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11159805.8 2011년03월25일
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11188571.1 2011년11월10일
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(56) 선행기술조사문헌
KR1020140097299 A

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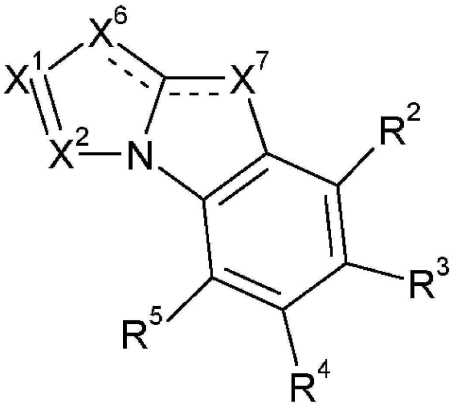
전체 청구항 수 : 총 6 항 심사관 : 허정오

(54) 발명의 명칭 **전자장치 응용을 위한 4H-이미다조[1,2-A]이미다졸**

(57) 요 약

본 발명은 화학식 I의 화합물, 그의 제조 방법 및 전자 소자, 특히 전계발광 소자에서의 그의 용도에 관한 것이다. 전계발광 소자에서 인광 방출체용 호스트 물질로서 사용되는 경우, 화학식 I의 화합물은 전계발광 소자의 개선된 효율, 안정성, 제조가능성, 또는 스펙트럼 특성을 제공할 수 있다.

<화학식 I>



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C09B 57/008 (2013.01)
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쉴트크네흐트, 크리스티안
미국 92124 캘리포니아주 샌디에고 파이잔 웨이 11442
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하이네마이어, 우테
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스위스 체하-4232 페렌 스타이넨뷜스트라쎄 173
와타나베, 소이치
독일 68165 만하임 베르더스트라쎄 17
렌나르츠, 크리스티안
독일 67105 쉬퍼슈타트 한스-푸르만-스트라쎄 24
바겐블라스트, 게르하르트
독일 67157 바헨하임 암 유데나커 8
월렙, 안느마리
스위스 체하-4232 페렌 스타이넨뷜스트라쎄 173
바르돈, 크리스티나
독일 79761 발트슈트 칼바리엔버크스트라쎄 5
베네디토, 플라비오, 루이츠
독일 67063 루드빅샤펜 스턴스트라쎄 40

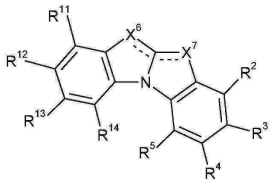
명 세 서

청구범위

청구항 1

하기 화학식 II의 화합물을 포함하는 전자 차단층.

<화학식 II>



상기 식에서,

X^6은 -N=이고 X^7은 $-NR^1-$이거나,

X^7은 =N-이고 X^6은 $-NR^1-$이고,

R^1은 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$의 기이고,

p는 0 또는 1이고, q는 0 또는 1이고, r은 0 또는 1이고,

A^1, A^2, A^3 및 A^4는 서로 독립적으로 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴렌기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴렌기이고, 여기서

기 A^1, A^2, A^3 및 A^4에 1개 이상의 기 $-(SiR^7R^8)-$가 개재될 수 있고, 단, A^1, A^2, A^3 및 A^4는 전자수송성 헤테로아릴렌기가 아니며;

R^2, R^3, R^4 및 R^5는 서로 독립적으로 H, 임의로 E에 의해 치환될 수 있고/거나 D가 개재될 수 있는 C_1-C_{25}알킬기; 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고;

R^6은 H, 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고;

R^7 및 R^8은 서로 독립적으로 C_1-C_{25}알킬기, 또는 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기이고;

R^{11}, R^{12}, R^{13} 및 R^{14}는 서로 독립적으로 H, 임의로 E에 의해 치환될 수 있고/거나 D가 개재될 수 있는 C_1-C_{25}알킬기; 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고,

D는 -CO-, -COO-, -S-, -SO-, $-SO_2-$, -O-, $-NR^{65}-$, $-SiR^{70}R^{71}-$, $-POR^{72}-$, $-CR^{63}=CR^{64}-$, 또는 -C≡C-이고,

E는 $-OR^{69}$, $-SR^{69}$, $-NR^{65}R^{66}$, $-COR^{68}$, $-COOR^{67}$, $-CONR^{65}R^{66}$, -CN, 또는 할로겐이고,

G는 E, 또는 C_1-C_{18}알킬기, C_6-C_{24}아릴기, 또는 F, C_1-C_{18}알킬, O가 개재된 C_1-C_{18}알킬에 의해 치환된 C_6-C_{24}아릴기, C_2-C_{30}헤테로아릴기, 또는 F, C_1-C_{18}알킬, O가 개재된 C_1-C_{18}알킬에 의해 치환된 C_2-C_{30}헤테로아릴기이고;

R^{63} 및 R^{64}는 서로 독립적으로 C_6-C_{18}아릴; C_1-C_{18}알킬, C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬; 또는

-O-가 개재된 C_1-C_{18}알킬이고;

R^{65} 및 R^{66}은 서로 독립적으로 C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이거나,

R^{65} 및 R^{66}은 함께 5 또는 6원 고리를 형성하고,

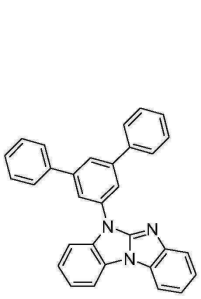
R^{67}은 C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴기; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

R^{68}은 H; C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴기; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

R^{69}는 C_6-C_{18}아릴; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

R^{70} 및 R^{71}은 서로 독립적으로 C_1-C_{18}알킬기, C_6-C_{18}아릴기, 또는 C_1-C_{18}알킬에 의해 치환된 C_6-C_{18}아릴기이고,

R^{72}는 C_1-C_{18}알킬기, C_6-C_{18}아릴기, 또는 C_1-C_{18}알킬에 의해 치환된 C_6-C_{18}아릴기이되, 단, 하기 화합물은 제외된다: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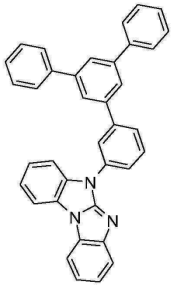
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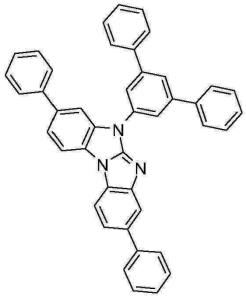
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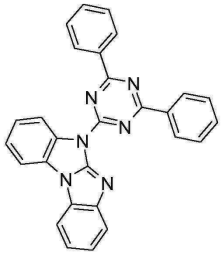
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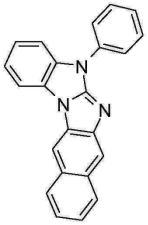
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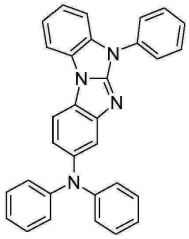
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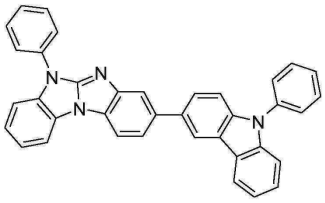
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청구항 2

제1항에 따른 전자 차단층을 포함하는 전자 소자.

청구항 3

제2항에 있어서, 전계발광 소자인 전자 소자.

청구항 4

제1항에 따른 전자 차단층을 포함하는, 고정식 화상 표시 장치 및 이동식 화상 표시 장치로 이루어진 군으로부터 선택되는, 장치.

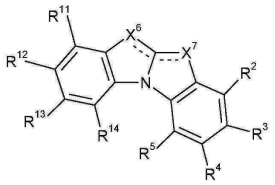
청구항 5

전자사진 광수용체, 광전 변환기, 유기 태양 전지 (유기 광기전), 스위칭 소자, 유기 발광 전계 효과 트랜지스터 (OLEFET), 이미지 센서, 색소 레이저 및 전계발광 소자를 위한 제1항에 따른 전자 차단층의 사용방법.

청구항 6

하기 화학식 II의 호스트 물질.

<화학식 II>



상기 식에서,

X^6은 -N=이고 X^7은 $-NR^1-$이거나,

X^7은 =N-이고 X^6은 $-NR^1-$이고,

R^1은 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$의 기이고,

p는 0 또는 1이고, q는 0 또는 1이고, r은 0 또는 1이고,

A^1, A^2, A^3 및 A^4는 서로 독립적으로 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴렌기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴렌기이고, 여기서

기 A^1, A^2, A^3 및 A^4에 1개 이상의 기 $-(SiR^7R^8)-$가 개재될 수 있고, 단, A^1, A^2, A^3 및 A^4는 전자수송성 헤테로아릴렌기가 아니며;

R^2, R^3, R^4 및 R^5는 서로 독립적으로 H, 임의로 E에 의해 치환될 수 있고/거나 D가 개재될 수 있는 C_1-C_{25}알킬기; 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고;

R^6은 H, 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고;

R^7 및 R^8은 서로 독립적으로 C_1-C_{25}알킬기, 또는 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기이고;

R^{11}, R^{12}, R^{13} 및 R^{14}는 서로 독립적으로 H, 임의로 E에 의해 치환될 수 있고/거나 D가 개재될 수 있는 C_1-C_{25}알킬기; 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고,

D는 -CO-, -COO-, -S-, -SO-, $-SO_2-$, -O-, $-NR^{65}-$, $-SiR^{70}R^{71}-$, $-POR^{72}-$, $-CR^{63}=CR^{64}-$, 또는 -C≡C-이고,

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G는 E, 또는 C_1-C_{18}알킬기, C_6-C_{24}아릴기, 또는 F, C_1-C_{18}알킬, O가 개재된 C_1-C_{18}알킬에 의해 치환된 C_6-C_{24}아릴기, C_2-C_{30}헤테로아릴기, 또는 F, C_1-C_{18}알킬, O가 개재된 C_1-C_{18}알킬에 의해 치환된 C_2-C_{30}헤테로아릴기이고;

R^{63} 및 R^{64}는 서로 독립적으로 C_6-C_{18}아릴; C_1-C_{18}알킬, C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬; 또는 -O-가 개재된 C_1-C_{18}알킬이고;

R^{65} 및 R^{66}은 서로 독립적으로 C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이거나,

R^{65} 및 R^{66}은 함께 5 또는 6원 고리를 형성하고,

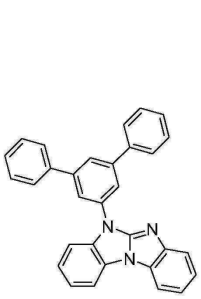
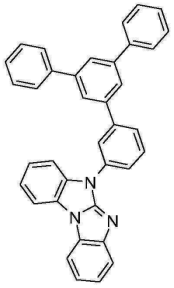
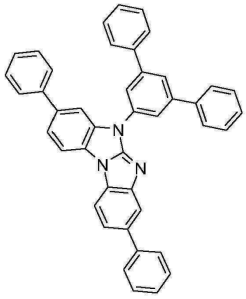
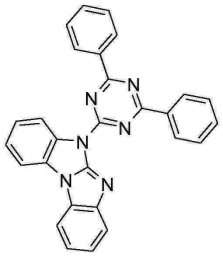
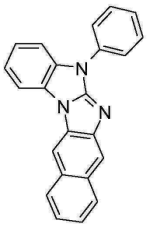
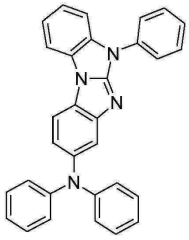
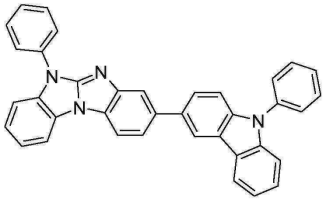
R^{67}은 C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴기; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

R^{68}은 H; C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴기; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

R^{69}는 C_6-C_{18}아릴; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

R^{70} 및 R^{71}은 서로 독립적으로 C_1-C_{18}알킬기, C_6-C_{18}아릴기, 또는 C_1-C_{18}알킬에 의해 치환된 C_6-C_{18}아릴기이고,

R^{72}는 C_1-C_{18}알킬기, C_6-C_{18}아릴기, 또는 C_1-C_{18}알킬에 의해 치환된 C_6-C_{18}아릴기이되, 단, 하기 화합물은 제외된다:


,

,

,

,

,

및

.

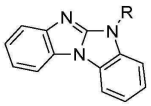
발명의 설명

기 술 분 야

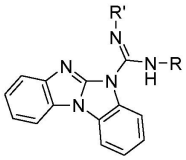
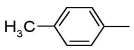
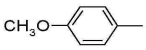
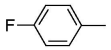
[0001] 본 발명은 화학식 I의 화합물, 그의 제조 방법 및 전자 소자, 특히 전계발광 소자에서의 그의 용도에 관한 것이다. 전계발광 소자에서 정공 수송 물질로서 사용될 경우, 화학식 I의 화합물은 전계발광 소자의 개선된 효율,

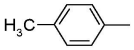
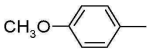
안정성, 제조가능성, 또는 스펙트럼 특성을 제공할 수 있다.

배 경 기 술

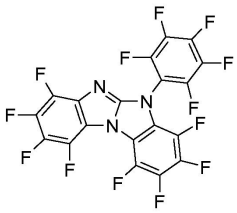
[0002] 문헌 [Khan, Misbahul Ain; Ribeiro, Vera Lucia Teixeira, Pakistan Journal of Scientific and Industrial Research 43 (2000) 168-170]은 1-(o-니트로페닐)- 및 1-(o-아지도페닐)벤즈이미다졸의 트리알킬 포스파이트-유도된 탈산소 및 열분해에 의한 벤즈이미다조[1,2-a]벤즈이미다졸  (R = H, Me, Et)의 합성을 기재한다.

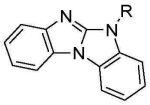
[0003] 문헌 [Pedro Molina et al. Tetrahedron (1994) 10029-10036]은 비스(2-아미노페닐)아민으로부터 유래된 비스(이미노포스포란)과 2당량의 이소시아네이트와의 아자 비티그(Wittig)-유형 반응이 벤즈이미다조[1,2,a]벤즈이미다졸 유도체를 직접 제공하였음을 보고한다.

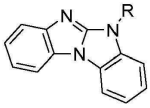
[0004]  (R = R' =  ,  ,  ,

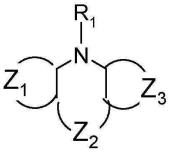
[0005]  ,  ; R =  및 R'=  , R = iso-프로필 및 R'= 에틸)

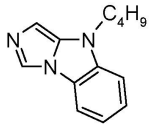
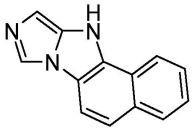
[0006] 문헌 [Kolesnikova, I. V.; Zhurnal Organicheskoi Khimii 25 (1989) 1689-95]은 5H-벤즈이미다조[1,2-a]벤즈이미다졸 1,2,3,4,7,8,9,10-옥타플루오로-5-(2,3,4,5,6-펜타플루오로페닐)의 합성을 기재한다.

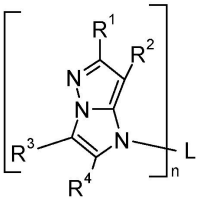
[0007] 

[0008] 문헌 [Achour, Reddouane; Zniber, Rachid, Bulletin des Societes Chimiques Belges 96 (1987) 787-92]은 벤즈이미다졸리논 유도체로부터 제조된 벤즈이미다조벤즈이미다졸  (R = H, $-CH(CH_3)_2$)의 합성을 기재한다.

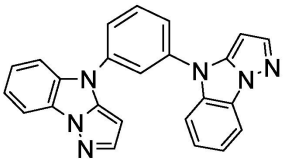
[0009] 문헌 [Hubert, Andre J.; Reimlinger, Hans, Chemische Berichte 103 (1970) 2828-35]은 벤즈이미다조벤즈이미다졸  (R = H, CH_3, )의 합성을 기재한다.

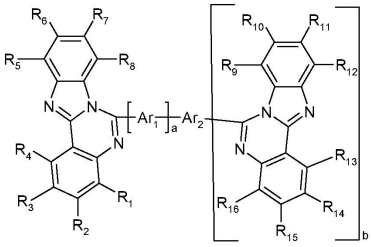
[0010] JP2001160488은 반대 애노드 및 캐소드 사이에 단일층 또는 다층 유기 화합물 필름을 갖는 발광층을 갖고, 여기서 유기 화합물 필름의 하나 이상의 층은 화학식  으로 나타내지는 1종 이상의 화합물을 함유하

는 것인 전계발광 소자를 기재한다. 하기 화합물이 명시적으로 개시되어 있다:  및  .

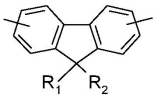
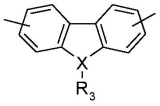
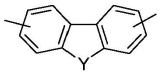
[0011] US20100244006은 캐소드; 애노드; 및 캐소드와 애노드 사이에 하나 이상의 유기층을 포함하는 유기 전계발광 소자에 관한 것이다. 하나 이상의 유기층은 하나 이상의 발광 물질을 함유하는 발광층을 포함한다. 하기 화학식 

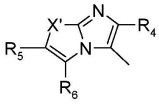
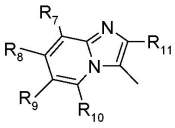
(I)로 나타내지는 화합물은 하나 이상의 유기층에 함유되고, 상기 식에서, n은 2 이상의 정수를 나타내고, L은 n-가 연결기를 나타내고, R^1, R^2, R^3, 및 R^4는 각각 독립적으로 수소 원자 또는 치환기를 나타낸다.

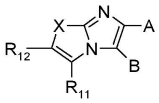
[0012] US20100244006에 기재된 화합물은 발광층에서 호스트로서 바람직하게 사용된다.  은 US20100244006에 개시된 화합물의 예를 나타낸다.

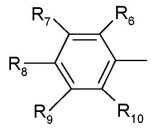
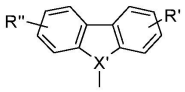
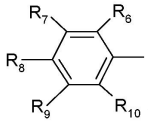
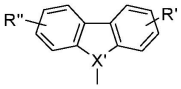
[0013] KR1020110008784는 화학식  의 신규 유기 발광 화합물 및 이를 포함하는 유기 전계발광 소자에 관한 것이다.

[0014] US2005079387은 화학식 Ar_1-Ar_2-Ar_3의 이미다졸 고리 함유 화합물 (청색 발광 호스트 화합물) 및 이를 사용하는 유기 전계발광 (EL) 표시 소자에 관한 것이다

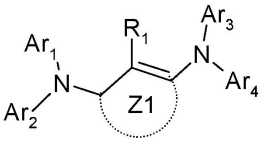
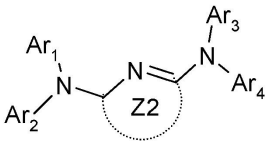
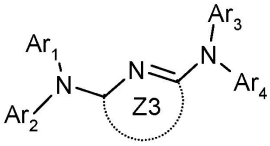
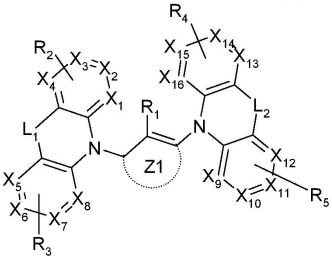
[0015] Ar_2는  ,  및  로 이루어진 군으로부터 선택되고,

[0016] Ar_1 및 Ar_3 각각은 독립적으로  및  로부터 선택되고, 여기서 X'는 O, 또는 S이다.

[0017] US2005074632는 화학식  의 이미다졸 고리 함유 화합물 및 이를 사용하는 유기 전계발광 (EL) 표시 소자에 관한 것이다. 특히, 이미다졸 고리-함유 화합물은 전계발광층과 같은 유기 필름을 위한 물질로서 도판트와 조합하여 또는 단독으로 사용될 수 있다.

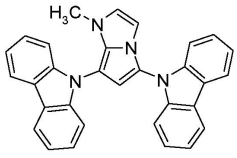
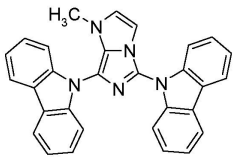
[0018] A는  , $-N(R_{13}R_{14})$, 및  로 이루어진 군으로부터 선택되고, B는  및  로 이루어진 군으로부터 선택된다. X는 O-, -S-, -Se- 및 -NH-로 이루어진 군으로부터 선택된다.

[0019] JP2007180147은 애노드와 캐소드에 의해 개재되며, 화학식 1, 2, 3 또는 4로 나타내지는 화합물을 함유하는 하나 이상의 발광층을 함유하는 유기 전계발광 소자에 관한 것이다:

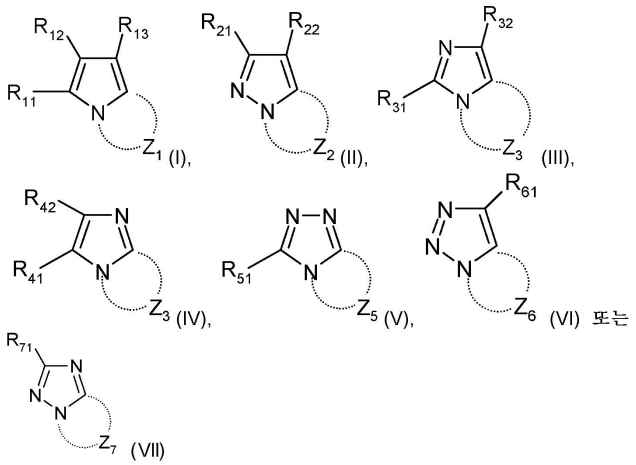

(1),

(2),

(3) 또는

(4)

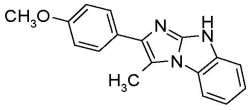
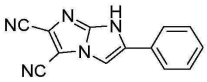
[0020] . Ar_1-Ar_4 = 방향족기 또는 방향족 헤테로시클릭기; R_1-R_5 = H 또는 치환기; Z_1 = 5 또는 6원의 헤테로시클릭 고리를 형성하는데 필요한 잔기; L_1, L_2 = 결합 또는 커플링기; 및 X_1-X_{16} = 탄소 또는 질소이다. Ar_1 및 Ar_2, 및 Ar_3 및 Ar_4의 한 부분에 새로운 고리가 형성될 수 있다.

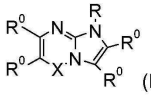
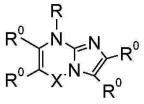
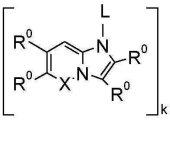
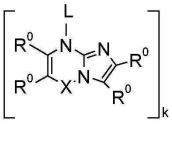
[0021] 하기 화합물이 명시적으로 개시되어 있다:

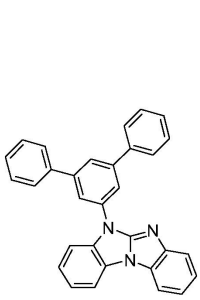
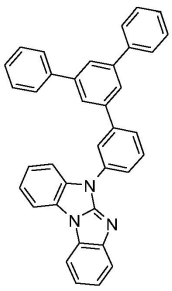
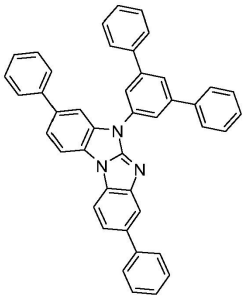
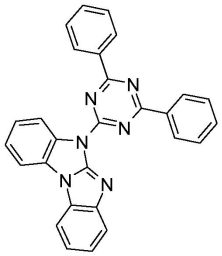
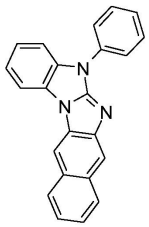
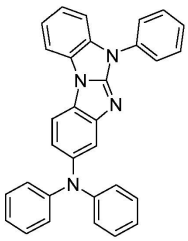
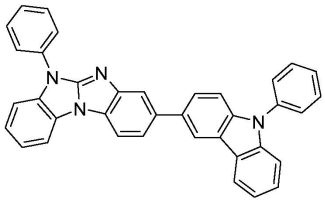
[0022]  및  .

[0023] US6551723은 발광층 또는 한 쌍의 전극 사이에 발광층을 함유하는 복수의 유기 화합물 박층을 포함하는 유기 전계발광 소자에 관한 것으로서, 여기서 유기 전계발광 소자 내 하나 이상의 층은 화학식 I 내지 VII로 나타내지는 하나 이상의 헤테로시클릭 화합물을 포함한다:

[0024]  . R_{11}, R_{12}, R_{13}, R_{21}, R_{22}, R_{31}, R_{32}, R_{41}, R_{42}, R_{51}, R_{61}, 및 R_{71}은 각각 독립적으로 수소 원자 또는 치환기이고; Z_1, Z_2, Z_3, Z_4, Z_5, Z_6, 및 Z_7은 5- 또는 6-원 고리를 형성하는데 필요한 원자단이다. 화학식 I 내지 VII로 나타내지는 화합물은 특히 발광층 및/또는 전자 주입층/전자 수송층에 첨가된다. 하기 화합물은 명시적으로 개시되어 있다:

[0025]  및  .

[0026] WO2011160757은 애노드, 캐소드 및 화학식  (I),  (II),  (III),  (IV)의 화합물(상기 식에서, X는 단일 결합일 수 있고 L은 2가 기일 수 있음)을 함유하는 하나 이상의 유기층을 포함하는 전자 소자에 관한 것이다. 하기 4H-이미다조[1,2-a]이미다졸 화합물이 명시적으로 개시되어 있다:

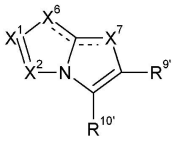
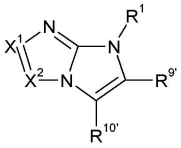
[0027]  ,  ,  ,  ,  ,  및  .

발명의 내용

[0028] 이러한 개발에도 불구하고, 전계발광 소자의 개선된 효율, 안정성, 제조가능성, 및/또는 스펙트럼 특성을 제공할 신규 정공 수송 물질을 포함하는 유기 발광 소자에 대한 필요성은 여전히 존재한다.

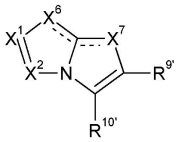
[0029] 따라서, 본 발명의 목적은, 상기 선행 기술과 관련하여, OLED에 사용하기에 적합한 추가의 물질 및 유기 전자장치(organic electronics)에서 추가의 응용을 제공하는 것이다. 더욱 특히, OLED에 사용하기 위한 정공 수송 물질, 전자/여기자 차단제 물질 및 매트릭스 물질을 제공하는 것이 가능해야 한다. 물질은 특히, 하나 이상의 인광 방출체, 특히 하나 이상의 녹색 방출체 또는 하나 이상의 청색 방출체를 포함하는 OLED에 적합해야 한다. 더욱이, 물질은 OLED의 양호한 효율, 양호한 작동 수명 및 열 응력에 대한 높은 안정성, 및 낮은 사용 및 작동 전압을 보장하는 OLED를 제공하기에 적합해야 한다.

발명을 실시하기 위한 구체적인 내용

[0030] 특정 이미다졸 유도체  (I'), 특히  ($R^{9'}$는 R^{9}의 의미를 갖고, $R^{10'}$는 R^{10}의 의미를 가짐)가 유기-전계발광 소자에 사용하기에 적합한 것으로 밝혀졌다. 특히, 특정 이미다졸 유도체는 양호한 효율 및 지속성을 갖는 인광 방출체를 위한 적합한 정공 수송 물질, 또는 호스트 물질이다.

[0031] 상기 목적은 화학식 I'의 화합물에 의해 해결되었다.

[0032] <화학식 I'>

[0033] 

[0034] 상기 식에서,

[0035] X^6은 -N=이고 X^7은 $-NR^1-$이거나,

[0036] X^7은 =N-이고 X^6은 $-NR^1-$이고,

[0037] R^1은 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$의 기이고,

[0038] p는 0 또는 1이고, q는 0 또는 1이고, r은 0 또는 1이고,

[0039] A^1, A^2, A^3 및 A^4는 서로 독립적으로 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴렌기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴렌기이고, 여기서

[0040] 기 A^1, A^2, A^3 및 A^4에 1개 이상의 기 $-(SiR^7R^8)-$가 개재될 수 있고;

[0041] R^6은 H, 기 $-(SiR^{20}R^{21}R^{22})$, 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고;

[0042] R^7 및 R^8은 서로 독립적으로 C_1-C_{25}알킬기, 또는 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기이고;

[0043] X^1은 N, 또는 CR^9이고;

[0044] X^2는 N, 또는 CR^{10}이고,

[0045] R^9, R^{10}, $R^{9'}$ 및 $R^{10'}$는 서로 독립적으로 H, 임의로 E에 의해 치환될 수 있고/거나 D가 개재될 수 있는 C_1-C_{25}알킬기; 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이거나,

[0046] R^9 및 R^{10} 및/또는 $R^{9'}$ 및 $R^{10'}$는 함께 임의로 치환될 수 있는 고리를 형성하고;

[0047] R^{20}, R^{21} 및 R^{22}는 서로 독립적으로 C_1-C_{25}알킬기, 또는 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기이고;

[0048] D는 -CO-, -COO-, -S-, -SO-, $-SO_2-$, -O-, $-NR^{65}-$, $-SiR^{70}R^{71}-$, $-POR^{72}-$, $-CR^{63}=CR^{64}-$, 또는 -C≡C-이고,

[0049] E는 $-OR^{69}$, $-SR^{69}$, $-NR^{65}R^{66}$, $-COR^{68}$, $-COOR^{67}$, $-CONR^{65}R^{66}$, -CN, 또는 할로겐이고,

[0050] G는 E, 또는 C_1-C_{18}알킬기, C_6-C_{24}아릴기, 또는 F, C_1-C_{18}알킬, 또는 O가 개재된 C_1-C_{18}알킬에 의해 치환된 C_6-C_{24}아릴기; C_2-C_{30}헤테로아릴기, 또는 F, C_1-C_{18}알킬, 또는 O가 개재된 C_1-C_{18}알킬에 의해 치환된 C_2-C_{30}헤테로아릴기이고;

[0051] R^{63} 및 R^{64}는 서로 독립적으로 C_6-C_{18}아릴; C_1-C_{18}알킬, C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬; 또는 -O-가 개재된 C_1-C_{18}알킬이고;

[0052] R^{65} 및 R^{66}은 서로 독립적으로 C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이거나,

[0053] R^{65} 및 R^{66}은 함께 5 또는 6원 고리를 형성하고,

[0054] R^{67}은 C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴기; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

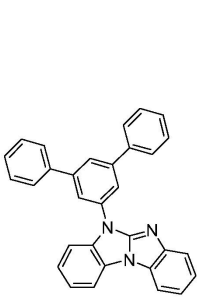
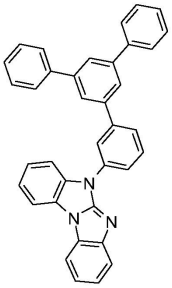
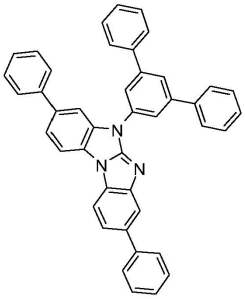
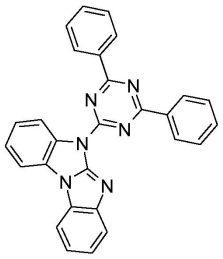
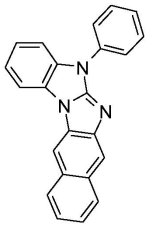
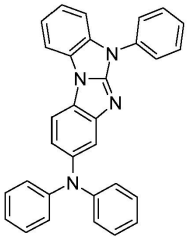
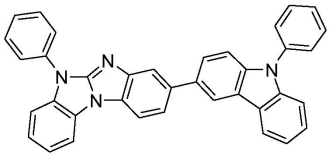
[0055] R^{68}은 H; C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴기; C_1-C_{18}알킬기; 또는 -O-가 개재

된 C_1-C_{18}알킬기이고,

[0056] R^{69}는 C_6-C_{18}아릴; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

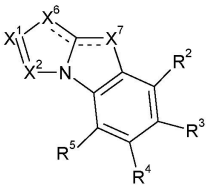
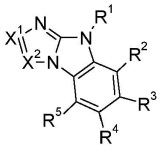
[0057] R^{70} 및 R^{71}은 서로 독립적으로 C_1-C_{18}알킬기, C_6-C_{18}아릴기, 또는 C_1-C_{18}알킬에 의해 치환된 C_6-C_{18}아릴기이고,

[0058] R^{72}는 C_1-C_{18}알킬기, C_6-C_{18}아릴기, 또는 C_1-C_{18}알킬에 의해 치환된 C_6-C_{18}아릴기이되, 단, 하기 화합물은 제외된다:

[0059]  ,  ,  ,  ,  ,  , 및  .

[0060] 특히 상기 목적은 화학식 I의 화합물

[0061] <화학식 I>

[0062]  , 특히  에 의해 해결되었고,

[0063] 상기 식에서,

[0064] X^6은 -N=이고 X^7은 $-NR^1$-이거나,

[0065] X^7은 =N-이고 X^6은 $-NR^1$-이고, 여기서

[0066] R^1은 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$의 기이고,

[0067] p는 0 또는 1이고, q는 0 또는 1이고, r은 0 또는 1이고,

[0068] A^1, A^2, A^3 및 A^4는 서로 독립적으로 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴렌기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴렌기이고, 여기서

[0069] 기 A^1, A^2, A^3 및 A^4에 1개 이상의 기 $-(SiR^7R^8)-$가 개재될 수 있고;

[0070] R^2, R^3, R^4 및 R^5는 서로 독립적으로 H, 임의로 E에 의해 치환될 수 있고/거나 D가 개재될 수 있는 C_1-C_{25}알킬기; 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고;

[0071] R^6은 H, 기 $-(SiR^{20}R^{21}R^{22})$, 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고;

[0072] R^7 및 R^8은 서로 독립적으로 C_1-C_{25}알킬기, 또는 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기이고;

[0073] X^1은 N, 또는 CR^9이고,

[0074] X^2는 N, 또는 CR^{10}이고,

[0075] R^9 및 R^{10}은 서로 독립적으로 H, 임의로 E에 의해 치환될 수 있고/거나 D가 개재될 수 있는 C_1-C_{25}알킬기; 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이거나,

[0076] R^9 및 R^{10}은 함께 임의로 치환될 수 있는 고리를 형성하고;

[0077] R^{20}, R^{21} 및 R^{22}는 서로 독립적으로 C_1-C_{25}알킬기, 또는 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기이고;

[0078] D는 -CO-, -COO-, -S-, -SO-, $-SO_2-$, -O-, $-NR^{65}-$, $-SiR^{70}R^{71}-$, $-POR^{72}-$, $-CR^{63}=CR^{64}-$, 또는 -C≡C-이고,

[0079] E는 $-OR^{69}$, $-SR^{69}$, $-NR^{65}R^{66}$, $-COR^{68}$, $-COOR^{67}$, $-CONR^{65}R^{66}$, -CN, 또는 할로겐이고,

[0080] G는 E, 또는 C_1-C_{18}알킬기, C_6-C_{24}아릴기, C_1-C_{18}알킬에 의해 치환된 C_6-C_{24}아릴기이고;

[0081] R^{63} 및 R^{64}는 서로 독립적으로 C_6-C_{18}아릴; C_1-C_{18}알킬, C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬; 또는 -O-가 개재된 C_1-C_{18}알킬이고;

[0082] R^{65} 및 R^{66}은 서로 독립적으로 C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이거나,

[0083] R^{65} 및 R^{66}은 함께 5 또는 6원 고리를 형성하고,

[0084] R^{67}은 C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴기; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

[0085] R^{68}은 H; C_6-C_{18}아릴기; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴기; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

[0086] R^{69}는 C_6-C_{18}아릴; C_1-C_{18}알킬 또는 C_1-C_{18}알콕시에 의해 치환된 C_6-C_{18}아릴; C_1-C_{18}알킬기; 또는 -O-가 개재된 C_1-C_{18}알킬기이고,

[0087] R^{70} 및 R^{71}은 서로 독립적으로 C_1-C_{18}알킬기, C_6-C_{18}아릴기, 또는 C_1-C_{18}알킬에 의해 치환된 C_6-C_{18}아릴기이고,

[0088] R^{72}는 C_1-C_{18}알킬기, C_6-C_{18}아릴기, 또는 C_1-C_{18}알킬에 의해 치환된 C_6-C_{18}아릴기이다.

[0089] 본 발명의 화합물은 전자사진 광수용체, 광전 변환기, 유기 태양 전지 (유기 광기전), 스위칭 소자, 예컨대 유기 트랜지스터, 예를 들어, 유기 FET 및 유기 TFT, 유기 발광 전계 효과 트랜지스터 (OLEFET), 이미지 센서, 색

소 레이저 및 전계발광 소자, 예를 들어, 유기 발광 다이오드 (OLED) 등에 사용될 수 있다.

[0090] 따라서, 본 발명의 추가의 대상은 본 발명에 따른 화합물을 포함하는 전자 소자이다. 전자 소자는 바람직하게는 전계발광 소자이다.

[0091] 화학식 I의 화합물은 원칙상 EL 소자의 임의의 층에 사용될 수 있지만, 바람직하게는 호스트, 정공 수송 및 전자 차단 물질로서 사용된다. 특히, 화학식 I의 화합물은 청색 발광 인광 방출체를 위한 호스트 물질로서 사용된다.

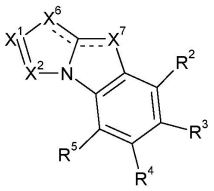
[0092] 따라서, 본 발명의 추가의 대상은 본 발명에 따른 화학식 I의 화합물을 포함하는 정공 수송층에 관한 것이다.

[0093] 본 발명의 추가의 대상은 본 발명에 따른 화학식 I의 화합물을 포함하는 발광층에 관한 것이다. 상기 실시양태에서 화합물 I의 화합물은 바람직하게는 호스트 물질로서 인광 방출체와 조합하여 사용된다.

[0094] 본 발명의 추가의 대상은 본 발명에 따른 화학식 I의 화합물을 포함하는 전자 차단층에 관한 것이다.

[0095] 화학식 I의 화합물은 특히 하기 화학식 I의 화합물이다.

[0096] <화학식 I>

[0097] 

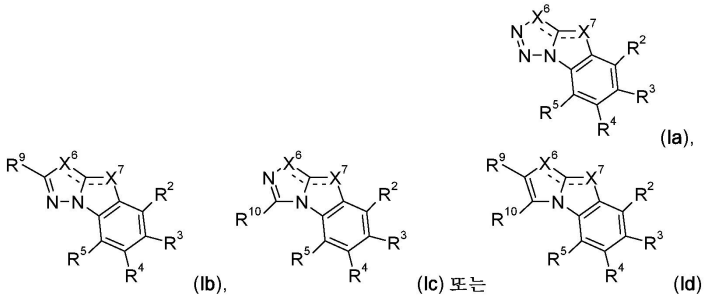
[0098] 상기 식에서,

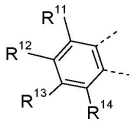
[0099] X^6은 -N=이고 X^7은 $-NR^1-$이거나,

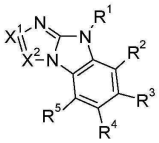
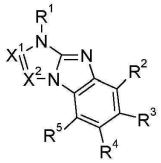
[0100] X^7은 =N-이고 X^6은 $-NR^1-$이고,

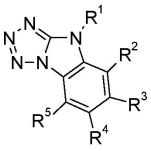
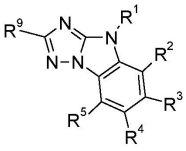
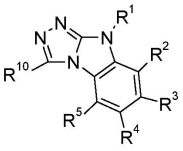
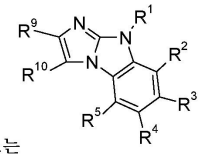
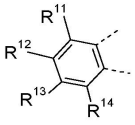
[0101] R^2, R^3, R^4 및 R^5는 서로 독립적으로 H, 임의로 E에 의해 치환될 수 있고/거나 D가 개재될 수 있는 C_1-C_{25}알킬기; 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고;

[0102] X^1, X^2, R^1, E, D 및 G는 상기 정의된 바와 같다.

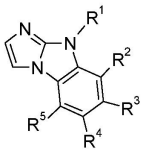
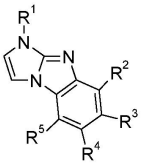
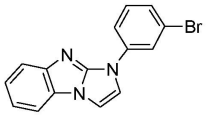
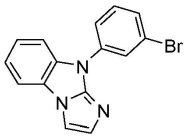
[0103] 화학식 I의 화합물은 화학식 

일 수 있고, X^6은 -N=이고 X^7은 $-NR^1-$이거나, X^7은 =N-이고 X^6은 $-NR^1-$이다. 화학식 Id의 화합물이 특히 바람직하며, 여기서 R^9 및 R^{10}은 함께 고리  를 형성하고, 여기서 R^{11}, R^{12}, R^{13} 및 R^{14}는 하기 정의된 바와 같다. R^{11}, R^{12}, R^{13} 및 R^{14}는 바람직하게는 H이다. R^2, R^3, R^4 및 R^5는 바람직하게는 H이다.

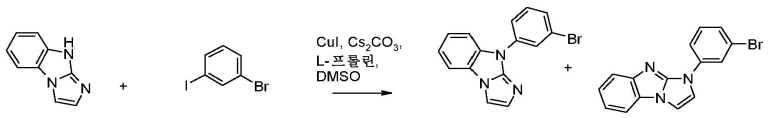
[0104] 바람직한 실시양태에서 화학식 I의 화합물은 화학식  의 화합물이다. 또 다른 바람직한 실시양태에서 화학식 I의 화합물은 화학식  의 화합물이다.

[0105] 바람직하게는, 화학식 I의 화합물은 화학식  (Ia'),  (Ib'),  (Ic') 또는  (Id') 의 화합물이다. 화학식 Ib' 및 Id'의 화합물이 바람직하다. 화학식 Id'의 화합물이 더욱 바람직하다. 훨씬 더 바람직한 것은 화학식 Id'의 화합물이고, 여기서 R^9 및 R^{10}은 함께 고리  를 형성하고, 여기서 R^{11}, R^{12}, R^{13} 및 R^{14}는 하기 정의된 바와 같다. R^{11}, R^{12}, R^{13} 및 R^{14}는 바람직하게는 H이다.

[0106] R^2, R^3, R^4 및 R^5는 바람직하게는 H이다.

[0107] 축 대칭이 아닌 화학식 I의 화합물, 예를 들어, 화학식 Id'의 화합물 (여기서, R^9 및 R^{10}은 H임) 등은 2개의 이성질체 형태로 존재할 수 있다:  (Id') 및  (Id"). 하기 화합물:  과  의 혼합물의 합성을 기재하는 실시예 2를 참조한다.

[0108] 4H-이미다조[1,2-a]벤즈이미다졸은 ARKIVOC 2002 (v) 48-61에 기재된 바와 같이 제조된다. 4H-이미다조[1,2-a]벤즈이미다졸과 1-브로모-3-아이오도-벤젠의 울만(Ullmann) 반응으로 2개의 이성질체가 대략 1 대 1의 비로 제공된다.

[0109] 

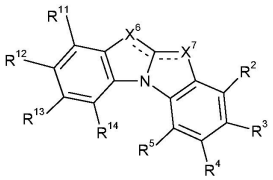
[0110] R^{20}, R^{21} 및 R^{22}는 바람직하게는 C_1-C_{18}알킬, 예컨대 메틸, 에틸, n-프로필, iso-프로필, n-부틸, 이소부틸, sec-부틸, t-부틸, 2-메틸부틸, n-펜틸, 이소펜틸, n-헥실, 2-에틸헥실, 또는 n-헵틸, C_6-C_{14}아릴, 예컨대 페닐, 나

프틸, 또는 비페닐릴이거나, G에 의해 치환된 C_6-C_{14}아릴, 예컨대 $-C_6H_4OCH_3$, $-C_6H_4OCH_2CH_3$, $-C_6H_3(OCH_3)_2$, 또는 $-C_6H_3(OCH_2CH_3)_2$, $-C_6H_4CH_3$, $-C_6H_3(CH_3)_2$, $-C_6H_2(CH_3)_3$, 또는 $-C_6H_4tBu$이다.

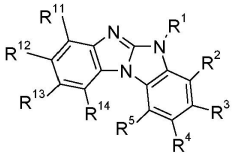
[0111] R^9 및 R^{10}은 바람직하게는 H, 또는 임의로 1개 이상의 C_1-C_8알킬기에 의해 치환될 수 있는 C_6-C_{14}아릴, 예컨대 페닐, 나프틸, 또는 비페닐릴; 또는 임의로 1개 이상의 C_1-C_8알킬기에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴, 예를 들어, 디벤조푸라닐 등이다.

[0112] 바람직한 실시양태에서 본 발명은 화학식 II, 특히 화학식 II'의 화합물에 관한 것이다.

[0113] <화학식 II>

[0114] 

[0115] <화학식 II'>

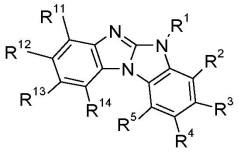
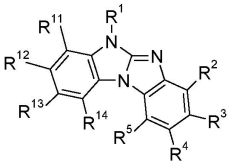
[0116] 

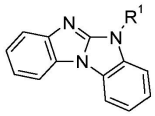
[0117] 상기 식에서,

[0118] X^6은 -N=이고 X^7은 $-NR^1-$이거나,

[0119] X^7은 =N-이고 X^6은 $-NR^1-$이고,

[0120] R^{11}, R^{12}, R^{13} 및 R^{14}는 서로 독립적으로 H, 임의로 E에 의해 치환될 수 있고/거나 D가 개재될 수 있는 C_1-C_{25}알킬기; 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고, E, D, G, R^1, R^2, R^3, R^4 및 R^5는 상기 정의된 바와 같다.

[0121] 바람직한 실시양태에서 화학식 II의 화합물은 화학식  의 화합물이다. 또 다른 바람직한 실시양태에서 화학식 II의 화합물은 화학식  의 화합물이다.

[0122] R^2, R^3, R^4, R^5, R^{11}, R^{12}, R^{13} 및 R^{14}가 H이고 R^1이 상기 정의된 바와 같은 화학식 II의 화합물이 훨씬 더 바람직하다:  (IIa).

[0123] R^6은 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기일 수 있다.

[0124] 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기 R^6은 전형적으로, 비치환되거나 치환될 수 있는, 페닐, 4-메틸페닐, 4-메톡시페닐, 나프틸, 특히 1-나프틸, 또는 2-나프틸, 비페닐릴, 터페닐릴, 피레닐, 2- 또는 9-플루오레닐, 페난트릴, 또는 안트릴이다.

[0125] 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기 R^6은, 5 내지 7개의 고리 원자를 갖는 고리 또는 축합 고리 시스템을 나타내며, 여기서 질소, 산소 또는 황은 가능한 헤테로 원자이고, 전형적으로, 적어도 6개의 공액 π-전자를 갖는 5 내지 30개의 원자를 갖는 헤테로시클릭기, 예컨대 티에닐, 벤조티오페닐, 디벤조티오페닐, 티안트레닐, 푸릴, 푸르푸릴, 2H-피라닐, 벤조푸라닐, 이소벤조푸라닐, 디벤조푸라닐, 페녹시티에닐, 피롤릴, 이미다졸릴, 피라졸릴, 피리딜, 비피리딜, 트리아지닐, 피리미디닐, 피라지닐, 피리다지닐, 인돌리지닐, 이소인돌릴, 인돌릴, 인다졸릴, 푸리닐, 퀴놀리지닐, 퀴놀릴, 이소퀴놀릴, 프탈라지닐, 나프티리디닐, 퀴녹살리닐, 퀴나졸리닐, 신놀리닐, 프테리디닐, 카르볼리닐, 벤조트리아졸릴, 벤족사졸릴, 페난트리디닐, 아크리디닐, 피리미디닐, 페난트롤리닐, 페나지닐, 이소티아졸릴, 페노티아지닐, 이속사졸릴, 푸라자닐, 4-이미다조[1,2-a]벤즈이미다조일, 5-벤즈이미다조[1,2-a]벤즈이미다졸일, 카르바졸릴, 또는 페녹사지닐이고, 이는 비치환되거나 치환될 수 있다. 게다가, C_2-C_{30}헤테로아릴기 R^6은 비치환되거나 치환될 수 있는 4H-[1,2,4]트리아졸로[1,5-a]벤즈이미다조일이다.

[0126] C_6-C_{24}아릴 및 C_2-C_{30}헤테로아릴기는 G에 의해 치환될 수 있고 바람직하게는 1개 이상의 C_1-C_8알킬기에 의해 치환된다.

[0127] 바람직한 C_2-C_{30}헤테로아릴기는 피리딜, 트리아지닐, 피리미디닐, 4-이미다조[1,2-a]벤즈이미다조일, 5-벤즈이미다조[1,2-a]벤즈이미다조일, 카르바졸릴, 디벤조푸라닐이고, 이는 비치환되거나 특히 C_6-C_{10}아릴, 또는 C_1-C_4알킬에 의해 치환된 C_6-C_{10}아릴, 또는 C_2-C_5헤테로아릴에 의해 치환될 수 있다. 4H-[1,2,4]트리아졸로[1,5-a]벤즈이미다조일은 또한 바람직한 C_2-C_{30}헤테로아릴기 R^6를 나타낸다.

[0128] A^1, A^2, A^3 및 A^4는 서로 독립적으로 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴렌기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴렌기이다. 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴렌기 A^1, A^2, A^3 및 A^4는 전형적으로, 비치환되거나 치환될 수 있는, 페닐렌, 4-메틸페닐렌, 4-메톡시페닐렌, 나프틸렌, 특히 1-나프틸렌, 또는 2-나프틸렌, 비페닐릴렌, 터페닐릴렌, 피레닐렌, 2- 또는 9-플루오레닐렌, 페난트릴렌, 또는 안트릴렌이다.

[0129] 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴렌기 A^1, A^2, A^3 및 A^4는, 5 내지 7개의 고리 원자를 갖는 고리 또는 축합 고리 시스템을 나타내며, 여기서 질소, 산소 또는 황은 가능한 헤테로 원자이고, 전형적으로, 적어도 6개의 공액 π-전자를 갖는 5 내지 30개의 원자를 갖는 헤테로시클릭기, 예컨대 티에닐렌, 벤조티오페닐렌, 디벤조티오페닐렌, 티안트레닐렌, 푸릴렌, 푸르푸릴렌, 2H-피라닐렌, 벤조푸라닐렌, 이소벤조푸라닐렌, 디벤조푸라닐렌, 페녹시티에닐렌, 피롤릴렌, 이미다졸릴렌, 피라졸릴렌, 피리딜렌, 비피리딜렌, 트리아지닐렌, 피리미디닐렌, 피라지닐렌, 피리다지닐렌, 인돌리지닐렌, 이소인돌릴렌, 인돌릴렌, 인다졸릴렌, 푸리닐렌, 퀴놀리지닐렌, 퀴놀릴렌, 이소퀴놀릴렌, 프탈라지닐렌, 나프티리디닐렌, 퀴녹살리닐렌, 퀴나졸리닐렌, 신놀리닐렌, 프테리디닐렌, 카르볼리닐렌, 벤조트리아졸릴렌, 벤족사졸릴렌, 페난트리디닐렌, 아크리디닐렌, 피리미디닐렌, 페난트롤리닐렌, 페나지닐렌, 이소티아졸릴렌, 페노티아지닐렌, 이속사졸릴렌, 푸라자닐렌, 카르바졸릴렌, 또는 페녹사지닐렌이고, 이는 비치환되거나 치환될 수 있다.

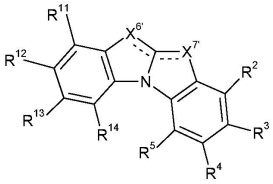
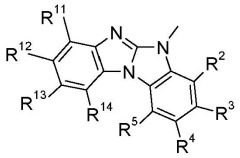
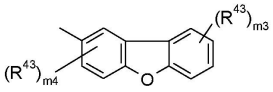
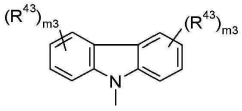
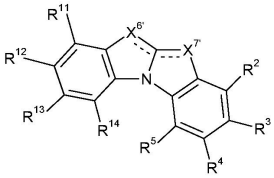
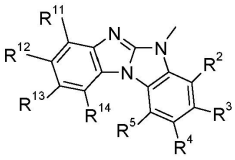
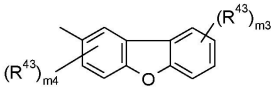
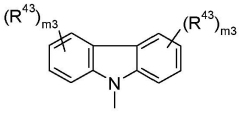
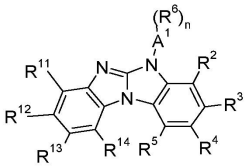
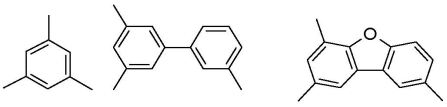
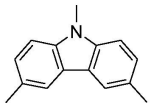
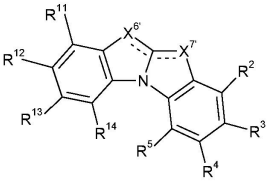
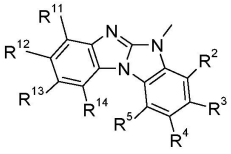
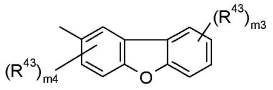
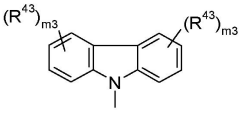
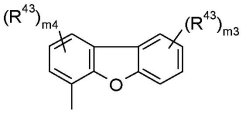
[0130] 바람직한 C_6-C_{24}아릴렌기는 비치환되거나 치환될 수 있는, 1,3-페닐렌, 3,3'-비페닐릴렌, 3,3'-m-터페닐렌, 2- 또는 9-플루오레닐렌, 페난트릴렌이다.

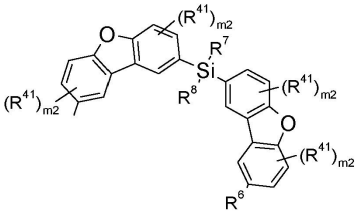
[0131] 바람직한 C_2-C_{30}헤테로아릴렌기는 비치환되거나 특히 C_6-C_{10}아릴, 또는 C_1-C_4알킬에 의해 치환된 C_6-C_{10}아릴, 또는 C_2-C_5헤테로아릴에 의해 치환될 수 있는, 피리딜렌, 트리아지닐렌, 피리미디닐렌, 카르바졸릴렌, 디벤조푸라닐렌이다.

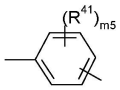
[0132] 더욱 바람직한 C_2-C_{30}헤테로아릴렌기는 임의로 1개 이상의 C_1-C_4알킬기에 의해 치환될 수 있는, 임의로 C_6-C_{10}아릴

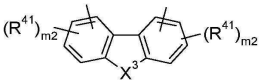
에 의해 치환될 수 있는, 카르바졸릴렌 및 디벤조푸라닐렌이다.

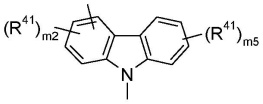
[0133] C_6-C_{24}아릴렌 및 C_2-C_{30}헤테로아릴렌기는 G에 의해 치환될 수 있고 바람직하게는 1개 이상의 C_1-C_8알킬기에 의해 치환된다.

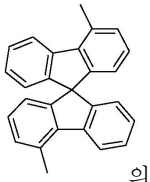
[0134] 용어 "C_2-C_{30}헤테로아릴기"가, 예를 들어, 화학식  , 특히  ,  및  의 기를 포함함에 따라, 기 A^1, A^2, A^3 및 A^4는, 예를 들어, 1개 이상의 화학식  , 특히  ,  및  의 기에 의해 치환될 수 있으므로, 예를 들어, 화학식  [n은 2, 또는 3, 특히 2임]의 화합물이 생성되고, 여기서 A^1은 화학식  , 또는  의 기이고, R^6은 화학식  , 특히  ,  및  의 기이다. 게다가, R^6은 화학식  의 기일 수 있다. $X^{6'}$는 -N=이고 $X^{7'}$는 -N<이거나, $X^{7'}$는 =N-이고 $X^{6'}$는 -N<이다. m3은 0 또는 1 내지 4의 정수이다. m4는 0 또는 1 내지 3의 정수이다.

[0135] R^1은 바람직하게는 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$의 기, 예를 들어, $-A^1-R^6$, $-A^1-A^2-R^6$, $-A^1-A^2-A^3-R^6$, $-A^1-A^2-A^3-A^4-R^6$, 또는  등이고, 여기서 A^1, A^2, A^3 및 A^4는 서로 독립적으로 화학식



, 

, 

, 또는 
의 기이고, 여기서

[0136] m5는 0 또는 1 내지 4의 정수이고,

[0137] m2는 0 또는 1 내지 3의 정수이고,

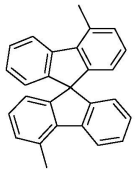
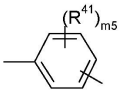
[0138] X^3은 -O-, -S-, 또는 $-NR^{15}-$이고,

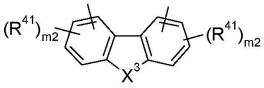
[0140] $*R^7$ 및 R^8은 C_1-C_{18}알킬기이고,

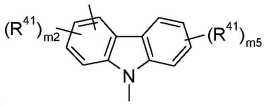
[0141] R^{15}는 C_1-C_{18}알킬기; -O-가 개재된 C_1-C_{18}알킬기; C_6-C_{18}아릴기; 1개 이상의 C_1-C_{18}알킬기, 또는 C_1-C_{18}알콕시기에 의해 치환된 C_6-C_{18}아릴기; C_2-C_{20}헤테로아릴기, 또는 1개 이상의 C_1-C_{18}알킬기에 의해 치환된 C_2-C_{20}헤테로아릴기이고,

[0142] R^{41}은 각 경우에 동일하거나 상이할 수 있고 F, C_1-C_{18}알킬, E에 의해 치환되고/거나 D가 개재된 C_1-C_{18}알킬, C_6-C_{24}아릴, G에 의해 치환된 C_6-C_{24}아릴, C_2-C_{20}헤테로아릴, 또는 G에 의해 치환된 C_2-C_{20}헤테로아릴이고,

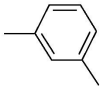
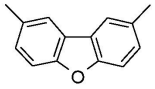
[0143] R^6, p, q, r, E, D 및 G는 상기 또는 하기에 정의된 바와 같다.

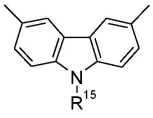
[0144] 화학식 
의 기는 화학식 

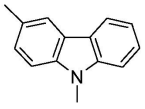
, 

또는 

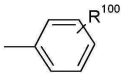
의 기보다 덜 바람직하다.

[0145] 더욱 바람직하게는, A^1, A^2, A^3 및 A^4는 서로 독립적으로 화학식 
, 

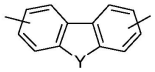
, 

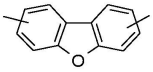
또는 

의 기이고, 여기서 R^{15}는 C_6-C_{18}아릴기; 또는 1개 이상의 C_1-C_{18}알킬기에 의해 치환된 C_6-C_{18}아릴기이다.

[0146] R^{15}는 바람직하게는 화학식 
, 또는 

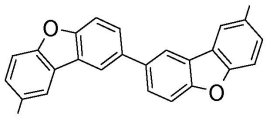
의 기이고, 여기서 R^{100}은 C_1-C_8알킬기이다.

[0147] 기 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$가 바람직하고, 여기서 A^1, A^2, A^3 및 A^4 중 하나 이상은 화학식 

의 기이고, 여기서 Y는 -O-, -S-, 또는 $-NR^{15}-$이고, 여기서 R^{15}는 상기 정의된 바와 같다. A^1, A^2, A^3 및 A^4 중 하나 이상이 화학식 

의 기인 기 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$가 더욱 바람직하다.

[0148] 바람직한 기 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 예를 하기에 나타냈다: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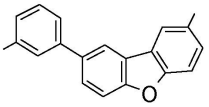
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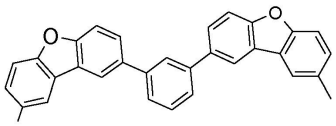
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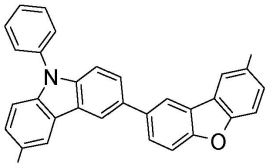
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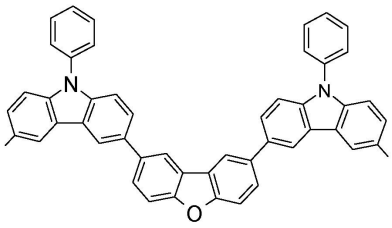
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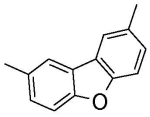
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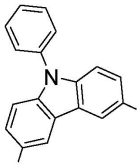
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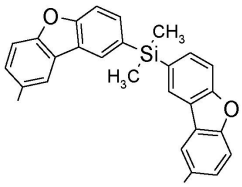
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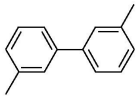
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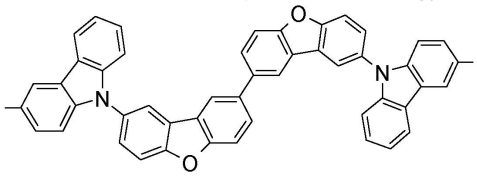
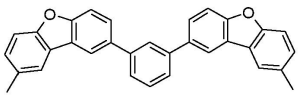
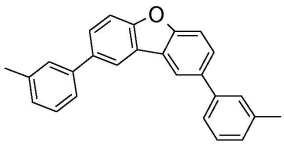


[0149] . 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 기의 추가 예는 화학식

,

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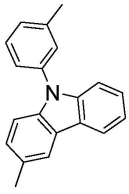
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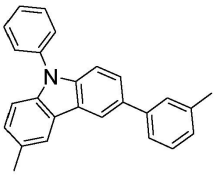
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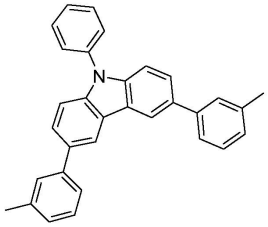
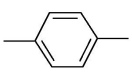

의 기이다.

[0150] 또 다른 바람직한 실시양태에서 R^1은 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$의 기, 예를 들어, $-A^1-R^6$, $-A^1-A^2-R^6$, $-A^1-A^2-A^3-R^6$, 또는 $-A^1-A^2-A^3-A^4-R^6$ 등이고, 여기서 기 A^1, A^2, A^3 및 A^4 중 하나 이상은 화학식

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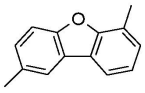
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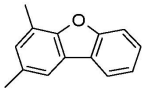
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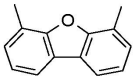
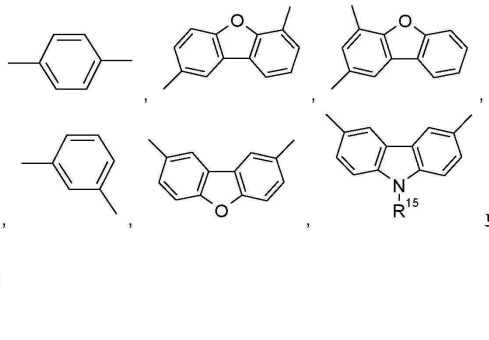
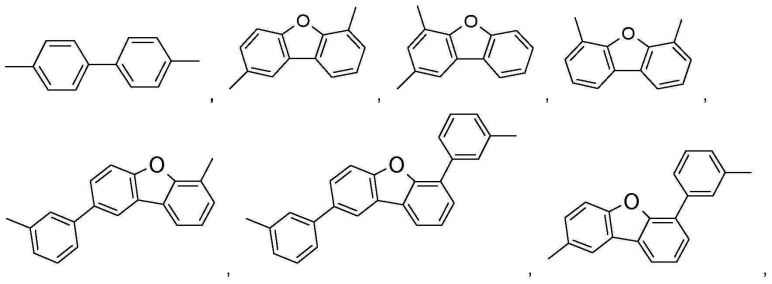
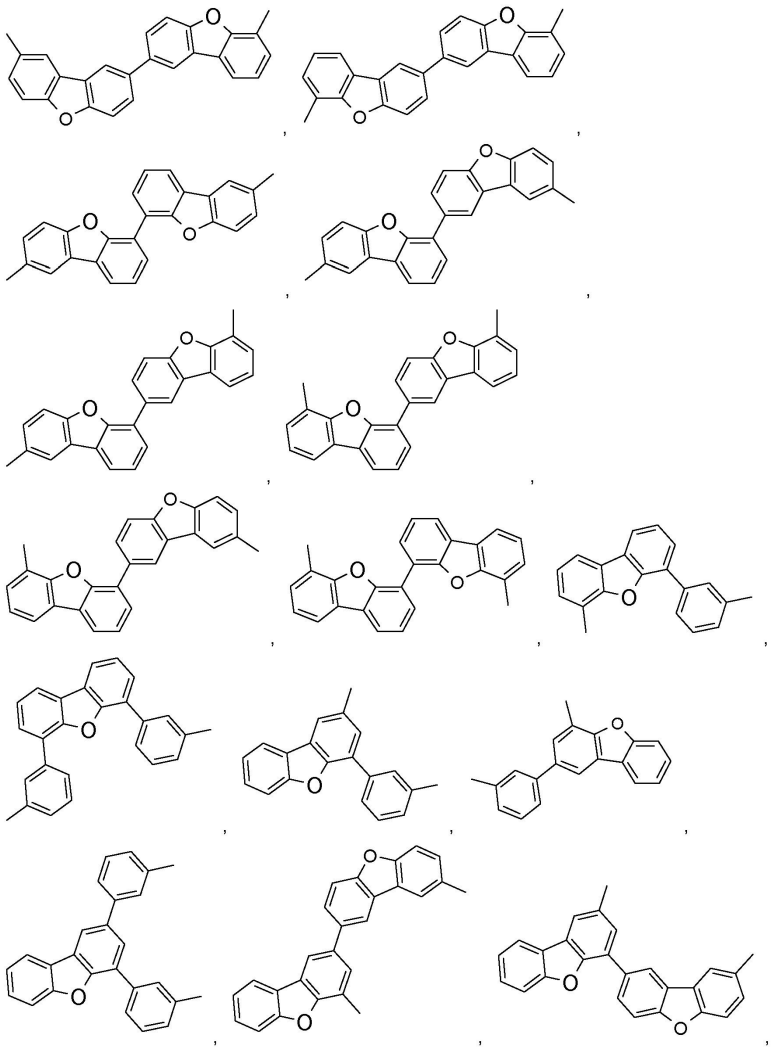

의 기이고; 그 나머지는 서로 독립적으로 화학



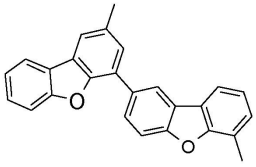
또는

식 의 기이고, 여기서 R^{15}는 C_6-C_{18}아릴기; 또는 1개 이상의 C_1-C_{18}알킬기에 의해 치환된 C_6-C_{18}아릴기이다. 바람직한 기 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 예를 하기에 나타냈다:





[0151]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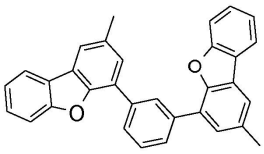
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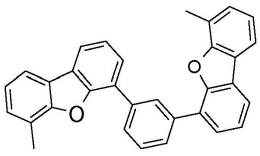
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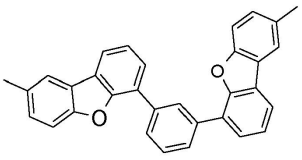
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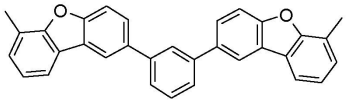
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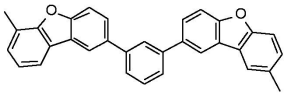
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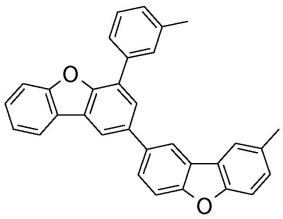
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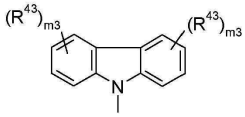
[0152]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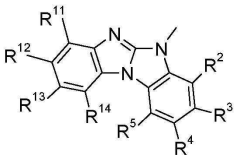
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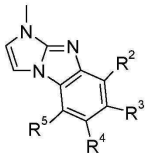
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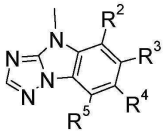
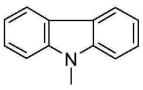


[0153] R^6은 특히 화학식 의 기, 매우 특히 화학식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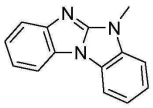
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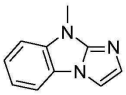
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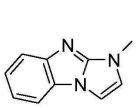
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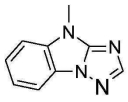
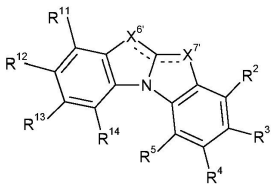
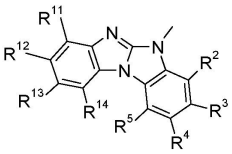
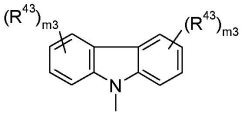
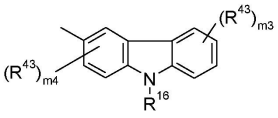

의 기이다. R^2, R^3, R^4, R^5, R^{11}, R^{12}, R^{13}, R^{14}, R^{43} 및 m3은 상기 정의된 바와 같다.



[0154] 본 발명의 바람직한 실시양태에서 R^6은 화학식 ($X^{6'}$는 -N=이고 $X^{7'}$는 -N<이거나, $X^{7'}$는 =N-이고 $X^{6'}$는 -N<임), 특히


,

,

의

기, 또는 기 $-(SiR^{20}R^{21}R^{22})$이고,

[0155] 여기서 R^2, R^3, R^4, R^5, R^{11}, R^{12}, R^{13} 및 R^{14}는 서로 독립적으로 H, 임의로 E에 의해 치환될 수 있고/거나 D가 개재될 수 있는 C_1-C_{25}알킬기; 임의로 G에 의해 치환될 수 있는 C_6-C_{24}아릴기, 또는 임의로 G에 의해 치환될 수 있는 C_2-C_{30}헤테로아릴기이고,

[0156] R^{16}은 C_6-C_{18}아릴기; 또는 1개 이상의 C_1-C_{18}알킬기에 의해 치환된 C_6-C_{18}아릴기이고,

[0157] R^{20}, R^{21} 및 R^{22}는 서로 독립적으로 C_6-C_{18}아릴기; 또는 1개 이상의 C_1-C_{18}알킬기에 의해 치환된 C_6-C_{18}아릴기이고,

[0158] R^{43}은 각 경우에 동일하거나 상이할 수 있고 F, C_1-C_{18}알킬, E에 의해 치환되고/거나 D가 개재된 C_1-C_{18}알킬, C_6-C_{24}아릴, G에 의해 치환된 C_6-C_{24}아릴, C_2-C_{20}헤테로아릴, 또는 G에 의해 치환된 C_2-C_{20}헤테로아릴이고,

[0159] m3은 0 또는 1 내지 4의 정수이고, m4는 0 또는 1 내지 3의 정수이고,

[0160] E, D, 및 G는 상기 또는 하기에 정의된 바와 같다.

[0161] D는 바람직하게는 -CO-, -COO-, -S-, -SO-, $-SO_2-$, -O-, $-NR^{65}-$이고, 여기서 R^{65}는 C_1-C_{18}알킬, 예컨대 메틸, 에틸, n-프로필, iso-프로필, n-부틸, 이소부틸, 또는 sec-부틸, 또는 C_6-C_{14}아릴, 예컨대 페닐, 톨릴, 나프틸, 또는 비페닐릴이다.

[0162] E는 바람직하게는 $-OR^{69}$; $-SR^{69}$; $-NR^{65}R^{65}$; $-COR^{68}$; $-COOR^{67}$; $-CONR^{65}R^{65}$; 또는 -CN이고; 여기서 R^{65}, R^{67}, R^{68} 및 R^{69}는 서로 독립적으로 C_1-C_{18}알킬, 예컨대 메틸, 에틸, n-프로필, iso-프로필, n-부틸, 이소부틸, sec-부틸, 헥실, 옥틸, 또는 2-에틸-헥실, 또는 C_6-C_{14}아릴, 예컨대 페닐, 톨릴, 나프틸, 또는 비페닐릴이다.

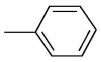
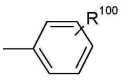
[0163] G는 E와 동일한 바람직한 정의를 갖고, C_1-C_{18}알킬, 예컨대 메틸, 에틸, n-프로필, iso-프로필, n-부틸, 이소부틸, sec-부틸, 헥실, 옥틸, 또는 2-에틸-헥실이거나, C_1-C_{18}퍼플루오로알킬, 예를 들어, $-CF_3$ 등이다.

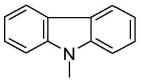
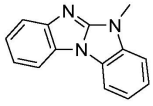
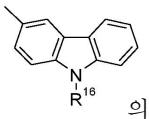
[0164] R^2, R^3, R^4, R^5, R^{11}, R^{12}, R^{13} 및 R^{14}는 바람직하게는 H이다.

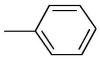
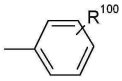
[0165] R^{43}은 바람직하게는 H, 또는 임의로 치환될 수 있는 C_6-C_{14}아릴, 예컨대 페닐, 톨릴, 나프틸, 또는 비페닐릴이다.

[0166] m3은 바람직하게는 0 또는 1, 가장 바람직하게는 0이다. m4는 바람직하게는 0 또는 1, 가장 바람직하게는 0이다.

[0167] m2는 바람직하게는 0 또는 1, 가장 바람직하게는 0이다. m5는 바람직하게는 0 또는 1, 가장 바람직하게는 0이다.

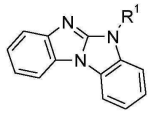
[0168] R^{20}, R^{21} 및 R^{22}는 바람직하게는 화학식  , 또는  의 기이고, 여기서 R^{100}은 C_1-C_8알킬기이다.

[0169] 더욱 바람직하게는, R^6은 화학식  ,  ,  , 또는  의 기이고, 여기서 R^{16}은 C_6-C_{18}아릴기; 또는 1개 이상의 C_1-C_{18}알킬기에 의해 치환된 C_6-C_{18}아릴기이다.

[0170] R^{16}은 바람직하게는 화학식  , 또는  의 기이고, 여기서 R^{100}은 C_1-C_8알킬기이다.

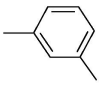
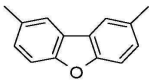
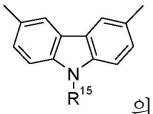
[0171] 바람직한 실시양태에서 본 발명은 화학식 II'의 화합물에 관한 것이다.

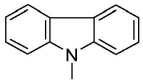
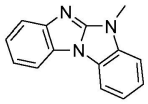
[0172] <화학식 II'>

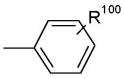
[0173] 

[0174] 상기 식에서,

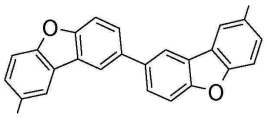
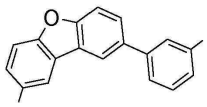
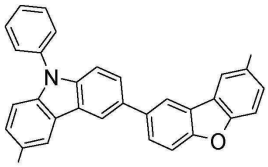
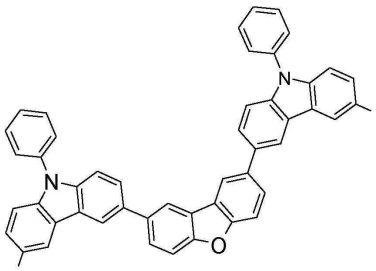
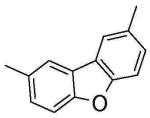
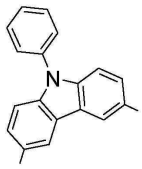
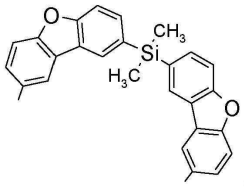
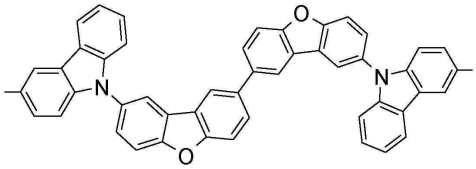
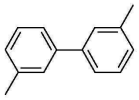
[0175] R^1은 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$의 기이고,

[0176] A^1, A^2, A^3 및 A^4는 서로 독립적으로 화학식  ,  , 또는  의 기이고,

[0177] R^6은  , 또는  의 기이고,

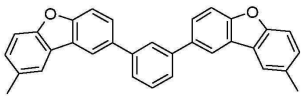
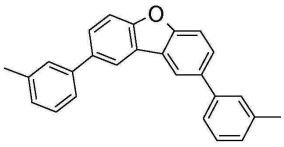
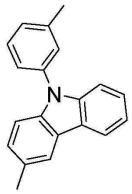
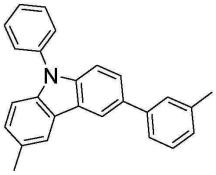
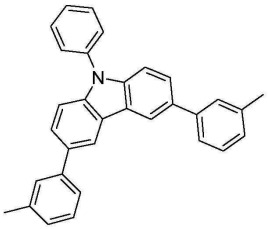
[0178] R^{15}는  , 또는  의 기이고, 여기서 R^{100}은 C_1-C_8알킬기이고, p, q 및 r은 상기 정의된 바와 같다.

[0179] 상기 실시양태에서 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 기는 특히 화학식


(IVa),

(IVb),

(IVc),

(IVd),

(IVe),

(IVf),

(IVg),

(IVh),

(IVi) 또는

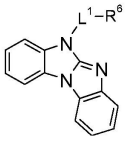
(IVj)

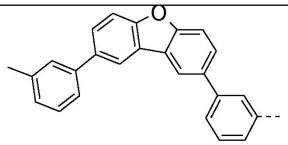
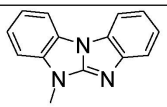
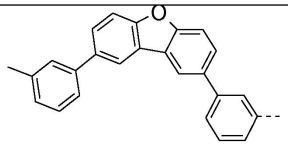
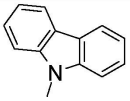
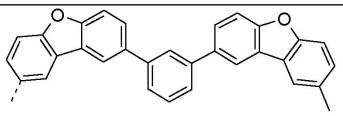
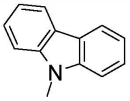
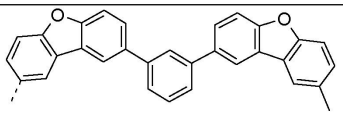
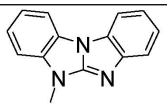
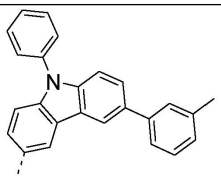
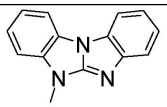
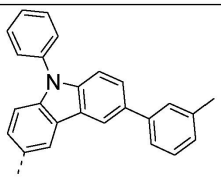
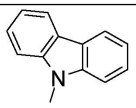
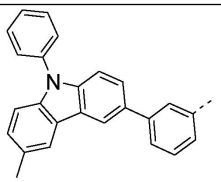
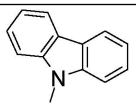
의 기이다. 화학식 $-A^1-(A^2)_p-(A^3)_q-$

$(A^4)_r$-의 기의 추가 예는 화학식  (IVk),  (IVl),  (IVm),  (IVn) 및  (IVo) 의 기이다.

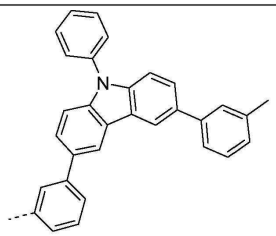
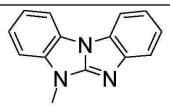
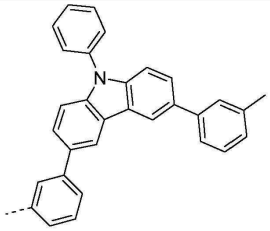
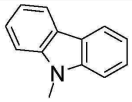
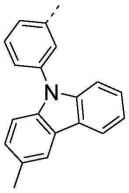
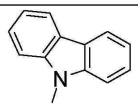
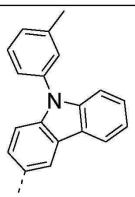
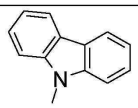
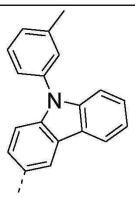
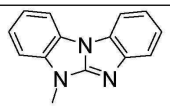
[0180] 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 현재 가장 바람직한 기는 화학식 IVa, IVb, IVe, IVl, IVk, IVs, IVv 및 VIj의 기이다.

[0181] 바람직한 화합물의 예는 청구항 8에 나타낸 화합물 A-1 내지 A-20, 특히 A-1 내지 A-19, 및 하기 표에 나타낸 화합물 A-21 내지 A-32이다:

[0182] 

화합물	$L^{1\,2)}$	R^6
A-21		
A-22		
A-23		
A-24		
A-25		
A-26		
A-27		

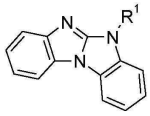
[0183]

A-28		
A-29		
A-30		
A-31		
A-32		

[0184]

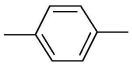
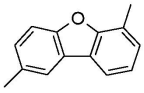
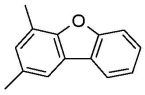
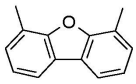
[0185] 또 다른 바람직한 실시양태에서 본 발명은 화학식 II'의 화합물에 관한 것이다.

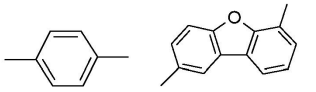
[0186] <화학식 II'>

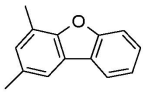
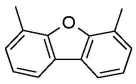
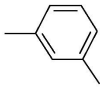
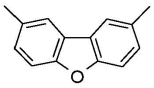
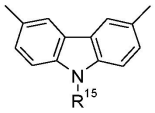
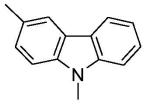
[0187] 

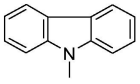
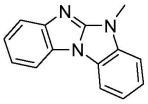
[0188] 상기 식에서,

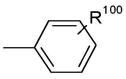
[0189] R^1은 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$의 기이고,

[0190] 여기서 기 A^1, A^2, A^3 및 A^4 중 하나 이상은 화학식  ,  ,  또는  의 기이고; 그 나머지는 서로 독립적으로

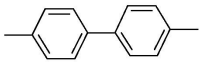







또는


화학식 의 기이고, R^6은 화학식  , 또는  의 기이고,

[0191] R^{15}는 화학식  , 또는  의 기이고, 여기서 R^{100}은 C_1-C_8알킬기이고, p, q 및 r은 상기 정의된 바와 같다.

[0192] 상기 실시양태에서 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 기는 특히 화학식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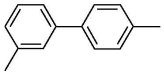
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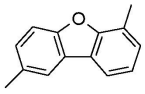
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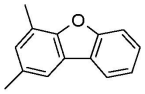
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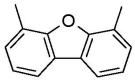
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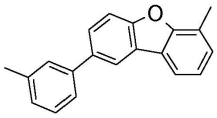
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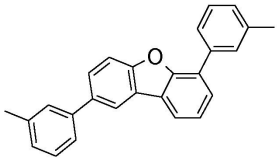
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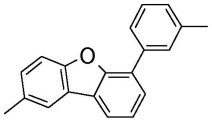
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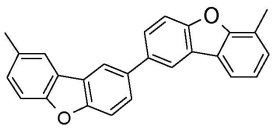
[0193]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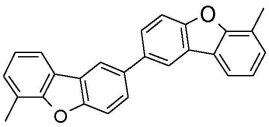
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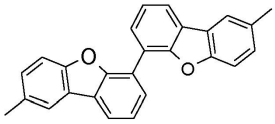
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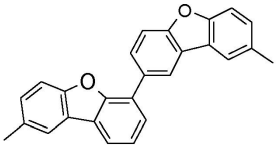
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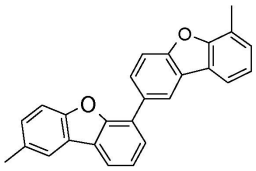
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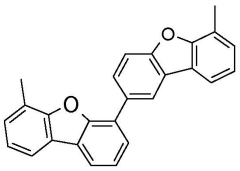
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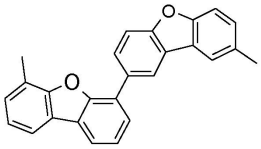
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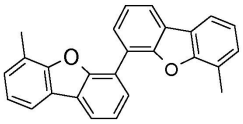
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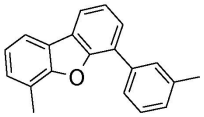
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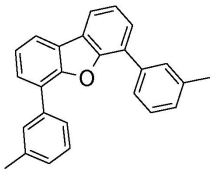
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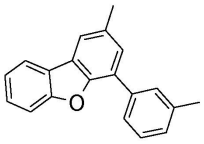
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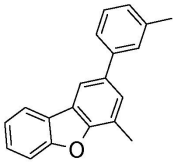
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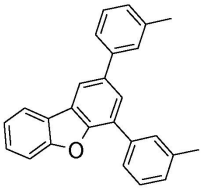
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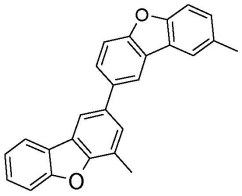
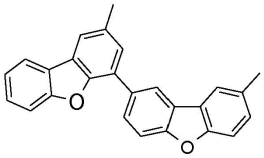
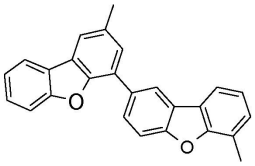
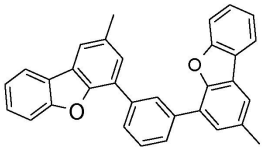
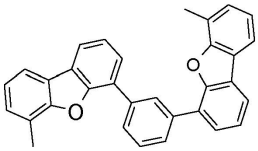
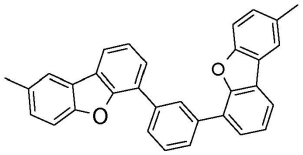
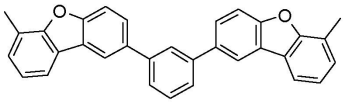
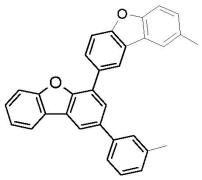
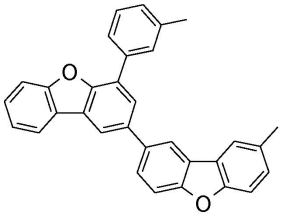
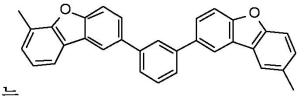

(VIl),

(VIm),

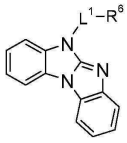
[0194]

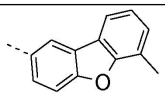
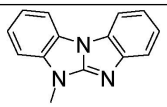
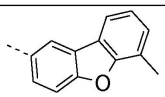
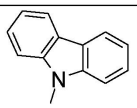
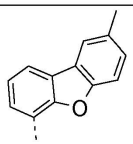
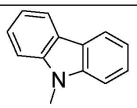
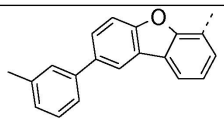
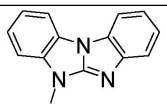
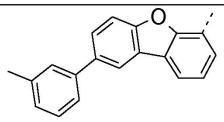
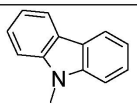
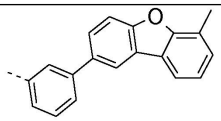
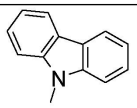
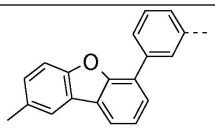
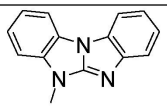
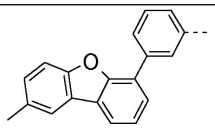
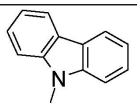
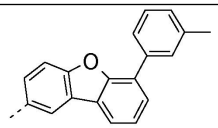
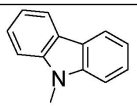
[0195]  (VIn),  (VIo),  (VIp),  (VIq),  (VIr),  (VIs),  (VIt) 또는  (VIu) 의 기이다.

[0196] $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 현재 가장 바람직한 기는 화학식 IVa, IVb, IVe, IVl, IVk, IVs, IVv 및 VIj의 기이다.

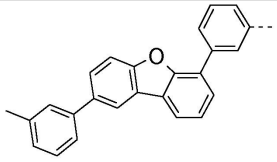
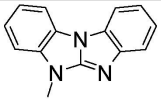
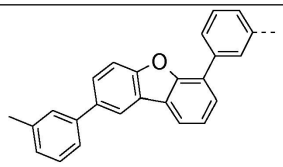
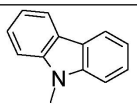
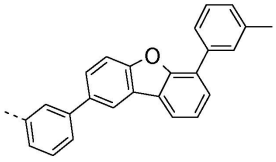
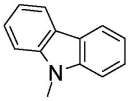
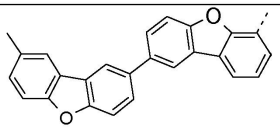
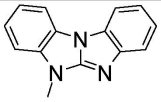
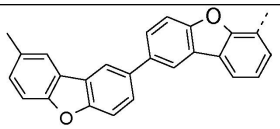
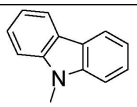
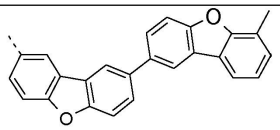
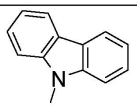
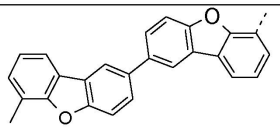
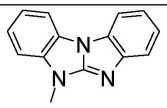
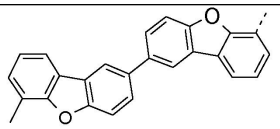
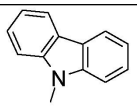
[0197] 화학식 I의 화합물이 청색, 또는 녹색 인광 방출체를 위한 호스트 물질로서, 또는 전자/여기자 차단 물질로서 사용되는 경우에, 화학식  의 기를 함유하는 기 $A^1-(A^2)_p-(A^3)_q-(A^4)_r-$, 즉 화학식 IVp 및 IVr의 기는 덜 바람직하다.

[0198] 바람직한 화합물의 예는 하기 표에 나타낸 화합물 C-1 내지 C-78이다.

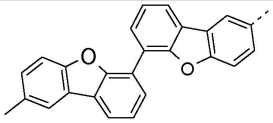
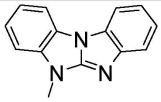
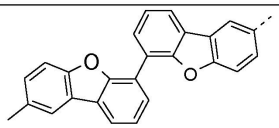
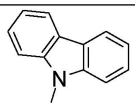
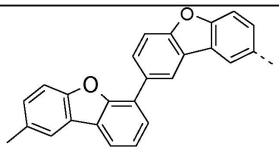
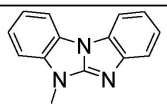
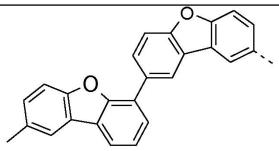
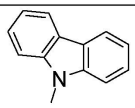
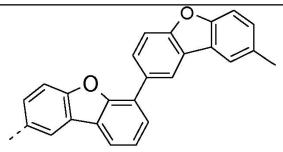
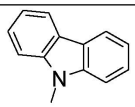
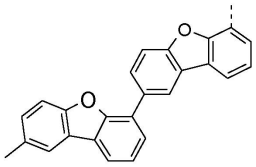
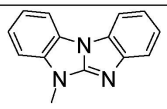
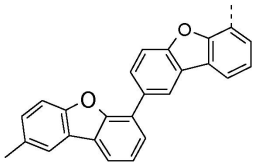
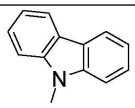
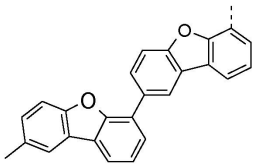
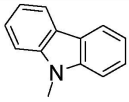
[0199] 

화합물	$L^{1\ 2)}$	R^6
C-1		
C-2		
C-3		
C-4		
C-5		
C-6		
C-7		
C-8		
C-9		

[0200]

C-10		
C-11		
C-12		
C-13		
C-14		
C-15		
C-16		
C-17		

[0201]

C-18		
C-19		
C-20		
C-21		
C-22		
C-23		
C-24		
C-25		

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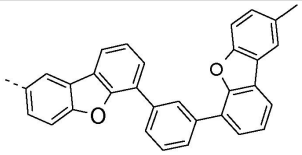
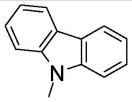
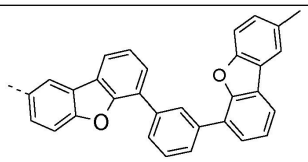
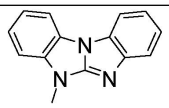
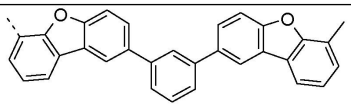
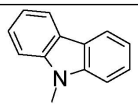
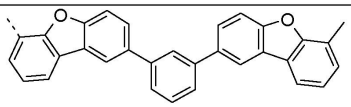
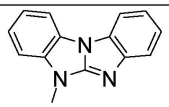
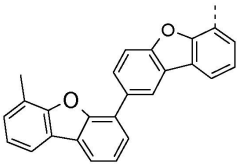
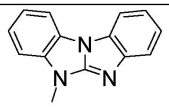
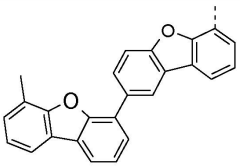
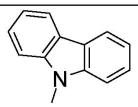
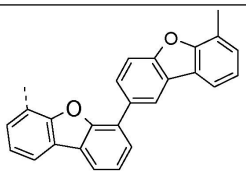
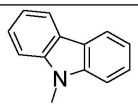
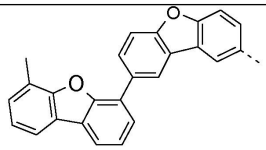
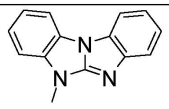
C-26		
C-27		
C-28		
C-29		
C-30		
C-31		
C-32		
C-33		

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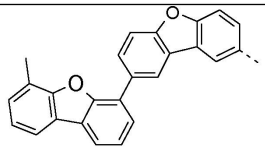
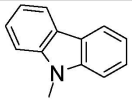
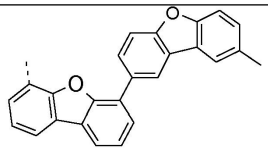
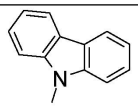
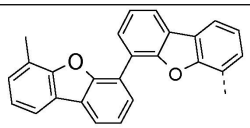
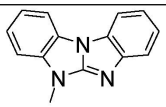
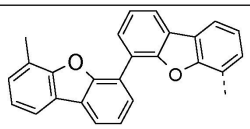
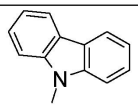
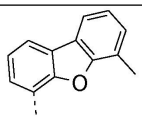
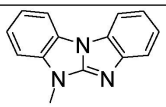
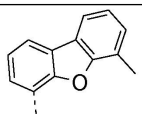
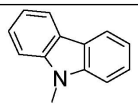
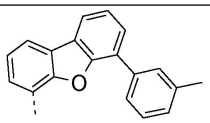
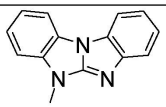
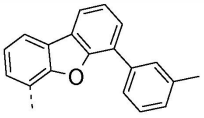
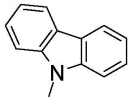
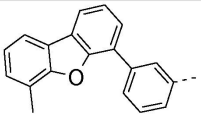
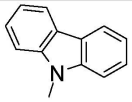
C-34		
C-35		
C-36		
C-37		
C-38		
C-39		
C-40		
C-41		
C-42		

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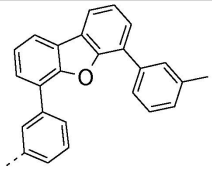
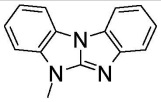
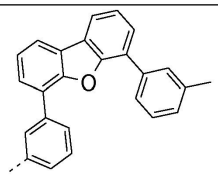
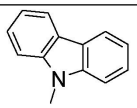
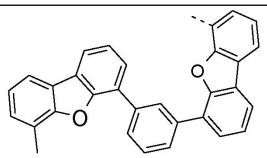
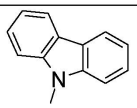
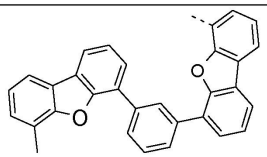
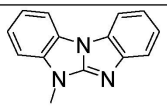
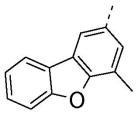
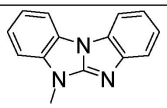
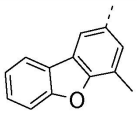
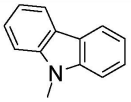
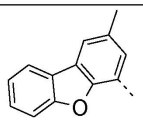
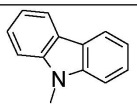
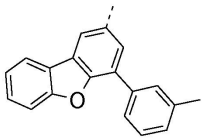
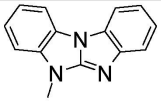
C-43		
C-44		
C-45		
C-46		
C-47		
C-48		
C-49		
C-50		

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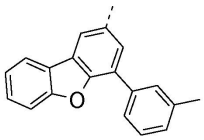
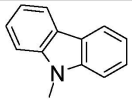
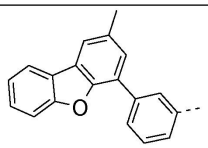
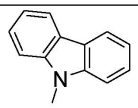
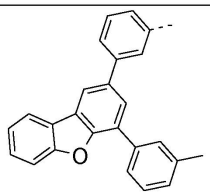
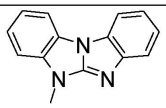
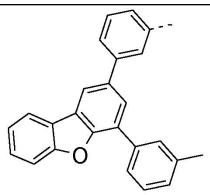
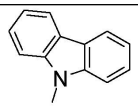
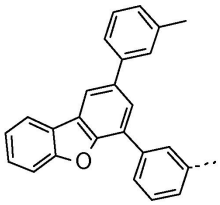
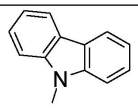
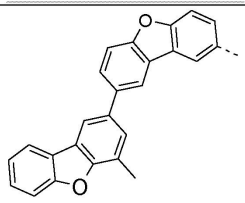
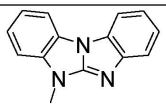
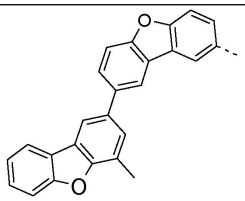
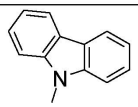
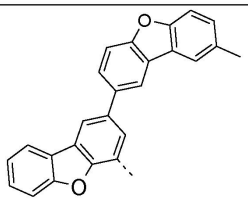
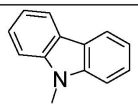
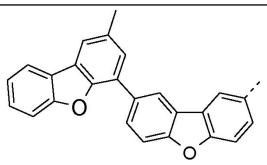
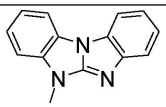
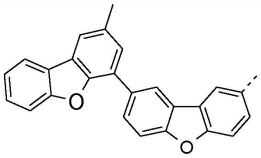
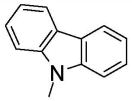
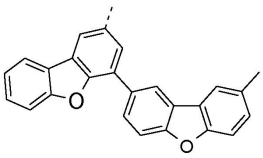
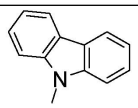
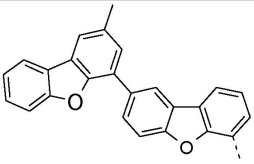
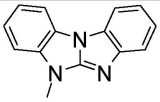
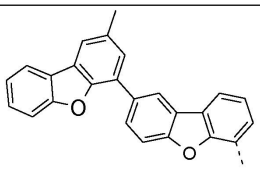
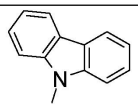
C-51		
C-52		
C-53		
C-54		
C-55		
C-56		

[0206]

C-57		
C-58		
C-59		
C-60		
C-61		
C-62		
C-63		

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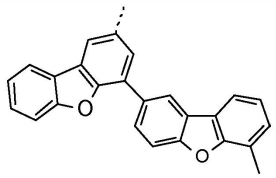
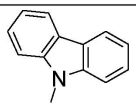
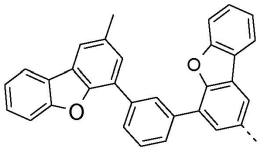
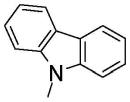
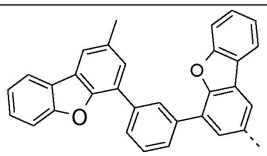
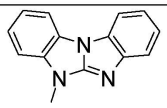
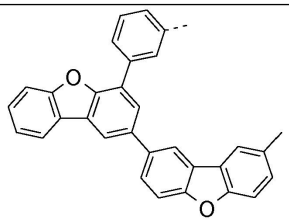
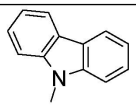
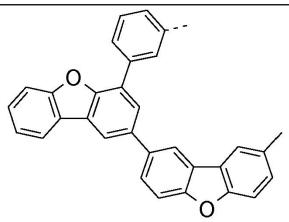
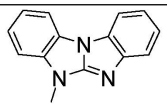
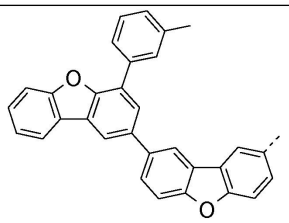
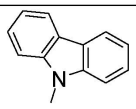
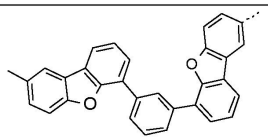
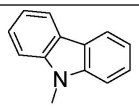
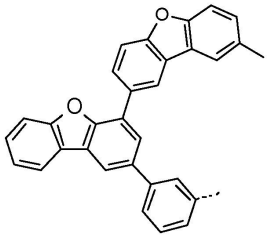
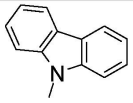
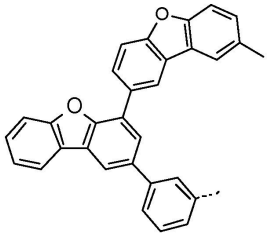
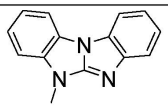
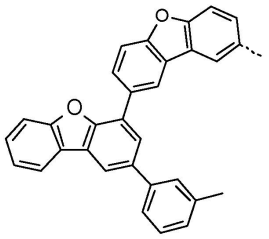
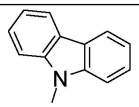
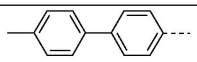
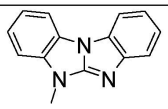
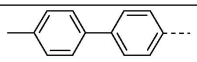
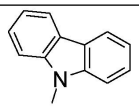
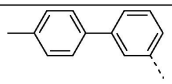
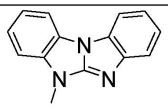
C-64		
C-65		
C-66		
C-67		
C-68		
C-69		

[0208]

[0209]

C-70		
C-71		
C-72		
C-73		
C-74		
C-75		
C-76		

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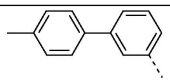
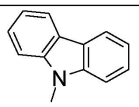
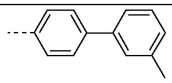
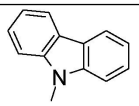
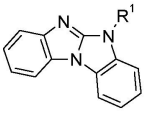
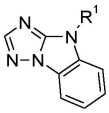
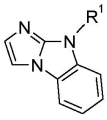
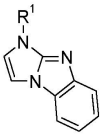
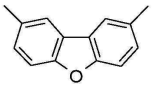
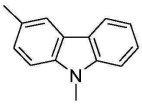
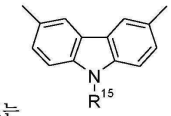
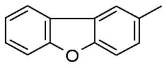
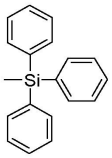
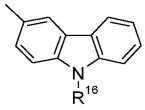
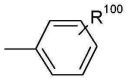
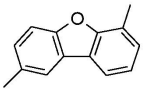
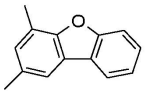
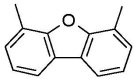
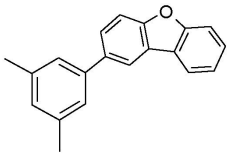
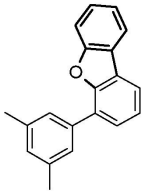
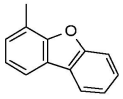
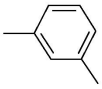
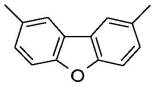
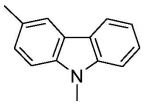
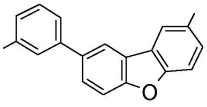
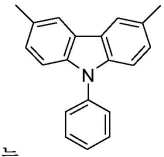
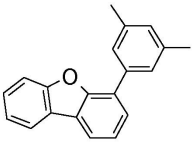
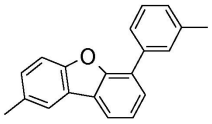
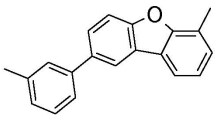
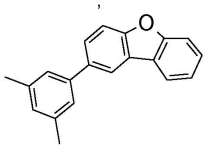
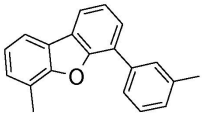
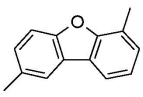
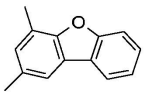
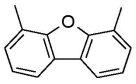
C-77		
C-78		

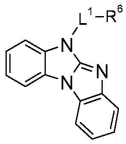
[0211] 또 다른 바람직한 실시양태에서 본 발명은 화학식  (II')의 화합물에 관한 것이다. 또 다른 바람직한 실시양태에서 본 발명은 화학식  (Ib'),  (Id') 및  (Id")의 화합물에 관한 것이다. 상기 실시양태에서 R^1은 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$의 기이고, 여기서

[0212] A^1, A^2, A^3 및 A^4는 서로 독립적으로 화학식  ,  ,  , 또는  의 기이고,

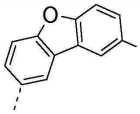
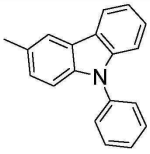
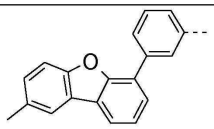
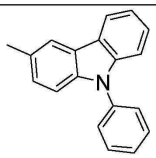
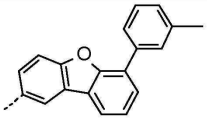
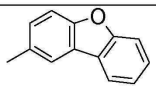
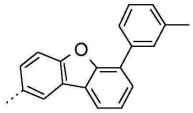
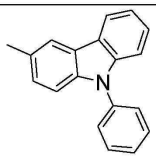
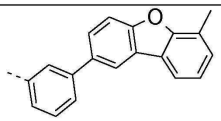
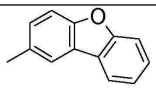
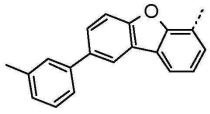
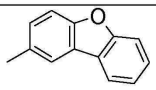
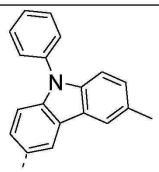
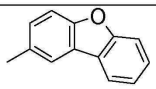
[0213] R^6은 화학식  ,  , 또는  의 기이고;

[0214] R^{15} 및 R^{16}은 화학식  , 또는  의 기이고, 여기서 R^{100}은 C_1-C_8알킬기이고, p, q 및 r은 상기 정의된 바와 같다. 게다가, A^1, A^2, A^3 및 A^4는 화학식  ,  ,  ,  , 또는  의 기를 나타낼 수 있다. 게다가, R^6은 화학식  의 기를 나타낼 수 있다. 상기 실시양태에서 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 기는 특히  ,  ,  ,  , 또는  화학식 의 기이다. 게다가, 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 기는 화학식  ,  ,  ,  ,  ,  ,  , 또는  의 기일 수 있다.

[0215] 바람직한 화합물의 예는 청구항 9에 나타낸 화합물 B-1 내지 B-5, 특히 B-1 내지 B-4, 및 하기 표에 나타낸 화합물 B-6 내지 B-35이다:

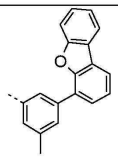
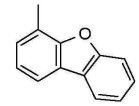
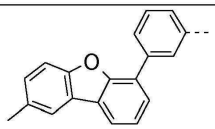
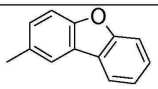
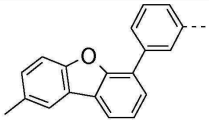
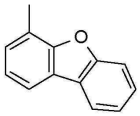
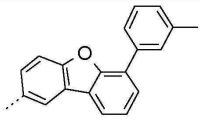
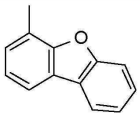
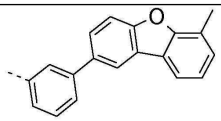
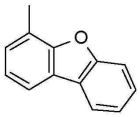
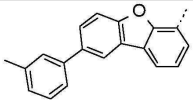
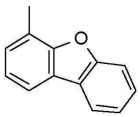
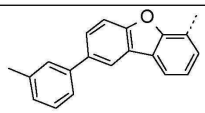
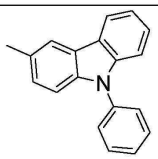
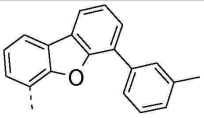
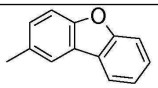
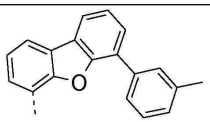
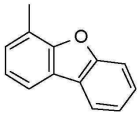


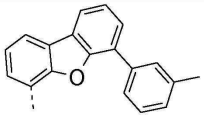
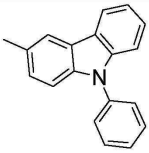
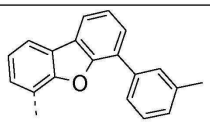
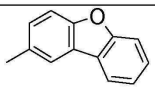
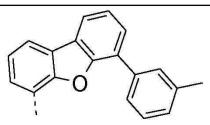
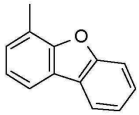
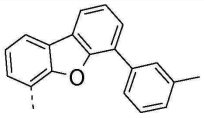
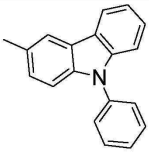
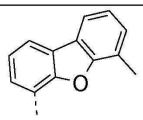
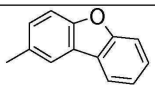
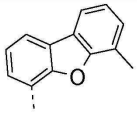
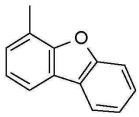
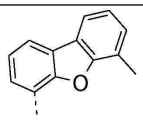
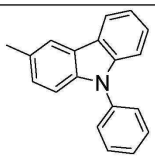
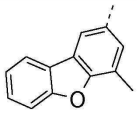
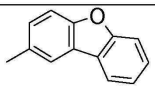
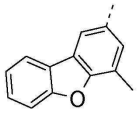
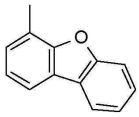
[0216]

화합물	L1 2)	R6
B-6		
B-7		
B-8		
B-9		
B-10		
B-11		
B-12		

[0217]

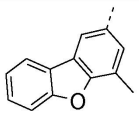
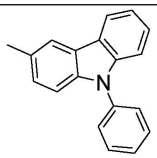
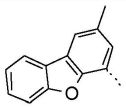
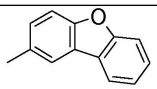
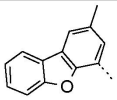
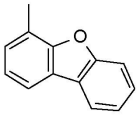
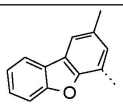
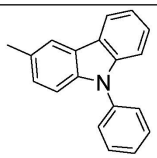
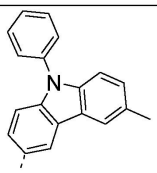
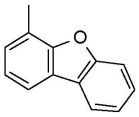
[0218]

B-13		
B-14		
B-15		
B-16		
B-17		
B-18		
B-19		
B-20		
B-21		

B-22		
B-23		
B-24		
B-25		
B-26		
B-27		
B-28		
B-29		
B-30		

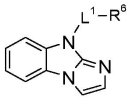
[0219]

[0220]

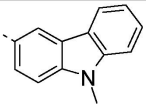
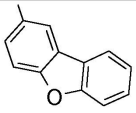
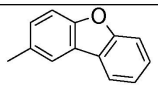
B-31		
B-32		
B-33		
B-34		
B-35		

[0221] 바람직한 화합물의 추가 예는 하기 표에 나타낸 화합물 J-1 내지 J-35, K-1 내지 K-35 및 L-1 내지 L-35이다.

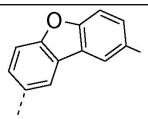
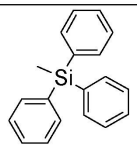
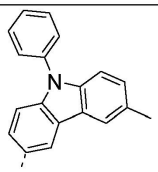
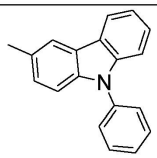
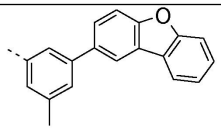
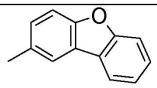
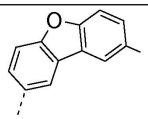
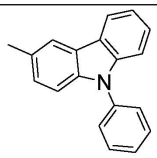
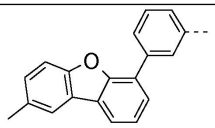
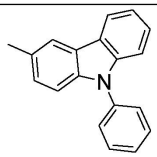
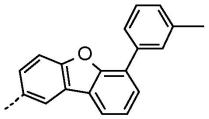
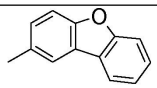
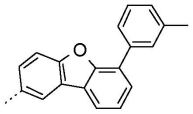
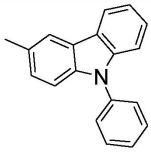
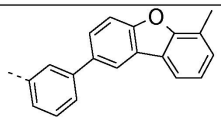
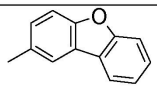
[0222]

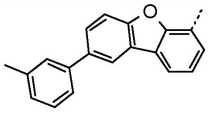
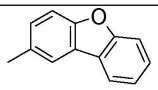
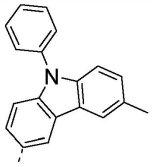
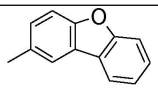
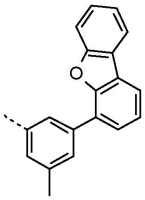
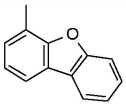
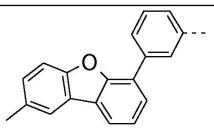
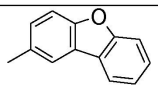
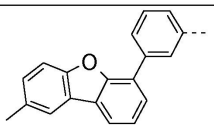
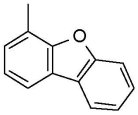
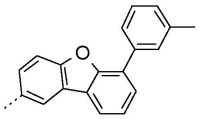
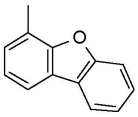
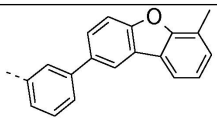
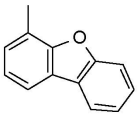
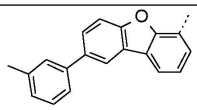
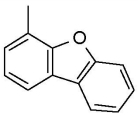


[0223]

화합물	L^1 3)	R^6
J-1		
J-2		

[0224]

J-3		
J-4		
J-5		
J-6		
J-7		
J-8		
J-9		
J-10		

J-11		
J-12		
J-13		
J-14		
J-15		
J-16		
J-17		
J-18		

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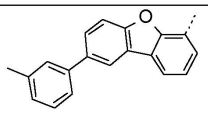
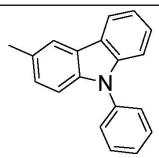
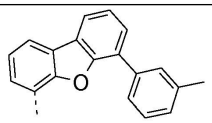
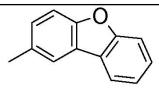
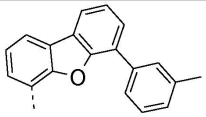
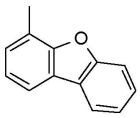
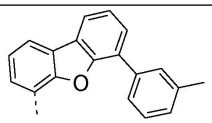
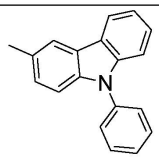
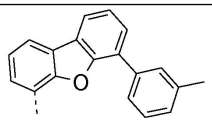
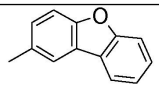
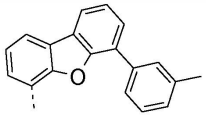
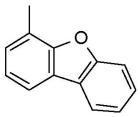
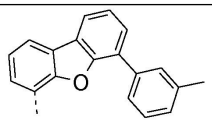
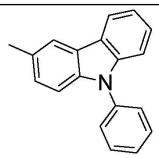
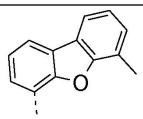
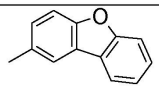
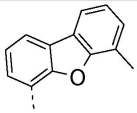
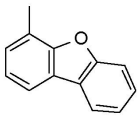
J-19		
J-20		
J-21		
J-22		
J-23		
J-24		
J-25		
J-26		
J-27		

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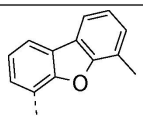
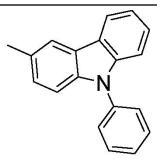
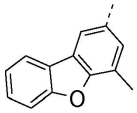
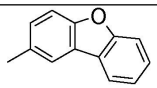
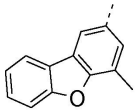
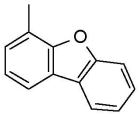
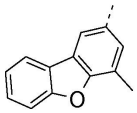
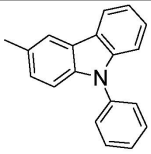
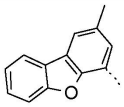
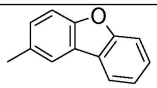
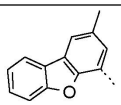
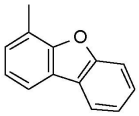
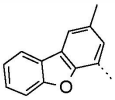
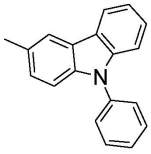
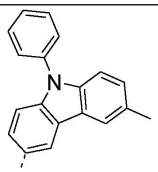
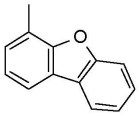
J-28		
J-29		
J-30		
J-31		
J-32		
J-33		
J-34		
J-35		

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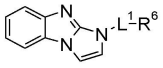
[0228] 

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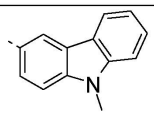
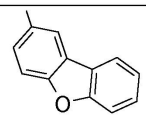
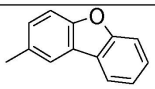
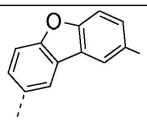
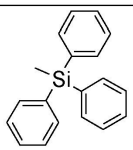
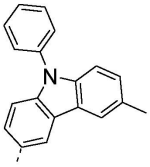
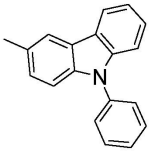
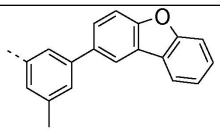
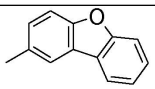
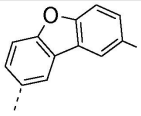
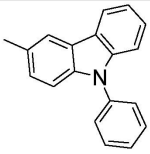
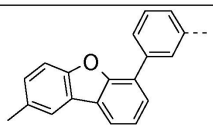
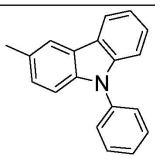
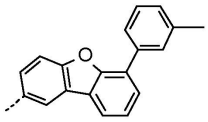
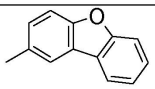
K-1		
K-2		
K-3		
K-4		
K-5		
K-6		
K-7		
K-8		

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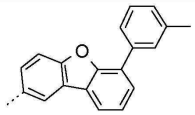
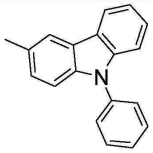
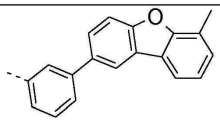
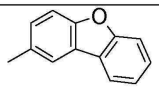
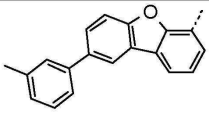
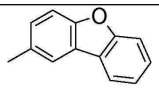
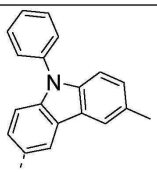
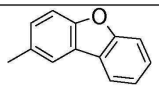
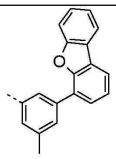
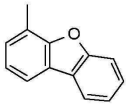
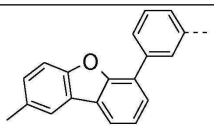
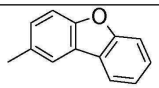
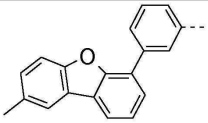
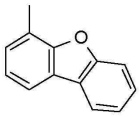
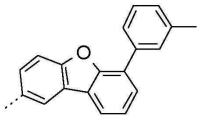
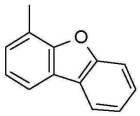
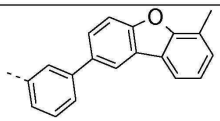
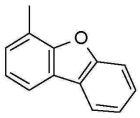
K-9		
K-10		
K-11		
K-12		
K-13		
K-14		
K-15		
K-16		
K-17		

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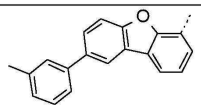
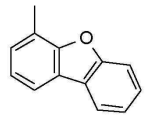
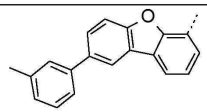
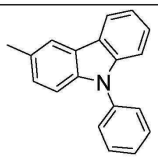
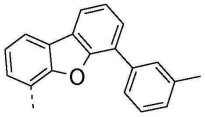
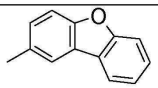
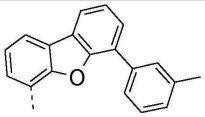
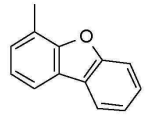
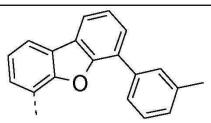
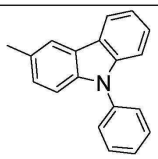
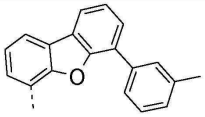
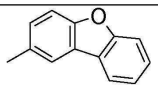
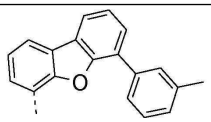
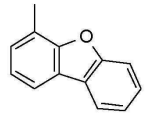
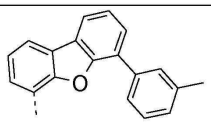
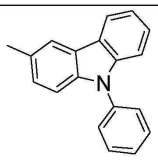
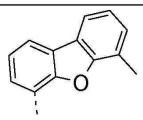
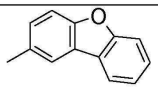
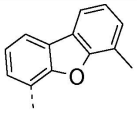
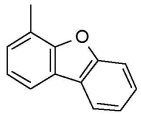
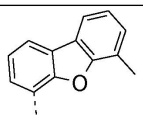
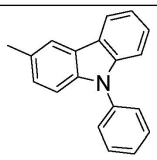
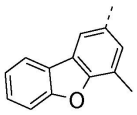
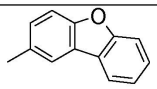
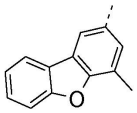
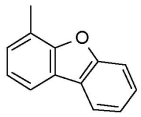
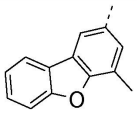
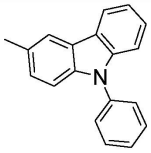
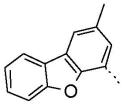
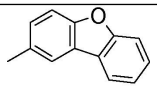
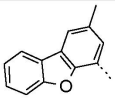
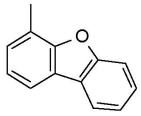
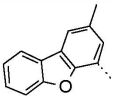
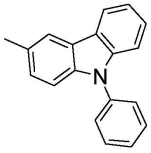
K-18		
K-19		
K-20		
K-21		
K-22		
K-23		
K-24		
K-25		
K-26		

K-27		
K-28		
K-29		
K-30		
K-31		
K-32		
K-33		
K-34		

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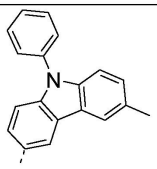
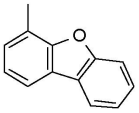
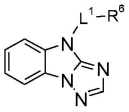
K-35		

[0233]

[0234]



[0235]

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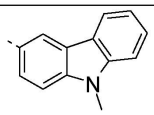
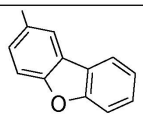
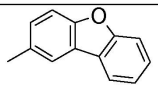
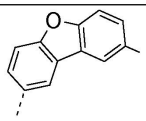
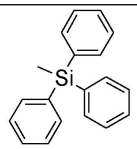
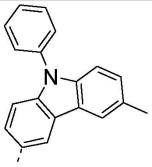
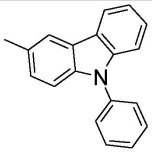
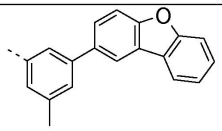
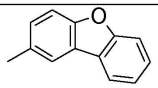
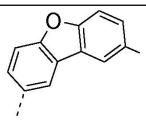
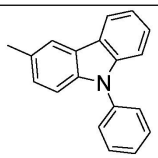
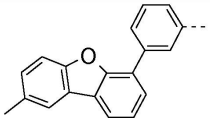
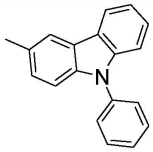
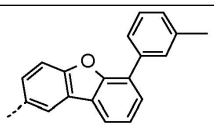
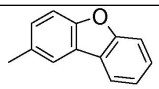
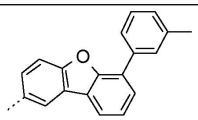
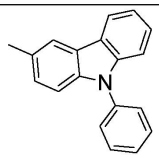
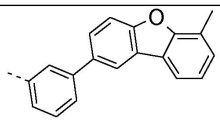
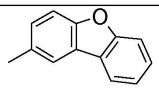
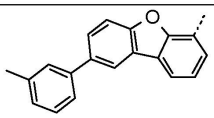
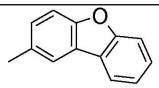
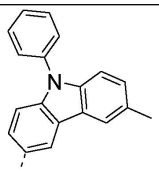
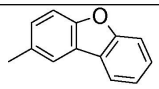
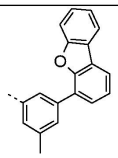
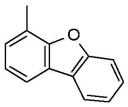
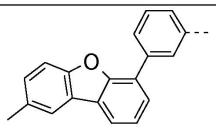
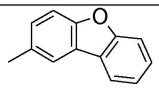
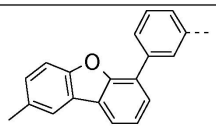
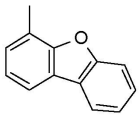
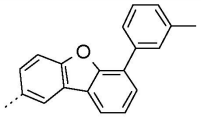
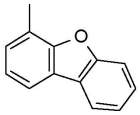
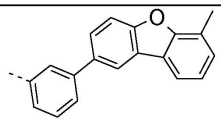
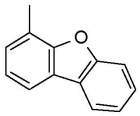
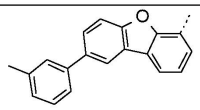
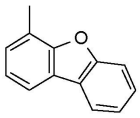
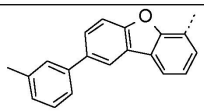
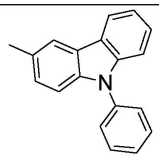
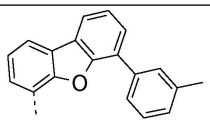
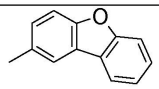
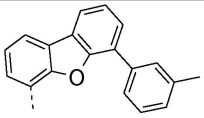
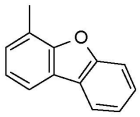
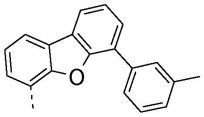
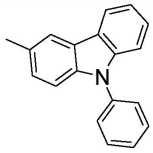
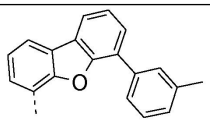
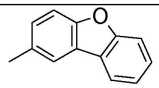
L-1		
L-2		
L-3		
L-4		
L-5		
L-6		

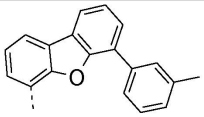
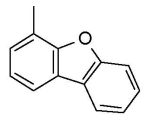
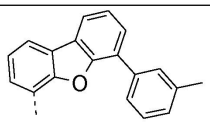
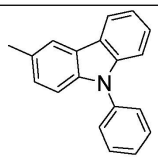
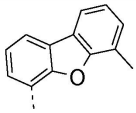
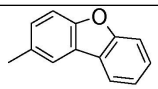
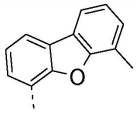
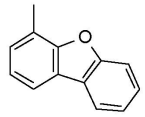
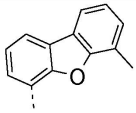
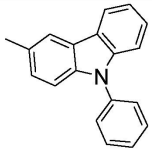
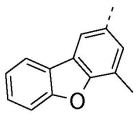
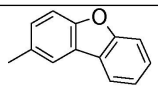
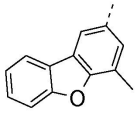
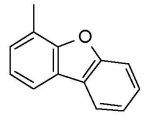
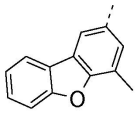
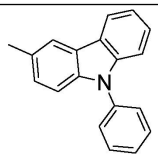
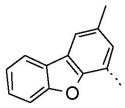
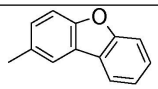
L-7		
L-8		
L-9		
L-10		
L-11		
L-12		
L-13		
L-14		

[0236]

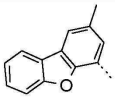
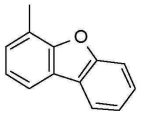
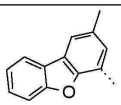
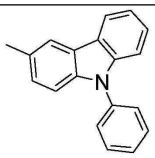
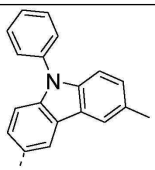
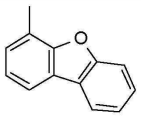
L-15		
L-16		
L-17		
L-18		
L-19		
L-20		
L-21		
L-22		
L-23		

[0237]

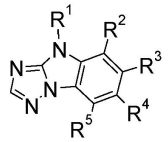
[0238]

L-24		
L-25		
L-26		
L-27		
L-28		
L-29		
L-30		
L-31		
L-32		

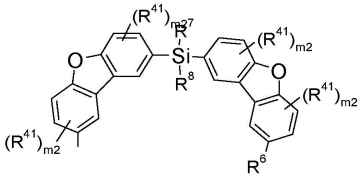
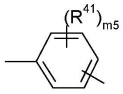
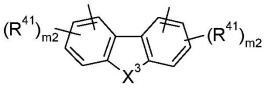
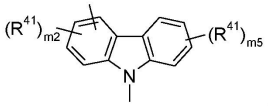
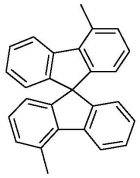
[0239]

L-33		
L-34		
L-35		

[0240] 또 다른 바람직한 실시양태에서 본 발명은 화학식  (Id'),  (Id"), 또는



(Ib)의 화합물에 관한 것이고, 여기서 R^1은 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$의 기이고; A^1, A^2, A^3, A^4, R^2, R^3, R^4, R^5, p, q 및 r은 상기 정의된 바와 같다.

[0241] R^1은 바람직하게는 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-R^6$, 또는  의 기이고, 여기서 A^1, A^2, A^3 및 A^4는 서로 독립적으로 화학식  ,  ,  또는  의 기이고, 여기서

[0242] m5는 0 또는 1 내지 4의 정수이고,

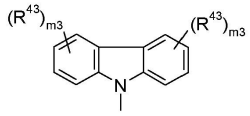
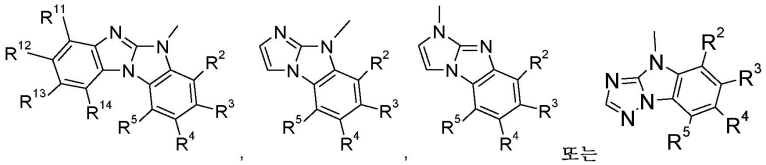
[0243] m2는 0 또는 1 내지 3의 정수이고,

[0244] X^3은 -O-, -S-, 또는 $-NR^{15}-$이고,

[0245] R^7 및 R^8은 C_1-C_{18}알킬기이고,

[0246] R^{15}는 C_1-C_{18}알킬기; -O-가 개재된 C_1-C_{18}알킬기; C_6-C_{18}아릴기; 1개 이상의 C_1-C_{18}알킬기, 또는 C_1-C_{18}알콕시기에 의해 치환된 C_6-C_{18}아릴기; C_2-C_{20}헤테로아릴기, 또는 1개 이상의 C_1-C_{18}알킬기에 의해 치환된 C_2-C_{20}헤테로아릴기이고,

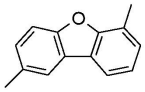
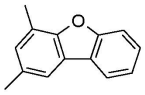
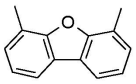
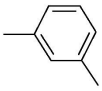
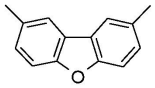
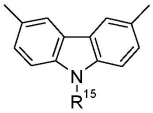
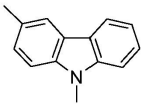
[0247] R^{41}은 각 경우에 동일하거나 상이할 수 있고 F, C_1-C_{18}알킬, E에 의해 치환되고/거나 D가 개재된 C_1-C_{18}알킬, C_6-C_{24}아릴, G에 의해 치환된 C_6-C_{24}아릴, C_2-C_{20}헤테로아릴, 또는 G에 의해 치환된 C_2-C_{20}헤테로아릴이고,

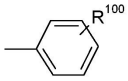
[0248] R^6은 바람직하게는 화학식  ,  또는 의 기이고,

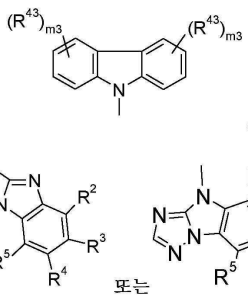
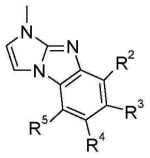
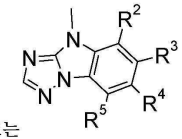
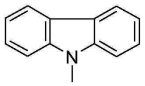
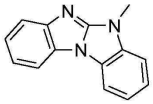
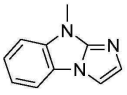
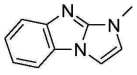
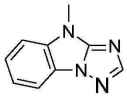
[0249] R^{43}은 각 경우에 동일하거나 상이할 수 있고 F, C_1-C_{18}알킬, E에 의해 치환되고/거나 D가 개재된 C_1-C_{18}알킬, C_6-C_{24}아릴, G에 의해 치환된 C_6-C_{24}아릴, C_2-C_{20}헤테로아릴, 또는 G에 의해 치환된 C_2-C_{20}헤테로아릴이고,

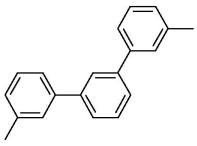
[0250] m3은 0 또는 1 내지 4의 정수이다. E, D, G, R^{11}, R^{12}, R^{13} 및 R^{14}는 상기 정의된 바와 같다.

[0251] R^2, R^3, R^4 및 R^5는 바람직하게는 수소이다.

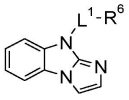
[0252] 바람직하게는, A^1, A^2, A^3 및 A^4는 서로 독립적으로 화학식  ,  ,  ,  ;  ,  ,  , 또는  의 기이고, 여기서 R^{15}는 C_6-C_{18}아릴기; 또는 1개 이상의 C_1-C_{18}알킬기에 의해 치환된 C_6-C_{18}아릴기이다.

[0253] R^{15}는 바람직하게는 화학식  , 또는  의 기이고, 여기서 R^{100}은 C_1-C_8알킬기이다.

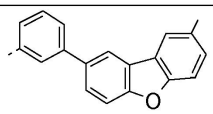
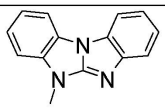
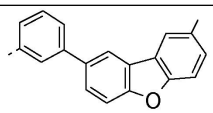
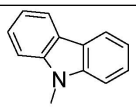
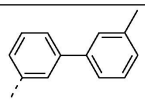
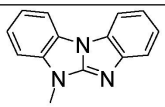
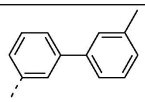
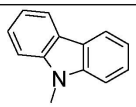
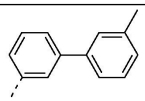
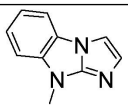
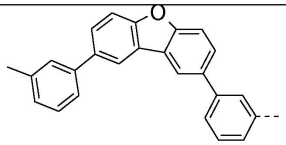
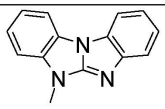
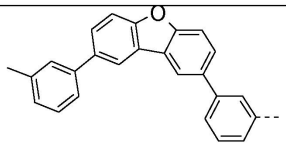
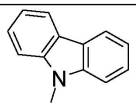
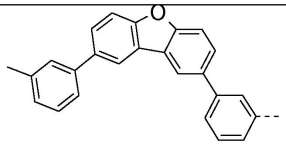
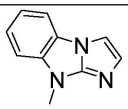
[0254] R^6은 화학식  ,  ,  , 또는  의 기, 특히 화학식  ,  ,  ,  , 또는  의 기이다. R^2, R^3, R^4, R^5, R^{11}, R^{12}, R^{13}, R^{14}, R^{43} 및 m3은 상기 정의된 바와 같다.

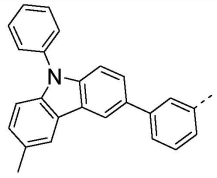
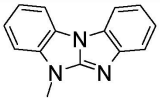
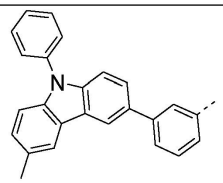
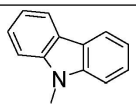
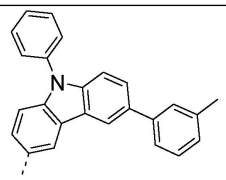
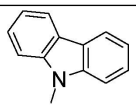
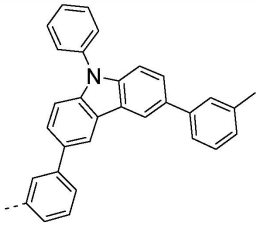
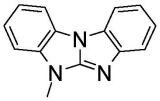
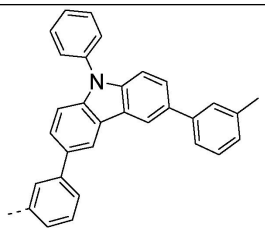
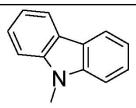
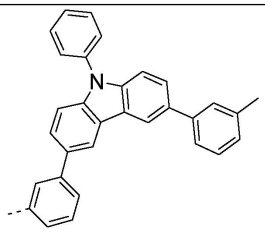
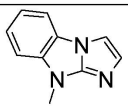
[0255] 상기 실시양태에서 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 기는 특히 화학식 IVa, IVb, IVc, IVd, IVe, IVf, IVg, IVh, IVi, IVj, IVk, IVl, IVm, IVn, IVo, IVp,  , IVq, IVr, IVs, IVt, IVu, IVv, IVw, IVx, IVy, IVz, VIa, VIb, VIc, VId, VIe, VIf, VIg, VIh, VIi, VIj, VIk, VIl, VIm, VIn, VIo, VIp, VIq, VIr, VIs, VIt, 또는 VIu의 기이다. 현재 가장 바람직한 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-$의 기는 화학식 IVa, IVb, IVe, IVl, IVk, IVs, IVv 및 VIj의 기이다.

[0256] 바람직한 화합물의 예는 하기 표에 나타낸 화합물 D-1 내지 D-144, E-1 내지 E-183뿐만 아니라 H-1 내지 H-264이다.

[0257] 

[0258]

화합물	L^{1} 3)	R^{6}
D-1		
D-2		
D-3		
D-4		
D-5		
D-6		
D-7		
D-8		

D-9		
D-10		
D-11		
D-12		
D-13		
D-14		

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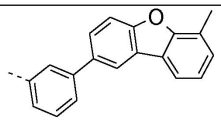
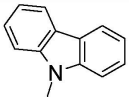
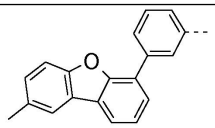
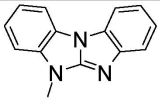
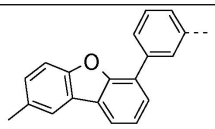
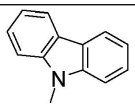
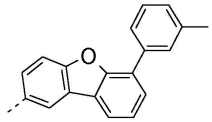
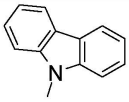
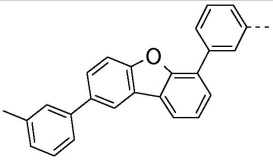
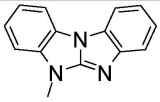
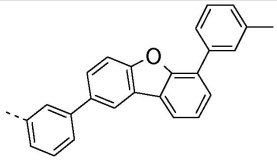
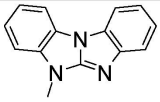
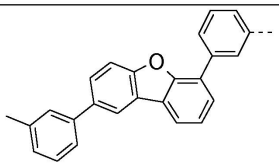
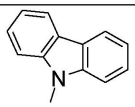
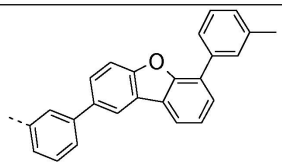
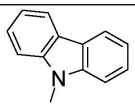
D-15		
D-16		
D-17		
D-18		
D-19		
D-20		
D-21		
D-22		

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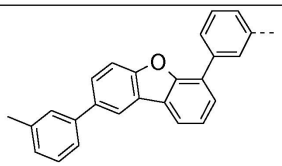
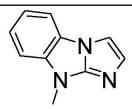
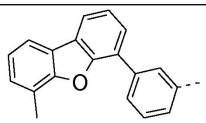
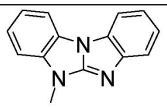
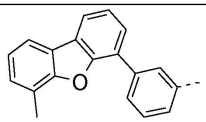
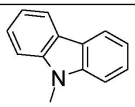
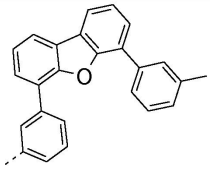
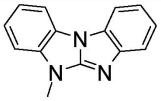
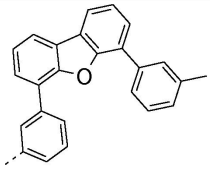
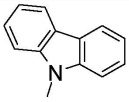
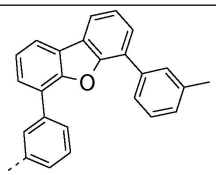
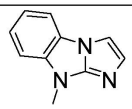
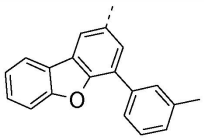
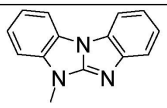
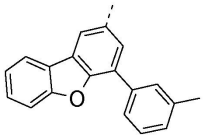
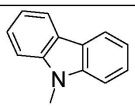
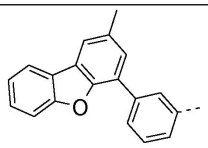
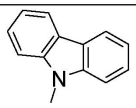
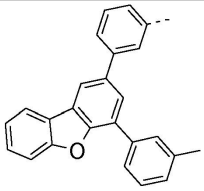
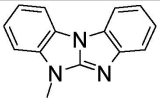
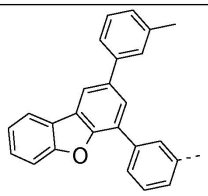
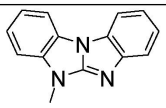
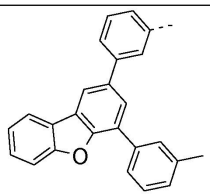
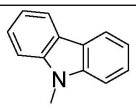
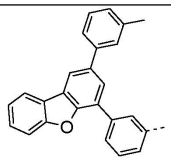
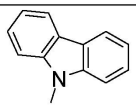
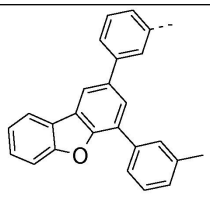
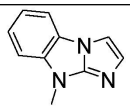
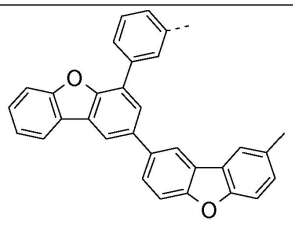
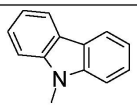
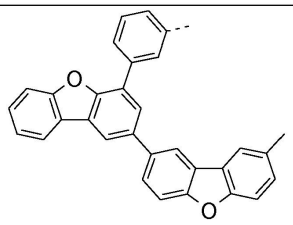
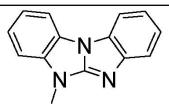
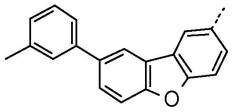
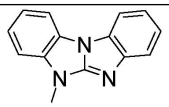
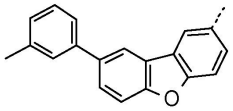
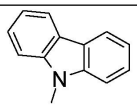
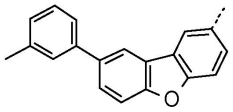
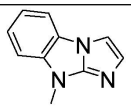
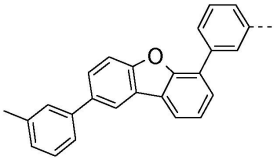
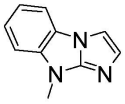
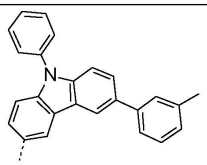
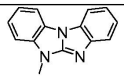
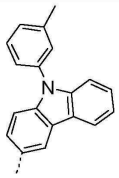
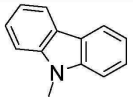
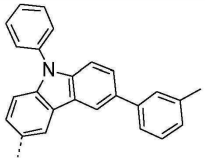
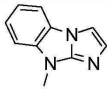
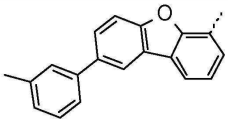
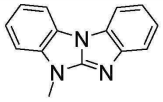
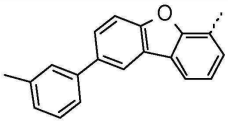
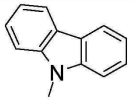
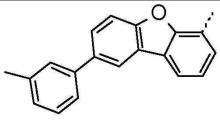
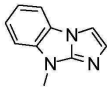
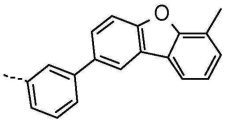
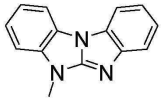
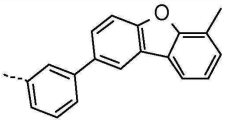
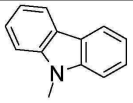
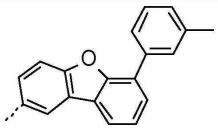
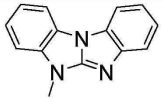
D-23		
D-24		
D-25		
D-26		
D-27		
D-28		
D-29		
D-30		

D-31		
D-32		
D-33		
D-34		
D-35		
D-36		

[0262]

[0263]

D-37		
D-38		
D-39		
D-40		
D-41		
D-42		
D-43		

D-44		
D-45		
D-46		
D-47		
D-48		
D-49		
D-50		
D-51		

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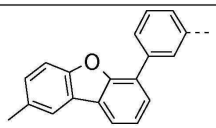
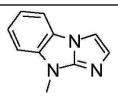
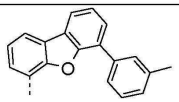
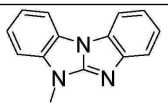
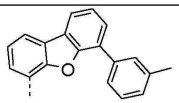
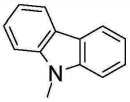
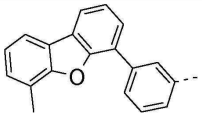
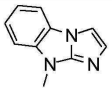
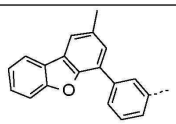
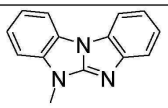
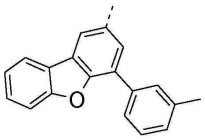
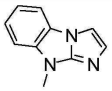
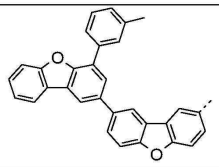
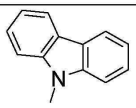
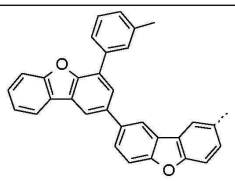
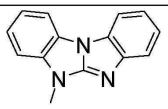
D-52		
D-53		
D-55		
D-56		
D-57		
D-58		
D-59		
D-60		

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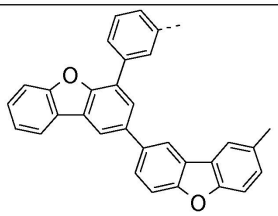
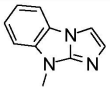
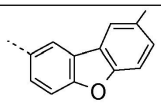
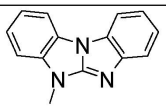
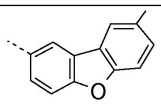
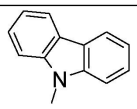
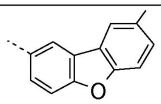
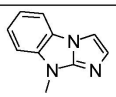
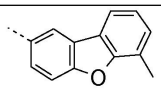
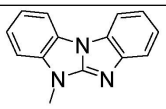
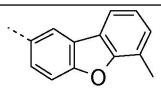
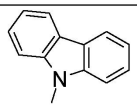
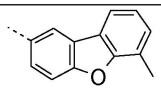
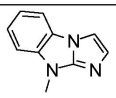
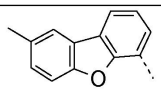
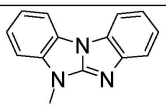
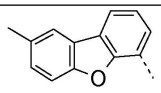
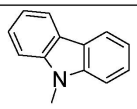
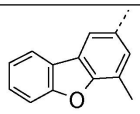
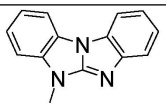
D-61		
D-62		
D-63		
D-64		
D-65		
D-66		
D-67		
D-68		
D-69		
D-70		

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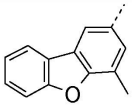
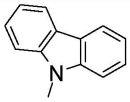
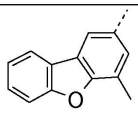
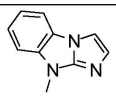
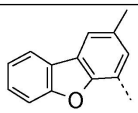
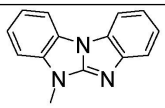
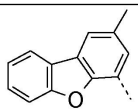
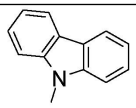
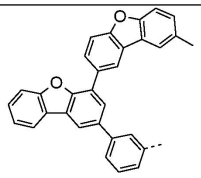
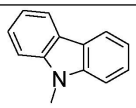
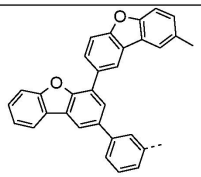
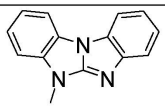
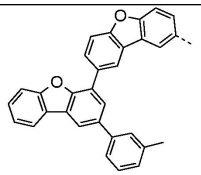
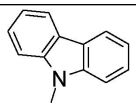
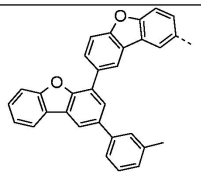
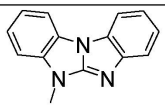
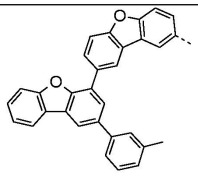
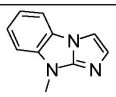
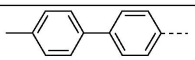
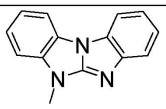
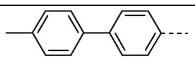
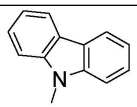
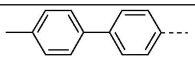
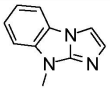
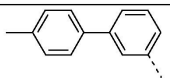
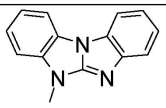
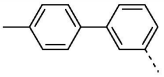
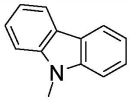
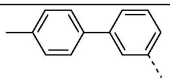
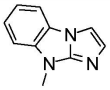
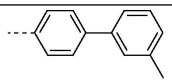
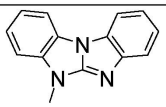
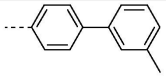
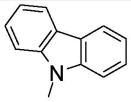
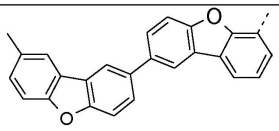
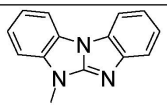
D-71		
D-72		
D-73		
D-74		
D-75		
D-76		
D-77		
D-78		

D-79		
D-80		
D-81		
D-82		
D-83		
D-84		
D-85		
D-86		
D-87		
D-88		

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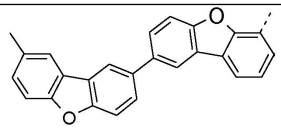
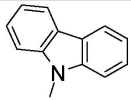
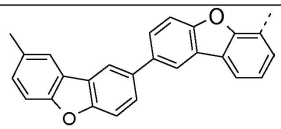
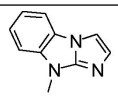
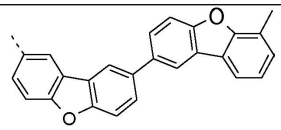
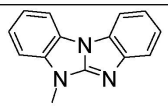
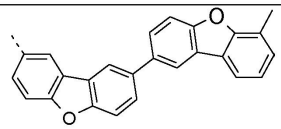
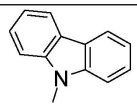
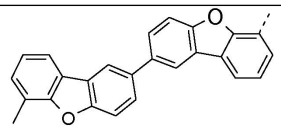
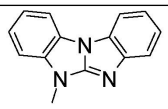
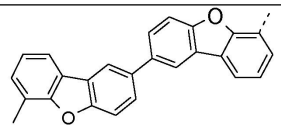
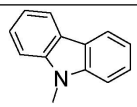
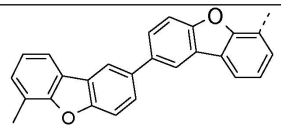
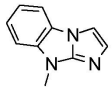
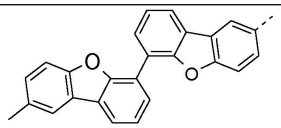
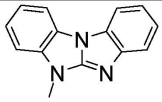
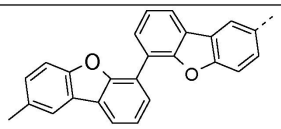
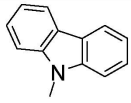
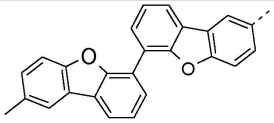
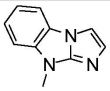
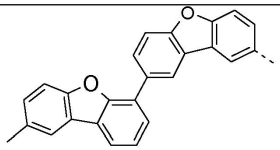
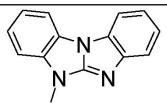
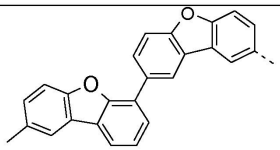
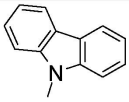
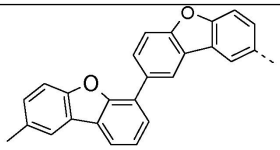
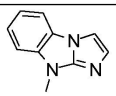
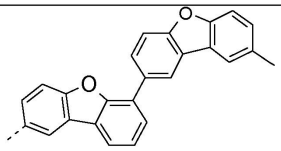
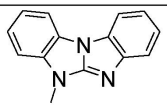
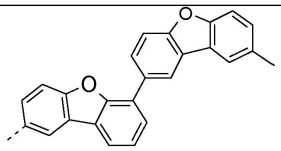
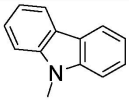
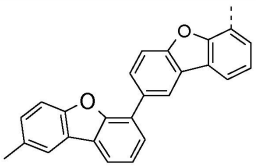
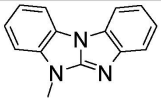
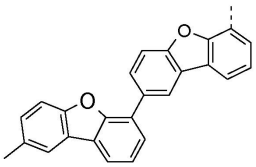
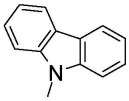
D-89		
D-90		
D-91		
D-92		
D-93		
D-94		
D-95		
D-96		
D-97		

D-98		
D-99		
D-100		
D-101		
D-102		
D-103		
D-104		
D-105		

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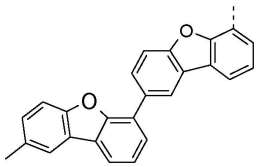
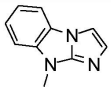
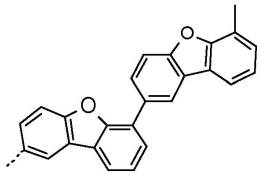
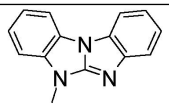
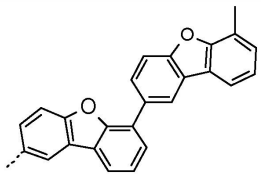
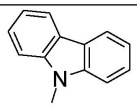
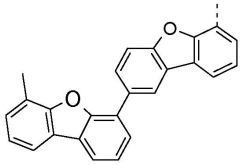
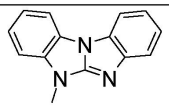
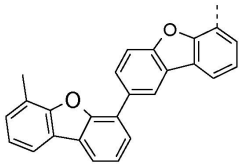
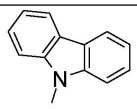
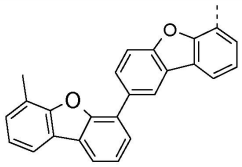
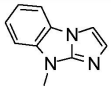
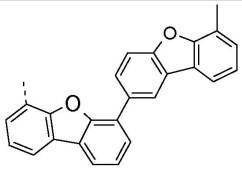
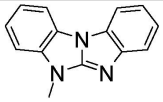
D-106		
D-107		
D-108		
D-109		
D-110		
D-111		
D-112		

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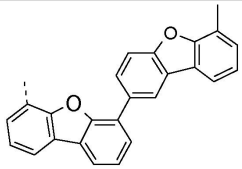
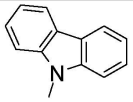
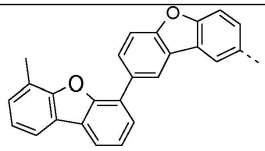
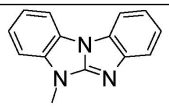
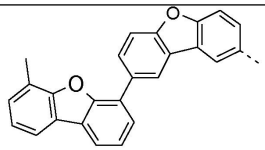
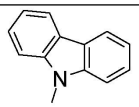
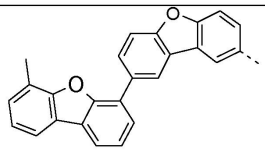
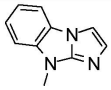
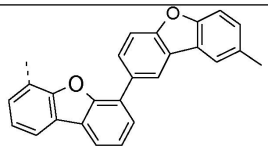
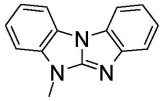
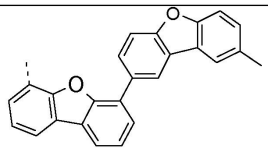
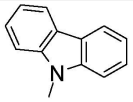
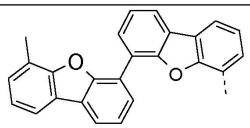
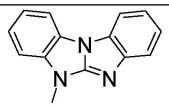
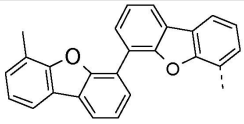
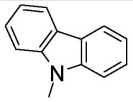
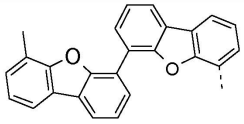
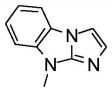
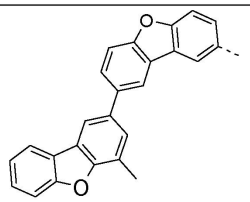
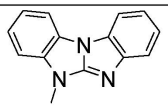
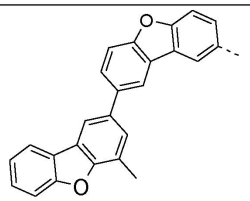
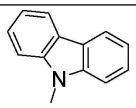
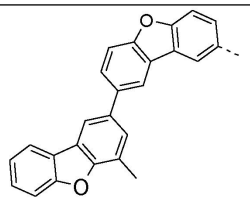
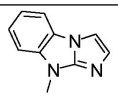
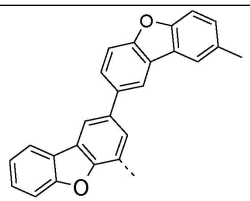
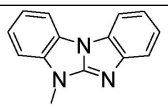
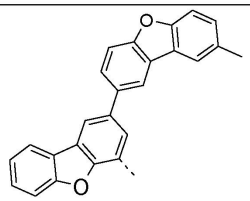
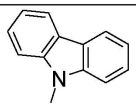
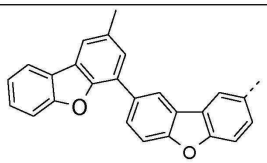
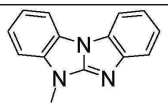
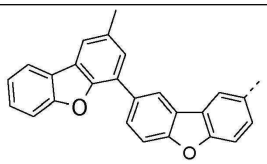
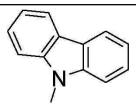
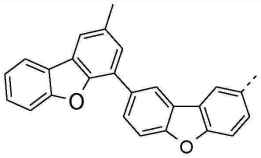
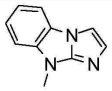
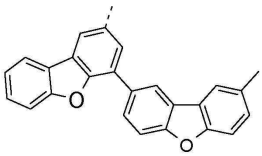
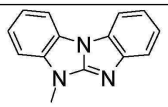
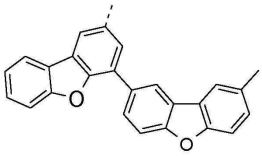
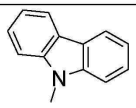
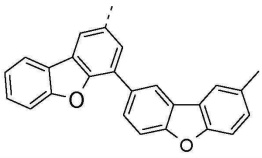
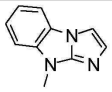
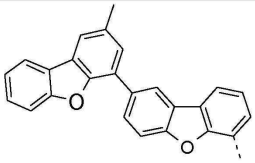
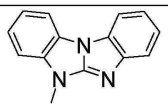
D-113		
D-114		
D-115		
D-116		
D-117		
D-118		
D-119		
D-120		

[0272]

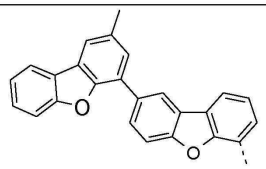
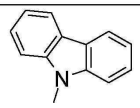
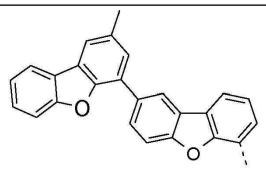
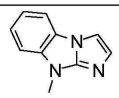
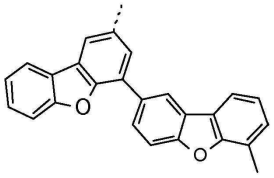
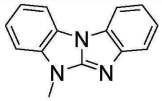
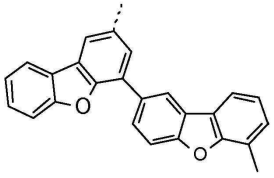
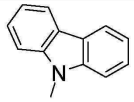
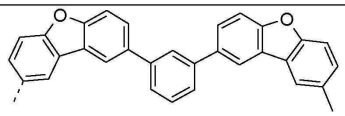
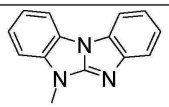
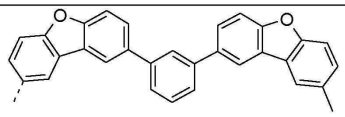
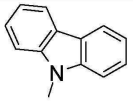
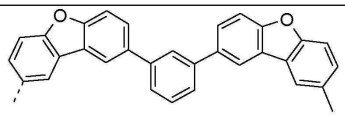
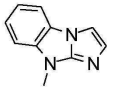
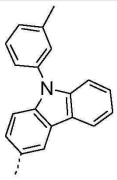
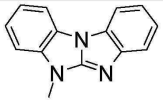
[0273]

D-121		
D-122		
D-123		
D-124		
D-125		
D-126		

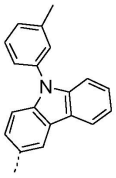
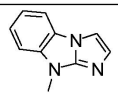
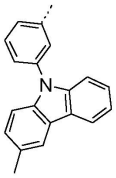
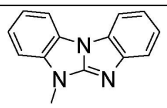
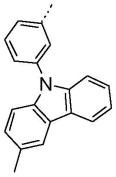
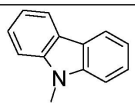
D-127		
D-128		
D-129		
D-130		
D-131		
D-132		
D-133		

[0274]

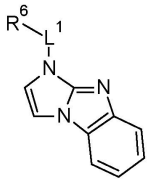
[0275]

D-134		
D-135		
D-136		
D-137		
D-138		
D-139		
D-140		
D-141		

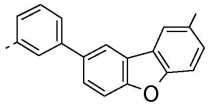
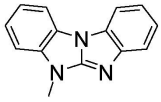
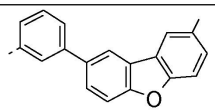
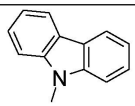
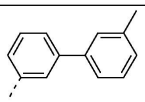
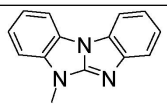
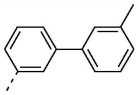
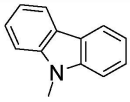
[0276]

D-142		
D-143		
D144		

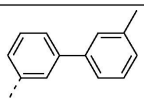
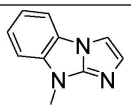
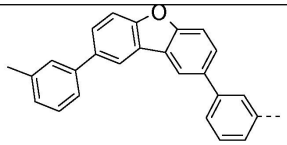
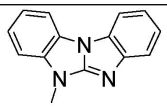
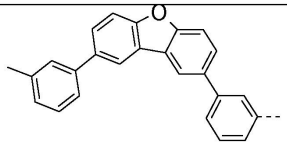
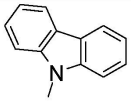
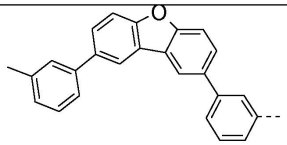
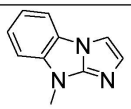
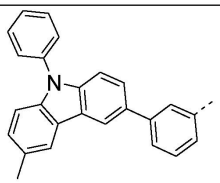
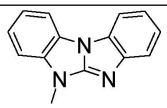
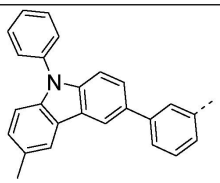
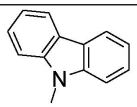
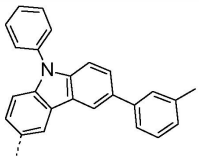
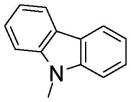
[0277]



[0278]

화합물	L^{1} 3)	R^{6}
E-1		
E-2		
E-3		
E-4		

[0279]

E-5		
E-6		
E-7		
E-8		
E-9		
E-10		
E-11		

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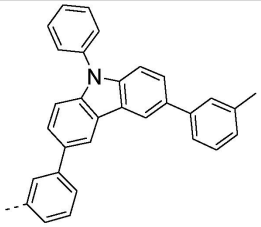
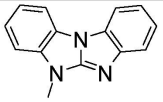
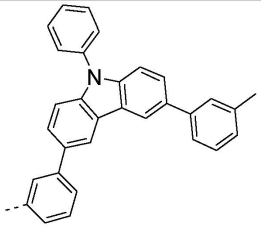
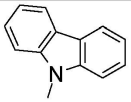
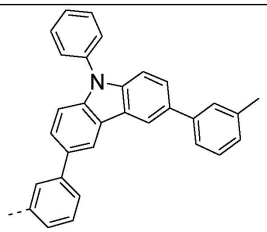
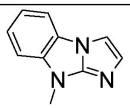
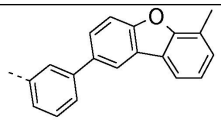
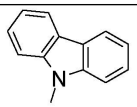
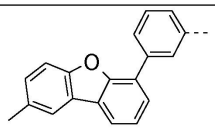
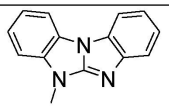
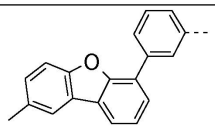
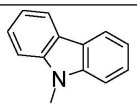
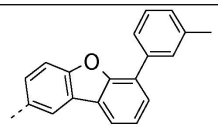
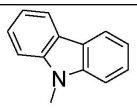
E-12		
E-13		
E-14		
E-15		
E-16		
E-17		
E-18		

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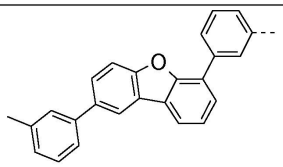
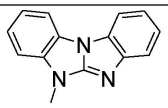
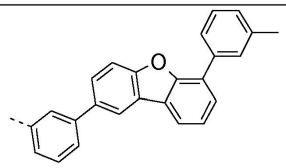
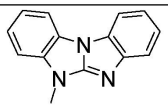
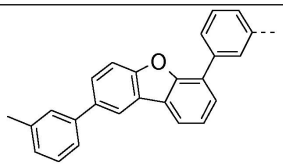
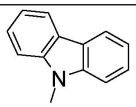
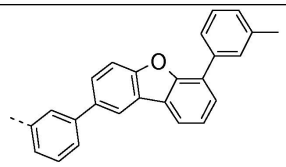
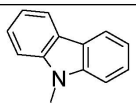
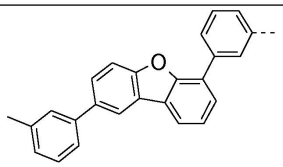
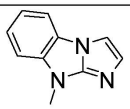
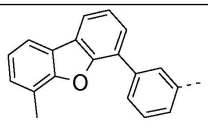
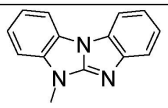
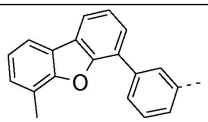
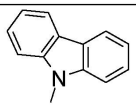
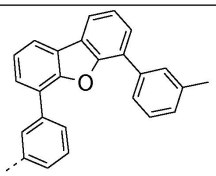
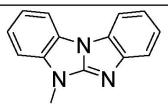
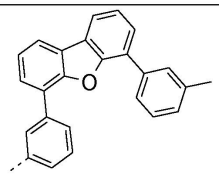
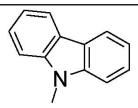
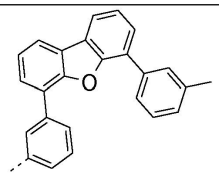
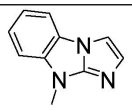
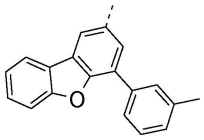
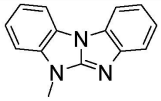
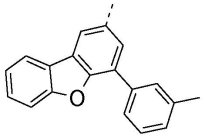
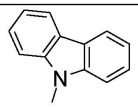
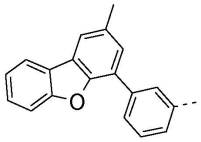
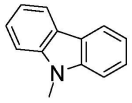
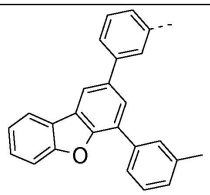
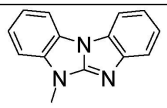
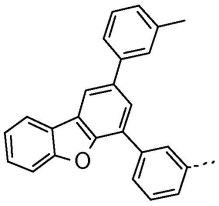
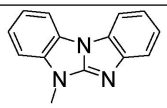
E-19		
E-20		
E-21		
E-22		
E-23		
E-24		
E-25		
E-26		

E-27		
E-28		
E-29		
E-30		
E-31		
E-32		
E-33		

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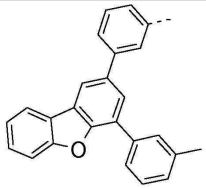
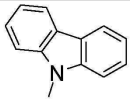
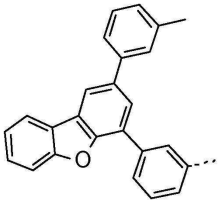
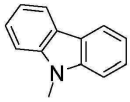
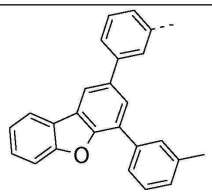
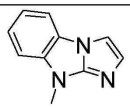
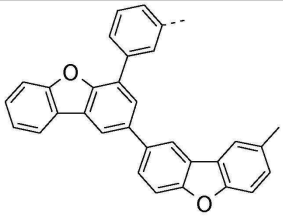
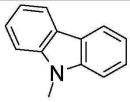
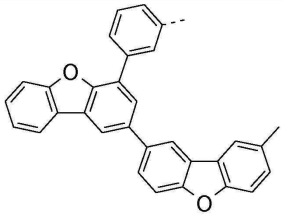
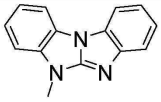
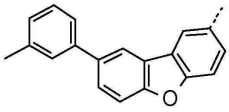
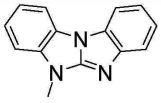
E-34		
E-35		
E-36		
E-37		
E-38		
E-39		

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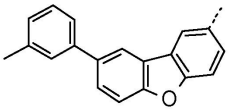
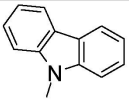
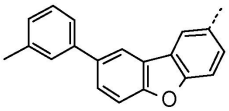
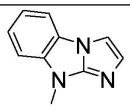
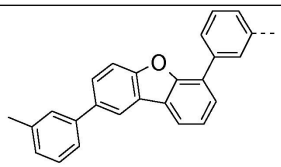
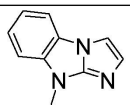
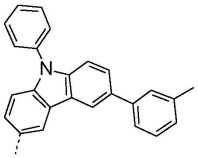
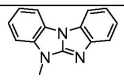
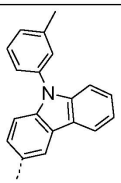
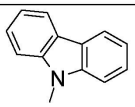
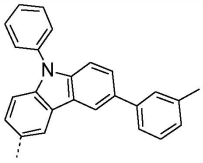
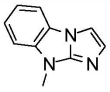
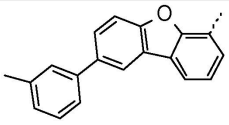
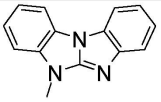
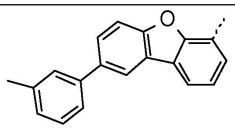
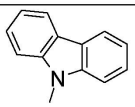
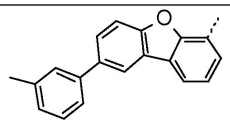
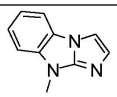
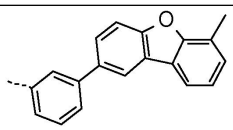
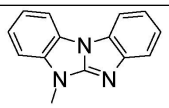
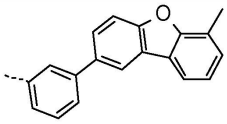
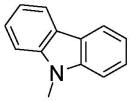
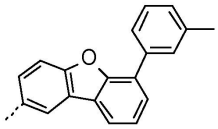
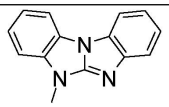
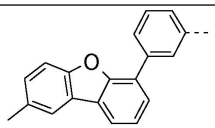
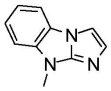
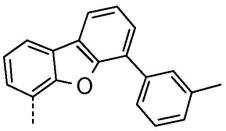
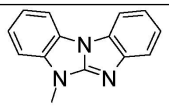
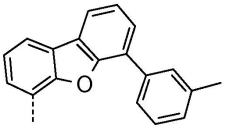
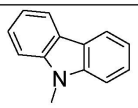
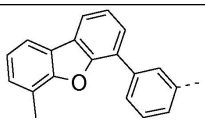
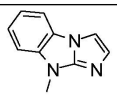
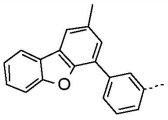
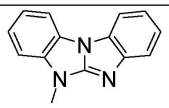
E-40		
E-41		
E-42		
E-43		
E-44		
E-45		
E-46		
E-47		

E-48		
E-49		
E-50		
E-51		
E-52		
E-53		
E-55		
E-56		
E-57		

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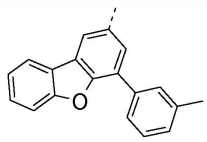
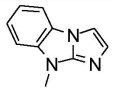
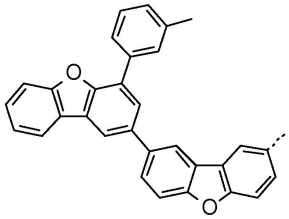
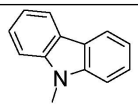
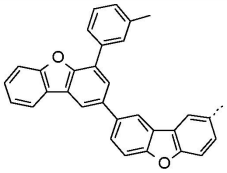
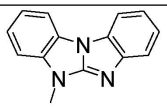
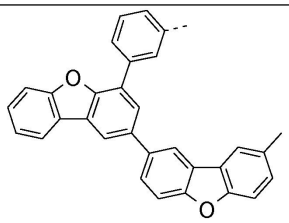
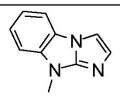
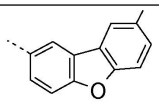
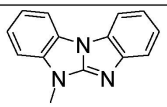
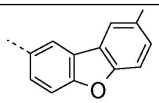
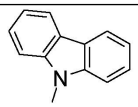
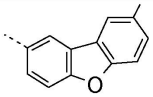
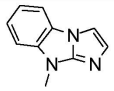
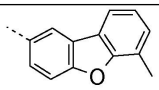
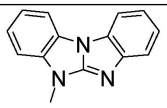
E-58		
E-59		
E-60		
E-61		
E-62		
E-63		
E-64		
E-65		

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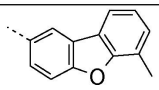
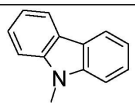
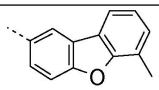
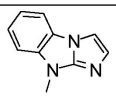
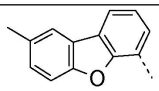
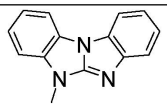
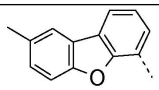
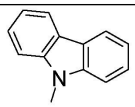
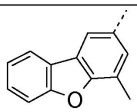
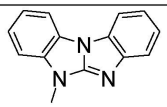
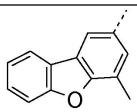
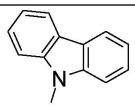
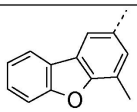
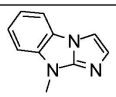
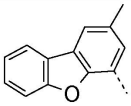
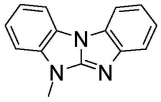
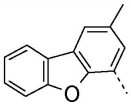
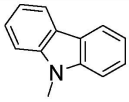
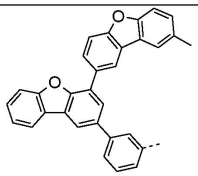
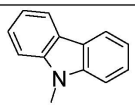
E-66		
E-67		
E-68		
E-69		
E-70		
E-71		
E-72		
E-73		
E-74		
E-75		

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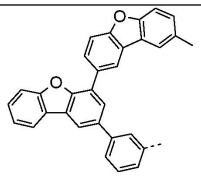
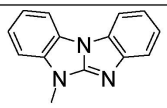
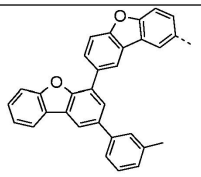
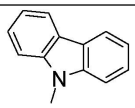
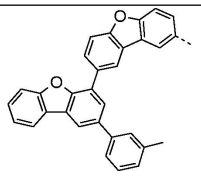
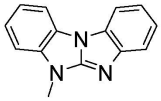
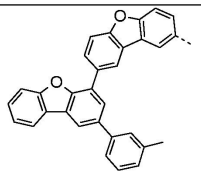
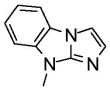
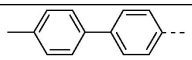
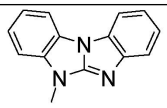
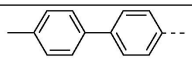
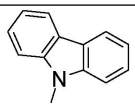
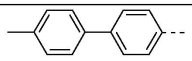
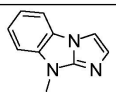
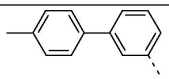
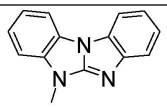
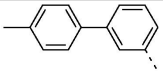
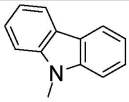
E-76		
E-77		
E-78		
E-79		
E-80		
E-81		
E-82		
E-83		
E-84		

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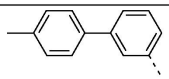
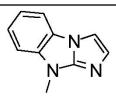
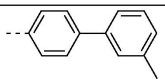
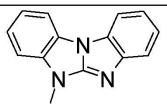
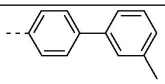
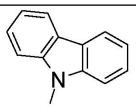
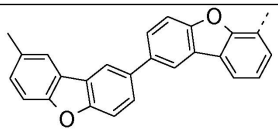
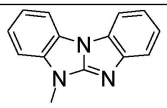
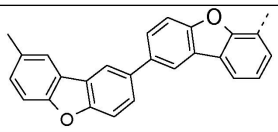
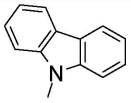
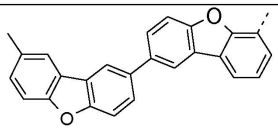
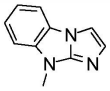
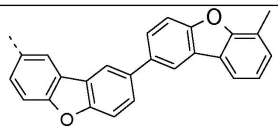
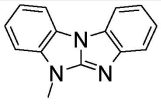
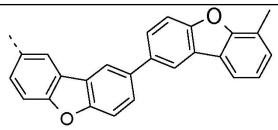
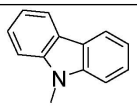
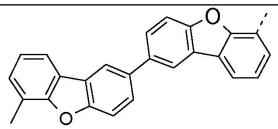
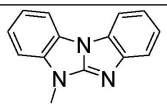
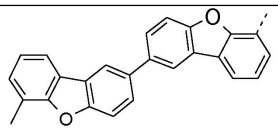
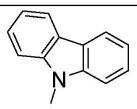
E-85		
E-86		
E-87		
E-88		
E-89		
E-90		
E-91		
E-92		
E-93		
E-94		

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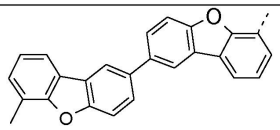
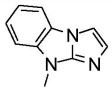
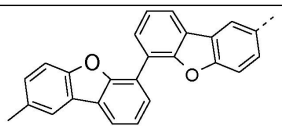
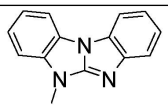
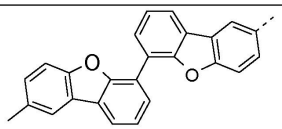
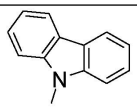
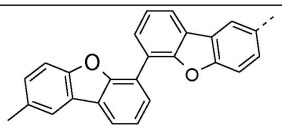
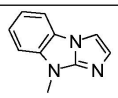
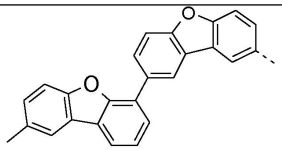
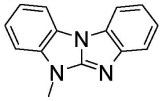
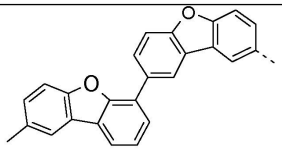
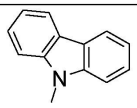
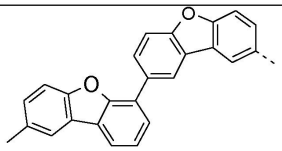
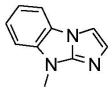
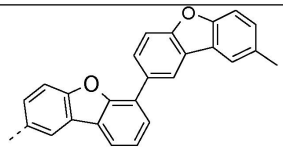
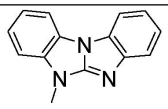
[0290]

E-95		
E-96		
E-97		
E-98		
E-99		
E-100		
E-101		
E-102		

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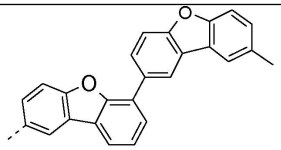
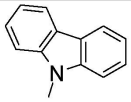
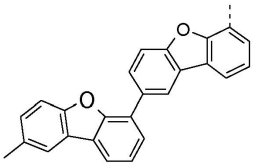
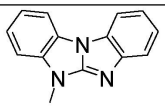
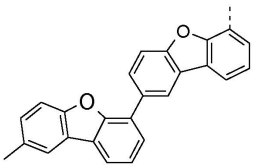
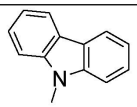
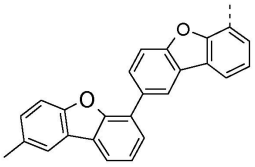
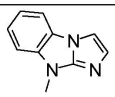
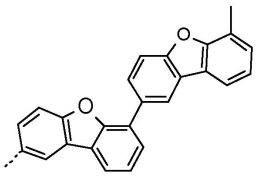
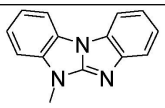
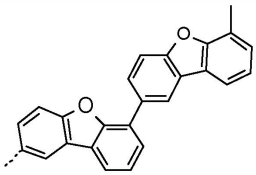
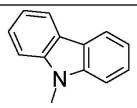
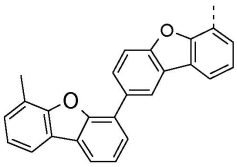
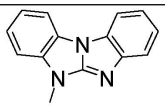
E-103		
E-104		
E-105		
E-106		
E-107		
E-108		
E-109		

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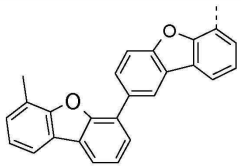
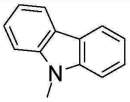
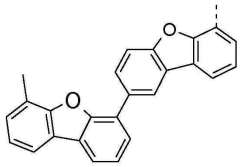
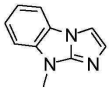
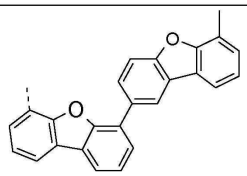
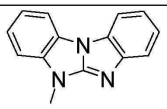
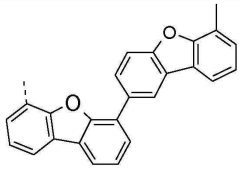
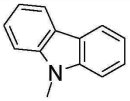
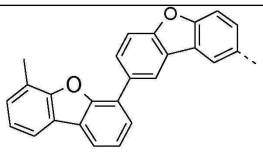
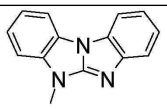
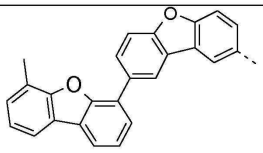
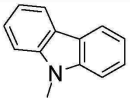
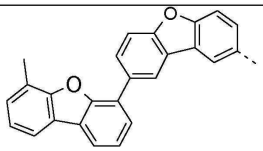
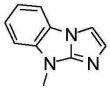
E-110		
E-111		
E-112		
E-113		
E-114		
E-115		
E-116		

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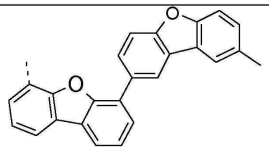
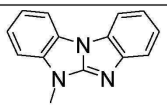
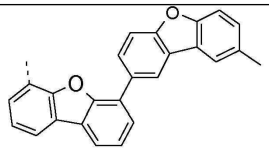
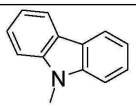
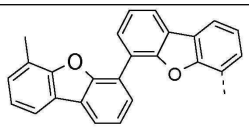
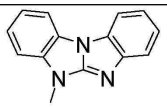
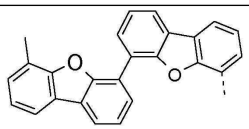
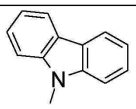
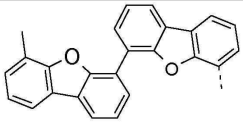
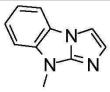
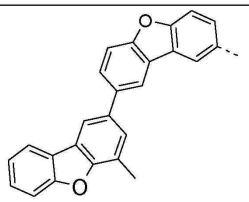
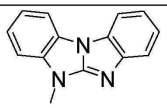
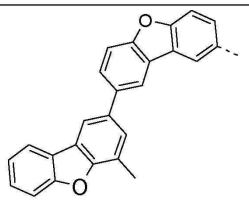
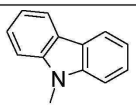
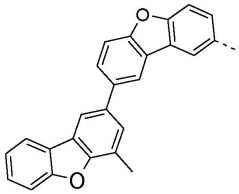
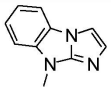
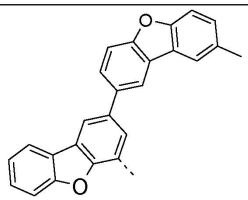
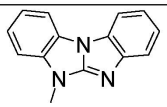
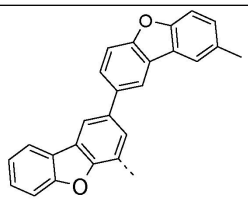
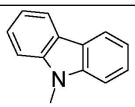
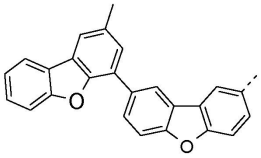
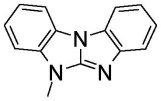
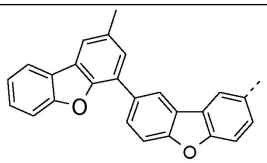
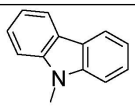
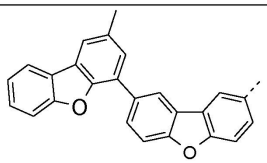
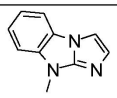
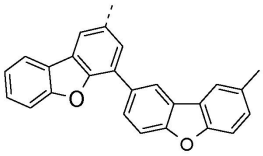
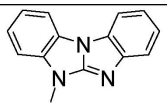
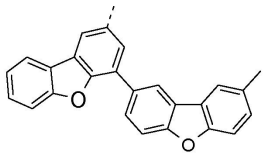
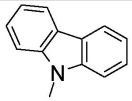
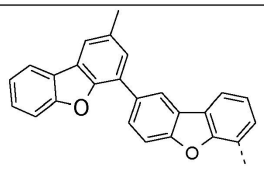
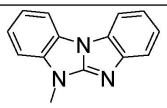
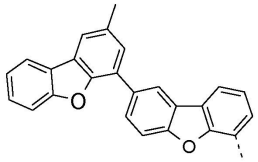
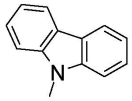
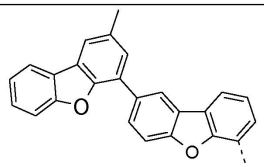
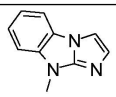
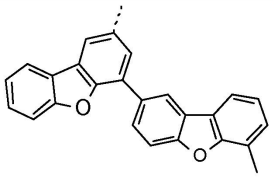
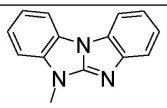
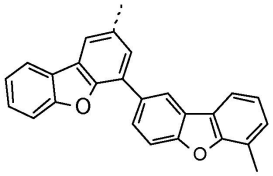
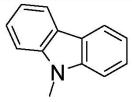
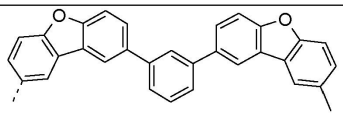
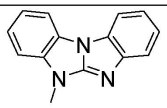
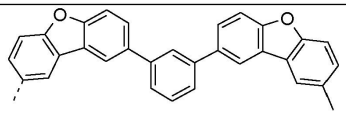
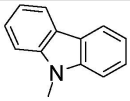
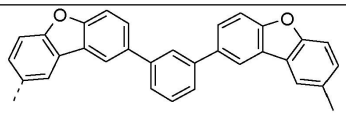
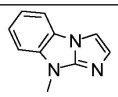
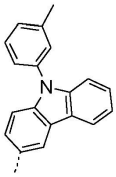
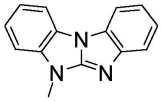
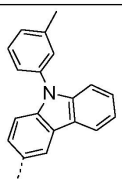
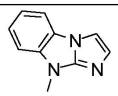
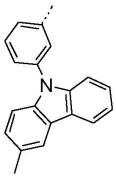
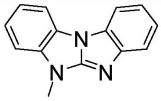
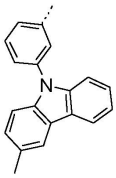
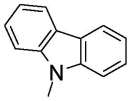
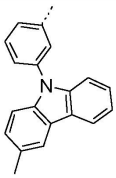
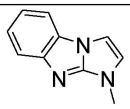
E-117		
E-118		
E-119		
E-120		
E-121		
E-122		
E-123		

E-124		
E-125		
E-126		
E-127		
E-128		
E-129		
E-130		

[0294]

[0295]

E-131		
E-132		
E-133		
E-134		
E-135		
E-136		
E-137		

E-138		
E-139		
E-140		
E-141		
E-142		
E-143		
E-144		

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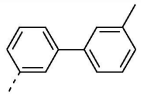
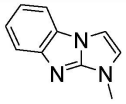
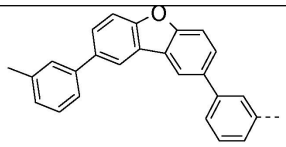
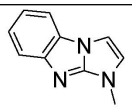
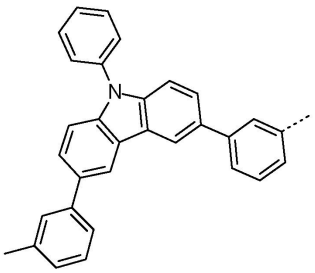
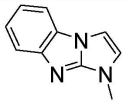
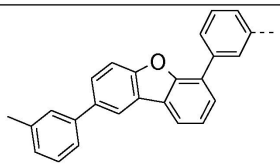
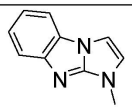
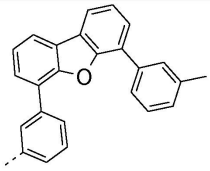
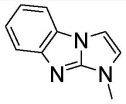
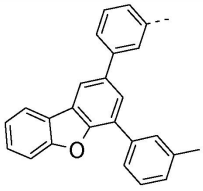
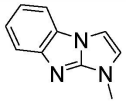
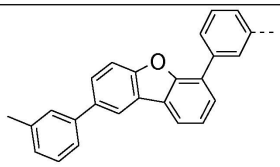
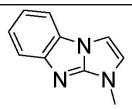
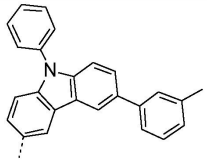
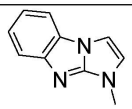
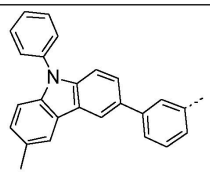
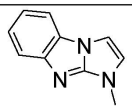
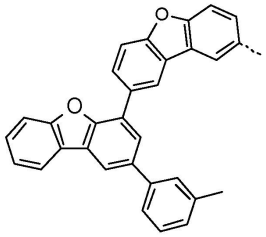
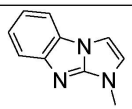
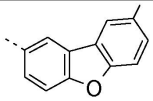
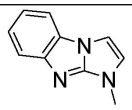
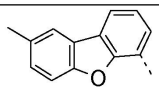
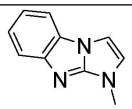
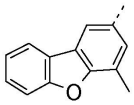
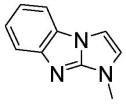
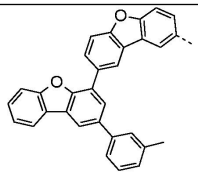
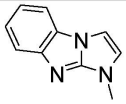
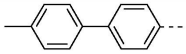
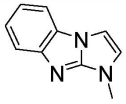
E-145		
E-146		
E-147		
E-148		
E-149		
E-150		
E-151		

E-152		
E-153		
E-154		
E-155		
E-156		
E-157		
E-158		
E-159		

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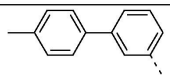
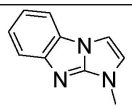
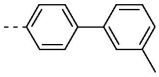
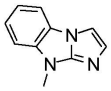
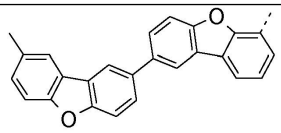
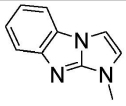
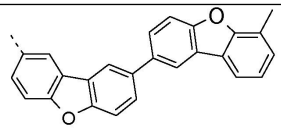
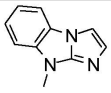
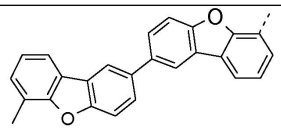
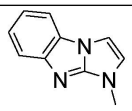
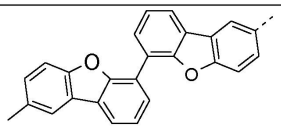
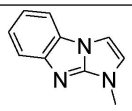
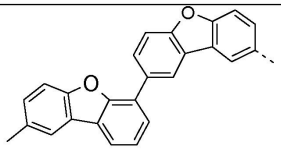
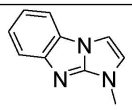
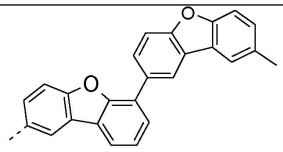
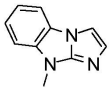
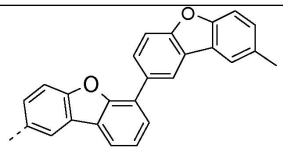
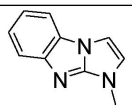
E-160		
E-161		
E-162		
E-163		
E-164		
E-165		
E-166		
E-167		
E-168		

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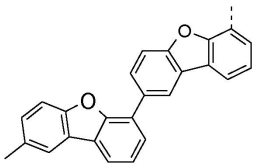
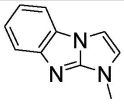
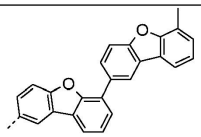
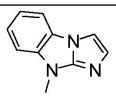
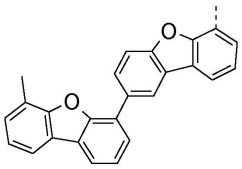
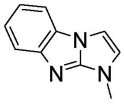
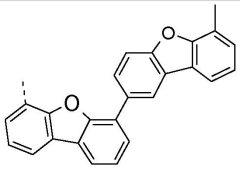
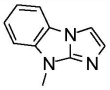
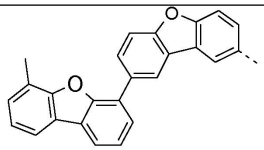
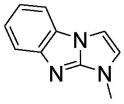
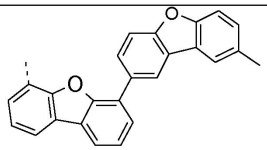
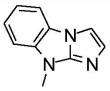
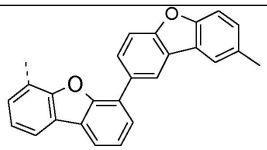
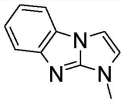
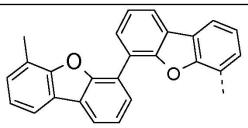
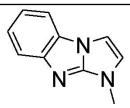
E-169		
E-170		
E-171		
E-172		
E-173		
E-174		
E-175		
E-176		

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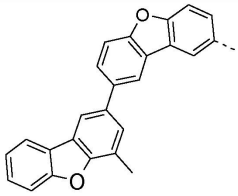
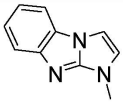
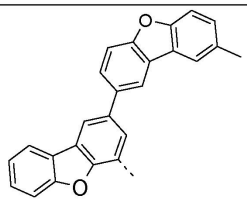
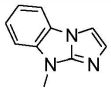
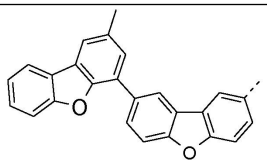
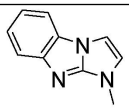
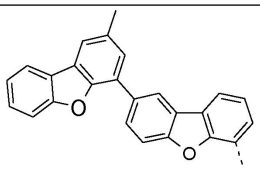
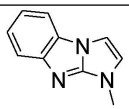
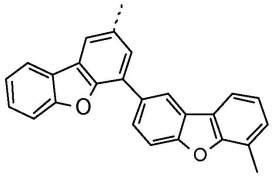
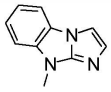
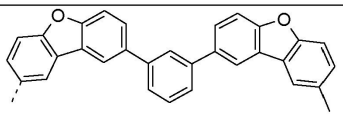
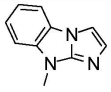
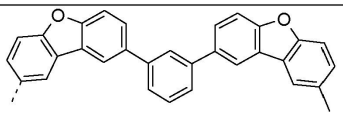
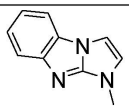
E-177		
E-178		
E-179		
E-180		
E-181		
E-182		
E-183		

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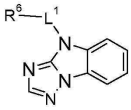
[0302] 

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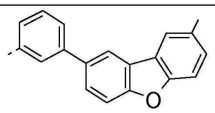
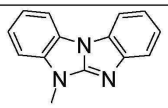
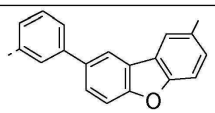
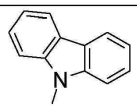
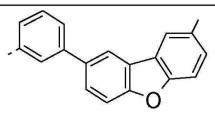
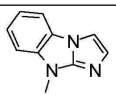
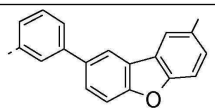
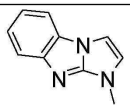
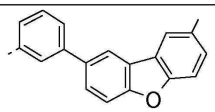
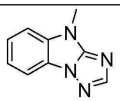
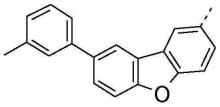
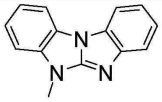
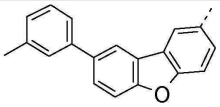
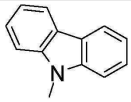
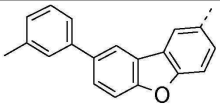
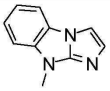
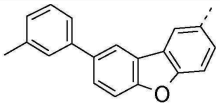
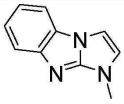
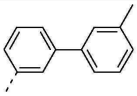
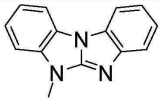
H-1		
H-2		
H-3		
H-4		
H-5		
H-6		
H-3		
H-4		
H-5		
H-6		

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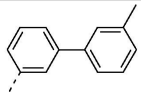
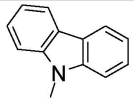
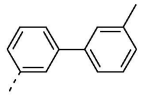
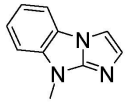
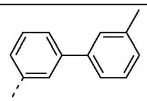
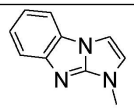
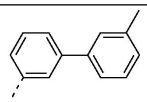
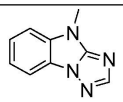
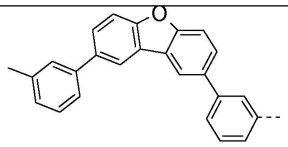
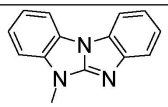
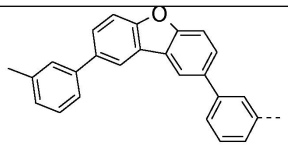
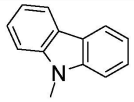
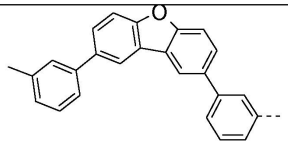
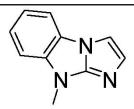
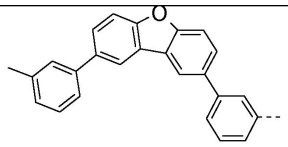
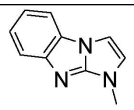
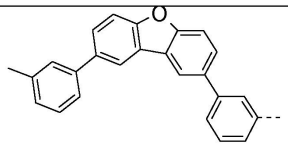
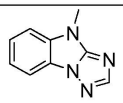
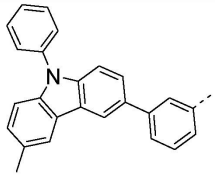
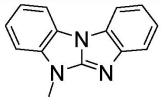
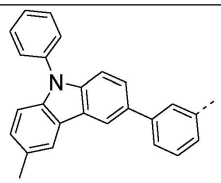
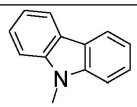
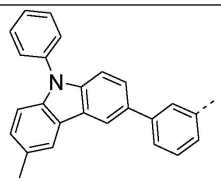
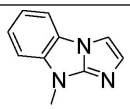
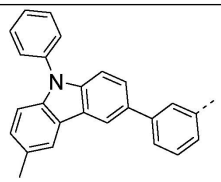
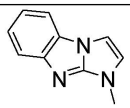
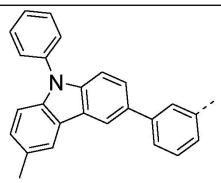
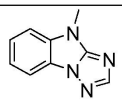
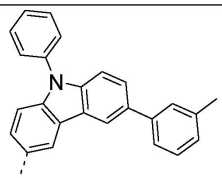
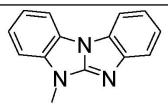
H-7		
H-8		
H-9		
H-10		
H-11		
H-12		
H-13		
H-14		
H-15		

H-16		
H-17		
H-18		
H-19		
H-20		
H-21		

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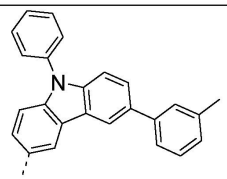
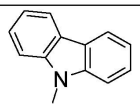
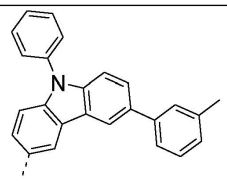
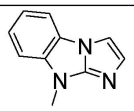
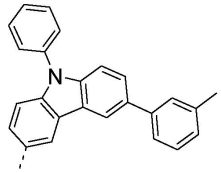
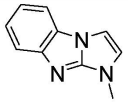
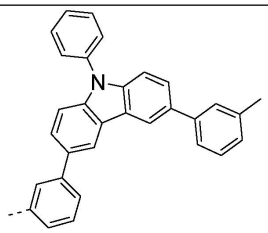
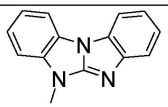
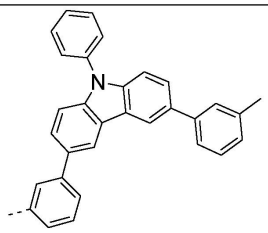
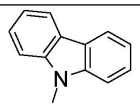
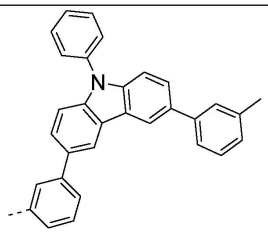
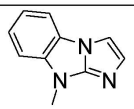
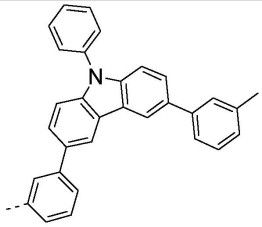
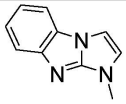
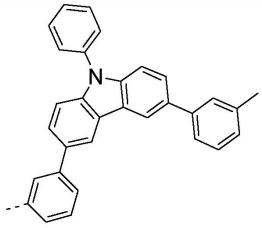
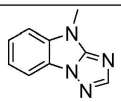
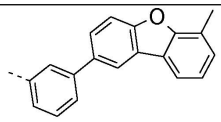
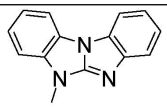
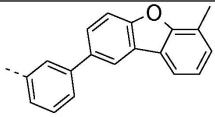
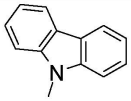
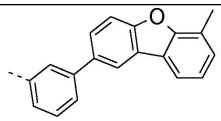
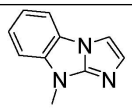
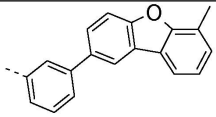
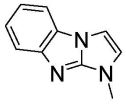
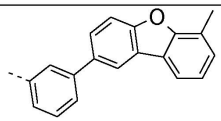
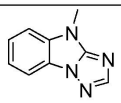
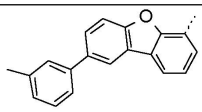
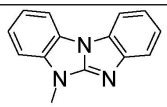
H-22		
H-23		
H-24		
H-25		
H-26		
H-27		

H-28		
H-29		
H-30		
H-31		
H-32		
H-33		
H-34		
H-35		

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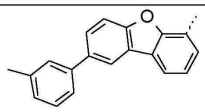
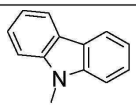
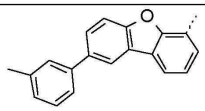
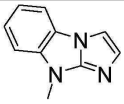
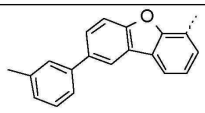
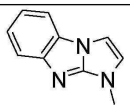
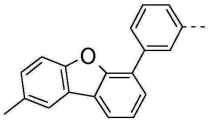
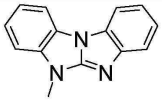
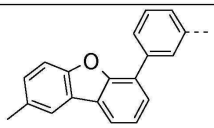
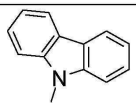
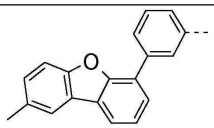
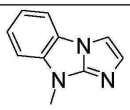
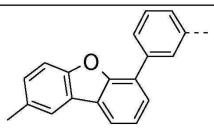
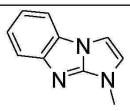
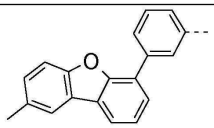
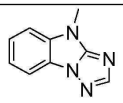
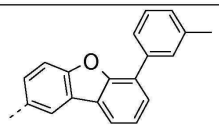
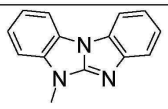
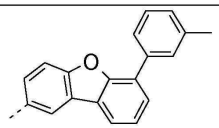
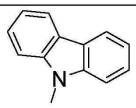
H-36		
H-27		
H-38		
H-39		
H-40		
H-41		
H-42		
H-43		
H-44		
H-45		

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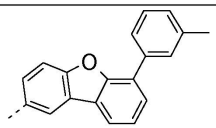
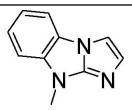
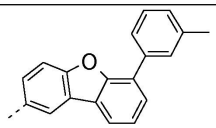
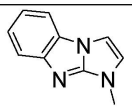
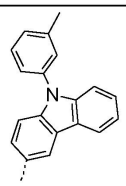
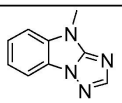
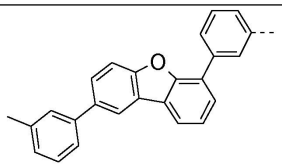
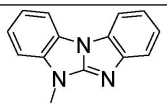
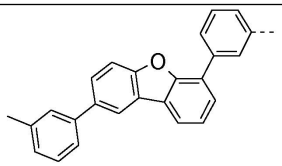
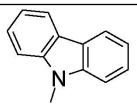
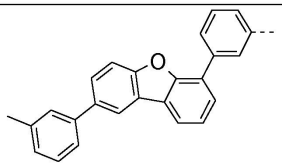
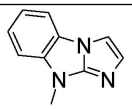
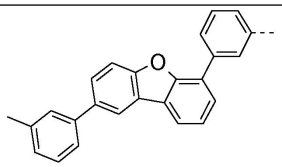
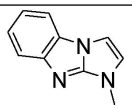
H-46		
H-47		
H-48		
H-49		
H-50		
H-51		
H-52		

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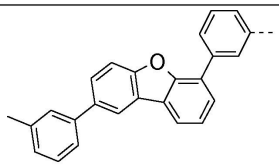
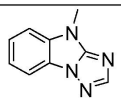
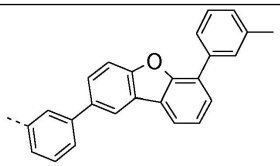
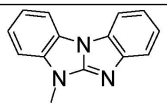
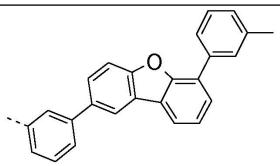
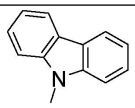
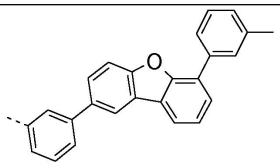
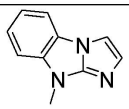
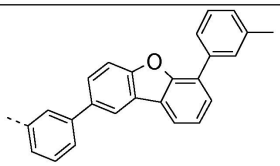
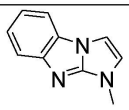
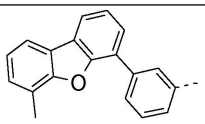
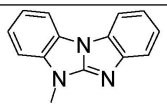
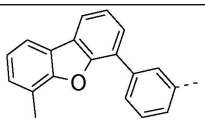
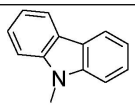
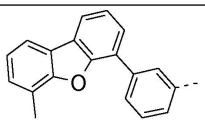
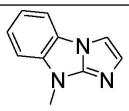
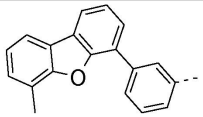
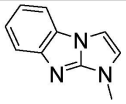
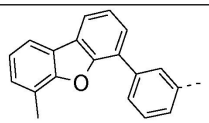
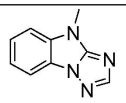
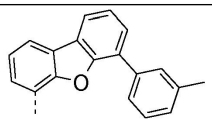
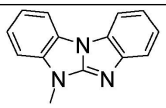
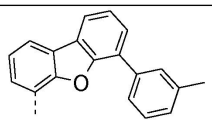
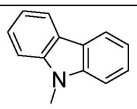
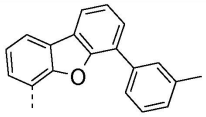
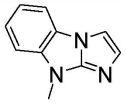
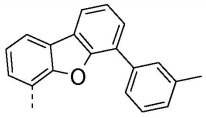
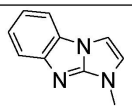
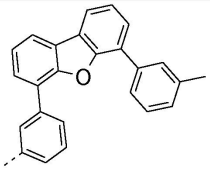
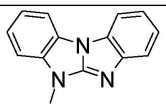
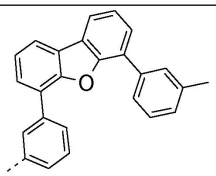
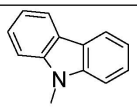
H-53		
H-54		
H-55		
H-56		
H-57		
H-58		
H-59		
H-60		

H-61		
H-62		
H-63		
H-64		
H-67		
H-68		
H-69		
H-70		

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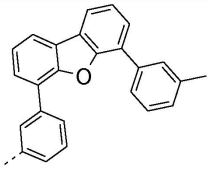
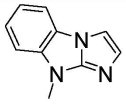
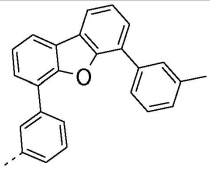
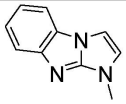
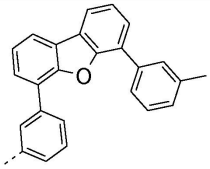
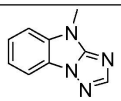
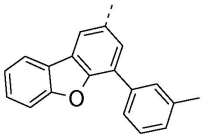
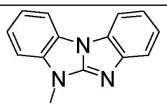
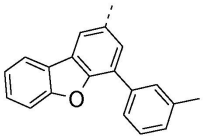
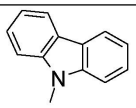
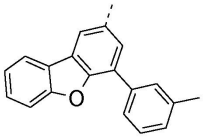
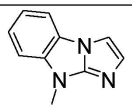
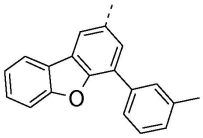
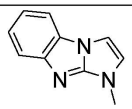
H-71		
H-72		
H-73		
H-74		
H-75		
H-76		
H-77		

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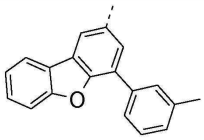
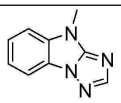
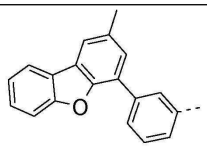
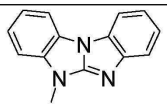
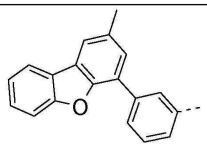
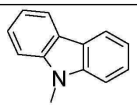
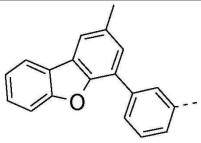
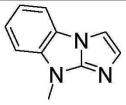
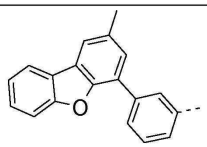
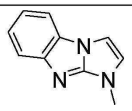
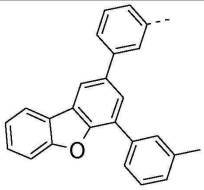
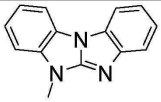
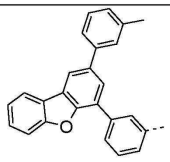
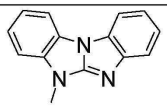
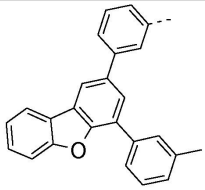
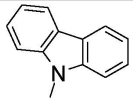
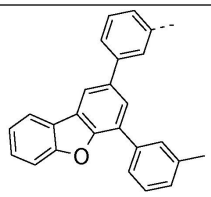
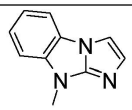
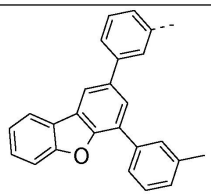
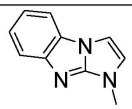
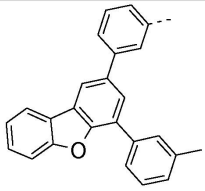
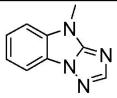
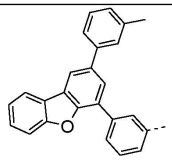
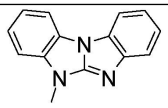
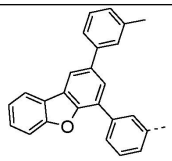
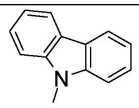
H-78		
H-79		
H-80		
H-81		
H-82		
H-83		
H-84		

H-85		
H-86		
H-87		
H-88		
H-89		
H-90		

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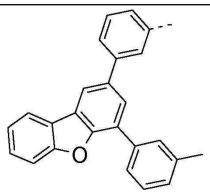
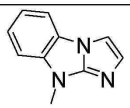
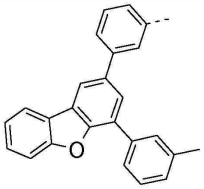
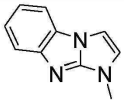
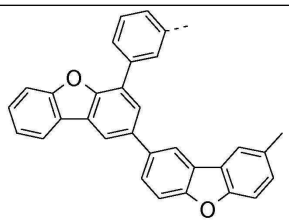
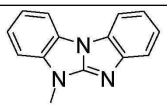
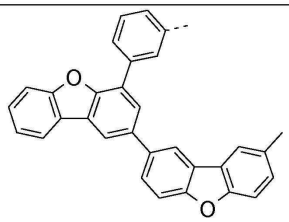
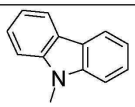
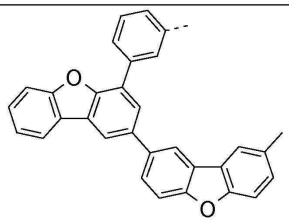
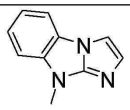
H-91		
H-92		
H-93		
H-94		
H-95		

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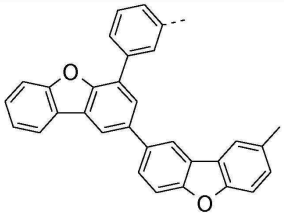
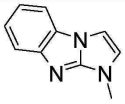
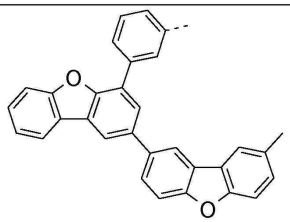
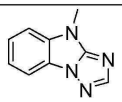
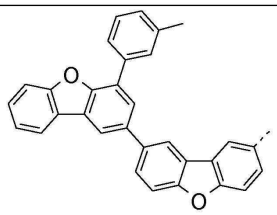
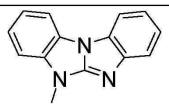
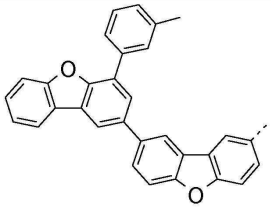
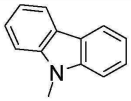
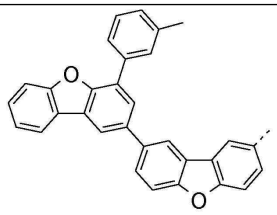
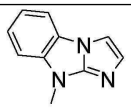
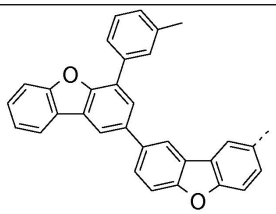
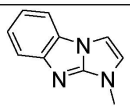
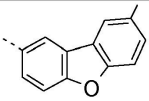
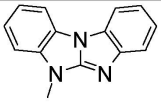
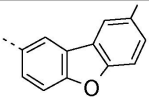
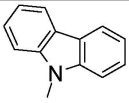
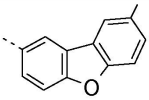
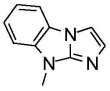
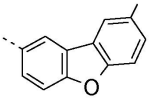
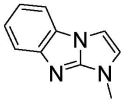
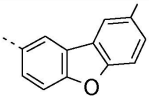
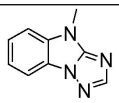
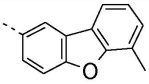
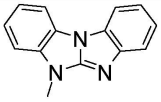
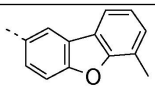
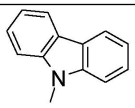
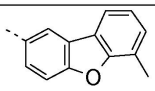
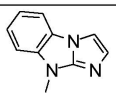
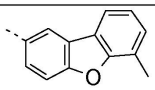
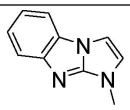
H-96		
H-97		
H-98		
H-99		
H-100		

H-101		
H-102		
H-103		
H-104		
H-105		
H-106		
H-107		
H-108		
H-109		
H-110		

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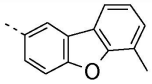
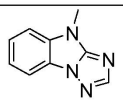
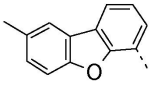
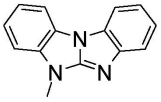
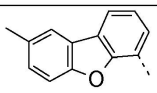
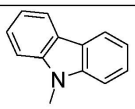
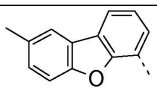
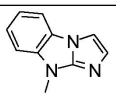
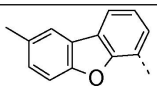
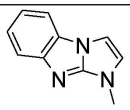
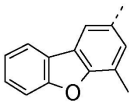
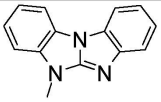
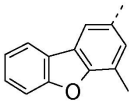
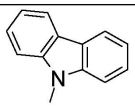
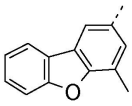
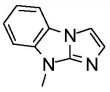
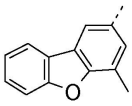
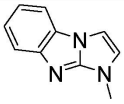
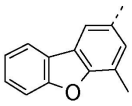
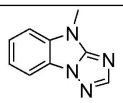
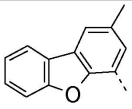
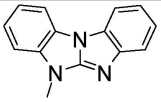
H-111		
H-112		
H-113		
H-114		
H-115		
H-116		
H-117		
H-118		
H-119		
H-120		
H-121		

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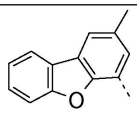
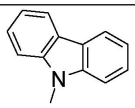
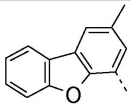
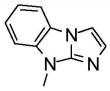
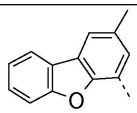
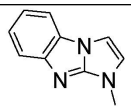
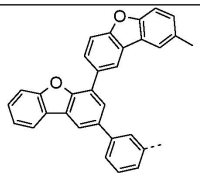
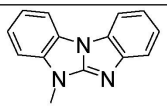
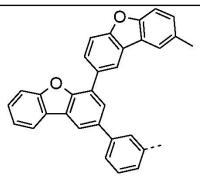
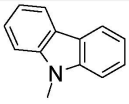
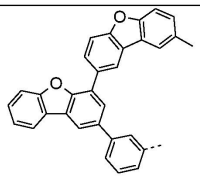
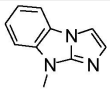
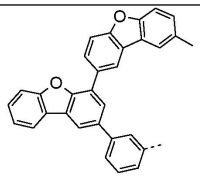
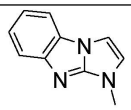
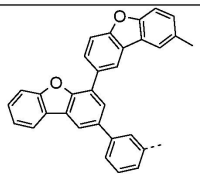
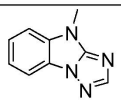
H-122		
H-123		
H-124		
H-125		
H-126		
H-127		
H-128		
H-129		

[0319]

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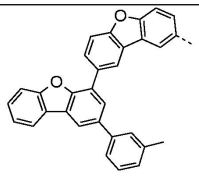
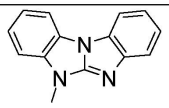
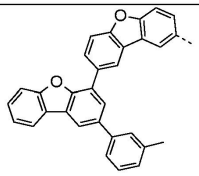
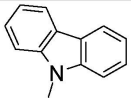
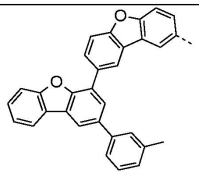
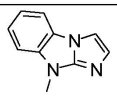
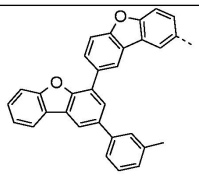
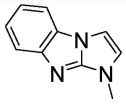
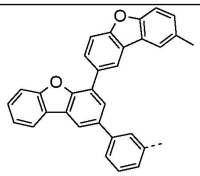
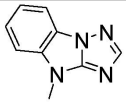
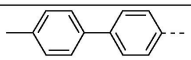
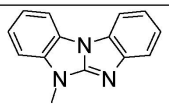
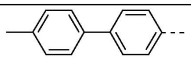
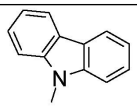
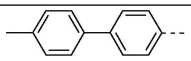
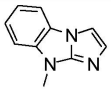
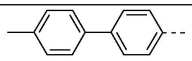
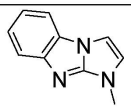
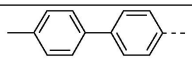
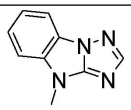
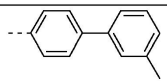
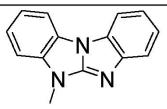
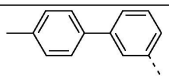
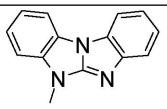
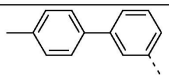
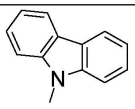
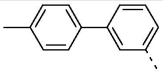
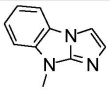
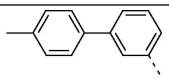
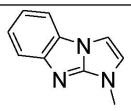
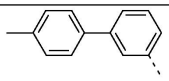
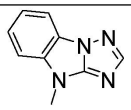
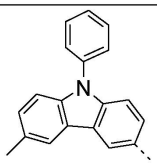
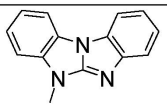
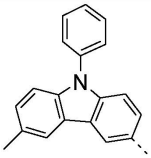
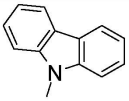
H-130		
H-131		
H-132		
H-133		
H-134		
H-135		
H-136		
H-137		

H-138		
H-139		
H-140		
H-141		
H-142		
H-143		
H-144		
H-145		
H-146		
H-147		

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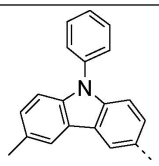
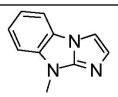
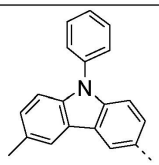
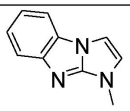
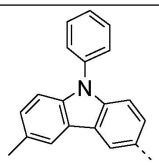
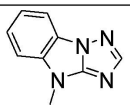
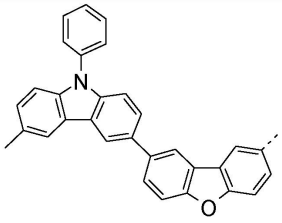
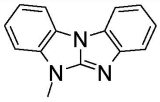
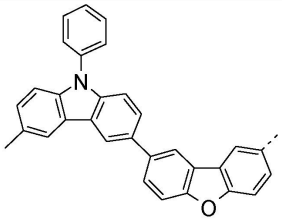
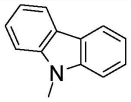
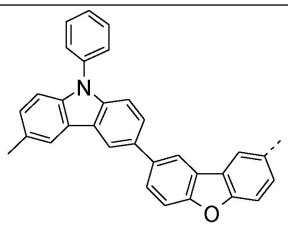
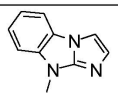
H-148		
H-149		
H-150		
H-151		
H-152		
H-153		

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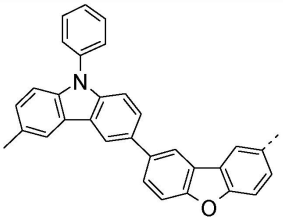
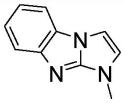
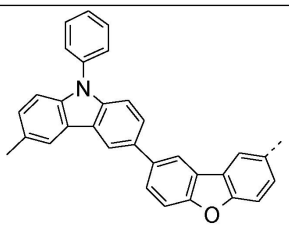
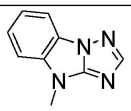
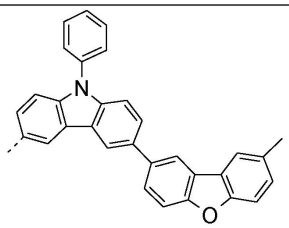
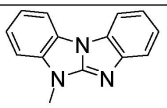
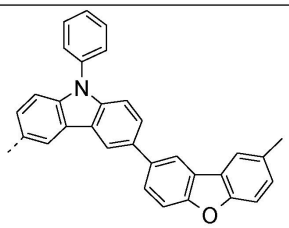
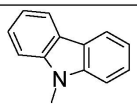
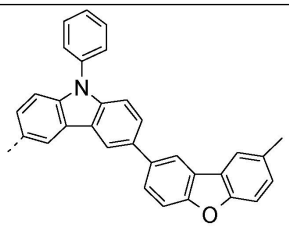
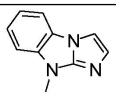
H-154		
H-155		
H-156		
H-157		
H-158		

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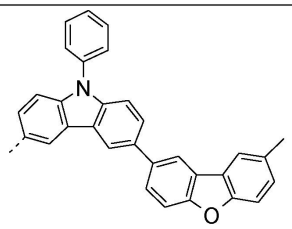
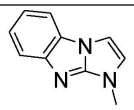
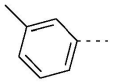
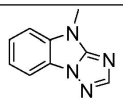
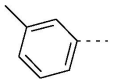
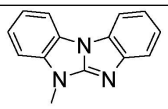
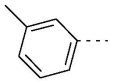
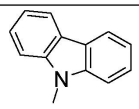
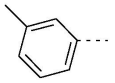
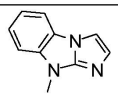
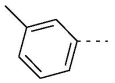
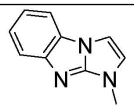
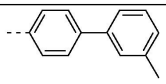
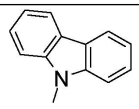
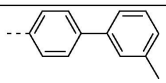
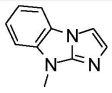
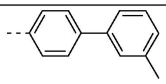
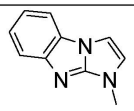
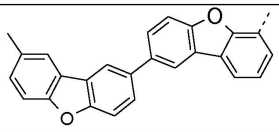
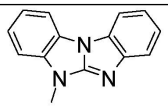
H-159		
H-160		
H-161		
H-162		
H-163		
H-164		
H-165		
H-166		
H-167		
H-168		

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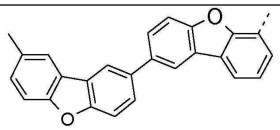
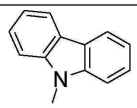
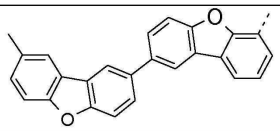
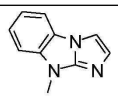
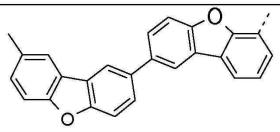
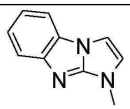
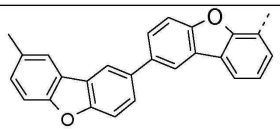
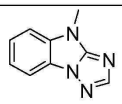
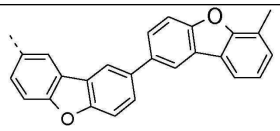
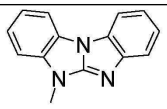
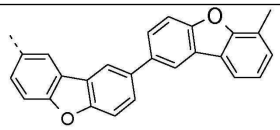
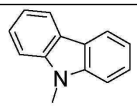
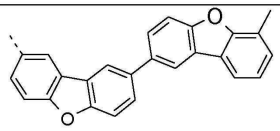
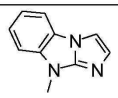
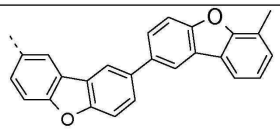
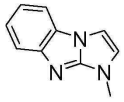
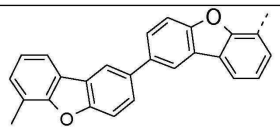
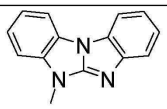
H-169		
H-170		
H-171		
H-172		
H-173		
H-174		
H-175		
H-176		
H-177		

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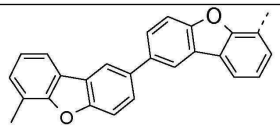
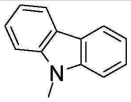
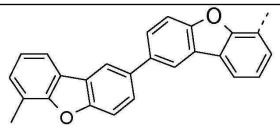
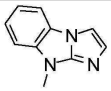
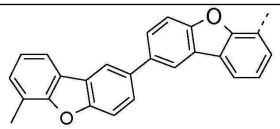
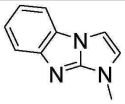
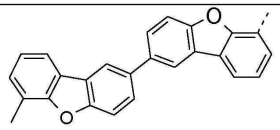
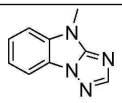
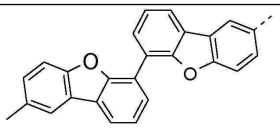
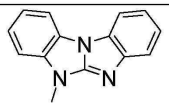
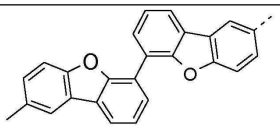
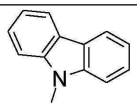
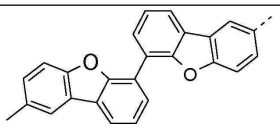
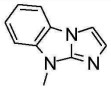
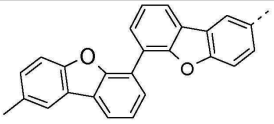
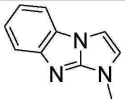
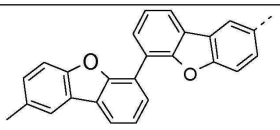
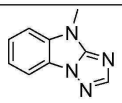
H-178		
H-179		
H-180		
H-181		
H-182		
H-183		
H-184		
H-185		
H-186		

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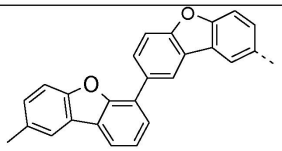
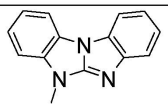
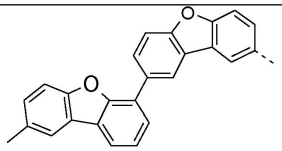
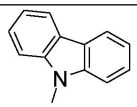
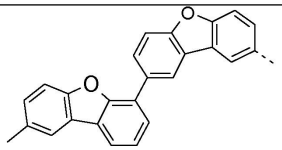
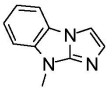
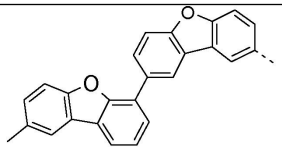
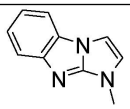
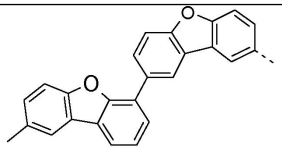
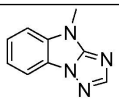
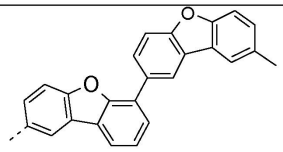
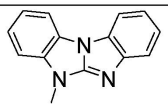
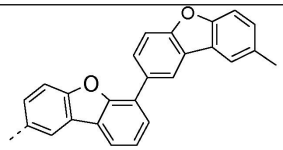
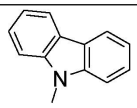
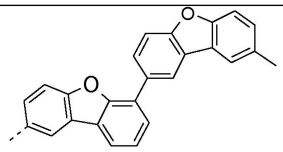
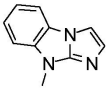
H-187		
H-188		
H-189		
H-190		
H-191		
H-192		
H-193		
H-194		

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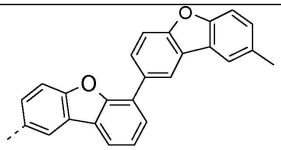
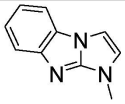
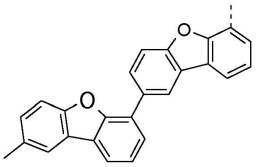
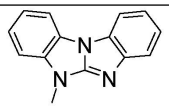
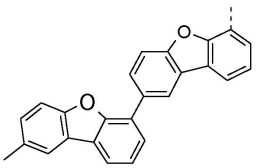
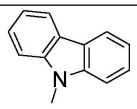
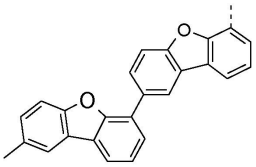
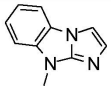
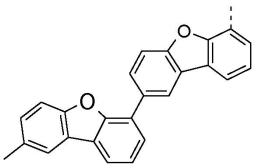
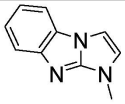
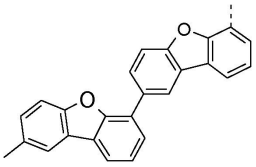
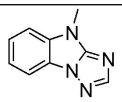
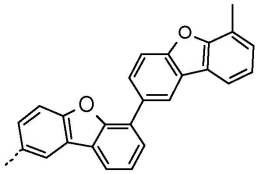
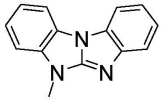
H-195		
H-196		
H-196		
H-197		
H-198		
H-199		
H-200		

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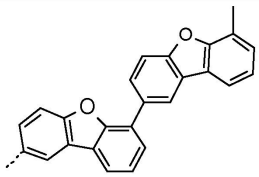
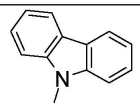
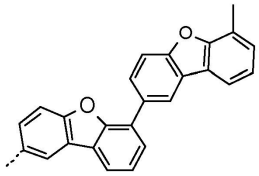
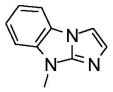
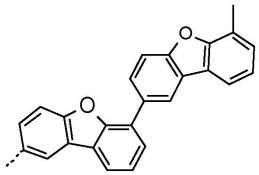
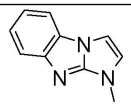
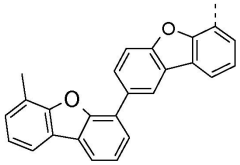
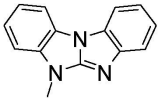
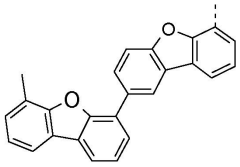
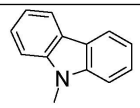
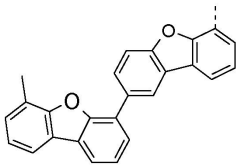
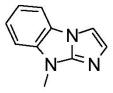
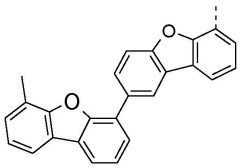
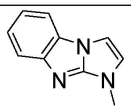
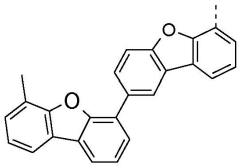
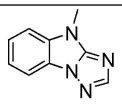
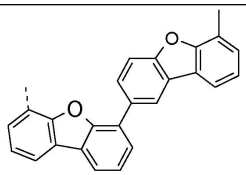
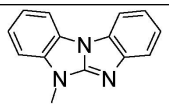
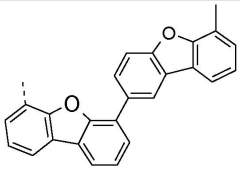
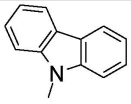
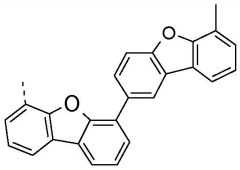
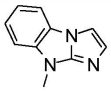
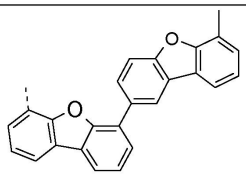
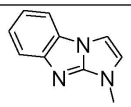
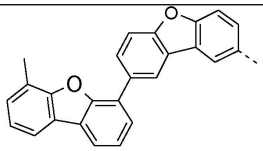
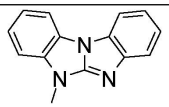
H-201		
H-202		
H-203		
H-204		
H-205		
H-206		

H-207		
H-208		
H-209		
H-210		
H-211		
H-212		
H-213		

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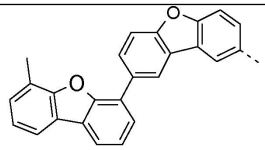
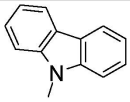
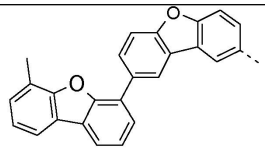
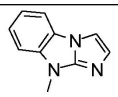
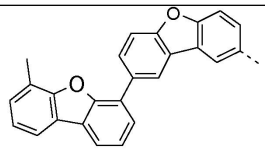
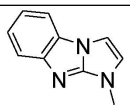
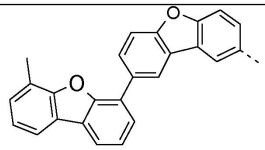
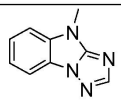
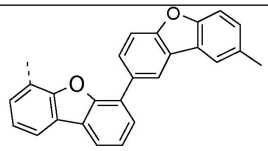
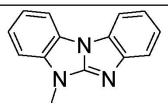
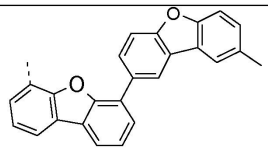
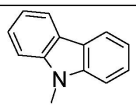
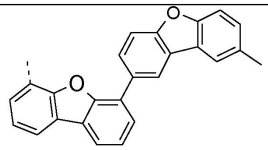
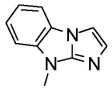
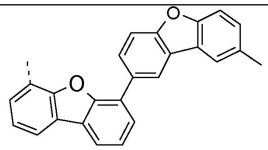
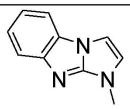
H-214		
H-215		
H-216		
H-217		
H-218		
H-219		
H-220		
H-221		

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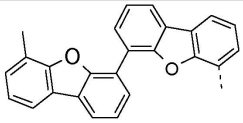
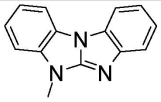
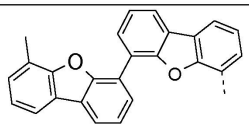
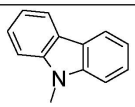
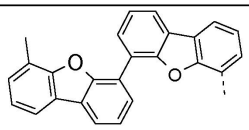
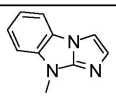
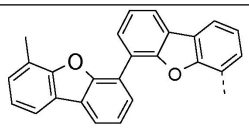
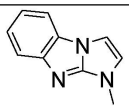
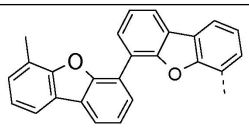
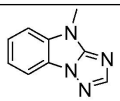
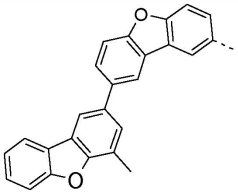
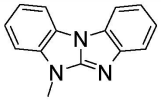
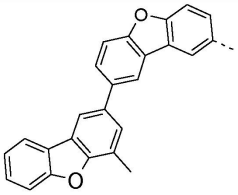
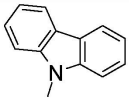
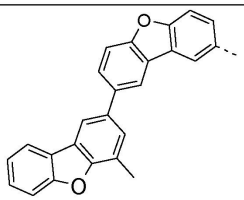
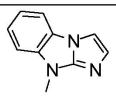
H-222		
H-223		
H-224		
H-225		
H-226		
H-227		
H-228		
H-229		

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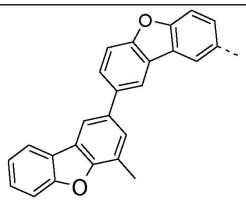
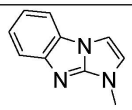
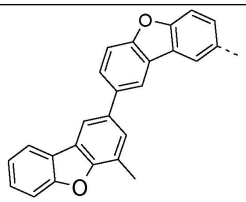
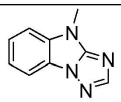
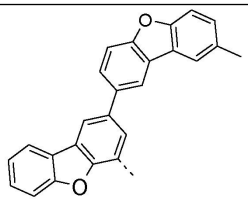
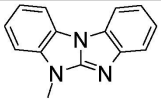
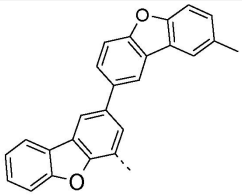
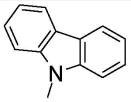
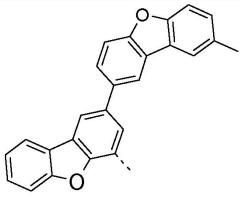
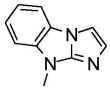
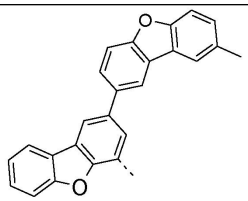
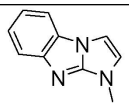
[0333]

H-230		
H-231		
H-232		
H-232		
H-233		
H-234		

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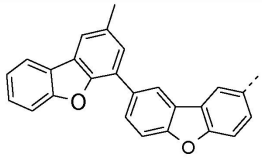
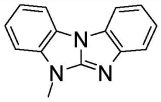
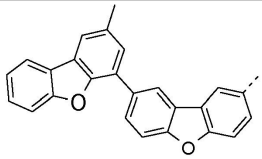
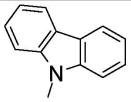
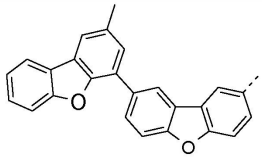
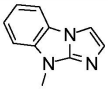
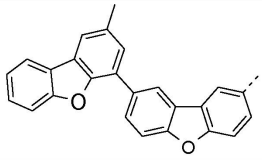
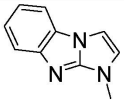
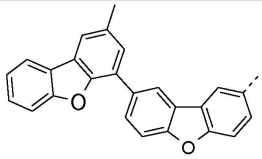
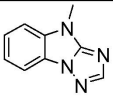
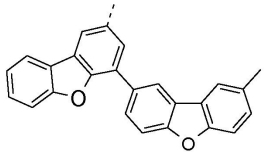
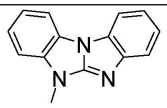
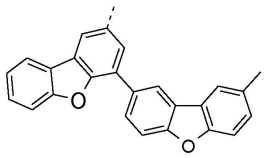
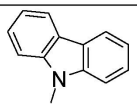
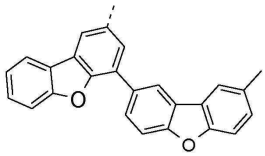
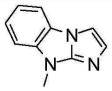
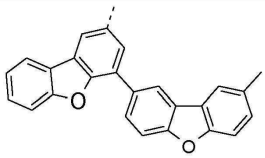
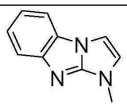
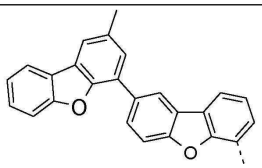
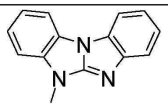
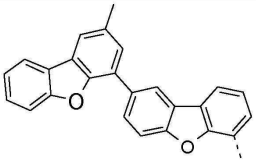
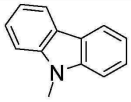
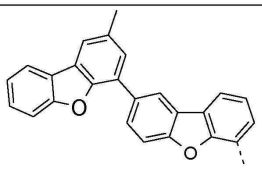
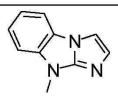
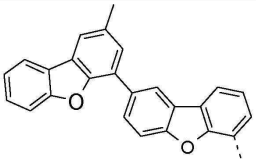
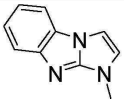
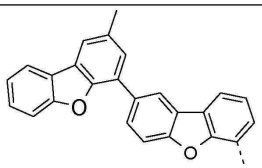
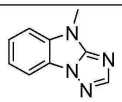
H-235		
H-236		
H-237		
H-238		
H-239		
H-240		
H-241		

H-242		
H-243		
H-244		
H-245		
H-246		
H-247		
H-248		

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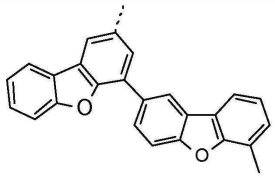
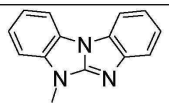
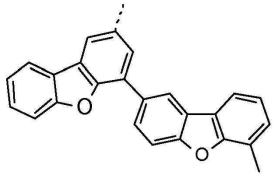
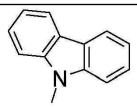
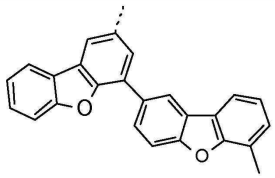
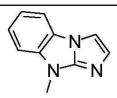
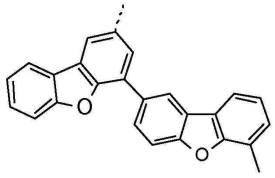
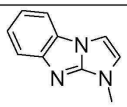
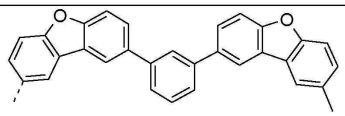
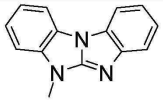
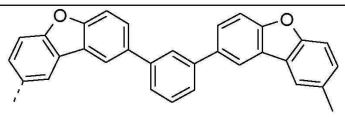
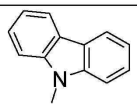
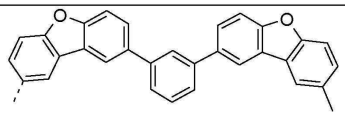
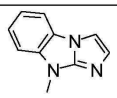
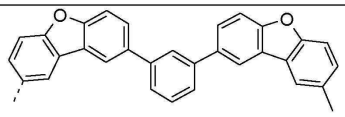
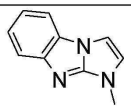
H-249		
H-250		
H-251		
H-251		
H-252		
H-253		
H-254		
H-255		

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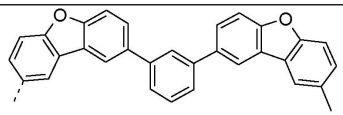
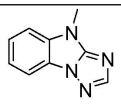
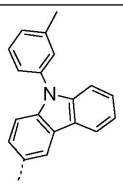
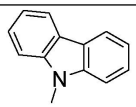
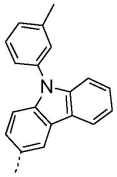
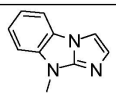
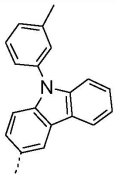
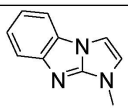
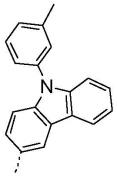
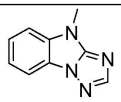
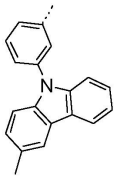
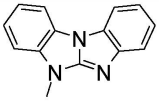
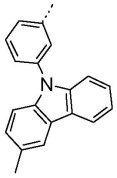
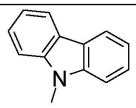
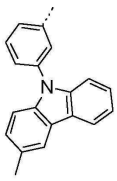
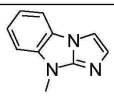
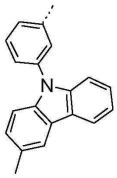
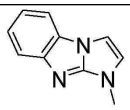
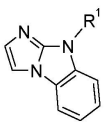
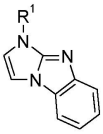
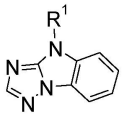
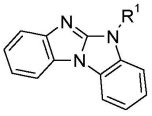
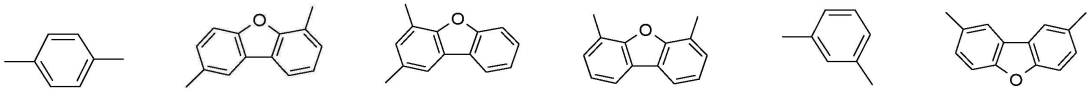
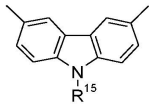
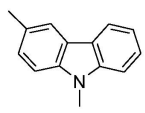
H-256		
H-257		
H-258		
H-259		
H-260		
H-261		
H-262		

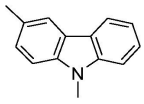
[0337]

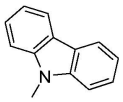
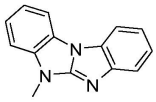
H-263		
H-264		

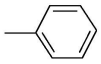
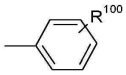
[0338]

[0339] 또 다른 바람직한 실시양태에서 본 발명은 화학식  ,  ,  , 또는  의

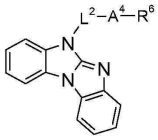
화합물에 관한 것이고, 여기서 R^1은 화학식 $-A^1-(A^2)_p-(A^3)_q-A^4-R^6$의 기이고; 여기서 A^1, A^2 및 A^3은 서로 독립적으로 화학식  ,  ,  의 기이고, 여기서 R^{15}는 C_6-C_{18}아릴기; 또는 1개 이상의 C_1-C_{18}알킬기에 의해 치환된 C_6-C_{18}아릴기이고,

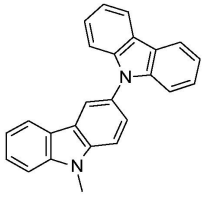
[0340] A^4는  의 기이고, 이는 N-원자를 통해 A^3에 결합되고;

[0341] R^6은 화학식  , 또는  의 기이고, p 및 q는 상기 정의된 바와 같다.

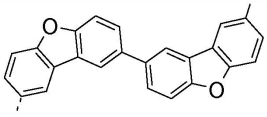
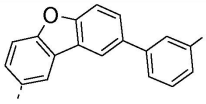
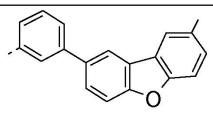
[0342] R^{15}는 바람직하게는 화학식  , 또는  의 기이고, 여기서 R^{100}은 C_1-C_8알킬기이다. 상기 실시 양태에서 화학식 $-A^1-(A^2)_p-(A^3)_q-$의 기는 특히 화학식 IVa, IVb, IVc, IVd, IVe, IVf, IVg, IVi, IVj, IVk, IVl, IVm, IVn, IVo, IVp, IVq, IVr, IVs, IVt, IVu, IVv, IVw, IVx, IVy, IVz, VIa, VIb, VIc, VId, VIe, VIf, VIg, VIh, VIi, VIj, VIk, VIl, VIm, VIn, VIo, VIp, VIq, VIr, VIs, VIt, 또는 VIu의 기이다. 현재 가장 바람직한 화학식 $-A^1-(A^2)_p-(A^3)_q-$의 기는 화학식 IVa, IVb, IVe, IVl, IVk, IVs, IVv 및 VIj의 기이다.

[0343] 화학식 I의 화합물이 청색, 또는 녹색 인광 방출체를 위한 호스트 물질로서, 또는 전자/여기자 차단 물질로서 사용되는 경우에, 화학식  의 기를 함유하는 기 $A^1-(A^2)_p-(A^3)_q-(A^4)_r-$, 즉 화학식 IVp 및 IVr의 기는 덜 바람직하다. 바람직한 화합물의 예는 하기 표에 나타낸 화합물 F-1 내지 F-62뿐만 아니라 G-1 내지 G-62이다.

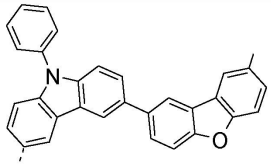
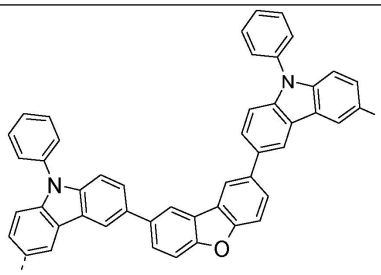
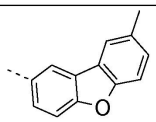
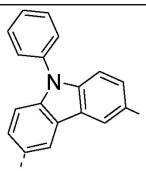
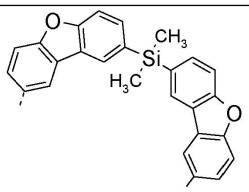
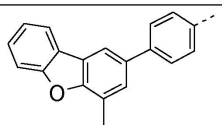
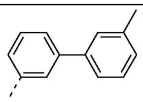
[0344] 

($-A^4-R^6$= )

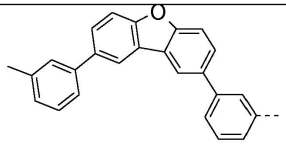
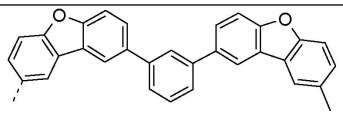
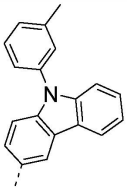
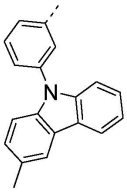
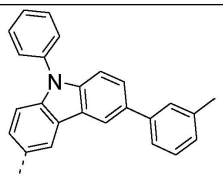
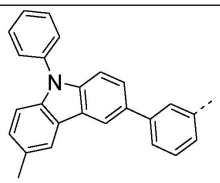
[0345]

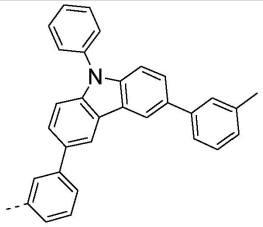
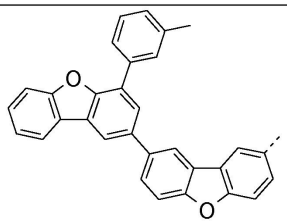
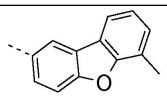
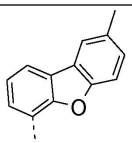
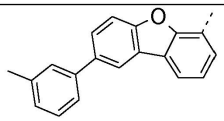
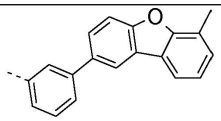
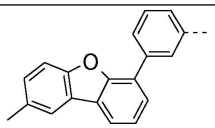
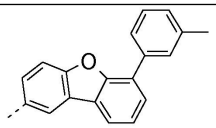
화합물	L2 2)
F-1	
F-2	
F-3	

[0346]

F-4	
F-5	
F-6	
F-7	
F-8	
F-9	
F-10	
F-11	

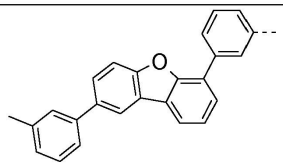
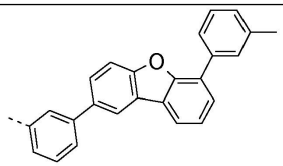
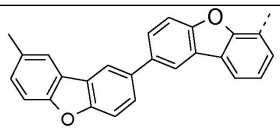
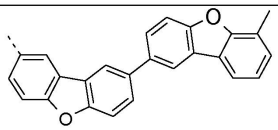
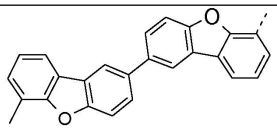
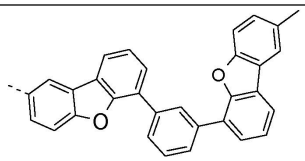
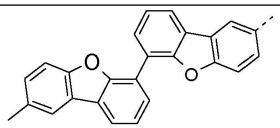
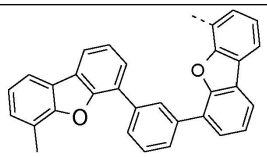
[0347]

F-12	
F-13	
F-14	
F-15	
F-16	
F-17	

F-18	
F-19	
F-20	
F-21	
F-22	
F-23	
F-24	
F-25	

[0348]

[0349]

F-26	
F-27	
F-28	
F-29	
F-30	
F-31	
F-32	
F-33	

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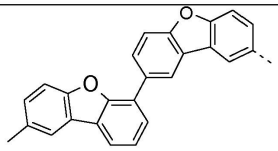
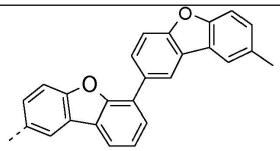
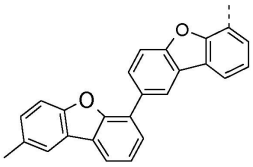
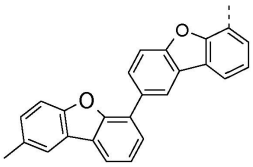
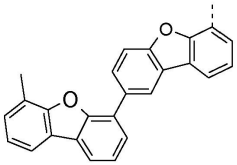
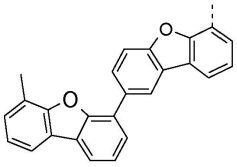
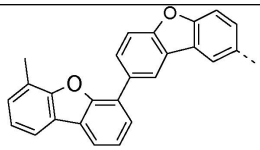
F-34	
F-35	
F-36	
F-37	
F-38	
F-39	
F-40	

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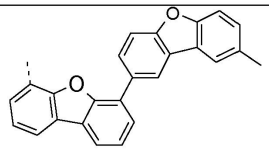
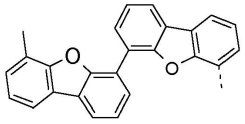
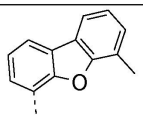
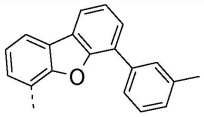
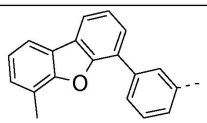
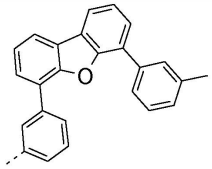
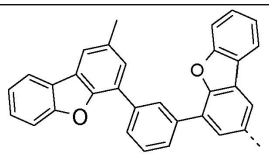
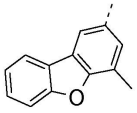
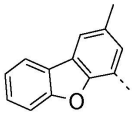
F-41	
F-42	
F-43	
F-44	
F-45	
F-46	
F-47	
F-48	
F-49	

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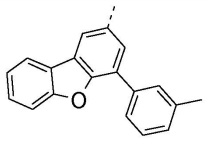
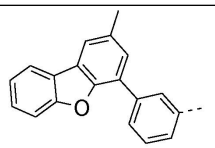
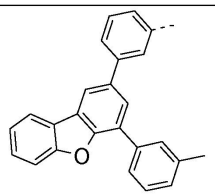
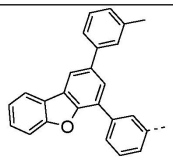
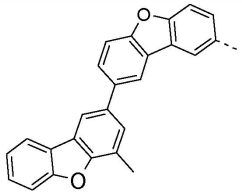
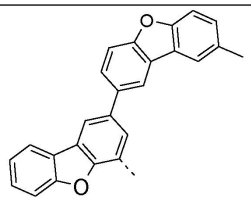
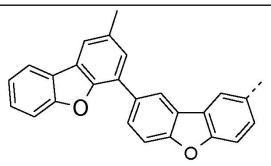
F-50	
F-51	
F-52	
F-53	
F-54	
F-55	
F-56	

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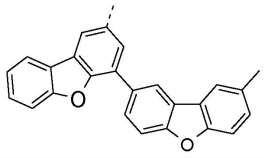
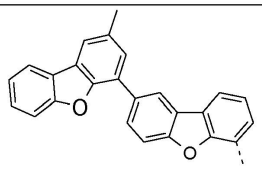
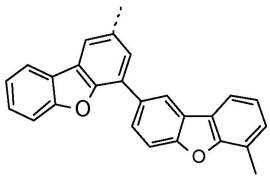
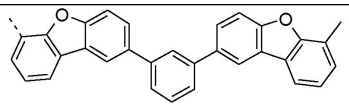
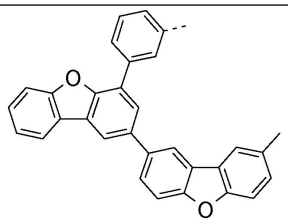
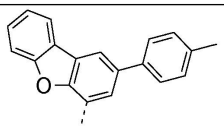
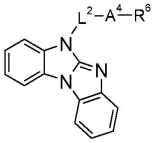
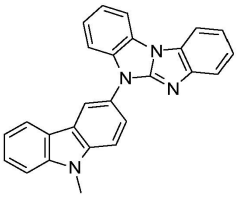
F-57	
F-58	
F-59	
F-60	
F-61	
F-62	

[0354] 

(-A4-R6= 

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[0355]

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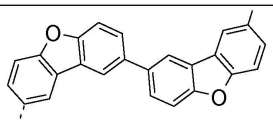
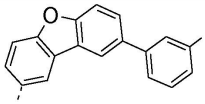
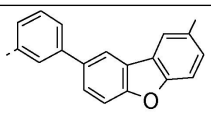
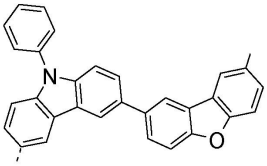
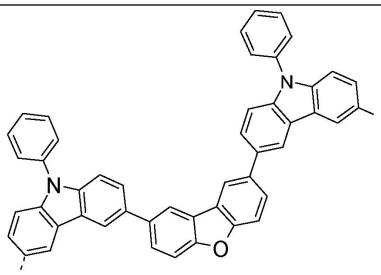
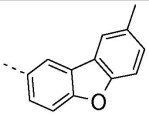
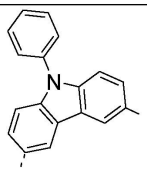
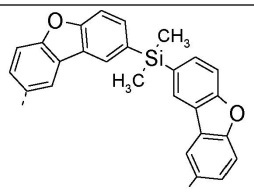
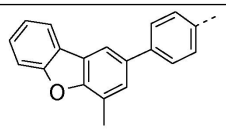
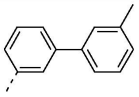
G-1	
G-2	
G-3	
G-4	
G-5	
G-6	
G-7	

G-8	
G-9	
G-10	
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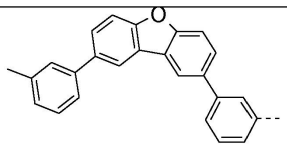
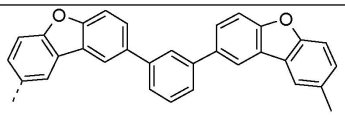
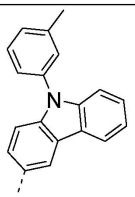
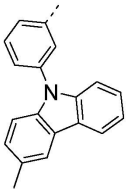
G-12	
G-13	
G-14	
G-15	

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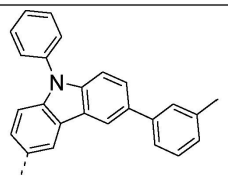
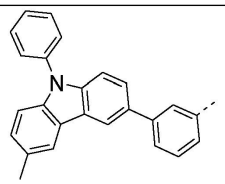
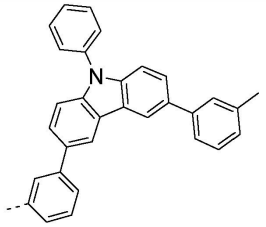
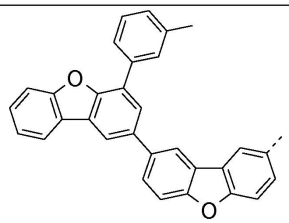
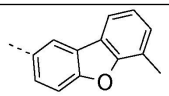
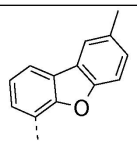
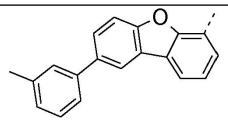
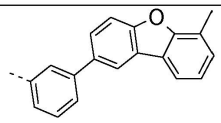
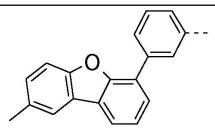
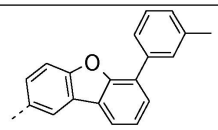
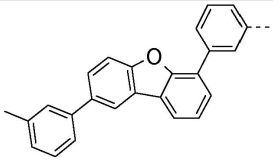
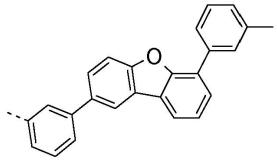
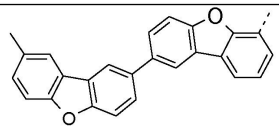
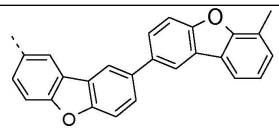
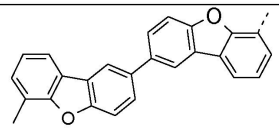
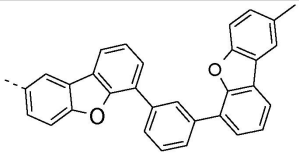
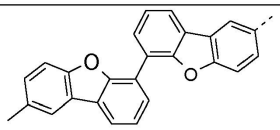
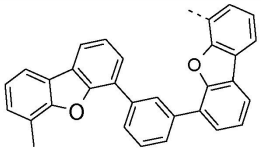
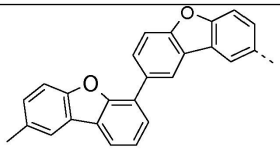
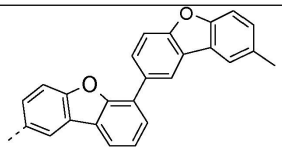
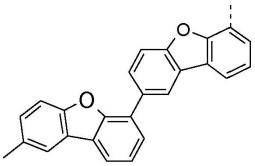
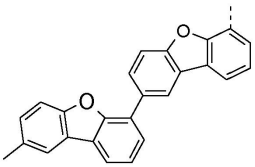
G-16	
G-17	
G-18	
G-19	
G-20	
G-21	
G-22	

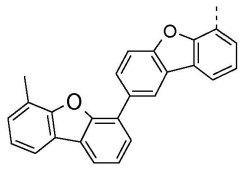
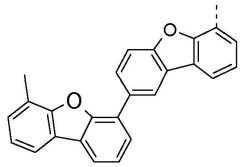
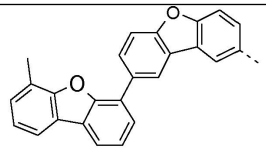
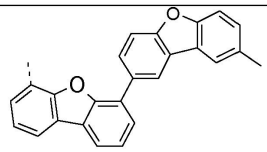
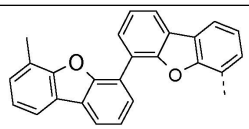
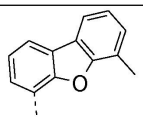
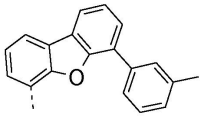
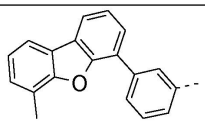
[0358]

G-23	
G-24	
G-25	
G-26	
G-27	
G-28	
G-29	
G-30	

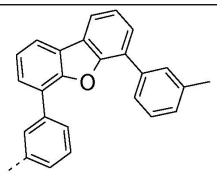
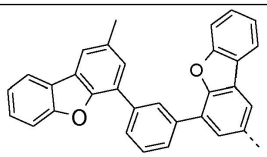
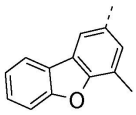
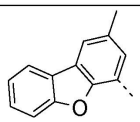
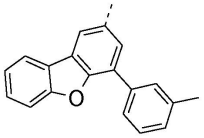
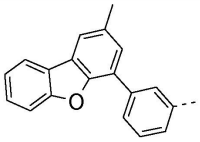
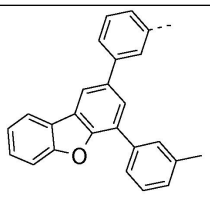
[0359]

G-31	
G-32	
G-33	
G-34	
G-35	
G-36	
G-37	

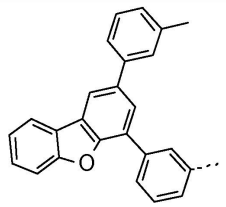
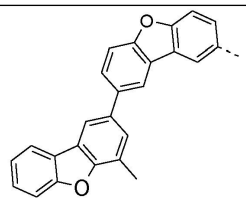
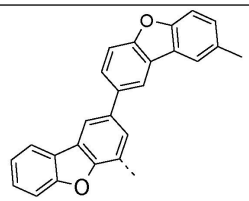
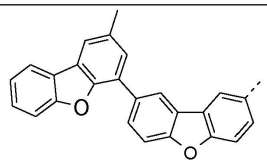
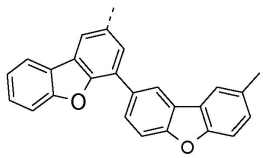
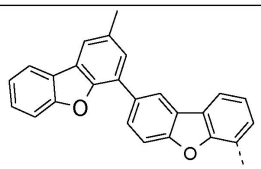
[0360]

G-38	
G-39	
G-40	
G-41	
G-42	
G-43	
G-44	
G-45	

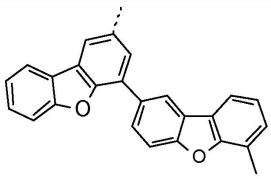
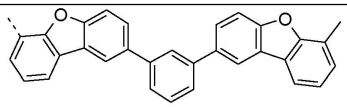
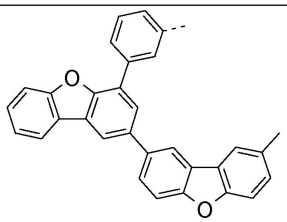
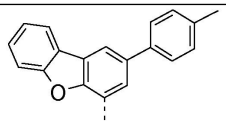
[0361]

G-46	
G-47	
G-48	
G-49	
G-50	
G-51	
G-52	

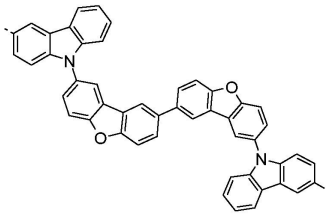
[0362]

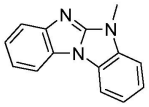
G-53	
G-54	
G-55	
G-56	
G-57	
G-58	

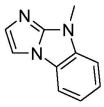
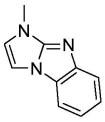
[0363]

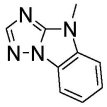
G-59	
G-60	
G-61	
G-62	

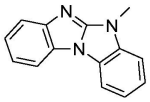
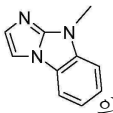
[0364] 상기 표에서 참조 기호 [1], [2], [3] 및 [4]는 하기 의미를 갖는다:

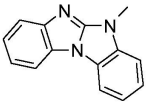
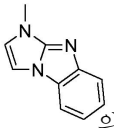
[0365] [1] L^1 =  .

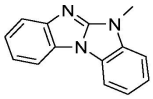
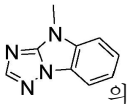
[0366] [2] 점선은 화학식  의 기에의 결합을 나타낸다.

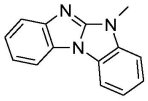
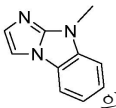
[0367] [3] 점선은 각각 화학식  및  의 기에의 결합을 나타낸다.

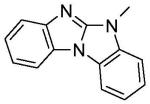
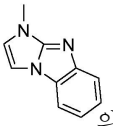
[0368] [4] 점선은 화학식  의 기에의 결합을 나타낸다.

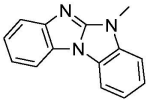
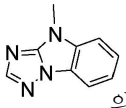
[0369] 또 다른 바람직한 실시양태에서 본 발명은 화학식  의 기를 화학식  의 기로 대체함으로써 화합물 F-1 내지 F-62로부터 생성되는 화합물 M-1 내지 M-62에 관한 것이다.

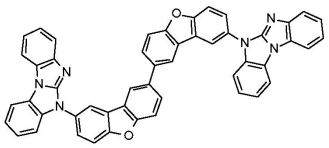
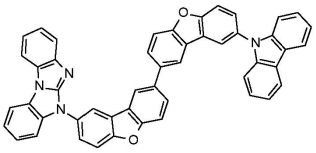
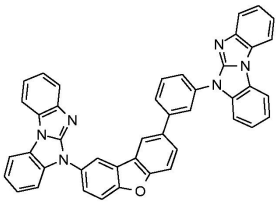
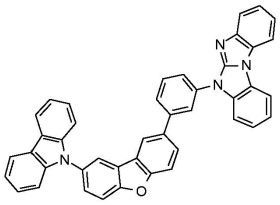
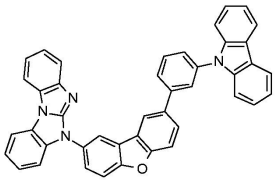
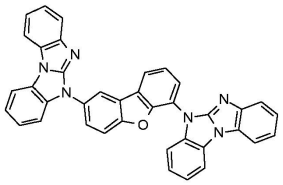
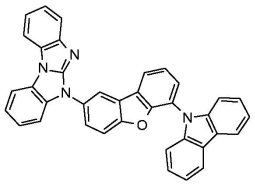
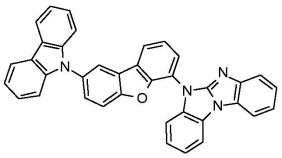
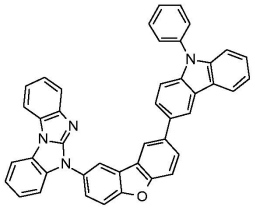
[0370] 또 다른 바람직한 실시양태에서 본 발명은 화학식  의 기를 화학식  의 기로 대체함으로써 화합물 F-1 내지 F-62로부터 생성되는 화합물 N-1 내지 N-62에 관한 것이다.

[0371] 또 다른 바람직한 실시양태에서 본 발명은 화학식  의 기를 화학식  의 기로 대체함으로써 화합물 F-1 내지 F-62로부터 생성되는 화합물 O-1 내지 O-62에 관한 것이다.

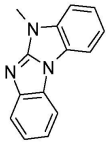
[0372] 또 다른 바람직한 실시양태에서 본 발명은 화학식  의 기를 화학식  의 기로 대체함으로써 화합물 G-1 내지 G-62로부터 생성되는 화합물 P-1 내지 P-62에 관한 것이다.

[0373] 또 다른 바람직한 실시양태에서 본 발명은 화학식  의 기를 화학식  의 기로 대체함으로써 화합물 G-1 내지 G-62로부터 생성되는 화합물 Q-1 내지 Q-62에 관한 것이다.

[0374] 또 다른 바람직한 실시양태에서 본 발명은 화학식  의 기를 화학식  의 기로 대체함으로써 화합물 G-1 내지 G-62로부터 생성되는 화합물 R-1 내지 R-62에 관한 것이다.


(A-1),

(A-2),

(C-4),

(A-5),

(C-9),

(C-1),

(C-2),

(C-3) 및

(B-6)

[0375] 현재 가장 바람직한 화합물은 화합물 이다.

[0376] 특히, 화학식  의 이미다졸 모이어티를 함유하는 화합물이 유기-전계발광 소자에서 사용하기에 적합한 것으로 밝혀졌다.

[0377] 할로겐은 플루오린, 염소, 브로민 및 아이오딘이다.

[0378] C_1-C_{25}알킬 (C_1-C_{18}알킬)은 전형적으로 가능한 경우 선형 또는 분지형이다. 예는 메틸, 에틸, n-프로필, 이소프로필, n-부틸, sec.-부틸, 이소부틸, tert.-부틸, n-펜틸, 2-펜틸, 3-펜틸, 2,2-디메틸프로필, 1,1,3,3-테트라메틸펜틸, n-헥실, 1-메틸헥실, 1,1,3,3,5,5-헥사메틸헥실, n-헵틸, 이소헵틸, 1,1,3,3-테트라메틸부틸, 1-메틸헵틸, 3-메틸헵틸, n-옥틸, 1,1,3,3-테트라메틸부틸 및 2-에틸헥실, n-노닐, 데실, 운데실, 도데실, 트리데실, 테트라데실, 펜타데실, 헥사데실, 헵타데실, 또는 옥타데실이다. C_1-C_8알킬은 전형적으로 메틸, 에틸, n-프로필, 이소프로필, n-부틸, sec.-부틸, 이소부틸, tert.-부틸, n-펜틸, 2-펜틸, 3-펜틸, 2,2-디메틸-프로필, n-헥실, n-헵틸, n-옥틸, 1,1,3,3-테트라메틸부틸 및 2-에틸헥실이다. C_1-C_4알킬은 전형적으로 메틸, 에틸, n-프로필, 이소프로필, n-부틸, sec.-부틸, 이소부틸, tert.-부틸이다.

[0379] C_1-C_{25}알콕시기 (C_1-C_{18}알콕시기)는 직쇄 또는 분지형 알콕시기, 예를 들어 메톡시, 에톡시, n-프로폭시, 이소프로폭시, n-부톡시, sec-부톡시 또는 tert-부톡시, 아밀옥시, 이소아밀옥시 또는 tert-아밀옥시, 헵틸옥시, 옥틸옥시, 이소옥틸옥시, 노닐옥시, 데실옥시, 운데실옥시, 도데실옥시, 테트라데실옥시, 펜타데실옥시, 헥사데실옥시, 헵타데실옥시 및 옥타데실옥시이다. C_1-C_8알콕시의 예는 메톡시, 에톡시, n-프로폭시, 이소프로폭시, n-부

톡시, sec-부톡시, 이소부톡시, tert.-부톡시, n-펜틸옥시, 2-펜틸옥시, 3-펜틸옥시, 2,2-디메틸프로폭시, n-헥실옥시, n-헵틸옥시, n-옥틸옥시, 1,1,3,3-테트라메틸부톡시 및 2-에틸헥실옥시, 바람직하게는 C_1-C_4알콕시, 예컨대 전형적으로 메톡시, 에톡시, n-프로폭시, 이소프로폭시, n-부톡시, sec-부톡시, 이소부톡시, tert.-부톡시이다.

[0380] 용어 "시클로알킬기"는 전형적으로, 비치환되거나 치환될 수 있는, C_4-C_{18}시클로알킬, 특히 C_5-C_{12}시클로알킬, 예컨대 시클로펜틸, 시클로헥실, 시클로헵틸, 시클로옥틸, 시클로노닐, 시클로데실, 시클로운데실, 시클로도데실, 바람직하게는 시클로펜틸, 시클로헥실, 시클로헵틸, 또는 시클로옥틸이다.

[0381] 임의로 치환될 수 있는 C_6-C_{24}아릴 (C_6-C_{18}아릴)은 전형적으로, 비치환되거나 치환될 수 있는, 페닐, 4-메틸페닐, 4-메톡시페닐, 나프틸, 특히 1-나프틸, 또는 2-나프틸, 비페닐릴, 터페닐릴, 피레닐, 2- 또는 9-플루오레닐, 페난트릴, 또는 안트릴이다.

[0382] C_2-C_{30}헤테로아릴은 5 내지 7개의 고리 원자를 갖는 고리 또는 축합 고리 시스템을 나타내며, 여기서 질소, 산소 또는 황은 가능한 헤테로 원자이고, 전형적으로, 적어도 6개의 공액 π-전자를 갖는 5 내지 30개의 원자를 갖는 헤테로시클릭기, 예컨대 티에닐, 벤조티오페닐, 디벤조티오페닐, 티안트레닐, 푸릴, 푸르푸릴, 2H-피라닐, 벤조푸라닐, 이소벤조푸라닐, 디벤조푸라닐, 페녹시티에닐, 피롤릴, 이미다졸릴, 피라졸릴, 피리딜, 비피리딜, 트리아지닐, 피리미디닐, 피라지닐, 피리다지닐, 인돌리지닐, 이소인돌릴, 인돌릴, 인다졸릴, 푸리닐, 퀴놀리지닐, 퀴놀릴, 이소퀴놀릴, 프탈라지닐, 나프티리디닐, 퀴녹살리닐, 퀴나졸리닐, 신놀리닐, 프테리디닐, 카르바졸릴, 카르볼리닐, 벤조트리아졸릴, 벤족사졸릴, 페난트리디닐, 아크리디닐, 피리미디닐, 페난트롤리닐, 페나지닐, 이소티아졸릴, 페노티아지닐, 이속사졸릴, 푸라자닐, 4-이미다조[1,2-a]벤즈이미다조일, 5-벤즈이미다조[1,2-a]벤즈이미다조일, 카르바졸릴, 또는 페녹사지닐이고, 이는 비치환되거나 치환될 수 있다.

[0383] C_6-C_{24}아릴 (C_6-C_{18}아릴) 및 C_2-C_{30} 헤테로아릴기는 바람직하게는 1개 이상의 C_1-C_8알킬기에 의해 치환된다.

[0384] 용어 "아릴 에테르기"는 전형적으로 C_{6-24}아릴옥시기, 즉 O-C_{6-24}아릴, 예를 들어, 페녹시 또는 4-메톡시페닐 등이다.

[0385] 상기-언급된 기의 가능한 치환기는 C_1-C_8알킬, 히드록실기, 메르캅토기, C_1-C_8알콕시, C_1-C_8알킬티오, 할로겐, 할로-C_1-C_8알킬, 또는 시아노기이다.

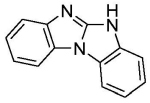
[0386] 치환기, 예를 들어 R^{41} 등이 기 내에 1회 초과로 존재하는 경우, 이는 각 경우에 상이할 수 있다.

[0387] 표현 "G에 의해 치환된"은 1개 이상의, 특히 1 내지 3개의 치환기 G가 존재할 수 있음을 의미한다.

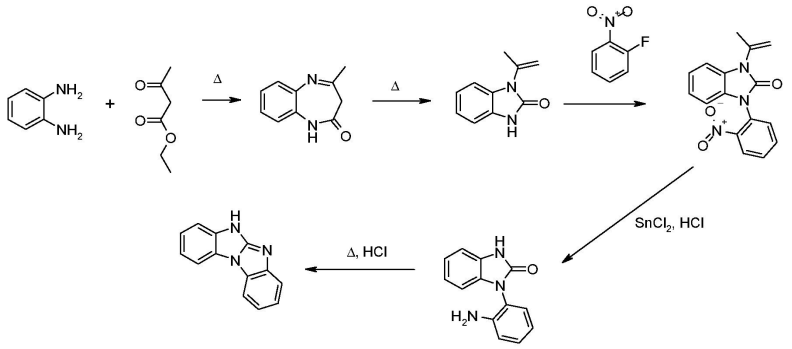
[0388] 상기 기재된 바와 같이, 상기 언급된 기는 E에 의해 치환될 수 있고/거나, 필요한 경우, D가 개재될 수 있다. 개재는 물론 기가 단일 결합에 의해 서로 결합된 2개 이상의 탄소 원자를 함유하는 경우에만 가능하고; C_6-C_{18}아릴은 개재되지 않으며; 개재된 아릴알킬은 알킬 모이어티에서 단위 D를 함유한다. 1개 이상의 E에 의해 치환되고/거나 1개 이상의 D가 개재된 C_1-C_{18}알킬은, 예를 들어, $(CH_2CH_2O)_{1-9}$-R^x (여기서 R^x는 H 또는 C_1-C_{10}알킬 또는 C_2-C_{10}알칸올 (예를 들어 CO-CH(C_2H_5)C_4H_9), CH_2-CH($OR^{y'}$)-CH_2-O-R^y이고, 여기서 R^y는 C_1-C_{18}알킬, C_5-C_{12}시클로알킬, 페닐, C_7-C_{15}페닐알킬이고, $R^{y'}$는 R^y와 동일한 정의를 포함하거나 H임);

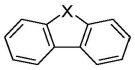
[0389] C_1-C_8알킬렌-COO-R^z, 예를 들어 CH_2COOR_z, CH(CH_3)$COOR^z$, C(CH_3)$_2$$COOR^z$ (여기서 R^z는 H, C_1-C_{18}알킬, $(CH_2CH_2O)_{1-9}$-R^x이고, R^x는 상기 나타낸 정의를 포함함);

[0390] CH_2CH_2-O-CO-CH=CH_2; CH_2CH(OH)CH_2-O-CO-C(CH_3)=CH_2이다.

[0391]  의 합성은, 예를 들어, 문헌 [Achour, Reddouane; Zniber, Rachid, Bulletin des Societes Chimiques Belges 96 (1987) 787-92]에 기재되어 있다.

[0392]



[0393] 화학식  의 적합한 베이스 골격은 상업적으로 시판되고 있거나 (특히 X가 S, O, NH인 경우에), 당업자에게 공지된 방법에 의해 수득될 수 있다. WO2010079051 및 EP1885818을 참조한다.

[0394] 할로겐화는 당업자에게 공지된 방법에 의해 수행할 수 있다. 화학식 II 2,8 위치 (디벤조푸란 및 디벤조티오펜) 또는 3,6 위치 (카르바졸)의 베이스 골격의 3 및 6 위치 (디브로민화) 또는 3 또는 6 위치 (모노브로민화)에서 브로민화 또는 아이오딘화가 바람직하다.

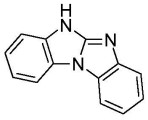
[0395] 임의로 치환된 디벤조푸란, 디벤조티오펜 및 카르바졸은 빙초산에서 또는 클로로포름 중에서 브로민 또는 NBS를 사용하여 2,8 위치 (디벤조푸란 및 디벤조티오펜) 또는 3,6 위치 (카르바졸)에서 디브로민화할 수 있다. 예를 들어, Br_2를 사용한 브로민화는 저온, 예를 들어 0℃에서 빙초산 또는 클로로포름 중에서 수행할 수 있다. 적합한 방법은, 예를 들어, X= NPh인 경우 문헌 [M. Park, J.R. Buck, C.J. Rizzo, Tetrahedron, 54 (1998) 12707-12714]에, 그리고 X= S인 경우 문헌 [W. Yang et al., J. Mater. Chem. 13 (2003) 1351]에 기재되어 있다. 게다가, 3,6-디브로모카르바졸, 3,6-디브로모-9-페닐카르바졸, 2,8-디브로모디벤조티오펜, 2,8-디브로모디벤조푸란, 2-브로모카르바졸, 3-브로모디벤조티오펜, 3-브로모디벤조푸란, 3-브로모카르바졸, 2-브로모디벤조티오펜 및 2-브로모디벤조푸란은 시판되고 있다.

[0396] 디벤조푸란 (및 디벤조티오펜에 관해 유사하게는)의 4 위치에서의 모노브로민화는, 예를 들어, 문헌 [J. Am. Chem. Soc. 1984, 106, 7150]에 기재되어 있다. 디벤조푸란 (디벤조티오펜)은 당업자에게 공지된 순서로 3 위치에서, 니트로화, 환원 및 후속 샌드마이어(Sandmeyer) 반응을 포함하여, 모노브로민화될 수 있다.

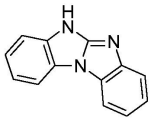
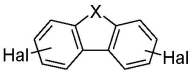
[0397] 디벤조푸란 또는 디벤조티오펜의 2 위치에서의 모노브로민화 및 카르바졸의 3 위치에서의 모노브로민화는 단지 1당량의 브로민 또는 NBS를 첨가하는 것을 제외하고, 디브로민화와 유사하게 수행한다.

[0398] 대안으로, 아이오딘화 디벤조푸란, 디벤조티오펜 및 카르바졸을 이용하는 것이 가능할 수도 있다. 제조는, 그 중에서도, 문헌 [Tetrahedron. Lett. 47 (2006) 6957-6960], [Eur. J. Inorg. Chem. 24 (2005) 4976-4984], [J. Heterocyclic Chem. 39 (2002) 933-941], [J. Am. Chem. Soc. 124 (2002) 11900-11907], [J. Heterocyclic Chem, 38 (2001) 77-87]에 기재되어 있다.

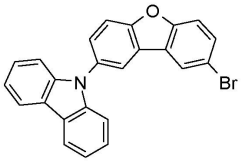
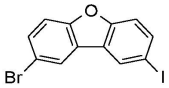
[0399] 친핵성 치환에 관해, Cl- 또는 F-치환 디벤조푸란, 디벤조티오펜 및 카르바졸이 필요하다. 염소화는, 그 중에서도, 문헌 [J. Heterocyclic Chemistry, 34 (1997) 891-900], [Org. Lett., 6 (2004) 3501-3504]; [J. Chem. Soc. [Section] C: Organic, 16 (1971) 2775-7], [Tetrahedron Lett. 25 (1984) 5363-6], [J. Org. Chem. 69 (2004) 8177-8182]에 기재되어 있다. 플루오르화는 문헌 [J. Org. Chem. 63 (1998) 878-880] 및 [J. Chem. Soc., Perkin Trans. 2, 5 (2002) 953-957]에 기재되어 있다.

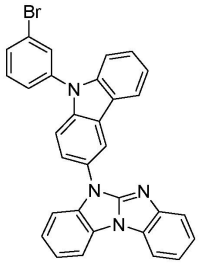
[0400] 기  의 도입을 염기의 존재하에 수행한다. 적합한 염기는 당업자에게 공지되어 있고 바람직하게는 알칼리 금속 및 알칼리 토금속 수산화물, 예컨대 NaOH, KOH, $Ca(OH)_2$, 알칼리 금속 수소화물, 예컨대 NaH, KH, 알칼리 금속 아미드, 예컨대 $NaNH_2$, 알칼리 금속 또는 알칼리 토금속 탄산염, 예컨대 K_2CO_3 또는 Cs_2CO_3, 및 알칼리 금속 알콕시드, 예컨대 NaOMe, NaOEt로 이루어진 군으로부터 선택된다. 게다가, 상기 언급된 염기의 혼합물

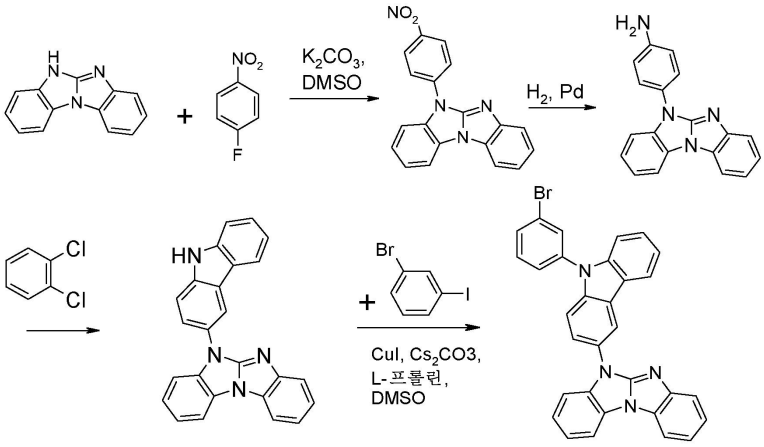
이 적합하다. NaOH, KOH, NaH 또는 K_2CO_3가 특히 바람직하다.

[0401] 헤테로아릴화는, 예를 들어,  의 화학식  의 할로겐화 화합물로의 구리 촉매에 의한 커플링 (울만 반응)에 의해 수행될 수 있다.

[0402] N-아릴화는, 예를 들어, 문헌 [H. Gilman and D. A. Shirley, J. Am. Chem. Soc. 66 (1944) 888]; [D. Li et al., Dyes and Pigments 49 (2001) 181-186] 및 [Eur. J. Org. Chem. (2007) 2147-151]에 개시되었다. 반응은 용매 중에서 또는 용융물 중에서 수행될 수 있다. 적합한 용매는, 예를 들어, (극성) 비프로톤성 용매, 예컨대 디메틸 술폭시드, 디메틸포름아미드, NMP, 트리데칸 또는 알콜이다.

[0403] 9-(8-브로모디벤조푸란-2-일)카르바졸  의 합성은 WO2010079051에 기재되어 있다. 2-브로모-8-아이오도-디벤조푸란  의 합성은 EP1885818에 기재되어 있다.

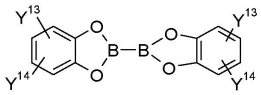
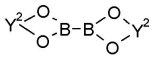
[0404] 화학식  의 화합물에 관한 가능한 합성 경로는 하기 반응식으로 나타냈다:

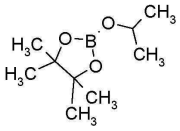
[0405] 

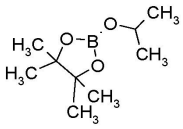
[0406] 문헌 [Angew. Chem. Int. Ed. 46 (2007) 1627-1629]을 참조한다.

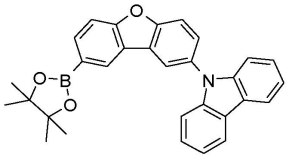
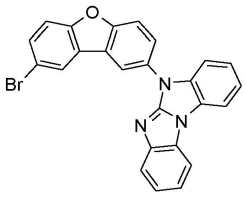
[0407] 디보론산 또는 디보로네이트기 함유 디벤조푸란, 디벤조티오펜 및 카르바졸은 경로 수를 증가시킴으로써 용이하게 제조할 수 있다. 합성 경로의 개요는, 예를 들어, 문헌 [Angew. Chem. Int. Ed. 48 (2009) 9240-9261]에 제시되어 있다.

[0408] 한 통상적인 경로에 의해 디보론산 또는 디보로네이트기 함유 디벤조푸란, 디벤조티오펜, 및 카르바졸은, 할로겐화 디벤조푸란, 디벤조티오펜 및 카르바졸을 용매, 예를 들어, 디메틸 포름아미드, 디메틸 술폭시드, 디옥산 및/또는 톨루엔 등 중에 촉매, 예를 들어, [1,1'-비스(디페닐포스피노)페로센]디클로로팔라듐(II), 착물 ($Pd(Cl)_2(dppf)$) 등, 및 염기, 예를 들어, 아세트산칼륨 등의 존재하에, $(Y^1O)_2B\text{-}B(OY^1)_2$,

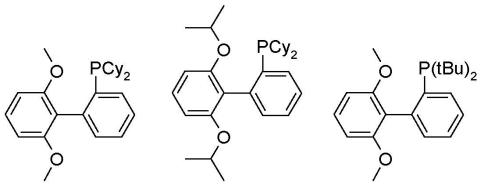
 , 또는  와 반응시킴으로써 수득할 수 있고 (문헌 [Prasad Appukkuttan et al., Synlett 8 (2003) 1204] 참조), 여기서 Y^1은 각 경우에 독립적으로 C_1-C_{18}알킬기이고 Y^2는 각 경우에 독립적으로 C_2-C_{10}알킬렌기, 예컨대 CY^3Y^4-CY^5Y^6-, 또는 CY^7Y^8-CY^9Y^{10}-$CY^{11}Y^{12}$-이고, 여기서 Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11} 및 Y^{12}는 서로 독립적으로 수소, 또는 C_1-C_{18}알킬기, 특히 $-C(CH_3)_2C(CH_3)_2-$, $-C(CH_3)_2CH_2C(CH_3)_2-$, 또는 $-CH_2C(CH_3)_2CH_2-$이고, Y^{13} 및 Y^{14}는 서로 독립적으로 수소, 또는 C_1-C_{18}알킬기이다.

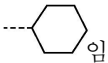
[0409] 디보론산 또는 디보로네이트기 함유 디벤조푸란, 디벤조티오펜 및 카르바졸 은 또한, 할로겐화 디벤조푸란, 디벤조티오펜 및 카르바졸을 알킬 리튬 시약, 예를 들어, n-부틸 리튬, 또는 t-부틸 리튬 등과, 이어서 보론산 에스테르, 예를 들어, B(이소프로폭시)$_3$, B(메톡시)$_3$, 또는  과 반응시킴으로써 제조할 수 있다 (문헌 [Synthesis (2000) 442-46] 참조).

[0410] 디보론산 또는 디보로네이트기 함유 디벤조푸란, 디벤조티오펜 및 카르바졸 은 또한 디벤조푸란, 디벤조티오펜 및 카르바졸을 리튬 아미드, 예를 들어, 리튬 디이소프로필아미드 (LDA) 등과 이어서 보론산 에스테르, 예를 들어, B(이소프로폭시)$_3$, B(메톡시)$_3$, 또는  등과 반응시킴으로써 제조할 수 있다 (문헌 [J. Org. Chem. 73 (2008) 2176-2181]).

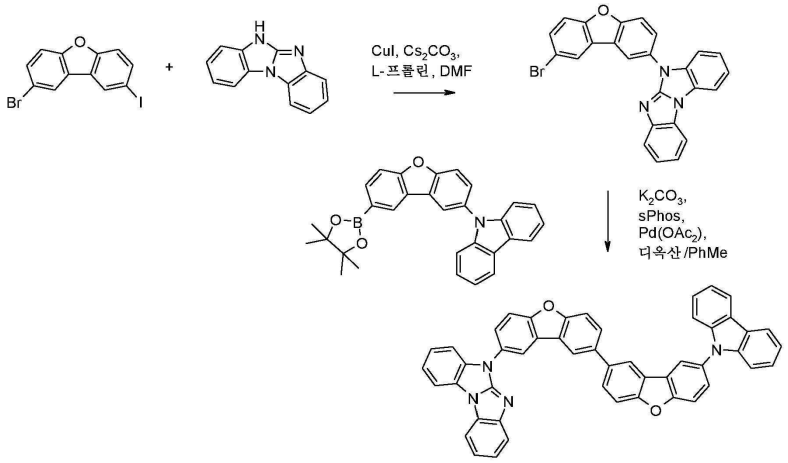
[0411] 디보론산 또는 디보로네이트기 함유 디벤조푸란, 디벤조티오펜 및 카르바졸, 예를 들어,  등은, 용매 중에서 및 촉매의 존재하에 등몰량의 할로겐화 디벤조푸란, 디벤조티오펜 및 카르바졸, 예를 들어,  등과 반응시킬 수 있다. 촉매는 μ-할로(트리이소프로필포스핀)(η^3-알릴)팔라듐(II) 유형 중 하나일 수 있다 (예를 들어 WO99/47474 참조).

[0412] 바람직하게는, 스즈키(Suzuki) 반응을 유기 용매, 예컨대 방향족 탄화수소 또는 통상의 극성 유기 용매, 예컨대 벤젠, 톨루엔, 크실렌, 테트라히드로푸란, 또는 디옥산, 또는 그의 혼합물, 가장 바람직한 톨루엔의 존재하에 수행한다. 통상, 용매의 양은 보론산 유도체의 몰당 1 내지 10 l의 범위로 선택된다. 또한 바람직하게는, 불활성 분위기, 예컨대 질소, 또는 아르곤 하에 반응을 수행한다. 추가로, 수성 염기, 예컨대 알칼리 금속 수산화물 또는 탄산염, 예컨대 NaOH, KOH, Na_2CO_3, K_2CO_3, Cs_2CO_3 등의 존재하에 반응을 수행하는 것이 바람직하고, 바람직하게는 K_2CO_3 수용액이 선택된다. 통상, 염기 대 보론산 또는 보론산 에스테르 유도체의 몰비는 0.5:1 내지 50:1, 매우 특히 1:1의 범위로 선택된다. 일반적으로, 반응 온도는 바람직하게는 환류 조건하에 40 내지 180℃의 범위로 선택된다. 바람직하게는, 반응 시간은 1 내지 80시간, 더욱 바람직하게는 20 내지 72시간의 범위로 선택된다. 바람직한 실시양태에서 커플링 반응 또는 중축합 반응을 위한 통상의 촉매, 바람직하게는 Pd-계 촉매가 사용되며, 이는 WO2007/101820에 기재되어 있다. 팔라듐 화합물은 폐쇄될 결합의 수를 기준으로 1:10000 내지 1:50, 바람직하게는 1:5000 내지 1:200의 비로 첨가된다. 예를 들어, 팔라듐(II) 염, 예컨대

$PdAc_2$ 또는 Pd_2dba_3의 사용 및 

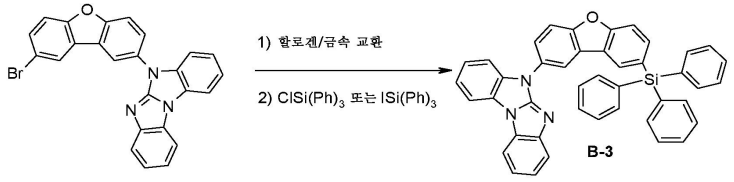
(여기서 Cy =  임)로 이루어진 군으로부터 선택된 리간드의 첨가가 바람직하다. 리간드는 Pd를 기준으로, 1:1 내지 1:10의 비로 첨가된다. 또한 바람직하게는, 촉매는 용액 또는 현탁액으로 첨가된다. 바람직하게는, 적절한 유기 용매, 예컨대 상기 기재된 것, 바람직하게는 벤젠, 톨루엔, 크실렌, THF, 디옥산, 더욱 바람직하게는 톨루엔, 또는 그의 혼합물이 사용된다. 용매의 양은 통상 보론산 유도체의 몰당 1 내지 10 l의 범위로 선택된다. 유기 염기, 예를 들어, 테트라알킬암모늄 히드록시드 등, 및 상 전이 촉매, 예를 들어 TBAB 등은 보론의 활성을 증진시킬 수 있다 (예를 들어, 문헌 [Leadbeater & Marco; Angew. Chem. Int. Ed. Eng. 42 (2003) 1407] 및 거기에 인용된 참조문헌 참조). 반응 조건의 다른 변화는 문헌 [T. I. Wallow and B. M. Novak in J. Org. Chem. 59 (1994) 5034-5037]; 및 [M. Remmers, M. Schulze, G. Wegner in Macromol. Rapid Commun. 17 (1996) 239-252] 및 [G. A. Molander und B. Canturk, Angew. Chem. , 121 (2009) 9404-9425]에 제시되어 있다.

[0413] 화합물 A-1에 관한 가능한 합성 경로는 하기 반응식으로 나타냈다:



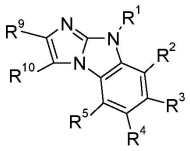
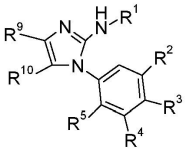
[0414]

[0415] 화합물 B-3에 관한 가능한 합성 경로는 하기 반응식으로 나타냈다:



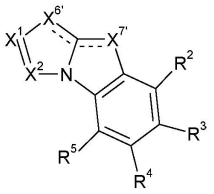
[0416]

[0417] 할로겐/금속 교환은 -78℃에서 nBuLi/THF, 또는 -78℃에서 tBuLi/THF를 사용하여 행한다. 이러한 화합물의 합성이 기재되어 있는 WO2010/079051을 참조한다.

[0418] 화학식  (Id')의 화합물은 또한, 화학식  의 화합물을 승온, 특히 100 내지 160℃의 온도에서 1 내지 72 h 동안 촉매, 예를 들어, 아세트산구리 ($Cu(OAc)_2$) 등; 리간드, 예를 들어, PPh_3, 및 1,10-페난트롤린 등; 염기, 예를 들어, 아세트산나트륨 (NaOAc), 탄산나트륨, 탄산칼륨, 탄산세슘, 인산칼륨, 및 탄산수소나트륨 등; 용매, 예를 들어, o-, m- 및 p-크실렌 등, 및 산소 (1 atm)의 존재하에 반응시킴으로써 합성할 수 있다. 문헌 [X. Wang et al. Org. Lett. 14 (2012) 452-455 [웹 공개: 2011년 12월 29일]]을 참조한다.

[0419] 화학식 V의 화합물은 본 발명의 화합물의 제조에서 중간체이고, 신규하며 본 발명의 추가의 대상을 형성한다.

[0420] <화학식 V>

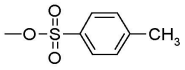
[0421] 

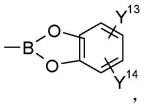
[0422] 상기 식에서,

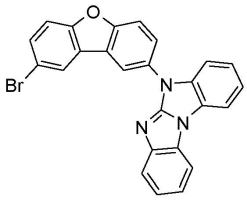
[0423] $X^{6'}$는 -N=이고 $X^{7'}$는 $-NR^{1'}-$이거나, $X^{7'}$는 -N=이고 $X^{6'}$는 $-NR^{1'}-$이고,

[0424] $R^{1'}$는 화학식 $-A^1-(A^2)_p-(A^3)_q-(A^4)_r-(R^{6'})_t$의 기이고, t는 1 또는 2, 특히 1이고;

[0425] p, q, r, A^1, A^2, A^3, A^4, X^1, X^2, R^2, R^3, R^4 및 R^5는 상기 정의된 바와 같다.

[0426] 한 실시양태에서 $R^{6'}$는 할로겐, 특히 Cl, Br, 또는 I; $-OS(O)_2CF_3$, $-OS(O)_2-$아릴, 특히  ; 또는 $-OS(O)_2CH_3$; 매우 특히 Br, 또는 I이다.

[0427] 또 다른 실시양태에서 $R^{6'}$는 ZnX^{12}, $-SnR^{207}R^{208}R^{209}$, $-B(OH)_2$, $-B(OY^1)_2$,  ,  , $-BF_4Na$, 또는 $-BF_4K$이고, 여기서 R^{207}, R^{208} 및 R^{209}는 동일하거나 상이하고 H 또는 C_1-C_6알킬이고, 이때 2개의 라디칼은 임의로 공통 고리를 형성하고 이들 라디칼은 임의로 분지 또는 비분지되고, X^{12}는 할로겐 원자, 특히 I, 또는 Br이고, Y^1은 각 경우에 독립적으로 C_1-C_{10}알킬기이고, Y^2는 각 경우에 독립적으로 C_2-C_{10}알킬렌기, 예컨대 $-CY^3Y^4-CY^5Y^6-$, 또는 $CY^7Y^8-CY^9Y^{10}-CY^{11}Y^{12}-$이고, 여기서 Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11} 및 Y^{12}는 서로 독립적으로 수소, 또는 C_1-C_{10}알킬기, 특히 $-C(CH_3)_2C(CH_3)_2-$, $-C(CH_3)_2CH_2C(CH_3)_2-$, 또는 $-CH_2C(CH_3)_2CH_2-$이고, Y^{13} 및 Y^{14}는 서로 독립적으로 수소 또는 C_1-C_{10}알킬기이다. p, q, r, A^1, A^2, A^3, A^4, X^1, X^2, R^2, R^3, R^4 및 R^5에 관해서는 화학식 I의 화합물에 관한 바람직한 정의가 동일하게 적용된다. 중간체의 예는 하기에 나타냈다: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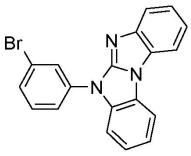
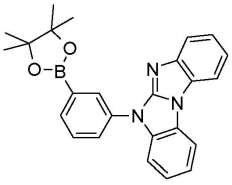

,

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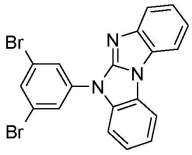
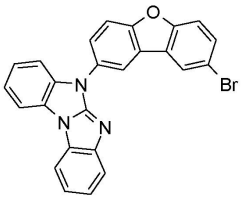
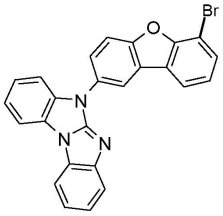

,

,

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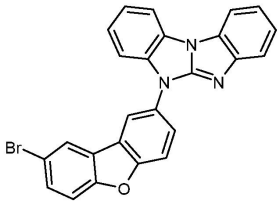
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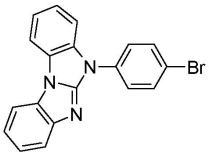
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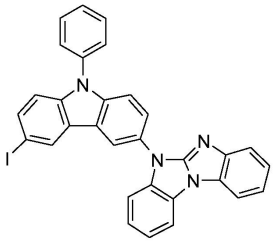
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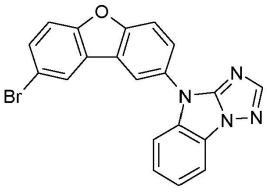
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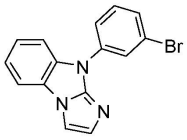
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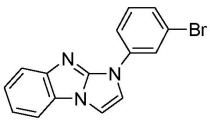
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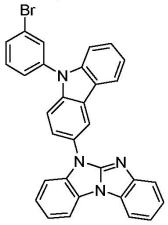
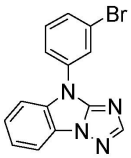

및

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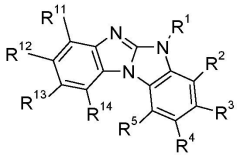
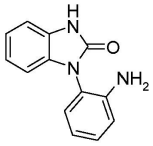
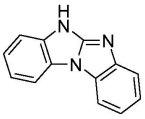
[0428]

[0429] 화학식 I의 화합물은, 예를 들어 스즈키-, 스틸(Stille)-, 또는 네기시(Negishi)-커플링 반응에 의한, 중간체 및 적합한 공반응물로부터 출발하여 수득될 수 있다.

[0430] 화학식  (II)의 화합물 (상기 식에서 R^2, R^3, R^4, R^5, R^{11}, R^{12}, R^{13} 및 R^{14}는 H이고, R^1은 상기 정의된 바와 같음)의 제조 방법은, (a) 화학식  (X)의 화합물을 H_3PO_4, 폴리인산, CH_3SO_3H/P_2O_5, CH_3SO_3H, 또는 황산에서 가열하여 화학식  (XI)의 화합물을 수득하는 단계; 및 (b) 화학식 XI의 화합물을 반응시켜 화학식 II의 화합물을 수득하는 단계를 포함할 수 있다. 단계 b)에 관한 다양한 예는 상기에 설명되어 있다. 단계 a)에서 140℃ 초과의 비점을 갖는 용매, 또는 용매의 혼합물, 예를 들어, 크실렌, 또는 메시틸렌 등이 존재할 수 있다. 화학식 X의 화합물을 불활성 기체, 예를 들어, 질소, 또는 아르곤의 분위기

하에, 140℃ 초과, 바람직하게는 160℃ 초과, 더욱 바람직하게는 180℃ 초과의 온도에서, 30분 내지 3주의 시간, 바람직하게는 1 내지 48 h 동안 교반한다.

[0431] 화학식 I의 화합물은 전하 캐리어 전도성이 필요한 응용에 사용하기에 특히 적합하고, 특히 예를 들어 스위칭 소자, 예컨대 유기 트랜지스터, 예를 들어 유기 FET 및 유기 TFT, 유기 태양 전지 및 유기 발광 다이오드(OLED)로부터 선택되는 유기 전자장치 응용에 사용하기에 적합하고, 화학식 I의 화합물은 발광층에서의 매트릭스 물질로서 및/또는 정공 및/또는 여기자 차단제 물질로서 및/또는 전자 및/또는 여기자 차단제 물질로서, 특히 인광 방출체와 조합하여 사용하기 위한 OLED에서 특히 적합한 것으로 밝혀졌다. 본 발명의 화학식 I의 화합물을 OLED에서 사용하는 경우에, 양호한 효율 및 긴 수명을 갖고 특히 낮은 사용 및 작동 전압에서 작동될 수 있는 OLED가 수득된다. 본 발명의 화학식 I의 화합물은 특히, 청색 및 녹색 방출체, 예를 들어 청색광 또는 암청색광 방출체 (이들은 특히 인광 방출체임)를 위한 매트릭스 및/또는 정공/여기자 차단제 물질로서 사용하기에 적합하다. 더욱이, 화학식 I의 화합물은 스위칭 소자 및 유기 태양 전지로부터 선택된 유기 전자장치 응용에서의 전도체/상보적 물질로서 사용될 수 있다.

[0432] 화학식 I의 화합물은 유기 전자장치 응용에서, 특히 OLED에서 매트릭스 물질 및/또는 정공/여기자 차단제 물질 및/또는 전자/여기자 차단제 물질 및/또는 정공 주입 물질 및/또는 전자 주입 물질 및/또는 정공 전도체 물질 (정공 수송 물질) 및/또는 전자 전도체 물질 (전자 수송 물질)로서, 바람직하게는 매트릭스 물질 및/또는 전자/여기자 차단제 및/또는 정공 수송 물질로서 사용될 수 있다. 본 발명의 화학식 I의 화합물은 더욱 바람직하게는 유기 전자장치 응용에서, 특히 OLED에서 매트릭스 물질로서 사용된다.

[0433] OLED의 발광층 또는 발광층들 중 하나에서, 방출체 물질을 화학식 I의 화합물의 매트릭스 물질 및 예를 들어, 양호한 정공 전도체 (정공 수송) 특성을 갖는 추가의 매트릭스 물질과 조합할 수도 있다. 이로써 이러한 발광층의 높은 양자 효율이 달성된다.

[0434] 화학식 I의 화합물이 발광층에서 매트릭스 물질로서 및 추가로 정공/여기자 차단제 물질 및/또는 전자/여기자 차단제 물질로서 사용되는 경우, 물질의 화학적 동일성 또는 유사성으로 인해, 발광층과 인접 정공/여기자 차단제 물질 및/또는 전자/여기자 차단제 물질 사이에 개선된 계면이 수득되고, 이는 동등한 휘도를 갖는 전압의 감소 및 OLED의 수명의 연장을 초래할 수 있다. 더욱이, 정공/여기자 차단제 물질 및/또는 전자/여기자 차단제 물질을 위한 및 발광층의 매트릭스를 위한 동일 물질의 사용으로 OLED의 제조 공정의 단순화가 가능해지며, 그 이유는 동일 공급원이 화학식 I의 화합물 중 하나의 물질의 기상 증착 공정에 사용될 수 있기 때문이다.

[0435] 유기 전자 소자의 적합한 구조는 당업자에게 공지되어 있고 하기에 명시되어 있다.

[0436] 유기 트랜지스터는 일반적으로 정공 수송 능력 및/또는 전자 수송 능력을 갖는 유기 층으로부터 형성된 반도체 층; 전도성 층으로부터 형성된 게이트 전극; 및 반도체 층과 전도성 층 사이에 도입된 절연층을 포함한다. 소스 전극 및 드레인 전극을 이러한 배치로 설치함으로써 트랜지스터 소자를 제조한다. 게다가, 당업자에게 공지된 추가의 층을 유기 트랜지스터에 존재시킬 수 있다.

[0437] 유기 태양 전지 (광전 변환 소자)는 일반적으로, 평행으로 배치된 2개의 플레이트-유형 전극 사이에 존재하는 유기 층을 포함한다. 유기 층은 콤(comb)-유형 전극상에 배열될 수 있다. 유기 층의 위치와 관련하여 특별한 제한은 없으며 전극의 물질과 관련하여 특별한 제한은 없다. 그러나, 평행으로 배치된 플레이트-유형 전극이 사용될 경우, 하나 이상의 전극이 바람직하게는 투명 전극, 예를 들어 ITO 전극 또는 플루오린-도핑된 주석 산화물 전극으로부터 형성된다. 유기 층은 2개의 서브층, 즉 p-유형 반도체 특성 또는 정공 수송 능력을 갖는 층, 및 n-유형 반도체 특성 또는 전자 수송 능력을 갖도록 형성된 층으로부터 형성된다. 게다가, 당업자에게 공지된 추가의 층을 유기 태양 전지에 존재시키는 것이 가능하다. 전자 수송 능력을 갖는 층은 화학식 I의 화합물을 포함할 수 있다.

[0438] 화학식 I의 화합물은 발광층 (바람직하게는 매트릭스 물질로서)에 뿐만 아니라 전자 차단층 (전자/여기자 차단제로서)에도 존재하는 것이 마찬가지로 가능하다.

[0439] 본 발명은 추가로, 애노드 An 및 캐소드 Ka 및 애노드 An와 캐소드 Ka 사이에 배열된 발광층 E, 및 적절한 경우 정공/여기자에 대한 하나 이상의 차단층, 전자/여기자에 대한 하나 이상의 차단층, 하나 이상의 정공 주입층, 하나 이상의 정공 전도체 층, 하나 이상의 전자 주입층 및 하나 이상의 전자 전도체 층으로 이루어진 군으로부터 선택된 하나 이상의 추가의 층을 포함하는 유기 발광 다이오드를 제공하고, 여기서 하나 이상의 화학식 I의 화합물이 발광층 E 및/또는 하나 이상의 추가의 층에 존재한다. 하나 이상의 화학식 I의 화합물은 바람직하게는 발광층 및/또는 정공 차단층에 존재한다.

[0440] 본 출원은 추가로 하나 이상의 화학식 I의 화합물을 포함하는 발광층에 관한 것이다.

[0441] *본 발명의 OLED의 구조*

[0442] 따라서 본 발명의 유기 발광 다이오드 (OLED)는 일반적으로 하기 구조를 갖는다:

[0443] 애노드 (An) 및 캐소드 (Ka), 및 애노드 (An)와 캐소드 (Ka) 사이에 배치된 발광층 E.

[0444] 본 발명의 OLED는, 예를 들어 - 바람직한 실시양태에서 - 하기 층으로부터 형성될 수 있다:

[0445] 1. 애노드

[0446] 2. 정공 전도체층

[0447] 3. 발광층

[0448] 4. 정공/여기자 차단층

[0449] 5. 전자 전도체층

[0450] 6. 캐소드

[0451] 상기 언급된 구조와 상이한 층 배열이 또한 가능하고, 당업자에게 공지되어 있다. 예를 들어, OLED가 언급된 층 모두를 갖는 것은 아닐 수 있고; 예를 들어, 층 (1) (애노드), (3) (발광층) 및 (6) (캐소드)을 갖는 OLED가 마찬가지로 적합하고, 이러한 경우에 층 (2) (정공 전도체 층) 및 (4) (정공/여기자 차단층) 및 (5) (전자 전도체 층)의 기능은 인접 층에 의해 추정된다. 층 (1), (2), (3) 및 (6), 또는 층 (1), (3), (4), (5) 및 (6)을 갖는 OLED가 마찬가지로 적합하다. 게다가, OLED는 정공 전도체 층 (2)과 발광층 (3) 사이에 전자/여기자 차단층을 가질 수 있다.

[0452] 게다가, 복수의 상기 언급된 기능 (전자/여기자 차단제, 정공/여기자 차단제, 정공 주입, 정공 전도, 전자 주입, 전자 전도)이 한 층에 조합되어 있고, 예를 들어 당해 층에 존재하는 단일 물질에 의해 추정되는 것이 가능하다. 예를 들어, 정공 전도체 층에 사용된 물질은, 한 실시양태에서, 여기자 및/또는 전자를 동시에 차단할 수 있다.

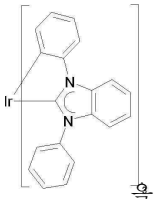
[0453] 더욱이, 상기 특정된 것 중에서 OLED의 개별 층은 차례차례 2개 이상의 층으로부터 형성될 수 있다. 예를 들어, 정공 전도체 층은 전극으로부터 정공이 주입되는 층, 및 정공 주입층에서 발광층 내로 정공을 멀리 수송하는 층으로부터 형성될 수 있다. 전자 전도체 층은 마찬가지로 복수의 층, 예를 들어 전극에 의해 전자가 주입되는 층, 및 전자 주입층으로부터 전자를 받아 이를 발광층 내로 수송하는 층으로 이루어질 수 있다. 언급된 이들 층은 각각 에너지 수준, 열 저항 및 전하 캐리어 이동성, 및 또한 유기 층 또는 금속 전극을 갖는 특정된 층의 에너지 차이와 같은 요인에 따라 선택된다. 당업자는 본 발명에 따라 방출체 물질로서 사용된 유기 화합물에 최적으로 부합되도록 OLED의 구조를 선택할 수 있다.

[0454] 특히 효율적인 OLED를 수득하기 위해, 예를 들어, 정공 전도체 층의 HOMO (최고 피점 분자 궤도(highest occupied molecular orbital))는 애노드의 작업 기능에 부합되어야 하고, 전자 전도체 층의 LUMO (최저 공 분자 궤도(lowest unoccupied molecular orbital))는 캐소드의 작업 기능에 부합되어야 하되, 단, 상기 언급된 층이 본 발명의 OLED에 존재한다.

[0455] 애노드 (1)는 양전하 캐리어를 제공하는 전극이다. 이는, 예를 들어, 금속, 다양한 금속의 혼합물, 금속 합금, 금속 산화물 또는 다양한 금속 산화물의 혼합물을 포함하는 물질로부터 형성될 수 있다. 대안으로, 애노드는 전도성 중합체일 수 있다. 적합한 금속은 금속 및 주족(main groups)의 금속, 전이 금속 및 란타노이드의 합금, 특히 원소 주기율표의 Ib족, IVa족, Va족 및 VIa족의 금속, 및 VIIIa족의 전이 금속을 포함한다. 애노드를 투명하게 하고자 할 경우, 일반적으로 원소 주기율표 (IUPAC 버전)의 IIb족, IIIb족 및 IVb족의 혼합된 금속 산화물, 예를 들어 인듐 주석 산화물(ITO)을 사용한다. 마찬가지로 애노드 (1)가, 예를 들어 문헌 [Nature, Vol. 357, pages 477 to 479 (June 11, 1992)]에 기재된 바와 같이, 유기 물질, 예를 들어 폴리아닐린을 포함하는 것이 가능하다. 애노드와 캐소드 둘 중 하나 이상은 형성된 광을 방출가능하게 하기 위해 적어도 부분적으로 투명해야 한다. 애노드 (1)용으로 사용된 물질은 바람직하게는 ITO이다.

[0456] 본 발명의 OLED의 층 (2)에 적합한 정공 전도체 물질은, 예를 들어 문헌 [Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 18, pages 837 to 860, 1996]에 개시되어 있다. 정공 수송 분자 및 중합체 둘 다는 정공 수송 물질로서 사용될 수 있다. 전형적으로 사용되는 정공 수송 분자는 트리스[N-(1-나프

틸)-N-(페닐아미노)]트리페닐아민 (1-NaphDATA), 4,4'-비스[N-(1-나프틸)-N-페닐아미노]비페닐 (α-NPD), N,N'-디페닐-N,N'-비스(3-메틸페닐)-[1,1'-비페닐]-4,4'-디아민 (TPD), 1,1-비스[(디-4-톨릴아미노)페닐]시클로헥산 (TAPC), N,N'-비스(4-메틸페닐)-N,N'-비스(4-에틸페닐)-[1,1'-(3,3'-디메틸)비페닐]-4,4'-디아민 (ETPD), 테트라키스(3-메틸페닐)-N,N,N',N'-2,5-페닐렌디아민 (PDA), α-페닐-4-N,N-디페닐아미노스티렌 (TPS), p-(디에틸아미노)벤즈알데히드 디페닐히드라존 (DEH), 트리페닐아민 (TPA), 비스[4-(N,N-디에틸아미노)-2-메틸페닐)(4-메틸페닐)메탄 (MPMP), 1-페닐-3-[p-(디에틸아미노)스티릴]-5-[p-(디에틸아미노)페닐]피라졸린 (PPR 또는 DEASP), 1,2-트랜스-비스(9H-카르바졸-9-일)시클로부탄 (DCZB), N,N,N',N'-테트라키스(4-메틸페닐)-(1,1'-비페닐)-4,4'-디아민 (TTB), 4,4',4"-트리스(N,N-디페닐아미노)트리페닐아민 (TDTA), 4,4',4"-트리스(N-카르바졸릴)트리페닐아민 (TCTA), N,N'-비스(나프탈렌-2-일)-N,N'-비스(페닐)벤지딘 (β-NPB), N,N'-비스(3-메틸페닐)-N,N'-비스(페닐)-9,9-스피로비플루오렌 (스피로-TPD), N,N'-비스(나프탈렌-1-일)-N,N'-비스(페닐)-9,9-스피로비플루오렌 (스피로-NPB), N,N'-비스(3-메틸페닐)-N,N'-비스(페닐)-9,9-디메틸플루오렌 (DMFL-TPD), 디[4-(N,N-디톨릴아미노)페닐]시클로헥산, N,N'-비스(나프탈렌-1-일)-N,N'-비스(페닐)-9,9-디메틸플루오렌, N,N'-비스(나프탈렌-1-일)-N,N'-비스(페닐)-2,2-디메틸벤지딘, N,N'-비스(나프탈렌-1-일)-N,N'-비스(페닐)벤지딘, N,N'-비스(3-메틸페닐)-N,N'-비스(페닐)벤지딘, 2,3,5,6-테트라플루오로-7,7,8,8-테트라시아노퀴노디메탄 (F4-TCNQ), 4,4',4"-트리스(N-3-메틸페닐-N-페닐아미노)트리페닐아민, 4,4',4"-트리스(N-(2-나프틸)-N-페닐-아미노)트리페닐아민, 피라지노[2,3-f][1,10]페난트롤린-2,3-디카르보니트릴 (PPDN), N,N,N',N'-테트라키스(4-메톡시페닐)벤지딘 (MeO-TPD), 2,7-비스[N,N-비스(4-메톡시페닐)아미노]-9,9-스피로비플루오렌 (MeO-스피로-TPD), 2,2'-비스[N,N-비스(4-메톡시페닐)아미노]-9,9-스피로비플루오렌 (2,2'-MeO-스피로-TPD), N,N'-디페닐-N,N'-디[4-(N,N-디톨릴아미노)페닐]벤지딘 (NTNPB), N,N'-디페닐-N,N'-디[4-(N,N-디페닐아미노)페닐]벤지딘 (NPNPB), N,N'-디(나프탈렌-2-일)-N,N'-디페닐벤젠-1,4-디아민 (β-NPP), N,N'-비스(3-메틸페닐)-N,N'-비스(페닐)-9,9-디페닐플루오렌 (DPFL-TPD), N,N'-비스(나프탈렌-1-일)-N,N'-비스(페닐)-9,9-디페닐플루오렌 (DPFL-NPB), 2,2',7,7'-테트라키스(N,N-디페닐아미노)-9,9'-스피로비플루오렌 (스피로-TAD), 9,9-비스[4-(N,N-비스(비페닐-4-일)아미노)페닐]-9H-플루오렌 (BPAPF), 9,9-비스[4-(N,N-비스(나프탈렌-2-일)아미노)페닐]-9H-플루오렌 (NPAPF), 9,9-비스[4-(N,N-비스(나프탈렌-2-일)-N,N'-비스페닐아미노)페닐]-9H-플루오렌 (NPBAPF), 2,2',7,7'-테트라키스[N-나프탈레닐(페닐)아미노]-9,9'-스피로비플루오렌 (스피로-2NPB), N,N'-비스(페난트렌-9-일)-N,N'-비스(페닐)벤지딘 (PAPB), 2,7-비스[N,N-비스(9,9-스피로비플루오렌-2-일)아미노]-9,9-스피로비플루오렌 (스피로-5), 2,2'-비스[N,N-비스(비페닐-4-일)아미노]-9,9-스피로비플루오렌 (2,2'-스피로-DBP), 2,2'-비스(N,N-디페닐아미노)-9,9-스피로비플루오렌 (스피로-BPA), 2,2',7,7'-테트라(N,N-디톨릴)아미노스피로비플루오렌 (스피로-TTB), N,N,N',N'-테트라나프탈렌-2-일벤지딘 (TNB), 포르피린 화합물 및 프탈로시아닌, 예컨대 구리 프탈로시아닌 및 산화티탄 프탈로시아닌으로 이루어진 군으로부터 선택된다. 전형적으로 사용되는 정공 수송 중합체는 폴리비닐카르바졸, (페닐메틸)폴리실란 및 폴리아닐린으로 이루어진 군으로부터 선택된다. 마찬가지로 정공 수송 분자를 폴리스티렌 및 폴리카르보네이트와 같은 중합체 내로 도핑함으로써 정공 수송 중합체를 수득하는 것이 가능하다. 적합한 정공 수송 분자는 상기에서 이미 언급된 분자이다.

[0457] 게다가 - 한 실시양태에서 - 카르벤 착물을 정공 수송 물질로서 사용하는 것이 가능하고, 하나 이상의 정공 전도체 물질의 밴드 갭(band gap)은 일반적으로, 사용되는 방출체 물질의 밴드 갭보다 더 크다. 본 출원의 맥락에서, "밴드 갭"은 삼중항 에너지(triplet energy)를 의미하는 것으로 이해된다. 적합한 카르벤 착물은, 예를 들어, WO 2005/019373 A2, WO 2006/056418 A2, WO 2005/113704, WO 2007/115970, WO 2007/115981 및 WO 2008/000727에 기재된 바와 같은 카르벤 착물이다. 적합한 카르벤 착물의 한 예는 화학식 

을 갖는 $Ir(dpbic)_3$이며, 이는 예를 들어 WO2005/019373에 개시되어 있다. 원칙상, 정공 전도체 층이 하나 이상의 화학식 I의 화합물을 정공 전도체 물질로서 포함하는 것이 가능하다.

[0458] 발광층 (3)은 하나 이상의 방출체 물질을 포함한다. 원칙상, 형광 또는 인광 방출체일 수 있고, 적합한 방출체 물질은 당업자에게 공지되어 있다. 적어도 1개의 방출체 물질은 바람직하게는 인광 방출체이다. 바람직하게 사용되는 인광 방출체 화합물은 금속 착물, 및 특히 금속 Ru, Rh, Ir, Pd 및 Pt의 착물, 특히 Ir의 착물을 기재로 하며, 중요성이 증가되었다. 화학식 I의 화합물은 발광층에서 매트릭스로서 사용될 수 있다.

[0459] 본 발명의 OLED에서 사용하기에 적합한 금속 착물은, 예를 들어 WO 02/60910 A1, US 2001/0015432 A1, US 2001/0019782 A1, US 2002/0055014 A1, US 2002/0024293 A1, US 2002/0048689 A1, EP 1 191 612 A2, EP 1 191 613 A2, EP 1 211 257 A2, US 2002/0094453 A1, WO 02/02714 A2, WO 00/70655 A2, WO 01/41512 A1, WO 02/15645 A1, WO 2005/019373 A2, WO 2005/113704 A2, WO 2006/115301 A1, WO 2006/067074 A1, WO 2006/056418, WO 2006121811 A1, WO 2007095118 A2, WO 2007/115970, WO 2007/115981, WO 2008/000727, WO2010129323, WO2010056669 및 WO10086089에 기재되어 있다.

[0460] 추가의 적합한 금속 착물은 시판되는 금속 착물 트리스(2-페닐피리딘)이리듐(III), 이리듐(III) 트리스(2-(4-톨릴)피리디네이토-N,$C^{2'}$), 비스(2-페닐피리딘)(아세틸아세토네이토)이리듐(III), 이리듐(III) 트리스(1-페닐이소퀴놀린), 이리듐(III) 비스(2,2'-벤조티에닐)피리디네이토-N,$C^{3'}$)(아세틸아세토네이트), 트리스(2-페닐퀴놀린)이리듐(III), 이리듐(III) 비스(2-(4,6-디플루오로페닐)피리디네이토-N,C^{2})피콜리네이트, 이리듐(III) 비스(1-페닐이소퀴놀린)(아세틸아세토네이트), 비스(2-페닐퀴놀린)(아세틸아세토네이토)이리듐(III), 이리듐(III) 비스(디-벤조[f,h]퀴녹살린)(아세틸아세토네이트), 이리듐(III) 비스(2-메틸디벤조[f,h]퀴녹살린)(아세틸아세토네이트) 및 트리스(3-메틸-1-페닐-4-트리메틸아세틸-5-피라졸리노)테르븀(III), 비스[1-(9,9-디메틸-9H-플루오렌-2-일)이소퀴놀린](아세틸아세토네이토)이리듐(III), 비스(2-페닐벤조티아졸레이토)(아세틸아세토네이토)이리듐(III), 비스(2-(9,9-디헥실플루오레닐)-1-피리딘)(아세틸아세토네이토)이리듐(III), 비스(2-벤조[b]티오펜-2-일-피리딘)(아세틸아세토네이토)이리듐(III)이다.

[0461] 게다가, 하기의 시판 물질이 적합하다: 트리스(디벤조일아세토네이토)모노(페난트롤린)유로퓸(III), 트리스(디벤조일메탄)모노(페난트롤린)유로퓸(III), 트리스(디벤조일메탄)모노(5-아미노페난트롤린)유로퓸(III), 트리스(디-2-나프토일메탄)모노(페난트롤린)유로퓸(III), 트리스-(4-브로모벤조일메탄)모노(페난트롤린)유로퓸(III), 트리스(디(비페닐)메탄)모노(페난트롤린)유로퓸(III), 트리스(디벤조일메탄)모노(4,7-디페닐-페난트롤린)유로퓸(III), 트리스(디벤조일메탄)모노(4,7-디-메틸페난트롤린)유로퓸(III), 트리스(디벤조일메탄)모노(4,7-디메틸페난트롤린디술폰산)유로퓸(III) 이나트륨 염, 트리스[디(4-(2-(2-에톡시에톡시)에톡시)벤조일메탄)]모노(페난트롤린)유로퓸(III) 및 트리스[디[4-(2-(2-에톡시에톡시)에톡시)벤조일메탄)]모노(5-아미노페난트롤린)유로퓸(III), 오스뮴(II) 비스(3-(트리플루오로메틸)-5-(4-tert-부틸피리딜)-1,2,4-트리아졸레이토)디페닐메틸포스핀, 오스뮴(II) 비스(3-(트리플루오로메틸)-5-(2-피리딜)-1,2,4-트리아졸)디메틸페닐포스핀, 오스뮴(II) 비스(3-(트리플루오로메틸)-5-(4-tert-부틸피리딜)-1,2,4-트리아졸레이토)디메틸페닐포스핀, 오스뮴(II) 비스(3-(트리플루오로메틸)-5-(2-피리딜)-피라졸레이토)디메틸페닐포스핀, 트리스[4,4'-디-tert-부틸(2,2')-비피리딘]루테늄(III), 오스뮴(II) 비스(2-(9,9-디부틸플루오레닐)-1-이소퀴놀린(아세틸아세토네이트).

[0462] 발광층은 바람직하게는 화학식 $[L]_{m1}[K]_{o}M[carbene]_{n1}$ (IX)의 화합물을 포함하며, 이는 WO 2005/019373 A2에 기재되어 있고, 상기 식에서, 기호는 하기 의미를 가진다:

[0463] M은 각각의 금속 원자에 관해 가능한 임의의 산화 상태의 Co, Rh, Ir, Nb, Pd, Pt, Fe, Ru, Os, Cr, Mo, W, Mn, Tc, Re, Cu, Ag 및 Au로 이루어진 군으로부터 선택된 금속 원자이고;

[0464] 카르벤은 비하전 또는 일음이온성 및 일좌배위, 이좌배위 또는 삼좌배위일 수 있는 카르벤 리간드이고, 카르벤 리간드는 또한 비스카르벤 또는 트리스카르벤 리간드일 수 있고;

[0465] L은 일음이온성 또는 이음이온성 리간드이고, 이는 일좌배위 또는 이좌배위일 수 있고;

[0466] K는 포스핀; 포스포네이트 및 그의 유도체, 아르세네이트 및 그의 유도체; 포스파이트; CO; 피리딘; 니트릴 및 M^1과 π 착물을 형성하는 공액 디엔으로 이루어진 군으로부터 선택된 비하전 일좌배위 또는 이좌배위 리간드이고;

[0467] n1은 카르벤 리간드의 개수이고, 여기서 n1은 1 이상이고, n1 > 1인 경우 화학식 I의 착물 중 카르벤 리간드는 동일하거나 상이할 수 있고;

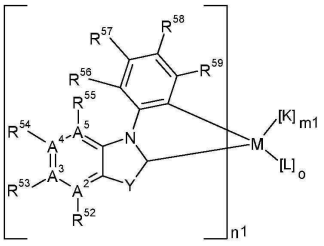
[0468] m은 리간드 L의 개수이고, 여기서 m1은 0 또는 ≥ 1일 수 있고, m > 1인 경우 리간드 L은 동일하거나 상이할 수 있고;

[0469] o는 리간드 K의 개수이고, 여기서 o는 0 또는 ≥ 1일 수 있고, o > 1인 경우 리간드 K는 동일하거나 상이할 수

있고;

[0470] 여기서 n1 + m1 + o의 합은 금속 원자의 산화 상태 및 배위 수 및 리간드 카르벤, L 및 K의 덴티시티(denticity) 및 또한 리간드, 카르벤 및 L의 전하에 따라 좌우되되, 단, n1은 1 이상이다.

[0471] 적합한 삼중 방출체인 카르벤 착물은 예를 들어 WO 2006/056418 A2, WO 2005/113704, WO 2007/115970, WO 2007/115981 및 WO 2008/000727, WO2009050281, WO2009050290, WO2011051404 및 WO2011073149에 기재되어 있다.

[0472] 화학식  (IXa)의 금속-카르벤 착물이 더욱 바람직하며, 이는 미국 특허 출원 번호 61/286046, 61/323885 및 유럽 특허 출원 10187176.2 (PCT/EP2010/069541)에 기재되어 있고, 상기 식에서 M, n1, Y, A^2, A^3, A^4, A^5, R^{51}, R^{52}, R^{53}, R^{54}, R^{55}, R^{56}, R^{57}, R^{58}, R^{59}, K, L, m1 및 o는 각각 하기와 같이 정의된다:

[0473] M은 Ir, 또는 Pt이고,

[0474] n1은 1, 2 및 3으로부터 선택된 정수이고,

[0475] Y는 NR^{51}, O, S 또는 $C(R^{25})_2$이고,

[0476] A^2, A^3, A^4, 및 A^5는 서로 독립적으로 N 또는 C이고, 여기서 2 A = 질소 원자이고 1개 이상의 탄소 원자는 고리 내에 2개의 질소 원자 사이에 존재하고,

[0477] R^{51}은 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 1 내지 20개의 탄소 원자를 갖는 선형 또는 분지형 알킬 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 3 내지 20개의 탄소 원자를 갖는 시클로알킬 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 6 내지 30개의 탄소 원자를 갖는 치환되거나 비치환된 아릴 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 총 5 내지 18개의 탄소 원자 및/또는 헤테로원자를 갖는 치환되거나 비치환된 헤테로아릴 라디칼이고,

[0478] R^{52}, R^{53}, R^{54} 및 R^{55}는 각각, A^2, A^3, A^4 및/또는 A^5가 N인 경우, 자유 전자쌍이거나, A^2, A^3, A^4 및/또는 A^5가 C인 경우, 각각 독립적으로 수소, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 1 내지 20개의 탄소 원자를 갖는 선형 또는 분지형 알킬 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 3 내지 20개의 탄소 원자를 갖는 시클로알킬 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 6 내지 30개의 탄소 원자를 갖는 치환되거나 비치환된 아릴 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 총 5 내지 18개의 탄소 원자 및/또는 헤테로원자를 갖는 치환되거나 비치환된 헤테로아릴 라디칼, 공여자 또는 수용자 작용을 갖는 기이거나,

[0479] R^{53} 및 R^{54}는 A^3 및 A^4와 함께 임의로 1개 이상의 추가의 헤테로원자가 개재되고 총 5 내지 18개의 탄소 원자 및/또는 헤테로원자를 갖는 임의로 치환되거나 비치환된 고리를 형성하고,

[0480] R^{56}, R^{57}, R^{58} 및 R^{59}는 각각 독립적으로 수소, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 1 내지 20개의 탄소 원자를 갖는 선형 또는 분지형 알킬 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 3 내지 20개의 탄소 원자를 갖는 시클로알킬 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 3 내지 20개의 탄소 원자를 갖는 시클로헤테로알킬 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 6 내지 30개의 탄소 원자를 갖는 비치환되거나 치환된 아릴 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 총 5 내지 18개의 탄소 원자 및/또는 헤테로원자를 갖는 치환되거나 비치

환된 헤테로아릴 라디칼, 공여자 또는 수용자 작용을 갖는 기이거나,

[0481] R^{56} 및 R^{57}, R^{57} 및 R^{58} 또는 R^{58} 및 R^{59}는 이들이 결합된 탄소 원자와 함께, 임의로 1개 이상의 헤테로원자가 개재되고 총 5 내지 18개의 탄소 원자 및/또는 헤테로원자를 갖는 포화, 불포화 또는 방향족, 임의로 치환된 고리를 형성하고/거나,

[0482] A^5가 C인 경우, R^{55} 및 R^{56}는 함께 임의로 헤테로원자, 방향족 단위, 헤테로방향족 단위 및/또는 관능기를 포함하고 총 1 내지 30개의 탄소 원자 및/또는 헤테로원자를 갖는 포화 또는 불포화, 선형 또는 분지형 브릿지를 형성하고, 여기에 탄소 원자 및/또는 헤테로원자를 포함하는 치환되거나 비치환된, 5- 내지 8-원 고리가 임의로 융합되고,

[0483] R^{25}는 독립적으로 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 1 내지 20개의 탄소 원자를 갖는 선형 또는 분지형 알킬 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 3 내지 20개의 탄소 원자를 갖는 시클로알킬 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 6 내지 30개의 탄소 원자를 갖는 치환되거나 비치환된 아릴 라디칼, 임의로 1개 이상의 헤테로원자가 개재되고, 임의로 1개 이상의 관능기를 함유하며 총 5 내지 18개의 탄소 원자 및/또는 헤테로원자를 갖는 치환되거나 비치환된 헤테로아릴 라디칼이고,

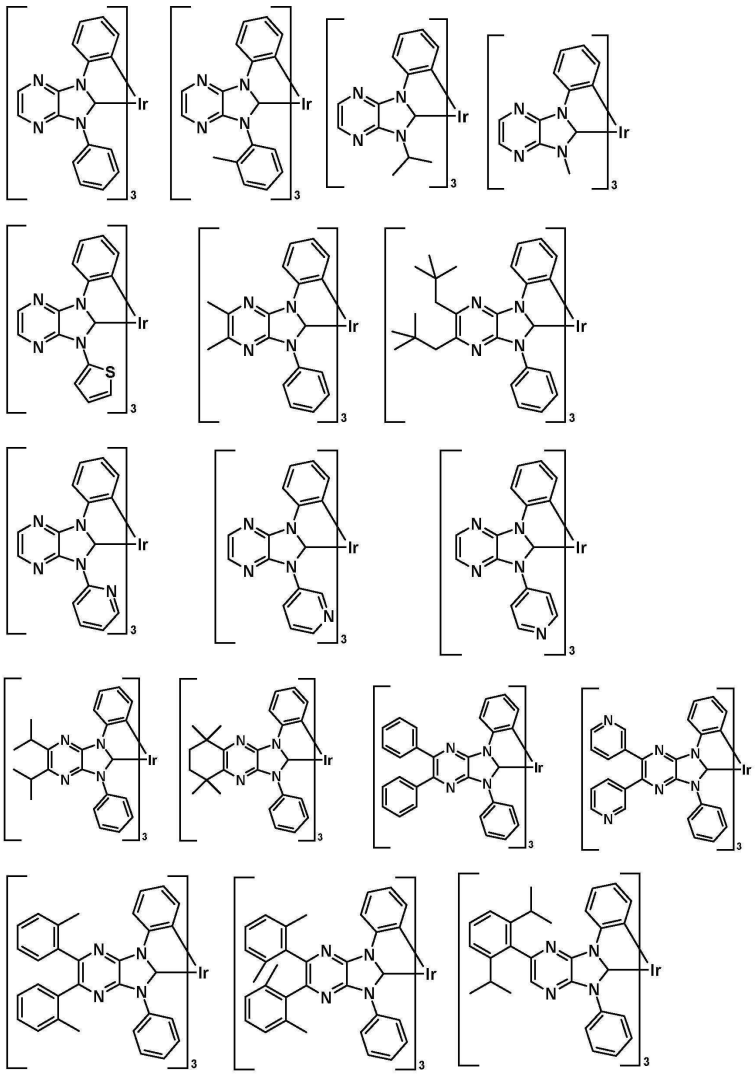
[0484] K는 비하전 일좌배위 또는 이좌배위 리간드이고,

[0485] L은 일음이온성 또는 이음이온성 리간드, 바람직하게는 일음이온성 리간드이고, 이는 일좌배위 또는 이좌배위일 수 있고,

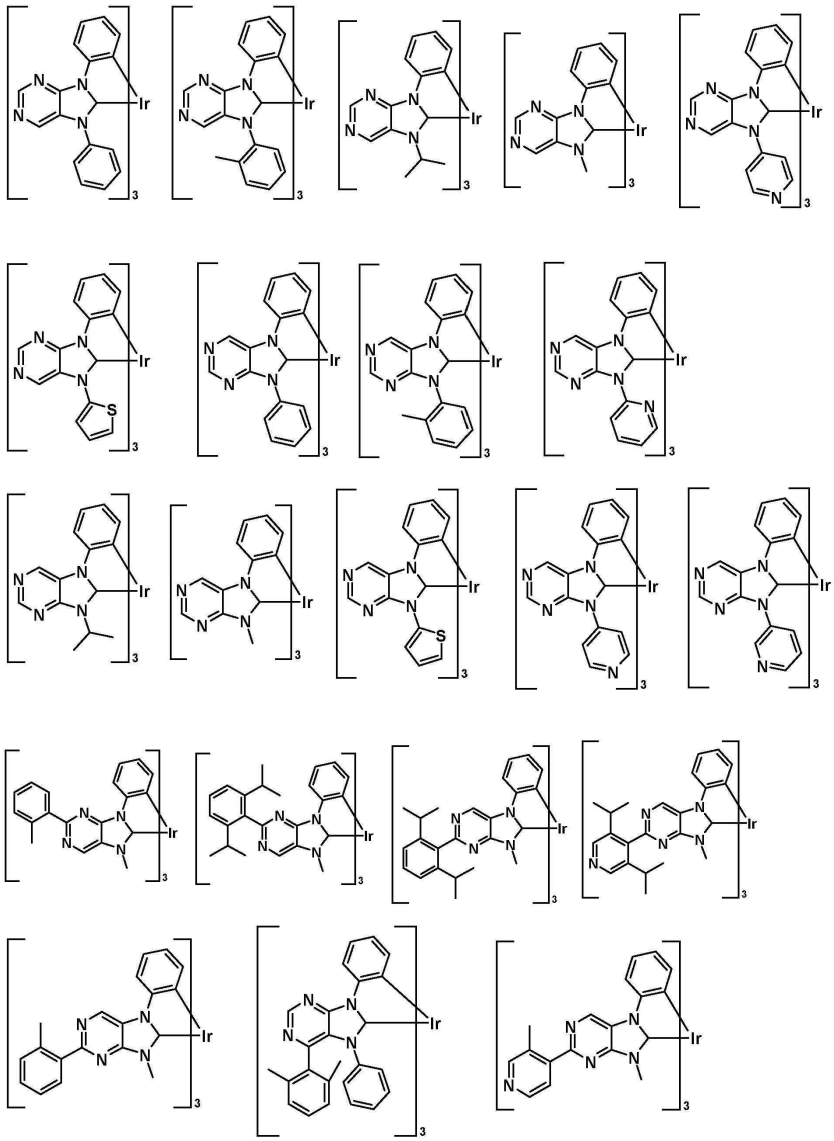
[0486] m1은 0, 1 또는 2이고, 여기서 m1이 2인 경우, K 리간드는 동일하거나 상이할 수 있고,

[0487] o는 0, 1 또는 2이고, 여기서 o이 2인 경우, L 리간드는 동일하거나 상이할 수 있다.

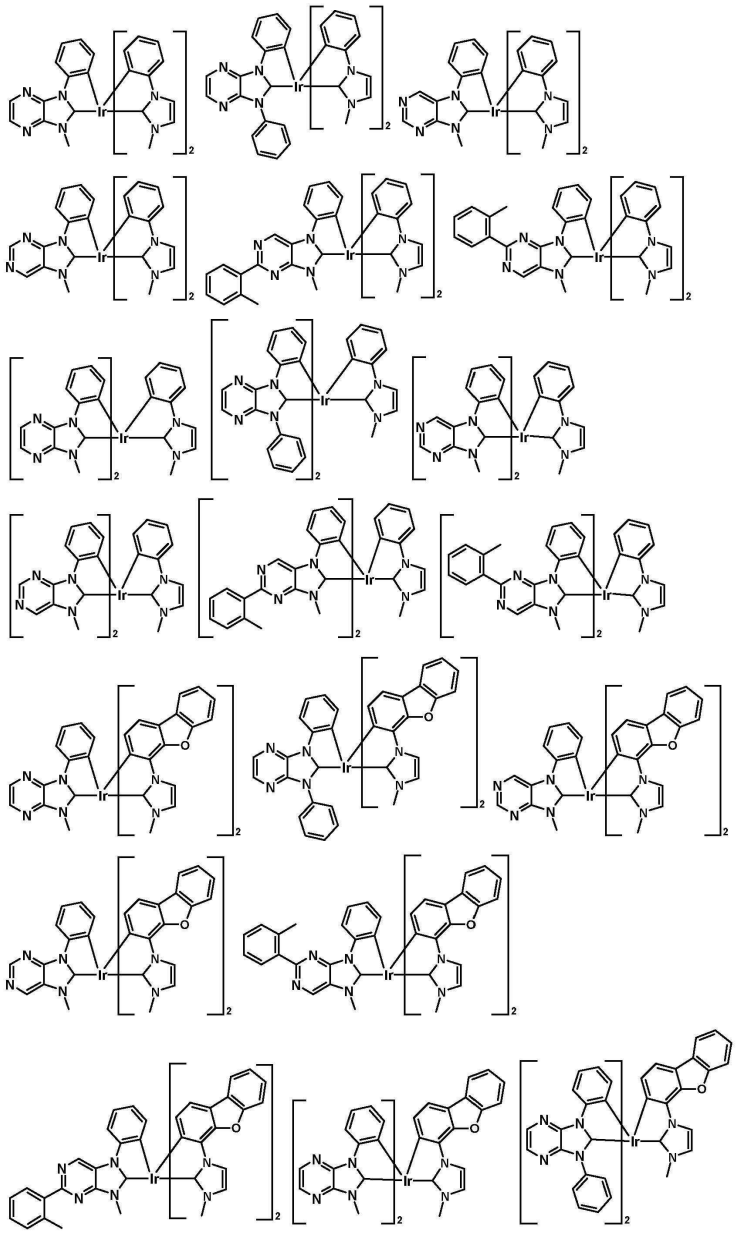
[0488] 화학식 IX의 화합물은 바람직하게는 하기 화학식의 화합물이다.



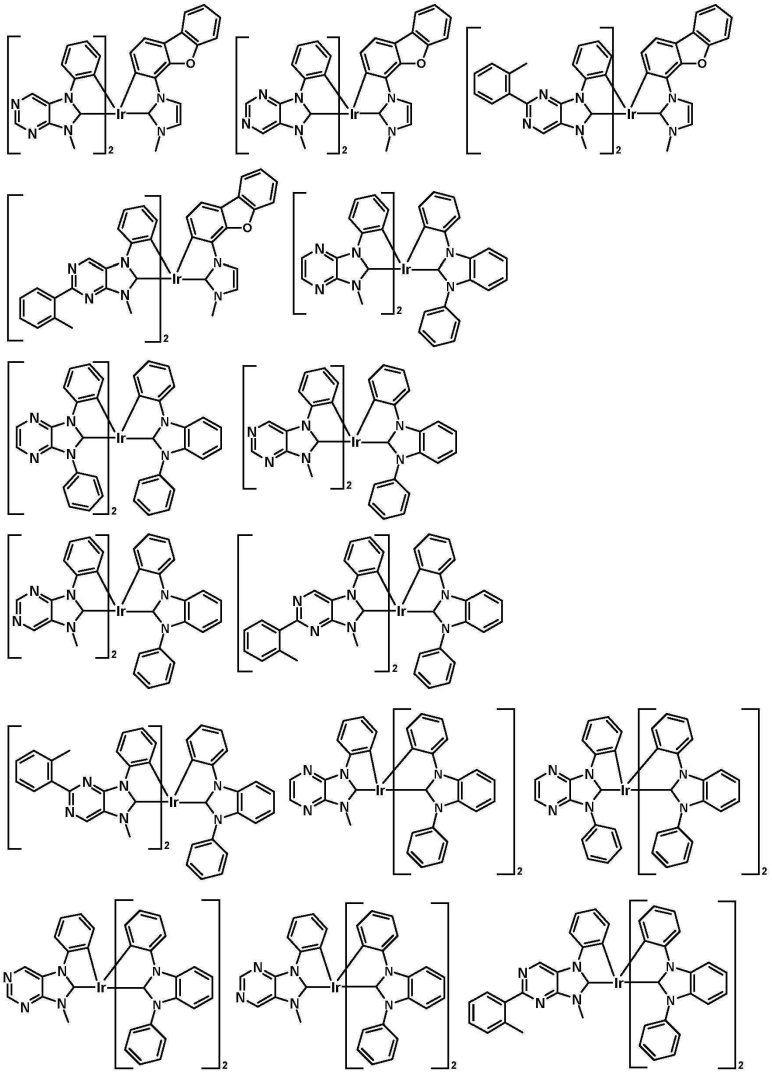
[0489]



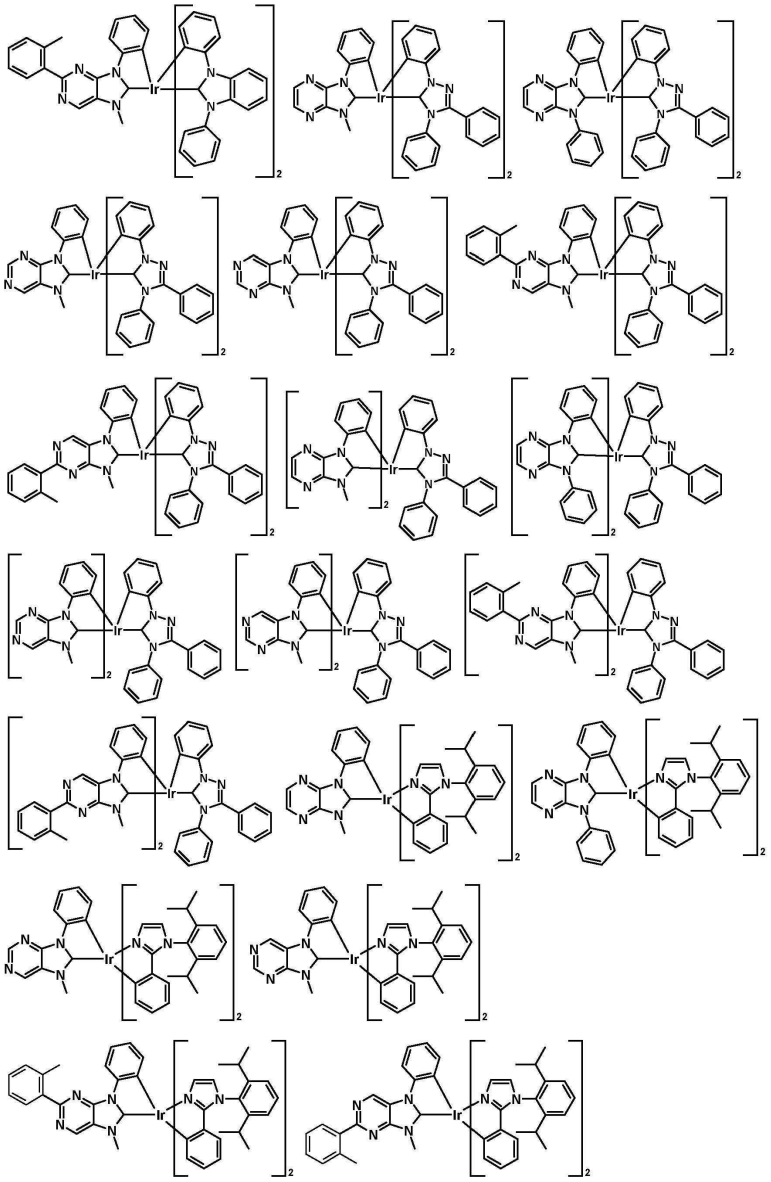
[0490]



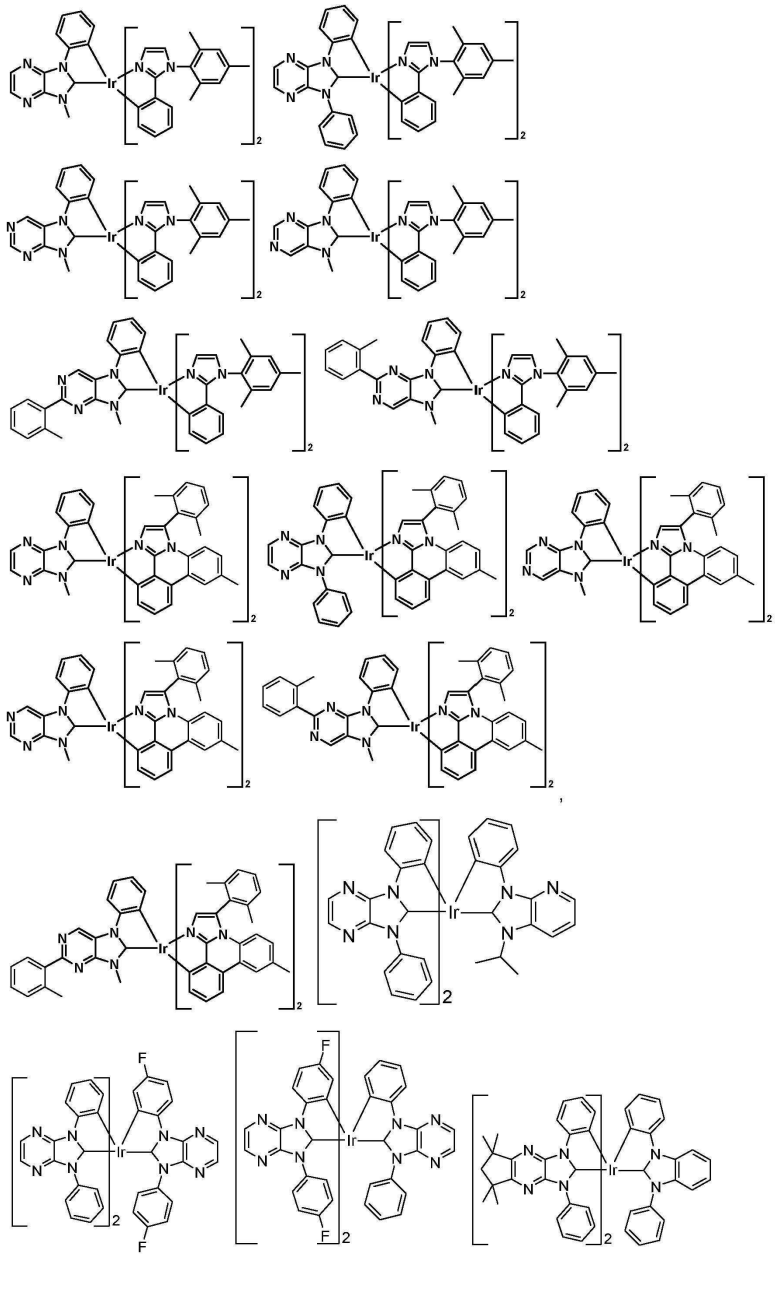
[0491]



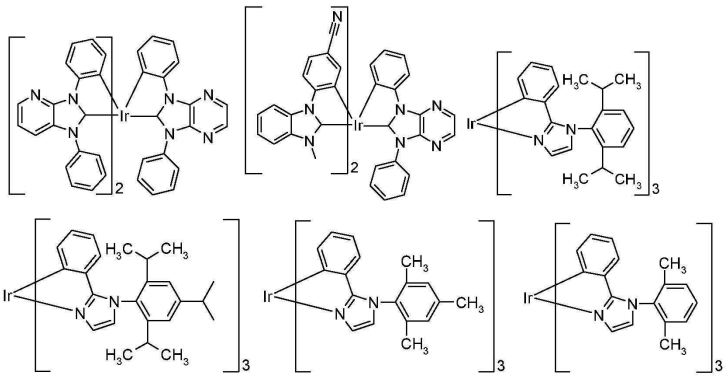
[0492]



[0493]



[0494]



[0495]

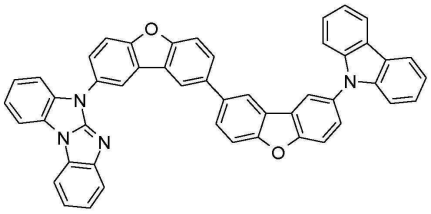
[0496] 동종 리간드(homoleptic) 금속-카르벤 착물은 면 이성질체 또는 자오선 이성질체의 형태로 존재할 수 있고, 면 이성질체가 바람직하다.

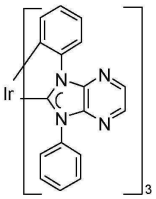
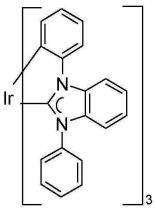
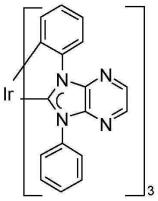
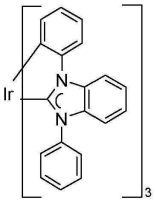
[0497] 이종 리간드(heteroleptic) 금속-카르벤 착물의 경우, 4개의 상이한 이성질체가 존재할 수 있고, 의사-면(pseudo-facial) 이성질체가 바람직하다.

[0498] 발광층은 방출체 물질 이외에 추가 성분을 포함할 수 있다. 예를 들어, 형광 염료를 발광층에 존재시켜 방출체

물질의 발광색을 변경시킬 수 있다. 또한 - 바람직한 실시양태에서 - 매트릭스 물질을 사용할 수 있다. 당해 매트릭스 물질은 중합체, 예를 들어 폴리(N-비닐카르바졸) 또는 폴리실란일 수 있다. 그러나, 매트릭스 물질은 소 분자, 예를 들어 4,4'-N,N'-디카르바졸비페닐 (CDP=CBP) 또는 3급 방향족 아민, 예를 들어 TCTA일 수 있다. 본 발명의 바람직한 실시양태에서, 하나 이상의 화학식 I의 화합물이 매트릭스 물질로서 사용된다.

[0499] 바람직한 실시양태에서, 발광층은 2 내지 40 중량%, 바람직하게는 5 내지 35 중량%의, 상기 언급된 방출체 물질 중 하나 이상 및 60 내지 98중량%, 바람직하게는 75 내지 95 중량%의, 상기 언급된 매트릭스 물질 중 하나 이상 - 한 실시양태에서 하나 이상의 화학식 I의 화합물 - 로부터 형성되고, 여기서 방출체 물질과 매트릭스 물질의 합계가 100 중량%가 되도록 첨가한다.

[0500] 특히 바람직한 실시양태에서, 발광층은 화합물 I의 화합물, 예를 들어, 

등, 및 바람직하게는 화학식  및  의 2개의 카르벤 착물을 포함한다. 상기 실시양태에서, 발광층은 2 내지 40 중량%, 바람직하게는 5 내지 35 중량%의  및 60 내지 98 중량%, 바람직하게는 65 내지 95 중량%의 화학식 I의 화합물 및  로부터 형성되고, 여기서 카르벤 착물과 화학식 I의 화합물의 합계가 100 중량%가 되도록 첨가한다

[0501] 따라서, 화학식 I의 화합물과 함께 OLED에서 매트릭스 물질 및/또는 정공/여기자 차단제 물질 및/또는 전자/여기자 차단제 물질 및/또는 정공 주입 물질 및/또는 전자 주입 물질 및/또는 정공 전도체 물질 및/또는 전자 전도체 물질로서, 바람직하게는 매트릭스 물질 및/또는 정공/여기자 차단제 물질로서 사용하기에 적합한 금속 착물은, 예를 들어, 또한 WO 2005/019373 A2, WO 2006/056418 A2, WO 2005/113704, WO 2007/115970, WO 2007/115981 및 WO 2008/000727에 기재된 바와 같은 카르벤 착물이다. 여기에서, 인용된 WO 출원의 개시 내용을 명시적으로 참조하고, 이들 개시 내용은 본 출원의 내용에 포함되는 것으로 고려되어야 한다.

[0502] 정공/여기자 차단층 (4)이 화학식 I의 화합물을 전혀 포함하지 않는 경우, OLED는 - 정공 차단층이 존재하는 경우 - OLED에 전형적으로 사용되는 정공 차단제 물질, 예컨대 2,6-비스(N-카르바졸릴)피리딘 (mCPy), 2,9-디메틸-4,7-디페닐-1,10-페난트롤린 (바토쿠프로인, (BCP)), 비스(2-메틸-8-퀴놀리네이토)-4-페닐페닐레이토)알루미늄(III) (BAlq), 페노티아진 *S,S*-디옥시드 유도체 및 1,3,5-트리스(N-페닐-2-벤질이미다졸릴)벤젠) (TPBI)을 갖고, TPBI는 또한 전자 전도성 물질로서 적합하다. 추가로 적합한 정공 차단제 및/또는 전자 전도체 물질은 2,2',2"-(1,3,5-벤젠트리일)트리스(1-페닐-1H-벤즈이미다졸), 2-(4-비페닐릴)-5-(4-tert-부틸페닐)-1,3,4-옥사디아졸, 8-히드록시퀴놀리노레이토리튬, 4-(나프탈렌-1-일)-3,5-디페닐-4H-1,2,4-트리아졸, 1,3-비스[2-(2,2'-비피리딘-6-일)-1,3,4-옥사디아조-5-일]벤젠, 4,7-디페닐-1,10-페난트롤린, 3-(4-비페닐릴)-4-페닐-5-tert-부틸페닐-1,2,4-트리아졸, 6,6'-비스[5-(비페닐-4-일)-1,3,4-옥사디아조-2-일]-2,2'-비피리딜, 2-페닐-9,10-디(나프탈렌-2-일)안트라센, 2,7-비스[2-(2,2'-비피리딘-6-일)-1,3,4-옥사디아조-5-일]-9,9-디메틸플루오

렌, 1,3-비스[2-(4-tert-부틸페닐)-1,3,4-옥사디아조-5-일]벤젠, 2-(나프탈렌-2-일)-4,7-디페닐-1,10-페난트롤린, 트리스-(2,4,6-트리메틸-3-(피리딘-3-일)페닐)보란, 2,9-비스(나프탈렌-2-일)-4,7-디페닐-1,10-페난트롤린, 1-메틸-2-(4-(나프탈렌-2-일)페닐)-1H-이미다조[4,5-f][1,10]-페난트롤린이다. 추가 실시양태에서, 정공/여기자 차단층 (4)으로서 또는 발광층 (3)에서 매트릭스 물질로서, 카르보닐 기를 포함하는 기를 통해 결합된 방향족 또는 헤테로방향족 환을 포함하는 화합물 (WO2006/100298에 기재된 바와 같음), 디실릴카르바졸, 디실릴벤조푸란, 디실릴벤조티오펜, 디실릴벤조포스폴, 디실릴벤조티오펜 S-옥시드 및 디실릴벤조티오펜 S,S-디옥시드로 이루어진 군으로부터 선택된 디실릴화합물 (예를 들어, 본 출원의 우선일에 아직 공개되지 않았던 PCT/EP2008/058207 및 PCT/EP2008/058106에 명시된 바와 같음), 및 WO2008/034758에 개시된 바와 같은 디실릴 화합물을 사용하는 것이 가능하다.

[0503] 본 발명의 OLED의 층 (5)에 적합한 전자 전도체 물질은 옥시노이드 화합물에 킬레이트화된 금속, 예컨대 2,2',2"-(1,3,5-페닐렌)트리스[1-페닐-1H-벤즈이미다졸] (TPBI), 트리스(8-퀴놀리노레이토)알루미늄 (Alq_3), 페난트롤린계 화합물, 예컨대 2,9-디메틸-4,7-디페닐-1,10-페난트롤린 (DDPA = BCP) 또는 4,7-디페닐-1,10-페난트롤린 (DPA), 및 아졸 화합물, 예컨대 2-(4-비페닐릴)-5-(4-t-부틸페닐)-1,3,4-옥사디아졸 (PBD) 및 3-(4-비페닐릴)-4-페닐-5-(4-t-부틸페닐)-1,2,4-트리아졸 (TAZ), 8-히드록시-퀴놀리노레이토리튬 (Liq), 4,7-디페닐-1,10-페난트롤린 (BPhen), 비스(2-메틸-8-퀴놀리노레이토)-4-(페닐페놀레이토)알루미늄 (BAlq), 1,3-비스[2-(2,2'-비피리딘-6-일)-1,3,4-옥사디아조-5-일]벤젠 (Bpy-OXD), 6,6'-비스[5-(비페닐-4-일)-1,3,4-옥사디아조-2-일]-2,2'-피리딜 (BP-OXD-Bpy), 4-(나프탈렌-1-일)-3,5-디페닐-4H-1,2,4-트리아졸 (NTAZ), 2,9-비스(나프탈렌-2-일)-4,7-디페닐-1,10-페난트롤린 (NBphen), 2,7-비스[2-(2,2'-비피리딘-6-일)-1,3,4-옥사디아조-5-일]-9,9-디메틸플루오렌 (Bby-FOXD), 1,3-비스[2-(4-tert-부틸페닐)-1,3,4-옥사디아조-5-일]벤젠 (OXD-7)을 포함한다. 트리스(2,4,6-트리메틸-3-(피리딘-3-일)페닐)보란 (3TPYMB), 1-메틸-2-(4-(나프탈렌-2-일)페닐)-1H-이미다조[4,5-f][1,10]페난트롤린 (2-NPIP), 2-페닐-9,10-디(나프탈렌-2-일)안트라센 (PADN), 2-(나프탈렌-2-일)-4,7-디페닐-1,10-페난트롤린 (HNBphen)을 포함한다. 층 (5)은 OLED 층들의 계면에서 여기자가 소광(quenching)되는 것을 막기 위해, 전자 수송을 용이하게 하는 역할뿐만 아니라, 완충층 또는 장벽층으로서도 역할을 할 수 있다. 층 (5)은 바람직하게는 전자의 이동성을 개선하고 여기자가 소광되는 것을 감소시킨다. 바람직한 실시양태에서, TPBI는 전자 전도체 물질로서 사용된다. 또 다른 바람직한 실시양태에서, BCP는 전자 전도체 물질로서 사용된다. 원칙상, 전자 전도체 층은 전자 전도체 물질로서 하나 이상의 화학식 I의 화합물을 포함할 수 있다.

[0504] 정공 전도체 물질 및 전자 전도체 물질로서 상기 언급된 물질들 중에서, 일부는 몇 가지 기능을 완수할 수 있다. 예를 들어 전자 전도성 물질 중 일부는, 이들이 낮은 HOMO를 가질 때, 동시에 정공 차단 물질이기도 하다. 이들은, 예를 들어 정공/여기자 차단층 (4)에 사용될 수 있다. 그러나, 정공/여기자 차단체로서의 기능은 또한 층 (5)에 의해 발휘되는 것이 마찬가지로 가능하므로, 층 (4)은 사용되지 않을 수 있다.

[0505] 전하 수송층은 또한 전자적으로 도핑되어, 첫째로 층 두께를 더 풍부하게 하도록 하고 (핀홀/단락을 피함), 둘째로 소자의 작동 전압을 최소화하도록, 사용되는 물질의 수송 특성을 개선할 수 있다. 예를 들어, 정공 전도체 물질은 전자 수용자로 도핑될 수 있고; 예를 들어, 프탈로시아닌 또는 아릴아민, 예컨대 TPD 또는 TDTA는 테트라플루오로테트라시안퀴노디메탄 (F4-TCNQ)으로 또는 MoO_3 또는 WO_3으로 도핑될 수 있다. 전자 전도체 물질은, 예를 들어 알칼리 금속, 예를 들어 리튬 함유 Alq_3으로 도핑될 수 있다. 게다가, 전자 전도체는 염, 예컨대 Cs_2CO_3, 또는 8-히드록시퀴놀레이토리튬 (Liq)으로 도핑될 수 있다. 전자 도핑은 당업자에게 공지되어 있고, 예를 들어, 문헌 [W. Gao, A. Kahn, J. Appl. Phys., Vol. 94, No. 1, 1 July 2003 (p-doped organic layer)]; [A. G. Werner, F. Li, K. Harada, M. Pfeiffer, T. Fritz, K. Leo. Appl. Phys. Lett., Vol. 82, No. 25, 23 June 2003] 및 [Pfeiffer et al., Organic Electronics 2003, 4, 89 - 103]에 개시되어 있다. 예를 들어, 카르벤 착물, 예를 들어 $Ir(dpbic)_3$ 이외에, 정공 전도체 층은 MoO_3 또는 WO_3으로 도핑될 수 있다. 예를 들어, 전자 전도체 층은 Cs_2CO_3으로 도핑된 BCP를 포함할 수 있다.

[0506] 캐소드 (6)는 전자 또는 음전하 캐리어를 도입하는 역할을 하는 전극이다. 캐소드에 적합한 물질은 원소 주기율표 (IUPAC 구버전)의 Ia족의 알칼리 금속, 예를 들어 Li, Cs, IIa족의 알칼리 토금속, 예를 들어 칼슘, 바륨 또는 마그네슘, IIb족의 금속 (란타니드 및 악티니드, 예를 들어 사마륨을 포함함)으로 이루어진 군으로부터 선택된다. 게다가, 알루미늄 또는 인듐과 같은 금속, 및 언급된 모든 금속의 조합물을 사용하는 것도 가능하다. 게다가, 알칼리 금속, 특히 리튬-포함 유기금속 화합물, 또는 알칼리 금속 플루오라이드, 예를 들어, LiF, CsF,

또는 KF 등을 유기 층과 캐소드 사이에 적용하여 작동 전압을 감소시킬 수 있다.

[0507] 본 발명에 따른 OLED는 게다가 당업자에게 공지된 추가의 층을 포함할 수 있다. 예를 들어, 양전하의 수송을 용이하게 하고/거나 층의 밴드 갭을 서로 부합시키는 층을 층 (2)과 발광층 (3) 사이에 적용할 수 있다. 대안으로, 이러한 추가의 층은 보호층으로서 역할을 할 수 있다. 유사한 방식으로, 부가적인 층을 발광층 (3)과 층 (4) 사이에 존재시켜 음전하의 수송을 용이하게 하고/거나 층 사이의 밴드 갭을 서로 부합시킬 수 있다. 대안으로, 당해 층은 보호층으로서 역할을 할 수 있다.

[0508] 바람직한 실시양태에서, 본 발명의 OLED는, 층 (1) 내지 (6) 이외에, 하기 언급된 다음 층 중 하나 이상을 포함한다:

[0509] - 2 내지 100 nm, 바람직하게는 5 내지 50 nm의 두께를 갖는 애노드 (1)와 정공 수송층 (2) 사이에 정공 주입층;

[0510] - 정공 수송층 (2)과 발광층 (3) 사이에 전자 차단층;

[0511] - 전자 수송층 (5)과 캐소드 (6) 사이에 전자 주입층.

[0512] 정공 주입층에 관한 물질은 구리 프탈로시아닌, 4,4',4"-트리스(N-3-메틸페닐-N-페닐아미노)트리페닐아민 (m-MTDATA), 4,4',4"-트리스(N-(2-나프틸)-N-페닐아미노)트리페닐아민 (2T-NATA), 4,4',4"-트리스(N-(1-나프틸)-N-페닐아미노)트리페닐아민 (1T-NATA), 4,4',4"-트리스(N,N-디페닐아미노)트리페닐아민 (NATA), 티탄 산화물 프탈로시아닌, 2,3,5,6-테트라플루오로-7,7,8,8-테트라시아노퀴노디메탄 (F4-TCNQ), 피라지노[2,3-f][1,10]페난트롤린-2,3-디카르보니트릴 (PPDN), N,N,N',N'-테트라키스(4-메톡시페닐)벤지딘 (MeO-TPD), 2,7-비스[N,N-비스(4-메톡시-페닐)아미노]-9,9-스피로비플루오렌 (MeO-스피로-TPD), 2,2'-비스[N,N-비스(4-메톡시-페닐)아미노]-9,9-스피로비플루오렌 (2,2'-MeO-스피로-TPD), N,N'-디페닐-N,N'-디-[4-(N,N-디톨릴아미노)페닐]벤지딘 (NTNPB), N,N'-디페닐-N,N'-디-[4-(N,N-디페닐-아미노)페닐]벤지딘 (NPNPB), N,N'-디(나프탈렌-2-일)-N,N'-디페닐벤젠-1,4-디아민 (α-NPP)으로부터 선택될 수 있다. 원칙상, 정공 주입층은 정공 주입 물질로서 하나 이상의 화학식 I의 화합물을 포함하는 것이 가능하다. 게다가, 중합체성 정공 주입 물질, 예컨대 폴리(N-비닐카르바졸) (PVK), 폴리티오펜, 폴리피롤, 폴리아닐린, 자기 도핑(self-dop) 중합체, 예를 들어, 술폰화 폴리(티오펜-3-[2[(2-메톡시에톡시)에톡시]-2,5-디일) (플렉스트로닉스(Plextronics)로부터 시판되는 플렉스코어(Plexcore)® OC 컨덕팅 잉크(Conducting Inks)) 등, 및 PEDOT/PSS로서도 칭해지는 공중합체, 예컨대 폴리(3,4-에틸렌디옥시티오펜)/폴리(4-스티렌술포네이트)를 사용할 수 있다.

[0513] 전자 주입층에 관한 물질로서, 예를 들어 LiF가 선택될 수 있다. 원칙상, 전자 주입층이 하나 이상의 화학식 I의 화합물을 전자 주입 물질로서 포함하는 것이 가능하다.

[0514] 당업자는 (예를 들어 전기화학적 연구를 토대로) 적합한 물질을 어떻게 선택해야 하는지 안다. 개별 층에 적합한 물질은 당업자에게 공지되어 있고, 예를 들어 WO 00/70655에 개시되어 있다.

[0515] 게다가, 본 발명의 OLED에 사용되는 층 중 일부는 전하 캐리어 수송의 효율을 증가시키기 위해 표면-처리해 두는 것이 가능하다. 언급된 각각의 층을 위한 물질의 선택은 바람직하게는 높은 효율 및 수명을 갖는 OLED를 수득함으로써 결정된다.

[0516] 본 발명의 OLED는 당업자에게 공지된 방법에 의해 제조될 수 있다. 일반적으로, 본 발명의 OLED는 개별 층의 적합한 기판 상으로의 연속 기상 증착에 의해 제조된다. 적합한 기판은, 예를 들어, 유리, 무기 반도체 또는 중합체 필름이다. 기상 증착에 관해, 통상적인 기법, 예컨대 열 증발, 화학적 기상 증착 (CVD), 물리적 기상 증착 (PVD) 등을 사용하는 것이 가능하다. 대안적 방법으로, OLED의 유기 층을, 당업자에게 공지된 코팅 기법을 사용하여, 적합한 용매 중 용액 또는 분산액으로부터 적용할 수 있다.

[0517] 일반적으로, 상이한 층은 하기 두께를 갖는다: 애노드 (1) 50 내지 500 nm, 바람직하게는 100 내지 200 nm; 정공 전도성 층 (2) 5 내지 100 nm, 바람직하게는 20 내지 80 nm, 발광층 (3) 1 내지 100 nm, 바람직하게는 10 내지 80 nm, 정공/여기자 차단층 (4) 2 내지 100 nm, 바람직하게는 5 내지 50 nm, 전자 전도성 층 (5) 5 내지 100 nm, 바람직하게는 20 내지 80 nm, 캐소드 (6) 20 내지 1000 nm, 바람직하게는 30 내지 500 nm. 캐소드와 관련하여 본 발명의 OLED에서 정공 및 전자의 재조합 구역의 상대적 위치 및 결과적으로 OLED의 발광 스펙트럼은, 다른 요인 중에서도, 각각의 층의 상대적 두께에 의해 영향을 받을 수 있다. 이는 전자 수송층의 두께가 바람직하게는, 재조합 구역의 위치가 다이오드의 광학 공진기 특성 및 결과적으로 발광체의 발광 파장에 부합되도록 선택되어야 함을 의미한다. OLED 중 개별 층의 층 두께의 비는 사용되는 물질에 따라 다르다. 사

용되는 임의의 부가적인 층의 층 두께는 당업자에게 공지되어 있다. 전자 전도성 층 및/또는 정공 전도성 층은 이들이 전기적으로 도핑되는 경우 명시된 층 두께보다 더 큰 두께를 갖는 것이 가능하다.

[0518] 바람직하게는 발광층 (바람직하게는 매트릭스 물질로서)에서 및/또는 정공/여기자 차단층에서 OLED의 하나 이상의 층에서 화학식 I의 화합물의 사용으로 인해 높은 효율 및 낮은 사용 및 작동 전압을 갖는 OLED를 수득 가능하게 된다. 종종, 화학식 I의 화합물의 사용에 의해 수득된 OLED는 게다가 높은 수명을 갖는다. OLED의 효율은 OLED의 다른 층을 최적화함으로써 부가적으로 개선될 수 있다. 예를 들어, 높은 효율 캐소드, 예컨대 Ca 또는 Ba는 적절한 경우 LiF의 중간층과 조합되어 사용될 수 있다. 작동 전압의 감소 또는 양자 효율의 증가를 초래하는 성형된 기판 및 신규 정공 수송 물질은 마찬가지로 본 발명의 OLED에서 사용가능하다. 더욱이, 부가적인 층을 OLED에 존재시켜 상이한 층의 에너지 수준을 조정하고 전계발광을 용이하게 할 수 있다.

[0519] OLED는 하나 이상의 제2 발광층을 추가로 포함할 수 있다. OLED의 전체 발광은 2개 이상의 발광층의 발광으로 이루어질 수 있고 또한 백색광을 포함할 수 있다.

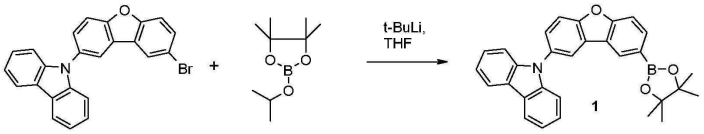
[0520] OLED는 전계발광이 유용한 모든 장치에서 사용될 수 있다. 적합한 소자는 바람직하게는 고정식 및 이동식 화상 표시 장치 및 조명 장치로부터 선택된다. 고정식 화상 표시 장치는, 예를 들어, 컴퓨터, 텔레비젼의 화상 표시 장치, 프린터, 주방용 기기 및 광고판, 조명 및 안내판에서의 화상 표시 장치이다. 이동식 화상 표시 장치는, 예를 들어, 휴대폰, 테블릿 PC, 휴대용 컴퓨터, 디지털 카메라, MP3 플레이어, 차량 및 버스와 기차의 행선지 표시에서의 화상 표시 장치이다. 본 발명의 OLED가 사용될 수 있는 추가의 소자는, 예를 들어 키보드; 의류 품목; 가구; 벽지이다.

[0521] 게다가, 본 발명은 하나 이상의 본 발명의 유기 발광 다이오드 또는 하나 이상의 본 발명의 발광층을 포함하는, 고정식 화상 표시 장치, 예컨대 컴퓨터, 텔레비젼의 화상 표시 장치, 프린터, 주방용 기기 및 광고판, 조명, 안내판에서의 화상 표시 장치, 및 이동식 화상 표시 장치, 예컨대 휴대폰, 테블릿 PC, 휴대용 컴퓨터, 디지털 카메라, MP3 플레이어, 차량 및 버스와 기차의 행선지 표시에서의 화상 표시 장치; 조명 장치; 키보드; 의류 품목; 가구; 벽지로 이루어진 군으로부터 선택된 소자에 관한 것이다.

[0522] 하기 실시예는 단지 예시를 목적으로 포함되어 있고 특허청구범위의 영역을 한정하는 것이 아니다. 달리 서술되지 않는 한, 모든 부 및 백분율은 중량 기준이다.

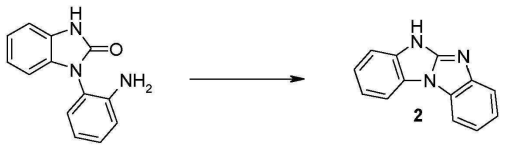
[0523] **실시예**

[0524] **실시예 1**

[0525] 

[0526] a) 펜탄 중 16.4 ml (27.9 mmol) t-부틸-리튬을 아르곤하에 -78℃에서 30 ml 물 유리 테트라히드로푸란 (THF) 중 5.00 g (12.1 mmol) 9-(8-브로모디벤조푸란-2-일)카르바졸의 용액 (그의 합성은 WO2010079051에 기재되어 있음)에 첨가하였다. 15분 후 2.93 g (15.8 mmol) 2-이소프로폭시-4,4,5,5-테트라메틸-1,3,2-디옥사보롤란을 서서히 첨가하였다. 반응 혼합물을 아르곤하에 -78℃에서 3시간 동안 교반하고 물에 붓고 수상을 디에틸 에테르로 추출하였다. 유기상을 황산마그네슘으로 건조시키고 용매를 제거하였다. 에테르로부터 결정화하여 2.57 g의 화합물 1 (수율: 46%)을 수득하였다.

[0527] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.18-8.23 (m, 3H), 8.05 (dd, J=8.3 Hz, J = 1.3 Hz, 1H), 7.80-7.82 (m, 1H), 7.64-7.70 (m, 2H), 7.43-7.49 (m, 4H), 7.28-7.37 (m, 2H), 1.43 (s, 12H).

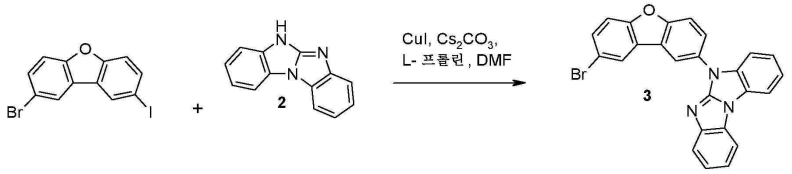
[0528] 

[0529] b) 11.3 g (50.0 mmol) 3-(2-아미노페닐)-1H-벤즈이미다졸-2-온을 180℃에서 50 g 폴리인산에 첨가하였다. 반응 혼합물을 질소하에 3 h 동안 220℃에서 교반하고 물에 부었다. 생성물을 여과해내고 물 및 메탄올로 세척하였다. 50 ml 30% 수산화나트륨 용액을 200 ml THF 중 생성물의 현탁액에 첨가하였다. 혼합물을 30분 동안 교

반하고 유기상을 분리하고, 황산마그네슘으로 건조시키고 용매를 증류해냈다. 9.26 g의 화합물 2 (수율: 89%)를 수득하였다.

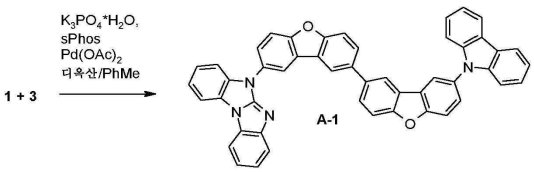
[0530] ^{1}H NMR (400 MHz, DMSO-d6): δ 7.88 (d, J= 7.7 Hz, 2H), 7.39 (d, J= 8.0 Hz, 2H), 7.12-7.16 (m, 2H), 6.97-7.01 (m, 2H).

[0531] 5H-벤즈이미다조[1,2-a]벤즈이미다졸 및 3-(2-아미노페닐)-1H-벤즈이미다졸-2-온의 합성은 문헌 [Bull. Soc. Chem. Belg. 96 (1987) 787]에 기재되어 있다.

[0532] 

[0533] c) 5.00 g (13.4 mmol) 2-브로모-8-아이오도-디벤조푸란 (그의 합성은EP1885818에 기재되어 있음), 8.74 g (26.8 mmol) 탄산세슘, 255 mg (1.34 mmol) 아이오딘화구리(I) 및 309 mg (2.68 mmol) L-프롤린을 질소하에 75 ml 디메틸포름아미드 중 2.78 g (13.4 mmol) 5H-벤즈이미다조[1,2-a]벤즈이미다졸에 첨가하였다. 반응 혼합물을 150℃에서 19 h 동안 가열하고 THF와 함께 히플로슈퍼 셀(Hyflo Super Cel)(R) 매질 (플루카(Fluka) 56678, CAS [91053-39-3]) 상에서 여과하였다. 유기상을 물로 세척하였다. 용매를 증류해냈다. 톨루엔/에틸 아세테이트 19/1을 사용하여 실리카겔 상에서 칼럼 크로마토그래피하여 화합물 3 (수율: 2.29 g (37.7%))을 수득하였다.

[0534] ^{1}H NMR (400 MHz, THF-d8): δ 8.66 (s, 1H), 8.41 (s, 1H), 8-01-8-16 (m, 3H), 7.89 (d, J= 8.8 Hz, 1H), 7.63-7.75(m, 4H), 7.25-7.49 (m, 4H).

[0535] 

[0536] d) 1.98 g (3.41 mmol)의 화합물 1 및 4.02 g (16.6 mmol) 삼염기성 인산칼륨 일수화물, 15 ml 디옥산, 60 ml 톨루엔 및 12 ml 물을 1.50 g (3.32 mmol)의 화합물 3에 첨가하였다. 혼합물을 아르곤으로 탈기하였다. 81 mg (0.199 mmol) 2-디시클로헥실포스피노-2',6'-디메톡시비페닐 (SPhos) 및 74 mg (0.033 mmol) 팔라듐(II) 아세테이트를 첨가하였다. 반응 혼합물을 아르곤으로 탈기하고 아르곤하에 100℃에서 4.5 h 동안 교반하였다. 40 ml의 1% 시안화나트륨 용액을 첨가하고 반응 혼합물을 1 h 동안 환류하였다. 디클로로메탄을 첨가하고, 유기상을 물로 세척하고 황산마그네슘으로 건조시켰다. 톨루엔 및 이어서 톨루엔 / 에틸 아세테이트 9 / 1을 사용하여 실리카겔 상에서 칼럼 크로마토그래피하여 화합물 A-1 (수율: 1.42 g (61%))을 수득하였다.

[0537] ^{1}H NMR (400 MHz, THF-d8): δ 8.71 (s, 1H), 8.54-8.58 (m, 2H), 8.41 (s, 1H), 8.20 (d, J= 7.8 Hz, 2H), 7.62-8.11 (m, 12H), 7.26-7.31 (m, 10H).

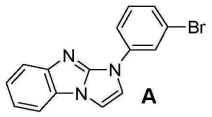
[0538] **실시예 2**

[0539] 4H-이미다조[1,2-a]벤즈이미다졸의 합성은 ARKIVOC 2002 (v) 48-61에 기재되어 있다.

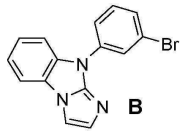
[0540] 

[0541] a) 200 ml 디메틸 술폭시드 (DMSO) 중 8.02 g (51.0 mmol) 4H-이미다조[1,2-a]벤즈이미다졸, 15.9 g (56.1 mmol) 1-브로모-3-아이오도-벤젠, 33.2 g (102 mmol) 탄산세슘, 1.94 g (10.2 mol) 아이오딘화구리(I) 및 2.35 g (20.4 mol) L-프롤린을 100℃에서 24 h 동안 교반하였다. 고체를 여과해내고 디클로로메탄으로 세척하였다. 유기상을 물로 세척하고 황산마그네슘으로 건조시켰다. 용매를 증류해냈다. 톨루엔 및 이어서 톨루엔/에틸 아세테이트 (20/1)를 사용하여 칼럼 크로마토그래피하여 생성물 혼합물 (3.89 g (24%) 이성질체 A 및 4.46 g (28%) 이성질체 B)을 수득하였다. 2개의 이성질체의 분리를 톨루엔/에틸 아세테이트 (톨루엔 100%, 톨루엔/에틸 아세테이트 95/5, 톨루엔/에틸 아세테이트 90/10 및 에틸아세테이트 100%)를 사용하여 구배 칼럼 크로마토그

래피에 의해 달성하였다.

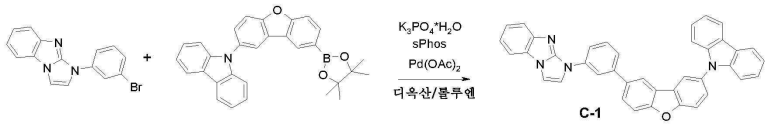
[0542] 

[0543] **1H NMR** (400 MHz, THF-d8): δ 8.54-8.56 (m, 1H), 8.33 (dd, J= 7.8 Hz, J= 1.4 Hz, 1H), 7.80 (d, J= 2.8 Hz, 1H), 7.76 (d, J= 2.8 Hz, 1H), 7.79 (d, J= 8.6 Hz, 2H), 7.39-7.46 (m, 2H), 7.20-7.29 (m, 1H), 7.12-7.16 (m, 1H).

[0544] 

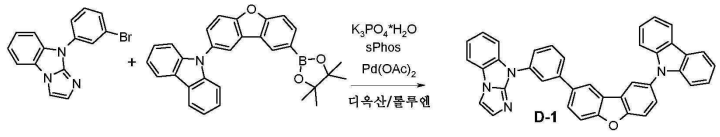
[0545] **1H NMR** (400 MHz, THF-d8): δ 8.23 (s, 1H), 7.95-7.97 (m, 1H), 7.70-7.74 (m, 2H), 7.56 (s, 1H), 7.45-7.53 (m, 2H), 7.24-7.33 (m, 2H), 7.17 (s, 1H).

[0546] b) 화합물 C-1의 합성을 화합물 A-1의 합성과 유사하게 수행하였다.

[0547] 

[0548] 1H NMR (400 MHz, THF-d8): 8.63 (s, 1H), 8.52 (s, 1H), 8.42 (s, 1H), 8.32-8.35 (m, 1H), 8.20-8.22 (m, 2H), 7.59-8.02 (m, 10H), 7.40-7.47 (m, 4H), 7.09-7.20 (m, 4H).

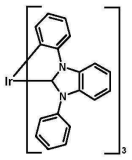
[0549] c) 실시예 2c)의 생성물의 합성을 화합물 A-1의 합성과 유사하게 수행하였다.

[0550] 

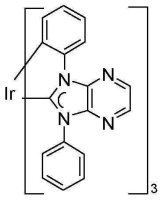
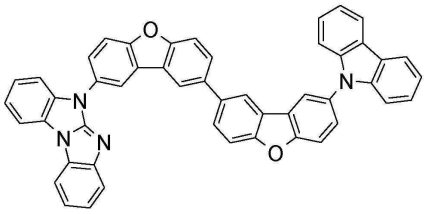
[0551] **1H NMR** (400 MHz, THF-d8): δ = 8.51 (d, J= 1.7 Hz, 1H), 8.41 (d, J= 2.1 Hz, 1H), 8.37-8.39 (m, 1H), 8.21 (s, 1H), 8.19 (s, 1H), 7.98 (dd, J= 8.6 Hz, J= 1.9 Hz, 1H), 7.91-7.94 (m, 2H), 7.65-7.82 (m, 6H), 7.57 (d, J= 1.5 Hz, 1H), 7.37-7.44 (m, 4H), 7.24-7.34 (m, 4H), 7.12 (d, J= 1.5 Hz, 1H).

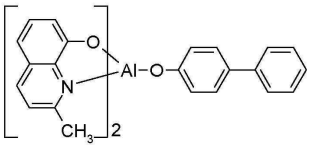
[0552] **적용 실시예 1 - 혼합 매트릭스**

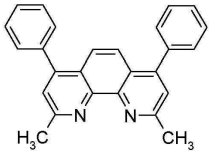
[0553] 애노드로서 사용되는 ITO 기판을 먼저 LCD 제조용 시판 세정제 (데코넥스(Deconex)® 20NS, 및 25오르간-액시드(ORGAN-ACID)® 중화제)로 세정한 다음 초음파 세정기(ultrasound bath) 중 아세톤/이소프로판올 혼합물 중에서 세정하였다. 존재할 수 있는 임의의 유기 잔사를 제거하기 위해, 기판을 추가의 25분 동안 오존 오븐 중에서 연속 오존류(ozone flow)에 노출시켰다. 당해 처리는 또한 ITO의 정공 주입 특성을 개선하였다. 그 다음 플렉스코어® OC AJ20-1000 (플렉스트로닉스 인코퍼레이티드(Plextronics Inc.)로부터 시판됨)을 스핀-코팅하고 건조시켜 정공 주입층 (~40 nm)을 형성시켰다.

[0554] 그 후, 하기 명시된 유기 물질을 약 10^{-7} -10^{-9}mbar에서 대략 0.5-5 nm/분의 속도로 청결한 기판에 기상 증착에 의해 적용하였다. 정공 수송 및 여기자 차단제로서, 

($Ir(dpbic)_3$) (제조에 관해, 출원 WO 2005/019373의 Ir 착물 (7) 참조)을 20 nm의 두께를 갖는 기판에 적용하고, 여기서 최초 10 nm를 MoO_x (~10%)로 도핑하여 전도도를 개선하였다.

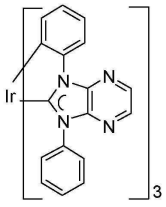
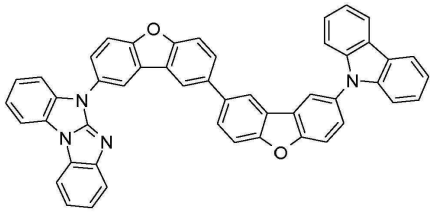
[0555] 후속적으로, 30 중량%의 방출체 화합물,  , 8 중량%의 화합물 $Ir(dpbic)_3$ 및 62 중량%의 화합물  (A-1)의 혼합물을 30 nm의 두께로 기상 증착에 의해 적용하였다.

[0556] 후속적으로, 물질 BAlq ()을 차단제로서 5 nm의 두께로 기상 증착에 의해 적용하였다.

[0557] 그 다음, Cs_2CO_3 도핑된 BCP () 층을 전자 수송층으로서 20 nm의 두께로 기상 증착에 의해 적용하고 최종적으로 100 nm-두께 Al 전극으로 소자를 완성하였다.

[0558] 모든 조립 부품을 불활성 질소 분위기 중에서 유리 뚜껑 및 게터(getter)로 밀봉하였다.

[0559] **적용 실시예 2 - 단일 매트릭스(Single-Matrix)**

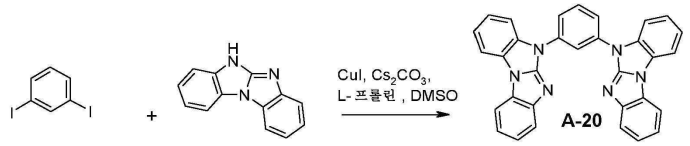
[0560] 발광층이 30 중량%의 화합물  및 70 중량%의 화합물  (A-1)만으로 이루어지고, 즉 화합물 $Ir(dpbic)_3$을 포함하지 않는 것을 제외하고, 적용 실시예 1에서와 같이 OLED의 제조 및 구축.

[0561] OLED를 특성화하기 위해, 전계발광 스펙트럼을 다양한 전류 및 전압에서 기록하였다. 게다가, 전류-전압 특성을 방출된 광 출력(light output)과 조합하여 측정하였다. 광 출력을 광도계를 사용한 보정에 의해 측광 파라미터로 변환시킬 수 있었다. 수명을 결정하기 위해, OLED를 일정 전류 밀도에서 작동시키고 광 출력의 감소를 기록하였다. 수명은 휘도가 초기 휘도의 절반으로 감소할 때까지 경과하는 시간으로서 정의하였다.

	EML	300nits에서의 전압 [V]	300nits에서의 EQE[1] [%]	4000nits에서의 수명 [h]	CIE
적용 실시예1	혼합 매트릭스	3.8 V	14.7 %	125 h	0.17 / 0.33
적용 실시예2	단일 매트릭스	3.6 V	14.2 %	65 h	0.17 / 0.34

[0562] 1) 외부 양자 효율 (EQE)은 물질 또는 소자로부터 배출되는 발생된 광자(photon)의 수 / 이를 통해 흐르는 전자의 수이다.

[0563] 실시예 3

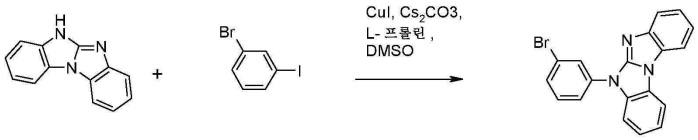
[0564]


[0565] 3.30 g (10 mmol) 1,3-디아이오도벤젠, 13.0 g (40.0 mmol) 탄산세슘, 1.90 g (1.00 mmol) 아이오딘화구리(I) 및 2.30 g (20.0 mmol) L-프롤린을 질소하에 100 ml 디메틸술폭시드 (DMSO) 중 4.56 g (22.0 mmol) 5H-벤즈이미다조[1,2-a]벤즈이미다졸에 첨가하였다. 반응 혼합물을 100℃에서 5 h 동안 교반하였다. 반응 혼합물을 물에 붓고 생성물을 여과해냈다. 생성물을 톨루엔으로부터 2회 결정화하였다. 수율 1.6 g (48%).

[0566] MS (APCI(pos): m/z = 489 (M^{+1}).

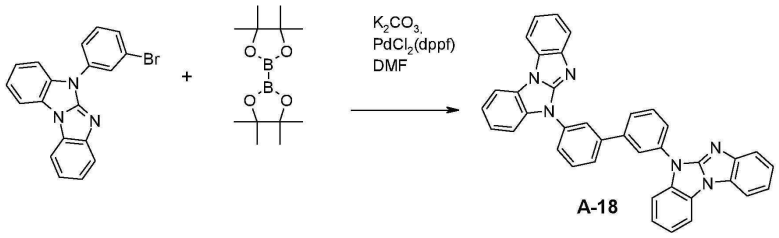
[0567] ^{1}H NMR (400 MHz, THF-d8): δ 8.79 (s, 1H), 8.22 (d, J= 8.4 Hz, 2H), 8.15-8.18 (m, 2H), 8.00-8.06 (m, 4H), 7.88 (t, J= 8.1 Hz, 1H) 7.71 (d, J= 7.9 Hz, 2H), 7.41-7.49 (m, 4H), 7.25-7.34 (m, 4H).

[0568] 실시예 4

[0569]


[0570] a) 7.78 g (25 mmol) 1-브로모-3-아이오도-벤젠, 16.3 g (50.0 mmol) 탄산세슘, 1.24 g (6.50 mmol) 아이오딘화구리(I) 및 1.50 g (13.0 mmol) L-프롤린을 질소하에 100 ml 디메틸술폭시드 (DMSO) 중 5.18 g (25.0 mmol) 5H-벤즈이미다조[1,2-a]벤즈이미다졸에 첨가하였다. 반응 혼합물을 100℃에서 18 h 동안 교반하였다. 반응 혼합물을 물에 부었다. 유기상을 디클로로메탄으로 추출하였다. 유기상을 황산마그네슘으로 건조시켰다. 용매를 증류해냈다. 톨루엔을 사용하여 실리카겔 상에서 칼럼 크로마토그래피하여 생성물을 수득하였다. 수율 8.35 g (92%).

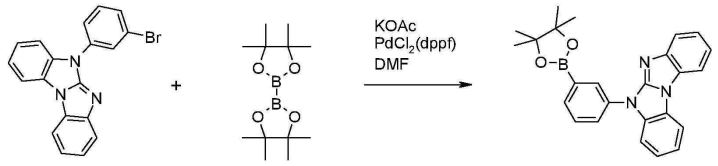
[0571] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.90-8.05 (m, 3H), 7.95-8.05 (m, 3H), 7.71 (d, J=7.9 Hz, 1H), 7.65 (d, J= 7.9 Hz, 1H). 7.50-7.65 (m, 2H), 7.26-7.45 (m, 4H).

[0572]


[0573] b) 20 ml DMF 중 실시예 4a)의 1.09 g (3.00 mmol)의 생성물, 690 mg (2.70 mmol) 4,4,5,5-테트라메틸-2-(4,4,5,5-테트라메틸-1,3,2-디옥사보롤란-2-일)-1,3,2-디옥사보롤란, 5.86 g (1.80 mmol) 탄산칼륨을 아르곤으로 탈기하였다. 1,1'-비스(디페닐포스피노)페로센)디클로로팔라듐(II)을 첨가하고 반응 혼합물을 아르곤으로 탈기하였다. 반응 혼합물을 80℃에서 18 h 동안 교반하였다. 생성물을 여과해내고 디메틸포름아미드 (DMF), 물 및 메탄올로 세척하였다. 수율 370 mg (44%).

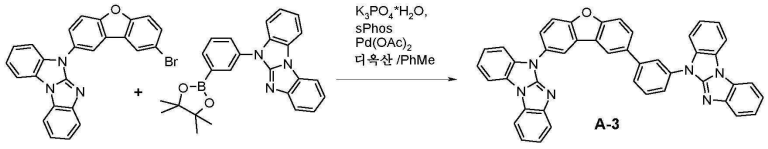
[0574] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 2H), 7.95-8.10 (m, 6H) 7.70-7.90 (m, 6H), 7.63 (d, J= 7.6 Hz, 2H), 7.20-7.45 (m, 8H).

[0575] 실시예 5

[0576]


[0577] a) 50 ml DMF 중 실시예 4a)의 5.78 g (16.0 mmol)의 생성물, 12.16 g (47.8 mmol) 4,4,5,5-테트라메틸-2-(4,4,5,5-테트라메틸-1,3,2-디옥사보롤란-2-일)-1,3,2-디옥사보롤란, 12.5 g (0.128 mol) 아세트산칼륨을 아르곤으로 탈기하였다. 1,1'-비스(디페닐포스피노)페로센)디클로로팔라듐(II)을 첨가하고 반응 혼합물을 아르곤으로 탈기하였다. 반응 혼합물을 60℃에서 22 h 동안 교반하고 물 중 염화나트륨의 포화 용액에 부었다. 수상을 테트라히드로푸란 (THF)으로 추출하고, 유기상을 황산마그네슘으로 건조시키고 용매를 증류해냈다. 생성물을 디에틸 에테르 및 시클로헥산으로부터 결정화하였다. 수율 3.62 g (59%).

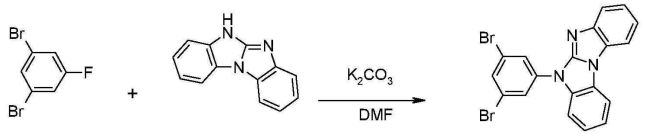
[0578] **1H NMR** (400 MHz, THF-d8): δ 8.26 (s, 1H), 8.09-8.10 (m, 1H), 8.07-8.09 (m, 2H), 7.86 (s, J= 7.6 Hz, 1H), 7.60-7.67 (m, 3H), 7.28-7.42 (m, 4H), 1.39 (s, 12H).

[0579]


[0580] b) 2.72 g (6.01 mmol) 5-(8-브로모디벤조푸란-2-일)벤즈이미다졸로[1,2-a]벤즈이미다졸 및 6.92 g (3.01 mmol) 삼염기성 인산칼륨 일수화물, 27 ml 디옥산, 100 ml 톨루엔 및 21 ml 물을 3.20 g (7.82 mmol)의 5-[3-(4,4,5,5-테트라메틸-1,3,2-디옥사보롤란-2-일)페닐]벤즈이미다졸로[1,2-a]벤즈이미다졸에 첨가하였다. 혼합물을 아르곤으로 탈기하였다. 148 mg (0.361 mmol) 2-디시클로헥실포스피노-2',6'-디메톡시비페닐 (SPhos) 및 135 mg (0.060 mmol) 팔라듐(II) 아세테이트를 첨가하였다. 반응 혼합물을 아르곤으로 탈기하고 아르곤하에 100℃에서 22 h 동안 교반하였다. 110 ml의 1% 시안화나트륨 용액을 첨가하고 반응 혼합물을 1 h 동안 환류하였다. 디클로로메탄을 첨가하고, 유기상을 물로 세척하고 황산마그네슘으로 건조시켰다. 생성물을 메탄올로 디콕션하였다(decoct) (수율: 1.62 g (41%)).

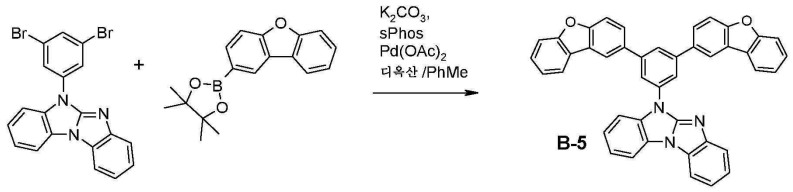
[0581] **1H NMR** (400 MHz, THF-d8): δ 8.69 (d, J= 1.1 Hz, 1H), 8.57 (d, J= 1.6 Hz, 1H), 8.42 (s, 1H), 8.05-8.08 (m, 1H), 7.89-7.99 (m, 6H), 7.80-7.85 (m, 2H) , 7.76-7.75 (m, 4H), 7.57-7.61 (m, 2H), 7.18-7.37 (m, 8H).

[0582] 실시예 6

[0583]


[0584] a) 200 ml DMF 중 20.0 g (78.8 mmol) 1,3-디브로모-5-플루오로-벤젠, 16.3 g (78.8 mmol) 6H-벤즈이미다졸로[1,2-a]벤즈이미다졸 및 43.5 g (0.315 mmol) 탄산칼륨을 170℃에서 17 h 동안 교반하였다. 반응 혼합물을 고온 상태로 여과하고 모액으로부터의 침전물을 냉각 후 여과하였다. 생성물을 물 및 에탄올로 세척하고 디에틸 에테르 및 에탄올로 디콕션하였다. 수율 21.2 g (61%).

[0585] **1H NMR** (400 MHz, THF-d8): δ 8.21-8.26 (m, 4H), 7.98-7.8.00 (m, 1H), 7.68-7.73 (m, 2H), 7.31-7.49 (m, 4H).

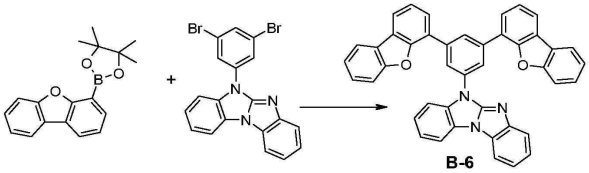
[0586]


[0587] b) 2.00 g (4.53 mmol) 5-(3,5-디브로모페닐)벤즈이미다졸로[1,2-a]벤즈이미다졸 및 4.15 g (3.00 mmol) 탄산

칼륨, 27 ml 디옥산, 100 ml 톨루엔 및 21 ml 물을 3.20 g (7.82 mmol)의 2-디벤조푸란-2-일-4,4,5,5-테트라메틸-1,3,2-디옥사보롤란에 첨가하였다. 혼합물을 아르곤으로 탈기하였다. 37 mg (0.090 mmol) 2-디시클로헥실포스피노-2',6'-디메톡시비페닐 (SPhos) 및 10 mg (0.0045 mmol) 팔라듐(II) 아세테이트를 첨가하였다. 반응 혼합물을 아르곤으로 탈기하고 아르곤하에 120℃에서 19 h 동안 교반하였다. 110 ml의 1% 시안화나트륨 용액을 첨가하고 반응 혼합물을 1 h 동안 환류하였다. 용매를 증류해냈다. 30 ml 톨루엔을 첨가하고, 생성물을 여과해내고, 물 및 시클로헥산으로 세척하고 메틸 부틸 케톤 (MEK)으로부터 결정화하였다. 수율 1.84 g (66%).

[0588] ^{1}H NMR (400 MHz, THF-d8): δ 8.21-8.26 (m, 4H), 7.98-7.8.00 (m, 1H), 7.68-7.73 (m, 2H), 7.31-7.49 (m, 4H).

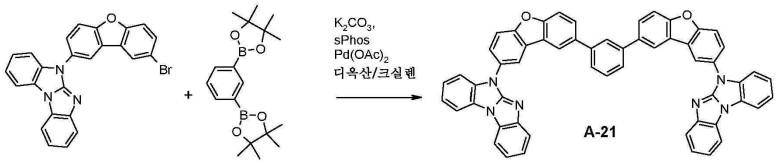
[0589] 실시예 7

[0590] 

[0591] 실시예 7의 생성물을 실시예 6에 기재된 절차와 유사하게 제조하였다.

[0592] ^{1}H NMR (400 MHz, DMSO-d6): δ 8.59 (d, J=1.5 Hz, 2H), 8.46-8.47 (m, 1H), 8.24-8.33 (m, 6H), 8.13 (d, J= 8.0 Hz, 1H), 7.99-8.01 (m, 2H), 7.78 (d, J= 8.2 Hz, 2H), 7.37-7.68 (m, 9H), 7.29-7.37 (m, 2H)

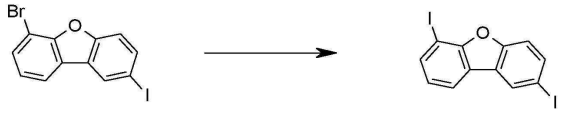
[0593] 실시예 8

[0594] 

[0595] 3.85 g (8.51 mmol) 5-(8-브로모디벤조푸란-2-일)벤즈이미다졸로[1,2-a]벤즈이미다졸 및 10.3 g (4.26 mmol) 삼염기성 인산칼륨 일수화물, 20 ml 디옥산, 80 ml 크실렌 및 16 ml 물을 2.01 g (4.09 mmol)의 4,4,5,5-테트라메틸-2-[3-(4,4,5,5-테트라메틸-1,3,2-디옥사보롤란-2-일)페닐]-1,3,2-디옥사보롤란에 첨가하였다. 혼합물을 아르곤으로 탈기하였다. 210 mg (0.511 mmol) 2-디시클로헥실포스피노-2',6'-디메톡시비페닐 (SPhos) 및 191 mg (0.085 mmol) 팔라듐(II) 아세테이트를 첨가하였다. 반응 혼합물을 아르곤으로 탈기하고 아르곤하에 100℃에서 22 h 동안 교반하였다. 110 ml의 1% 시안화나트륨 용액을 첨가하고 반응 혼합물을 1 h 동안 환류하였다. 디클로로메탄을 첨가하였다. 유기상을 물로 세척하고 황산마그네슘으로 건조시켰다. 생성물을 디에틸에테르로 디콕션하였다. 수율 1.31 g (39%).

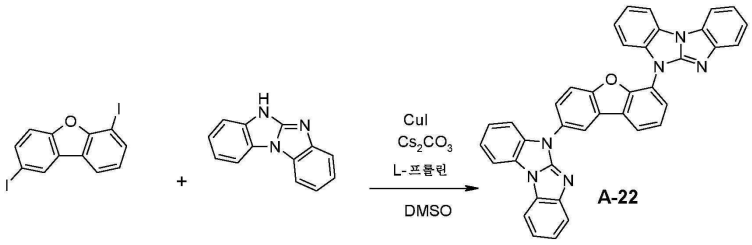
[0596] ^{1}H NMR (400 MHz, DMF-d7): δ 8.90 (d, J= 1.7 Hz, 2H), 8.86 (d, J= 2.2 Hz, 2H), 8.37 (s, 1H), 8.26-8.31 (m, 4H), 8.14-8.21 (m, 4H), 8.08-8.11 (m, 2H), 7.94-7.96 (m, 2H), 7.89-7.93 (m, 2H), 7.76-7.78 (m, 2H), 7.66-7.71 (m, 3H), 7.32-7.49 (m, 8H)

[0597] 실시예 9

[0598] 

[0599] a) 2,6-디아이오도-디벤조푸란을 WO2011/111423의 실시예 13에 따라 제조하고 시클로헥산으로부터 결정화함으로써 정제하였다.

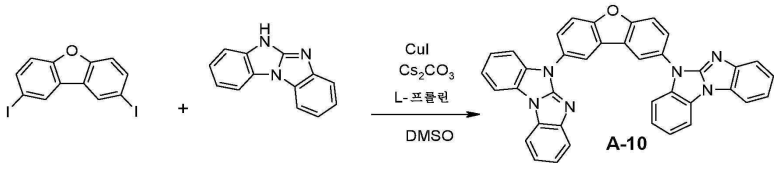
[0600]



[0601] b) 실시예 9의 생성물을 실시예 5에 기재된 절차와 유사하게 제조하였다.

[0602] 실시예 10

[0603]

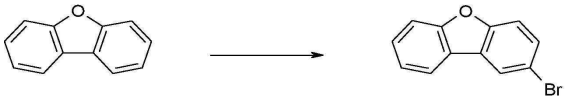


[0604] 4.20 g (10 mmol) 2,8-디아이오도디벤조푸란, 13.0 g (40.0 mmol) 탄산세슘, 1.90 g (1.00 mmol) 아이오딘화구리(I) 및 2.30 g (20.0 mmol) L-프롤린을 질소하에100 ml 디메틸술폭시드 (DMSO) 중 4.56 g (22.0 mmol) 5H-벤즈이미다조[1,2-a]벤즈이미다졸에 첨가하였다. 반응 혼합물을 100℃에서 24 h 동안 교반하고, 여과하고 디클로로메탄으로 세척하였다. 유기상을 황산마그네슘으로 건조시키고 용매를 증류해냈다. 생성물을 에테르로부터 결정화하였다. 수율 4.7 g (81%)

[0605] ^{1}H NMR (400 MHz, THF-d8): δ 8.73 (d, J= 1.2 Hz, 2H), 8.14 (d, J= 2.3 Hz, J=8.8 Hz, 2H), 7.96-8.02 (m, 4H), 7.92 (d, J=8.8 Hz, 2H), 7.70-7.73 (m, 2H), 7.62 (d, J= 7.1 Hz, 2H), 7.25-7.40 (m, 8 H).

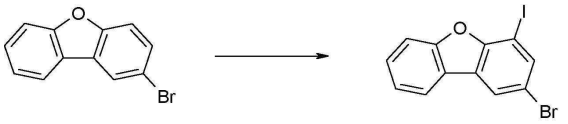
[0606] 실시예 11

[0607]



[0608] a) 2-브로모-디벤조푸란을 문헌 [E. Hand, J. Org. Chem. 62 (1997) 1348]에 따라 제조하고 tert-부틸 메틸 에테르 (TBME)로부터 결정화하여 정제하였다.

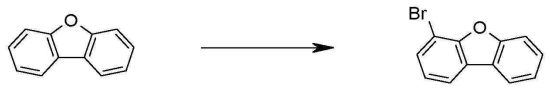
[0609]



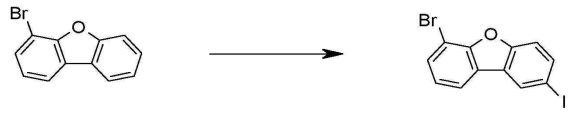
[0610] b) 47.27 g (0.199 mol)의 2-브로모-벤조푸란을 440 ml 건조 THF에 용해시키고 아르곤하에 -78℃로 냉각하였다. 1 h 이내에 리튬 디이소프로필아미드 (LDA; 250 ml의 건조 THF 중 81.2 ml (0.219 mol) n-부틸리튬 (헥산 중 2.7M) 및 20.18 g (0.199 mol) 디이소프로필아민으로부터 제조됨)의 용액을, 온도를 -73℃ 이하로 유지하면서 첨가하였다. 생성된 황색 용액을 -78℃에서 2 h 동안 교반하였다. 그 다음 150 ml 건조 THF에 용해된 50.6 g (0.199 mol) 아이오딘의 용액을, 온도를 -73℃ 이하로 유지하면서 50분 이내에 첨가하였다. 생성된 갈색 용액을 실온으로 가온하고, 500 ml의 완충제 용액 pH = 7에 붓고 2N HCl을 사용하여 pH = 7로 중화시켰다. 유기 용매를 증발시키고 수성상을 에틸아세테이트로 3회 추출하였다. 합해진 유기상을 물로 3회 세척하고, 황산마그네슘으로 건조시키고, 여과하고 용매를 증발시켰다. 시클로헥산/TBME = 1:1로부터 2회 결정화하여 35.0 g의 2-브로모-4-아이오도-디벤조푸란 (수율: 45.6%)을 수득하였다.

[0611] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 1.8 Hz, 1H), 7.95 (d, J = 1.8 Hz, 1H), 7.85 (d, J = 8 Hz, 1H), 7.63 (d, J = 8 Hz, 1H), 7.51 (t, J = 8 Hz, 1H), 7.37 (t, J = 8 Hz, 1H).

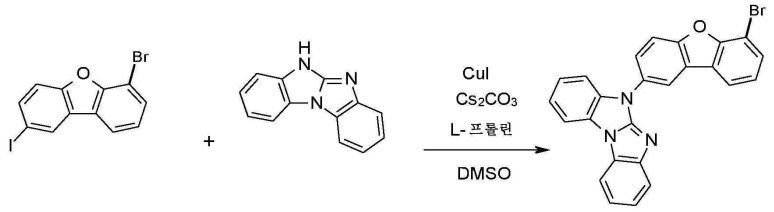
[0612] 실시예 12

[0613] 

[0614] a) 4-브로모-디벤조푸란을 US2011/0006670의 실시예 1에 따라 제조하고 메탄올로부터 결정화하여 정제하였다.

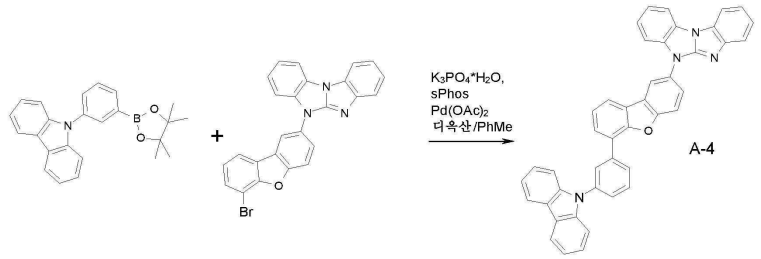
[0615] 

[0616] b) 6-브로모-2-아이오도-디벤조푸란을 US2011/0006670의 실시예 1에 따라 제조하고 2-프로판올로부터 결정화하여 정제하였다.

[0617] 

[0618] c) 1.00 g (2.68 mmol) 6-브로모-2-아이오도-디벤조푸란, 1.75 g (5.36 mmol) 탄산세슘, 130 mg (0.67 mmol) 아이오딘화구리(I) 및 150 mg (1.34 mmol) L-프롤린을 질소하에 20 ml DMSO 중 670 mg (3.22 mmol) 5H-벤즈이미다조[1,2-a]벤즈이미다졸에 첨가하였다. 반응 혼합물을 100℃에서 18 h 동안 교반하고 여과하였다. THF 및 톨루엔을 유기상에 첨가하고 유기상을 물로 세척하였다. 유기상을 황산마그네슘으로 건조시키고 용매를 증류해냈다. 생성물을 추가 정제 없이 단계 d)에서 사용할 수 있었다 (수율 = 650 mg (78%)).

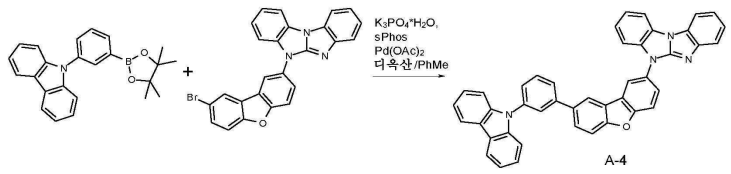
[0619] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, J = 2.2 Hz, 1H), 8.13-8.19 (m, 2H), 7.96-8.07 (m, 3H), 7.66-7.78 (m, 3H), 7.25-7.45 (m, 5H).

[0620] 

[0621] d) 실시예 12의 생성물을 실시예 5에 기재된 절차와 유사하게 제조하였다.

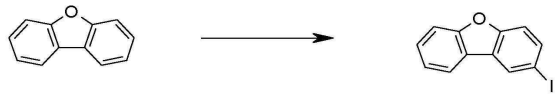
[0622] MS (APCI(pos), m/z): 615.5 (M^{+1}). ^{1}H NMR (400 MHz, THF-d8): 8.68 (d, J= 2.1 Hz, 1H), 8.34 (t, J = 1.8 Hz, 1H), 8.21 (d, J= 7.7 Hz, 3H), 7.85-7.15 (m, 7 H), 7.65-7.77 (m, 5 H), 7.47-7.58 (m, 3H), 7.28-7.44 (m, 6 H).

[0623] 실시예 13

[0624] 

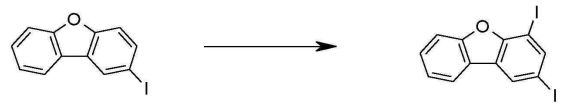
[0625] 9-[3-(4,4,5,5-테트라메틸-1,3,2-디옥사보롤란-2-일)페닐]카르바졸의 합성은 문헌 [Chem. Mater. 20 (2008) 1691-693]에 기재되어 있다. 실시예 21의 생성물을 실시예 5에 기재된 절차와 유사하게 제조하였다.

[0626] 실시예 14

[0627] 

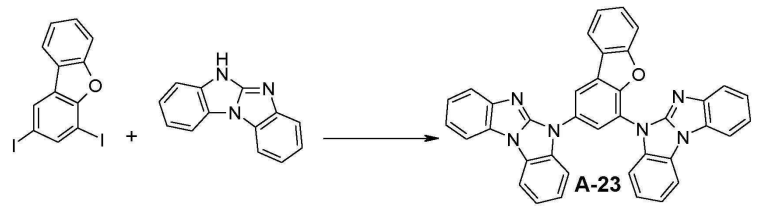
[0628] 2-아이오도-디벤조푸란을 문헌 [A. Kryska, Journal of Chemical Research, Miniprint 10 (1999) 2501]에 따라 제조하고 메탄올로부터 결정화하여 정제하였다.

[0629] 실시예 15

[0630] 

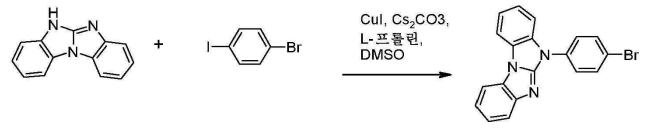
[0631] a) 2,4-디아이오도-디벤조푸란을 2-아이오도-디벤조푸란 (실시예 14)으로부터 출발하여, 실시예 11에 기재된 절차와 유사하게 제조하고 2-프로판올로부터 결정화하여 정제하였다 (수율: 80%).

[0632] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 8.07 (s, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H).

[0633] 

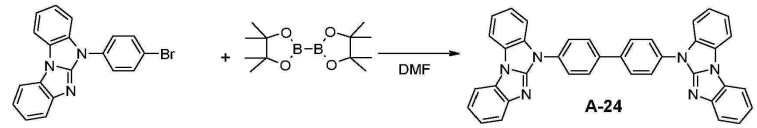
[0634] b) 실시예 15의 생성물을 실시예 10에 기재된 절차와 유사하게 제조하였다.

[0635] 실시예 16

[0636] 

[0637] a) 7.00 g (24.7 mmol) 1-브로모-4-아이오도-벤젠, 10.5 g (32.2 mmol) 탄산세슘, 2.36 g (12.4 mmol) 아이오딘화구리(I) 및 2.85 g (24.7 mmol) L-프롤린을 질소하에 80 ml DMSO 중 5.13 g (24.7 mmol) 5H-벤즈이미다조[1,2-a]벤즈이미다졸에 첨가하였다. 반응 혼합물을 100℃에서 15 h 및 150℃에서 4 h 동안 교반하고, 디클로로메탄을 사용하여 히플로 상에서 여과하였다. 유기상을 물로 세척하였다. 유기상을 황산마그네슘으로 건조시켰다. 생성물을 디에틸에테르 및 메틸 에틸 케톤 (MEK)으로 디콕션하였다. 수율: 2.90 g (77%).

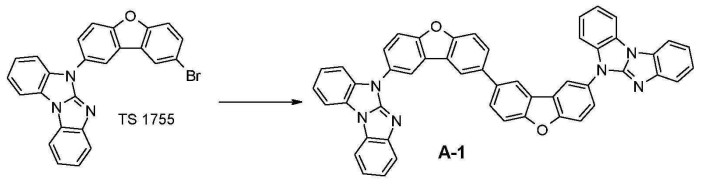
[0638] ^{1}H NMR (400 MHz, DMF-d7): δ 7.93-8.10 (m, 4H), 7.78-7.92 (m, 2H), 7.72-7.79 (m, 1H), 7.49-7.71 (m, 1H), 7.31-7.49 (m 4H).

[0639] 

[0640] b) 실시예 16b)의 생성물을 실시예 4b)에 기재된 절차와 유사하게 제조하였다.

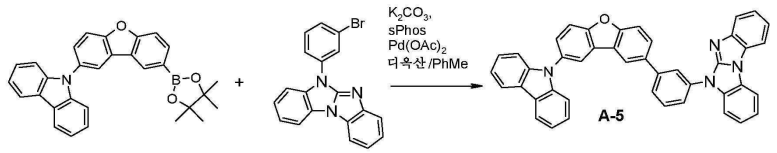
[0641] ^{1}H NMR (400 MHz, DMF-d7): δ = 8.19-8.33 (m, 10H), 7.83-7.87 (m, 2H), 7.73-7.77 (m, 2H), 7.35-7.54 (m, 4H). 한 신호는 DMF에 의해 커버됨
MS (APCI(pos), m/z): 565 (M^{+1}).

[0642] 실시예 17

[0643] 

[0644] 실시예 17의 생성물을 실시예 4b)에 기재된 절차와 유사하게 제조하였다.

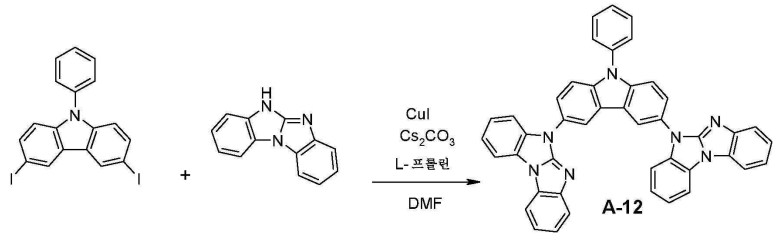
[0645] 실시예 18

[0646] 

[0647] 실시예 18의 생성물을 실시예 5b)에 기재된 절차와 유사하게 제조하였다.

[0648] MS (APCI(pos), m/z): 615 (M^{+1}).

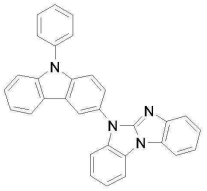
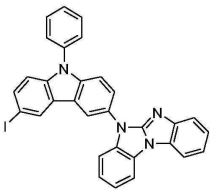
[0649] 실시예 19

[0650] 

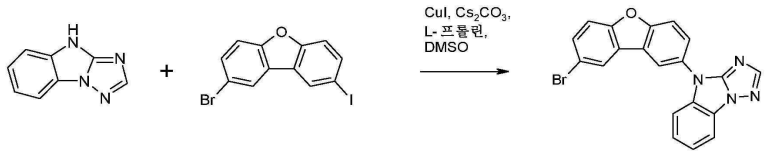
[0651] 2 g (4.04 mmol) 3,6-디아이오도-9-페닐-카르바졸, 5.26 g (16.2 mmol) 탄산세슘, 190 mg (0.101 mmol) 아이오딘화구리(I) 및 233 mg (2.02 mmol) L-프롤린을 질소하에 40 ml DMSO 중 1.84 g (8.89 mmol) 5H-벤즈이미다조[1,2-a]벤즈이미다졸에 첨가하였다. 반응 혼합물을 150℃에서 10 h 동안 교반하고, 히플로 슈퍼 셀(R) 매질(플루카 56678, CAS [91053-39-3]) 상에서 여과하고 디클로로메탄으로 세척하였다. 유기상을 황산마그네슘으로 건조시키고 용매를 증류해냈다. 시클로헥산/톨루엔 (시클로헥산 100%, 시클로헥산/톨루엔 10/1, 시클로헥산/톨루엔 4/1)을 사용하여 구배 칼럼 크로마토그래피하여 생성물 (수율: 70 mg (3%))을 수득하였다.

[0652] MS (APCI(pos), m/z): 654 (M^{+1}).
^{1}H NMR (400 MHz, THF-d8): δ = 8.81 (d, J=1.9 Hz, 2H), 7.99-7.05 (m, 6H), 7.70-7.83 (m, 11H), 7.22-7.41 (m, 8H).

[0653] 화합물 A-12 이외에 하기 화합물을 HPLC-MS에 의해 검출하였다:

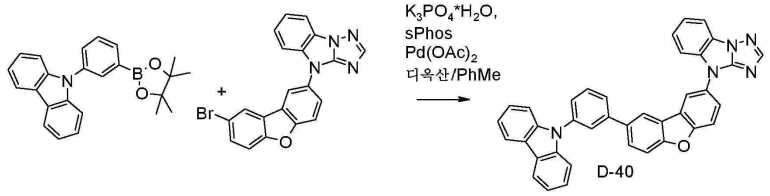
[0654] 
(MS (APCI(pos), m/z): 449 (M^{+1})).

(MS (APCI(pos), m/z): 575 (M^{+1})).

[0655] 실시예 20

[0656] 

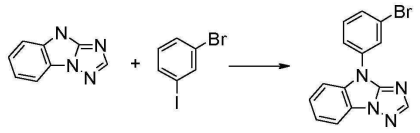
[0657] a) 실시예 20a)의 생성물을 실시예 1c)에 기재된 절차와 유사하게 제조하였다. 4H-[1,2,4]트리아졸로[1,5-a]벤즈이미다졸의 합성 및 그의 합성에 사용된 출발 물질에 관해서는 문헌 [J. Heterocyclic Compounds (1989) 168] 및 [J. Org. Chem 42 (1977) 542]을 참조한다.

[0658] MS (MALDI-MS (, m/z): 403 (M^{+1}).

[0659] 

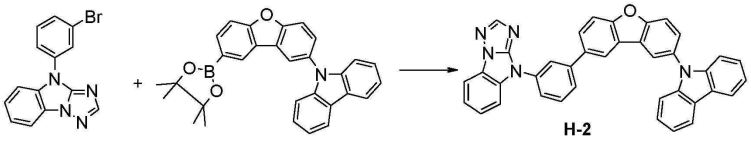
[0660] b) 실시예 20b)의 생성물을 실시예 13에 기재된 절차와 유사하게 제조하였다.

[0661] **실시예 21**

[0662] 

[0663] a) 5 g (31.6 mmol) 4H-[1,2,4]트리아졸로[1,5-a]벤즈이미다졸, 20.6 g (63.2 mmol) 탄산세슘, 1.5 g (7.9 mmol) 아이오딘화구리(I), 및 910 mg (7.9 mmol) L-프롤린을 질소하에 60 mL DMSO 중 17.8 g (8 mL) (63.2 mmol) 1-브로모-3-아이오도벤젠에 첨가하였다. 반응 혼합물을 85℃에서 15 h 동안 교반하였다. 반응 혼합물을 디클로로메탄을 사용하여 실리카겔을 통해 여과하였다. 유기상을 물, NaCl 용액으로 세척하고, 황산나트륨으로 건조시켰다. 생성물을 디에틸에테르로 디콕션하였다 (수율: 8.0 g (80%)).

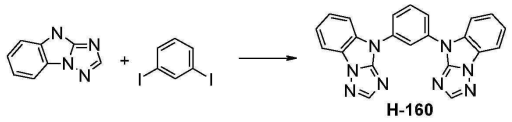
[0664] ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.02 (s, 1H), 7.98 (s, 1H), 7.90-7.88 (m, 1H), 7.71-7.68 (m, 1H), 7.60-7.58 (d, 1H), 7.52-7.48 (t, 1H), 7,46-7.40 (m, 2H). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 155.05 (d, 1C), 153.47 (s, 1C), 136.82 (s, 1C), 134.23 (s, 1C), 131.63 (d, 1C), 130.78 (d, 1C), 126.69 (d, 1C), 124.95 (s, 1C), 124.87 (d, 1C), 123.50 (s, 1C), 123.26 (d, 1C), 122.45 (d, 1C), 112.15 (d, 1C), 111.66 (d, 1C).

[0665] 

[0666] b) 40 mL 톨루엔 중 1.25 g (4 mmol) 4-(3-브로모페닐)-[1,2,4]트리아졸로[1,5-a]벤즈이미다졸, 2.4 g (5.2 mmol) 9-[8-(4,4,5,5-테트라메틸-1,3,2-디옥사보롤란-2-일)디벤조푸란-2-일]카르바졸, 및 4.3 g (20 mmol) 인산칼륨을 아르곤하에 디옥산/물 40 mL/10 mL 중 90 mg (0.03 mmol) 팔라듐(II)아세테이트, 100 mg (0.24 mmol) 2-디시클로헥실포스피노-2,6-디메톡시비페닐 (SPhos)에 첨가하였다. 반응 혼합물을 85℃에서 15 h 동안 교반하고 디클로로메탄을 사용하여 셀라이트를 통해 여과하였다. 유기상을 물, NaCl 용액으로 세척하고, 황산나트륨으로 건조시켰다 (수율: 1.75 g (77%)).

[0667] ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.41 (d, 1H), 8.37 (d, 1H), 8.34 (d, 2H), 8.25 (t, 1H), 8.17 (s, 1H), 8.06-8.04 (m, 3H), 7.93-7.86 (m, 4H), 7.84 (d, 1H), 7.82 (d, 1H), 7.59-7.54 (m, 6H), 7.47-7.43 (m, 2H). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 157.22 (s, 1C), 155.97 (s, 1C), 155.07 (d, 1C), 153.80 (s, 1C), 143.30 (s, 1C), 141.80 (s, 2C), 136.12 (s, 1C), 135.79 (s, 1C), 134.68 (s, 1C), 133.14 (s, 1C), 130.81 (d, 1C), 127.78 (d, 1C), 127.31 (d, 1C), 126.79 (d, 1C), 126.36 (d, 2C), 125.87 (s, 1C), 124.91 (s, 1C), 124.89 (s, 1C), 124.76 (d, 1C), 123.51 (d, 2C), 122.92 (d, 1C), 122.88 (d, 1C), 120.61 (d, 2C), 120.31 (d, 1C),120.26 (d, 2C), 122.65 (d, 1C), 120.03 (d, 1C), 113.40 (d, 1C), 112.66 (d, 1C), 112.21 (d, 1C), 111.58 (d, 1C), 110.02 (d, 2C).

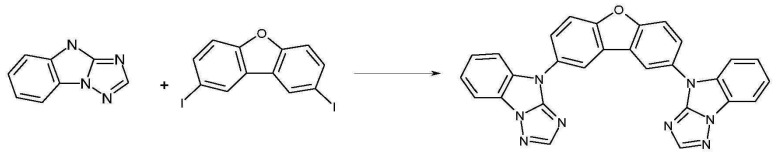
[0668] 실시예 22

[0669] 

[0670] 10 mL DMSO 중 160 mg (0.48 mmol) 1,3-디아이오도벤젠 및 170 mg (1.06 mmol) 4H-[1,2,4]트리아졸로[1,5-a]벤즈이미다졸을 아르곤하에 15분 동안 교반하였다. 625 mg (1.9 mmol) 탄산세슘, 120 mg (1.06 mmol) L-프롤린, 및 90 mg (0.48 mmol) 아이오딘화구리(I)를 첨가하였다. 반응 혼합물을 100℃에서 15 h 동안 교반하고 디클로로메탄을 사용하여 셀라이트를 통해 여과하였다. 유기상을 물, NaCl 용액으로 세척하고, 황산나트륨으로 건조시켰다. 생성물을 이소프로판올로부터 결정화하였다 (수율: 130 mg (69%)).

[0671] ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.35 (s, 1H), 8.06 (s, 2H), 7.94-7.84 (m, 7H), 7.50-7.42 (m, 4H). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 155.12 (d, 2C), 153.59 (s, 2C), 137.10 (s, 2C), 134.27 (s, 2C), 131.07 (d, 1C), 125.09 (s, 2C), 125.06, (d, 2C), 123.39 (d, 2C), 121.80 (d, 2C), 118.36 (d, 1C), 112.51 (d, 2C), 111.73 (d, 2C).

[0672] 실시예 23

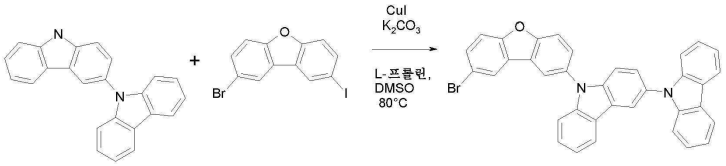
[0673] 

[0674] 10 mL DMSO 중 1 g (2.4 mmol) 2,8-디아이오도디벤조푸란 및 840 mg (5.3 mmol) 4H-[1,2,4]트리아졸로[1,5-a]벤즈이미다졸을 아르곤하에 15분 동안 교반하였다. 3.1 g mg (9.6 mmol) 탄산세슘, 550 mg (4.8 mmol) L-프롤린, 및 460 mg (2.4 mmol) 아이오딘화구리(I)를 첨가하였다. 갈색 반응 혼합물을 100℃에서 15 h 동안 교반하였다. 물을 반응 혼합물에 첨가하고 여과하고 메탄올로 세척하였다. 생성물을 톨루엔으로 결정화하였다 (수율: 330 mg (28%)).

[0675] ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.38 (s, 1H), 8.05 (s, 2H), 7.92-7.85 (m, 8H), 7.42-7.13 (dd, 2H)

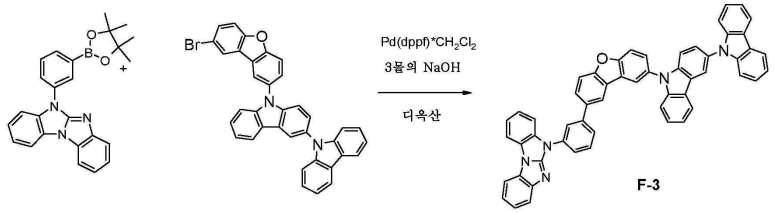
[0676] 실시예 24

[0677] 9-(9*H*-카르바졸-3-일)-9*H*-카르바졸을 문헌 절차 (J. Org. Chem, 2008, 73, 1809)에 따라 제조하였다.

[0678] 

[0679] a) 실시예 24a)의 생성물을 실시예 10의 절차에 따라 제조하였다. 정제: FC (SiO_2, 시클로헥산/CH_2Cl_2 4:1). 수율: 85%.

[0680] **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.34 (s, 1H), 8.18 (m, 5H), 7.87 (d, 1H), 7.77 (d, 1H), 7.67 (d, 1H), 7.59 (m, 3H), 7.51-7.39 (m, 6H), 7.31 (m, 3H).

[0681] 

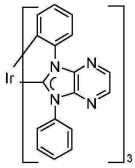
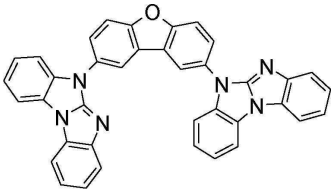
[0682] b) Pd(dppf)*CH_2Cl_2 (8 mg, 0.01 mmol)를 디옥산 (5 mL) 및 NaOH (3 M, 0.25 mL) 중 5-[3-(4,4,5,5-테트라메틸

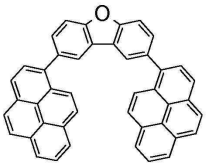
-1,3,2-디옥사보롤란-2-일)페닐]벤즈이미다졸로[1,2-a]벤즈이미다졸 (133 mg, 0.33 mmol), 실시예 24a)의 생성물 (144 mg, 0.25 mmol)의 탈기된 (Ar) 혼합물에 첨가하였다. 반응 혼합물을 80℃에서 8 h 동안 가열하고 셀라이트 및 FC (SiO_2, CH_2Cl_2) 상에서 여과하여 생성물 (수율: 50 mg, 26%)을 수득하였다.

[0683] ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.33 (2xs, 2+1H), 8.18 (m, 4H), 7.88 (m, 5H), 7.81-7.73 (m, 4H), 7.69-7.62 (m, 3H), 7.56 (d, 1H), 7.49 (d, 2H), 7.42-7.27 (m, 11H).

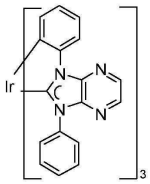
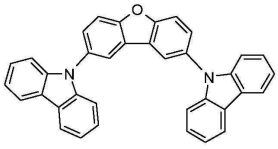
[0684] **적용 실시예 3**

[0685] ITO 기재의 제조뿐만 아니라 완전한 다이오드의 후속 특성화는 하기 층의 조성이 상이한 것을 제외하고, 적용 실시예 1에 상당하였다:

[0686] 정공 수송 및 여기자 차단제로서, Ir(dpbic)$_3$를 20 nm 두께의 기판에 적용하고, 여기서 먼저 10 nm을 MoO_3 (~10%)로 도핑하여 전도성을 개선하였다. 후속적으로, 30 중량%의 방출체 화합물,  ; 15 중량%의 화합물 Ir(dpbic)$_3$ 및 55 중량%의 화합물  (A-10)을 30 nm의 두께로 기상 증착에 의해 적용하였다.

[0687] 후속적으로, 화합물 A-10을 정공 차단제로서 5 nm의 두께로 기상 증착에 의해 적용하였다. 후속적으로 50 중량%의 물질  과 50 중량%의 물질  의 혼합물을 20 nm의 두께로 전자 수송층으로서 증발시켰다. 최종적으로 ~2 nm KF를 전자 주입층으로서 증착시키고 100 nm 두께의 Al 전극이 소자를 완성하였다.

[0688] **비교 적용 실시예 1**

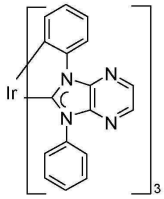
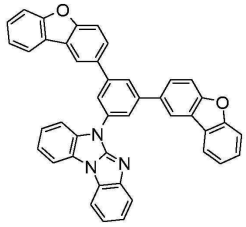
[0689] 하기를 제외하고, OLED의 제조 및 구축을 적용 실시예 3에서와 같이 행하였다: 정공 수송층에서 Ir(dpbic)$_3$ 중 MoO_3의 도핑 농도는 5 중량%이었다. 발광층은 30 중량%의 화합물  , 15 중량%의 화합물 Ir(dpbic)$_3$ 및 55 중량%의 화합물  (Ref-1)로 이루어졌다. 정공 차단층은 화합물 Ref-1로 이루어졌고 전자 수송층은 25 nm 두께였다.

	호스트 물질	300nits에서의 전압 [V]	300nits에서의 EQE [%]	4000nits에서의 수명 *
적용 실시예 3	A-10	4.02	14.0 %	100
비교 적용 실시예 1	Ref-1	4.00	10.8%	20

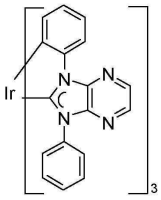
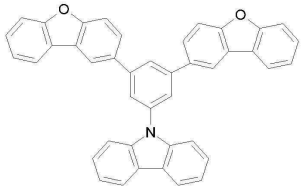
* 적용 실시예 3의 측정된 수명을 100으로 설정하고 비교 적용 실시예 1의 수명은 적용 실시예 3의 수명과 관련하여 명시하였다

[0690]

[0691] **적용 실시예 4**

[0692] 하기를 제외하고, OLED의 제조 및 구축을 적용 실시예 3에서와 같이 행하였다: MoO_3 및 $Ir(dpbic)_3$를 갖는 정공 수송층은 15 nm이었고 도핑되지 않은 전자 차단제, $Ir(dpbic)_3$은 단지 5 nm 두께이었다. 발광층은 30 중량%의 화합물  , 10 중량%의 화합물 $Ir(dpbic)_3$ 및 60 중량%의 화합물  (B-5)로 이루어졌고, 두께는 40 nm이었다. 정공 차단층은 물질 B-5로 이루어졌다.

[0693] **비교 적용 실시예 2**

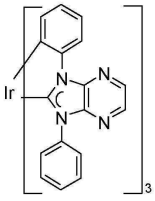
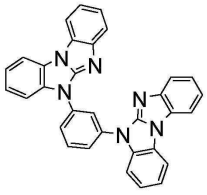
[0694] 하기를 제외하고, OLED의 제조 및 구축을 적용 실시예 3에서와 같이 행하였다: 발광층은 30 중량%의 화합물  , 10 중량%의 화합물 $Ir(dpbic)_3$ 및 60 중량%의 화합물  (Ref-2)로 이루어졌고, 두께는 40 nm이었다. 정공 차단층은 화합물 Ref-2로 이루어졌다.

	호스트 물질	300nits에서의 전압 [V]	4000nits에서의 수명 *
적용 실시예 4	B-5	4.55	100
비교 적용 실시예 2	Ref-2	4.34	70

* 적용 실시예 4의 측정된 수명을 100으로 설정하고 비교 적용 실시예 2의 수명은 적용 실시예 4의 수명과 관련하여 명시하였다.

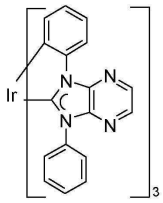
[0695]

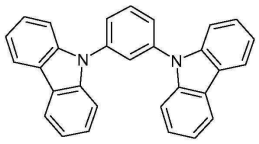
[0696] **적용 실시예 5**

[0697] 하기를 제외하고, OLED의 제조 및 구축을 적용 실시예 1에서와 같이 행하였다: 발광층은 30 중량%의 화합물  , 10 중량%의 화합물 $Ir(dpbic)_3$ 및 60 중량%의 화합물  (A-20)로 이루어졌고, 두께는 30 nm이었다. 전자 수송층은 25 nm 두께이었다.

[0698] **비교 적용 실시예 3**

[0699] 하기를 제외하고, OLED의 제조 및 구축은 적용 실시예 1에서와 같이 행하였다: 발광층은 30 중량%의 화합물



, 10 중량%의 화합물 $Ir(dpbic)_3$ 및 60 중량%의 화합물  (Ref-3)으로 이루어졌고, 두께는 30 nm이었다. 정공 차단층은 25 nm 두께이었다.

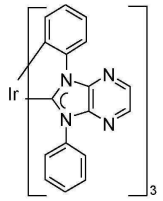
	호스트 물질	300nits 에서의 전압 [V]	300nits 에서의 EQE [%]
적용 실시예 5	A-20	3.43	11.3
비교 적용 실시예 3	Ref-3	3.81	13.6

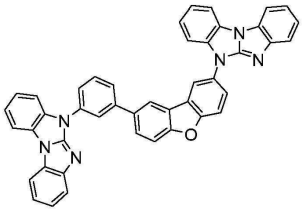
* 적용 실시예 5의 측정된 수명을 100으로 설정하고 비교 적용 실시예 3의 수명은 적용 실시예 5의 수명과 관련하여 명시하였다.

[0700]

[0701] 적용 실시예 6

[0702] 하기를 제외하고, OLED의 제조 및 구축을 적용 실시예 3에서와 같이 행하였다: 발광층은 30 중량%의 화합물



, 10 중량%의 화합물 $Ir(dpbic)_3$ 및 60 중량%의 화합물  (A-3)으로 이루어졌고, 두께는 40 nm이었다. 정공 차단층은 물질 A-3으로 이루어졌다.

	호스트 물질	300nits 에서의 전압 [V]	300nits 에서의 EQE [%]	CIE
적용 실시예 6	A-20	4.56	12.8	0.18 / 0.36

[0703]