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(54) **MATERIALS FOR ORGANIC  
ELECTROLUMINESCENT DEVICES**

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(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.

### MATERIALS FOR ORGANIC ELECTROLUMINESCENT DEVICES

**[0001]** The present invention relates to materials for use in electronic devices, in particular in organic electroluminescent devices, and to electronic devices comprising these materials.

**[0002]** The structure of organic electroluminescent devices (OLEDs) in which organic semiconductors are employed as functional materials is described, for example, in U.S. Pat. No. 4,539,507, U.S. Pat. No. 5,151,629, EP 0676461 and WO 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).

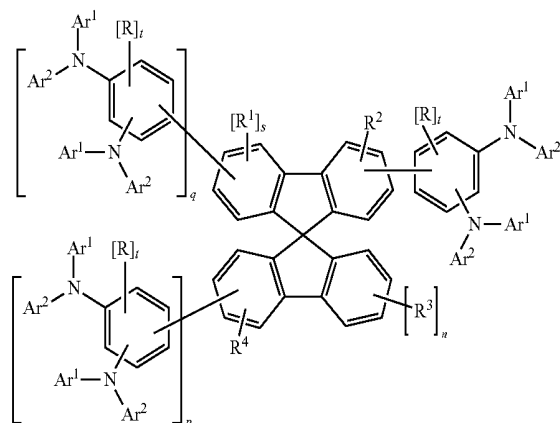
**[0003]** In accordance with the prior art, the hole-transport materials used in the hole-transport layer or in the hole-injection layer are, in particular, triaryl-amine derivatives which frequently contain at least two triarylamino groups or at least one triarylamino group and at least one carbazole group. These compounds are frequently derived from diarylamino-substituted triphenyl-amines (TPA type), from diarylamino-substituted biphenyl derivatives (TAD type) or combinations of these base compounds. Use is also frequently made of spirobifluorene derivatives which are for example substituted by diarylamino groups (for example in accordance with EP 676461 or U.S. Pat. No. 7,714,145). There is still a demand here for alternative materials that can be used in OLEDs devices in order to obtain devices with good properties in terms of efficiency, lifetime and operating voltage.

**[0004]** Therefore, 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-transport or exciton-blocking layer or as matrix material in an emitting layer.

**[0005]** It has now been found that certain compounds described below in greater detail achieve this object and result in very good properties 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 compounds according to the invention as hole-transport material or as matrix material. The materials generally have high thermal stability and can therefore be sublimed without decomposition and without a residue. The present invention therefore relates to these materials and to electronic devices which comprise compounds of this type.

**[0006]** The present invention therefore relates to a compound of the following formula (1):

formula (1)



where the following applies to the symbols and indices used:

**[0007]**  $Ar^1$ ,  $Ar^2$  is on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 60 C aromatic ring atoms, which may in each case also be substituted by one or more radicals  $R^5$ ,  $Ar^1$  and  $Ar^2$  here may also be connected to one another by a group E;

**[0008]** E is on each occurrence, identically or differently, a single bond,  $N(R^5)$ , O, S,  $C(R^5)_2$ ,  $C(R^5)_2-C(R^5)_2$ ,  $Si(R^5)_2$  or  $B(R^5)$ ;

**[0009]**  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  are selected on each occurrence, identically or differently, from the group consisting of D, F, Cl, Br, I, CN,  $Si(R^6)_3$ ,  $N(R^6)_2$ , 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  $R^6$ , where in each case one or more non-adjacent  $CH_2$  groups may be replaced by  $Si(R^6)_2$ ,  $C=NR^6$ ,  $P(=O)(R^6)$ , SO,  $SO_2$ ,  $NR^6$ , O, S or  $CONR^6$  and where one or more H atoms may be replaced by D, F, Cl, Br or I, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , an aryloxy or heteroaryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals  $R^6$ , or an aralkyl or heteroaralkyl group having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , where two or more adjacent substituents  $R^1$  or  $R^2$  or  $R^3$  or  $R^4$  may optionally form a mono- or polycyclic ring system, which may be substituted by one or more radicals  $R^6$ ;

**[0010]** R is selected on each occurrence, identically or differently, from the group consisting of D, F, Cl, Br, I, CN,  $Si(R^6)_3$ , 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  $R^6$ , where in each case one or more non-adjacent  $CH_2$  groups may be replaced by  $Si(R^6)_2$ ,  $C=NR^6$ ,  $P(=O)(R^6)$ , SO,  $SO_2$ ,  $NR^6$ , O, S or  $CONR^6$  and where one or more H atoms may be replaced by D, F, Cl, Br or I, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , an aryloxy or heteroaryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals  $R^6$ , or an aralkyl or heteroaralkyl group having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , where two or more adjacent substituents R may optionally form a mono- or polycyclic ring system, which may be substituted by one or more radicals  $R^6$ ;

**[0011]**  $R^5$  is selected on each occurrence, identically or differently, from the group consisting of H, D, F, Cl, Br, I, CN,  $Si(R^6)_3$ ,  $N(R^6)_2$ , 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  $R^6$ , where in each case one or more non-adjacent  $CH_2$  groups may be replaced by  $Si(R^6)_2$ ,  $C=NR^6$ ,  $P(=O)(R^6)$ , SO,  $SO_2$ ,  $NR^6$ , O, S or  $CONR^6$  and where one or more H atoms may be replaced by D, F, Cl, Br or I, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , an aryloxy or heteroaryloxy-

loxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R<sup>6</sup>, or an aralkyl or heteroaralkyl group having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R<sup>6</sup>, where two or more adjacent substituents R<sup>5</sup> may optionally form a mono- or polycyclic ring system, which may be substituted by one or more radicals R<sup>6</sup>;

**[0012]** R<sup>6</sup> is selected from the group consisting of H, D, F, an aliphatic hydrocarbon radical having 1 to 20 C atoms or an aromatic or heteroaromatic ring system having 5 to 30 aromatic ring atoms, in which one or more H atoms may be replaced by D or F, where two or more adjacent substituents R<sup>6</sup> may form a mono- or polycyclic ring system with one another;

**[0013]** m is 0, 1, 2 or 3;

**[0014]** n is 0, 1, 2, 3 or 4;

**[0015]** p, q are, identically or differently, 0 or 1;

**[0016]** r, s are, identically or differently, 0, 1, 2, 3 or 4; where p+r≤4 and q+s≤4.

**[0017]** t is, on each occurrence, identically or differently, 0, 1, 2 or 3.

**[0018]** An aryl group in the sense of this invention is taken to mean either a simple aromatic ring, i.e. benzene, or a condensed (annelated) aryl group, for example naphthalene or phenanthrene. By contrast, aromatic groups linked to one another by a single bond, such as, for example, biphenyl or fluorene, are not referred to as an aryl group, but instead as an aromatic ring system.

**[0019]** A heteroaryl group in the sense of the present invention comprises at least one heteroatom in the aromatic ring, preferably a heteroatom selected from N, O and S. A heteroaryl group may comprise only a simple heteroaromatic ring, such as e. g. pyridine, triazine, or thiophene, or it may be a condensed (annelated) heteroaryl group, such as quinoline or carbazole.

**[0020]** An aromatic ring system in the sense of this invention contains 6 to 60 C atoms in the ring system, where the aromatic ring system may be built up e.g. from benzene, naphthalene, phenanthrene, fluorene and spirobifluorene or combinations of these groups. An aromatic ring system in the sense of this invention is, in particular, also intended to be taken to mean a system in which, in addition, a plurality of aryl groups is linked to one another directly or via a carbon atom. Thus, for example, systems such as biphenyl, terphenyl, quaterphenyl, fluorene, 9,9'-spirobifluorene, 9,9'-diaryl-fluorene, etc., in particular, are also intended to be taken to be aromatic ring systems in the sense of this invention. The aromatic ring system here by definition contains no amino groups. Triaryl amino groups are thus not covered by the definition of an aromatic ring system.

**[0021]** An analogous definition applies to the term heteroaromatic ring system, which is to be understood to be a combination of two or more interconnected aryl or heteroaryl groups, at least one of them being a heteroaryl group.

**[0022]** An aralkyl group is to be understood to be an alkyl group which is substituted by an aryl group, where the aryl group is defined as above, and the alkyl group may have 1 to 20 C atoms, and may be substituted as defined above for alkyl groups, and may have one or more CH<sub>2</sub> groups replaced as defined above for alkyl groups. In the aralkyl group, the alkyl group is the group which bonds to the rest of the compound. An analogous definition applies to the

term heteroaralkyl group, only that a heteroaryl group is present instead of an aryl group.

**[0023]** An aryloxy group is to be understood to be an aryl group bonded via a divalent (ether) oxygen atom. An analogous definition applies to the term heteroaryloxy group, only that a heteroaryl group is present instead of an aryl group.

**[0024]** For the purposes of the present invention, an aliphatic hydrocarbon radical or an alkyl group or an alkenyl or alkynyl group, which may typically contain 1 to 40 or also 1 to 20 C atoms and in which, in addition, individual H atoms or CH<sub>2</sub> groups may be substituted by the above-mentioned groups, 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, neopentyl, cyclopentyl, n-hexyl, neoheptyl, cyclohexyl, n-heptyl, cycloheptyl, n-octyl, cyclooctyl, 2-ethylhexyl, trifluoromethyl, pentafluoroethyl, 2,2,2-trifluoro-ethyl, ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl, cycloheptenyl, octenyl, cyclooctenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl or octynyl.

**[0025]** An alkoxy group having 1 to 40 C atoms is preferably taken to mean methoxy, trifluoromethoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy, n-pentoxy, s-pentoxy, 2-methylbutoxy, n-hexoxy, cyclohexyloxy, n-heptoxy, cycloheptyloxy, n-octyloxy, cyclooctyloxy, 2-ethylhexyloxy, pentafluoroethoxy or 2,2,2-trifluoroethoxy.

**[0026]** A thioalkyl group having 1 to 40 C atoms is taken to mean, in particular, methylthio, ethylthio, n-propylthio, i-propylthio, n-butylthio, i-butylthio, s-butylthio, t-butylthio, n-pentylthio, s-pentylthio, n-hexylthio, cyclohexylthio, n-heptylthio, cycloheptylthio, n-octylthio, cyclooctylthio, 2-ethyl hexylthio, trifluoromethylthio, pentafluoroethylthio, 2,2,2-trifluoroethylthio, ethenylthio, propenylthio, butenylthio, pentenylthio, cyclopentenylthio, hexenylthio, cyclohexenylthio, heptenylthio, cycloheptenylthio, octenylthio, cyclooctenylthio, ethynylthio, propynylthio, butynylthio, pentynylthio, hexynylthio, heptynylthio or octynylthio.

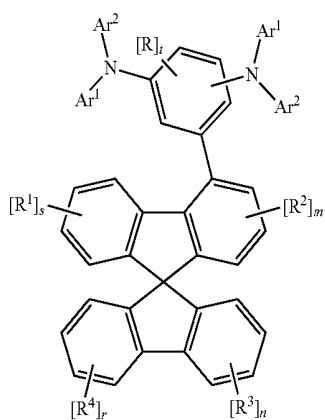
**[0027]** In general, alkyl, alkoxy or thioalkyl groups in accordance with the present invention can be straight-chain, branched or cyclic, where one or more non-adjacent CH<sub>2</sub> groups may be replaced by the above-mentioned groups; furthermore, one or more H atoms may also be replaced by D, F, Cl, Br, I, CN or NO<sub>2</sub>, preferably F, Cl or CN, further preferably F or CN, particularly preferably CN.

**[0028]** Preferably, the two amino groups on the diamino-phenyl group are located in meta-position to each other. Particularly preferably, they are located in meta-position to each other and to the bond to the spirobifluorene.

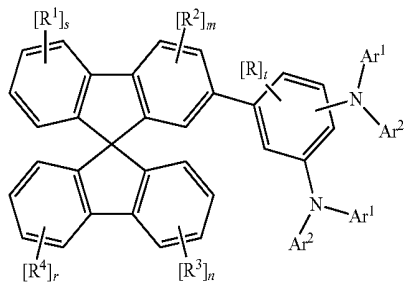
**[0029]** In a preferred embodiment of the invention, p+q=0 or 1. The compound according to the invention thus preferably contains one or two diaminobenzene groups. Particularly preferably, p+q=0, and the compound according to the invention contains one diaminobenzene group.

**[0030]** In a preferred embodiment of the invention, the compound of the formula (1) is selected from the compounds of the following formulae (2) to (9),

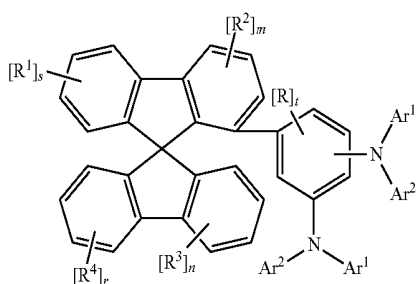
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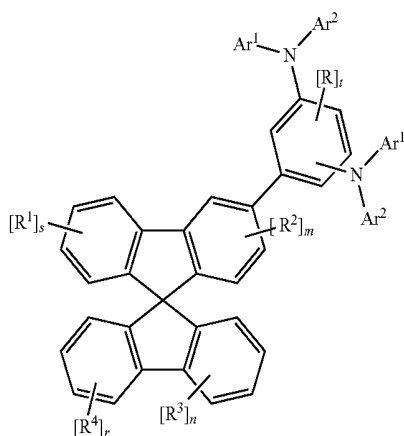
formula (2)



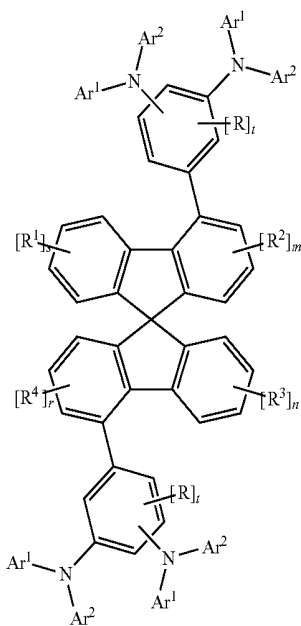
formula (3)



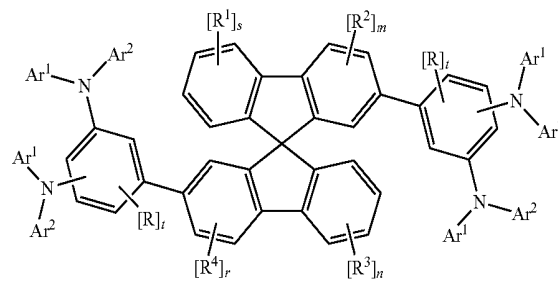
formula (4)



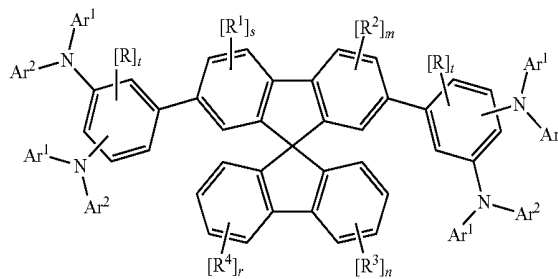
formula (5)



formula (6)

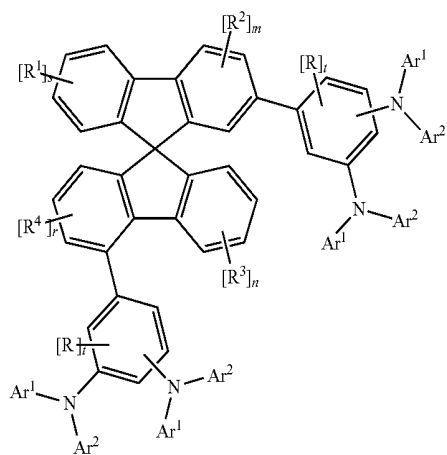


formula (7)



formula (8)

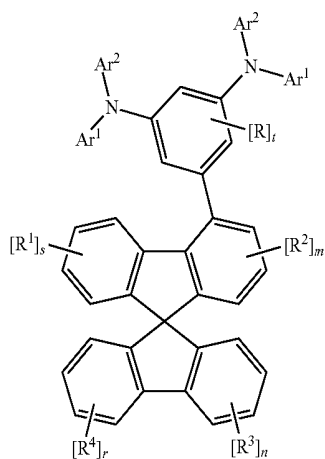
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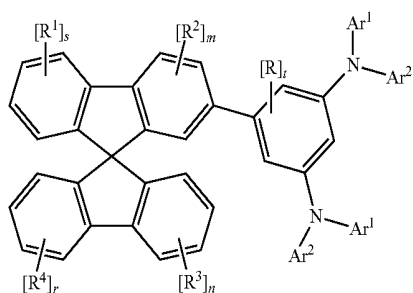
formula (9)

where the symbols and indices used have the meanings given above.

[0031] In a particularly preferred embodiment of the invention, the compounds of the formulae (2) to (9) are selected from the compounds of the following formulae (2a) to (9a),



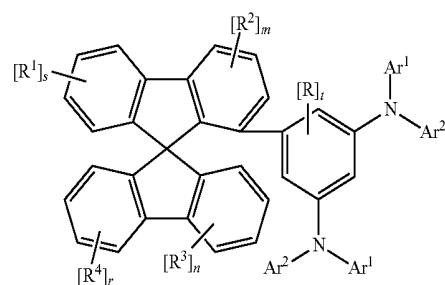
formula (2a)



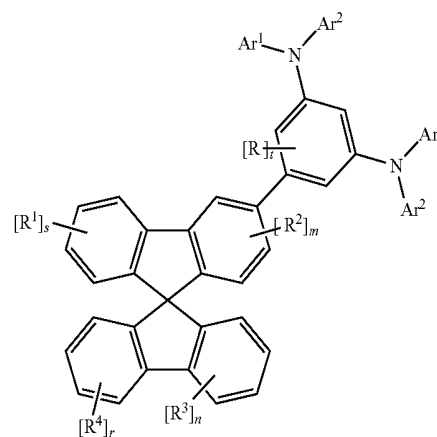
formula (3a)

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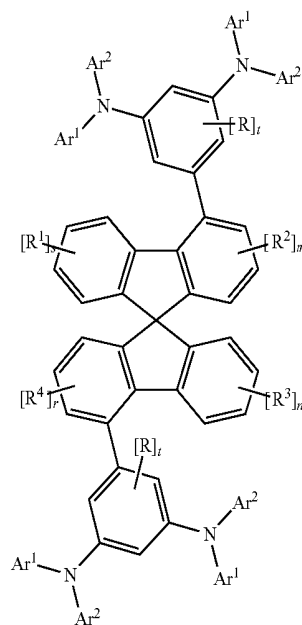
formula (4a)



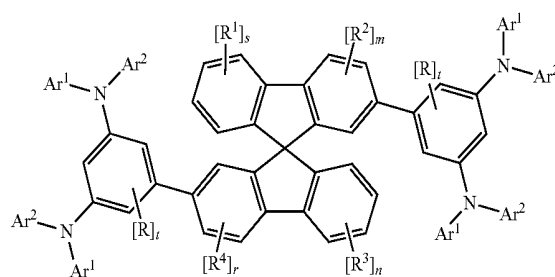
formula (5a)



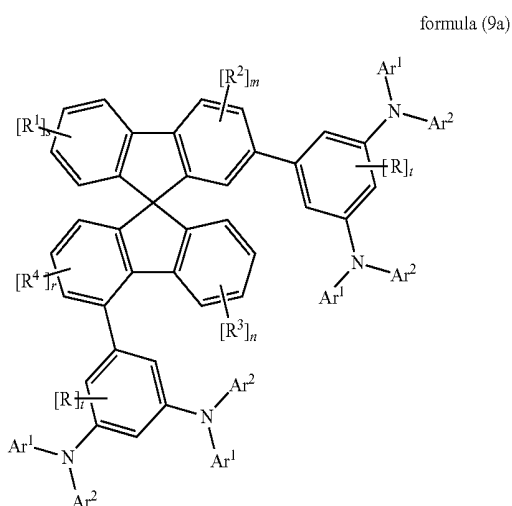
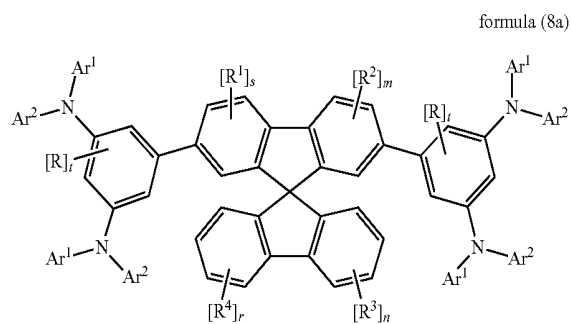
formula (6a)



formula (7a)

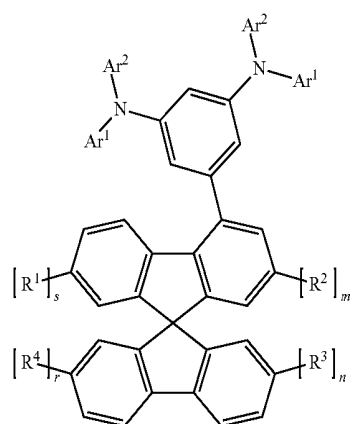


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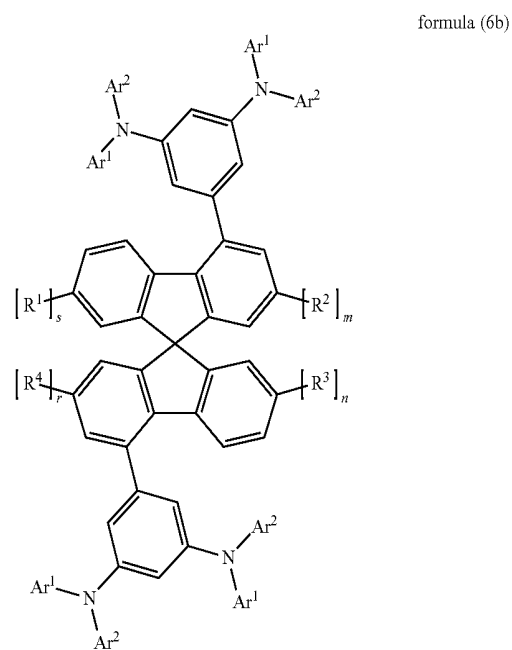
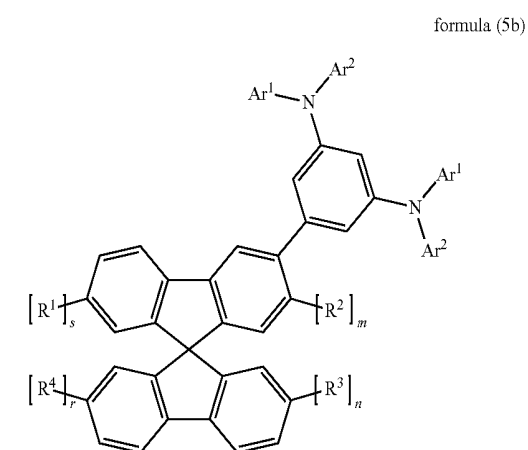
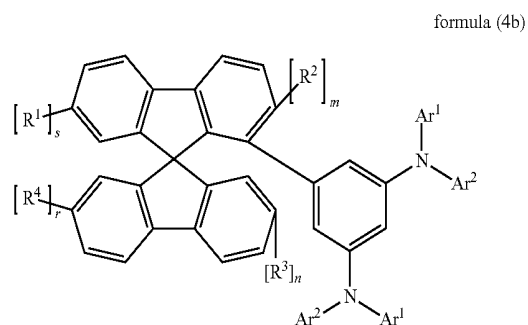
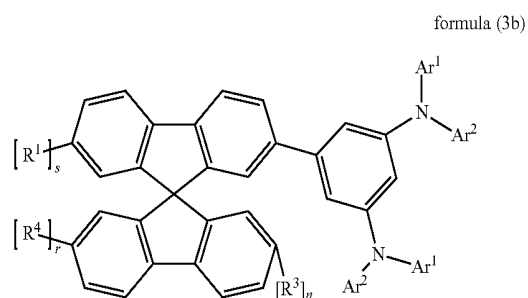


where the symbols and indices used have the meanings given above.

**[0032]** Very particular preference is given to the compounds of the following formulae (2b) to (9b),

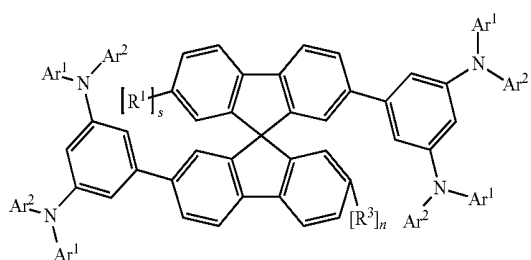


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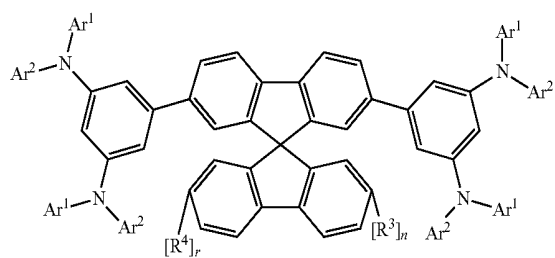


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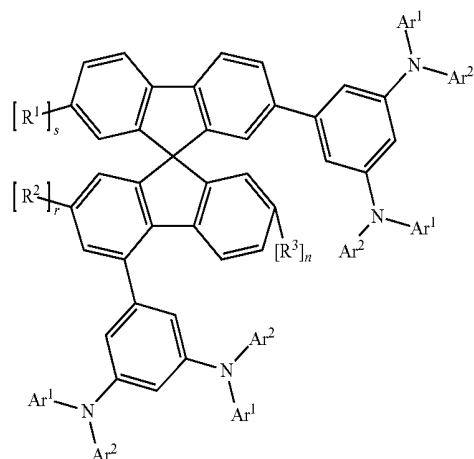
formula (7b)



formula (8b)

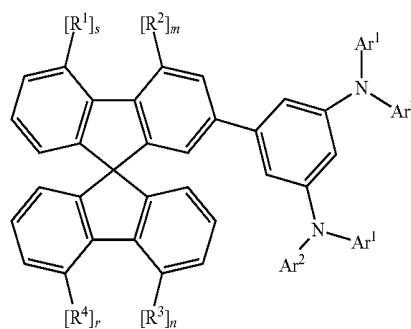


formula (9b)

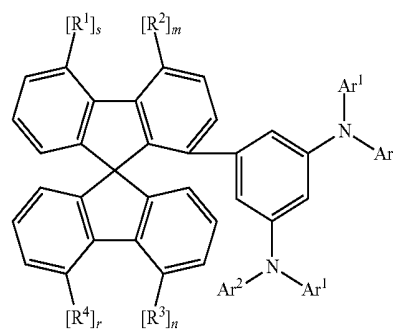


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formula (3c)



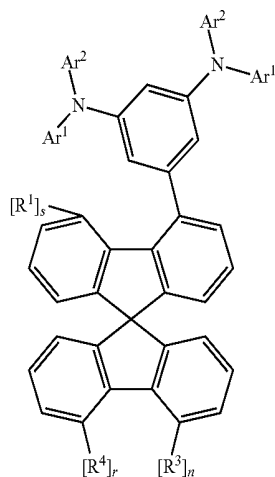
formula (4c)



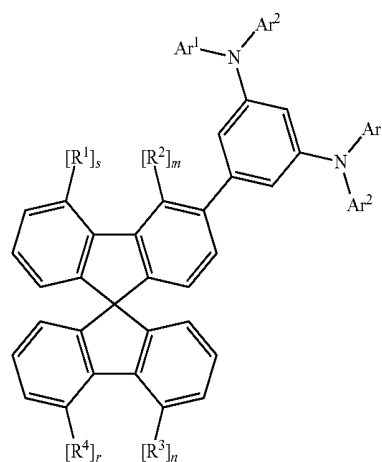
where  $m$ ,  $n$ ,  $r$  and  $s$  are, identically or differently, 0 or 1 and the other symbols used have the meanings given above.

**[0033]** Further very particular preference is given to the compounds of the following formulae (2c) to (9c),

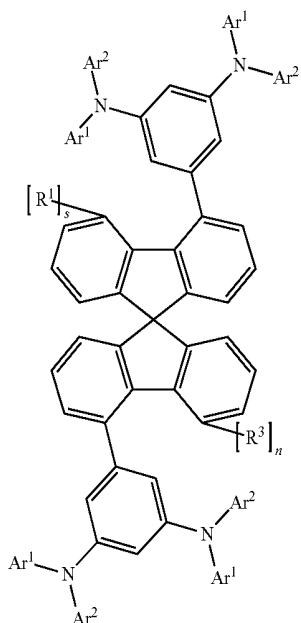
formula (2c)



formula (5c)

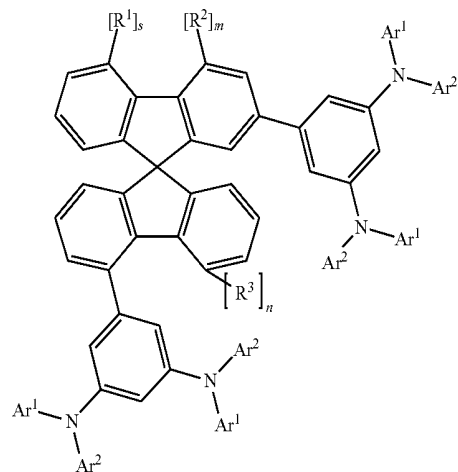


-continued



formula (6c)

-continued



formula (9c)

where m, n, r and s are, identically or differently, 0 or 1 and the other symbols used have the meanings given above.

**[0034]** In a particularly preferred embodiment of the invention, the compound according to the invention contains only one diaminobenzene group. This thus preferably relates to compounds of the formulae (2), (3), (4) and (5) or (2a), (3a), (4a) and (5a) or (2b), (3b), (4b) and (5b), or (2c), (3c), (4c) and (5c).

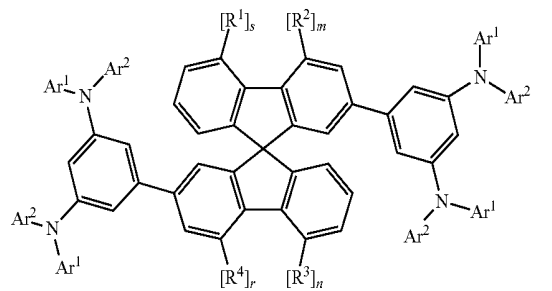
**[0035]** In a further preferred embodiment of the invention, the diaminobenzene groups are bonded in the 2-position or in the 4-position of the spirobifluorene. This thus preferably relates to the compounds of the formulae (2) and (3) or (2a) and (3a) or (2b) and (3b).

**[0036]** Very particular preference is given to the compounds of the formula (2) or (2a) or (2b) or (2c).

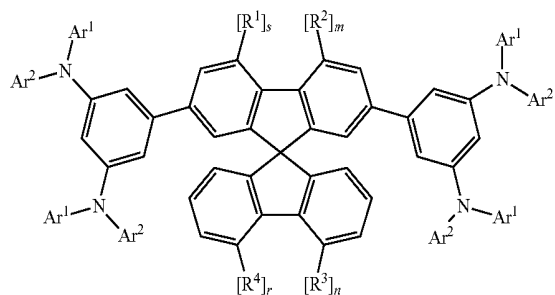
**[0037]** At least one of the groups Ar<sup>1</sup> and Ar<sup>2</sup> is selected, identically or differently, on each occurrence, from phenyl, fluorenyl, spirobifluorenyl, biphenyl, terphenyl, quaterphenyl, carbazoyl, dibenzofuranyl and dibenzothiophenyl, each of which may be substituted by one or more radicals R<sup>5</sup>.

**[0038]** The groups Ar<sup>1</sup> and Ar<sup>2</sup> here are preferably selected, identically or differently on each occurrence, from the group consisting of phenyl, fluorenyl, spirobifluorenyl, biphenyl, terphenyl, quaterphenyl, carbazoyl, dibenzofuranyl and dibenzothiophenyl, each of which may be substituted by one or more radicals R<sup>5</sup>.

**[0039]** The groups Ar<sup>1</sup> and Ar<sup>2</sup> here are very preferably selected, identically or differently on each occurrence, from the groups of the following formulae (10) to (66),

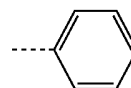


formula (7c)

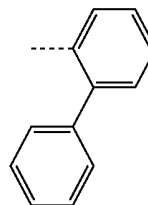


formula (8c)

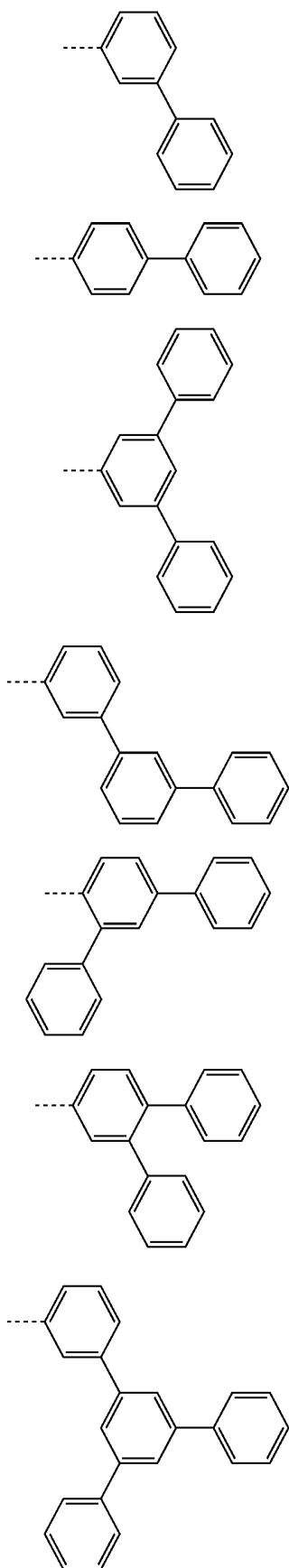
formula (10)



formula (11)



-continued



formula (12)

formula (13)

formula (14)

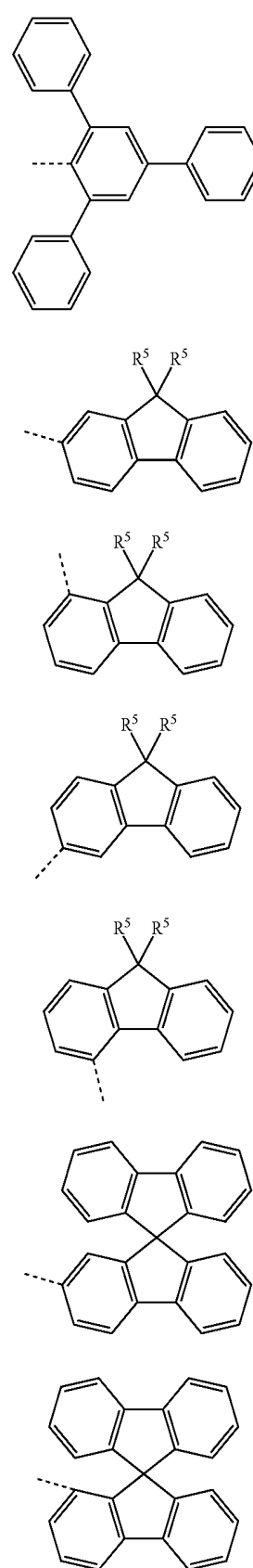
formula (15)

formula (16)

formula (17)

formula (18)

-continued



formula (19)

formula (20)

formula (21)

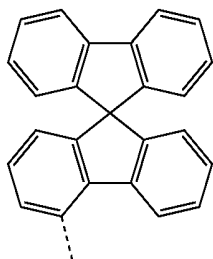
formula (22)

formula (23)

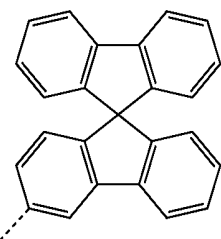
formula (24)

formula (25)

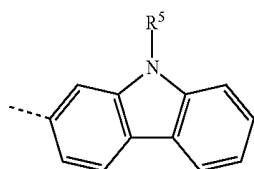
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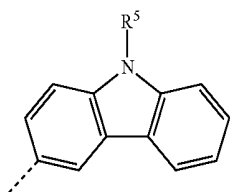
formula (26)



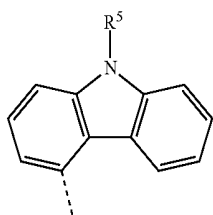
formula (27)



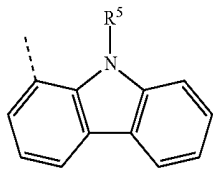
formula (28)



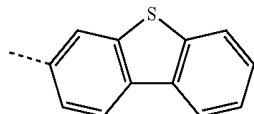
formula (29)



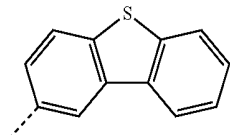
formula (30)



formula (31)

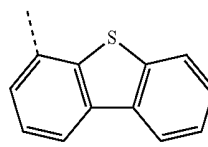


formula (32)

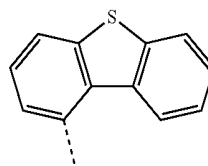


formula (33)

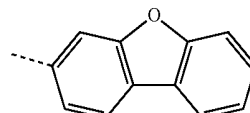
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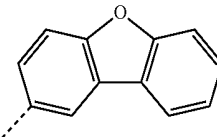
formula (34)



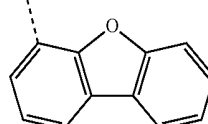
formula (35)



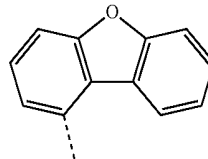
formula (36)



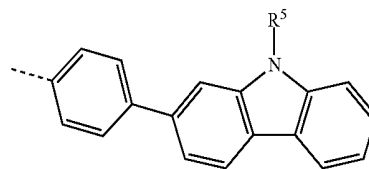
formula (37)



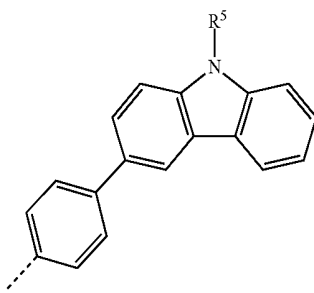
formula (38)



formula (39)

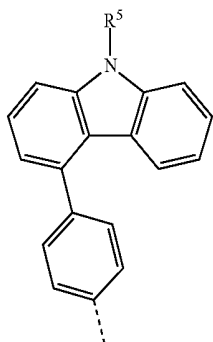


formula (40)



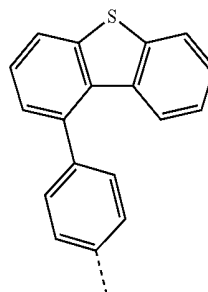
formula (41)

-continued

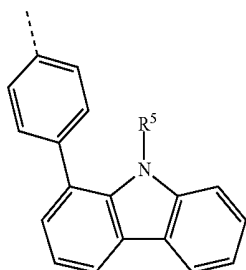


formula (42)

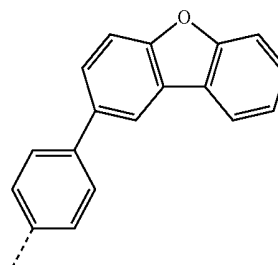
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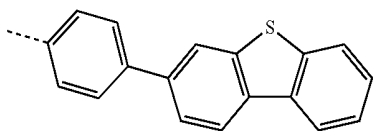
formula (47)



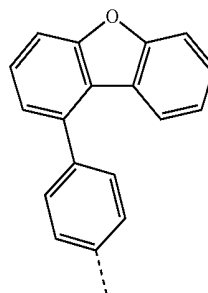
formula (43)



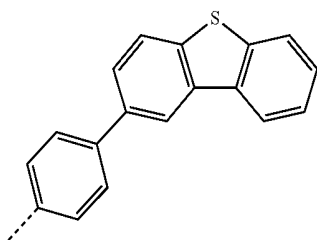
formula (48)



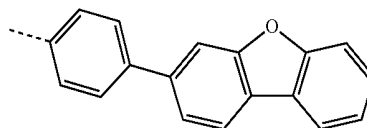
formula (44)



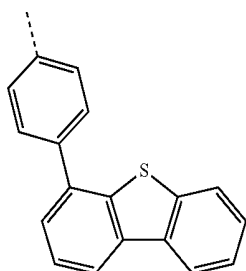
formula (49)



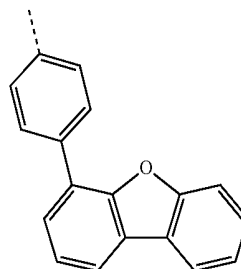
formula (45)



formula (50)

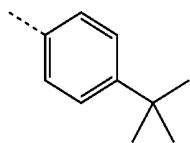


formula (46)

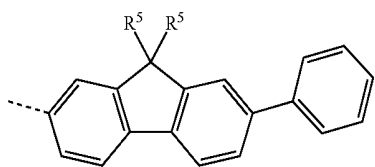


formula (51)

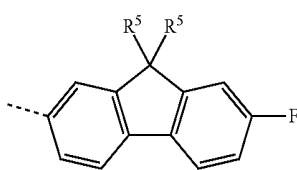
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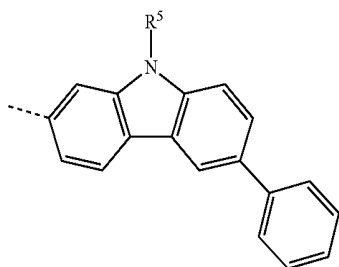
formula (52)



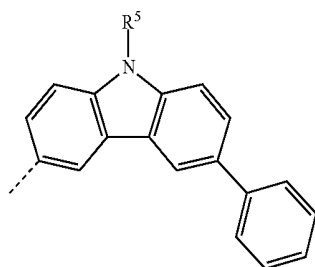
formula (53)



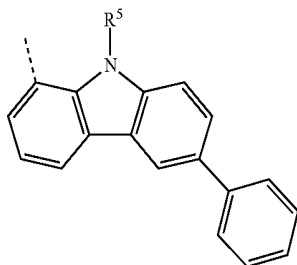
formula (54)



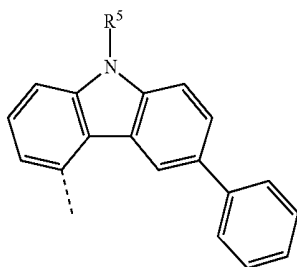
formula (55)



formula (56)



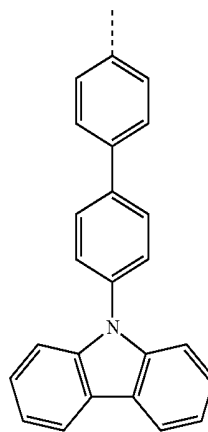
formula (57)



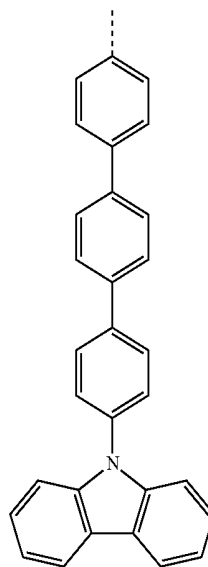
formula (58)

-continued

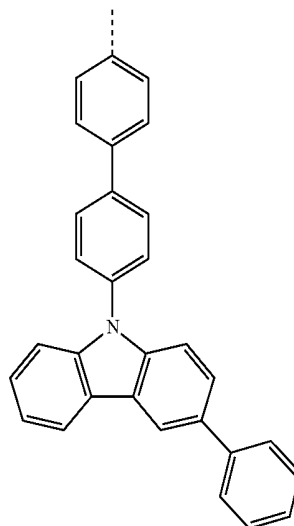
formula (59)



formula (60)

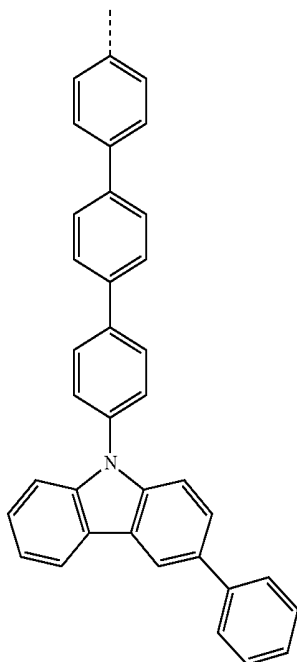


formula (61)

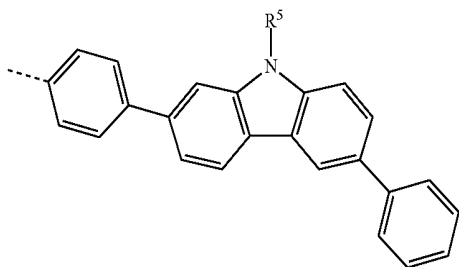


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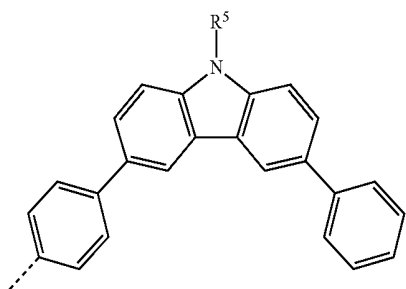
formula (62)



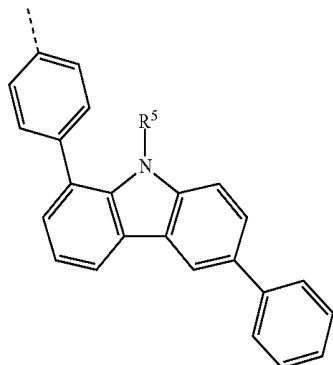
formula (63)



formula (64)

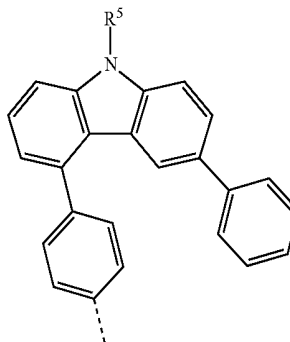


formula (65)



-continued

formula (66)



where the dashed bond indicates the bond to the nitrogen, and the groups may be substituted by one or more radicals  $R^5$ , but are preferably unsubstituted.

**[0040]**  $R^5$  in the groups of the formulae (20) to (23), (53) and (54) preferably stands, identically or differently, for an alkyl group having 1 to 10 C atoms, in particular for methyl, or a phenyl group, which may be substituted by one or more radicals  $R^6$ .

**[0041]** Preferred groups  $Ar^1$  and  $Ar^2$  are selected, identically or differently on each occurrence, from the group consisting of the above-mentioned formulae (10), (11), (12), (13), (20), (21), (22), (23), (32), (33), (34), (35), (36), (37), (38), (39), (40), (41), (42), (43), (44), (45), (46), (47), (48), (49), (50) and (51). All possible combinations of these groups are equally possible here.

**[0042]** Particularly preferred is that  $Ar^1$  and  $Ar^2$  are selected, identically or differently on each occurrence, from the group consisting of the above-mentioned formulae (10), (11), (13), (20), (36), (37), (38), (41), (46) and (51).

**[0043]** Furthermore,  $R^5$  in the groups of the formulae (28) to (31) and (40) to (43) and (55) to (58) and (63) to (66) preferably stands for a phenyl group, an ortho-biphenyl group, a meta-biphenyl group, a para-biphenyl group, a terphenyl group, a 1-naphthyl group, or a 2-naphthyl group which may be substituted by one or more radicals  $R^6$ .

**[0044]** Preferably,  $Ar^1$  and  $Ar^2$  are selected, identically or differently on each occurrence, from the groups of the formulae (10), (13) and (20), which may be substituted by one or more radicals  $R^5$ .

**[0045]** At least one of the groups  $Ar^1$  and  $Ar^2$  is particularly preferably a group of the formula (10), (13) or (20).

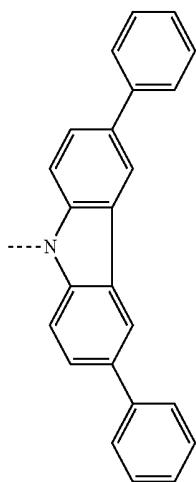
**[0046]** The two groups  $Ar^1$  and  $Ar^2$  of the above-mentioned formulae (11) to (66) which are bonded to the nitrogen may be combined with one another as desired.

**[0047]** In a preferred embodiment of the invention, the groups  $Ar^1$  and  $Ar^2$  are selected differently from one another.

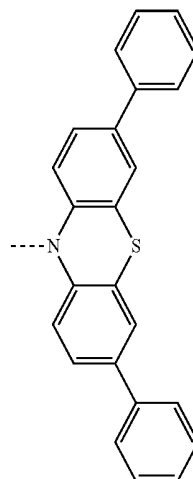
**[0048]** In a further preferred embodiment of the invention, the groups  $Ar^1$  and  $Ar^2$  are selected identically.

**[0049]** If the groups  $Ar^1$  and  $Ar^2$  in the compounds of the formula (1) and (2) to (9) or the preferred embodiments are linked to one another by a group E, the group  $-NAr^1Ar^2$  preferably has the structure of one of the following formulae (67) to (74),

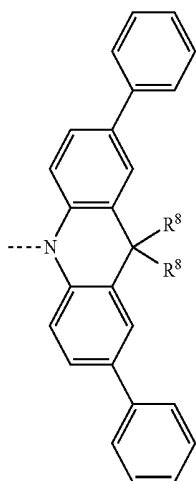
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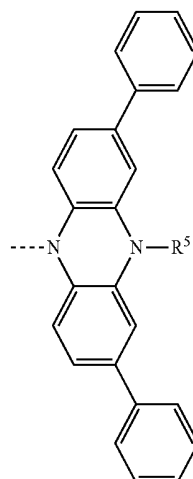
formula (67)



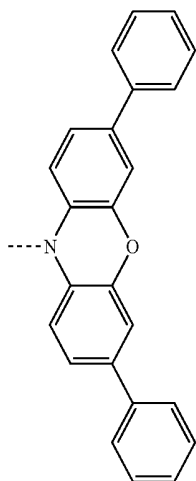
formula (70)



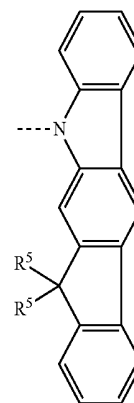
formula (68)



formula (71)

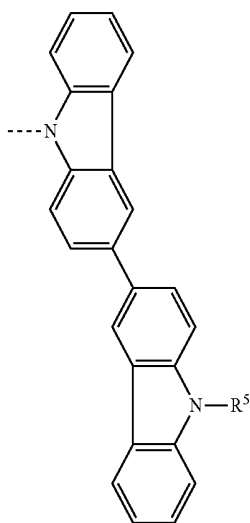


formula (69)

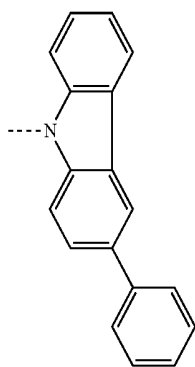


formula (72)

-continued



formula (73)



formula (74)

where the symbols used have the meanings given above, and the dashed bond indicates the bond to the spirobifluorene. These groups may also be substituted by one or more radicals  $R^5$ , but are preferably unsubstituted.

**[0050]**  $R^5$  in the group of the formula (68) and (72) preferably stands, identically or differently, for an alkyl group having 1 to 10 C atoms, in particular for methyl, or a phenyl group, which may be substituted by one or more radicals  $R^6$ .

**[0051]** Furthermore,  $R^5$  in the group of the formula (71) and (73) preferably stands for a phenyl group, which may be substituted by one or more radicals  $R^6$ .

**[0052]** In a preferred embodiment of the invention,  $R^1$  to  $R^4$  are selected, identically or differently on each occurrence, from the group consisting of 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  $R^6$ , 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, and an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ .

**[0053]** In a particularly preferred embodiment of the invention,  $R^1$  to  $R^4$  are selected on each occurrence, identically or differently, from the group consisting of F, a straight-chain alkyl group having 1 to 5 C atoms, a branched or cyclic alkyl group having 3 to 6 C atoms, or an aromatic

or heteroaromatic ring system having 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ .

**[0054]** Most preferably,  $R^1$  to  $R^4$  are selected, identically or differently, from F,  $N(R^6)_2$ , phenyl, methyl and tert-butyl.

**[0055]** In another preferred embodiment of the invention, R is selected, identically or differently on each occurrence, from the group consisting of 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  $R^6$ , 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, and an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ .

**[0056]** In a particularly preferred embodiment of the invention, R is selected on each occurrence, identically or differently, from the group consisting of F, a straight-chain alkyl group having 1 to 5 C atoms, a branched or cyclic alkyl group having 3 to 6 C atoms, or an aromatic or heteroaromatic ring system having 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ .

**[0057]** Most preferably, R is selected from F, phenyl, methyl and tert-butyl.

**[0058]** In a further preferred embodiment of the invention, the radical  $R^5$  which is bonded to  $Ar^1$  or  $Ar^2$  is selected, identically or differently on each occurrence, from the group consisting of H, F, CN, a straight-chain alkyl group having 1 to 10 C atoms, a branched or cyclic alkyl group having 3 to 10 C atoms or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, each of which may be substituted by one or more radicals  $R^6$ .

**[0059]** In a particularly preferred embodiment of the invention, the radical  $R^5$  which is bonded to  $Ar^1$  or  $Ar^2$  is selected, identically or differently on each occurrence, from the group consisting of H, a straight-chain alkyl group having 1 to 5 C atoms, a branched or cyclic alkyl group having 3 to 6 C atoms or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, each of which may be substituted by one or more radicals  $R^6$ .

**[0060]** The radicals  $R^1$  to  $R^6$  here preferably contain no condensed aryl or heteroaryl groups in which more than two aromatic or heteroaromatic six-membered rings are condensed directly onto one another, i.e., for example, no anthracene or pyrene groups. The radicals  $R^1$  to  $R^6$  particularly preferably contain absolutely no condensed aryl or heteroaryl groups in which aromatic or heteroaromatic six-membered rings are condensed directly onto one another, i.e. also, for example, no naphthalene groups.

**[0061]** It may furthermore be preferred for the two substituents  $R^5$  in the 9-position of a fluorene together to form a cycloalkyl ring, preferably having 3 to 8 C atoms, particularly preferably having 5 or 6 C atoms.

**[0062]** Likewise, the two substituents  $R^5$  in formula (68) and (72) may form a ring system with one another and thus form a Spiro system, for example a cycloalkyl ring, preferably having 3 to 8 C atoms, particularly preferably having 5 or 6 C atoms.

**[0063]** 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.

**[0064]** Particular preference is given to compounds of the formulae (1) and (2) to (9) and (2a) to (9a) and (2b) to (9b) and (2c) to (9c), in which the preferred embodiments mentioned above occur simultaneously. Particular preference is therefore given to compounds for which:

**[0065]**  $Ar^1$ ,  $Ar^2$  are, identically or differently, a group of one of the formulae (10) to (66);

**[0066]** or  $-NAr^1Ar^2$  stands for a group of one of the formulae (67) to (74);

**[0067]** E is on each occurrence, identically or differently, a single bond or  $C(R^1)_2$ ,  $N(R^1)$ , O or S;

**[0068]**  $R^1$  to  $R^4$  are selected, identically or differently on each occurrence, from the group consisting of 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  $R^6$ , 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 system having 5 to 24 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ ;

**[0069]** R is selected, identically or differently on each occurrence, from the group consisting of 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  $R^6$ , 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, and an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ .

**[0070]**  $R^5$  is, if the radical  $R^5$  is bonded to  $Ar^1$  or  $Ar^2$ , selected, identically or differently on each occurrence, from the group consisting of H, F, CN,  $N(R^6)_2$ , a straight-chain alkyl group having 1 to 10 C atoms, a branched or cyclic alkyl group having 3 to 10 C atoms or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, each of which may be substituted by one or more radicals  $R^6$ ;

**[0071]** or  $R^5$  which is bonded to the carbon bridge in the formulae (20) to (23), (53), (54), (68) and (72) is, identically or differently, an alkyl group having 1 to 10 C atoms, in particular methyl, or a phenyl group, which may be substituted by one or more radicals  $R^6$ ;

**[0072]** or  $R^5$  which is bonded to the nitrogen bridge in the formulae (28) to (31), (40) to (43) or (55) to (58), (63) to (66), (71) and (73) is a phenyl group, which may be substituted by one or more radicals  $R^6$ ;

**[0073]**  $R^6$  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 or an aromatic ring system having 5 to 24 C atoms;

**[0074]** m is 0 or 1;

**[0075]** n is 0 or 1;

**[0076]** p q is 0 or 1;

**[0077]** r is 0 or 1;

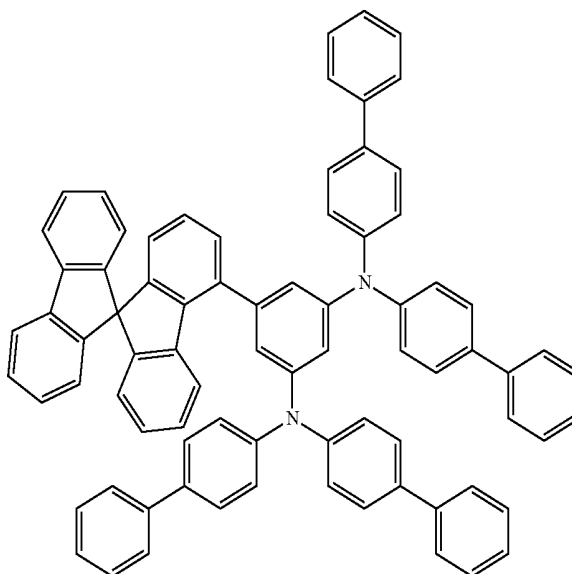
**[0078]** s is 0 or 1;

**[0079]** t is 0 or 1.

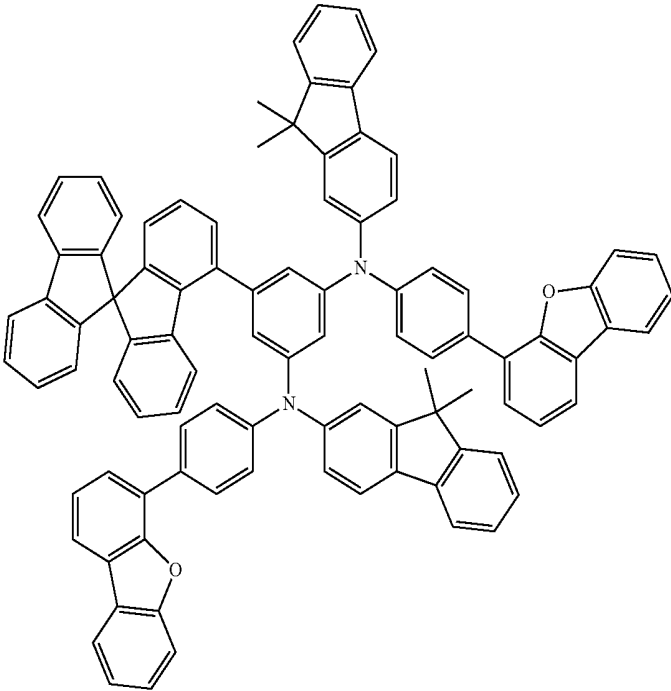
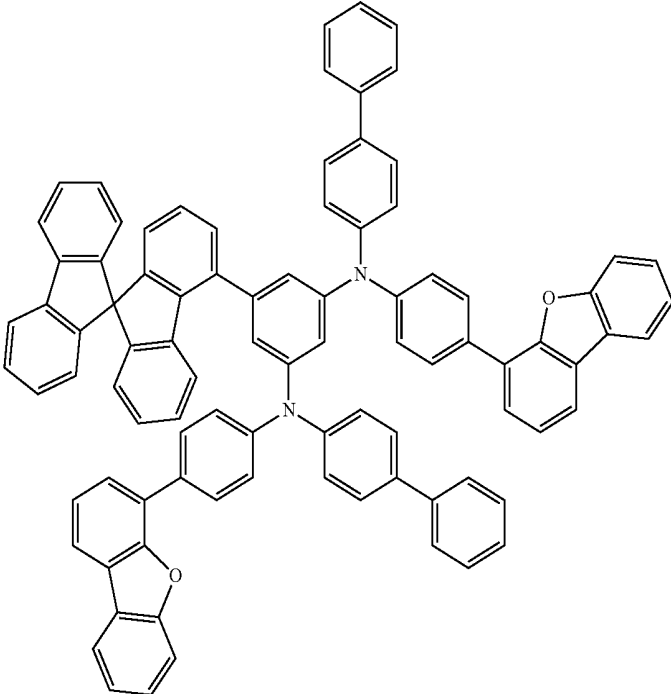
**[0080]** More preferably, in the compounds listed above,  $R^1$  to  $R^4$  is selected, identically or differently, from H, F,  $N(R^6)_2$ , phenyl, methyl and tert-butyl.

**[0081]** Still more preferably, in the compounds listed above, t is 0.

**[0082]** Examples of suitable compounds according to the invention are the compounds shown in the following table:

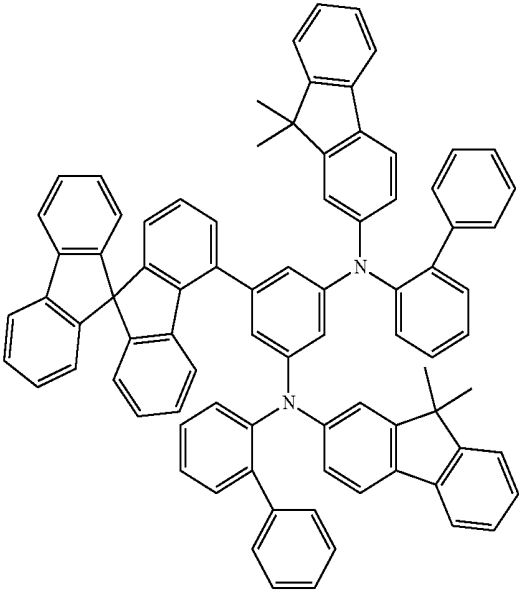
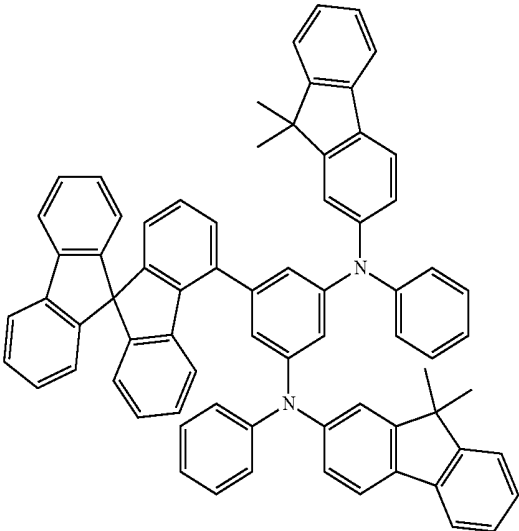


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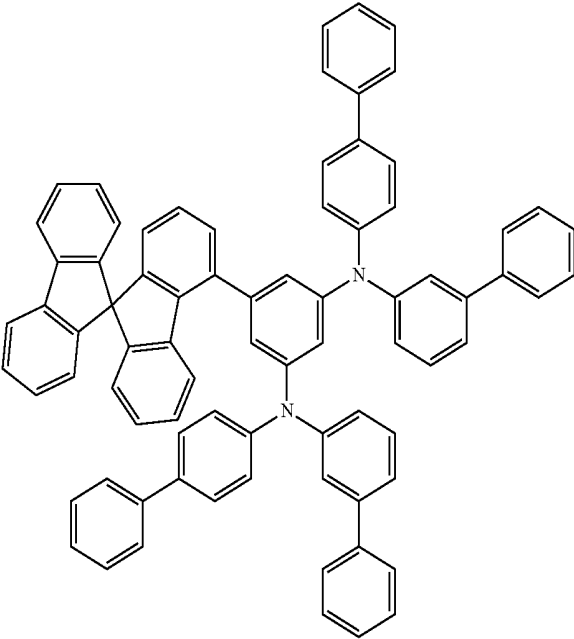
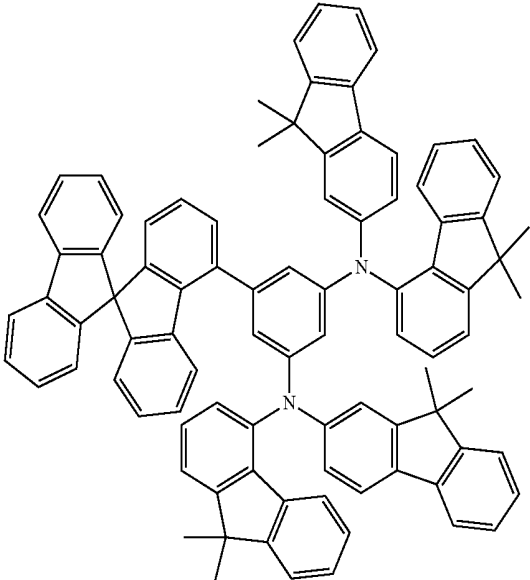
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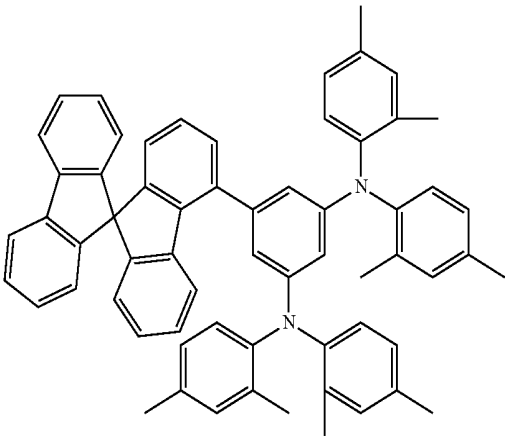
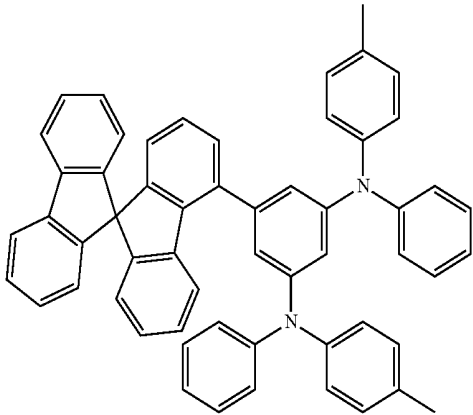
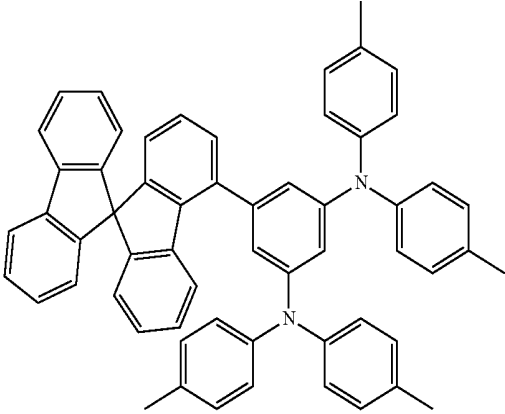
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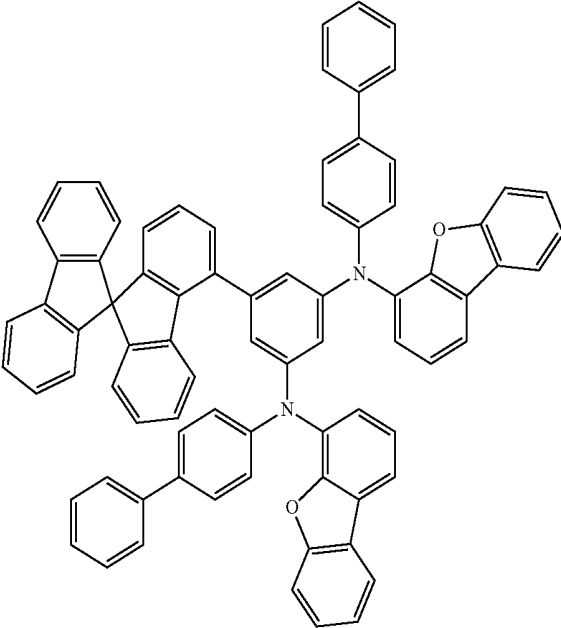
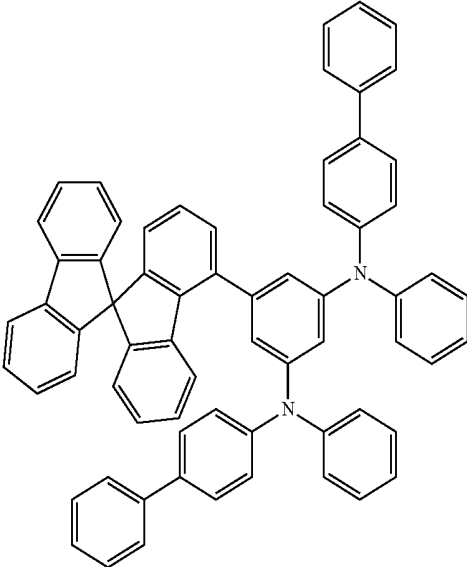
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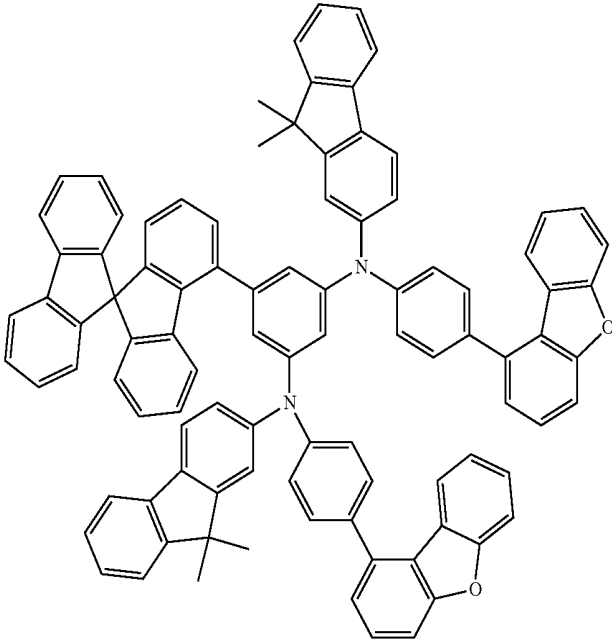
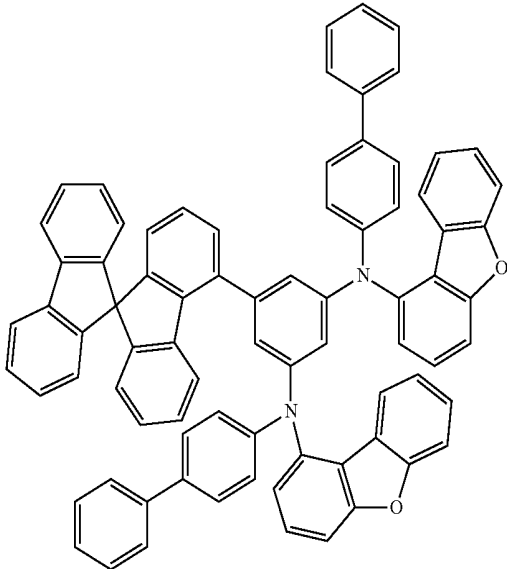
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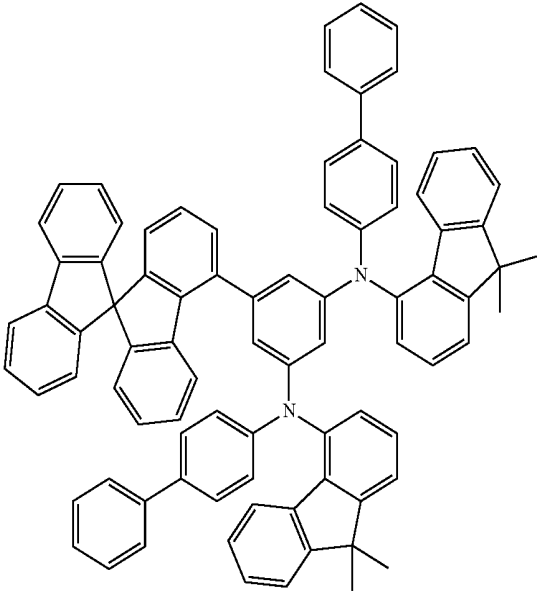
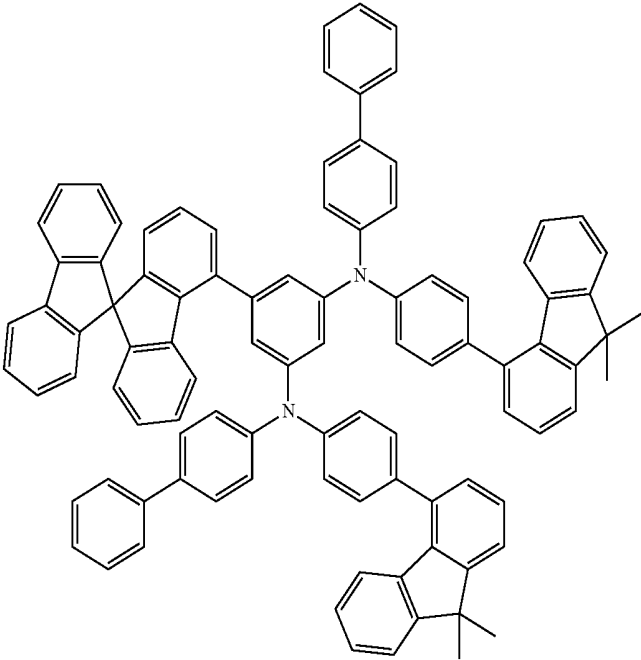
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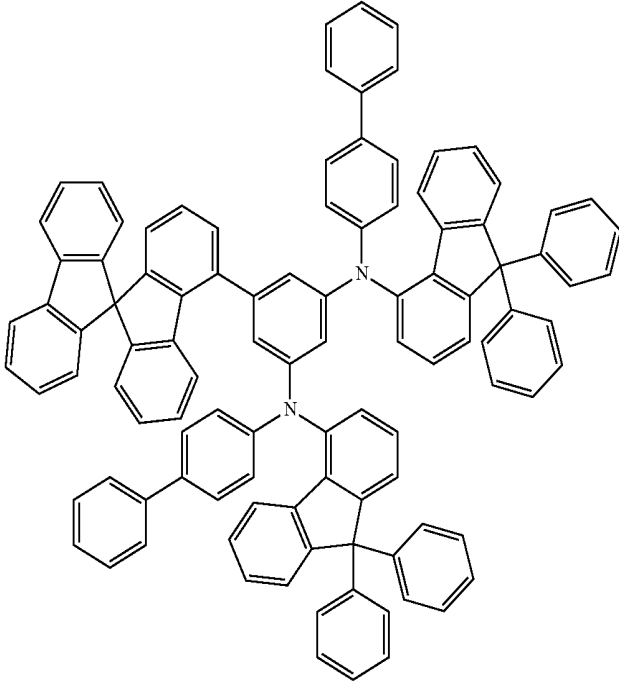
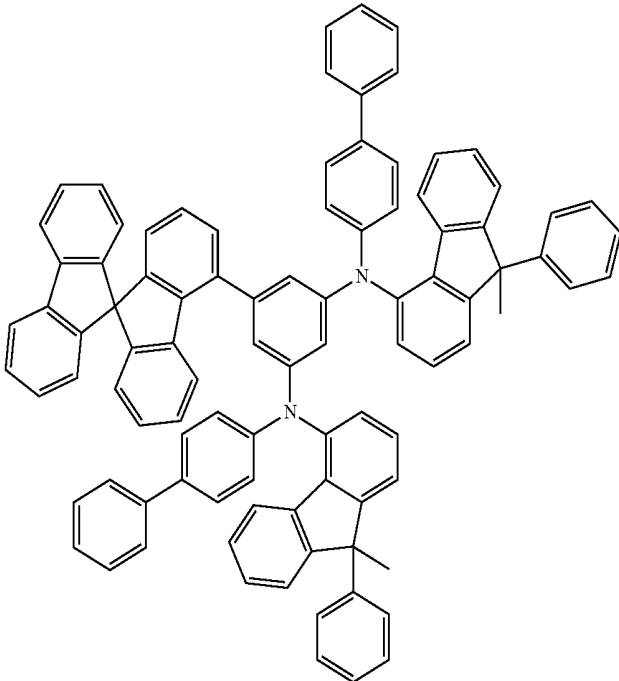


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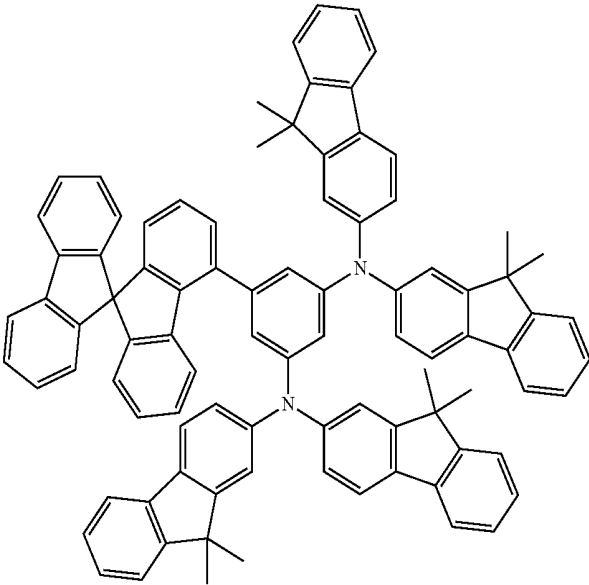
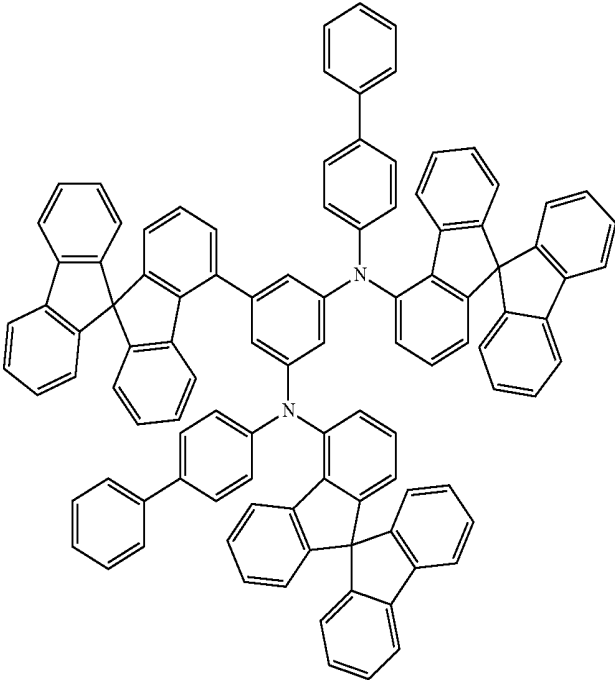


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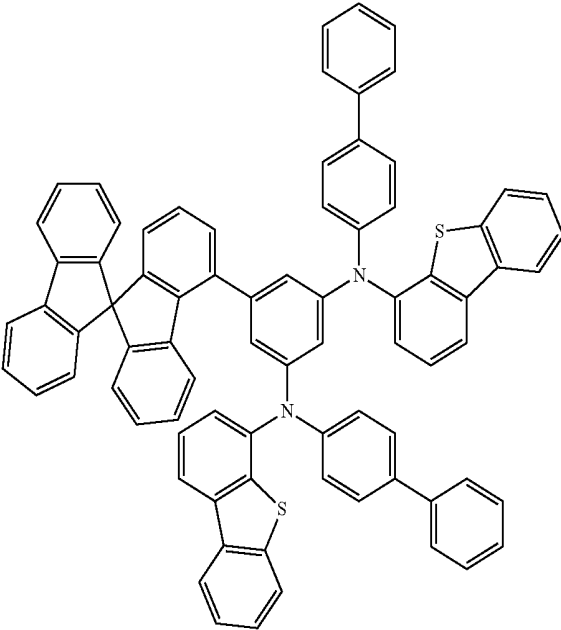
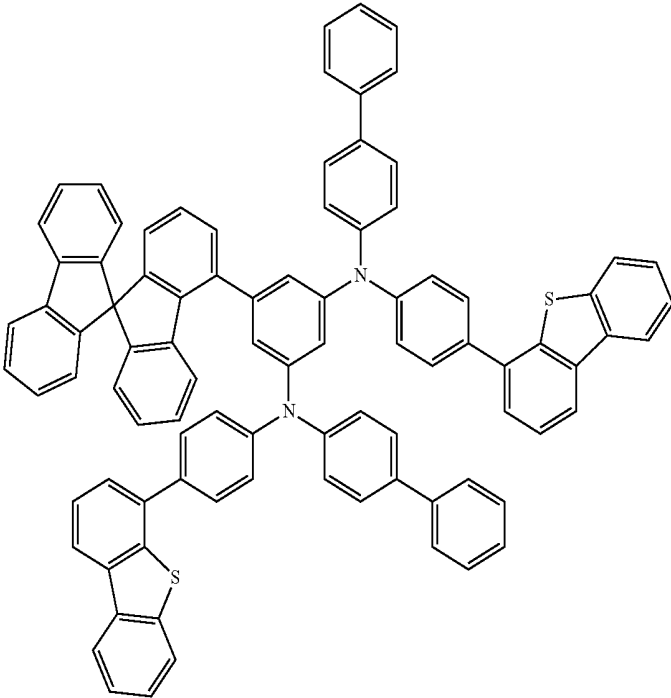
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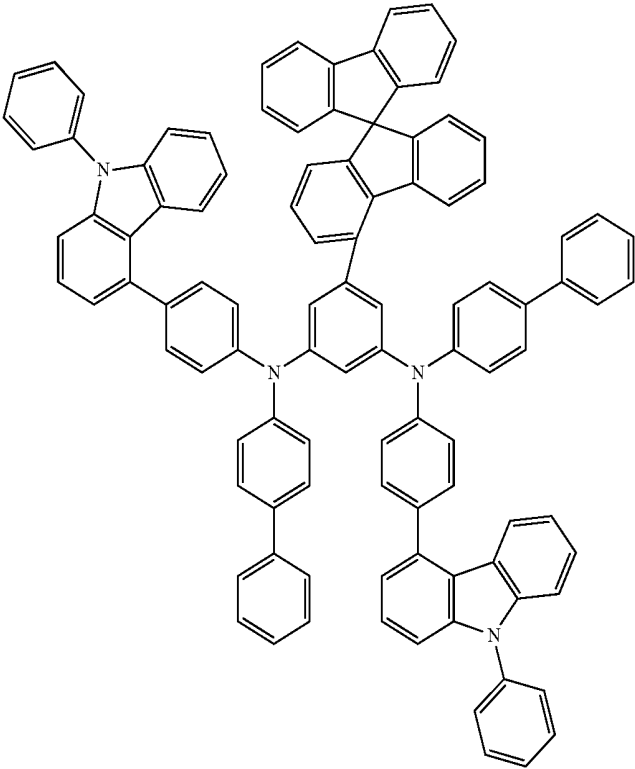
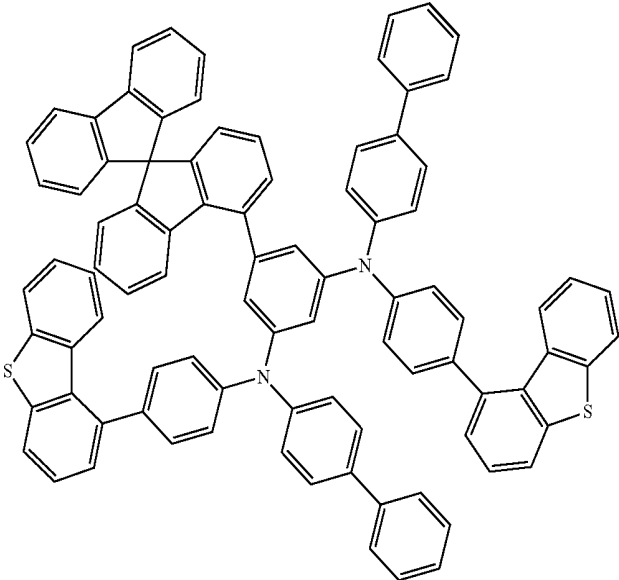
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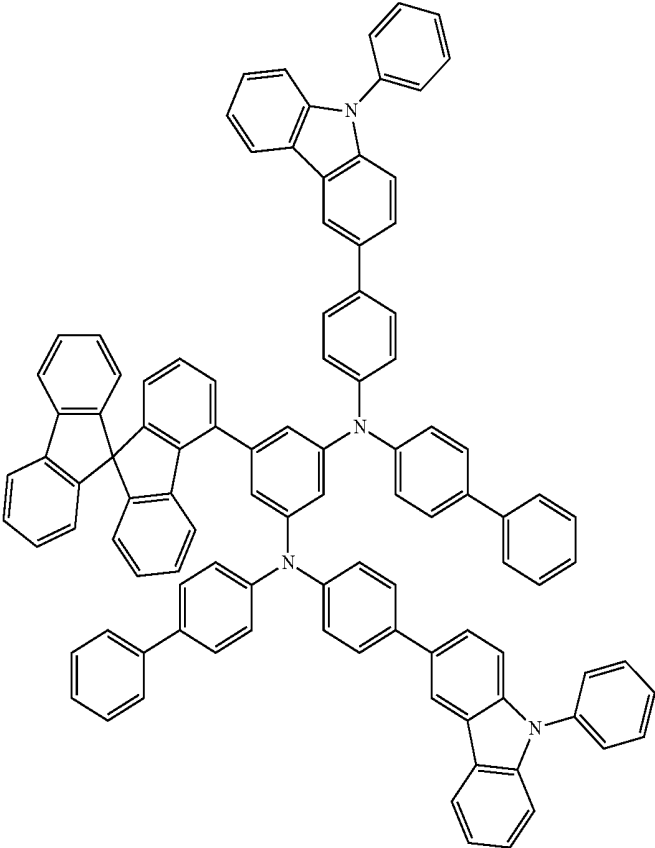
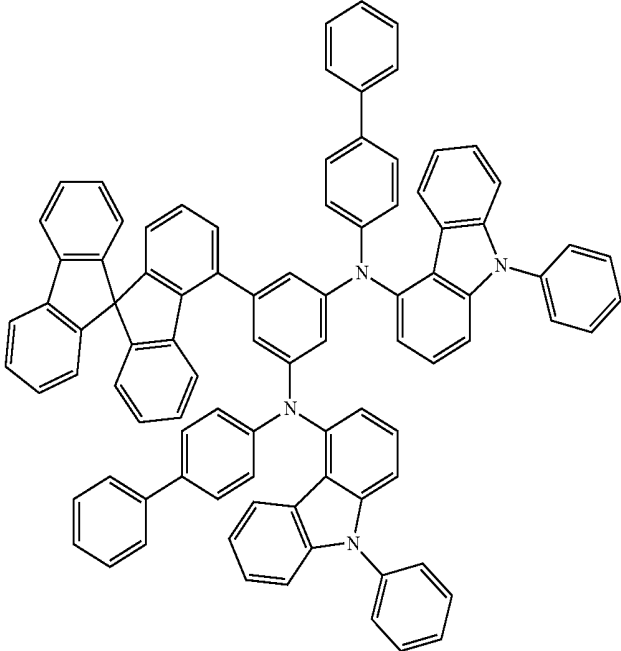


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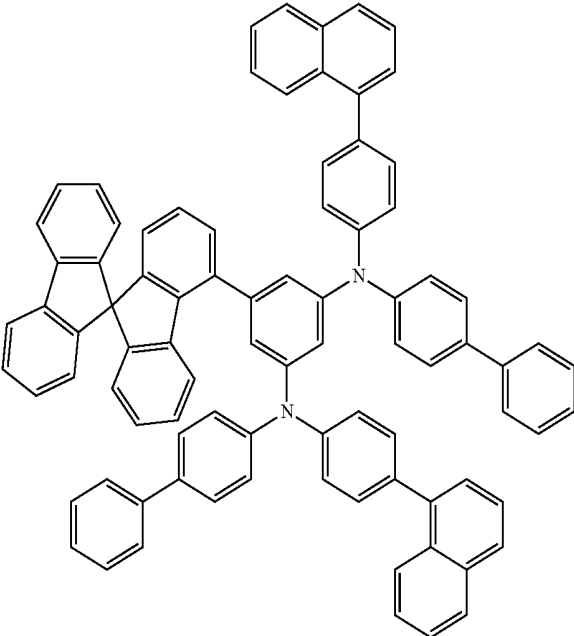
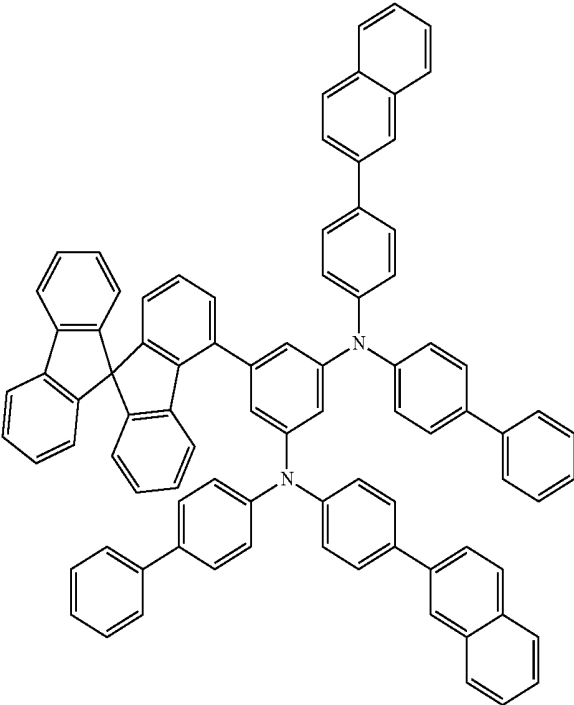


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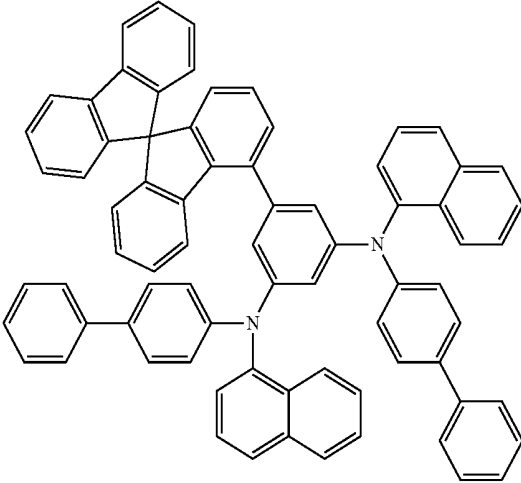
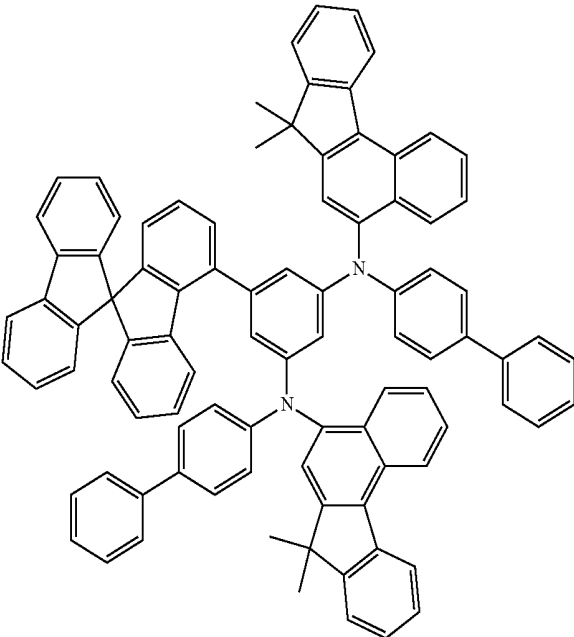
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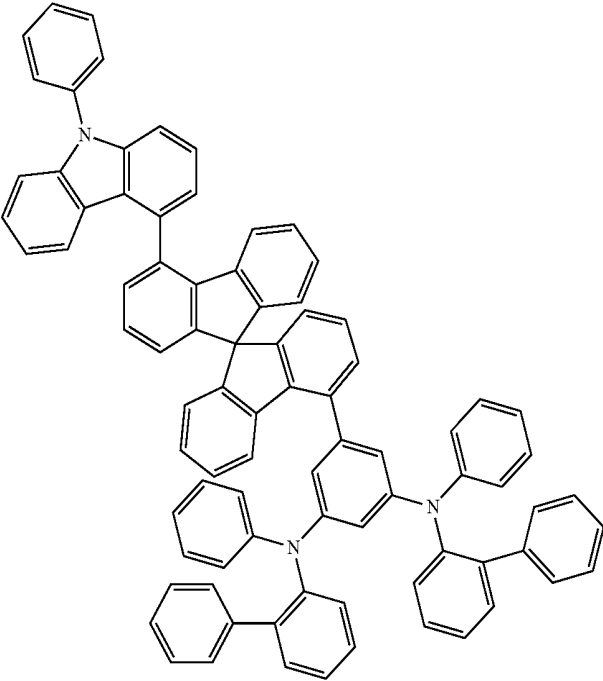
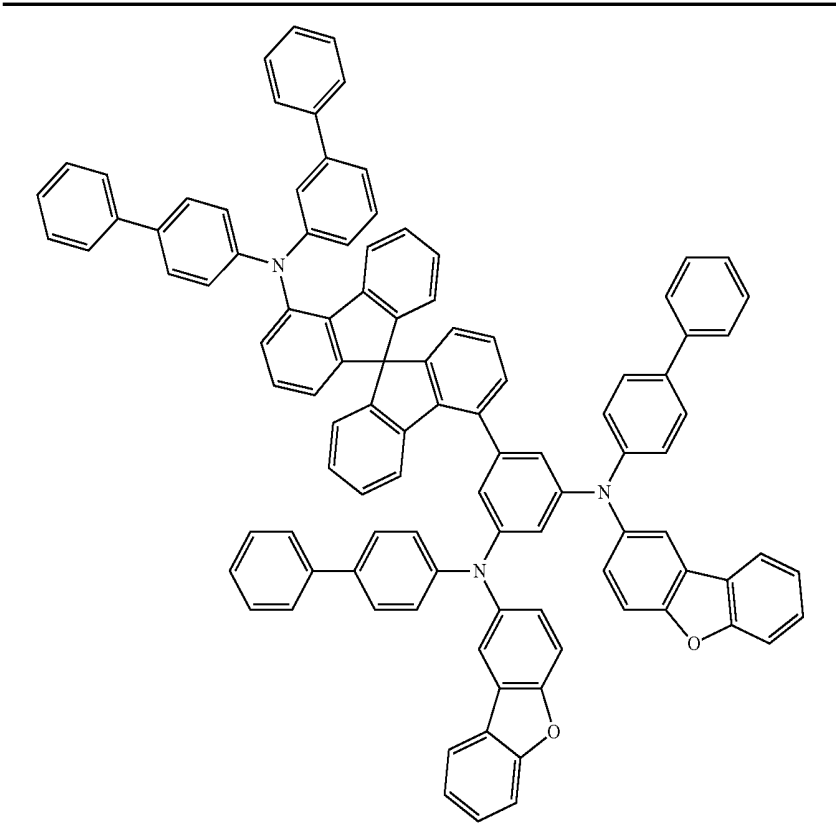


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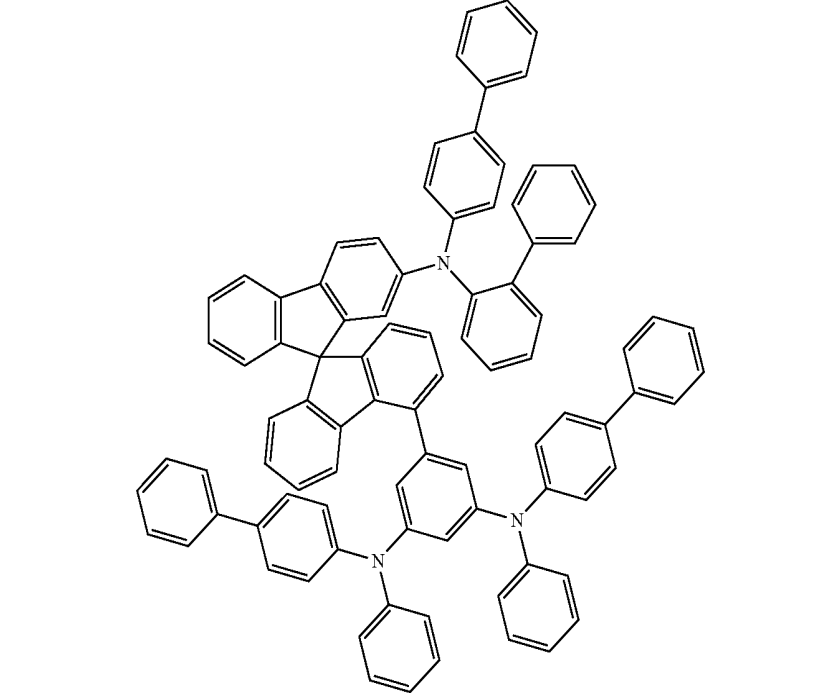
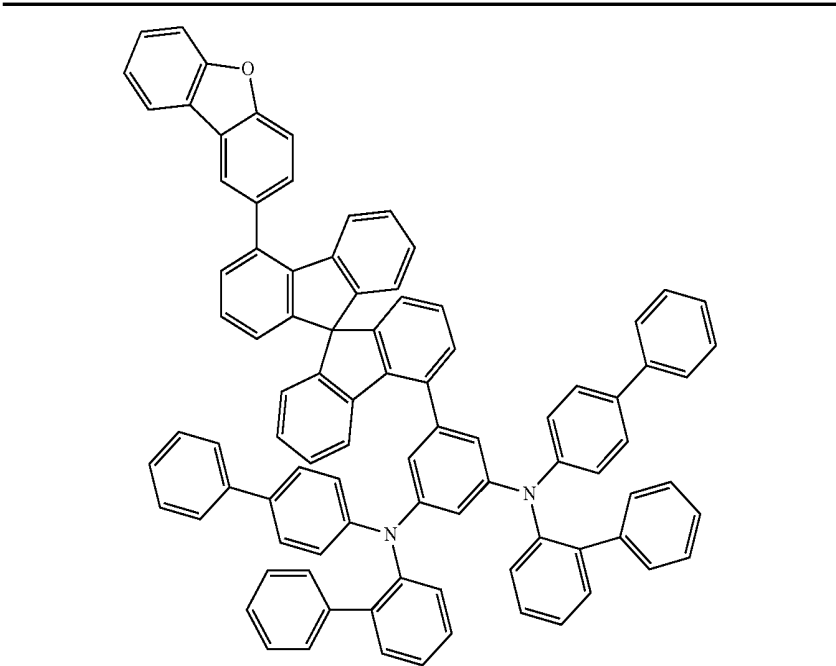
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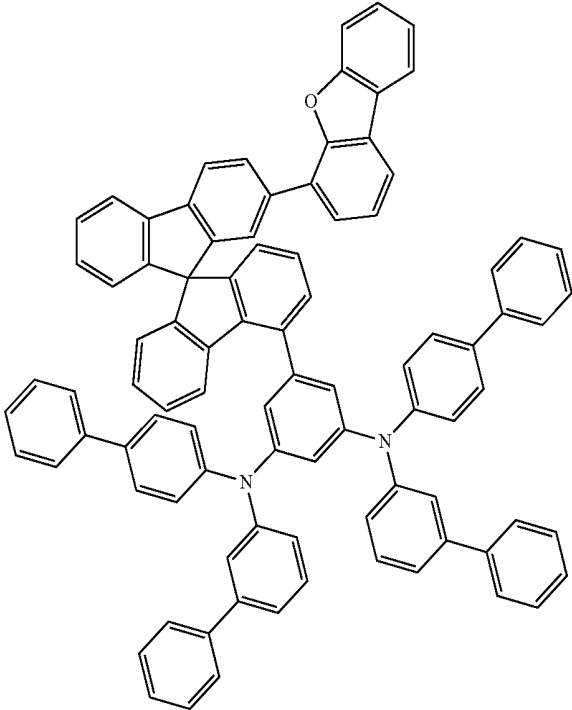
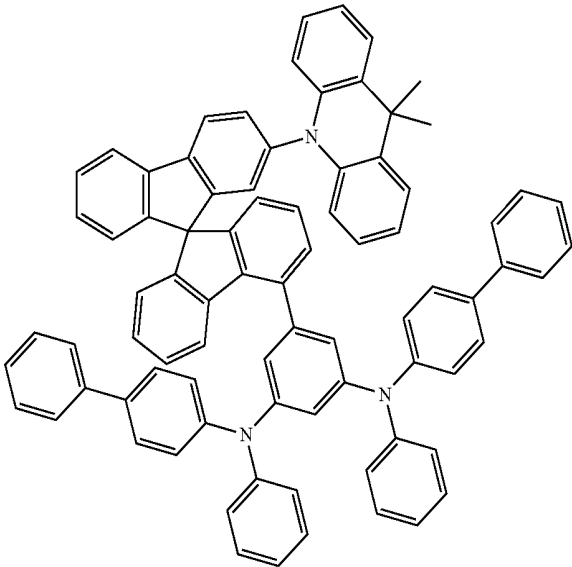


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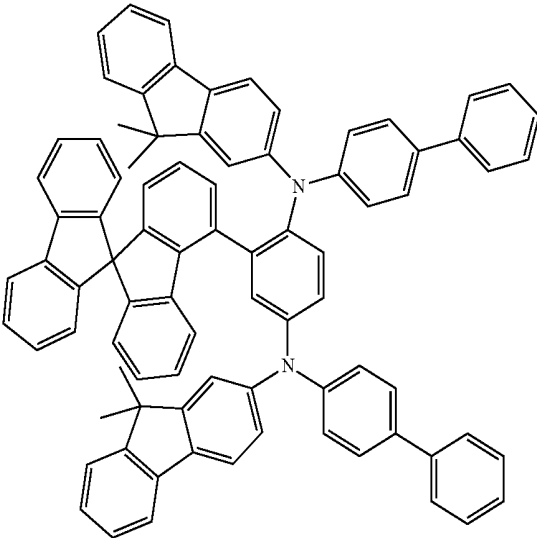
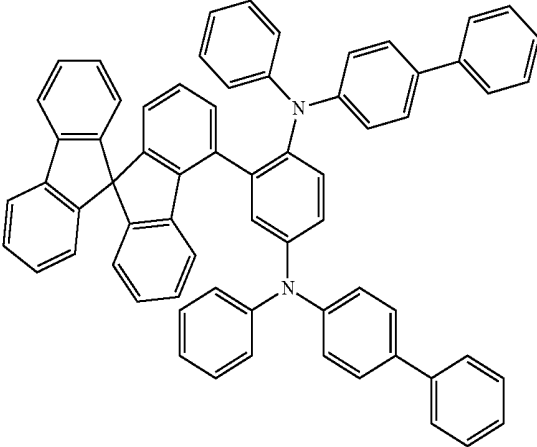
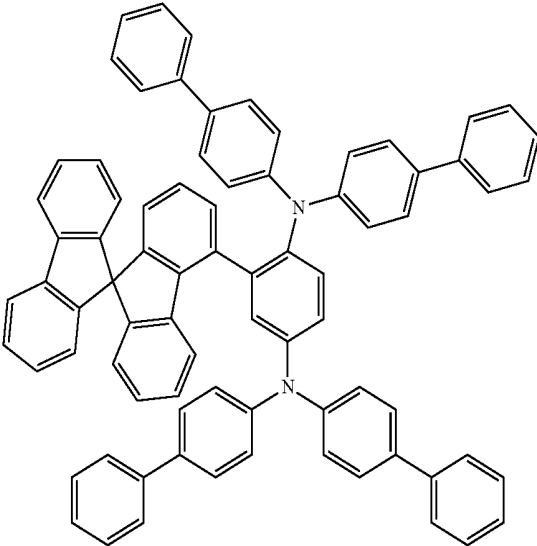


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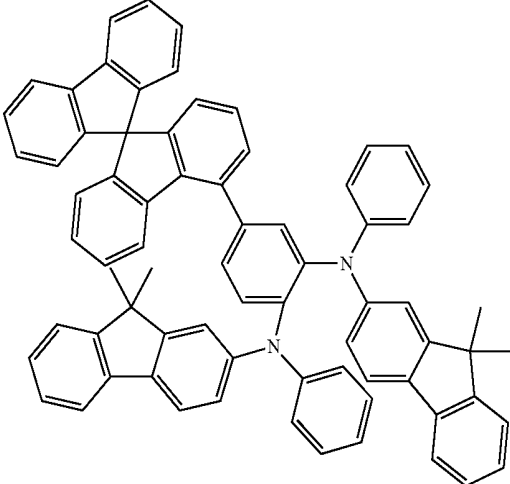
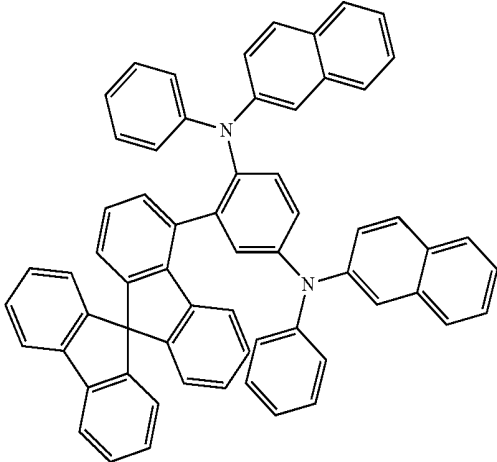
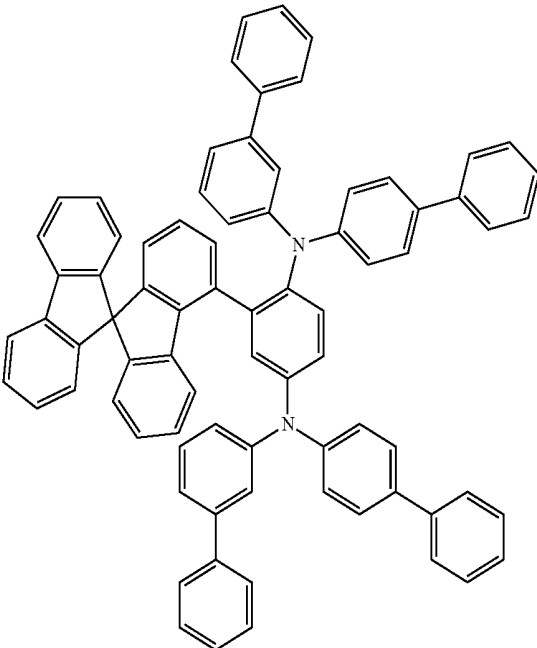
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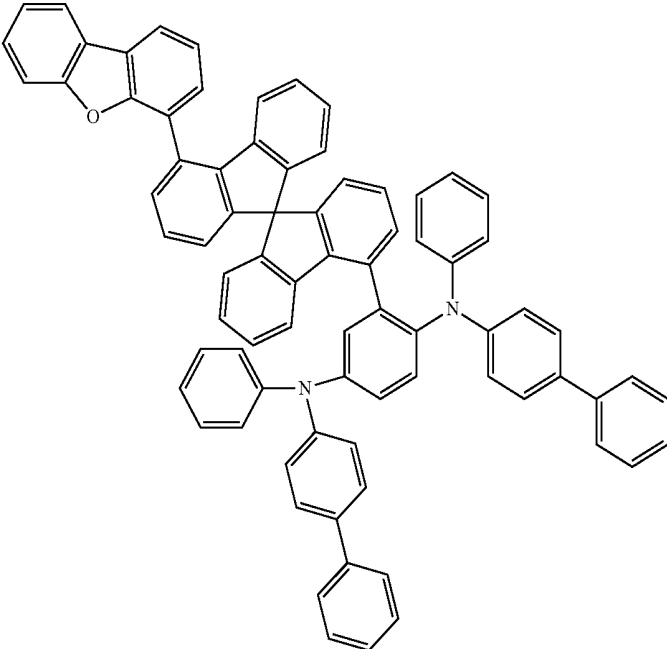
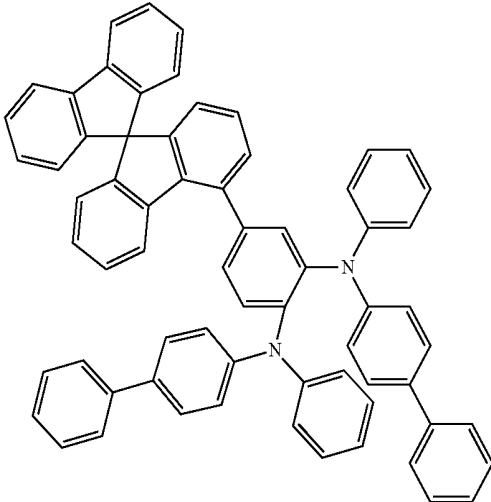


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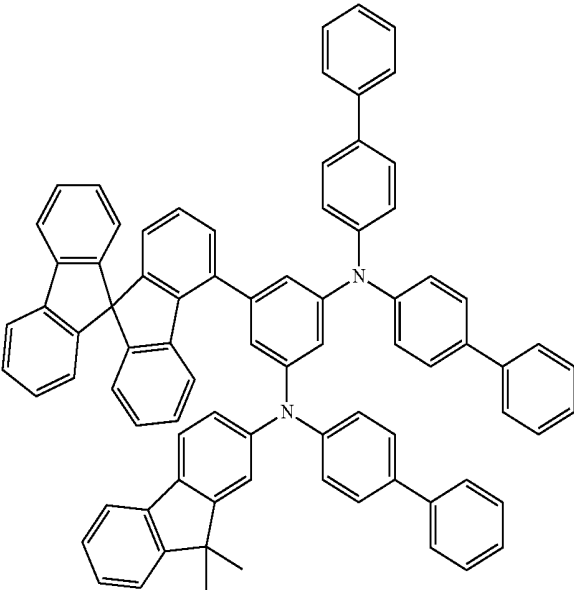
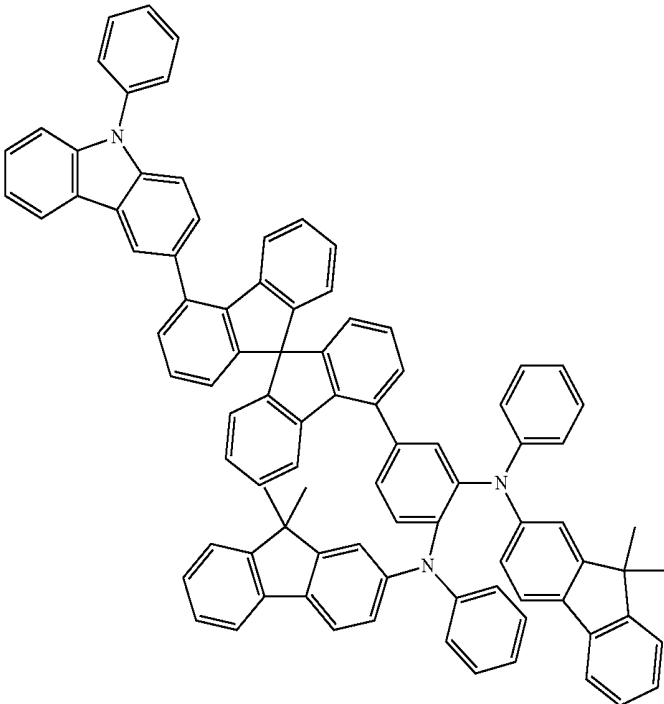
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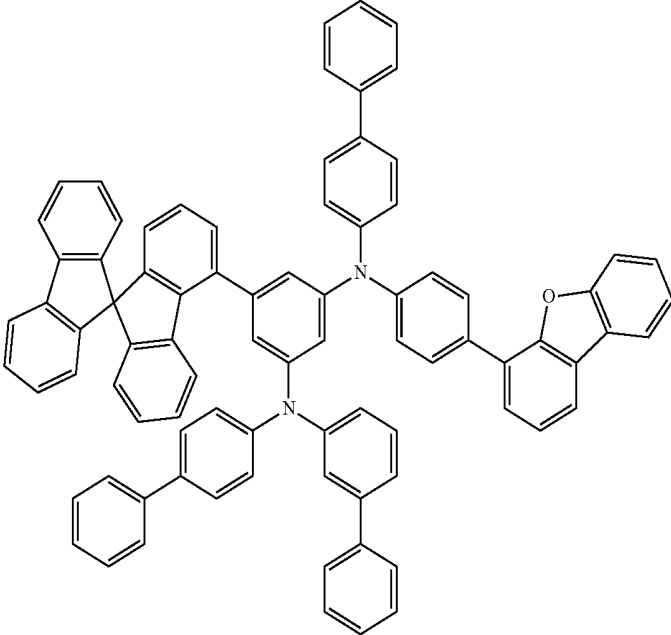
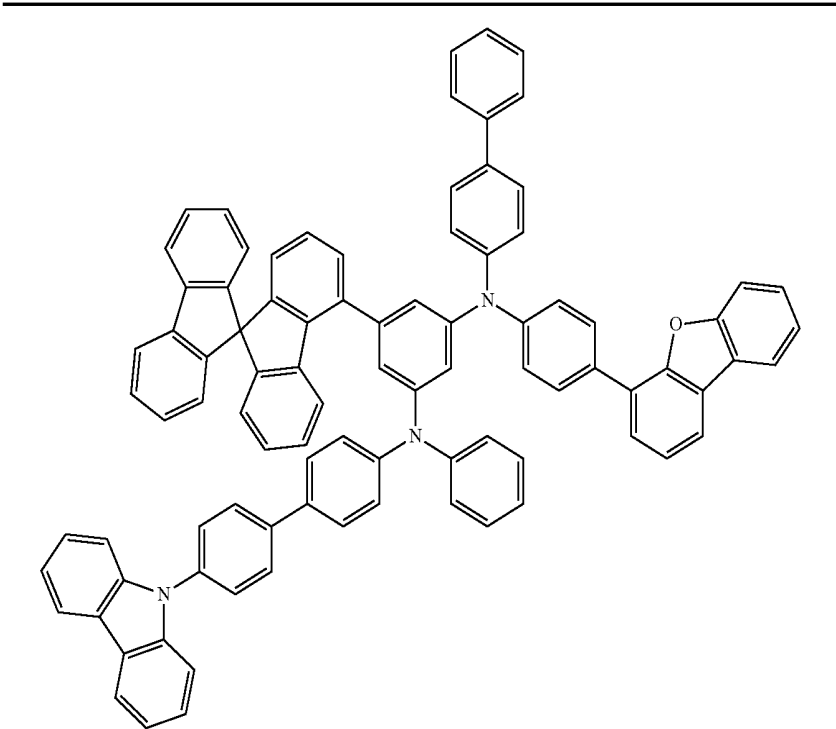


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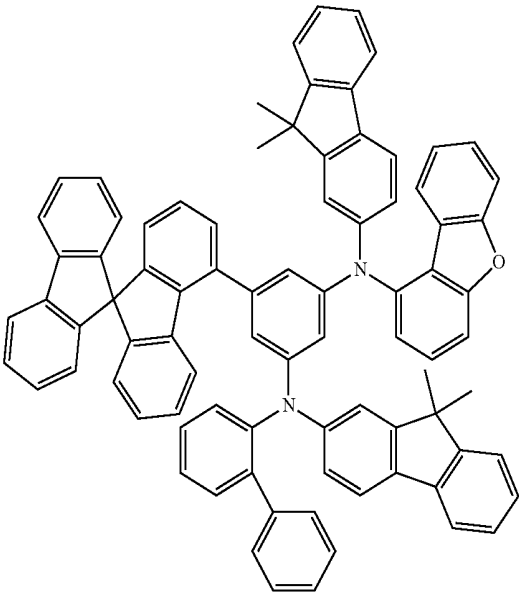
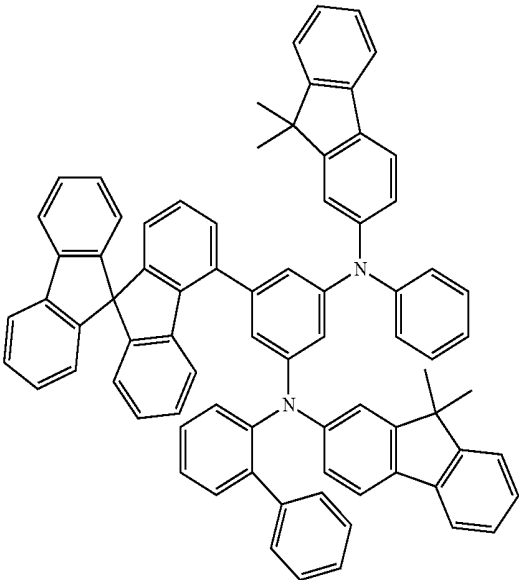


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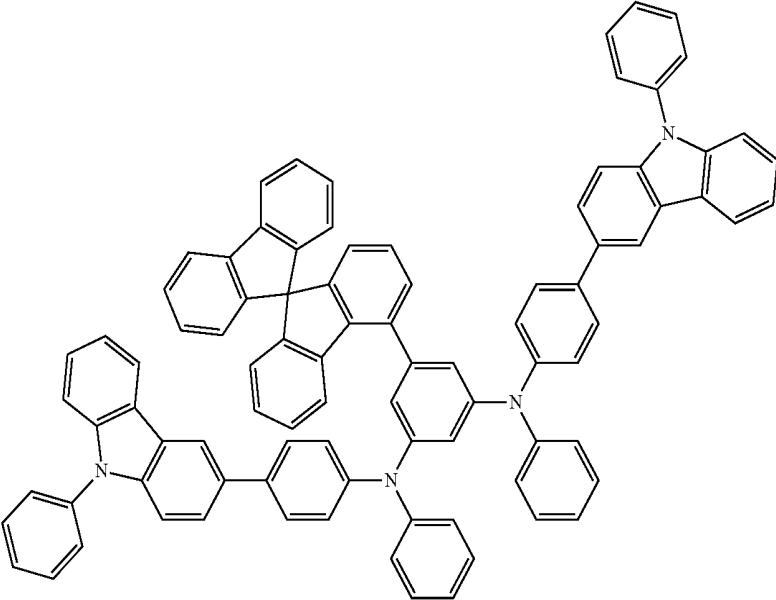
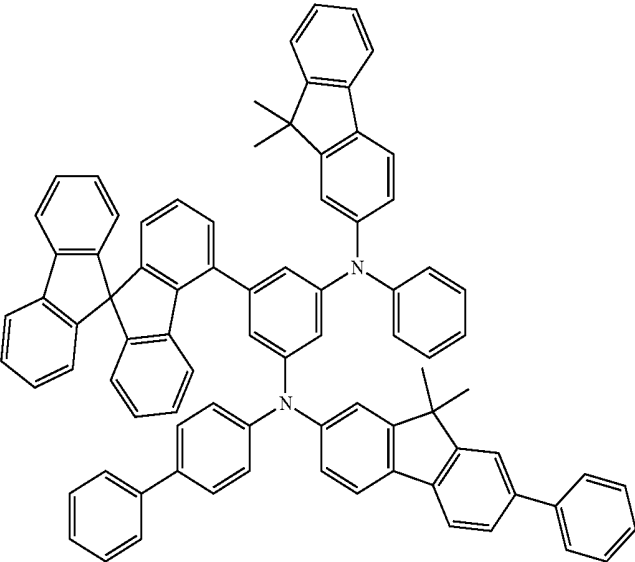
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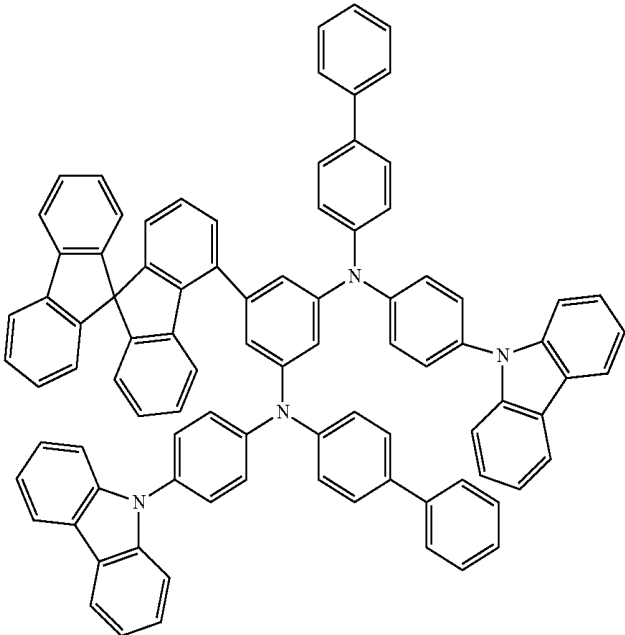
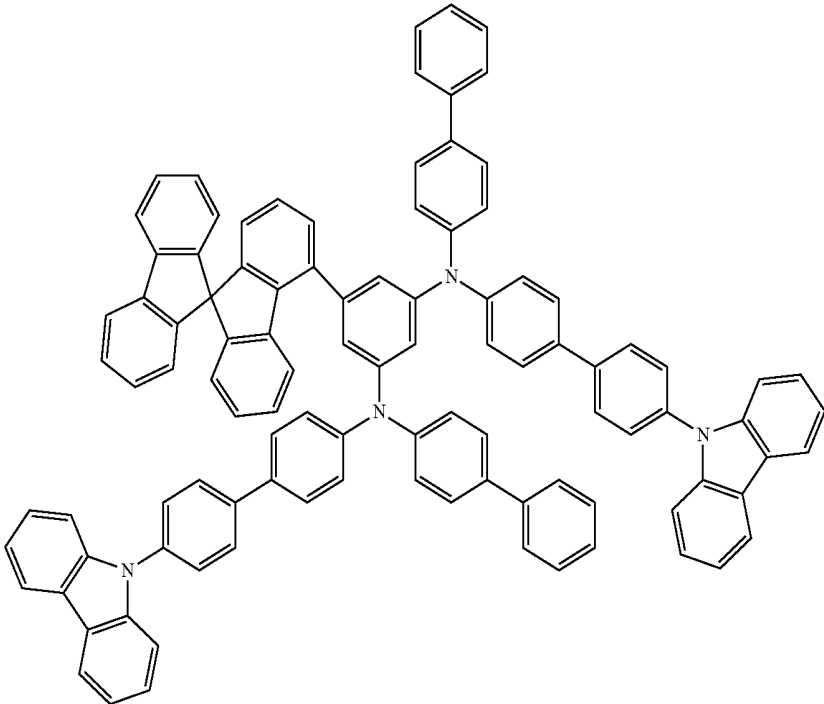
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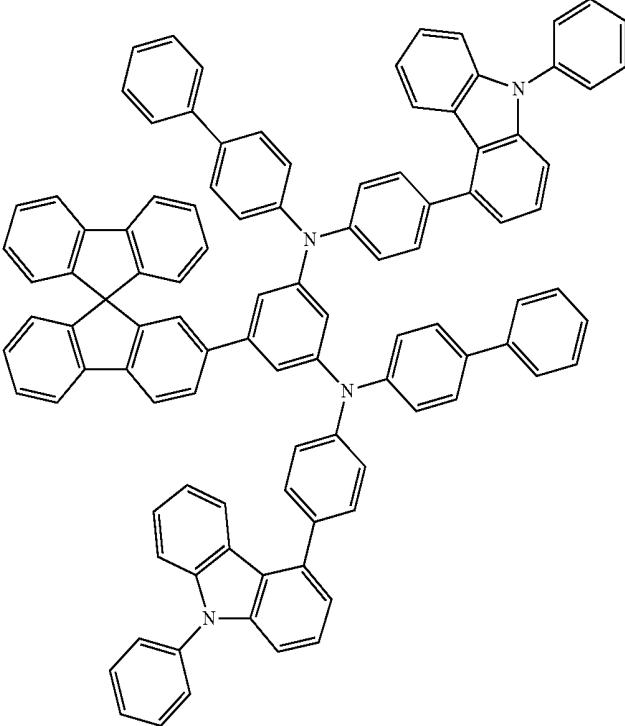
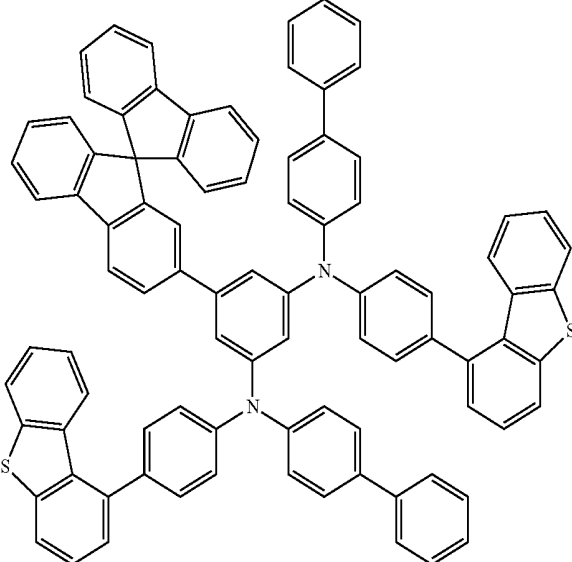
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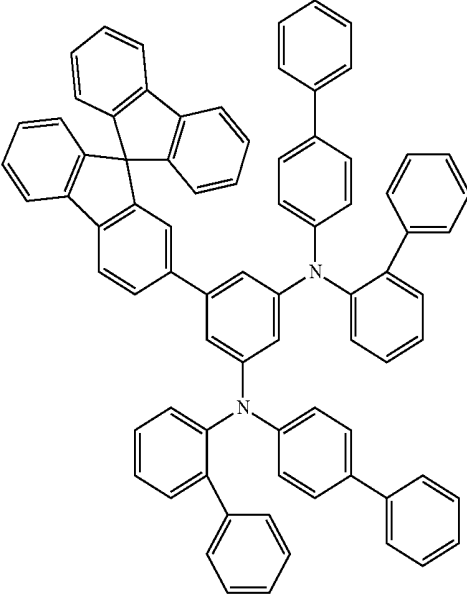
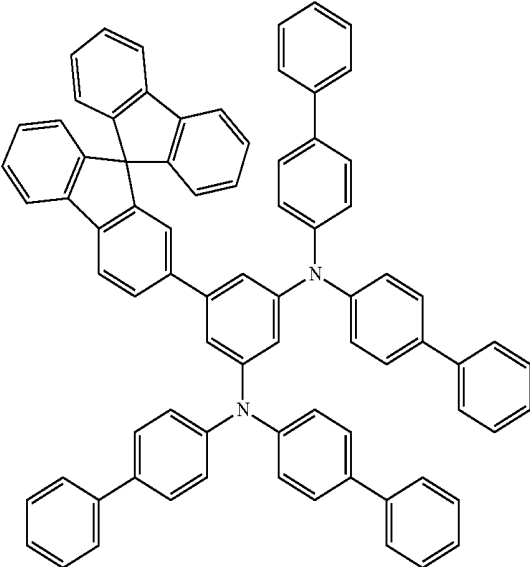
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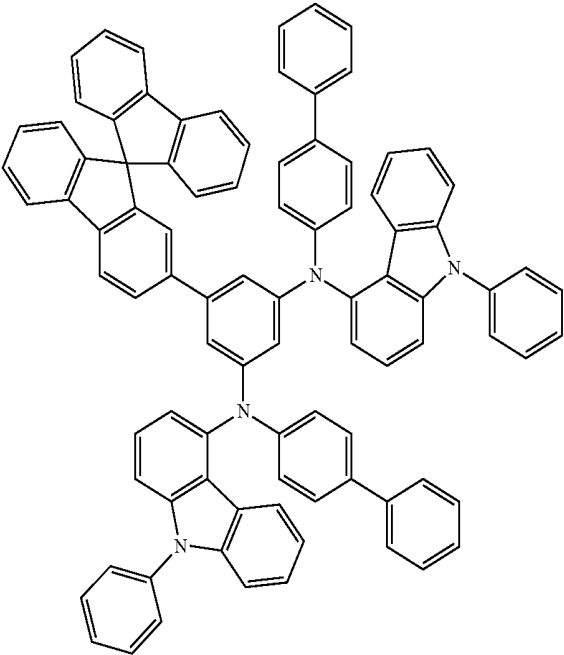
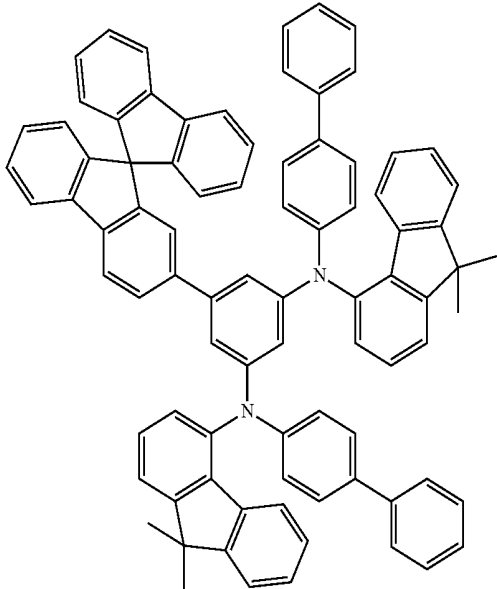
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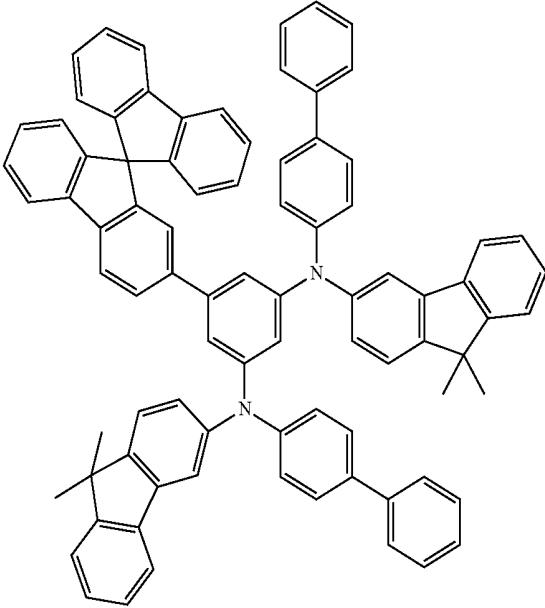
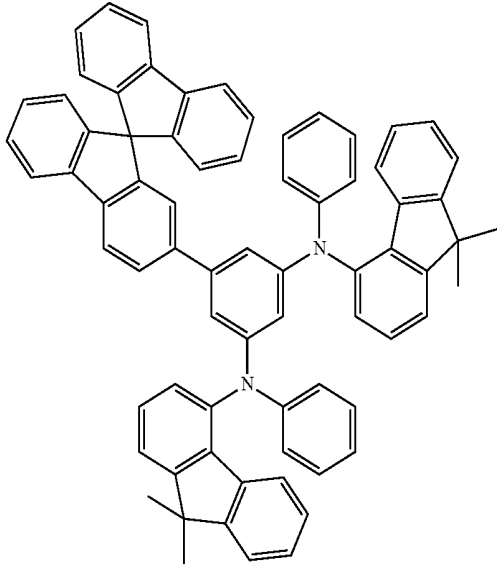
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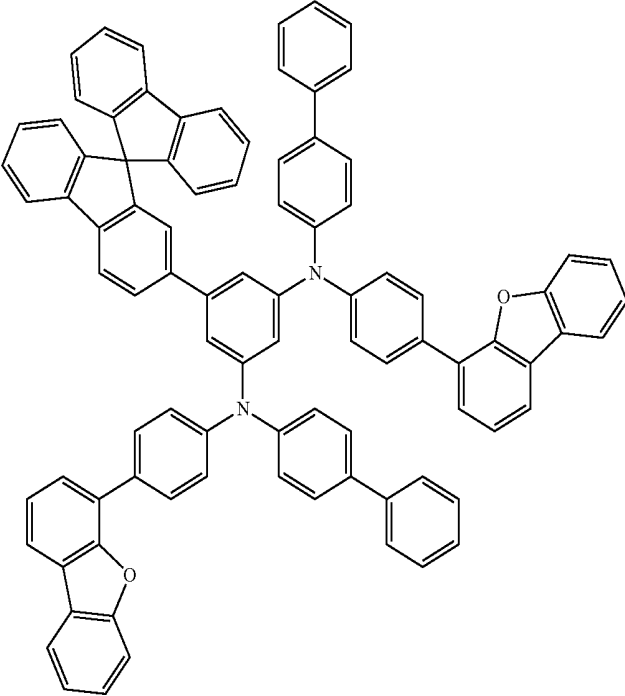
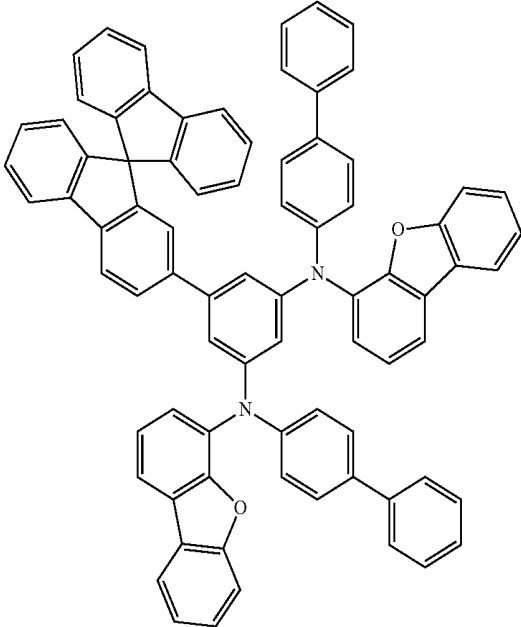


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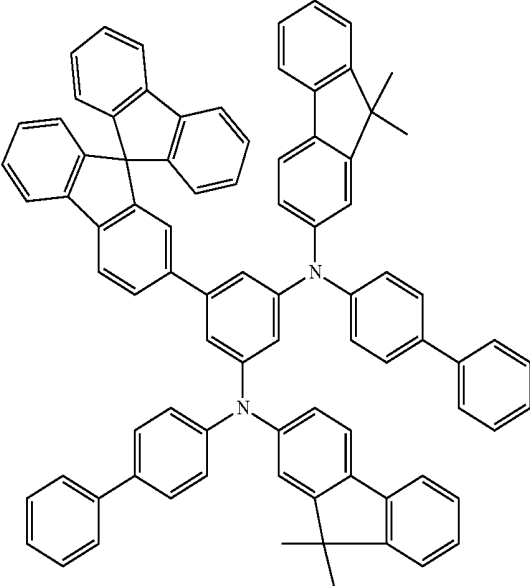
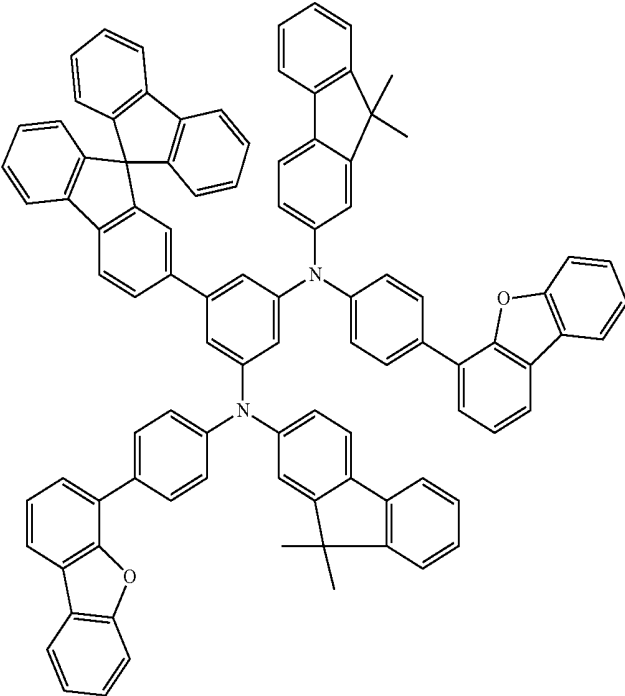


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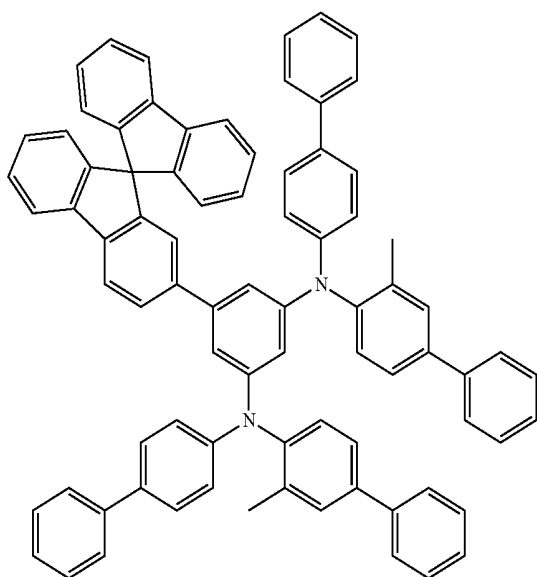
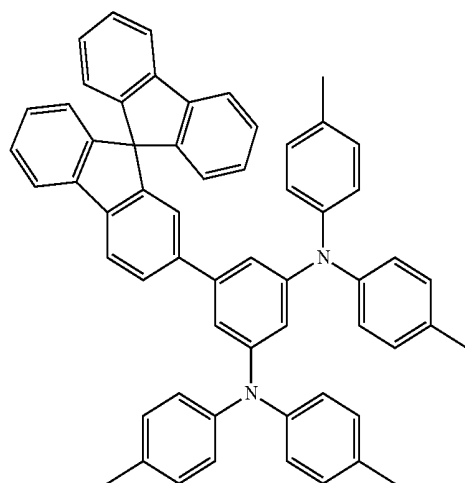
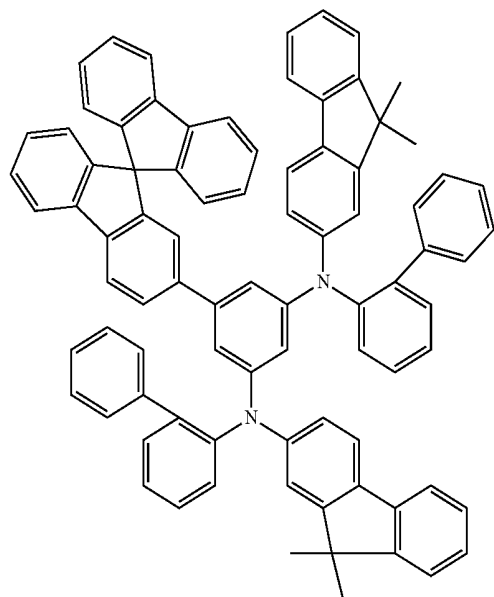
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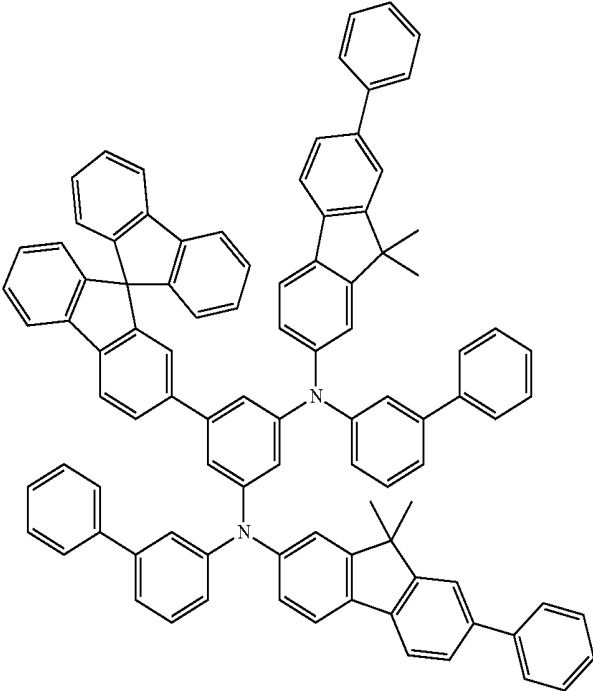
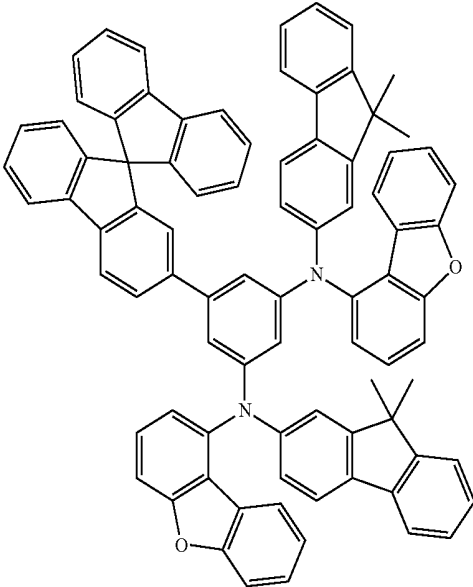
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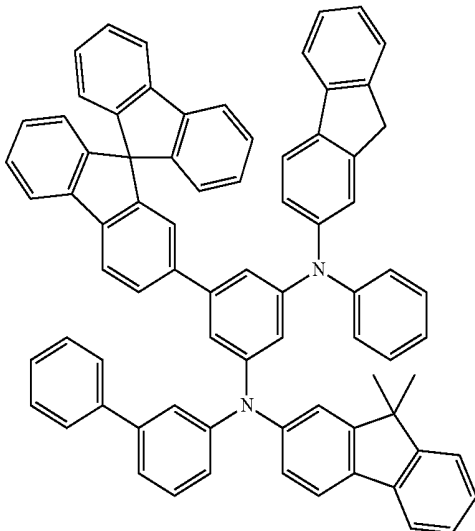
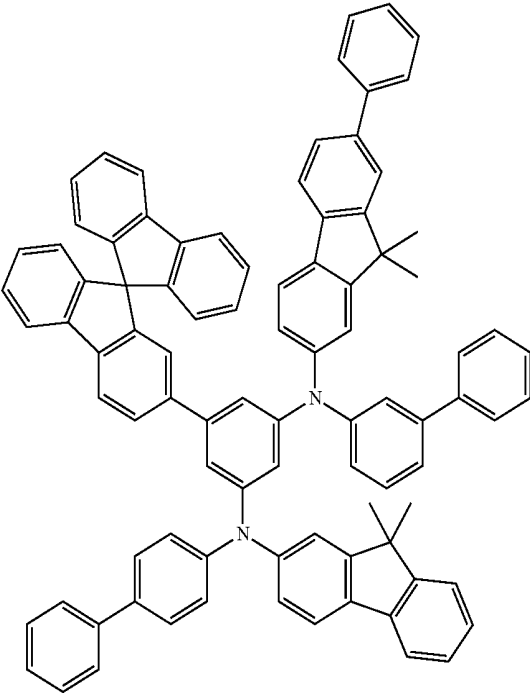
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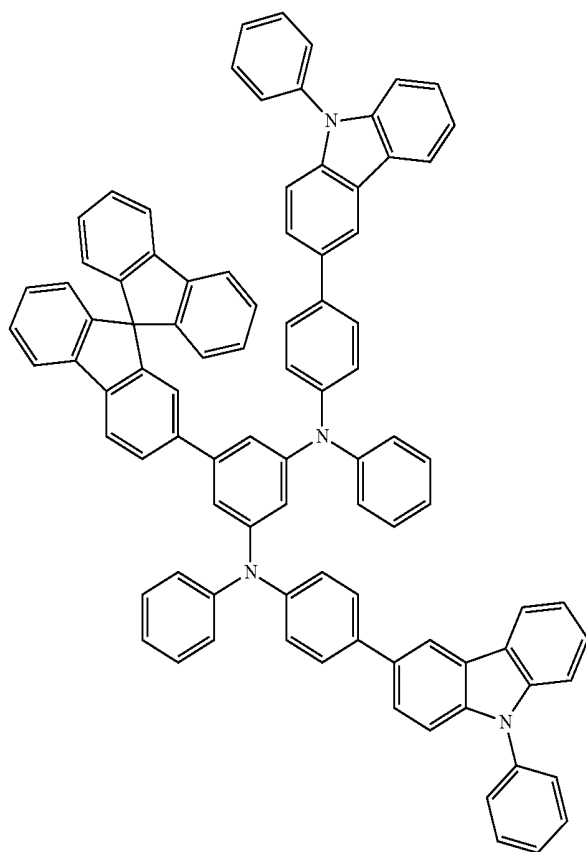
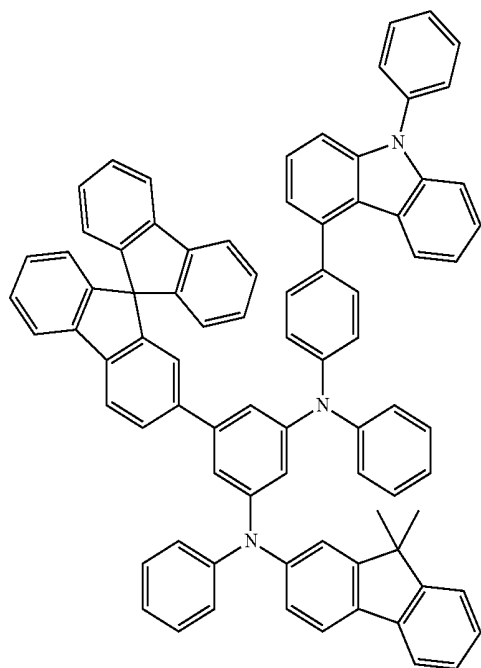
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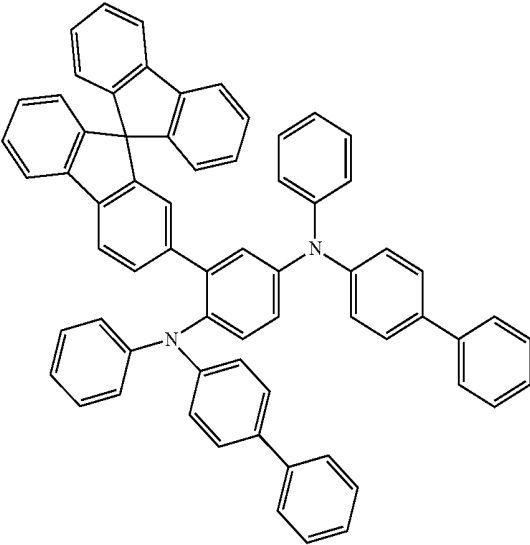
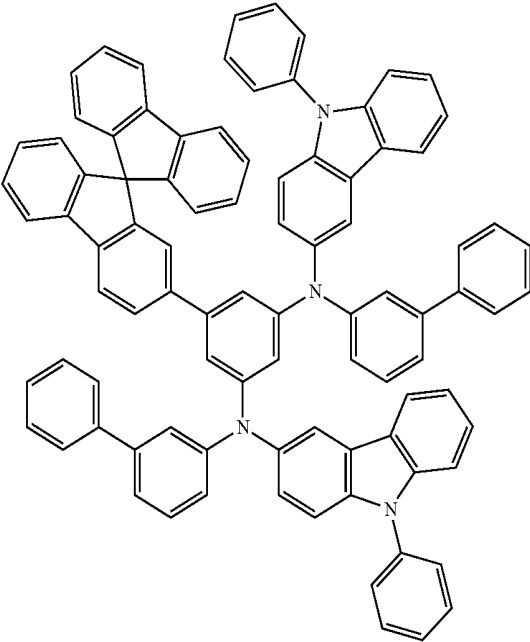
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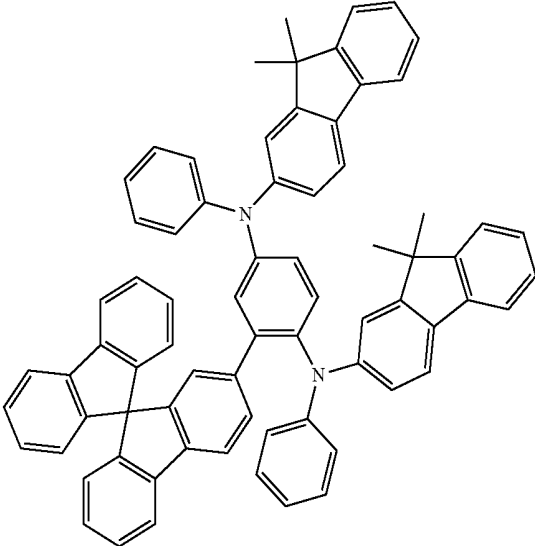
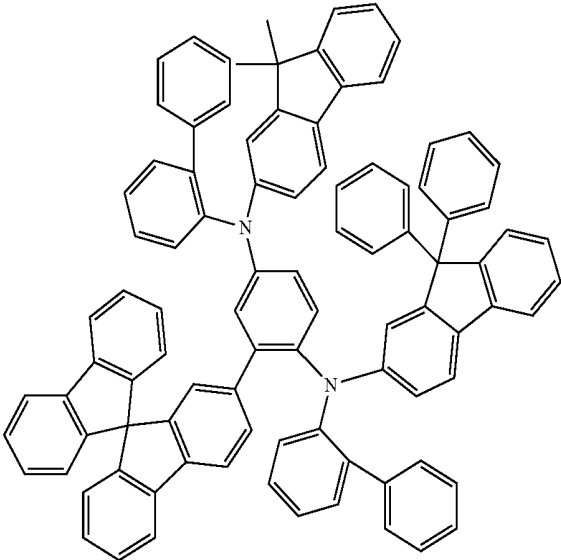
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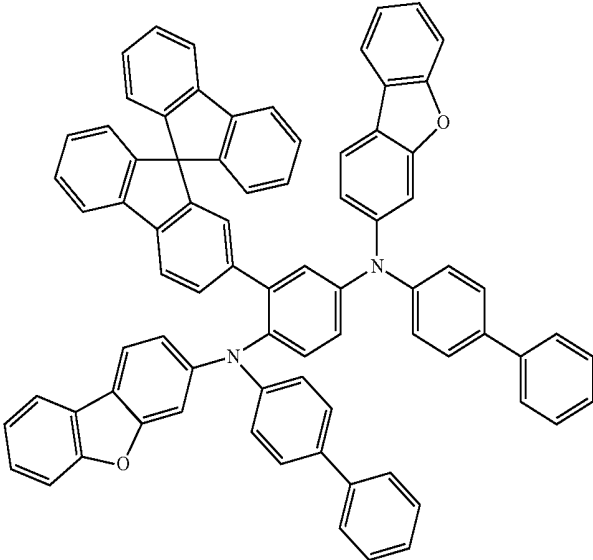
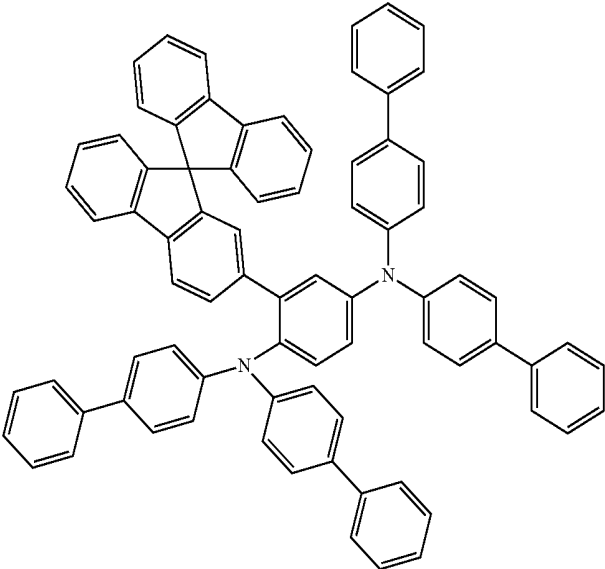
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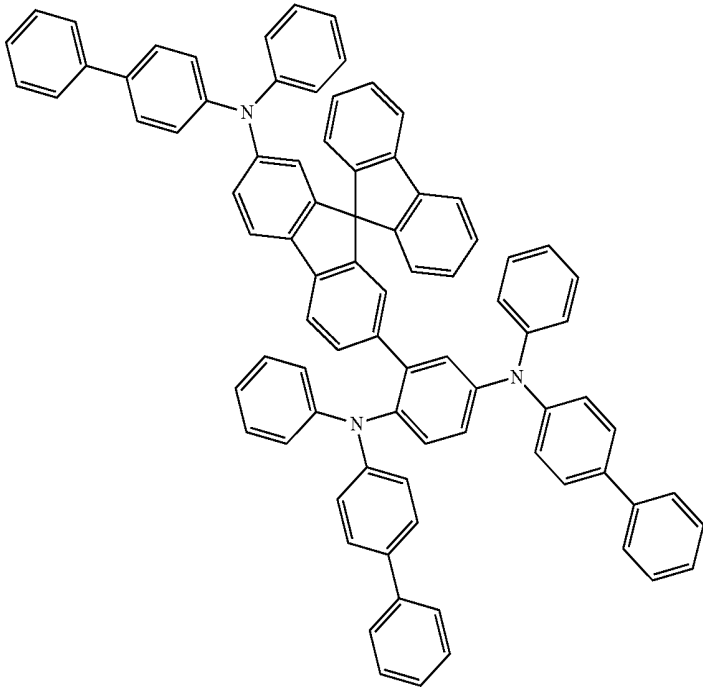
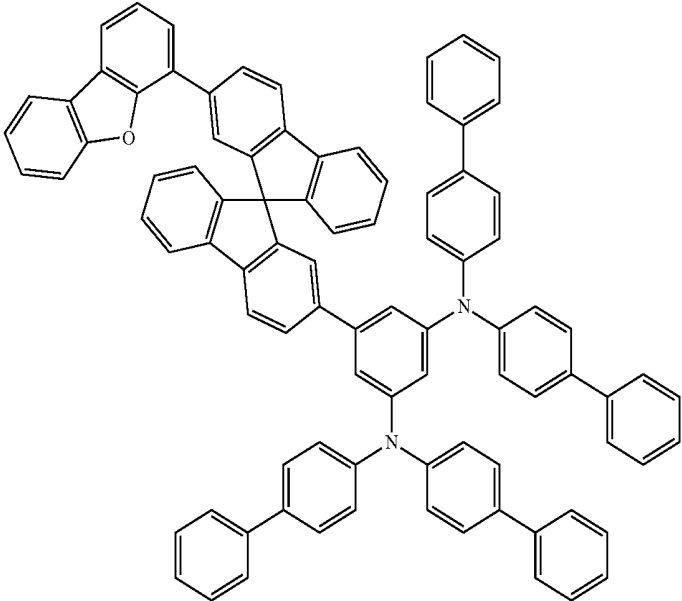
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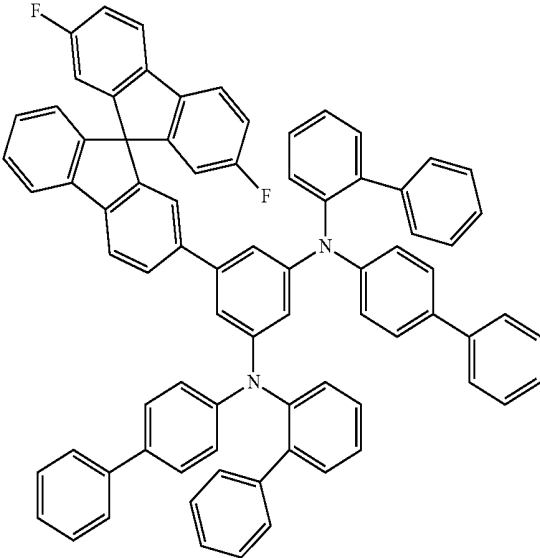
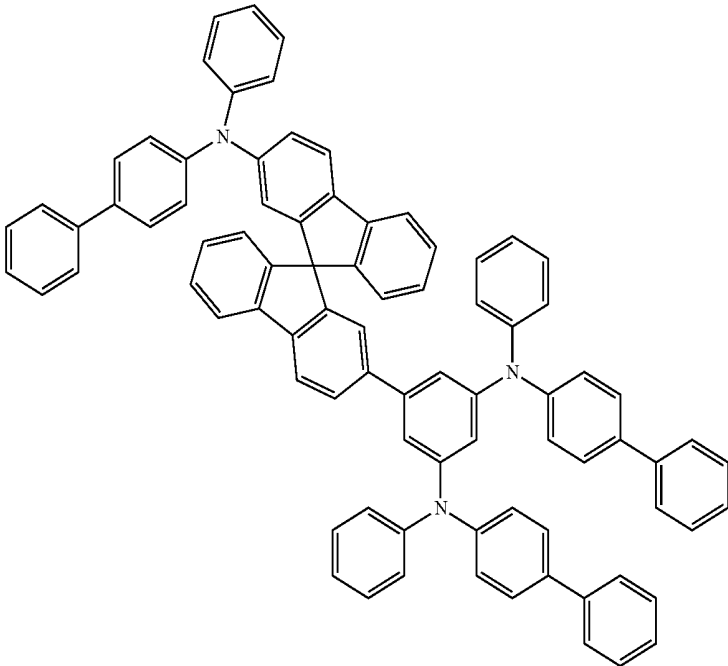
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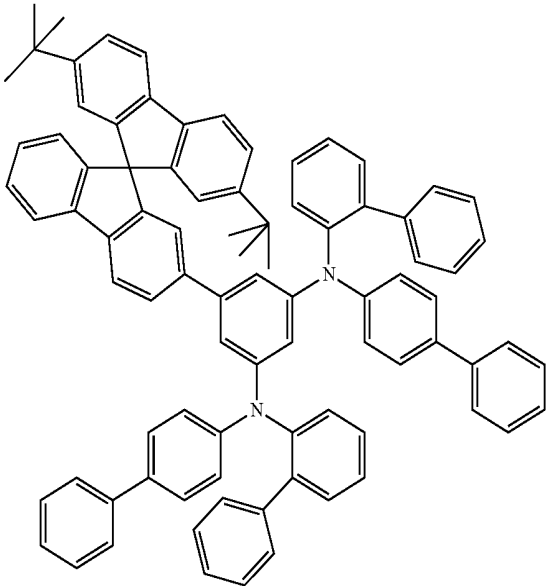
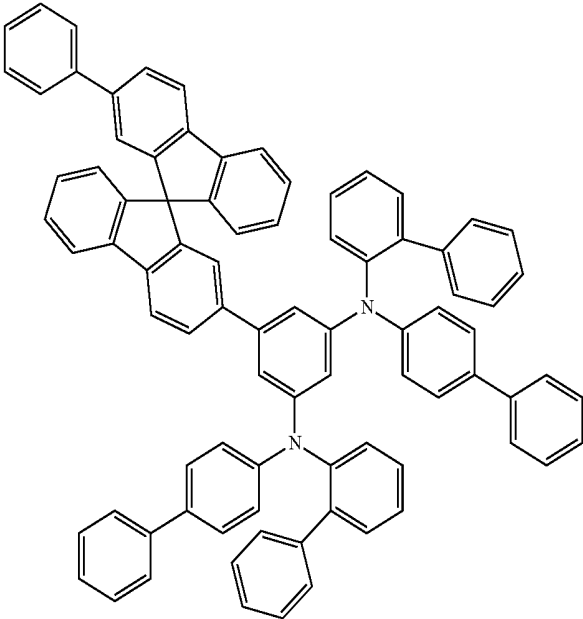
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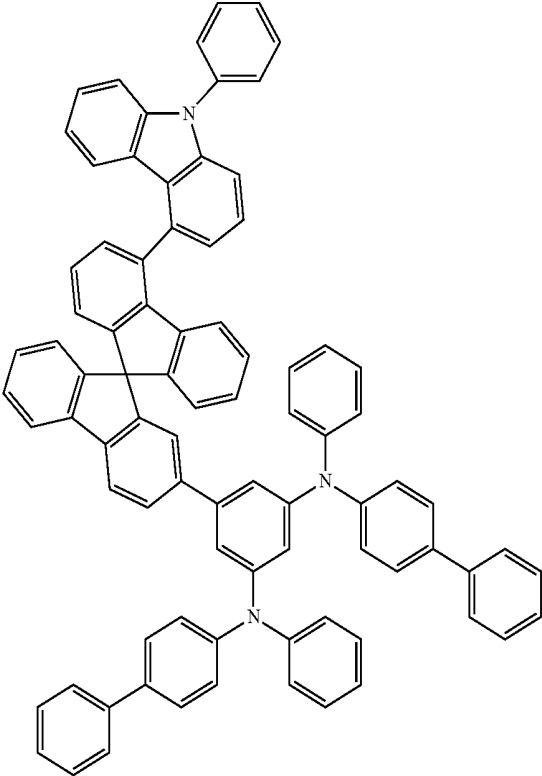
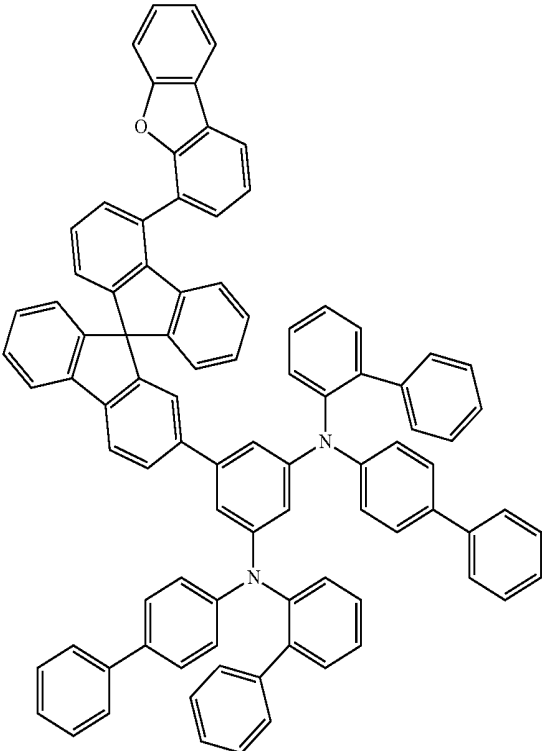


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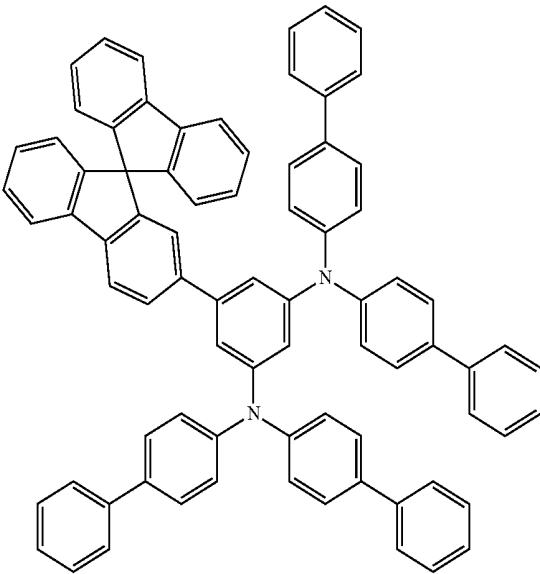
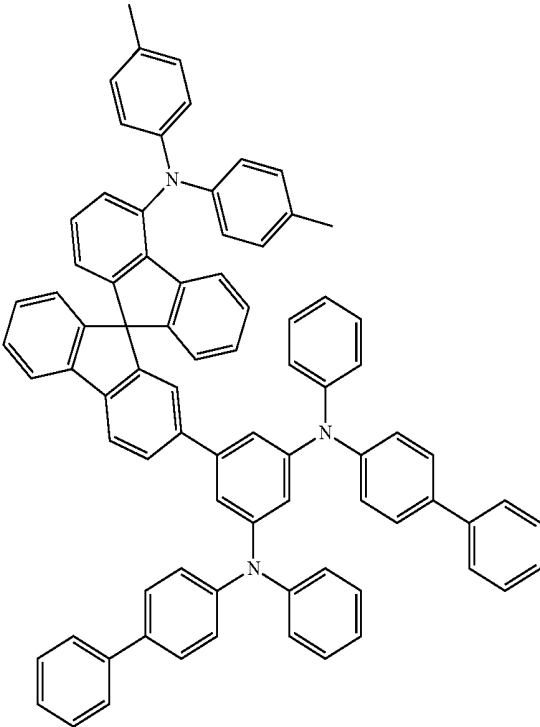


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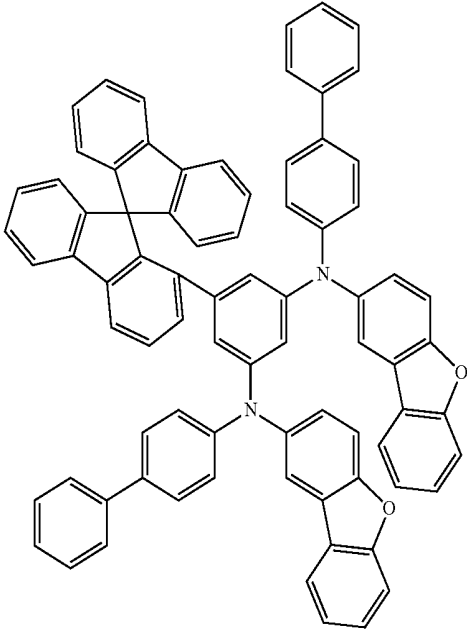
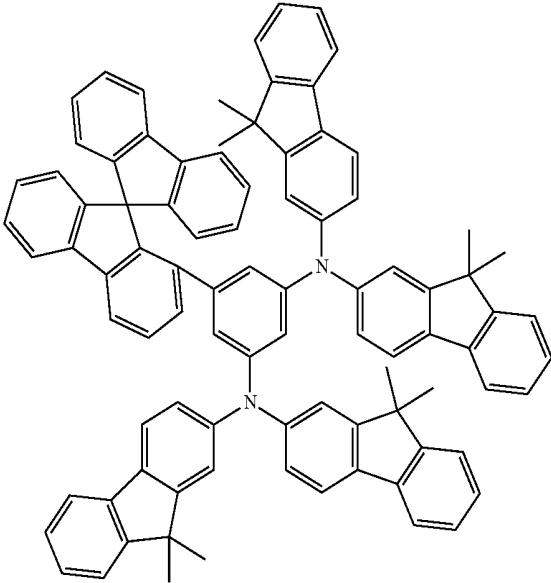
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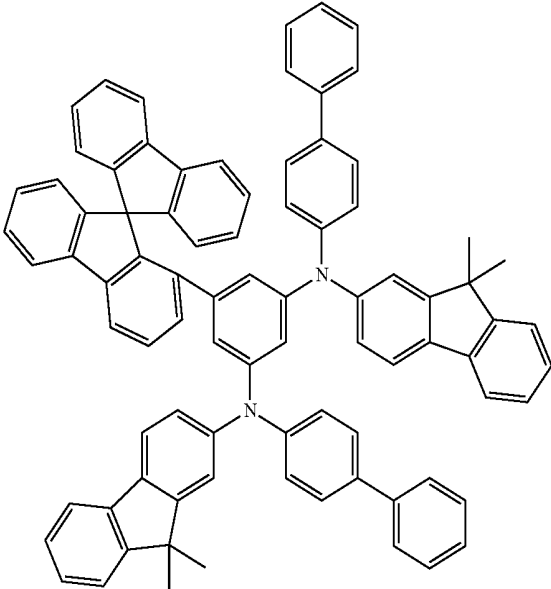
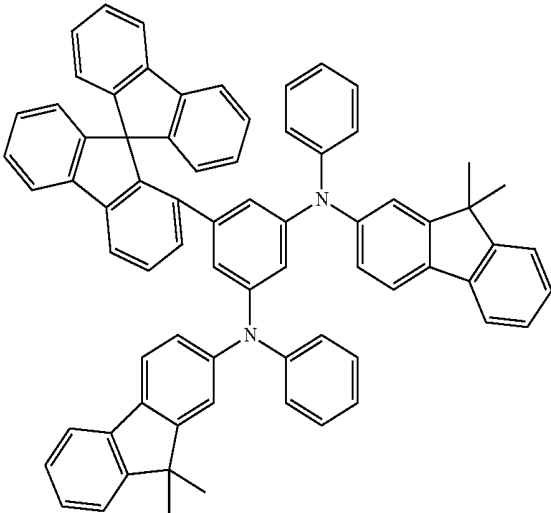
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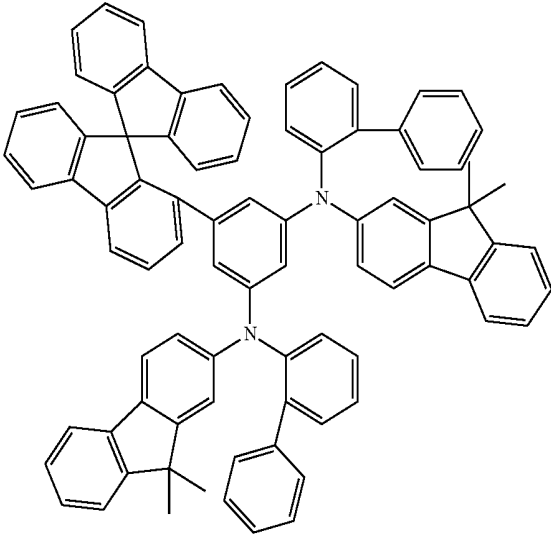
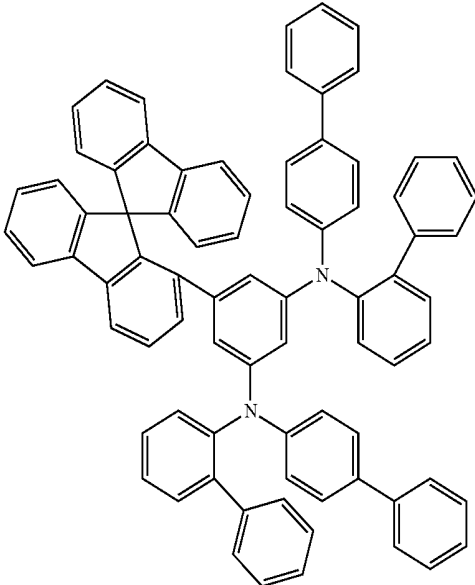
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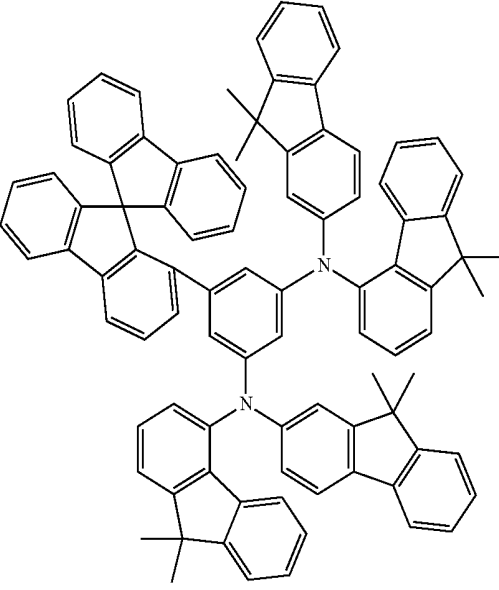
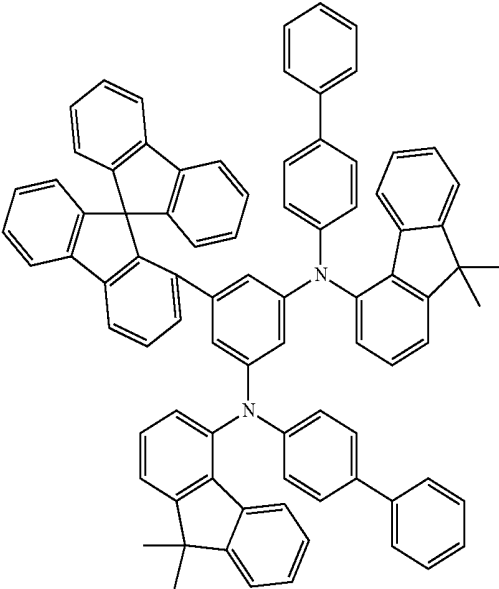
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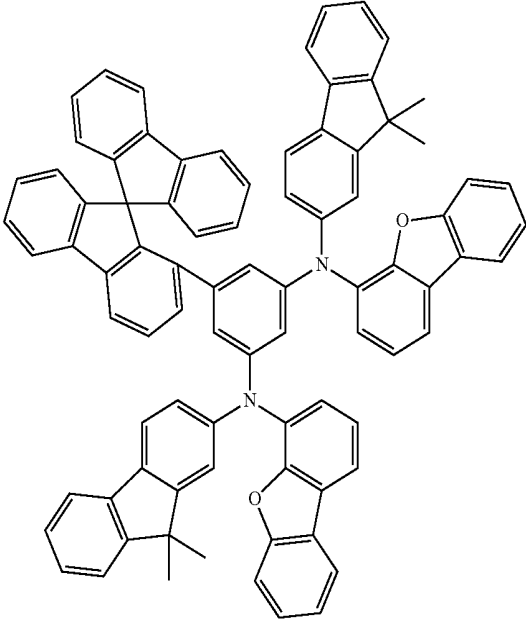
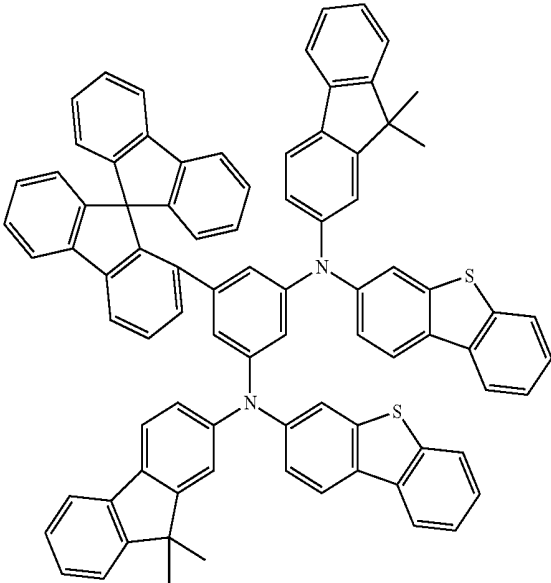
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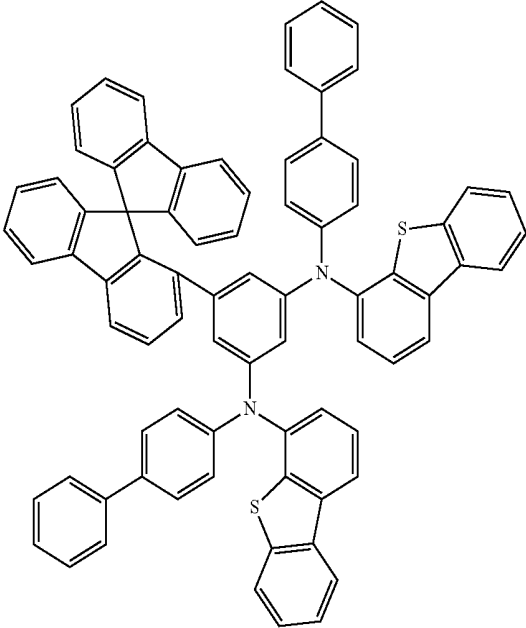
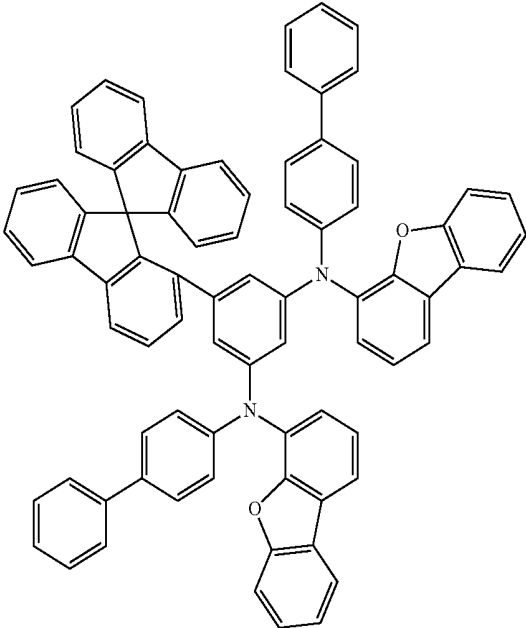
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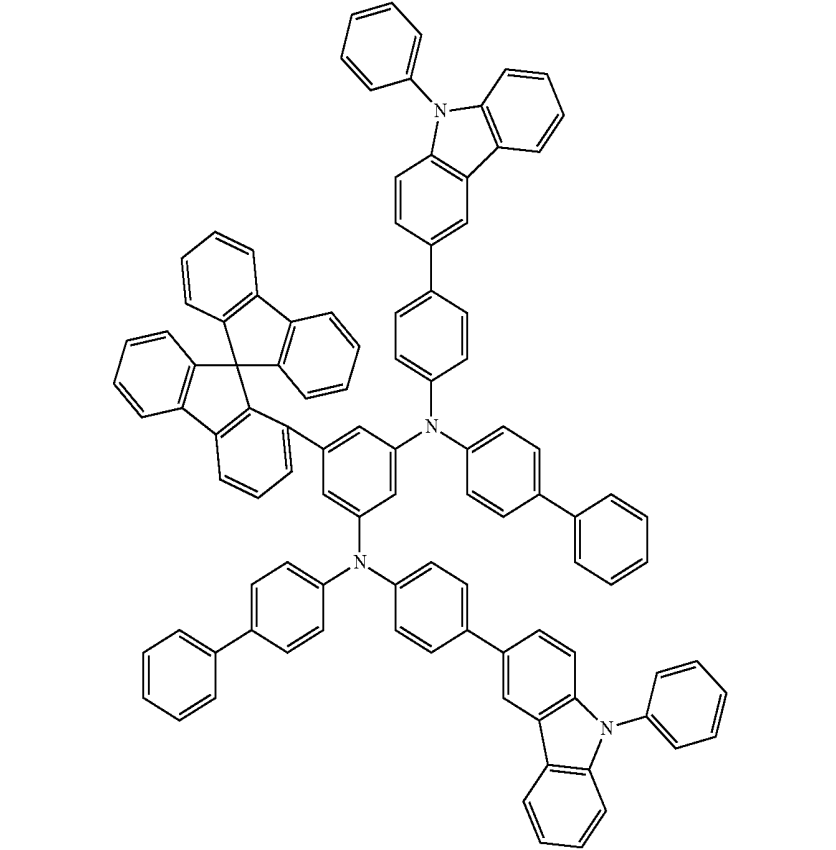
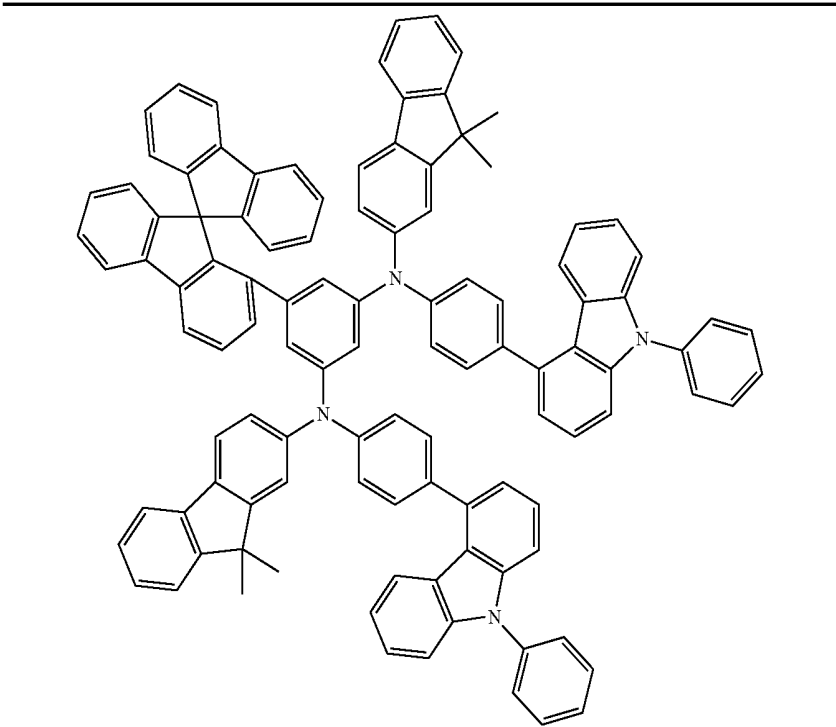


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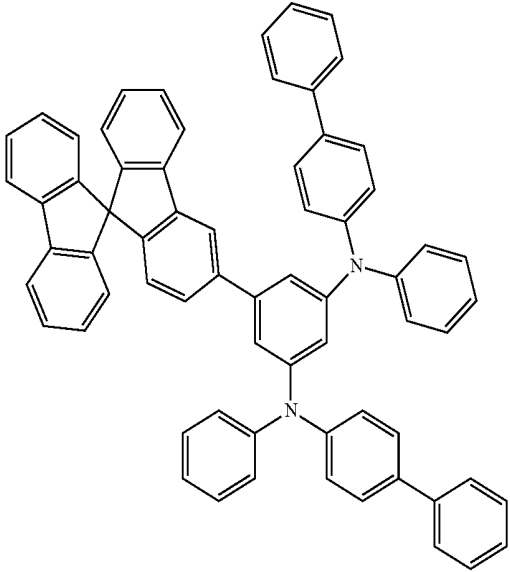
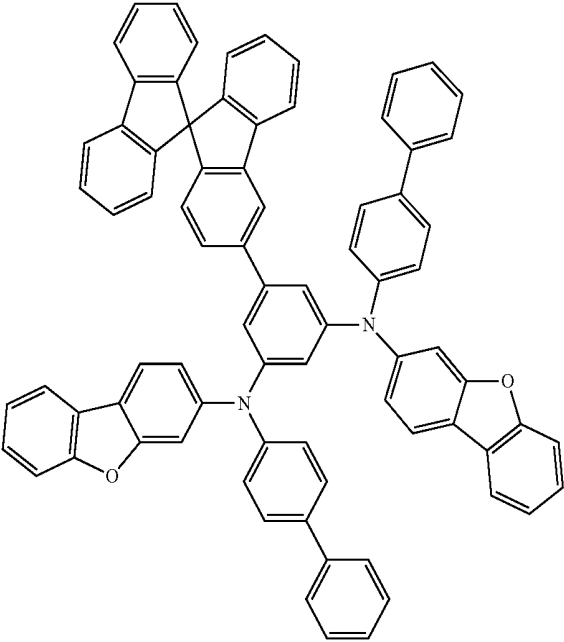


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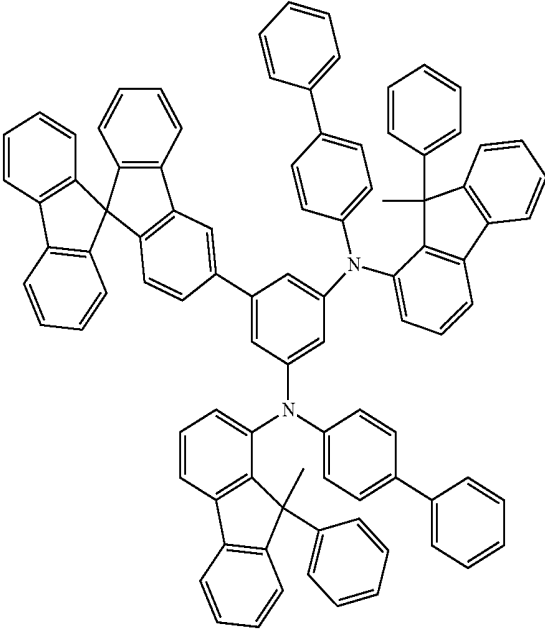
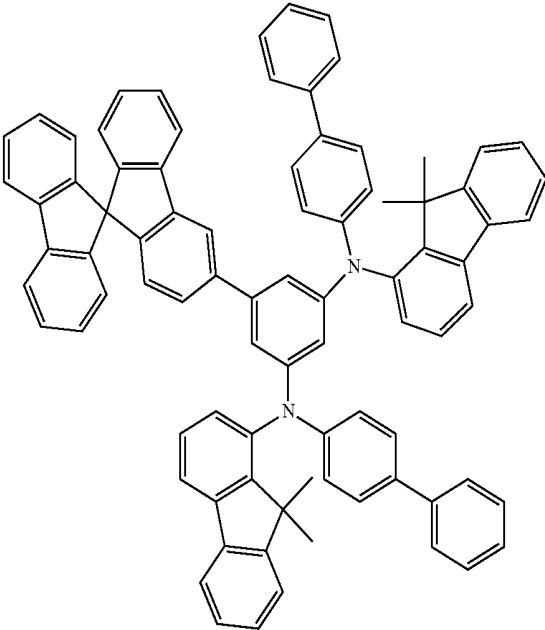
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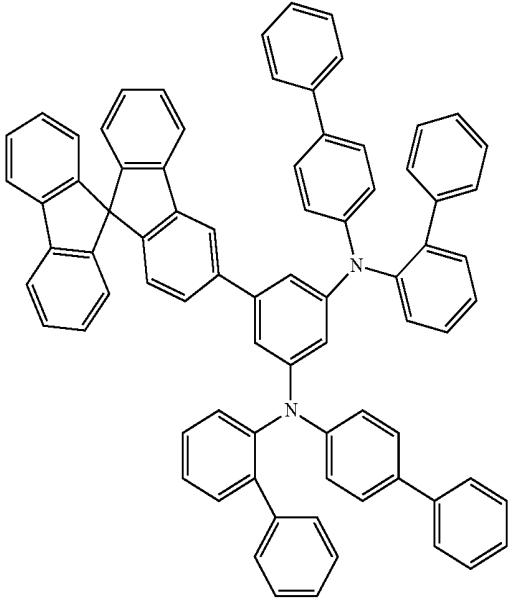
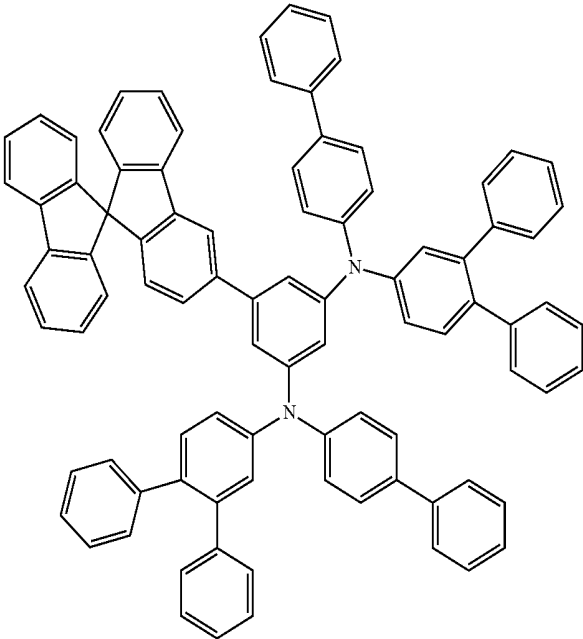
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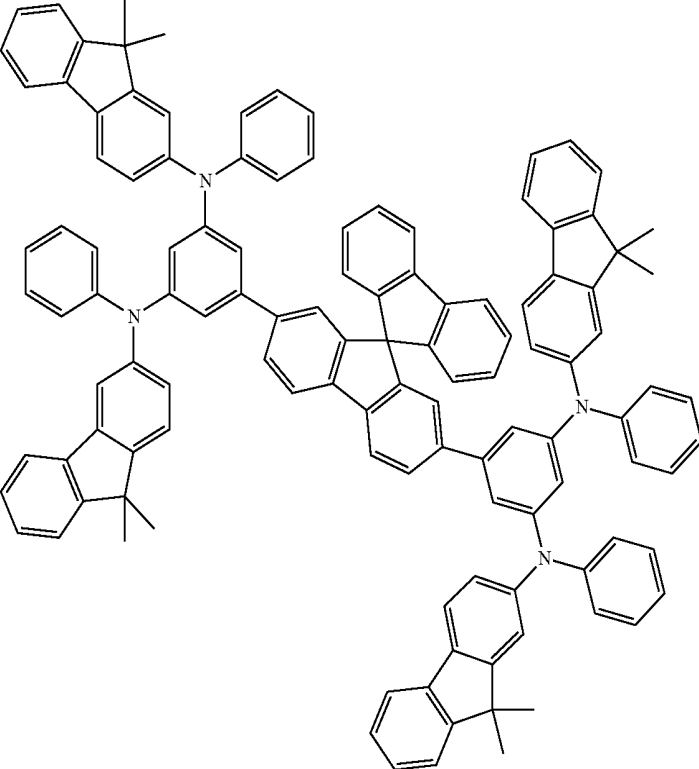
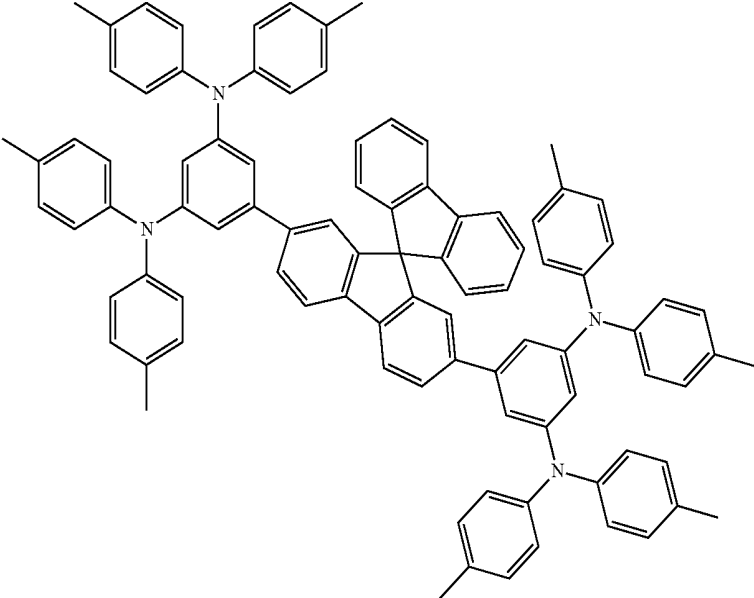
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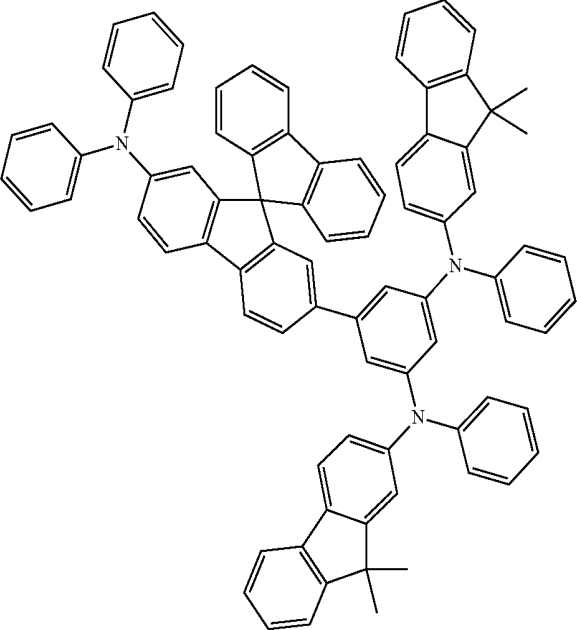
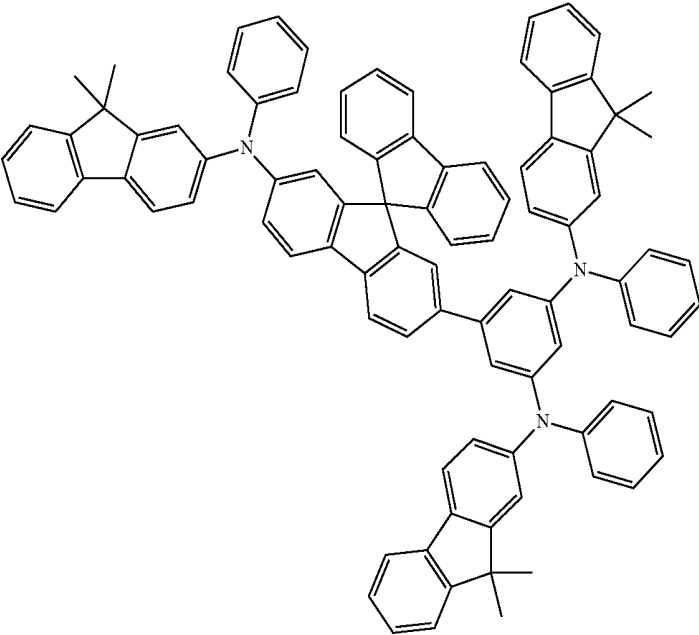
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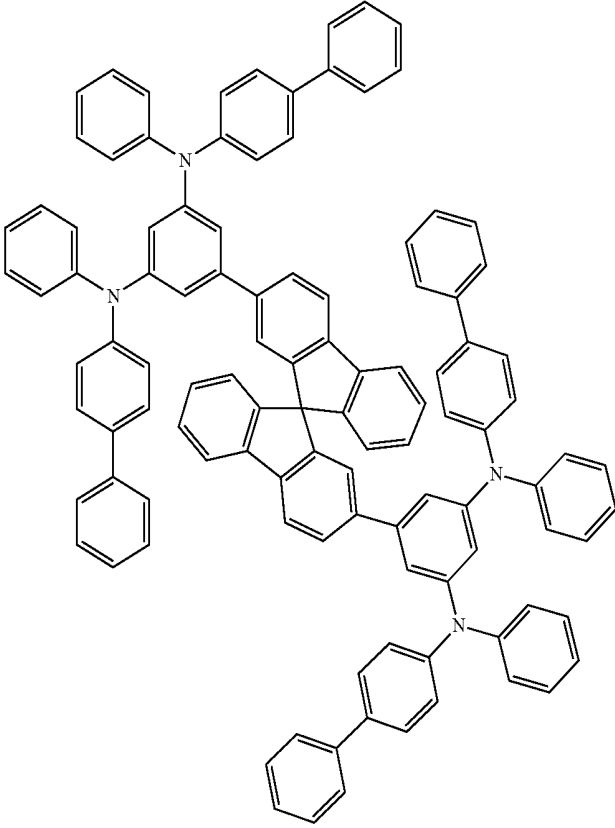
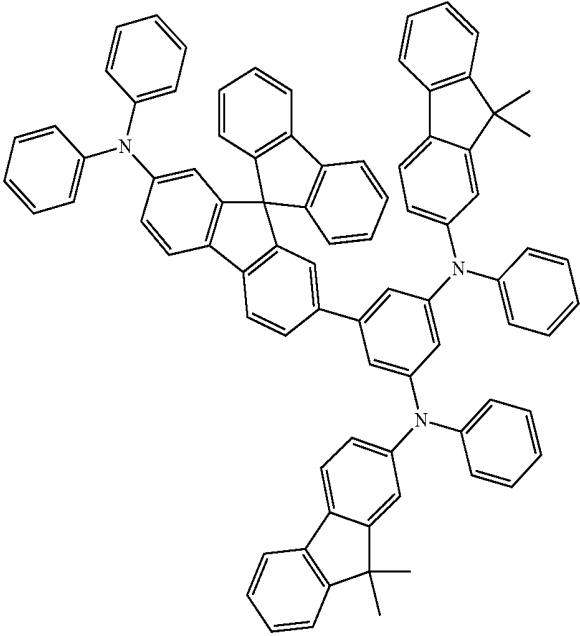


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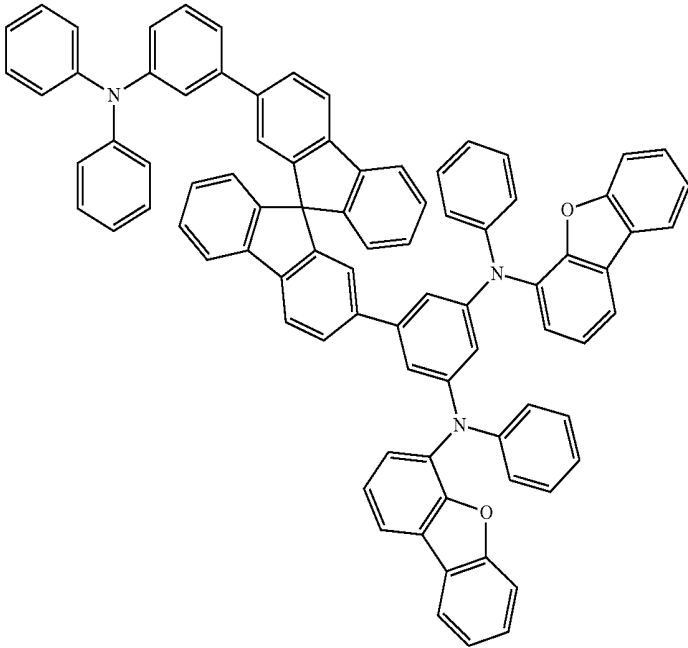
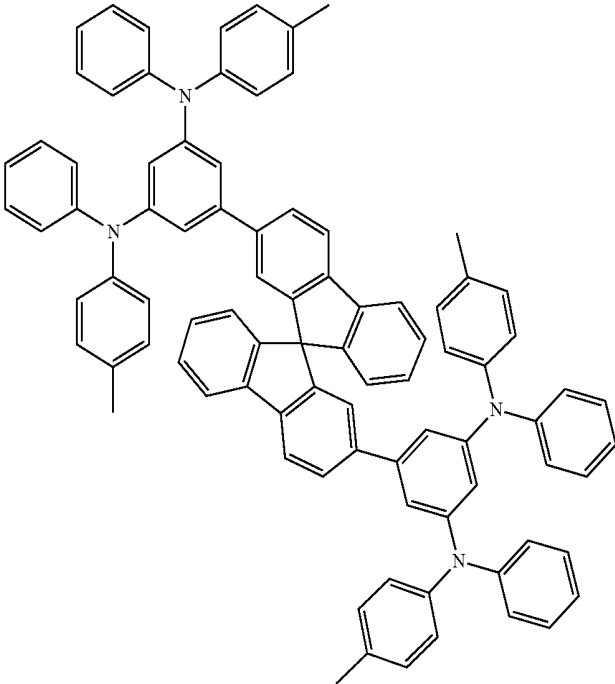


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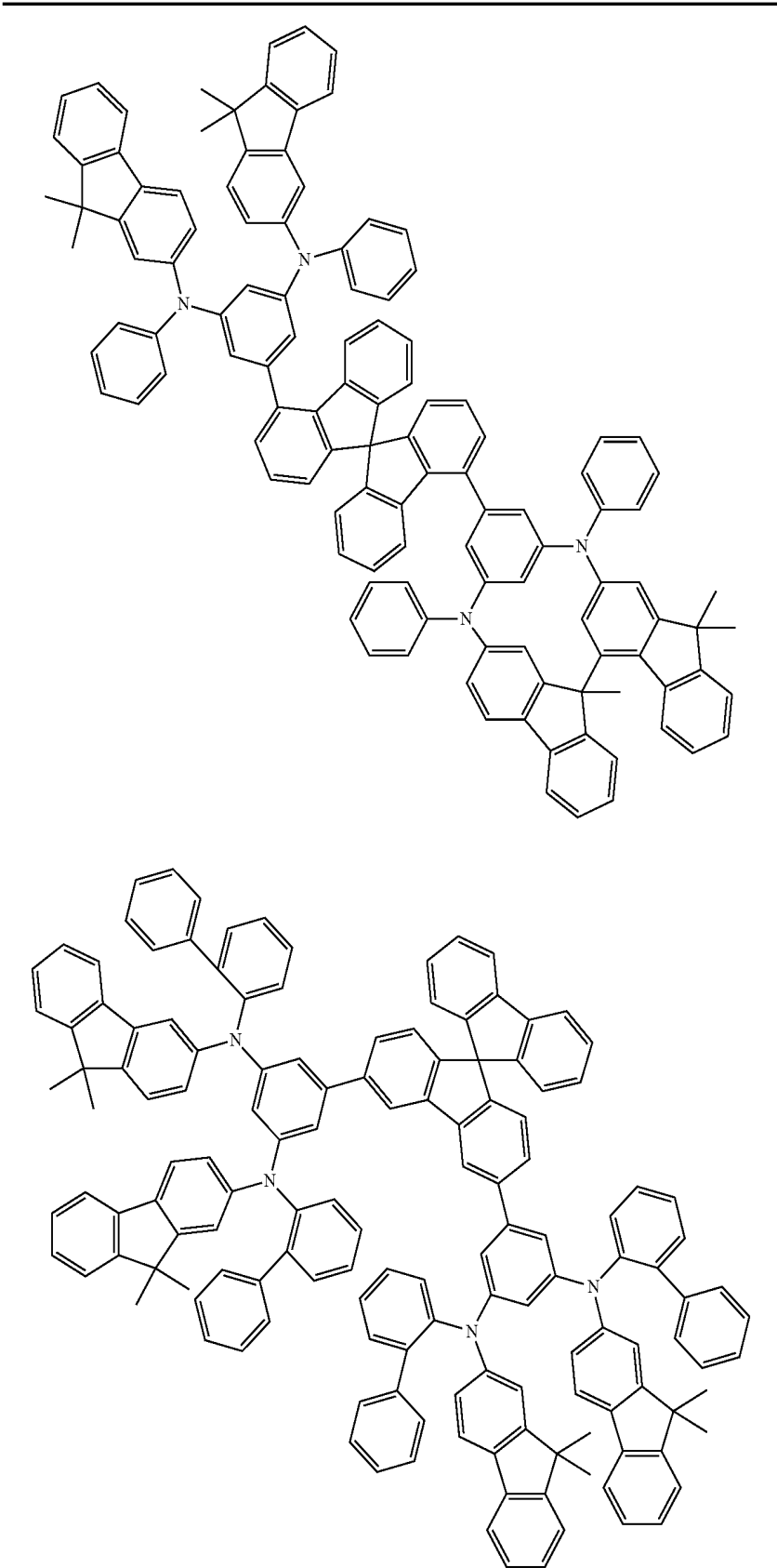


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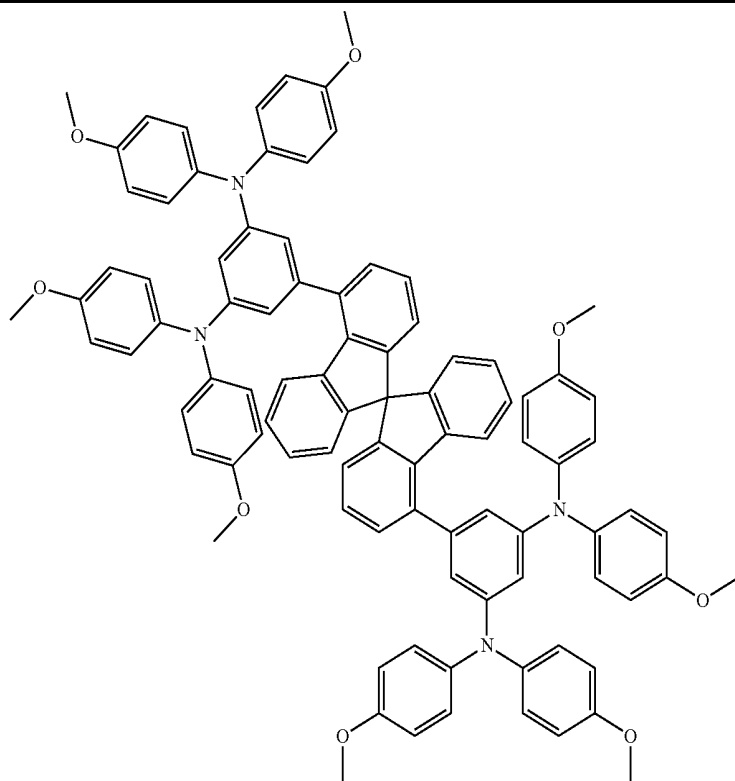
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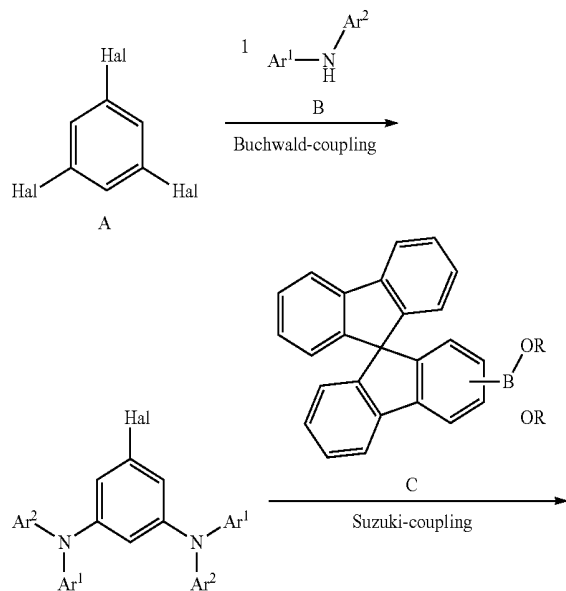


**[0083]** The compounds according to the invention can be prepared by synthetic steps known to the person skilled in the art, such as, for example, halogenation, Hartwig-Buchwald coupling and Suzuki coupling.

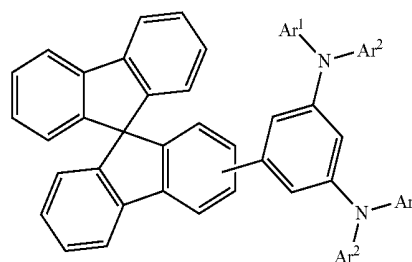
**[0084]** The synthesis of a diaminobenzene-spirobifluorene is shown in scheme 1, where two access routes to the diaminobenzene-spirobifluorene are shown.

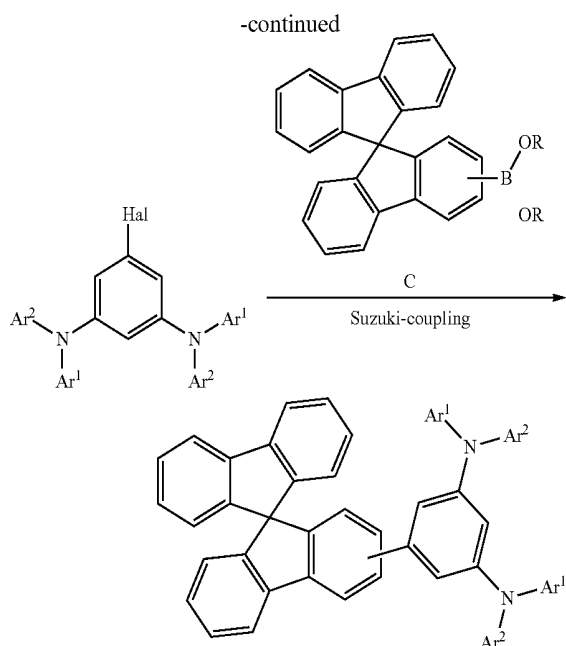
Scheme 1:

a) First route



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**[0085]** A halogenated diaminobenzene group is synthesized from a corresponding trihalogenated benzene group (compound A) by introduction of two diarylamino groups, as shown in scheme 1a. Alternatively, the diarylamino groups can be successively introduced using compound B<sub>1</sub> and B<sub>2</sub> in order to obtain a halogenated diaminobenzene compound with two different diarylamino-groups, as shown in Scheme 1b. Finally, the spirobifluorene group is introduced by a C—C Suzuki coupling reaction between a boronic ester derivative C and the halogenated diaminobenzene.

**[0086]** The compounds according to the invention described above, in particular compounds which are substituted by reactive leaving groups, such as bromine, iodine, triflate, 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.

**[0087]** 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 R<sup>1</sup> to R<sup>5</sup>. Depending on the 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.

**[0088]** 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 04/113468), 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 these units. The polymers, oligomers and dendrimers usually also contain further units, for example emitting (fluorescent or phosphorescent) units, such as, for example, vinyltriarylamines (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 triarylamines.

**[0089]** The polymers, oligomers and dendrimers according to the invention have advantageous properties, in particular long lifetimes, high efficiencies and good colour coordinates.

**[0090]** 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:

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

**[0091]** 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.

**[0092]** The present invention thus also relates to a process for the preparation of the polymers, oligomers and dendrimers according to the invention, which 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, such as, for example, in Frechet, Jean M. J.; Hawker, Craig J., "Hyperbranched 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 characterization of dendritic molecules", Materials Science and Technology (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.

**[0093]** The compounds according to the invention are suitable for use in an electronic device. An electronic device here is taken to mean a device which comprises at least one layer which comprises at least one organic compound. However, the component here may also comprise inorganic materials or also layers built up entirely from inorganic materials.

**[0094]** The present invention therefore furthermore relates to the use of the compounds according to the invention in an electronic device, in particular in an organic electroluminescent device.

**[0095]** The present invention still furthermore relates to an electronic device comprising at least one compound according to the invention. The preferences stated above likewise apply to the electronic devices.

**[0096]** 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 transistors (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 (D. M. Koller et al., *Nature Photonics* 2008, 1-4), but preferably organic electroluminescent devices (OLEDs), particularly preferably phosphorescent OLEDs.

**[0097]** 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.

**[0098]** 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 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.

**[0099]** 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 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 red emission (for the basic structure see, for example, WO 2005/011013). 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.

**[0100]** 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 embodiments 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 in an emitting layer, in particular for phosphorescent emitters. The preferred embodiments indicated above also apply to the use of the materials in organic electronic devices.

**[0101]** 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 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.

**[0102]** 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.

**[0103]** The compound of the formula (1) or the preferred embodiments is particularly preferably employed in a hole-transport or exciton-blocking layer.

**[0104]** 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.

**[0105]** If the compound according to formula (1) is employed as a hole transporting material in a hole transporting layer, a hole injection layer, an exciton blocking layer or an electron blocking layer, the compound may be used as a pure material, i.e. in a proportion of 100% in the layer, or it may be used in combination with one or more other materials. According to a preferred embodiment, in this case, the one or other compound which is used in combination with the compound according to formula (1) is a p-dopant. Preferred p-dopants to be used are electron

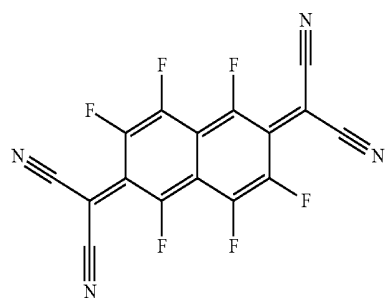
acceptor compounds, preferably such electron acceptor compounds which can oxidize one or more of the other compounds of the mixture.

**[0106]** The p-dopant is preferably present in a concentration of 0.1 to 20 Vol-%, preferably 0.5 to 12 Vol-%, more preferably 1 to 8 Vol-% and most preferably 2 to 6 Vol-% in the layer comprising the compound according to the invention.

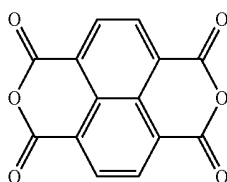
**[0107]** Particularly preferred p-dopants to be used in combination with the compounds according to the invention are the compounds disclosed in one or more of the following documents: WO 2011/073149, EP 1968131, EP 2276085, EP 2213662, EP 1722602, EP 2045848, DE 102007031220, U.S. Pat. No. 8,044,390, U.S. Pat. No. 8,057,712, WO 2009/003455, WO 2010/094378, WO 2011/120709, US 2010/0096600 and WO 2012/095143.

**[0108]** Highly preferred p-dopants to be used in the devices according to the invention are quinodimethanes, azaindenofluorendiones, azaphenalenenes, azatriphenylenes, I<sub>2</sub>, metal halogenides, preferably transition metal halogenides, metal oxides, preferably transition metal oxides or metal oxides comprising at least one metal of the third main group, and transition metal complexes, preferably complexes of Cu, Co, Ni, Pd or Pt with ligands having at least one binding oxygen atom. Preferred are furthermore transition metal oxides such as rhenium oxides, molybdenum oxides and tungsten oxides, more preferably Re<sub>2</sub>O<sub>7</sub>, MoO<sub>3</sub>, WO<sub>3</sub> and ReO<sub>3</sub>.

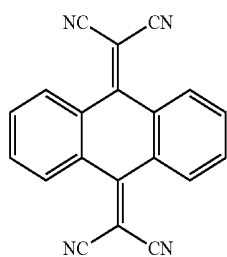
**[0109]** Preferred p-dopants are furthermore the following compounds:



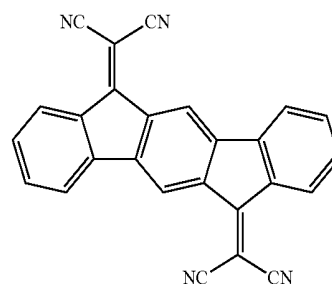
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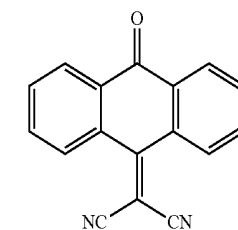
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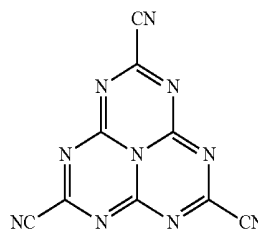
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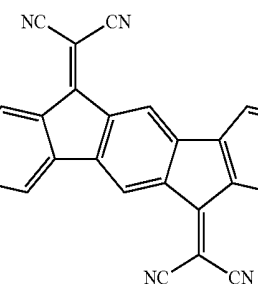
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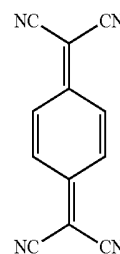
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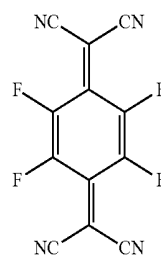
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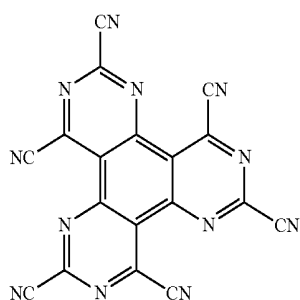


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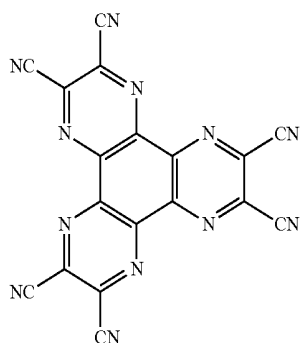


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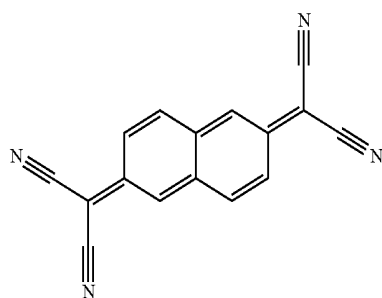
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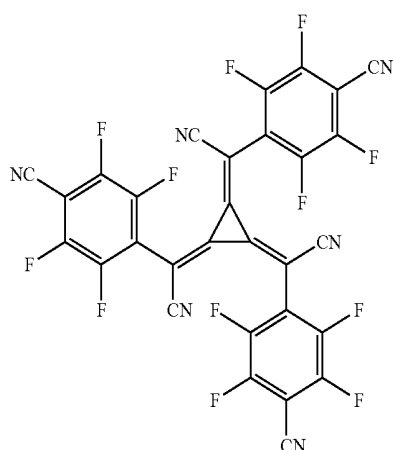
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(D-13)

**[0110]** In a further preferred embodiment of the invention, the compound of the formula (1) or the preferred embodiment is employed as matrix material for a fluorescent or phosphorescent compound, in particular for a phosphorescent compound, in an emitting layer. The organic electroluminescent 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.

**[0111]** If the compound of the formula (1) or the preferred embodiment 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 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.

**[0112]** The mixture comprising the compound of the formula (1) or the preferred embodiment and the emitting compound comprises between 99.9 and 1% by weight, preferably between 99 and 10% by weight, particularly preferably between 97 and 60% by weight, in particular between 95 and 80% by weight, of the compound of the formula (1) or the preferred embodiment, based on the entire mixture comprising emitter and matrix material. Correspondingly, the mixture comprises between 0.1 and 99% by 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 same numerical values apply, with the percentage in this case being indicated in % by vol. in each case.

**[0113]** A particularly preferred embodiment of the present invention is the use of the compound of the formula (1) or the preferred embodiment as matrix material for a phosphorescent emitter in combination with a further matrix material. Particularly suitable matrix materials which can be employed in combination with the compounds of the formula (1) or the preferred embodiment are aromatic ketones, aromatic phosphine oxides or aromatic sulfoxides or sulfones, for example in accordance with WO 2004/013080, WO 2004/093207, WO 2006/005627 or WO 2010/006680, triaryl amines, carbazole derivatives, for example CBP (N,N-bis(carbazolyl)biphenyl), 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.

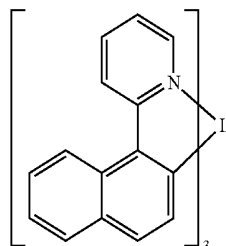
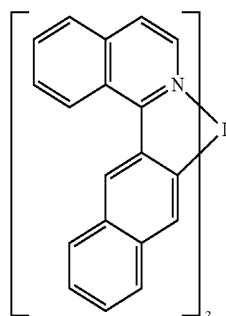
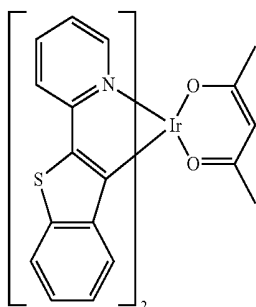
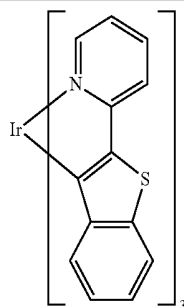
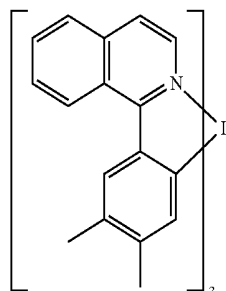
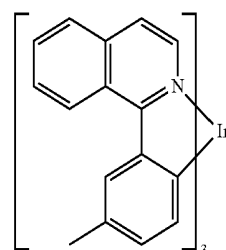
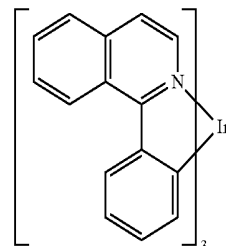
[0114] It is likewise possible to use two or more phosphorescent emitters in the mixture. In this case, the emitter which emits at shorter wavelength acts as co-host in the mixture.

[0115] 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.

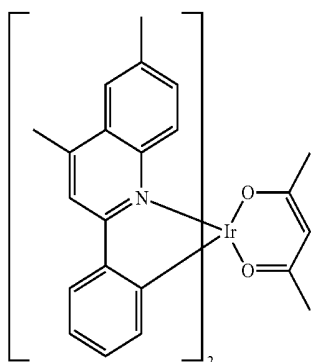
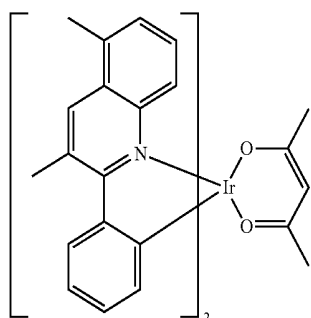
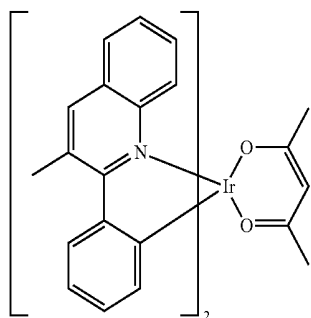
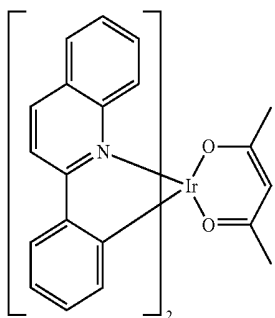
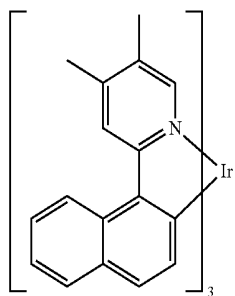
[0116] Examples of the emitters described above are revealed by the applications WO 2000/70655, WO 2001/41512, WO 2002/02714, WO 2002/15645, EP 1191613, EP 1191612, EP 1191614, WO 2005/033244, WO 2005/019373, US 2005/0258742, WO 2009/146770, WO 2010/015307, WO 2010/031485, WO 2010/054731, WO 2010/054728, 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.

[0117] Examples of triplet emitters to be used in the devices according to the present application are shown in the following table.

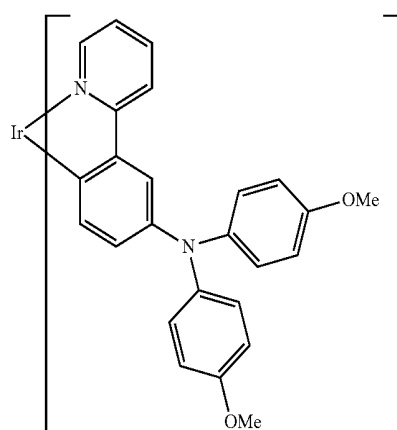
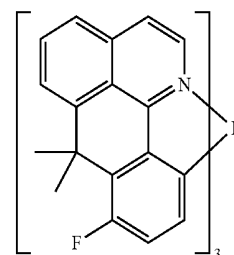
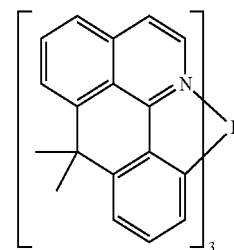
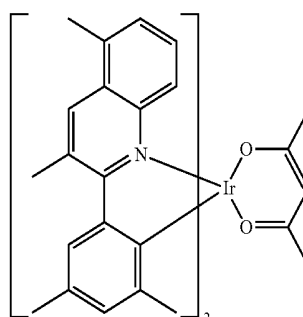
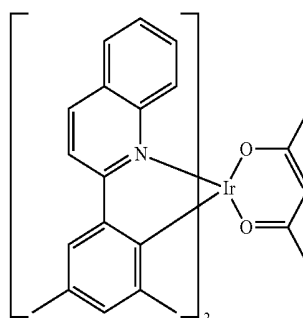
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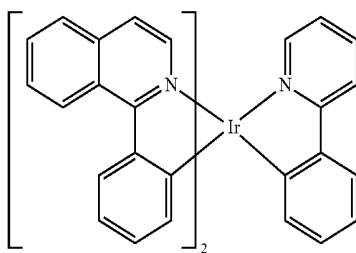
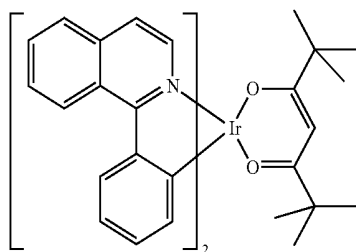
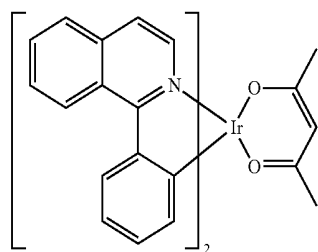
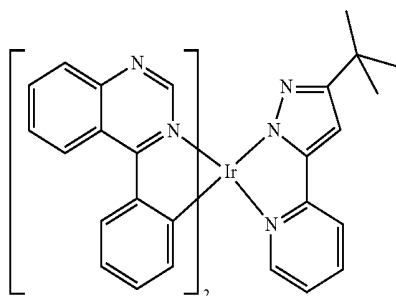
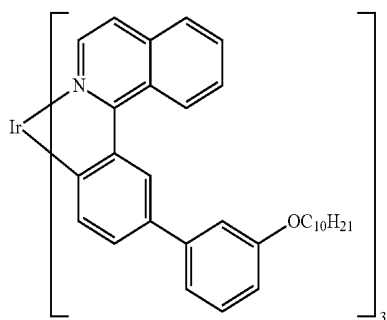
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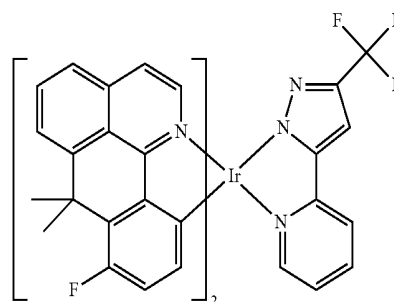
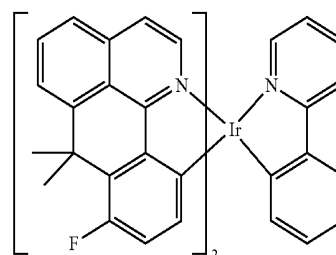
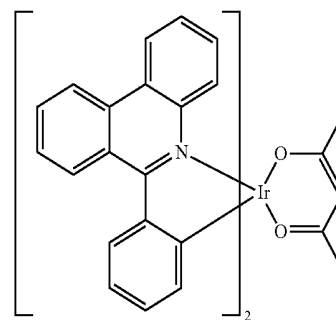
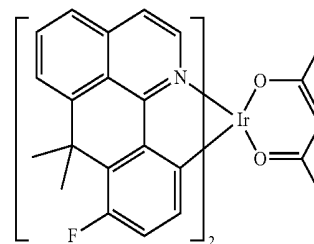
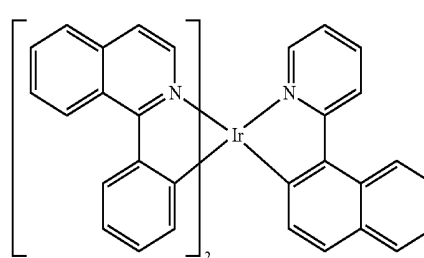
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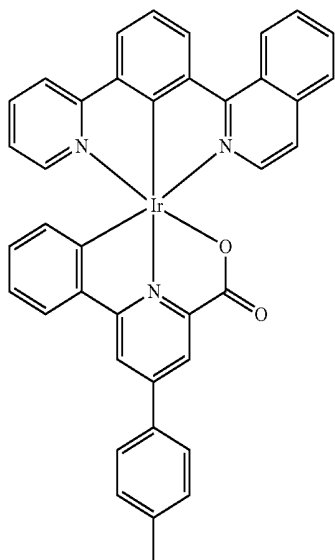
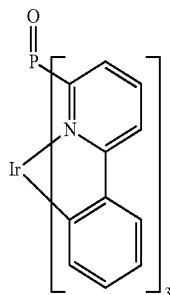
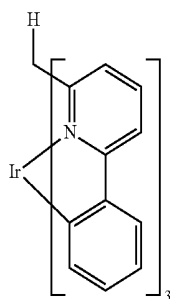
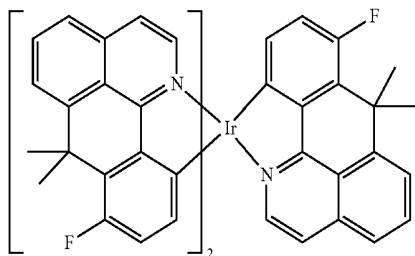
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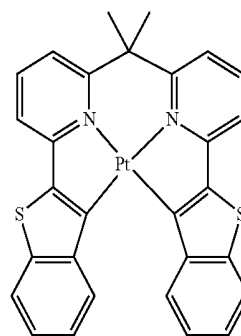
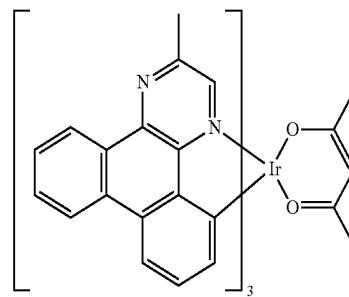
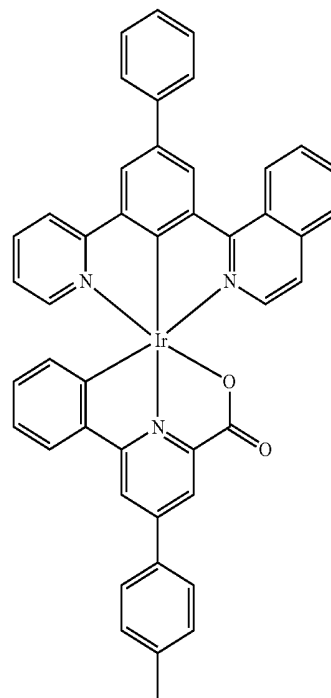
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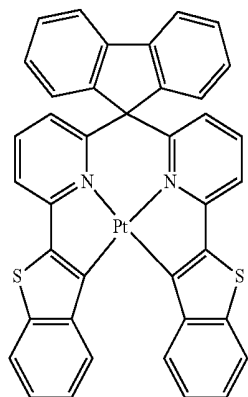
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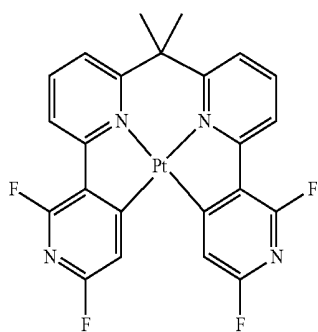
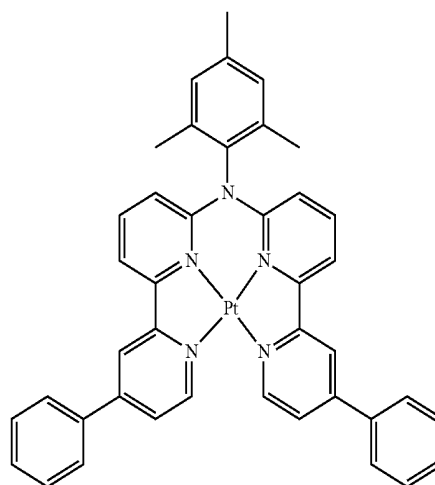
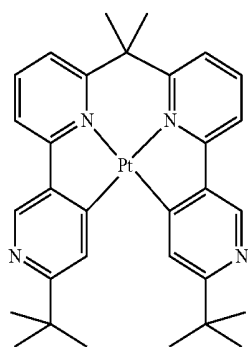
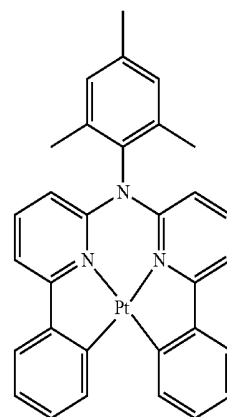
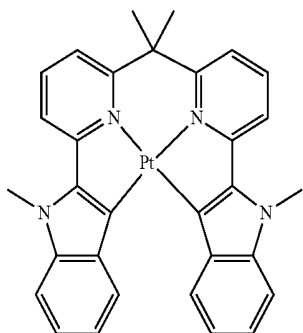
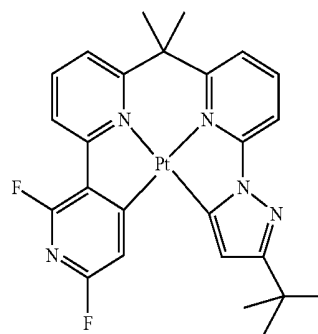
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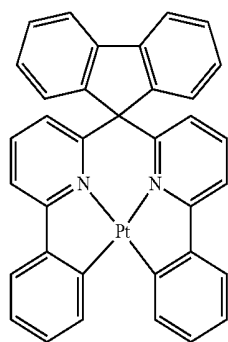
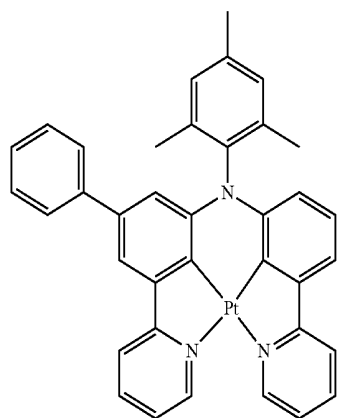
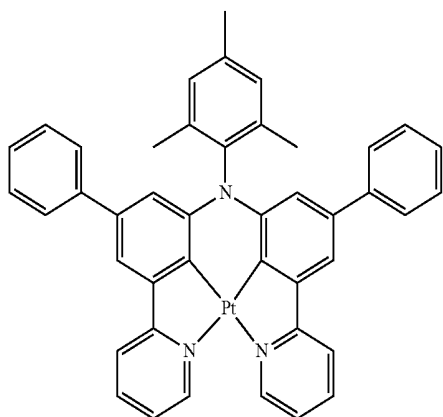
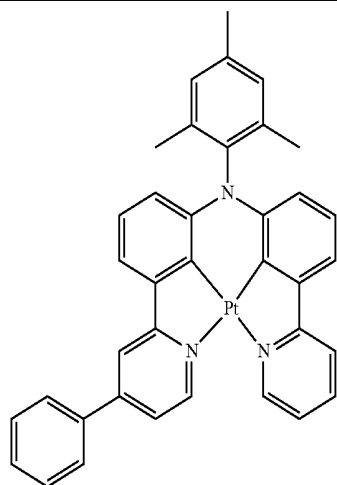
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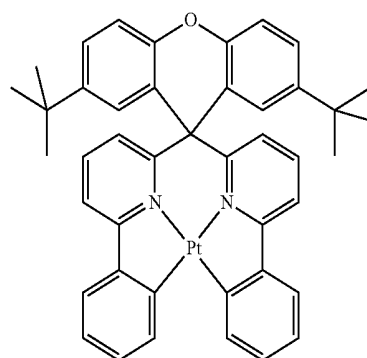
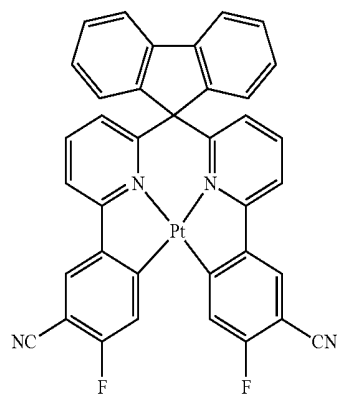
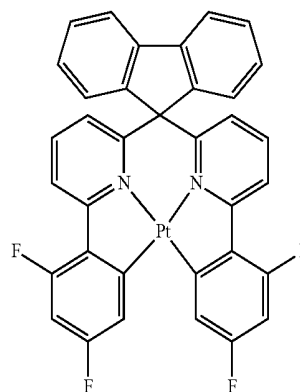
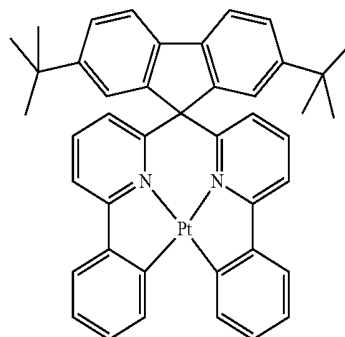
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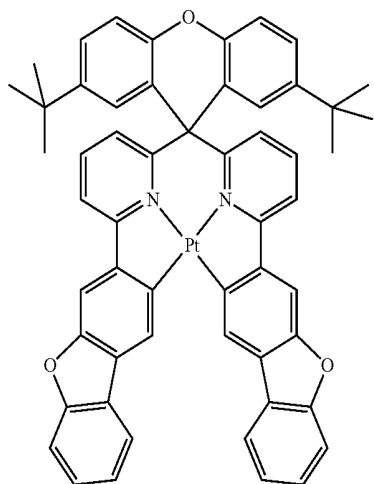
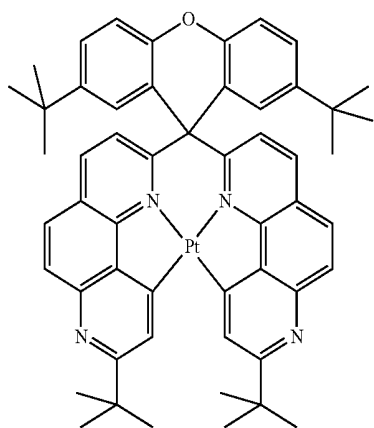
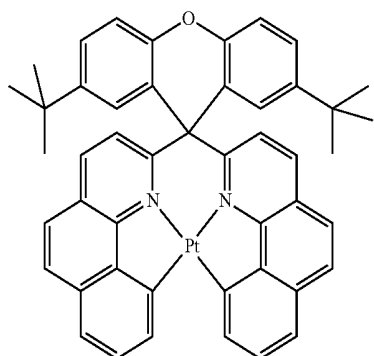
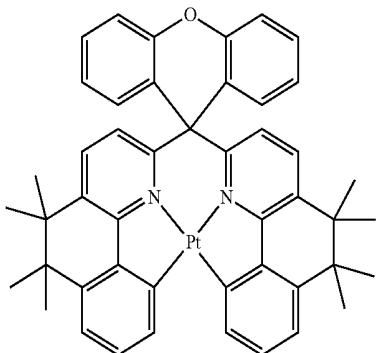
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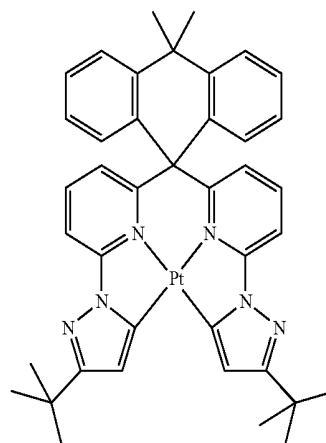
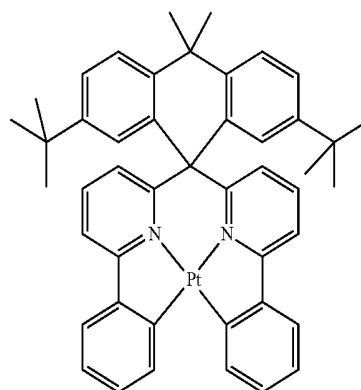
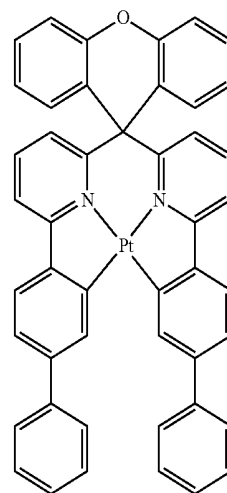
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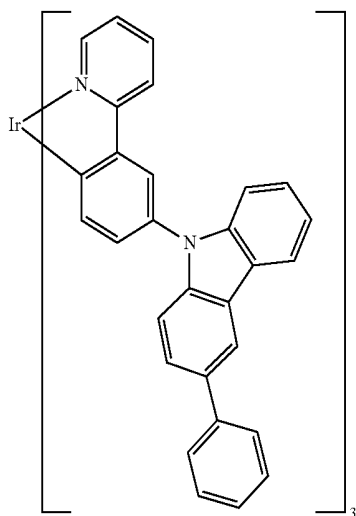
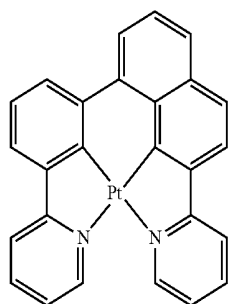
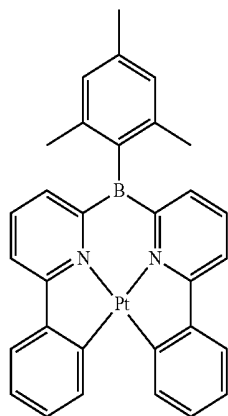
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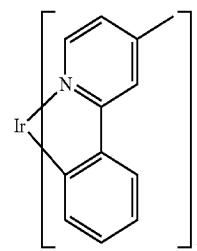
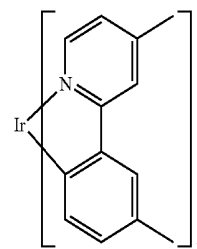
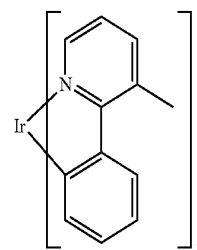
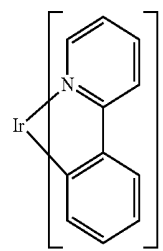
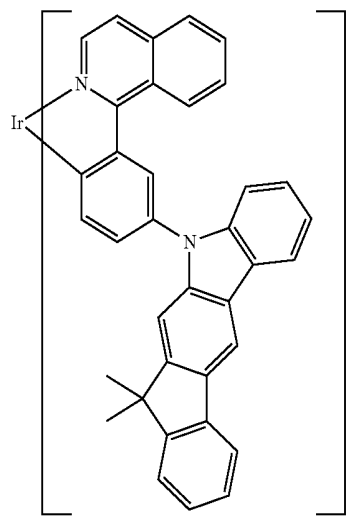
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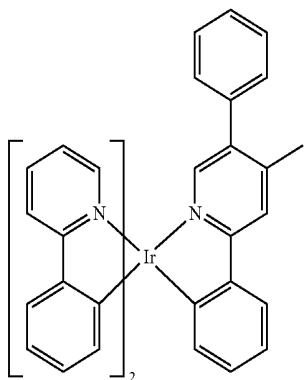
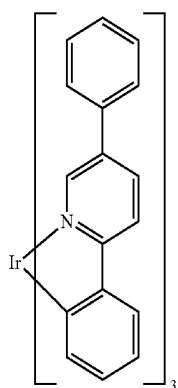
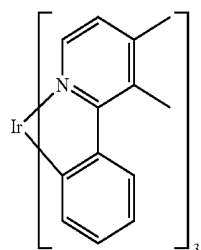
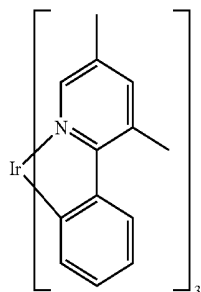
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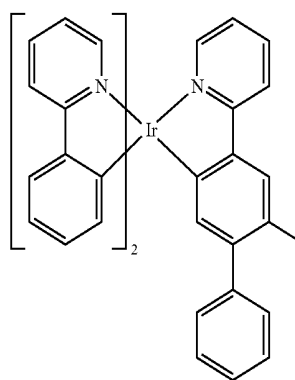
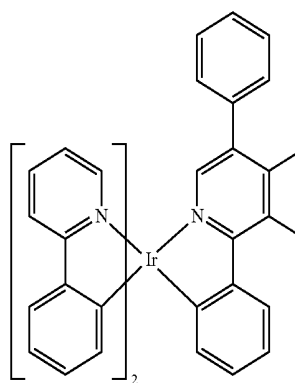
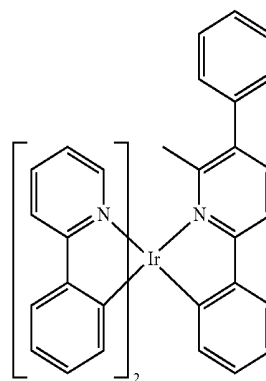
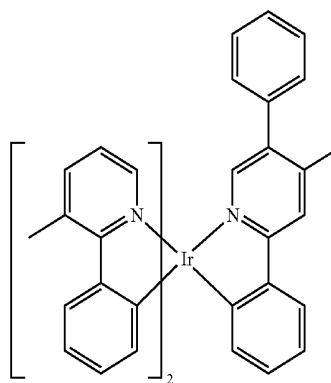
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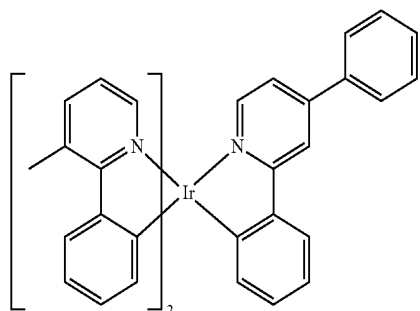
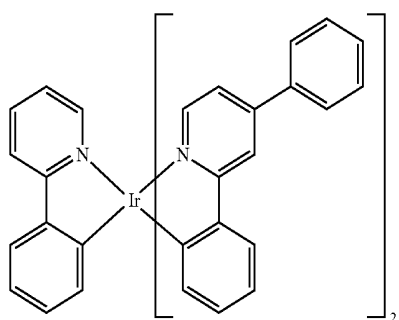
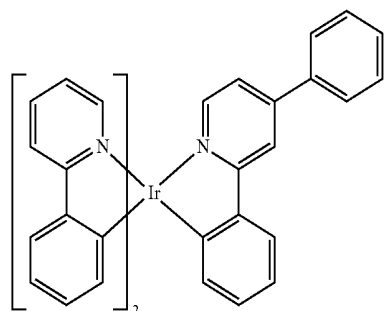
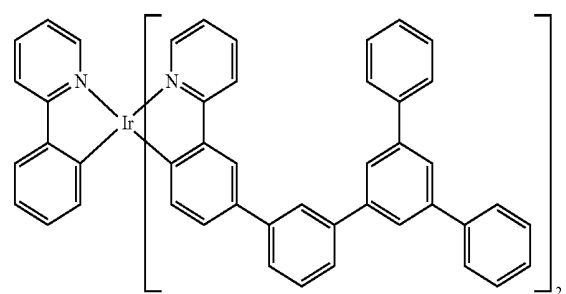
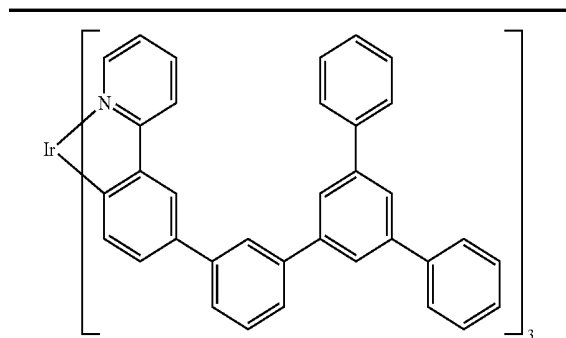
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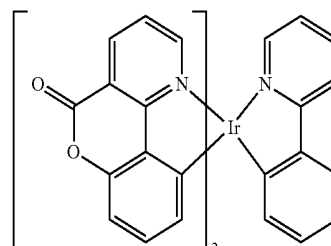
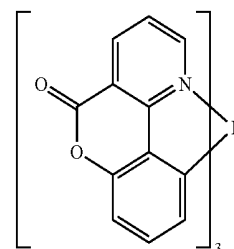
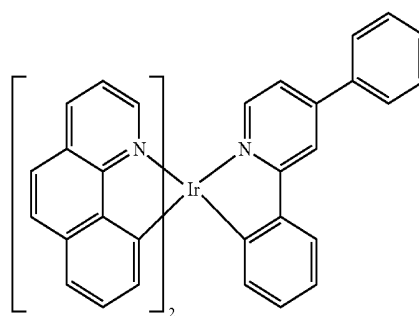
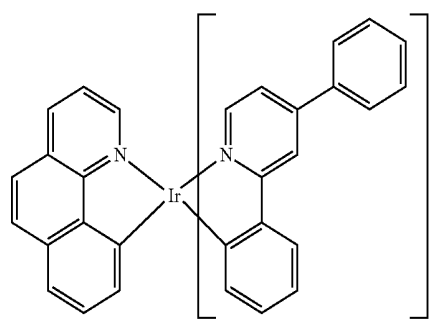
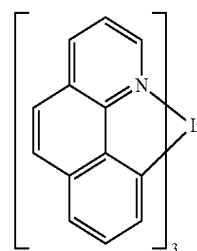
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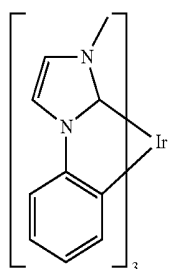
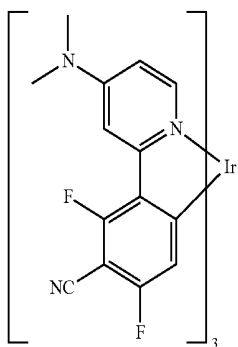
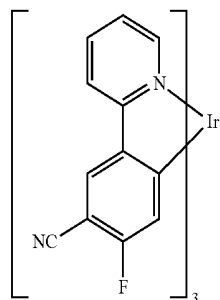
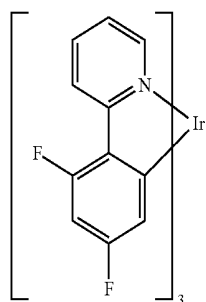
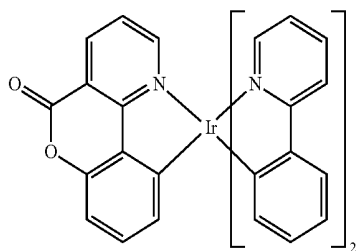
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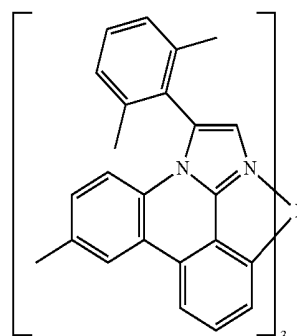
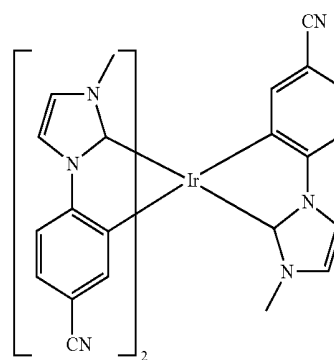
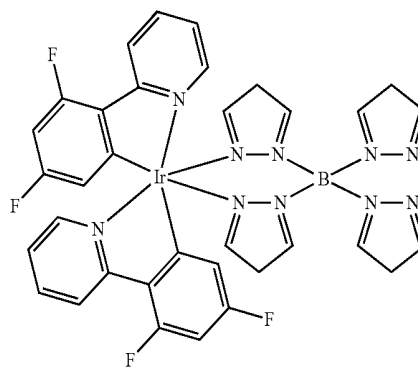
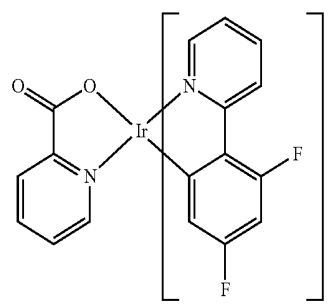
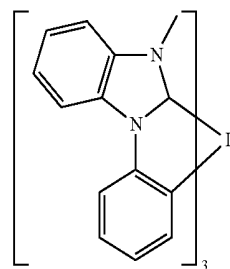
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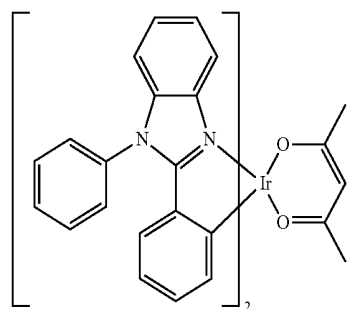
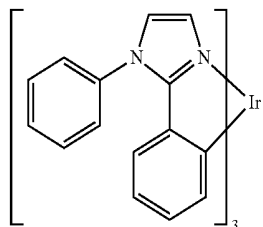
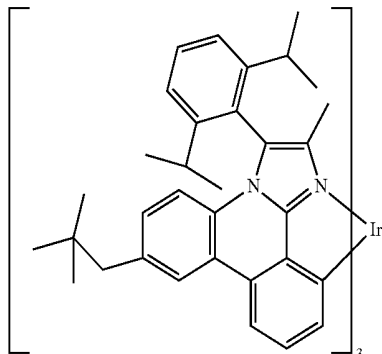
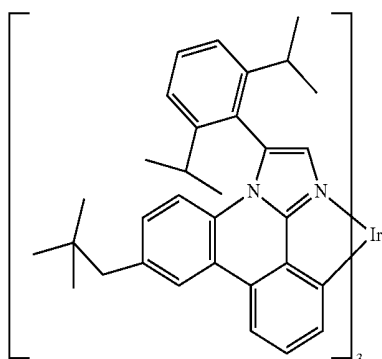
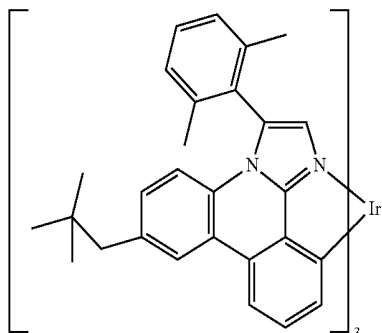
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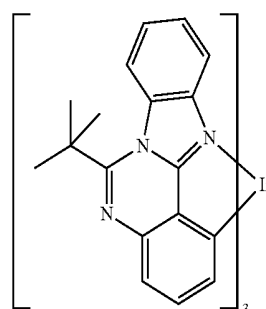
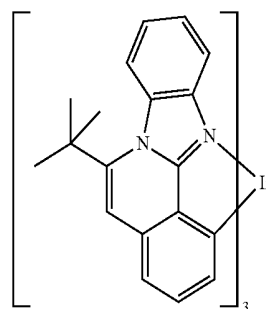
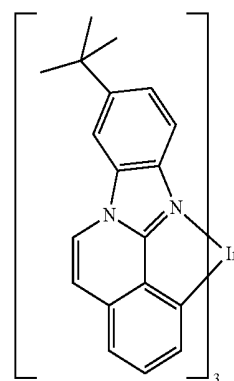
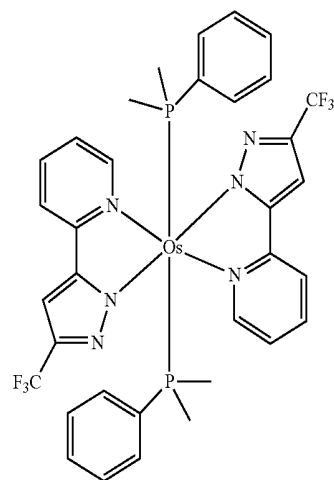
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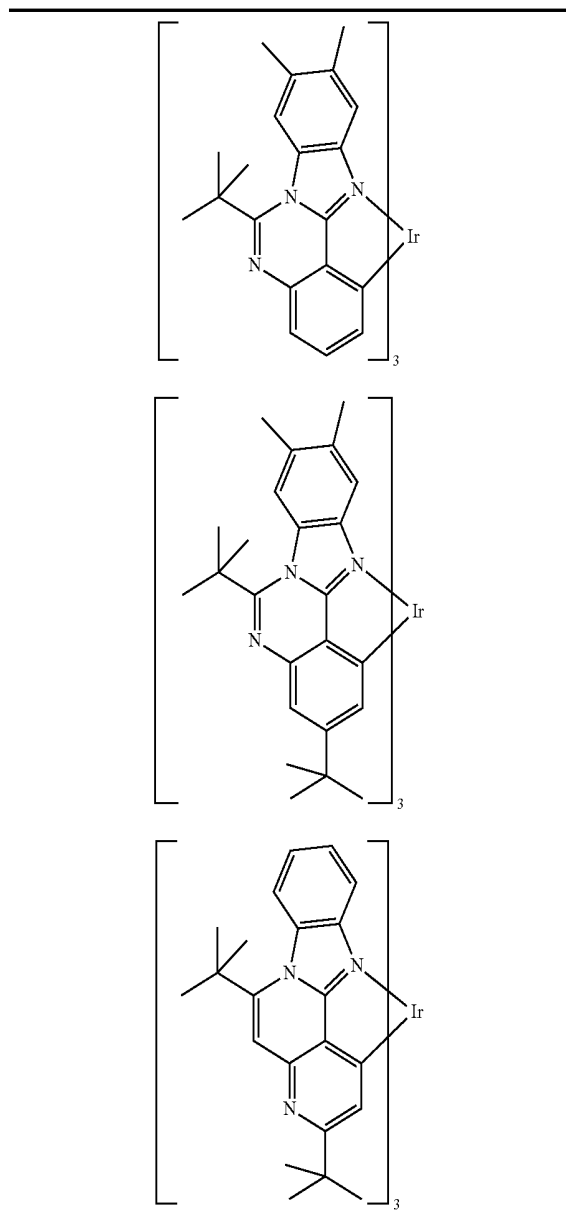
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[0118] In a further embodiment of the invention, the organic electroluminescent device according to the invention does not comprise a separate hole-injection layer and/or hole-transport layer and/or hole-blocking layer and/or electron-transport layer, 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 directly adjacent to the emitting layer, as described, for example, in WO 2009/030981.

[0119] 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.

[0120] 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.

[0121] Preferred fluorescent emitter materials are selected from the class of the arylamines. An arylamine or aromatic amine in the sense of this invention is taken to mean a compound which contains three substituted or unsubstituted aromatic or heteroaromatic ring systems bonded directly to the nitrogen. At least one of these aromatic or heteroaromatic ring systems is preferably a condensed ring system, particularly preferably having at least 14 aromatic ring atoms. Preferred examples thereof are aromatic anthracenamines, aromatic anthracenediamines, aromatic pyrenamines, aromatic pyrenediamines, aromatic chrysenamines or aromatic chrysenediamines. An aromatic anthracenamine is taken to mean a compound in which one diarylamino group is bonded directly to an anthracene group, preferably in the 9-position. An aromatic anthracenediamine is taken to mean a compound in which two diarylamino groups are bonded directly to an anthracene group, preferably in the 9,10-position. Aromatic pyrenamines, pyrenediamines, chrysenamines and chrysenediamines are defined analogously thereto, where the diarylamino groups are preferably bonded to the pyrene in the 1-position or in the 1,6-position. Further preferred emitter materials are selected from indenofluorenamines or indenofluorenediamines, for example in accordance with WO 06/122630, benzoindenofluorenamines or benzoindenofluorenediamines, for example in accordance with WO 08/006449, and dibenzoindenofluorenamines or dibenzoindenofluorenediamines, for example in accordance with WO 07/140847. Examples of emitter materials from the class of the styrylamines are substituted or unsubstituted tristilbenamines or the emitter materials described in WO 06/000388, WO 06/058737, WO 06/000389, WO 07/065549 and WO 07/115610. Preference is furthermore given to the condensed hydrocarbons disclosed in the application WO 10/012328.

[0122] Matrix materials which can be used, preferably for fluorescent dopants, are materials from various classes of substance. Preferred matrix materials are selected from the classes of the oligoarylenes (for example 2,2',7,7'-tetraphenylspirobifluorene in accordance with EP 676461 or dinaphthylanthracene), in particular the oligoarylenes containing condensed aromatic groups, the oligoarylenevinylens (for example DPVBi or spiro-DPVBi in accordance with EP 676461), the polyodal metal complexes (for example in accordance with WO 04/081017), the hole-conducting compounds (for example in accordance with WO 04/058911), the electron-conducting compounds, in particular ketones, phosphine oxides, sulfoxides, etc. (for example in accordance with WO 05/084081 and WO 05/084082), the atropisomers (for example in accordance with WO 06/048268), the boronic acid derivatives (for example in accordance with WO 06/117052) or the benzanthracenes (for example in accordance with WO 08/145239). Suitable matrix materials are furthermore preferably the compounds according to the invention. Apart from the compounds according to the invention, particularly preferred matrix materials are selected from the classes of the oligoarylenes, comprising

naphthalene, anthracene, benzanthracene and/or pyrene or atropisomers of these compounds, the oligoarylenevinylenes, the ketones, the phosphine oxides and the sulfoxides. Very particularly preferred matrix materials are selected from the classes of the oligoarylenes, comprising anthracene, benzanthracene, benzophenanthrene and/or pyrene or atropisomers of these compounds. An oligoarylene in the sense of this invention is intended to be taken to mean a compound in which at least three aryl or arylene groups are bonded to one another.

[0123] Besides the compounds according to the invention, suitable charge-transport materials, as can be used in the hole-injection or hole-transport layer or in the electron-transport layer of the organic electroluminescent device according to the invention, are, for example, the compounds disclosed in Y. Shirota et al., *Chem. Rev.* 2007, 107(4), 953-1010, or other materials as are employed in these layers in accordance with the prior art.

[0124] 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.

[0125] 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 through a nozzle and thus structured (for example M. S. Arnold et al., *Appl. Phys. Lett.* 2008, 92, 053301).

[0126] 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, offset 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.

[0127] 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.

[0128] 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.

[0129] For the processing of the compounds according to the invention from the liquid phase, for example by spin coating or by printing processes, formulations of the compounds according to the invention are necessary. These

formulations can be, for example, solutions, dispersions or emulsions. It may be preferred to use mixtures of two or more solvents for this purpose. Suitable and preferred solvents are, for example, toluene, anisole, o-, m- or p-xylene, methyl benzoate, mesitylene, tetralin, veratrol, THF, methyl-THF, THP, chlorobenzene, dioxane, phenoxytoluene, in particular 3-phenoxy-toluene, (-)-fenchone, 1,2,3,5-tetramethylbenzene,

1,2,4,5-tetramethylbenzene, 1-methylnaphthalene, 2-methylbenzothiazole, 2-phenoxy-ethanol, 2-pyrrolidinone, 3-methylanisole, 4-methylanisole, 3,4-dimethylanisole, 3,5-dimethylanisole, acetophenone,  $\alpha$ -terpineol, benzothiazole, butyl benzoate, cumene, cyclohexanol, cyclohexanone, cyclohexylbenzene, decalin, dodecylbenzene, ethyl benzoate, indane, methyl benzoate, NMP, p-cymene, phenetol, 1,4-diisopropylbenzene, dibenzyl ether, diethylene glycol butyl methyl ether, triethylene glycol butyl methyl ether, diethylene glycol dibutyl ether, triethylene glycol dimethyl ether, diethylene glycol monobutyl ether, tripropylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, 2-isopropyl-naphthalene, pentylbenzene, hexylbenzene, heptylbenzene, octylbenzene, 1,1-bis(3,4-dimethylphenyl)ethane or mixtures of these solvents.

[0130] The invention therefore furthermore relates to a formulation, in particular a solution, dispersion or emulsion, comprising at least one compound of the formula (I) or at least one polymer, oligomer or dendrimer containing at least one unit of the formula (I), and at least one solvent, preferably 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.

[0131] 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.

[0132] 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.

## EXAMPLES

### A) Synthesis Examples

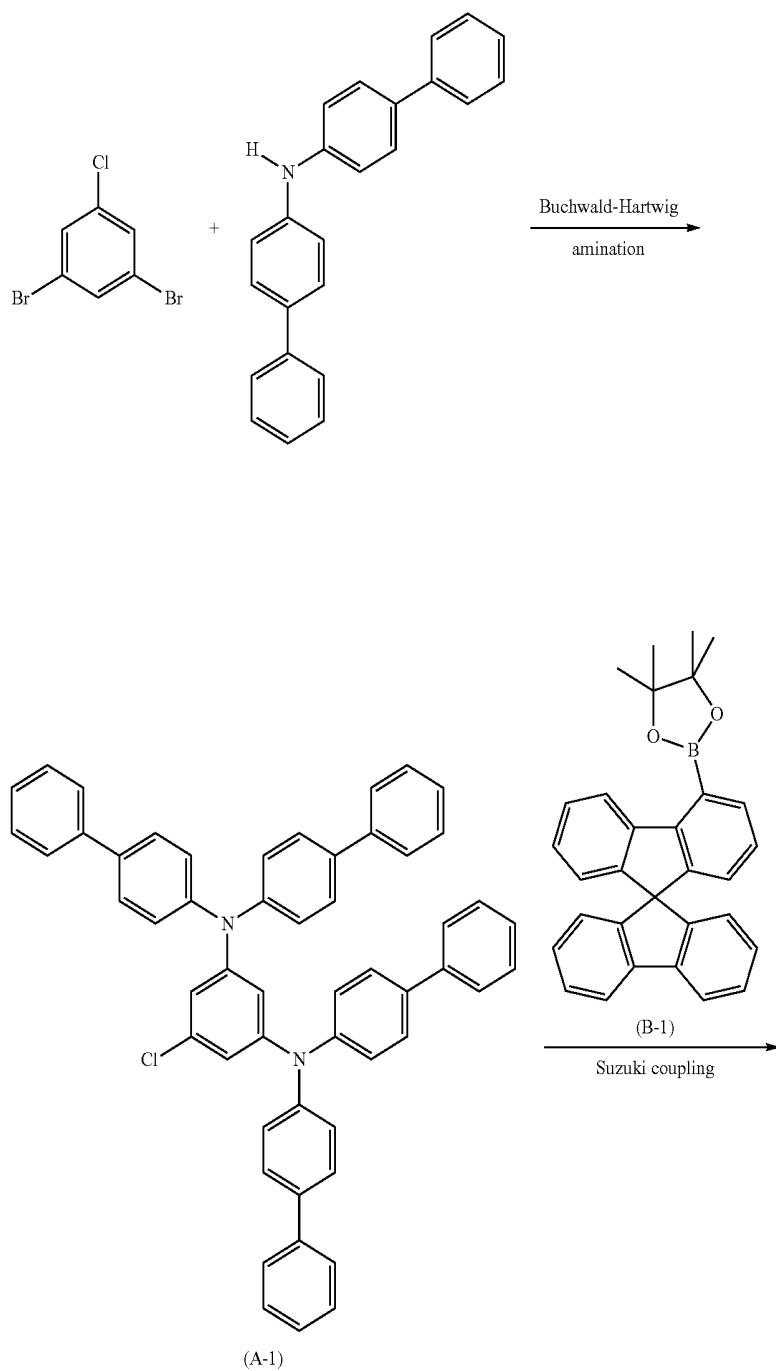
#### Examples

[0133] 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.

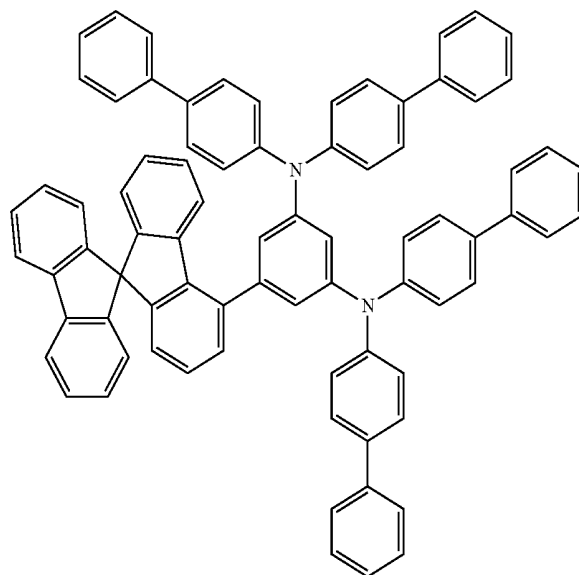
## Example 1

## Synthesis of Compound (1-1)

[0134]



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(1-1)

Intermediate (A-1): Synthesis of N,N,N',N'-Tetra-kis-biphenyl-4-yl-5-chloro-benzene-1,3-diamine

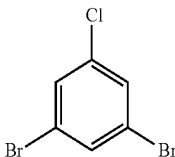
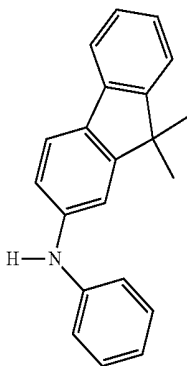
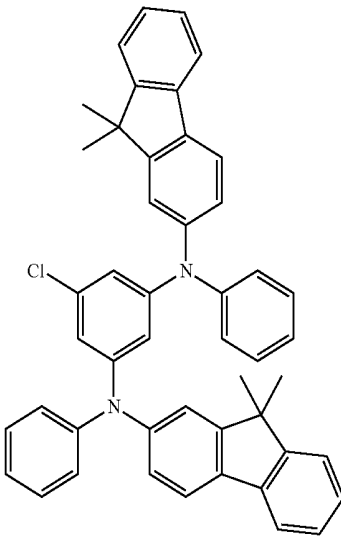
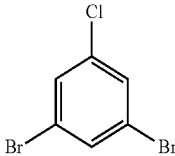
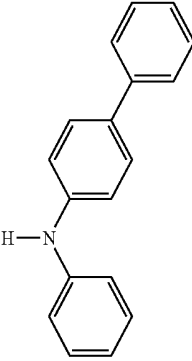
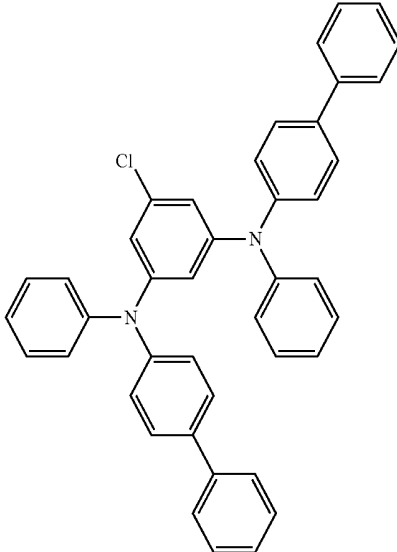
**[0135]** Tri-tert-butylphosphine (11.1 mL of a 1.0 M solution in toluene, 11.1 mmol), palladium acetate (1.25 g, 5.55 mmol) and cesium carbonate (75.0 g, 232 mmol) are added to a solution of bis-biphenyl-4-yl-amine (CAS Nr. 102113-98-4) (59.0 g, 185 mmol) and 1,3-Dibromo-5-chloro-ben-

zene (25 g, 92 mol) in degassed toluene (600 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 heptane/toluene. Yield: 67.7 g, 75%.

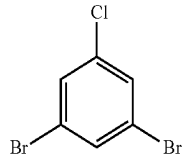
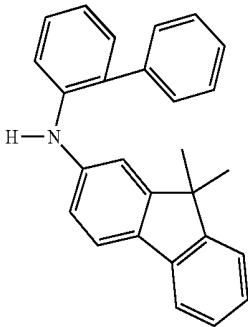
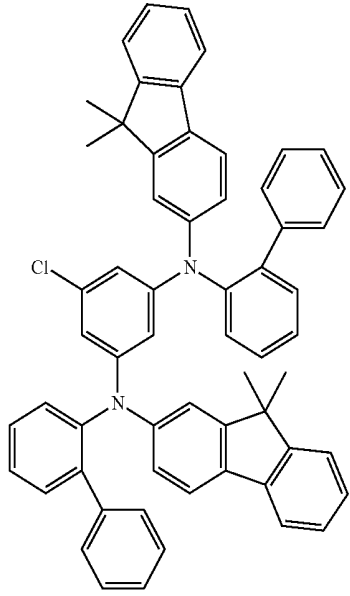
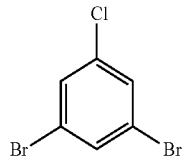
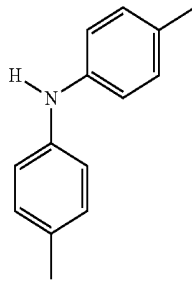
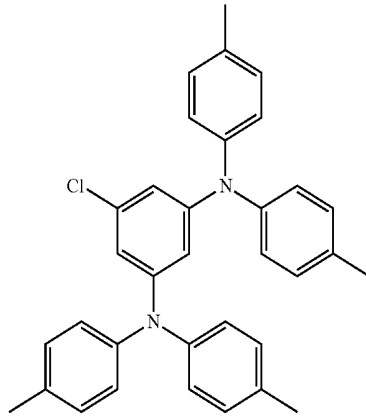
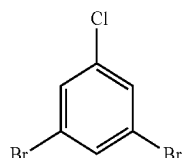
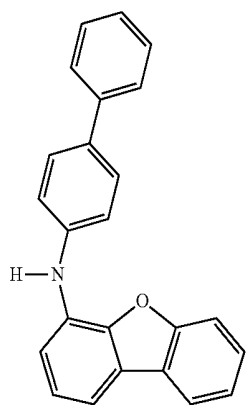
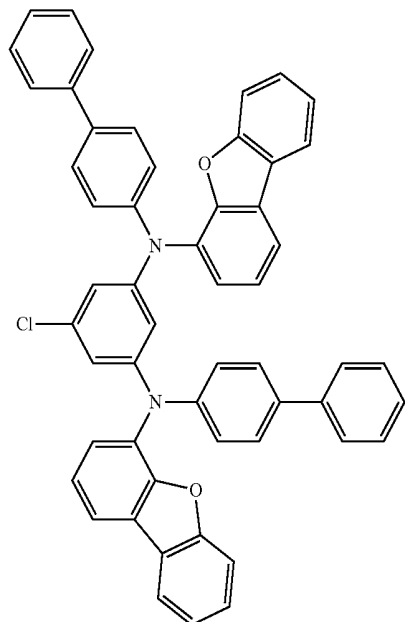
**[0136]** The following compounds are obtained analogously:

	Educt 1	Amine	Product	Yield
A-2	 [14862-52-3]	 [1267248-50-9]		65%

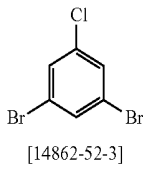
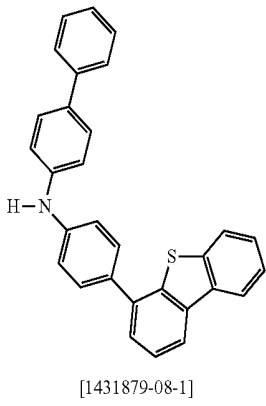
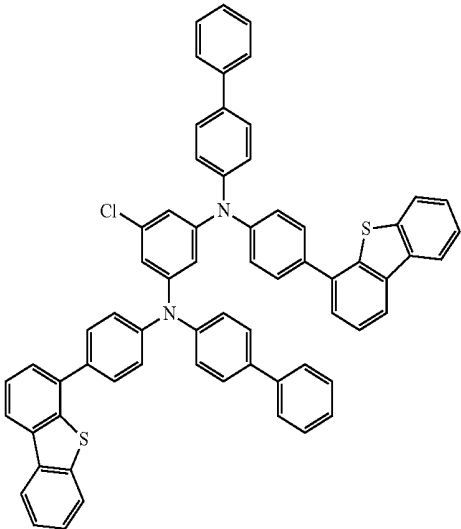
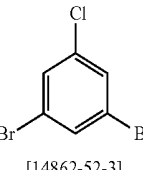
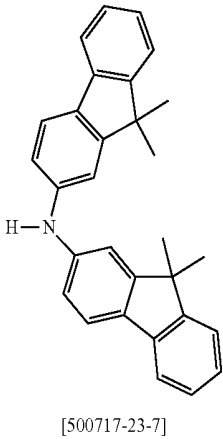
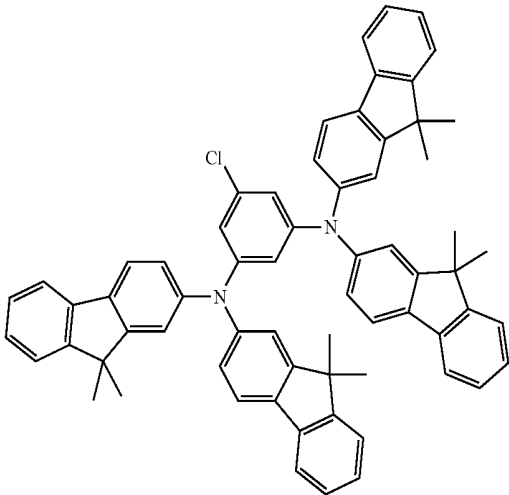
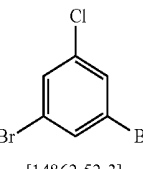
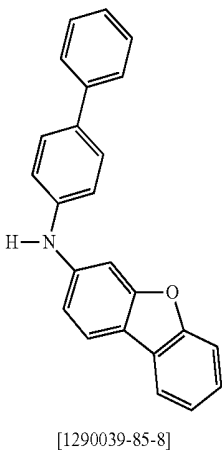
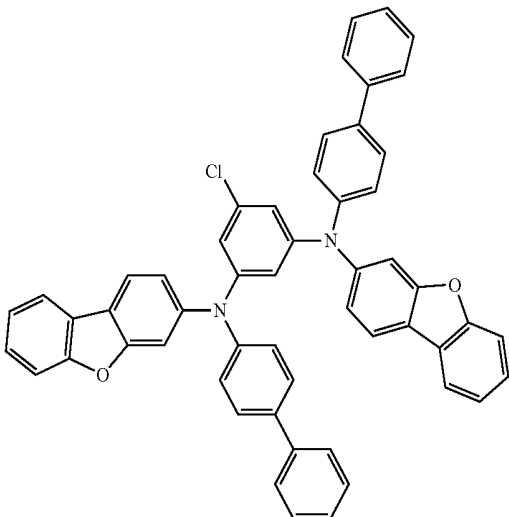
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Educt 1	Amine	Product	Yield
A-3	 [14862-52-3]	 [355832-04-1] 	71%
A-4	 [14862-52-3]	 [32228-99-2] 	80%

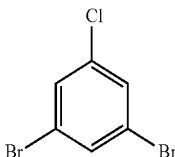
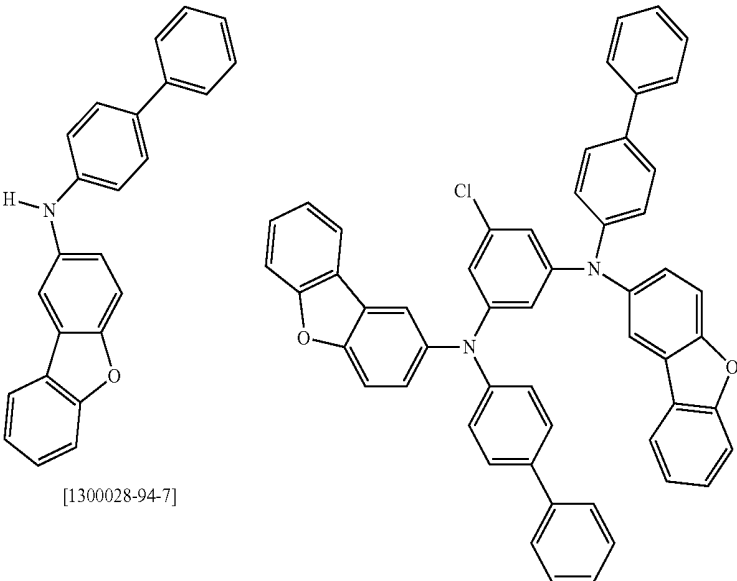
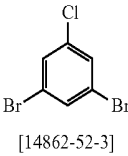
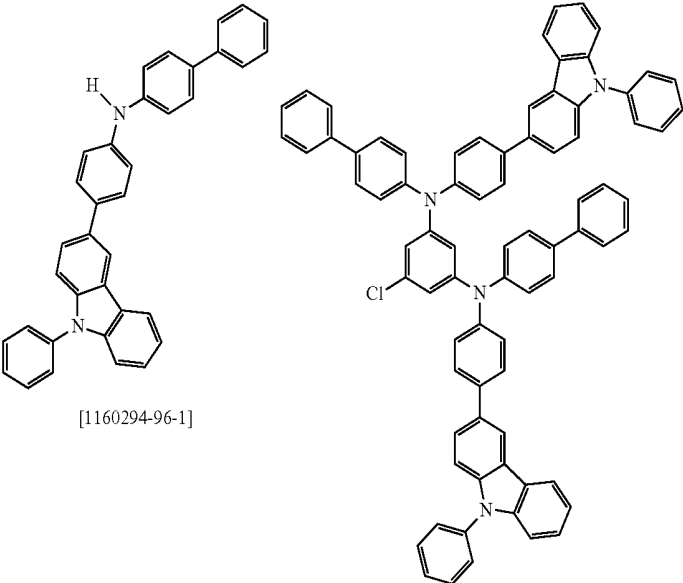
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A-5	Educt 1	Amine	Product	Yield
A-5	 [14862-52-3]	 [1198395-24-2]		80%
A-6	 [14862-52-3]	 [620-93-9]		87%
A-7	 [14862-52-3]	 [1318338-47-4]		76%

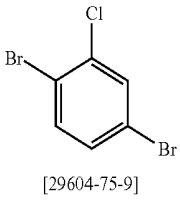
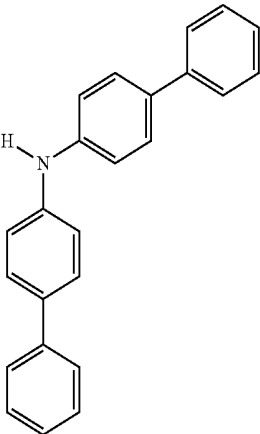
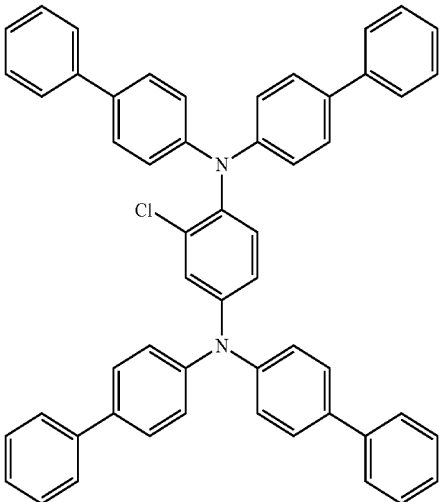
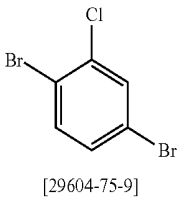
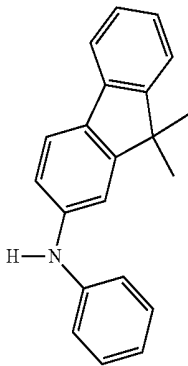
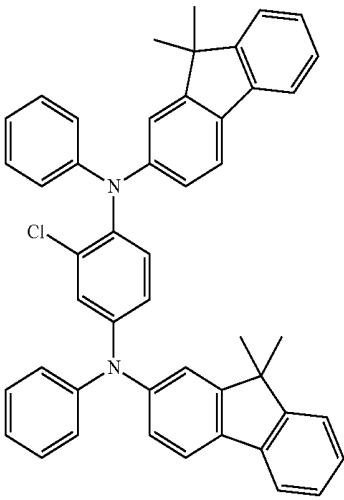
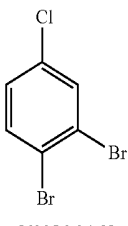
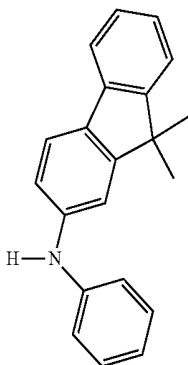
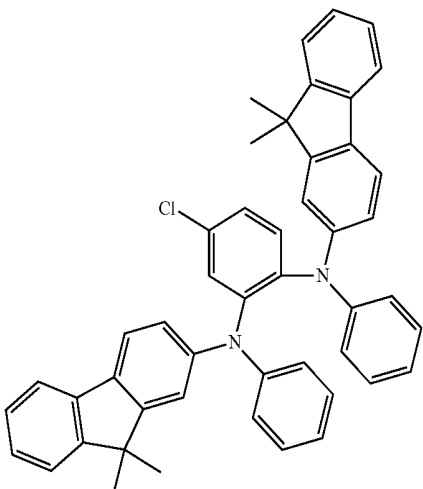
-continued

Educt 1	Amine	Product	Yield	
A-8	 <p>[14862-52-3]</p>	 <p>[1431879-08-1]</p>		73%
A-9	 <p>[14862-52-3]</p>	 <p>[500717-23-7]</p>		70%
A-10	 <p>[14862-52-3]</p>	 <p>[1290039-85-8]</p>		81%

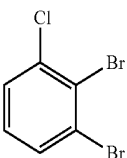
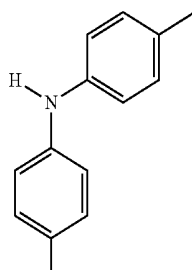
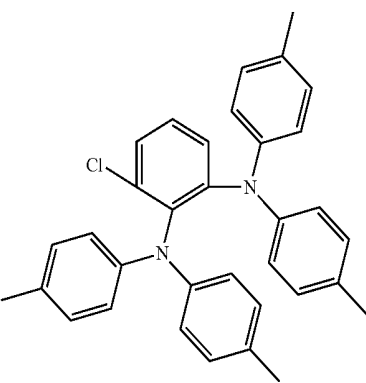
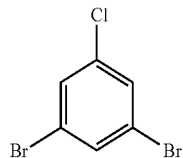
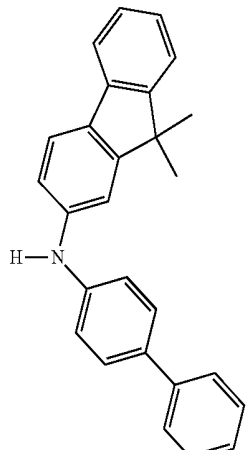
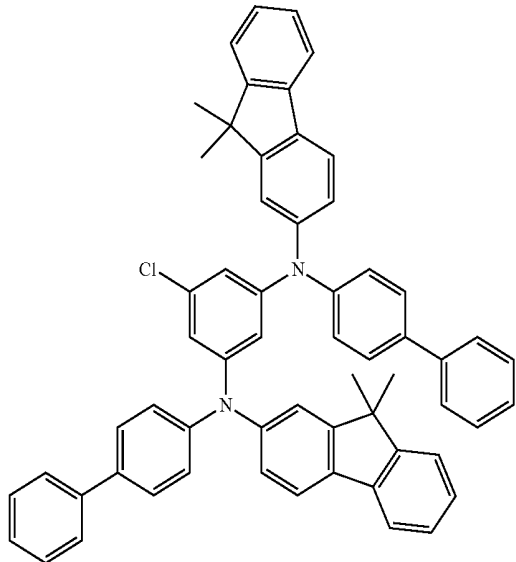
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Educt 1	Amine	Product	Yield
A-11	 [14862-52-3]	 [1300028-94-7]	83%
A-12	 [14862-52-3]	 [1160294-96-1]	78%

-continued

Educt 1	Amine	Product	Yield	
A-13	 [29604-75-9]	 [102113-98-4]		68%
A-14	 [29604-75-9]	 [355832-04-1]		74%
A-15	 [69956-24-3]	 [355832-04-1]		61%

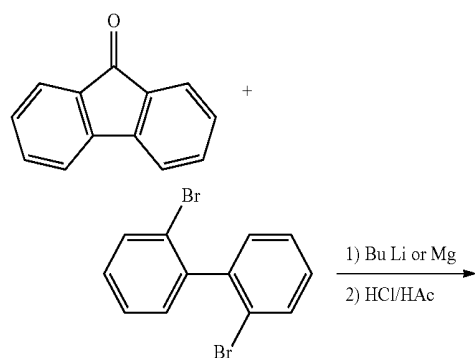
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A-16	Educt 1	Amine	Product	Yield
	 [104514-49-0]	 [620-93-9]		40%
	 [14862-52-3]	 [897671-69-1]		71%

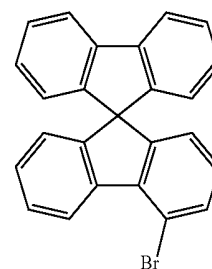
Intermediate (B-1): Synthesis of the Spirobifluorene-Boronester Derivatives

1a) Synthesis of 4-bromospiro-9,9''-bifluorene

[0137]



-continued

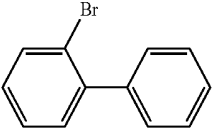
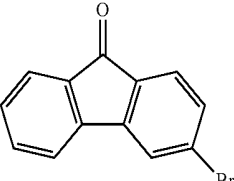
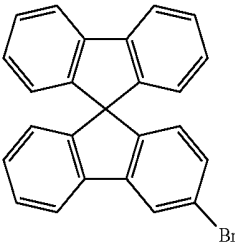
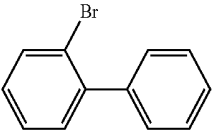
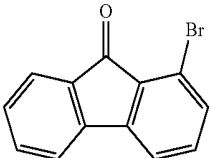
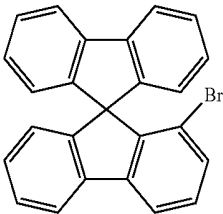
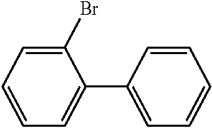
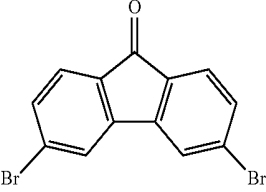
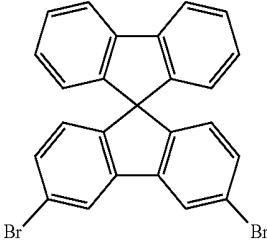
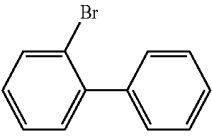
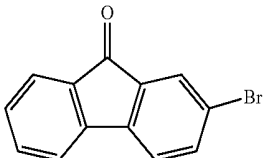
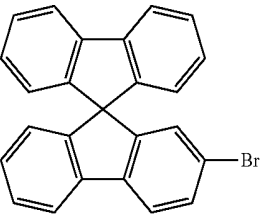
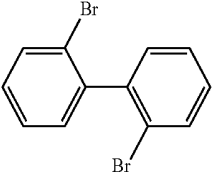
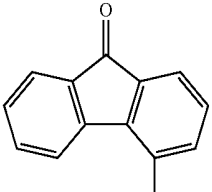
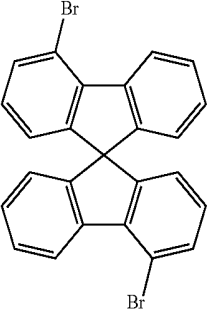


**[0138]** 60 g (188.5 mmol) 2,2'-Dibromo-biphenyl (CAS 13029-09-9) is dissolved in 750 mL of dry THF and cooled down to  $-78^{\circ}\text{C}$ . 75.4 mL (188.5 mmol) of a 2.5M solution of nBuLi in heptane is added dropwise. After 1 h a solution of 34.6 g of fluorenone (188.5 mmol) (CAS 486-25-9) in 250 mL of THF is added dropwise. The reaction mixture is allowed to reach the room temperature overnight, then quenched with saturated  $\text{NH}_4\text{Cl}$  (100 mL) solution, the mixture is stirred briefly, the organic phase is separated off, and the solvent is removed in vacuum. The residue is suspended in 500 ml of glacial acetic acid at  $40^{\circ}\text{C}$ ., 0.5 ml of conc. hydrochloric acid is added to the suspension, and

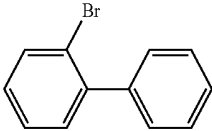
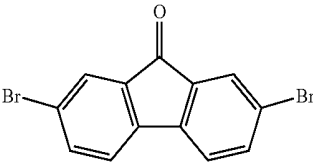
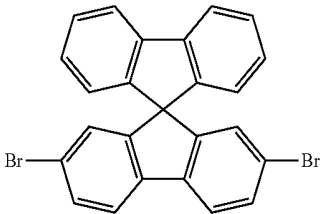
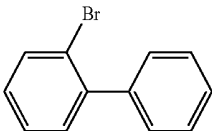
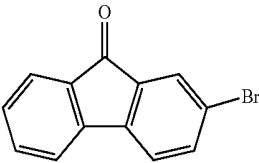
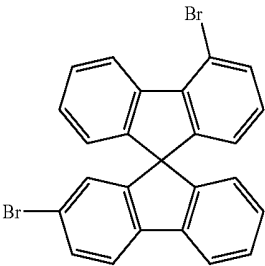
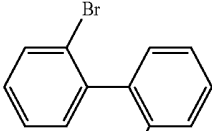
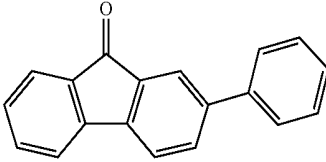
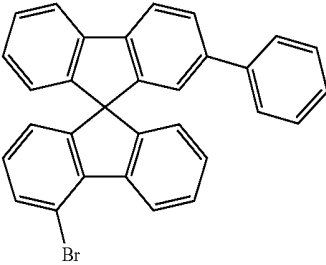
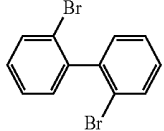
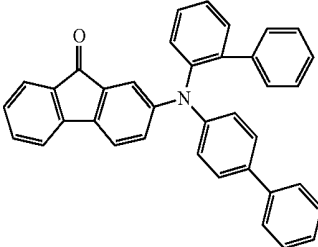
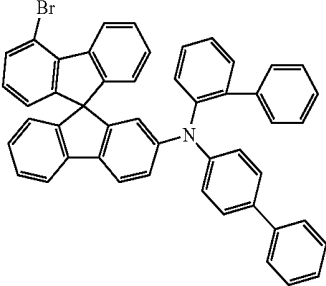
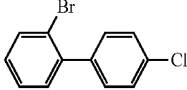
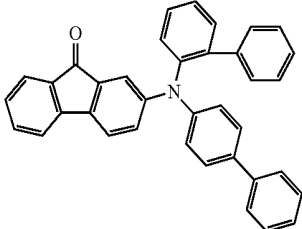
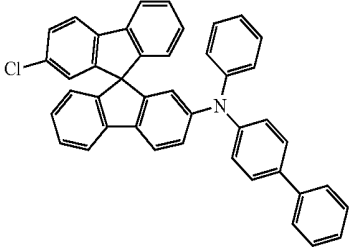
the mixture is subsequently stirred at 100° C. for a further 2 h. After cooling, the precipitated solid is filtered off with suction, washed once with 100 ml of glacial acetic acid, three times with 100 ml of ethanol each time and finally

recrystallized from dioxane. Yield: 70.1 g (169 mmol), 90%; purity about 98% according to <sup>1</sup>H-NMR.

[0139] The synthesis of further brominated spirobifluorene derivatives is carried out analogously:

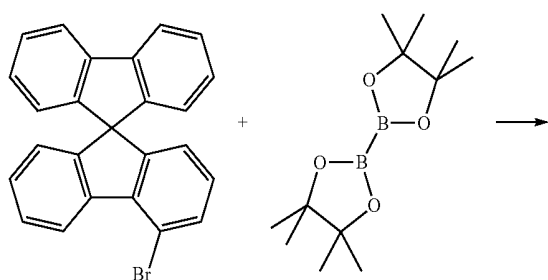
	Br-biphenyl	Br-fluorenone	Product: Br-spirobifluorene	Yield
1b	 [2052-07-5]	 [2041-19-2]		85%
1c	 [2052-07-5]	 [36804-63-4]		68%
1d	 [2052-07-5]	 [216312-73-1]		85%
1e	 [2052-07-5]	 [3096-56-8]		91%
1f	 [13029-09-9]	 [4269-17-4]	 [1257321-41-7]	90%

-continued

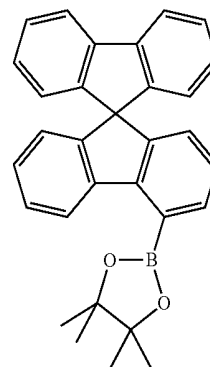
	Br-biphenyl	Br-fluorenone	Product: Br-spirobifluorene	Yield
1g	 [2052-07-5]	 [14348-75-5]		78%
1h	 [13029-09-9]	 [3096-56-8]		75%
1i	 [13029-09-9]	 [3096-49-9]		71%
1j	 [13029-09-9]			68%
1k	 [179526-95-5]			70%

## 2a) Synthesis of 4-bromospiro-9,9'-bifluorene (B-1)

[0140]



-continued

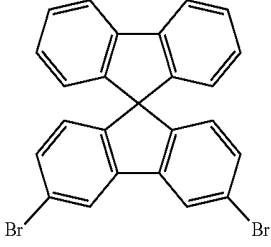
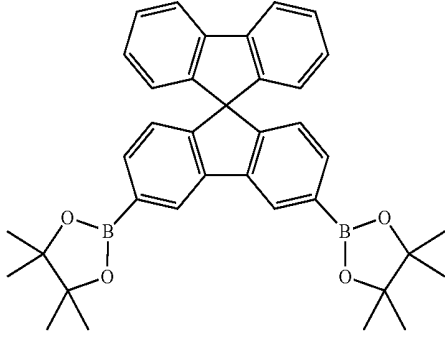
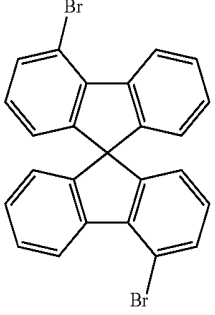
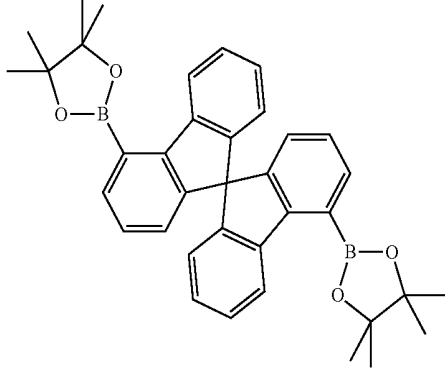
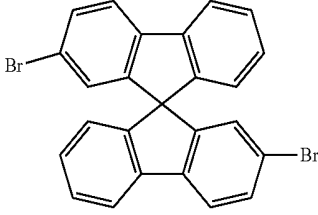
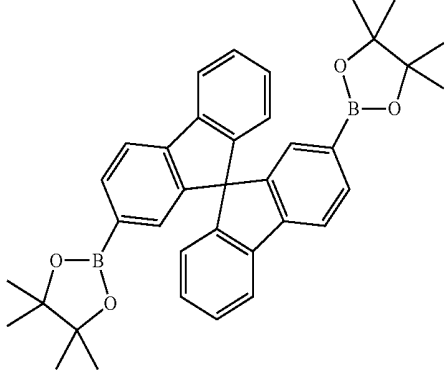
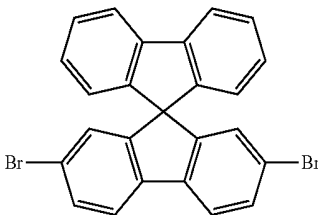
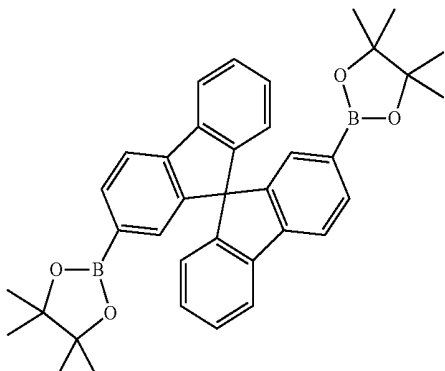


**[0141]** 60 g (152 mmol) 4-bromospiro-9,9'-bifluorene, 47.2 g (182.1 mmol) bis-pinacolatodiboron, 3.72 g (4.55 mmol) 1,1'-bis(diphenylphosphino)ferrocene-palladium(II) dichloride dichloromethane complex, 44.7 g (455 mmol) potassium acetate and 600 ml of toluene is heated under reflux for 16 h. After cooling, 200 ml of water are added, the mixture is stirred for a further 30 min., the organic phase is separated off, filtered through a short Celite bed, and the solvent is then removed in vacuum. The residue is recrystallised several times from heptanes/toluene. Yield: 67.1 g, 96%.

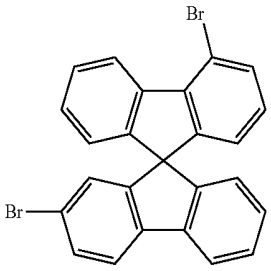
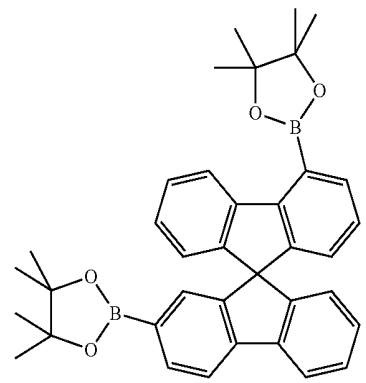
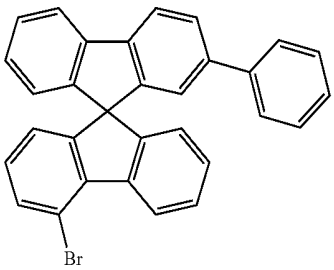
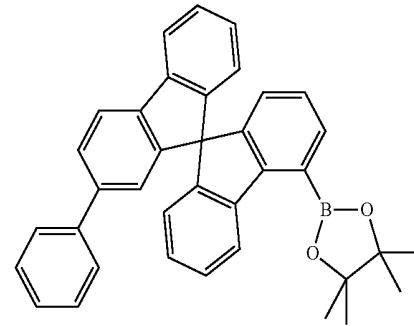
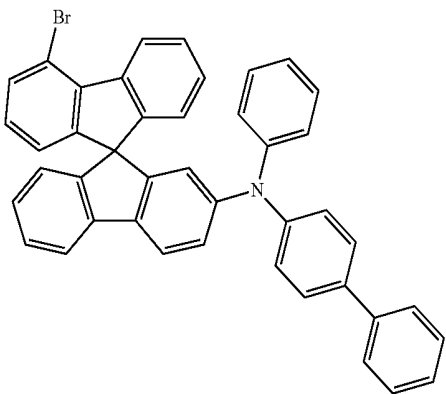
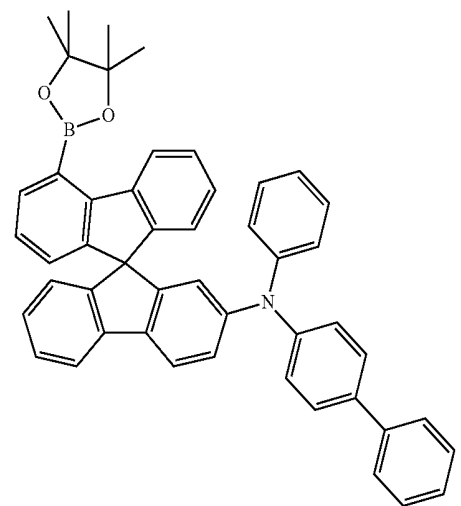
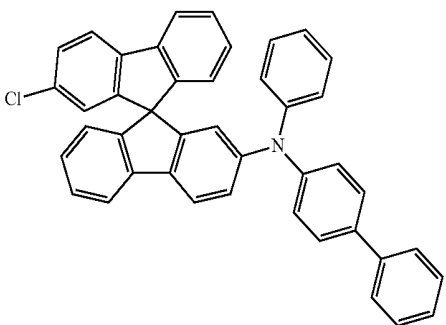
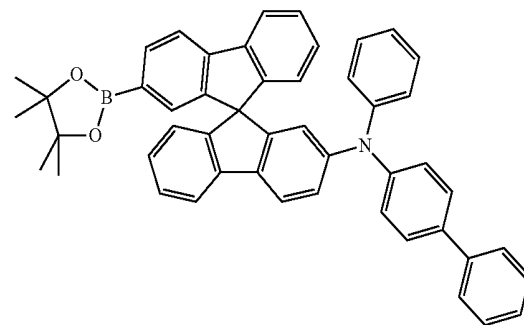
**[0142]** The synthesis of further spirobifluorene boronic ester derivatives is carried out analogously:

Br-spirobifluorene	Product	Yield
B-2 		90%
B-3 		67%
B-4 		87%

-continued

Br-spirobifluorene	Product	Yield
B-5 		85%
B-6 		85%
B-7 		90%
B-8 		92%

-continued

Br-spirobifluorene	Product	Yield
B-9 		85%
B-10 		93%
B-11 		92%
B-12 		87%

## Synthesis of Compound (1.1)

**[0143]** 392 mg (0.53 mmol) Palladium dichloride-bis(tricyclohexylphosphine), 39  $\mu$ L hydrazinium hydroxide (0.8 mmol) and sodium metaborate (11 g, 40 mmol) are added to a solution of 20 g (27 mmol) of N,N,N',N'-tetrakis-biphenyl-4-yl-5-chloro-benzene-1,3-diamine (A-1) and 10 g (28 mmol) 4-Spirobifluoreneboronic ester (B1) in 430 mL THF, 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 organic phases are dried and evaporated in vacuum. The residue is recrystallised from heptane/toluene and sublimated in vacuum. Compound (1-1) is obtained in the form of a pale-yellow solid (21.0 g, 76% of theory).

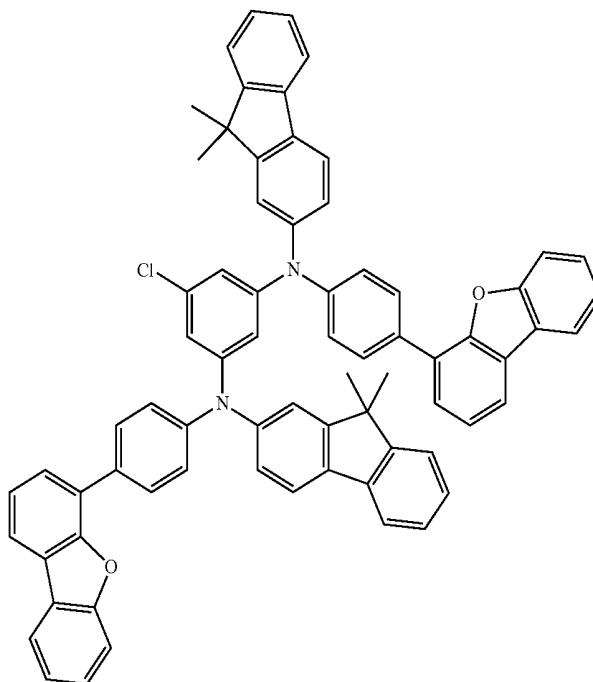
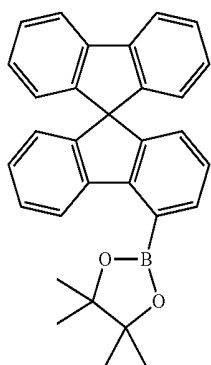
ene and filtered through Celite. The filtrate is extended with water, re-extracted with toluene, and the combined organic phases are dried and evaporated in vacuum. The residue is recrystallised from heptane/toluene and sublimated in vacuum. Compound (1-1) is obtained in the form of a pale-yellow solid (21.0 g, 76% of theory).

**[0144]** The synthesis of compound 1-2 to 1-29 is carried out analogously. After recrystallisation the materials are sublimated or tempered under high vacuum.

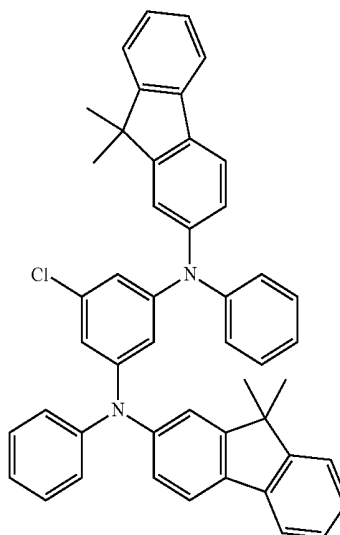
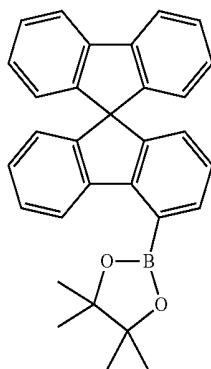
Intermediate B

Intermediate A

1-2

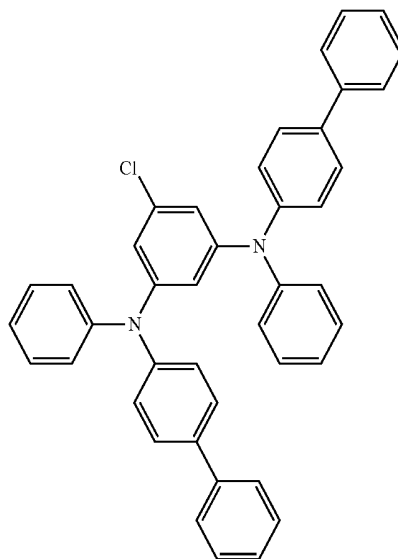
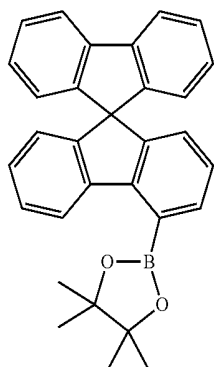


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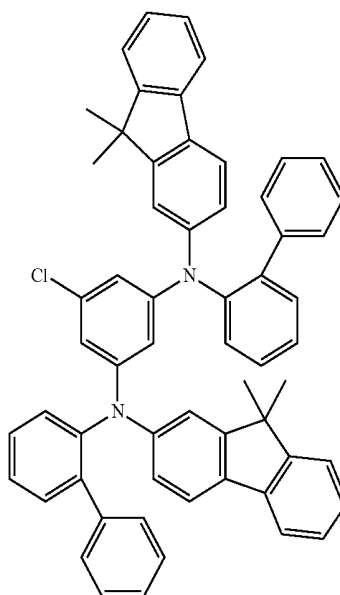
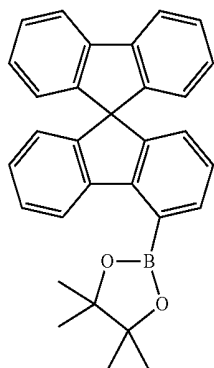


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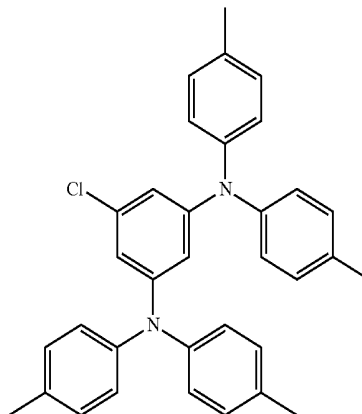
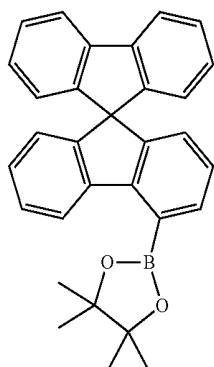
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1-5



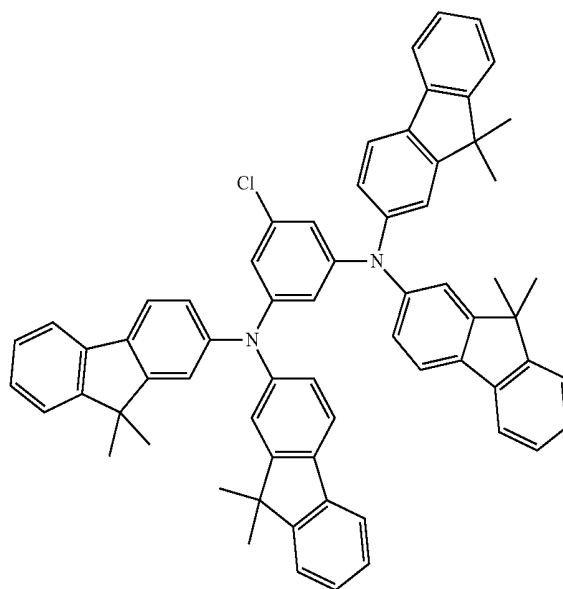
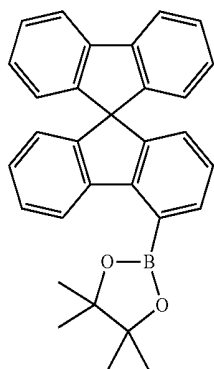
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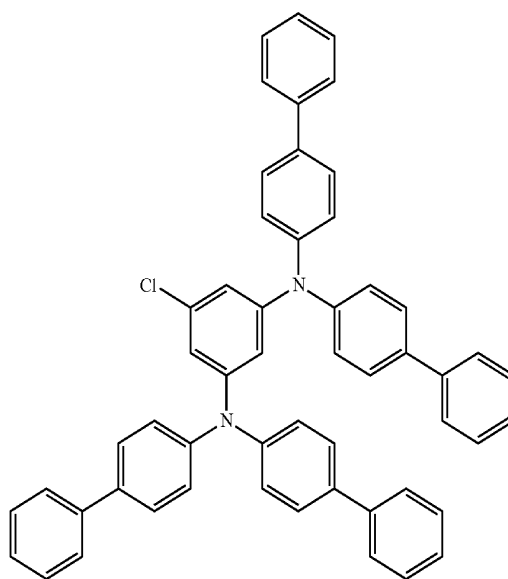
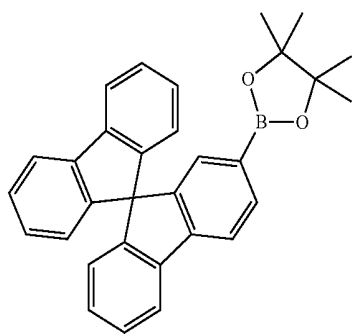
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1-7



1-8

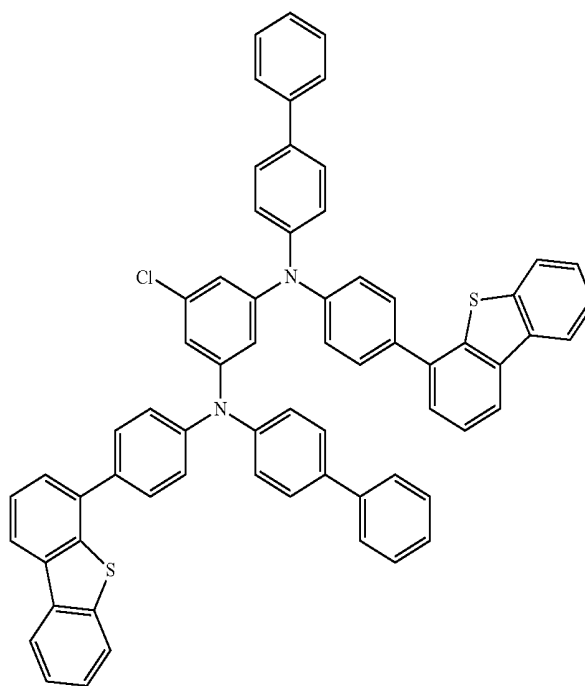
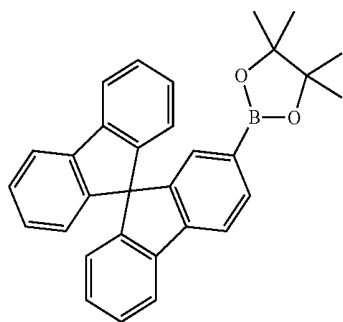


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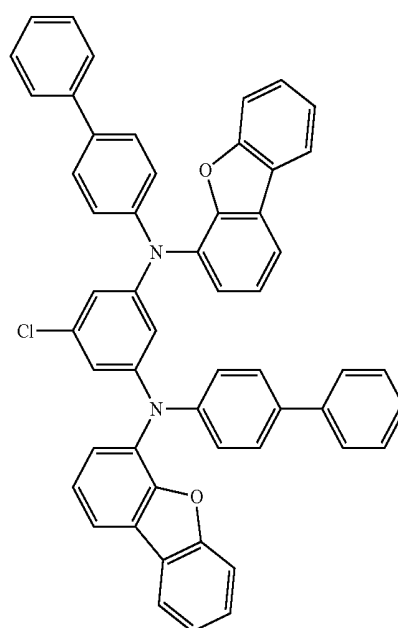
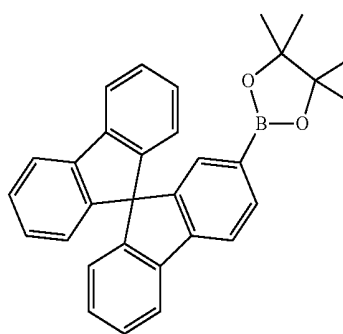
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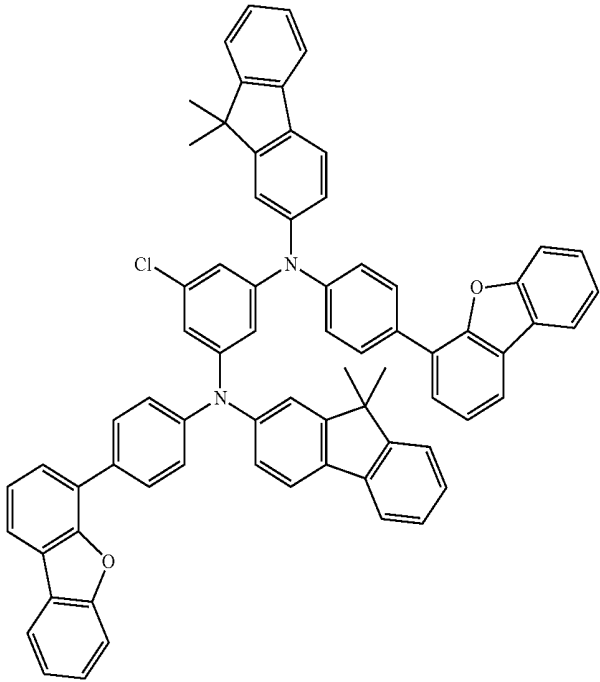
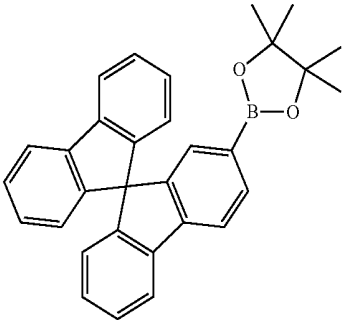
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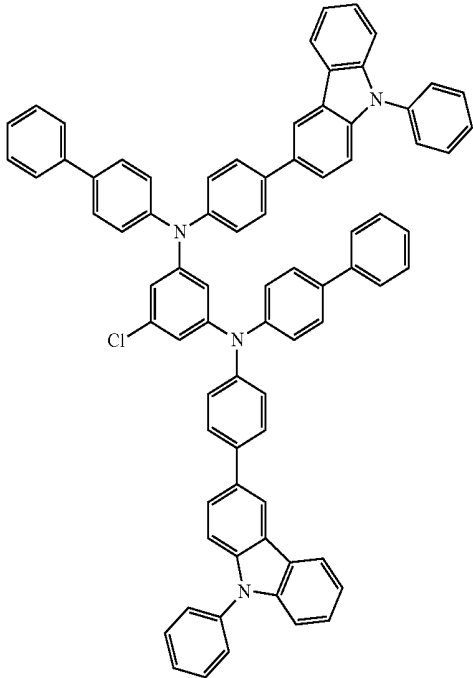
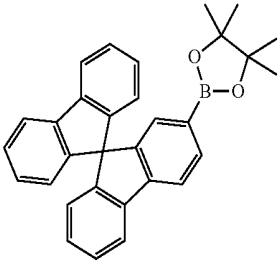
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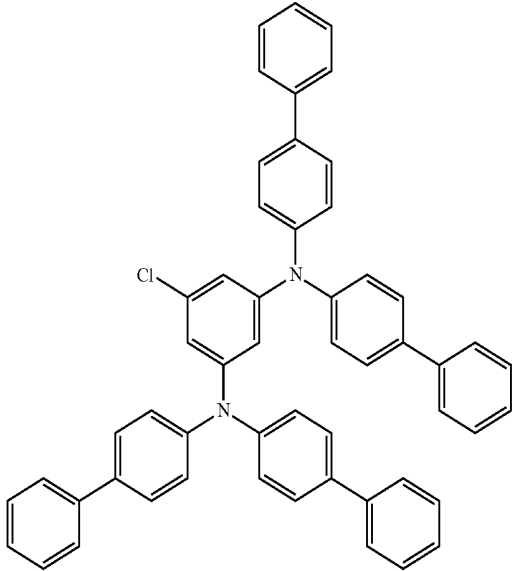
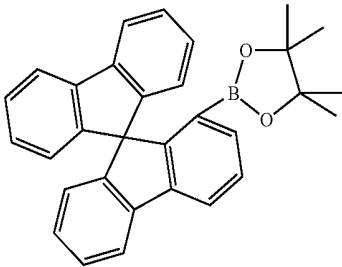
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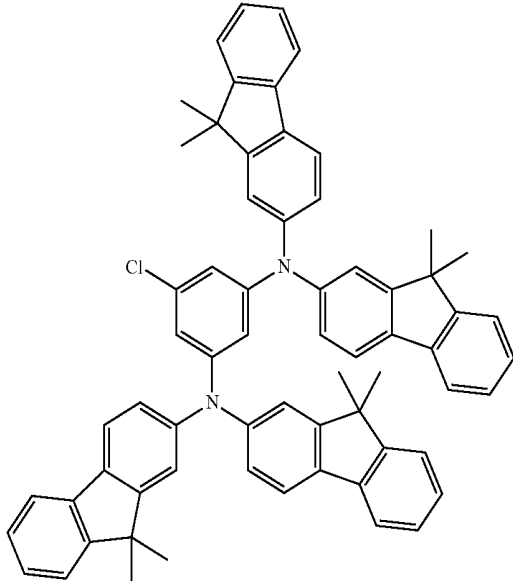
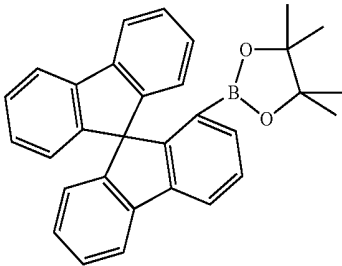
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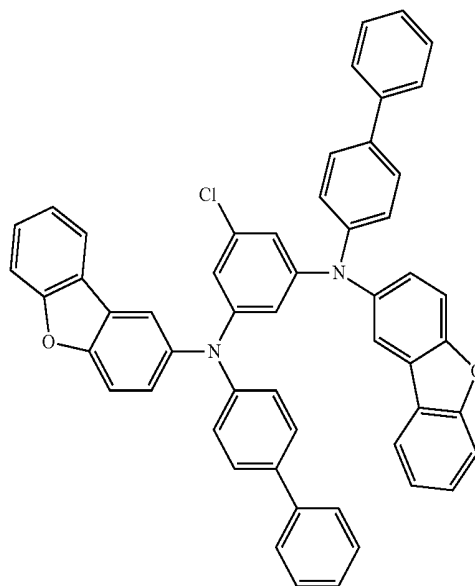
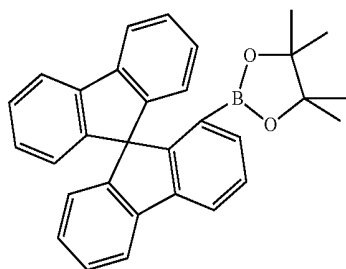


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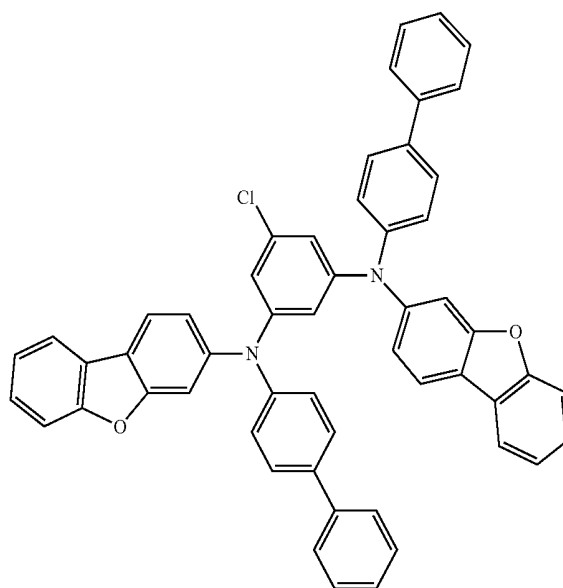
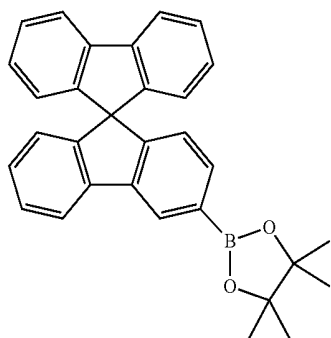


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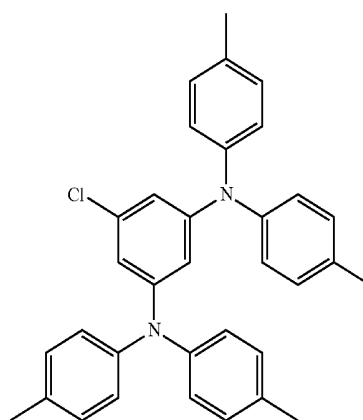
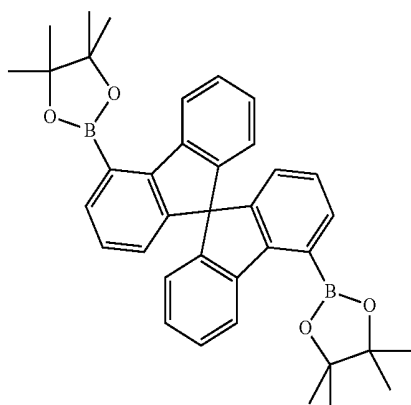
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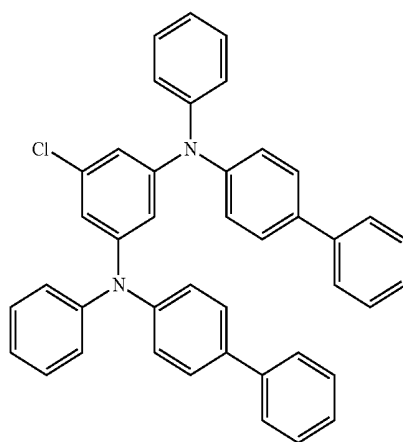
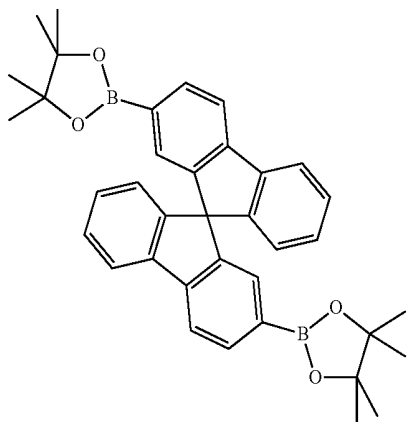


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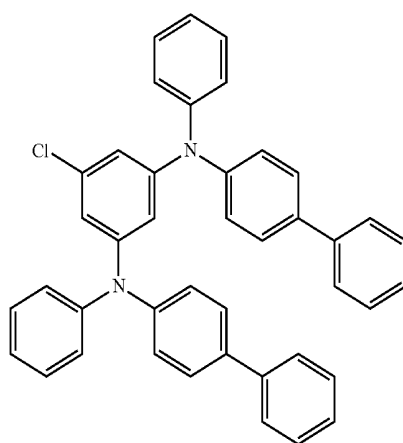
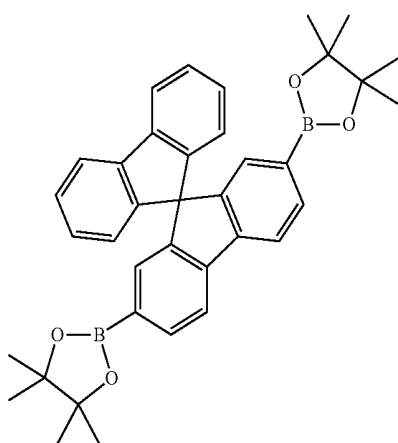


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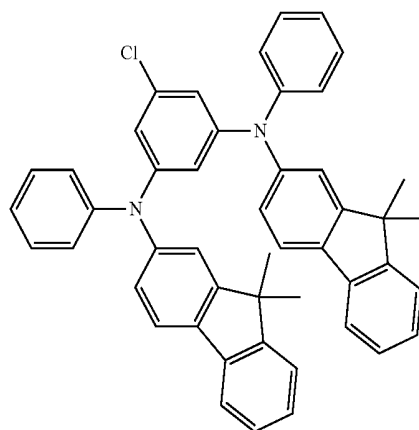
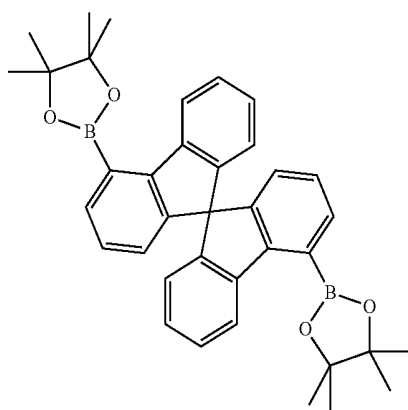
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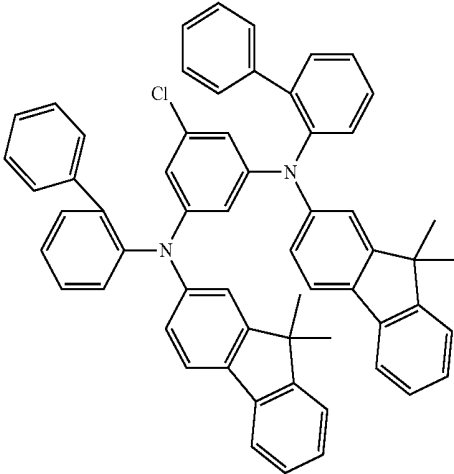
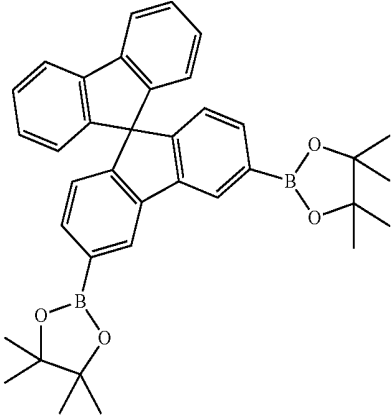


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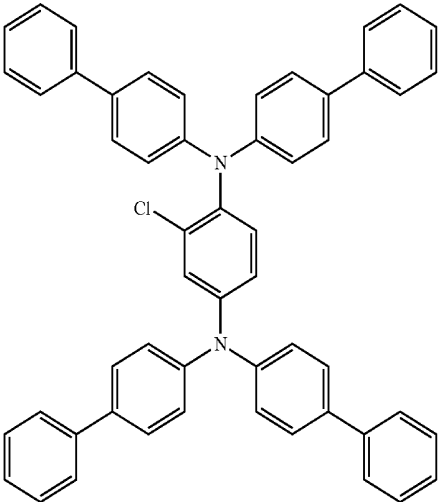
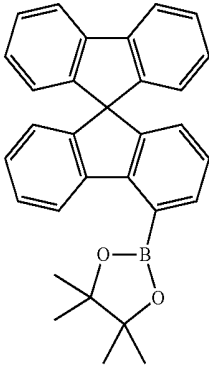


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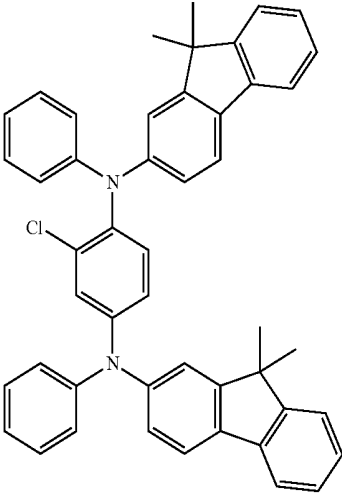
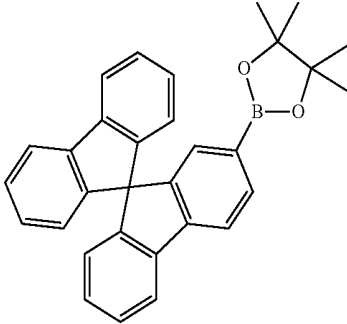
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1-23

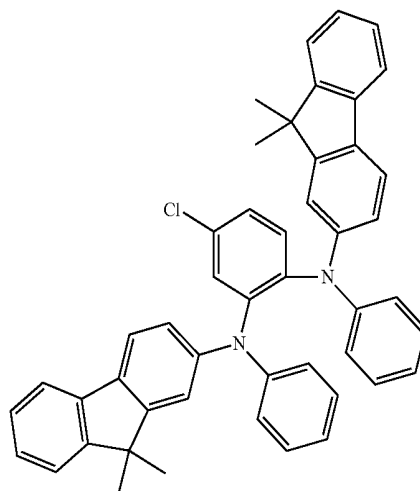
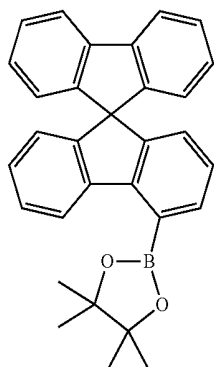


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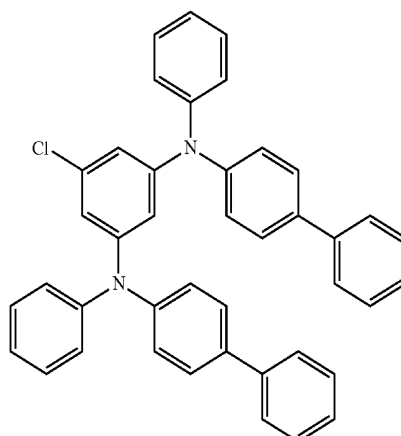
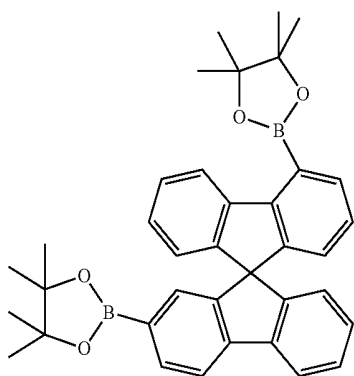


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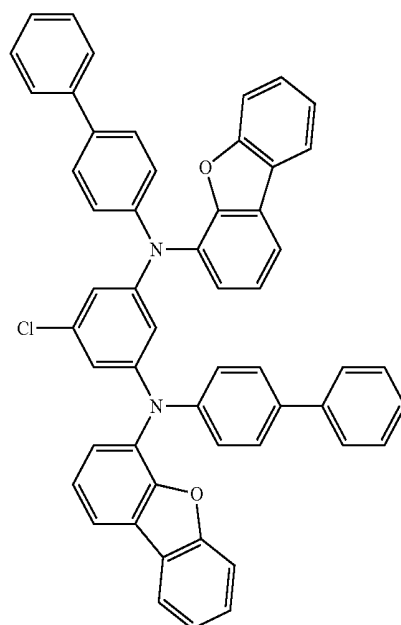
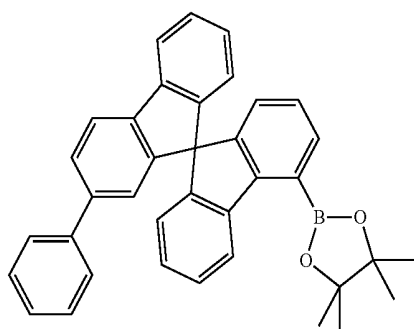
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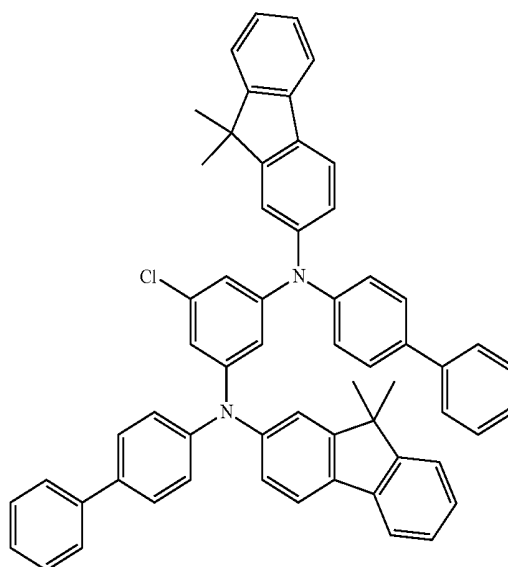
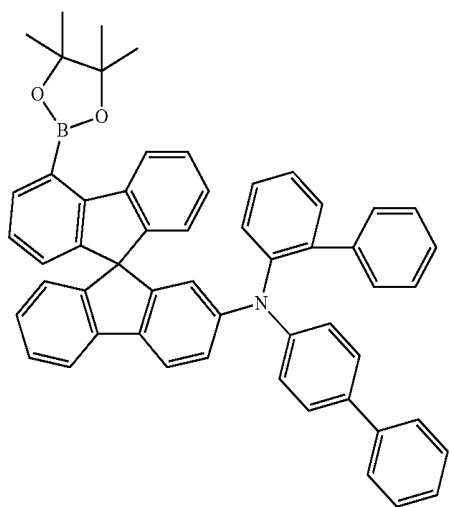


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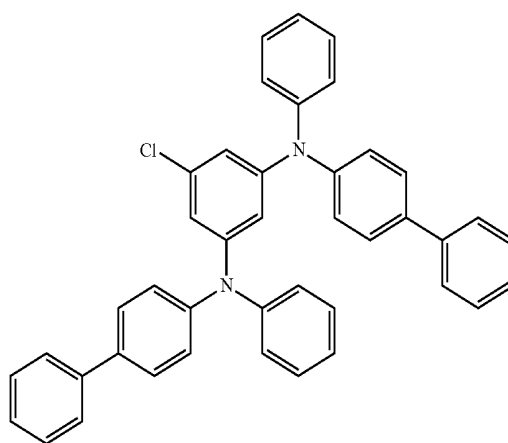
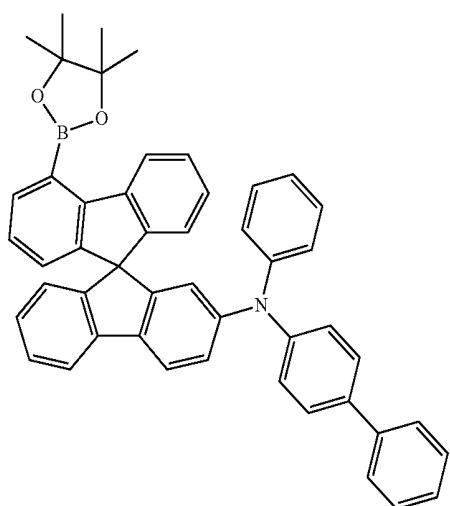


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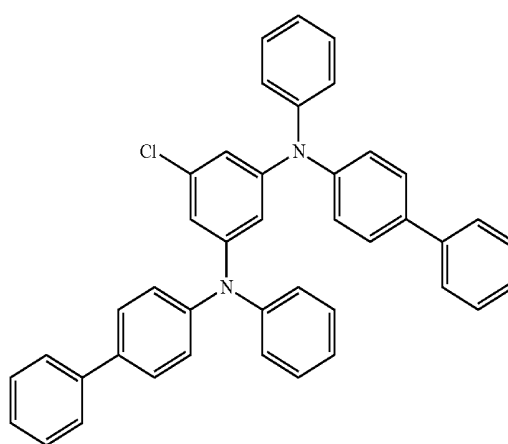
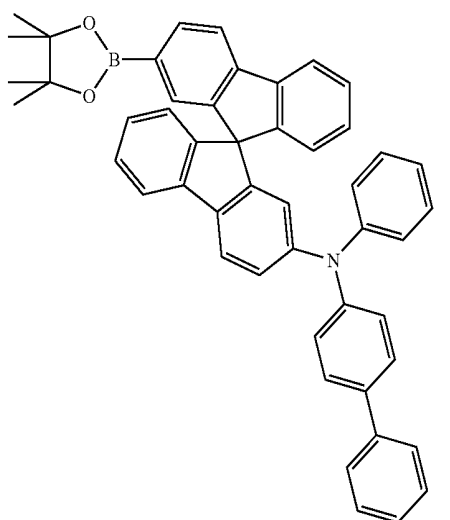
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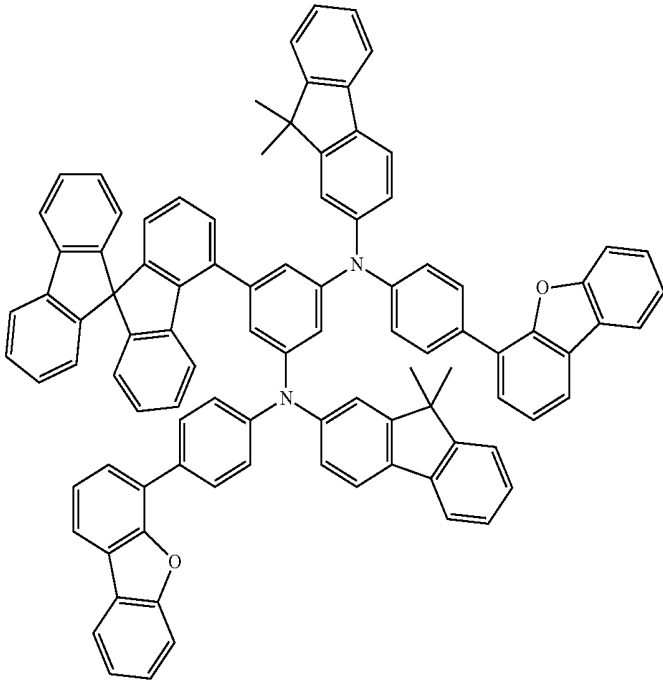
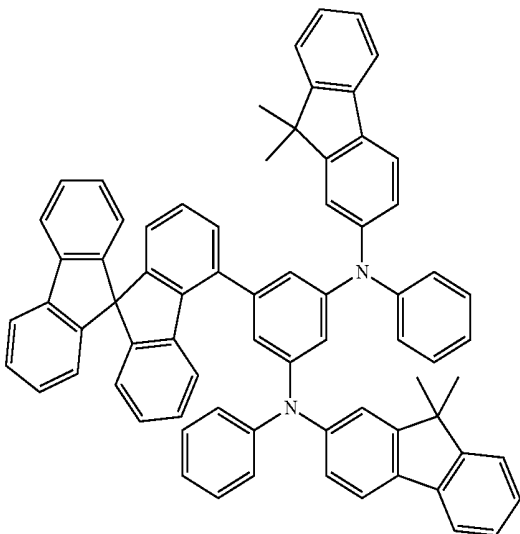
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1-30



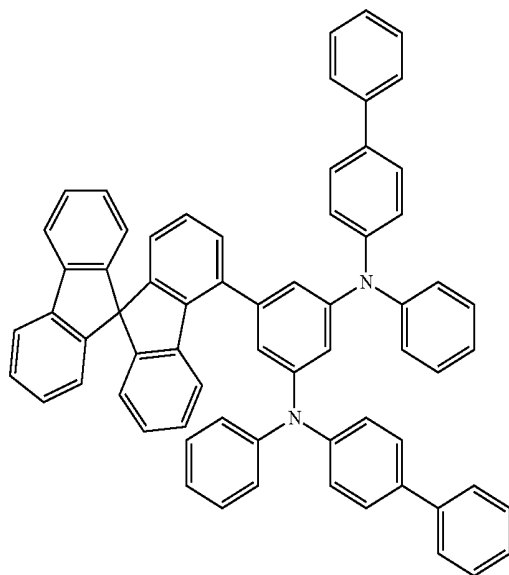
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Product	Yield
1-2	78%
 <p>The chemical structure of product 1-2 is a complex polycyclic molecule. It features a central benzene ring substituted at the 1 and 4 positions with two nitrogen atoms. Each nitrogen atom is bonded to a 2,2-dimethyl-1H-indene group. The central benzene ring is also substituted at the 2 and 5 positions with two indeno[1,2-b]fluorene groups. The 3 and 6 positions of the central benzene ring are substituted with two 2,2-dimethyl-1H-indene groups. The overall structure is highly symmetric and contains multiple fused ring systems.</p>	78%
1-3	81%
 <p>The chemical structure of product 1-3 is a complex polycyclic molecule, similar to product 1-2. It features a central benzene ring substituted at the 1 and 4 positions with two nitrogen atoms. Each nitrogen atom is bonded to a 2,2-dimethyl-1H-indene group. The central benzene ring is also substituted at the 2 and 5 positions with two indeno[1,2-b]fluorene groups. The 3 and 6 positions of the central benzene ring are substituted with two 2,2-dimethyl-1H-indene groups. The overall structure is highly symmetric and contains multiple fused ring systems.</p>	81%

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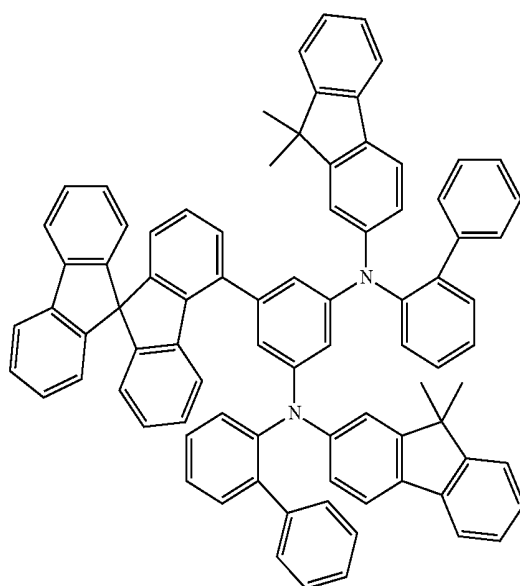
1-4

75%



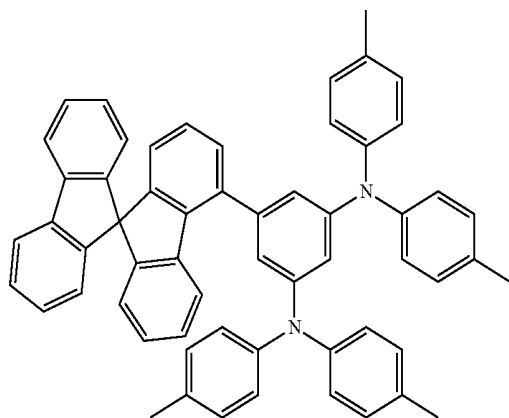
1-5

68%



1-6

70%

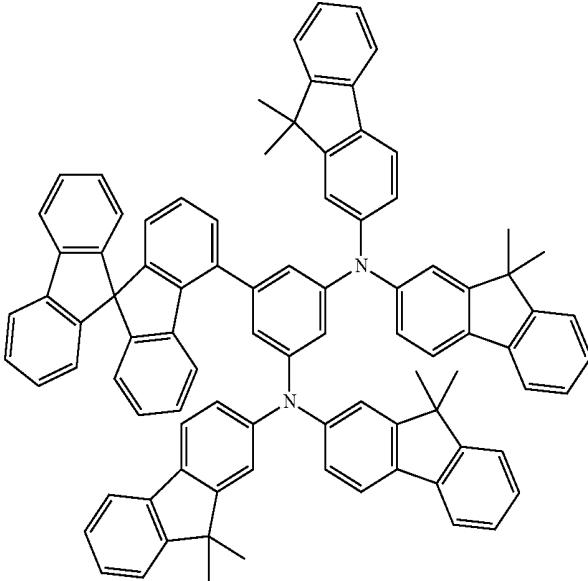


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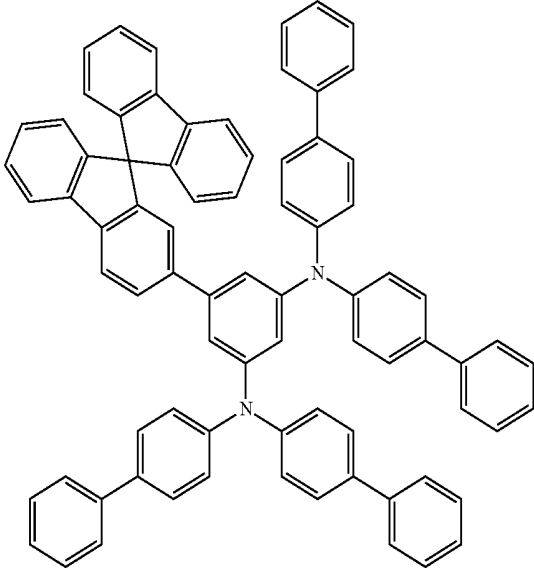
1-7

65%



1-8

77%

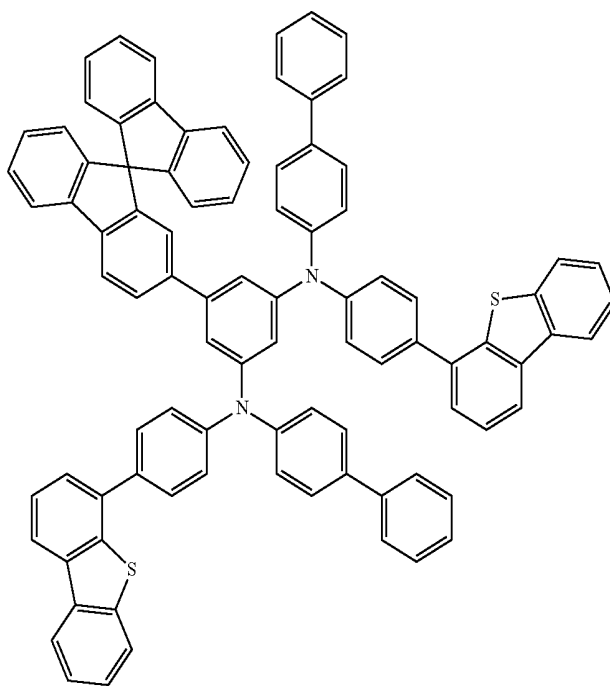


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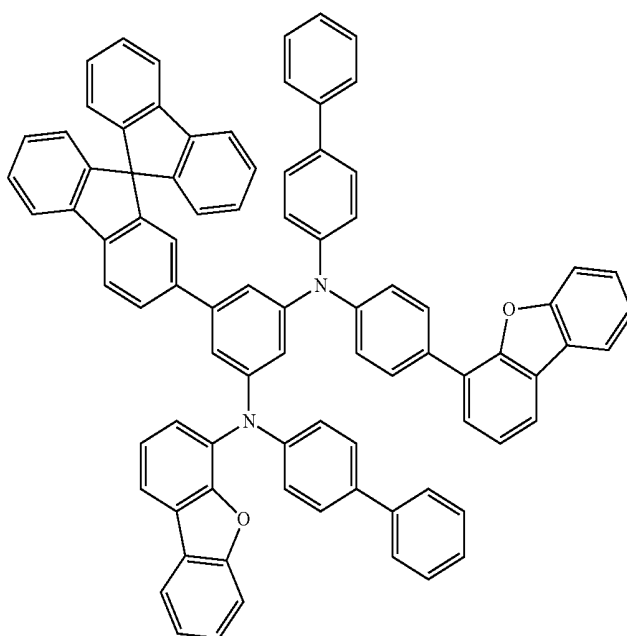
1-9

68%



1-10

71%



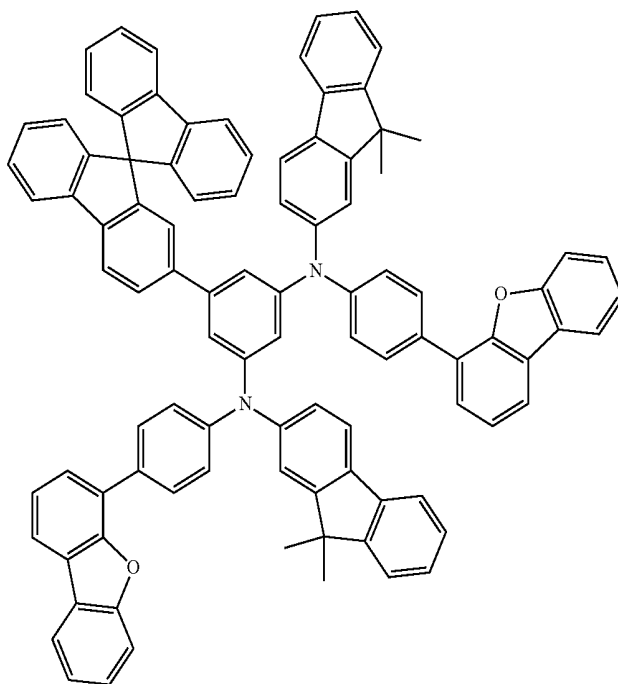
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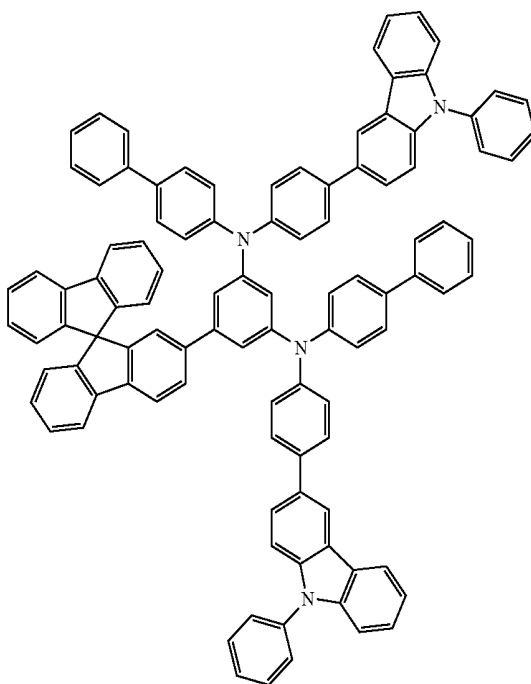
1-11

71%



1-12

80%



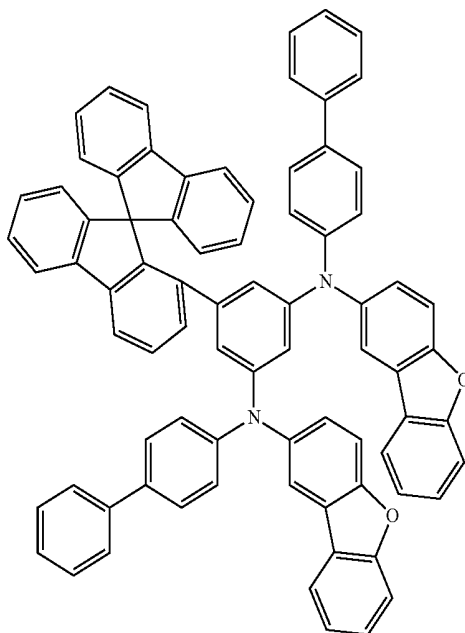


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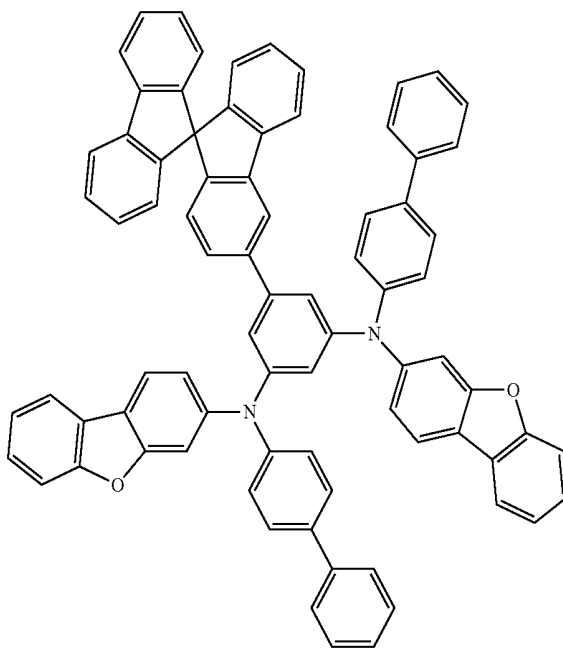
1-16

70%



1-17

83%

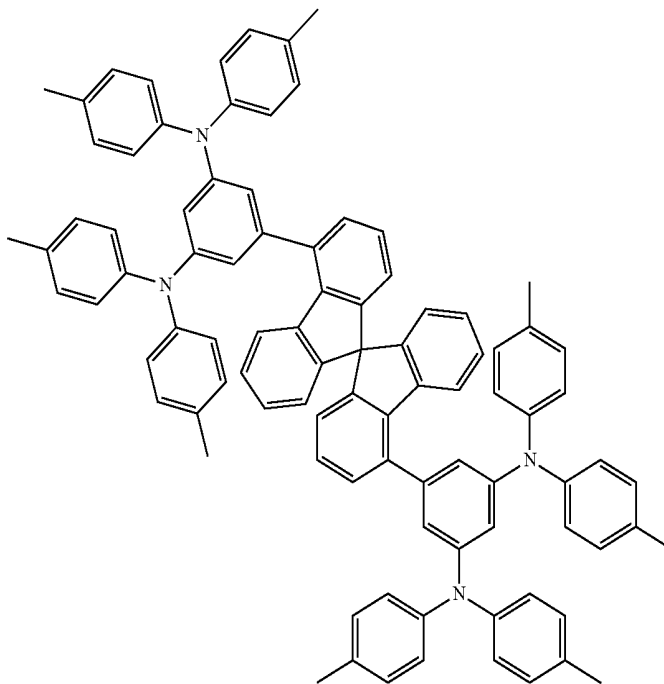


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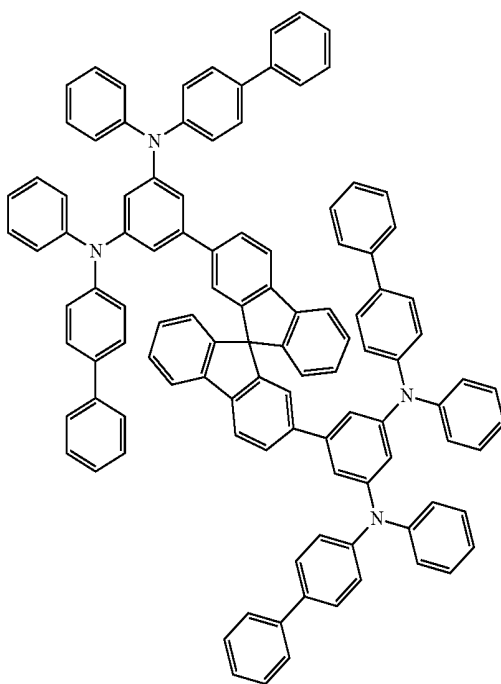
1-18

65%



1-19

73%



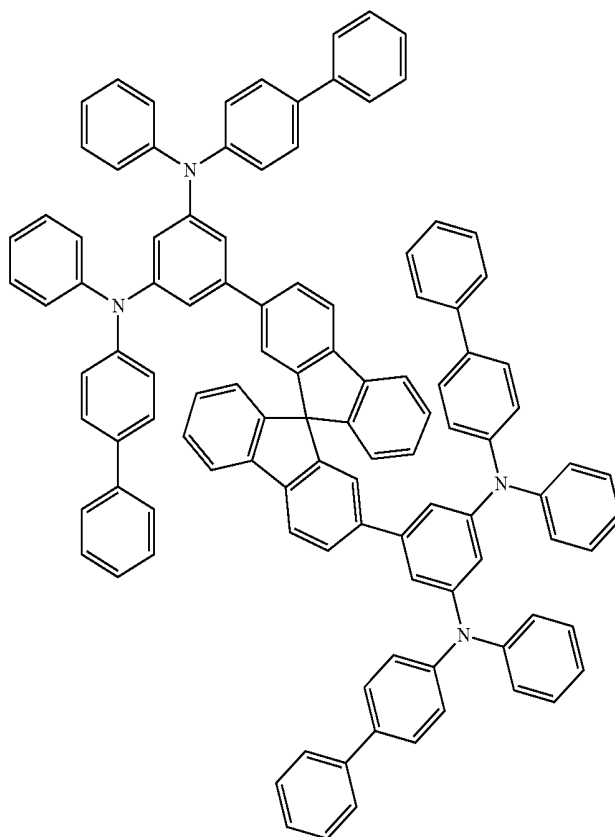
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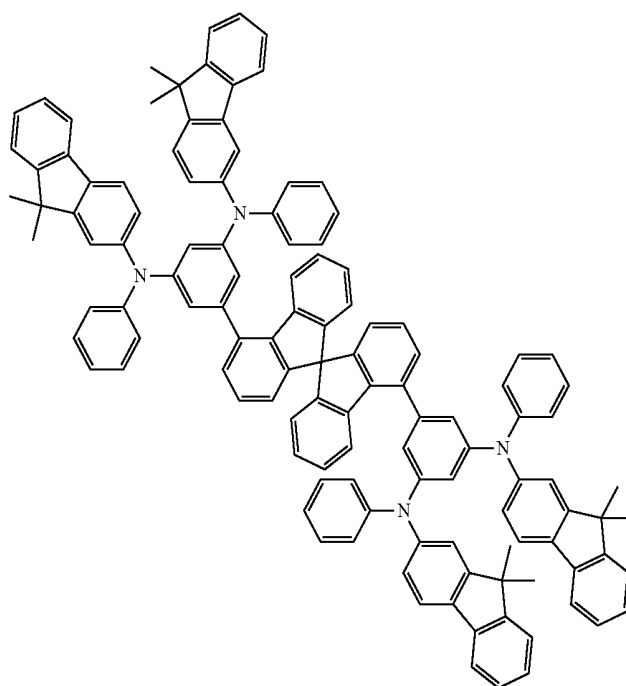
1-20

77%



1-21

60%



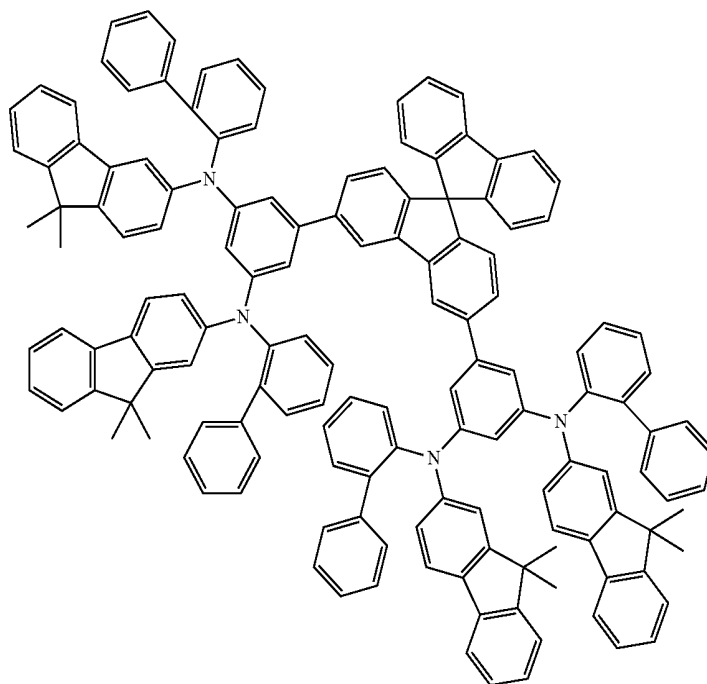
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1-22

64%





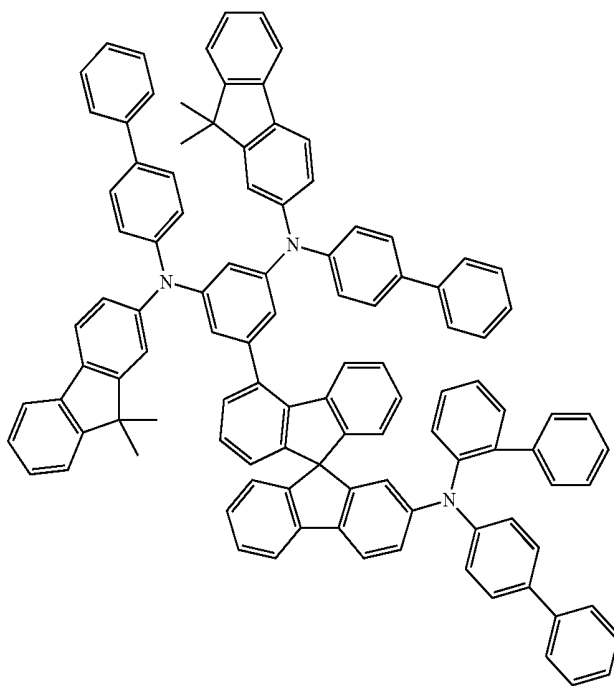


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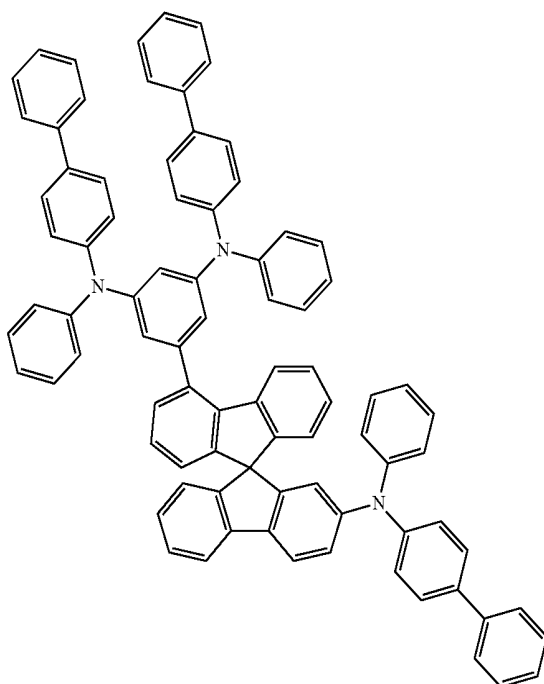
1-28

69%



1-29

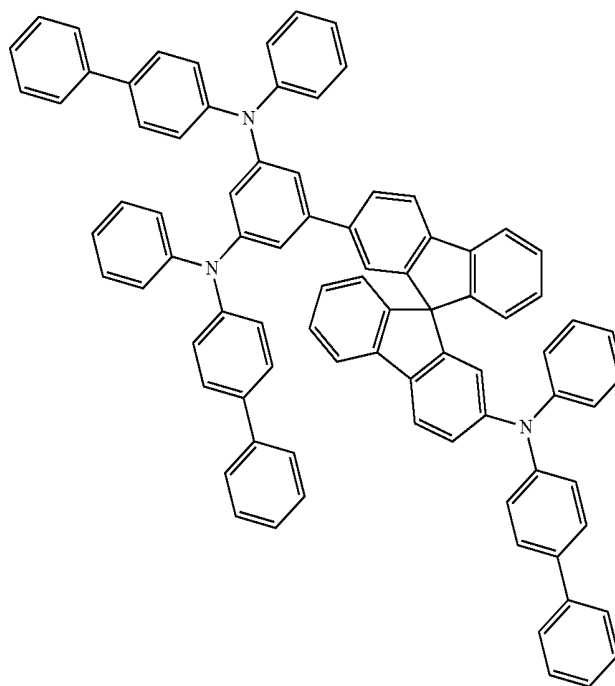
73%



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1-30

60%



### B) Device Examples

**[0145]** OLEDs according to the invention and OLEDs in accordance with the prior art are produced by a general process in accordance with WO2004/058911, which is adapted to the circumstances described here (layer-thickness variation, materials).

**[0146]** The substrates used are glass plates coated with structured ITO (indium tin oxide) in a thickness of 50 nm. The OLEDs basically have the following layer structure: substrate/hole-injection layer (HIL)/hole-transport layer (HTL)/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 100 nm. The precise structure of the OLEDs is pointed out at each experiment described below. The structures of the materials used for the production of the OLEDs are shown in Table 1.

**[0147]** All materials are applied by thermal vapour deposition in a vacuum chamber. The emission layer 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 coevaporation. An expression such as H1:SEB (5%) means that material H1 is present in the layer in a proportion by volume of 95% and SEB is present in the layer in a proportion of 5%. A layer composition, where only the percentage of the second material is given adds up to 100%

with the percentage of the first material. Analogously, the electron-transport layer may also consist of a mixture of two materials.

**[0148]** The OLEDs are characterised by standard methods. For this purpose, the external quantum efficiency (EQE, measured in percent) as a function of the luminous density, calculated from current/voltage/luminous density characteristic lines (IUL characteristic lines) assuming Lambertian emission characteristics, and the lifetime are determined. The expression EQE @ 10 mA/cm<sup>2</sup> denotes the external quantum efficiency at an operating luminous density of 10 mA/cm<sup>2</sup>. LT80 @ 60 mA/cm<sup>2</sup> is defined as the time until the luminance of the OLED device drops to 80% of its initial luminous intensity at a constant driving current density of 60 mA/cm<sup>2</sup>. The data obtained for the various OLEDs are summarised in the text below.

### Use of Compounds According to the Invention as Hole-Transport Materials in Fluorescent OLEDs

**[0149]** 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. The samples comprising the compounds according to the invention exhibit both high efficiency (Table 2 and 3) and also high lifetime (Table 3).

TABLE 1

Structures of the materials used

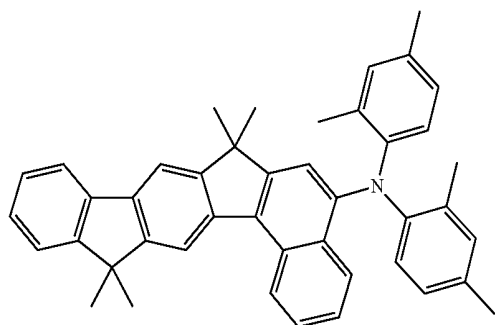
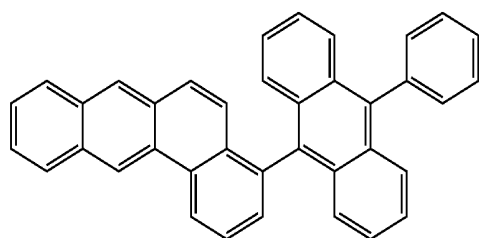
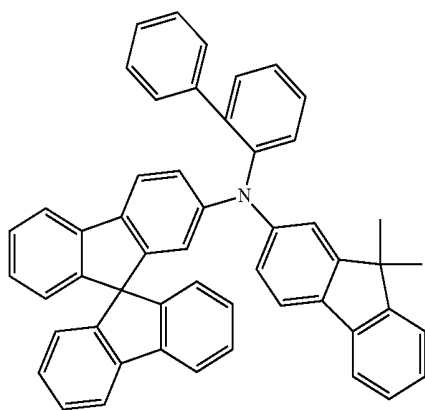
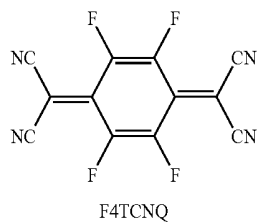
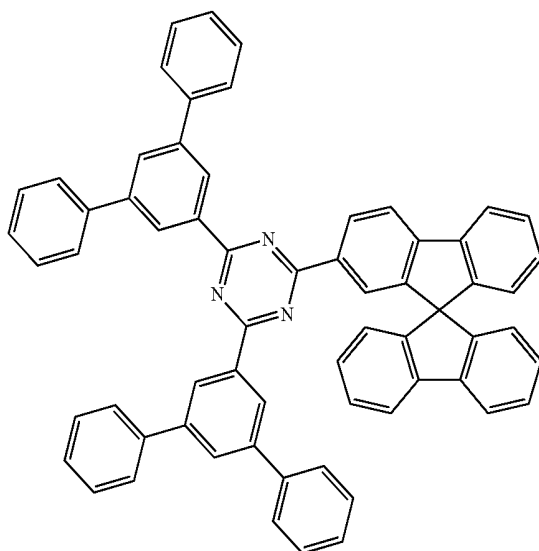
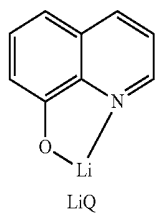


TABLE 1-continued

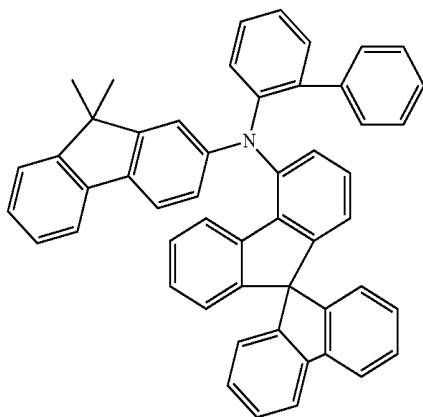
Structures of the materials used



ETM



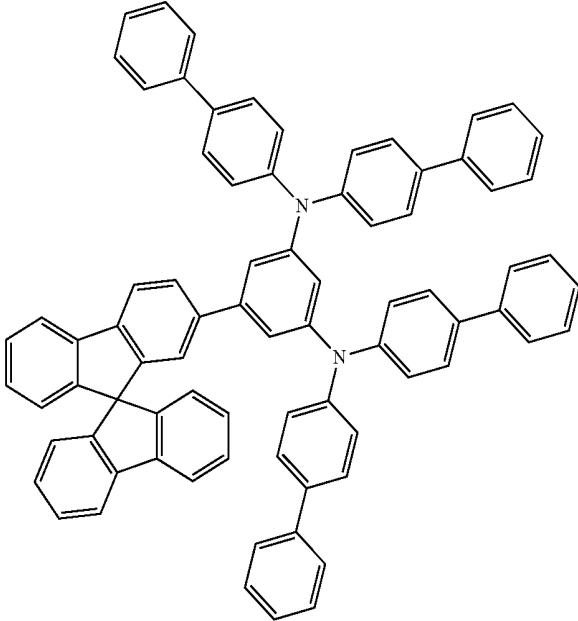
LiQ



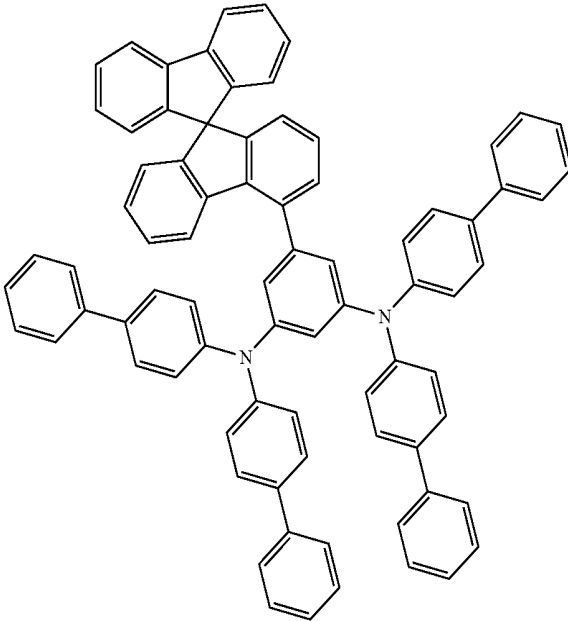
HTM

TABLE 1-continued

Structures of the materials used



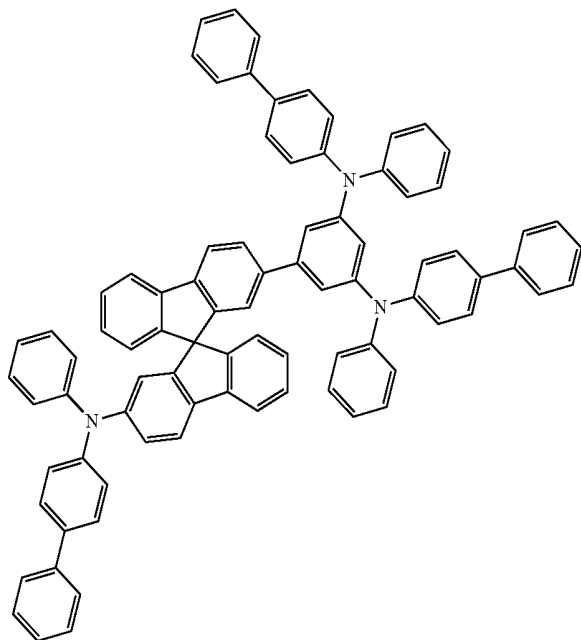
HTM1



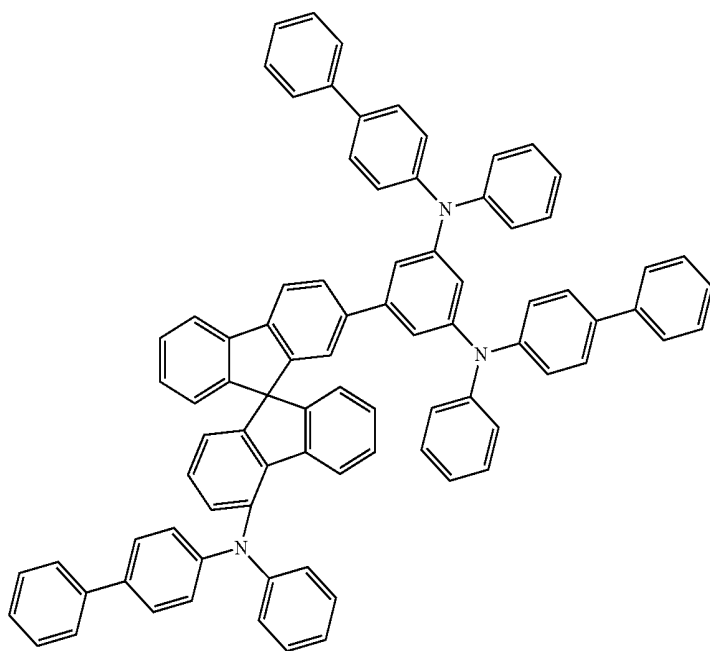
HTM2

TABLE 1-continued

Structures of the materials used



HTM3



HTM4

## Example 1

**[0150]** Singlet blue devices with the following structures (E1, E2, E3 and E4) were produced:

TABLE 2

Structure of the OLEDs and results				
Layer type [Thickness (nm)]	E1	E2	E3	E4
HIL	HIM:F4TCNQ	HIM:F4TCNQ	HIM:F4TCNQ	HIM:F4TCNQ
[20]	(5%)	(5%)	(5%)	(5%)
HTL	HIM	HIM	HIM	HIM
[175]				
EBL	HTM1	HTM2	HTM3	HTM4
[20]				
EML	H1:SEB	H1:SEB	H1:SEB	H1:SEB
[20]	(5%)	(5%)	(5%)	(5%)
ETL	ETM:LiQ	ETM:LiQ	ETM:LiQ	ETM:LiQ
[30]	(50%)	(50%)	(50%)	(50%)
EIL	LiQ	LiQ	LiQ	LiQ
[1]				
EQE@10 mA/ cm <sup>2</sup> (%)	8.3	8.9	9.0	9.3

**[0151]** Further singlet blue devices with the structures E5 and E6 were produced:

TABLE 3

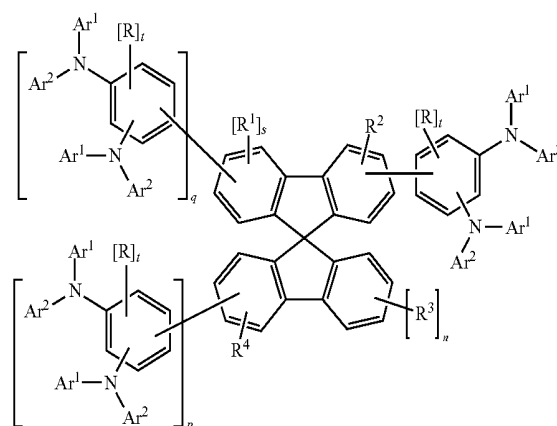
Structure of the OLEDs and results		
Layer type [Thickness (nm)]	E5	E6
HIL	HTM1:F4TCNQ	HTM2:F4TCNQ
[20]	(5%)	(5%)
HTL	HTM1	HTM2
[180]		
EBL	HTM	HTM
[10]		
EML	H1:SEB	H1:SEB
[20]	(5%)	(5%)
ETL	ETM:LiQ	ETM:LiQ
[30]	(50%)	(50%)
EIL	LiQ	LiQ
[1]		
EQE @ 10 mA/cm <sup>2</sup> (%)	7.8	8.0
LT80 @ 60 mA/cm <sup>2</sup> (h)	360	370

**[0152]** All devices exhibit an operating voltage of 3.9V-4.0V at a driving current density of 10 mA/cm<sup>2</sup>.

**1.-18.** (canceled)

**19.** A compound of formula (1):

formula (1)



where the following applies to the symbols and indices used:

Ar<sup>1</sup>, Ar<sup>2</sup> is on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 6 C aromatic ring atoms, which may in each case also be substituted by one or more radicals R<sup>5</sup>, Ar<sup>1</sup> and Ar<sup>2</sup> here may also be connected to one another by a group E;

E is on each occurrence, identically or differently, a single bond, N(R<sup>5</sup>), O, S, C(R<sup>5</sup>)<sub>2</sub>, C(R<sup>5</sup>)<sub>2</sub>-C(R<sup>5</sup>)<sub>2</sub>, Si(R<sup>5</sup>)<sub>2</sub> or B(R<sup>5</sup>);

$R^1, R^2, R^3, R^4$  are selected on each occurrence, identically or differently, from the group consisting of D, F, Cl, Br, I, CN,  $Si(R^6)_3$ ,  $N(R^6)_2$ , 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  $R^6$ , where in each case one or more non-adjacent  $CH_2$  groups may be replaced by  $Si(R^6)_2$ ,  $C=NR^6$ ,  $P(=O)(R^6)$ , SO,  $SO_2$ ,  $NR^6$ , O, S or  $CONR^6$  and where one or more H atoms may be replaced by D, F, Cl, Br or I, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , an aryloxy or heteroaryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals  $R^6$ , or an aralkyl or heteroaralkyl group having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , where two or more adjacent substituents  $R^1$  or  $R^2$  or  $R^3$  or  $R^4$  may optionally form a mono- or polycyclic ring system, which may be substituted by one or more radicals  $R^6$ ;

R is selected on each occurrence, identically or differently, from the group consisting of D, F, Cl, Br, I, CN,  $Si(R^6)_3$ , 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  $R^6$ , where in each case one or more non-adjacent  $CH_2$  groups may be replaced by  $Si(R^6)_2$ ,  $C=NR^6$ ,  $P(=O)(R^6)$ , SO,  $SO_2$ ,  $NR^6$ , O, S or  $CONR^6$  and where one or more H atoms may be replaced by D, F, Cl, Br or I, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , an aryloxy or heteroaryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals  $R^6$ , or an aralkyl or heteroaralkyl group having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , where two or more adjacent substituents  $R^5$  may optionally form a mono- or polycyclic ring system, which may be substituted by one or more radicals  $R^6$ ;

$R^5$  is selected on each occurrence, identically or differently, from the group consisting of H, D, F, Cl, Br, I, CN,  $Si(R^6)_3$ ,  $N(R^6)_2$ , 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  $R^6$ , where in each case one or more non-adjacent  $CH_2$  groups may be replaced by  $Si(R^6)_2$ ,  $C=NR^6$ ,  $P(=O)(R^6)$ , SO,  $SO_2$ ,  $NR^6$ , O, S or  $CONR^6$  and where one or more H atoms may be replaced by D, F, Cl, Br or I, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , an aryloxy or heteroaryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals  $R^6$ , or an aralkyl or heteroaralkyl group having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ , where two or

more adjacent substituents  $R^5$  may optionally form a mono- or polycyclic ring system, which may be substituted by one or more radicals  $R^6$ ;

$R^6$  is selected from the group consisting of H, D, F, an aliphatic hydrocarbon radical having 1 to 20 C atoms or an aromatic or heteroaromatic ring system having 5 to 30 C atoms, in which one or more H atoms may be replaced by D or F, where two or more adjacent substituents  $R^6$  may form a mono- or polycyclic ring system with one another;

m is 0, 1, 2 or 3;

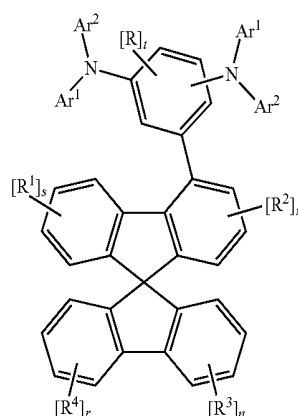
n is 0, 1, 2, 3 or 4;

p, q are, identically or differently, 0 or 1;

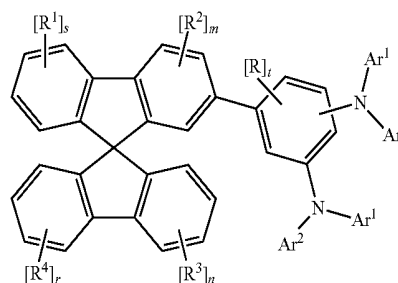
r, s are, identically or differently, 0, 1, 2, 3 or 4; where  $p+r \leq 4$  and  $q+s \leq 4$ ;

t is, on each occurrence, identically or differently, 0, 1, 2 or 3.

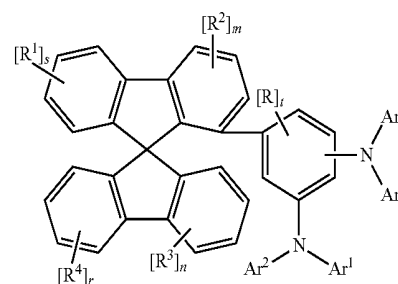
20. The compound according to claim 19, selected from compounds of the following formulae (2) to (9),



formula (2)

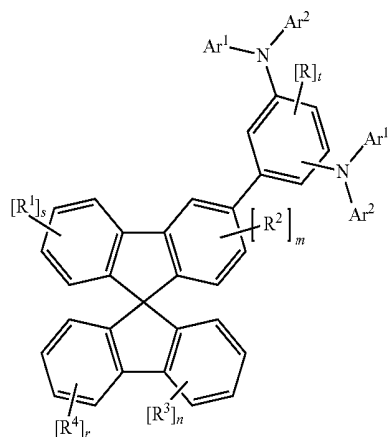


formula (3)



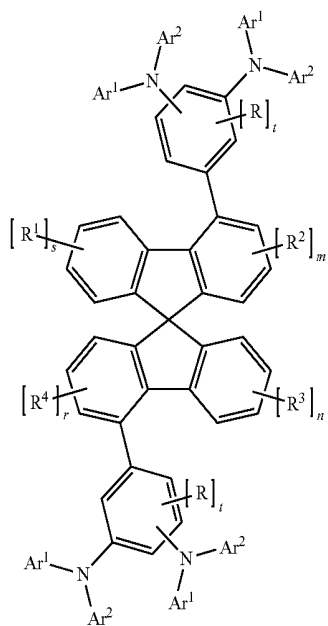
formula (4)

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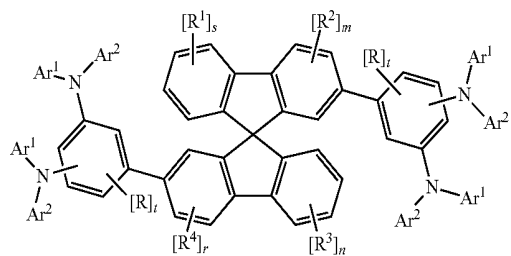


formula (5)

formula (6)

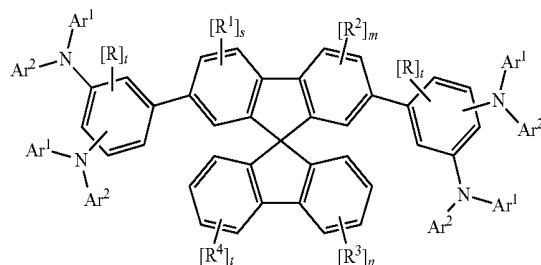


formula (7)

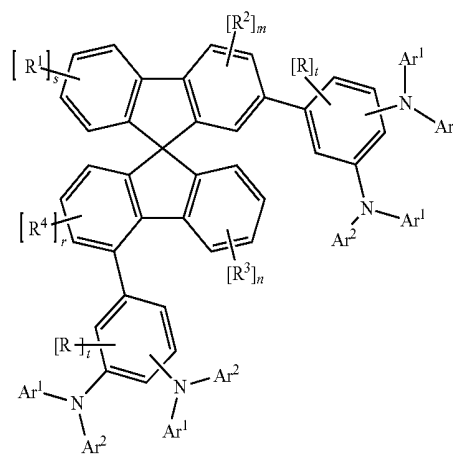


-continued

formula (8)



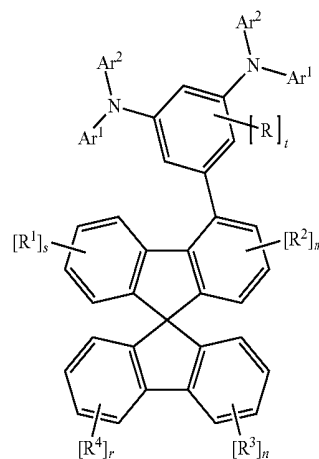
formula (9)



formula (2a)

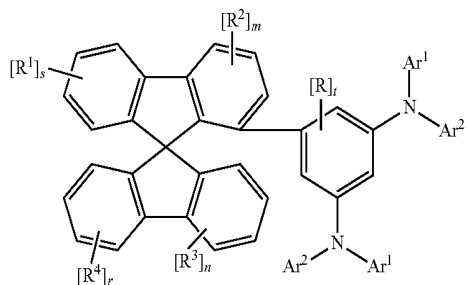
where the symbols and indices used are defined as in claim 19.

21. The compound according to claim 19, selected from compounds of the following formulae (2a) to (9a),



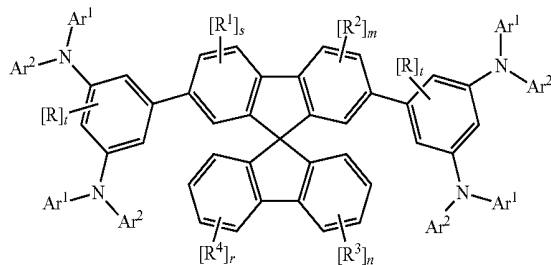
formula (3a)

-continued



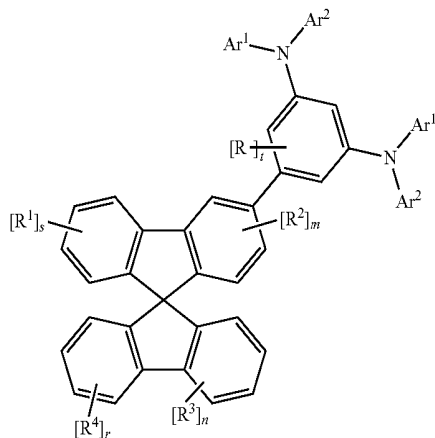
formula (4a)

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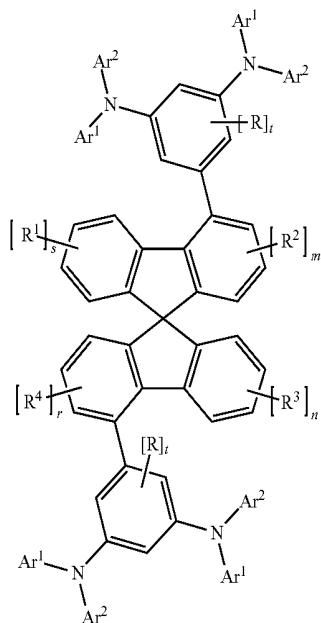


formula (8a)

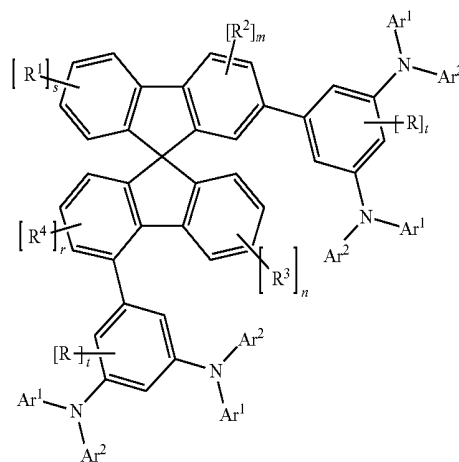
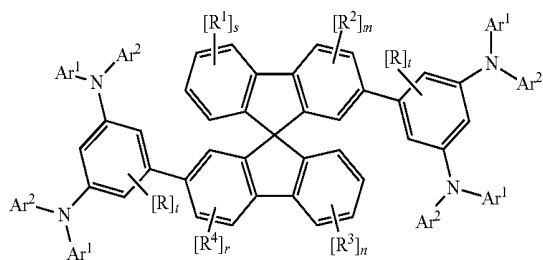
formula (5a)



formula (6a)



formula (7a)

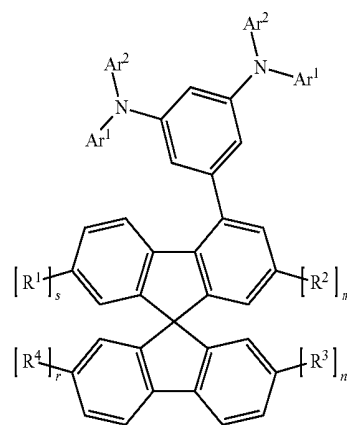


formula (9a)

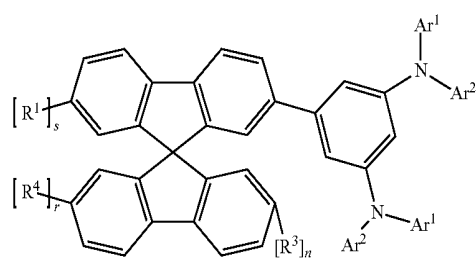
where the symbols and indices used are defined as in claim 19.

22. The compound according to claim 19, selected from compounds of the following formulae (2b) to (9b),

formula (2b)

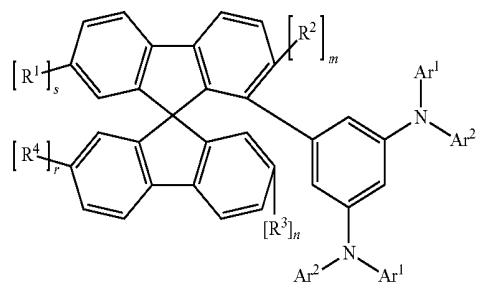


formula (3b)

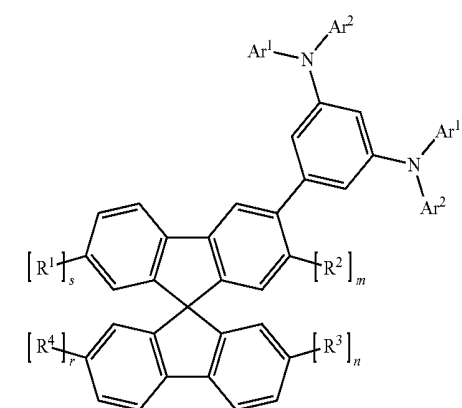


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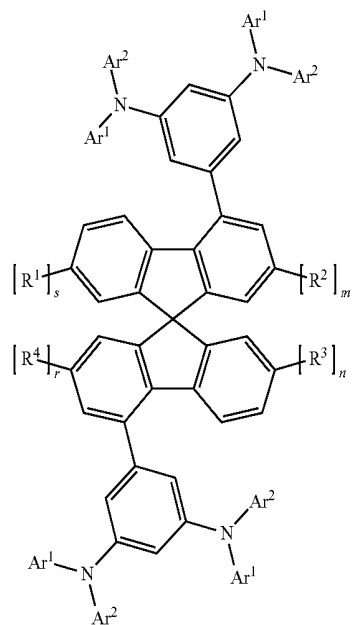
formula (4b)



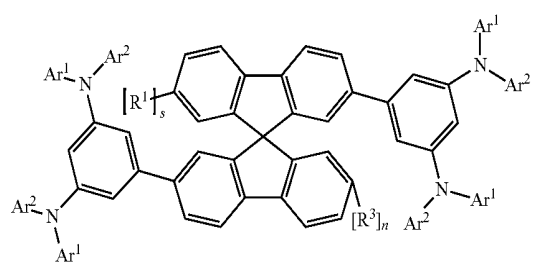
formula (5b)



formula (6b)

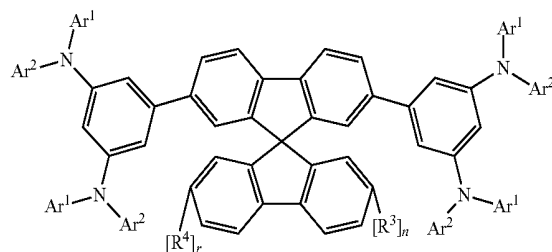


formula (7b)

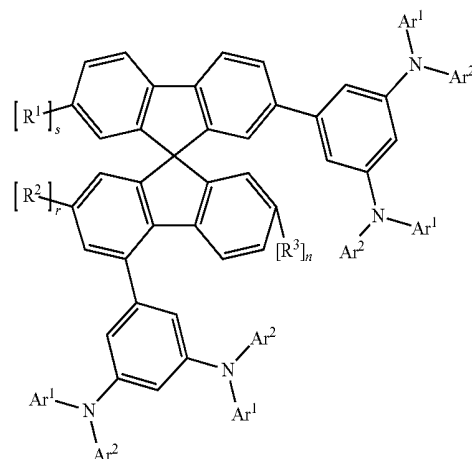


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formula (8b)



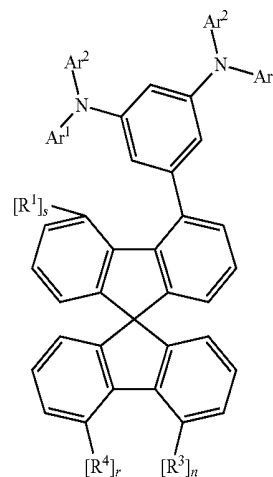
formula (9b)



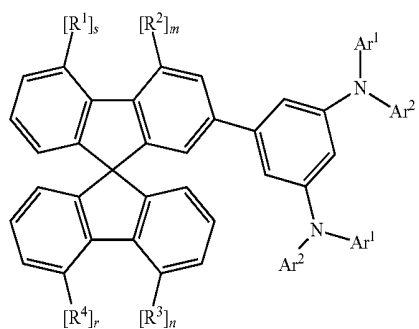
where  $m$ ,  $n$ ,  $r$  and  $s$  are, identically or differently, 0 or 1;  
and the other symbols used are defined as claim 19.

23. The compound according to claim 19, selected from compounds of the following formula (2c) or (9c),

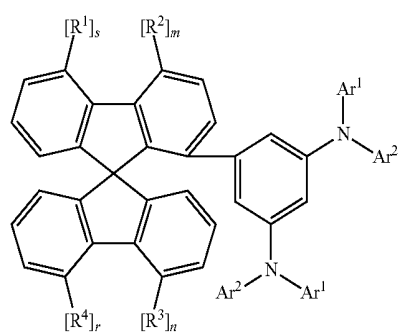
formula (2c)



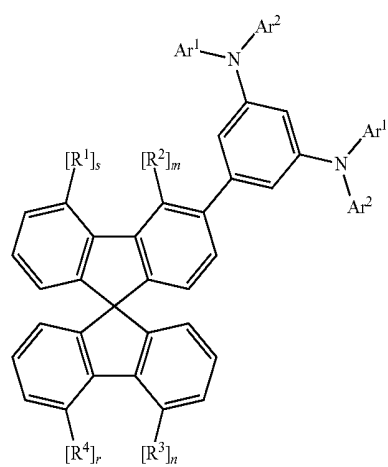
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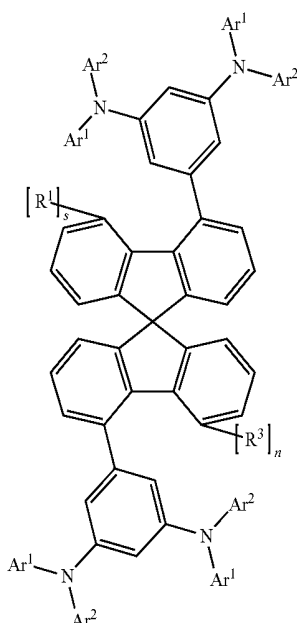
formula (3c)



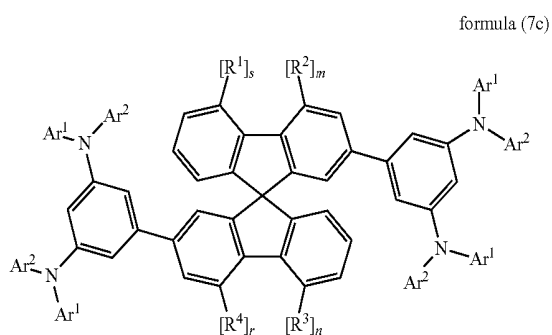
formula (4c)



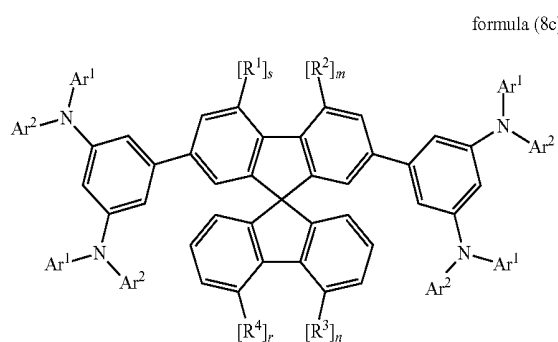
formula (5c)



formula (6c)

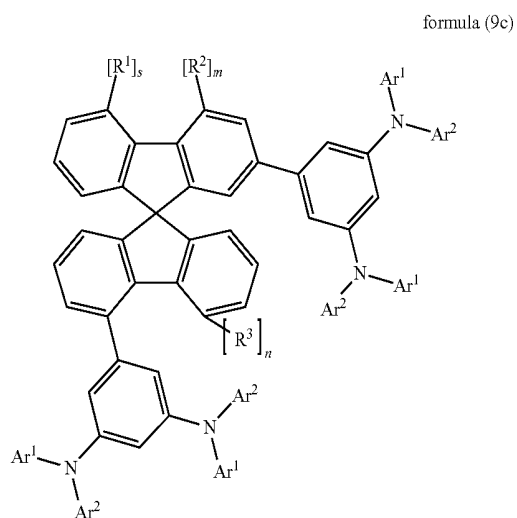


formula (7c)



formula (8c)

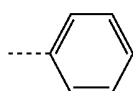
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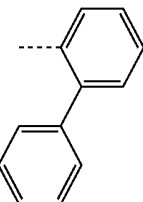
where  $m$ ,  $n$ ,  $r$  and  $s$  are, identically or differently, 0 or 1;  
and the other symbols used are defined as claim 19.

24. The compound according to claim 19, wherein at least one of the groups  $Ar^1$  and  $Ar^2$  is selected, identically or differently, on each occurrence, from phenyl, fluorenyl, spirobifluorenyl, biphenyl, terphenyl, quaterphenyl, carbazoyl, dibenzofuranyl and dibenzothiophenyl, each of which may be substituted by one or more radicals  $R^5$ .

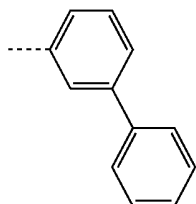
25. Compound according to claim 19, wherein at least one of the groups  $Ar^1$  and  $Ar^2$  are selected, identically or differently on each occurrence, from the groups of the following formulae (10) to (66),



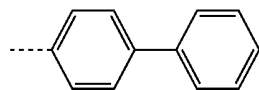
formula (10)



formula (11)

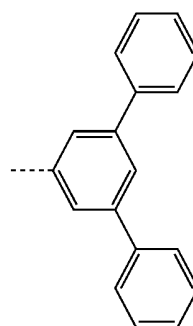


formula (12)

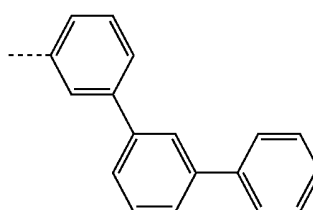


formula (13)

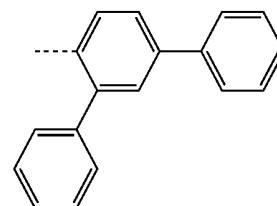
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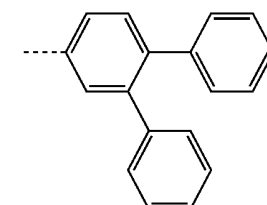
formula (14)



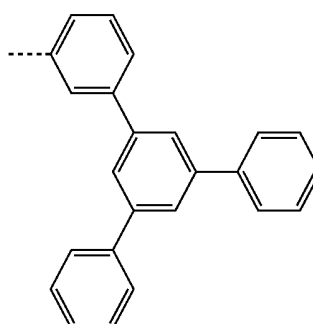
formula (15)



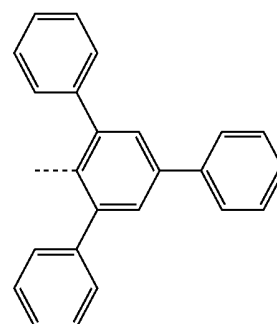
formula (16)



formula (17)

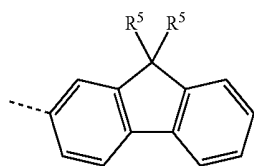


formula (18)

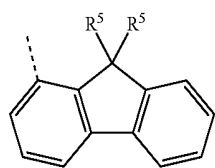


formula (19)

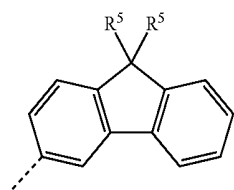
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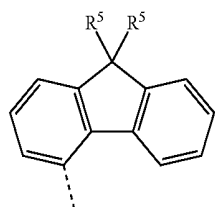
formula (20)



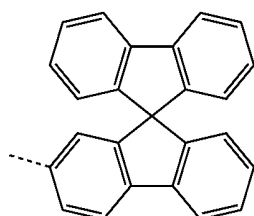
formula (21)



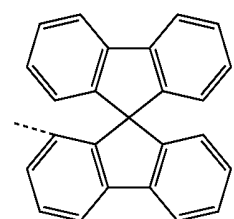
formula (22)



formula (23)

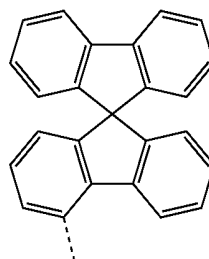


formula (24)

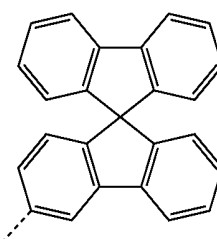


formula (25)

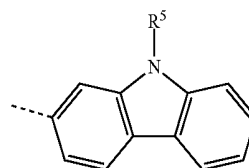
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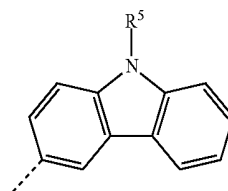
formula (26)



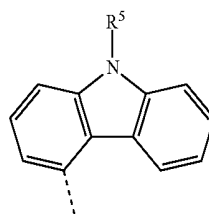
formula (27)



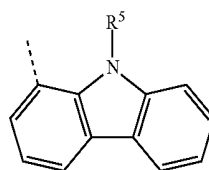
formula (28)



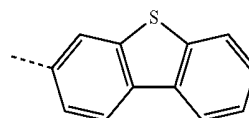
formula (29)



formula (30)

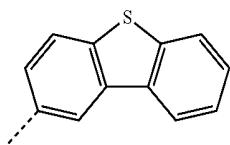


formula (31)

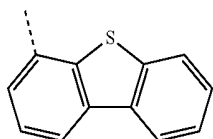


formula (32)

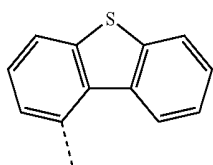
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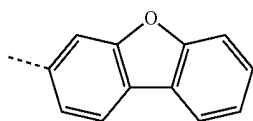
formula (33)



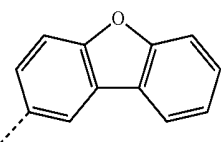
formula (34)



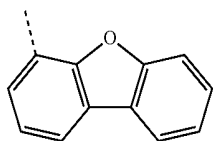
formula (35)



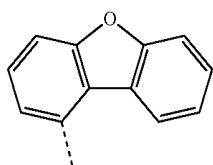
formula (36)



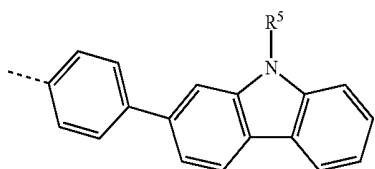
formula (37)



formula (38)

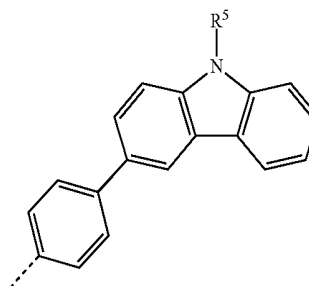


formula (39)

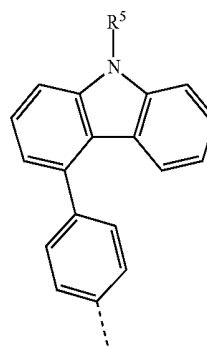


formula (40)

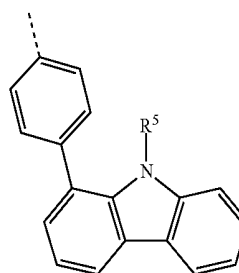
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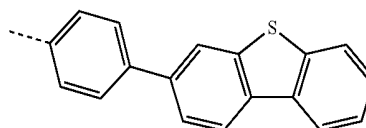
formula (41)



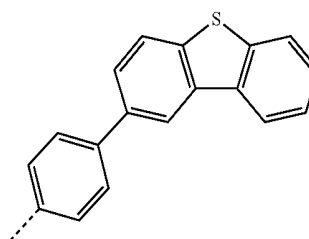
formula (42)



formula (43)

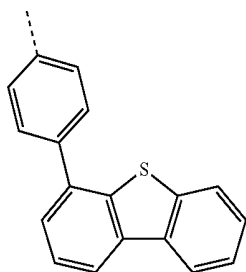


formula (44)

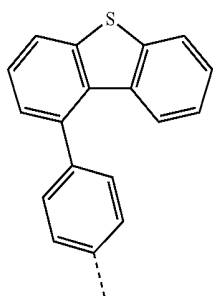


formula (45)

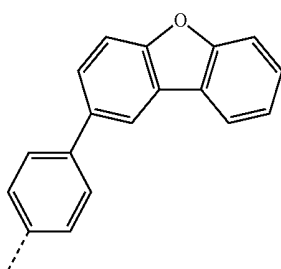
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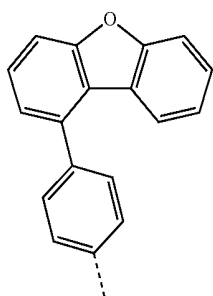
formula (46)



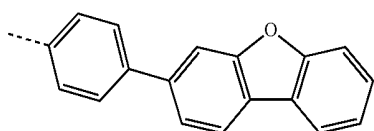
formula (47)



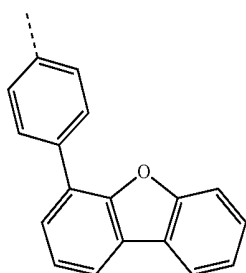
formula (48)



formula (49)

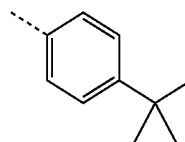


formula (50)

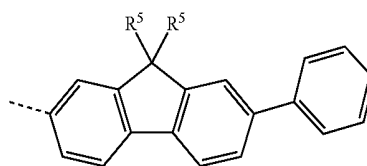


formula (51)

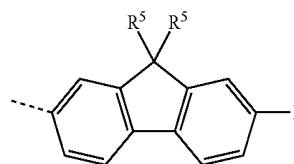
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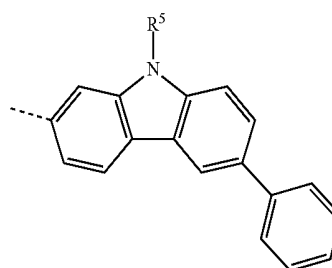
formula (52)



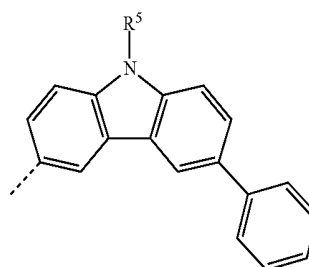
formula (53)



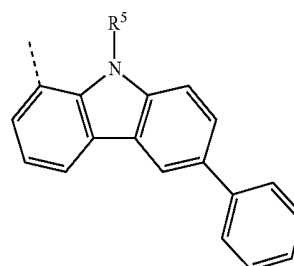
formula (54)



formula (55)

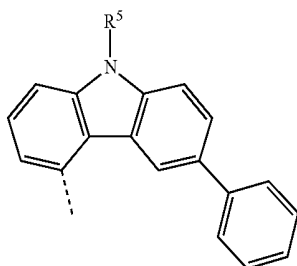


formula (56)



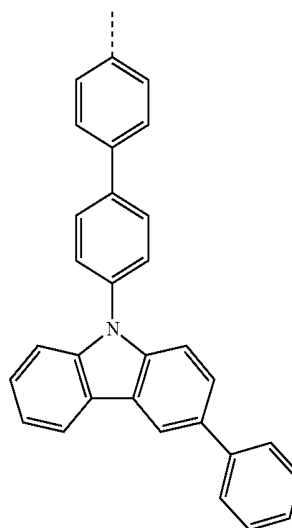
formula (57)

-continued



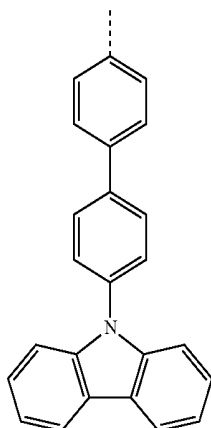
formula (58)

-continued



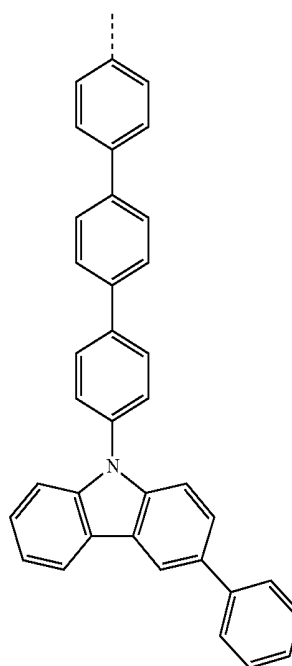
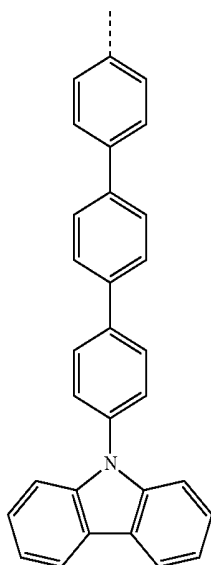
formula (61)

formula (59)

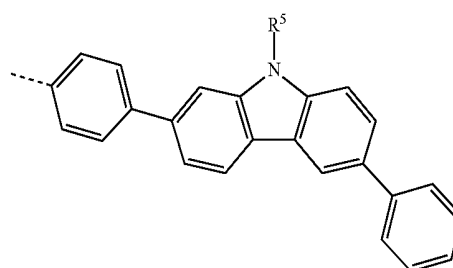


formula (62)

formula (60)

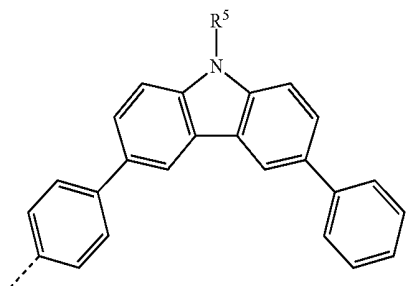


formula (63)

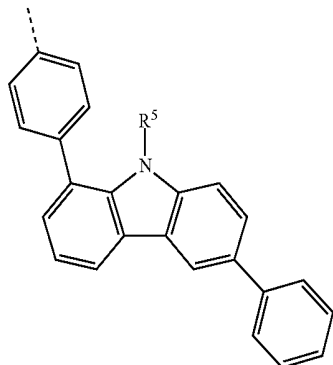


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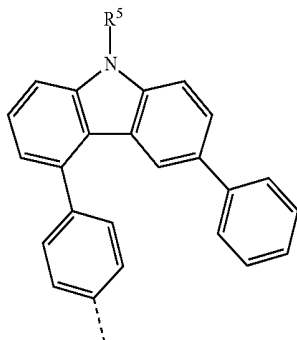
formula (64)



formula (65)



formula (66)



where the dashed bond indicates the bond to the nitrogen, and the groups may be substituted by one or more radicals  $R^5$ .

26. The compound according to claim 19, wherein the groups  $Ar^1$  and  $Ar^2$  are selected identically.

27. The compound according to claim 19, wherein the groups  $Ar^1$  and  $Ar^2$  are selected differently from one another.

28. The compound according to claim 19, wherein  $R^1$  to  $R^4$  are selected, identically or differently on each occurrence, from the group consisting of 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  $R^6$ , 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, or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ .

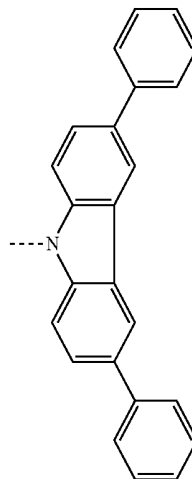
29. The compound according to claim 19, wherein the radical  $R^5$  which is bonded to  $Ar^1$  or  $Ar^2$  is selected, identically or differently on each occurrence, from the group consisting of H, F, CN,  $N(R^6)_2$ , a straight-chain alkyl group having 1 to 10 C atoms, a branched or cyclic alkyl group having 3 to 10 C atoms or an aromatic or heteroaromatic ring

system having 5 to 24 aromatic ring atoms, each of which may be substituted by one or more radicals  $R^6$ .

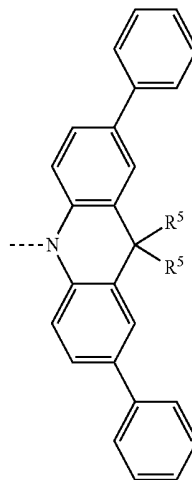
30. The compound according to claim 19, wherein:

$Ar^1$ ,  $Ar^2$  are, identically or differently, a group of one of the formulae (10) to (66); or  $-NAr^1Ar^2$  stands for a group of one of the formulae (67) to (74);

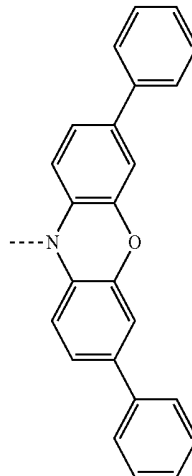
formula (67)



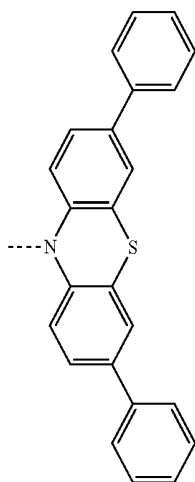
formula (68)



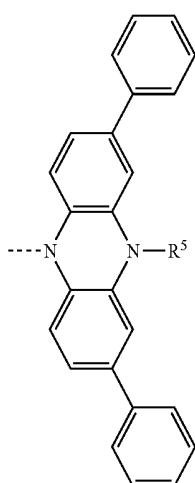
formula (69)



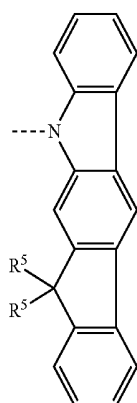
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formula (70)

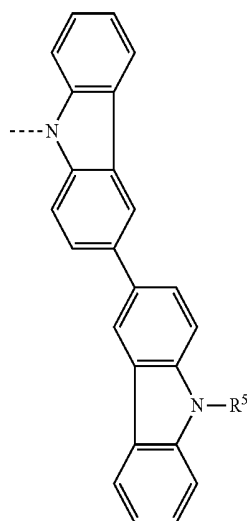


formula (71)

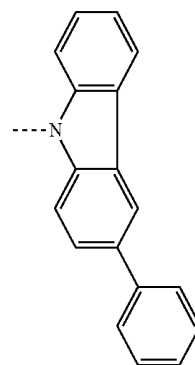


formula (72)

-continued



formula (73)



formula (74)

E is on each occurrence, identically or differently, a single bond or  $C(R^5)_2$ ,  $N(R^5)$ , O or S;

$R^1$  to  $R^4$  are selected, identically or differently on each occurrence, from the group consisting of H, 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  $R^6$ , 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, or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ ;

R is selected, identically or differently on each occurrence, from the group consisting of 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  $R^6$ , 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, or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, which may in each case be substituted by one or more radicals  $R^6$ .

$R^5$  is, if the radical  $R^5$  is bonded to  $Ar^1$  or  $Ar^2$ , selected, identically or differently on each occurrence, from the group consisting of H, F, CN,  $N(R^6)_2$ , a straight-chain alkyl group having 1 to 10 C atoms, a branched or cyclic alkyl group having 3 to 10 C atoms or an

aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, each of which may be substituted by one or more radicals  $R^6$ ;

or  $R^5$  which is bonded to the carbon bridge in the formulae (20) to (23), (53), (54), (68) and (72) is, identically or differently, an alkyl group having 1 to 10 C atoms, or a phenyl group, which may be substituted by one or more radicals  $R^6$ ;

or  $R^5$  which is bonded to the nitrogen bridge in the formulae (28) to (31), (40) to (43) or (55) to (58), (63) to (66), (71) and (73) is a phenyl group, which may be substituted by one or more radicals  $R^6$ ;

$R^6$  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 or an aromatic ring system having 5 to 24 C atoms;

m is 0 or 1;

n is 0 or 1;

p+q is 0 or 1;

r is 0 or 1;

s is 0 or 1;

t is 0 or 1.

**31.** An oligomer, a polymers or a dendrimer comprising one or more compounds according to claim **19**, where the bond(s) to the polymer, oligomer or dendrimers may be localised at any desired positions in formula (I).

**32.** A formulation comprising at least one compound according to claim **19** and at least one solvent.

**33.** A process for the preparation of a compound according to claim **19**, comprising a C—C Suzuki coupling reaction between a spirobifluorene boronic ester derivative and an halogenated diaminobenzene.

**34.** A method comprising utilizing the compound according to claim **19** in an electronic device.

**35.** An electronic device comprising at least one compound according to claim **19**, 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, organic dye-sensitised solar cells, organic optical detectors, organic photoreceptors, organic field-quench devices, light-emitting electrochemical cells, organic laser diodes and organic plasmon emitting devices.

**36.** The electronic device according to claim **35**, selected from organic electroluminescent devices, wherein the compound according to claim **19** is comprised as hole-transport material in a hole-transport or hole-injection or exciton-blocking or electron-blocking layer, or is comprised as matrix material for fluorescent or phosphorescent emitters in an emitting layer.

\* \* \* \* \*

专利名称(译)	用于有机电致发光器件的材料		
公开(公告)号	<a href="#">US20170338414A1</a>	公开(公告)日	2017-11-23
申请号	US15/526909	申请日	2015-10-23
申请(专利权)人(译)	MERCK PATENT GMBH		
当前申请(专利权)人(译)	MERCK PATENT GMBH		
[标]发明人	MUJICA FERNAUD TERESA MONTENEGRO ELVIRA PFISTER JOCHEN		
发明人	MUJICA-FERNAUD, TERESA MONTENEGRO, ELVIRA PFISTER, JOCHEN		
IPC分类号	H01L51/00 C07D333/76 C07D307/91 C07D219/14 C07D209/86 C07C217/92 C07C211/61 H01L51/50 C07C211/54		
CPC分类号	H01L51/0032 H01L51/5088 H01L51/5096 C07D333/76 C07C217/92 C07D209/86 C07C211/54 C07C211/61 C07D219/14 C07D307/91 H01L51/0052 H01L51/0059 H01L51/006 H01L51/0061 H01L51/0072 H01L51/0073 H01L51/0074 H01L51/5056 C07C2603/18 C07C2603/94 Y02E10/549 H01L51/0056		
其他公开文献	US10510960		
外部链接	<a href="#">Espacenet</a> <a href="#">USPTO</a>		

摘要(译)

本发明涉及式(1)化合物,其适用于电子器件,特别是有机电致发光器件,并涉及包含这些化合物的电子器件。

formula (1)

