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(54) **Title:** MATERIALS FOR ELECTRONIC DEVICES

(57) **Abstract:** The present application relates to heterospirobifluorene compounds and to electronic devices, in particular organic electroluminescent devices, comprising the heterospirobifluorene derivatives.

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Materials for electronic devices

The present application relates to a heterospirobifluorene compound of a formula (I) defined in greater detail below. The compound is preferably used in an electronic device, particularly preferably in an organic electroluminescent device (OLED).

Electronic devices in the context of this application are understood to mean what are called “organic electronic devices”, which contain organic semiconductor materials as functional materials. More particularly, these devices are understood to mean organic electroluminescent (EL) devices, especially organic light emitting diodes (OLEDs). The design and general operating principle of OLEDs are well known to the skilled person.

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

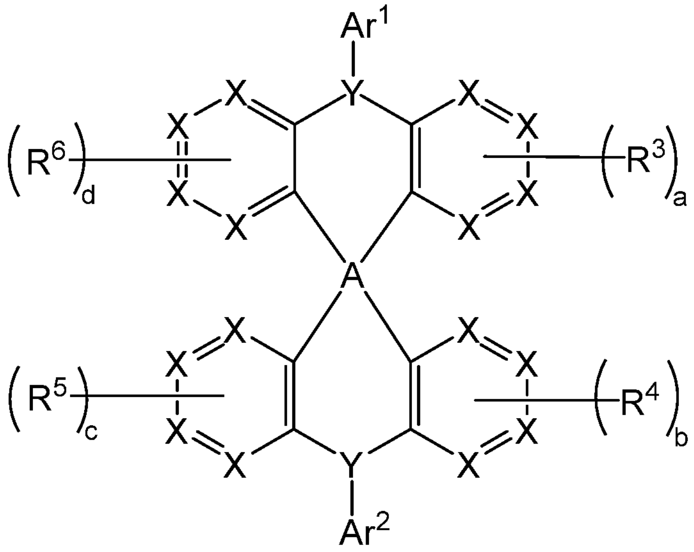
A great influence on the performance data of electronic devices is possessed by layers having a hole-transporting function, for example hole-injecting layers, hole transport layers, electron blocking layers and also emitting layers. For use in these layers, there is a continuous search for new materials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

In the prior art, triarylamine compounds in particular, such as spirobifluorenamines and fluorenamines, are known as hole transporting materials and hole transporting matrix materials for electronic devices. The use of acridine derivatives in OLEDs, and more particularly of spirobisacridine, is also disclosed in the prior art, for example in JP 2002-265938, KR 2011-0120075 or WO 2015/158411. However, there is still a need for improvement with respect to the above-mentioned properties.

It has now been found that spirobisacridine compounds which conform to the formula (I) defined below are highly suitable for use in OLEDs. They are suitable, in particular, for use in a hole-transporting layer, and more particularly for use in an electron-blocking layer.

The compounds found have one or more properties selected from very good hole-conducting properties, very good electron-blocking properties, high oxidation stability, good solubility, and high temperature stability. When used in OLEDs, they result in one or more advantageous properties of the OLEDs selected from long lifetime, high quantum efficiency and low operating voltage.

The present invention relates to a compound of the formula (I)



formula (I),

where the following applies to the symbols and indices occurring:

A is C or Si;

Y is on each occurrence, identically or differently, N or P;

X is on each occurrence, identically or differently, CR^1 or N;

Ar^1, Ar^2 are on each occurrence, identically or differently, an aromatic ring system having 6 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^2, or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^2; where at least one of the two groups Ar^1 and Ar^2 is an aromatic ring system having 12 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^2, or a heteroaromatic ring system having 12 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^2;

R^3, R^4, R^5, R^6 are selected on each occurrence, identically or differently from D, F, C(=O)R, CF_3, OCF_3, CN, $Si(R)_3$, $N(R)_2$, $P(=O)(R)_2$, S(=O)R, $S(=O)_2R$, straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, alkenyl or alkynyl groups having 2 to 20 C atoms, where the said alkyl, alkoxy, alkenyl and alkynyl groups may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F; aromatic ring systems having 6 to 40 aromatic ring atoms, which may be substituted by one or more radicals R, or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R;

R^1, R^2 are selected on each occurrence, identically or differently, from H, D, F, C(=O)R, CF_3, OCF_3, CN, $Si(R)_3$, $N(R)_2$, $P(=O)(R)_2$, S(=O)R, $S(=O)_2R$, straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, alkenyl or alkynyl groups having 2 to 20 C atoms, where the said alkyl, alkoxy, alkenyl and alkynyl groups may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F; aromatic ring systems having 6 to 40 aromatic ring atoms, which may be substituted by one or more radicals R, or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R; where two or more radicals R^1 or R^2 may be linked to one another and may form a ring; where the said alkyl, alkoxy, alkenyl and alkynyl groups and the said aromatic ring systems and heteroaromatic ring systems may each be substituted by one or more radicals R; and where one or more CH_2 groups in the said alkyl, alkoxy, alkenyl and alkynyl groups may be replaced by -RC=CR-, -C≡C-, $Si(R)_2$, C=O, C=NR, -C(=O)O-, -C(=O)NR-, NR, P(=O)(R), -O-, -S-, SO or SO_2;

R is selected on each occurrence, identically or differently, from H, D, F, C(=O)R´, CF_3, OCF_3, CN, $Si(R')_3$, $N(R')_2$, $P(=O)(R')_2$, S(=O)R´, $S(=O)_2R'$, straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, alkenyl or alkynyl groups having 2 to 20 C atoms, where one or more H atoms in the above-mentioned groups may be replaced by D or F, aromatic ring systems having 6 to 40 aromatic ring atoms and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more radicals R may be linked to one another and may form a ring; where the said alkyl, alkoxy, alkenyl and alkynyl groups and the said aromatic ring systems and heteroaromatic ring systems may each be substituted by one or more radicals R´; and where one or more CH_2 groups in the said alkyl, alkoxy, alkenyl and alkynyl groups may be replaced by -R´C=CR´-, -C≡C-, $Si(R')_2$, C=O, C=NR´, -C(=O)O-, -C(=O)NR´-, NR´, P(=O)(R´), -O-, -S-, SO or SO_2;

R´ is selected on each occurrence, identically or differently, from H, D, F, CN, alkyl groups having 1 to 20 C atoms, aromatic ring systems having 6 to 40 aromatic ring atoms and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more radicals R´ may be linked to one another and may form a ring; and where the said alkyl groups, aromatic ring systems and heteroaromatic ring systems may be substituted by F or CN;

a, b, c, d are on each occurrence, identically or differently, 0, 1, 2, 3 or 4; where at least one of the indices a, b, c and d is equal to 1; and

at least one radical R^3, R^4, R^5 or R^6 is present in the compound of formula (I), which stands for F, $Si(R)_3$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where the said alkyl, alkoxy or thioalkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F.

If an index a, b, c or d is equal to 0, the corresponding group R^3, R^4, R^5 or R^6 is not present.

If an index a, b, c or d is equal to 1, the corresponding group R^3, R^4, R^5 or R^6 is bonded to one of the groups X of the ring. This group X is then equal to C, corresponding to the tetravalence of carbon.

The following definitions apply to the chemical groups used as general definitions. They only apply insofar as no more specific definitions are given.

An aryl group in the sense of this invention contains 6 to 60 aromatic ring atoms, none of which is a heteroatom. An aryl group in the sense of this invention is taken to mean either a simple aromatic ring, i.e. benzene, or a condensed aromatic polycyclic ring system, for example naphthalene, phenanthrene or anthracene. A condensed aromatic polycyclic ring system in the sense of the present application consists of two or more simple aromatic rings condensed with one another. Condensation between rings here is taken to mean that the rings share at least one edge with one another.

A heteroaryl group in the sense of this invention contains 5 to 60 aromatic ring atoms, at least one of which is a heteroatom. The heteroatoms of the heteroaryl group are preferably selected from N, O and S. A heteroaryl group in the sense of this invention 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 heteroaromatic polycyclic ring system, for example quinoline or carbazole. A condensed heteroaromatic polycyclic ring system in the sense of the present application consists of two or more simple heteroaromatic rings condensed with one another. Condensation between rings here is taken to mean that the rings share at least one edge with one another.

An aryl or heteroaryl group, which may in each case be substituted by the above-mentioned radicals and which may be linked to the aromatic or heteroaromatic ring system via any desired positions, is taken to mean, in particular, groups derived from benzene, naphthalene, anthracene, phenanthrene, pyrene, dihydropyrene, chrysene, perylene, triphenylene, fluoranthene, benzanthracene, benzophenanthrene, tetracene, pentacene, benzopyrene, furan, benzofuran, isobenzofuran, dibenzofuran, thiophene, benzothiophene, isobenzothiophene, dibenzothiophene, pyrrole, indole, isoindole, carbazole, pyridine, quinoline, isoquinoline, acridine, phenanthridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, phenothiazine, phenoxazine, pyrazole, indazole, imidazole, benzimidazole, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, oxazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, benzothiazole, pyridazine, benzopyridazine, pyrimidine, benzopyrimidine, quinoxaline, pyrazine, phenazine, naphthyridine, azacarbazole, benzocarboline, phenanthroline, 1,2,3-triazole, 1,2,4-triazole, benzotriazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, tetrazole, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine, 1,2,3,5-tetrazine, purine, pteridine, indolizine and benzothiadiazole.

An aromatic ring system in the sense of this invention contains 6 to 60 C atoms in the ring system and includes no heteroatoms as aromatic ring atoms. An aromatic ring system in the sense of this invention therefore contains no heteroaryl groups. An aromatic ring system in the sense of this invention is intended to be taken to mean a system which does not necessarily contain only aryl groups, but instead in which, in addition, a plurality of aryl groups may be connected by a single bond or by a non-aromatic unit, such as, for example, one or more optionally substituted C, Si, N, O or S atoms. The non-aromatic unit here preferably contains less than 10% of the atoms other than H, based on the total number of atoms other than H in the system. Thus, for example, systems such as 9,9'-spirobifluorene, 9,9'-diarylfluorene, triarylamine, diaryl ether and stilbene are also intended to be taken to be aromatic ring systems in the sense of this invention, as are systems in which two or more aryl groups are connected, for example, by a linear or cyclic alkyl, alkenyl or alkynyl group or by a silyl group. Furthermore, systems in which two or more aryl groups are linked to one another via single bonds are also taken to be aromatic ring systems in the sense of this invention, such as, for example, systems such as biphenyl and terphenyl.

A heteroaromatic ring system in the sense of this invention contains 5 to 60 aromatic ring atoms, at least one of which is a heteroatom. The heteroatoms of the heteroaromatic ring system are preferably selected from N, O and/or S. A heteroaromatic ring system corresponds to the above-mentioned definition of an aromatic ring system, but contains at least one heteroatom as one of the aromatic ring atoms. It consequently differs from an aromatic ring system in the sense of the definition of the present application, which, in accordance with this definition, cannot contain a heteroatom as aromatic ring atoms.

An aromatic ring system having 6 to 60 aromatic ring atoms or a heteroaromatic ring system having 5 to 60 aromatic ring atoms are taken to mean, in particular, groups derived from the groups mentioned above under aryl groups and heteroaryl groups and from biphenyl, terphenyl, quaterphenyl, fluorene, spirobifluorene, dihydrophenanthrene, dihydropyrene, tetrahydropyrene, indenofluorene, truxene, isotruxene, spirotruxene, spiroisotruxene, indenocarbazole, or from combinations of these groups.

For the purposes of the present invention, a straight-chain alkyl group having 1 to 40 C atoms or a branched or cyclic alkyl group having 3 to 40 C atoms or an alkenyl or alkynyl group having 2 to 40 C atoms, in which, in addition, individual H atoms or CH_2 groups may be substituted by the groups mentioned above under the definition of the radicals, is preferably taken to mean the radicals methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, 2-methylbutyl, n-pentyl, s-pentyl, cyclopentyl, neopentyl, n-hexyl, cyclohexyl, neohexyl, n-heptyl, cycloheptyl, n-octyl, cyclooctyl, 2-ethylhexyl, trifluoromethyl, pentafluoroethyl, 2,2,2-trifluoroethyl, ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl, cycloheptenyl, octenyl, cyclooctenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl or octynyl.

An alkoxy or thioalkyl group having 1 to 40 C atoms, in which, in addition, individual H atoms or CH_2 groups may be substituted by the groups mentioned above in the definition of the radicals, is preferably taken to mean methoxy, trifluoromethoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy, n-pentoxy, s-pentoxy, 2-methylbutoxy, n-hexoxy, cyclohexyloxy, n-heptoxy, cycloheptyloxy, n-octyloxy, cyclooctyloxy, 2-ethylhexyloxy, pentafluoroethoxy, 2,2,2-trifluoroethoxy, methylthio, ethylthio, n-propylthio, i-propylthio, n-butylthio, i-butylthio, s-butylthio, t-butylthio, n-pentylthio, s-pentylthio, n-hexylthio, cyclohexylthio, n-heptylthio, cycloheptylthio, n-octylthio, cyclooctylthio, 2-ethylhexylthio, trifluoromethylthio, pentafluoroethylthio, 2,2,2-trifluoroethylthio, ethenylthio, propenylthio, butenylthio, pentenylthio, cyclopentenylthio, hexenylthio, cyclohexenylthio, heptenylthio, cycloheptenylthio, octenylthio, cyclooctenylthio, ethynylthio, propynylthio, butynylthio, pentynylthio, hexynylthio, heptynylthio 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 mean, inter alia, that the two radicals are linked to one another by a chemical bond. 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.

According to a preferred embodiment, the compound of the formula (I) contains no arylamino group as substituent. An arylamino group in the sense of the present application is taken to mean a group in which one or more aryl or heteroaryl groups, preferably three aryl or heteroaryl groups, are bonded to a nitrogen atom.

According to a further preferred embodiment of the invention, the compound of the formula (I) contains no condensed aryl group having more than 10 aromatic ring atoms and no condensed heteroaryl group having more than 14 aromatic ring atoms.

According to a further preferred embodiment of the invention, the compound of the formula (I) is used as a non-light emitting hole-transport material in a layer having a hole-transporting function, for example hole-injecting layers, hole transport layers, electron blocking layers.

According to another preferred embodiment of the invention, the compound of the formula (I) is used as a non-light emitting host material having hole-transporting properties in combination with an emitter in an emitting layer.

Preferably, precisely 1, 2, 3 or 4 indices selected from the indices a, b, c and d in formula (I) are equal to 1 or 2.

Preferably, precisely 1, 2 or 3 indices selected from the indices a, b, c and d are equal to 1 or 2, particularly preferably precisely 1 or 2 indices selected from the indices a, b, c and d are equal to 1 or 2.

According to a preferred embodiment of the invention, the index a is equal to 1, and the indices b, c and d are equal to 0.

According to an alternative preferred embodiment, the indices a and b are equal to 1, and the indices c and d are equal to 0.

According to another preferred embodiment, the index a is equal to 2, and the indices b, c and d are equal to 0.

A is preferably a carbon atom.

Y is preferably a nitrogen atom.

Preferably at most three groups X, particularly preferably at most two groups X, and very particularly preferably at most one group X, per six-membered ring in the compound of the formula (I) are equal to N.

Preferably, not more than 2 directly adjacent groups X in a ring are equal to N.

X is preferably equal to CR^1, where R^1 is preferably selected, identically or differently, from H and D.

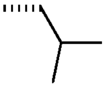
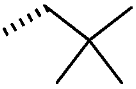
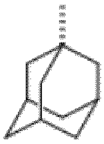
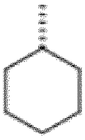
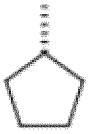
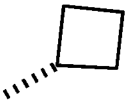
Preferably, Ar^1 and Ar^2 are selected on each occurrence, identically or differently, from aromatic ring systems having 6 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2, or from heteroaromatic ring systems having 5 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2, where at least one of the two groups Ar^1 and Ar^2 is an aromatic ring system having 12 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2, or a heteroaromatic ring system having 12 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2. More preferably, both of the groups Ar^1 and Ar^2 are selected on each occurrence, identically or differently, from aromatic ring systems having 12 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2, and heteroaromatic ring systems having 12 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2. Even more preferably, both of the groups Ar^1 and Ar^2 are selected on each occurrence, identically or differently, from aromatic ring systems having 12 to 18 aromatic ring atoms, which may be substituted by one or more radicals R^2.

More preferably, at least one of the two groups Ar^1 and Ar^2 is a biphenyl, terphenyl or fluorenyl group, which may be substituted by one or more radicals R^2. Even more preferably, the two groups Ar^1 and Ar^2 are selected, identically or differently, from the group consisting of biphenyl, terphenyl and fluorenyl, which may be substituted by one or more radicals R^2.

Preferably, R^3, R^4, R^5, R^6 are selected on each occurrence, identically or differently from F, CF_3, OCF_3, $Si(R)_3$, straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, where the said alkyl, alkoxy and thioalkyl groups may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F; aromatic ring systems having 6 to 40 aromatic ring atoms, which may be substituted by one or more radicals R, or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R.

According to the present invention, at least one radical R^3, R^4, R^5 or R^6 is present in the compound of formula (I), which stands for F, $Si(R)_3$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where the said alkyl, alkoxy or thioalkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F. Preferably, at least one radical R^3, R^4, R^5 or R^6 is present in the compound of formula (I), which stands for a straight-chain alkyl group having 1 to 20 C atoms, more preferably 1 to 10 C atoms, even more preferably 2 to 10 C atoms, branched or cyclic alkyl group having 3 to 20, more preferably 3 to 10 C atoms, where the said alkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F.

Examples of the at least one radical R^3, R^4, R^5 or R^6 present in the compound of formula (I), which stands for F, $Si(R)_3$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where the said alkyl, alkoxy or thioalkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F, are depicted below:

$-CH_3$		$-CH_2CH_3$
R-1	**R-2**	**R-3**
		
R-4	**R-5**	**R-6**
		
R-7	**R-8**	**R-9**
	$-CF_2CF_3$	$-OCF_3$
R-10	**R-11**	**R-12**
$-SCF_3$	$-SF_5$	$-OCF_2CF_3$
R-13	**R-14**	**R-15**
$-SCF_2CF_3$	-F	$-CF_3$
R-16	**R-17**	**R-18**
$Si-(Ph)_3$	$C-(Ph)_3$	$-OCH_2CH_3$
R-19	**R-20**	**R-21**
$-OCH_3$	$-SCH_3$	$-Si(CH_3)_3$
R-22	**R-23**	**R-24**
$-Si(CH_3)2t\text{-}Bu$	$-Si(iPr)_3$	$-Si(CH_3)_2Ph$
R-25	**R-26**	**R-27**
$-CD_3$	$-CD_2-CD_3$	$-C(CD_3)_3$
R-28	**R-29**	**R-30**

$-CD_2-(CD_3)_2$	$-OCD_3$	$-SCD_3$
R-31	**R-32**	**R-33**
$-Si(CD_3)_3$	$-CD_2(CH_3)_2$	$-CD_2(CH_3)_3$
R-34	**R-35**	**R-36**

Preferably, at least one of the radicals R^3, R^4, R^5, R^6 is selected from one of the groups of the formulae R-1 to R-10, more preferably R-2 to R-7. Even more preferably, all the groups R^3, R^4, R^5, R^6 are selected, identically or differently, from one of the groups of the formulae R-1 to R-10, particularly preferably from R-2 to R-7.

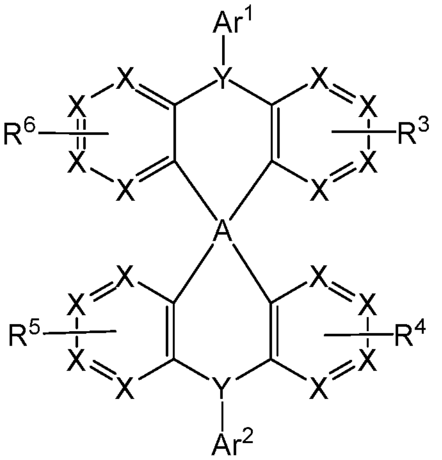
In accordance with a preferred embodiment, all the radical R^3, R^4, R^5 and R^6 present in the compound of formula (I), stand identically or differently, for F, $Si(R)_3$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where the said alkyl, alkoxy or thioalkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F. Preferably, all the radical R^3, R^4, R^5 and R^6 present in the compound of formula (I), stand, identically or differently, for a straight-chain alkyl group having 1 to 20 C atoms, more preferably 1 to 10 C atoms, even more preferably 2 to 10 C atoms, branched or cyclic alkyl group having 3 to 20, more preferably 3 to 10 C atoms, where the said alkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F.

In accordance with another preferred embodiment, the compounds of formula (I) comprise:
at least one radical R^3, R^4, R^5 or R^6 which stands for F, $Si(R)_3$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where the said alkyl, alkoxy or thioalkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F, and

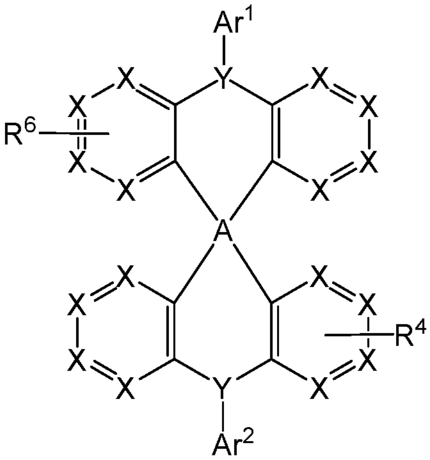
at least one radical R^3, R^4, R^5 or R^6 which stands for an aromatic ring system having 6 to 40 aromatic ring atoms, which may be substituted by one or more radicals R, or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R.

More preferably, the compounds of formula (I) comprise:
at least one radical R^3, R^4, R^5 or R^6 which stands for a straight-chain alkyl group having 1 to 20 C atoms, more preferably 1 to 10 C atoms, even more preferably 2 to 10 C atoms, branched or cyclic alkyl group having 3 to 20 C atoms, more preferably 3 to 10 C atoms, where the said alkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F, and
at least one radical R^3, R^4, R^5 or R^6 which stands for aromatic ring systems having 6 to 30, preferably 6 to 18 aromatic ring atoms, which may be substituted by one or more radicals R, or a heteroaromatic ring system having 5 to 30, preferably 6 to 18 aromatic ring atoms, which may be substituted by one or more radicals R.

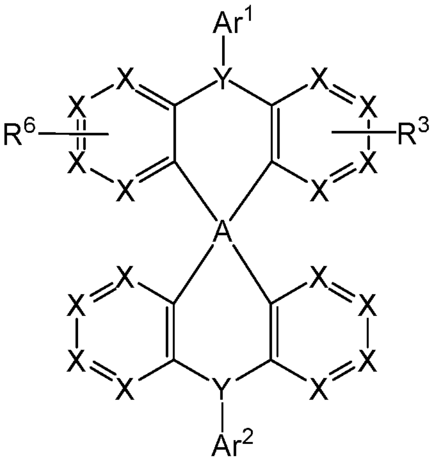
Preferably, the compound of the formula (I) are selected from one of the formulae (I-1) to (I-7),



formula (I-1)



formula (I-2)



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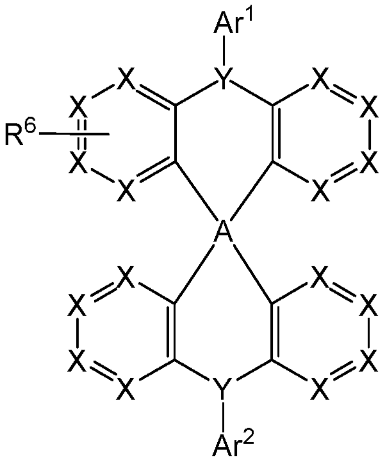
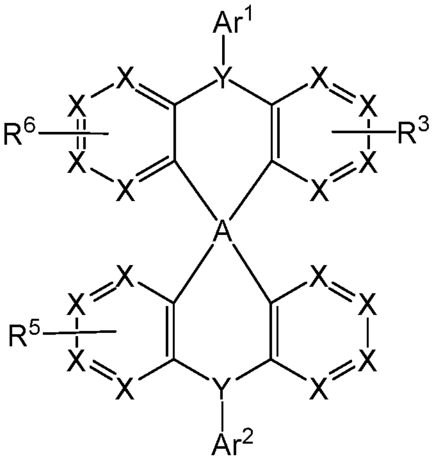
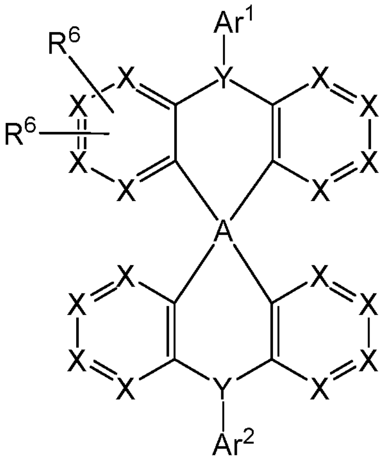


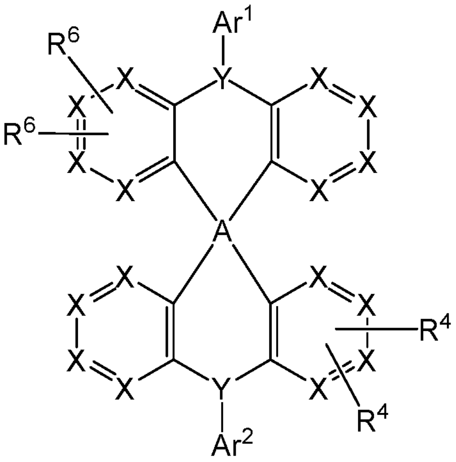
formula (I-4)



formula (I-5)



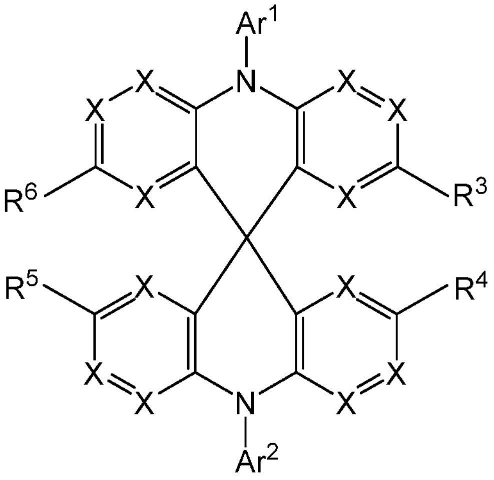
formula (I-6)



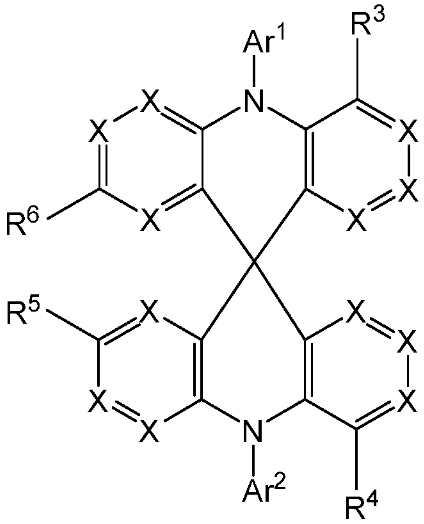
formula (I-7)

where the symbols and indices occurring are as defined above.

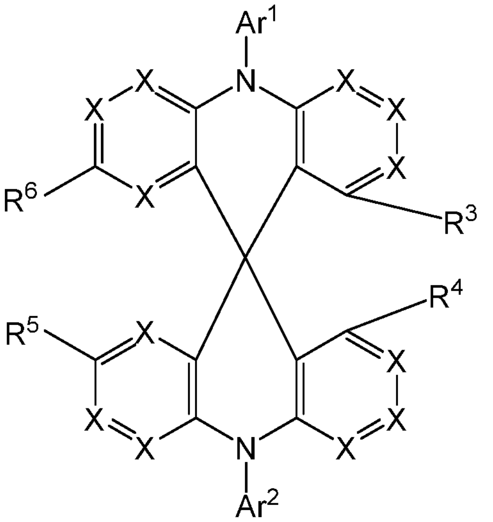
More preferably, the compound of the formula (I) are selected from one of the formulae (I-1-1) to (I-7-1),



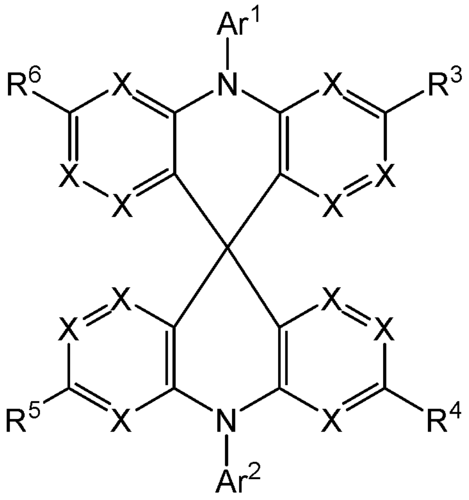
formula (I-1-1)



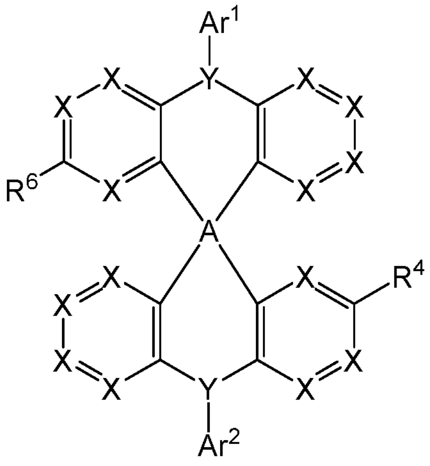
formula (I-1-2)



formula (I-1-3)



formula (I-1-4)



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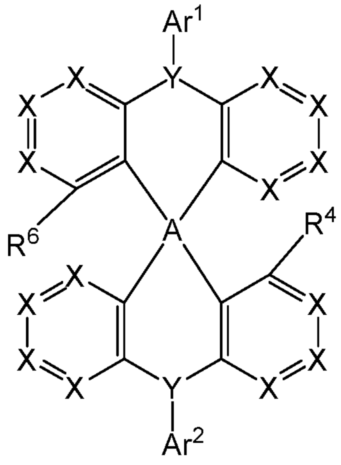
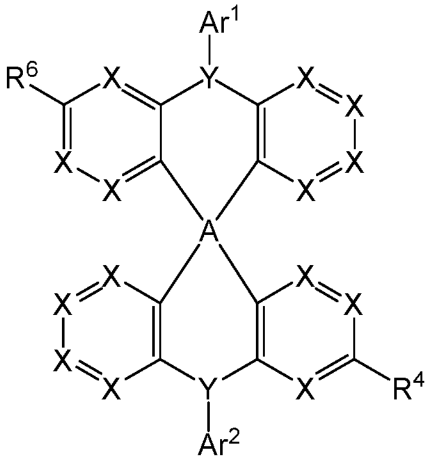
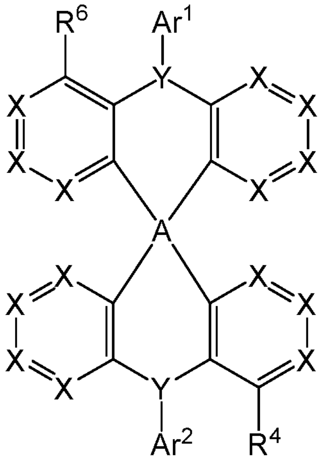


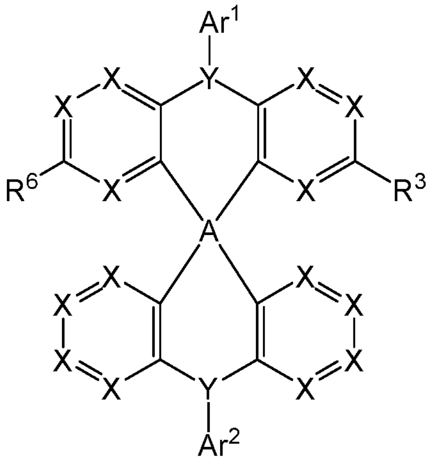
formula (I-2-2)



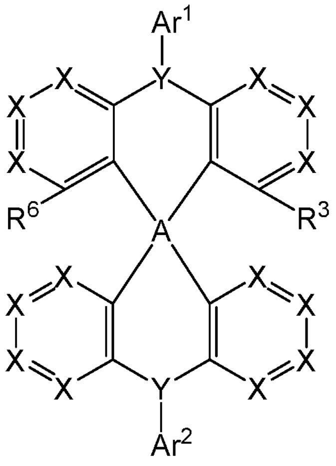
formula (I-2-3)



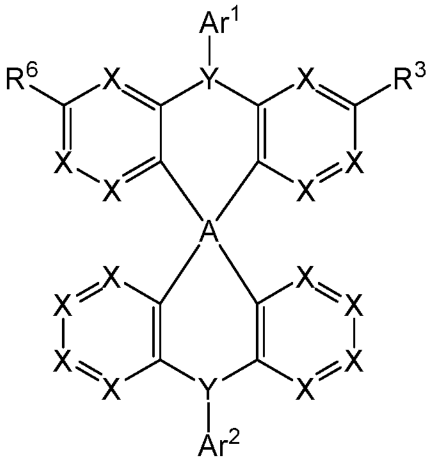
formula (I-2-4)



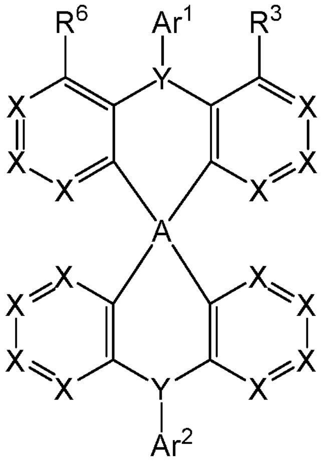
formula (I-3-1)



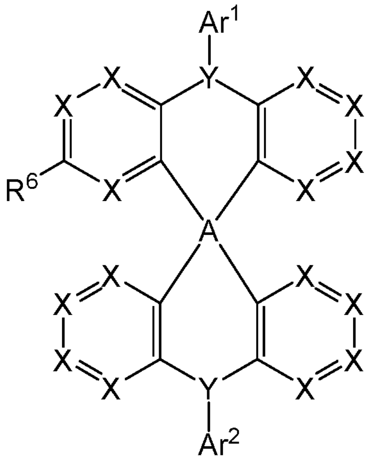
formula (I-3-2)



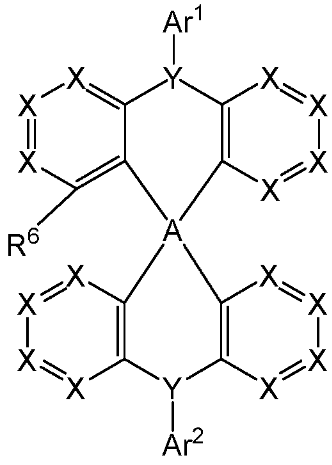
formula (I-3-3)



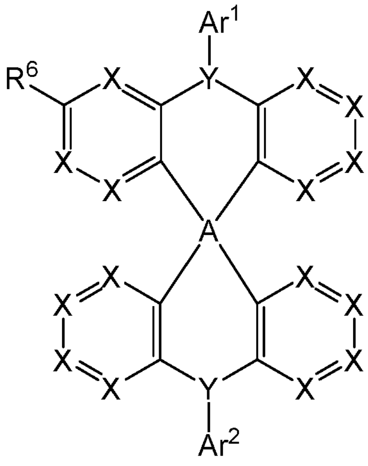
formula (I-3-4)



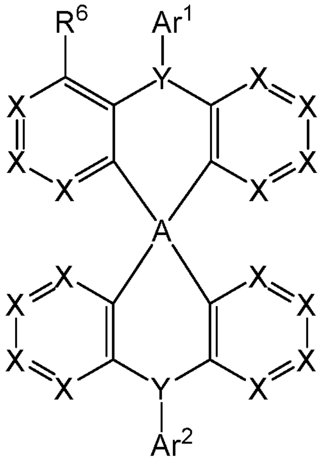
formula (I-4-1)



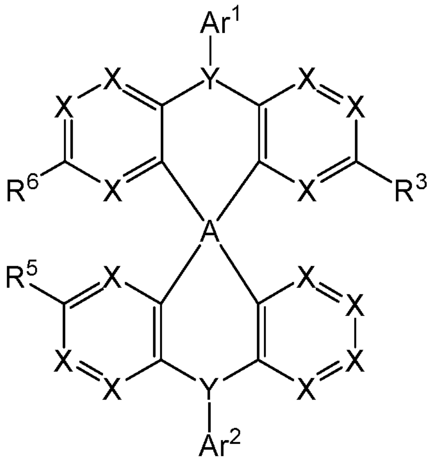
formula (I-4-2)



formula (I-4-3)



formula (I-4-4)



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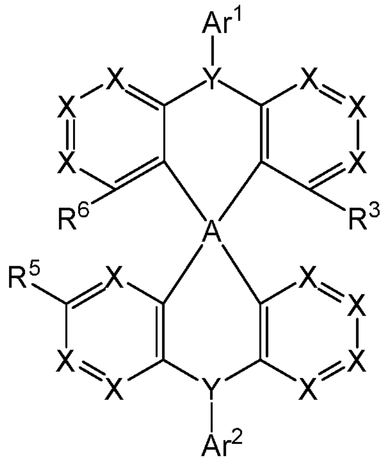
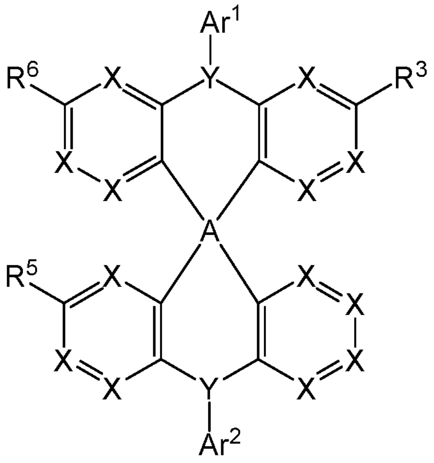
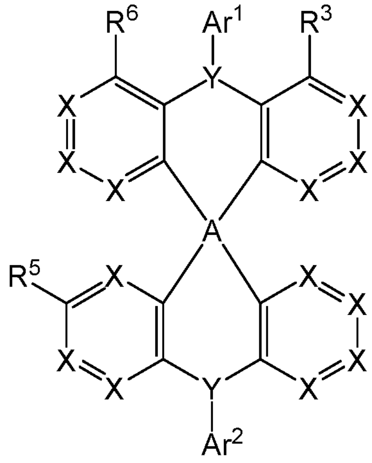


formula (I-5-2)



formula (I-5-3)



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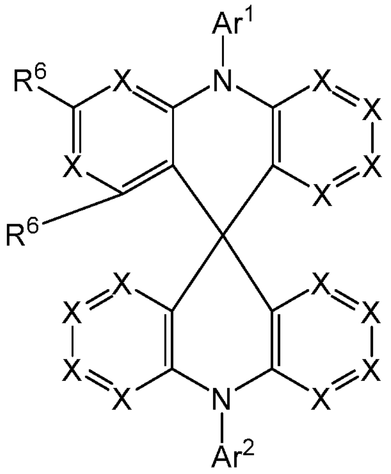
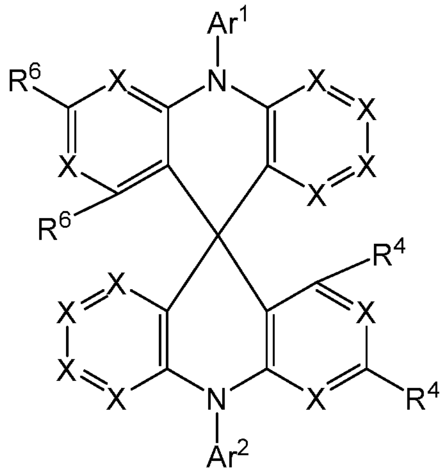


formula (I-6-1)



formula (I-7-1)

where the symbols and indices occurring are as defined above.

Even more preferably, the compound of the formula (I) are selected from the compounds of formulae (I-1-1) to (I-7-1), where Ar^1, Ar^2, R^3, R^4, R^5, R^6 correspond to the above-mentioned preferred embodiments for these groups and where:

X stands for CR^1, where R^1 is selected, identically or differently, from H and D.

Among formulae (I-1-1) to (I-7-1), the formulae (I-1-1), (I-2-1), (I-3-1), (I-4-1), (I-5-1), (I-6-1) and (I-7-1) are preferred, the formulae (I-2-1), (I-3-1), (I-4-1) and (I-6-1) are very preferred, and the formulae (I-2-1) and (I-4-1) are particularly preferred.

Preferably, in formulae (I-1) to (I-7) and (I-1-1) to (1-7-1):

- the radical R^6 is selected from F, $Si(R)_3$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where the said alkyl, alkoxy or thioalkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F; and
- the radicals R^3, R^4, R^5 are selected, identically or differently, from D, F, C(=O)R, CF_3, OCF_3, CN, $Si(R)_3$, $N(R)_2$, $P(=O)(R)_2$, S(=O)R, $S(=O)_2R$, straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, alkenyl or alkynyl groups having 2 to 20 C atoms, where the said alkyl, alkoxy, thioalkyl, alkenyl and alkynyl groups may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F; aromatic ring systems having 6 to 40 aromatic ring atoms, which may be substituted by one or more radicals R, or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R.

More preferably, in formulae (I-1) to (I-7) and (I-1-1) to (1-7-1):

- the radical R^6 is selected from F, $Si(R)_3$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where the said alkyl, alkoxy or thioalkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F; and

- the radicals R^3, R^4, R^5 are selected, identically or differently, from F, $Si(R)_3$, a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, where the said alkyl, alkoxy or thioalkyl groups may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F; aromatic ring systems having 6 to 30, preferably 6 to 18 aromatic ring atoms, which may be substituted by one or more radicals R, or a heteroaromatic ring system having 5 to 30, preferably 6 to 18 aromatic ring atoms, which may be substituted by one or more radicals R.

Preferably, the compound of formula (I) is a deuterated compound. The term “deuterated compound” refers here to a compound in which deuterium is present in at least 100 times the natural abundance level. A higher deuteration degree than in nature can be achieved by using building blocks which have been previously enriched with deuterium via a deuteration method or by submitting a compound to a deuteration method.

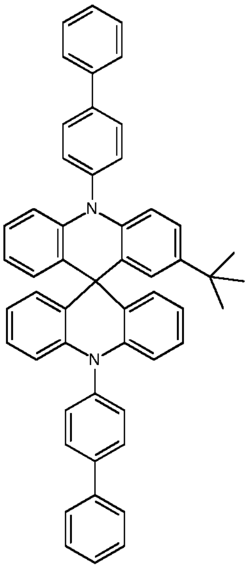
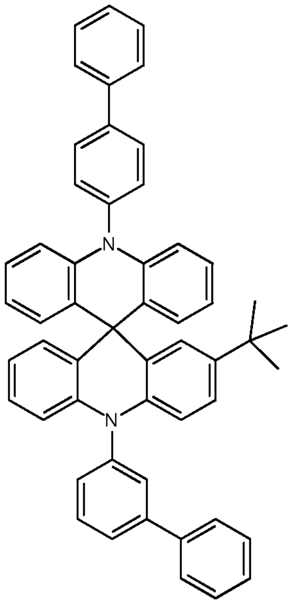
In accordance with the present invention, the deuteration degree corresponds to the number of deuterium atoms in a compound on the total number of deuterium atoms and protium atoms in the compound in %, as follows:

Deuteration degree (%) = $(N_D * 100) / (N_P + N_D)$
where:
N_D is the number of deuterium atoms in the compound
N_P is the number of deuterium and protium atoms in the compounds

Unless specified otherwise, the term hydrogen in the present invention design the protium isotope of hydrogen, which accounts for more that 99.98% of the natural occurring hydrogen in the oceans.

Preferably, the compound of formula (I) has a deuteration degree higher than 20%, 40%, 60% or 80%.

Examples of compounds of the formula (I) are depicted in the following table: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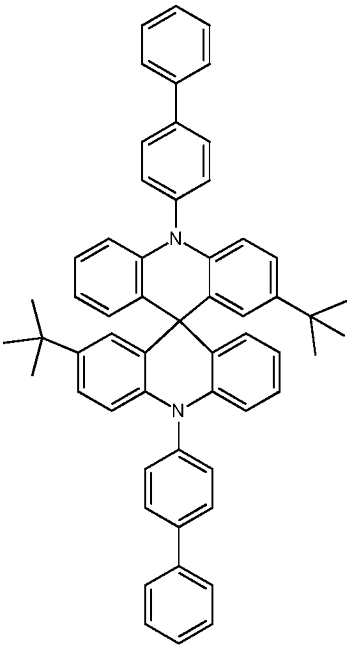	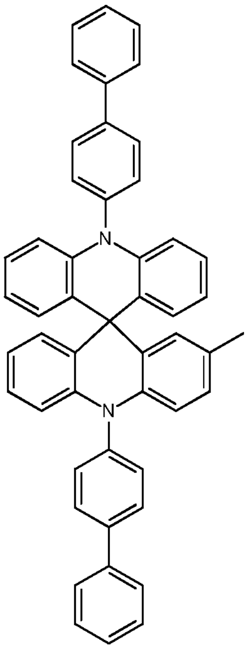
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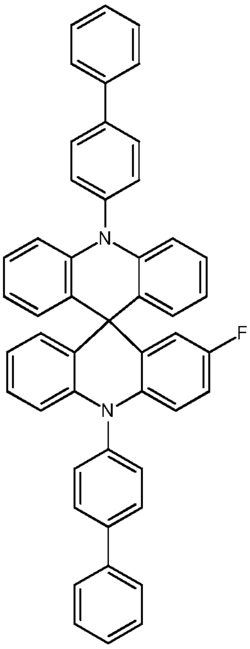	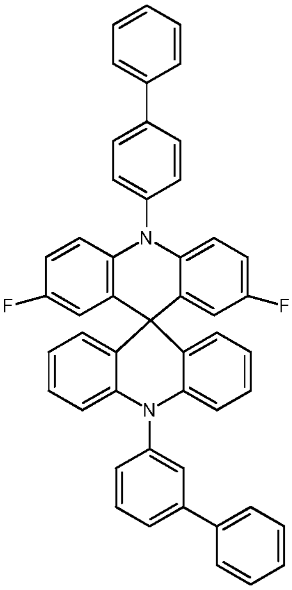
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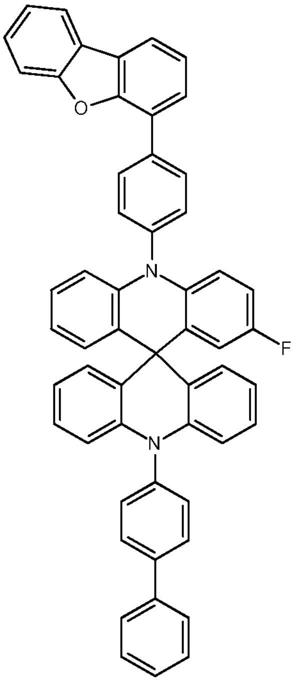	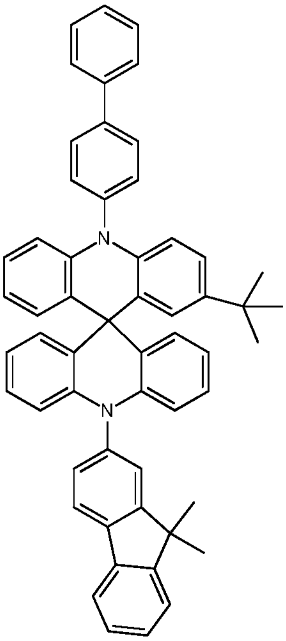
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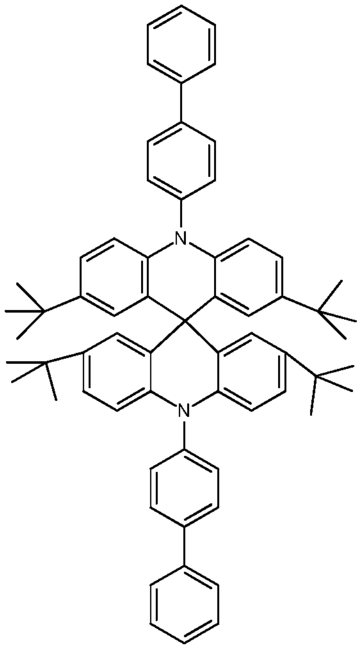	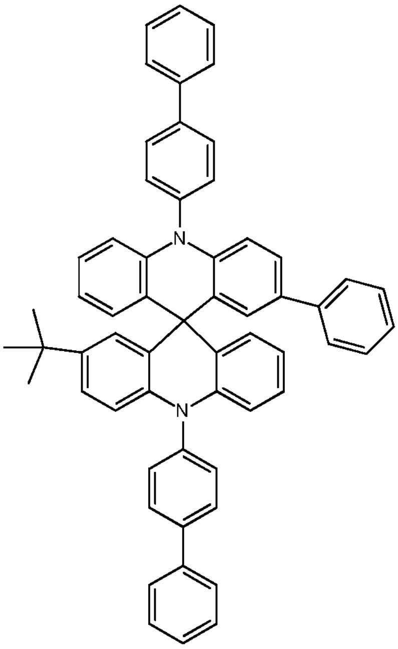
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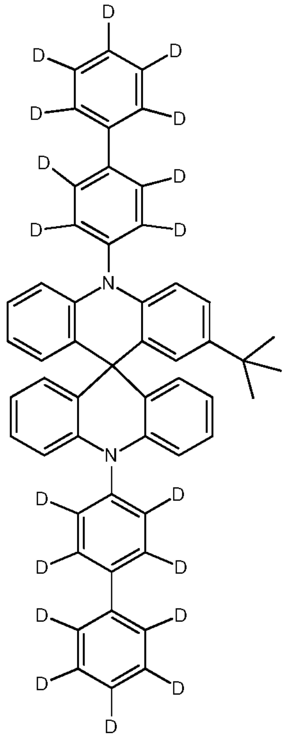	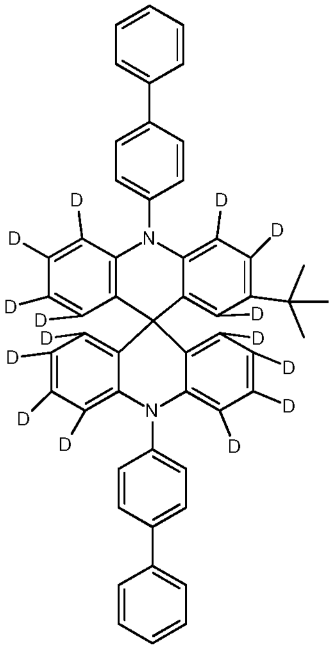
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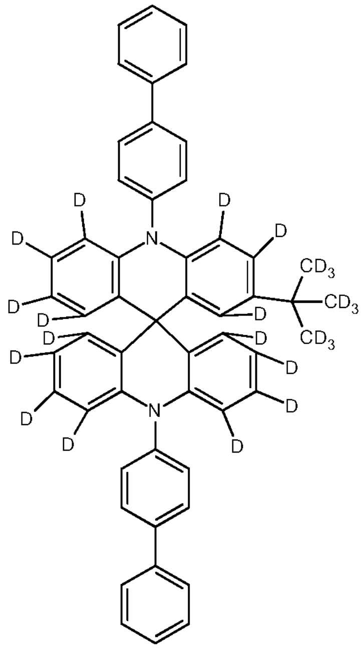	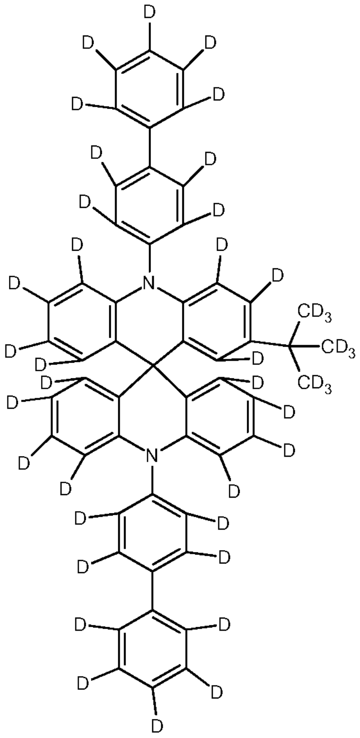
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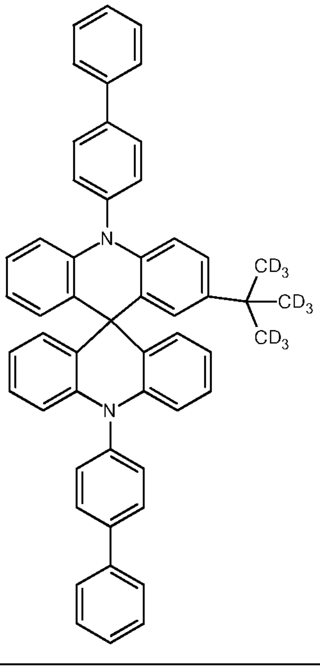	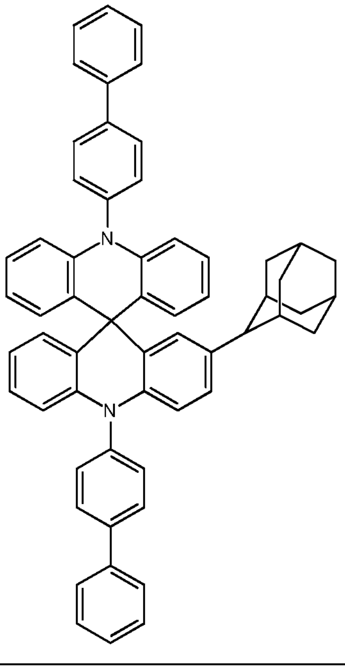
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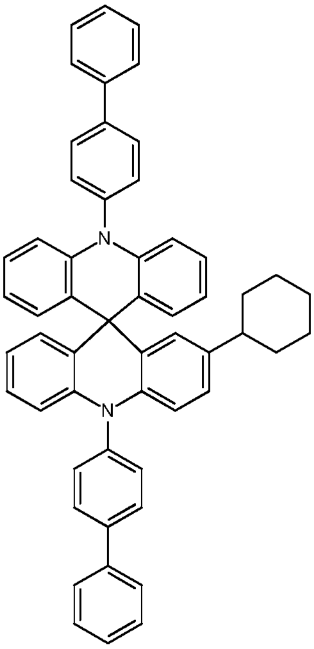	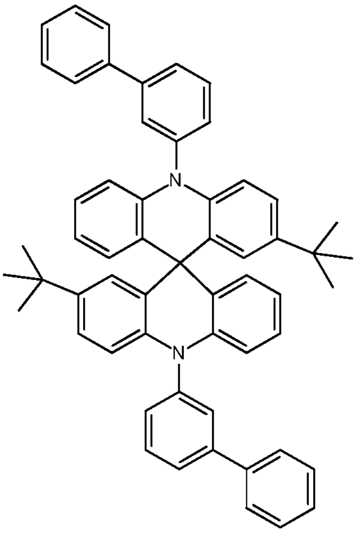
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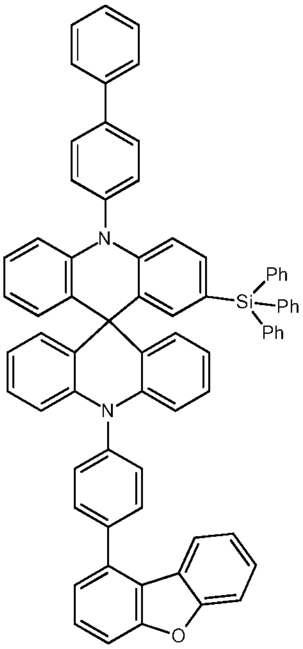	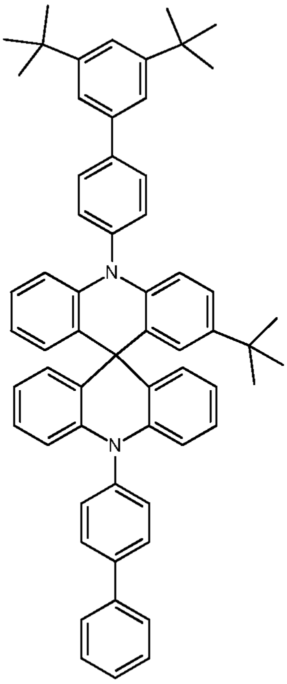
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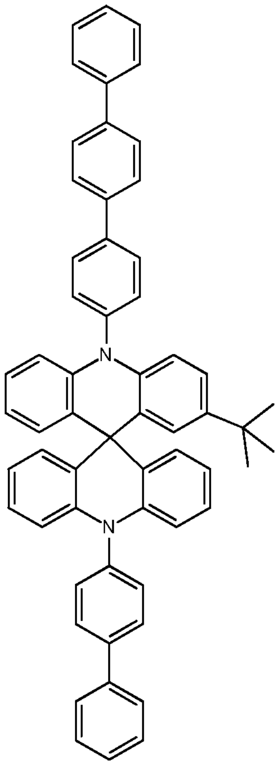	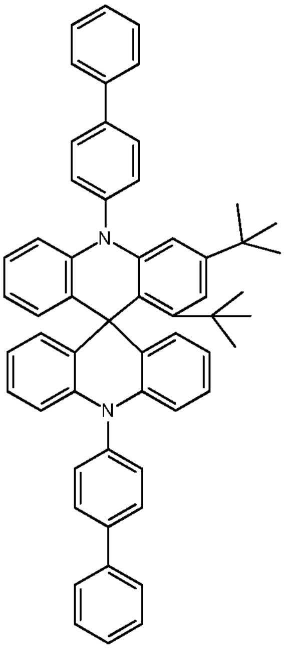
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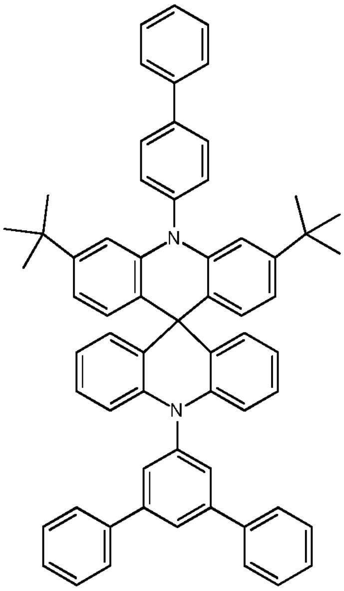	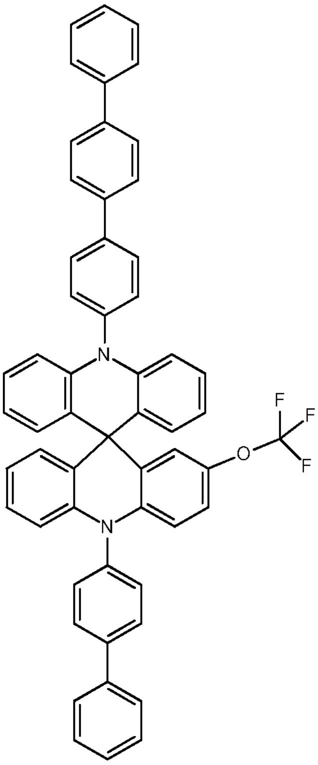
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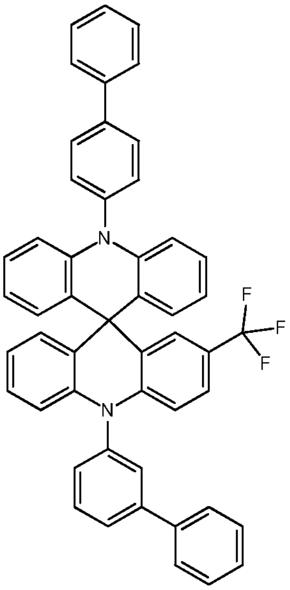	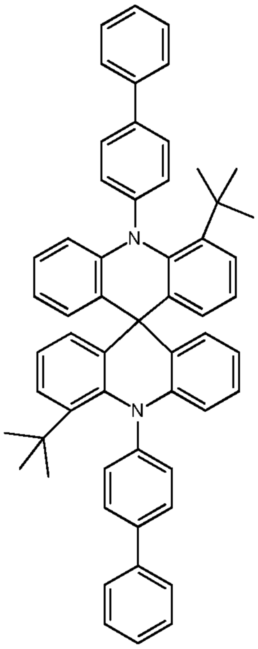
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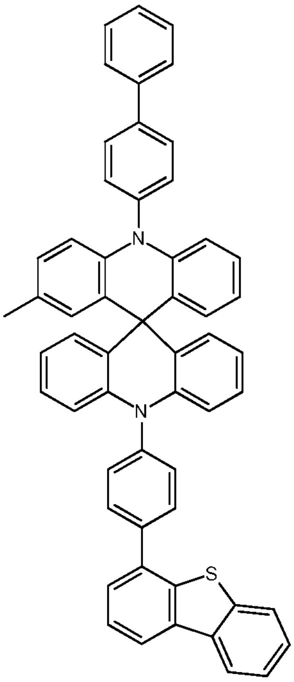	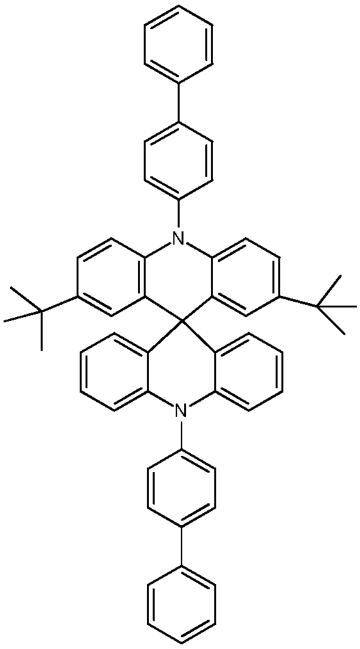
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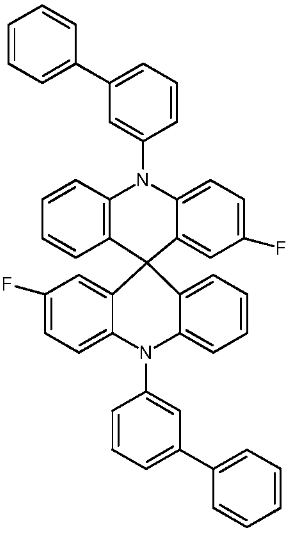	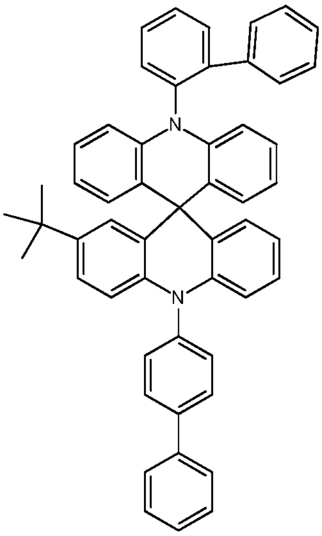
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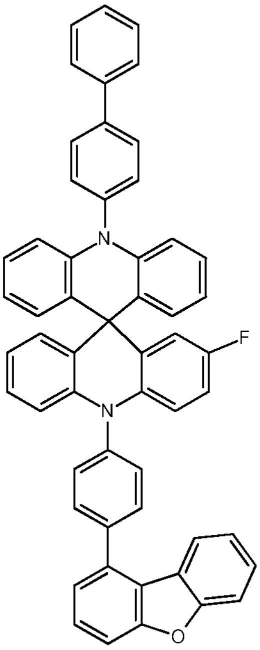	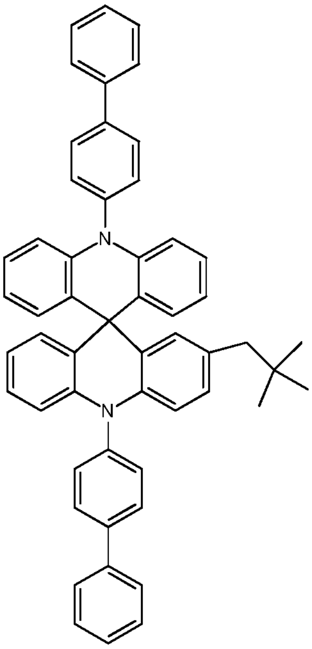
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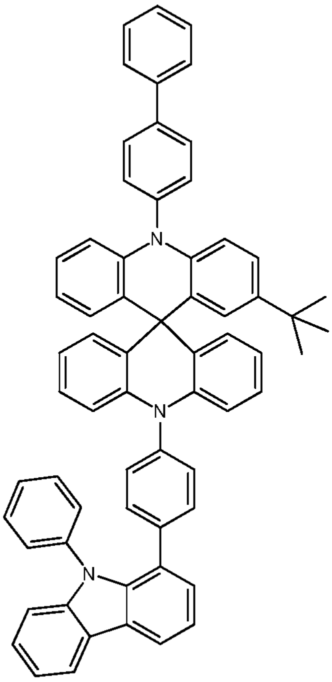	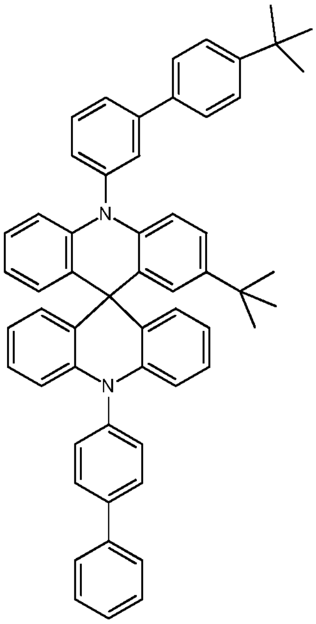
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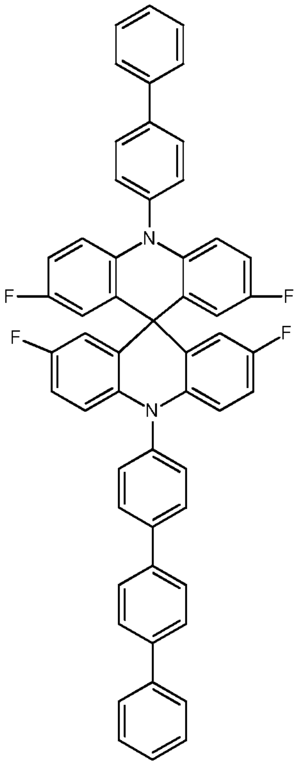	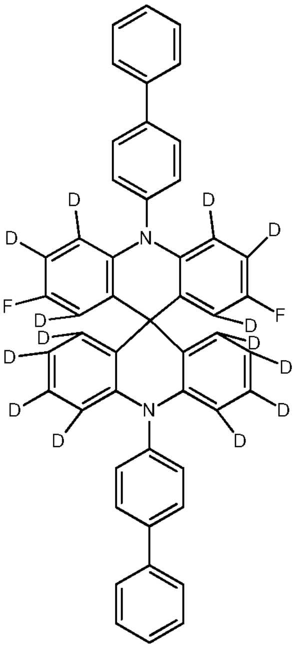
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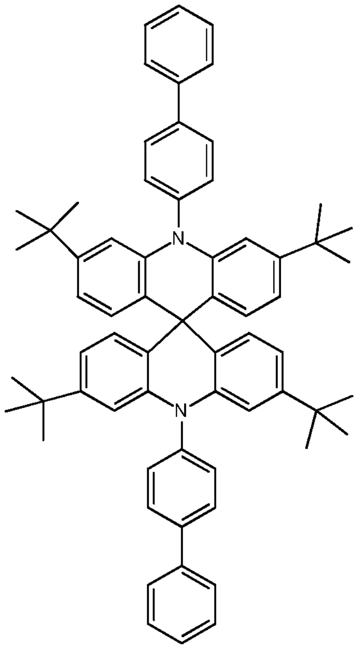	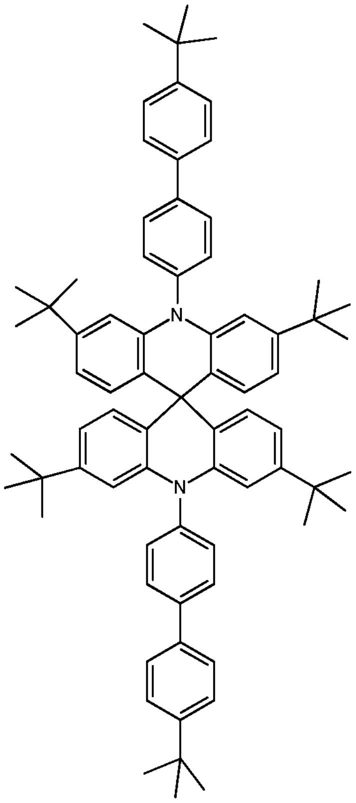
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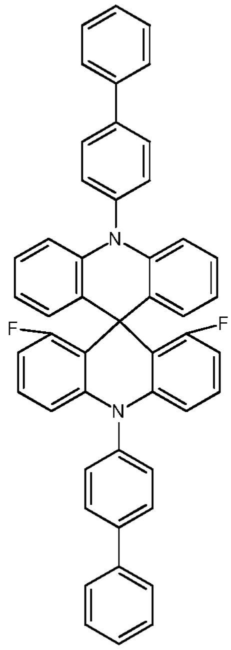	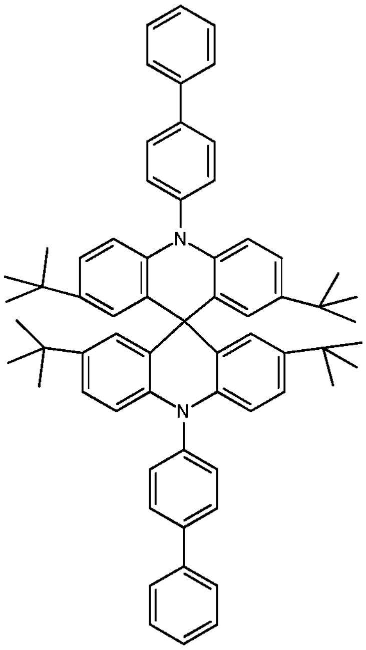
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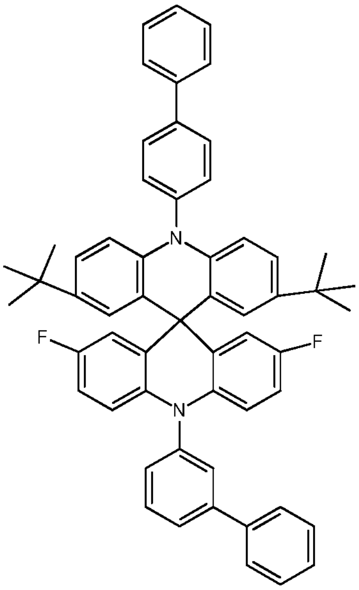	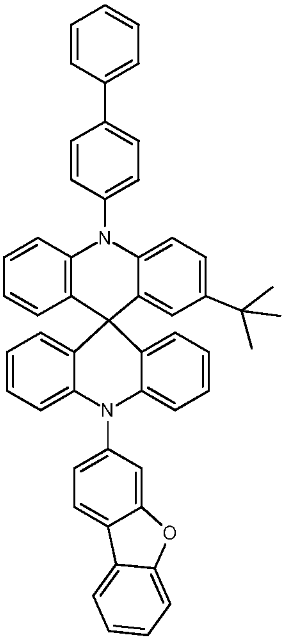
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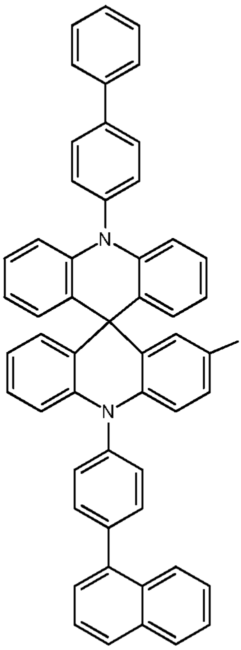	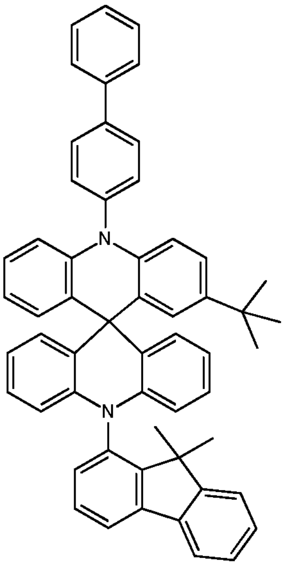
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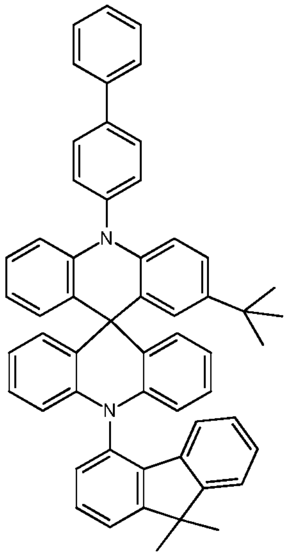	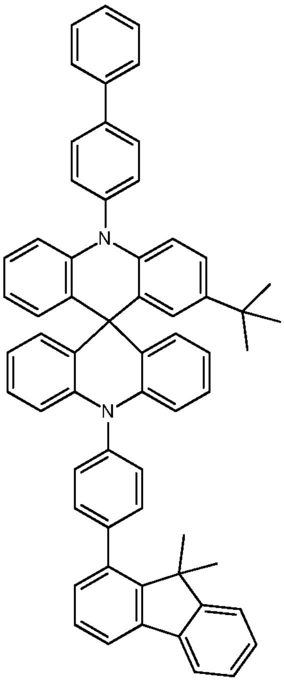
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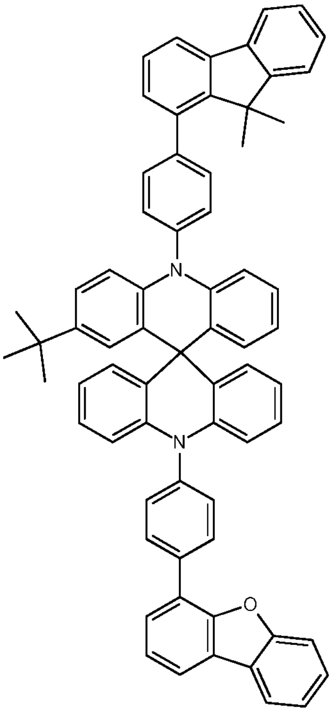	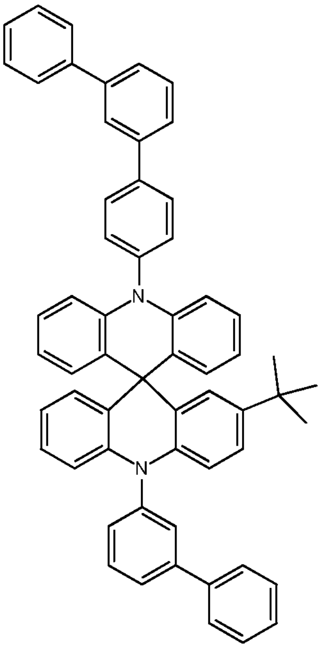
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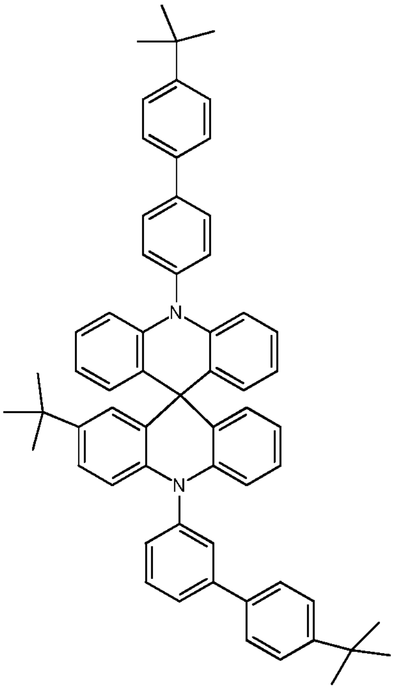	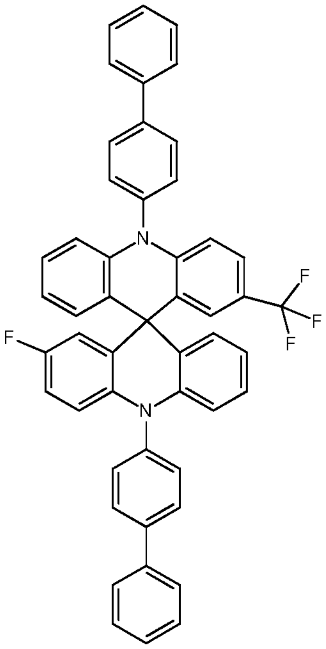
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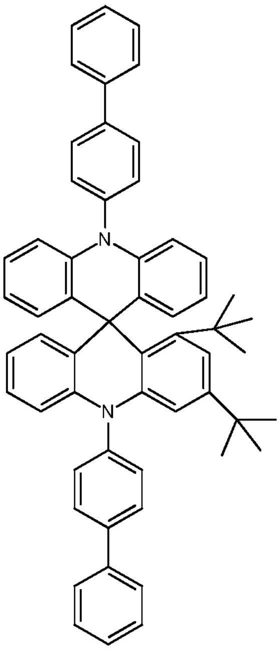	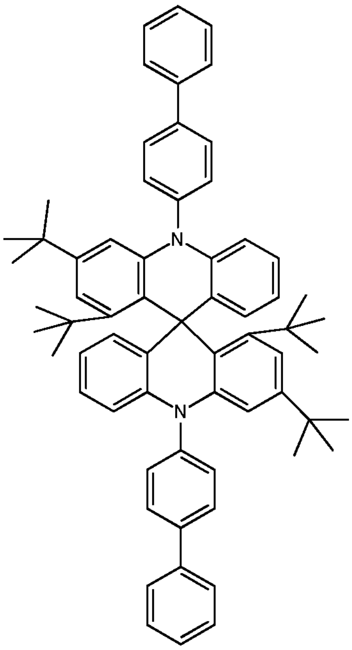
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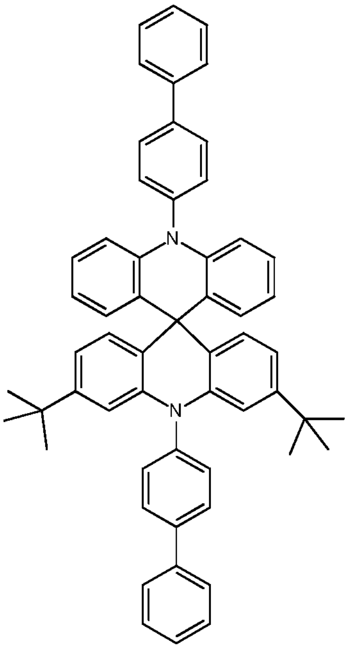	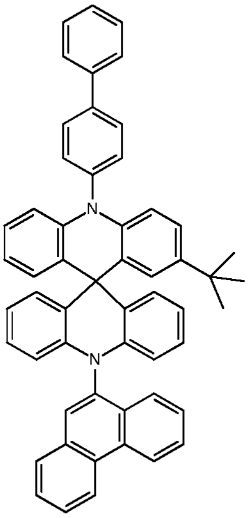
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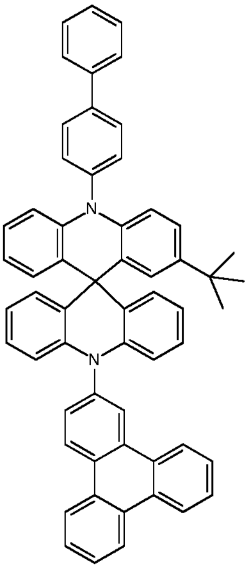	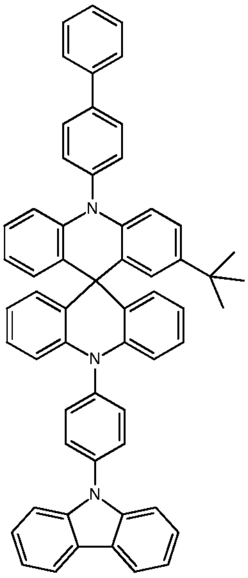
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The compounds of the formula (I) can be prepared using known reactions of organic chemistry, for example using bromination reactions, Buchwald coupling reactions and Suzuki coupling reactions.

General processes for the preparation of the compounds of the formula (I) are shown in the application WO2015/158411. Additionally, specific examples of processes for the preparation of compounds of the formula (I) are shown in the working examples.

The compounds according to the present invention may be used or applied together with further organic functional materials, which are commonly used in electronic devices according to the prior art. A great variety of suitable organic functional materials is known to those skilled in the art in the field of electronic devices. The present invention therefore further provides for a composition comprising one or more compounds of formula (I), or one or more polymers, oligomers or dendrimers containing one or more compounds of formula (I), and at least one further organic functional material selected from the group consisting of fluorescent emitters, phosphorescent emitters, host materials, matrix materials, electron transporting materials, electron injecting materials, hole transporting materials, hole injecting materials, electron blocking materials, hole blocking materials, wide band gap materials, delayed fluorescent emitters and delayed fluorescent hosts.

Delayed fluorescent emitters and delayed fluorescent hosts are well known in the art and disclosed in, e.g., Ye Tao et al., Adv. Mater. 2014, 26, 7931-7958, M. Y. Wong et al., Adv. Mater. 2017, 29, 1605444, WO 2011/070963, WO 2012/133188, WO 2015/022974 and WO 2015/098975. Typically, the delayed fluorescent materials (emitters and/or hosts) are characterized in that they exhibit a rather small gap between their singlet energy (S_1) and triplet energy (T_1). Preferably ΔE_{ST} is equal to or smaller than 0.5 eV, very preferably equal to or smaller than 0.3 eV, particularly preferably equal to or smaller than 0.2 eV and most preferably equal to or small than 0.1 eV, wherein ΔE_{ST} represents the difference between the singlet energy (S_1) and the triplet energy (T_1).

Within the present invention, wide band gap materials are understood to mean a material as disclosed in US 7,294,849, which is characterized in having a band gap of at least 3 eV, preferably at least 3.5 eV and very preferably at least 4.0 eV, wherein the term “band gap” means the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Such systems exhibit particularly advantageous performance characteristics in electroluminescent devices.

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

The invention therefore further provides a formulation, especially a solution, dispersion or emulsion, comprising at least one compound of formula (I), or oligomers, polymers or dendrimers containing one or more compounds of formula (I), or at least one composition comprising one or more compounds of formula (I) and at least one further organic functional material, as described above, and at least one solvent, preferably an organic solvent. The way in which such solutions can be prepared is known to those skilled in the art and is described, for example, in WO 2002/072714, WO 2003/019694 and the literature cited therein.

The compounds of the invention are suitable for use in electronic devices, especially in organic electroluminescent devices such as OLEDs. Depending on the substitution, the compounds are used in different functions and layers.

The invention therefore further provides for the use of the compound of formula (I), or an oligomer, polymers or dendrimer containing one or more compounds of formula (I), or a composition comprising one or more compounds of formula (I) and at least one further organic functional material, as described above, in an electronic device. This electronic device is preferably selected from the group consisting of organic integrated circuits (OICs), organic field-effect transistors (OFETs), organic thin-film transistors (OTFTs), organic solar cells (OSCs), organic optical detectors, organic photoreceptors and, more preferably, organic electroluminescent devices (EL devices). Preferred EL devices are organic light-emitting transistors (OLETs), organic field-quench devices (OFQDs), organic light-emitting electrochemical cells (OLECs, LECs, LEECs), organic laser diodes (O-lasers) and organic light emitting diodes (OLEDs), of which OLEDs are most preferred.

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

Particularly preferably, the electronic device is an organic light emitting diode (OLED), also known as organic electroluminescent diode or device comprising anode, cathode and at least one organic layer formed between anode and cathode, characterized in that at least one organic layer, which may be an emitting layer, a hole transport layer or another layer, preferably an emitting layer or a hole transport layer, particularly preferably a hole transport layer, comprises at least one compound of formula (I).

A hole transport layer is located between the anode and emitting layer and supports the transport of holes across it so they can reach the emitting layer. Preferably, an OLED comprises a hole transport region comprising one or more hole-transport layers including hole injection layers, hole transport layers and electron blocking layers. A hole injection layer (HIL) is preferably located between the anode and another hole transport layer. The hole injection layer injects the holes in the adjacent hole transport layer. An electron-blocking layer (EBL) (also called auxiliary layer) is preferably located between a hole transport layer and the emitting layer, more preferably the electron blocking layer is adjacent to the emitting layer. The electron blocking layer blocks the electrons and confines them within the emitting layer. The electron blocking layer may comprise one or more electron blocking layers.

In accordance with a preferred embodiment, the electronic device is an organic light emitting diode (OLED) comprising anode, at least one hole transport layer, at least one emitting layer, at least one electron transport layer and cathode, where the at least one hole transport layer comprises a compound of formula (I).

In accordance with a very preferred embodiment, the electronic device is an organic light emitting diode (OLED) comprising anode, at least one hole transport layer, at least one light emitting layer, at least one electron transport layer and cathode, where the at least one hole transport layer comprises a compound of formula (I) and, where the at least one hole transport layer is formed between the anode and the light emitting layer and the at least one electron transport layer is formed between the light emitting layer and the cathode.

In accordance with a particularly preferred embodiment, the electronic device is an organic light emitting diode (OLED) comprising anode, a hole transport layer, a light emitting layer, an electron transport layer and cathode, where the hole transport layer includes a first hole transport layer and a second hole transport layer, where the first hole transport layer is formed between the anode and the second hole transport layer and the second hole transport layer is formed between the first hole transport layer and the emitting layer, and where the second hole transport layer comprises a compound of formula (I). Preferably, the second hole-transport layer is an electron-blocking layer. More preferably, the second hole-transport layer is an electron-blocking layer adjacent to the light emitting layer. The electron-blocking layer may include one, two or more electron-blocking layers, where one of the electron blocking layers comprises the compound of formula (I).

More specifically, it is preferred that the electronic device is an organic light emitting diode (OLED) comprising, in the following order:

- An anode
- A first hole transport layer

- An electron blocking layer
- A light emitting layer
- An electron transport layer
- A cathode,

where the at least one electron blocking layer comprises a compound of formula (I).

In accordance with a very preferred embodiment, the sequence of layers in the OLED is as follows:
substrate,
anode,
optionally hole-injection layer HIL, preferably p-doped, p-HIL
first hole-transport layer HTL
electron blocking layer EBL_1
optionally second electron blocking layer EBL_2
emitting layer EML
optionally a hole-blocking layer HBL,
an electron-transport layer ETL,
optionally an electron-injection layer EIL, and
a cathode, where either EBL_1 or, when present, EBL_2 comprises a compounds of formula (I), and where further layers may additionally be present in the OLED.

Within the present invention, the term “organic layer” is understood to mean any layer of an electronic device which comprises one or more organic compounds as functional materials.

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

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

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

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

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

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

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

In a preferred embodiment of the invention, the compounds of formula (I) are used as hole-transporting material. In that case, the compounds are preferably present in a hole transport layer, an electron blocking layer or a hole injection layer. Particular preference is given to use in an electron blocking layer.

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

Hole injection layers and electron blocking layers are understood in the context of the present application to be specific embodiments of hole transport layers. A hole injection layer, in the case of a plurality of hole transport layers between the anode and emitting layer, is a hole transport layer which directly adjoins the anode or is separated therefrom only by a single coating of the anode. An electron blocking layer, in the case of a plurality of hole transport layers between the anode and emitting layer, is that hole transport layer which directly adjoins the emitting layer on the anode side. Preferably, the OLED of the invention comprises two, three or four hole-transporting layers between the anode and emitting layer, at least one of which preferably contains a compound of formula (I), and more preferably exactly one or two contain a compound of formula (I).

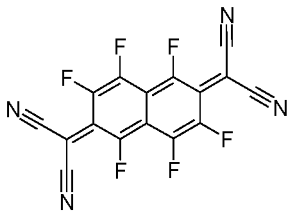
If the compound of formula (I) is used as hole transport material in a hole transport layer, a hole injection layer or an electron blocking layer, the compound can be used as pure material, i.e. in a proportion of 100%, in the hole transport layer, or it can be used in combination with one or more further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

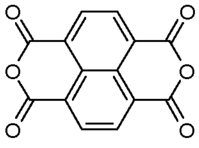
Particularly preferred embodiments of p-dopants are the compounds disclosed in WO 2011/073149, EP 1968131, EP 2276085, EP 2213662, EP 1722602, EP 2045848, DE 102007031220, US 8044390, US 8057712, WO 2009/003455, WO 2010/094378, WO 2011/120709, US 2010/0096600, WO 2012/095143 and DE 102012209523.

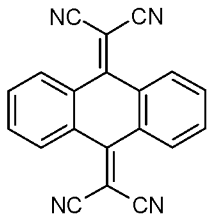
Particularly preferred p-dopants are quinodimethane compounds, azaindenofluorenediones, azaphenalenes, azatriphenylenes, I_2, metal halides, preferably transition metal halides, metal oxides, preferably metal oxides containing at least one transition metal or a metal of main group 3, and transition metal complexes, preferably complexes of Cu, Co, Ni, Pd and Pt with ligands containing at least one oxygen atom as bonding site. Preference is further given to transition metal oxides as dopants, preferably oxides of rhenium, molybdenum and tungsten, more preferably Re_2O_7, MoO_3, WO_3 and ReO_3.

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

Preferred p-dopants are especially the following compounds:







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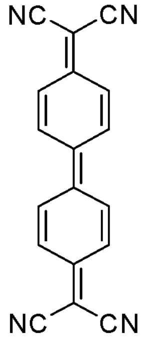

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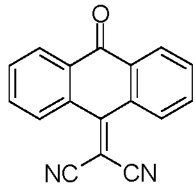

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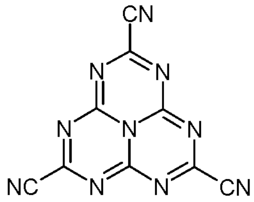

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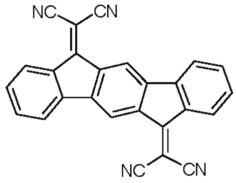

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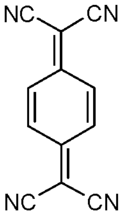

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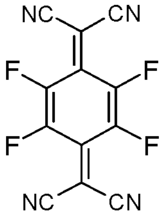

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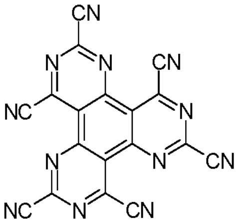

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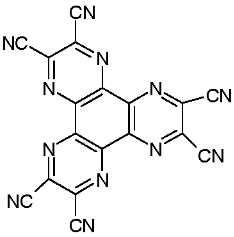

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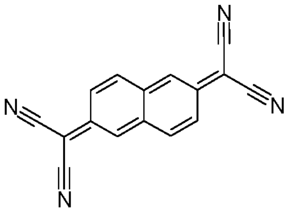

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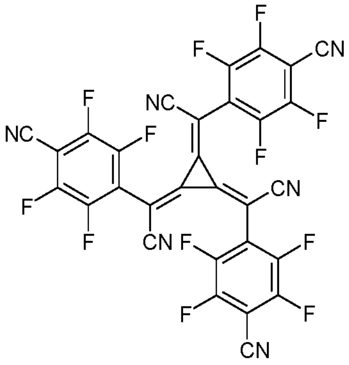
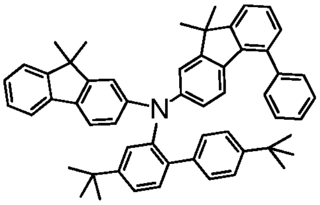
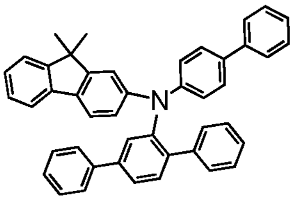
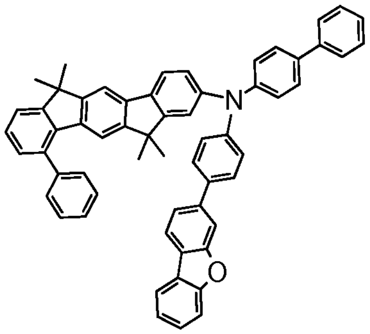


(D-13)

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

Further hole transport materials that can be used in any of the layers that require materials with hole transporting capabilities, e.g. hole injection layer (HIL), hole transport layer (HTL), electron blocking layer (EBL) or the emissive layer (EML) are listed in the following table. The compounds can be prepared easily according to the disclosure cited for each of the compounds. The compounds HT-1 to HT-33 exhibit excellent stability and electronic devices comprising the compounds show high efficiencies, low voltages and improved lifetimes.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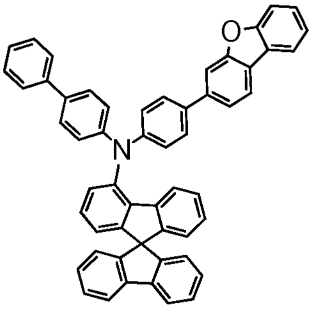	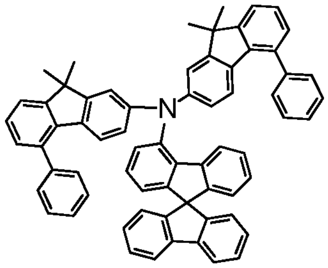	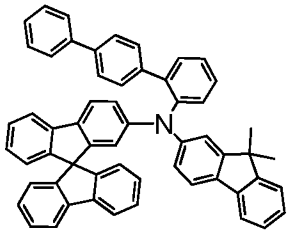
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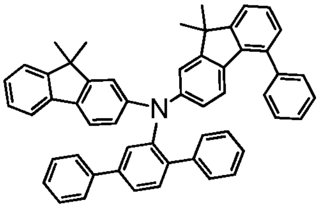	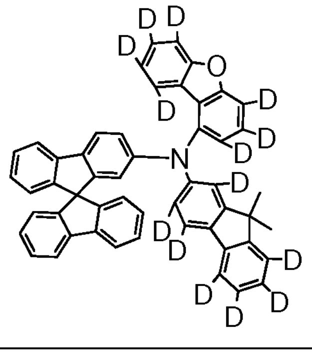	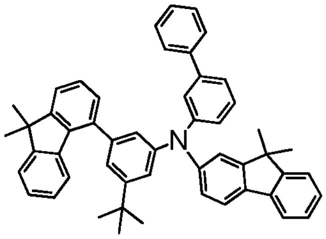

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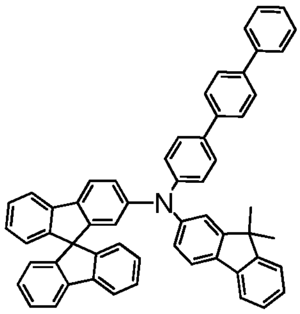	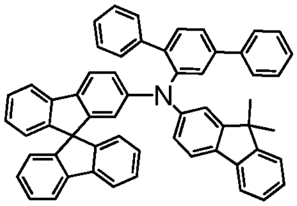	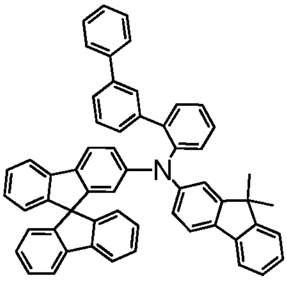
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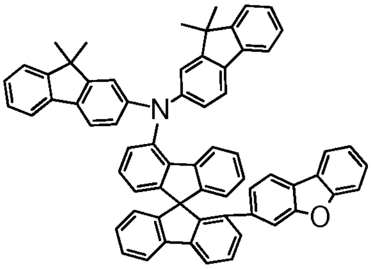	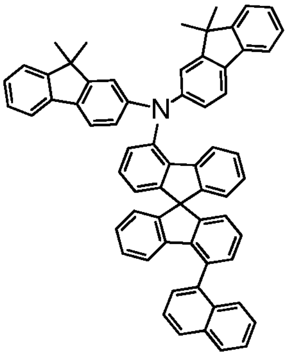	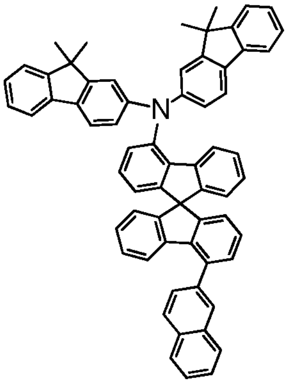
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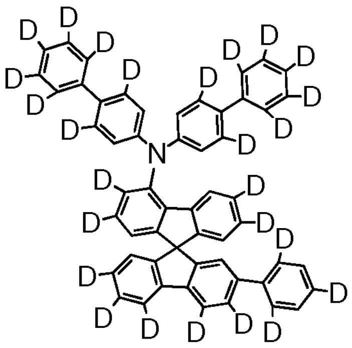	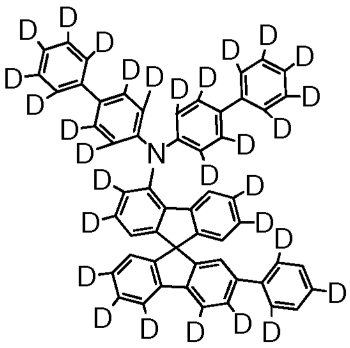	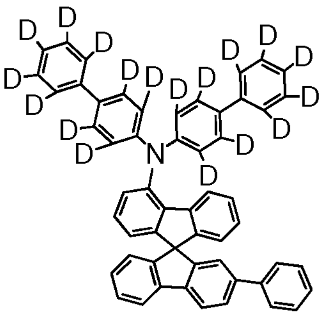
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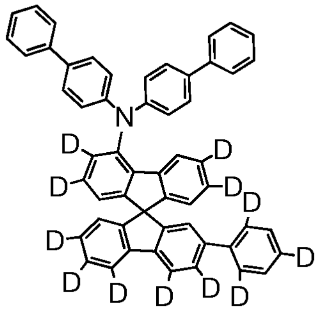	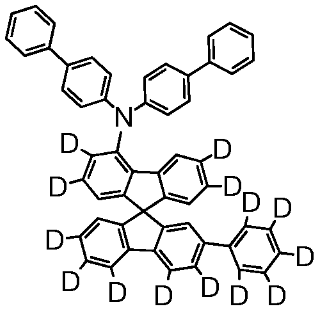	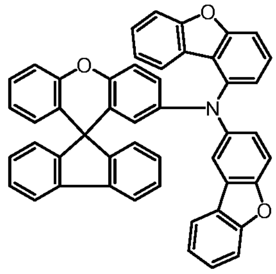
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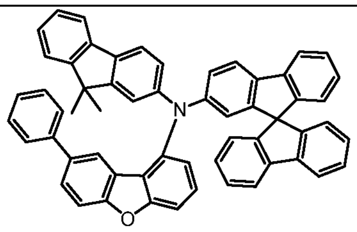	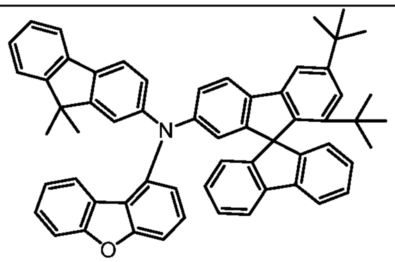	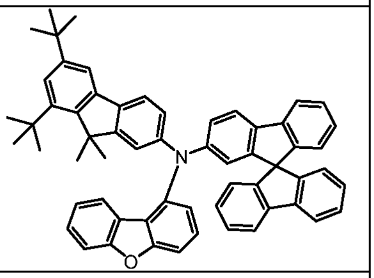
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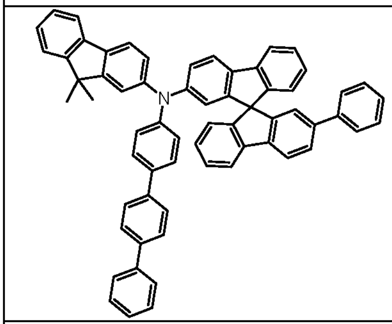	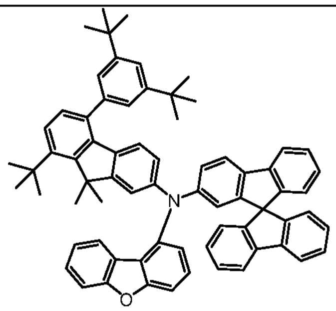	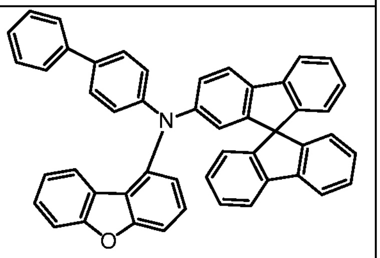
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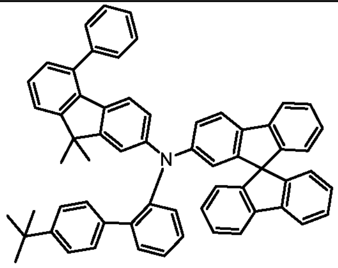	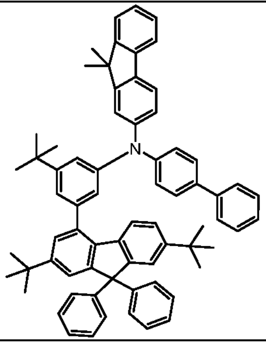	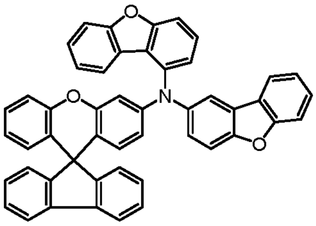
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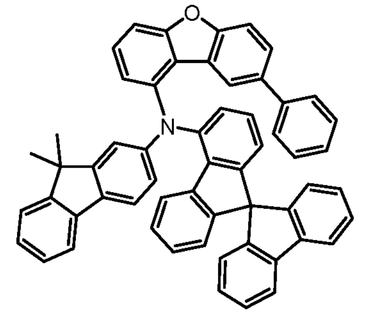
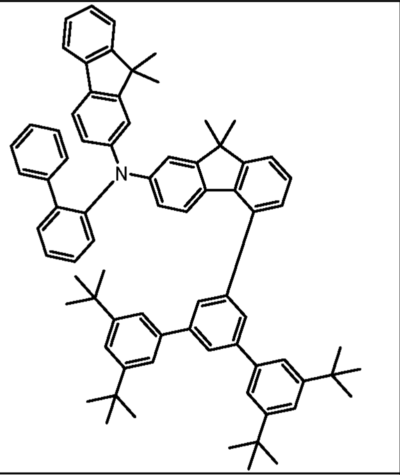
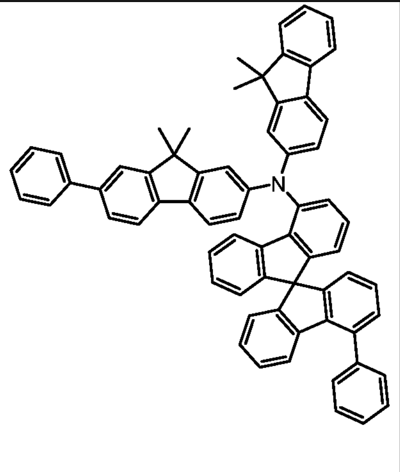
		
HT-31 WO2017/102064	HT-32 WO2019/115577 WO2022/108068	HT-33 WO2013/120577 WO2017/102063

The teachings on the use of the compounds and the methods of making the compounds contained in the above patent applications are hereby expressly incorporated by reference into the present disclosure. The compounds HT-1 to HT-33 exhibit excellent properties when used in OLEDs, in particular excellent lifetime and efficiency. This is particularly the case when they are used in a hole transport layer of the OLED.

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

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

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

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

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

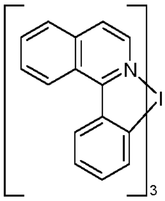
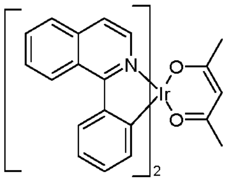
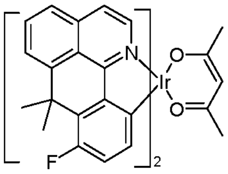
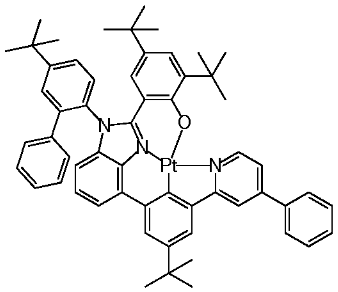
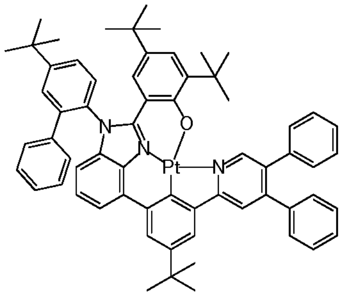
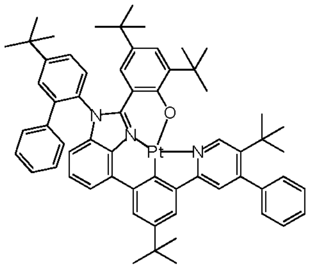
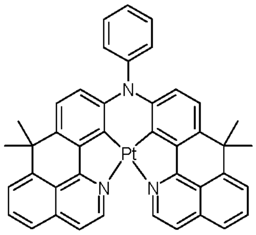
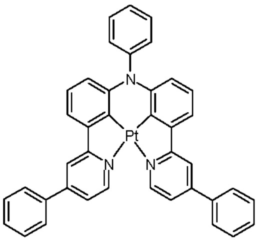
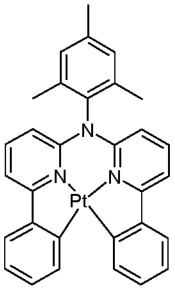
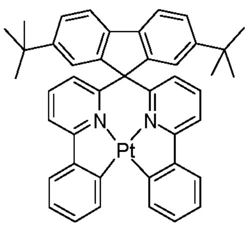
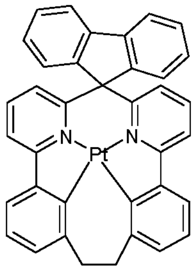
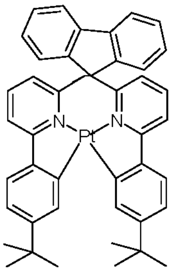
The mixed matrix systems may comprise one or more emitting compounds, preferably one or more phosphorescent emitting compounds. In general, mixed matrix systems are preferably used in phosphorescent organic light emitting diode.

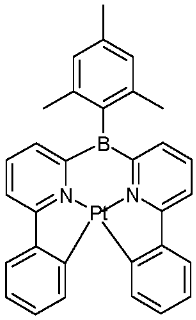
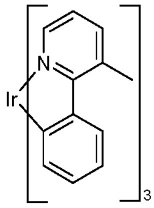
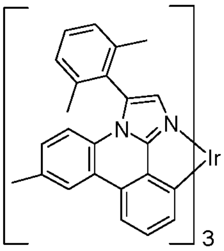
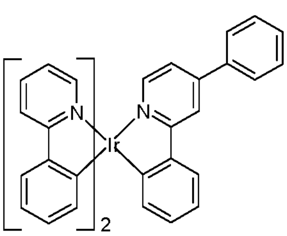
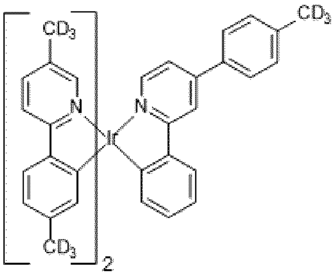
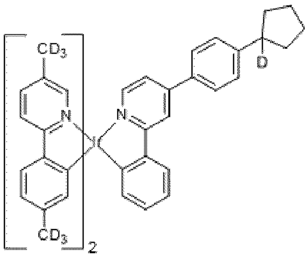
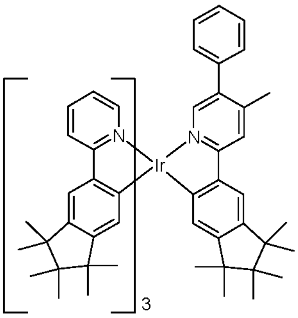
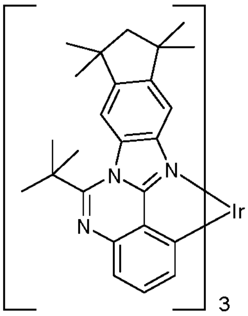
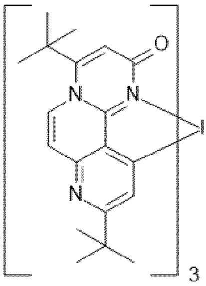
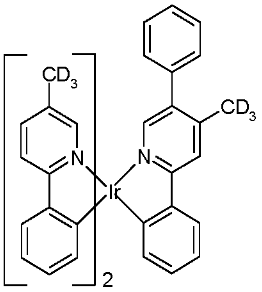
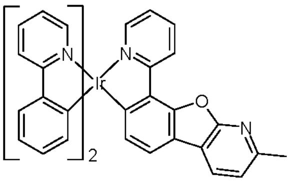
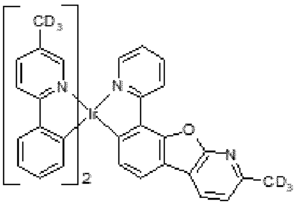
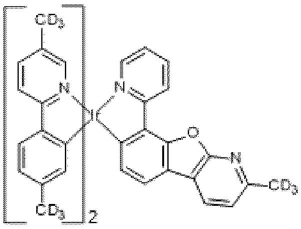
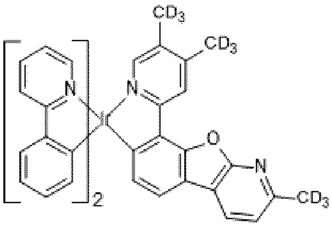
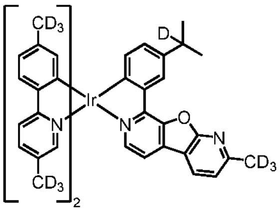
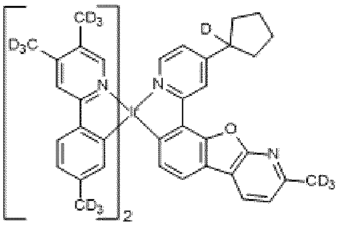
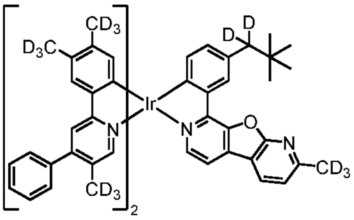
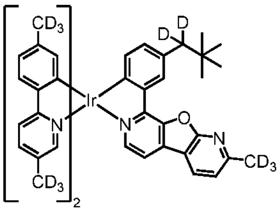
Particularly suitable matrix materials which can be used in combination with the compounds of the invention as matrix components of a mixed matrix system are selected from the preferred matrix materials specified below for phosphorescent emitting compounds or the preferred matrix materials for fluorescent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

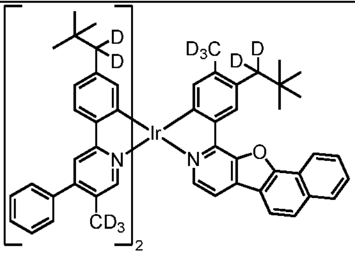
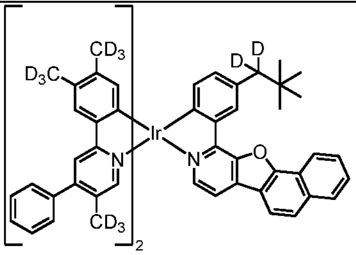
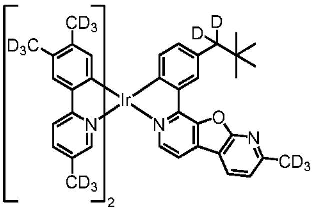
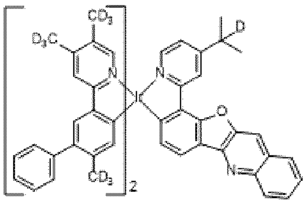
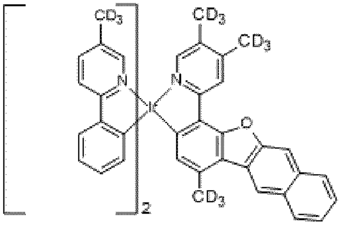
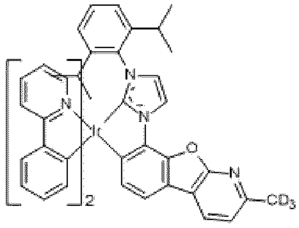
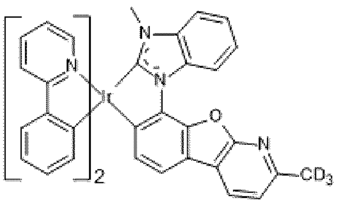
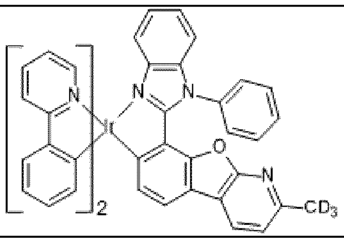
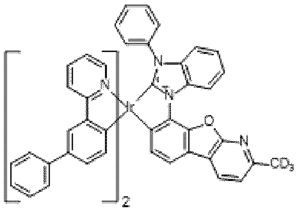
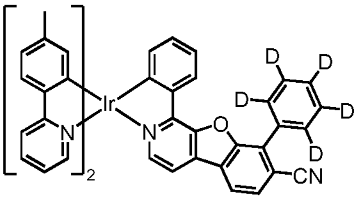
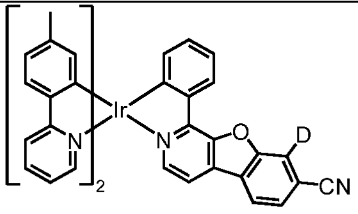
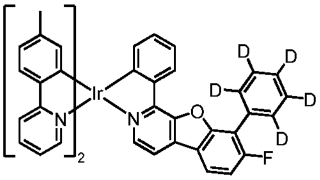
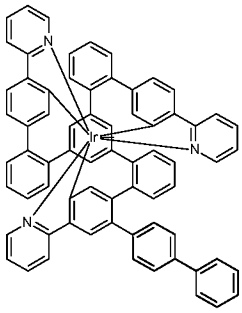
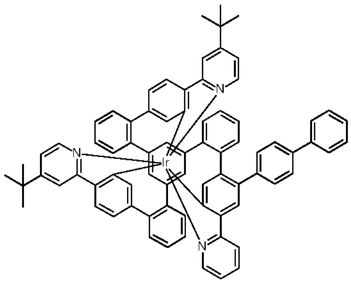
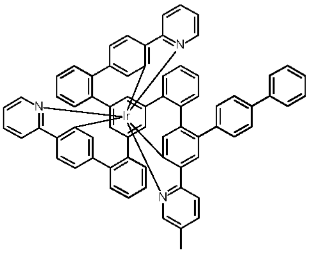
Preferred phosphorescent emitting compounds for use in mixed matrix systems are the same as detailed further up as generally preferred phosphorescent emitter materials.

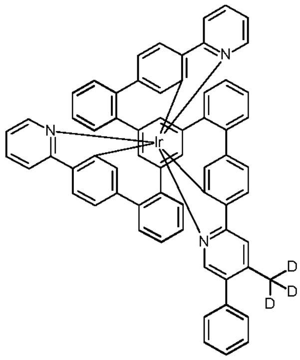
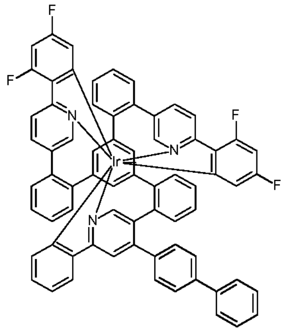
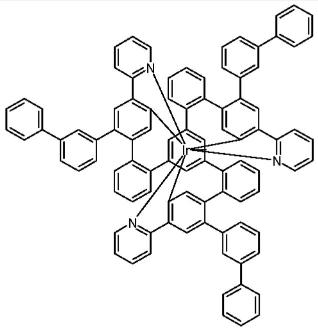
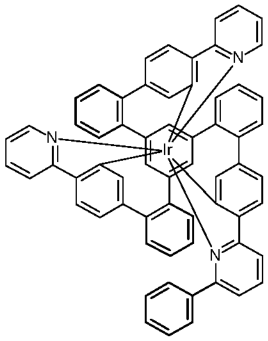
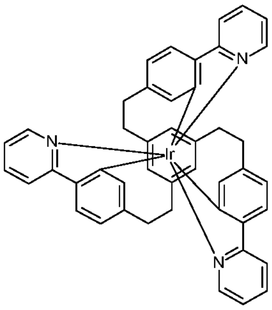
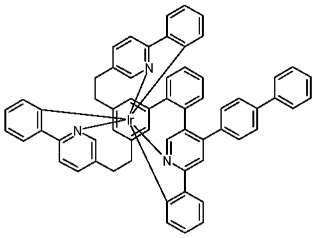
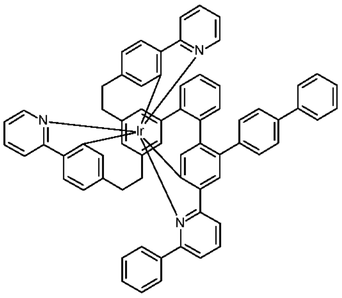
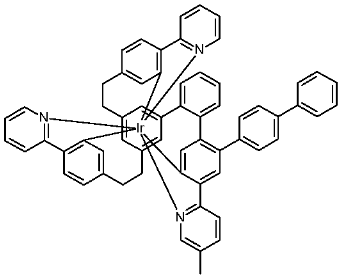
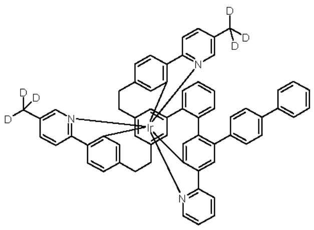
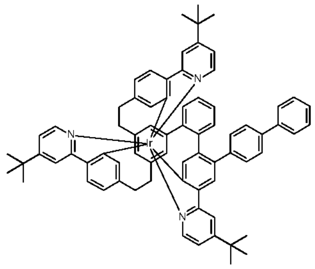
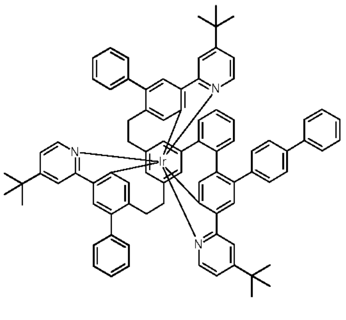
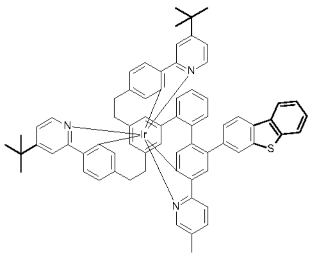
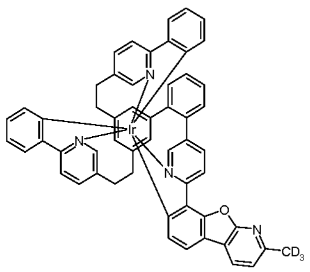
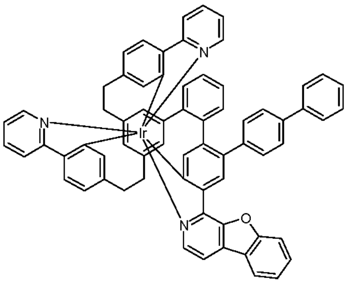
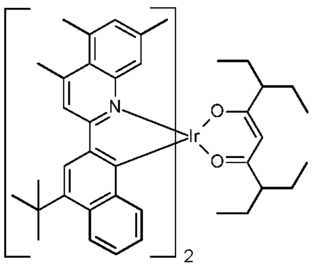
Preferred embodiments of the different functional materials in the electronic device are listed hereinafter.

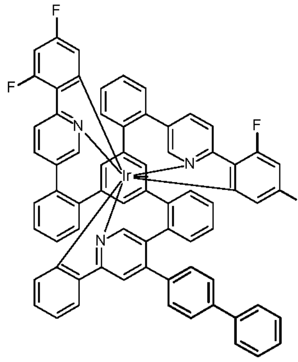
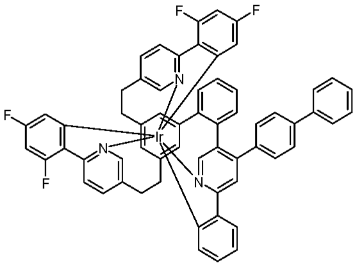
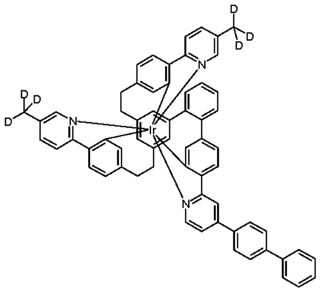
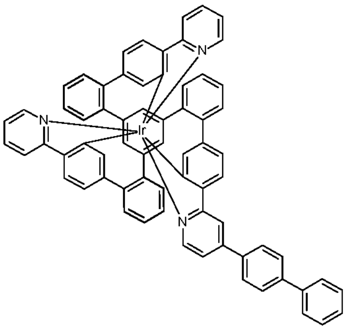
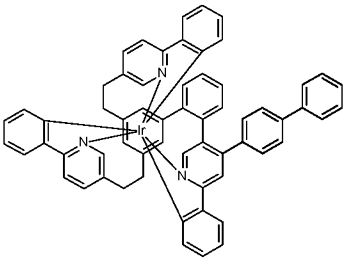
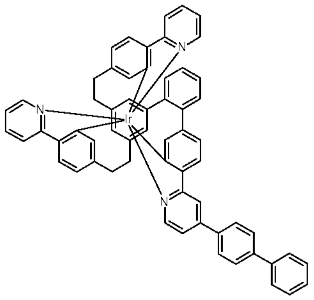
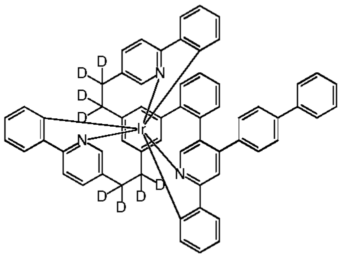
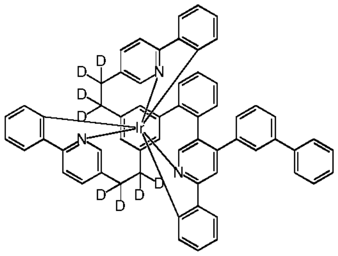
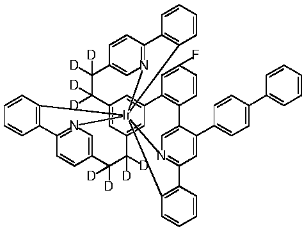
Preferred phosphorescent emitting compounds are the following ones:

Preferred fluorescent emitting compounds are selected from the class of the arylamines. An arylamine or an aromatic amine in the context of this invention is understood to mean a compound containing three substituted or unsubstituted aromatic or heteroaromatic ring systems bonded directly to the nitrogen. Preferably, at least one of these aromatic or heteroaromatic ring systems is a fused ring system, more preferably having at least 14 aromatic ring atoms. Preferred examples of these are aromatic anthracenamines, aromatic anthracenediamines, aromatic pyrenamines, aromatic pyrenediamines, aromatic chrysenamines or aromatic chrysenediamines. An aromatic anthracenamine is understood to mean a compound in which a diarylamino group is bonded directly to an anthracene group, preferably in the 9 position. An aromatic anthracenediamine is understood to mean a compound in which two diarylamino groups are bonded directly to an anthracene group, preferably in the 9,10 positions. Aromatic pyrenamines, pyrenediamines, chrysenamines and chrysenediamines are defined analogously, where the diarylamino groups are bonded to the pyrene preferably in the 1 position or 1,6 positions. Further preferred emitting compounds are indenofluorenamines or -fluorenediamines, for example according to WO 2006/108497 or WO 2006/122630, benzoindenofluorenamines or -fluorenediamines, for example according to WO 2008/006449, and dibenzoindenofluoreneamines or -diamines, for example according to WO 2007/140847, and the indenofluorene derivatives having fused aryl groups disclosed in WO 2010/012328. Likewise, preferred are the pyrenearylamines disclosed in WO 2012/048780 and in WO 2013/185871. Likewise, preferred are the benzoindenofluorenamines disclosed in WO 2014/037077, the benzofluorenamines disclosed in WO 2014/106522, the extended benzoindenofluorenes disclosed in WO 2014/111269 and in WO 2017/036574, the phenoxazines disclosed in WO 2017/028940 and in WO 2017/028941, and the fluorene derivatives bonded to furan units or to thiophene units that are disclosed in WO 2016/150544.

Useful matrix materials, preferably for fluorescent emitting compounds, include materials of various substance classes. Preferred matrix materials are selected from the classes of the oligoarylenes (e.g. 2,2‘,7,7‘-tetraphenylspirobifluorene according to EP 676461 or dinaphthylanthracene), especially of the oligoarylenes containing fused aromatic groups, the oligoarylenevinylenes (e.g. DPVBi or spiro-DPVBi according to EP 676461), the polypodal metal complexes (for example according to WO 2004/081017), the hole-conducting compounds (for example according to WO 2004/058911), the electron-conducting compounds, especially ketones, phosphine oxides, sulphoxides, etc. (for example according to WO 2005/084081 and WO 2005/084082), the atropisomers (for example according to WO 2006/048268), the boronic acid derivatives (for example according to WO 2006/117052) or the benzanthracenes (for example according to WO 2008/145239). Particularly preferred matrix materials are selected from the classes of the oligoarylenes comprising naphthalene, anthracene, benzanthracene and/or pyrene or atropisomers of these compounds, the oligoarylenevinylenes, the ketones, the phosphine oxides and the sulphoxides. Very particularly preferred matrix materials are selected from the classes of the oligoarylenes comprising anthracene, benzanthracene, benzophenanthrene and/or pyrene or atropisomers of these compounds. An oligoarylene in the context of this invention shall be understood to mean a compound in which at least three aryl or arylene groups are bonded to one another. Preference is further given to the anthracene derivatives disclosed in WO 2006/097208, WO 2006/131192, WO 2007/065550, WO 2007/110129, WO 2007/065678, WO 2008/145239, WO 2009/100925, WO 2011/054442 and EP 1553154, the pyrene compounds disclosed in EP 1749809, EP 1905754 and US 2012/0187826, the benzanthracenylanthracene compounds disclosed in WO 2015/158409, the indenobenzofurans disclosed in WO 2017/025165, and the phenanthrylanthracenes disclosed in WO 2017/036573.

Preferred matrix materials for phosphorescent emitting compounds are, as well as the compounds of the formula (I), aromatic ketones, aromatic phosphine oxides or aromatic sulphoxides or sulphones, for example according to WO 2004/013080, WO 2004/093207, WO 2006/005627 or WO 2010/006680, triarylamines, carbazole derivatives, e.g. CBP (N,N-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 according to WO 2007/063754 or WO 2008/056746, indenocarbazole derivatives, for example according to WO 2010/136109, WO 2011/000455 or WO 2013/041176, azacarbazole derivatives, for example according to EP 1617710, EP 1617711, EP 1731584, JP 2005/347160, bipolar matrix materials, for example according to WO 2007/137725, silanes, for example according to WO 2005/111172, azaboroles or boronic esters, for example according to WO 2006/117052, triazine derivatives, for example according to WO 2010/015306, WO 2007/063754 or WO 2008/056746, zinc complexes, for example according to EP 652273 or WO 2009/062578, diazasilole or tetraazasilole derivatives, for example according to WO 2010/054729, diazaphosphole derivatives, for example according to WO 2010/054730, bridged carbazole derivatives, for example according to US 2009/0136779, WO 2010/050778, WO 2011/042107, WO 2011/088877 or WO 2012/143080, triphenylene derivatives, for example according to WO 2012/048781, or lactams, for example according to WO 2011/116865 or WO 2011/137951.

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

Preferably, the inventive OLED comprises two or more different hole-transporting layers. The compound of the formula (I) may be used here in one or more of or in all the hole-transporting layers. In a preferred embodiment, the compound of the formula (I) is used in exactly one or exactly two hole-transporting layers, and other compounds, preferably aromatic amine compounds, are used in the further hole-transporting layers present. Further compounds which are used alongside the compounds of the formula (I), preferably in hole-transporting layers of the OLEDs of the invention, are especially indenofluorenamine derivatives (for example according to WO 06/122630 or WO 06/100896), the amine derivatives disclosed in EP 1661888, hexaazatriphenylene derivatives (for example according to WO 01/049806), amine derivatives with fused aromatics (for example according to US 5,061,569), the amine derivatives disclosed in WO 95/09147, monobenzoindenofluorenamines (for example according to WO 08/006449), dibenzoindenofluorenamines (for example according to WO 07/140847), spirobifluorenamines (for example according to WO 2012/034627 or WO 2013/120577), fluorenamines (for example according to WO 2014/015937, WO 2014/015938, WO 2014/015935 and WO 2015/082056), spirodibenzopyranamines (for example according to WO 2013/083216), dihydroacridine derivatives (for example according to WO 2012/150001), spirodibenzofurans and spirodibenzothiophenes, for example according to WO 2015/022051, WO 2016/102048 and WO 2016/131521, phenanthrenediarylamines, for example according to WO 2015/131976, spirotribenzotropolones, for example according to WO 2016/087017, spirobifluorenes with meta-phenyldiamine groups, for example according to WO 2016/078738, spirobisacridines, for example according to WO 2015/158411, xanthenediarylamines, for example according to WO 2014/072017, and 9,10-dihydroanthracene spiro compounds with diarylamino groups according to WO 2015/086108.

Very particular preference is given to the use of spirobifluorenes substituted by diarylamino groups in the 4 position as hole-transporting compounds, especially to the use of those compounds that are claimed and disclosed in WO 2013/120577, and to the use of spirobifluorenes substituted by diarylamino groups in the 2 position as hole-transporting compounds, especially to the use of those compounds that are claimed and disclosed in WO 2012/034627.

Materials used for the electron transport layer may be any materials as used according to the prior art as electron transport materials in the electron transport layer. Especially suitable are aluminum complexes, for example Alq_3, zirconium complexes, for example Zrq_4, lithium complexes, for example Liq, benzimidazole derivatives, triazine derivatives, pyrimidine derivatives, pyridine derivatives, pyrazine derivatives, quinoxaline derivatives, quinoline derivatives, oxadiazole derivatives, aromatic ketones, lactams, boranes, diazaphosphole derivatives and phosphine oxide derivatives. Further suitable materials are derivatives of the abovementioned compounds as disclosed in JP 2000/053957, WO 2003/060956, WO 2004/028217, WO 2004/080975 and WO 2010/072300.

Preferred cathodes of the electronic device are metals having a low work function, metal alloys or multilayer structures composed of various metals, for example alkaline earth metals, alkali metals, main group metals or lanthanoids (e.g. Ca, Ba, Mg, Al, In, Mg, Yb, Sm, etc.). Additionally, suitable are alloys composed of an alkali metal or alkaline earth metal and silver, for example an alloy composed of magnesium and silver. In the case of multilayer structures, in addition to the metals mentioned, it is also possible to use further metals having a relatively high work function, for example Ag or Al, in which case combinations of the metals such as Ca/Ag, Mg/Ag or Ba/Ag, for example, are generally used. It may also be preferable to introduce a thin interlayer of a material having a high dielectric constant between a metallic cathode and the organic semiconductor. Examples of useful materials for this purpose are alkali metal or alkaline earth metal fluorides, but also the corresponding oxides or carbonates (e.g. LiF, Li_2O, BaF_2, MgO, NaF, CsF, Cs_2CO_3, etc.). It is also possible to use lithium quinolinate (LiQ) for this purpose. The layer thickness of this layer is preferably between 0.5 and 5 nm.

Preferred anodes are materials having a high work function. Preferably, the anode has a work function of greater than 4.5 eV versus vacuum. Firstly, metals having a high redox potential are suitable for this purpose, for example Ag, Pt or Au. Secondly, metal/metal oxide electrodes (e.g. $Al/Ni/NiO_x$, Al/PtO_x) may also be preferred. For some applications, at least one of the electrodes has to be transparent or partly transparent in order to enable the irradiation of the organic material (organic solar cell) or the emission of light (OLED, O-laser). Preferred anode materials here are conductive mixed metal oxides. Particular preference is given to indium tin oxide (ITO) or indium zinc oxide (IZO). Preference is further given to conductive doped organic materials, especially conductive doped polymers. In addition, the anode may also consist of two or more layers, for example of an inner layer of ITO and an outer layer of a metal oxide, preferably tungsten oxide, molybdenum oxide or vanadium oxide.

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

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

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

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

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

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

The compounds according to the present invention and the electronic devices according to the present invention, respectively, exhibit the following surprising and advantageous effects compared to the prior art:

1 The compounds according to the present invention are particularly suitable as hole-transporting materials in an electron blocking layer in electronic devices, such as electroluminescent devices, which is particularly due to their very good very good electron-blocking properties and hole-conducting properties

2. The compounds according to the present invention are characterized by low sublimation temperature, high thermal stability, high oxidation stability, high glass transition temperature and high solubility, which is advantageous in terms of their processability, for example from the liquid phase or from the gaseous phase and makes them particularly suitable for being used in electronic devices.

3. When used in electronic devices, in particular as hole-transporting materials, the compounds according to the present invention lead to excellent results in terms of lifetime, operating voltage and quantum efficiency of the devices.

4. The compounds containing deuterium are more thermally stable, the devices containing the compounds show a longer lifetime and an improved efficiency

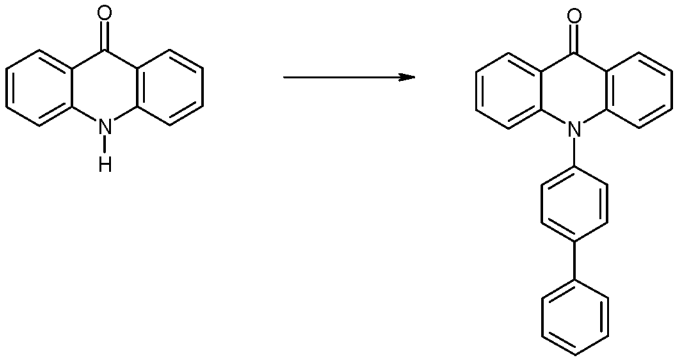
The invention is described in more detail below with the help of examples which are not to be considered as limiting the scope of the invention.

Examples

A) Synthesis Examples

A-1) Synthesis of symmetrical basic structures

Step 1: 10-{[1,1'-biphenyl]-4-yl}-9,10-dihydroacridin-9-one 1a



100 g (0.5 mol) of 10H-acridin-9-one, 140 g (0.6 mol) of 4-bromobiphenyl, 9.6 g (0.05 mol) of CuI, 104.0 g (0.75 mol) of potassium carbonate and 22.0 ml (0.1 mol) of 2,2,6,6-tetramethylheptane-3,5-dione are dissolved in 600 ml of dimethylformamide under a protective atmosphere. The reaction mixture is heated at the boil for 48 h under a protective atmosphere. Water is subsequently added to the mixture. The solid is filtered off with suction, washed with water and ethanol and recrystallised from toluene.

Yield: 167 g (0.48 mol), 96% of theory.

The following compounds can be obtained analogously:

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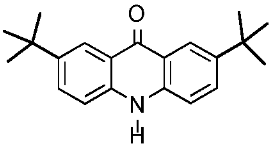
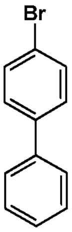
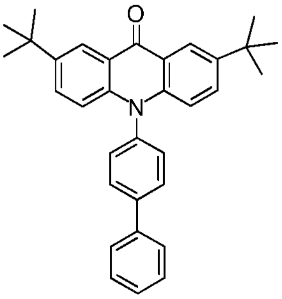
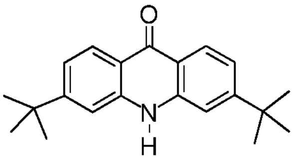
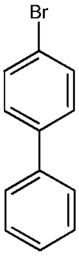
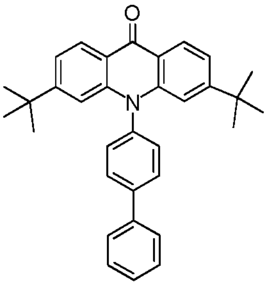
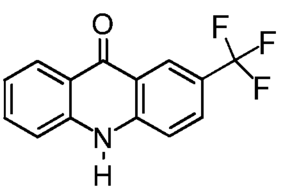
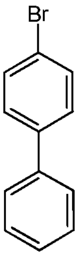
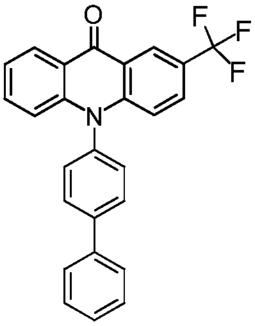
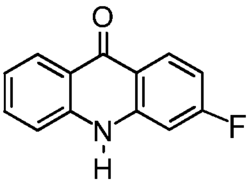
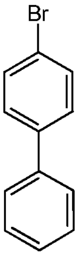
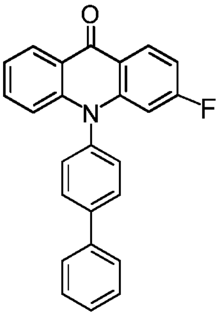
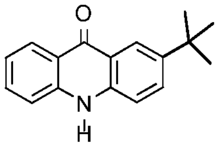
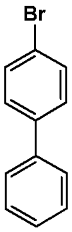
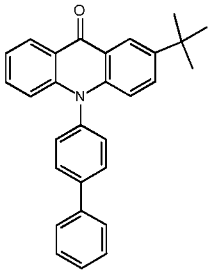
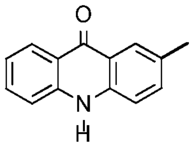
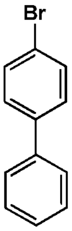
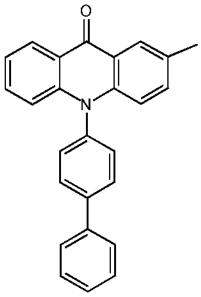
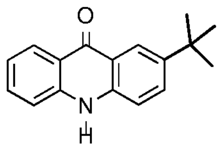
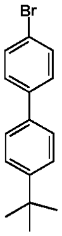
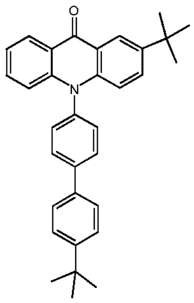
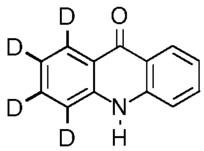
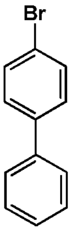
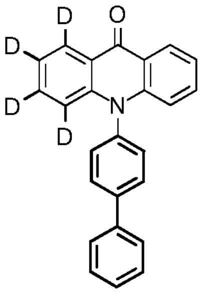
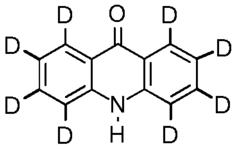
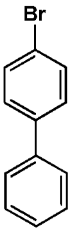
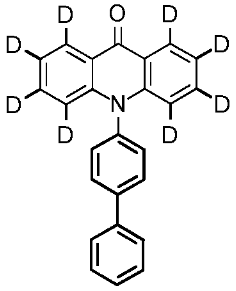
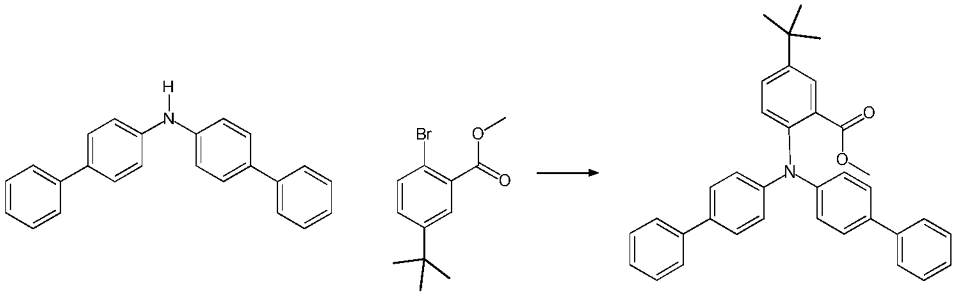
		
		
		
		

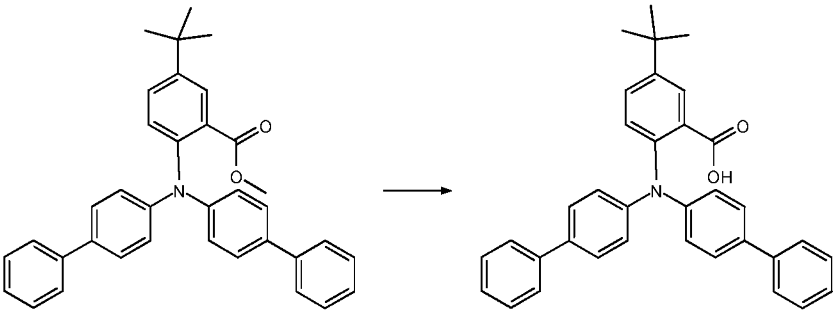
A-2) Synthesis of asymmetrical acridinones

Step 1: Methyl 2-[bis({[1,1'-biphenyl]-4-yl})amino]-5-tert-butylbenzoate 2a



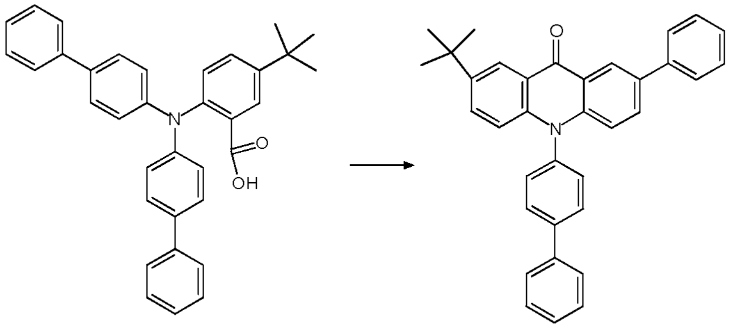
50 g (155.5 mmol) of bisbiphenyl-4-ylamine, 66.9 g (246.9 mmol) of methyl 2-bromo-5-tert-butylbenzoate, 21.5 g (155.5 mmol) of potassium carbonate, 22.1 g (155.5 mmol) of sodium sulfate and 0.9 g (15.5 mmol) of copper powder are suspended in 210 ml of nitrobenzene. The reaction mixture is heated at 220°C for 6 h. After cooling, the mixture is filtered through Celite, and the nitrobenzene is distilled off. The residue is filtered through silica gel (heptane/dichloromethane 1:1). The product is obtained in the form of a solid. The yield is 64 g (80% of theory).

Step 2: 2-[bis({[1,1'-biphenyl]-4-yl})amino]-5-tert-butylbenzoic acid 3a



114.2 g (2722 mmol) of LiOH*H_2O are added to a solution of 62 g (121.1 mmol) of methyl benzoate in 294 ml of dioxane and 294 ml of water. The reaction mixture is heated at 105°C for 16 h. After cooling, ethyl acetate is added, the mixture is added to 1500 ml of 10% citric acid solution and extracted with ethyl acetate. The combined organic phases are dried and evaporated in vacuo. The residue is used in the next step without further purification.

Step 3: 10-{[1,1'-biphenyl]-4-yl}-2-tert-butyl-7-phenyl-9,10-dihydroacridin-9-one 4a



62 g (124.5 mmol) of benzoic acid are dissolved in 364 ml of methanesulfonic acid, and the mixture is stirred overnight at 60°C. After cooling, the mixture is slowly added to ice/water, and the solid which has precipitated out is filtered off with suction. The solid is dissolved in ethyl acetate and washed with a 20% sodium hydrogencarbonate solution. The combined organic phases are dried and evaporated in vacuo. The residue is recrystallised from MeOH. The yield is 56 g (94% of theory).

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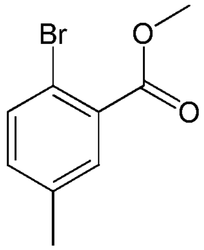
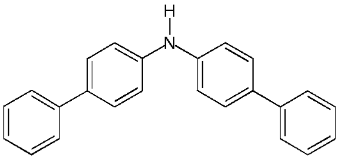
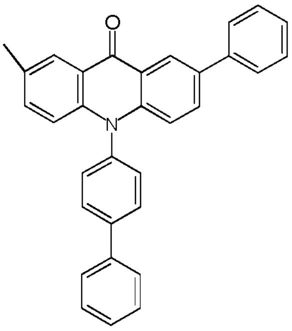
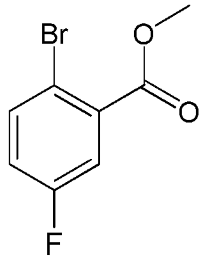
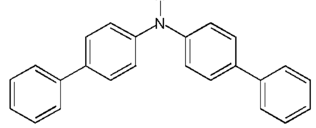
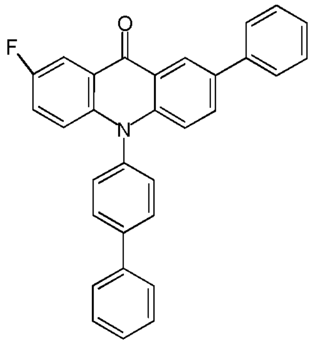
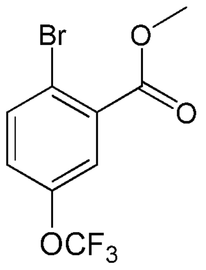
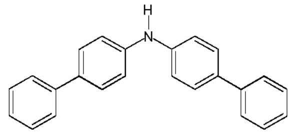
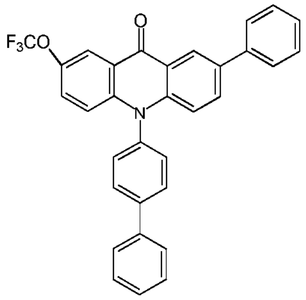
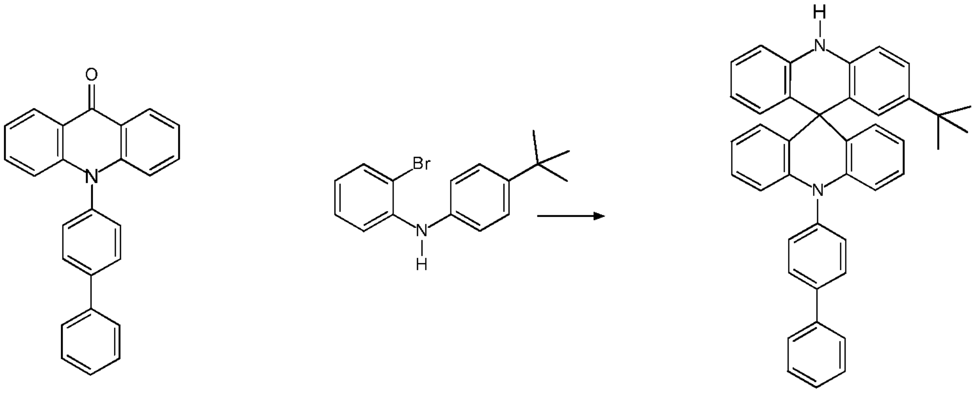
		

A-4) Formation of the spiro unit

10'-{[1,1'-biphenyl]-4-yl}-2-tert-butyl-10H,10'H-9,9'-spirobi[acridine] 5a



42.6 g (140 mmol) of 2-bromo-N-(4-tert-butylphenyl)aniline are initially introduced in 350 ml of absolute THF, cooled to -78°C, and 112 ml (280 mmol) of 2.5 M n-BuLi in THF are added. The mixture is subsequently thawed to -10°C and stirred at this temperature for a further 1 h. 30 g (86 mmol) of 10-biphenyl-4-yl-2,7-diphenyl-10H-acridin-9-one dissolved in 600 ml of THF are slowly added. The mixture is then stirred at room temperature for a further 24 h. 100 ml of ammonium chloride solution are added, stirring is continued briefly, the organic phase is separated off, and the solvent is removed in vacuo. The residue is suspended in 750 ml of warm glacial acetic acid at 40°C, 60 ml of conc. hydrochloric acid are added to the suspension, and the mixture is subsequently stirred at room temperature for a further 8 h. After cooling, the solid which has precipitated out is filtered off with suction, washed once with 100 ml of water, three times with 100 ml of ethanol each time and finally recrystallised from heptane. Yield: 35.3 g (54 mmol), 74% of theory.

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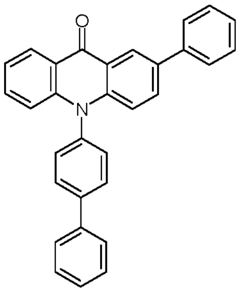
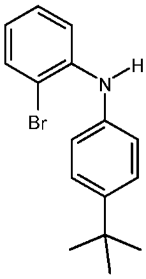
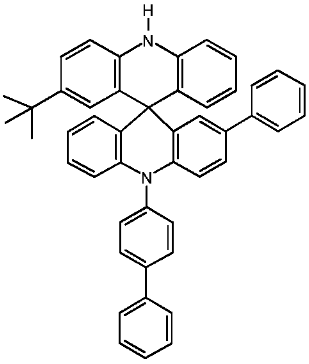
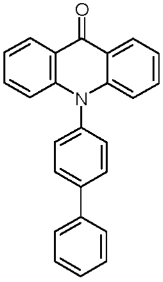
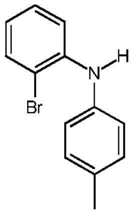
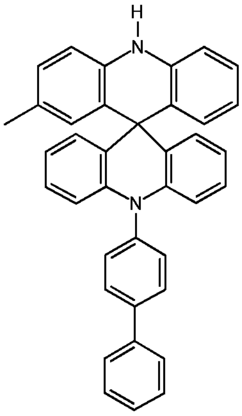
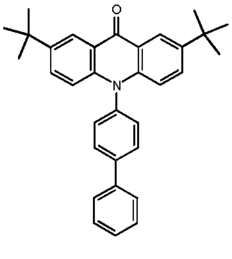
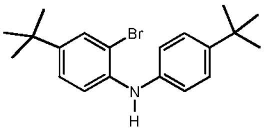
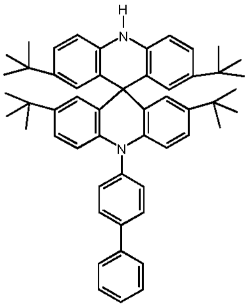
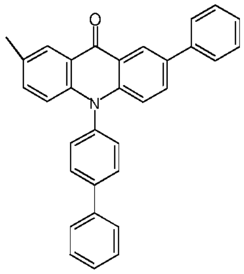
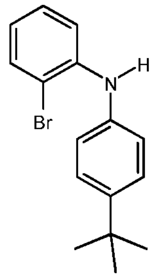
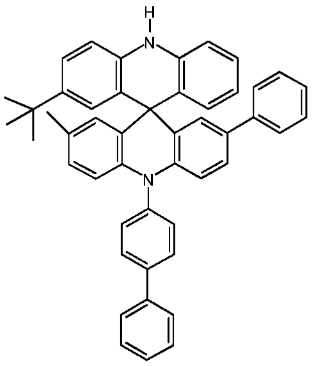
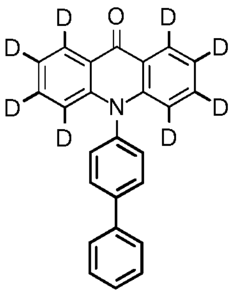
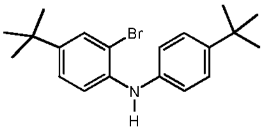
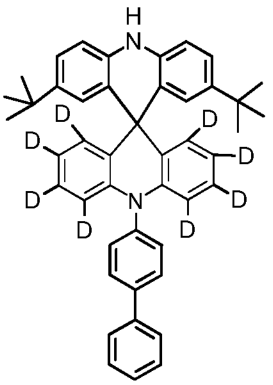
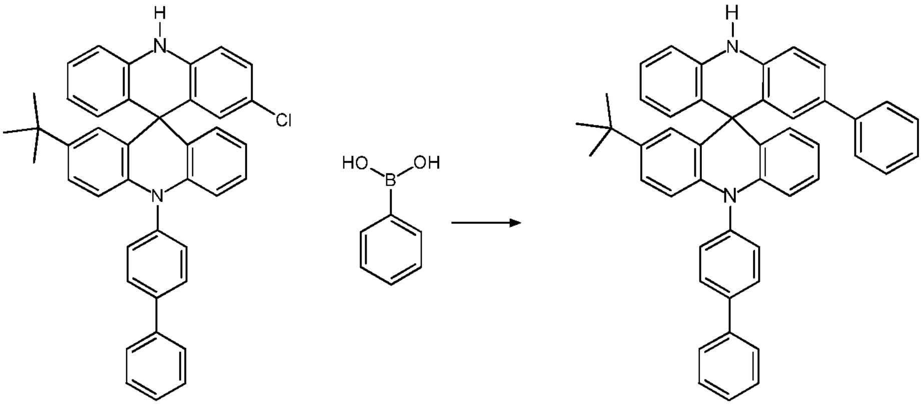
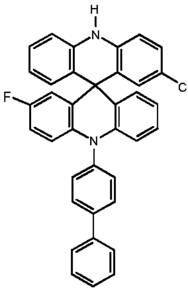
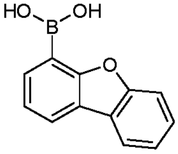
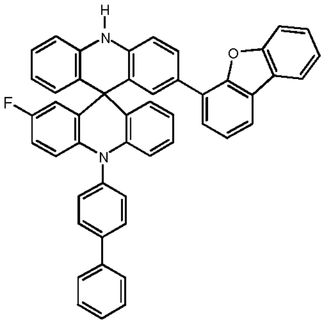
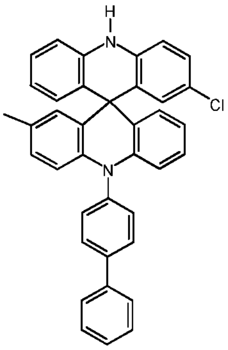
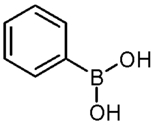
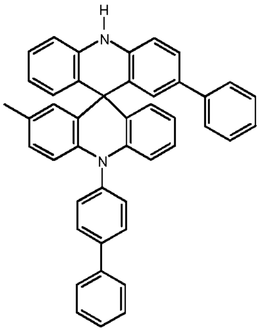
		
		
		

A-5) Suzuki reaction : 10'-{[1,1'-biphenyl]-4-yl}-7'-tert-butyl-2-phenyl-10H,10'H-9,9'-spirobi[acridine] 6a



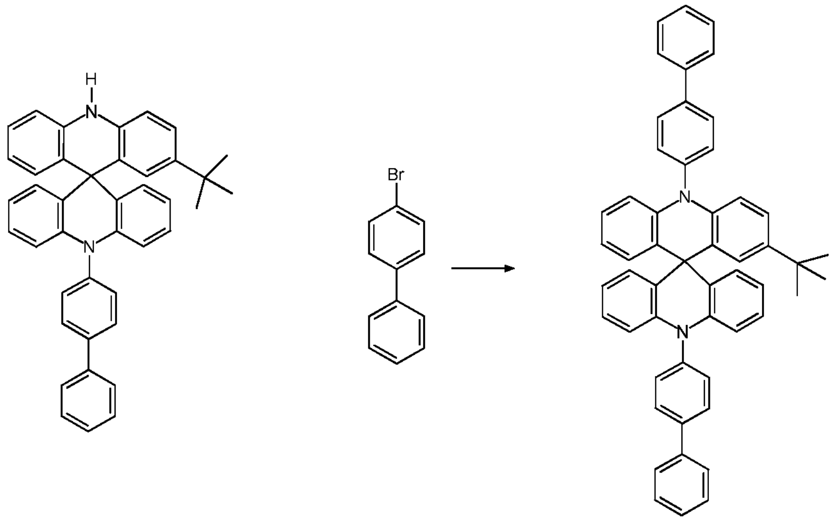
5.4 g (44.3 mmol) of benzeneboronic acid, 17.4 g (29.5 mmol) of 10-biphenyl-4-yl-2-chloro-9,9-dimethyl-9,10-dihydroacridine and 8.9 g (59.1 mmol) of CsF are suspended in 250 ml of dioxane. 1.1 g (1.5 mmol) of $PdCl_2(PCy_3)_2$ are added to this suspension, and the reaction mixture is heated under reflux for 16 h. After cooling, the mixture is filtered through silica gel, washed three times with 200 ml of water and subsequently evaporated to dryness. The residue is filtered through silica gel (heptane/ethyl acetate). The product is obtained in the form of a solid. The yield is 16.7 g (90% of theory).

Starting material 1	Starting material 2	Product
		
		

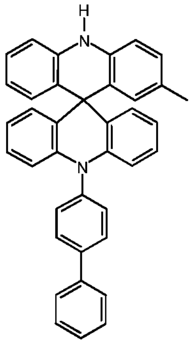
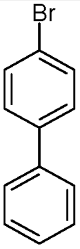
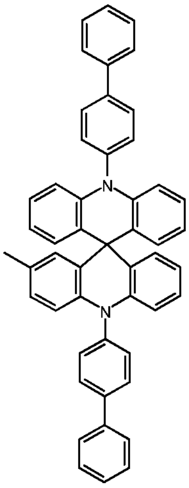
A-6) Buchwald reaction

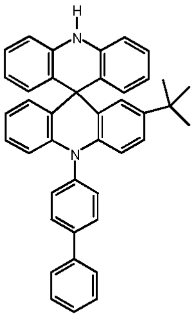
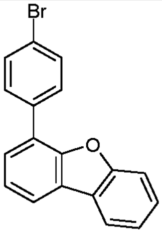
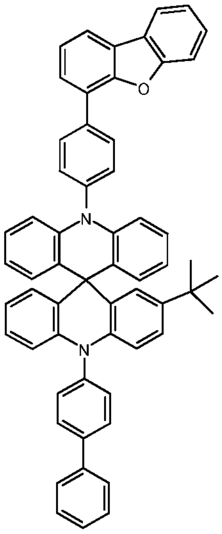
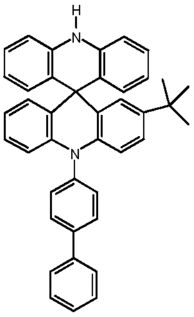
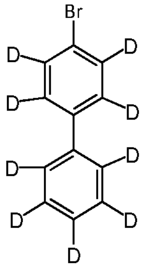
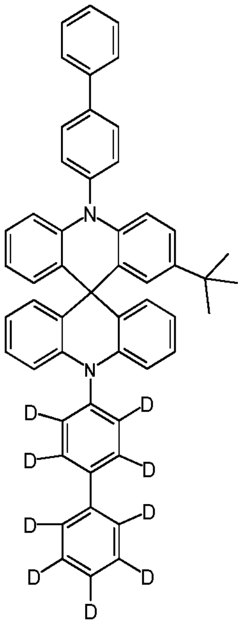
10,10'-bis({[1,1'-biphenyl]-4-yl})-2-tert-butyl-10H,10'H-9,9'-spirobi[acridine]

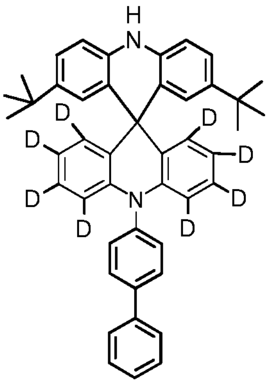
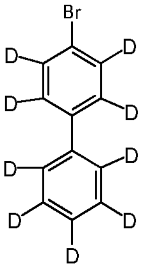
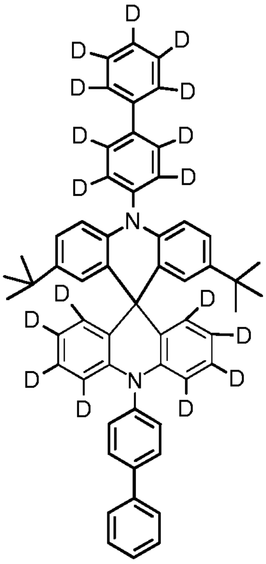
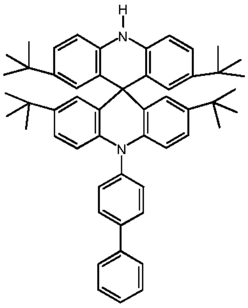
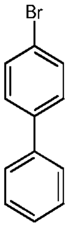
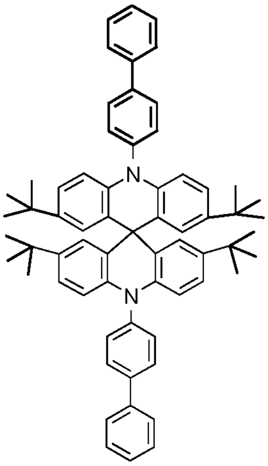
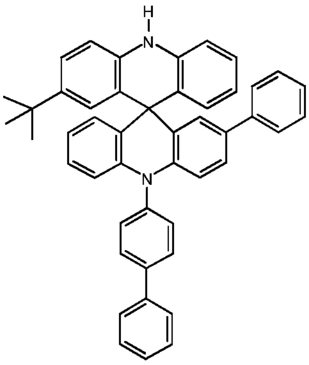
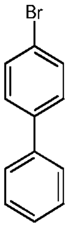
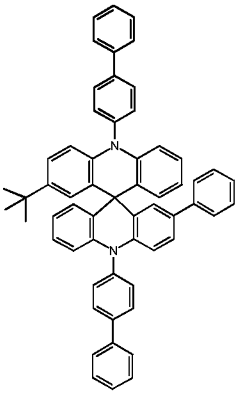
7a

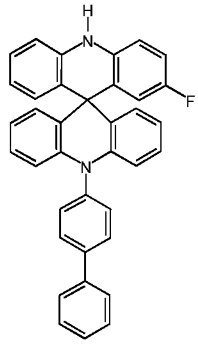
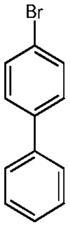
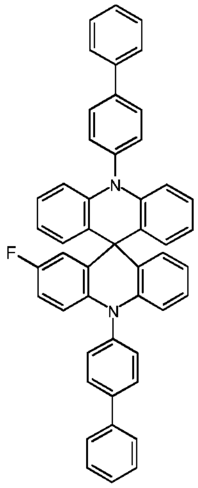
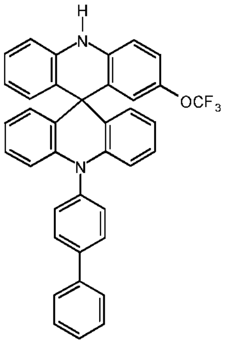
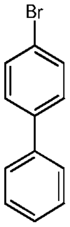
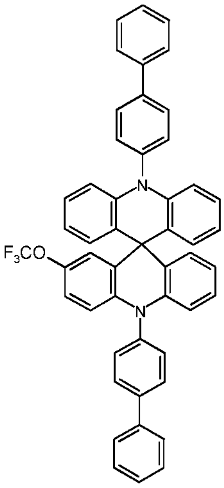


A degassed suspension of 11.1 g (46.7 mmol) of 4-bromobiphenyl, 24.9 g (44.9 mmol) of the spirobisacridine in 480 ml of toluene and 11.9 g (121.3 mmol) of NaO*t*Bu is saturated with N_2 for 1 h. 1.07 g (1.9 mmol) of DPPF and 1.38 g (1.9 mmol) of palladium(II) acetate are then added. The reaction mixture is heated under reflux overnight. After cooling, the organic phase is filtered through silica gel and subsequently evaporated to dryness. The residue is recrystallised from toluene/heptane. Yield: 15.7 g (49% of theory).

Starting material 1	**Starting material 2**	**Product**
		

B) Device examples

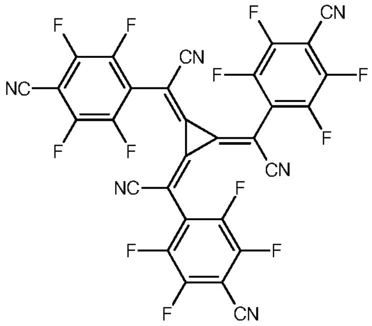
1) General production process for the OLEDs and characterization of the OLEDs

Glass plaques which have been coated with structured ITO (indium tin oxide) in a thickness of 50 nm are the substrates to which the OLEDs are applied.

The OLEDs basically have the following layer structure: substrate / hole injection layer (HIL) / hole transport layer (HTL) / electron blocker layer (EBL) / emission layer (EML) / electron transport layer, optionally with second layer (ETL) / electron injection layer (EIL) and finally a cathode. The cathode is formed by an aluminium layer of thickness 100 nm. The exact structure of the OLEDs can be found in the tables which follow. The materials used for production of the OLEDs are shown in a table below.

All materials are applied by thermal vapour deposition in a vacuum chamber. In this case, the emission layer consists of at least one matrix material (host material) and an emitting dopant which is added to the matrix material(s) in a particular proportion by volume by co-evaporation. Details given in such a form as H:SEB (95%:5%) mean here that the material H is present in the layer in a proportion by volume of 95% and SEB in a proportion of 5%.
In an analogous manner, the electron transport layer and the hole injection layer also consist of a mixture of two materials. The structures of the materials that are used in the OLEDs are shown in Table 3.

The OLEDs are characterized in a standard manner. For this purpose, the electroluminescence spectra, the external quantum efficiency (EQE, measured in %) as a function of the luminance, calculated from current-voltage-luminance characteristics assuming Lambertian radiation characteristics, and the lifetime are determined. The parameter EQE @ 10 mA/cm² refers to the external quantum efficiency which is attained at 10 mA/cm². The parameter U @ 10 mA/cm^2 refers to the operating voltage at 10 mA/cm^2. The lifetime LT is defined as the time after which the luminance drops from the starting luminance to a certain proportion in the course of operation with constant current density. An LT80 figure means here that the lifetime reported corresponds to the time after which the luminance has dropped to 80% of its starting value. The figure @60 or 40 mA/cm^2 means here that the lifetime in question is measured at 60 or 40 mA/cm^2.

Table 1: Structures of the compounds

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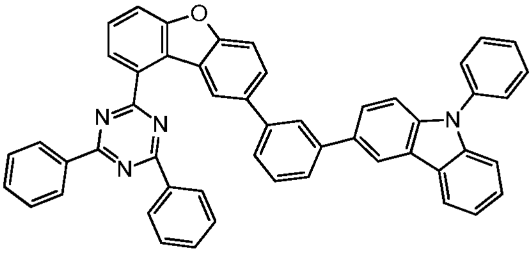	
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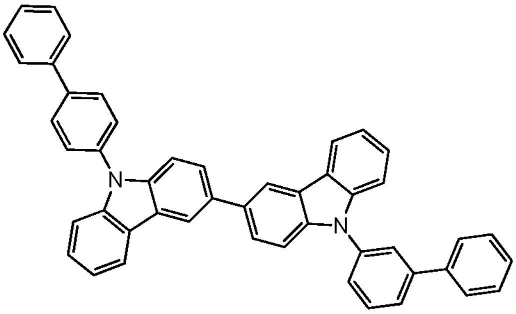	
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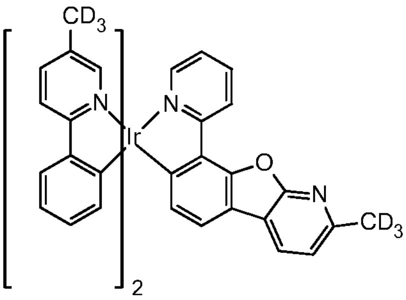
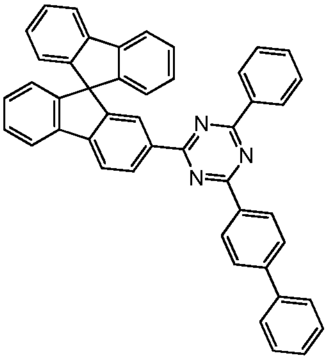
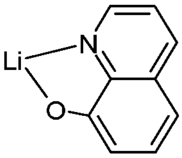
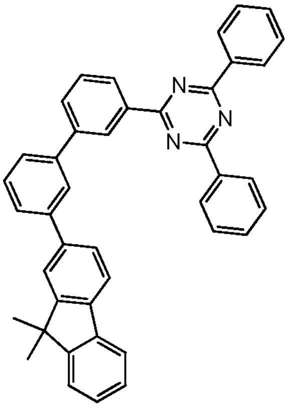
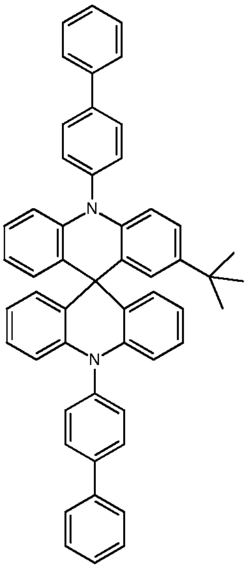
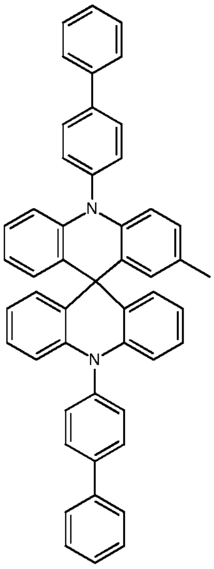
	
TEG	ETM
	
LiQ	HBM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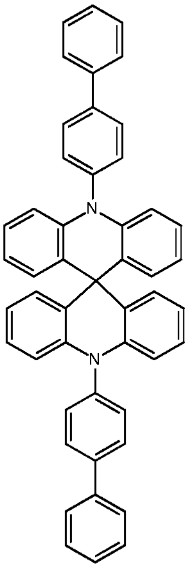
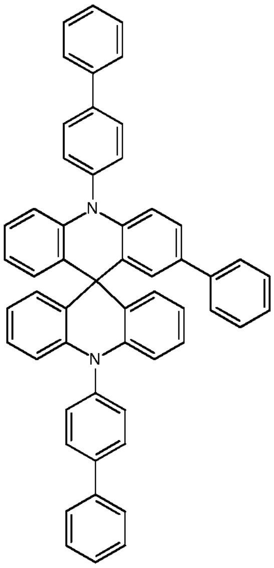
	
C1(HTM-0216)	C2(HTM-0238)

1) Inventive OLEDs containing a compound of the formula (I) in the EBL of green-phosphorescing OLEDs

Devices as shown in the following table are produced:

Table 2: Structure of the OLEDs							
Bsp.	***HIL***	***HTL1***	***EBL***	***EML***	***HBL***	***ETL1***	***EIL***

	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm
1	HTM: p-Dotand (3%) 10 nm	HTM 50 nm	C1 30 nm	TMM-1 (32%): TMM-2 (60%):TEG(8%) 35 nm	HBM 5 nm	ETM:LiQ (50:50%) 30 nm	LiQ 1 nm
2	HTM: p- Dotand (3%) 10 nm	HTM 50 nm	C2 30 nm	TMM-1 (32%): TMM-2 (60%):TEG(8%) 35 nm	HBM 5 nm	ETM:LiQ (50:50%) 30 nm	LiQ 1 nm
3	HTM: p- Dotand (3%) 10 nm	HTM 50 nm	INV1 30 nm	TMM-1 (32%): TMM-2 (60%):TEG(8%) 35 nm	HBM 5 nm	ETM:LiQ (50:50%) 30 nm	LiQ 1 nm
4	HTM: p- Dotand (3%) 10 nm	HTM 50 nm	INV2 30 nm	TMM-1 (32%): TMM-2 (60%):TEG(8%) 35 nm	HBM 5 nm	ETM:LiQ (50:50%) 30 nm	LiQ 1 nm

As shown in Table 3, the compounds of the invention lead to OLEDs having very good performances, more particularly in terms of operating voltages, in comparison with the compounds of the prior art, for a comparable or better efficiency and lifetime.,

Table 3: Results of the OLED devices

Ex.	U @ 10 mA/cm² (V)	EQE @ 10 mA/cm² (%)
1	4.0	23.6
2	3.9	22.9
3	3.6	24.4
4	3.5	23.6

2) Inventive OLEDs containing a compound of the formula (I) in the HIL and HTL of blue-fluorescent OLEDs

Devices as shown in the following table are produced:

Table 4: Structure of the OLEDs

Ex.	*HIL*	*HTL1*	*EBL*	*EML*	*HBL*	*ETL*	*EIL*
	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm	Thickness / nm
5	HTM: p-Dotand (3%) 10 nm	HTM 185 nm	C1 5 nm	H:SEB(3%) 20 nm	HBM 5 nm	ETM:LiQ(50%) 30 nm	LiQ 1 nm
6	HTM: p- Dotand (3%) 10 nm	HTM 185 nm	C2 5 nm	H:SEB(3%) 20 nm	HBM 5 nm	ETM:LiQ(50%) 30 nm	LiQ 1 nm
7	HTM: p- Dotand (3%) 10 nm	HTM 185 nm	INV1 5 nm	H:SEB(3%) 20 nm	HBM 5 nm	ETM:LiQ(50%) 30 nm	LiQ 1 nm
8	HTM: p- Dotand (3%) 10 nm	HTM 185 nm	INV2 5 nm	H:SEB(3%) 20 nm	HBM 5 nm	ETM:LiQ(50%) 30 nm	LiQ 1 nm

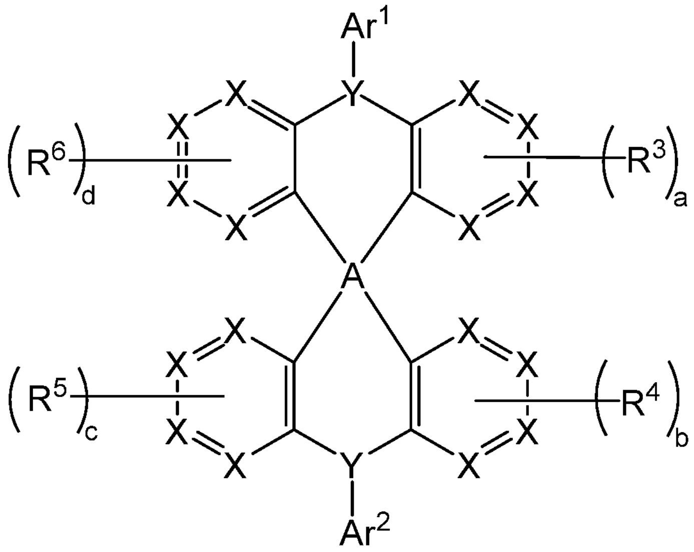
As shown in Table 5, the compounds of the invention lead to OLEDs having very good performances, more particularly in terms of operating voltages, in comparison with the compounds of the prior art for a comparable or better efficiency and lifetime.

Table 5: Results of the OLED devices

Ex.	U @ 10 mA/cm² (V)	EQE @ 10 mA/cm² (%)
5	3.8	10.8
6	3.7	10.7
7	3.4	10.8
8	3.5	10.8

Patent Claims

1. Compound of the formula (I)



formula (I),

where the following applies to the symbols and indices occurring:

A is C or Si;

Y is on each occurrence, identically or differently, N or P;

X is on each occurrence, identically or differently, CR^1 or N;

Ar^1, Ar^2 are on each occurrence, identically or differently, an aromatic ring system having 6 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^2, or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^2; where at least one of the two groups Ar^1 and Ar^2 is an aromatic ring system having 12 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^2, or a heteroaromatic ring system having 12 to 40 aromatic ring atoms, which may be substituted by one or more radicals R^2;

R^3, R^4, R^5, R^6 are selected on each occurrence, identically or differently from D, F, C(=O)R, CF_3, OCF_3, CN, $Si(R)_3$, $N(R)_2$, $P(=O)(R)_2$, S(=O)R, $S(=O)_2R$, straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, alkenyl or alkynyl groups having 2 to 20 C atoms, where the said alkyl, alkoxy, alkenyl and alkynyl groups may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F; aromatic ring systems having 6 to 40 aromatic ring atoms, which may be substituted by one or more radicals R, or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R;

R^1, R^2 are selected on each occurrence, identically or differently, from H, D, F, C(=O)R, CF_3, OCF_3, CN, $Si(R)_3$, $N(R)_2$, $P(=O)(R)_2$, S(=O)R, $S(=O)_2R$, straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, alkenyl or alkynyl groups having 2 to 20 C atoms, where the said alkyl, alkoxy, alkenyl and alkynyl groups may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F; aromatic ring systems having 6 to 40 aromatic ring atoms, which may be substituted by one or more radicals R, or a heteroaromatic ring system having 5 to 40 aromatic ring atoms, which may be substituted by one or more radicals R; where two or more radicals R^1 or R^2 may be linked to one another and may form a ring; where the said alkyl, alkoxy, alkenyl and alkynyl groups and the said aromatic ring systems and heteroaromatic ring systems may each be substituted by one or more radicals R; and where one or more CH_2 groups in the said alkyl, alkoxy, alkenyl and alkynyl groups may be replaced by -RC=CR-, -C≡C-, $Si(R)_2$, C=O, C=NR, -C(=O)O-, -C(=O)NR-, NR, P(=O)(R), -O-, -S-, SO or SO_2;

R is selected on each occurrence, identically or differently, from H, D, F, C(=O)R´, CF_3, OCF_3, CN, $Si(R´)_3$, $N(R´)_2$, $P(=O)(R´)_2$, S(=O)R´, $S(=O)_2R´$, straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, alkenyl or alkynyl groups having 2 to 20 C atoms, where one or more H atoms in the above-mentioned groups may be replaced by D or F, aromatic ring systems having 6 to 40 aromatic ring atoms and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more radicals R may be linked to one another and may form a ring; where the said alkyl, alkoxy, alkenyl and alkynyl groups and the said aromatic ring systems and heteroaromatic ring systems may each be substituted by one or more radicals R´; and where one or more CH_2 groups in the said alkyl, alkoxy, alkenyl and alkynyl groups may be replaced by -R´C=CR´-, -C≡C-, $Si(R´)_2$, C=O, C=NR´, -C(=O)O-, -C(=O)NR´-, NR´, P(=O)(R´), -O-, -S-, SO or SO_2;

R´ is selected on each occurrence, identically or differently, from H, D, F, CN, alkyl groups having 1 to 20 C atoms, aromatic ring systems having 6 to 40 aromatic ring atoms and heteroaromatic ring systems having 5 to 40 aromatic ring atoms; where two or more radicals R´ may be linked to one another and may form a ring; and where the said alkyl groups, aromatic ring systems and heteroaromatic ring systems may be substituted by F or CN;

a, b, c, d are on each occurrence, identically or differently, 0, 1, 2, 3 or 4; where at least one of the indices a, b, c and d is equal to 1; and

at least one radical R^3, R^4, R^5 or R^6 is present in the compound of formula (I), which stands for F, $Si(R)_3$, a straight-chain alkyl, alkoxy or thioalkyl group having 1 to 20 C atoms, branched or cyclic alkyl, alkoxy or thioalkyl group having 3 to 20 C atoms, where the said alkyl, alkoxy or thioalkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F.

2. Compound according to Claim 1, characterised in that precisely 1, 2, 3 or 4 indices selected from the indices a, b, c and d in formula (I) are equal to 1 or 2.

3. Compound according to one or more of Claims 1 or 2, characterised in that A is a carbon atom.

4. Compound according to one or more of Claims 1 to 3, characterised in that Y is a nitrogen atom.

5. Compound according to one or more of Claims 1 to 4, characterised in that X is equal to CR^1, where R^1 is selected, identically or differently, from H and D.

6. Compound according to one or more of Claims 1 to 5, characterised in that Ar^1 and Ar^2 are selected on each occurrence, identically or differently, from aromatic ring systems having 6 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2, or from heteroaromatic ring systems having 5 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2, where at least one of the two groups Ar^1 and Ar^2 is an aromatic ring system having 12 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2, or a heteroaromatic ring system having 12 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2.

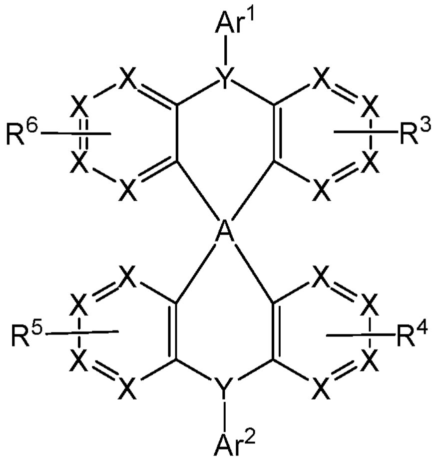
7. Compound according to one or more of Claims 1 to 6, characterised in that both of the groups Ar^1 and Ar^2 are selected on each occurrence, identically or differently, from aromatic ring systems having 12 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2, and heteroaromatic ring systems having 12 to 24 aromatic ring atoms, which may be substituted by one or more radicals R^2.

8. Compound according to one or more of Claims 1 to 7, characterised in that R^3, R^4, R^5 and R^6 stand, identically or differently, for a straight-chain alkyl group having 1 to 20 C atoms, branched or cyclic alkyl group having 3 to 20 C atoms, where the said alkyl group may be in each case substituted by one

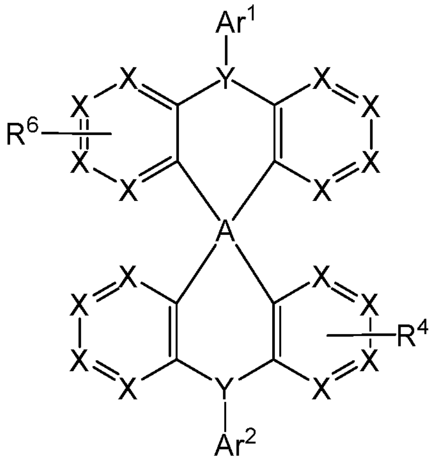
or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F.

9. Compound according to one or more of Claims 1 to 7, characterized in that the compound of formula (I) comprises:
at least one radical R^3, R^4, R^5 or R^6 which stands for a straight-chain alkyl group having 1 to 20 C atoms, branched or cyclic alkyl group having 3 to 20 C atoms, where the said alkyl group may be in each case substituted by one or more radicals R and where one or more H atoms in the above-mentioned groups may be replaced by D or F, and
at least one radical R^3, R^4, R^5 or R^6, which stands for aromatic ring systems having 6 to 18 aromatic ring atoms, which may be substituted by one or more radicals R, or a heteroaromatic ring system having 6 to 18 aromatic ring atoms, which may be substituted by one or more radicals R.

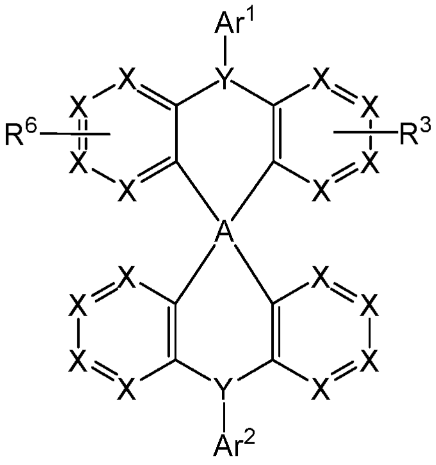
10. Compound according to one or more of claims 1 to 9, characterised in that the compound of the formula (I) conforms to one of the formulae (I-1) to (I-7),



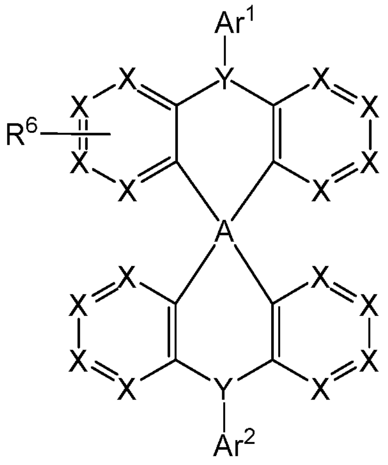
formula (I-1)



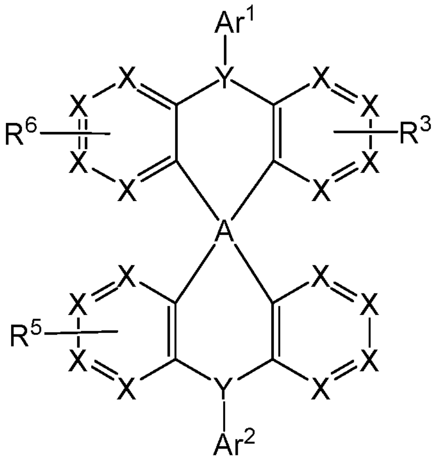
formula (I-2)



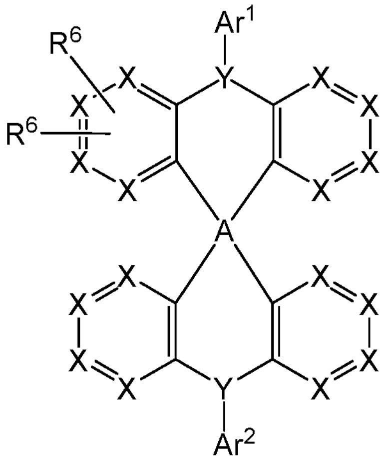
formula (I-3)



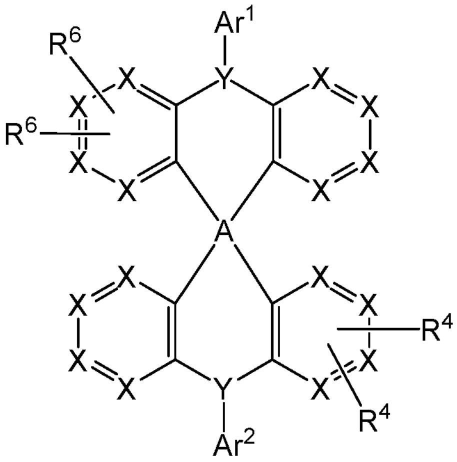
formula (I-4)



formula (I-5)



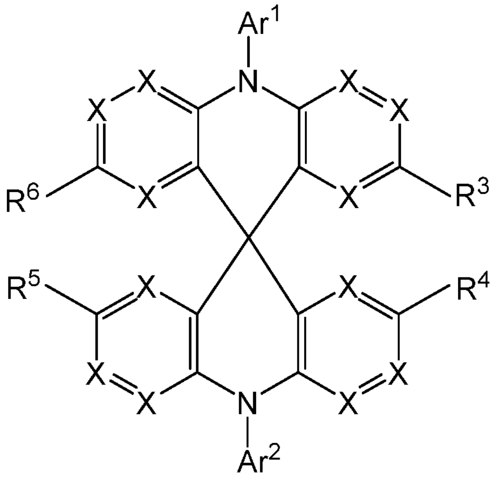
formula (I-6)



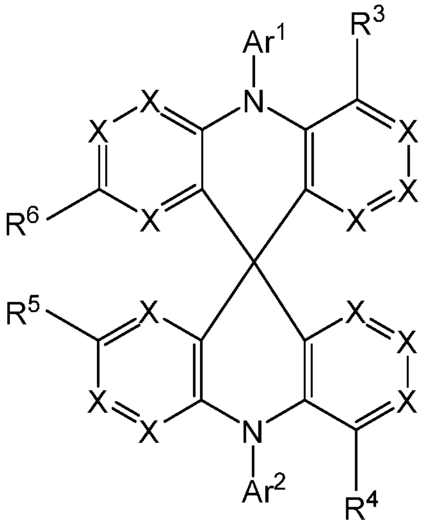
formula (I-7)

where the symbols and indices occurring are defined in accordance with one or more of Claims 1 to 9.

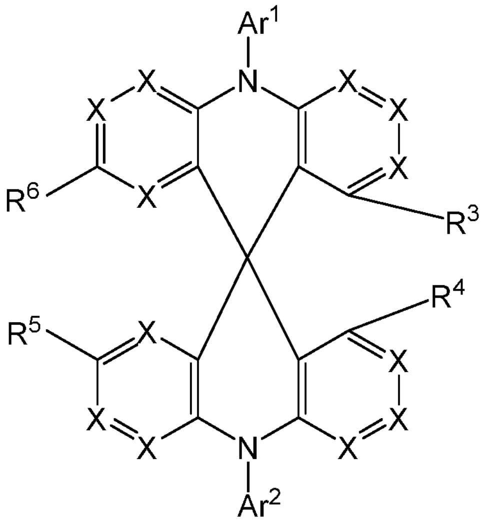
11. Compound according to one or more of Claims 1 to 10, characterised in that the compound of the formula (I) conforms to one of the formulae (I-1-1) to (I-7-1),



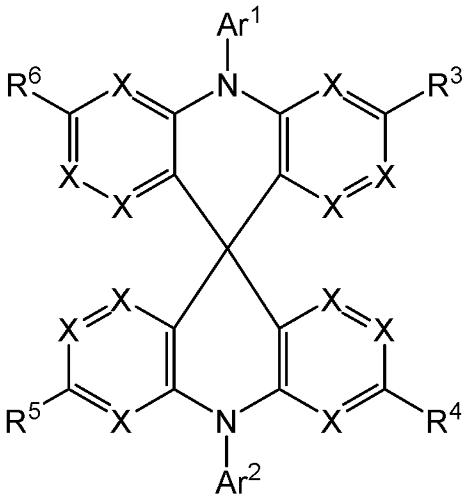
formula (I-1-1)



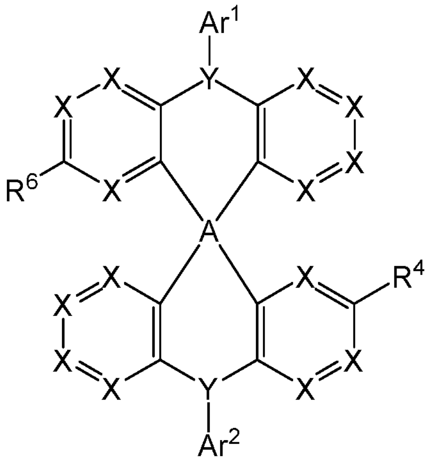
formula (I-1-2)



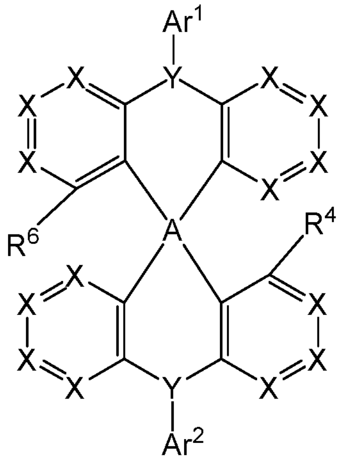
formula (I-1-3)



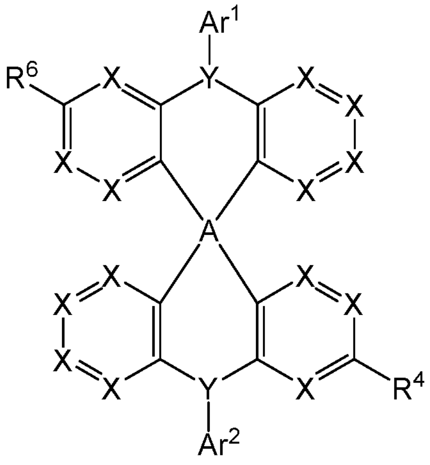
formula (I-1-4)



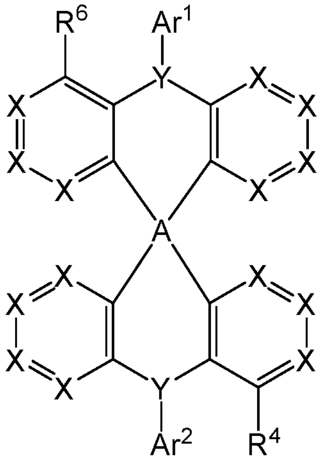
formula (I-2-1)



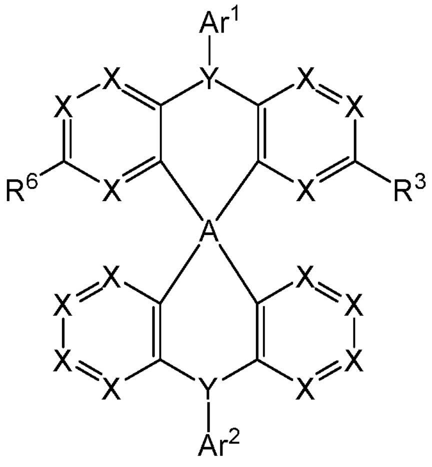
formula (I-2-2)



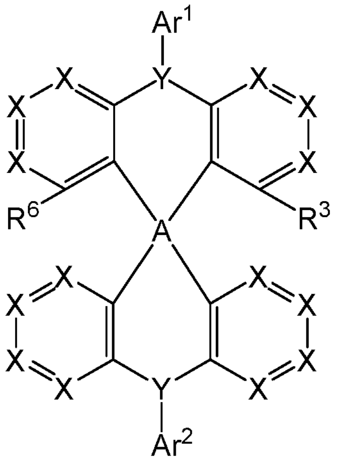
formula (I-2-3)



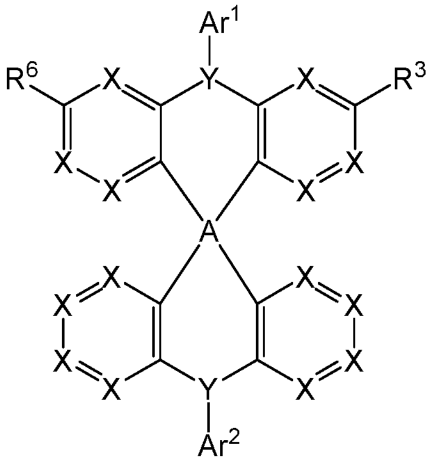
formula (I-2-4)



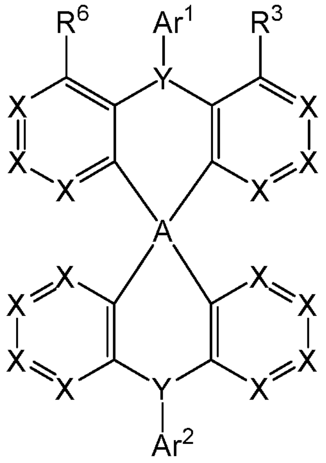
formula (I-3-1)



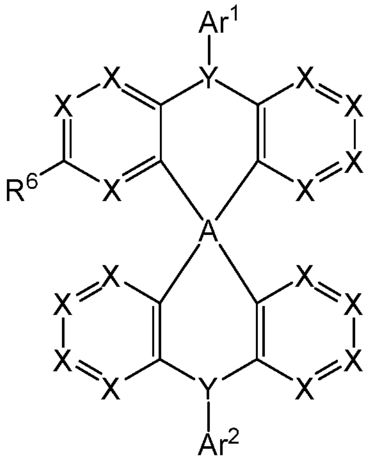
formula (I-3-2)



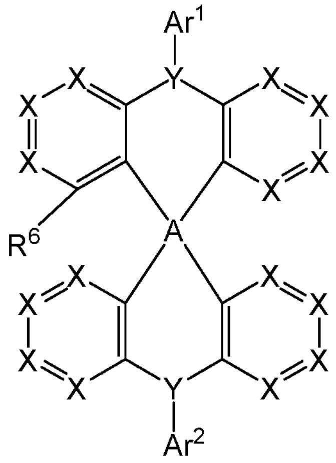
formula (I-3-3)



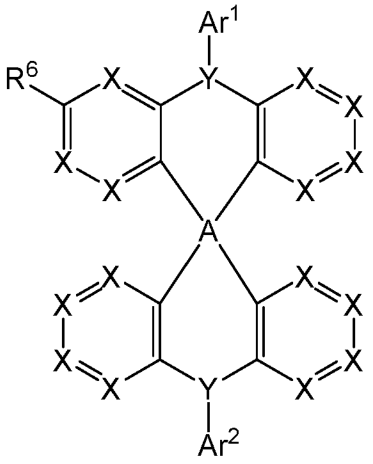
formula (I-3-4)



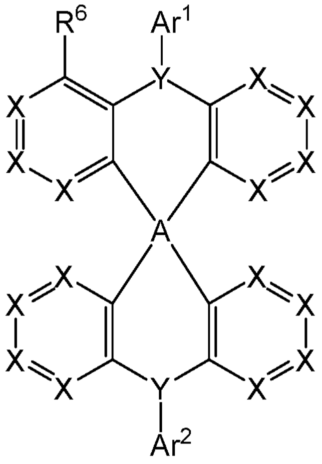
formula (I-4-1)



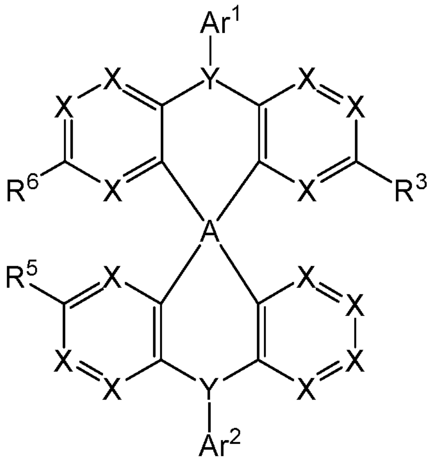
formula (I-4-2)



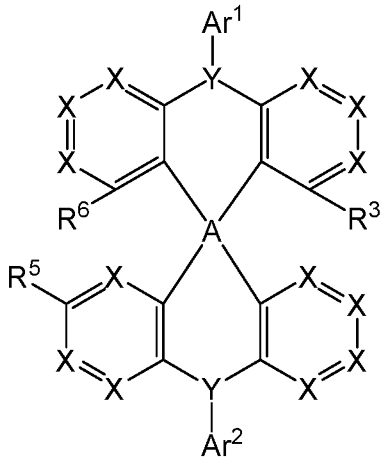
formula (I-4-3)



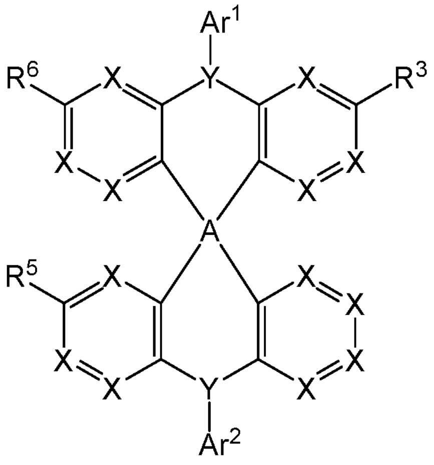
formula (I-4-4)



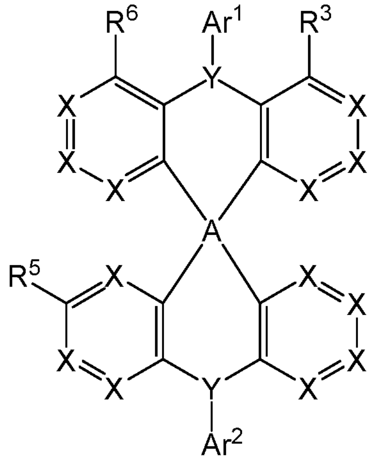
formula (I-5-1)



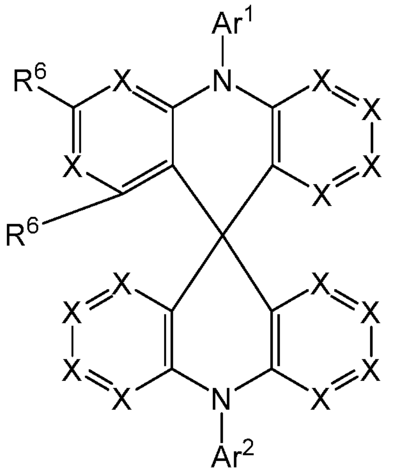
formula (I-5-2)



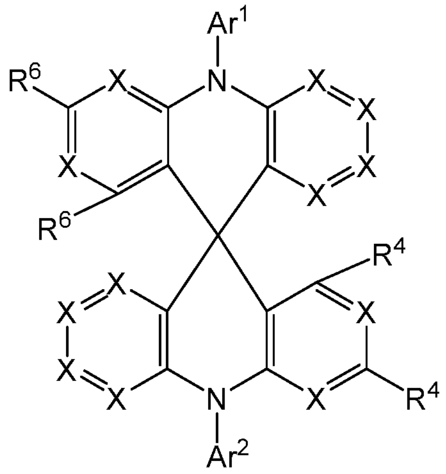
formula (I-5-3)



formula (I-5-4)



formula (I-6-1)



formula (I-7-1)

where the symbols and indices occurring are defined in accordance with one or more of Claims 1 to 9.

12. Compound according to Claim 11, characterised in that it is selected from compounds of formulae (I-1-1), (I-2-1), (I-3-1), (I-4-1), (I-5-1), (I-6-1) and (I-7-1), where:
    X stands for CR^1, where R^1 is selected, identically or differently, from H and D.

13. Compound according to one or more of the preceding claims, characterized in that the compound is a deuterated compound.

14. Compound according to one or more of the preceding claims, characterized in that the compound has a deuteration degree higher than 20%, 40%, 60% or 80%.

15. Use of a compound according to one or more of Claims 1 to 14 in an electronic device.

16. Organic light emitting diode comprising anode, cathode, and an organic layer formed between anode and cathode, said organic layer comprises at least one compound according to one or more of Claims 1 to 14.

17. Organic light emitting diode according to claim 16, characterized in that said organic layer is a hole transport layer.

18. Organic light emitting diode according to claim 16 or 17, characterized in that it comprises in the following sequence: anode, a hole transport layer, a light emitting layer, an electron transport layer and cathode, where the hole transport layer includes a first hole transport layer and a second hole transport layer, where
    the first hole transport layer is formed between the anode and the second hole transport layer;
    the second hole transport layer is formed between the first hole transport layer and the emitting layer, and
    where the second hole transport layer comprises a compound of formula (I).

19. Organic light emitting diode according to claim 18, characterized in that it the second hole transport layer is an electron-blocking layer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/069311

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D471/10
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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2015/158411 A1 (MERCK PATENT GMBH [DE]) 22 October 2015 (2015-10-22) claim 1 -----	1-19
Y	CN 1 338 499 A (UNIV QINGHUA [CN]) 6 March 2002 (2002-03-06) Examples; claim 1 -----	1-19
X	WO 2019/173646 A1 (EXXONMOBIL RES & ENG CO [US]; GEORGIA TECH RES INST [US]) 12 September 2019 (2019-09-12) page 38 -----	1-6, 10-12

☐ Further documents are listed in the continuation of Box C.

☒ 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

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search 7 October 2024	Date of mailing of the international search report 21/10/2024
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 Baston, Eckhard

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/069311

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