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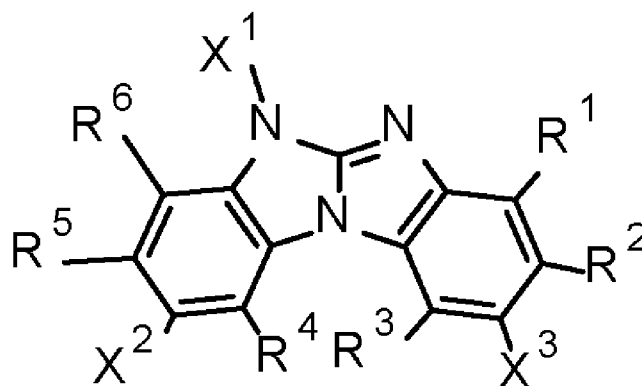
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BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
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MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
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(54) Title: 2,9-FUNCTIONALIZED BENZIMIDAZOLO[1,2-A]BENZIMIDAZOLES AS HOSTS FOR ORGANIC LIGHT EMITTING DIODES (OLEDs)



(I)

(57) Abstract: The present invention relates to compounds of formula (I), a process for their production and their use in electronic devices, especially electroluminescent devices. When used as charge transport material and/or host material for phosphorescent emitters in electroluminescent devices, the compounds of formula (I) may provide improved efficiency and reduced driving voltage of electroluminescent devices.

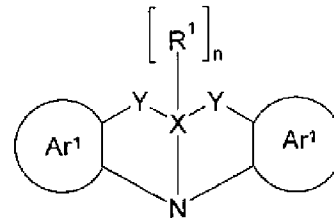
2,9-Functionalized Benzimidazolo[1,2-a]benzimidazoles as Hosts for Organic Light Emitting Diodes (OLEDs)

Description

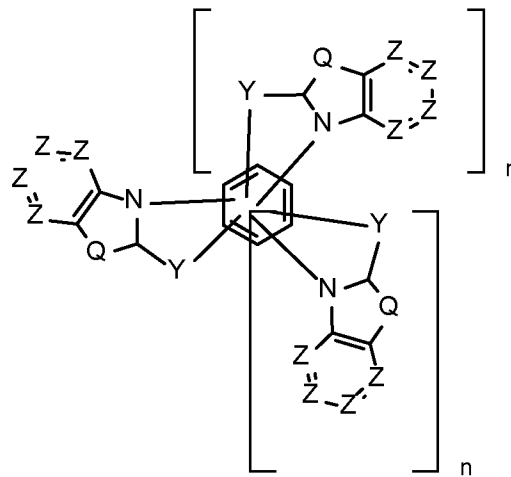
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The present invention relates to compounds of formula I, a process for their production and their use in electronic devices, especially electroluminescent devices. When used as hole transport material in electroluminescent devices, the compounds of formula I may provide improved efficiency, stability, manufacturability, or spectral characteristics of electrolumi-

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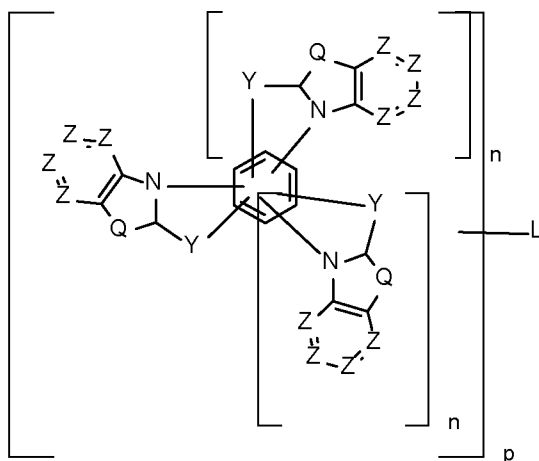
DE102012000064 describes compounds of formula and their use in organic light emitting devices (OLEDs). Among others X can be C. If X is C, n is 1. WO2012139692 relates to electronic devices which comprise an anode, a cathode and at least one organic layer, where the organic layer comprises one or more substituted ben-



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zene compounds of formula

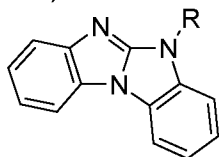
(I), or



(II). Y can be S and n can be 0 or 1, Z is

CR¹ or N. R¹ can be an aromatic or hetero aromatic ring system.

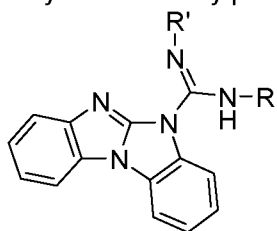
Khan, Misbahul Ain; Ribeiro, Vera Lucia Teixeira, Pakistan Journal of Scientific and Industrial Research 43 (2000) 168-170 describes the synthesis of benzimidazo[1,2-



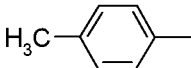
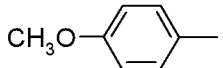
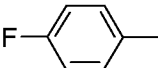
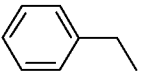
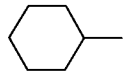
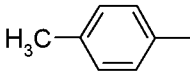
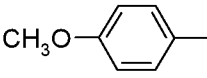
a]benzimidazoles (R = H, Me, Et) by trialkyl phosphite-induced deoxygenation and thermolysis of 1-(o-nitrophenyl)- and 1-(o-azidophenyl)benzimidazoles.

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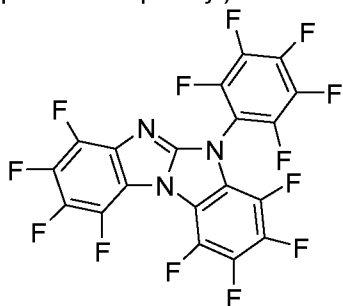
Pedro Molina et al. Tetrahedron (1994) 10029-10036 reports that aza Wittig-type reaction of bis(iminophosphoranes), derived from bis(2-aminophenyl)amine with two equivalents of isocyanate directly provided benzimidazo[1,2,a]benzimidazole derivatives.



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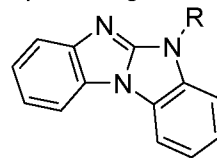
(R = R' = , , , , ; R =  and R' = , R = iso-propyl and R' = ethyl)

Kolesnikova, I. V.; Zhurnal Organicheskoi Khimii 25 (1989) 1689-95 describes the synthesis of 5H-benzimidazo[1,2-a]benzimidazole 1,2,3,4,7,8,9,10-octafluoro-5-(2,3,4,5,6-pentafluorophenyl).



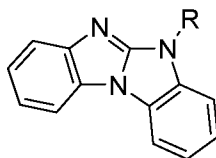
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Achour, Reddouane; Zniber, Rachid, Bulletin des Societes Chimiques Belges 96 (1987)



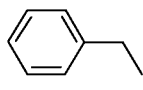
787-92 describes the synthesis of benzimidazobenzimidazoles (-CH(CH₃)₂) which were prepared from benzimidazolinone derivatives.

Hubert, Andre J.; Reimlinger, Hans, Chemische Berichte 103 (1970) 2828-35 describes the

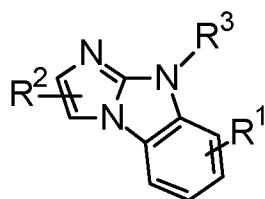


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synthesis of benzimidazobenzimidazoles

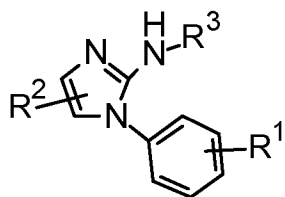
(R = H, CH₃, ).

X. Wang et al. *Org. Lett.* **2012**, 14, 452-455 discloses a highly efficient copper-catalyzed



synthesis for compounds of formula

, wherein compounds of for-

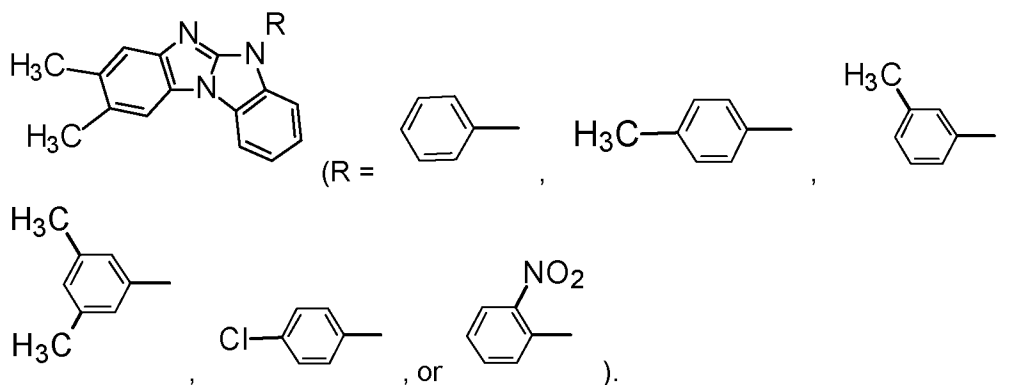


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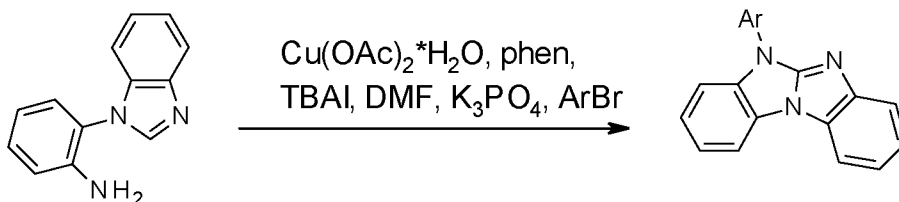
are reacted in the presence of copper acetate

(Cu(OAc)₂)/PPh₃/1,10-phenanthroline/sodium acetate and oxygen in m-xylene (1 atm) at

- 5 elevated temperature [published on web: December 29, 2011]. Among others the following compounds can be prepared by the described synthesis method:

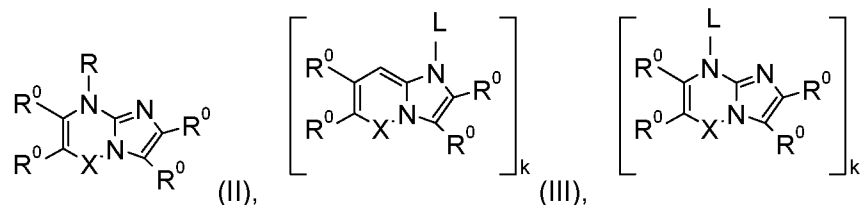
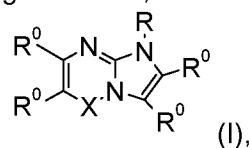


10 In *Eur. J. Org. Chem.* **2014**, 5986–5997 a new synthesis of benzimidazo[1,2-a]benzimidazole is described.

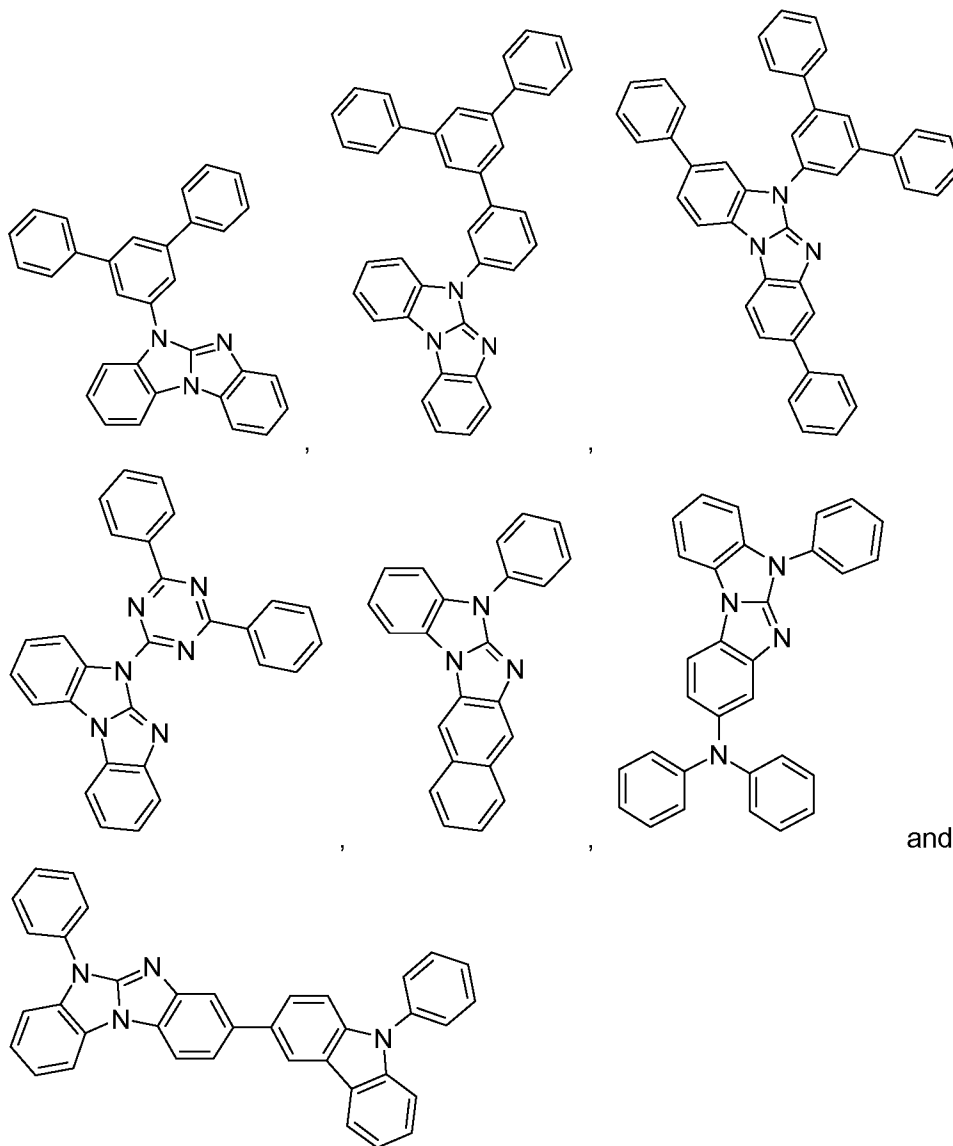


WO2011/160757 relates to an electronic device comprising an anode, cathode and at least

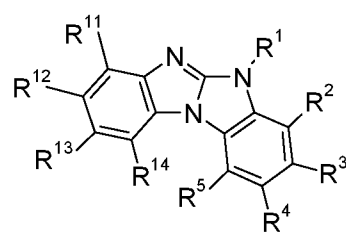
one organic layer which contains a compound of formulae



- 15 be a single bond and L may be a divalent group. The following 4H-imidazo[1,2-a]imidazole compounds are explicitly disclosed:

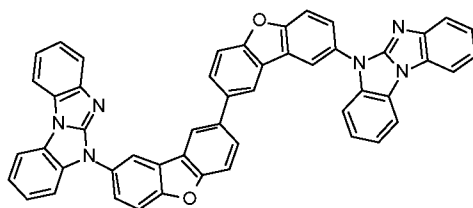


and



WO2012/130709 relates to 4H-Imidazo[1,2-a]imidazoles,

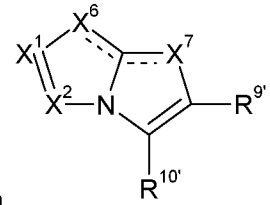
, such



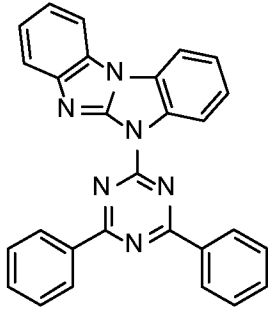
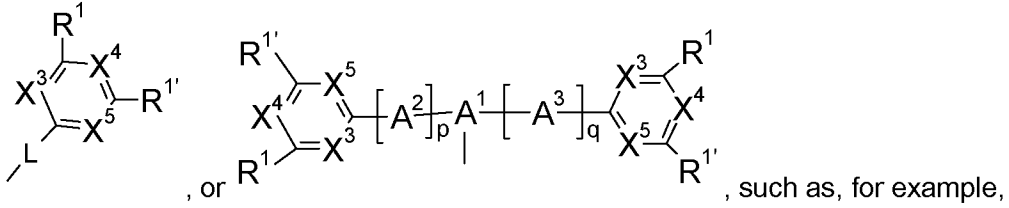
5 as , for example,

(A-1), a process for their produc-

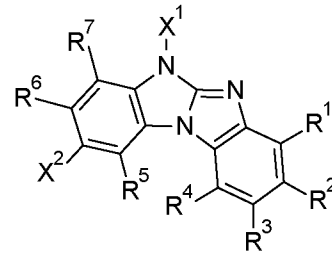
tion and their use in electronic devices, especially electroluminescent devices.



WO2013/068376 describes 4H-imidazo[1,2-a]imidazoles of formula wherein X⁶ is -N= and X⁷ is -NR⁶-, or X⁷ is =N- and X⁶ is -NR⁶-, R⁶ is a group of formula



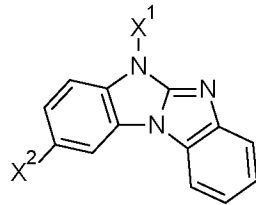
5 ; a process for their production and their use in electronic devices, especially electroluminescent devices.



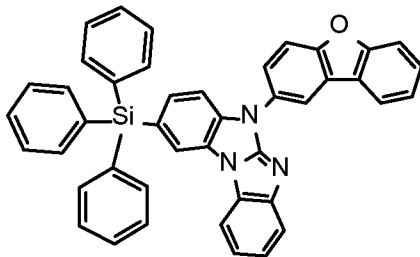
WO2014/009317 relates to compounds of formula

(I), espe-

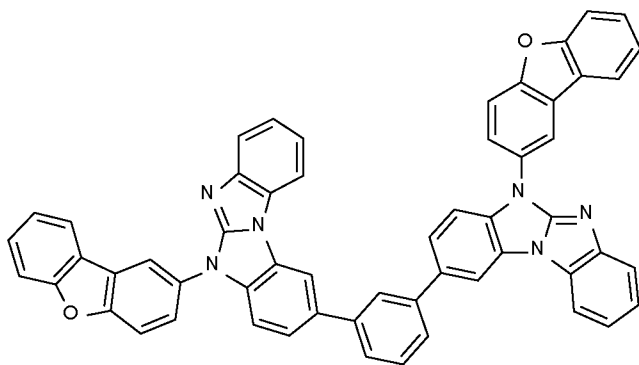
cially compounds of formula



(Ia), such as, for example,



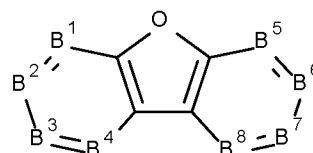
(B-1) and



(A-42), a process for their produc-

tion and their use in electronic devices, especially electroluminescent devices. The 2,5-disubstituted benzimidazo[1,2-a]benzimidazole derivatives are suitable hole transporting materials, or host materials for phosphorescent emitters.

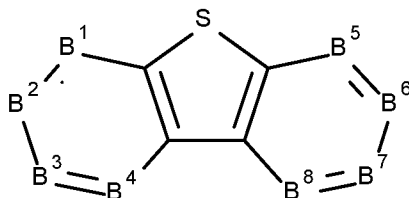
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WO2014/044722 relates to compounds of formula (I), which are characterized in that they substituted by benzimidazo[1,2-a]benzimidazo-5-yl and/or benzimidazo[1,2-a]benzimidazo-2,5-ylene groups and in that at least one of the substituents B¹, B², B³, B⁴, B⁵, B⁶, B⁷ and B⁸ represents N, a process for their production and their use in electronic devices, especially electroluminescent devices.

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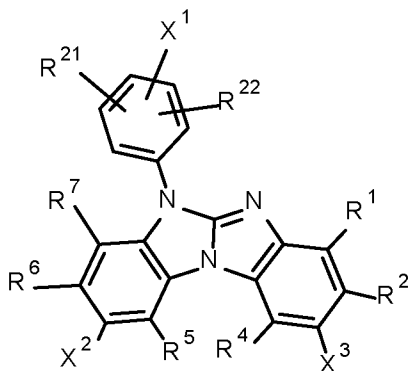
European patent application no. 13191100.0 relates to compounds of formula



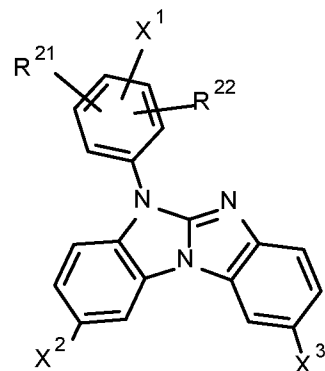
(I), which are characterized in that they are substituted by benzimidazo[1,2-a]benzimidazo-5-yl and/or benzimidazo[1,2-a]benzimidazo-2,5-ylene groups and in that at least one of the substituents B¹, B², B³, B⁴, B⁵, B⁶, B⁷ and B⁸ represents N; a process for their production and their use in electronic devices, especially electroluminescent devices.

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European patent application no. 14162667.1 relates to compounds of the formula

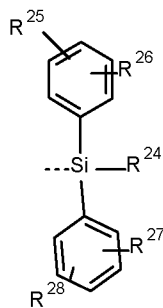


(I), especially



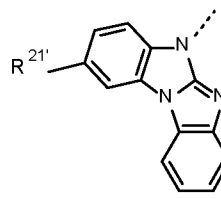
(Ia),

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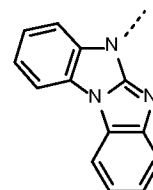


wherein X¹ is H, a group of formula

, or

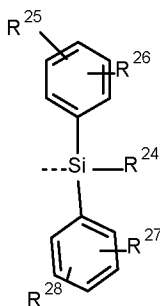


;

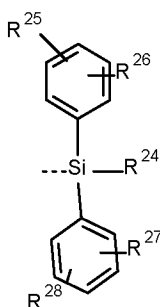


, or

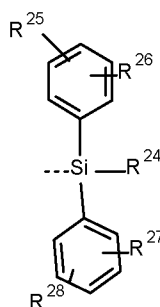
X² and X³ are independently of each other H, or a group of formula



; wherein at least one of X¹, X² and X³ is a group of formula

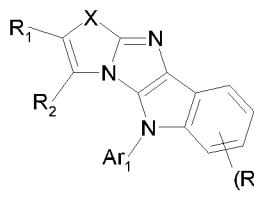


, or comprises a group of formula



- 5 Benzimidazo[1,2-a]benzimidazo-5-yl and benzimidazo[1,2-a]benzimidazo-2-ylsubstituted benzimidazolo[2,1-b][1,3]benzothiazole derivatives are described in PCT/EP2014/066174. Azabenzimidazo[2,1-a]benzimidazoles for electronic applications are described in European patent application no. 14183598.3.

- 10 KR 10-2015-0034029 discloses compounds of the formula



(R₃)_n (formula I), wherein

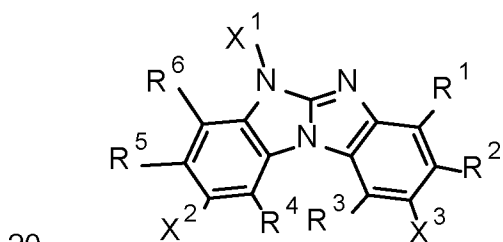
X is according to all examples O or S, and the position of R₃ – if present at all – is not defined. The compound of formula I is used in organic light emitting devices.

- 15 Notwithstanding these developments, there remains a need for organic light emitting devices comprising new hole transport materials to provide improved efficiency, stability, manufacturability, and/or spectral characteristics of electroluminescent devices.

Accordingly, it is an object of the present invention, with respect to the aforementioned prior art, to provide further materials suitable for use in OLEDs and further applications in organic electronics. More particularly, it should be possible to provide hole transport materials, electron/exciton blocker materials and matrix materials for use in OLEDs. The materials should be suitable especially for OLEDs which comprise at least one phosphorescence emitter, especially at least one green emitter or at least one blue emitter. Furthermore, the materials should be suitable for providing OLEDs which ensure good efficiencies, good operative lifetimes and a high stability to thermal stress, and a low use and operating voltage of the OLEDs.

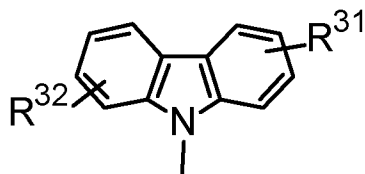
Certain 2,5,9-functionalized benzimidazolo[1,2-a]benzimidazoles derivatives are found to be suitable for use in organo-electroluminescent devices. In particular, certain 2,5,9-functionalized benzimidazolo[1,2-a]benzimidazole derivatives are suitable hole transporting, electron blocking, or host materials for phosphorescent emitters with good efficiency and durability. The good hole transporting and/or hole injection properties of this materials can lead to an reduced driving voltage.

Said object has been solved by compounds of the formula

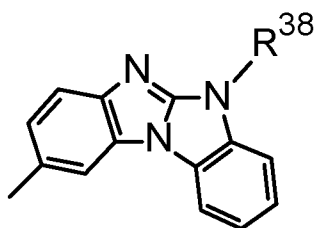
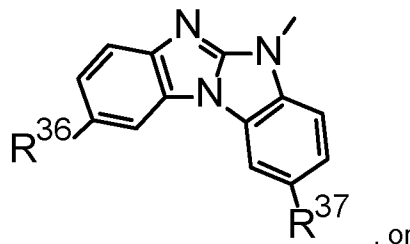
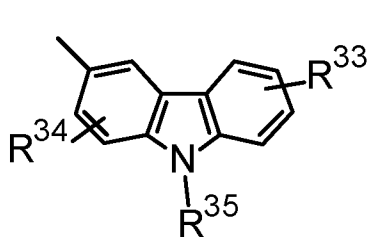


(I), wherein

- R¹, R², R³, R⁴, R⁵ and R⁶ are independently of each other H, a C₁-C₂₅alkyl group, which can optionally be substituted by E and or interrupted by D; a C₆-C₂₄aryl group, which can optionally be substituted by G, or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G;
- X¹ is a group of formula $-(A^1)_o-(A^2)_p-(A^3)_q-(A^4)_r-R^{16}$,
 o is 0, or 1, p is 0, or 1, q is 0, or 1, r is 0, or 1,
 A¹, A², A³ and A⁴ are independently of each other a C₆-C₂₄arylen group, which can optionally be substituted by G, or a C₂-C₃₀heteroarylen group, which can optionally be substituted by G; wherein
- X² and X³ are independently of each other a group of formula $-(A^5)_v-(A^6)_s-(A^7)_t-(A^8)_u-R^{15}$, or $-NR^{10}R^{11}$,
 v is 0, or 1, s is 0, or 1, t is 0, or 1, u is 0, or 1,
 A⁵, A⁶, A⁷ and A⁸ are independently of each other a C₆-C₂₄arylen group, which can optionally be substituted by G, or a C₂-C₃₀heteroarylen group, which can optionally be substituted by G; wherein
- R¹⁰ and R¹¹ are independently of each other a C₆-C₂₄aryl group, which can optionally be substituted by G; or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G; or R¹⁰ and R¹¹ together with the nitrogen atom to which they are bonded form a heteroaromatic ring, or ring system;

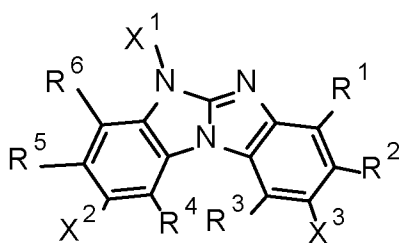


R¹⁵ is a group of formula



- R³¹, R³², R³³, R³⁴, R³⁶ and R³⁷ are independently of each other H, or a C₁-C₂₅alkyl group;
- 5 R³⁵ and R³⁸ are independently of each a C₆-C₁₀aryl group, which can optionally be substituted by one, or more C₁-C₂₅alkyl groups;
- R¹⁶ is a C₆-C₂₄aryl group, which can optionally be substituted by G; or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G;
- D is -CO-, -COO-, -S-, -SO-, -SO₂-, -O-, -NR⁶⁵-, -SiR⁷⁰R⁷¹-, -POR⁷²-, -CR⁶³=CR⁶⁴-, or -C≡C,
- 10 E is -OR⁶⁹, -SR⁶⁹, -NR⁶⁵R⁶⁶, -COR⁶⁸, -COOR⁶⁷, -CONR⁶⁵R⁶⁶, -CN, or halogen,
- G is E, or a C₁-C₁₈alkyl group, a C₆-C₂₄aryl group, a C₆-C₂₄aryl group, which is substituted by F, C₁-C₁₈alkyl, or C₁-C₁₈alkyl which is interrupted by O; a C₂-C₃₀heteroaryl group, or a C₂-C₃₀heteroaryl group, which is substituted by F, C₁-C₁₈alkyl, or C₁-C₁₈alkyl which is interrupted by O;
- 15 R⁶³ and R⁶⁴ are independently of each other H, C₆-C₁₈aryl; C₆-C₁₈aryl which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; C₁-C₁₈alkyl; or C₁-C₁₈alkyl which is interrupted by -O-;
- R⁶⁵ and R⁶⁶ are independently of each other a C₆-C₁₈aryl group; a C₆-C₁₈aryl which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-; or
- 20 R⁶⁵ and R⁶⁶ together form a five or six membered ring,
- R⁶⁷ is a C₆-C₁₈aryl group; a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-;
- R⁶⁸ is H; a C₆-C₁₈aryl group; a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-;
- 25 R⁶⁹ is a C₆-C₁₈aryl; a C₆-C₁₈aryl, which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-;
- R⁷⁰ and R⁷¹ are independently of each other a C₁-C₁₈alkyl group, a C₆-C₁₈aryl group, or a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl, and
- R⁷² is a C₁-C₁₈alkyl group, a C₆-C₁₈aryl group, or a C₆-C₁₈aryl group, which is substituted by
- 30 C₁-C₁₈alkyl.

In a further embodiment, said object has been solved by compounds of the formula



(I), wherein

R¹, R², R³, R⁴, R⁵ and R⁶ are independently of each other H, a C₁-C₂₅alkyl group, which can optionally be substituted by E and or interrupted by D; a C₆-C₂₄aryl group, which can optionally be substituted by G, or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G;

X¹ is a group of formula $-(A^1)_o-(A^2)_p-(A^3)_q-(A^4)_r-R^{16}$,

o is 0, or 1, p is 0, or 1, q is 0, or 1, r is 0, or 1,

A¹, A², A³ and A⁴ are independently of each other a C₆-C₂₄arylen group, which can optionally be substituted by G, or a C₂-C₃₀heteroarylen group, which can optionally be substituted by G; wherein

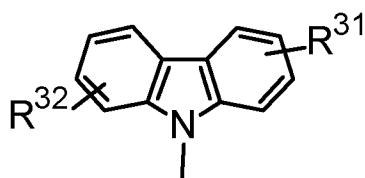
X² and X³ are independently of each other a group of formula $-(A^5)_v-(A^6)_s-(A^7)_t-(A^8)_u-R^{15}$, or $-NR^{10}R^{11}$,

v is 0, or 1, s is 0, or 1, t is 0, or 1, u is 0, or 1,

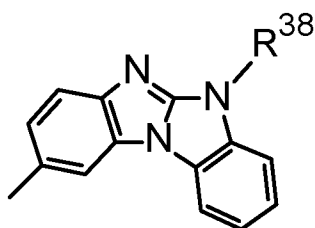
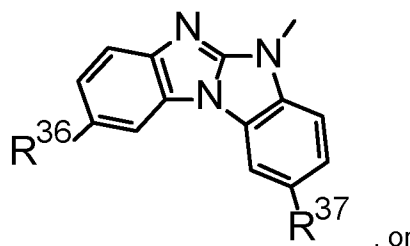
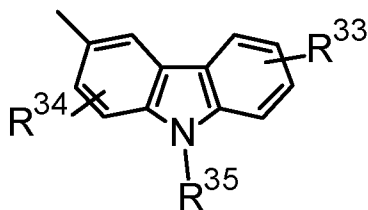
A⁵, A⁶, A⁷ and A⁸ are independently of each other a C₆-C₂₄arylen group, which can optionally be substituted by G, or a C₂-C₃₀heteroarylen group, which can optionally be substituted by G; wherein

R¹⁰ and R¹¹ are independently of each other a C₆-C₂₄aryl group, which can optionally be substituted by G; or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G; or

R¹⁰ and R¹¹ together with the nitrogen atom to which they are bonded form a heteroaromatic ring, or ring system;



R¹⁵ is a group of formula



R³¹, R³², R³³, R³⁴, R³⁶ and R³⁷ are independently of each other H, or a C₁-C₂₅alkyl group;

R³⁵ and R³⁸ are independently of each a C₆-C₁₀aryl group, which can optionally be substituted by one, or more C₁-C₂₅alkyl groups;

R¹⁶ is a C₆-C₂₄aryl group, which can optionally be substituted by G; or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G;

5 D is -CO-, -COO-, -S-, -SO-, -SO₂-, -O-, -NR⁶⁵-, -SiR⁷⁰R⁷¹-, -POR⁷²-, -CR⁶³=CR⁶⁴-, or -C≡C, E is -OR⁶⁹-, -SR⁶⁹-, -NR⁶⁵R⁶⁶-, -COR⁶⁸-, -COOR⁶⁷-, -CONR⁶⁵R⁶⁶-, -CN, or halogen,

G is E, or a C₁-C₁₈alkyl group, a C₆-C₂₄aryl group, a C₆-C₂₄aryl group, which is substituted by F, C₁-C₁₈alkyl, or C₁-C₁₈alkyl which is interrupted by O; a C₂-C₃₀heteroaryl group, or a C₂-C₃₀heteroaryl group, which is substituted by F, C₁-C₁₈alkyl, or C₁-C₁₈alkyl which is interrupted by O;

R⁶³ and R⁶⁴ are independently of each other H, C₆-C₁₈aryl; C₆-C₁₈aryl which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; C₁-C₁₈alkyl; or C₁-C₁₈alkyl which is interrupted by -O-;

R⁶⁵ and R⁶⁶ are independently of each other a C₆-C₁₈aryl group; a C₆-C₁₈aryl which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-;

R⁶⁵ and R⁶⁶ together form a five or six membered ring,

R⁶⁷ is a C₆-C₁₈aryl group; a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-;

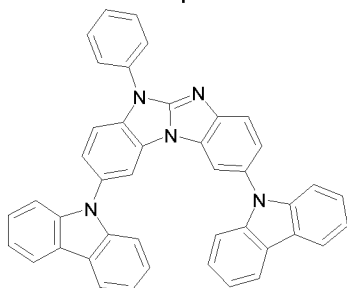
R⁶⁸ is H; a C₆-C₁₈aryl group; a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-;

R⁶⁹ is a C₆-C₁₈aryl; a C₆-C₁₈aryl, which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-;

R⁷⁰ and R⁷¹ are independently of each other a C₁-C₁₈alkyl group, a C₆-C₁₈aryl group, or a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl, and

25 R⁷² is a C₁-C₁₈alkyl group, a C₆-C₁₈aryl group, or a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl,

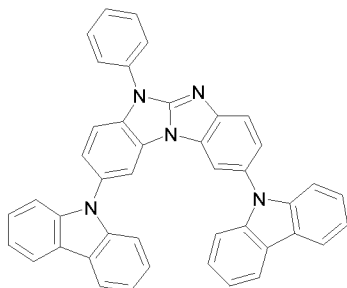
wherein a compound of formula



is excluded.

30

In a further embodiment, said object has been solved by a compound of the formula



The compounds of the present invention may be used for electrophotographic photoreceptors, photoelectric converters, organic solar cells (organic photovoltaics), switching elements, such as organic transistors, for example, organic FETs and organic TFTs, organic light emitting field effect transistors (OLEFETs), image sensors, dye lasers and electroluminescent devices, such as, for example, organic light-emitting diodes (OLEDs).

Accordingly, a further subject of the present invention is directed to an electronic device, comprising a compound according to the present invention. The electronic device is preferably an electroluminescent device.

The compounds of formula I can in principal be used in any layer of an EL device, but are preferably used as host, hole transport and/or electron/exciton blocking material. Particularly, the compounds of formula I are used as host material for green, especially blue light emitting phosphorescent emitters.

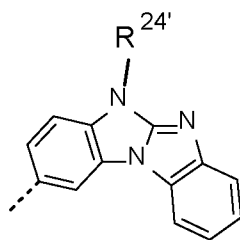
Hence, a further subject of the present invention is directed to a hole transport layer, comprising a compound of formula I according to the present invention.

A further subject of the present invention is directed to an emitting layer, comprising a compound of formula I according to the present invention. In said embodiment a compound of formula I is preferably used as host material in combination with a phosphorescent emitter.

A further subject of the present invention is directed to an electron/exciton blocking layer, comprising a compound of formula I according to the present invention.

Specific examples of the compound represented by the formula (I) are given below. The compound represented by the formula (I) is not limited to the following specific examples.

D is preferably -CO-, -COO-, -S-, -SO-, -SO₂-, -O-, -NR⁶⁵-, wherein R⁶⁵ is C₁-C₁₈alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, or sec-butyl, or C₆-C₁₄aryl, such as phenyl, tolyl, naphthyl, or biphenyl, or C₂-C₃₀heteroaryl, such as, for example, benzimid-



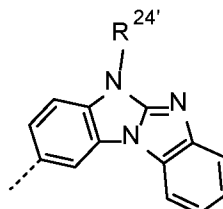
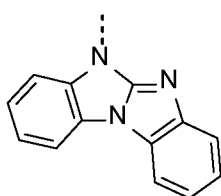
azo[1,2-a]benzimidazo-2-yl (), carbazolyl, dibenzofuranyl, which can be unsubstituted or substituted especially by C₆-C₁₀aryl, or C₆-C₁₀aryl, which is substituted by C₁-C₄alkyl; or C₂-C₁₃heteroaryl.

E is preferably -OR⁶⁹-, -SR⁶⁹-, -NR⁶⁵R⁶⁵-, -COR⁶⁸-, -COOR⁶⁷-, -CONR⁶⁵R⁶⁵-, or -CN; wherein R⁶⁵, R⁶⁷, R⁶⁸ and R⁶⁹ are independently of each other C₁-C₁₈alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, or C₆-C₁₄aryl, such as phenyl, tolyl, naphthyl, or biphenyl.

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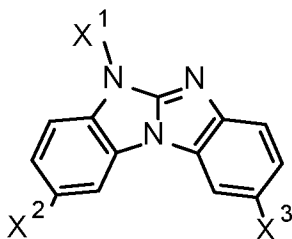
G is preferably $-OR^{69}$; $-SR^{69}$; $-NR^{65}R^{65}$; a C_1 - C_{18} alkyl group, a C_6 - C_{14} aryl group, a C_6 - C_{14} aryl group, which is substituted by F, or C_1 - C_{18} alkyl; a C_2 - C_{13} heteroaryl group, or a C_2 - C_{13} heteroaryl group, which is substituted by F, or C_1 - C_{18} alkyl; or $-Si(R^{12})(R^{13})(R^{14})$; where-
 5 in R^{65} , R^{67} , R^{68} and R^{69} are independently of each other C_1 - C_{18} alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, or C_6 - C_{14} aryl, such as phenyl, tolyl, naphthyl, or biphenyl; R^{12} , R^{13} and R^{14} are independently of each other a C_6 - C_{14} aryl group, which can optionally be substituted by C_1 - C_{18} alkyl; or a C_2 - C_{13} heteroaryl group, which can optionally be substituted by C_1 - C_{18} alkyl.

10 A C_2 - C_{13} heteroaryl group is for example, benzimidazo[1,2-a]benzimidazo-5-yl



(), benzimidazo[1,2-a]benzimidazo-2-yl (), benzimidazo[2,1-b][1,3]benzothiazolyl, carbazolyl, dibenzofuranyl, which can be unsubstituted or substituted, especially by C_6 - C_{10} aryl, or C_6 - C_{10} aryl, which is substituted by C_1 - C_4 alkyl; or C_2 - C_{13} heteroaryl. Preferably, R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are H. Accordingly, in a preferred

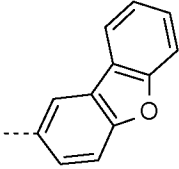
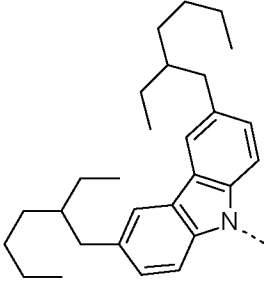
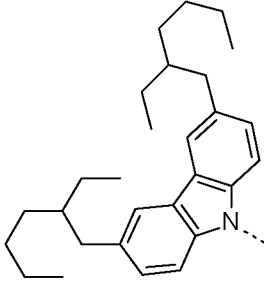
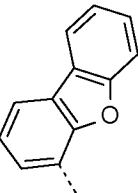
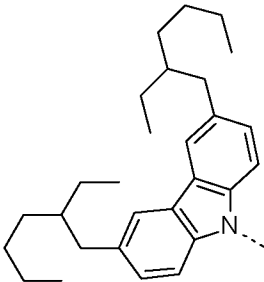
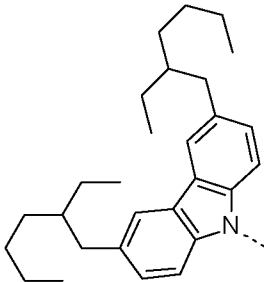
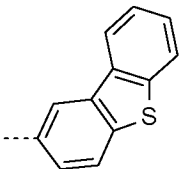
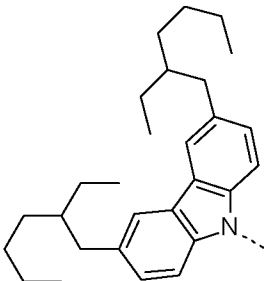
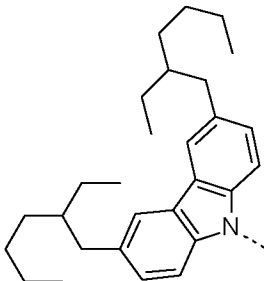
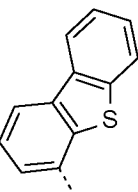
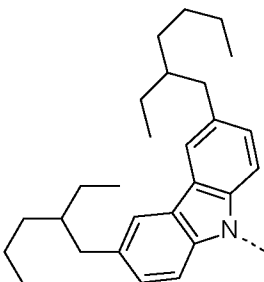
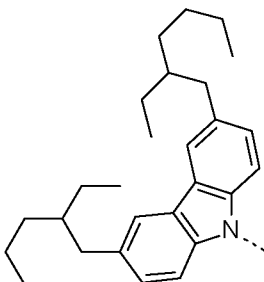
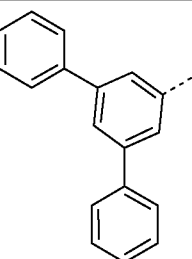
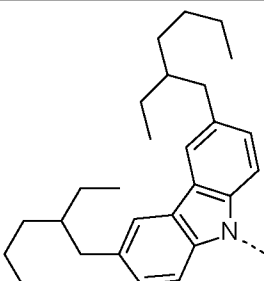
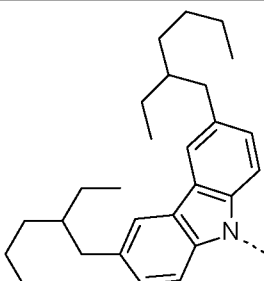
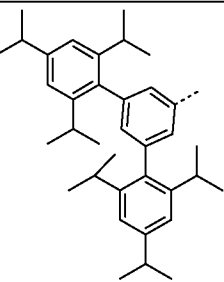
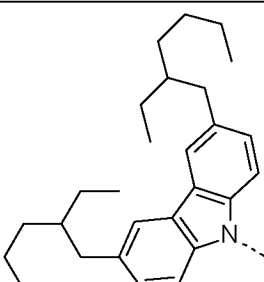
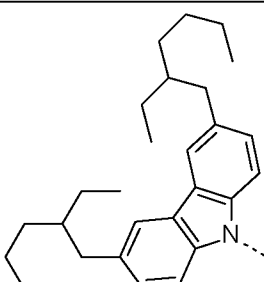
15 embodiment the present invention is directed to compounds of formula

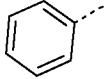
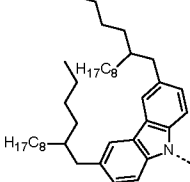
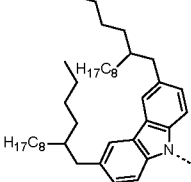
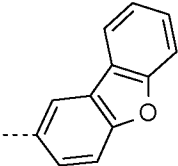
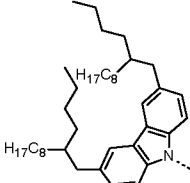
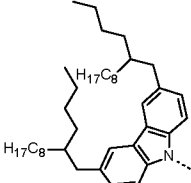
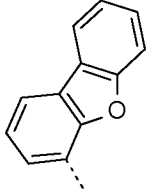
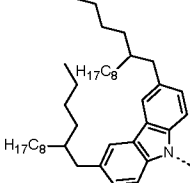
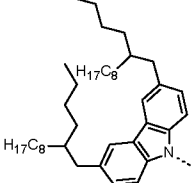
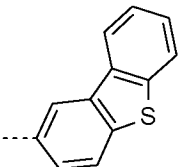
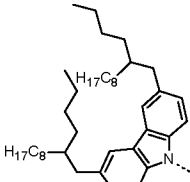
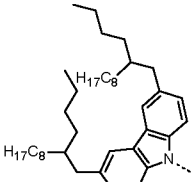
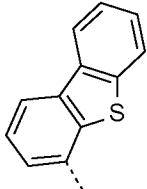
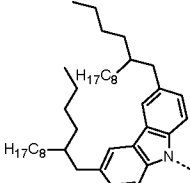
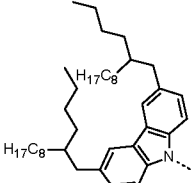
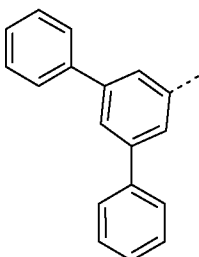
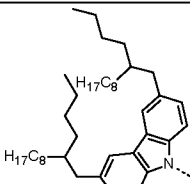
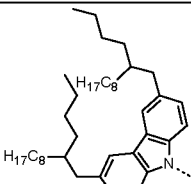
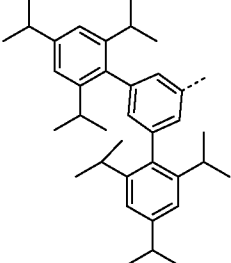
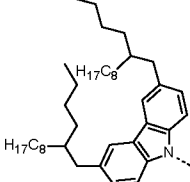
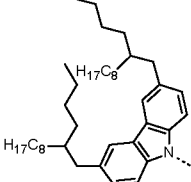
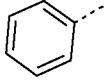
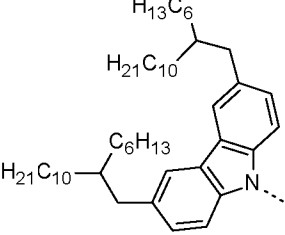
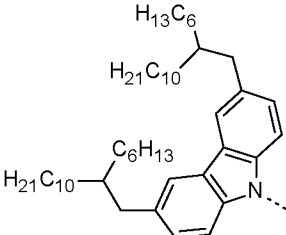


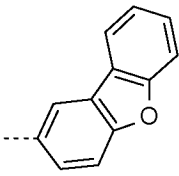
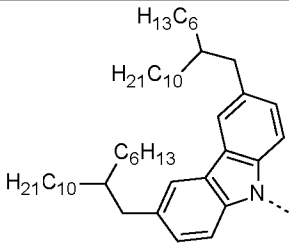
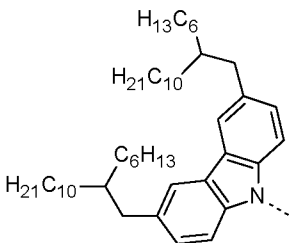
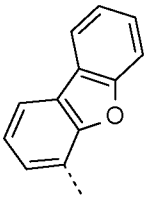
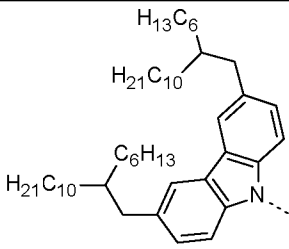
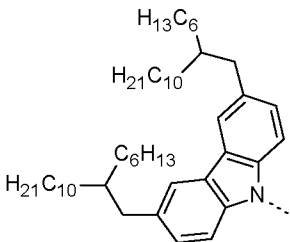
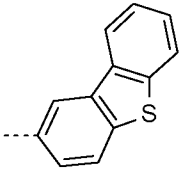
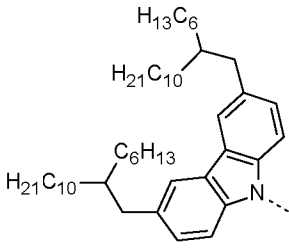
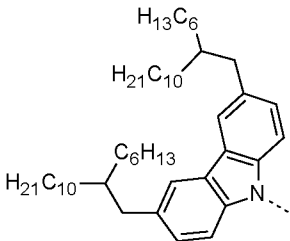
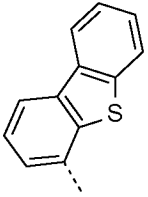
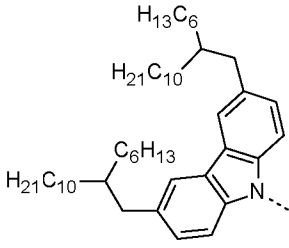
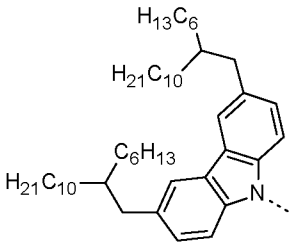
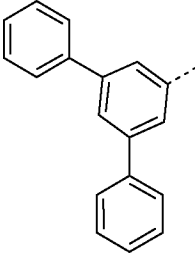
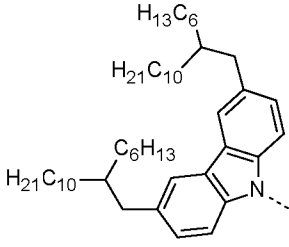
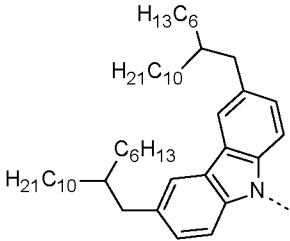
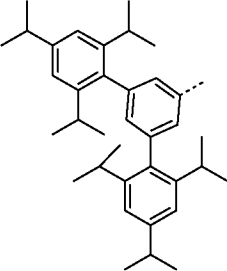
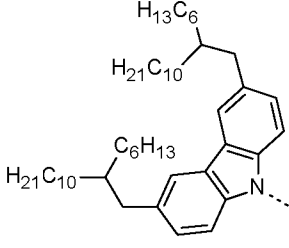
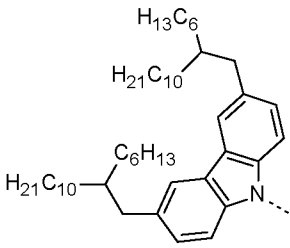
(Ia), wherein X^1 , X^2 and X^3 are defined above, or below.

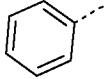
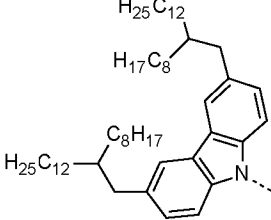
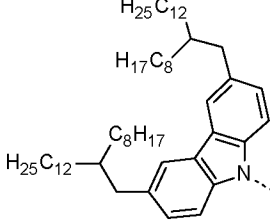
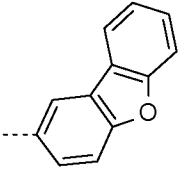
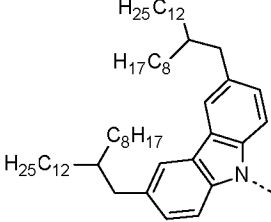
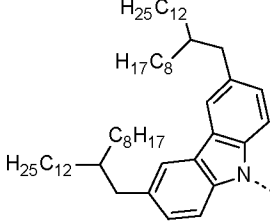
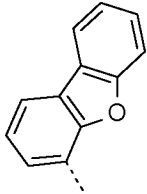
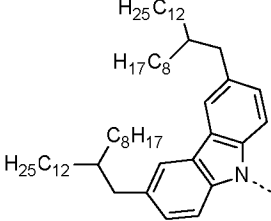
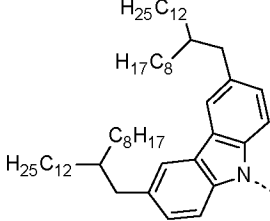
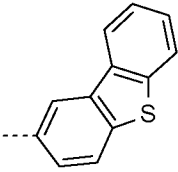
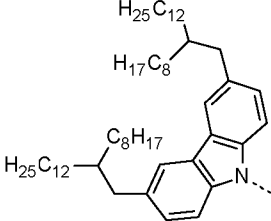
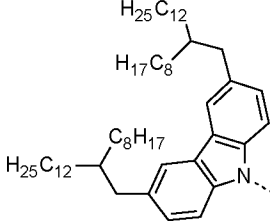
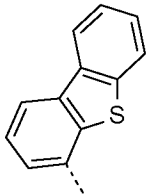
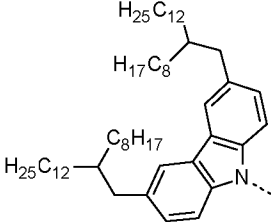
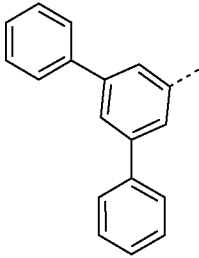
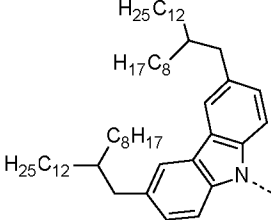
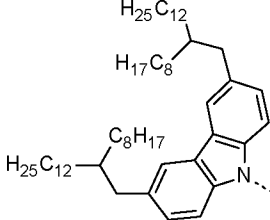
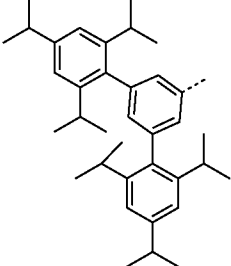
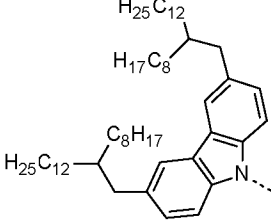
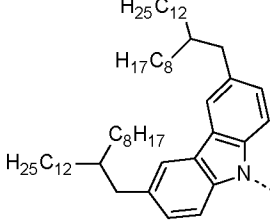
Compounds of formula (Ia), wherein at least one of X^1 , X^2 and X^3 is substituted by a C_1 - C_{25} alkyl group; are suitable materials for solution processable OLEDs. Examples of such
 20 compounds are shown in the table below.

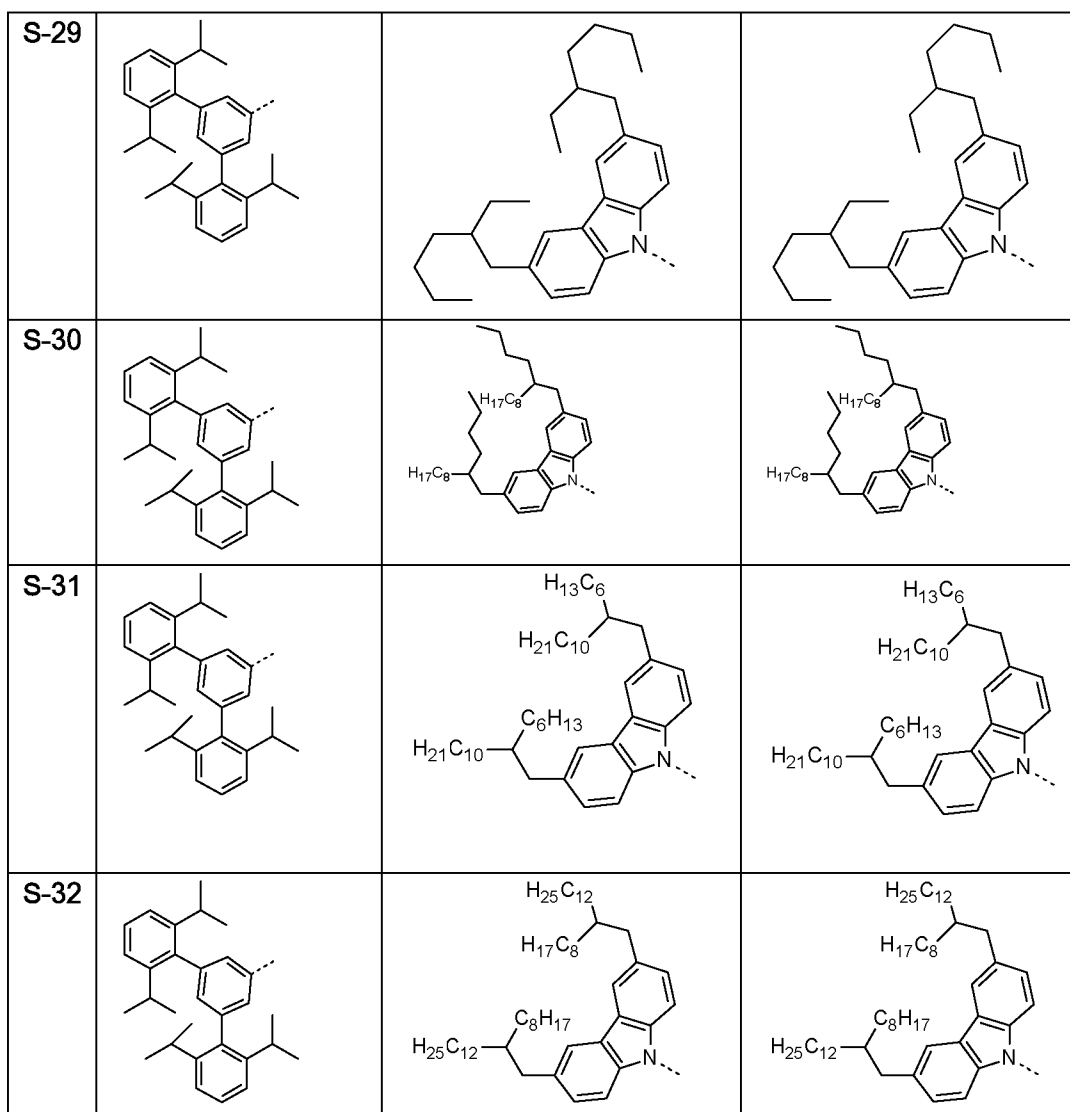
Cpd.	X^1	X^2	X^3
S-1			

<p>S-2</p>			
<p>S-3</p>			
<p>S-4</p>			
<p>S-5</p>			
<p>S-6</p>			
<p>S-7</p>			

<p>S-8</p>			
<p>S-9</p>			
<p>S-10</p>			
<p>S-11</p>			
<p>S-12</p>			
<p>S-13</p>			
<p>S-14</p>			
<p>S-15</p>			

<p>S-16</p>			
<p>S-17</p>			
<p>S-18</p>			
<p>S-19</p>			
<p>S-20</p>			
<p>S-21</p>			

<p>S-22</p> 		
<p>S-23</p> 		
<p>S-24</p> 		
<p>S-25</p> 		
<p>S-26</p> 		
<p>S-27</p> 		
<p>S-28</p> 		



----- indicates the bonding to the benzimidazolo[1,2-a]benzimidazole.
 X¹ is a group of the formula $-(A^1)_o-(A^2)_p-(A^3)_q-(A^4)_r-R^{16}$.

o is 0, or 1, p is 0, or 1, q is 0, or 1, r is 0, or 1. Preferably, q is 0 and r is 0.

5

For the group of formula $-(A^1)_o-(A^2)_p-(A^3)_q-(A^4)_r-R^{16}$ the following preferences apply.

A¹, A², A³ and A⁴ are independently of each other a C₆-C₂₄arylen group, which can optionally be substituted by G, or a C₂-C₃₀heteroarylen group, which can optionally be substituted by G.

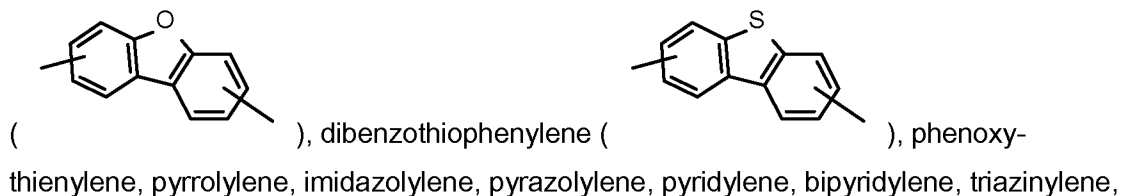
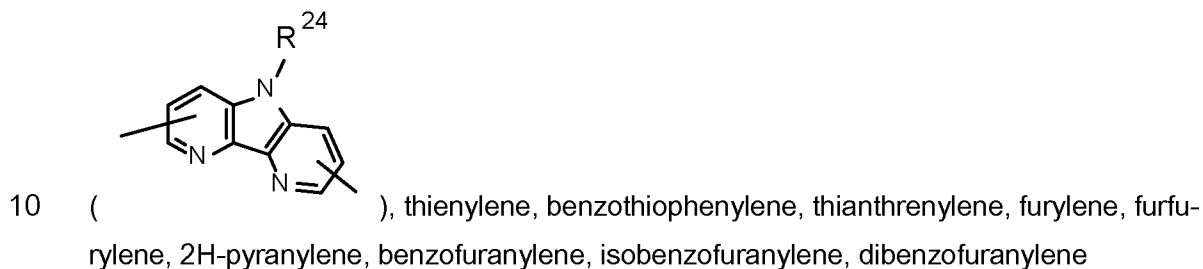
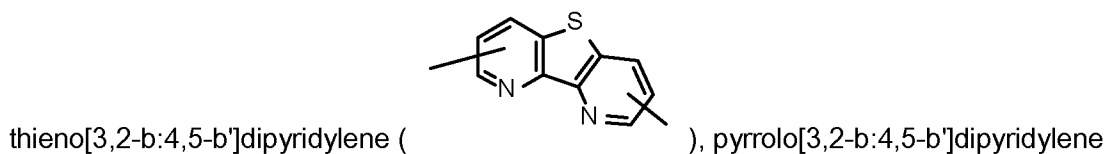
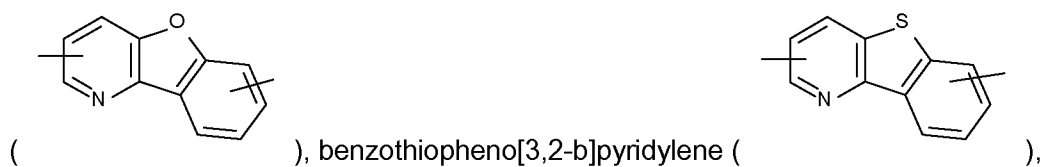
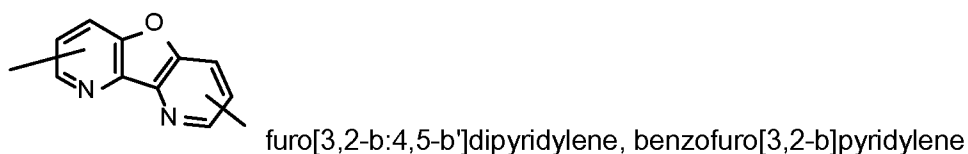
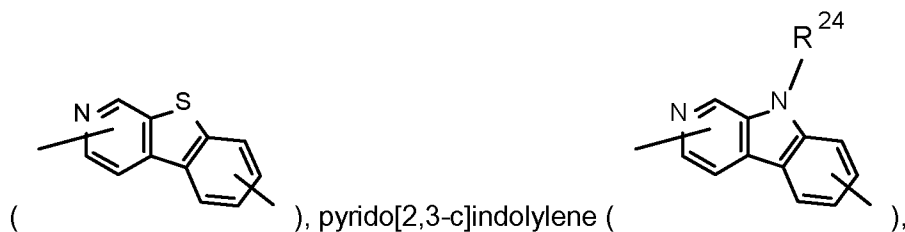
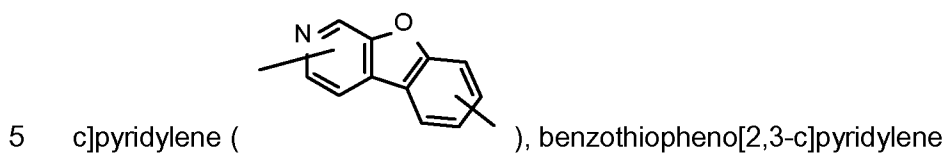
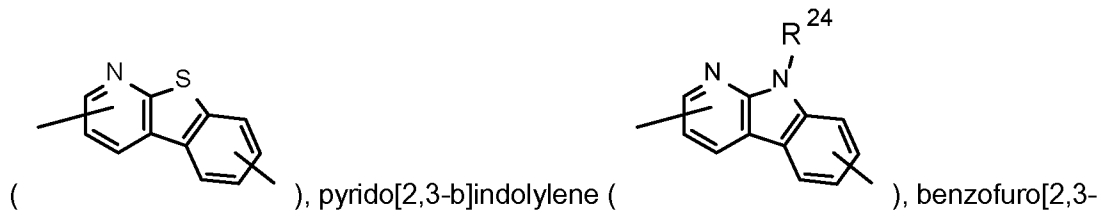
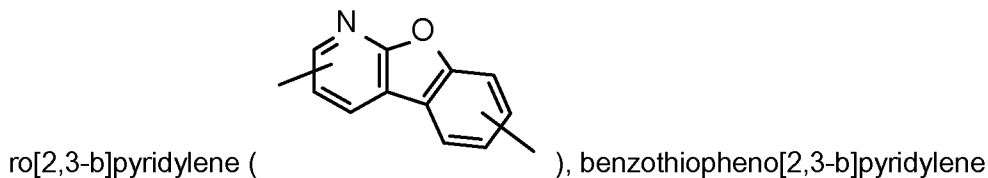
10

The C₆-C₂₄arylen groups A¹, A², A³ and A⁴ which optionally can be substituted by G, are typically phenylene, 4-methylphenylene, 4-methoxyphenylene, naphthylene, especially 1-naphthylene, or 2-naphthylene, biphenylene, terphenylene, pyrenylene, 2- or 9-fluorenylene, phenanthrylene, or anthrylene, which may be unsubstituted or substituted.

15

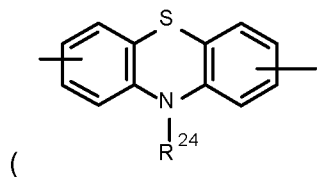
The C₂-C₃₀heteroarylen groups A¹, A², A³ and A⁴, which optionally can be substituted by G, represent a ring with five to seven ring atoms or a condensed ring system, wherein nitrogen,

oxygen or sulfur are the possible hetero atoms, and is typically a heterocyclic group with five to 30 atoms having at least six conjugated-electrons such as, for example, benzofu-

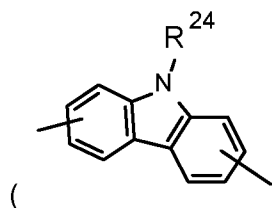


pyrimidinylene, pyrazinylene, pyridazinylene, indolizinylen, isoindolylen, indolylen, indazolylene, purinylene, quinolizinylen, chinolylen, isochinolylen, phthalazinylene, naphthyridinylene, chinoxalinylen, chinazolinylen, cinnolinylen, pteridinylene, carbolinylen, benzotriazolylene, benzoxazolylene, phenanthridinylene, acridinylene, pyrimidinylene, phenanthrolinylen, phenazinylene, isothiazolylene, phenothiazinylene

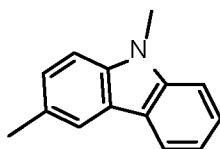
5



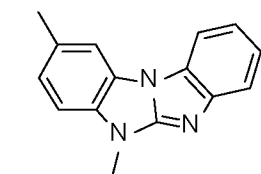
(), isoxazolylene, furazanylene, carbazolylene



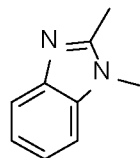
, or



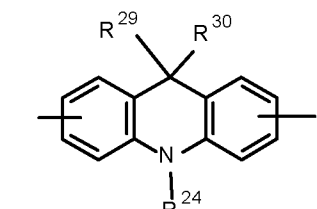
), benzimidazo[1,2-a]benzimidazo-2,5-ylene



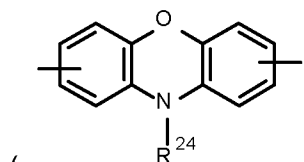
(), benzimidazo-1,2-ylene (



), 9,9-dialkylacridinylene



(; R²⁹ and R³⁰ are C₁-C₂₅alkyl), or phenoxazinylene



10 (), which can be unsubstituted or substituted. R²⁴ is a C₆-C₂₄aryl group, or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G, wherein G is as defined in above.

15 Preferred C₆-C₂₄arylen groups are 1,3-phenylene, 1,4-phenylene, 3,3'-biphenylene, 3,3'-m-terphenylene, 2- or 9-fluorenylene, phenanthrylene, which may be unsubstituted or substituted, especially by C₆-C₁₀aryl, C₆-C₁₀aryl which is substituted by C₁-C₄alkyl; or C₂-C₁₄heteroaryl.

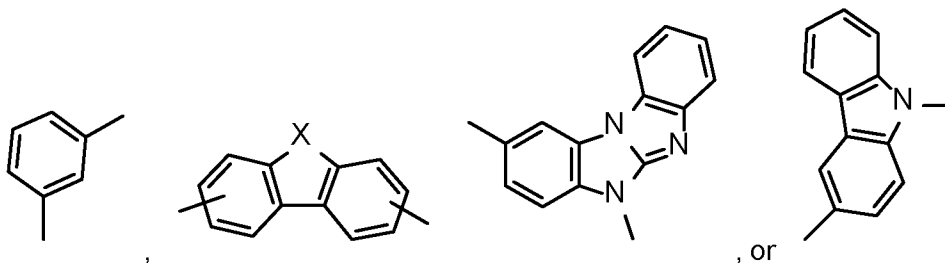
20 More preferred C₂-C₃₀heteroarylen groups are thienylene, benzothiophenylene, thianthrenylene, furylene, furfurylene, 2H-pyranylene, benzofuranylene, isobenzofuranylene, dibenzofuranylene, dibenzothiophenylene, phenoxythienylene, pyrrolylene, phenothiazin-10-ylene, imidazolylene, indolizinylen, isoindolylen, indolylen, indazolylene, carbazolylene, benzimidazo[1,2-a]benzimidazo-2,5-ylene, phenoxazin-10-ylene, or 9,9-dialkylacridin-10-ylene, which can be unsubstituted or substituted.

The C₆-C₂₄arylen and C₂-C₃₀heteroarylen groups may be substituted by G.

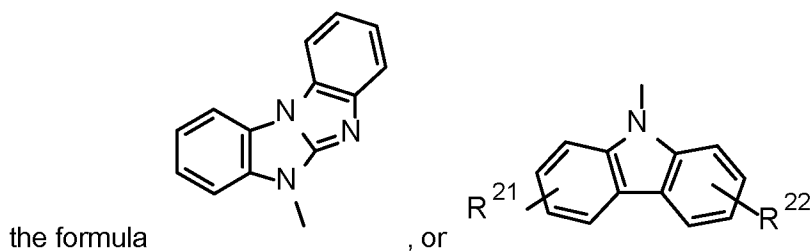
G is preferably C₁-C₁₈alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, -CF₃, a C₆-C₁₄aryl group, a C₆-C₁₄aryl group, which is substituted by F, or C₁-C₁₈alkyl; a C₂-C₁₃heteroaryl group, or a C₂-C₁₃heteroaryl group, which is substituted by F, or C₁-C₁₈alkyl.

Benzimidazo[1,2-a]benzimidazo-5-yl, benzimidazo[1,2-a]benzimidazo-2-yl, carbazolyl and dibenzofuranyl are examples of a C₂-C₁₃heteroarylgroup. Phenyl, 1-naphthyl and 2-naphthyl are examples of a C₆-C₁₄aryl group.

Preferably, A¹, A², A³ and A⁴ are independently of each other a group of the formula



X is O, S, or NR²⁵, and R²⁵ a phenyl group, or a C₁-C₁₈alkyl group, with the proviso that o is 1, if R¹⁶ is a group of



the formula

R¹⁶ may be a C₆-C₂₄aryl group, which can optionally be substituted by G, or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G.

The C₆-C₂₄aryl group R¹⁶, which optionally can be substituted by G, is typically phenyl, 4-methylphenyl, 4-methoxyphenyl, naphthyl, especially 1-naphthyl, or 2-naphthyl, biphenyl, terphenyl, pyrenyl, 2- or 9-fluorenyl, phenanthryl, or anthryl, or triphenylenyl (especially triphenylen-2-yl), which may be unsubstituted or substituted.

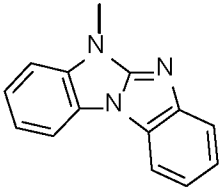
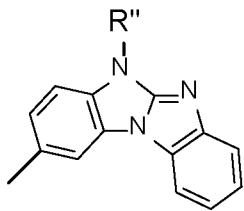
The C₂-C₃₀heteroaryl group R¹⁶, which optionally can be substituted by G, represent a ring with five to seven ring atoms or a condensed ring system, wherein nitrogen, oxygen or sulfur are the possible hetero atoms, and is typically a heterocyclic group with five to 30 atoms having at least six conjugated π -electrons such as 9H-pyrido[2,3-b]indolyl, benzofuro[2,3-b]pyridyl, benzothiopheno[2,3-b]pyridyl, 9H-pyrido[2,3-c]indolyl, benzofuro[2,3-c]pyridyl, benzothiopheno[2,3-c]pyridyl, furo[3,2-b:4,5-b']dipyridyl, pyrrolo[3,2-b:4,5-b']dipyridyl, thieno[3,2-b:4,5-b']dipyridyl, thienyl, benzothiophenyl, dibenzothiophenyl, thianthrenyl, furyl, furfuryl, 2H-pyranyl, benzofuranyl, isobenzofuranyl, dibenzofuranyl, phenoxythienyl, pyrrol-yl, imidazolyl, pyrazolyl, pyridyl, bipyridyl, triazinyl, pyrimidinyl, pyrazinyl, pyridazinyl, in-

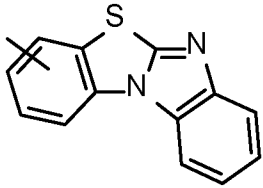
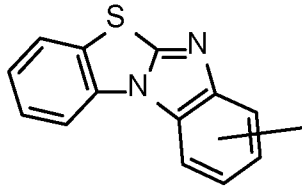
doliziny, isoindoly, indoly, indazolyl, puriny, quinoliziny, chinoly, isochinoly, phthalaziny, naphthyridiny, chinoxaliny, chinazoliny, cinnoliny, pteridiny, carboliny, benzotriazolyl, benzoxazolyl, phenanthridiny, acridiny, pyrimidiny, phenanthroliny, phenaziny, isothiazolyl, phenothiaziny, isoxazolyl, furazany, benzimidazo[1,2-a]benzimidazo-5-yl, benzimidazo[1,2-a]benzimidazo-2-yl, benzimidazolo[2,1-b][1,3]benzothiazolyl, carbazolyl, 9-phenylcarbazolyl, azabenzimidazo[1,2-a]benzimidazolyl, or phenoxaziny, which can be unsubstituted or substituted.

The C₆-C₂₄aryl and C₂-C₃₀heteroaryl groups may be substituted by G.

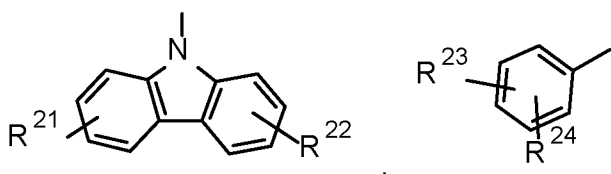
G is preferably C₁-C₁₈alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl; -CF₃, a C₆-C₁₄aryl group, a C₆-C₁₄aryl group, which is substituted by F, or C₁-C₁₈alkyl; a C₂-C₁₃heteroaryl group, or a C₂-C₁₃heteroaryl group, which is substituted by F, or C₁-C₁₈alkyl.

Preferred C₂-C₃₀heteroaryl groups are pyridyl, triazinyl, pyrimidinyl, especially 9H-pyrido[2,3-b]indolyl, benzofuro[2,3-b]pyridyl, benzothiopheno[2,3-b]pyridyl, 9H-pyrido[2,3-c]indolyl, benzofuro[2,3-c]pyridyl, benzothiopheno[2,3-c]pyridyl, furo[3,2-b:4,5-b']dipyridyl, pyrrolo[3,2-b:4,5-b']dipyridyl, thieno[3,2-b:4,5-b']dipyridyl, benzimidazo[1,2-a]benzimidazo-5-yl

() , benzimidazo[1,2-a]benzimidazo-2-yl ( ; R'' is C₆-C₁₀aryl, or C₆-C₁₀aryl, which is substituted by C₁-C₄alkyl; or C₂-C₁₄heteroaryl), benzimid-

azolo[2,1-b][1,3]benzothiazolyl (, or ), carbazolyl, dibenzofuranyl, or dibenzothiophenyl, which can be unsubstituted or substituted especially by C₆-C₁₀aryl, or C₆-C₁₀aryl, which is substituted by C₁-C₄alkyl; or C₂-C₁₄heteroaryl.

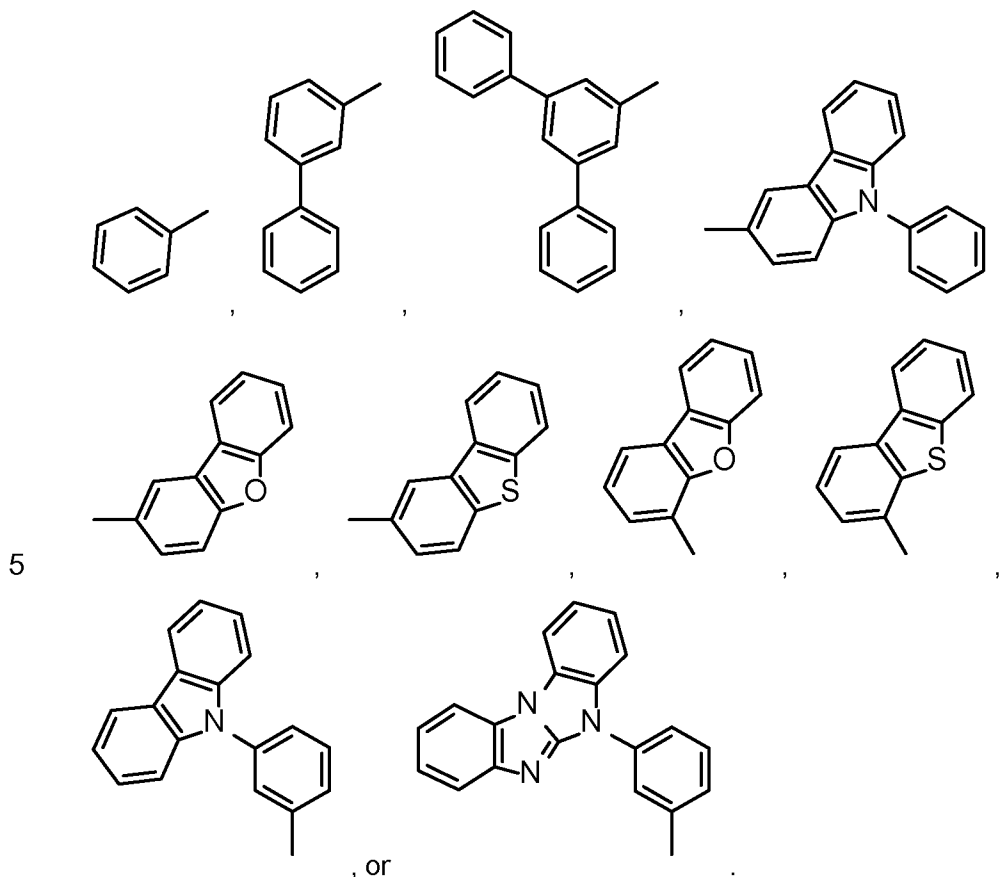
Most preferred, R¹⁶ is a group of the formula



R²¹ and R²² are independently of each other H, a phenyl group, or a C₁-C₁₈alkyl group;

R²³ and R²⁴ are independently of each other H, a phenyl group, or a C₁-C₁₈alkyl group.

Most preferred, X¹ is a group of the formula



For the group of formula $-(A^5)_v-(A^6)_s-(A^7)_t-(A^8)_u-R^{15}$ the following preferences apply.

10 v is 0, or 1, s is 0, or 1, t is 0, or 1, u is 0, or 1. Preferably, t is 0 and u is 0.

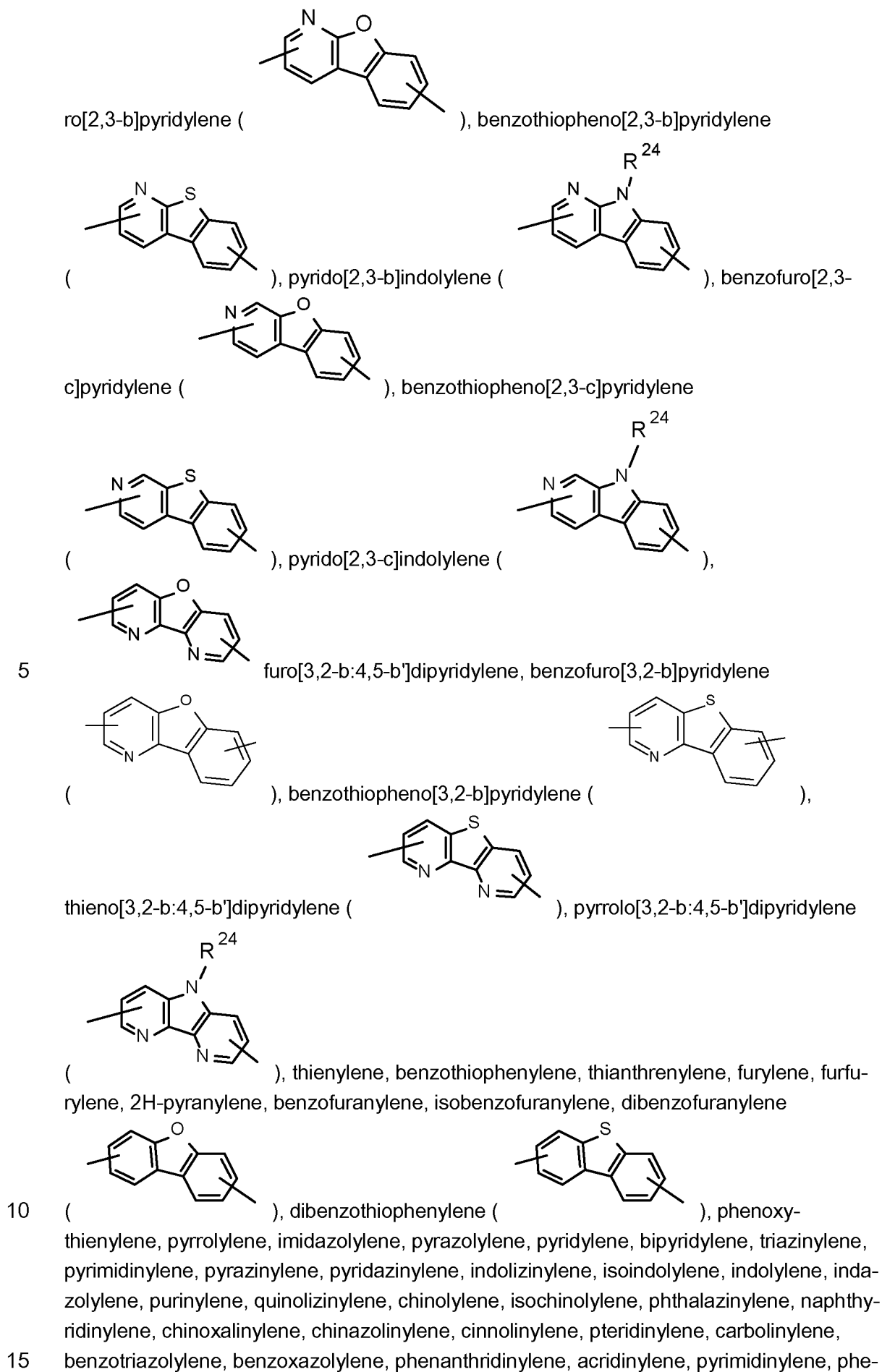
A⁵, A⁶, A⁷ and A⁸ are independently of each other a C₆-C₂₄arylen group, which can optionally be substituted by G, or a C₂-C₃₀heteroarylen group, which can optionally be substituted by G.

15

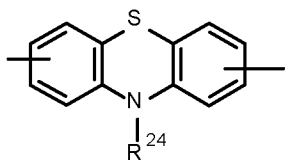
The C₆-C₂₄arylen groups A⁵, A⁶, A⁷ and A⁸ which optionally can be substituted by G, are typically phenylene, 4-methylphenylene, 4-methoxyphenylene, naphthylene, especially 1-naphthylene, or 2-naphthylene, biphenylene, terphenylene, pyrenylene, 2- or 9-fluorenylene, phenanthrylene, or anthrylene, which may be unsubstituted or substituted.

20

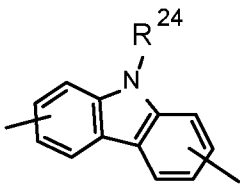
The C₂-C₃₀heteroarylen groups A⁵, A⁶, A⁷ and A⁸, which optionally can be substituted by G, represent a ring with five to seven ring atoms or a condensed ring system, wherein nitrogen, oxygen or sulfur are the possible hetero atoms, and is typically a heterocyclic group with five to 30 atoms having at least six conjugated-electrons such as, for example, benzofu-



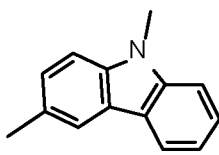
nanthrolinylene, phenazinylene, isothiazolylene, phenothiazinylene



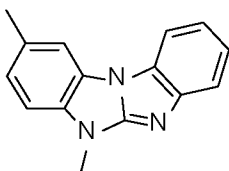
(), isoxazolylene, furazanylene, carbazolylene



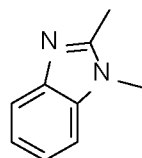
, or



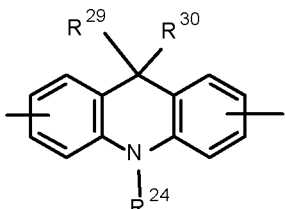
(), benzimidazo[1,2-a]benzimidazo-2,5-ylene



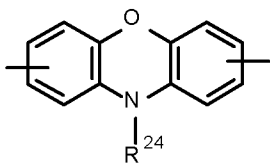
(), benzimidazo-1,2-ylene (



), 9,9-dialkylacridinylene



5 (); R²⁹ and R³⁰ are C₁-C₂₅alkyl), or phenoxazinylene



(), which can be unsubstituted or substituted. R²⁴ is a C₆-C₂₄aryl group, or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G, wherein G is as defined in above.

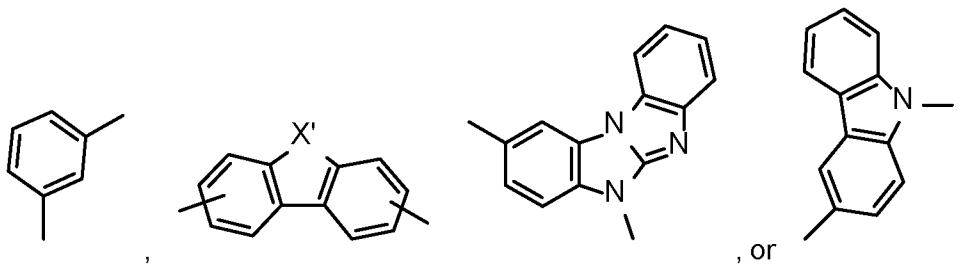
- 10 Preferred C₆-C₂₄arylen groups are 1,3-phenylene, 1,4-phenylene, 3,3'-biphenylene, 3,3'-m-terphenylene, 2- or 9-fluorenylene, phenanthrylene, which may be unsubstituted or substituted, especially by C₆-C₁₀aryl, C₆-C₁₀aryl which is substituted by C₁-C₄alkyl; or C₂-C₁₄heteroaryl.
- 15 Preferred C₂-C₃₀heteroarylen groups are indolylene, carbazolylene, benzimidazo[1,2-a]benzimidazo-2,5-ylene, phenoxazin-10-ylene, or 9,9-dialkylacridin-10-ylene, which can be unsubstituted or substituted. A further preferred C₂-C₃₀heteroarylen group is dibenzofuranylene, which can be unsubstituted or substituted.
- 20 The C₆-C₂₄arylen and C₂-C₃₀heteroarylen groups may be substituted by G.

G is preferably C₁-C₁₈alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, -CF₃, a C₆-C₁₄aryl group, a C₆-C₁₄aryl group, which is substituted by F, or C₁-C₁₈alkyl; a C₂-C₁₃heteroaryl group, or a C₂-C₁₃heteroaryl group, which is substituted by F, or C₁-C₁₈alkyl.

25

Benzimidazo[1,2-a]benzimidazo-5-yl, benzimidazo[1,2-a]benzimidazo-2-yl, carbazolyl and dibenzofuranyl are examples of a C₂-C₁₃heteroarylgroup. Phenyl, 1-naphthyl and 2-naphthyl are examples of a C₆-C₁₄aryl group.

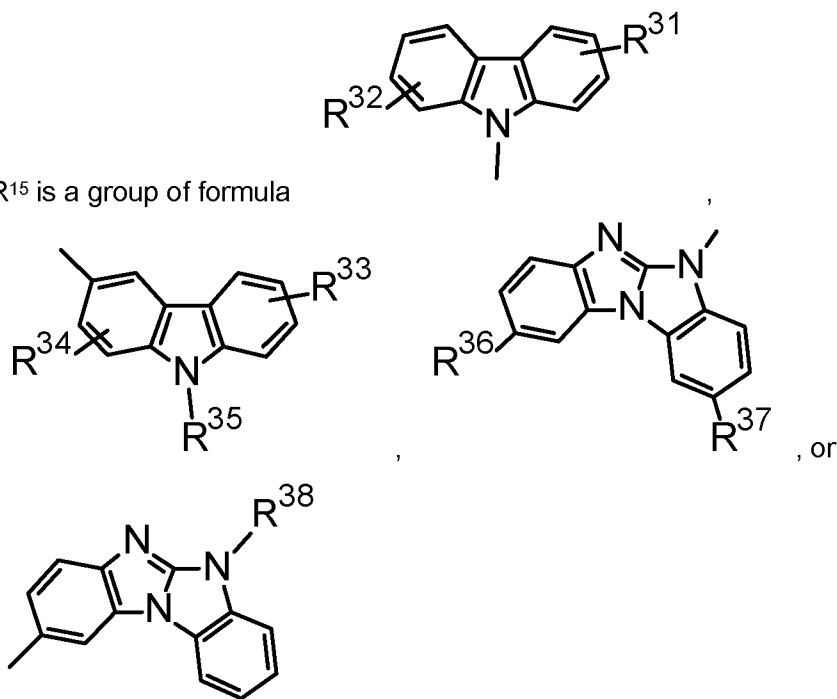
5 More preferred, A⁵, A⁶, A⁷ and A⁸ are independently of each other a group of the formula



X' is O, S, or NR^{25'}, and

R^{25'} a phenyl group, or a C₁-C₁₈alkyl group.

10 R¹⁵ is a group of formula

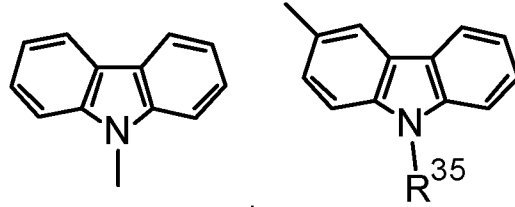


; wherein

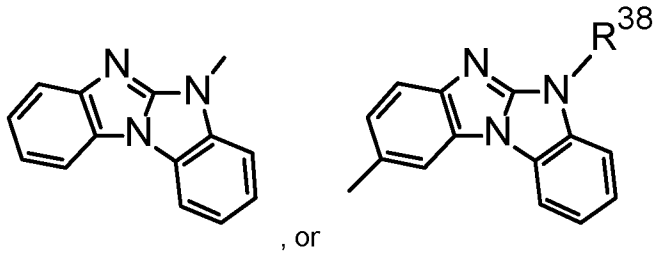
R³¹, R³², R³³, R³⁴, R³⁶ and R³⁷ are independently of each other H, or a C₁-C₂₅alkyl group;

R³⁵ and R³⁸ are independently of each other a C₆-C₁₀aryl group, which can optionally be substituted by one, or more C₁-C₂₅alkyl groups.

15



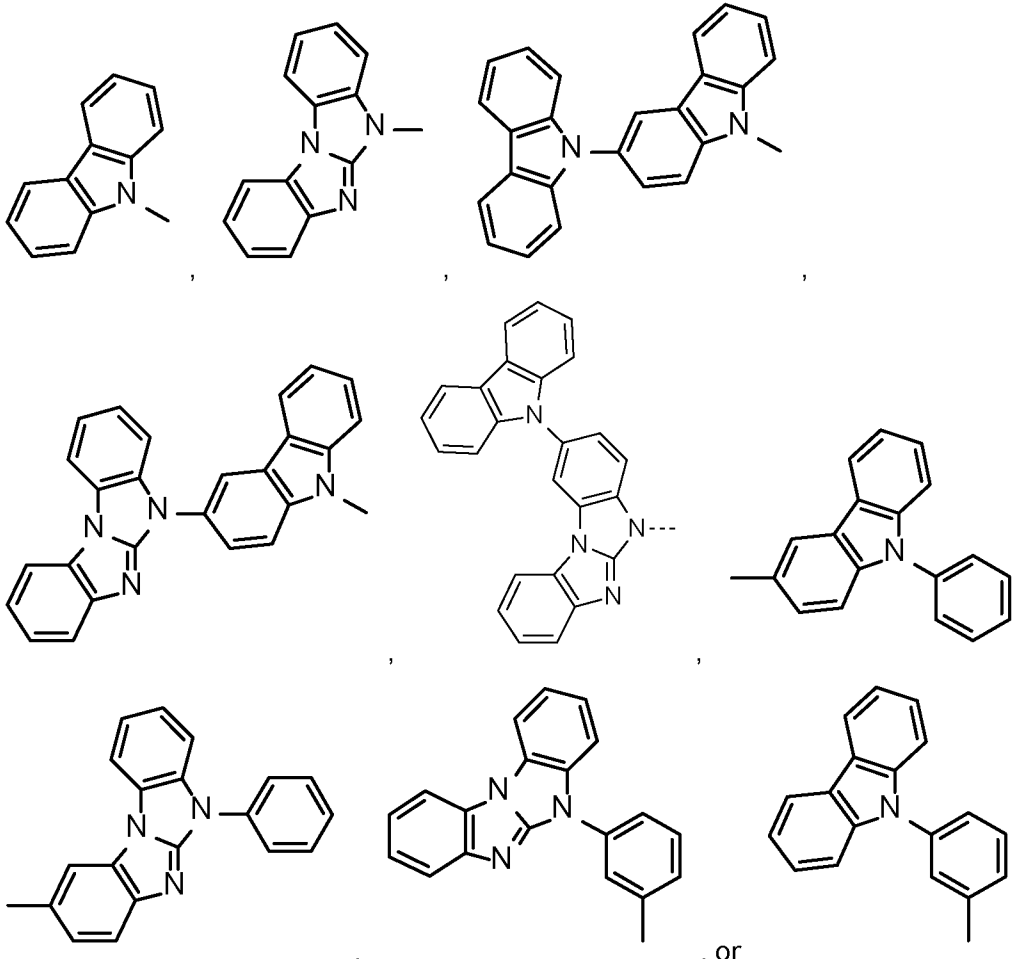
Preferably, R¹⁵ is a group of the formula



R³⁵ and R³⁸ are independently of each other a phenyl group, which can optionally be substituted by one, or more C₁-C₂₅alkyl groups.

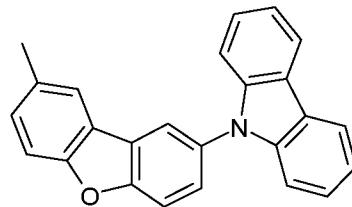
5

Most preferred, X² and X³ are independently of each other a group of the formula

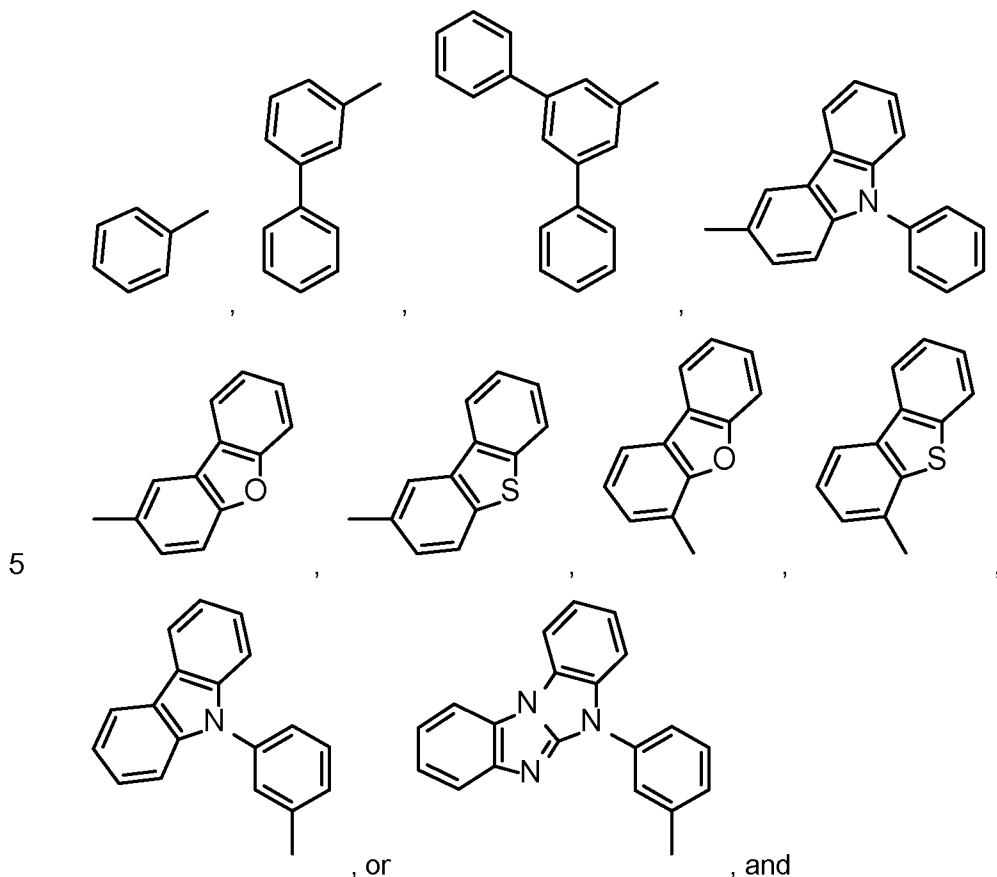
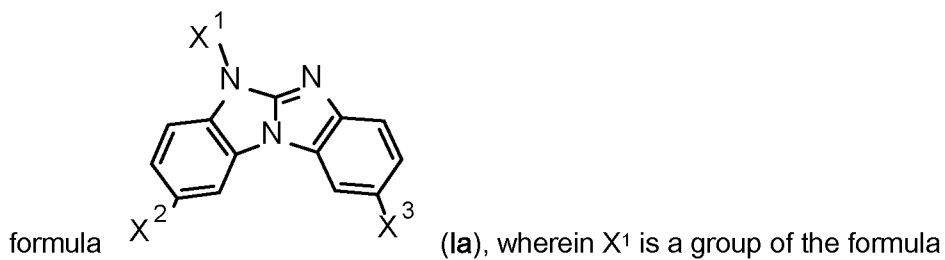


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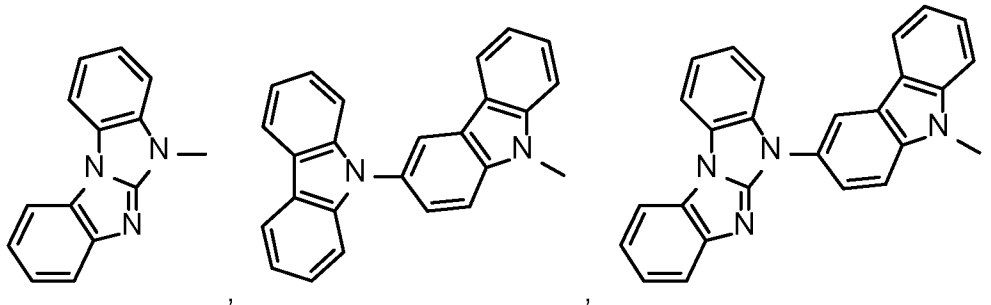
tionally, a most preferred, X² and X³ group is X² and X³ may be different, but are preferably the same.

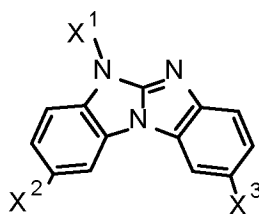
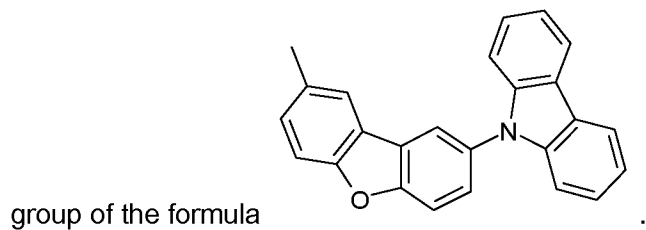
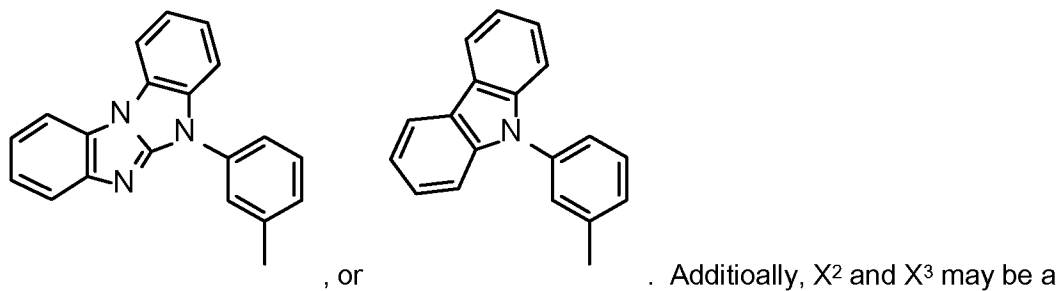
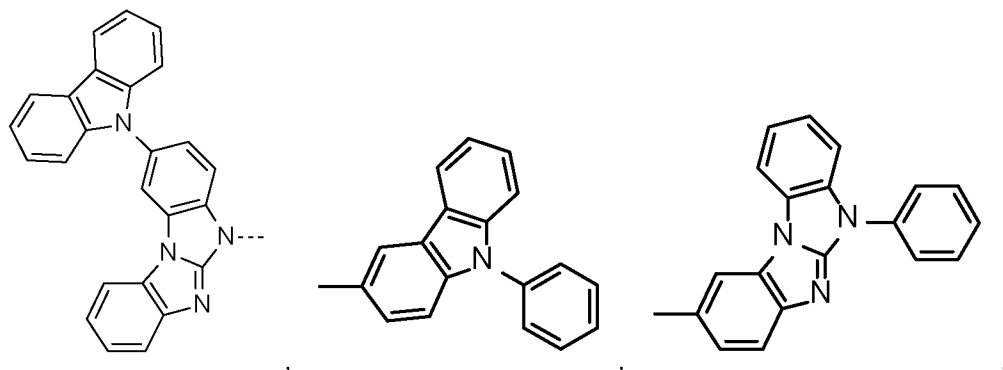


In a particularly preferred embodiment the present invention is directed to compounds of



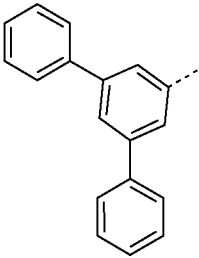
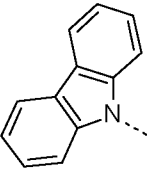
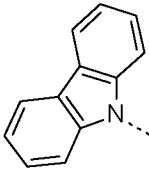
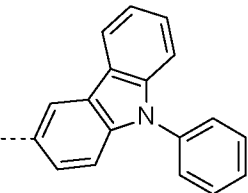
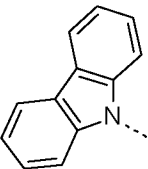
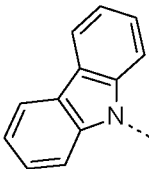
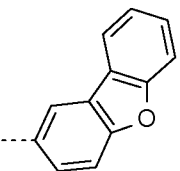
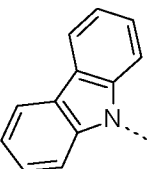
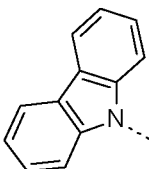
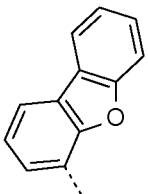
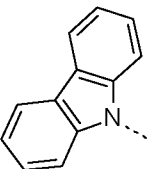
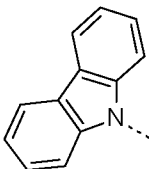
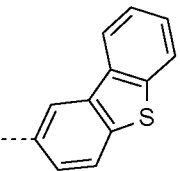
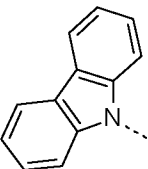
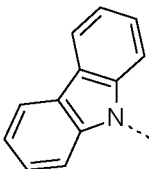
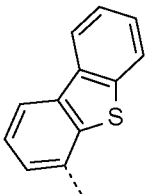
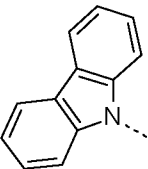
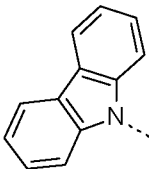
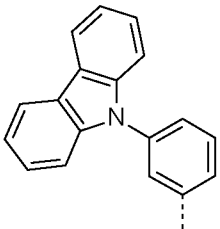
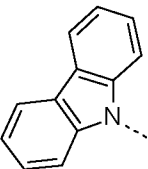
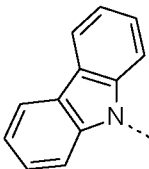
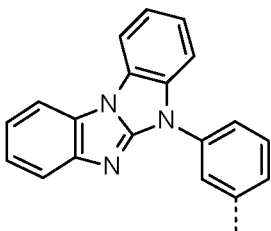
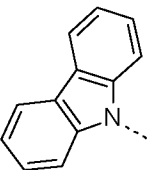
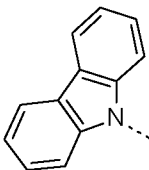
X² and X³ are independently of each other a group of the formula

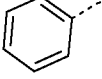
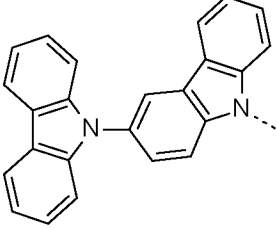
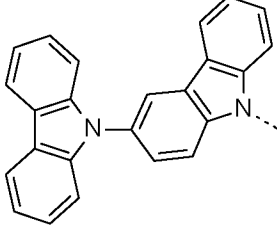
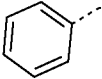
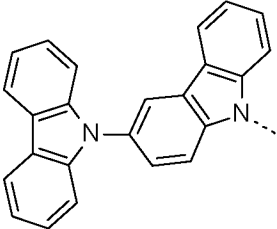
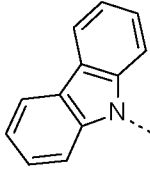
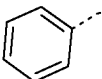
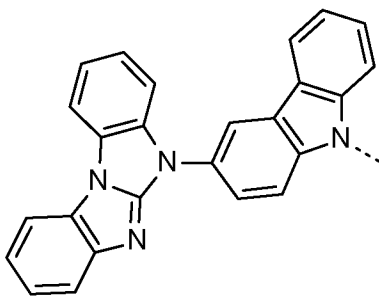
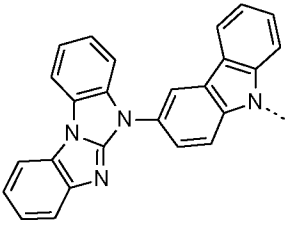
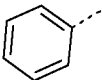
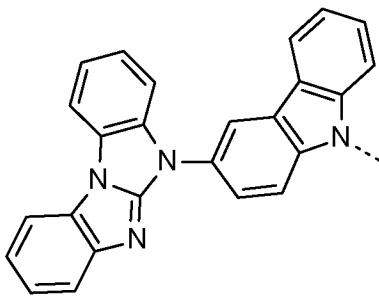
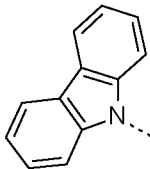
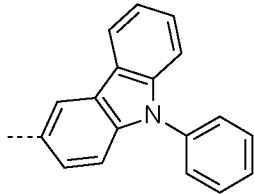
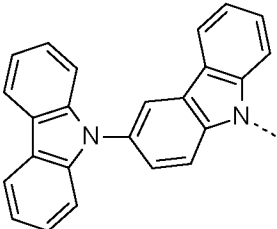
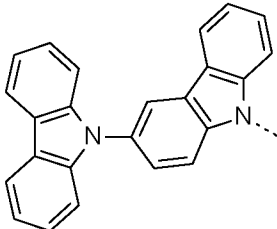
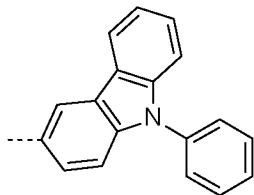
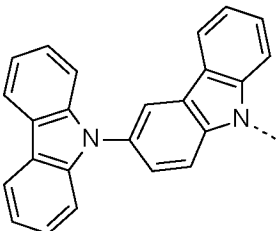
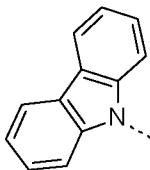


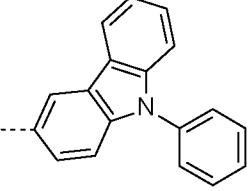
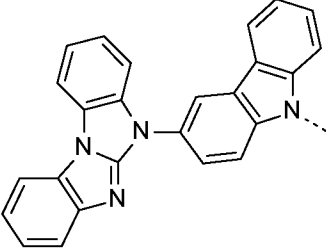
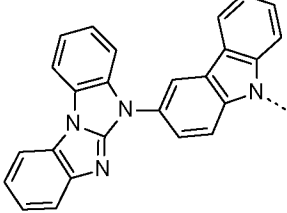
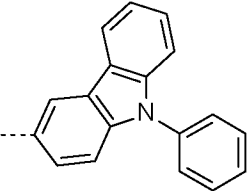
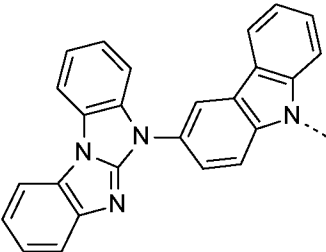
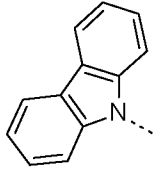
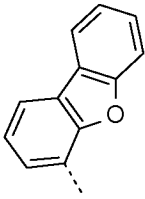
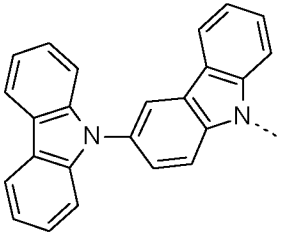
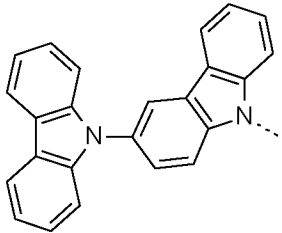
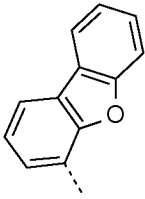
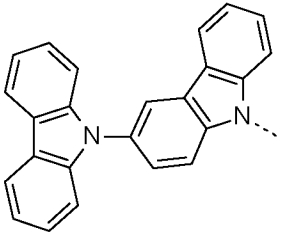
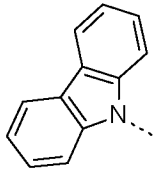
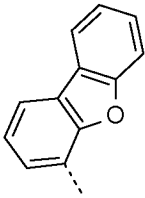
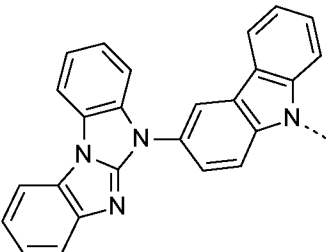
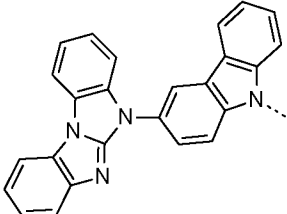
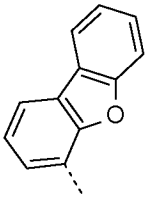
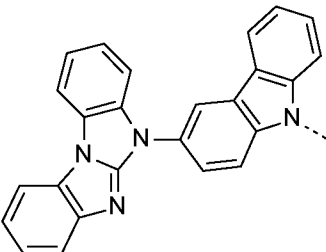
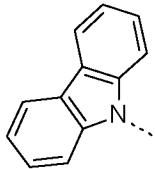
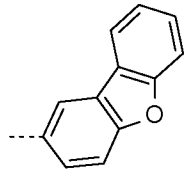
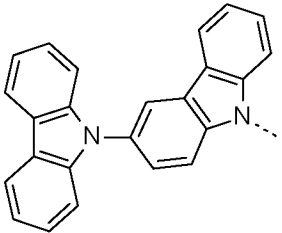
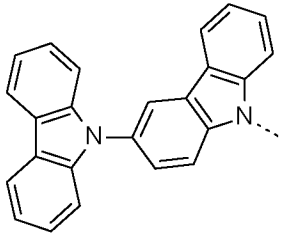


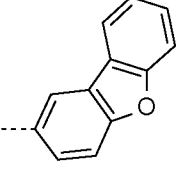
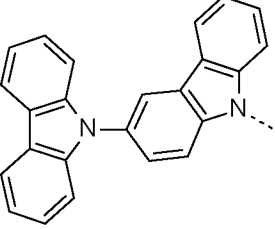
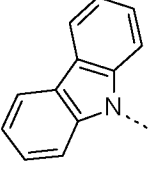
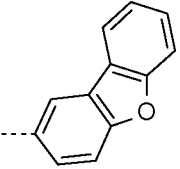
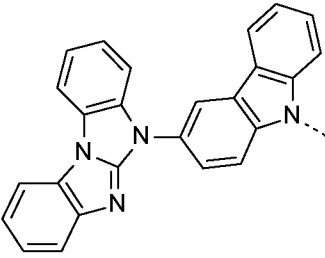
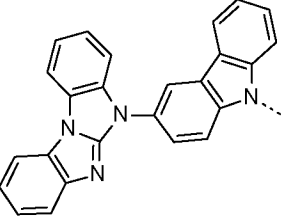
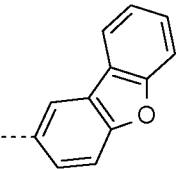
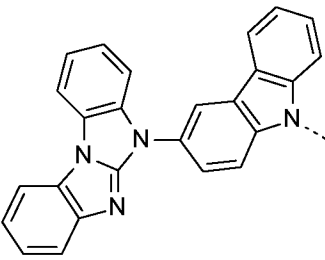
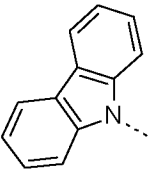
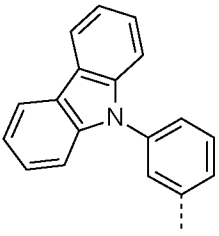
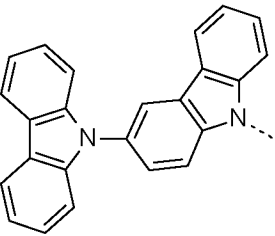
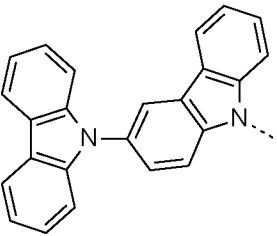
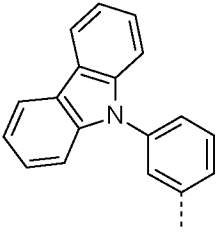
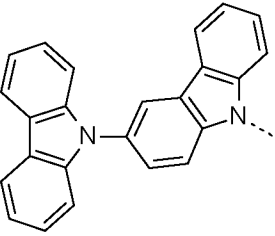
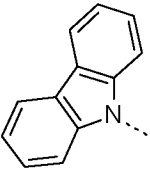
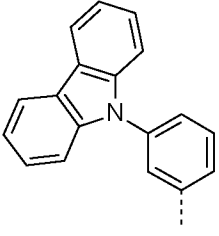
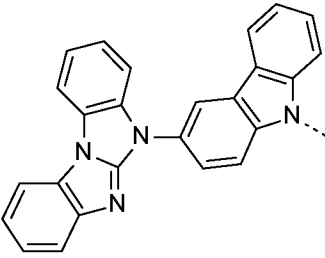
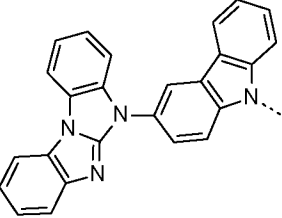
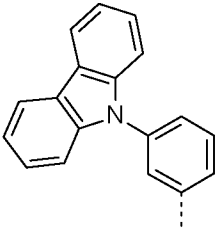
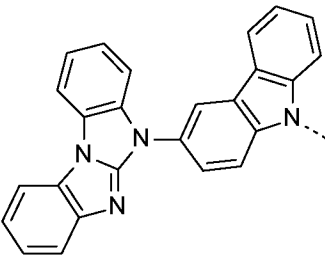
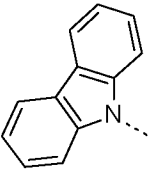
5 Examples of compounds of formula (Ia) are shown in the table below.

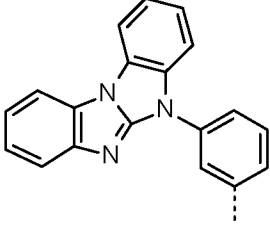
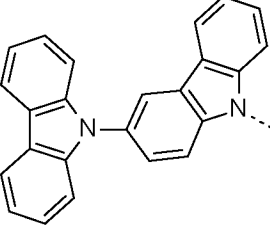
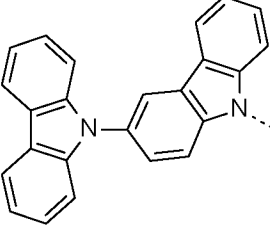
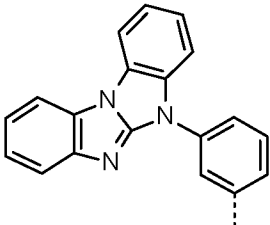
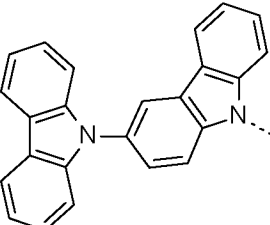
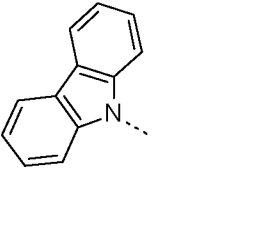
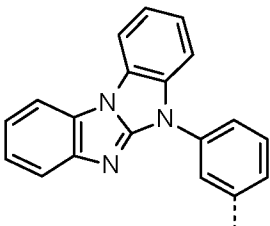
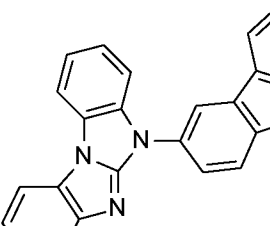
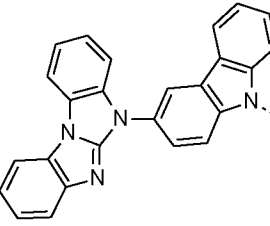
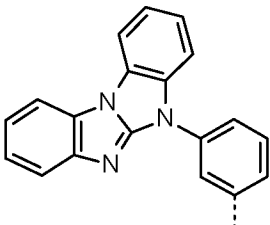
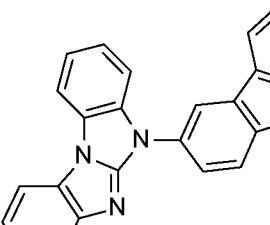
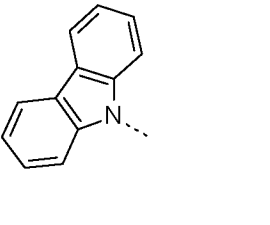

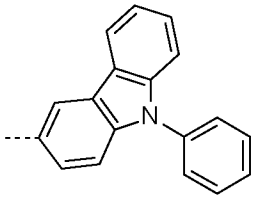
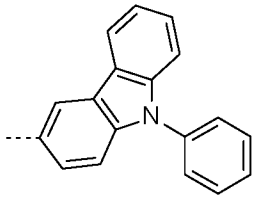

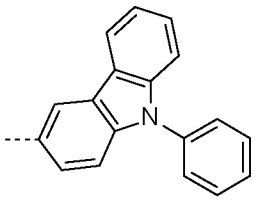
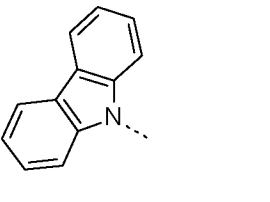

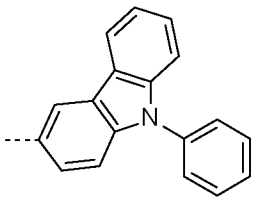
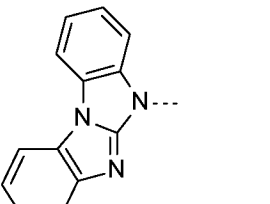
Cpd.	X ¹	X ²	X ³
A-1			
A-2			

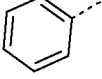
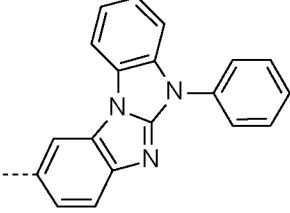
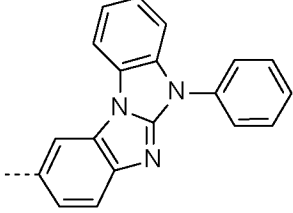
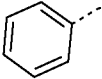
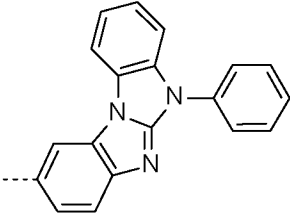
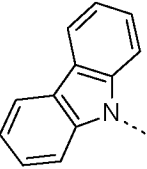
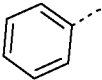
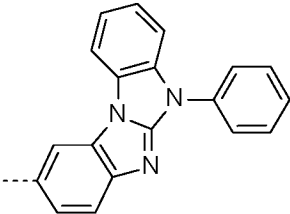
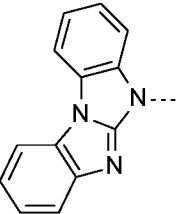
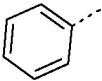
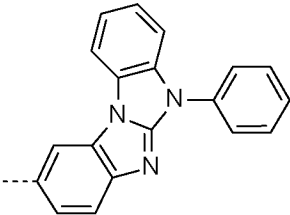
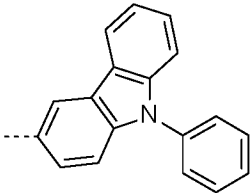
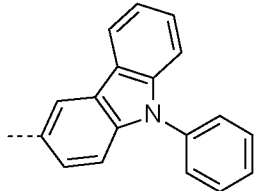
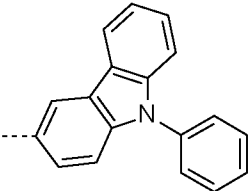
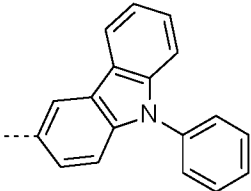
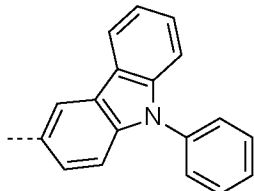
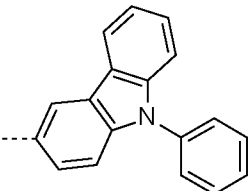
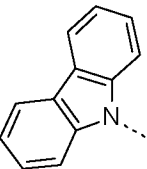
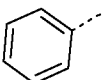
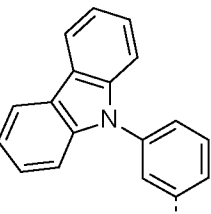
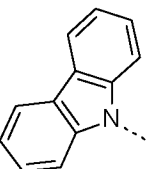
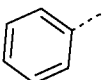
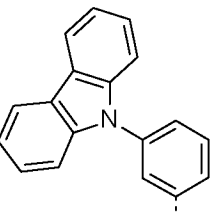
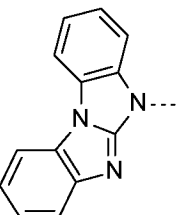
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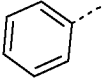
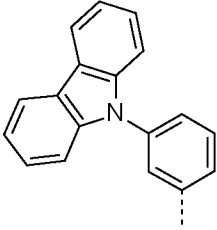
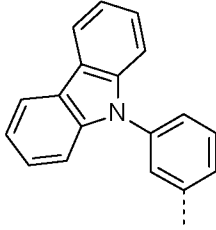
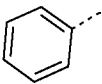
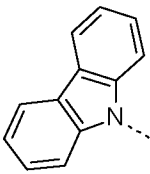
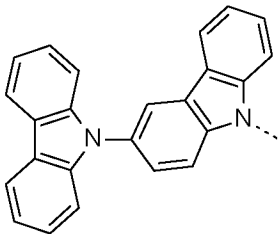
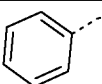
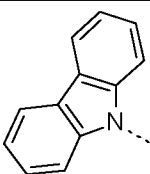
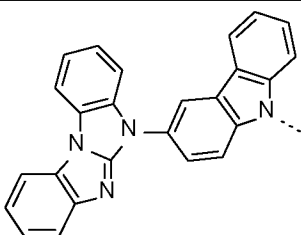
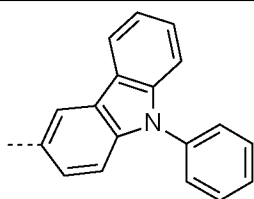
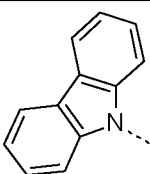
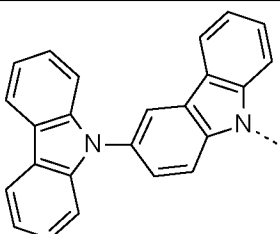
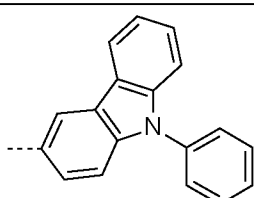
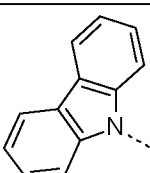
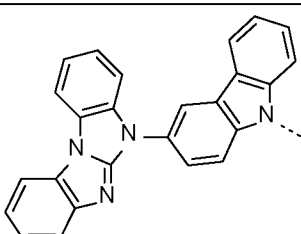
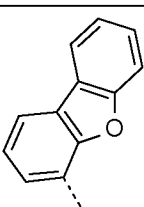
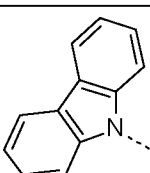
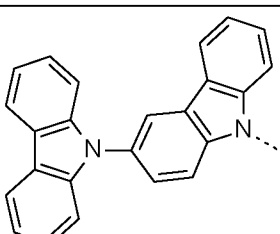
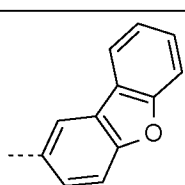
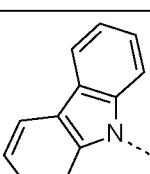
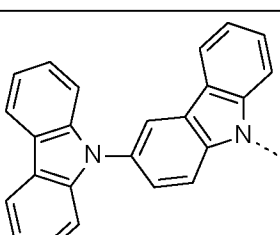
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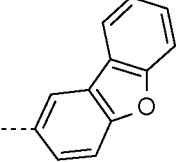
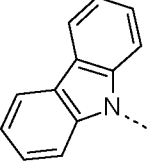
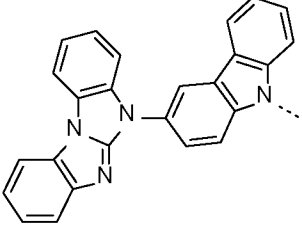
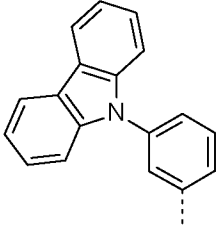
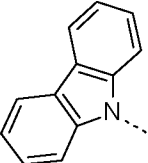
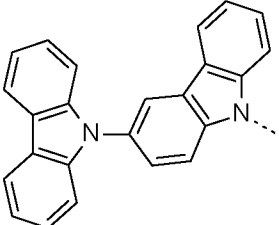
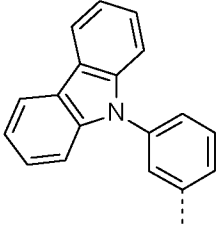
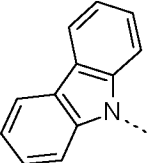
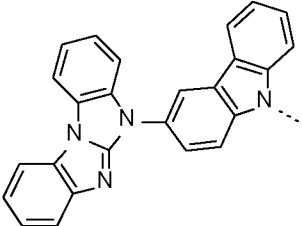
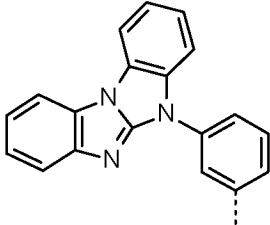
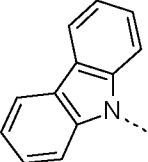
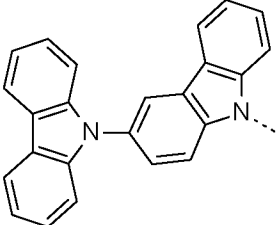
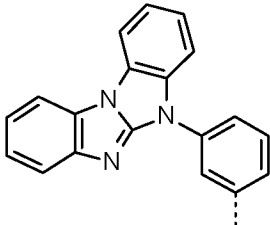
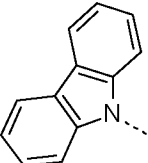
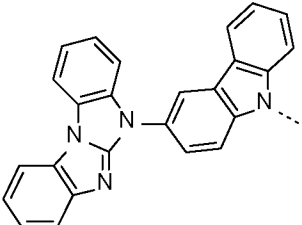
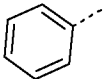
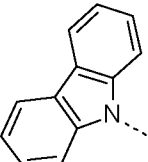
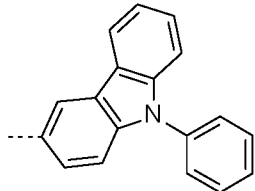
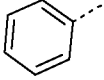
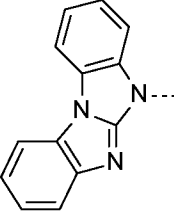
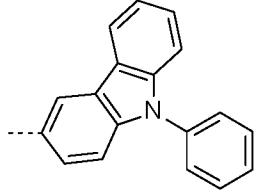
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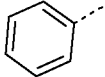
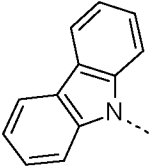
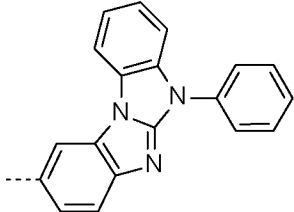
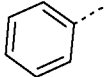
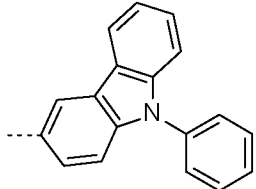
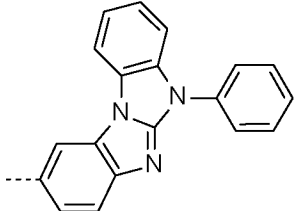
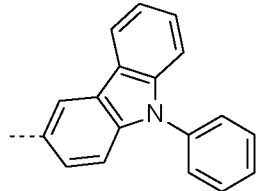
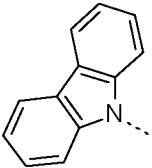
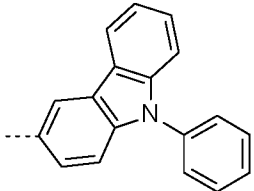
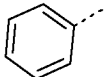
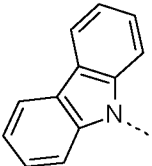
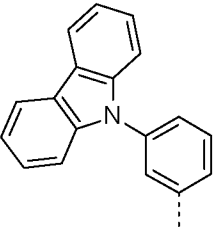
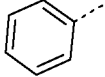
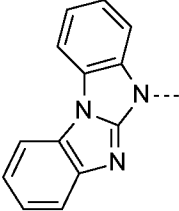
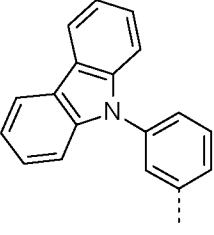
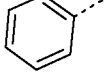
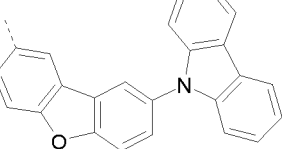
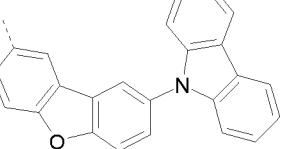
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----- indicates the bonding to the benzimidazolo[1,2-a]benzimidazole.

Compounds A-1 to A-64 and A-65 are preferred, compounds A-1, A-2, A-3, A-5, A-11, A-13, A-23, A-25, A-35, A-38, A-46 and A-59 and A-65 are particularly preferred.

5 Halogen is fluorine, chlorine, bromine and iodine.

C₁-C₂₅alkyl (C₁-C₁₈alkyl) is typically linear or branched, where possible. Examples are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, 1,1,3,3-tetramethylpentyl, n-hexyl, 1-methylhexyl, 1,1,3,3,5,5-hexamethylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl, n-nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, or octadecyl. C₁-C₈alkyl is typically

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methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethyl-propyl, n-hexyl, n-heptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl. C₁-C₄alkyl is typically methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl.

5

C₁-C₂₅alkoxy groups (C₁-C₁₈alkoxy groups) are straight-chain or branched alkoxy groups, e.g. methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy, amyloxy, isoamyloxy or tert-amyloxy, heptyloxy, octyloxy, isooctyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy and octadecyloxy. Examples of C₁-C₈alkoxy are methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.-butoxy, isobutoxy, tert.-butoxy, n-pentyloxy, 2-pentyloxy, 3-pentyloxy, 2,2-dimethylpropoxy, n-hexyloxy, n-heptyloxy, n-octyloxy, 1,1,3,3-tetramethylbutoxy and 2-ethylhexyloxy, preferably C₁-C₄alkoxy such as typically methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.-butoxy, isobutoxy, tert.-butoxy.

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The term "cycloalkyl group" is typically C₅-C₁₂cycloalkyl, such as cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl, preferably cyclopentyl, cyclohexyl, cycloheptyl, or cyclooctyl, which may be unsubstituted or substituted.

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C₆-C₂₄aryl (C₆-C₁₈aryl), which optionally can be substituted, is typically phenyl, 4-methylphenyl, 4-methoxyphenyl, naphthyl, especially 1-naphthyl, or 2-naphthyl, biphenyl, terphenyl, pyrenyl, 2- or 9-fluorenyl, phenanthryl, or anthryl, which may be unsubstituted or substituted. Phenyl, 1-naphthyl and 2-naphthyl are examples of a C₆-C₁₀aryl group.

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C₇-C₂₅aralkyl is typically benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, α,α-dimethylbenzyl, ω-phenyl-butyl, ω,ω-dimethyl-ω-phenyl-butyl, ω-phenyl-dodecyl, ω-phenyl-octadecyl, ω-phenyl-eicosyl or ω-phenyl-docosyl, preferably C₇-C₁₈aralkyl such as benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, α,α-dimethylbenzyl, ω-phenyl-butyl, ω,ω-dimethyl-ω-phenyl-butyl, ω-phenyl-dodecyl or ω-phenyl-octadecyl, and particularly preferred C₇-C₁₂aralkyl such as benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, α,α-dimethylbenzyl, ω-phenyl-butyl, or ω,ω-dimethyl-ω-phenyl-butyl, in which both the aliphatic hydrocarbon group and aromatic hydrocarbon group may be unsubstituted or substituted. Preferred examples are benzyl, 2-phenylethyl, 3-phenylpropyl, naphthylethyl, naphthylmethyl, and cumyl.

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C₂-C₃₀heteroaryl represents a ring with five to seven ring atoms or a condensed ring system, wherein nitrogen, oxygen or sulfur are the possible hetero atoms, and is typically a heterocyclic group with five to 30 atoms having at least six conjugated π-electrons such as thienyl, benzothiophenyl, dibenzothiophenyl, thianthrenyl, furyl, furfuryl, 2H-pyranyl, benzofuranyl, isobenzofuranyl, dibenzofuranyl, phenoxythienyl, pyrrolyl, imidazolyl, pyrazolyl, pyridyl, bipyridyl, triazinyl, pyrimidinyl, pyrazinyl, pyridazinyl, indoliziny, isoindolyl, indolyl, indazolyl, purinyl, quinoliziny, chinolyl, isochinolyl, phthalazinyl, naphthyridinyl, chinoxaliny, chinazoliny, cinnoliny, pteridinyl, carbazolyl, carboliny, benzotriazolyl, benzoxazolyl, phenanthridinyl, acridinyl, pyrimidinyl, phenanthroliny, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, 4-imidazo[1,2-a]benzimidazolyl, 5-benzimidazo[1,2-a]benzimidazolyl, benzimidazolo[2,1-b][1,3]benzothiazolyl, carbazolyl, or phenoxazinyl, which can be unsubstituted or substituted. Benzimidazo[1,2-a]benzimidazo-5-yl, benzimidazo[1,2-

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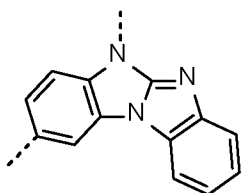
a]benzimidazo-2-yl, carbazolyl and dibenzofuranyl are examples of a C₂-C₁₄heteroaryl group.

C₆-C₂₄arylen groups, which optionally can be substituted by G, are typically phenylene, 4-methylphenylene, 4-methoxyphenylene, naphthylene, especially 1-naphthylene, or 2-naphthylene, biphenylene, terphenylene, pyrenylene, 2- or 9-fluorenylene, phenanthrylene, or anthrylene, which may be unsubstituted or substituted. Preferred C₆-C₂₄arylen groups are 1,3-phenylene, 3,3'-biphenylene, 3,3'-m-terphenylene, 2- or 9-fluorenylene, phenanthrylene, which may be unsubstituted or substituted.

10

C₂-C₃₀heteroarylen groups, which optionally can be substituted by G, represent a ring with five to seven ring atoms or a condensed ring system, wherein nitrogen, oxygen or sulfur are the possible hetero atoms, and is typically a heterocyclic group with five to 30 atoms having at least six conjugated π -electrons such as thienylene, benzothiophenylene, dibenzothiophenylene, thianthrenylene, furylene, furfurylene, 2H-pyranylene, benzofuranylene, isobenzofuranylene, dibenzofuranylene, phenoxythienylene, pyrrolylene, imidazolylene, pyrazolylene, pyridylene, bipyridylene, triazinylene, pyrimidinylene, pyrazinylene, pyridazinylene, indolizinylene, isoindolylene, indolylene, indazolylene, purinylene, quinolizinylene, chinolylene, isochinolylene, phthalazinylene, naphthyridinylene, chinoxalinylene, chinazolinylene, cinnolinylene, pteridinylene, carbolinylene, benzotriazolylene, benzoxazolylene, phenanthridinylene, acridinylene, pyrimidinylene, phenanthrolinylene, phenazinylene, isothiazolylene, phenothiazinylene, isoxazolylene, furazanylene, carbazolylene, benzimidazo[1,2-a]benzimidazo-2,5-ylene, or phenoxazinylene, which can be unsubstituted or substituted. Preferred C₂-C₃₀heteroarylen groups are pyridylene, triazinylene, pyrimidinylene, carbazolylene, dibenzofuranylene and benzimidazo[1,2-a]benzimidazo-2,5-ylene

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(), which can be unsubstituted or substituted, especially by C₆-C₁₀aryl, C₆-C₁₀aryl which is substituted by C₁-C₄alkyl; or C₂-C₁₄heteroaryl.

Possible substituents of the above-mentioned groups are C₁-C₈alkyl, a hydroxyl group, a mercapto group, C₁-C₈alkoxy, C₁-C₈alkylthio, halogen, halo-C₁-C₈alkyl, or a cyano group. The C₆-C₂₄aryl (C₆-C₁₈aryl) and C₂-C₃₀heteroaryl groups are preferably substituted by one, or more C₁-C₈alkyl groups.

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If a substituent occurs more than one time in a group, it can be different in each occurrence.

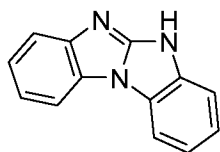
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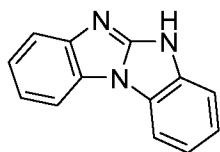
Halo-C₁-C₈alkyl is an alkyl group where at least one of the hydrogen atoms is replaced by a halogen atom. Examples are -CF₃, -CF₂CF₃, -CF₂CF₂CF₃, -CF(CF₃)₂, -(CF₂)₃CF₃, and -C(CF₃)₃.

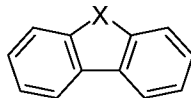
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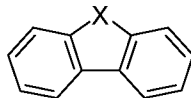
The wording "substituted by G" means that one, or more, especially one to three substituents G might be present.

- As described above, the aforementioned groups may be substituted by E and/or, if desired, interrupted by D. Interruptions are of course possible only in the case of groups containing at least 2 carbon atoms connected to one another by single bonds; C₆-C₁₈aryl is not interrupted; interrupted arylalkyl contains the unit D in the alkyl moiety. C₁-C₁₈alkyl substituted by one or more E and/or interrupted by one or more units D is, for example, (CH₂CH₂O)₁₋₉-R^x, where R^x is H or C₁-C₁₀alkyl or C₂-C₁₀alkanoyl (e.g. CO-CH(C₂H₅)C₄H₉), CH₂-CH(OR^y)-CH₂-O-R^y, where R^y is C₁-C₁₈alkyl, C₅-C₁₂cycloalkyl, phenyl, C₇-C₁₅phenylalkyl, and R^y embraces the same definitions as R^y or is H;
- C₁-C₈alkylene-COO-R^z, e.g. CH₂COOR^z, CH(CH₃)COOR^z, C(CH₃)₂COOR^z, where R^z is H, C₁-C₁₈alkyl, (CH₂CH₂O)₁₋₉-R^x, and R^x embraces the definitions indicated above; CH₂CH₂-O-CO-CH=CH₂; CH₂CH(OH)CH₂-O-CO-C(CH₃)=CH₂.
- An alkyl group substituted by E is, for example, an alkyl group where at least one of the hydrogen atoms is replaced by F. Examples are -CF₃, -CF₂CF₃, -CF₂CF₂CF₃, -CF(CF₃)₂, -(CF₂)₃CF₃, and -C(CF₃)₃.



The synthesis of  is described, for example, in Achour, Reddouane; Zniber, Rachid, Bulletin des Societes Chimiques Belges 96 (1987) 787-92.



- Suitable base skeletons of the formula  are either commercially available (especially in the cases when X is S, O, NH), or can be obtained by processes known to those skilled in the art. Reference is made to WO2010079051 and EP1885818.

- The halogenation can be performed by methods known to those skilled in the art. Preference is given to brominating or iodinating in the 3 and 6 positions (dibromination) or in the 3 or 6 positions (monobromination) of the base skeleton of the formula 2,8 positions (dibenzofuran and dibenzothiophene) or 3,6 positions (carbazole).

- Optionally substituted dibenzofurans, dibenzothiophenes and carbazoles can be dibrominated in the 2,8 positions (dibenzofuran and dibenzothiophene) or 3,6 positions (carbazole) with bromine or NBS in glacial acetic acid or in chloroform. For example, the bromination with Br₂ can be effected in glacial acetic acid or chloroform at low temperatures, e.g. 0°C. Suitable processes are described, for example, in M. Park, J.R. Buck, C.J. Rizzo, Tetrahedron, 54 (1998) 12707-12714 for X= NPh, and in W. Yang et al., J. Mater. Chem. 13 (2003) 1351 for X= S. In addition, 3,6-dibromocarbazole, 3,6-dibromo-9-phenylcarbazole, 2,8-dibromodibenzothiophene, 2,8-dibromodibenzofuran, 2-bromocarbazole, 3-bromodibenzothiophene, 3-bromodibenzofuran, 3-bromocarbazole, 2-bromodibenzothiophene and 2-bromodibenzofuran are commercially available.

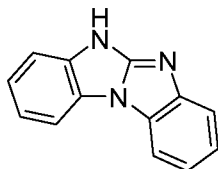
- Monobromination in the 4 position of dibenzofuran (and analogously for dibenzothiophene) is described, for example, in J. Am. Chem. Soc. 1984, 106, 7150. Dibenzofuran (diben-

zothiophene) can be monobrominated in the 3 position by a sequence known to those skilled in the art, comprising a nitration, reduction and subsequent Sandmeyer reaction.

Monobromination in the 2 position of dibenzofuran or dibenzothiophene and monobromination in the 3 position of carbazole are effected analogously to the dibromination, with the exception that only one equivalent of bromine or NBS is added.

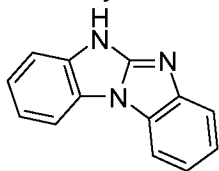
Alternatively, it is also possible to utilize iodinated dibenzofurans, dibenzothiophenes and carbazoles. The preparation is described, inter alia, in Tetrahedron. Lett. 47 (2006) 6957-6960, Eur. J. Inorg. Chem. 24 (2005) 4976-4984, J. Heterocyclic Chem. 39 (2002) 933-941, J. Am. Chem. Soc. 124 (2002) 11900-11907, J. Heterocyclic Chem, 38 (2001) 77-87.

For the nucleophilic substitution, Cl- or F-substituted dibenzofurans, dibenzothiophenes and carbazoles are required. The chlorination is described, inter alia, in 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. The fluorination is described in J. Org. Chem. 63 (1998) 878-880 and J. Chem. Soc., Perkin Trans. 2, 5 (2002) 953-957.

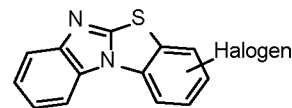


The introduction of the group is performed in the presence of a base. Suitable bases are known to those skilled in the art and are preferably selected from the group consisting of alkali metal and alkaline earth metal hydroxides such as NaOH, KOH, Ca(OH)₂, alkali metal hydrides such as NaH, KH, alkali metal amides such as NaNH₂, alkali metal or alkaline earth metal carbonates such as K₂CO₃ or Cs₂CO₃, and alkali metal alkoxides such as NaOMe, NaOEt. In addition, mixtures of the aforementioned bases are suitable. Particular preference is given to NaOH, KOH, NaH or K₂CO₃.

Heteroarylation can be affected, for example, by copper-catalyzed coupling of

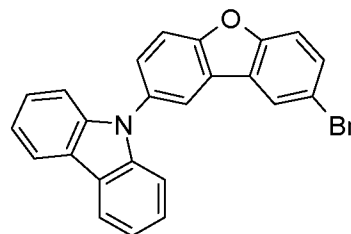


to a halogenated compound of the formula

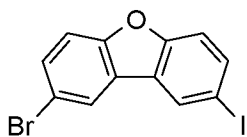


(Ullmann reaction).

The N-arylation is, for example, disclosed in H. Gilman and D. A. Shirley, J. Am. Chem. Soc. 66 (1944) 888; D. Li et al., Dyes and Pigments 49 (2001) 181 – 186 and Eur. J. Org. Chem. (2007) 2147-2151. The reaction can be performed in solvent or in a melt. Suitable solvents are, for example, (polar) aprotic solvents such as dimethyl sulfoxide, dimethylformamide, N-methyl-2-pyrrolidone (NMP), tridecane or alcohols.



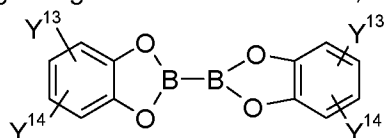
The synthesis of 9-(8-bromodibenzofuran-2-yl)carbazole, is described in WO2010079051. The synthesis of 2-bromo-8-iodo-dibenzofurane,



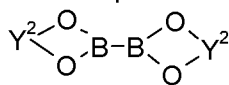
, is described in EP1885818.

- 5 Diboronic acid or diboronate group containing dibenzofurans, dibenzothiophenes and carbazoles can be readily prepared by an increasing number of routes. An overview of the synthetic routes is, for example, given in *Angew. Chem. Int. Ed.* 48 (2009) 9240 – 9261.

- 10 By one common route diboronic acid or diboronate group containing dibenzofurans, dibenzothiophenes, and carbazoles can be obtained by reacting halogenated dibenzofurans,

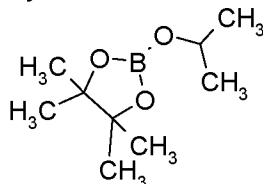


dibenzothiophenes and carbazoles with $(Y^1O)_2B-B(OY^1)_2$,



- or in the presence of a catalyst, such as, for example, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II), complex $(Pd(Cl)_2(dppf))$, and a base, such as, for example, potassium acetate, in a solvent, such as, for example, dimethyl formamide, dimethyl sulfoxide, dioxane and/or toluene (cf. Prasad Appukkuttan et al., *Synlett* 8 (2003) 1204), wherein Y^1 is independently in each occurrence a C_1-C_{18} alkylgroup and Y^2 is independently in each occurrence a C_2-C_{10} alkylene group, such as $-CY^3Y^4-CY^5Y^6-$, or $-CY^7Y^8-CY^9Y^{10}-CY^{11}Y^{12}-$, wherein $Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11}$ and Y^{12} are independently of each other hydrogen, or a C_1-C_{18} alkylgroup, especially $-C(CH_3)_2C(CH_3)_2-$, $-C(CH_3)_2CH_2C(CH_3)_2-$, or $-CH_2C(CH_3)_2CH_2-$, and Y^{13} and Y^{14} are independently of each other hydrogen, or a C_1-C_{18} alkylgroup.

- 25 Diboronic acid or diboronate group containing dibenzofurans, dibenzothiophenes and carbazoles can also be prepared by reacting halogenated dibenzofurans, dibenzothiophenes and carbazoles with alkyl lithium reagents, such as, for example, n-butyl lithium, or t-butyl lithium, followed by reaction with boronic esters, such as, for example, $B(isopropoxy)_3$,

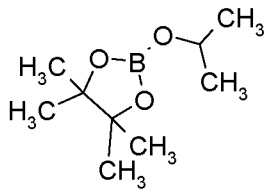


$B(methoxy)_3$, or

(cf. *Synthesis* (2000) 442–446).

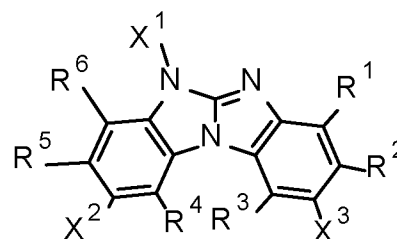
- 30 Diboronic acid or diboronate group containing dibenzofurans, dibenzothiophenes and carbazoles can also be prepared by reacting dibenzofurans, dibenzothiophenes and carbazoles with lithium amides, such as, for example, lithium diisopropylamide (LDA) followed by

reaction with boronic esters such as, for example, B(isopropoxy)₃, B(methoxy)₃, or



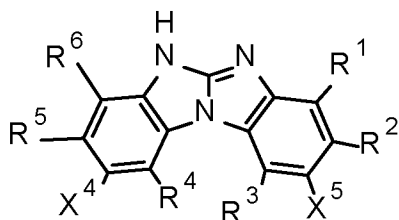
(J. Org. Chem. 73 (2008) 2176-2181).

The synthesis of the compounds of formula (I) can be done in analogy to methods known in the literature.

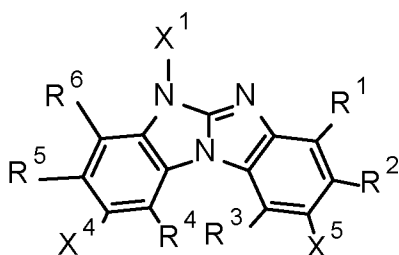


- 5 A process for the preparation of a compound of formula (I) comprises

a) selective arylation of a compound of formula



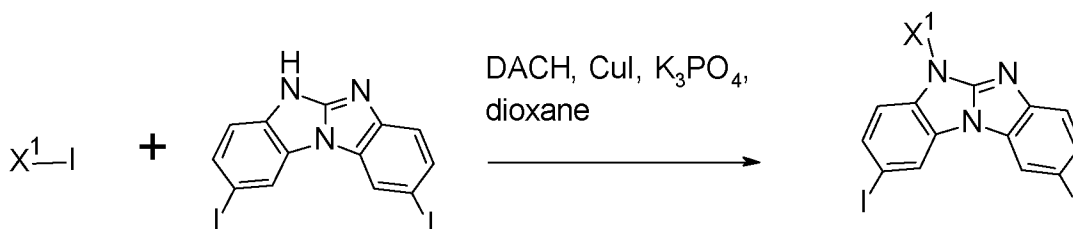
(II) to obtain a compound of formula



(III), and

- 10 b) Ullmann coupling of the compound of formula (III) with an arylamine, to obtain the compound of formula (I), or
Suzuki coupling of the compound of formula (III) with a boronic ester to obtain the compound of formula (I), wherein
 X^4 and X^5 are independently of each other Cl, Br, or I; and
- 15 R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , X^1 , X^2 and X^3 are as defined above.

Arylation of 2,9-diiodo-6H-benzimidazo[1,2-a]benzimidazole can, for example, be done under Ullman conditions with aryl iodides.

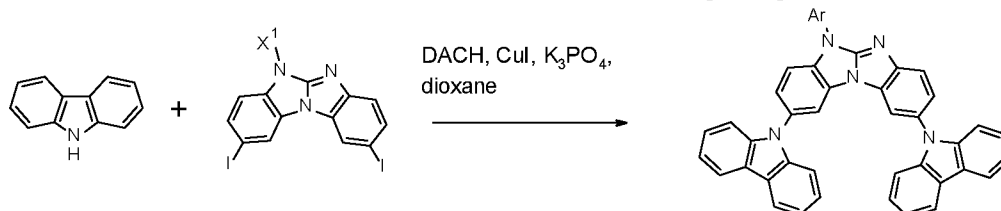


Reaction conditions for Ullmann reactions are, for example, described in Angew Chem Int Ed Engl., 48 (2009) 6954-71 WO14009317, WO12130709, J. Am. Chem. Soc. 131 (2009) 2009-2251, J. Org. Chem, 70 (2005) 5165.

- 5 Typically the Ullmann coupling of the compound of formula (II) with a compound of formula X¹-Y (Y is Br, or I, especially I) is done in the presence of copper, or a copper salt, such as, for example, CuI, CuBr, Cu₂O, or CuO, and a ligand, such as, for example, L-proline, trans-cyclohexane-1,2-diamine (DACH), 1,10-phenanthroline in a solvent, such as, for example, dimethylsulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMA), N-
- 10 methylpyrrolidone (NMP) and dioxane, or a solvent mixture. The reaction temperature is dependent on the reactivity of the starting materials, but is generally in the range of 25 to 200 °C.

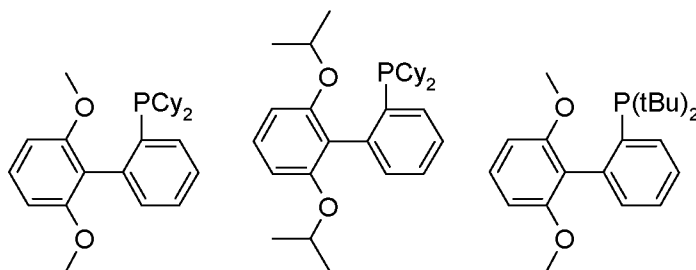
- 15 Typically the Ullmann coupling of the compound of formula (III) with an arylamine is done in the presence of copper, or a copper salt, such as, for example, CuI, CuBr, Cu₂O, or CuO, and a ligand, such as, for example, L-proline, trans-cyclohexane-1,2-diamine (DACH), 1,10-phenanthroline in a solvent, such as, for example, dimethylsulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMA), N-methylpyrrolidone (NMP) and dioxane, or a solvent mixture. The reaction temperature is dependent on the reactivity of the starting materials, but is generally in the range of 25 to 200 °C.
- 20

Carbazole or benzimidazolo[1,2-a]benzimidazole units can be coupled under Ullmann conditions on the X¹ substituted 2,9-diiodo-6H-benzimidazolo[1,2-a]benzimidazole.

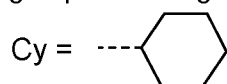


- 25 Typically the Suzuki reaction is carried out in the presence of a catalyst and a base in an organic solvent, or a solvent mixture. Generally, the reaction temperature is in the range of from 40 to 180°C.
- Preferably, the Suzuki reaction is carried out in the presence of an organic solvent, such as an aromatic hydrocarbon or a usual polar organic solvent, such as benzene, toluene, xy-
- 30 lene, tetrahydrofuran, or dioxane, or mixtures thereof, most preferred toluene. Usually, the amount of the solvent is chosen in the range of from 1 to 10 l per mol of boronic acid derivative. Also preferred, the reaction is carried out under an inert atmosphere such as nitrogen, or argon. Further, it is preferred to carry out the reaction in the presence of an aqueous base, such as an alkali metal hydroxide or carbonate such as NaOH, KOH, Na₂CO₃,
- 35 K₂CO₃, Cs₂CO₃ and the like, preferably an aqueous K₂CO₃ solution is chosen. Usually, the molar ratio of the base to boronic acid or boronic ester derivative is chosen in the range of from 0.5:1 to 50:1, very especially 1:1. Generally, the reaction temperature is chosen in the range of from 40 to 180°C, preferably under reflux conditions. Preferred, the reaction time is chosen in the range of from 1 to 80 hours, more preferably from 20 to 72 hours. In a preferred embodiment a usual catalyst for coupling reactions or for polycondensation reactions
- 40 is used, preferably Pd-based, which is described in WO2007/101820. The palladium compound is added in a ratio of from 1:10000 to 1:50, preferably from 1:5000 to 1:200, based

on the number of bonds to be closed. Preference is given, for example, to the use of palladium(II) salts such as PdAc₂ or Pd₂dba₃ and to the addition of ligands selected from the



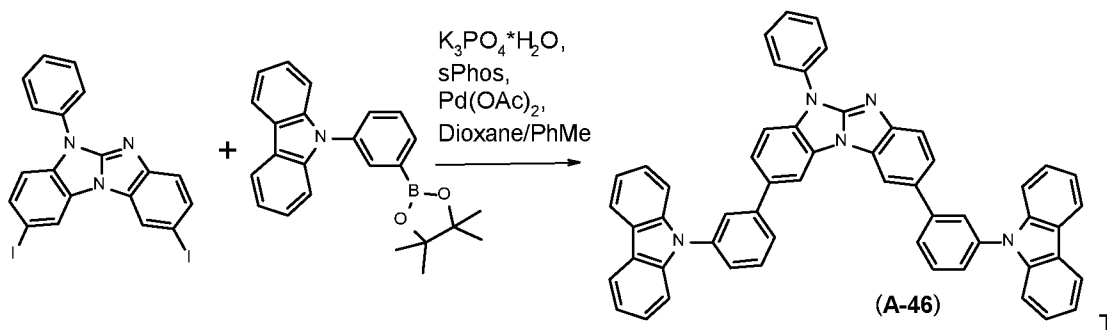
group consisting of



; wherein

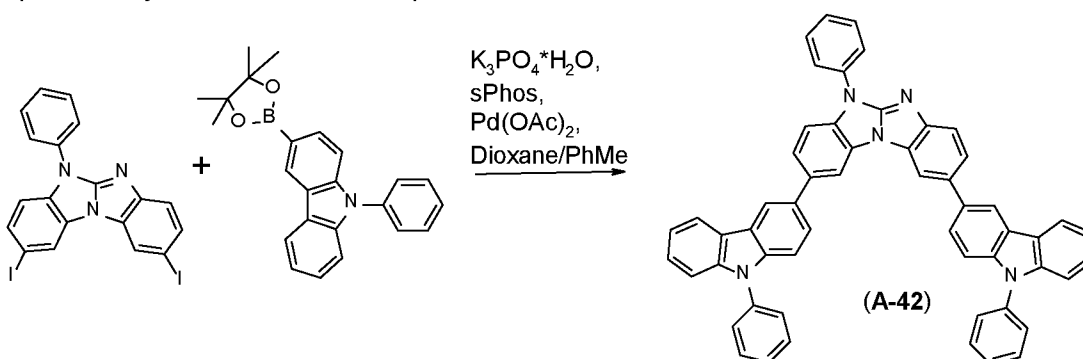
- The ligand is added in a ratio of from 1:1 to 1:10, based on Pd. Also preferred, the catalyst is added as in solution or suspension. Preferably, an appropriate organic solvent such as the ones described above, preferably benzene, toluene, xylene, THF, dioxane, more preferably toluene, or mixtures thereof, is used. The amount of solvent usually is chosen in the range of from 1 to 10 l per mol of boronic acid derivative. Organic bases, such as, for example, tetraalkylammonium hydroxide, and phase transfer catalysts, such as, for example TBAB, can promote the activity of the boron (see, for example, Leadbeater & Marco; *Angew. Chem. Int. Ed. Eng.* 42 (2003) 1407 and references cited therein). Other variations of reaction conditions are given by T. I. Wallow and B. M. Novak in *J. Org. Chem.* 59 (1994) 5034-5037; and M. Remmers, M. Schulze, G. Wegner in *Macromol. Rapid Commun.* 17 (1996) 239-252 and G. A. Molander und B. Canturk, *Angew. Chem.* , 121 (2009) 9404 – 9425.

A possible synthetic route for compound **A-46** is shown in the reaction scheme below:



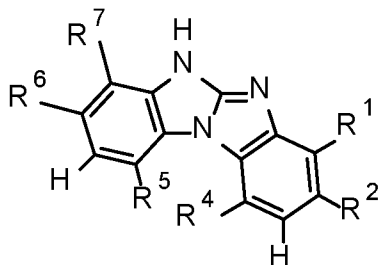
The synthesis of 9-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]carbazole is described in *Chem. Mater.* 20 (2008) 1691–1693.

- 20 A possible synthetic route for compound **A-42** is shown in the reaction scheme below:



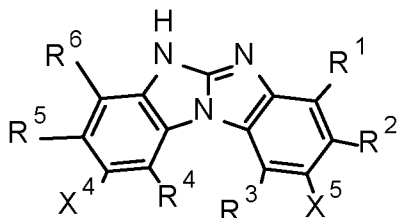
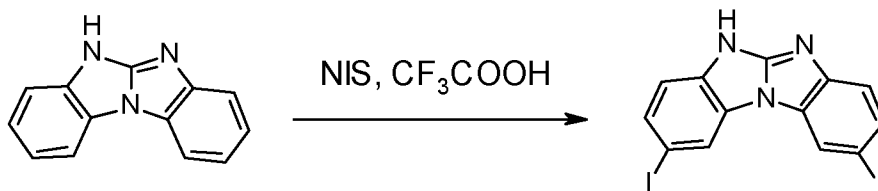
The synthesis of 9-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole is described in WO12023947.

The compound of formula (II) is prepared by halogenation of a compound of formula



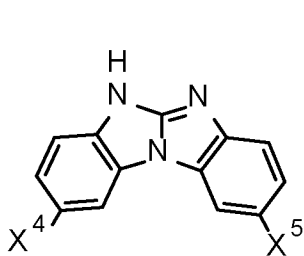
(IV).

5 Bishalogenation of benzimidazo[1,2-a]benzimidazole can be done, for example, with N-iodosuccinimide (NIS), N-bromosuccinimide, diacetoxyiodo benzene and iodine.

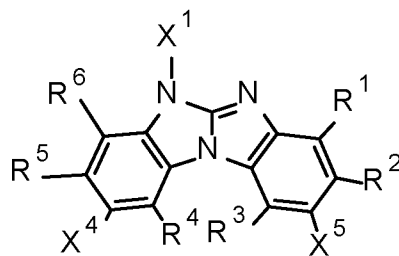


The compounds of formula

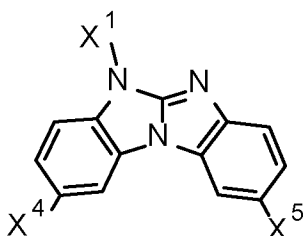
(II), especially



(IIa), and

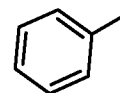


(III), especially

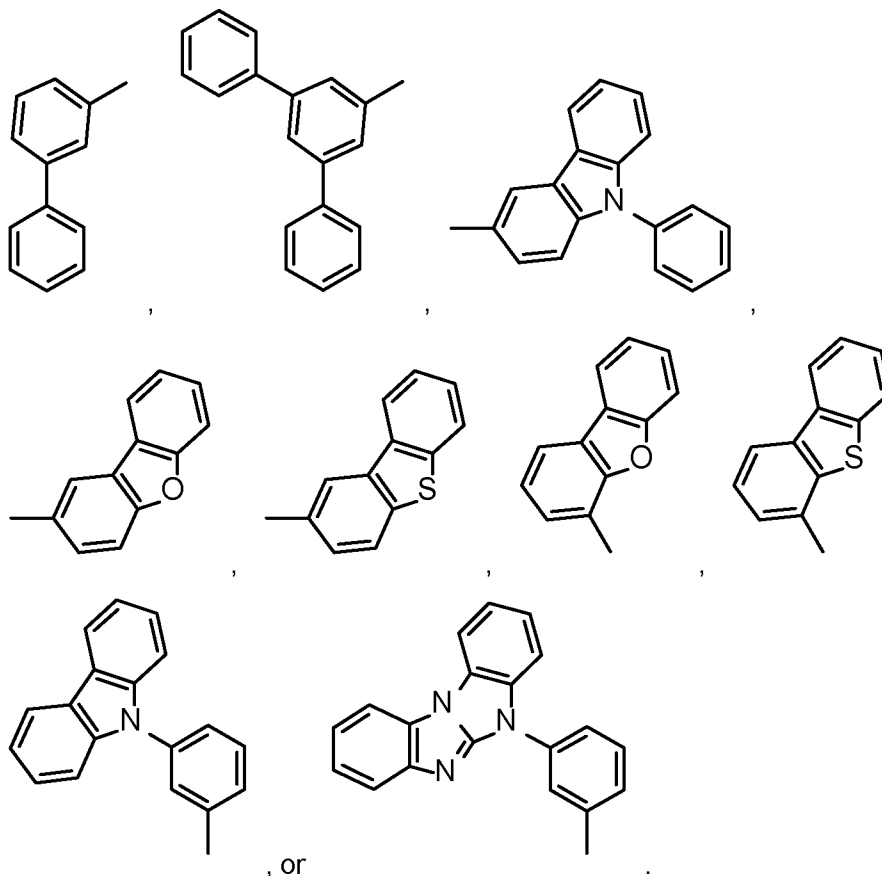


(IIIa) are intermediates in the production of the compounds of

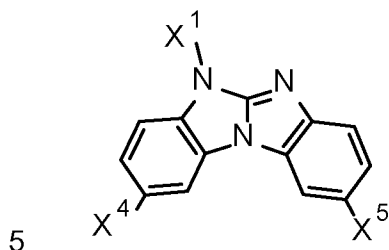
10 formula (I), are new and form a further subject of the present invention. X⁴ and X⁵ are independently of each other Cl, Br, or I. X⁴ and X⁵ are preferably I. R¹, R², R³, R⁴, R⁵, R⁶ and X¹ are defined above. For R¹, R², R³, R⁴, R⁵, R⁶ and X¹ the same preferences apply as in case



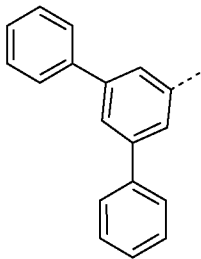
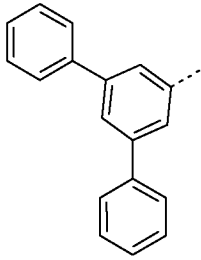
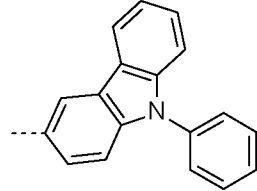
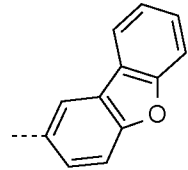
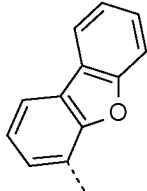
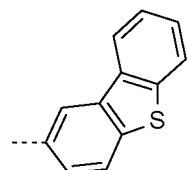
of the compounds of formula (I). Preferably, X¹ is a group of formula

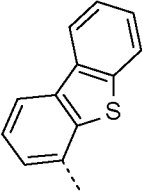
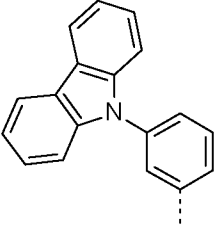
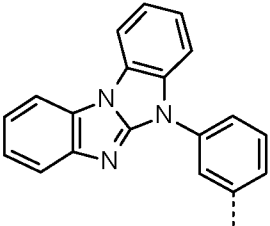


Examples of compounds of formula (II) and (III) are shown below:



Cpd.	X ¹	X ²	X ³
I-1	H	Cl	Cl
I-2	H	Br	Br
I-3	H	I	I
I-4		Cl	Cl
I-5	"	Br	Br
I-6	"	I	I
I-7		Cl	Cl
I-8	"	Br	Br
I-9	"	I	I

I-10		Cl	Cl
I-11	“	Br	Br
I-12	“	I	I
I-13		Cl	Cl
I-14	“	Br	Br
I-15	“	I	I
I-16		Cl	Cl
I-17	“	Br	Br
I-18	“	I	I
I-19		Cl	Cl
I-20	“	Br	Br
I-21	“	I	I
I-22		Cl	Cl
I-23	“	Br	Br
I-24	“	I	I
I-25		Cl	Cl
I-26	“	Br	Br
I-27	“	I	I

I-28		Cl	Cl
I-29	“	Br	Br
I-30	“	I	I
I-31		Cl	Cl
I-32	“	Br	Br
I-33	“	I	I
I-34		Cl	Cl
I-35	“	Br	Br
I-36	“	I	I

indicates the bonding to the benzimidazolo[1,2-a]benzimidazole.

It has been found that the compounds of the formula I are particularly suitable for use in applications in which charge carrier conductivity is required, especially for use in organic electronics applications, for example selected from switching elements such as organic transistors, e.g. organic FETs and organic TFTs, organic solar cells and organic light-emitting diodes (OLEDs), the compounds of the formula I being particularly suitable in OLEDs for use as matrix material in a light-emitting layer and/or as electron and/or exciton blocker material and/or as hole transport material, especially in combination with a phosphorescence emitter. In the case of use of the inventive compounds of the formula I in OLEDs, OLEDs which have good efficiencies and a long lifetime and which can be operated especially at a low use and operating voltage are obtained. The inventive compounds of the formula I are suitable especially for use as matrix and/or electron/exciton blocker materials for blue and green emitters, for example light blue or deep blue emitters, these being especially phosphorescence emitters. Furthermore, the compounds of the formula I can be used as conductor/complementary materials in organic electronics applications selected from switching elements and organic solar cells.

The compounds of the formula I can be used as matrix material and/or electron/exciton blocker material and/or hole transport material (hole conductor material). The inventive compounds of the formula I are preferably used as matrix materials in organic electronics applications, especially in OLEDs.

In the emission layer or one of the emission layers of an OLED, it is also possible to combine an emitter material with a matrix material of the compound of the formula I and a further matrix material which has, for example, a good electron transport property. This achieves a high quantum efficiency of this emission layer.

When a compound of the formula I is used as matrix (host) material in an emission layer and additionally as electron/exciton blocker material, owing to the chemical identity or similarity of the materials, an improved interface between the emission layer and the adjacent electron/exciton blocker material, which can lead to a decrease in the voltage with equal luminance and to an extension of the lifetime of the OLED. Moreover, the use of the same material for electron/exciton blocker material and for the matrix of an emission layer allows the production process of an OLED to be simplified, since the same source can be used for the vapor deposition process of the material of one of the compounds of the formula I.

Suitable structures of organic electronic devices are known to those skilled in the art and are specified below.

The organic transistor generally includes a semiconductor layer formed from an organic layer with charge transport capacity; a gate electrode formed from a conductive layer; and an insulating layer introduced between the semiconductor layer and the conductive layer. A source electrode and a drain electrode are mounted on this arrangement in order thus to produce the transistor element. In addition, further layers known to those skilled in the art may be present in the organic transistor.

The organic solar cell (photoelectric conversion element) generally comprises an organic layer present between two plate-type electrodes arranged in parallel. The organic layer may be configured on a comb-type electrode. There is no particular restriction regarding the site of the organic layer and there is no particular restriction regarding the material of the electrodes. When, however, plate-type electrodes arranged in parallel are used, at least one electrode is preferably formed from a transparent electrode, for example an ITO electrode or a fluorine-doped tin oxide electrode. The organic layer is formed from two sublayers, i.e. a layer with p-type semiconductor properties or hole transport capacity, and a layer formed with n-type semiconductor properties or charge transport capacity. In addition, it is possible for further layers known to those skilled in the art to be present in the organic solar cell. The layers with charge transport capacity may comprise the compounds of formula I.

It is likewise possible that the compounds of the formula I are present both in the light-emitting layer (preferably as matrix material) and in the blocking layers (as electron/exciton blockers).

The present invention further provides an organic light-emitting diode comprising an anode (a) and a cathode (i) and a light-emitting layer (e) arranged between the anode (a) and the cathode (i), and if appropriate at least one further layer selected from the group consisting of at least one blocking layer for holes/excitons, at least one blocking layer for electrons/excitons, at least one hole injection layer, at least one hole transport layer, at least

one electron injection layer and at least one electron transport layer, wherein the at least one compound of the formula I is present in the light-emitting layer (e) and/or in at least one of the further layers. The at least one compound of the formula I is preferably present in the light-emitting layer and/or the electron/exciton blocking layers.

5

In a preferred embodiment of the present invention, at least one compound of the formula I, especially a compound of the formula (Ia-1), is used as hole transport material. Examples of preferred compounds of formula I are compounds A-1 to A-64 and A-65 shown above. Compounds A-1, A-2, A-3, A-5, A-11, A-13, A-23, A-25, A-35, A-38, A-46 and A-59 and A-65 are particularly preferred.

10

In another preferred embodiment of the present invention, at least one compound of the formula I, especially a compound of the formula (Ia-1), is used as electron/exciton blocker material. Examples of preferred compounds of formula I are compounds A-1 to A-64 and A-65 shown above. Compounds A-1, A-2, A-3, A-5, A-11, A-13, A-23, A-25, A-35, A-38, A-46 and A-59 and A-65 are particularly preferred.

15

The present application further relates to a light-emitting layer comprising at least one compound of the formula I.

20

Structure of the inventive OLED

The inventive organic light-emitting diode (OLED) thus generally has the following structure:

25

an anode (a) and a cathode (i) and a light-emitting layer (e) arranged between the anode (a) and the cathode (i).

The inventive OLED may, for example - in a preferred embodiment - be formed from the following layers:

30

1. Anode (a)
2. Hole transport layer (c)
3. Light-emitting layer (e)
4. Blocking layer for holes/excitons (f)
5. Electron transport layer (g)

35

6. Cathode (i)

Layer sequences different than the aforementioned structure are also possible, and are known to those skilled in the art. For example, it is possible that the OLED does not have all of the layers mentioned; for example, an OLED with layers (a) (anode), (e) (light-emitting layer) and (i) (cathode) is likewise suitable, in which case the functions of the layers (c) (hole transport layer) and (f) (blocking layer for holes/excitons) and (g) (electron transport layer) are assumed by the adjacent layers. OLEDs which have layers (a), (c), (e) and (i), or layers (a), (e), (f), (g) and (i), are likewise suitable. In addition, the OLEDs may have a blocking layer for electrons/excitons (d) between the hole transport layer (c) and the Light-emitting layer (e).

40
45

It is additionally possible that a plurality of the aforementioned functions (electron/exciton blocker, hole/exciton blocker, hole injection, hole conduction, electron injection, electron conduction) are combined in one layer and are assumed, for example, by a single material present in this layer. For example, a material used in the hole transport layer, in one embodiment, may simultaneously block excitons and/or electrons.

Furthermore, the individual layers of the OLED among those specified above may in turn be formed from two or more layers. For example, the hole transport layer may be formed from a layer into which holes are injected from the electrode, and a layer which transports the holes away from the hole-injecting layer into the light-emitting layer. The electron conduction layer may likewise consist of a plurality of layers, for example a layer in which electrons are injected by the electrode, and a layer which receives electrons from the electron injection layer and transports them into the light-emitting layer. These layers mentioned are each selected according to factors such as energy level, thermal resistance and charge carrier mobility, and also energy difference of the layers specified with the organic layers or the metal electrodes. The person skilled in the art is capable of selecting the structure of the OLEDs such that it is matched optimally to the organic compounds used in accordance with the invention.

In a preferred embodiment the OLED according to the present invention comprises in this order:

- (a) an anode,
- (b) optionally a hole injection layer,
- (c) optionally a hole transport layer,
- (d) optionally an exciton blocking layer
- (e) an emitting layer,
- (f) optionally a hole/ exciton blocking layer
- (g) optionally an electron transport layer,
- (h) optionally an electron injection layer, and
- (i) a cathode.

In a particularly preferred embodiment the OLED according to the present invention comprises in this order:

- (a) an anode,
- (b) optionally a hole injection layer,
- (c) a hole transport layer,
- (d) an exciton blocking layer
- (e) an emitting layer,
- (f) a hole/ exciton blocking layer
- (g) an electron transport layer, and
- (h) optionally an electron injection layer, and
- (i) a cathode.

The properties and functions of these various layers, as well as example materials are known from the prior art and are described in more detail below on basis of preferred embodiments.

5

Anode (a):

The anode is an electrode which provides positive charge carriers. It may be composed, for example, of materials which comprise a metal, a mixture of different metals, a metal alloy, a metal oxide or a mixture of different metal oxides. Alternatively, the anode may be a
10 conductive polymer. Suitable metals comprise the metals of groups 11, 4, 5 and 6 of the Periodic Table of the Elements, and also the transition metals of groups 8 to 10. When the anode is to be transparent, mixed metal oxides of groups 12, 13 and 14 of the Periodic Table of the Elements are generally used, for example indium tin oxide (ITO). It is likewise possible that the anode (a) comprises an organic material, for example polyaniline, as
15 described, for example, in Nature, Vol. 357, pages 477 to 479 (June 11, 1992). Preferred anode materials include conductive metal oxides, such as indium tin oxide (ITO) and indium zinc oxide (IZO), aluminum zinc oxide (AlZnO), and metals. Anode (and substrate) may be sufficiently transparent to create a bottom-emitting device. A preferred transparent substrate and anode combination is commercially available ITO (anode) deposited on glass
20 or plastic (substrate). A reflective anode may be preferred for some top-emitting devices, to increase the amount of light emitted from the top of the device. At least either the anode or the cathode should be at least partly transparent in order to be able to emit the light formed. Other anode materials and structures may be used.

25 **Hole injection layer (b):**

Generally, injection layers are comprised of a material that may improve the injection of charge carriers from one layer, such as an electrode or a charge generating layer, into an adjacent organic layer. Injection layers may also perform a charge transport function. The hole injection layer may be any layer that improves the injection of holes from anode into an
30 adjacent organic layer. A hole injection layer may comprise a solution deposited material, such as a spin-coated polymer, or it may be a vapor deposited small molecule material, such as, for example, CuPc or MTDATA. Polymeric hole-injection materials can be used such as poly(N-vinylcarbazole) (PVK), polythiophenes, polypyrrole, polyaniline, self-doping polymers, such as, for example, sulfonated poly(thiophene-3-[2[(2-methoxyethoxy)ethoxy]-
35 2,5-diyl]) (Plexcore® OC Conducting Inks commercially available from Plextronics), and copolymers such as poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) also called PEDOT/PSS.

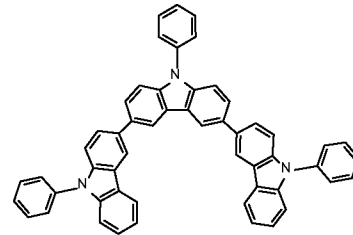
Hole transport layer (c):

40 Either hole-transporting molecules or polymers may be used as the hole transport material.

In a preferred embodiment of the present invention, at least one compound of the formula I, especially a compound of the formula (Ia-1), is used as hole transport material. Examples of preferred compounds of formula I are compounds A-1 to A-64 and A-65 shown above.

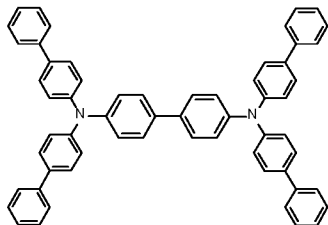
45 Compounds A-1, A-2, A-3, A-5, A-11, A-13, A-23, A-25, A-35, A-38, A-46 and A-59 and A-65 are particularly preferred.

Additional suitable hole transport materials for layer (c) of the inventive OLED are disclosed, for example, in Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Vol. 18, pages 837 to 860, 1996, US20070278938, US2008/0106190, US2011/0163302 (tri-aryl amines with (di)benzothiophen/(di)benzofuran; Nan-Xing Hu et al. Synth. Met. 111 (2000) 421 (indolocarbazoles), WO2010002850 (substituted phenylamine compounds) and WO2012/16601 (in particular the hole transport materials mentioned on pages 16 and 17 of WO2012/16601). Combination of different hole transport material may be used. Reference



(HTL1-1)

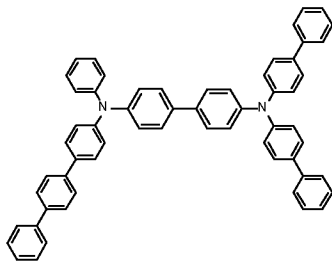
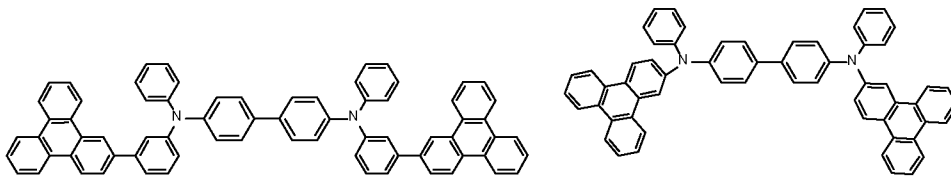
is made, for example, to WO2013/022419, wherein



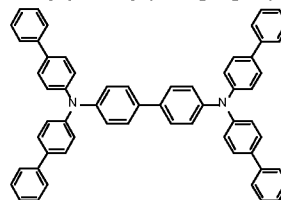
(HTL2-1) constitute the hole transport layer.

10

Customarily used hole-transporting molecules are selected from the group consisting of



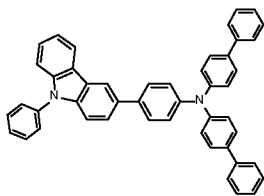
(4-phenyl-N-(4-phenylphenyl)-N-[4-[4-(N-[4-(4-phenyl-



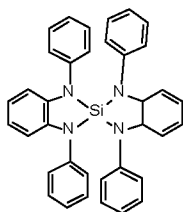
(4-phenyl-N-(4-

phenyl)phenyl]anilino)phenyl]phenyl]aniline),
phenyl)phenyl)-N-[4-[4-(4-phenyl-N-(4-phenylphenyl)anilino)phenyl]phenyl]aniline),

15

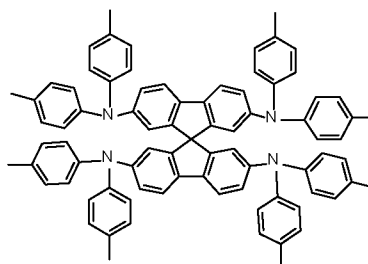


(4-phenyl-N-[4-(9-phenylcarbazol-3-yl)phenyl]-N-(4-



phenylphenyl)aniline),

(1,1',3,3'-tetraphenylspiro[1,3,2-benzodiazasilole-



2,2'-3a,7a-dihydro-1,3,2-benzodiazasilole]],

(N2,N2,N2',N2',N7,N7,N7',N7'-octakis(p-tolyl)-9,9'-spirobi[fluorene]-2,2',7,7'-tetramine), 4,4'-

bis[N-(1-naphthyl)-N-phenylamino]biphenyl (α -NPD), N,N'-diphenyl-N,N'-bis(3-

5 methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), 1,1-bis[(di-4-tolylamino)phenyl]-
cyclohexane (TAPC), N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl)-

biphenyl]-4,4'-diamine (ETPD), tetrakis(3-methylphenyl)-N,N,N',N'-2,5-phenylenediamine

(PDA), α -phenyl-4-N,N-diphenylaminostyrene (TPS), p-(diethylamino)benzaldehyde diphe-

nylhydrazone (DEH), triphenylamine (TPA), bis[4-(N,N-diethylamino)2-methylphenyl](4-

10 methylphenyl)methane (MPMP), 1-phenyl-3-[p-(diethylamino)styryl]5-[p-
(diethylamino)phenyl]pyrazoline (PPR or DEASP), 1,2-trans-bis(9H-carbazol9-yl)-

cyclobutane (DCZB), N,N,N',N'-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TTB),

fluorine compounds such as 2,2',7,7'-tetra(N,N-di-tolyl)amino-9,9'-spirobifluorene (spiro-

TTB), N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)9,9'-spirobifluorene (spiro-NPB) and 9,9-

15 bis(4-(N,N-bis-biphenyl-4-yl-amino)phenyl)-9Hfluorene, benzidine compounds such as N,N'-
bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine and porphyrin compounds such as copper

phthalocyanines. In addition, polymeric hole-injection materials can be used such as

poly(N-vinylcarbazole) (PVK), polythiophenes, polypyrrole, polyaniline, self-doping poly-

mers, such as, for example, sulfonated poly(thiophene-3-[2[(2-methoxyethoxy)ethoxy]-2,5-

20 diyl) (Plexcore® OC Conducting Inks commercially available from Plextronics), and copolymers such as poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) also called PE-
DOT/PSS. Preferred examples of a material of the hole injecting layer are a porphyrin

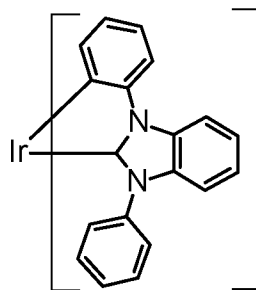
compound, an aromatic tertiary amine compound, or a styrylamine compound. Particu-

larly preferable examples include an aromatic tertiary amine compound such as hexa-

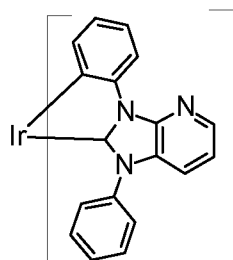
25 cyano-hexaazatriphenylene (HAT).

In a preferred embodiment it is possible to use metal carbene complexes as hole transport materials. Suitable carbene complexes are, for example, carbene complexes as described in WO2005/019373A2, WO2006/056418 A2, WO2005/113704, WO2007/115970,

30 WO2007/115981, WO2008/000727 and PCT/EP2014/055520. One example of a suitable



carbene complex is Ir(DPBIC)₃ with the formula: $\text{Ir}(\text{DPBIC})_3$ (HTM-1). Another example of a suitable carbene complex is Ir(ABIC)₃ with the



la: $\text{Ir}(\text{ABIC})_3$ (HTM-2).

- 5 The hole-transporting layer may also be electronically doped in order to improve the transport properties of the materials used, in order firstly to make the layer thicknesses more generous (avoidance of pinholes/short circuits) and in order secondly to minimize the operating voltage of the device. Electronic doping is known to those skilled in the art and is disclosed, for example, in W. Gao, A. Kahn, J. Appl. Phys., Vol. 94, 2003, 359 (p-doped organic layers); A. G. Werner, F. Li, K. Harada, M. Pfeiffer, T. Fritz, K. Leo, Appl. Phys. Lett., Vol. 82, No. 25, 2003, 4495 and Pfeiffer et al., Organic Electronics 2003, 4, 89 - 103 and K. Walzer, B. Maennig, M. Pfeiffer, K. Leo, Chem. Soc. Rev. 2007, 107, 1233. For example it is possible to use mixtures in the hole-transporting layer, in particular mixtures which lead to electrical p-doping of the hole-transporting layer. p-Doping is achieved by the
- 10 addition of oxidizing materials. These mixtures may, for example, be the following mixtures: mixtures of the abovementioned hole transport materials with at least one metal oxide, for example MoO₂, MoO₃, WO_x, ReO₃ and/or V₂O₅, preferably MoO₃ and/or ReO₃, more preferably MoO₃, or mixtures comprising the aforementioned hole transport materials and one or more compounds selected from 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ), 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane, bis(tetra-n-butylammonium)tetracyanodiphenodimethane, 2,5-dimethyl-7,7,8,8-tetracyanoquinodimethane, tetracyanoethylene, 11,11,12,12-tetracyanonaphtho[2,6]-quinodimethane, 2-fluoro-7,7,8,8-tetracyanoquinodimethane, 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane, dicyanomethylene-1,3,4,5,7,8-hexafluoro-6H-naphthalen-2-ylidene)malononitrile (F₆-TNAP), Mo(tfd)₃ (from Kahn et al., J. Am. Chem. Soc. 2009, 131 (35), 12530–12531), compounds as described in EP1988587, US2008265216, EP2180029, US20100102709, WO2010132236, EP2180029 and quinone compounds as mentioned in EP2401254. Preferred mixtures comprise the aforementioned carbene complexes, such as, for example, the carbene complexes HTM-1 and HTM-2, and MoO₃ and/or ReO₃, especially MoO₃. In a particularly preferred embodiment the hole transport layer comprises from 0.1 to 10 wt % of MoO₃ and 90 to 99.9 wt % carbene complex, especially of the carbene complex HTM-1 and HTM-2, wherein the total amount of the MoO₃ and the carbene complex is 100 wt %.
- 15
- 20
- 25
- 30

Exciton blocking layer (d):

Blocking layers may be used to reduce the number of charge carriers (electrons or holes) and/or excitons that leave the emissive layer. An electron/exciton blocking layer (d) may be disposed between the first emitting layer (e) and the hole transport layer (c), to block electrons from emitting layer (e) in the direction of hole transport layer (c). Blocking layers may also be used to block excitons from diffusing out of the emissive layer. Suitable metal complexes for use as electron/exciton blocker material are, for example, carbene complexes as described in WO2005/019373A2, WO2006/056418A2, WO2005/113704, WO2007/115970, WO2007/115981, WO2008/000727 and PCT/EP2014/055520. Explicit reference is made here to the disclosure of the WO applications cited, and these disclosures shall be considered to be incorporated into the content of the present application. One example of a suitable carbene complex is compound **HTM-1** and **HTM-2**.

In a preferred embodiment of the present invention, at least one compound of the formula I, especially a compound of the formula (**Ia-1**), is used as electron/exciton blocker material. Examples of preferred compounds of formula I are compounds **A-1** to **A-64** and **A-65** shown above. Compounds **A-1**, **A-2**, **A-3**, **A-5**, **A-11**, **A-13**, **A-23**, **A-25**, **A-35**, **A-38**, **A-46** and **A-59** and **A-65** are particularly preferred.

Emitting layer (e)

The light-emitting layer (e) comprises at least one emitter material. In principle, it may be a fluorescence or phosphorescence emitter, suitable emitter materials being known to those skilled in the art. The at least one emitter material is preferably a phosphorescence emitter. The phosphorescence emitter compounds used with preference are based on metal complexes, and especially the complexes of the metals Ru, Rh, Ir, Pd and Pt, in particular the complexes of Ir, have gained significance. The compounds of the formula I can be used as the matrix in the light-emitting layer.

Suitable metal complexes for use in the inventive OLEDs are described, for example, in documents 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, WO10086089, US2011/0057559, WO2011/106344, US2011/0233528, WO2012/048266 and WO2012/172482.

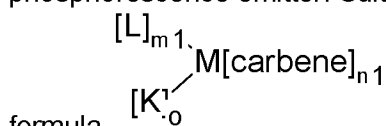
Further suitable metal complexes are the commercially available metal complexes tris(2-phenylpyridine)iridium(III), iridium(III) tris(2-(4-tolyl)pyridinato-N,C^{2'}), bis(2-phenylpyridine)(acetylacetonato)iridium(III), iridium(III) tris(1-phenylisoquinoline), iridium(III) bis(2,2'-benzothienyl)pyridinato-N,C^{3'})(acetylacetonate), tris(2-phenylquinoline)iridium(III), iridium(III) bis(2-(4,6-difluorophenyl)pyridinato-N,C^{2'})picolinate, iridium(III) bis(1-phenylisoquinoline)(acetylacetonate), bis(2-phenylquinoline)(acetylacetonato)iridium(III), iridium(III) bis(di-benzof[h]quinoxaline)(acetylacetonate), iridium(III) bis(2-methyl-di-

benzo[f,h]quinoxaline)(acetylacetonate) and tris(3-methyl-1-phenyl-4-trimethylacetyl-5-pyrazolino)terbium(III), bis[1-(9,9-dimethyl-9H-fluoren-2-yl)isoquinoline](acetylacetonato)iridium(III), bis(2-phenylbenzothiazolato)(acetylacetonato)iridium(III), bis(2-(9,9-dihexylfluorenyl)-1-pyridine)(acetylacetonato)iridium(III), bis(2-benzo[b]thiophen-2-ylpyridine)(acetylacetonato)iridium(III).

In addition, the following commercially available materials are suitable:
 tris(dibenzoylacetonato)mono(phenanthroline)europium(III), tris(dibenzoylmethane)-mono(phenanthroline)europium(III), tris(dibenzoylmethane)mono(5-aminophenanthroline)-europium(III), tris(di-2-naphthoylmethane)mono(phenanthroline)europium(III), tris(4-bromobenzoylmethane)mono(phenanthroline)europium(III), tris(di(biphenyl)methane)-mono(phenanthroline)europium(III), tris(dibenzoylmethane)mono(4,7-diphenylphenanthroline)europium(III), tris(dibenzoylmethane)mono(4,7-di-methylphenanthroline)europium(III), tris(dibenzoylmethane)mono(4,7-dimethylphenanthroline)disulfonic acid)europium(III) disodium salt, tris[di(4-(2-(2-ethoxyethoxy)ethoxy)benzoylmethane)]mono(phenanthroline)europium(III) and tris[di[4-(2-(2-ethoxyethoxy)ethoxy)benzoylmethane)]mono(5-aminophenanthroline)europium(III), osmium(II) bis(3-(trifluoromethyl)-5-(4-tert-butylpyridyl)-1,2,4-triazolato)diphenylmethylphosphine, osmium(II) bis(3-(trifluoromethyl)-5-(2-pyridyl)-1,2,4-triazole)dimethylphenylphosphine, osmium(II) bis(3-(trifluoromethyl)-5-(4-tert-butylpyridyl)-1,2,4-triazolato)dimethylphenylphosphine, osmium(II) bis(3-(trifluoromethyl)-5-(2-pyridyl)pyrazolato)dimethylphenylphosphine, tris[4,4'-di-tert-butyl(2,2')-bipyridine]ruthenium(III), osmium(II) bis(2-(9,9-dibutylfluorenyl)-1-isoquinoline)(acetylacetonate).

Preferred phosphorescence emitters are carbene complexes. Suitable phosphorescent blue emitters are specified in the following publications: WO2006/056418A2, WO2005/113704, WO2007/115970, WO2007/115981, WO2008/000727, WO2009050281, WO2009050290, WO2011051404, US2011/057559 WO2011/073149, WO2012/121936A2, US2012/0305894A1, WO2012/170571, WO2012/170461, WO2012/170463, WO2006/121811, WO2007/095118, WO2008/156879, WO2008/156879, WO2010/068876, US2011/0057559, WO2011/106344, US2011/0233528, WO2012/048266, WO2012/172482, PCT/EP2014/064054 and PCT/EP2014/066272.

Preferably, the light emitting layer (e) comprises at least one carbene complex as phosphorescence emitter. Suitable carbene complexes are, for example, compounds of the



formula (IX), which are described in WO 2005/019373 A2, wherein the symbols have the following meanings:

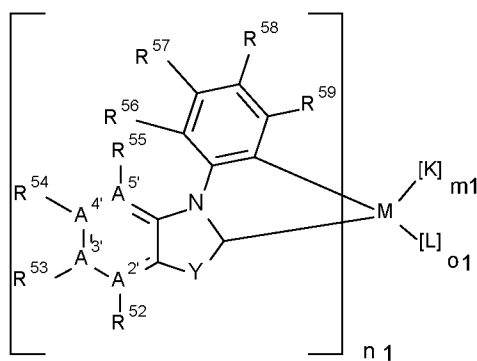
M is a metal atom selected from the group consisting of Co, Rh, Ir, Nb, Pd, Pt, Fe, Ru, Os, Cr, Mo, W, Mn, Tc, Re, Cu, Ag and Au in any oxidation state possible for the respective metal atom;

Carbene is a carbene ligand which may be uncharged or monoanionic and monodentate, bidentate or tridentate, with the carbene ligand also being able to be a biscarbene or triscarbene ligand;

L is a monoanionic or dianionic ligand, which may be monodentate or bidentate;

- K is an uncharged monodentate or bidentate ligand selected from the group consisting of phosphines; phosphonates and derivatives thereof, arsenates and derivatives thereof; phosphites; CO; pyridines; nitriles and conjugated dienes which form a π complex with M¹;
- n₁ is the number of carbene ligands, where n₁ is at least 1 and when n₁ > 1 the carbene ligands in the complex of the formula I can be identical or different;
- 5 m₁ is the number of ligands L, where m₁ can be 0 or ≥ 1 and when m₁ > 1 the ligands L can be identical or different;
- o is the number of ligands K, where o can be 0 or ≥ 1 and when o > 1 the ligands K can be identical or different;
- 10 where the sum n₁ + m₁ + o is dependent on the oxidation state and coordination number of the metal atom and on the denticity of the ligands carbene, L and K and also on the charge on the ligands, carbene and L, with the proviso that n₁ is at least 1.

More preferred are metal-carbene complexes of the general formula

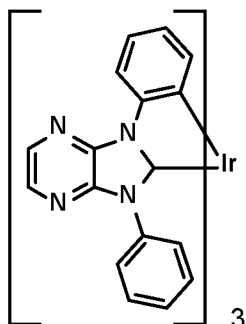


- 15 (IXa), which are described in WO2011/073149,

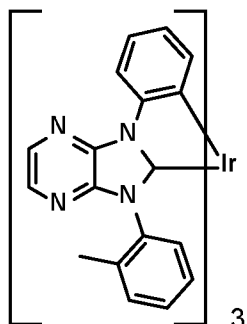
where M, n₁, Y, A^{2'}, A^{3'}, A^{4'}, A^{5'}, R⁵¹, R⁵², R⁵³, R⁵⁴, R⁵⁵, R⁵⁶, R⁵⁷, R⁵⁸, R⁵⁹, K, L, m₁ and o₁ are each defined as follows:

- M is Ir, or Pt,
- n₁ is an integer selected from 1, 2 and 3,
- 20 Y is NR⁵¹, O, S or C(R²⁵)₂,
- A^{2'}, A^{3'}, A^{4'}, and A^{5'} are each independently N or C, where 2 A' = nitrogen atoms and at least one carbon atom is present between two nitrogen atoms in the ring,
- R⁵¹ is a linear or branched alkyl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 1 to 20 carbon atoms, cycloalkyl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 3 to 20 carbon atoms, substituted or unsubstituted aryl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 6 to 30 carbon atoms, substituted or unsubstituted heteroaryl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having a total of 5 to 18 carbon atoms and/or heteroatoms,
- 30 R⁵², R⁵³, R⁵⁴ and R⁵⁵ are each, if A^{2'}, A^{3'}, A^{4'} and/or A^{5'} is N, a free electron pair, or, if A^{2'}, A^{3'}, A^{4'} and/or A^{5'} is C, each independently hydrogen, linear or branched alkyl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 1 to 20 carbon atoms, cycloalkyl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 3 to 20 carbon atoms, substituted or unsubstituted aryl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 6 to 30 carbon atoms, substituted or unsubstituted heteroaryl radical optionally interrupted by at least one het-

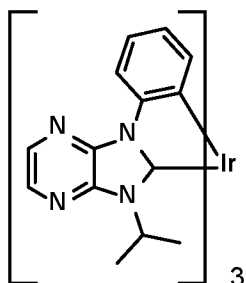
- eroatom, optionally bearing at least one functional group and having a total of 5 to 18 carbon atoms and/or heteroatoms, group with donor or acceptor action, or
R⁵³ and R⁵⁴ together with A³ and A⁴ form an optionally substituted, unsaturated ring optionally interrupted by at least one further heteroatom and having a total of 5 to 18 carbon atoms and/or heteroatoms,
- 5 R⁵⁶, R⁵⁷, R⁵⁸ and R⁵⁹ are each independently hydrogen, linear or branched alkyl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 1 to 20 carbon atoms, cycloalkyl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 3 to 20 carbon atoms, cycloheteroalkyl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 3 to 20 carbon atoms, substituted or unsubstituted aryl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 6 to 30 carbon atoms, substituted or unsubstituted heteroaryl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having a total of 5 to 18 carbon atoms and/or heteroatoms, group with donor or acceptor action, or
- 10 R⁵⁶ and R⁵⁷, R⁵⁷ and R⁵⁸ or R⁵⁸ and R⁵⁹, together with the carbon atoms to which they are bonded, form a saturated, unsaturated or aromatic, optionally substituted ring optionally interrupted by at least one heteroatom and having a total of 5 to 18 carbon atoms and/or heteroatoms, and/or
- 15 if A⁵¹ is C, R⁵⁵ and R⁵⁶ together form a saturated or unsaturated, linear or branched bridge optionally comprising heteroatoms, an aromatic unit, heteroaromatic unit and/or functional groups and having a total of 1 to 30 carbon atoms and/or heteroatoms, to which is optionally fused a substituted or unsubstituted, five- to eight-membered ring comprising carbon atoms and/or heteroatoms,
- 20 R²⁵ is independently a linear or branched alkyl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 1 to 20 carbon atoms, cycloalkyl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 3 to 20 carbon atoms, substituted or unsubstituted aryl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having 6 to 30 carbon atoms, substituted or unsubstituted heteroaryl radical optionally interrupted by at least one heteroatom, optionally bearing at least one functional group and having a total of 5 to 18 carbon atoms and/or heteroatoms,
- 25 K is an uncharged mono- or bidentate ligand,
- 30 L is a mono- or dianionic ligand, preferably monoanionic ligand, which may be mono- or bidentate,
- 35 m₁ is 0, 1 or 2, where, when m₁ is 2, the K ligands may be the same or different, o₁ is 0, 1 or 2, where, when o₁ is 2, the L ligands may be the same or different.
- 40 The compound of formula IX is preferably a compound of the formula:



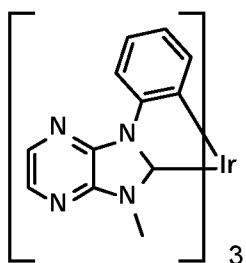
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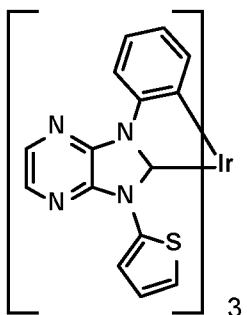
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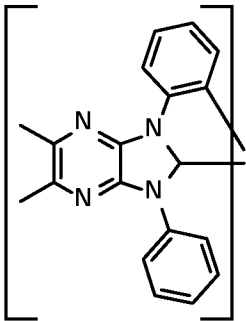
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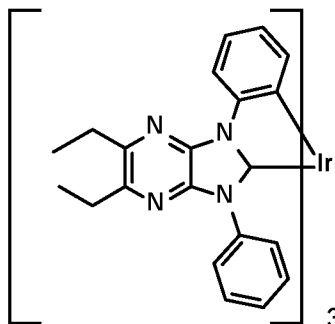
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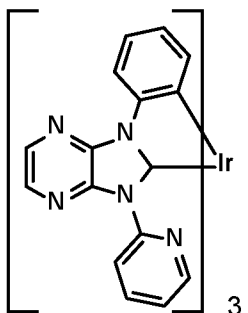
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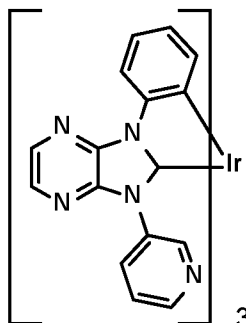
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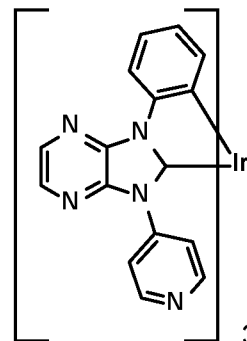
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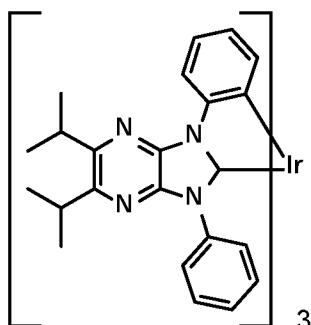
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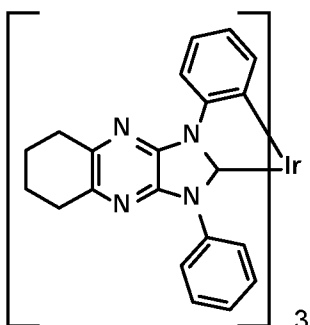
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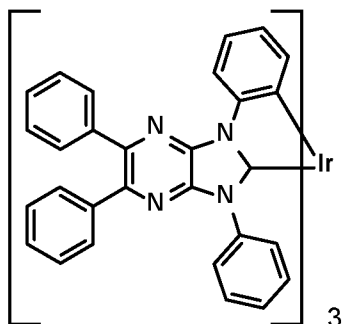
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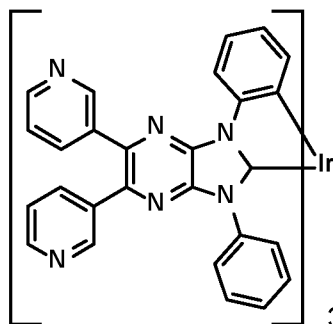
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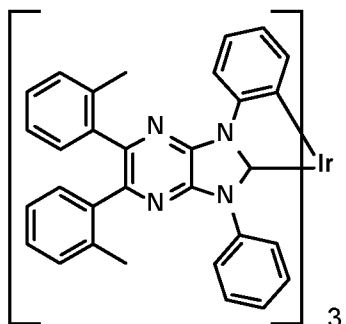
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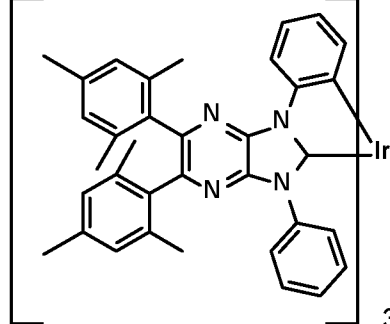
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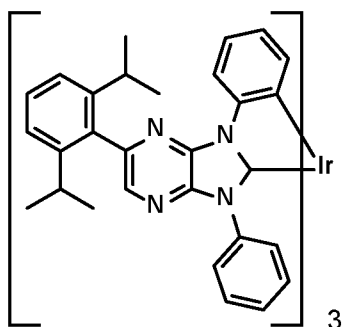
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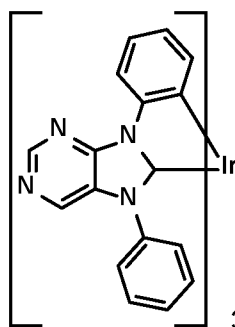
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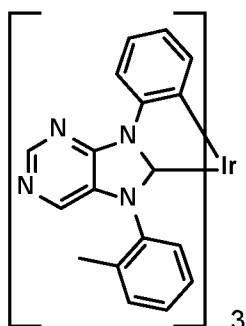
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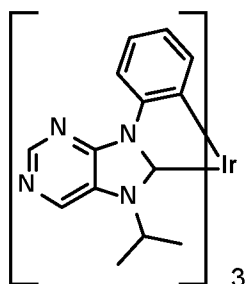
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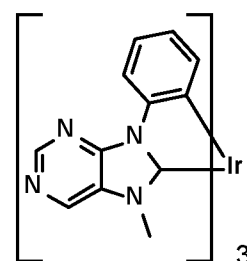
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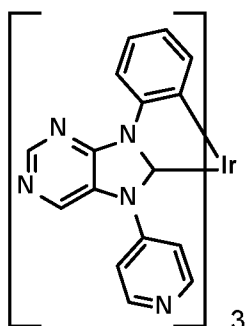
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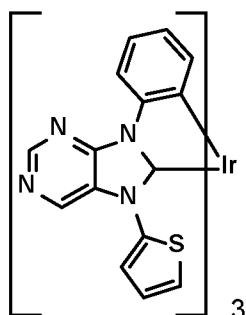
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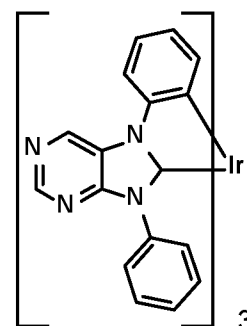
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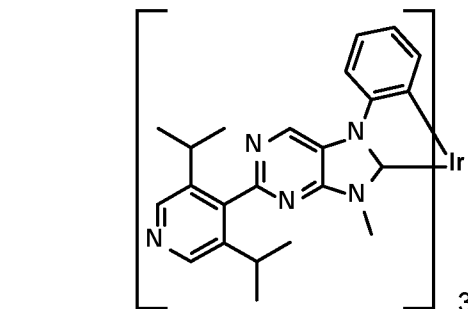
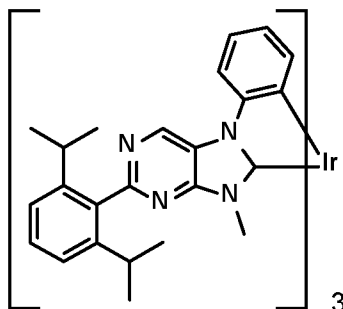
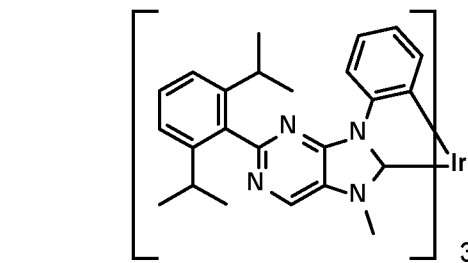
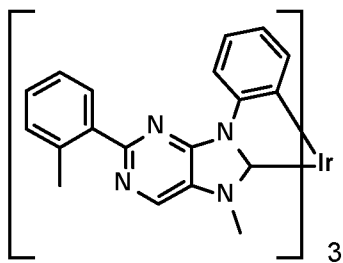
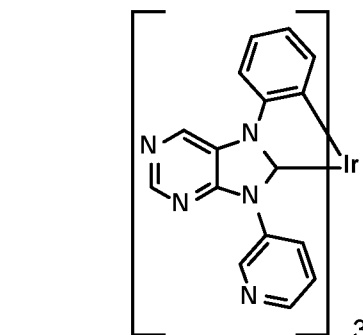
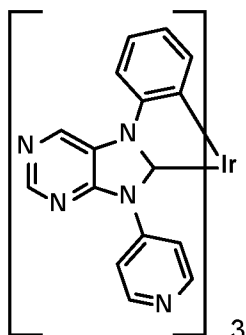
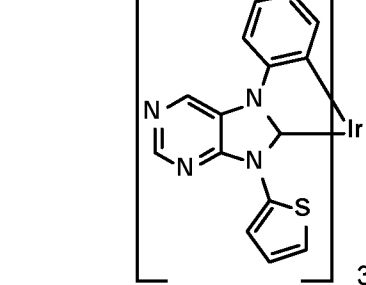
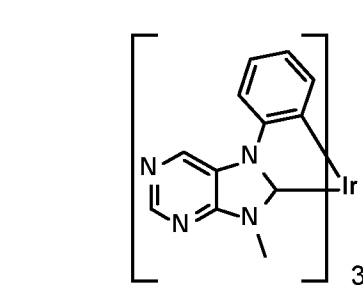
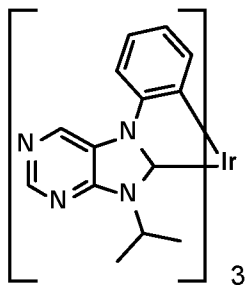
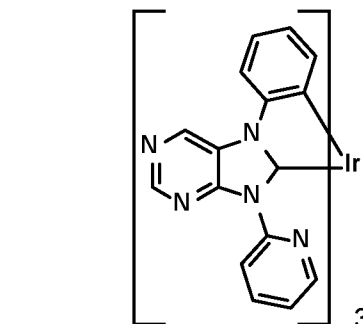
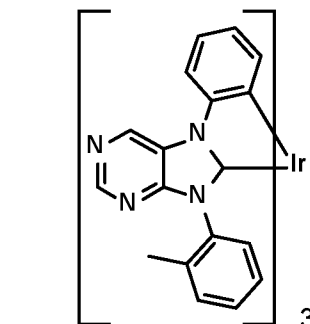
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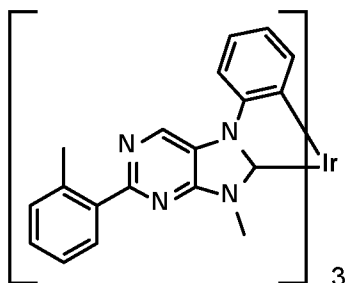


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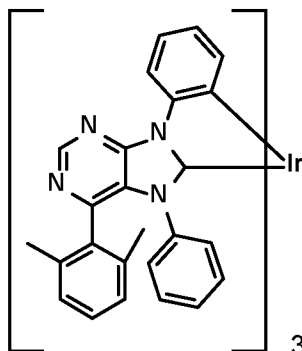


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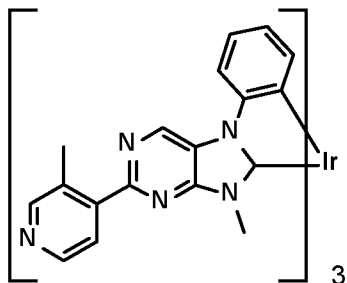




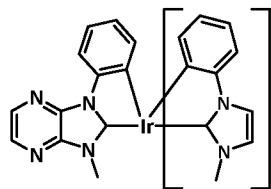
(BE-36),



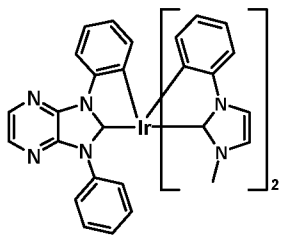
(BE-37),



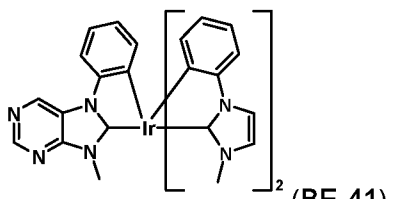
(BE-38),



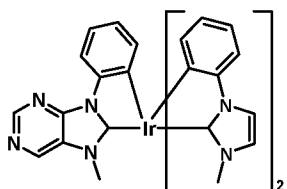
(BE-39),



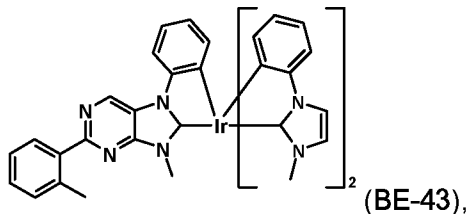
(BE-40),



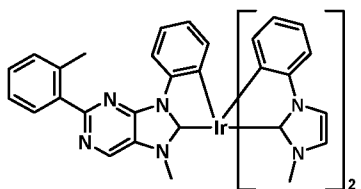
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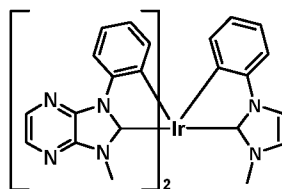
(BE-42),



(BE-43),

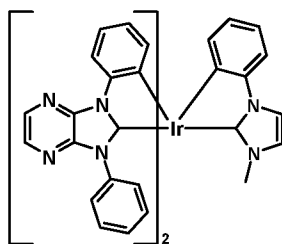


(BE-44),

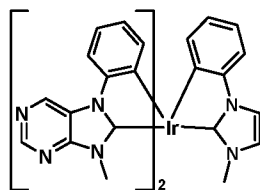


(BE-45),

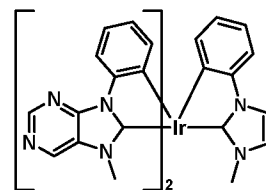
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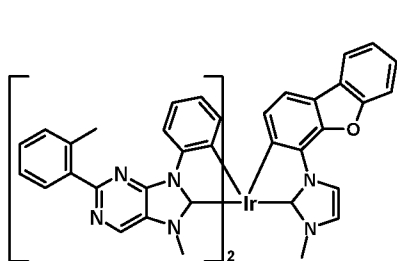
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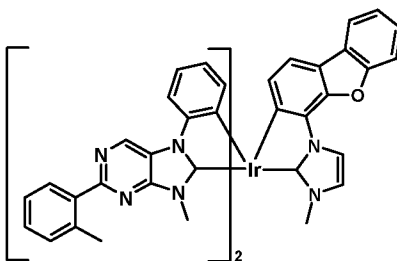
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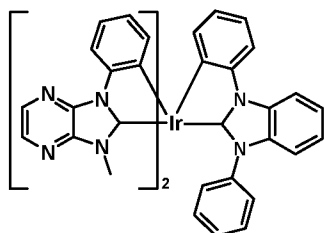
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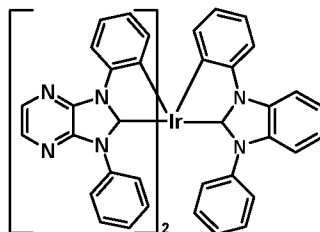
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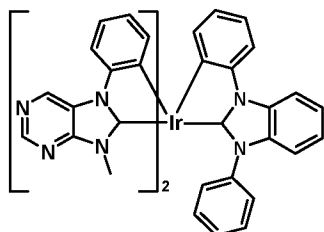
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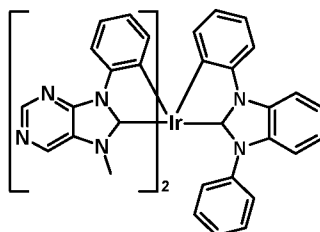
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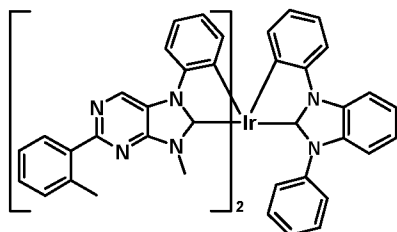
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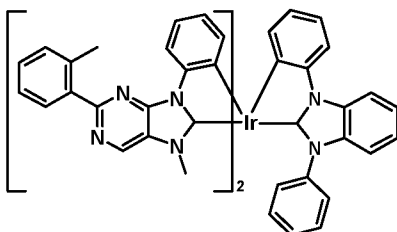
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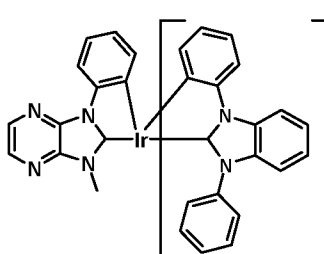
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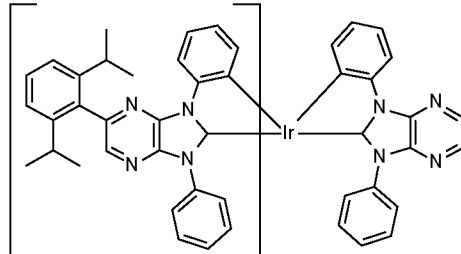
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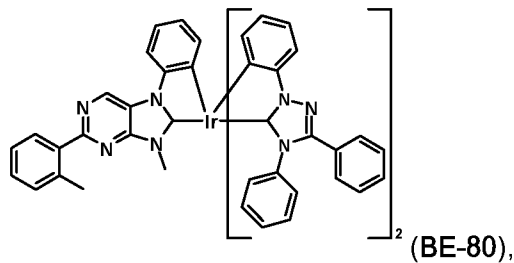
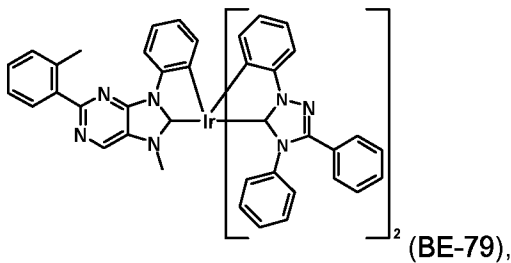
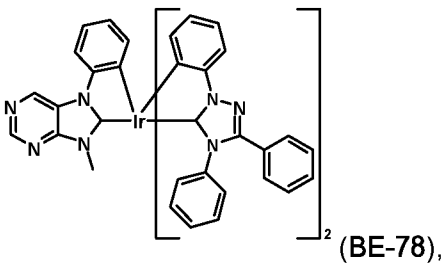
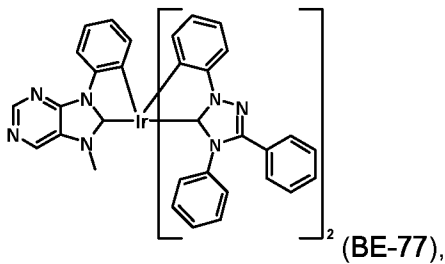
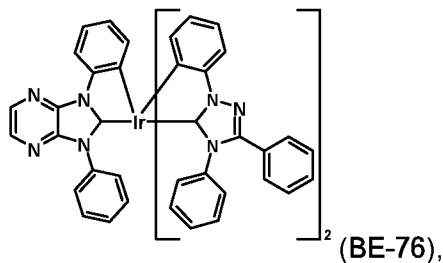
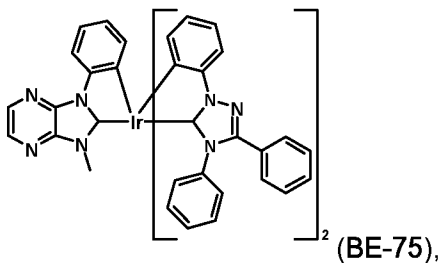
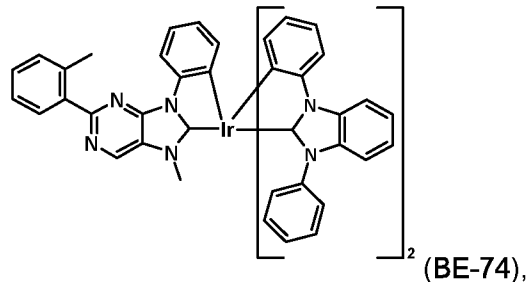
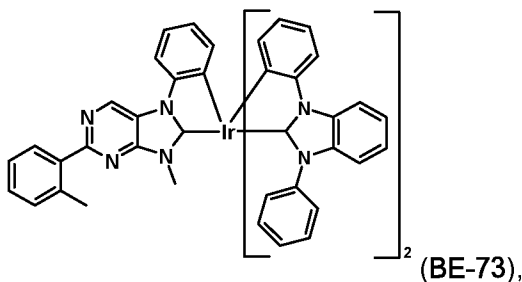
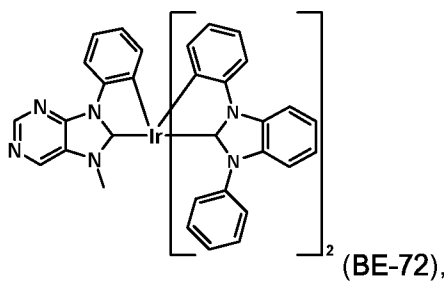
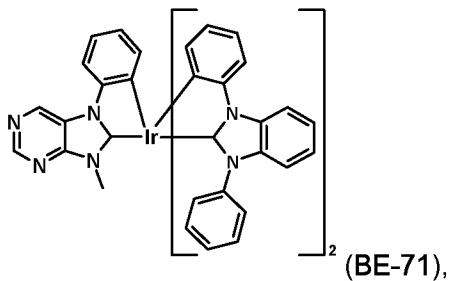
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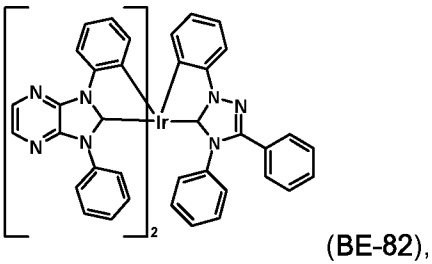
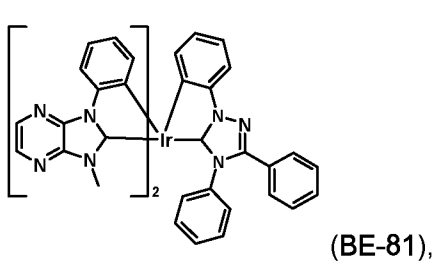
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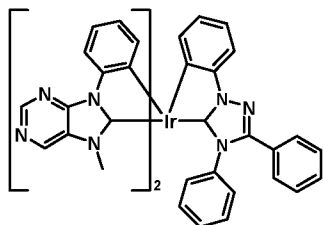


(BE-70),

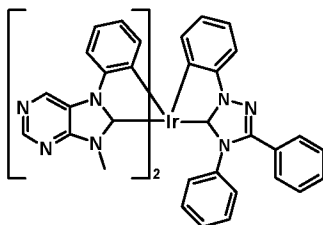


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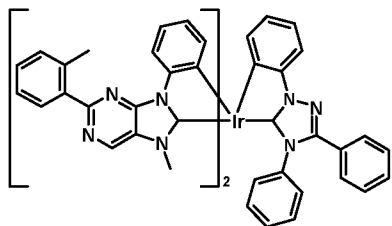




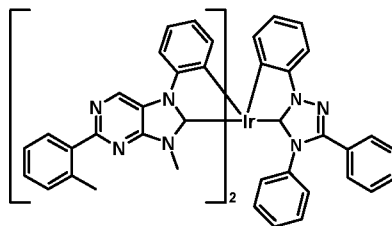
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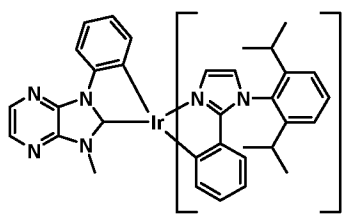
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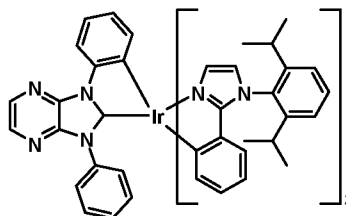
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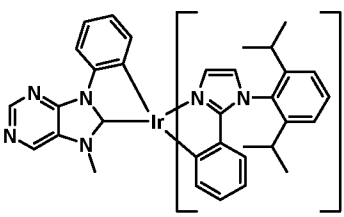
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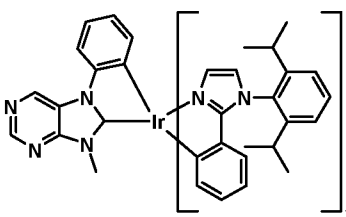
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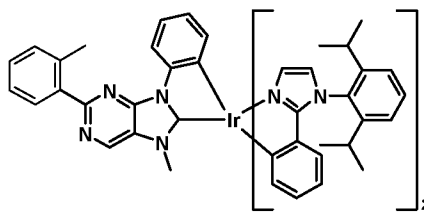
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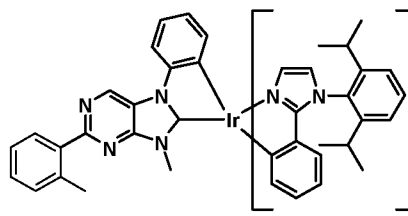
(BE-88),



(BE-89),

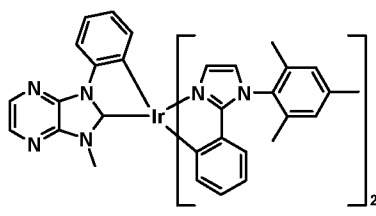


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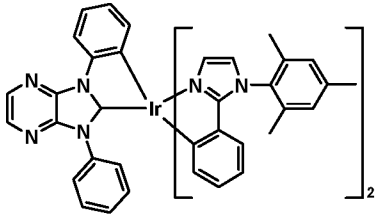


(BE-91),

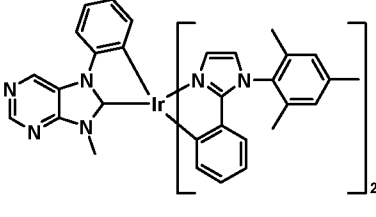
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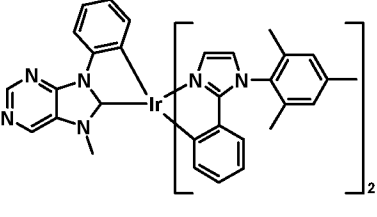
(BE-92),



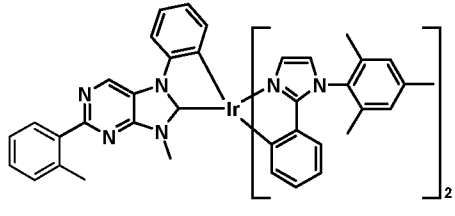
(BE-93),



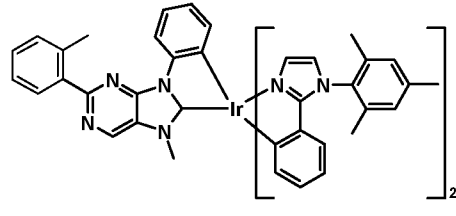
(BE-94),



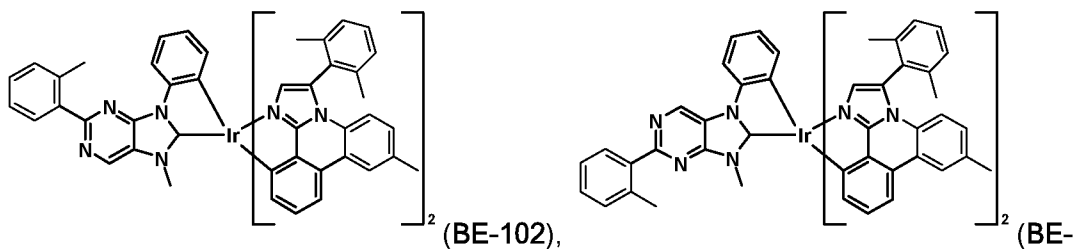
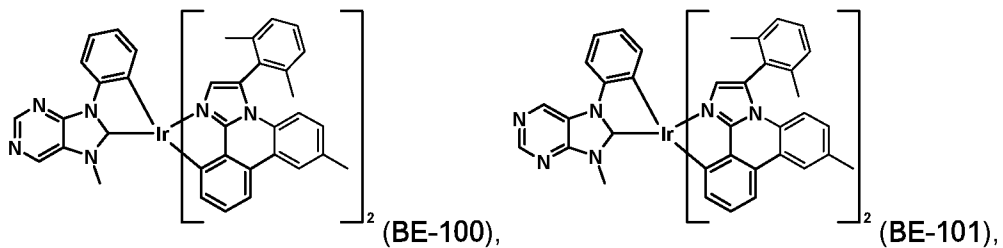
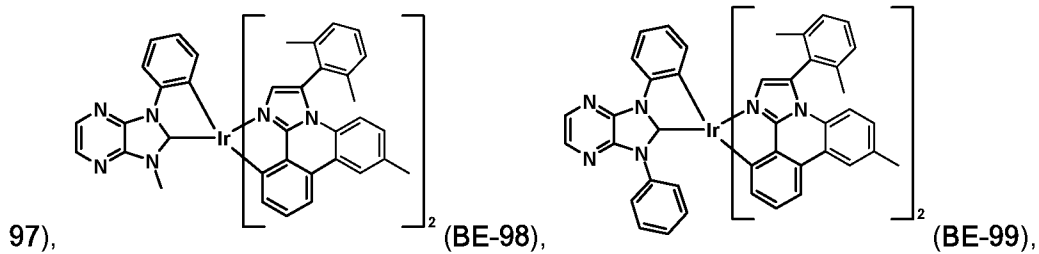
(BE-95),



(BE-96),

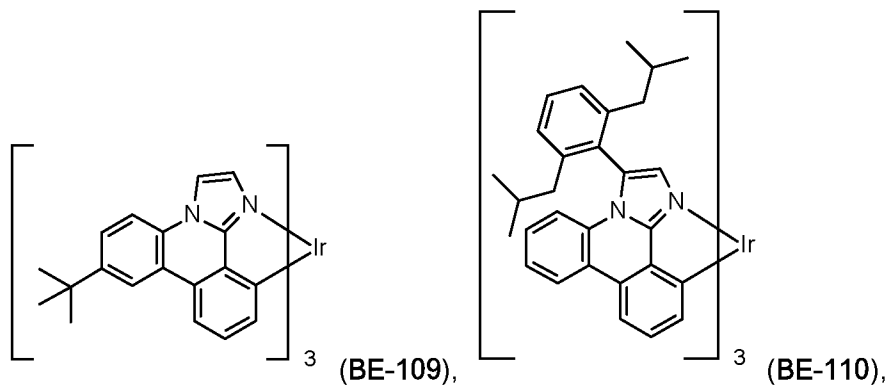
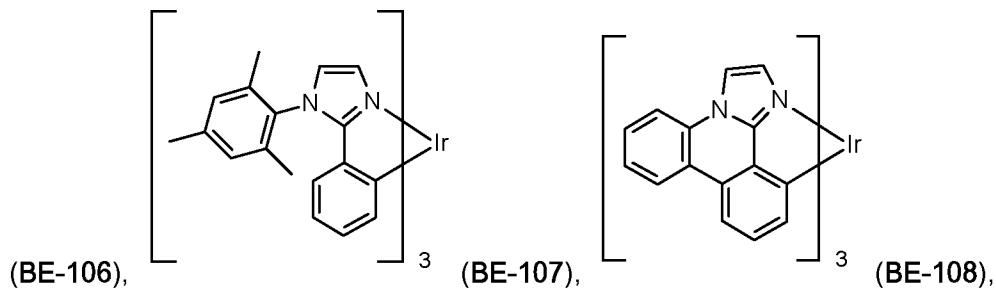
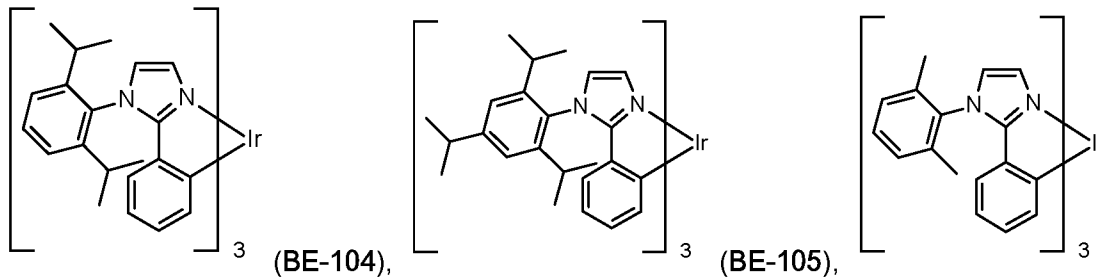


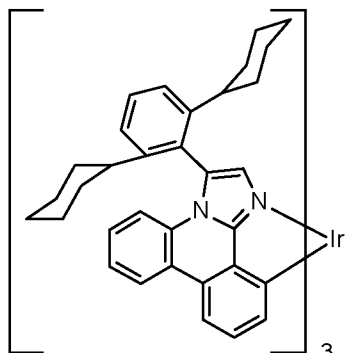
(BE-



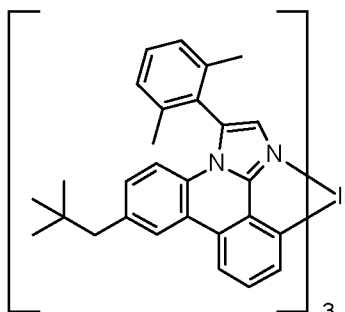
103).

5 Further suitable non-carbene emitter materials are mentioned below:

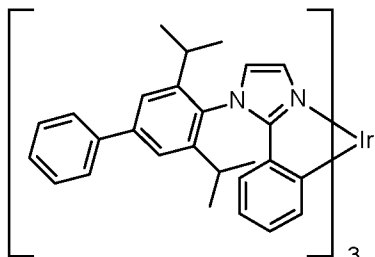




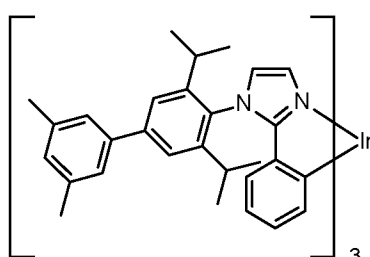
(BE-111),



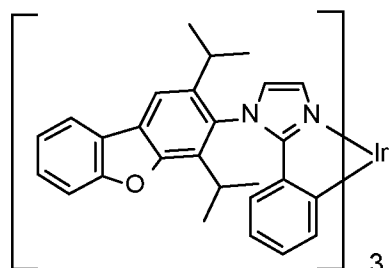
(BE-112),



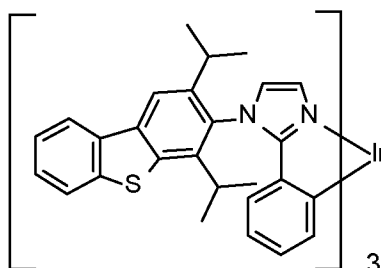
(BE-113),



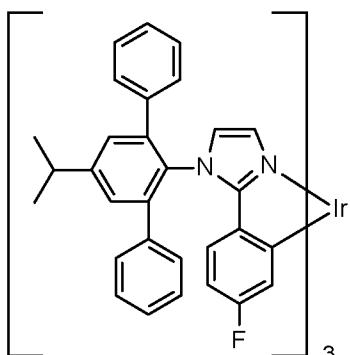
(BE-114),



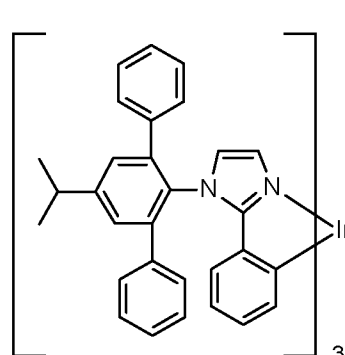
(BE-115),



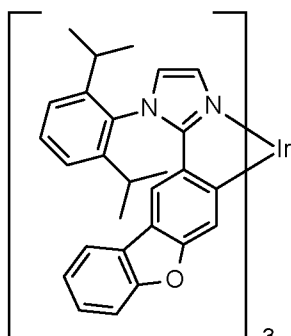
(BE-116),



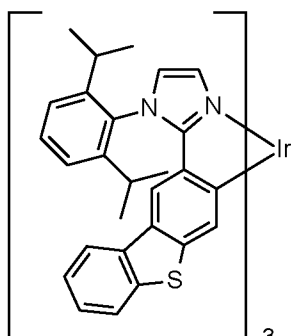
(BE-117),



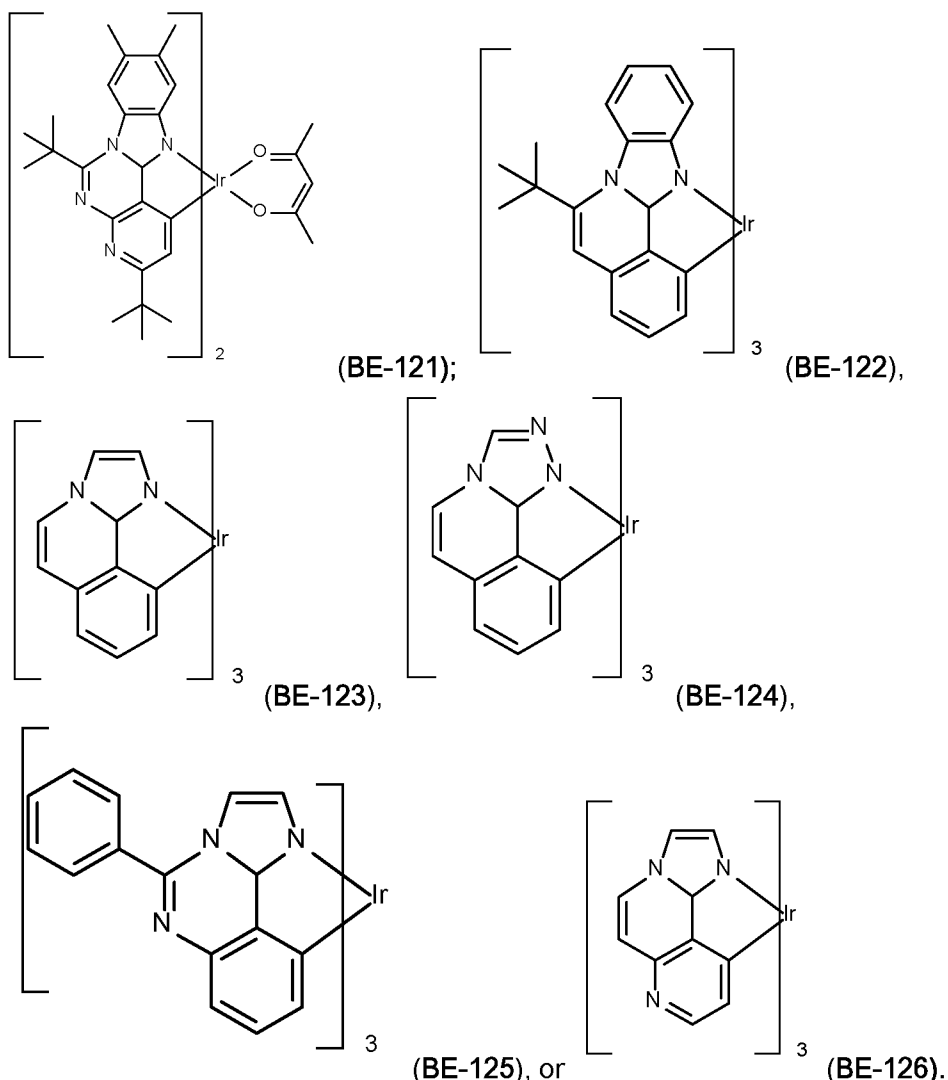
(BE-118),



(BE-119),



(BE-120),



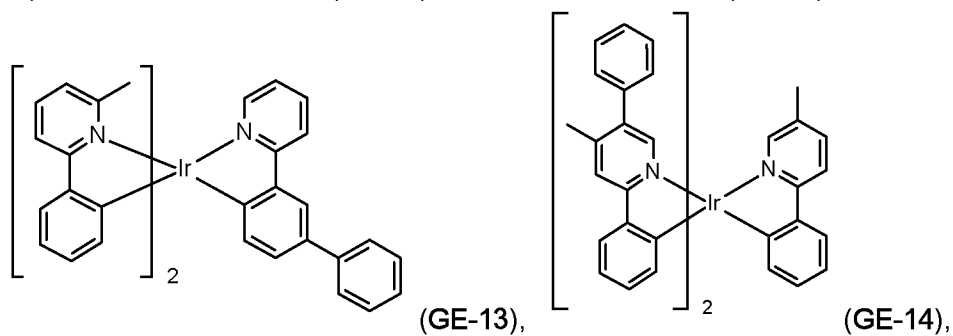
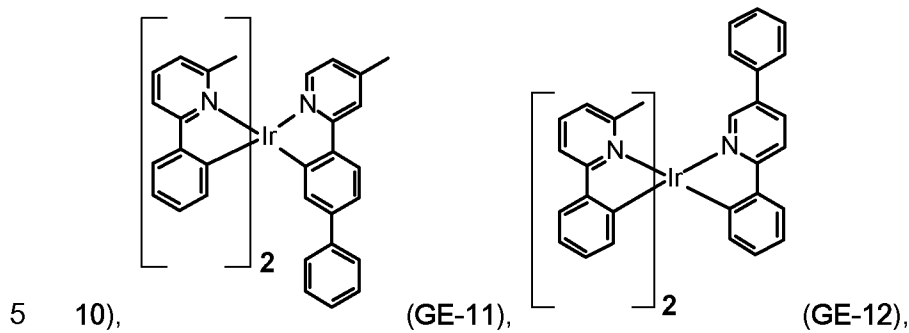
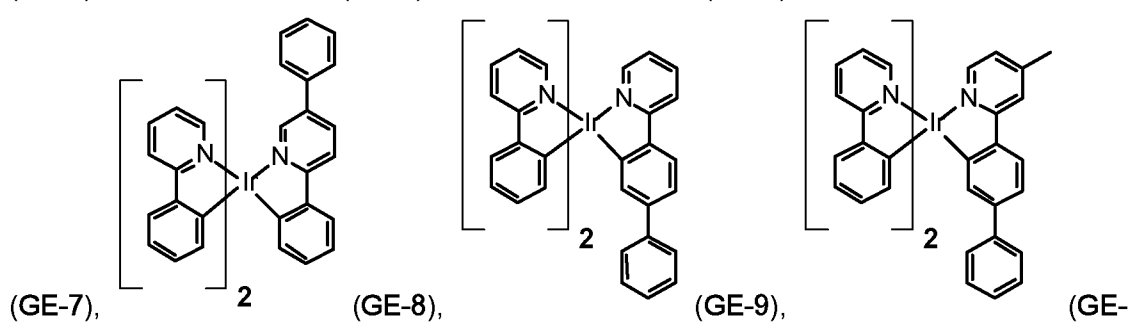
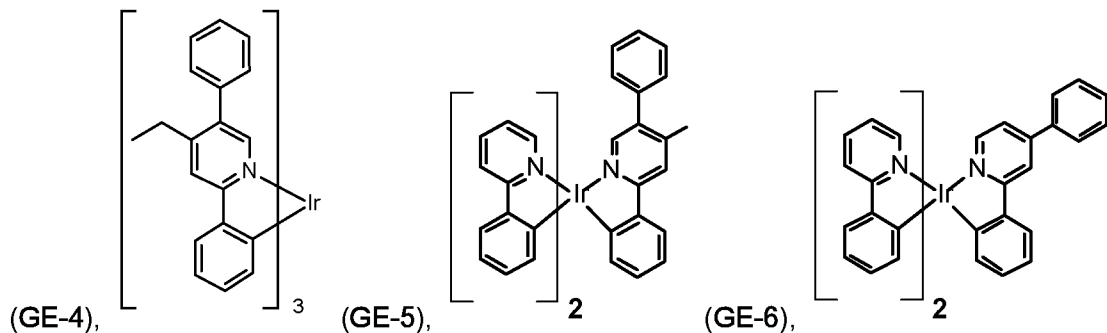
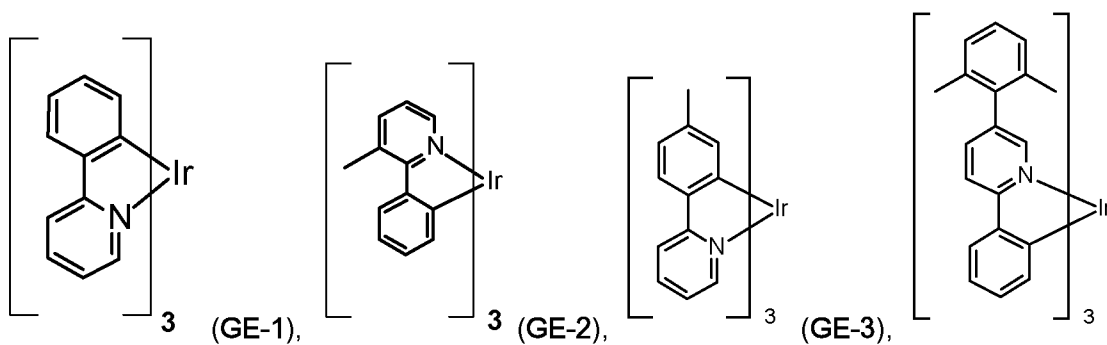
- 5 The compound of formula IX is more preferably a compound (BE-1), (BE-2), (BE-7), (BE-12), (BE-16), (BE-64), or (BE-70). The most preferred phosphorescent blue emitters are compounds (BE-1) and (BE-12).

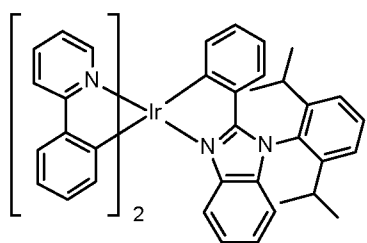
10 The homoleptic metal-carbene complexes may be present in the form of facial or meridional isomers, preference being given to the facial isomers.

Suitable carbene complexes of formula (IX) and their preparation process are, for example, described in WO2011/073149.

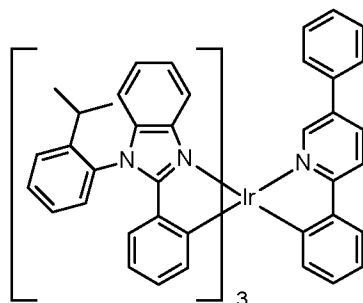
- 15 The compounds of the present invention can also be used as host for phosphorescent green emitters. Suitable phosphorescent green emitters are, for example, specified in the following publications: WO2006014599, WO20080220265, WO2009073245, WO2010027583, WO2010028151, US20110227049, WO2011090535, WO2012/08881, WO20100056669, WO20100118029, WO20100244004, WO2011109042, 20 WO2012166608, US20120292600, EP2551933A1; US6687266, US20070190359, US20070190359, US20060008670; WO2006098460, US20110210316, WO2012053627; US6921915, US20090039776; and JP2007123392.

Examples of suitable phosphorescent green emitters are shown below:

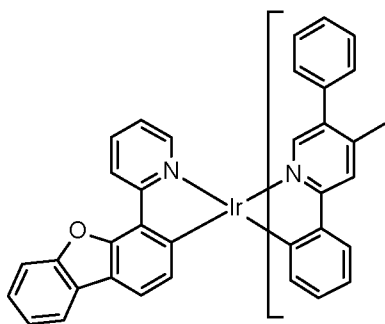




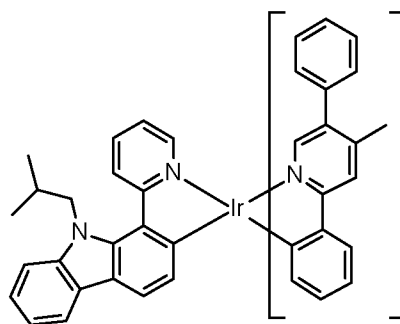
(GE-15),



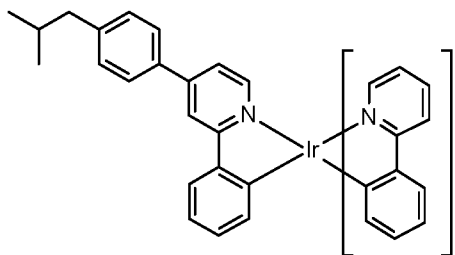
(GE-16),



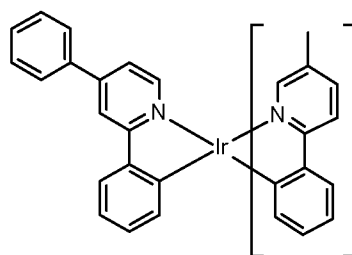
(GE-17),



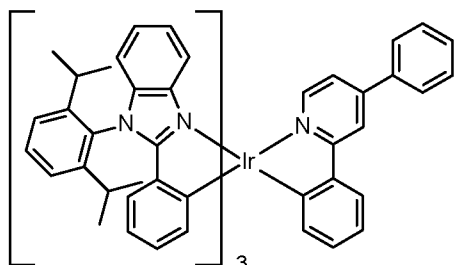
(GE-18),



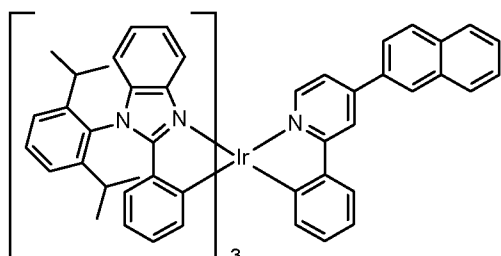
(GE-19),



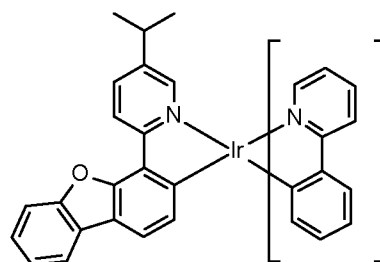
(GE-20),



(GE-21),

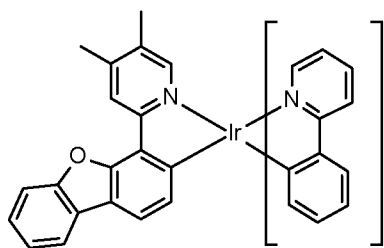


(GE-22),

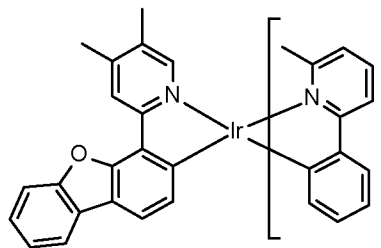


(GE-

5

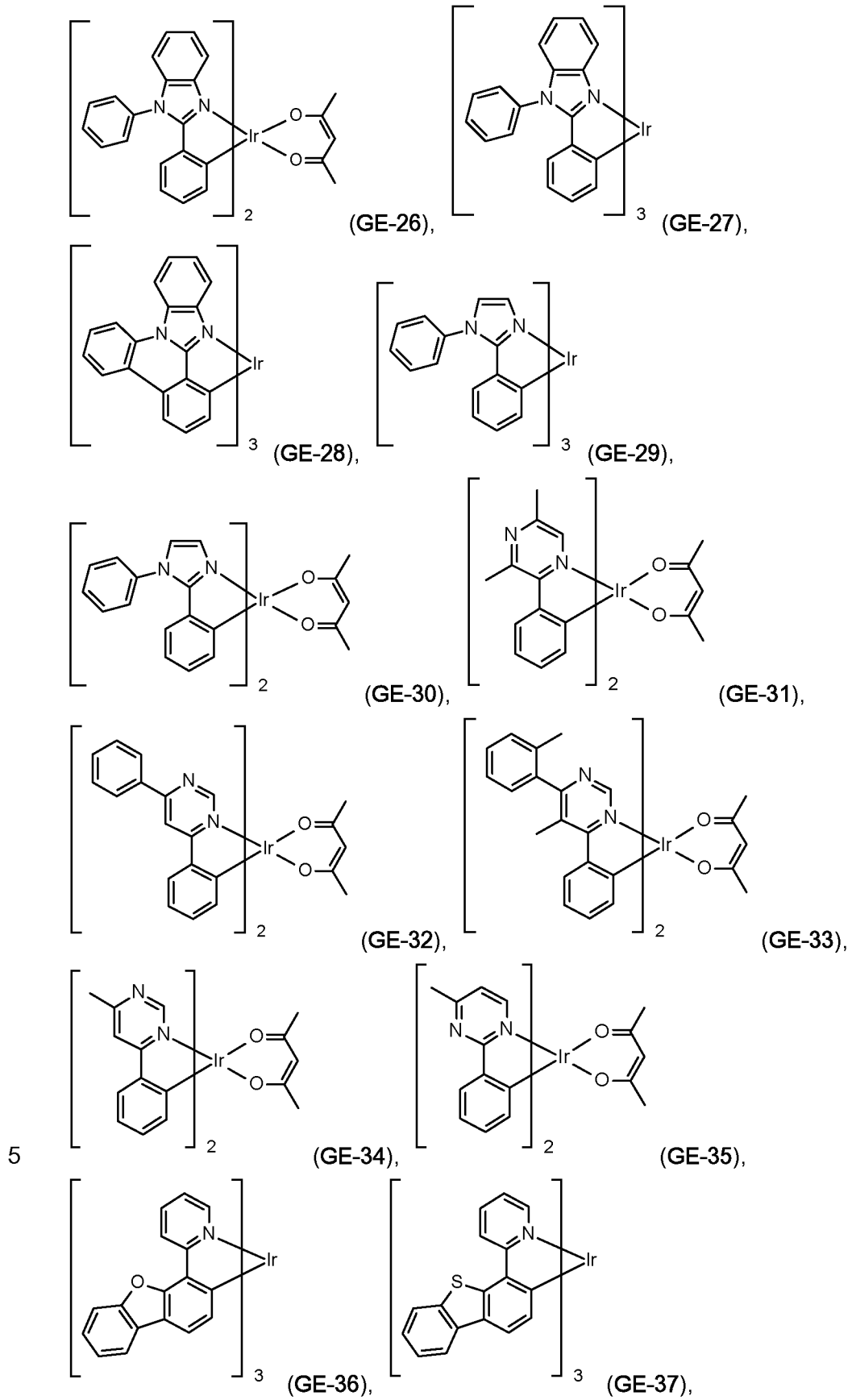


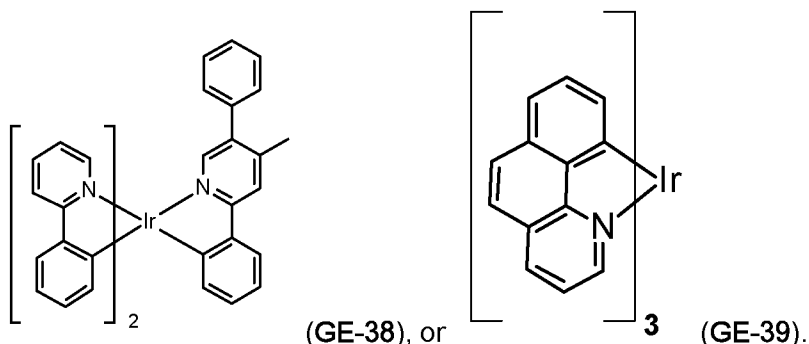
(GE-24),



(GE-

23),
25),





Host (matrix) materials

The light-emitting layer may comprise further components in addition to the emitter material. For example, a fluorescent dye may be present in the light-emitting layer in order to alter the emission color of the emitter material. In addition - in a preferred embodiment - a matrix material can be used. This matrix material may be a polymer, for example poly(N-vinylcarbazole) or polysilane. The matrix material may, however, be a small molecule, for example 4,4'-N,N'-dicarbazolebiphenyl (CDP=CBP) or tertiary aromatic amines, for example TCTA.

In another preferred embodiment of the present invention, at least one compound of the formula I, especially a compound of the formula (Ia-1), is used as matrix material. Examples of preferred compounds of formula I are compounds A-1 to A-64 and A-65 shown above. Compounds A-1, A-2, A-3, A-5, A-11, A-13, A-23, A-25, A-35, A-38, A-46 and A-59 and A-65 are particularly preferred.

In a preferred embodiment, the light-emitting layer is formed from 2 to 40% by weight, preferably 5 to 35% by weight, of at least one of the aforementioned emitter materials and 60 to 98% by weight, preferably 75 to 95% by weight, of at least one of the aforementioned matrix materials - in one embodiment at least one compound of the formula I - where the sum total of the emitter material and of the matrix material adds up to 100% by weight.

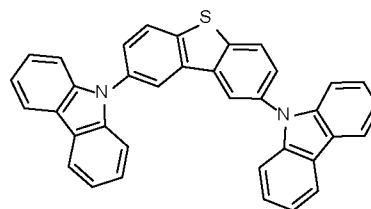
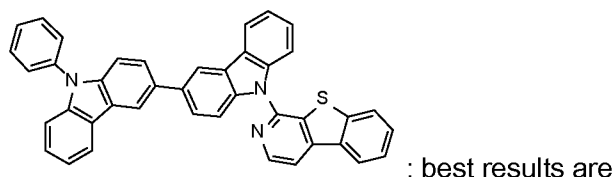
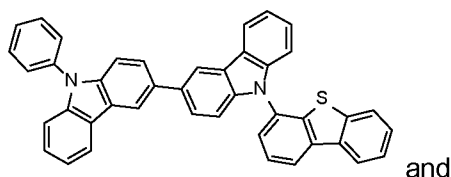
Suitable metal complexes for use together with the compounds of the formula I as matrix material in OLEDs are, for example, also carbene complexes as described in WO 2005/019373 A2, WO 2006/056418 A2, WO 2005/113704, WO 2007/115970, WO 2007/115981 and WO 2008/000727.

Further suitable host materials, which may be small molecules or (co)polymers of the small molecules mentioned, are specified in the following publications: WO2007108459 (H-1 to H-37), preferably H-20 to H-22 and H-32 to H-37, most preferably H-20, H-32, H-36, H-37, WO2008035571 A1 (Host 1 to Host 6), JP2010135467 (compounds 1 to 46 and Host-1 to Host-39 and Host-43), WO2009008100 compounds No.1 to No.67, preferably No.3, No.4, No.7 to No. 12, No.55, No.59, No. 63 to No.67, more preferably No. 4, No. 8 to No. 12, No. 55, No. 59, No.64, No.65, and No. 67, WO2009008099 compounds No. 1 to No. 110, WO2008140114 compounds 1-1 to 1-50, WO2008090912 compounds OC-7 to OC-36 and the polymers of Mo-42 to Mo-51, JP2008084913 H-1 to H-70, WO2007077810 compounds 1 to 44, preferably 1, 2, 4-6, 8, 19-22, 26, 28-30, 32, 36, 39-44, WO201001830 the polymers of monomers 1-1 to 1-9, preferably of 1-3, 1-7, and 1-9, WO2008029729 the (poly-

mers of) compounds 1-1 to 1-36, WO20100443342 HS-1 to HS-101 and BH-1 to BH-17, preferably BH-1 to BH-17, JP2009182298 the (co)polymers based on the monomers 1 to 75, JP2009170764, JP2009135183 the (co)polymers based on the monomers 1-14, WO2009063757 preferably the (co)polymers based on the monomers 1-1 to 1-26,
 5 WO2008146838 the compounds a-1 to a-43 and 1-1 to 1-46, JP2008207520 the (co)polymers based on the monomers 1-1 to 1-26, JP2008066569 the (co)polymers based on the monomers 1-1 to 1-16, WO2008029652 the (co)polymers based on the monomers 1-1 to 1-52, WO2007114244 the (co)polymers based on the monomers 1-1 to 1-18, JP2010040830 the compounds HA-1 to HA-20, HB-1 to HB-16, HC-1 to HC-23 and the
 10 (co)polymers based on the monomers HD-1 to HD-12, JP2009021336, WO2010090077 the compounds 1 to 55, WO2010079678 the compounds H1 to H42, WO2010067746, WO2010044342 the compounds HS-1 to HS-101 and Poly-1 to Poly-4, JP2010114180 the compounds PH-1 to PH-36, US2009284138 the compounds 1 to 111 and H1 to H71, WO2008072596 the compounds 1 to 45, JP2010021336 the compounds H-1 to H-38, preferably H-1, WO2010004877 the compounds H-1 to H-60, JP2009267255 the compounds
 15 1-1 to 1-105, WO2009104488 the compounds 1-1 to 1-38, WO2009086028, US2009153034, US2009134784, WO2009084413 the compounds 2-1 to 2-56, JP2009114369 the compounds 2-1 to 2-40, JP2009114370 the compounds 1 to 67, WO2009060742 the compounds 2-1 to 2-56, WO2009060757 the compounds 1-1 to 1-76, WO2009060780 the compounds 1-1 to 1-70, WO2009060779 the compounds 1-1 to 1-42, WO2008156105 the compounds 1 to 54, JP2009059767 the compounds 1 to 20, JP2008074939 the compounds 1 to 256, JP2008021687 the compounds 1 to 50, WO2007119816 the compounds 1 to 37, WO2010087222 the compounds H-1 to H-31, WO2010095564 the compounds HOST-1 to HOST-61, WO2007108362, WO2009003898,
 20 WO2009003919, WO2010040777, US2007224446, WO06128800, WO2012014621, WO2012105310, WO2012/130709 and European patent applications EP12175635.7 and EP12185230.5. and EP12191408.9 (in particular page 25 to 29 of EP12191408.9).

The above-mentioned small molecules are more preferred than the above-mentioned
 30 (co)polymers of the small molecules.

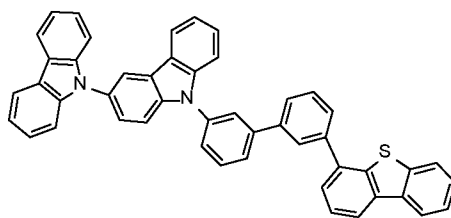
Further suitable second host materials, are described in WO2011137072 (for example,



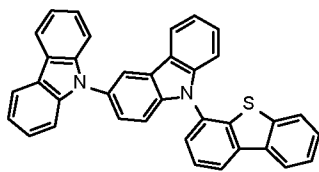
achieved if said compounds are combined with

);

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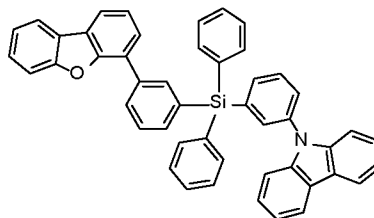
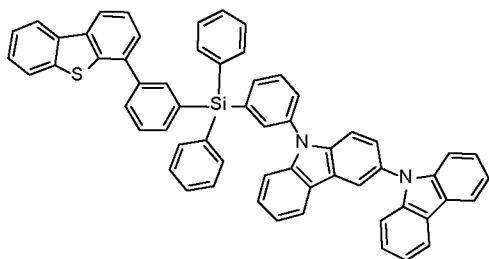


WO2012048266 (for example,

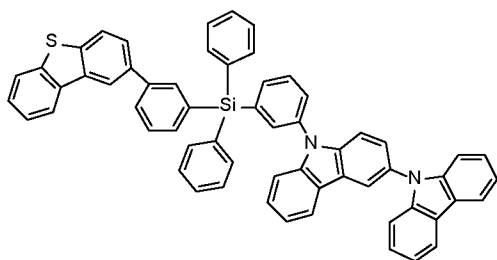


and

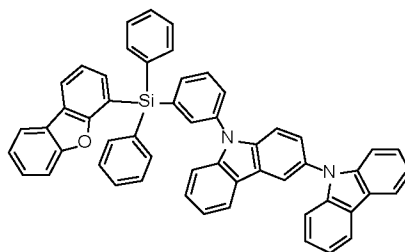
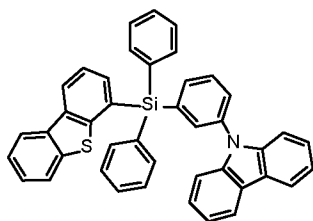
); WO2012162325 (for example,



and



); and EP2551932 (for example,

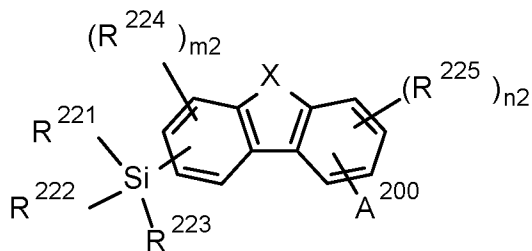


5

and

).

In a particularly preferred embodiment, one or more compounds of the general formula (X) specified hereinafter are used as second host material.



(X), wherein

10 X is NR, S, O or PR;

R is aryl, heteroaryl, alkyl, cycloalkyl, or heterocycloalkyl;

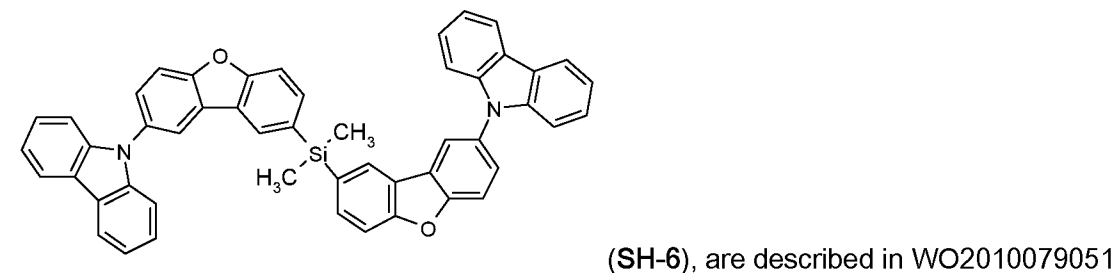
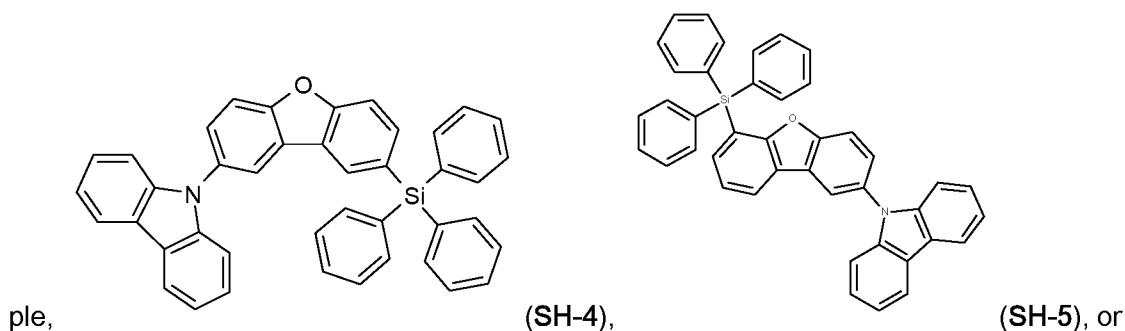
A²⁰⁰ is -NR²⁰⁶R²⁰⁷, -P(O)R²⁰⁸R²⁰⁹, -PR²¹⁰R²¹¹, -S(O)₂R²¹², -S(O)R²¹³, -SR²¹⁴, or -OR²¹⁵;

R²²¹, R²²² and R²²³ are independently of each other aryl, heteroaryl, alkyl, cycloalkyl, or heterocycloalkyl, wherein at least one of the groups R²²¹, R²²², or R²²³ is aryl, or heteroaryl;

R²²⁴ and R²²⁵ are independently of each other alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, a group A²⁰⁰, or a group having donor, or acceptor characteristics;

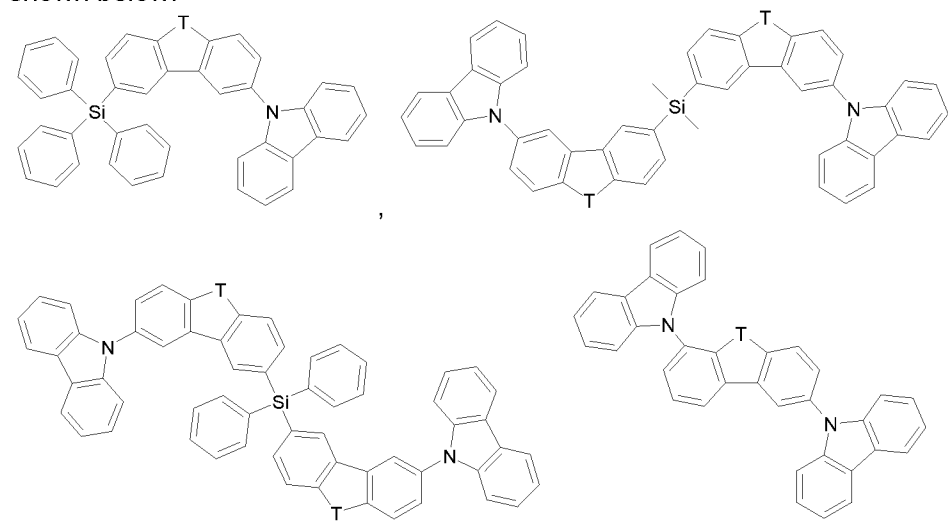
n₂ and m₂ are independently of each other 0, 1, 2, or 3;

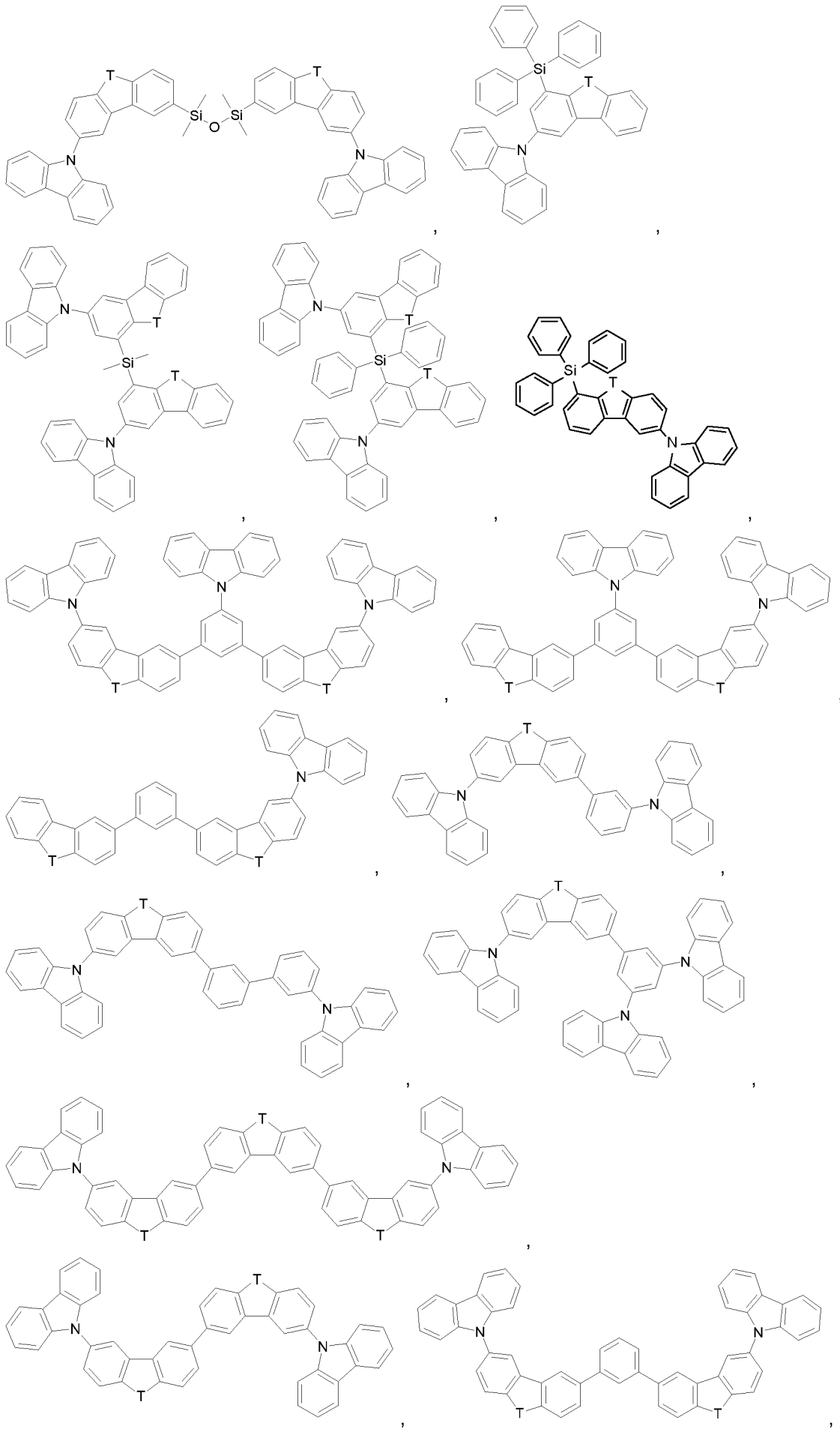
R²⁰⁶ and R²⁰⁷ form together with the nitrogen atom a cyclic residue having 3 to 10 ring atoms, which can be unsubstituted, or which can be substituted with one, or more substituents selected from alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and a group having donor, or acceptor characteristics; and/or which can be annulated with one, or more further cyclic residues having 3 to 10 ring atoms, wherein the annulated residues can be unsubstituted, or can be substituted with one, or more substituents selected from alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and a group having donor, or acceptor characteristics; and R²⁰⁸, R²⁰⁹, R²¹⁰, R²¹¹, R²¹², R²¹³, R²¹⁴ und R²¹⁵ are independently of each other aryl, heteroaryl, alkyl, cycloalkyl, or heterocycloalkyl. Compounds of formula X, such as, for exam-

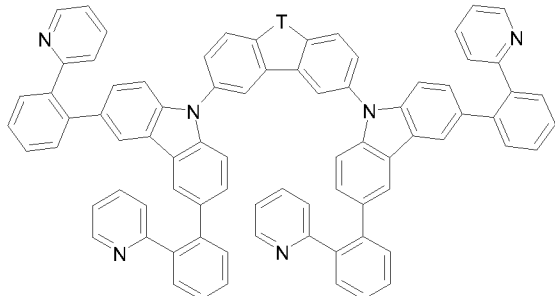
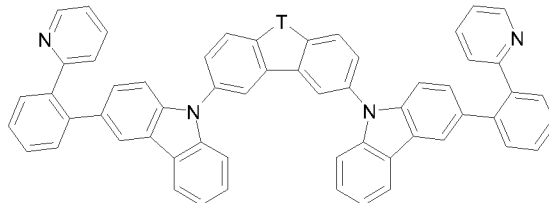
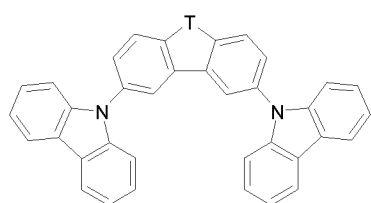
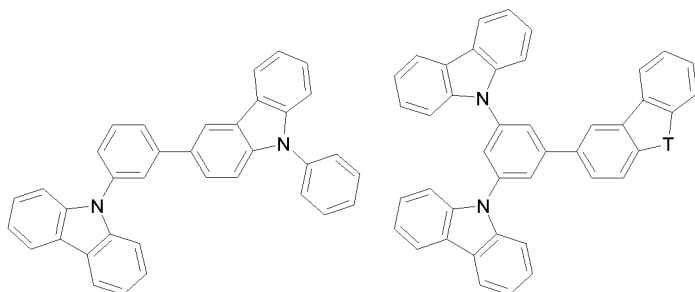
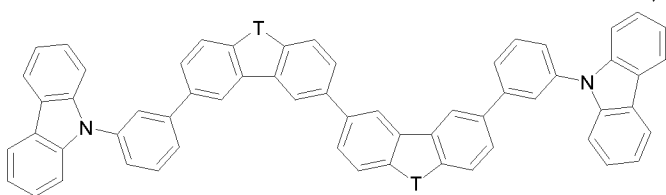
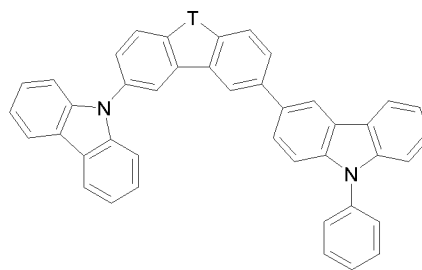
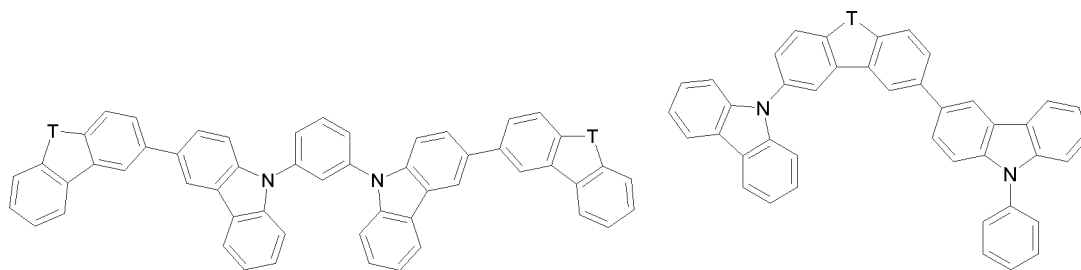


(in particular pages on 19 to 26 and in tables on pages 27 to 34, pages 35 to 37 and pages 42 to 43).

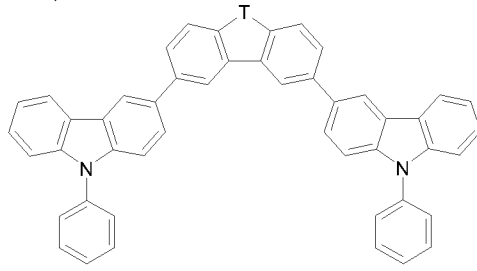
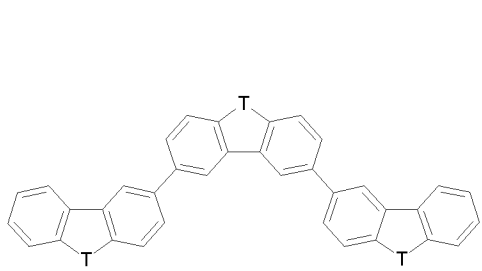
Additional host materials on basis of dibenzofuran are, for example, described in US2009066226, EP1885818B1, EP1970976, EP1998388, EP2034538 and European patent application no. 14160197.1. Examples of particularly preferred host materials are shown below:

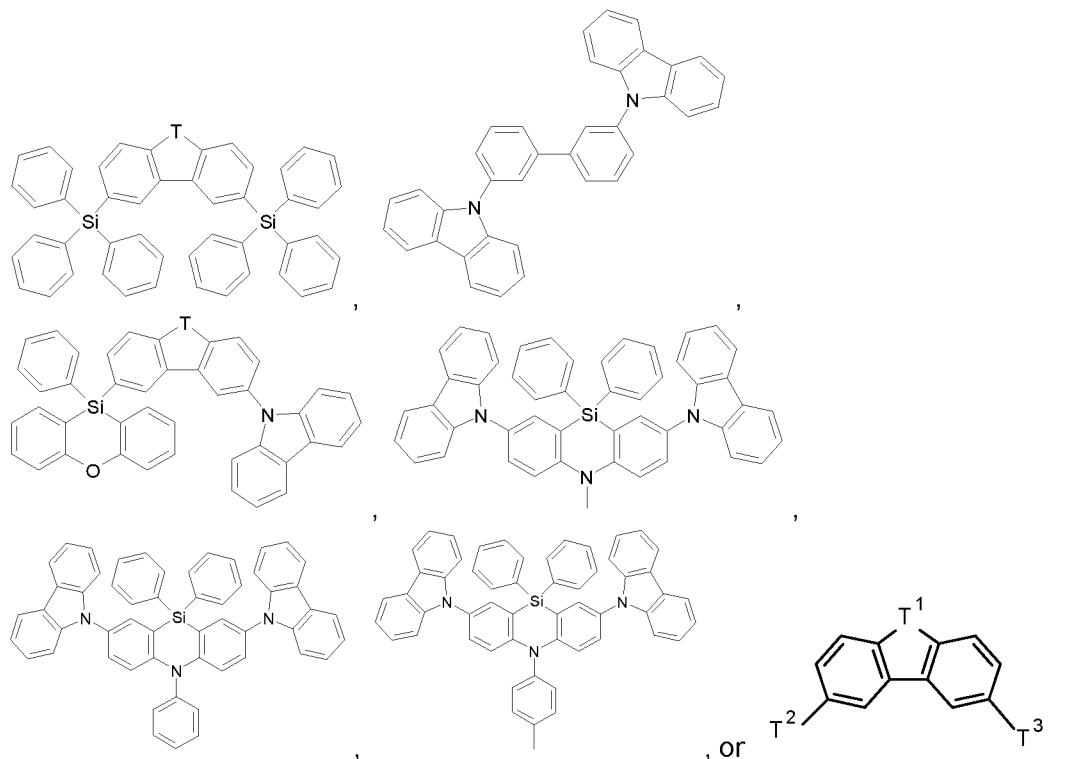




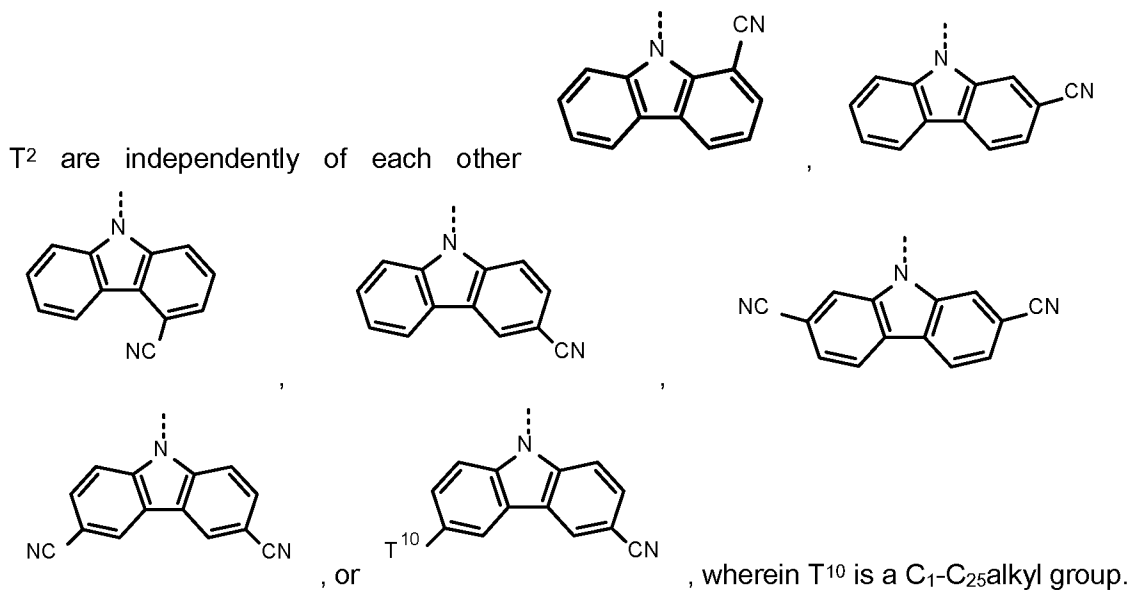


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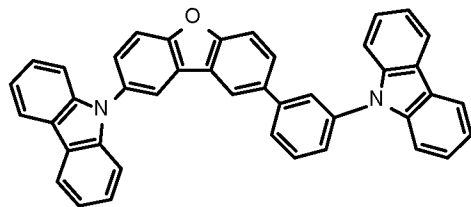




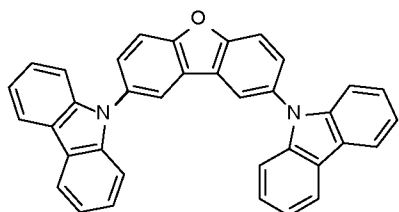
In the above-mentioned compounds T is O, or S, preferably O. If T occurs more than one time in a molecule, all groups T have the same meaning. T¹ and



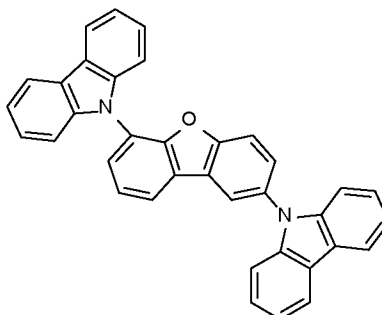
Compounds



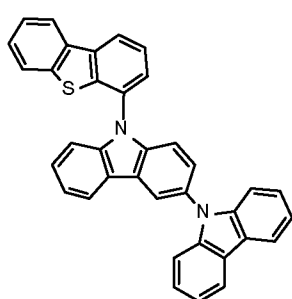
(SH-1),



(SH-2),

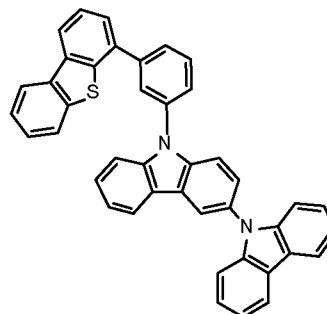


(SH-3), SH-4,

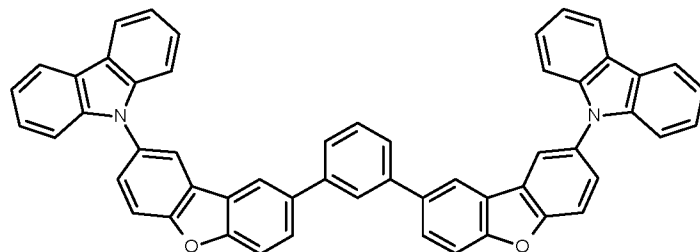


SH-5, SH-6,

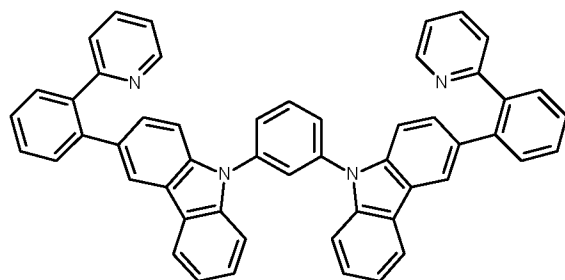
(SH-7),



(SH-8),

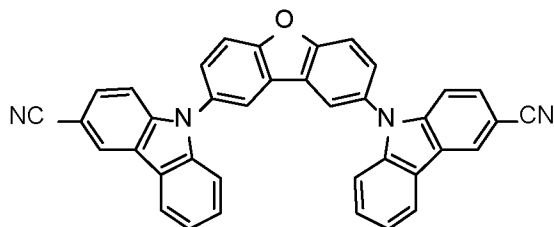


(SH-9),



(SH-10)

5



and

(SH-11) are most preferred.

Hole/exciton blocking layer (f):

Blocking layers may be used to reduce the number of charge carriers (electrons or holes) and/or excitons that leave the emissive layer. The hole blocking layer may be disposed between the emitting layer (e) and electron transport layer (g), to block holes from leaving layer (e) in the direction of electron transport layer (g). Blocking layers may also be used to
5 block excitons from diffusing out of the emissive layer.

Additional hole blocker materials typically used in OLEDs are 2,6-bis(N-carbazolyl)pyridine (mCPy), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproin, (BCP)), bis(2-methyl-8-quinolinato)-4-phenylphenylato)aluminum(III) (BALq), phenothiazine S,S-dioxide
10 derivates and 1,3,5-tris(N-phenyl-2-benzylimidazolyl)benzene (TPBI), TPBI also being suitable as electron-transport material. Further suitable hole blockers and/or electron conductor materials are 2,2',2''-(1,3,5-benzenetriyl)tris(1-phenyl-1-H-benzimidazole), 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, 8-hydroxyquinolinolitolithium, 4-(naphthalen-1-yl)-3,5-diphenyl-4H-1,2,4-triazole, 1,3-bis[2-(2,2'-bipyridin-6-yl)-1,3,4-oxadiazole-5-yl]benzene, 4,7-diphenyl-1,10-phenanthroline, 3-(4-biphenyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole, 6,6'-bis[5-(biphenyl-4-yl)-1,3,4-oxadiazole-2-yl]-2,2'-bipyridyl, 2-phenyl-9,10-di(naphthalene-2-yl)anthracene, 2,7-bis[2-(2,2'-bipyridin-6-yl)-1,3,4-oxadiazole-5-yl]-9,9-dimethylfluorene, 1,3-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazole-5-yl]benzene, 2-(naphthalene-2-yl)-4,7-diphenyl-1,10-phenanthroline, tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane, 2,9-bis(naphthalene-2-yl)-4,7-diphenyl-1,10-phenanthroline, 1-methyl-2-(4-(naphthalene-2-yl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthroline. In a further embodiment, it is possible to use compounds which comprise aromatic or heteroaromatic rings joined via groups comprising carbonyl groups, as disclosed in WO2006/100298, disilyl compounds selected from the group consisting of disilylcarbazoles, disilylbenzofurans, disilylbenzothiophenes, disilylbenzophospholes, disilylbenzothiophene S-oxides and disilylbenzothiophene S,S-dioxides, as specified, for example, in PCT applications
25 WO2009/003919 and WO2009003898 and disilyl compounds as disclosed in WO2008/034758, as a blocking layer for holes/excitons (f).

30 In another preferred embodiment compounds (SH-1), (SH-2), (SH-3), SH-4, SH-5, SH-6, (SH-7), (SH-8), (SH-9), (SH-10) and (SH-11) may be used as hole/exciton blocking materials.

Electron transport layer (g):

35 Electron transport layer may include a material capable of transporting electrons. Electron transport layer may be intrinsic (undoped), or doped. Doping may be used to enhance conductivity. Suitable electron-transporting materials for layer (g) of the inventive OLEDs comprise metals chelated with oxinoid compounds, such as tris(8-hydroxyquinolato)aluminum (Alq₃), compounds based on phenanthroline such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (DDPA = BCP), 4,7-diphenyl-1,10-phenanthroline (Bphen), 2,4,7,9-tetraphenyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline (DPA) or phenanthroline derivatives disclosed in EP1786050, in EP1970371, or in EP1097981, andazole compounds such as 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) and 3-(4-biphenyl)-4phenyl-5-(4-t-butylphenyl)-1,2,4-
45 triazole (TAZ).

It is likewise possible to use mixtures of at least two materials in the electron-transporting layer, in which case at least one material is electron-conducting. Preferably, in such mixed electron-transport layers, at least one phenanthroline compound is used, preferably BCP, or at least one pyridine compound according to the formula (VIII) below, preferably a compound of the formula (VIIIaa) below. More preferably, in mixed electron-transport layers, in addition to at least one phenanthroline compound, alkaline earth metal or alkali metal hydroxyquinolate complexes, for example Liq, are used. Suitable alkaline earth metal or alkali metal hydroxyquinolate complexes are specified below (formula VII). Reference is made to WO2011/157779.

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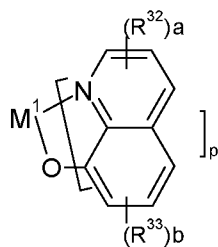
The electron-transport layer may also be electronically doped in order to improve the transport properties of the materials used, in order firstly to make the layer thicknesses more generous (avoidance of pinholes/short circuits) and in order secondly to minimize the operating voltage of the device. Electronic doping is known to those skilled in the art and is disclosed, for example, in W. Gao, A. Kahn, J. Appl. Phys., Vol. 94, No. 1, 1 July 2003 (p-doped organic layers); A. G. Werner, F. Li, K. Harada, M. Pfeiffer, T. Fritz, K. Leo, Appl. Phys. Lett., Vol. 82, No. 25, 23 June 2003 and Pfeiffer et al., Organic Electronics 2003, 4, 89 - 103 and K. Walzer, B. Maennig, M. Pfeiffer, K. Leo, Chem. Soc. Rev. 2007, 107, 1233. For example, it is possible to use mixtures which lead to electrical n-doping of the electron-transport layer. n-Doping is achieved by the addition of reducing materials. These mixtures may, for example, be mixtures of the abovementioned electron transport materials with alkali/alkaline earth metals or alkali/alkaline earth metal salts, for example Li, Cs, Ca, Sr, Cs₂CO₃, with alkali metal complexes, for example 8-hydroxyquinolatolithium (Liq), and with Y, Ce, Sm, Gd, Tb, Er, Tm, Yb, Li₃N, Rb₂CO₃, dipotassium phthalate, W(hpp)₄ from EP1786050, or with compounds described in EP1837926B1, EP1837927, EP2246862 and WO2010132236.

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In a preferred embodiment, the electron-transport layer comprises at least one compound of the general formula (VII)



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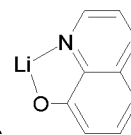
R^{32} and R^{33} are each independently F, C₁-C₈-alkyl, or C₆-C₁₄-aryl, which is optionally substituted by one or more C₁-C₈-alkyl groups, or two R^{32} and/or R^{33} substituents together form a fused benzene ring which is optionally substituted by one or more C₁-C₈-alkyl groups;

35

a and b are each independently 0, or 1, 2 or 3,

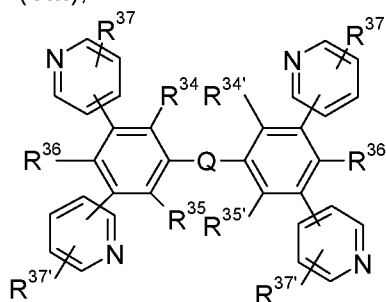
M^1 is an alkaline metal atom or alkaline earth metal atom,

p is 1 when M^1 is an alkali metal atom, p is 2 when M^1 is an earth alkali metal atom.



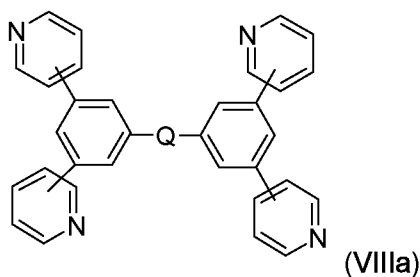
A very particularly preferred compound of the formula (VII) is (Liq), which may be present as a single species, or in other forms such as Li_gQ_g in which g is an integer, for example Li_6Q_6 . Q is an 8-hydroxyquinolate ligand or an 8-hydroxyquinolate derivative.

- 5 In a further preferred embodiment, the electron-transport layer comprises at least one compound of the formula (VIII),

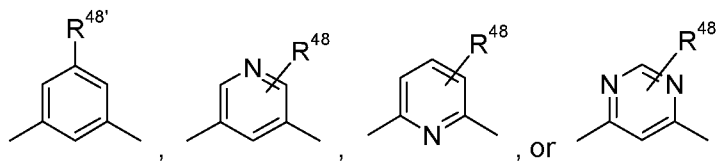


(VIII), in which

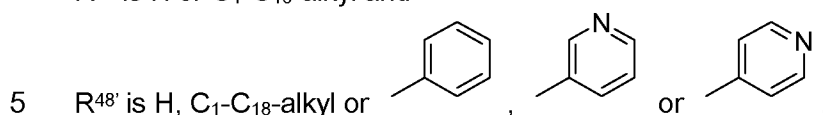
- R^{34} , R^{35} , R^{36} , R^{37} , $R^{34'}$, $R^{35'}$, $R^{36'}$ and $R^{37'}$ are each independently H, $\text{C}_1\text{-C}_{18}$ -alkyl, $\text{C}_1\text{-C}_{18}$ -alkyl which is substituted by E and/or interrupted by D, $\text{C}_6\text{-C}_{24}$ -aryl, $\text{C}_6\text{-C}_{24}$ -aryl which is substituted by G, $\text{C}_2\text{-C}_{20}$ -heteroaryl or $\text{C}_2\text{-C}_{20}$ -heteroaryl which is substituted by G, Q is an arylene or heteroarylene group, each of which is optionally substituted by G; D is $-\text{CO}-$; $-\text{COO}-$; $-\text{S}-$; $-\text{SO}-$; $-\text{SO}_2-$; $-\text{O}-$; $-\text{NR}^{40}-$; $-\text{SiR}^{45}\text{R}^{46}-$; $-\text{POR}^{47}-$; $-\text{CR}^{38}=\text{CR}^{39}-$; or $-\text{C}\equiv\text{C}-$;
- E is $-\text{OR}^{44}$; $-\text{SR}^{44}$; $-\text{NR}^{40}\text{R}^{41}$; $-\text{COR}^{43}$; $-\text{COOR}^{42}$; $-\text{CONR}^{40}\text{R}^{41}$; $-\text{CN}$; or F;
- 15 G is E, $\text{C}_1\text{-C}_{18}$ -alkyl, $\text{C}_1\text{-C}_{18}$ -alkyl which is interrupted by D, $\text{C}_1\text{-C}_{18}$ -perfluoroalkyl, $\text{C}_1\text{-C}_{18}$ -alkoxy, or $\text{C}_1\text{-C}_{18}$ -alkoxy which is substituted by E and/or interrupted by D, in which
- R^{38} and R^{39} are each independently H, $\text{C}_6\text{-C}_{18}$ -aryl; $\text{C}_6\text{-C}_{18}$ -aryl which is substituted by $\text{C}_1\text{-C}_{18}$ -alkyl or $\text{C}_1\text{-C}_{18}$ -alkoxy; $\text{C}_1\text{-C}_{18}$ -alkyl; or $\text{C}_1\text{-C}_{18}$ -alkyl which is interrupted by $-\text{O}-$;
- 20 R^{40} and R^{41} are each independently $\text{C}_6\text{-C}_{18}$ -aryl; $\text{C}_6\text{-C}_{18}$ -aryl which is substituted by $\text{C}_1\text{-C}_{18}$ -alkyl or $\text{C}_1\text{-C}_{18}$ -alkoxy; $\text{C}_1\text{-C}_{18}$ -alkyl; or $\text{C}_1\text{-C}_{18}$ -alkyl which is interrupted by $-\text{O}-$; or R^{40} and R^{41} together form a 6-membered ring;
- R^{42} and R^{43} are each independently $\text{C}_6\text{-C}_{18}$ -aryl; $\text{C}_6\text{-C}_{18}$ -aryl which is substituted by $\text{C}_1\text{-C}_{18}$ -alkyl or $\text{C}_1\text{-C}_{18}$ -alkoxy; $\text{C}_1\text{-C}_{18}$ -alkyl; or $\text{C}_1\text{-C}_{18}$ -alkyl which is interrupted by $-\text{O}-$,
- 25 R^{44} is $\text{C}_6\text{-C}_{18}$ -aryl; $\text{C}_6\text{-C}_{18}$ -aryl which is substituted by $\text{C}_1\text{-C}_{18}$ -alkyl or $\text{C}_1\text{-C}_{18}$ -alkoxy; $\text{C}_1\text{-C}_{18}$ -alkyl; or $\text{C}_1\text{-C}_{18}$ -alkyl which is interrupted by $-\text{O}-$,
- R^{45} and R^{46} are each independently $\text{C}_1\text{-C}_{18}$ -alkyl, $\text{C}_6\text{-C}_{18}$ -aryl or $\text{C}_6\text{-C}_{18}$ -aryl which is substituted by $\text{C}_1\text{-C}_{18}$ -alkyl,
- R^{47} is $\text{C}_1\text{-C}_{18}$ -alkyl, $\text{C}_6\text{-C}_{18}$ -aryl or $\text{C}_6\text{-C}_{18}$ -aryl which is substituted by $\text{C}_1\text{-C}_{18}$ -alkyl.
- 30 Preferred compounds of the formula (VIII) are compounds of the formula (VIIIa)



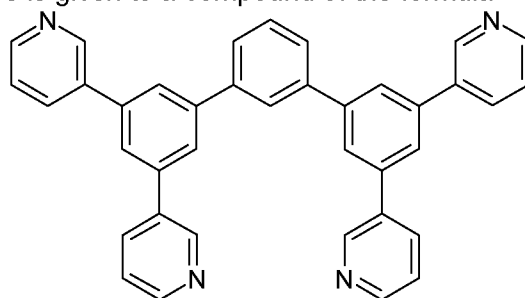
in which Q is:



R⁴⁸ is H or C₁-C₁₈-alkyl and



Particular preference is given to a compound of the formula



(ETM-2).

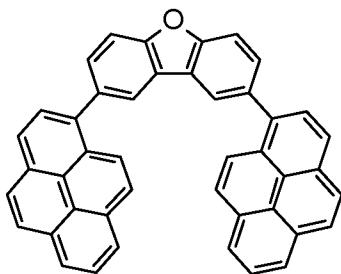
10 In a further, very particularly preferred embodiment, the electron-transport layer comprises a compound Liq and a compound **ETM-2**.

15 In a preferred embodiment, the electron-transport layer comprises the compound of the formula (VII) in an amount of 99 to 1% by weight, preferably 75 to 25% by weight, more preferably about 50% by weight, where the amount of the compounds of the formulae (VII) and the amount of the compounds of the formulae (VIII) adds up to a total of 100% by weight.

20 The preparation of the compounds of the formula (VIII) is described in J. Kido et al., Chem. Commun. (2008) 5821–5823, J. Kido et al., Chem. Mater. 20 (2008) 5951–5953 and JP2008/127326, or the compounds can be prepared analogously to the processes disclosed in the aforementioned documents.

25 It is likewise possible to use mixtures of alkali metal hydroxyquinolate complexes, preferably Liq, and dibenzofuran compounds in the electron-transport layer. Reference is made to WO2011/157790. Dibenzofuran compounds **A-1** to **A-36** and **B-1** to **B-22** described in

WO2011/157790 are preferred, wherein dibenzofuran compound



(A-10; = ETM-1) is most preferred.

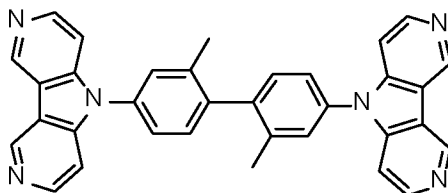
In a preferred embodiment, the electron-transport layer comprises Liq in an amount of 99 to 1% by weight, preferably 75 to 25% by weight, more preferably about 50% by weight, where the amount of Liq and the amount of the dibenzofuran compound(s), especially ETM-1, adds up to a total of 100% by weight.

In a preferred embodiment, the electron-transport layer comprises at least one phenanthroline derivative and/or pyridine derivative.

In a further preferred embodiment, the electron-transport layer comprises at least one phenanthroline derivative and/or pyridine derivative and at least one alkali metal hydroxyquinolate complex.

In a further preferred embodiment, the electron-transport layer comprises at least one of the dibenzofuran compounds A-1 to A-36 and B-1 to B-22 described in WO2011/157790, especially ETM-1.

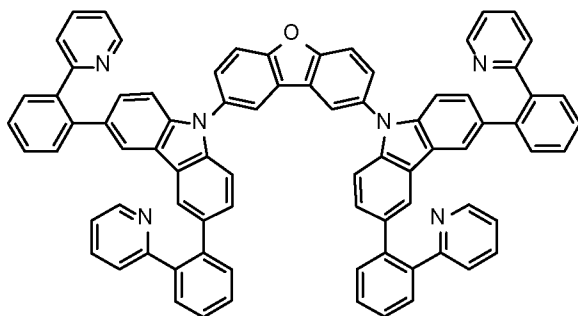
In a further preferred embodiment, the electron-transport layer comprises a compound described in WO2012/111462, WO2012/147397, WO2012/14621, such as, for example, a



compound of formula

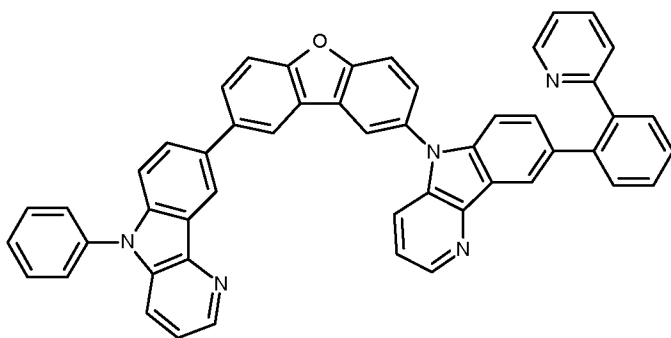
(ETM-3), US2012/0261654,

such as, for example, a compound of formula



(ETM-4), and WO2012/115034, such as

for example, such as, for example, a compound of formula



(ETM-5).

Electron injection layer (h):

- 5 The electron injection layer may be any layer that improves the injection of electrons into an adjacent organic layer. Lithium-comprising organometallic compounds such as 8-hydroxyquinolatolithium (Liq), CsF, NaF, KF, Cs₂CO₃ or LiF may be applied between the electron transport layer (g) and the cathode (i) as an electron injection layer (h) in order to reduce the operating voltage.

10

Cathode (i):

- The cathode (i) is an electrode which serves to introduce electrons or negative charge carriers. The cathode may be any metal or nonmetal which has a lower work function than the anode. Suitable materials for the cathode are selected from the group consisting of alkali metals of group 1, for example Li, Cs, alkaline earth metals of group 2, metals of group 12 of the Periodic Table of the Elements, comprising the rare earth metals and the lanthanides and actinides. In addition, metals such as aluminum, indium, calcium, barium, samarium and magnesium, and combinations thereof, may be used.

15

- 20 In general, the different layers, if present, have the following thicknesses:

- anode (a): 500 to 5000 Å (ångström), preferably 1000 to 2000 Å;
 hole injection layer (b): 50 to 1000 Å, preferably 200 to 800 Å,
 hole-transport layer (c): 50 to 1000 Å, preferably 100 to 800 Å,
 exciton blocking layer (d): 10 to 500 Å, preferably 50 to 100 Å,
 25 light-emitting layer (e): 10 to 1000 Å, preferably 50 to 600 Å,
 hole/ exciton blocking layer (f): 10 to 500 Å, preferably 50 to 100 Å,
 electron-transport layer (g): 50 to 1000 Å, preferably 200 to 800 Å,
 electron injection layer (h): 10 to 500 Å, preferably 20 to 100 Å,
 cathode (i): 200 to 10 000 Å, preferably 300 to 5000 Å.

30

The person skilled in the art is aware (for example on the basis of electrochemical studies) of how suitable materials have to be selected. Suitable materials for the individual layers are known to those skilled in the art and are disclosed, for example, in WO 00/70655.

- 35 In addition, it is possible that some of the layers used in the inventive OLED have been surface-treated in order to increase the efficiency of charge carrier transport. The selection of the materials for each of the layers mentioned is preferably determined by obtaining an OLED with a high efficiency and lifetime.

The inventive OLED can be produced by methods known to those skilled in the art. In general, the inventive OLED is produced by successive vapor deposition of the individual layers onto a suitable substrate. Suitable substrates are, for example, glass, inorganic semiconductors or polymer films. For vapor deposition, it is possible to use customary techniques, such as thermal evaporation, chemical vapor deposition (CVD), physical vapor deposition (PVD) and others. In an alternative process, the organic layers of the OLED can be applied from solutions or dispersions in suitable solvents, employing coating techniques known to those skilled in the art.

10

Use of the compounds of the formula I in at least one layer of the OLED, preferably in the light-emitting layer (preferably as a matrix material), charge transport layer and/or in the charge/exciton blocking layer makes it possible to obtain OLEDs with high efficiency and with low use and operating voltage. Frequently, the OLEDs obtained by the use of the compounds of the formula I additionally have high lifetimes. The efficiency of the OLEDs can additionally be improved by optimizing the other layers of the OLEDs. For example, high-efficiency cathodes such as Ca or Ba, if appropriate in combination with an intermediate layer of LiF, can be used. Moreover, additional layers may be present in the OLEDs in order to adjust the energy level of the different layers and to facilitate electroluminescence.

20

The OLEDs may further comprise at least one second light-emitting layer. The overall emission of the OLEDs may be composed of the emission of the at least two light-emitting layers and may also comprise white light.

25

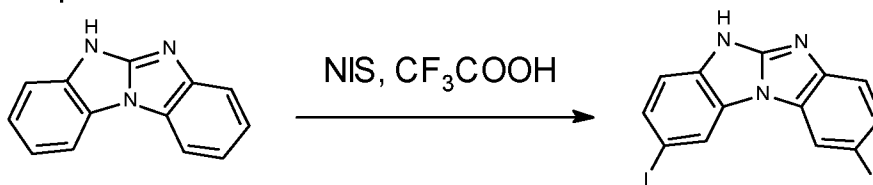
The OLEDs can be used in all apparatus in which electroluminescence is useful. Suitable devices are preferably selected from stationary and mobile visual display units and illumination units. Stationary visual display units are, for example, visual display units of computers, televisions, visual display units in printers, kitchen appliances and advertising panels, illuminations and information panels. Mobile visual display units are, for example, visual display units in cellphones, tablet PCs, laptops, digital cameras, MP3 players, vehicles and destination displays on buses and trains. Further devices in which the inventive OLEDs can be used are, for example, keyboards; items of clothing; furniture; wallpaper. In addition, the present invention relates to a device selected from the group consisting of stationary visual display units such as visual display units of computers, televisions, visual display units in printers, kitchen appliances and advertising panels, illuminations, information panels, and mobile visual display units such as visual display units in cellphones, tablet PCs, laptops, digital cameras, MP3 players, vehicles and destination displays on buses and trains; illumination units; keyboards; items of clothing; furniture; wallpaper, comprising at least one inventive organic light-emitting diode or at least one inventive light-emitting layer.

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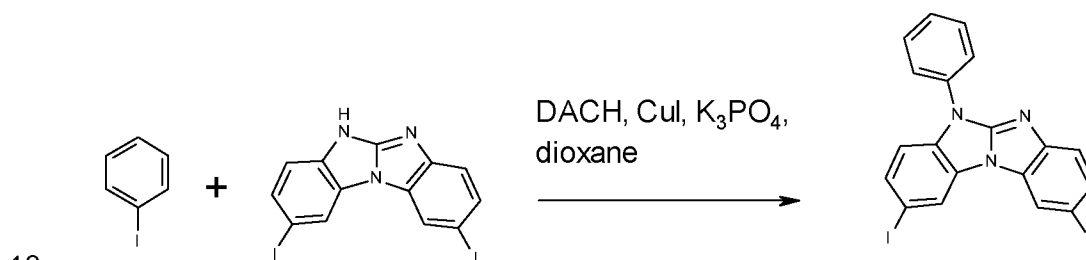
The following examples are included for illustrative purposes only and do not limit the scope of the claims. Unless otherwise stated, all parts and percentages are by weight.

Examples

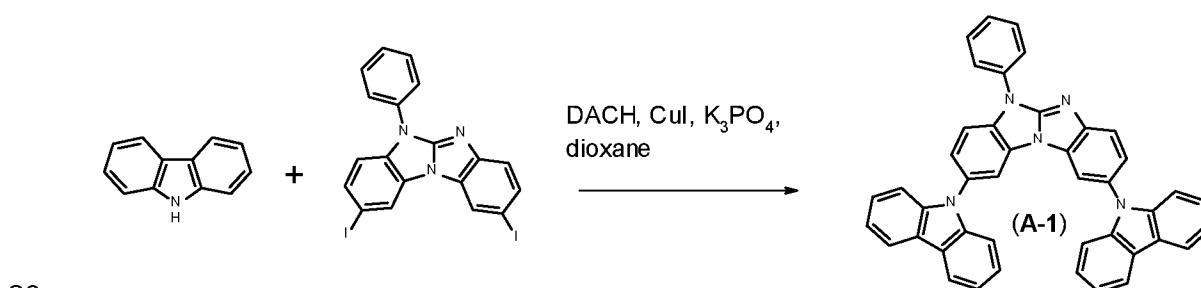
Example 1



- 5 a) 20 g (96.5 mmol) 6H-benzimidazo[1,2-a]benzimidazole is dissolved in 400 ml trifluoroacetic acid under nitrogen. 43.4 g (193 mmol) N-Iodosuccinimide is added in 10 minutes. The reaction mixture is stirred at 25 °C for 24 h under nitrogen. The precipitated product is filtered off and crystallized from trifluoroacetic acid (yield: 19.2 g (43 %)).
¹H NMR (400 MHz, TFA-d₁): δ 8.77-8.78 (m, 2H), 8.34-8.37 (m, 2H), 7.91-7.94 (m, 1H).



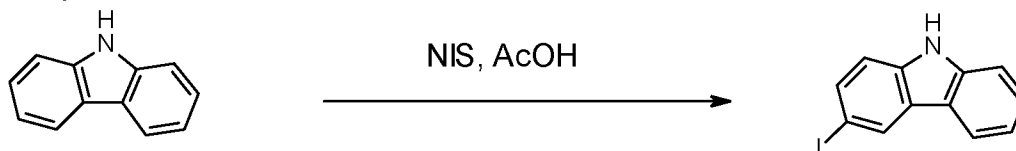
- 10 b) 16.5 g (35.9 mmol) 2,9-diiodo-6H-benzimidazo[1,2-a]benzimidazole, 22 g (108 g) iodo-benzene, 500 mg (2.63 mmol) copper iodide, 22.9 g (107 mmol) potassium phosphate and 35.0 g (307 mmol) trans-cyclohexane-1.2-diamine (DACH) in 100 ml dioxane are refluxed under nitrogen for 9 h. The solids are filtered off and are washed with chloroform. The organic phase is washed with water and is dried with magnesium sulfate. The solvent is removed in vacuum. Column chromatography on silica gel with chloroform results in the product (yield: 6.30 g (33 %)).
¹H NMR (400 MHz, CDCl₃): δ 8.15 (d, J= 1.3 Hz, 1H), 8.12 (d, J= 1.4 Hz, 1H), 7.77-7.81 (m, 2H), 7.61-7.69 (m, 4H), 7.49-7.55 (m 2H), 7.30-7.34 (m, 1H).



- 20 c) 4.00 g (7.48 mmol) 2,9-diiodo-5-phenyl-benzimidazo[1,2-a]benzimidazole, 3.12 g (18.8 mmol) carbazole, 280 mg (1.50 mmol) copper iodide, 6.35 g (29.9 mmol) potassium phosphate and 260 mg (2.24 mmol) trans-cyclohexane-1.2-diamine (DACH) in 80 ml dioxane are refluxed under nitrogen for 24 h. 7.00 g (61.4 mmol) trans-cyclohexane-1.2-diamine (DACH) are added and the reaction mixture is refluxed under nitrogen for 48 h.
 25 The solids are filtered off and are washed with dioxane. Chloroform is added and the organic phase is washed with water, 1 % solution of amino propanol, 20 % ammonia solution and water. Column chromatography on silica gel with chloroform result in the product (yield: 3.95 g (86 %)).

¹H NMR (400 MHz, CDCl₃): δ 8.16 (s, 2H), 8.13 (s, 2H), 7.92-8.02 (m, 5H), 7.71-7.82 (m, 3H), 7.54-7.59 (m, 3H), 7.36-7.41 (m, 8H), 7.24-7.32 (m, 6H).

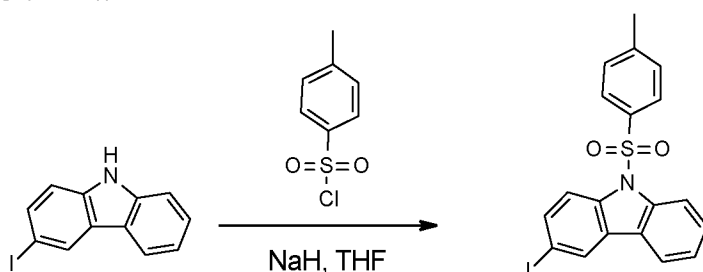
Example 2



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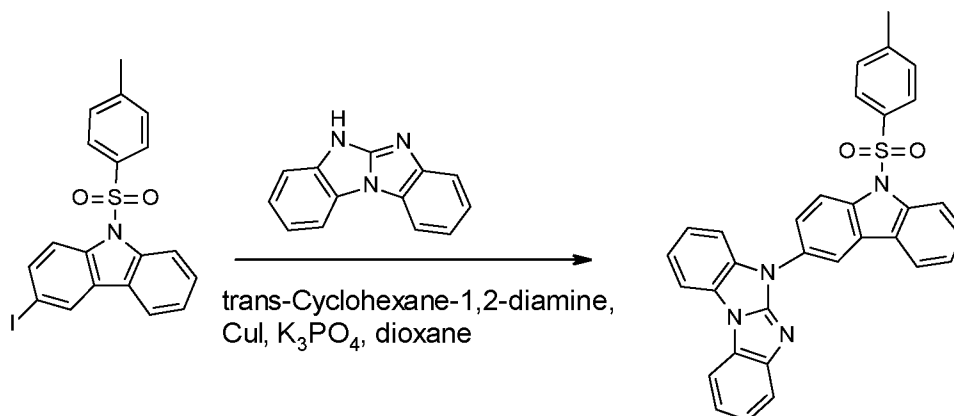
a) 76.9 g (0.460 mol) carbazole and 104 g (0.460 mol) 1-iodopyrrolidine-2,5-dione (NIS) in 100 ml acetic acid are stirred under nitrogen at 20 °C. After 5 h the product is filtered off. The product is crystallized from 900 ml ethanol using 2 g charcoal. The ethanol solution is filtered hot. The ethanol solution is cooled to 20 °C and the product is filtered off (yield: 59.5 g (44 %)).

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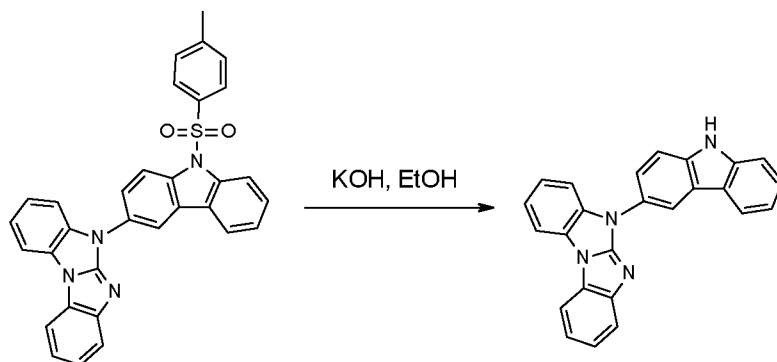
b) 19.7 g (67.0 mmol) 3-iodo-9H-carbazole and 2.95 g (73.7 mmol) sodium hydride 60 % dispersion in mineral oil in 500 ml tetrahydrofuran (THF) are stirred at 50 °C under nitrogen for 1h. 12.8 g (67.0 mmol) 4-methylbenzenesulfonyl chloride in 100 ml THF are added at 20 °C. The reaction mixture is stirred for 1 h at 20 °C and is then stirred for 1 h at 50 °C. The solution is filtered and the solvent is distilled off. 200 ml ethyl acetate are added and the organic phase is washed with a solution of citric acid, sodium hydrogen carbonate and water. The solvent is partly removed until the product starts to crystallize. The product is filtered off and washed with methanol (yield: 23 g (79 %)).



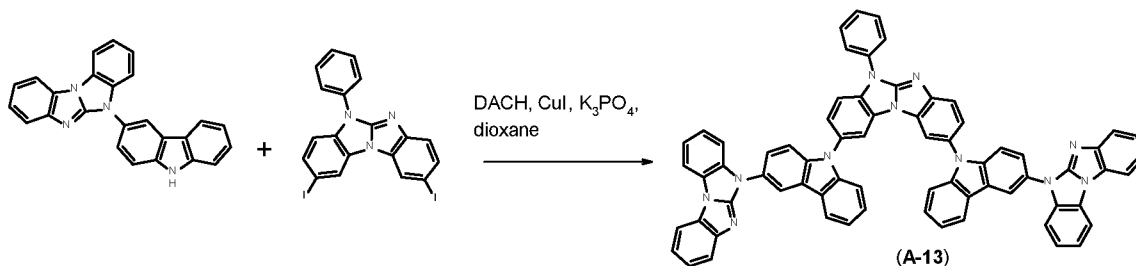
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c) 36.0 g (174 mmol) 6H-benzimidazo[1,2-a]benzimidazole, 77.8 g (174 mmol) 3-iodo-9-(p-tolylsulfonyl) carbazole, 106 g (0.500 mol) potassium phosphate, 5.5 g (28.9 mmol) copper iodide, and 111 g (0.972 mol) trans-cyclohexane-1,2-diamine in 900 ml dioxane are stirred at 100 °C 48 h under nitrogen. The product is filtered off, washed with dioxane, and ethanol and is used without purification in the next reaction step.

25

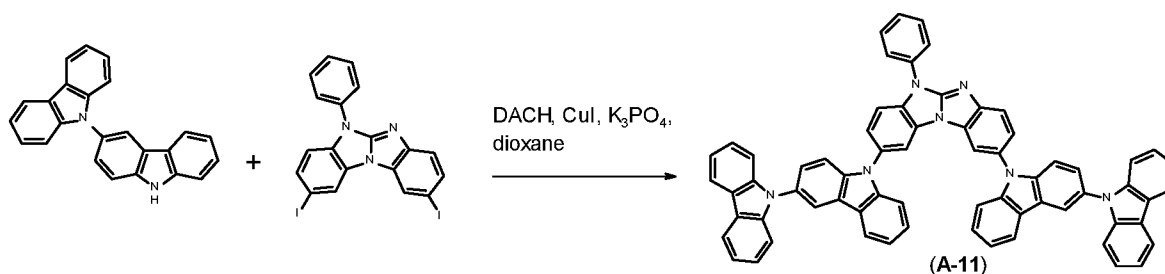


- d) A solution of 11.3 g (202 mmol) potassium hydroxide in 500 ml ethanol is added under nitrogen within 5 minutes to 53 g (101 mmol) 5-[9-(p-tolylsulfonyl)carbazol-3-yl]benzimidazo[1,2-a]benzimidazole in 500 ml boiling ethanol. After 5 h the product is filtered off and is washed with ethanol, water and methanol (yield: 32 g (85.4 %)).
- 5 $^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 11.6 (s, 1H), 8.57 (d, $J=7.8$ Hz, 1H), 8.22-8.28 (m, 3H), 7.74-7.82 (m, 2H), 7.57-7.62 (m, 2H), 7.38-7.54 (m, 4H), 7.27-7.34 (m, 2H), 7.20-7.24 (m, 1H).



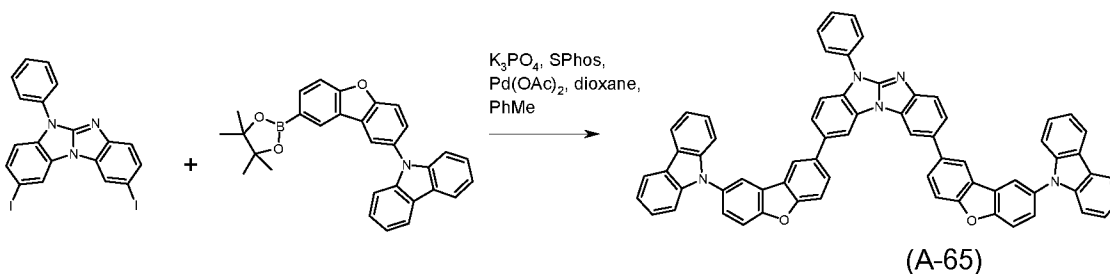
- 10 e) The product is prepared in analogy to the method described in example 1c).

Example 3



- 15 The synthesis of 3-carbazol-9-yl-9H-carbazole is described in J. Org. Chem. 73 (2008) 1809-1817. The product is prepared in analogy to the method described in example 1c).

Example 4



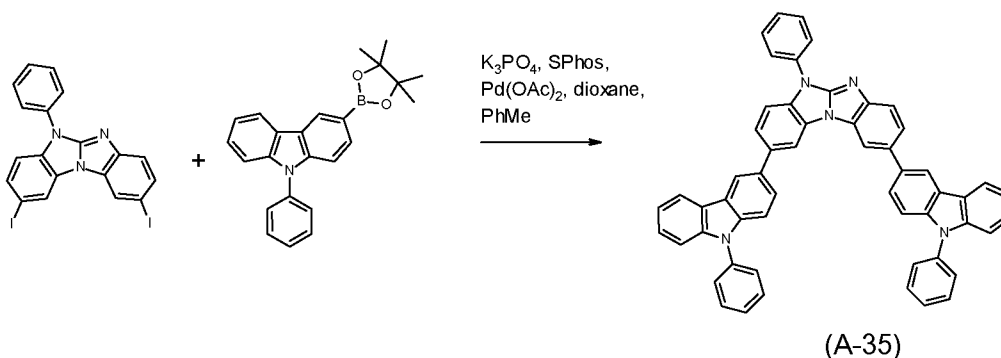
20

The synthesis of 9-[8-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)dibenzofuran-2-yl]carbazole is described in WO12130709A1.

4.82 g (10.5 mmol) 9-[8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzofuran-2-yl]carbazole, 2.78 g (5.20 mmol) 2,9-diiodo-5-phenyl-benzimidazolo[1,2-a]benzimidazole, 6.62 g (31.0 mmol) potassium phosphate tribasic in 30 ml dioxane, 70 ml toluene and 20 ml water are degased with argon. 0.1 g (0.445 mmol) palladium(II)acetate is added and the reaction mixture is degased with argon. 460 mg (1.121 mmol) SPhos (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl) is added and the reaction mixture is degased with argon. The reaction mixture is stirred at 80 °C under argon for 18 h. The organic layer is washed with a 1 wt% solution of NaCN in water and then the organic phase is washed with water. The organic phase is dried with magnesium sulfate and the solvent is removed in vacuum. Column chromatography on silica gel with dichloromethane gives 2.19 g (45 wt%) of the product.

¹H NMR (300 MHz, DMSO-d₆): δ, 7.25-7.53 (m, 13H), 7.65-7.86 (m, 10H), 7.93-8.07 (m, 6H), 8.24-8.27 (d, 4H), 8.52-8.53 (d, 2H), 8.67-8.68 (m, 4H)

Example 5



The synthesis of 9-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole is described in WO2012/023947A1.

3.95 g (10.7 mmol) 9-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole, 2.70 g (5.05 mmol) 2,9-diiodo-5-phenyl-benzimidazolo[1,2-a]benzimidazole, 5.36 g (25.0 mmol) potassium phosphate tribasic in 20 ml dioxane, 40 ml toluene and 20 ml water are degased with argon. 0.1 g (0.445 mmol) palladium(II)acetate is added and the reaction mixture is degased with argon. 460 mg (1.121 mmol) SPhos (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl) is added and the reaction mixture is degased with argon. The reaction mixture is stirred at 80 °C under argon for 18 h.

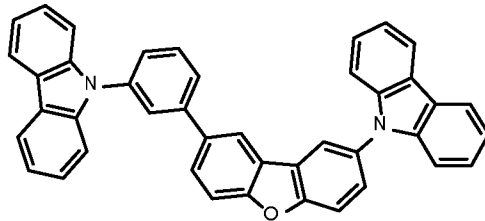
The organic layer is washed with a 1 wt% solution of NaCN in water and then the organic phase is washed with water. The organic phase is dried with magnesium sulfate and the solvent is removed in vacuum.

Column chromatography on silica gel with chloroform and then chloroform/methanol 99/1 gives 1.80 g (47 wt%) of the product.

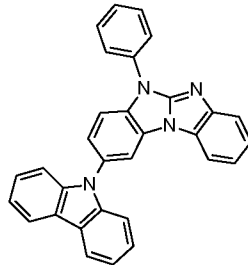
¹H NMR (400 MHz, DMSO-d₆): δ, 7.34-7.39 (m, 2H), 7.43-7.61 (m, 9H), 7.69-7.89 (m, 14H), 8.00-8.04 (t, 4H), 8.46-8.47 (t, 2H), 8.84-8.89 (m, 4H)

Comparative application example 1

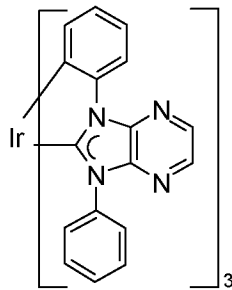
The ITO substrate used as the anode is first cleaned with an isopropanol in an ultrasonic bath. To eliminate any possible organic residues, the substrate is exposed to a continuous ozone flow in an ozone oven for further 30 minutes. This treatment also improves the hole injection properties of the ITO. Then Plexcore® OC AJ20-1000 (commercially available from Plextronics Inc.) is spin-coated and dried to form a hole injection layer (~40 nm). Thereafter, the organic materials specified below are applied by vapor deposition to the Plexcore® coated substrate at a rate of approx. 0.5-5 nm/min at about 10⁻⁷ -10⁻⁹ mbar. As a



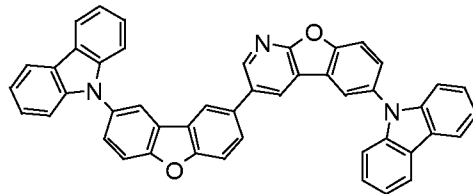
hole transport, compound (SH-1) is applied by vapor deposition in a thickness of 10 nm doped with MoOx (~10%) to improve the conduc-



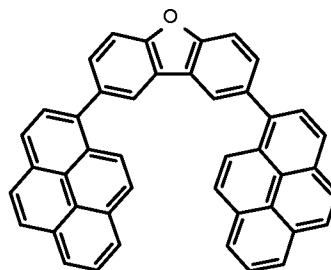
tivity. As exciton and electron blocker, (CC-1) is applied to the substrate with a thickness of 10 nm. Subsequently, a mixture of 10% by weight of emitter com-



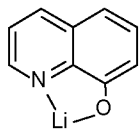
ound, (BE-1), 45% by weight of compound (CC-1) and 45% by weight



of compound (CC-2) are applied by vapor deposition in a thickness of 40 nm. Subsequently, material (CC-2) is applied by vapour deposition with a thickness of 5 nm as a blocker. Thereafter, a 20 nm thick electron transport layer is



deposited consisting of 50% by weight of (ETM-1), and of

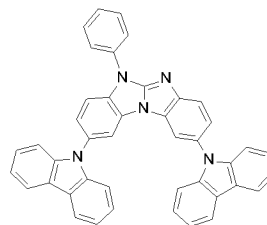


50% of (Liq). Finally a 2 nm KF layer serves as an electron injection layer and a 100 nm-thick Al electrode completes the device.

All fabricated parts are sealed with a glass lid and a getter in an inert nitrogen atmosphere.

5 Application Example 1

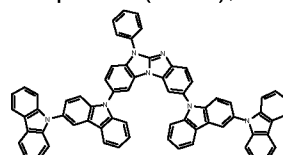
Comparative Application Example 1 is repeated except that compound (CC-1), which is



used as exciton blocker and host, is replaced by compound (A-1).

Application Example 2

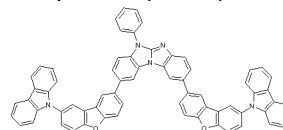
10 Comparative Application Example 1 is repeated except that compound (CC-1), which is



used as exciton blocker and host, is replaced by compound (A-11).

Application Example 3

Comparative Application Example 1 is repeated except that compound (CC-1), which is



15 used as exciton blocker and host, is replaced by compound (A-65).

OLED characterization

To characterize the OLED, electroluminescence spectra are recorded at various currents and voltages. In addition, the current-voltage characteristic is measured in combination with the light output emitted. The light output is converted to photometric parameters by calibration with a photometer. The results are shown in Table 1. Data are given at luminance (L) = 1000 Cd/m² except otherwise stated.

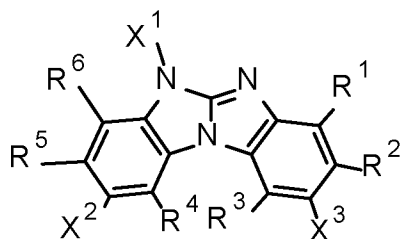
Table 1

Appl. Ex.	Host	U [V]
1	(A-1)	3.35
2	(A-11)	3.25
3	(A-65)	3.30
Comp. Appl. Ex. 1	(CC-1)	3.55

25 It is evident that the driving voltage U is decreased by replacing host (CC-1) by (A-1), (A-11) or (A-65), which is very important property to realise high efficiency device.

Claims

1. A compound of the formula



(I), wherein

5 R¹, R², R³, R⁴, R⁵ and R⁶ are independently of each other H, a C₁-C₂₅alkyl group, which can optionally be substituted by E and or interrupted by D; a C₆-C₂₄aryl group, which can optionally be substituted by G, or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G;

10 X¹ is a group of formula $-(A^1)_o-(A^2)_p-(A^3)_q-(A^4)_r-R^{16}$,

o is 0, or 1, p is 0, or 1, q is 0, or 1, r is 0, or 1,

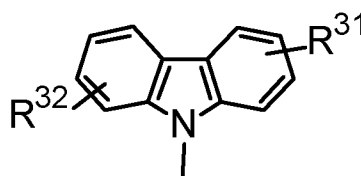
A¹, A², A³ and A⁴ are independently of each other a C₆-C₂₄arylen group, which can optionally be substituted by G, or a C₂-C₃₀heteroarylen group, which can optionally be substituted by G; wherein

15 X² and X³ are independently of each other a group of formula $-(A^5)_v-(A^6)_s-(A^7)_t-(A^8)_u-R^{15}$, or $-NR^{10}R^{11}$,

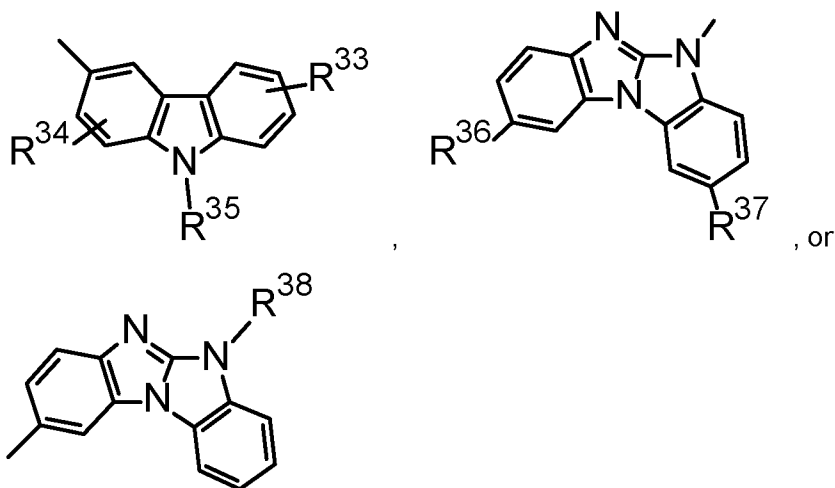
v is 0, or 1, s is 0, or 1, t is 0, or 1, u is 0, or 1,

A⁵, A⁶, A⁷ and A⁸ are independently of each other a C₆-C₂₄arylen group, which can optionally be substituted by G, or a C₂-C₃₀heteroarylen group, which can optionally be substituted by G; wherein

20 R¹⁰ and R¹¹ are independently of each other a C₆-C₂₄aryl group, which can optionally be substituted by G; or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G; or R¹⁰ and R¹¹ together with the nitrogen atom to which they are bonded form a heteroaromatic ring, or ring system;



25 R¹⁵ is a group of formula



R³¹, R³², R³³, R³⁴, R³⁶ and R³⁷ are independently of each other H, or a C₁-C₂₅alkyl group;

5 R³⁵ and R³⁸ are independently of each a C₆-C₁₀aryl group, which can optionally be substituted by one, or more C₁-C₂₅alkyl groups;

R¹⁶ is a C₆-C₂₄aryl group, which can optionally be substituted by G; or a C₂-C₃₀heteroaryl group, which can optionally be substituted by G;

10 D is -CO-, -COO-, -S-, -SO-, -SO₂-, -O-, -NR⁶⁵-, -SiR⁷⁰R⁷¹-, -POR⁷²-, -CR⁶³=CR⁶⁴-, or -C≡C-,

E is -OR⁶⁹-, -SR⁶⁹-, -NR⁶⁵R⁶⁶-, -COR⁶⁸-, -COOR⁶⁷-, -CONR⁶⁵R⁶⁶-, -CN, or halogen,

15 G is E, or a C₁-C₁₈alkyl group, a C₆-C₂₄aryl group, a C₆-C₂₄aryl group, which is substituted by F, C₁-C₁₈alkyl, or C₁-C₁₈alkyl which is interrupted by O; a C₂-C₃₀heteroaryl group, or a C₂-C₃₀heteroaryl group, which is substituted by F, C₁-C₁₈alkyl, or C₁-C₁₈alkyl which is interrupted by O;

R⁶³ and R⁶⁴ are independently of each other H, C₆-C₁₈aryl; C₆-C₁₈aryl which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; C₁-C₁₈alkyl; or C₁-C₁₈alkyl which is interrupted by -O-;

20 R⁶⁵ and R⁶⁶ are independently of each other a C₆-C₁₈aryl group; a C₆-C₁₈aryl which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-; or

R⁶⁵ and R⁶⁶ together form a five or six membered ring,

R⁶⁷ is a C₆-C₁₈aryl group; a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-,

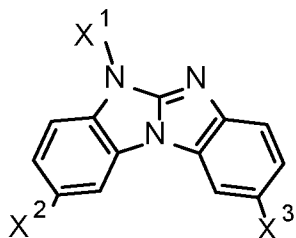
25 R⁶⁸ is H; a C₆-C₁₈aryl group; a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-,

R⁶⁹ is a C₆-C₁₈aryl; a C₆-C₁₈aryl, which is substituted by C₁-C₁₈alkyl, or C₁-C₁₈alkoxy; a C₁-C₁₈alkyl group; or a C₁-C₁₈alkyl group, which is interrupted by -O-,

30 R⁷⁰ and R⁷¹ are independently of each other a C₁-C₁₈alkyl group, a C₆-C₁₈aryl group, or a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl, and

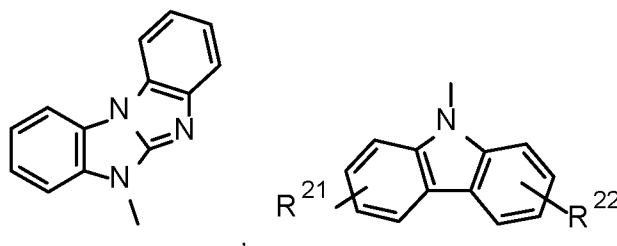
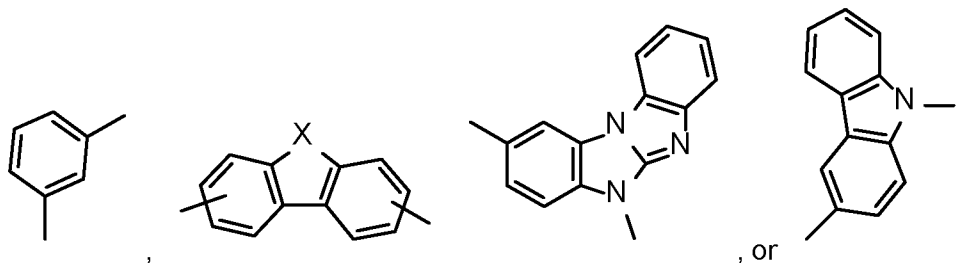
R⁷² is a C₁-C₁₈alkyl group, a C₆-C₁₈aryl group, or a C₆-C₁₈aryl group, which is substituted by C₁-C₁₈alkyl.

35 2. The compound according to claim 1, which is a compound of formula

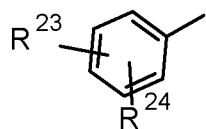


(Ia), wherein X¹, X² and X³ are defined in claim 1.

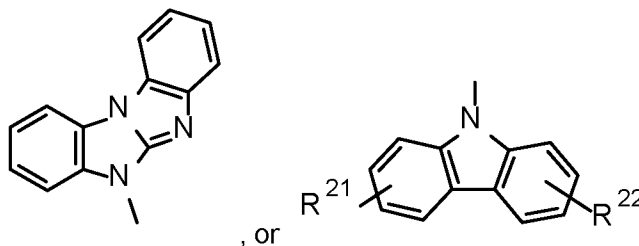
3. The compound according to any of claims 1 to 2, wherein
 X¹ is a group of the formula $-(A^1)_o-(A^2)_p-(A^3)_q-(A^4)_r-R^{16}$,
 5 o is 0, or 1, p is 0, or 1, q is 0, or 1, r is 0, or 1,
 A¹, A², A³ and A⁴ are independently of each other a group of the formula



R¹⁶ is a group of the formula



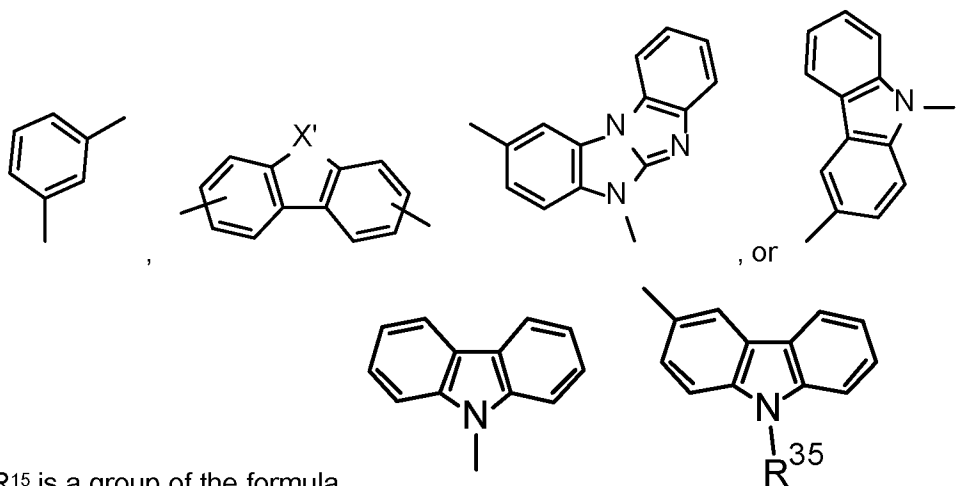
- 10 R²¹ and R²² are independently of each other H, a phenyl group, or a C₁-C₁₈alkyl group;
 R²³ and R²⁴ are independently of each other H, a phenyl group, or a C₁-C₁₈alkyl group;
 X is O, S, or NR²⁵, and
 15 R²⁵ a phenyl group, or a C₁-C₁₈alkyl group, with the proviso that o is 1, if R¹⁶ is a



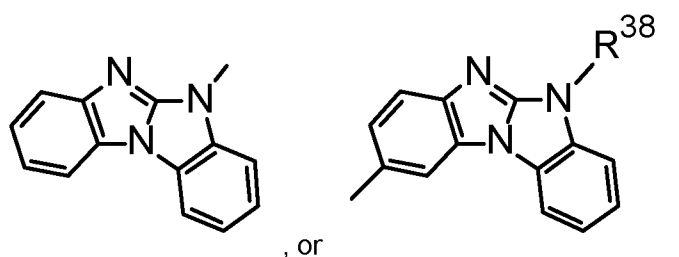
group of the formula

4. The compound according to claim 1, 2 or 3 wherein
 X² and X³ are independently of each other a group of formula $-(A^5)_v-(A^6)_s-(A^7)_t-(A^8)_u-$
 20 R¹⁵,
 v is 0, or 1, s is 0, or 1, t is 0, or 1, u is 0, or 1,

A⁵, A⁶, A⁷ and A⁸ are independently of each other a group of the formula

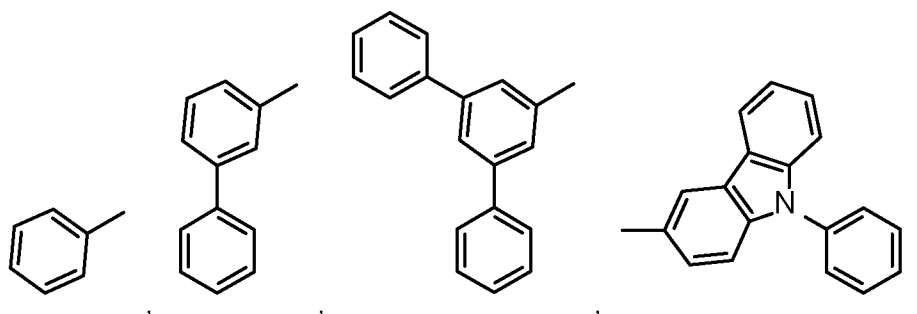


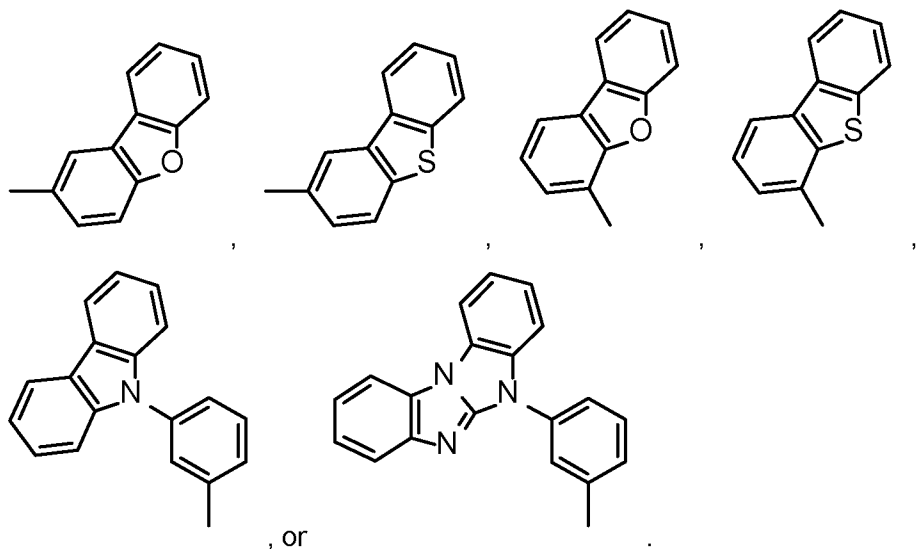
R¹⁵ is a group of the formula



- 5 R³⁵ and R³⁸ are independently of each other a phenyl group, which can optionally be substituted by one, or more C₁-C₂₅alkyl groups;
 X' is O, S, or NR^{25'}, and
 R^{25'} a phenyl group, or a C₁-C₁₈alkyl group.

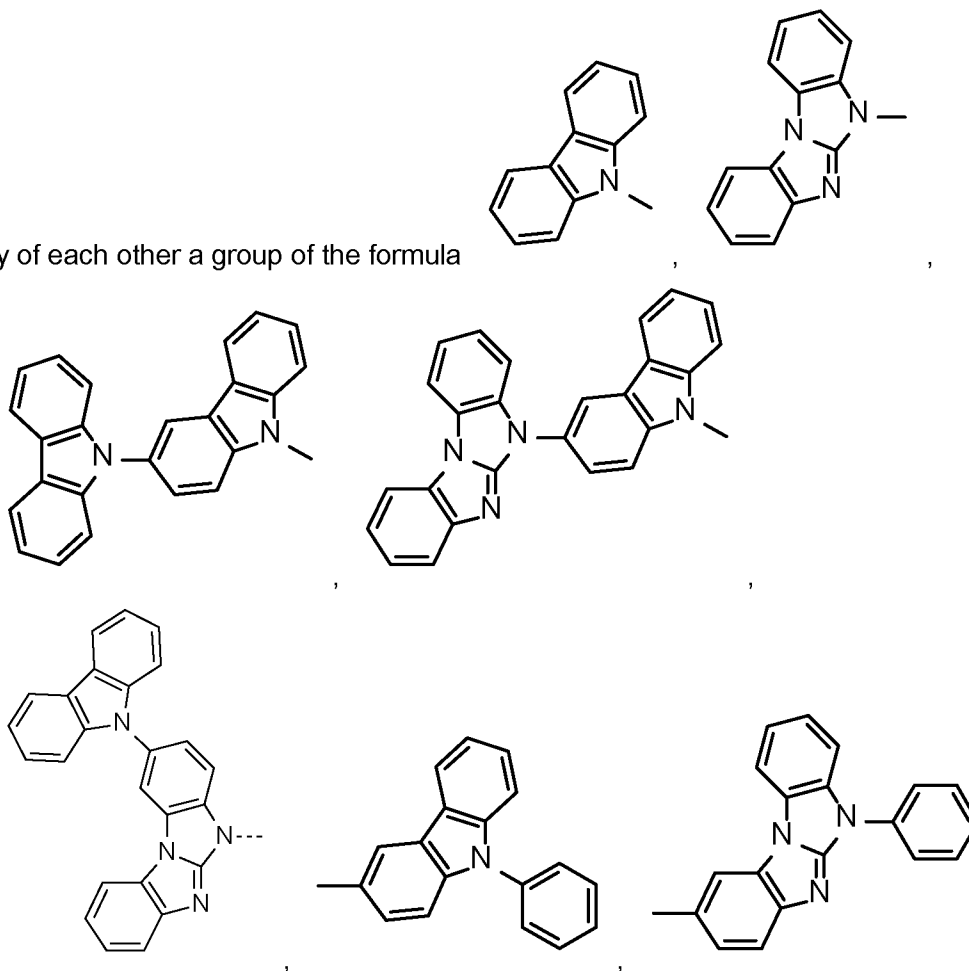
- 10 5. The compound according to any of claims 1 to 4, wherein X¹ is a group of the formula

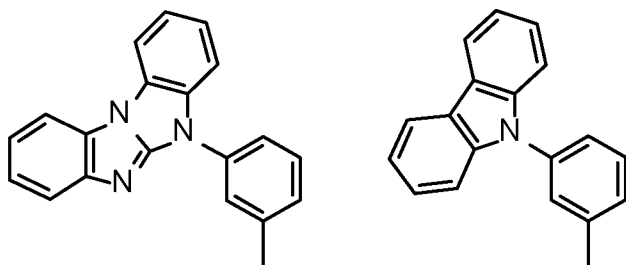




6. The compound according to any of claims 1 to 5, wherein X² and X³ are independent-

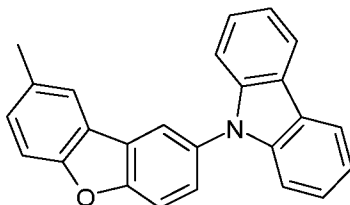
5 ly of each other a group of the formula





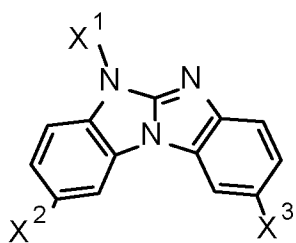
, or

; additionally, X² and X³ may be



a group of the formula

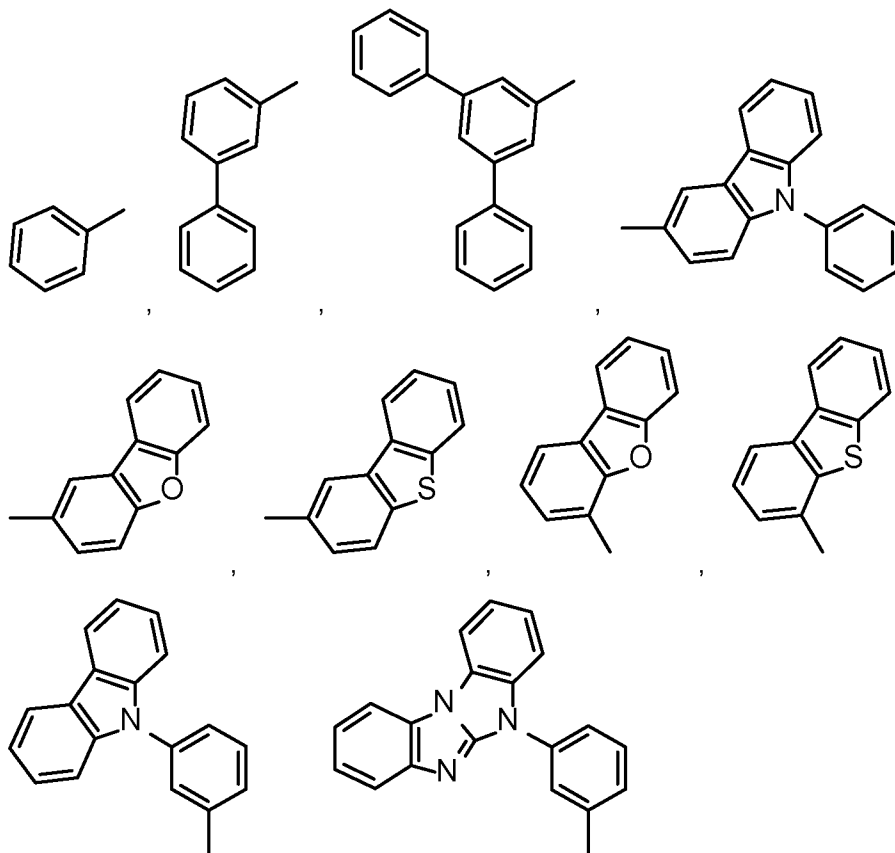
7. The compound according to any of claims 1 to 6, which is a compound of formula



5

(Ia), wherein

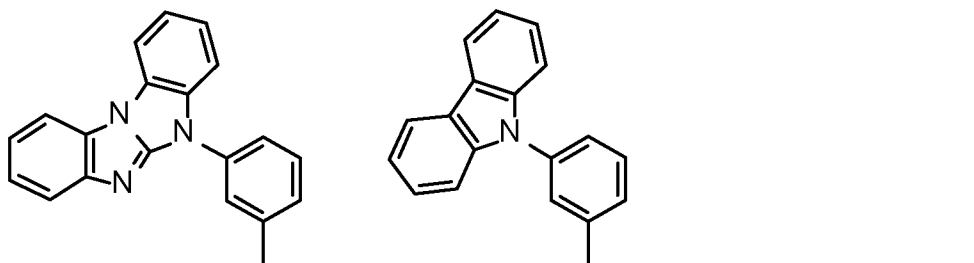
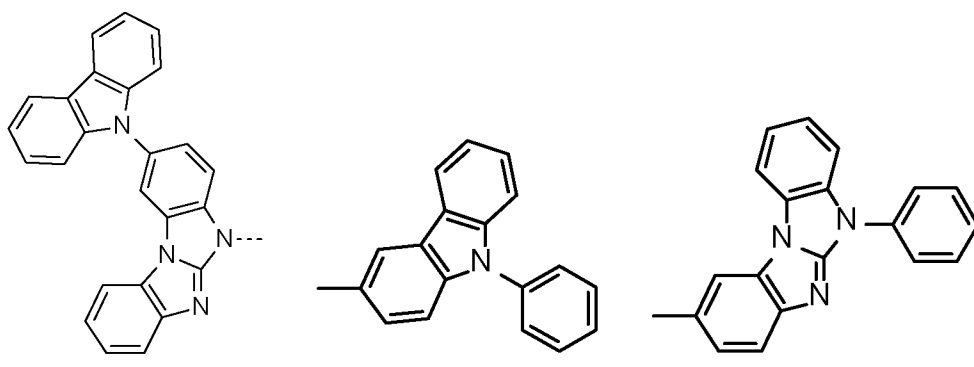
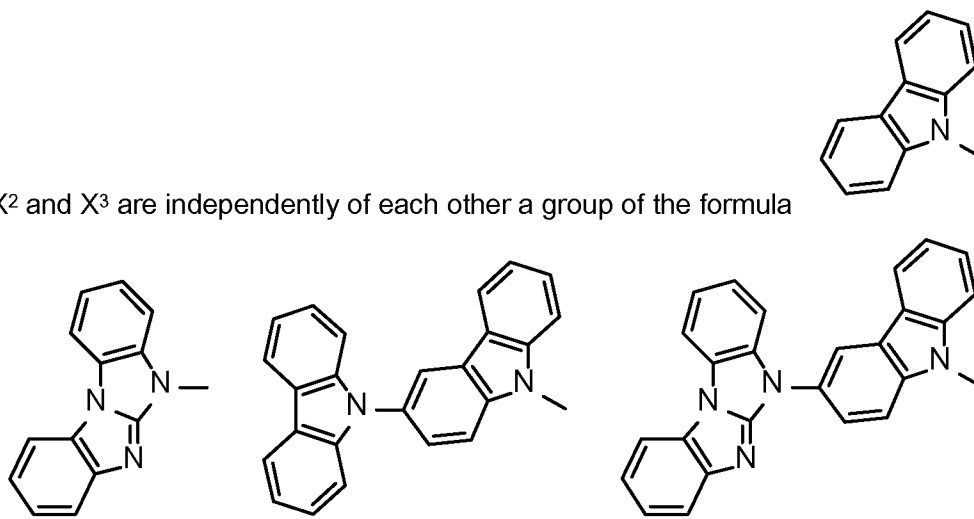
X¹ is a group of the formula



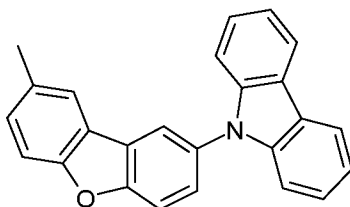
, or

, and

X² and X³ are independently of each other a group of the formula



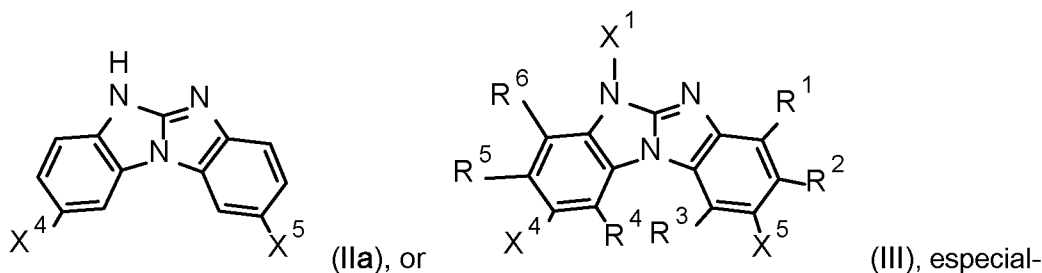
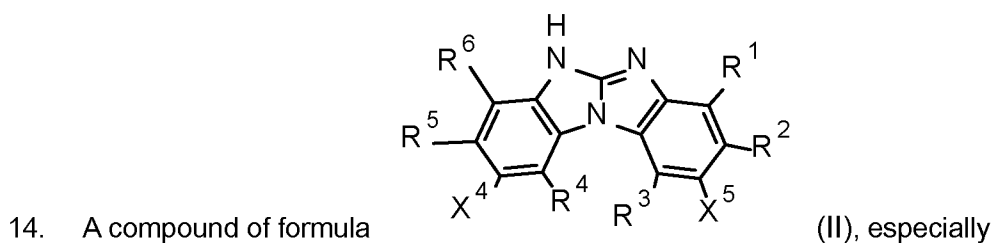
, or ; additionally, X² and X³ may be



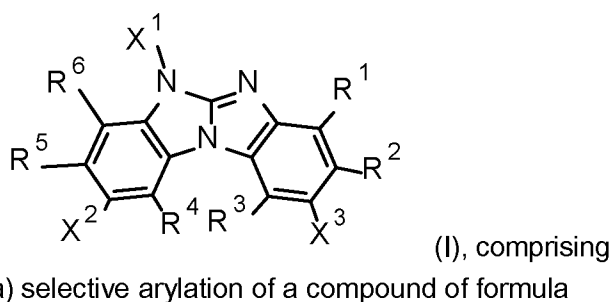
5 a group of the formula

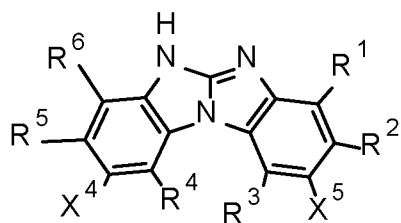
- 8. An electronic device, comprising a compound according to any of claims 1 to 7.
- 9. The electronic device according to claim 8, which is an electroluminescent device.
- 10. A hole transport layer, an electron/exciton blocking layer, or an emitting layer comprising a compound according to any of claims 1 to 7.
- 11. The emitting layer according to claim 10, comprising a compound according to any of claims 1 to 7 as host material in combination with a phosphorescent emitter.

12. An apparatus selected from the group consisting of stationary visual display units; mobile visual display units; illumination units; keyboards; items of clothing; furniture; wallpaper, comprising the organic electronic device according to claim 8, or 9, or the hole transport layer, the electron/exciton blocking layer, or the emitting layer according to claim 10.
13. Use of the compounds of formula I according to any of claims 1 to 7 for electrophotographic photoreceptors, photoelectric converters, organic solar cells, switching elements, organic light emitting field effect transistors, image sensors, dye lasers and electroluminescent devices.

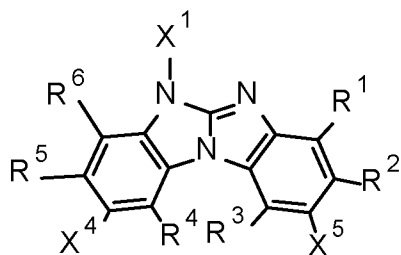


15. ly (IIIa), wherein X⁴ and X⁵ are independently of each other Cl, Br, or I and R¹, R², R³, R⁴, R⁵, R⁶ and X¹ are defined in claim 1.
15. A process for the preparation of a compound of formula



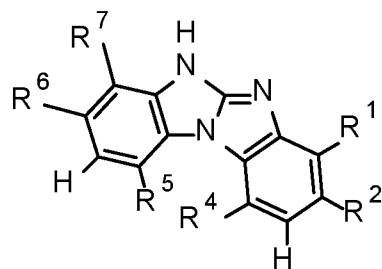


(II) to obtain a compound of formula



(III),

- b) Ullmann coupling of the compound of formula (III) with an arylamine, to obtain the compound of formula (I), or
- 5 Suzuki coupling of the compound of formula (III) with a boronic esters to obtain the compound of formula (I), wherein
- X^4 and X^5 are independently of each other Cl, Br, or I; and
- R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , X^1 , X^2 and X^3 are as defined in claim 1.
- 10 16. The process according to claim 15, wherein the compound of formula (II) is prepared



by halogenation of a compound of formula

(IV).

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/055667A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D487/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/009317 A1 (BASF SE [DE]; BASF SCHWEIZ AG [CH]) 16 January 2014 (2014-01-16) claim 1	1-16
A	----- KOLESNIKOVA T V ET AL: "REACTIONS OF N-POLYFLUOROPHENYLCARBONIMIDOYL DICHLORIDES WITH PRIMARY AND SECONDARY AMINES, KINETICS AND MECHANISM. SYNTHESIS OF POLYFLUORINATED CARBODIIMIDES, CHLOROFORMAMIDINES, GUANIDINES AND BENZIMIDAZOLES", JOURNAL OF FLUORINE CHEMISTRY, ELSEVIER, NL, vol. 40, 1 January 1988 (1988-01-01), pages 217-246, XP002914639, ISSN: 0022-1139, DOI: 10.1016/S0022-1139(00)83067-5 example XIII -----	14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

7 October 2015

Date of mailing of the international search report

16/10/2015

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Baston, Eckhard

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2015/055667

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014009317	A1	16-01-2014	
		CN 104395316 A	04-03-2015
		EP 2872512 A1	20-05-2015
		KR 20150036402 A	07-04-2015
		TW 201410678 A	16-03-2014
		US 2015207083 A1	23-07-2015
		WO 2014009317 A1	16-01-2014
