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(54) Title: MULTIFLUORINATED CONDUCTOR MATERIAL FOR LEDS FOR IMPROVING THE LIGHT OUTCOUPLING

(57) Abstract: Conductor material for LEDs for improving the light outcoupling, wherein the conductor material is selected from the group comprising hole conductor material, electron conductor material and/or emitter material, the conductor material comprises at least one conductive fluorinated organic substance having at least one fluorinated alkyl substituent, one fluorinated alkenyl substituent and/or one fluorinated alkynyl substituent, wherein at least two fluorine atoms are bonded to at least one carbon atom of the fluorinated substituent, and the conductive fluorinated organic substance has a refractive index of > 1.30 and < 1.55 .

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Multifluorinated conductor material for LEDs for improving the light outcoupling

The present invention relates to a conductor material for LEDs for improving the light outcoupling, to an organic light-emitting diode (OLED) or polymer light-emitting diode (polyLED) comprising the conductor material and also to luminous means which comprise such an organic light-emitting diode (OLED) or polymer light-emitting diode (polyLED).

OLEDs are known in the prior art. Typical OLEDs comprise small molecules and are made in a number of layers in the vacuum sublimation method. The simplest form of an organic light-emitting diode OLED consists of three layers. For an application in the field of flat screens, glass coated with ITO (indium tin oxide layer) is used as transparent support and first electrode. Calcium or aluminum, for example, is applied as second electrode to the polymer located thereon. At least two and at most about 7-8 layers are often used in an overall thickness of about 100 nm. The substrate consists of glass which is coated with the transparent conductive material ITO that serves as anode. The cathode consists of thin sputtered metal layers which adjoin the organic layers. The organic materials in which light is generated typically have a refractive index of 1.7. This value applies in the case of a wavelength in the near infrared; at about 1000 nm. Most materials have absorption in the blue or ultraviolet spectral range; the refractive index increases steeply in the direction of these resonance points. The light outcoupling from the layers takes place with a relatively high refractive index of about 1.7 – 1.8. The ITO has a refractive index in the range of 1.7-1.9.

Both organic light-emitting diodes OLEDs, for example consisting of small molecules, and those consisting of polymers, polyLEDs, have the disadvantage of too low a outcoupling efficiency, which usually outcouples only 20% up to a maximum of 50% of the light generated in the component. The rest of the light is coupled into waveguide modes which pass the light into the substrate or into the light-generating layer itself, where it is ultimately absorbed.

In the prior art there are a large number of organic light-generating materials. By way of example, EP-A2 0 848 579 describes a compound with a triphenylamine structure and a total of six $\text{CF}_3\text{-CPh}_2\text{-CF}_3$ substituents, this material being suitable for use in an electroluminescent element.

The organic materials used in the prior art as conductor material have a high outcoupling loss. For diodes such as OLEDs or polyLEDs, the outcoupling loss is the greatest source of loss for light emission from the diode. There is therefore a great need for a diode layer, particularly for applications in the display sector, with improved light outcoupling, i.e. a reduction of the outcoupling loss to improve the light generation of a diode.

It is an object of the present invention to provide in particular a conductor material for LEDs with improved light outcoupling properties.

In order to achieve this object, according to the invention a conductor material for LEDs for improving the light outcoupling is provided, wherein

- the conductor material is selected from the group comprising hole conductor material, electron conductor material and/or emitter material,
- the conductor material comprises at least one conductive fluorinated organic substance having at least one fluorinated alkyl substituent, one fluorinated alkenyl substituent and/or one fluorinated alkynyl substituent, wherein at least two fluorine atoms are bonded to at least one carbon atom of the fluorinated substituent, and
- the conductive fluorinated organic substance has a refractive index of ≥ 1.30 and ≤ 1.55 .

It has now surprisingly been found that a conductor material layer based on conductive fluorinated organic substances having a refractive index of ≥ 1.30 and ≤ 1.55 outcouples generated light considerably better than conductor material layers consisting of substances having a higher refractive index, with the outcoupling of light increasing as the refractive index of the conductive fluorinated organic substances according to the invention in the light-emitting layer decreases. Consequently, conductive fluorinated organic substances which have a refractive index of ≤ 1.50 and ≥ 1.30 , preferably of ≤ 1.45 and ≥ 1.34 , more preferably of ≤ 1.43 and ≥ 1.35 , particularly preferably of ≤ 1.41 and ≥ 1.37 and most preferably a refractive index of ≤ 1.41 and ≥ 1.39 , are particularly suitable. Further suitable conductive fluorinated organic substances may have a refractive index of 1.349, 1.352, 1.361 or 1.407, with a mean deviation of the refractive index of ± 0.002 .

Besides an advantageous refractive index of ≥ 1.30 and ≤ 1.55 , these materials also have a low dielectric constant ϵ .

Within the context of this invention, the conductor material may be a hole conductor material, electron conductor material and/or emitter material.

The conductive fluorinated organic substances according to the invention are thus particularly suitable as conductor material for the production of layers, for example for LEDs such as OLEDs or polyLEDs. Corresponding organic light-emitting diodes (OLEDs) or polymer light-emitting diodes (polyLEDs) according to the invention may comprise one or more layers of at least one conductive fluorinated organic substance with a refractive index of ≤ 1.50 and ≥ 1.30 , preferably of ≤ 1.45 and ≥ 1.34 , more preferably of ≤ 1.43 and ≥ 1.35 , particularly preferably of ≤ 1.41 and ≥ 1.37 and most preferably a refractive index of ≤ 1.40 and ≥ 1.39 .

OLEDs and/or polyLEDs according to the invention may be used in particular for luminous means. Such luminous means may comprise at least one, preferably 2 to 10, OLEDs and/or polyLEDs. The number of OLEDs and/or polyLEDs in the luminous means according to the invention may also be considerably higher.

Diodes according to the invention, such as OLEDs and/or polyLEDs may be contained in luminous means such as lamps, lights, beamers, segment-based and pixel-based display elements, background lighting systems of LCD displays of all kinds, emergency lighting and the like.

In order to improve the light outcoupling, it is therefore preferred that at least one light-outcoupling layer of the LED comprises at least one conductive fluorinated organic substance according to the invention. According to the invention, it is advantageous if the layer comprises, based on the overall weight of the layer, at least 20% by weight, preferably at least 30% by weight, more preferably at least 40% by weight, even more preferably at least 50% by weight, still more preferably at least 60% by weight, yet more preferably at least 70% by weight and most preferably at least 80% by weight of at least one of the conductive fluorinated organic substances according to the invention. One or more layers may also consist entirely of at least one, preferably at least 2 to 10, conductive fluorinated organic substances according to the invention.

The diode, in particular LED or OLED, may comprise at least one layer according to the invention, preferably 2 to 10 and more preferably 3 to 7 layers according to the invention. Layers formed according to the invention may comprise identical or different conductive fluorinated organic substances. Moreover, the weight content of the conductive fluorinated organic substances used according to the invention in the respective layers, based on the respective overall weight of the layer, may be identical or different.

It may be advantageous for the light outcoupling if the mean refractive index of all substances of at least one layer formed according to the invention is in the range of

≤ 1.5 and ≥ 1.3 , preferably of ≤ 1.45 and ≥ 1.34 , more preferably of ≤ 1.43 and ≥ 1.35 , particularly preferably of ≤ 1.41 and ≥ 1.37 and most preferably in the range of ≤ 1.41 and ≥ 1.39 .

The light outcoupling for a diode with at least one layer formed according to the invention, measured in lumens, with the layer having a mean refractive index D of ≥ 1.3 and ≤ 1.5 , may be for example around at least 5%, preferably around at least 10%, more preferably around at least 15%, even more preferably around at least 20%, still more preferably around at least 30% and most preferably around at least 40%, compared to the same arrangement but consisting of a conductor material having a higher mean refractive index D of $X = 1.8$.

Typical values for the layer thicknesses in a diode, in particular an OLED, are 15 – 150 nm for the ITO and 50 – 300 nm for the organic layers.

According to the invention, it has been found that conductor materials in which a number of hydrogen atoms are replaced by fluorine atoms and which then have a refractive index D of ≥ 1.30 and ≤ 1.55 are suitable according to the invention. Substances with perfluorinated linear or branched alkyl, alkenyl and/or alkynyl radicals or substituents with at least 4 carbon atoms, preferably 5 to 20 carbon atoms, in the chain have proven to be particularly advantageous for use as conductor materials for forming a diode layer.

Hereinbelow, substances which can be used according to the invention will be given, it being possible for these substances to be used for example as electron or hole conductors, in particular in OLEDs.

Conductive fluorinated organic substances that are suitable according to the invention may be selected from the group comprising aryl compounds, perfluorinated adamantane, triphenylamine compounds, carbazole compounds, oxadiazole compounds, triazole compounds, triazine compounds, fluorene compounds, hexaphenylbenzene compounds, phenanthroline compounds, pyridine compounds, polyfluorene with perfluorinated side chains, conjugated polymers, poly-para-phenylene vinylene (PPV), polyvinylcarbazole, metal complexes, in particular metal complexes comprising Al, Ga and/or Zn as metal ion, quinoline compounds, acetylacetonate compounds, bipyridine compounds, phenanthroline compounds and/or metal complexes comprising carboxylic acids as ligand.

Conductive fluorinated organic substances that are suitable according to the invention preferably have at least one fluorinated substituent in the form of a linear or branched alkyl, alkenyl and/or alkynyl radical or substituent.

Fluorinated substituents for which C_mF_{m+X} are preferred, in which
 5 $m = 1$ to 30, preferably $m = 2$ to 20, more preferably $m = 4$ to 17, even more preferably 6 to 15; and

$X = 0$ to $m+1$, with m being an integer. X is preferably at least 1 and at most $2 \cdot m + 1$.

According to one embodiment according to the invention, $m = 4$ to 18 and $X =$
 10 m to $2 \cdot m + 1$.

According to a further embodiment according to the invention, $m = 8$ to 16 and $X = m$ to $2 \cdot m + 1$.

According to a further embodiment according to the invention, $m = 10$ to 14 and $X = m$ to $2 \cdot m + 1$.

15 The maximum number of X is limited by the maximum possible number of fluorine atoms for the respective substituent. Thus, X is greater for an unsaturated linear alkyl radical or substituent than compared to a linear unsaturated radical or substituent with the same chain length.

The conductive fluorinated organic substance may be a monomer, oligomer or
 20 polymer, wherein the conductive fluorinated substance preferably comprises conjugated double and/or triple bonds and may preferably have a molecular weight of ≥ 100 and $\leq 300,000$, more preferably ≥ 1000 and $\leq 200,000$, even more preferably $\geq 10,000$ and $\leq 200,000$ and yet more preferably $\geq 50,000$ and $\leq 100,000$. The molecular weight for polymers that can be used according to the invention may also be considerably greater than
 25 300,000.

Within the context of this invention, the terms "alkyl, alkenyl, alkynyl, alkoxy, aryl, alkylene, arylene, amines, halogen, carboxylate derivatives, cycloalkyl, carbonyl derivatives, heterocycloalkyl, heteroaryl, heteroarylene, sulfonate, sulfate, phosphonate, phosphate, phosphine, phosphine oxide", unless stated otherwise, represent:

30 alkyl = linear or branched C_1 - C_{20} -alkyl, preferably ethyl, propyl, isopropyl, tert-butyl, butyl, pentane.

alkenyl = C_2 - C_{20} -alkenyl.

alkynyl = C_2 - C_{20} -alkynyl.

cycloalkyl = C_3 - C_{10} -cycloalkyl.

alkoxy = C₁-C₆-alkoxy.

alkylene = methylene; 1,1-ethylene; 1,2-ethylene; 1,1-propylidene; 1,2-propylene; 1,3-propylene; 2,2-propylidene; butan-2-ol-1,4-diyl; propan-2-ol-1,3-diyl; 1,4-butylene; cyclohexane-1,1-diyl; cyclohexane-1,2-diyl; cyclohexane-1,3-diyl; cyclohexane-1,4-diyl; cyclopentane-1,1-diyl; cyclopentane-1,2-diyl; and/or cyclopentane-1,3-diyl.

aryl = homo- or heteroaromatics having a molecular weight of ≤ 300 .

arylene = 1,2-phenylene; 1,3-phenylene; 1,4-phenylene; 1,2-naphthalenylene; 1,3-naphthalenylene; 1,4-naphthalenylene; 2,3-naphthalenylene; 1-hydroxy-2,3-phenylene; 1-hydroxy-2,4-phenylene; 1-hydroxy-2,5-phenylene; and/or 1-hydroxy-2,6-phenylene.

heteroaryl = pyridinyl; pyrimidinyl; pyrazinyl; triazolyl; pyridazinyl; 1,3,5-triazinyl; quinolinyl; isoquinolinyl; quinoxalinyl; imidazolyl; pyrazolyl; benzimidazolyl; thiazolyl; oxazolidinyl; pyrrolyl; carbazolyl; indolyl; and/or isoindolyl.

heteroarylene = pyridinediyl; quinolinediyl; pyrazodiyl; pyrazolediyl; triazolediyl; pyrazinediyl; and/or imidazolediyl; in particular pyridine-2,3-diyl; pyridine-2,4-diyl; pyridine-2,5-diyl; pyridine-2,6-diyl; pyridine-3,4-diyl; pyridine-3,5-diyl; quinoline-2,3-diyl; quinoline-2,4-diyl; quinoline-2,8-diyl; isoquinoline-1,3-diyl; isoquinoline-1,4-diyl; pyrazole-1,3-diyl; pyrazole-3,5-diyl; triazole-3,5-diyl; triazole-1,3-diyl; pyrazine-2,5-diyl; and/or imidazole-2,4-diyl.

C1-C6-heterocycloalkyl = piperidinyl; piperidine; 1,4-piperazine, tetrahydrothiophene; tetrahydrofuran; 1,4,7-triazacyclononane; 1,4,8,11-tetraazacyclotetradecane; 1,4,7,10,13-pentaazacyclopentadecane; 1,4-diaza-7-thiacyclononane; 1,4-diaza-7-oxacyclononane; 1,4,7,10-tetraazacyclododecane; 1,4-dioxane; 1,4,7-trithiacyclononane; pyrrolidine; and/or tetrahydropyran.

heterocycloalkylene = piperidin-1,2-ylene; piperidin-2,6-ylene; piperidin-4,4-ylidene; 1,4-piperazin-1,4-ylene; 1,4-piperazin-2,3-ylene; 1,4-piperazin-2,5-ylene; 1,4-piperazin-2,6-ylene; 1,4-piperazin-1,2-ylene; 1,4-piperazin-1,3-ylene; 1,4-piperazin-1,4-ylene; tetrahydrothiophen-2,5-ylene; tetrahydrothiophen-3,4-ylene; tetrahydrothiophen-2,3-ylene; tetrahydrofuran-2,5-ylene; tetrahydrofuran-3,4-ylene; tetrahydrofuran-2,3-ylene; pyrrolidin-2,5-ylene; pyrrolidin-3,4-ylene; pyrrolidin-2,3-ylene; pyrrolidin-1,2-ylene; pyrrolidin-1,3-ylene; pyrrolidin-2,2-ylidene; 1,4,7-triazacyclonon-1,4-ylene; 1,4,7-triazacyclonon-2,3-ylene; 1,4,7-triazacyclonon-2,9-ylene; 1,4,7-triazacyclonon-3,8-ylene; 1,4,7-triazacyclonon-2,2-ylidene; 1,4,8,11-tetraazacyclotetradec-1,4-ylene; 1,4,8,11-tetraazacyclotetradec-1,8-ylene; 1,4,8,11-tetraazacyclotetradec-2,3-ylene; 1,4,8,11-tetraazacyclotetradec-2,5-ylene; 1,4,8,11-tetraazacyclotetradec-1,2-ylene; 1,4,8,11-

tetraazacyclotetradec-2,2-ylidene; 1,4,7,10-tetraazacyclododec-1,4-ylene; 1,4,7,10-tetraazacyclododec-1,7-ylene; 1,4,7,10-tetraazacyclododec-1,2-ylene; 1,4,7,10-tetraazacyclododec-2,3-ylene; 1,4,7,10-tetraazacyclododec-2,2-ylidene; 1,4,7,10,13-pentaazacyclopentadec-1,4-ylene; 1,4,7,10,13-pentaazacyclopentadec-1,7-ylene; 1,4,7,10,13-pentaazacyclopentadec-2,3-ylene; 1,4,7,10,13-pentaazacyclopentadec-1,2-ylene; 1,4,7,10,13-pentaazacyclopentadec-2,2-ylidene; 1,4-diaza-7-thiacyclonon-1,4-ylene; 1,4-diaza-7-thiacyclonon-1,2-ylene; 1,4-diaza-7-thiacyclonon-2,3-ylene; 1,4-diaza-7-thiacyclonon-6,8-ylene; 1,4-diaza-7-thiacyclonon-2,2-ylidene; 1,4-diaza-7-oxacyclonon-1,4-ylene; 1,4-diaza-7-oxacyclonon-1,2-ylene; 1,4-diaza-7-oxacyclonon-2,3-ylene; 1,4-diaza-7-oxacyclonon-6,8-ylene; 1,4-diaza-7-oxacyclonon-2,2-ylidene; 1,4-dioxan-2,3-ylene; 1,4-dioxan-2,6-ylene; 1,4-dioxan-2,2-ylidene; tetrahydropyran-2,3-ylene; tetrahydropyran-2,6-ylene; tetrahydropyran-2,5-ylene; tetrahydropyran-2,2-ylidene; 1,4,7-trithiacyclonon-2,3-ylene; 1,4,7-trithiacyclonon-2,9-ylene; and/or 1,4,7-trithiacyclonon-2,2-ylidene.

heterocycloalkyl = pyrrolinyl; pyrrolidinyl; morpholinyl; piperidinyl; piperazinyl; hexamethyleneimine; 1,4-piperazinyl; tetrahydrothiophenyl; tetrahydrofuranyl; 1,4,7-triazacyclononan-yl; 1,4,8,11-tetraazacyclotetradecan-yl; 1,4,7,10,13-pentaazacyclopentadecan-yl; 1,4-diaza-7-thiacyclononan-yl; 1,4-diaza-7-oxacyclononan-yl; 1,4,7,10-tetraazacyclododecan-yl; 1,4-dioxan-yl; 1,4,7-trithiacyclononan-yl; tetrahydropyran-yl; and/or oxazolidin-yl.

amines = $-N(R)_2$ in which each R independently of one another is selected from the group comprising: H; C_1 - C_6 -alkyl; C_1 - C_6 -alkyl- C_6H_5 ; and/or phenyl, wherein both Rs may form an $-NC_3$ to $-NC_5$ heterocyclic ring closure.

halogen = F; Cl; Br and/or I, particularly preferably F.

sulfonate = $-S(O)_2OR$, in which R = H; C_1 - C_6 -alkyl; phenyl; C_1 - C_6 -alkyl- C_6H_5 ; Li; Na; K; Cs; Mg; and/or Ca.

sulfate = $-OS(O)_2OR$, in which R = H; C_1 - C_6 -alkyl; phenyl; C_1 - C_6 -alkyl- C_6H_5 ; Li; Na; K; Cs; Mg; and/or Ca.

sulfone: $-S(O)_2R$, in which R = H; C_1 - C_6 -alkyl; phenyl; C_1 - C_6 -alkyl- C_6H_5 and/or amines (to form sulfonamide) selected from the group comprising: $-NR'_2$, in which each R' independently of one another is selected from the group comprising: H; C_1 - C_6 -alkyl; C_1 - C_6 -alkyl- C_6H_5 ; and/or phenyl, wherein if both R's = C_1 - C_6 -alkyl, the R's together may form an $-NC_3$ to $-NC_5$ heterocyclic ring closure.

carboxylate derivatives = $-C(O)OR$, in which R is selected from the group comprising: H; C_1 - C_{20} -alkyl; phenyl; C_1 - C_6 -alkyl- C_6H_5 ; Li; Na; K; Cs; Mg; and/or Ca.

carbonyl derivatives = $-C(O)R$, in which R is selected from the group comprising: H; C_1 - C_6 -alkyl; phenyl; C_1 - C_6 -alkyl- C_6H_5 and/or amine (to form amide) selected from the group comprising: $-NR'_2$, in which each R' independently of one another is selected from the group comprising: H; C_1 - C_6 -alkyl; C_1 - C_6 -alkyl- C_6H_5 ; and/or phenyl, wherein if both
 5 R's = C_1 - C_6 -alkyl, the R's together may form an $-NC_3$ to $-NC_5$ heterocyclic ring closure.

phosphonate = $-P(O)(OR)_2$, in which each R independently of one another is selected from the group comprising: H; C_1 - C_6 -alkyl; phenyl; C_1 - C_6 -alkyl- C_6H_5 ; Li; Na; K; Cs; Mg; and/or Ca.

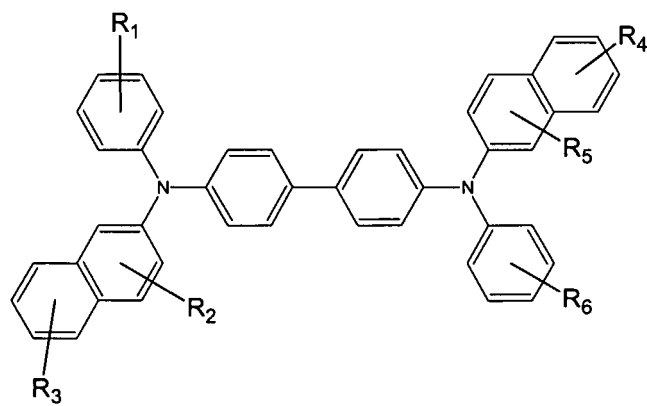
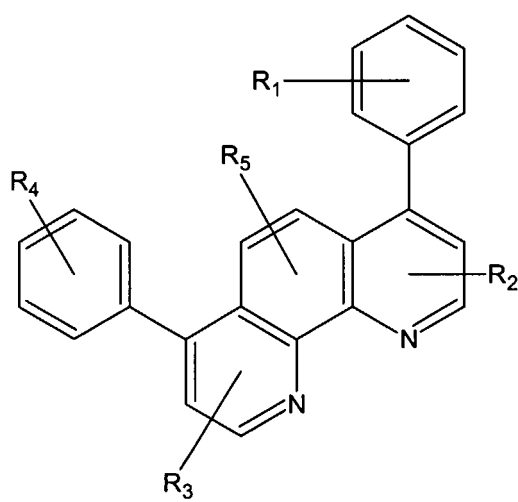
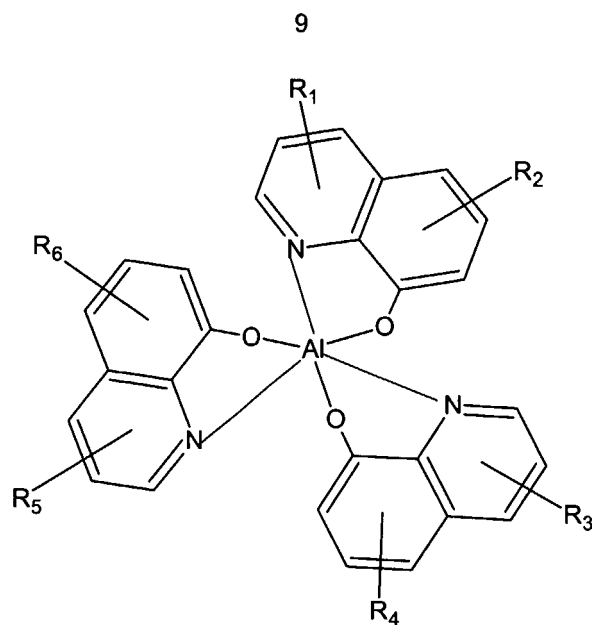
phosphate = $-OP(O)(OR)_2$, in which each R independently of one another is
 10 selected from the group comprising: H; C_1 - C_6 -alkyl; phenyl; C_1 - C_6 -alkyl- C_6H_5 ; Li; Na; K; Cs; Mg; and/or Ca.

phosphine = $-P(R)_2$, in which each R independently of one another is selected from the group comprising: H; C_1 - C_6 -alkyl; phenyl; C_1 - C_6 -alkyl- C_6H_5 .

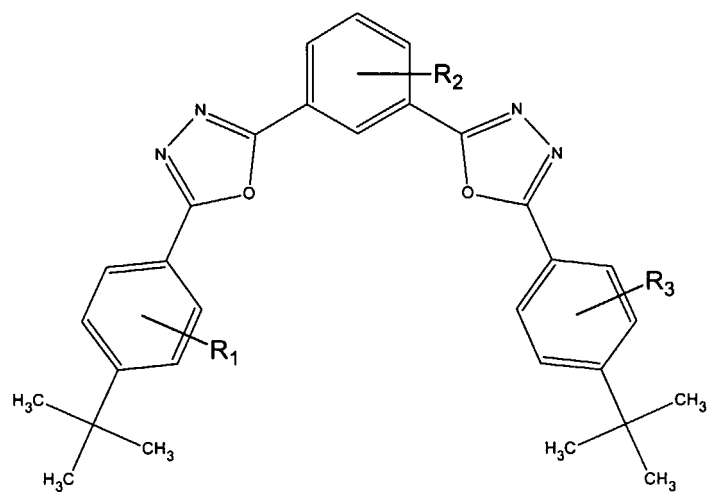
phosphine oxide = $-P(O)R_2$, in which each R independently of one another is
 15 selected from the group comprising: H; C_1 - C_6 -alkyl; phenyl; C_1 - C_6 -alkyl- C_6H_5 and/or amine (to form phosphonamidate) selected from the group comprising: $-NR'_2$, in which each R' independently of one another is selected from the group comprising: H; C_1 - C_6 -alkyl; C_1 - C_6 -alkyl- C_6H_5 ; and/or phenyl, wherein if both R's = C_1 - C_6 -alkyl, the R's together may form an $-NC_3$ to $-NC_5$ heterocyclic ring closure.

20 $R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8$ and/or R_9 are identical or different and are selected from the group comprising hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxy, aryl, alkylene, arylene, amines, halogen, carboxylate derivatives, cycloalkyl, carbonyl derivatives, heterocycloalkyl, heteroaryl, heteroarylene, sulfonate, sulfate, phosphonate, phosphate, phosphine and/or phosphine oxide, at least one radical R selected from the group $R_1, R_2, R_3,$
 25 R_4, R_5, R_6, R_7, R_8 and/or R_9 representing a fluorinated alkyl substituent, a fluorinated alkenyl substituent and/or a fluorinated alkynyl substituent in which at least two fluorine atoms are bonded to at least one carbon atom.

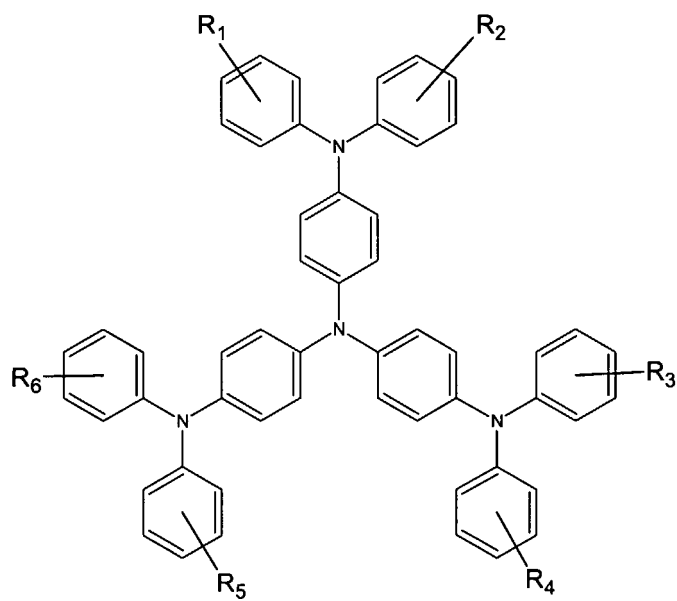
A conductive fluorinated organic substance that can be used according to the invention may preferably be selected from the group comprising at least one compound
 30 having one of the following structural formulae I to XX:



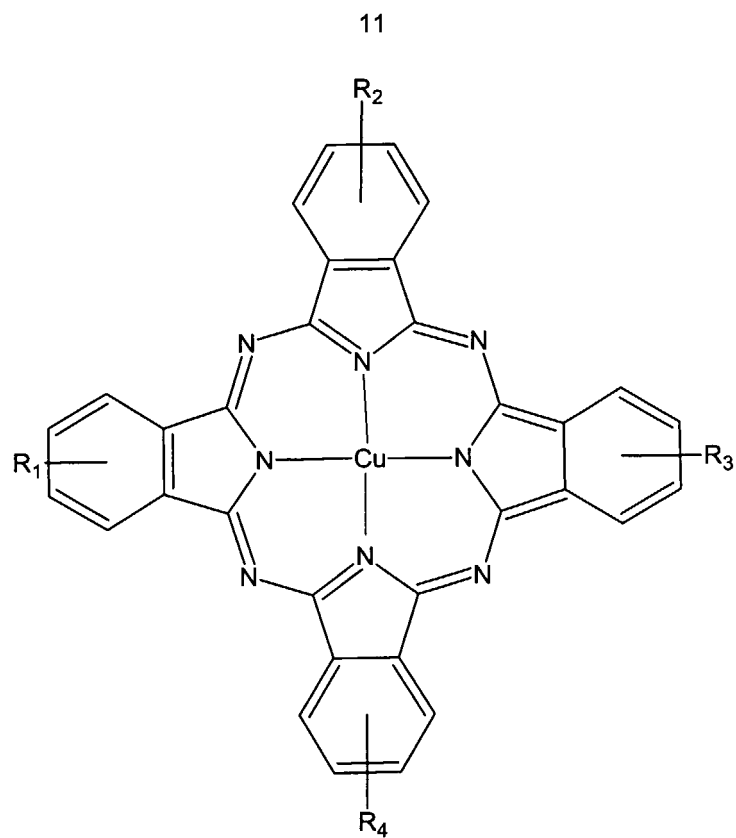
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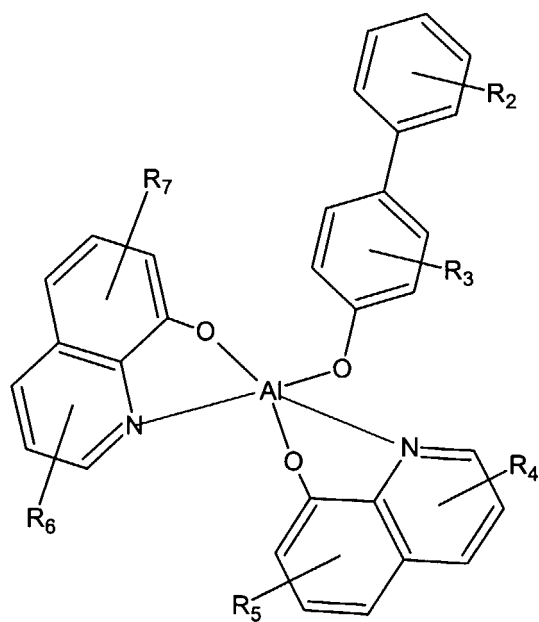
Formula IV



Formula V

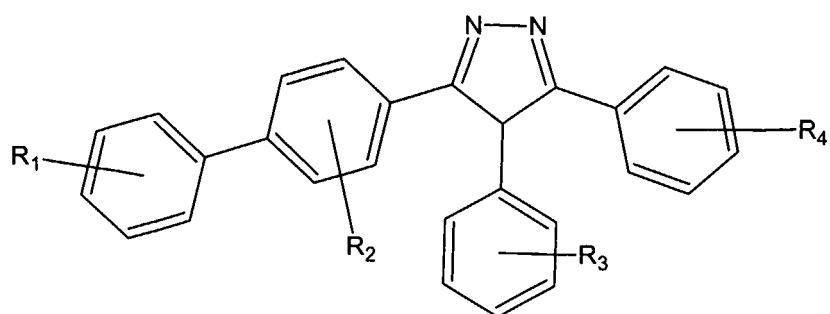


Formula VI

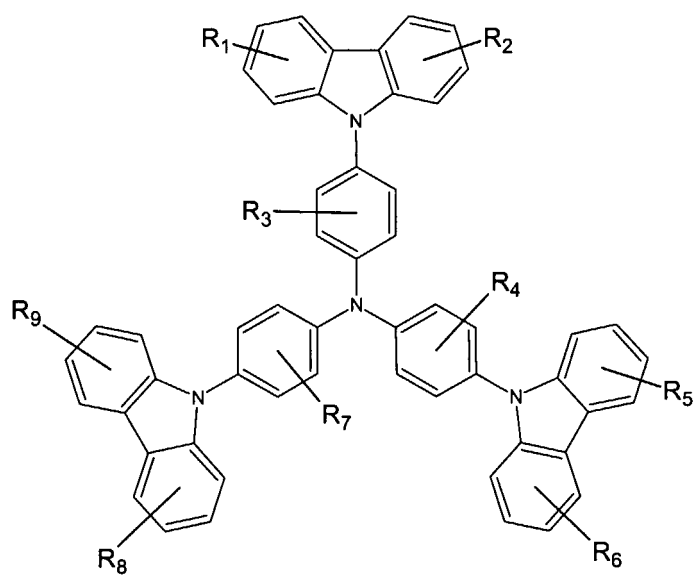


Formula VII

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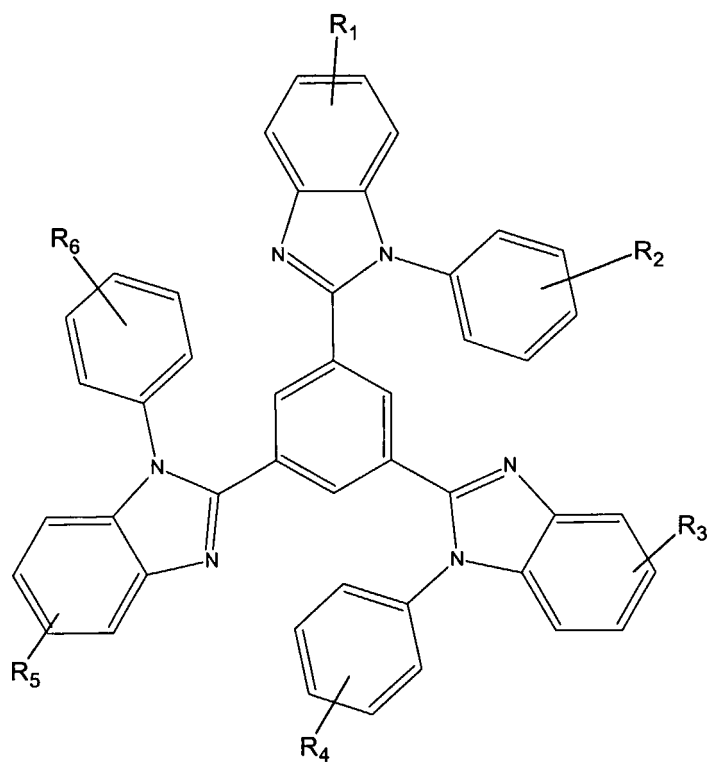


Formula VIII

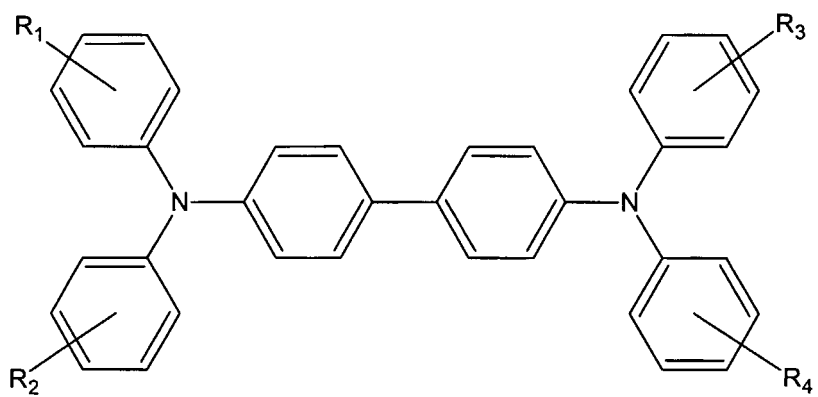


Formula IX

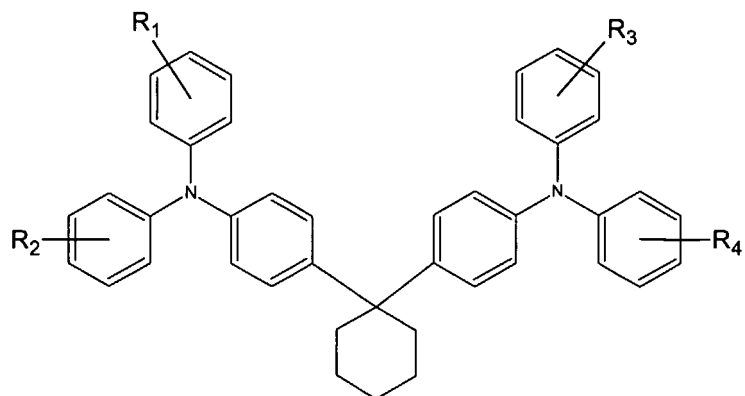
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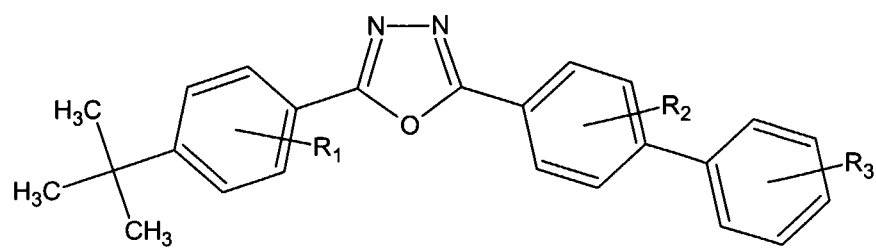
Formula X



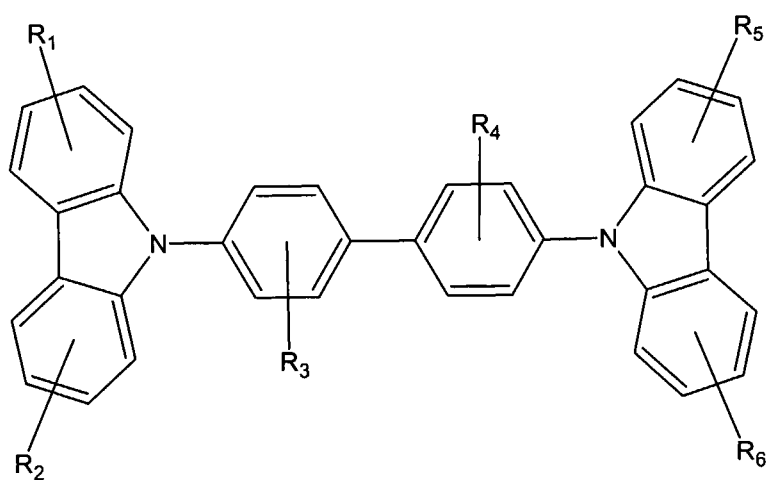
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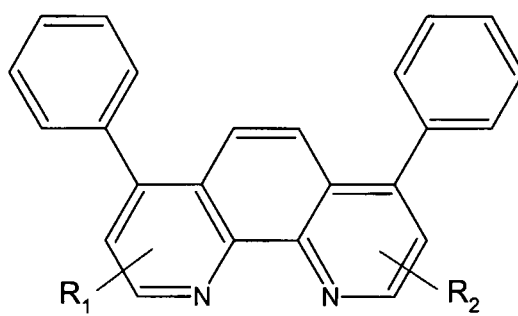
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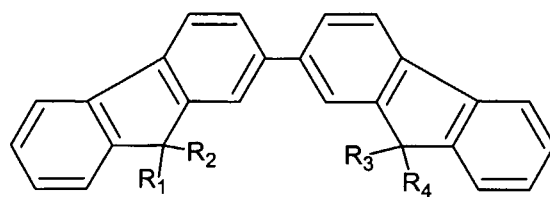
Formula XIII



Formula XIV

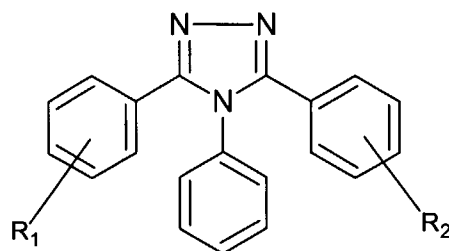


Formula XV

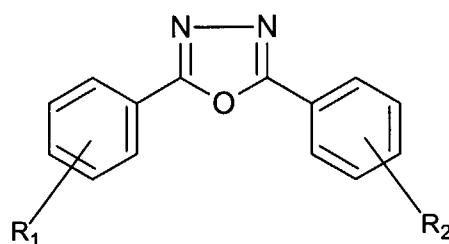


Formula XVI

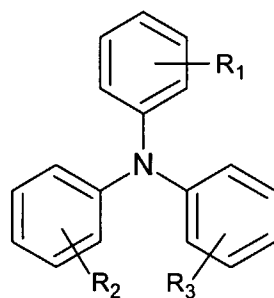
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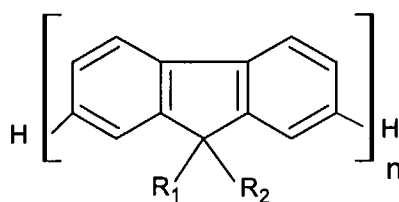
Formula XVII



Formula XVIII



Formula XIX



Formula XX

in which R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈ and/or R₉ are at least partially identical
 or different and are selected from the group comprising hydrogen, hydroxyl, alkyl, alkenyl,
 alkynyl, alkoxy, aryl, alkylene, arylene, amines, halogen, carboxylate derivatives, cycloalkyl,

carbonyl derivatives, heterocycloalkyl, heteroaryl, heteroarylene, sulfonate, sulfate, phosphonate, phosphate, phosphine and/or phosphine oxide,

wherein at least one radical R selected from the group R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈ and/or R₉ represents a fluorinated alkyl substituent, a fluorinated alkenyl substituent and/or a fluorinated alkynyl substituent in which at least two fluorine atoms are bonded to at least one carbon atom;

in which n = 1 to 10,000,000, preferably 10 to 1,000,000, more preferably 100 to 500,000, even more preferably 500 to 250,000, particularly preferably 1000 to 100,000 and most preferably 5000 to 50,000.

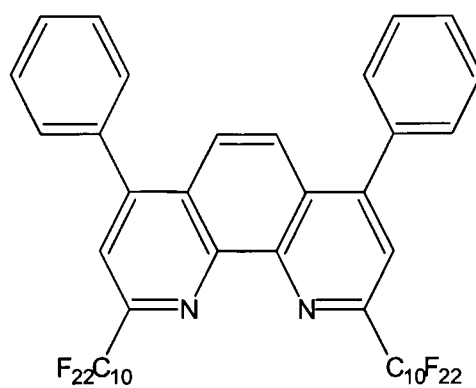
Preferably, at least one of the compounds according to formulae I to XX has at least one radical R selected from the group R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈ and/or R₉ which represents a fluorinated alkyl substituent, a fluorinated alkenyl substituent and/or a fluorinated alkynyl substituent which has at least 3 to 20 carbon atoms, preferably 4 to 15 carbon atoms, more preferably 5 to 12 carbon atoms and even more preferably 6 to 10 carbon atoms, to which at least seven fluorine atoms are bonded.

According to a further embodiment of the present invention, at least one of the compounds according to formulae I to XX has at least one radical R selected from the group R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈ and/or R₉ which represents a fluorinated alkyl substituent, a fluorinated alkenyl substituent and/or a fluorinated alkynyl substituent which

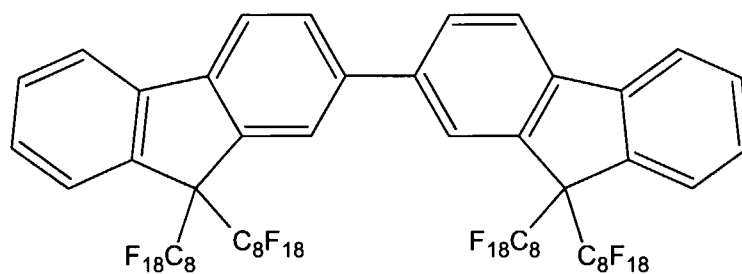
- has at least 4 carbon atoms, to which at least 7 to 9 fluorine atoms are bonded,
- preferably has at least 6 carbon atoms, to which at least 7 to 13 fluorine atoms are bonded,
- more preferably has at least 8 carbon atoms, to which at least 7 to 17 fluorine atoms are bonded,
- even more preferably has at least 10 carbon atoms, to which at least 7 to 21 fluorine atoms are bonded, and/or
- most preferably at least one alkyl substituent, alkenyl substituent and/or alkynyl substituent is perfluorinated.

According to the invention, most suitable conductive fluorinated organic substances may preferably be selected from the group comprising at least one compound having one of the following structural formulae XXI to XXVI:

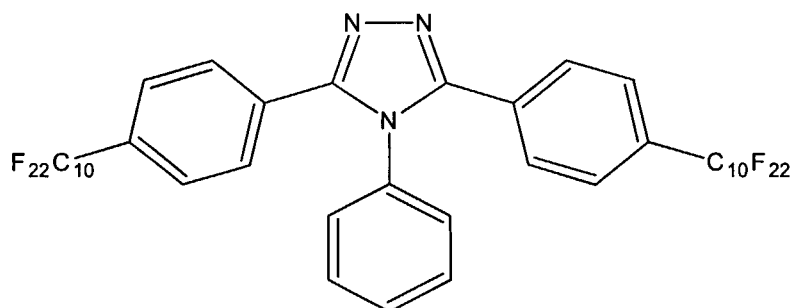
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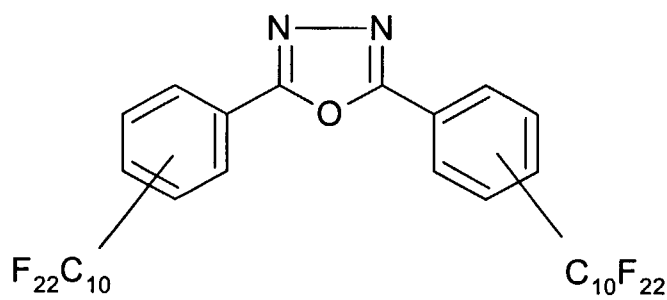
Formula XXI



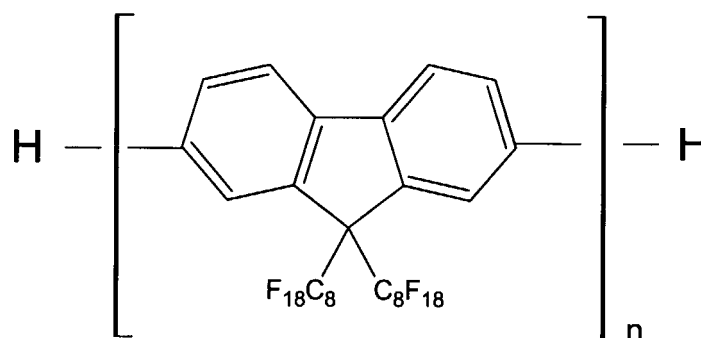
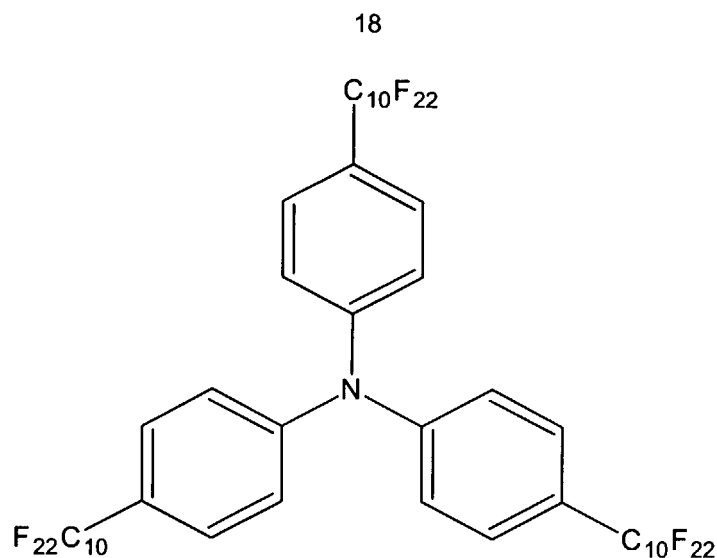
Formula XXII



Formula XXIII



Formula XXIV



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in which $n = 1$ to 10,000,000, preferably 10 to 1,000,000, more preferably 100 to 500,000, even more preferably 500 to 250,000, particularly preferably 1000 to 100,000 and most preferably 5000 to 50,000.

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For conductive fluorinated organic substances that can be used according to the invention and have a triphenylamine structure, it is advantageous if these have a fluorinated alkyl substituent, a fluorinated alkenyl substituent and/or a fluorinated alkynyl substituent which

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- has at least 4 carbon atoms, to which at least 7 to 9 fluorine atoms are bonded,
- preferably has at least 6 carbon atoms, to which at least 7 to 13 fluorine atoms are bonded,
- more preferably has at least 8 carbon atoms, to which at least 7 to 17 fluorine atoms are bonded, and/or

- most preferably has at least 10 carbon atoms, to which at least 7 to 21 fluorine atoms are bonded,

with the maximum number of fluorine atoms being limited by the respective alkyl substituent, alkenyl substituent and/or alkynyl substituent.

5 The refractive indices relate to a temperature of 23°C and a wavelength of $\lambda = 550$ nm and are given to an accuracy of ± 0.01 unless stated otherwise. A variable angle spectroscopic ellipsometer M2000V from J.A. Woollam was used to measure the refractive index.

10 In many OLEDs, the following layer structure is used: a first electrode, the anode, is located on a substrate. Adjoining the anode there is a hole-conductive layer, an emitting layer, an electron-conductive layer and a cathode. The holes are transported from the hole-conductive layer, which also facilitates the injection of holes from the anode, into the emitting layer. The emitting layer contains for example a matrix of a hole conductor or electron conductor material in which the light-emitting molecules are embedded. In the
15 emitting layer, the holes meet electrons which are transported from the cathode via the electron-conductive layer into the emitting layer. By recombination of the electrons and holes, excitons are produced which upon return to the basic state release energy. The light-emitting molecules in the emitting layer are excited directly or by energy transfer.

Since in most cases the holes are the majority charge carriers, it is
20 advantageous to add a so-called hole blocking layer between the emitting layer and the electron-conductive layer, which hole blocking layer prevents the transport of holes to the cathode. One disadvantage is that the holes pile up at the interface between emitting layer and hole blocking layer and build up a positive space charge at that point. The OLED thereby acts as a lossy capacitor.

25 It has been found that as the capacitance increases, the quantum efficiency of an OLED decreases. Causes of this are interactions between the excitons and charge carriers or charges (polarons), which may lead to undesirable quenching of the excitons. These interactions may arise in an amplified manner in the positive space charge zone which is located in the emitting layer.

30 At a given geometric size (area A, electrode spacing d) of a capacitor, the capacitance C is calculated according to the formula

$$C = (\epsilon \cdot \epsilon_0 \cdot A) / d$$

wherein ϵ_0 is the dielectric constant of empty space ($8.854 \cdot 10^{-12}$ As/Vm) and ϵ is the dielectric constant of the material of the dielectric.

A reduction in the capacitance C may be achieved by reducing the dielectric constant ϵ of the material of the dielectric, in this case the materials in the layers between anode and cathode and specifically in particular the materials in the emitting layer and the hole blocking layer. In this case, it is advantageous that the dielectric constant ϵ of the materials is < 5 , preferably < 4 and particularly preferably < 3 . A dielectric constant $\epsilon < 2.8$ is very particularly preferred and a dielectric constant $\epsilon < 2.5$ is even more particularly preferred. These materials have no permanent dipole moment and can be polarized only with difficulty.

By virtue of the reduced capacitance C , the stored charge in the OLED is reduced even at a constant voltage. A reduced space charge reduces the reactions between excitons and charge carriers or charges and thus prevents the undesirable quenching of the excitons.

The above-described materials according to the invention have such a low dielectric constant ϵ , and by using them as matrix in the emitting layer and/or in the hole blocking layer it is possible for the capacitance C to be lowered and for the quantum efficiency of an OLED to be increased. For instance, the calculated dielectric constant ϵ of 2,2',7,7'-tetraphenyl-9,9'-spirobifluorene (spiro-quarterphenyl) is 3.57 and the calculated dielectric constant ϵ of hexaphenylbenzene is 3.03.

CLAIMS:

1. A conductor material for LEDs for improving the light outcoupling, wherein
 - the conductor material is selected from the group comprising hole conductor material, electron conductor material and/or emitter material,
 - the conductor material comprises at least one conductive fluorinated organic substance having at least one fluorinated alkyl substituent, one fluorinated alkenyl substituent and/or one fluorinated alkynyl substituent, wherein at least two fluorine atoms are bonded to at least one carbon atom of the fluorinated substituent, and
 - the conductive fluorinated organic substance has a refractive index of ≥ 1.30 and ≤ 1.55 .
2. A conductor material as claimed in claim 1, wherein the fluorinated substituent is a linear or branched alkyl, alkenyl and/or alkynyl substituent.
3. A conductor material as claimed in claim 1 or 2, wherein C_mF_{m+X} applies in respect of at least one fluorinated substituent, in which
 - $m = 1$ to 20 , preferably $m = 2$ to 16 , more preferably $m = 4$ to 12 ; and
 - $X = 1$ to $m+1$, with m being an integer.
4. A conductor material as claimed in any of claims 1 to 3, wherein the conductive fluorinated organic substance is a monomer, oligomer or polymer, the conductive fluorinated substance preferably comprising conjugated double and/or triple bonds and preferably having a molecular weight of ≥ 100 and $\leq 300,000$.
5. A conductor material as claimed in any of claims 1 to 4, wherein the conductive fluorinated organic substance is selected from the group comprising aryl compounds, perfluorinated adamantane, triphenylamine compounds, carbazole compounds, oxadiazole compounds, triazole compounds, triazine compounds, fluorene compounds, hexaphenylbenzene compounds, phenanthroline compounds, pyridine compounds, polyfluorene with perfluorinated side chains, conjugated polymers, poly-para-phenylene

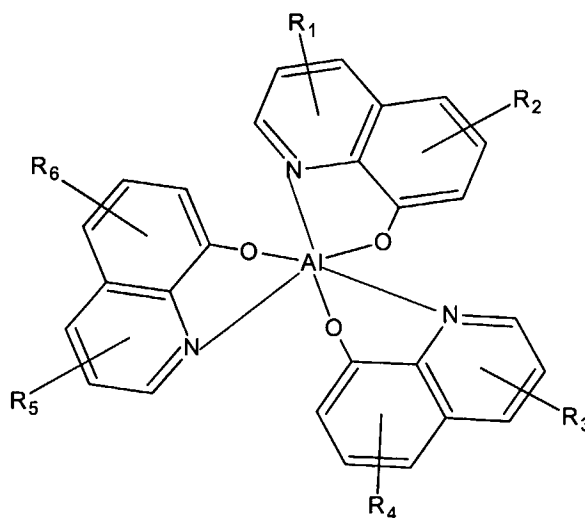
vinylene (PPV), polyvinylcarbazole, metal complexes, in particular metal complexes comprising Al, Ga and/or Zn as metal ion, quinoline compounds, acetylacetonate compounds, bipyridine compounds, phenanthroline compounds and/or metal complexes comprising carboxylic acids as ligand.

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6. A conductor material as claimed in any of claims 1 to 5, wherein the conductive fluorinated organic substance preferably has a refractive index of ≤ 1.50 , more preferably a refractive index of ≤ 1.45 , even more preferably a refractive index of ≤ 1.40 , particularly preferably a refractive index of ≤ 1.39 and most preferably a refractive index of ≤ 1.37 .

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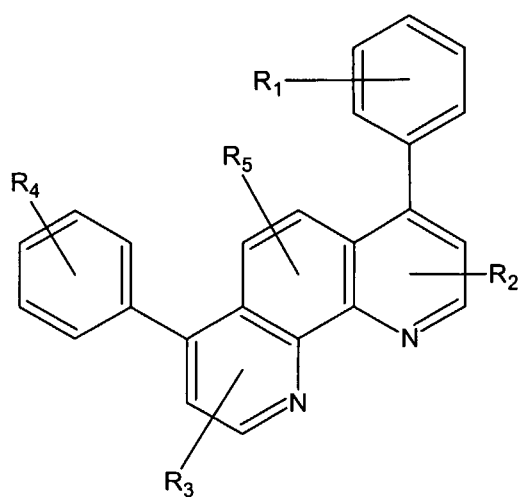
7. A conductor material as claimed in any of claims 1 to 6, wherein the conductive fluorinated organic substance is selected from the group comprising at least one compound having one of the following structural formulae I to XX:



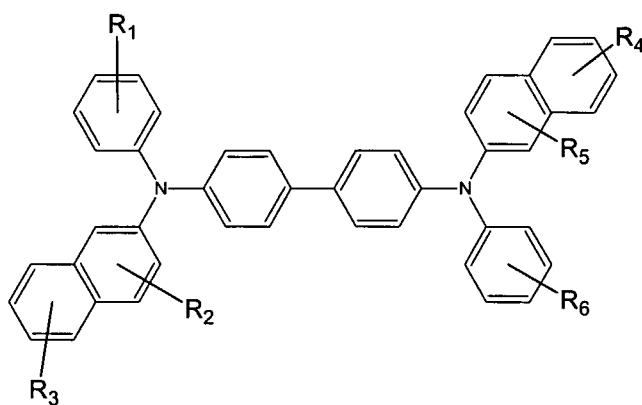
Formula I

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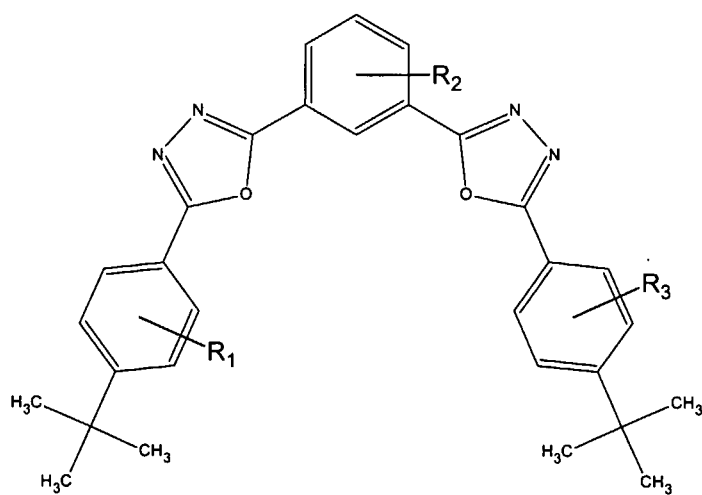


Formula II



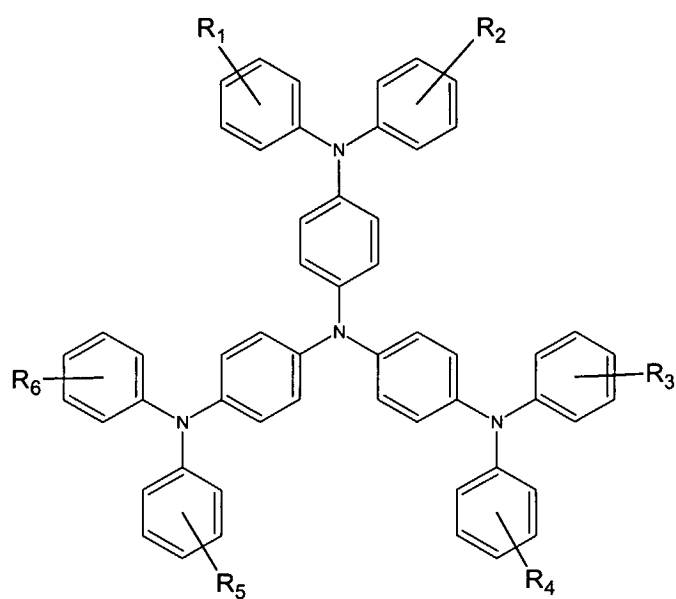
Formula III

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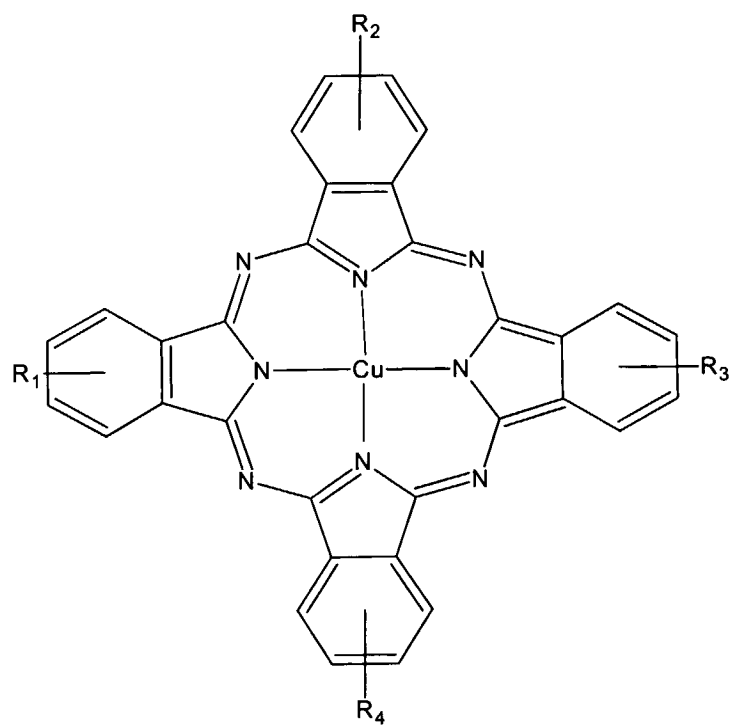


Formula IV

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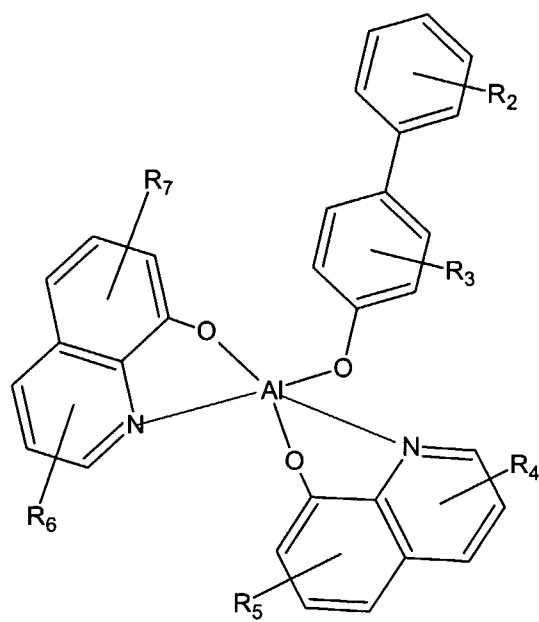


Formula V

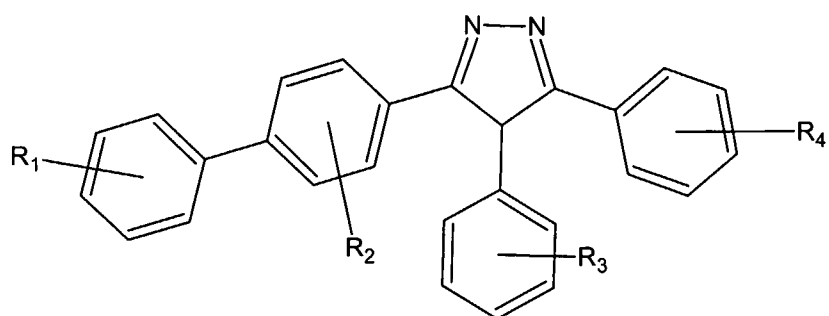


Formula VI

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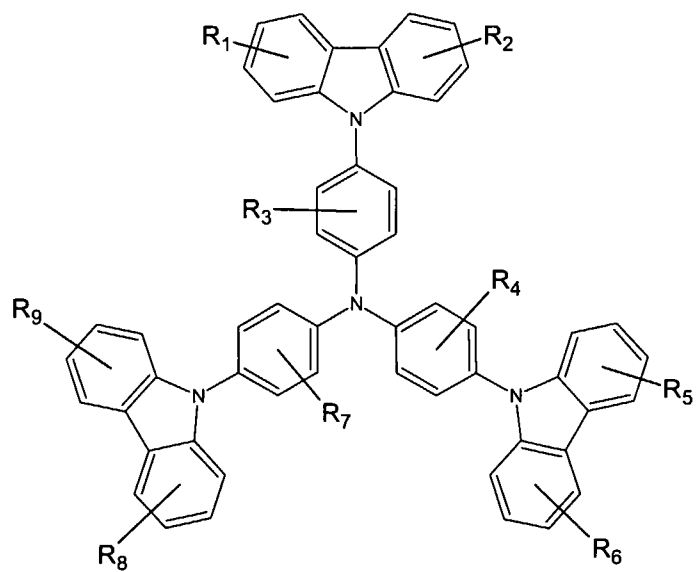


Formula VII



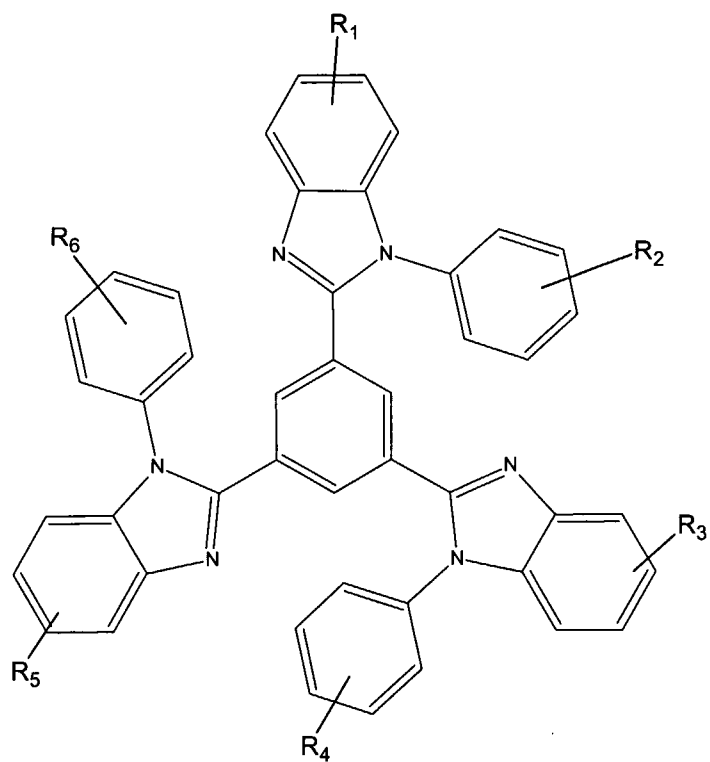
Formula VIII

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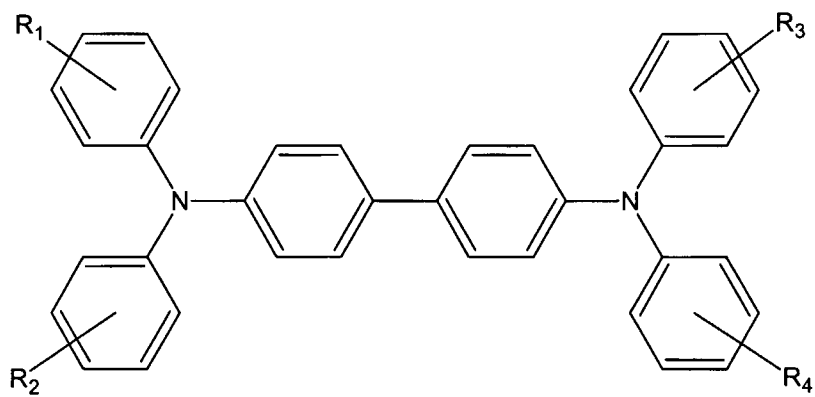
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Formula IX



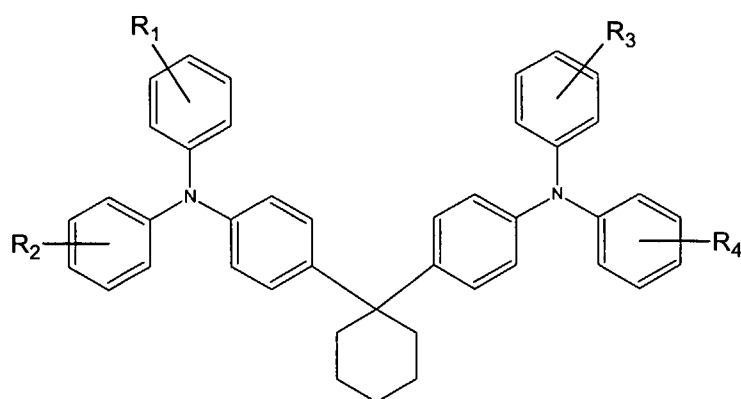
Formula X

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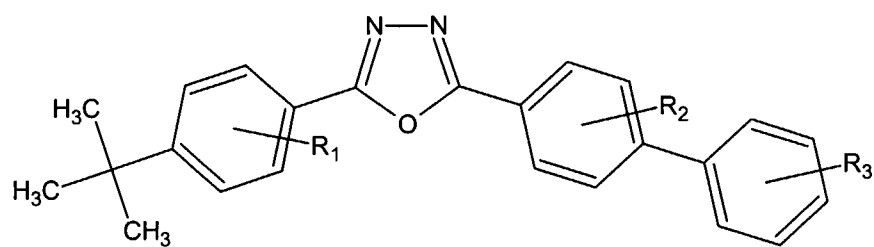


Formula XI

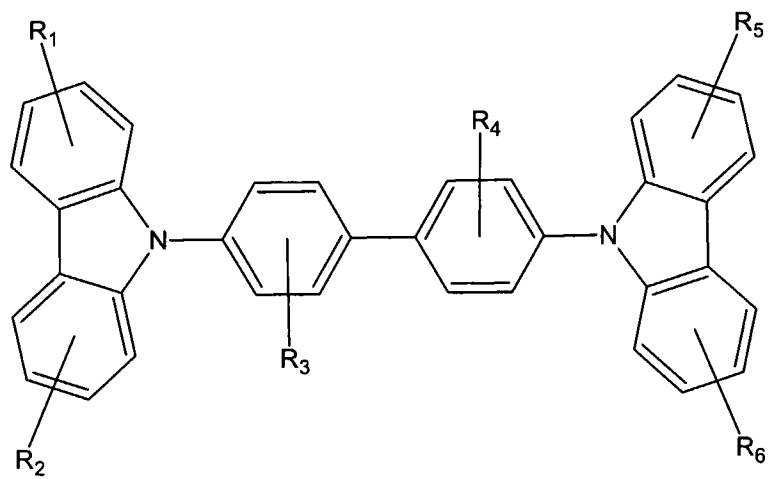
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Formula XII

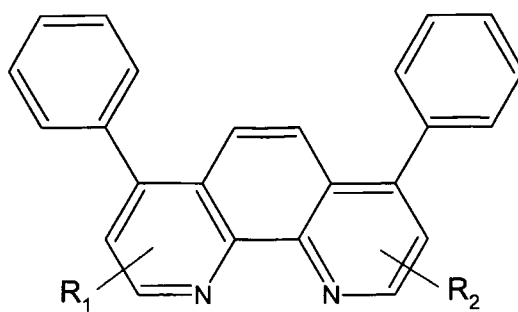


Formula XIII

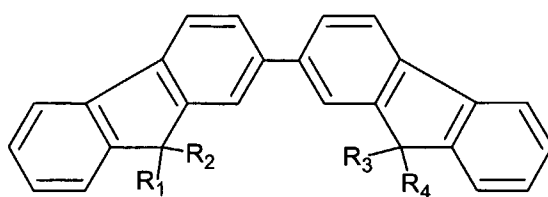


Formula XIV

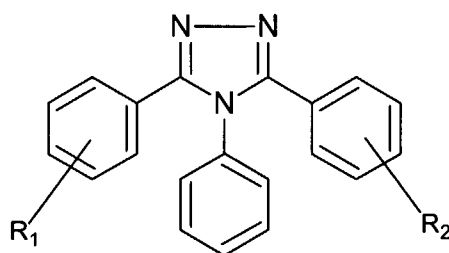
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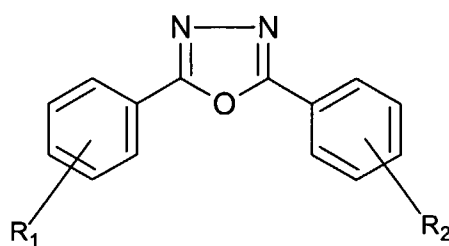
Formula XV



Formula XVI



Formula XVII

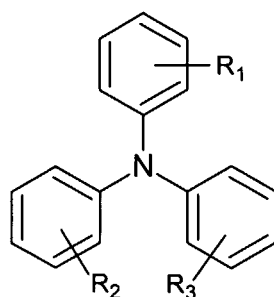


Formula XVIII

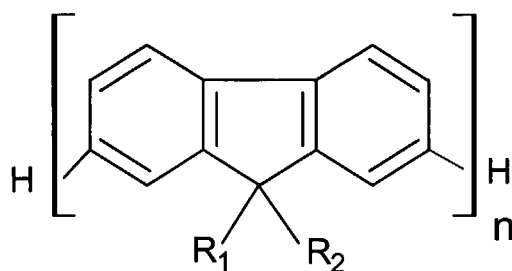
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Formula XIX



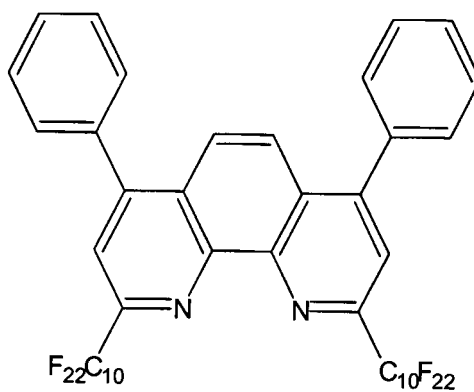
Formula XX

in which R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and R_9 are at least partially identical or different and are selected from the group comprising hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxy, aryl, alkylene, arylene, amines, halogen, carboxylate derivatives, cycloalkyl, carbonyl derivatives, heterocycloalkyl, heteroaryl, heteroarylene, sulfonate, sulfate, phosphonate, phosphate, phosphine and/or phosphine oxide, wherein at least one R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and/or R_9 represents a fluorinated alkyl substituent, a fluorinated alkenyl substituent and/or a fluorinated alkynyl substituent in which at least two fluorine atoms are bonded to at least one carbon atom; and

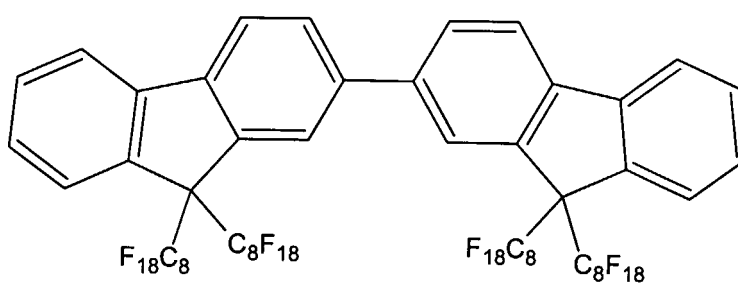
in which $n = 1$ to 10,000,000, preferably 10 to 1,000,000, more preferably 100 to 500,000, even more preferably 500 to 250,000, particularly preferably 1000 to 100,000 and most preferably 5000 to 50,000.

8. A conductor material as claimed in any of claims 1 to 7, wherein the conductive fluorinated organic substance is selected from the group comprising at least one compound having one of the following structural formulae XXI to XXVI:

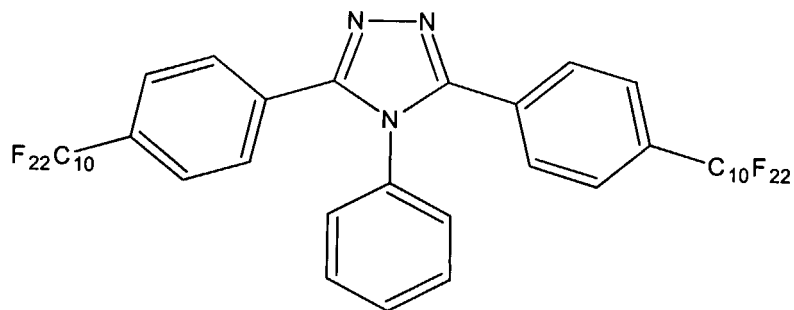
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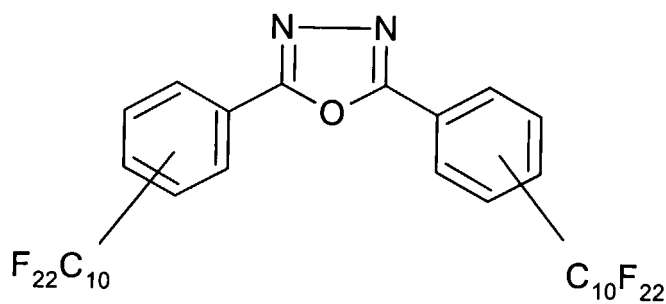
Formula XXI



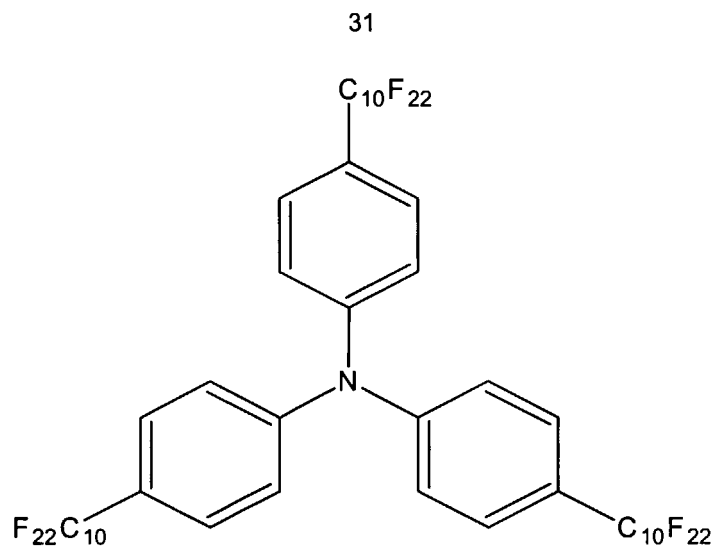
Formula XXII



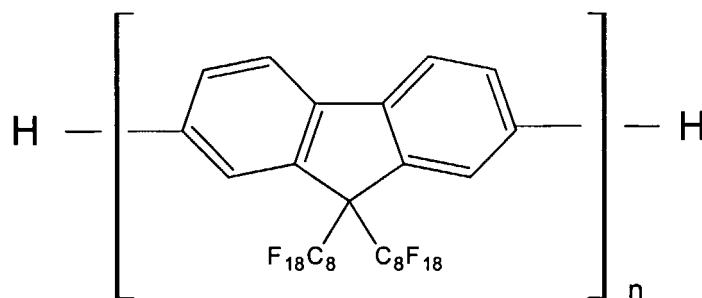
Formula XXIII



Formula XXIV



Formula XXV



Formula XXVI

in which $n = 1$ to 10,000,000, preferably 10 to 1,000,000, more preferably 100 to 500,000, even more preferably 500 to 250,000, particularly preferably 1000 to 100,000 and most preferably 5000 to 50,000.

9. A diode, in particular an organic light-emitting diode (OLED) or polymer light-emitting diode (polyLED), comprising one or more layers having a refractive index of $\geq X$ and ≤ 1.5 and/or one or more layers which comprise at least one conductive fluorinated organic substance as claimed in any of the preceding claims 1 to 8.

10. A luminous means comprising at least one diode, in particular an OLED and/or polyLED as claimed in claim 9.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB2004/050999

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L51/30

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)

IPC 7 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 practical, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/45184 A (BROWN BEVERLEY ANNE ; LEEMING STEPHEN WILLIAM (GB); YEATES STEPHEN GEO) 6 June 2002 (2002-06-06) formula 10 page 8, line 20 - line 24 -----	1-8
X	EP 0 848 579 A (TOYO INK MFG CO) 17 June 1998 (1998-06-17) cited in the application tables 1, structure, 7 -----	1-7
X	EP 0 917 216 A (LG ELECTRONICS INC) 19 May 1999 (1999-05-19) chemical formula II page 12 ----- -/--	1-7

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

30 August 2004

Date of mailing of the international search report

23. 11. 2004

Name and mailing address of the ISA

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Authorized officer

Wolfbauer, G

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB2004/050999

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>HOSHINO S ET AL: "DEVICE PERFORMANCE OF AN N-CHANNEL ORGANIC THIN-FILM TRANSISTOR WITH LiF/Al BILAYER SOURCE AND DRAIN ELECTRODES"</p> <p>JAPANESE JOURNAL OF APPLIED PHYSICS, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, JP, vol. 41, no. 7A, PART 2, 1 July 2002 (2002-07-01), pages L808-L810, XP001151607</p> <p>ISSN: 0021-4922</p> <p>figure 1</p> <p>-----</p>	1-7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2004/050999

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

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

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

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

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-8

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

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

1. claims: 1-8

A fluorinated organic conductor material for LEDs.

1.1. claims: 1-7

A conductor material represented by chemical Formula I.

1.2. claims: 1-8

A conductor material represented by chemical Formula II, XV and XXI.

1.3. claims: 1-7

A conductor material represented by chemical Formula III.

1.4. claims: 1-7

A conductor material represented by chemical Formula IV.

1.5. claims: 1-7

A conductor material represented by chemical Formula V.

1.6. claims: 1-7

A conductor material represented by chemical Formula VI.

1.7. claims: 1-7

A conductor material represented by chemical Formula VII.

1.8. claims: 1-7

A conductor material represented by chemical Formula VIII.

1.9. claims: 1-7

A conductor material represented by chemical Formula IX.

1.10. claims: 1-7

A conductor material represented by chemical Formula X.

1.11. claims: 1-7

A conductor material represented by chemical Formula XI.

1.12. claims: 1-7

A conductor material represented by chemical Formula XII.

1.13. claims: 1-7

A conductor material represented by chemical Formula XIII.

1.14. claims: 1-7

A conductor material represented by chemical Formula XIV.

1.15. claims: 1-8

A conductor material represented by chemical Formula XVI, XX, XXII and XXVI.

1.16. claims: 1-8

A conductor material represented by chemical Formula XVII and XXIII.

1.17. claims: 1-8

A conductor material represented by chemical Formula XVIII and XXIV.

1.18. claims: 1-8

A conductor material represented by chemical Formula XIX and XXV.

2. claims: 9-10

A diode comprising at least one conductive fluorinated organic substance.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB2004/050999

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专利名称(译)	用于LED的多氟化导体材料，用于改善光输出耦合		
公开(公告)号	EP1647062A1	公开(公告)日	2006-04-19
申请号	EP2004744403	申请日	2004-06-24
[标]申请(专利权)人(译)	皇家飞利浦电子股份有限公司		
申请(专利权)人(译)	飞利浦知识产权及标准部GMBH 皇家飞利浦电子N.V.		
当前申请(专利权)人(译)	皇家飞利浦电子N.V. 飞利浦知识产权及标准部GMBH		
发明人	BOERNER, H.F., PHILIPS I.P. & STANDARDS GMBH		
IPC分类号	H01L51/30 H01L51/00 H01L51/50 H01L51/52		
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优先权	2003102032 2003-07-07 EP		
其他公开文献	EP1647062B1		
外部链接	Espacenet		

摘要(译)

用于改善光输出耦合的LED的导体材料，其中导体材料选自包括空穴导体材料，电子导体材料和/或发射体材料的组，导体材料包括至少一种具有至少一个氟化烷基的导电氟化有机物质取代基，一个氟化链烯基取代基和/或一个氟化炔基取代基，其中至少两个氟原子与氟化取代基的至少一个碳原子键合，并且导电氟化有机物质具有> _ 1.30和<_的折射率1.55。