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Pfister et al.

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(54) **MATERIALS FOR ELECTRONIC DEVICES**

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H01L 51/5016 (2013.01); Y02E 10/549
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(71) Applicant: **Merck Patent GmbH**, Darmstadt (DE)

(72) Inventors: **Jochen Pfister**, Seeheim-Jugenheim (DE); **Frank Stieber**, Einhausen (DE); **Elvira Montenegro**, Weinheim (DE); **Teresa Mujica-Fernaud**, Darmstadt (DE)

(58) **Field of Classification Search**

CPC H01L 51/0058; H01L 51/006; H01L 51/0061; H01L 51/0074; H01L 51/5012; H01L 51/5016; H01L 51/5056; H01L 51/506

See application file for complete search history.

(73) Assignee: **Merck Patent GmbH**, Darmstadt (DE)

(56) **References Cited**

U.S. PATENT DOCUMENTS

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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257/40

(21) Appl. No.: **15/538,277**

FOREIGN PATENT DOCUMENTS

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(65) **Prior Publication Data**

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(30) **Foreign Application Priority Data**

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Primary Examiner — Stephen W Smoot

(74) *Attorney, Agent, or Firm* — Drinker Biddle & Reath LLP

(51) **Int. Cl.**

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H01L 51/00 (2006.01)

H01L 51/05 (2006.01)

H01L 51/42 (2006.01)

(57) **ABSTRACT**

The present application relates to spirobifluorene derivatives of a formula (I), to the use thereof in electronic devices, especially in organic electroluminescent devices (OLEDs), where they may be used in hole-transporting function, and to processes for preparing said derivatives. The compounds have one or more properties selected from very good hole-conducting properties, very good electron-blocking properties, high glass transition temperature, high oxidation stability, good solubility and high thermal stability.

(52) **U.S. Cl.**

CPC **H01L 51/0074** (2013.01); **H01L 51/006** (2013.01); **H01L 51/0058** (2013.01); **H01L 51/0059** (2013.01); **H01L 51/0061** (2013.01); **H01L 51/506** (2013.01); **H01L 51/5012** (2013.01); **H01L 51/5056** (2013.01); **H01L**

21 Claims, No Drawings

MATERIALS FOR ELECTRONIC DEVICES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a national stage application (under 35 U.S.C. § 371) of PCT/EP2015/002475, filed Dec. 8, 2015, which claims benefit of European Application No. 14004355.5, filed Dec. 22, 2014, both of which are incorporated herein by reference in their entirety.

The present application relates to a spirobifluorene derivative of a formula (I) defined hereinafter which is suitable for use in electronic devices, especially organic electroluminescent devices (OLEDs).

BACKGROUND OF THE INVENTION

Electronic devices in the context of this application are understood to mean what are called organic electronic devices, which contain organic semiconductor materials as functional materials. More particularly, these are understood to mean OLEDs.

The structure of OLEDs in which organic compounds are used 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. In general, the term OLEDs is understood to mean electronic devices which have one or more layers comprising organic compounds and emit light on application of electrical voltage.

In electronic devices, especially OLEDs, there is great interest in improving the performance data, especially lifetime, efficiency and operating voltage. In these aspects, it has not yet been possible to find any entirely satisfactory solution.

A great influence on the performance data of electronic devices is possessed by layers having a hole-transporting function, for example hole-injecting layers, hole transport layers, electron blocker layers and also emitting layers. For use in these layers, there is a continuous search for new materials having hole-transporting properties.

It is known in the prior art that triaryl amines can be used in these layers as materials having hole-transporting properties. The triaryl amines may be monoaryl amines as described, for example, in JP 1995/053955, WO 2006/123667 and JP 2010/222268, or bis- or other oligoamines, as described, for example, in U.S. Pat. No. 7,504,163 or US 2005/0184657. Known examples of triarylamine compounds as materials having hole-transporting properties for OLEDs include tris-*p*-biphenylamine, *N,N'*-di-1-naphthyl-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) and 4,4', 4''-tris(3-methylphenylphenylamino)triphenylamine (MT-DATA).

Additionally known in the prior art is the use of spirobifluorene-arylamino compounds in OLEDs, including as hole transport materials (WO 2012/034627 and WO 2013/120577).

BRIEF SUMMARY OF THE INVENTION

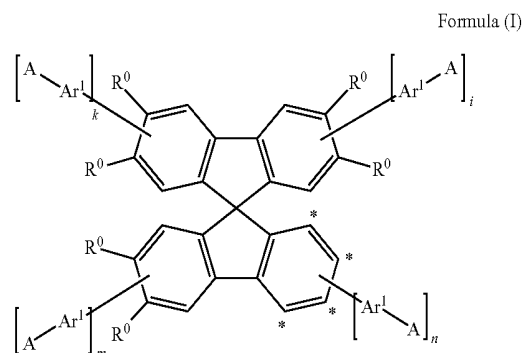
In the course of studies relating to novel materials for use in OLEDs, it has now been found that, surprisingly, compounds having an arylamine or carbazole group and having a spirobifluorene unit fused onto a benzothiophene unit are of outstanding suitability for use in OLEDs, especially as materials having hole-transporting function.

The compounds found have one or more properties selected from very good hole-conducting properties, very

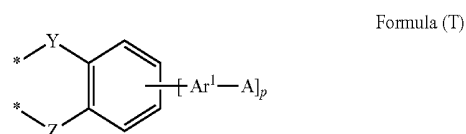
good electron-blocking properties, high glass transition temperature, high oxidation stability, good solubility and high thermal stability. When the compounds found are used in OLEDs, especially in hole-transporting function, very good device performance data, especially very good lifetime and quantum efficiency of the devices, are observed.

DETAILED DESCRIPTION OF THE INVENTION

The present invention therefore provides a compound of the formula (I)



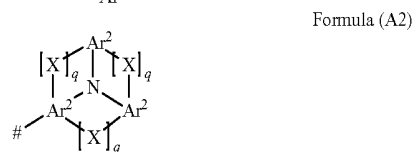
which has a group of the formula (T)



bonded at two adjacent positions marked by * to the base structure of formula (I), where the condensation is such that any bond marked by * in formula (T) is attached at a position marked by * to the base structure of formula (I)

which may be substituted at one or more positions shown as unsubstituted in the base structure of formula (I) and the group of the formula (T) by an R¹ radical; and which has the following definitions of the variables:

A is the same or different at each instance and is a group of the formula (A1), (A2) or (A3) which is bonded via the bond marked with # and may be substituted at one or more positions shown as unsubstituted by an R² radical;



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Ar¹ is the same or different at each instance and is a single bond or an aromatic or heteroaromatic ring system which has 6 to 30 aromatic ring atoms and may be substituted by one or more R² radicals;

Ar² is the same or different at each instance and is an aromatic or heteroaromatic ring system which has 6 to 30 aromatic ring atoms and may be substituted by one or more R² radicals;

X is the same or different at each instance and is a single bond or a group selected from BR², C(R²)₂, Si(R²)₂, C=O, O, S, S=O, SO₂, NR², PR² and P(=O)R²;

Y is selected from O, S and Se;

Z is selected from O, S, Se and a single bond, where Z is not a single bond when Y is O;

R⁰ is the same or different at each instance and is selected from H, D, F, CN, Si(R³)₃, straight-chain alkyl or alkoxy groups having 1 to 20 carbon atoms, branched or cyclic alkyl or alkoxy groups having 3 to 20 carbon atoms, alkenyl or alkynyl groups having 2 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms, and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where the alkyl, alkoxy, alkenyl and alkynyl groups mentioned and the aromatic ring systems and heteroaromatic ring systems mentioned may each be substituted by one or more R³ radicals; and where one or more CH₂ groups in the alkyl, alkoxy, alkenyl and alkynyl groups mentioned may be replaced by —R³C=CR³—, —C≡C—, Si(R³)₂, C=O, C=NR³, —C(=O)O—, —C(=O)NR³—, NR³, P(=O)(R³), —O—, —S—, SO or SO₂;

R¹ is the same or different at each instance and is selected from H, D, F, C(=O)R³, CN, Si(R³)₃, P(=O)(R³)₂, OR³, S(=O)R³, S(=O)₂R³, straight-chain alkyl or alkoxy groups having 1 to 20 carbon atoms, branched or cyclic alkyl or alkoxy groups having 3 to 20 carbon atoms, alkenyl or alkynyl groups having 2 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms, and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more R¹ radicals may be joined to one another and may form a ring; where the alkyl, alkoxy, alkenyl and alkynyl groups mentioned and the aromatic ring systems and heteroaromatic ring systems mentioned may each be substituted by one or more R³ radicals; and where one or more CH₂ groups in the alkyl, alkoxy, alkenyl and alkynyl groups mentioned may be replaced by —R³C=CR³—, —C≡C—, Si(R³)₂, C=O, C=NR³, —C(=O)O—, —C(=O)NR³—, NR³, P(=O)(R³), —O—, —S—, SO or SO₂;

R² is the same or different at each instance and is selected from H, D, F, C(=O)R³, CN, Si(R³)₃, N(R³)₂, P(=O)(R³)₂, OR³, S(=O)R³, S(=O)₂R³, straight-chain alkyl or alkoxy groups having 1 to 20 carbon atoms, branched or cyclic alkyl or alkoxy groups having 3 to 20 carbon atoms, alkenyl or alkynyl groups having 2 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms, and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more R² radicals may be joined to one another and may form a ring; where the alkyl, alkoxy, alkenyl and alkynyl groups mentioned and the aromatic ring systems and heteroaromatic ring systems mentioned may each be substituted by one or more R³ radicals; and where one or more CH₂ groups in the alkyl, alkoxy, alkenyl and alkynyl groups mentioned may be replaced by —R³C=CR³—, —C≡C—, Si(R³)₂, C=O, C=NR³,

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—C(=O)O—, —C(=O)NR³—, NR³, P(=O)(R³), —O—, —S—, SO or SO₂;

R³ is the same or different at each instance and is selected from H, D, F, C(=O)R⁴, CN, Si(R⁴)₃, N(R⁴)₂, P(=O)(R⁴)₂, OR⁴, S(=O)R⁴, S(=O)₂R⁴, straight-chain alkyl or alkoxy groups having 1 to 20 carbon atoms, branched or cyclic alkyl or alkoxy groups having 3 to 20 carbon atoms, alkenyl or alkynyl groups having 2 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms, and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more R¹ or R² radicals may be joined to one another and may form a ring; where the alkyl, alkoxy, alkenyl and alkynyl groups mentioned and the aromatic ring systems and heteroaromatic ring systems mentioned may each be substituted by one or more R⁴ radicals; and where one or more CH₂ groups in the alkyl, alkoxy, alkenyl and alkynyl groups mentioned may be replaced by —R⁴C=CR⁴—, —C≡C—, Si(R⁴)₂, C=O, C=NR⁴, —C(=O)O—, —C(=O)NR⁴—, NR⁴, P(=O)(R⁴), —O—, —S—, SO or SO₂;

R⁴ is the same or different at each instance and is selected from H, D, F, CN, alkyl groups having 1 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more R⁴ radicals may be joined to one another and may form a ring; and where the alkyl groups, aromatic ring systems and heteroaromatic ring systems mentioned may be substituted by F or CN;

q is the same or different at each instance and is 0 or 1, where at least one q in formula (A2) is 1;

i, k, m, n and p are the same or different at each instance and are 0 or 1, where at least one of these indices is 1.

The groups in square brackets with the indices i, k, m, n and p may generally, and in the structures which follow as well, be bonded to the spirobifluorene base skeleton only in those positions shown as unsubstituted. More particularly, they cannot be bonded in positions that bear an R⁰ radical.

An aryl group in the context of this invention contains 6 to 40 aromatic ring atoms of which none is a heteroatom. An aryl group in the context of this invention is understood to mean either a simple aromatic cycle, i.e. benzene, or a fused aromatic polycycle, for example naphthalene, phenanthrene or anthracene. A fused aromatic polycycle in the context of the present application consists of two or more simple aromatic cycles fused to one another. Fusion between cycles is understood here to mean that the cycles share at least one edge with one another.

A heteroaryl group in the context of this invention contains 5 to 40 aromatic ring atoms of which at least one is a heteroatom. The heteroatoms of the heteroaryl group are preferably selected from N, O and S. A heteroaryl group in the context of this invention is understood to mean either a simple heteroaromatic cycle, for example pyridine, pyrimidine or thiophene, or a fused heteroaromatic polycycle, for example quinoline or carbazole. A fused heteroaromatic polycycle in the context of the present application consists of two or more simple heteroaromatic cycles fused to one another. Fusion between cycles is understood here to mean that the cycles share at least one edge with one another.

An aryl or heteroaryl group, each of which may be substituted by the abovementioned radicals and which may be joined to the aromatic or heteroaromatic system via any desired positions, is especially understood to mean groups derived from benzene, naphthalene, anthracene, phenanthrene, pyrene, dihydropyrene, chrysene, perylene, triph-

enylene, fluoranthene, benzanthracene, benzophenanthrene, tetracene, pentacene, benzopyrene, furan, benzofuran, isobenzofuran, dibenzofuran, thiophene, benzothiophene, isobenzothiophene, dibenzothiophene, pyrrole, indole, isoindole, carbazole, pyridine, quinoline, isoquinoline, acridine, phenanthridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, phenothiazine, phenoxazine, pyrazole, indazole, imidazole, benzimidazole, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, oxazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, benzothiazole, pyridazine, benzopyridazine, pyrimidine, benzopyrimidine, quinoxaline, pyrazine, phenazine, naphthyridine, azacarbazole, benzocarboline, phenanthroline, 1,2,3-triazole, 1,2,4-triazole, benzotriazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, tetrazole, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-tetrazine, purine, pteridine, indolizine and benzothiadiazole.

An aromatic ring system in the context of this invention contains 6 to 40 carbon atoms in the ring system and does not include any heteroatoms as aromatic ring atoms. An aromatic ring system in the context of this invention therefore does not contain any heteroaryl groups. An aromatic ring system in the context of this invention shall be understood to mean a system which does not necessarily contain only aryl groups but in which it is also possible for a plurality of aryl groups to be bonded by a single bond or by a non-aromatic unit, for example one or more optionally substituted C, Si, N, O or S atoms. In this case, the nonaromatic unit comprises preferably less than 10% of the atoms other than H, based on the total number of atoms other than H in the system. For example, systems such as 9,9'-spirobifluorene, 9,9'-diarylfuorene, triarylamine, diaryl ethers and stilbene are also to be regarded as aromatic ring systems in the context of this invention, and likewise systems in which two or more aryl groups are joined, for example, by a linear or cyclic alkyl, alkenyl or alkynyl group or by a silyl group. In addition, systems in which two or more aryl groups are joined to one another via single bonds are also to be regarded as aromatic ring systems in the context of this invention, for example systems such as biphenyl and terphenyl.

A heteroaromatic ring system in the context of this invention contains 5 to 40 aromatic ring atoms, at least one of which is a heteroatom. The heteroatoms of the heteroaromatic ring system are preferably selected from N, O and/or S. A heteroaromatic ring system corresponds to the above-mentioned definition of an aromatic ring system, but has at least one heteroatom as one of the aromatic ring atoms. In this way, it differs from an aromatic ring system in the sense of the definition of the present application, which, according to this definition, cannot contain any heteroatom as aromatic ring atom.

An aromatic ring system having 6 to 40 aromatic ring atoms or a heteroaromatic ring system having 5 to 40 aromatic ring atoms is especially understood to mean groups derived from the groups mentioned above under aryl groups and heteroaryl groups, and from biphenyl, terphenyl, quaterphenyl, fluorene, spirobifluorene, dihydrophenanthrene, dihydropyrene, tetrahydropyrene, indenofluorene, truxene, isotruxene, spirotruxene, spiroisotruxene, indenocarbazole, or from combinations of these groups.

In the context of the present invention, a straight-chain alkyl group having 1 to 20 carbon atoms and a branched or

cyclic alkyl group having 3 to 20 carbon atoms and an alkenyl or alkynyl group having 2 to 40 carbon atoms in which individual hydrogen atoms or CH₂ groups may also be replaced by the groups mentioned above in the definition of the radicals are preferably understood to mean the methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, 2-methylbutyl, n-pentyl, s-pentyl, cyclopentyl, neopentyl, n-hexyl, cyclohexyl, neoheptyl, n-heptyl, cycloheptyl, n-octyl, cyclooctyl, 2-ethylhexyl, trifluoromethyl, pentafluoroethyl, 2,2,2-trifluoroethyl, ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl, cycloheptenyl, octenyl, cyclooctenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl or octynyl radicals.

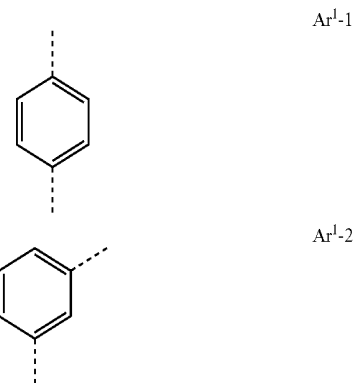
An alkoxy or thioalkyl group having 1 to 20 carbon atoms in which individual hydrogen atoms or CH₂ groups may also be replaced by the groups mentioned above in the definition of the radicals is preferably understood to mean methoxy, trifluoromethoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy, n-pentoxy, s-pentoxy, 2-methylbutoxy, n-hexoxy, cyclohexyloxy, n-heptoxy, cycloheptyloxy, n-octyloxy, cyclooctyloxy, 2-ethylhexyloxy, pentafluoroethoxy, 2,2,2-trifluoroethoxy, methylthio, ethylthio, n-propylthio, i-propylthio, n-butylthio, i-butylthio, s-butylthio, t-butylthio, n-pentylthio, s-pentylthio, n-hexylthio, cyclohexylthio, n-heptylthio, cycloheptylthio, n-octylthio, cyclooctylthio, 2-ethylhexylthio, trifluoromethylthio, pentafluoroethylthio, 2,2,2-trifluoroethylthio, ethenylthio, propenylthio, butenylthio, pentenylthio, cyclopentenylthio, hexenylthio, cyclohexenylthio, heptenylthio, cycloheptenylthio, octenylthio, cyclooctenylthio, ethynylthio, propynylthio, butynylthio, pentynylthio, hexynylthio, heptynylthio or octynylthio.

The wording that two or more radicals together may form a ring, in the context of the present application, shall be understood to mean, inter alia, that the two radicals are joined to one another by a chemical bond. In addition, however, the abovementioned wording shall also be understood to mean that, if one of the two radicals is hydrogen, the second radical binds to the position to which the hydrogen atom was bonded, forming a ring.

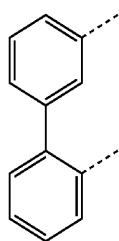
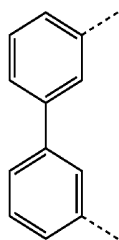
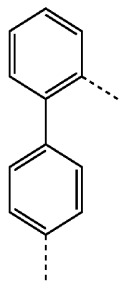
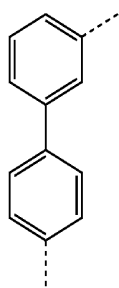
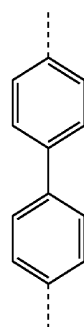
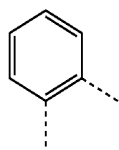
It is preferable that A is a group of the formula (A-1) or (A-3), more preferably a group of the formula (A-1).

It is preferable that Ar¹ is the same or different at each instance and is selected from a single bond and a divalent group derived from benzene, biphenyl, terphenyl, fluorene, spirobifluorene, indenofluorene, carbazole, dibenzofuran or dibenzothiophene, each optionally substituted by R² radicals, or a combination of two or more of these groups, but not more than 30 aromatic ring atoms may be present in Ar¹.

Ar¹ groups are preferably selected from groups of the following formulae:



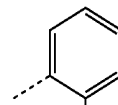
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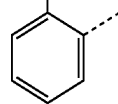
Ar¹-3

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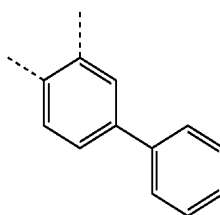


Ar¹-4

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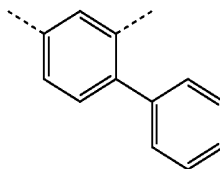
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Ar¹-5

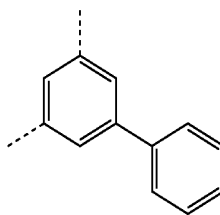
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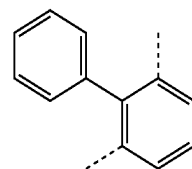
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Ar¹-6

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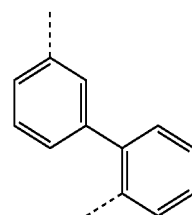
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Ar¹-7

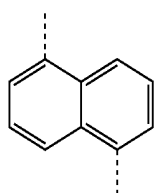
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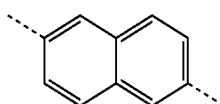
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Ar¹-8

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Ar¹-9

Ar¹-10

Ar¹-11

Ar¹-12

Ar¹-13

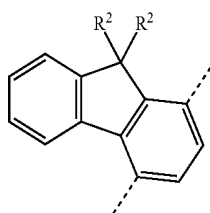
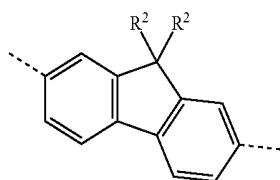
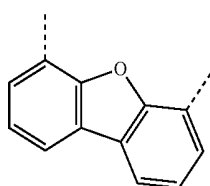
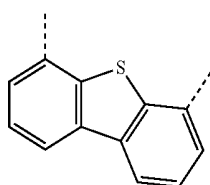
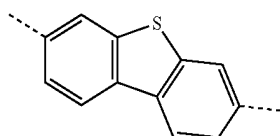
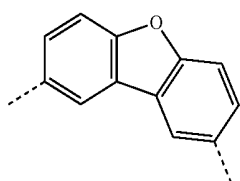
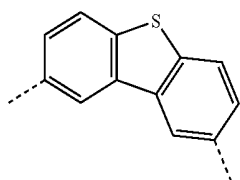
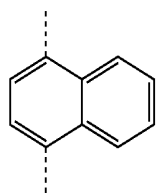
Ar¹-14

Ar¹-15

Ar¹-16

9

-continued



10

-continued

Ar¹-17

5

Ar¹-18

15

Ar¹-19

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Ar¹-20

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Ar¹-21

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Ar¹-22

45

Ar¹-23

55

Ar¹-24

65

Ar¹-25

Ar¹-26

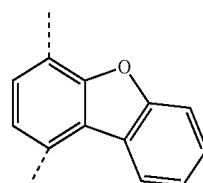
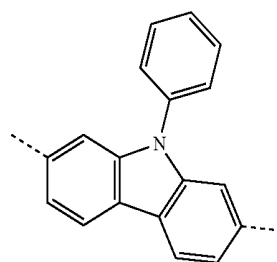
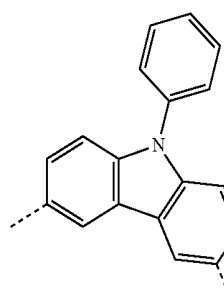
Ar¹-27

Ar¹-28

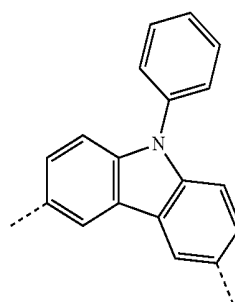
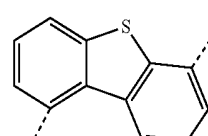
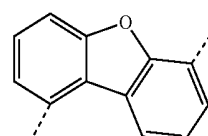
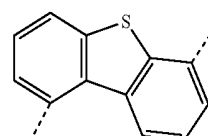
Ar¹-29

Ar¹-30

Ar¹-31

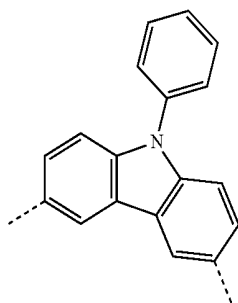


Ar^s-11



11

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Ar¹-32

5

10

15

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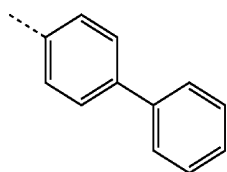
25

where the dotted bonds represent the bonds to the radical of the formula and the groups may be substituted at the free positions by one or more R² radicals, but are preferably unsubstituted at the free positions.

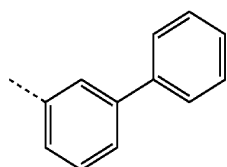
R² in the groups of the formulae (Ar¹-23) and (Ar¹-24) is preferably the same or different and is an alkyl group having 1 to 10 carbon atoms, especially methyl, or is a phenyl group which may be substituted by one or more R³ radicals and is preferably unsubstituted. Two alkyl groups R² may also form a ring with formation of a spiro group, preferably a cyclohexyl ring or a cyclopentyl ring.

It is preferable that Ar² is the same or different at each instance and is selected from an aromatic or heteroaromatic ring system which has 6 to 25 aromatic ring atoms and may be substituted by one or more R² radicals. Particular preference is given to phenyl, biphenyl, terphenyl, fluorenyl, spirobifluorenyl, indenofluorenyl, naphthyl, phenanthrenyl, furanyl, benzofuranyl, dibenzofuranyl, thiophenyl, benzothioiophenyl, dibenzothioiophenyl, carbazolyl, indolocarbazolyl and indenocarbazolyl, each of which may be substituted by one or more R² radicals.

Ar² groups are preferably the same or different at each instance and are selected from groups of the following formulae:

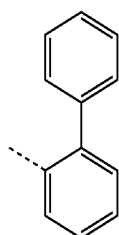
Ar²-1

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Ar²-2

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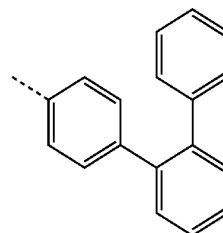
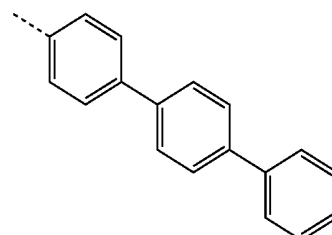
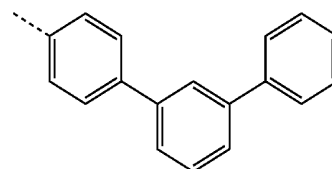
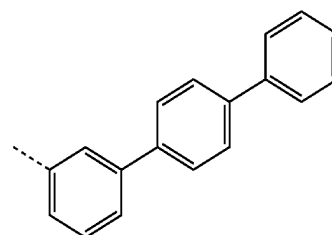
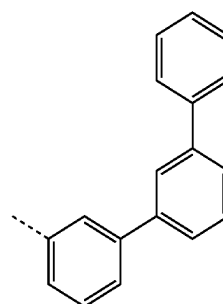
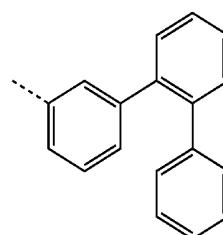
Ar²-3

60

65

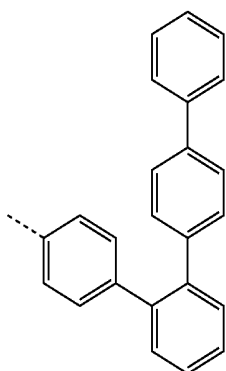
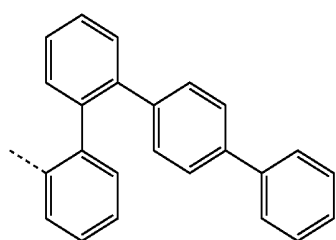
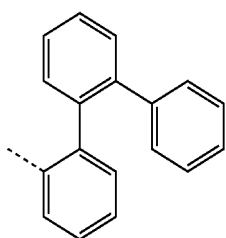
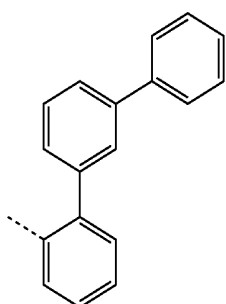
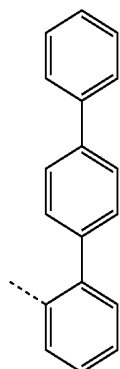
12

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Ar²-4Ar²-5Ar²-6Ar²-7Ar²-8Ar²-9

13

-continued



14

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Ar²-10

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Ar²-11

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Ar²-12

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Ar²-13

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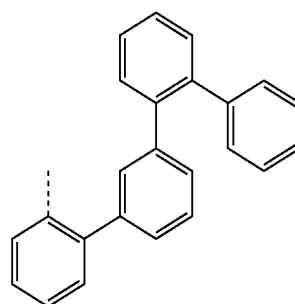
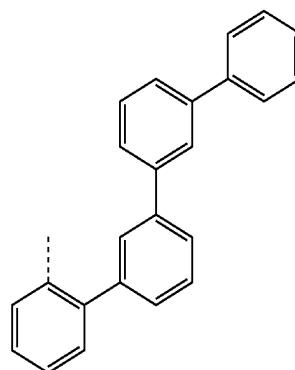
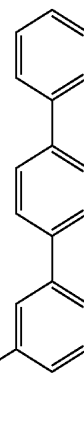
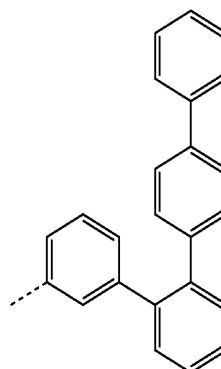
Ar²-14

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65

Ar²-15



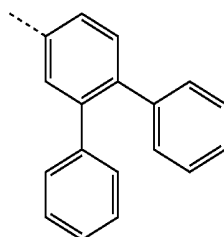
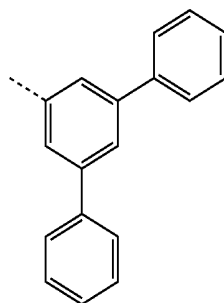
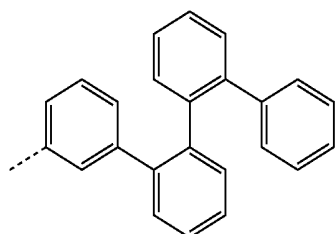
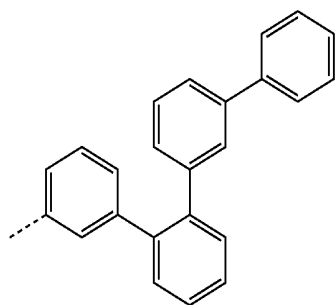
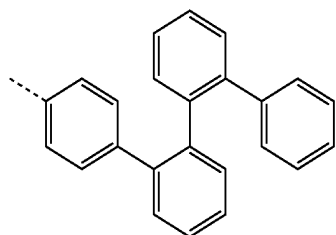
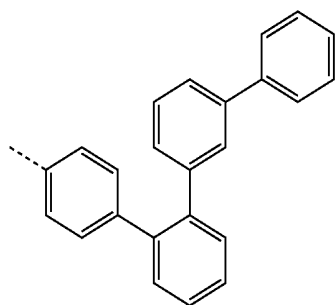
Ar²-16

Ar²-17

Ar²-18

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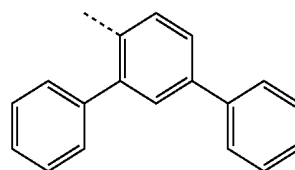


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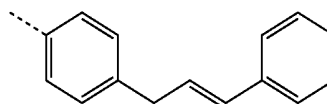
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Ar²-19

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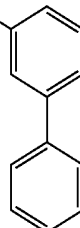


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Ar²-20

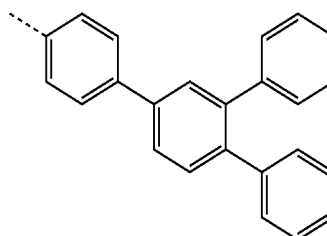
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Ar²-21

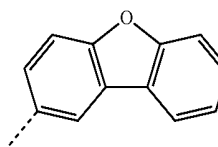
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Ar²-22

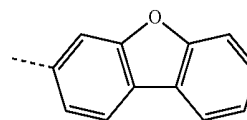
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Ar²-23

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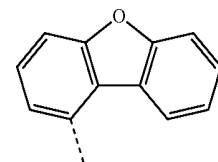


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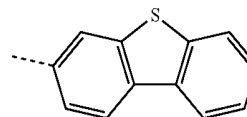
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Ar²-24

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65



Ar²-25

Ar²-26

Ar²-27

Ar²-28

Ar²-29

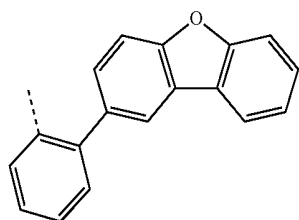
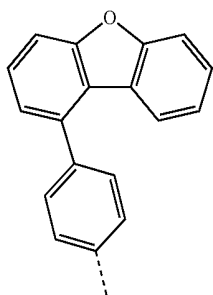
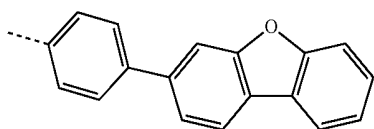
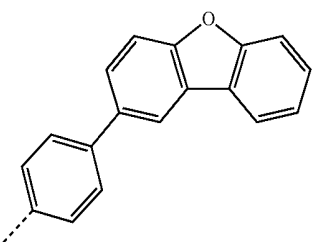
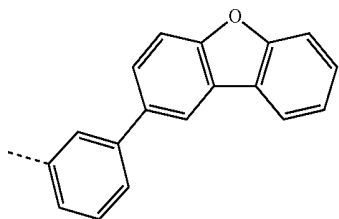
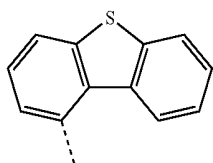
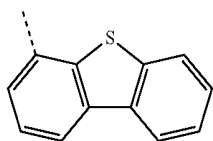
Ar²-30

Ar²-31

Ar²-32

Ar²-33

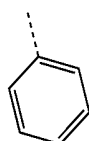
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18
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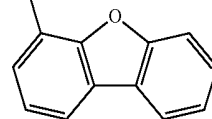
Ar²-34

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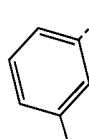
Ar²-35

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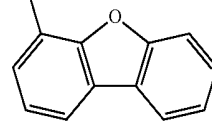


Ar²-36

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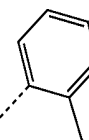


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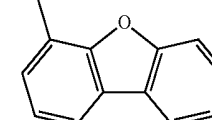


Ar²-37

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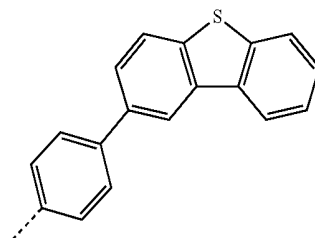
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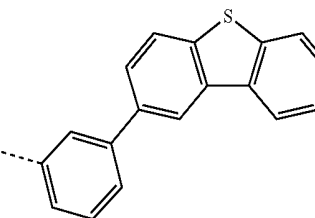
Ar²-38

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Ar²-39

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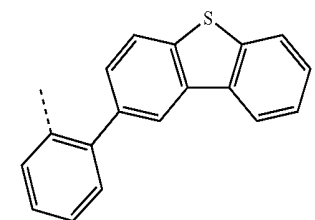


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Ar²-40

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Ar²-41

Ar²-42

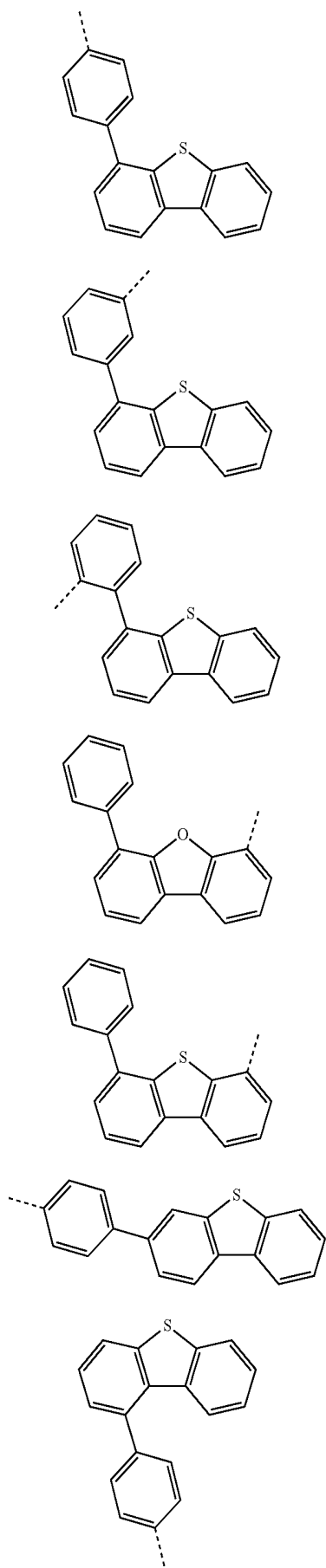
Ar²-43

Ar²-44

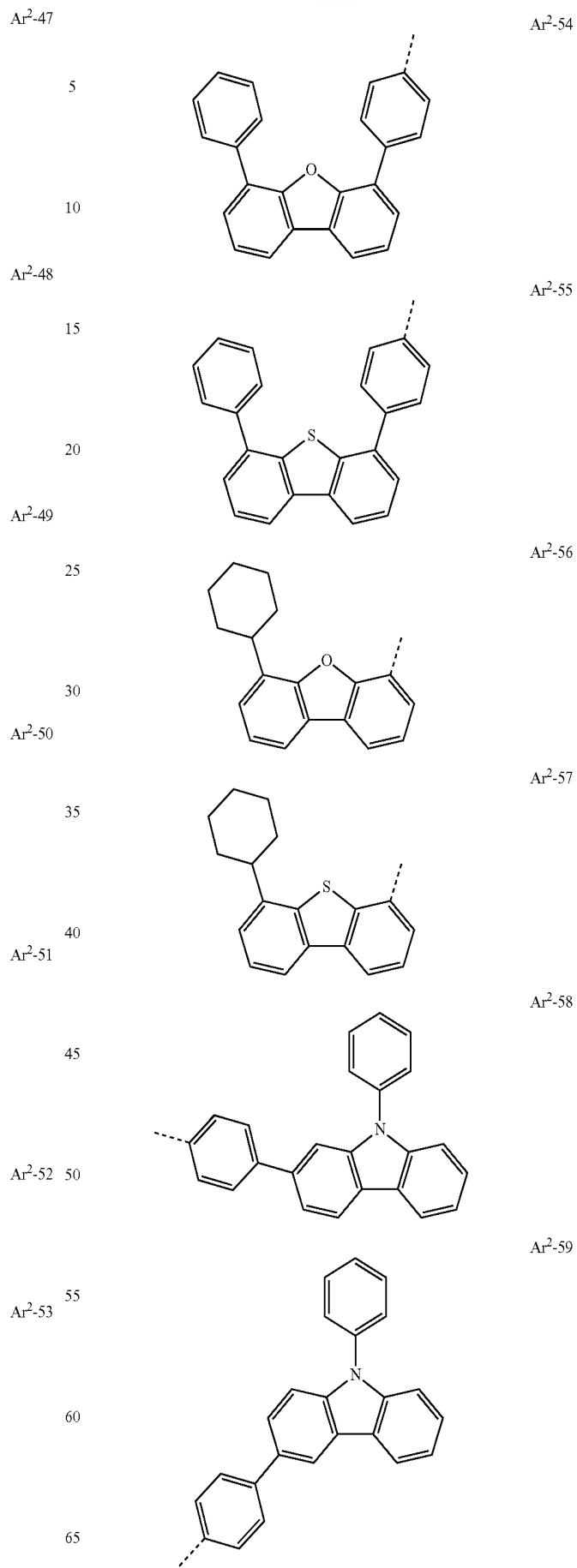
Ar²-45

Ar²-46

19
-continued



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-continued



Ar²-47

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Ar²-48

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Ar²-49

25

30

Ar²-50

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Ar²-51

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Ar²-52

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Ar²-53

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Ar²-54

Ar²-55

Ar²-56

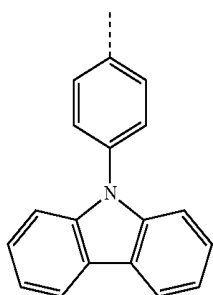
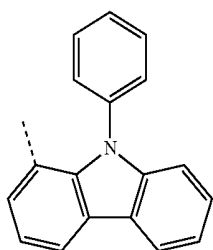
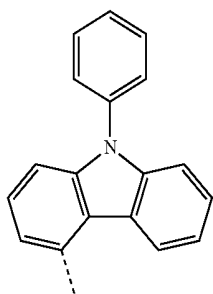
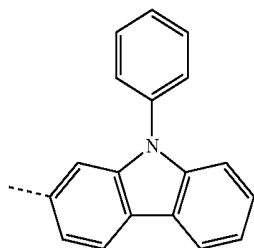
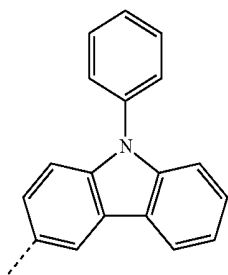
Ar²-57

Ar²-58

Ar²-59

21

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22

-continued

Ar²-60

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Ar²-61

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Ar²-62

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Ar²-63

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Ar²-64

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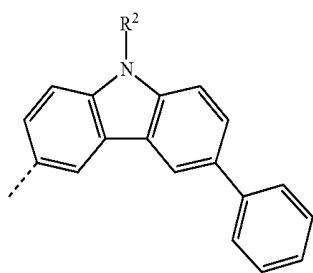
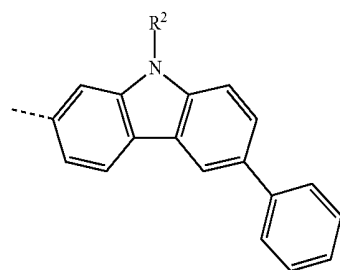
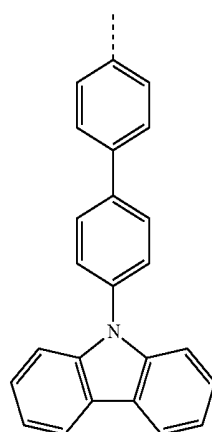
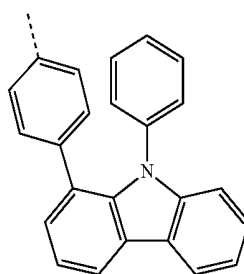
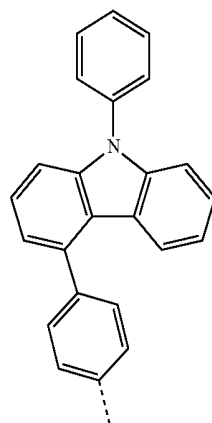
Ar²-65

Ar²-66

Ar²-67

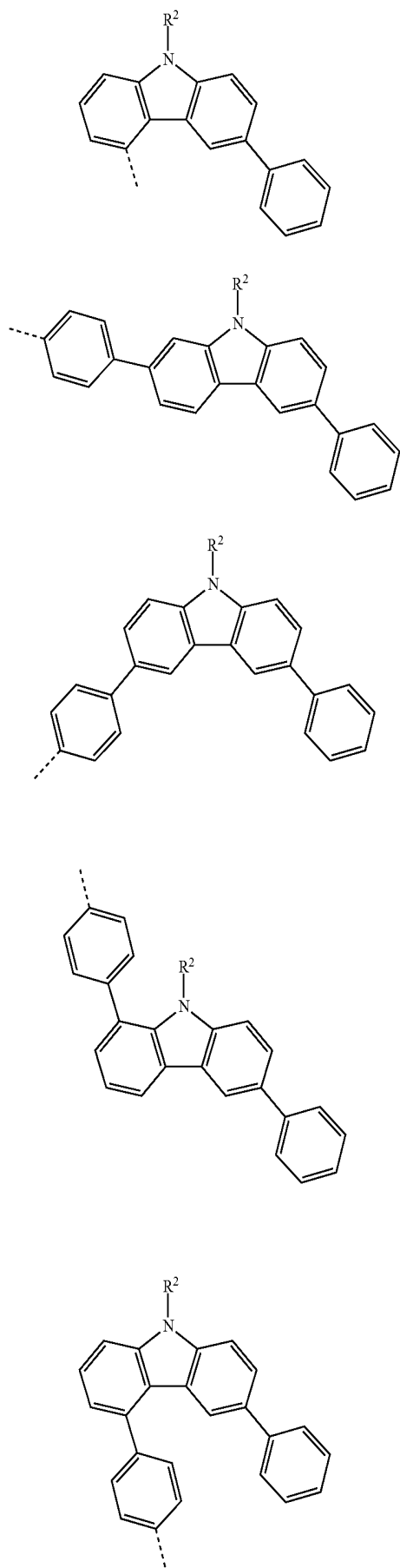
Ar²-68

Ar²-69



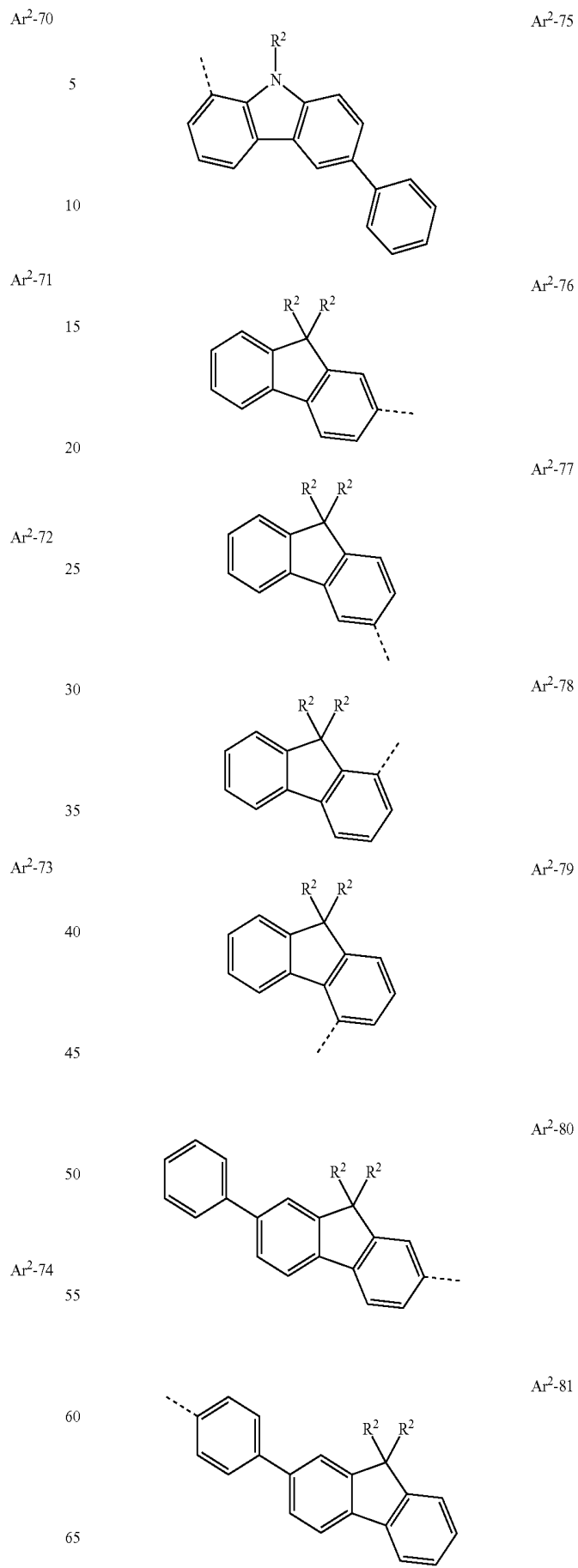
23

-continued



24

-continued



Ar²-70

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Ar²-71

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Ar²-72

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Ar²-73

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Ar²-74

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Ar²-75

Ar²-76

Ar²-77

Ar²-78

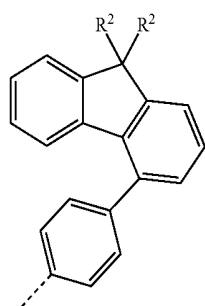
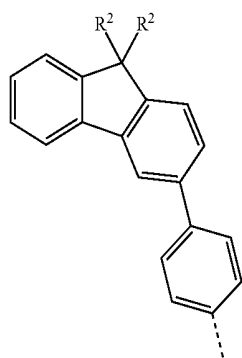
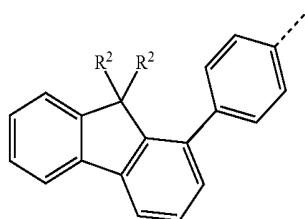
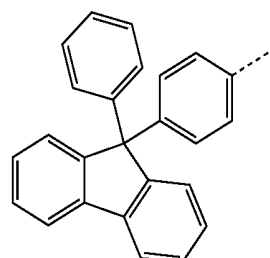
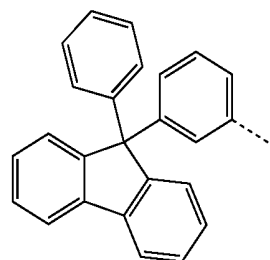
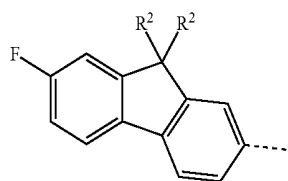
Ar²-79

Ar²-80

Ar²-81

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Ar²-82

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Ar²-83

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Ar²-84

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Ar²-85

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Ar²-86

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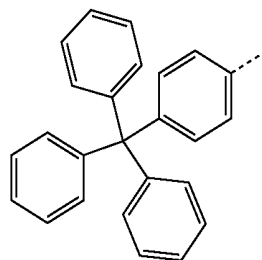
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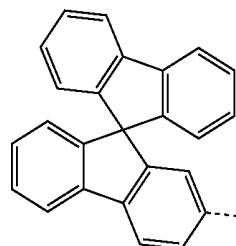
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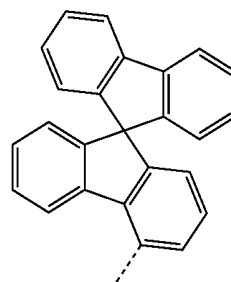
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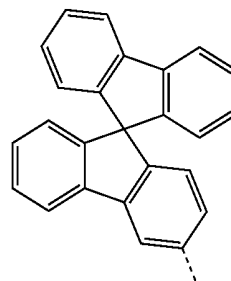
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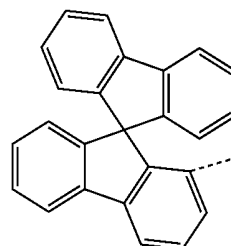
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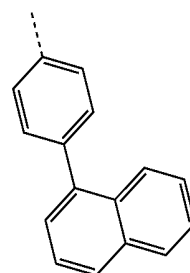
Ar²-91



Ar²-92

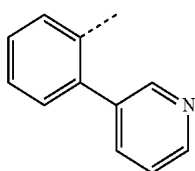
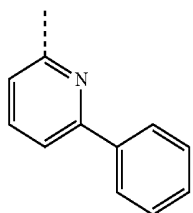
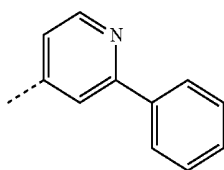
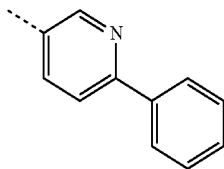
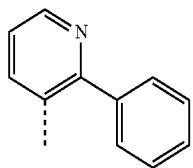
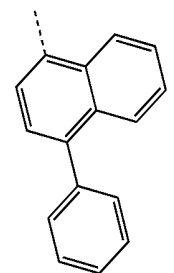
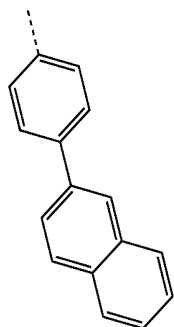


Ar²-93



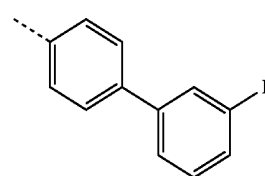
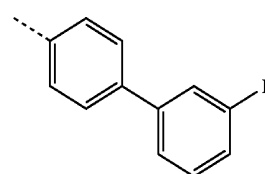
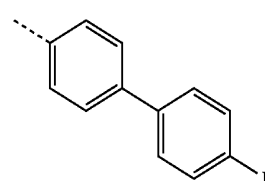
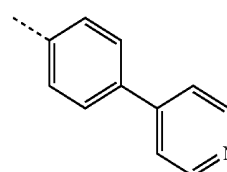
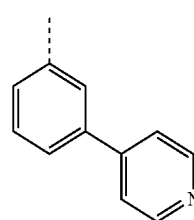
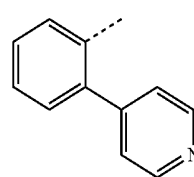
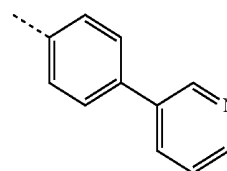
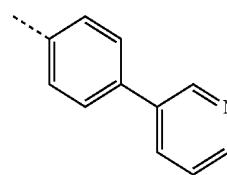
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Ar²-94

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Ar²-95

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Ar²-96

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Ar²-97

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Ar²-98

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Ar²-99

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Ar²-100

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Ar²-101

Ar²-102

Ar²-103

Ar²-104

Ar²-105

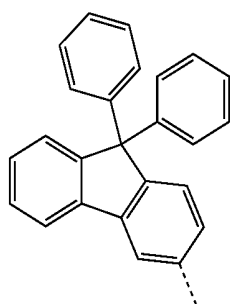
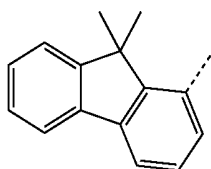
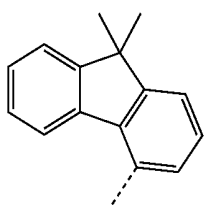
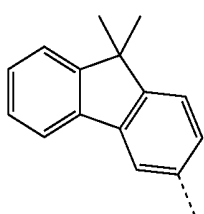
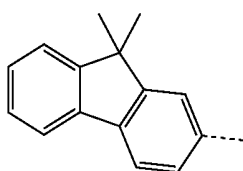
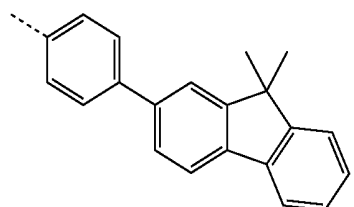
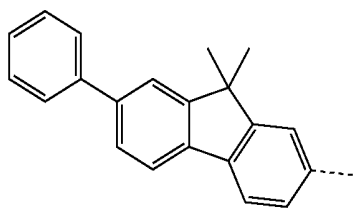
Ar²-106

Ar²-107

Ar²-108

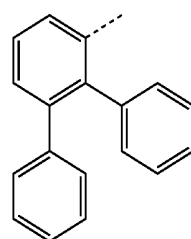
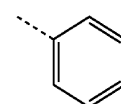
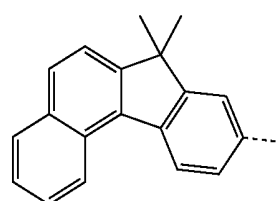
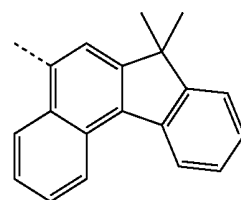
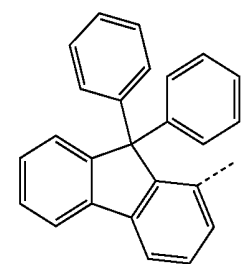
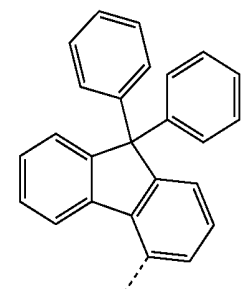
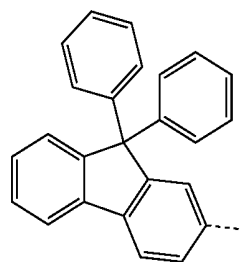
29

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Ar²-109

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Ar²-110

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Ar²-111

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Ar²-112

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Ar²-113

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Ar²-114

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Ar²-115

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Ar²-116

Ar²-117

Ar²-118

Ar²-119

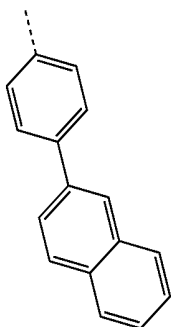
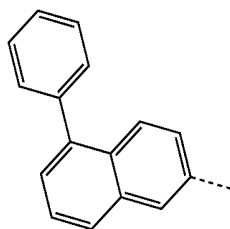
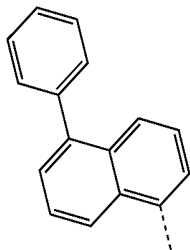
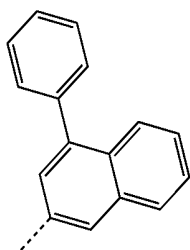
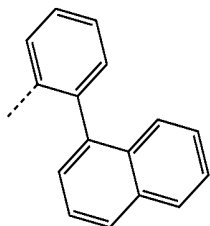
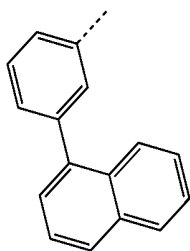
Ar²-120

Ar²-121

Ar²-122

31

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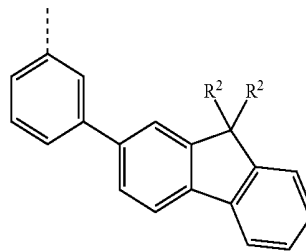


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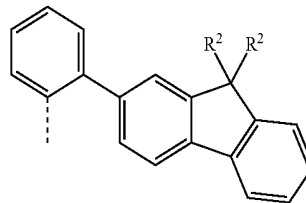
Ar²-123

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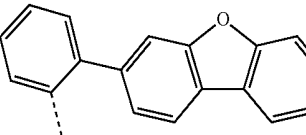
Ar²-124

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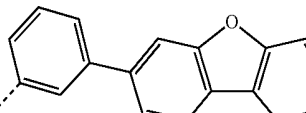
Ar²-125

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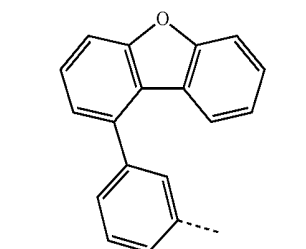
Ar²-126

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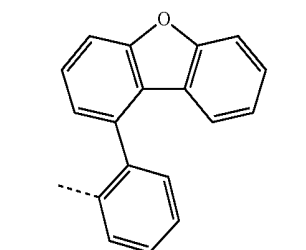
Ar²-127

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Ar²-128

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Ar²-129

Ar²-130

Ar²-131

Ar²-132

Ar²-133

Ar²-134

55 where the dotted bond represents the bond to the nitrogen and the groups may be substituted at the free positions by one or more R² radicals, but are preferably unsubstituted at the free positions.

60 R² in the groups of the formulae (Ar²-68) to (Ar²-82), (Ar²-85) to (Ar²-87), (Ar²-129) and (Ar²-130) is preferably the same or different and is an alkyl group having 1 to 10 carbon atoms, especially methyl, or a phenyl group which may be substituted by one or more R³ radicals and is preferably unsubstituted. Two alkyl groups R² may also form a ring with formation of a spiro group, preferably a cyclohexyl ring or a cyclopentyl ring.

It is preferable that X is the same or different at each instance and is selected from a single bond or a group selected from $C(R^2)_2$, $C=O$, O , S and NR^2 ; more preferably, X is a single bond.

R^0 is preferably the same or different at each instance and is selected from H, D, F, straight-chain alkyl or alkoxy groups having 1 to 10 carbon atoms, branched or cyclic alkyl or alkoxy groups having 3 to 10 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms and heteroaromatic ring systems having 5 to 40 aromatic ring atoms, where said alkyl and alkoxy groups and said aromatic ring systems and heteroaromatic ring systems may each be substituted by one or more R^3 radicals. More preferably, R^0 is the same or different at each instance and is H, F, a straight-chain alkyl group having 1 to 10 carbon atoms, a branched or cyclic alkyl group having 3 to 10 carbon atoms, an aromatic ring system having 6 to 30 aromatic ring atoms or a heteroaromatic ring system having 5 to 30 aromatic ring atoms, where said alkyl groups and said aromatic ring systems and said heteroaromatic ring systems may each be substituted by one or more R^3 radicals. Most preferably, R^0 is H.

Preferably, R^1 and R^2 are the same or different at each instance and are H, D, F, CN, $Si(R^3)_3$, a straight-chain alkyl or alkoxy group having 1 to 10 carbon atoms, a branched or cyclic alkyl or alkoxy group having 3 to 10 carbon atoms or an aromatic or heteroaromatic ring system having 6 to 30 aromatic ring atoms, where two or more R^1 or R^2 radicals may be joined to one another and may form a ring, where said alkyl and alkoxy groups and said aromatic and heteroaromatic ring systems may each be substituted by one or more R^3 radicals, and where one or more CH_2 groups in the alkyl and alkoxy groups mentioned may be replaced by $-C\equiv C-$, $-R^3C=CR^3-$, $Si(R^3)_2$, $C=O$, $C=NR^3$, $-NR^3-$, $-O-$, $-S-$, $-C(=O)O-$ or $-C(=O)NR^3-$.

More preferably, R^1 and R^2 are the same or different at each instance and are H, D, F, CN, a straight-chain alkyl group having 1 to 10 carbon atoms or a branched or cyclic alkyl group having 3 to 10 carbon atoms, or an aromatic or heteroaromatic ring system having 6 to 25 aromatic ring atoms, where said alkyl and alkoxy groups and said aromatic or heteroaromatic ring systems may each be substituted by one or more R^3 radicals. Most preferably, R^1 and R^2 are the same or different at each instance and are H, F, CN, methyl, tert-butyl, phenyl, biphenyl, dibenzofuran, dibenzothio-
phene or carbazole.

Preferably, R^3 is the same or different at each instance and is H, D, F, CN, $Si(R^4)_3$, $N(R^4)_2$, a straight-chain alkyl or alkoxy group having 1 to 10 carbon atoms or a branched or cyclic alkyl or alkoxy group having 3 to 10 carbon atoms or an aromatic or heteroaromatic ring system having 5 to 30 aromatic ring atoms, where two or more R^3 radicals may be joined to one another and may form a ring, where said alkyl and alkoxy groups and said aromatic or heteroaromatic ring systems may each be substituted by one or more R^4 radicals, and where one or more CH_2 groups in the alkyl and alkoxy groups mentioned may be replaced by $-C\equiv C-$, $-R^4C=CR^4-$, $Si(R^4)_2$, $C=O$, $C=NR^4$, $-NR^4-$, $-O-$, $-S-$, $-C(=O)O-$ or $-C(=O)NR^4-$. More preferably, R^3 is the same or different at each instance and is H, D, F, CN, $N(R^4)_2$, a straight-chain alkyl group having 1 to 10 carbon atoms or a branched or cyclic alkyl group having 3 to 10 carbon atoms, or an aromatic or heteroaromatic ring system having 6 to 25 aromatic ring atoms, where

said alkyl and alkoxy groups and said aromatic or heteroaromatic ring systems may each be substituted by one or more R^4 radicals.

It is preferable that p is 1. In this case, it is further preferable that all the other indices k, i, m and n are 0.

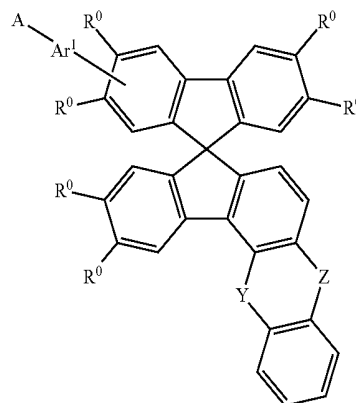
It is preferable that k is 1. In this case, it is further preferable that all the other indices i, m, n and p are 0.

It is further preferable that the sum of the indices i, k, m, n and p is 1 or 2, more preferably 1.

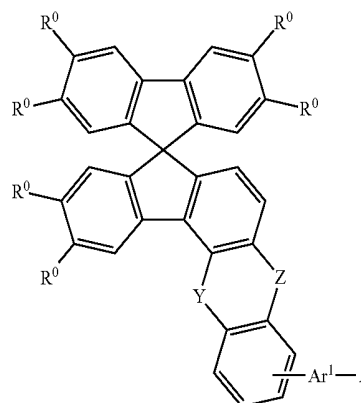
Preferably, the Y group is S, and the Z group is O, S or a single bond. More preferably, the Y group is S, and the Z group is a single bond.

Preferred embodiments of the compounds of the formula (I) correspond to the following formulae:

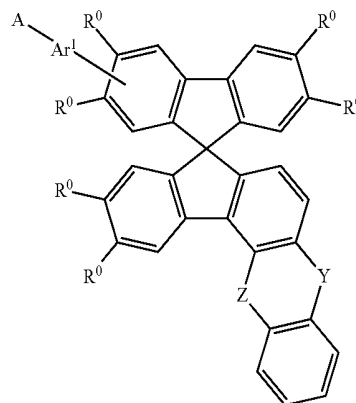
Formula (I-1)



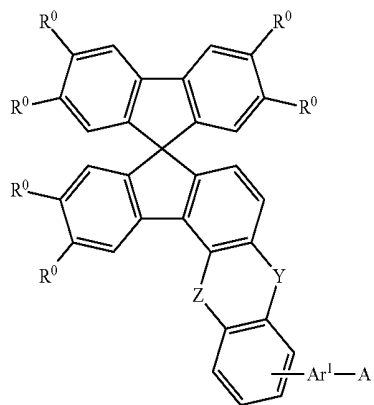
Formula (I-2)



Formula (I-3)



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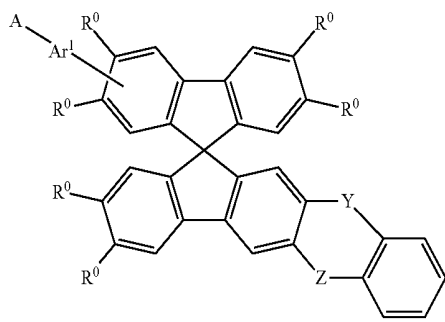
Formula (I-4)

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Formula (I-5)

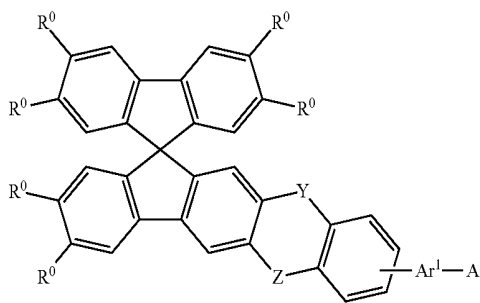


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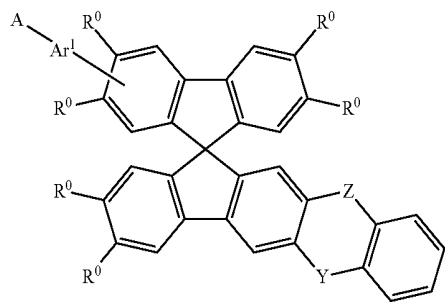
Formula (I-6)



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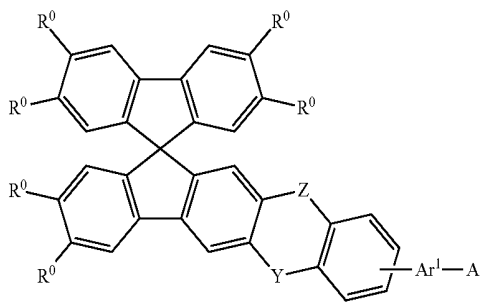
Formula (I-7)



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Formula (I-8)

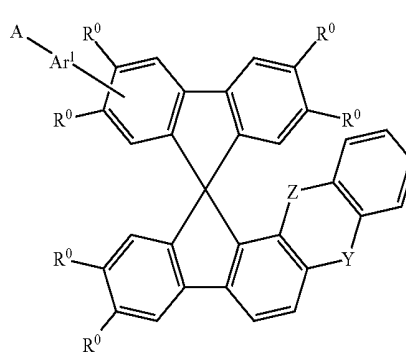


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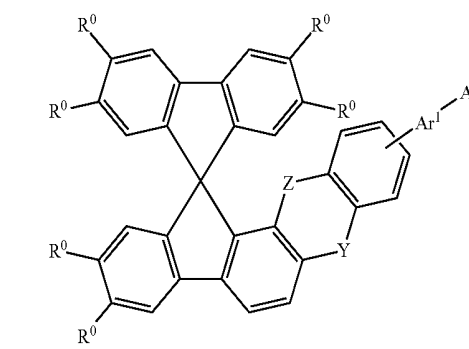
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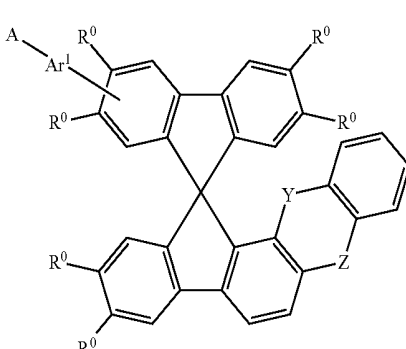
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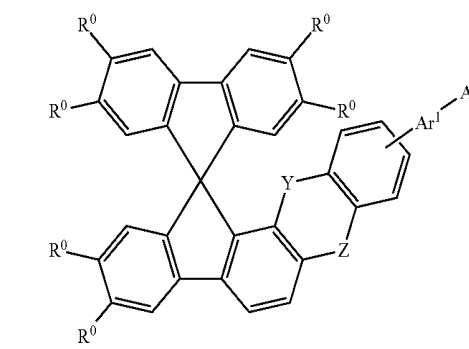
Formula (I-9)



Formula (I-10)

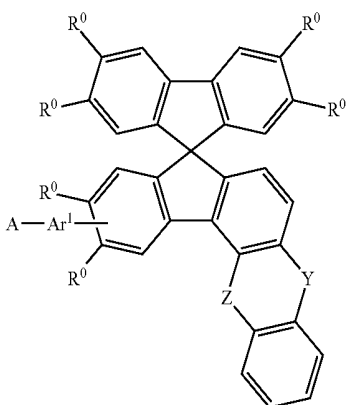
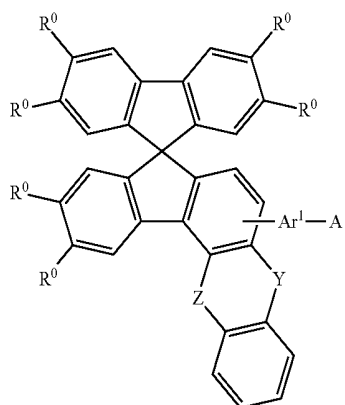
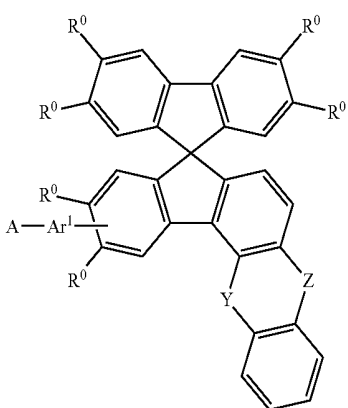
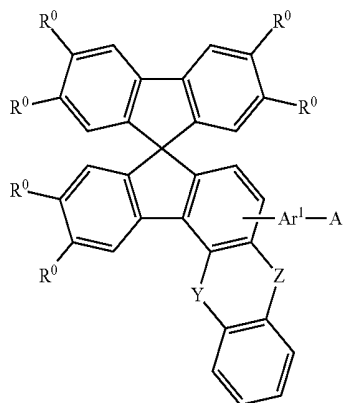


Formula (I-11)



Formula (I-12)

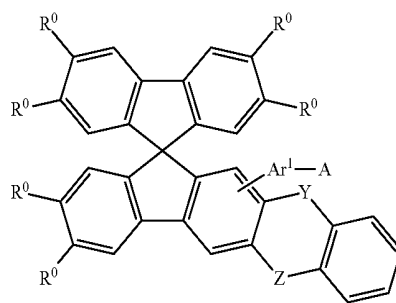
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38
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Formula (I-13)

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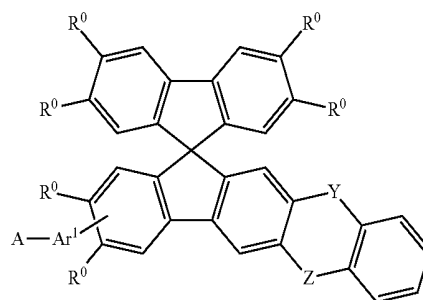
Formula (I-17)

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Formula (I-14)

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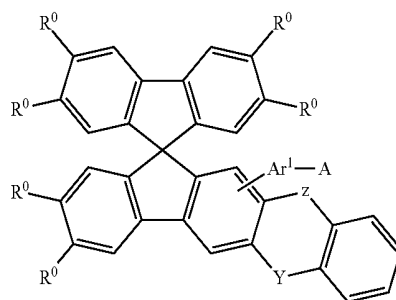


Formula (I-18)

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Formula (I-15)

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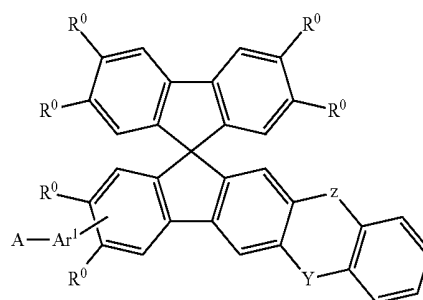
Formula (I-19)

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Formula (I-16)

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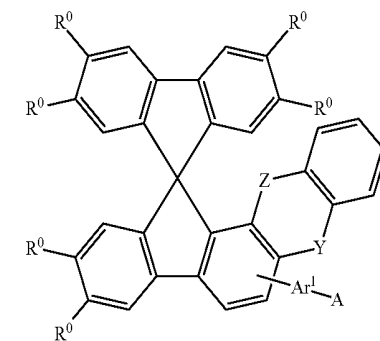
Formula (I-20)

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Formula (I-16)

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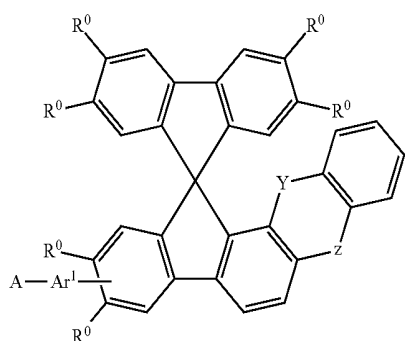
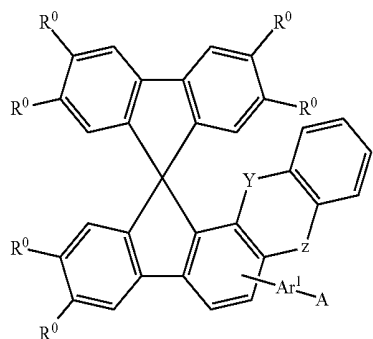
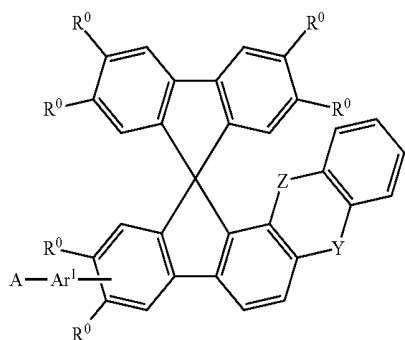


Formula (I-21)

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Formula (I-22)

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Formula (I-23)

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Formula (I-24)

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where the symbols that occur are as defined above, and the compounds may be substituted at positions shown as unsubstituted by R^1 radicals.

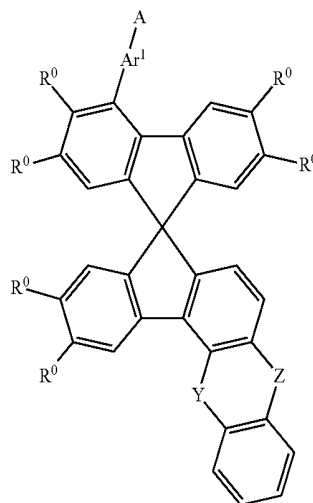
Particular preference among the formulae specified is given to the formulae (I-1) to (I-12).

For formulae (I-1) to (I-24), in particular, the preferred embodiments of R^0 , Ar^1 and A apply. Preferably, for formulae (I-1) to (I-24), the Y group is S, and the Z group is O, S or a single bond; more preferably, the Y group is S, and the Z group is a single bond. It is additionally especially preferable for the abovementioned formulae that R^0 is H.

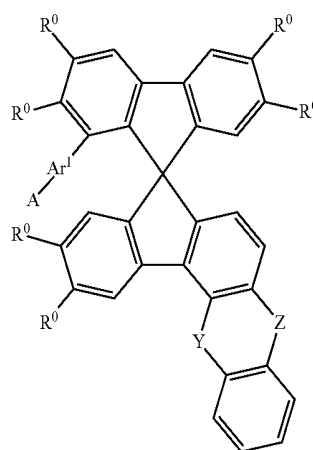
Most preferred among the formulae (I-1), (I-3), (I-5), (I-7), (I-9) and (I-11) are the following formulae:

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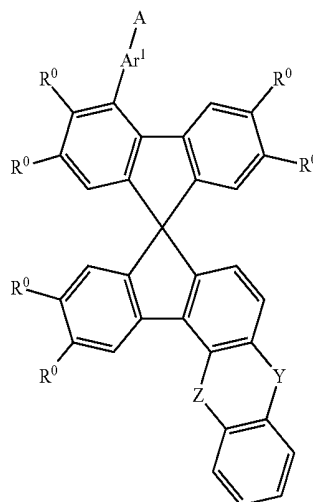
Formula (I-1A)



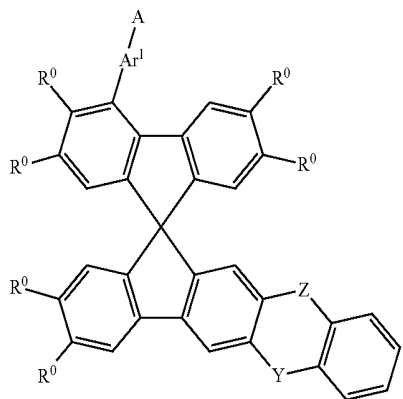
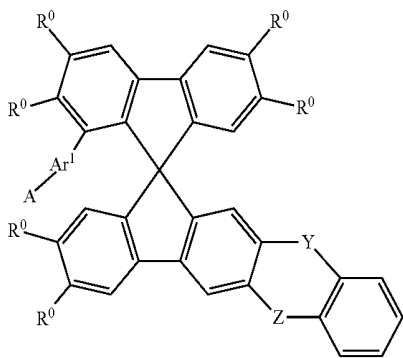
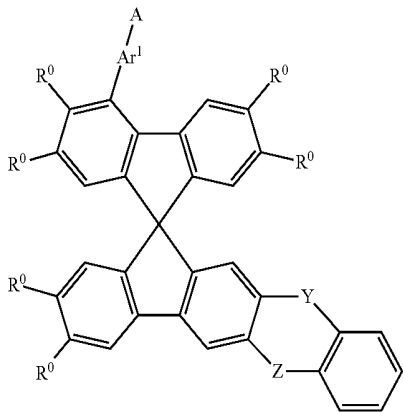
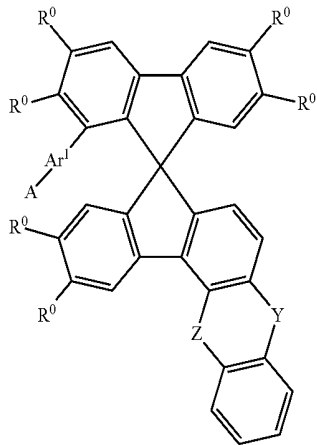
Formula (I-1B)



Formula (I-3A)

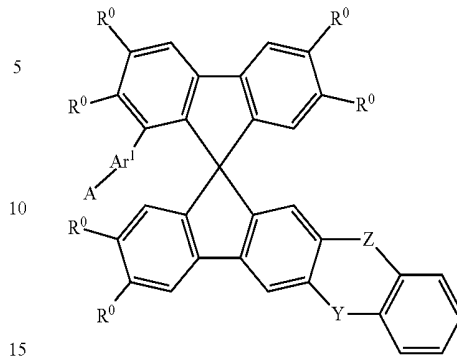


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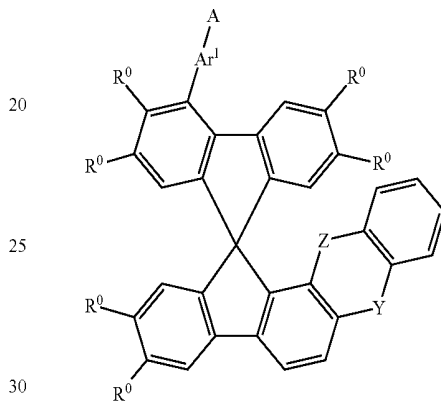
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Formula (I-3B)



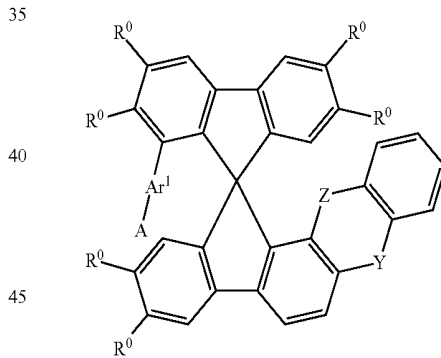
Formula (I-7B)

Formula (I-5A)



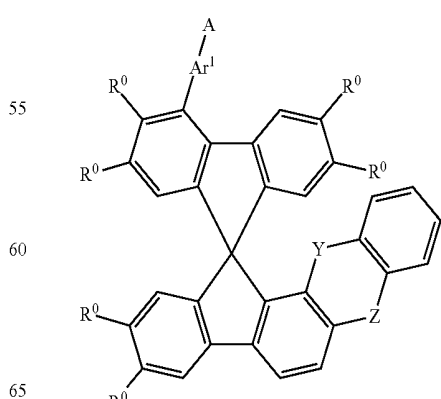
Formula (I-9A)

Formula (I-5B)



Formula (I-9B)

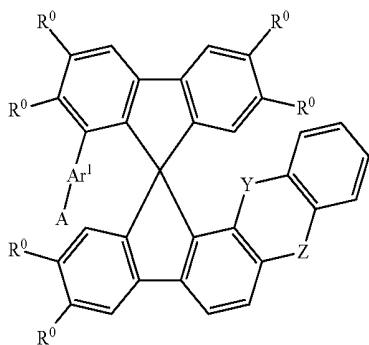
Formula (I-7A)



Formula (I-11A)

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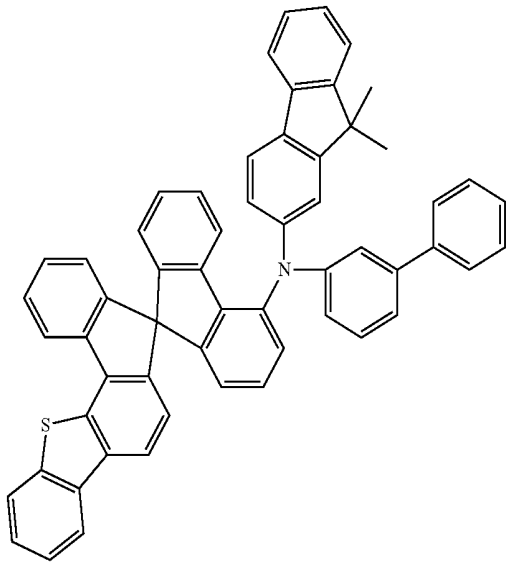
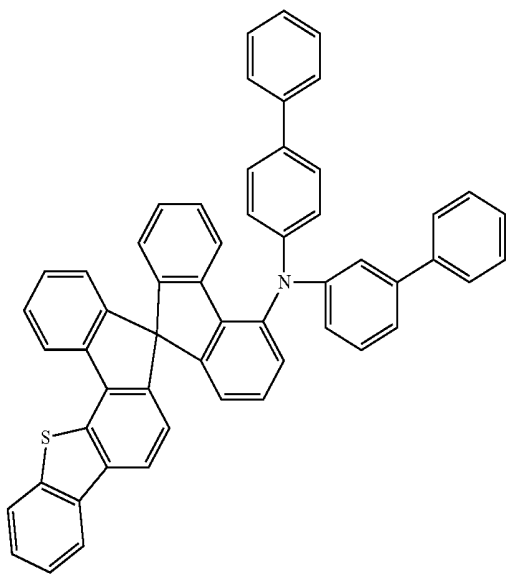
Formula (I-11B)



where the symbols that occur are as defined above, and the compounds may be substituted at positions shown as unsubstituted by R¹ radicals.

For the formulae just mentioned, in particular, the preferred embodiments of R⁰, Ar¹ and A apply. Preferably, the Y group is S, and the Z group is O, S or a single bond; more preferably, the Y group is S, and the Z group is a single that R⁰ is H.

The following explicit compounds are preferred embodiments of the compounds of the formula (I):



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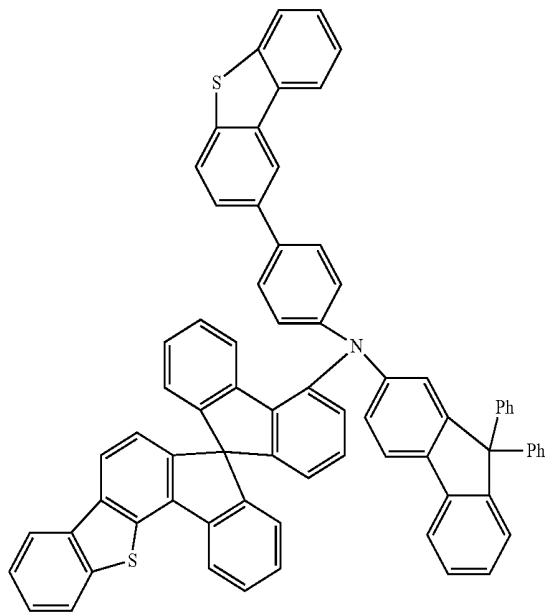
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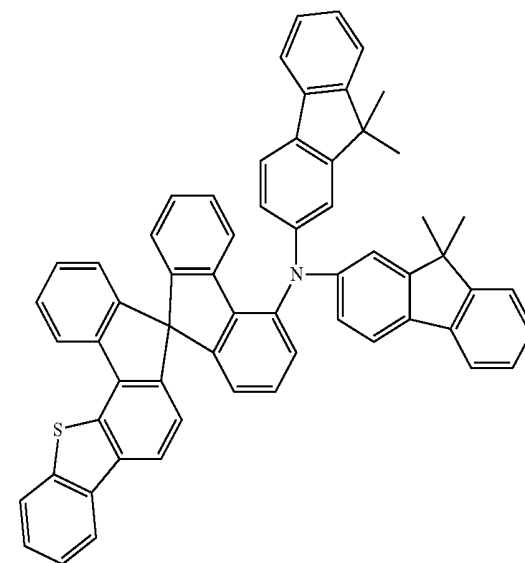
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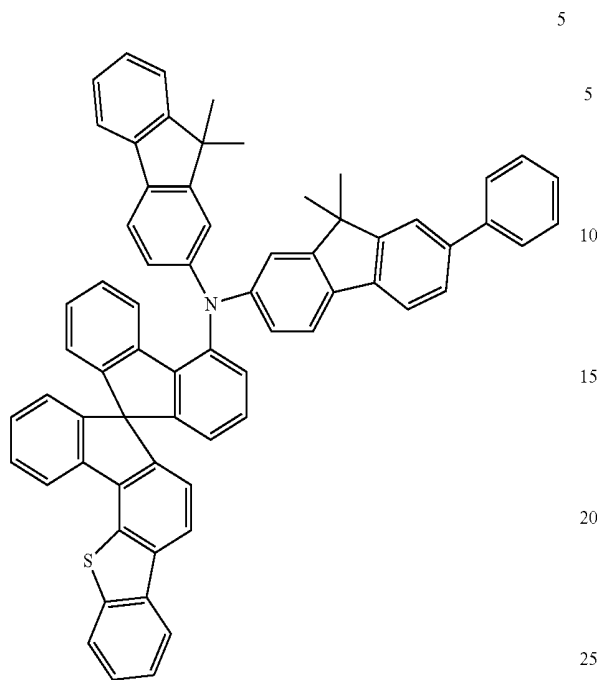
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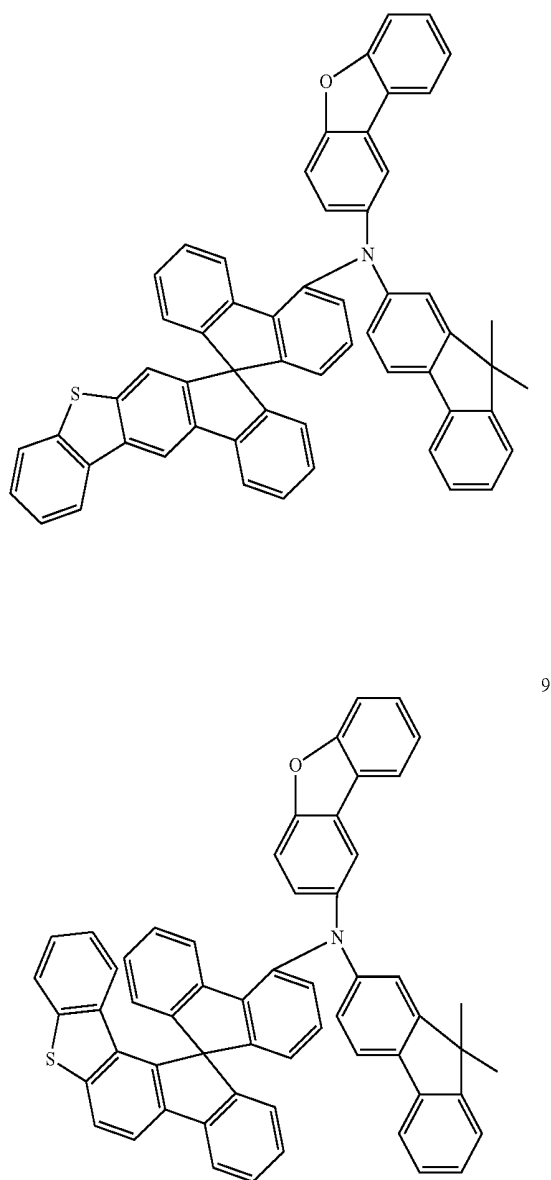
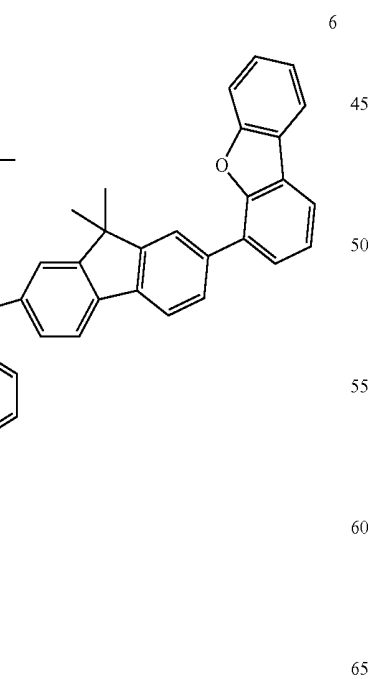
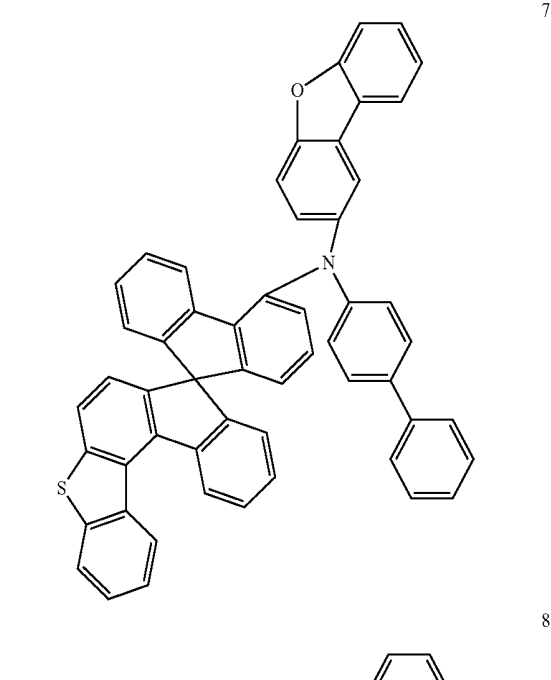
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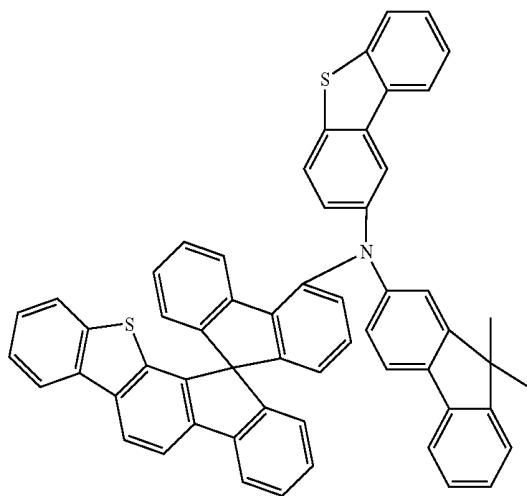
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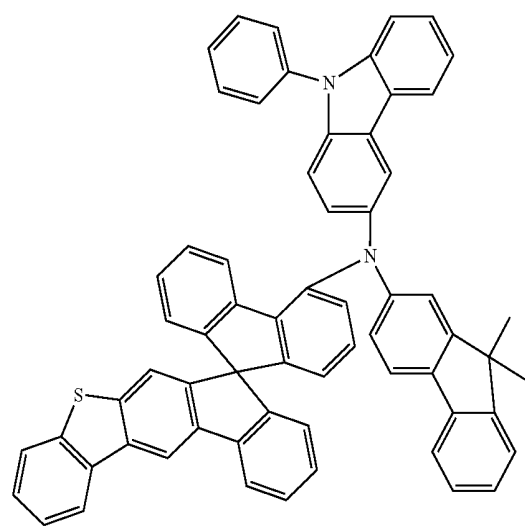
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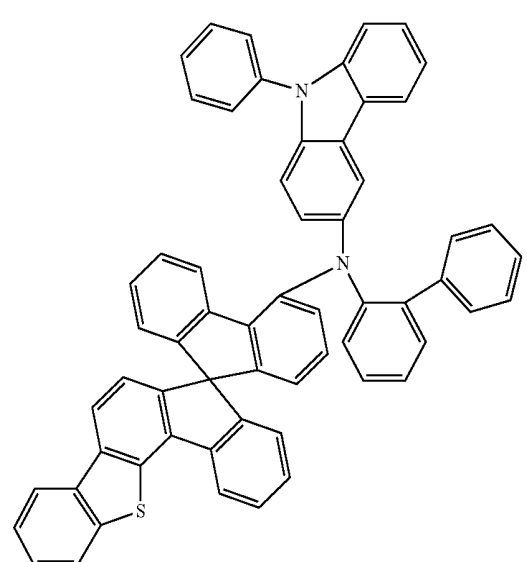
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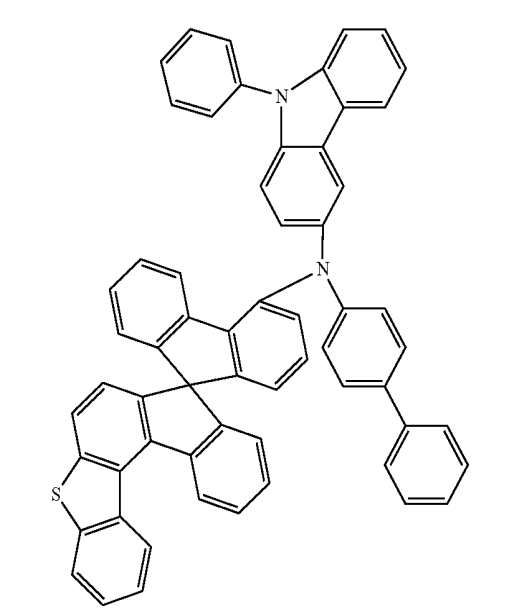
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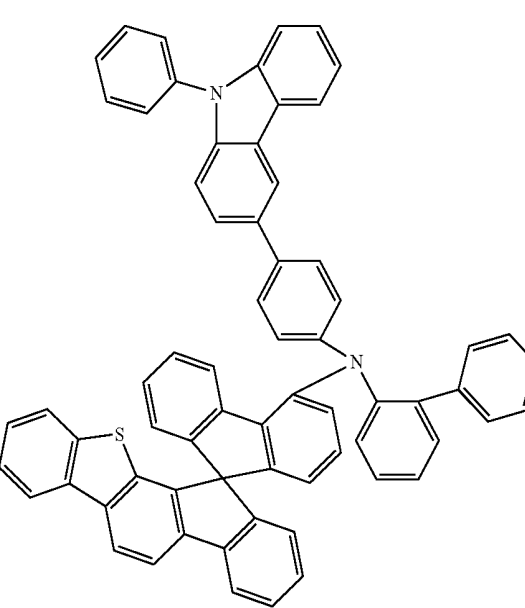
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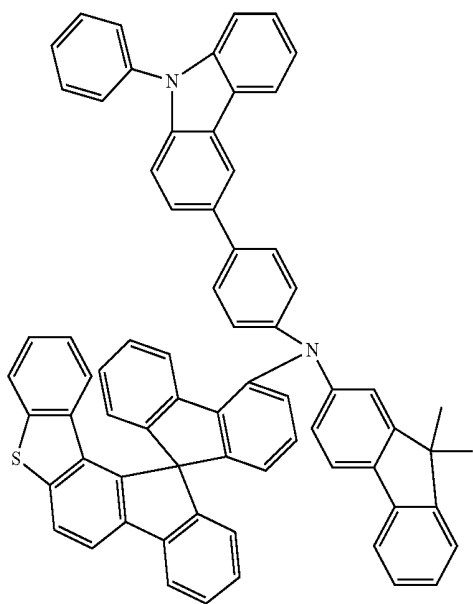
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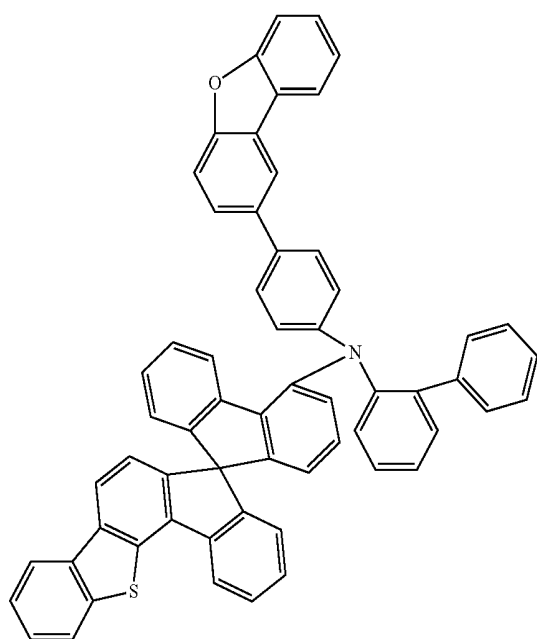
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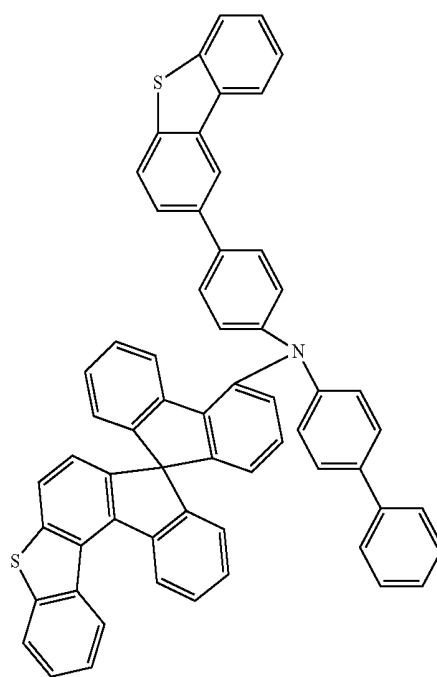
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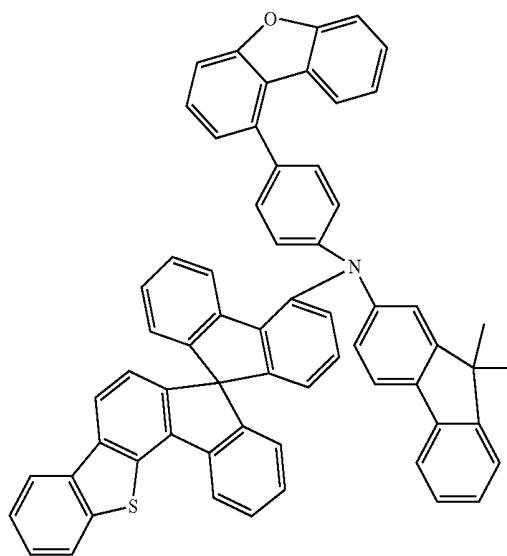
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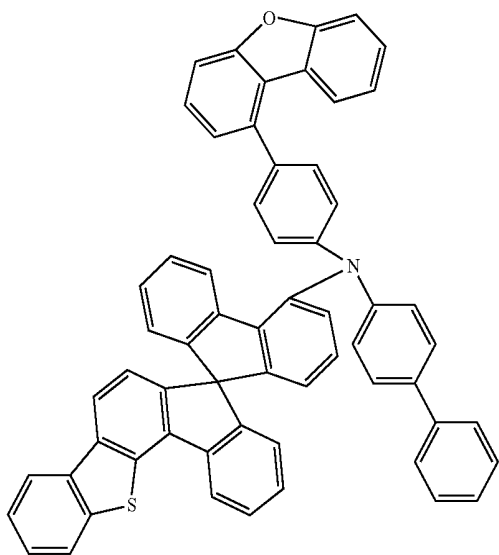
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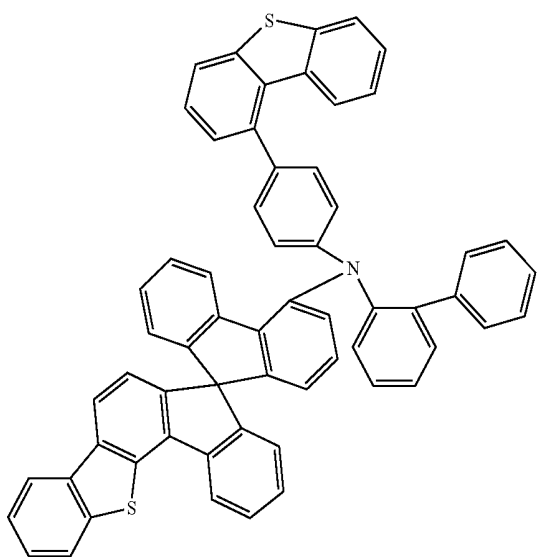
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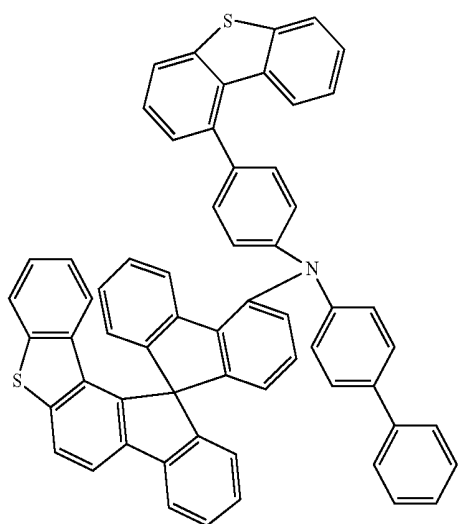
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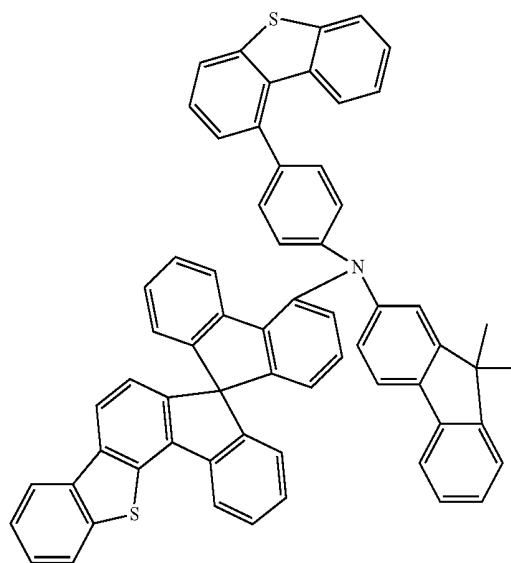
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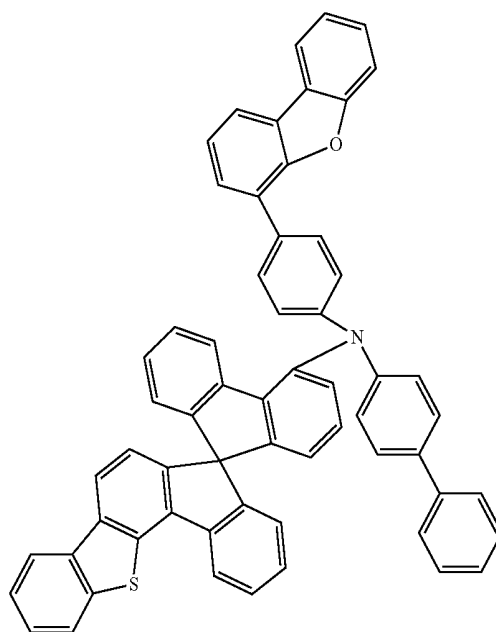
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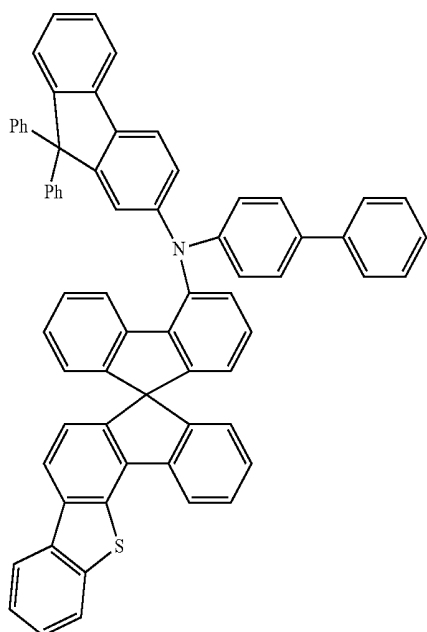
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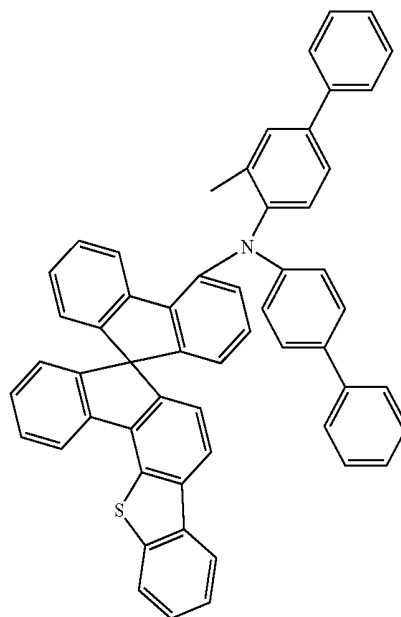
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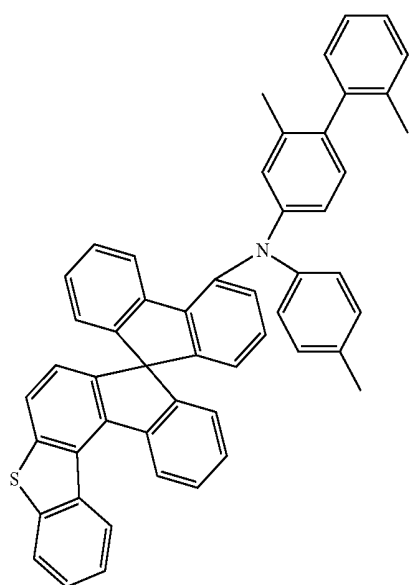
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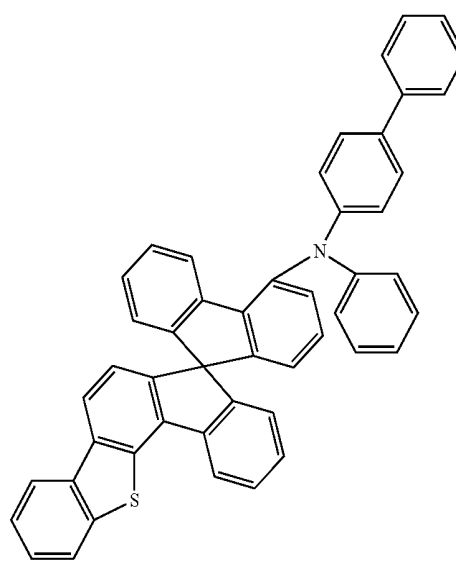


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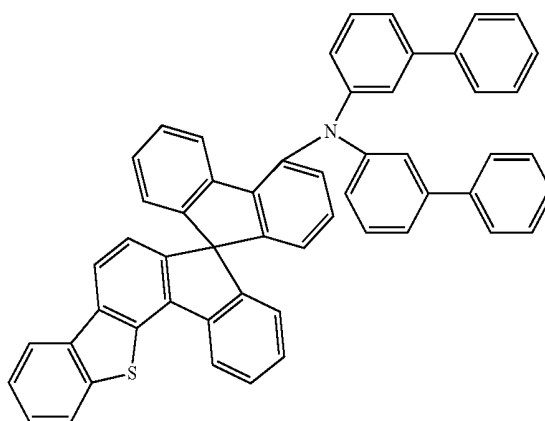
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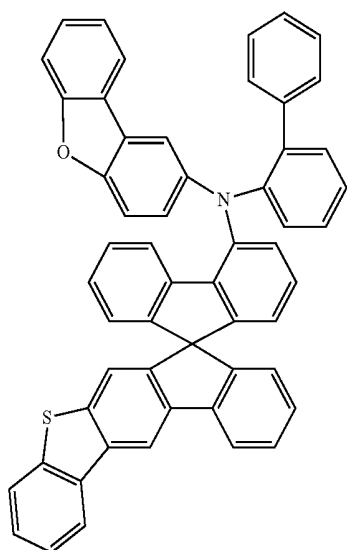
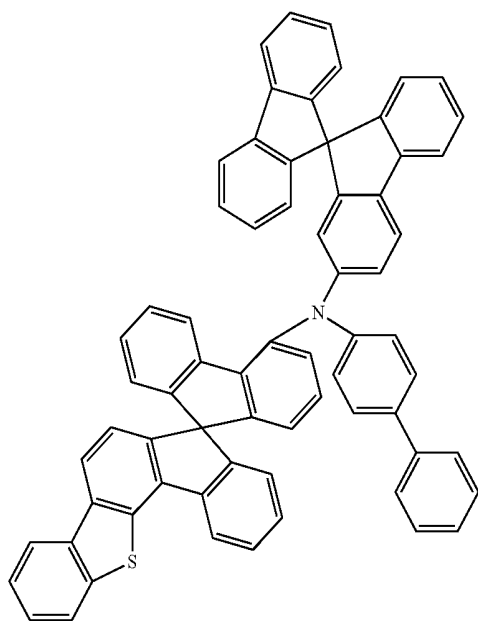
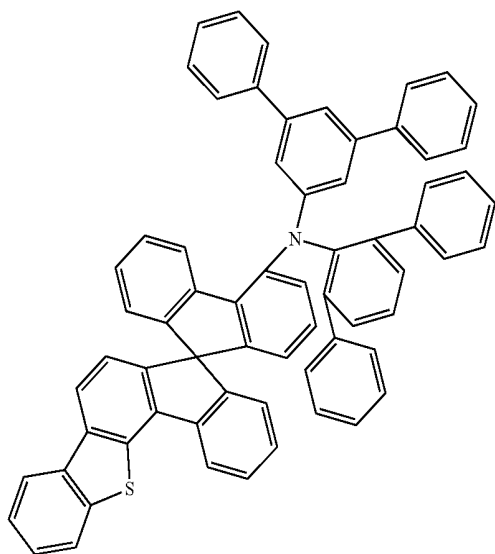
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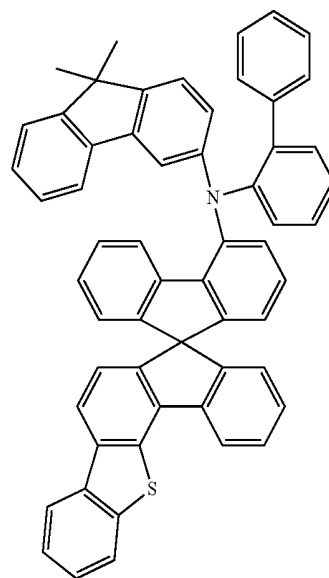
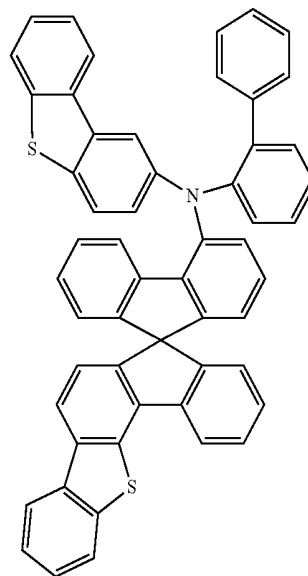
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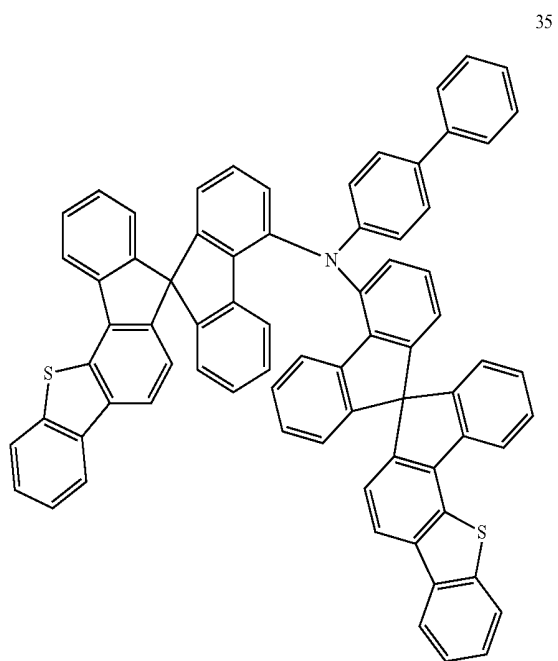
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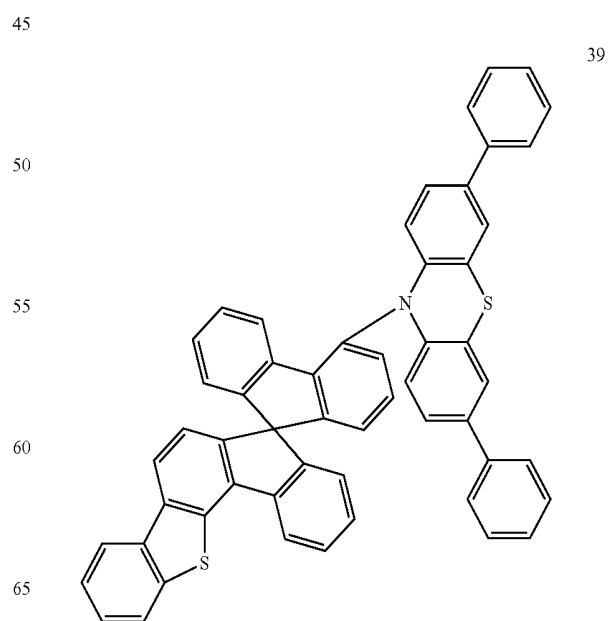
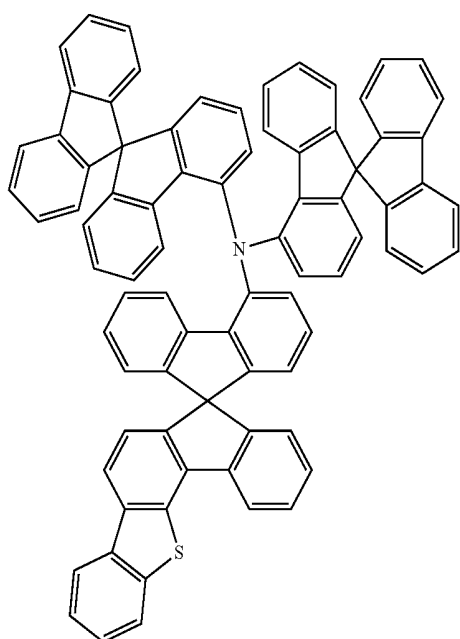
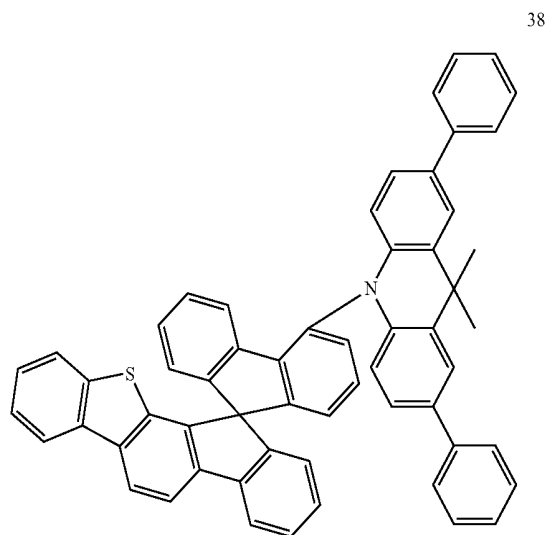
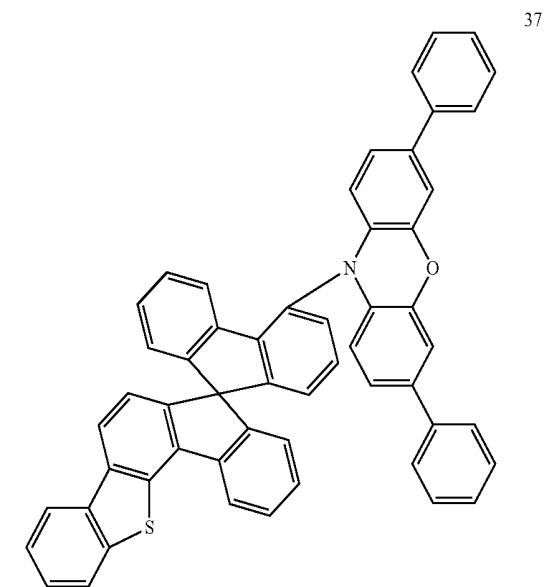
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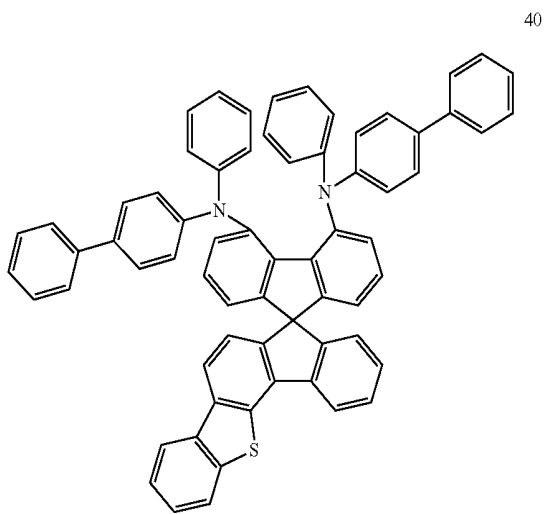
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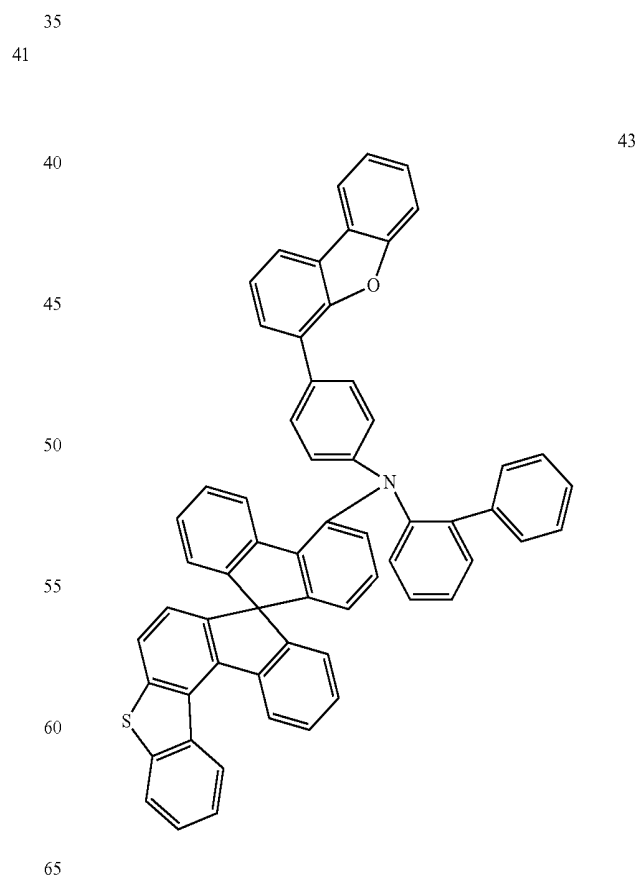
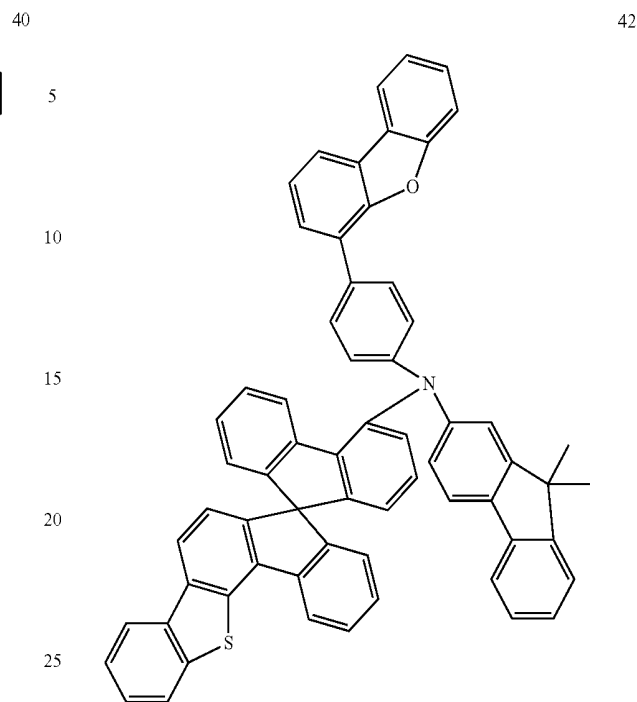
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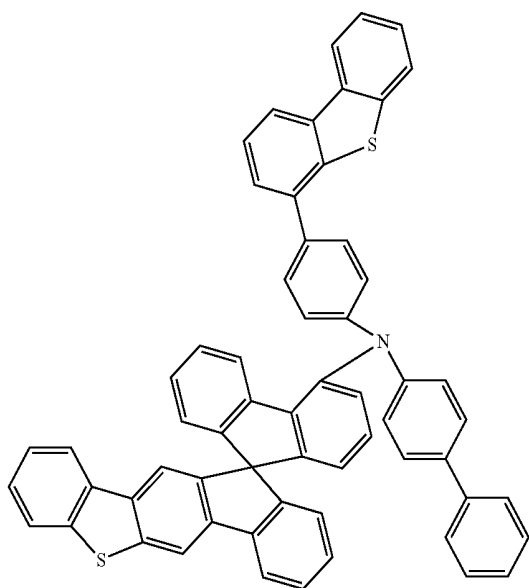
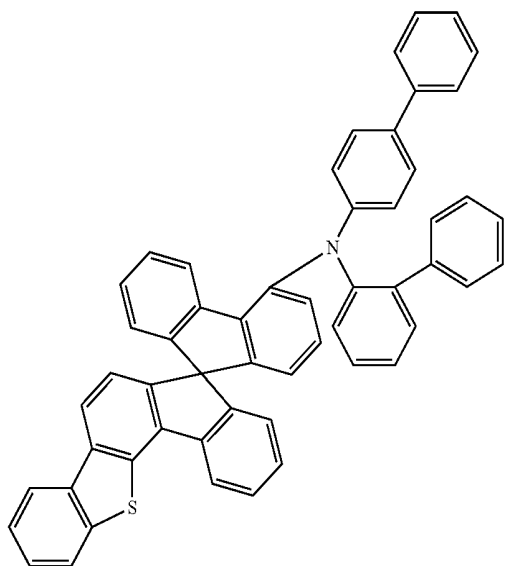
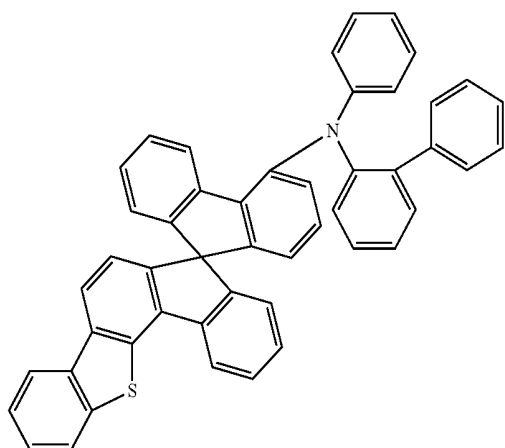
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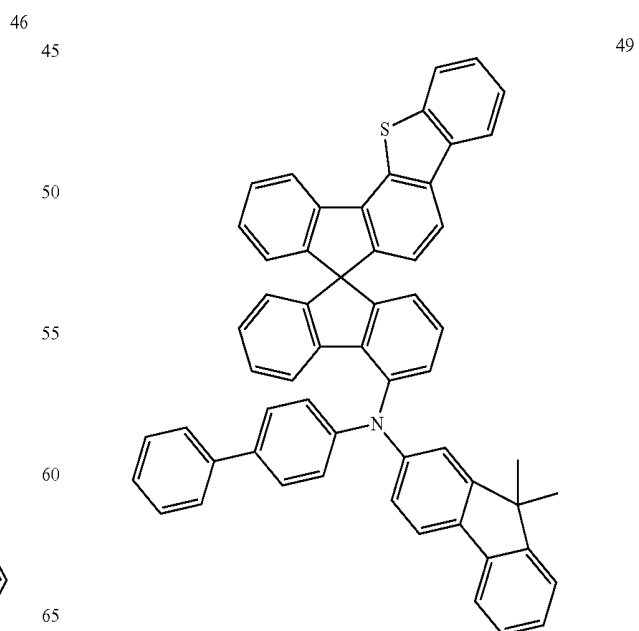
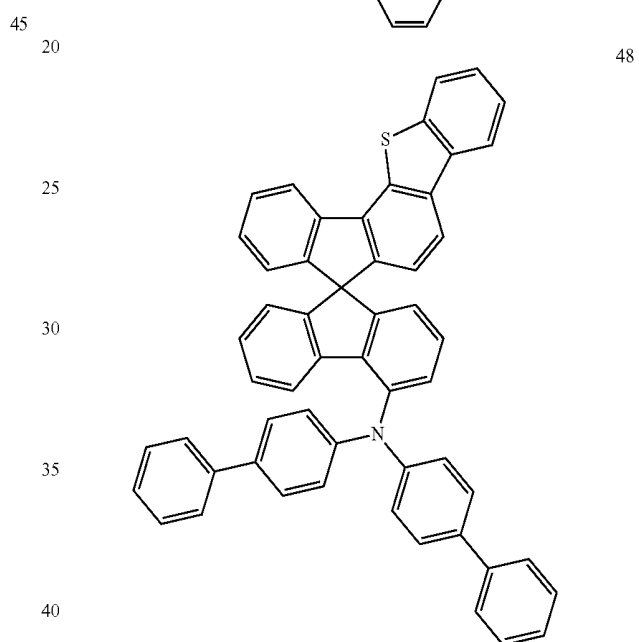
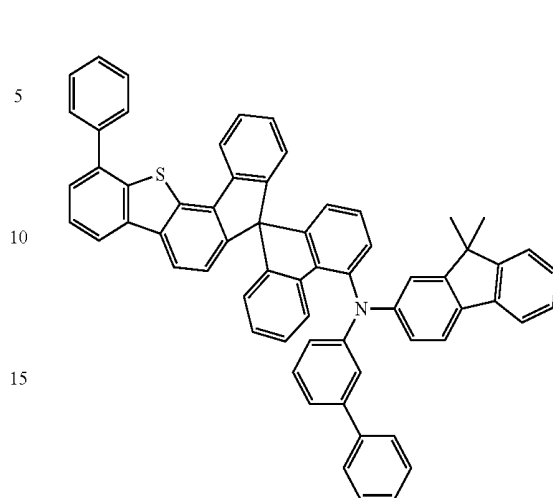
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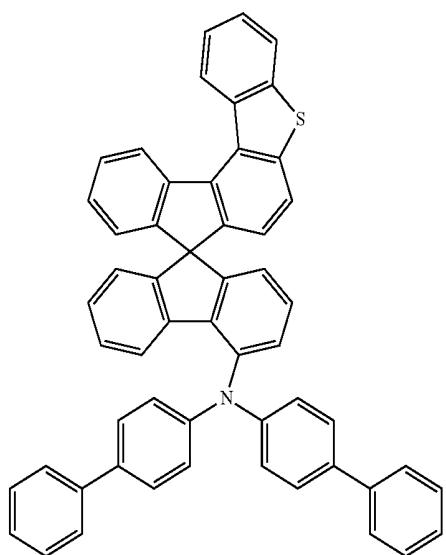
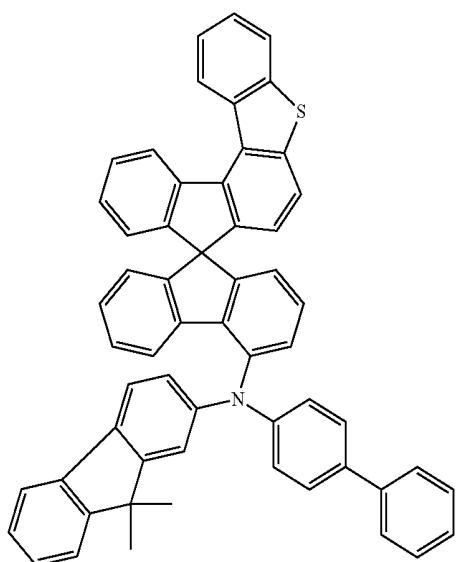
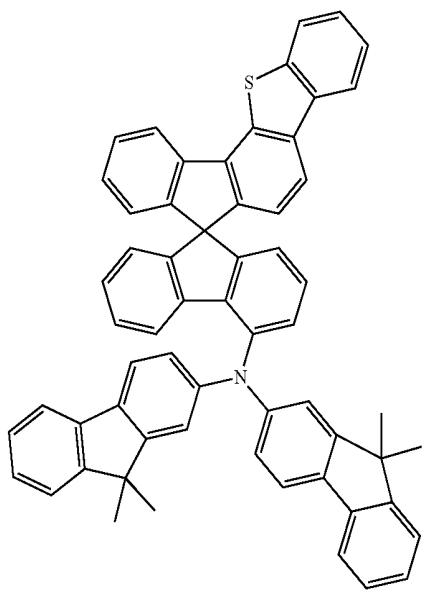
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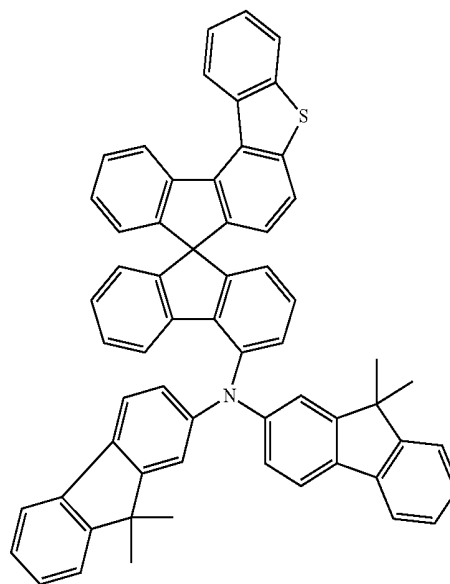
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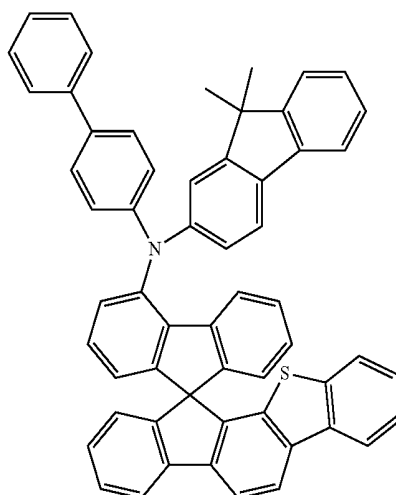
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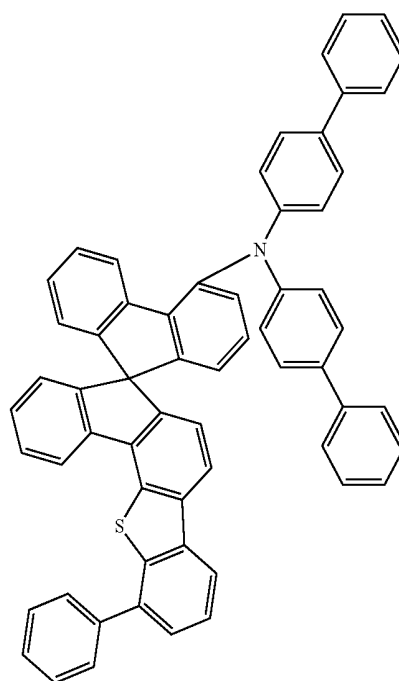
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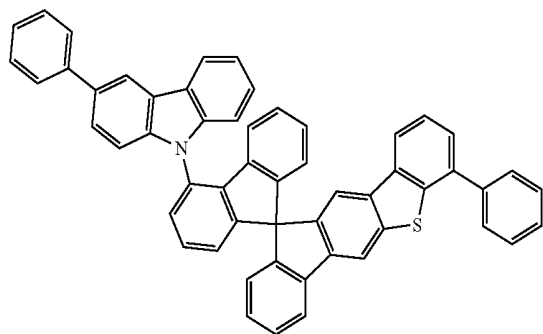
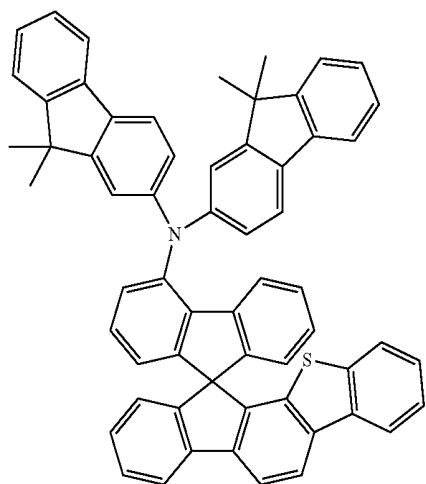
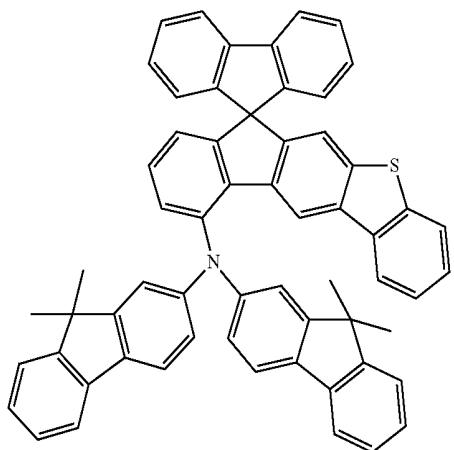
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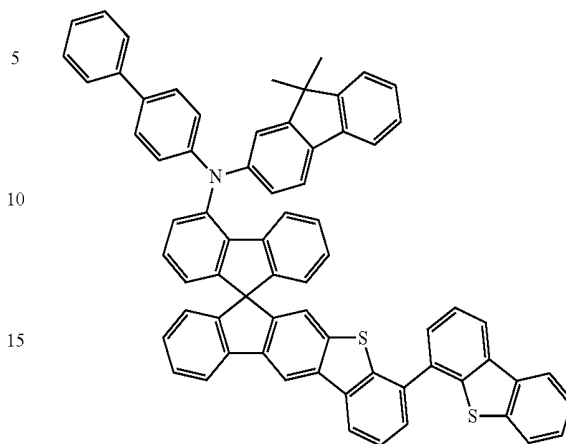


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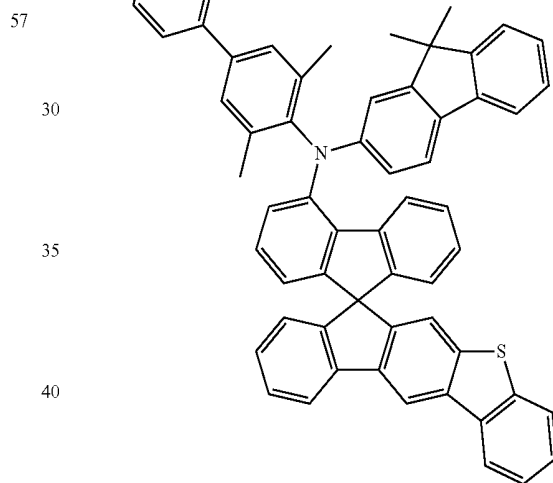
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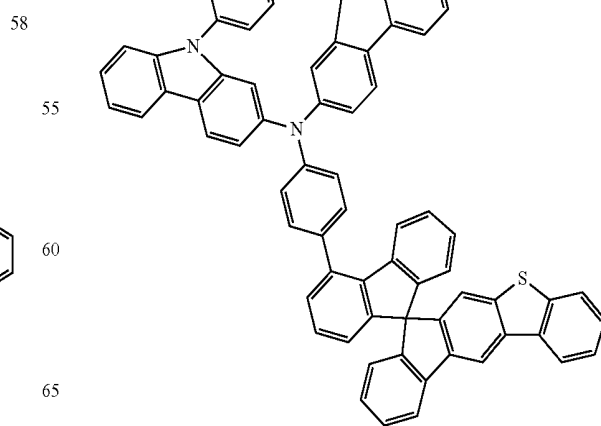
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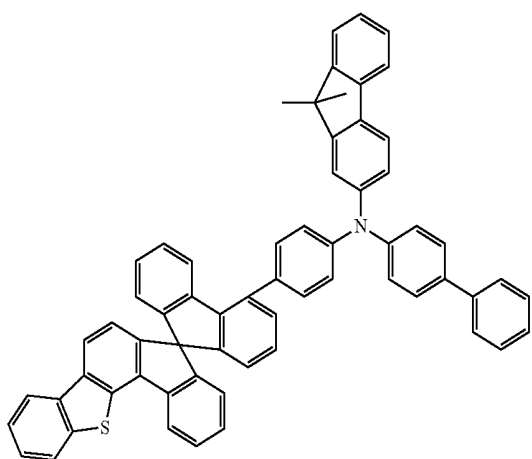
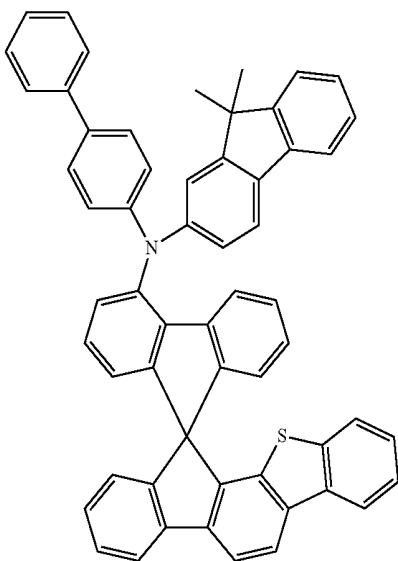
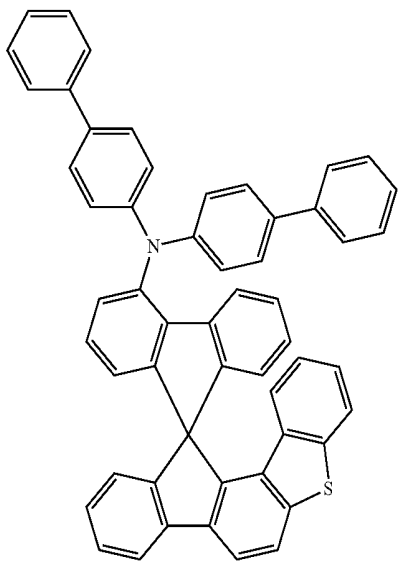
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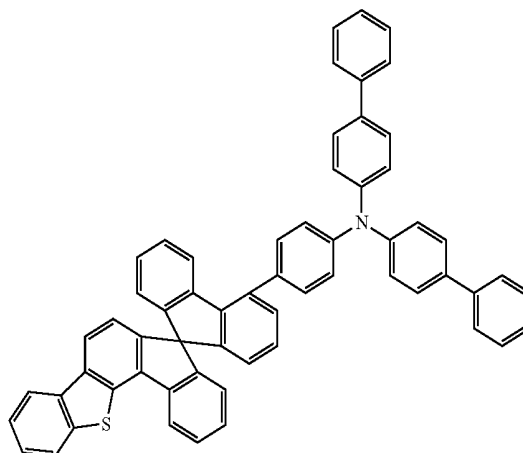
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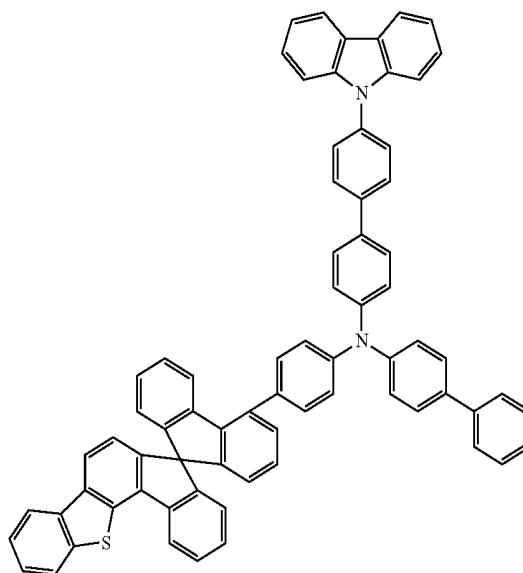
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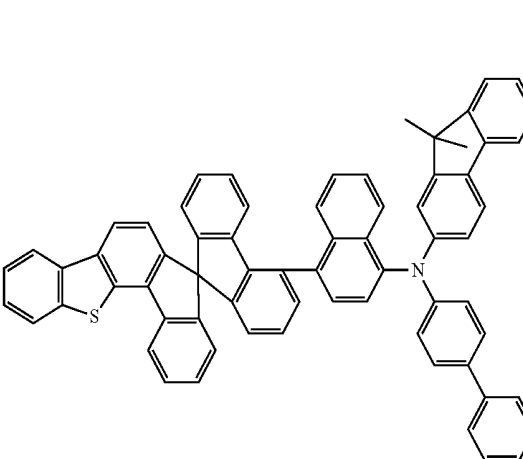
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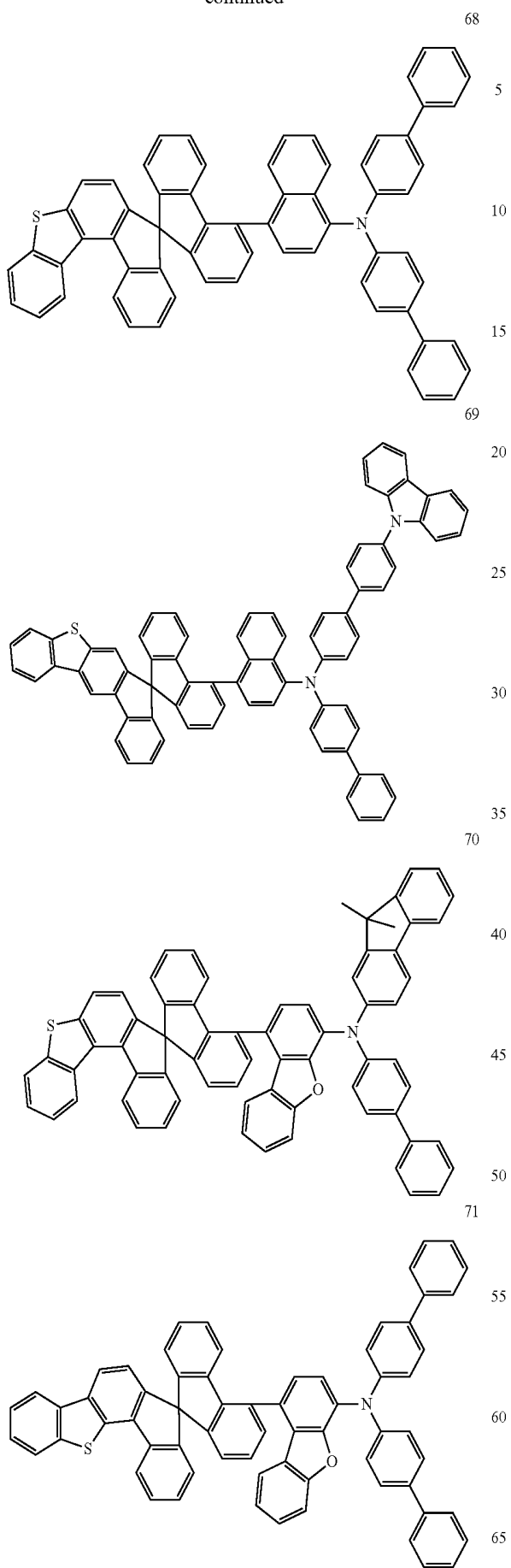
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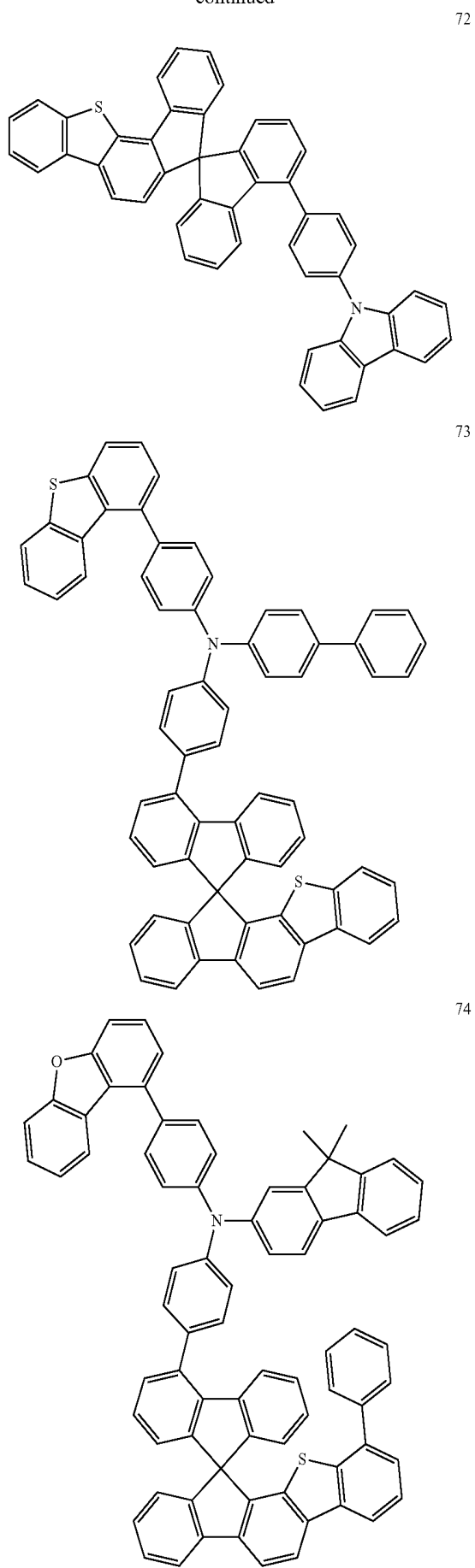
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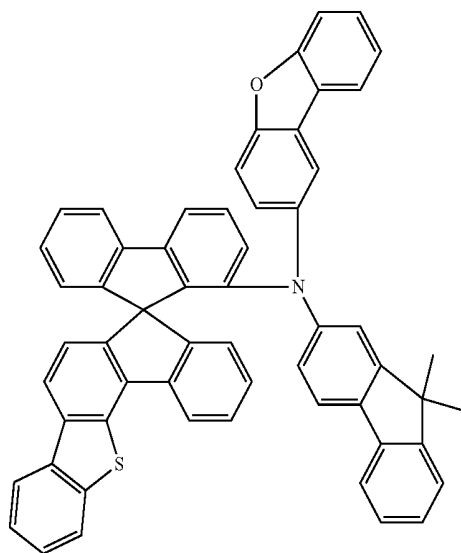
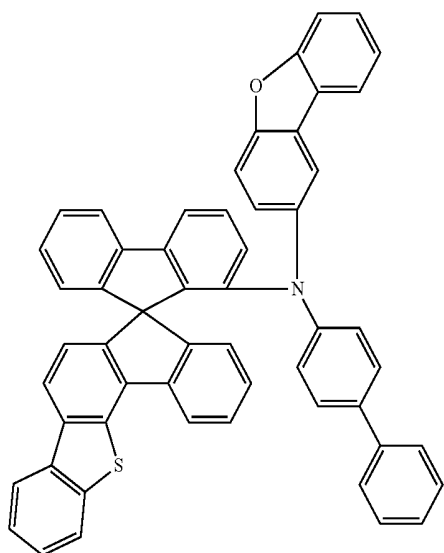
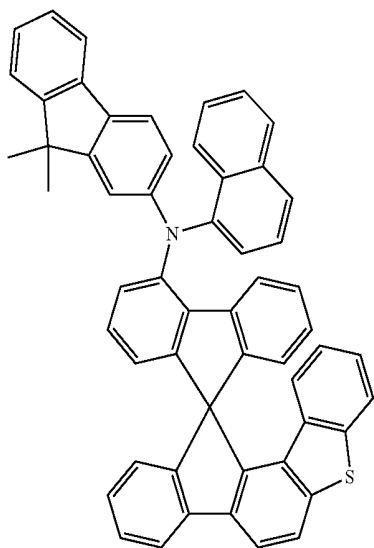
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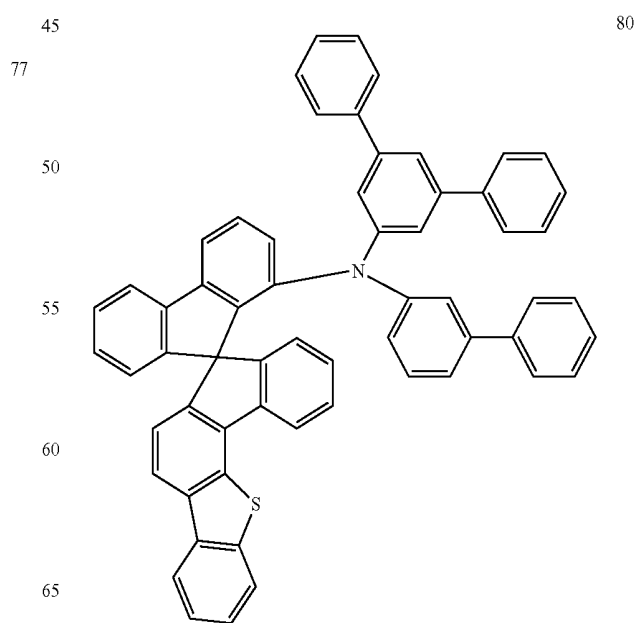
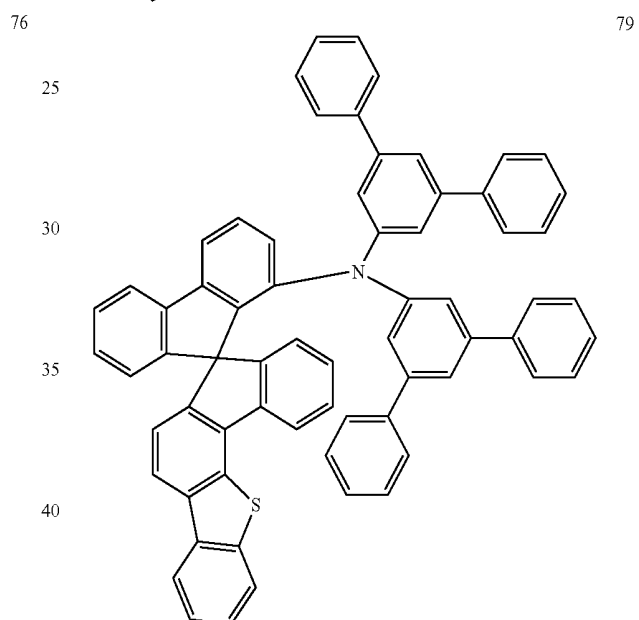
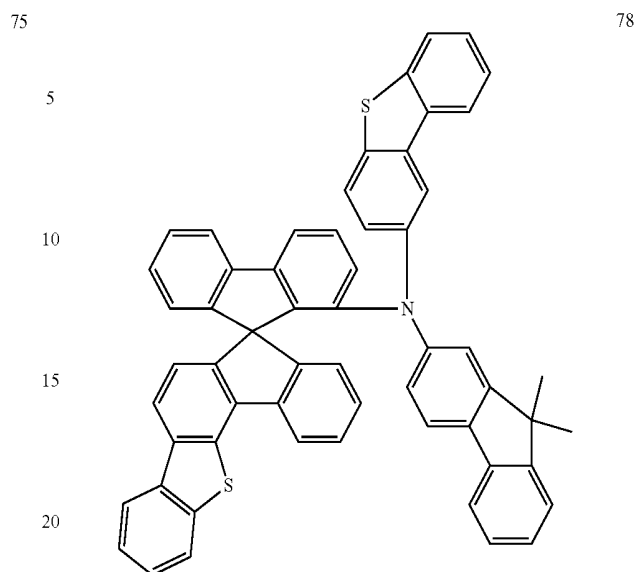
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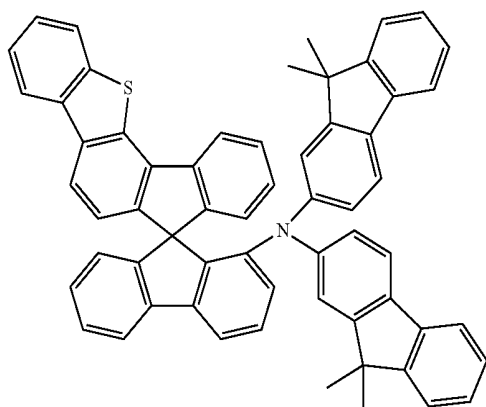
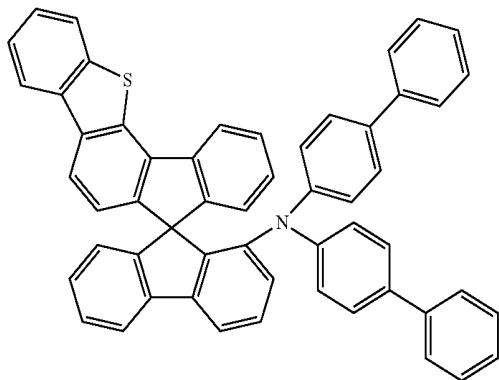
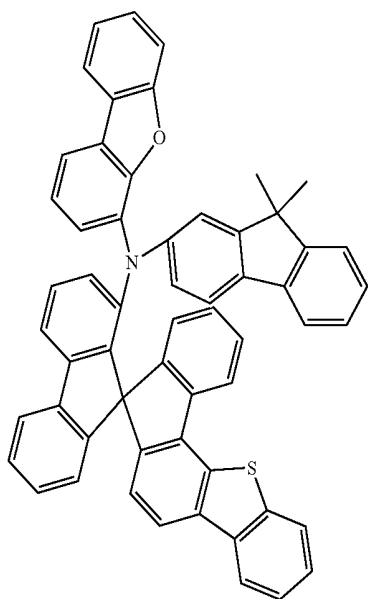


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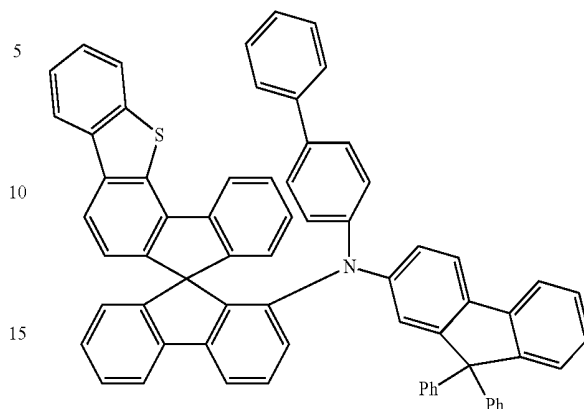


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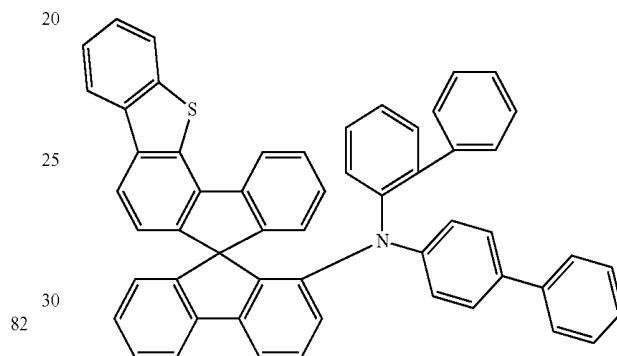
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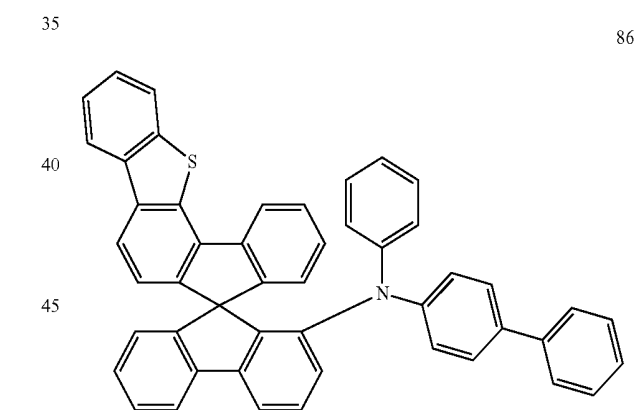
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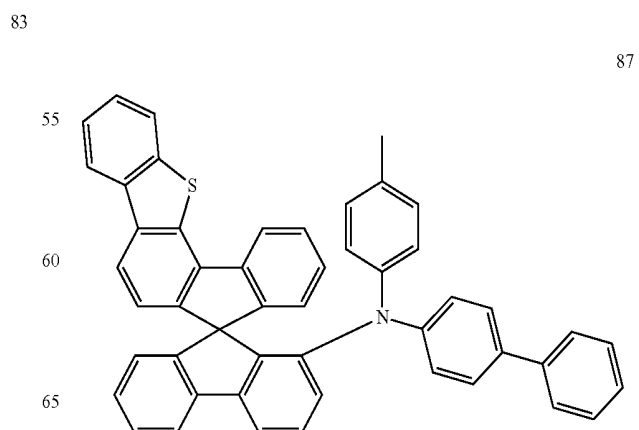


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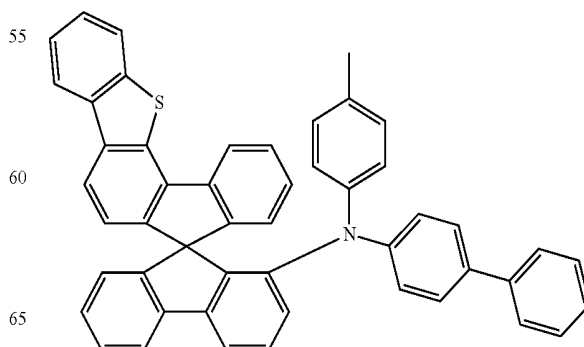
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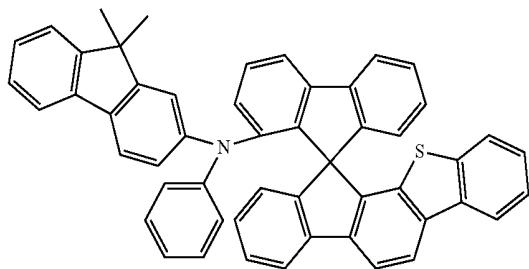
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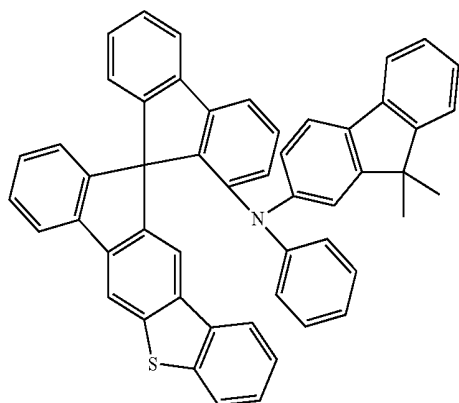
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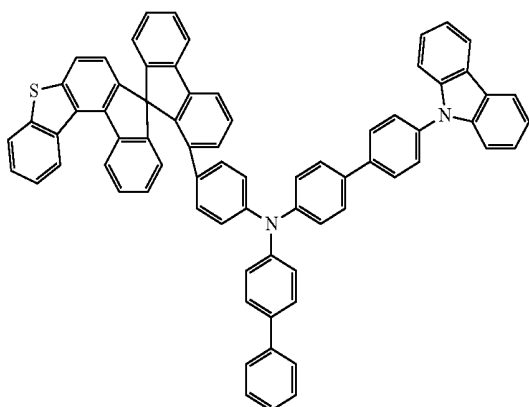
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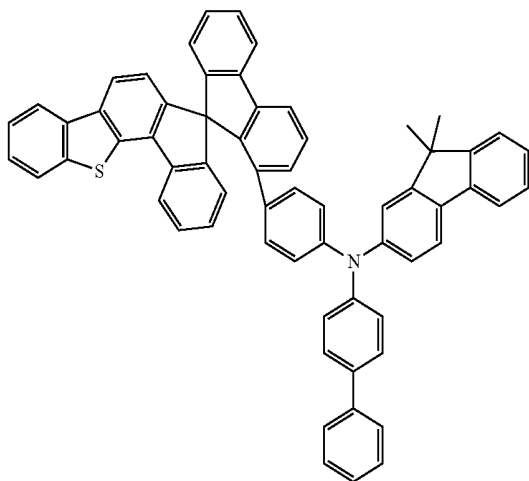
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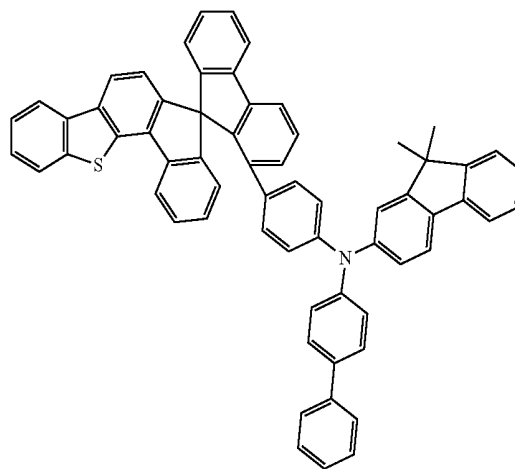
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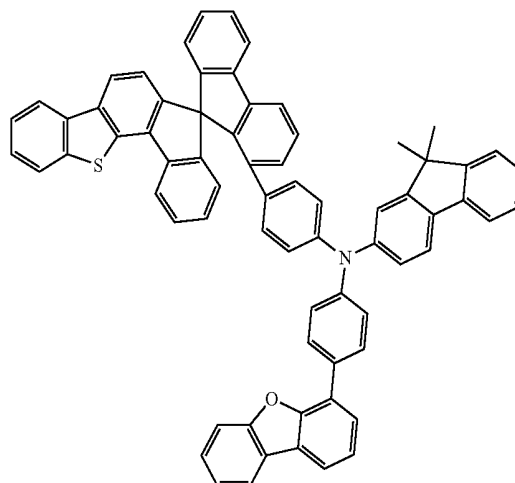
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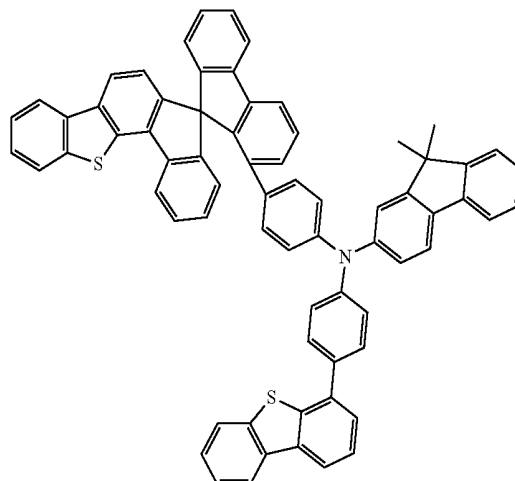
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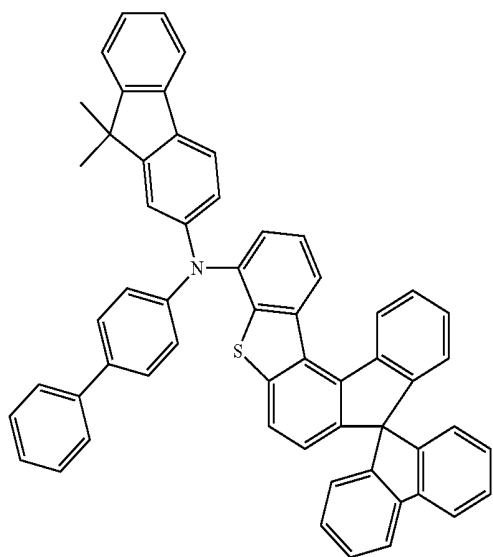
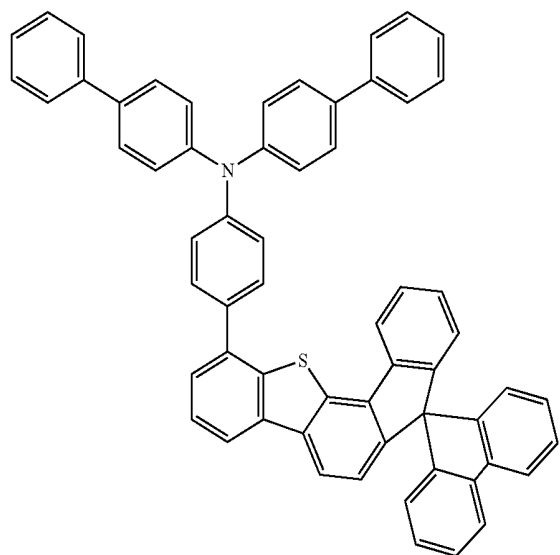
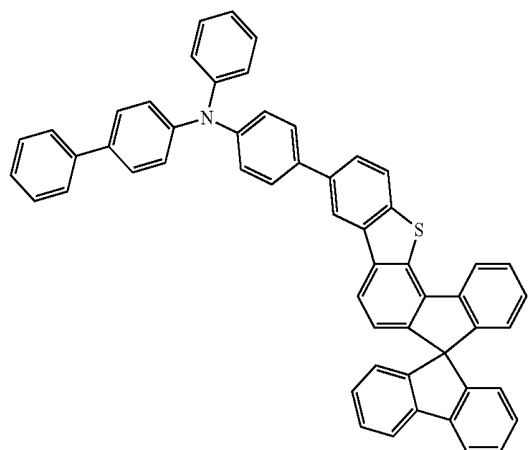


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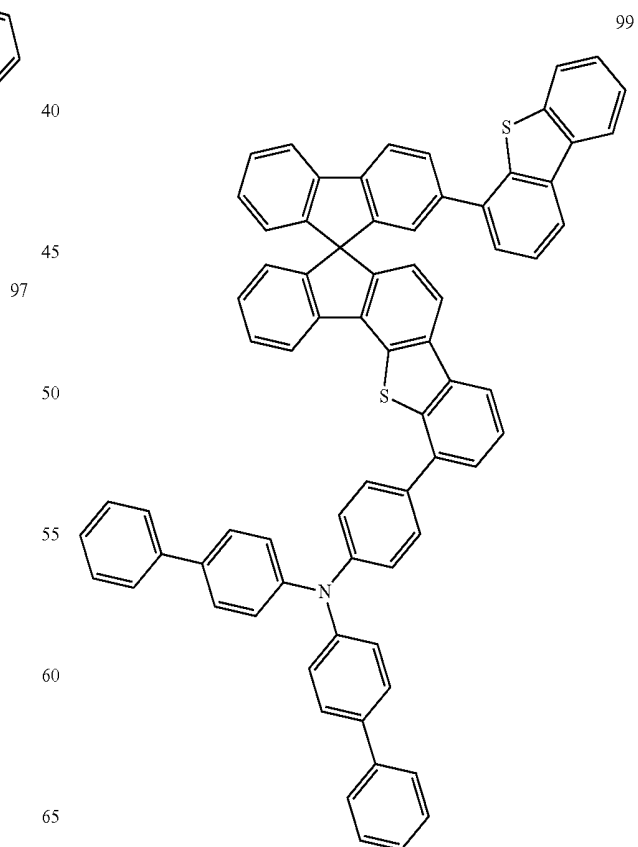
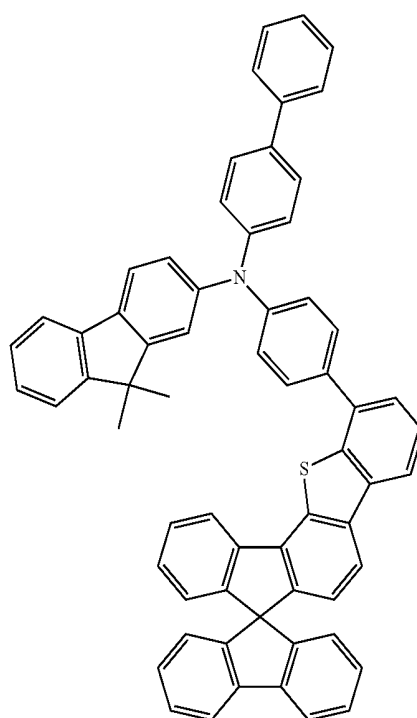
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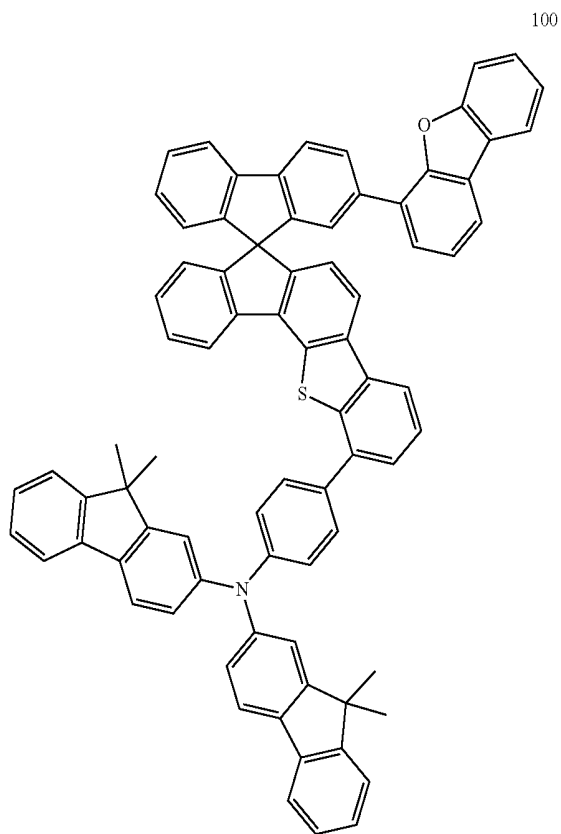


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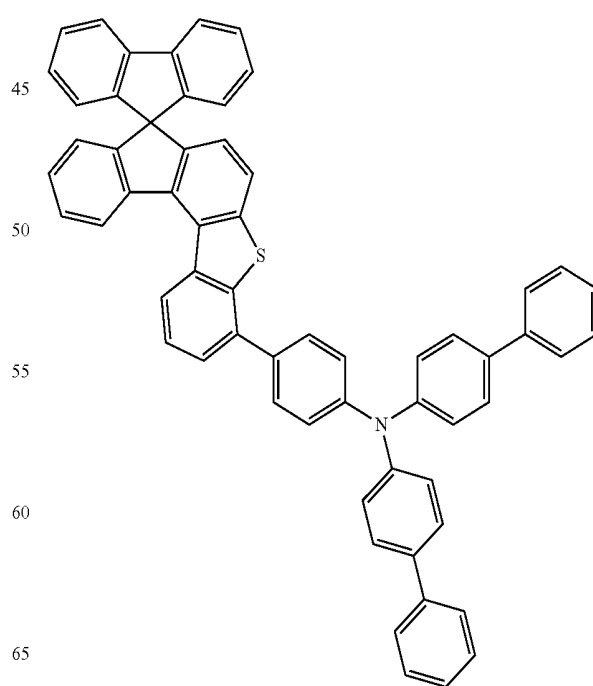
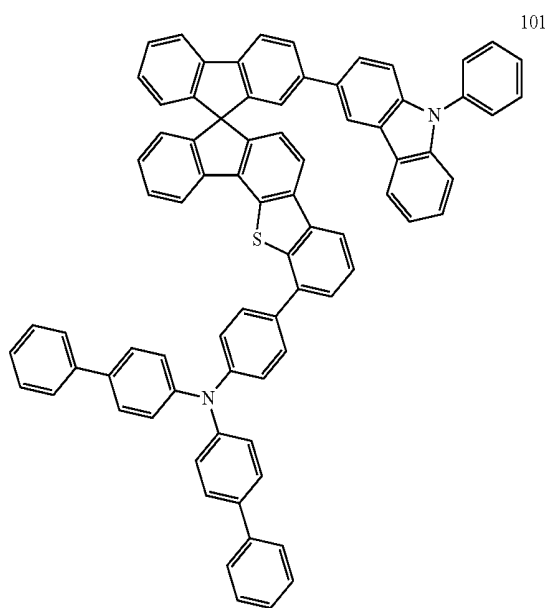
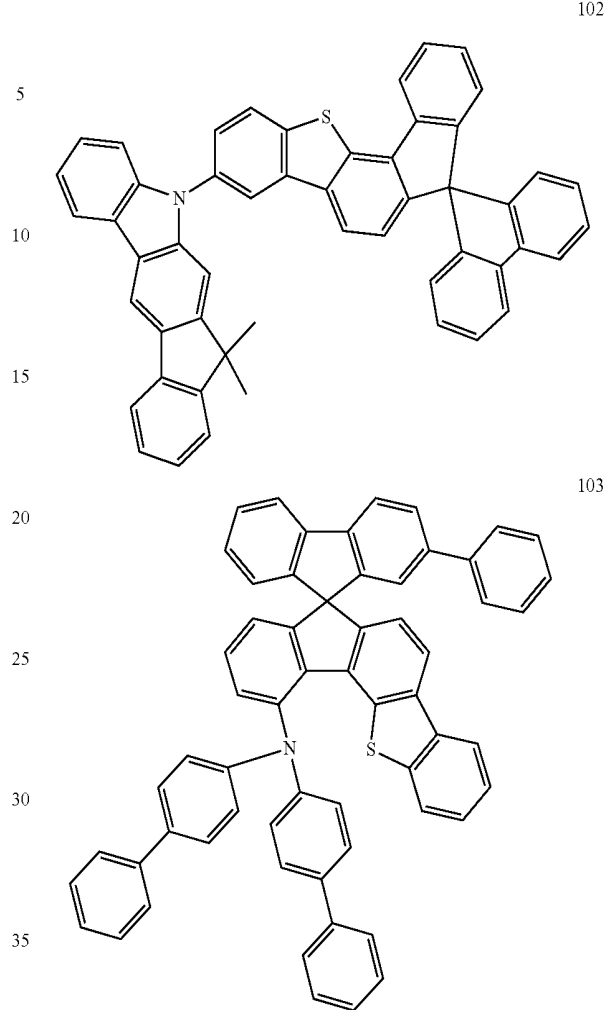
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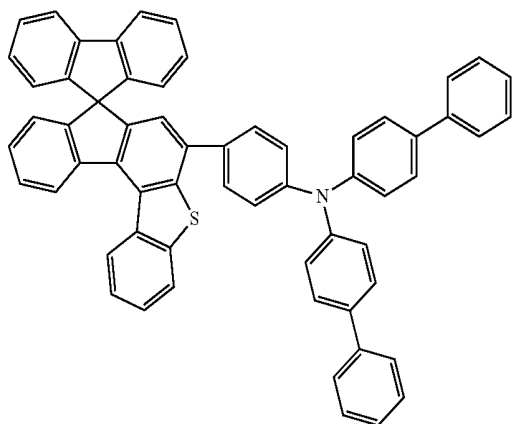
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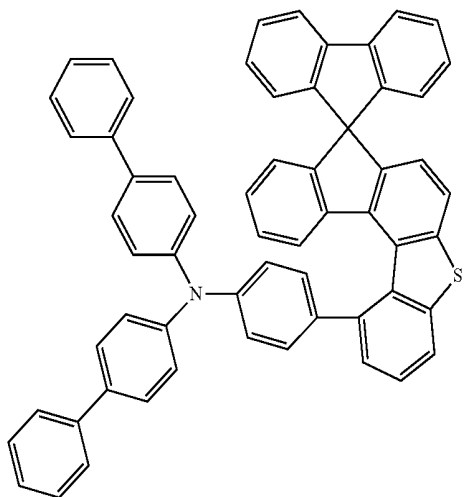
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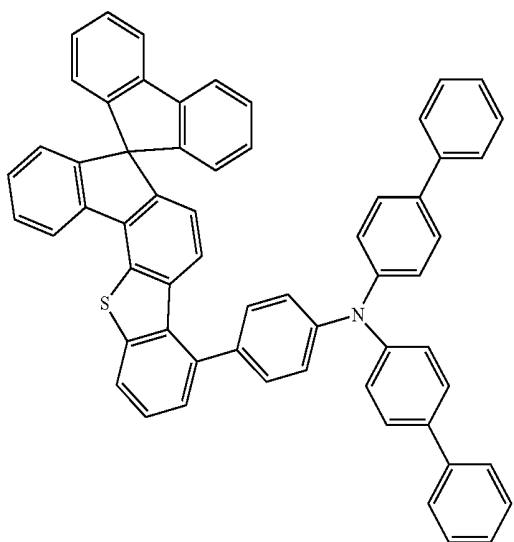
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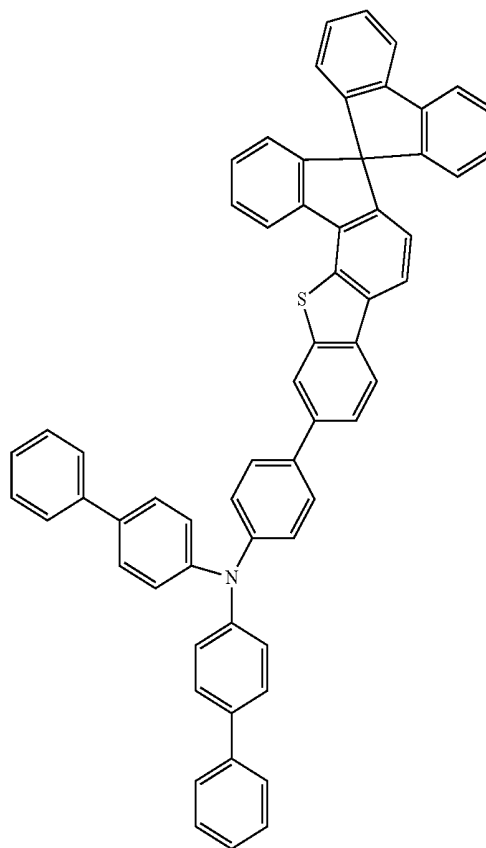
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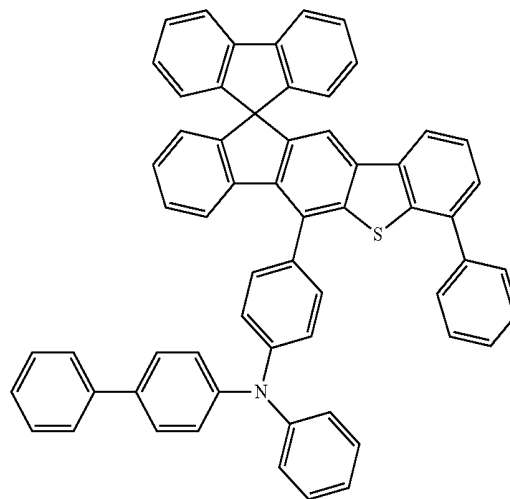
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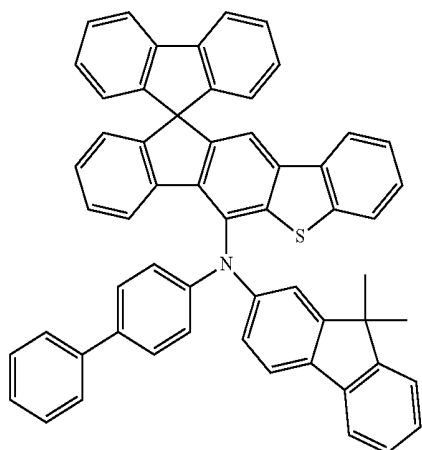


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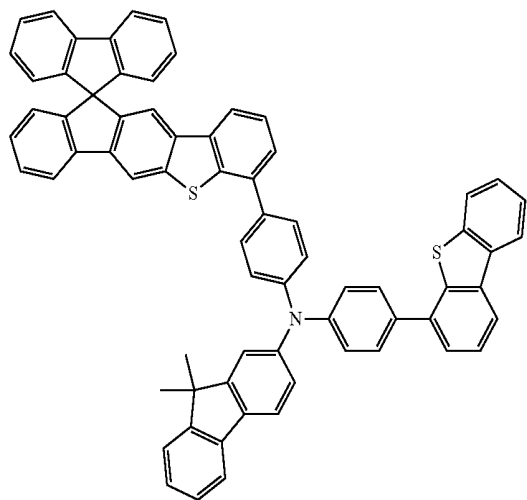
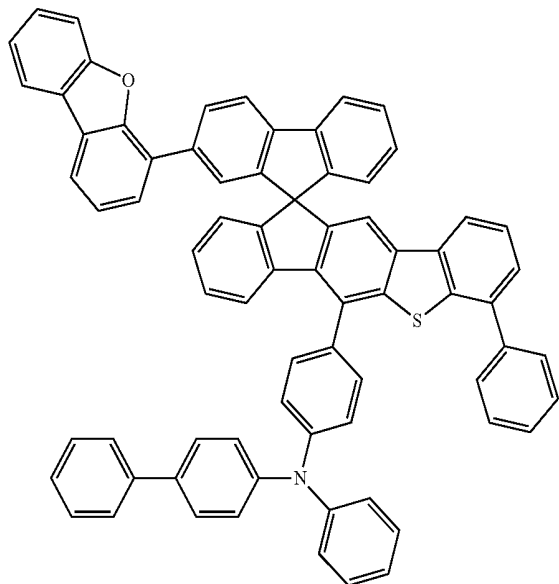
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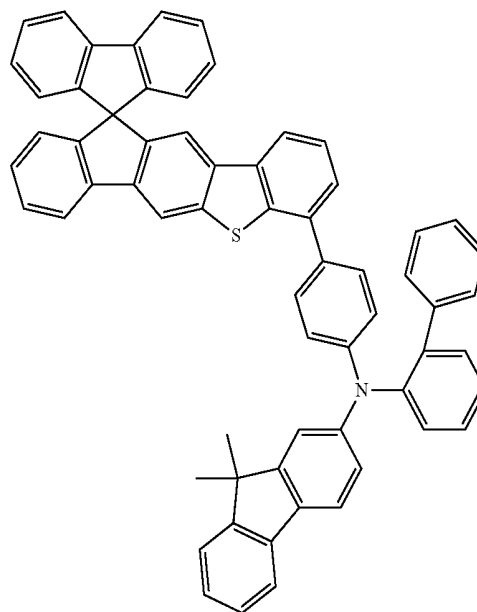
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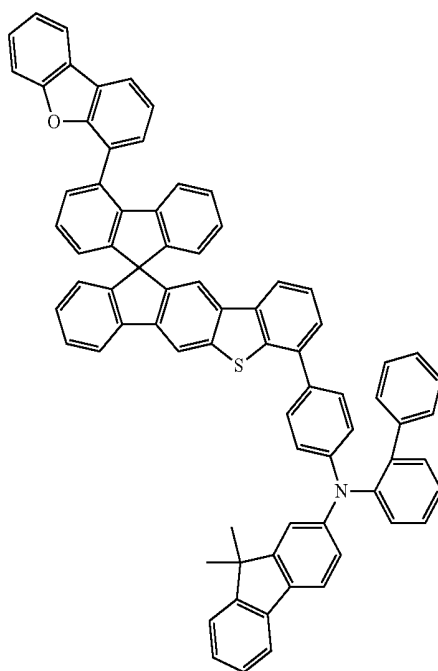


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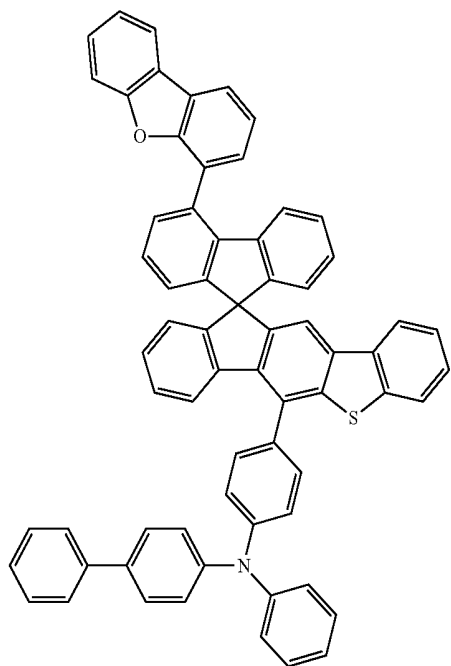
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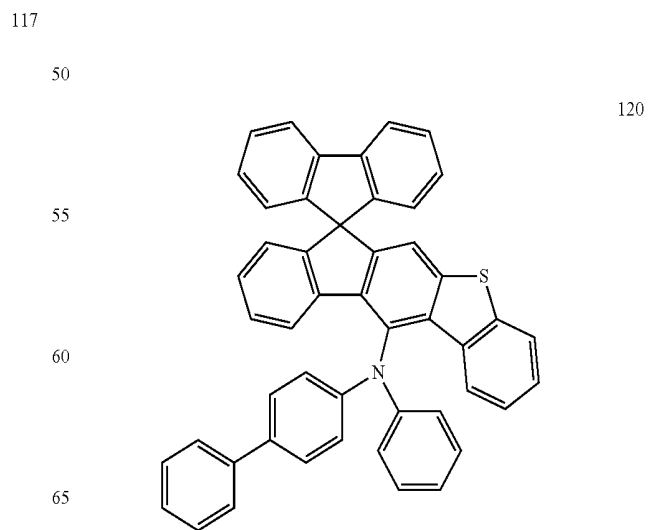
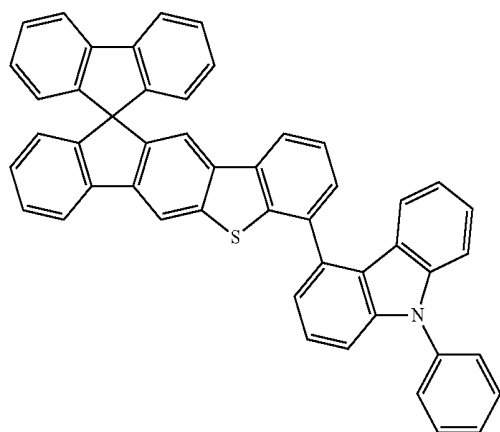
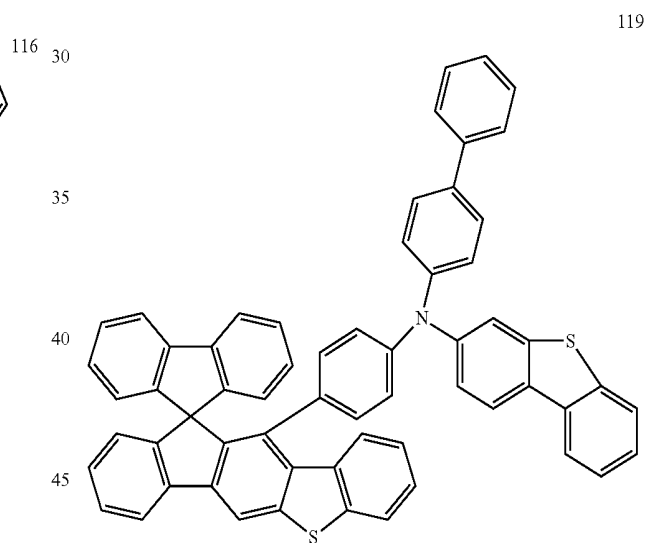
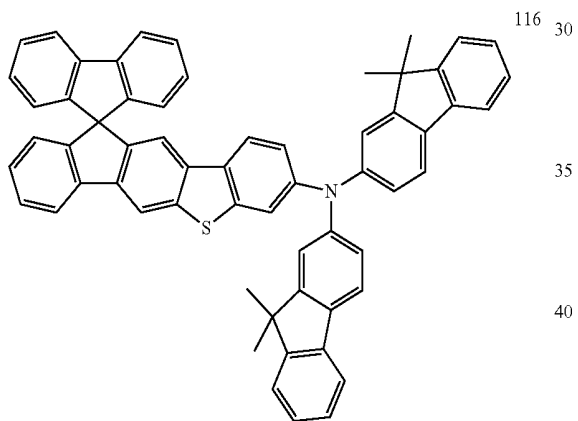
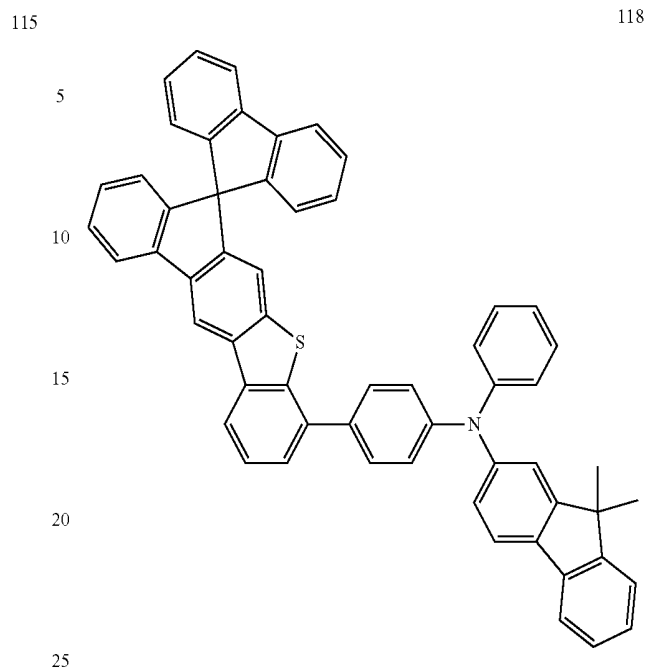
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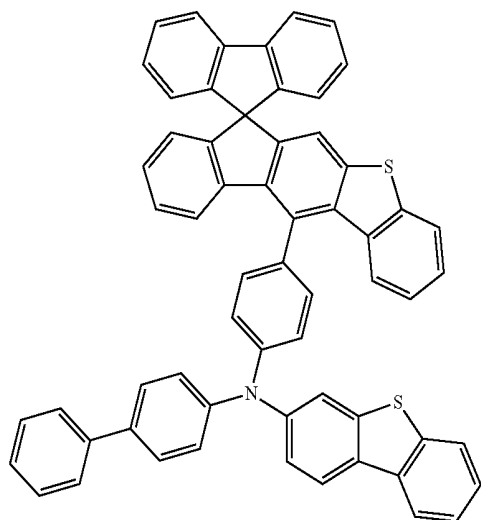


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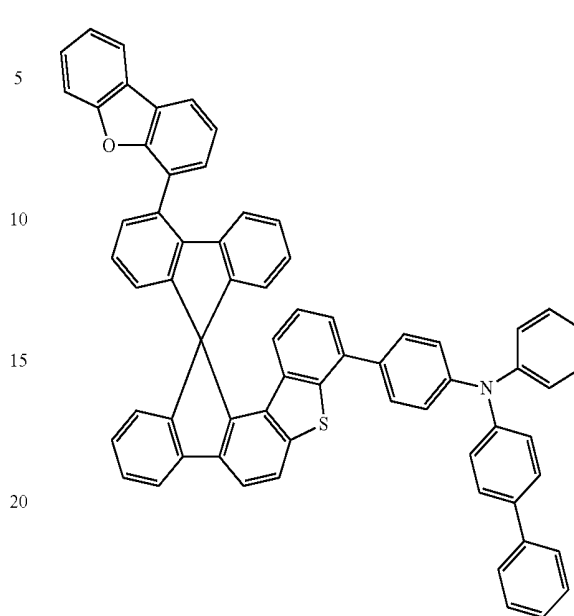
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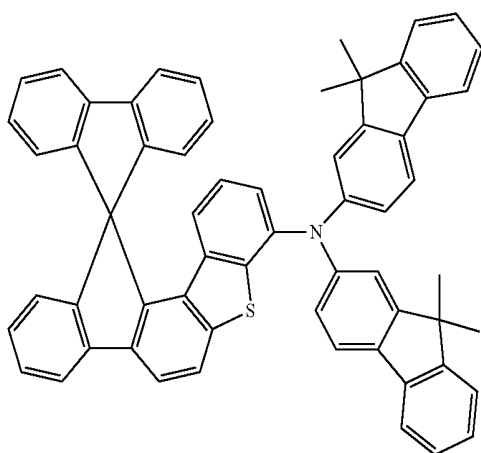
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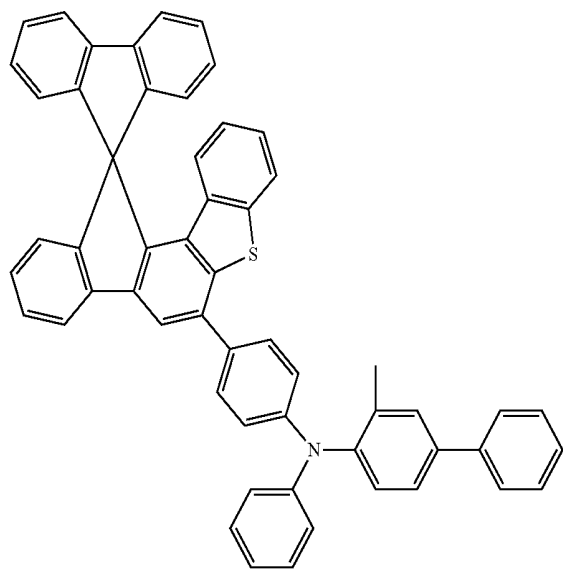
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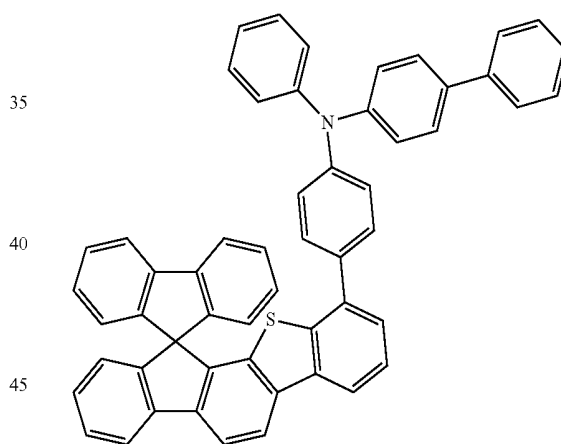


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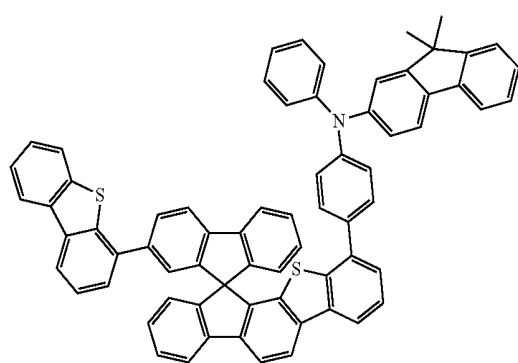


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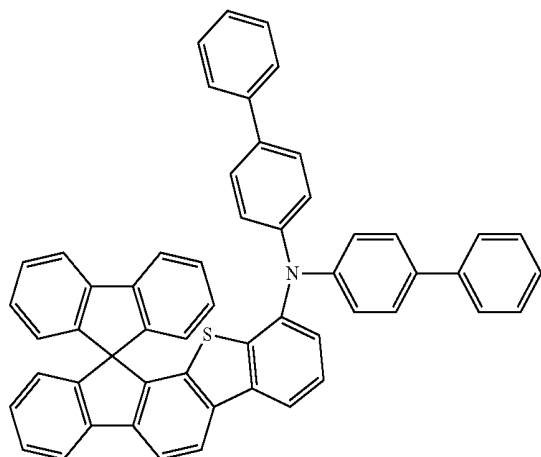
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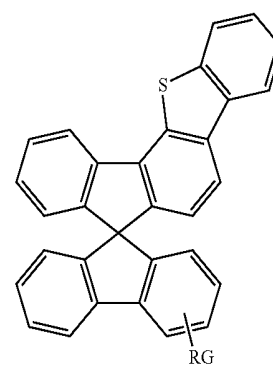
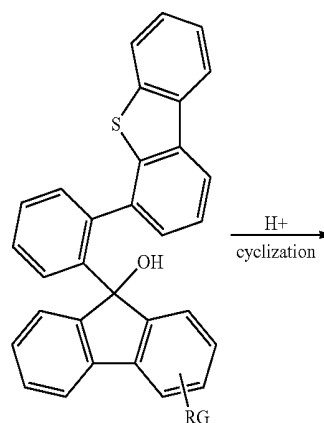
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Formula (Z-1)

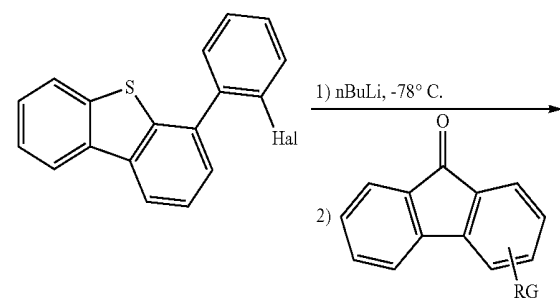
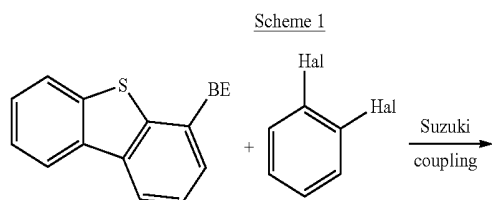
BE: boronic acid derivative
 Hal: halogen atom
 RG: reactive group, preferably Br

The synthesis of the compounds of formula (I) can be conducted using processes and reaction types known in the prior art, for example halogenation, organometallic addition, Buchwald coupling and Suzuki coupling.

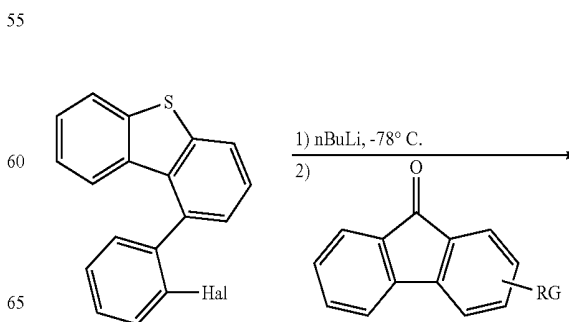
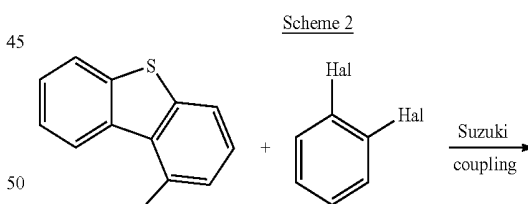
Schemes 1 to 8 show possible synthesis routes for preparation of the inventive compounds. They serve to elucidate the invention to the person skilled in the art, and should not be interpreted in a restrictive manner. The person skilled in the art will be able, within the scope of his common knowledge in the art, to modify the synthesis routes shown, or to develop other routes if this appears to be more advantageous.

In all the synthesis schemes that follow, the compounds are shown in unsubstituted form. This does not rule out the presence of any desired substituents in the processes.

Scheme 1 shows a suitable synthesis for the intermediate of formula (Z-1).

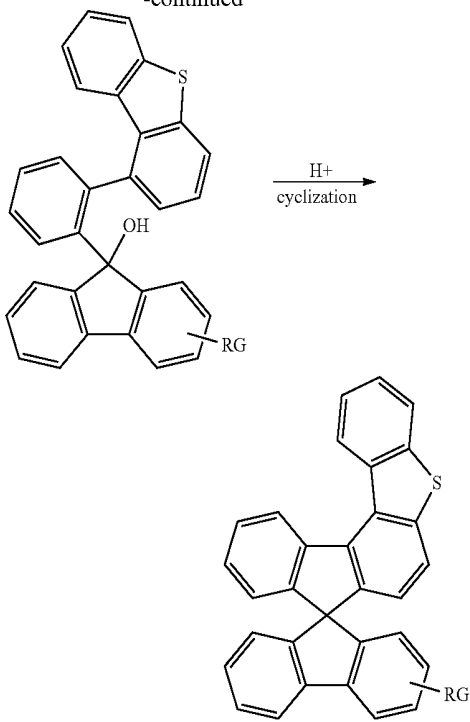


Scheme 2 shows a suitable synthesis for the intermediate of formula (Z-2).



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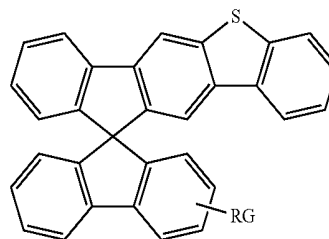
Formula (Z-2)

BE: boronic acid derivative
Hal: halogen atom
RG: reactive group, preferably Br

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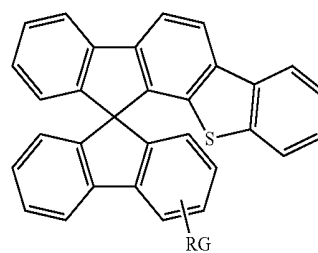
Formula (Z-3)

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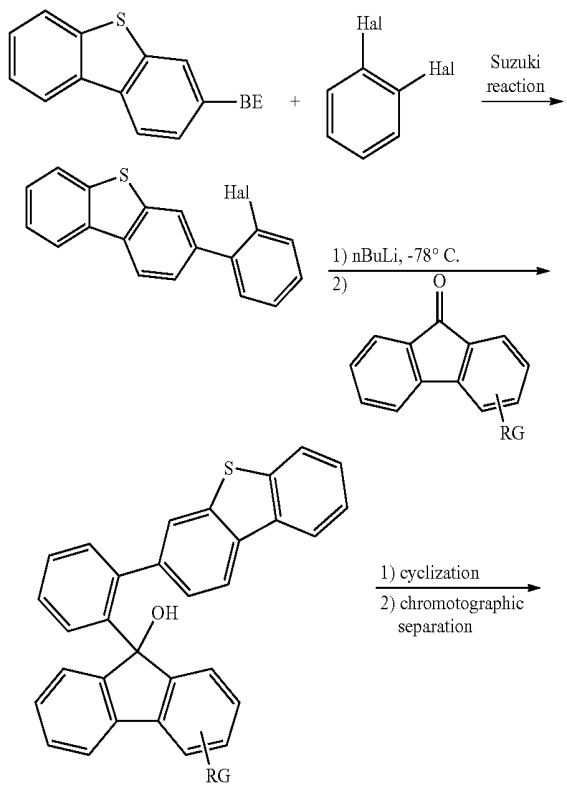
Formula (Z-4)

BE: boronic acid derivative
Hal: halogen atom
RG: reactive group, preferably Br

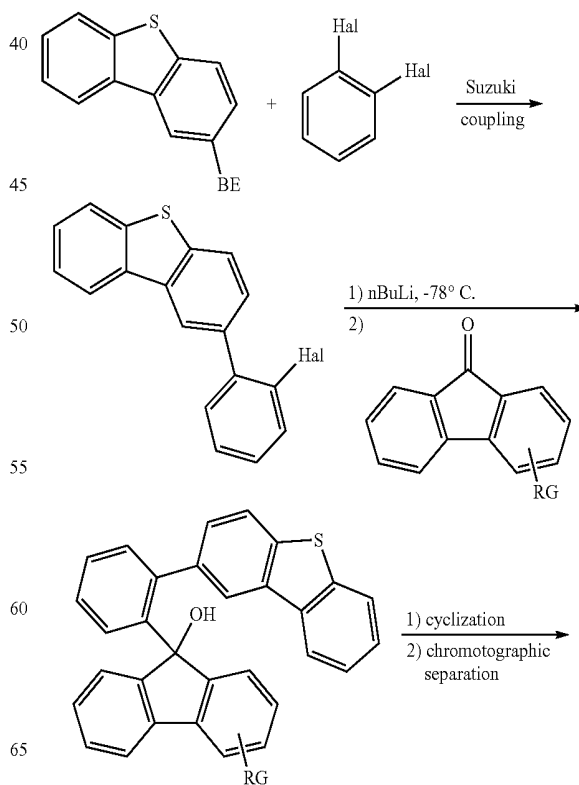
Scheme 3 shows a suitable synthesis for intermediates of formulae (Z-3) and (Z-4).

Scheme 4 shows a suitable alternative synthesis for intermediates of formulae (Z-5) and (Z-6).

Scheme 3



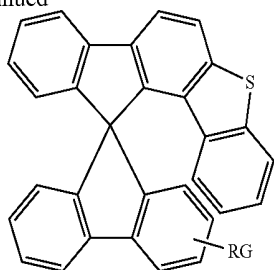
Scheme 4



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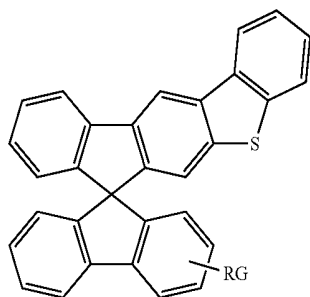
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Formula (Z-5)

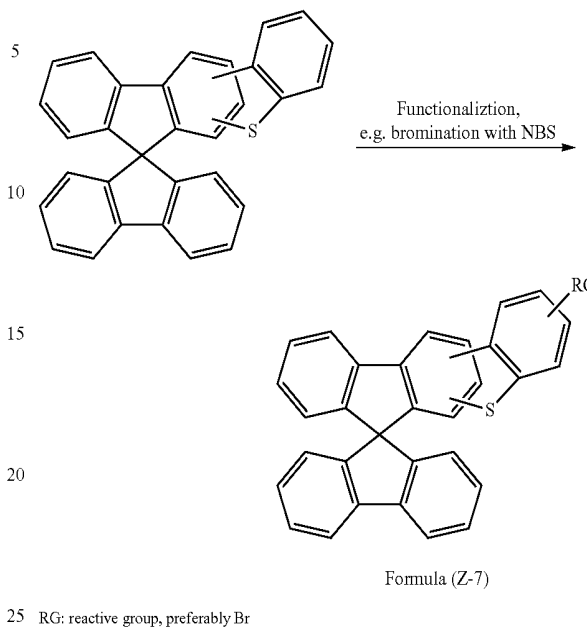
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Formula (Z-6)

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Scheme 5



Functionalization,
e.g. bromination with NBS

Formula (Z-7)

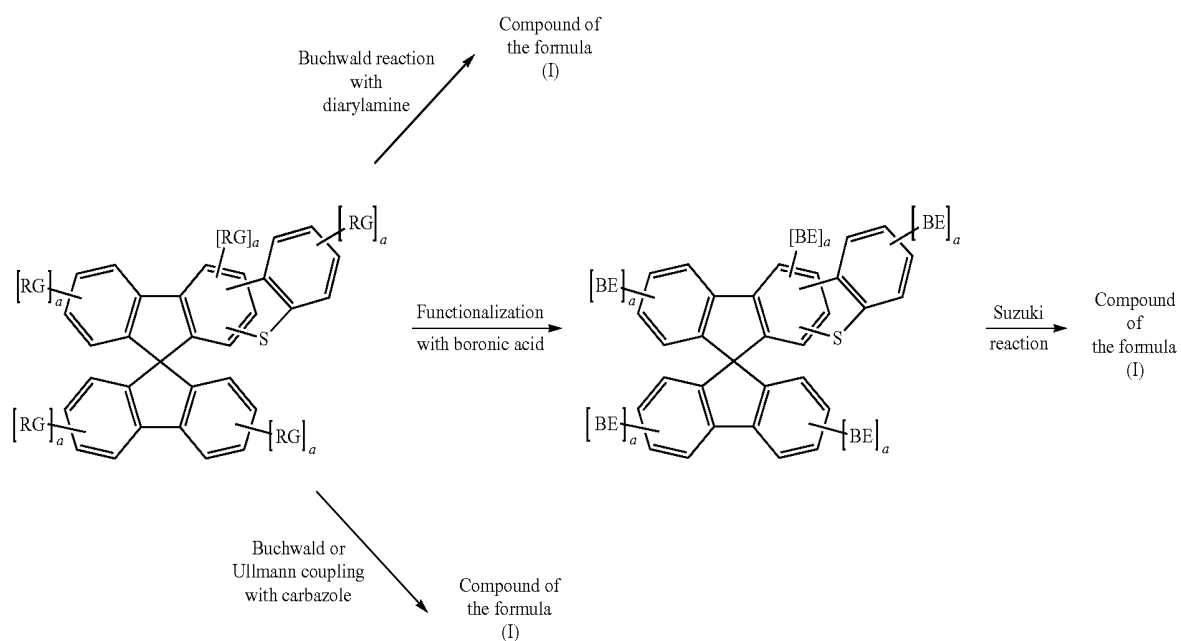
25 RG: reactive group, preferably Br

BE: boronic acid derivative
Hal: halogen atom
RG: reactive group, preferably Br

The synthesis units shown above may be provided with a reactive group, for example bromine, on the benzothiophene unit, as shown by the following scheme (formula (Z-7)):

30 The intermediates of the formulae (Z-1) to (Z-7) provided with reactive groups, as shown above, are versatile synthesis units which can be converted to compounds of the formula (I) as shown by the following scheme:

Scheme 6

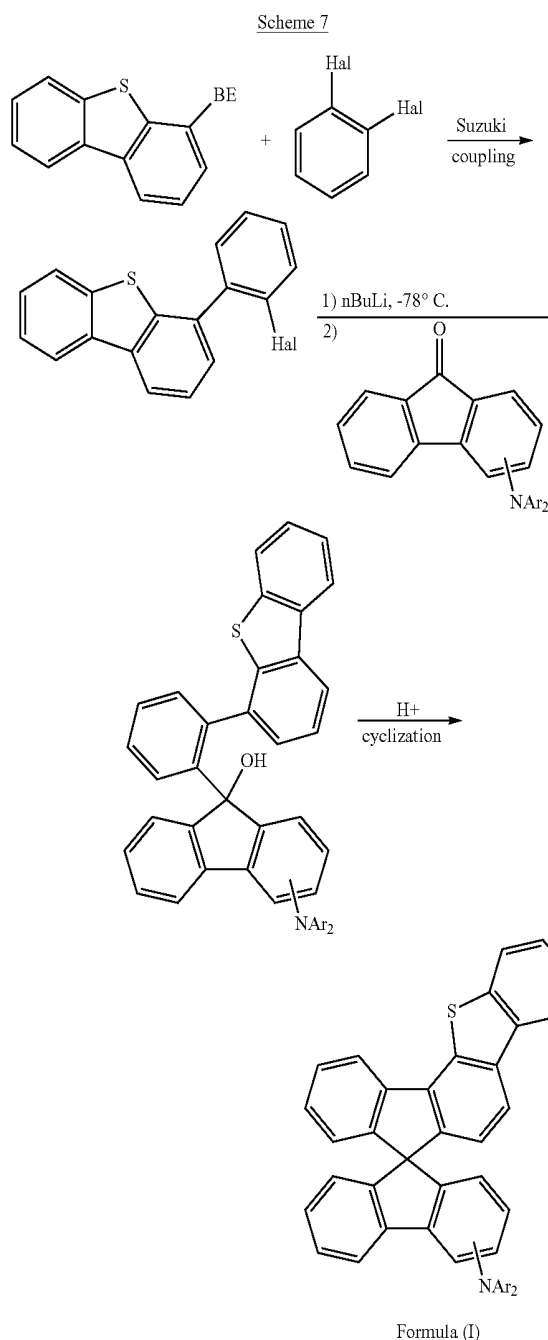


RG: reactive group, preferably bromine
BE: boronic acid derivative
a = 0 or 1

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The process shown in Scheme 6, via the functionalization with boronic acid (middle), is especially suitable for preparing compounds in which a diarylamine or a carbazole is bonded to the spirobifluorene unit via an arylene or heteroarylene spacer.

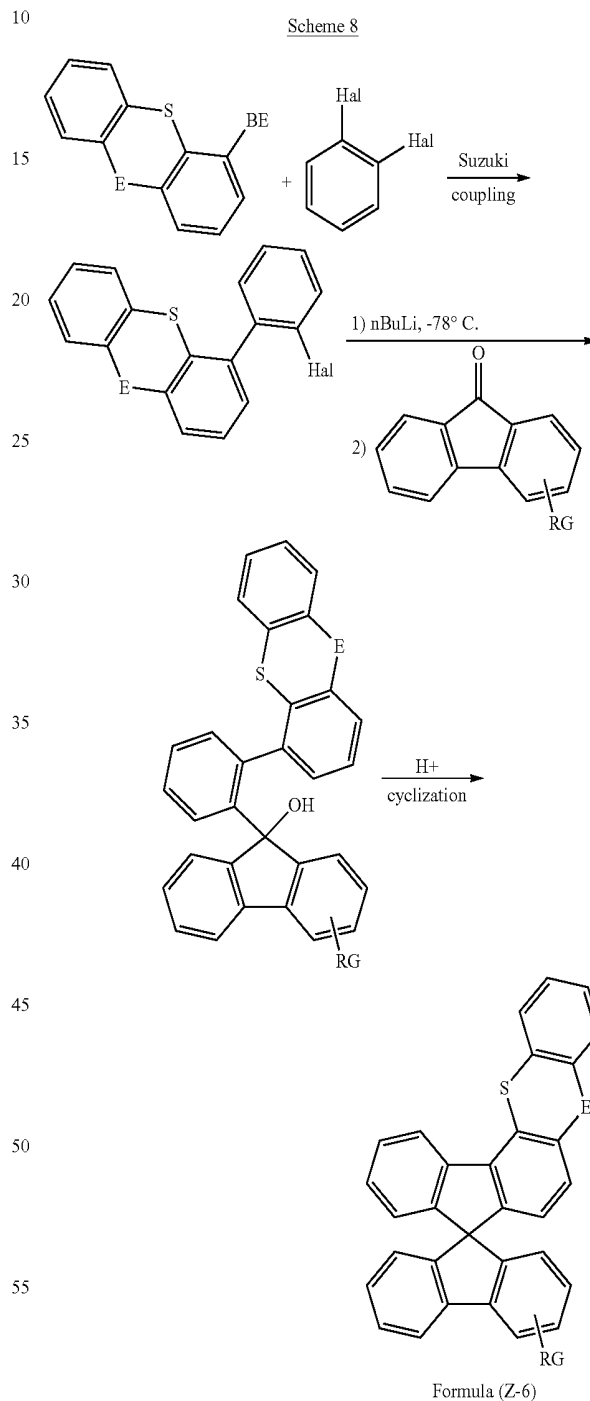
According to an alternative process for preparing the inventive compounds (Scheme 7), the procedure is analogous to Schemes 1 to 4, except that a diarylamino group is present in place of the reactive RG group in the fluorenone derivative. Scheme 7 merely shows the reaction analogous to Scheme 1. However, it is also possible in the same way to modify the processes according to Schemes 2 to 4, in each case by exchange of the RG group for a corresponding diarylamino group.



BE: boronic acid derivative
Hal: halogen atom
NAr₂: diarylamino group

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According to a modification of the processes shown in Schemes 1 to 4 and 7, it is also possible to use analogous compounds, for example thianthrene derivatives, rather than dibenzothiophene derivatives in the synthesis of the base skeleton. This is shown by way of example in Scheme 8. Again, modifications are possible, in a corresponding manner to Schemes 2 to 5.



E: O, S, Se, preferably O or S
BE: boronic acid derivative
Hal: halogen atom
RG: reactive group, preferably Br

The compounds of the formula (Z-6) obtained can, as shown in Scheme 6, be converted further to the final compounds of formula (I). It is also possible to use the

thianthrene derivatives to conduct modifications to the synthesis according to Scheme 7.

The present application thus provides a process for preparing a compound of the formula (I), characterized in that either

A) first the spirobifluorene base skeleton substituted by a reactive group is prepared by reacting a dibenzothiophenyl derivative with a fluorenone derivative bearing the reactive group and, in a later step, via an organometallic coupling reaction, a diarylamino or carbazole group or an aryl or heteroaryl group substituted by a diarylamino or carbazole group is introduced at the position of the reactive group, or

B) the reaction of a dibenzothiophenyl derivative with a fluorenone bearing a diarylamino or carbazole group or an aryl or heteroaryl group substituted by a diarylamino or carbazole group is involved, or

C) first a spirobifluorene base skeleton is prepared by reacting a dibenzothiophenyl derivative with a fluorenone derivative, then the latter is functionalized with a reactive group and, in a later step, via an organometallic coupling reaction, a diarylamino or carbazole group or an aryl or heteroaryl group substituted by a diarylamino or carbazole group is introduced at the position of the reactive group.

The reactive group is preferably a halogen atom, more preferably Br. The organometallic coupling reaction is preferably a Buchwald coupling or a Suzuki coupling.

The above-described compounds, especially compounds substituted by reactive leaving groups, such as bromine, iodine, chlorine, boronic acid or boronic ester, may find use as monomers for production of corresponding oligomers, dendrimers or polymers. Suitable reactive leaving groups are, for example, bromine, iodine, chlorine, boronic acids, boronic esters, amines, alkenyl or alkynyl groups having a terminal C—C double bond or C—C triple bond, oxiranes, oxetanes, groups which enter into a cycloaddition, for example a 1,3-dipolar cycloaddition, for example dienes or azides, carboxylic acid derivatives, alcohols and silanes.

The invention therefore further provides oligomers, polymers or dendrimers containing one or more compounds of formula (I), wherein the bond(s) to the polymer, oligomer or dendrimer may be localized at any desired positions substituted by R⁰, R¹ or R² in formula (I). According to the linkage of the compound of formula (I), the compound is part of a side chain of the oligomer or polymer or part of the main chain. An oligomer in the context of the invention is understood to mean a compound formed from at least three monomer units. A polymer in the context of the invention is understood to mean a compound formed from at least ten monomer units. The inventive polymers, oligomers or dendrimers may be conjugated, partly conjugated or nonconjugated. The inventive oligomers or polymers may be linear, branched or dendritic. In the structures having linear linkage, the units of formula (I) may be joined directly to one another, or they may be joined to one another via a bivalent group, for example via a substituted or unsubstituted alkylene group, via a heteroatom or via a bivalent aromatic or heteroaromatic group. In branched and dendritic structures, it is possible, for example, for three or more units of formula (I) to be joined by a trivalent or higher-valency group, for example via a trivalent or higher-valency aromatic or heteroaromatic group, to give a branched or dendritic oligomer or polymer.

For the repeat units of formula (I) in oligomers, dendrimers and polymers, the same preferences apply as described above for compounds of formula (I).

For preparation of the oligomers or polymers, the monomers of the invention are homopolymerized or copolymer-

ized with further monomers. Suitable and preferred comonomers are chosen from fluorenes (for example according to EP 842208 or WO 2000/22026), spirobifluorenes (for example according to EP 707020, EP 894107 or WO 2006/061181), paraphenylenes (for example according to WO 1992/18552), carbazoles (for example according to WO 2004/070772 or WO 2004/113468), thiophenes (for example according to EP 1028136), dihydrophenanthrenes (for example according to WO 2005/014689 or WO 2007/006383), cis- and trans-indenofluorenes (for example according to WO 2004/041901 or WO 2004/113412), ketones (for example according to WO 2005/040302), phenanthrenes (for example according to WO 2005/104264 or WO 2007/017066) or else a plurality of these units. The polymers, oligomers and dendrimers typically contain still further units, for example emitting (fluorescent or phosphorescent) units, for example vinyltriarylamines (for example according to WO 2007/068325) or phosphorescent metal complexes (for example according to WO 2006/003000), and/or charge transport units, especially those based on triarylamines.

The inventive polymers and oligomers are generally prepared by polymerization of one or more monomer types, of which at least one monomer leads to repeat units of the formula (I) in the polymer. Suitable polymerization reactions are known to those skilled in the art and are described in the literature. Particularly suitable and preferred polymerization reactions which lead to formation of C—C or C—N bonds are the SUZUKI polymerization, the YAMAMOTO polymerization, the STILLE polymerization and the HARTWIG-BUCHWALD polymerization.

How the polymerization can be conducted by these methods and how the polymers can then be separated from the reaction medium and purified is known to those 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.

For the processing of the inventive compounds from the liquid phase, for example by spin-coating or by printing methods, formulations of the inventive compounds are required. These formulations may, for example, be solutions, dispersions or emulsions. For this purpose, it may be preferable to use mixtures of two or more solvents. Suitable and preferred solvents are, for example, toluene, anisole, o-, m- or p-xylene, methyl benzoate, mesitylene, tetralin, veratrole, THF, methyl-THF, THP, chlorobenzene, dioxane, phenoxytoluene, especially 3-phenoxytoluene, (–)-fenchone, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, 1-methylnaphthalene, 2-methylbenzothiazole, 2-phenoxyethanol, 2-pyrrolidinone, 3-methylanisole, 4-methylanisole, 3,4-dimethylanisole, 3,5-dimethylanisole, acetophenone, α -terpineol, benzothiazole, butyl benzoate, cumene, cyclohexanol, cyclohexanone, cyclohexylbenzene, decalin, dodecylbenzene, ethyl benzoate, indane, methyl benzoate, NMP, p-cymene, phenetole, 1,4-diisopropylbenzene, dibenzyl ether, diethylene glycol butyl methyl ether, triethylene glycol butyl methyl ether, diethylene glycol dibutyl ether, triethylene glycol dimethyl ether, diethylene glycol monobutyl ether, tripropylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, 2-isopropylphenylbenzene, pentylbenzene, hexylbenzene, heptylbenzene, octylbenzene, 1,1-bis(3,4-dimethylphenyl)ethane or mixtures of these solvents.

The invention therefore further provides a formulation, especially a solution, dispersion or emulsion, comprising at least one compound of formula (I) or at least one polymer, oligomer or dendrimer containing at least one unit of formula (I) and at least one solvent, preferably an organic solvent. The way in which such solutions can be prepared is

known to those skilled in the art and is described, for example, in WO 2002/072714, WO 2003/019694 and the literature cited therein.

The inventive compounds are suitable for use in electronic devices, especially in organic electroluminescent devices (OLEDs). Depending on the substitution, the compounds are used in different functions and layers.

The invention therefore further provides for the use of the compound of formula (I) in an electronic device. This electronic device is preferably selected from the group consisting of organic integrated circuits (OICs), organic field-effect transistors (OFETs), organic thin-film transistors (OTFTs), organic light-emitting transistors (OLETs), organic solar cells (OSCs), organic optical detectors, organic photoreceptors, organic field-quench devices (OFQDs), organic light-emitting electrochemical cells (OLECs), organic laser diodes (O-lasers) and more preferably organic electroluminescent devices (OLEDs).

The invention further provides, as already set out above, an electronic device comprising at least one compound of formula (I). This electronic device is preferably selected from the abovementioned devices.

It is more preferably an organic electroluminescent device (OLED) comprising anode, cathode and at least one emitting layer, characterized in that at least one organic layer, which may be an emitting layer, a hole transport layer or another layer, comprises at least one compound of formula (I).

Apart from the cathode, anode and emitting layer, the organic electroluminescent device may also comprise further layers. These are selected, for example, from in each case one or more hole injection layers, hole transport layers, hole blocker layers, electron transport layers, electron injection layers, electron blocker layers, exciton blocker layers, interlayers, charge generation layers (IDMC 2003, Taiwan; Session 21 OLED (5), T. Matsumoto, T. Nakada, J. Endo, K. Mod, N. Kawamura, A. Yokoi, J. Kido, *Multiphoton Organic EL Device Having Charge Generation Layer*) and/or organic or inorganic p/n junctions.

The sequence of the layers of the organic electroluminescent device comprising the compound of the formula (I) is preferably as follows: anode-hole injection layer-hole transport layer-optionally further hole transport layer-optionally electron blocker layer-emitting layer-optionally hole blocker layer-electron transport layer-electron injection layer-cathode. It is additionally possible for further layers to be present in the OLED.

The inventive organic electroluminescent device may contain two or more emitting layers. More preferably, these emission layers in this case have several emission maxima between 380 nm and 750 nm overall, such that the overall result is white emission; in other words, various emitting compounds which may fluoresce or phosphoresce and which emit blue, green, yellow, orange or red light are used in the emitting layers. Especially preferred are three-layer systems, i.e. systems having three emitting layers, where the three layers show blue, green and orange or red emission (for the basic construction see, for example, WO 2005/011013). The inventive compounds are preferably present in the hole transport layer, hole injection layer or electron blocker layer.

It is preferable in accordance with the invention when the compound of formula (I) is used in an electronic device comprising one or more phosphorescent emitting compounds. In this case, the compound may be present in different layers, preferably in a hole transport layer, an electron blocker layer, a hole injection layer or an emitting layer.

The term "phosphorescent emitting compounds" typically encompasses compounds where the emission of light is effected through a spin-forbidden transition, for example a transition from an excited triplet state or a state having a higher spin quantum number, for example a quintet state.

Suitable phosphorescent emitting compounds (=triplet emitters) are especially compounds which, when suitably excited, emit light, preferably in the visible region, and also contain at least one atom of atomic number greater than 20, preferably greater than 38, and less than 84, more preferably greater than 56 and less than 80. Preference is given to using, as phosphorescent emitting compounds, compounds containing copper, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold or europium, especially compounds containing iridium, platinum or copper. In the context of the present invention, all luminescent iridium, platinum or copper complexes are considered to be phosphorescent emitting compounds.

Examples of the above-described emitting compounds can be found in applications WO 00/70655, WO 01/41512, WO 02/02714, WO 02/15645, EP 1191613, EP 1191612, EP 1191614, WO 05/033244, WO 05/019373 and US 2005/0258742. In general, all phosphorescent complexes as used for phosphorescent OLEDs according to the prior art and as known to those skilled in the art in the field of organic electroluminescent devices are suitable. It is also possible for the person skilled in the art, without exercising inventive skill, to use further phosphorescent complexes in combination with the compounds of formula (I) in organic electroluminescent devices. Further examples are listed in a table which follows.

It is also possible in accordance with the invention to use the compound of formula (I) in an electronic device comprising one or more fluorescent emitting compounds.

In a preferred embodiment of the invention, the compounds of formula (I) are used as hole transport material. In that case, the compounds are preferably present in a hole transport layer, an electron blocker layer or a hole injection layer.

A hole transport layer according to the present application is a layer having a hole-transporting function between the anode and emitting layer.

Hole injection layers and electron blocker layers are understood in the context of the present application to be specific embodiments of hole transport layers. A hole injection layer, in the case of a plurality of hole transport layers between the anode and emitting layer, is a hole transport layer which directly adjoins the anode or is separated therefrom only by a single coating of the anode. An electron blocker layer, in the case of a plurality of hole transport layers between the anode and emitting layer, is that hole transport layer which directly adjoins the emitting layer on the anode side.

If the compound of formula (I) is used as hole transport material in a hole transport layer, a hole injection layer or an electron blocker layer, the compound can be used as pure material, i.e. in a proportion of 100%, in the hole transport layer, or it can be used in combination with one or more further compounds. In a preferred embodiment, the organic layer containing the compound of the formula (I) then additionally contains one or more p-dopants. p-Dopants used according to the present invention are preferably those organic electron acceptor compounds capable of oxidizing one or more of the other compounds in the mixture.

Particularly preferred embodiments of p-dopants are the compounds disclosed in WO 2011/073149, EP 1968131, EP 2276085, EP 2213662, EP 1722602, EP 2045848, DE

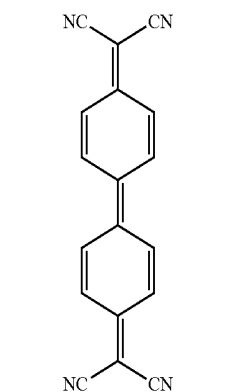
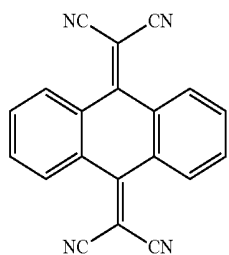
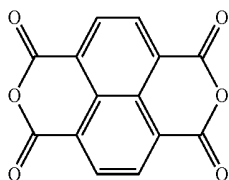
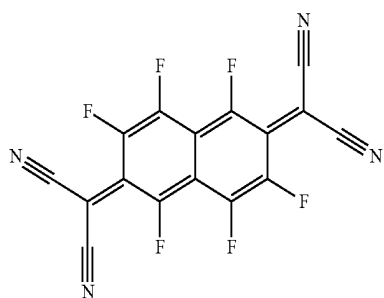
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102007031220, U.S. Pat. No. 8,044,390, U.S. Pat. No. 8,057,712, WO 2009/003455, WO 2010/094378, WO 2011/120709, US 2010/0096600, WO 2012/095143 and DE 102012209523.

Particularly preferred p-dopants are quinodimethane compounds, azaindenofluorenediones, azaphenalenenes, azatriphenylenes, I₂, metal halides, preferably transition metal halides, metal oxides, preferably metal oxides containing at least one transition metal or a metal of main group 3, and transition metal complexes, preferably complexes of Cu, Co, Ni, Pd and Pt with ligands containing at least one oxygen atom as bonding site. Preference is further given to transition metal oxides as dopants, preferably oxides of rhenium, molybdenum and tungsten, more preferably Re₂O₇, MoO₃, WO₃ and ReO₃.

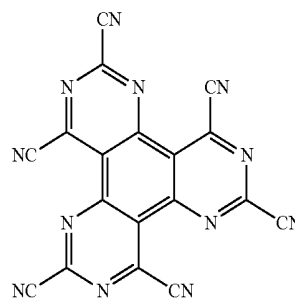
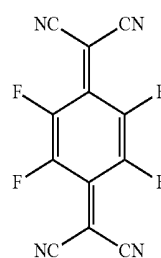
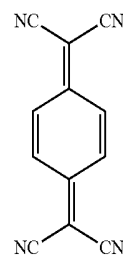
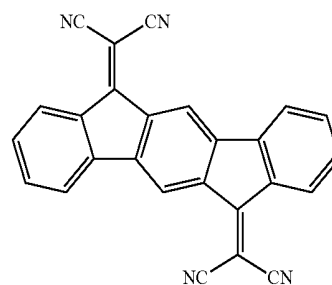
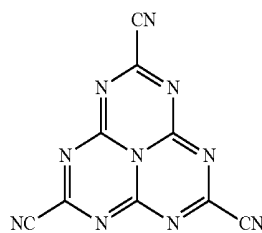
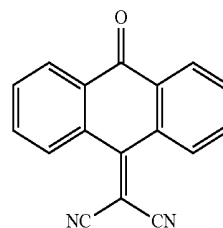
The p-dopants are preferably in substantially homogeneous distribution in the p-doped layers. This can be achieved, for example, by coevaporation of the p-dopant and the hole transport material matrix.

Preferred p-dopants are especially the following compounds:



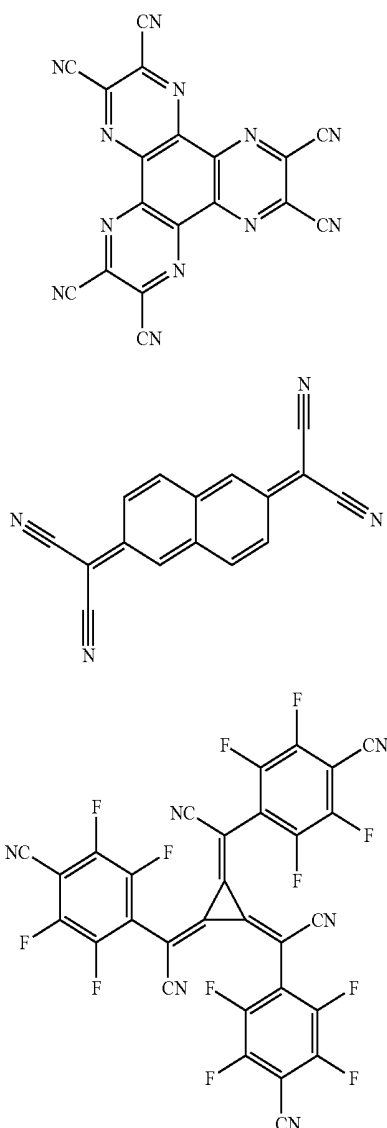
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103

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In a further preferred embodiment of the invention, the compound of formula (I) is used as hole transport material in combination with a hexaazatriphenylene derivative as described in US 2007/0092755. Particular preference is given here to using the hexaazatriphenylene derivative in a separate layer.

In a further embodiment of the present invention, the compound of the formula (I) is used in an emitting layer as matrix material in combination with one or more emitting compounds, preferably phosphorescent emitting compounds.

The proportion of the matrix material in the emitting layer in this case is between 50.0% and 99.9% by volume, preferably between 80.0% and 99.5% by volume, and more preferably between 92.0% and 99.5% by volume for fluorescent emitting layers and between 85.0% and 97.0% by volume for phosphorescent emitting layers.

Correspondingly, the proportion of the emitting compound is between 0.1% and 50.0% by volume, preferably between 0.5% and 20.0% by volume, and more preferably between 0.5% and 8.0% by volume for fluorescent emitting layers and between 3.0% and 15.0% by volume for phosphorescent emitting layers.

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(D-11) An emitting layer of an organic electroluminescent device may also comprise systems comprising a plurality of matrix materials (mixed matrix systems) and/or a plurality of emitting compounds. In this case too, the emitting compounds are generally those compounds having the smaller proportion in the system and the matrix materials are those compounds having the greater proportion in the system. In individual cases, however, the proportion of a single matrix material in the system may be less than the proportion of a single emitting compound.

(D-12) 15 It is preferable that the compounds of formula (I) are used as a component of mixed matrix systems. The mixed matrix systems preferably comprise two or three different matrix materials, more preferably two different matrix materials. Preferably, in this case, one of the two materials is a material having hole-transporting properties and the other material is a material having electron-transporting properties. The compound of the formula (I) is preferably the matrix material having hole-transporting properties. The desired electron-transporting and hole-transporting properties of the mixed matrix components may, however, also be combined mainly or entirely in a single mixed matrix component, in which case the further mixed matrix component(s) fulfil(s) other functions. The two different matrix materials may be present in a ratio of 1:50 to 1:1, preferably 1:20 to 1:1, more preferably 1:10 to 1:1 and most preferably 1:4 to 1:1. Preference is given to using mixed matrix systems in phosphorescent organic electroluminescent devices. One source of more detailed information about mixed matrix systems is the application WO 2010/108579.

(D-13) 20 The mixed matrix systems may comprise one or more emitting compounds, preferably one or more phosphorescent emitting compounds. In general, mixed matrix systems are preferably used in phosphorescent organic electroluminescent devices.

35 Particularly suitable matrix materials which can be used in combination with the inventive compounds as matrix components of a mixed matrix system are selected from the preferred matrix materials specified below for phosphorescent emitting compounds or the preferred matrix materials for fluorescent emitting compounds, according to what type of emitting compound is used in the mixed matrix system.

40 Preferred phosphorescent emitting compounds for use in mixed matrix systems are the same as detailed further up as generally preferred phosphorescent emitter materials.

Preferred embodiments of the different functional materials in the electronic device are listed hereinafter.

Preferred phosphorescent emitting compounds have already been mentioned above.

50 Preferred fluorescent emitting compounds are selected from the class of the arylamines. An arylamine or an aromatic amine in the context of this invention is understood to mean a compound containing three substituted or unsubstituted aromatic or heteroaromatic ring systems bonded directly to the nitrogen. Preferably, at least one of these aromatic or heteroaromatic ring systems is a fused ring system, more preferably having at least 14 aromatic ring atoms. Preferred examples of these are aromatic anthraceneamines, aromatic anthracenediamines, aromatic pyreneamines, aromatic pyrenediamines, aromatic chryseneamines or aromatic chrysenediamines. An aromatic anthraceneamine is understood to mean a compound in which a diarylamino group is bonded directly to an anthracene group, preferably in the 9 position. An aromatic anthracenediamine is understood to mean a compound in which two diarylamino groups are bonded directly to an anthracene group, preferably in the 9,10 positions. Aromatic pyreneam-

ines, pyrenediamines, chryseneamines and chrysenediamines are defined analogously, where the diarylamino groups in the pyrene are bonded preferably in the 1 position or 1,6 positions. Further preferred emitting compounds are indenofluoreneamines or -diamines, for example according to WO 2006/108497 or WO 2006/122630, benzoindenofluoreneamines or -diamines, for example according to WO 2008/006449, and dibenzoindenofluoreneamines or -diamines, for example according to WO 2007/140847, and the indenofluorene derivatives having fused aryl groups disclosed in WO 2010/012328. Likewise preferred are the pyrenearylamines disclosed in WO 2012/048780 and in WO 2013/185871. Likewise preferred are the benzoindenofluoreneamines disclosed in WO 2014/037077, the benzoindenofluoreneamines disclosed in WO 2014/106522 and the extended benzoindenofluorenes disclosed in WO 2014/111269.

Useful matrix materials, preferably for fluorescent emitting compounds, include materials of various substance classes. Preferred matrix materials are selected from the classes of the oligoarylenes (e.g. 2,2',7,7'-tetraphenylspirobifluorene according to EP 676461 or dinaphthylanthracene), especially of the oligoarylenes containing fused aromatic groups, the oligoarylenevinylens (e.g. DPVBi or spiro-DPVBi according to EP 676461), the polypodal metal complexes (for example according to WO 2004/081017), the hole-conducting compounds (for example according to WO 2004/058911), the electron-conducting compounds, especially ketones, phosphine oxides, sulphoxides, etc. (for example according to WO 2005/084081 and WO 2005/084082), the atropisomers (for example according to WO 2006/048268), the boronic acid derivatives (for example according to WO 2006/117052) or the benzanthracenes (for example according to WO 2008/145239). 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 oligoarylenevinylens, the ketones, the phosphine oxides and the sulphoxides. 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 context of this invention shall be understood to mean a compound in which at least three aryl or arylene groups are bonded to one another. Preference is further given to the anthracene derivatives disclosed in WO 2006/097208, WO 2006/131192, WO 2007/065550, WO 2007/110129, WO 2007/065678, WO 2008/145239, WO 2009/100925, WO 2011/054442 and EP 1553154, and the pyrene compounds disclosed in EP 1749809, EP 1905754 and US 2012/0187826.

Preferred matrix materials for phosphorescent emitting compounds are, as well as the compounds of the formula (I), aromatic ketones, aromatic phosphine oxides or aromatic sulphoxides or sulphones, for example according to WO 2004/013080, WO 2004/093207, WO 2006/005627 or WO 2010/006680, triarylamines, carbazole derivatives, e.g. CBP (N,N-bis(carbazolyl)biphenyl) 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 according to WO 2007/063754 or WO 2008/056746, indenocarbazole derivatives, for example according to WO 2010/136109, WO 2011/000455 or WO 2013/041176, azacarbazole derivatives, for example according to EP 1617710, EP 1617711, EP 1731584, JP 2005/347160, bipolar matrix materials, for example according to WO 2007/137725, silanes, for example according to WO 2005/111172, azaboroles or boronic esters, for example

according to WO 2006/117052, triazine derivatives, for example according to WO 2010/015306, WO 2007/063754 or WO 2008/056746, zinc complexes, for example according to EP 652273 or WO 2009/062578, diazasilole or tetrazasilole derivatives, for example according to WO 2010/054729, diazaphosphole derivatives, for example according to WO 2010/054730, bridged carbazole derivatives, for example according to US 2009/0136779, WO 2010/050778, WO 2011/042107, WO 2011/088877 or WO 2012/143080, triphenylene derivatives, for example according to WO 2012/048781, or lactams, for example according to WO 2011/116865 or WO 2011/137951.

Suitable charge transport materials as usable in the hole injection or hole transport layer or electron blocker layer or in the electron transport layer of the electronic device of the invention are, as well as the compounds of the formula (I), for example, the compounds disclosed in Y. Shirota et al., Chem. Rev. 2007, 107(4), 953-1010, or other materials as used in these layers according to the prior art.

Preferably, the inventive OLED comprises two or more different hole-transporting layers. The compound of the formula (I) may be used here in one or more of or in all the hole-transporting layers. According to a preferred embodiment, the compound of the formula (I) is used in exactly one hole-transporting layer, and other compounds, preferably aromatic amine compounds, are used in the further hole-transporting layers present.

Materials used for the electron transport layer may be any materials as used according to the prior art as electron transport materials in the electron transport layer. Especially suitable are aluminium complexes, for example Alq₃, zirconium complexes, for example Zrq₄, lithium complexes, for example Liq, benzimidazole derivatives, triazine derivatives, pyrimidine derivatives, pyridine derivatives, pyrazine derivatives, quinoxaline derivatives, quinoline derivatives, oxadiazole derivatives, aromatic ketones, lactams, boranes, diazaphosphole derivatives and phosphine oxide derivatives. Further suitable materials are derivatives of the above-mentioned compounds as disclosed in JP 2000/053957, WO 2003/060956, WO 2004/028217, WO 2004/080975 and WO 2010/072300.

Preferred cathodes of the electronic device are metals having a low work function, metal alloys or multilayer structures composed of various metals, for example alkaline earth metals, alkali metals, main group metals or lanthanoids (e.g. Ca, Ba, Mg, Al, In, Mg, Yb, Sm, etc.). Additionally suitable are alloys composed of an alkali metal or alkaline earth metal and silver, for example an alloy composed of magnesium and silver. In the case of multilayer structures, in addition to the metals mentioned, it is also possible to use further metals having a relatively high work function, for example Ag or Al, in which case combinations of the metals such as Ca/Ag, Mg/Ag or Ba/Ag, for example, are generally used. It may also be preferable to introduce a thin interlayer of a material having a high dielectric constant between a metallic cathode and the organic semiconductor. Examples of useful materials for this purpose are alkali metal or alkaline earth metal fluorides, but also the corresponding oxides or carbonates (e.g. LiF, Li₂O, BaF₂, MgO, NaF, CsF, Cs₂CO₃, etc.). It is also possible to use lithium quinolate (LiQ) for this purpose. The layer thickness of this layer is preferably between 0.5 and 5 nm.

Preferred anodes are materials having a high work function. Preferably, the anode has a work function of greater than 4.5 eV versus vacuum. Firstly, metals having a high redox potential are suitable for this purpose, for example Ag, Pt or Au. Secondly, metal/metal oxide electrodes (e.g. Al/Ni/

NiO_x, Al/PtO_x) may also be preferred. For some applications, at least one of the electrodes has to be transparent or partly transparent in order to enable the irradiation of the organic material (organic solar cell) or the emission of light (OLED, O-LASER). Preferred anode materials here are conductive mixed metal oxides. Particular preference is given to indium tin oxide (ITO) or indium zinc oxide (IZO). Preference is further given to conductive doped organic materials, especially conductive doped polymers. In addition, the anode may also consist of two or more layers, for example of an inner layer of ITO and an outer layer of a metal oxide, preferably tungsten oxide, molybdenum oxide or vanadium oxide.

The device is structured appropriately (according to the application), contact-connected and finally sealed, in order to rule out damaging effects by water and air.

In a preferred embodiment, the electronic device is characterized in that one or more layers are coated by a sublimation process. In this case, the materials are applied by vapour deposition in vacuum sublimation systems at an initial pressure of less than 10⁻⁵ mbar, preferably less than 10⁻⁶ mbar. In this case, however, it is also possible that the initial pressure is even lower, for example less than 10⁻⁷ mbar.

Preference is likewise given to an electronic device, characterized in that one or more layers are coated by the OVPD (organic vapour phase deposition) method or with the aid of a carrier gas sublimation. In this case, the materials are applied at a pressure between 10⁻⁵ mbar and 1 bar. A

special case of this method is the OVJP (organic vapour jet printing) method, in which the materials are applied directly by a nozzle and thus structured (for example M. S. Arnold et al., Appl. Phys. Lett. 2008, 92, 053301).

Preference is additionally given to an electronic device, characterized in that one or more layers are produced from solution, for example by spin-coating, or by any printing method, for example screen printing, flexographic printing, nozzle printing or offset printing, but more preferably LITI (light-induced thermal imaging, thermal transfer printing) or inkjet printing. For this purpose, soluble compounds of formula (I) are needed. High solubility can be achieved by suitable substitution of the compounds.

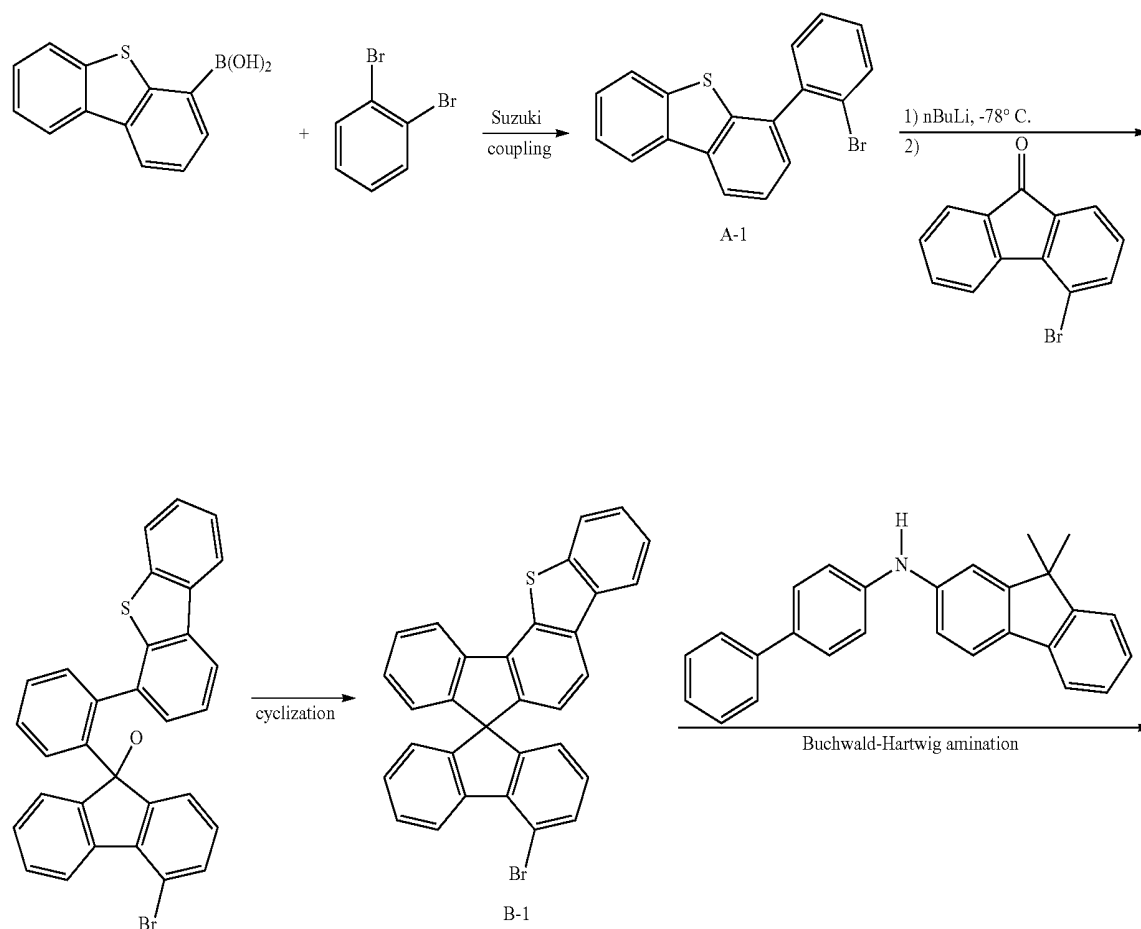
It is further preferable that an electronic device of the invention is produced by applying one or more layers from solution and one or more layers by a sublimation method.

According to the invention, the electronic devices comprising one or more compounds of formula (I) can be used in displays, as light sources in lighting applications and as light sources in medical and/or cosmetic applications (e.g. light therapy).

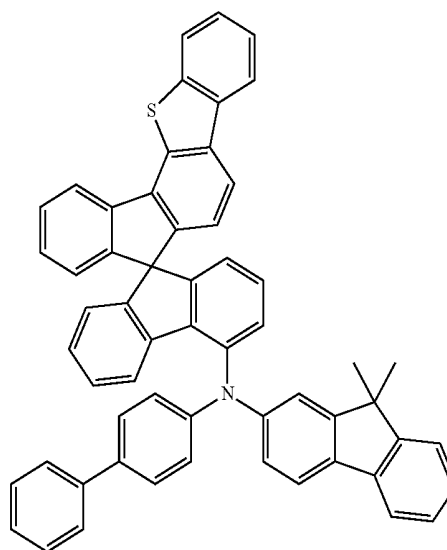
WORKING EXAMPLES

A) Synthesis Examples

Example 1: Synthesis of Compounds (1-1) to (1-14)



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(1-1)

Synthesis of 4-(2-bromophenyl)dibenzothiophene
A-1

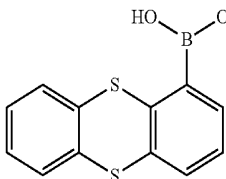
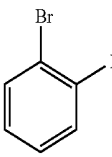
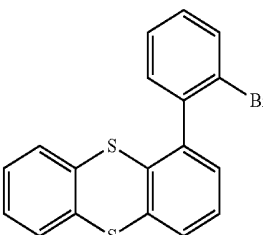
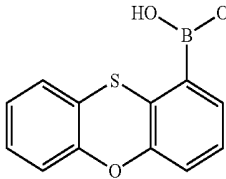
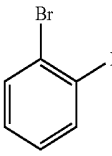
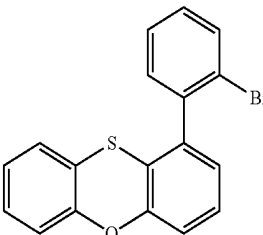
80 g (351 mmol) of dibenzothiophene-4-boronic acid (CAS: 108847-20-7), 83 g (351 mmol) of 1,2-dibromobenzene and 8.2 g (7.02 mmol) of $\text{Pd}(\text{Ph}_3\text{P})_4$ are suspended in 700 ml of dioxane. Added gradually to this suspension are 440 ml (877 mmol) of potassium carbonate solution (2 M),

and the reaction mixture is heated under reflux for 18 h. After cooling, the organic phase is removed, filtered through silica gel, washed three times with 200 ml of water and then concentrated to dryness. The residue is purified by chromatography on silica gel. Yield: 95 g (280 mmol), 80% of theory, purity by HPLC >97%.

In a manner analogous to the synthesis of compound A-1 described, the following compounds are prepared:

	Reactant 1	Reactant 2	Product	Yield
A-2	 668983-97-9			73%
A-3	 1245943-60-5			61%
A-4	 108847-24-1			78%

-continued

	Reactant 1	Reactant 2	Product	Yield
A-5	 108847-76-3			83%
A-6	 636607-99-3			75%

Synthesis of Intermediate B-1

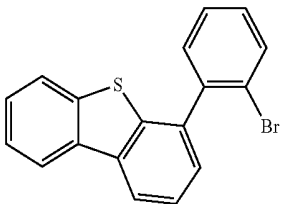
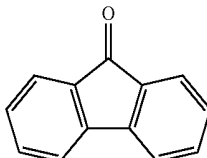
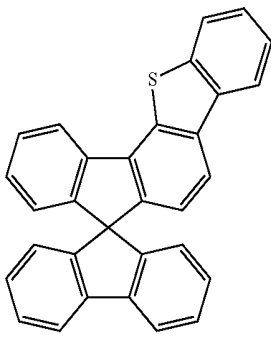
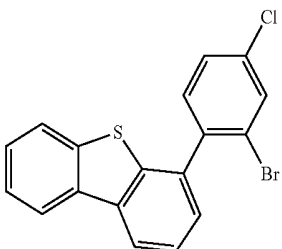
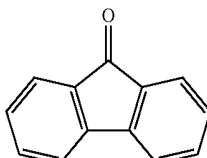
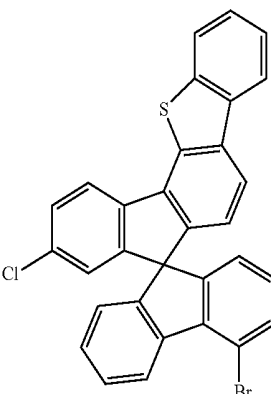
56.3 g (166 mmol) of 4-(2-bromophenyl)dibenzothio- phene A-1 are initially charged in 700 ml of THF at -78°C . At this temperature, 70 ml of BuLi (2.5 M in hexane) are added dropwise. After 1 hour, 45.2 g (174 mmol) of fluorene-9-one in 200 ml of THF are added dropwise. The mixture is left to stir at room temperature overnight, added to ice-water and extracted with dichloromethane. The combined organic phases are washed with water and dried over sodium sul-

25

phate. The solvent is removed under reduced pressure and the residue, without further purification, is heated with 90 ml of HCl and 1 l of AcOH at 75°C overnight. After cooling, the precipitated solid is filtered off with suction and washed twice with 150 ml of water and three times with 150 ml each time of ethanol, and finally recrystallized from heptane. Yield: 54 g (107 mmol), 65%; purity about 98% by ^1H NMR.

30

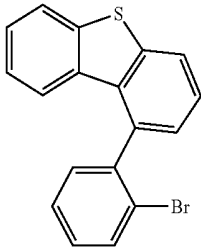
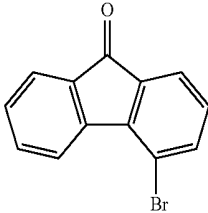
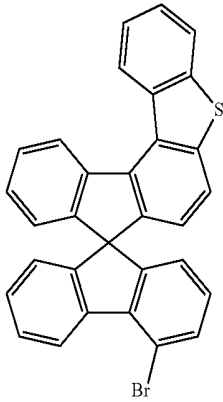
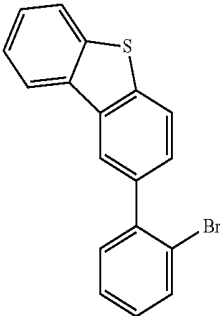
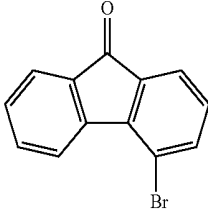
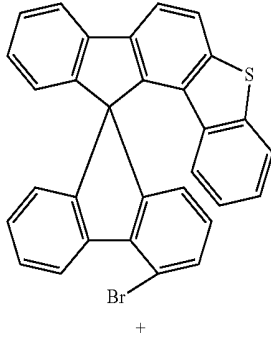
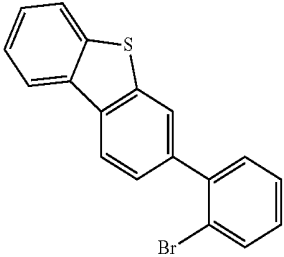
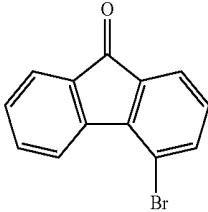
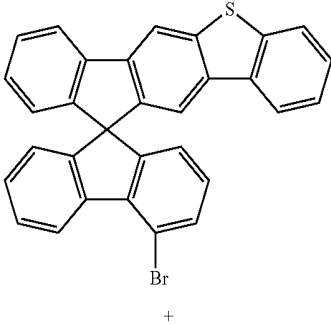
In a manner analogous to the synthesis of compound B-1 described, the following compounds are prepared:

	Reactant 1	Reactant 2	Product	Yield
B-2		 [486-25-9]		70%
B-3		 [4269-17-4]		62%

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114

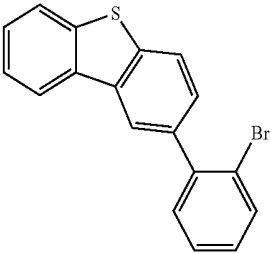
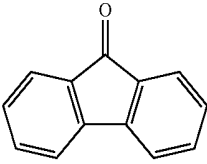
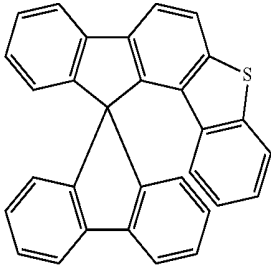
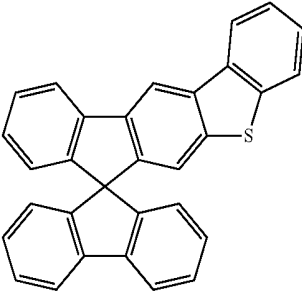
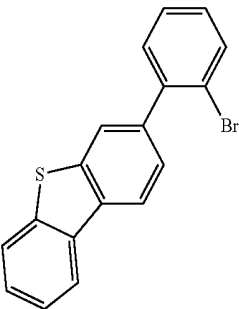
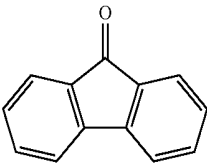
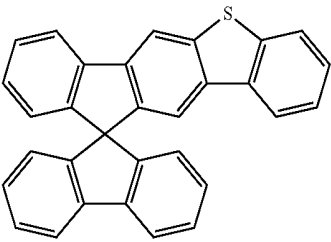
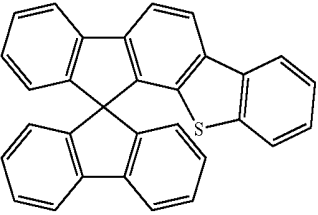
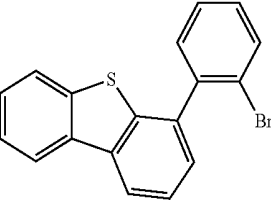
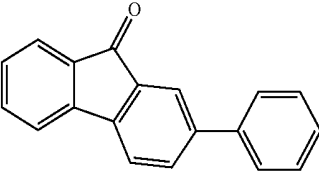
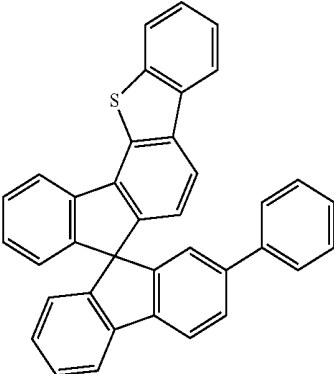
-continued

	Reactant 1	Reactant 2	Product	Yield
B-4		 [4269-17-4]		75%
B-5		 [4269-17-4]	 +	68%
B-6		 [4269-17-4]	 +	70%

115

116

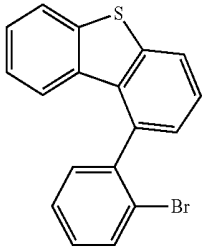
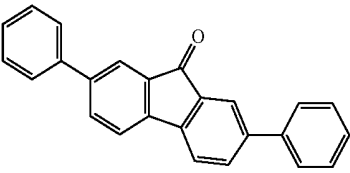
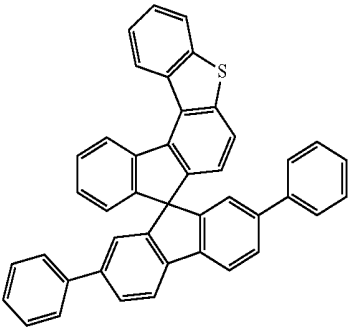
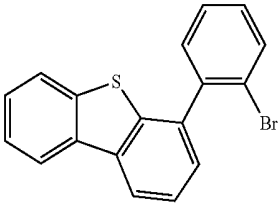
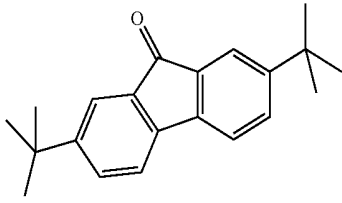
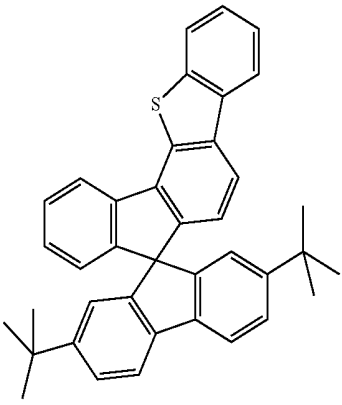
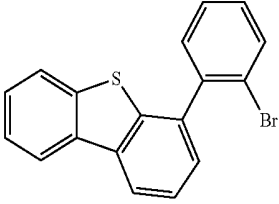
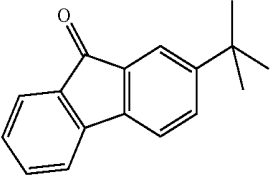
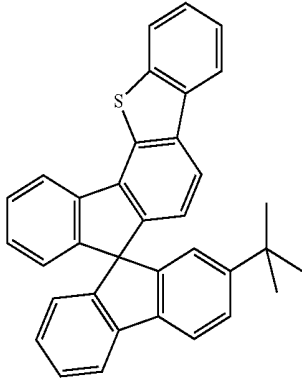
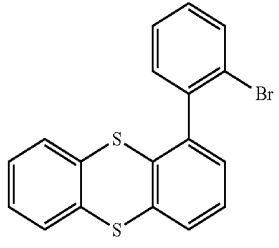
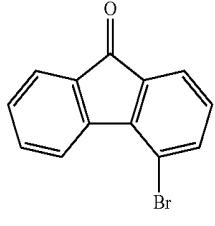
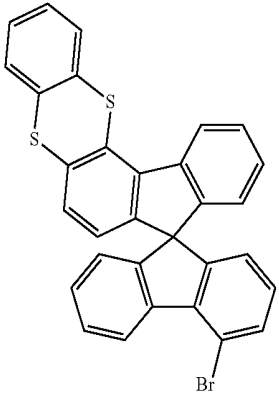
-continued

	Reactant 1	Reactant 2	Product	Yield
B-7			 +	65%
				
B-8			 +	80%
				
B-9		 [3096-49-9]		

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-continued

	Reactant 1	Reactant 2	Product	Yield
B-10		 [115033-91-5]		64%
B-11		 [58775-13-6]		71%
B-12		 [58775-11-4]		70%
B-13		 [4269-17-4]		56%

-continued

	Reactant 1	Reactant 2	Product	Yield
B-14				72%

Synthesis of Compound (1-1)

14.3 g (39.5 mmol) of biphenyl-4-yl(9,9-dimethyl-9H-fluoren-2-yl)amine and 19.8 g (39.5 mol) of the bromo-spiro 25
 derivative B-1 are dissolved in 350 ml of toluene. The solution is degassed and saturated with N₂. Thereafter, 1.55 ml (1.55 mmol) of a 1 M tri-tert-butylphosphine solution and 173 mg (1.44 mmol) of Pd(AcO)₂ are added thereto, and then 9.5 g of sodium tert-butoxide (98.7 mmol) are added. The reaction mixture is heated to boiling under a protective atmosphere for 4 h. The mixture is subsequently partitioned 30
 between toluene and water, and the organic phase is washed

20

three times with water and dried over Na₂SO₄ and concentrated by rotary evaporation. After the crude product has been filtered through silica gel with toluene, the remaining residue is recrystallized from heptane/toluene and finally sublimed under high vacuum. The purity is 99.9% (HPLC). The yield of compound (1-1) is 22 g (73% of theory).

Synthesis of compounds (1-2) to (1-14)

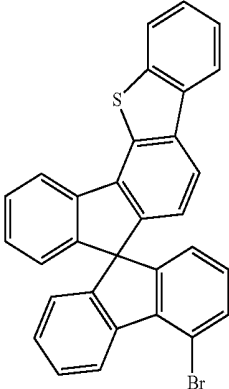
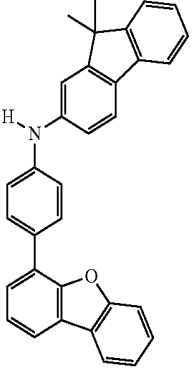
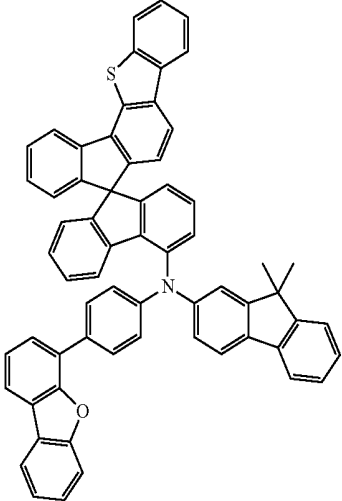
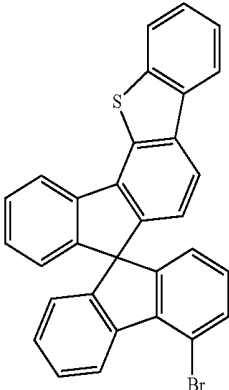
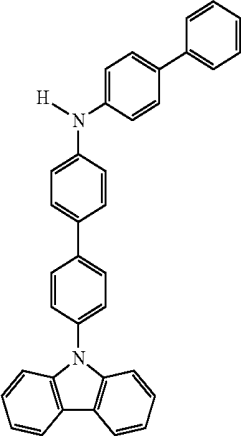
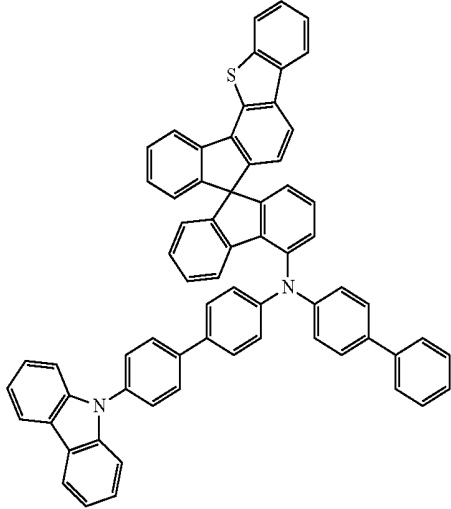
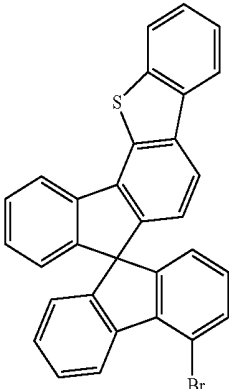
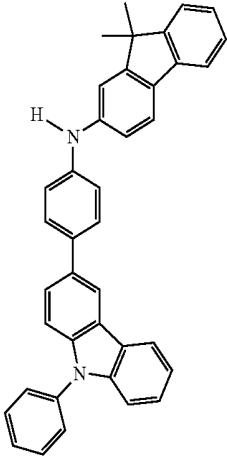
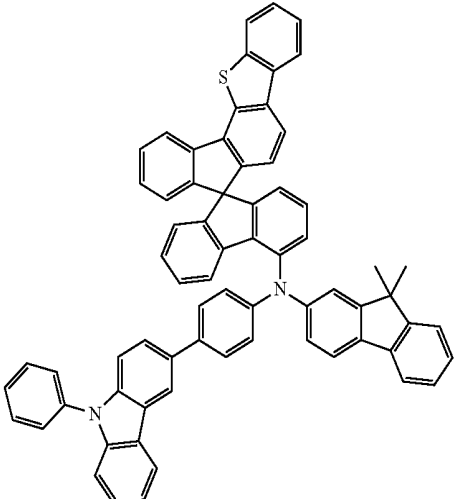
In a manner analogous to the synthesis of compound (1-1) described in Example 1, the following compounds (1-2) to (1-14) are also prepared:

	Reactant 1	Reactant 2	Product	Yield
1-2				78%
1-3				78%

121

122

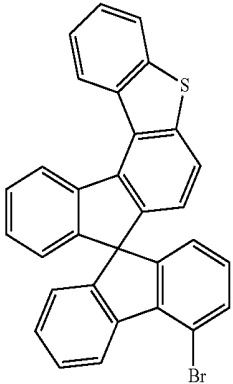
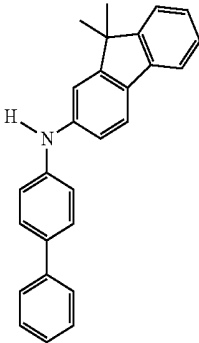
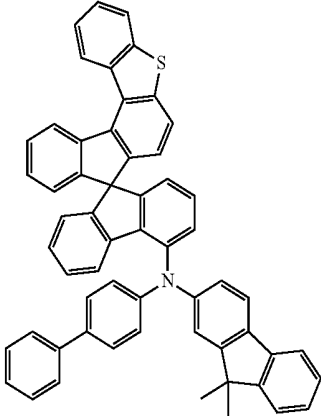
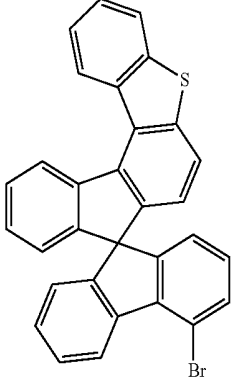
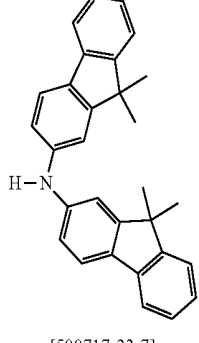
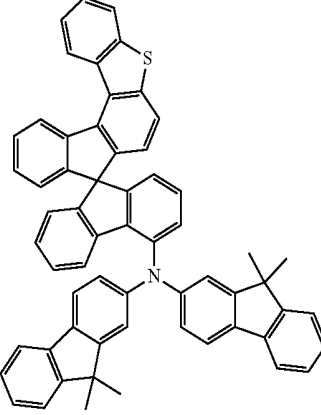
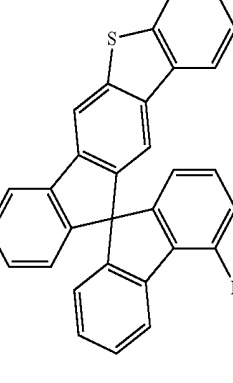
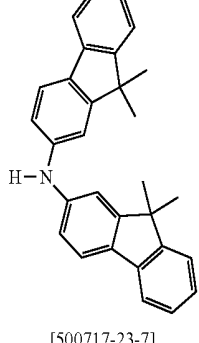
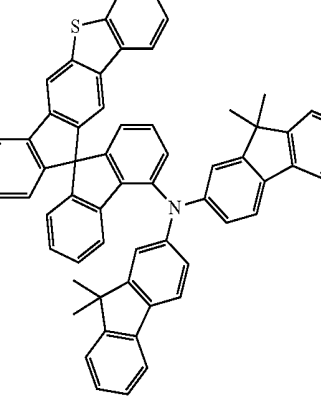
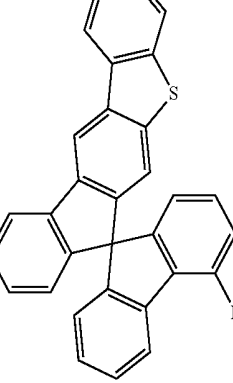
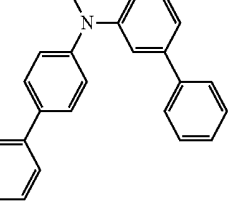
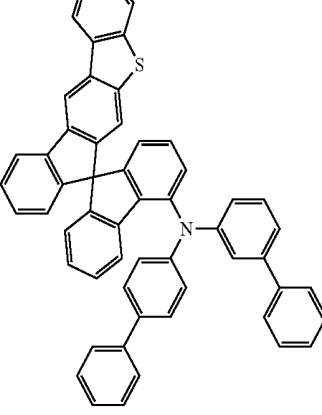
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	Reactant 1	Reactant 2	Product	Yield
1-4				83%
1-5				66%
1-6				67%

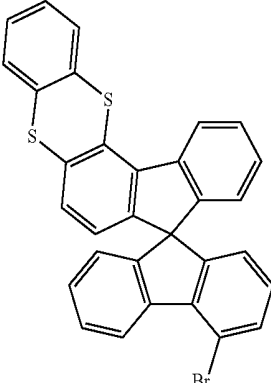
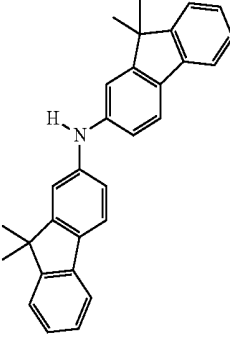
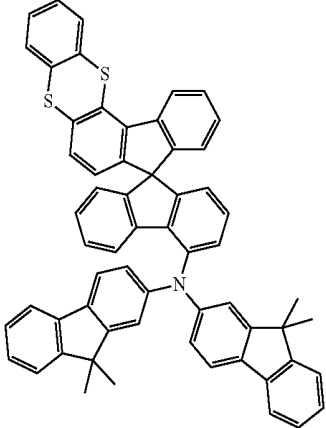
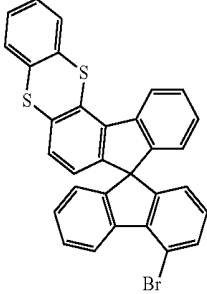
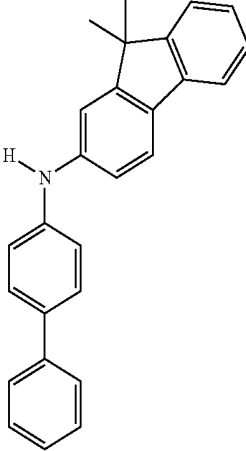
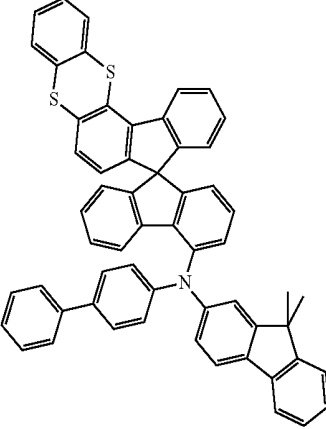
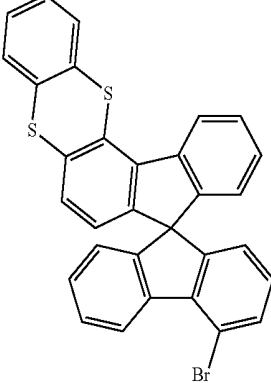
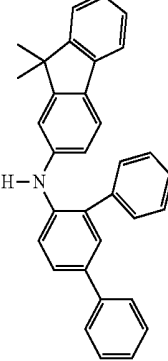
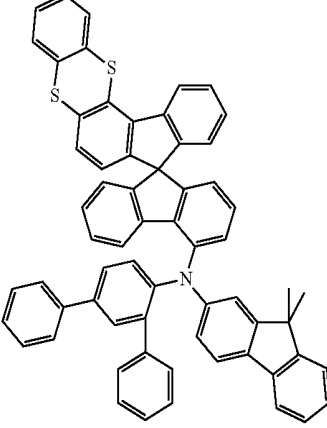
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124

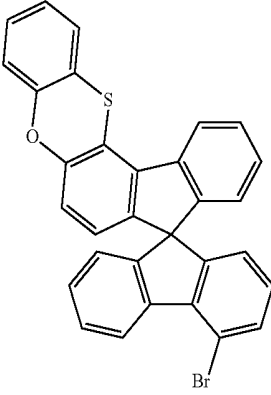
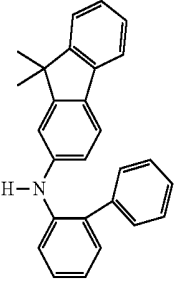
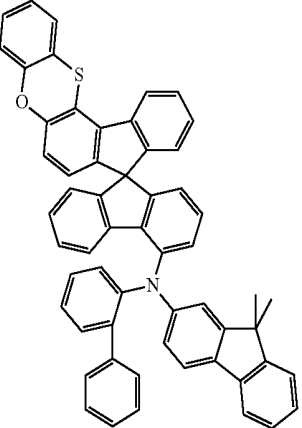
-continued

	Reactant 1	Reactant 2	Product	Yield
1-7				79%
1-8		 [500717-23-7]		77%
1-9		 [500717-23-7]		72%
1-10				68%

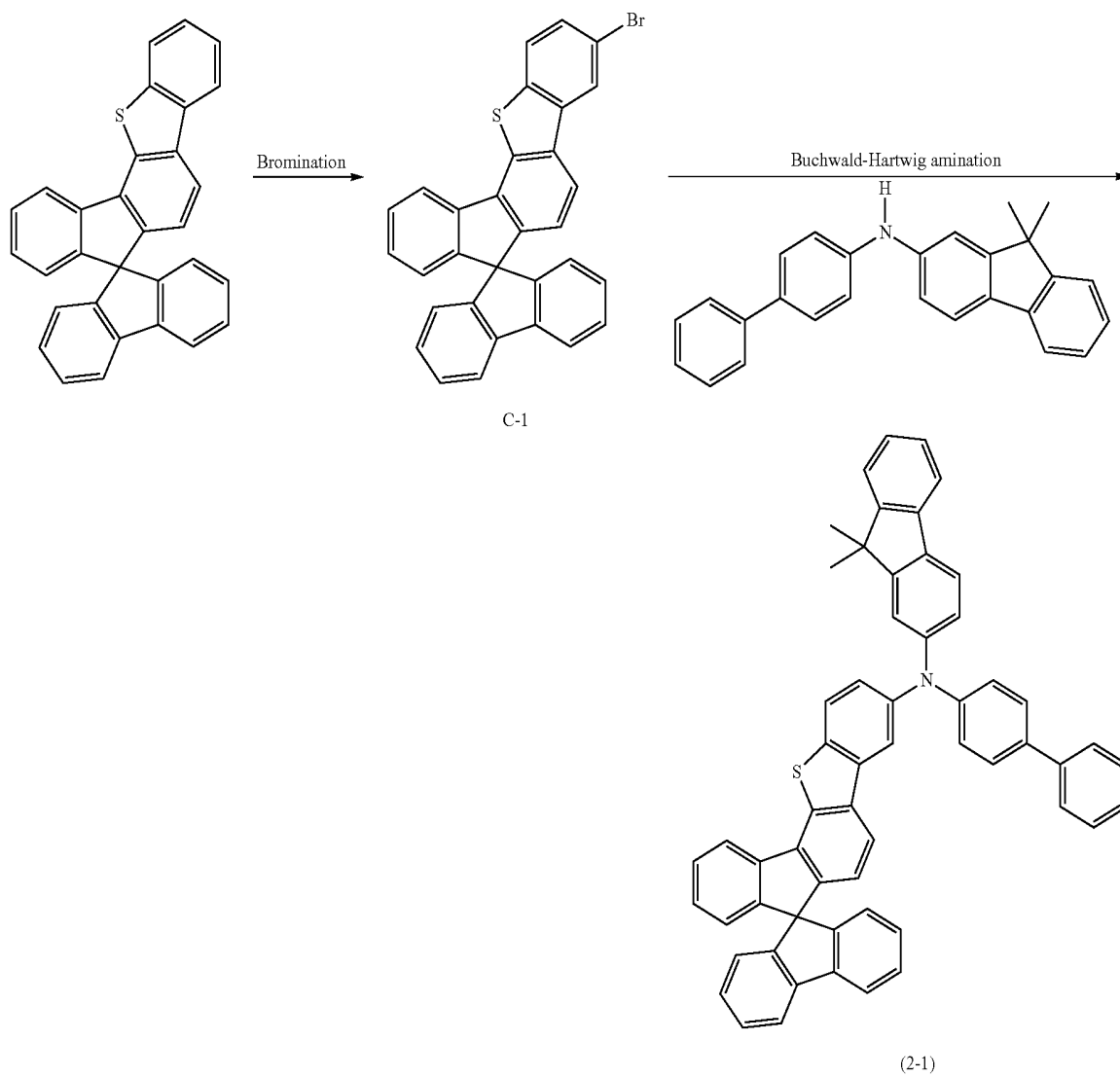
-continued

Reactant 1	Reactant 2	Product	Yield
1-11 			68%
1-12 			74%
1-13 			67%

-continued

	Reactant 1	Reactant 2	Product	Yield
1-14				71%

Example 2: Synthesis of Compounds (2-1) to
(2-12)



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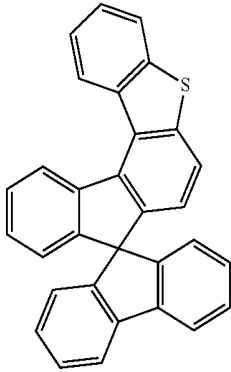
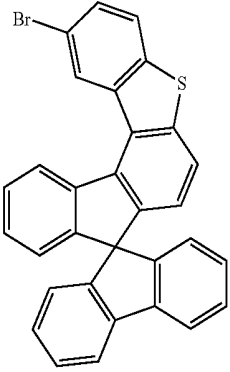
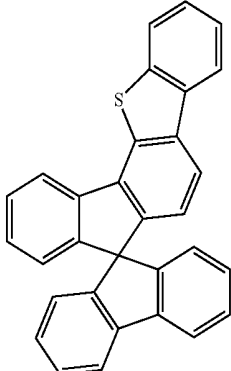
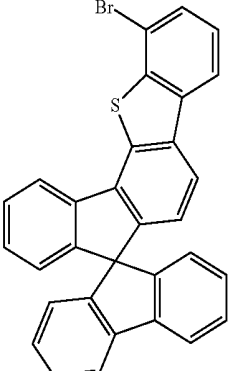
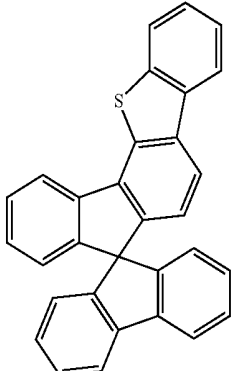
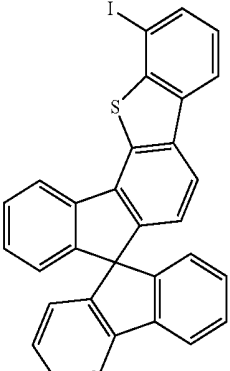
Synthesis of Intermediate C-1

18 g (44 mmol) of the starting compound are dissolved in 200 ml of acetonitrile, and 7.5 g (42 mmol) of N-bromosuccinimide are added in portions at room temperature. On completion of conversion, water and ethyl acetate are added

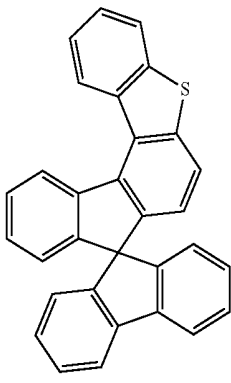
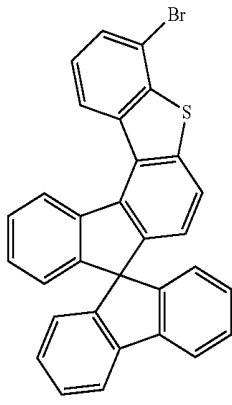
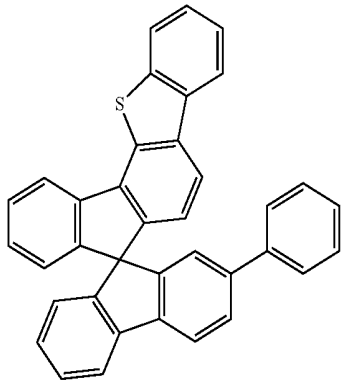
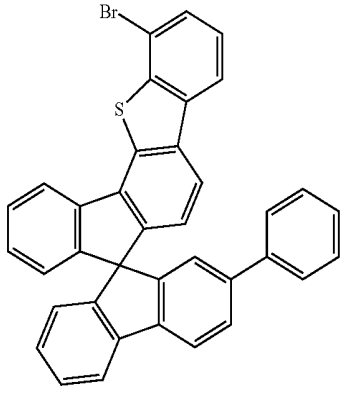
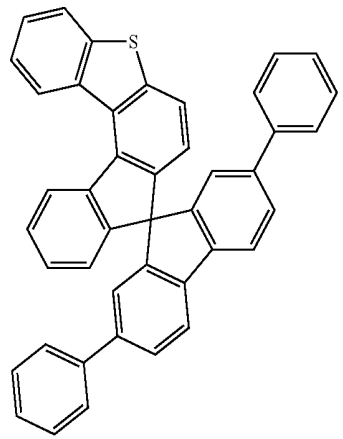
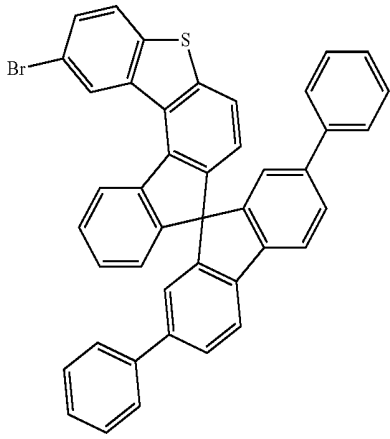
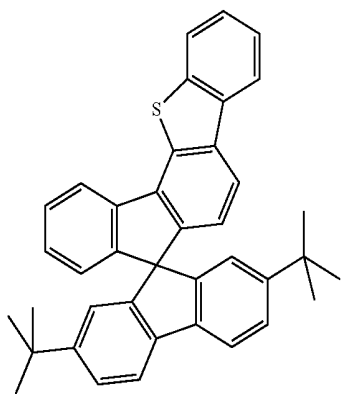
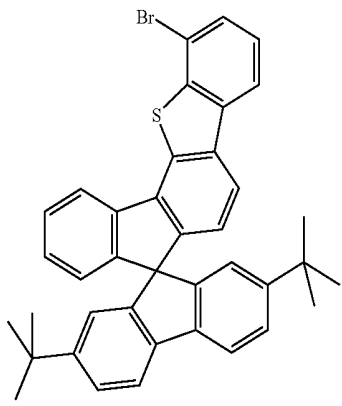
130

thereto, and the organic phase is removed, dried and concentrated. The crude product is subsequently stirred repeatedly with hot MeOH. Yield: 16.13 g (75%) of the bromo-spiro derivative C-1.

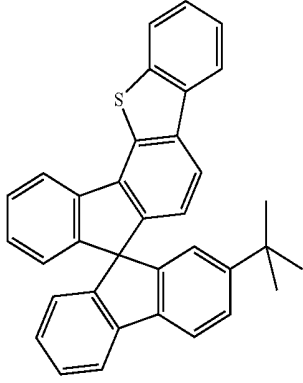
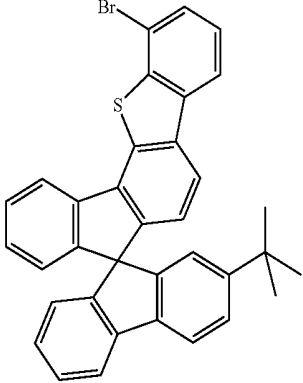
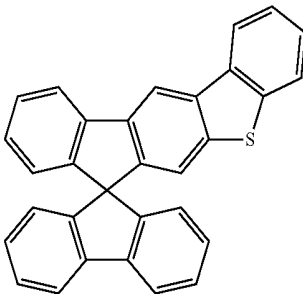
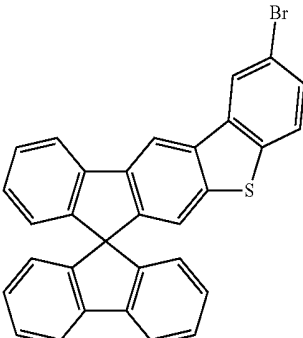
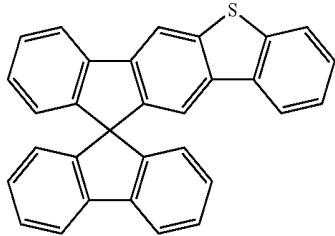
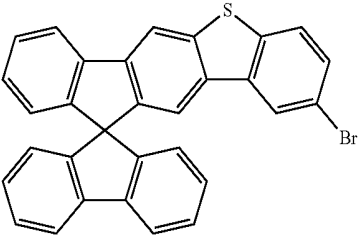
In an analogous manner, the following brominated compounds are prepared:

	Reactant 1	Brominating reagent	Product	Yield
C-2		NBS		68%
C-3		1) nBuLi, -78° C. 2) BrCH ₂ -CH ₂ Br		50%
C-4		1) nBuLi, -78° C. 2) I ₂		45%

-continued

	Reactant 1	Brominating reagent	Product	Yield
C-5		1) nBuLi, -78° C. 2) BrCH ₂ -CH ₂ Br		40%
C-6		1) nBuLi, -78° C. 2) BrCH ₂ -CH ₂ Br		40%
C7		NBS		66%
C-8		1) nBuLi, -78° C. 2) BrCH ₂ -CH ₂ Br		50%

-continued

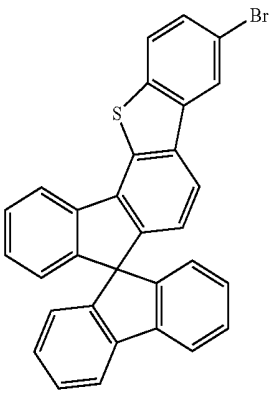
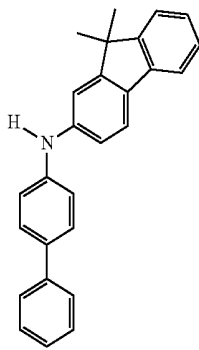
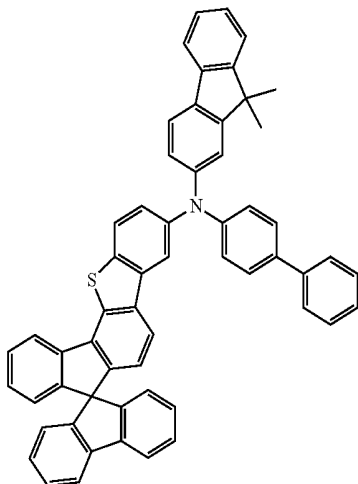
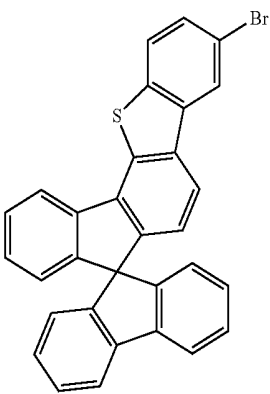
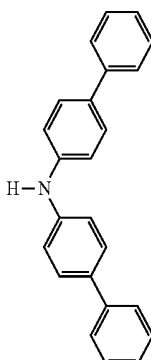
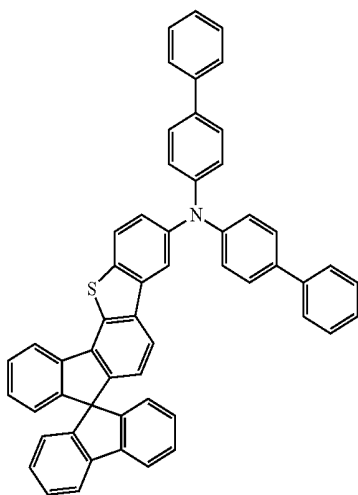
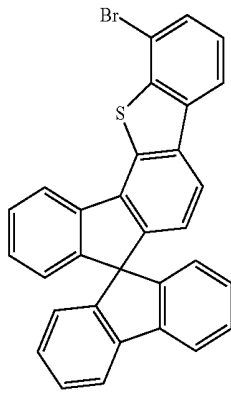
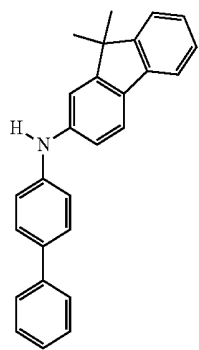
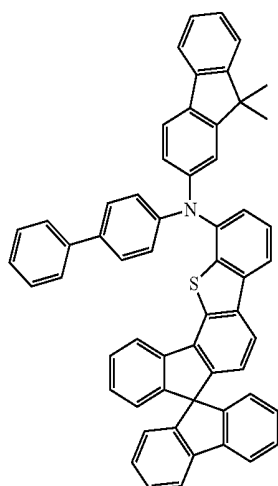
	Reactant 1	Brominating reagent	Product	Yield
C-9		1) nBuLi, -78° C. 2) BrCH ₂ -CH ₂ Br		48%
C-10		NBS		61%
C-11		NBS		60%

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Synthesis of compounds (2-1) to (2-12)

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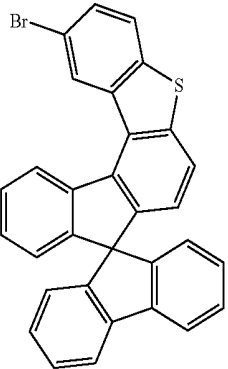
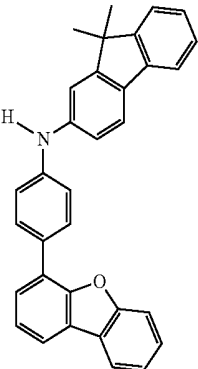
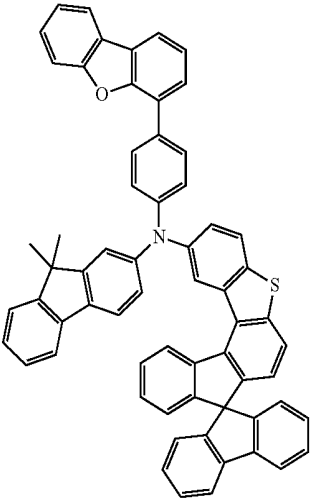
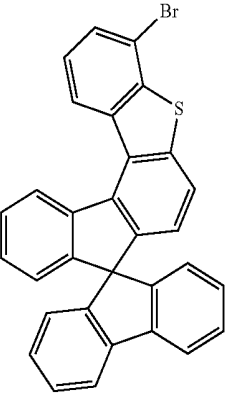
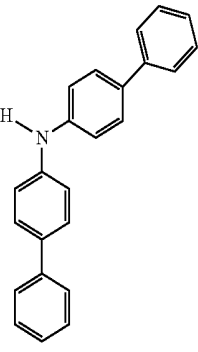
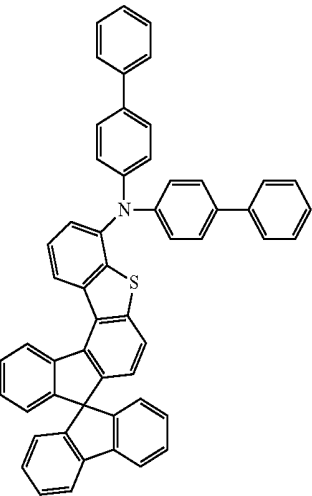
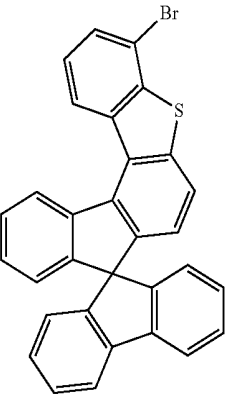
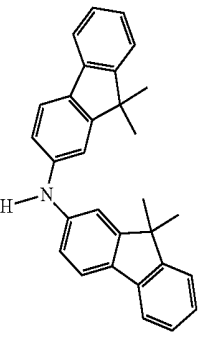
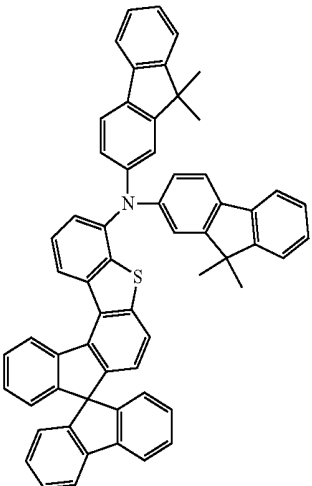
In a manner analogous to the synthesis of compound (1-1) described in Example 1, the following compounds (2-1) to (2-12) are also prepared:

	Reactant 1	Reactant 2	Product	Yield
2-1		 [102113-98-4]		76%
2-2		 [102113-98-4]		80%
2-3		 [102113-98-4]		71%

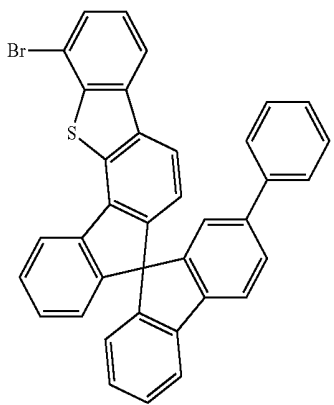
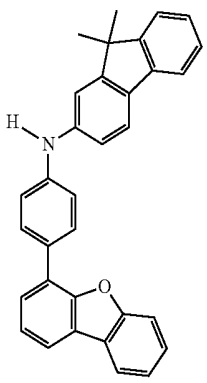
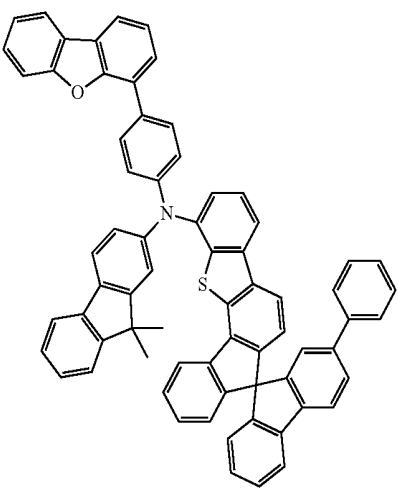
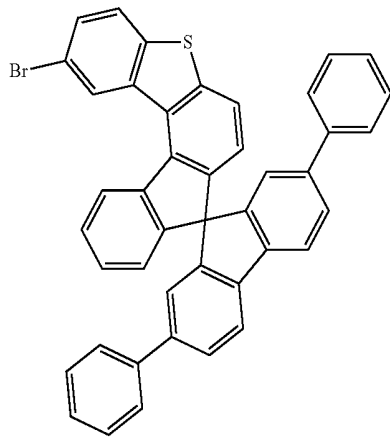
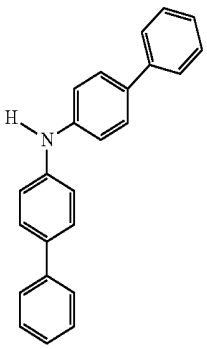
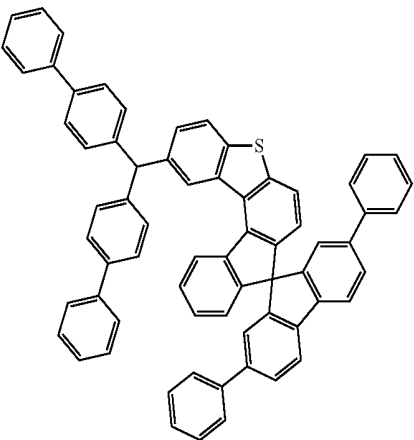
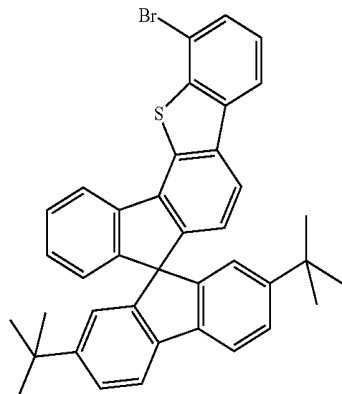
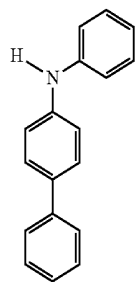
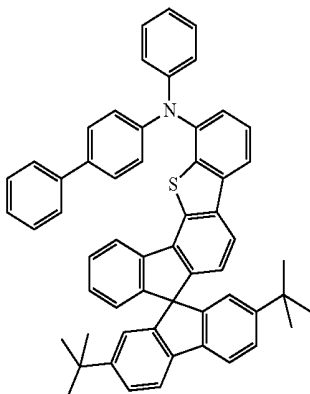
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-continued

	Reactant 1	Reactant 2	Product	Yield
2-4				78%
2-5				82%
2-6				77%

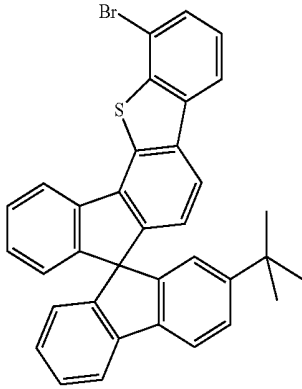
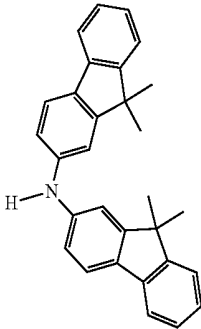
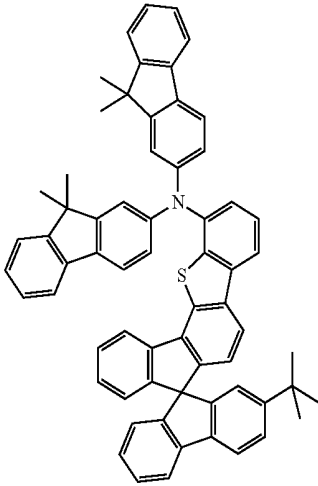
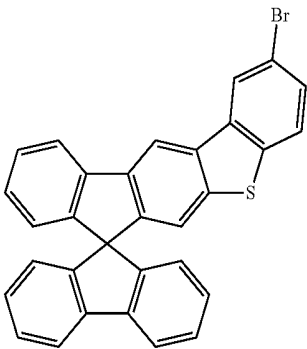
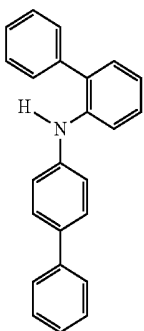
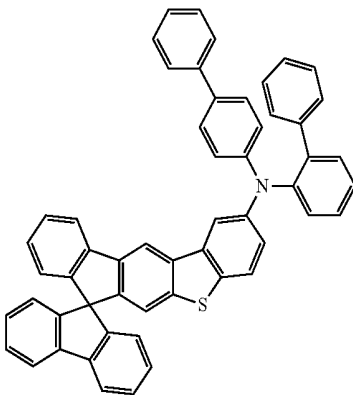
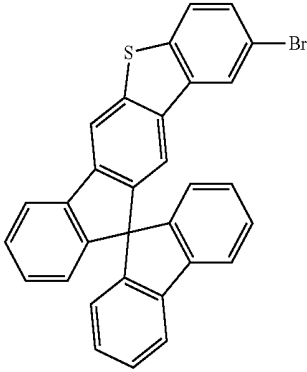
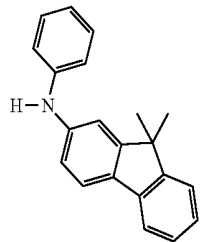
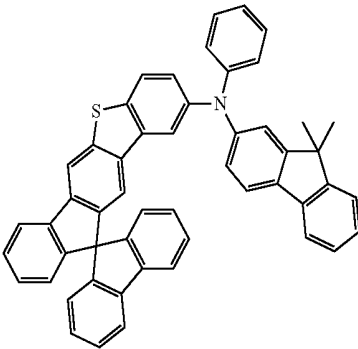
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	Reactant 1	Reactant 2	Product	Yield
2-7				75%
2-8				81%
2-9				83%

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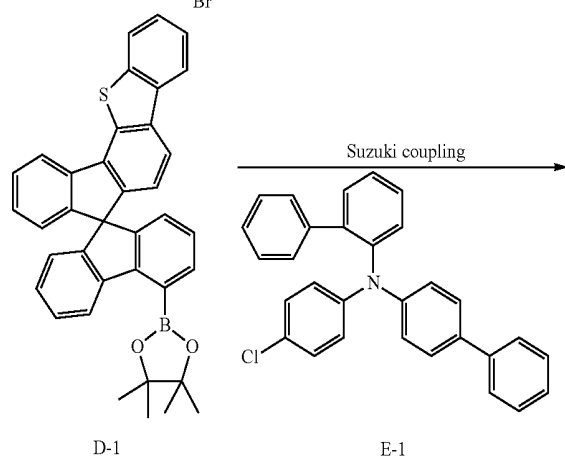
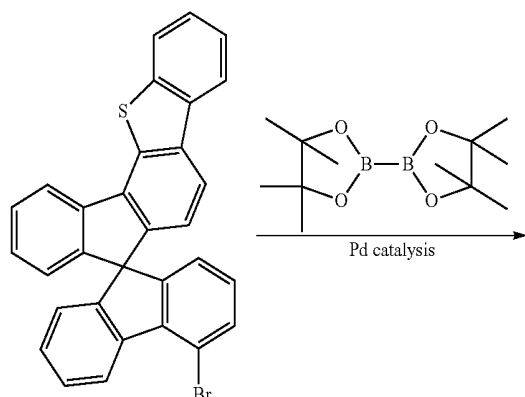
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-continued

	Reactant 1	Reactant 2	Product	Yield
2-10				75%
2-11				75%
2-12				79%

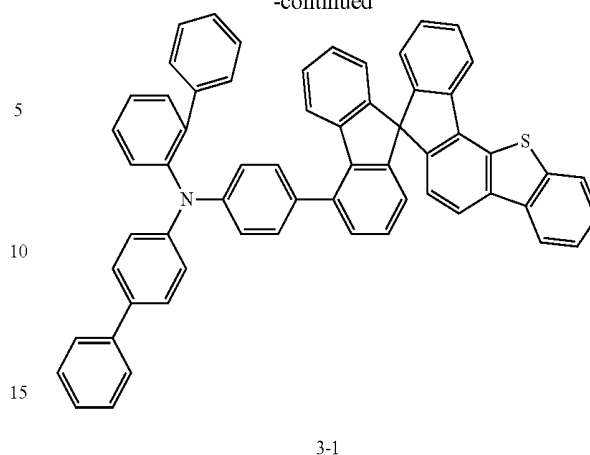
143

Example 3: Synthesis of Compounds 3-1 to 3-11



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-continued



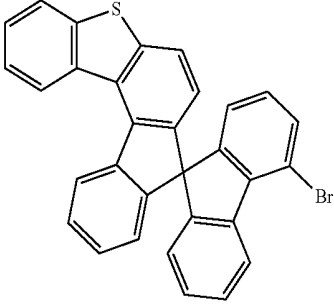
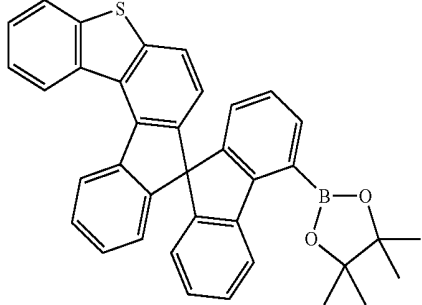
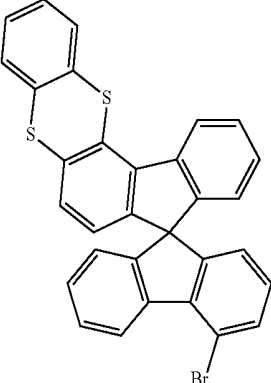
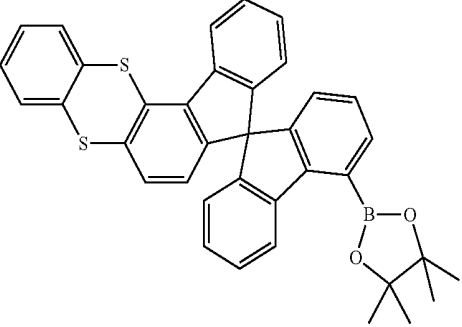
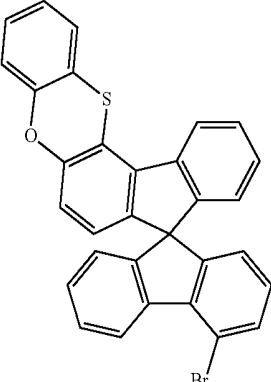
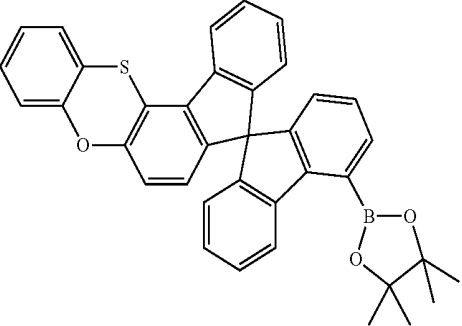
Spirofluorene-Boronic Ester Derivative (D-1)

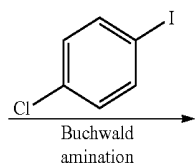
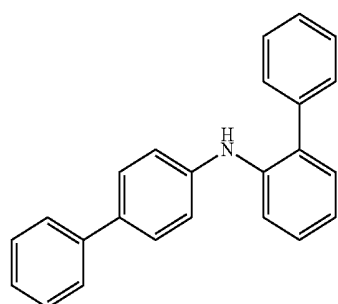
25 g (49.9 mmol) of the spirofluorene-bromo derivative, 14 g (55 mmol) of bis(pinacolato)diborane and 14.7 g (150 mmol) of potassium acetate are suspended in 400 ml of DMF. To this suspension is added 1.22 g (1.5 mmol) of 1,1-bis(diphenylphosphino)ferrocenedichloropalladium(II) complex with DCM. The reaction mixture is heated under reflux for 16 h. After cooling, the organic phase is removed, washed three times with 400 mL of water and then concentrated to dryness. The residue is recrystallized from toluene (25 g, 92% yield).

In a manner analogous thereto, the following compounds are prepared:

Reactant 1	Product	Yield
D-2		80%
D-3		83%

-continued

	Reactant 1	Product	Yield
D-4			88%
D-5			88%
D-6			76%

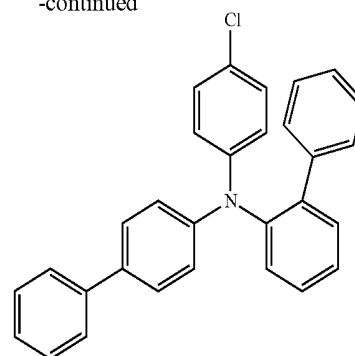
Biphenyl-2-yl(biphenyl-4-yl)(4-chlorophenyl)amine
(E-1)

50

55

60

-continued



23.8 g of biphenyl-2-yl(biphenyl-4-yl)amine (74 mmol) and 21.2 g of 4-chloriodobenzene (89 mmol) are dissolved in 500 ml of toluene. The solution is degassed and saturated with N₂. Thereafter, 3 ml (3 mmol) of a 1 M tri-tert-

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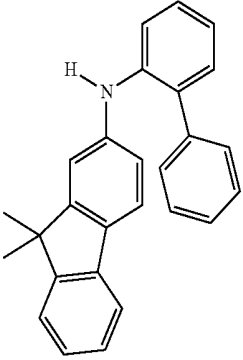
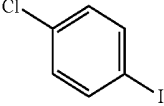
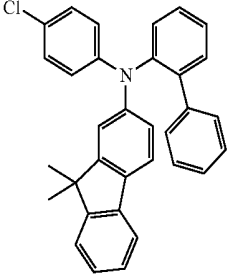
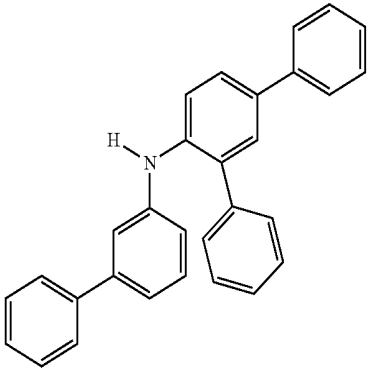
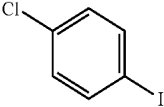
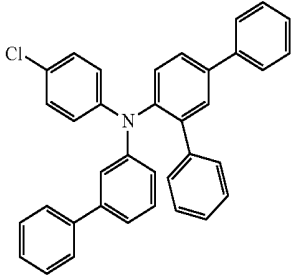
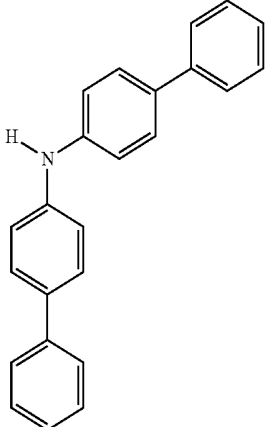
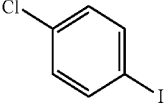
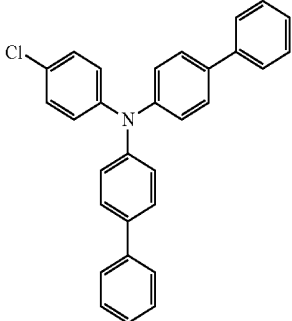
butylphosphine solution and 0.33 g (1.48 mmol) of palladium(II) acetate are added thereto, and then 10.7 g of sodium tert-butoxide (111 mmol) are added.

The reaction mixture is heated to boiling under a protective atmosphere for 12 h. The mixture is subsequently partitioned between toluene and water, and the organic phase is washed three times with water and dried over Na_2SO_4 and

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concentrated by rotary evaporation. After the crude product has been filtered through silica gel with toluene, the remaining residue is recrystallized from heptane/toluene. The yield is 29 g (90% of theory).

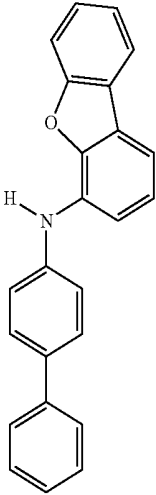
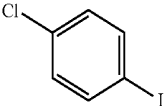
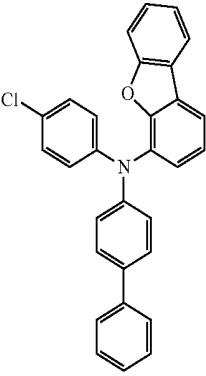
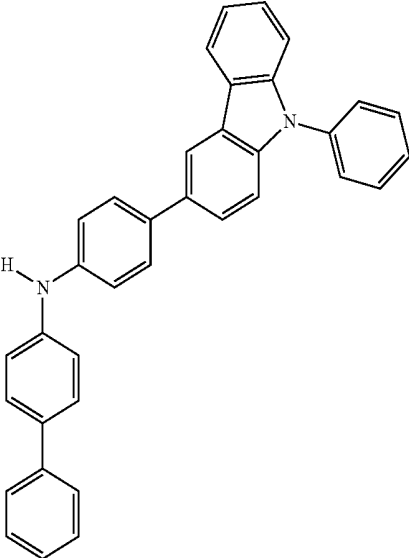
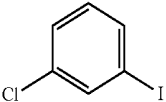
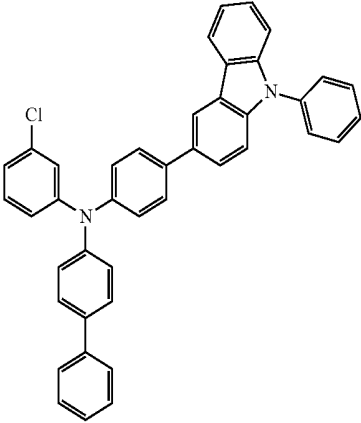
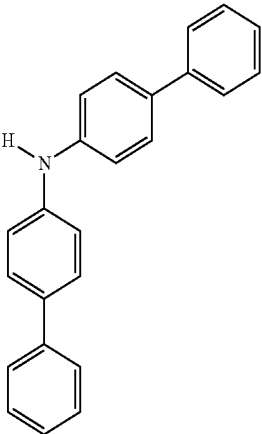
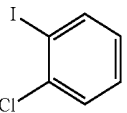
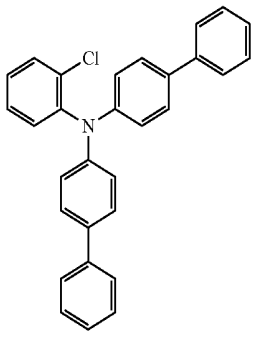
In a manner analogous thereto, the following compounds are prepared:

	Reactant 1	Reactant 2	Product	Yield
E-2				78%
E-3				80%
E-4				81%

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-continued

	Reactant 1	Reactant 2	Product	Yield
E-5				92%
E-6				85%
E-7				75%

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Synthesis of Compound (3-1)

19.05 g (35 mmol) of spirofluorene pinacolboronic ester derivative D-1 and 19.0 g (35 mmol) of chloro derivative E-1 are suspended in 300 ml of dioxane and 10.6 g of caesium fluoride (69.4 mmol). 1.3 g (1.73 mmol) of bis (tricyclohexylphosphine)palladium dichloride are added to this suspension, and the reaction mixture is heated under reflux for 24 h. After cooling, the organic phase is removed, filtered through silica gel, washed three times with 100 ml of water and then concentrated to dryness. After the crude

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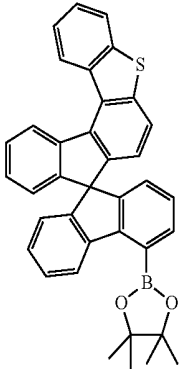
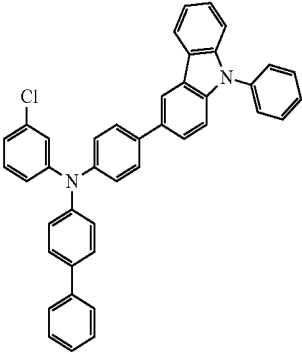
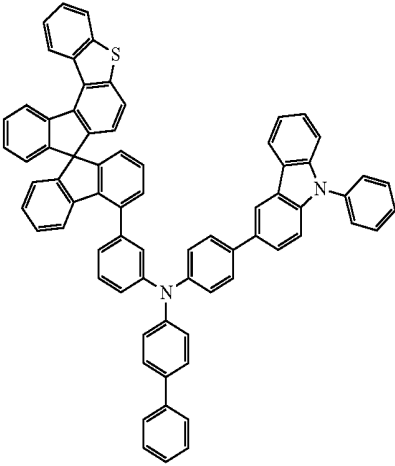
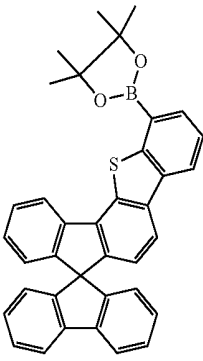
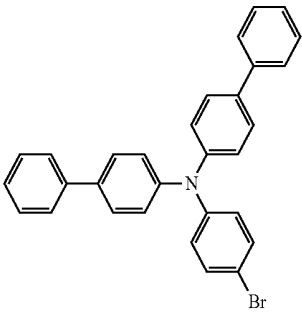
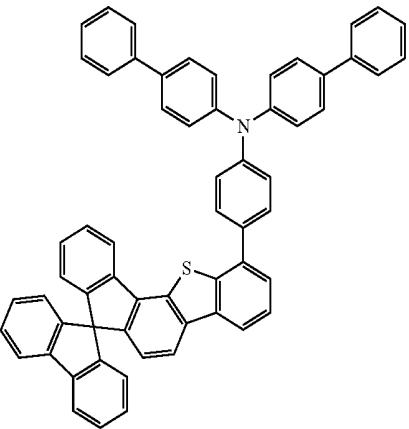
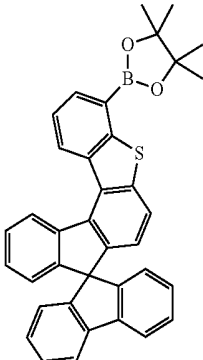
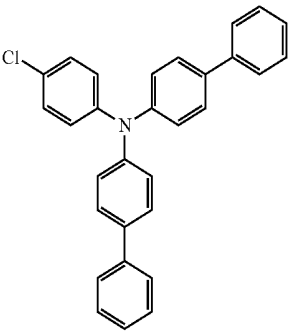
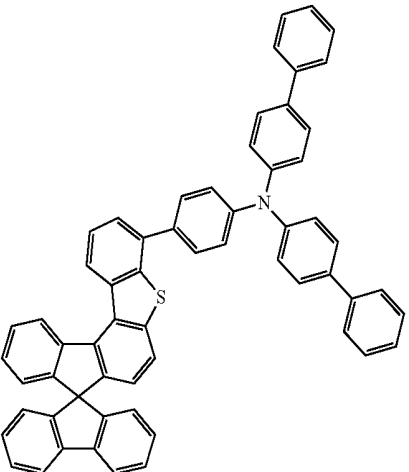
product has been filtered through silica gel with toluene, the remaining residue is recrystallized from heptane/toluene and finally sublimed under high vacuum. The purity is 99.9%. The yield is 21.3 g (75% of theory).

Synthesis of Compounds (3-2) to (3-11)

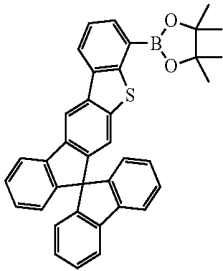
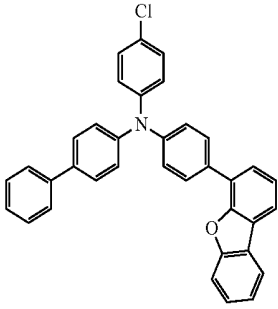
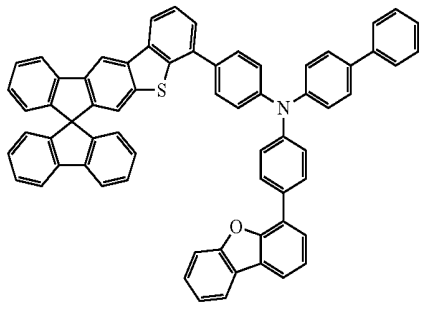
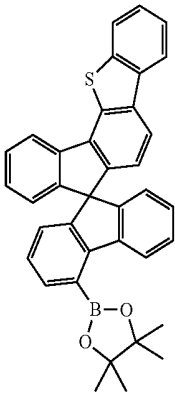
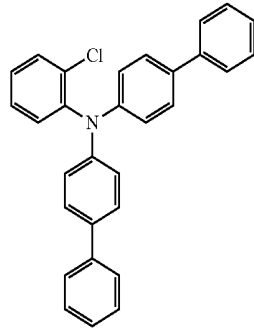
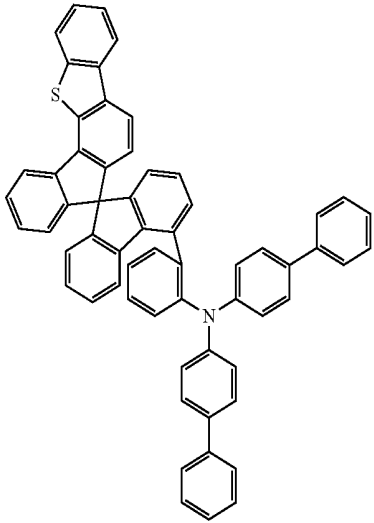
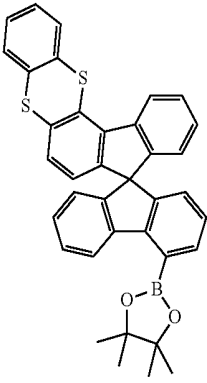
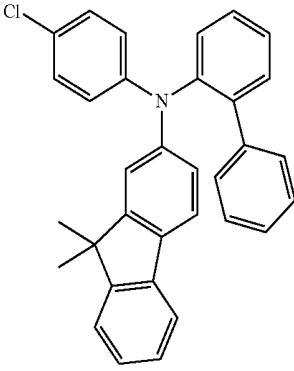
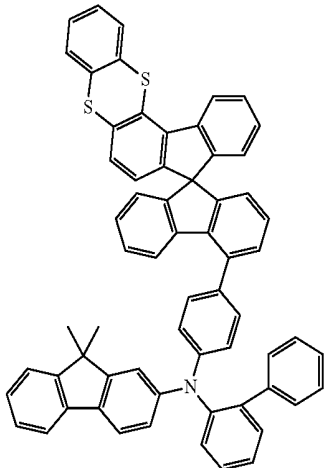
In a manner analogous to the synthesis of compound (3-1) described in Example 1, the following compounds (3-2) to (3-11) are also prepared:

	Reactant 1	Reactant 2	Product	Yield
3-2				78%
3-3				71%
3-4				82%

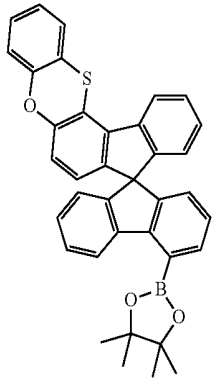
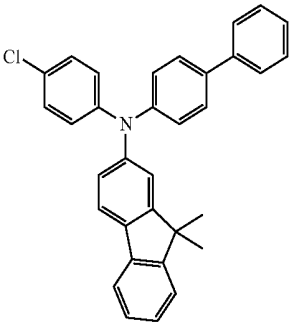
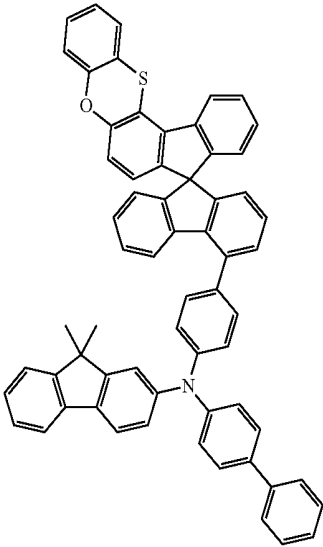
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	Reactant 1	Reactant 2	Product	Yield
3-5				89%
3-6				69%
3-7				75%

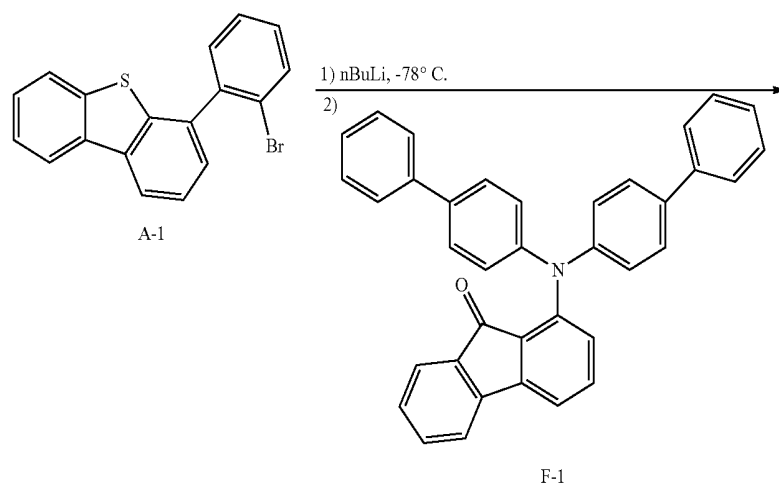
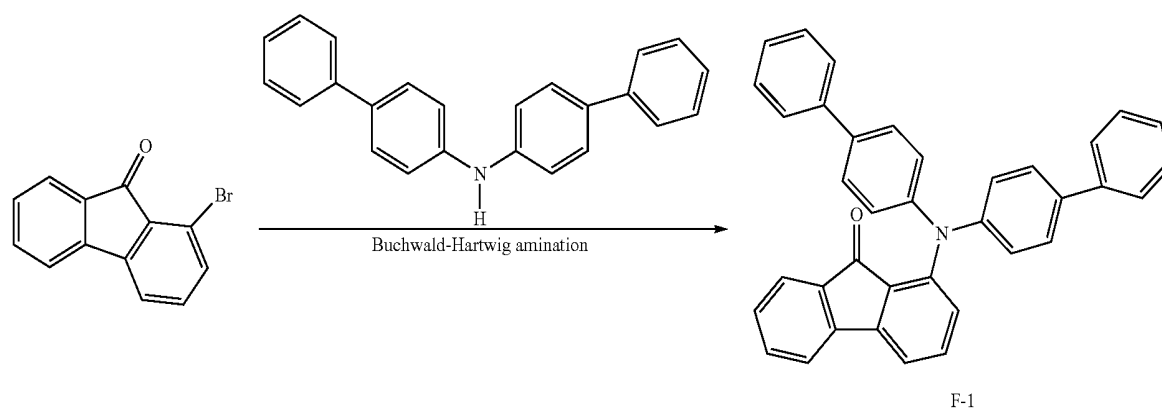
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	Reactant 1	Reactant 2	Product	Yield
3-8				72%
3-9				63%
3-10				75%

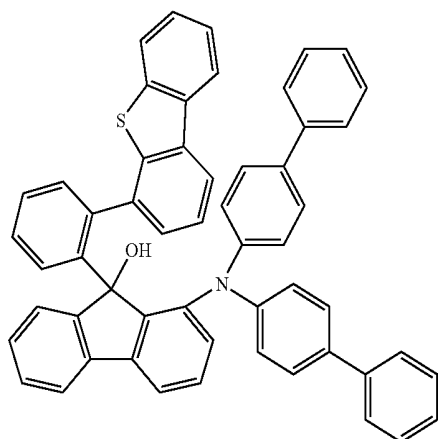
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	Reactant 1	Reactant 2	Product	Yield
3-11				77%

Example 4: Synthesis of Compounds 4-1 to 4-9



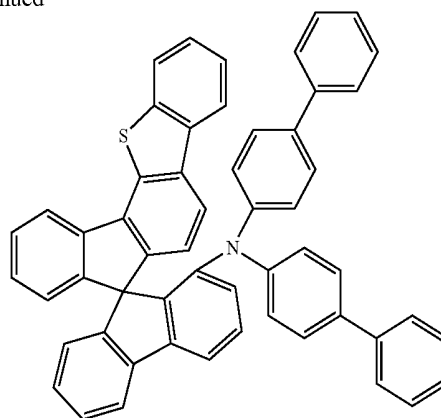
159



-continued

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cyclization



(4-1)

20

Synthesis of compounds F-1 to F-5

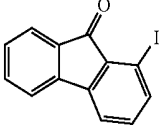
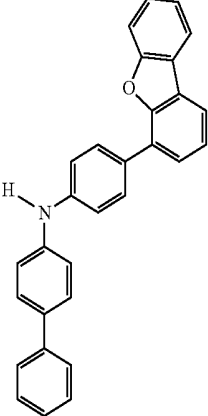
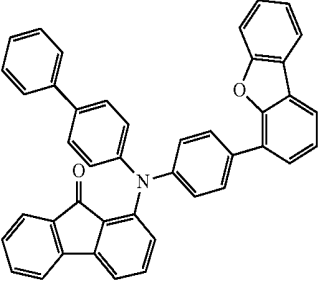
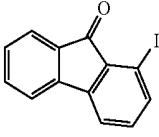
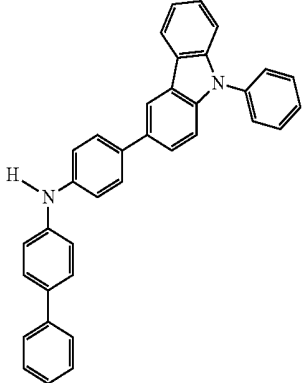
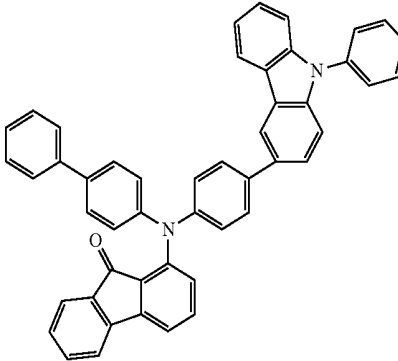
27 g (85 mmol) of bis(biphenyl)amine and 22.0 g (85 mmol) of 1-bromofluorenone are dissolved in 170 ml of toluene. The solution is degassed and saturated with N_2 . Thereafter, 4 ml (1.7 mmol) of a 10% tri-tert-butylphosphine solution and 0.2 g (0.89 mmol) of $Pd(AcO)_2$ are added thereto, and then 12.2 g of sodium tert-butoxide (127 mmol)

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are added. The reaction mixture is heated to boiling under a protective atmosphere for 12 h. The mixture is subsequently partitioned between toluene and water, and the organic phase is washed three times with water and dried over Na_2SO_4 and concentrated by rotary evaporation. After the crude product has been filtered through silica gel with toluene, the remaining residue is recrystallized from heptane/toluene. The yield of compound F-1 is 34 g (80% of theory).

	Reactant 1	Reactant 2	Product	Yield
F-2				67%
F-3				75%

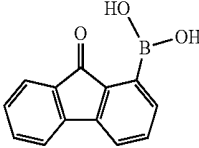
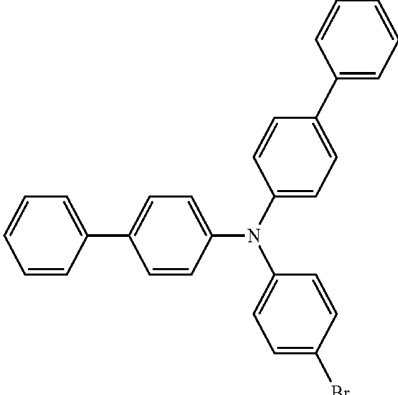
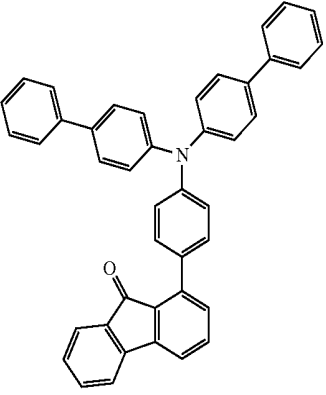
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	Reactant 1	Reactant 2	Product	Yield
F-4				80%
F-5				78%

Synthesis of Compounds F-6 to F-8

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In a manner analogous to the synthesis of compound (3-1) described in Example 1, the following compounds (F-6) to (F-8) are also prepared:

	Reactant 1	Reactant 2	Product	Yield
F-6				89%

-continued

	Reactant 1	Reactant 2	Product	Yield
F-7				85%
F-8				75%

Synthesis of Compounds 4-1 to 4-9

30 g (88 mmol) of 4-(2-bromophenyl)dibenzothiophene are initially charged in 300 ml of THF at -78°C . At this temperature, 39 ml of BuLi (2.5 M in hexane) are added dropwise. After 1 hour, 44 g (88 mmol) of fluorenone F-1 in 200 ml of THF are added dropwise. The mixture is left to stir at room temperature overnight, added to ice-water and extracted with dichloromethane. The combined organic phases are washed with water and dried over sodium sul-

35

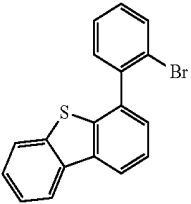
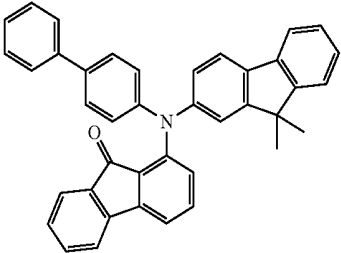
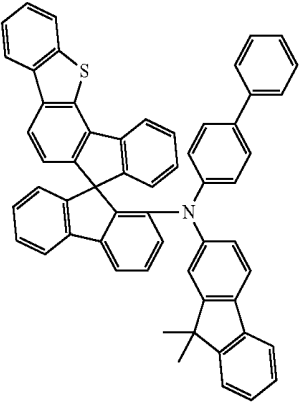
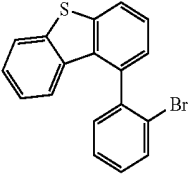
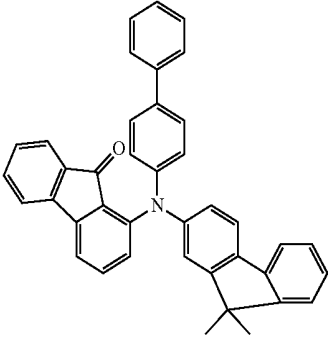
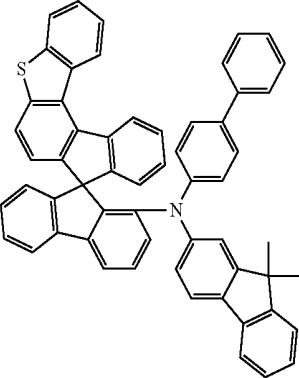
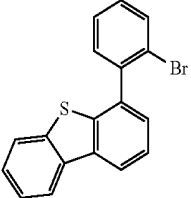
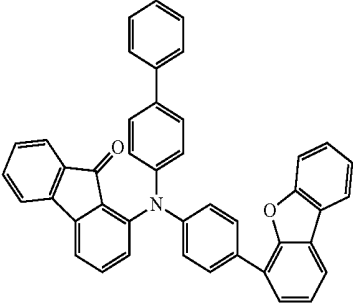
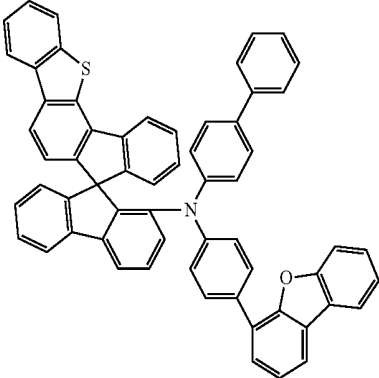
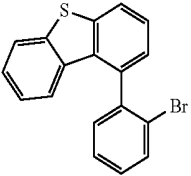
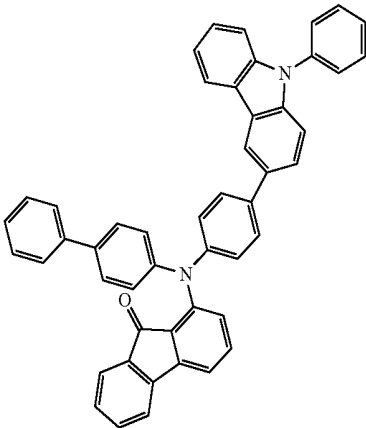
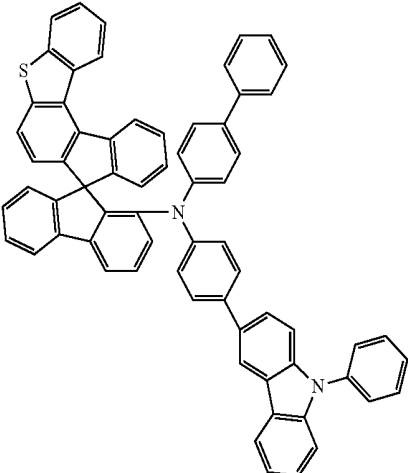
phate. The solvent is removed under reduced pressure and the residue, without further purification, is heated under reflux with 100 ml of HCl and 1200 ml of AcOH at 75°C . overnight. After cooling, the precipitated solid is filtered off with suction and washed once with 100 ml of water and three times with 100 ml each time of ethanol, recrystallized from heptane and finally sublimed under high vacuum. Yield: 40 g (53 mmol), 60%; purity: about 99.9% by HPLC.

40

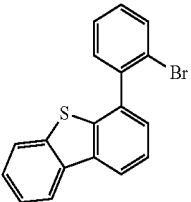
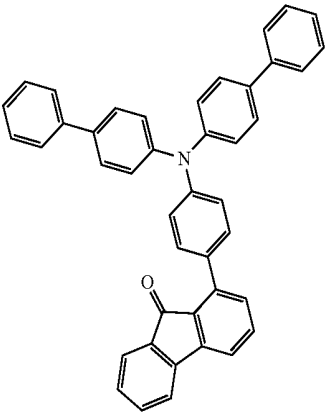
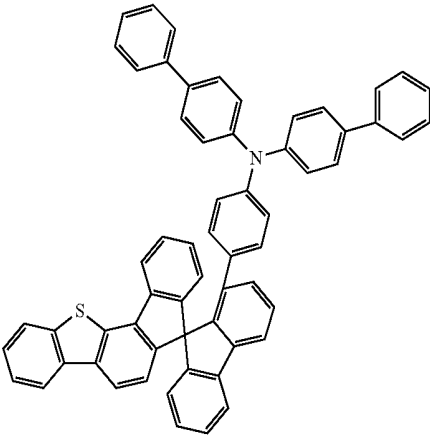
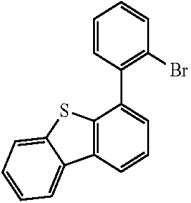
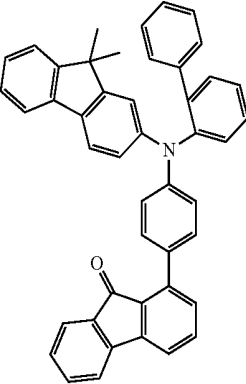
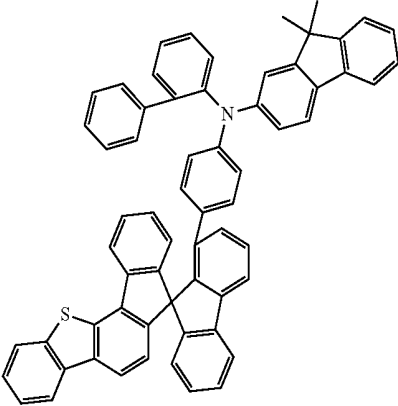
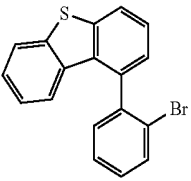
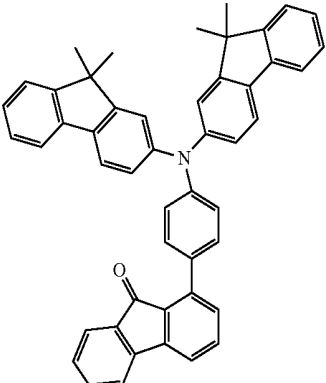
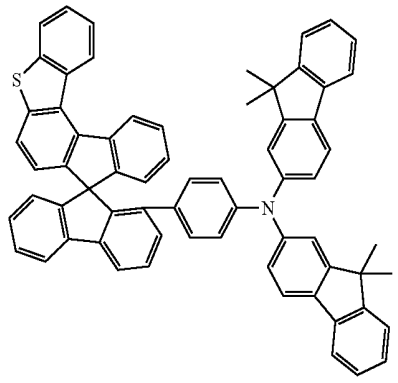
In an analogous manner, it is possible to prepare the further compounds 4-2 to 4-9:

	Reactant 1	Reactant 2	Product	Yield
4-2				50%

-continued

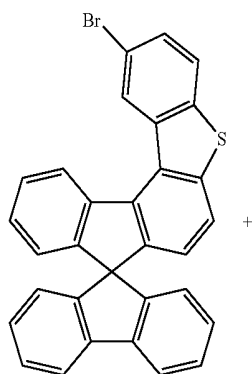
	Reactant 1	Reactant 2	Product	Yield
4-3				61%
4-4				48%
4-5				49%
4-6				45%

-continued

Reactant 1	Reactant 2	Product	Yield
4-7 			60%
4-8 			52%
4-9 			60%

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Example 5: Synthesis of Compounds 5-1 to 5-3



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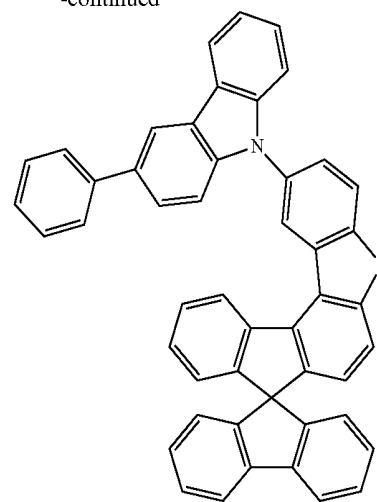
-continued

5

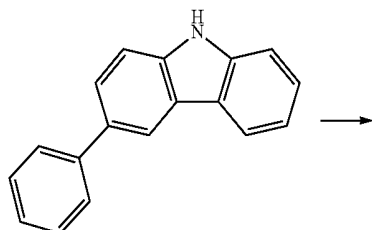
10

15

20



5-1



25

30

35

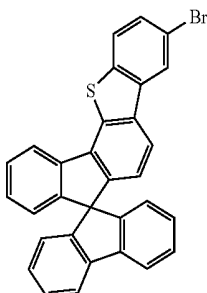
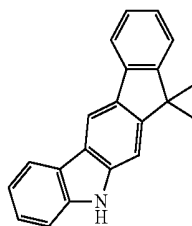
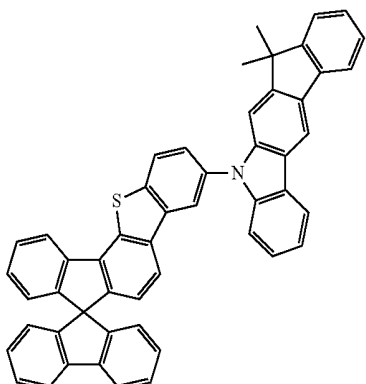
40

10.5 g (43 mmol) of 3-phenylcarbazole and 18 g (36 mmol) of the bromo-spiro derivative are dissolved in 30 ml of toluene. The solution is degassed and saturated with N_2 . Thereafter, 1.44 ml (1.44 mmol) of a 1 M tri-tert-butylphosphine solution and 660 mg (0.72 mmol) of $Pd_2(dba)_3$ are added thereto, and then 5.28 g of sodium tert-butoxide (53.8 mmol) are added. The reaction mixture is heated to boiling under a protective atmosphere for 24 h. The mixture is subsequently partitioned between toluene and water, and the organic phase is washed three times with water and dried over Na_2SO_4 and concentrated by rotary evaporation. After the crude product has been filtered through silica gel with toluene, the remaining residue is recrystallized from heptane/toluene and finally sublimed under high vacuum. The purity is 99.9% (HPLC). The yield of compound (5-1) is 14 g (60% of theory).

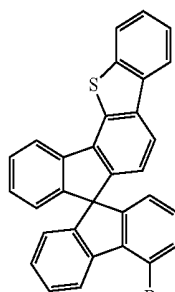
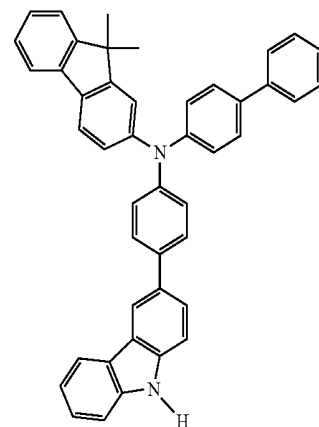
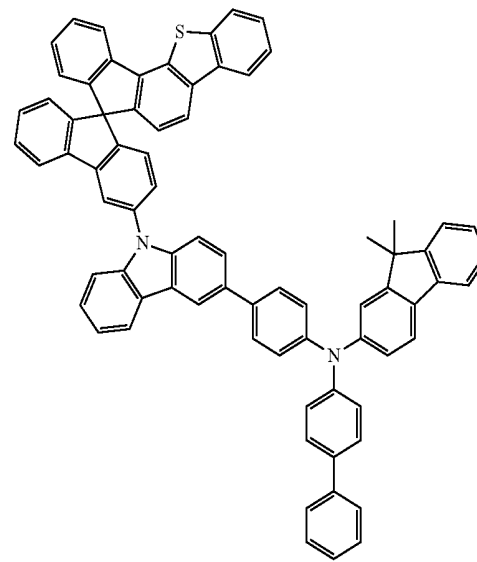
Synthesis of Compounds (5-2) and (5-3)

In a manner analogous to the synthesis of compound (5-1) described in Example 1, the following compounds (5-2) and (5-3) are also prepared:

In an analogous manner, the following compounds are obtained:

Reactant 1	Reactant 2	Product	Yield
5-2 	 1257220-47-5		50%

-continued

Reactant 1	Reactant 2	Product	Yield
5-3 	 1427738-11-1		45%

B) Device Examples

OLEDs of the invention and OLEDs according to the prior art are produced by a general method according to WO 04/058911, which is adapted to the circumstances described here (e.g. materials).

In the inventive examples which follow, the data for various OLEDs are presented. Substrates used are glass plates coated with structured ITO (indium tin oxide) of thickness 50 nm. The OLEDs have the following layer structure: substrate/p-doped hole transport layer (HIL1)/hole transport layer (HTL)/p-doped hole transport layer (HTL2)/electron blocker 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 of thickness 100 nm. The materials required for production of the OLEDs are shown in Table 1.

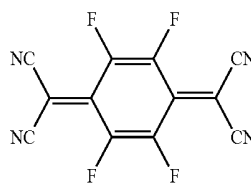
All materials are applied by thermal vapour deposition in a vacuum chamber. In this case, the emission layer always

consists of at least one matrix material (host material) and an emitting dopant (emitter) which is added to the matrix material(s) in a particular proportion by volume by co-evaporation. Details given in such a form as H1:SEB(5%) mean here that the material H1 is present in the layer in a proportion by volume of 95% and SEB in a proportion by volume of 5%. In an analogous manner, the electron transport layers or the hole injection layers may also consist of a mixture of two or more materials.

The OLEDs are characterized in a standard manner. For this purpose, the external quantum efficiency (EQE, measured in percent) is determined as a function of luminance, calculated from current-voltage-luminance characteristics (IUL characteristics) assuming Lambertian radiation characteristics, and the lifetime. The parameter EQE @ 10 mA/cm² refers to the external quantum efficiency at a current density of 10 mA/cm². LD80 @ 60 mA/cm² is the lifetime before the OLED, given a starting brightness at constant current of 60 mA/cm², has fallen to 80% of the starting intensity.

TABLE 1

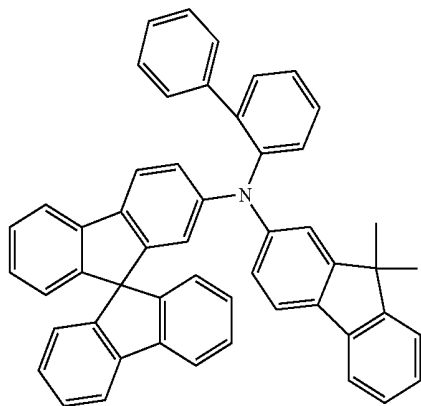
Structures of the materials used



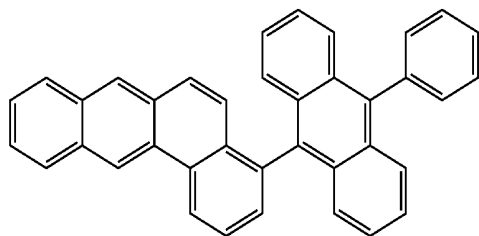
F4TCNQ

Structures of the materials used

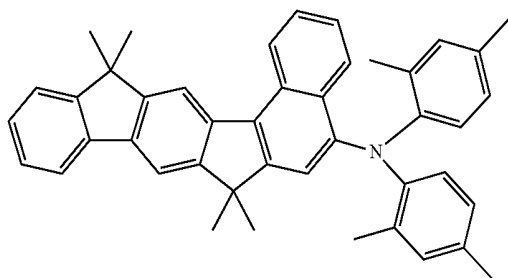
HIM



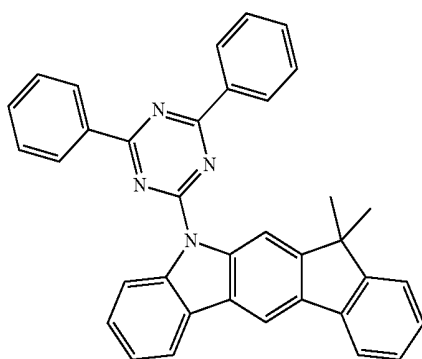
H1



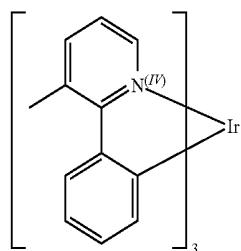
SEB



H2

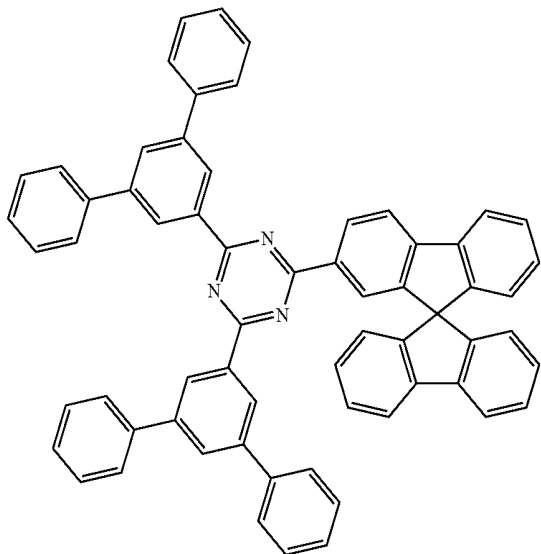


TEG

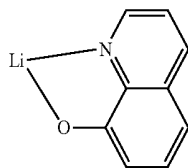


Structures of the materials used

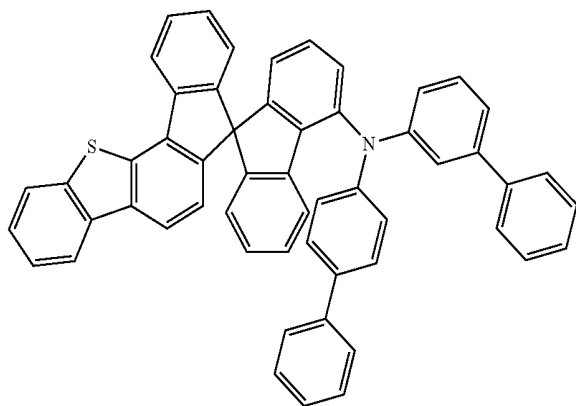
ETM



LiQ



HTM1



HTM2

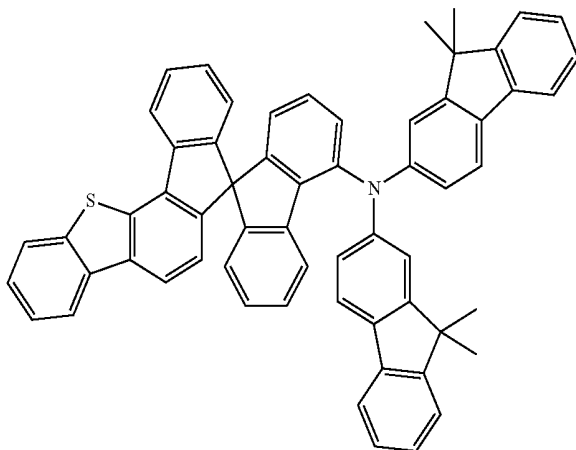
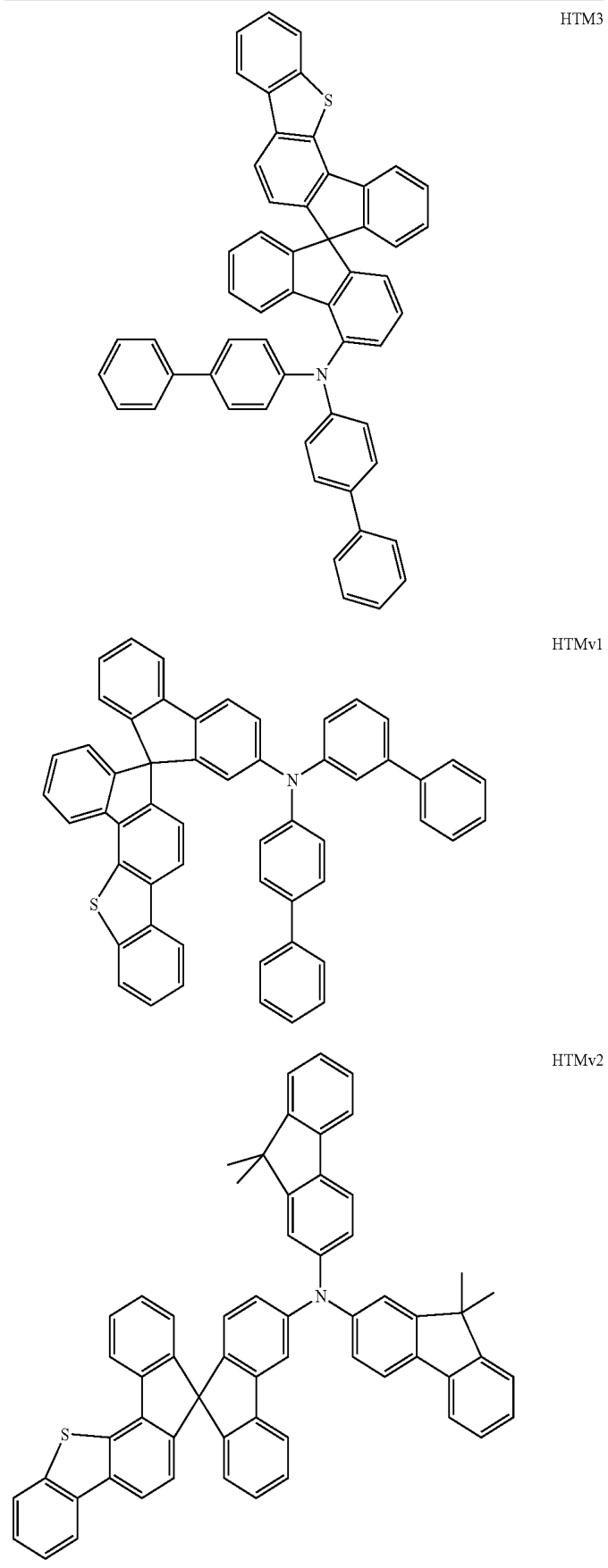


TABLE 1-continued

Structures of the materials used



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Example 1

The inventive compound HTM1 and the comparative compound HTMv1 are compared with one another in a blue-emitting OLED stack. The structure of the stack is as follows: HIM:F4TCNQ(5%)(20 nm)/HIM(155 nm)/HTM1:F4TCNQ(5%)(20 nm)/HTM1(20 nm)/H1:SEB(5%)(20 nm)/ETM:LiQ(50%)(30 nm)/LiQ(1 nm). In the comparative example, rather than HTM1, HTMv1 is used in all relevant layers.

The evaluation of the external quantum efficiencies at 10 mA/cm² for the experiments conducted shows the following results: HTM1 achieves 7.7% EQE, whereas HTMv1 achieves only 7.0%. The lifetimes of the devices produced until a drop to 80% of the starting intensity at a constant current of 60 mA/cm² show the advantage of compound HTM1 even more clearly. These extend to 380 hours in the case of HTM1, whereas HTMv1 achieves only 270 hours.

Example 2

The same two materials as in Example 1 are used to produce a triplet green component having the following structure: HIM:F4TCNQ(5%)(20 nm)/HIM(210 nm)/HTM1:F4TCNQ(5%)(20 nm)/HTM1(20 nm)/H2:TEG(10%)(30 nm)/ETM:LiQ(50%)(40 nm)/LiQ(1 nm). In the comparative example, HTM1 is replaced by HTMv1.

The external quantum efficiencies show a similar trend to that in the blue-emitting OLED of Example 1. The external quantum efficiency for HTM1 at 2 mA/cm² in this experiment is 19.4%. The component comprising HTMv1 achieves 19.1%. The lifetime of HTM1 here too is much higher than for the comparative HTM. HTM1 at 20 mA/cm² has a lifetime before a drop to 80% of the starting intensity of 160 hours. HTMv1 has an LT80 of 110 hours.

Example 3

In a further experiment, the compounds HTM2 and HTMv2 are compared. Here, the different performance data are even more clearly distinguishable. Again, the blue singlet stack (cf. Example 1) with the following structure is used: HIM:F4TCNQ(5%)(20 nm)/HIM(155 nm)/HTM2:F4TCNQ(5%)(20 nm)/HTM2(20 nm)/H1:SEB(5%)(20 nm)/ETM:LiQ(50%)(30 nm)/LiQ(1 nm), with insertion of HTMv2 rather than HTM2 at all appropriate points in the stack in the comparative experiment.

In the evaluation of the experimental data, the experiment comprising HTM2 shows an external quantum efficiency at 10 mA/cm² of 7.9%, whereas HTMv2 shows only 7.3%. The lifetimes show a clear difference between the two materials. The stack comprising HTM2 has a lifetime LT80 at 60 mA/cm² of 330 hours. HTMv2 under the same conditions achieves only 190 hours.

Example 4

Similar trends are seen as well in the triplet green component tested. The stack is analogous to the above-described green-emitting OLED stack (cf. example 3): HIM:F4TCNQ(5%)(20 nm)/HIM(210 nm)/HTM2:F4TCNQ(5%)(20)/HTM2(20)/H2:TEG(10%)(30 nm)/ETM:LiQ(50%)(40 nm)/LiQ(1 nm). In the comparative experiment, again, HTM2 is replaced by HTMv2.

The external quantum efficiency at 2 mA/cm² for HTM2 is 19.2%; HTMv2 achieves only 17.7%. The LT80 @ 20

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mA/cm² in the HTM2 stack is 170 hours, and in the comparative structure comprising HTMv2 100 hours.

Example 5

Finally, the compound HTM3 is also tested in a singlet blue stack. This has the following structure: (HIM:F4TCNQ(5%)(20 nm)/HIM(155 nm)/HTM3:F4TCNQ(5%)(20 nm)/HTM3(20 nm)/H1:SEB(5%)(20 nm)/ETM:UQ(50%)(30 nm)/LiQ(1 nm)). The compound HTM3 here exhibits an external quantum efficiency at 10 mA/cm² of 7.6%. The lifetime to 80% and 60 mA/cm² is 340 hours.

Example 6

In a triplet green component having the following structure: HIM:F4TCNQ(5%)(20 nm)/HIM(210 nm)/HTM3:F4TCNQ(5%)(20 nm)/HTM3(20 nm)/H2:TEG(10%)(30 nm)/ETM:LiQ(50%)(40 nm)/LiQ(1 nm), the compound HTM3 shows an external quantum efficiency at 2 mA/cm² of 17.8% and a lifetime LT80 @ 20 mA/cm² of 150 hours.

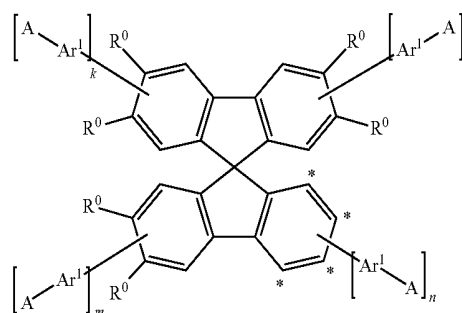
In summary, the device examples show that excellent performance data are achieved in OLEDs with the inventive compounds, especially excellent lifetime and quantum efficiency, both in systems comprising fluorescent emitters and in systems comprising phosphorescent emitters.

Substitution by an arylamino group in the specific position on the spirobifluorene as present in the compounds HTM1 to HTM3 additionally leads to much improved device performance compared to substitution in the 2 and 3 positions as exists in comparative examples HTMv1 and HTMv2.

The invention claimed is:

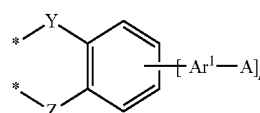
1. A compound of the formula (I)

Formula (I)



which has a group of the formula (T)

Formula (T)



bonded at two adjacent positions marked by * to the base structure of formula (I), where the condensation is such that any bond marked by * in formula (T) is attached at a position marked by * to the base structure of formula (I);

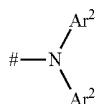
which optionally substituted at one or more positions shown as unsubstituted in the base structure of formula (I) and the group of the formula (T) by an R¹ radical;

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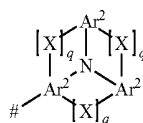
wherein the group —Ar¹-A can only be bonded at one or more positions shown as unsubstituted in the base structure of formula (I); and

which has the following definitions of the variables:

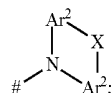
A is the same or different at each instance and is a group of the formula (A1), (A2) or (A3) which is bonded via the bond marked with # and optionally substituted at one or more positions shown as unsubstituted by an R² radical;



Formula (A1)



Formula (A2)



Formula (A3)

Ar¹ is the same or different at each instance and is a single bond or an aromatic or heteroaromatic ring system which has 6 to 30 aromatic ring atoms and optionally substituted by one or more R² radicals;

Ar² is the same or different at each instance and is an aromatic or heteroaromatic ring system which has 6 to 30 aromatic ring atoms and optionally substituted by one or more R² radicals;

X is the same or different at each instance and is a single bond or a group selected from BR², C(R²)₂, Si(R²)₂, C=O, O, S, S=O, SO₂, NR², PR² and P(=O)R²;

Y is selected from O and S;

Z is selected from O, S, and a single bond, where Z is not a single bond when Y is O;

R⁰ is H;

R¹ is the same or different at each instance and is selected from H, D, F, C(=O)R³, CN, Si(R³)₃, P(=O)(R³)₂, OR³, S(=O)R³, S(=O)₂R³, straight-chain alkyl or alkoxy groups having 1 to 20 carbon atoms, branched or cyclic alkyl or alkoxy groups having 3 to 20 carbon atoms, alkenyl or alkynyl groups having 2 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms, and heteroaromatic ring systems having 5

to 40 aromatic ring atoms; where two or more R¹ radicals optionally joined to one another and optionally form a ring; where the alkyl, alkoxy, alkenyl and alkynyl groups mentioned and the aromatic ring systems and heteroaromatic ring systems mentioned optionally each be substituted by one or more R³ radicals; and where one or more CH₂ groups in the alkyl, alkoxy, alkenyl and alkynyl groups mentioned optionally be replaced by —R³C=CR³—, —C≡C—, Si(R³)₂, C=O, C=NR³, —C(=O)O—, —C(=O)NR³—, NR³, P(=O)(R³), —O—, —S—, SO or SO₂;

R² is the same or different at each instance and is selected from H, D, F, C(=O)R³, CN, Si(R³)₃, N(R³)₂, P(=O)(R³)₂, OR³, S(=O)R³, S(=O)₂R³, straight-chain alkyl or alkoxy groups having 1 to 20 carbon atoms, branched or cyclic alkyl or alkoxy groups having 3 to 20 carbon atoms, alkenyl or alkynyl groups having 2

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20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms, and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more R² radicals optionally be joined to one another and optionally form a ring; where the alkyl, alkoxy, alkenyl and alkynyl groups mentioned and the aromatic ring systems and heteroaromatic ring systems mentioned optionally each be substituted by one or more R³ radicals; and where one or more CH₂ groups in the alkyl, alkoxy, alkenyl and alkynyl groups mentioned optionally be replaced by —R³C=CR³—, —C≡C—, Si(R³)₂, C=O, C=NR³, —C(=O)O—, —C(=O)NR³—, NR³, P(=O)(R³), —O—, —S—, SO or SO₂;

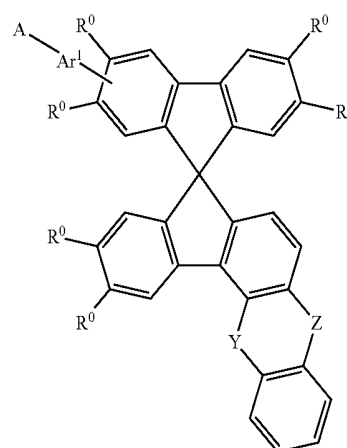
R³ is the same or different at each instance and is selected from H, D, F, C(=O)R⁴, CN, Si(R⁴)₃, N(R⁴)₂, P(=O)(R⁴)₂, OR⁴, S(=O)R⁴, S(=O)₂R⁴, straight-chain alkyl or alkoxy groups having 1 to 20 carbon atoms, branched or cyclic alkyl or alkoxy groups having 3 to 20 carbon atoms, alkenyl or alkynyl groups having 2 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms, and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more R¹ or R² radicals optionally be joined to one another and optionally form a ring; where the alkyl, alkoxy, alkenyl and alkynyl groups mentioned and the aromatic ring systems and heteroaromatic ring systems mentioned optionally each be substituted by one or more R⁴ radicals; and where one or more CH₂ groups in the alkyl, alkoxy, alkenyl and alkynyl groups mentioned optionally be replaced by —R⁴C=CR⁴—, —C≡C—, Si(R⁴)₂, C=O, C=NR⁴, —C(=O)O—, —C(=O)NR⁴—, NR⁴, P(=O)(R⁴), —O—, —S—, SO or SO₂;

R⁴ is the same or different at each instance and is selected from H, D, F, CN, alkyl groups having 1 to 20 carbon atoms, aromatic ring systems having 6 to 40 aromatic ring atoms and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more R⁴ radicals optionally be joined to one another and optionally form a ring; and where the alkyl groups, aromatic ring systems and heteroaromatic ring systems mentioned optionally be substituted by F or CN;

q is the same or different at each instance and is 0 or 1, where at least one q in formula (A2) is 1;

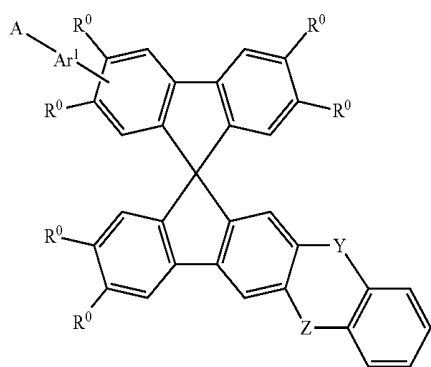
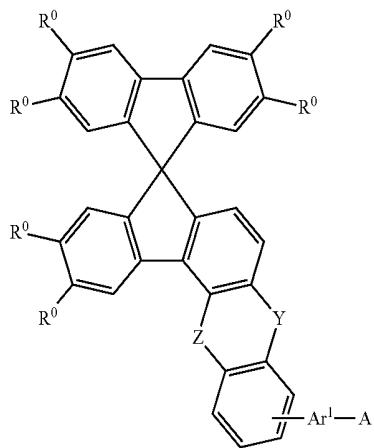
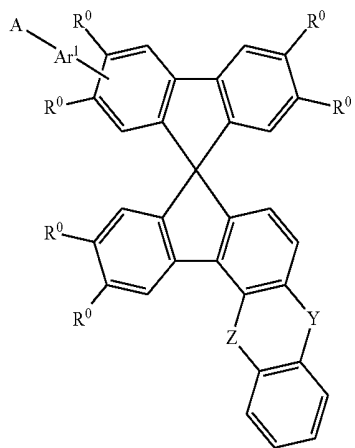
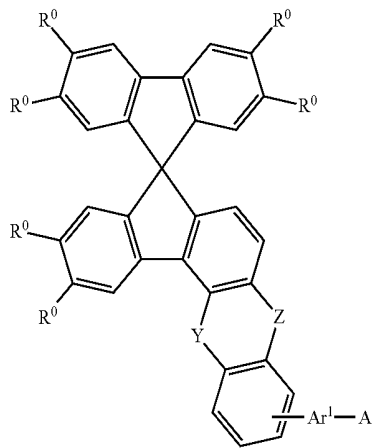
i, k, m, n and p are the same or different at each instance and are 0 or 1, where at least one of these indices is 1.

2. The compound according to claim 1, wherein it corresponds to one of the following formulae:



Formula (I-1)

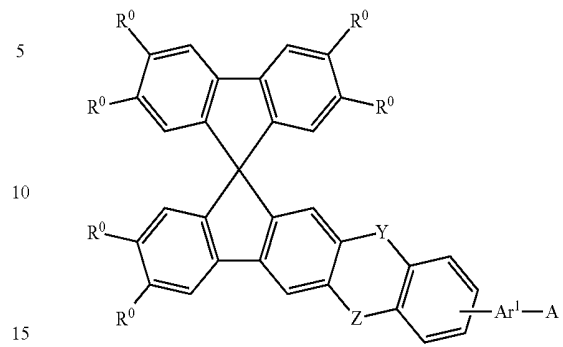
183
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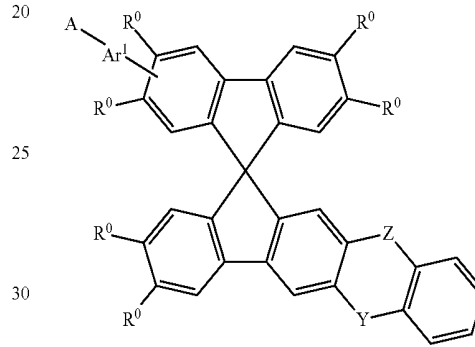
Formula (I-2)

Formula (I-6)



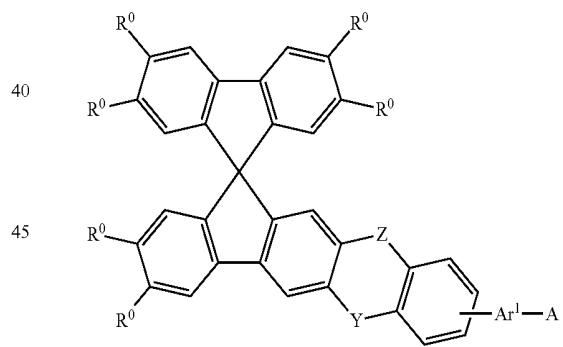
Formula (I-3)

Formula (I-7)



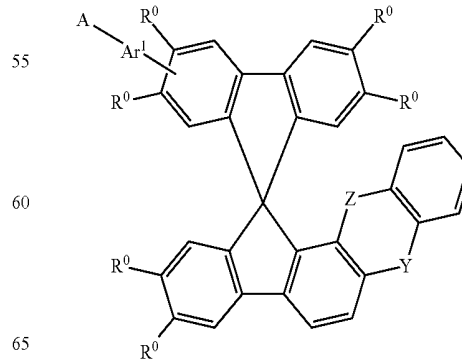
Formula (I-4)

Formula (I-8)



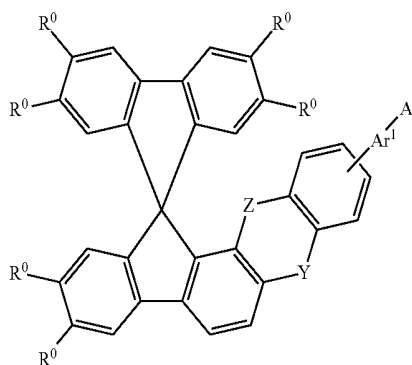
Formula (I-5)

Formula (I-9)

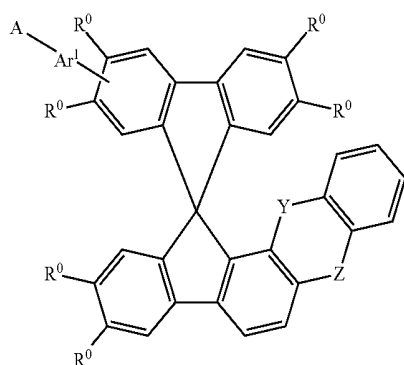


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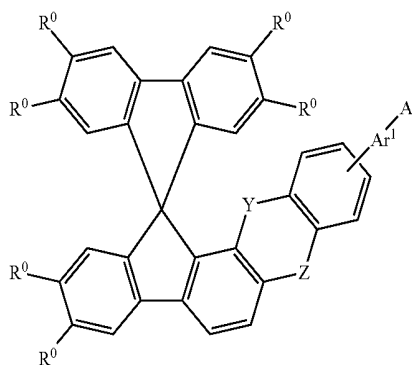
-continued



Formula (I-10)



Formula (I-11)



Formula (I-12)

where the symbols that occur are as defined in claim 1, wherein the group $-\text{Ar}^1\text{-A}$ can only be bonded at one or more positions shown as unsubstituted in the base structure of formulae (I-1) through (I-12); and the compounds optionally be substituted at positions shown as unsubstituted by R^1 radicals.

3. The compound according to claim 1, wherein A is a group of the formula (A-1).

4. The compound according to claim 1, wherein Ar^1 is the same or different at each instance and is selected from a single bond and a divalent group derived from benzene, biphenyl, terphenyl, fluorene, spirobifluorene, indenofluorene, carbazole, dibenzofuran or dibenzothiophene, each optionally substituted by R^2 radicals, or a combination of

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two or more of these groups, but not more than 30 aromatic ring atoms optionally present in Ar^1 .

5. The compound according to claim 1, wherein Ar^2 is the same or different at each instance and is selected from phenyl, biphenyl, terphenyl, fluorenyl, spirobifluorenyl, indenofluorenyl, naphthyl, phenanthrenyl, furanyl, benzofuranyl, dibenzofuranyl, thiophenyl, benzothiophenyl, dibenzothiophenyl, carbazolyl, indolocarbazolyl and indenocarbazolyl, each of which optionally substituted by one or more R^2 radicals.

6. The compound according to claim 1, wherein X is a single bond.

7. The compound according to claim 1, wherein R^1 and R^2 are the same or different at each instance and are H, D, F, CN, a straight-chain alkyl group having 1 to 10 carbon atoms or a branched or cyclic alkyl group having 3 to 10 carbon atoms, or an aromatic or heteroaromatic ring system having 6 to 25 aromatic ring atoms, where said alkyl and alkoxy groups and said aromatic or heteroaromatic ring systems each optionally substituted by one or more R^3 radicals.

8. The compound according to claim 1, wherein p is 1, and in that all the other indices k, i, m and n are 0, or wherein k is 1, and in that all the other indices m, n and p are 0.

9. The compound according to claim 1, wherein the sum total of the indices i, k, m, n and p is 1.

10. The compound according to claim 1, wherein the Y group is S, and the Z group is O, S or a single bond.

11. The compound according to claim 1, wherein the Y group is S, and the Z group is a single bond.

12. A process for preparing a compound according to claim 1, comprising either

A) first preparing a spirobifluorene base skeleton substituted by a reactive group by reacting a dibenzothiophenyl derivative with a fluorenone derivative bearing the reactive group and, in a later step, via an organometallic coupling reaction, a diarylamino or carbazole group or an aryl or heteroaryl group substituted by a diarylamino or carbazole group is introduced at the position of the reactive group, or

B) reacting a dibenzothiophenyl derivative with a fluorenone bearing a diarylamino or carbazole group or an aryl or heteroaryl group substituted by a diarylamino or carbazole group is involved, or

C) first preparing a spirobifluorene base skeleton by reacting a dibenzothiophenyl derivative with a fluorenone derivative, then the latter is functionalized with a reactive group and, in a later step, via an organometallic coupling reaction, a diarylamino or carbazole group or an aryl or heteroaryl group substituted by a diarylamino or carbazole group is introduced at the position of the reactive group.

13. An oligomer, polymer or dendrimer containing one or more compounds of the formula (I) according to claim 1, wherein the bond(s) to the polymer, oligomer or dendrimer optionally localized at any desired positions substituted by R^0 , R^1 or R^2 in formula (I).

14. A formulation comprising at least one compound according to claim 1, or at least one polymer, oligomer or dendrimer according to claim 13, and at least one solvent.

15. A method comprising utilizing the compound according to claim 1, or the oligomer, polymer or dendrimer according to claim 13, in an electronic device.

16. An electronic device comprising at least one compound according to claim 1 or at least one oligomer, polymer or dendrimer according to claim 13.

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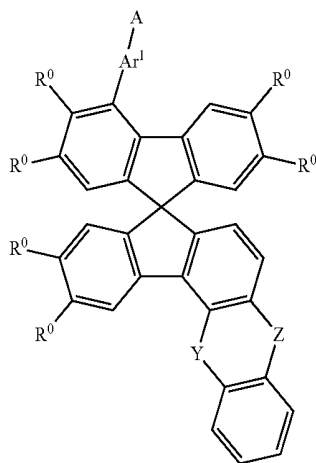
17. The electronic device according to claim 16, selected from the group consisting of organic integrated circuits (OICs), organic field-effect transistors (OFETs), organic thin-film transistors (OTFTs), organic light-emitting transistors (OLETs), organic solar cells (OSCs), organic optical detectors, organic photoreceptors, organic field-quench devices (OFQDs), organic light-emitting electrochemical cells (OLECs), organic laser diodes (O-lasers) and organic electroluminescent devices (OLEDs).

18. The electronic device according to claim 17, wherein the at least one compound or the at least one oligomer, polymer or dendrimer is present in a layer selected from hole transport layers and emitting layers.

19. The electronic device according to claim 18, wherein the at least one compound or the at least one oligomer, polymer or dendrimer is present in an emitting layer together with one or more phosphorescent emitters.

20. The electronic device according to claim 18, wherein the at least one compound or the at least one oligomer, polymer or dendrimer is present in a hole transport layer together with one or more p-dopants.

21. The compound according to claim 1, wherein it corresponds to one of the following formulae:

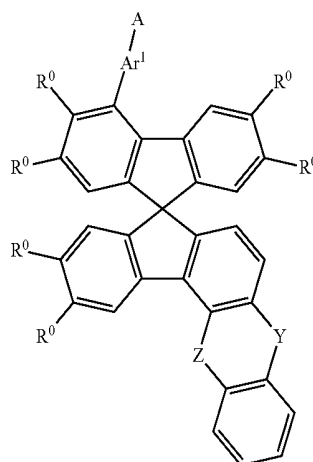


Formula (I-1A)

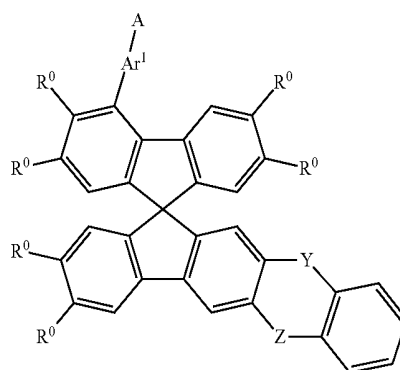
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-continued

Formula (I-3A)



Formula (I-5A)



Formula (I-7A)

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专利名称(译)	电子设备用材料		
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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	PFISTER JOCHEN STIEBER FRANK MONTENEGRO ELVIRA MUJICA FERNAUD TERESA		
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摘要(译)

本申请涉及式 (I) 的螺二芴衍生物, 其在电子器件中的用途, 特别是在有机电致发光器件 (OLED) 中的用途, 其中它们可用于空穴传输功能, 以及制备所述衍生物的方法。该化合物具有一种或多种选自非常好的空穴传导性质, 非常好的电子阻挡性能, 高玻璃化转变温度, 高氧化稳定性, 良好的溶解性和高热稳定性的性质。

Formula (I)

