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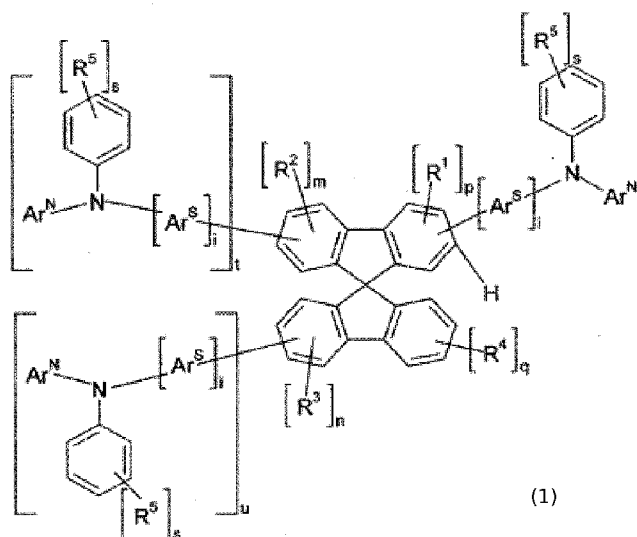
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(54) Title: MATERIALS FOR ORGANIC ELECTROLUMINESCENT DEVICES

(57) Abstract: The present invention relates to compounds of the formula (1) which are suitable for use in electronic devices, in particular organic electroluminescent devices, and to electronic devices which comprise these compounds.



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Materials for organic electroluminescent devices

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

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The structure of organic electroluminescent devices (OLEDs) in which organic semiconductors are employed as functional materials is described, for example, in US 4,539,507, US 5,151,629, EP 0676461 and WO 10 98/27136. The emitting materials employed here are increasingly organo-metallic complexes which exhibit phosphorescence instead of fluorescence (M. A. Baldo *et al.*, *Appl. Phys. Lett.* **1999**, *75*, 4-6).

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In accordance with the prior art, the hole-transport materials used in the hole-transport layer or in the hole-injection layer are, in particular, triarylamine derivatives which frequently contain at least two triarylamino groups or at least one triarylamino group and at least one carbazole group. These compounds are frequently derived from diarylamino-substituted triphenylamines (TPA type), from diarylamino-substituted biphenyl derivatives (TAD type) or combinations of these base compounds. Furthermore, for example, use is made of spirobifluorene derivatives which are substituted by one to four diarylamino groups (for example in accordance with EP 20 676461, US 7,714,145 or EP2814906). In the case of these compounds, there is furthermore a need for improvement both in the case of fluorescent and in the case of phosphorescent OLEDs, in particular with respect to efficiency, lifetime and operating voltage on use in an organic 25 electroluminescent device.

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The object of the present invention is to provide compounds which are suitable for use in a fluorescent or phosphorescent OLED, in particular a phosphorescent OLED, for example as hole-transport material in a hole-

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transport or exciton-blocking layer or as matrix material in an emitting layer.

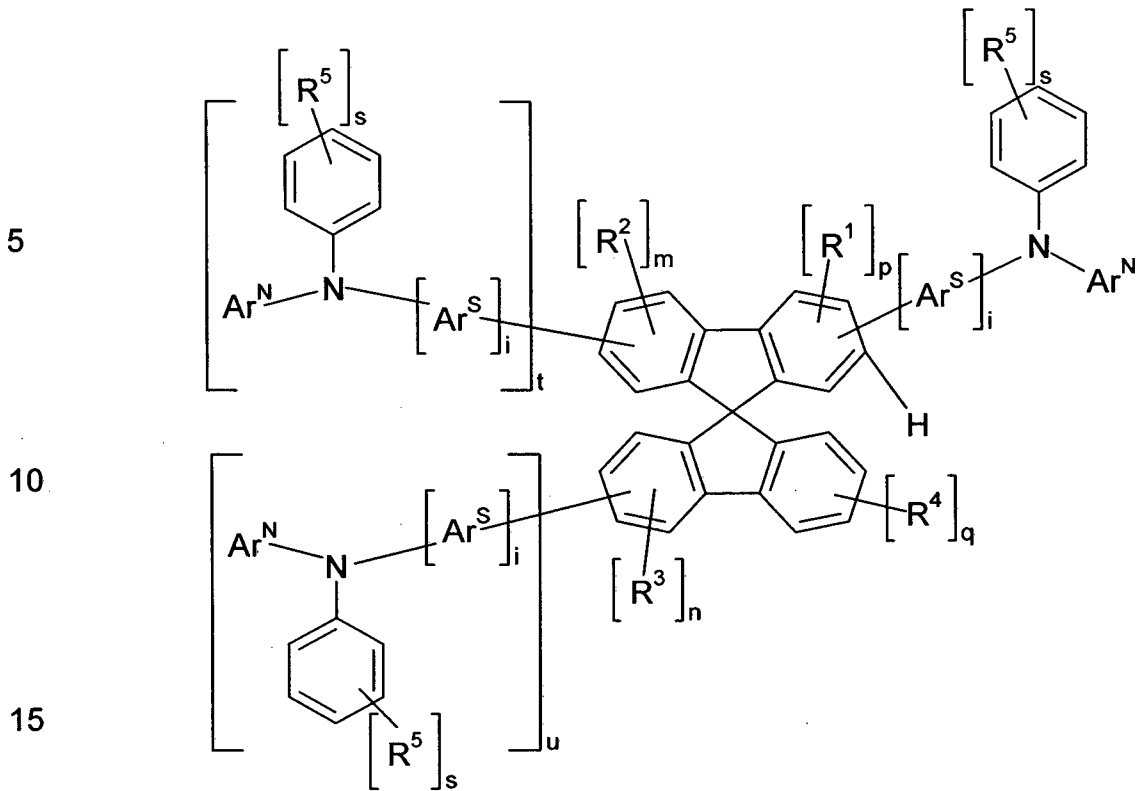
5 It has now been found that certain compounds described below in greater detail achieve this object and result in significant improvements in the organic electroluminescent device, in particular with respect to the lifetime, the efficiency and the operating voltage. This applies to phosphorescent and fluorescent electroluminescent devices, especially on use of the
10 compounds according to the invention as hole-transport material or as matrix material. Furthermore, the compounds described below contain a rigid planar Spiro unit and flexible structure elements in the outer periphery, whereby the flexibility of the molecule center is reduced and the solubility is increased by the substituents. Additionally, the compounds
15 described below exhibit an improved oxidation stability in solutions in comparison with conventional diamines compounds. This leads to an easier cleaning and second to an easier handling of these compounds. More particularly, the storage stability of solutions for printing processes, which comprise these compounds, is significantly improved. Finally, the
20 compounds of the present invention generally have high thermal stability and can therefore be sublimed without decomposition and without a residue. The present invention therefore relates to these compounds and to electronic devices which comprise compounds of this type.

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The present invention therefore relates to a compound of the following formula (1):

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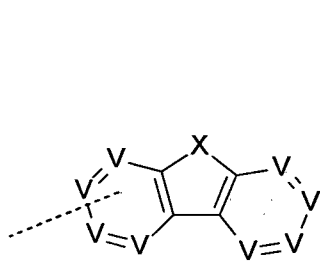


formula (1)

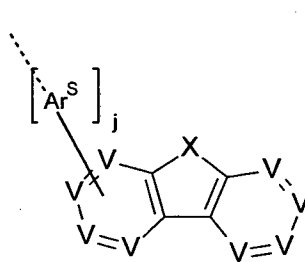
20 where the following applies to the symbols and indices used:

Ar^N is a group of one of the following formulae (2-1) to (2-3)

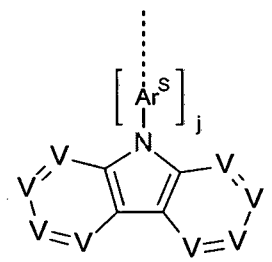
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30 formula (2-1)



formula (2-2)



formula (2-3)

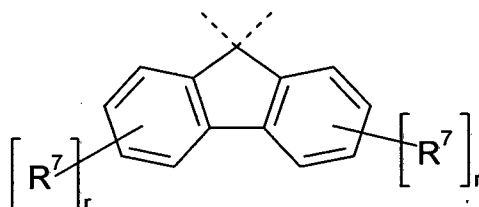
35 V is, identically or differently, equal to CR^6 or N ; with the proviso that when the bonding to a nitrogen atom depicted in formula (1) takes place via a group V , then V stands for a C atom; and

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where the dashed bonds indicate the bonding to a nitrogen atom depicted in formula (1);

X is a divalent bridge selected from the group consisting of B(R⁰), C(R⁰)₂, Si(R⁰)₂, C=O, C=NR⁰, C=C(R⁰)₂, O, S, S=O, SO₂, N(R⁰), P(R⁰) and P(=O)R⁰;

or X is a group of the following formula (3),



formula (3)

where the dashed bonds indicate the bonding to the 5-membered ring of formula (2-1) or (2-2);

R⁰ is selected on each occurrence, identically or differently, from the group consisting of H, D, F, Cl, Br, I, CHO, CN, C(=O)Ar¹, P(=O)(Ar¹)₂, S(=O)Ar¹, S(=O)₂Ar¹, NO₂, Si(R⁸)₃, B(OR⁸)₂, OSO₂R⁸, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R⁸, where in each case one or more non-adjacent CH₂ groups may be replaced by R⁸C=CR⁸, C≡C, Si(R⁸)₂, Ge(R⁸)₂, Sn(R⁸)₂, C=O, C=S, C=Se, P(=O)(R⁸), SO, SO₂, O, S or CONR⁸ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, an aromatic or heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may in each case be substituted by one or more radicals R⁸, an aryloxy group having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R⁸, where two

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substituents R^0 attached to the same C or Si atom may optionally form a mono- or polycyclic aliphatic ring system, which may be substituted by one or more radicals R^8 ; with the proviso that when two R^0 are attached to the same C atom, then at least one R^0 is selected from the group consisting of H, D, F, CN, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R^8 .

R^1 , R^2 , R^3 , R^4 , R^6 or R^7 are selected on each occurrence, identically or differently, from the group consisting of H, D, F, Cl, Br, I, CHO, CN, $C(=O)Ar^1$, $P(=O)(Ar^1)_2$, $S(=O)Ar^1$, $S(=O)_2Ar^1$, NO_2 , $Si(R^8)_3$, $B(OR^8)_2$, OSO_2R^8 , a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R^8 , where in each case one or more non-adjacent CH_2 groups may be replaced by $R^8C=CR^8$, $C\equiv C$, $Si(R^8)_2$, $Ge(R^8)_2$, $Sn(R^8)_2$, $C=O$, $C=S$, $C=Se$, $P(=O)(R^8)$, SO , SO_2 , O, S or $CONR^8$ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 , an aromatic or heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may in each case be substituted by one or more radicals R^8 , an aryloxy group having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^8 , where two or more adjacent substituents R^1 , two or more adjacent substituents R^2 , two or more adjacent substituents R^3 , two or more adjacent substituents R^4 , two or more adjacent substituents R^6 or two or more adjacent substituents R^7 may optionally form a mono- or polycyclic, aliphatic ring system or aromatic ring system, which may be substituted by one or more radicals R^8 ;

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R^5 is selected on each occurrence, identically or differently, from the group consisting of H, D, F, Cl, Br, I, CHO, CN, C(=O)Ar¹, P(=O)(Ar¹)₂, S(=O)Ar¹, S(=O)₂Ar¹, NO₂, Si(R⁸)₃, B(OR⁸)₂, OSO₂R⁸, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R⁸, where in each case one or more non-adjacent CH₂ groups may be replaced by R⁸C=CR⁸, C≡C, Si(R⁸)₂, Ge(R⁸)₂, Sn(R⁸)₂, C=O, C=S, C=Se, P(=O)(R⁸), SO, SO₂, O, S or CONR⁸ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, where two or more adjacent substituents R⁵ may optionally form a mono- or polycyclic aliphatic ring system, which may be substituted by one or more radicals R⁸;

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R^8 is selected on each occurrence, identically or differently, from the group consisting of H, D, F, Cl, Br, I, CN, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, where in each case one or more non-adjacent CH₂ groups may be replaced by SO, SO₂, O, S 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 60 C atoms, where two or more adjacent substituents R⁸ may optionally form a mono- or polycyclic, aliphatic ring system;

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Ar¹, Ar^S are on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may in each case also be substituted by one or more radicals R⁸;

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t, u are, identically or differently, 0 or 1;

m, n, q, r are, identically or differently, 0, 1, 2, 3 or 4, where $t + m \leq 4$ and $u + n \leq 4$;

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p is 0, 1 or 2;

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i is 0, 1 or 2, wherein $i = 0$ or $j = 0$ means that the group Ar^s is absent and replaced by a single bond;

j is 1, 2 or 3;

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s is 0, 1, 2, 3, 4 or 5.

For the purposes of the present application, the following definitions of chemical groups apply:

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An aryl group in the sense of this invention contains 6 to 60 aromatic ring atoms; a heteroaryl group in the sense of this invention contains 5 to 60 aromatic ring atoms, at least one of which is a heteroatom. The heteroatoms are preferably selected from N, O and S. This represents the basic definition. If other preferences are indicated in the description of the present invention, for example with respect to the number of aromatic ring atoms or the heteroatoms present, these apply.

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An aryl group or heteroaryl group here is taken to mean either a simple aromatic ring, i.e. benzene, or a simple heteroaromatic ring, for example pyridine, pyrimidine or thiophene, or a condensed (annellated) aromatic or heteroaromatic polycycle, for example naphthalene, phenanthrene, quinoline or carbazole. A condensed (annellated) aromatic or heteroaromatic polycycle in the sense of the present application consists of two or more simple aromatic or heteroaromatic rings condensed with one another.

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An aryl or heteroaryl group, which may in each case be substituted by the above-mentioned radicals and which may be linked to the aromatic or heteroaromatic ring system via any desired positions, is taken to mean, in particular, groups derived from benzene, naphthalene, anthracene, phenanthrene, pyrene, dihydropyrene, chrysene, perylene, fluoranthene, benzanthracene, benzophenanthrene, tetracene, pentacene, benzopyrene, furan, benzofuran, isobenzofuran, dibenzofuran, thiophene, benzothiophene, isobenzothiophene, dibenzothiophene, pyrrole, indole, isoindole, carbazole, 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, quinoxalinimidazole, oxazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, benzothiazole, pyridazine, benzopyridazine, pyrimidine, benzopyrimidine, quinoxaline, pyrazine, phenazine, 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.

An aryloxy group in accordance with the definition of the present invention is taken to mean an aryl group, as defined above, which is bonded via an oxygen atom. An analogous definition applies to heteroaryloxy groups.

An aromatic ring system in the sense of this invention contains 6 to 60 C atoms in the ring system. A heteroaromatic ring system in the sense of this invention contains 5 to 60 aromatic ring atoms, at least one of which is a heteroatom. The heteroatoms are preferably selected from N, O and/or S. An aromatic or heteroaromatic ring system in the sense of this invention is

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intended to be taken to mean a system which does not necessarily contain only aryl or heteroaryl groups, but instead in which, in addition, a plurality of aryl or heteroaryl groups may be connected by a non-aromatic unit (preferably less than 10% of the atoms other than H), such as, for example, an sp^3 -hybridised C, Si, N or O atom, an sp^2 -hybridised C or N atom or an sp -hybridised C atom. Thus, for example, systems such as 9,9'-spirobifluorene, 9,9'-diarylfluorene, triarylamine, diaryl ether, stilbene, etc., are also intended to be taken to be aromatic ring systems in the sense of this invention, as are systems in which two or more aryl groups are connected, for example, by a linear or cyclic alkyl, alkenyl or alkynyl group or by a silyl group. Furthermore, systems in which two or more aryl or heteroaryl groups are linked to one another via single bonds are also taken to be aromatic or heteroaromatic ring systems in the sense of this invention, such as, for example, systems such as biphenyl, terphenyl or diphenyltriazine.

An aromatic or heteroaromatic ring system having 5 - 60 aromatic ring atoms, which may in each case also be substituted by radicals as defined above and which may be linked to the aromatic or heteroaromatic group via any desired positions, is taken to mean, in particular, groups derived from benzene, naphthalene, anthracene, benzanthracene, phenanthrene, benzophenanthrene, pyrene, chrysene, perylene, fluoranthene, naphthalene, pentacene, benzopyrene, biphenyl, biphenylene, terphenyl, terphenylene, quaterphenyl, fluorene, spirobifluorene, dihydrophenanthrene, dihydropyrene, tetrahydropyrene, cis- or trans-indenofluorene, 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, quinoxalinimidazole, oxazole, benzoxazole, naphthoxazole, anthroxazole,

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phenanthroxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, benzothiazole, pyridazine, benzopyridazine, pyrimidine, benzopyrimidine, quinoxaline, 1,5-diazaanthracene, 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, or combinations of these groups.

For the purposes of the present invention, a straight-chain alkyl group having 1 to 40 C atoms or a branched or cyclic alkyl group having 3 to 40 C atoms or an alkenyl or alkynyl group having 2 to 40 C atoms, in which, in addition, individual H atoms or CH₂ groups may be substituted by the groups mentioned above under the definition of the radicals, is preferably taken to mean the radicals methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, 2-methylbutyl, n-pentyl, s-pentyl, cyclopentyl, neopentyl, n-hexyl, cyclohexyl, neohexyl, n-heptyl, cycloheptyl, n-octyl, cyclooctyl, 2-ethylhexyl, trifluoromethyl, pentafluoroethyl, 2,2,2-trifluoroethyl, ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl, cycloheptenyl, octenyl, cyclooctenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl or octynyl. An alkoxy or thioalkyl 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, 2,2,2-trifluoroethoxy, 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-trifluoro-

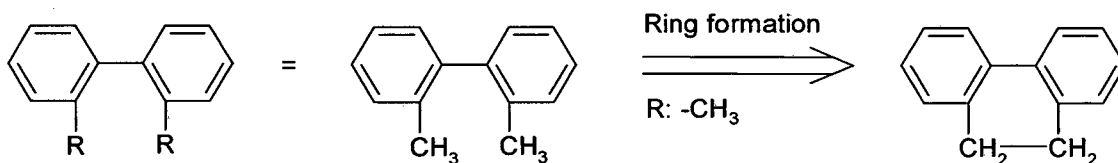
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ethylthio, ethenylthio, propenylthio, butenylthio, pentenylthio, cyclopentenylthio, hexenylthio, cyclohexenylthio, heptenylthio, cycloheptenylthio, octenylthio, cyclooctenylthio, ethynylthio, propynylthio, butynylthio, pentynylthio, hexynylthio, heptynylthio or octynylthio.

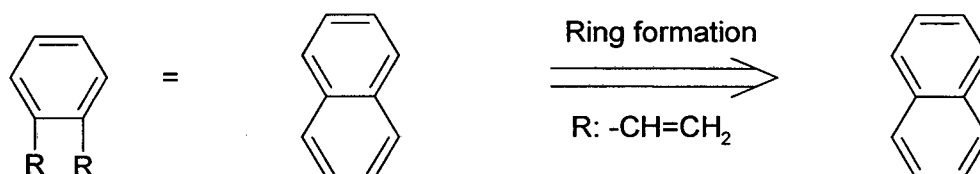
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The formulation that two or more radicals may form a ring with one another is, for the purposes of the present application, intended to be taken to mean, inter alia, that the two radicals are linked to one another by a chemical bond. This is illustrated by the following schemes:

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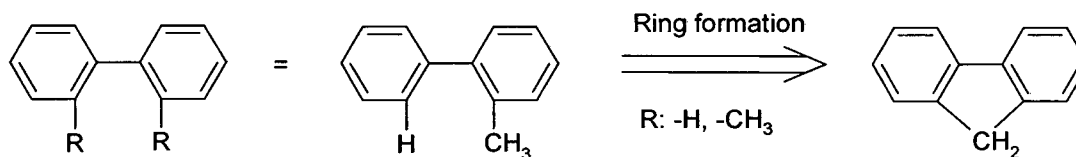
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Furthermore, however, the above-mentioned formulation is also intended to be taken to mean that, in the case where one of the two radicals represents hydrogen, the second radical is bonded at the position to which the hydrogen atom was bonded, with formation of a ring. This is illustrated by the following scheme:

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In accordance with a preferred embodiment, there is a maximum of two groups V per 6-membered ring that stand for N in formula (2-1), (2-2) and (2-3). More preferably, there is maximum one group V per 6-membered

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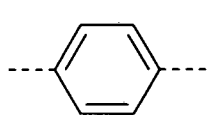
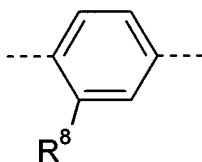
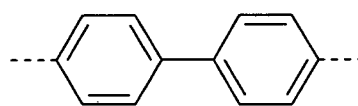
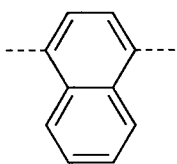
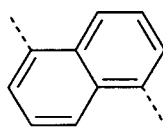
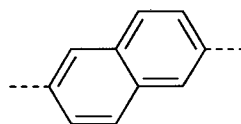
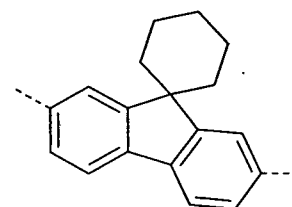
ring that stands for N in formula (2). More particularly preferably, V stands for CR^6 or C if it is bonded to a nitrogen atom depicted in formula (1).

According to a preferred embodiment, $t + u = 0$ or 1. More preferably, $t + u = 0$.

It is furthermore preferred that the index i is equal to 0.

The group Ar^S is preferably, identically or differently on each occurrence, selected from aromatic or heteroaromatic ring systems having 6 to 18 aromatic ring atoms, which may in each case also be substituted by one or more radicals R^8 .

Particularly preferable groups Ar^S are selected from the groups of formulae (Ar^S -1) to (Ar^S -15) below:

Ar^S-1Ar^S-2Ar^S-3Ar^S-4Ar^S-5Ar^S-6Ar^S-7

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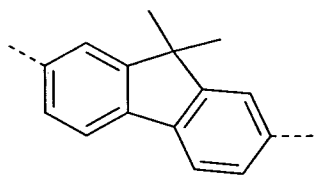
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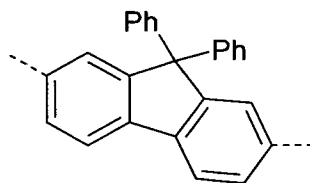
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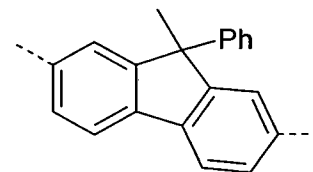
- 13 -



Ar^S-8

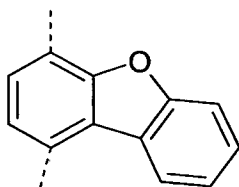


Ar^S-9

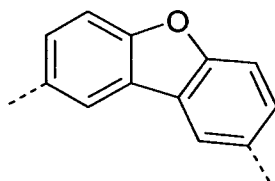


Ar^S-10

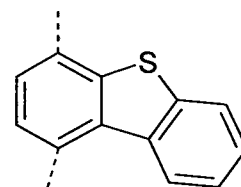
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Ar^S-11



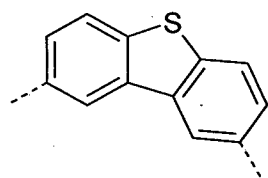
Ar^S-12



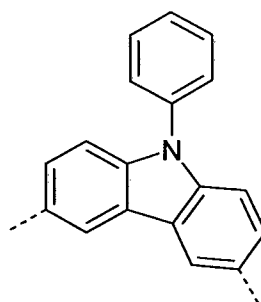
Ar^S-13

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Ar^S-14



Ar^S-15

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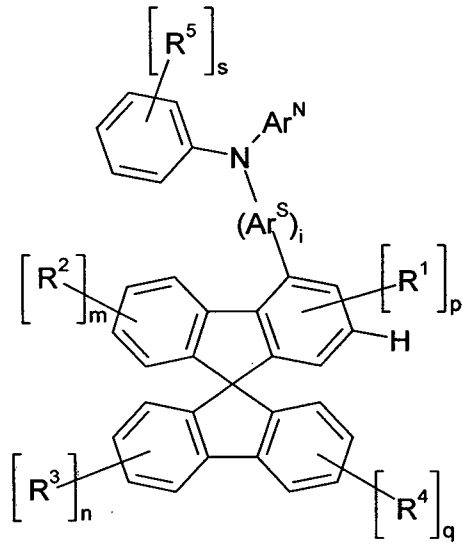
where the dashed bonds indicates the bonds to the spirobifluorene and to the amine, and where the groups may be substituted at each free position by a group R⁸ but are preferably unsubstituted.

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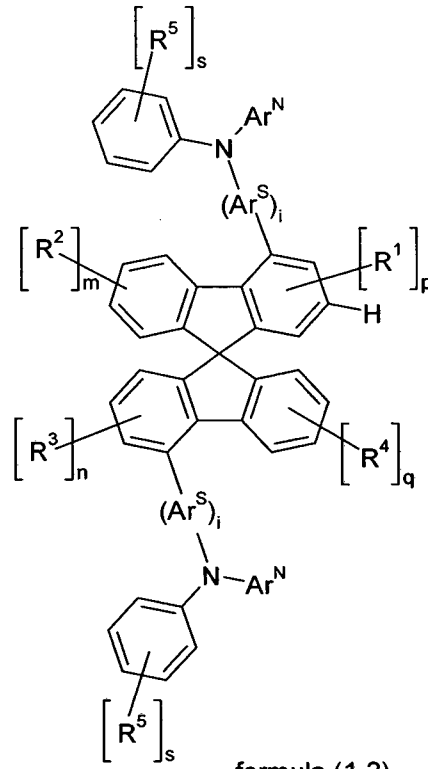
In a preferred embodiment of the invention, the compound of the formula (1) is selected from the compounds of the following formulae (1-1) to (1-9),

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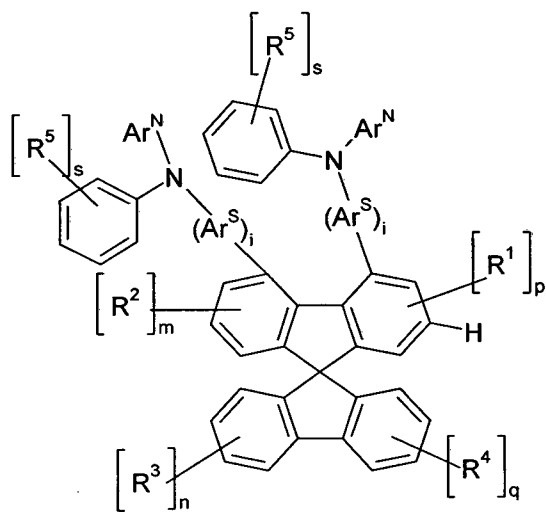


formula (1-1)

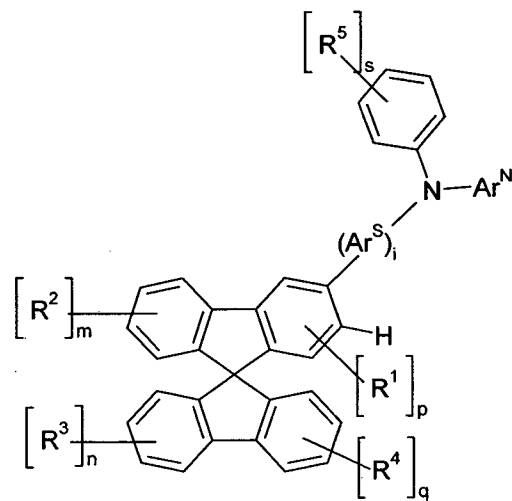


formula (1-2)

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formula (1-3)

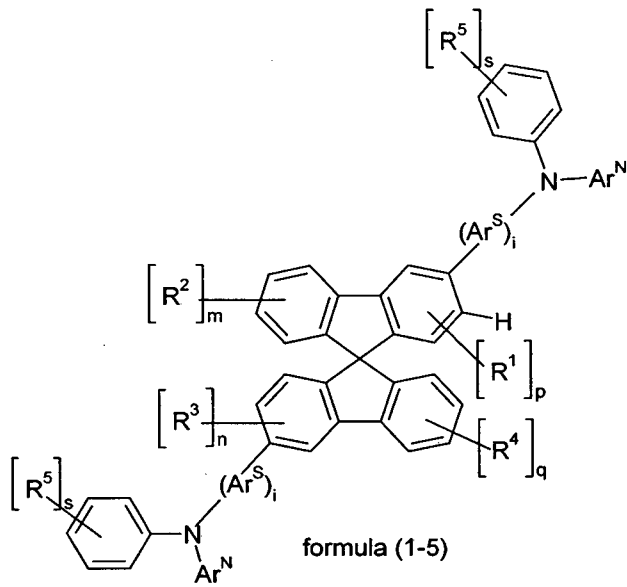


formula (1-4)

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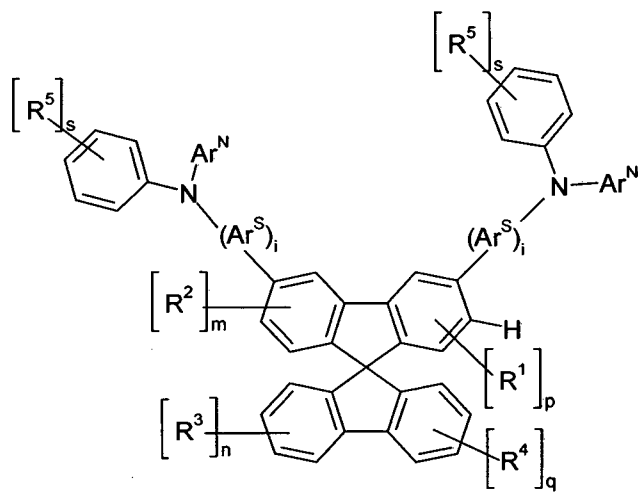
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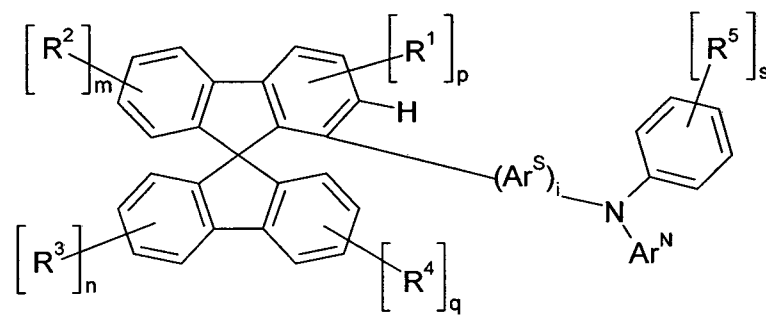
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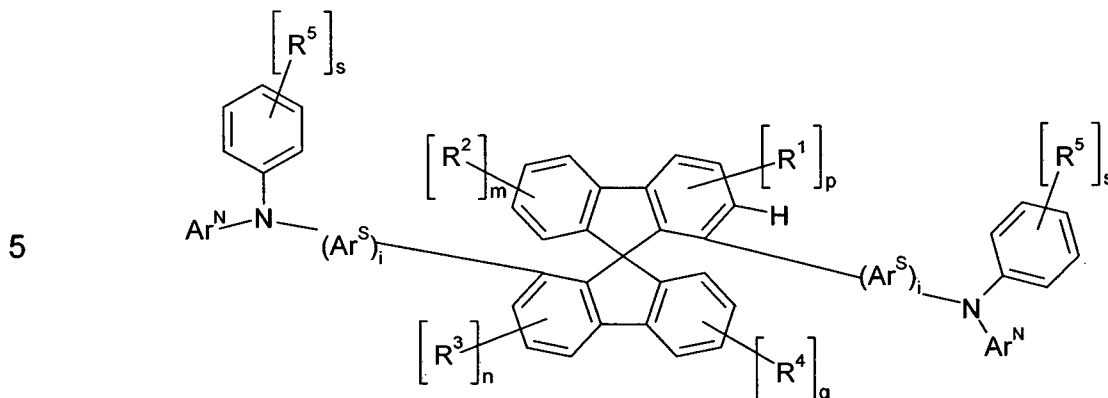


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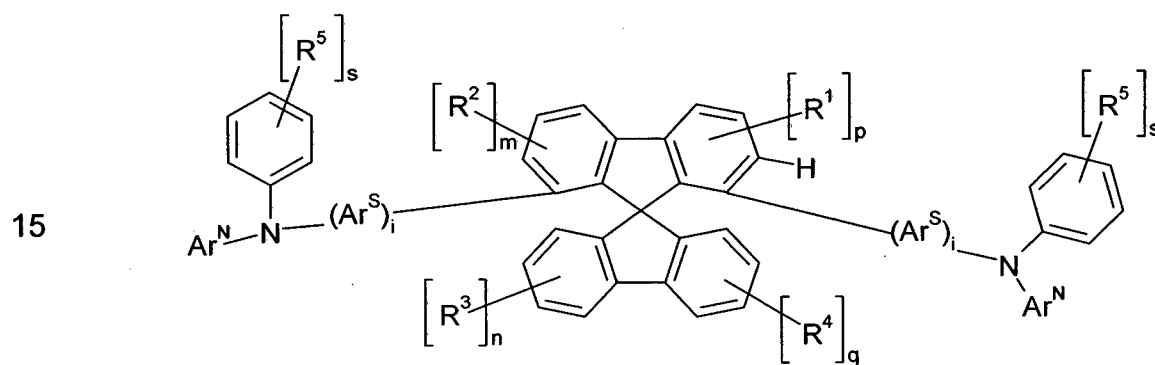


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formula (1-8)

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formula (1-9)

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where the symbols and indices used have the same meanings as indicated above.

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Furthermore, for the compounds of formulae (1-1) to (1-9), it is preferred that $i = 0$.

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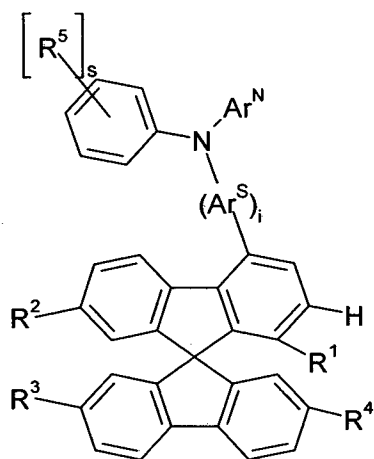
In a particularly preferred embodiment of the invention, the compounds of formulae (1-1) to (1-9) are selected from the compounds of the following formulae (1-1a) to (1-9a),

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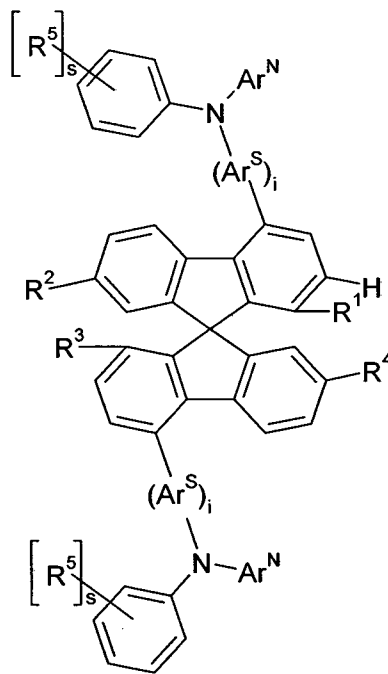
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formula (1-1a)

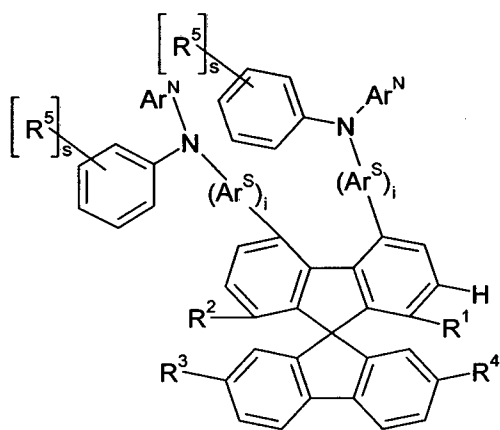


formula (1-2a)

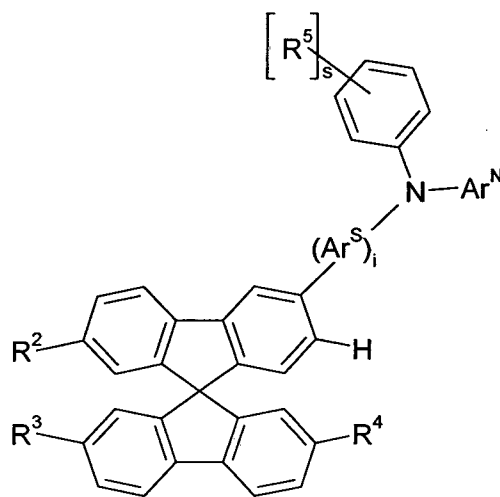
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formula (1-3a)

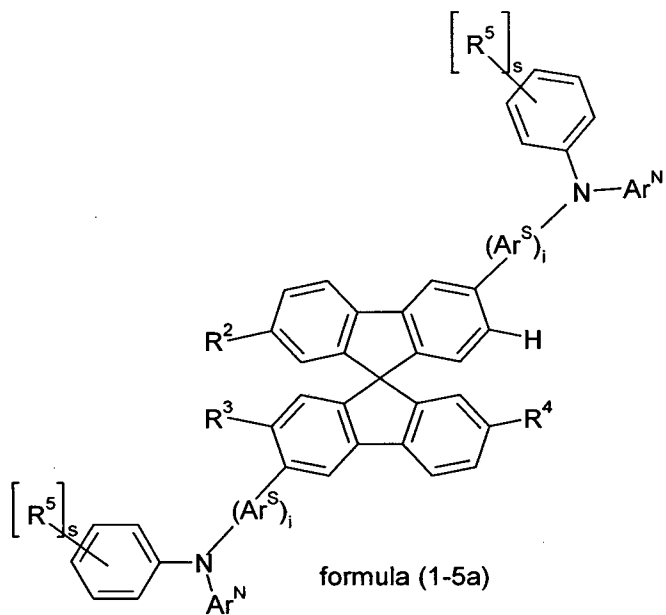


formula (1-4a)

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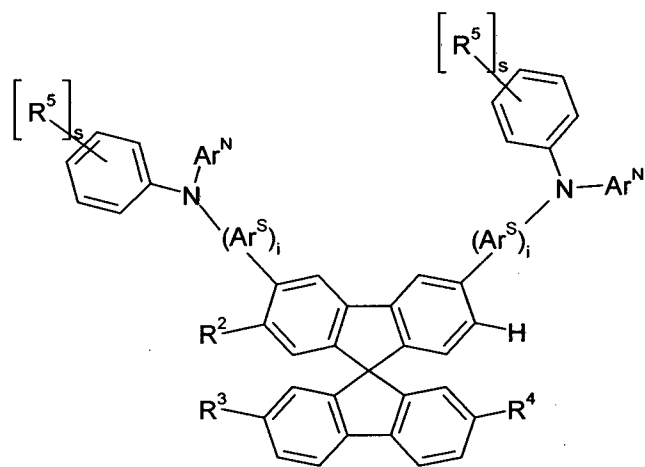
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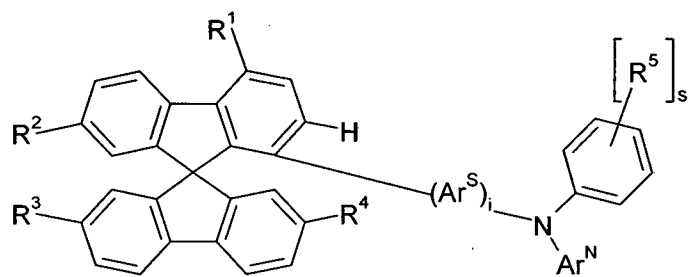
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formula (1-6a)

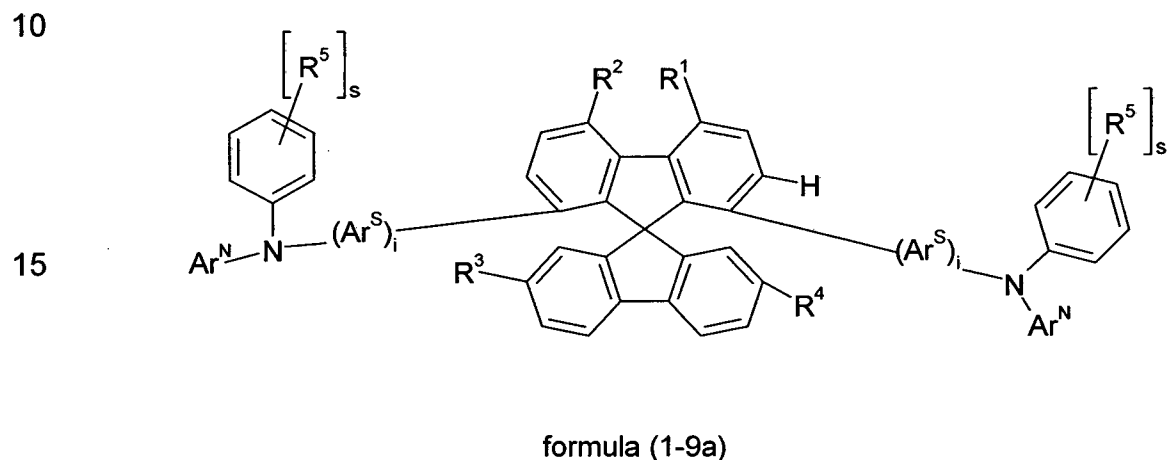
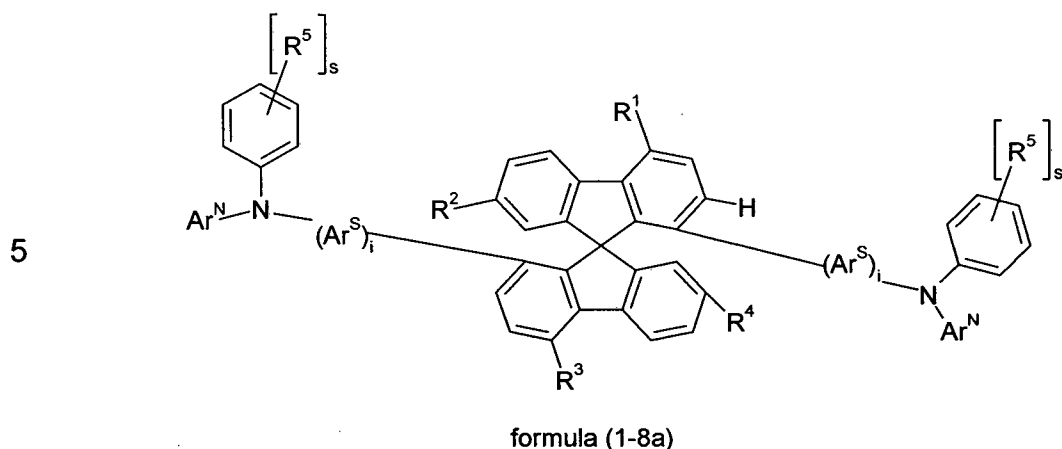
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formula (1-7a)

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- 19 -



20 where the symbols and indices used have the meanings as indicated above.

For the compounds of formulae (1-1a) to (1-1b) above, it is preferred that i is equal to 0.

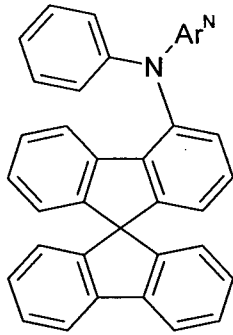
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In a very particularly preferred embodiment of the invention, the compounds of formulae (1-1a) to (1-9a) are selected from the compounds of the following formulae (1-1b) to (1-9b),

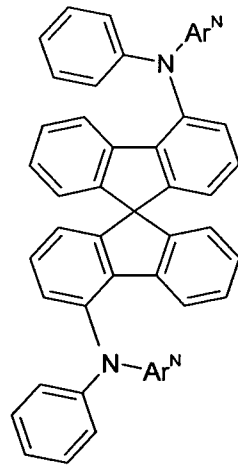
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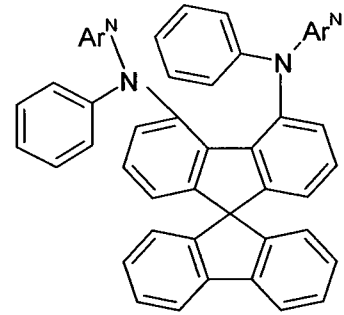
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formula (1-1b)



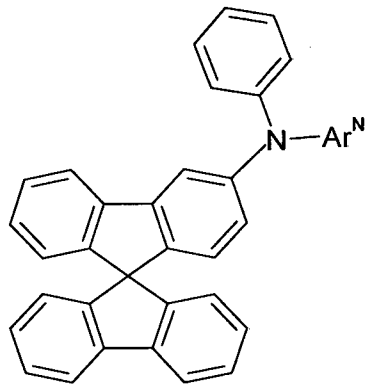
formula (1-2b)



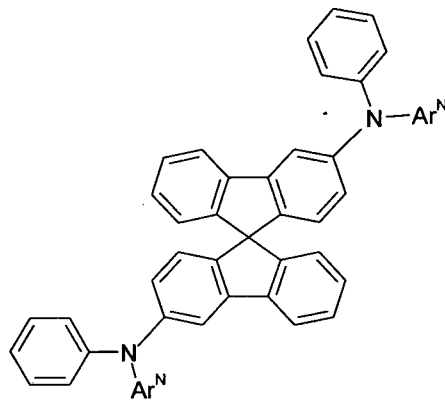
formula (1-3b)

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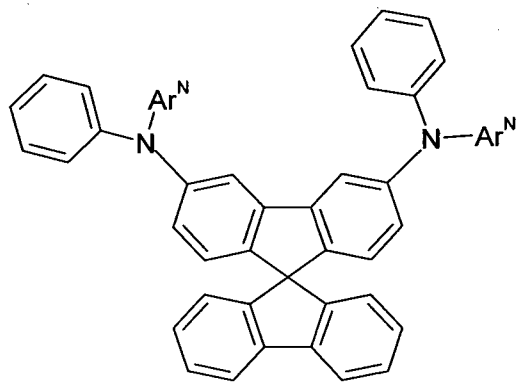
formula (1-4b)



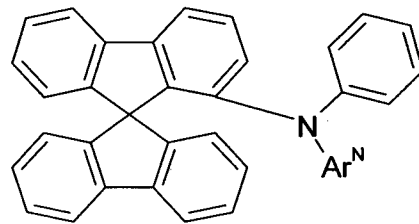
formula (1-5b)

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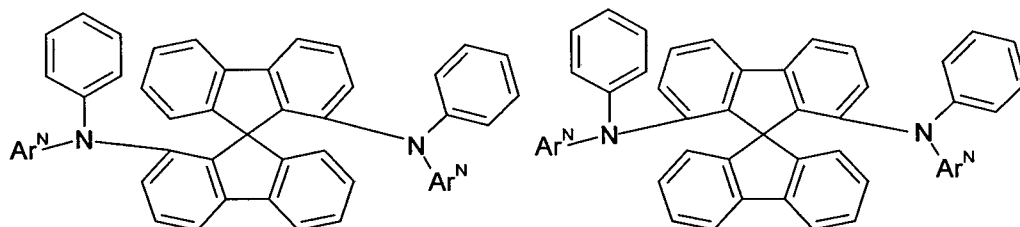
formula (1-6b)



formula (1-7b)

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formula (1-8b)

formula (1-9b)

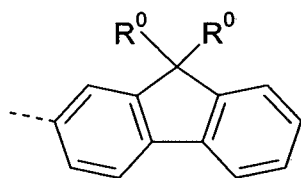
where the symbol Ar^N has the same meanings as indicated above.

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According to a preferred embodiment, the group Ar^N is selected from the groups of formulae (2-1) or (2-2), and very preferably (2-1).

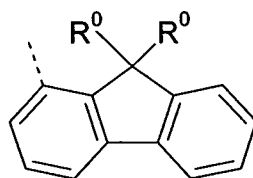
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According to a further preferred embodiment, the group Ar^N is selected from the groups of the following formulae (20) to (84),

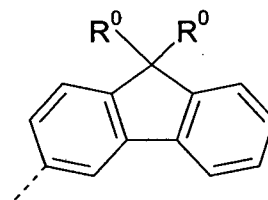


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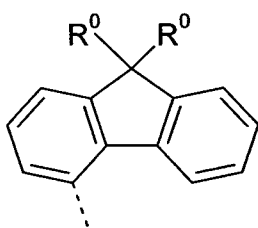
formula (20)



formula (21)

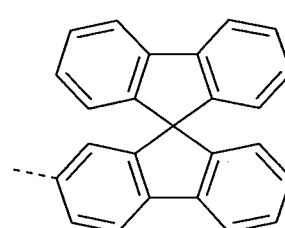


formula (22)

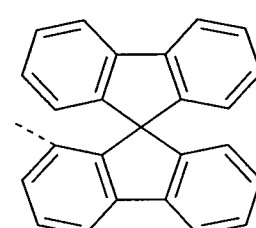


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formula (23)



formula (24)

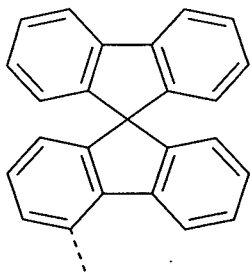


formula (25)

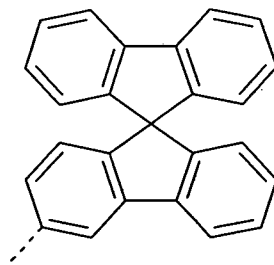
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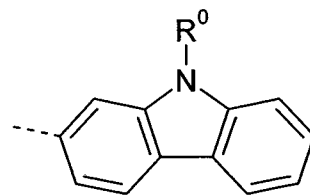
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formula (26)

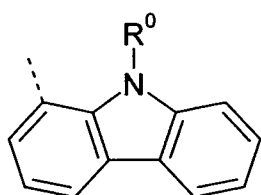


formula (27)

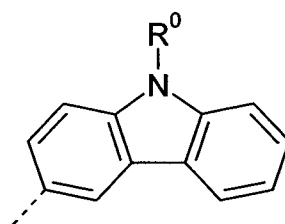


formula (28)

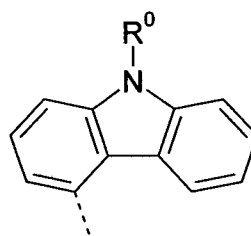
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formula (29)

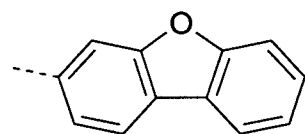


formula (30)

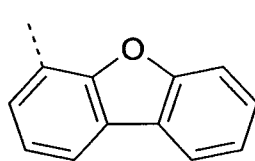


formula (31)

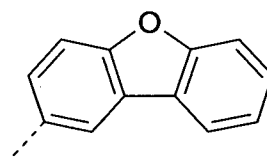
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formula (32)

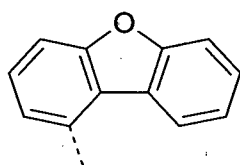


formula (33)

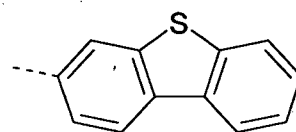


formula (34)

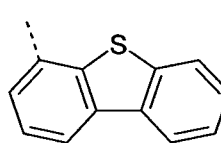
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formula (35)

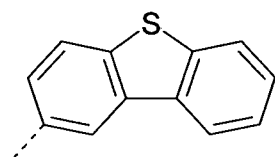


formula (36)

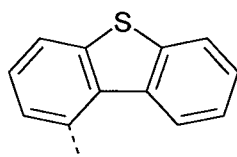


formula (37)

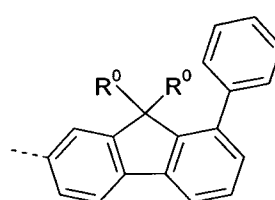
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formula (38)

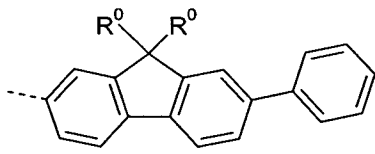


formula (39)

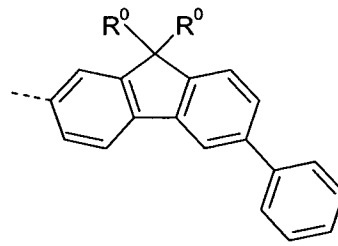


formula (40)

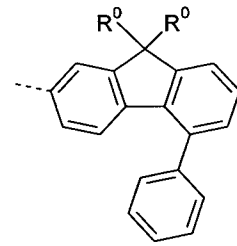
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formula (41)

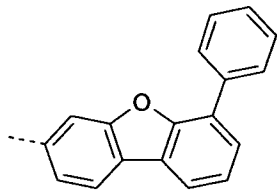


formula (42)

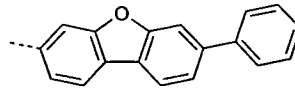


formula (43)

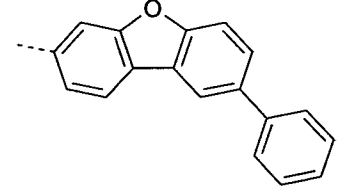
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formula (44)

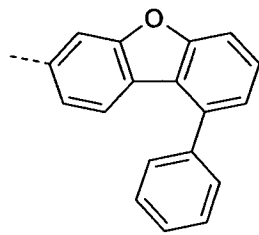


formula (45)

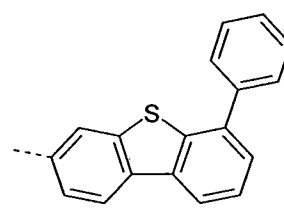


formula (46)

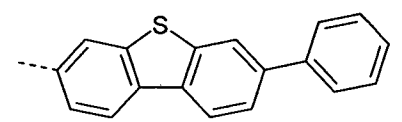
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formula (47)

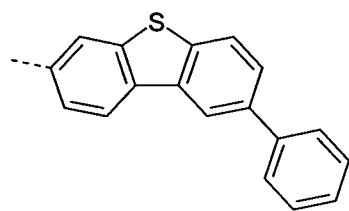


formula (48)

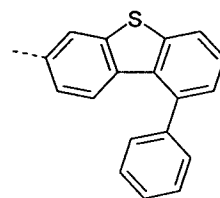


formula (49)

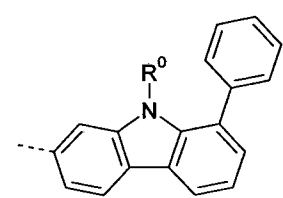
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formula (50)

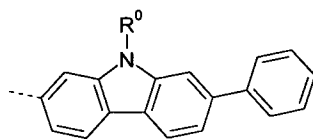


formula (51)

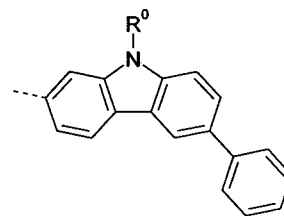


formula (52)

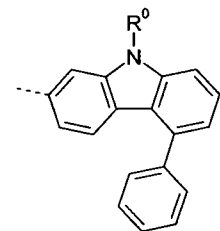
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formula (53)



formula (54)

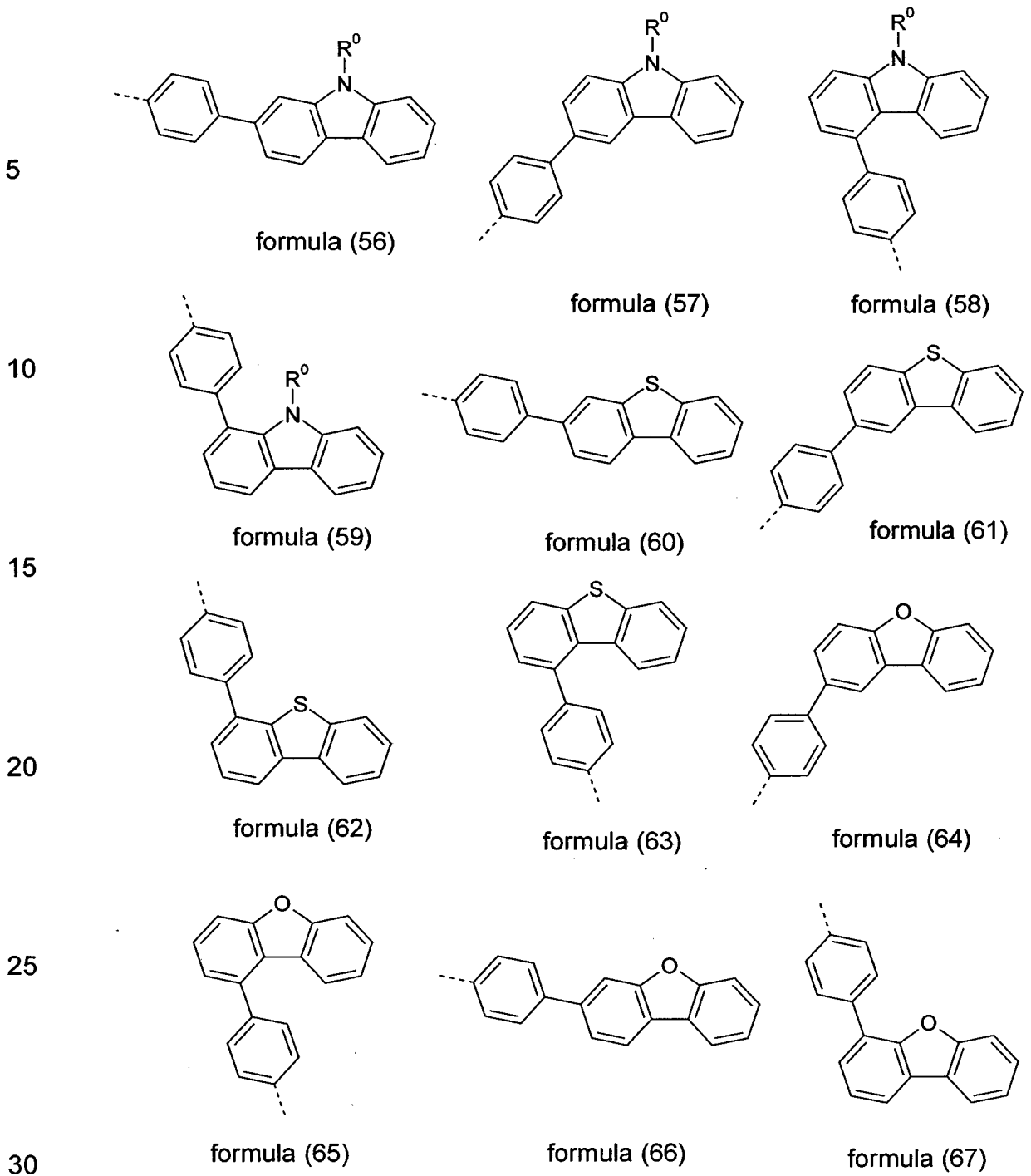


formula (55)

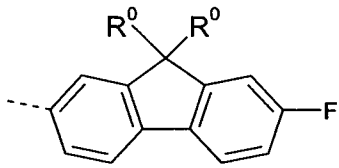
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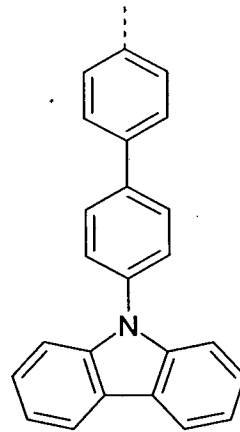
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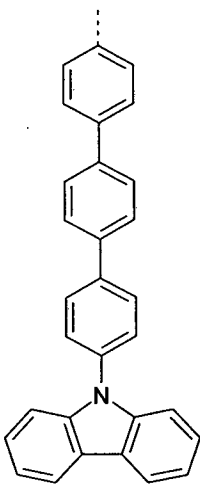


formula (68)

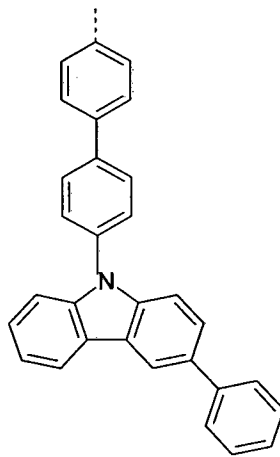


formula (69)

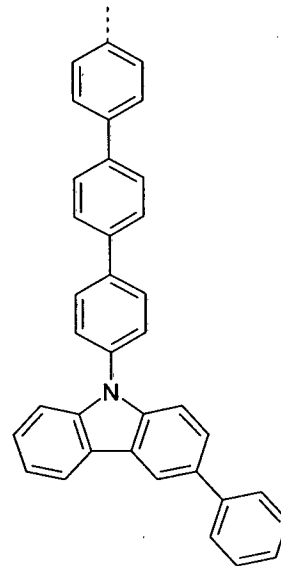
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formula (70)

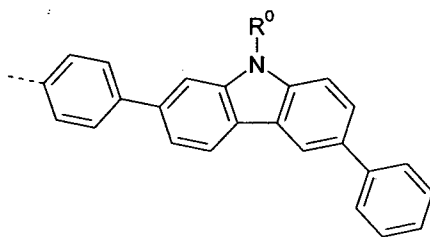


formula (71)

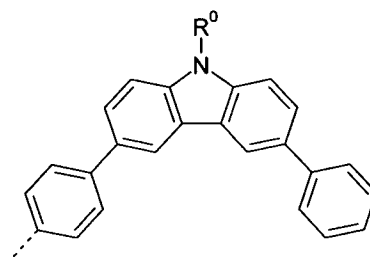


formula (72)

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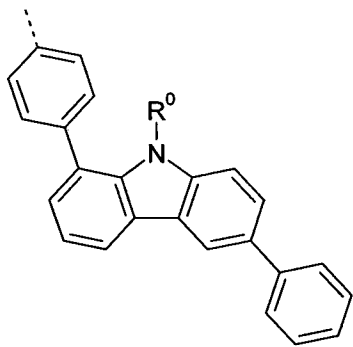
formula (73)



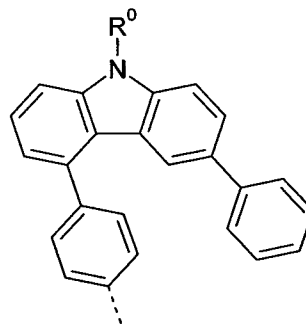
formula (74)

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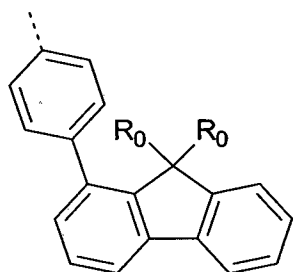


formula (75)

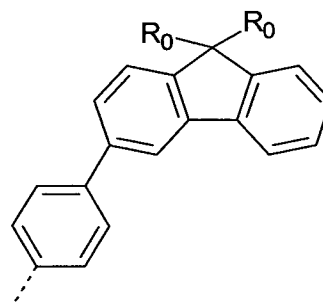


formula (76)

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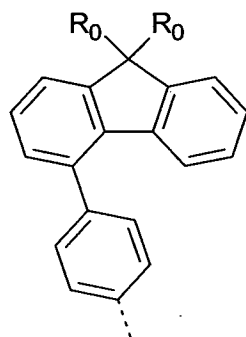


formula (77)

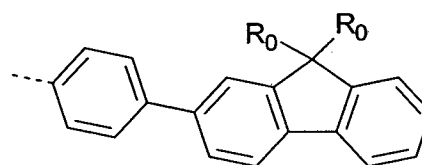


formula (78)

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formula (79)



formula (80)

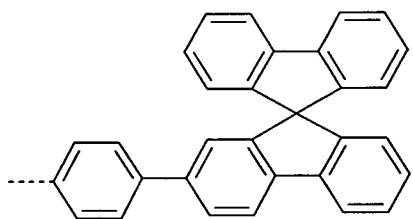
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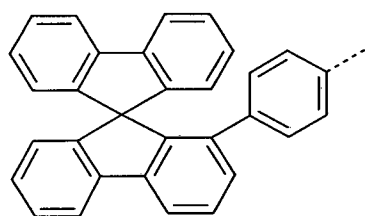
- 27 -

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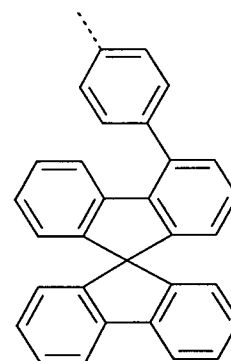
formula (81)

10

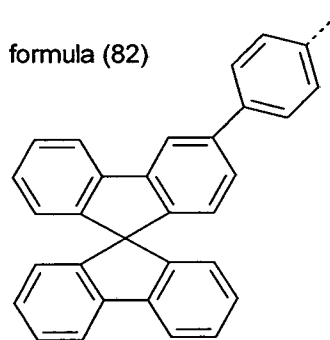


formula (83)

15



formula (82)



formula (84)

20

where the dashed bond indicates the bond to a nitrogen atom depicted in formula (1), where R^0 has the same meaning as indicated above and where the groups of formulae (20) to (84) may be substituted by one or more radicals R^8 .

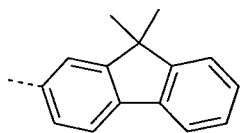
25

The group Ar^N here is particularly preferably selected from the groups of formulae (20) to (23), (40) to (43) and (68), very particularly preferably from the groups of formulae (20) to (23).

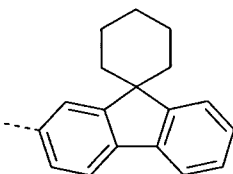
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Preferred structures of the formulae (20) to (23) are structures of formulae (20-a) to (23-i) as represented below:

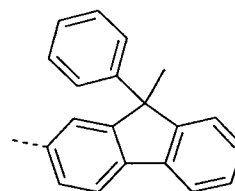
35



formula (20-a)

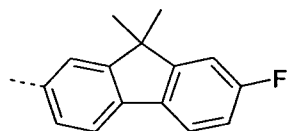


formula (20-b)

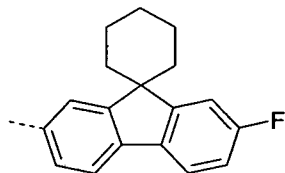


formula (20-c)

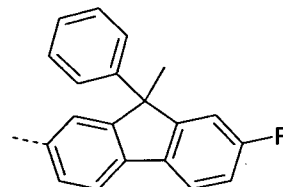
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formula (20-d)

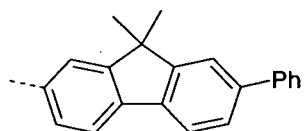


formula (20-e)

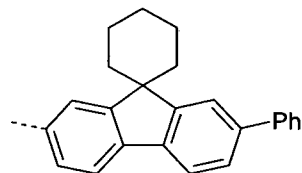


formula (20-f)

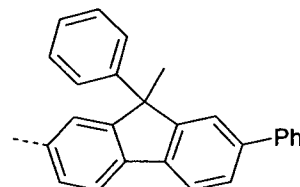
10



formula (20-g)

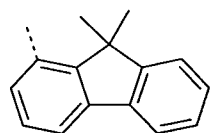


formula (20-h)

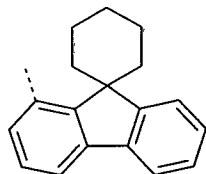


formula (20-i)

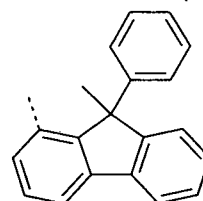
15



formula (21-a)

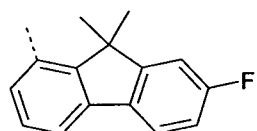


formula (21-b)

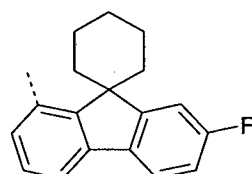


formula (21-c)

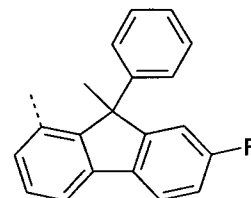
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formula (21-d)

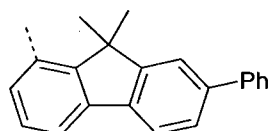


formula (21-e)

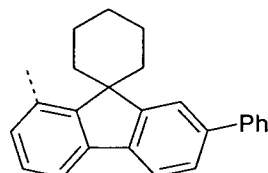


formula (21-f)

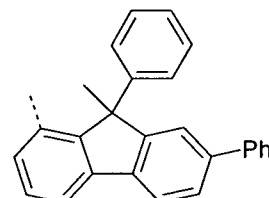
25



formula (21-g)



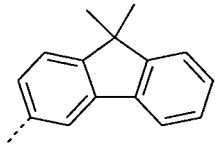
formula (21-h)



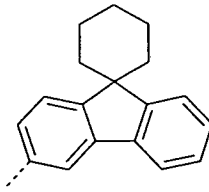
formula (21-i)

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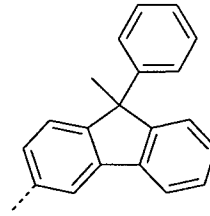
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formula (22-a)

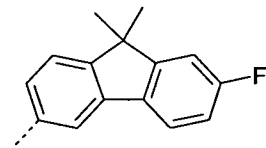


formula (22-b)

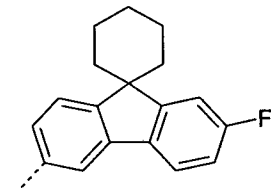


formula (22-c)

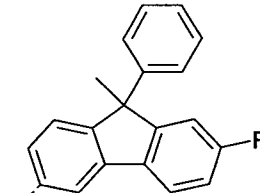
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formula (22-d)

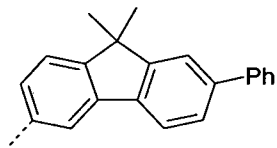


formula (22-e)

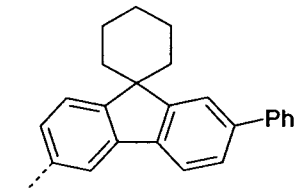


formula (22-f)

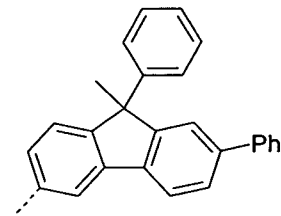
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formula (22-g)

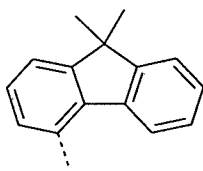


formula (22-h)

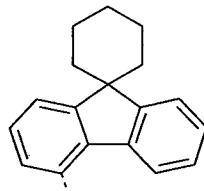


formula (22-i)

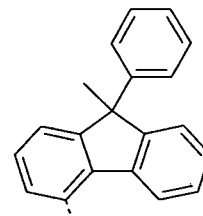
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formula (23-a)

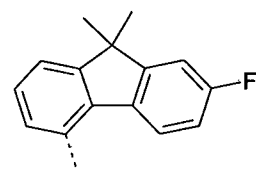


formula (23-b)

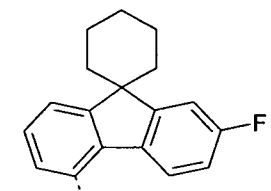


formula (23-c)

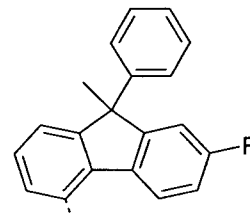
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formula (23-d)

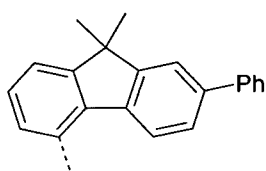


formula (23-e)

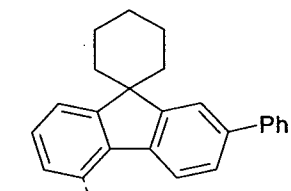


formula (23-f)

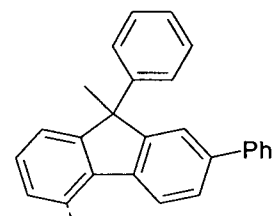
25



formula (23-g)



formula (23-h)



formula (23-i)

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- 30 -

5 In a preferred embodiment of the invention, R¹ to R⁴ are selected, identically or differently on each occurrence, from the group consisting of H, D, F, CN, a straight-chain alkyl or alkoxy group having 1 to 10 C atoms or a branched or cyclic alkyl or alkoxy group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R⁸, where one or more non-adjacent CH₂ groups may be replaced by O and where one or more H atoms may be replaced by F, an aromatic or heteroaromatic ring system having 6 to 24 aromatic ring atoms, which may in each case be substituted by one or more radicals R⁸.

10 In a particularly preferred embodiment of the invention, R¹ to R⁴ are selected on each occurrence, identically or differently, from the group consisting of H, D, F, CN, a straight-chain alkyl group having 1 to 5 C atoms or a branched or cyclic alkyl group having 3 to 6 C atoms, an aryl or hetero-aryl group having 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R⁸.

20 R¹ to R⁴ in the compounds of the formulae (1), (1-1) to (1-9) and (1-1a) to (1-9a) are very particularly preferably selected, identically or differently on each occurrence, from the group consisting of F, CN, methyl, tert-Butyl or phenyl.

25 In a further a preferred embodiment of the invention, R⁵ is selected from the group consisting of H, D, F, CN, a straight-chain alkyl or alkoxy group having 1 to 10 C atoms or a branched or cyclic alkyl or alkoxy group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R⁸, where one or more non-adjacent CH₂ groups may be replaced by O and where one or more H atoms may be replaced by F.

30 In a further preferred embodiment of the invention, R⁶ and R⁷ are selected, identically or differently on each occurrence, from the group consisting of H, D, F, CN, a straight-chain alkyl or alkoxy group having 1 to 10 C atoms

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5 or a branched or cyclic alkyl or alkoxy group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R^8 , where one or more non-adjacent CH_2 groups may be replaced by O and where one or more H atoms may be replaced by F, an aryl or heteroaryl ring system having 5 to 14 aromatic ring atoms, which may in each case be substituted by one or more radicals R^8 .

10 It is furthermore preferred that R^0 is selected on each occurrence, identically or differently, from the group consisting of H, D, F, CN, a straight-chain alkyl or alkoxy group having 1 to 10 C atoms or a branched or cyclic alkyl or alkoxy group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R^8 , where in each case one or more non-adjacent CH_2 groups may be replaced by O and where one or more H atoms may be replaced by D, F or CN, an aromatic or heteroaromatic ring system having 5 to 14 aromatic ring atoms, which may in each case be substituted by one or more radicals R^8 , where two substituents R^0 may optionally form a monocyclic aliphatic ring system, which may be substituted by one or more radicals R^8 ; with the proviso that when two R^0 are attached to the same C atom, then at least one R^0 is selected from the group consisting of H, D, F, CN, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R^8 .

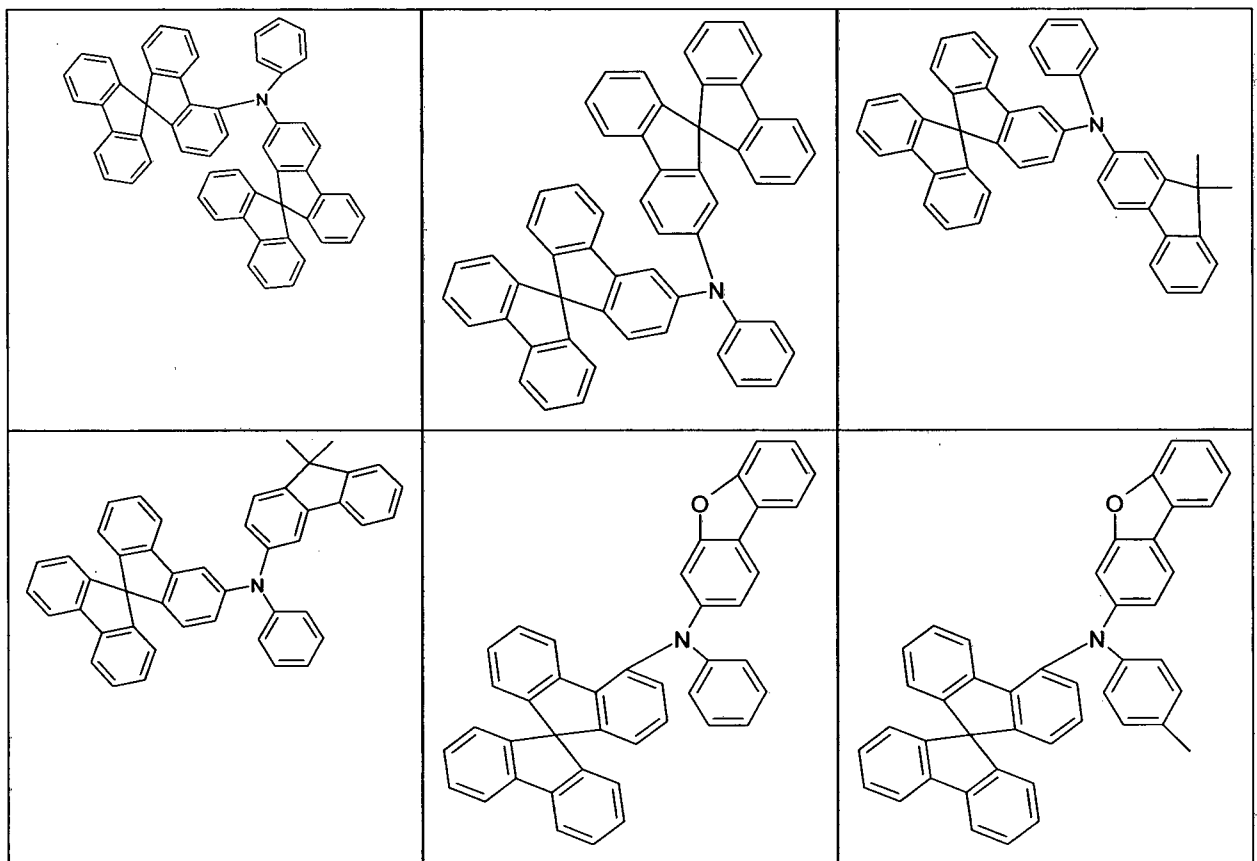
25
30 It is particularly preferred that R^0 is selected on each occurrence, identically or differently, from the group consisting of H, a straight-chain alkyl group having 1 to 10 C atoms or a branched or cyclic alkyl group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R^8 . It is very particularly preferred that R^0 is selected from H or methyl.

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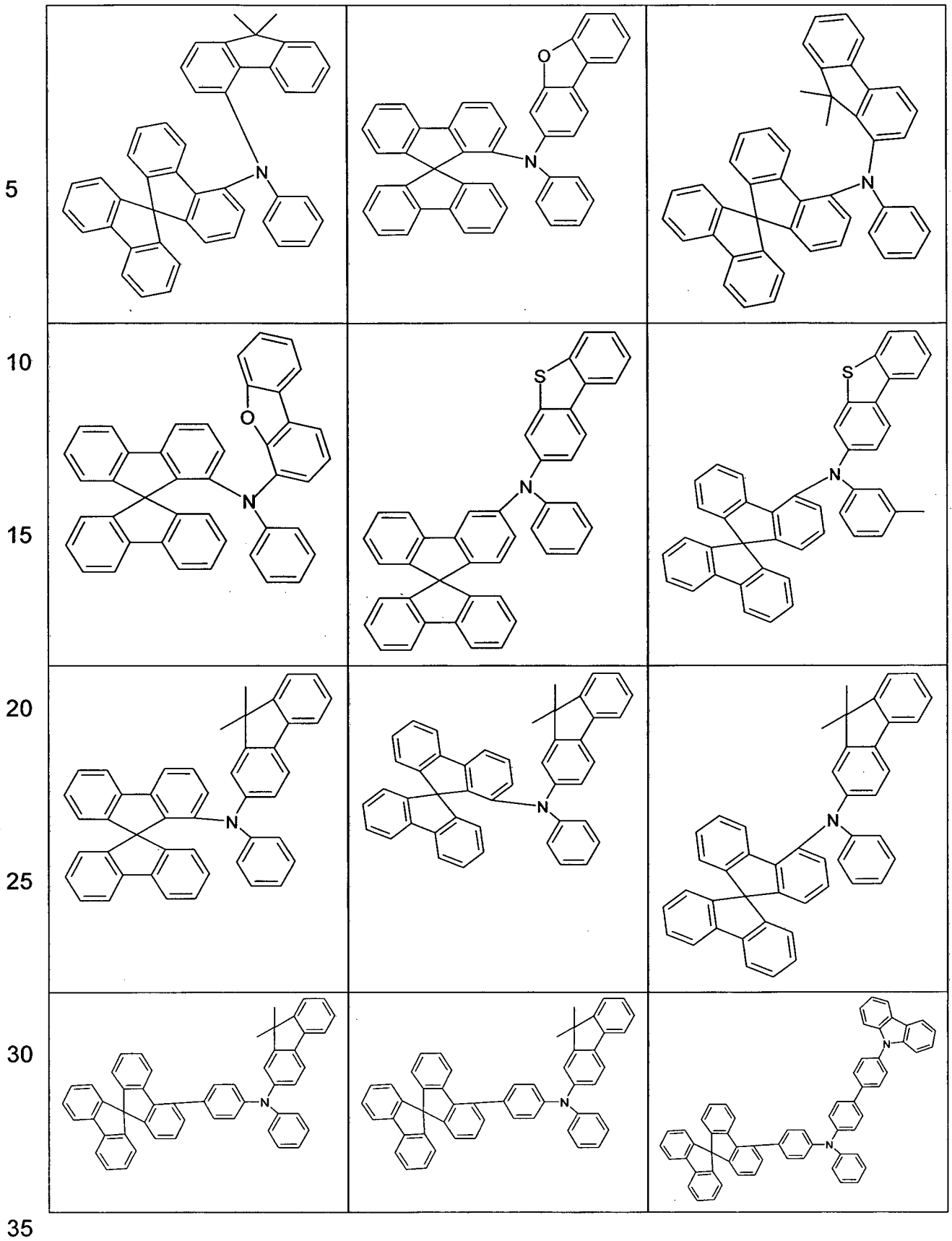
- 32 -

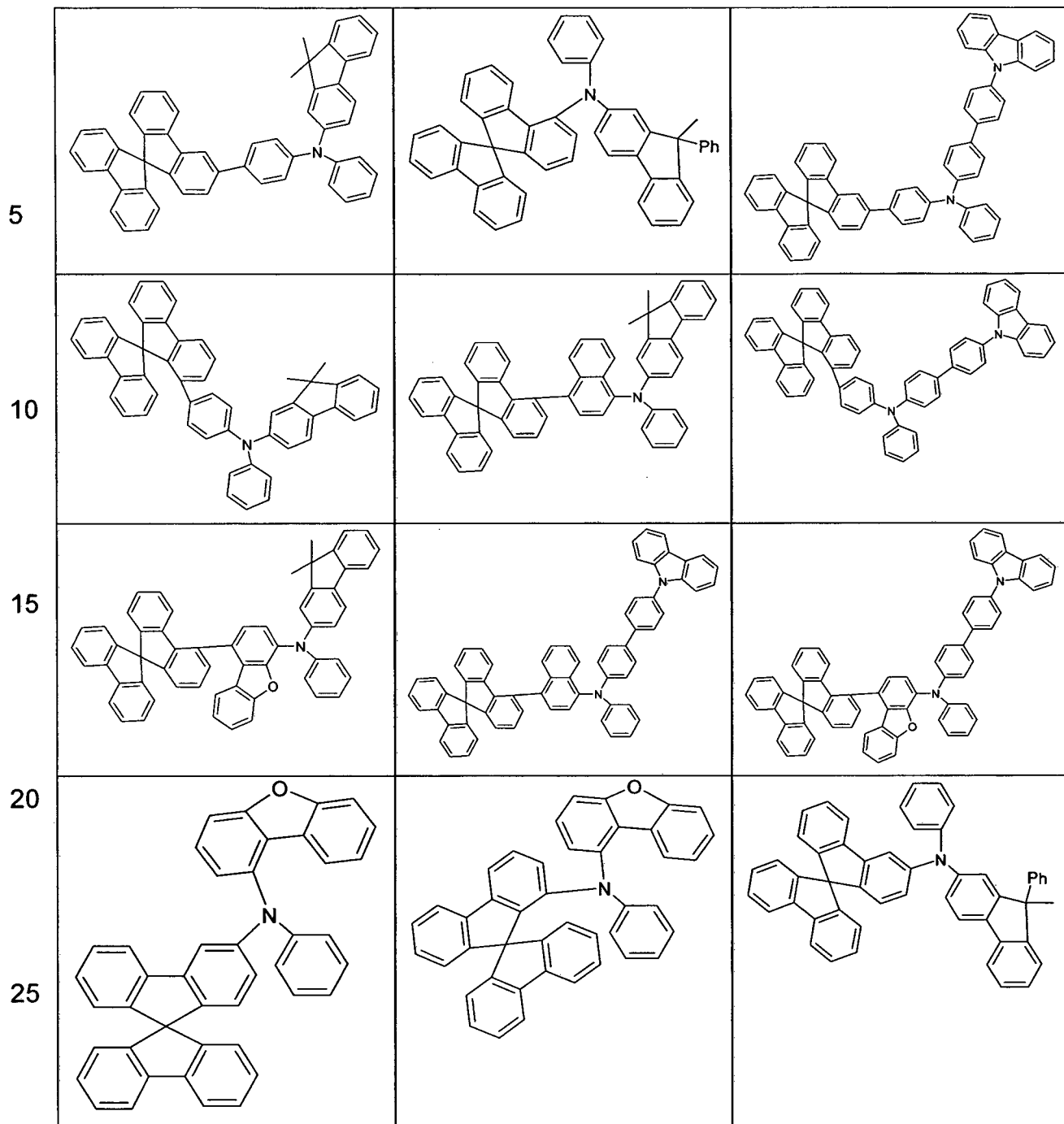
For compounds which are processed by vacuum evaporation, the alkyl groups preferably have not more than four C atoms, particularly preferably not more than 1 C atom. For compounds which are processed from solution, suitable compounds are also those which are substituted by linear, branched or cyclic 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.

Examples of suitable compounds according to the invention are the compounds shown in the following table:



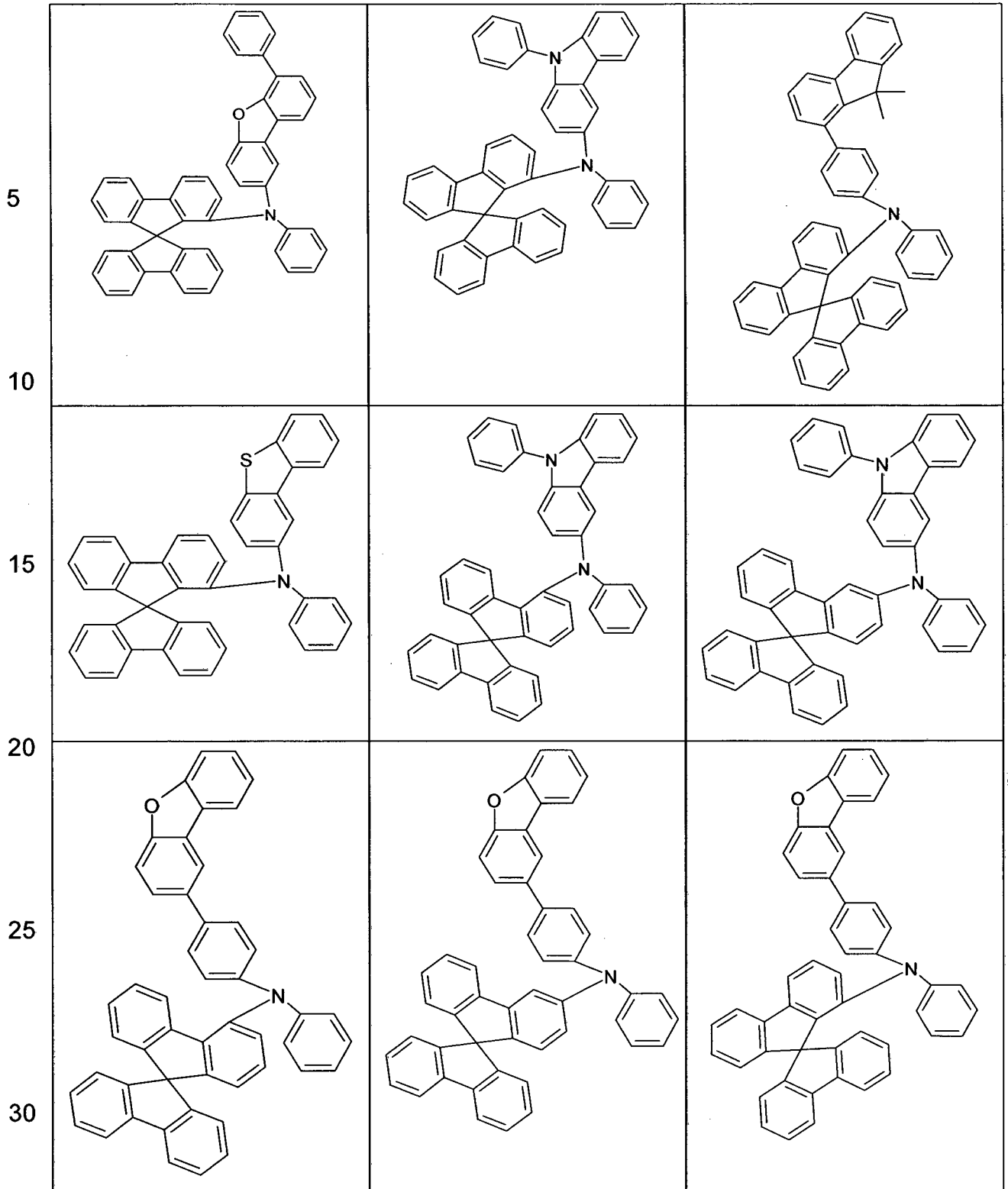
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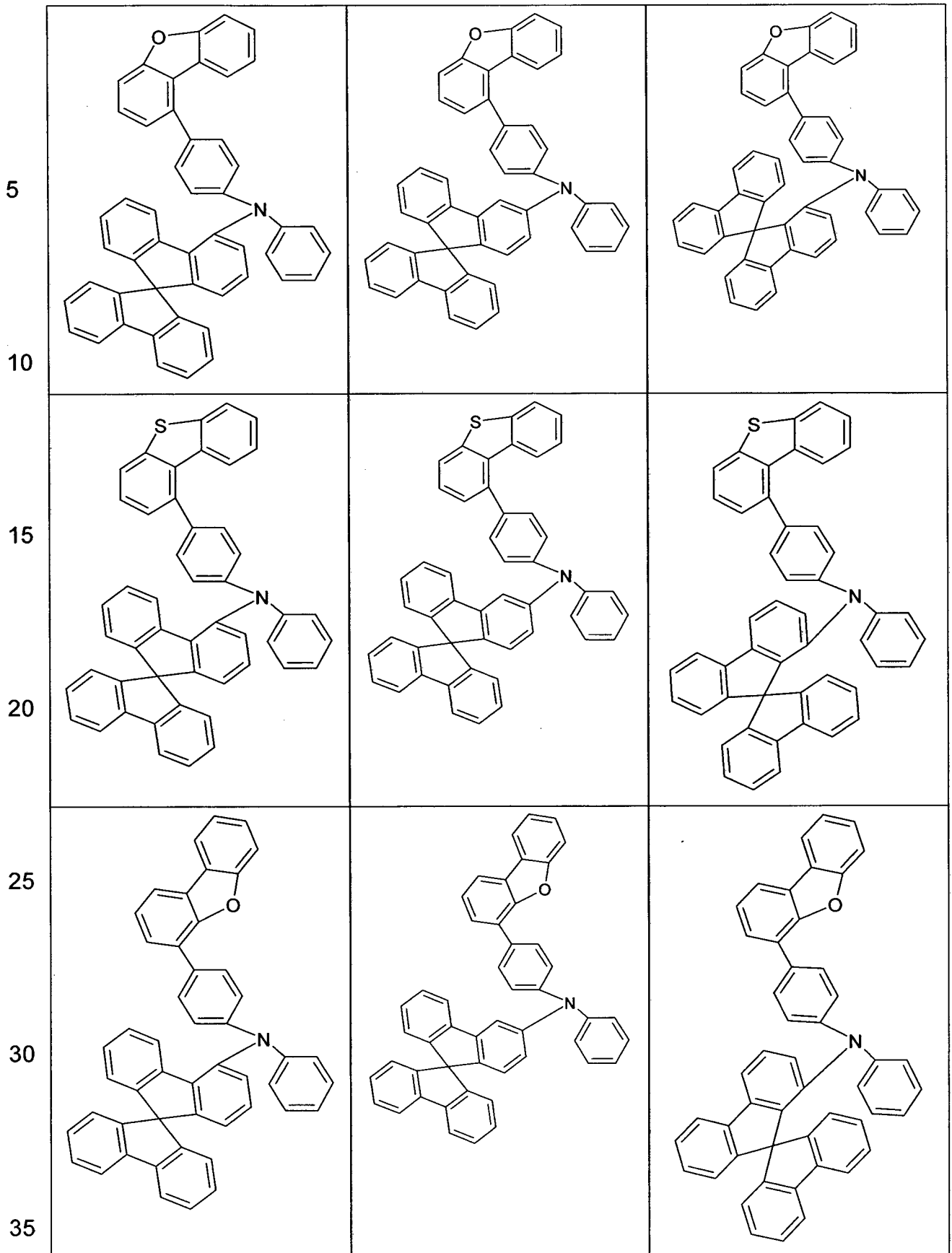


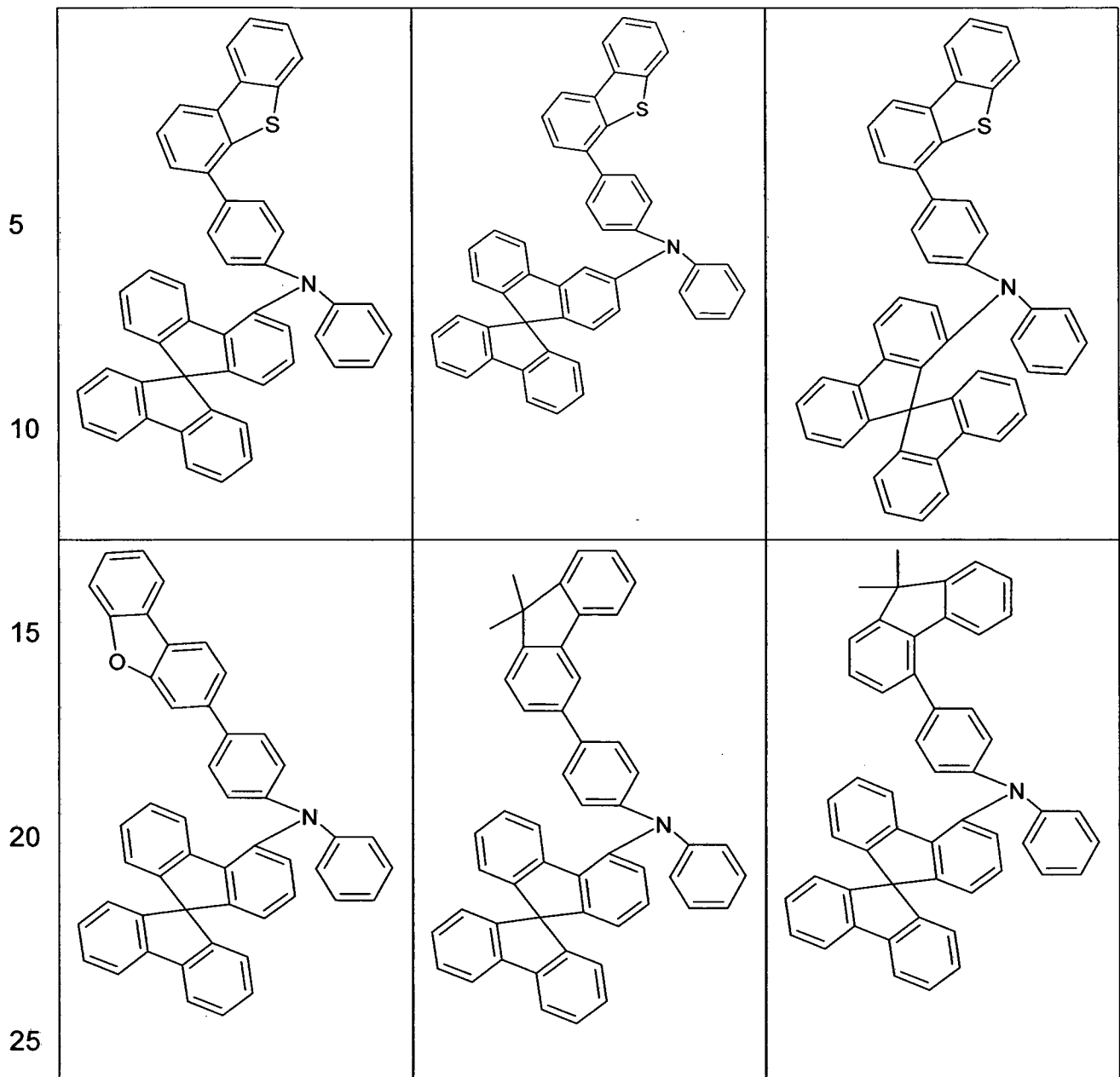


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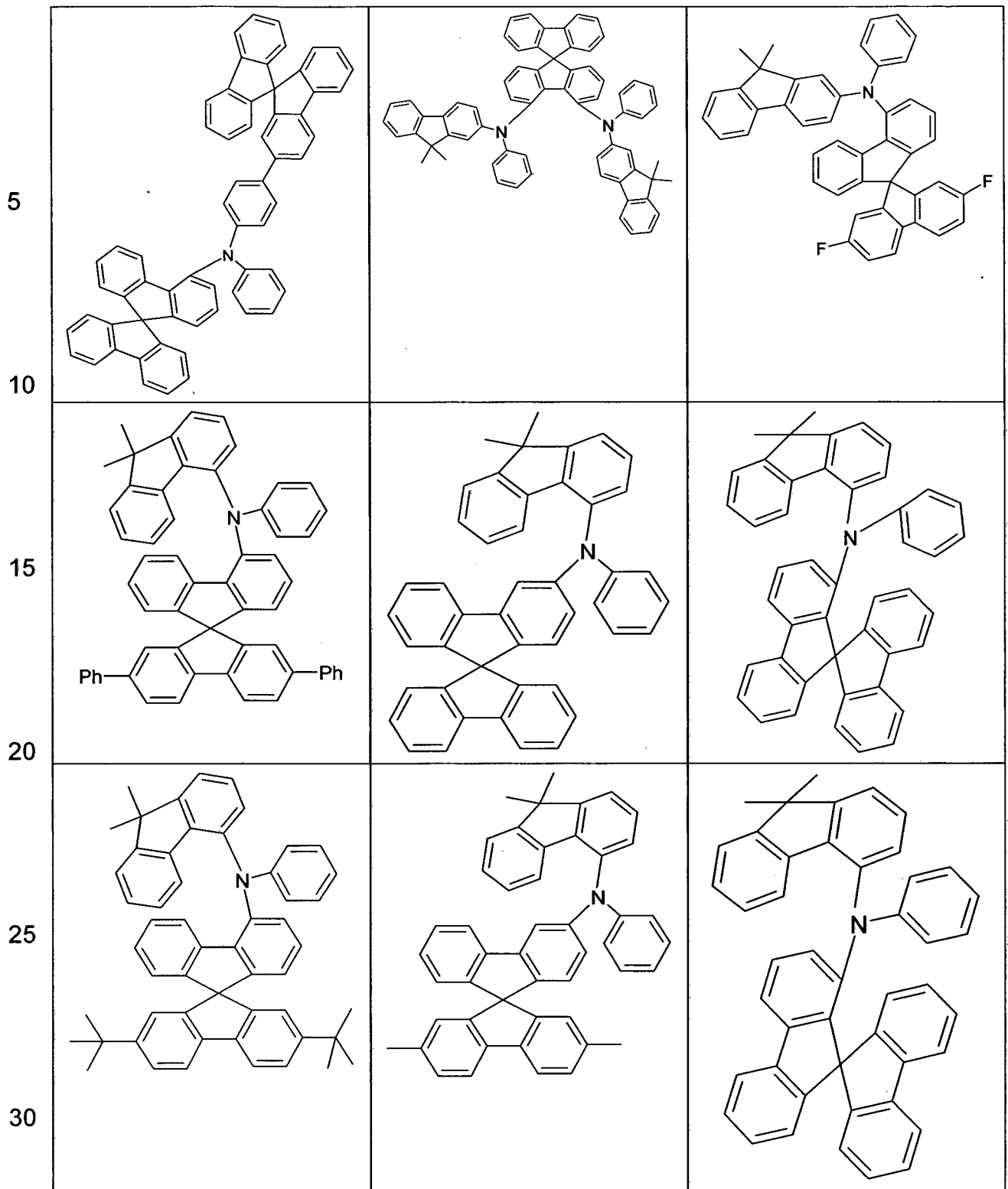


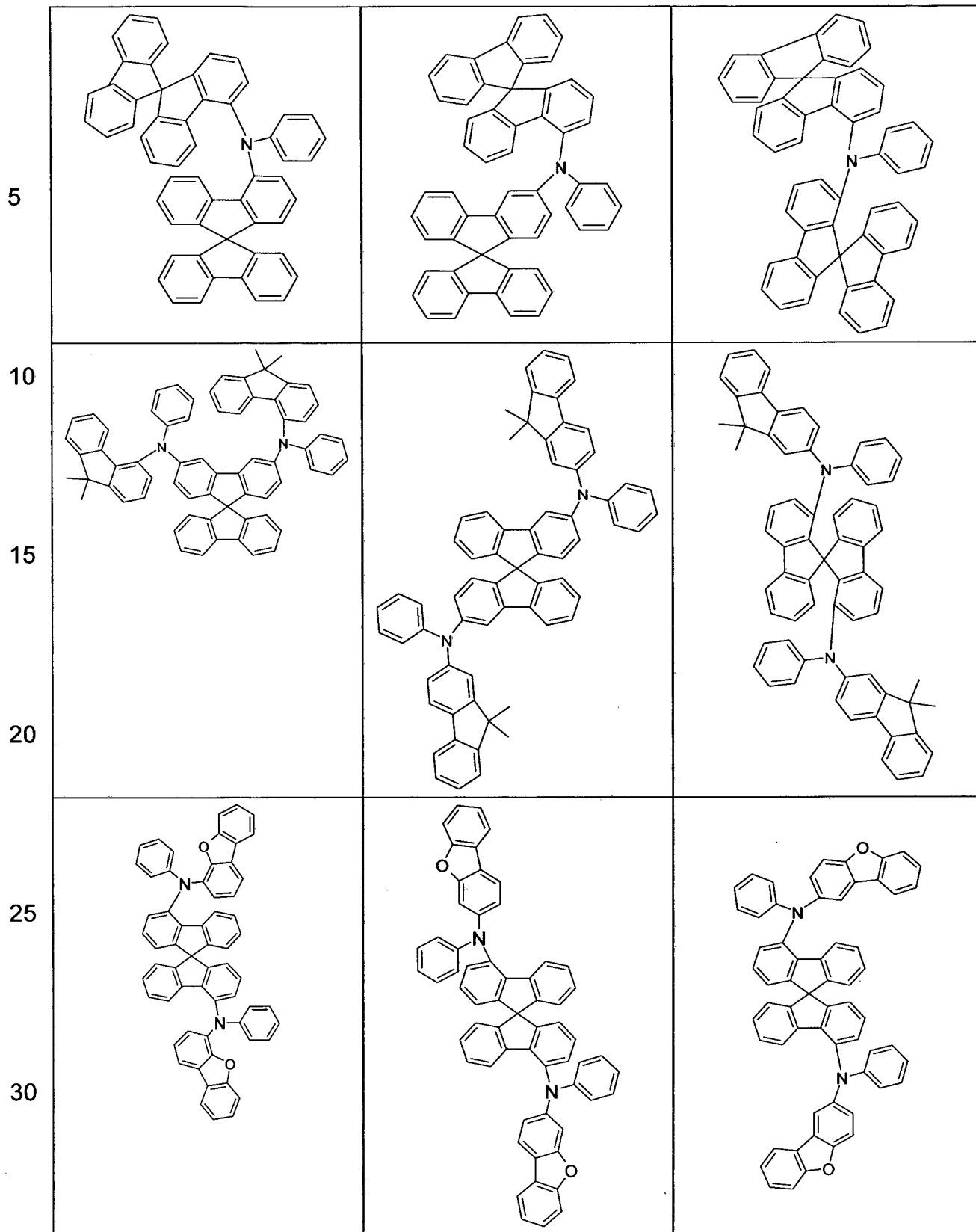


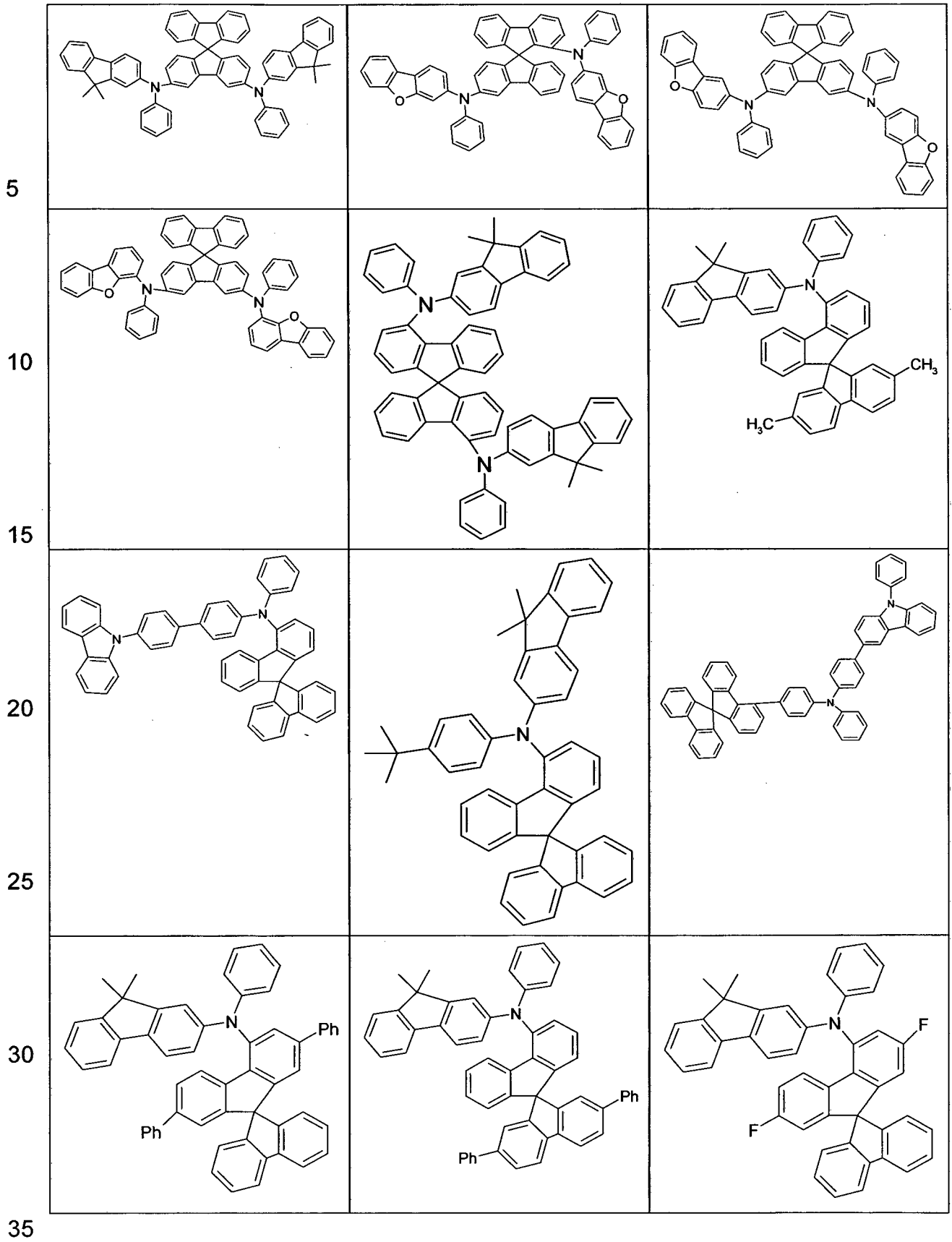


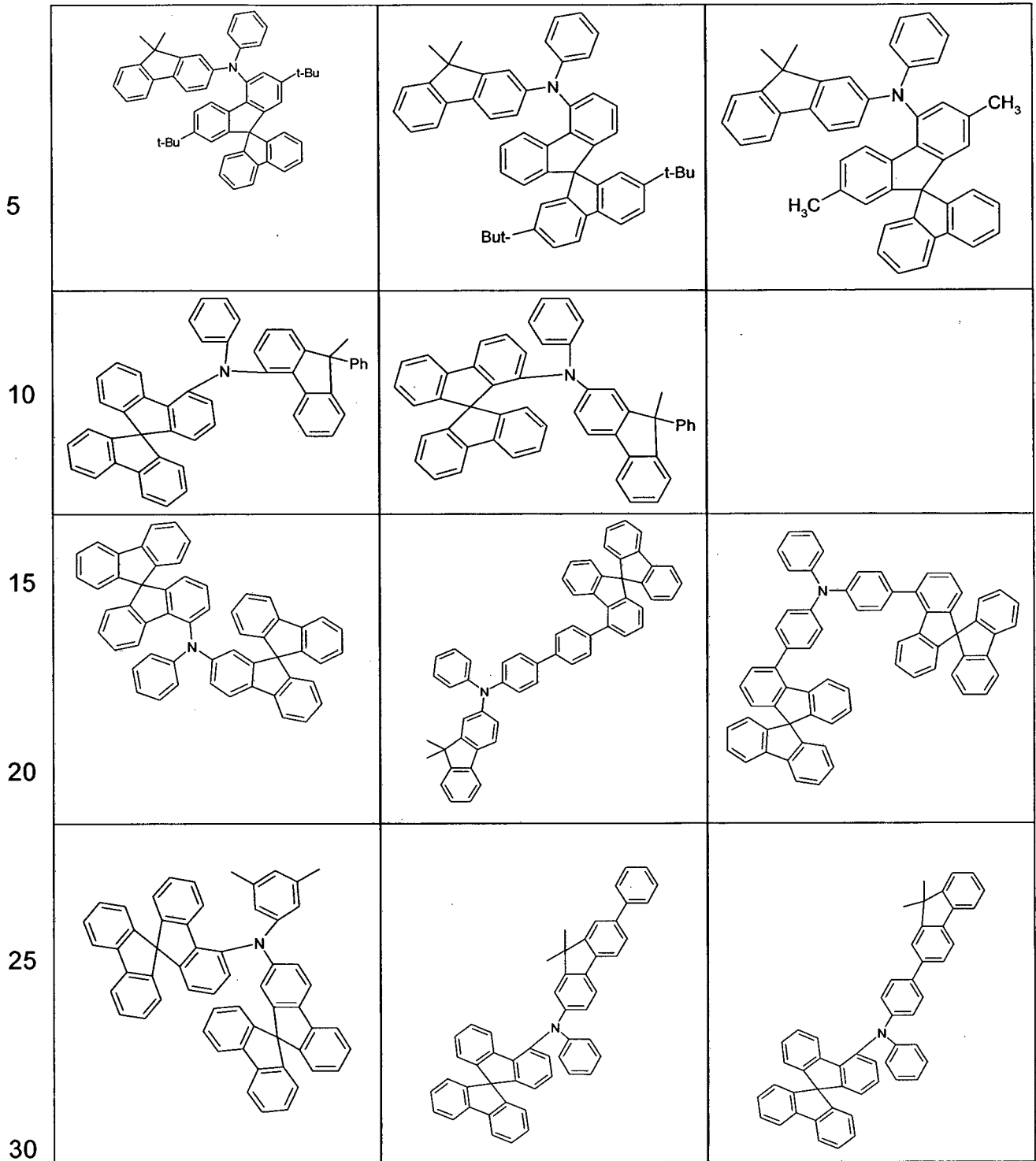
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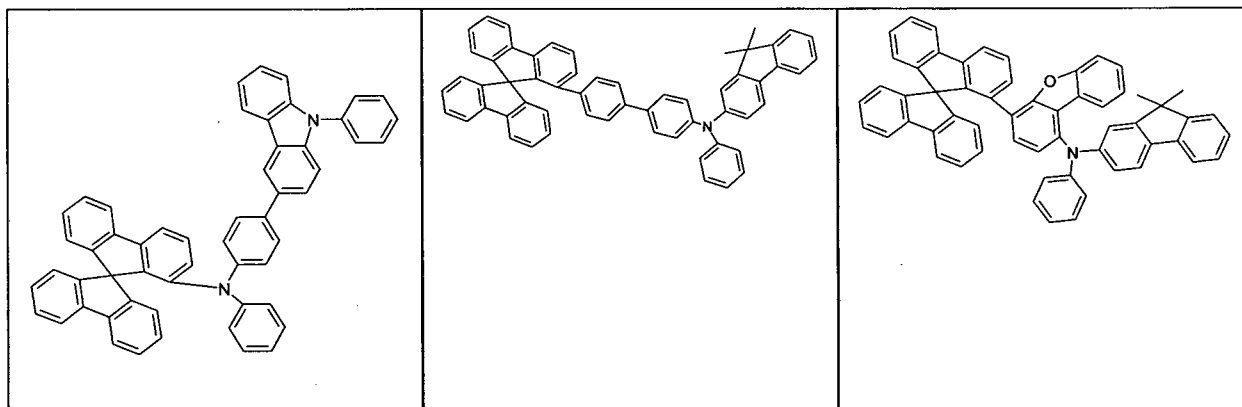
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The compounds according to the invention can be prepared by synthetic steps known to the person skilled in the art, such as, for example, bromination, Ullmann arylation, Hartwig-Buchwald coupling, etc.

15

The syntheses generally start from the 1-, 3- or 4-halogenated, in particular brominated, spirobifluorene derivatives, followed by a C-N coupling reaction, for example a Hartwig-Buchwald coupling or an Ullmann coupling, for introduction of the diarylamino group. Analogously, another suitable leaving group, for example tosylate or triflate, can be used instead of the halogen. The synthesis of 1-diarylaminospirobifluorene is shown in Scheme 1, where two different access routes to the brominated starting compound are shown.

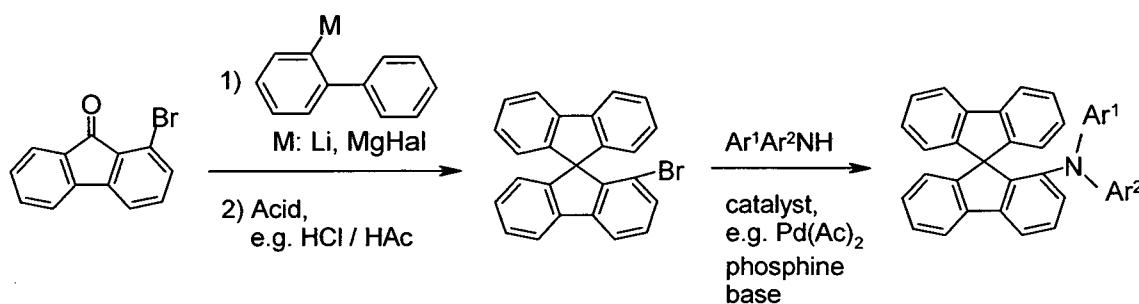
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Scheme 1:

a) Classical spiro synthesis:

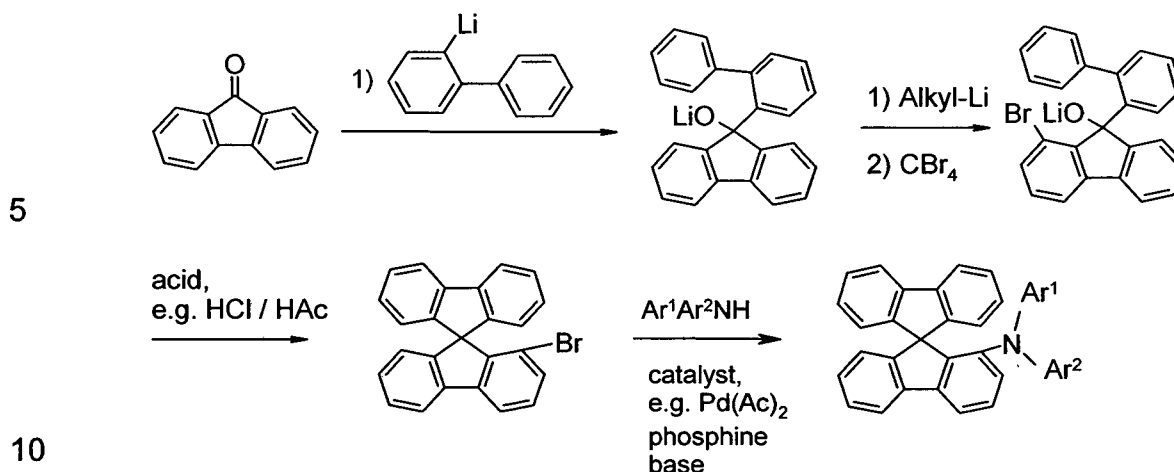
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b) Directional lithiation of fluorenol:



Analogously to the classical spiro synthesis shown above, the corresponding spirobifluorene derivatives which are halogenated in the 3- or 4-position can be synthesised by employing the corresponding 3- or 4-halogen-substituted fluorenone as starting material. Likewise, corresponding substituted structures can also be synthesised entirely analogously.

15

The present invention therefore furthermore relates to a process for the preparation of a compound of the formula (1), characterised in that the diarylamino group is introduced by a C-N coupling reaction between a 1- or 3- or 4-halogenated spirobifluorene and a diarylamine.

20

The compounds according to the invention described above, in particular compounds which are substituted by reactive leaving groups, such as bromine, iodine, boronic acid or boronic acid ester, can be used as monomers for the preparation of corresponding oligomers, dendrimers or polymers. The oligomerisation or polymerisation here is preferably carried out via the halogen functionality or the boronic acid functionality.

25

30

The invention therefore furthermore relates to oligomers, polymers or dendrimers comprising one or more compounds of the formula (1), where the bond(s) to the polymer, oligomer or dendrimer may be localised at any desired positions in formula (1) substituted by R¹ to R⁵. Depending on the

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linking of the compound of the formula (1), the compound is part of a side chain of the oligomer or polymer or part of the main chain. An oligomer in the sense of this invention is taken to mean a compound which is built up from at least three monomer units. A polymer in the sense of the invention is taken to mean a compound which is built up from at least ten monomer units. The polymers, oligomers or dendrimers according to the invention may be conjugated, partially conjugated or non-conjugated. The oligomers or polymers according to the invention may be linear, branched or dendritic. In the structures linked in a linear manner, the units of the formula (1) may be linked directly to one another or linked to one another via a divalent group, for example via a substituted or unsubstituted alkylene group, via a heteroatom or via a divalent aromatic or heteroaromatic group. In branched and dendritic structures, three or more units of the formula (1) may, for example, be linked via a trivalent or polyvalent group, for example via a trivalent or polyvalent aromatic or heteroaromatic group, to give a branched or dendritic oligomer or polymer. The same preferences as described above for compounds of the formula (1) apply to the recurring units of the formula (1) 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. Suitable and preferred comonomers are selected from fluorenes (for example in accordance with EP 842208 or WO 00/22026), spirobifluorenes (for example in accordance with EP 707020, EP 894107 or WO 06/061181), para-phenylenes (for example in accordance with WO 92/18552), carbazoles (for example in accordance with WO 04/070772 or WO 04/113468), thiophenes (for example in accordance with EP 1028136), dihydrophenanthrenes (for example in accordance with WO 05/014689 or WO 07/006383), cis- and trans-indenofluorenes (for example in accordance with WO 04/041901 or WO 04/113412), ketones (for example in accordance with WO 05/040302), phenanthrenes (for example in accordance with WO 05/104264 or WO 07/017066) or also a plurality of

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5 these units. The polymers, oligomers and dendrimers usually also contain further units, for example emitting (fluorescent or phosphorescent) units, such as, for example, vinyltriaryl amines (for example in accordance with WO 07/068325) or phosphorescent metal complexes (for example in accordance with WO 06/003000), and/or charge-transport units, in particular those based on triaryl amines.

10 The polymers, oligomers and dendrimers according to the invention have advantageous properties, in particular long lifetimes, high efficiencies and good colour coordinates.

15 The polymers and oligomers according to the invention are generally prepared by polymerisation of one or more types of monomer, at least one monomer of which results in recurring units of the formula (1) in the polymer. Suitable polymerisation reactions are known to the person skilled in the art and are described in the literature. Particularly suitable and preferred polymerisation reactions which result in C-C or C-N links are the following:

- 20
- (A) SUZUKI polymerisation;
 - (B) YAMAMOTO polymerisation;
 - (C) STILLE polymerisation; and
 - 25 (D) HARTWIG-BUCHWALD polymerisation.

30 The way in which the polymerisation can be carried out by these methods and the way in which the polymers can then be separated off from the reaction medium and purified is known to the person skilled in the art and is described in detail in the literature, for example in WO 2003/048225, WO 2004/037887 and WO 2004/037887.

35 The present invention thus also relates to a process for the preparation of the polymers, oligomers and dendrimers according to the invention, which

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is characterised in that they are prepared by SUZUKI polymerisation, YAMAMOTO polymerisation, STILLE polymerisation or HARTWIG-
BUCHWALD polymerisation. The dendrimers according to the invention
can be prepared by processes known to the person skilled in the art or
analogously thereto. Suitable processes are described in the literature,
5 such as, for example, in Frechet, Jean M. J.; Hawker, Craig J., "Hyper-
branched polyphenylene and hyperbranched polyesters: new soluble,
three-dimensional, reactive polymers", *Reactive & Functional Polymers*
(1995), 26(1-3), 127-36; Janssen, H. M.; Meijer, E. W., "The synthesis and
10 characterization of dendritic molecules", *Materials Science and Technol-
ogy* (1999), 20 (Synthesis of Polymers), 403-458; Tomalia, Donald A.,
"Dendrimer molecules", *Scientific American* (1995), 272(5), 62-6; WO
02/067343 A1 and WO 2005/026144 A1.

15 The compounds according to the invention are suitable for use in an elec-
tronic device. An electronic device here is taken to mean a device which
comprises at least one layer which comprises at least one organic com-
20 pound. However, the component here may also comprise inorganic materi-
als or also layers built up entirely from inorganic materials.

25 The present invention therefore furthermore relates to the use of the com-
pounds according to the invention in an electronic device, in particular in
an organic electroluminescent device.

30 The present invention still furthermore relates to an electronic device com-
prising at least one compound according to the invention. The preferences
stated above likewise apply to the electronic devices.

35 The electronic device is preferably selected from the group consisting of
organic electroluminescent devices (organic light-emitting diodes, OLEDs),
organic integrated circuits (O-ICs), organic field-effect transistors
(O-FETs), organic thin-film transistors (O-TFTs), organic light-emitting tran-

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sistors (O-LETs), organic solar cells (O-SCs), organic dye-sensitised solar cells (ODSSCs), 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
5 (D. M. Koller *et al.*, *Nature Photonics* **2008**, 1-4), but preferably organic electroluminescent devices (OLEDs), particularly preferably phosphorescent OLEDs.

10 The organic electroluminescent devices and the light-emitting electrochemical cells can be employed for various applications, for example for monochromatic or polychromatic displays, for lighting applications or for medical and/or cosmetic applications, for example in phototherapy.

15 The organic electroluminescent device comprises a cathode, an 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
20 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.

25 The organic electroluminescent device here may comprise one emitting layer or a plurality of emitting layers. If a plurality of emission layers is present, these preferably have in total a plurality of emission maxima between
30 380 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 preference is given to systems having three emitting layers, where the three layers exhibit blue, green and orange or
35 red emission (for the basic structure see, for example, WO 2005/011013).

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It is possible here for all emitting layers to be fluorescent or for all emitting layers to be phosphorescent or for one or more emitting layers to be fluorescent and one or more other layers to be phosphorescent.

5 The compound according to the invention in accordance with the embodiments indicated above can be employed here in different layers, depending on the precise structure. Preference is given to an organic electroluminescent device comprising a compound of the formula (1) or the preferred
10 embodiments as hole-transport material in a hole-transport or hole-injection or exciton-blocking layer or as matrix material for fluorescent or phosphorescent emitters, in particular for phosphorescent emitters. The preferred embodiments indicated above also apply to the use of the materials in organic electronic devices.

15 In a preferred embodiment of the invention, the compound of the formula (1) or the preferred embodiments is employed as hole-transport or hole-injection material in a hole-transport or hole-injection layer. The emitting
20 layer here can be fluorescent or phosphorescent. A hole-injection layer in the sense of the present invention is a layer which is directly adjacent to the anode. A hole-transport layer in the sense of the present invention is a layer which is located between a hole-injection layer and an emitting layer.

25 In still a further preferred embodiment of the invention, the compound of the formula (1) or the preferred embodiments is employed in an exciton-blocking layer. An exciton-blocking layer is taken to mean a layer which is directly adjacent to an emitting layer on the anode side.

30 The compound of the formula (1) or the preferred embodiments is particularly preferably employed in a hole-transport or exciton-blocking layer.

35 If the compound of the formula (1) is employed as a hole-transport material in a hole-transport layer, a hole-injection layer or an exciton-

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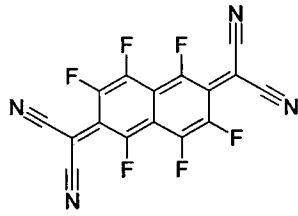
blocking layer, then the compound of formula (1) can be used in such a layer as a single material, i.e. in a proportion of 100%, or the compound of formula (1) can be used in combination with one or more further compounds in such a layer. According to a preferred embodiment, the organic layer comprising the compound of formula (1) additionally
5 comprises one or more p-dopants. Preferred p-dopant for the present invention are organic compounds that can accept electrons (electron acceptors) and can oxidize one or more of the other compounds present in the mixture.

10 Particularly preferred embodiments of p-dopants are described in WO 2011/073149, EP 1968131, EP 2276085, EP 2213662, EP 1722602, EP 2045848, DE 102007031220, US 8044390, US 8057712, WO
15 2009/003455, WO 2010/094378, WO 2011/120709, US 2010/0096600, WO 2012/095143 and DE 102012209523.

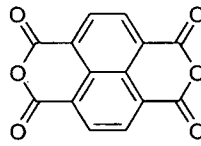
20 Particularly preferred as p-dopants are quinodimethane compounds, azaindenofluorendione, azaphenalene, azatriphenylene, I₂, metal halides, preferably transition metal halides, metal oxides, preferably metal oxides containing at least one transition metal or a metal of the 3rd main group and transition metal complexes, preferably complexes of Cu, Co, Ni, Pd and Pt with ligands containing at least one oxygen atom as binding site.
25 Also preferred are transition metal oxides as dopants, preferably oxides of rhenium, molybdenum and tungsten, particularly preferably Re₂O₇, MoO₃, WO₃ and ReO₃.

30 The p-dopants are preferably distributed substantially uniformly in the p-doped layers. This can be achieved for example by co-evaporation of the p-dopant and of the hole-transport material matrix.

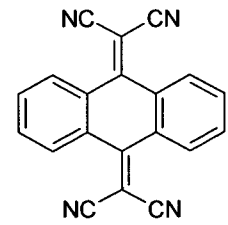
35 Particularly preferred p-dopants are selected from the compounds (D-1) to (D-13):



(D-1)

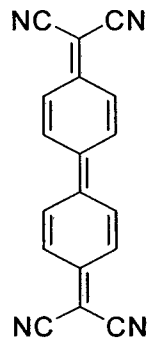


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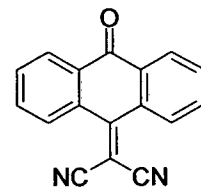


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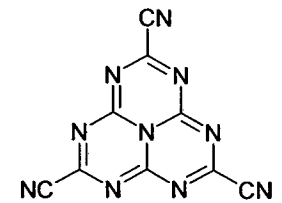
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(D-4)



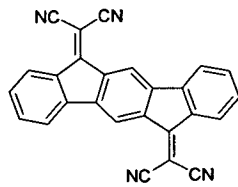
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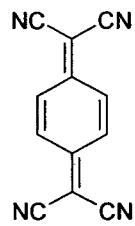
(D-6)

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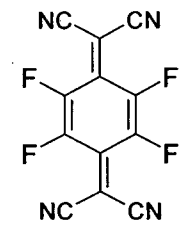
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(D-7)



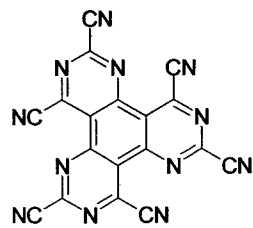
(D-8)



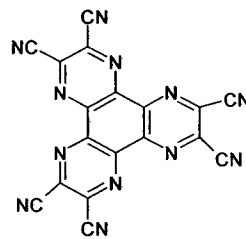
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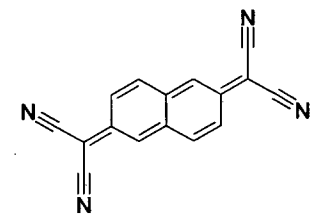
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(D-10)



(D-11)

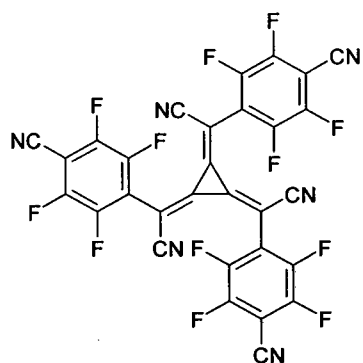


(D-12)

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(D-13)

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In an embodiment of the invention, the compound of the formula (1) or the preferred embodiments is used in a hole-transport or -injection layer in combination with a layer which comprises a hexaazatriphenylene derivative, in particular hexacyanohexaazatriphenylene (for example in accordance with EP 1175470). Thus, for example, preference is given to a combination which looks as follows: anode – hexaazatriphenylene derivative – hole-transport layer, where the hole-transport layer comprises one or more compounds of the formula (1) or the preferred embodiments. It is likewise possible in this structure to use a plurality of successive hole-transport layers, where at least one hole-transport layer comprises at least one compound of the formula (1) or the preferred embodiments. A further preferred combination looks as follows: anode – hole-transport layer – hexaazatriphenylene derivative – hole-transport layer, where at least one of the two hole-transport layers comprises one or more compounds of the formula (1) or the preferred embodiments. It is likewise possible in this structure to use a plurality of successive hole-transport layers instead of one hole-transport layer, where at least one hole-transport layer comprises at least one compound of the formula (1) or the preferred embodiments.

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In a further preferred embodiment of the invention, the compound of the formula (1) or the preferred embodiments is employed as matrix material for a fluorescent or phosphorescent compound, in particular for a phosphorescent compound, in an emitting layer. The organic electrolumines-

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cent device here may comprise one emitting layer or a plurality of emitting layers, where at least one emitting layer comprises at least one compound according to the invention as matrix material.

5 If the compound of the formula (1) or the preferred embodiments is employed as matrix material for an emitting 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
10 is taken to mean the luminescence from an excited state having a spin multiplicity > 1 , in particular from an excited triplet state. For the purposes of this application, all luminescent complexes containing transition metals or lanthanoids, in particular all luminescent iridium, platinum and copper complexes, are to be regarded as phosphorescent compounds.

15 The mixture comprising the matrix material, which comprises the compound of the formula (1) or the preferred embodiments, and the emitting compound comprises between 99.9 and 1% by weight, preferably
20 between 99 and 10% by weight, particularly preferably between 97 and 60% by weight, in particular between 95 and 80% by weight, of the matrix material, based on the entire mixture comprising emitter and matrix material. Correspondingly, the mixture comprises between 0.1 and 99% by
25 weight, preferably between 1 and 90% by weight, particularly preferably between 3 and 40% by weight, in particular between 5 and 20% by weight, of the emitter, based on the entire mixture comprising emitter and matrix material. The limits indicated above apply, in particular, if the layer is applied from solution. If the layer is applied by vacuum evaporation, the
30 same numerical values apply, with the percentage in this case being indicated in % by vol. in each case.

35 A particularly preferred embodiment of the present invention is the use of the compound of the formula (1) or the preferred embodiments as matrix material for a phosphorescent emitter in combination with a further matrix

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material. Particularly suitable matrix materials which can be employed in combination with the compounds of the formula (1) or the preferred embodiments 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, triarylaminines, carbazole derivatives, for example CBP (N,N-biscarbazolylbiphenyl), m-CBP or the carbazole derivatives disclosed in WO 2005/039246, US 2005/0069729, JP 2004/288381, EP 1205527 or WO 2008/086851, indolocarbazole derivatives, for example in accordance with WO 2007/063754 or WO 2008/056746, indenocarbazole derivatives, for example in accordance with WO 2010/136109 or WO 2011/000455, 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 2010/015306, WO 2007/063754 or WO 08/056746, zinc complexes, for example in accordance with EP 652273 or WO 2009/062578, fluorene derivatives, for example in accordance with WO 2009/124627, diazasilole or tetraazasilole derivatives, for example in accordance with WO 2010/054729, diazaphosphole derivatives, for example in accordance with WO 2010/054730, or bridged carbazole derivatives, for example in accordance with US 2009/0136779, WO 2010/050778, WO 2011/042107 or WO 2011/088877. It is furthermore possible to use an electronically neutral co-host which has neither hole-transporting nor electron-transporting properties, as described, for example, in WO 2010/108579.

It is likewise possible to use two or more phosphorescent emitters in the mixture. In this case, the emitter which emits at shorter wavelength acts as co-host in the mixture.

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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 atomic number. The phosphorescent 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, platinum or copper.

Examples of the emitters described above are revealed by the applications WO 2000/70655, 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 2009/146770, WO 2010/015307, WO 2010/031485, WO 2010/054731, WO 2010/054728, WO 2010/086089, WO 2010/099852, WO 2010/102709, WO 2011/157339 or WO 2012/007086. In general, all phosphorescent complexes as 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 inventive step.

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 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 identical or similar to the metal complex in the emitting layer as hole-transport or hole-injection material

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directly adjacent to the emitting layer, as described, for example, in WO 2009/030981.

5 It is furthermore possible to use the compound of the formula (1) or the preferred embodiments both in a hole-transport layer or exciton-blocking layer and as matrix in an emitting layer.

10 In the further layers of the organic electroluminescent device according to the invention, it is possible to use all materials as usually employed in accordance with the prior art. The person skilled in the art will therefore be able, without inventive step, to employ all materials known for organic electroluminescent devices in combination with the compounds of the formula (1) according to the invention or the preferred embodiments.

15 Preference is furthermore given to an organic electroluminescent device, characterised in that one or more layers are applied by means of a sublimation process, in which the materials are vapour-deposited in vacuum sublimation units at an initial pressure of usually 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.

25 Preference is likewise given to an organic electroluminescent device, characterised in that one or more layers are applied 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 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
30 through a nozzle and thus structured (for example M. S. Arnold *et al.*, *Appl. Phys. Lett.* **2008**, 92, 053301).

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5 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, LITI (light induced thermal imaging, thermal transfer printing), ink-jet printing, screen printing, flexographic printing, off-
10 set printing or nozzle printing. Soluble compounds, which are obtained, for example, by suitable substitution, are necessary for this purpose. These processes are also particularly suitable for the compounds according to the invention, since these generally have very good solubility in organic solvents.

15 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 deposition. Thus, for example, the emitting layer can be applied from solution and the electron-transport layer by vapour deposition.

20 These processes are generally known to the person skilled in the art and can be applied by him without inventive step to organic electroluminescent devices comprising the compounds according to the invention.

25 The processing of the compounds according to the invention from the liquid phase, for example by spin coating or by printing processes, requires formulations of the compounds according to the invention. These formulations can be, for example, solutions, dispersions or mini-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-
30 xylene, methyl benzoate, dimethylanisole, mesitylene, tetralin, veratrol, THF, methyl-THF, THP, chlorobenzene, dioxane or mixtures of these solvents.

35 The present invention therefore furthermore relates to a formulation, in particular a solution, dispersion or mini-emulsion, comprising at least one

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5 compound of the formula (1) or the preferred embodiments indicated above and at least one solvent, in particular an organic solvent. The way in which solutions of this type can be prepared is known to the person skilled in the art and is described, for example, in WO 2002/072714, WO 2003/019694 and the literature cited therein.

10 The present invention furthermore relates to mixtures comprising at least one compound of the formula (1) or the preferred embodiments indicated above and at least one further compound. The further compound can be, for example, a fluorescent or phosphorescent dopant if the compound according to the invention is used as matrix material. The mixture may then also additionally comprise a further material as additional matrix material.

15 The compounds according to the invention and the organic electroluminescent devices according to the invention are distinguished by the following surprising advantages over the prior art:

- 20
1. The compounds according to the invention are very highly suitable for use in a hole-transport or hole-injection layer in an organic electroluminescent device. They are also suitable, in particular, for use in a layer which is directly adjacent to a phosphorescent emitting layer, since the
25 compounds according to the invention do not extinguish the luminescence.
 2. The compounds according to the invention, employed as matrix material for fluorescent or phosphorescent emitters, result in very high efficiencies and long lifetimes. This applies, in particular, if the compounds are employed as matrix material together with a further matrix material and a phosphorescent emitter.
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3. The compounds according to the invention, employed in organic electroluminescent devices, result in high efficiencies and in steep current/voltage curves with low use and operating voltages.
- 5 4. The compounds according to the invention contain a rigid planar Spiro unit and flexible structure elements in the outer periphery, whereby the flexibility of the molecule center is reduced and the solubility is increased by the substituents.
- 10 5. The compounds according to the invention exhibit an improved oxidation stability in solutions in comparison with conventional diamines compounds. This leads to an easier cleaning and second to an easier handling of these compounds. More particularly, the storage
15 stability of solutions for printing processes, which comprise these compounds, is significantly improved.
- 20 6. The compounds of the present invention have high thermal stability and can therefore be sublimed without decomposition and without a residue.

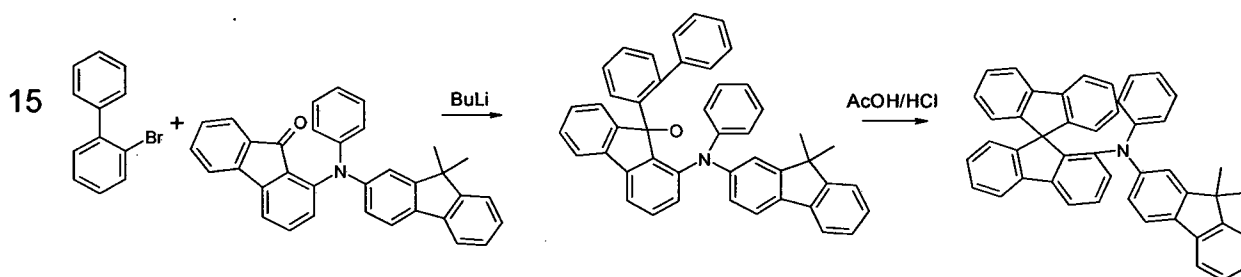
25 These above-mentioned advantages are not accompanied by an impairment in the other electronic properties.

30 The invention is explained in greater detail by the following examples, without wishing to restrict it thereby. On the basis of the descriptions, the person skilled in the art will be able 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 use the process according to the invention.

35

Examples:**A) Synthesis examples**

The following syntheses are carried out under a protective-gas atmosphere, unless indicated otherwise. The starting materials can be purchased from ALDRICH or ABCR. The numbers in square brackets in the case of the starting materials known from the literature are the corresponding CAS numbers.

Synthesis of phenyl-(9,9'-dimethylfluorenyl)-1-spiro-9,9'-bifluorenylamine

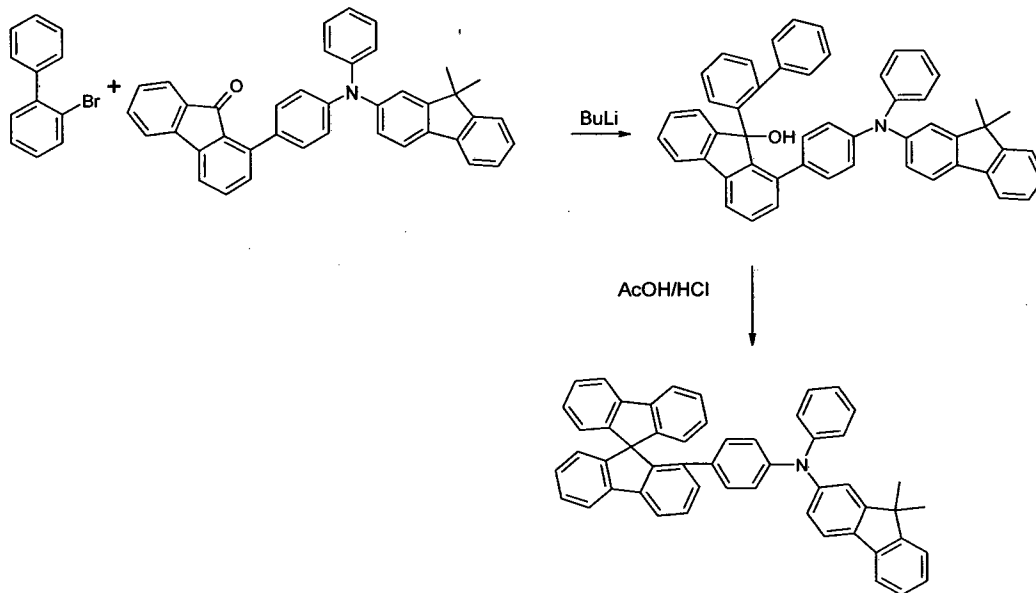
A solution of 2-Bromo-biphenyl (17 g, 70 mmol) in THF (90ml) is treated with 35 mL of *n*-BuLi (2,1 M in hexane, 70 mmol) under argon at -78 °C. The mixture is stirred for 30 minutes. A solution of phenyl-(9,9'-dimethylfluorenyl)amine-9H-Fluoren-9-one (38 g, 82 mmol) in 90 mL THF is added dropwise. The reaction proceeds at -78 °C for 30 minutes and then is stirred at room temperature overnight. The reaction is quenched with water and extracted with ethyl acetate. The intermediate alcohol is obtained after the solvent is removed (31 g, 64%). Without further purification, a mixture of the alcohol, acetic acid (700 mL) and concentrated HCl (62 mL) is refluxed for 2 hours. After cooling, the mixture is filtered and washed with water. The residue is crystallised from toluene. The crude product is extracted in a Soxhlet extractor (toluene) and purified by zone sublimation in vacuo. The product is isolated in the

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form of a pale-yellow solid (13 g, 27 % of theory, purity > 99.99% according to HPLC).

Similar to this phenyl-(9,9'-dimethylfluorenyl)-1-(4-phenyl)-spiro-9,9'-bifluorenylamine was synthesized:

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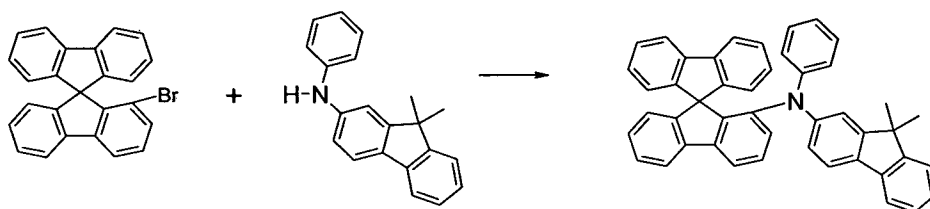
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Example 3a: Synthesis of phenyl-2-(9,9'-dimethylfluorenyl)-1-spiro-9,9'-bifluorenylamine

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Tri-*tert*-butylphosphine (2.7 ml of a 1.0 M solution in toluene, 2.7 mmol), palladium acetate (307 mg, 1.4 mmol) and sodium *tert*-butoxide (9.8 g, 102 mmol) are added to a solution of phenyl-(9,9-dimethyl-9*H*-fluoren-2-yl)-amine (20.5 g, 71 mmol) and 4-bromo-9,9'-spirobifluorene (27 g, 68 mmol) in degassed toluene (500 ml), and the mixture is heated under reflux for 2 h. The reaction mixture is cooled to room temperature, extended with toluene and filtered through Celite. The filtrate is evaporated in vacuo, and

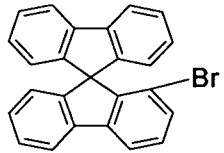
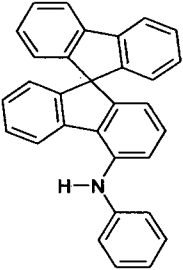
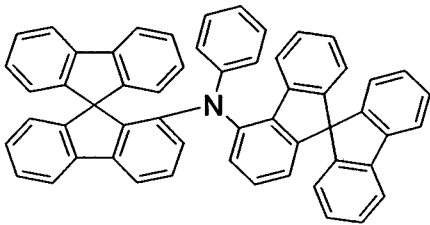
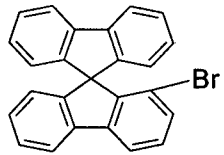
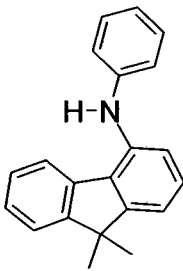
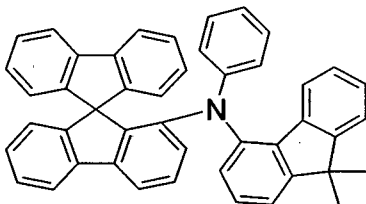
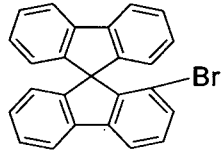
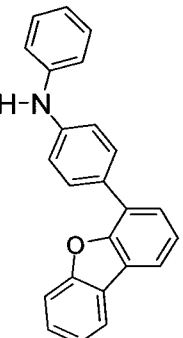
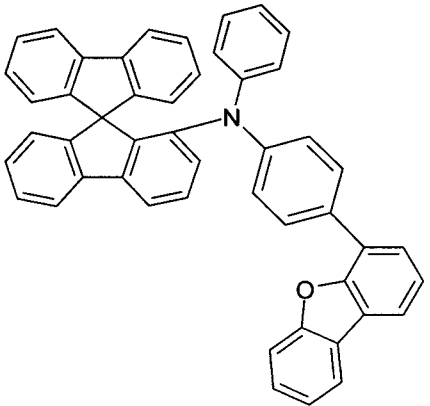
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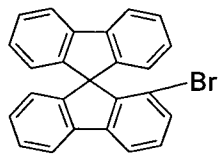
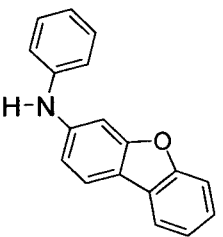
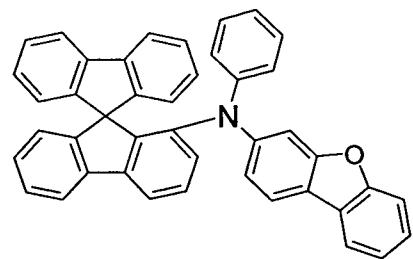
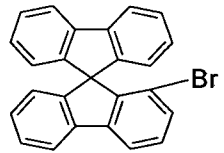
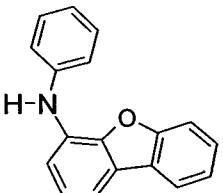
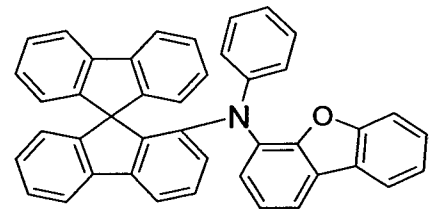
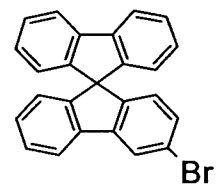
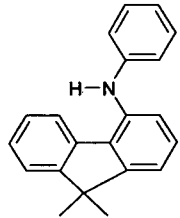
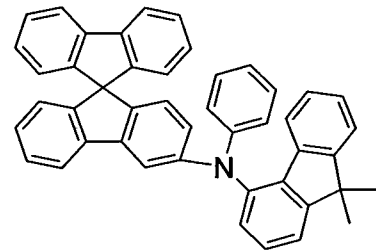
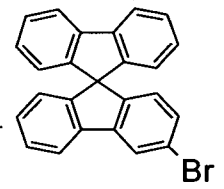
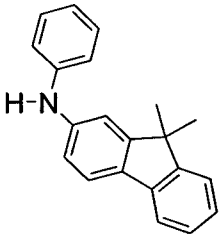
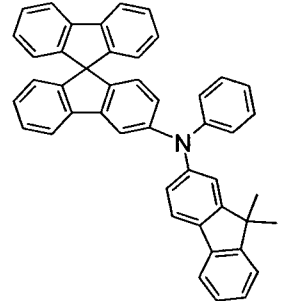
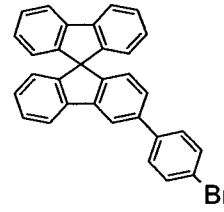
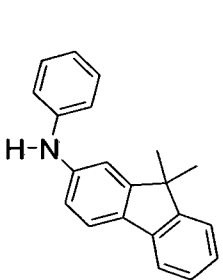
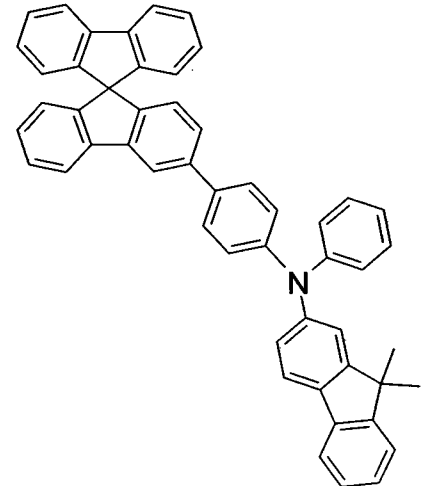
the residue is crystallised from ethyl acetate/heptane. The crude product is extracted in a Soxhlet extractor (toluene) and purified by zone sublimation in vacuo twice ($p = 3 \times 10^{-4}$ mbar, $T = 298^\circ\text{C}$). The product is isolated in the form of a pale-yellow solid (8 g, 20 % of theory, purity > 99.99% according to HPLC).

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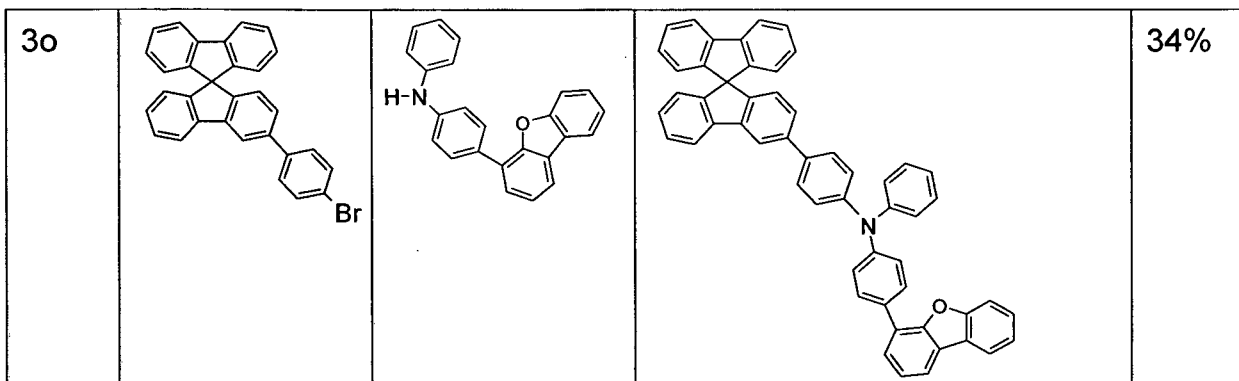
The following compounds are obtained analogously:

Ex.	Br-spiro	Amine	Product	Yield
10 3b				43%
15 20 3c				56%
25 30 3d		 [955959-21-9]		61%

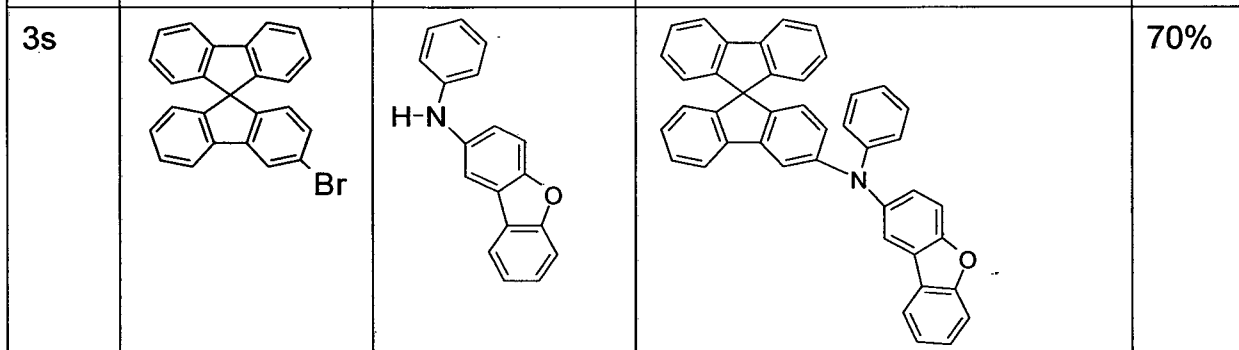
35

5	3e		 [406488-87-2]		72%
10	3k				64%
15	3l				56%
20	3m		 [355832-04-1]		66%
25 30 35	3n				46%

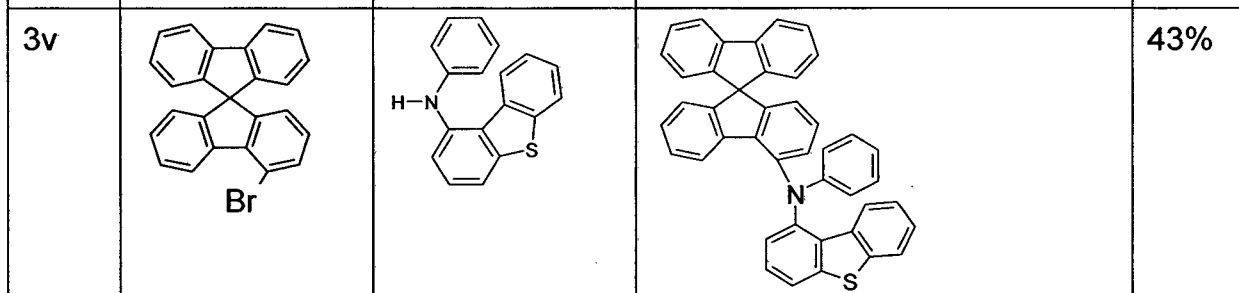
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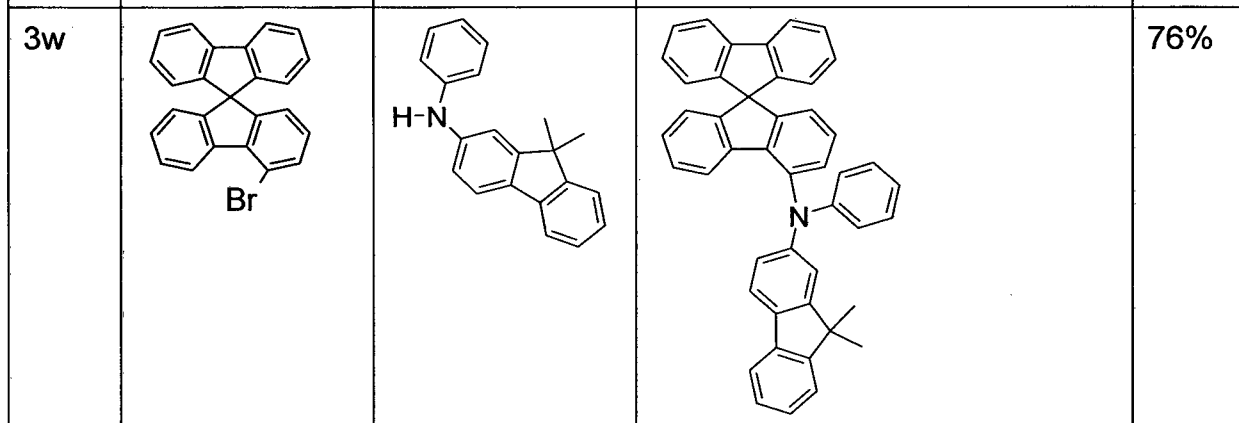
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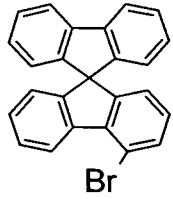
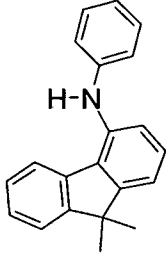
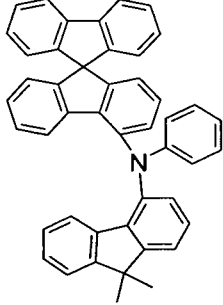
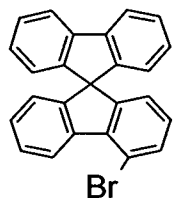
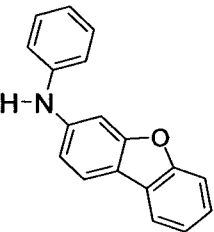
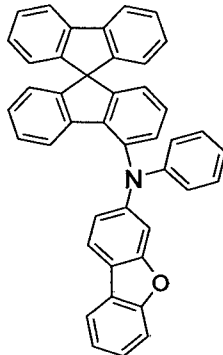
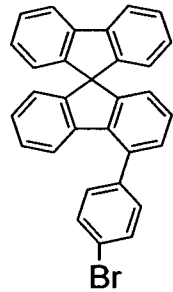
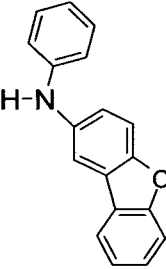
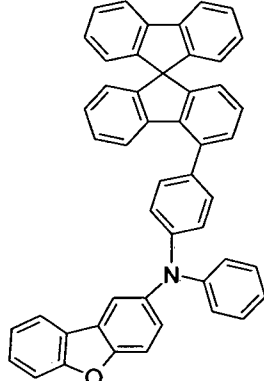
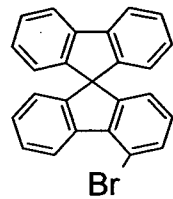
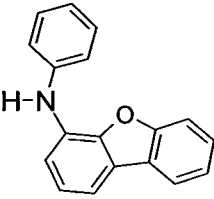
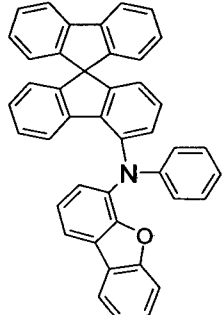


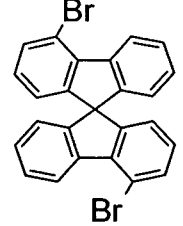
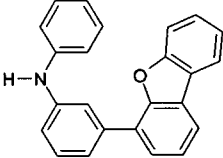
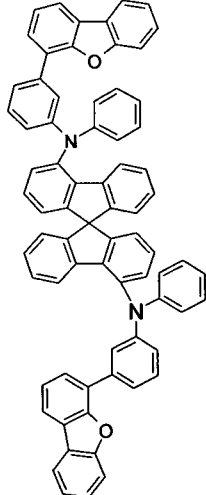
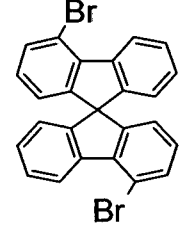
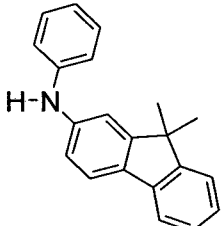
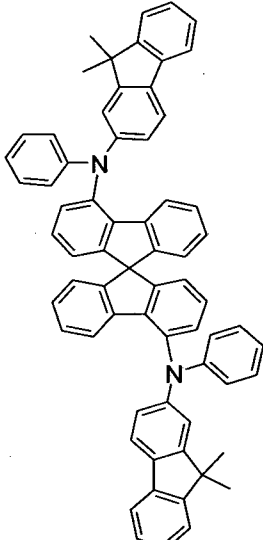
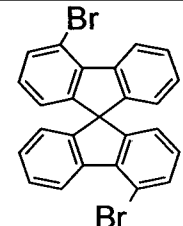
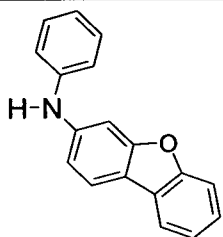
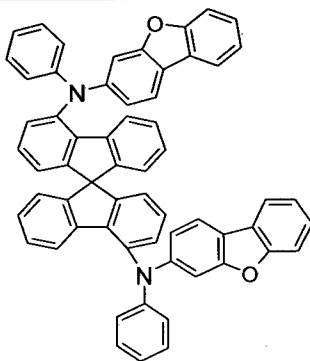
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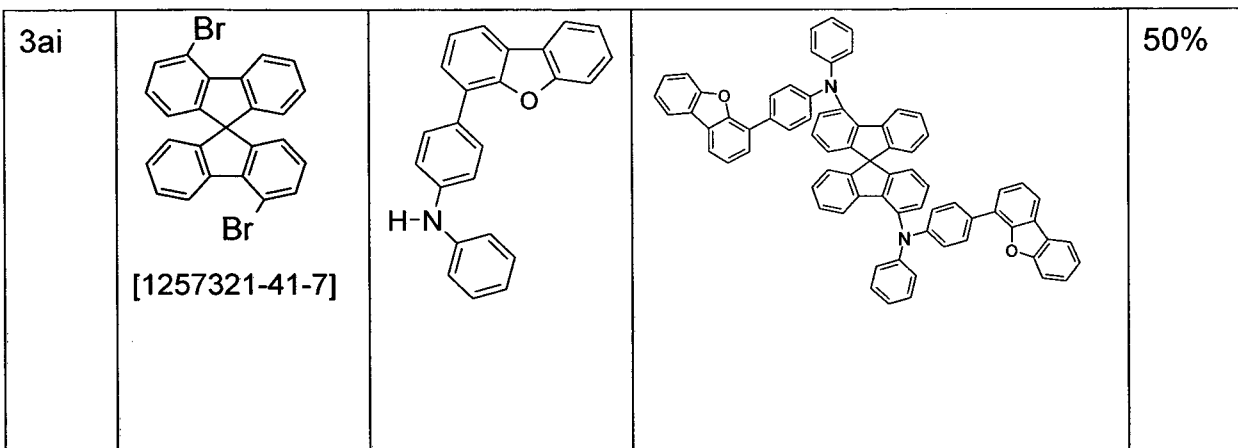
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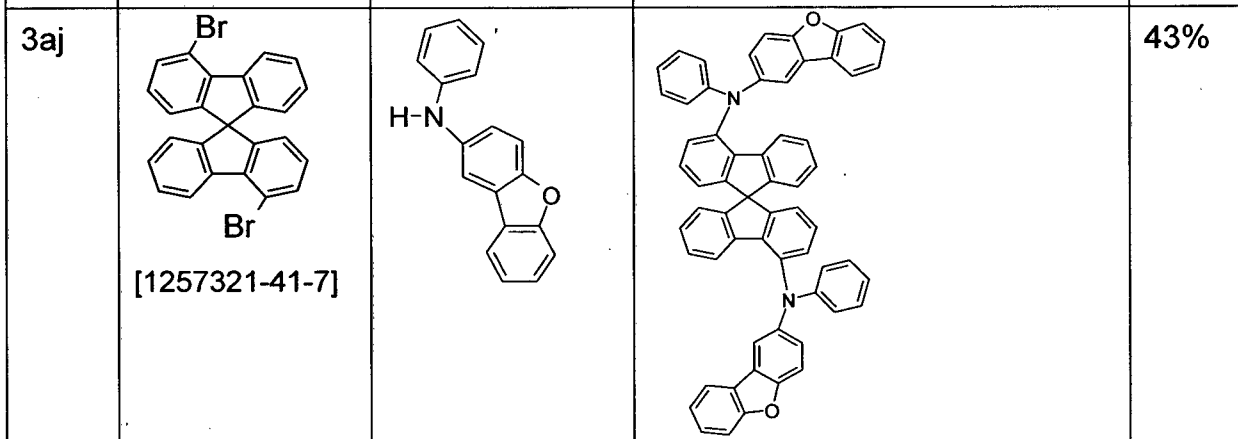
5	3x				41%
10	3y				50%
15	3z				59%
25	3aa				71%

<p>5</p>	<p>3af</p>  <p>[1257321-41-7]</p>			<p>48%</p>
<p>15</p> <p>20</p>	<p>3ag</p>  <p>[1257321-41-7]</p>			<p>46%</p>
<p>25</p> <p>30</p>	<p>3ah</p>  <p>[1257321-41-7]</p>			<p>41%</p>

5

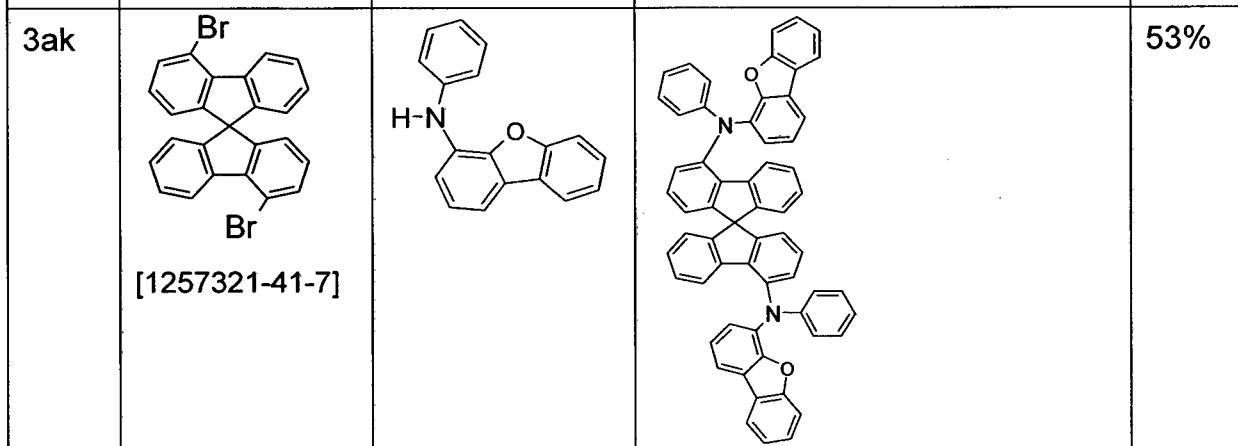


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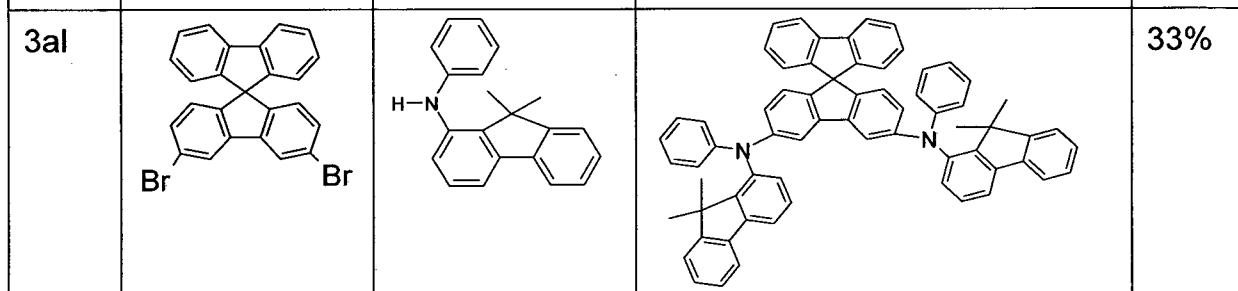
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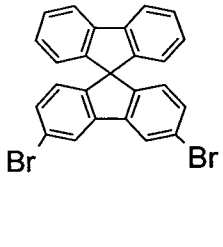
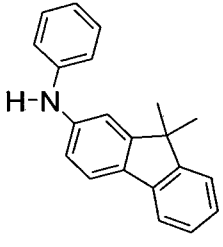
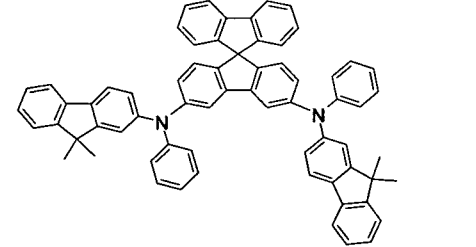
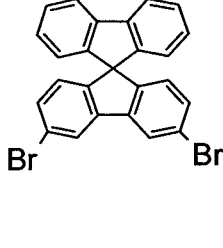
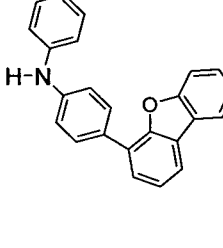
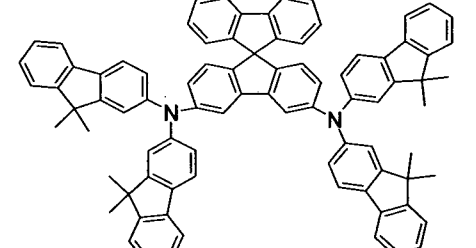
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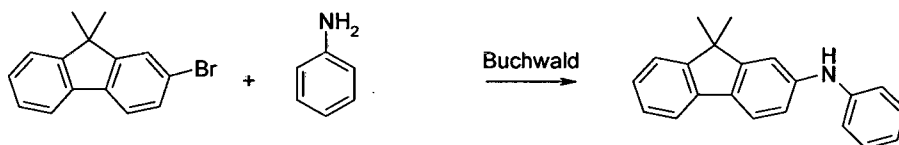
35

- 67 -

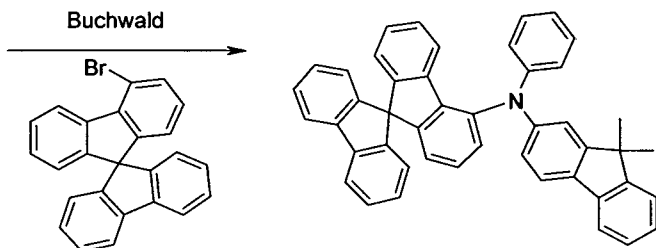
5	3am				46%
10	3an				41%

Example 4a: Synthesis of biphenyl-2-yl-(9,9-dimethyl-9H-fluoren-2-yl)-(9,9'-spirobifluoren-4-yl)amine

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a) Synthesis of phenyl-(9,9-dimethyl-9H-fluoren-2-yl)amine

1,1'-Bis(diphenylphosphino)ferrocene (1.5 g, 2.7 mmol), palladium acetate (616 mg, 2.7 mmol) and sodium *tert*-butoxide (22.9 g, 238 mmol) are added to a solution of phenyl-amine (17.0 g, 183 mmol) and 2-bromo-9,9-dimethyl-9H-fluorene (50.0 g, 183 mmol) in degassed toluene (400 ml), and the mixture is heated under reflux for 20 h. The reaction mixture is cooled to room temperature, extended with toluene and filtered through Celite. The filtrate is extended with water, re-extracted with toluene, and the combined

- 68 -

organic phases are dried and evaporated in vacuo. The residue is filtered through silica gel (heptane/dichloromethane) and crystallised from isopropanol. Phenyl-(9,9-dimethyl-9*H*-fluoren-2-yl)amine is obtained in the form of a pale-yellow solid (49.0 g, 95% of theory).

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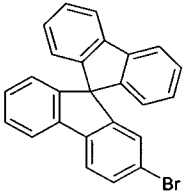
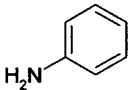
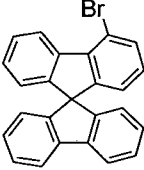
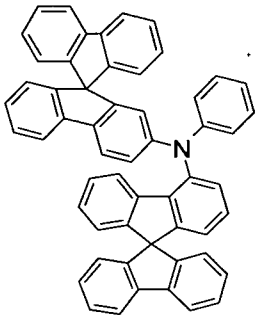
b) Synthesis of phenyl-(9,9-dimethyl-9*H*-fluoren-2-yl)-(9,9'-spiro-bifluoren-4-yl)amine

Tri-*tert*-butylphosphine (4.4 ml of a 1.0 M solution in toluene, 4.4 mmol), palladium acetate (248 mg, 1.1 mmol) and sodium *tert*-butoxide (16.0 g, 166 mmol) are added to a solution of phenyl-(9,9-dimethyl-9*H*-fluoren-2-yl)amine (40.0 g, 140 mmol) and 4-bromo-9,9'-spirobifluorene (56.9 g, 144 mmol) in degassed toluene (500 ml), and the mixture is heated under reflux for 2 h. The reaction mixture is cooled to room temperature, extended with toluene and filtered through Celite. The filtrate is evaporated in vacuo, and the residue is crystallised from ethyl acetate/heptane. The crude product is extracted in a Soxhlet extractor (toluene) and purified by zone sublimation in vacuo twice ($p = 3 \times 10^{-4}$ mbar, $T = 298^{\circ}\text{C}$). The product is isolated in the form of a pale-yellow solid (20.4 g, 24% of theory, purity > 99.99% according to HPLC).

10

The following compounds are obtained analogously:

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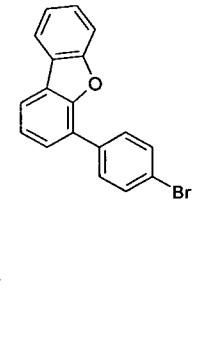
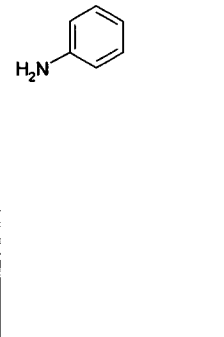
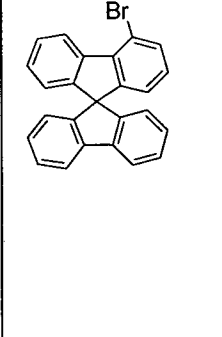
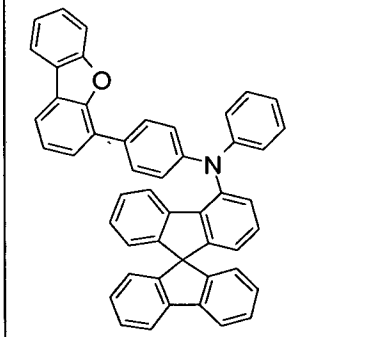
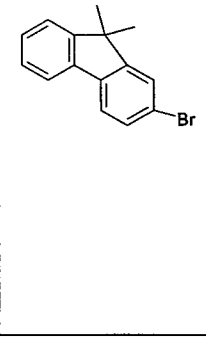
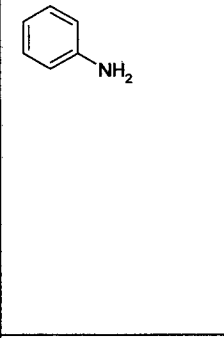
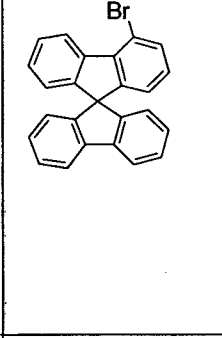
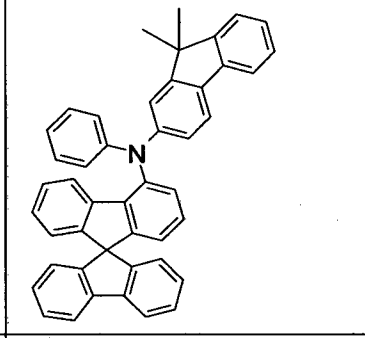
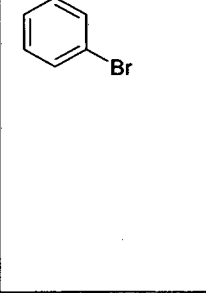
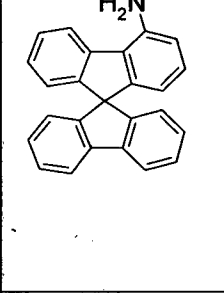
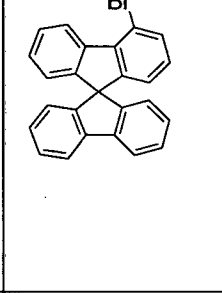
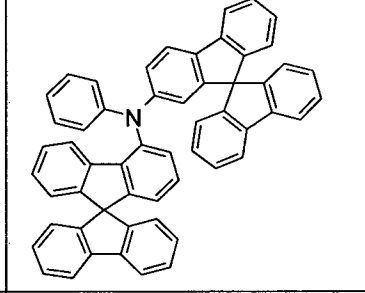
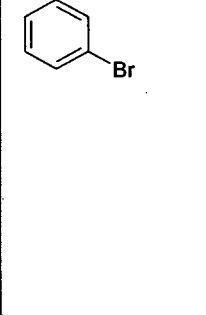
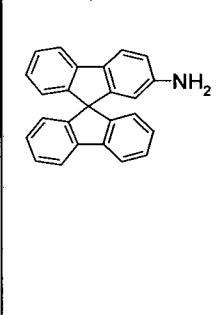
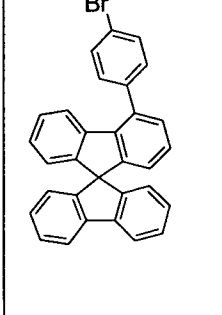
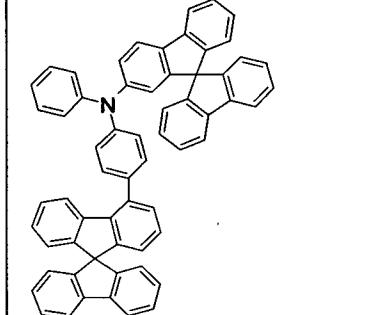
Ex.	Starting material 1	Starting material 2	Starting material 3	Product	Yield
4b			 [1161009-88-6]		78%

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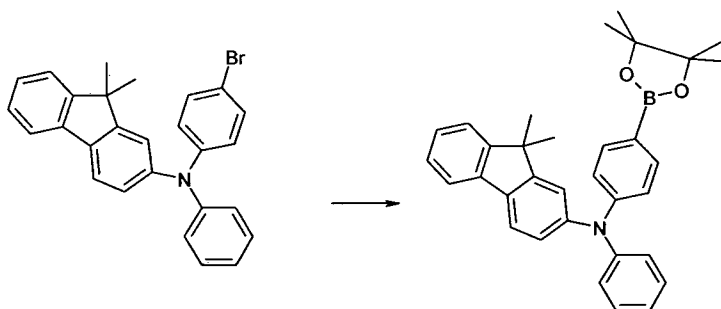
5	4c					73%
10	4d					75%
15	4e					79%
20	4f					78%

30 **Example 5a: Synthesis of Synthesis of Biphenyl-4-yl-(9,9-dimethyl-9H-fluoren-2-yl)-[4-(9,9'-spiro-bifluoren-4-yl)-phenyl]-amine**

35 **a) Synthesis of Biphenyl-4-yl-(9,9-dimethyl-9H-fluoren-2-yl)(4,4,5,5tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-amine**

- 70 -

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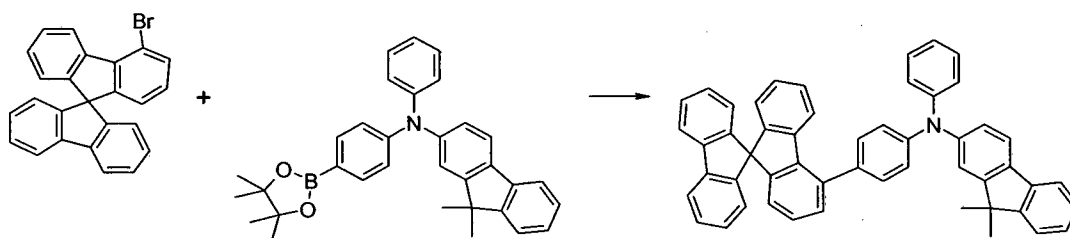
102 g (231 mmol) of phenyl-(4-bromo-phenyl)-(9,9-dimethyl-9H-fluoren-2-yl)-amine, 4,8 g (5,9 mmol) of Pd(dppf)Cl₂, 61,6 g (238 mmol) of bis(pinacolato)diboron and 58,3 g (594 mmol) of potassium acetate are dissolved in 1300 mL of 1,4-dioxane. The reaction mixture is refluxed and agitated under an argon atmosphere for 12 hours and after cooling to room temperature, the mixture is filtered through Celite. The filtrate is evaporated in vacuo, and the residue is crystallised from heptane. The product is isolated in the form of a pale-yellow solid (87 g, 78% of theory).

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b) Synthesis of phenyl-(9,9-dimethyl-9H-fluoren-2-yl)-[4-(9,9'-spiro-bifluoren-4-yl)-phenyl]-amine

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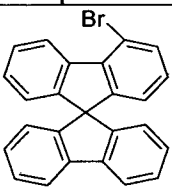
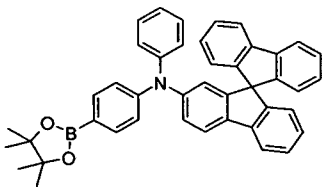
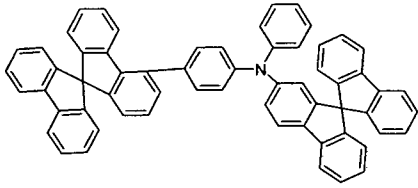
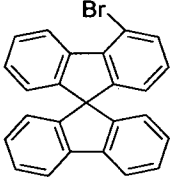
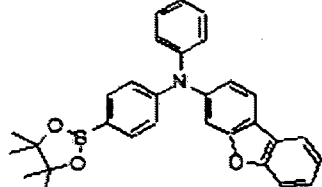
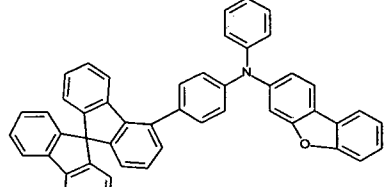
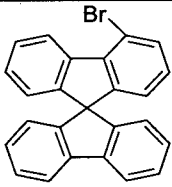
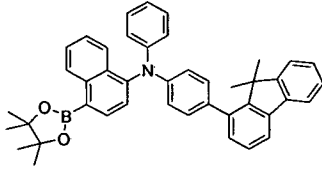
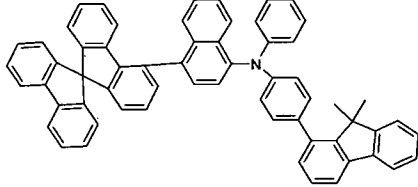
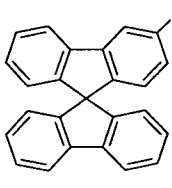
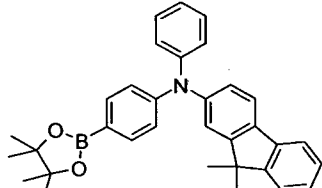
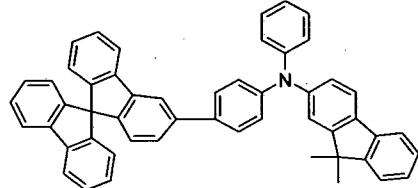
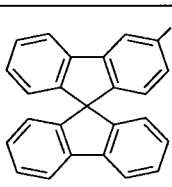
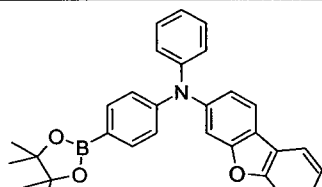
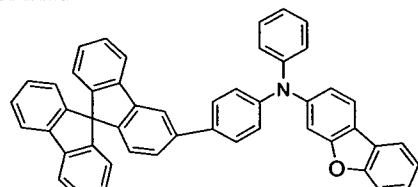
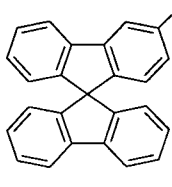
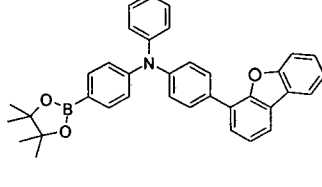
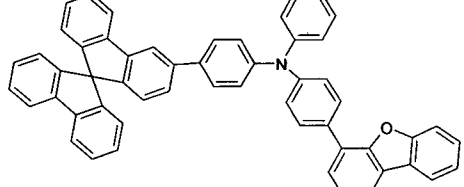
24 g (49,4 mmol) of phenyl-(9,9-dimethyl-9H-fluoren-2-yl)-[4-(9,9'-spiro-bifluoren-4-yl)-phenyl]-amine, 20 g (49,4 mmol) of 4-bromospiro-bifluorene, 1,8 g (2,5 mmol) of PdCl₂(Cy)₃, 15 g (99 mmol) of cesium fluoride are dissolved in 500 mL of toluene. The reaction mixture is refluxed and agitated under an argon atmosphere for 12 hours and after cooling to room temperature, the mixture is filtered through Celite. The filtrate is evaporated in vacuo, and the residue is crystallised from heptane.

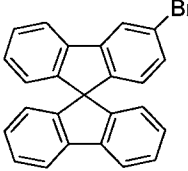
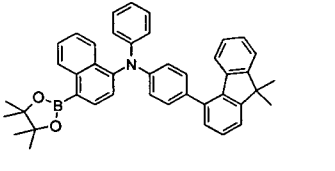
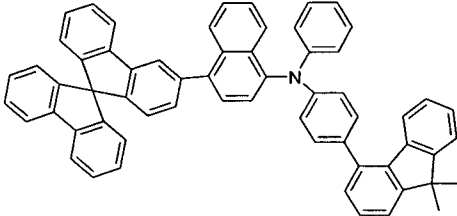
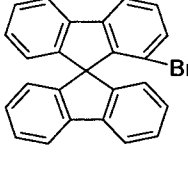
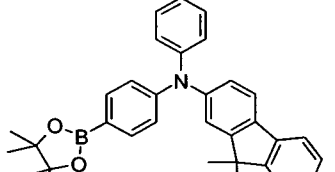
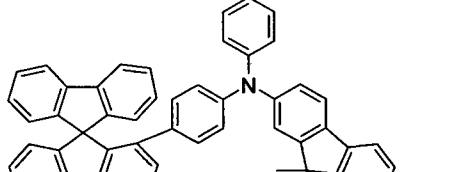
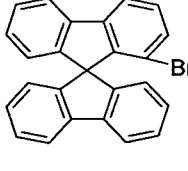
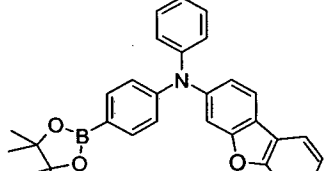
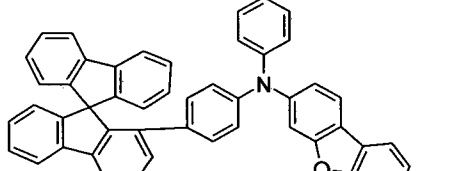
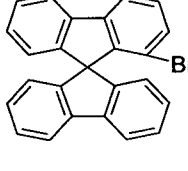
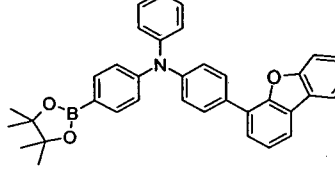
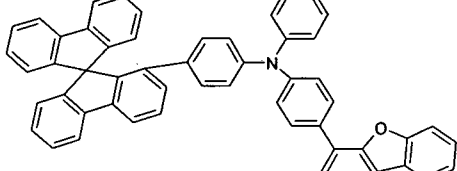
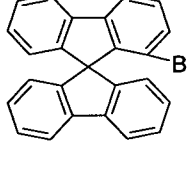
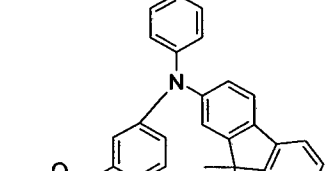
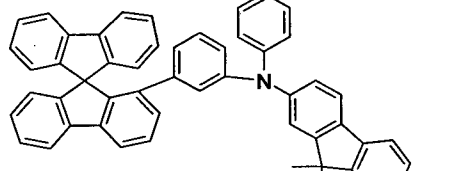
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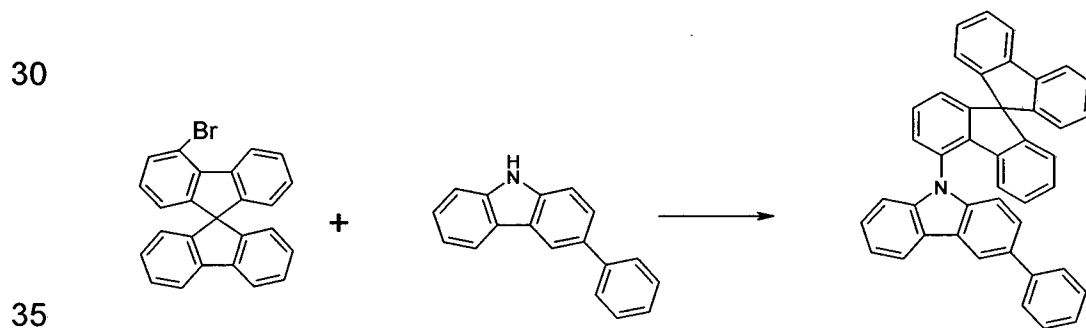
The crude product is extracted in a Soxhlet extractor (toluene) and purified by zone sublimation in vacuo twice. The product is isolated in the form of a pale-yellow solid (9 g, 57% of theory, purity > 99.99% according to HPLC).

5 The following compounds are synthesized analogously:

Ex.	Br-Spiro	Amine	Product	Yield
10 5b				43%
15 5c				55%
20 5d				60%
25 5e				63%
30 5f				70%
35 5g				75%

5h				55%
5i				64%
5j				60%
5k				67%
5l				58%

Example 6a: 9-Spiro-4-yl-3,6-diphenyl-9H-carbazol



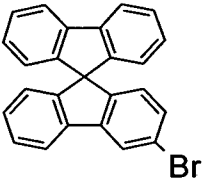
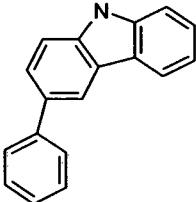
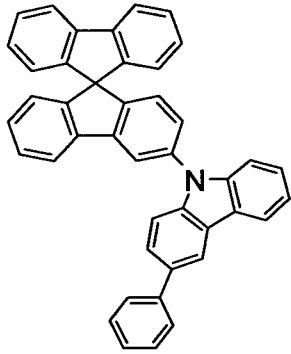
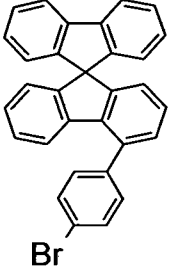
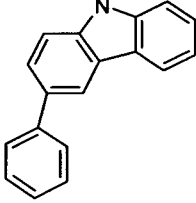
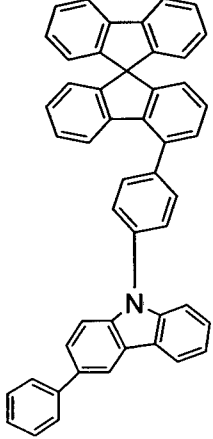
- 73 -

19.2 g (47 mmol) 4-Brom-9-spirobifluorene, 15 g (62 mmol) 3-phenyl-9-H-carbazole and 29.2 g Rb_2CO_3 are suspended in 250 mL p-Xylol. To the suspension are given 0.95 g (4,2 mmol) $\text{Pd}(\text{OAc})_2$ and 12.6 ml of a 1M solution of Tri-tert-butylphosphine. The mixture is stirred 24 h under reflux.

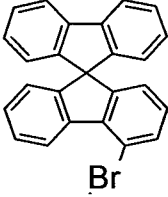
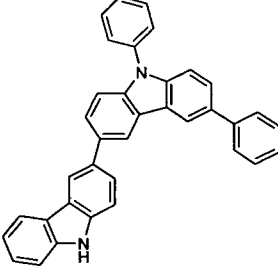
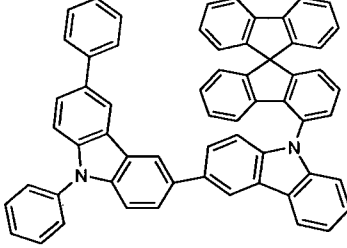
5 After cooling the organic phase is separated, washed three times with 150 mL water and is subsequently concentrated to dryness in vacuo. The residue is hot extracted with toluene, recrystallized three times from toluene and subsequently sublimated at high vacuum. Yield is 19.6 g (35 mmol) corresponding to 75 % of theory. Purity is according to HPLC

10 99.9 %.

The following compounds are obtained analogously:

	starting material 1	starting material 2	product	yield
15 6b				76%
20				
25 6c				65%
30				

35

5 6d				77%
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B) Devices examples

10 OLEDs according to the invention and OLEDs in accordance with the prior art are produced by a general process in accordance with WO 2004/058911, which is adapted to the circumstances described here (layer-thickness variation, materials).

15 The data for various OLEDs are presented in Examples E1, E2 and E3 below (see Tables 1 to 4). The substrates used are glass plates coated with structured ITO (indium tin oxide) in a thickness of 50nm. The OLEDs basically have the following layer structure: substrate / hole-injection layer
 20 (HIL) / hole-transport layer (HTL) / hole-injection layer (HIL) / electron-blocking layer (EBL) / emission layer (EML) / electron-transport layer (ETL) / electron-injection layer (EIL) and finally a cathode. The cathode is formed by an aluminium layer with a thickness of 100nm. The precise structure of the OLEDs is shown in Table 1 and 3. The materials required for the
 25 production of the OLEDs are shown in Table 5.

30 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 H1:SEB(5%) here means that
 35 material H1 is present in the layer in a proportion by volume of 95% and

- 75 -

SEB is present in the layer in a proportion of 5%. Analogously, the electron-transport layer may also consist of a mixture of two materials. The OLEDs are characterised by standard methods. For this purpose, the current efficiency (measured in cd/A), the power efficiency (measured in lm/W) and the external quantum efficiency (EQE, measured in per cent) as a function of the luminous density, calculated from current/voltage/luminous density characteristic lines (UIL characteristic lines) assuming Lambertian emission characteristics, and the lifetime are determined. The expression EQE @ 10mA/cm² denotes the external quantum efficiency at an operating current density of 10mA/cm². LT80 @ 5000cd/m² is the lifetime until the OLED has dropped from a luminance of 5000cd/m² to 80% of the initial intensity, i.e. to 4000cd/m². The data for the various OLEDs are summarised in Tables 2 and 4.

Use of compounds according to the invention as hole-transport materials in fluorescent and phosphorescent OLEDs

In particular, compounds according to the invention are suitable as HIL, HTL or EBL in OLEDs. They are suitable as a single layer, but also as mixed component as HIL, HTL, EBL or within the EML. Compared with components which comprise reference materials (HTMV1, HTMV2, HTMV3), the samples comprising the compounds according to the invention exhibit both higher efficiencies and also significantly improved lifetimes. They were tested both in singlet blue and also in triplet green OLED devices.

Table 1: Structure of the OLEDs

Ex.	HIL	HTL	EBL	EML	ETL	EIL
	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm
E1	HIL:F4TCNQ(5%) 20nm	HIL 170nm	HTM1 20nm	H1:SEB(5%) 20 nm	ETM:LiQ(50%) 30 nm	LiQ 1nm
E2	HIL:F4TCNQ(5%) 20nm	HIL 170nm	HTM2 20nm	H1:SEB(5%) 20 nm	ETM:LiQ(50%) 30 nm	LiQ 1nm
V1	HIL:F4TCNQ(5%)	HIL	HTMV1	H1:SEB(5%)	ETM:LiQ(50%)	LiQ

	20nm	170nm	20nm	20 nm	30 nm	1nm
V2	HIL:F4TCNQ(5%) 20nm	HIL 170nm	HTMV2 20nm	H1:SEB(5%) 20 nm	ETM:LiQ(50%) 30 nm	LiQ 1nm
V3	HIL:F4TCNQ(5%) 20nm	HIL 170nm	HTMV3 20nm	H1:SEB(5%) 20 nm	ETM:LiQ(50%) 30 nm	LiQ 1nm

5

Table 2: Data for the OLEDs

Ex.	EQE	LT80
	@ 10mA/cm ²	@ 5000 cd/m ²
	%	[h]
E1	9.1	240
E2	9.0	180
V1	8.8	110
V2	9.0	150
V3	8.4	180

10

15

Table 3: Structure of the OLEDs

Ex.	HIL	HTL	HIL	EBL	EML	ETL	EIL
	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm
E3	HIL:F4TCNQ 20 nm	HIL 210nm	HTM1:F4TCNQ 20nm	HTM1 20nm	H2:TEG(10%) 30 nm	ETM1(50%):LiQ(50%) 40 nm	LiQ 1nm
V4	HIL: F4TCNQ 20 nm	HIL 210nm	HTMV1:F4TCNQ 20nm	HTMV1 20nm	H2:TEG(10%) 30 nm	ETM1(50%):LiQ(50%) 40 nm	LiQ 1nm
V5	HIL: F4TCNQ 20 nm	HIL 210nm	HTMV2:F4TCNQ 20nm	HTMV2 20nm	H2:TEG(10%) 30 nm	ETM1(50%):LiQ(50%) 40 nm	LiQ 1nm

20

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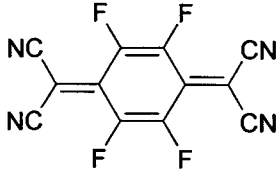
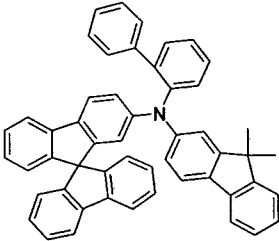
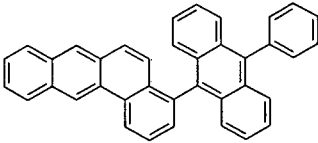
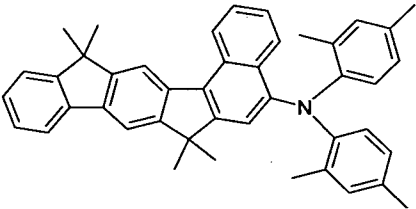
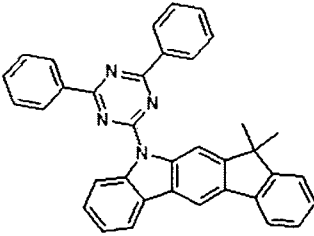
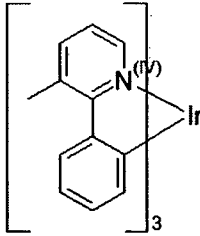
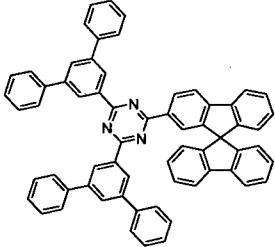
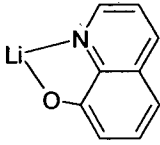
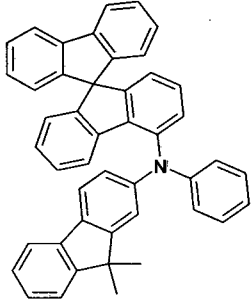
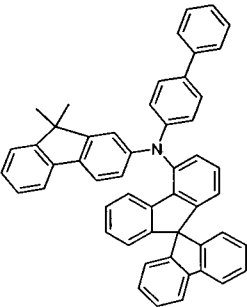
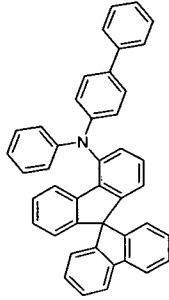
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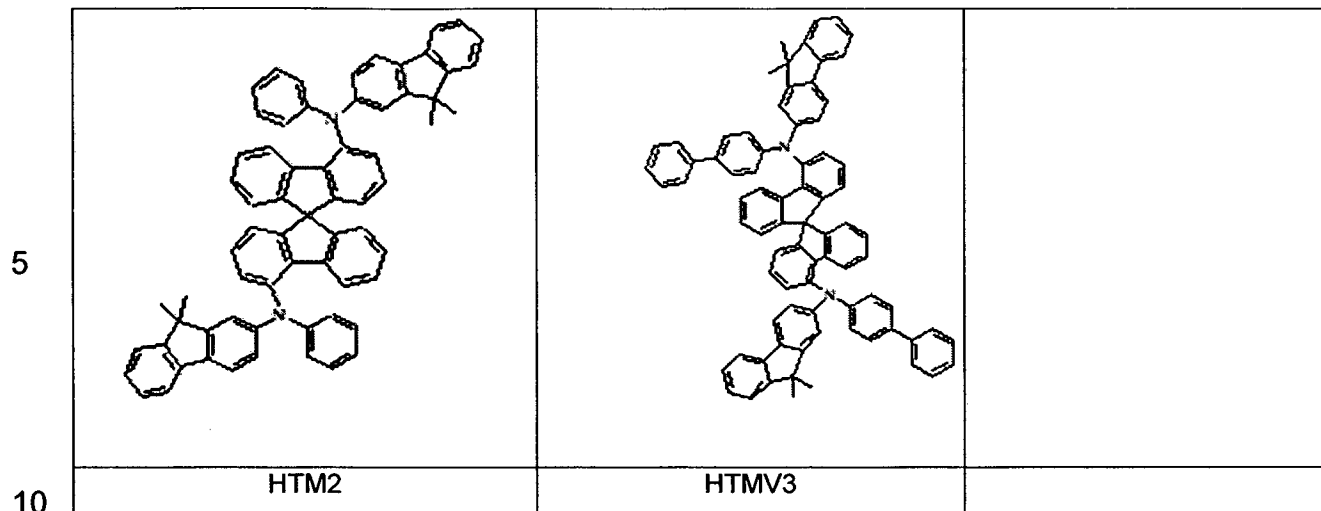
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Table 4: Data for the OLEDs

Ex.	EQE	LT80
	@ 2mA/cm ²	@ 10000cd/m ²
	%	[h]
E3	21.6	240
V4	19.7	240
V5	19.9	230

Table 5 – Structures of the materials used

5			
	F4TCNQ	HIM	H1
10			
	SEB	H2	TEG
15			
20	ETM	LIQ	
25			
30	HTM1	HTMV1	HTMV2



5

10

15

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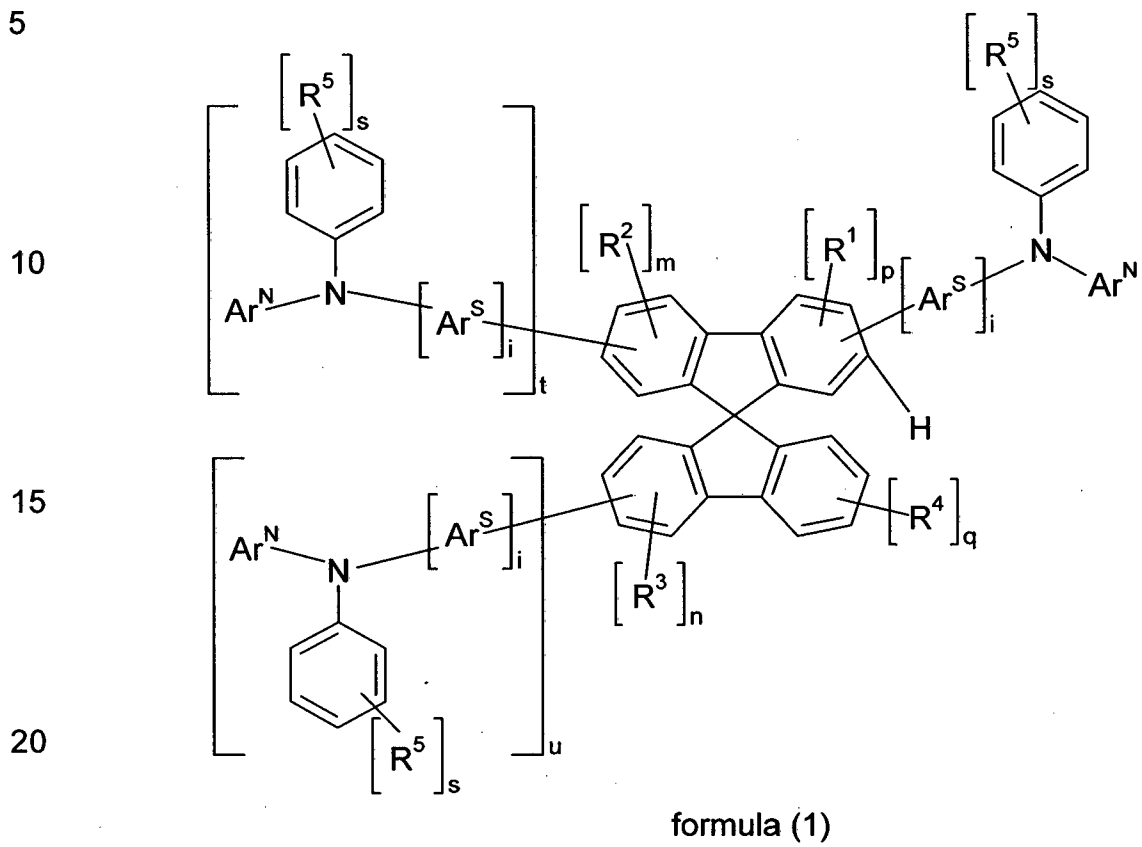
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Patent Claims

1. Compound of the formula (1),

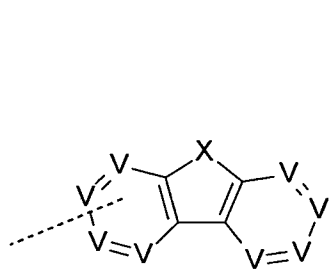


where the following applies to the symbols and indices used:

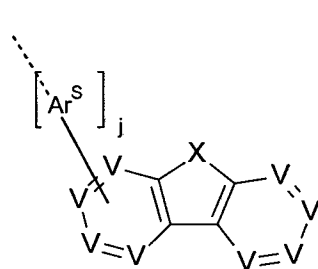
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Ar^N is a group of one of the following formulae (2-1) to (2-3)

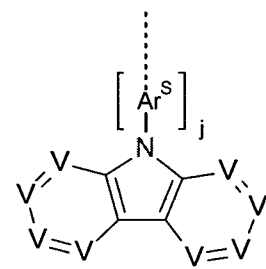
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formula (2-1)



formula (2-2)



formula (2-3)

35

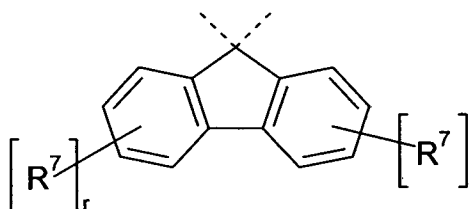
- 80 -

V is, identically or differently, equal to CR⁶ or N; with the proviso that when the bonding to a nitrogen atom depicted in formula (1) takes place via a group V, then V stands for a C atom; the dashed bonds indicate the bonding to a nitrogen atom depicted in formula (1);

5

X is a divalent bridge selected from the group consisting of B(R⁰), C(R⁰)₂, Si(R⁰)₂, C=O, C=NR⁰, C=C(R⁰)₂, O, S, S=O, SO₂, N(R⁰), P(R⁰) and P(=O)R⁰;
or X is a group of the following formula (3),

10



15

formula (3)

where the dashed bonds indicate the bonding to the 5-membered ring of formula (2-1) or (2-2);

20

R⁰ is selected on each occurrence, identically or differently, from the group consisting of H, D, F, Cl, Br, I, CHO, CN, C(=O)Ar¹, P(=O)(Ar¹)₂, S(=O)Ar¹, S(=O)₂Ar¹, NO₂, Si(R⁸)₃, B(OR⁸)₂, OSO₂R⁸, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R⁸, where in each case one or more non-adjacent CH₂ groups may be replaced by R⁸C=CR⁸, C≡C, Si(R⁸)₂, Ge(R⁸)₂, Sn(R⁸)₂, C=O, C=S, C=Se, P(=O)(R⁸), SO, SO₂, O, S or CONR⁸ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, an aromatic or heteroaromatic ring system having 5 to 40 aromatic ring atoms,

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which may in each case be substituted by one or more radicals R^8 , an aryloxy group having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^8 , where two substituents R^0 attached to the same C or Si atom may optionally form a mono- or polycyclic aliphatic ring system, which may be substituted by one or more radicals R^8 ; with the proviso that when two R^0 are attached to the same C atom, then at least one R^0 is selected from the group consisting of H, D, F, CN, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R^8 .

R^1, R^2, R^3, R^4, R^6 or R^7 are selected on each occurrence, identically or differently, from the group consisting of H, D, F, Cl, Br, I, CHO, CN, $C(=O)Ar^1$, $P(=O)(Ar^1)_2$, $S(=O)Ar^1$, $S(=O)_2Ar^1$, NO_2 , $Si(R^8)_3$, $B(OR^8)_2$, OSO_2R^8 , a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R^8 , where in each case one or more non-adjacent CH_2 groups may be replaced by $R^8C=CR^8$, $C\equiv C$, $Si(R^8)_2$, $Ge(R^8)_2$, $Sn(R^8)_2$, $C=O$, $C=S$, $C=Se$, $P(=O)(R^8)$, SO, SO_2 , O, S or $CONR^8$ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 , an aromatic or heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may in each case be substituted by one or more radicals R^8 , an aryloxy group having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^8 , where two or more adjacent substituents R^1 , two or more adjacent substituents R^2 , two or more adjacent substituents R^3 , two or more adjacent substituents R^4 , two or more adjacent substituents R^6 or two or more adjacent

- 82 -

substituents R^7 may optionally form a mono- or polycyclic, aliphatic ring system or aromatic ring system, which may be substituted by one or more radicals R^8 ;

5 R^5 is selected on each occurrence, identically or differently, from the group consisting of H, D, F, Cl, Br, I, CHO, CN, C(=O)Ar¹, P(=O)(Ar¹)₂, S(=O)Ar¹, S(=O)₂Ar¹, NO₂, Si(R⁸)₃, B(OR⁸)₂, OSO₂R⁸, a straight-chain alkyl, alkoxy or thioalkyl group having
10 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R^8 , where in each case one or more non-adjacent CH₂ groups may be replaced by R⁸C=CR⁸, C≡C, Si(R⁸)₂, Ge(R⁸)₂, Sn(R⁸)₂, C=O, C=S, C=Se, P(=O)(R⁸), SO,
15 SO₂, O, S or CONR⁸ and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, where two or more adjacent substituents R^5 may optionally form a mono- or polycyclic aliphatic ring system, which may be substituted by
20 one or more radicals R^8 ;

R^8 is selected on each occurrence, identically or differently, from the group consisting of H, D, F, Cl, Br, I, CN, a straight-chain
25 alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, where in each case one or more non-adjacent CH₂ groups may be replaced by SO, SO₂, O, S and where one or more H atoms may be replaced by D, F, Cl, Br or I, an aromatic
30 or heteroaromatic ring system having 6 to 60 C atoms, where two or more adjacent substituents R^8 may optionally form a mono- or polycyclic, aliphatic ring system;

35 Ar¹, Ar^S are on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 40 aromatic ring

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atoms, which may in each case also be substituted by one or more radicals R⁸;

t, u are, identically or differently, 0 or 1;

5

m, n, q, r are, identically or differently, 0, 1, 2, 3 or 4, where $t + m \leq 4$ and $u + n \leq 4$;

10

p is 0, 1 or 2;

i is 0, 1 or 2, wherein $i = 0$ or $j = 0$ means that the group Ar^s is absent and replaced by a single bond;

15

j is 1, 2 or 3;

s is 0, 1, 2, 3, 4 or 5.

20

2. Compound according to claim 1, characterised in that $t + u = 0$ or 1.

3. Compound according to claim 1 or 2, characterised in that the index i is 0.

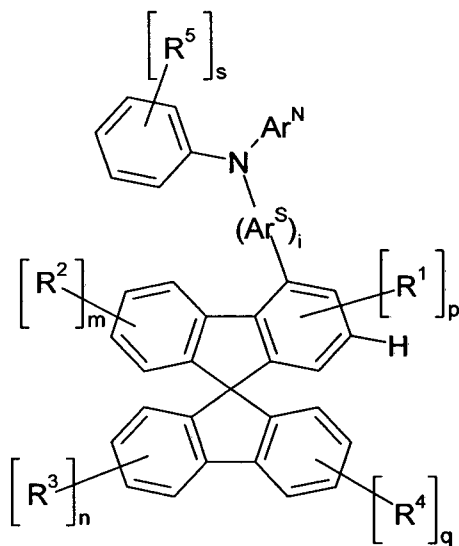
25

4. Compound according to one or more of the preceding claims, selected from the compounds of the formulae (1-1) to (1-9),

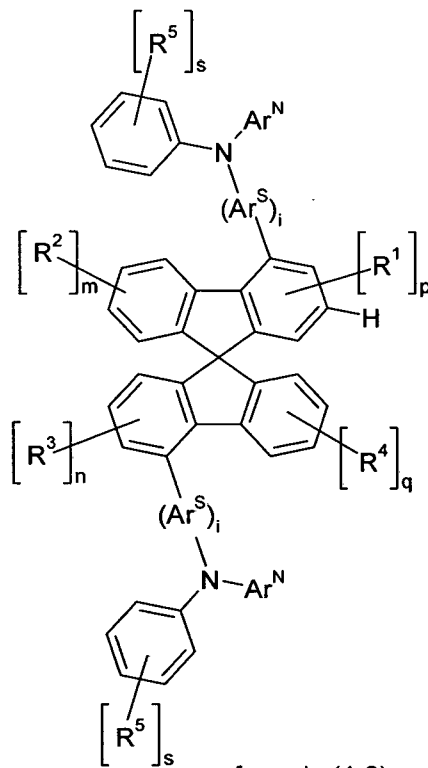
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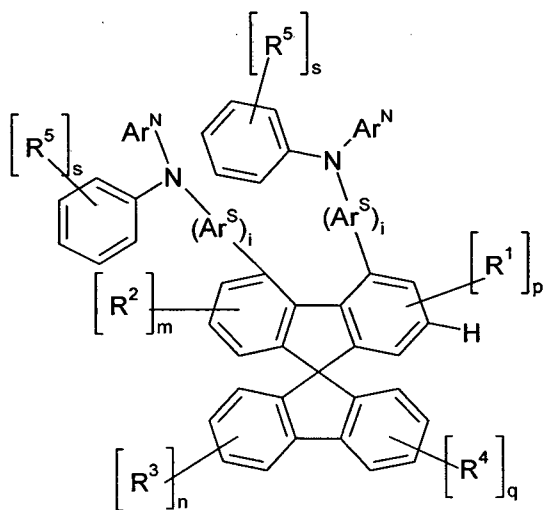


formula (1-1)

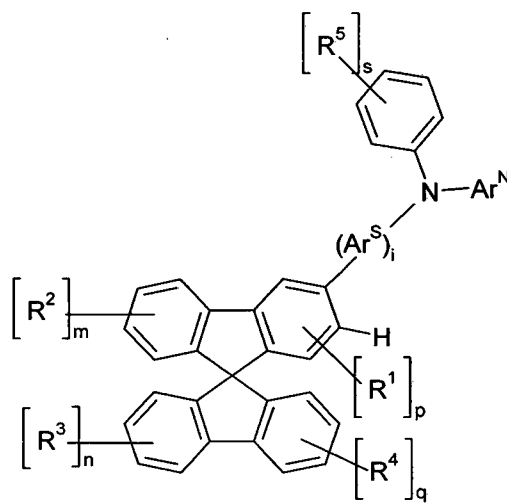


formula (1-2)

20



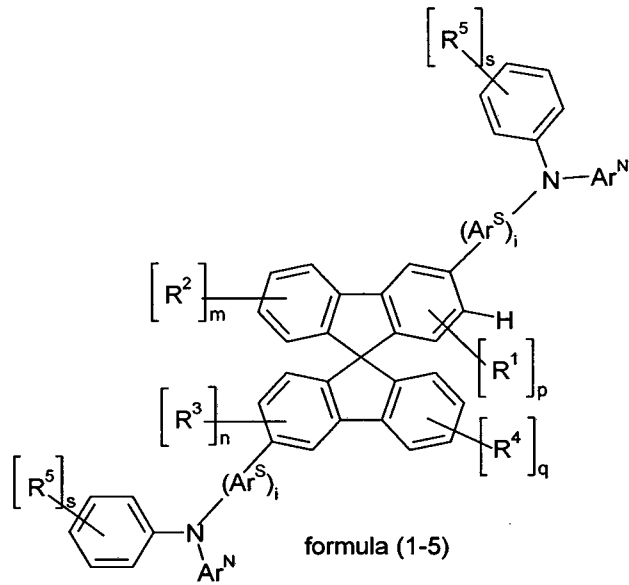
formula (1-3)



formula (1-4)

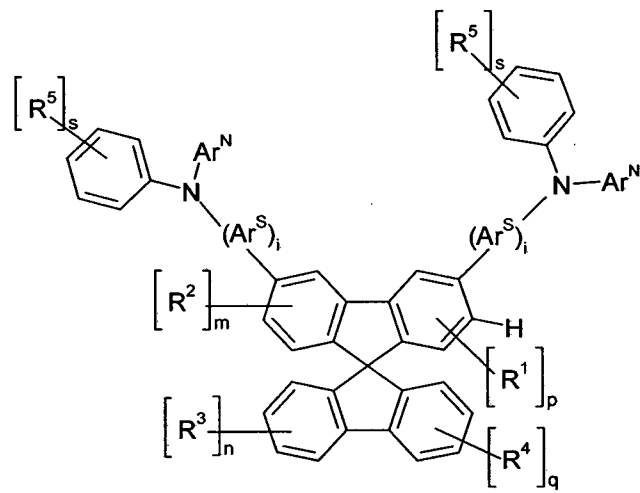
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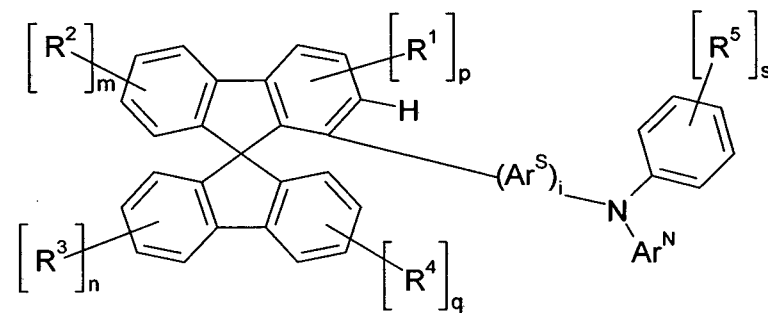
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formula (1-6)

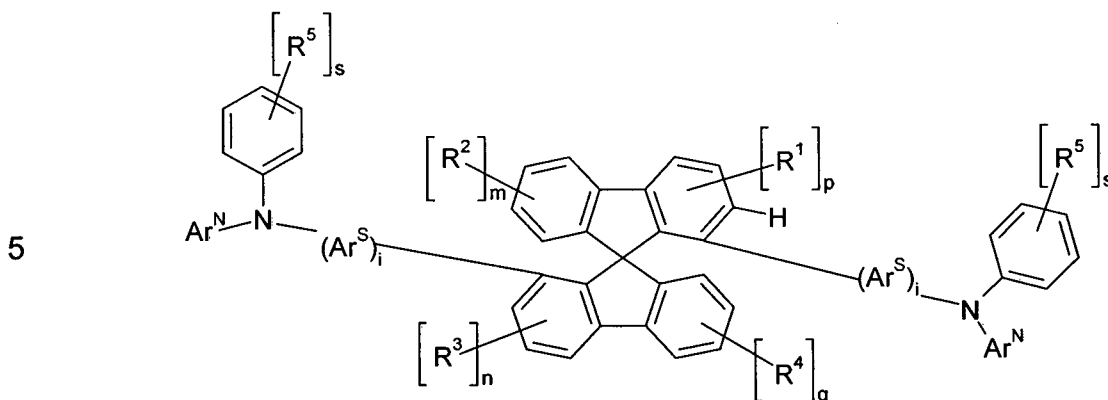
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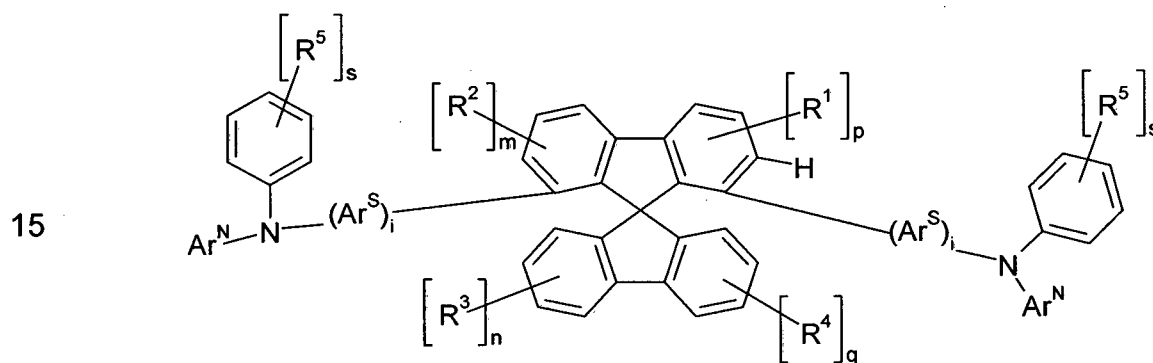
formula (1-7)

35



formula (1-8)

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formula (1-9)

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where the symbols and indices used have the meanings given in claim 1.

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5. Compound according to one or more of the preceding claims, selected from the compounds of the formulae (1-1a) to (1-9a)

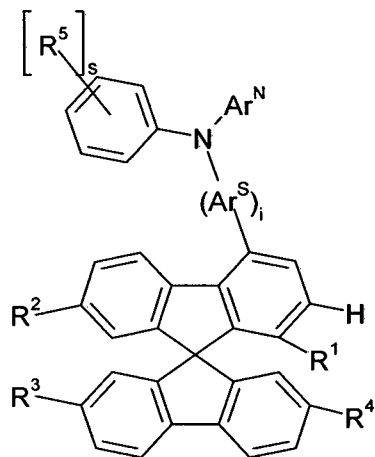
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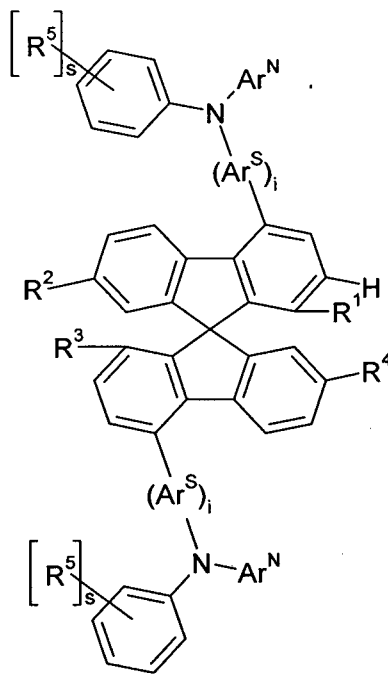
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formula (1-1a)

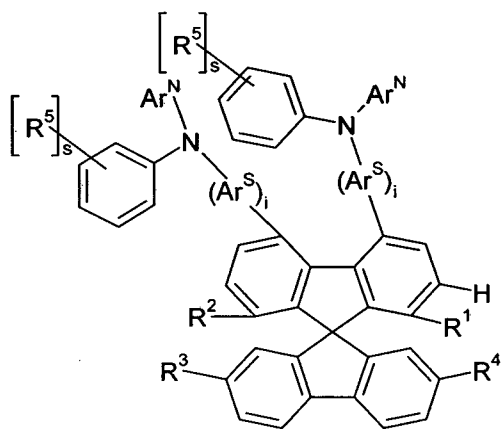


formula (1-2a)

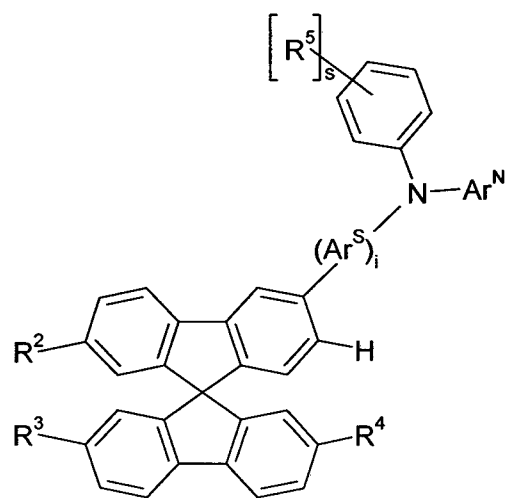
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formula (1-3a)

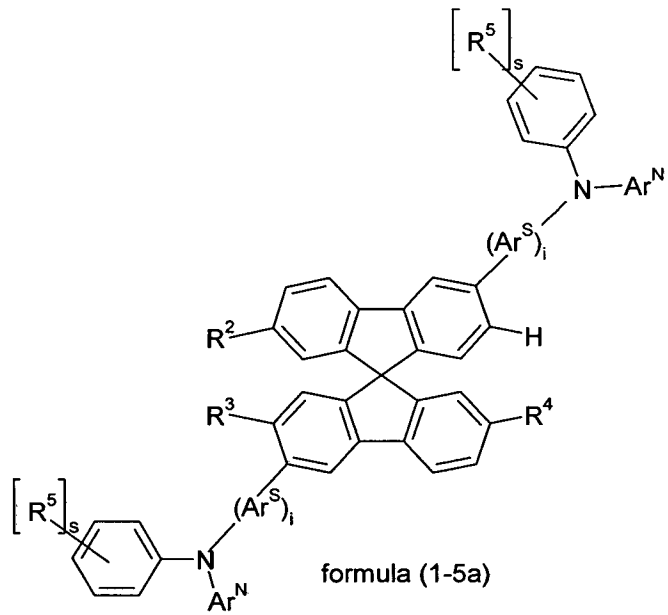


formula (1-4a)

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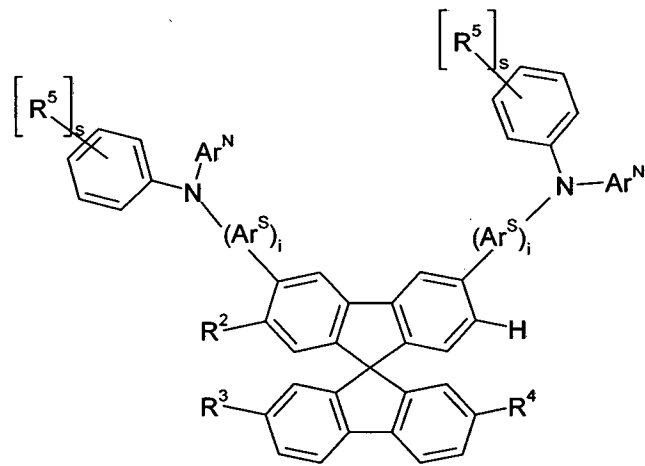
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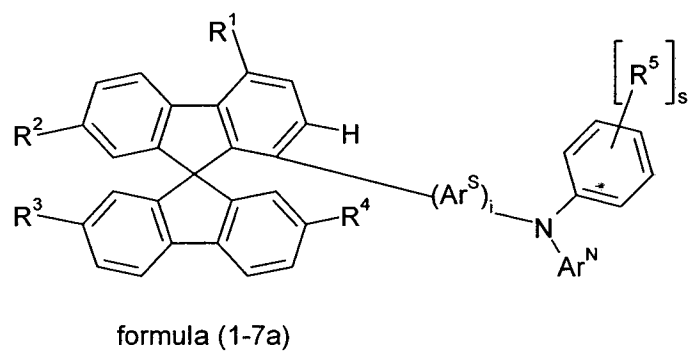
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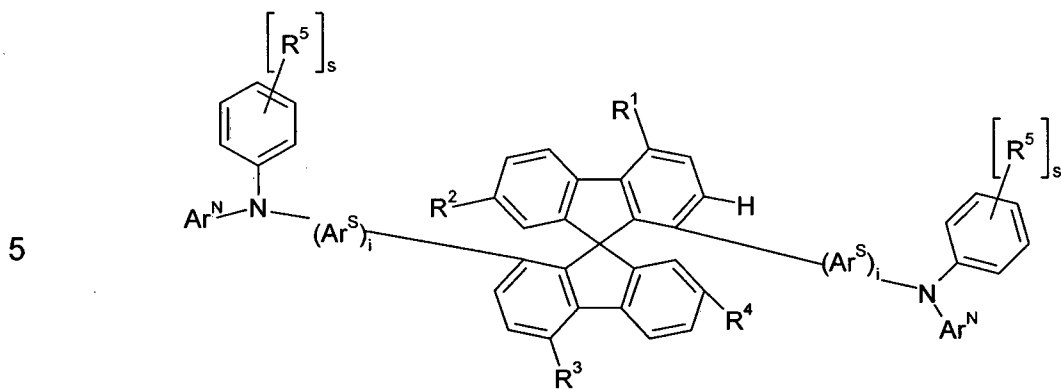
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formula (1-6a)

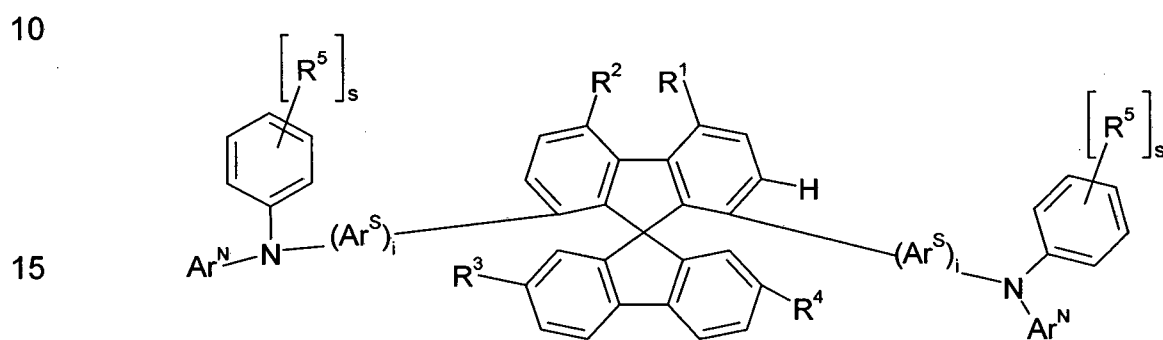
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formula (1-8a)



formula (1-9a)

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where the symbols and indices used have the meanings given in claim 1.

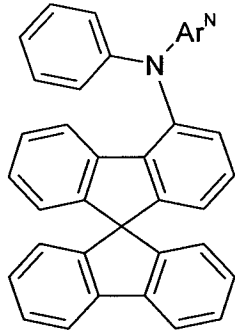
25

6. Compound according to one or more of the preceding claims, selected from the compounds of the formulae (1-1b) to (1-9b)

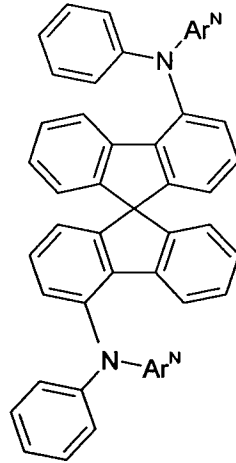
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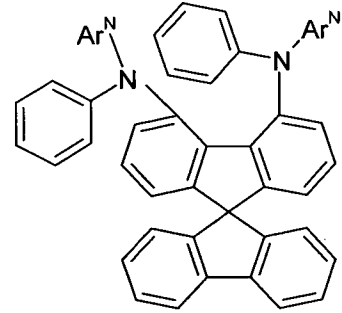
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formula (1-1b)



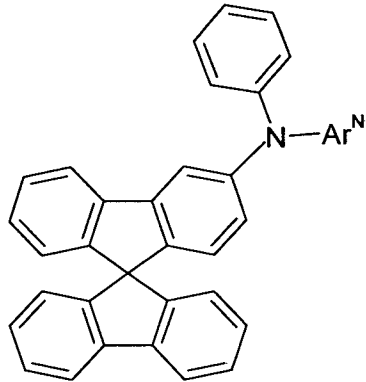
formula (1-2b)



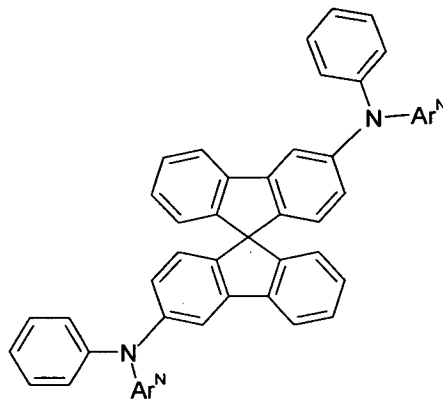
formula (1-3b)

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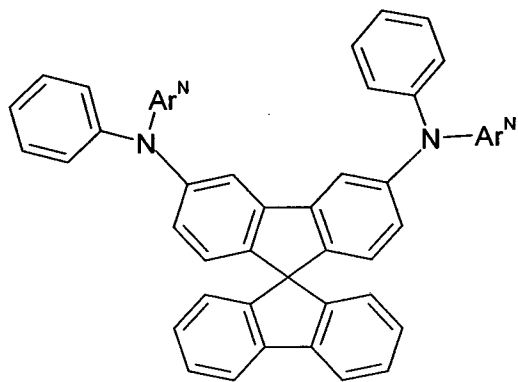
formula (1-4b)



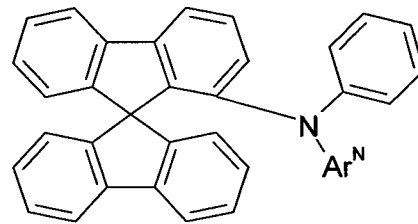
formula (1-5b)

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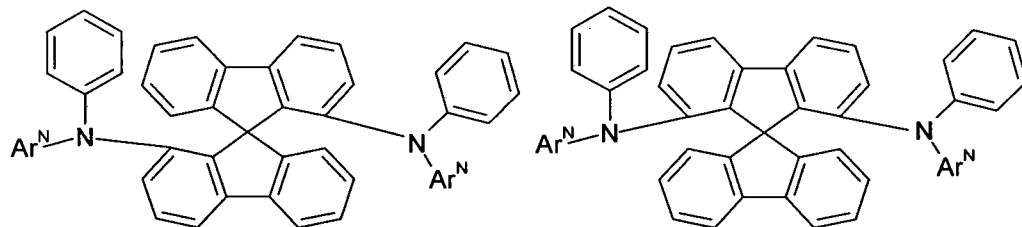
formula (1-6b)



formula (1-7b)

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formula (1-8b)

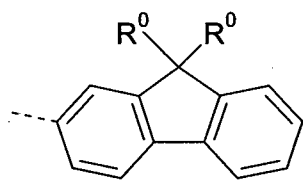
formula (1-9b)

10

where the symbol Ar^N has the same meanings as in claim 1.

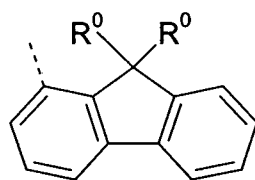
7. Compound according to one or more of the preceding claims, characterized in that the group Ar^N is selected from the groups of formulae (20) to (84)

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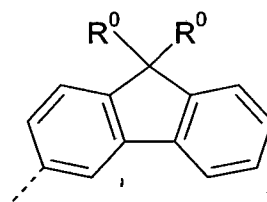


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formula (20)

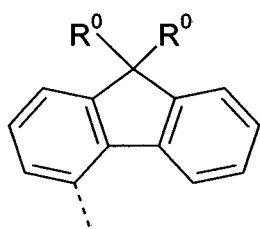


formula (21)

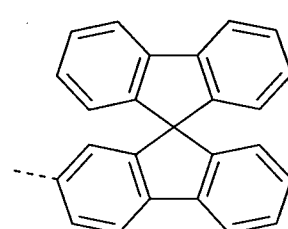


formula (22)

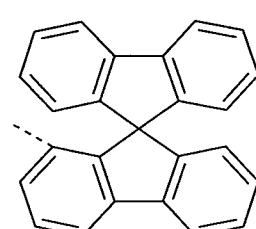
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formula (23)



formula (24)

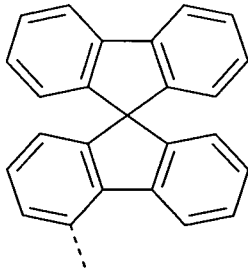


formula (25)

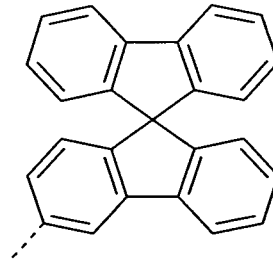
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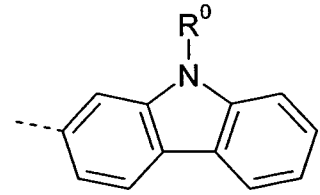
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formula (26)

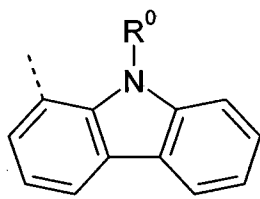


formula (27)

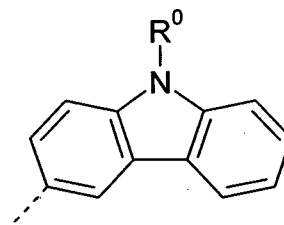


formula (28)

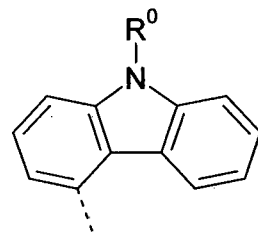
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formula (29)

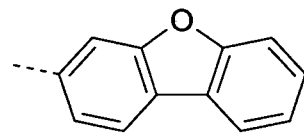


formula (30)

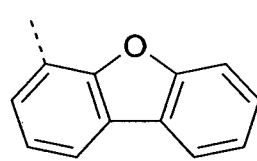


formula (31)

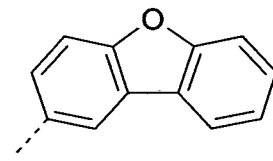
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formula (32)

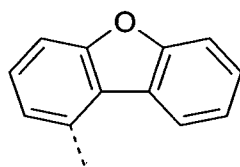


formula (33)

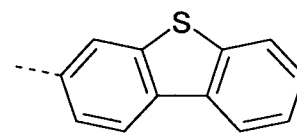


formula (34)

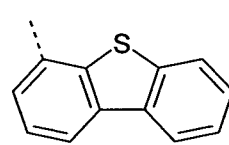
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formula (35)

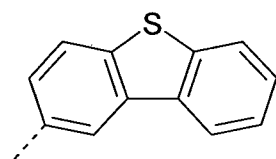


formula (36)

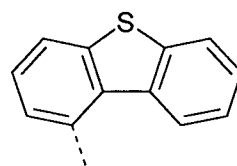


formula (37)

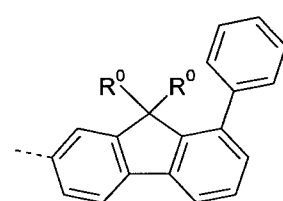
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formula (38)



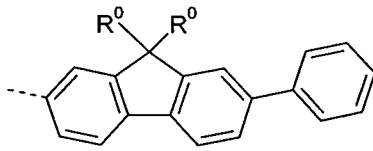
formula (39)



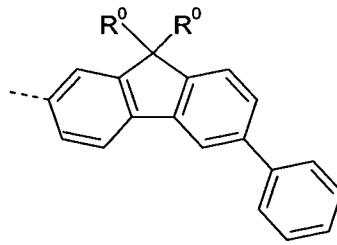
formula (40)

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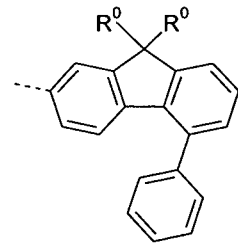
- 93 -



formula (41)

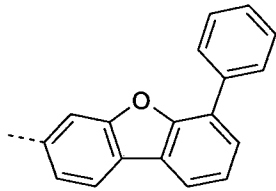


formula (42)

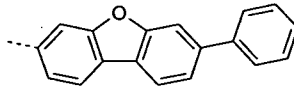


formula (43)

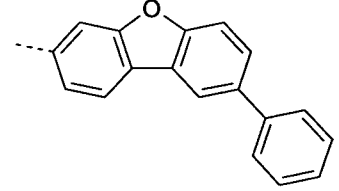
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formula (44)

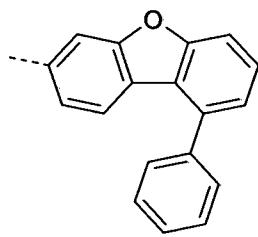


formula (45)

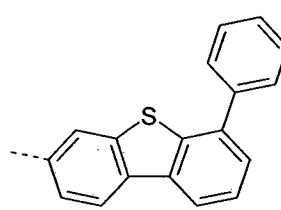


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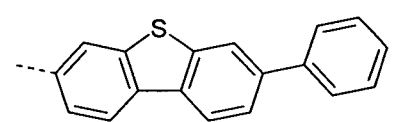
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formula (47)

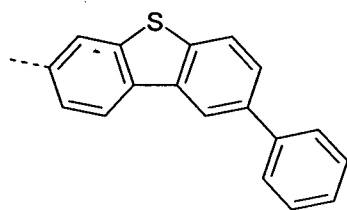


formula (48)

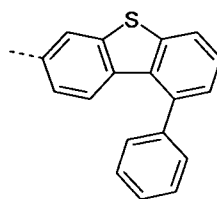


formula (49)

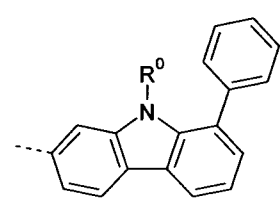
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formula (50)

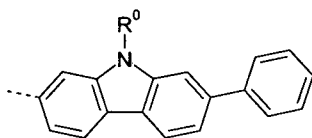


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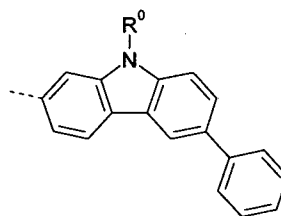


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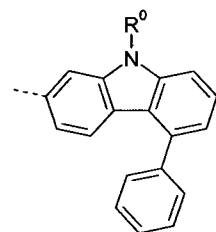
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formula (53)

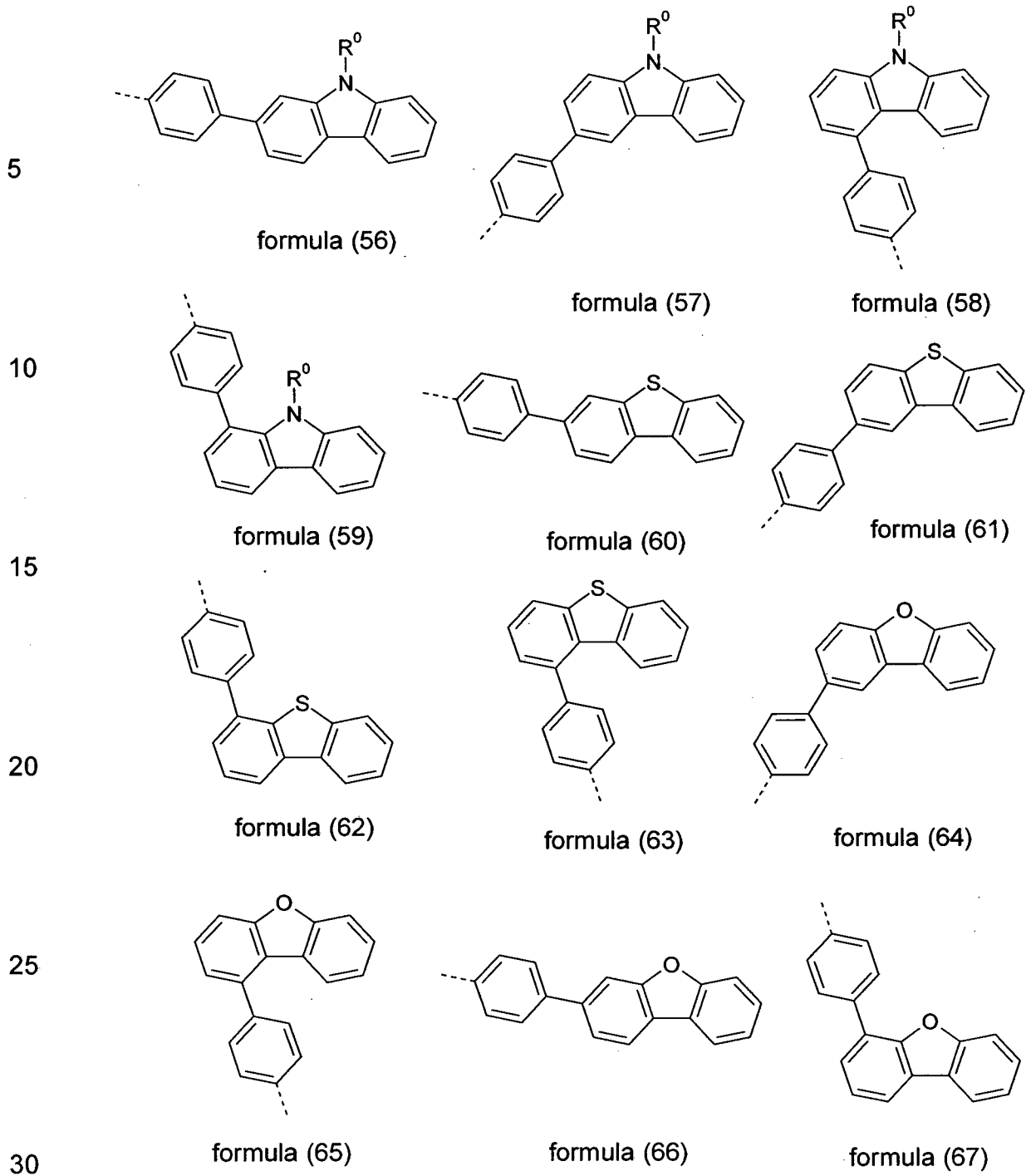


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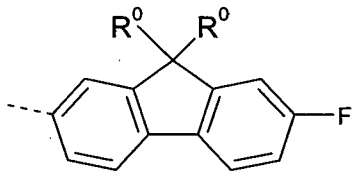


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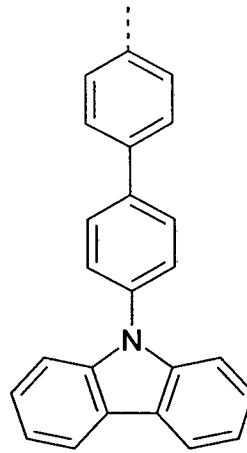
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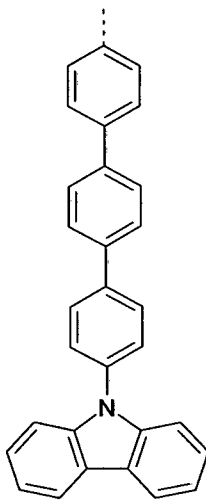
formula (68)



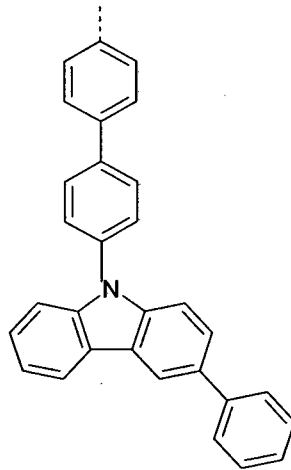
formula (69)

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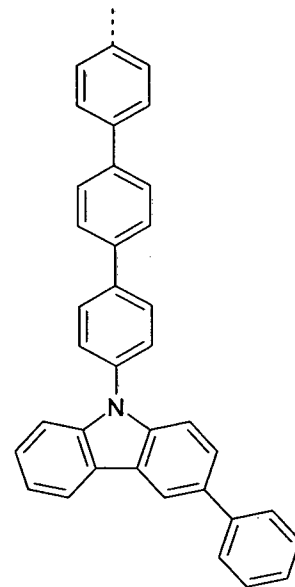
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formula (70)



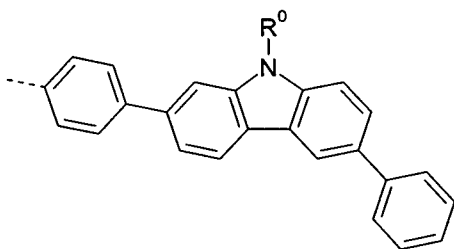
formula (71)



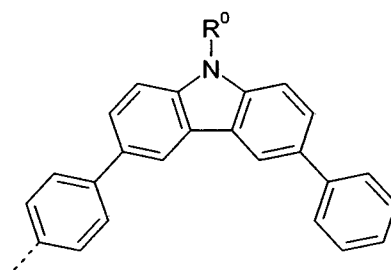
formula (72)

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formula (73)

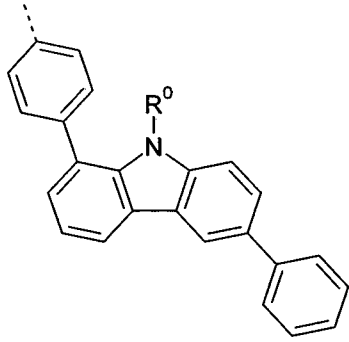


formula (74)

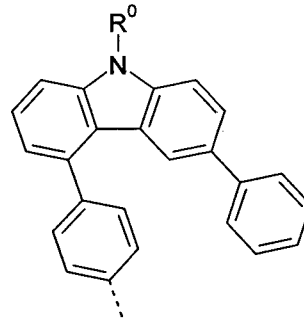
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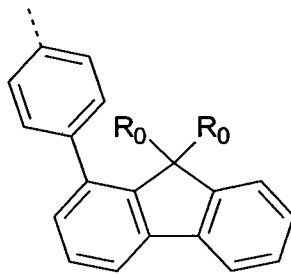


formula (75)

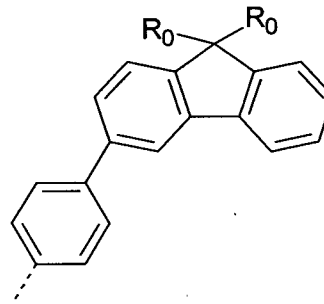


formula (76)

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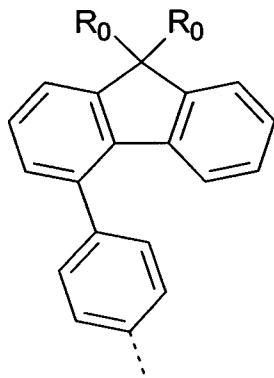


formula (77)

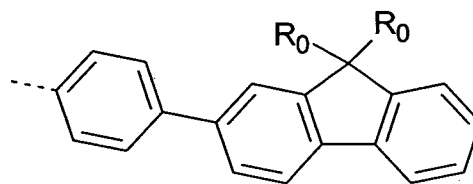


formula (78)

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formula (79)



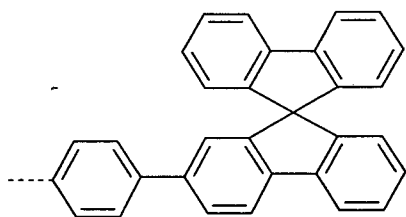
formula (80)

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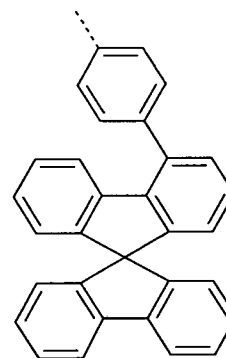
- 97 -

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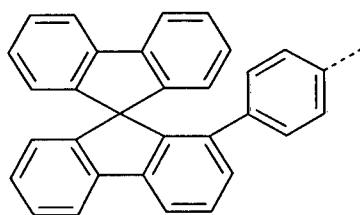
formula (81)

10



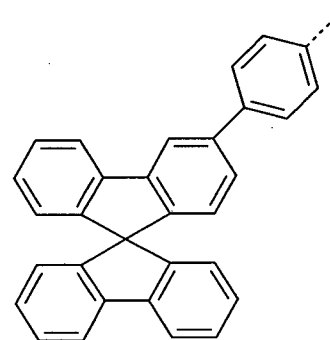
formula (82)

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formula (83)

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formula (84)

where the dashed bond indicates the bond to a nitrogen atom depicted in formula (1), where R^0 has the same meaning as in claim 1 and where the groups of formulae (20) to (84) may be substituted by one or more radicals R^8 .

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8. Compound according to one or more of the preceding claims, characterised in that R^1 to R^4 are selected, identically or differently on each occurrence, from the group consisting of H, D, F, CN, a straight-chain alkyl or alkoxy group having 1 to 10 C atoms or a branched or cyclic alkyl or alkoxy group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R^8 , where one or more non-adjacent CH_2 groups may be replaced by O and where one or more H atoms may be replaced by F, an aromatic or heteroaromatic ring

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system having 6 to 24 aromatic ring atoms, which may in each case be substituted by one or more radicals R⁸.

- 5 9. Compound according to one or more of the preceding claims, characterised in that R⁵ is selected from the group consisting of H, D, F, CN, a straight-chain alkyl or alkoxy group having 1 to 10 C atoms or a branched or cyclic alkyl or alkoxy group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R⁸, where
10 one or more non-adjacent CH₂ groups may be replaced by O and where one or more H atoms may be replaced by F.
- 15 10. Compound according to one or more of the preceding claims, characterised in that R⁶ and R⁷ are selected, identically or differently on each occurrence, from the group consisting of H, D, F, CN, a
20 straight-chain alkyl or alkoxy group having 1 to 10 C atoms or a branched or cyclic alkyl or alkoxy group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R⁸, where one or more non-adjacent CH₂ groups may be replaced by O and where one or more H atoms may be replaced by F, an aryl or heteroaryl ring
25 system having 5 to 14 aromatic ring atoms, which may in each case be substituted by one or more radicals R⁸.
- 30 11. Compound according to one or more of the preceding claims, characterised in that R⁰ is selected on each occurrence, identically or differently, from the group consisting of H, D, F, CN, a straight-chain
35 alkyl or alkoxy group having 1 to 10 C atoms or a branched or cyclic alkyl or alkoxy group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R⁸, where in each case one or more non-adjacent CH₂ groups may be replaced by O and where one or more H atoms may be replaced by D, F or CN, an aromatic or
heteroaromatic ring system having 5 to 14 aromatic ring atoms, which may in each case be substituted by one or more radicals R⁸, where

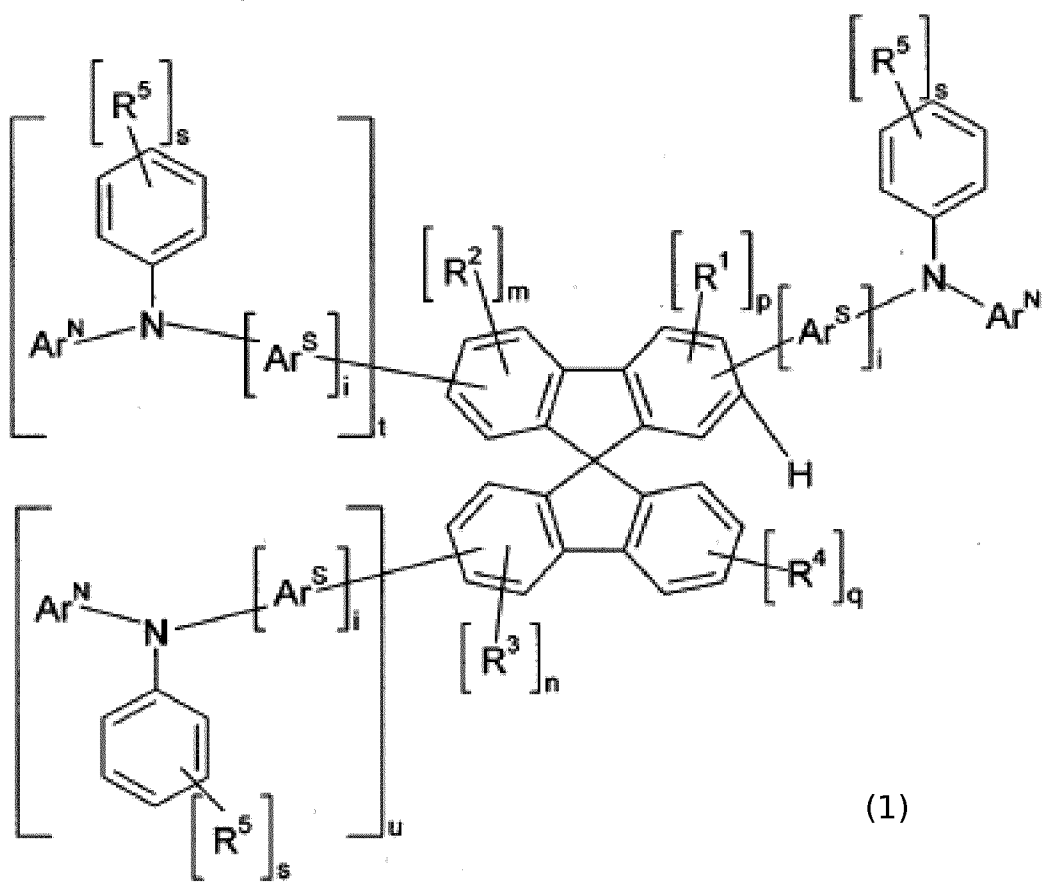
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- two substituents R^0 may optionally form a monocyclic aliphatic ring system, which may be substituted by one or more radicals R^8 ; with the proviso that when two R^0 are attached to the same C atom, then at least one R^0 is selected from the group consisting of H, D, F, CN, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 40 C atoms or a branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 40 C atoms, each of which may be substituted by one or more radicals R^8 .
- 5
12. Compound according to one or more of the preceding claims, characterised in that R^0 is selected on each occurrence, identically or differently, from the group consisting of H, a straight-chain alkyl group having 1 to 10 C atoms or a branched or cyclic alkyl group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R^8 .
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13. Process for the preparation of a compound according to one or more of the preceding claims, characterised in that the diarylamino group is introduced by a C-N coupling reaction between a diarylamine compound and a halogenated spirobifluorene compound.
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14. Formulation comprising at least one compound according to one or more of the claims 1 to 12 and at least one solvent.
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15. Use of a compound according to one or more of claims 1 to 12 in an electronic device, in particular in an organic electroluminescent device.
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16. Electronic device comprising at least one compound according to one or more of claims 1 to 12, preferably 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
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field-quench devices, light-emitting electrochemical cells, organic laser diodes and organic plasmon emitting devices.

- 5 17. Electronic device according to claim 16, which is an organic electro-luminescent device, characterised in that the compound according to one or more of claims 1 to 12 is employed as hole-transport material in a hole-transport or hole-injection or exciton-blocking or electron-blocking layer or as matrix material for fluorescent or phosphorescent emitters.
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/001120

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C07C211/61 C07D333/76 C07D209/82 C07D307/91 C09K11/06
 H01L51/50
 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)
 C07C C07D C09K 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, WPI Data, 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.
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X	WO 2012/034627 A1 (MERCK PATENT GMBH [DE]; PFLUMM CHRISTOF [DE]; PARHAM AMIR HOSSAIN [DE]) 22 March 2012 (2012-03-22) claims; examples -----	1-17
X	WO 2013/120577 A1 (MERCK PATENT GMBH [DE]) 22 August 2013 (2013-08-22) page 113 - page 122; claims; examples ----- -/--	1-17

Further documents are listed in the continuation of Box C.

See patent family annex.

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Date of the actual completion of the international search

8 September 2016

Date of mailing of the international search report

19/09/2016

Name and mailing address of the ISA/

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Zervas, Brigitte

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/001120

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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Information on patent family members

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