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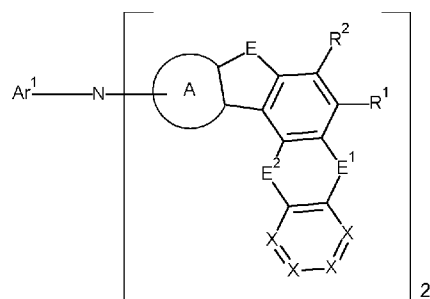
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(54) Title: MATERIALS FOR ORGANIC ELECTROLUMINESCENT DEVICES



(1)

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

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Materials for organic electroluminescent devices

The present invention relates to a compound of the formula (1), to the use of the compound in an electronic device, and to an electronic device comprising a compound of the formula (1). The present invention furthermore
5 relates to a process for the preparation of a compound of the formula (1) and to a formulation comprising one or more compounds of the formula (1).

The development of functional compounds for use in electronic devices is
10 currently the subject of intensive research. The aim is, in particular, the development of compounds with which improved properties of electronic devices in one or more relevant points can be achieved, such as, for example, power efficiency and lifetime of the device as well as colour
15 coordinates of the emitted light.

In accordance with the present invention, the term electronic device is taken to mean, inter alia, organic integrated circuits (OICs), organic field-effect
20 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).
25

Of particular interest is the provision of compounds for use in the last-mentioned electronic devices called OLEDs. The general structure and the functional principle of OLEDs are known to the person skilled in the art and
30 are described, for example, in US 4539507.

Further improvements are still necessary with respect to the performance data of OLEDs, in particular with a view to broad commercial use, for
35 example in display devices or as light sources. Of particular importance in this connection are the lifetime, the efficiency and the operating voltage of

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the OLEDs and as well as the colour values achieved. In particular, in case of blue-emitting OLEDs, there is potential for improvement with respect to the lifetime and the efficiency of the devices.

5 An important starting point for achieving the said improvements is the choice of the emitter compound and of the host compound employed in the electronic device.

10 Blue-fluorescent emitters known from the prior art are a multiplicity of compounds. Arylamines containing one or more condensed aryl are known from the prior. Arylamines containing dibenzofuran groups (for example in US 2017/0012214) are also known from the prior art.

15 However, there is still a need for further fluorescent emitters, especially blue-fluorescent emitters, which may be employed in OLEDs and lead to OLEDs having very good properties in terms of lifetime, color emission and efficiency. More particularly, there is a need for blue-fluorescent emitters
20 combining very high efficiencies, very good life time and suitable color coordinates.

Furthermore, it is known that an OLED may comprise different layers, which may be applied either by vapour deposition in a vacuum chamber or by
25 processing from a solution. The processes based on vapour deposition lead to good results but such processes are complex and expensive. Therefore, there is a need for OLED materials that can be easily and reliably processed from solution. In this case, the materials should have good
30 solubility properties in the solution that comprises them. Additionally, the OLED materials that are processed from a solution should be able to orientate themselves in the deposited film to improve the overall efficiency of the OLED. The term orientation means here the horizontal molecular
35 orientation of the compounds, as explained in Zhao et al., Horizontal

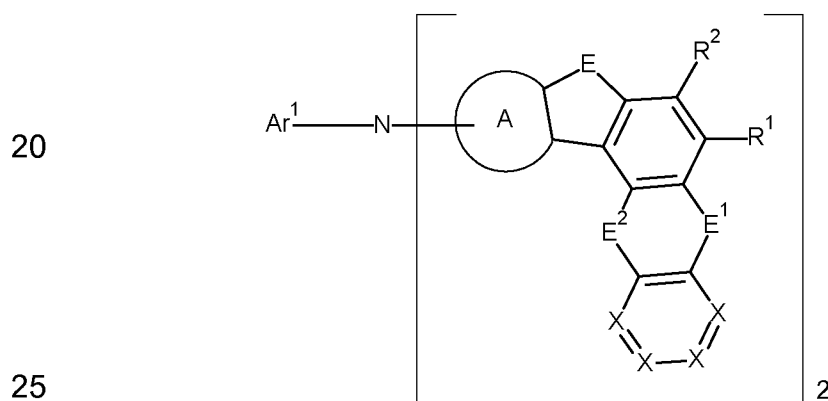
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molecular orientation in solution-processed organic light-emitting diodes, Appl. Phys. Lett. 106063301, 2015.

The present invention is thus based on the technical object of providing compounds which are suitable for use in electronic devices, such as OLEDs, more particularly as blue-fluorescent emitters or matrix materials and, which are suitable for vacuum processing or for solution processing.

In investigations on novel compounds for use in electronic devices, it has now been found, that compounds of formula (1) as defined below are eminently suitable for use in electronic devices. In particular, they achieve one or more, preferably all, of the above-mentioned technical objects.

The invention thus relates to compounds of formula (1),



formula (1)

where the following applies to the symbols and indices used:

A stands on each occurrence, identically or differently, for an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R³; wherein the ring A is condensed on the five-membered ring comprising E via two adjacent carbon atoms, as depicted in formula (1);

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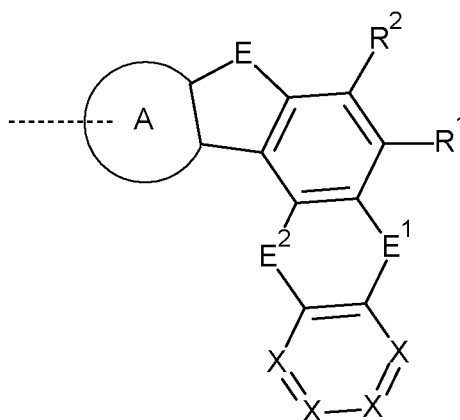
Ar¹ stands for:

- an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R⁴;
- a group of formula (Ar1-1),

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10

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formula (Ar1-1)

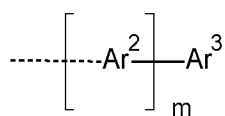
where the dashed bond indicates the bonding to the nitrogen atom as depicted in formula (1); or

20

- a group ArL;

ArL stands for a group of formula (ArL-1),

25



formula (ArL-1)

30

where the dashed bond in formula (ArL-1) indicates the bonding to the structure of formula (1);

X stands on each occurrence, identically or differently, for CR³ or N;

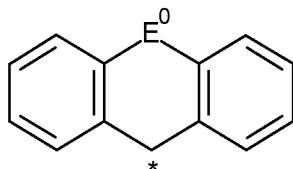
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E is on each occurrence, identically or differently, selected from $-BR^0-$, $-C(R^0)_2-$, $-C(R^0)_2-C(R^0)_2-$, $-C(R^0)_2-O-$, $-C(R^0)_2-S-$, $-R^0C=CR^0-$, $-R^0C=N-$, $Si(R^0)_2$, $-Si(R^0)_2-Si(R^0)_2-$, $-C(=O)-$, $-C(=NR^0)-$, $-C(=C(R^0)_2)-$, $-O-$, $-S-$, $-S(=O)-$, $-SO_2-$, $-N(R^0)-$, $-P(R^0)-$ and $-P(=O)R^0-$; or E is a group of

5

formula (E-1),



10

formula (E-1)

where the symbol * in formula (E-1) indicates the corresponding group E in formula (1); and

15

E^0 is identically or differently on each occurrence, selected from the group consisting of a single bond, $-BR^0-$, $-C(R^0)_2-$, $-C(R^0)_2-C(R^0)_2-$, $-C(R^0)_2-O-$, $-C(R^0)_2-S-$, $-R^0C=CR^0-$, $-R^0C=N-$, $Si(R^0)_2$, $-Si(R^0)_2-Si(R^0)_2-$, $-C(=O)-$, $-C(=NR^0)-$, $-C(=C(R^0)_2)-$, $-O-$, $-S-$, $-S(=O)-$, $-SO_2-$, $-N(R^0)-$, $-P(R^0)-$ and $-P(=O)R^0-$;

20

E^1 , E^2 are identically or differently on each occurrence, selected from the group consisting of a single bond, $-C(R^0)_2-$, $Si(R^0)_2$, $-O-$ and $-S-$; with the proviso that, in a ring comprising the groups E^1 and E^2 , one of the group E^1 and E^2 , is a single bond, $-C(R^0)_2-$ or $Si(R^0)_2$, and the other group is O or S;

25

R^0 , R^1 , R^2 , R^3 , R^4 stand on each occurrence, identically or differently, for:

30

- H, D, F, Cl, Br, I, CHO, CN, $N(Ar)_2$, $C(=O)Ar$, $P(=O)(Ar)_2$, $S(=O)Ar$, $S(=O)_2Ar$, NO_2 , $Si(R)_3$, $B(OR)_2$ or OSO_2R ; or

35

- a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 40 C atoms or branched or a cyclic alkyl, alkoxy or thioalkyl groups having

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- 3 to 40 C atoms, each of which may be substituted by one or more radicals R, where in each case one or more non-adjacent CH₂ groups may be replaced by RC=CR, C≡C, Si(R)₂, Ge(R)₂, Sn(R)₂, C=O, C=S, C=Se, P(=O)(R), SO, SO₂, O, S or CONR and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂; or
- 5 - an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R, or an aryloxy groups having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R; or
- 10 - for a group Ar_L, which may be substituted by one or more radicals R; and where two adjacent substituents R⁰, two adjacent substituents R¹ and R², two adjacent substituents R³ and/or two adjacent substituents R⁴, may form a mono- or polycyclic, aliphatic ring system or aromatic ring
- 15 system, which may be substituted by one or more radicals R;

Ar², Ar³ stand on each occurrence, identically or differently, for an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R;

20

m is an integer selected from 1 to 10;

R stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CHO, CN, N(Ar)₂, C(=O)Ar, P(=O)(Ar)₂, S(=O)Ar, S(=O)₂Ar, NO₂, Si(R')₃, B(OR')₂, OSO₂R', a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 40 C atoms or branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 40 C atoms, each of which may be

25 substituted by one or more radicals R', where in each case one or more non-adjacent CH₂ groups may be replaced by R'C=CR', C≡C, Si(R')₂, Ge(R')₂, Sn(R')₂, C=O, C=S, C=Se, P(=O)(R'), SO, SO₂, O, S or CONR' and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, an aromatic or heteroaromatic ring systems having 5 to 60

30 aromatic ring atoms, which may in each case be substituted by one or

35

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more radicals R', or an aryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R', where two adjacent substituents R may form a mono- or polycyclic, aliphatic ring system or aromatic ring system, which may be substituted by one or more radicals R';

5

Ar is an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, which may in each case also be substituted by one or more radicals R';

10

R' stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms or branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, where in each case one or more non-adjacent CH₂ groups may be replaced by SO, SO₂, O, S and where one or more H atoms may be replaced by D, F, Cl, Br or I, or an aromatic or heteroaromatic ring system having 5 to 24 C atoms;

20

with the proviso that, when the ring A stands for a benzene ring, then the group R¹ or the group R² is selected from an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R.

25

Preferably, when the ring A stands for a benzene ring, then the group R¹ is selected from an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R.

30

Adjacent substituents in the sense of the present invention are substituents which are bonded to atoms which are linked directly to one another or which are bonded to the same atom.

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

5 An aryl group in the sense of this invention contains 6 to 60 aromatic ring atoms, preferably 6 to 40 aromatic ring atoms, more preferably 6 to 20 aromatic ring atoms; a heteroaryl group in the sense of this invention contains 5 to 60 aromatic ring atoms, preferably 5 to 40 aromatic ring atoms, more preferably 5 to 20 aromatic ring atoms, at least one of which is a heteroatom. The heteroatoms are preferably selected from N, O and S.
10 This represents the basic definition. If other preferences are indicated in the description of the present invention, for example with respect to the number of aromatic ring atoms or the heteroatoms present, these apply.

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

25 An aryl or heteroaryl group, which may in each case be substituted by the above-mentioned radicals and which may be linked to the aromatic or heteroaromatic ring system via any desired positions, is taken to mean, in particular, groups derived from benzene, naphthalene, anthracene, phen-
anthrene, pyrene, dihydropyrene, chrysene, perylene, fluoranthene, benz-
30 anthracene, benzophenanthrene, tetracene, pentacene, benzopyrene, furan, benzofuran, isobenzofuran, dibenzofuran, thiophene, benzothio-
phene, isobenzothiophene, dibenzothiophene, pyrrole, indole, isoindole, carbazole, pyridine, quinoline, isoquinoline, acridine, phenanthridine, benzo-
35 5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, phenothiazine,

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phenoxazine, pyrazole, indazole, imidazole, benzimidazole, naphthimi-
dazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalini-
midazole, oxazole, benzoxazole, naphthoxazole, anthroxazole, phenan-
throxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, benzothiazole, pyridazine,
5 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-oxa-
diazole, 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,
10 1,2,3-triazine, tetrazole, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-
tetrazine, purine, pteridine, indolizine and benzothiadiazole.

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

An aromatic ring system in the sense of this invention contains 6 to 60 C
20 atoms in the ring system, preferably 6 to 40 C atoms, more preferably 6 to
20 C atoms. A heteroaromatic ring system in the sense of this invention
contains 5 to 60 aromatic ring atoms, preferably 5 to 40 aromatic ring
atoms, more preferably 5 to 20 aromatic ring atoms, at least one of which is
a heteroatom. The heteroatoms are preferably selected from N, O and/or S.
25 An aromatic or heteroaromatic ring system in the sense of this invention is
intended to be taken to mean a system which does not necessarily contain
only aryl or heteroaryl groups, but instead in which, in addition, a plurality of
aryl or heteroaryl groups may be connected by a non-aromatic unit
30 (preferably less than 10% of the atoms other than H), such as, for example,
an sp³-hybridised C, Si, N or O atom, an sp²-hybridised C or N atom or an
sp-hybridised C atom. Thus, for example, systems such as 9,9'-spirobifluo-
rene, 9,9'-diarylfuorene, triarylamine, diaryl ether, stilbene, etc., are also
35 intended to be taken to be aromatic ring systems in the sense of this inven-
tion, as are systems in which two or more aryl groups are connected, for

- 10 -

example, by a linear or cyclic alkyl, alkenyl or alkynyl group or by a silyl group. Furthermore, systems in which two or more aryl or heteroaryl groups are linked to one another via single bonds are also taken to be aromatic or heteroaromatic ring systems in the sense of this invention, such as, for
5 example, systems such as biphenyl, terphenyl or diphenyltriazine.

An aromatic or heteroaromatic ring system having 5 - 60 aromatic ring atoms, which may in each case also be substituted by radicals as defined above and which may be linked to the aromatic or heteroaromatic group via
10 any desired positions, is taken to mean, in particular, groups derived from benzene, naphthalene, anthracene, benzanthracene, phenanthrene, benzophenanthrene, pyrene, chrysene, perylene, fluoranthene, naphthacene, pentacene, benzopyrene, biphenyl, biphenylene, terphenyl, terphenylene, quaterphenyl, fluorene, spirobifluorene, dihydrophenanthrene, dihydro-
15 pyrene, tetrahydropyrene, cis- or trans-indenofluorene, truxene, isotruxene, spirotruxene, spiroisotruxene, furan, benzofuran, isobenzofuran, dibenzofuran, thiophene, benzothiophene, isobenzothiophene, dibenzothiophene, pyrrole, indole, isoindole, carbazole, indolocarbazole, indenocarbazole, pyridine, quinoline, isoquinoline, acridine, phenanthridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, phenothiazine, phenoxazine, pyrazole, indazole, imidazole, benzimidazole, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, oxazole,
20 benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, benzothiazole, pyridazine, benzopyridazine, pyrimidine, benzopyrimidine, quinoxaline, 1,5-diazaanthracene, 2,7-diazapyrene, 2,3-diazapyrene, 1,6-diazapyrene, 1,8-diazapyrene, 4,5-diazapyrene, 4,5,9,10-tetraazaperylene, pyrazine, phenazine, phenoxazine, phenothiazine, fluorubin, naphthyridine, azacarbazole, benzocarboline, phenanthroline, 1,2,3-triazole, 1,2,4-triazole, benzotriazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, tetrazole, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine,
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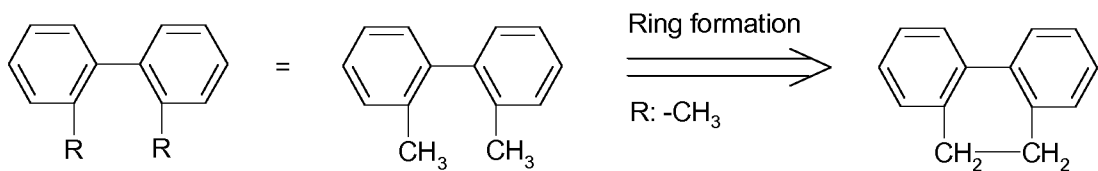
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1,2,3,5-tetrazine, purine, pteridine, indolizine and benzothiadiazole, or combinations of these groups.

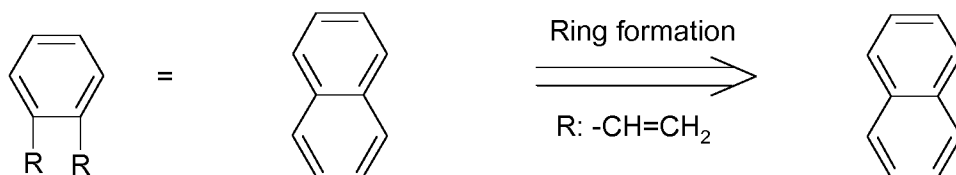
For the purposes of the present invention, a straight-chain alkyl group
5 having 1 to 40 C atoms or a branched or cyclic alkyl group having 3 to 40 C
atoms or an alkenyl or alkynyl group having 2 to 40 C atoms, in which, in
addition, individual H atoms or CH₂ groups may be substituted by the
groups mentioned above under the definition of the radicals, is preferably
taken to mean the radicals methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl,
10 s-butyl, t-butyl, 2-methylbutyl, n-pentyl, s-pentyl, cyclopentyl, neopentyl,
n-hexyl, cyclohexyl, neohexyl, n-heptyl, cycloheptyl, n-octyl, cyclooctyl,
2-ethylhexyl, trifluoromethyl, pentafluoroethyl, 2,2,2-trifluoroethyl, ethenyl,
propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl,
15 cycloheptenyl, octenyl, cyclooctenyl, ethynyl, propynyl, butynyl, pentynyl,
hexynyl or octynyl. An alkoxy or thioalkyl group having 1 to 40 C atoms is
preferably taken to mean methoxy, trifluoromethoxy, ethoxy, n-propoxy,
i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy, n-pentoxy, s-pentoxy,
20 2-methylbutoxy, n-hexoxy, cyclohexyloxy, n-heptoxy, cycloheptyloxy,
n-octyloxy, cyclooctyloxy, 2-ethylhexyloxy, pentafluoroethoxy, 2,2,2-tri-
fluoroethoxy, 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,
25 2-ethylhexylthio, trifluoromethylthio, pentafluoroethylthio, 2,2,2-trifluoroethyl-
thio, ethenylthio, propenylthio, butenylthio, pentenylthio, cyclopentenylthio,
hexenylthio, cyclohexenylthio, heptenylthio, cycloheptenylthio, octenylthio,
cyclooctenylthio, ethynylthio, propynylthio, butynylthio, pentynylthio,
30 hexynylthio, heptylthio or octynylthio.

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

- 12 -



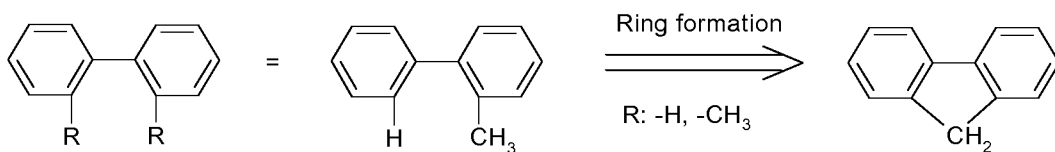
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Furthermore, however, the above-mentioned formulation is also intended to be taken to mean that, in the case where one of the two radicals represents hydrogen, the second radical is bonded at the position to which the hydrogen atom was bonded, with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

15



20

In accordance with a preferred embodiment, the ring A is selected from the group consisting of phenyl, naphthyl, anthracene, phenanthrene, fluorene, dibenzothiophene, dibenzofurane or carbazole, which may in each case be substituted by one or more radicals R³.

25

Preferably, Ar¹ stands for:

- an aromatic or heteroaromatic ring system having 5 to 40, preferably 5 to 30, more preferably 5 to 30, particularly preferably 6 to 30 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R⁴;
- a group of formula (Ar1-1) as depicted above; or
- a group ArL.

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Very preferably, Ar¹ stands for:

- phenyl, biphenyl, fluorene, spirobifluorene, naphthalene, phenanthrene, dibenzofuran, dibenzothiophene, carbazole, pyridine, pyrimidine, pyrazine, pyridazine, triazine, benzopyridine, benzopyridazine, benzopyrimidine or quinazoline, or a combination of two or three of these groups, each of which may be substituted by one or more radicals R⁴;
- a group of formula (Ar1-1) as depicted above; or
- a group ArL.

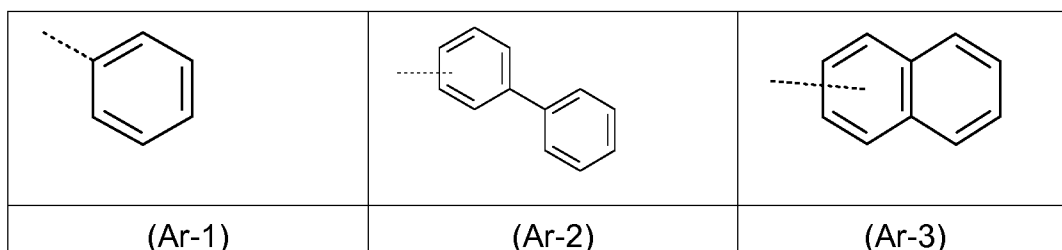
Particularly preferably, Ar¹ stands for:

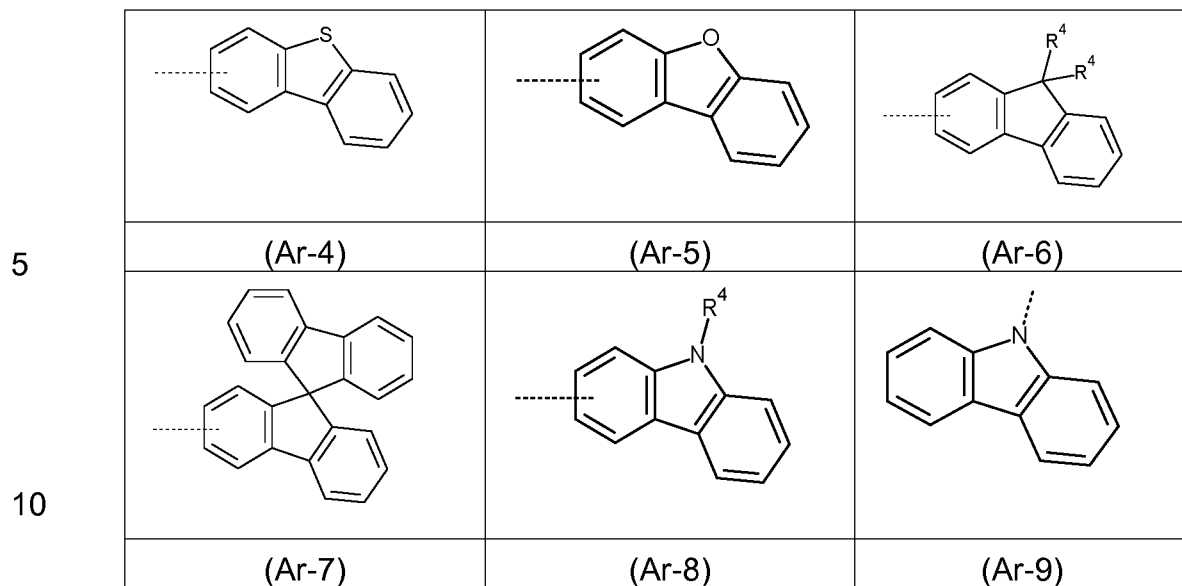
- phenyl, biphenyl, fluorene, spirobifluorene, naphthalene, phenanthrene, dibenzofuran, dibenzothiophene, carbazole or a combination of two or three of these groups, each of which may be substituted by one or more radicals R⁴;
- a group of formula (Ar1-1) as depicted above; or
- a group ArL.

Very particularly preferably, Ar¹ stands for:

- an aromatic or heteroaromatic ring system of one of the formulae (Ar-1) to (Ar-9) as depicted below;
- a group of formula (Ar1-1) as depicted above; or
- a group ArL.

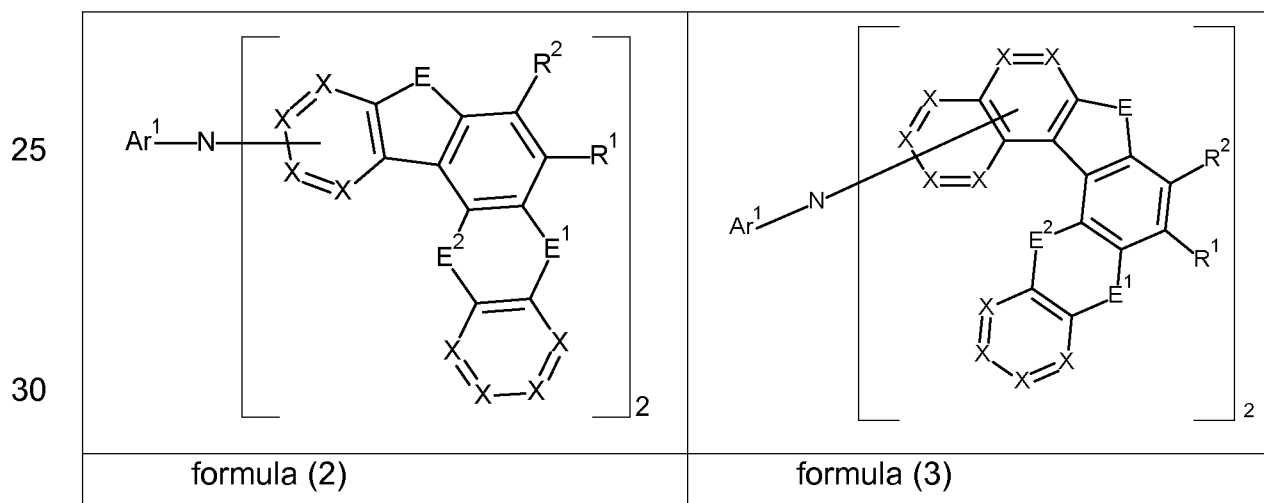
Structure of the aromatic or heteroaromatic ring systems of formulae (Ar-1) to (Ar-9) are represented in the table below:



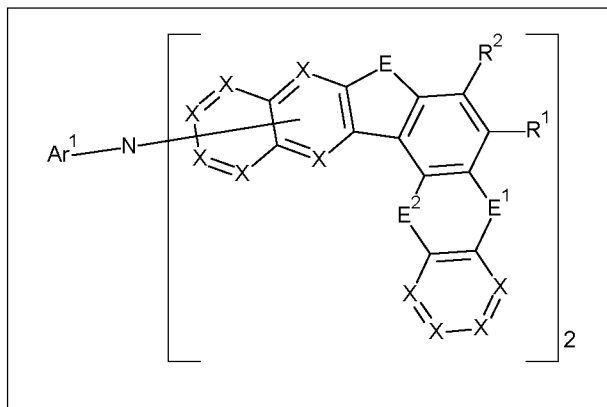


In formulae (Ar-1) to (Ar-9), the dashed bond indicates the bonding to the nitrogen of the structure of formula (1); and the groups of formulae (Ar-1) to (Ar-9) may be substituted at each free position by a group R⁴, which has the same meaning as above.

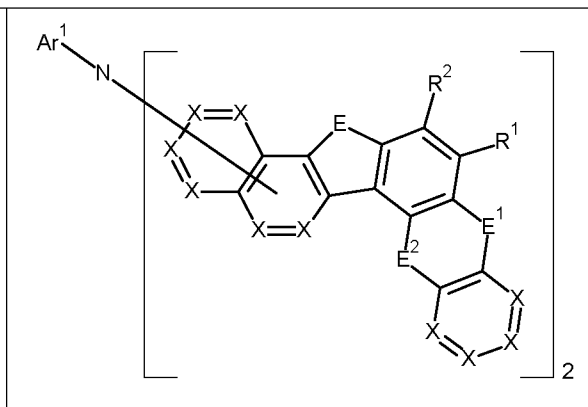
Preferably, the compounds of formula (1) are selected from the compounds of formulae (2) to (41),



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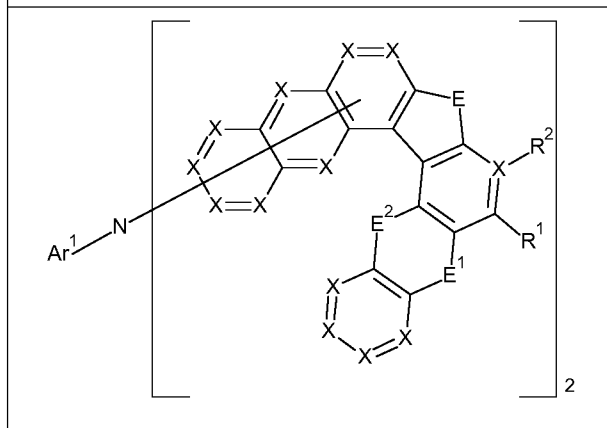


formula (4)

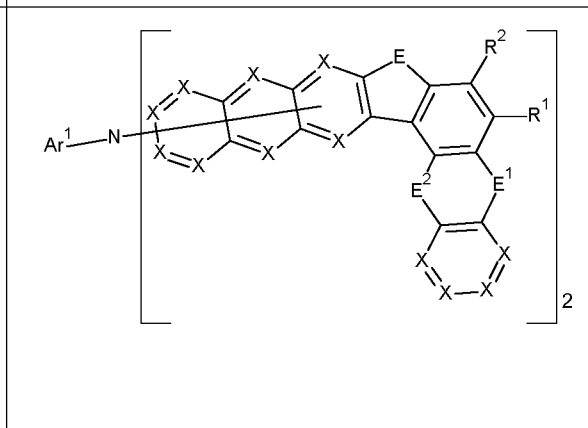


formula (5)

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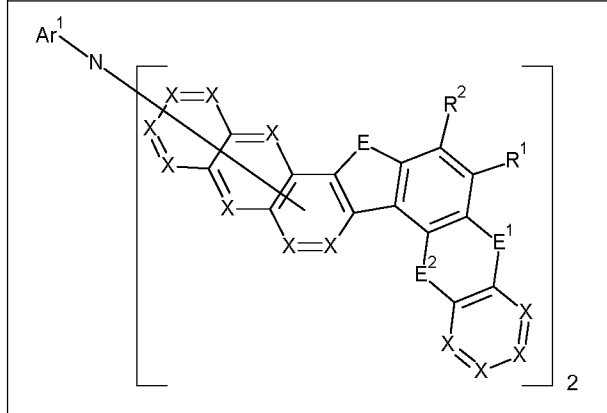


formula (6)

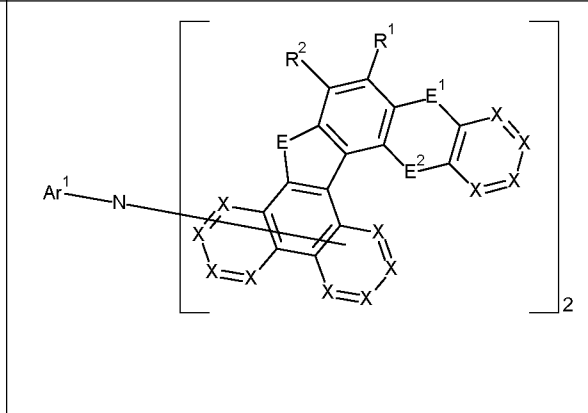


formula (7)

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formula (8)

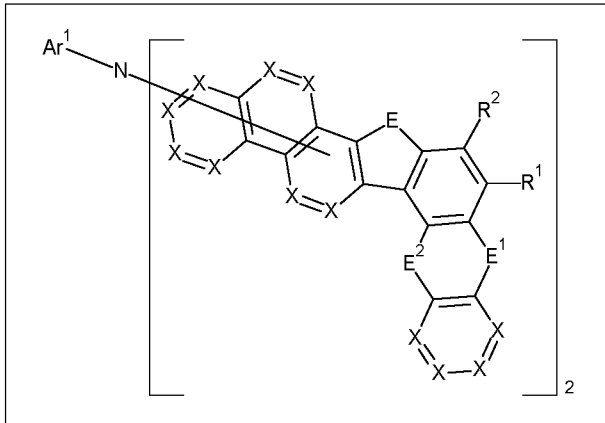


formula (9)

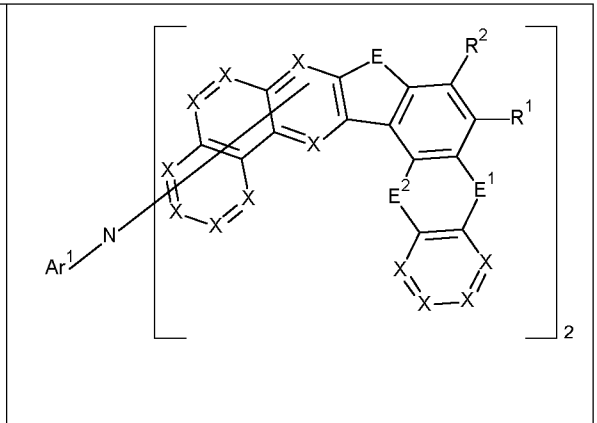
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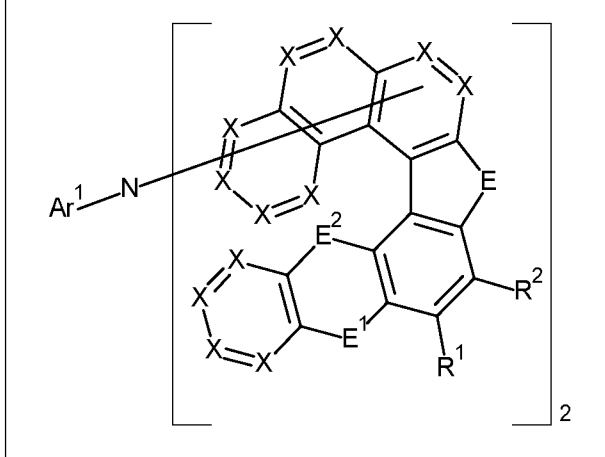


formula (10)

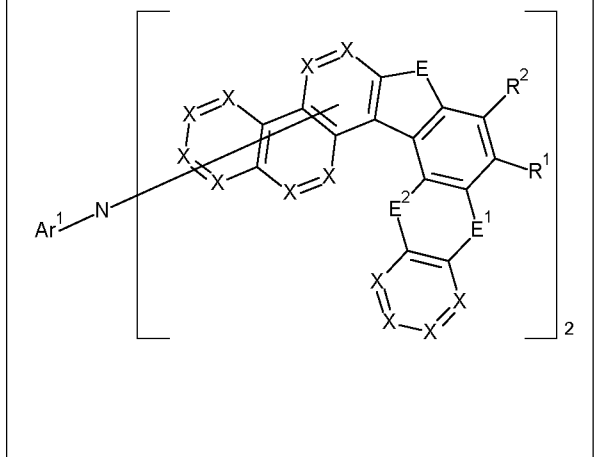


formula (11)

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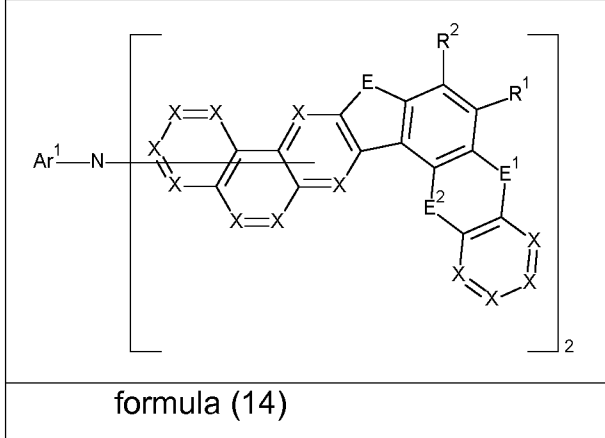


formula (12)

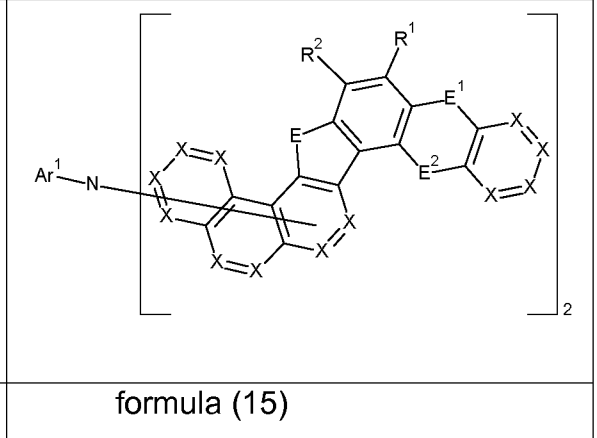


formula (13)

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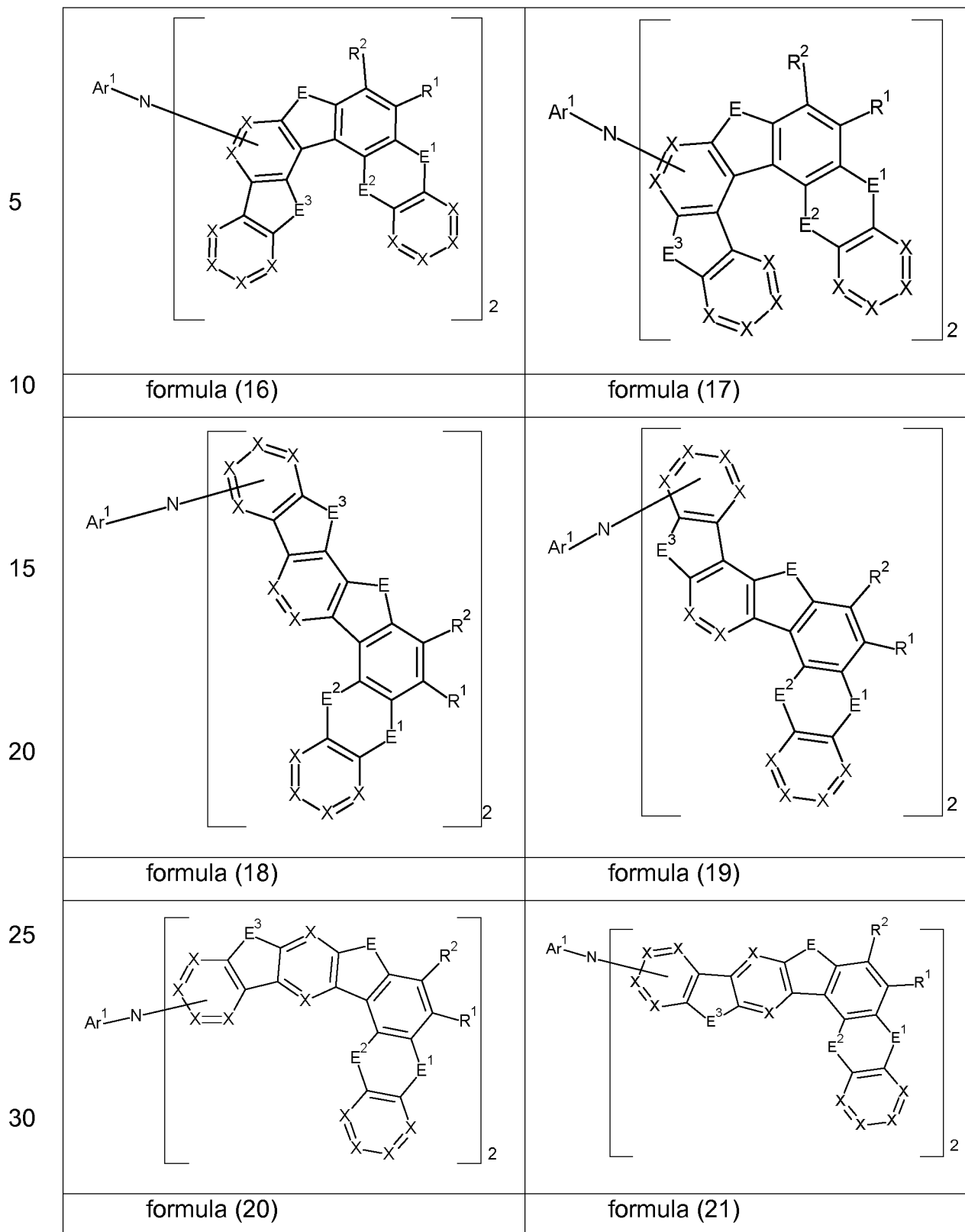
formula (14)

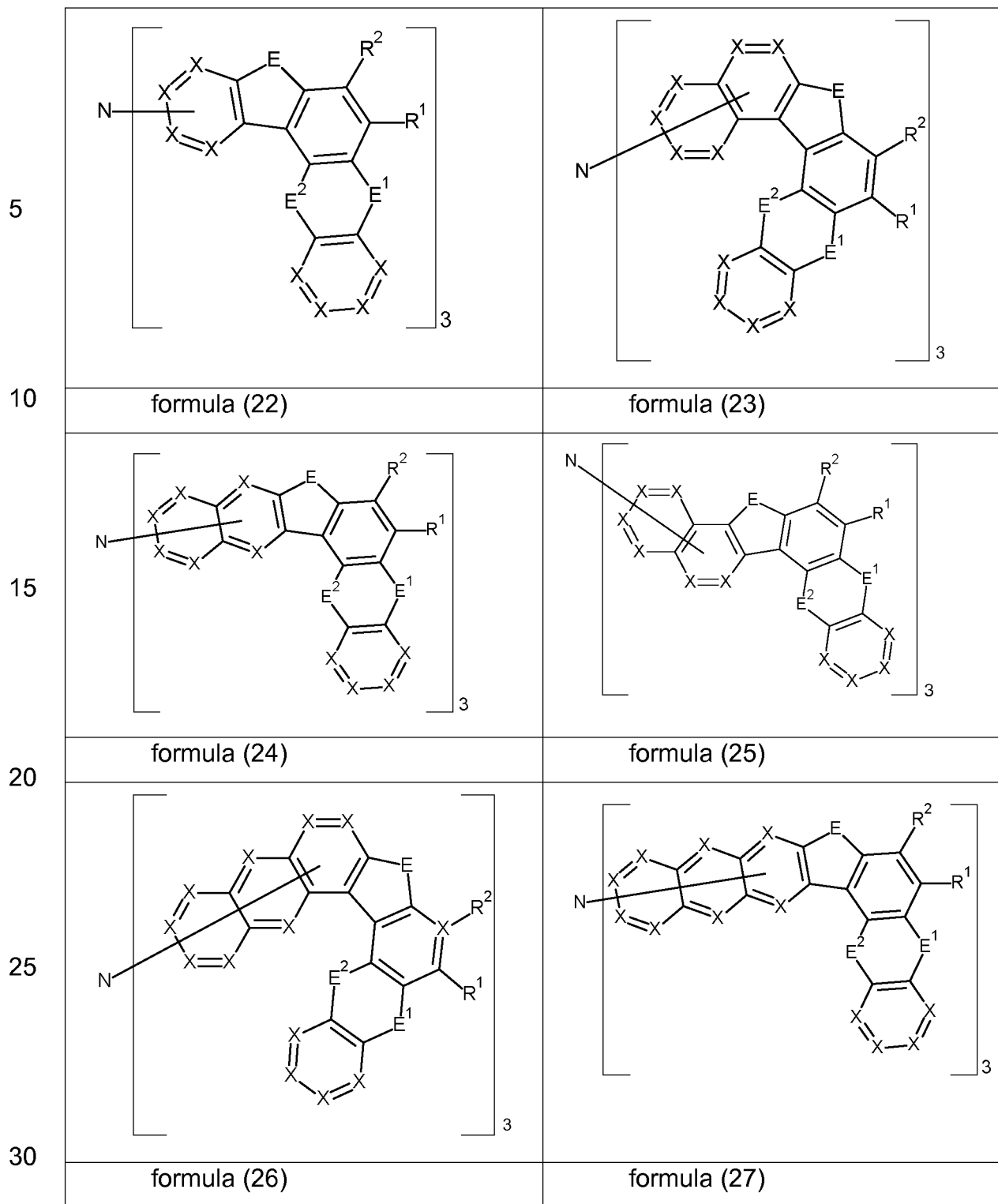


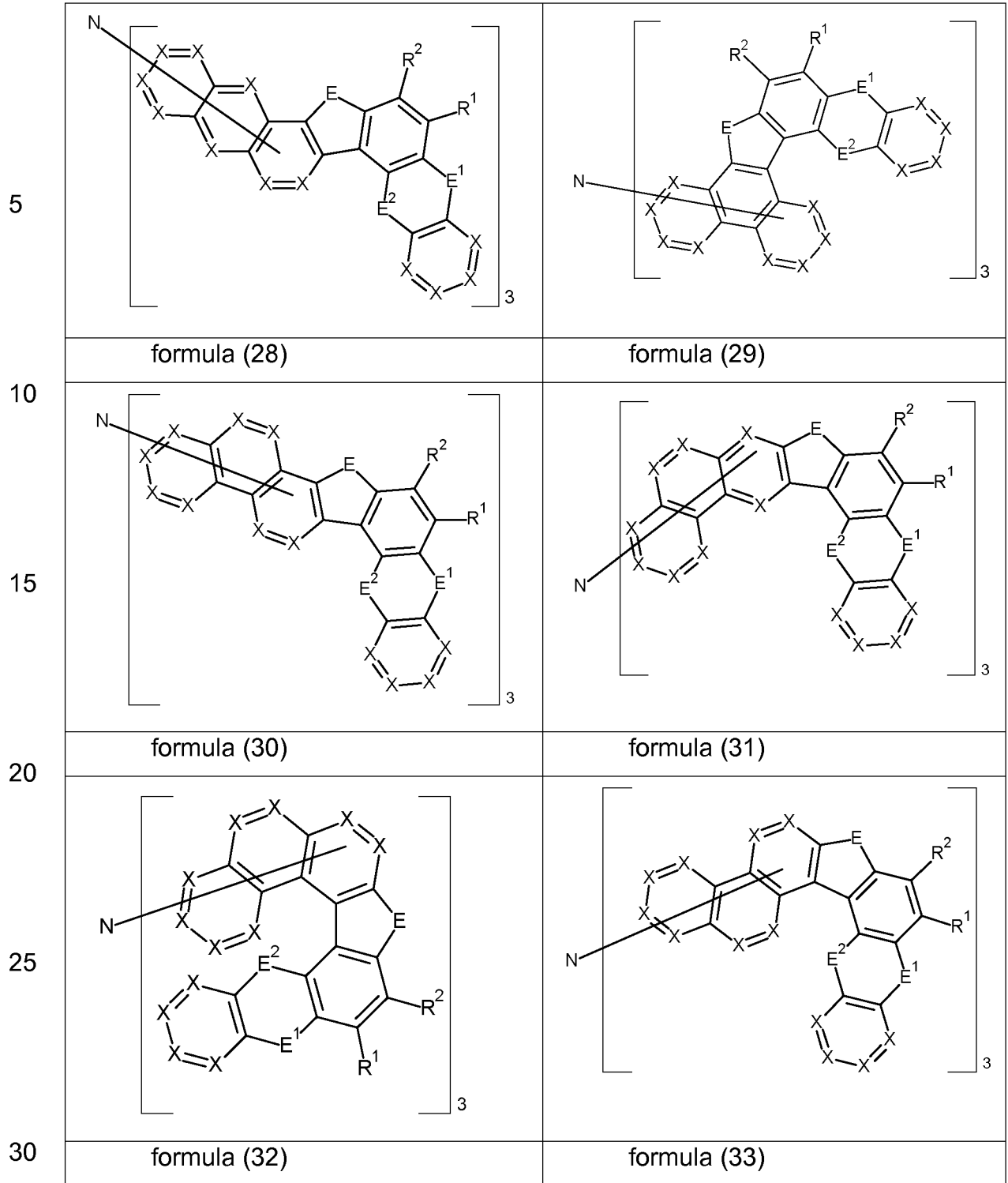
formula (15)

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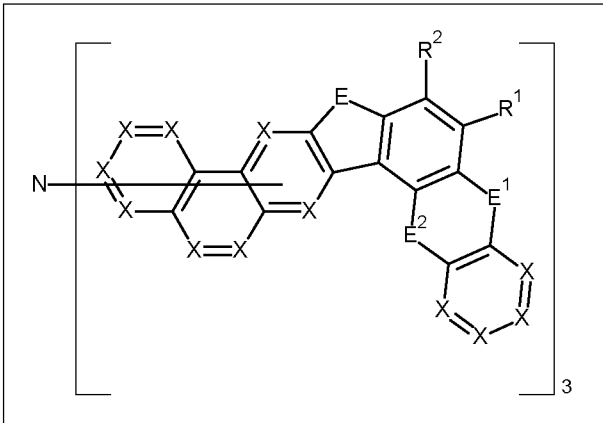
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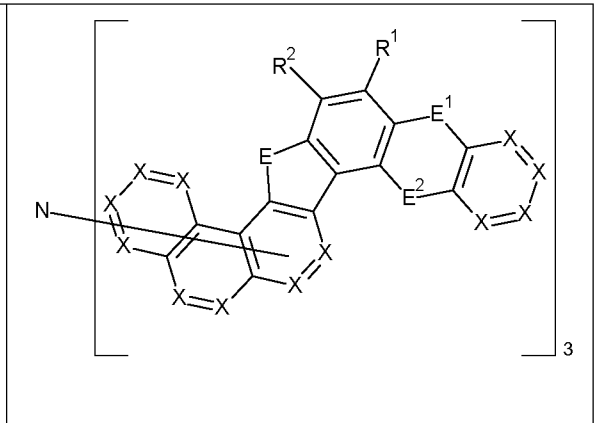




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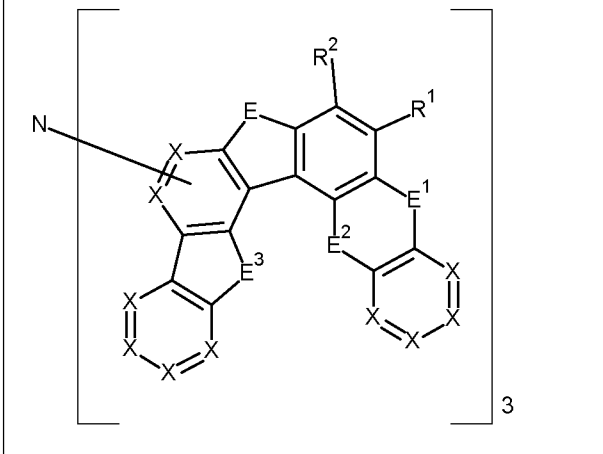


formula (34)

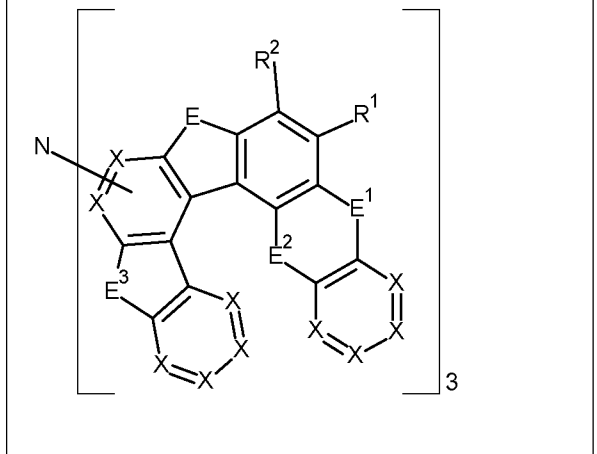


formula (35)

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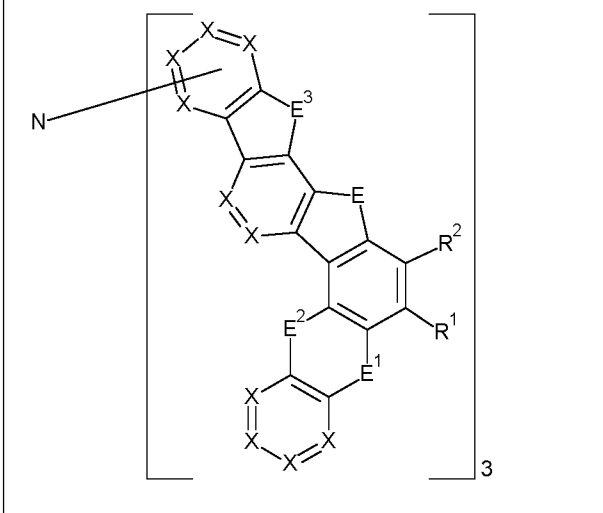


formula (36)

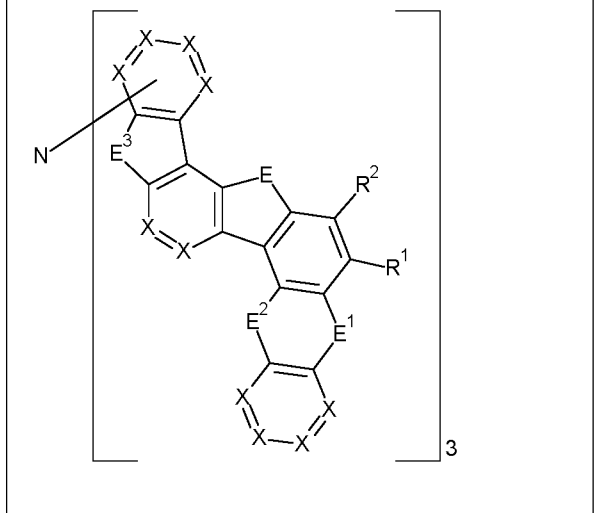


formula (37)

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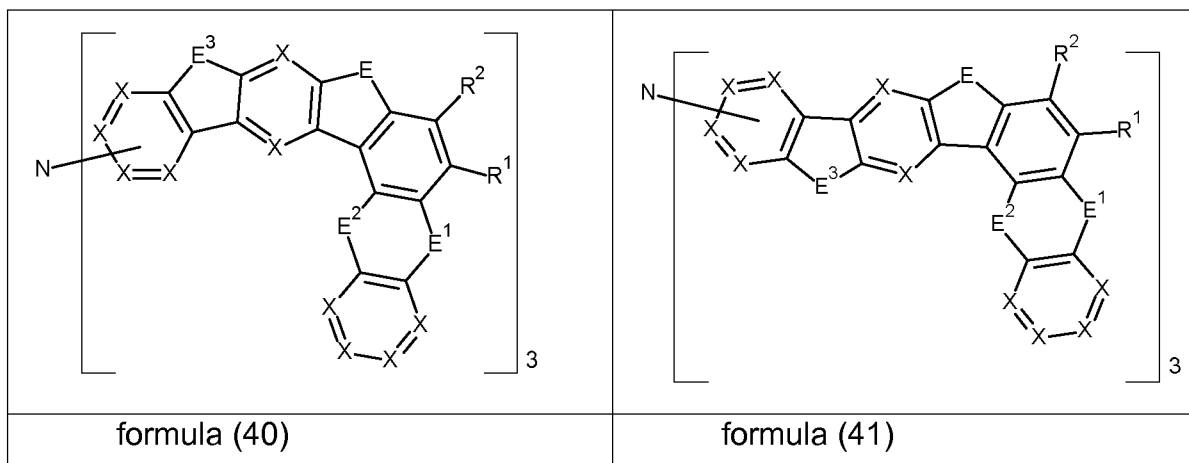


formula (38)



formula (39)

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where the symbols Ar¹, E, E¹, E², R¹ and R² have the same meaning as above; and where

15

X is CR² or N; or X stands for C if a group -NAr¹ is bonded to X; and

E³ is on each occurrence, identically or differently, selected from -C(R⁰)₂-, -O-, -S- or -N(R⁰)-; wherein R⁰ has the same meaning as above.

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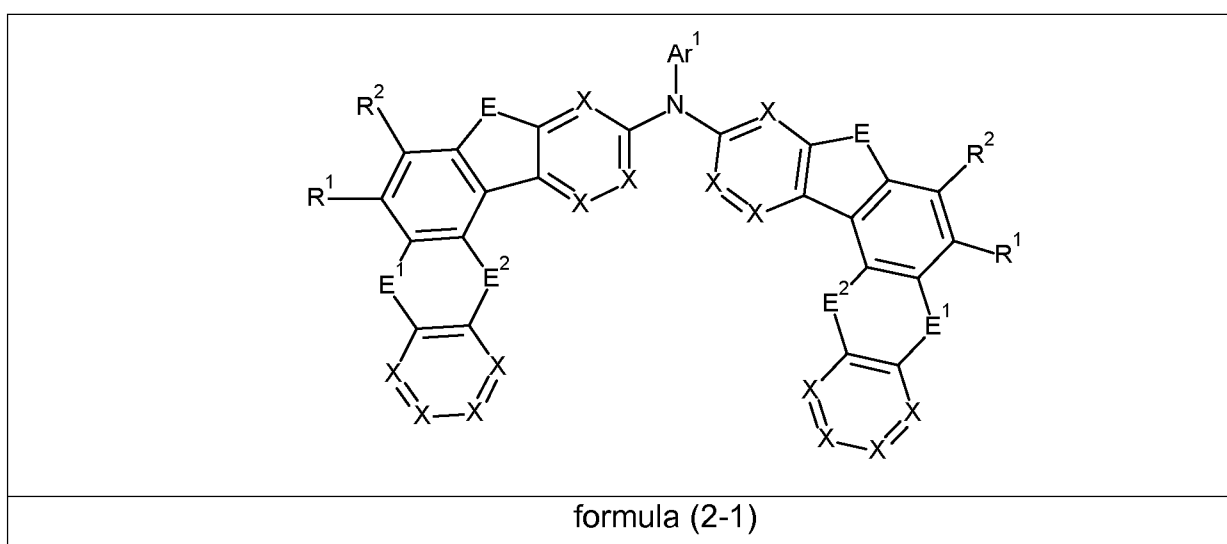
Preferably, E³ stands for -C(R⁰)₂-.

Very preferably, the compounds of formula (1) are selected from the compounds of formulae (2-1) to (41-1),

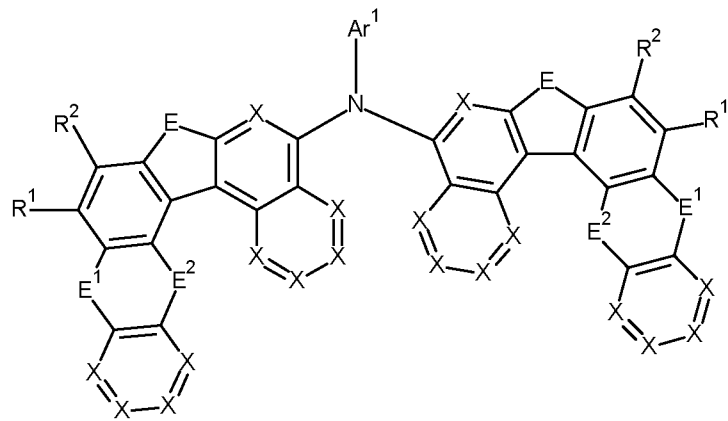
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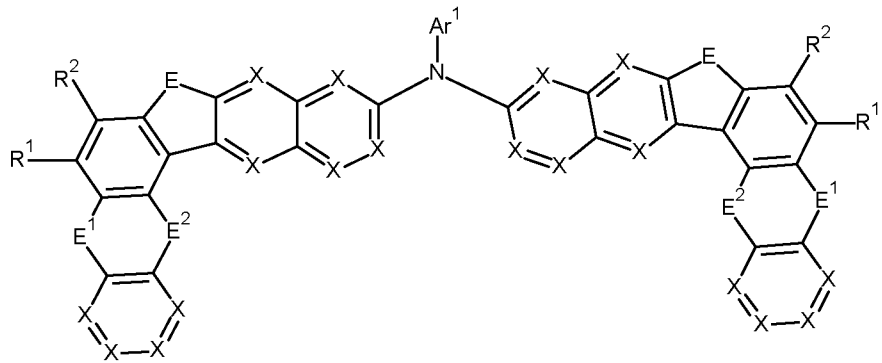
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formula (3-1)

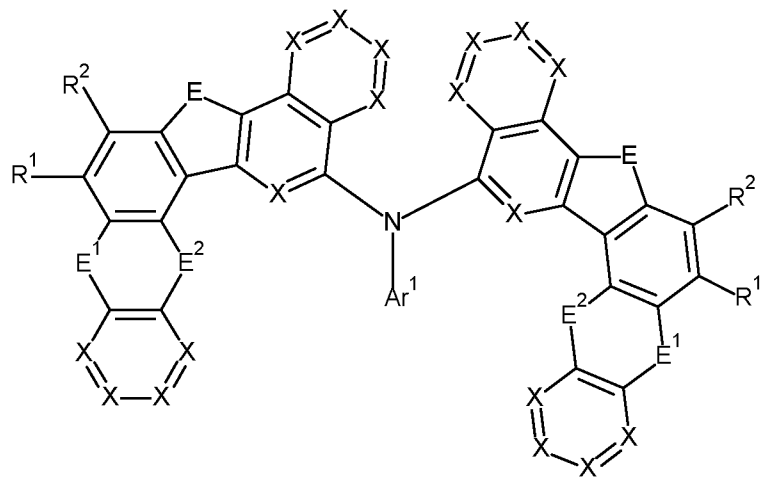
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formula (4-1)

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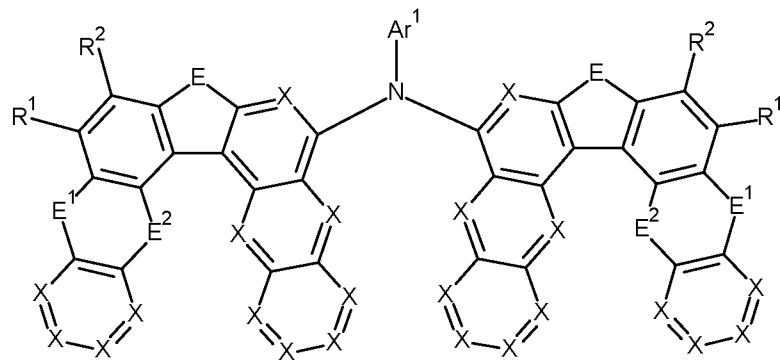


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formula (5-1)

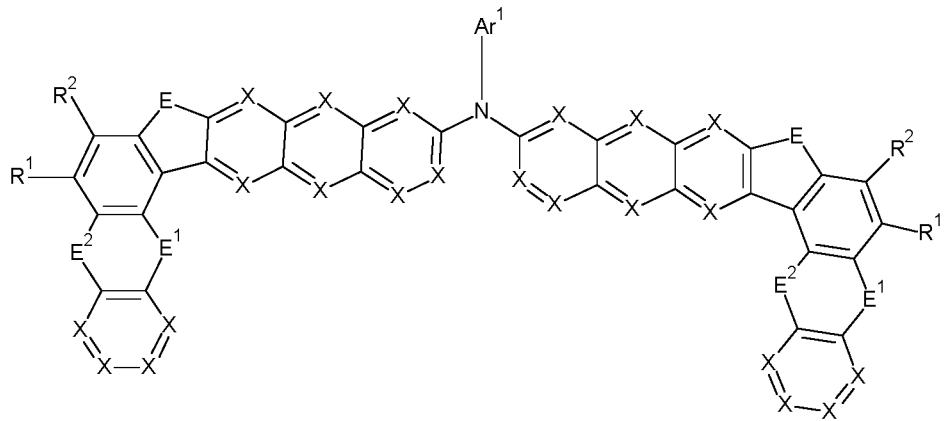
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formula (6-1)

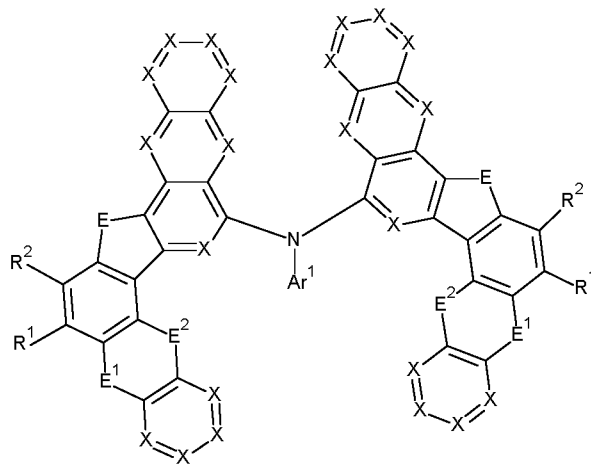
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formula (7-1)

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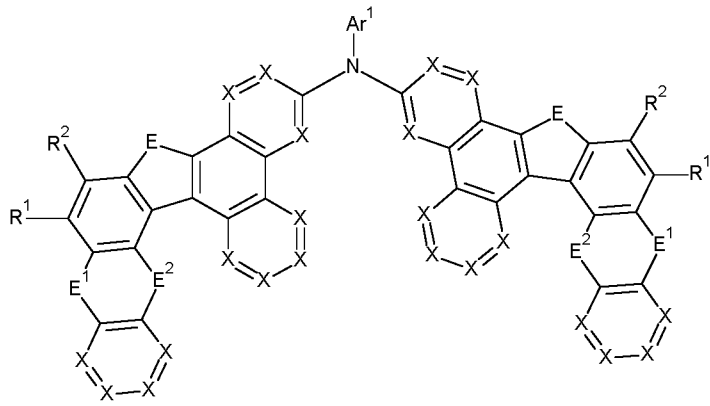
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formula (8-1)

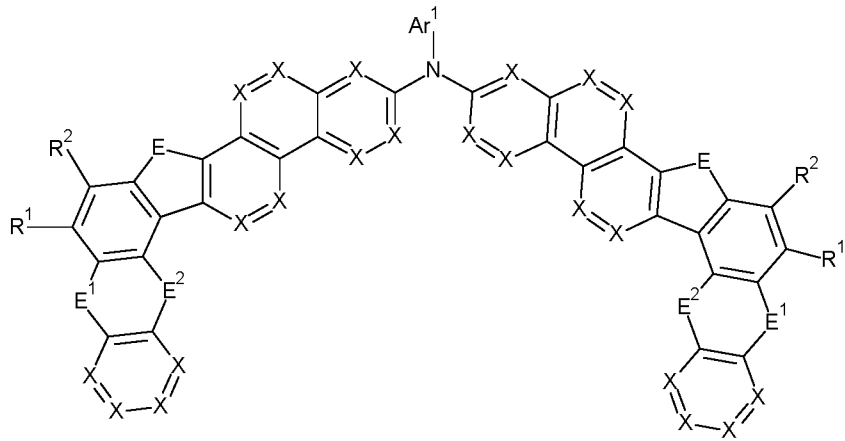
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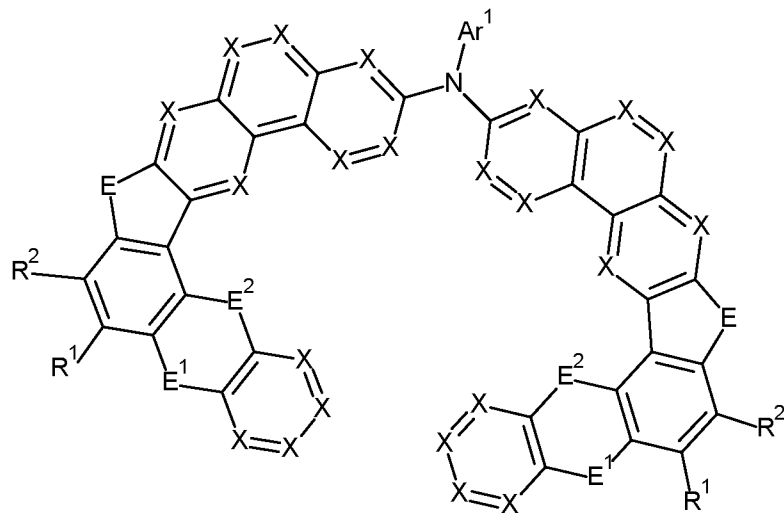
formula (9-1)

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formula (10-1)

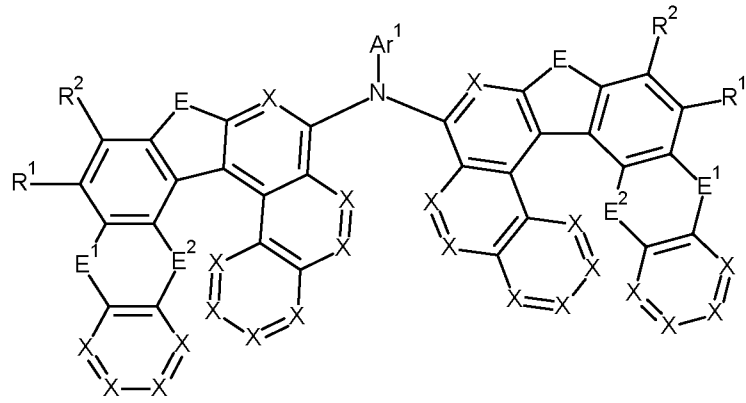
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formula (11-1)

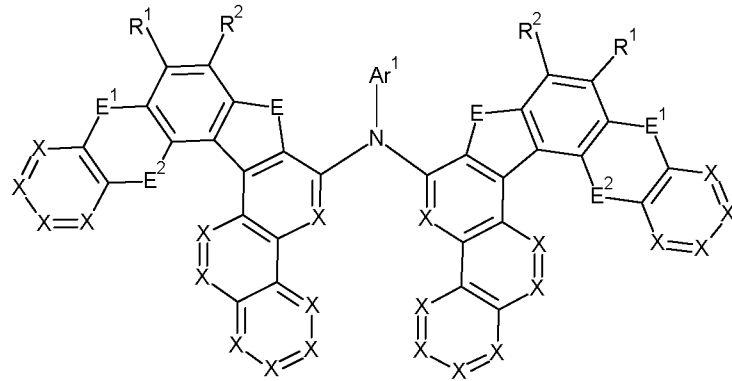
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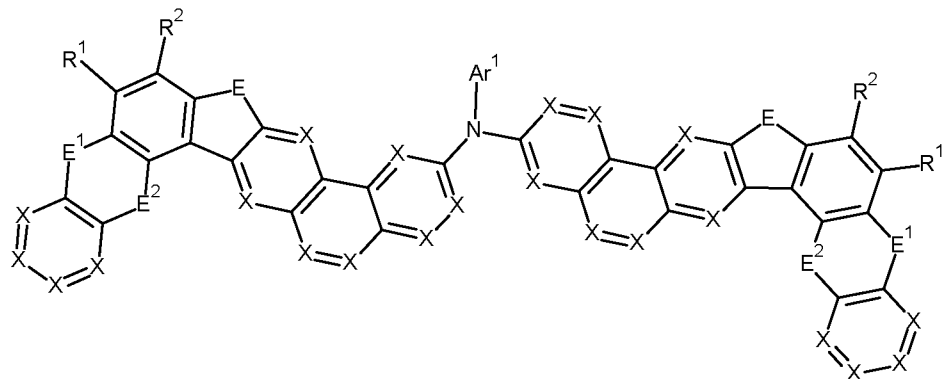
formula (12-1)

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formula (13-1)

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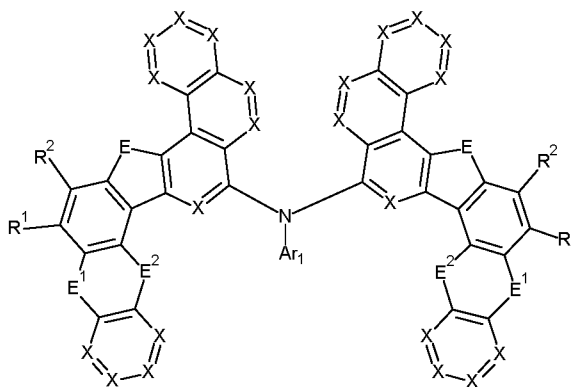


formula (14-1)

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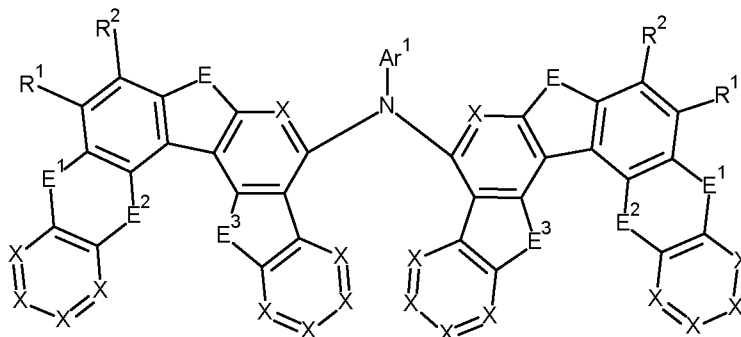
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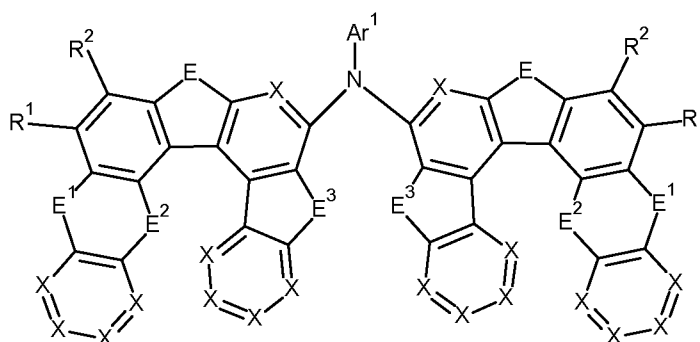
formula (15-1)

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formula (16-1)

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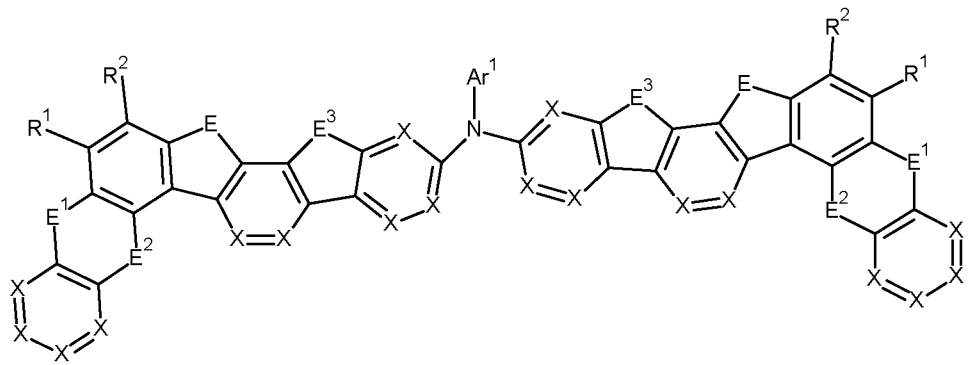


formula (17-1)

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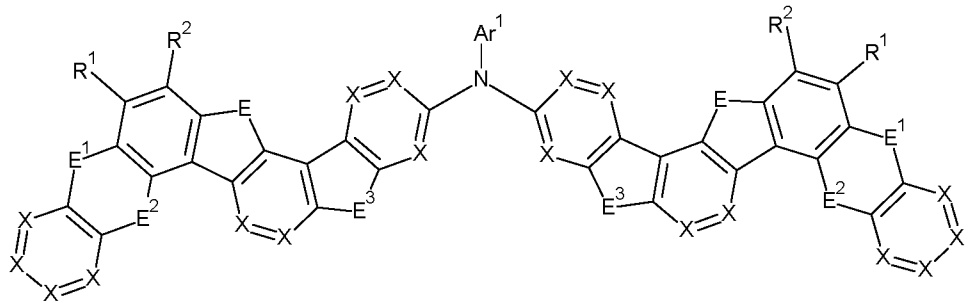
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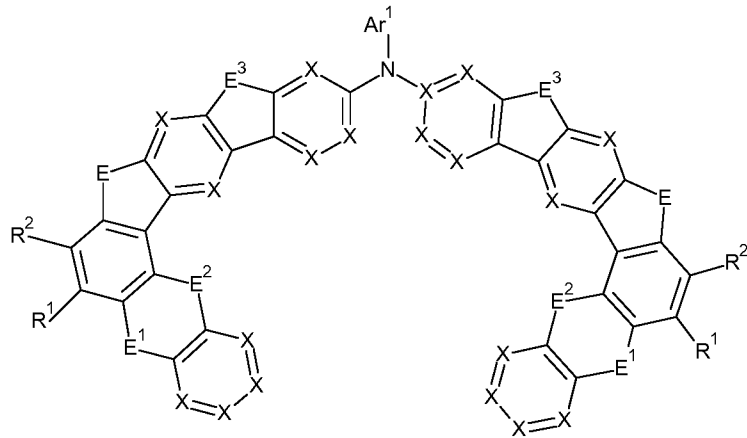
formula (18-1)

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formula (19-1)

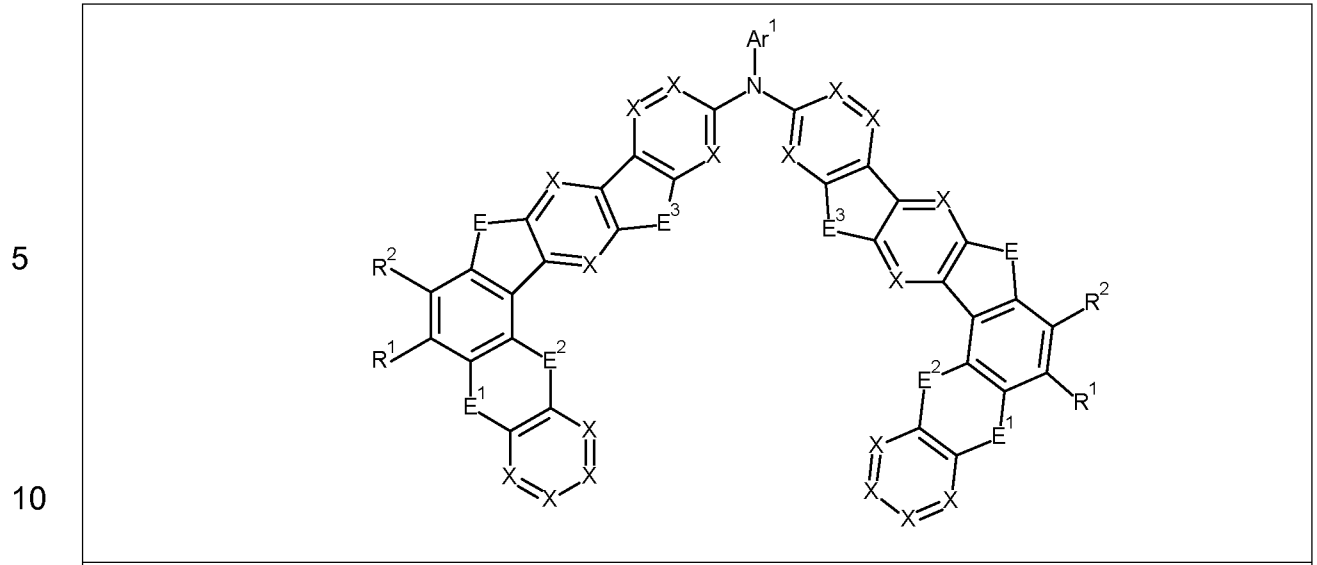
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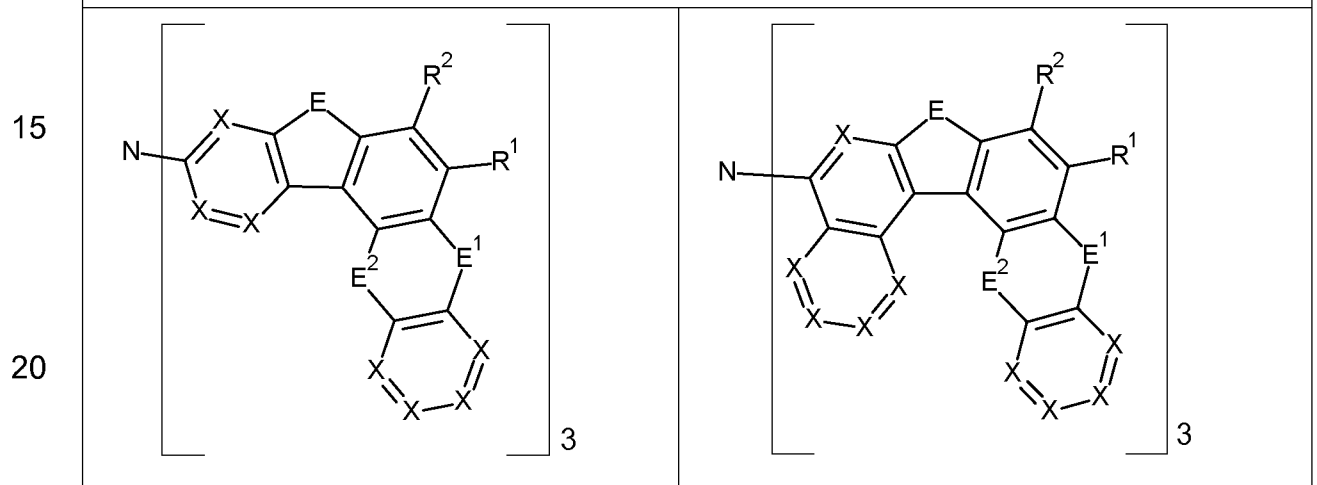
formula (20-1)

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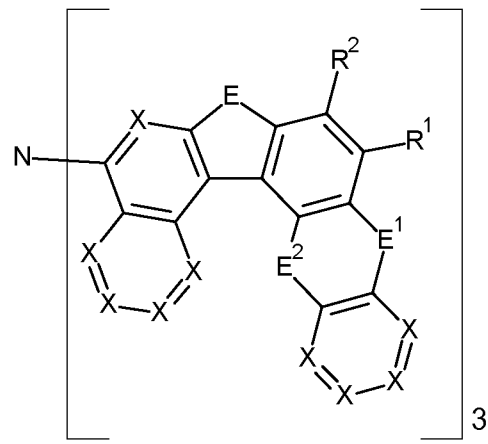
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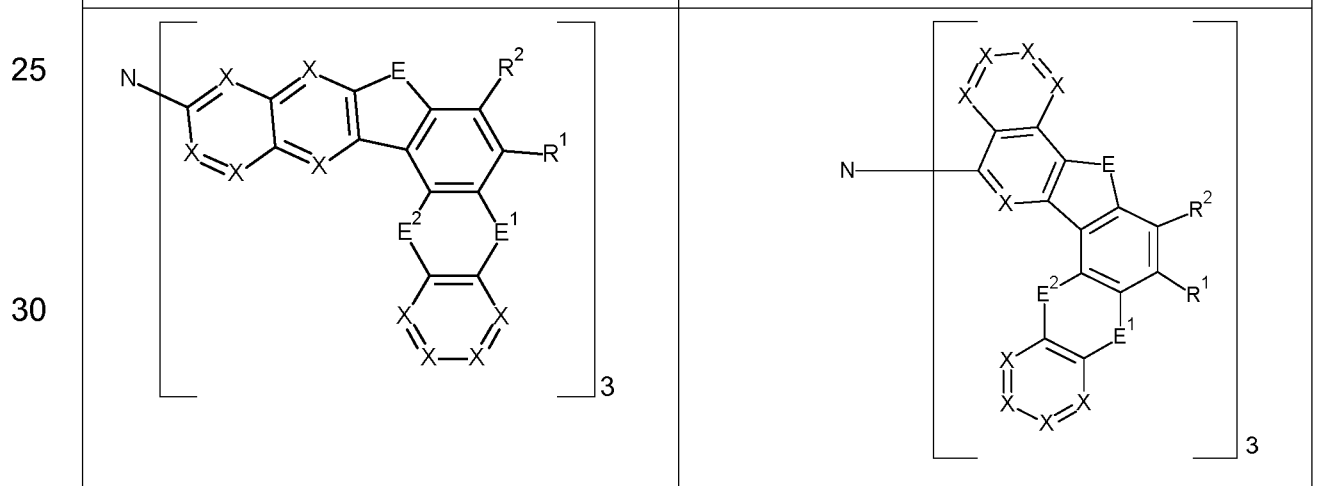
formula (21-1)



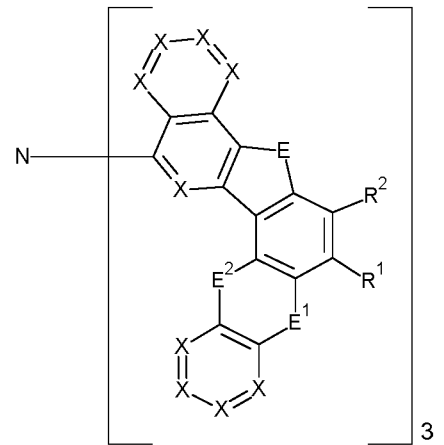
formula (22-1)



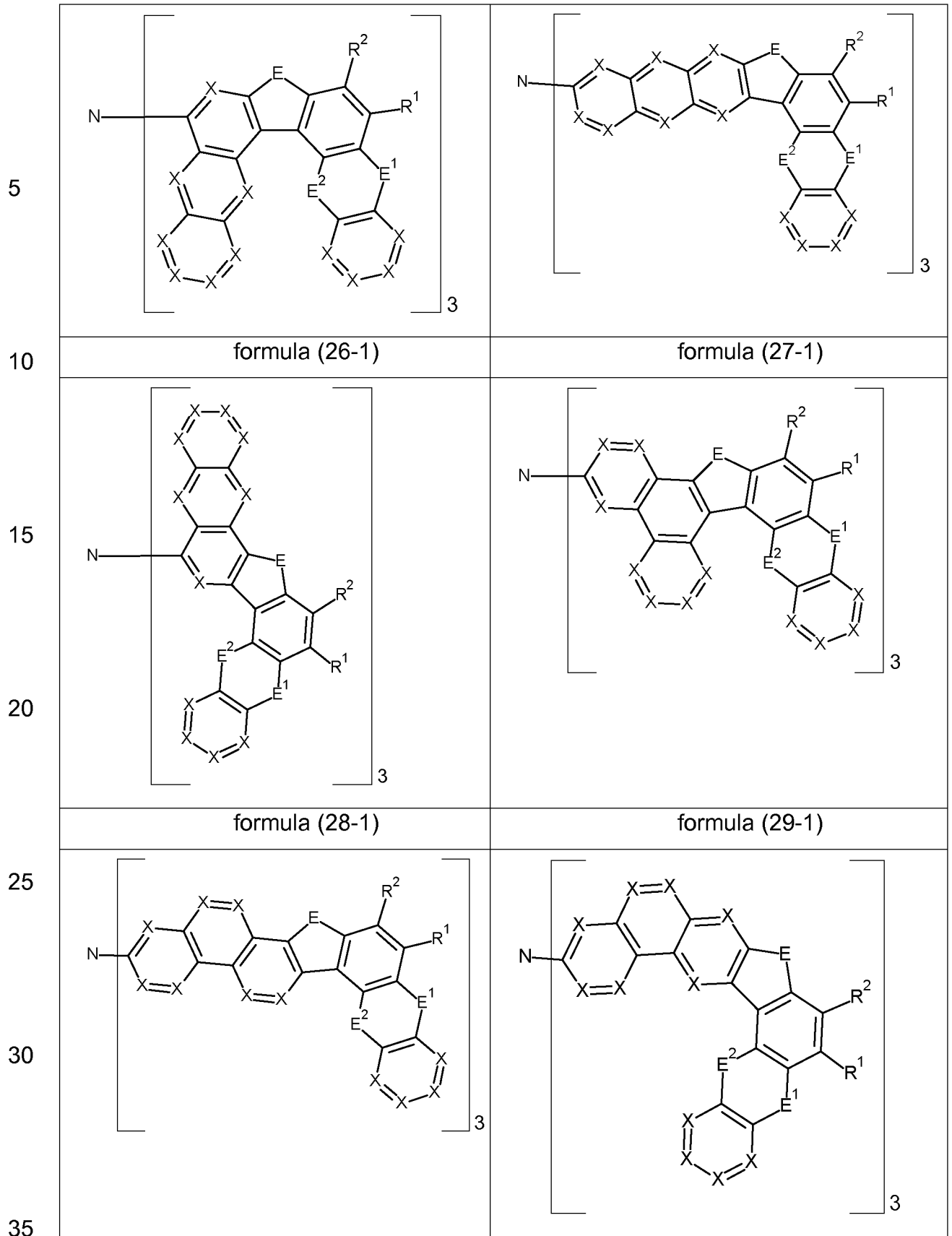
formula (23-1)

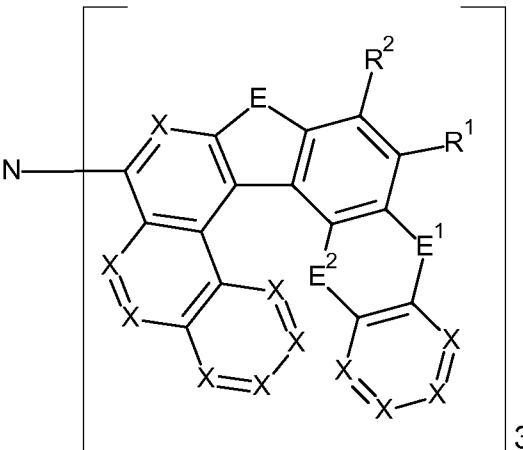
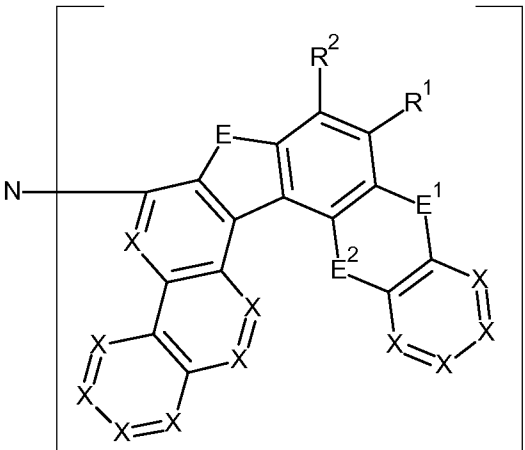
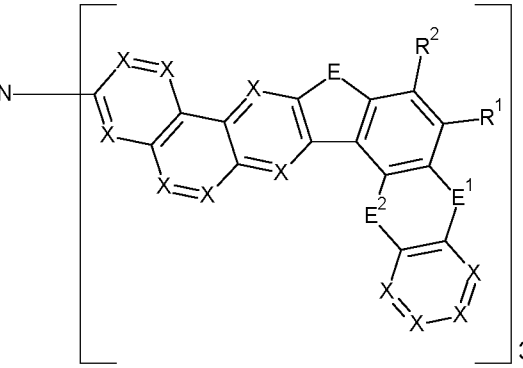
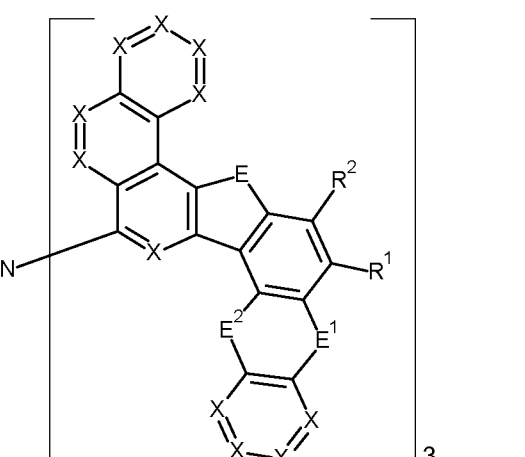
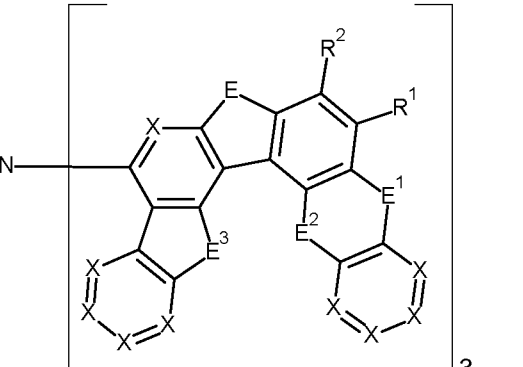
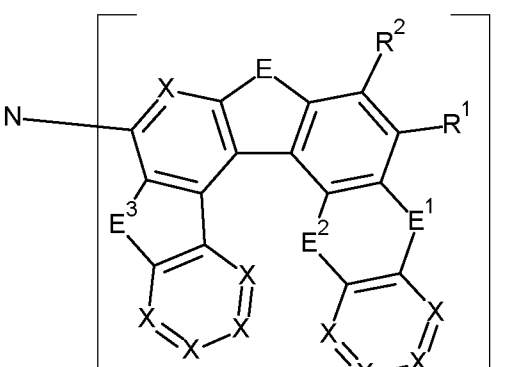


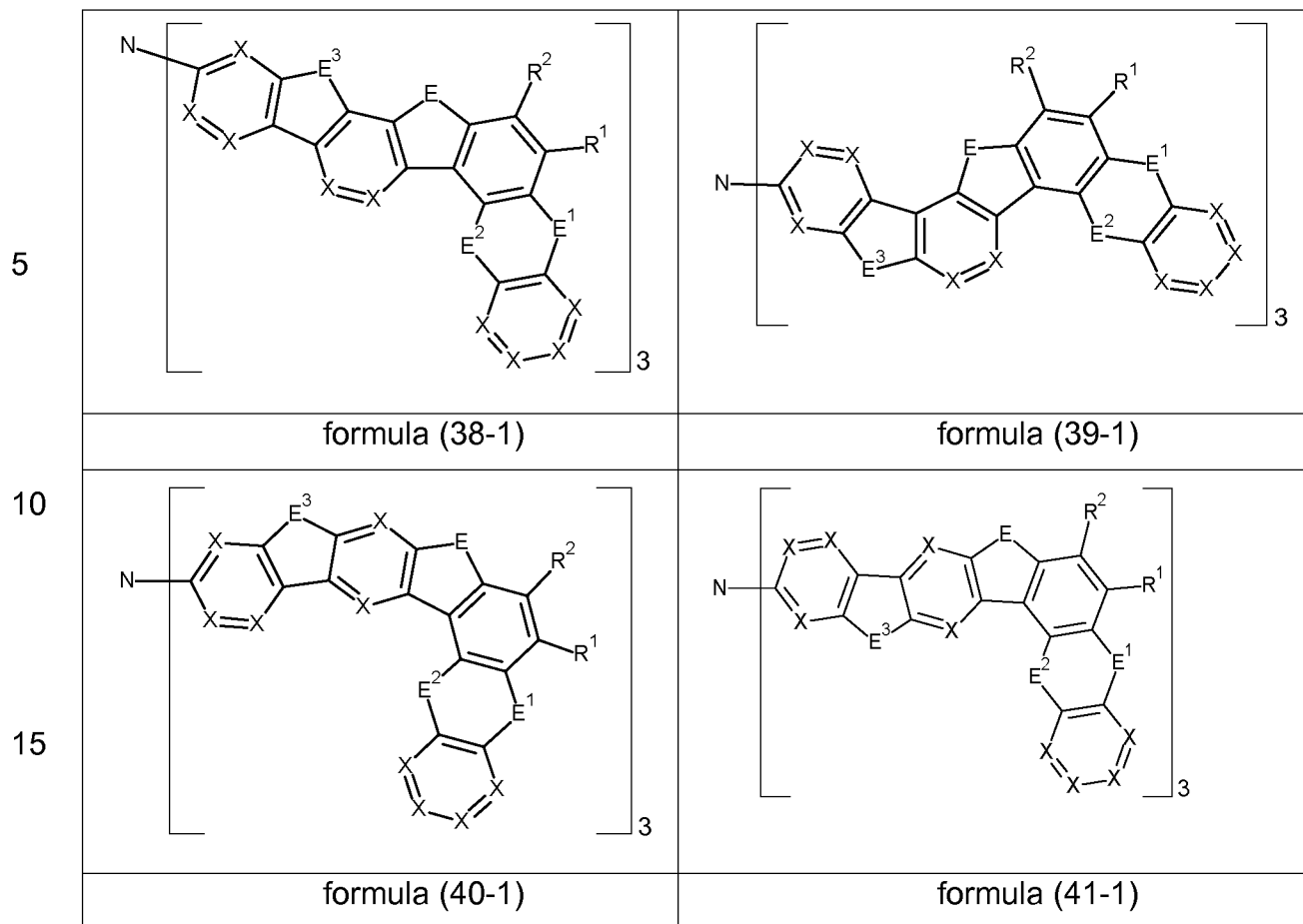
formula (24-1)



formula (25-1)

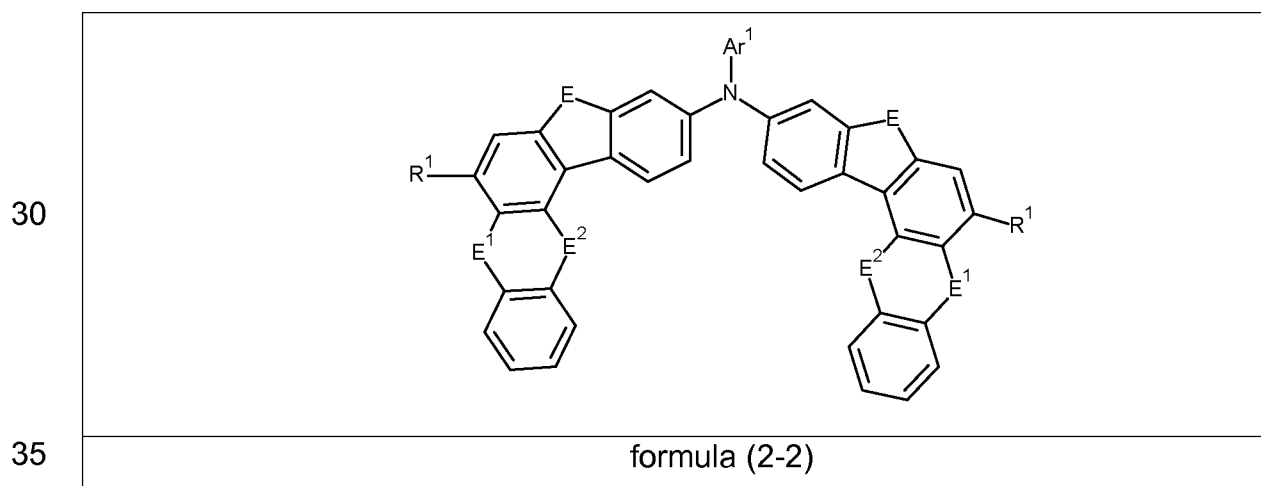


<p>5</p> <p>10</p>	<p>formula (30-1)</p> 	<p>formula (31-1)</p> 
<p>15</p> <p>20</p>	<p>formula (32-1)</p> 	<p>formula (33-1)</p> 
<p>25</p> <p>30</p>	<p>formula (34-1)</p> 	<p>formula (35-1)</p> 
<p>35</p>	<p>formula (36-1)</p>	<p>formula (37-1)</p>

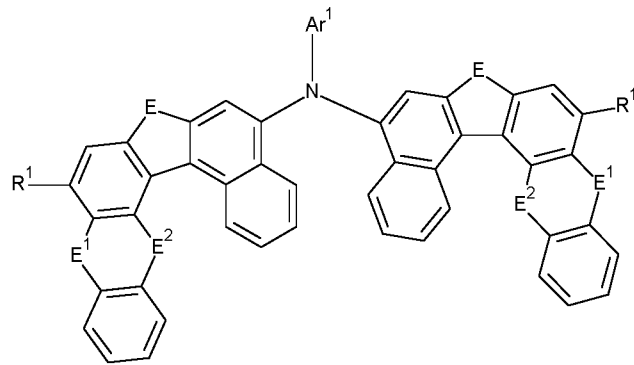


20 where the symbols X, Ar¹, E, E¹, E², E³, R¹ and R² have the same meaning as above.

Particularly preferably, the compounds of formula (1) are selected from the
 25 compounds of formulae (2-2) to (41-2),

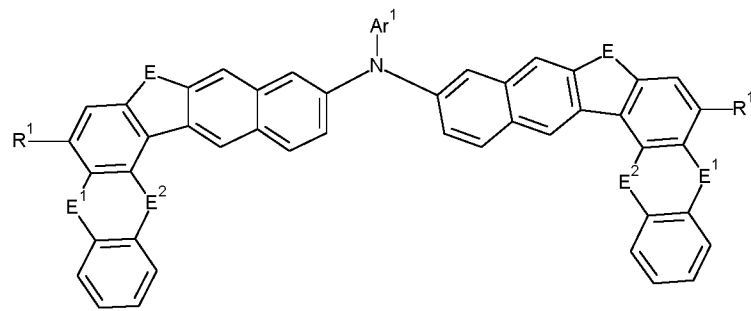


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formula (3-2)

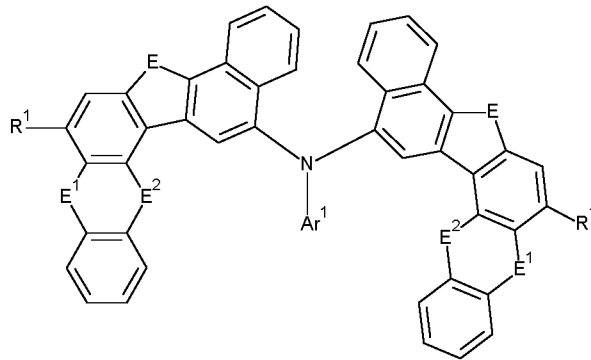
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formula (4-2)

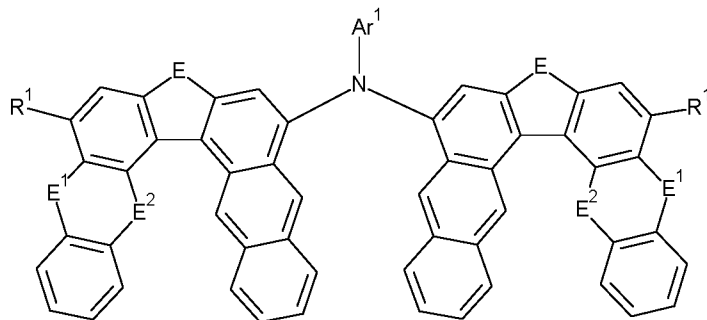
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formula (5-2)

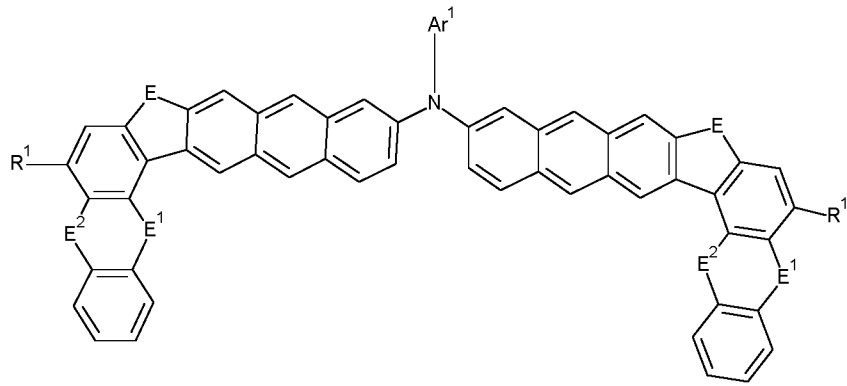
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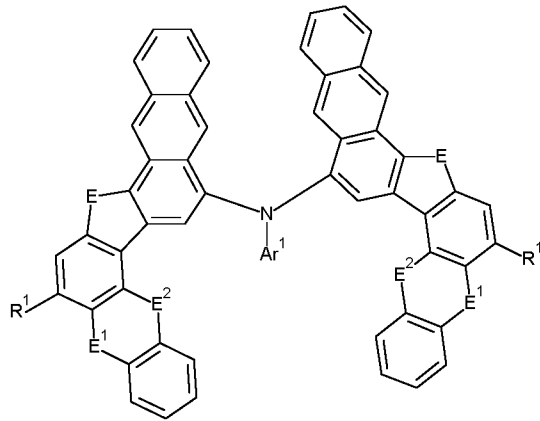
formula (6-2)

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formula (7-2)

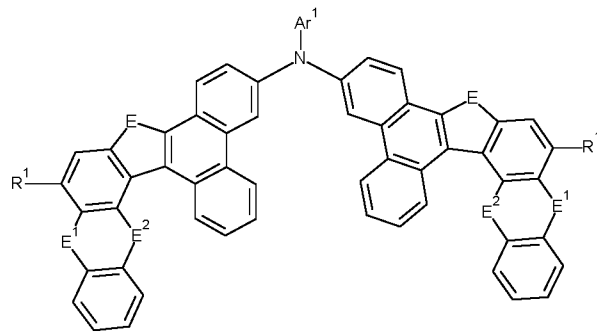
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formula (8-2)

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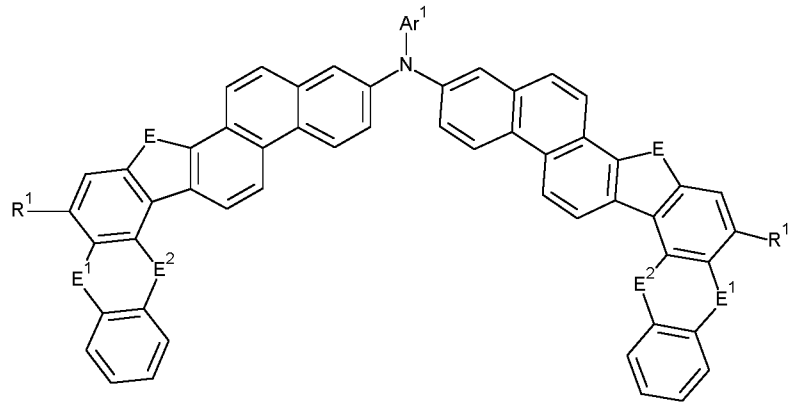
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formula (9-2)

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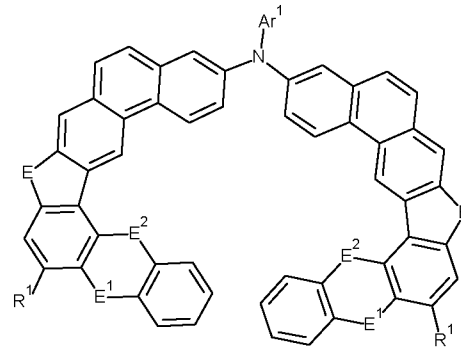
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formula (10-2)

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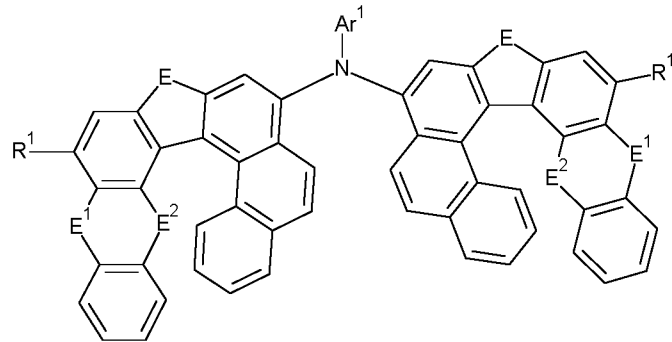
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formula (11-2)

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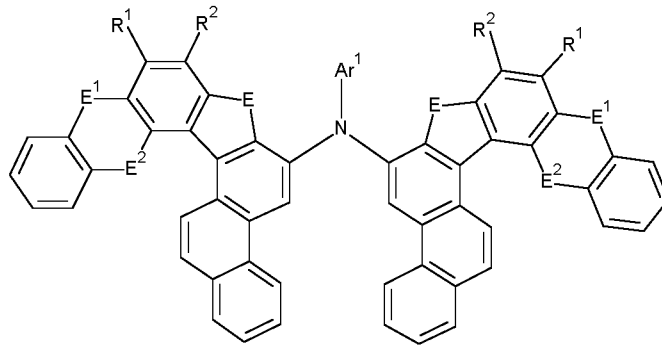
formula (12-2)

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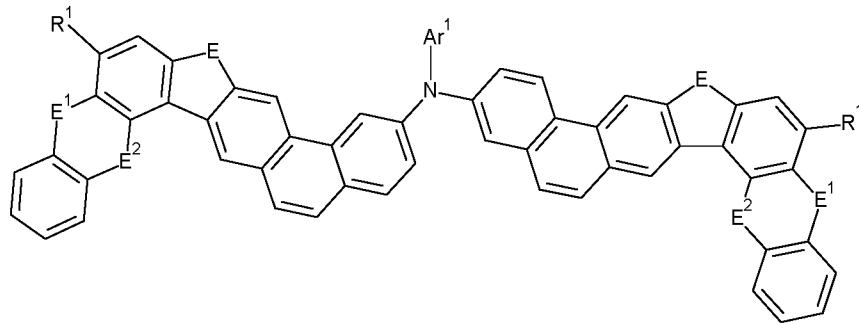
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formula (13-2)

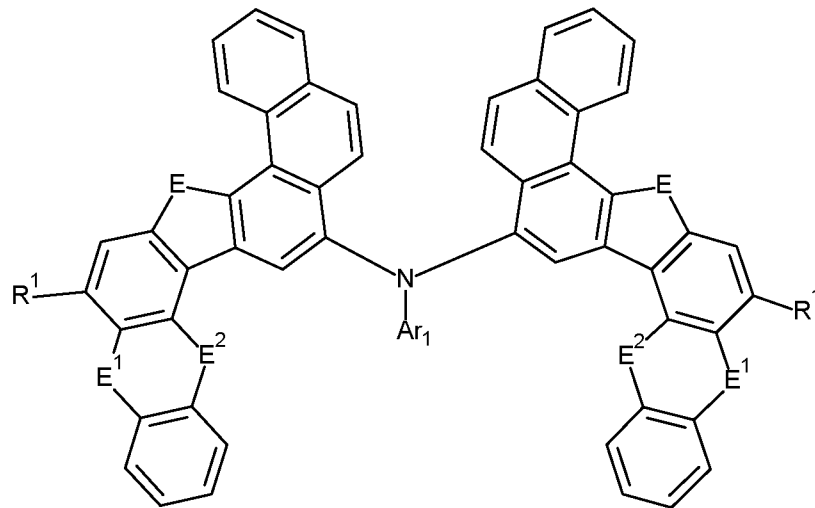
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formula (14-2)

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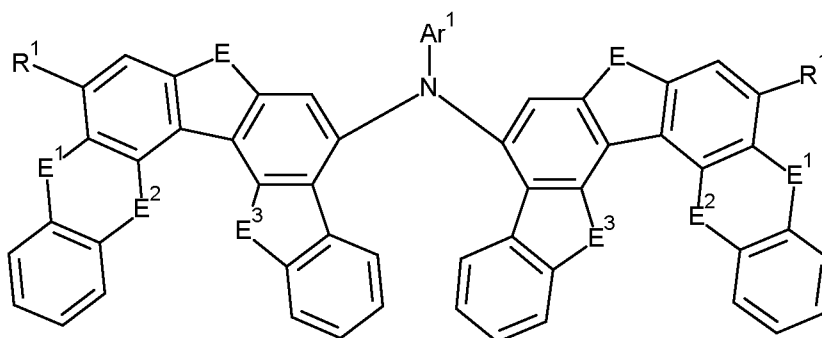
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formula (15-2)

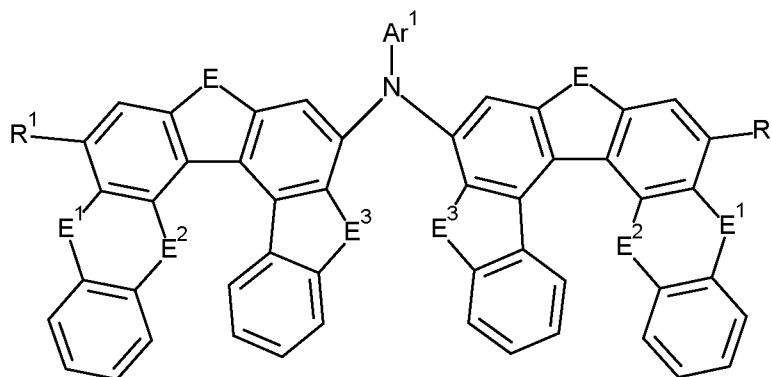
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formula (16-2)

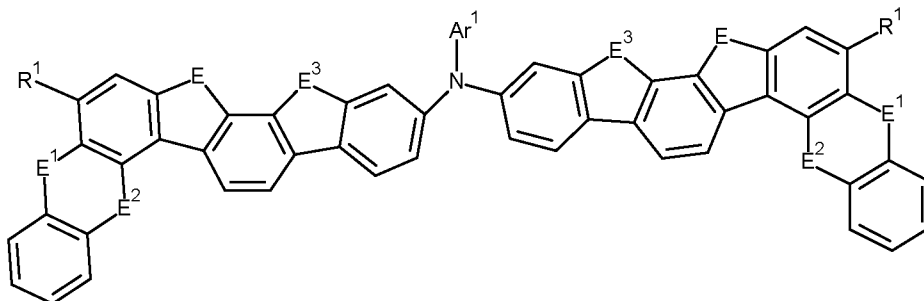
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formula (17-2)

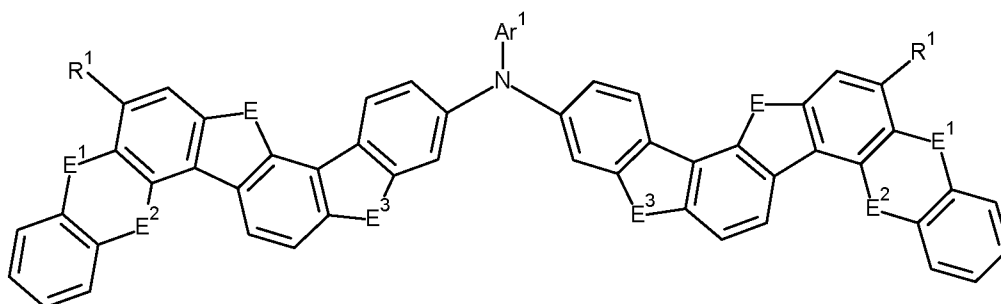
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formula (18-2)

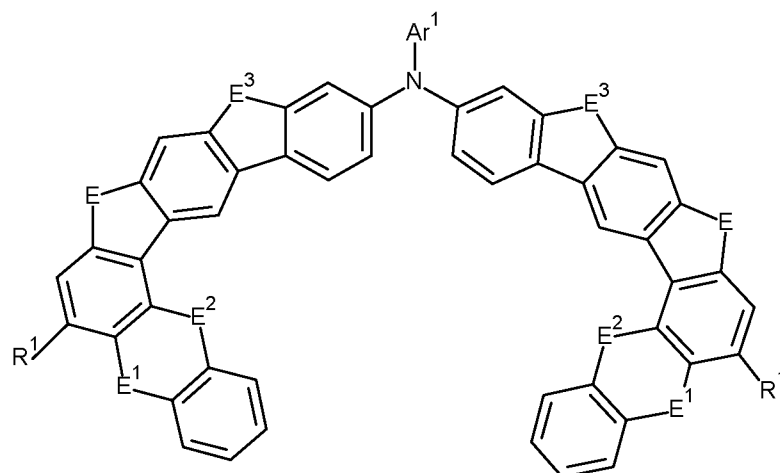
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formula (19-2)

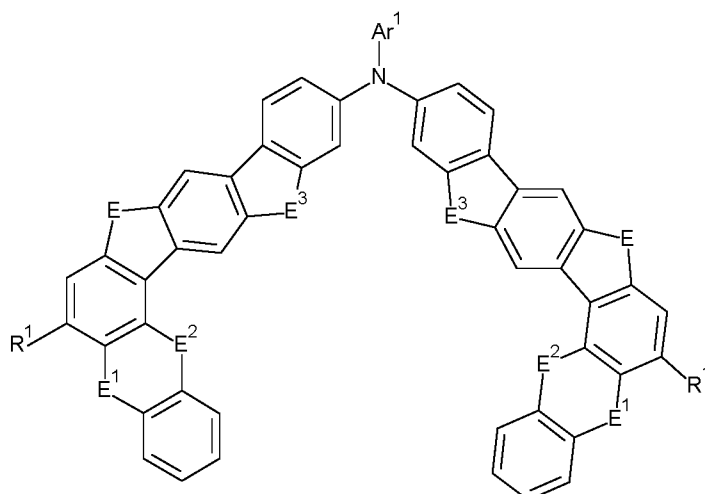
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formula (20-2)

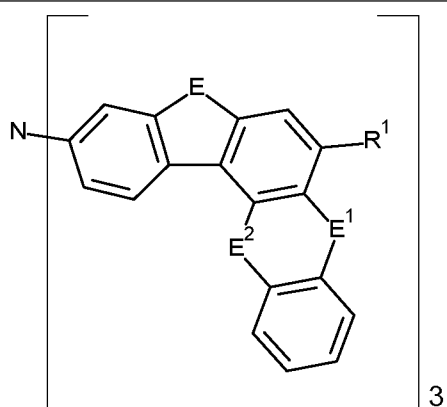
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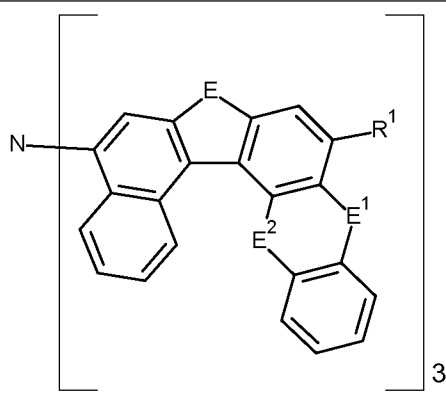
formula (21-2)

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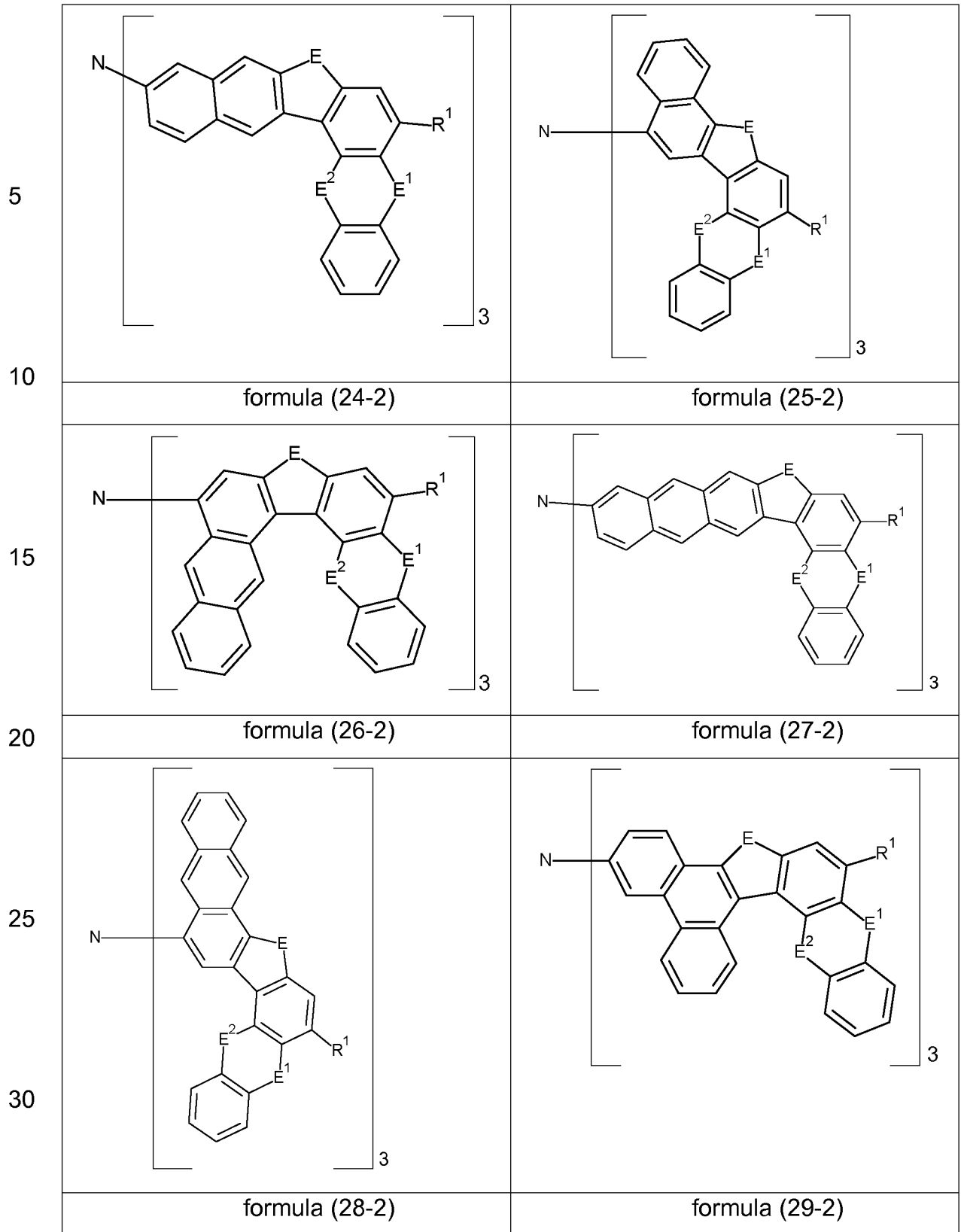
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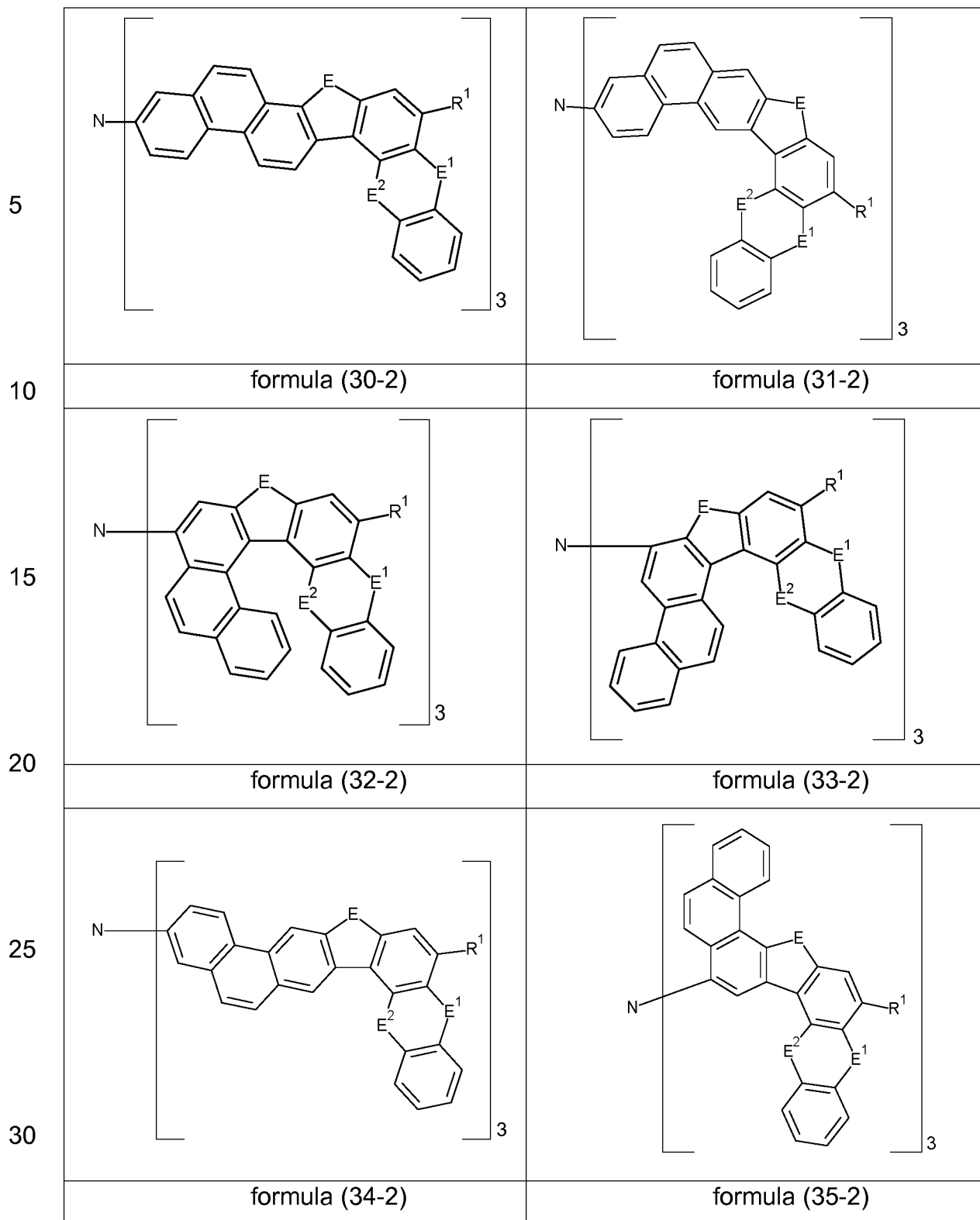
formula (22-2)

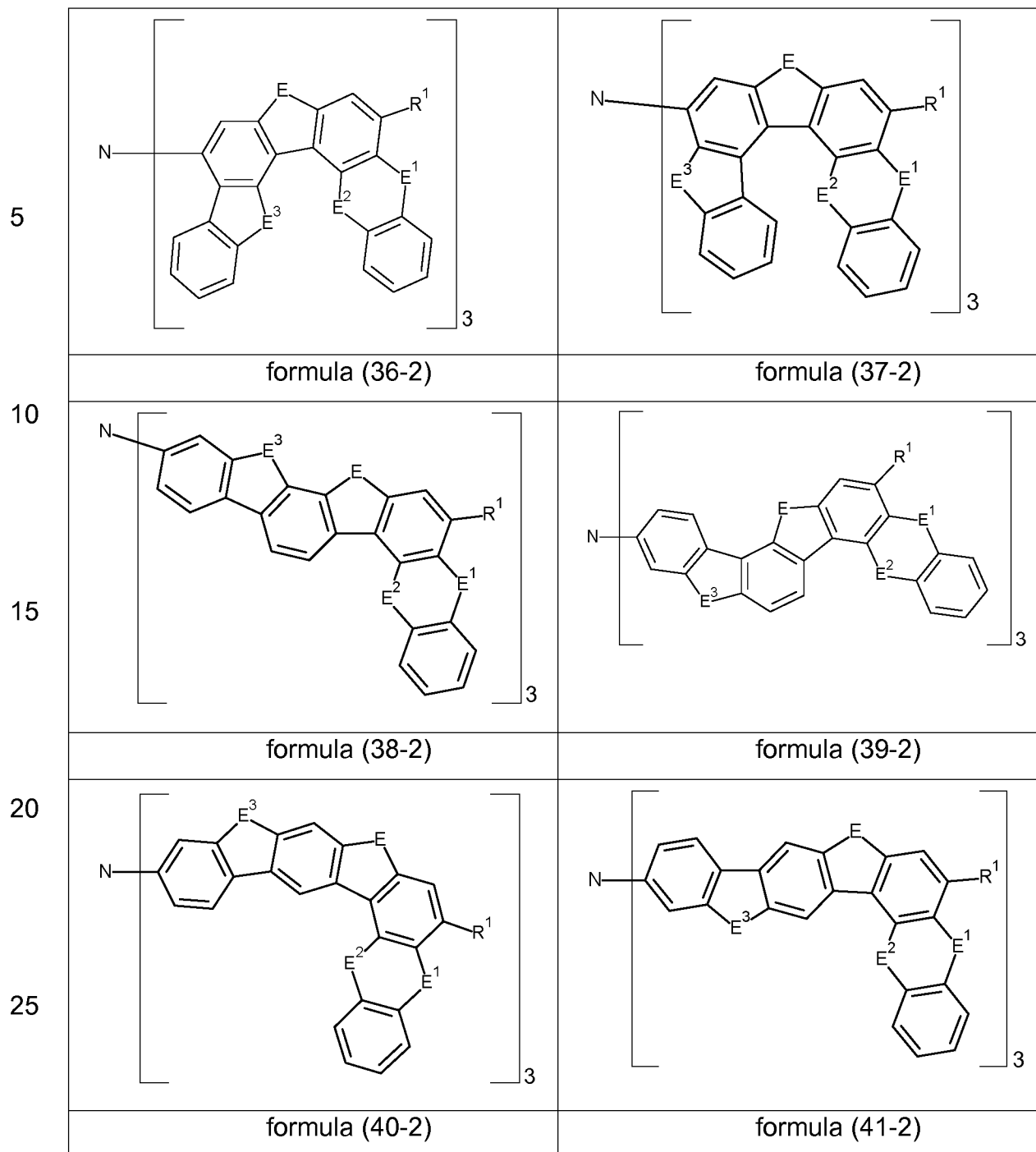


35

formula (23-2)







30 where the symbols X, Ar¹, E, E¹, E², E³ and R¹ have the same meaning as above.

Preferably, R¹, R², R³, R⁴ stand on each occurrence, identically or differ-
 35 ently, for:

- 41 -

- H, D, F, N(Ar)₂, Si(R)₃; or
- a straight-chain alkyl or alkoxy groups having 1 to 20, preferably 1 to 10 C atoms or branched or a cyclic alkyl or alkoxy groups having 3 to 20, preferably 3 to 10 C atoms, each of which may be substituted by one or more radicals R, where in each case one or more non-adjacent CH₂ groups may be replaced by RC=CR, O or S and where one or more H atoms may be replaced by D or F; or
- an aromatic or heteroaromatic ring systems having 5 to 40, preferably 5 to 20 aromatic ring atoms, which may in each case be substituted by one or more radicals R; or
- for a group ArL as defined above, which may be substituted by one or more radicals R;

and where two adjacent substituents R¹ and R², two adjacent substituents R³ and/or two adjacent substituents R⁴, may form a mono- or polycyclic, aliphatic ring system or aromatic ring system, which may be substituted by one or more radicals R;

More preferably, R¹ and R² stand on each occurrence, identically or differently, for H, D, F, a straight-chain alkyl group having 1 to 10 C atoms or a branched or a cyclic alkyl group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R, an aromatic or heteroaromatic ring systems having 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R, or for a group ArL, which may be substituted by one or more radicals R, where ArL stands for a group of formula (ArL-1) as defined above.

In accordance with a preferred embodiment, the groups R¹ and R² are on each occurrence, identically or differently, selected from H, a straight-chain alkyl group having 1 to 10 C atoms, an aromatic or heteroaromatic ring systems having 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R, or a group ArL of formula (ArL-1) as defined above.

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In accordance with a very preferred embodiment, at least one of the groups R^1 and R^2 present in the same ring corresponds to a group ArL of formula (ArL-1) as defined above.

5 In accordance with a particularly preferred embodiment, the group R^1 corresponds to a group ArL of formula (ArL-1) as defined above.

10 In accordance with a preferred embodiment, R^3 , R^4 stand on each occurrence, identically or differently, for H, D, F, a straight-chain alkyl group having 1 to 10 C atoms or branched or a cyclic alkyl having 3 to 10 C atoms, each of which may be substituted by one or more radicals R, where one or more H atoms may be replaced by D or F; or an aromatic or heteroaromatic ring systems having 5 to 18 aromatic ring atoms, which may
15 in each case be substituted by one or more radicals R; where two adjacent substituents R^3 and/or two adjacent substituents R^4 , may form a mono- or polycyclic, aliphatic ring system or aromatic ring system, which may be substituted by one or more radicals R.

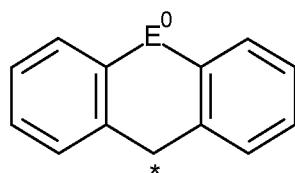
20 In accordance with a preferred embodiment, R stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl or alkoxy groups having 1 to 20, preferably 1 to 10 C atoms or branched or cyclic alkyl or alkoxy groups having 3 to 20, preferably 3 to 10 C atoms,
25 each of which may be substituted by one or more radicals R' , where one or more H atoms may be replaced by D or F, an aromatic or heteroaromatic ring systems having 5 to 40, preferably 5 to 20 aromatic ring atoms, which may in each case be substituted by one or more radicals R' . More
30 preferably, R stands on each occurrence, identically or differently, for H, a straight-chain alkyl having 1 to 10 C atoms or branched or cyclic alkyl group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R' , an aromatic or heteroaromatic ring systems having 5 to 18
35 aromatic ring atoms, which may in each case be substituted by one or more radicals R' .

- 43 -

In accordance with a preferred embodiment, R' stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl group having 1 to 10 C atoms or branched or cyclic alkyl group having 3 to 10 C atoms, or an aromatic or heteroaromatic ring system having 5 to 18 C atoms.

In accordance with a preferred embodiment, the groups E¹, E² are, identically or differently, on each occurrence, selected from the group consisting of a single bond, -O- and -S-; with the proviso that, in a ring comprising the groups E¹ and E², one of the group E¹ and E² is a single bond, and the other group is O or S. Very preferably, in a ring comprising the groups E¹ and E², E¹ is O and E² is a single bond or E¹ is a single bond and E² is O.

In accordance with a preferred embodiment, the group E is on each occurrence, identically or differently, selected from -C(R⁰)₂-, -Si(R⁰)₂-, -O-, -S-, -N(R⁰)-; or E is a group of formula (E-1),



formula (E-1)

where the symbol * in formula (E-1) indicates the corresponding group E in formula (1) and where E⁰ has the same meaning as above.

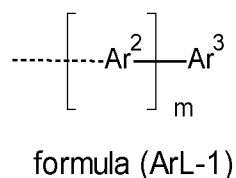
In accordance with a very preferred embodiment, the group E stands for -C(R⁰)₂-.

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In accordance with another very preferred embodiment, the group E stands for a group of formula (E-1) where, E⁰ stands for a single bond or -C(R⁰)₂.

In accordance with the invention, the group Ar_L stands for a group of the following formula (Ar_L-1),



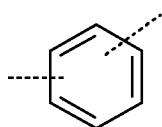
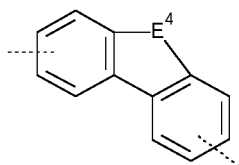
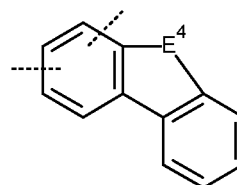
where the dashed bond in formula (Ar_L-1) indicates the bonding to the structure of formula (1).

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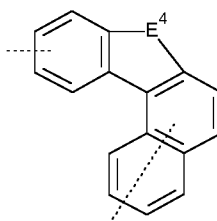
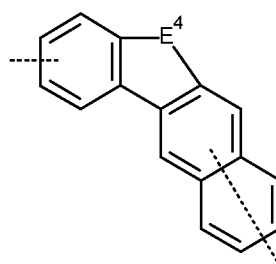
Preferably, m is an integer selected from 1 to 6, very preferably from 1 to 4.

In formula (Ar_L-1), it is preferred that the group Ar² is selected from the groups of formulae (Ar₂-1) to (Ar₂-25),

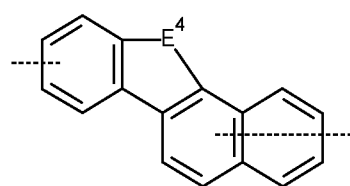
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(Ar₂-1)(Ar₂-2)(Ar₂-3)

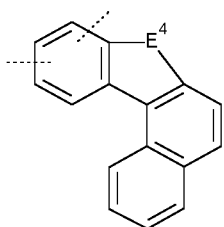
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(Ar₂-4)(Ar₂-5)

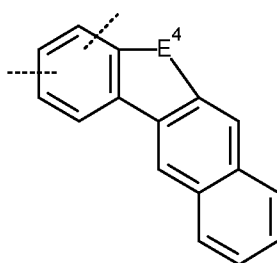
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(Ar₂-6)

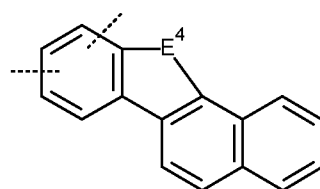
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(Ar2-7)

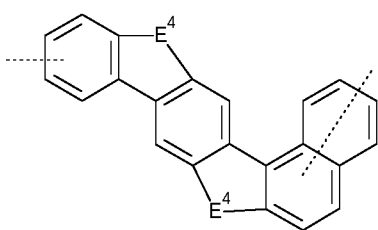


(Ar2-8)

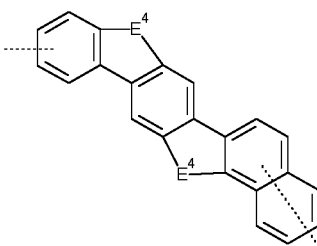


(Ar2-9)

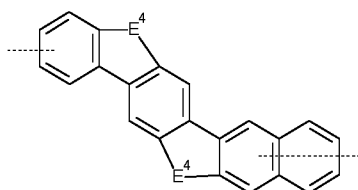
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(Ar2-10)

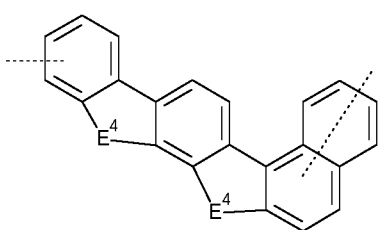


(Ar2-11)

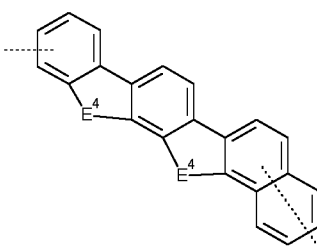


(Ar2-12)

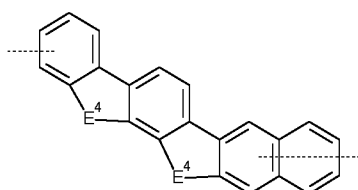
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(Ar2-13)

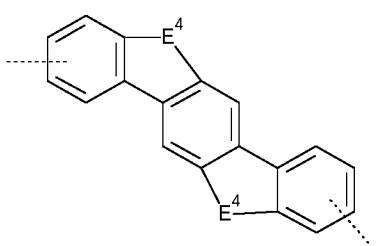


(Ar2-14)

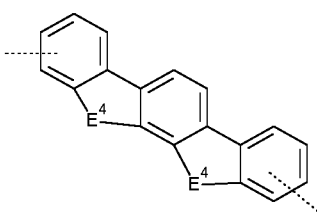


(Ar2-15)

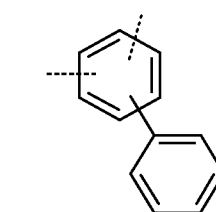
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(Ar2-16)

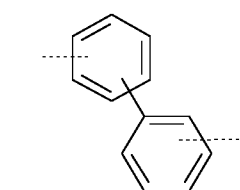


(Ar2-17)

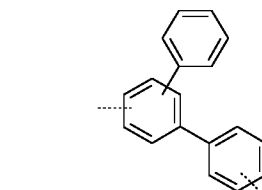


(Ar2-18)

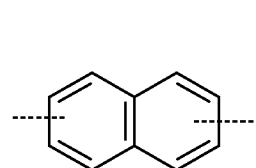
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(Ar2-19)



(Ar2-20)



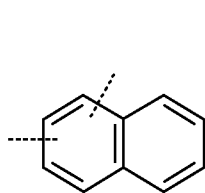
(Ar2-21)

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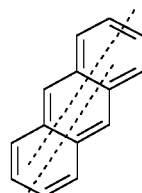
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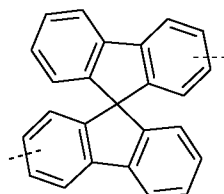


(Ar2-22)

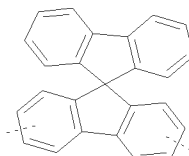


(Ar2-23)

5



(Ar2-24)



(Ar2-25)

10

where the dashed bonds indicate the bonding to the structure of formula (1) and to a group Ar^2 or Ar^3 and the groups of formulae (Ar2-1) to (Ar2-25) may be substituted at each free position by a group R, which has the same meaning as above and where

15

E^4 is selected from $-B(R^0)$, $-C(R^0)_2$, $-C(R^0)_2-C(R^0)_2$, $-Si(R^0)_2$, $-C(=O)$, $-C(=NR^0)$, $-C(C(R^0))_2$, $-O$, $-S$, $-S(=O)$, $-SO_2$, $-N(R^0)$, $-P(R^0)$ and $-P(=O)R^0$, where the substituent R^0 has the same meaning as above.

20

Preferably, E^4 is selected from $-C(R^0)_2$, $-Si(R^0)_2$, $-O$, $-S$ or $-N(R^0)$, where the substituent R^0 has the same meaning as above

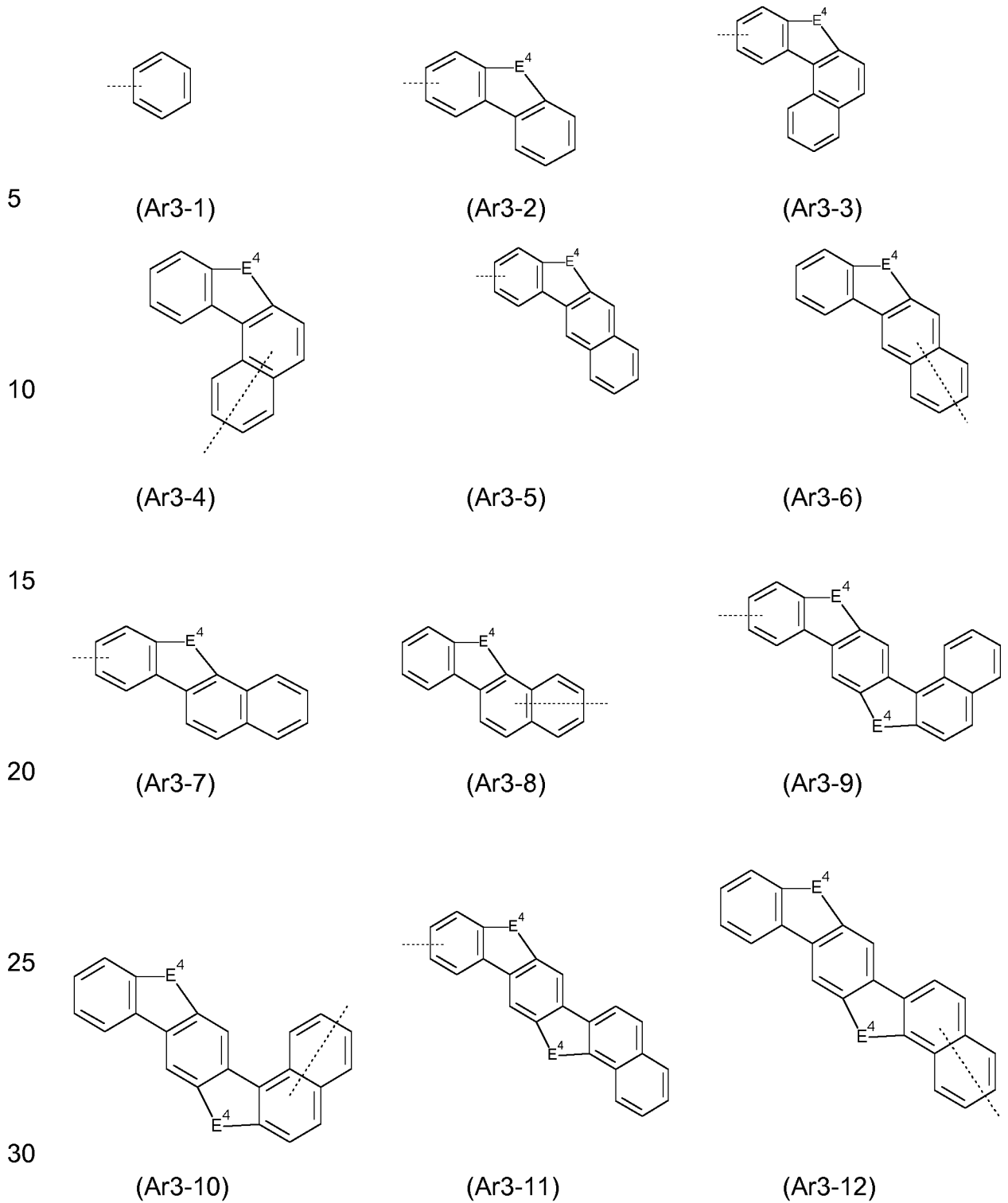
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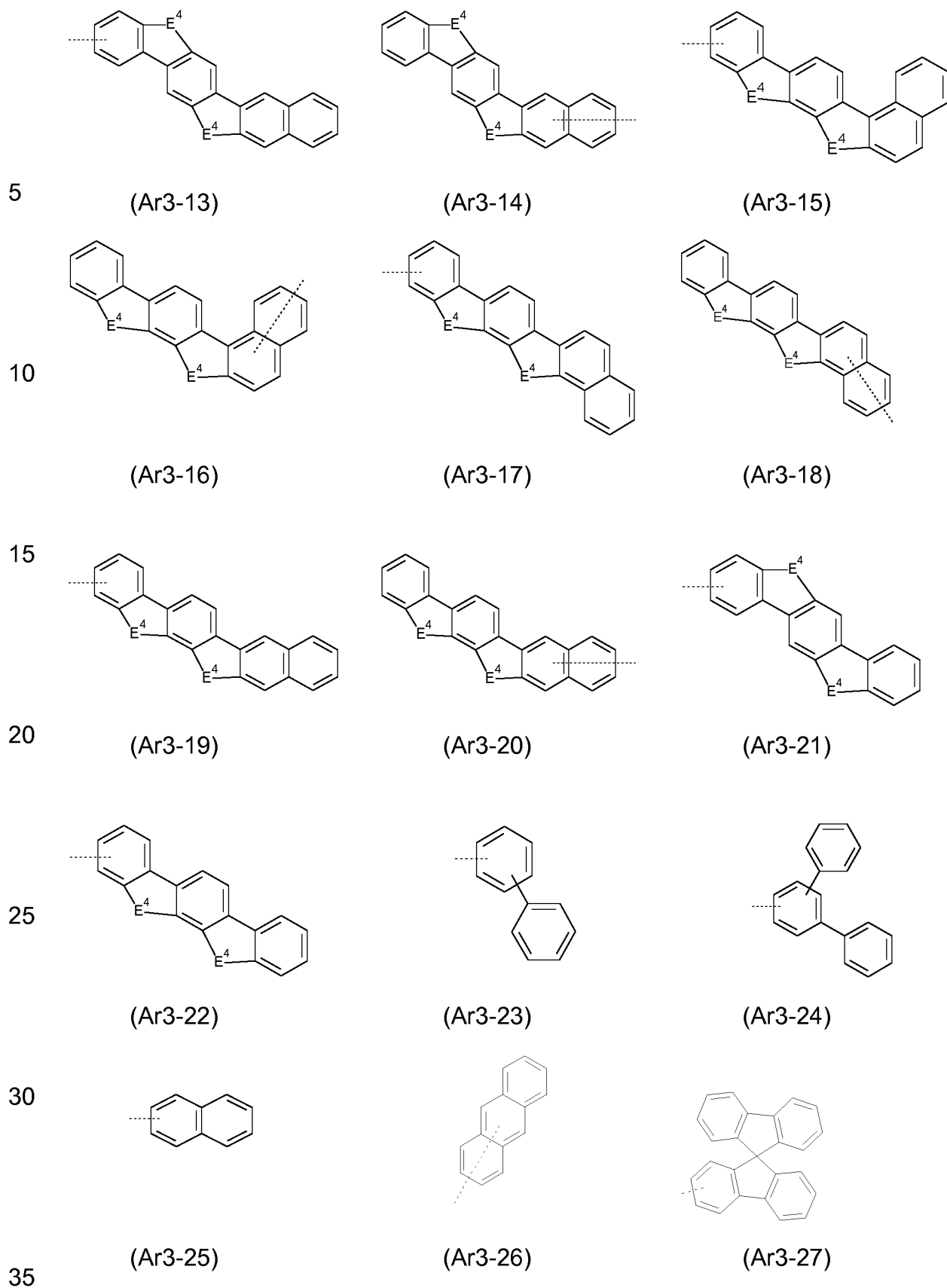
Among formulae (Ar2-1) to (Ar2-25), following formulae are preferred: (Ar2-1), (Ar2-2), (Ar2-3), (Ar2-18), (Ar2-19), (Ar2-20), (Ar2-21), (Ar2-22) and (Ar2-25).

30

Furthermore, in formula (ArL-1), it is preferred that Ar^3 is on each occurrence, identically or differently, selected from the group consisting of the groups of formulae (Ar3-1) to (Ar3-27),

35





- 49 -

where the dashed bond indicates the bonding to Ar^2 and where E^4 has the same meaning as above and the groups of formulae (Ar3-1) to (Ar3-27) may be substituted at each free position by a group R, which has the same meaning as above.

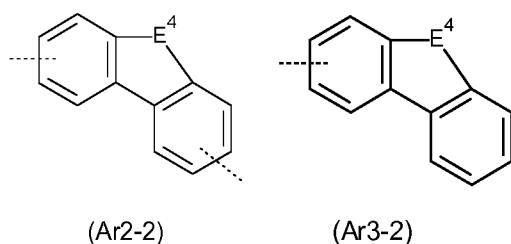
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Among formulae (Ar3-1) to (Ar2-27), following formulae are preferred: (Ar3-1), (Ar3-2), (Ar3-23), (Ar3-24), (Ar3-25) and (Ar3-27).

10

In accordance with a preferred embodiment at least one group Ar^2 stands for a group of formula (Ar2-2) and/or at least one group Ar^3 stands for a group of formula (Ar3-2),

15



where

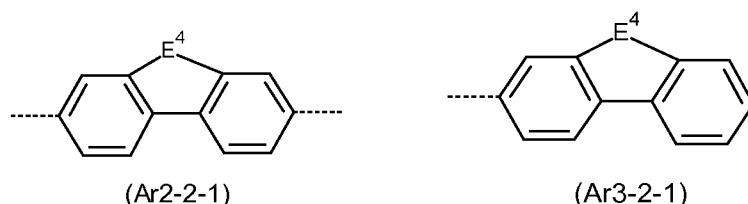
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the dashed bonds in formula (Ar2-2) indicate the bonding to the structure of formula (1) and to a group Ar^2 or Ar^3 ; and the dashed bond in formula (Ar3-2) indicates the bonding to Ar^2 ; and E^4 has the same meaning as in above; and the groups of formulae (Ar2-2) and (Ar3-2) may be substituted at each free position by a group R, which has the same meaning as above.

25

In accordance with a very preferred embodiment, at least one group Ar^2 stands for a group of formula (Ar2-2-1) and/or at least one group Ar^3 stands for a group of formula (Ar3-2-1),

30



35

where

- 50 -

the dashed bonds in formula (Ar2-2-1) indicate the bonding to the structure of formula (1) and to a group Ar² or Ar³;

the dashed bond in formula (Ar3-2-1) indicates the bonding to Ar²;

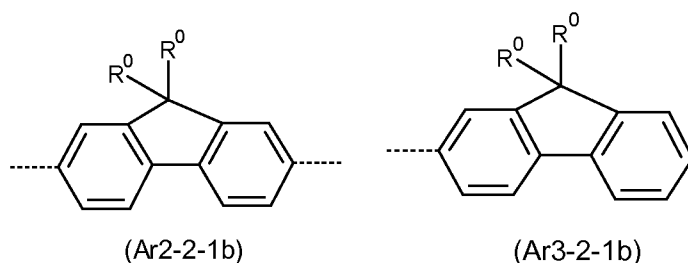
E⁴ has the same meaning as above; and

5 the groups of formulae (Ar2-2-1) and (Ar3-2-1) may be substituted at each free position by a group R, which has the same meaning as above.

In accordance with a particularly preferred embodiment, at least one group Ar² stands for a group of formula (Ar2-2-1b) and/or at least one group Ar³ stands for a group of formula (Ar3-2-1b),

10

15



where

20 the dashed bonds in formula (Ar2-2-1b) indicate the bonding to the structure of formula (1) and to a group Ar² or Ar³;

the dashed bond in formula (Ar3-2-1b) indicates the bonding to Ar²;

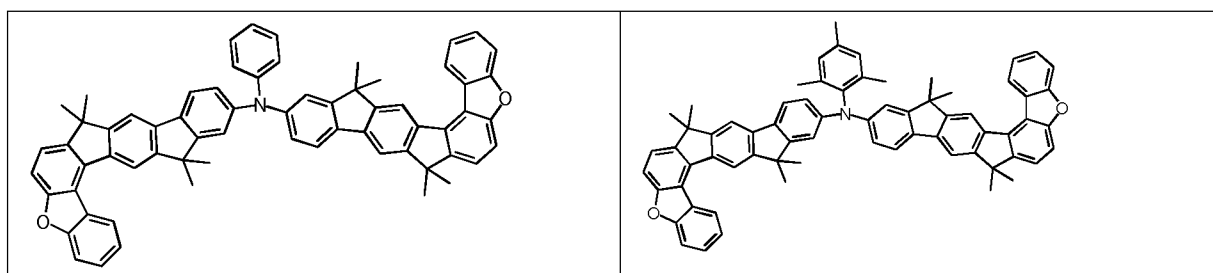
R⁰ has the same meaning as above; and

25

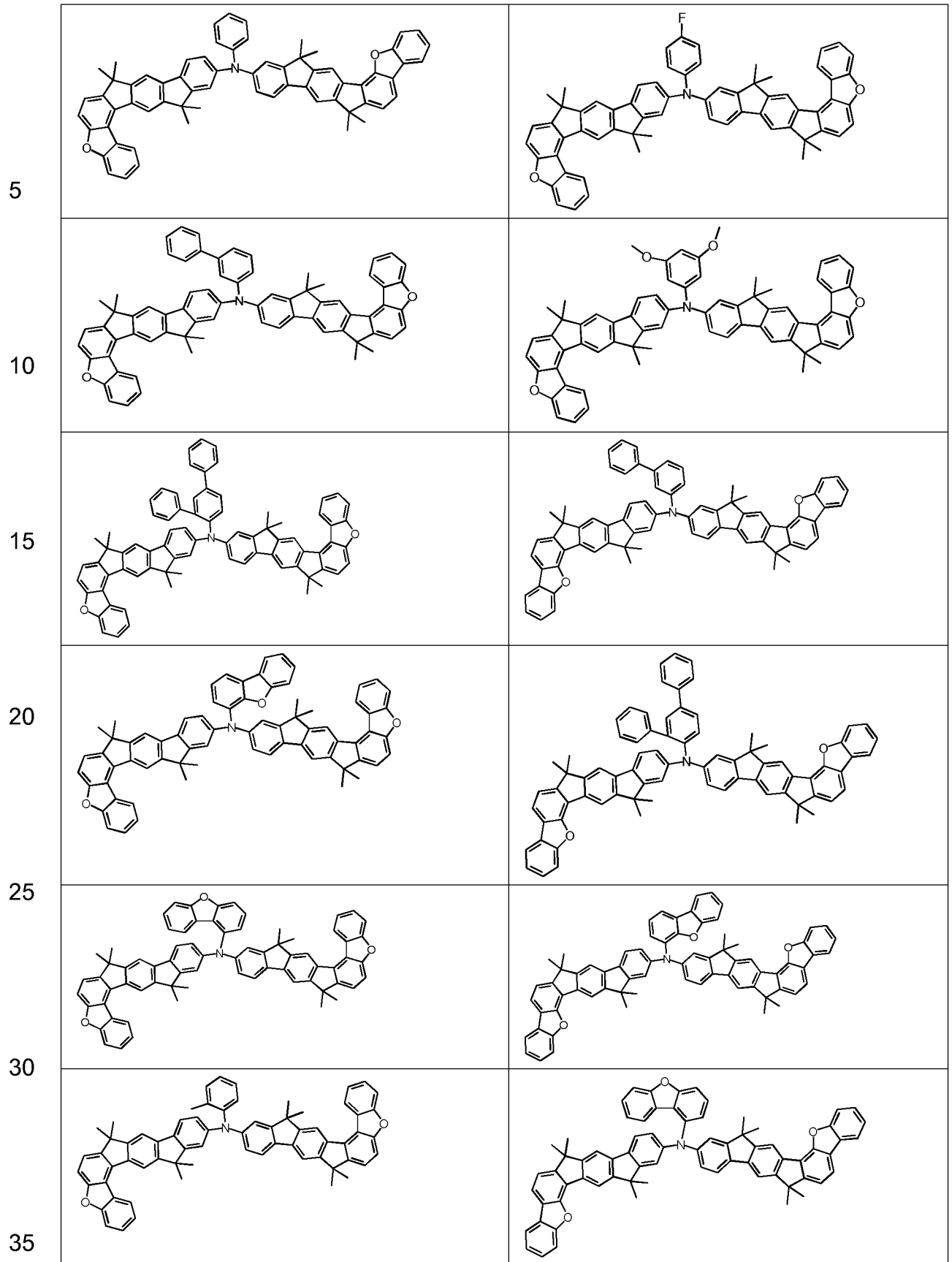
the groups of formulae (Ar2-2-1b) and (Ar3-2-1b) may be substituted at each free position by a group R, which has the same meaning as above.

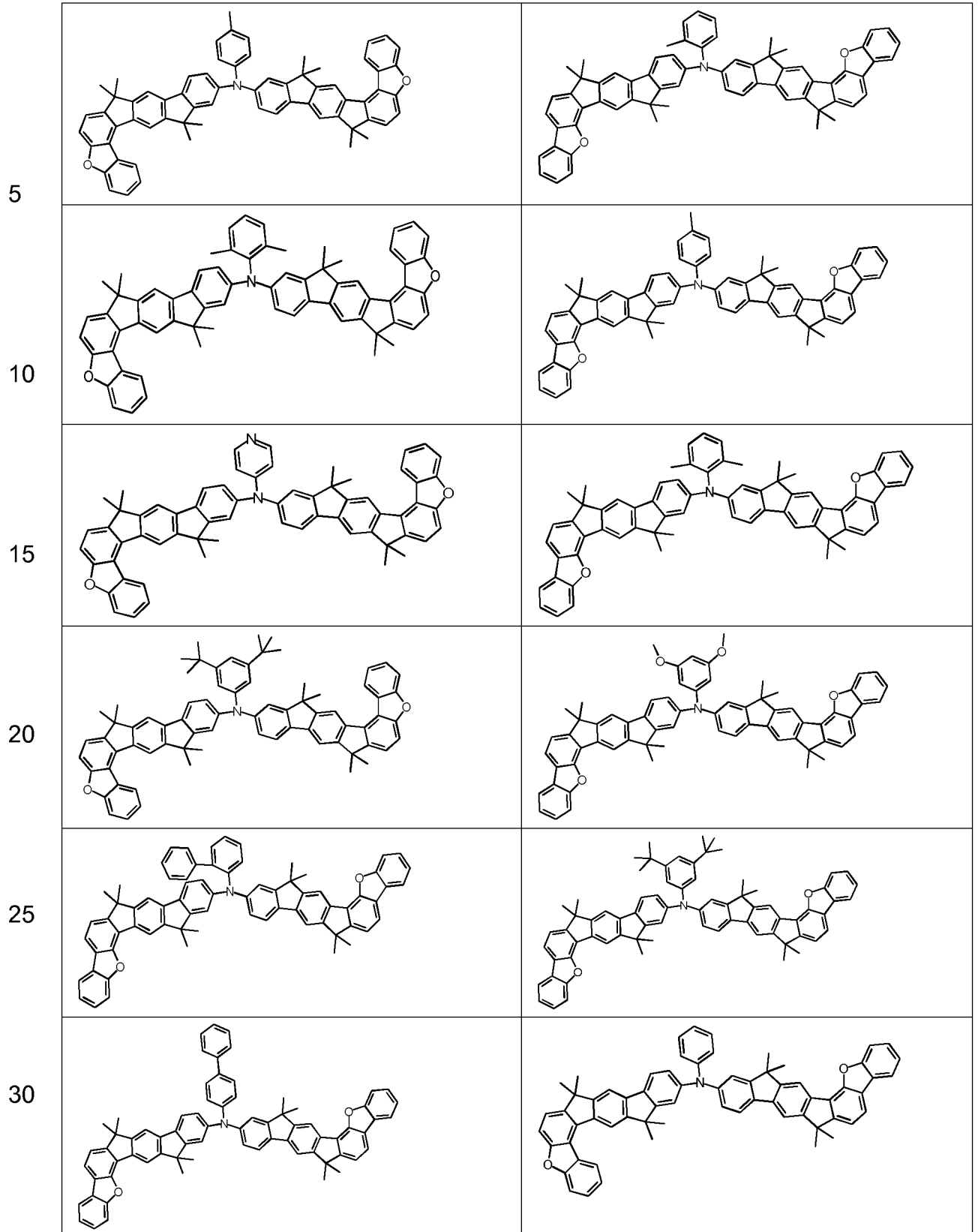
The following compounds are examples of compounds of formula (1):

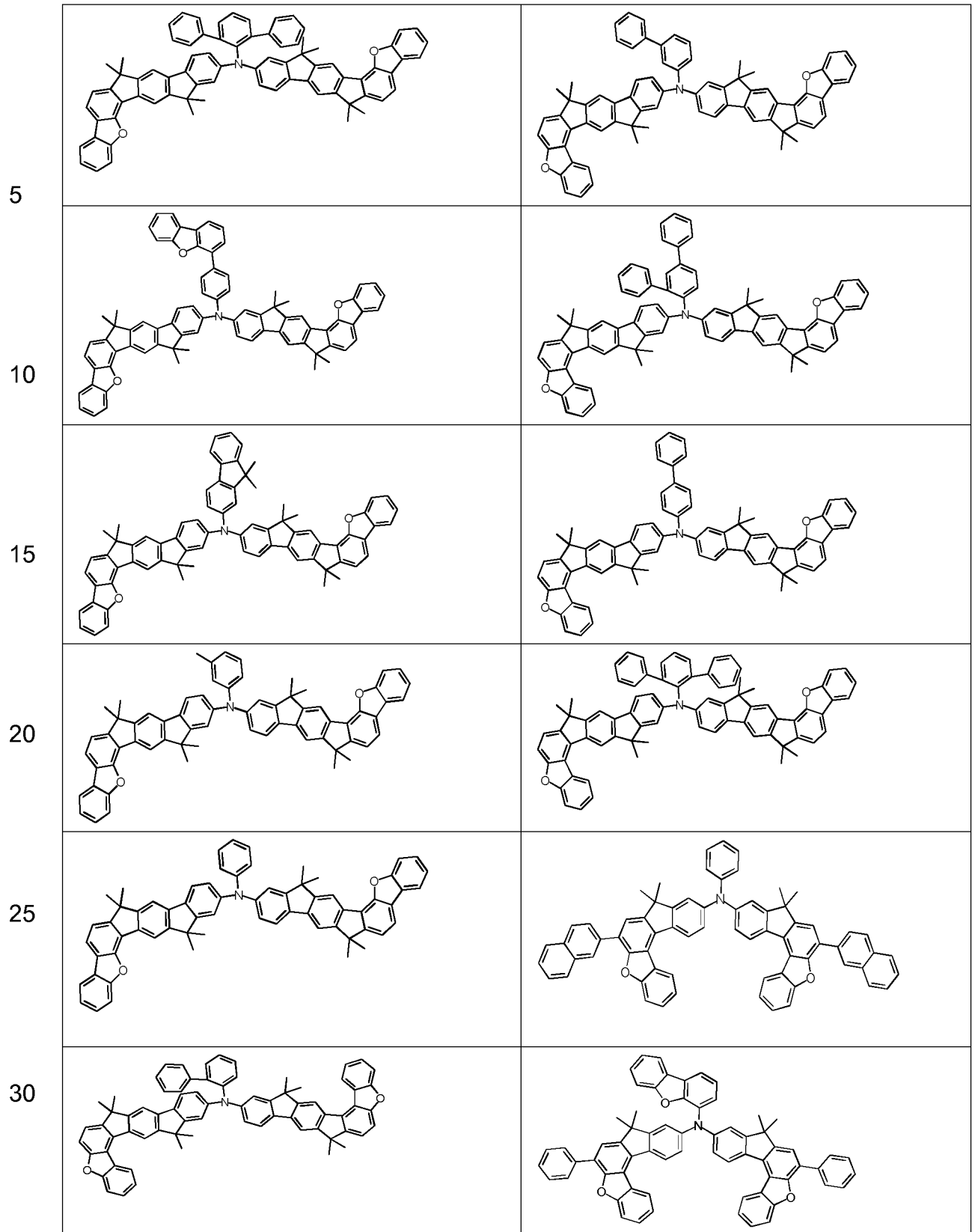
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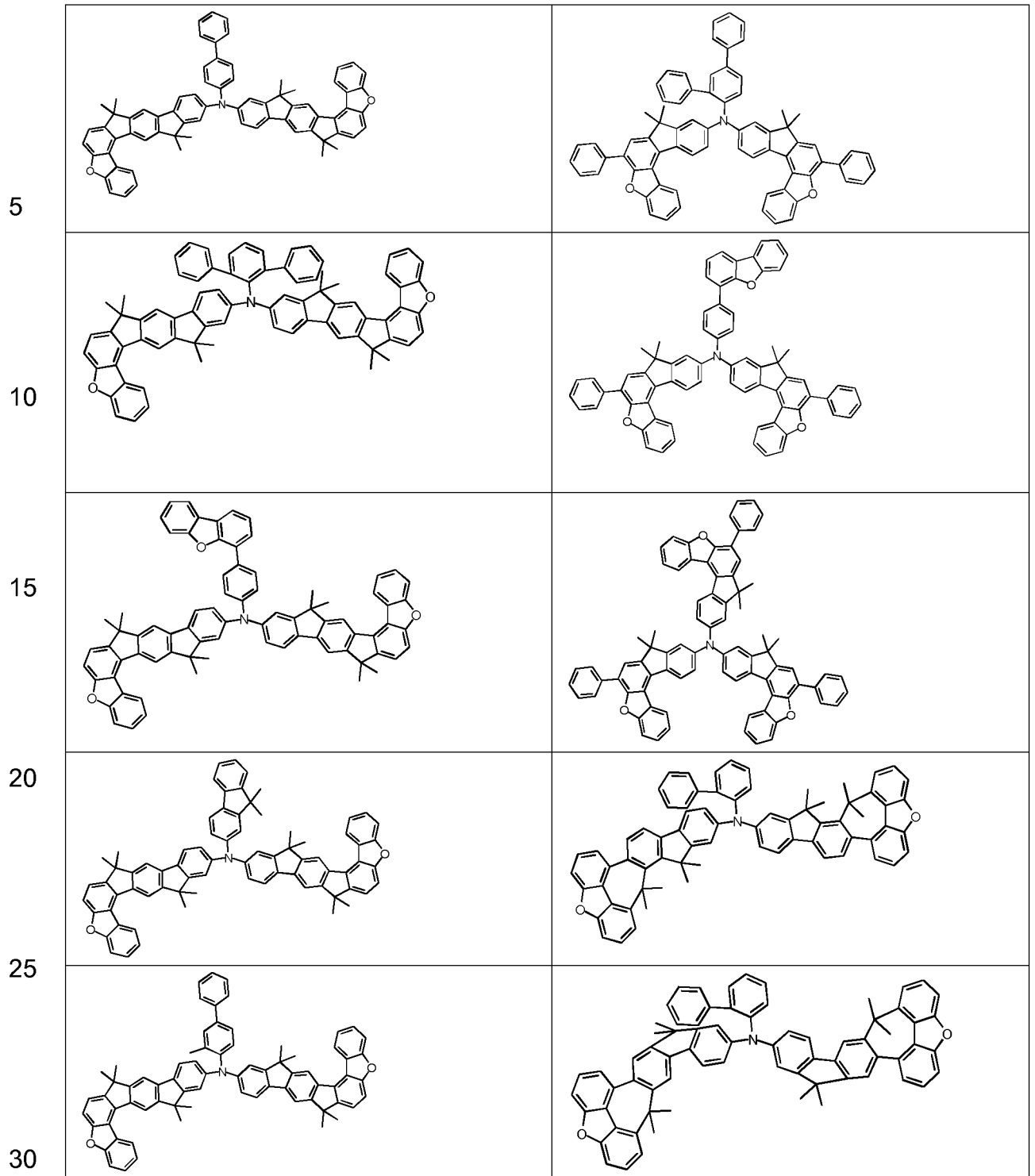


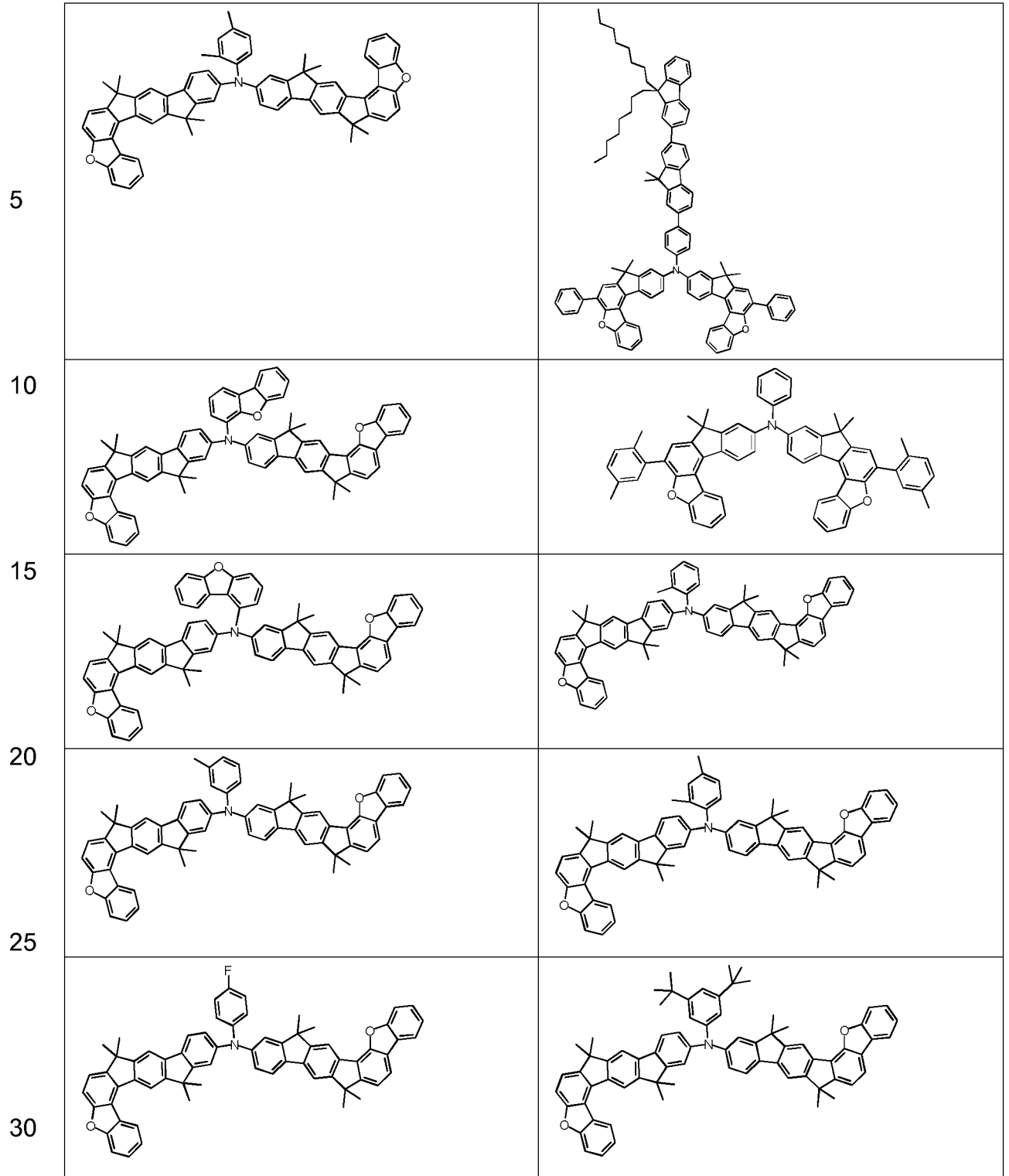
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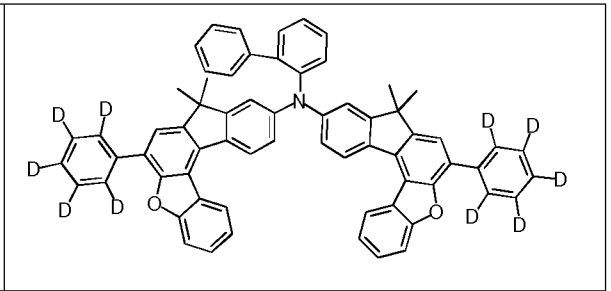
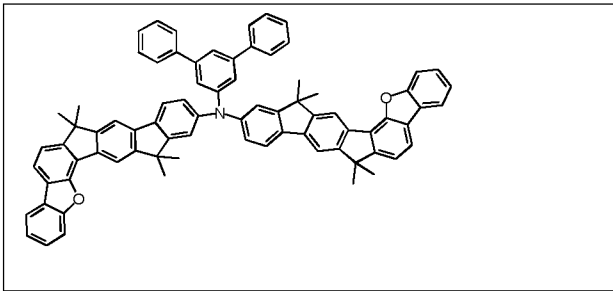




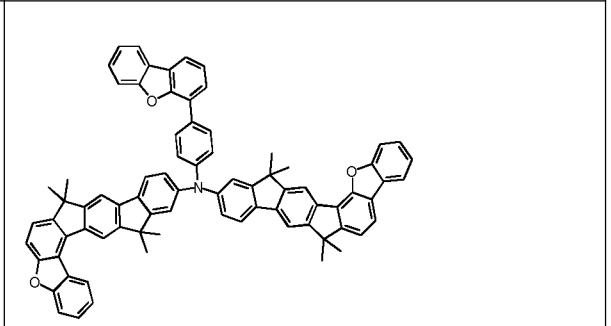
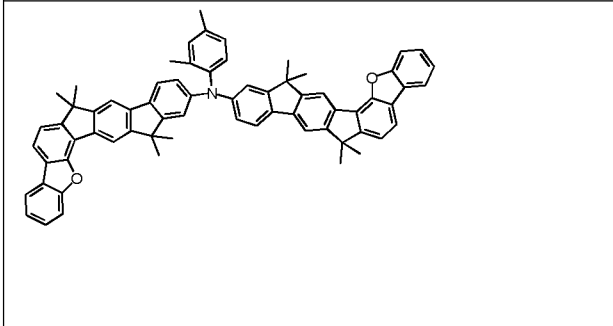




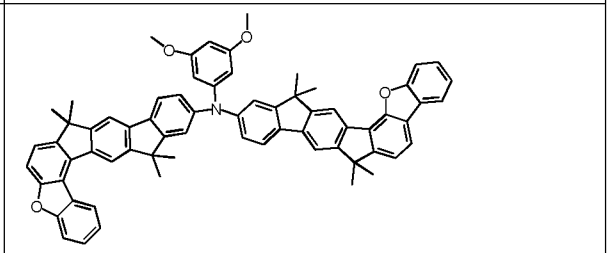
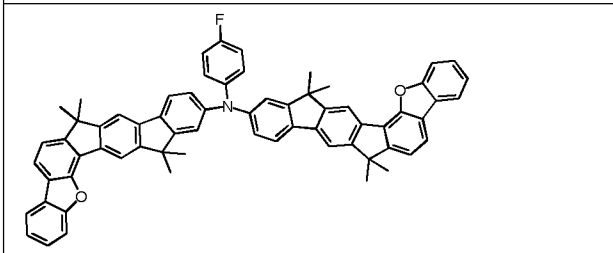
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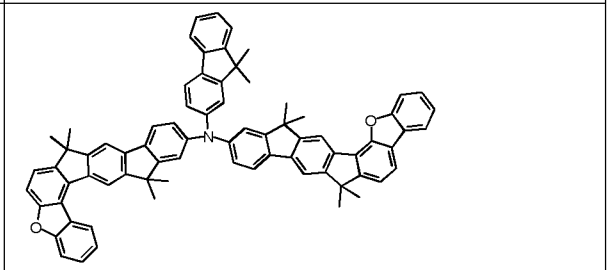
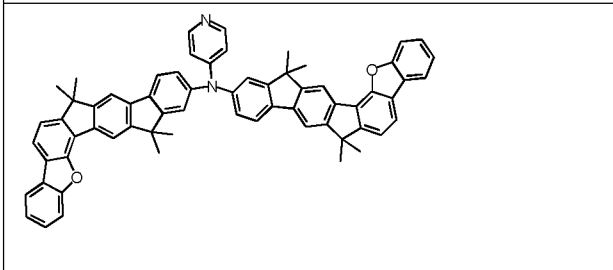
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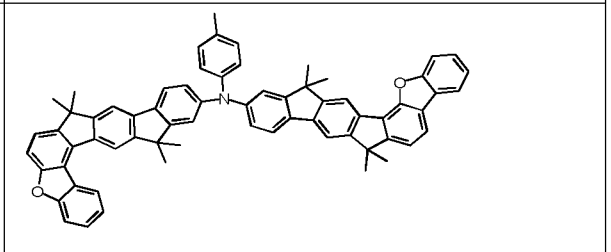
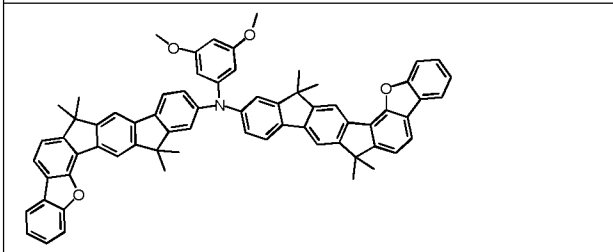
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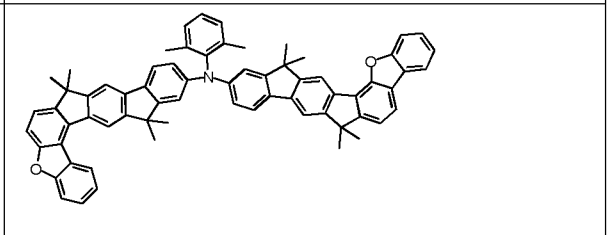
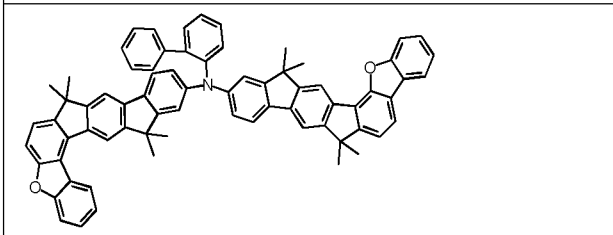
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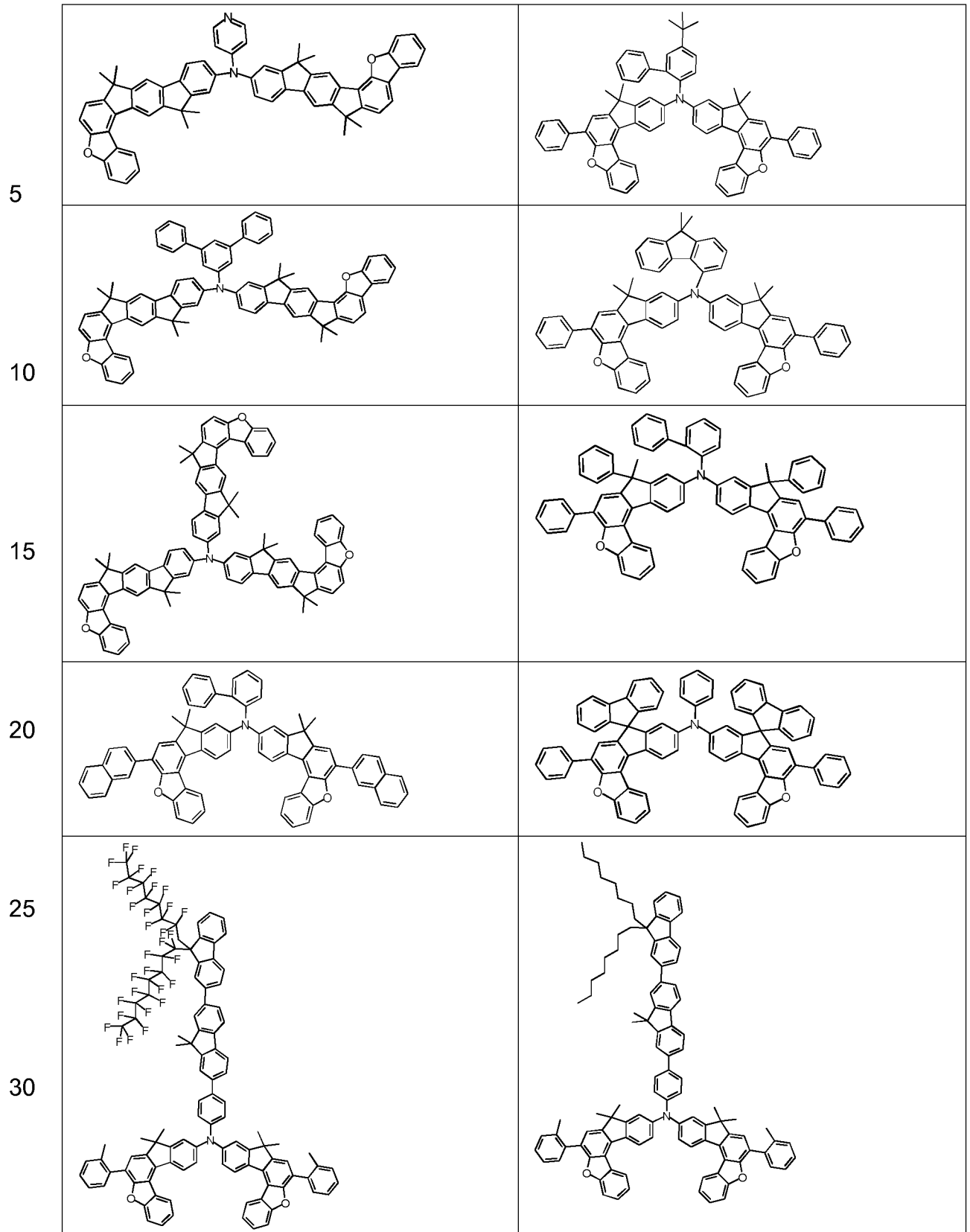
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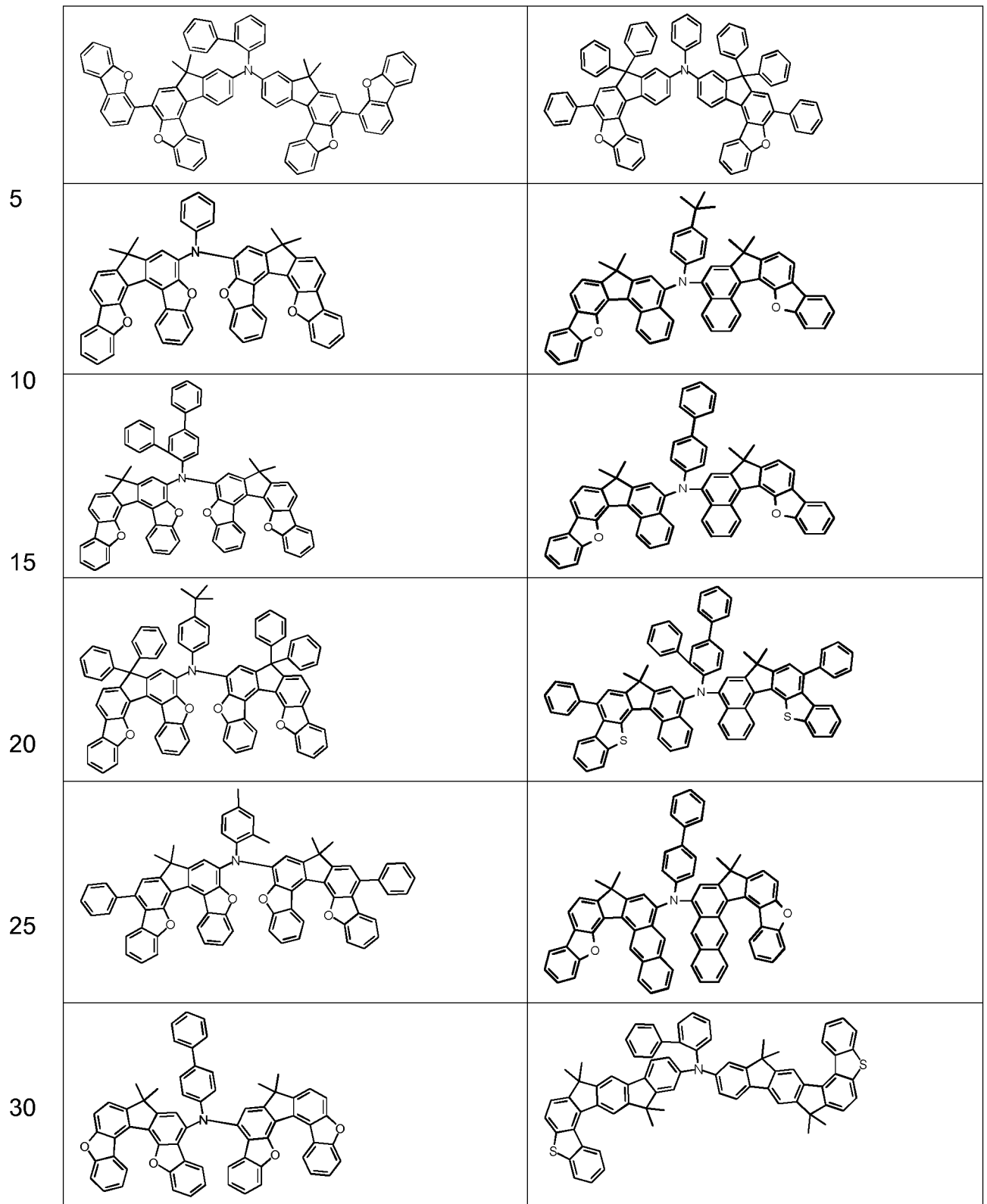


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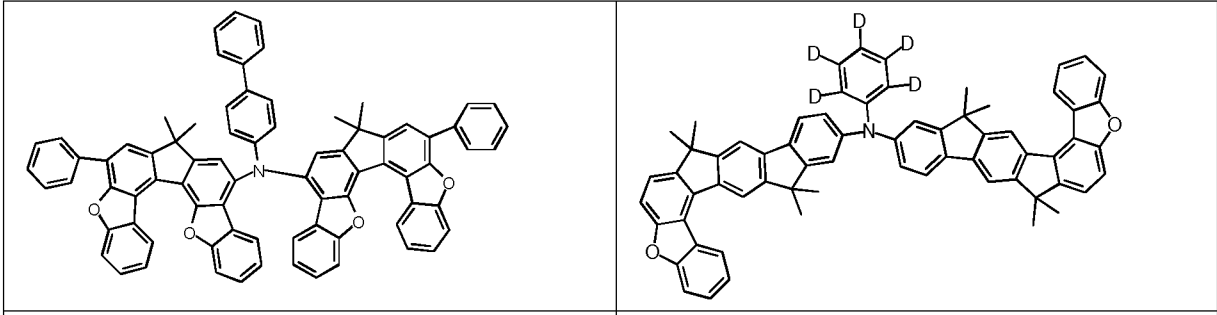


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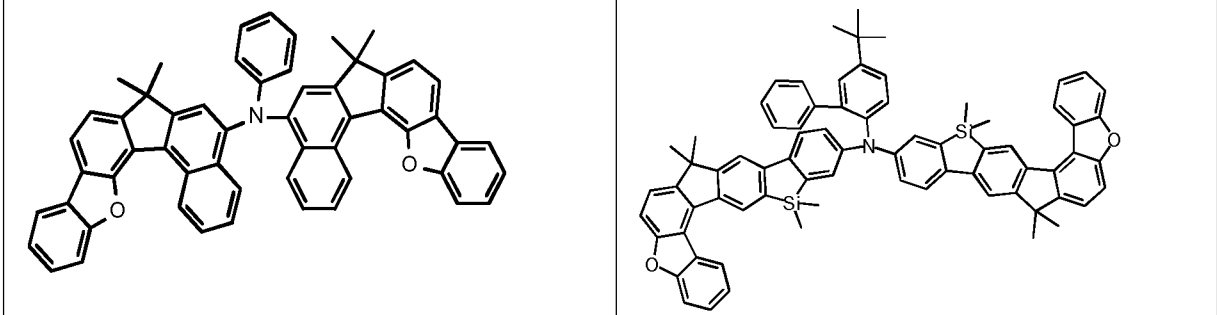




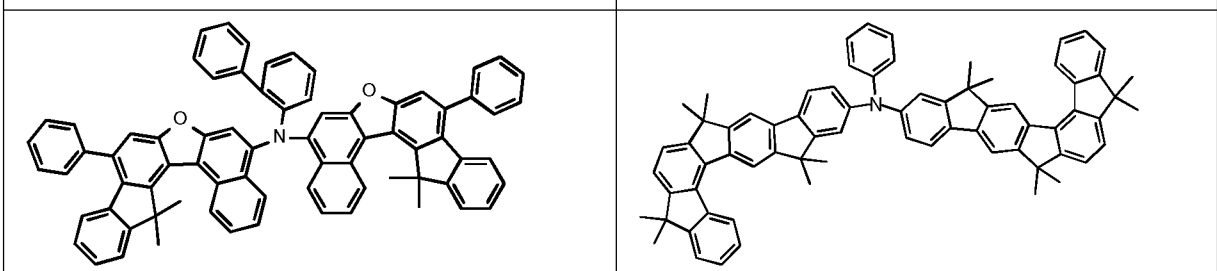
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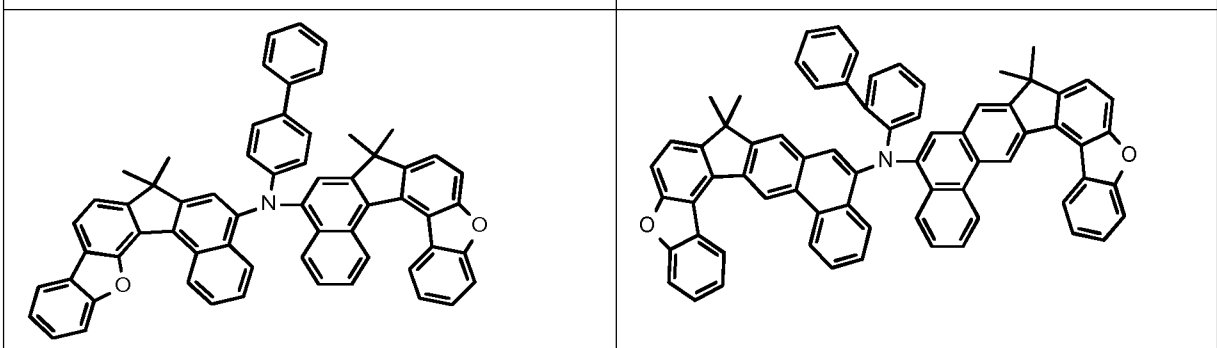
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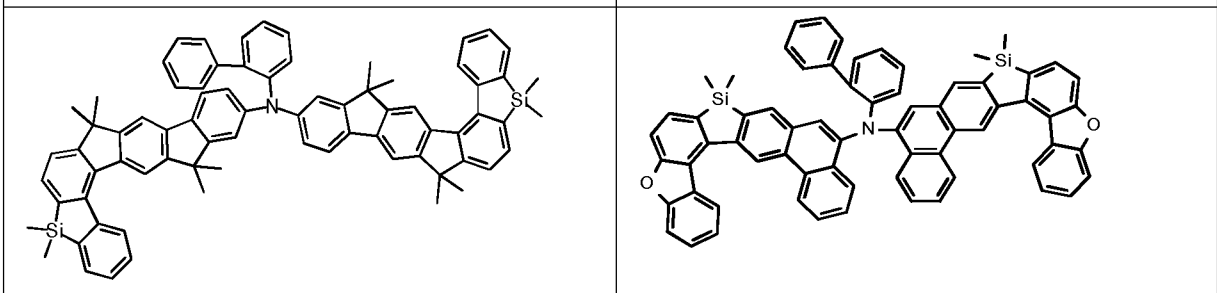
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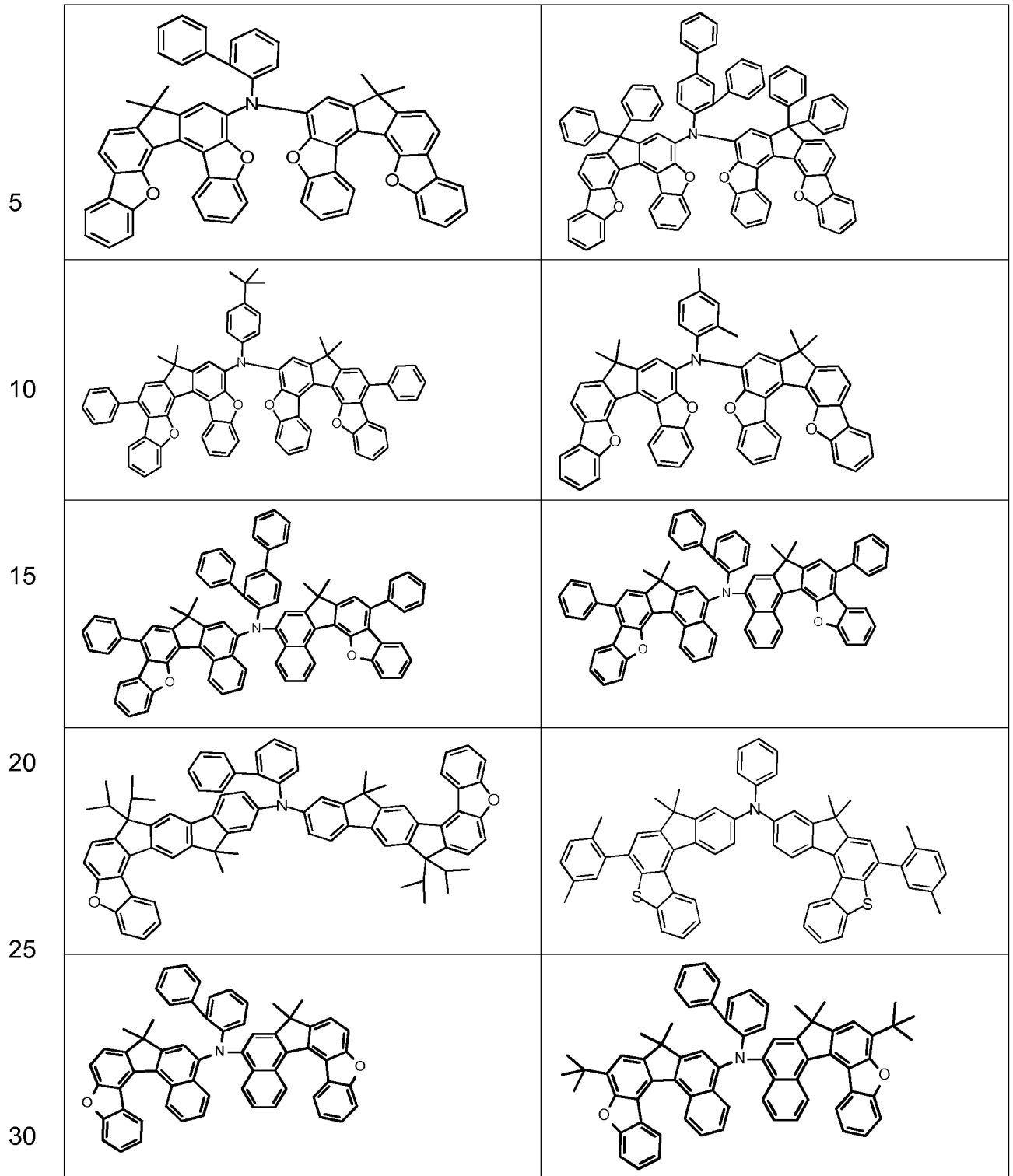


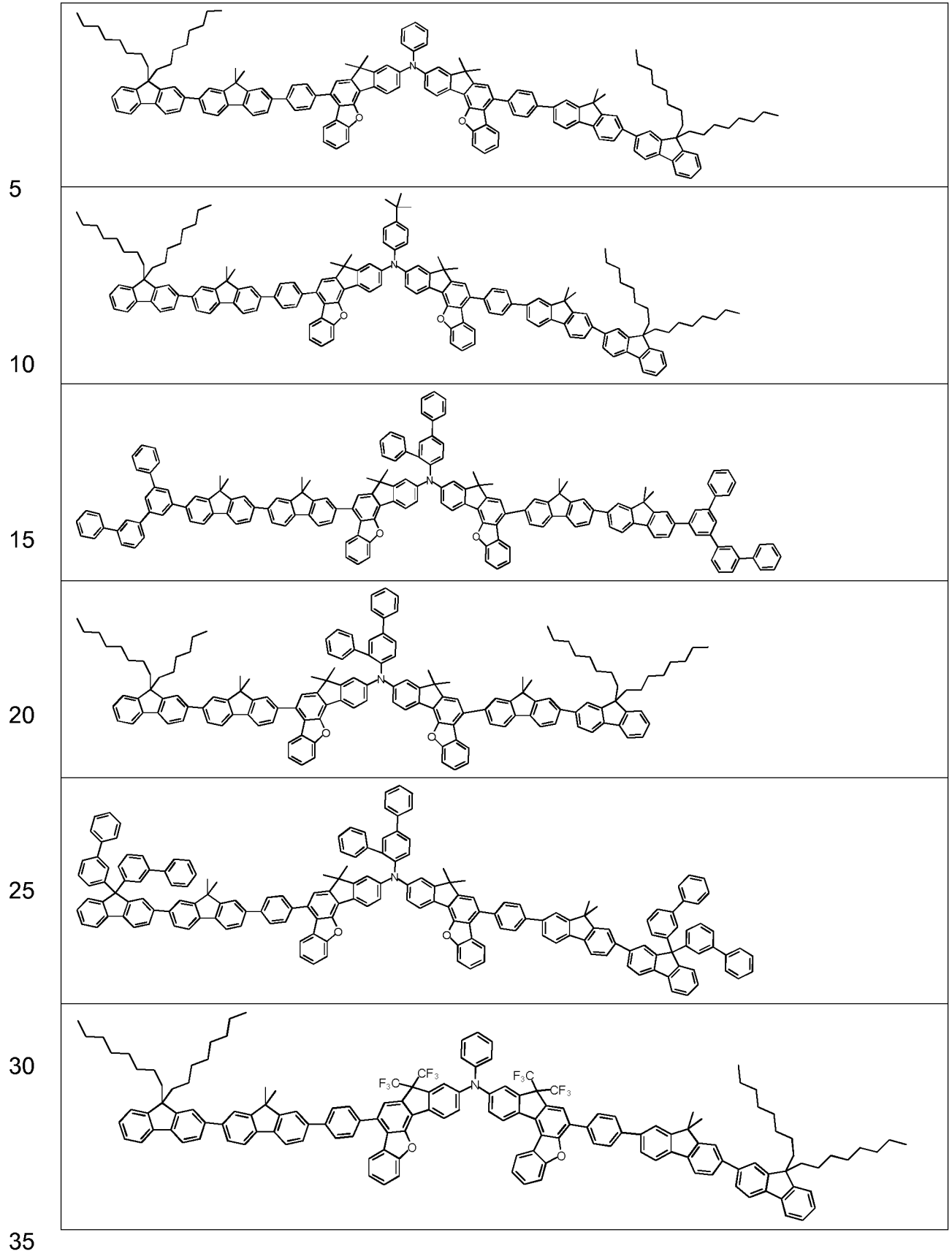
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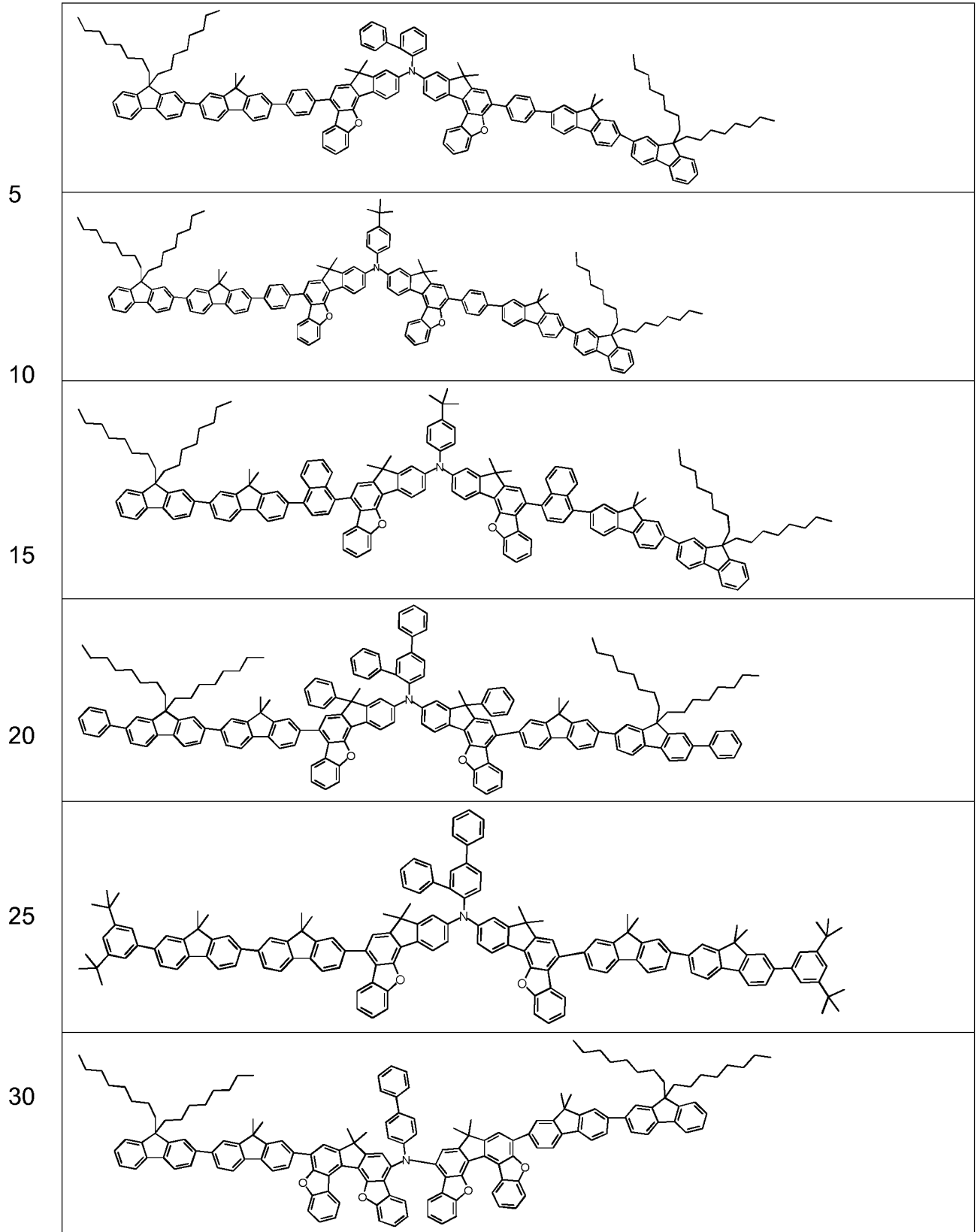


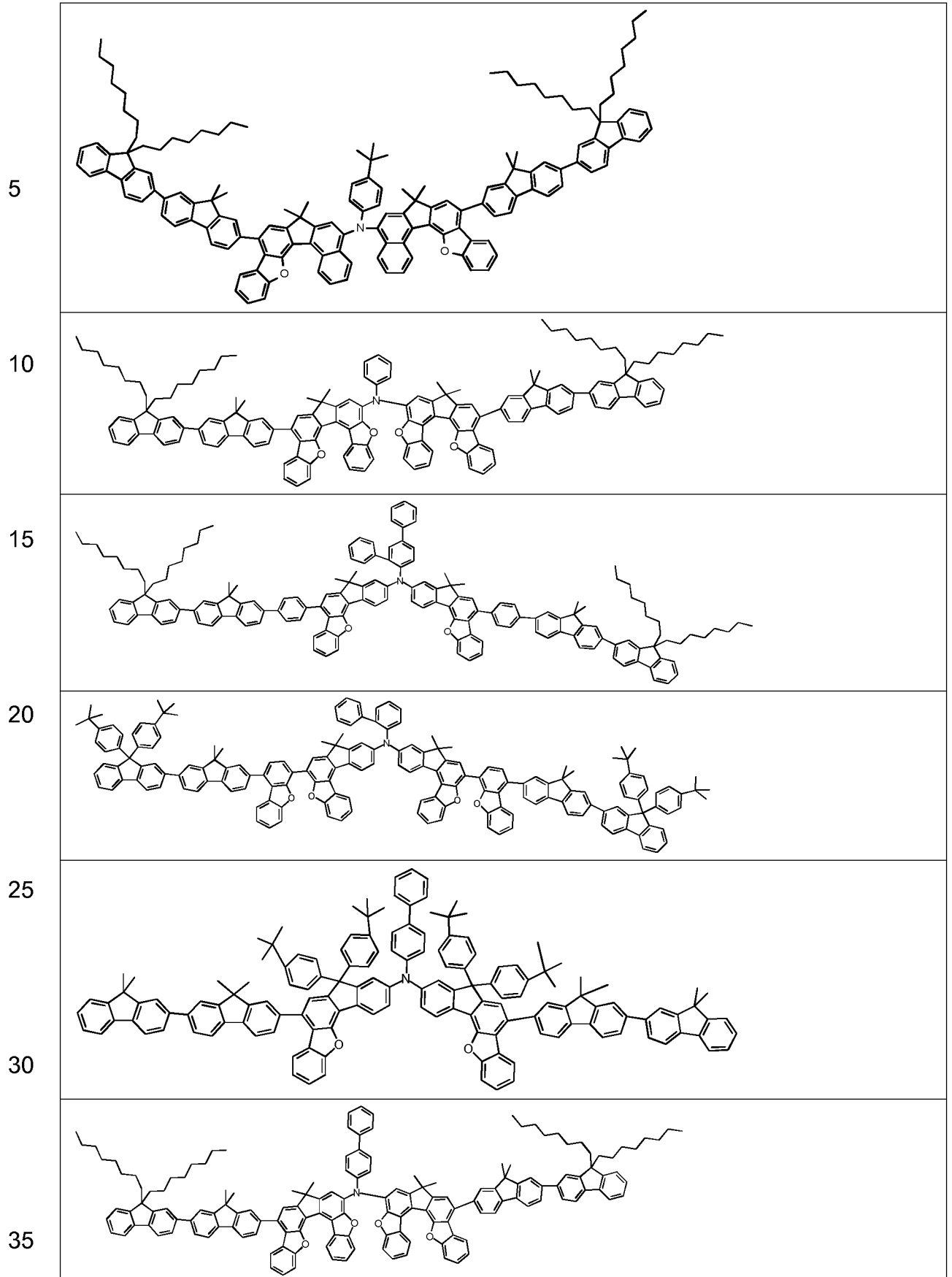
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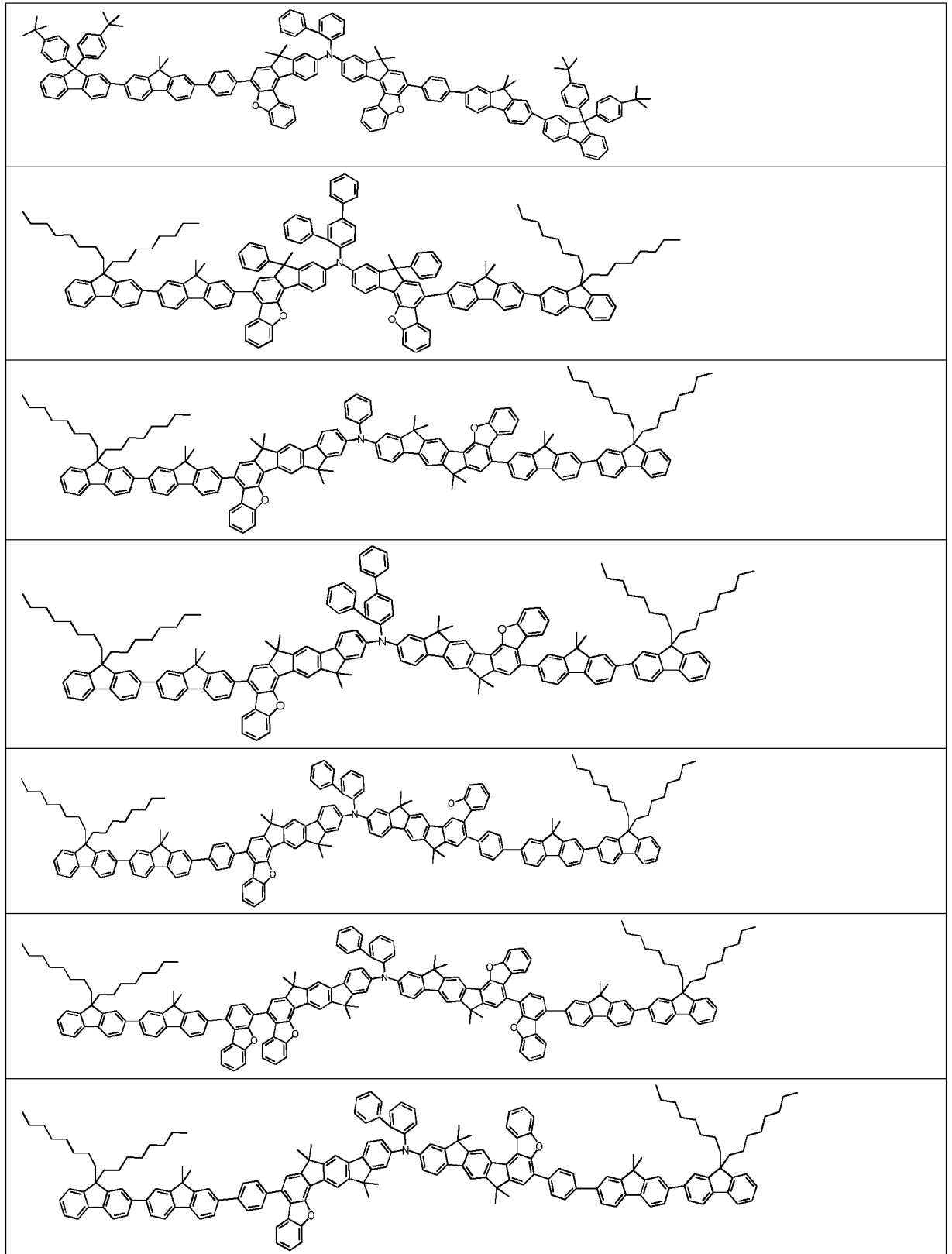
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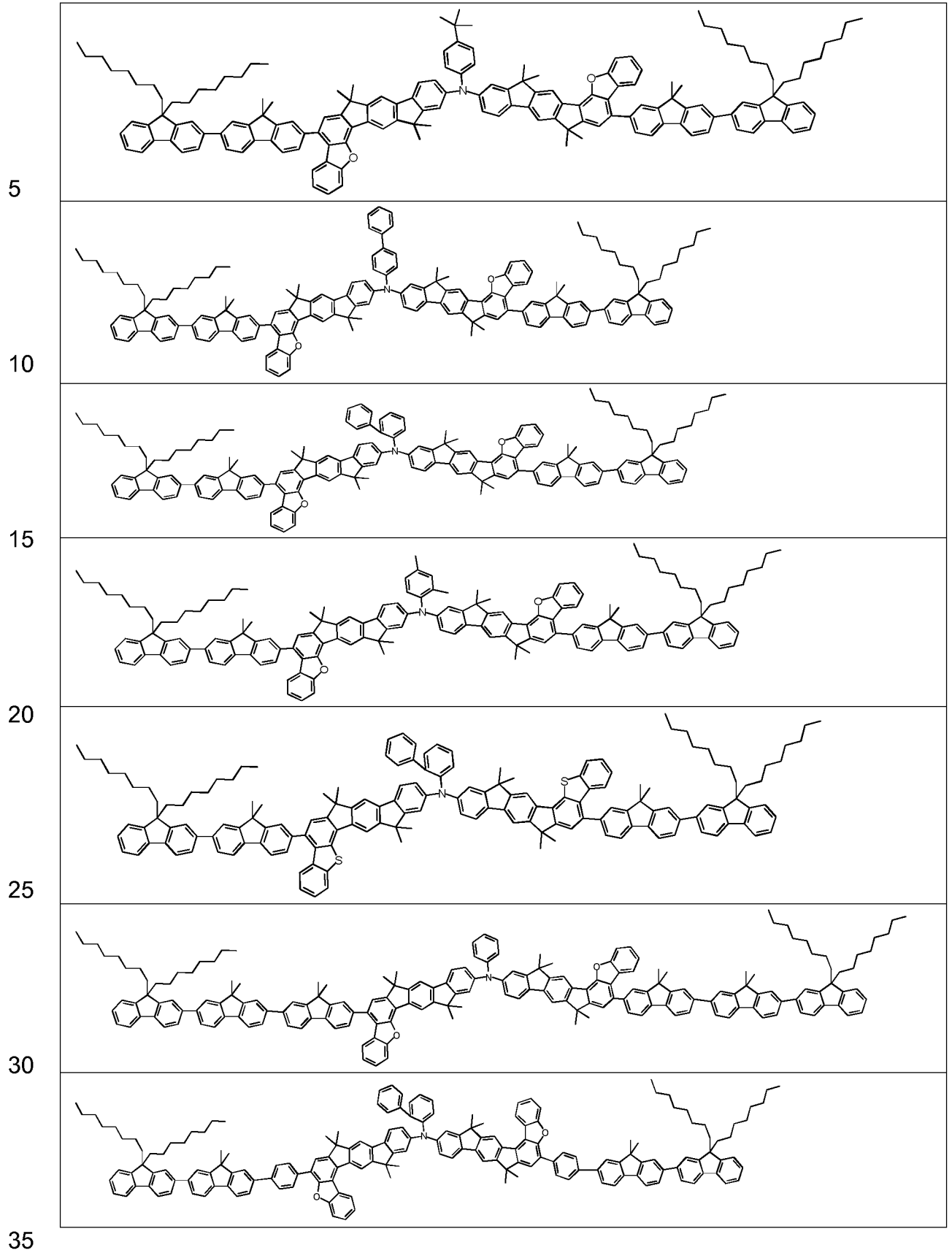




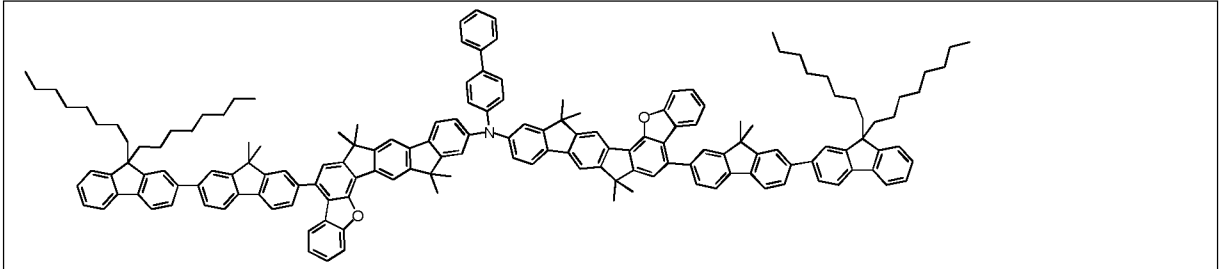




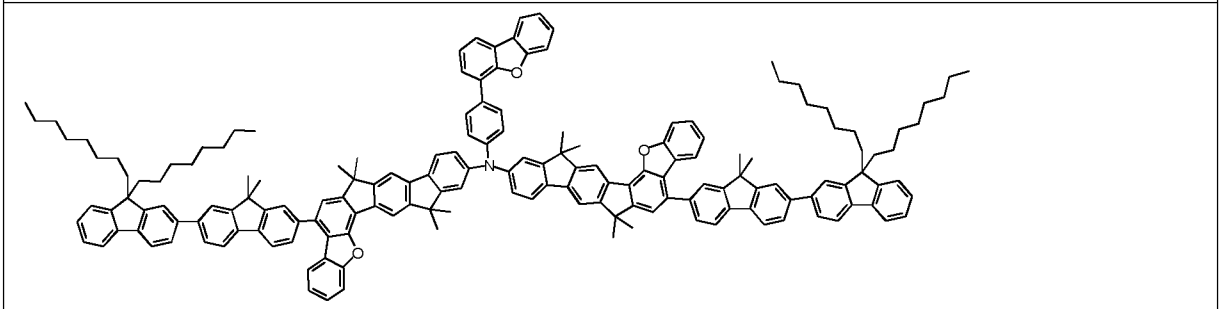




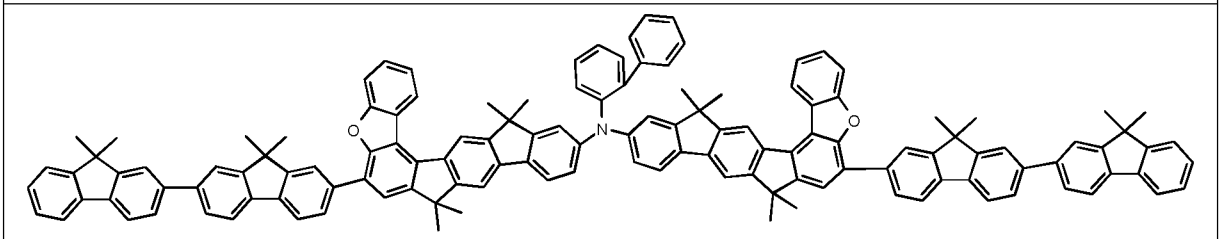
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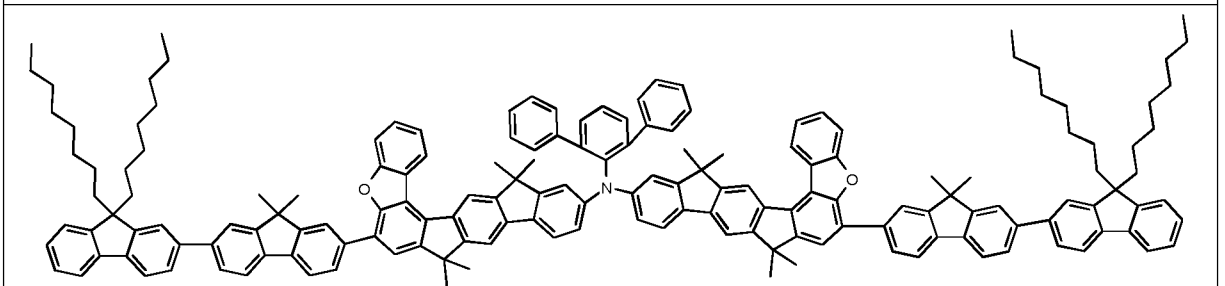
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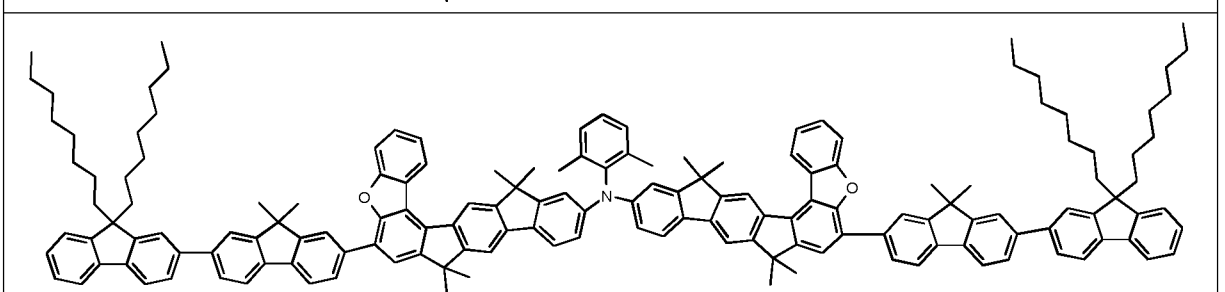
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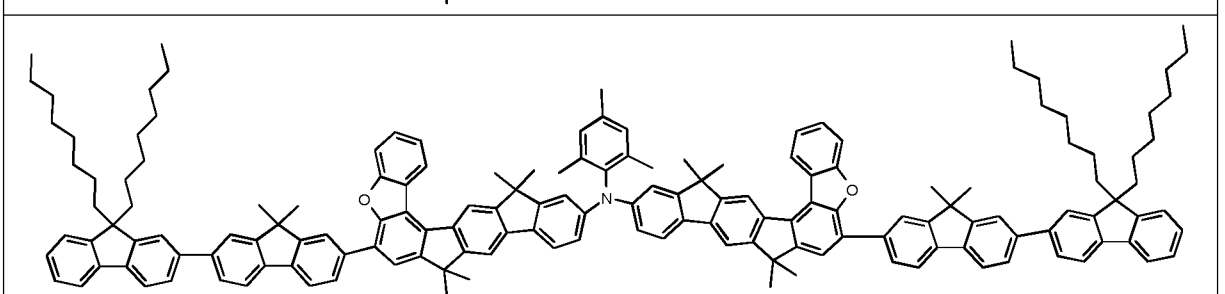
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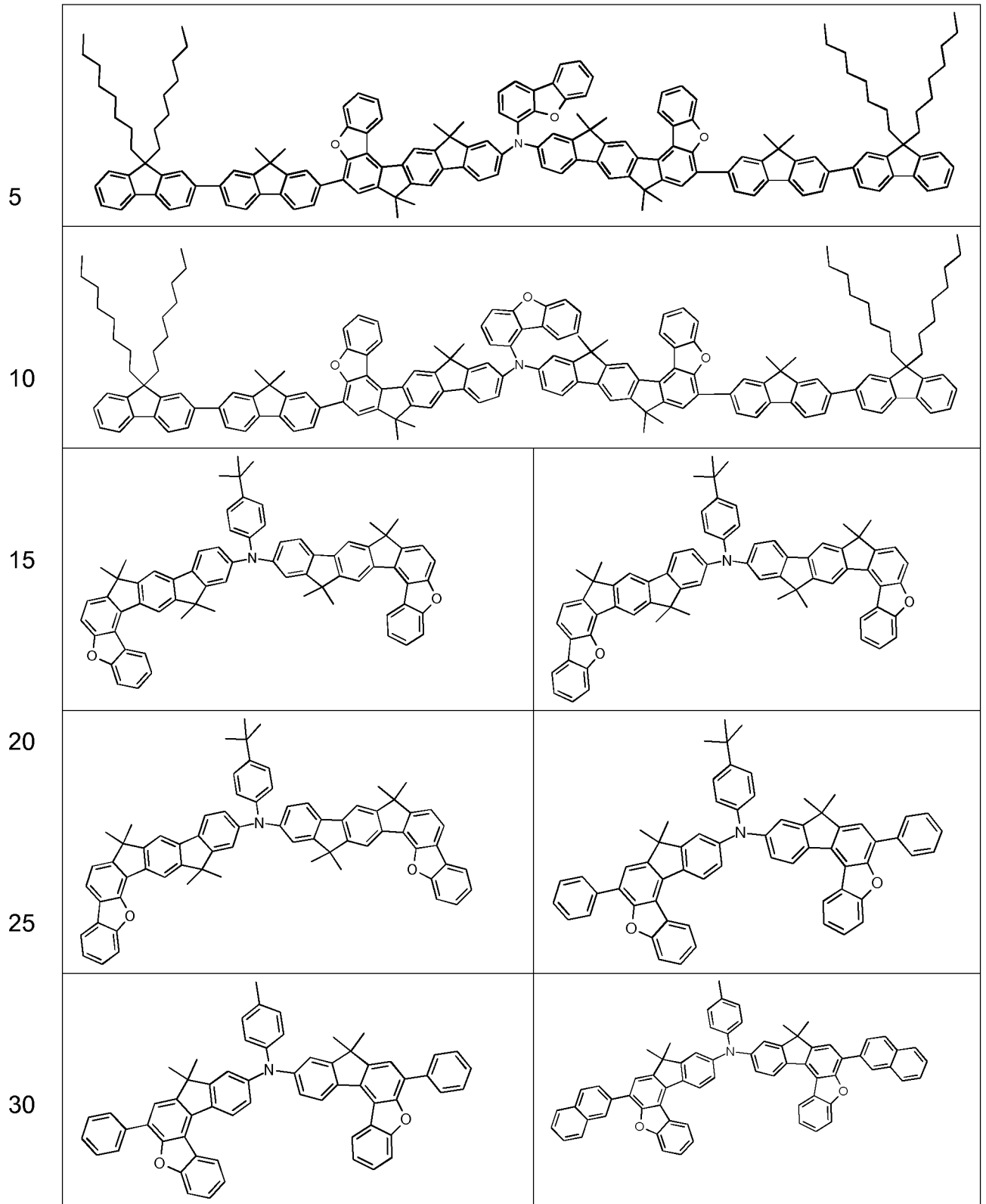
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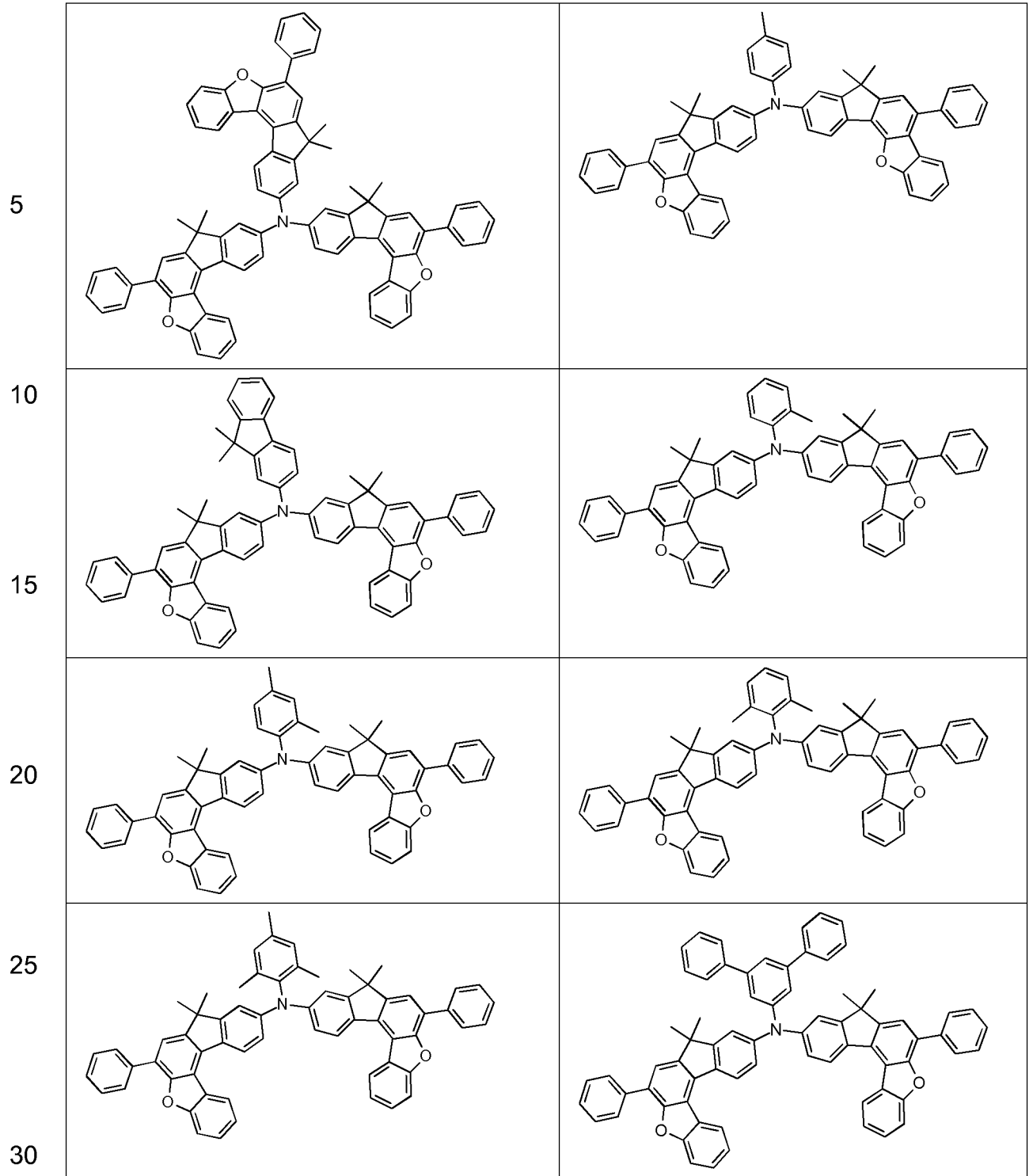
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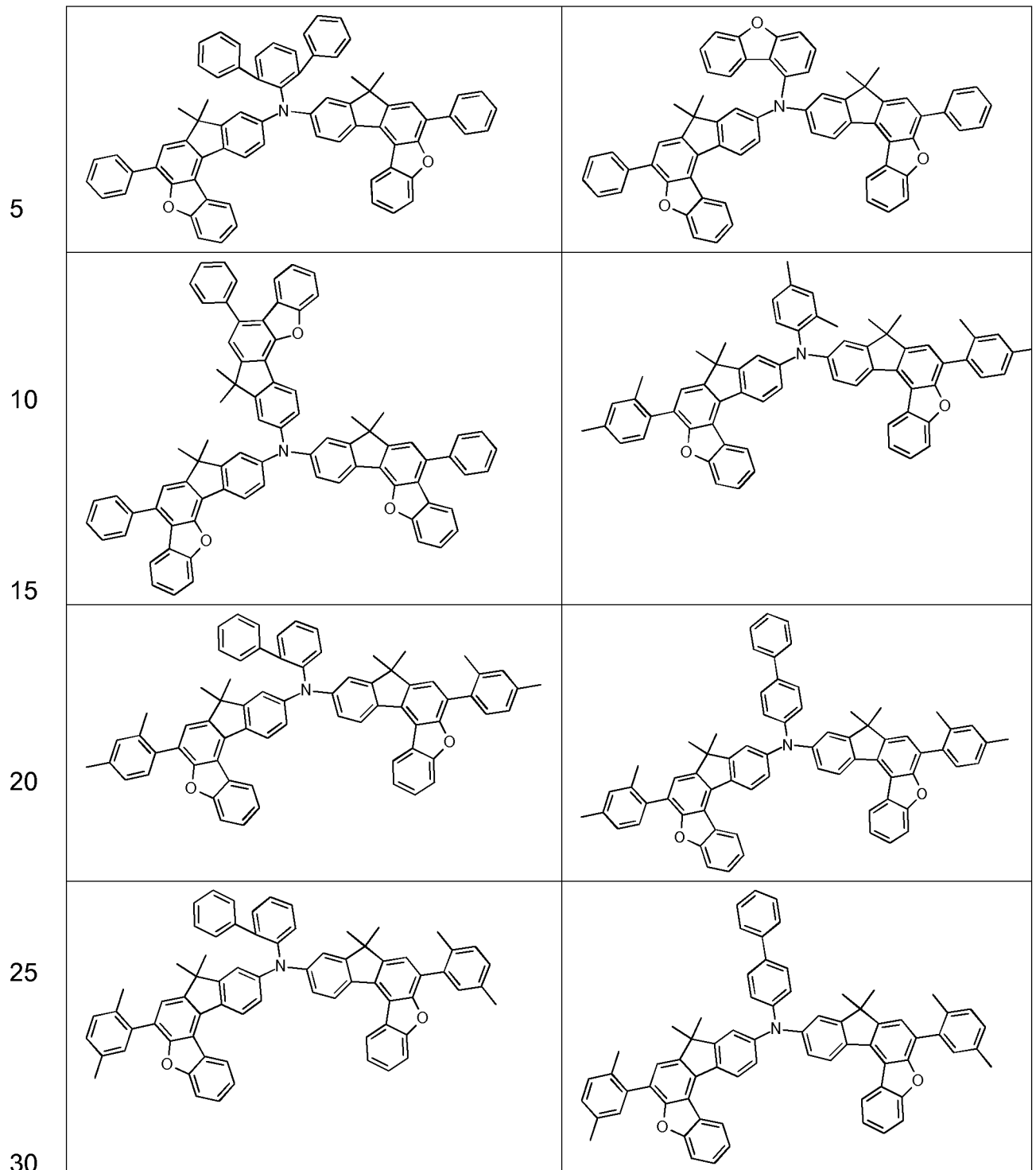


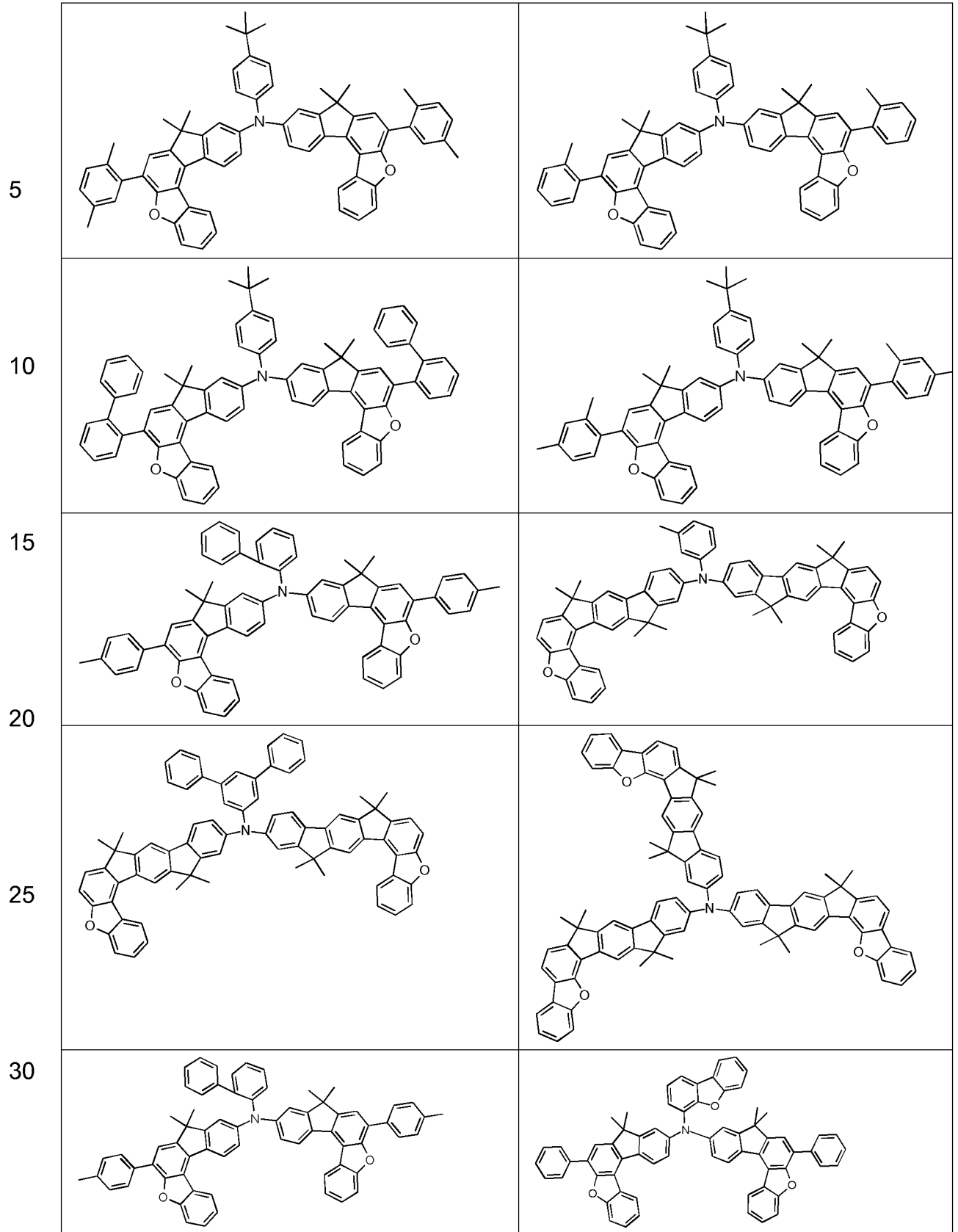
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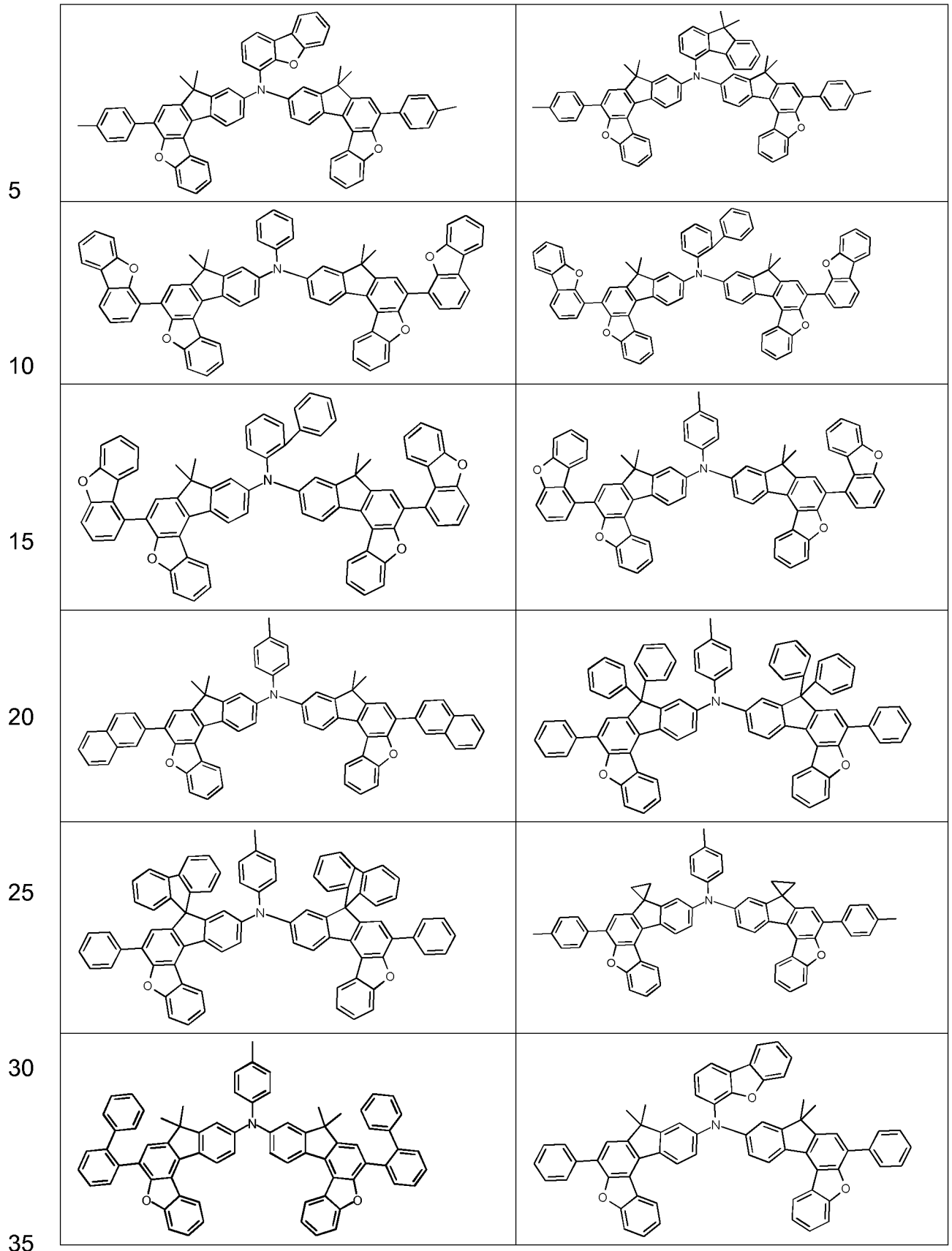
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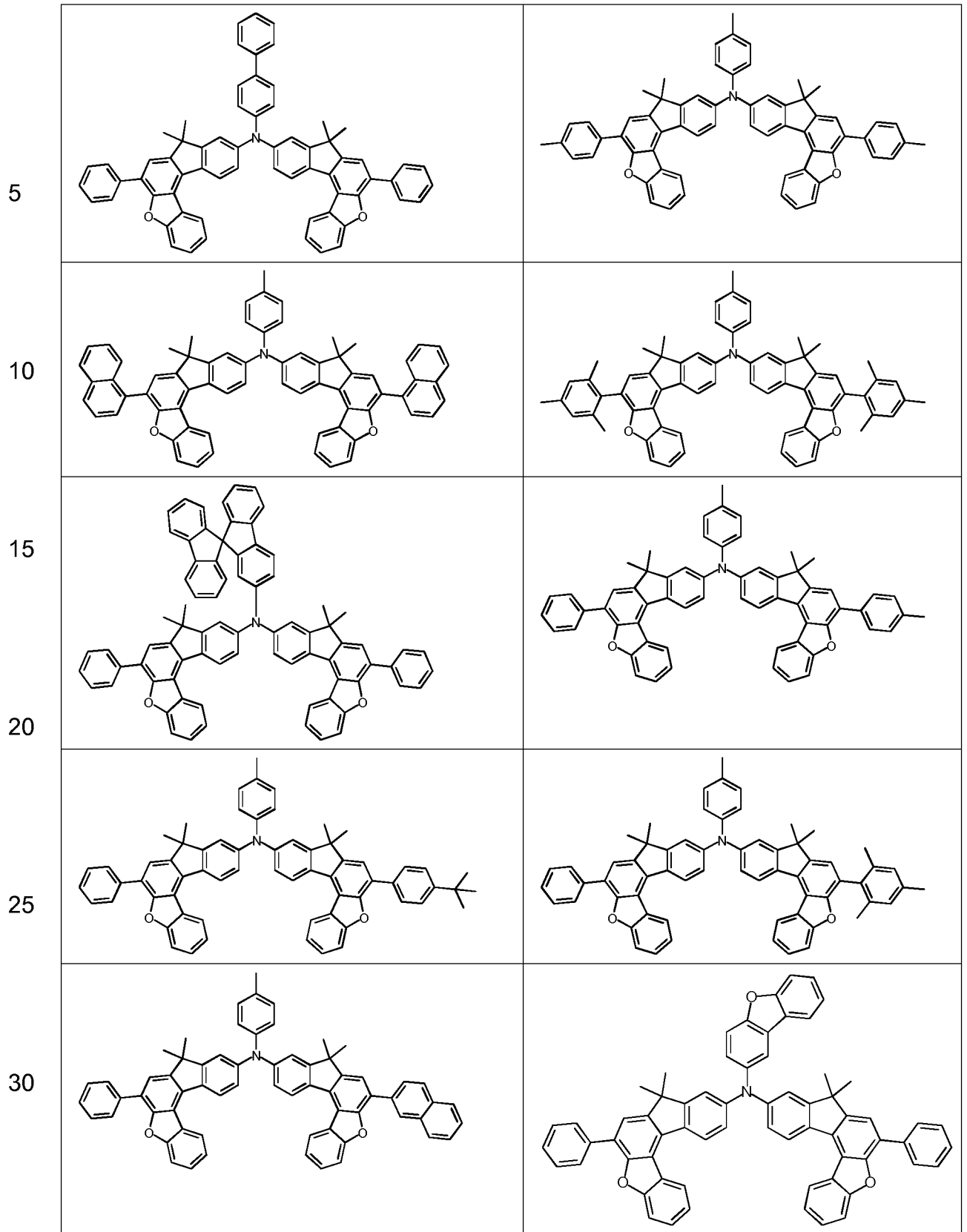




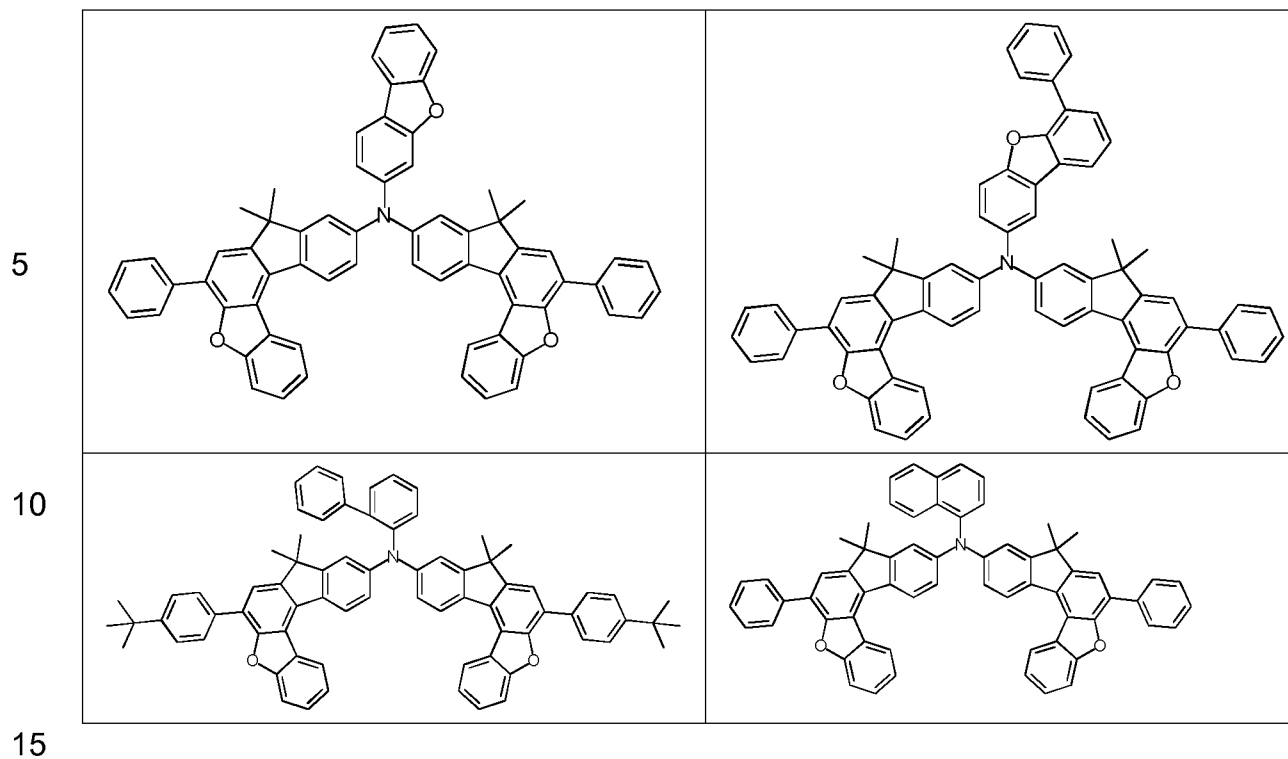


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The compounds according to the invention can be prepared by synthesis steps known to the person skilled in the art, such as, for example, bromination, Suzuki coupling, Ullmann coupling, Hartwig-Buchwald coupling, etc.

20 An example of a suitable synthesis process is depicted in general terms in Schemes 1 to 3 below.

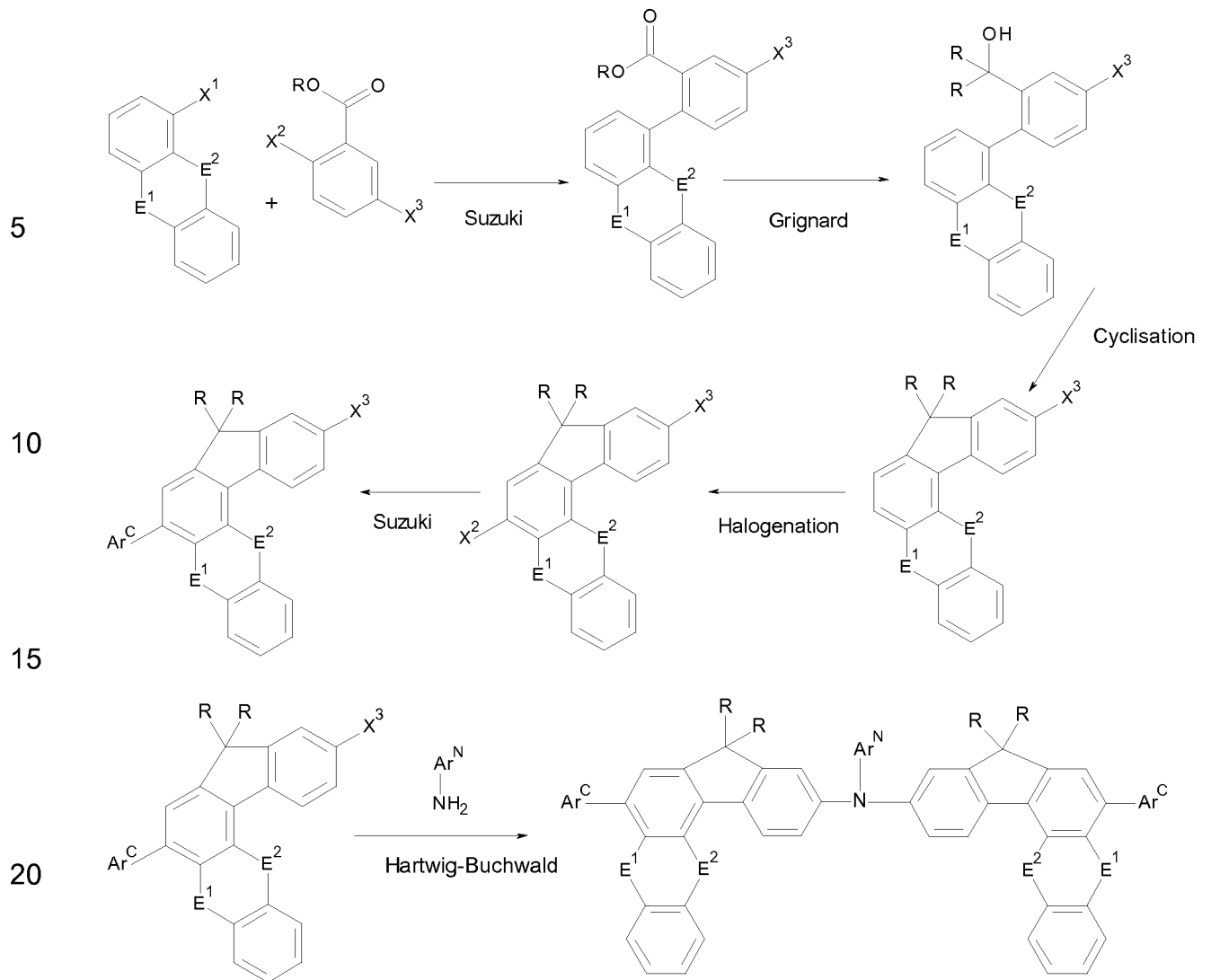
Scheme 1

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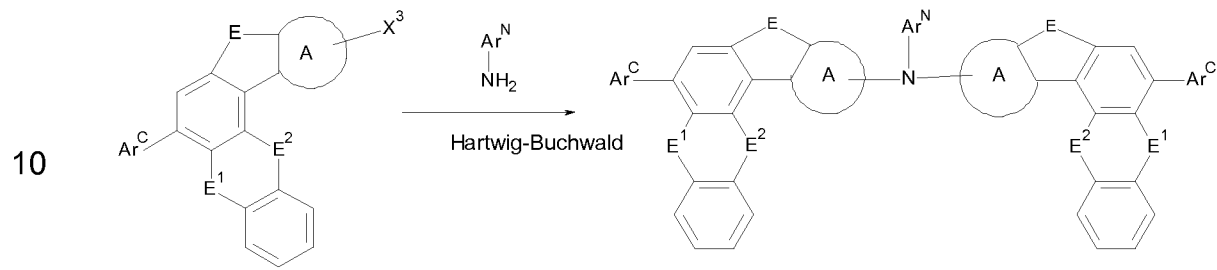
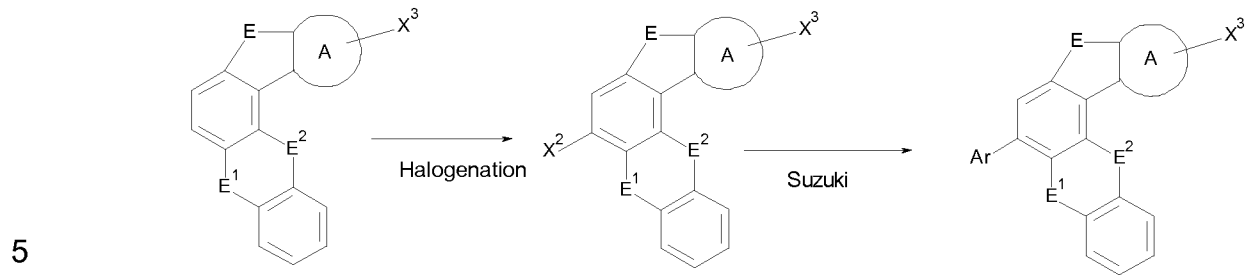
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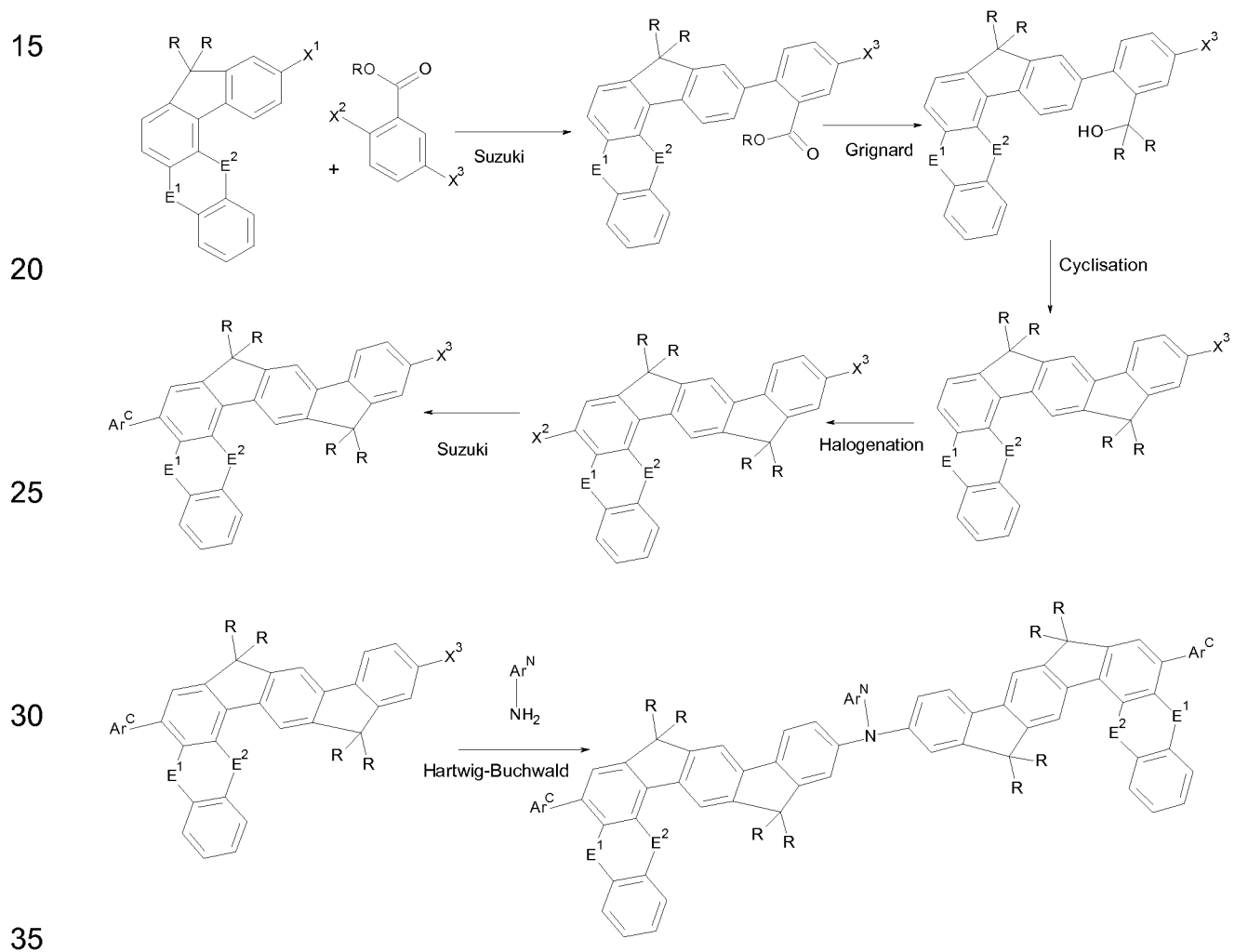


Scheme 2

- 75 -



Scheme 3

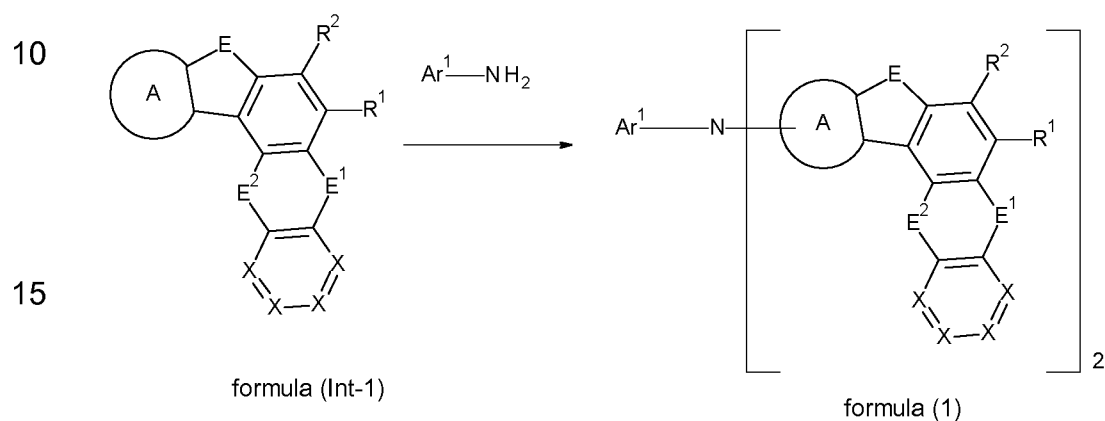


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In Schemes 1 to 3, the symbols E, E¹, E², R and the ring A have the same meaning as above, the symbols X¹, X² and X³ represent a leaving group (like an halogen or a boronic ester) and the symbols Ar^N or Ar^C represent aromatic or heteroaromatic ring systems.

5

The compounds of formula (1) may be synthesized as described above, where a group of formula (Int-1) reacts with an amine of formula Ar¹-NH₂ in order to obtain a group of formula (1):



20

The present invention therefore relates to a process for the synthesis of the compounds according to the invention, comprising a step where a group of formula (Int-1) reacts with an amine of formula Ar¹-NH₂.

25

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

30

Suitable and preferred solvents are, for example, toluene, anisole, o-, m- or p-xylene, methyl benzoate, mesitylene, tetralin, veratrol, THF, methyl-THF, THP, chlorobenzene, dioxane, phenoxytoluene, in particular 3-phenoxytoluene, (-)-fenchone, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, 1-methylnaphthalene, 2-methylbenzothiazole, 2-phenoxy-

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ethanol, 2-pyrrolidinone, 3-methylanisole, 4-methylanisole, 3,4-dimethyl-
anisole, 3,5-dimethylanisole, acetophenone, α -terpineol, benzothiazole,
butyl benzoate, cumene, cyclohexanol, cyclohexanone, cyclohexylbenzene,
decalin, dodecylbenzene, ethyl benzoate, indane, methyl benzoate, NMP,
5 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 di-
10 methyl ether, 2-isopropyl-naphthalene, pentylbenzene, hexylbenzene,
heptylbenzene, octylbenzene, 1,1-bis(3,4-dimethylphenyl)ethane or
mixtures of these solvents.

The present invention therefore furthermore relates to a formulation com-
15 prising a compound according to the invention and at least one further
compound. The further compound may be, for example, a solvent, in parti-
cular one of the above-mentioned solvents or a mixture of these solvents.
However, the further compound may also be at least one further organic or
20 inorganic compound which is likewise employed in the electronic device, for
example an emitting compound, in particular a phosphorescent dopant,
and/or a further matrix material. Suitable emitting compounds and further
matrix materials are indicated below in connection with the organic electro-
luminescent device. This further compound may also be polymeric.
25

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

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

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5 The present invention again furthermore relates to an electronic device comprising at least one of the compounds or mixtures according to the invention mentioned above. The preferences stated above for the compound also apply to the electronic devices.

10 The electronic device is preferably selected from the group consisting of organic electroluminescent devices (OLEDs, PLEDs), organic integrated circuits (O-ICs), organic field-effect transistors (O-FETs), organic thin-film transistors (O-TFTs), organic light-emitting transistors (O-LETs), organic solar cells (O-SCs), organic dye-sensitised solar cells, organic optical detectors, organic photoreceptors, organic field-quench devices (O-FQDs), light-emitting electrochemical cells (LECs), organic laser diodes (O-lasers)
15 and "organic plasmon emitting devices" (D. M. Koller *et al.*, *Nature Photonics* **2008**, 1-4), preferably organic electroluminescent devices (OLEDs, PLEDs), in particular phosphorescent OLEDs.

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

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where the three layers exhibit blue, green and orange or red emission (for the basic structure see, for example, WO 2005/011013). These can be fluorescent or phosphorescent emission layers or hybrid systems, in which fluorescent and phosphorescent emission layers are combined with one
5 another.

The compound according to the invention in accordance with the embodiments indicated above can be employed in various layers, depending on the precise structure and on the substitution. Preference is given to an
10 organic electroluminescent device comprising a compound of the formula (1) or in accordance with the preferred embodiments as fluorescent emitters, emitters showing TADF (Thermally Activated Delayed Fluorescence), matrix material for fluorescent emitters. Particularly
15 preferred is an organic electroluminescent device comprising a compound of the formula (1) or in accordance with the preferred embodiments as fluorescent emitters, more particularly blue-emitting fluorescent compound.

The compounds of formula (1) can also be employed in an electron-transport layer and/or in an electron-blocking or exciton-blocking layer and/or in a hole-transport layer, depending on the precise substitution. The preferred embodiments indicated above also apply to the use of the
20 materials in organic electronic devices.

The compound according to the invention is particularly suitable for use as blue-emitting emitter compound. The electronic device concerned may comprise a single emitting layer comprising the compound according to the
30 invention or it may comprise two or more emitting layers. The further emitting layers here may comprise one or more compounds according to the invention or alternatively other compounds.

If the compound according to the invention is employed as a fluorescent emitting compound in an emitting layer, it is preferably employed in
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- 80 -

combination with one or more matrix materials. A matrix material here is taken to mean a material which is present in the emitting layer, preferably as the principal component, and which does not emit light on operation of the device.

5

The proportion of the emitting compound in the mixture of the emitting layer is between 0.1 and 50.0%, preferably between 0.5 and 20.0%, particularly preferably between 1.0 and 10.0%. Correspondingly, the proportion of the matrix material or matrix materials is between 50.0 and 99.9%, preferably

10

between 80.0 and 99.5%, particularly preferably between 90.0 and 99.0%.

15

The specifications of the proportions in % are, for the purposes of the present application, taken to mean % by vol. if the compounds are applied from the gas phase and % by weight if the compounds are applied from solution.

20

Preferred matrix materials for use in combination with fluorescent emitting compounds are selected from the classes of the oligoarylenes (for example 2,2',7,7'-tetraphenylspirobifluorene in accordance with EP 676461 or dinaphthylanthracene), in particular the oligoarylenes containing condensed aromatic groups, the oligoarylenevinylens (for example DPVBi or spiro-DPVBi in accordance with EP 676461), the polypodal metal complexes (for example in accordance with WO 2004/081017), the hole-conducting compounds (for example in accordance with WO 2004/058911), the electron-conducting compounds, in particular ketones, phosphine oxides, sulfoxides, etc. (for example in accordance with WO 2005/084081 and WO 2005/084082), the atropisomers (for example in accordance with WO 2006/048268), the boronic acid derivatives (for example in accordance with WO 2006/117052) or the benzantracenes (for example in accordance with WO 2008/145239). Particularly preferred matrix materials are selected from the classes of the oligoarylenes, comprising naphthalene, anthracene, benzantracene and/or pyrene or atropisomers of these compounds, the oligoarylenevinylens, the ketones, the phosphine oxides and the

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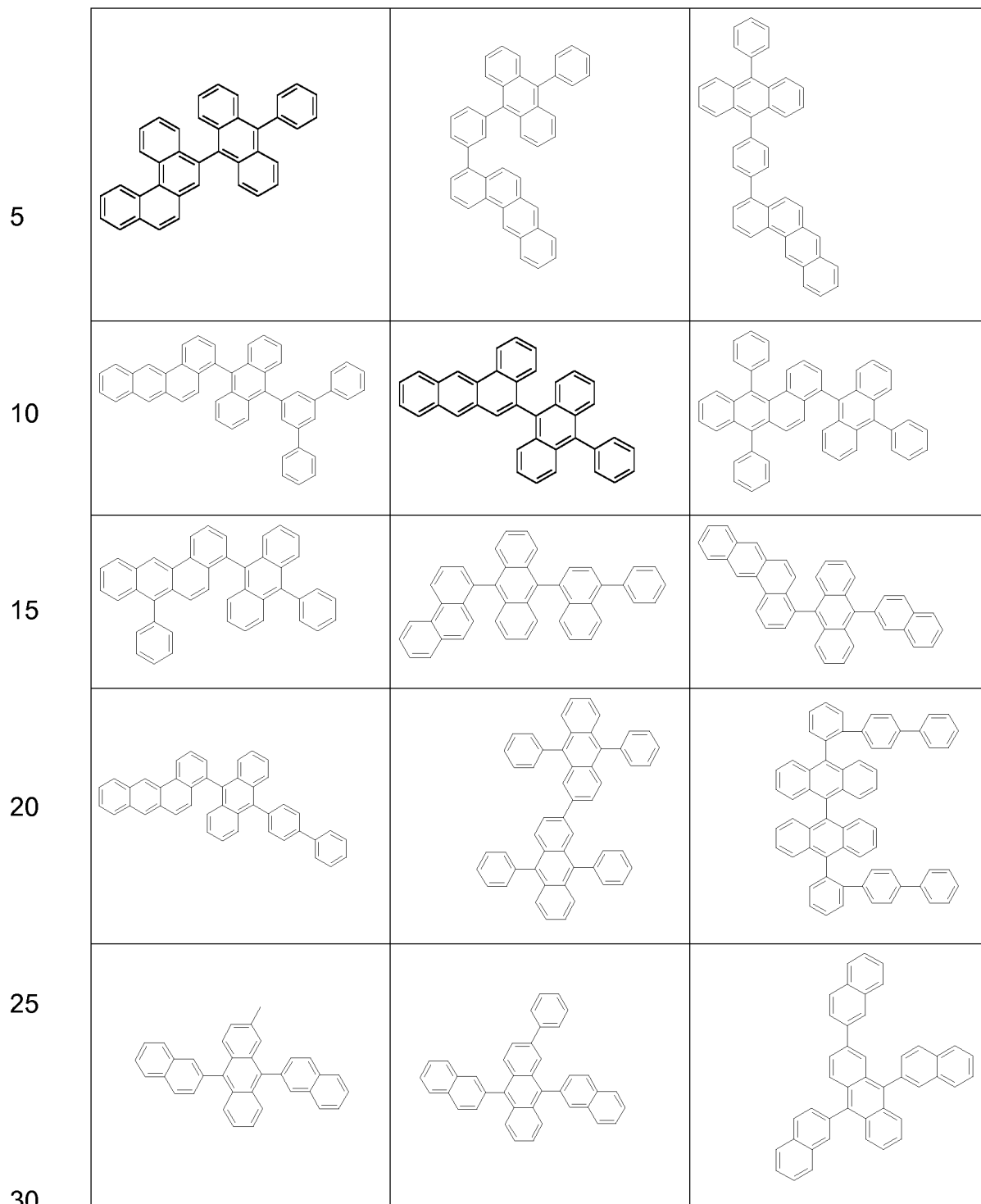
- 81 -

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

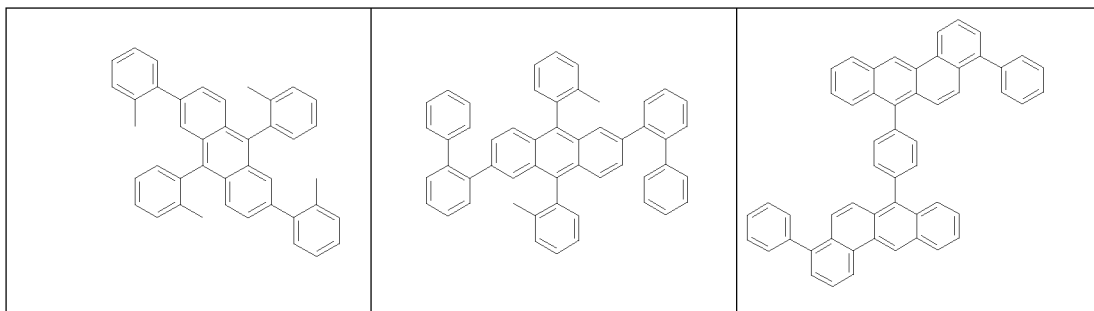
10 Particularly preferred matrix materials for use in combination with the compounds of the formula (1) in the emitting layer are depicted in the following table.

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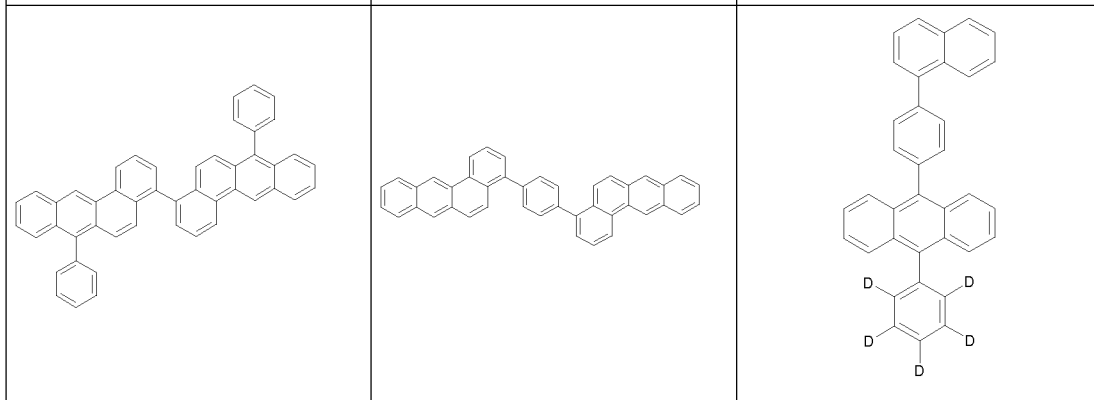
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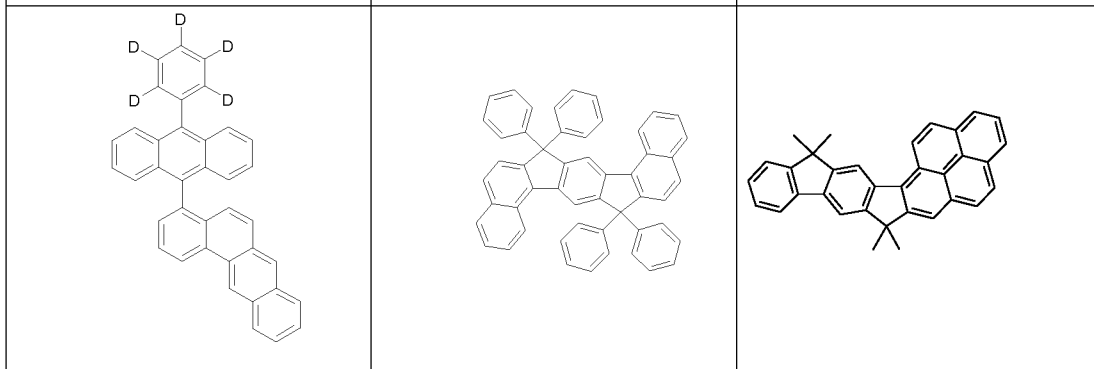
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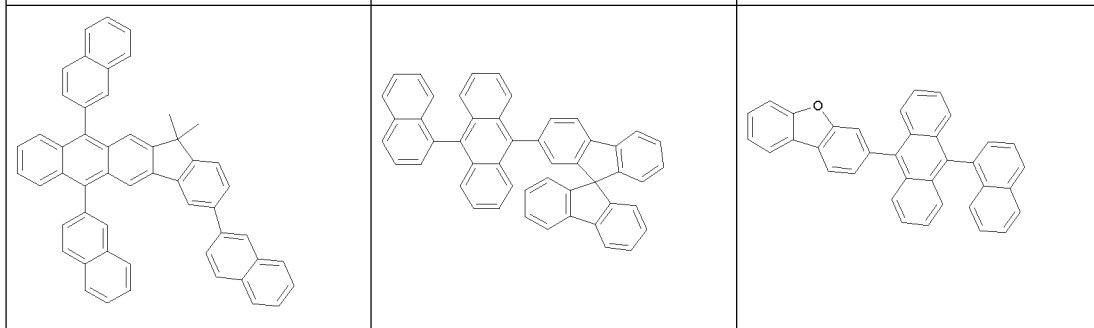
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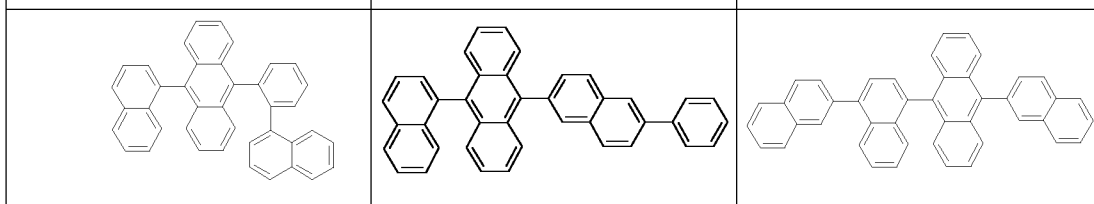
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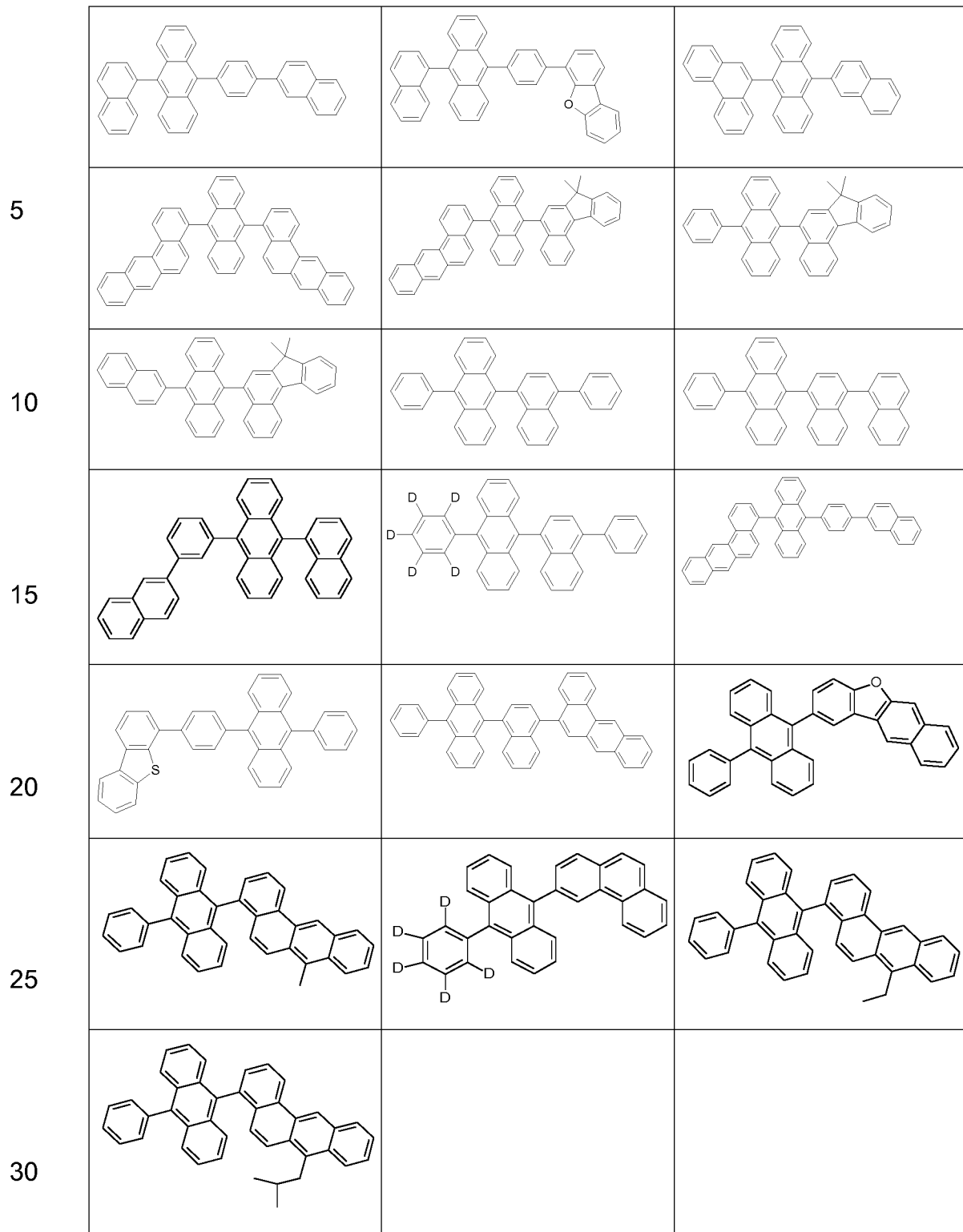


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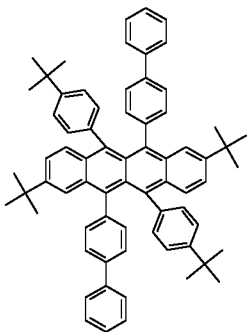
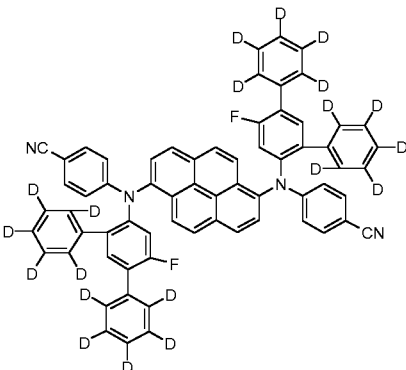
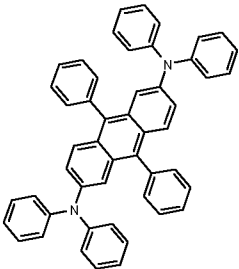
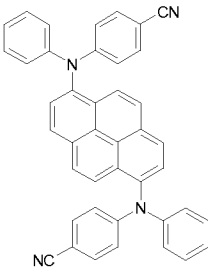
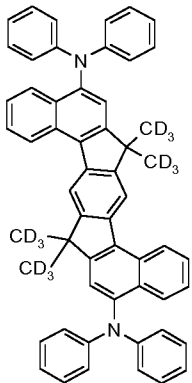
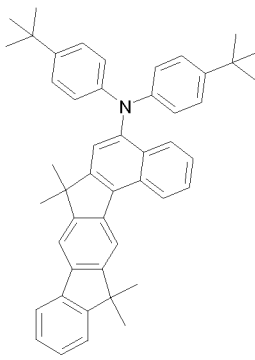
If the compound according to the invention is employed as a fluorescent emitting compound in an emitting layer, it may be employed in combination with one or more other fluorescent emitting compounds.

Preferred fluorescent emitters, besides the compounds according to the invention, are selected from the class of the arylamines. An arylamine in the sense of this invention is taken to mean a compound which contains three substituted or unsubstituted aromatic or heteroaromatic ring systems bonded directly to the nitrogen. At least one of these aromatic or heteroaromatic ring systems is preferably a condensed ring system, particularly preferably having at least 14 aromatic ring atoms. Preferred examples thereof are aromatic anthracenamines, aromatic anthracenediamines, aromatic pyrenamines, aromatic pyrenediamines, aromatic chrysenamines or aromatic chrysenediamines. An aromatic anthracenamine is taken to mean a compound in which one diarylamino group is bonded directly to an anthracene group, preferably in the 9-position. An aromatic anthracenediamine is taken to mean a compound in which two diarylamino groups are bonded directly to an anthracene group, preferably in the 9,10-position. Aromatic pyrenamines, pyrenediamines, chrysenamines and chrysenediamines are defined analogously thereto, where the diarylamino groups are preferably bonded to the pyrene in the 1-position or in the 1,6-position. Further preferred emitters are indenofluorenamines or indenofluorenediamines, for example in accordance with WO 2006/108497 or WO 2006/122630, benzoindenofluorenamines or benzoindenofluorenediamines, for example in accordance with WO 2008/006449, and dibenzoindenofluorenamines or dibenzoindenofluorenediamines, for example in accordance with WO 2007/140847, and the indenofluorene derivatives containing condensed aryl groups which are disclosed in WO 2010/012328. Still further preferred emitters are benzanthracene derivatives as disclosed in WO 2015/158409, anthracene derivatives as disclosed in WO 2017/036573, fluorene dimers like in WO 2016/150544 or phenoxazine derivatives as disclosed in WO 2017/028940 and WO 2017/028941. Preference is likewise given to the pyrenarylamines disclosed in WO 2012/048780 and WO 2013/185871. Preference is likewise given to the benzoindenofluorenamines disclosed in WO 2014/037077, the benzofluorenamines disclosed in

WO 2014/106522 and the indenofluorenes disclosed in WO 2014/111269 or WO 2017/036574.

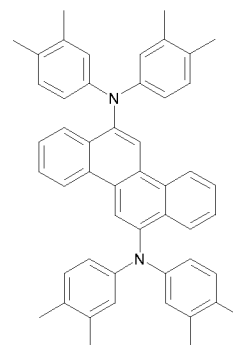
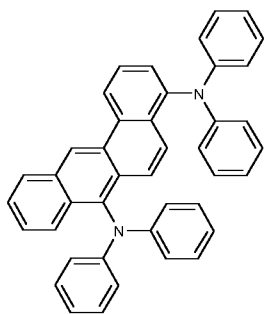
5 Examples of preferred fluorescent emitting compounds, besides the compounds according to the invention, which can be used in combination with the compounds of the invention in an emitting layer or which can be used in another emitting layer of the same device are depicted in the following table:

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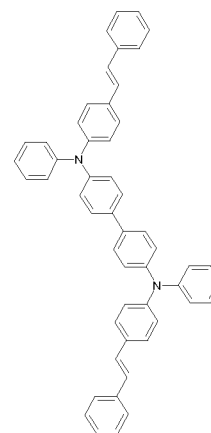
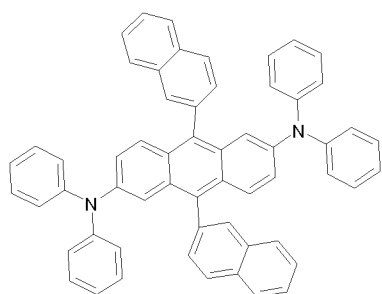
	
	
	

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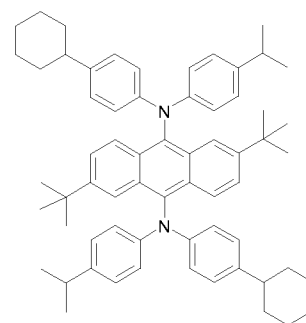
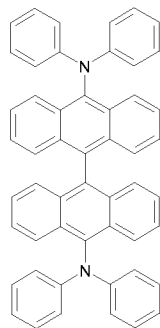


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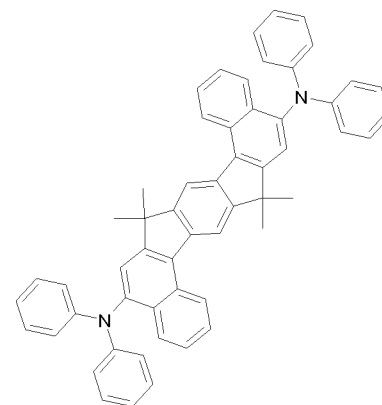
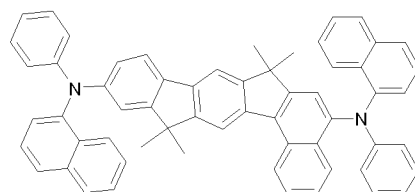
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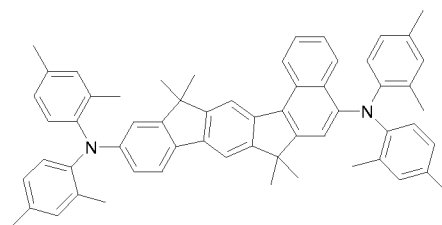
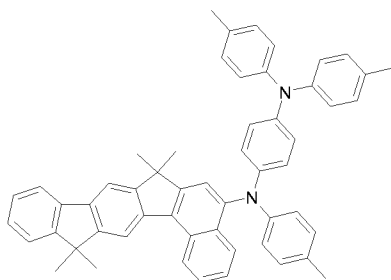
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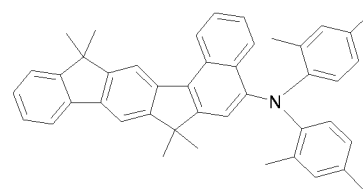
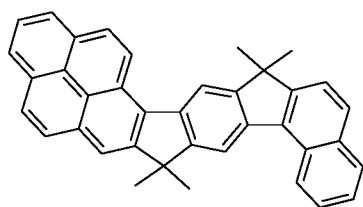


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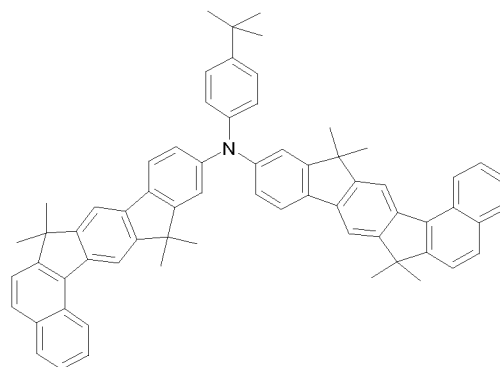
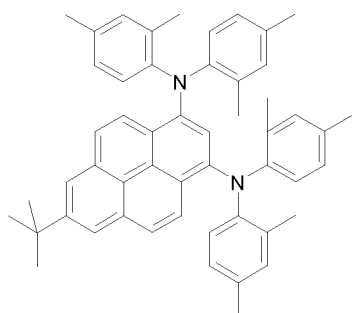
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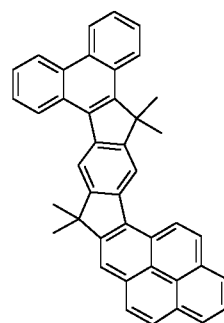
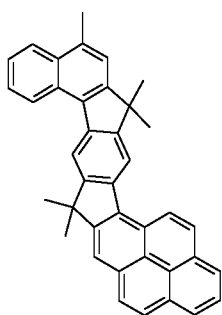
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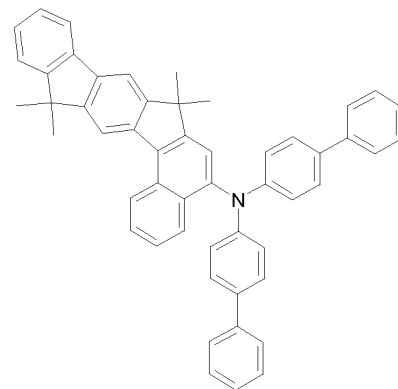
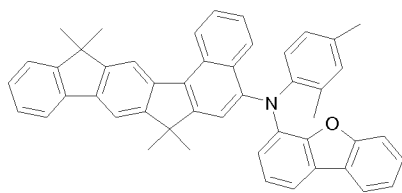


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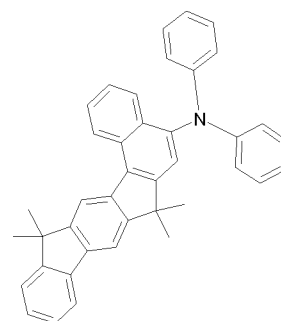
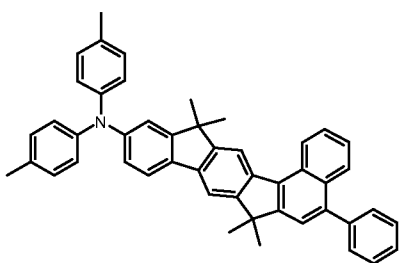
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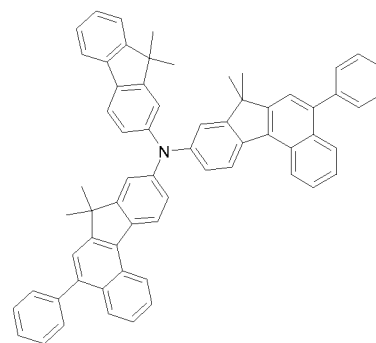
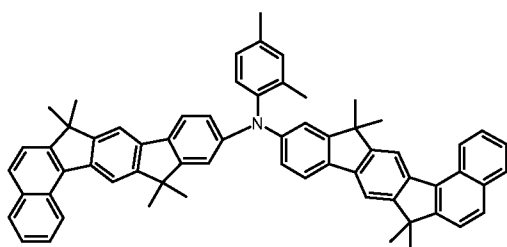
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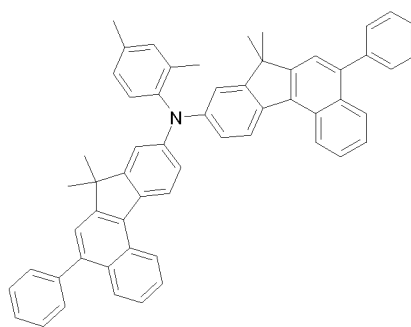
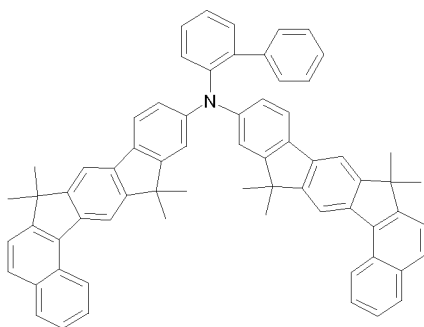


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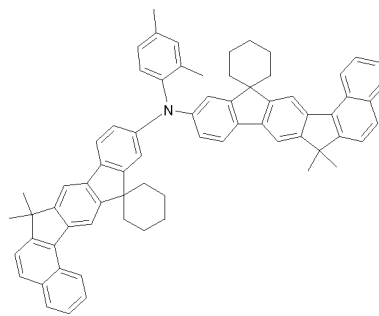
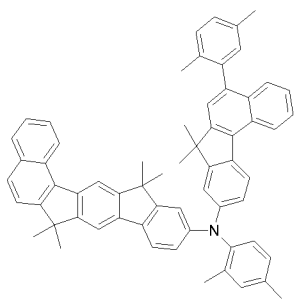
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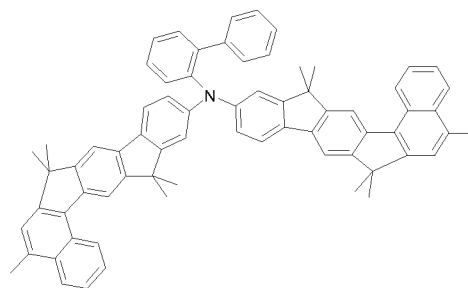
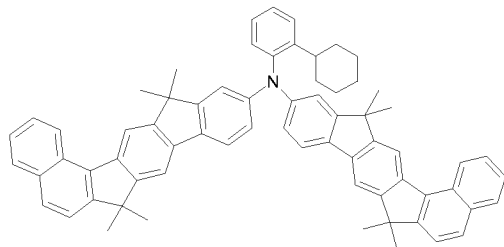
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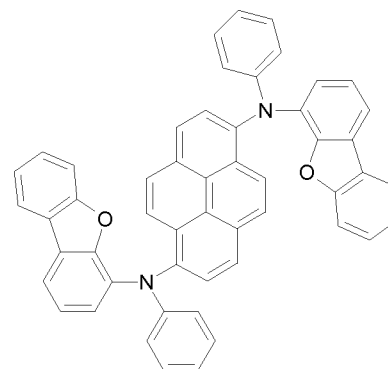
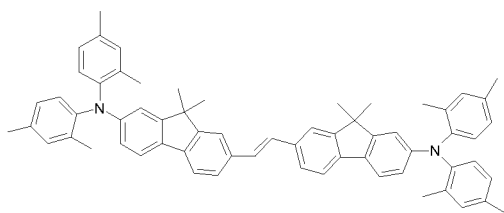
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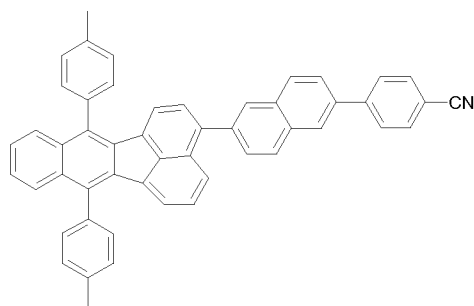
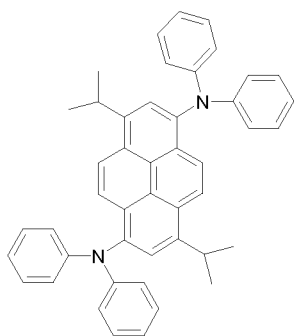


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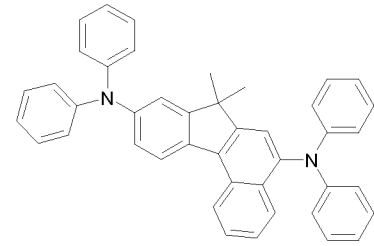
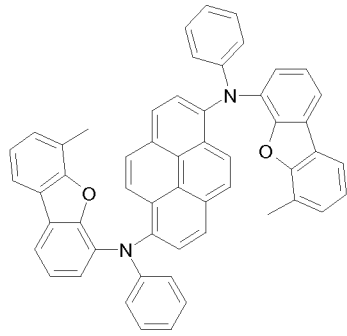
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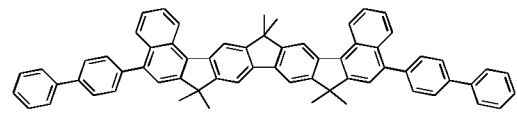
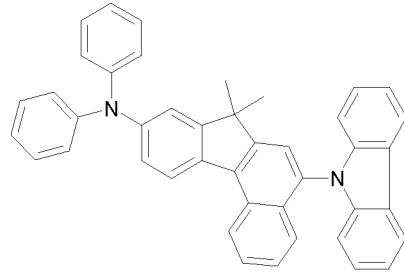
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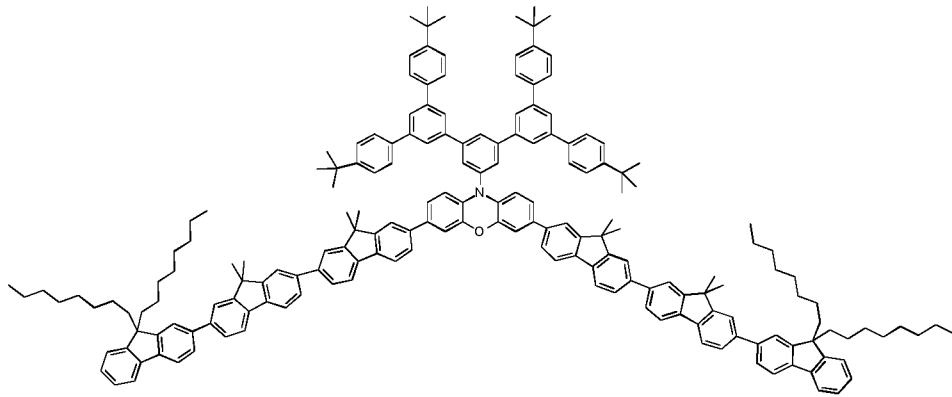
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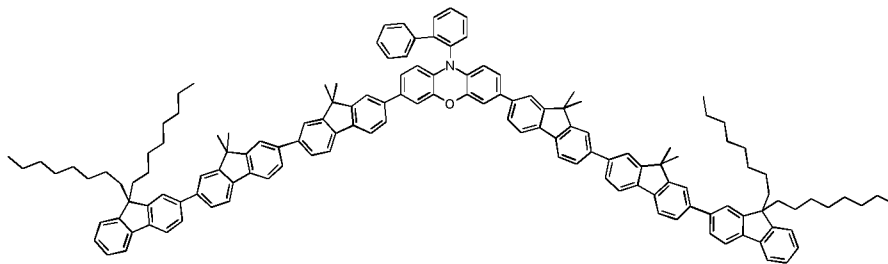


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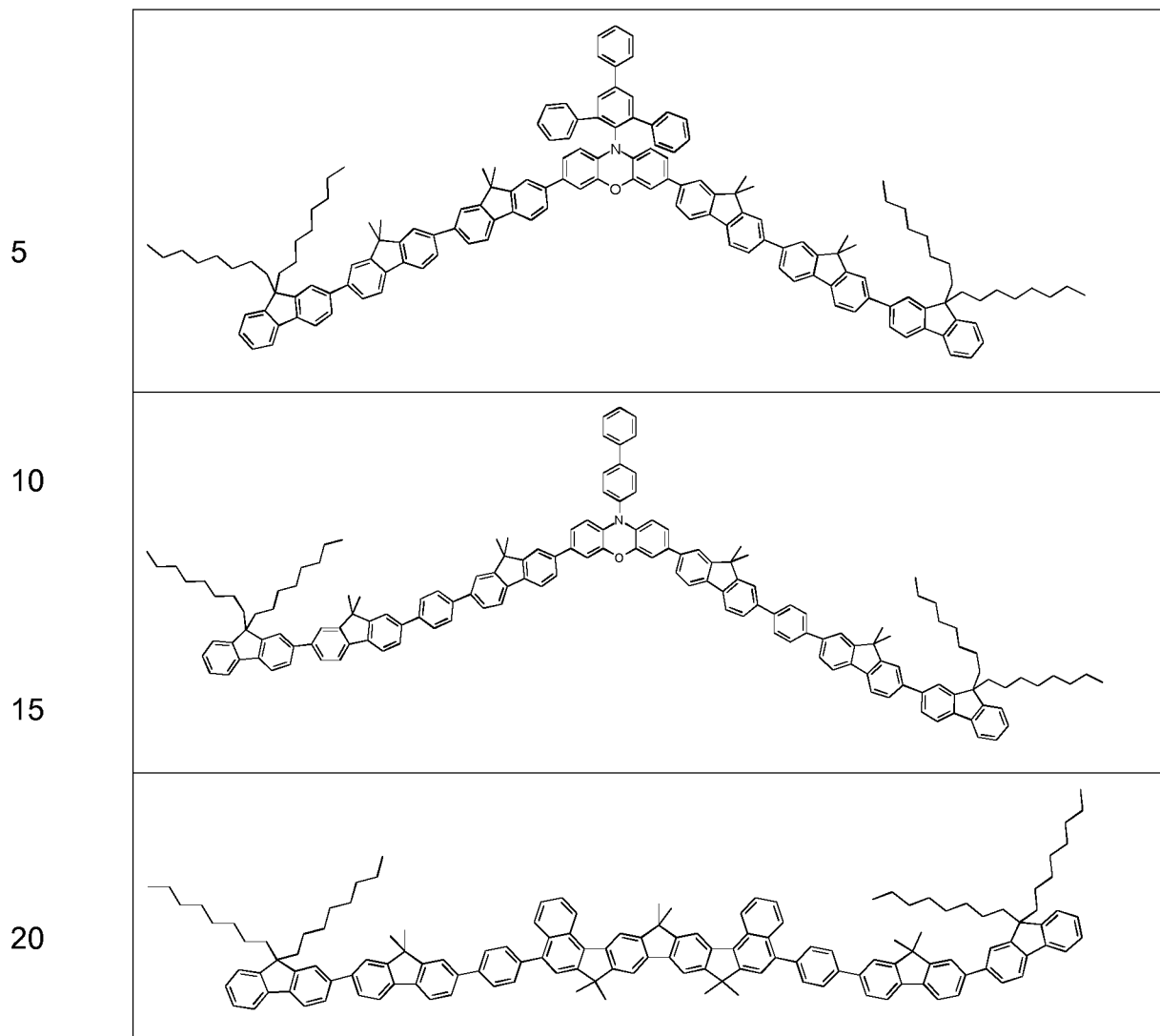
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The compounds according to the invention can also be employed in other layers, for example as hole-transport materials in a hole-injection or hole-transport layer or electron-blocking layer or as matrix materials in an emitting layer, preferably as matrix materials for phosphorescent emitters.

If the compound of the formula (I) is employed as hole-transport material in a hole-transport layer, a hole-injection layer or an electron-blocking layer, the compound can be employed as pure material, i.e. in a proportion of 100%, in the hole-transport layer, or it can be employed in combination with one or more further compounds. According to a preferred embodiment, the organic layer comprising the compound of the formula (I) then additionally

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comprises one or more p-dopants. The p-dopants employed in accordance with the present invention are preferably organic electron-acceptor compounds which are able to oxidise one or more of the other compounds of the mixture.

5

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 102007031220, US 8044390, US 8057712, WO 2009/003455, WO 2010/094378, WO 2011/120709, US 2010/0096600 and WO 2012/095143.

10

If the compound of the formula (I) is employed as matrix material in combination with a phosphorescent emitter in an emitting layer, the phosphorescent emitter is preferably selected from the classes and embodiments of phosphorescent emitters indicated below. Furthermore, one or more further matrix materials are preferably present in the emitting layer in this case.

15

20

So-called mixed-matrix systems of this type preferably comprise two or three different matrix materials, particularly preferably two different matrix materials. It is preferred here for one of the two materials to be a material having hole-transporting properties and for the other material to be a material having electron-transporting properties. The compound of the formula (I) is preferably the material having hole-transporting properties.

25

However, the desired electron-transporting and hole-transporting properties of the mixed-matrix components may also be combined mainly or completely in a single mixed-matrix component, where the further mixed-matrix component or components satisfy other functions. The two different matrix materials may be present here in a ratio of 1:50 to 1:1, preferably 1:20 to 1:1, particularly preferably 1:10 to 1:1 and very particularly prefera-

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bly 1:4 to 1:1. Mixed-matrix systems are preferably employed in phosphorescent organic electroluminescent devices. Further details on mixed-matrix systems are contained, inter alia, in the application WO 2010/108579.

5 Particularly suitable matrix materials which can be used as matrix components of a mixed-matrix system in combination with the compounds according to the invention are selected from the preferred matrix materials for phosphorescent emitters indicated below or the preferred matrix materials for fluorescent emitters, depending on what type of emitter compound is
10 employed in the mixed-matrix system.

Generally preferred classes of material for use as corresponding functional materials in the organic electroluminescent devices according to the invention are indicated below.
15

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

For the purposes of the present invention, all luminescent iridium, platinum or copper complexes are regarded as phosphorescent compounds.
30

Examples of the phosphorescent emitters described above are revealed by the applications WO 2000/70655, WO 2001/41512, WO 2002/02714, WO 2002/15645, EP 1191613, EP 1191612, EP 1191614, WO 2005/
35 033244, WO 2005/019373 and US 2005/0258742. In general, all phospho-

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rescent complexes as used in accordance with the prior art for phosphorescent OLEDs and as are known to the person skilled in the art in the area of organic electroluminescent devices are suitable for use in the devices according to the invention. The person skilled in the art will also be able to employ further phosphorescent complexes without inventive step in combination with the compounds according to the invention in OLEDs.

Preferred matrix materials for phosphorescent emitters are aromatic ketones, aromatic phosphine oxides or aromatic sulfoxides or sulfones, for example in accordance with WO 2004/013080, WO 2004/093207, WO 2006/005627 or WO 2010/006680, triarylamines, carbazole derivatives, for example CBP (N,N-biscarbazolylbiphenyl) or the carbazole derivatives disclosed in WO 2005/039246, US 2005/0069729, JP 2004/288381, EP 1205527 or WO 2008/086851, indolocarbazole derivatives, for example in accordance with WO 2007/063754 or WO 2008/056746, indenocarbazole derivatives, for example in accordance with WO 2010/136109, WO 2011/000455 or WO 2013/041176, azacarbazole derivatives, for example in accordance with EP 1617710, EP 1617711, EP 1731584, JP 2005/347160, bipolar matrix materials, for example in accordance with WO 2007/137725, silanes, for example in accordance with WO 2005/111172, azaboroles or boronic esters, for example in accordance with WO 2006/117052, triazine derivatives, for example in accordance with WO 2010/015306, WO 2007/063754 or WO 2008/056746, zinc complexes, for example in accordance with EP 652273 or WO 2009/062578, diazasilole or tetraazasilole derivatives, for example in accordance with WO 2010/054729, diazaphosphole derivatives, for example in accordance with WO 2010/054730, bridged carbazole derivatives, for example in accordance with US 2009/0136779, WO 2010/050778, WO 2011/042107, WO 2011/088877 or WO 2012/143080, triphenylene derivatives, for example in accordance with WO 2012/048781, or lactams, for example in accordance with WO 2011/116865 or WO 2011/137951.

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

Materials which can be used for the electron-transport layer are all materials as are used in accordance with the prior art as electron-transport materials in the electron-transport layer. Particularly 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. Furthermore 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 hole-transport materials which can be used in a hole-transport, hole-injection or electron-blocking layer in the electroluminescent device according to the invention are indenofluorenamine derivatives (for example in accordance with WO 06/122630 or WO 06/100896), the amine derivatives disclosed in EP 1661888, hexaazatriphenylene derivatives (for example in accordance with WO 01/049806), amine derivatives containing condensed aromatic rings (for example in accordance with US 5,061,569), the amine derivatives disclosed in WO 95/09147, monobenzoidenofluorenamines (for example in accordance with WO 08/006449), dibenzoidenofluorenamines (for example in accordance with WO 07/140847), spirobifluorenamines (for example in accordance with WO 2012/034627 or WO 2013/120577), fluorenamines (for example in accordance with the as

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yet unpublished applications EP 12005369.9, EP 12005370.7 and EP 12005371.5), spirodibenzopyranamines (for example in accordance with WO 2013/083216) and dihydroacridine derivatives (for example in accordance with WO 2012/150001). The compounds according to the invention can also be used as hole-transport materials.

The cathode of the organic electroluminescent device preferably comprises metals having a low work function, metal alloys or multilayered structures comprising various metals, such as, for example, alkaline-earth metals, alkali metals, main-group metals or lanthanoids (for example Ca, Ba, Mg, Al, In, Mg, Yb, Sm, etc.). Also suitable are alloys comprising an alkali metal or alkaline-earth metal and silver, for example an alloy comprising magnesium and silver. In the case of multilayered structures, further metals which have a relatively high work function, such as, for example, Ag or Al, can also be used in addition to the said metals, in which case combinations of the metals, such as, for example, Ca/Ag, Mg/Ag or Ag/Ag, are generally used. It may also be preferred to introduce a thin interlayer of a material having a high dielectric constant between a metallic cathode and the organic semiconductor. Suitable for this purpose are, for example, alkali metal fluorides or alkaline-earth metal fluorides, but also the corresponding oxides or carbonates (for example LiF, Li₂O, BaF₂, MgO, NaF, CsF, Cs₂CO₃, etc.). Furthermore, lithium quinolate (LiQ) can be used for this purpose. The layer thickness of this layer is preferably between 0.5 and 5 nm.

The anode preferably comprises materials having a high work function. The anode preferably has a work function of greater than 4.5 eV vs. vacuum. Suitable for this purpose are on the one hand metals having a high redox potential, such as, for example, Ag, Pt or Au. On the other hand, metal/metal oxide electrodes (for example Al/Ni/NiO_x, Al/PtO_x) may also be preferred. For some applications, at least one of the electrodes must be transparent or partially transparent in order to facilitate either irradiation of

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the organic material (organic solar cells) or the coupling-out of light (OLEDs, O-lasers). 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 furthermore given to conductive, doped organic materials, in particular conductive doped polymers.

The device is appropriately (depending on the application) structured, provided with contacts and finally sealed, since the lifetime of the devices according to the invention is shortened in the presence of water and/or air.

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

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

Preference is furthermore given to an organic electroluminescent device, characterised in that one or more layers are produced from solution, such as, for example, by spin coating, or by means of any desired printing process, such as, for example, screen printing, flexographic printing, nozzle printing or offset printing, but particularly preferably LITI (light induced

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thermal imaging, thermal transfer printing) or ink-jet printing. Soluble compounds of the formula (I) are necessary for this purpose. High solubility can be achieved through suitable substitution of the compounds.

5 Also possible are hybrid processes, in which, for example, one or more layers are applied from solution and one or more further layers are applied by vapour deposition. Thus, it is possible, for example, to apply the emitting layer from solution and to apply the electron-transport layer by vapour deposition.

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

15 In accordance with the invention, the electronic devices comprising one or more compounds according to the invention can be employed in displays, as light sources in lighting applications and as light sources in medical and/or cosmetic applications (for example light therapy).

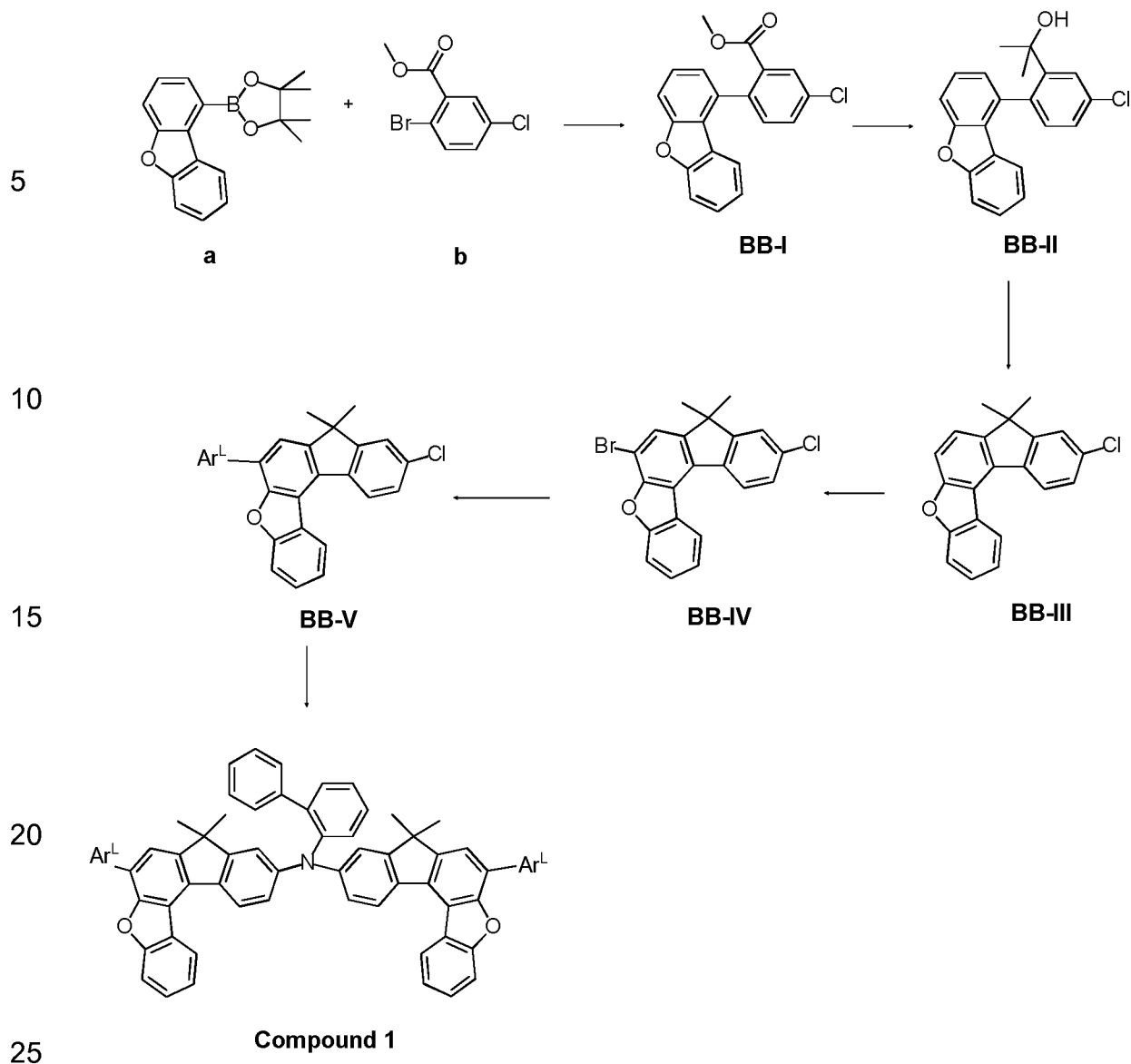
20 The invention will now be explained in greater detail by the following examples, without wishing to restrict it thereby.

A) Syntheses Examples

25 Scheme synthesis example Compound 1

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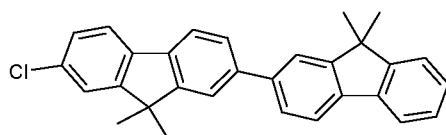
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Synthesis of the group ArL

Synthesis of compound Int1.1

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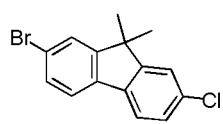
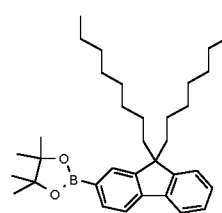
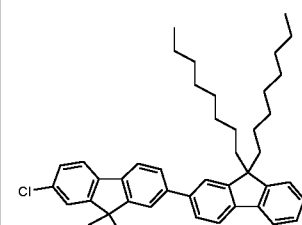
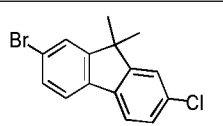
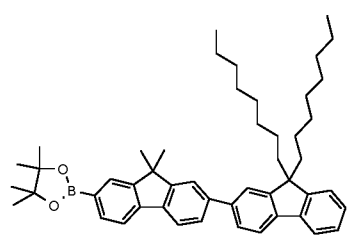
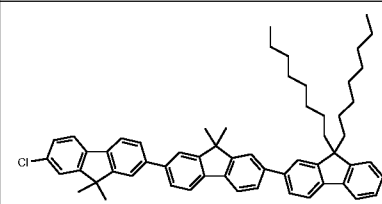
30 g (97.5 mmol) 2-Bromo-7-Chloro-9,9-dimethyl-9H-fluorene (see JP 2003277305 A), 25.5 g (107.3 mmol) (9,9-dimethylfluoren-2-yl)boronic acid 90 g (390mmol), 0.9 g (4 mmol) palladium(II)acetate and 3.6 g (11.7 mmol) tri(o-tolyl)-phosphine are mixed in 1 L toluene, dioxane, water (1:1:1) and stirred at reflux overnight. After cooling down to room temperature, 200 mL toluene are added and the organic phase is separated and washed with water (2 x 200 mL), the combined organic phases are concentrated under reduced pressure. The residue is purified by recrystallization from toluene/heptane.

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Yield: 39.1 g (93 mmol; 96 %).

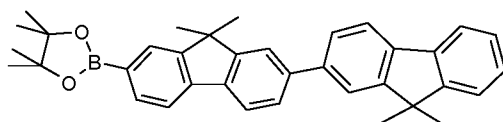
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Following compounds can be synthesized in an analogous manner:

Comp.	Starting material	Starting material	Product
15 Int1.2			
20 Int1.3		ArL2 (see below) 	

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Synthesis of ArL1



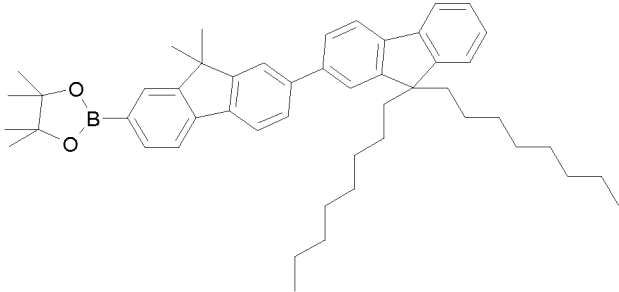
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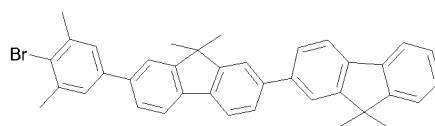
40 g (95 mmol) Int1.1, 38.6 g (152 mmol) bis-(pinacolato)-diboron, 4.2 g (5.7 mmol) trans-dichloro(tricyclohexylphosphine)palladium(II) and 28 g (285 mmol) potassium acetate are mixed in 400 mL dioxane and stirred for 16 h at reflux. The reaction mixture is allowed to cool to room temperature and 400 mL toluene are added. The organic phase is separated, washed with water (2 x 200 mL) and filtered through Celite. The solution is concentrated to dryness under reduced pressure. The residue is purified by recrystallization from toluene/heptane.

Yield: 36 g (70 mmol; 74 %).

Following compounds can be synthesized in an analogous manner:

Compound	Starting material	Product
ArL2	Int1.2	

Synthesis of Int1.4



5.5 g (17.8 mmol) 2-Bromo-5-iodo-1,3-dimethylbenzene, 6.5 g (12.7 mmol) ArL1, 366 mg (0.3 mmol) tetrakis(triphenylphosphine)-palladium(0) and 2.7 g (13 mmol) sodium carbonate are mixed in 200 mL toluene, ethanol and water (2:1:1) and stirred for 16 hours at 90 °C. After cooling down to room temperature, 100 mL toluene are added, the organic phase is separated and washed with water (2 x 50 mL). The organic phase is concentrated to dryness

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under reduced pressure. The residue is purified by recrystallization from toluene/heptane.

Yield: 6.2 g (11 mmol; 86 %).

The following compounds can be synthesized in an analogous manner:

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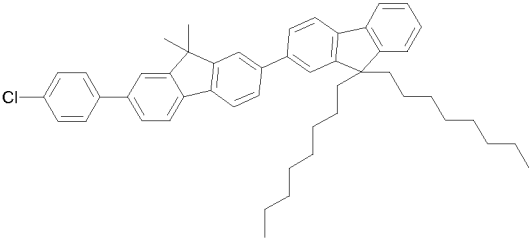
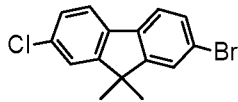
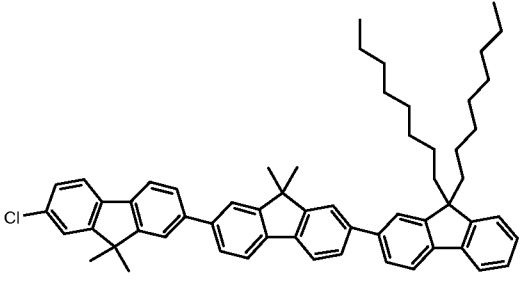
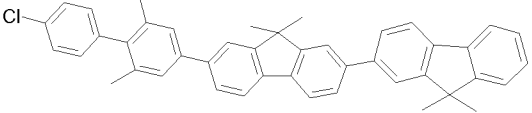
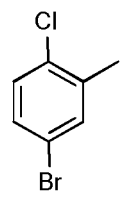
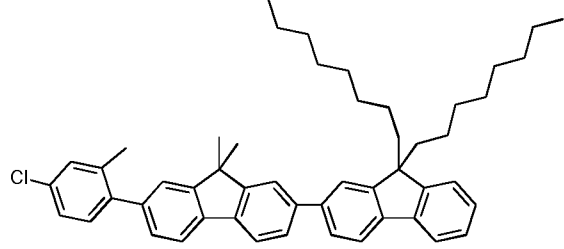
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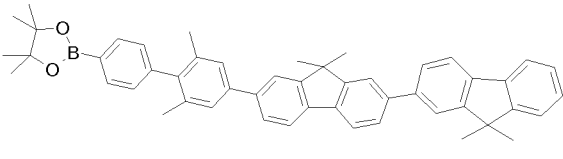
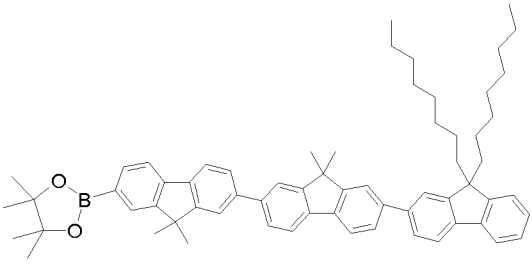
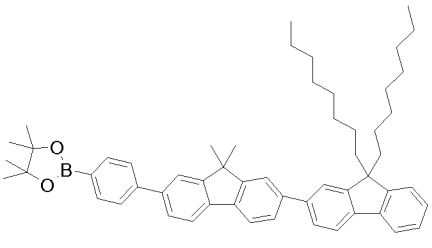
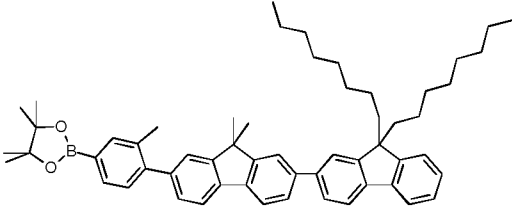
Compound	Starting material	Starting material	Product
Int1.5	ArL2	CAS 106-93-8	
Int1.6	ArL2	 JP 2003277305 A	
Int1.7	CAS 1679-18-1	Int1.4	
Int1.8	ArL2	 CAS 14495-51-3	

Synthesis of ArL3 to ArL6:

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Compounds ArL3 to ArL6 can be synthesized in an analogous manner to ArL1:

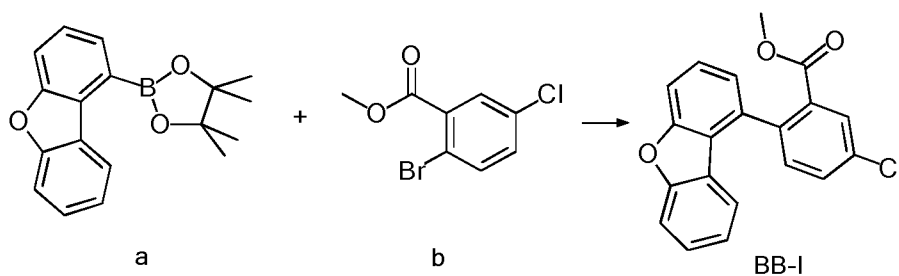
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Compound	Starting material	Product
ArL3	Int1.7	
ArL4	Int1.6	
ArL5	Int1.5	
ArL6	Int1.8	

Synthesis building block BB-I:

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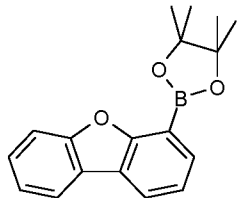
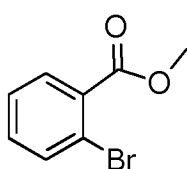
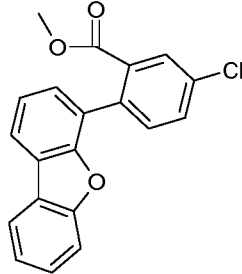
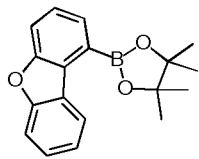
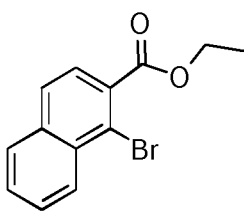
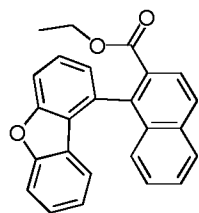
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117.9 g (401 mmol) starting material **a**, 100 g (401 mmol) starting material **b** and 203.1 g (882 mmol) potassium phosphate monohydrate are mixed in 1.6 L toluene/water/dioxane (2:1:1) and degassed. To the mixture, palladium

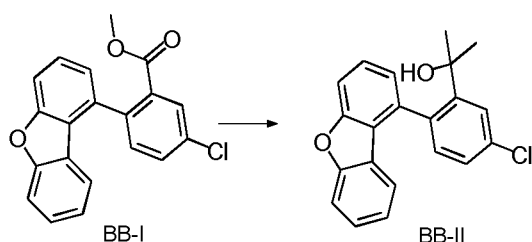
- 105 -

acetate (0.9 g, 4 mmol) and tri-*ortho*-tolylphosphine (2.44 g, 8 mmol) are added and the mixture is stirred at reflux for 16 h. After cooling the mixture to room temperature, the phases are separated. The aqueous phase is further extracted with ethyl acetate (2 x 300 mL). The combined organic phases are washed multiple times with water, dried over sodium sulfate and finally removed in vacuum. The crude is filtered over a plug of SiO₂/Al₂O₃ using ethyl acetate as solvent. After removing the solvent in vacuum, an oil is obtained in quantitative yield.

The following compounds can be synthesized in an analogous manner:

Compound	Starting material	Starting material	Product
BB-I.a	 CAS 912824-85-2		
BB-I.b			

Synthesis BB-II:

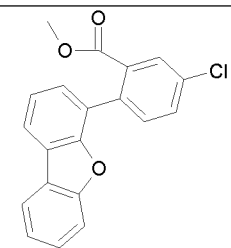
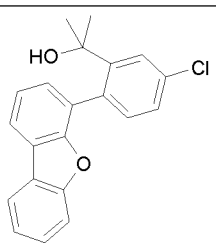
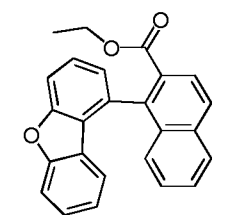
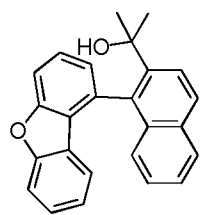


MeMgCl (461 mL, 3 M in THF, 1.38 mol) is added dropwise to a pre-cooled THF suspension (0 °C, 1.5 L) of compound BB-I (135 g, 0.4 mol) and CeCl₃

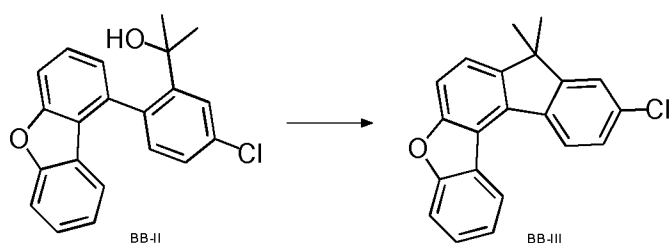
- 106 -

(199 g, 0.8 mol). After completion of the reaction, a saturated aqueous solution of NH_4Cl is added to quench the excess of MeMgCl , and the organic phase is extracted three times with ethyl acetate. The organic fractions are combined and washed with water and brine, successively. The volatiles were removed in vacuum to yield the desired product. 129 g (96 %).

The following compounds can be synthesized in an analogous manner:

Compound	Starting material	Product
BB-II.a		
BB-II.b		

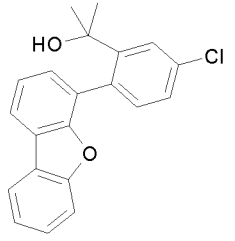
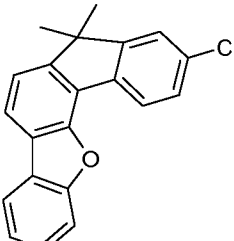
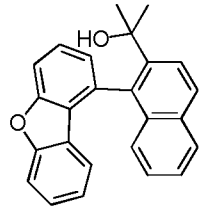
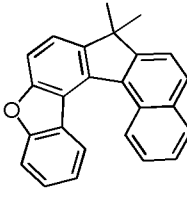
Synthesis BB-III:



To a solution of compound BB-II (129 g, 383 mmol) in toluene (1 L), 50 g of Amberlyst-15 are added. The mixture is stirred at reflux overnight. The mixture is cooled down to room temperature and the Amberlyst-15 filtered off. The solvent is removed in vacuum and the crude product is purified by column chromatography (SiO_2 , heptane). Yield: 106.2 g (87 %).

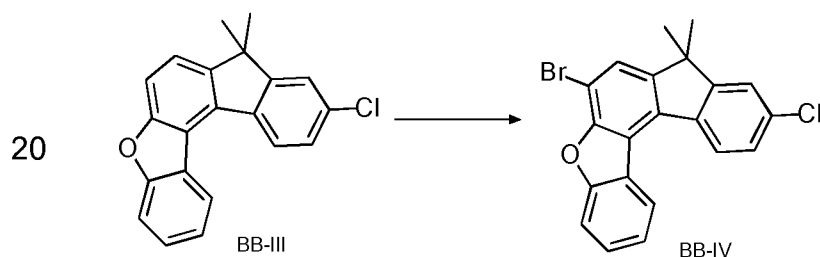
- 107 -

The following compounds can be synthesized in an analogous manner:

Compound	Starting material	Product
5 BB-III.a		
10 BB-III.b		

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Synthesis BB-IV:



25 To a solution of compound BB-III (100 g, 314 mmol) in CH₂Cl₂ (1.2 L), N-bromosuccinimide (55.83 g, 314 mmol) and HBr (32 % solution in acetic acid, 0.5 mL) are added. The reaction is heated at 30 °C for 4 days. After completion of the reaction, Na₂S₂O₃ (300 mL, saturated aqueous solution) is added and the mixture is stirred vigorously for 30 minutes. The phases are separated and the organic phase is washed several times with water. The solvent is removed in vacuum and the crude product vigorously stirred with ethanol to yield a white solid. Yield: 119.8 g (96%).

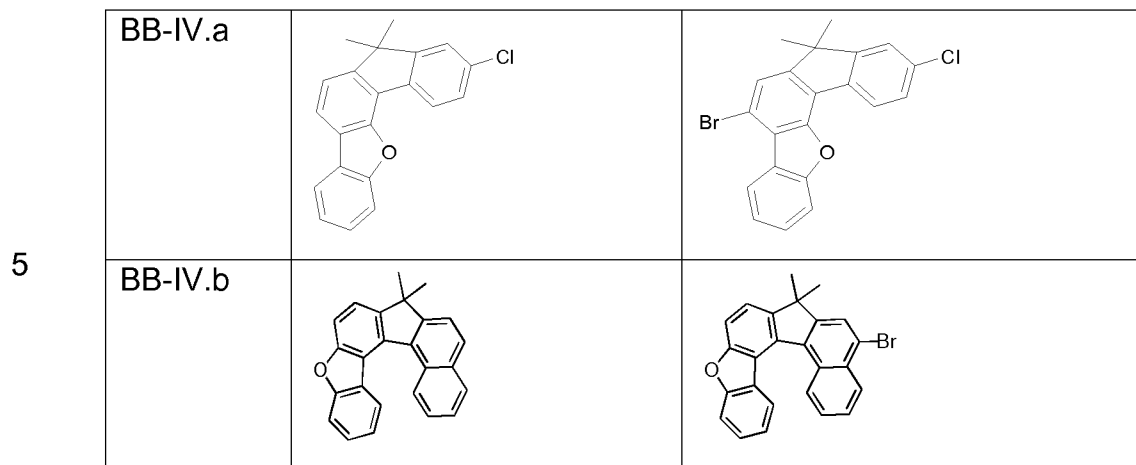
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The following compounds can be synthesized in an analogous manner:

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Compound	Starting material	Product

- 108 -



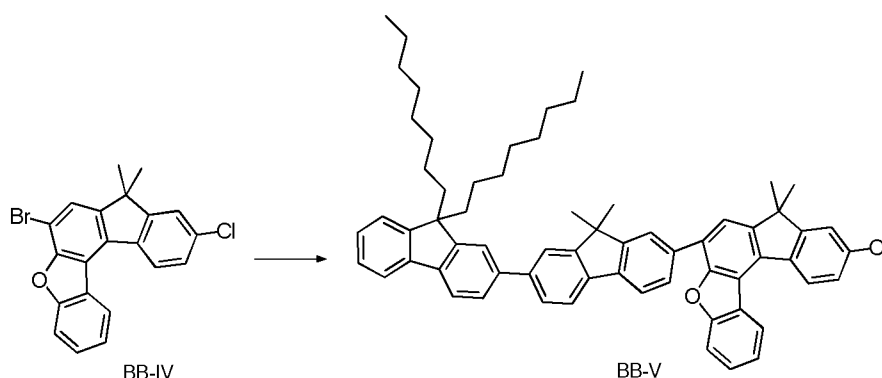
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Synthesis Intermediate BB-V:

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30.0 g (75.4 mmol) BB-IV, 53.7 g (75.4 mmol) ArL2 and 16.0 g (151 mmol) sodium carbonate are mixed in 600 mL toluene/dioxane/water (2:1:2) and degassed. To the mixture, Tetrakis(triphenylphosphine)palladium (2.2 g, 1.9 mmol) is added and the mixture is stirred at reflux for 4 h. After cooling the mixture to room temperature, 400 mL of ethyl acetate is added and the phases are separated. The organic phase is washed multiple times with water and the solvent is removed in vacuum. Afterwards, the organic phase is filtrated over a plug of silica using ethyl acetate as solvent. The solvent is removed in vacuum and the crude product vigorously stirred with ethanol to yield a white solid. Yield: 64.4 g (95%).

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The following compounds can be synthesized in an analogous manner:

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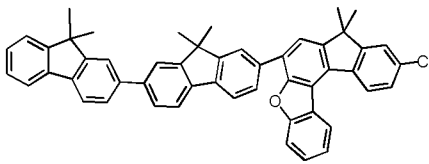
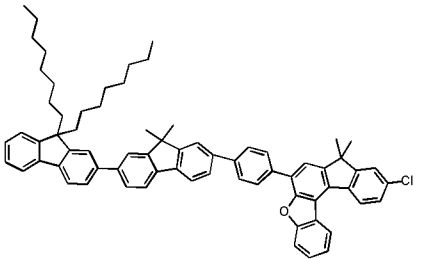
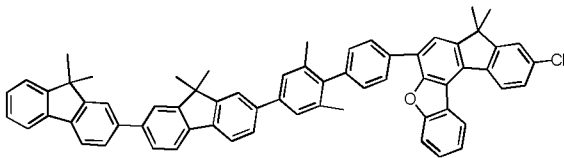
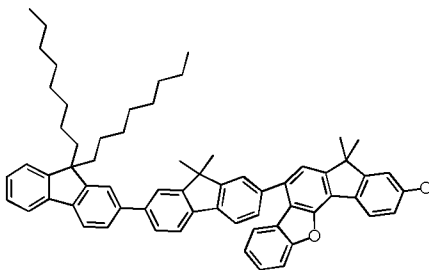
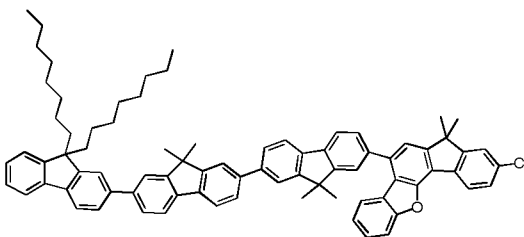
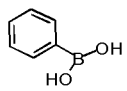
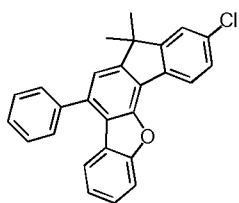
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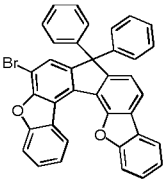
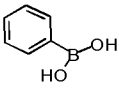
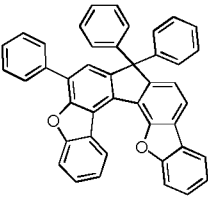
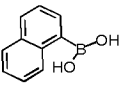
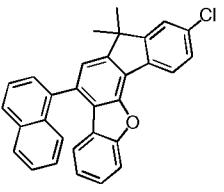
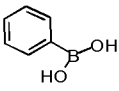
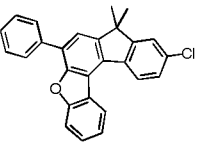
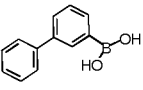
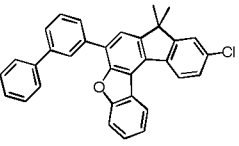
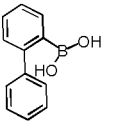
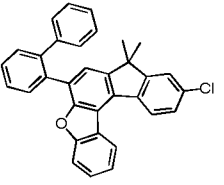
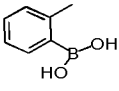
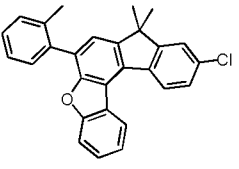
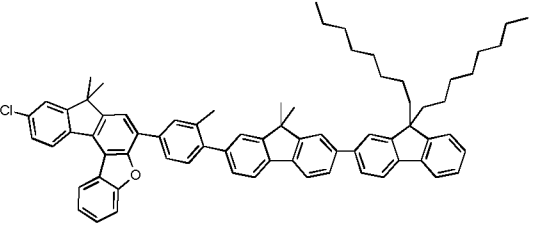
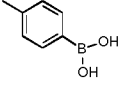
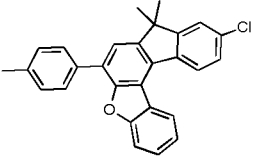
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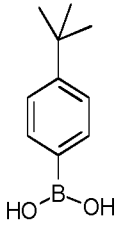
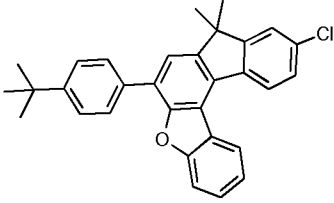
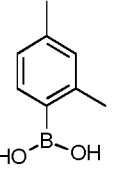
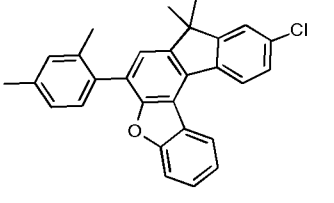
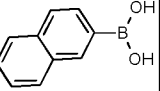
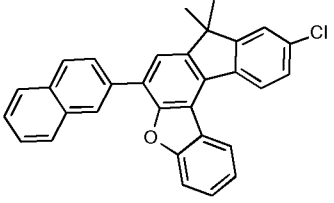
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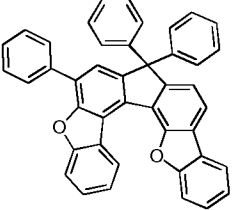
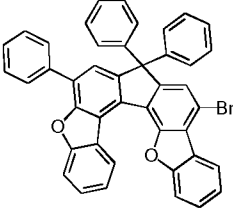
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Comp.	Starting material	Starting material	Product
BB-V.a	BB-IV	ArL1	
BB-V.b	BB-IV	ArL5	
BB-V.c	BB-IV	ArL3	
BB-V.d	BB-IV.a	ArL2	
BB-V.e	BB-IV.a	ArL4	
BB-V.f	BB-IV.a		

5	<p>BB-V.g</p>  <p>1831917-17-9</p>		
10	<p>BB-V.h</p> <p>BB-IV.a</p>		
15	<p>BB-V.i</p> <p>BB-IV</p>		
20	<p>BB-V.j</p> <p>BB-IV</p>		
25	<p>BB-V.k</p> <p>BB-IV</p>		
30	<p>BB-V.l</p> <p>BB-IV</p>		
35	<p>BB-V.m</p> <p>BB-IV</p>	<p>ArL6</p>	
40	<p>BB-V.n</p> <p>BB-IV</p>		

5	BB-V.o.	BB-IV		
10	BB-V.p.	BB-IV		
15	BB-V.q.	BB-IV		

The following compound can be synthesized in an analogous manner like compound BB-IV:

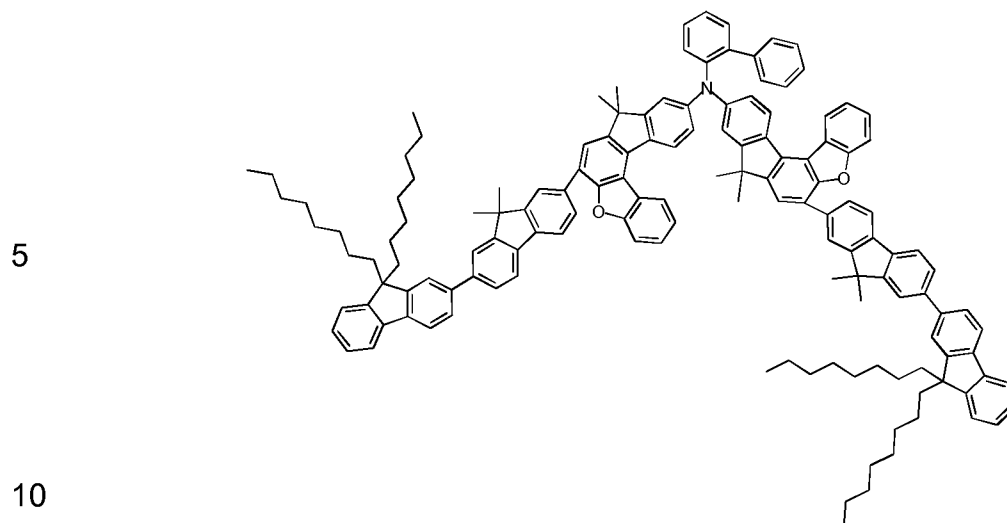
20	Starting material	Product
25		

Synthesis Compound 1:

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2.28 g (13.5 mmol) biphenyl-2-ylamine, 24.2 g (27.0 mmol) BB-V and 7.75 g (80.6 mmol) sodium tertbutylate are mixed in 300 mL toluene and degassed. Afterwards, 563 mg (1.4 mmol) S-Phos and 151 mg (0.7 mmol) palladium acetate are added and the mixture is stirred at reflux for 16 h. After cooling the mixture at room temperature, 200 mL of water is added and the phases are separated. The crude product is filtrate over a plug of aluminium oxide using toluene as solvent. The product is further purified by several recrystallizations from toluene/heptane. Yield: 7.7 g (45 %).

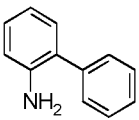
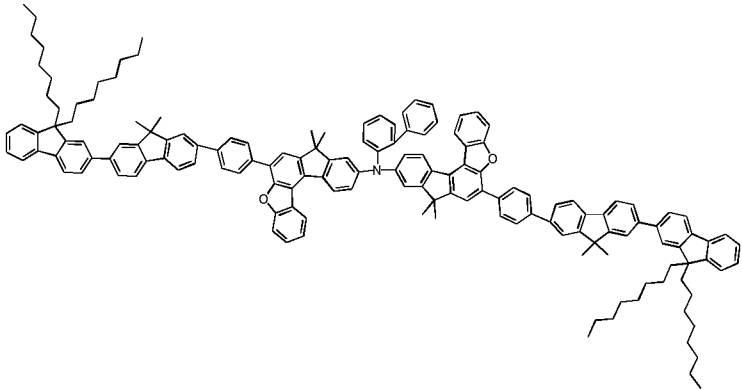
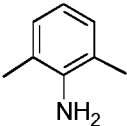
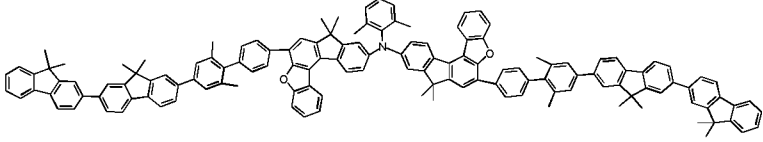
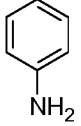
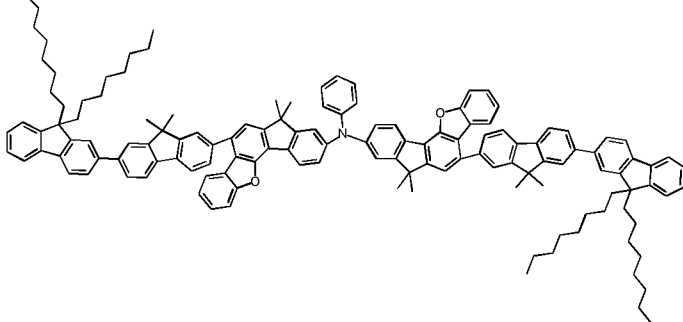
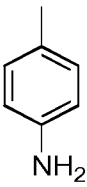
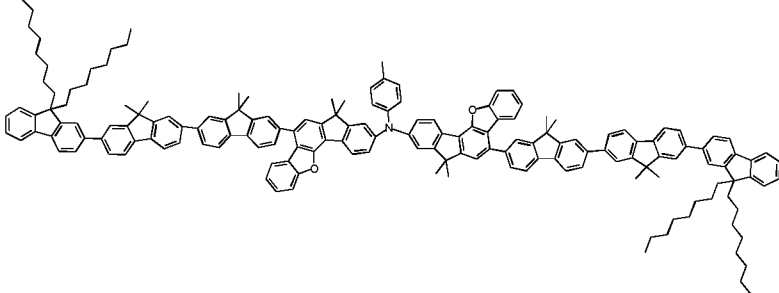
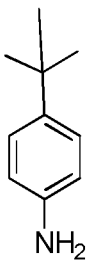
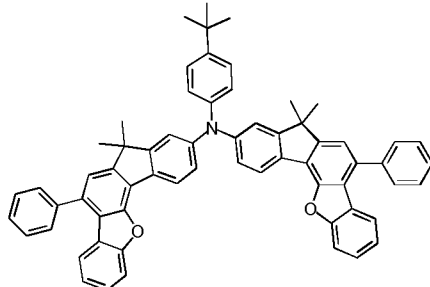
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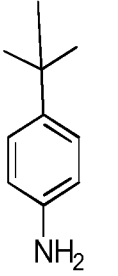
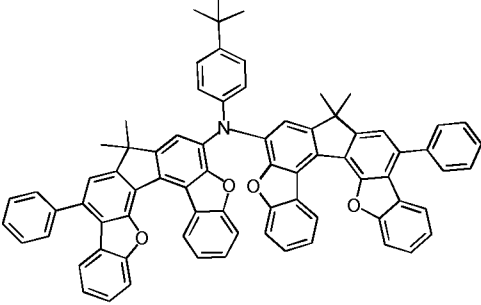
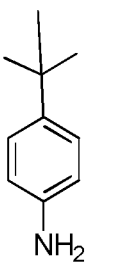
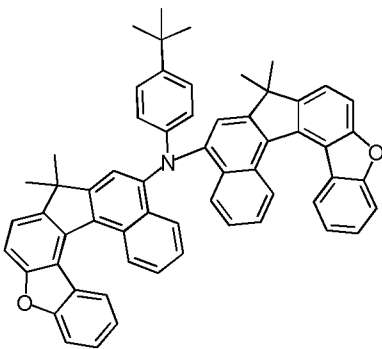
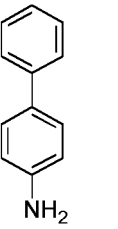
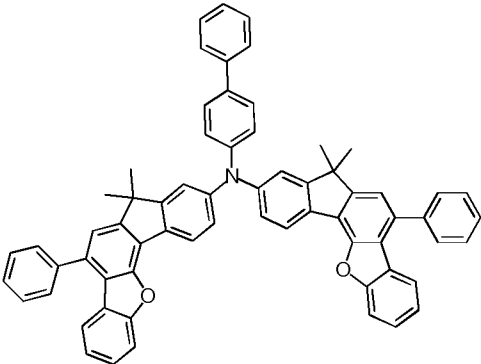
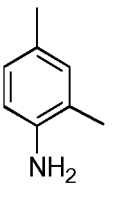
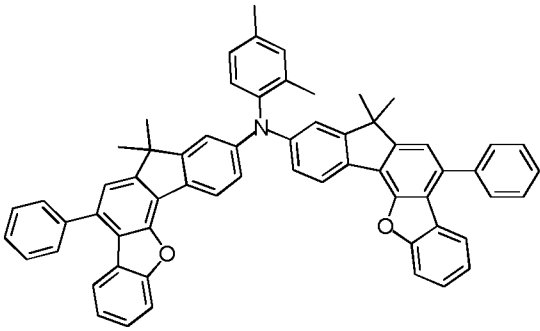
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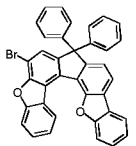
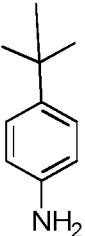
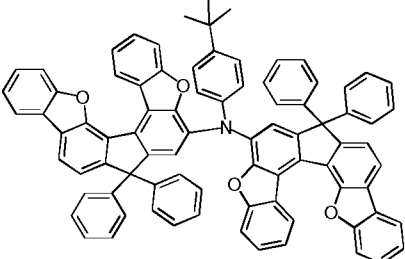
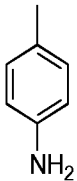
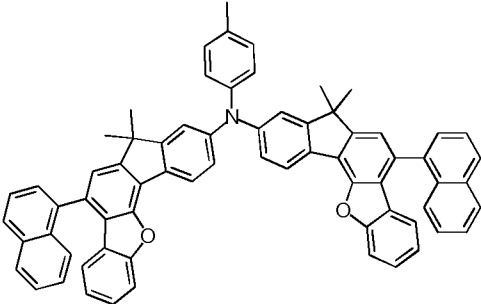
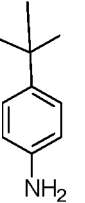
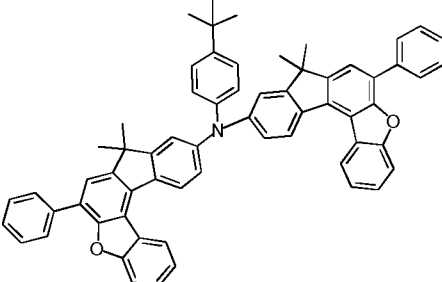
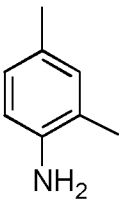
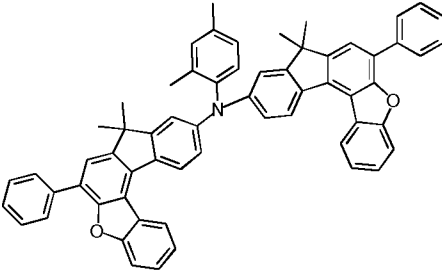
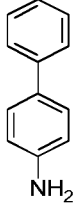
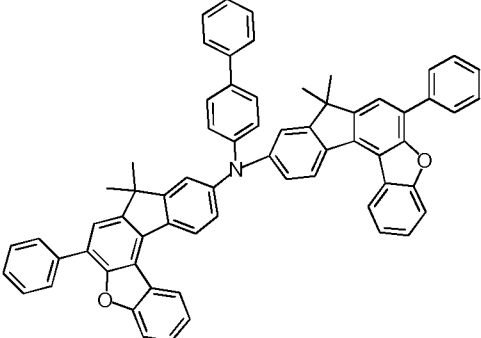
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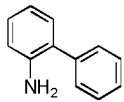
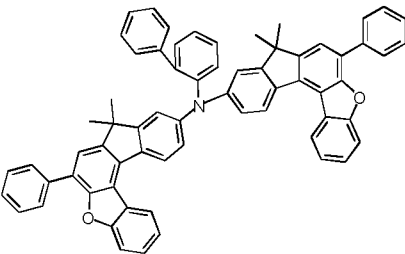
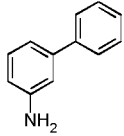
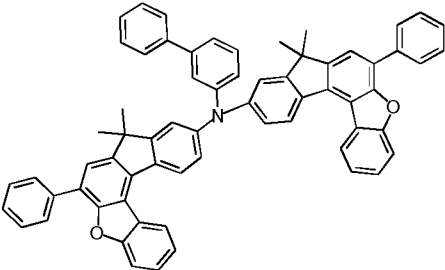
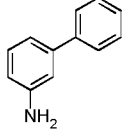
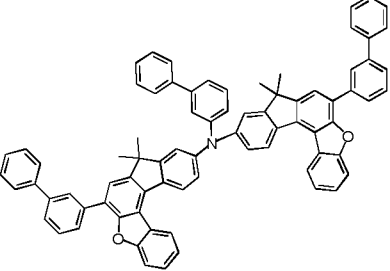
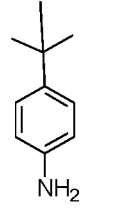
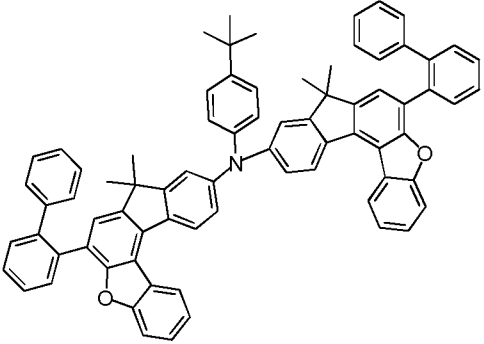
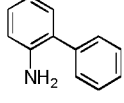
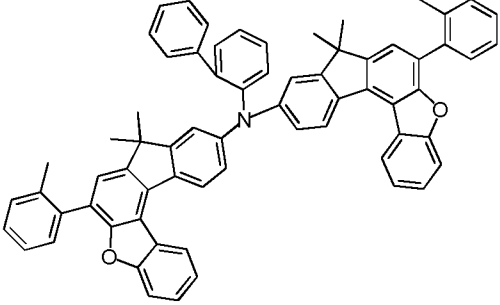
Comp.	Starting material	Starting material	Product
25	BB-V.a		
30			

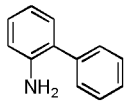
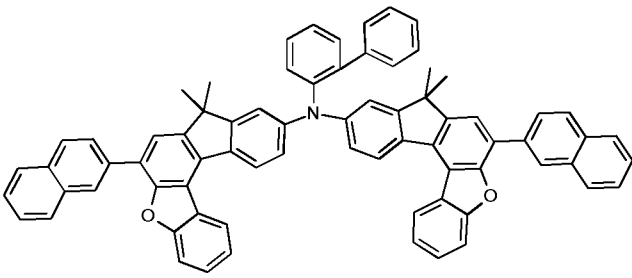
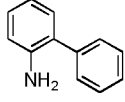
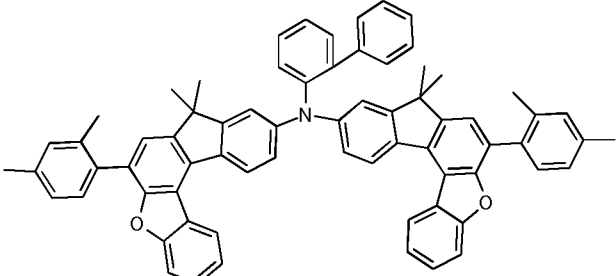
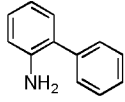
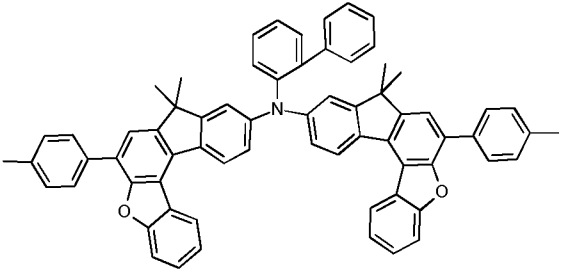
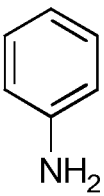
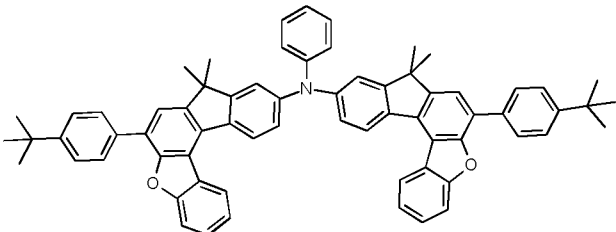
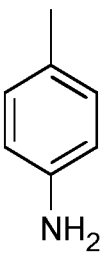
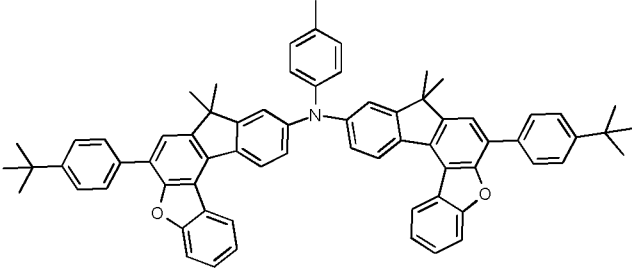
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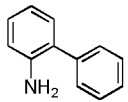
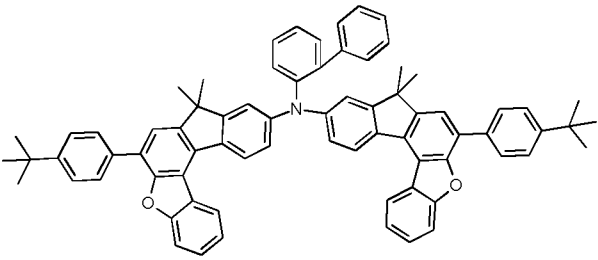
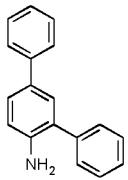
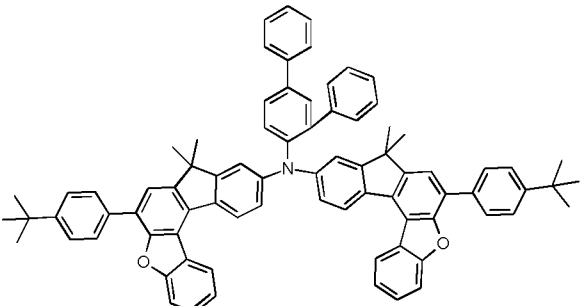
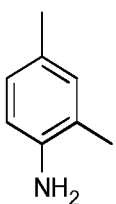
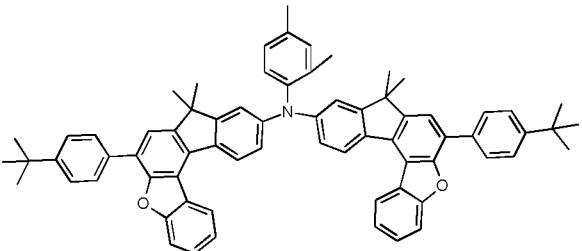
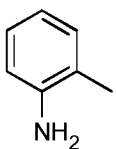
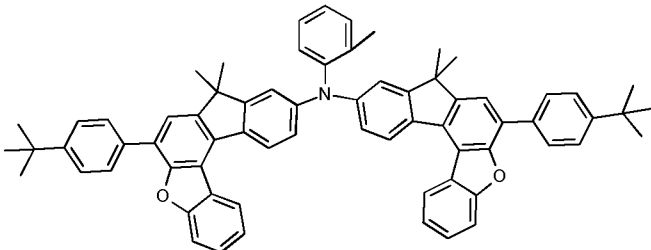
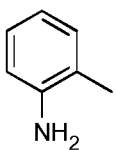
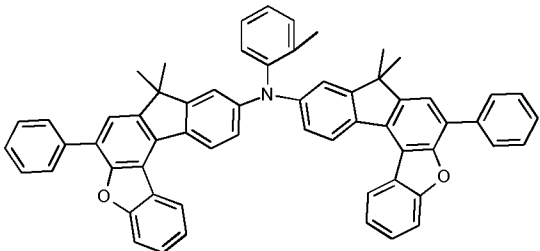
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<p>10</p>	<p>4</p>	<p>BB-V.c</p>		
<p>15</p>	<p>5</p>	<p>BB-V.d</p>		
<p>20</p>	<p>6</p>	<p>BB-V.e</p>		
<p>30</p>	<p>7</p>	<p>BB-V.f</p>		

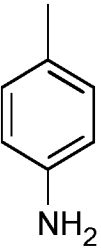
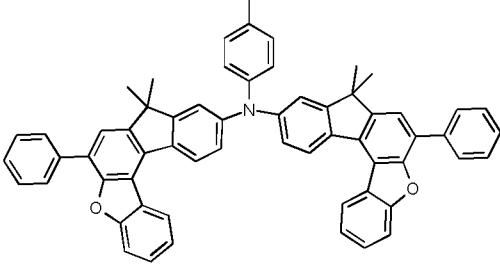
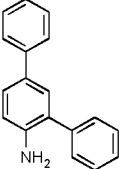
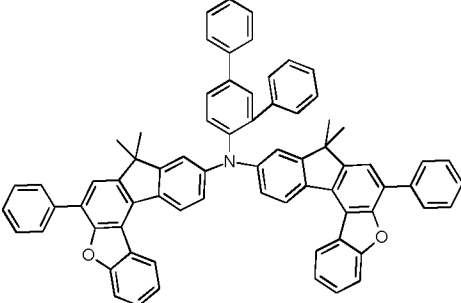
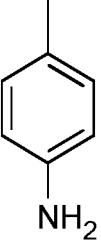
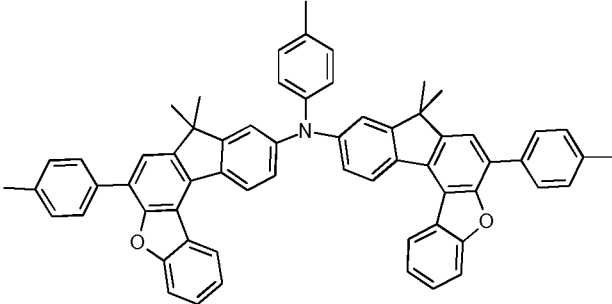
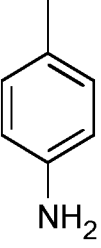
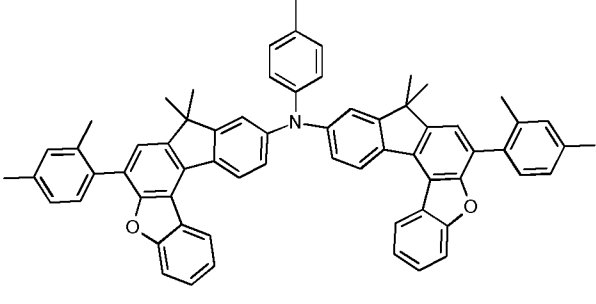
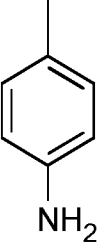
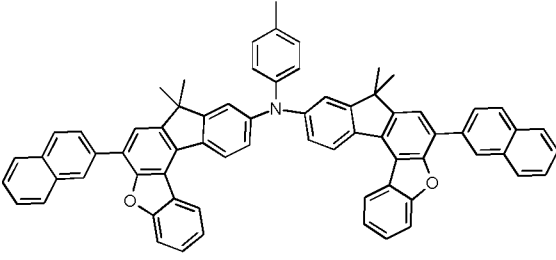
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10	9	BB-IV.b		
15	10	BB-V.f		
25	11	BB-V.f		

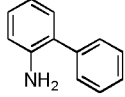
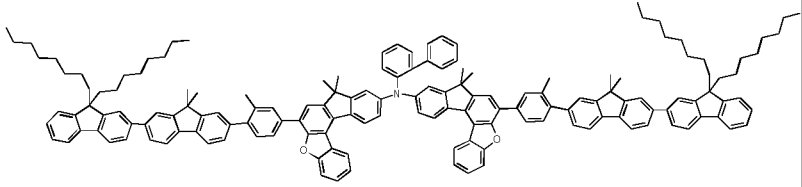
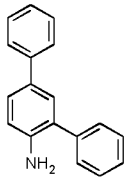
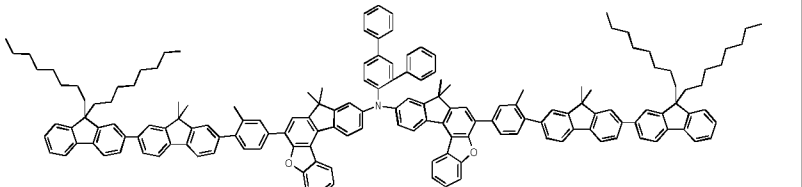
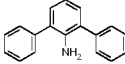
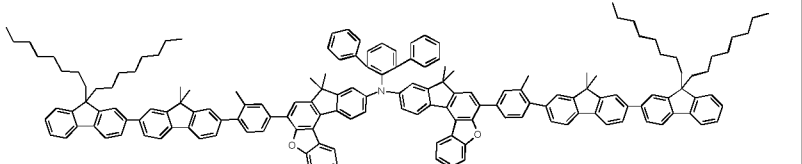
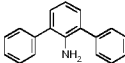
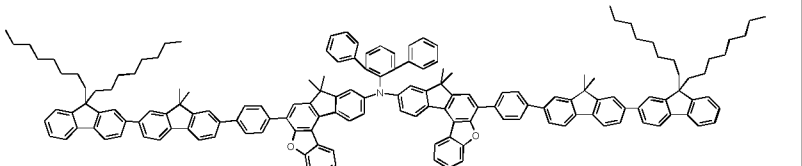
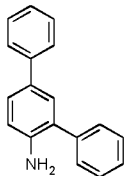
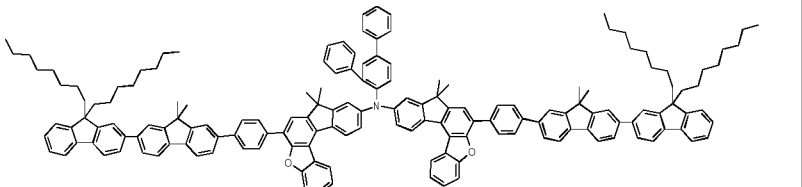
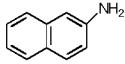
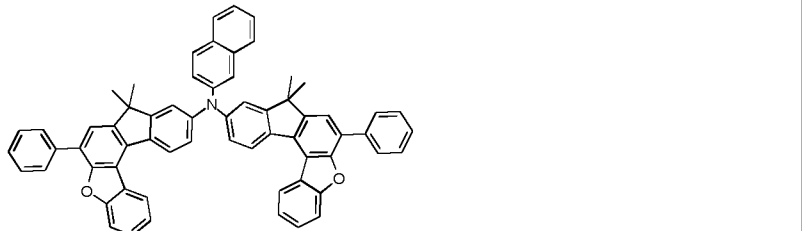
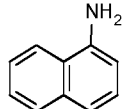
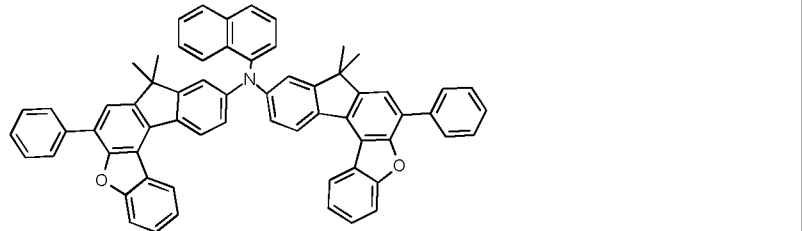
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<p>10</p>	<p>13</p> <p>BB-V.h</p>		
<p>15</p> <p>20</p>	<p>14</p> <p>BB-V.i</p>		
<p>25</p>	<p>15</p> <p>BB-V.i</p>		
<p>30</p> <p>35</p>	<p>16</p> <p>BB-V.i</p>		

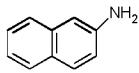
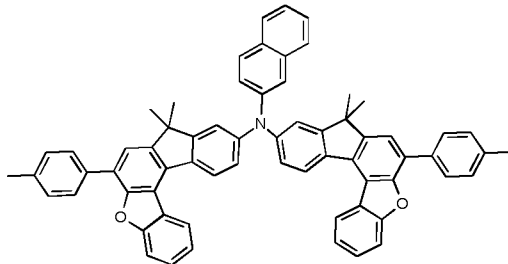
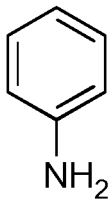
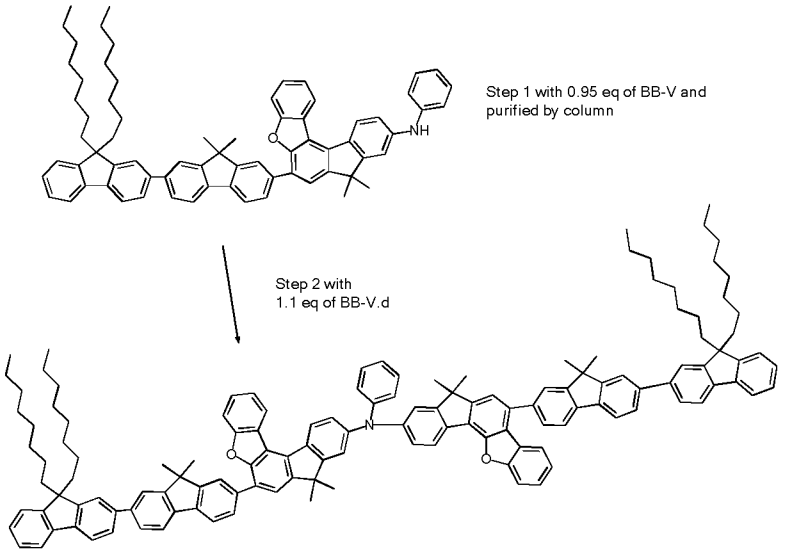
5	17	BB-V.i		
10	18	BB-V.i		
15	19	BB-V.j		
20	20	BB-V.k		
30	21	BB-V.l		

5	22	BB-V.q		
10	23	BB-V.p		
15	24	BB-V.n		
20	25	BB-V.o		
30	26	BB-V.o		

5	27	BB-V.o		
10	28	BB-V.o		
15	29	BB-V.o		
20	30	BB-V.o		
25	31	BB-V.i		

5	32	BB-V.i		
10	33	BB-V.i		
15	34	BB-V.n		
20	35	BB-V.p		
30	36	BB-V.q		

	37	BB-V.m		
5	38	BB-V.m		
10	39	BB-V.m		
15	40	BB-V.b		
20	41	BB-V.b		
25	42	BB-V.i		
30	43	BB-V.i		

<p>44</p>	<p>BB-V.n</p>		
<p>45</p>	<p>BB-V</p>		 <p>Step 1 with 0.95 eq of BB-V and purified by column</p> <p>Step 2 with 1.1 eq of BB-V.d</p>

20 **Synthesis examples part 2:**

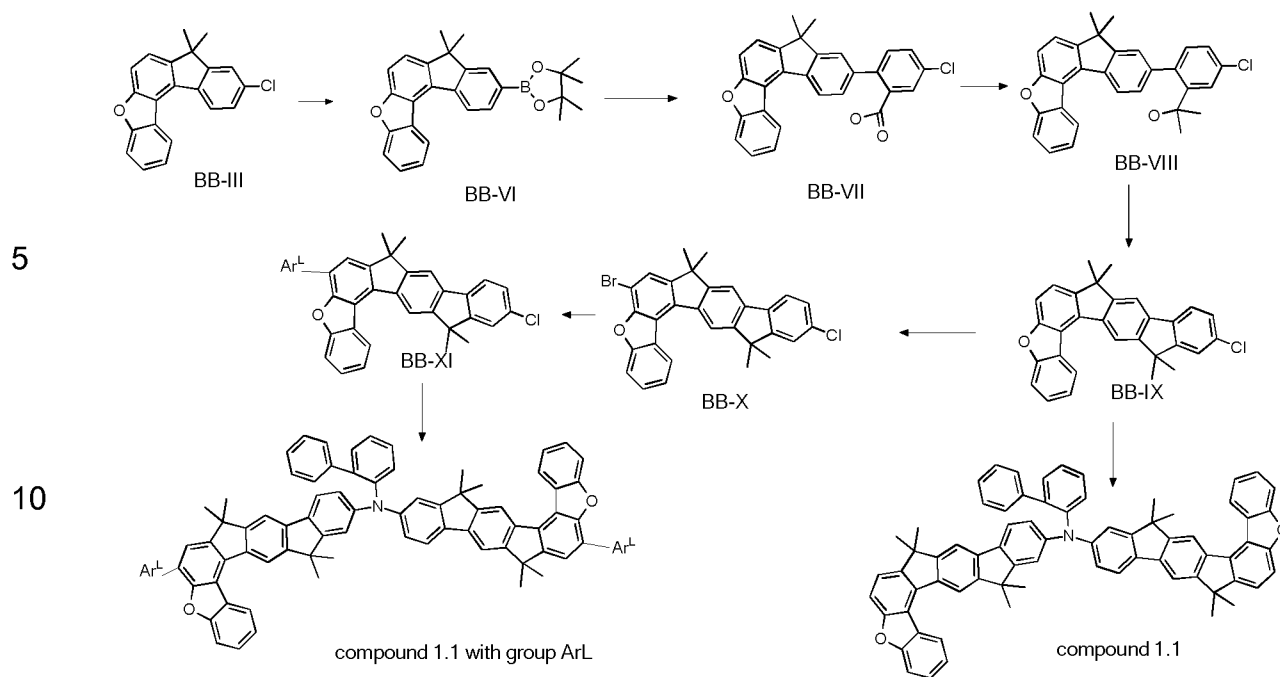
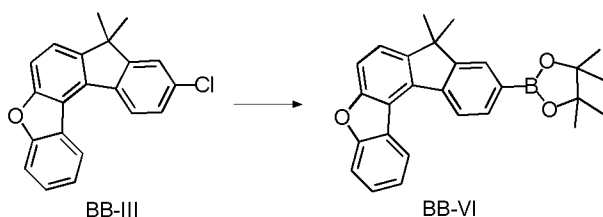
Scheme synthesis example Compound 1.1

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**Synthesis BB-VI:**

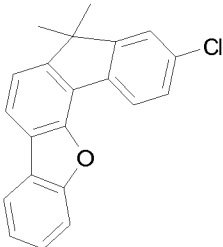
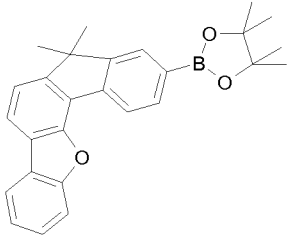
10-Chloro-8,8-dimethyl-8H-5-oxa-indeno[2,1-c]fluorene (30.00 g; 94.1 mmol), bis-(pinacolato)-diboron (28.68 g; 112.9 mmol) and potassium acetate (18.47 g; 188.2 mmol) are dissolved in 800 mL 1,4-dioxane.

XPhos Palladacycle Gen 3 (CAS:1445085-55-1; 1.59 g; 1.882 mmol) and bis-(pinacolato)-diboron (28.68 g; 112.9 mmol) are added and the reaction mixture is stirred at 100 °C overnight. After complete conversion, the reaction mixture is cooled down to room temperature and water and toluene are added. The phases are separated and the organic phase is washed several times with water. The combined organic phases are filtrated over silica with toluene as eluent. The solvent is removed in vacuum and the crude product vigorously stirred with ethanol to yield a white solid.

Yield: 34.2 g (83.4 mmol; 88%)

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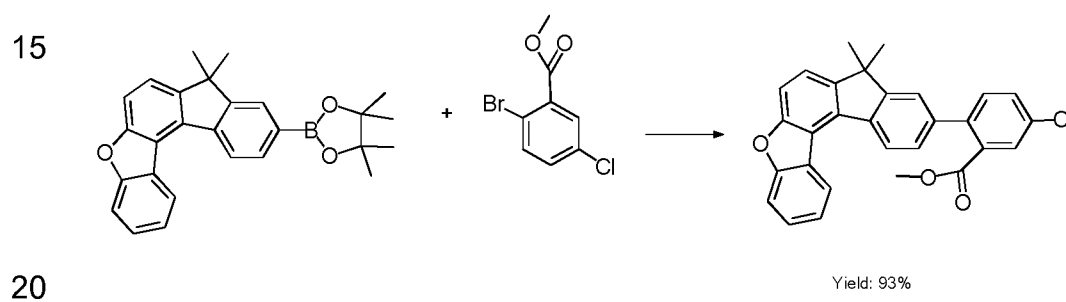
The following compound can be synthesized in an analogous manner:

Compound	Starting material	Product
5 BB-VI.a		

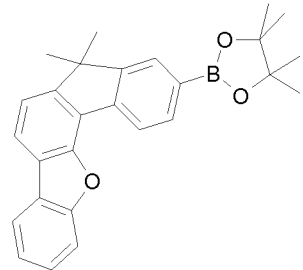
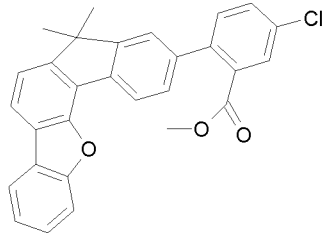
10

Synthesis of BB-VII:

Synthesis of BB-VII is done analog to BB-I:



The following compound can be synthesized in an analogous manner:

Compound	Starting material	Product
25 BB-VII.a		

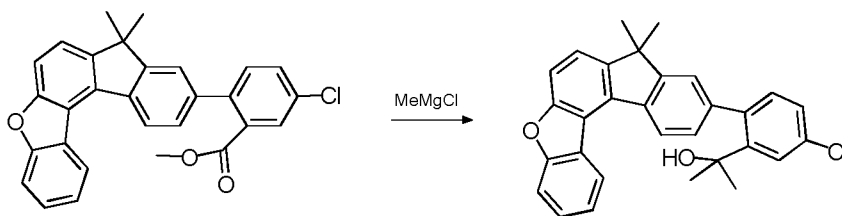
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Synthesis of BB-VIII:

Synthesis of BB-VIII is done analog to BB-II:

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Yield: 87%

The following compound can be synthesized in an analogous manner:

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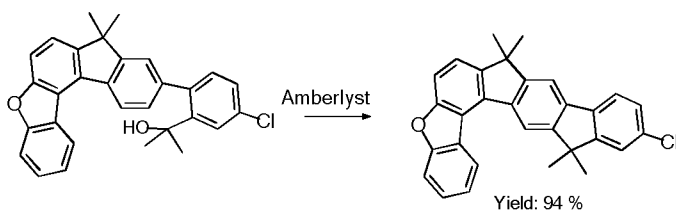
Compound	Starting material	Product
BB-VIII.a		

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Synthesis of BB-IX:

Synthesis of BB-IX is done analog to BB-III:

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Yield: 94 %

The following compound can be synthesized in an analogous manner:

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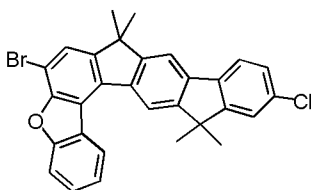
Compound	Starting material	Product
BB-IX.a		

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Synthesis of BB-X:

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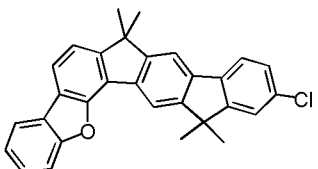
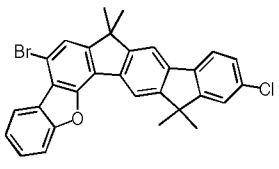
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To a solution of compound BB-IX (100 g, 229 mmol) in CH_2Cl_2 (1.2 L), N-bromosuccinimide (40.71 g, 314 mmol) and HBr (32 % solution in acetic acid, 0.5 mL) are added. The reaction is heated at 30 °C for 4 days. After completion of the reaction, $\text{Na}_2\text{S}_2\text{O}_3$ (300 mL, saturated aqueous solution) is added and the mixture is stirred vigorously for 30 minutes. The phases are separated and the organic phase is washed several times with water. The solvent is removed in vacuum and the crude product vigorously stirred with ethanol to yield a white solid. Yield: 101.2 g (86%).

The following compound can be synthesized in an analogous manner:

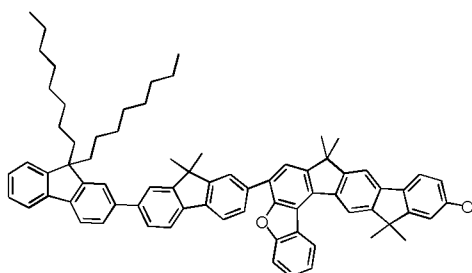
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Compound	Starting material	Product
BB-X.a		

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Synthesis of BB-XI:

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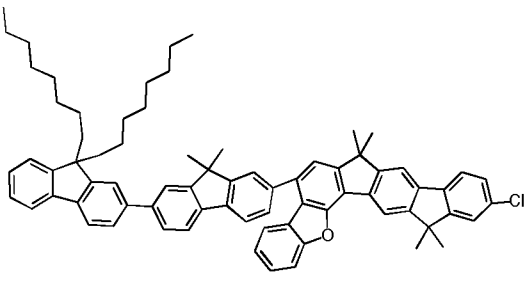
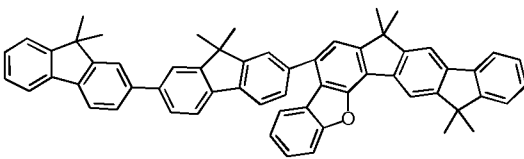
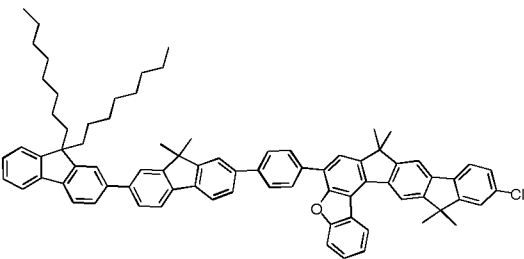
35

30.0 g (58.4 mmol) BB-X, 42.5 g (60.0 mmol) ArL2 and 16.0 g (151 mmol) sodium carbonate are mixed in 600 mL toluene/dioxane/water (2:1:2) and

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degassed. To the mixture, tetrakis(triphenylphosphine)palladium (2.2 g, 1.9 mmol) is added and the mixture is stirred at reflux for 4 h. After cooling the mixture to room temperature, 400 mL of ethyl acetate is added and the phases are separated. The organic phase is washed multiple times with water and the solvent is removed in vacuum. Afterwards, the organic phase is filtrated over a plug of silica using ethyl acetate as solvent. The solvent is removed in vacuum and the crude product vigorously stirred with ethanol to yield a white solid. Yield: 48.1 g (84%).

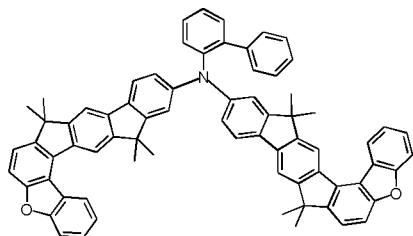
The following compounds can be synthesized in an analogous manner:

Comp.	Starting Material	Starting Material	Product
BB-XI.a	BB-X.a	ArL2	
BB-XI.b	BB-X.a	ArL1	
BB-XI.c	BB-X	ArL5	

Synthesis of compound 1.1:

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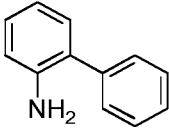
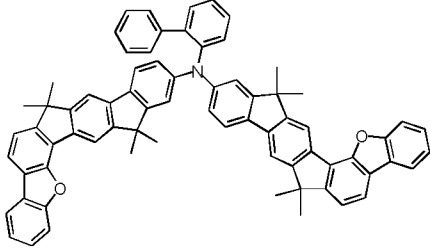
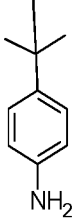
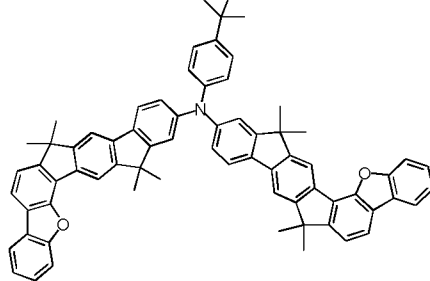
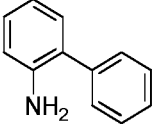
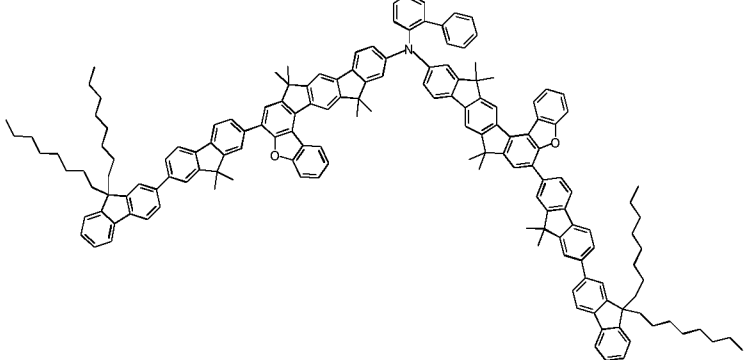
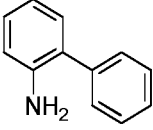
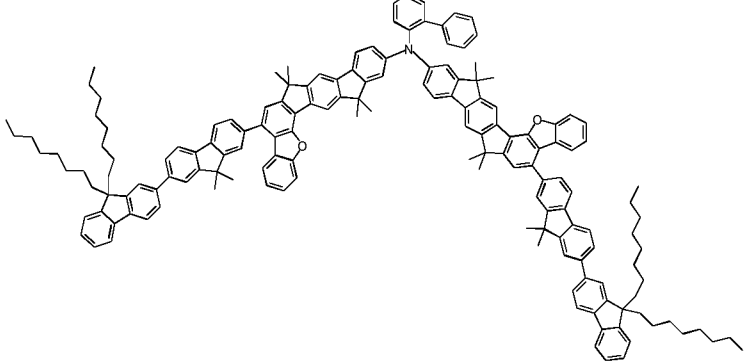
5

2.00 g (11.8 mmol) biphenyl-2-ylamine, 11.31 g (26.0 mmol) BB-IX and 6.82 g (70.9 mmol) sodium tertbutylate are mixed in 300 mL toluene and degassed. Afterwards, 563 mg (1.4 mmol) S-Phos and 151 mg (0.7 mmol) palladium acetate are added and the mixture is stirred at reflux for 16 h. After cooling the mixture at room temperature, 200 mL of water is added and the phases are separated. The crude product is filtrate over a plug of aluminium oxide using toluene as solvent. The product is further purified by several recrystallizations from toluene/heptane. Yield: 6.7 g (59 %).

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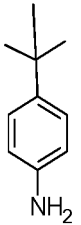
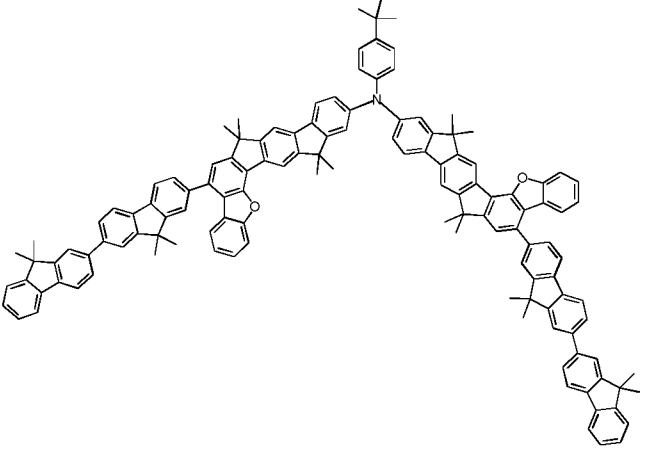
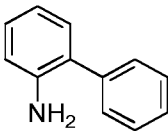
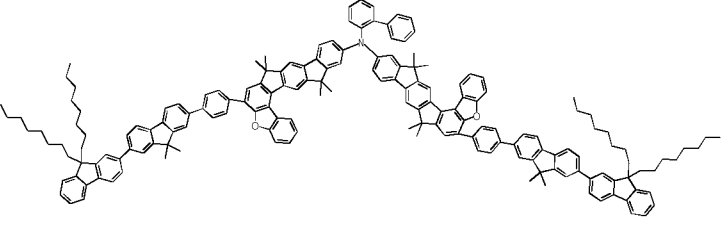
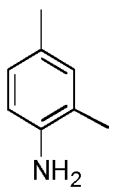
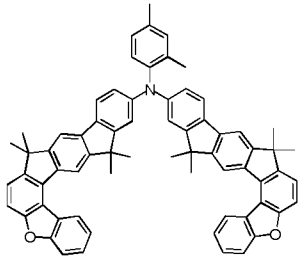
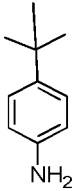
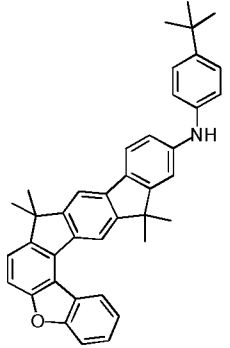
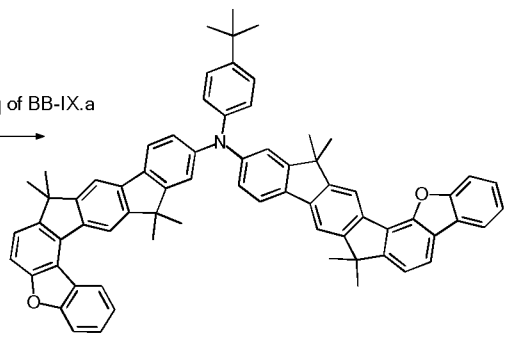
The following compounds can be synthesized in an analogous manner:

Comp.	SM	SM	Product
20 1.2	BB-IX		
25 1.3	BB-IX		
30 1.4	BB-IX		
35			

5	1.5	BB-IX.a		
10	1.6	BB-IX.a		
15	1.7	BB-XI		
20	1.8	BB-XI.a		

30

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5	1.9	BB-XI.b		
10	1.10	BB-XI.c		
15	1.11	BB-IX		
25 30 35	1.12	BB-IX		<p data-bbox="1029 1467 1324 1523">Step 1 with 0.95 eq of BB-IX and purified by column</p>  <p data-bbox="750 1691 1005 1724">Step 2 with 1.1 eq of BB-IX.a</p> 

B) Fabrication of OLEDs

The manufacturing of the OLED devices is performed accordingly to WO 04/05891 with adapted film thicknesses and layer sequences. The following examples V1, E1 to E9 show data of various OLED devices.

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Substrate pre-treatment of examples V1, E1 to E9:

Glass plates with structured ITO (50 nm, indium tin oxide) are coated with a buffer of 20 nm PEDOT:PSS (Poly(3,4-ethylenedioxythiophene) poly(styrene-sulfonate, CLEVIOS™ P VP Al 4083 from Heraeus Precious Metals GmbH Germany, spin-coated from a water-based solution) to form the substrates on which the OLED devices are fabricated.

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The OLED devices have in principle the following layer structure:

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- Substrate,
- ITO (50 nm),
- Buffer (20 nm),
- Hole transporting layer (HTL),
- Optional interlayer (IL)
- Emissive layer (EML),
- Optional hole blocking layer (HBL),
- Electron transporting layer (ETL),
- Electron injection layer (EIL),
- Cathode.

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The cathode is formed by an aluminium layer with a thickness of 100 nm. The detailed stack sequence is shown in table A. The materials used for the OLED fabrication are presented in table C.

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All materials are applied by thermal vapour deposition in a vacuum chamber. The emission layer here always consists of at least one matrix material (host material=H) and an emitting dopant (emitter=D), which is mixed with the matrix material or matrix materials in a certain proportion by volume by co-evaporation. An expression such as H1:D1 (97%:3%) here

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means that material H1 is present in the layer in a proportion by volume of 97%, whereas D1 is present in the layer in a proportion of 3%. Analogously, the electron-transport layer may also consist of a mixture of two or more materials.

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The OLED devices are characterised by standard methods. For this purpose, the electroluminescence spectra, the current efficiency (measured in cd/A), power efficiency (lm/W) and the external quantum efficiency (EQE, measured in % at 1000 cd/m²) are determined from

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current/voltage/luminance characteristic lines (IUL characteristic lines) assuming a Lambertian emission profile. The electroluminescence (EL) spectra are recorded at a luminous density of 1000 cd/m² and the CIE 1931 x and y coordinates are then calculated from the EL spectrum. U1000 is defined as the voltage at luminous density of 1000 cd/m². SE1000 represents the current efficiency, LE1000 the power efficiency at 1000 cd/m². EQE1000 is defined as the external quantum efficiency at luminous density of 1000 cd/m². The device data of various OLED devices is summarized in table B. The example V1 represents the comparative example according to the state-of-the-art. The examples E1 to E9 show data of inventive OLED devices.

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In the following section several examples are described in more detail to show the advantages of the inventive OLED devices.

Use of inventive compounds as emitting material in fluorescent OLEDs

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The inventive compounds are especially suitable as an emitter (dopant) when blended into a fluorescent blue matrix to form the emissive layer of a fluorescent blue OLED device. The representative examples are D1 to D9. Comparative compound for the state-of-the-art is represented by SdT1 (structures see table C). The use of the inventive compound as an emitter

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(dopant) in a fluorescent blue OLED device results in significantly improved device data (E1 to E9) (device data see table B).

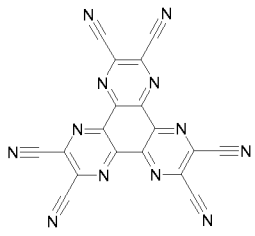
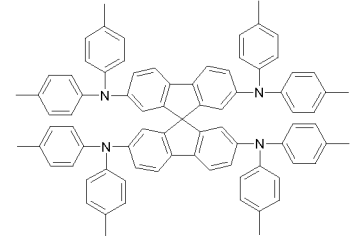
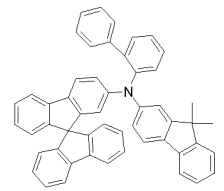
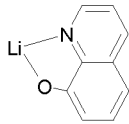
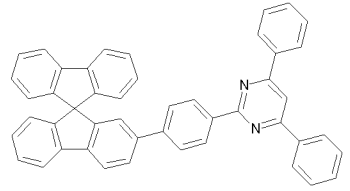
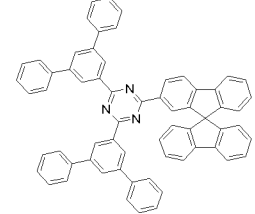
Table A: Device stack of vapor processed OLEDs

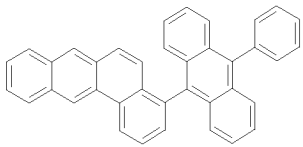
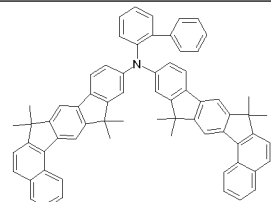
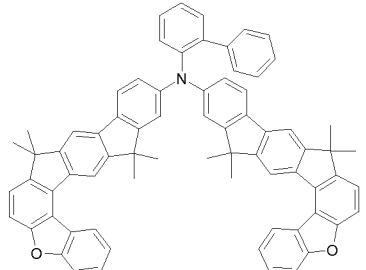
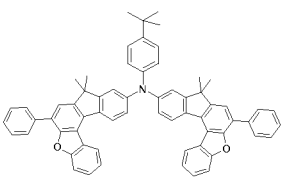
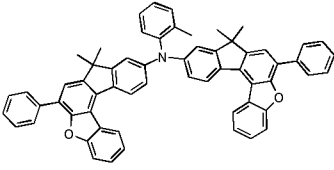
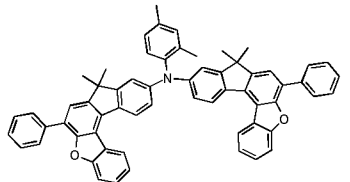
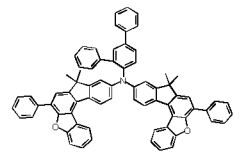
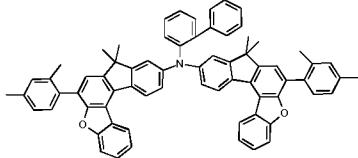
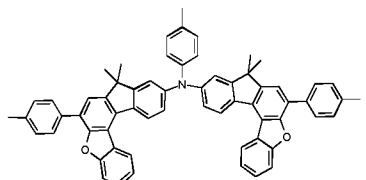
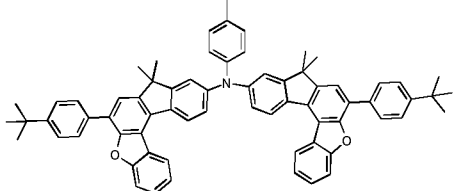
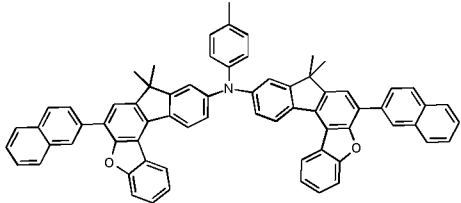
Ex.	HTL [nm]	IL [nm]	EBL [nm]	EML [nm]	HBL [nm]	ETL [nm]	EIL [nm]
5 V1	SpA1 140nm	HATC N 5nm	SpMA1 20nm	H1:SdT1 (97%:3%) 20nm	HBM 10nm	ETM:LiQ (50%:50%) 20nm	LiQ 1nm
10 E1	SpA1 140nm	HATC N 5nm	SpMA1 20nm	H1:D1 (97%:3%) 20nm	HBM 10nm	ETM:LiQ (50%:50%) 20nm	LiQ 1nm
E2	SpA1 140nm	HATC N 5nm	SpMA1 20nm	H1:D2 (97%:3%) 20nm	HBM 10nm	ETM:LiQ (50%:50%) 20nm	LiQ 1nm
15 E3	SpA1 140nm	HATC N 5nm	SpMA1 20nm	H1:D3 (97%:3%) 20nm	HBM 10nm	ETM:LiQ (50%:50%) 20nm	LiQ 1nm
E4	SpA1 140nm	HATC N 5nm	SpMA1 20nm	H1:D4 (97%:3%) 20nm	HBM 10nm	ETM:LiQ (50%:50%) 20nm	LiQ 1nm
20 E5	SpA1 140nm	HATC N 5nm	SpMA1 20nm	H1:D5 (97%:3%) 20nm	HBM 10nm	ETM:LiQ (50%:50%) 20nm	LiQ 1nm
E6	SpA1 140nm	HATC N 5nm	SpMA1 20nm	H1:D6 (97%:3%) 20nm	HBM 10nm	ETM:LiQ (50%:50%) 20nm	LiQ 1nm
E7	SpA1 140nm	HATC N 5nm	SpMA1 20nm	H1:D7 (97%:3%) 20nm	HBM 10nm	ETM:LiQ (50%:50%) 20nm	LiQ 1nm
30 E8	SpA1 140nm	HATC N 5nm	SpMA1 20nm	H1:D8 (97%:3%) 20nm	HBM 10nm	ETM:LiQ (50%:50%) 20nm	LiQ 1nm
E9	SpA1 140nm	HATC N 5nm	SpMA1 20nm	H1:D9 (97%:3%) 20nm	HBM 10nm	ETM:LiQ (50%:50%) 20nm	LiQ 1nm
35							

Table B: Device data of vapor processed OLEDs

Ex.	U1000 (V)	SE1000 (cd/A)	LE1000 (lm/W)	EQE1000 (%)	CIE x/y @ 1000 cd/m ²
V1	4.4	5.7	4.1	7.1	0.15/0.09
E1	4.3	6.2	4.5	8.3	0.15/0.08
E2	4.3	7.8	5.6	8.5	0.14/0.10
E3	4.4	6.1	4.4	7.8	0.15/0.08
E4	4.3	6.6	4.8	8.2	0.15/0.09
E5	4.3	8.0	5.8	8.4	0.14/0.10
E6	4.4	6.7	4.8	8.5	0.16/0.09
E7	4.3	7.9	5.8	8.3	0.14/0.10
E8	4.4	8.2	5.9	8.5	0.14/0.11
E9	4.3	8.4	6.1	8.2	0.14/0.11

Table C: Structural formulae of vapor processed OLED materials

 <p>HATCN</p>	 <p>SpA1</p>
 <p>SpMA1</p>	 <p>LiQ</p>
 <p>HBM</p>	 <p>ETM</p>

		
5	H1	SdT1
		
10	D1	D2
		
15	D3	D4
		
20	D5	D6
		
25	D7	D8
		
30	D9	

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Fabrication of solution processed OLED devices

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The production of solution-based OLEDs has already been described many times in the literature, for example in WO 2004/037887 and WO 2010/097155. The process is adapted to the circumstances described below (layer-thickness variation, materials).

5

The inventive material combinations are used in the following layer sequence:

- substrate,
- ITO (50 nm),
- 10 - Buffer (40 nm),
- emission layer (EML) (40 nm),
- hole-blocking layer (HBL) (10 nm),
- electron-transport layer (ETL) (30 nm),
- 15 - cathode (Al) (100 nm).

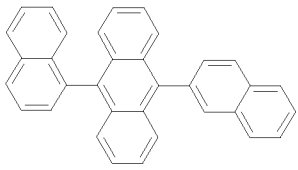
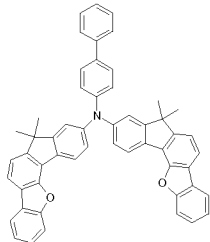
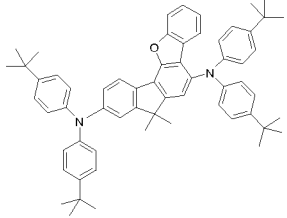
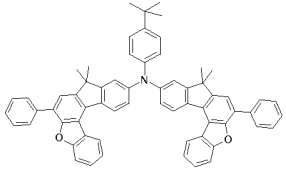
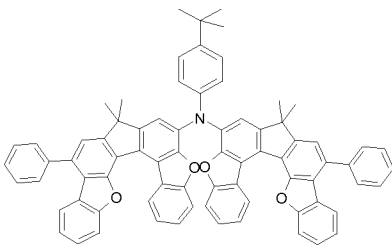
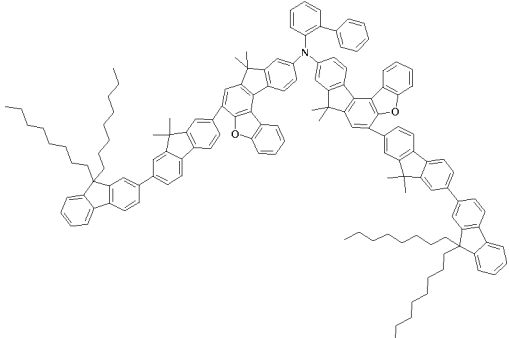
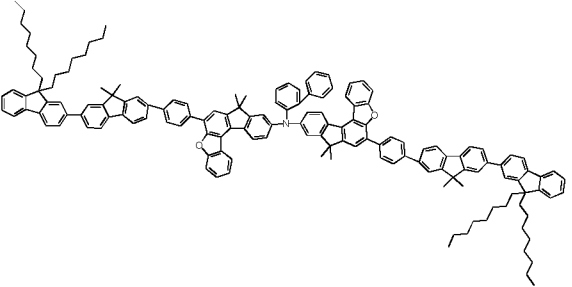
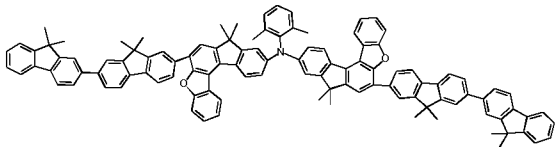
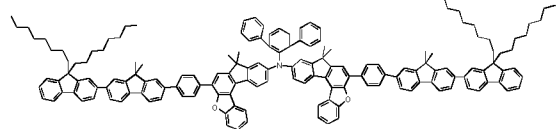
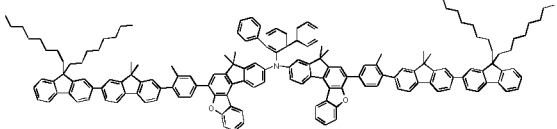
Glass plates coated with structured ITO (indium tin oxide) in a thickness of 50 nm serve as substrate. These are coated with the buffer (PEDOT:PSS) Clevios P VP Al 4083 (Heraeus Clevios GmbH, Leverkusen). The spin coating of the buffer is carried out from water in air. The layer is subsequently dried by heating at 180°C for 10 minutes. The emission layers are applied to the glass plates coated in this way.

25

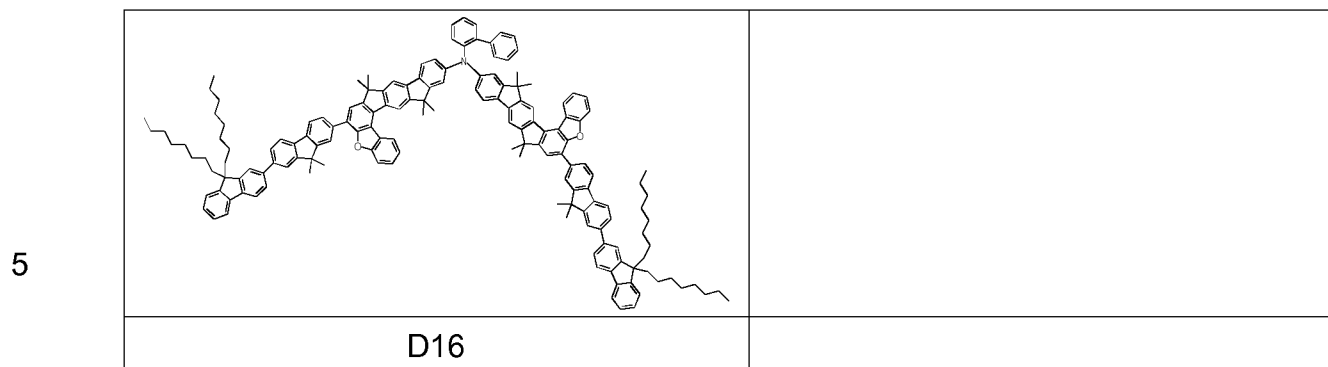
The emission layer (EML) is composed of the matrix material (host material) H2 and the emitting dopant (emitter) D2. Both materials are present in the emission layer in a proportion of 97 % by weight H2 and 3 % by weight D2. The mixture for the emission layer is dissolved in toluene. The solids content of such solutions is about 9 mg/ml if, as here, the layer thickness of 40 nm which is typical for a device is to be achieved by means of spin coating. The layers are applied by spin coating in an inert-gas atmosphere and dried by heating at 120°C for 10 minutes. The materials used in the present case are shown in table D.

35

Table D: Structural formulae of the solution processed materials in the EML

<p>5</p> 	
<p>H2</p>	<p>SdT2</p>
<p>10</p> 	
<p>SdT3</p>	<p>D2</p>
<p>15</p> 	
<p>D10</p>	<p>D11</p>
<p>25</p> 	
<p>D12</p>	<p>D13</p>
<p>30</p> 	
<p>D14</p>	<p>D15</p>

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10 The materials for the hole-blocking layer and electron-transport layer are likewise applied by thermal vapour deposition in a vacuum chamber and are shown in table C. The hole-blocking layer (HBL) consists of ETM. The electron-transport layer (ETL) consists of the two materials ETM and LiQ, which are mixed with one another in a proportion by volume of 50% each by co-evaporation. The cathode is formed by the thermal evaporation of an

 15 aluminium layer with a thickness of 100 nm.

20 The OLEDs are characterised by standard methods. For this purpose, the electroluminescence spectra are recorded, the current efficiency (measured in cd/A) and the external quantum efficiency (EQE, measured in percent) as a function of the luminous density assuming Lambert emission characteristics are calculated from current/voltage/luminous density characteristic lines (IUL characteristic lines). The electroluminescence spectra

 25 are recorded at a luminous density of 1000 cd/m², and the CIE 1931 x and y colour coordinates are calculated from this data. The term EQE1000 denotes the external quantum efficiency at an operating luminous density of 1000 cd/m².

30 The properties of the various OLEDs are summarised in table E. Examples V2 and V3 are the comparative examples, whereas E10 to E17 show properties of OLEDs containing materials of the present invention.

35 Table E: Device data of solution processed OLEDs

- 138 -

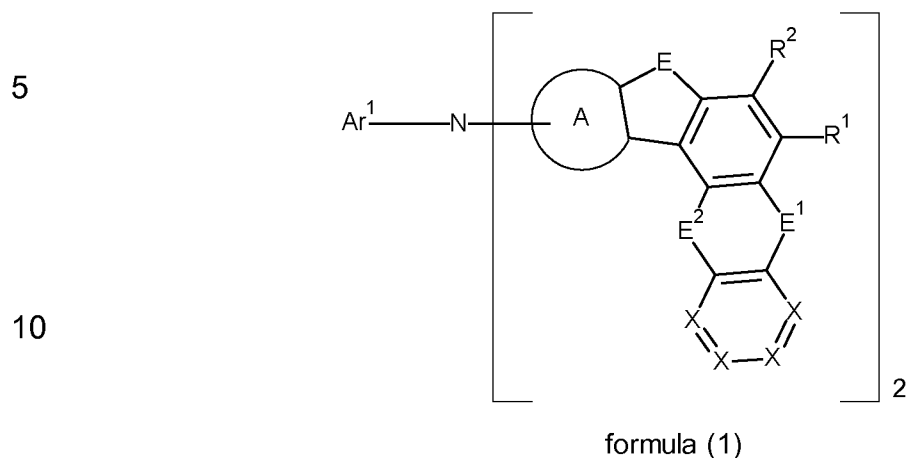
Example	EML host	EML dopant	EQE1000 [%]	CIE x/y
V2	H2	SdT2	1.9	0.15 / 0.05
V3	H2	SdT3	3.2	0.14 / 0.14
E10	H2	D2	3.8	0.14 / 0.14
E11	H2	D10	3.9	0.13 / 0.15
E12	H2	D11	4.5	0.15 / 0.17
E13	H2	D12	4.6	0.15 / 0.16
E14	H2	D13	4.3	0.15 / 0.16
E15	H2	D14	4.4	0.15 / 0.16
E16	H2	D15	4.7	0.14 / 0.15
E17	H2	D16	4.6	0.14 / 0.15

Table E shows that use of materials (D2, D10 to D16) according to the present invention give rise to improvements over the prior art (SdT2 and SdT3) when used as fluorescent blue emitters, in particular with respect to efficiency.

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Patent Claims

1. Compound of the formula (1),



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

A stands on each occurrence, identically or differently, for an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R^3 ; wherein the ring A is condensed on the five-membered ring comprising E via two adjacent carbon atoms, as depicted in formula (1);

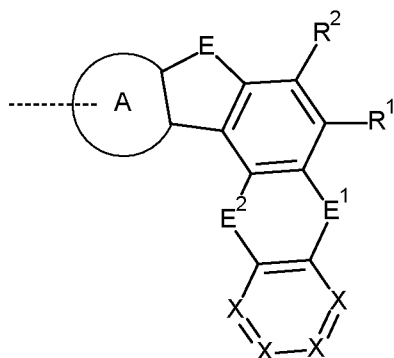
20

Ar^1 stands for:

- 25
- an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R^4 ;
 - a group of formula (Ar1-1),
- 30

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5

formula (Ar1-1)

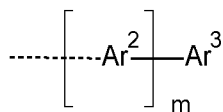
10

where the dashed bond indicates the bonding to the nitrogen atom as depicted in formula (1); or

- a group ArL;

15

ArL stands for a group of formula (ArL-1),



formula (ArL-1)

20

where the dashed bond in formula (ArL-1) indicates the bonding to the structure of formula (1);

25

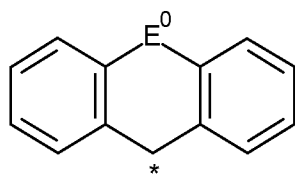
X stands on each occurrence, identically or differently, for CR³ or N;

30

E is on each occurrence, identically or differently, selected from -BR⁰-, -C(R⁰)₂-, -C(R⁰)₂-C(R⁰)₂-, -C(R⁰)₂-O-, -C(R⁰)₂-S-, -R⁰C=CR⁰-, -R⁰C=N-, Si(R⁰)₂-, -Si(R⁰)₂-Si(R⁰)₂-, -C(=O)-, -C(=NR⁰)-, -C(=C(R⁰)₂)-, -O-, -S-, -S(=O)-, -SO₂-, -N(R⁰)-, -P(R⁰)- and -P((=O)R⁰)-; or E is a group of formula (E-1),

35

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formula (E-1)

5

where the symbol * in formula (E-1) indicates the corresponding group E in formula (1); and

10

E^0 is identically or differently on each occurrence, selected from the group consisting of a single bond, $-BR^0-$, $-C(R^0)_2-$, $-C(R^0)_2-C(R^0)_2-$, $-C(R^0)_2-O-$, $-C(R^0)_2-S-$, $-R^0C=CR^0-$, $-R^0C=N-$, $Si(R^0)_2$, $-Si(R^0)_2-Si(R^0)_2-$, $-C(=O)-$, $-C(=NR^0)-$, $-C(=C(R^0)_2)-$, $-O-$, $-S-$, $-S(=O)-$, $-SO_2-$, $-N(R^0)-$, $P(R^0)-$ and $-P(=O)R^0-$;

15

E^1 , E^2 are identically or differently on each occurrence, selected from the group consisting of a single bond, $-C(R^0)_2-$, $Si(R^0)_2$, $-O-$ and $-S-$; with the proviso that, in a ring comprising the groups E^1 and E^2 , one of the group E^1 and E^2 , is a single bond, $-C(R^0)_2-$ or $Si(R^0)_2$, and the other group is O or S;

20

R^0 , R^1 , R^2 , R^3 , R^4 stand on each occurrence, identically or differently, for:

25

- H, D, F, Cl, Br, I, CHO, CN, $N(Ar)_2$, $C(=O)Ar$, $P(=O)(Ar)_2$, $S(=O)Ar$, $S(=O)_2Ar$, NO_2 , $Si(R)_3$, $B(OR)_2$ or OSO_2R ;
- a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 40 C atoms or branched or a cyclic alkyl, alkoxy or thioalkyl groups having 3 to 40 C atoms, each of which may be substituted by one or more radicals R, where in each case one or more non-adjacent CH_2 groups may be replaced by $RC=CR$, $C\equiv C$, $Si(R)_2$, $Ge(R)_2$, $Sn(R)_2$, $C=O$, $C=S$, $C=Se$, $P(=O)(R)$, SO, SO_2 , O, S or CONR and

30

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where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂;

- an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R, or an aryloxy groups having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R; or
- for a group ArL, which may be substituted by one or more radicals R;

and where two adjacent substituents R⁰, two adjacent substituents R¹ and R², two adjacent substituents R³ and/or two adjacent substituents R⁴, may form a mono- or polycyclic, aliphatic ring system or aromatic ring system, which may be substituted by one or more radicals R;

Ar², Ar³ stand on each occurrence, identically or differently, for an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R;

m is an integer selected from 1 to 10;

R stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CHO, CN, N(Ar)₂, C(=O)Ar, P(=O)(Ar)₂, S(=O)Ar, S(=O)₂Ar, NO₂, Si(R')₃, B(OR')₂, OSO₂R', a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 40 C atoms or branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 40 C atoms, each of which may be substituted by one or more radicals R', where in each case one or more non-adjacent CH₂ groups may be replaced by R'C=CR', C≡C, Si(R')₂, Ge(R')₂, Sn(R')₂, C=O, C=S, C=Se, P(=O)(R'), SO, SO₂, O, S or CONR' and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R', or an aryloxy group having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R', where two

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adjacent substituents R may form a mono- or polycyclic, aliphatic ring system or aromatic ring system, which may be substituted by one or more radicals R';

5 Ar is an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms, which may in each case also be substituted by one or more radicals R';

10 R' stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms or branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, where in each case one or more non-adjacent CH₂ groups may be replaced by SO, SO₂, O, S and where one or more H atoms
15 may be replaced by D, F, Cl, Br or I, or an aromatic or heteroaromatic ring system having 5 to 24 C atoms;

with the proviso that, when the ring A stands for a benzene ring, then the
20 group R¹ or the group R² is selected from an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R.

25 2. Compound according to claim 1, characterized in that the ring A is selected from the group consisting of phenyl, naphthyl, anthracene, phenanthrene, fluorene, dibenzothiophene, dibenzofurane or carbazole, which may in each case be substituted by one or more radicals R³.

30 3. Compound according to one or more of claim 1 or 2, characterized in that Ar¹ stands for:

- phenyl, biphenyl, fluorene, spirobifluorene, naphthalene, phenanthrene, dibenzofuran, dibenzothiophene, carbazole, pyridine, pyrimidine,
35 pyrazine, pyridazine, triazine, benzopyridine, benzopyridazine, benzopyrimidine or quinazoline, or a combination of two or three of

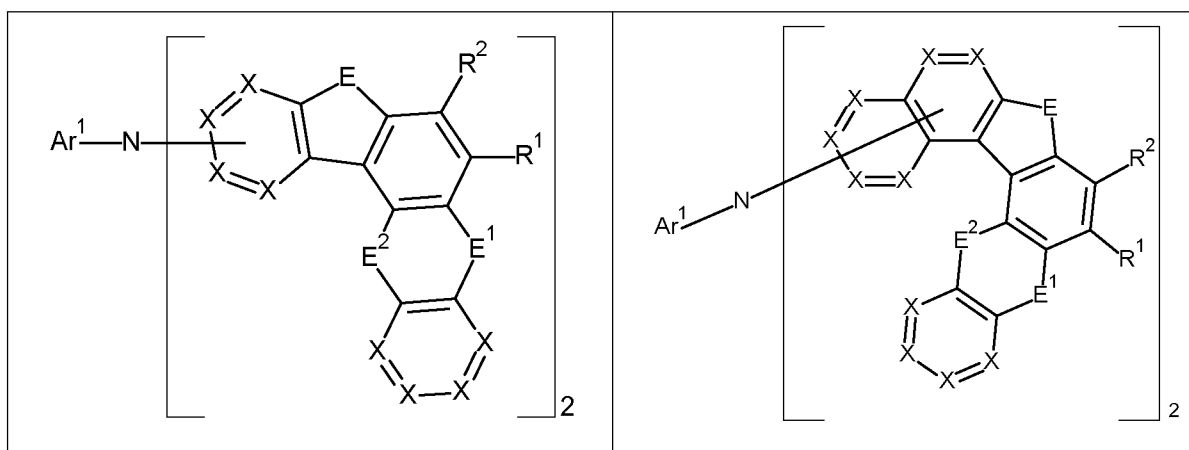
these groups, each of which may be substituted by one or more radicals R⁴;

- a group of formula (Ar1-1) as depicted above; or
- a group ArL.

5

4. Compound according to one or more of the preceding claims, selected from compounds of formulae (2) to (41),

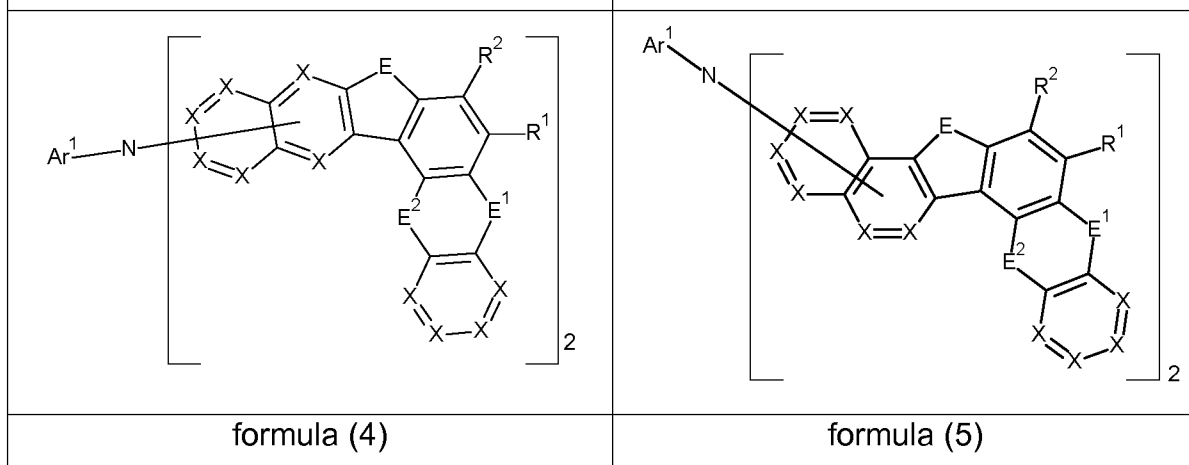
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formula (2)

formula (3)

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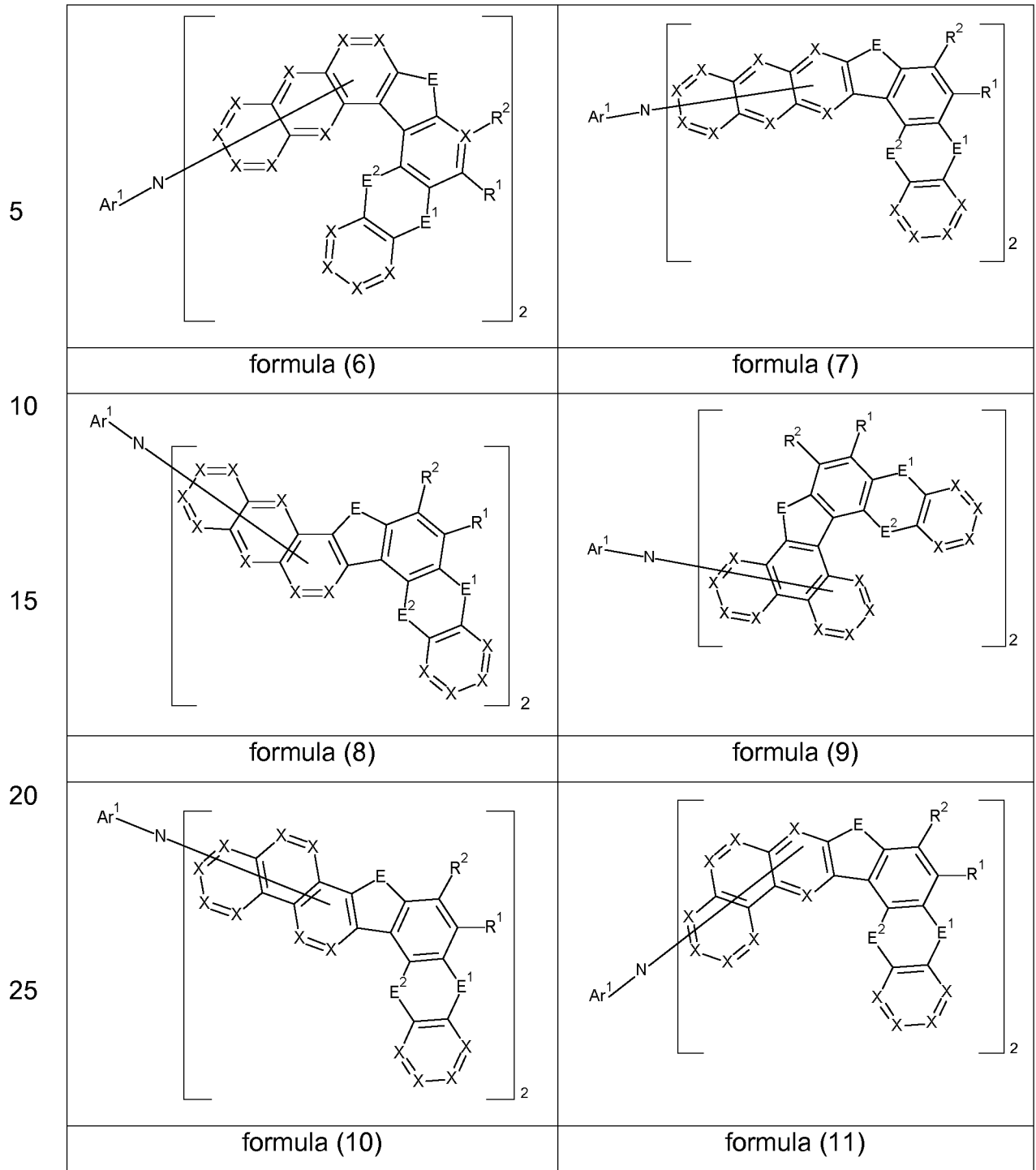


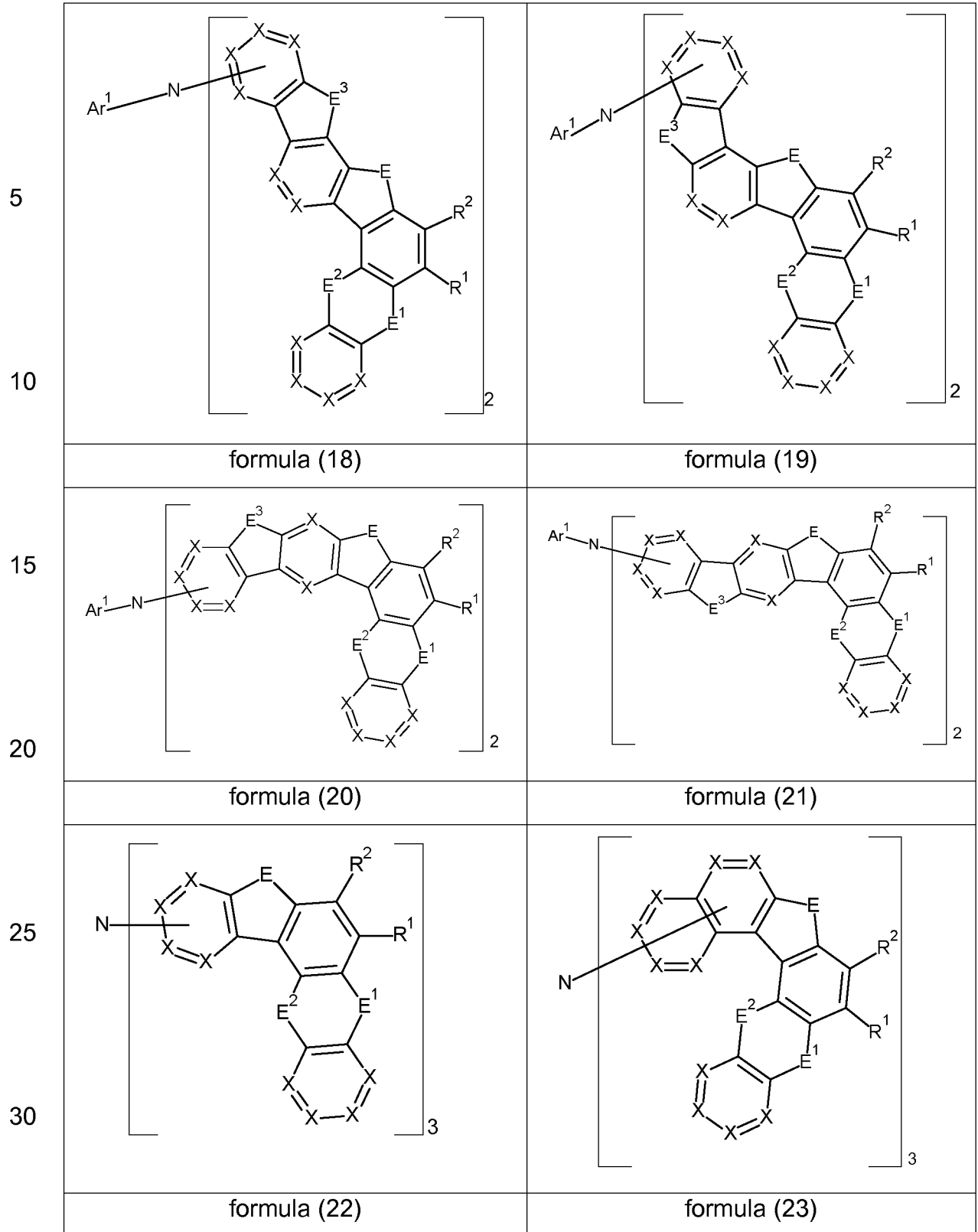
formula (4)

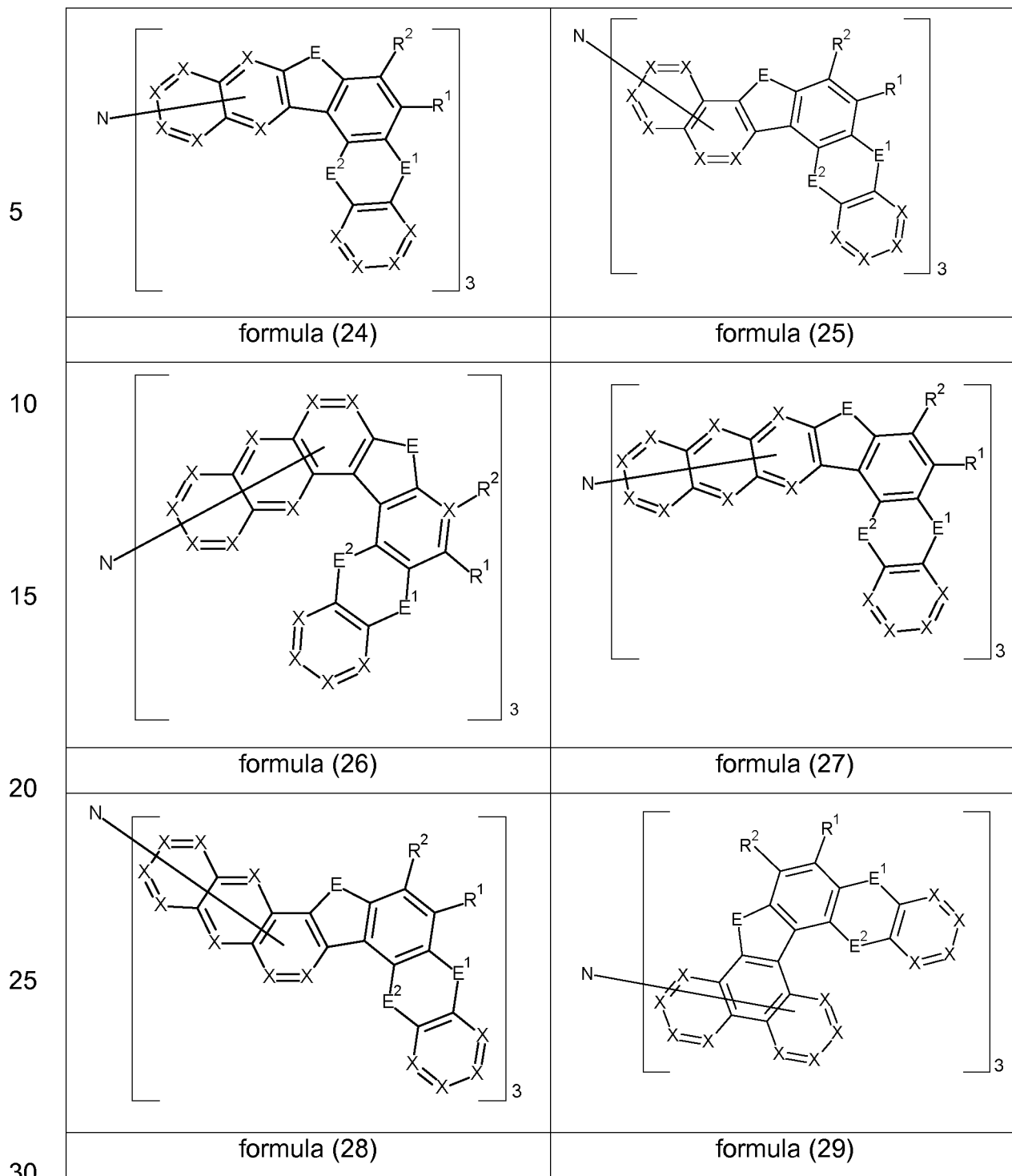
formula (5)

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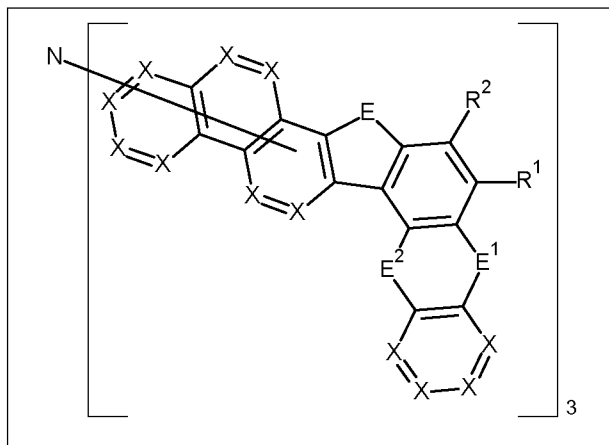
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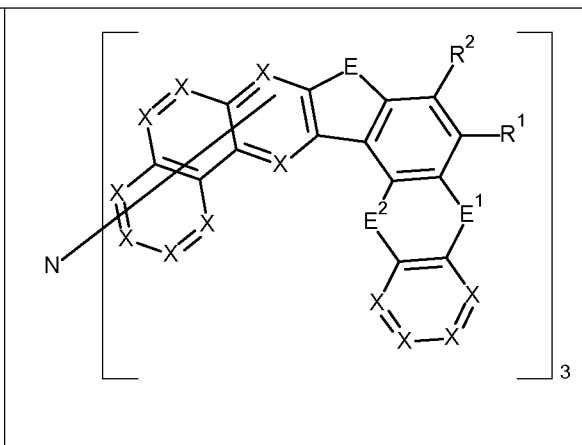




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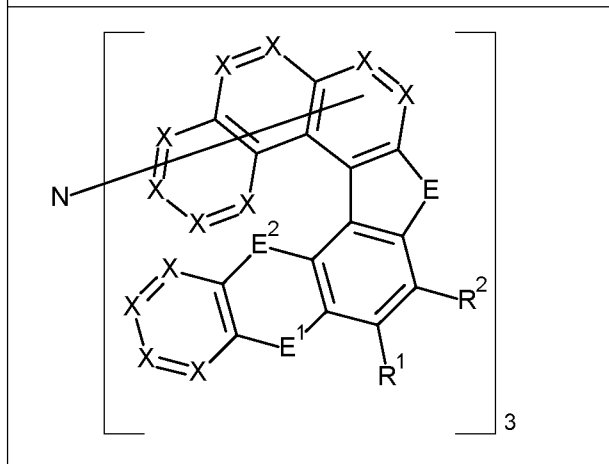


formula (30)

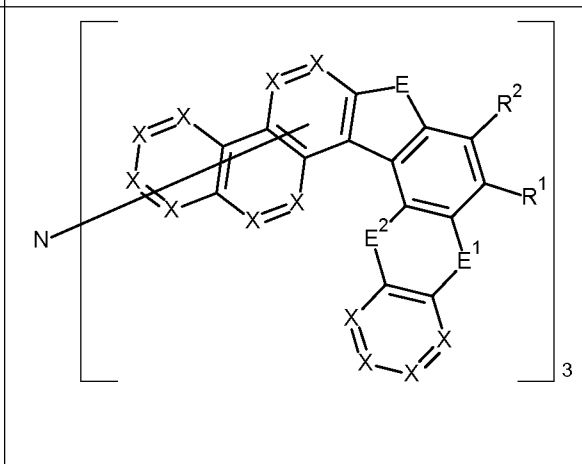


formula (31)

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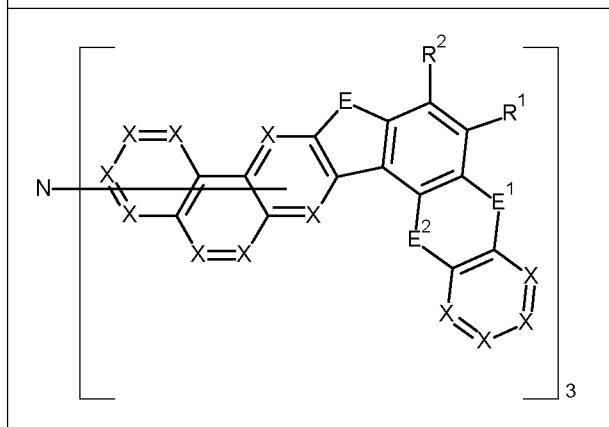


formula (32)

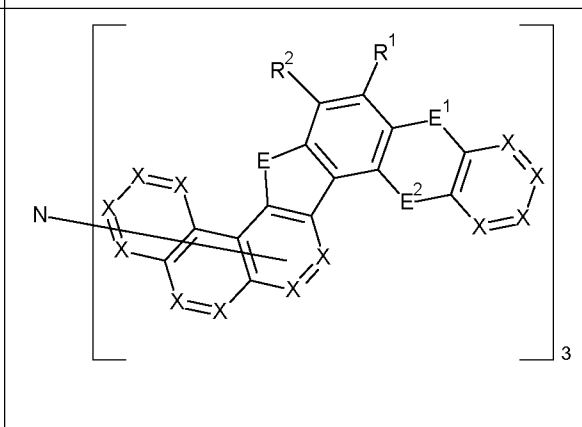


formula (33)

20



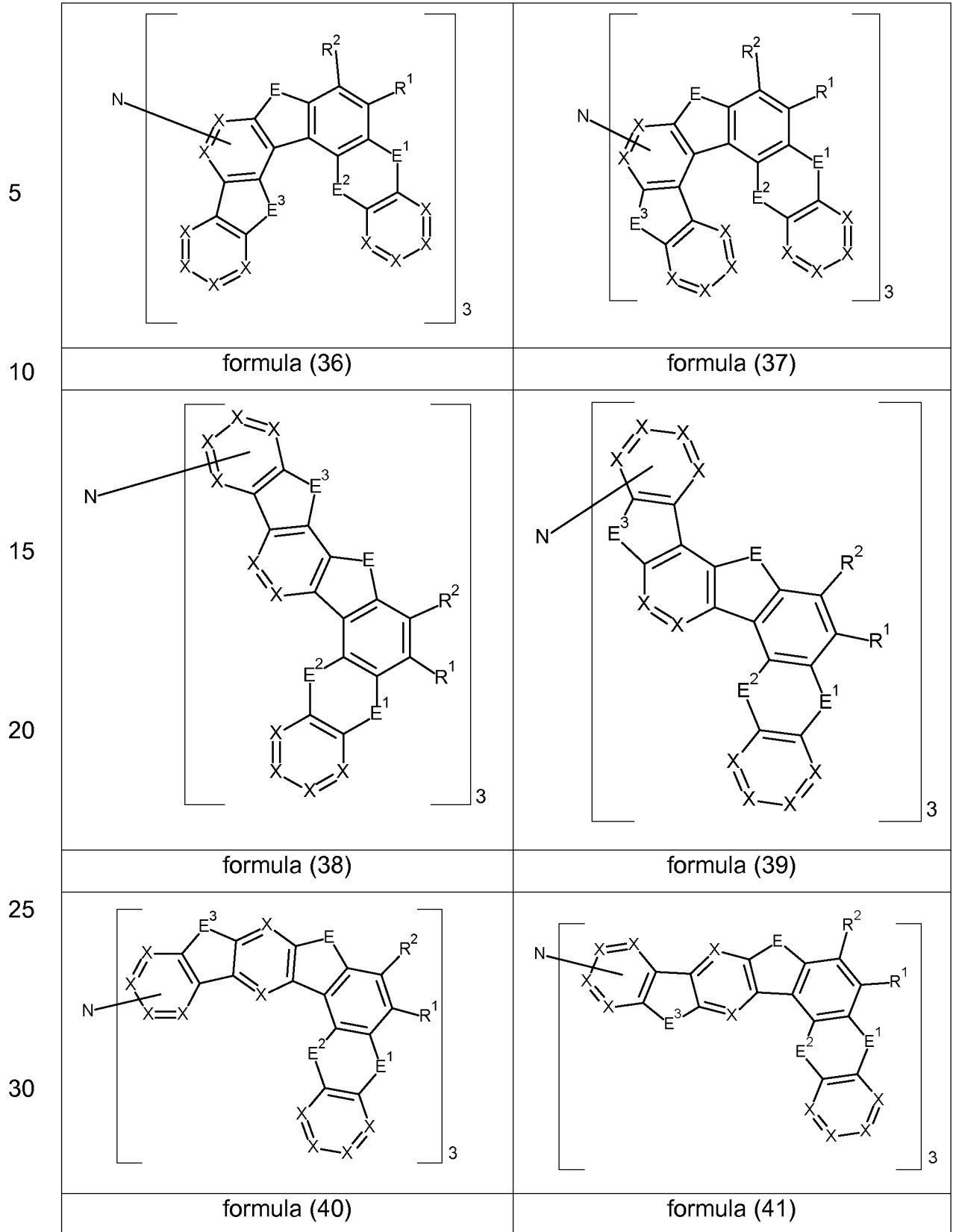
formula (34)



formula (35)

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- 151 -

where the symbols Ar^1 , E, E^1 , E^2 , R^1 and R^2 have the same meaning as in claim 1; and where

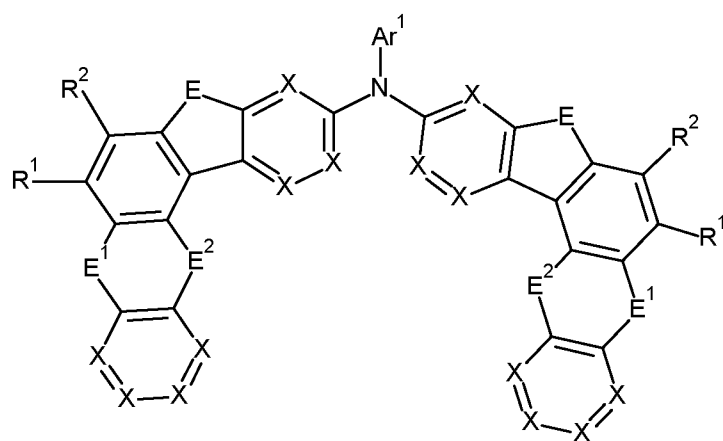
X is CR^2 or N; or X stands for C if a group $-NAr^1$ is bonded to X; and

E^3 is on each occurrence, identically or differently, selected from

5 $-C(R^0)_2-$, $-O-$, $-S-$ or $-N(R^0)-$; where R^0 has the same meaning as in claim 1.

5. Compound according to one or more of the preceding claims, selected from compounds of formulae (2-1) to (41-1),

10

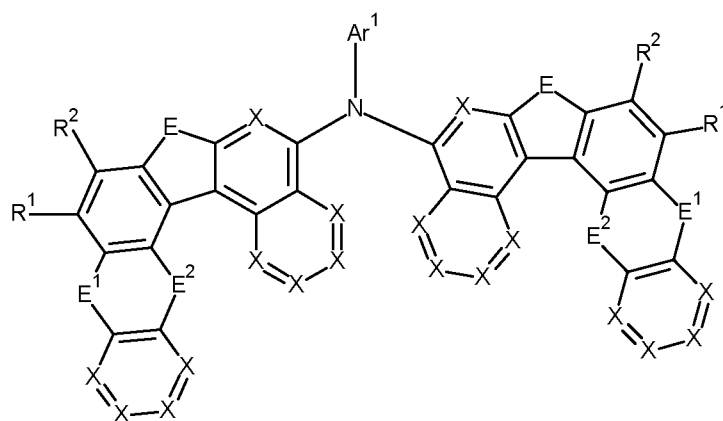


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formula (2-1)

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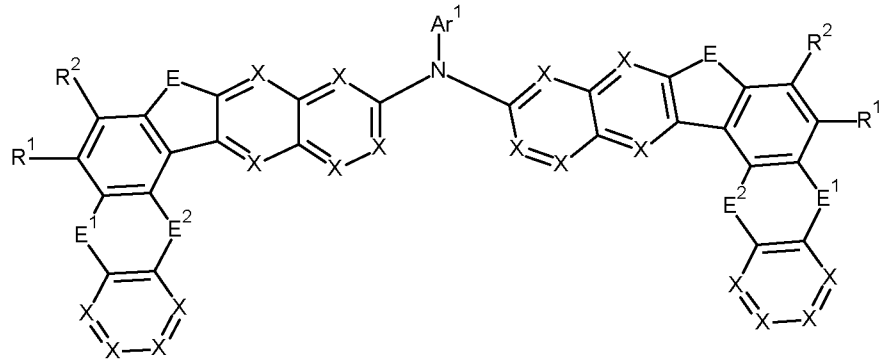


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formula (3-1)

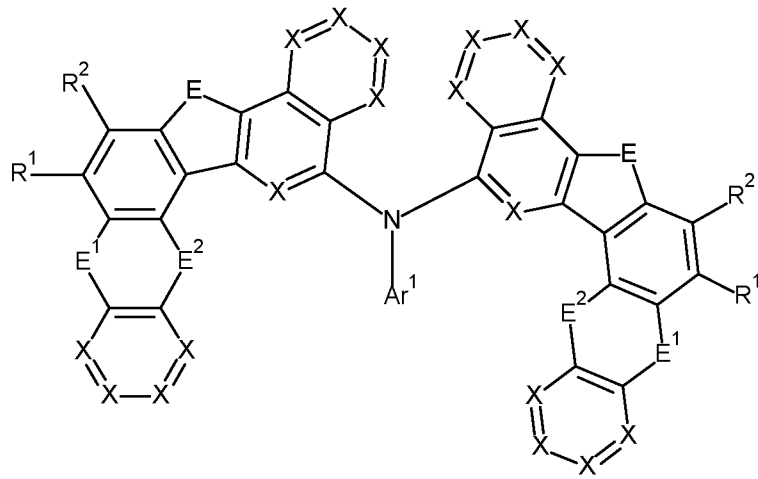
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formula (4-1)

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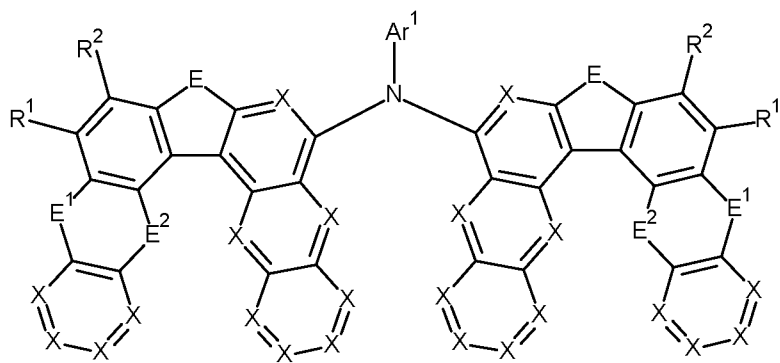


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formula (5-1)

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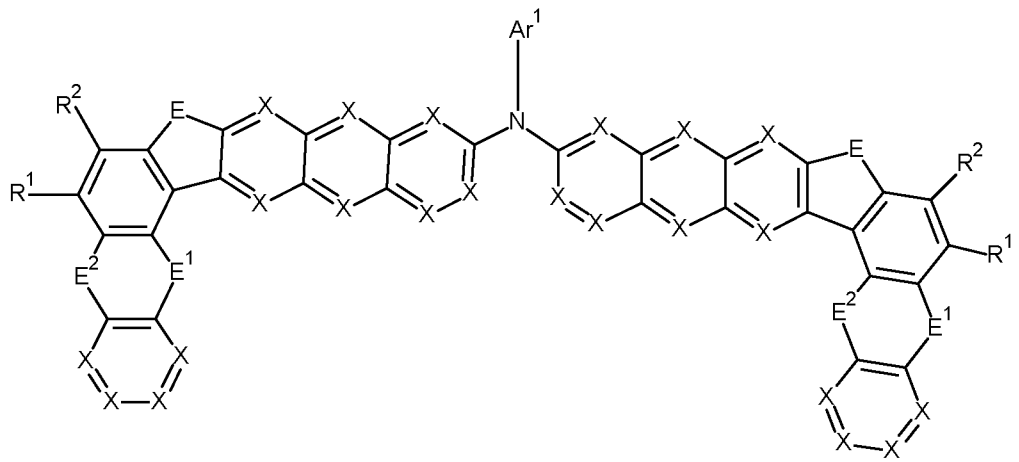


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formula (6-1)

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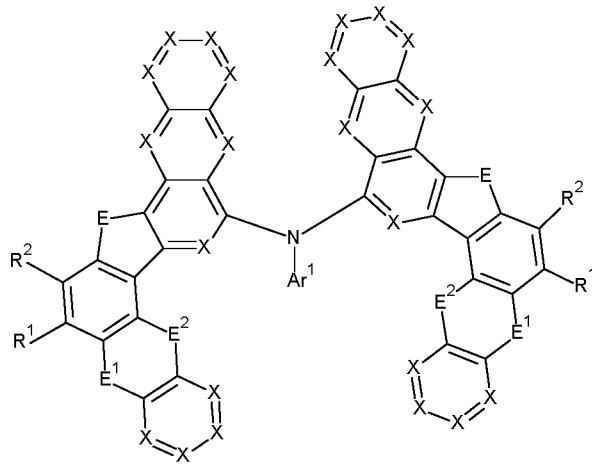
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formula (7-1)

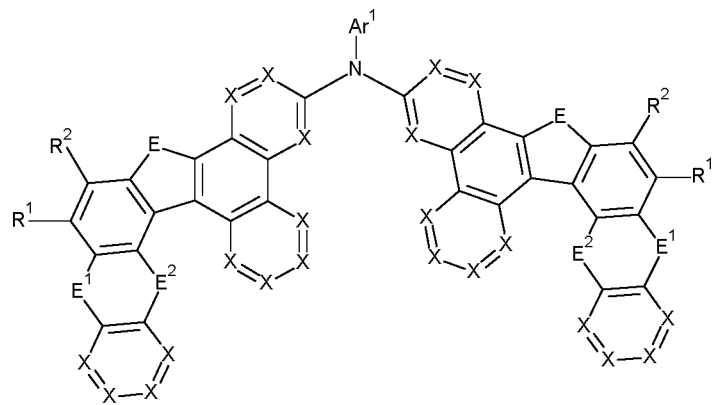
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formula (8-1)

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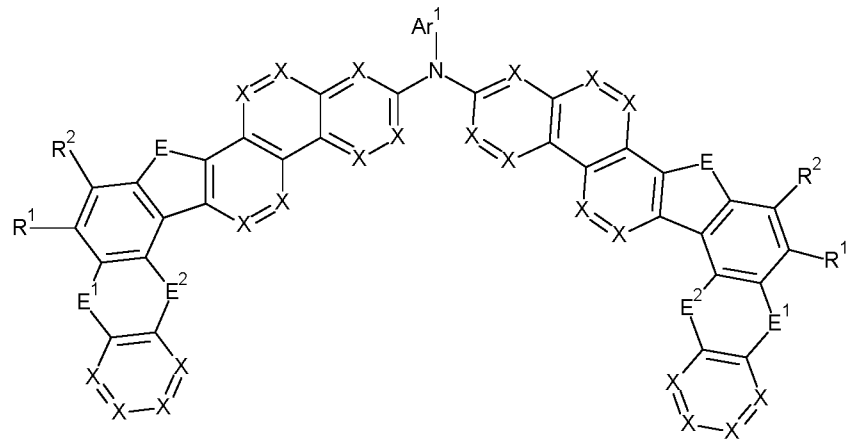


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formula (9-1)

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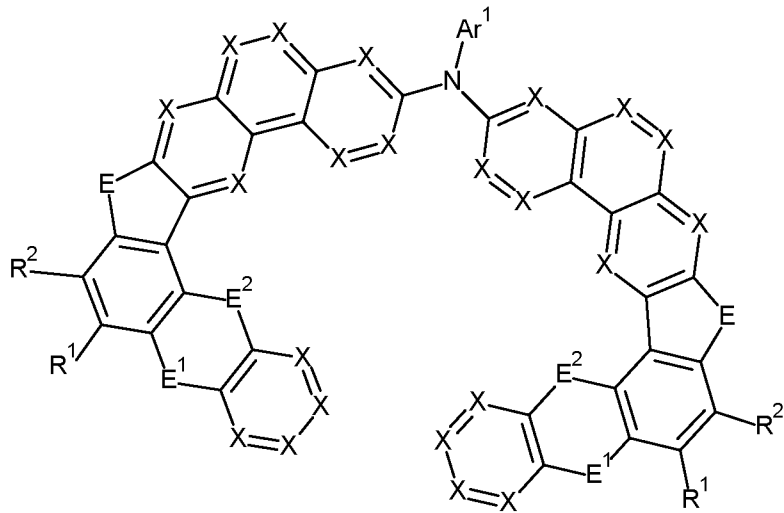
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formula (10-1)

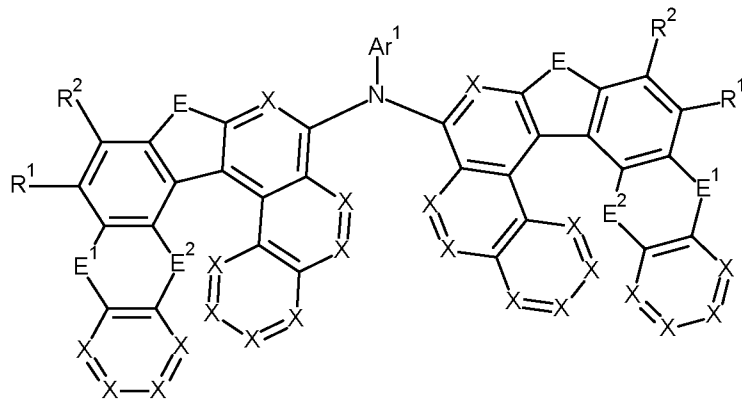
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formula (11-1)

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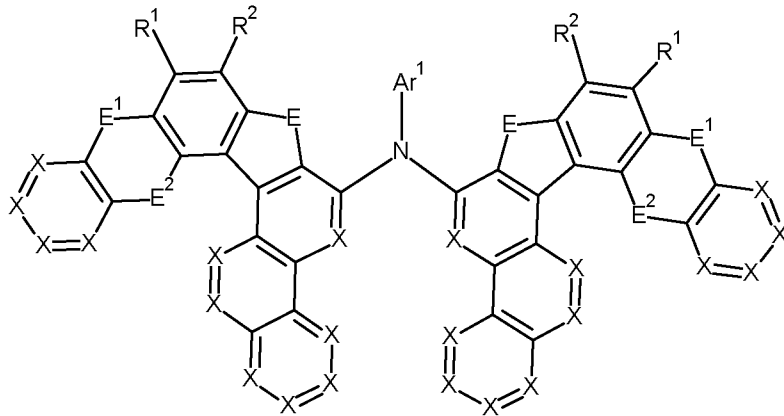


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formula (12-1)

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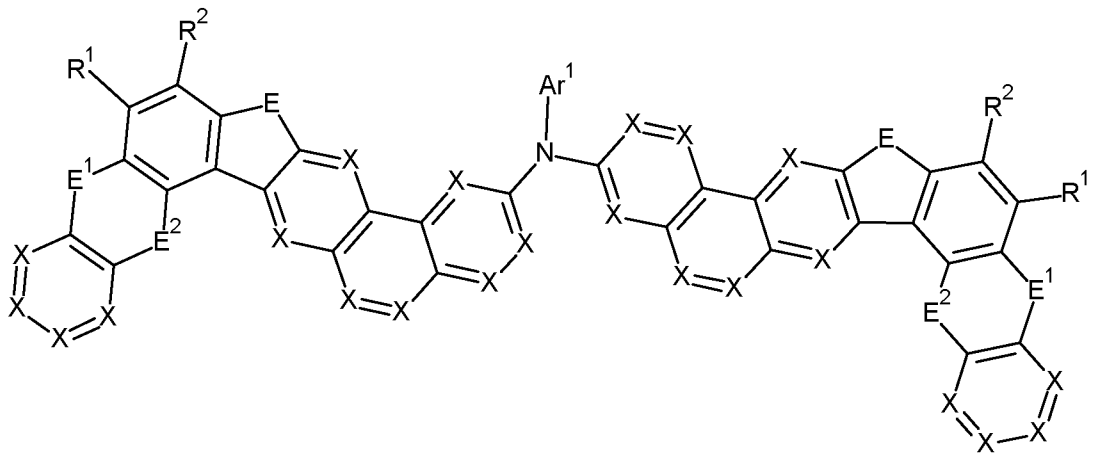
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formula (13-1)

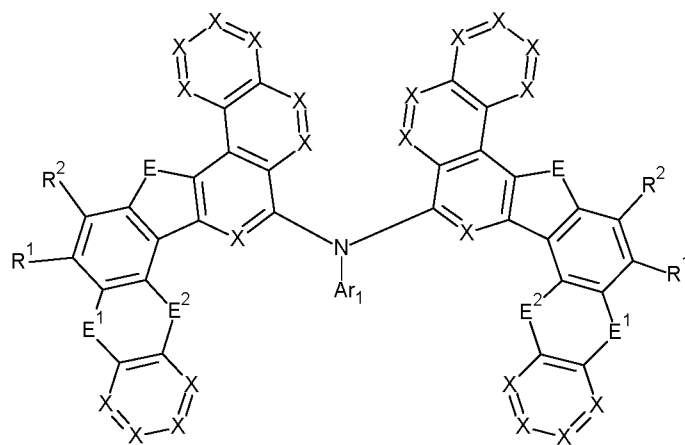
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formula (14-1)

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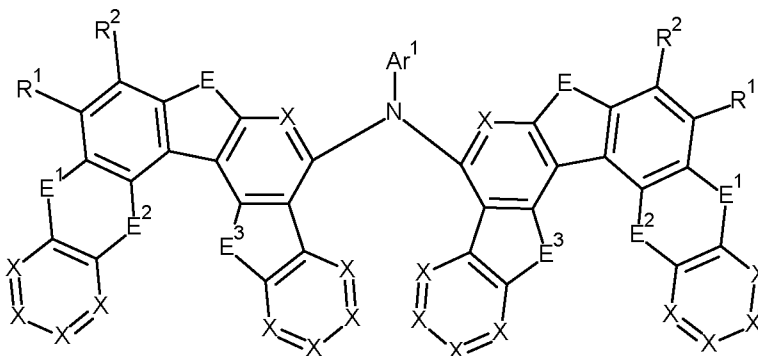


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formula (15-1)

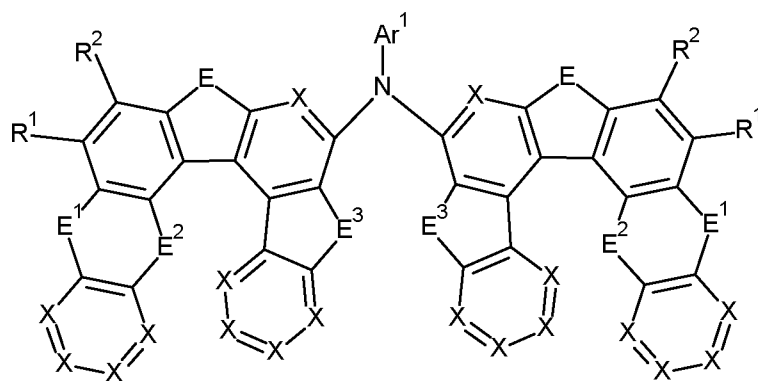
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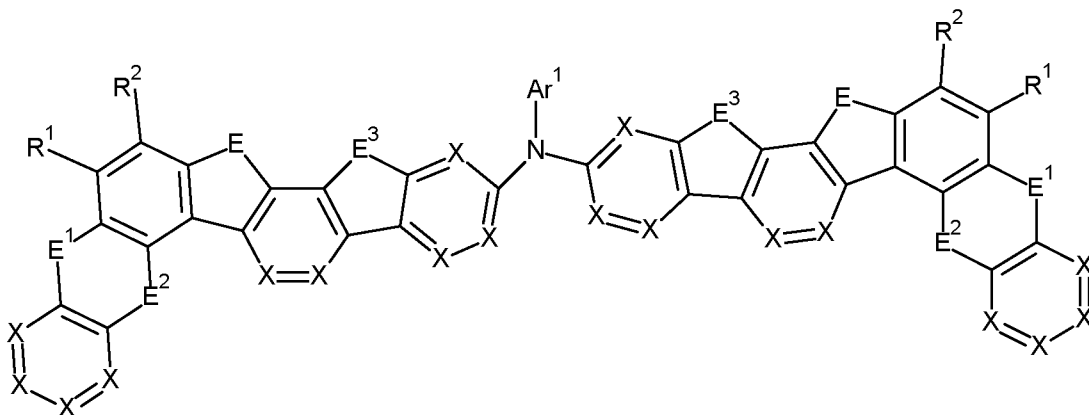
formula (16-1)

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formula (17-1)

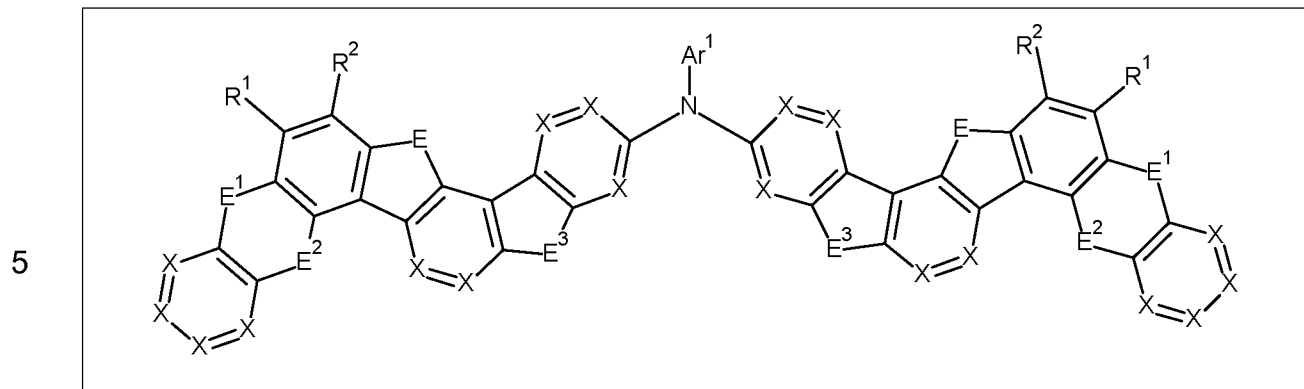
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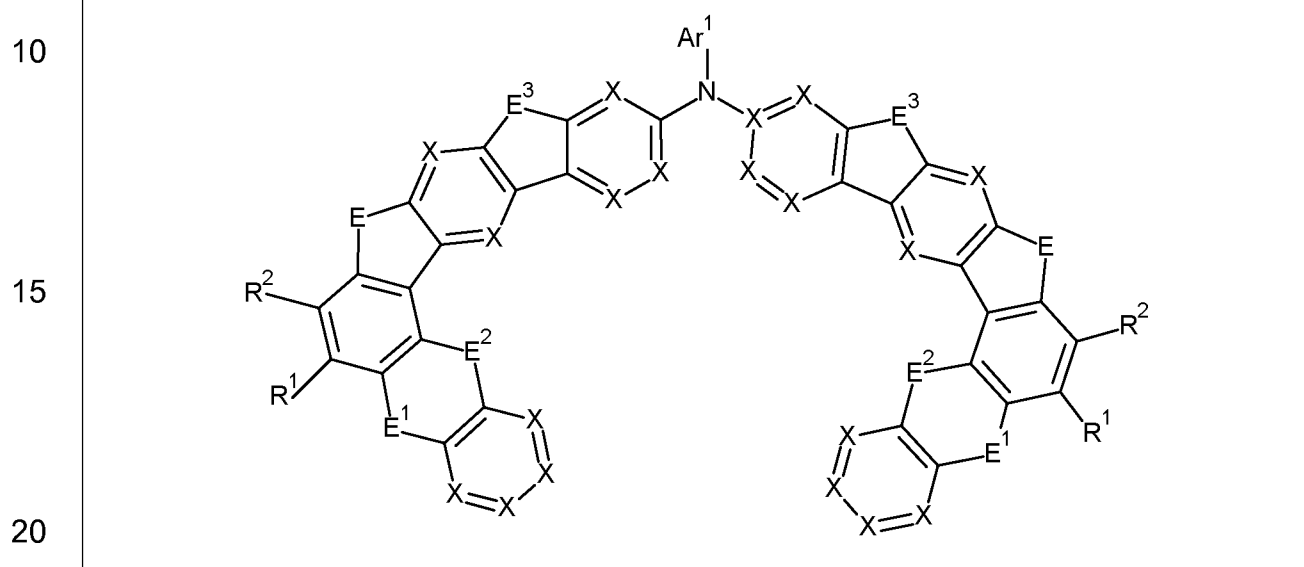
formula (18-1)

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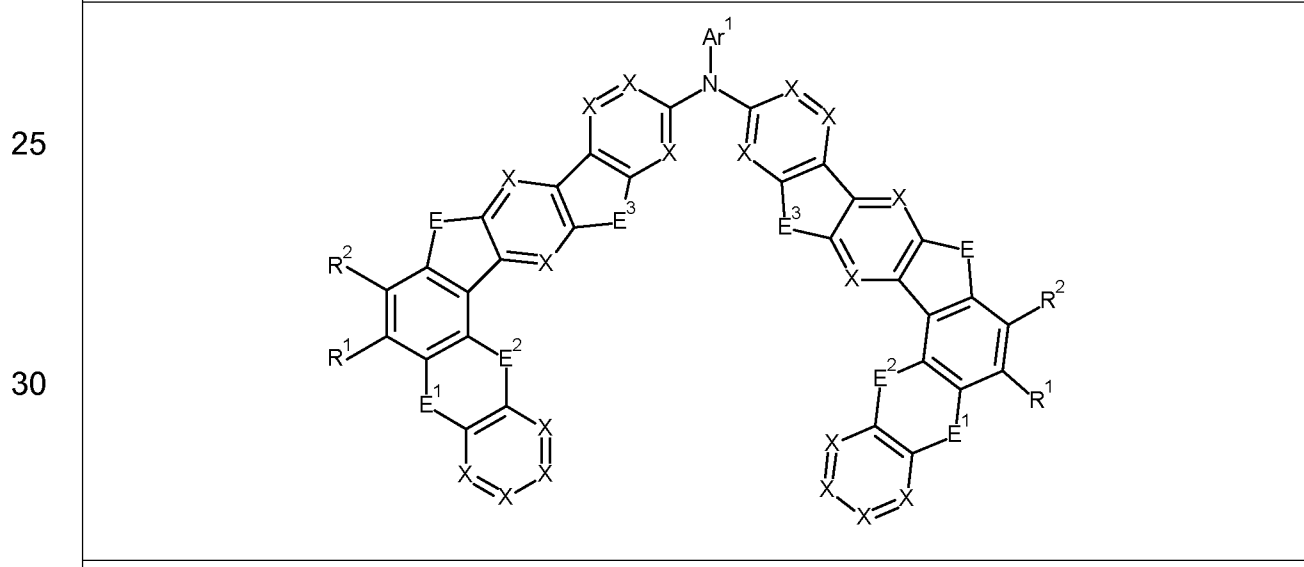
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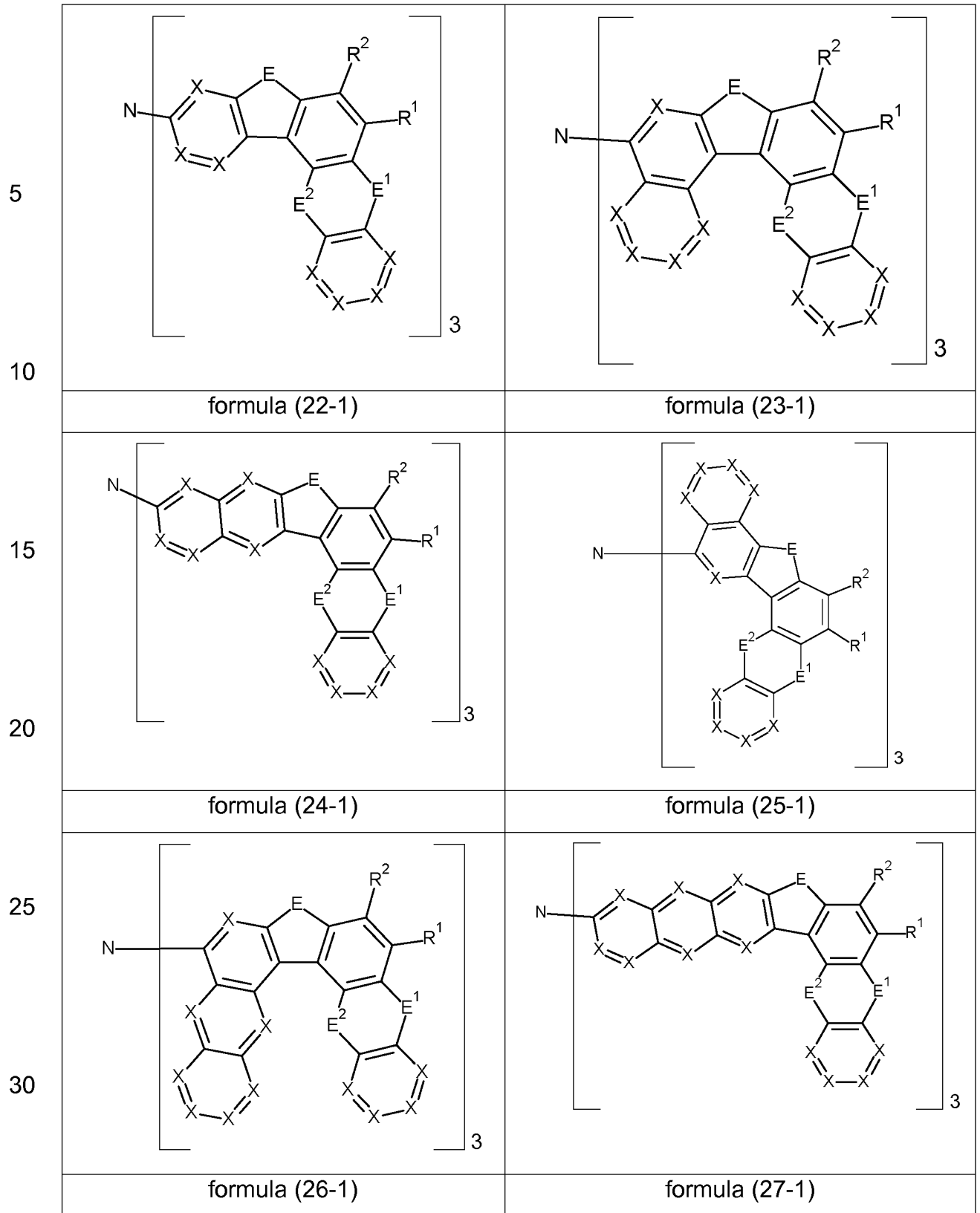
formula (19-1)



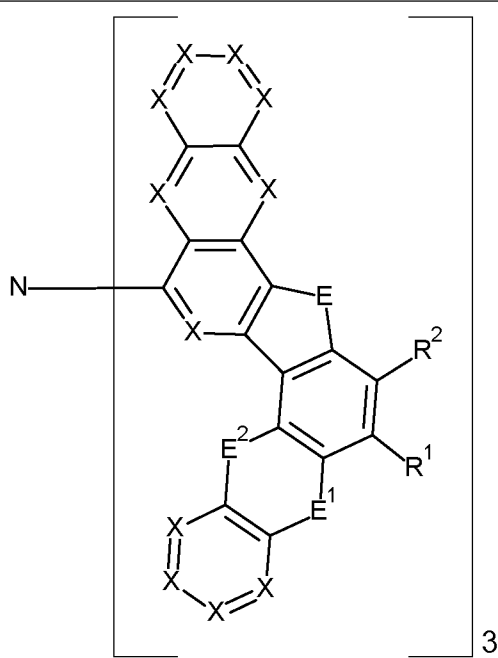
formula (20-1)



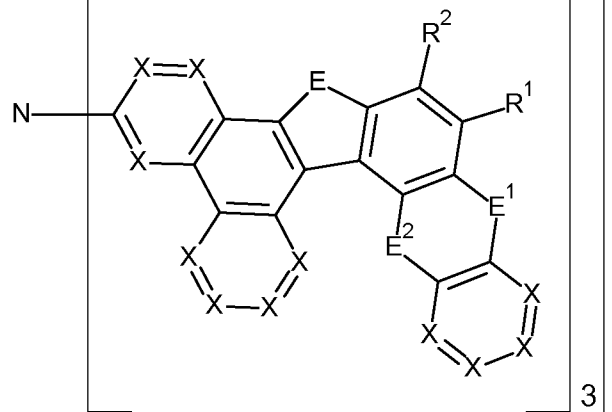
formula (21-1)



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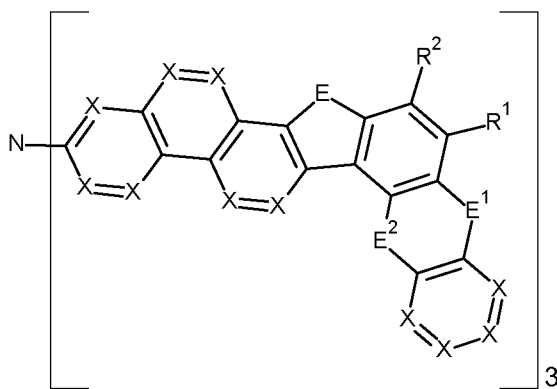


formula (28-1)

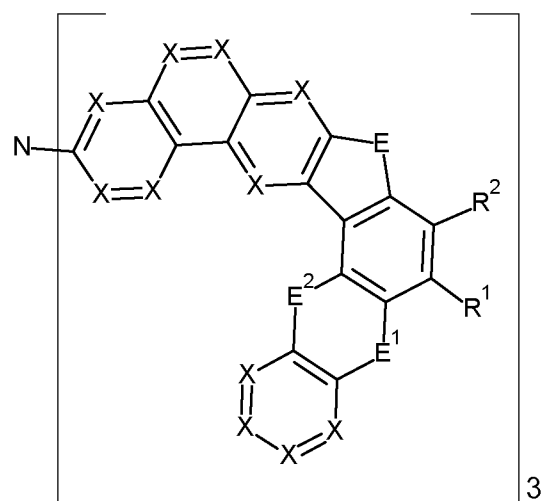


formula (29-1)

15



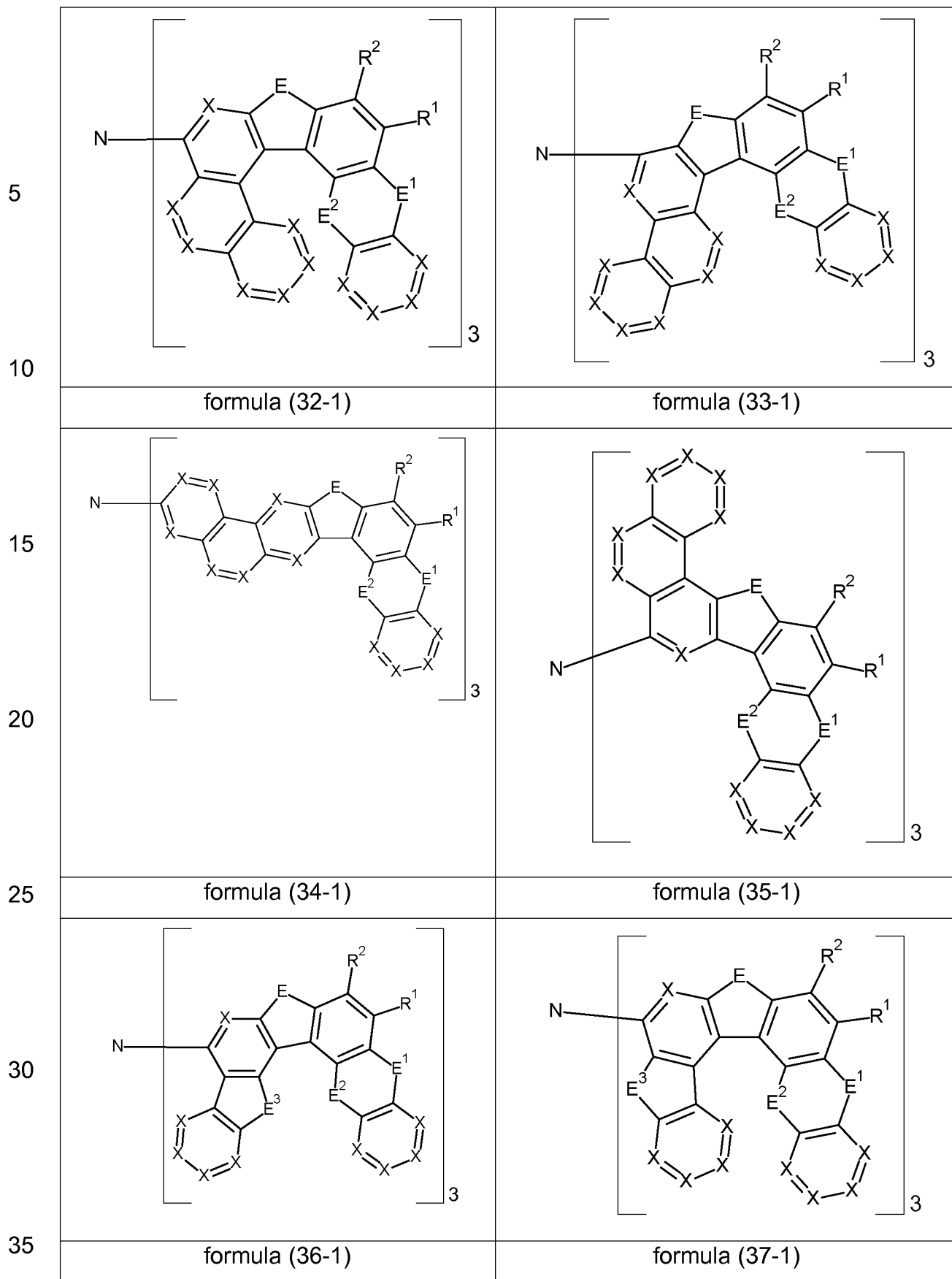
formula (30-1)



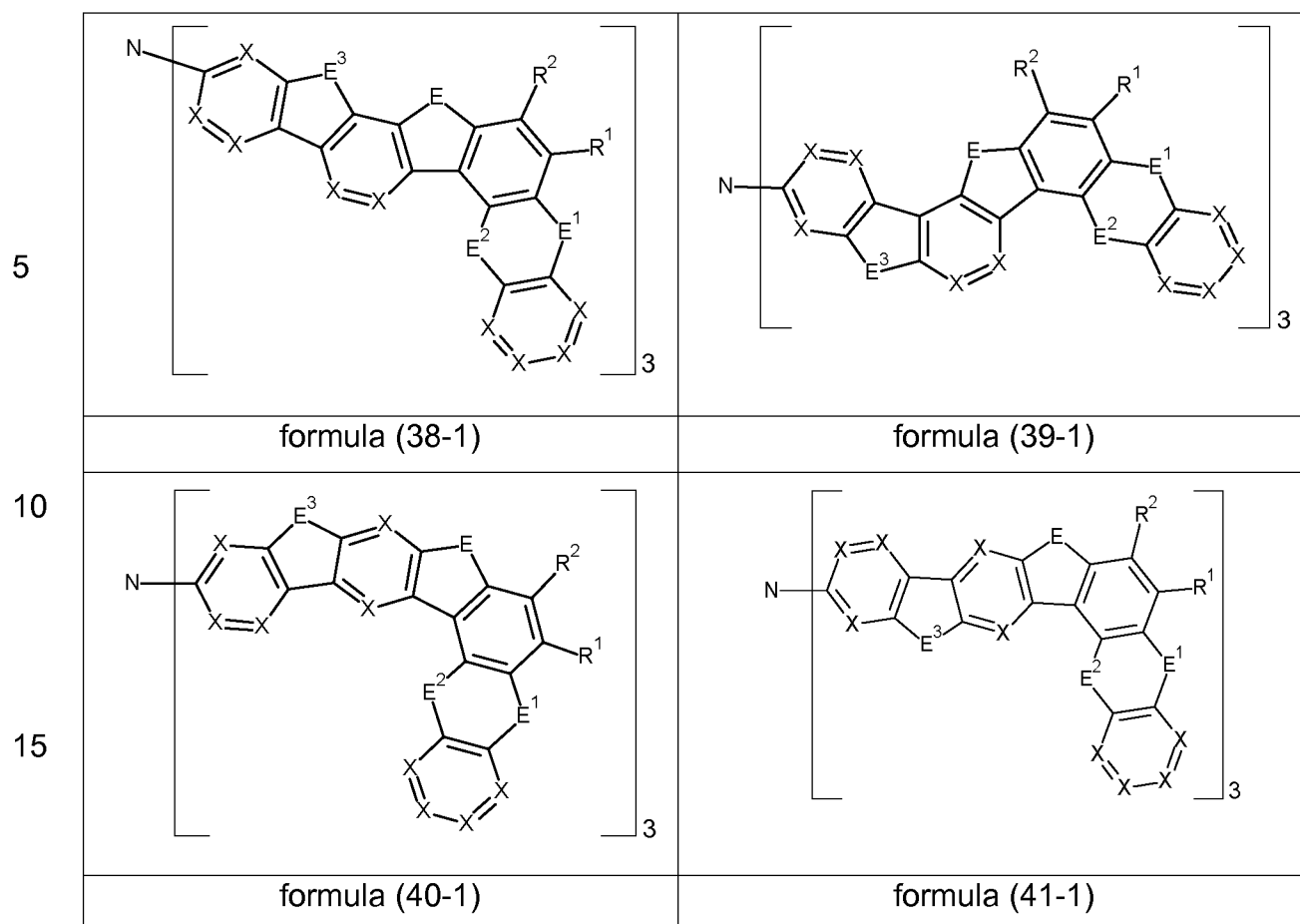
formula (31-1)

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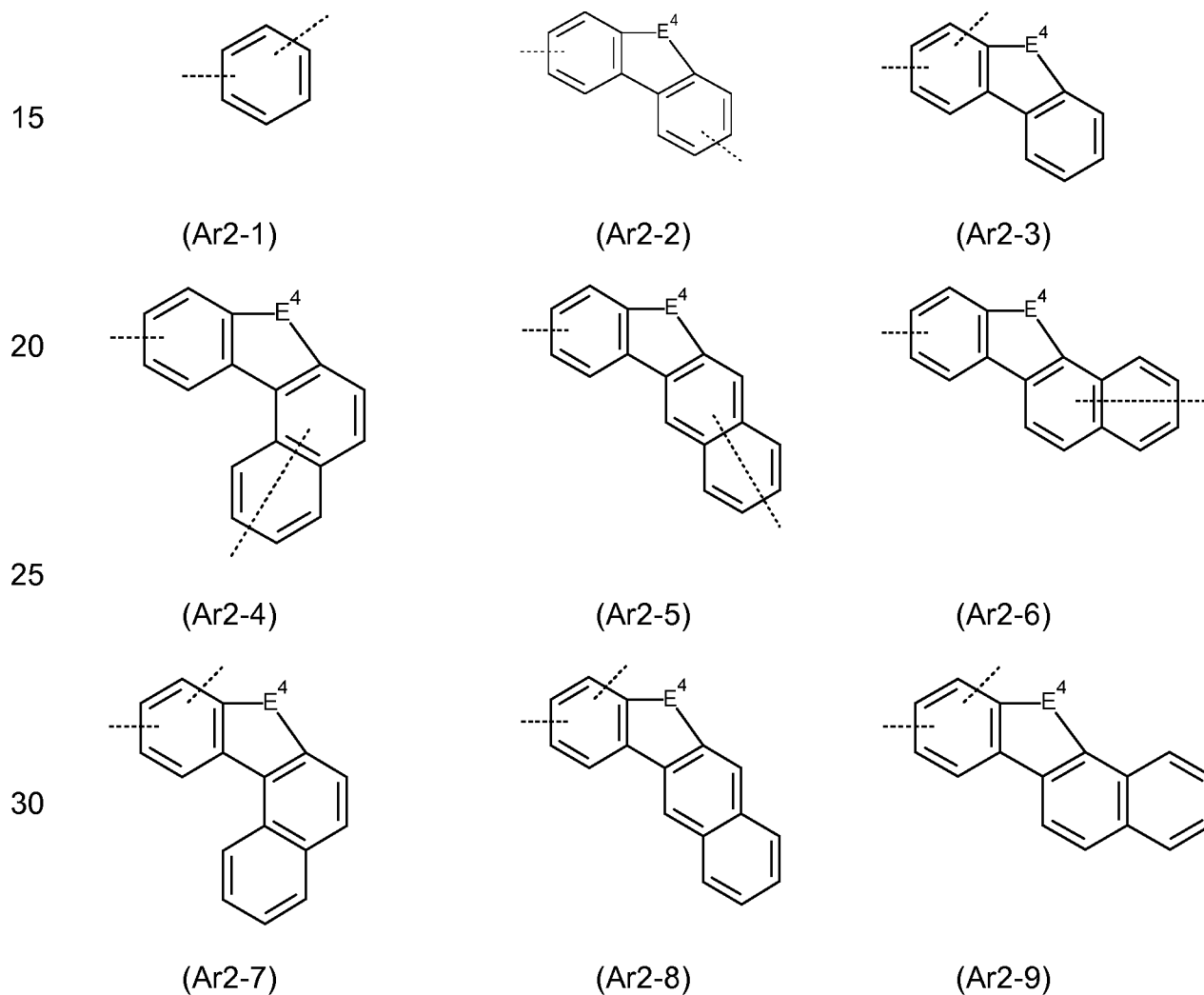
20 where the symbols X, Ar¹, E, E¹, E², R¹ and R² have the same meaning as in claim 1 and the symbol E³ has the same meaning as in claim 3.

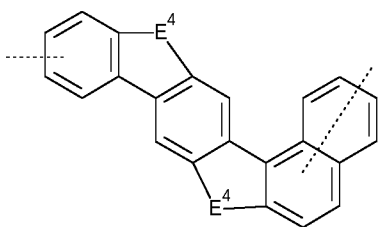
6. Compound according to one or more of the preceding claims,
 25 characterized in that at least one of the groups R¹ and R² present in the same ring corresponds to a group Ar_L of formula (Ar_L-1) as defined in claim 1.

7. Compound according to one or more of the preceding claims,
 30 characterized in that E¹, E² are, identically or differently, on each occurrence, selected from the group consisting of a single bond, -O- and -S-; with the proviso that, in a ring comprising the groups E¹ and E², one of the group E¹ and E² is a single bond, and the other group is O or S.
 35

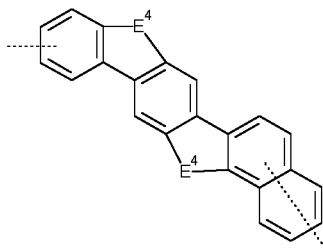
- 162 -

8. Compound according to one or more of the preceding claims, characterized in that, in a ring comprising the groups E^1 and E^2 , E^1 is O and E^2 is a single bond or E^1 is a single bond and E^2 is O.
9. Compound according to one or more of the preceding claims, characterized in that E is $-C(R^0)_2-$.
10. Compound according to one or more of the preceding claims, characterized in that the group Ar^2 in formula (ArL-1) is selected from the groups of formulae (Ar2-1) to (Ar2-25),

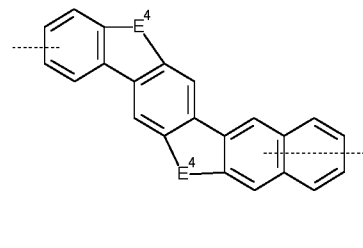




(Ar2-10)

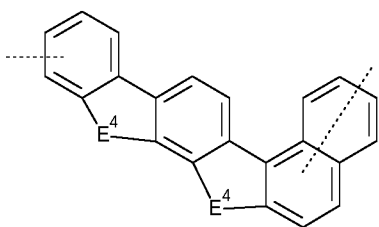


(Ar2-11)

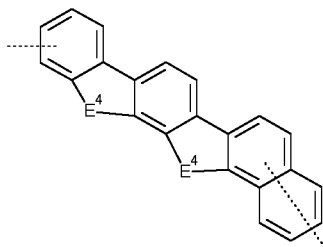


(Ar2-12)

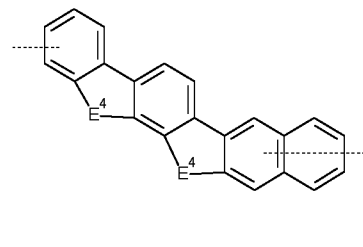
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(Ar2-13)

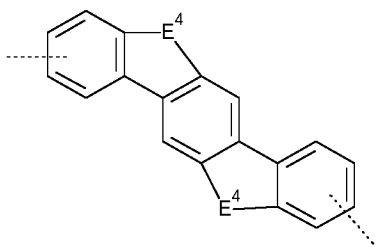


(Ar2-14)

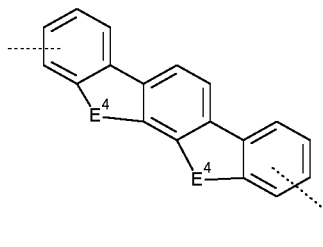


(Ar2-15)

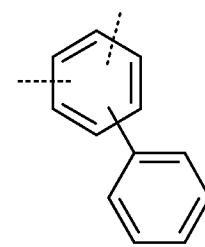
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(Ar2-16)

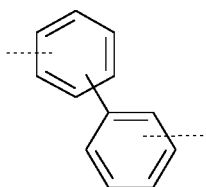


(Ar2-17)

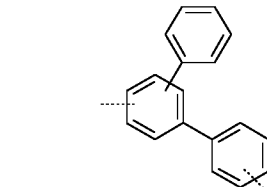


(Ar2-18)

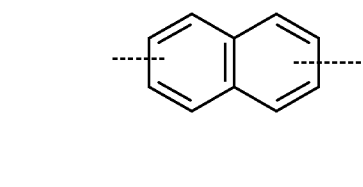
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(Ar2-19)



(Ar2-20)



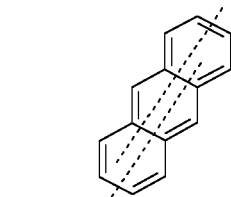
(Ar2-21)

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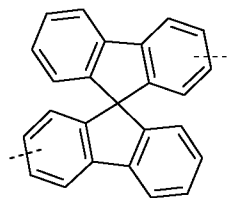
(Ar2-22)



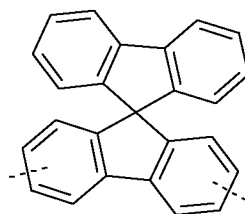
(Ar2-23)

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(Ar2-24)



(Ar2-25)

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where the dashed bonds indicate the bonding to the structure of formula (1) and to a group Ar^2 or Ar^3 and the groups of formulae (Ar2-1) to (Ar2-25) may be substituted at each free position by a group R, which has the same meaning as in claim 1 and where

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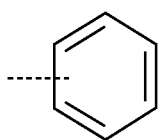
15

E^4 is selected from $-B(R^0)$, $-C(R^0)_2$, $-C(R^0)_2-C(R^0)_2-$, $-Si(R^0)_2$, $-C(=O)-$, $-C(=NR^0)-$, $-C(C(R^0))_2-$, $-O-$, $-S-$, $-S(=O)-$, $-SO_2-$, $-N(R^0)-$, $-P(R^0)-$ and $-P(=O)R^0-$, where the substituent R^0 has the same meaning as in claim 1.

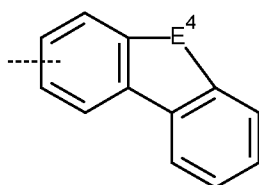
11. Compound according to one or more of the preceding claim, characterized in that Ar^3 is on each occurrence, identically or differently, selected from the group consisting of the groups of formulae (Ar3-1) to (Ar3-27),

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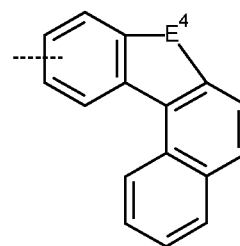
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(Ar3-1)



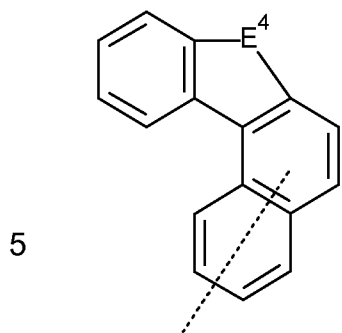
(Ar3-2)



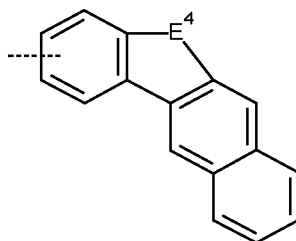
(Ar3-3)

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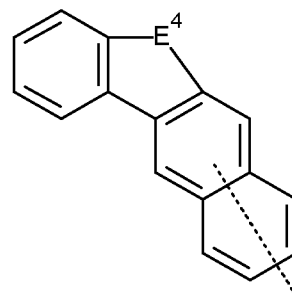
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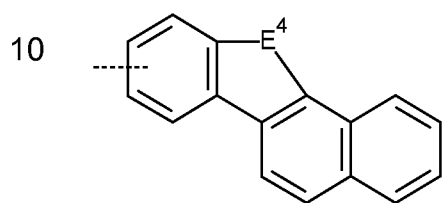
(Ar3-4)



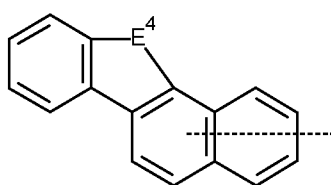
(Ar3-5)



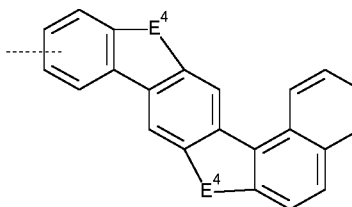
(Ar3-6)



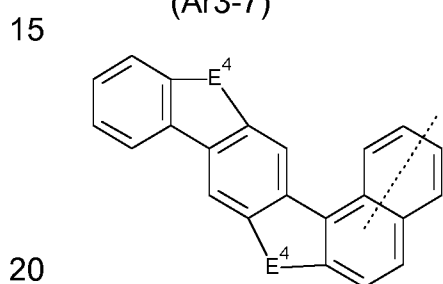
(Ar3-7)



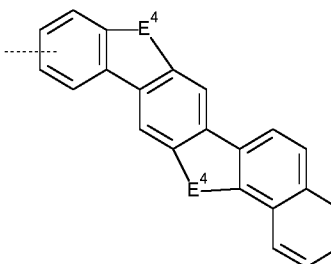
(Ar3-8)



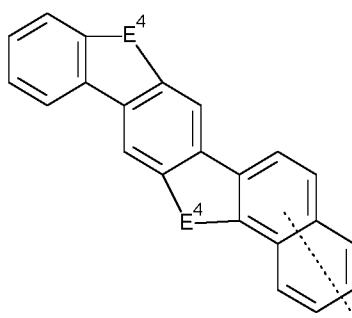
(Ar3-9)



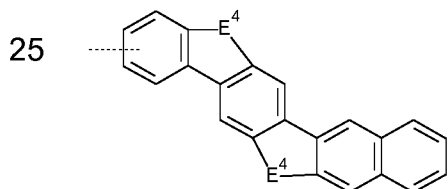
(Ar3-10)



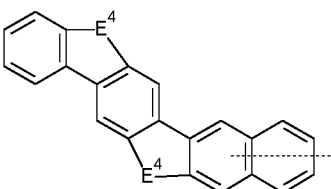
(Ar3-11)



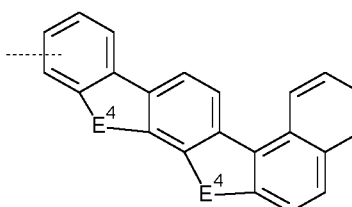
(Ar3-12)



(Ar3-13)



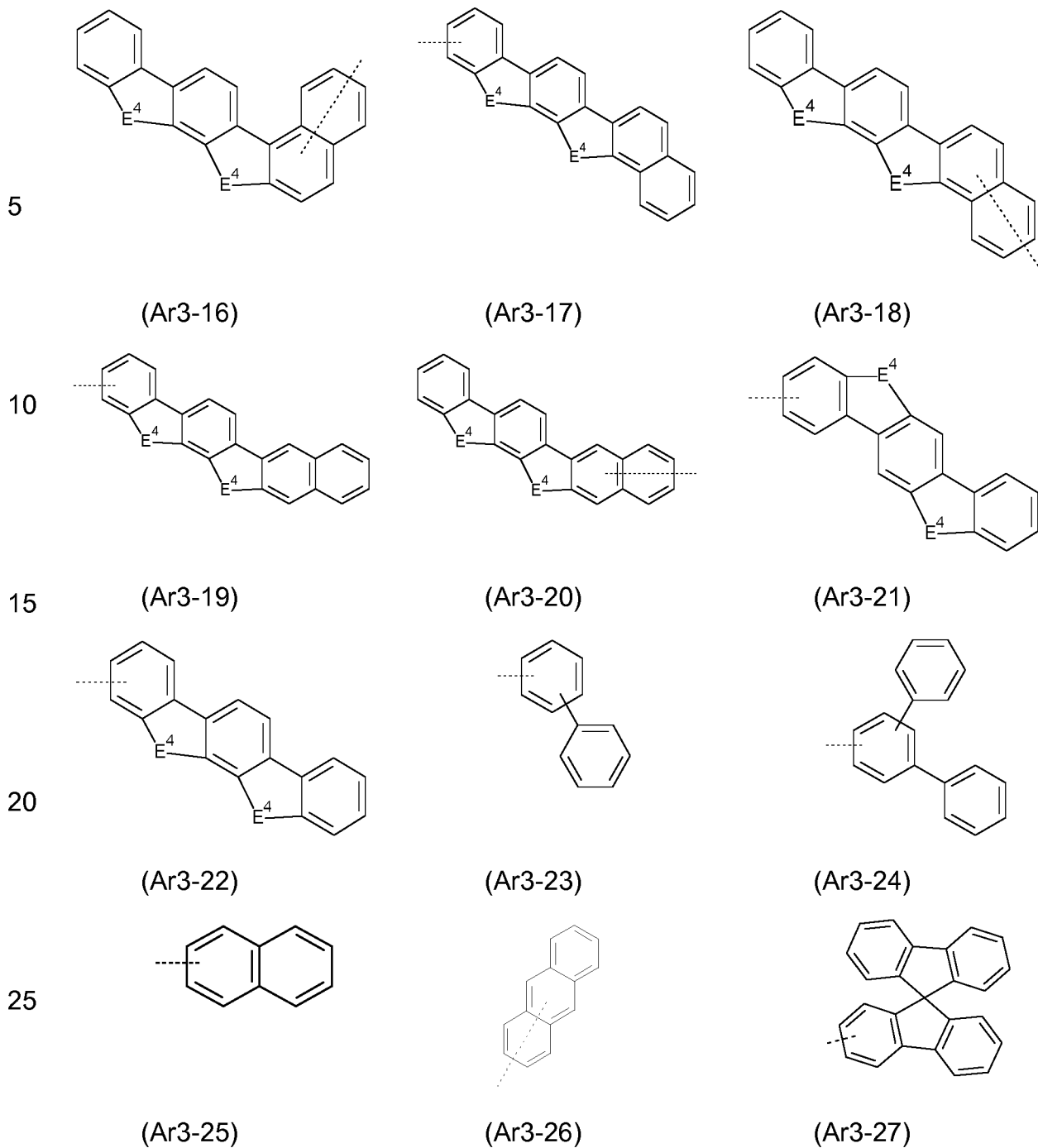
(Ar3-14)



(Ar3-15)

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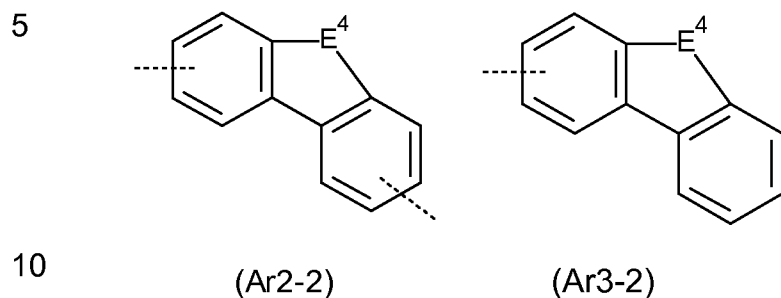


30 where the dashed bond indicates the bonding to Ar² and where E⁴ has the same meaning as in claim 11 and the groups of formulae (Ar3-1) to (Ar3-27) may be substituted at each free position by a group R, which has the same meaning as in claim 1.

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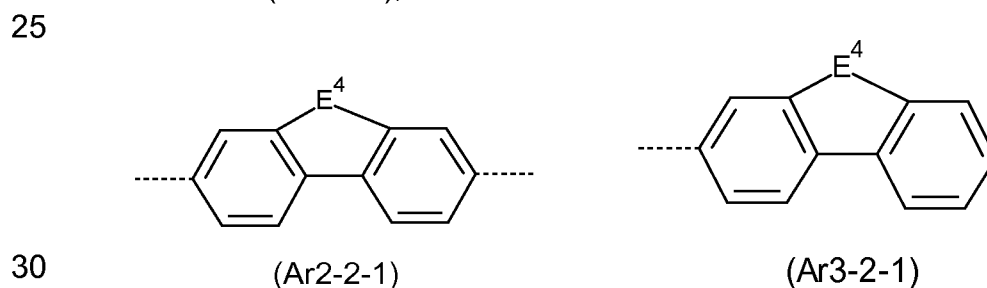
12. Compound according to one or more of the preceding claims, characterized in that, in formula (ArL-1), at least one group Ar^2 stands for a group of formula (Ar2-2) and/or at least one group Ar^3 stands for a group of formula (Ar3-2),



where

- the dashed bonds in formula (Ar2-2) indicate the bonding to the structure of formula (1) and to a group Ar^2 or Ar^3 ; and the dashed bond in formula (Ar3-2) indicates the bonding to Ar^2 ; and E^4 has the same meaning as in claim 16; and the groups of formulae (Ar2-2) and (Ar3-2) may be substituted at each free position by a group R, which has the same meaning as in claim 1.

- 20
13. Compound according to one or more of the preceding claims, characterized in that, in formula (ArL-1), at least one group Ar^2 stands for a group of formula (Ar2-2-1) and/or at least one group Ar^3 stands for a group of formula (Ar3-2-1),



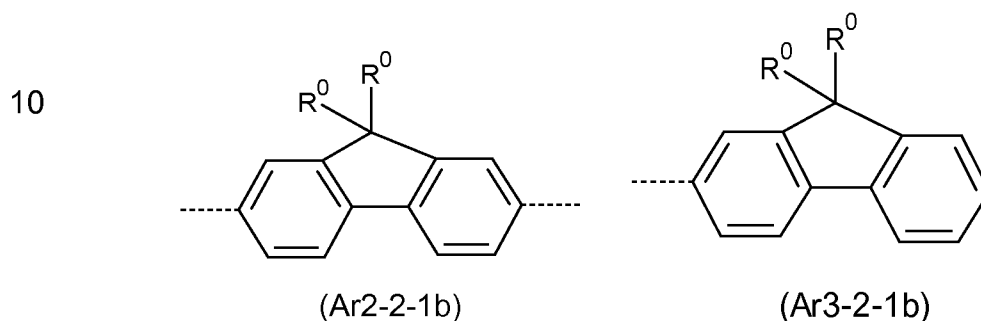
where

- the dashed bonds in formula (Ar2-2-1) indicate the bonding to the structure of formula (1) and to a group Ar^2 or Ar^3 ;
- 35 the dashed bond in formula (Ar3-2-1) indicates the bonding to Ar^2 ;
- E^4 has the same meaning as in claim 16; and

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the groups of formulae (Ar2-2-1) and (Ar3-2-1) may be substituted at each free position by a group R, which has the same meaning as in claim 1.

14. Compound according to one or more of the preceding claims,
 5 characterized in that, in formula (ArL-1), at least one group Ar² stands for a group of formula (Ar2-2-1b) and/or at least one group Ar³ stands for a group of formula (Ar3-2-1b),



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where

the dashed bonds in formula (Ar2-2-1b) indicate the bonding to the structure of formula (1) and to a group Ar² or Ar³;

the dashed bond in formula (Ar3-2-1b) indicates the bonding to Ar²;

20 R⁰ has the same meaning as in claim 1; and

the groups of formulae (Ar2-2-1b) and (Ar3-2-1b) may be substituted at each free position by a group R, which has the same meaning as in claim 1.

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15. Formulation comprising at least one compound according to one or more of the claims 1 to 14 and at least one solvent.

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16. Electronic device comprising at least one compound according to one or more of claims 1 to 14, selected from the group consisting of organic electroluminescent devices, organic integrated circuits, organic field-effect transistors, organic thin-film transistors, organic light-emitting transistors, organic solar cells, dye-sensitised organic solar cells, organic optical
 35 detectors, organic photoreceptors, organic field-quench devices, light-

- 169 -

emitting electrochemical cells, organic laser diodes and organic plasmon emitting devices.

17. Electronic device according to claim 16, which is an organic electrolumi-
5 nescent device, characterised in that the compound according to one or
more of claims 1 to 14 is employed as a fluorescent emitter or as a matrix
material for fluorescent emitters.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/078011

A. CLASSIFICATION OF SUBJECT MATTER INV. C07D307/93 C07D493/04 C09K11/00 H01L51/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C07D C09K H01L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, EMBASE, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 902 463 A1 (CHEIL IND INC [KR]) 5 August 2015 (2015-08-05) compounds C-1 to C-8, C-17 to C-24 and D-1 to D-32; page 32 - page 35; claims 1, 10, 13; examples 8, 9	1-17
A	----- CN 106 892 914 A (NANJING TOPTO SEMICONDUCTOR MAT CO LTD) 27 June 2017 (2017-06-27) synthetic intermediates 13, 22, 31, 41, 55 and 65	1-17
A	----- WO 2011/021803 A2 (DUKSAN HIGH METAL CO LTD [KR]; PARK JUNGHWAN [KR]; KIM DAESUNG [KR]; P) 24 February 2011 (2011-02-24) compounds 26-33, 47-50, 70-77, 90-93	1-17
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 21 November 2018	Date of mailing of the international search report 12/02/2019	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Moriggi, J	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2018/078011

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-17(partially)

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-17(partially)

The compounds according to formula (1) of current claim 1 in which A is an aromatic ring system, the formulations containing them and the corresponding devices

2. claims: 1-17(partially)

the compounds according to formula (1) of current claim 1 in which A is a heteroaromatic ring system, the formulations containing them and the corresponding devices

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/078011

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2902463	A1	05-08-2015	CN 105121594 A
			EP 2902463 A1
			JP 6167180 B2
			JP 2016502500 A
			KR 20140042554 A
			US 2015137111 A1
			WO 2014051232 A1

CN 106892914	A	27-06-2017	NONE

WO 2011021803	A2	24-02-2011	KR 20110018688 A
			WO 2011021803 A2
