(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 September 2012 (13.09.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/121561 A1

(51) International Patent Classification:
C07D 403/14 (2006.01) *C07D 401/14* (2006.01)
C07D 409/14 (2006.01) *C09K 11/06* (2006.01)
C07D 405/14 (2006.01) *H01L 27/32* (2006.01)
C07D 403/04 (2006.01) *H01L 51/54* (2006.01)

(21) International Application Number:
PCT/KR2012/001712

(22) International Filing Date:
8 March 2012 (08.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10-2011-0020492 8 March 2011 (08.03.2011) KR

(71) Applicant *(for all designated States except US)*: **ROHM AND HAAS ELECTRONIC MATERIALS KOREA LTD.** [KR/KR]; 736, Baekseok-dong, Cheonan-si, Chungcheongnam-do 331-980 (KR).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **AHN, Hee-choon** [KR/KR]; 105, Sinheung Villa, 355-1, Mangpo-dong, Yeongtong-gu, Suwon-si, Gyeonggi-do 443-400 (KR). **YOON, Seok-keun** [KR/KR]; 205, 342-4, Sin-dong, Yeongtong-gu, Suwon-si, Gyeonggi-do 443-390 (KR). **MOON, Doo-hyeon** [KR/KR]; 104-101, World Meridian 2 Cha Apt., Jinan-dong, Hwaseong-si, Gyeonggi-do 445-718 (KR). **KIM, Hee-sook** [KR/KR]; 101, 340-22, Sin-dong, Yeongtong-gu, Suwon-si, Gyeonggi-do 443-390 (KR). **LEE, Su-hyun** [KR/KR]; 141-501, Hanil Town Apt., Jowon 2-dong, Jangan-gu, Suwon-si, Gyeonggi-do 440-709 (KR). **SHIN, Hyo-nim** [KR/KR]; 204-701, EG The One Apt., Botdeulmaeul 2-danji, Sampyeong-dong, Bundang-gu, Seongnam-si, Gyeonggi-do 463-892 (KR). **LEE, Kyung-joo** [KR/KR]; 210-1001, Hyundai Hometown Apt., Dohwa-dong, Mapo-gu, Seoul 121-773 (KR). **PARK, Kyoung-jin** [KR/KR]; A202, Donghyeon Villa, 124-13, Hadaewon-dong, Jungwon-gu, Seongnam-si, Gyeonggi-do 462-110 (KR). **KIM, Nam-kyun** [KR/KR]; 510-1601, Kumho Bestville Apt., 867, Sanghyeon-dong, Suji-gu, Yongin-si, Gyeonggi-do 448-130 (KR). **CHO, Young-jun** [KR/KR]; 204-701, EG The One Apt., Botdeulmaeul 2-danji, Sampyeong-dong, Bundang-gu, Seongnam-si, Gyeonggi-do 463-892 (KR). **KWON, Hyuck-joo** [KR/KR]; 105-2003, Hillstate Apt., Samseong-dong, Gangnam-gu, Seoul 135-877 (KR). **KIM, Bong-ok** [KR/KR]; 208-401, Hillstate Apt., 50, Samseong-dong, Gangnam-gu, Seoul 135-877 (KR).

(74) Agent: **CHANG, Hoon**; Korean Re Bldg. 5F, #80, Soosong-dong, Chongro-ku, Seoul 110-733 (KR).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, 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, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2012/121561 A1

(54) Title: NOVEL ORGANIC ELECTROLUMINESCENT COMPOUNDS AND ORGANIC ELECTROLUMINESCENT DEVICE USING THE SAME

(57) Abstract: The present invention relates to a novel organic electroluminescent compound and an organic electroluminescent device using the same. Said organic luminescent compound provides an organic electroluminescent device which has high luminous efficiency and a long operation lifetime and requires a low driving voltage improving power efficiency and power consumption.

Description

Title of Invention: NOVEL ORGANIC ELECTROLUMINESCENT COMPOUNDS AND ORGANIC ELECTROLUMINESCENT DEVICE USING THE SAME

Technical Field

[1] The present invention relates to novel organic electroluminescent compounds and organic electroluminescent device using the same.

Background Art

[2] An electroluminescent (EL) device is a self-light-emitting device which has advantages over other types of display devices in that it provides a wider viewing angle, a greater contrast ratio, and has a faster response time. An organic EL device was first developed by Eastman Kodak, by using small molecules (aromatic diamines) and aluminum complexes in a light-emitting layer [Appl. Phys. Lett. 51, 913, 1987].

[3] The most important factor to determine luminous efficiency in an organic EL device is a light-emitting materials. Until now, fluorescent materials have been widely used as light-emitting material. However, in view of electroluminescent mechanisms, phosphorescent materials theoretically show four (4) times higher luminous efficiency than fluorescent materials. Thus, recently, phosphorescent materials have been investigated.

[4] Iridium(III) complexes have been widely known as phosphorescent material, including bis(2-(2'-benzothienyl)-pyridinato-N,C3')iridium(acetylacetonate) ((acac)Ir(btp)$_2$), tris(2-phenylpyridine)iridium (Ir(ppy)$_3$) and bis(4,6-difluorophenylpyridinato-N,C2)picolinate iridium (Firpic) as red, green and blue materials, respectively.

[5] In order to improve color purity, luminous efficiency and stability, light-emitting materials can be used as one prepared by mixing a dopant with a host material. In the host material/dopant system, the host material has a great influence on the efficiency and performance of an EL device, and thus is important.

[6] At present, 4,4'-N,N'-dicarbazol-biphenyl (CBP) is the most widely known host material for phosphorescent materials. Further, Pioneer (Japan) developed a high performance organic EL device employing, as a host material, bathocuproine (BCP) or aluminum(III)bis(2-methyl-8-quinolinate)(4-phenylphenolate) (BAlq) which had been a material used for a hole blocking layer.

[7] Though these phosphorous host materials provide good light-emitting characteristics, they have the following disadvantages: (1) Due to their low glass transition temperature and poor thermal stability, their degradation may occur during a high-temperature deposition process in a vacuum. (2) The power efficiency of an organic

EL device is given by [(π/voltage) × current efficiency], and thus the power efficiency is inversely proportional to the voltage. Though an organic EL device comprising phosphorescent materials provides better current efficiency (cd/A) than one comprising fluorescent materials, a significantly high driving voltage is required to be applied to an organic EL device, thereby resulting in poor power efficiency (lm/W). (3) Further, the operation lifetime of an organic EL device is short and luminous efficiency is still required to be improved.

[8] International Patent Publication No. WO 2006/049013 discloses compounds for organic electroluminescent materials whose backbone has a condensed bicycle group. However, it does not disclose compounds having a nitrogen-containing condensed bicyclic group, which is formed by condensing two 6-membered rings; a carbazolic group; and an aryl or heteroaryl group. Further, an organic EL device comprising said compounds fails to provide good luminous efficiency, operation lifetime and driving voltage.

Disclosure of Invention

Technical Problem

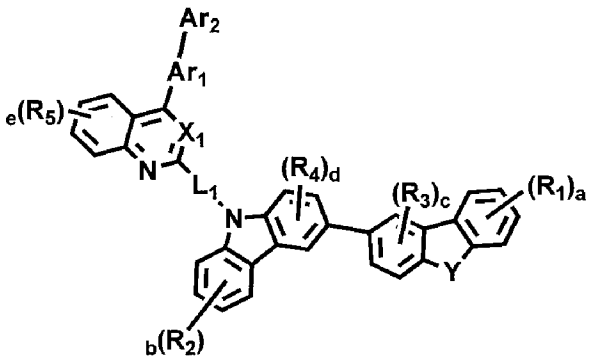
[9] An object of the present invention is to provide organic electroluminescent compounds imparting excellent luminous efficiency, long operation lifetime and low driving voltage to a device; and an organic electroluminescent device using said compounds.

Solution to Problem

[10] The present inventors found that the above object can be achieved by a compound represented by the following formula 1:

[11] [Formula 1]

[12]



[13] wherein

[14] L_1 represents a single bond, a substituted or unsubstituted 5- to 30-membered heteroarylene group, a substituted or unsubstituted (C6-C30)arylene group, or a substituted or unsubstituted (C6-C30)cycloalkylene group;

[15] X_1 represents CH or N;

[16] Y represents -O-, -S-, -$CR_{11}R_{12}$- or -NR_{13}-;

[17] Ar_1 represents a single bond, a substituted or unsubstituted 5- to 30-membered heteroarylene group, a substituted or unsubstituted (C6-C30)arylene group, or a substituted or unsubstituted (C1-C30)alkylene group;

[18] Ar_2 represents hydrogen, deuterium, a substituted or unsubstituted (C1-C30)alkyl group, a substituted or unsubstituted (C6-C30)aryl group, or a substituted or unsubstituted 5- to 30-membered heteroaryl group;

[19] R_1 to R_5 each independently represent hydrogen, deuterium, a halogen, a substituted or unsubstituted (C1-C30)alkyl group, a substituted or unsubstituted (C6-C30)aryl group, a substituted or unsubstituted 5- to 30-membered heteroaryl group, a substituted or unsubstituted (C3-C30)cycloalkyl group, a substituted or unsubstituted 5- to 7-membered heterocycloalkyl group, a substituted or unsubstituted (C6-C30)aryl(C1-C30)alkyl group, a substituted or unsubstituted (C6-C30)aryl group fused with at least one (C3-C30)cycloalkyl group, a 5- or 7-membered heterocycloalkyl group fused with at least one substituted or unsubstituted (C6-C30)aromatic ring, (C3-C30)cycloalkyl group fused with at least one substituted or unsubstituted (C6-C30)aromatic ring, -$NR_{14}R_{15}$, -$SiR_{16}R_{17}R_{18}$, -SR_{19}, -OR_{20}, a substituted or unsubstituted (C2-C30)alkenyl group, a substituted or unsubstituted (C2-C30)alkynyl group, a cyano group, a nitro group, or a hydroxyl group; or are linked to an adjacent substituent via a substituted or unsubstituted (C3-C30)alkylene group or a substituted or unsubstituted (C3-C30)alkenylene group to form a mono- or polycyclic alicyclic ring or a mono- or polycyclic aromatic ring whose carbon atom(s) may be substituted by at least one hetero atom selected from nitrogen, oxygen and sulfur;

[20] R_{11} to R_{20} have the same meaning as one of R_1 to R_5;

[21] a, b and e each independently represent an integer of 1 to 4; where a, b or e is an integer of 2 or more, each of R_1, each of R_2 or each of R_5 is the same or different;

[22] c and d each independently represent an integer of 1 to 3; where c or d is an integer of 2 or more, each of R_3 or each of R_4 is the same or different; and

[23] the heterocycloalkyl group and the heteroaryl(ene) group contain at least one hetero atom selected from B, N, O, S, P(=O), Si and P.

[24] Herein, "(C1-C30)alkyl(ene)" is a linear or branched alkyl(ene) having 1 to 30, preferably 1 to 20, more preferable 1 to 10 carbon atoms and includes methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, etc.; "(C2-C30) alkenyl(ene)" is a linear or branched alkenyl(ene) having 2 to 30, preferably 2 to 20, more preferably 1 to 10 carbon atoms and includes vinyl, 1-propenyl, 2-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 2-methylbut-2-enyl, etc.; "(C2-C30)alkynyl" is a linear or branched alkynyl having 2 to 30, preferably 2 to 20, more preferably 1 to 10 carbon atoms and includes ethynyl, 1-propynyl, 2-propynyl, 1-butynyl, 2-butynyl, 3-butynyl,

1-methylpent-2-ynyl, etc.; "(C1-C30)alkoxy" is a linear or branched alkoxy having 1 to 30, preferably 2 to 20, more preferably 2 to 10 carbon atoms and includes methoxy, ethoxy, propoxy, isopropoxy, 1-ethylpropoxy, etc.; "(C3-C30)cycloalkyl" is a mono- or polycyclic hydrocarbon having 3 to 30, preferably 3 to 20, more preferably 3 to 7 carbon atoms and includes cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, etc.; "(C6-C30)cycloalkylene" is one formed by removing hydrogen from cycloalkyl having 6 to 30, preferably 6 to 20, more preferably 6 or 7 carbon atoms; and "5- to 7-membered heterocycloalkyl" is a cycloalkyl having at least one hetero atom selected from B, N, O, S, P(=O), Si and P, preferably N, O and S, and carbon atoms as remaining ring backbone atoms other than said hetero atom and includes tetrahydrofuran, pyrrolidine, tetrahydropyran, etc. Further, "(C6-C30)aryl(ene)" is a monocyclic ring or fused ring derived from an aromatic hydrocarbon and having preferably 6 to 20 ring backbone carbon atoms; and includes phenyl, biphenyl, terphenyl, naphthyl, fluorenyl, phenanthrenyl, anthracenyl, indenyl, triphenylenyl, pyrenyl, tetracenyl, perylenyl, chrysenyl, naphthacenyl, fluoranthenyl, etc. Further, "5- or 30-membered heteroaryl(ene)" is an aryl having at least one, preferably 1 to 4 hetero atom selected from the group consisting of B, N, O, S, P(=O), Si and P, and carbon atoms as remaining ring backbone atoms other than said hetero atom; is a monocyclic ring or fused ring condensed with at least benzene ring; has preferably 5 to 21 ring backbone atoms; may be partially saturated; may be one formed by linking at least one heteroaryl or aryl group to a heteroaryl group via a single bond(s); and includes a monocyclic ring-type heteroaryl including furyl, thiophenyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, thiadiazolyl, isothiazolyl, isoxazolyl, oxazolyl, oxadiazolyl, triazinyl, tetrazinyl, triazolyl, tetrazolyl, furazanyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, etc. and a fused ring-type heteroaryl including benzofuranyl, benzothiophenyl, isobenzofuranyl, dibenzofuranyl, dibenzothiophenyl, benzoimidazolyl, benzothiazolyl, benzoisothiazolyl, benzoisoxazolyl, benzoxazolyl, isoindolyl, indolyl, indazolyl, benzothiadiazolyl, quinolyl, isoquinolyl, cinnolinyl, quinazolinyl, quinoxalinyl, carbazolyl, phenoxazinyl, phenanthridinyl, benzodioxolyl, etc.

[25] Preferably, substituents of formula I are as follows:

[26] L_1 represents preferably a single bond, a substituted or unsubstituted 5- or 30-membered heteroarylene group or a substituted or unsubstituted (C6-C30)arylene group, more preferably a single bond or a substituted or unsubstituted (C6-C30)arylene group.

[27] X represents preferably N.

[28] Y represents preferably -O-, -S-, $-CR_{11}R_{12}-$ (wherein R_{11} and R_{12} each independently represent a substituted or unsubstituted (C1-C30)alkyl group) or $-NR_{13}-$ (wherein R_{13} represents a halogen, deuterium, a substituted or unsubstituted (C6-C30)aryl group, or

a substituted or unsubstituted 5- or 30-membered heteroaryl group).

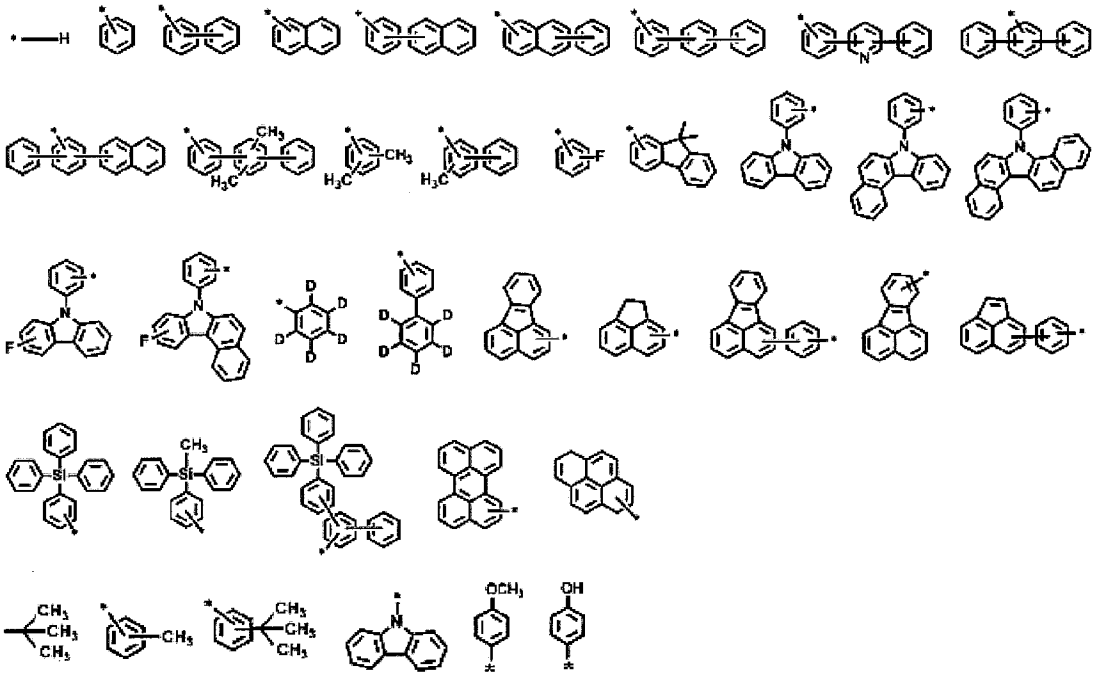
[29] R_1 and R_2 each independently represent hydrogen, a substituted or unsubstituted (C6-C30)aryl group, a substituted or unsubstituted 5- or 30-membered heteroaryl group, $-NR_{14}R_{15}$ (wherein R_{14} and R_{15} each independently represent a substituted or unsubstituted (C1-C30)alkyl group or a substituted or unsubstituted (C6-C30)aryl group) or a hydroxyl group, more preferably hydrogen or a substituted or unsubstituted (C6-C30)aryl group.

[30] R_3 to R_5 each independently represent hydrogen or a substituted or unsubstituted (C1-C30)alkyl group, more preferably hydrogen.

[31] a to e each independently represent an integer of 1.

[32] $*-Ar_1-Ar_2$

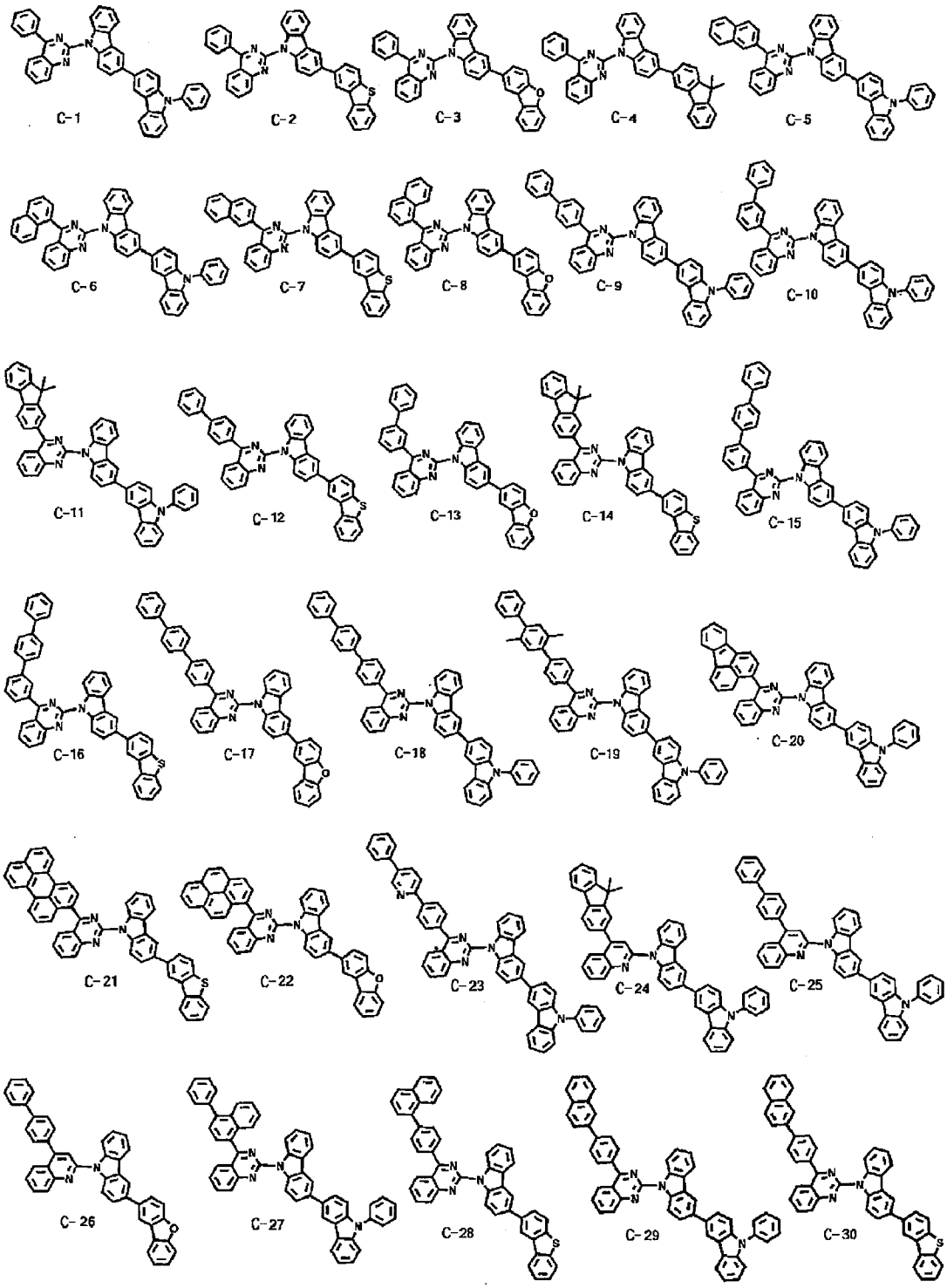
is selected from the following structures:

[33] 

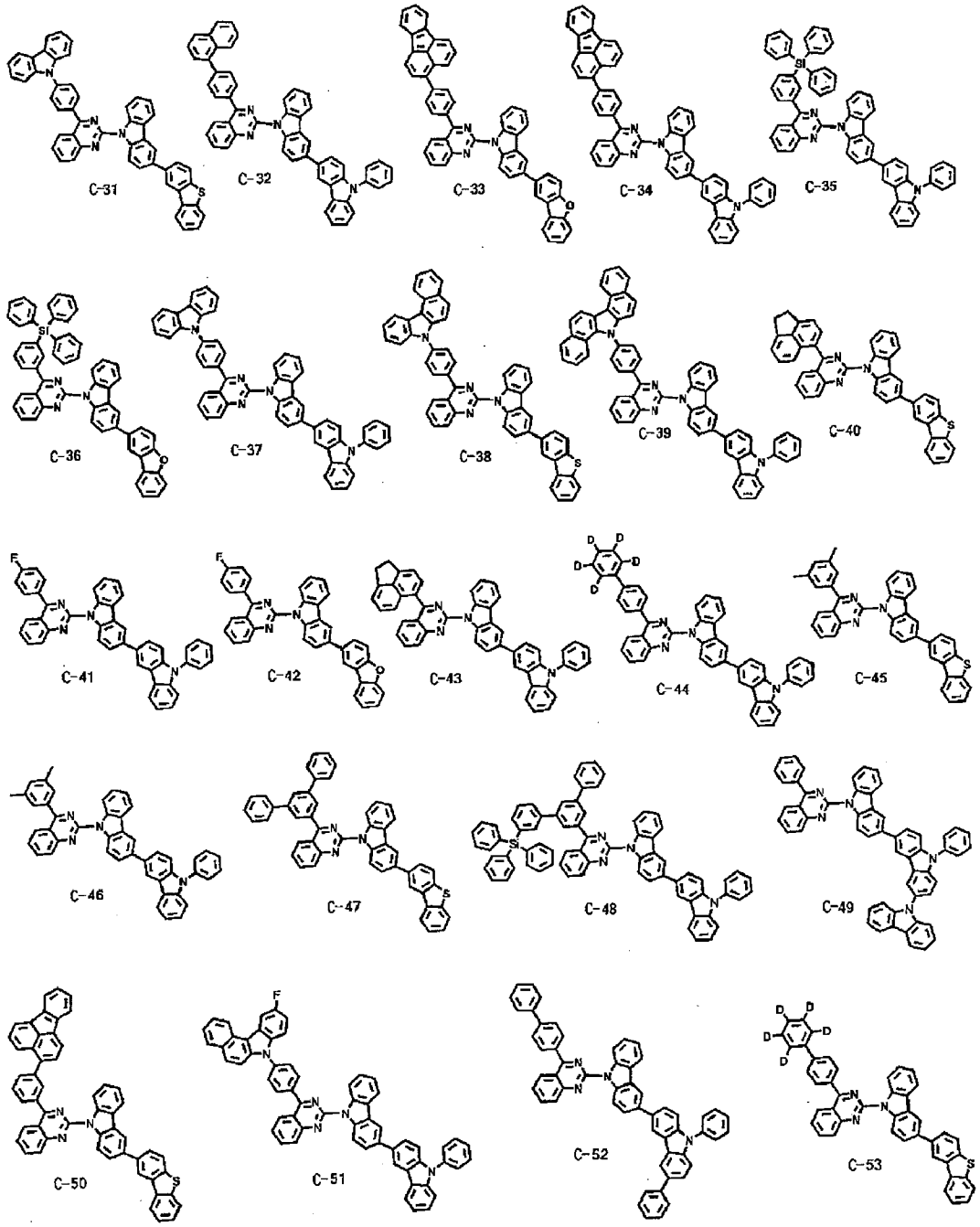
[34] Herein, substituents of the substituted (C1-C30)alkyl group, the substituted (C2-C30)alkenyl group, the substituted (C2-C30)alkynyl group, the substituted (C6-C30)cycloalkylene group, the substituted (C3-C30)cycloalkyl group, the substituted 5- to 7-membered heterocycloalkyl group, the substituted (C6-C30)aryl(ene) group, the substituted 5- to 30-membered heteroaryl(ene) group and the substituted aromatic ring represented by said L_1, Ar_1, Ar_2, R_1 to R_5 and R_{11} to R_{20} each independently is at least one selected from the group consisting of deuterium, a halogen, a cyano group, a carboxyl group, a nitro group, a hydroxyl group, a (C1-C30)alkyl group, a halo(C1-C30)alkyl group, a (C2-C30)alkenyl group, a (C2-C30)alkynyl group, a (C1-C30)alkoxy group, a (C1-C30)alkylthio group, a (C3-C30)cycloalkyl group, a (C3-C30)cycloalkenyl group, a 5- to 7-membered heterocycloalkyl group, a

(C6-C30)aryl group, a (C6-C30)aryloxy group, a (C6-C30)arylthio group, a 5- to 30-membered heteroaryl group, a 5- to 30-membered heteroaryl group substituted by a (C6-C30)aryl group, a (C6-C30)aryl group substituted by a 5- to 30-membered heteroaryl group, a tri(C1-C30)alkylsilyl group, a tri(C6-C30)arylsilyl group, a di(C1-C30)alkyl(C6-C30)arylsilyl group, a (C1-C30)alkyldi(C6-C30)arylsilyl group, an amino group, a mono or di(C1-C30)alkylamino group, a mono or di(C6-C30)arylamino group, a (C1-C30)alkyl(C6-C30)arylamino group, a (C1-C30)alkylcarbonyl group, a (C1-C30)alkoxycarbonyl group, a (C1-C30)arylcarbonyl group, a di(C6-C30)arylbornyl group, a di(C1-C30)alkylbornyl group, a (C1-C30)alkyl(C6-C30)arylbornyl group, a (C6-C30)aryl(C1-C30)alkyl group and a (C1-C30)alkyl(C6-C30)aryl group. Preferably, said substituents are at least one selected from the group consisting of deuterium, a halogen, a (C1-C30)alkyl group, a halo(C1-C30)alkyl group, a (C6-C30)aryl group, a 5- to 30-membered heteroaryl group, a tri(C1-C30)alkylsilyl group, a tri(C6-C30)arylsilyl group, a di(C1-C30)alkyl(C6-C30)arylsilyl group, a (C1-C30)alkyldi(C6-C30)arylsilyl group, a hydroxyl group and a (C1-C30)alkoxy group.

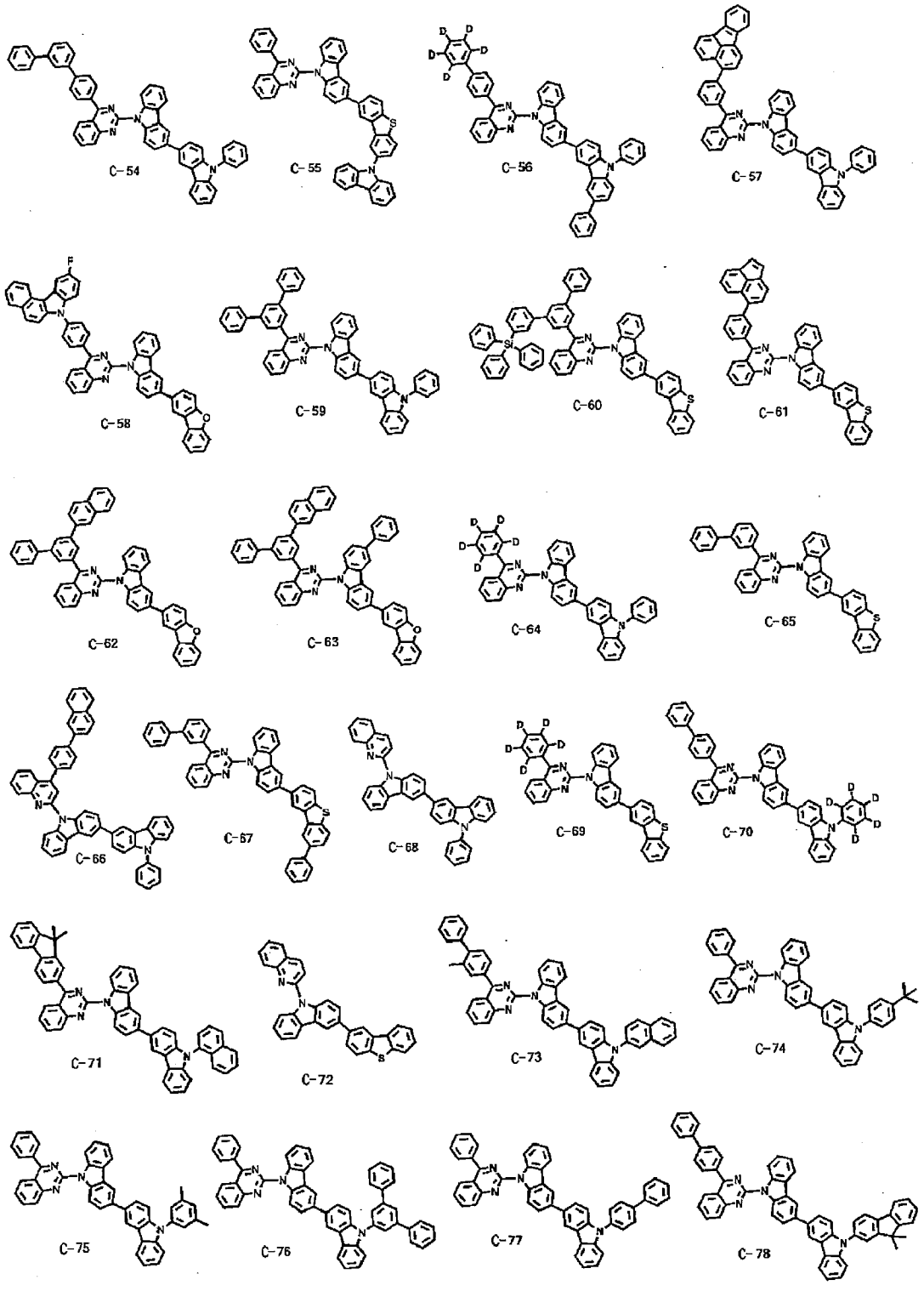
[35] Organic electroluminescent compounds according to the present invention include the following, but are not limited thereto:


C-1
C-2
C-3
C-4
C-5
C-6
C-7
C-8
C-9
C-10
C-11
C-12
C-13
C-14
C-15
C-16
C-17
C-18
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30

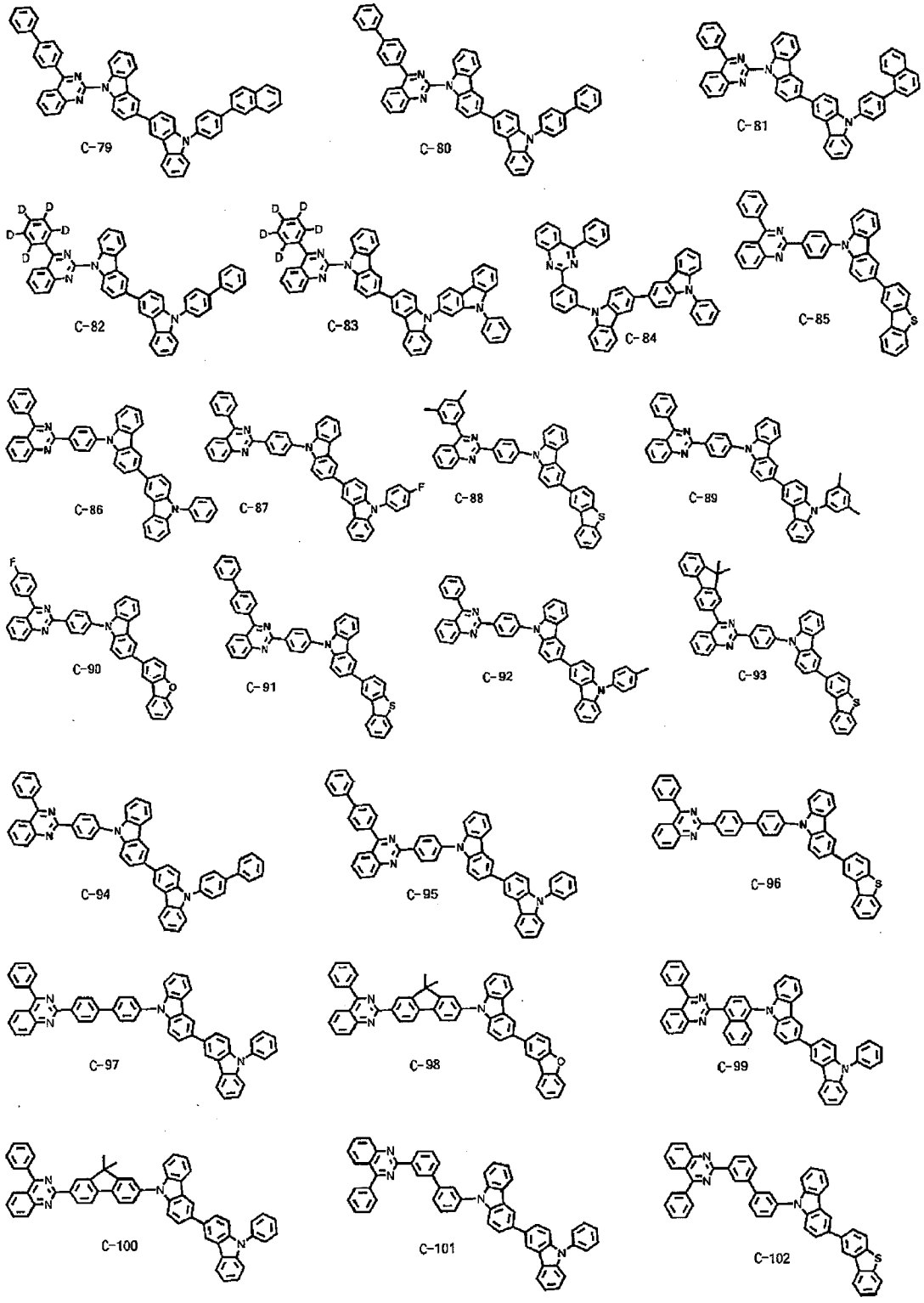
[36]


C-31
C-32
C-33
C-34
C-35
C-36
C-37
C-38
C-39
C-40
C-41
C-42
C-43
C-44
C-45
C-46
C-47
C-48
C-49
C-50
C-51
C-52
C-53

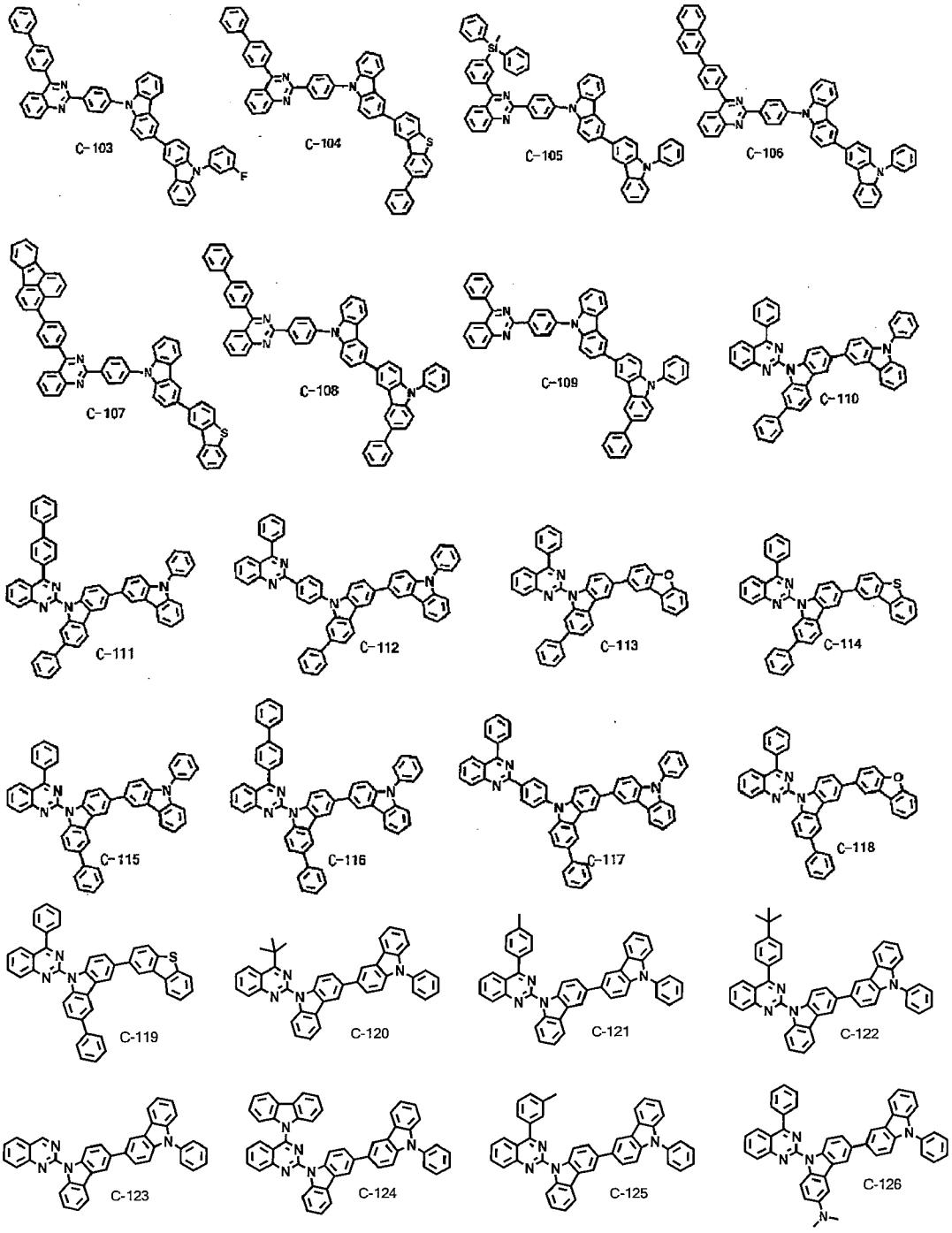
[37]


C-54
C-55
C-56
C-57
C-58
C-59
C-60
C-61
C-62
C-63
C-64
C-65
C-66
C-67
C-68
C-69
C-70
C-71
C-72
C-73
C-74
C-75
C-76
C-77
C-78

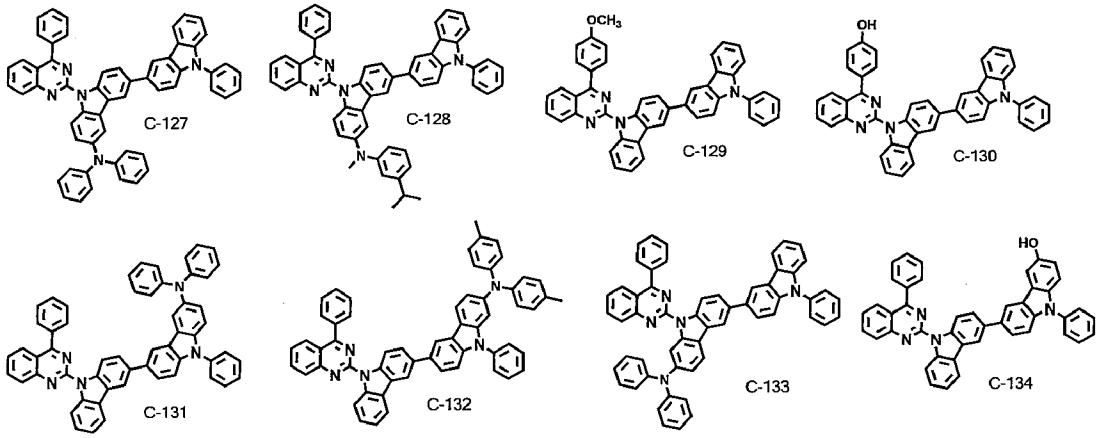
[38]


C-79
C-80
C-81
C-82
C-83
C-84
C-85
C-86
C-87
C-88
C-89
C-90
C-91
C-92
C-93
C-94
C-95
C-96
C-97
C-98
C-99
C-100
C-101
C-102

[39]


C-103
C-104
C-105
C-106
C-107
C-108
C-109
C-110
C-111
C-112
C-113
C-114
C-115
C-116
C-117
C-118
C-119
C-120
C-121
C-122
C-123
C-124
C-125
C-126

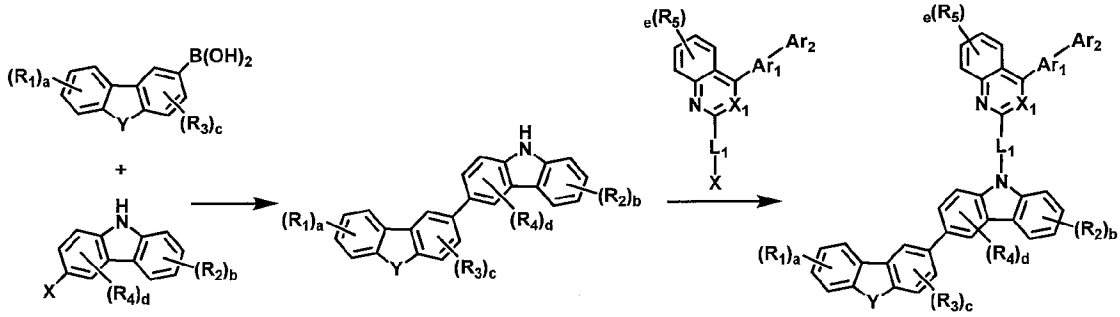
[40]



[41] Organic electroluminescent compounds according to the present invention can be prepared by well-known methods in the art, for example, according to the following scheme 1.

[42] [Scheme 1]

[43]



[44] wherein, R_1 to R_5, Ar_1, Ar_2, Y, X_1, L_1, a, b, c, d and e are as defined in formula 1 above, and X represents a halogen.

[45] Further, the present invention provides an organic electroluminescent device comprising the organic electroluminescent compound of formula 1.

[46] Said organic electroluminescent device comprises a first electrode, a second electrode and at least one organic layer between said first electrode and said second electrode. Said organic layer comprises at least one organic electroluminescent compound of formula 1. Further, said organic layer comprises a light-emitting layer in which the organic electroluminescent compound of formula 1 is comprised as a host material. Where the organic electroluminescent compound of formula 1 is comprised as a host material in the light-emitting layer, said light-emitting layer further comprises at least one phosphorescent dopant. In the organic electroluminescent device of the present invention, said phosphorescent dopant is not particularly limited, but may be selected from compounds represented by the following formula 2:

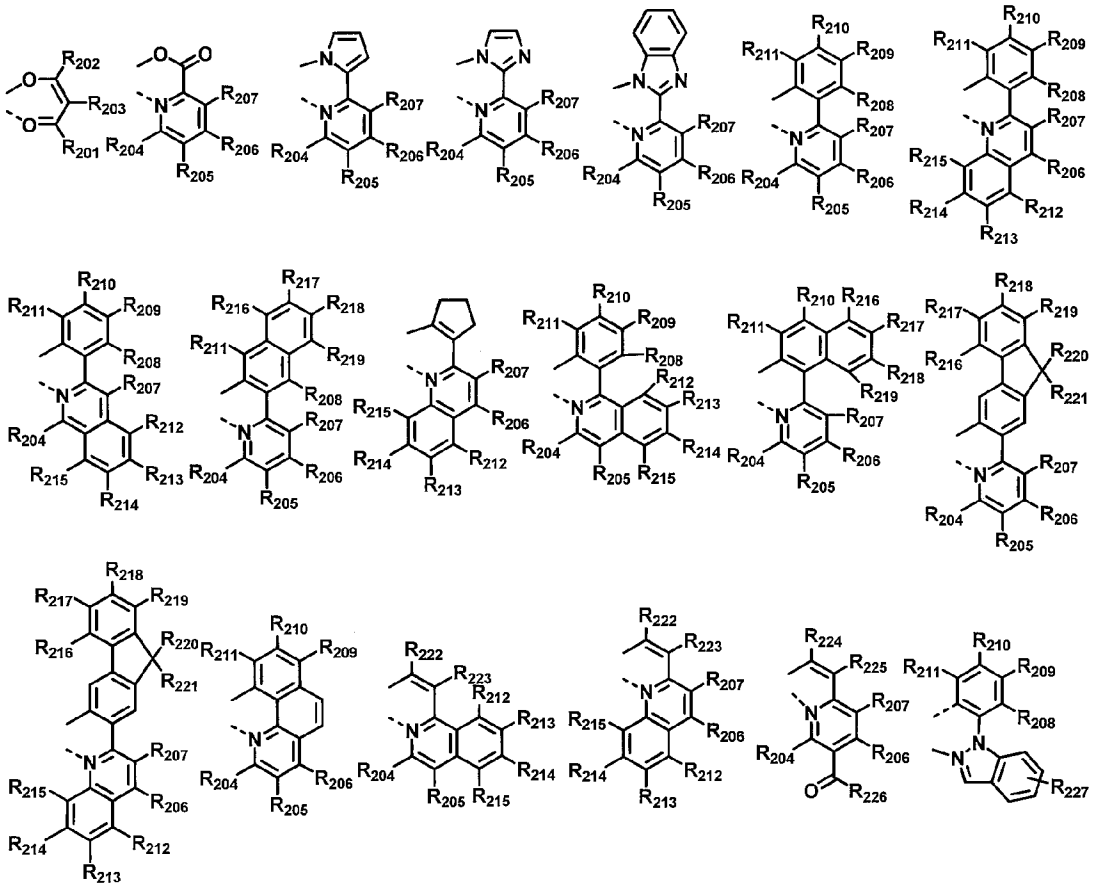
[47] [Formula 2]

[48] $M^1L^{101}L^{102}L^{103}$

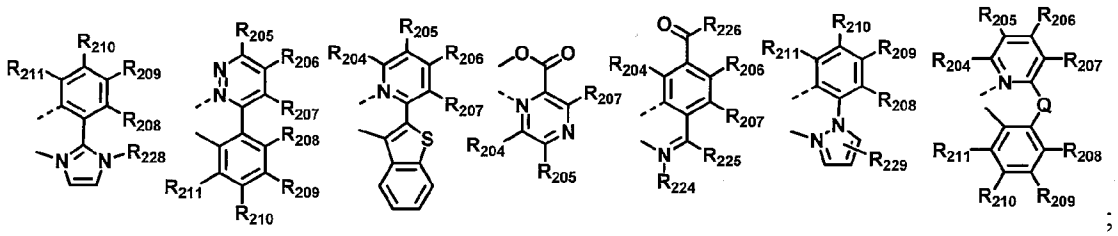
[49] wherein

[50] M_1 is selected from the group consisting of Ir, Pt, Pd and Os; L^{101}, L^{102} and L^{103} each independently are selected from the following structures:

[51]



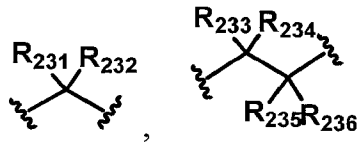
[52]



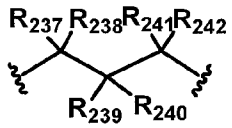
;

[53] R_{201} to R_{203} each independently represent hydrogen, deuterium, a (C1-C30)alkyl group unsubstituted or substituted by a halogen(s), a (C6-C30)aryl group unsubstituted or substituted by a (C1-C30)alkyl group(s), or a halogen; R_{204} to R_{219} each independently represent hydrogen, deuterium, a substituted or unsubstituted (C1-C30)alkyl group, a substituted or unsubstituted (C1-C30)alkoxy group, a substituted or unsubstituted (C3-C30)cycloalkyl group, a substituted or unsubstituted (C2-C30)alkenyl group, a substituted or unsubstituted (C6-C30)aryl group, a substituted or unsubstituted mono- or di-(C1-C30)alkylamino group, a substituted or unsubstituted mono- or di-(C6-C30)arylamino group, SF_5, a substituted or unsubstituted tri(C1-C30)alkylsilyl group, a substituted or unsubstituted di(C1-C30)alkyl(C6-C30)arylsilyl group, a sub-

stituted or unsubstituted tri(C6-C30)arylsilyl group, a cyano group or a halogen; R_{220} to R_{223} each independently represent hydrogen, deuterium, a (C1-C30)alkyl group unsubstituted or substituted by a halogen(s), or a (C6-C30)aryl group unsubstituted or substituted by a (C1-C30)alkyl group(s); R_{224} and R_{225} each independently represent hydrogen, deuterium, a substituted or unsubstituted (C1-C30)alkyl group, a substituted or unsubstituted (C6-C30)aryl group, or a halogen, or R_{224} and R_{225} may be linked to each other via a (C3-C12)alkylene group or (C3-C12)alkenylene group with or without a fused ring, to form a mono- or polycyclic alicyclic ring or a mono- or polycyclic aromatic ring; R_{226} represents a substituted or unsubstituted (C1-C30)alkyl group, a substituted or unsubstituted (C6-C30)aryl group, a substituted or unsubstituted 5- or 30-membered heteroaryl group or a halogen; R_{227} to R_{229} each independently represent hydrogen, deuterium, a substituted or unsubstituted (C1-C30)alkyl group, a substituted or unsubstituted (C6-C30)aryl group or a halogen; Q represents



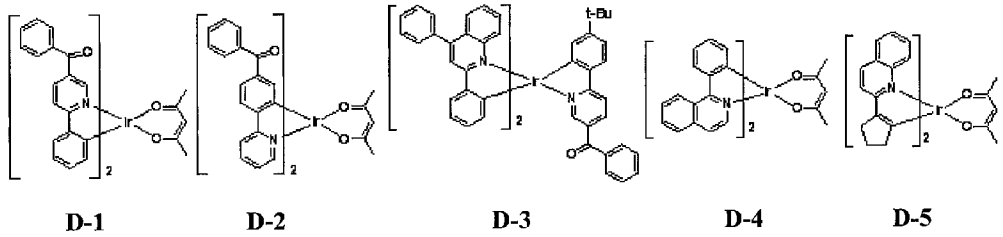
or



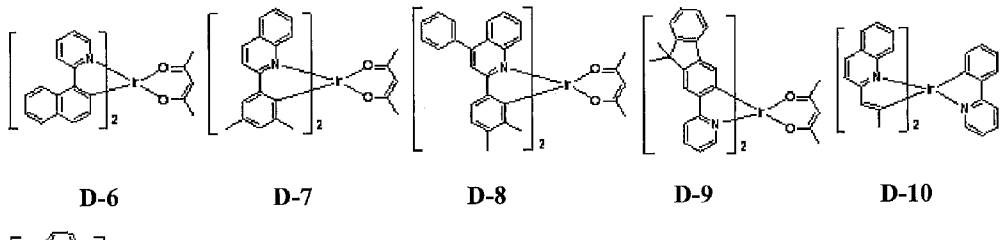
; R_{231} to R_{242} each independently represent hydrogen, deuterium, a (C1-C30)alkyl group unsubstituted or substituted by a halogen(s), a (C1-C30)alkoxy group, a halogen, a substituted or unsubstituted (C6-C30)aryl group, a cyano group, a substituted or unsubstituted (C5-C30)cycloalkyl group, or each of R_{231} to R_{242} may be linked to an adjacent substituent via (C2-C30) alkylene group or (C2-C30)alkenylene group to form a spiro ring or a fused ring or may be linked to R_{207} or R_{208} via (C2-C30) alkylene group or (C2-C30)alkenylene group to form a saturated or unsaturated fused ring.

[54] The dopants of formula 2 include the following, but are not limited thereto:

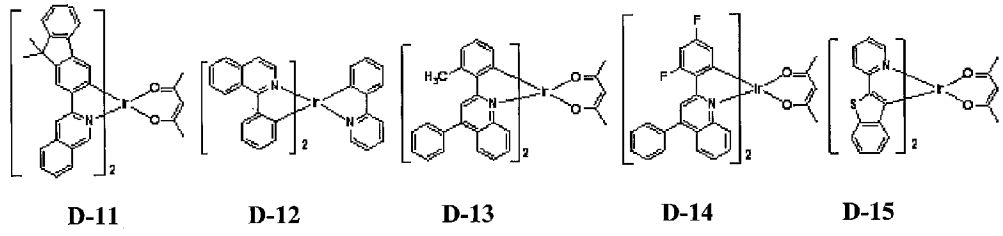
[55]



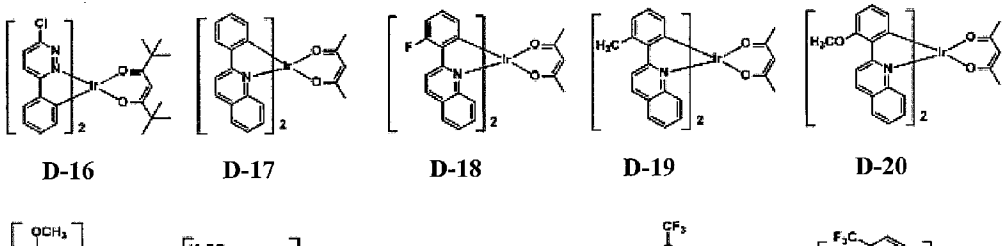
D-1 D-2 D-3 D-4 D-5



D-6 D-7 D-8 D-9 D-10

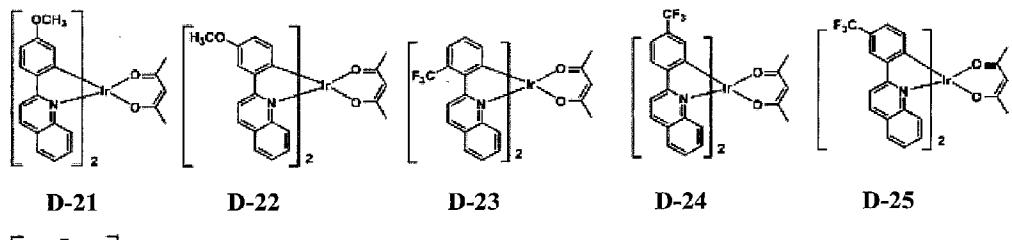


D-11 D-12 D-13 D-14 D-15

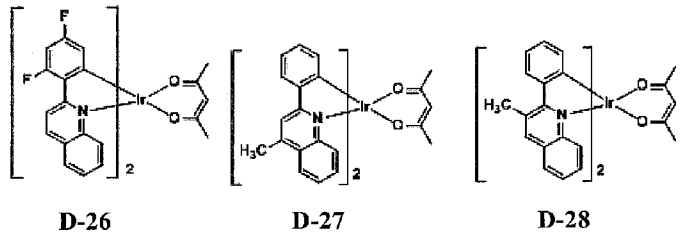


D-16 D-17 D-18 D-19 D-20

[56]



D-21 D-22 D-23 D-24 D-25



D-26 D-27 D-28

[57] The organic electroluminescent device according to the present invention may further comprise, in addition to the organic electroluminescent compound according to the present invention, at least one amine-based compound selected from the group consisting of arylamine-based compounds and styrylarylamine-based compounds.

[58] In the organic electroluminescent device according to the present invention, the organic layer may further comprise at least one metal selected from the group consisting of metals of Group 1, metals of Group 2, transition metals of the 4th period, transition metals of the 5th period, lanthanides and organic metals of d-transition

elements of the Periodic Table, or at least one complex compound comprising said metal. The organic layer may comprise a light-emitting layer and a charge generating layer.

[59] The organic electroluminescent device according to the present invention may emit a white light by further comprising in addition to the organic electroluminescent compound according to the present invention, at least one light-emitting layer which comprises a blue electroluminescent compound, a red electroluminescent compound or a green electroluminescent compound. If necessary, the organic electroluminescent device may further comprise a yellow light-emitting layer or an orange light-emitting layer.

[60] Preferably, in the organic electroluminescent device according to the present invention, at least one layer (hereinafter, "a surface layer") selected from a chalcogenide layer, a metal halide layer and a metal oxide layer may be placed on an inner surface(s) of one or both electrode(s). Specifically, it is preferred that a chalcogenide layer of silicon or aluminum is placed on an anode surface of an electroluminescent medium layer, and a metal halide layer or metal oxide layer is placed on a cathode surface of an electroluminescent medium layer. Such a surface layer provides operation stability for the organic electroluminescent device. Preferably, said chalcogenide includes $SiO_X(1\leq X\leq 2)$, $AlO_X(1\leq X\leq 1.5)$, SiON, SiAlON, etc.; said metal halide includes LiF, MgF_2, CaF_2, a rare earth metal fluoride, etc.; and said metal oxide includes Cs_2O, Li_2O, MgO, SrO, BaO, CaO, etc.

[61] Preferably, in the organic electroluminescent device according to the present invention, a mixed region of an electron transport compound or a mixed region of a hole transport compound and an oxidative dopant may be placed on at least one surface of a pair of electrodes. In that case, the electron transport compound is reduced to an anion, and thus facilitates injecting and transporting electrons to an electroluminescent medium. Further, the hole transport compound is oxidized to a cation, and thus facilitates injecting and transporting holes to an electroluminescent medium. Preferably, the oxidative dopant includes various Lewis acids and acceptor compounds; and the reductive dopant includes alkali metals, alkali metal compounds, alkaline earth metals, rare-earth metals, and mixtures thereof. A reductive dopant layer may be employed as a charge generating layer to prepare an electroluminescent device having two or more electroluminescent layers and emitting a white light.

Advantageous Effects of Invention

[62] The organic electroluminescent compound according to the present invention provides an organic electroluminescent device which has high luminous efficiency and a long operation lifetime and requires a low driving voltage improving power ef-

ficiency and power consumption.

Mode for the Invention

[63] Hereinafter, examples are provided for preparing the organic electroluminescent compounds, and properties of the organic electroluminescent devices using them.

[64] The abbreviations used in the examples have the following meanings:

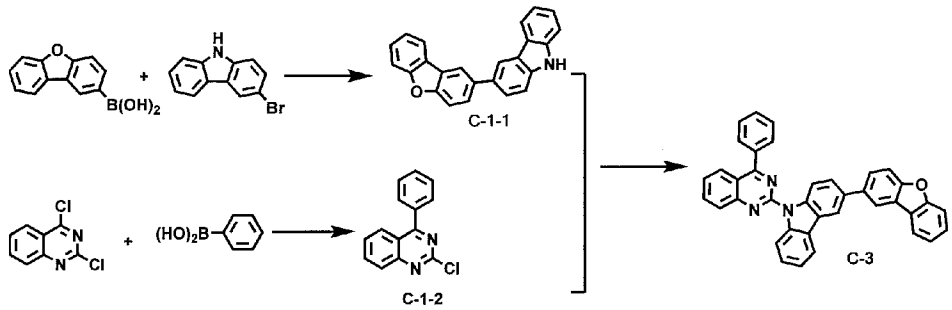
[65] Ph: phenyl, MeOH: methanol, EtOH: ethanol, MC: methylene chloride, EA: ethyl acetate,

[66] DMF: dimethylformamide, n-Bu: normal-butyl, i-Pr: isopropyl, Me: methyl,

[67] THF: tetrahydrofuran, EDA: ethylene diamine, NBS: N-bromosuccinimide

[68] [Preparation example 1] Preparation of compound C-3

[69]



[70] Preparation of compound C-1-1

[71] Dibenzo[b,d]furan-2-yl boronic acid (10.33 g, 48.76 mmol), 3-bromo-9H-carbazole (10 g, 40.63 mmol), K_2CO_3 (13.5 g,97.52 mmol) and $Pd(PPh_3)_4$ (2.35 g, 2.03 mmol) were added to toluene 200 mL, EtOH 50 mL and purified water 50 mL. After stirring the reaction mixture for 3 hours at 90 to 100°C, the mixture was cooled to room temperature. An aqueous layer was removed from the mixture by a gravity separation. The obtained organic layer was concentrated, was triturated with MC, and then was filtered to obtain compound C-1-1 (9.75 g, 72%).

[72] Preparation of compound C-1-2

[73] After dissolving 2,4-dichloroquinazoline (30 g, 151 mmol), phenylboronic acid (9.2 g, 75.3 mmol), $Pd(PPh_3)_4$ (2.6 g, 2.3 mmol) and Na_2CO_3 (16 g, 150 mmol) in toluene (300 mL) and distilled water (75 mL), the reaction mixture was stirred for 2 hours at 90°C. The mixture was distillated under reduced pressure to obtain an organic layer, and then was triturated with MeOH. The obtained solid was dissolved in MC, was filtered through silica, and then was triturated with MC and hexane to obtain compound C-1-2 (9.3 g, 51.4%).

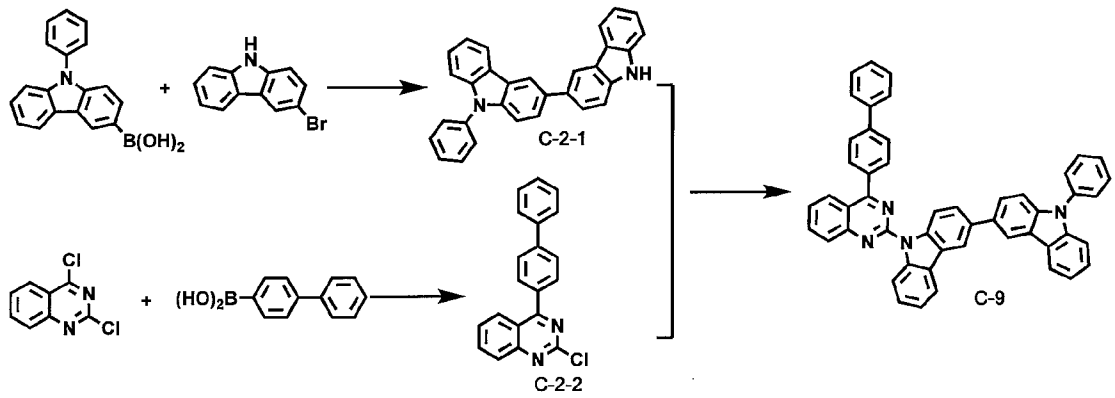
[74] Preparation of compound C-3

[75] After suspending compound C-1-1 (5.3 g, 14.7 mmol) and compound C-1-2 (5 g, 15.8 mmol) in DMF 80 mL. 60% NaH (948 mg, 22 mmol) was added to the mixture at room temperature. The obtained reaction mixture was stirred for 12 hours. After adding purified water (1 L), the mixture was filtered under reduced pressure. The

obtained solid was triturated with MeOH/EA, was dissolved in MC, was filtered through silica, and then was triturated with MC/n-hexane to obtain compound C-3 (5 g, 51.5%).

[76] [Preparation example 2] Preparation of compound C-9

[77]



[78] Preparation of compound C-2-1

[79] 9-phenyl-9H-carbazol-3-yl boronic acid (14 g, 48.76 mmol), 3-bromo-9H-carbazole (10 g, 40.63 mmol), K_2CO_3 (13.5 g, 97.52 mmol) and $Pd(PPh_3)_4$ (2.35 g, 2.03 mmol) were added to toluene 200 mL, EtOH 50 mL and purified water 50 mL. After stirring the reaction mixture for 3 hours at 90 to 100°C, the mixture was cooled to room temperature. An aqueous layer was removed from the mixture by a gravity separation. The obtained organic layer was concentrated, was triturated with MC, and then was filtered to obtain compound C-2-1 (12 g, 72%).

[80] Preparation of compound C-2-2

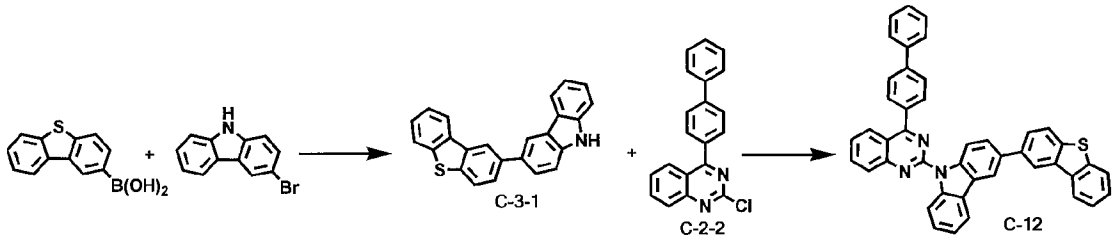
[81] 2,4-dichloroquinazoline (20 g, 0.1 mol), biphenyl-4-yl boronic acid (18.9 g, 0.1 mol), $Pd(PPh_3)_4$ (3.5 g, 3.01 mmol) and Na_2CO_3 (31.9 g, 0.3 mol) were added to toluene 800 mL, EtOH 200 mL and purified water 200 mL. After stirring the reaction mixture for 3 hours at 70 to 80°C, an aqueous layer was removed from the mixture by a gravity separation. The obtained organic layer was concentrated, and then was purified by silica column chromatography to obtain compound C-2-2 (15 g, 47%).

[82] Preparation of compound C-9

[83] After suspending compound C-2-2 (4.6 g, 14.7 mmol) and compound C-2-1 (5 g, 12.2 mmol) in DMF 80 mL, 60% NaH (881 g, 22 mmol) was added to the mixture at room temperature. The obtained reaction mixture was stirred for 12 hours. After adding purified water (1 L), the mixture was filtered under reduced pressure. The obtained solid was triturated with MeOH/EA, was dissolved in MC, was filtered through silica, and then was triturated with MC/n-hexane to obtain compound C-9 (4 g, 47.4%).

[84] [Preparation example 3] Preparation of compound C-12

[85]



[86] Preparation of compound C-3-1

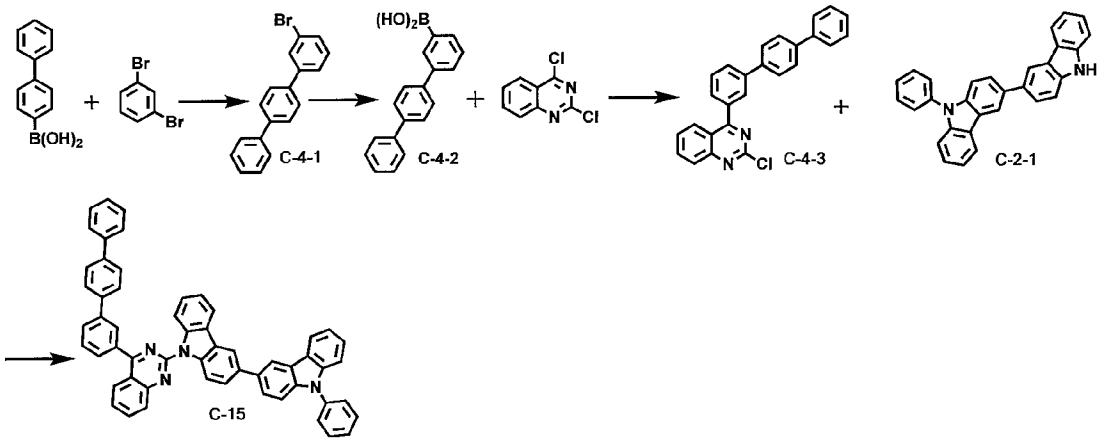
[87] Dibenzo[b,d]thiophen-2-yl boronic acid (10.33 g, 48.76 mmol), 3-bromo-9H-carbazole (10 g, 40.63 mmol), K_2CO_3 (13.5 g,97.52 mmol), and $Pd(PPh_3)_4$ (2.35 g,2.03 mmol) were added to toluene 200 mL, EtOH 50 mL and purified water 50 mL. After stirring the reaction mixture for 3 hours at 90 to 100°C, the mixture was cooled to room temperature. An aqueous layer was removed from the mixture by a gravity separation. The obtained organic layer was concentrated, was triturated with MC, and then was filtered to obtain compound C-3-1 (9.75 g, 72%).

[88] Preparation of compound C-12

[89] After suspending compound C-3-1 (5.5 g, 15.8 mmol) and compound C-2-2 (5 g, 15.8 mmol) in DMF 80 mL, 60% NaH (948 mg, 22 mmol) was added to the mixture at room temperature. The obtained reaction mixture was stirred for 12 hours. After adding purified water (1 L), the mixture was filtered under reduced pressure. The obtained solid was triturated with MeOH/EA, was dissolved in MC, was filtered through silica, and then was triturated with MC/n-hexane. Compound C-12 (5.2 g, 52%) was obtained.

[90] [Preparation example 4] Preparation of compound C-15

[91]



[92] Preparation of compound C-4-1

[93] After dissolving biphenyl-4-yl boronic acid (157 g, 554 mmol), 1,3-dibromobenzene (100 g, 581.7 mmol), $Pd(PPh_3)_4$ (13 g, 11.08 mmol) and Na_2CO_3 (150 g, 1.385 mol) in toluene(3.5 L), EtOH (0.7 L) and distilled water (0.7 L), the reaction mixture was stirred for 3 hours at 90°C. The mixture was extracted with EA and distilled water, was

dissolved in chloroform (10 L) by heat, and then was filtered through silica. After triturating the resultant with EA and hexane, the resultant was triturated with EA and MeOH to obtain compound C-4-1 (94 g, 60%).

[94] Preparation of compound C-4-2

[95] After dissolving compound C-4-1 (55 g, 178 mmol) in THF (800 mL), 2.5 M n-BuLi in hexane (106 mL, 267 mmol) was added to the reaction mixture at -78℃, and then the mixture was stirred for 1 hour. $B(Oi\text{-}Pr)_3$ (82 mL, 356 mmol) was added slowly to the mixture, and then the mixture was stirred for 2 hours. The mixture was quenched by adding 2 M HCl, was extracted with distilled water and EA, and then was recrystallized with hexane and acetone. Compound C-4-2 (43 g, 88.0%) was obtained.

[96] Preparation of compound C-4-3

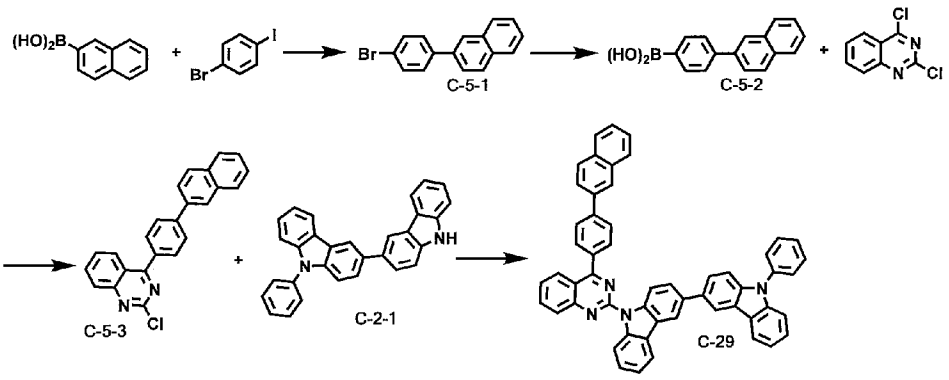
[97] 2,4-dichloroquinazoline (20 g, 73 mmol), compound C-4-2 (15 g, 73 mmol), $Pd(PPh_3)_4$ (2.5 g, 2.2 mmol) and Na_2CO_3 (23 g,241 mmol) were dissolved in toluene(500 mL), EtOH (100 mL) and distilled water (100 mL), and then was stirred for 5 hours at 100°C. The reaction mixture was distillated under reduced pressure to obtain an organic layer, and then was triturated with MeOH. The obtained solid was dissolved in MC, was filtered through silica, and then was triturated with MC and hexane to obtain compound C-4-3 (19.5 g, 68%).

[98] Preparation of compound C-15

[99] After suspending compound C-2-1 (5 g, 12.2 mmol) and compound C-4-3 (4.6 g, 11.6 mmol) in DMF 80 mL, 60% NaH (881 mg, 22 mmol) was added to the mixture at room temperature. The obtained reaction mixture was stirred for 12 hours. After adding purified water (1 L), the mixture was filtered under reduced pressure. The obtained solid was triturated with MeOH/EA, was triturated with DMF, and then was triturated with EA/THF. The resultant was dissolved in MC, was filtered through silica, and then was triturated with MeOH/EA. Compound C-15 (5.1 g, 57%) was obtained.

[100] [Preparation example 5] Preparation of compound C-29

[101]



[102] Preparation of compound C-5-1

[103] After dissolving 2-naphthylboronic acid (157 g, 554 mmol), 1-bromo-4-iodobenzene (100 g, 581.7 mmol), $Pd(PPh_3)_4$ (13 g, 11.08 mmol) and Na_2CO_3 (150 g, 1.385 mol) in toluene(3.5 L), EtOH (0.7 L) and distilled water (0.7 L), the reaction mixture was stirred for 3 hours at 90°C. The mixture was extracted with EA and distilled water, was dissolved in chloroform (10 L) by heat, and then was filtered through silica. After triturating the resultant with EA and hexane, the resultant was triturated with EA and MeOH to obtain compound C-5-1 (94 g, 60%).

[104] Preparation of compound C-5-2

[105] After dissolving compound C-5-1 (94 g, 332 mmol) in THF (800 mL), 2.5 M n-BuLi in hexane (80 mL, 386.4 mmol) was added to the reaction mixture at -78°C, and then the mixture was stirred for 1 hour. $B(OMe)_3$ (28 mL, 498 mmol) was added slowly to the mixture, and then the mixture was stirred for 2 hours. The mixture was quenched by adding 2 M HCl, was extracted with distilled water and EA, and then was recrystallized with hexane and acetone. Compound C-5-2 (57 g, 67.0%) was obtained.

[106] Preparation of compound C-5-3

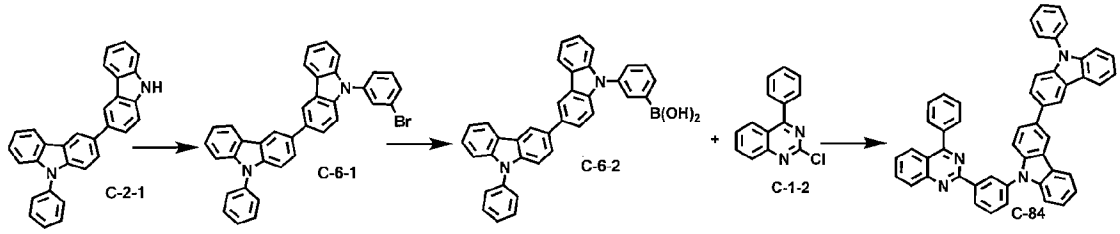
[107] 2,4-dichloroquinazoline (46 g, 230 mmol), compound C-5-2 (57 g, 230 mmol), $Pd(PPh_3)_4$ (10.6 g, 9.2 mmol) and Na_2CO_3 (73 g, 690 mmol) were dissolved in toluene(1.1 L), EtOH (230 mL) and distilled water (350 mL), and then was stirred for 5 hours at 100°C. The reaction mixture was distillated under reduced pressure to obtain an organic layer, and then was triturated with MeOH. The obtained solid was dissolved in MC, was filtered through silica, and then was triturated with MC and hexane to obtain compound C-5-3 (51 g, 99.9%).

[108] Preparation of compound C-29

[109] After suspending compound C-2-1 (5 g, 12.2 mmol) and compound C-5-3 (4.5 g, 12.2 mmol) in DMF 80 mL, 60% NaH (881mg, 22 mmol) was added to the mixture at room temperature. The obtained reaction mixture was stirred for 12 hours. After adding purified water (1 L), the mixture was filtered under reduced pressure. The obtained solid was triturated with MeOH/EA, was triturated with DMF, and then was triturated with EA/THF. The resultant was dissolved in MC, was filtered through silica, and then was triturated with MeOH/EA. Compound C-29 (1.8 g, 20%) was obtained.

[110] [Preparation example 6] Preparation of compound C-84

[111]



[112] Preparation of compound C-6-1

[113] Compound C-2-1 (14 g, 34.3 mmol), 1,3-dibromobenzene (48.5 g, 171.4 mmol), CuI (3.3 g, 17.1 mmol), K_3PO_4 (21.8 g, 102.9 mmol) and EDA (2.3 mL, 34.3 mmol) were added to toluene 500 mL. The reaction mixture was stirred under reflux for 1 day, was extracted with EA, and then was distilled under reduced pressure. After purifying the resultant by column chromatography with MC/Hexane, compound C-6-1 (15.5 g, 80.1%) was obtained.

[114] Preparation of compound C-6-2

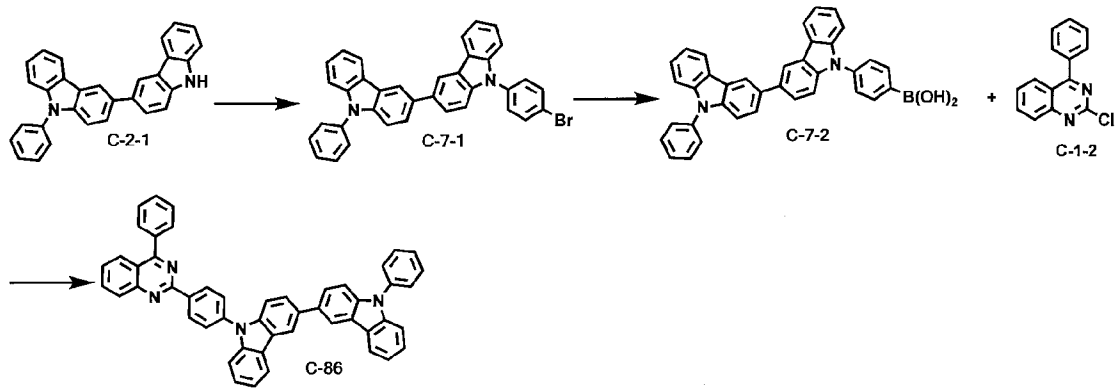
[115] After dissolving compound C-6-1 (15.5 g, 27.5 mmol) in THF (250 mL), 2.5 M n-BuLi in hexane (17.6 mL, 44 mmol) was added thereto at -78°C. The reaction mixture was stirred for 1 hour. $B(Oi\text{-}Pr)_3$ (12.6 mL, 55 mmol) was added slowly to the mixture, and then the mixture was stirred for 2 hours. The mixture was quenched by adding 2 M HCl, was extracted with distilled water and EA, and then was recrystallized with hexane and MC. Compound C-6-2 (8.7 g, 60%) was obtained.

[116] Preparation of compound C-84

[117] After compound C-1-2 (2.3 g, 9.5 mmol), compound C-6-2 (6 g, 11.3 mmol), $Pd(PPh_3)_4$(532mg, 0.46 mmol) and Na_2CO_3 (2.9 g, 27.6 mmol) were dissolved in toluene(55 mL), EtOH(14 mL) and distilled water (14 mL), the reaction mixture was stirred for 2 hours at 90°C. The mixture was extracted with distilled water and EA. After purifying the resultant by a column chromatography with MC and hexane, compound C-84 (2.4 g, 36.9%) was obtained.

[118] [Preparation example 7] Preparation of compound C-86

[119]



[120] Preparation of compound C-7-1

[121] Compound C-2-1 (14 g, 34.3 mmol), 1-bromo-4-iodobenzene (48.5 g, 171.4 mmol), CuI (3.3 g, 17.1 mmol), K_3PO_4 (21.8 g, 102.9 mmol) and EDA (2.3 mL, 34.3 mmol) were added to toluene 500 mL. The reaction mixture was stirred under reflux for 1 day, was extracted with EA, and then was distilled under reduced pressure. After purifying the resultant by column chromatography with MC/Hexane, compound C-7-1 (15.5 g, 80.1%) was obtained.

[122] Preparation of compound C-7-2

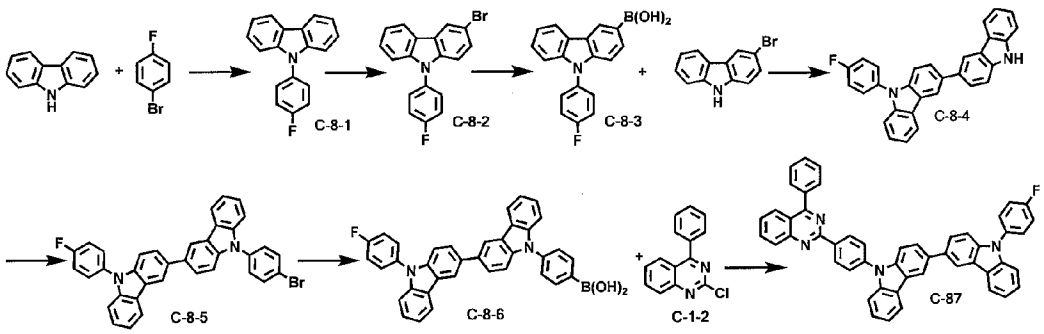
[123] After dissolving compound C-7-1 (15.5 g, 27.5 mmol) in THF (250 mL), 2.5 M n-BuLi in hexane (17.6 mL, 44 mmol) was added thereto at -78°C. The reaction mixture was stirred for 1 hour. $B(Oi\text{-}Pr)_3$ (12.6 mL, 55 mmol) was added slowly to the mixture, and then the mixture was stirred for 2 hours. The mixture was quenched by adding 2 M HCl, was extracted with distilled water and EA, and then was recrystallized with MC and hexane. Compound C-7-2 (8.7 g, 60%) was obtained.

[124] Preparation of compound C-86

[125] After compound C-1-2 (2.3 g, 9.5 mmol), compound C-7-2 (6 g, 11.3 mmol), $Pd(PPh_3)_4$ (532mg, 0.46 mmol) and Na_2CO_3 (2.9 g, 27.6 mmol) were dissolved in toluene(55 mL), EtOH(14 mL) and distilled water (14 mL), the reaction mixture was stirred for 2 hours at 90°C. The mixture was extracted with distilled water and EA. After purifying the resultant by a column chromatography with MC and hexane, compound C-86 (2.4 g, 36.9%) was obtained.

[126] [Preparation example 8] Preparation of compound C-87

[127]



[128] Preparation of compound C-8-1

[129] 9H-carbazole (20 g, 119.6 mmol), 1-bromo-4-fluorobenzene (40 mL, 358.8 mmol), CuI (23 g, 119.6 mmol), K_3PO_4 (117 g, 357 mmol) and EDA (16 mL, 238 mmol) were added to toluene 500 mL. The reaction mixture was stirred under reflux for 1 day, was extracted with EA, and then was distilled under reduced pressure. After purifying the resultant by column chromatography with MC/Hexane, compound C-8-1 (42 g, 67%) was obtained.

[130] Preparation of compound C-8-2

[131] After dissolving compound C-8-1 (5 g, 19.1 mmol) in DMF(100 mL), NBS (3.4 g, 19.1 mmol) was added thereto. The reaction mixture was stirred for 1 day, was extracted with EA, and then was distilled under reduced pressure. After purifying the resultant by column chromatography with MC/Hexane, compound C-8-2 (5.6 g, 86%) was obtained.

[132] Preparation of compound C-8-3

[133] After dissolving C-8-2 (5.6 g, 16.5 mmol) in THF (85 mL), 2.5 M n-BuLi in hexane

(7.2 mL, 18.2 mmol) was added thereto at -78°C. The reaction mixture was stirred for 1 hour. $B(Oi\text{-}Pr)_3$ (5.7 mL, 24.7 mmol) was added slowly to the mixture, and then the mixture was stirred for 2 hours. The mixture was quenched by adding 2 M HCl, was extracted with distilled water and EA, and then was recrystallized with MC and hexane. Compound C-8-3 (8.7 g, 60%) was obtained.

[134] Preparation of compound C-8-4

[135] Compound C-8-3 (14 g, 48.76 mmol), 3-bromo-9H-carbazole (10 g, 40.63 mmol), K_2CO_3 (13.5 g, 97.52 mmol) and $Pd(PPh_3)_4$ (2.35 g, 2.03 mmol) were added to toluene 200 mL, EtOH 50 mL, and purified water 50 mL. After stirring the reaction mixture for 3 hours at 90 to 100°C, the mixture was cooled to room temperature. An aqueous layer was removed from the mixture by a gravity separation. The obtained organic layer was concentrated, was recrystallized with MC, and then was filtered to obtain compound C-8-4 (12 g, 72%).

[136] Preparation of compound C-8-5

[137] Compound C-8-4 (14 g, 34.3 mmol), 1-bromo-4-iodobenzene (48.5 g, 171.4 mmol), CuI (3.3 g, 17.1 mmol), K_3PO_4 (21.8 g, 102.9 mmol) and EDA (2.3 mL, 34.3 mmol) were added to toluene 500 mL. The reaction mixture was stirred under reflux for 1 day, was extracted with EA, and then was distilled under reduced pressure. After purifying the resultant by column chromatography with MC/Hexane, compound C-8-5 (15.5 g, 80.1%) was obtained.

[138] Preparation of compound C-8-6

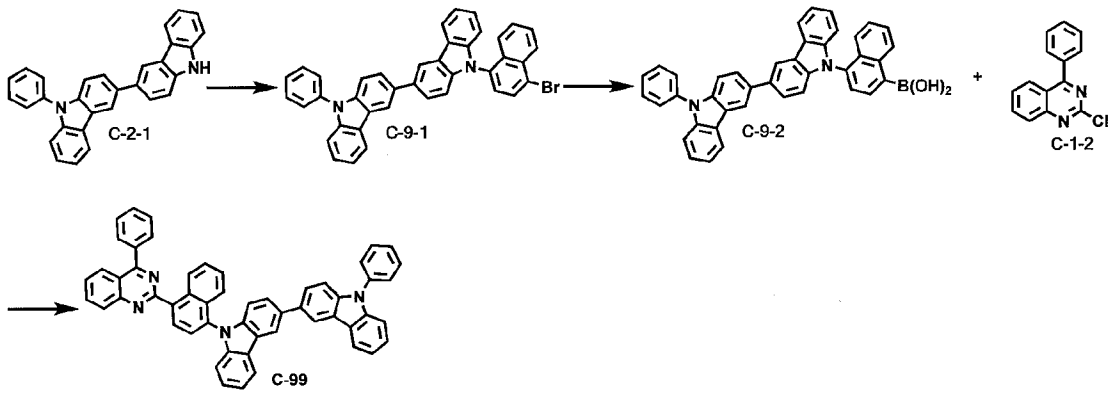
[139] After dissolving compound C-8-5 (15.5 g, 27.5 mmol) in THF (250 mL), 2.5 M n-BuLi in hexane (17.6 mL, 44 mmol) was added to the reaction mixture at -78℃, and then the mixture was stirred for 1 hour. $B(Oi\text{-}Pr)_3$ (12.6 mL, 55 mmol) was added slowly to the mixture, and then the mixture was stirred for 2 hours. The mixture was quenched by adding 2 M HCl, was extracted with distilled water and EA, and then was recrystallized with MC and hexane. Compound C-8-6 (8.7 g, 60%) was obtained.

[140] Preparation of compound C-87

[141] After dissolving compound C-1-2 (2.3 g, 9.5 mmol), compound C-8-6 (6 g, 11.3 mmol), $Pd(PPh_3)_4$(532mg, 0.46 mmol) and Na_2CO_3 (2.9 g, 27.6 mmol) in toluene(55 mL), EtOH(14 mL), and distilled water (14 mL), the reaction mixture was stirred for 2 hours at 90°C, and then was extracted with distilled water and EA. After purifying the resultant by a column chromatography with MC and hexane, compound C-87 (2.4 g, 36.9%) was obtained.

[142] [Preparation example 9] Preparation of compound C-99

[143]



[144] Preparation of compound C-9-1

[145] Compound C-2-1 (16 g, 39.17 mmol), 1,4-dibromonaphthalene (28 g, 97.92 mmol), CuI (7.7 g, 40.43 mmol), $CsCO_3$ (38.4 g, 117.86 mmol) and KI (13 g, 78.3 mmol) were added to toluene 400 mL. After adding ethylenediamine (5.12 mL, 78.3 mmol) thereto, the reaction mixture was stirred under reflux for 30 hours. After completing the reaction, the mixture was cooled to room temperature and was extracted with MC/ purified water. The obtained organic layer was concentrated. After purifying the resultant by a silica column chromatography, compound C-9-1 (7.1 g, 30%) was obtained.

[146] Preparation of compound C-9-2

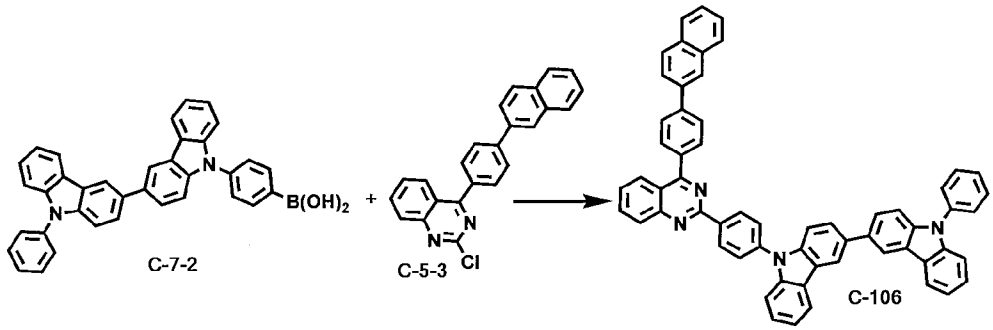
[147] After dissolving compound C-9-1 (6 g, 9.78 mmol) in THF (60 mL), 2.5 M n-BuLi in hexane (5.9 mL, 14.7 mmol) was added thereto at -78°C. The reaction mixture was stirred for 1 hour. $B(Oi\text{-}Pr)_3$ (4.5 mL, 19.6 mmol) was added slowly to the mixture, and then the mixture was stirred for 12 hours. After completing the reaction, purified water 20 mL was slowly dropped stepwise to the mixture. Thereafter, the mixture was extracted with MC/NH4Cl aq. The obtained organic layer was concentrated, and then was filtered through silica to obtain compound C-9-2 (4.5 g, 79.5%).

[148] Preparation of compound C-99

[149] After adding compound C-9-2 (4.5 g, 7.78 mmol), compound C-1-2 (2 g, 8.56 mmol), Na_2CO_3 (2.5 g, 23.34 mmol) and $Pd(PPh_3)_4$ (0.45 g, 0.39 mmol) to toluene 40 mL, EtOH 10 mL and purified water 10 mL, the reaction mixture was stirred for 12 hours at 115 to 120°C. After completing the reaction, the mixture was cooled to room temperature. An aqueous layer was removed from the mixture by a gravity separation. After purifying the obtained organic layer by a silica column chromatography, compound C-99 (3 g, 52.6%) was obtained.

[150] [Preparation example 10] Preparation of compound C-106

[151]

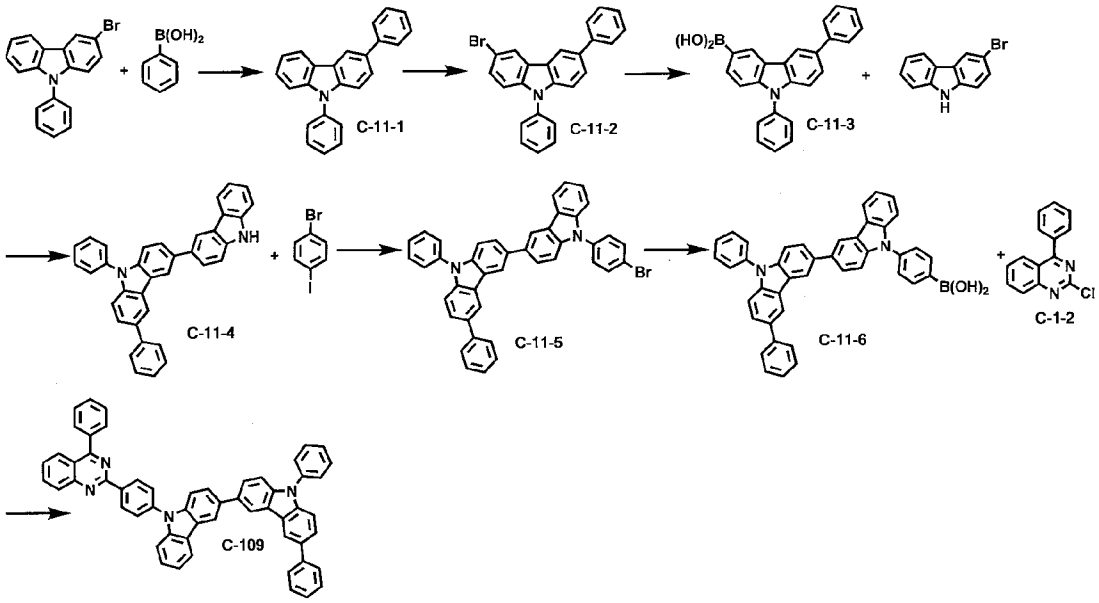


[152] Preparation of compound C-106

[153] After dissolving compound C-7-2 (2.5 g, 4.73 mmol), compound C-5-3 (1.7 g, 4.73 mmol), $Pd(PPh_3)_4$ (273mg, 0.24 mmol) and Na_2CO_3 (1.5 g, 14.2 mmol) in toluene(55 mL), EtOH(14 mL) and distilled water (14 mL), the reaction mixture was stirred for 2 hours at 90°C, and then was extracted with distilled water and EA. After purifying the resultant by a column chromatography with MC and hexane, compound C-106 (2.3 g, 59.7%) was obtained.

[154] [Preparation example 11] Preparation of compound C-109

[155]



[156] Preparation of compound C-11-1

[157] After dissolving 3-bromo-9-phenyl-9H-carbazole (10 g, 31.06 mmol), phenylboronic acid (3.75 g, 31.06 mmol), K_2CO_3 (12.9 g, 93.18 mmol) and $Pd(PPh_3)_4$ (1.8 g, 1.55 mmol) in toluene 150 mL, EtOH 40 mL and purified water 40 mL, the reaction mixture was stirred for 3 hours at 90 to 100°C. After completing the reaction, the mixture was cooled to room temperature. An aqueous layer was removed from the mixture by a gravity separation. After purifying the obtained organic layer by a silica column chromatography, compound C-11-1 (6.4 g, 65%) was obtained.

[158] Preparation of compound C-11-2

[159] After dissolving compound C-11-1 (6.4 g, 20.06 mmol) in DMF 100 mL, NBS (3.6 g, 20.06 mmol) was added thereto. The reaction mixture was stirred for 3 hours. After completing the reaction, the mixture was extracted with MC/purified water. After purifying the resultant by a silica column chromatography, compound C-11-2 (4.8 g, 60%) was obtained.

[160] Preparation of compound C-11-3

[161] After dissolving compound C-11-2 (4.8 g, 12.06 mmol) in THF (60 mL), 2.5 M n-BuLi in hexane (6.3 mL, 15.68 mmol) was added thereto at -78°C. The reaction mixture was stirred for 1 hour. $B(Oi\text{-}Pr)_3$ (4.5 g, 24.12 mmol) was added slowly to the mixture, and then the mixture was stirred for 12 hours. After completing the reaction, purified water 20 mL was slowly dropped stepwise to the mixture. Thereafter, the mixture was extracted with MC/NH_4Cl aq. The obtained organic layer was concentrated, was filtered through silica, and then was crystallized with MC/hexane to obtain compound C-11-3 (3 g, 70%).

[162] Preparation of compound C-11-4

[163] 3-bromo-9H-carbazole (2 g, 8.26 mmol), compound C-11-3 (3 g, 8.26 mmol), Pd(PPh3)4 (0.48 g, 0.4 mmol) and K_2CO_3 (3.4 g, 24.78 mmol) were added to toluene 40 mL, EtOH 10 mL and purified water 10 mL. The reaction mixture was stirred for 15 hours at 70 to 80°C. After completing the reaction, an aqueous layer was removed from the mixture by a gravity separation. The obtained organic layer was concentrated. After purifying the resultant by a silica column chromatography, compound C-11-4 (3.2 g, 80%) was obtained.

[164] Preparation of compound C-11-5

[165] After adding compound C-11-4 (3.2 g, 6.6 mmol), iodobromobenzene (3.7 g, 13.21 mmol), CuI (1.5 g, 7.9 mmol) and K_3PO_4 (2.8 g, 13.2 mmol) to toluene 33 mL, ethylenediamine (0.47 g, 7.9 mmol) was added thereto. The reaction mixture was stirred under reflux for 30 hours. After completing the reaction, the mixture was cooled to room temperature, and then was extracted with MC/purified water. The obtained organic layer was concentrated. After purifying the resultant by a silica column chromatography, compound C-11-5 (3.3 g, 80%) was obtained.

[166] Preparation of compound C-11-6

[167] After dissolving compound C-11-5 (3.3 g, 5.16 mmol) in THF (25 mL), 2.5 M n-BuLi in hexane (2.6 mL, 6.7 mmol) was added thereto at -78°C. The reaction mixture was stirred for 1 hour. $B(Oi\text{-}Pr)_3$ (1.9 g, 10.3 mmol) was added slowly to the mixture, and then the mixture was stirred for 12 hours. After completing the reaction, purified water 10 mL was slowly dropped stepwise to the mixture. Thereafter, the mixture was extracted with MC/NH_4Cl aq. The obtained organic layer was concentrated, was filtered through silica, and then was recrystallized with MC/hexane to obtain

compound C-11-6 (2.5 g, 80%).

[168] Preparation of compound C-109

[169] After adding C-11-6 (2.5 g, 4.14 mmol), compound C-1-2 (1 g, 4.55 mmol), Na_2CO_3 (1.3 g, 12.42 mmol) and $Pd(PPh_3)_4$ (0.24 g, 0.2 mmol) to toluene 20 mL, EtOH 5 mL and purified water 5 mL, the reaction mixture was stirred for 12 hours at 115 to 120℃. After completing the reaction, the mixture was cooled to room temperature. An aqueous layer was removed from the mixture by a gravity separation. After purifying the obtained organic layer by a silica column chromatography, compound C-109 (2.2 g, 70%) was obtained.

[170] Compounds C-1, C-5, C-6, C-10, C-11, C-18, C-52, C-68, C-95, C-103 and C-120 to C-125 were prepared by employing the methods of preparation examples 1 to 11. Physicochemical properties of all the prepared compounds are shown in the following Table 1.

[171] [Table 1]

[172]

Compound	Yield (%)	UV (nm)	PL (nm)	mp (°C)	MS/EIMS	
					Found	Calculated
C-1	62	306	516	219	613	612.72
C-3	51.5				538	537.61
C-5	48	324	525	234	663	662.78
C-6	47	356	513	245	663	662.78
C-9	47.4	342	523	265	688	688.26
C-10	53	304	517	204	689	688.82
C-11	44	308	511	248	729	728.88
C-12	52				630	629.77
C-15	57	304	517	227	764	764.29
C-18	51	354	527	310	765	764.91
C-29	20	342	531	262	738	738.28
C-52	61	310	522	221	765	764.91
C-68	59	304	427	131	536	535.64
C-84	36.9	304	383	168	688	688.26
C-86	36.9	304	446	168	688	688.26
C-87	36.9				706	706.26
C-95	50	344	460	205	765	764.91
C-99	52.6	305	464	210	738	738.28
C-103	43	304	443	197	707	706.81
C-106	59.7				814	814.31
C-109	70	305	448	187	764	764.29
C-120	45	306	467	210	593	592.73
C-121	47	308	515	235	627	626.75
C-122	53	338	505	274	669	668.83
C-123	56	304	427	131	537	536.62
C-124	51	340	513	281	702	701.81
C-125	50	306	508	196	627	626.75

[173] [Example 1] Production of an OLED device using the organic electroluminescent compound according to the present invention

[174] A transparent electrode indium tin oxide (ITO) thin film (15 Ω/sq) on a glass substrate for an organic light-emitting diode (OLED) device (Samsung Corning, Republic of Korea) was subjected to an ultrasonic washing with trichloroethylene, acetone, ethanol and distilled water, sequentially, and then was stored in isopropanol. Then, the ITO substrate was mounted on a substrate holder of a vacuum vapor depositing apparatus. N^1-(naphthalen-1-yl)-N^4,N^4-diphenylbenzene-1,4-diamine was introduced into a cell of said vacuum vapor depositing apparatus, and then the pressure in the chamber of said apparatus was controlled to achieve 10^{-6} torr. Thereafter, an

electric current was applied to the cell to evaporate the above introduced material, thereby forming a hole injection layer having a thickness of 60 nm on the ITO substrate. Then, N,N'-di(4-biphenyl)-N,N'-di(4-biphenyl)-4,4'-diaminobiphenyl was introduced into another cell of said vacuum vapor depositing apparatus, and was evaporated by applying electric current to the cell, thereby forming a hole transport layer having a thickness of 20 nm on the hole injection layer. Thereafter, compound C-1 was introduced into one cell of the vacuum vapor depositing apparatus, as a host material, and compound D-7 was introduced into another cell as a dopant. The two materials were evaporated at different rates and was deposited in a doping amount of 4 to 20 wt% to form a light-emitting layer having a thickness of 30 nm on the hole transport layer. Then, 9,10-di(1-naphthyl)-2-(4-phenyl-1-phenyl-1H-benzo[d]imidazole)anthracene was introduced into one cell and lithium quinolate was introduced into another cell. The two materials were evaporated at different rates and was deposited in a doping amount of 30 to 70 wt% to form an electron transport layer having a thickness of 30 nm on the light-emitting layer. Then, after depositing lithium quinolate as an electron injection layer having a thickness of 1 to 2 nm on the electron transport layer, an Al cathode having a thickness of 150 nm was deposited by another vacuum vapor deposition apparatus on the electron injection layer. Thus, an OLED device was produced. All the material used for producing the OLED device were those purified by vacuum sublimation at 10^{-6} torr.

[175] The produced OLED device shows red emission having a luminance of 1,020 cd/m^2 at a driving voltage of 4.3 V and a current density of 7.5 mA/cm^2. Further, the minimum time for a luminance of 5,000 nit to be reduced to 90% of the luminance was 140 hours.

[176] [Examples 2 to 11] Production of an OLED device using the organic electroluminescent compound according to the present invention

[177] OLED devices were produced in the same manner as one of Example 1, except for using those shown in the below Table 2 as a host material and a dopant.

[178] [Comparative Example 1] Production of an OLED device using conventional electroluminescent compounds

[179] OLED device was produced in the same manner as one of Example 1, except that a light-emitting layer having a thickness of 30 nm was deposited on the hole transport layer by using 4,4'-N,N'-dicarbazol-biphenyl (CBP) as a host material and $(piq)_2$ Ir(acac) [bis-(1-phenylisoquinolyl)iridium(III) acetylacetonate] as a dopant and that a hole blocking layer having a thickness of 10 nm was deposited by using aluminum(III) bis(2-methyl-8-quinolinato)-4-phenylphenolate.

[180] The produced OLED device shows red emission having a luminance of 1,000 cd/m^2

at a driving voltage of 5.5 V and a current density of 12.5 mA/cm^2. Further, minimum time for a luminance of 5,000 nit to be reduced to 90% of the luminance was 15 hours.

[181] The results of examples and comparative example are shown in the following Table 2.

[182] [Table 2]

[183]

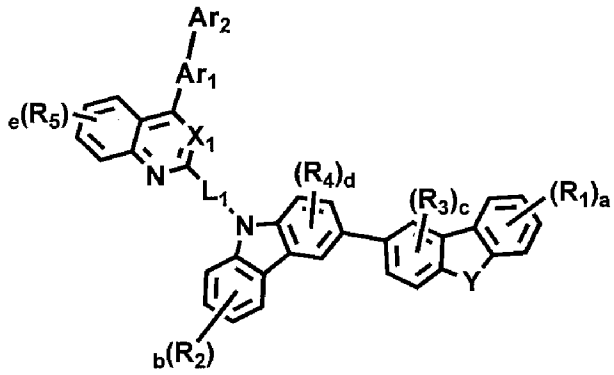
	Host Material	Dopant	Driving Voltage (V)	Current Density (mA/cm^2)	Luminance (cd/m^2) /Color	Minimum Time Required for a Luminance of 5,000 nit to Be Reduced to 90%
Example 1	C-1	D-7	4.3	7.5	1,020/Red	140
Example 2	C-4	D-11	4.0	10.2	1,030/Red	70
Example 3	C-9	D-7	4.4	7.8	1,050/Red	140
Example 4	C-13	D-7	4.3	8.3	1,100/Red	150
Example 5	C-28	D-11	4.2	9.8	1,030/Red	70
Example 6	C-52	D-11	4.4	10.2	1,070/Red	80
Example 7	C-67	D-7	4.5	7.1	1,010/Red	140
Example 8	C-99	D-11	4.2	10.6	1,080/Red	80
Example 9	C-11	D-11	4.0	10.2	1,050/Red	100
Example 10	C-86	D-11	4.1	9.8	1,070/Red	100
Example 11	C-121	D-7	4.2	7.2	1,080/Red	120
Comparative Example 1	CBP	$(piq)_2Ir$ (acac)	5.5	12.5	1,000/Red	15

[184] As shown in Table 2, the organic electroluminescent compounds according to the present invention have superior properties than those of conventional electroluminescent compounds, and thus provide an organic electroluminescent device which has high luminous efficiency and a long operation lifetime and requires a low driving voltage improving power efficiency and power consumption.

Claims

[Claim 1] An organic electroluminescent compound represented by the following formula 1:

[Formula 1]



wherein

L^1 represents a single bond, a substituted or unsubstituted 5- to 30-membered heteroarylene group, a substituted or unsubstituted (C6-C30)arylene group, or a substituted or unsubstituted (C6-C30)cycloalkylene group;

X_1 represents CH or N;

Y represents -O-, -S-, $-CR_{11}R_{12}-$ or $-NR_{13}-$;

Ar_1 represents a single bond, a substituted or unsubstituted 5- to 30-membered heteroarylene group, a substituted or unsubstituted (C6-C30)arylene group, or a substituted or unsubstituted (C1-C30)alkylene group;

Ar_2 represents hydrogen, deuterium, a substituted or unsubstituted (C1-C30)alkyl group, a substituted or unsubstituted (C6-C30)aryl group, or a substituted or unsubstituted 5- to 30-membered heteroaryl group;

R_1 to R_5 each independently represent hydrogen, deuterium, a halogen, a substituted or unsubstituted (C1-C30)alkyl group, a substituted or unsubstituted (C6-C30)aryl group, a substituted or unsubstituted 5- to 30-membered heteroaryl group, a substituted or unsubstituted (C3-C30)cycloalkyl group, a substituted or unsubstituted 5- to 7-membered heterocycloalkyl group, a substituted or unsubstituted (C6-C30)aryl(C1-C30)alkyl group, a substituted or unsubstituted (C6-C30)aryl group fused with at least one (C3-C30)cycloalkyl group, a 5- or 7-membered heterocycloalkyl group fused with at least one substituted or unsubstituted (C6-C30)aromatic ring, (C3-C30)cycloalkyl

group fused with at least one substituted or unsubstituted (C6-C30)aromatic ring, $-NR_{14}R_{15}$, $-SiR_{16}R_{17}R_{18}$, $-SR_{19}$, $-OR_{20}$, a substituted or unsubstituted (C2-C30)alkenyl group, a substituted or unsubstituted (C2-C30)alkynyl group, a cyano group, a nitro group, or a hydroxyl group; or are linked to an adjacent substituent via a substituted or unsubstituted (C3-C30)alkylene group or a substituted or unsubstituted (C3-C30)alkenylene group to form a mono- or polycyclic alicyclic ring or a mono- or polycyclic aromatic ring whose carbon atom(s) may be substituted by at least one hetero atom selected from nitrogen, oxygen and sulfur;

R_{11} to R_{20} have the same meaning as one of R_1 to R_5;

a, b and e each independently represent an integer of 1 to 4; where a, b or e is an integer of 2 or more, each of R_1, each of R_2 or each of R_5 is the same or different;

c and d each independently represent an integer of 1 to 3; where c or d is an integer of 2 or more, each of R_3 or each of R_4 is the same or different; and

the heterocycloalkyl group and the heteroaryl(ene) group contain at least one hetero atom selected from B, N, O, S, P(=O), Si and P.

[Claim 2] The organic electroluminescent compound according to claim 1, characterized in that substituents of the substituted (C1-C30)alkyl group, the substituted (C2-C30)alkenyl group, the substituted (C2-C30)alkynyl group, the substituted (C6-C30)cycloalkylene group, the substituted (C3-C30)cycloalkyl group, the substituted 5- to 7-membered heterocycloalkyl group, the substituted (C6-C30)aryl(ene) group, the substituted 5- to 30-membered heteroaryl(ene) group and the substituted aromatic ring represented by said L_1, Ar_1, Ar_2, R_1 to R_5 and R_{11} to R_{20} each independently is at least one selected from the group consisting of deuterium, a halogen, a cyano group, a carboxyl group, a nitro group, a hydroxyl group, a (C1-C30)alkyl group, a halo(C1-C30)alkyl group, a (C2-C30)alkenyl group, a (C2-C30)alkynyl group, a (C1-C30)alkoxy group, a (C1-C30)alkylthio group, a (C3-C30)cycloalkyl group, a (C3-C30)cycloalkenyl group, a 5- to 7-membered heterocycloalkyl group, a (C6-C30)aryl group, a (C6-C30)aryloxy group, a (C6-C30)arylthio group, a 5- to 30-membered heteroaryl group, a 5- to 30-membered heteroaryl group substituted by a (C6-C30)aryl group, a (C6-C30)aryl group substituted by a 5- to 30-membered heteroaryl group, a tri(C1-C30)alkylsilyl group, a tri(C6-C30)arylsilyl group, a

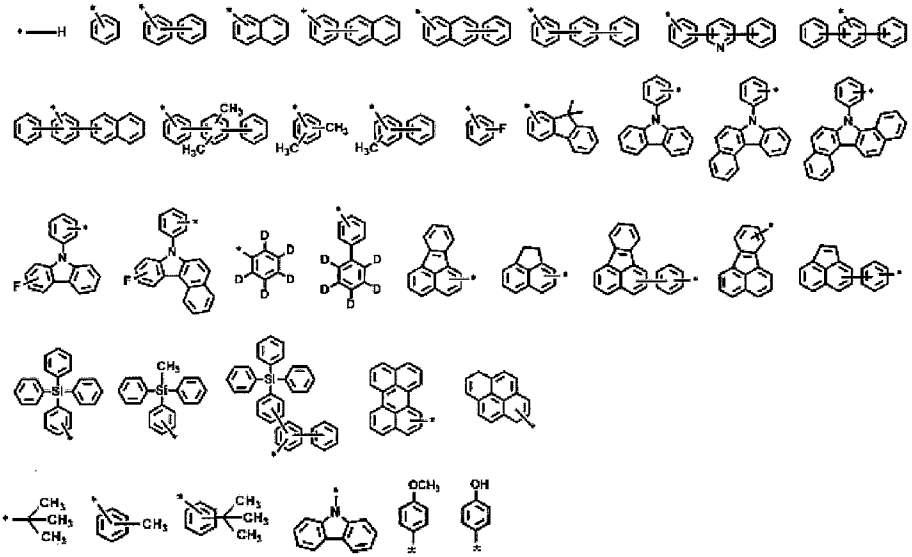
di(C1-C30)alkyl(C6-C30)arylsilyl group, a (C1-C30)alkyldi(C6-C30)arylsilyl group, an amino group, a mono or di(C1-C30)alkylamino group, a mono or di(C6-C30)arylamino group, a (C1-C30)alkyl(C6-C30)arylamino group, a (C1-C30)alkylcarbonyl group, a (C1-C30)alkoxycarbonyl group, a (C1-C30)arylcarbonyl group, a di(C6-C30)arylbornyl group, a di(C1-C30)alkylbornyl group, a (C1-C30)alkyl(C6-C30)arylbornyl group, a (C6-C30)aryl(C1-C30)alkyl group and a (C1-C30)alkyl(C6-C30)aryl group.

[Claim 3] The organic electroluminescent compound according to claim 1, characterized in that L_1 represents a single bond, a substituted or unsubstituted 5- or 30-membered heteroarylene group or a substituted or unsubstituted (C6-C30)arylene group; and Y represents -O-, -S-, -$CR_{11}R_{12}$- (wherein R_{11} and R_{12} each independently represent a substituted or unsubstituted (C1-C30)alkyl group) or -NR_{13}- (wherein R_{13} represents a halogen, deuterium, a substituted or unsubstituted (C6-C30)aryl group, or a substituted or unsubstituted 5- or 30-membered heteroaryl group).

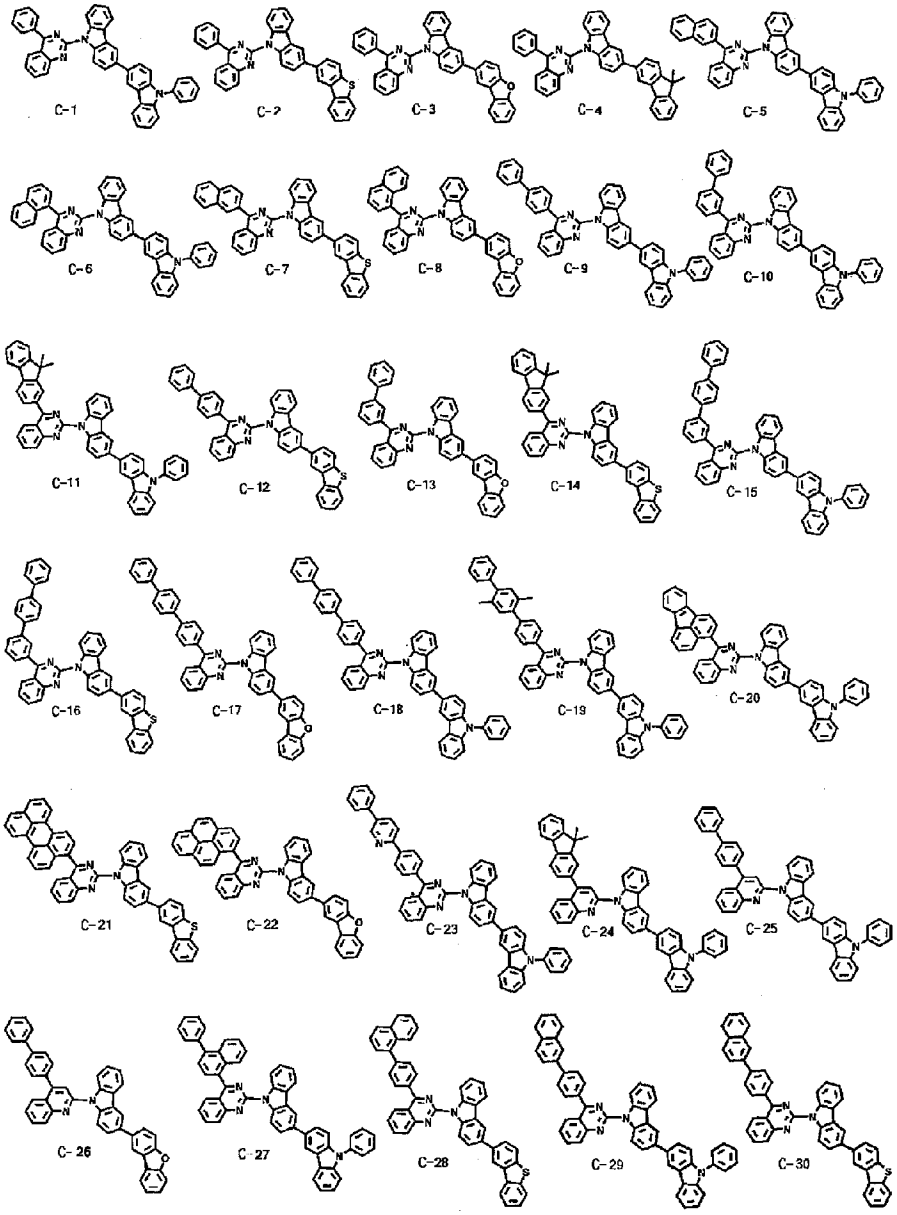
[Claim 4] The organic electroluminescent compound according to claim 1, characterized in that

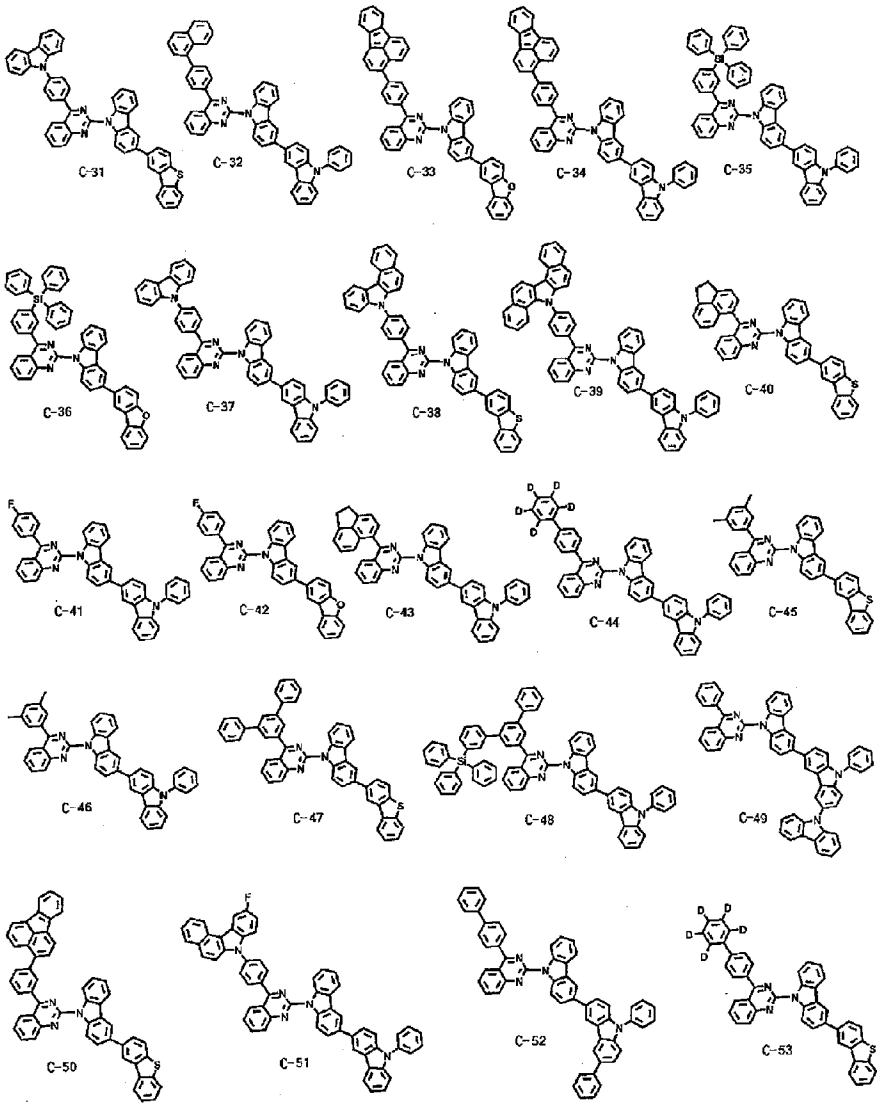
$*-Ar_1-Ar_2$

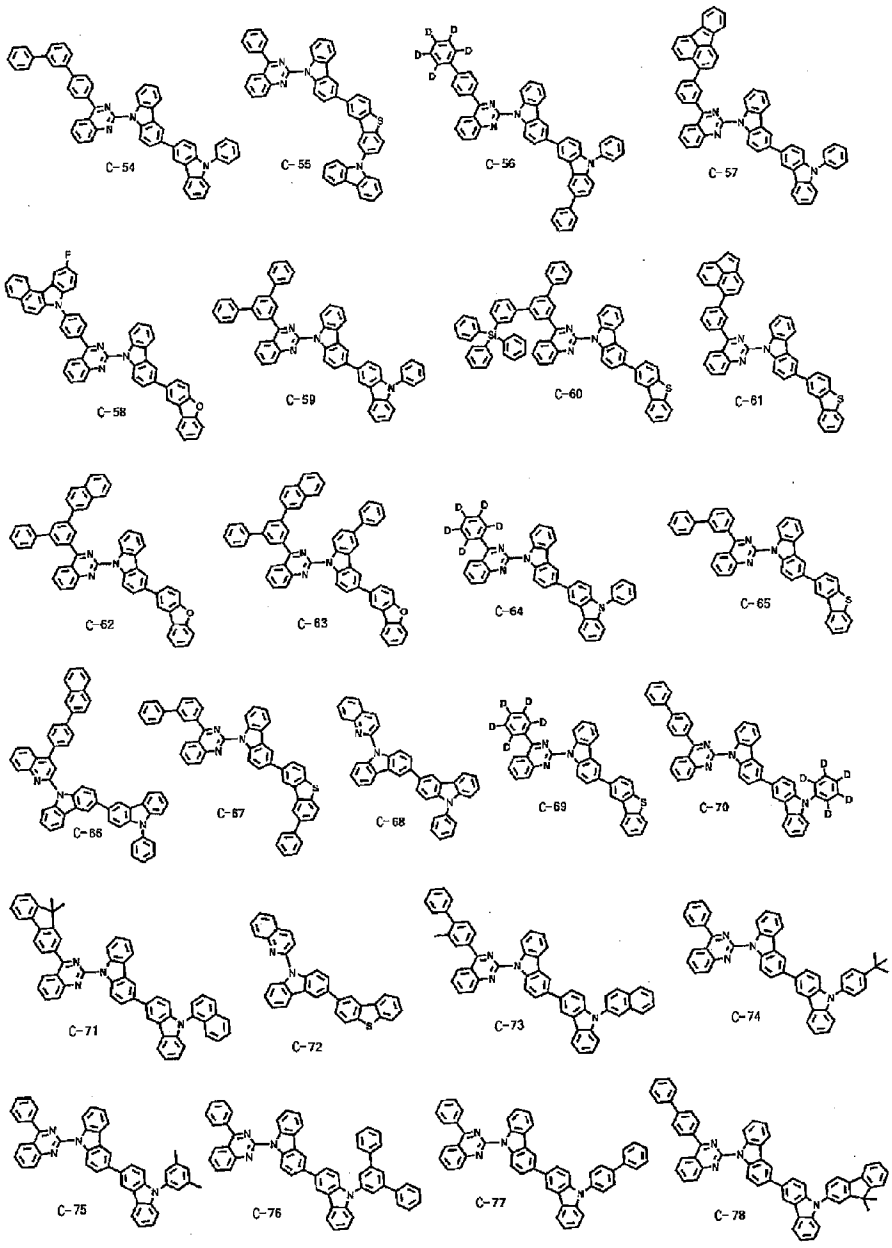
is selected from the following structures:

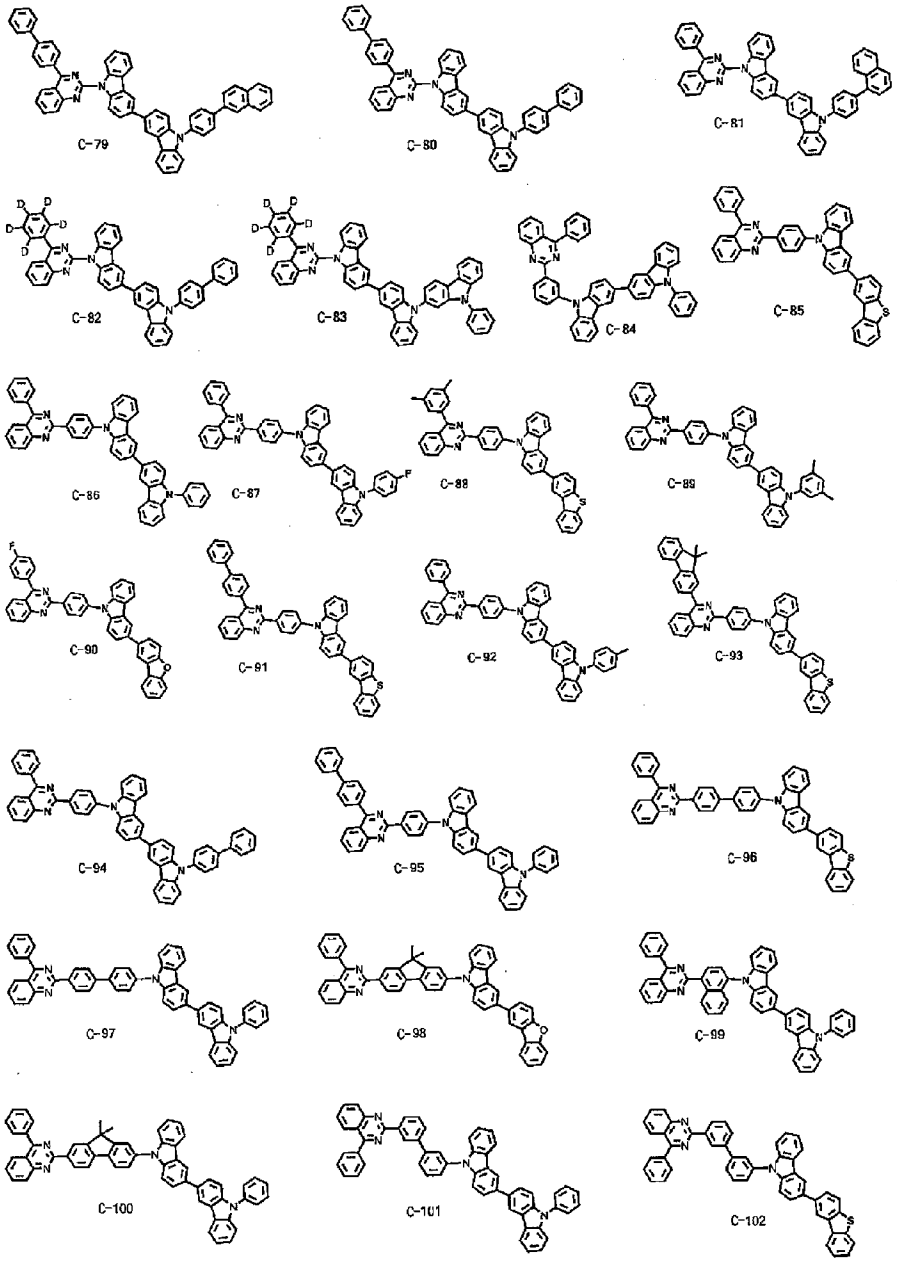


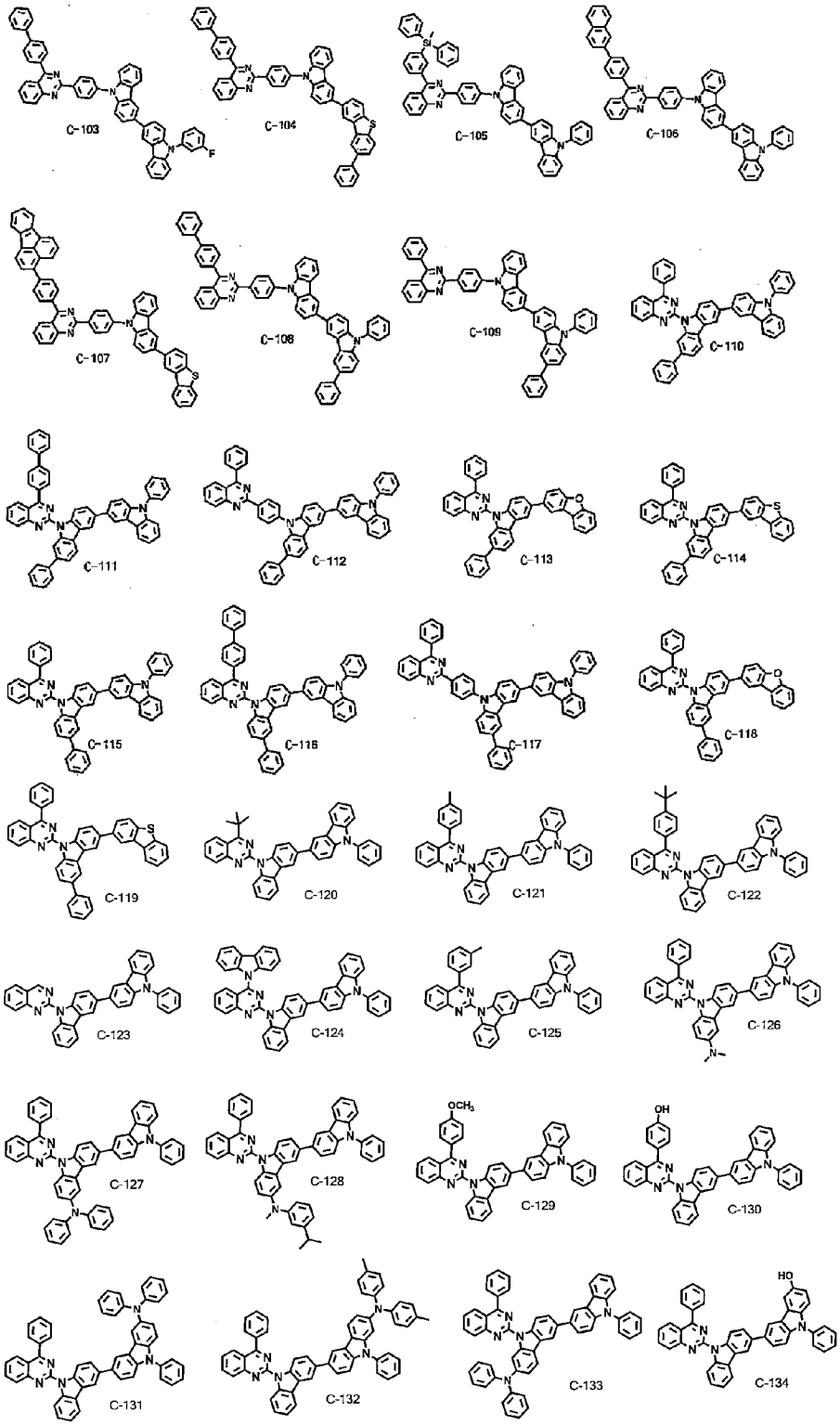
[Claim 5] The organic electroluminescent compound according to claim 1, characterized in that said compound is selected from the group consisting of:


C-1
C-2
C-3
C-4
C-5
C-6
C-7
C-8
C-9
C-10
C-11
C-12
C-13
C-14
C-15
C-16
C-17
C-18
C-19
C-20
C-21
C-22
C-23
C-24
C-25
C-26
C-27
C-28
C-29
C-30


C-31
C-32
C-33
C-34
C-35
C-36
C-37
C-38
C-39
C-40
C-41
C-42
C-43
C-44
C-45
C-46
C-47
C-48
C-49
C-50
C-51
C-52
C-53


C-54
C-55
C-56
C-57
C-58
C-59
C-60
C-61
C-62
C-63
C-64
C-65
C-66
C-67
C-68
C-69
C-70
C-71
C-72
C-73
C-74
C-75
C-76
C-77
C-78


C-79
C-80
C-81
C-82
C-83
C-84
C-85
C-86
C-87
C-88
C-89
C-90
C-91
C-92
C-93
C-94
C-95
C-96
C-97
C-98
C-99
C-100
C-101
C-102



[Claim 6] An organic electroluminescent device comprising the organic electroluminescent compound according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2012/001712

A. CLASSIFICATION OF SUBJECT MATTER

C07D 403/14 (OCT 2005) C07D 409/14 (OCT 2005) C07D 405/14 (OCT 2005) C07D 403/04 (OCT 2005)
C07D 401/14 (OCT 2005) C09K 11/06 (OCT 2005) H01L 27/32 (OCT 2005) H01L 51/54 (OCT 2005)

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)

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)
STN: databases REGISTRY and CAPLUS, structure search based on formula I of claim 1

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] 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	Date of mailing of the international search report
17 July 2012	18 July 2012

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
Email address: pct@ipaustralia.gov.au
Facsimile No.: +61 2 6283 7999

Authorized officer

Chetan Makani
AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No. 0262832896

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/KR2012/001712**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/019156 A1 (ROHM AND HAAS ELECTRONIC MATERIALS KOREA LTD.) 17 February 2011 See compounds 8 and 27 on pages 7 and 8, claims 1 and 6, abstract	1–6
P,A	US 2011/0278552 A1 (NUMATA et al.) 17 November 2011 See the examples starting at page 4	1–6
E	WO 2012/036482 A1 (ROHM AND HAAS ELECTRONIC MATERIALS KOREA LTD.) 22 March 2012 See compounds from page 11 onwards	1–6
P,X	KR 2012/013173 A (CHEIL INDUSTRIES INC.) 14 February 2012 See compounds 10b and 10c on pages 10 and 13	1, 3–6
P,X	WO 2011/132683 A1 (IDEMITSU KOSAN CO., LTD.) 27 October 2011 See the first two compounds on page 38	1, 3–6

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/KR2012/001712**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
WO 2011/019156 A1	17 Feb 2011	KR 20110015836 A	17 Feb 2011
		TW 201120186 A	16 Jun 2011
		WO 2011019156 A1	17 Feb 2011
US 2011/0278552 A1	17 Nov 2011	US 2011278552 A1	17 Nov 2011
		WO 2011122132 A1	06 Oct 2011
		WO 2011125680 A1	13 Oct 2011
WO 2012/036482 A1	22 Mar 2012	KR 20120030009 A	27 Mar 2012
		WO 2012036482 A1	22 Mar 2012
KR 2012/013173 A	14 Feb 2012	None	
WO 2011/132683 A1	27 Oct 2011	CN 102421772 A	18 Apr 2012
		CN 102439004 A	02 May 2012
		EP 2415769 A1	08 Feb 2012
		EP 2423209 A1	29 Feb 2012
		KR 20120034648 A	12 Apr 2012
		US 2011278555 A1	17 Nov 2011
		US 2011279020 A1	17 Nov 2011
		US 2012138911 A1	07 Jun 2012
		US 2012138912 A1	07 Jun 2012
		WO 2011132683 A1	27 Oct 2011
		WO 2011132684 A1	27 Oct 2011

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.