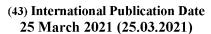
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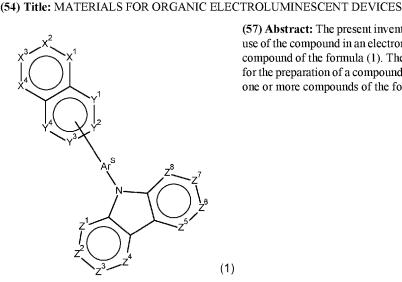
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(57) **Abstract:** The present invention relates to a compound of the formula (1), to the use of the compound in an electronic device, and to an electronic device comprising a compound of the formula (1). The present invention furthermore relates to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

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Materials for organic electroluminescent devices

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

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The structure of organic electroluminescent devices (OLEDs) in which organic semiconductors are employed as functional materials is described, for example in US 4539507. The emitting materials employed here are very often organometallic complexes which exhibit phosphorescence. For quantum-mechanical reasons, an up to four-fold increase in efficiency is possible using phosphorescent instead of fluorescent emitters. In general, however, there is still a need for improvement in the case of OLEDs, in particular also in the case of OLEDs which exhibit triplet emission (phosphorescence), for example with respect to efficiency, operating voltage and lifetime.

The properties of phosphorescent OLEDs are not only determined by the triplet emitters but also by the other materials used together with triplet emitters in OLEDs, such as matrix materials, also called host materials.

Improvements in these materials and their charge-transport properties can thus also result in significant improvements in the OLED properties.

Thus, the choice of the matrix material in an emission layer comprising a phosphorescent emitter has a great influence on OLEDs properties, especially in terms of efficiency. The matrix material limits the quenching of excited states of emitter molecules by energy transfer.

The object of the present invention is the provision of compounds, which are suitable for use in an OLED. More particularly, the object of the present invention is the provision of compounds, which are particularly suitable as

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matrix material for phosphorescent emitters in an OLED, but also as hole-transport material (HTM), electron-blocking material (EBM), electron-transport material (ETM), hole-blocking material (HBM) depending on the specific structure and radicals present in the compound. A further object of the present invention is to provide further organic semiconductors for organic electroluminescent devices to provide the person skilled in the art with a greater possible choice of materials for the production of OLEDs.

Compounds comprising lactam derivatives and their use as OLEDs materials, more particularly as matrix materials for phosphorescent emitters, are known from the prior art (for example in WO 2013/064206).

Surprisingly, it has now been found that certain compounds comprising lactam moieties combined with naphthalene moieties, as described in greater detail below, exhibit excellent properties when they are employed in OLEDs, particularly when employed as matrix material for red phosphorescent emitters. Indeed, these compounds lead to OLEDs exhibiting better properties in terms of lifetime and/or efficiency and/or electroluminescent emission. In addition, these compounds have a high glass transition temperature and a good thermal stability, which is an important property for OLED materials, especially when the materials are vapor-deposited via a vacuum process.

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The present invention therefore relates to these compounds and to electronic devices, in particular organic electroluminescent devices, which comprise compounds of this type. The present invention also relates to mixtures and formulations comprising this mixture.

The present invention relates to a compound of the formula (1),

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formula (1)

where the following applies to the symbols and indices used:

Ar^s stands on each occurrence, identically or differently, for a single bond or for an aromatic or heteroaromatic ring system having 5 to 30 aromatic ring atoms, which may be substituted by one or more radicals R;

 X^1 to X^4 stand on each occurrence, identically or differently, for CR¹ or 25 N;

Y¹ to Y⁴ stand on each occurrence, identically or differently, for CR² or N; with the proviso that the group Ar^S as depicted in formula (1) is bonded to one of the group Y¹, Y², Y³ or Y⁴ which stands for C; and exactly two non-adjacent groups Y, namely Y¹ and Y⁴, Y¹ and Y³ or Y² and Y⁴ stand for N;

characterized in that:

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Z¹ to Z⁸ stand on each occurrence, identically or differently, for CR³ or N; where at least two adjacent groups Z selected from Z¹-Z², Z²-Z³, Z³-Z⁴, Z⁵-Z⁶, Z⁶-Z⁷ and Z⁷-Z⁸ form together an heteroaromatic ring system selected from the groups of formula (Het-1) or (Het-2),

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where, in (Het-1) and (Het-2), the signs * indicate the bonding positions to Z¹-Z², Z²-Z³, Z³-Z⁴, Z⁵-Z⁶, Z⁶-Zⁿ or Zⁿ-Z⁶ in formula (1);

 Z^9 to Z^{12} stand on each occurrence, identically or differently, for CR³ or N;

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

and at least two adjacent groups Z, selected from Z^1 - Z^2 , Z^2 - Z^3 , Z^3 - Z^4 , Z^5 - Z^6 , Z^6 - Z^7 , Z^7 - Z^8 , Z^9 - Z^{10} , Z^{10} - Z^{11} and Z^{11} - Z^{12} , form together an aromatic ring of formula (Aro-1),

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$$Z_{13}^{16}$$
 Z_{14}^{15}

(Aro-1)

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where Z^{13} to Z^{16} stand on each occurrence, identically or differently, for CR³ or N; and where the signs * indicate the bonding positions to Z^1 - Z^2 , Z^2 - Z^3 , Z^3 - Z^4 , Z^5 - Z^6 , Z^6 - Z^7 , Z^7 - Z^8 Z^9 - Z^{10} , Z^{10} - Z^{11} or Z^{11} - Z^{12} ;

R¹, R² and R³ stand on each occurrence, identically or differently, for H, D,

F, CI, Br, I, CHO, CN, C(=O)Ar, $P(=O)(Ar)_2$, S(=O)Ar, $S(=O)_2Ar$, $N(R)_2$,

N(Ar)₂, NO₂, Si(R)₃, B(OR)₂, OSO₂R, a straight-chain alkyl, alkoxy or

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thioalkyl groups having 1 to 40 C atoms or branched or a cyclic alkyl, alkoxy or thioalkyl groups having 3 to 40 C atoms, each of which may be substituted by one or more radicals R, where in each case one or more non-adjacent CH₂ groups may be replaced by RC=CR, C=C, Si(R)₂, Ge(R)₂, Sn(R)₂, C=O, C=S, C=Se, P(=O)(R), SO, SO₂, O, S or CONR

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and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R, or an aryloxy groups having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R; where two adjacent radicals R¹ may form an aliphatic or aromatic ring system together, which may be substituted by one or more radicals R, where one radical R² and one radical R¹ may form a ring, which may be substituted by one or more radicals R, and where two adjacent radicals

R³ may form an aliphatic or aromatic ring system together, which may be

substituted by one or more radicals R;

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- R stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CHO, CN, C(=0)Ar, P(=0)(Ar)₂, S(=0)Ar, S(=0)₂Ar, N(R')₂, N(Ar)₂, NO₂, Si(R´)₃, B(OR´)₂, OSO₂R´, a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 40 C atoms or branched or a cyclic alkyl, alkoxy or 5 thioalkyl groups having 3 to 40 C atoms, each of which may be substituted by one or more radicals R´, where in each case one or more non-adjacent CH₂ groups may be replaced by R´C=CR´, C≡C, Si(R´)₂, $Ge(R')_2$, $Sn(R')_2$, C=O, C=S, C=Se, P(=O)(R'), SO, SO_2 , O, S or CONR'10 and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R', or an aryloxy groups having 5 to 60 aromatic ring 15 atoms, which may be substituted by one or more radicals R; where two adjacent radicals R may form an aliphatic or aromatic ring system together, which may be substituted by one or more radicals R';
- Ar is, on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case also be substituted by one or more radicals R´;
- 25 R´ stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms or branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, where in each case one or more non-adjacent CH₂ groups may be replaced by SO, SO₂, O, S and where one or more H atoms may be replaced by D, F, Cl, Br or I, or an aromatic or heteroaromatic ring system having 5 to 24 aromatic ring atoms.

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

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

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

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

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

dazole, 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.

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

An aromatic ring system in the sense of this invention contains 6 to 60 C atoms in the ring system. A heteroaromatic ring system in the sense of this invention contains 5 to 60 aromatic ring atoms, at least one of which is a heteroatom. The heteroatoms are preferably selected from N, O and/or S. An aromatic or heteroaromatic ring system in the sense of this invention is intended to be taken to mean a system which does not necessarily contain only aryl or heteroaryl groups, but instead in which, in addition, a plurality of aryl or heteroaryl groups may be connected by a non-aromatic unit (preferably less than 10% of the atoms other than H), such as, for example, an sp³-hybridised C, Si, N or O atom, an sp²-hybridised C or N atom or an sp-hybridised C atom. Thus, for example, systems such as 9,9'-spirobifluorene, 9,9'-diarylfluorene, triarylamine, diaryl ether, stilbene, etc., are also intended to be taken to be aromatic ring systems in the sense of this invention, as are systems in which two or more aryl groups are connected, for example, by a linear or cyclic alkyl, alkenyl or alkynyl group or by a silyl group. Furthermore, systems in which two or more aryl or heteroaryl groups are linked to one another via single bonds are also taken to be aromatic or

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heteroaromatic ring systems in the sense of this invention, such as, for example, systems such as biphenyl, terphenyl or diphenyltriazine.

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

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

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

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$$\begin{array}{c} \text{ring formation} \\ \text{R} \\ \text{R} \\ \text{R} \end{array} = \begin{array}{c} \text{Ring formation} \\ \text{R: -CH}_3 \\ \text{R: -CH} \\ \text{R: -CH}_2 \\ \end{array}$$

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

Preferably, in the six-membered ring comprising Y¹ to Y⁴, the group Y⁴ stands for N, the group Y³ is bonded to the group Ar⁵ so that Y³ stands for C and one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR². More preferably, the group Y⁴ stands for N, the group Y³ is bonded to the group Ar⁵ so that Y³ stands for C, the group Y² stands for N and the group Y¹ stands for CR².

Preferably, the groups X^1 to X^4 stand on each occurrence, identically or differently, for CR^1 .

In accordance with a preferred embodiment, Ar^S is a single bond so that the compounds of formula (1) correspond to the compounds of the formula (1A):

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$$X^3$$
 X^2
 X^4
 X^4

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formula (1A)

where the symbols have the same meaning as above.

In accordance with another preferred embodiment, the group Ar^s is an aromatic or heteroaromatic ring system having 5 to 18 aromatic ring atoms, which may in each case also be substituted by one or more radicals R.

More preferably, the group Ar^s stands on each occurrence, identically or differently, for phenyl, biphenyl, fluorene, spirobifluorene, naphthalene, phenanthrene, anthracene, dibenzofuran, dibenzothiophene, carbazole, pyridine, pyrimidine, pyrazine, pyridazine, triazine, benzopyridine, benzopyridazine, benzopyrimidine and quinazoline, each of which may be substituted by one or more radicals R.

In accordance with a very preferred embodiment, the group Ar^S stands on each occurrence, identically or differently, for phenyl, biphenyl, fluorene, dibenzofuran, dibenzothiophene and carbazole, each of which may be substituted by one or more radicals R.

Examples of suitable groups Ar^S are the groups (Ar^S-1) to (Ar^S-22) depicted in the table below:

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	Ar ^s -1	Ar ^s -2	Ar ^s -3
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4.5	Ar ^s -4	Ar ^s -5	Ar ^s -6
15			
20	Ar ^s -7	Ar ^s -8	Ar ^s -9
25	S.		S
	Ar ^s -10	Ar ^s -11	Ar ^s -12
30	R ^{CO}	RCO	RNO NO
	Ar ^s -13	Ar ^s -14	Ar ^s -15
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5	RNO		
	Ar ^s -16	Ar ^s -17	Ar ^s -18
10			·
15	Ar ^s -19	Ar ^s -20	Ar ^s -21
13	\s\		
20	Ar ^s -22		

where the dashed bonds indicate the bonds to the structure of formula (1), and where the groups (Ar^S-1) to (Ar^S-22) may be substituted at each free position by a radical R and where:

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 R^{N0} , R^{C0} are on each occurrence, identically or differently, H, D, F, Cl, Br, I, CN, a straight-chain alkyl, alkoxy or thioalkoxy group having 1 to 40, preferably 1 to 20, more preferably 1 to 10 C atoms or cyclic alkyl, alkoxy or thioalkoxy group having 3 to 40, preferably 3 to 20, more preferably 3 to 10 C atoms, each of which may be substituted by one or more radicals R, where one or more non-adjacent CH_2 groups may be replaced by (R)C=C(R), $C\equiv C$, O or S and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 , or an aromatic or heteroaromatic ring system having 5 to 60, preferably 5 to 40, more preferably 5 to 30, very more

preferably 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R, where optionally two adjacent radicals R^{c0} can form a mono- or polycyclic, aliphatic, aromatic or heteroaromatic ring system with one another.

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Examples of very suitable groups Ar^S are the groups (Ar^S-23) to (Ar^S-67) depicted in the table below:

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Ar ^s -23	Ar ^s -24	Ar ^s -25
Ar ^s -26	Ar ^s -27	Ar ^s -28
Ar ^s -29	Ar ^s -30	Ar ^s -31
Ar ^s -32	Ar ^s -33	Ar ^s -34

5	Ar ^s -35	Ar ^s -36	Ar ^s -37
	``.		
10	Ar ^s -38	Ar ^s -39	Ar ^s -40
15	Ar ^s -41	Ar ^s -42	Ar ^s -43
20	S S	S S	S S
	Ar ^s -44	Ar ^s -45	Ar ^s -46
25	s		
	Ar ^s -47	Ar ^s -48	Ar ^s -49
30			
35	Ar ^s -50	Ar ^s -51	Ar ^s -52
50			

5			
	Ar ^s -53	Ar ^s -54	Ar ^s -55
10			
	Ar ^s -56	Ar ^s -57	Ar ^s -58
15			
20	Ar ^s -59	Ar ^s -60	Ar ^s -61
25			
	Ar ^s -62	Ar ^s -63	Ar ^s -64
30			S
	Ar ^s -65	Ar ^s -66	Ar ^s -67
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where the dashed bonds indicate the bonds to the structure of formula (1) and where the groups (Ar^S-23) to (Ar^S-67) may be substituted at each free position by a radical R.

- Preferably, the group R^N stands for an aromatic or heteroaromatic ring system having 5 to 60, preferably 5 to 40, more preferably 5 to 24 aromatic ring atoms, very preferably 6 to 18 aromatic ring atoms, which may be in each case substituted by one or more radicals R.
- More preferably, the group R^N stands on each occurrence, identically or differently, for phenyl, biphenyl, terphenyl, quaterphenyl, fluorene, spirobifluorene, naphthalene, anthracene, phenanthrene, triphenylene, fluoranthene, indole, benzofuran, benzothiophene, dibenzofuran, dibenzothiophene, carbazole, indenocarbazole, indolocarbazole, phenanthroline, pyridine, pyrimidine, pyrazine, pyridazine, triazine, quinolone, benzopyridine, benzopyridazine, benzopyrimidine, quinazoline, benzimidazole, or a combination of two or three of these groups, each of which may be substituted by one or more radicals R.

Examples of very suitable groups R^N are the groups of formulae (RN-1) to (RN-22) listed in the table below:

25 30 (RN-1) (RN-2) (RN-3)

5		R ^{CO} R ^{CO}	
	(RN-4)	(RN-5)	(RN-6)
10		RNO NO	
	(RN-7)	(RN-8)	(R N -9)
15	s s	N N	
	(RN-10)	(RN-11)	(RN-12)
20	N		
25	(RN-13)	(RN-14)	(RN-15)
30			
	(RN-16)	(RN-17)	(RN-18)

5	(RN-19)	(RN-20)	(RN-21)
10			
	(RN-22)		

where:

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- the dashed bond indicates the bonding to the nitrogen group of the lactam ring in formula (1);

- the group R^{C0} and R^{N0} have the same meaning as above; and

- the groups of formulae (RN-1) to (RN-22) may be substituted at each free position by a radical R.

Among the groups of formulae (RN-1) to (RN-22), the groups of formulae (RN-1), (RN-2), (RN-3), (RN-4), (RN-5), (RN-6), (RN-7), (RN-8), (RN-9) and (RN-10) are preferred.

In accordance with a preferred embodiment, the compounds of formula (1) are selected from the compounds of the formulae (2) to (13),

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- 22 -

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- 23 -

where

- the symbols X¹-X⁴, Ar^s and R^N have the same meaning as above;
- Z¹-Z¹² stand on each occurrence, identically or differently, for CR³ or N;

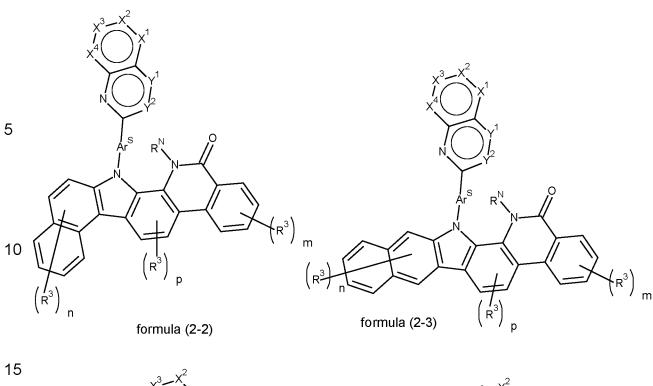
- in formulae (2), (3), (6) and (7), at least two adjacent groups Z, selected from to Z¹-Z², Z²-Z³, Z³-Z⁴, Z⁵-Z⁶, Z⁹-Z¹⁰, Z¹⁰-Z¹¹ and Z¹¹-Z¹², form together an aromatic ring of formula (Aro-1) as defined in claim 1;
- in formulae (4), (5), (8) and (9), at least two adjacent groups Z, selected from to Z¹-Z², Z²-Z³, Z³-Z⁴, Z²-Z³, Z³-Z¹0, Z¹0-Z¹¹ and Z¹¹-Z¹², form together an aromatic ring of formula (Aro-1) as defined in claim 1; and where
 - in formulae (10), (11), (12) and (13), at least two adjacent groups Z, selected from Z¹-Z², Z²-Z³, Z³-Z⁴, Z9-Z¹0, Z¹0-Z¹¹ and Z¹¹-Z¹², form together an aromatic ring of formula (Aro-1) as defined in claim 1;
 - one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR².
- In accordance with a very preferred embodiment, the compounds of formula (1) are selected from the compounds of formulae (2-1) to (2-7) or (3-1) to (3-7),

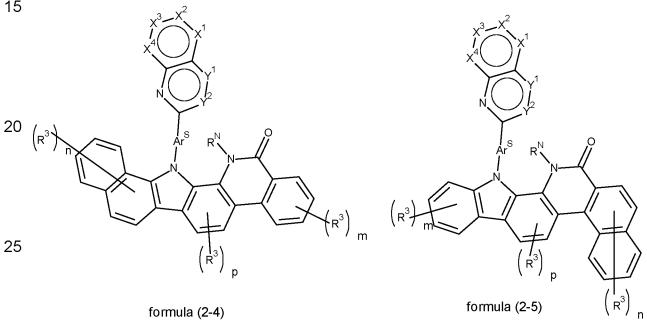
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10

$$(R^3)$$
 m (R^3) m

formula (2-1)





- 26 -

5
$$\begin{pmatrix}
R^{3} \\
R^{3}
\end{pmatrix}_{p}$$
formula (2-6)

formula (2-7)

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- 27 -

formula (3-5)

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formula (3-4)

- 28 -

where

15 X¹-X⁴, Ar^S, R³ and R^N have the same meaning as above; one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR²;

p is an integer of 0 to 2;

m is an integer of 0 to 4; and

n is an integer of 0 to 6.

In accordance with another very preferred embodiment, the compound of formula (1) are selected from the compounds of formulae (4-1) to (4-7) or (5-1) to (5-7),

30

formula (4-2)

- 30 -

- 31 -

formula (5-2)

- 32 -

35 where

- 33 -

 X^1 - X^4 , Ar^S , R^3 and R^N have the same meaning as above; one group Y^1 or Y^2 corresponds to N and the other group Y^1 or Y^2 corresponds to CR^2 ;

p is an integer of 0 to 2;

m is an integer of 0 to 4; and n is an integer of 0 to 6.

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In accordance with another very preferred embodiment, the compounds of formula (1) are selected from compounds of formulae (6-1) to (6-7) or (7-1) to (7-7),

formula (6-1)

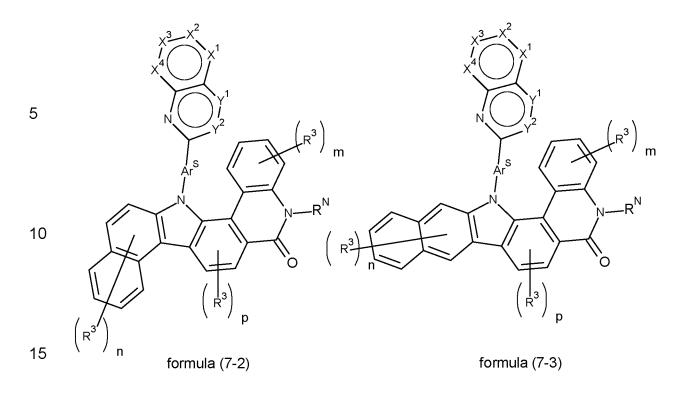
- 34 -

formula (6-5)

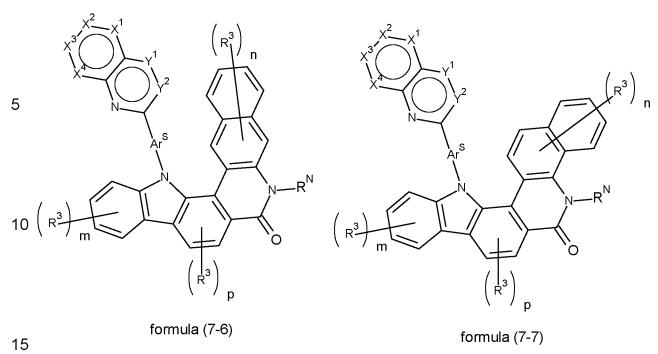
- 35 -

formula (7-1)

- 36 -



- 37 -



where

- X¹-X⁴, Ar^S, R³ and R^N have the same meaning as above;
- one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR²;

20 - p is an integer of 0 to 2;

- m is an integer of 0 to 4; and
- n is an integer of 0 to 6.
- In accordance with still another very preferred embodiment, the compounds of formula (1) are selected from compounds of formulae (8-1) to (8-7) or (9-1) to (9-7),

- 38 -

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- 39 -

$$\begin{array}{c}
X^3 \\
X^2 \\
X^4 \\
X^4 \\
X^4 \\
X^2 \\
X^4 \\
X^2 \\
X^3 \\
X^4 \\
X^3 \\
X^4 \\
X^3 \\
X^4 \\
X^4 \\
X^3 \\
X^4 \\
X^4$$

formula (9-1)

35 where formula (9-6)

- 42 -

- X^1 - X^4 , Ar^S , R^3 and R^N have the same meaning as above;

- one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR²;
- p is an integer of 0 to 2;
- 5 m is an integer of 0 to 4; and
 - n is an integer of 0 to 6.

In accordance with still another very preferred embodiment, the compounds of formula (1) are selected from the compounds of formulae (10-1) to (10-6) or (11-1) to (11-6),

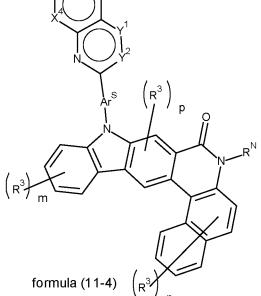
- 43 -

- 44 -

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$$R^3$$
 R^3
 R^3

formula (11-3)



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- 45 -

where

- X¹-X⁴, Ar^S, R³ and R^N have the same meaning as above;
- one group Y^1 or Y^2 corresponds to N and the other group Y^1 or Y^2 corresponds to CR^2 ;
 - p is an integer of 0 to 2;
 - m is an integer of 0 to 4; and
 - n is an integer of 0 to 6.

In accordance with another very preferred embodiment, the compounds of formula (1) are selected from compounds of formulae (12-1) to (12-6) or (13-1) to (13-6),

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- 46 -

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formula (12-4)

- 47 -

- 48 -

5
$$\left(\mathbb{R}^{3}\right)$$
 $\left(\mathbb{R}^{3}\right)$ $\left($

formula (13-6)

where

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- X¹-X⁴, Ar^S, R³ and R^N have the same meaning as above;
- one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR²;
 - p is an integer of 0 to 2;
 - m is an integer of 0 to 4; and

formula (13-5)

- n is an integer of 0 to 6.

- 49 -

In accordance with a particularly preferred embodiment, the compounds of formula (1) are selected from the compounds of formulae (2-1a) to (2-7a) or (3-1a) to (3-7a),

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$$R^3$$

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formula (2-1a)

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- 51 -

formula (3-2a) formula (3-3a)

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- 52 -

 $25 \text{where } R^1, \ R^2, \ R^3 \ \text{and} \ R^N \ \text{have the same meaning as above}.$

In accordance with another particularly preferred embodiment, the compound of formula (1) are selected from the compounds of formulae (4-1a) to (4-7a) or (5-1a) to (5-7a),

- 53 -

formula (4-1a)

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- 54 -

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formula (4-6a)

- 55 -

formula (5-1a)

- 56 -

where R¹, R², R³ and R^N have the same meaning as above.

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In accordance with another particularly preferred embodiment, the compounds of formula (1) are selected from compounds of formulae (6-1a) to (6-7a) or (7-1a) to (7-7a),

- 57 -

$$R^{1}$$
 N
 N
 R^{3}
 N
 R^{N}

formula (6-1a)

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- 58 -

formula (6-5a)

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- 59 -

formula (7-1a)

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- 60 -

where R^1 , R^2 , R^3 and R^N have the same meaning as above.

In accordance with still another particularly preferred embodiment, the compounds of formula (1) are selected from compounds of formulae (8-1a) to (8-7a) or (9-1a) to (9-7a),

- 61 -

formula (8-2a)

formula (8-3a)

- 62 -

formula (8-6a)

formula (8-7a)

- 63 -

$$R^{1}$$
 R^{2}
 R^{3}
 R^{3}
 R^{3}

formula (9-1a)

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- 64 -

where R^1 , R^2 , R^3 and R^N have the same meaning as above. In accordance with still another particularly preferred embodiment, the compounds of formula (1) are selected from the compounds of formulae (10-1a) to (10-6a) or (11-1a) to (11-6a),

formula (9-6a)

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formula (9-7a)

- 65 -

formula (10-3a)

- 66 -

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formula (11-1a)

R³

formula (11-2a)

- 67 -

where R^1 , R^2 , R^3 and R^N have the same meaning as above.

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In accordance with another very preferred embodiment, the compounds of formula (1) are selected from compounds of formulae (12-1a) to (12-6a) or (13-1a) to (13-6a),

- 68 -

formula (12-3a) formula (12-4a)

- 69 -

- 70 -

where R¹, R², R³ and R^N have the same meaning as above

formula (13-5a)

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Preferably, R¹, R³ stand on each occurrence, identically or differently, for H, D, F, CN, a straight-chain alkyl group having 1 to 20 C atoms or branched or a cyclic alkyl group having 3 to 20 C atoms, each of which may be substituted by one or more radicals R, where in each case one or more non-adjacent CH₂ groups may be replaced by RC=CR, C=C, O or S and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, an aromatic or heteroaromatic ring systems having 5 to 40, preferably 5 to 30, more preferably 5 to 18 aromatic ring atoms, which may in each case be

formula (13-6a)

substituted by one or more radicals R, or an aryloxy group having 5 to 40, preferably 5 to 30, more preferably 5 to 18 aromatic ring atoms, which may be substituted by one or more radicals R, where two radicals R¹ may form a monocyclic or polycyclic, aliphatic, aromatic or heteroaromatic ring system with one another, which may be substituted by one or more radicals R, and where two where two radicals R³ may form a monocyclic or polycyclic, aliphatic, aromatic or heteroaromatic ring system with one another, which may be substituted by one or more radicals R. When two radicals R¹ or R³ form a ring, they preferably form a condensed benzene ring as exemplified below:

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More preferably, R¹, R³ stand on each occurrence, identically or differently, for H, D, CN, a straight-chain alkyl group having 1 to 10 C atoms or branched or a cyclic alkyl group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R, an aromatic or heteroaromatic ring systems having 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R, where two radicals R¹ may form a condensed benzene ring with one another, which may be substituted by one or more radicals R, and where two where two radicals R³ may form a condensed benzene ring with one another, which may be substituted by one or more radicals R.

Preferably, R² stands on each occurrence, identically or differently, for H, D, F, a straight-chain alkyl group having 1 to 20 C atoms or branched or a cyclic alkyl group having 3 to 20 C atoms, each of which may be substituted by one or more radicals R, where in each case one or more non-adjacent CH₂ groups may be replaced by RC=CR, C≡C, O or S and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, an aromatic or heteroaromatic ring systems having 5 to 40, preferably 5 to 30, more preferably 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R, or an aryloxy group having 5 to 40, preferably 5 to 30, more preferably 5 to 18 aromatic ring atoms, which may be substituted by one or more radicals R.

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More preferably, R² stands on each occurrence, identically or differently, for H, D, F, a straight-chain alkyl group having 1 to 10 C atoms or branched or a cyclic alkyl group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R, or an aromatic or heteroaromatic ring systems having 5 to 60, preferably 5 to 40, more preferably 5 to 30, very more preferably 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R.

Very preferably, R² stands on each occurrence, identically or differently, for an aromatic or heteroaromatic ring systems having 5 to 60, preferably 5 to 40, more preferably 5 to 30, very more preferably 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R.

Particularly preferably, R² stands for an aromatic or heteroaromatic ring system having selected from benzene, naphthalene, anthracene, benzanthracene, phenanthrene, triphenylene (also called benzophenanthrene), pyrene, chrysene, perylene, fluoranthene, naphthacene, pentacene, benzopyrene, biphenyl, biphenylene, terphenyl, terphenylene, quaterphenyl, fluorene, spirobifluorene, indenofluorene, furan, benzofuran, dibenzofuran, thiophene, benzothiophene, dibenzothiophene,

pyrrole, indole, isoindole, carbazole, indolocarbazole, indenocarbazole, pyridine, quinoline, isoquinoline, acridine, phenanthridine, benzoquinoline, phenothiazine, phenoxazine, imidazole, benzimidazole, naphthimidazole, phenanthrimidazole, pyrimidine, benzopyrimidine, quinoxaline, pyrazine, phenazine, phenoxazine, phenothiazine, azacarbazole, triazine, or combinations of these groups. Very particularly preferably, the group R² is selected from the group consisting of from benzene, naphthalene, phenanthrene, triphenylene, fluoranthene, biphenyl, terphenyl, quaterphenyl, fluorene, spirobifluorene, indenofluorene, dibenzofuran, dibenzothiophene, carbazole, indolocarbazole, indenocarbazole, pyridine, quinoline, benzoquinoline, pyrimidine, benzopyrimidine, quinoxaline, phenoxazine, phenothiazine, azacarbazole, pyrazine, triazine, or combinations of these groups.

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Preferably, R stands on each occurrence, identically or differently, for H, D, F, CN, a straight-chain alkyl or alkoxy group having 1 to 20 C atoms or branched or cyclic alkyl or alkoxy group having 3 to 20 C atoms, each of which may be substituted by one or more radicals R´, an aromatic or heteroaromatic ring systems having 5 to 40, preferably 5 to 30, more preferably 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R´, where two radicals R may form a ring system with one another, which may be substituted by one or more radicals R´. More preferably, R stands on each occurrence, identically or differently, for H, D, F, CN, a straight-chain alkyl group having 1 to 10 C atoms or branched or cyclic alkyl group having 3 to 10 C atoms, each of which may be substituted by one or more radicals R´, an aromatic or heteroaromatic ring systems having 5 to 18 aromatic ring atoms, which may in each case be substituted by one or more radicals R´.

Preferably, Ar is an aromatic or heteroaromatic ring system having 5 to 18 aromatic ring atoms, which may in each case also be substituted by one or more radicals R´.

Preferably, R´ stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl or alkoxy group having 1 to 20, preferably 1 to 10, more preferably 1 to 5 C atoms or branched or cyclic alkyl or alkoxy group having 3 to 20, preferably 1 to 10, more preferably 1 to 5 C atoms, where one or more H atoms may be replaced by D, F, Cl, Br or I, or an aromatic or heteroaromatic ring system having 5 to 24 C, preferably 5 to 18 C atoms.

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

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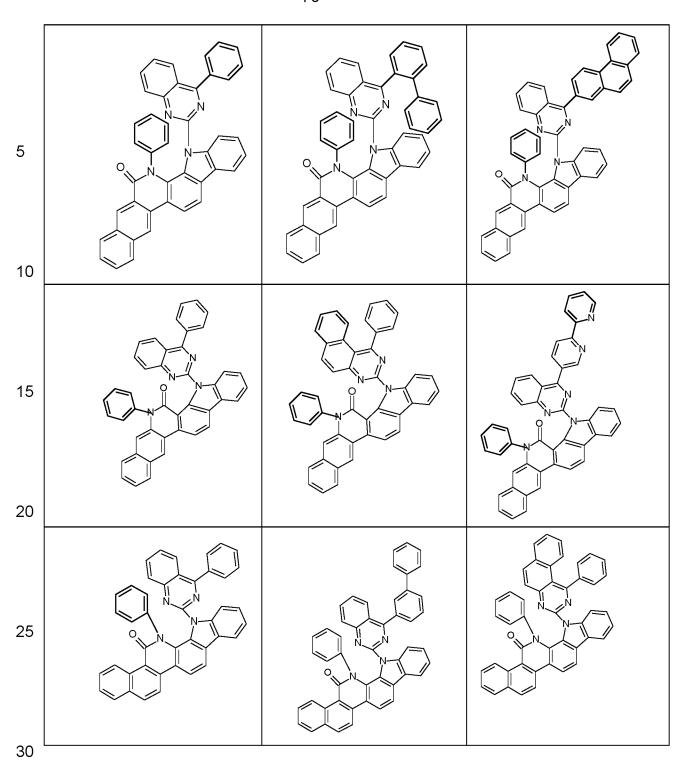
5		
		2
15		
20		
25		
30		

5		
15		
20		
25		
30		

5		
10		
15		
20		
25		

- 78 -

5		
10		
15		
20		
25		



5		
15		
25		

5		
15 20		
25 30		

- 83 -

The compounds according to the invention can be prepared by synthesis steps known to the person skilled in the art, such as, for example, bromination, Suzuki coupling, Ullmann coupling, Hartwig-Buchwald coupling, etc. Examples of suitable synthesis processes are depicted in general terms in Schemes 1-3.

Scheme 1

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Scheme 2

- 84 -

Scheme 3

Advanced Synthesis & Catalysis, 357(2-3), 366-370; 2015

- 85 -

In schemes 1, 2 and 3:

 X^1 , X^2 = leaving group, more preferably halogen

Quin = quinozaline or quinoxaline derivative

Ar = aromatic or heteroaromatic ring system

 Ar^{1} , Ar^{2} and Ar^{3} = aromatic or heteroaromatic ring systems.

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Furthermore, the compounds shown in the above schemes may be substituted at any free positions with any organic radicals.

The present invention therefore relates to a process for the synthesis of the compounds according to the invention, comprising:

- (i) the synthesis of a polycyclic compound comprising at least three aryl or heteroaryl groups, whereas two aryl or heteroaryl groups are connected via a 6-membered lactam ring and two aryl or heteroaryl groups are connected via a pyrrole ring;
- (ii) Introduction of a quinazoline or quinoxaline group via a C-N coupling reaction between the nitrogen atom of the compound obtained in step (i) and a quinazoline or quinoxaline group.

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The present invention therefore relates to another process for the synthesis of the compounds according to the invention, comprising:

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- (i) C-C coupling reaction between a carbazole derivative comprising a quinazoline or quinoxaline group and an aryl or heteroaryl group;
- (ii) formation of a lactam bridge between the carbazole derivative and the aryl or heteroaryl group of step (i).

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

- 86 -

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preferably organic solvents. The solvents are very preferably selected from hydrocarbons, alcohols, esters, ethers, ketones and amines. 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, in particular 3-phenoxytoluene, (-)-fenchone, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, 1-methylnaphthalene, 1-ethylnaphthalene, decylbenzene, phenyl naphthalene, menthyl isovalerate, para tolyl isobutyrate, cyclohexal hexanoate, ethyl para toluate, ethyl ortho toluate, ethyl meta toluate, decahydronaphthalene, ethyl 2-methoxybenzoate, dibutylaniline, dicyclohexylketone, isosorbide dimethyl ether, decahydronaphthalene, 2methylbiphenyl, ethyl octanoate, octyl octanoate, diethyl sebacate, 3,3dimethylbiphenyl, 1,4-dimethylnaphthalene, 2,2'-dimethylbiphenyl, 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, 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 present invention therefore furthermore relates to a formulation comprising a compound according to the invention and at least one further compound. The further compound may be, for example, a solvent, in particular one of the above-mentioned solvents or a mixture of these solvents. However, the further compound may also be at least one further organic or inorganic compound which is likewise employed in the electronic device, for example an emitting compound, in particular a phosphorescent dopant,

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and/or a further matrix material. Suitable emitting compounds and further matrix materials are indicated below in connection with the organic electro-luminescent device. This further compound may also be polymeric.

PCT/EP2020/075693

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

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

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

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

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The organic electroluminescent device comprises a cathode, an anode and at least one emitting layer. Apart from these layers, it may also comprise

further layers, for example in each case one or more hole-injection layers, hole-transport layers, hole-blocking layers, electron-transport layers, electron-injection layers, exciton-blocking layers, electron-blocking layers and/or charge-generation layers. It is likewise possible for interlayers, which have, for example, an exciton-blocking function, to be introduced between two emitting layers. However, it should be pointed out that each of these layers does not necessarily have to be present. The organic electroluminescent device here may comprise one emitting layer or a plurality of emitting layers. If a plurality of emission layers are present, these preferably have in total a plurality of emission maxima between 380 nm and 750 nm, resulting overall in white emission, i.e. various emitting compounds which are able to fluoresce or phosphoresce are used in the emitting layers. Particular preference is given to systems having three emitting layers, where the three layers exhibit blue, green and orange or red emission (for the basic structure see, for example, WO 2005/011013). These can be fluorescent or phosphorescent emission layers or hybrid systems, in which fluorescent and phosphorescent emission layers are combined with one another.

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The compound according to the invention in accordance with the embodiments indicated above can be employed in various layers, depending on the precise structure. Preference is given to an organic electroluminescent device comprising a compound of the formula (1) or in accordance with the preferred embodiments as matrix material for fluorescent emitters, phosphorescent emitters or emitters showing TADF (Thermally Activated Delayed Fluorescence), in particular for phosphorescent emitters, and/or in an electron-transport layer and/or in an electron-blocking or exciton-blocking layer and/or in a hole-transport layer, depending on the precise substitution. The preferred embodiments indicated above also apply to the use of the materials in organic electronic devices.

In a preferred embodiment of the invention, the compound of the formula (1) or in accordance with the preferred embodiments is employed as matrix

material for a fluorescent or phosphorescent compound, in particular for a phosphorescent compound, in an emitting layer. The organic electroluminescent device here may comprise one emitting layer or a plurality of emitting layers, where at least one emitting layer comprises at least one compound according to the invention as matrix material.

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If the compound of the formula (1) or in accordance with the preferred embodiments is employed as matrix material for an emitting compound in an emitting layer, it is preferably employed in combination with one or more phosphorescent materials (triplet emitters). Phosphorescence in the sense of this invention is taken to mean the luminescence from an excited state having spin multiplicity > 1, in particular from an excited triplet state. For the purposes of this application, all luminescent transition-metal complexes and luminescent lanthanide complexes, in particular all iridium, platinum and copper complexes, are to be regarded as phosphorescent compounds.

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Preferably, when the compounds of the formula (1) or in accordance with the preferred embodiments are employed as matrix materials for an emitting compound in an emitting layer, they are preferably employed in combination with one or more phosphorescent material (triplet emitters).

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The mixture comprising the compound of the formula (1) or in accordance with the preferred embodiments and the emitting compound comprises between 99 and 1% by vol., preferably between 98 and 10% by vol., particularly preferably between 97 and 60% by vol., in particular between 95 and 80% by vol., of the compound of the formula (1) or in accordance with the preferred embodiments, based on the entire mixture comprising emitter and matrix material. Correspondingly, the mixture comprises between 1 and 99% by vol., preferably between 2 and 90% by vol., particularly preferably between 3 and 40% by vol., in particular between 5 and 20% by vol., of the emitter, based on the entire mixture comprising emitter and matrix material.

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Suitable phosphorescent compounds (= triplet emitters) are, in particular, compounds which emit light, preferably in the visible region, on suitable excitation and in addition contain at least one atom having an atomic number greater than 20, preferably greater than 38 and less than 84, particularly preferably greater than 56 and less than 80, in particular a metal having this atomic number. The phosphorescent emitters used are preferably compounds which contain copper, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold or europium, in particular compounds which contain iridium or platinum. For the purposes of the present invention, all luminescent compounds which contain the above-mentioned metals are regarded as phosphorescent compounds.

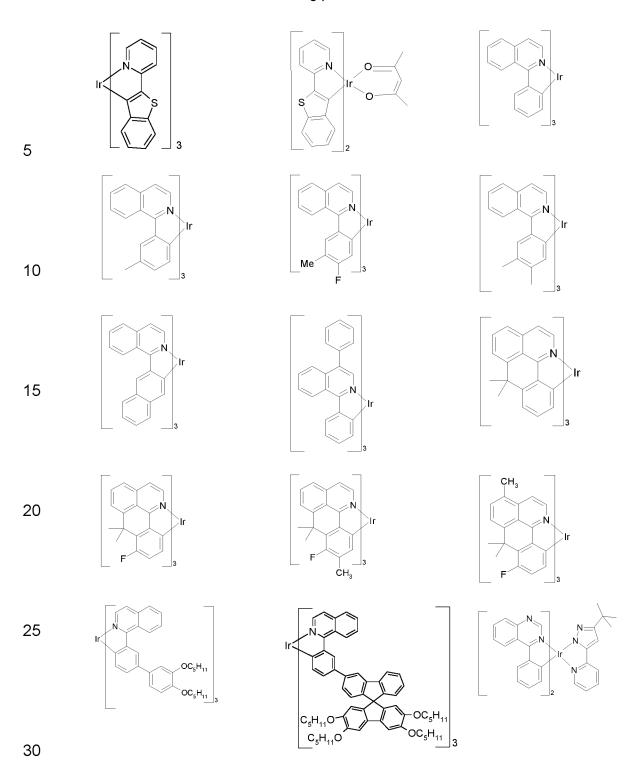
Examples of the emitters described above are revealed by the applications 15 WO 00/70655, WO 2001/41512, WO 2002/02714, WO 2002/15645, EP 1191613, EP 1191612, EP 1191614, WO 05/033244, WO 05/019373, US 2005/0258742, WO 2009/146770, WO 2010/015307, WO 2010/031485, WO 2010/054731, WO 2010/054728, WO 2010/086089, WO 2010/099852, WO 2010/102709, WO 2011/032626, WO 2011/066898, WO 2011/157339, 20 WO 2012/007086, WO 2014/008982, WO 2014/023377, WO 2014/094962, WO 2014/094961, WO 2014/094960, WO 2016/124304, WO 2016/125715, WO 2017/032439 as well as the not yet published applications WO 2018/011186 and WO 2018/041769. In general, all phosphorescent 25 complexes as used in accordance with the prior art for phosphorescent OLEDs and as are known to the person skilled in the art in the area of organic electroluminescence are suitable, and the person skilled in the art will be able to use further phosphorescent complexes without inventive step.

Examples of suitable phosphorescent emitters are the phosphorescent emitters listed in the table below:

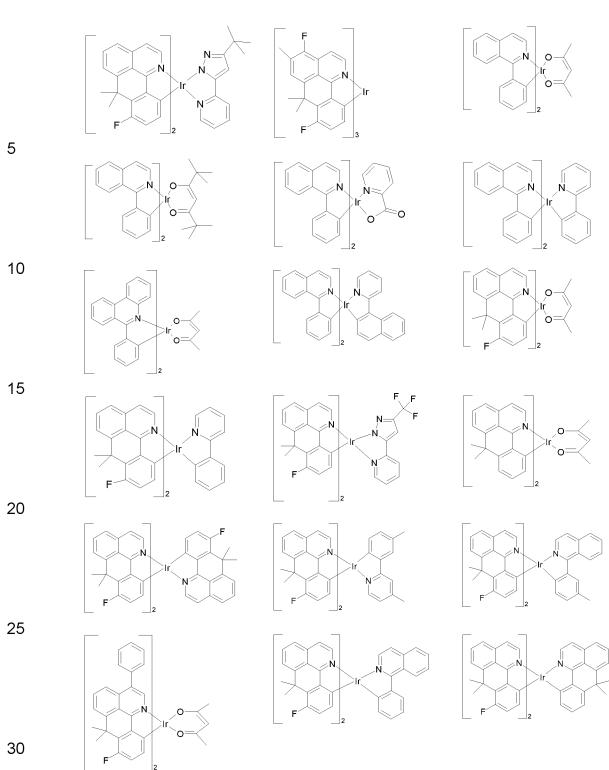
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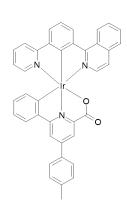
- 91 -

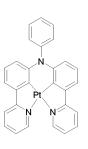


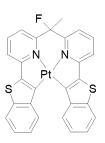
- 92 -



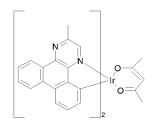
- 93 -







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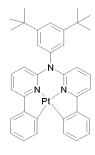


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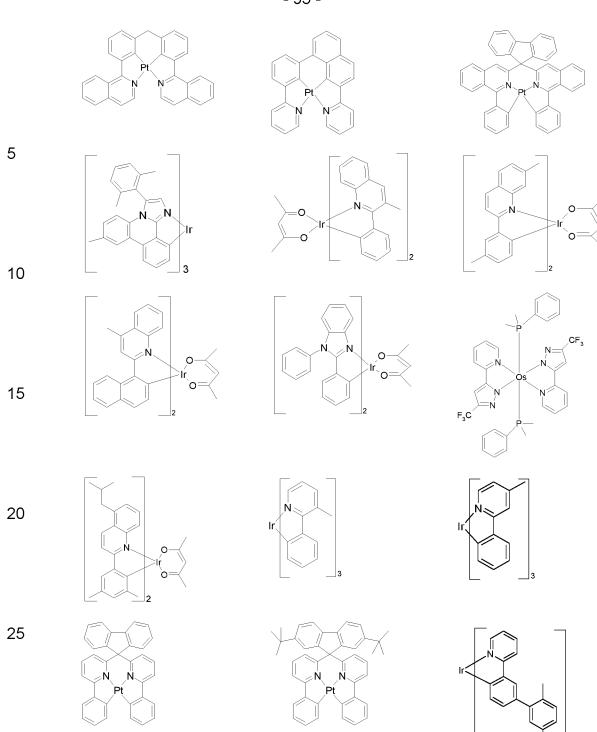
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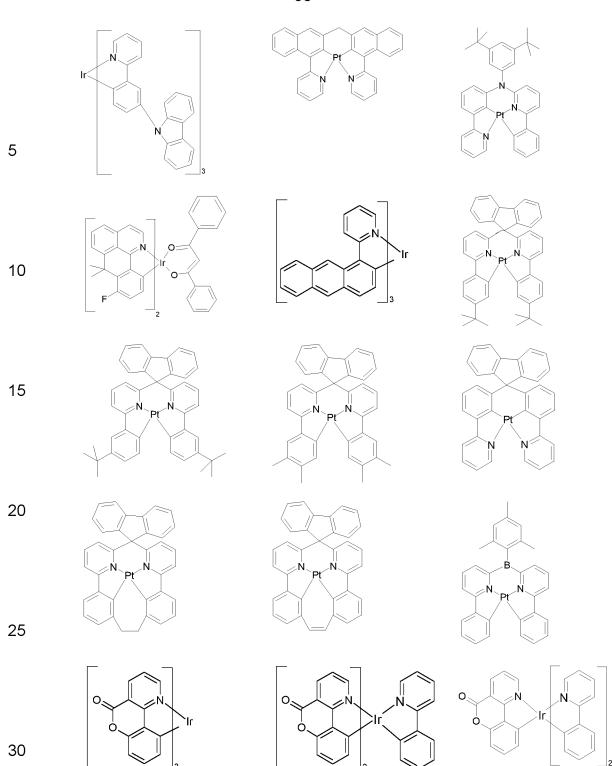


25 N Pt N

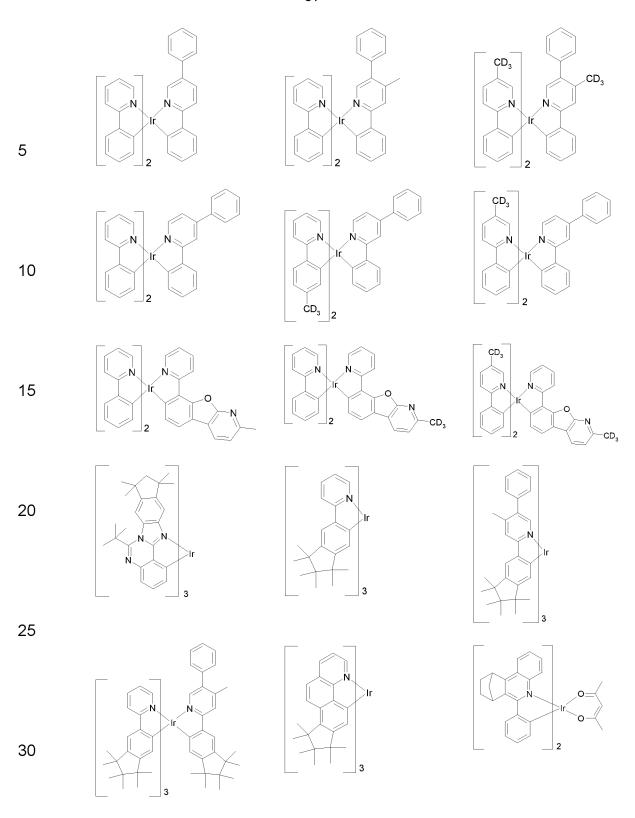
- 95 -



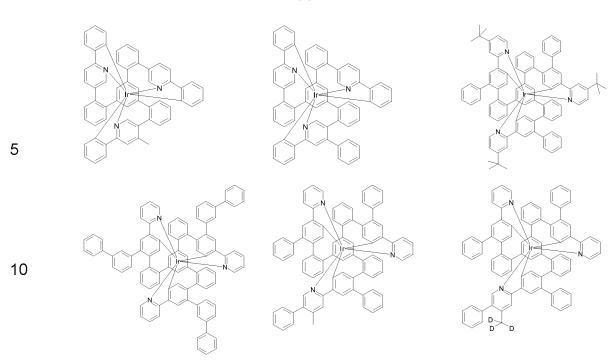
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Suitable phosphorescent materials (= triplet emitters) that can be advantageously combined with the compounds of formula (1) are, as mentioned above, compounds which emit a red light on suitable excitation, which means phosphorescent materials having an excited triplet state level (T1) comprised between 550 and 800 nm, more particularly 550-680 nm.

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A further preferred embodiment of the present invention is the use of the compound of the formula (1) or in accordance with the preferred embodiments as matrix material for a phosphorescent emitter in combination with a further matrix material. Particularly suitable matrix materials which can be employed in combination with the compounds of the formula (1) or in accordance with the preferred embodiments are aromatic ketones, aromatic phosphine oxides or aromatic sulfoxides or sulfones, for example in accordance with WO 2004/013080, WO 2004/093207, WO 2006/005627 or WO 2010/006680, triarylamines, carbazole derivatives, for example CBP (N,N-biscarbazolylbiphenyl) or the carbazole derivatives disclosed in WO 2005/039246, US 2005/0069729, JP 2004/288381, EP 1205527 or WO

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2008/086851, indolocarbazole derivatives, for example in accordance with WO 2007/063754 or WO 2008/056746, indenocarbazole derivatives, for example in accordance with WO 2010/136109 and WO 2011/000455, azacarbazole derivatives, for example in accordance with EP 1617710, EP 1617711, EP 1731584, JP 2005/347160, bipolar matrix materials, for example in accordance with WO 2007/137725, silanes, for example in accordance with WO 005/111172, azaboroles or boronic esters, for example in accordance with WO 2006/117052, triazine derivatives, for example in accordance with WO 2010/015306, WO 2007/063754 or WO 2008/056746, 10 zinc complexes, for example in accordance with EP 652273 or WO 2009/062578, diazasilole or tetraazasilole derivatives, for example in accordance with WO 2010/054729, diazaphosphole derivatives, for example in accordance with WO 2010/054730, bridged carbazole derivatives, for 15 example in accordance with US 2009/0136779, WO 2010/050778, WO 2011/042107, WO 2011/088877 or in accordance with EP 11003232.3, triphenylene derivatives, for example in accordance with WO 2012/048781, or lactams, for example in accordance with WO 2011/116865 or WO 2011/137951. A further phosphorescent emitter which emits at shorter 20 wavelength than the actual emitter may likewise be present in the mixture as co-host.

Preferred co-host materials are triarylamine derivatives, lactams, carbazole derivatives and indenocarbazole derivatives. Preferred co-host materials are very particularly carbazole derivatives and indenocarbazole derivatives.

The compounds of the formula (1) or in accordance with the preferred embodiments are particularly suitable as matrix material alone or in combination with a further matrix material for a phosphorescent emitter.

In a further embodiment of the invention, the organic electroluminescent device according to the invention does not comprise a separate holeinjection layer and/or hole-transport layer and/or hole-blocking layer and/or electron-transport layer, i.e. the emitting layer is directly adjacent to the hole-

injection layer or the anode, and/or the emitting layer is directly adjacent to the electron-transport layer or the electron-injection layer or the cathode, as described, for example, in WO 2005/053051. It is furthermore possible to use a metal complex which is identical or similar to the metal complex in the emitting layer as hole-transport or hole-injection material directly adjacent to the emitting layer, as described, for example, in WO 2009/030981.

It is furthermore possible to employ the compounds according to the invention in a hole-blocking or electron-transport layer. This applies, in particular, to compounds according to the invention which do not have a carbazole structure. These may preferably also be substituted by one or more further electron-transporting groups, for example benzimidazole groups.

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

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For example, the compound according to the invention can also be used as a matrix for semiconducting light-emitting nanoparticles. In the context of the present invention, the term "nano" denotes a size in the range from 0.1 to 999 nm, preferably from 1 to 150 nm. In a preferred embodiment, the semiconducting light-emitting nano-particle is a quantum material ("Quantum sized material"). The term "quantum material" in the sense of the present invention refers to the size of the semiconductor material itself without further connections or a further surface modification, which shows the so-called quantum confinement effect, as for example in ISBN: 978-3-662-44822-9. In one embodiment of the invention, the total size of the quantum material is in the range from 1 to 100 nm, more preferably from 1 to 30 nm

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and particularly preferably from 5 to 15 nm. In this case, the core of the semiconducting light-emitting nano-particle can vary. Suitable examples are CdS, CdSe, CdTe, ZnS, ZnSe, ZnSeS, ZnTe, ZnO, GaAs, GaP, GaSb, HgS, HgSe, HgSe, HgTe, InAs, InP, InPS, InPZnS, InPZn, InPGa, InSb, AlAs, AIP, AISb, Cu₂S, Cu₂Se, CuInS₂, CuInSe₂, Cu₂(ZnSn)S₄, Cu₂(InGa) S₄, TiO₂, or a combination of said materials. In a preferred embodiment, the core of the semiconductive light-emitting particle contains one or more elements of group 13 and one or more elements of group 15 of the periodic system of the elements, for example GaAs, GaP, GaSb, InAs, InP, InPS, InPZnS, InPZn, InPGa, InSb, AlAs, AlP, AlSb, CuInS₂, CuInSe₂, Cu₂(InGa)S₄ or a combination of the mentioned materials. Particularly preferably, the core contains In- and P-atoms, z. InP, InPS, InPZnS, InPZn or InPGa. In a further embodiment of the invention, the nanoparticle contains one or more shell layers, which comprise a first element from the group 12, 13 or 14 of the periodic table and a second element from the group 15 or 16 of the periodic table. Preferably, all shell layers contain a first element from the group 12, 13 or 14 of the periodic system and a second element from the group 15 or 16 of the periodic system. In a preferred embodiment of the invention, at least one of the shell layers contains a first element from the group 12 and a second element from the group 16 of the periodic table, for example CdS, CdZnS, ZnS, ZnSe, ZnSSe, ZnSSeTe, CdS/ZnS, ZnSe/ZnS or ZnS/ZnSe. Particularly preferably, all shell layers contain a first element from the group 12 and a second element from the group 16 of the periodic table.

Preference is furthermore given to an organic electroluminescent device, characterised in that one or more layers are applied by means of a sublimation process, in which the materials are vapour-deposited in vacuum sublimation units at an initial pressure of less than 10⁻⁵ mbar, preferably less than 10⁻⁶ mbar. However, it is also possible for the initial pressure to be even lower or higher, for example less than 10⁻⁷ mbar.

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

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- Preference is furthermore given to an organic electroluminescent device, characterised in that one or more layers are produced from solution, such as, for example, by spin coating, or by means of any desired printing process, such as, for example, ink-jet printing, LITI (light induced thermal imaging, thermal transfer printing), screen printing, flexographic printing, offset printing or nozzle printing. Soluble compounds, which are obtained, for example, by suitable substitution, are necessary for this purpose.
- Also possible are hybrid processes, in which, for example, one or more layers are applied from solution and one or more further layers are applied by vapour deposition. Thus, it is possible, for example, to apply the emitting layer from solution and to apply the electron-transport layer by vapour deposition.

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

The compounds according to the invention generally have very good properties on use in organic electroluminescent devices. In particular, the lifetime on use of the compounds according to the invention in organic electroluminescent devices is significantly better compared with similar compounds in accordance with the prior art. The other properties of the organic electroluminescent device, in particular the efficiency and the volt-

age, are likewise better or at least comparable. Furthermore, the compounds have a high glass transition temperature and high thermal stability.

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

A) Syntheses Examples

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Unless otherwise stated, the following syntheses are carried out in a protective gas atmosphere in dried solvents. The compounds according to the invention can be synthesised by means of synthesis methods known to the skilled person.

a) 5-(2-chloroanilino)benzo[c]fluoren-7-one

43 g (140 mmol) of 5-bromobenzo[c]fluoren-7-one, 17.9 g (140 mmol) of 2-chloroaniline, 68.2 g (710 mmol) of sodium tert-butylate, 613 mg (3 mmol) of palladium(II)acetate and 3.03 g (5 mmol) of dppf are dissolved in 1.3 L of toluene and stirred under reflux for 5 hours. The reaction mixture is cooled down to room temperature, mixed with toluene and filtered via Celite. The filtrate is concentrated under vacuum and the residue of toluene/heptane is crystallized. The product is isolated as a colourless solid. Yield: 38 g (107 mmol) 77% of the theory.

The following compounds can be produced analogously:

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		Educt 1	Educt 2	Product	Yield
5	1a	[52086-21-2]	NH ₂ CI		83%
10	2a	Br (64356-33-8)	NH ₂ CI	CI HN	75%
15	3a	[2129981-13-9]	NH ₂	NH O	81%
20	4a	[2102312-08-1]	NH ₂	NH O	79%
25	5a	[2129981-13-9]	NH ₂ CI 7285-66-7	E T	87%
35	6a	Br [2084129-34-8]	NH ₂	CI	80%

b) Cyclisation

36.2 g (102 mmol) of 5-(2-chloroanilino)benzo[c]fluoren-7-one, 56 g (409 mmol) of potassium carbonate, 4.5 g (12 mmol) of tricyclohexyl phosphine tetrafluoroborate and 1.38 g (6 mmol) of palladium(II)acetate are suspended in 500 mL of dimethylacetamide and stirred under reflux for 6 hours. After cooling, the reaction mixture is mixed with 300 ml water and 400 mL and stirred for 30 minutes. The organic phase is then spearated and filtered over a short Celite bed. The solvend is then removed under vacuum. The raw product is extracted via a hot extraction with toluene and recrystallized from toluene. The product is isolated as a beige-coloured solid (21g, 66 mmol, corresponds to 65% of the theory).

The following compounds can be produced analogously:

	Educt Product		Yield
1b	NH CI	H. H.	68%

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5	2b	CI N	HN	72%
10 15	3b		NH O	76%
20	4b	H O C C	NH NH	75%
25	5b	NH O	NH O	68%
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c) 5-(2-nitrophenyl)benzo[c]fluoren-7-one

A well stirred degassed suspension of 30 g (183.8 mmol) of B-(2-nitrophenyl)-benzeneboronic acid, 57 g (184 mmol) of 5-bromobenzo[c]fluoren-7-one and 66.5 g (212.7 mmol) of potassium carbonate in a mixture of 250 ml water and 250 ml THF is mixed with 1.7 g (1.49 mmol) of Pd(PPh₃)₄ and heated for 17 h under reflux. After cooling, the organic phase is separated, washed three times with 200 ml water and once with 200 ml saturated aqueous saline solution, dried over magnesium sulphate and rotated to dryness. The grey residue is recrystallized from hexane. The precipitated crystals are extracted, washed with MeOH and dried in vacuum; yield: 58.9 g, (167 mmol), 91% of theory.

The following compounds can be produced analogously:

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		Educt1	Educt 2	Product	Yield
5	1c	[2129981-13-9]	O /4 /4 /0- B O H HO [5570-19-4]		81%
				O //4	
15	2c	Br (64356-33-8)	0 /4 /0- B O H HO [5570-19-4]		87%
20					
25	3c	[2129981-13-9]	NO ₂ B(OH) ₂	N+O	85%
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d) Carbazole synthesis

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A mixture of 84.2 g (240 mmol) of 5-(2-nitrophenyl)benzo[c]fluoren-7-one and 290.3 ml (1669 mmol) of triethyl phosphite is heated for 12 h under reflux. The remaining triethyl phosphite is then distilled (72-76 °C / 9 mm Hg). A mixture of Water/MeOH (1:1) is added to the residue, which is then filtered and recrystallized.

Yield: 53.5 g, (168 mmol), 70 % of theorie.

The following compounds can be produced analogously:

	Educt 1	Product	Yield
1d		HN	78%
2d	N O O		72%

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e) Methyl 2-[11-(4-phenylquinazolin-2-yl)benzo[a]carbazol-5yl]benzoate

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35 g (70 mmol) of 5-bromo-11-(4-phenylquinazolin-2-yl)benzo[a]carbazole, 13,4 g (75 mmol) of (2-methoxycarbonylphenyl)boronic acid and 14,7 g (139 mmol) of sodium carbonate are suspended in 200 mL toluene, 52 mL ethanol and 100 mL water. Then, 80 mg (0,69 mmol) of tetrakisphenylphosphine-palladium(0) are added to this suspension and the reaction mixture is heated for 16 h under reflux. After cooling, the organic phase is separated, filtered over silica gel, washed three times with 200 mL water and then concentrated to dryness. The residue is recrystallized from heptane/dichloromethane.

The yield is 31.8 g (57 mmol), corresponding to 81 % of the theory.

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The following compounds can be produced analogously:

		Educt1	Educt 2	Product	Yield
5	1e	[1656982-97-6]	Br [610-94-6]		80%
15	2e	[2054893-54-6] _{HO} B—OH	[1692877-64-7]		83%
25	3e	Br N N N N N N N N N N N N N N N N N N N	HO B OH [374538-03-1]		85%
30	4e	[2113711-86-5] B—OH	[610-94-6]		87%

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		ı		
5	5e	[1907704-71-5]	HO B H [374538-03-1]	81%
10	6e	[1627508-12-6]	HO B H [374538-03-1]	82%
20	7e	[2103210-71-3] B-O	[610-94-6]	88%
25 30	8e	[1843211-19-7]	[89555-39-5]	89%

f) Ketone synthesis:

24,4 g (44 mmol) of methyl 2-[11-(4-phenylquinazolin-2-yl)benzo[a]carbazol-5-yl]benzoate are introduced in 220 ml of concentrated H₂SO₄ and stirred for 2 hours. When the reaction is complete, the mixture is carefully poured on ice and extracted with toluene, separated and concentrated with the rotary evaporator, the precipitated solid is aspirated and washed with water and ethanol.

The yield is 18.8 g (36 mmol), corresponding to 82 % of the theory.

The following compounds can be prepared analogously:

		Educt 1	Product	Yield
25				
30	1f			87%

5	2f		85%
10	3f		80%
15 20	4f		83%
25	5f		85%
30	6f		80%

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g) Ketoxime synthesis

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76.8 g (147 mmol) of the compound **(f)** is introduced in 300 ml pyridine/ 200 methanol. Then, 20.5 g hydroxylammonium chloride are slowly added to the mixture, which is heated for 3,5 hours at 60°C. When the reaction is complete, the precipitated solid is aspirated and washed with water and 1 mol HCl and then with methanol.

The yield is 71 g (132 mmol), corresponding to 90 % of theory.

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The following compounds can be made analogously:

		Educt 1	Product	Yield
5	1g		OH NOH	87%
10				
			N	
15	2g		N OH	81%
20	3g		OH NNNN	85%
25	4g			79%
30			ОН	

5	5g		OH NOH	83%
10	6g		OH N	82%
15	7g		OH NO H	76%
25	8g	NH O	HO NH	74%
30	9g	H	OH NOH	75%

5	10g	HN	63%
10	11g	NH NOH	67%
20	12g	HNOH	69%
25	13g	NH OH	71%
30	14g	NH NOH	74%
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h) Lactame synthesis (Beckmann-rearrangement)

75 g (141 mmol) of compound **(g)** is placed in 300 ml of polyphosphoric acid and heated to 170 °C for 12 hours. When the reaction is complete, the

mixture is placed on ice and extracted with ethyl acetic acid, separated and concentrated. The precipitated solid is aspirated and washed with ethanol. The isomers are chromatographically separated.

Yield: 70 g (130 mmol) of the mixture i(a)+i(b), corresponding to 94% of the 5 theory, purity: 98,0 % n. HPLC. After recrystallization from ethyl acetate/toluene (1:2): 32g (43%) i(a) and 38g (51.6%) i(b) are obtained.

The following compounds can be made analogously:

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10		Educt 1	Product (a)	Product (b)	Yield
15	1h	N OH			51%/45%
20	2h	H H			50%/41%
30	3h	D H D D D D D D D D D D D D D D D D D D		O NH N N	47%/42%

5	4h	N N OH	N N N N N N N N N N N N N N N N N N N		38%/40%
10	5h	OH		NH NH	40%/35%
15	6h	DOH NOH			43%/39%
20	7h	N OH			42%/39%
25	8h	HO N	ON H	NH HO	44% / 37%
35	9h	H H H H H H H H H H H H H H H H H H H	H	H	35%/ 38%

5	10h	H H H H H H H H H H H H H H H H H H H	HN ONH	HN	39%/ 45%
10	11h	NH NOH	NH ONH	NH HO	38%/ 37%
15	12h	E O D D D D D D D D D D D D D D D D D D	H	H	33%/ 45%
20	13h	NH OH	NH ONH	NH HO	41% / 32%
30	14h	DH DH	NH ON THE STATE OF	NH HO	48% / 30%

j) Ullmann reaction

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13,5 g (25 mmol, 1.00 eq.) of compound **h(a)**, 21.3ml (128 mmol, 5.2 eq.) of 3-bromobiphenyl and 7.20 g of potassium carbonate (52.1 mmol, 2.10 eq.)

are mixed in 220 ml dried DMF and inerted in argon. Then, 0.62 g (2.7 mmol, 0.11eq) of 1,3-di(2-pyridyl)-1,3-propanedione and 0.52 g (2.7 mmol, 0.11eq) of copper(I) iodide are added int the mixture, which is heated at 140 °C for three days. When the reaction is complete, the mixture is carefully concentrated with the rotary evaporator, the precipitated solid is aspirated and washed with water and ethanol. The raw product is purified twice using a hot extractor (toluene/heptane 1:1) and the resulting solid is recrystallized from toluene. After sublimation, 8.2 g (12 mmol, 48 % of the theory) of the desired target compound is obtained.

The following compounds can be produced analogously:

		Educt 1	Educt 2	Product	Yield
5	1j			N N N N N N N N N N N N N N N N N N N	79%
10	2 j	NH NH			68 %
15	3j	HIN			57%
20	4 j				59%
25		NH			
30	5j			N N N N N N N N N N N N N N N N N N N	63%
35			[20442-79-9]		

5	6j	S S S S S S S S S S S S S S S S S S S	[502161-03-7]	68%
10	7 j	A H H H H H H H H H H H H H H H H H H H		71%
15	8j			63%
20	9j		[20442-79-9]	77%
30	10j			65%

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5	12j			64%
10	13j	Z Z Z O	[20442-79-9]	67%
20	14j		[20442-79-9]	61%
25	15j			72%

5	16j			68%
10	17j	N N N N O CN		59%
15	18j			64%
25	19j		[20442-79-9]	60%

5	21j			69%
10	22j		[20442-79-9]	65%
20	23j		[20442-79-9]	69%
25	25j	N N N N N N N N N N N N N N N N N N N		63%
30	26j			67%

25 i) Nucleophile substitution:

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20,3 g (61 mmol) of a lactame compound **(8h)** is dissolved in 300 ml of dimethylformamide in an inert atmosphere and mixed with 3 g of NaH in mineral oil (60%, 75 mmol). After 1 h at room temperature, a solution of 24 g (63 mmol) of 2-chloro-4-phenyl-benzo[h]quinazoline in 150 mL of dimethylformamide is added to the mixture drop by drop. The reaction mixture is then stirred for 12 h at room temperature. After this time, the reaction mixture is poured on ice and extracted three times with dichloromethane. The combined organic phases are dried over Na₂SO₄ and concentrated. The residue is recrystallized with toluene.

Yield: 28.9 g (49 mmol), correspond to 81 % of the theory.

The following compounds can be produced analogously:

		Educt 1	Educt 2	Product	Yield
20	3i	HE TO THE TOTAL PROPERTY OF THE TOTAL PROPER	CI N N N N N N N N N N N N N N N N N N N		68%
25	4i	NH HO	N N CI [6484-25-9]		71%
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5	5i	HZ TZ O	CI N CN [1292317-90-8]	CN H	65%
10	6i		[30169-34-7]		62%
20	11i	THE	4786-80-5]		60%
25	13i	H Z Z	CI N N N N N N N N N N N N N N N N N N N	NH NH	67%

B) Fabrication of OLEDs

The use of the inventive materials in OLEDs is presented in the following examples E4 to E12 (see Table 1).

Pretreatment for examples E1 to E12:

Glass plates coated with structured ITO (indium tin oxide, 50 nm) are treated with an oxygen plasma followed by an argon plasma before coating. These

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plasma-treated glass plates form the substrates on which the OLEDs are applied.

In principle, the OLEDs have the following layer structure: substrate /
optional interlayer (IL) / hole injection layer (HIL) / hole transport layer (HTL)
/ electron blocking layer (EBL) / emission layer (EML) / optional hole
blocking layer (HBL) / electron transport layer (ETL) / optional electron
injection layer (EIL) and finally a cathode. The cathode is formed by a 100
nm thick aluminium layer. The exact structure of the OLEDs is shown in
Table 1. The materials used for the OLED fabrication are listed in Table 2.
The data of the OLEDs are listed in Tables 3 and 4.

All materials are applied by thermal vapour deposition in a vacuum

15 chamber. The emission layer here always consists of at least one matrix material (host material) and an emitting dopant (emitter), which is admixed with the matrix material or matrix materials in a certain proportion by volume by co-evaporation.

An expression such as IC1:EG1:TER1 (45%:45%:10%) here means that the material IC1 is present in the layer in a proportion by volume of 45%, EG1 is present in the layer in a proportion by volume of 45% and TER1 is present in the ayer in a proportion by volume of 10%. Analogously, the electron-transport layer may also consist of a mixture of two materials.

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The OLEDs are characterized by standard methods.

For this purpose, the electroluminescence spectra and the external quantum efficiency (EQE, measured in %) are determined as a function of luminance, calculated from current-voltage-luminance characteristics assuming a Lambertian radiation characteristic. The electroluminescence spectra are determined at a brightness of 1000 cd/m² and the CIE 1931 x and y colour coordinates are determined. U 1000, in Table 3 below, corresponds to the operating voltage required for getting a luminance of 1000 cd/m² and EQE 1000 corresponds to the external quantum efficiency at 1000 cd/m².

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Lifetime LT is defined as the time in hours (h), after which the starting brightness at constant current density j_0 , is reduced to a certain level L1 in % of the starting brightness.

L1 = 95% in Table 3 below means, that the given lifetime LT corresponds to the time after which the brightness is reduced to 95% of its starting value. The results are shown in Table 3.

Use of the inventive materials in OLEDs

The inventive compounds EG1 to EG6 can be used in the examples E4 to E11 as matrix material in the emission layer of red phosphorescent OLEDs.

Table 4 summarizes the results of some examples. The use of the inventive compounds as matrix material for phosphorescent OLEDs leads to OLEDs having better performances in terms of operating voltage, external quantum efficiency and lifetime, in comparison with OLEDs comprising the comparative compounds V1 and V2.

Table 1: Structures of the OLEDs

Ex.	HIL nm	HTL nm	EBL nm	EML nm	HBL nm	ETL nm	EIL nm
	HATCN	SpMA1	SpMA3	V1:TER5	ST2	ST2:LiQ	LiQ 1nm
E1	5nm	125nm	10nm	(97%:3%) 35nm	10nm	(50%:50%) 30nm	
E2	HATCN	SpMA1	SpMA3	V2:TER5	ST2	ST2:LiQ	LiQ 1nm
	5nm	125nm	10nm	(97%:3%) 35nm	10nm	(50%:50%) 30nm	
	HATCN	SpMA1	SpMA3	V2:IC3:TER5	ST2	ST2:LiQ	LiQ 1nm
E3	5nm	125nm	10nm	(72%:25%:3%)	10nm	(50%:50%) 30nm	
				35nm			
E4	HATCN	SpMA1	SpMA3	EG1:TER5	ST2	ST2:LiQ	LiQ 1nm
L4	5nm	125nm	10nm	(97%:3%) 35nm	10nm	(50%:50%) 30nm	
	HATCN	SpMA1	SpMA3	EG1:IC2:TER5	ST2	ST2:LiQ	LiQ 1nm
E5	5nm	125nm	10nm	(72%:25%:3%)	10nm	(50%:50%) 30nm	
				35nm			
	HATCN	SpMA1	SpMA3	EG1:IC3:TER5	ST2	ST2:LiQ	LiQ 1nm
E6	5nm	125nm	10nm	(72%:25%:3%)	10nm	(50%:50%) 30nm	
				35nm			

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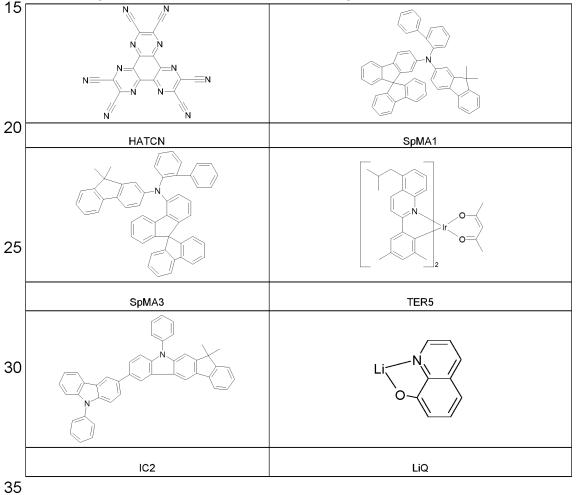
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		HATCN	SpMA1	SpMA3	EG2:IC3:TER5	ST2	ST2:LiQ	LiQ 1nm
	E7	5nm	125nm	10nm	(72%:25%:3%)	10nm	(50%:50%) 30nm	
					35nm			
		HATCN	SpMA1	SpMA3	EG3:IC3:TER5	ST2	ST2:LiQ	LiQ 1nm
	E8	5nm	125nm	10nm	(72%:25%:3%)	10nm	(50%:50%) 30nm	
					35nm			
5		HATCN	SpMA1	SpMA3	EG4:IC3:TER5	ST2	ST2:LiQ	LiQ 1nm
	E9	5nm	125nm	10nm	(72%:25%:3%)	10nm	(50%:50%) 30nm	
					35nm			
		HATCN	SpMA1	SpMA3	EG5:IC3:TER5	ST2	ST2:LiQ	LiQ 1nm
	E10	5nm	125nm	10nm	(72%:25%:3%)	10nm	(50%:50%) 30nm	
					35nm			
10		HATCN	SpMA1	SpMA3	EG6:IC3:TER5	ST2	ST2:LiQ	LiQ 1nm
10	E11	5nm	125nm	10nm	(72%:25%:3%)	10nm	(50%:50%) 30nm	
					35nm			

Table 2: Structures of the materials used in OLEDs



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5		
	ST2	IC3
10		
15		
	V1	V2
20		
	EG1(5j)	EG2 (10j)
30		
	EG3 (27j)	EG4 (25j)

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Table 3: OLEDs data

Ex.	U1000	CIE x/y bei	jo	EQE	L1	LT
	(V)	1000 cd/m ²	(mA/cm²)	1000	(%)	(h)
				%		
E1	4,6	0.67/0.34	20	14	95	330
E2	3.9	0.67/0.33	20	15	95	610
E3	3.6	0.67/0.34	20	16	95	780
E4	3.2 0.67/0.33		20	19	95	890
E5	3.3	0.67/0.33	20	20	95	1230
E6	3.4	0.67/0.33	20	21	95	980
E7	3.5	0.67/0.34	20	19.1	95	1001
E8	3.4	0.67/0.33	20	19,6	95	1180
E9	3.4	0.67/0.34	20	18,9	95	1210
E10	3.4	0.67/0.33	20	19,1	95	990
E11	3.3	0.67/0.34	20	20	95	1245

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Patent Claims

1. Compound of the formula (1),

5
$$\begin{array}{c} x^3 \\ x^4 \\ y^3 \\ y^3 \\ y^2 \\ y^3 \\ y^2 \\ y^3 \\ y^2 \\ y^3 \\ y^4 \\ y^3 \\ y^2 \\ y^3 \\ y^3 \\ y^2 \\ y^3 \\ y^$$

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formula (1)

where the following applies to the symbols and indices used:

Ar^s stands on each occurrence, identically or differently, for a single bond or for an aromatic or heteroaromatic ring system having 5 to 30 aromatic ring atoms, which may be substituted by one or more radicals R;

 X^1 to X^4 stand on each occurrence, identically or differently, for CR^1 or N;

Y¹ to Y⁴ stand on each occurrence, identically or differently, for CR² or N; with the proviso that the group Ar^S as depicted in formula (1) is bonded to one of the group Y¹, Y², Y³ or Y⁴ which stands for C; and exactly two non-adjacent groups Y, namely Y¹ and Y⁴, Y¹ and Y³ or Y² and Y⁴ stand for N;

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characterized in that:

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Z¹ to Z⁸ stand on each occurrence, identically or differently, for CR³ or N; where at least two adjacent groups Z selected from Z¹-Z², Z²-Z³, Z³-Z⁴, Z⁵-Z⁶, Z⁶-Z⁷ and Z⁷-Z⁸ form together an heteroaromatic ring system selected from groups of formula (Het-1) or (Het-2),

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$$* \underbrace{\sum_{Z^{12}}^{N} Z^{11}}_{*} \underbrace{\sum_{Z^{10}}^{12} Z^{9}}_{*} \times \underbrace{\sum_{Z^{10}}^{N} Z^{9}}_{*} \times$$

where

the signs * indicate the bonding positions to Z^1 - Z^2 , Z^2 - Z^3 , Z^3 - Z^4 , Z^5 - Z^6 , Z^6 - Z^7 or Z^7 - Z^8 in formula (1);

Z⁹ to Z¹² stand on each occurrence, identically or differently, for CR³ or N;

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

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60 aromatic ring atoms, which may be substituted by one or more radicals R;

and at least two adjacent groups Z, selected from Z^1 - Z^2 , Z^2 - Z^3 , Z^3 - Z^4 , Z^5 - Z^6 , Z^6 - Z^7 , Z^7 - Z^8 , Z^9 - Z^{10} , Z^{10} - Z^{11} and Z^{11} - Z^{12} , form together an aromatic ring of formula (Aro-1),

*
$$Z^{16}$$

* Z^{13}

(Aro-1)

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where Z¹³ to Z¹⁶ stand on each occurrence, identically or differently, for CR³ or N; and where the signs * indicate the bonding positions to Z¹-Z², Z²-Z³, Z³-Z⁴, Z⁵-Z⁶, Z⁶-Z⁷, Z⁷-Z⁸ Z⁹-Z¹⁰, Z¹⁰-Z¹¹ or Z¹¹-Z¹²;

R¹, R² and R³ stand on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CHO, CN, C(=0)Ar, $P(=0)(Ar)_2$, S(=0)Ar, $S(=0)_2Ar$, N(R)₂, N(Ar)₂, NO₂, Si(R)₃, B(OR)₂, OSO₂R, a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 40 C atoms or branched or a cyclic alkyl, alkoxy or thioalkyl groups having 3 to 40 C atoms, each of which may be substituted by one or more radicals R, where in each case one or more non-adjacent CH₂ groups may be replaced by RC=CR, C=C, Si(R)₂, Ge(R)₂, Sn(R)₂, C=O, C=S, C=Se, P(=O)(R), SO, SO₂, O, S or CONR and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂, an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R, or an aryloxy groups having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R; where two adjacent radicals R¹ may form an aliphatic or aromatic ring system together, which may be substituted by one or more radicals R, where one radical R² and one radical R¹ may form a ring, which may be

substituted by one or more radicals R, and where two adjacent radicals R³ may form an aliphatic or aromatic ring system together, which may be substituted by one or more radicals R;

- R stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, 5 CHO, CN, C(=0)Ar, P(=0)(Ar)₂, S(=0)Ar, S(=0)₂Ar, N(R')₂, N(Ar)₂, NO₂, Si(R´)₃, B(OR´)₂, OSO₂R´, a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 40 C atoms or branched or a cyclic alkyl, alkoxy or thioalkyl groups having 3 to 40 C atoms, each of which may be 10 substituted by one or more radicals R´, where in each case one or more non-adjacent CH₂ groups may be replaced by R´C=CR´, C=C, Si(R´)₂, Ge(R')2, Sn(R')2, C=O, C=S, C=Se, P(=O)(R'), SO, SO2, O, S or CONR' and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN 15 or NO₂, an aromatic or heteroaromatic ring systems having 5 to 60 aromatic ring atoms, which may in each case be substituted by one or more radicals R', or an aryloxy groups having 5 to 60 aromatic ring atoms, which may be substituted by one or more radicals R'; where two adjacent radicals R may form an aliphatic or aromatic ring system 20 together, which may be substituted by one or more radicals R';
 - Ar is, on each occurrence, identically or differently, an aromatic or heteroaromatic ring system having 5 to 60 aromatic ring atoms, which may in each case also be substituted by one or more radicals R´;

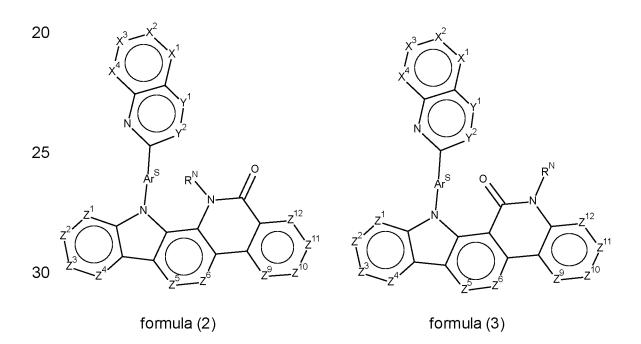
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R stands on each occurrence, identically or differently, for H, D, F, Cl, Br, I, CN, a straight-chain alkyl, alkoxy or thioalkyl groups having 1 to 20 C atoms or branched or cyclic alkyl, alkoxy or thioalkyl groups having 3 to 20 C atoms, where in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

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- 2. Compound according to claim 1, characterized in that:
 - Y⁴ stands for N;

- Y³ is bonded to the group Ar^S in formula (1) and stands for C;
- one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR².
- 3. Compound according to claim 1 or 2, characterized in that Y² stands for N and Y¹ stands for CR².
- 4. Compound according to one or more of the preceding claims, characterized in that it X¹ to X⁴ stand on each occurrence, identically or differently, for CR¹.
- 5. Compound according to one or more of the preceding claims, characterized in that it is selected from the compounds of one of the formulae (2) to (13),



WO 2021/052924

formula (7)

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$$z^{2}$$
 z^{2}
 $z^{$

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formula (6)

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$$z^{2}$$
 z^{2}
 z^{2}
 z^{2}
 z^{2}
 z^{2}
 z^{2}
 z^{2}
 z^{2}
 z^{2}

Formula (8)

 z^{2}
 z^{2}

20
$$x^3$$
 x^4 x^4 x^5 x

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$$z^{2}$$
 z^{3}
 z^{2}
 z^{4}
 z^{2}
 z^{2}

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formula (12)

formula (13)

where

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- the symbols X¹-X⁴, Ar^S and R^N have the same meaning as in claim 1;

- Z¹-Z¹² stand on each occurrence, identically or differently, for CR³ or N;

in formulae (2), (3), (6) and (7), at least two adjacent groups Z, selected from to Z¹-Z², Z²-Z³, Z³-Z⁴, Z⁵-Z⁶, Z⁰-Z¹⁰, Z¹⁰-Z¹¹ and Z¹¹-Z¹², form together an aromatic ring of formula (Aro-1) as defined in claim 1;

in formulae (4), (5), (8) and (9), at least two adjacent groups Z, selected from to Z¹-Z², Z²-Z³, Z³-Z⁴, Z²-Z³, Z³-Z⁴, Z²-Z³, Z³-Z¹¹, Z¹¹-Z¹¹ and Z¹¹-Z¹², form together an aromatic ring of formula (Aro-1) as defined in claim 1; and where

in formulae (10), (11), (12) and (13), at least two adjacent groups Z, selected from Z¹-Z², Z²-Z³, Z³-Z⁴, Z9-Z¹0, Z¹0-Z¹¹ and Z¹¹-Z¹², form together an aromatic ring of formula (Aro-1) as defined in claim 1;

one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR².

6. Compound according to one or more of the preceding claims, characterized in that it is selected from the compounds of formulae (2-1) to (2-7) or (3-1) to (3-7),

- 147 -

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$$(R^{2})$$
 (R^{3}) $(R$

formula (2-7)

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formula (2-6)

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formula (3-7)

5(
$$\mathbb{R}^3$$
) \mathbb{R}^N (\mathbb{R}^3) \mathbb{R}^N (\mathbb{R}^3) \mathbb{R}^N formula (3-4) \mathbb{R}^3 \mathbb{R}^N (\mathbb{R}^3) \mathbb{R}^N \mathbb{R}^N \mathbb{R}^N \mathbb{R}^3 \mathbb{R}^N $\mathbb{R}^$

where

X¹-X⁴, Ar^s, R³ and R^N have the same meaning as in claim 1;
one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR²;
p is an integer of 0 to 2;
m is an integer of 0 to 4; and

n is an integer of 0 to 6.

7. Compound according to one or more of the claims 1 to 5, characterized in that it is selected from compounds of formulae (4-1) to (4-7) or (5-1) to (5-7),

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$$(R^3)$$
 R^N
 (R^3)
 R^N

formula (4-1)

formula (4-2)

$$\left(\mathbb{R}^3\right)_{m}$$

formula (4-3)

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- 152 -

formula (5-2)

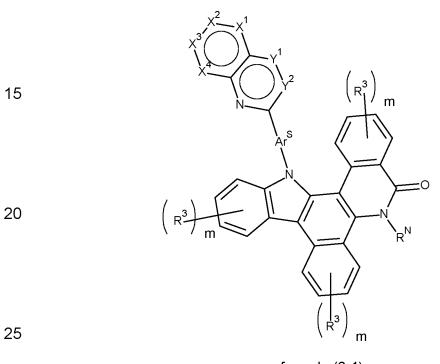
- 153 -

35 where

- 154 -

X¹-X⁴, ArS, R³ and RN have the same meaning as in claim 1; one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR²; p is an integer of 0 to 2; m is an integer of 0 to 4; and n is an integer of 0 to 6.

8. Compound according to one or more of the claims 1 to 5, characterized in that it is selected from compounds of formulae (6-1) to (6-7) or (7-1) to (7-7),



formula (6-1)

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- 156 -

formula (7-1)

- 157 -

- 158 -

where

- X¹-X⁴, Ar^S, R³ and R^N have the same meaning as in claim 1;
- one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR²;

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- p is an integer of 0 to 2;
- m is an integer of 0 to 4; and
- n is an integer of 0 to 6.

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9. Compound according to one or more of the claims 1 to 5, characterized in that it is selected from compounds of formulae (8-1) to (8-7) or (9-1) to (9-7),

- 159 -

formula (8-1)

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(R³) p

(R³) p

formula (8-2) formula (8-3)

- 160 -

formula (8-6)

- 161 -

$$(R^3)$$
 m (R^3) m (R^3) m

formula (9-1)

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35 where

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- X¹-X⁴, Ar^S, R³ and R^N have the same meaning as in claim 1;
- one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR²;
- p is an integer of 0 to 2;
- 5 m is an integer of 0 to 4; and
 - n is an integer of 0 to 6.
 - 10. Compound according to one or more of the claims 1 to 5, characterized in that it is selected from the compounds of formulae (10-1) to (10-6) or (11-1) to (11-6),

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- 165 -

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$$R^3$$
 R^3
 R

- 166 -

where

- X¹-X⁴, Ar^S, R³ and R^N have the same meaning as in claim 1;
- one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR²;
 - p is an integer of 0 to 2;
 - m is an integer of 0 to 4; and
 - n is an integer of 0 to 6.

11. Compound according to one or more of the claims 1 to 5, characterized in that it is selected from compounds of formulae (12-1) to (12-6) or (13-1) to (13-6),

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20
$$\left(\mathbb{R}^{3}\right)$$
 $\left(\mathbb{R}^{3}\right)$ \left

formula (12-3)

formula (12-4)

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- 169 -

formula (13-3)

formula (13-4)

where

- X¹-X⁴, Ar^s, R³ and R^N have the same meaning as in claim 1;
- one group Y¹ or Y² corresponds to N and the other group Y¹ or Y² corresponds to CR²;
 - p is an integer of 0 to 2;
 - m is an integer of 0 to 4; and
 - n is an integer of 0 to 6.

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- 12. Compound according to one or more of the preceding claims, characterized in that R^N stands on each occurrence, identically or differently, for phenyl, biphenyl, terphenyl, quaterphenyl, fluorene, spirobifluorene, naphthalene, anthracene, phenanthrene, triphenylene, fluoranthene, indole, benzofuran, benzothiophene, dibenzofuran, dibenzothiophene, carbazole, indenocarbazole, indolocarbazole, phenanthroline, pyridine, pyrimidine, pyrazine, pyridazine, triazine, quinolone, benzopyridine, benzopyridazine, benzopyrimidine, quinazoline, benzimidazole, or a combination of two or three of these groups, each of which may be substituted by one or more radicals R.
- 15 13. Formulation comprising at least one compound according to one or more of the claims 1 to 12 and at least one solvent.
- 14. Electronic device comprising at least one compound according to one ormore of claims 1 to 12.
 - 15. Electronic device according to claim 14, characterized in that it is selected from the group consisting of organic electroluminescent devices, organic integrated circuits, organic field-effect transistors, organic thin-film transistors, organic light-emitting transistors, organic solar cells, dyesensitised organic solar cells, organic optical detectors, organic photoreceptors, organic field-quench devices, light-emitting electrochemical cells, organic laser diodes and organic plasmon emitting devices.

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16. Electronic device according to claim 14 or 15, which is an organic electroluminescent device, characterised in that the compound according to one or more of claims 1 to 12 is employed as a matrix material for emitters, a hole-transport-material or an electron-transport material.

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- 17. Electronic device according to claim 16, characterised in that the compound according to one or more of claims 1 to 12 is employed as a matrix material in an emitting layer comprising at least one compound according to one or more of claims 1 to 12 and at least one emitter.
- 18. Electronic device according to claim 17, characterized in that the emitting layer comprises:
 - a compound according to one or more of claims 1 to 12 as a first matrix material;
 - a second matrix material, which is different from the first matrix material;
 - and at least one emitter.

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19. Electronic device according to claim 18, characterized in that the second matrix material is selected from lactams, carbazole derivatives and indenocarbazole derivatives.

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20. Electronic device according to one or more of the claims 17 to 19, characterized in that the emitter is a phosphorescent material.

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INTERNATIONAL SEARCH REPORT

International application No PCT/EP2020/075693

A. CLASSIFICATION OF SUBJECT MATTER INV. C07D471/04 H01L51/00 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) C07D H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

Further documents are listed in the continuation of Box C.

C. DOCUM	ENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
А	WO 2013/064206 A1 (MERCK PATENT GMBH [DE]) 10 May 2013 (2013-05-10) cited in the application Example 9b in the table on page 52; claim 1; tables 1-3	1-20
А	EP 2 080 762 A1 (NIPPON STEEL CHEMICAL CO [JP]) 22 July 2009 (2009-07-22) compounds 25, 26 on page 9, compound 56 on page 12, compound 86 on page 16; claims 1,2,6	1-20
А	WO 2018/138039 A1 (MERCK PATENT GMBH [DE]) 2 August 2018 (2018-08-02) compounds in tables on pages 111-119, especially 1c, 8c, 9c, 10c, 11c, 14c, 16c, 21c, 22c, 25c, 26c, 27v, 29c, 31c; claims 1-6,15	1-20
	-/	

* Special categories of cited documents :	"T" later document published after the international filing date or priority	
"A" document defining the general state of the art which is not considered to be of particular relevance	date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
 "E" earlier application or patent but published on or after the international filing date "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 	 "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 	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family	
Date of the actual completion of the international search	Date of mailing of the international search report	
13 October 2020	22/10/2020	
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 Guspanová, Jana	

X See patent family annex.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/075693

A W0 2018/166932 A1 (MERCK PATENT GMBH [DE]) 1-20 20 September 2018 (2018-09-20) compounds EG8 on page 146 and EG18 to EG20 on page 147; claims 1,16,19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2020/075693

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