



(51) International Patent Classification:

C07D 405/14 (2006.01) *C07D 403/14* (2006.01)
C07D 407/14 (2006.01) *H01L 27/32* (2006.01)
C07D 409/14 (2006.01) *H01L 51/54* (2006.01)

(21) International Application Number:

PCT/EP2016/000834

(22) International Filing Date:

19 May 2016 (19.05.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15001718.4 10 June 2015 (10.06.2015) EP

(71) Applicant: **MERCK PATENT GMBH** [DE/DE]; Frankfurter Strasse 250, 64293 Darmstadt (DE).

(72) Inventors: **PARHAM, Amir Hossain**; Roemischer Ring 26, 60486 Frankfurt am Main (DE). **JATSCH, Anja**; Hattsteiner Strasse 12, 60489 Frankfurt am Main (DE). **EBERLE, Thomas**; Willy-Brandt-Strasse 6, 76829 Landau (DE). **GROSSMANN, Tobias**; Reuterallee 71, 64297 Darmstadt (DE). **KROEBER, Jonas Valentin**; Fahrgasse 4, 60311 Frankfurt am Main (DE). **DOBELMANN-MARA, Lars**; Holzhofallee 16, 64295 Darmstadt (DE).

(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, BN, 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, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: MATERIALS FOR ORGANIC ELECTROLUMINESCENT DEVICES

(57) Abstract: The present invention relates to compounds which are suitable for use in electronic devices, and to electronic devices, in particular organic electroluminescent devices, comprising these compounds. The compounds have a a dibenzofuran, dibenzothiophene or a fluorene group substituted in the 1-position, either directly or through a linking group, to a carbon atom of a heteroaromatic group with one or two nitrogen atoms in a bicyclic 6/6 core, or to a carbon or nitrogen atom of a heteroaromatic group with two nitrogen atoms in a bicyclic 5/6 core and is further substituted with a group selected from dibenzofuran, dibenzothiophene, fluorene or carbazole.



WO 2016/198144 A1

Materials for organic electroluminescent devices

5 The present invention relates to materials for use in electronic devices, in particular in organic electroluminescent devices, and to electronic devices, in particular organic electroluminescent devices, comprising these materials.

10 The structure of organic electroluminescent devices (OLEDs) in which organic semiconductors are employed as functional materials is described, for example, in US 4539507, US 5151629, EP 0676461 and WO 98/27136.

15 The emitting materials employed here are increasingly organometallic complexes which exhibit phosphorescence instead of fluorescence. For quantum-mechanical reasons, an up to four-fold increase in the energy and power efficiency is possible using organometallic compounds as phosphorescence emitters. In general, however, there is still a need for improvement in the case of OLEDs, in particular also in the case of OLEDs which exhibit triplet emission (phosphorescence), for example with respect to efficiency, operating voltage and lifetime.

20 The properties of phosphorescent OLEDs are not only determined by the triplet emitters employed. In particular, the other materials used, such as matrix materials, hole-blocking materials, electron-transport materials, hole-transport materials and electron- or exciton-blocking materials, are also of particular importance here. Improvements in these materials can thus also result in significant improvements in the OLED properties.

25 There are many materials that can be employed as matrix materials for phosphorescent emitters in organic electroluminescent devices. Further improvements are desirable here, in particular with respect to the efficiency, the lifetime and the thermal stability of the materials. The object of the present invention is the provision of compounds which are suitable for use in an OLED, in particular as matrix material for phosphorescent emitters, but also as electron-transport materials although other uses such as hole-transport and/or electron-blocking materials are also possible. A further object of the present invention is to provide further organic semiconductors for organic electroluminescent devices so as to provide the person skilled in

30

35

the art with a greater possible choice of materials for the production of OLEDs.

5 It is known that compounds with aromatic heterocyclic groups such as carbazoles, dibenzofurans, dibenzothiophenes, fluorenes, quinazolines, quinoxalines and benzimidazoles are useful in OLEDs, generally as hosts for light emitting materials or for their charge-carrying properties. Compounds with combinations of at least three of these classes are known.

10 WO 2012/134124, WO 2012/169821, WO 2013/187689, WO 2012/121561, WO 2012/050371, WO 2012/036482, WO 2012/141499, KR 201310263, KR 2012132815, KR 2012116272, KR 2012109744, KR 2012038060, KR 2013102673 and KR 20120033017 describe OLEDs with quinazolone groups substituted with (among others) dibenzofuran, dibenzothiophene or
15 fluorene groups as well as carbazolyl groups.

US 2014/0114069 discloses OLEDs with quinazoline substituted (either directly or through a link) through the nitrogen of a carbazole group which may be further substituted with dibenzofuran, dibenzothiophene or fluorene
20 groups.

US 2013/0306959 discloses OLED with compounds of the formula A-B-(Cz)_n where A, B and C are all aromatic heterocyclic groups, where A and B can include (among many others) quinazolines, quinoxalines, benzimidazoles, dibenzofurans and dibenzothiophenes and Cz can also include
25 carbazoles as well.

CN 103467447 discloses OLEDs with quinazoline compounds substituted with carbazole groups and can be further substituted with (among others) dibenzofuran, dibenzothiophene and fluorene groups.
30

WO 2013/154325 and WO 2014/104585 disclose OLEDs with bis-carbazolyl groups that may be substituted with (among others) quinazolines, dibenzofurans, dibenzothiophenes and fluorenes.

WO 2014/088290 discloses OLEDs with carbazole groups that have an annulated benzene ring which can be substituted with quinazolines, quinoxalines, dibenzofurans, dibenzothiophenes and fluorenes.

5 KR 2014013351, US 2014/0027744 and US 2012/0133274 describe OLEDs with compounds that may contain combinations of 2-(N-phenylbenzimidazole), N-phenylcarbazole, dibenzofuran and dibenzothiophene groups.

10 JP 2012-222268 discloses OLEDs with compounds with combinations of carbazole, dibenzofuran, dibenzothiophene and N-benzimidazole groups.

15 WO 2013/022145 discloses OLEDs with compounds with N-phenylbenzimidazole and carbazole groups which may be substituted with (among other) dibenzofuran and dibenzothiophene groups.

20 WO 2010/044607 discloses OLEDs with compounds with N-phenylbenzimidazole and carbazole groups which may be substituted with (among other) dibenzofuran, dibenzothiophene and fluorene groups.

25 JP 2012-049518 discloses OLEDs with substituted dibenzofuran, dibenzothiophene and N-phenylcarbazole groups.

30 KR 2012104067 discloses dibenzothiophene derivatives substituted in the 1- position with quinoline and N-(1-phenylbenzimidazole) groups. The benzimidazole may be connected either directly through the nitrogen or through an aryl linking group to the nitrogen.

35 WO 2011/106344 discloses dibenzofuran, dibenzothiophene or fluorene compounds substituted in the 1- or 4- positions with a N-(1-phenylbenzimidazole) as ligands for phosphorescent metal complexes.

Begoin *et al.*, *Helv. Chem. Acta.*, 96, 853 (2013) discloses 1-(N-(1-phenylbenzimidazole)) substituted dibenzofurans and dibenzothiophenes.

40 Additional general disclosures for compounds with a combination of three different kinds of aromatic heterocyclic groups can be found in

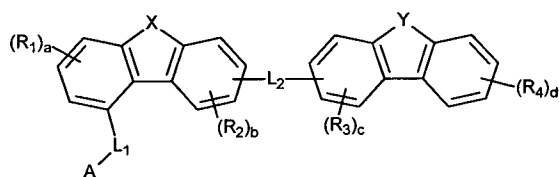
WO 2012/033108; JP 20141883315; US 2011/0147792; KR 2014122680;
 KR 2014127073; US 2014/0284584; WO 2012/033108; US 2014/001460;
 KR 2014080002 and US 8685543.

5 US 7651790 discloses OLEDs with a compound of A-C-B where A is a hole-transporting group (including, among others, carbazoles), B is an electron-transporting group (including triazines, fluorenes and spirofluorenes among others) and C is a bond or a linking group.

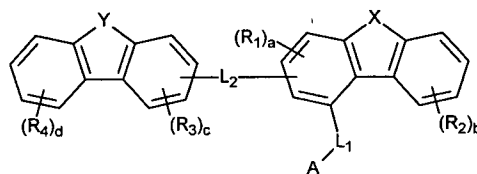
10 Lee et al., Chem. Europ. J., 19, 1194 (2013) compares the effects on OLED performance of attaching a N-phenylcarbazole group (through the phenyl group) in the 2, 3 or 4 positions of a dibenzofuran.

15 Surprisingly, it has been found that certain compounds described in greater detail below achieve this object, are highly suitable for use in OLEDs and result in improvements in the organic electroluminescent device. The improvements here relate, in particular, to the lifetime of the device, although other characteristics can also be improved. The present invention therefore relates to these compounds and to electronic devices, in particular
 20 organic electroluminescent devices, which comprise compounds of this type.

The present invention relates to a compound according to Formula (1) or (2):



25 Formula (1)



Formula (2)

where:

X is an oxygen, sulfur or CZ₁Z₂;

30 Y is an oxygen, sulfur, CZ₁Z₂ or NAr₁;

5 Z₁ and Z₂ are on each occurrence, identically or differently, H, D, F, a straight-chain alkyl, alkoxy or thioalkoxy group having 1 to 40 C atoms or a straight-chain alkenyl or alkynyl group having 2 to 40 C atoms or a branched or cyclic alkyl, alkenyl, alkynyl, alkoxy or thioalkoxy group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R₅, where one or more, preferably non-adjacent CH₂ groups may be replaced by (R₅)C=C(R₅), C≡C, Si(R₅)₂, Ge(R₅)₂, Sn(R₅)₂, C=O, C=S, C=Se, C=N(R₅), P(=O)(R₅), SO, SO₂, N(R₅)₂, O, S or CON(R₅)₂ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, or an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R₅, or an aryloxy or heteroaryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R₅, where Z₁ and Z₂ may be connected together to form a spiro ring system;

10 R₁, R₂, R₃ and R₄ is on each occurrence, identically or differently, selected from the group consisting of H, D, F, Cl, Br, I, CN, Si(R₅)₃, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl with 3-40 C atoms which may be substituted by one or more radicals R₅, wherein each one or more non-adjacent CH₂ groups by may be replaced Si(R₅)₂, C=NR₅, P(=O)(R₅), SO, SO₂, NR₅, O, S or CONR₅ and where one or more H atoms may be replaced by D, F, Cl, Br or I, an aromatic or heteroaromatic ring system having 6 to 40 carbon atoms which may be substituted by one or more radicals R₅, an aryloxy group having 5 to 60 aromatic ring atoms which may be substituted by one or more radicals R₅, or an aralkyl group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R₅, where two or more adjacent substituents R₁, R₂, R₃ and R₄ can form a mono- or polycyclic, aliphatic, aromatic or heteroaromatic ring system with one another and which may be substituted with one or more radicals R₅; where R₅ is selected from the group consisting of H, D, F, an aliphatic hydrocarbon radical having 1 to 20 carbon atoms or an aromatic or heteroaromatic ring system having 5 to 30 C atoms; R₆ is the same as R₁ but excluding H or D;

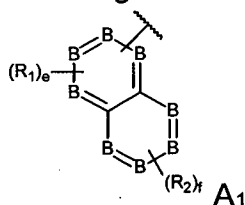
15 Ar₁ and Ar₂ are on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 30 aromatic ring atoms, which may be substituted by one or more radicals R₅ and where optionally

two or more adjacent substituents R_5 can form a mono- or polycyclic-
aliphatic, aromatic or heteroaromatic ring system with one another;

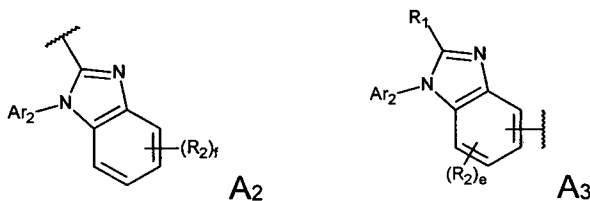
a, b, c are on each occurrence, identically or differently, are 0, 1, 2 or 3
where a is not 3 in Formula (2) and d is independently 0, 1, 2, 3 or 4;

5 L_1 and L_2 are on each occurrence, identically or differently, a direct bond
or an aromatic or heteroaromatic ring system having 5-30 aromatic ring
atoms, which may be substituted by one or more non-aromatic radicals R_5 ;

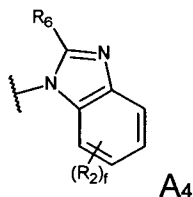
A is a heterocyclic group according to Formula A_1 :



10 where only one or two of B are nitrogen atoms and the others are carbon
atoms, R_1 and R_2 are as previously defined, e is 0, 1, 2 or 3, f is 0, 1, 2, 3 or
4, and wherein A_1 is connected to the remainder of the compound through a
carbon atom; or A is a heterocyclic group selected from the group of
Formula A_2 or A_3 :

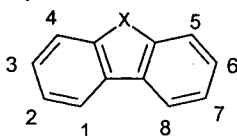


15 where Ar_2 , R_1 , R_2 , e and f are as previously defined; or A is a heterocyclic
group according to A_4 :



where Ar_2 , R_2 , R_6 , e and f are as previously defined.

20 In the sense of this invention, the following numbering system for the central
nucleus to which A is attached ($X = O, S$ or CZ_1Z_2) will be used:



For convenience, the same numbering system will also be used for a carbazole substituent ($X=NAr_1$).

5 The compounds of Formulae (1) or (2) can be generally described as having a central nucleus that is a dibenzofuran ($X=O$), a dibenzothiophene ($X=S$) or a fluorene ($X=CZ_1Z_2$). The 1-position of the compound of Formulae (1) and (2) is connected (either directly or through a linking group L_1) to a carbon atom of a heteroaromatic group with one or two nitrogen atoms in a bicyclic 6/6 core. Alternatively, the 1-position is connected (either directly or through
10 a linking group L_1) to a carbon or nitrogen atom of a heteroaromatic group with two nitrogen atoms in a bicyclic 5/6 core, which is a benzimidazole. In either of these alternatives, the compounds of Formulae (1) and (2) also have at least one substituent selected from a dibenzofuran ($Y=O$), dibenzothiophene ($Y=S$), fluorene ($Y=CZ_1Z_2$) or carbazole ($Y=NAr_1$) attached via
15 any of its 1- to 8- positions to any of the 2- to 8- positions of the central nucleus.

In the sense of the invention, the terms "dibenzofuran, dibenzothiophene, fluorene (including spirofluorene), or carbazole" include not only the parent
20 heterocycle but also include any analogues that have annulated monocyclic- or polycyclic-, aliphatic, aromatic or heteroaromatic rings. An annulated ring is one that has two adjacent ring atoms in common with another ring.

An aryl group in the context of this invention contains from 6 to 24 carbon
25 atoms; a heteroaryl group within the meaning of this invention containing from 2 to 24 carbon atoms and at least one heteroatom, with the proviso that the sum of carbon atoms and hetero atoms is at least 5. The heteroatoms are preferably selected from N, O and S. Among an aryl or heteroaryl group is either a simple aromatic ring, for example benzene, or a simple
30 heteroaromatic ring, for example pyridine, pyrimidine, thiophene, etc., or a fused aryl or heteroaryl, such as naphthalene, anthracene, phenanthrene, quinoline, isoquinoline, etc.

An aromatic ring system in the sense of this invention contains from 6 to 40
35 carbon atoms in the ring system. A heteroaromatic ring system in the sense of this invention contains 1 to 40 carbon atoms and at least one heteroatom

in the ring system, with the proviso that the sum of carbon atoms and hetero atoms is at least 5 results. The heteroatoms are preferably selected from N, O and S. An aromatic or heteroaromatic ring system in the context of this invention is to be understood as a system that does not necessarily contain
5 only aryl or heteroaryl groups, but in which a plurality of aryl or heteroaryl groups are connected by a non-aromatic moiety, such as, for example, a C, N or O atom or a carbonyl group. For example, systems such as 9,9'-spiro-bifluorene, 9,9-diarylfluorene, triarylamine, stilbene, etc., are aromatic ring systems for the purposes of this invention. Also included are systems in
10 which two or more aryl groups are connected, for example, by a linear or cyclic alkyl group or by a silyl group. Furthermore, to systems in which two or more aryl or heteroaryl groups are directly bonded to each other, such, for example, biphenyl, terphenyl or quaterphenyl be understood also as an aromatic or heteroaromatic ring system.

15 For the purposes of this invention, a cyclic alkyl, alkoxy or thioalkoxy means a monocyclic, bicyclic or a polycyclic group.

In the present invention, a C1 to C40 alkyl group, in which individual H
20 atoms or CH₂ groups may be substituted by the above-mentioned groups, include methyl, ethyl, n-propyl, i-propyl, cyclopropyl, n-butyl, i-butyl, s-butyl, t-butyl, cyclobutyl, 2-methylbutyl, n-pentyl, s-pentyl, t-pentyl, 2-pentyl, neo-pentyl, cyclopentyl, n hexyl, s-hexyl, t-hexyl, 2-hexyl, 3-hexyl, neo-hexyl, cyclohexyl, 1-methylcyclopentyl, 2-methylpentyl, n-heptyl, 2-heptyl, 3-heptyl,
25 4-heptyl, cycloheptyl, 1-methylcyclohexyl, n-octyl, 2-ethylhexyl, cyclooctyl, 1-bicyclo [2,2,2] octyl, 2-bicyclo [2.2.2] octyl, 2- (2,6-dimethyl) octyl, 3- (3,7-dimethyl) octyl, adamantyl, trifluoromethyl, pentafluoroethyl, 2,2,2-trifluoroethyl, 1,1-dimethyl-n-hex-1-yl, 1,1-dimethyl-n-hept- 1-yl, 1,1-dimethyl-n-oct-1-yl, 1,1-dimethyl-n-dec-1-yl, 1,1-dimethyl-n-dodec-1-yl, 1,1-dimethyl-n-tetradec-1-yl, 1,1-dimethyl-n-hexadec-1-yl, 1,1-dimethyl-n-octadec-1-yl, 1,1-diethyl-n-hex-1-yl, 1,1-diethyl-n-hept-1-yl, 1,1-diethyl-n-oct-1-yl, 1,1-diethyl-n-dec-1-yl, 1,1-diethyl-n-dodec-1-yl, 1,1-diethyl-n-tetradec-1-yl, 1,1-diethyl-n-hexadec-1-yl, 1,1-diethyl-n-octadec-1-yl, 1-(n-propyl) cyclohex-1-yl, 1-(n-butyl)cyclohex-1-yl, 1-(N-hexyl) -cyclohex-1-yl, 1-(n-octyl)-cyclohex-1-yl and
35 1-(n-decyl)cyclohex-1-yl. Examples of an alkenyl group include ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl,

cycloheptenyl, octenyl, cyclooctenyl or cyclooctadienyl. Examples of an alkynyl group include, for example, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl or octynyl. An alkoxy group having 1 to 40 C atoms is preferably taken to mean methoxy, trifluoromethoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy, n-pentoxy, s-pentoxy, 2-methylbutoxy, n-hexoxy, cyclohexyloxy, n-heptoxy, cycloheptyloxy, n-octyloxy, cyclooctyloxy, 2-ethylhexyloxy, pentafluoroethoxy and 2,2,2-trifluoroethoxy. A thioalkyl group having 1 to 40 C atoms is taken to mean, in particular, methylthio, ethylthio, n-propylthio, i-propylthio, n-butylthio, i-butylthio, s-butylthio, t-butylthio, n-pentylthio, s-pentylthio, n-hexylthio, cyclohexylthio, n-heptylthio, cycloheptylthio, n-octylthio, cyclooctylthio, 2-ethylhexylthio, trifluoromethylthio, pentafluoroethylthio, 2,2,2-trifluoroethylthio, ethenylthio, propenylthio, butenylthio, pentenylthio, cyclopentenylthio, hexenylthio, cyclohexenylthio, heptenylthio, cycloheptenylthio, octenylthio, cyclooctenylthio, ethynylthio, propynylthio, butynylthio, pentynylthio, hexynylthio, heptynylthio or octynylthio. In general, alkyl, alkoxy or thioalkyl groups in accordance with the present invention may be straight-chain, branched or cyclic, where one or more non-adjacent CH₂ groups may be replaced by the above-mentioned groups; furthermore, one or more H atoms may also be replaced by D, F, Cl, Br, I, CN or NO₂, preferably F, Cl or CN, further preferably F or CN, particularly preferably CN..

An aromatic or heteroaromatic ring system having 5-60 aromatic ring atoms which may be substituted with residues above yet and which can be linked via any position on the aromatic or heteroaromatic compounds, for example, groups are understood to be derived from benzene, naphthalene, anthracene, benzanthracene, phenanthrene, benzophenanthrene, pyrene, chrysene, perylene, fluoranthene, benzfluoranthene, naphthacene, pentacene, benzopyrene, biphenyl, biphenyl, terphenyl, fluorene, spirobifluorene, dihydrophenanthrene, dihydropyrene, tetrahydropyrene, *cis*- or *trans*-indenofluorene, *cis*- or *trans*-Monobenzoindenofluorene, *cis*- or *trans*-dibenzoindenofluorene, truxene, isotruxene, spirotruxene, spiroisotruxene, furan, benzofuran, isobenzofuran, dibenzofuran, thiophene, benzothiophene, isobenzothiophene, dibenzothiophene, pyrrole, indole, isoindole, carbazole, indolocarbazole, indenocarbazole, pyridine, quinoline, isoquinoline, acridine, phenanthridine, benzo-5,6-quinoline, benzo-6,7-

quinoline, benzo-7,8-quinoline, phenothiazine, phenoxazine, pyrazole, indazole, imidazole, benzimidazole, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, chinoxalinimidazole, oxazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, benzothiazole, pyridazine, benzopyridazin, pyrimidine, benzpyrimidine, quinoxaline, 1,5-diaza-anthracene, 2,7-diazapyrene, 2,3-diazapyrene, 1,6-diazapyrene, 1,8-diazapyrene, 4,5-diazapyrene, 4,5,9,10-tetraazaperylene, pyrazine, phenazine, phenoxazine, phenothiazine, fluorubin, naphthyridine, azacarbazole, benzocarboline, phenanthroline, 1,2,3-triazole, 1,2,4-triazole, benzotriazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, tetrazole, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-tetrazine, purine, pteridine, indolizine and benzothiadiazole.

In the above, R_1 to R_4 refers to a first substituent and R_5 is a secondary substituent on $R_1 - R_4$ or in the case of structure A_4 , a first substituent. Any of $R_1 - R_4$ and R_5 can be chosen independently from the groups as described. Adjacent radicals or adjacent substituents in the sense of the present application are taken to mean substituents which are bonded to C atoms which are in turn bonded directly to one another or substituents which are bonded to the same C atom.

In compounds which are processed by vacuum evaporation, the alkyl groups preferably have not more than five C atoms, particularly preferably not more than 4 C atoms, very particularly preferably not more than 1 C atom. For compounds which are processed from solution, suitable compounds are also those which are substituted by alkyl groups, in particular branched alkyl groups, having up to 10 C atoms or which are substituted by oligoarylene groups, for example *ortho*-, *meta*-, *para*- or branched terphenyl or quaterphenyl groups.

If the compounds of the formula (1) or (2) or the preferred embodiments are used as matrix material for a phosphorescent emitter or in a layer which is directly adjacent to a phosphorescent layer, it is furthermore preferred for $R_1 - R_6$, Z_1 , Z_2 , Ar_1 and Ar_2 of the compound to contain no condensed aryl or

heteroaryl groups in which more than two six-membered rings are condensed directly onto one another. It is generally advantageous for the triplet energy of the compound used as a matrix material or in an adjacent layer to be the same or greater than the phosphorescent material in the emitting layer.

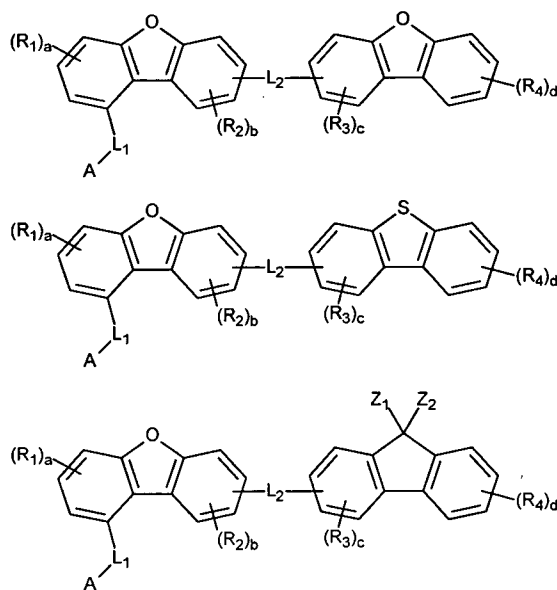
The compounds according to the invention described above, in particular compounds which are substituted by reactive leaving groups, such as bromine, iodine, chlorine, boronic acid or boronic acid ester, or by reactive, polymerisable groups, such as olefins, styrenes, acrylates or oxetanes, can be used as monomers for the generation of corresponding oligomers, dendrimers or polymers. The oligomerisation or polymerisation here preferably takes place via the halogen functionality or the boronic acid functionality or via the polymerisable group. It is furthermore possible to crosslink the polymers via groups of this type. The compounds and polymers according to the invention can be employed as crosslinked or uncrosslinked layer.

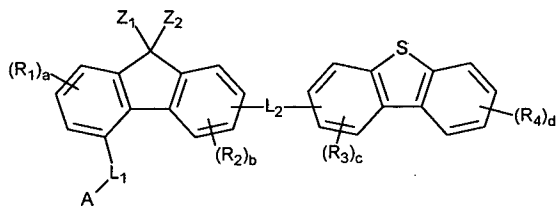
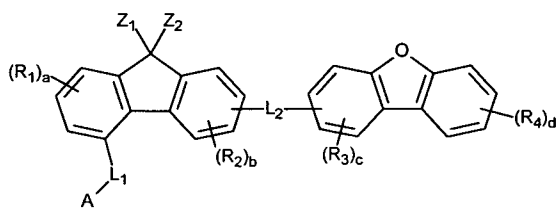
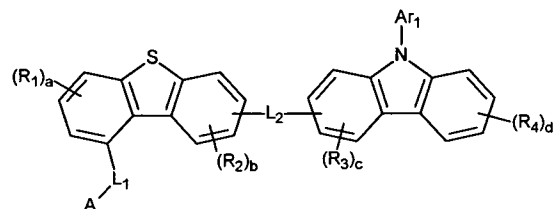
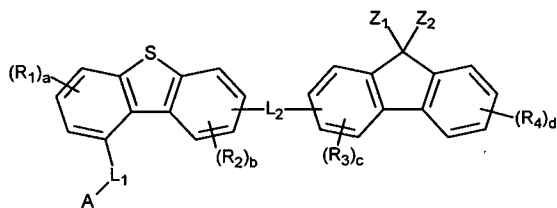
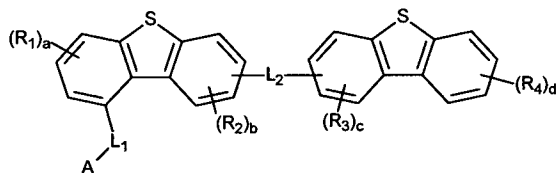
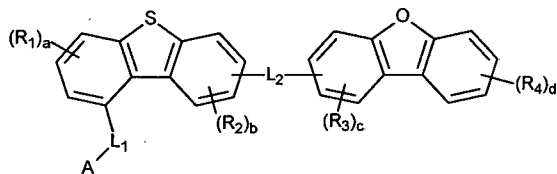
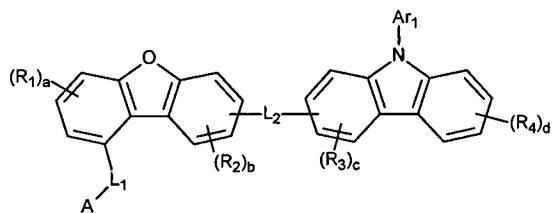
The invention therefore furthermore relates to oligomers, polymers or dendrimers containing one or more of the compounds according to the invention indicated above, where one or more bonds from the compound according to the invention to the polymer, oligomer or dendrimer are present at one or more positions instead of substituents. Depending on the linking of the compound according to the invention, this forms a side chain of the oligomer or polymer or is linked in the main chain or forms the core of a dendrimer. The polymers, oligomers or dendrimers may be conjugated, partially conjugated or non-conjugated. The oligomers or polymers may be linear, branched or dendritic. The same preferences as described above apply to the recurring units of the compounds according to the invention in oligomers, dendrimers and polymers.

For the preparation of the oligomers or polymers, the monomers according to the invention are homopolymerised or copolymerised with further monomers. Preference is given to homopolymers or copolymers in which the units of the formula (1) or the preferred embodiments indicated above are present to the extent of 0.01 to 99.9 mol%, preferably 5 to 90 mol%, particularly

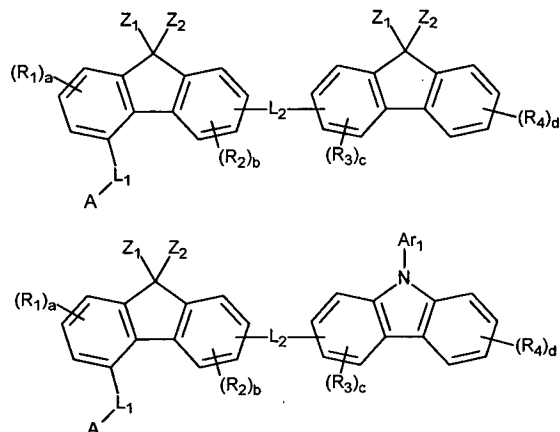
preferably 20 to 80 mol%. Suitable and preferred comonomers which form the polymer backbone are selected from fluorenes (for example in accordance with EP 842208 or WO 2000/22026), spirobifluorenes (for example in accordance with EP 707020, EP 894107 or WO 2006/061181), para-phenylenes (for example in accordance with WO 92/18552), carbazoles (for example in accordance with WO 2004/070772 or WO 2004/113468), thiophenes (for example in accordance with EP 1028136); dihydro-phenanthrenes (for example in accordance with WO 2005/014689), cis- and trans-indenofluorenes (for example in accordance with WO 2004/041901 or WO 2004/113412), ketones (for example in accordance with WO 2005/040302), phenanthrenes (for example in accordance with WO 2005/104264 or WO 2007/017066) or also a plurality of these units. The polymers, oligomers and dendrimers may also contain further units, for example hole-transport units, in particular those based on triarylamines, and/or electron-transport units. In addition, the polymers may contain triplet emitters, either copolymerised or mixed in as a blend. In particular, the combination of the oligomers, polymers or dendrimers according to the invention with triplet emitters leads to particularly good results.

X and Y may be the same or different in any combination. In particular, all of the following combinations (shown for Formula (1), but it should be understood that the same combinations apply to Formula (2) as well) are possible:



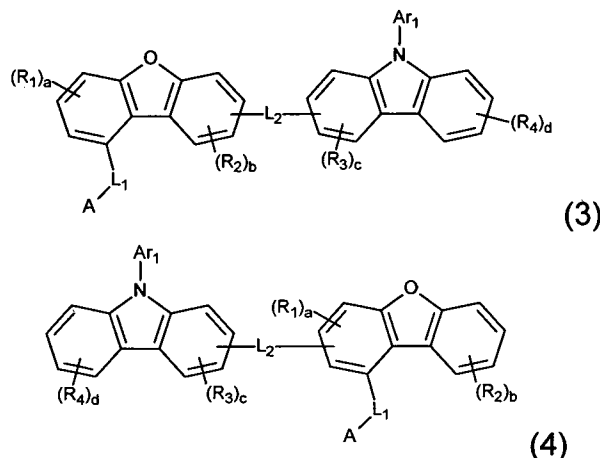


5



5

It is preferred that X is oxygen or sulfur and Y is oxygen, sulfur, CZ₁Z₂ or NAr₁ in both Formulae (1) and (2). It is also preferred that Y is NAr₁ and X is oxygen, sulfur or CZ₁Z₂ in both Formulae (1) and (2). It is most preferred that X is oxygen and Y is NAr₁ as shown in Formulae (3) and (4):



10

In any of Formulae (1)-(4), it is preferred that c is 0, d is 0, 1 or 2 and when d is 2, the two R₄ groups are adjacent and form a monocyclic- or polycyclic, aromatic or heteroaromatic annulated ring system.

15

Whenever X or Y (or both) is CZ₁Z₂ (a fluorene derivative), it is preferred that Z₁ and Z₂ are on each occurrence, identically or differently, an alkyl group of 1-10 carbon atoms or an aryl group of between 6-30 carbon atoms. For both alkyl and aryl groups, the two Z groups may be attached together to form a spiro ring system. Examples of suitable alkyl groups for Z₁ and Z₂ are methyl, ethyl, hexyl and decyl. Of these, methyl groups are highly preferred.

20

Examples of aryl groups are phenyl and naphthyl. The aryl groups may be further substituted with additional alkyl, aryl or heteroatoms. Of these,

substituted or unsubstituted phenyl groups such as *p*-methylphenyl are preferred. Particularly preferred are 9,9'-diphenyl groups. It is preferred for both X and Y that Z₁ and Z₂ are identical, although X and Y may individually have the same or different identical Z groups.

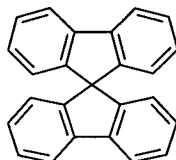
5

Two identical or different Z₁ and Z₂ groups may also be connected together to form a 9,9'-spiro ring system. For example, two alkyl Z groups can be connected to form spiro compounds such as 9,9'-cyclopentyl or 9,9'-cyclohexyl:



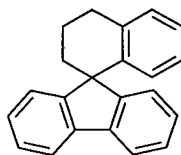
10

Alternatively, two aryl Z groups may be connected to form spiro compounds such as a 9,9'-spirobifluorene:



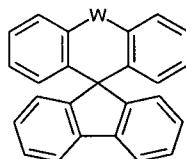
15

which may be further substituted. Particularly preferred are unsubstituted 9,9'-spirobifluorenes. Also contemplated are unsymmetrical spiro compounds where Z₁ is an alkyl and Z₂ is an aryl such as:



20

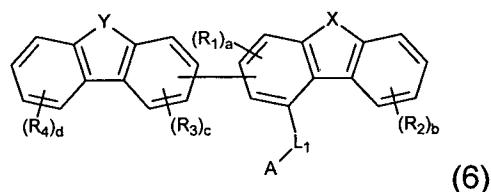
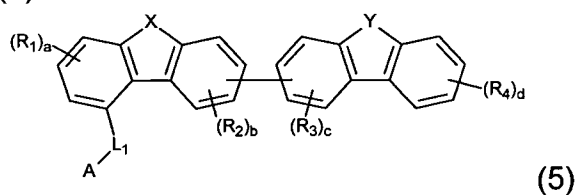
Further contemplated are spirofluorene derivatives where the spiro group is further elaborated with additional substituents or forms heterocyclic spiro groups. Some examples of this type of heterocyclic spirofluorene derivative are:



where W is oxygen, sulfur, N-Aryl, SO₂ or C=O.

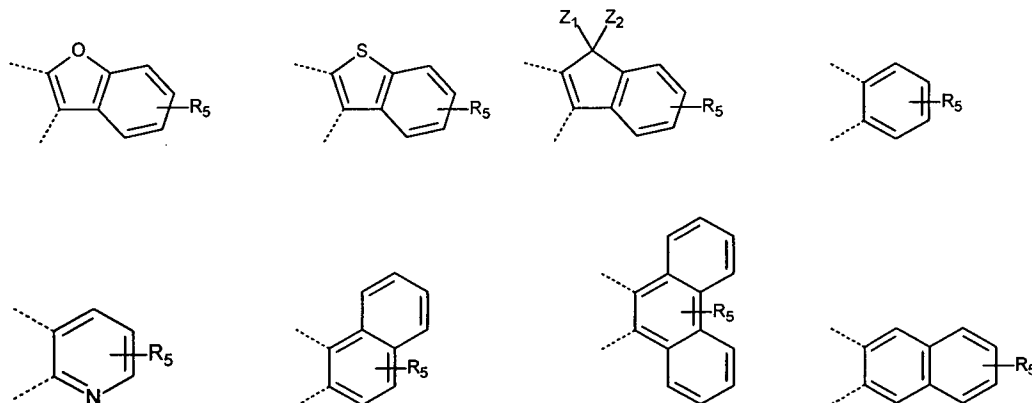
The group containing Y is connected through any of the 1- to 8- positions to the central nucleus (which contains X and the -L₁-A group) and not through the 9-position. It is understood that when Y is NAr₁, the carbazole group is not connected to the central nucleus through the Ar₁ group or the nitrogen of the carbazole group either. It is preferred for Formulae (1) and (2) that the 7-
 5 position of the group containing X is connected (either directly or through L₂) to the 2-position of the group containing Y.

L₂ is a linking group that connects the group containing X to the group containing Y. It may be a direct bond so that a carbon atom of the group containing X (in any of the 2- to 8- positions) is connected via a single bond to a carbon atom in the group containing Y (in any of the 1- to 8- positions). If L₂ is not a direct bond, then it is an aromatic or heteroaromatic ring system having 5-30 aromatic ring atoms, which may be substituted by one or more
 10 non-aromatic radicals R₅. For example, L₂ can be a *meta*- or *para*-phenylene group, a polycyclic aromatic group such as naphthyl or a fluorene, or a polycyclic heteroaromatic group such as dibenzofuran or dibenzothiophene, any of which can be further substituted. If L₂ is an
 15 aromatic or heteroaromatic ring system, then L₂ is connected to both the group containing X and the group containing Y by single bonds. Thus, it is understood that the group containing X and the group containing Y are not annulated to each other. It is preferred that L₂ is a direct bond as shown in
 20 Formulae (5) and (6):



The group containing X may be substituted with R₁ and R₂ substituents. The group containing Y may be substituted with R₃ and R₄ substituents. If there are any two adjacent R₁ – R₄ groups, they may be combined to form an
 30 annulated monocyclic or polycyclic aromatic or heteroaromatic ring. For

example, any two adjacent R₃ or R₄ groups may be represented by the following annulated groups:

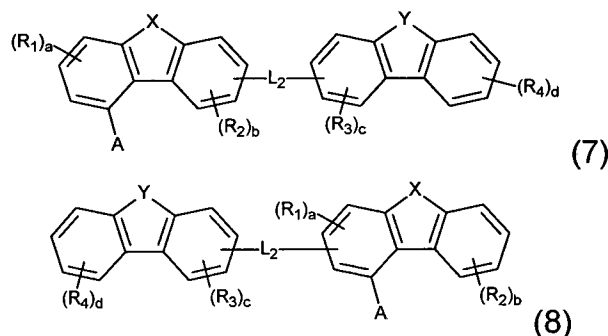


5

The group -L₁-A is located in the 1- position of the group containing X and L₁ is selected independently of L₂. It may be a direct bond so that a carbon atom in the 1-position of the group containing X is connected to A by a single bond. Alternatively, if L₁ is not a direct bond, then it is an aromatic or heteroaromatic ring system having 5-30 aromatic ring atoms, which may be substituted by one or more non-aromatic radicals R₅. For example, L₁ can be a *meta*- or *para*-phenylene group, a polycyclic aromatic group such as naphthyl or a fluorene, or a polycyclic heteroaromatic group such as dibenzofuran or dibenzothiophene, any of which can be further substituted. If L₁ is an aromatic or heteroaromatic ring system, then L₁ is connected to both the group containing X and A by single bonds. It is preferred that L₁ is a single bond as in Formulae (7) and (8):

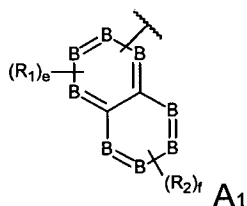
10

15

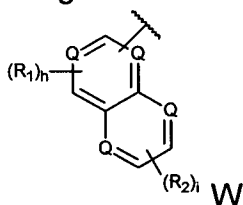


20

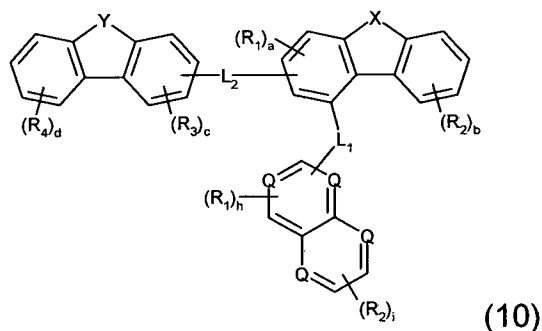
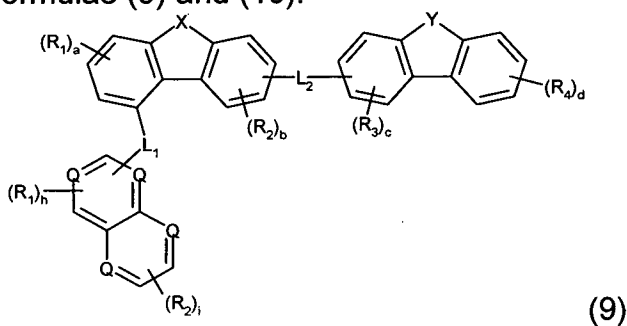
One option for A is a heterocyclic group according to Formula A₁:



5 where only one or two of B are nitrogen atoms and the others are carbon atoms. If there is no substituent on the carbon atom, an H atom is bound to the corresponding carbon atom. The site where A₁ is connected to L₁ or the group containing X is where B is a carbon atom and not a nitrogen. A preferred version of A₁ is according to formula W:

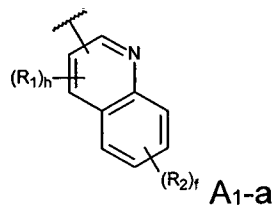


10 where at least one but at most only two Q are nitrogen and the others are carbon and h and i are independently 0, 1 or 2. This embodiment corresponds to formulae (9) and (10):

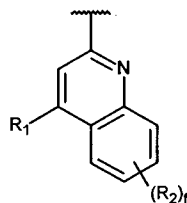


15 where at most only two Q are nitrogen and the others are carbon and h and i are independently 0, 1 or 2.

In one embodiment of Formulae (9) and (10) where only one Q is nitrogen, then W is a quinoline derivative according to formula A_{1-a}:

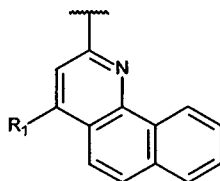


In this embodiment, one preferred structure for the quinoline derivative is:



and a specific example of a suitable structure for a quinoline derivative of this embodiment is:

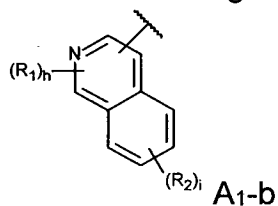
5



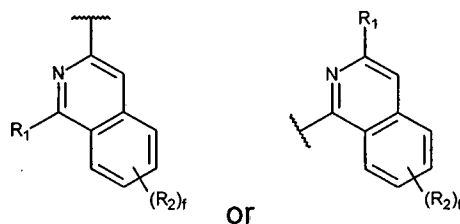
In this embodiment of Formulae (9) and (10) with A1-a, the most preferred structure is where f is 0.

10

In another embodiment of Formulae (9) and (10) where one Q is nitrogen, then W is an isoquinoline derivative according to formula A1-b:



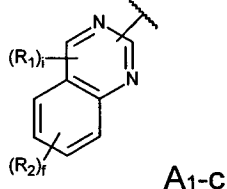
In this embodiment, two preferred structures for the isoquinoline derivative are:



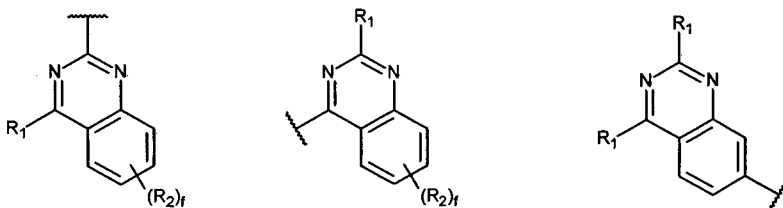
15

and the most preferred structures for Formulae (9) and (10) with A1-b are where f is 0.

In Formulas (9) and (10) when two Q are nitrogen, then W can be a quinazoline derivative according to A_{1-c}:

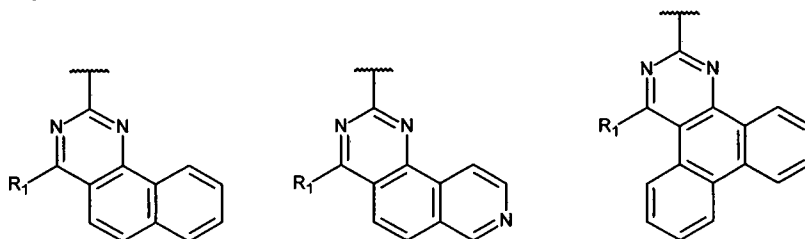


where i is 0 or 1. In this embodiment, three preferred structures for A_{1-c} are:



5

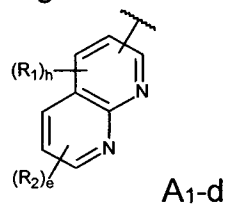
and some specific examples of preferred structures include:



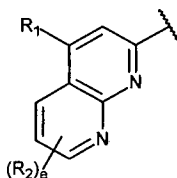
In this embodiment of Formulae (9) and (10) with A_{1-c}, it is most preferred that f is 0.

10

In another embodiment when two Q of W are nitrogen, then W can be a naphthyridine derivative according to A_{1-d}:



In this embodiment, a preferred structure for A_{1-d} is:

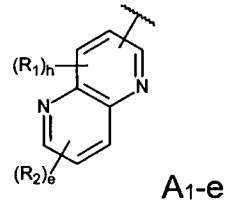


15

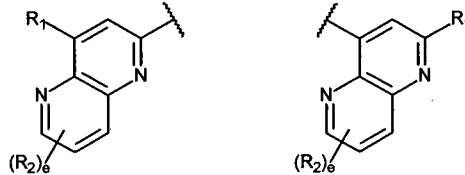
and the most preferred for Formulae (9) and (10) with A_{1-d} are where e is 0.

In yet another embodiment when two Q of W are nitrogen, then W can be a

pyrido[3,2-b]pyridine derivative according to A1-e:



and where preferred structures are:

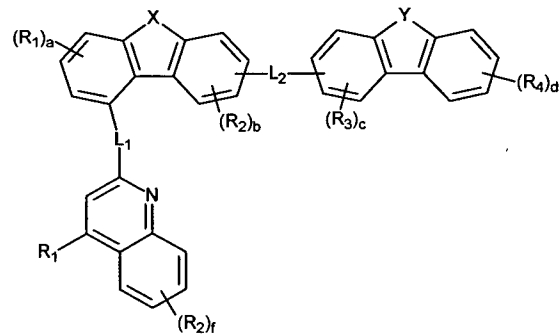


5 and the most preferred for Formulae (9) and (10) with A1-e are where e is 0.

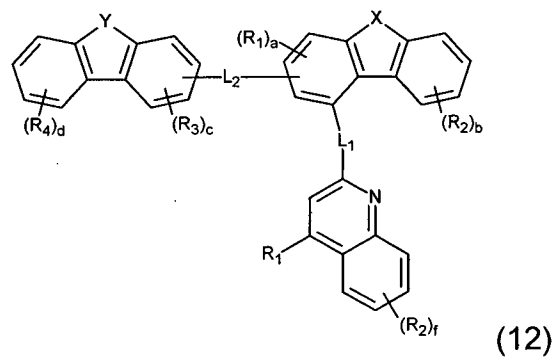
In A1-a, A1-b, A1-c, A1-d or A1-e, it is understood any two adjacent R₁ or R₂ groups may be combined to form an annulated monocyclic or polycyclic aromatic or heteroaromatic ring. In the sense of the invention, it is understood that a derivative encompasses such annulated groups.

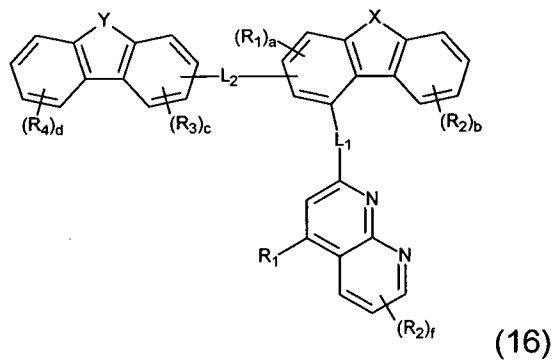
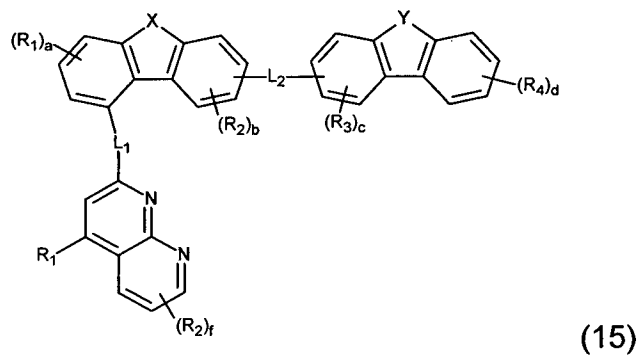
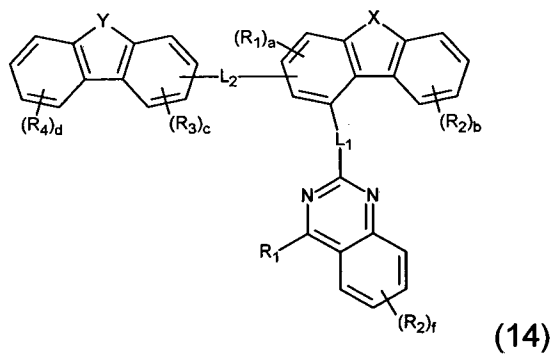
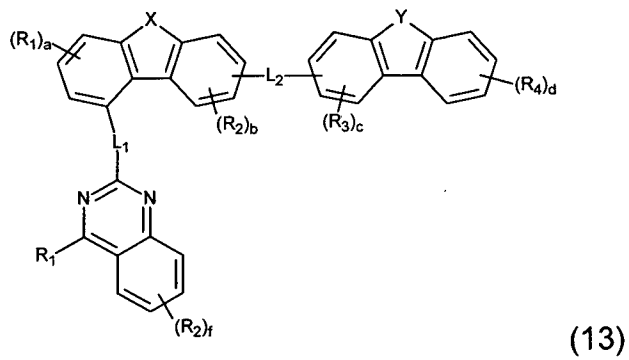
10

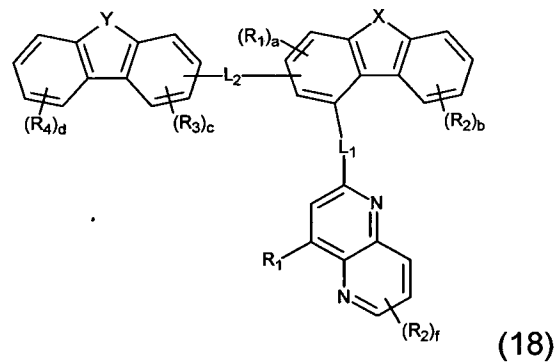
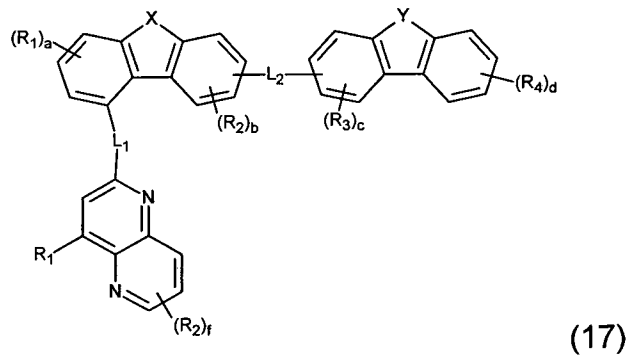
Of these embodiments, the preferred are according to Formulae (11)-(12) with A1-a, Formulae (13) – (14) with A1-c, Formulae (15)-(16) with A1-d and Formulae (17)-(18) with A1-e :



15







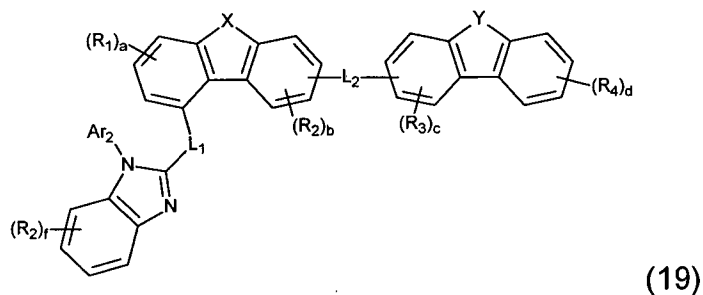
In Formulae (11) – (18), it is preferred that f is 0.

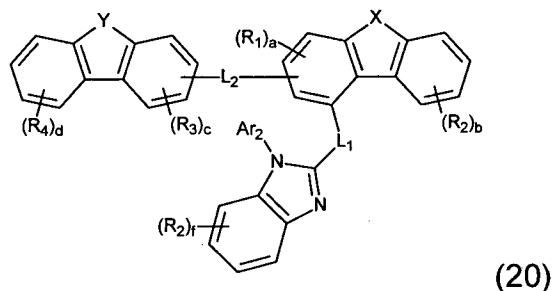
5

In some embodiments, A can be a benzimidazole derivative as illustrated in A₂, A₃ and A₄. The benzimidazole derivative can be attached to the 1-position of the group containing X (either directly or via L₁) by a carbon atom as in A₂ or A₃, or through the 1-nitrogen as in A₄.

10

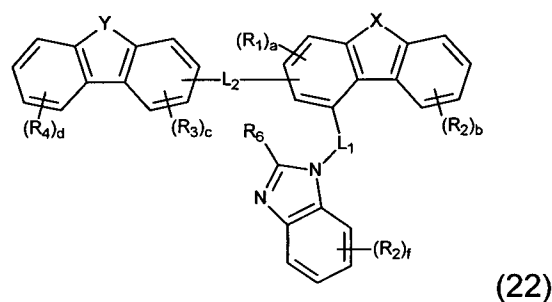
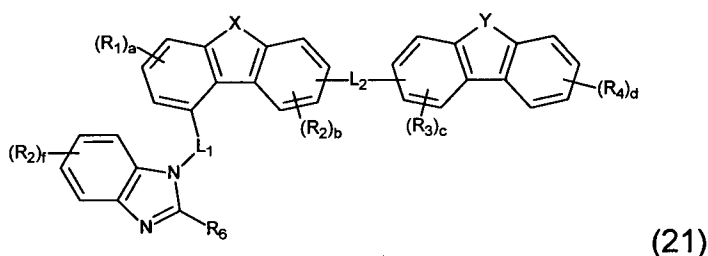
One preferred embodiment is according to A₂ as shown in Formulae (19) and (20):





For Formula (19) and (20), it is preferred that f is 0. In another embodiment related to (19) and (20), it is preferred that Ar₂ is phenyl. In yet another embodiment related to (19) and (20), it is preferred that L₁ is a direct bond or a phenyl group.

Another preferred embodiment is according to A₄ as shown in Formulae (21) and (22):

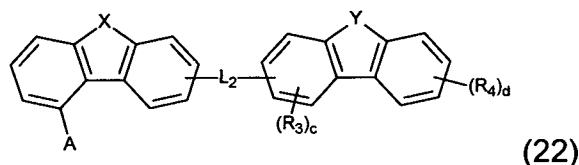


For Formula (21) and (22), it is preferred that f is 0. In another embodiment related to (21) and (22), it is preferred that R₁ is phenyl. In yet another embodiment related to (21) and (22), it is preferred that L₁ is a direct bond or a phenyl group. It is preferred in another embodiment of (21) and (22) that R₆ is an alkyl group of 1 to 12 C atoms or an aromatic or heteroaromatic ring system having 5 to 30 aromatic ring atoms, and most preferably, phenyl.

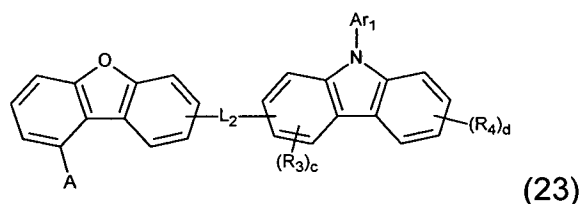
Other preferred embodiments are where the A group is attached to a different ring of the group containing X than the group containing Y as in

Formulae (1), (3), (5), (7), (9), (11), (13), (15), (17), (19) or (21). In any of these embodiments, it is preferred that a and b are both 0, and more preferred that a, b and c are all 0. It is most preferred that a, b and c is 0, d is 0 or 2 and when d is 2, the two R₄ groups are adjacent and form a monocyclic- or polycyclic- aromatic or heteroaromatic annulated ring system

The preferred embodiments mentioned above can be combined with one another in any combination as desired. In a particularly preferred embodiment of the invention, multiple preferences mentioned above can occur simultaneously. For example, the following formulae include some preferred combinations of features.



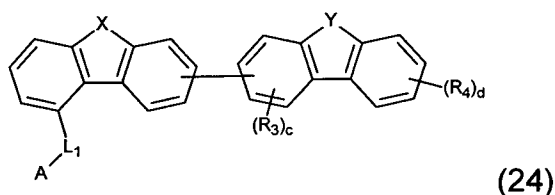
In one embodiment according to Formula (22), it is most preferred that X is oxygen and Y is NAr₁. In another embodiment according to Formula (22), it is most preferred that L₂ is a direct bond. In yet another embodiment according to Formula (22), it is most preferred that c is 0, d is 0 or 2 and when d is 2, the two R₄ groups are adjacent and form a monocyclic- or polycyclic- aromatic or heteroaromatic annulated ring system. In yet another embodiment according to Formula (22), it is most preferred that A is a quinazoline group according to A₁-b.



In one embodiment according to Formula (23), it is preferred that c is 0. In another embodiment according to Formula (23), it is preferred that L₂ is a direct bond. In yet another embodiment according to Formula (23), it is most preferred that c is 0, d is 0 or 2 and when d is 2, the two R₄ groups are adjacent and form a monocyclic- or polycyclic- aromatic or heteroaromatic annulated ring system. In yet another embodiment according to Formula (23), it is preferred that A is a quinazoline group, and more preferably, A is

a quinoline derivative according to A₁-a, and even more preferably where h and f are 0. In yet another embodiment according to Formula (23), it is preferred that A is a quinazoline group according to A₁-b, and more preferably where i and f are 0.

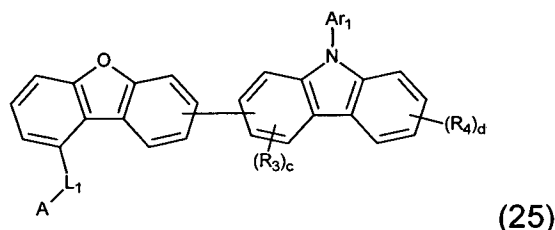
5



10

In one embodiment according to Formula (24), it is preferred that X is oxygen and Y is NAr₁. In yet another embodiment according to Formula (23), L₁ is a *meta*- or *para*- phenyl group. In yet another embodiment according to Formula (23), it is most preferred that c is 0, d is 0 or 2 and when d is 2, the two R₄ groups are adjacent and form a monocyclic- or polycyclic, aromatic or heteroaromatic annulated ring system. In yet another embodiment according to Formula (24), it is most preferred that A is a quinazoline group according to A₁-b where f is 0 or a benzimidazole according to A₄ where L₁ is a direct bond or a *meta*- or *para*- phenyl group and f is 0. For Formula (24), if A is according to A₄, it is most preferred that L₁ is a *meta*- or *para*- phenyl group and Ar₁ is a phenyl group.

15



20

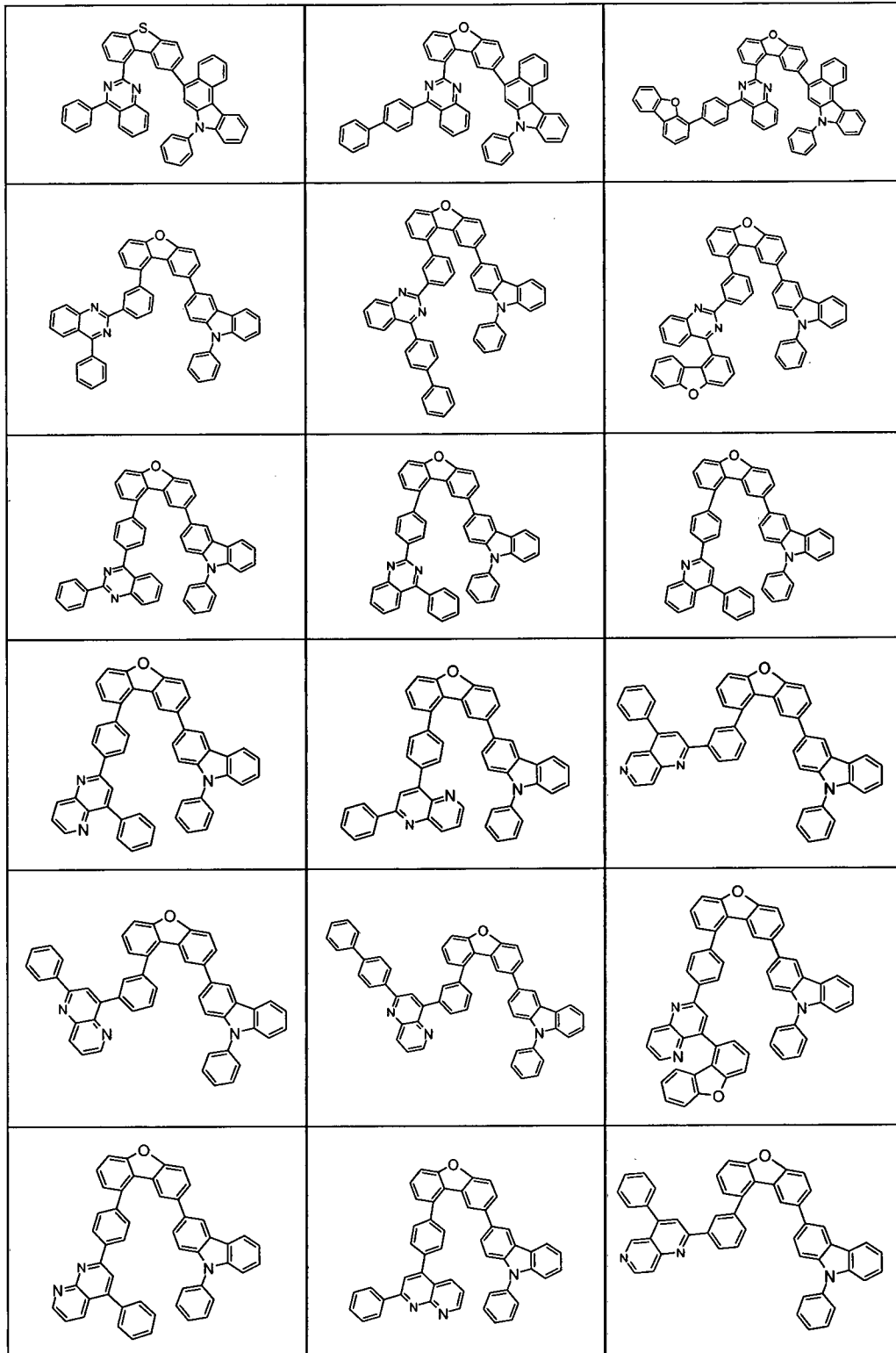
In one embodiment according to Formula (25), it is preferred that A is according to A₂, A₃ or A₄, and more preferred where e and f are 0. In yet another embodiment according to Formula (25), L₁ is a *meta*- or *para*- phenyl group. In yet another embodiment according to Formula (25), it is most preferred that c is 0, d is 0 or 2 and when d is 2, the two R₄ groups are adjacent and form a monocyclic- or polycyclic- aromatic or heteroaromatic annulated ring system. In yet another embodiment according to Formula (25), it is most preferred that A is a benzimidazole according to A₄ where L₁ is a direct bond or a *meta*- or *para*- phenyl group and f is 0. For Formula

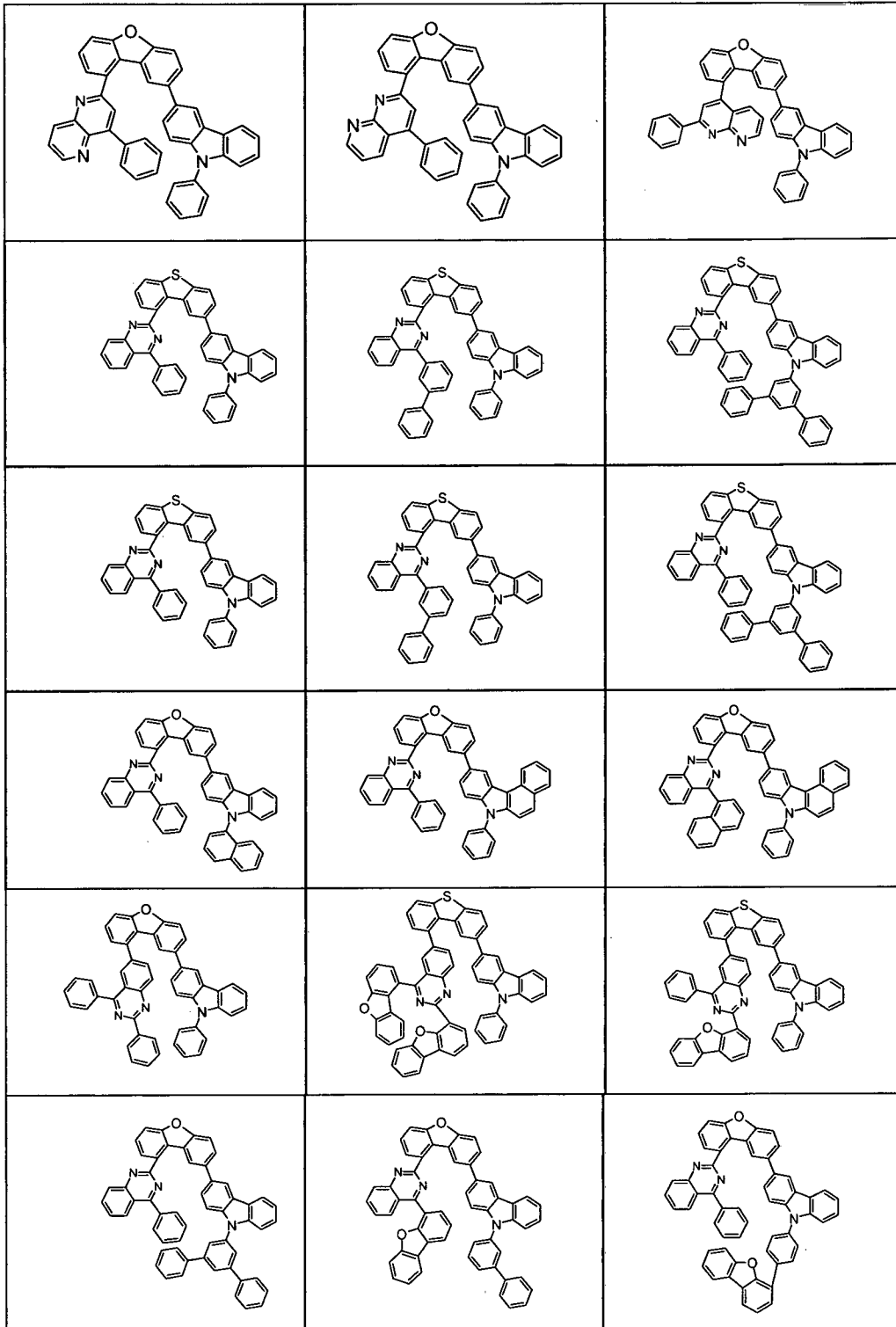
25

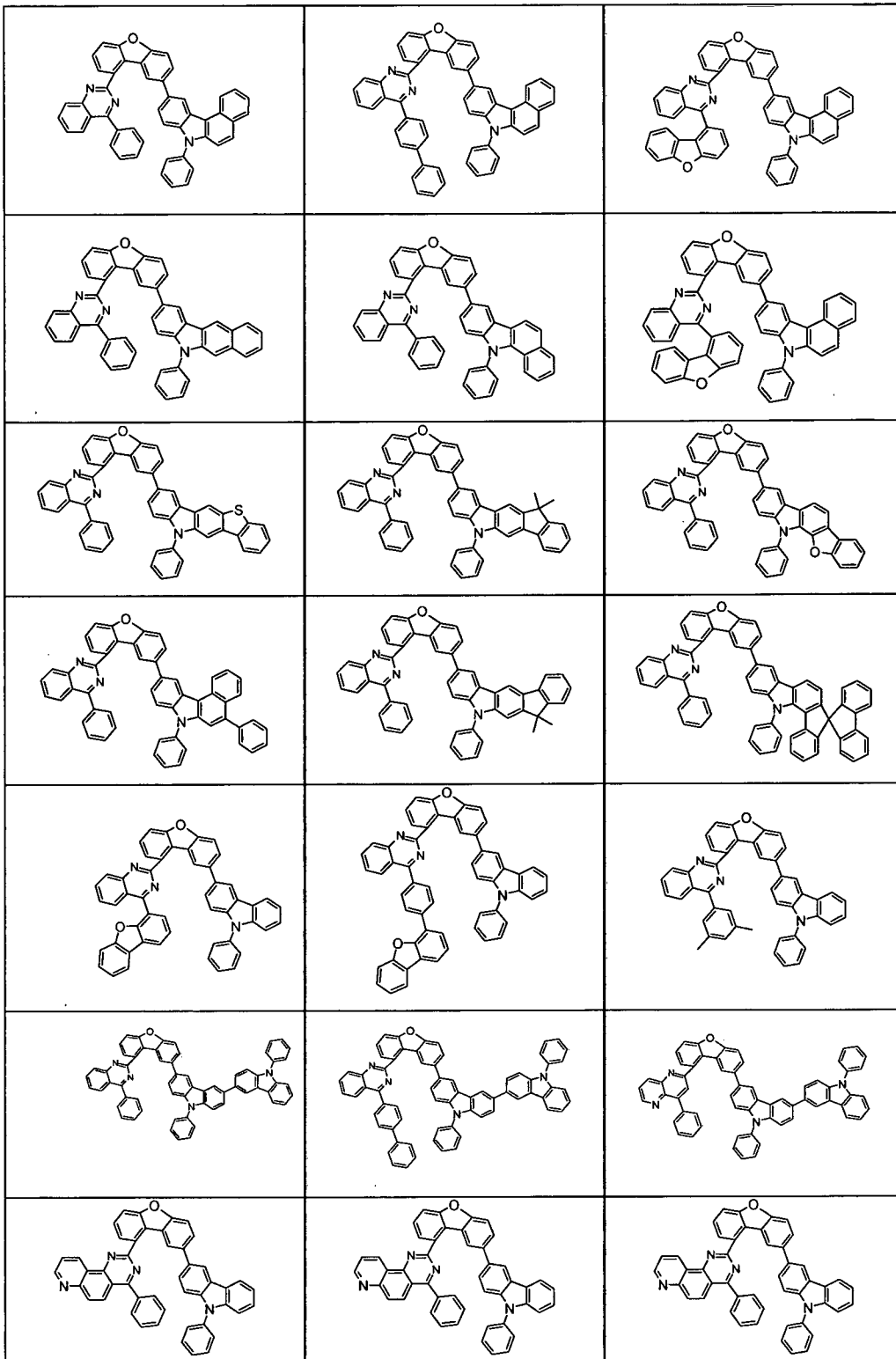
(25), if A is according to A₄, it is most preferred that L₁ is a *meta*- or *para*-phenyl group and Ar₂ is a phenyl group.

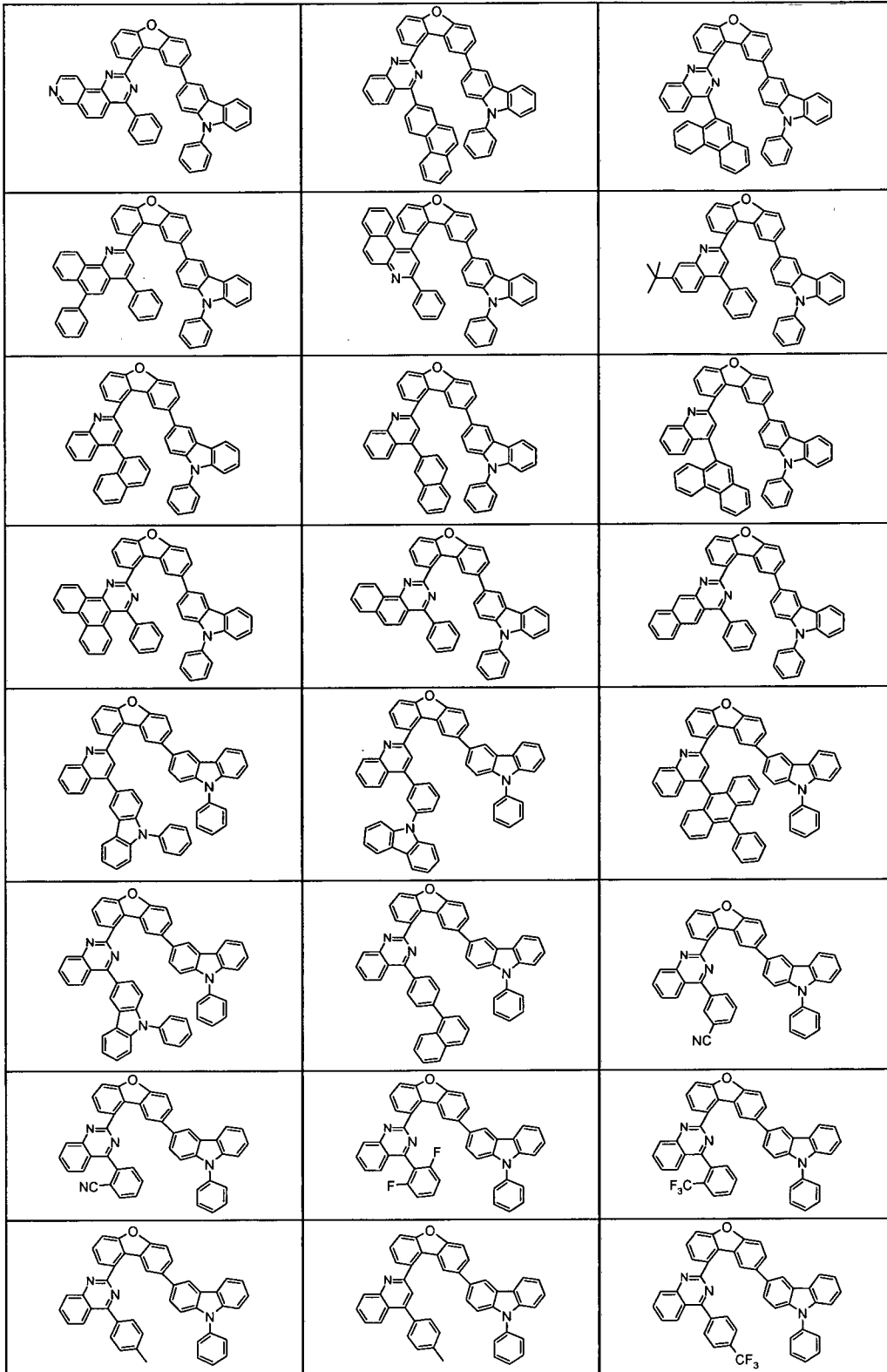
5

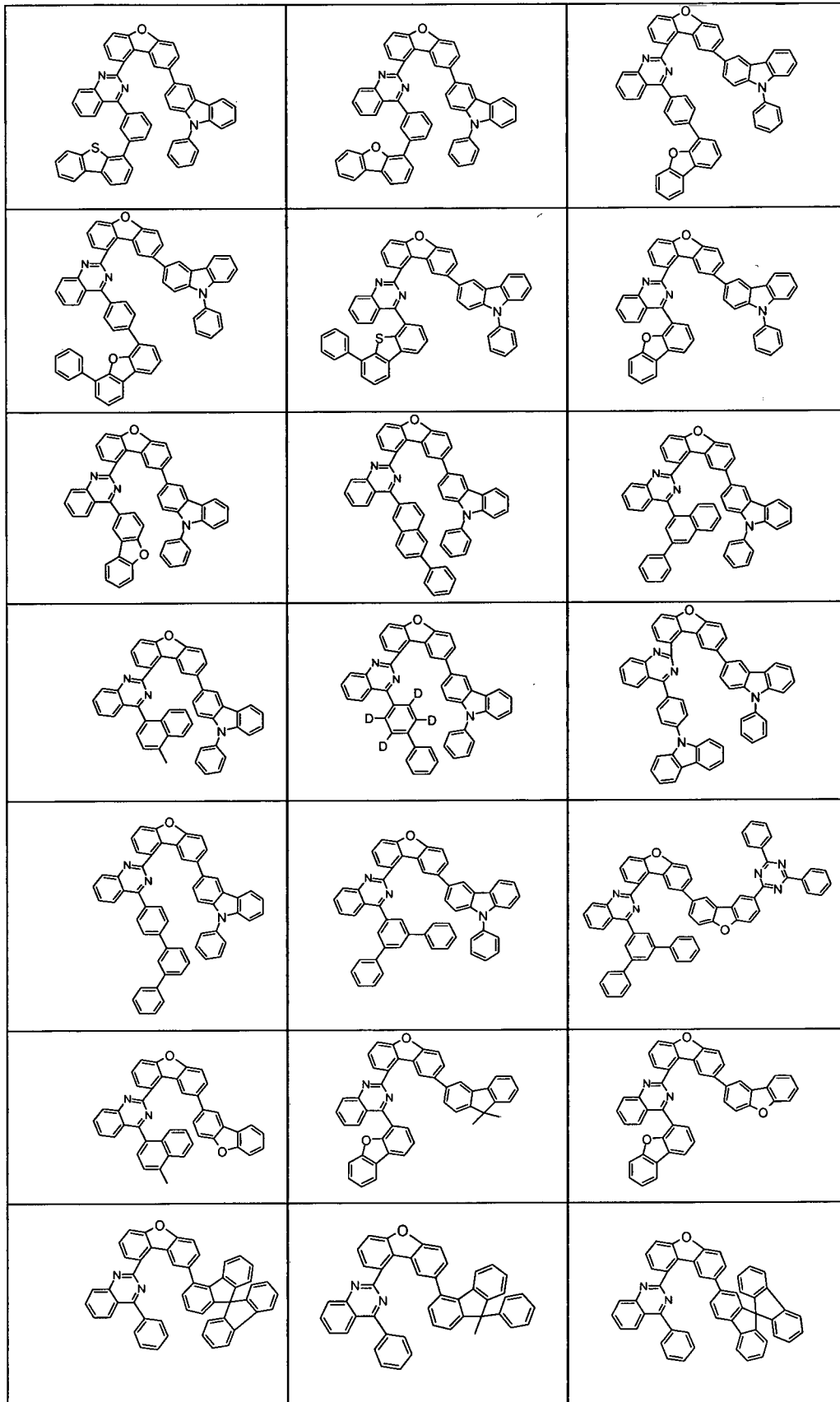
Examples of compounds in accordance with the embodiments indicated above are the compounds shown in the following table.

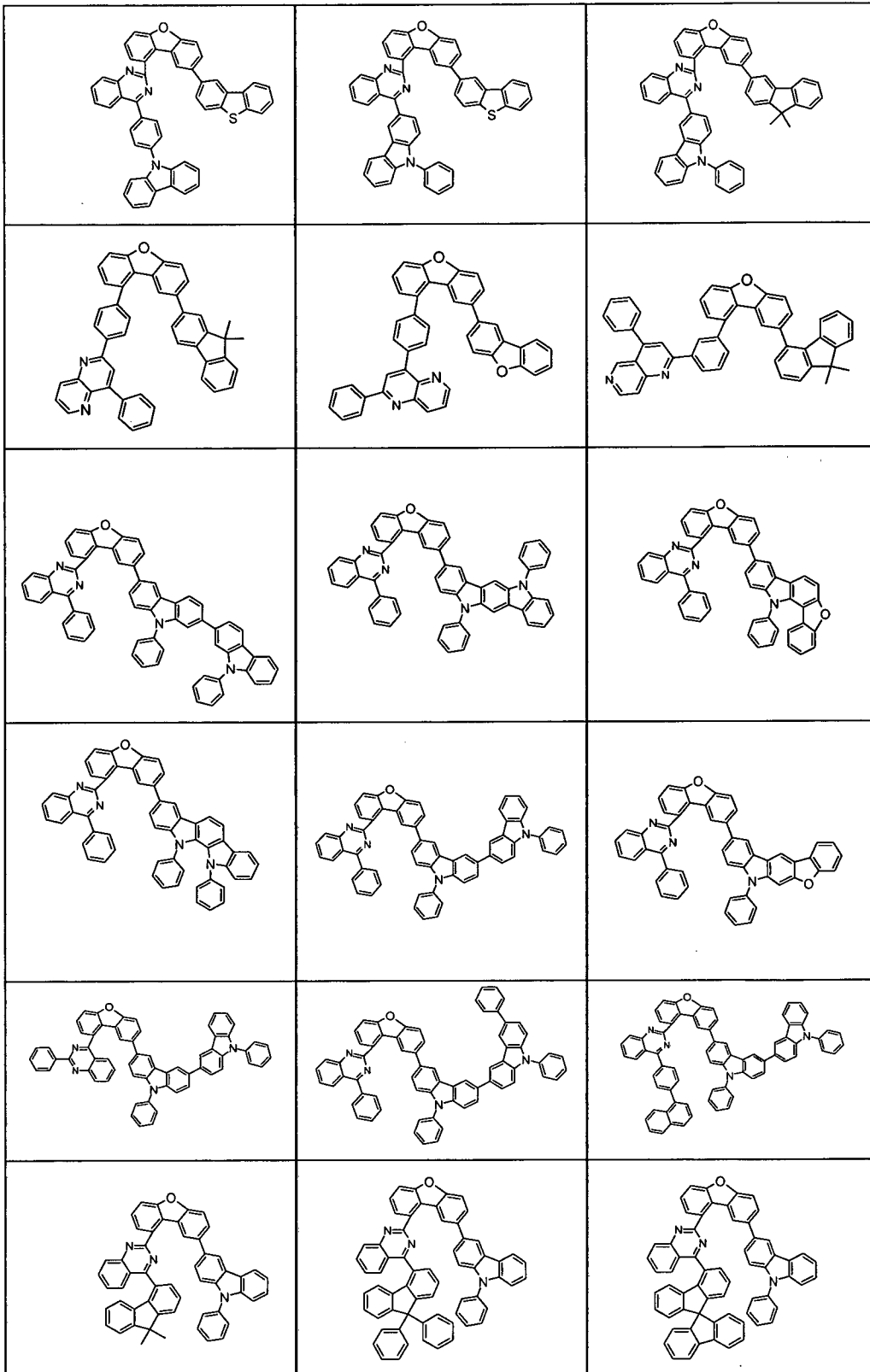


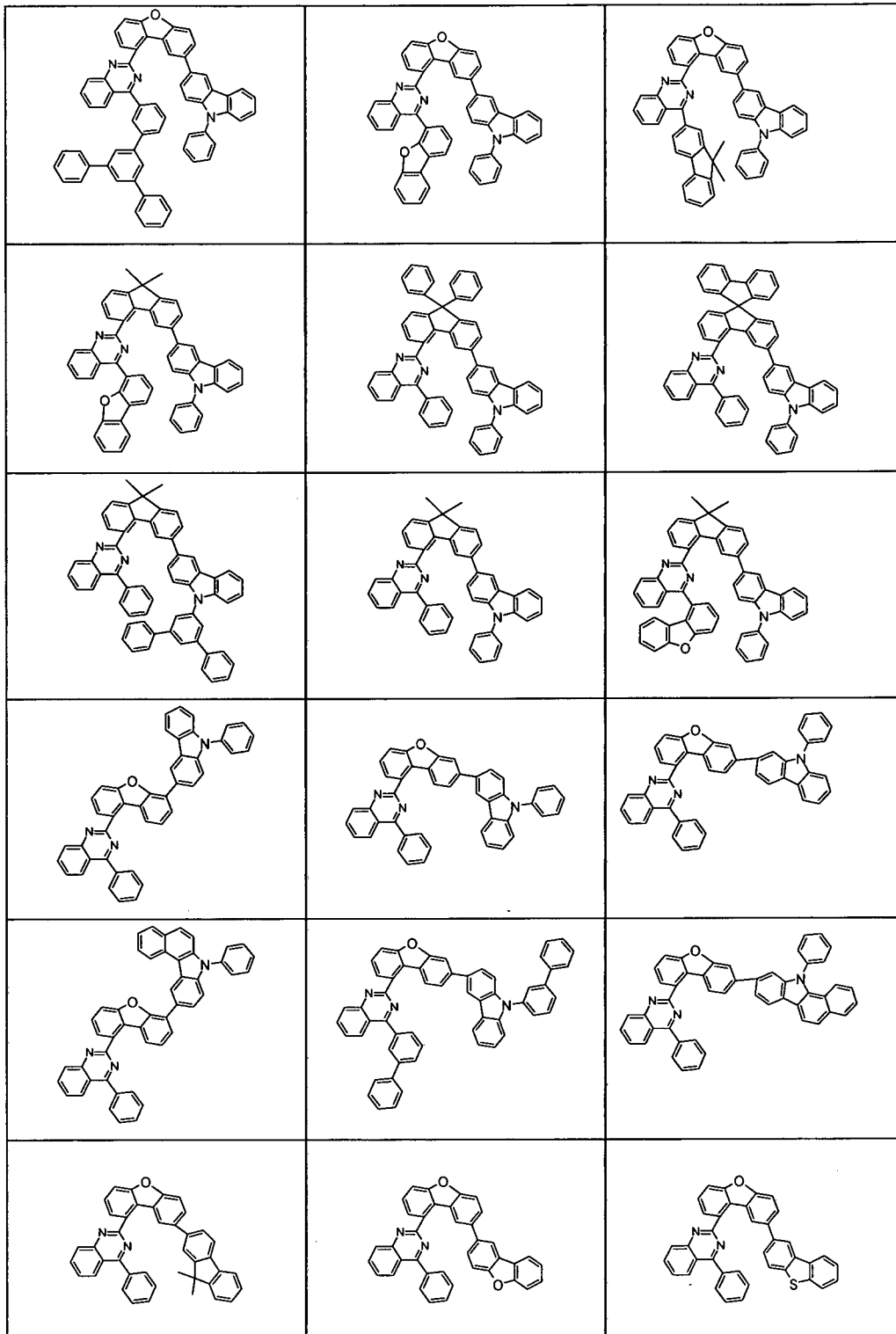


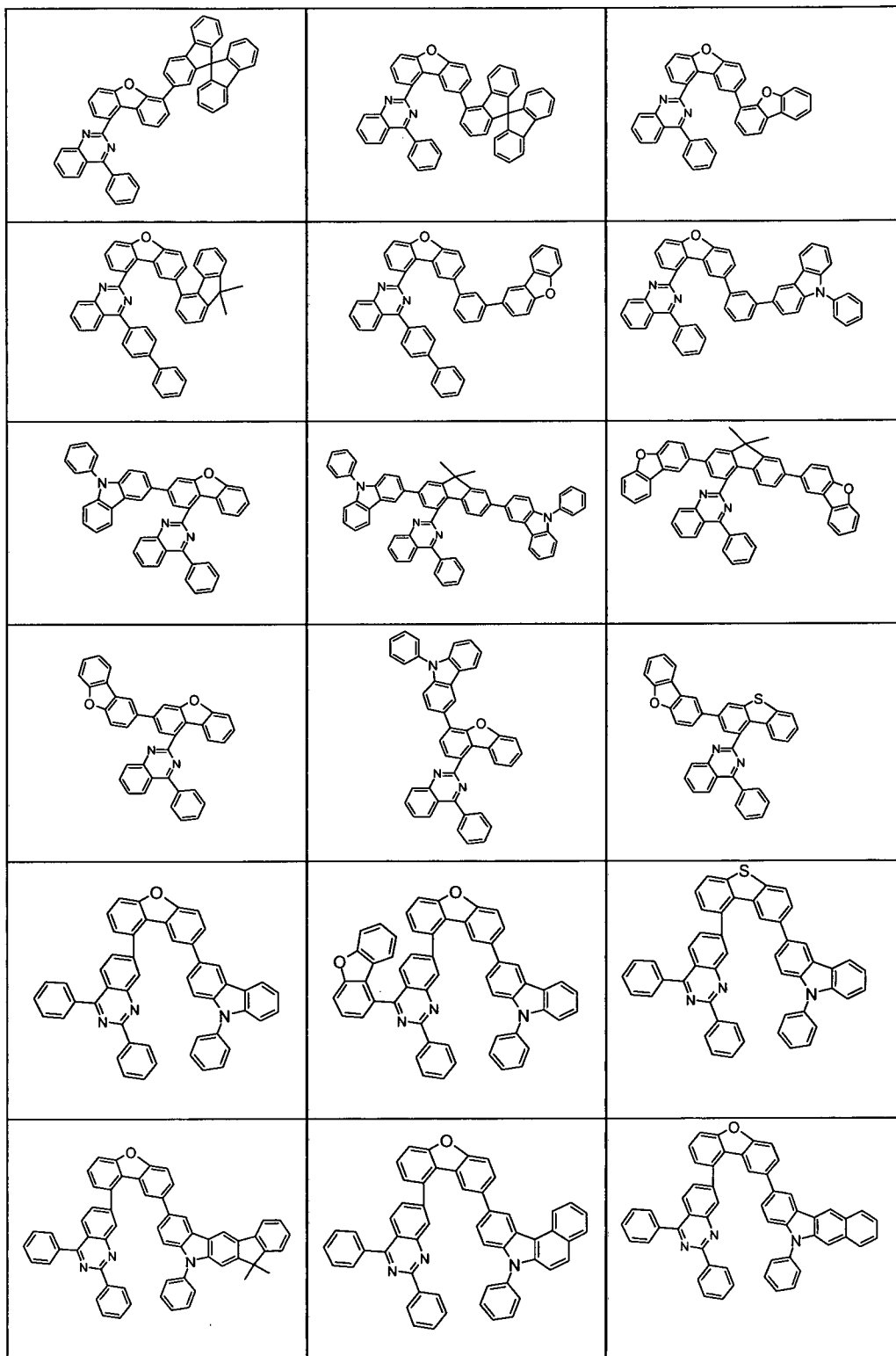


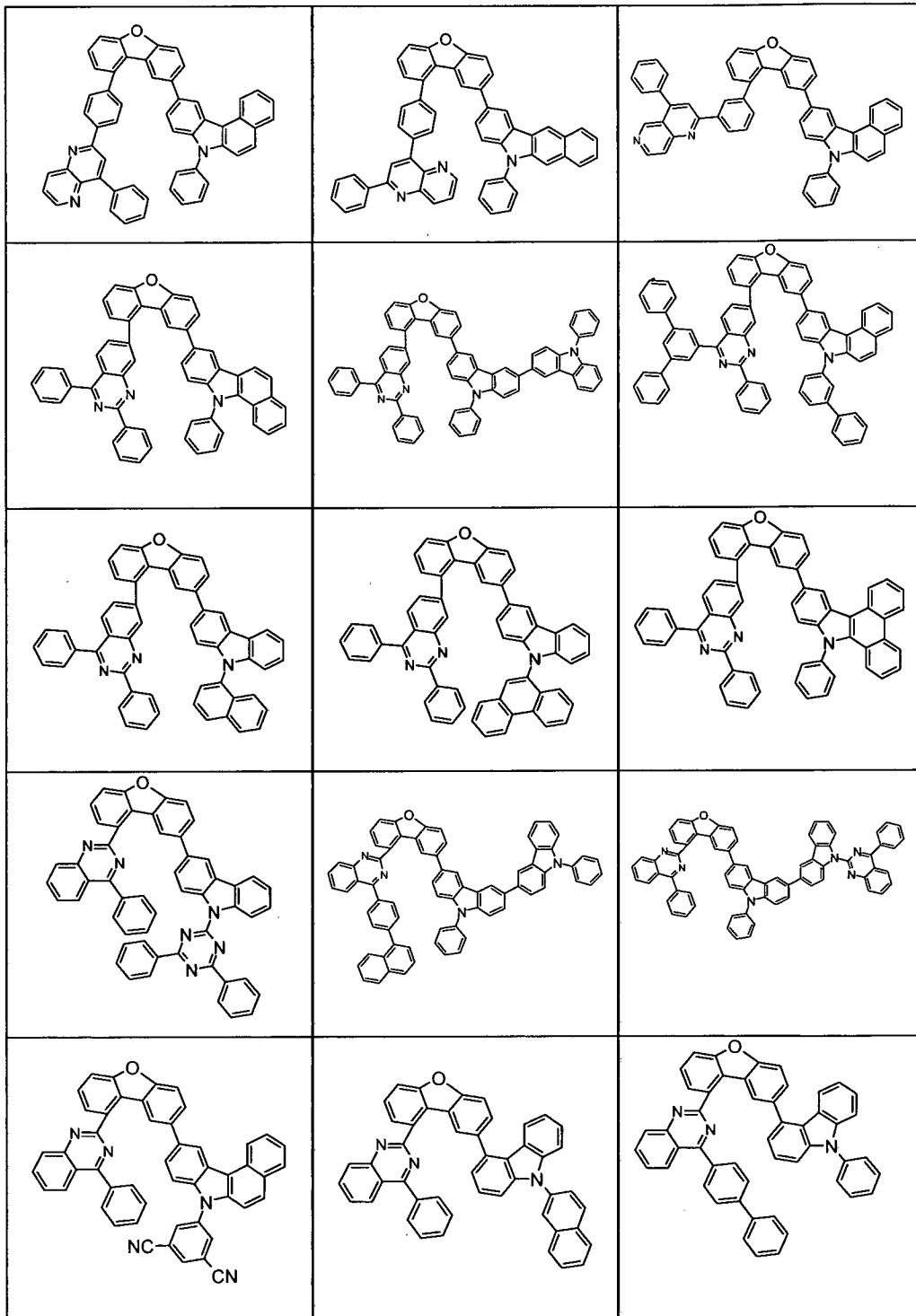


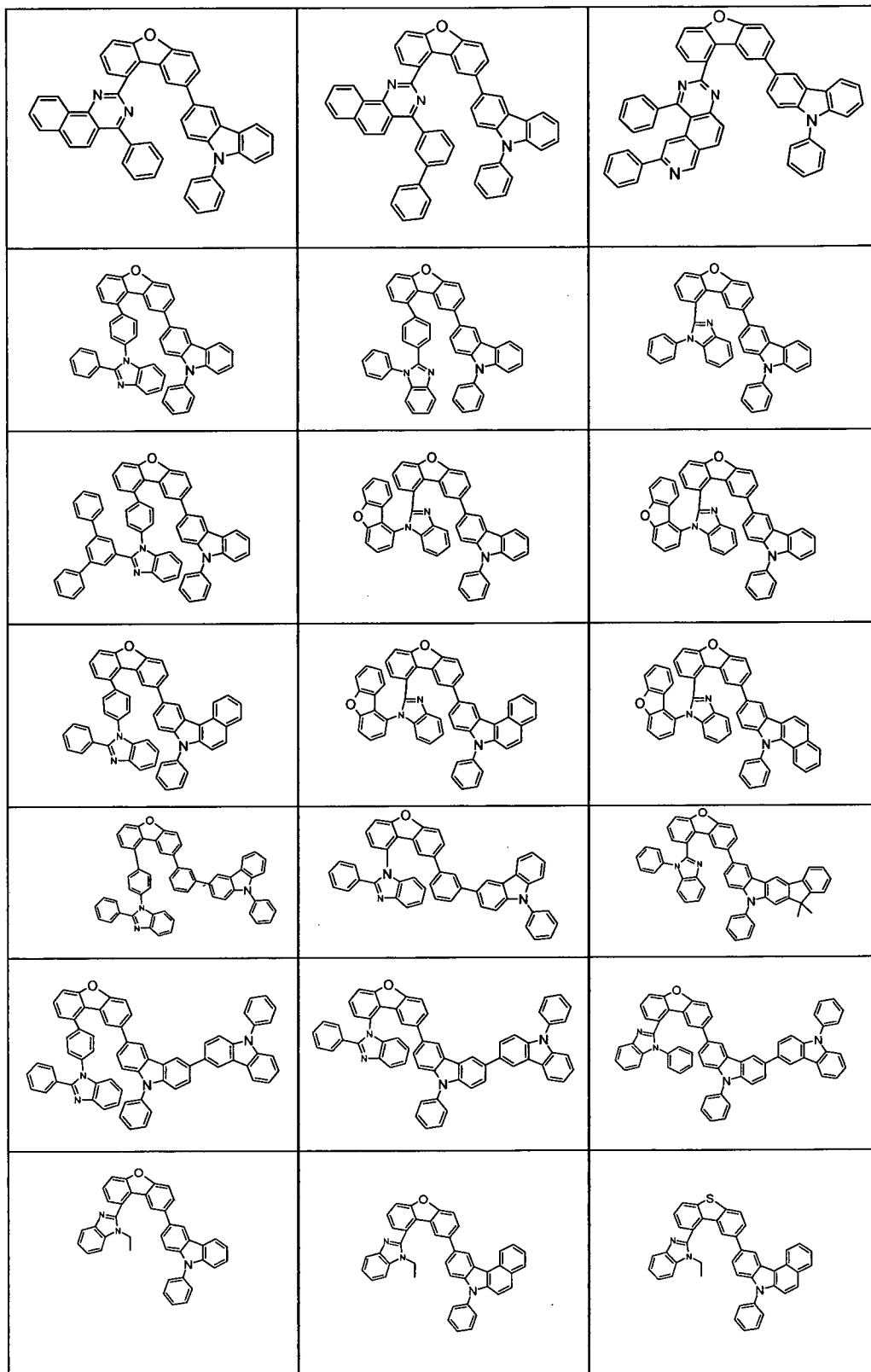


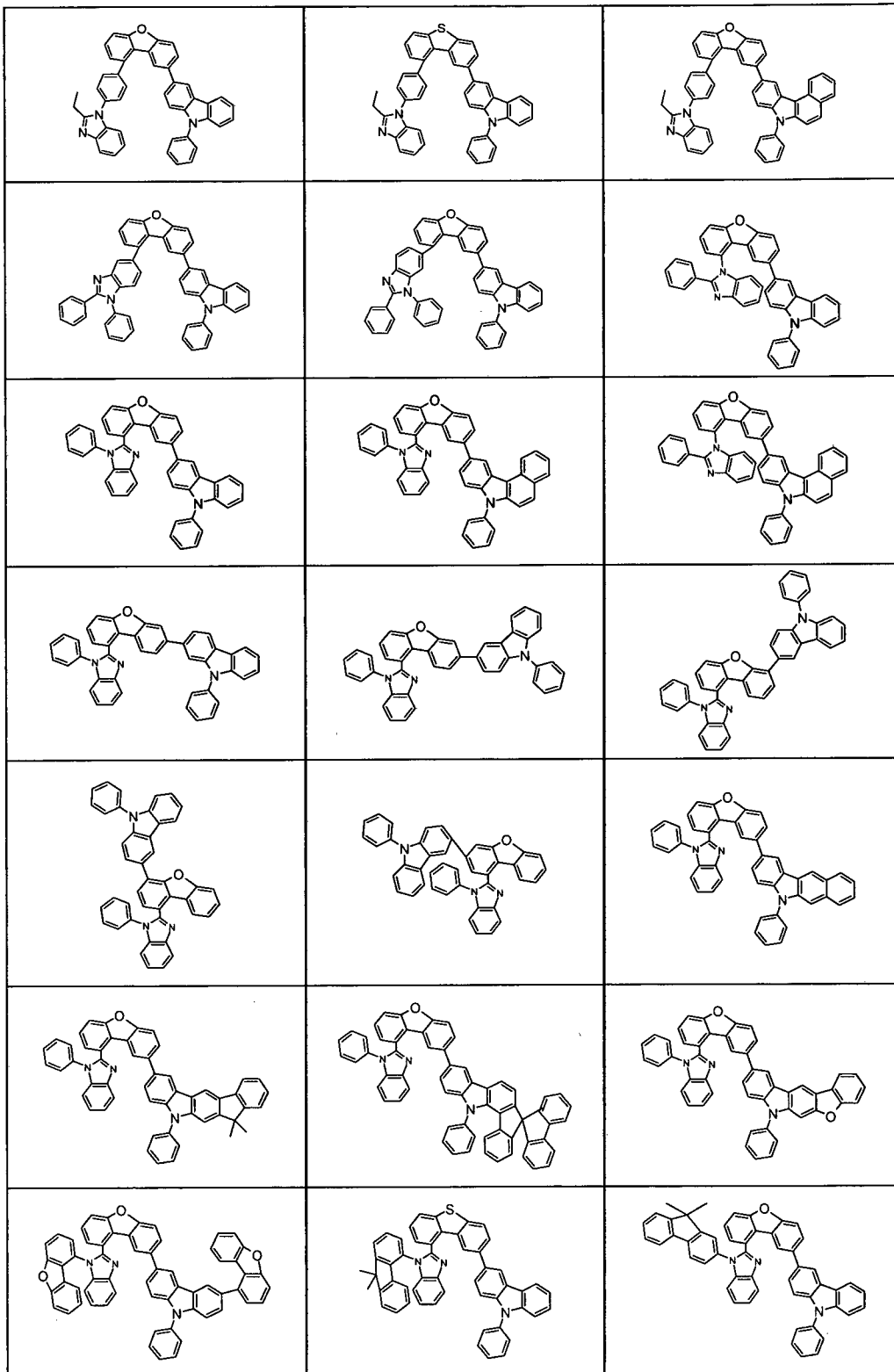


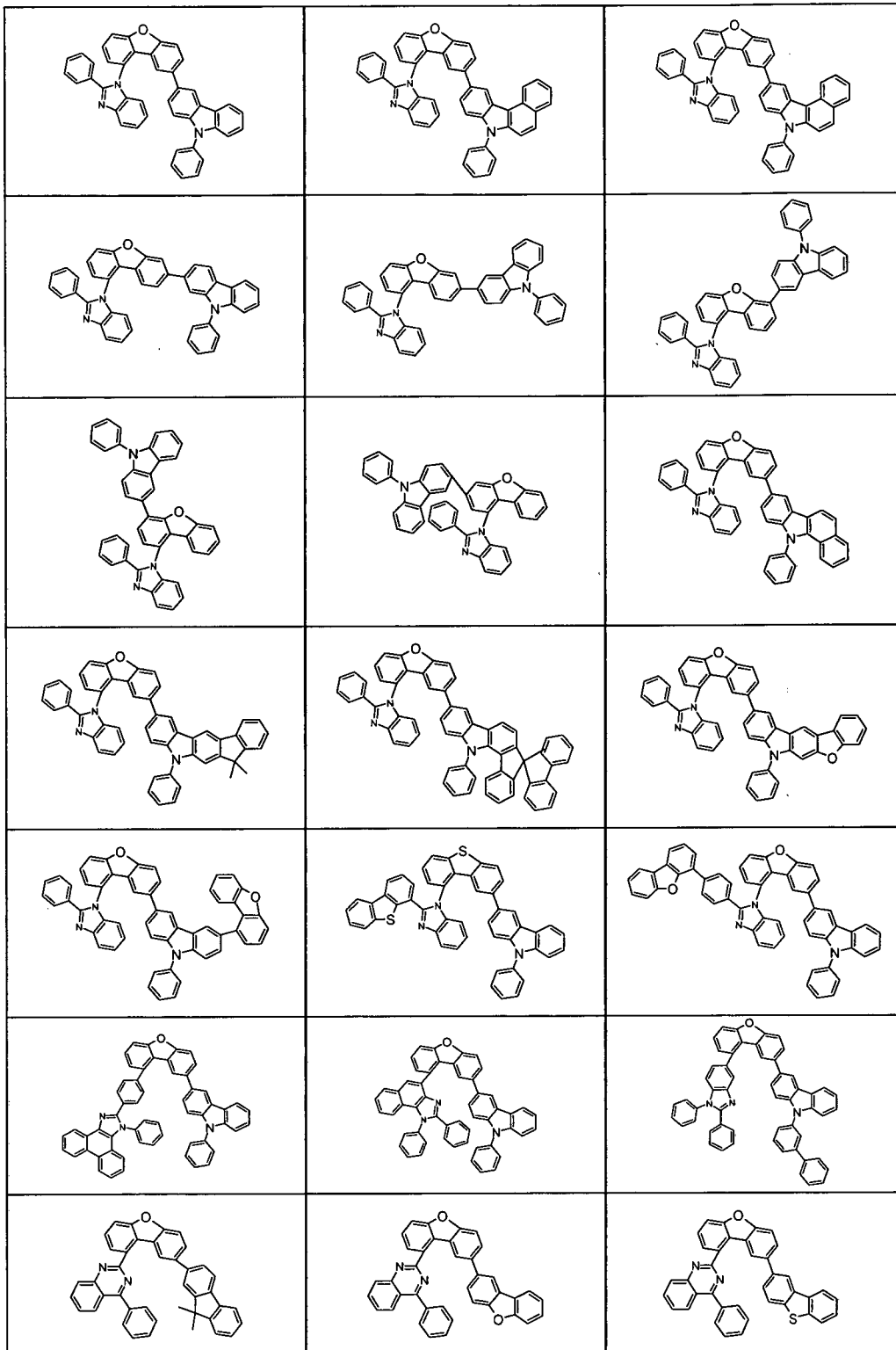


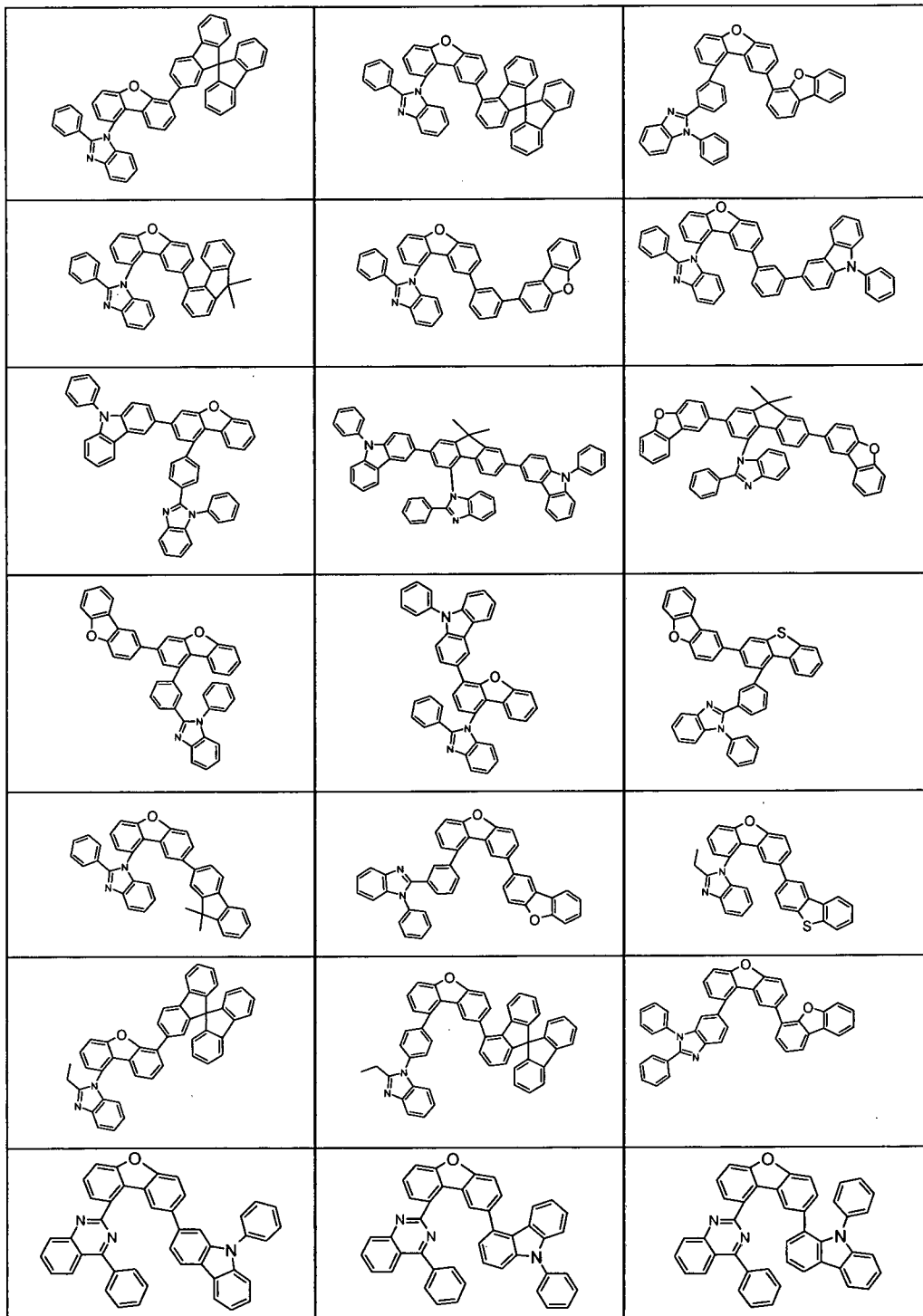


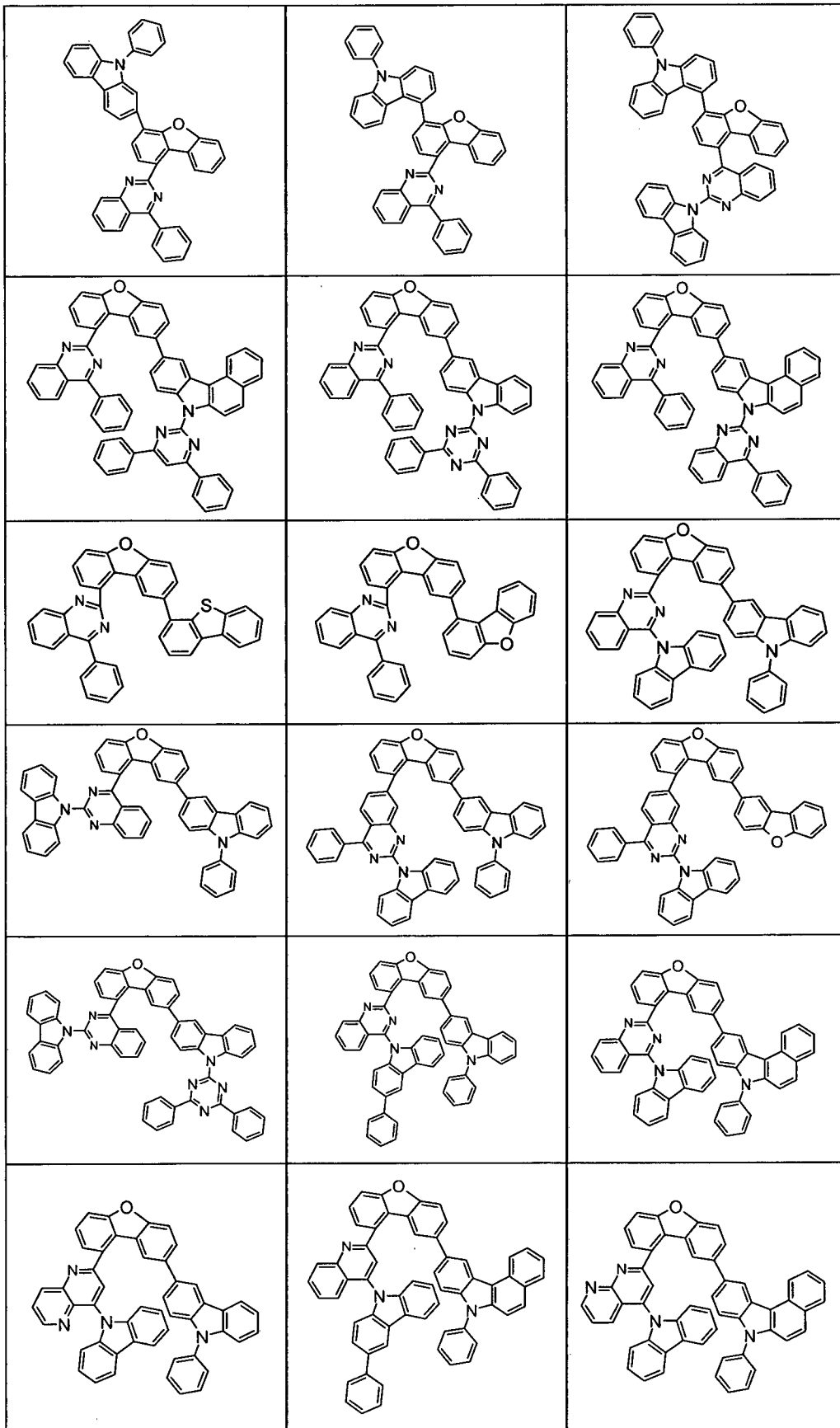












The compounds according to the invention are suitable for use in an electronic device, in particular in an organic electroluminescent device. The present invention therefore furthermore relates to the use of a compound according to the invention in an electronic device, in particular in an organic electroluminescent device. The present invention still furthermore relates to an electronic device comprising at least one compound according to the invention. An electronic device in the sense of the present invention is a device which comprises at least one layer which comprises at least one organic compound. The component may also comprise inorganic materials or also layers which are built up entirely from inorganic materials.

The electronic device is preferably selected from the group consisting of organic electroluminescent devices (OLEDs), organic integrated circuits (O-ICs), organic field-effect transistors (O-FETs), organic thin-film transistors (O-TFTs), organic light-emitting transistors (O-LETs), organic solar cells (O-SCs), dye-sensitised organic solar cells (DSSCs), organic optical detectors, organic photoreceptors, organic field-quench devices (O-FQDs), light-emitting electrochemical cells (LECs), organic laser diodes (O-lasers) and "organic plasmon emitting devices", but preferably organic electroluminescent devices (OLEDs), particularly preferably phosphorescent OLEDs.

The organic electroluminescent device comprises cathode, anode and at least one emitting layer. Apart from these layers, it may also comprise further layers, for example in each case one or more hole-injection layers, hole-transport layers, hole-blocking layers, electron-transport layers, electron-injection layers, exciton-blocking layers, electron-blocking layers and/or charge-generation layers. Interlayers, which have, for example, an exciton-blocking function, may likewise be introduced between two emitting layers. However, it should be pointed out that each of these layers does not necessarily have to be present. The organic electroluminescent device here may comprise one emitting layer, or it may comprise a plurality of emitting layers. If a plurality of emission layers are present, these preferably have in total a plurality of emission maxima between 380 nm and 750 nm, resulting overall in white emission, i.e. various emitting compounds which are able to fluoresce or phosphoresce are used in the emitting layers. Particular

5 preference is given to systems having three emitting layers, where the three layers exhibit blue, green and orange or red emission (for the basic structure see, for example, WO 2005/011013). The organic electroluminescent device according to the invention may also be a tandem OLED, in particular also for white-emitting OLEDs.

10 The compound according to the invention in accordance with the embodiments indicated above can be employed in various layers, depending on the precise structure. Preference is given to an organic electroluminescent device comprising a compound of the formulae (1) or (2) or the preferred
15 embodiments indicated above as matrix material for phosphorescent or fluorescent emitters, in particular for phosphorescent emitters, and/or in an electron-blocking or exciton-blocking layer and/or in a hole-transport layer and/or in a hole-blocking layer and/or in a hole-blocking or electron-transport layer, depending on the precise substitution.

20 In a preferred embodiment of the invention, the compound according to the invention is employed as matrix material for a phosphorescent compound in an emitting layer. The organic electroluminescent device here may comprise one emitting layer, or it may comprise a plurality of emitting layers, where at least one emitting layer comprises at least one compound according to the invention as matrix material.

25 If the compound according to the invention is employed as matrix material for a phosphorescent compound in an emitting layer, it is preferably employed in combination with one or more phosphorescent materials (triplet emitters). Phosphorescence in the sense of this invention is taken to mean the luminescence from an excited state having relatively high spin multiplicity, i.e. a spin state > 1 , in particular from an excited triplet state. In the
30 sense of this application, all luminescent complexes containing transition metals or lanthanides, in particular all iridium, platinum and copper complexes, are to be regarded as phosphorescent compounds.

35 The mixture of the compound according to the invention and the emitting compound comprises between 99 and 1% by vol., preferably between 98 and 10% by vol., particularly preferably between 97 and 60% by vol., in

particular between 95 and 80% by vol., of the compound according to the invention, based on the entire mixture comprising emitter and matrix material. Correspondingly, the mixture comprises between 1 and 99% by vol., preferably between 2 and 90% by vol., particularly preferably between 3 and 40% by vol., in particular between 5 and 20% by vol., of the emitter, based on the entire mixture comprising emitter and matrix material.

A further preferred embodiment of the present invention is the use of the compound according to the invention as matrix material for a phosphorescent emitter in combination with a further matrix material. Particularly suitable matrix materials which can be employed in combination with the compounds according to the invention are aromatic ketones, aromatic phosphine oxides or aromatic sulfoxides or sulfones, for example in accordance with WO 2004/013080, WO 2004/093207, WO 2006/005627 or WO 2010/006680, triaryl amines, carbazole derivatives, for example CBP (N,N-bis-carbazolylbiphenyl) or the carbazole derivatives disclosed in WO 2005/039246, US 2005/0069729, JP 2004/288381, EP 1205527, WO 2008/086851 or WO 2013/041176, indolocarbazole derivatives, for example in accordance with WO 2007/063754 or WO 2008/056746, indenocarbazole derivatives, for example in accordance with WO 2010/136109, WO 2011/000455, WO 2013/041176 or WO 2013/056776, azacarbazole derivatives, for example in accordance with EP 1617710, EP 1617711, EP 1731584, JP 2005/347160, bipolar matrix materials, for example in accordance with WO 2007/137725, silanes, for example in accordance with WO 2005/111172, azaboroles or boronic esters, for example in accordance with WO 2006/117052, triazine derivatives, for example in accordance with WO 2007/063754, WO 2008/056746, WO 2010/015306, WO 2011/057706, WO 2011/060859 or WO 2011/060877, zinc complexes, for example in accordance with EP 652273 or WO 2009/062578, diazasilole or tetraazasilole derivatives, for example in accordance with WO 2010/054729, diazaphosphole derivatives, for example in accordance with WO 2010/054730, bridged carbazole derivatives, for example in accordance with WO 2011/042107, WO 2011/060867, WO 2011/088877 and WO 2012/143080, or triphenylene derivatives, for example in accordance with WO 2012/048781. A further phosphorescent emitter which emits at shorter wavelength than the actual emitter may likewise be present in the mixture as

co-host, or a compound which does not participate in the charge transport to a significant extent, if at all, as described, for example, in WO 2010/108579.

5 Suitable phosphorescent compounds (= triplet emitters) are, in particular, compounds which emit light, preferably in the visible region, on suitable excitation and in addition contain at least one atom having an atomic number greater than 20, preferably greater than 38 and less than 84, particularly preferably greater than 56 and less than 80, in particular a metal having this
10 atomic number. The phosphorescence emitters used are preferably compounds which contain copper, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold or europium, in particular compounds which contain iridium or platinum.

15 Examples of the emitters described above are revealed by the applications WO 00/70655, WO 2001/41512, WO 2002/02714, WO 2002/15645, EP 1191613, EP 1191612, EP 1191614, WO 2005/033244, WO 2005/019373, US 2005/0258742, WO 2010/086089, WO 2011/157339, WO 2012/007086, WO 2012/163471, WO 2013/000531 and WO 2013/020631. Also suitable are, for example, the metal complexes disclosed in the unpublished
20 applications EP 12005187.5 and EP 12005715.3. In general, all phosphorescent complexes as are used in accordance with the prior art for phosphorescent OLEDs and as are known to the person skilled in the art in the area of organic electroluminescence are suitable, and the person skilled in the art will be able to use further phosphorescent complexes without
25 inventive step.

The compounds according to the invention are also suitable, in particular, as matrix materials for phosphorescent emitters in organic electroluminescent devices, as described, for example, in US 2011/0248247 and
30 US 2012/0223633. In these multicoloured display components, an additional blue emission layer is applied by vapour deposition over the entire area to all pixels, also those having a colour other than blue. It has been found here, surprisingly, that the compounds according to the invention, when employed as matrix materials for the red and/or green pixels, continue to result in very
35 good lifetime and emission together with the vapour-deposited blue emission layer.

5 In a further embodiment of the invention, the organic electroluminescent device according to the invention does not comprise a separate hole-injection layer and/or hole-transport layer and/or hole-blocking layer and/or
10 electron-transport layer, i.e. the emitting layer is directly adjacent to the hole-injection layer or the anode, and/or the emitting layer is directly adjacent to the electron-transport layer or the electron-injection layer or the cathode, as described, for example, in WO 2005/053051. It is furthermore possible to use a metal complex which is the same as or similar to the metal complex in
15 the emitting layer as hole-transport or hole-injection material directly adjacent to the emitting layer, as described, for example, in WO 2009/030981.

20 In a further embodiment of the invention, the compound according to the invention is employed in a hole-transport layer or in an electron-blocking layer or exciton-blocking layer.

25 In still a further preferred embodiment of the invention, the compound according to the invention is employed as electron-transport material in an electron-transport or electron-injection layer. The emitting layer here may be fluorescent or phosphorescent. If the compound is employed as electron-transport material, it may be preferred for it to be doped, for example with alkali-metal complexes, such as, for example, LiQ (lithium hydroxy-quinolate) or with an alkali metal, such as Li.

30 In still a further preferred embodiment of the invention, the compound according to the invention is employed in a hole-blocking layer. A hole-blocking layer is taken to mean a layer which is directly adjacent to an emitting layer on the cathode side.

35 In the further layers of the organic electroluminescent device according to the invention, all materials can be used as are usually employed in accordance with the prior art. The person skilled in the art will therefore be able to employ all materials which are known for organic electroluminescent devices in combination with the compounds of the formula (1) according to the

invention or the preferred embodiments indicated above without inventive step.

5 Preference is furthermore given to an organic electroluminescent device, characterised in that one or more layers are coated by means of a sublimation process, in which the materials are applied by vapour deposition in vacuum sublimation units at an initial pressure of less than 10^{-5} mbar, preferably less than 10^{-6} mbar. However, it is also possible for the initial pressure to be even lower, for example less than 10^{-7} mbar.

10 Preference is likewise given to an organic electroluminescent device, characterised in that one or more layers are coated by means of the OVPD (organic vapour phase deposition) process or with the aid of carrier-gas sublimation, in which the materials are applied at a pressure between
15 10^{-5} mbar and 1 bar. A special case of this process is the OVJP (organic vapour jet printing) process, in which the materials are applied directly through a nozzle and are thus structured (for example M. S. Arnold *et al.*, *Appl. Phys. Lett.* **2008**, 92, 053301).

20 Preference is furthermore given to an organic electroluminescent device, characterised in that one or more layers are produced from solution, such as, for example, by spin coating, or by means of any desired printing process, such as, for example, screen printing, flexographic printing, offset
25 printing, LITI (light induced thermal imaging, thermal transfer printing), ink-jet printing or nozzle printing. Soluble compounds, which are obtained, for example, by suitable substitution, are necessary for this purpose. Also possible are hybrid processes, in which, for example, one or more layers are applied from solution and one or more further layers are applied by vapour
30 deposition.

35 For the processing of the compounds according to the invention from the liquid phase, for example by spin coating or by printing processes, formulations of the compounds according to the invention are necessary. These formulations can be, for example, solutions, dispersions or emulsions. It may be preferred to use mixtures of two or more solvents for this purpose. Suitable and preferred solvents are, for example, toluene, anisole, o-, m- or

p-xylene, methyl benzoate, mesitylene, tetralin, veratrol, THF, methyl-THF, THP, chlorobenzene, dioxane, phenoxytoluene, in particular 3-phenoxytoluene, hexamethylindane, (-)-fenchone, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, 1-methylnaphthalene, 2-methylbenzothiazole, 2-phenoxyethanol, 2-pyrrolidinone, 3-methylanisole, 4-methylanisole, 3,4-dimethylanisole, 3,5-dimethylanisole, acetophenone, α -terpineol, benzothiazole, butyl benzoate, cumene, cyclohexanol, cyclohexanone, cyclohexylbenzene, decalin, dodecylbenzene, ethyl benzoate, indane, methyl benzoate, NMP, p-cymene, phenetole, 1,4-diisopropylbenzene, dibenzyl ether, diethylene glycol butyl methyl ether, triethylene glycol butyl methyl ether, diethylene glycol dibutyl ether, triethylene glycol dimethyl ether, diethylene glycol monobutyl ether, tripropylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, 2-isopropyl-naphthalene, pentylbenzene, hexylbenzene, heptylbenzene, octylbenzene, 1,1-bis(3,4-dimethylphenyl)ethane or mixtures of these solvents.

The present invention furthermore relates to a formulation comprising a compound according to the invention and at least one further compound. The further compound may be, for example, a solvent, in particular one of the above-mentioned solvents or a mixture of these solvents. However, the further compound may also be at least one further organic or inorganic compound which is likewise employed in the electronic device, for example an emitting compound and/or a further matrix material. Suitable emitting compounds and further matrix materials are indicated above in connection with the organic electroluminescent device. This further compound may also be polymeric.

dibenzofuran, dibenzothiophene or a fluorene group substituted in the 1-position, either directly or through a linking group, to a carbon atom of a heteroaromatic group with one or two nitrogen atoms in a bicyclic 6/6 core, or to a carbon or nitrogen atom of a heteroaromatic group with two nitrogen atoms in a bicyclic 5/6 core and are further substituted with a group selected from dibenzofuran, dibenzothiophene, fluorene or carbazole.

All of the above processes are generally known to the person skilled in the art and can be applied without inventive step to organic electroluminescent devices comprising the compounds according to the invention.

5 The compounds according to the invention and the organic electroluminescent devices according to the invention are distinguished by one or more of the following surprising advantages over the prior art:

10 1. The compounds according to the invention, employed as matrix material for fluorescent or phosphorescent emitters, result in long lifetimes. This applies, in particular, if the compounds are employed as matrix material for a phosphorescent emitter.

15 2. The compounds according to the invention result in very low operating voltages. This applies, in particular, if the compounds are employed as matrix material for a phosphorescent emitter.

20 These above-mentioned advantages are not accompanied by an impairment in the other electronic properties.

25 The invention is explained in greater detail by the following examples without wishing to restrict it thereby. The person skilled in the art will be able to use the descriptions to carry out the invention throughout the range disclosed and prepare further compounds according to the invention without inventive step and use them in electronic devices or apply the process according to the invention.

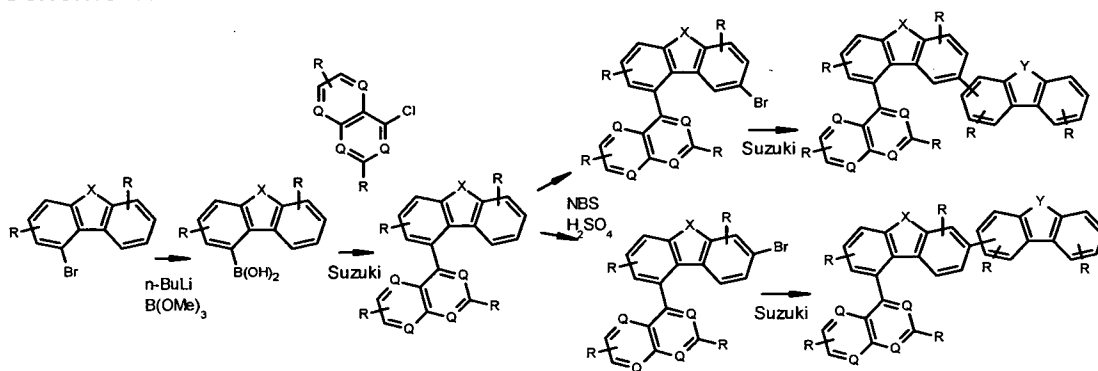
Examples

30 The following syntheses are carried out, unless indicated otherwise, under a protective-gas atmosphere in dried solvents. The solvents and reagents can be purchased from ALDRICH or ABCR. The numbers indicated in the case of the starting materials which are not commercially available are the corresponding CAS numbers.

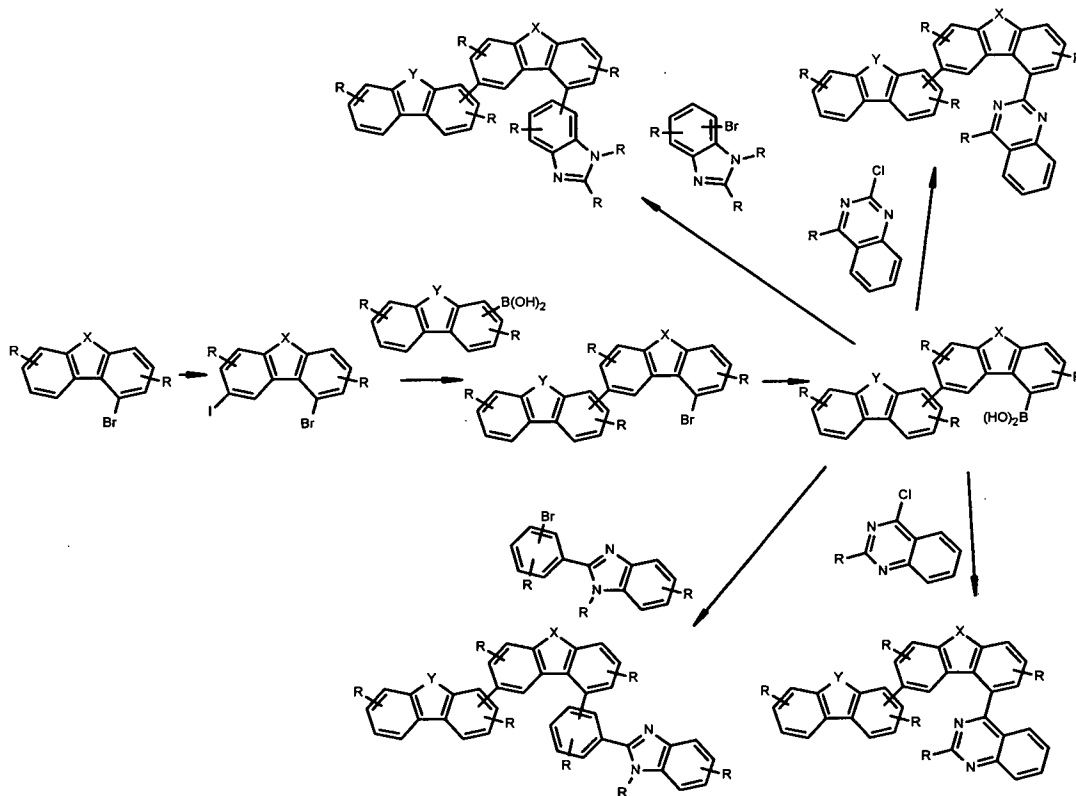
35 Generally, there are two general processes for forming compounds of formulae (1) or (2). The first (illustrated in Scheme 2) is where an

intermediate with a group containing X (i.e. dibenzofuran, dibenzothiophene or a fluorene group) and the group containing Y (i.e. dibenzofuran, dibenzothiophene, fluorene or carbazole) is obtained by a C-C coupling, such as Suzuki, Negishi, Yamamoto, Grignard-Cross, Stille, Hartwig-Buchwald or Ullmann, between the two groups. The heterocyclic A (or L₁-A) group is added to this intermediate by subsequent functionization (i.e. halogenation, followed by formation of a boron containing group) and another C-C coupling reaction with A (or L₁-A) compound. In the case where A is a benzotriazole attached via nitrogen, the coupling reaction is by any known C-N coupling reactions including both a nucleophilic aromatic substitution reaction or a Pd-catalysed coupling reaction. Alternatively, a second process (illustrated in Schemes 1 and 3) is where the A (or L₁-A) group is attached to the group containing X by any of same methods described above. The resulting intermediate is then functionized by any of the methods described for the first process, and the group containing Y is then added to the intermediate by a C-C coupling reaction. For example, some of the compounds of the invention may be made by the following synthetic schemes:

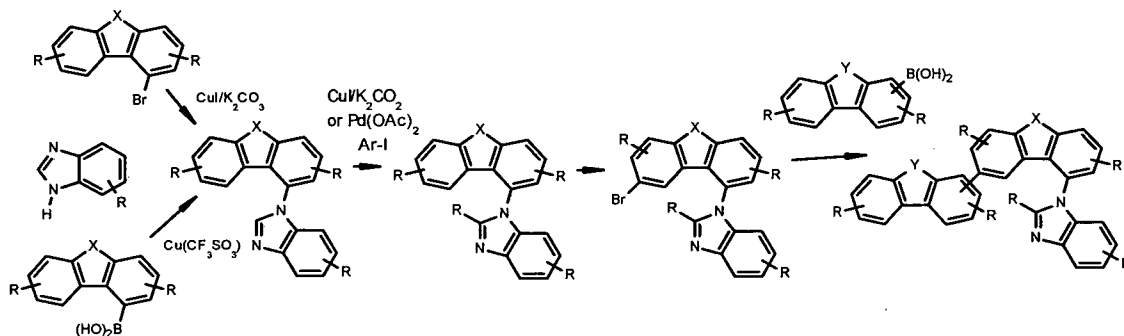
20 Scheme 1:



Scheme 2:



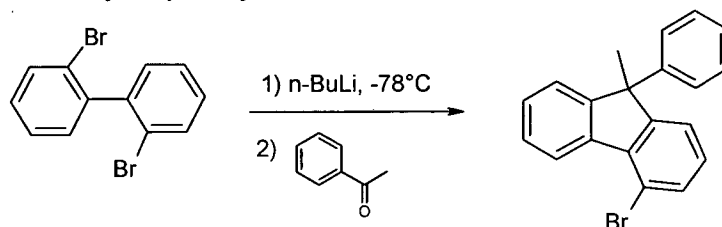
Scheme 3:



5

Synthesis Examples:

a) 4-bromo-9-methyl-9-phenyl-9H-fluorene



30 g (94 mmol) of 2,2'-dibromobiphenyl are dissolved in 200 ml of dried THF in a flask which has been dried by heating. The reaction mixture is cooled to

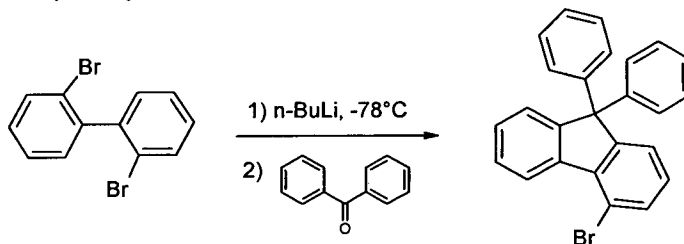
10

-78°C. 37.7 ml of a 2.5 M solution of n-butyllithium in hexane (94 mmol) are slowly added dropwise (duration: about 1 h) at this temperature. The batch is stirred at -70°C for a further 1 h. 11.1 ml of acetophenone (94 mmol) are subsequently dissolved in 100 ml of THF and added dropwise at -70°C.

5 When the addition is complete, the reaction mixture is slowly warmed to room temperature, quenched using NH₄Cl and subsequently evaporated in a rotary evaporator. 300 ml of acetic acid are carefully added to the evaporated solution, and 50 ml of fuming HCl are subsequently added. The batch is heated to 75°C and kept there for 6 h, during which a white solid precipitates out.

10

b) 4-bromo-9,9-diphenyl-9H-fluorene



15

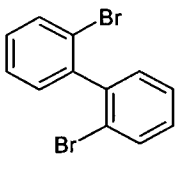
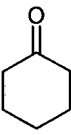
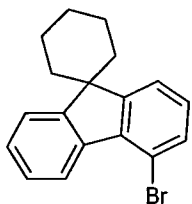
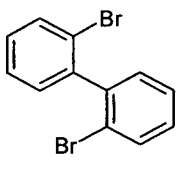

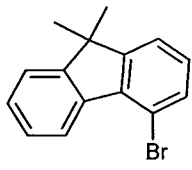
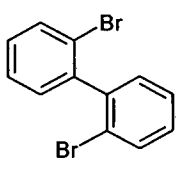
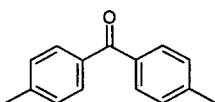
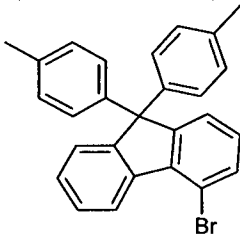
37 g (152 mmol) of 2,2'-dibromobiphenyl are dissolved in 300 ml of dried THF in a flask which has been dried by heating. The reaction mixture is cooled to -78°C. 75 ml of a 15% solution of n-butyllithium in hexane (119 mmol) are slowly added dropwise (duration: about 1 hour) at this temperature. The batch is stirred at -70°C for a further 1 h. 21.8 g of benzophenone (119 mmol) are subsequently dissolved in 100 ml of THF and added dropwise at -70°C. When the addition is complete, the reaction mixture is slowly warmed to room temperature, quenched using NH₄Cl and subsequently evaporated in a rotary evaporator. 510 ml of acetic acid are carefully added to the evaporated solution, and 100 ml of fuming HCl are subsequently added. The batch is heated to 75°C and kept at this

20

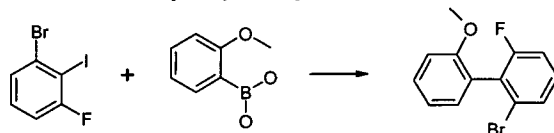
25

30

The following brominated compounds b1-b3 were prepared analogously:

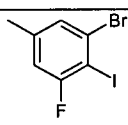
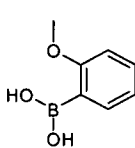
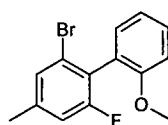
	Reactant 1	Reactant 2	Product	Yield
b1				78%
b2				70%
b3				82%

c) 6-Bromo-2-fluoro-2'-methoxy-biphenyl

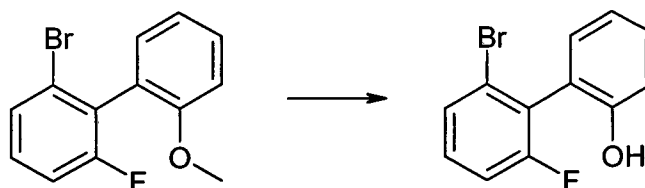


200 g (664 mmol) of 1-bromo-3-fluoro-2-iodobenzene, 101 g (664 mmol) of
 5 2-methoxyphenylboronic acid and 137.5 g (997 mmol) of sodium tetraborate
 are dissolved in 1000 ml of THF and 600 ml of water and degassed. 9.3 g
 (13.3 mmol) of bis(triphenylphosphine)palladium(II) chloride and 1 g (20
 mmol) of hydrazinium hydroxide are added. The reaction mixture is
 subsequently stirred at 70°C for 48 h under a protective-gas atmosphere.
 10 The cooled solution is diluted with toluene, washed a number of times with
 water, dried and evaporated. The product is purified by column
 chromatography on silica gel with toluene/heptane (1:2). Yield: 155 g (553
 mmol), 83% of theory.

15 The following compound c1 was prepared analogously:

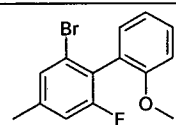
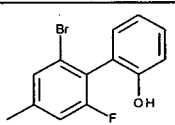
	Reactant 1	Reactant 2	Product	Yield
c1	 [1000576-09-9]			77%

d) 6'-bromo-2'-fluoro-biphenyl-2-ol

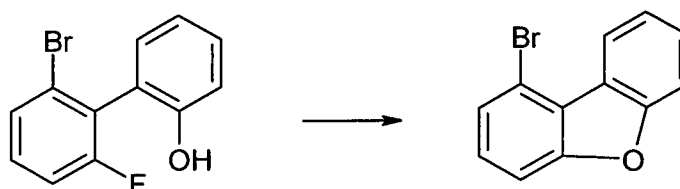


112 g (418 mmol) of 6-bromo-2-fluoro-2'-methoxybiphenyl are dissolved in 2 l of dichloromethane and cooled to 5°C. 41.01 ml (431 mmol) of boron tribromide are added dropwise to this solution over the course of 90 min., and stirring is continued overnight. Water is subsequently slowly added to the mixture, and the organic phase is washed three times with water, dried over Na₂SO₄, evaporated in a rotary evaporator and purified by chromatography. Yield: 104 g (397 mmol), 98% of theory.

The following compound d1 was prepared analogously:

	Reactant	Product	Yield
d1			92%

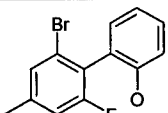
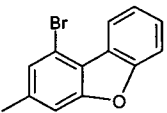
e) 1-Bromo-dibenzofuran



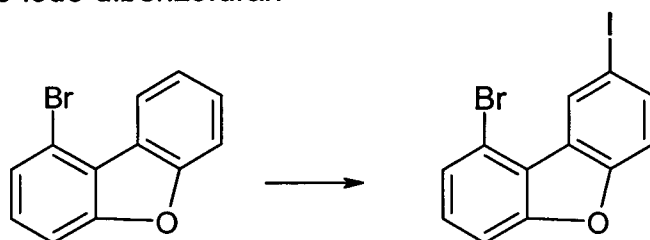
111 g (416 mmol) of 6-bromo-2'-fluorobiphenyl-2-ol are dissolved in 2 l of SeccoSolv® DMF (max 0.003% of H₂O) and cooled to 5°C. 20 g (449 mmol) of sodium hydride (60% suspension in paraffin oil) are added in portions to

5 this solution, and the mixture is stirred for a further 20 min. after the addition is complete and then heated at 100°C for 45 min. After cooling, 500 ml of ethanol are slowly added to the mixture, which is then evaporated to dryness in a rotary evaporator and purified by chromatography. Yield: 90 g (367 mmol), 88.5% of theory.

The following compound e1 was prepared analogously:

	Reactant	Product	Yield
e1			81%

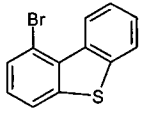
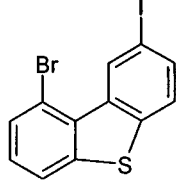
f) 1-bromo-8-iodo-dibenzofuran

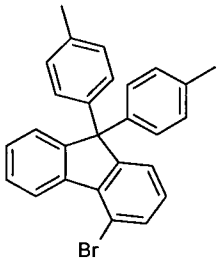
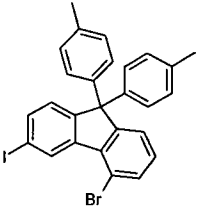
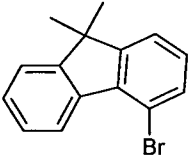
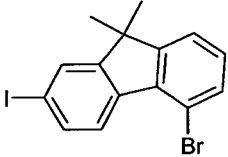


10 20 g (80 mmol) of dibenzofuran-1-boronic acid, 2.06 g (40.1 mmol) of iodine, 3.13 g (17.8 mmol) of iodic acid, 80 ml of acetic acid, 5 ml of sulfuric acid, 5 ml of water and 2 ml of chloroform are stirred at 65° for 3 hours. After cooling, water is added to the mixture, and the solid which has precipitated out is filtered off with suction and washed three times with water. The residue is recrystallised from toluene and from dichloromethane/heptane. The yield is 25.6 g (68 mmol), corresponding to 85% of theory.

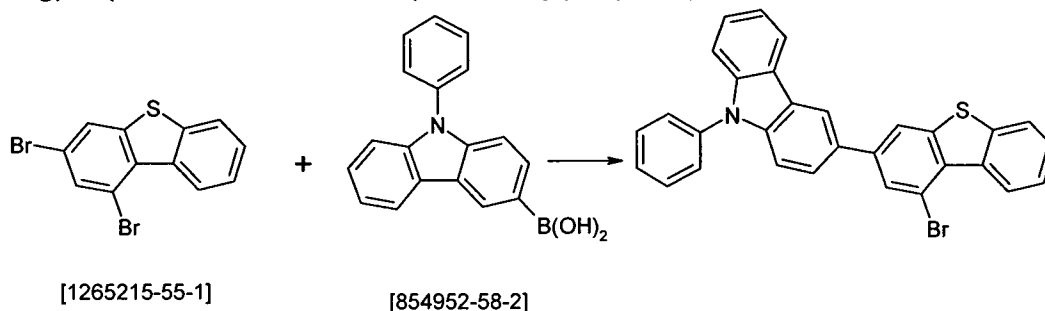
15

The following compounds were prepared analogously:

	Reactant	Product	Yield
f1	 [65642-94-6]		81%

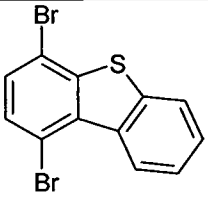
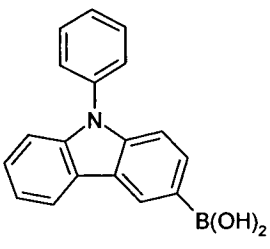
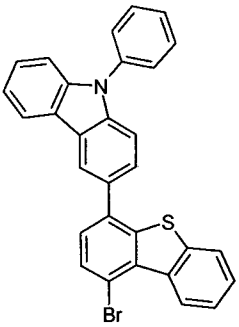
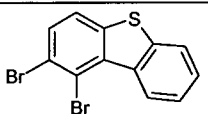
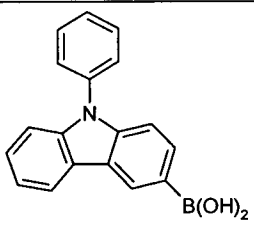
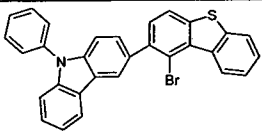
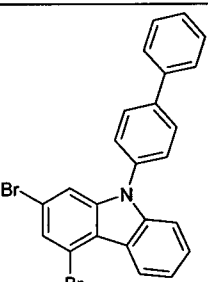
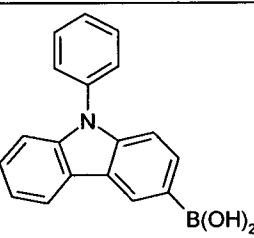
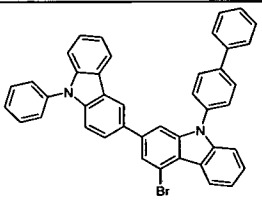
f2			84%
f3			78%

g) 3-(1-bromo-dibenzothiophene-3-yl)-9-phenyl-9H-carbazole

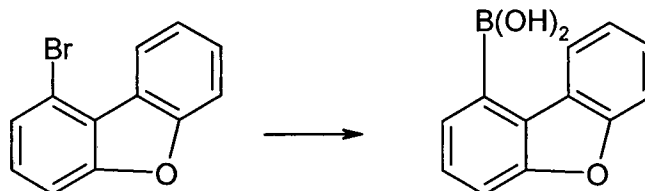


22 g (66 mmol) of 1,3-dibromodibenzothiophene, 17 g (664 mmol) of
 5 2-N-phenylcarbazole-3-boronic acid and 13.7 g (100 mmol) of sodium
 tetraborate are dissolved in 100 ml of THF and 60 ml of water and
 degassed. 0. g (1.3 mmol) of bis(triphenylphosphine)palladium(II) chloride
 and 1 g (20 mmol) of hydrazinium hydroxide are added. The reaction
 10 mixture is subsequently stirred at 70°C for 48 h under a protective-gas
 atmosphere. The cooled solution is diluted with toluene, washed a number
 of times with water, dried and evaporated. The product is purified by column
 chromatography on silica gel with toluene/heptane (1:2). Yield: 13.2 g (26
 mmol), 40% of theory.

15 The following compounds were prepared analogously:

	Reactant 1	Reactant 2	Product	Yield
g1	 [1225467-30-0]	 [854952-58-2]		27%
g2	 [1225467-28-6]	 [854952-58-2]		24%
g3	 [1453088-13-5]	 [854952-58-2]		31%

h) dibenzofuran-1-boronic acid

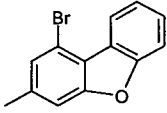
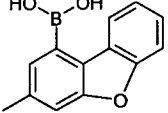
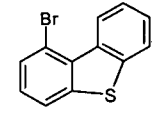
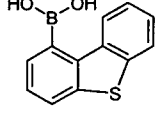
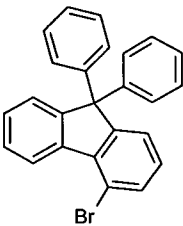
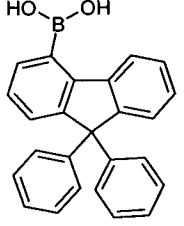
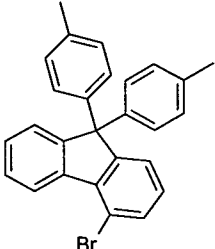
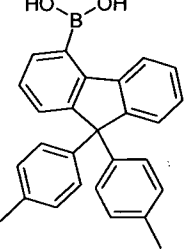
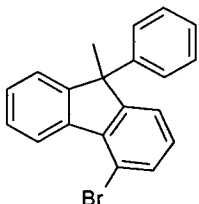
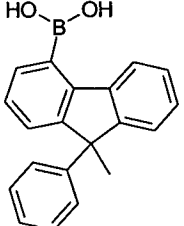
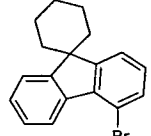
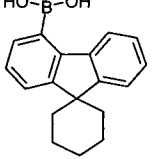


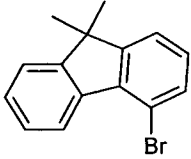
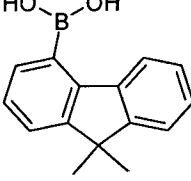
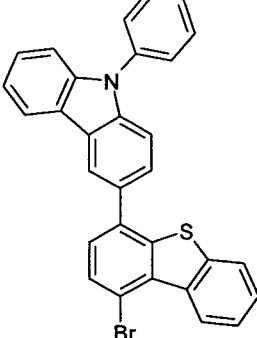
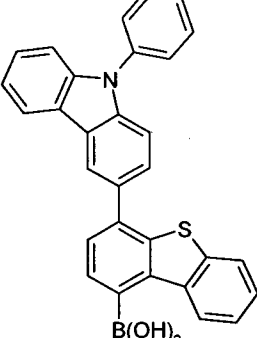
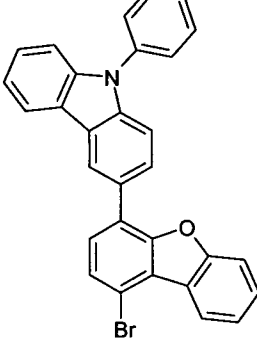
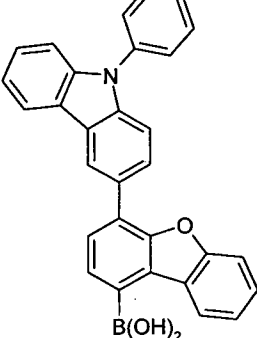
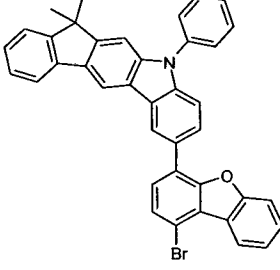
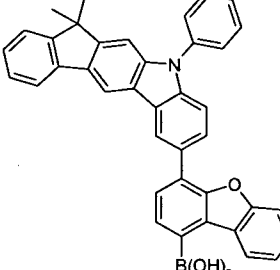
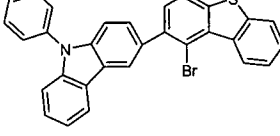
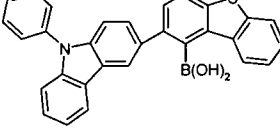
5 180 g (728 mmol) of 1-bromodibenzofuran are dissolved in 1500 ml of dry THF and cooled to -78°C . 305 ml (764 mmol / 2.5 M in hexane) of n-butyllithium are added over the course of about 5 min. at this temperature, and the mixture is subsequently stirred at -78°C for a further 2.5 h. 151 g (1456 mmol) of trimethyl borate are added as rapidly as possible at this temperature, and the reaction is slowly allowed to come to room temperature

(about 18 h). The reaction solution is washed with water, and the solid which has precipitated out and the organic phase are dried azeotropically with toluene. The crude product is washed by stirring with toluene/methylene chloride at about 40°C and filtered off with suction. Yield: 146 g (690 mmol), 95% of theory.

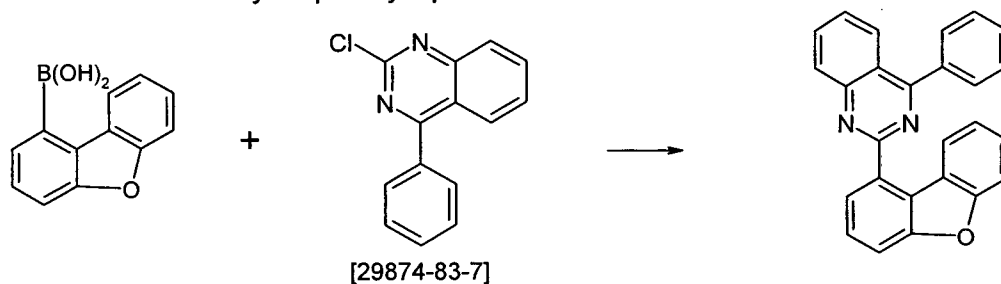
5

The following compounds were prepared analogously:

	Reactant	Product	Yield
h1			81%
h2	 [65642-94-6]		73%
h3			78%
h4			81%
h5			86%
h6			83%

h7			85%
h8	 <p>K1</p>		80%
h9			83%
h10			82%
h11			81%

j) 2-Dibenzofuran-1-yl-4-phenyl-quinazoline



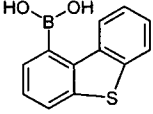
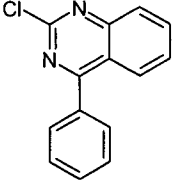
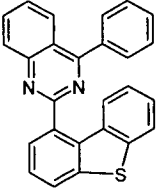
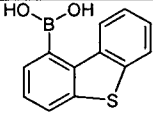
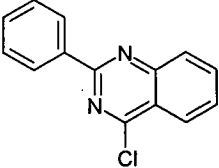
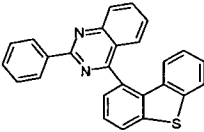
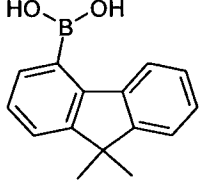
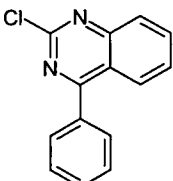
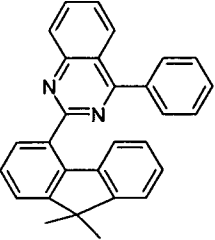
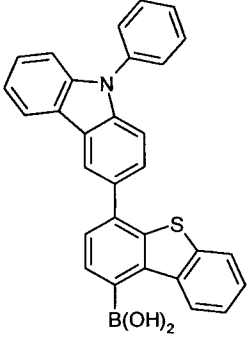
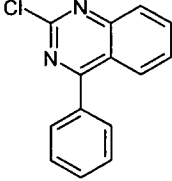
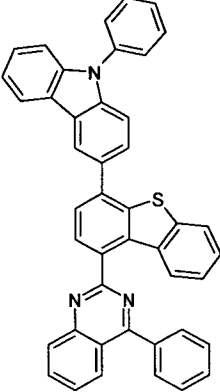
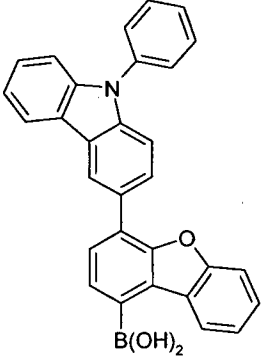
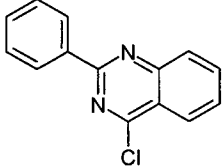
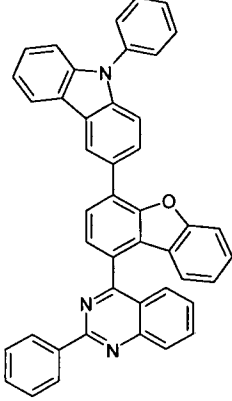
5

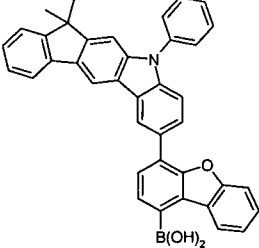
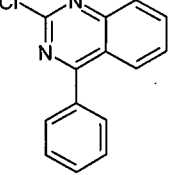
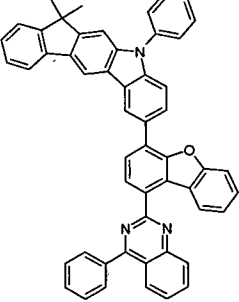
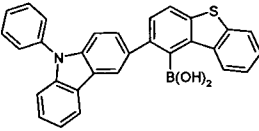
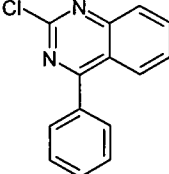
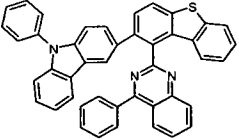
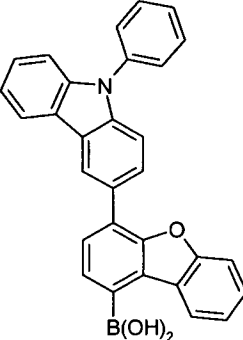
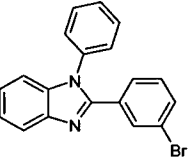
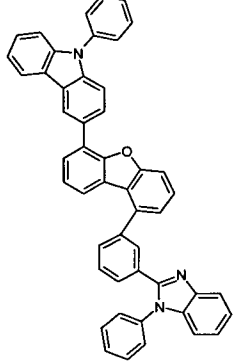
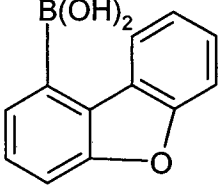
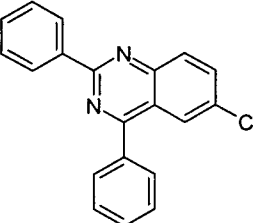
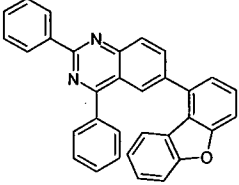
23 g (110.0 mmol) of dibenzofuran-1-boronic acid, 29.5 g (110.0 mmol) of 2-chloro-4-phenyl-quinazoline and 26 g (210.0 mmol) of sodium carbonate are suspended in 500 ml of ethylene glycol diamine ether and 500 ml of water. 913 mg (3.0 mmol) of tri-*o*-tolylphosphine and then 112 mg (0.5 mmol) of palladium(II) acetate are added to this suspension, and the reaction mixture is heated under reflux for 16 h. After cooling, the organic phase is separated off, filtered through silica gel, washed three times with 200 ml of water and subsequently evaporated to dryness. The residue is recrystallised from toluene and from dichloromethane/heptane. The yield is 32 g (86 mmol), corresponding to 80% of theory.

10

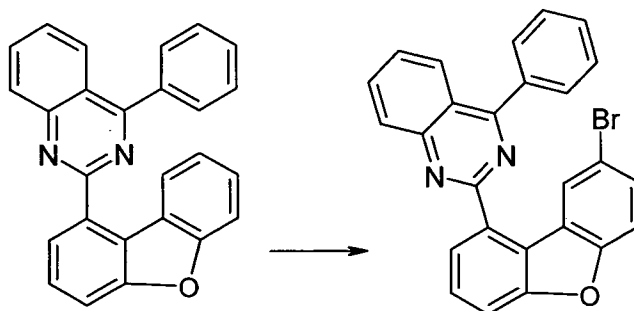
The following compounds were prepared analogously:

	Reactant 1	Reactant 2	Product	Yield
j1		 [29874-83-7]		78%
j2		 [6484-25-9]		70%
j3		 [1292317-90-8]		71%

j4		 <p>[29874-83-7]</p>		77%
j5		 <p>[6484-25-9]</p>		76%
j6		 <p>[29874-83-7]</p>		74%
j7	 <p>B(OH)₂</p>	 <p>[29874-83-7]</p>		75%
j8	 <p>B(OH)₂</p>	 <p>[6484-25-9]</p>		71%

<p>j9</p>		 <p>[29874-83-7]</p>		<p>64%</p>
<p>j10</p>		 <p>[29874-83-7]</p>		<p>59%</p>
<p>j11</p>		 <p>[760212-40-6]</p>		<p>67%</p>
<p>j12</p>		 <p>[30169-34-7]</p>		<p>71%</p>

i) 2-(8-bromo-dibenzofuran-1-yl)-4-phenyl-quinazoline

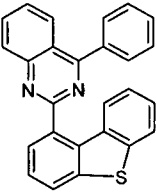
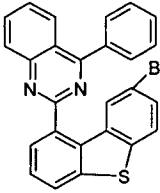
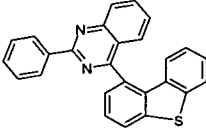
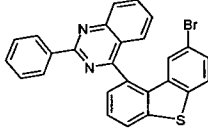
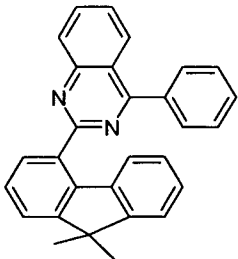
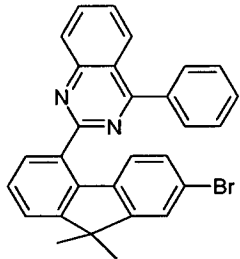
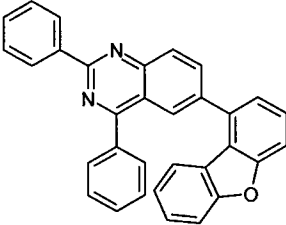
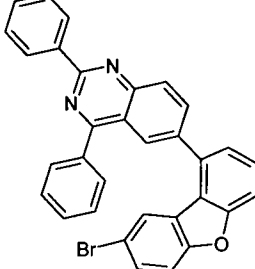


5 70.6 g (190.0 mmol) of 2-dibenzofuran-1-yl-4-phenylquinazoline are suspended in 2000 ml of acetic acid (100%) and 2000 ml of sulfuric acid (95-98%). 34 g (190 mmol) of NBS are added in portions to this suspension, and the mixture is stirred in the dark for 2 hours. Water/ice are then added, and the solid is separated off and rinsed with ethanol. The residue is recrystallised from toluene. The yield is 59 g (130 mmol), corresponding to 69% of theory.

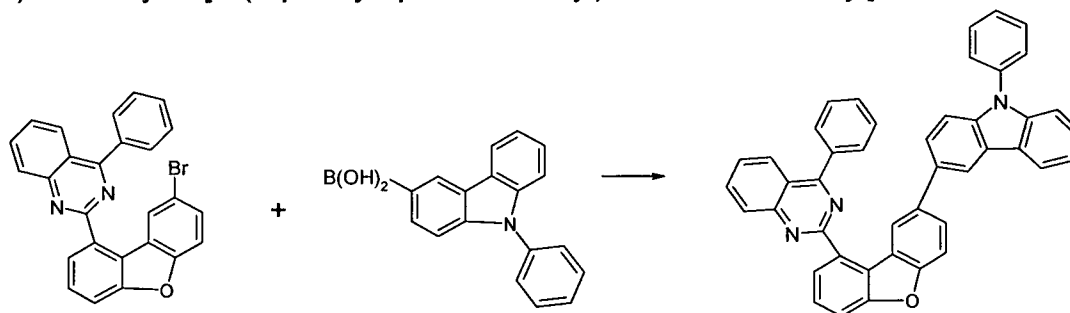
10 In the case of the thiophene derivatives, nitrobenzene is employed instead of sulfuric acid and elemental bromine is employed instead of NBS.

The following compounds were prepared analogously:

	Reactant	Product	Yield
i1			70%
i2			73%
i3			71%

i4			62%
i5			60%
i6			65%
i7			69%

k) 9-Phenyl-3-[9-(4-phenylquinazolin-2-yl)-dibenzofuran-2-yl]-9H-carbazole



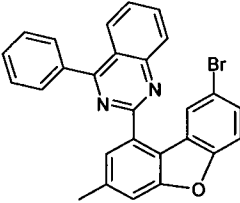
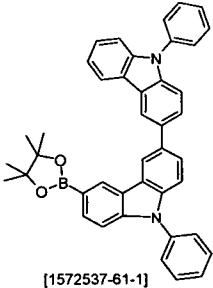
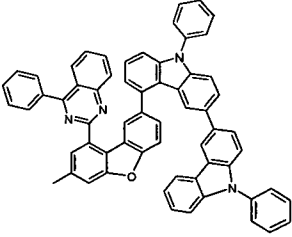
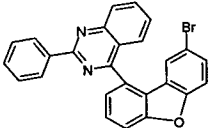
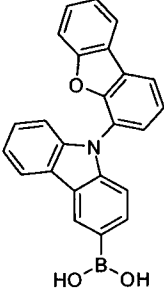
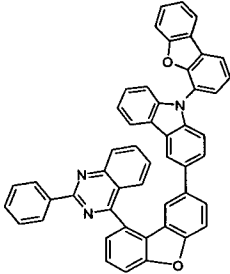
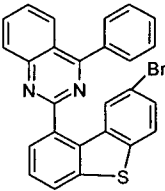
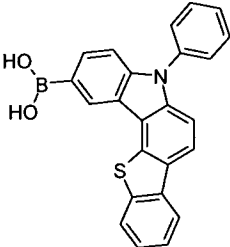
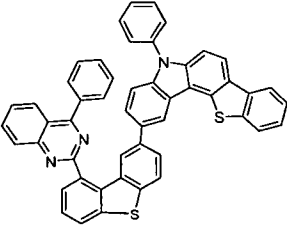
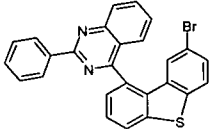
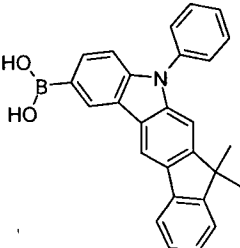
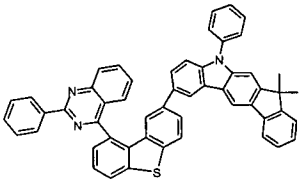
5

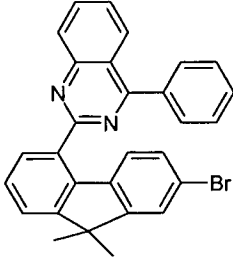
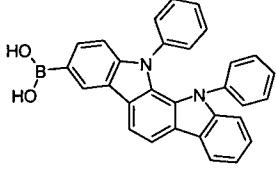
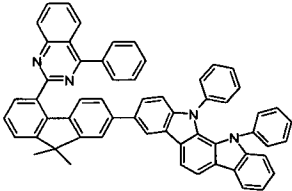
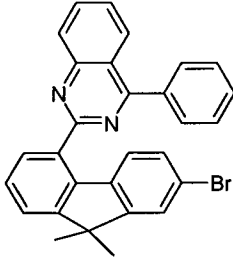
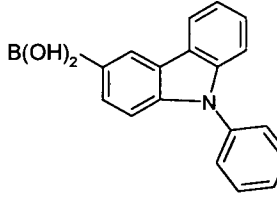
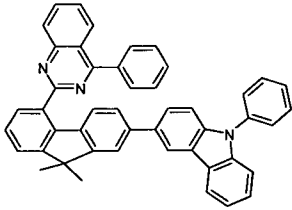
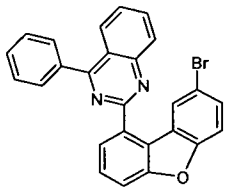
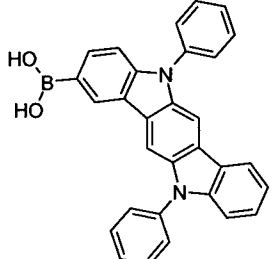
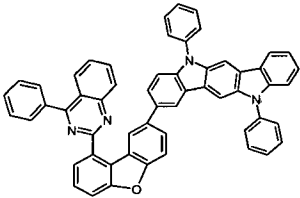
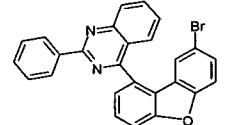
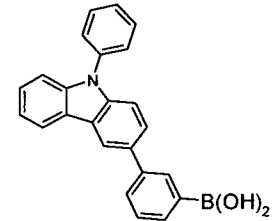
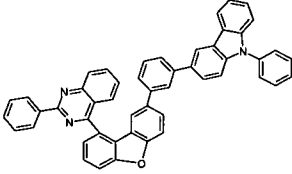
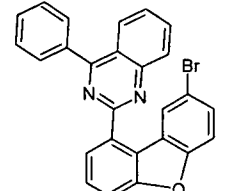
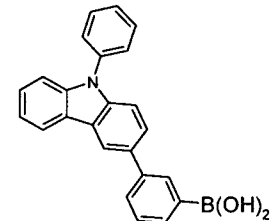
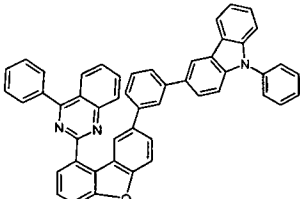
70.3 g (156 mmol) of 2-(8-bromodibenzofuran-1-yl)-4-phenylquinazoline, 50 g (172 mmol) of N-phenylcarbazole-3-boronic acid and 36 g (340 mmol) of sodium carbonate are suspended in 1000 ml of ethylene glycol diamine ether and 280 ml of water. 1.8 g (1.5 mmol) of tetrakis(triphenylphosphine)-palladium(0) are added to this suspension, and the reaction mixture is heated under reflux for 16 h. After cooling, the organic phase is separated

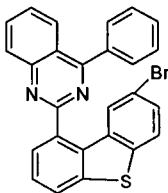
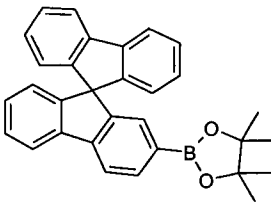
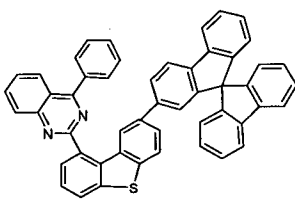
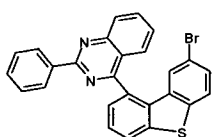
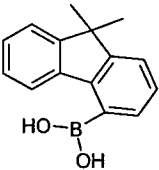
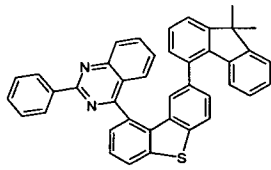
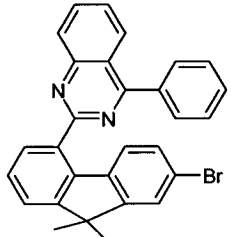
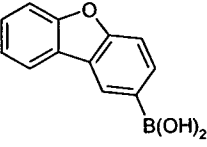
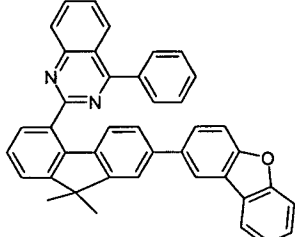
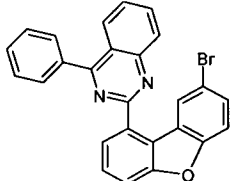
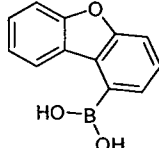
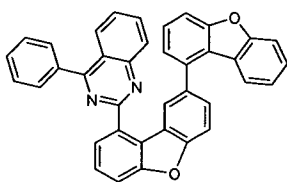
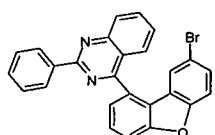
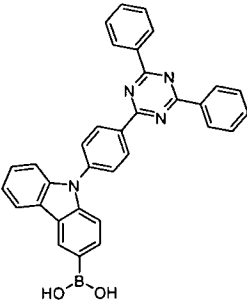
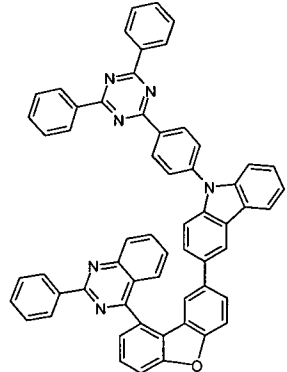
off, filtered through silica gel, washed three times with 200 ml of water and subsequently evaporated to dryness. The product is purified by column chromatography on silica gel with toluene/heptane (1:2) and finally sublimed in a high vacuum ($p = 5 \times 10^{-7}$ mbar) (purity 99.9%). The yield is 68 g (112 mmol), corresponding to 72% of theory.

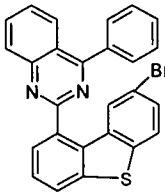
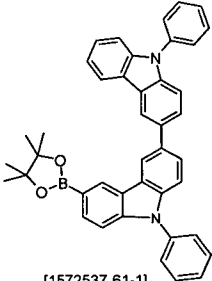
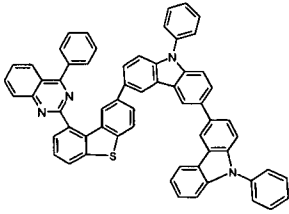
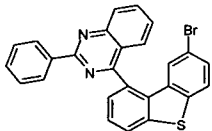
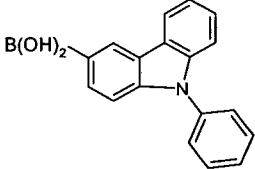
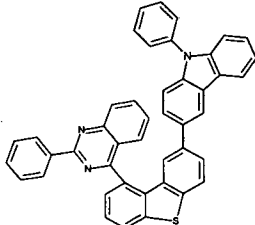
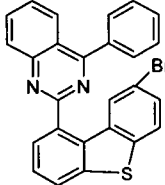
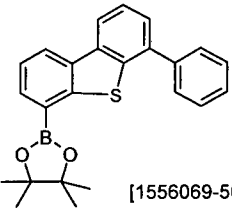
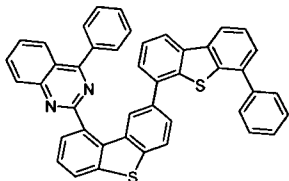
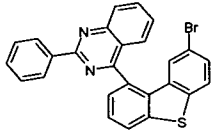
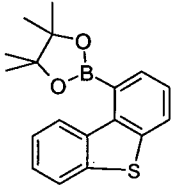
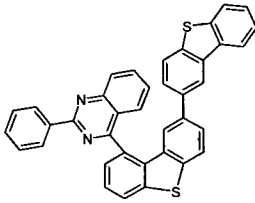
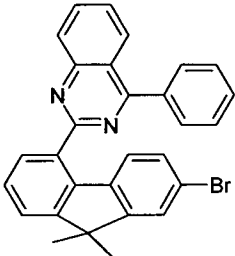
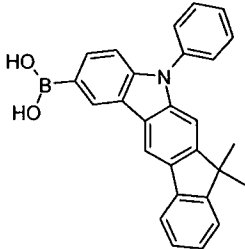
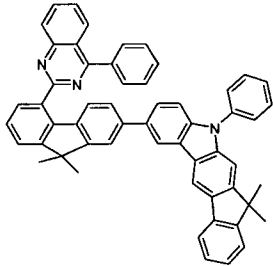
5

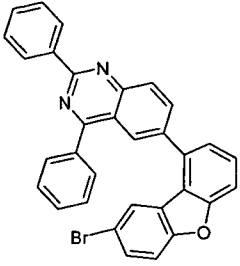
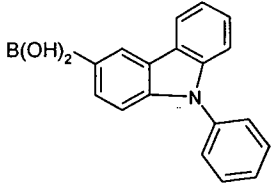
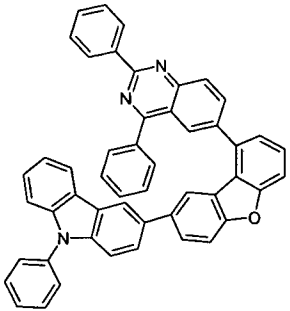
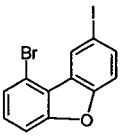
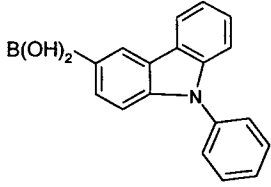
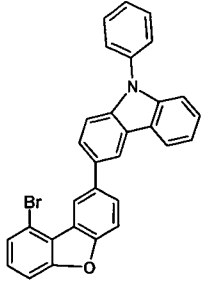
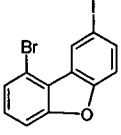
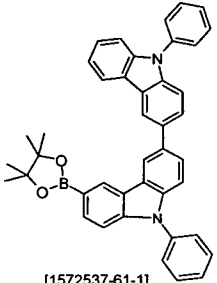
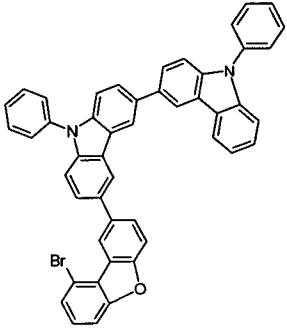
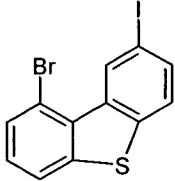
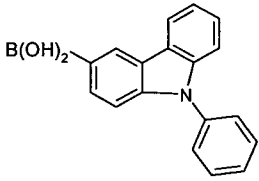
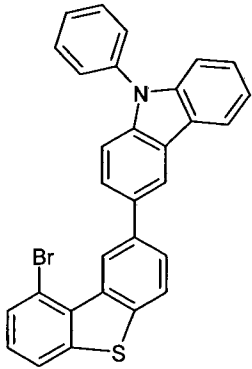
The following compounds were prepared analogously:

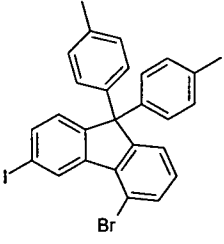
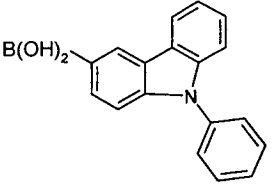
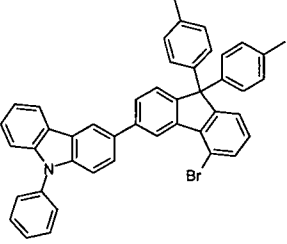
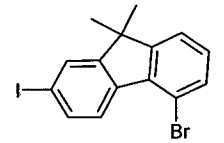
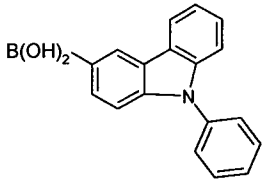
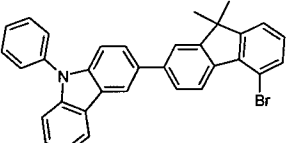
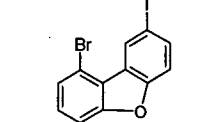
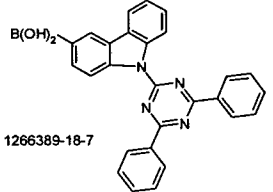
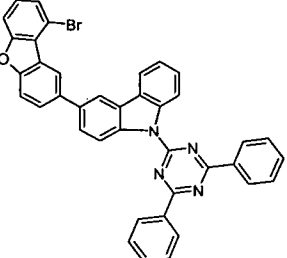
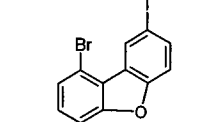
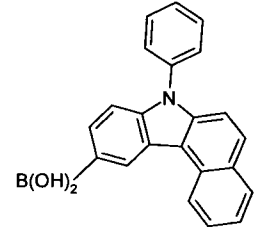
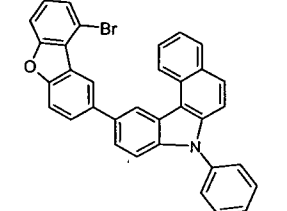
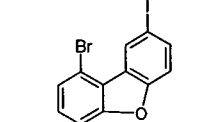
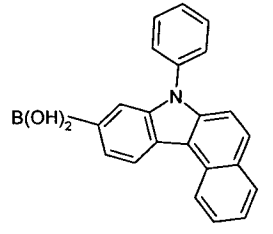
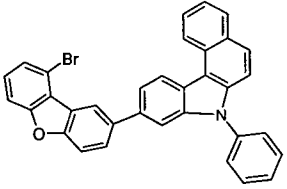
	Reactant 1	Reactant 2	Product	Yield
k1		 [1572537-61-1]		60%
k2		 HO-B-OH [1547397-15-8]		65%
k4		 HO-B-OH [1391729-63-7]		53%
k5		 HO-B-OH [1379585-25-7]		58%

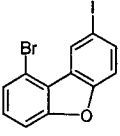
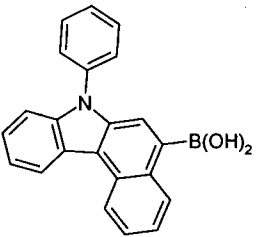
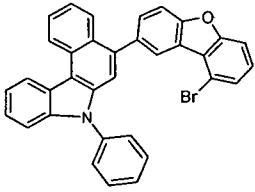
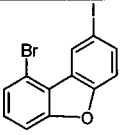
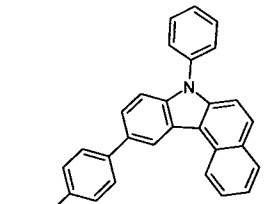
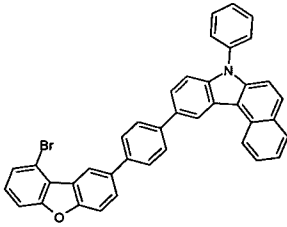
<p>k6</p>		 <p>[1373359-67-1]</p>		<p>52%</p>
<p>k7</p>		 <p>854952-58-2</p>		<p>69%</p>
<p>k8</p>		 <p>[1314019-74-3]</p>		<p>67%</p>
<p>k9</p>		 <p>[854952-60-6]</p>		<p>69%</p>
<p>k10</p>		 <p>[854952-60-6]</p>		<p>55%</p>

<p>k11</p>		 <p>[1557257-88-1]</p>		<p>69%</p>
<p>k12</p>		 <p>HO-B OH</p> <p>[1246022-50-3]</p>		<p>71%</p>
<p>k13</p>		 <p>B(OH)₂</p> <p>[402936-15-6]</p>		<p>74%</p>
<p>k14</p>		 <p>HO-B OH</p> <p>[162607-19-4]</p>		<p>67%</p>
<p>k15</p>		 <p>HO-B OH</p>		<p>65%</p>

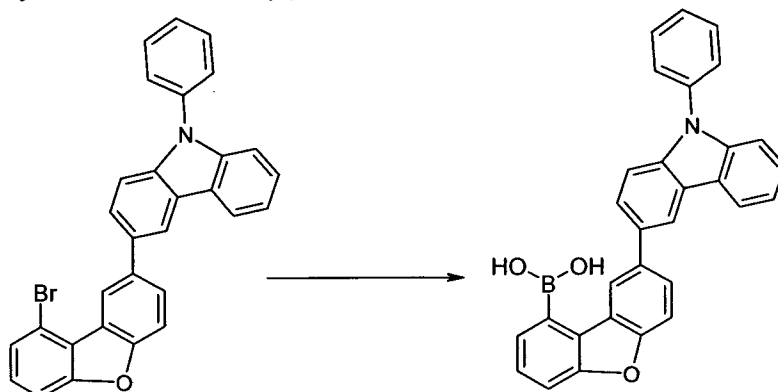
<p>k16</p>		 <p>[1572537-61-1]</p>		<p>82%</p>
<p>k17</p>		 <p>854952-58-2</p>		<p>51%</p>
<p>k18</p>		 <p>[1556069-50-1]</p>		<p>62%</p>
<p>k19</p>		 <p>[1434286-69-7]</p>		<p>77%</p>
<p>k20</p>		 <p>[1379585-25-7]</p>		<p>64%</p>

<p>k21</p>		<p>$B(OH)_2$</p>  <p>854952-58-2</p>		<p>72%</p>
<p>k22</p>		<p>$B(OH)_2$</p>  <p>854952-58-2</p>		<p>66%</p>
<p>k23</p>		 <p>[1572537-61-1]</p>		<p>75%</p>
<p>k24</p>		<p>$B(OH)_2$</p>  <p>854952-58-2</p>		<p>78%</p>

<p>k25</p>		<p>B(OH)₂</p>  <p>854952-58-2</p>	 <p>70%</p>
<p>k26</p>		<p>B(OH)₂</p>  <p>854952-58-2</p>	 <p>76%</p>
<p>k27</p>		<p>B(OH)₂</p>  <p>1266389-18-7</p>	 <p>70%</p>
<p>k28</p>		<p>B(OH)₂</p>  <p>1246562-39-9</p>	 <p>74%</p>
<p>k29</p>		<p>B(OH)₂</p>  <p>1357572-68-9</p>	 <p>73%</p>

k30		 1357573-03-5		72%
k31		 1426392-81-5		69%

l) 8-(9-phenyl-9H-carbazol-3-yl)-dibenzofuran-1-boronic acid



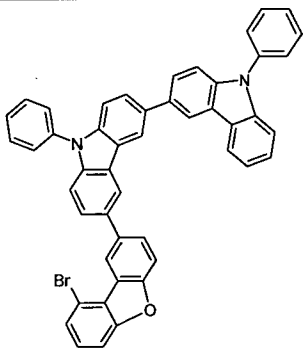
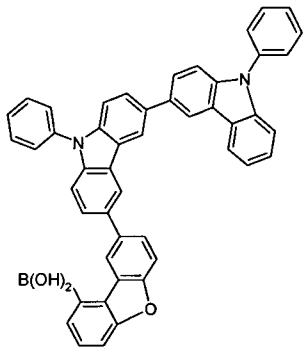
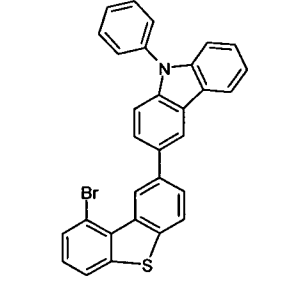
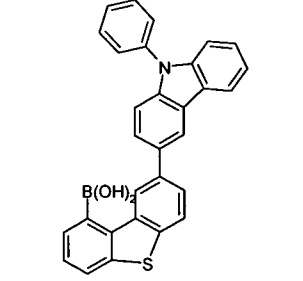
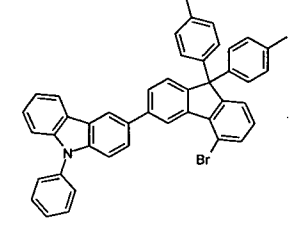
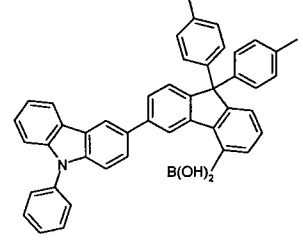
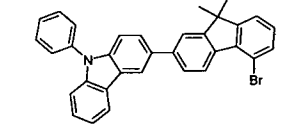
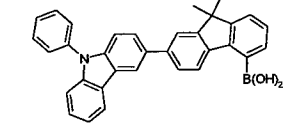
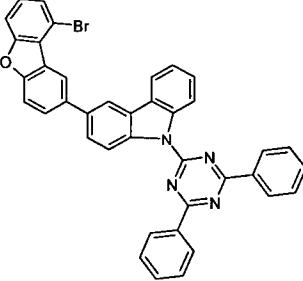
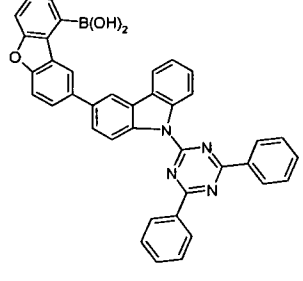
5

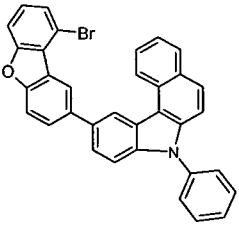
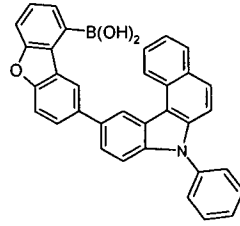
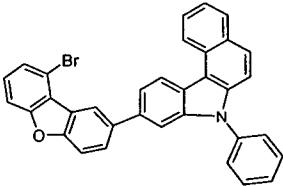
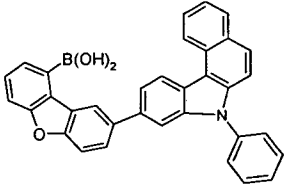
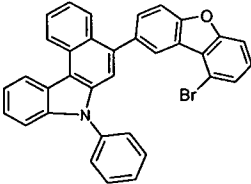
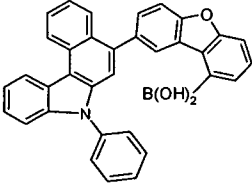
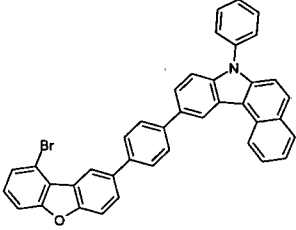
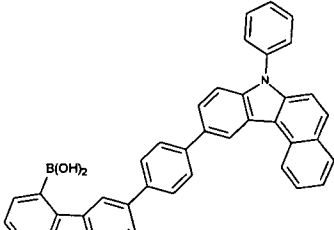
20 g (182 mmol) of 3-(9-bromodibenzofuran-2-yl)-9-phenyl-9H-carbazole are dissolved in 400 ml of dry THF and cooled to -78°C . 77 ml (190 mmol / 2.5 M in hexane) of n-butyllithium are added over the course of about 5 min. at this temperature, and the mixture is subsequently stirred at -78°C for a further 2.5 h. 38 g (365 mmol) of trimethyl borate are added as rapidly as possible at this temperature, and the reaction is slowly allowed to come to RT (about 18 h). The reaction solution is washed with water, and the solid which has precipitated out and the organic phase are dried azeotropically with toluene. The crude product is washed by stirring with toluene/methylene chloride at about 40°C and filtered off with suction. Yield: 16.7 g (690 mmol), 90% of theory.

10

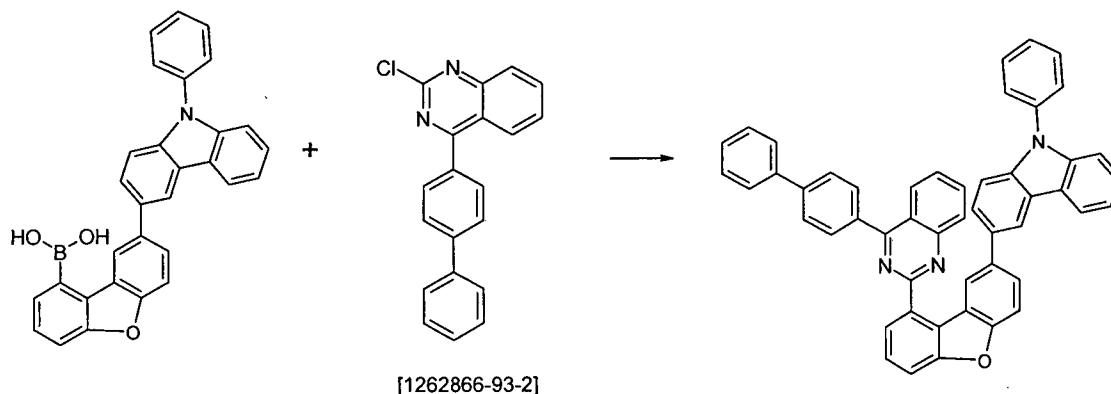
15

The following compounds were prepared analogously:

	Reactant	Product	Yield
I1			81%
I2			84%
I3			78%
I4			77%
I5			72%

16			77%
17			75%
18			70%
19			71%

m) 3-[9-(4-biphenyl-4-yl-quinazolin-2-yl)-dibenzofuran-2-yl]-9-phenyl-9H-carbazole

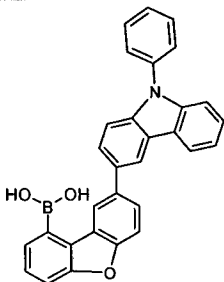
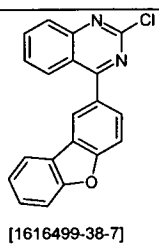
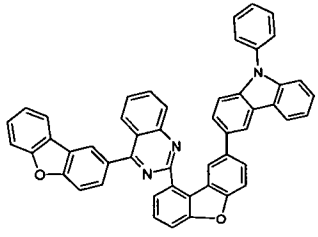
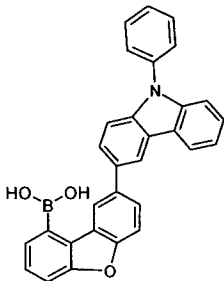
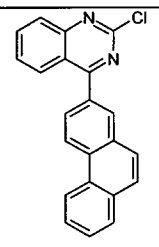
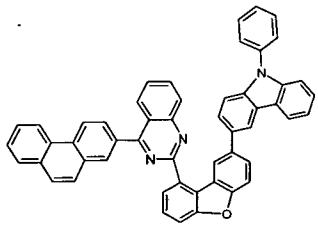
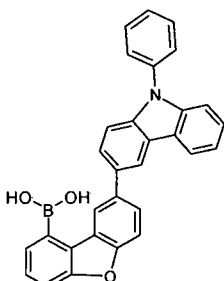
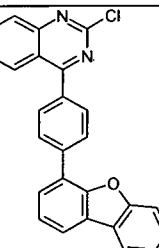
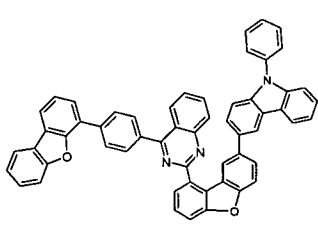


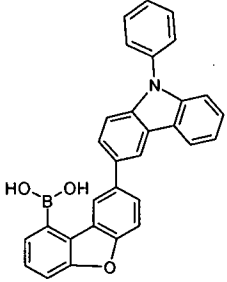
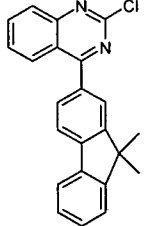
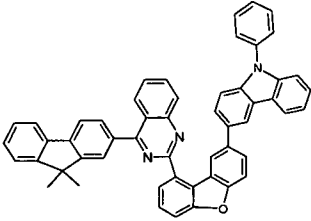
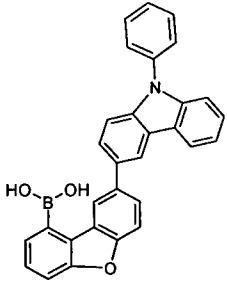
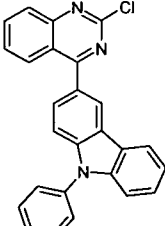
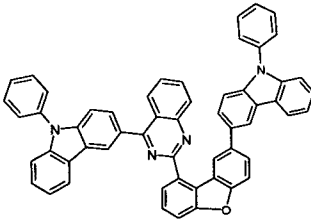
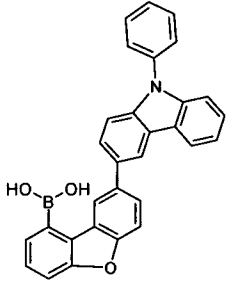
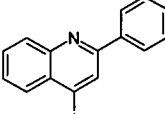
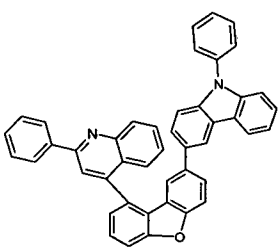
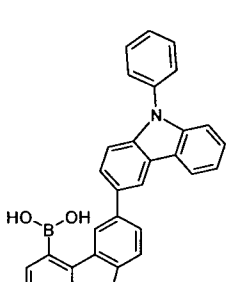
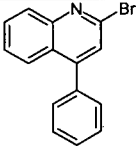
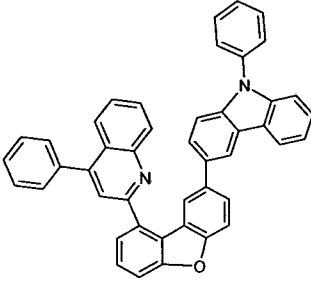
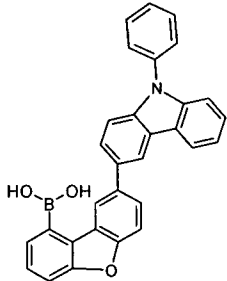
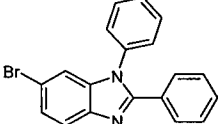
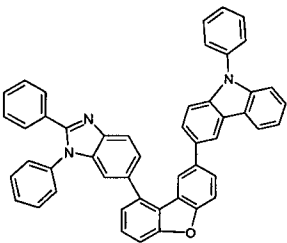
5

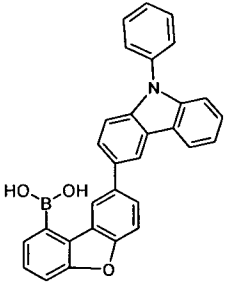
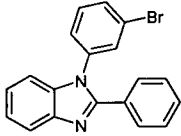
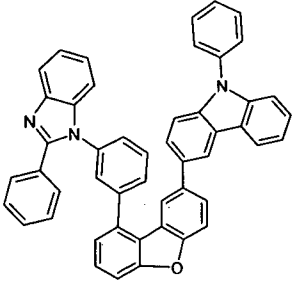
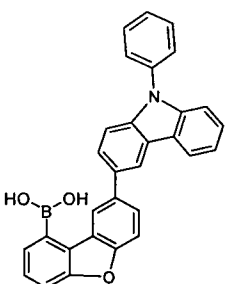
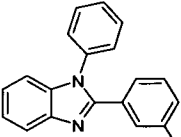
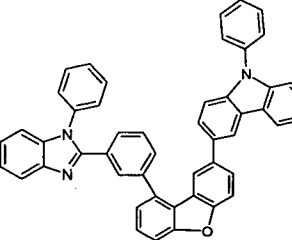
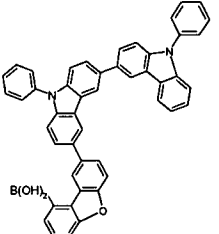
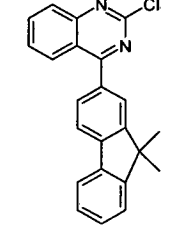
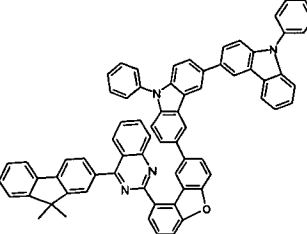
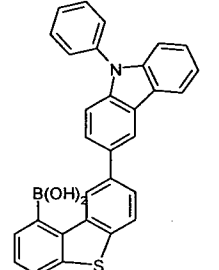
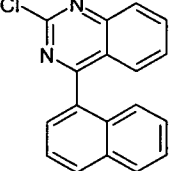
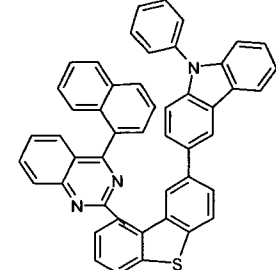
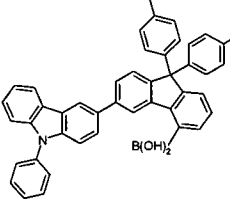
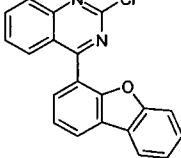
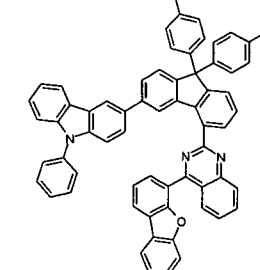
49.8 g (110.0 mmol) of 8-(9-phenyl-9H-carbazol-3-yl)dibenzofuran-1-boronic acid, 34 g (110.0 mmol) of 4-biphenyl-4-yl-2-chloroquinazoline and 26 g (210.0 mmol) of sodium carbonate are suspended in 500 ml of ethylene

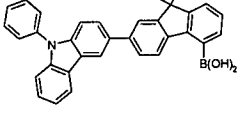
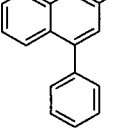
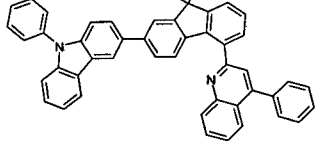
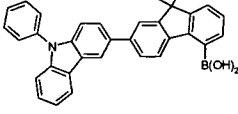
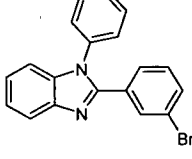
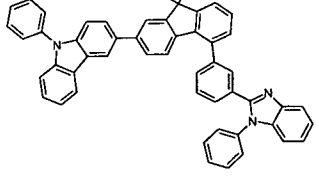
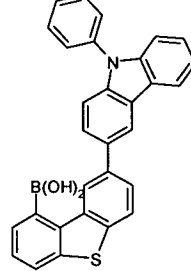
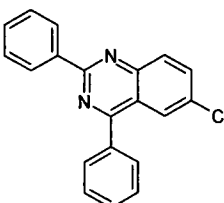
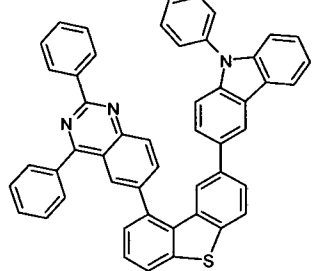
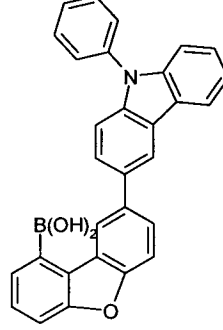
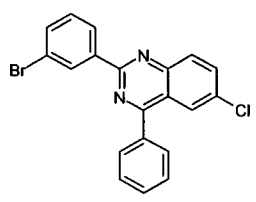
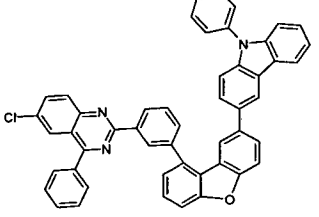
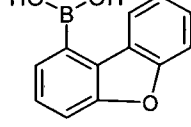
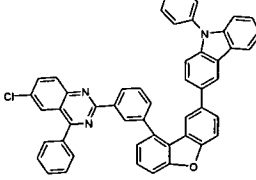
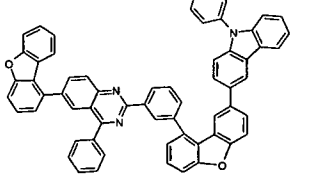
glycol diamine ether and 500 ml of water. 913 mg (3.0 mmol) of tri-*o*-tolylphosphine and then 112 mg (0.5 mmol) of palladium(II) acetate are added to this suspension, and the reaction mixture is heated under reflux for 16 h. After cooling, the organic phase is separated off, filtered through silica gel, washed three times with 200 ml of water and subsequently evaporated to dryness. The product is purified by column chromatography on silica gel with toluene/heptane (1:2) and finally sublimed in a high vacuum ($p = 5 \times 10^{-7}$ mbar) (purity 99.9%). The yield is 60 g (87 mmol), corresponding to 80% of theory.

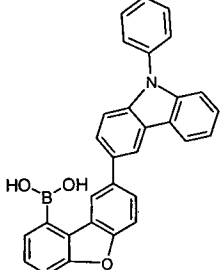
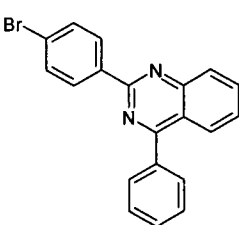
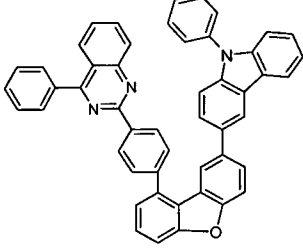
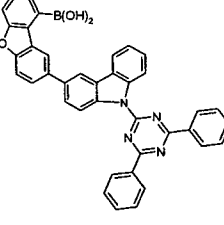
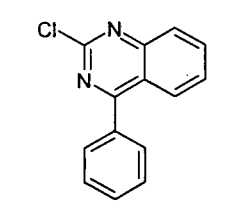
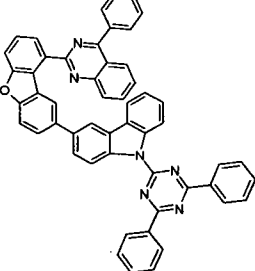
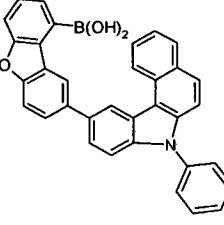
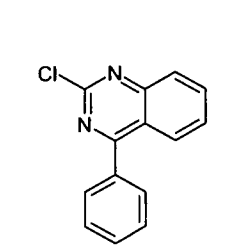
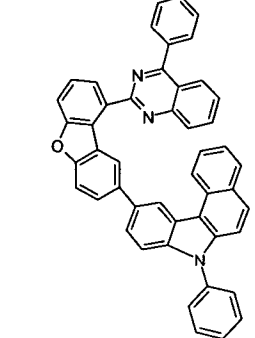
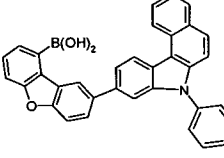
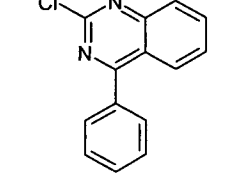
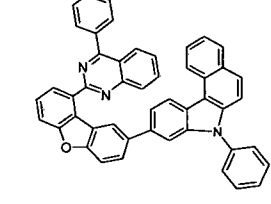
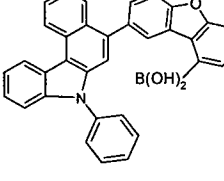
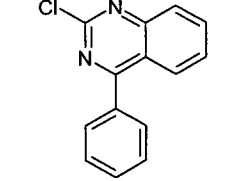
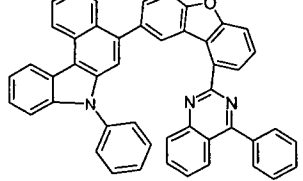
The following compounds were prepared analogously:

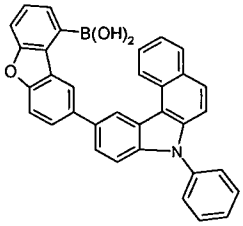
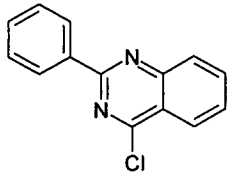
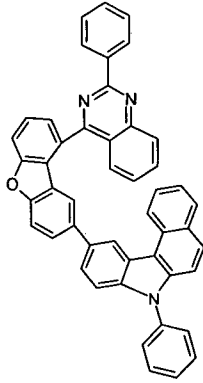
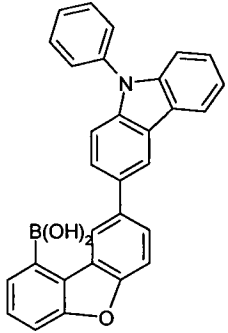
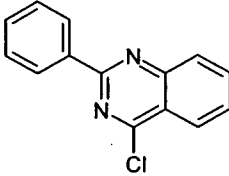
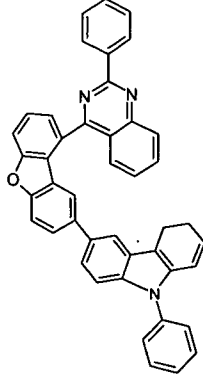
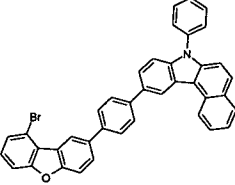
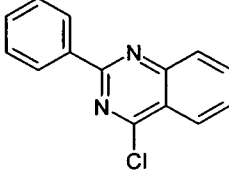
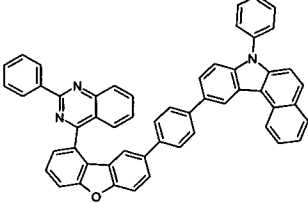
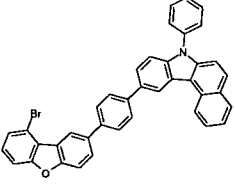
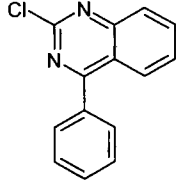
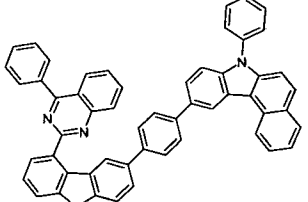
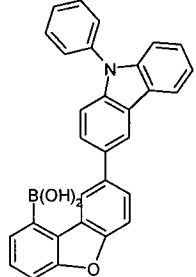
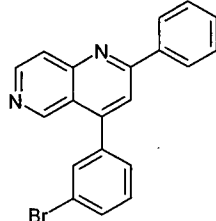
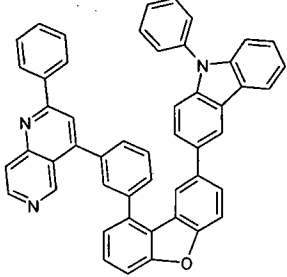
	Reactant 1	Reactant 2	Product	Yield
m1				78%
m2				76%
m3				72%

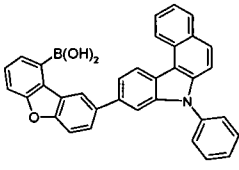
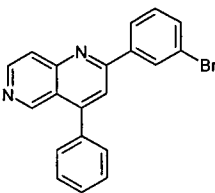
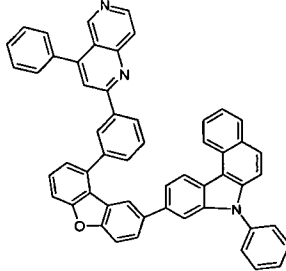
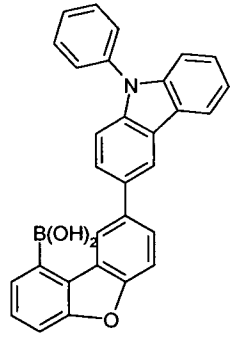
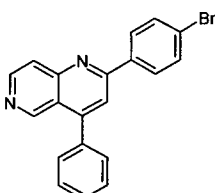
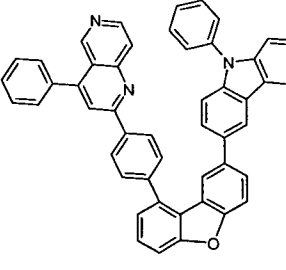
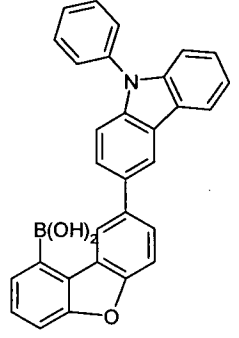
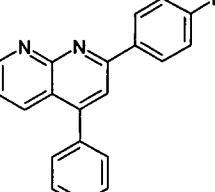
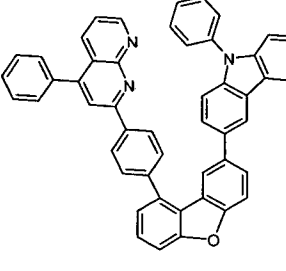
<p>m4</p>		 <p>[1373265-66-7]</p>		<p>69%</p>
<p>m5</p>		 <p>[1373317-91-9]</p>		<p>81%</p>
<p>m6</p>		 <p>[643017-61-2]</p>		<p>88%</p>
<p>m7</p>		 <p>[857206-12-3]</p>		<p>79%</p>
<p>m8</p>		 <p>[760212-55-3]</p>		<p>75%</p>

<p>m9</p>		 <p>[1171247-63-4]</p>		<p>83%</p>
<p>m10</p>		 <p>[760212-40-6]</p>		<p>76%</p>
<p>m11</p>		 <p>[1373265-66-7]</p>		<p>71%</p>
<p>m12</p>		 <p>[1413376-86-9]</p>		<p>80%</p>
<p>m13</p>		 <p>[14003252-55-0]</p>		<p>75%</p>

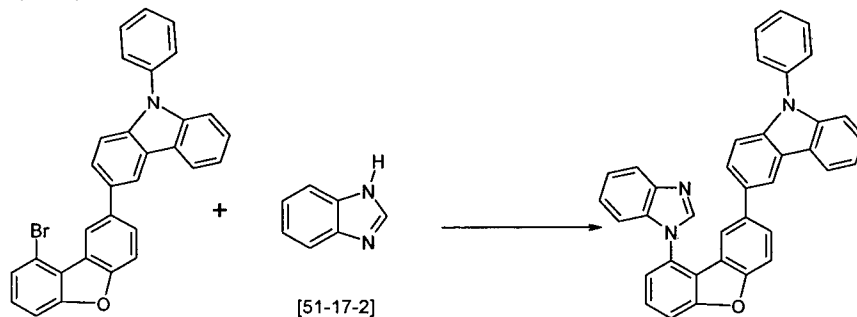
<p>m14</p>		 <p>[5855-56-1]</p>	 <p>74%</p>
<p>m15</p>		 <p>[760212-40-6]</p>	 <p>73%</p>
<p>m16</p>		 <p>[30169-34-7]</p>	 <p>69%</p>
<p>m17</p>		 <p>[1257084-12-0]</p>	 <p>59%</p>
<p>m18</p>		 <p>m17</p>	 <p>73%</p>

<p>m19</p>		 <p>[540466-42-0]</p>		<p>78%</p>
<p>m20</p>		 <p>[29874-83-7]</p>		<p>70%</p>
<p>m21</p>		 <p>[29874-83-7]</p>		<p>73%</p>
<p>m22</p>		 <p>[29874-83-7]</p>		<p>67%</p>
<p>m23</p>		 <p>[29874-83-7]</p>		<p>68%</p>

<p>m24</p>		 <p>[6484-25-9]</p>		<p>76%</p>
<p>m25</p>		 <p>[6484-25-9]</p>		<p>79%</p>
<p>m26</p>		 <p>[6484-25-9]</p>		<p>77%</p>
<p>m27</p>		 <p>[29874-83-7]</p>		<p>78%</p>
<p>m30</p>		 <p>[1632307-99-3]</p>		<p>75%</p>

m31		 [1632307-97-1]		76%
m32		 [1632307-96-0]		78%
m33		 [1632294-77-9]		73%

n) 3-(9-benzimidazol-1-yl-dibenzofuran-2-yl)-9-phenyl-9H-carbazole



k21

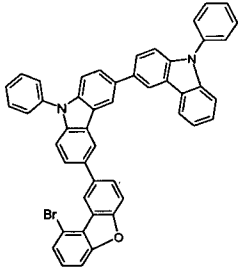
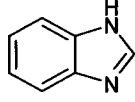
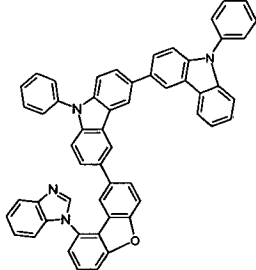
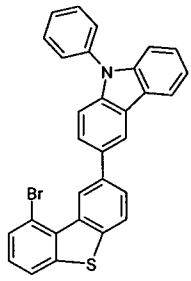
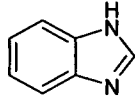
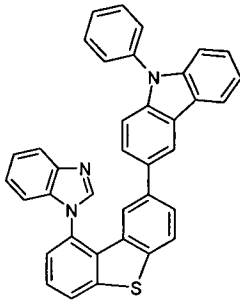
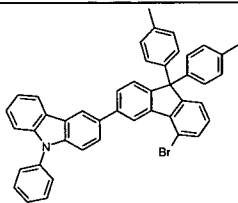
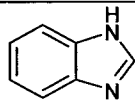
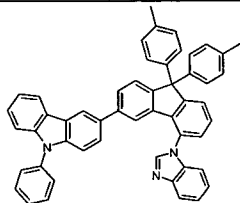
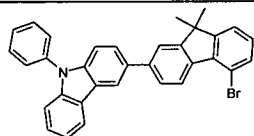
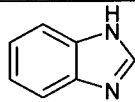
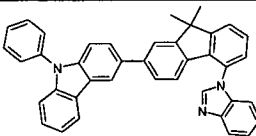
5

10 g (84.7 mmol) of benzimidazole, 42 g (127.4 mmol) of CsCO₃, 2.4 g (14.7 mmol) of CuI and 30.7 g (63 mmol) of 3-(9-bromodibenzofuran-2-yl)-9-phenyl-9H-carbazole are suspended in 100 ml of degassed DMF under a protective gas, and the reaction mixture is heated under reflux at 120°C for

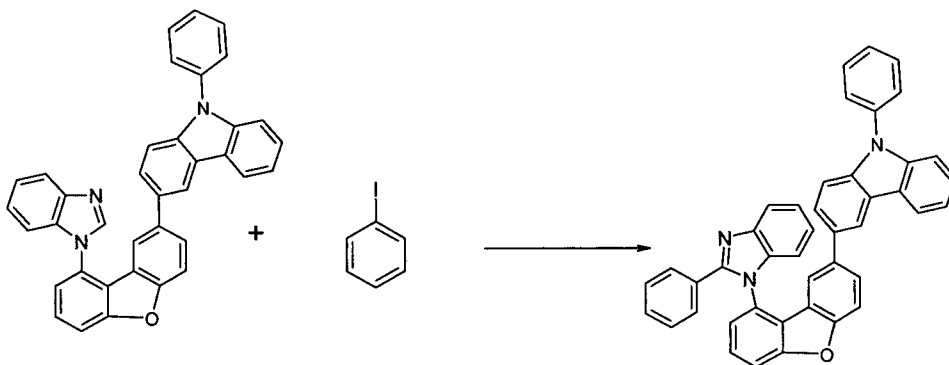
40 h. After cooling, the solvent is removed in vacuo, the residue is dissolved in dichloromethane, and water is added. The organic phase is then separated off and filtered through silica gel. The yield is 28 g (53 mmol), corresponding to 87% of theory.

5

The following compounds are prepared analogously:

	Reactant 1	Reactant 2	Product	Yield
n1	 k22	 [51-17-2]		80%
n2	 k23	 [51-17-2]		83%
n3	 k24	 [51-17-2]		79%
n4	 K25	 [51-17-2]		86%

o) 9-phenyl-3-[9-(2-phenyl-benzimidazol-1-yl)-dibenzofuran-2-yl]-9H-carbazole



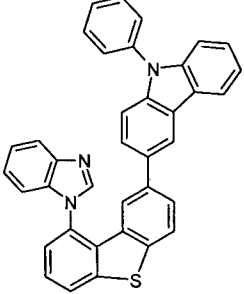
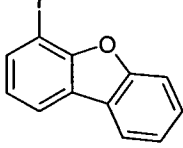
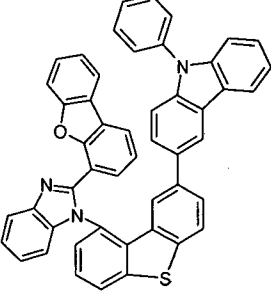
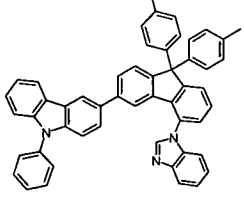
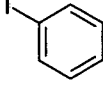
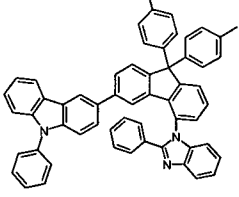
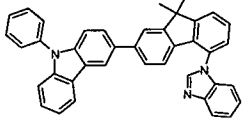
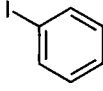
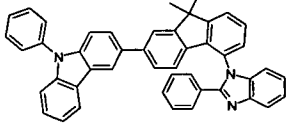
5

26 g (50 mmol) of 3-(9-benzimidazol-1-yl)dibenzofuran-2-yl)-9-phenyl-9H-carbazole, 560 mg (25 mmol) of Pd(OAc)₂, 19.3 g (118 mmol) of CuI and 20.8 g (100 mmol) of iodobenzene are suspended in 300 ml of degassed DMF under a protective gas, and the reaction mixture is heated under reflux at 140°C for 24 h. After cooling, the solvent is removed in vacuo, the residue is dissolved in dichloromethane, and water is added. The organic phase is then separated off and filtered through silica gel. The product is purified by column chromatography on silica gel with toluene/heptane (1:2) and finally sublimed in a high vacuum ($p = 5 \times 10^{-7}$ mbar) (purity 99.9%). The yield is 17.8 g (30 mmol), corresponding to 60% of theory.

10

The following compounds were prepared analogously:

	Reactant 1	Reactant 2	Product	Yield
o1		 [144981-85-1]		55%
o2				53% %

o3		 [65344-26-5]		47%
o4				44%
o5				51%

Fabrication of OLEDs

The following examples V1-V7 and E1-E11 (see Table 1 and 2) show data for various OLEDs.

5

Substrate pre-treatment of examples V1-7 and E1-E1a: Glass plates with structured ITO (50 nm, indium tin oxide) form the substrates on which the OLEDs are processed. Before evaporation of the OLED materials, the substrates are pre-baked for 15 minutes at 250°C, followed by an O₂ plasma treatment for 130 seconds.

10

The OLEDs have in principle the following layer structure: substrate / optional hole-injection layer (HIL) / hole-transport layer (HTL) / optional interlayer (IL) / electron-blocking layer (EBL) / emission layer (EML) / optional hole-blocking layer (HBL) / electron-transport layer (ETL) / optional electron-injection layer (EIL) and finally a cathode. The cathode is formed by an aluminium layer with a thickness of 100 nm. The exact layer structure

15

(and layer thickness) is denoted in Table 1. The materials used for the OLED fabrication are presented in Table 3.

5 All materials are applied by thermal vapour deposition in a vacuum chamber. The emission layer here always consists of at least one matrix material (host material) and an emitting dopant (emitter), which is admixed with the matrix material or matrix materials in a certain proportion by volume by co-evaporation. An expression such as IC1:M1:TEG1 (55%:35%:10%) here means that material IC1 is present in the layer in a proportion by
10 volume of 55%, M1 is present in the layer in a proportion of 35% and TEG1 is present in the layer in a proportion of 10%. Analogously, the electron-transport layer may also consist of a mixture of two materials.

15 The OLEDs are characterised by standard methods. For this purpose, the electroluminescence spectra, the current efficiency (CE1000, measured in cd/A at 1000 cd/m²), the luminous efficacy (LE1000, measured in lm/W at 1000 cd/m²), the external quantum efficiency (EQE1000, measured in % at 1000 cd/m²) and the voltage (U1000, measured at 1000 cd/m² in V) are determined from current/ voltage/luminance characteristic lines (IUL
20 characteristic lines) assuming a Lambertian emission profile. The electroluminescence (EL) spectra are recorded at a luminous density of 10³ (1000) cd/m² and the CIE 1931 x and y coordinates are then calculated from the EL spectrum.

25 For selected experiments, the lifetime is determined. The lifetime is defined as the time after which the luminous density has dropped to a certain proportion from a certain initial luminous density L₁ when the OLED is driven at a constant current. The starting condition L₀; j₀ = 4000 cd/m² and L₁ = 70% in Table 2 indicates that the in column LT denoted lifetime corresponds
30 to the time in hours (h) needed to fade the OLED from a starting luminous density of 4000 cd/m² to 2800 cd/m². Accordingly, the lifetime of the starting condition L₀; j₀ = 20mA/cm², L₁ = 80% is the time needed to fade the OLED operated at the constant current of 20mA/cm² to 80% of the initial luminous
35 density.

The device data of various OLEDs is summarized in Table 2. The examples V1-V7 are comparison examples according to the state-of-the-art using comparison compounds XXCE1 to XXCE7. The examples E1-E11 show data of inventive OLEDs using inventive examples Inv-1 to Inv-11.

5

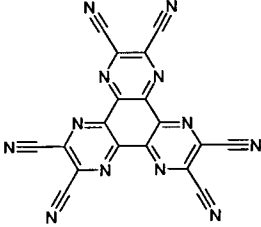
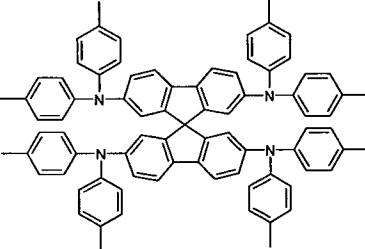
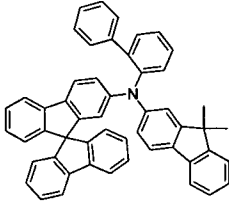
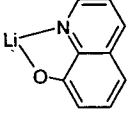
Table 1: OLED structure

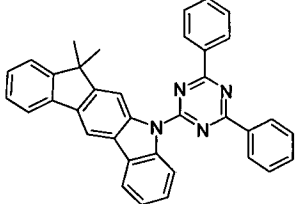
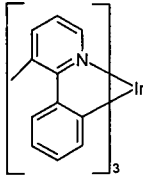
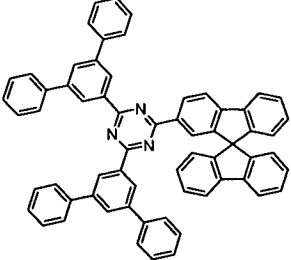
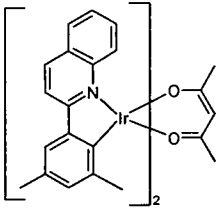
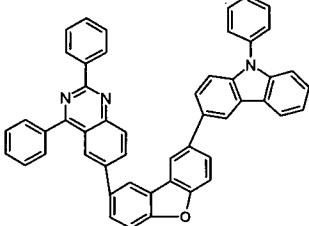
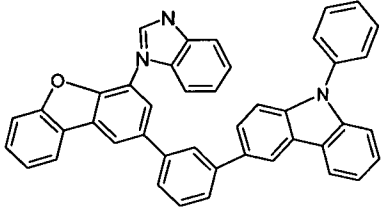
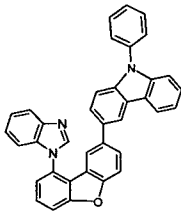
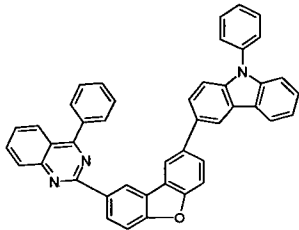
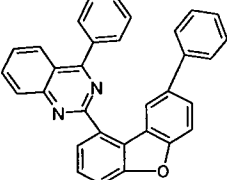
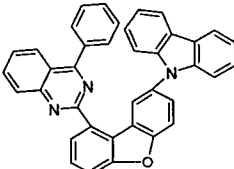
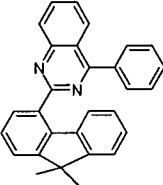
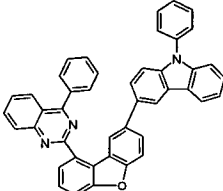
No.	HTL	IL	EBL	EML	HBL	ETL
V1	SpMA1 140nm	---	---	XXCE1:TER4 (95%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
V2	SpA1 70nm	HATCN 5nm	SpMA1 110nm	IC1:TEG1 (90%:10%) 30nm	XXCE2 10nm	ST2:LiQ (50%:50%) 30nm
V3	SpA1 70nm	HATCN 5nm	SpMA1 110nm	IC1:TEG1 (90%:10%) 30nm	XXCE3 10nm	ST2:LiQ (50%:50%) 30nm
V4	SpMA1 140nm	---	---	XXCE4:TER4 (95%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
V5	SpMA1 140nm	---	---	XXCE5:TER4 (95%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
V6	SpMA1 140nm	---	---	XXCE6:TER4 (95%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
V7	SpMA1 140nm	---	---	IC1:TER4 (95%:5%) 40nm	XXCE7 10nm	ST2:LiQ (50%:50%) 25nm
E1	SpMA1 140nm	---	---	Inv-1:TER4 (95%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
E2	SpMA1 140nm	---	---	Inv-2:TER4 (95%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
E3	SpMA1 140nm	---	---	Inv-3:TEG1:TER4 (80%:15%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
E4	SpMA1 140nm	---	---	Inv-4:SpMA1:TER4 (65%:30%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
E5	SpMA1 140nm	---	---	Inv-5:TEG1:TER4 (85%:10%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
E6	SpMA1 140nm	---	---	Inv-6:TER4 (97%:3%) 40nm	---	ST2:LiQ (50%:50%) 35nm
E7	SpMA1 140nm	---	---	Inv-7:TEG1:TER4 (85%:10%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
E8	SpMA1 140nm	---	---	Inv-8:TER4 (95%:5%) 40nm	---	ST2:LiQ (50%:50%) 35nm
E9	SpA1 70nm	HATCN 5nm	SpMA1 110nm	IC1:TEG1 (90%:10%) 30nm	Inv-9 10nm	ST2:LiQ (50%:50%) 30nm
E10	SpA1 70nm	HATCN 5nm	SpMA1 110nm	IC1:TEG1 (90%:10%) 30nm	---	Inv-10:LiQ (50%:50%) 30nm
E11	SpMA1 140nm	---	---	Inv-11:TER4 (97%:3%) 40nm	IC1 10nm	ST2:LiQ (50%:50%) 25nm

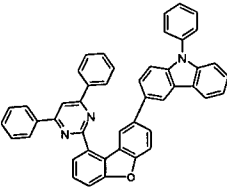
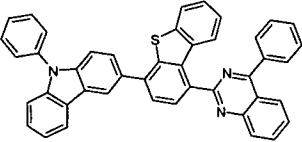
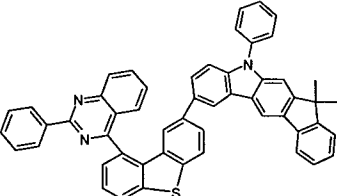
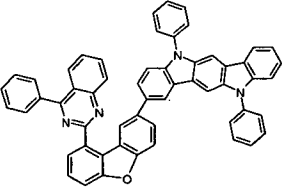
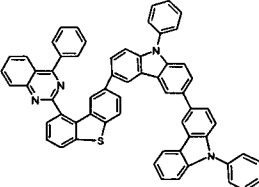
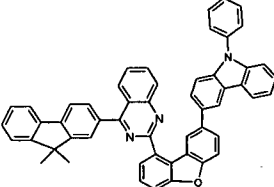
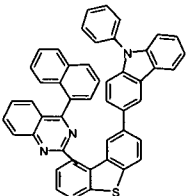
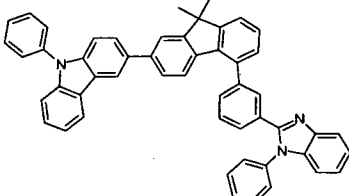
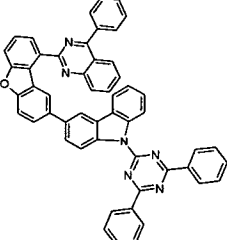
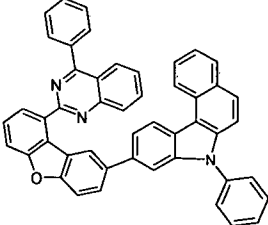
Table 2: OLED device data

Example	U1000 (V)	CE1000 (cd/A)	LE1000 (lm/W)	EQE 1000	CIE x/y at 10 ³ cd/m ²	Lo; jo	L ₁ %	LT (h)
V1	4.8	16.1	10.5	14.4%	0.67/0.33	20 mA/cm ²	80	740
V2	3.5	61	55	17.3%	0.33/0.62	20 mA/cm ²	80	120
V3	3.3	63	60	17.5%	0.32/0.63	20 mA/cm ²	80	125
V4	4.7	16.6	11.1	14.7%	0.67/0.33	20 mA/cm ²	80	870
V5	4.5	16.9	11.8	14.9%	0.66/0.34	20 mA/cm ²	80	820
V6	4.8	16.7	10.9	14.6%	0.66/0.34	20 mA/cm ²	80	770
V7	4.8	16.8	11.0	14.7%	0.66/0.33	20 mA/cm ²	80	1010
E1	4.7	16.7	11.2	14.8%	0.67/0.33	20 mA/cm ²	80	1120
E2	4.6	16.8	11.5	14.9%	0.67/0.33	20 mA/cm ²	80	900
E3	4.2	19.6	14.7	17.8%	0.67/0.33	20 mA/cm ²	80	1330
E4	4.4	17.4	12.4	15.6%	0.67/0.33	20 mA/cm ²	80	1170
E5	4.3	19.5	14.2	17.0%	0.66/0.34	20 mA/cm ²	80	1240
E6	4.6	17.0	11.6	15.0%	0.67/0.33	20 mA/cm ²	80	1090
E7	4.3	19.1	14.0	16.9%	0.67/0.33	20 mA/cm ²	80	1140
E8	4.7	16.5	11.0	14.6%	0.67/0.33	20 mA/cm ²	80	1020
E9	3.5	63	57	17.1%	0.33/0.63	20 mA/cm ²	80	135
E10	3.6	64	56	17.2%	0.33/0.63	20 mA/cm ²	80	115
E11	4.6	17.3	11.8	15.1%	0.66/0.34	20 mA/cm ²	80	1100

Table 3: Structures of OLED Materials

	
HATCN	SpA1
	
SpMA1	LiQ

	
<p>IC1</p>	<p>TEG1</p>
	
<p>ST2</p>	<p>TER4</p>
	
<p>XXCE1 (comp)</p>	<p>XXCE2 (comp)</p>
	
<p>XXCE3 (comp)</p>	<p>XXCE4 (comp)</p>
	
<p>XXCE5 (comp)</p>	<p>XXCE6 (comp)</p>
	
<p>XXCE7</p>	<p>Inv-1</p>

	
Inv-2	Inv-3
	
Inv-4	Inv-5
	
Inv-6	Inv-7
	
Inv-8	Inv-9
	
Inv-10	Inv-11

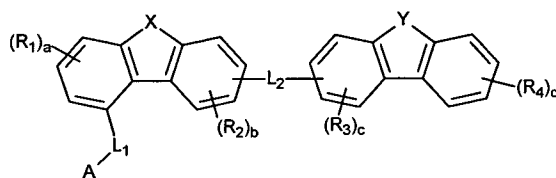
5

As can be seen in Table 2, OLEDs containing the compounds of the invention provide improved performance, without regard to whether it is located in the light-emitting layer as a host (i.e. E1-E8), in a hole-blocking layer (i.e. E9) or in an electron-transporting layer (i.e. E10). For example, inventive OLEDs E1, E2, E6 and E8, using inventive compounds as a host for a red phosphorescent emitter, are the same as comparative OLEDs V1 and V4-6 but have improved lifetime. In particular, comparison compound

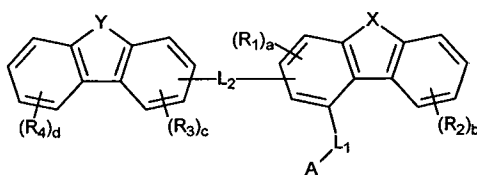
XXCE4 (V4), which has a diazine heterocycle in the 2-position, has a LT of 870 h. However, E1, which is identical to V4 except for using the inventive compound Inv-1, which is identical for XXCE4 except that the diazine is located in the 1-position, has a LT of 1120 h, for an improvement of 29%.
5 Likewise, E9, where an inventive compound is used as a host for a green phosphorescent emitter, shows better lifetime than V2 and V3. Even better results are seen when an inventive compound is used in more than one layer (i.e. E11) is compared to a comparative (i.e. V7) without the inventive
10 compound.

Patent Claims

1. A compound according to Formula (1) or (2):



Formula (1)



Formula (2)

where:

X is oxygen, sulfur or CZ₁Z₂;

Y is oxygen, sulfur, CZ₁Z₂ or NAr₁;

Z₁ and Z₂ are on each occurrence, identically or differently, H, D, F, a straight-chain alkyl, alkoxy or thioalkoxy group having 1 to 40 C atoms or a straight-chain alkenyl or alkynyl group having 2 to 40 C atoms or a branched or cyclic alkyl, alkenyl, alkynyl, alkoxy or thioalkoxy group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R₅, where one or more, preferably non-adjacent CH₂ groups may be replaced by (R₅)C=C(R₅), C≡C, Si(R₅)₂, Ge(R₅)₂, Sn(R₅)₂, C=O, C=S, C=Se, C=N(R₅), P(=O)(R₅), SO, SO₂, N(R₅)₂, O, S or CON(R₅)₂ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, or an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R₅, or an aryloxy or heteroaryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R₅, where Z₁ and Z₂ may be connected together to form a spiro ring system;

R₁, R₂, R₃ and R₄ is on each occurrence, identically or differently, selected from the group consisting of H, D, F, Cl, Br, I, CN, Si(R₅)₃, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl with 3-40 C atoms which may be substituted by one or more radicals R₅, wherein each one or more non-adjacent CH₂ groups by may be replaced Si(R₅)₂, C=NR₅, P(=O)(R₅), SO,

SO₂, NR₅, O, S or CONR₅ and where one or more H atoms may be replaced by D, F, Cl, Br or I, an aromatic or heteroaromatic ring system having 6 to 40 carbon atoms which may be substituted by one or more radicals R₅, an aryloxy group having 5 to 60 aromatic ring atoms which may be substituted by one or more radicals R₅, or an aralkyl group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R₅, where two or more adjacent substituents R₁, R₂, R₃ and R₄ can form a mono- or polycyclic, aliphatic, aromatic or heteroaromatic ring system with one another and which may be substituted with one or more radicals R₅;

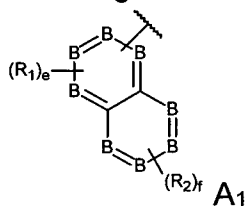
R₅ is selected from the group consisting of H, D, F, an aliphatic hydrocarbon radical having 1 to 20 carbon atoms or an aromatic or heteroaromatic ring system having 5 to 30 C atoms;

Ar₁ is an aromatic or heteroaromatic ring system having 5 to 30 aromatic ring atoms, which may be substituted by one or more radicals R₅ and where optionally two or more adjacent substituents R₅ can form a mono- or polycyclic, aliphatic, aromatic or heteroaromatic ring system with one another;

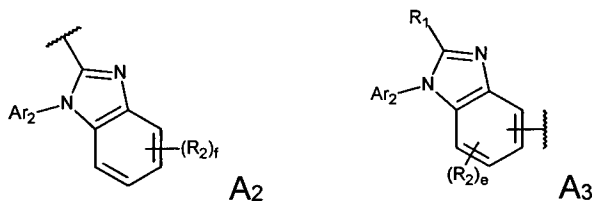
a, b, c are on each occurrence, identically or differently, are 0, 1, 2 or 3, where a is not 3 in Formula (2), and d is independently 0, 1, 2, 3 or 4;

L₁ and L₂ are on each occurrence, identically or differently, a direct bond or an aromatic or heteroaromatic ring system having 5-30 aromatic ring atoms, which may be substituted by one or more non-aromatic radicals R₅;

A is a heterocyclic group according to Formula A₁:



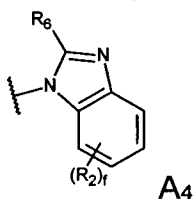
where only one or two of B are nitrogen atoms and the others are carbon atoms, R₁ and R₂ are as previously defined, e is 0, 1, 2 or 3, f is 0, 1, 2, 3 or 4, and wherein A₁ is connected to the remainder of the compound through a carbon atom; or A is a heterocyclic group selected from the group of Formula A₂ or A₃:



where R_1 , R_2 , e and f are as previously defined; and

Ar_2 is an aromatic or heteroaromatic ring system having 5 to 30 aromatic ring atoms, which may be substituted by one or more radicals R_5 and where optionally two or more adjacent substituents R_5 can form a mono- or polycyclic, aliphatic, aromatic or heteroaromatic ring system with one another;

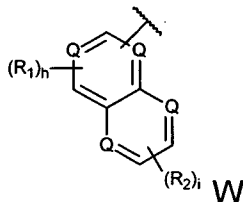
or A is a heterocyclic group according to A_4 :



where R_2 , e and f are as previously defined; and

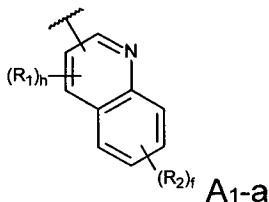
R_6 is the same as R_1 but excluding H or D.

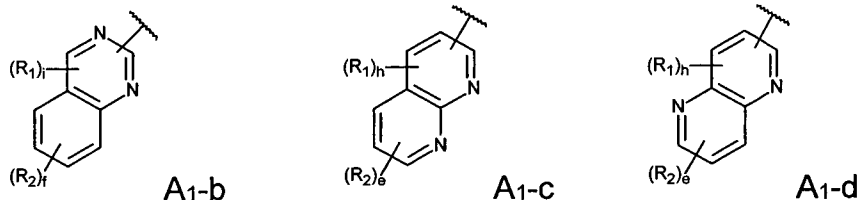
2. A compound according to claim 1 where A_1 is according to formula W:



where only one or two of Q are nitrogen atoms and the others are carbon atoms.

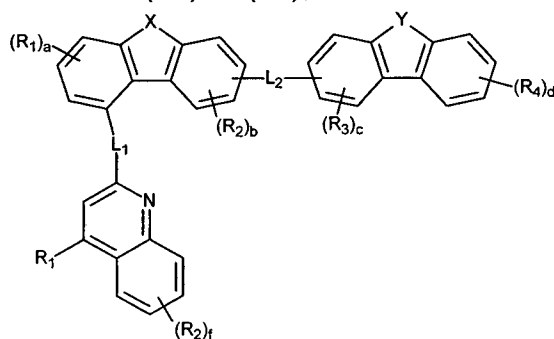
3. A compound according to claim 2 where one Q is nitrogen so that W group is according to A_1 -a or where two Q are nitrogen so that W is according to any of A_1 -b, A_1 -c and A_1 -d:



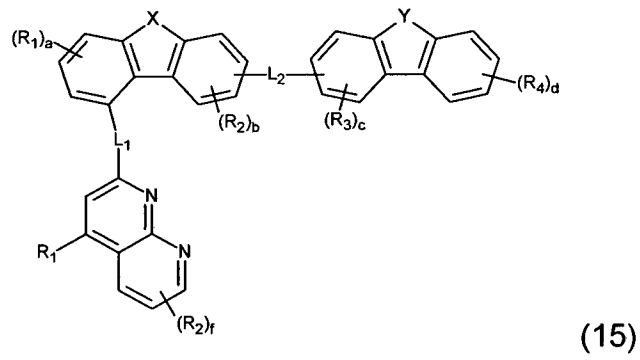
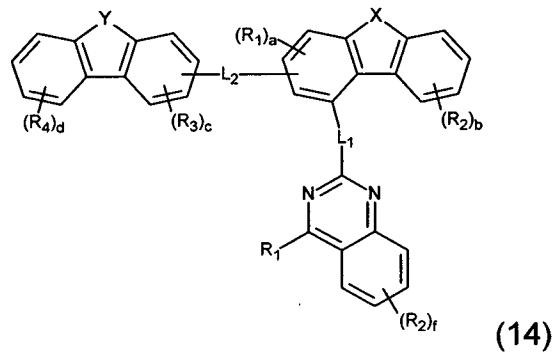
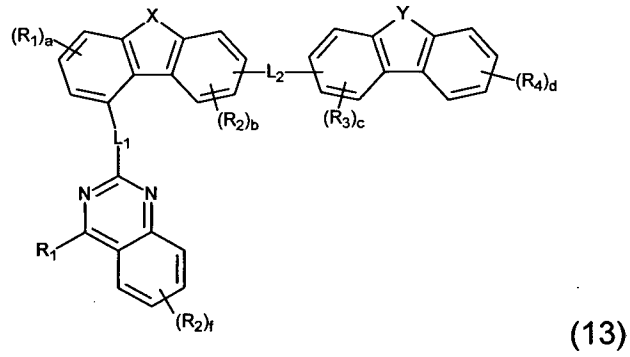
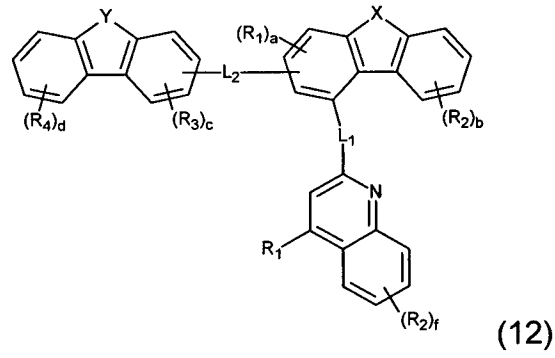


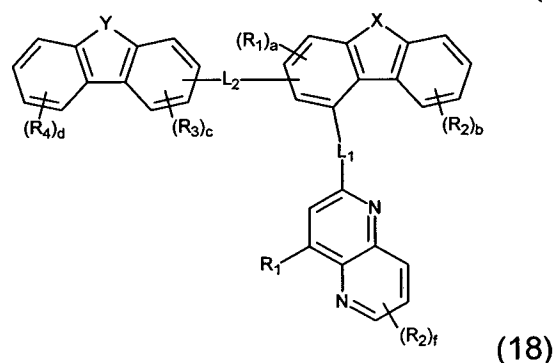
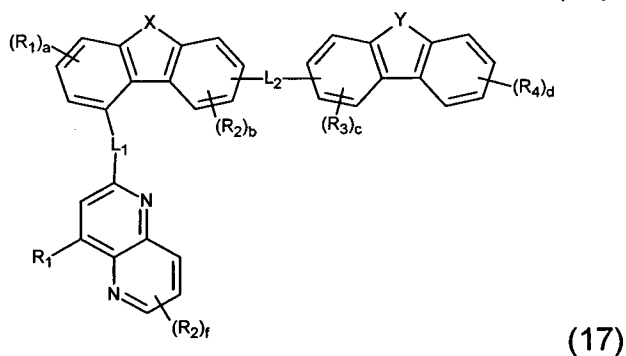
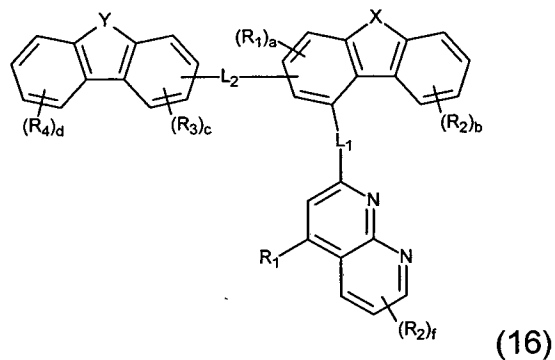
where the symbols and indices have the meanings as defined in claim 1.

- 5
4. A compound according to one or more of claims 1 to 3 where X is oxygen and Y is NAr₁.
5. A compound according to one or more of claims 1 to 4 where L₁ is a direct bond or a phenylene group.
- 10
6. A compound according to one or more of claims 1 to 5 where L₂ is a direct bond or a phenylene group.
7. A compound according to one or more of claims 1 to 6 where whenever X or Y is CZ₁Z₂, Z₁ and Z₂ are identical alkyl groups of 1-10 carbon atoms or aryl groups of between 6-30 carbon atoms.
- 15
8. A compound according to one or more of claims 1 to 7 where c is 0, d is 0 or 2 and when d is 2, the two R₄ groups are adjacent and form a monocyclic- or polycyclic, aromatic or heteroaromatic annulated ring system.
- 20
9. A compound according to one or more of claims 1 to 8 according to any one of Formulae (11) to (18);



(11)





where the symbols and indices are defined as in claim 1.

5

10. A compound according to one or more of claims 1 to 9, characterised in that it contains no condensed aryl or heteroaryl groups in which more than two six-membered rings are condensed directly onto one another.

10

11. An oligomer, polymer or dendrimer containing one or more of the compounds according to one or more of claims 1 to 10, where one or more bonds from the compound to the polymer, oligomer or dendrimer are present instead of substituents at one or more positions.

15

12. A formulation comprising at least one compound according to one or more of claims 1 to 10 or an oligomer, polymer or dendrimer according to claim 11 and at least one solvent.
- 5 13. The use of a compound according to one or more of claims 1 to 10 or an oligomer, polymer or dendrimer according to claim 11 in an electronic device.
- 10 14. An electronic device comprising at least one compound according to one or more of claims 1 to 10 or an oligomer, polymer or dendrimer according to claim 11, in particular selected from the group consisting of organic electroluminescent devices, organic integrated circuits, organic field-effect transistors, organic thin-film transistors, organic light-emitting transistors, organic solar cells, dye-sensitised organic solar cells, organic optical detectors, organic photoreceptors, organic field-quench devices, light-emitting electrochemical cells, organic laser diodes and organic plasmon emitting devices.
- 15
- 20 15. An electronic device according to claim 14, which is an organic electroluminescent device, characterised in that the compound according to one or more of claims 1 to 10 or claim 11 is employed as matrix material for phosphorescent or fluorescent emitters and/or in an electron-blocking or exciton-blocking layer and/or in a hole-transport layer and/or in a hole-blocking layer and/or in a hole-blocking or
- 25 electron-transport layer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/000834

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C07D405/14 C07D407/14 C07D409/14 C07D403/14 H01L27/32
 H01L51/54
 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 H01L
 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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 2015 0012835 A (DUKSAN HI-METAL CO., LTD., S. KOREA) 4 February 2015 (2015-02-04) paragraph [0095]; compounds P-17, P-18, P19 claims 1-4 -----	1-15
X	JP 2013 131518 A (KONICA MINOLTA INC) 4 July 2013 (2013-07-04) page 36; compound 12 claim 1 -----	1-15
X	KR 2012 0033017 A (ROHM & HAAS ELECT MATERIALS [KR]) 6 April 2012 (2012-04-06) cited in the application paragraph [0039]; compounds 27, 28 claim 1 -----	1-15
	-/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>
---	---

Date of the actual completion of the international search 9 August 2016	Date of mailing of the international search report 16/08/2016
---	---

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Samsam Bakhtiary, M
--	--

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/000834

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/067425 A1 (ROHM & HAAS ELECT MATERIALS [KR]; SHIN HYO NIM [KR]; KIM CHI SIK [KR];) 24 May 2012 (2012-05-24) cited in the application claims 1,5 -----	1-15
A	WO 2013/187689 A1 (ROHM & HAAS ELECT MATERIALS [KR]) 19 December 2013 (2013-12-19) cited in the application claims 1,5 -----	1-15
A	WO 2012/036482 A1 (ROHM & HAAS ELECT MATERIALS [KR]; SHIN HYO NIM [KR]; HWANG SOO-JIN [KR]) 22 March 2012 (2012-03-22) cited in the application claims 1,3,5 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2016/000834

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 20150012835 A	04-02-2015	NONE	
JP 2013131518 A	04-07-2013	JP 5857724 B2	10-02-2016
		JP 2013131518 A	04-07-2013
KR 20120033017 A	06-04-2012	NONE	
WO 2012067425 A1	24-05-2012	CN 103313979 A	18-09-2013
		CN 104356137 A	18-02-2015
		EP 2640726 A1	25-09-2013
		JP 2014503497 A	13-02-2014
		KR 20120052879 A	24-05-2012
		TW 201229202 A	16-07-2012
		US 2014077179 A1	20-03-2014
		WO 2012067425 A1	24-05-2012
WO 2013187689 A1	19-12-2013	CN 104364345 A	18-02-2015
		EP 2841527 A1	04-03-2015
		JP 2015527972 A	24-09-2015
		KR 20130139535 A	23-12-2013
		TW 201406924 A	16-02-2014
		US 2015133662 A1	14-05-2015
		WO 2013187689 A1	19-12-2013
WO 2012036482 A1	22-03-2012	CN 103221406 A	24-07-2013
		EP 2616462 A1	24-07-2013
		JP 2013539750 A	28-10-2013
		KR 20120030009 A	27-03-2012
		TW 201224110 A	16-06-2012
		WO 2012036482 A1	22-03-2012