(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 024 049 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
25.08.2021 Bulletin 2021/34

(51) Int Cl.:
H01L 51/54 *(2006.01)* ***C07C 13/00*** *(2006.01)*
H01L 51/50 *(2006.01)*

(21) Application number: **14193716.9**

(22) Date of filing: **18.11.2014**

(54) **Fluorinated aromatic small molecules as functional additives for dispersion of conductive polymers**

Fluorierte aromatische kleine Moleküle als funktionale Additive zur Dispergierung von leitfähigen Polymeren

Petites molécules aromatiques fluorées comme additifs fonctionnels pour la dispersion de polymères conducteurs

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(43) Date of publication of application:
25.05.2016 Bulletin 2016/21

(60) Divisional application:
21174566.6

(73) Proprietor: **Heraeus Deutschland GmbH & Co. KG**
63450 Hanau (DE)

(72) Inventors:
- **Lövenich, Wilfried**
  51469 Bergisch Gladbach (DE)
- **Kausch-Busies, Nina**
  51467 Bergisch Gladbach (DE)
- **Ponomarenko, Sergei Anatolievich**
  107589 Moskau (RU)
- **Elschner, Andreas**
  45468 Mülheim (DE)
- **Kononevich, Yuriy N.**
  127051 Moskau (RU)
- **Tereshchenko, Alexey S.**
  141304 Moskau (RU)

(74) Representative: **Herzog IP Patentanwalts GmbH**
Steinstraße 16-18
40212 Düsseldorf (DE)

(56) References cited:
EP-A1- 1 405 849 **EP-A1- 1 640 372**
JP-A- 2006 222 010 **JP-A- 2007 176 921**

- **YANG LIU ET AL: "Novel sulfonated thin-film composite nanofiltration membranes with improved water flux for treatment of dye solutions", JOURNAL OF MEMBRANE SCIENCE, ELSEVIER, vol. 394, 28 December 2011 (2011-12-28), pages 218-229, XP028397860, ISSN: 0376-7388, DOI: 10.1016/J.MEMSCI.2011.12.045 [retrieved on 2012-01-03]**
- **LIU CUIBO ET AL: "Selective C4-F bond cleavage/C-O bond formation of polyfluoroarenes with phenols and benzyl", JOURNAL OF FLUORINE CHEMISTRY, vol. 156, 4 September 2013 (2013-09-04), pages 51-60, XP028786007, ISSN: 0022-1139, DOI: 10.1016/J.JFLUCHEM.2013.08.013**
- **None**

EP 3 024 049 B1

Description

[0001] The present invention relates to a composition comprising a compound, to a process for the preparation of a conductive layer using this composition, to a conductive layer comprising the compound and to electronic components comprising this conductive layer.

[0002] Electrically conducting polymers have been used in a variety of organic electronic devices, including in the development of electroluminescent (EL) devices for use in light emissive displays. With respect to EL devices, such as organic light emitting diodes (OLEDs) containing conducting polymers, such devices generally have the following configuration:

anode/hole injection layer/EL polymer/cathode

[0003] The anode is typically any material that has the ability to inject holes into the otherwise filled π-band of the semiconducting, EL polymer, such as, for example, indium/tin oxide (ITO). The anode is optionally supported on a glass or plastic substrate. The EL polymer is typically a conjugated semiconducting polymer such as poly(paraphenylenevinylene) or polyfluorene. The cathode is typically any material (such as, e.g., Ca or Ba) that has the ability to inject electrons into the otherwise empty π^*-band of the semiconducting, EL polymer.

[0004] The hole injection layer (also referred to as "buffer layer") is typically a conducting polymer and facilitates the injection of holes from the anode into the EL polymer layer. Typical conducting polymers employed as hole injection layer include polyaniline and polydioxythiophenes. A well known conductive polymer that is used to prepare conductive layers in organic electronic devices is a complex of poly(3,4-ethylenedioxythiophene) and polystyrene sulfonic acid, also referred to as "PEDOT/PSS". However, an OLED the hole injection layer which is based on PEDOT/PSS is usually characterized by an unsatisfying performance, in particular by a comparatively short life time and a low efficiency and luminescence.

[0005] In order to improve the performance of an OLED the hole injection layer which is based on PEDOT/PSS the prior art suggest to add certain additives to the PEDOT/PSS-dispersions used to form the hole injection layer.

[0006] US 2005/0209388 A1, for example, suggest to substitute the polystyrene sulfonic acid by colloid-forming polymeric acids such as NAFION®, wherein according to the teaching of US 2005/0209388 A1 the compositions disclosed therein are obtained by oxidatively polymerizing the thiophene monomers in the presence of NAFION®. US 2004/124504 A1 suggests to improve the performance of an OLED the hole injection layer of which is based on PEDOT/PSS by adding a plurality of nanoparticles to the dispersions. Suitable nanoparticles disclosed in US 2004/124504 A1 are perfluorethylene sulfonates such as NAFION®. However, using NAFION® as an additive in hole injection layers of an OLED has the disadvantage that these fluorinated sulfonic acid polymers are expensive, not soluble in water (they merely form a colloid) and that they are insoluble in organic solvents. These disadvantages limit their compatibility with conductive polymer dispersions especially at higher concentration.

[0007] WO 2009/096352 A1 discloses a "charge transport varnish" comprising specific low molecular weight fluorinated sulfonic acids and conductive polymers such as polyanilline. This varnish may have a beneficial effect on OLED performance (i.e. low-voltage drive and luminescence efficiency) if applied as a thin film. The fluorinated sulfonic acids are soluble in water and in highly polar organic solvents such as DMF. A general applicability of these substances has not be shown, in particularly a beneficial effect of the described low molecular weight fluorinated sulfonic acids when used in combination with PEDOT/PSS. Moreover, the solubility of the fluorinated sulfonic acids disclosed in WO 2009/096352 A1 in solvents other than water is low.

[0008] JP 2006 222010 A discloses a polymer electrolyte material that includes a polyarylene ether-based compound comprising an ionic group.

[0009] EP 1 640 372 A1 discloses a 1,4-benzodioxanesulfonic acid compound and its use as an electron acceptor. The mode of use includes a varnish containing the electron acceptor, a charge transporting thin film formed from the varnish, and an organic electroluminescence device having said charge transporting thin film.

[0010] Yang Liu et al. (Journal of Membrane Science, vol. 394 (2011), pages 218-229) disclose sulfonated thin-film composite nanofiltration membranes with improved water flux for treatment of dye solutions.

[0011] JP 2007 176921 A discloses a benzonitrile compound which can be suitably used in applications of an additive controlling a refractive index without adversely affecting various properties such as thermal properties possessed by a resin such as a transparent resin, its manufacturing method, a resin additive containing this benzonitrile compound, and a resin composition.

[0012] Liu Cuibo et al. (Journal of Fluorine Chemistry, vol. 156 (2013), pages 51-60) disclose selective C4-F bond cleavage/C-O bond formation of polyfluoroarenes with phenols and benzyl alcohols.

[0013] EP 1 405 849 A1 discloses aromatic vinyl compounds, using the term "aromatic" in a broad sense, so as to include ring structures of relatively low resonance energy such as maleimide rings. Also disclosed are methods of preparing such compounds, and their use as polymeric materials.

[0014] It was therefore an object of the present invention to overcome the disadvantages of the prior art in the field of organic electronic devices, in particular of OLEDs the hole injection layer of which is based on conductive polymers such

as PEDOT/PSS.

[0015] In particular, it was an object of the present invention to provide a low molecular weight additive with a tailored solubility in water or organic solvents that, when used in combination with conductive polymers such as PEDOT/PSS for the preparation of conductive layers in organic electronic devices, in particular for the preparation of a hole injection layer in an OLED, helps to improve the performance of these electronic devices. In contrast to complex polymers such as NAFION® the low-molecular weight additives should by obtainable by a simple 1-2 step synthesis from commercially available precursors.

[0016] A contribution to the solution of at least one of the above objects is provided by the subject matter of the category-forming independent claims, wherein the therefrom dependent subclaims represent preferred embodiments of the present invention, whose subject matter likewise make a contribution to solving at least one object.

[0017] A contribution towards solving these objects is made by a composition as defined in claim 1, wherein the composition comprises at least one conductive polymer, at least one solvent and at least one compound having a general formula Ia

$$k\text{-}[X\text{-}A]_n \qquad Ia$$

wherein

K represents an aromatic group in which at least one hydrogen atom may be substituted by a functional group selected from the group consisting of a sulfonic acid group, a sulfuric acid group, an ammonium group, an aliphatic group, and $-CO_2M$, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+};
X is O;
A represents a fluorinated or perfluorinated aromatic group;
n represents an integer in the range from 2 to 6.

[0018] In accordance with claim 1 the conductive polymer comprises a complex of a polythiophene and a polyanion.

[0019] It is preferred that in the compound in the composition according to the present invention the functional group (i. e. the functional group with which at least one hydrogen atom of the aromatic group K may be substituted) is a functional group selected from the group consisting of

i) $-SO_3M$, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+},

ii) $-OSO_3M$, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+},

iii) $-CO_2M$, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+},

iv) an ammonium group selected from the group consisting of $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, and $-N(C_5H_{11})_4^+$, and

v) an alkyl group selected from the group consisting of $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ and $-C_{12}H_{25}$.

Functional groups i), ii), iii) and iv) are preferred if the compounds in the composition according to the present invention are used in water-based compositions, whereas functional group v) (or compounds in which no hydrogen atoms are substituted by any of these functional groups i) to v)) are preferred for compositions that are based on organic solvents.

[0020] According to preferred embodiments of the compound in the composition according to the present invention 1, 2, 3 or 4 hydrogen atoms, preferably 1 or 2 hydrogen atoms of the aromatic group K are substituted by one of the above mentioned functional groups selected from the group consisting of a sulfonic acid group, a sulfuric acid group, an ammonium group and an aliphatic group.

[0021] As in the compound in the composition according to the present invention two or more hydrogen atoms of the aromatic group K may be substituted by any of the above mentioned functional groups, these groups may be identical or different. However, according to a particularly preferred embodiment of the compound in the composition according to the present invention the functional group is $-SO_3M$, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+}, and if more than one hydrogen atom of the aromatic group K is substituted by a functional group, all these groups are $-SO_3M$ groups, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+}.

[0022] According to a first embodiment of the compound in the composition according to the present invention K represents a monocyclic aromatic group and the structural subunit Ia' of formula Ia

$K\text{-}[\text{-}X\text{-}A]_n$ Ia

has a general structure selected from the group consisting of general formulae IIa to IIk as defined in claim 4.

[0023] From the compounds of the first embodiment particularly preferred compounds are those in which X represents O and in which the following combinations for substituent R per entity K are fulfilled:

n = 2, and

R = 1 × $\text{-}SO_3M$ and 3 × H or R = 2 × $\text{-}SO_3M$ and 2 × H,

or

n = 3, and

R = 3 × H and 3 × $\text{-}SO_3M$,

wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+}.

[0024] According to a second embodiment of the compound in the composition according to the present invention K represents a bicyclic aromatic group (i. e. K is based on a naphthalene group).

[0025] According to a first variant of the second embodiment of the compound in the composition according to the present invention n represents 2 and the structural subunit Ia' of formula Ia

$K\text{-}[\text{-}X\text{-}A]_n$ Ia

has a general structure selected from the group consisting of general formulae IIIa to IIIj as defined in claim 6.

[0026] In context with this first variant of the second embodiment compounds are particularly preferred in which X represents O and in which the following combinations for substituent R per entity K are fulfilled:

R = 2 × $\text{-}SO_3M$ and 4 × H,

or

R = 3 × $\text{-}SO_3M$ and 3 × H,

wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+}.

[0027] According to a second variant of the second embodiment of the compound in the composition according to the present invention n represents 3 and the structural subunit Ia' of formula Ia

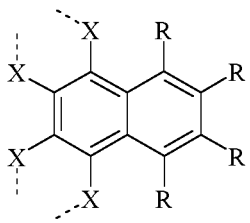
$K\text{-}[\text{-}X\text{-}A]_n$ Ia

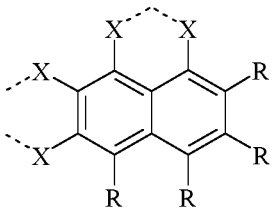
has a general structure selected from the group consisting of general formulae IVa to IV1 as defined in claim 8.

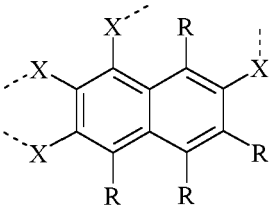
[0028] According to a third variant of the second embodiment of the compound in the composition according to the present invention n represents 4 and the structural subunit Ia' of formula Ia

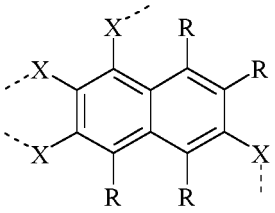
$K\text{-}[\text{-}X\text{-}A]_n$ Ia

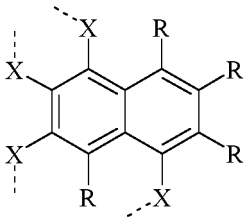
has a general structure selected from the group consisting of general formulae Va to Vi:

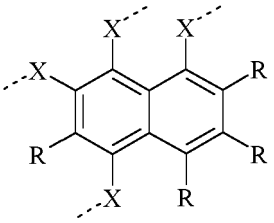

Va

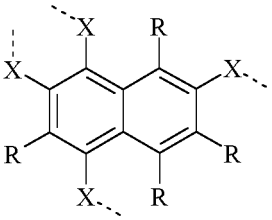

Vb

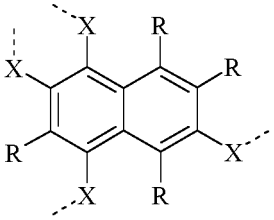

Vc

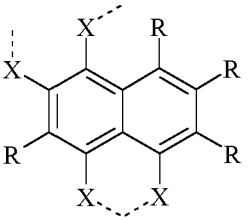

Vd


Ve


Vf


Vg


Vh

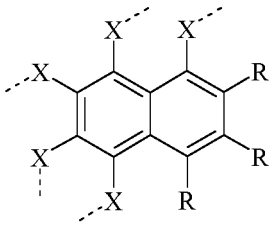

Vi

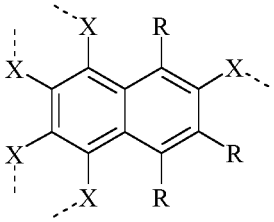
wherein R is selected from the group consisting of H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ and $-C_{12}H_{25}$, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+} and wherein the dotted line indicates the bond to A.

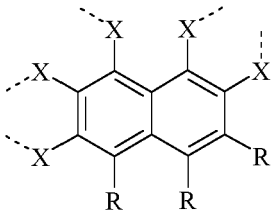
[0029] According to a fourth variant of the second embodiment of the compound in the composition according to the present invention n represents 5 and the structural subunit Ia' of formula Ia

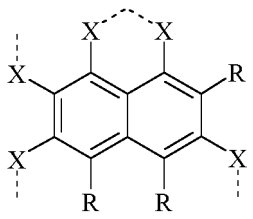
$$K\text{-}[\text{-}X\text{-}A]_n \qquad \text{Ia}$$

has a general structure selected from the group consisting of general formulae VIa to VIe:

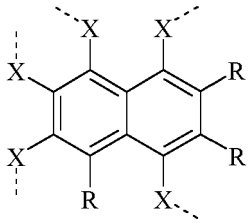

VIa


VIb


VIc



VId



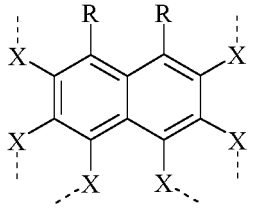
VIe

wherein R is selected from the group consisting of H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ and $-C_{12}H_{25}$, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+} and wherein the dotted line indicates the bond to A.

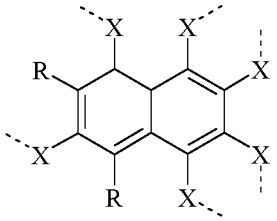
[0030] According to a fifth variant of the second embodiment of the compound in the composition according to the present invention n represents 6 and the structural subunit Ia' of formula Ia

$$K\text{-}[\text{-}X\text{-}A]_n \qquad \text{Ia}$$

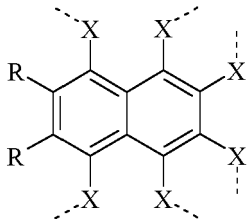
has a general structure selected from the group consisting of general formulae VIIa to VIIj:



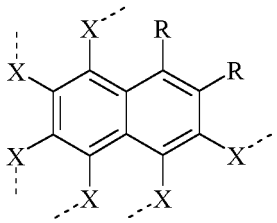
VIIa



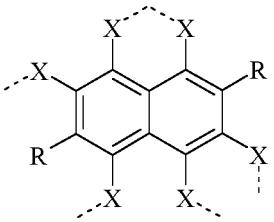
VIIb



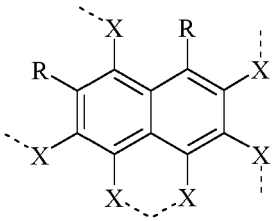
VIIc



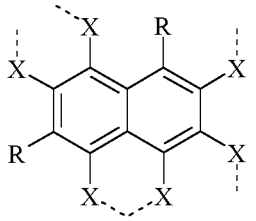
VIId



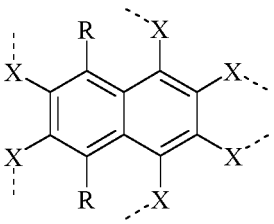
VIIe



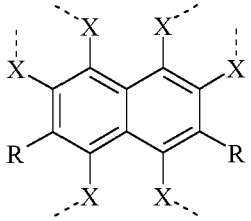
VIIf



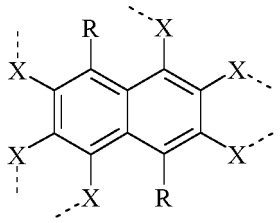
VIIg



VIIh



VIIi



VIIj

wherein R is selected from the group consisting of H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ and $-C_{12}H_{25}$, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+} and wherein the dotted line indicates the bond to A.

[0031] According to a third embodiment of the compound in the composition according to the present invention K represents a tricyclic aromatic group (i. e. K is based on a anthracene group or a phenanthrene group) and the structural subunit Ia' of formula Ia

$$K\text{-}[\text{-}X\text{-}A]_n \qquad \text{Ia}$$

has a general structure selected from the group consisting of general formulae VIIIa to VIIIr as defined in claim 12.

[0032] In context with the third embodiment compounds are particularly preferred in which X represents O and in which the following combinations for substituent R per entity K are fulfilled:

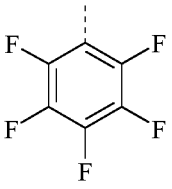
R = 2 × $-SO_3M$ and 6 × H,

or

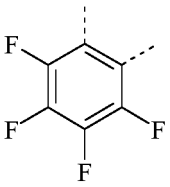
R = 3 × $-SO_3M$ and 5 × H,

wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+}.

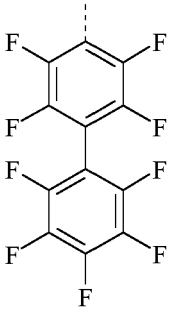
[0033] In the compound in the composition according to the present invention A represents a fluorinated or perfluorinated aromatic group, more preferably a perfluorinated aromatic group. In this context it is particularly preferred that A has a general structure selected from the group consisting of general formulae IXa to IXo:



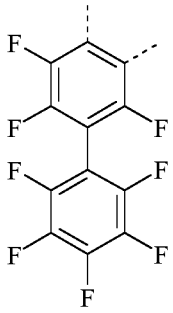
IXa



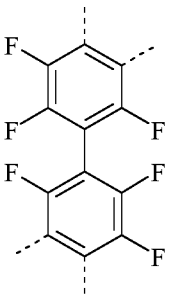
IXb



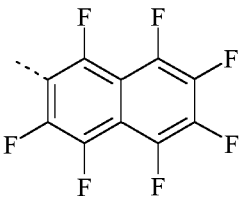
IXc



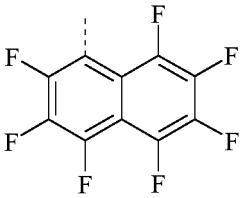
IXd



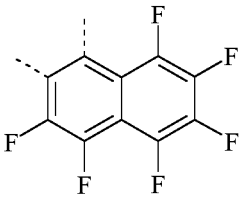
IXe



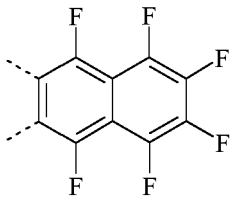
IXf



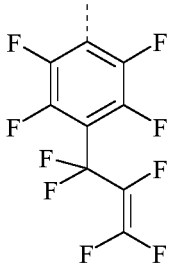
IXg



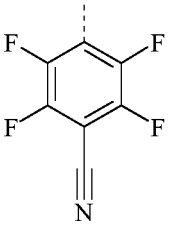
IXh



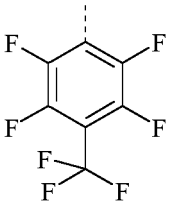
IXi



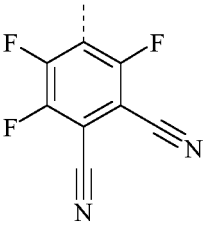
IXj



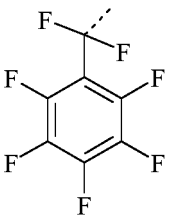
IXk



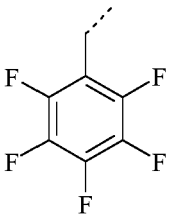
IXl



IXm



IXn



IXo

wherein the dotted line indicates the bond to X.

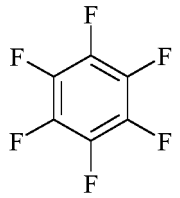
[0034] Particularly preferred embodiments of the compound in the composition according to the present invention have a general structure selected from the group consisting of general formulae Xd to Xg as defined in claim 14 or the corresponding salts thereof.

[0035] It should be noted that, although in general formulae Xd to Xg the functional groups are shown to be $-SO_3H$ groups, these groups can of course also be partially or completely neutralized and can therefore also be present in the form of $-SO_3M$ groups, in which M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+}.

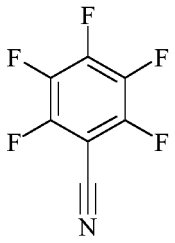
[0036] The compound in the composition according to the present invention can be prepared in a simply one-step synthesis by reacting the mono- or polycyclic aromatic or heteroaromatic system K in which at least one hydrogen atom may be substituted by the above mentioned functional groups and in which at the position at which X is attached the corresponding acid form -XH is present, i.e.

- a group -OH in case of X = O,

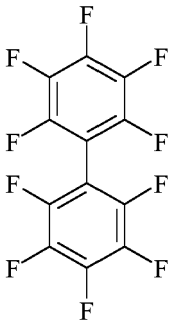
with a fluorinated or perfluorinated aromatic compound, preferably with a perfluorinated aromatic compound having a general structure selected from the group consisting of general formulae XIa to XIh:



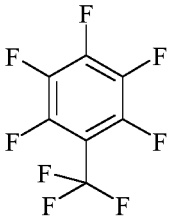
XIa



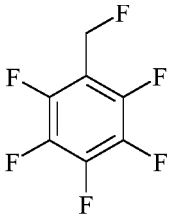
XIb



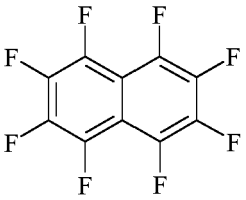
XIc



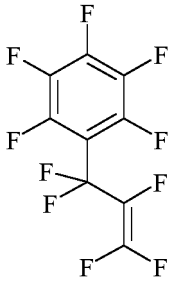
XId



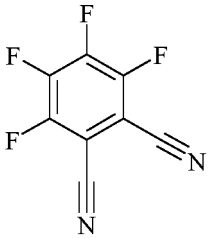
XIe



XIf



XIg



XIh

in a nucleophilic aromatic substitution reaction, preferably in the presence of a suitable catalyst. Catalysts that can be used for this purpose can be selected from the group consisting of lithium, potassium, lithium hydride, sodium hydride, lithium t-butoxide, sodium t-butoxide, potassium t-butoxide, lithium-diisopropylamide, n-butyllithium, s-butyllithium, t-butyllithium, lithium hexamethyldisilazide, sodium hexamethyldisilazide, potassium hexamethyldisilazide, lithium hydroxide, sodium hydroxide, potassium hydroxide, barium hydroxide, barium oxide, lithium carbonate, sodium carbonate, potassium carbonate, cesium carbonate, calcium carbonate, sodium hydrogen carbonate, triethylamine, diisopropylethylamine, tetramethylethylenediamine, triethylenediamine, pyridine, dimethylaminopyridine, imidazole and the like, and dehydration condensing agents such as hydrochloric acid, sulfuric acid, diphosphorus pentaoxide, aluminum (III) chloride, boron trifluoride diethyl ether complex, ethyl aluminum dichloride, diethyl aluminum chloride and the like. Preferred catalysts are selected from the group consisting of sodium hydroxide, sodium carbonate and potassium carbonate.

[0037] The reaction can be performed in any solvent in which the educts (i. e. the mono- or polycyclic aromatic or heteroaromatic system K in which at the position at which X is attached the corresponding acid form -XH is used and the fluorinated or perfluorinated aromatic compound) can be dissolved or dispersed. Preferably an aprotic polar organic solvent is used, which is preferably selected from the group consisting N,N-dimethylformamide, N,N-dimethyacetamide, N-methylpyrrolidone, 1,3-dimethyl-2-imidazolidinone, dimethylsulfoxide, tetrahydrofuran and dioxane.

[0038] The possible reaction temperature generally ranges from -50°C to the boiling point of a solvent used and is preferably within a range of 0 to 140°C. The reaction time is usually at 0.1 to 100 hours. After completion of the reaction, purification can be made by distilling off of the reaction solvent, protonation of the sulfonate by means of a cationic exchange resins, extraction operations with a solvent such as methanol or the like, or by precipitation.

[0039] The composition according to the present invention is preferably a dispersion or a solution, particularly preferred dispersion.

[0040] Polyanions and polythiophene are present in the composition according to the present invention especially in a weight ratio of 0.5 : 1 to 50 : 1, preferably of 1 : 1 to 30 : 1, more preferably 2 : 1 to 20 : 1. The weight of the conjugated polymer corresponds here to the initial weight of the monomers used, assuming that there is full conversion in the polymerization.

[0041] As a further component the composition according to the present invention also comprises at least one solvent II).

[0042] Preferred solvents are

- water,
- organic solvents selected from the group consisting of aliphatic hydrocarbons, such as heptane, hexane, pentane, octane,
- terpenes or petroleum ether,
- aromatic hydrocarbons such as benzene, toluene, xylene, mesitylene, biphenyl,
- ethers, such as diethylether, diisopropylether, methyltertbutylether dibutylether, diphenylether, anisole and ethylenglycol ethers such as polyethylenglycol (PEG), ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monophenyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, propylen glycol monopropyl ether, dipropylen glycol monomethylether, dipropylen glycol dimethylether, diethylene glycol monomethyl ether or ethylene glycol dibutyl ether,
- esters such as methylacetate, ethylacetate, propylacetate or butylacetate, methylbenzoate, ethylbenzoate, propylbenzoate, butylbenzoate, γ-butyrolactone, δ-valerolactone, γ-valerolactone, ethylene glycol methyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, propylene glycol methyl ether acetate,
- halogenated hydrocarbons such as dichloromethane, dichloroethane, chlorobenzene, chloroform, tetrachloromethane, trichloroethane or trichloroethene,
- aliphatic nitriles such as acetonitrile,
- aliphatic sulphoxides and sulphones such as dimethylsulfoxide or sulfolane,
- aliphatic carboxylic acids such as acetic acid,
- aliphatic carboxylic acid amides such as acetamide, dimethyl acetamide or dimethylformamide and ketones such as acetone or methyl-t-butyl ketone,
- alcohols such as methanol, ethanol, propanol, butanol, hexanol, terpineol, 1,2-propandiol, ethylenglycol or dodecanol,
- acetals such as glyme (dimethoxyethane), diglyme, tetraglyme, or dioxolane,
- carbonates such as propylene carbonate or ethylene carbonate
- and other solvent classes like oligo- or polysiloxanes,
- and mixtures of at least two of these solvents.

[0043] It is preferred that the composition according to the present invention comprises the at least one compound III) in an amount of 0.01 to 10 wt.-%, preferably 0.1 to 7.5 wt.-% and most preferably 0.5 to 5 wt.-%, in each case based on the total weight of the composition. The weight ratio of the at least one compound III) and the total weight of polythiophene and polyanion is preferably in the range from 1 : 100 to 100 : 1, more preferably in the range from 1 : 10 to 10 : 1 and most preferably in the range from 1 : 5 to 5 : 1.

[0044] Besides at least one conductive polymer I), at least one solvent II) and at least one compound III) the composition according to the present invention may comprise further additives IV) being different from components I), II) and III), such as

- surface-active substances, e.g. anionic surfactants, such as e.g. alkylbenzenesulphonic acids and salts, paraffinsulphonates, alcohol sulphonates, ether sulphonates, sulphosuccinates, phosphate esters, alkyl ether carboxylic acids or carboxylates, cationic surfactants, such as e.g. quaternary alkylammonium salts, nonionic surfactants, such as e.g. linear alcohol ethoxylates, oxo alcohol ethoxylates, alkylphenol ethoxylates or alkyl polyglucosides,

- adhesion promoters, such as e.g. organofunctional silanes or hydrolysates thereof, e.g. 3-glycidoxypropyltrialkoxysilane, 3-aminopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane,

vinyltrimethoxysilane or octyltriethoxysilane, or

- crosslinking agents, such as melamine compounds, masked isocyanates, functional silanes - e.g. tetraethoxysilane, alkoxysilane hydrolysates, e.g. based on tetraethoxysilane, epoxysilanes, such as 3-glycidoxypropyltrialkoxysilane, epoxides or oxetanes, amines, quaternary amines, polyamines or quaternary polyamines,

- binders, such as, for example, polyalkylene glycols, polyacrylates, polyurethanes, polyesters, polyethers, polyamides or polyvinyl alcohol, or

- additives which increase the conductivity, such as, for example, polyalkylene glycols, in particular polyethylene glycols or polypropylene glycols, polyglycerols or mixtures of these, polyols, such as propylene glycol and ethylene glycol, sulphoxides, such as dimethylsulphoxide, carboxylic acid amides, such as methylacetamide, dimethylacetamide, dimethylformamide, N-methylpyrrolidone, N-cyclohexylpyrrolidone, ionic liquids, sugars, such as sorbitol.

[0045] The amount of these additives will of course depend on the nature of the additive, but is usually in the range from 0 to 20 wt.-%, more preferably from 1 to 15 wt.-% and most preferably from 2.5 to 10 wt.-%, based on the total weight of the composition.

[0046] Preferably, the composition according to the present invention comprises, in each case based on the total weight of the composition,

I) 0.01 to 10 wt.-%, more preferably 0.1 to 7.5 wt.-% and most preferably 0.5 to 5 wt.-%, of the conductive polymer;

III) 0.01 to 10 wt.-%, more preferably 0.1 to 7.5 wt.-% and most preferably 0.2 to 5 wt.-%, of the at least one compound according to the present invention;

IV) 0 to 20 wt.-%, more preferably from 1 to 15 wt.-% and most preferably from 2.5 to 10 wt.-%, of further additives IV) being different from components I), II) and III),

wherein the reminder is the solvent II).

[0047] It is furthermore preferable for the composition according to the present invention to have a pH in a range of from 1 to 12, particularly preferably in a range of from 4 to 8, at a temperature of 25 °C. The viscosity at 20 °C of the composition according to the present invention is preferably less than 1,000 mPas, preferably less than 400 mPas.

[0048] The solids content of the composition according to the present invention is preferably in a range of from 0.1 to 10 wt.%, particularly preferably in a range of from 0.5 to 7.5 wt.% and most preferably in a range of from 1 to 5 wt.%.

[0049] The composition according to the present invention can be obtained by various processes.

- According to a first embodiment, the composition according to the present invention can be obtained by oxidatively polymerizing the monomers used to prepare the conductive polymer I) (3,4-ethylenedioxythiophene), in the presence of the compound III) in an appropriate solvent. The solvent used for the polymerization reaction can be the solvent II) that is present in the composition according to the present invention, however, it is also possible to substitute the solvent used for the polymerization reaction by a different solvent (such a process is disclosed, for example, in US 6,692,662 B2) or to add a further solvent to the solvent used for the polymerisation reaction to obtain a solvent mixture.

- According to a second (and preferred) embodiment, the composition according to the present invention can be obtained by simply adding the compound III) to a composition that already comprises the conductive polymer I), preferably to an aqueous PEDOT/PSS-dispersion. In this case it is also possible that the solvent used for the polymerization reaction can be the solvent II) that is present in the composition according to the present invention or that the solvent used for the polymerization reaction is substituted by a different solvent as disclosed, for example, in US 6,692,662 B2 or that a further solvent is added to the solvent used for the polymerization reaction to obtain a solvent mixture.

[0050] If necessary, the mixture of components I), II) and III) obtained by one of the above mentioned processes is heated until all the components are dissolved, wherein the maximum temperature will of course depend on the boiling point of the solvent that is used.

[0051] A contribution towards solving the above mentioned objects is also made by a process for the preparation of a conductive layer as defined in claim 16

[0052] In process step (PI) a substrate is superimposed with the composition according to the present invention (or with a composition comprising the solvent and either the conductive polymer I) or the compound III)). All layers which

can be employed in electronic components, such as, for example, in an OLED, are suitable as the substrate. Thus, in particular, the substrate can be one which is furnished with a preferably transparent base electrode, the substrate itself preferably also being transparent. Glass, PET or other transparent plastics, for example, can be employed as transparent substrate, onto which a transparent electrically conductive electrode is then introduced, such as e.g. an electrode made of indium - tin oxide (ITO), doped zinc- or tin oxide or a conductive polymer. Particularly suitable transparent plastic substrates are, for example, polycarbonates, polyesters, such as e.g. PET and PEN (polyethyleneterephthalate and polyethylenenaphthalinedicarboxylate), copolycarbonates, polyacrylates, polysulphones, poly-ethersulphones (PES), polyimides, polyethylene, polypropylene, cyclic polyolefins or cyclic olefin copolymers (COC), hydrated styrene polymers or hydrated styrene copolymers. Suitable polymer bases can, for example, also be films such as polyester films, PES films from the Sumitomo company or polycarbonate films from the Bayer AG company (Makrofol®). According to the invention, ITO coated glass is particularly preferred as substrate.

[0053] Superimposing the substrate with the composition according to the present invention or with a composition comprising the solvent II) and either the conductive polymer I) or the compound III) can then be accomplished by known methods, for example by spin coating, dipping, pouring, dropping on, injecting, spraying, knife application, spreading or printing, for example inkjet, screen, intaglio, offset or pad printing, in a wet film thickness of 0.1 μm to 250 μm, preferably in a wet film thickness of 0.5 μm to 50 μm, and then dried at a temperature of 20°C to 200°C.

[0054] In process step (P2) the solvent II) that is contained in the composition that has been applied is then at least partially removed to obtain an electrically conductive layer comprising the conductive polymer I) and the compound III), said removal preferably being performed by simple evaporation.

[0055] According to a particularly preferred embodiment of the process according to the present invention process steps (PI) and (P2) are is just two steps in the manufacture of an OLED. As stated above, an OLED usually comprises

an anode
a hole injection layer
an emitter layer and
a cathode,

wherein the hole injection layer is preferably prepared by the process according to the present invention. The OLED may comprise further layers, such as an electron injection layer that is located between the electroluminescence layer and the cathode.

[0056] The OLED the hole injection layer of which has been prepared using the composition according to the present invention can, for example, exhibit any of the following layer structures (a) to (h):

(a) anode/
hole injection layer/
at least one emitter layer/
cathode;

(b) anode/
hole injection layer/
hole transport layer/
at least one emitter layer/
cathode;

(c) anode/
hole injection layer/
at least one emitter layer/
electron injection layer/
cathode;

(d) anode/
hole injection layer/
hole transport layer/
at least one emitter layer/
electron injection layer/
cathode;

(e) anode/

hole injection layer/
at least one emitter layer/
electron transport layer/
cathode;

(f) anode/
hole injection layer/
hole transport layer/
at least one emitter layer/
electron transport layer/
cathode;

(g) anode/
hole injection layer/
at least one emitter layer/
electron transport layer/
electron injection layer/
cathode;

(h) anode/
hole injection layer/
hole transport layer/
at least one emitter layer/
electron transport layer/
electron injection layer/
cathode.

[0057] The layer structures (a) to (h) can be embodied either with the anode located next to the substrate, the substrate being, for example, glass or a transparent plastic film, or with the cathode located next to the substrate.

[0058] The anode layer is preferably based on indium tin oxide, indium zinc oxide, fluorine-doped tin oxide, tungsten trioxide, titanium dioxide, molybdenum trioxide, aluminium zinc oxide, gallium indium zinc oxide, aluminium, silver, palladium, copper, gold, platinum, and alloys thereof, for example silver- palladium-copper and molybdenum-chrome.

[0059] Suitable materials for the emitter layer are conjugated polymers such as polyphenylenevinylenes and/or polyfluorenes, for example, the polyparaphenylenevinylene derivatives and polyfluorene derivatives described in WO-A-90/13148, or emitters from the class of low molecular emitters, also termed "small molecules" in technical circles, such as aluminium complexes, such as, for example, tris(8-hydroxyquinolinato)aluminium (Alq_3), fluorescence dyes, e.g. quinacridones, or phosphorescent emitters such as, for example, $Ir(ppy)_3$. Further suitable materials for the emitter layer are described e.g. in DE-A-196 27 071. Particularly preferred as emitter layer, according to the invention, is tris(8-hydroxyquinolinato)aluminium (Alq_3).

[0060] Preferred as the injection layer are single Ca layers or a stack structure consisting of a Ca layer and another layer, which consists of one or more materials selected from the group IA and IIA metals of the periodic table, excluding Ca, which exhibit a work function from 1.5 to 3.0 eV, and oxides, halogenides and carbonates thereof. Examples of group IA metals of the periodic table which exhibit a work function from 1.5 to 3.0 eV, and oxides, halogenides and carbonates thereof, are lithium, lithium fluoride, sodium oxide, lithium oxide and lithium carbonate. Examples of group IIA metals of the periodic table, excluding Ca, which exhibit a work function from 1.5 to 3.0 eV, and oxides, halogenides and carbonates thereof, are strontium, magnesium oxide, magnesium fluoride, strontium fluoride, barium fluoride, strontium oxide and magnesium carbonate.

[0061] The electron transport layer can consist of materials such as, for example, oxadiazol derivatives, anthraquinodimethane or derivatives thereof, benzoquinone or derivatives thereof, naphthoquinone or derivatives thereof, anthraquinone or derivatives thereof, tetracyanoanthraquinodimethane or derivatives thereof, fluorenone derivatives, diphenyldicyanoethylene or derivatives thereof, diphenoquinone derivatives and metal complexes of 8-hydroxyquinoline or derivatives thereof, polyquinoline or derivatives thereof, polyquinoxaline or derivatives thereof or polyfluorene or derivatives thereof.

[0062] Particularly suitable materials for the cathode layer are transparent or translucent materials with a relatively low work function (preferably lower than 4.0 eV). Examples of this type of material are metals, such as lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), Be, magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), aluminium (Al), scandium (Sc), vanadium (V), Zn, yttrium (Y), indium (In), cerium (Ce), samarium (Sm), Eu, Tb and ytterbium (Yb); alloys consisting of two or more of these metals; alloys consisting of one or more of these metals and

one or more metals selected from Au, Ag, Pt, Cu, manganese (Mn), titanium (Ti), cobalt (Co), nickel (Ni), wolfram (W) and tin (Sn); graphite or graphite intercalation compounds; and metal oxides, such as, for example, ITO and tin oxide. Particularly preferable is the use of aluminium as the cathode layer.

[0063] The application of the emitter layer, of the electron injection layer and of the cathode injection layer can be carried out in a manner known to a person skilled in the art, preferably through vapour coating such as is described, for instance, in WO-A-2009/0170244.

[0064] A contribution towards solving the above mentioned objects is also made by a conductive layer as defined in claim 17. In this context it is also preferred that the weight ratio of the at least one compound III)and the total weight of polythiophene and polyanion in the conductive layer is preferably in the range from 1 : 100 to 100 : 1, more preferably in the range from 1 : 10 to 10 : 1 and most preferably in the range from 1 : 5 to 5 : 1.

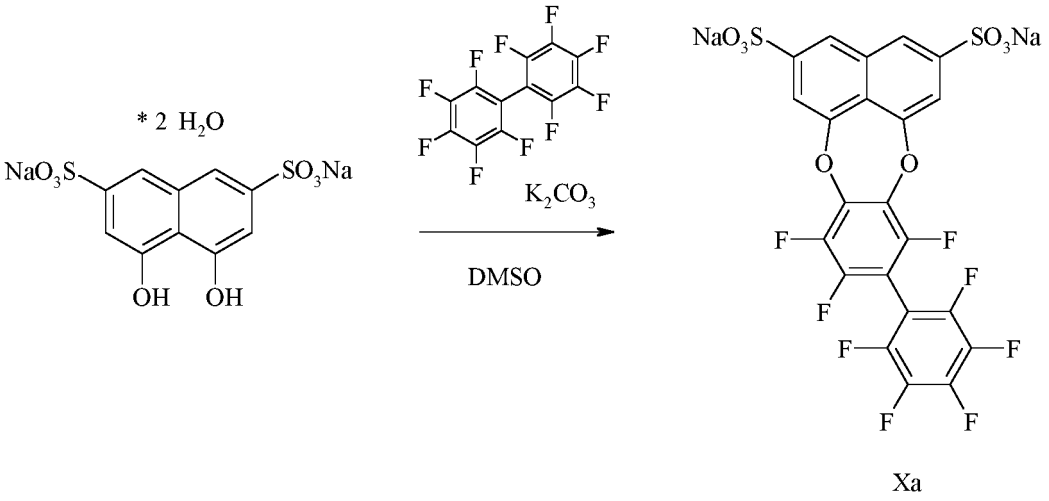
[0065] A contribution towards solving the above mentioned objects is also made by a an electronic component comprising a conducting layer obtainable by the process according to the present invention or comprising a conductive layer according to the present invention. According to a preferred embodiment of the electronic component according to the present invention this electronic component is an OLED, a display, an organic solar cell, a hybrid solar cell, a field effect transistor, or a thermoelectric generator. In case of an OLED it is furthermore preferred that the hole injection layer of the OLED is obtainable by the process according to the present invention or corresponds to a conductive layer according to the present invention.

[0066] The invention will now be further illustrated by means of non-limiting examples.

Examples

Example 1A: synthesis of compound Xa

[0067]



Xa

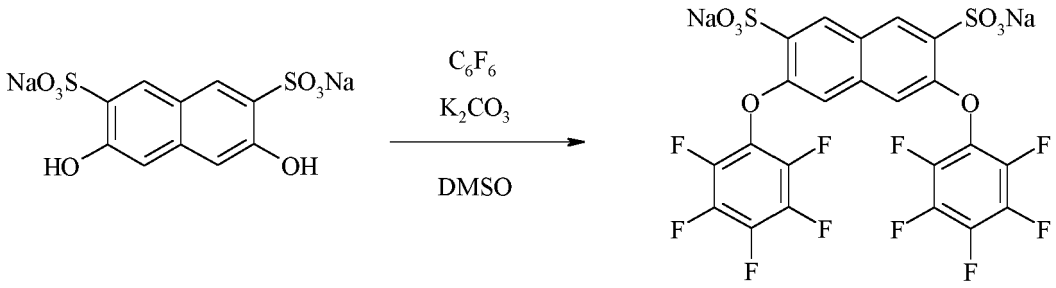
[0068] Chromotropic acid disodium salt (2.00 g, 0.005 mol), potassium carbonate (2.76 g, 0.005 mol), decafluorobiphenyl (8.35 g, 0.025 mol) and 50 ml of DMSO were stirred under heating at 120 - 130°C during 40 hours. The reaction was controlled by ^{1}H-NMR spectroscopy. After completion of the reaction it was cooled down to room temperature and filtered from the solid, containing the rest of K_2CO_3 and the by-product KF. DMSO from the filtrate was evaporated under vacuum (1 mbar) and excess of decafluorobiphenyl was sublimed. 20 mL of water were added to the residue and the product was precipitated as a white solid, which was filtered and washed with cold water. The filter cake was dried under vacuum to give 2.27 g of the pure compound Xa, which correspond to the isolated yield of 69 %.

[0069] ^{1}H NMR (300 MHz, DMSO-d6) δ = 8.12 (s, 2H), 7.65 (d, J = 15.9 Hz, 2H); ^{19}F NMR (282 MHz, DMSO-d6) δ = -55.6 (m), -59.5 (m), -60.2 (m), -70.0 (m), -78.7 (m), -82.7 (m).

[0070] Prior to formulation compound Xa was recrystallized. It was dissolved in H_2O (solid content 1 %) and heated to 90°C. The hot solution was filtered through a syringe filter (PVDF, 0.8 μm) and concentrated.

Example 1B: synthesis of compound Xe

[0071]



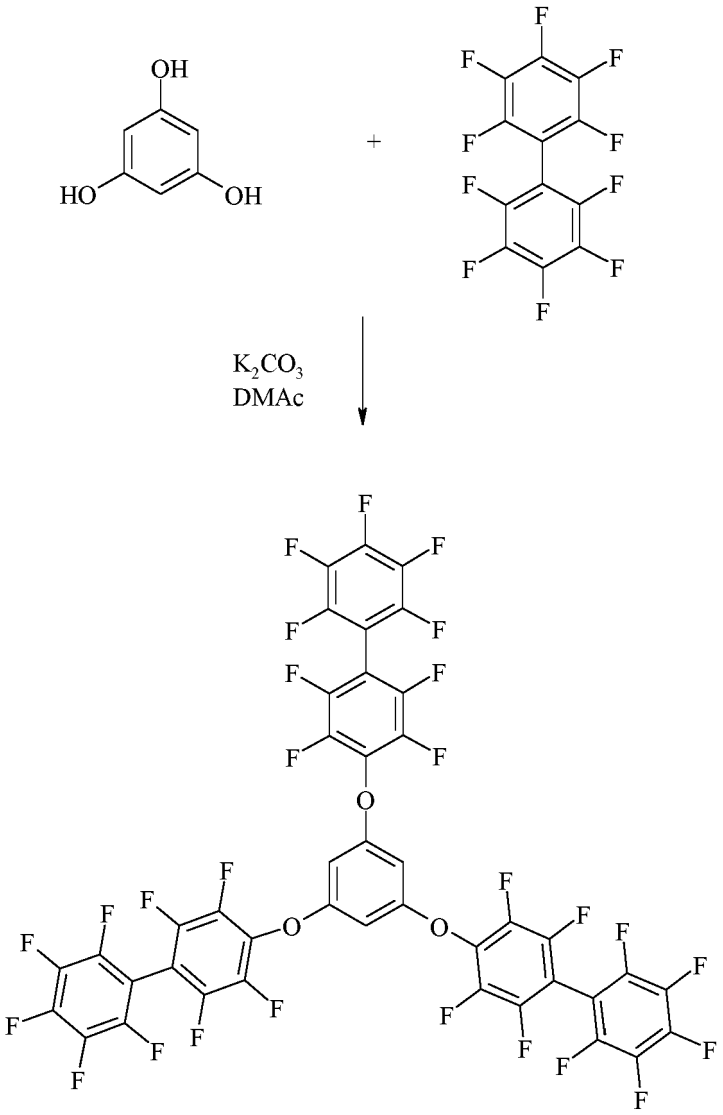
Xe

[0072] 3,6-Dihydroxynaphthalene-2,7-disulfonic acid disodium salt was reacted with hexaflourobenzene and potassium carbonate (1 : 4 : 10 mole ratio) in DMF (at concentration of 40 g of 3,6-dihydroxynaphthalene-2,7-disulfonic acid disodium salt per 1 L of DMF) at 130°C. The reaction was controlled by ^{1}H-NMR spectroscopy. After 20 h of heating at 120 - 130°C the reaction was complete according to ^{1}H-NMR spectroscopy. The mixture was cooled to room temperature and filtered from the solid, containing the rest of K_2CO_3 and the by-product KF. DMSO and the excess of hexafluorobenzene from the filtrate were evaporated under vacuum (1 mbar). Water (10 mL per 25 mL of the initial amount of DMSO) was added to the residue and the product was precipitated as a white solid, which was filtered, washed with water and dried under vacuum (1 mbar) to give the first portion of compound Xe. The filtrate formed was evaporated up to approximately 50% of its initial volume and cooled overnight in the refrigerator at 4°C. A new portion of the product was precipitated as a white solid, which was filtered again, washed with water and dried in vacuum (1 mbar) to give the second portion of compound Xe as a white solid. The total yield of compound Xe was 67%.

[0073] ^{1}H NMR (300 MHz, DMSO) δ 8.31 (s, 2H), 7.07 (s, 2H); ^{19}F NMR (282 MHz, DMSO) δ = - 76.0 (m), -83.0 (m), -84.3 (m).

Example 1C: synthesis of compound Xg (soluble in organic solvents)

[0074]

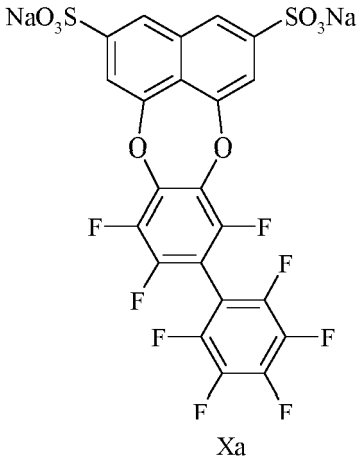


Xg

[0075] K_2CO_3 (1.1 g, 0.008 mol) and decafluorobiphenyl (3 g, 0.009 mol) were suspended in dry N,N-dimethylacetamide (10 ml) and heated to 100°C. 1,3,5-Trihydroxybenzene (0.25 g, 0.002 mol) dissolved in DMAc (10 ml) was added slowly over a period of 4 h at 92 - 97°C. After complete addition the reaction mixture was heated to 120°C until TLC confirmed complete consumption of starting material. The mixture was concentrated and to the residue a dilute NH_4Cl-solution (1 g NH_4Cl/20 ml H_2O) was slowly added. The aqueous phase was extracted 3 times with MTBE. The combined organic layers were washed with brine and dried over Na_2SO_4. After evaporation of solvents the clear yellow highly viscous oil was purified by column chromatography over SiO_2 (eluent: toluene). The product was isolated as a light yellow highly viscous oil (2.1 g, 0.002 mol, quant.).
LC-MS (ESI; H_2O/MeCN Grad. 0.8g/L NH4OAc) M = 1068; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.49.

Example 2: formulation of a dispersion of PEDOT:PSS with compound Xa (not forming part of the claimed invention)

[0076]



Xa

Example 2A (solid content of compound Xa = 0.7%):

[0077] 0.42 g of compound Xa were dissolved in 30 g Clevios P VPAI 4083 (Heraeus Precious Metals GmbH & Co. KG, 1.5% solid content). 24 g of water were added and the mixture was stirred for 30 min at room temperature and then heated (1 h, 40°C) until all solids were dissolved completely. The mixture was cooled to room temperature (1 h), 6 g of ethanol were added and the mixture was stirred for another 30 min. After aging for 3 h the dispersion was filtered subsequently through 0.8 μm and 0.45 μm syringe filters (PVDF).

Example 2B (solid content of compound Xa = 0.47%):

[0078] 0.28 g of compound Xa were dissolved in 40 g Clevios P VPAI 4083 (Heraeus Precious Metals GmbH & Co. KG, 1.5% solid content). 14 g of water were added and the mixture was stirred for 30 min at room temperature and then heated (1 h, 40°C) until all solids were dissolved completely. The mixture was cooled to room temperature (1 h), 6 g of ethanol were added and the mixture was stirred for another 30 min. After aging for 3 h the dispersion was filtered subsequently through 0.8 μm and 0.45 μm syringe filters (PVDF).

Example 2C (solid content of compound Xa = 0.3%):

[0079] 0.18 g of compound Xa were dissolved in 40 g Clevios P VPAI 4083 (Heraeus Precious Metals GmbH & Co. KG, 1.5% solid content). 14 g of water were added and the mixture was stirred for 30 min at room temperature and then heated (1 h, 40°C) until all solids were dissolved completely. The mixture was cooled to room temperature (1 h), 6 g of ethanol were added and the mixture was stirred for another 30 min. After aging for 3 h the dispersion was filtered subsequently through 0.8 μm and 0.45 μm syringe filters (PVDF).

Example 2D (solid content of compound Xa = 1.05%):

[0080] 0.63 g of compound Xa were dissolved in 30 g Clevios P VPAI 4083 (Heraeus Precious Metals GmbH & Co. KG, 1.5% solid content). 24 g of water were added and the mixture was stirred for 30 min at room temperature and then heated (1 h, 55°C) until all solids were dissolved completely. The mixture was cooled to room temperature (1 h), 6 g of ethanol were added and the mixture was stirred for another 30 min. After aging for 3 h the dispersion was filtered through a 0.8 μm syringe filter (PVDF). For filtration through 0.45 μm syringe filter 3 h ultrasonic treatment (Sonorex R1028, Bandelin) was necessary prior to filtration.

Example 3: fabrication of an OLED with a conductive layer containing compound Xa (not forming part of the claimed invention)

[0081] The dispersion obtained in Examples 2A-2D was used to construct organic light emitting diodes (OLEDs). The procedure for producing the OLEDs was as follows:

i) Preparation of the substrate
ITO-coated glass is cut into pieces 50 mm × 50 mm in size (substrates) and is structured with photo resist into 8 contact lines - each 2 mm in width at their ends. Thereafter, the substrates are cleaned in 0.3 % strength Mucasol

solution in an ultrasound bath, rinsed with distilled water and spin-dried in a centrifuge. Immediately before coating, the ITO-coated sides are activated for 10 min in a UV/ozone reactor (PR-100, UVP Inc., Cambridge, GB).

ii) Application of the hole-injecting layer

About 5 ml of the dispersion according to Examples 2A-2D are filtered (Millipore HV, 0.45 μm). The cleaned ITO-coated substrate is laid on a spin-coater (Carl Suss RC8) and the filtered solution is distributed on the ITO-coated side of the substrate. The excess solution is then spun off by rotating the plate for 30 sec. The spin-speed was adjusted to obtain always a layer thickness of 50 nm (dried film) determined with a stylus profilometer (Dektak 150, Bruker). Thereafter, the substrate coated in this way is dried on a hotplate at 200°C for 5 min.

iii) Application of the hole transport and the emitter layer

The ITO substrates coated with the dispersion from Examples 2A-2D are transferred into a vapor deposition unit (Univex 350, Leybold). Under a pressure below 10^{-3} Pa, first 60 nm of a hole transport layer of NPB (N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine) and then 50 nm of an emitter layer of A1Q3 (tris-(8-hydroxyquinoline)-aluminium) are vapor-deposited in succession at a vapor deposition rate of 1 Å/sec.

iv) Application of the metal cathode

The layer system is then transferred into a glove box with an N_2 atmosphere and an integrated vapor deposition unit (Auto306 Vacuum Coater, Edwards), and metal electrodes are vapor-deposited. For this, the substrate is laid on a shadow mask with the layer system downwards. The shadow mask comprised rectangular slots of 2 mm width which intersected the ITO strips and are orientated perpendicular to these. A 0.5 nm thick LiF layer and then a 200 nm thick Al layer are vapor-deposited successively from two vapor deposition boats under a pressure of p <= 10^{-3} Pa. The vapor deposition rates were 1 Å/s for LiF and 10 Å/s for Al. The area of the individual OLEDs is 4.0 mm^2.

v) Layer stack overview

Example 3A: ITO//Formulation from Example 2A (50nm)//NPB//ALQ//LiF//Al
Example 3B: ITO//Formulation from Example 2B (50nm)//NPB//ALQ//LiF//Al
Example 3C: ITO//Formulation from Example 2C (50nm)//NPB//ALQ//LiF//Al
Example 3D: ITO//Formulation from Example 2D (50nm)//NPB//ALQ//LiF//Al

vi) Characterization of the OLED

The two electrodes of the organic LED are connected (contacted) to a source/measuring unit (Keithley 2400) via electrical leads. The positive pole is connected to the ITO electrode and the negative pole is connected to the metal electrode. The dependency of the OLED current and the electroluminescence intensity (detection is with a photodiode (EG&G C30809E) + electrometer (Keithley 6415)) on the voltage is plotted. The lifetime of the OLED-device is then determined by allowing a constant current of I = 3.84 mA to flow through the arrangement and monitoring the voltage and light intensity as a function of time.

[0082] The characteristic Data for the OLEDs is summarized in table 1.

Comparative Example 4: fabrication of an OLED not containing compound Xa

[0083] The procedure is the same as in Example 3, with the difference that in the second process step Clevios P VP AI4083 (Heraeus Precious Metals GmbH & Co. KG), regarded as standard in OLED construction, was used solely as the interlayer instead of the dispersions according to the invention from example 2A-2D. Clevios © P VP AI4083 was deposited according to Example 3. The film thickness was 50 nm.

[0084] The characteristic Data for the OLEDs is summarized in table 1.

Layer stack:

Comparative Example 4 ITO// Clevios P VP AI4083 (50nm)//NPB//ALQ//LiF//Al

Example 5: determination of resistivity

[0085] The resistivity of Clevios™ films is determined by measuring the film's sheet resistance and its layer thickness. The films are prepared by depositing 1-2 ml of the polymer dispersion on a 50 mm × 50 mm glass-substrate. Prior deposition the glass-substrate of 1 mm thickness is thoroughly cleaned in 0.3 % strength Mucasol solution in an ultrasound

bath, rinsed with distilled water and spin-dried in a centrifuge. As a final step the surface to be coated on is activated by UV/Ozone exposure (PR-100UV/Ozone UVP, Cambridge, GB) for 15 min. Next the glass-substrate is placed in a chuck of a spin-coater (Carl Süss RC8). The overlaying dispersion is removed by rotating the glass-plate at 1000 rpm for 30 sec. A thin uniform film is obtained. The film is conveyed to a heat-plate set to 130°C and left there for 5 min to dry.

[0086] In a next step the film is covered with a shadow mask. The mask is made of a 100 μm-thick steel-sheet of size 50 mm × 50 mm exhibiting 6 parallel slits machined in the centre (Length L: 25.0mm, width b: 3.0mm, slit-separation: a = 500 μm). The mask is held by a magnet from the backside of the coated substrate. The substrate is mounted in a vacuum-evaporator with electro-thermally heated boats for Ag-evaporation (Univex 350, Leybold). The vessel is evacuated to a pressure of 6×10^{-4}°Pa. When this pressure is reached, Ag is thermally evaporated at a rate of 20 Å/sec until a final electrode-thickness of 2000 Å is reached.

[0087] The resistance R between adjacent Ag-electrodes is measured with an electrometer (Keithley 616) in a home-built set-up in which the sample is mounted in a vacuum chamber and Au-contact pins are pressed on the Ag-electrodes.

[0088] The film's thickness d is determined by scratching the film off the substrate with a razor blade and scanning the stylus of a mechanical profilometer (Dektak 150, Bruker) across the scratch.

[0089] Finally the resistivity "ro" is calculated my multiplying the sheet resistance with the layer thickness according to ro=R×L/b×d.

[0090] The resistivities of films made of dispersions according to Example 2A-2D are shown in table 1.

Example 6: comparison of the OLEDs from Examples 3 and 4

[0091] The graphs plotting current and electroluminescence against voltage and the lifetime measurements for the OLEDs from Examples 3 and 4 were compared.

Table 1: OLED-characteristics from Examples 3 and 4 wherein the values were normalized to the comparative example 4.

		IVL-Characteristics at U=5.0V			Lifetime @ I= 48mA/cm^2			
	specific resistance (Ohm×cm)	I (mA/cm^2)	L (cd/m^2)	Efficiency (cd/A)	U (t=0) (Volt)	L(t=0) (cd/m^2)	t(80%) (h)	t(50%) (h)
Ex. 3A	0.13	1.48	1.58	1.05	0.90	1.01	2.2	2.6
Ex. 3B	0.11	1.33	1.24	0.93	0.95	0.93	2.79	2.94
Ex. 3C	0.1	1.3	1.34	1.03	0.90	0.92	2.2	2.18
Ex. 3D	0.1	1.5	1.72	1.14	0.89	1.01	1.8	2.57
Comp. Ex. 4 (AI4083)	1	1	1	1	1	1	1	1

[0092] A significant increase of lifetime compared to the standard (Comparative Example 4) can be observed for all Examples 3A-3D.

Claims

1. A composition comprising

I) at least one conductive polymer,
II) at least one solvent and
III) at least one compound having a general formula Ia

$$K\text{-}[\text{-}X\text{-}A]_n \qquad \text{Ia}$$

wherein

K represents an aromatic group in which at least one hydrogen atom may be substituted by a functional

group selected from the group consisting of a sulfonic acid group, a sulfuric acid group, an ammonium group, an aliphatic group, and-CO_2M, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+};
X is O;
A represents a fluorinated or perfluorinated aromatic group;
n represents an integer in the range from 2 to 6;

characterized in that the conductive polymer comprises a complex of a polythiophene and a polyanion.

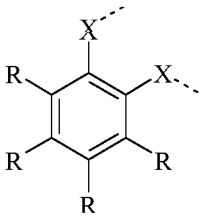
2. The composition according to claim 1, wherein the functional group is selected from the group consisting of

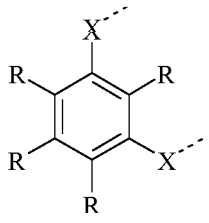
i) -SO_3M, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+},
i) -OSO_3M, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+},
ii) -CO_2M, wherein M is selected from the group consisting of H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} and Mg^{2+},
iii) an ammonium group selected from the group consisting of -$N(CH_3)_4^+$, -$N(CH_2CH_3)_4^+$, -$N(C_3H_7)_4^+$, -$N(C_4H_9)_4^+$, and -$N(C_5H_{11})_4^+$, and
iv) an alkyl group selected from the group consisting of -CH_3, -C_2H_5, -C_3H_7, -C_4H_9, -C_5H_{11}, -C_6H_{13}, -C_7H_{15}, -C_8H_{17}, -C_9H_{19}, -$C_{10}H_{21}$, -$C_{11}H_{23}$ and -$C_{12}H_{25}$.

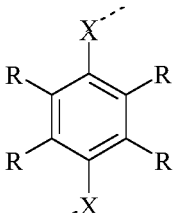
3. The composition according to anyone of claims 1 to 2, wherein K represents a monocyclic aromatic group and wherein the structural subunit Ia' of formula Ia

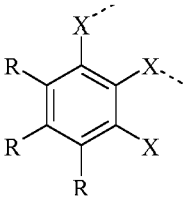
$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

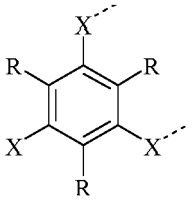
has a general structure selected from the group consisting of general formulae IIa to IIk:

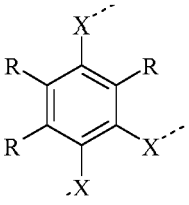

IIa

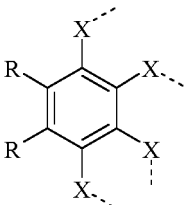

IIb

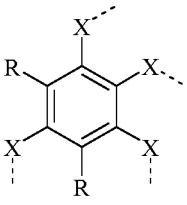

IIc

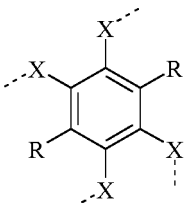

IId

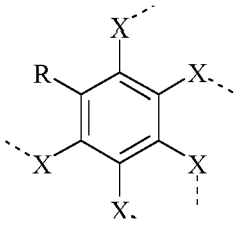

IIe


IIf


IIg


IIh


IIj



IIIk

wherein

- R is selected from the group consisting of H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$, and $-C_{12}H_{25}$, wherein M is as defined in claim 2 and

wherein the dotted line indicates the bond to A.

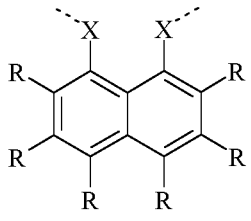
4. The composition according to claim 3, wherein the following combinations for substituent R per entity K are fulfilled:

n = 2, and
R = 1 × $-SO_3M$ and 3 × H or R = 2 × $-SO_3M$ and 2 × H,
or
n = 3, and
R = 3 × H or R = 3 × $-SO_3M$,
wherein M is as defined in claim 2.

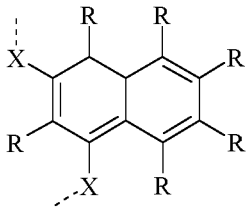
5. The composition according to anyone of claims 1 to 2, wherein K represents a bicyclic aromatic group, n represents 2 and wherein the structural subunit Ia' of formula Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

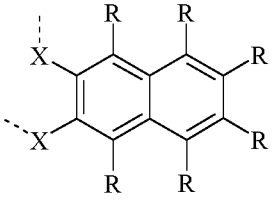
has a general structure selected from the group consisting of general formulae IIIa to IIIj:



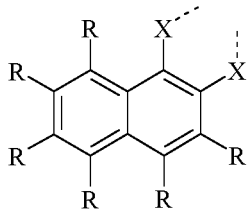
IIIa



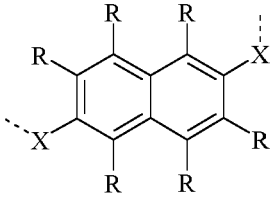
IIIb



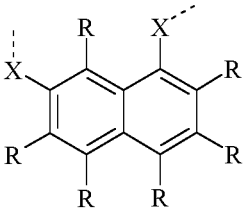
IIIc



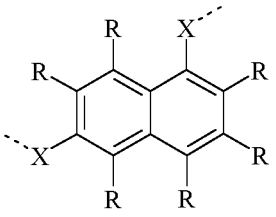
IIId



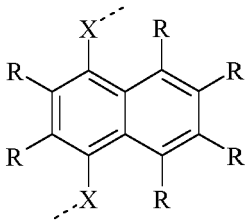
IIIe



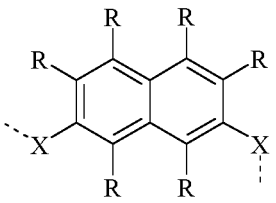
IIIf



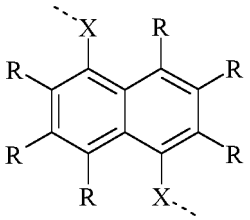
IIIg



IIIh



IIIi



IIIj

wherein

- R is selected from the group consisting of H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$, and $-C_{12}H_{25}$, wherein M is as defined in claim 2 and

wherein the dotted line indicates the bond to A.

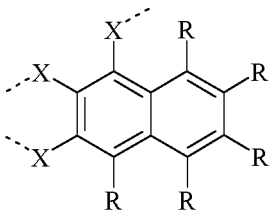
6. The composition according to claim 5, wherein the following combinations for substituent R per entity K are fulfilled:

R = 2 × $-SO_3M$ and 4 × H,
or
R = 3 × $-SO_3M$ and 3 × H,
wherein M is as defined in claim 2.

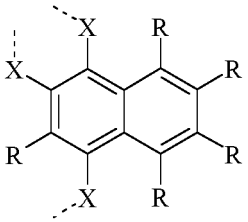
7. The composition according to anyone of claims 1 to 2, wherein K represents a bicyclic aromatic group, n represents 3 and wherein the structural subunit Ia' of formula Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

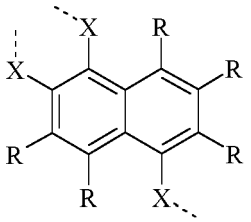
has a general structure selected from the group consisting of general formulae IVa to IV1:



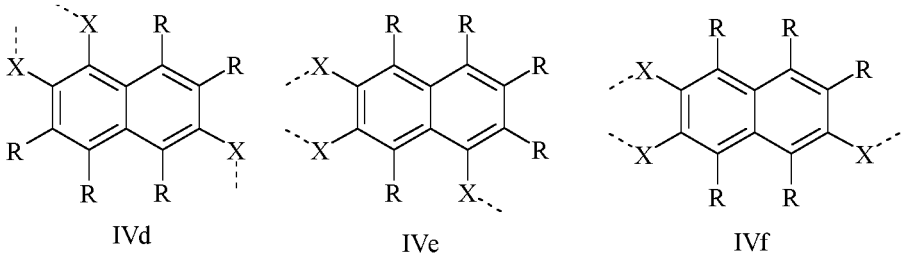
IVa

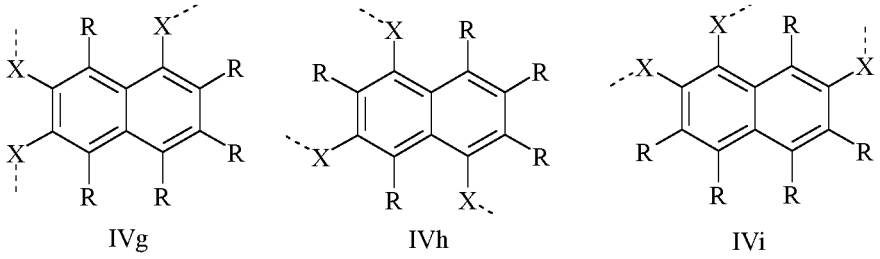


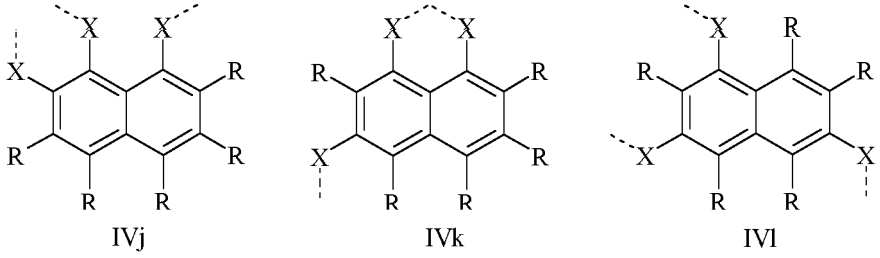
IVb



IVc


IVd IVe IVf


IVg IVh IVi

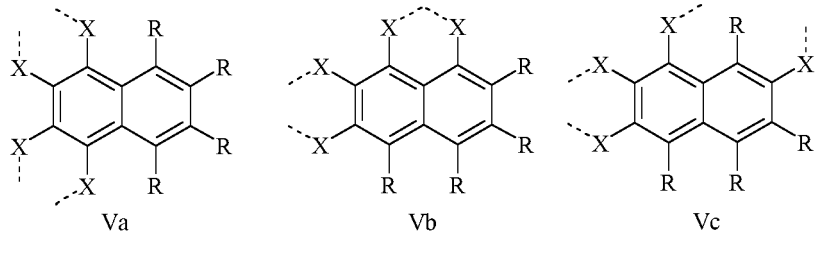

IVj IVk IVl

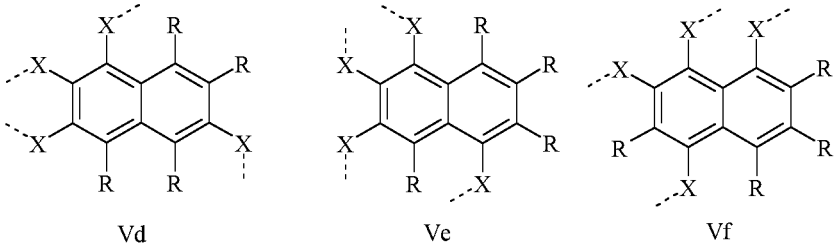
wherein R is selected from the group consisting of H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$, and $-C_{12}H_{25}$, wherein M is as defined in claim 2 and wherein the dotted line indicates the bond to A.

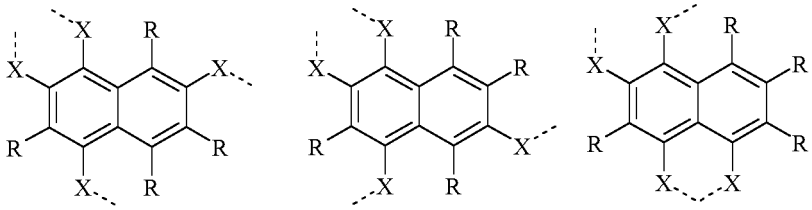
8. The composition according to anyone of claims 1 to 2, wherein K represents a bicyclic aromatic group, n represents 4 and wherein the structural subunit Ia' of formula Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

has a general structure selected from the group consisting of general formulae Va to Vi:


Va Vb Vc


Vd Ve Vf



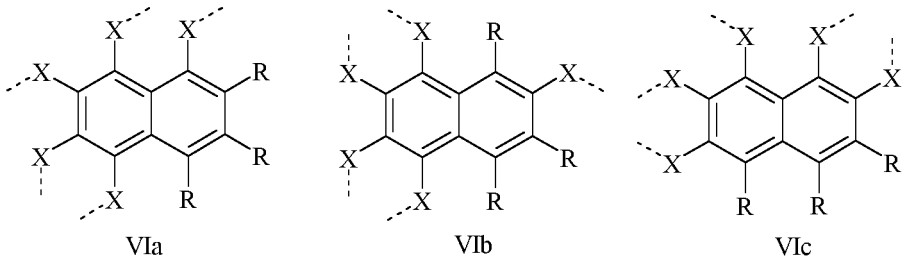
Vg Vh Vi

wherein R is selected from the group consisting of H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$, and $-C_{12}H_{25}$, wherein M is as defined in claim 2 and wherein the dotted line indicates the bond to A.

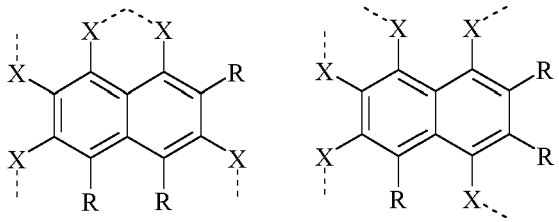
9. The composition according to anyone of claims 1 to 2, wherein K represents a bicyclic aromatic group, n represents 5 and wherein the structural subunit Ia' of formula Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

has a general structure selected from the group consisting of general formulae VIa to VIe:



VIa VIb VIc



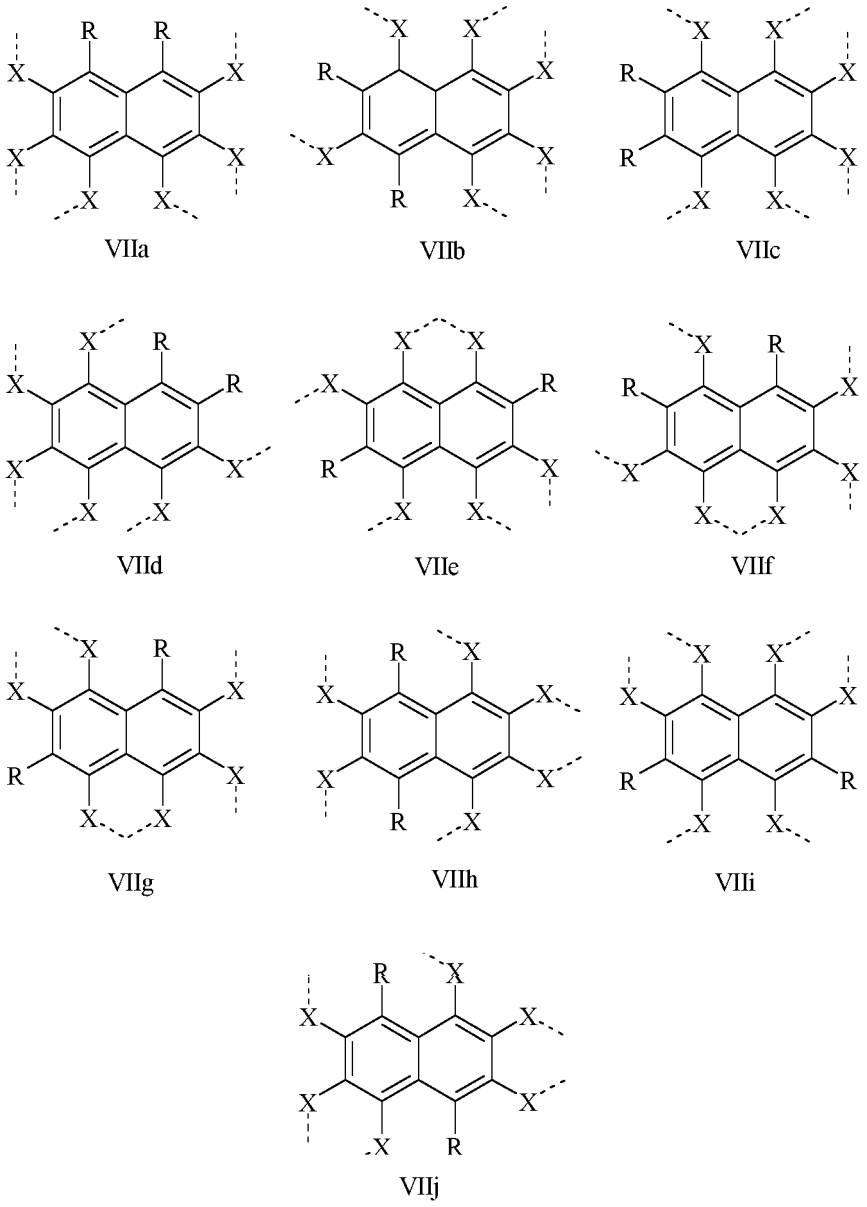
VId VIe

wherein R is selected from the group consisting of H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ and $-C_{12}H_{25}$, wherein M is as defined in claim 2 and wherein the dotted line indicates the bond to A.

10. The composition according to anyone of claims 1 to 2, wherein K represents a bicyclic aromatic group, n represents 6 and wherein the structural subunit Ia' of formula Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

has a general structure selected from the group consisting of general formulae VIIa to VIIj:



VIIa VIIb VIIc

VIId VIIe VIIf

VIIg VIIh VIIi

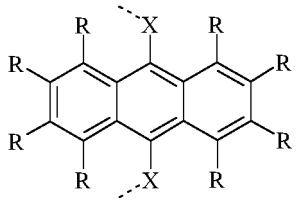
VIIj

wherein R is selected from the group consisting of H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ and $-C_{12}H_{25}$, wherein M is as defined in claim 2 and wherein the dotted line indicates the bond to A.

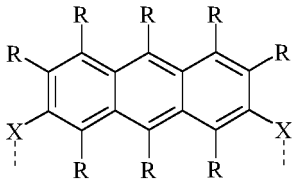
11. The composition according to anyone of claims 1 to 2, wherein K represents a tricyclic aromatic group and wherein the structural subunit Ia' of formula Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

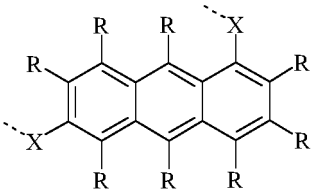
has a general structure selected from the group consisting of general formulae VIIa to VIIIr:



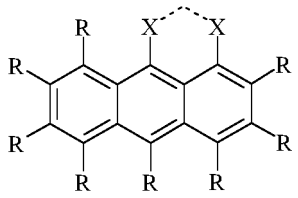
VIIIa



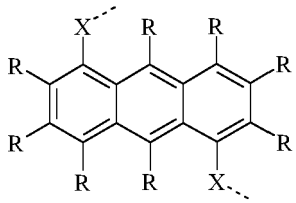
VIIIb



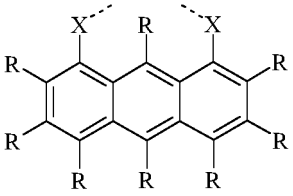
VIIIc



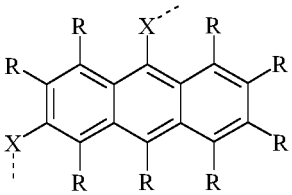
VIIId



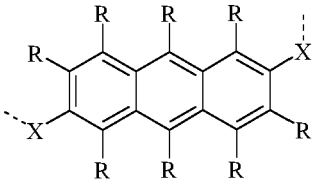
VIIIe



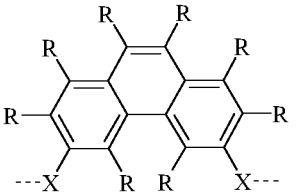
VIIIf



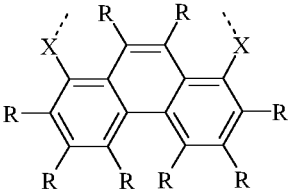
VIIIg



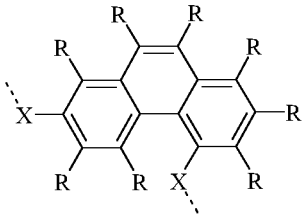
VIIIh



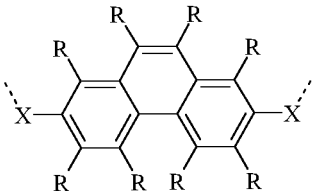
VIIIi



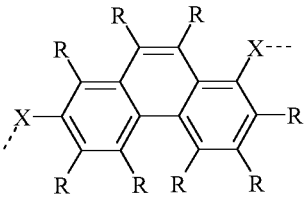
VIIIj



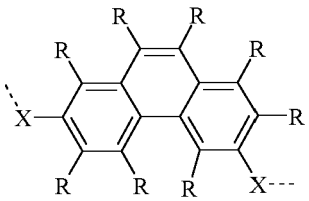
VIIIk



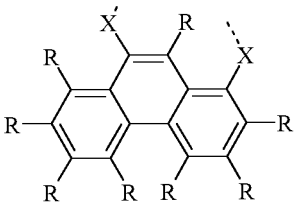
VIIIl



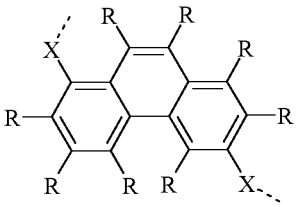
VIIIm



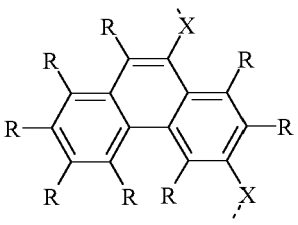
VIIIn



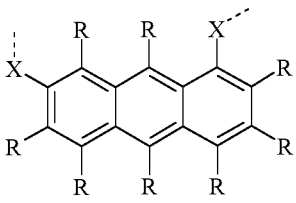
VIIIo



VIIIp



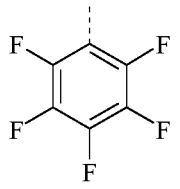
VIIIq



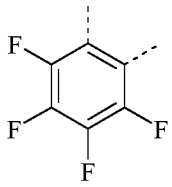
VIIIr

wherein R is selected from the group consisting of H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ and $-C_{12}H_{25}$, wherein M is as defined in claim 2 and wherein the dotted line indicates the bond to A.

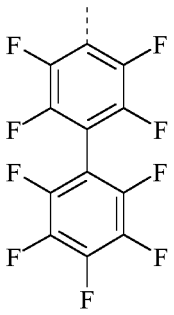
12. The composition according to anyone of claims 1 to 11, wherein A has a general structure selected from the group consisting of general formulae IXa to IXo:



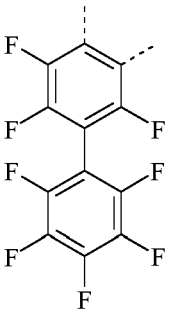
IXa



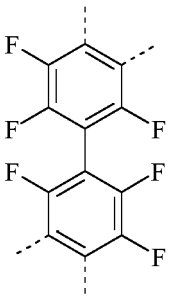
IXb



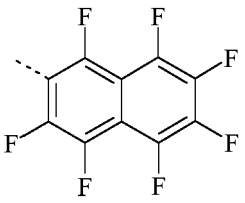
IXc



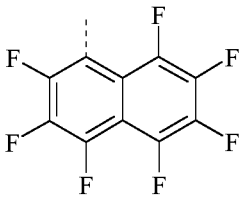
IXd



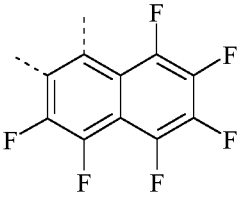
IXe



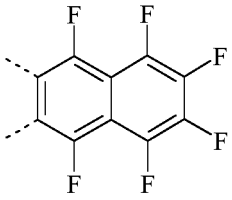
IXf



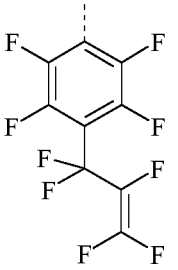
IXg



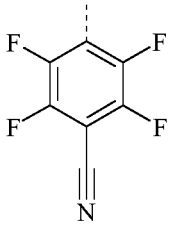
IXh



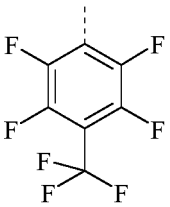
IXi



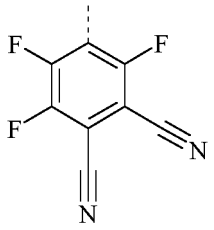
IXj



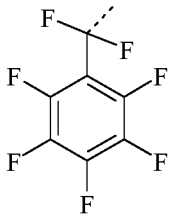
IXk



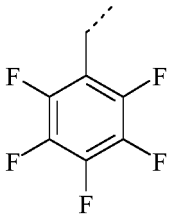
IXl



IXm



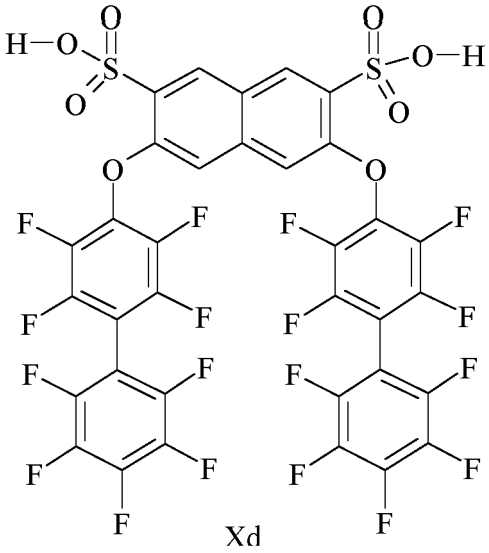
IXn



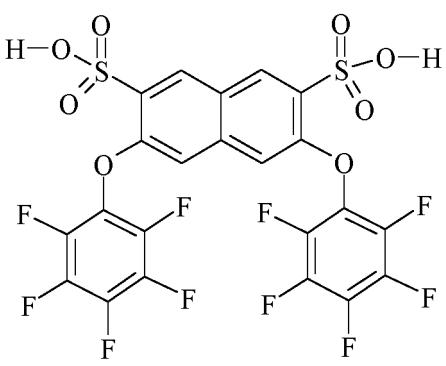
IXo

wherein the dotted line indicates the bond to X.

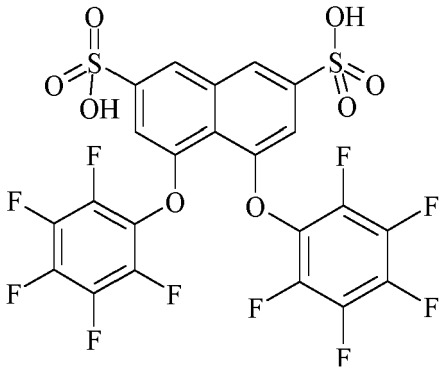
13. The composition according to anyone of claims 1 to 12, wherein the compound has a general structure selected from the group consisting of general formulae Xd to Xg or the corresponding salts thereof:



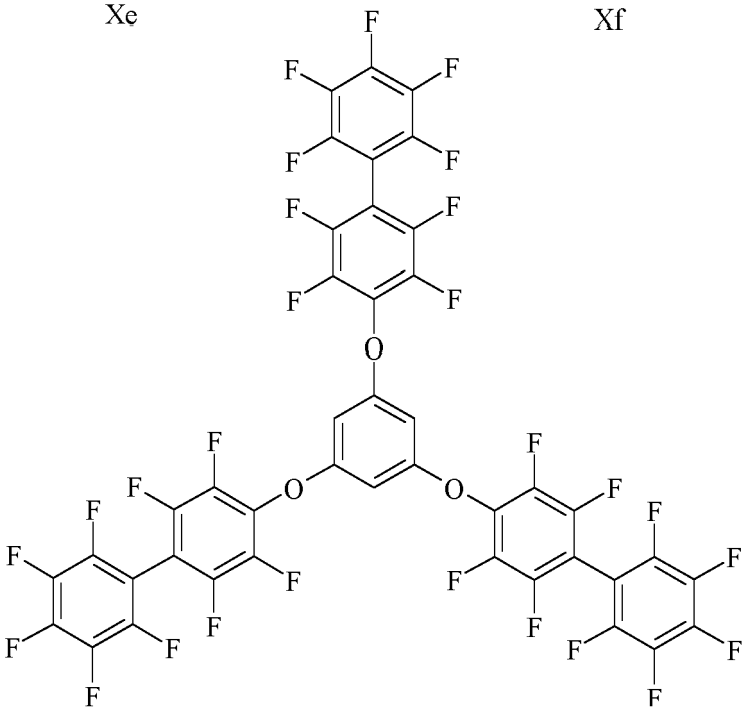
Xd



Xe



Xf



Xg

14. The composition according to anyone of claims 1 to 13, wherein the solvent II) is water, an organic solvent selected from the group consisting of alcohols, aliphatic hydrocarbons, aromatic hydrocarbons, ethers, halogenated hydrocarbons, aliphatic nitriles, aliphatic carboxylic acids, aliphatic carboxylic acid and ketones or a mixture of at least two of these solvents.

15. A process for the preparation of a conductive layer, which comprises the process steps:

(PI) superimposing a substrate with the composition according to anyone of claims 1 to 14; or first superimposing a substrate with a composition comprising the solvent II) as defined in claims 1 and 14 and the compound III) as defined in anyone of claims 1 to 13, at least partial removal of the solvent and then superimposing the substrate with a composition according to anyone of claims 1 to 14 or with a composition comprising the solvent II) as defined in claims 1 and 14 and the conductive polymer I) as defined in claim 1; or first superimposing a substrate with a composition comprising the solvent II) as defined in claims 1 and 14 and the conductive polymer I) as defined in claim 1, at least partial removal of the solvent and then superimposing the substrate with the composition according to anyone of claims 1 to 14 or with a composition comprising the solvent II) as defined in claims 1 and 14 and the compound III) as defined in anyone of claims 1 to 13;
(P2) at least partial removal of the solvent.

16. A conductive layer comprising at least one compound as defined in anyone of claims 1 to 13 and at least one conductive polymer, wherein the conductive polymer comprises a complex of a polythiophene and a polyanion.

17. An electronic component comprising a conducting layer obtainable by the process according to claim 15 or comprising a conductive layer according to claim 16.

18. The electronic component according to claim 17, wherein the electronic component is an OLED, a display, an organic solar cell, a hybrid solar cell, a field effect transistor, or a thermoelectric generator.

Patentansprüche

1. Zusammensetzung umfassend

I) mindestens ein leitfähiges Polymer,
II) mindestens ein Lösungsmittel und
III) mindestens eine Verbindung mit einer allgemeinen Formel Ia

$$K\text{-}[\text{-}X\text{-}A]_n \qquad \text{Ia}$$

wobei

K stellt eine aromatische Gruppe dar, bei der mindestens ein Wasserstoffatom durch eine funktionelle Gruppe, ausgewählt aus der Gruppe bestehend aus einer Sulfonsäuregruppe, einer Schwefelsäuregruppe, einer Ammoniumgruppe, einer aliphatischen Gruppe und $-CO_2M$ substituiert sein kann, wobei M ausgewählt ist aus der Gruppe bestehend aus H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} und Mg^{2+};
X is O;
A repräsentiert eine fluorierte oder perfluorierte aromatische Gruppe;
n steht für eine ganze Zahl im Bereich von 2 bis 6;

dadurch gekennzeichnet, dass das leitfähige Polymer einen Komplex aus einem Polythiophen und einem Polyanion umfasst.

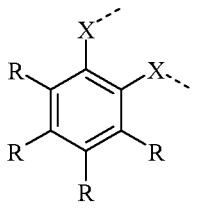
2. Zusammensetzung nach Anspruch 1, wobei die funktionelle Gruppe ausgewählt ist aus der Gruppe bestehend aus

i) $-SO_3M$, wobei M ausgewählt ist aus der Gruppe bestehend aus H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} und Mg^{2+},
i) $-OSO_3M$, wobei M ausgewählt ist aus der Gruppe bestehend aus H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} und Mg^{2+},
ii) $-CO_2M$, wobei M ausgewählt ist aus der Gruppe bestehend aus H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} und Mg^{2+},
iii) eine Ammoniumgruppe, ausgewählt aus der Gruppe bestehend aus $-N(CH_3)_4^+$,- $N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$ und $-N(C_5H_{11})_4^+$, und
iv) eine Alkylgruppe ausgewählt aus der Gruppe bestehend aus $-CH_3$,- C_2H_5, -C3H7, -C4H9, $-C_5H_{11}$, $-C_6HI_3$, $-C_7HI_5$, $-C_8HI_7$, $-C_9HI_9$, $-C_{10}H_2I$, $-C_{11}H_{23}$ und $-C_{12}H_{25}$.

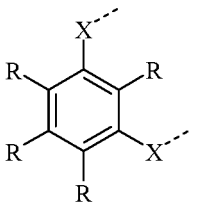
3. Zusammensetzung nach einem der Ansprüche 1 bis 2, wobei K eine monocyclische aromatische Gruppe darstellt und wobei die strukturelle Untereinheit Ia' der Formel Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

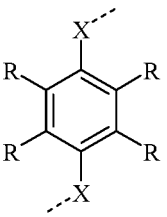
eine allgemeine Struktur aufweist, die ausgewählt ist aus der Gruppe bestehend aus den allgemeinen Formeln IIa bis IIk:



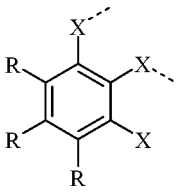
IIa



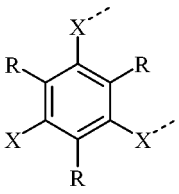
IIb



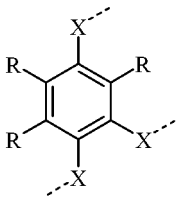
IIc



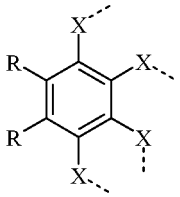
IId



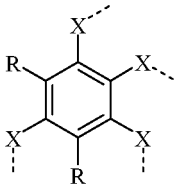
IIe



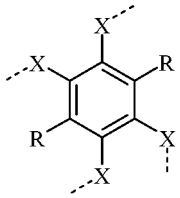
IIf



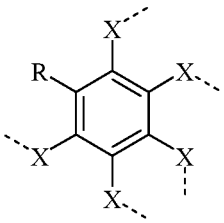
IIg



IIh



IIj



IIk

wobei

-R ausgewählt ist aus der Gruppe bestehend aus H, $+SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$,- C_2H_5, -C3H7, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H2l$, $-C_{11}H_{23}$ und $-C_{12}H_{25}$, wobei M wie in Anspruch 2 definiert ist und
wobei die gestrichelte Linie die Bindung an A anzeigt.

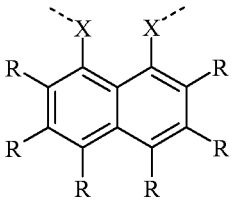
4. Zusammensetzung nach Anspruch 3, wobei die folgenden Kombinationen für Substituent R pro Einheit K erfüllt sind:

n = 2, und
R = 1 × $-SO_3M$ und 3 × - SO_3M und 2 × H,
oder
n = 3, und
R = 3 × H oder 3 ×$-SO_3M$,
wobei M wie in Anspruch 2 definiert ist.

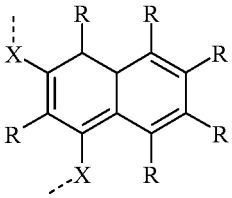
5. Zusammensetzung nach einem der Ansprüche 1 bis 2, wobei K eine bicyclische aromatische Gruppe darstellt, n für 2 steht und wobei die strukturelle Untereinheit Ia' der Formel Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

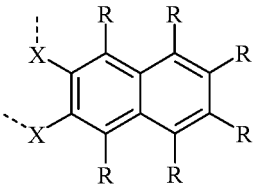
eine allgemeine Struktur aufweist, die aus der Gruppe ausgewählt ist, die aus den allgemeinen Formeln IIIa bis IIIj besteht:



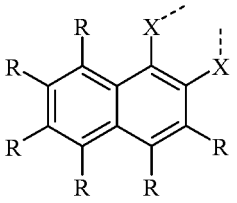
IIIa



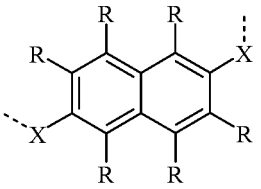
IIIb



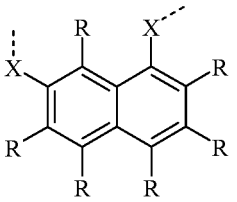
IIIc



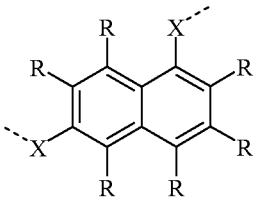
IIId



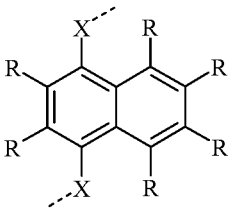
IIIe



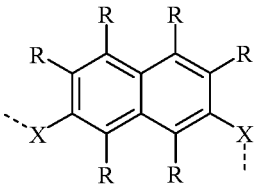
IIIf



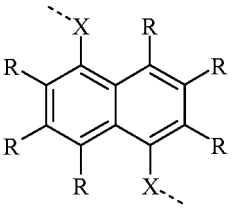
IIIg



IIIh



IIIi



IIIj

wobei

-R ausgewählt ist aus der Gruppe bestehend aus H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$,- C_2H_5, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ und $-C_{12}H_{25}$, wobei M wie in Anspruch 2 definiert ist und
wobei die gestrichelte Linie die Bindung an A anzeigt.

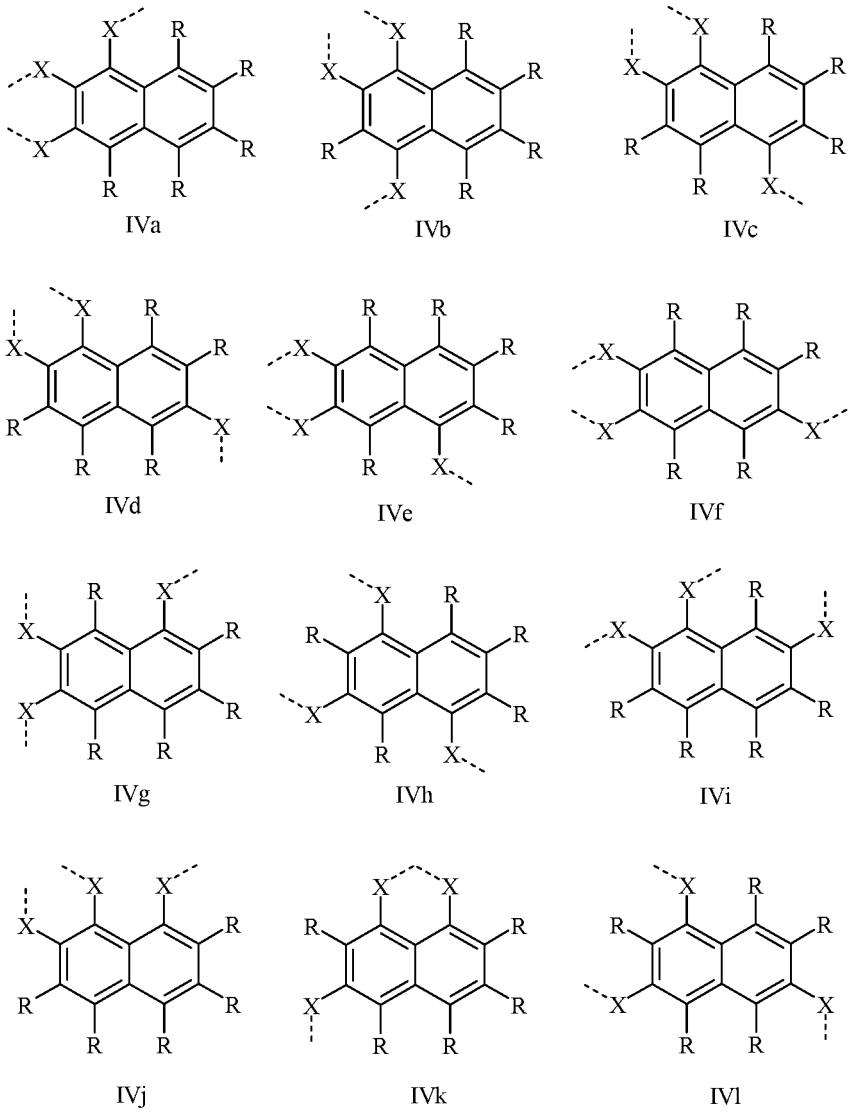
6. Zusammensetzung nach Anspruch 5, wobei die folgenden Kombinationen für Substituent R pro Einheit K erfüllt sind:

R = 2 × $-SO_3M$ und 4 × H,
oder
R = 3 × $-SO_3M$ und 3 xH,
wobei M wie in Anspruch 2 definiert ist.

7. Zusammensetzung nach einem der Ansprüche 1 bis 2, wobei K eine bicyclische aromatische Gruppe darstellt, n für 3 steht und wobei die strukturelle Untereinheit Ia' der Formel Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

eine allgemeine Struktur aufweist, die ausgewählt ist aus der Gruppe bestehend aus den allgemeinen Formeln IVa bis IVl:

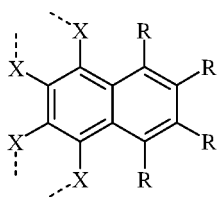


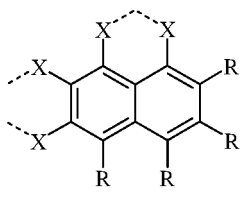
Wobei
-R ausgewählt ist aus der Gruppe bestehend aus H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$,- C_2H_5, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ und $-C_{12}H_{25}$, wobei M wie in Anspruch 2 definiert ist und wobei die gestrichelte Linie die Bindung zu A anzeigt.

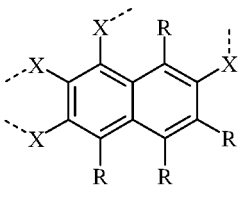
8. Zusammensetzung nach einem der Ansprüche 1 bis 2, wobei K eine bicyclische aromatische Gruppe darstellt, n 4 bedeutet und wobei die strukturelle Untereinheit Ia' der Formel Ia

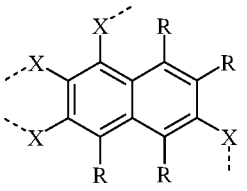
$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

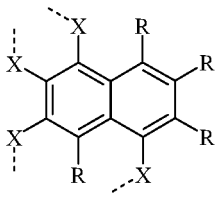
eine allgemeine Struktur aufweist, die aus der Gruppe ausgewählt ist, die aus den allgemeinen Formeln Va bis Vi besteht:

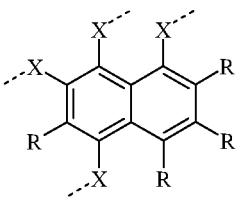

Va

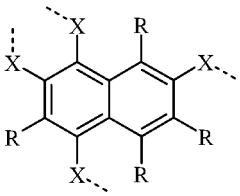

Vb

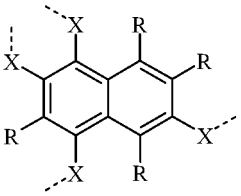

Vc

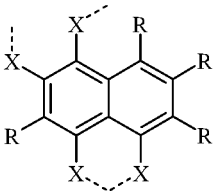

Vd


Ve


Vf


Vg


Vh

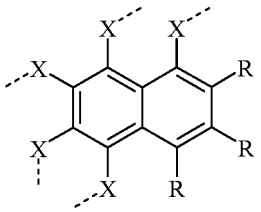

Vi

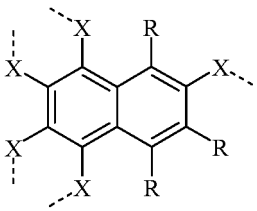
Wobei
-R ausgewählt ist aus der Gruppe bestehend aus H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$,- C_2H_5, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ und $-C_{12}H_{25}$, wobei M wie in Anspruch 2 definiert ist und wobei die gestrichelte Linie die Bindung zu A anzeigt.

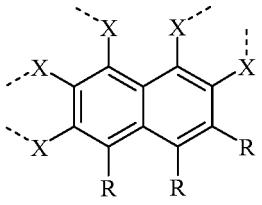
9. Zusammensetzung nach einem der Ansprüche 1 bis 2, wobei K eine bicyclische aromatische Gruppe darstellt, n für 5 steht und wobei die strukturelle Untereinheit Ia' der Formel Ia

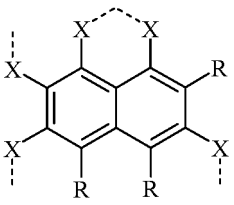
$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

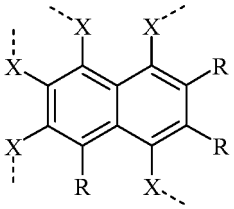
eine allgemeine Struktur aufweist, die ausgewählt ist aus der Gruppe bestehend aus den allgemeinen Formeln VIa bis VIe:


VIa


VIb


VIc


VId

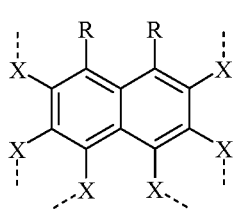

VIe

Wobei -R ausgewählt ist aus der Gruppe bestehend aus H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$,- C_2H_5, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ und $-C_{12}H_{25}$, wobei M wie in Anspruch 2 definiert ist und wobei die gestrichelte Linie die Bindung zu A anzeigt.

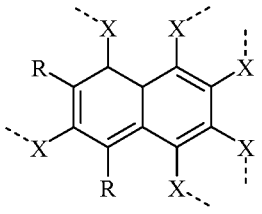
10. Zusammensetzung nach einem der Ansprüche 1 bis 2, wobei K eine bicyclische aromatische Gruppe darstellt, n für 6 steht und wobei die strukturelle Untereinheit Ia' der Formel Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

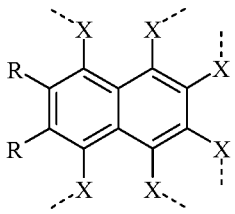
eine allgemeine Struktur aufweist, die aus der Gruppe ausgewählt ist, die aus den allgemeinen Formeln VIIa bis VIIj besteht:



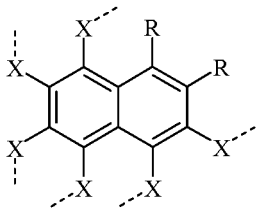
VIIa



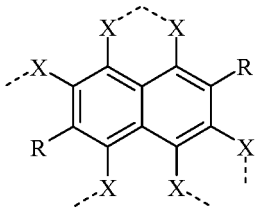
VIIb



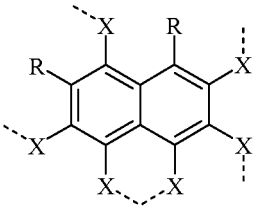
VIIc



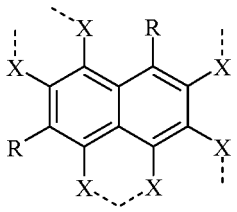
VIId



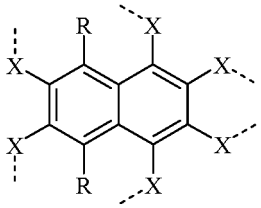
VIIe



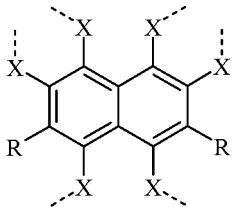
VIIf



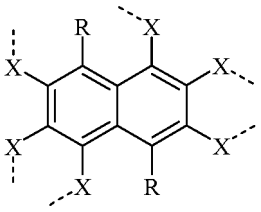
VIIg



VIIh



VIIi



VIIj

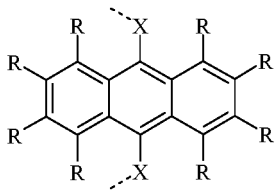
Wobei
-R ausgewählt ist aus der Gruppe bestehend aus H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$,- C_2H_5, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ und $-C_{12}H_{25}$, wobei M wie in Anspruch 2 definiert ist und wobei die gestrichelte Linie die Bindung zu A anzeigt.

11. Zusammensetzung nach einem der Ansprüche 1 bis 2, wobei K eine tricyclische aromatische Gruppe darstellt und

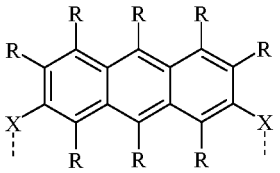
wobei die strukturelle Untereinheit Ia' der Formel Ia

$$K\text{-}[\text{-}X]_n \qquad \text{Ia'}$$

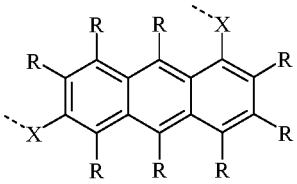
eine allgemeine Struktur aufweist, die aus der Gruppe ausgewählt ist, die aus den allgemeinen Formeln VIIIa bis VIIIr besteht:



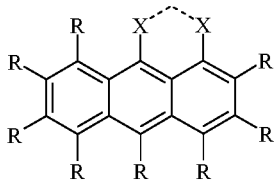
VIIIa



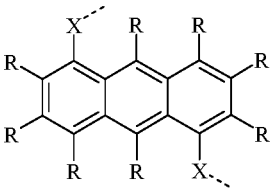
VIIIb



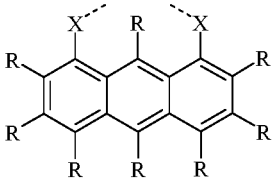
VIIIc



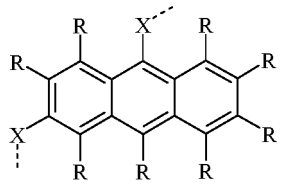
VIIId



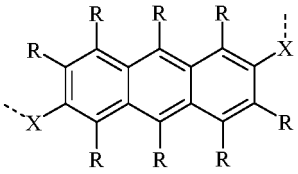
VIIIe



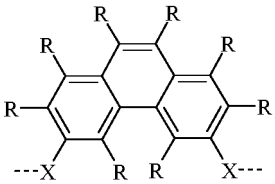
VIIIf



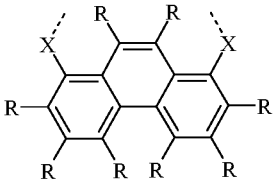
VIIIg



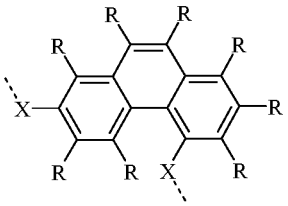
VIIIh



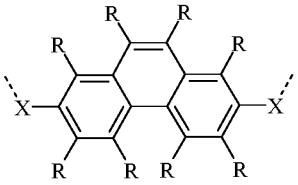
VIIIi



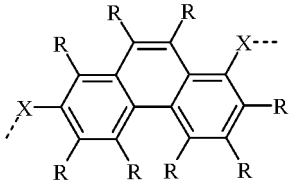
VIIIj



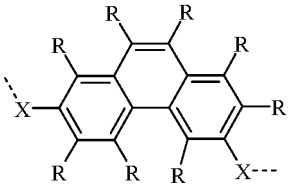
VIIIk



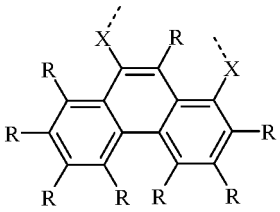
VIIIl



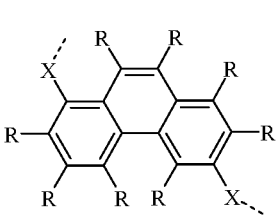
VIIIm



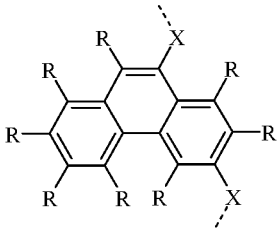
VIIIn



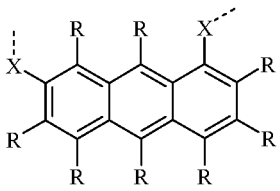
VIIIo



VIIIp



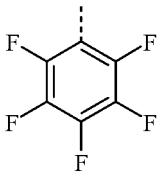
VIIIq



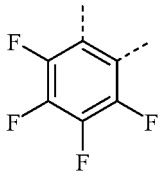
VIIIr

Wobei
-R ausgewählt ist aus der Gruppe bestehend aus H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$,- C_2H_5, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ und $-C_{12}H_{25}$, wobei M wie in Anspruch 2 definiert ist und wobei die gestrichelte Linie die Bindung zu A anzeigt.

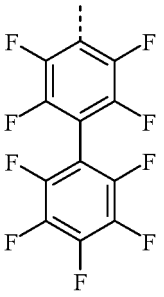
12. Zusammensetzung nach einem der Ansprüche 1 bis 11, wobei A eine allgemeine Struktur aufweist, die ausgewählt ist aus der Gruppe bestehend aus den allgemeinen Formeln IXa bis IXo:



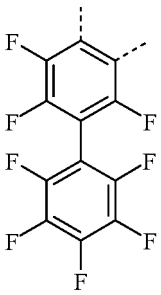
IXa



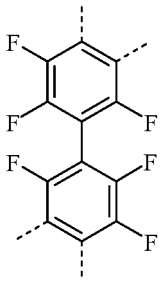
IXb



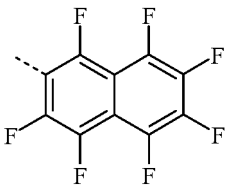
IXc



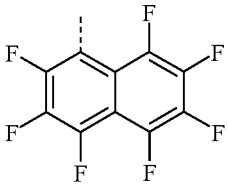
IXd



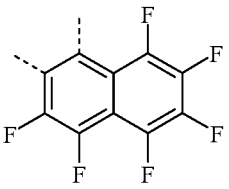
IXe



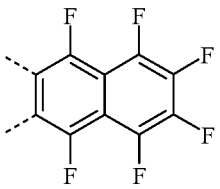
IXf



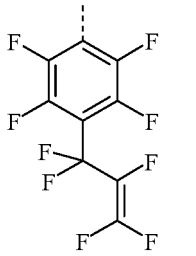
IXg



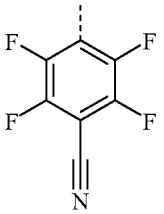
IXh



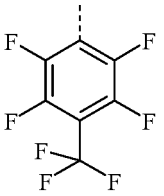
IXi



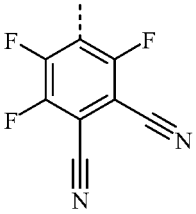
IXj



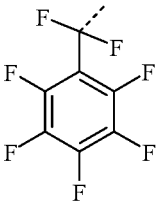
IXk



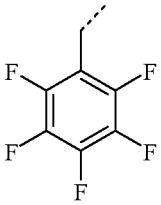
IXl



IXm



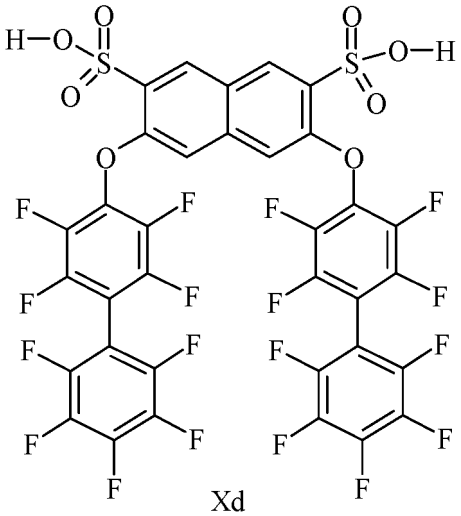
IXn



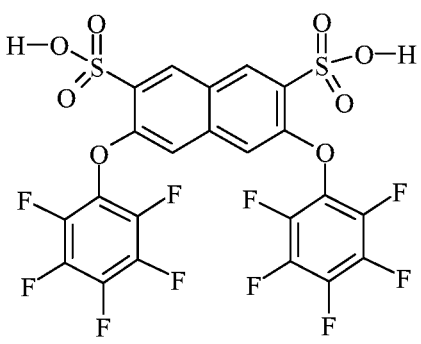
IXo

wobei die gestrichelte Linie die Bindung an X anzeigt.

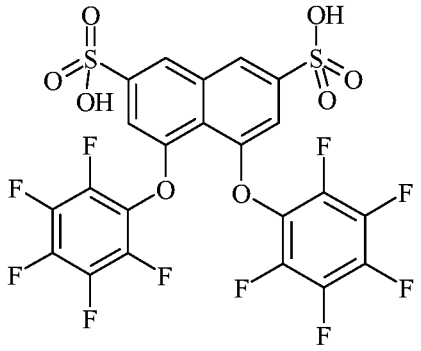
13. Zusammensetzung nach einem der Ansprüche 1 bis 12, wobei die Verbindung eine allgemeine Struktur aufweist, ausgewählt aus der Gruppe bestehend aus den allgemeinen Formeln Xd bis Xg oder den entsprechenden Salzen davon:



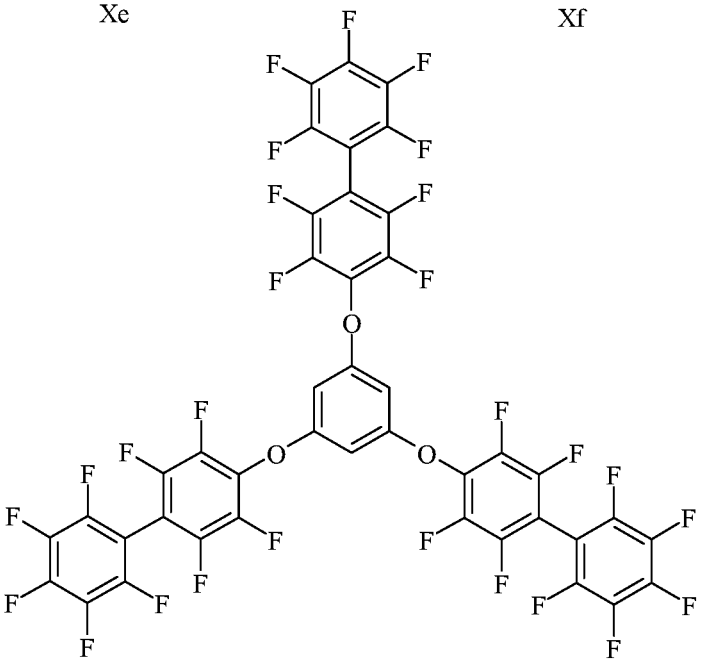
Xd



Xe



Xf



Xg

14. Zusammensetzung nach einem der Ansprüche 1 bis 12, wobei das Lösungsmittel II) Wasser, ein organisches Lösungsmittel, ausgewählt aus der Gruppe bestehend aus Alkoholen, aliphatischen Kohlenwasserstoffen, aromatischen Kohlenwasserstoffen, Ethern, halogenierten Kohlenwasserstoffen, aliphatischen Nitrilen, aliphatischen Carbonsäuren, aliphatischen Carbonsäuren und Ketonen oder eine Mischung aus mindestens zwei dieser Lösungsmittel ist.

15. Ein Verfahren zur Herstellung einer leitfähigen Schicht, das die Verfahrensschritte umfasst:

(P1) Bedecken eines Substrats mit der Zusammensetzung nach einem der Ansprüche 1 bis 14;
oder
erstes Überlagern eines Substrats mit einer Zusammensetzung, die das Lösungsmittel II) gemäß den Ansprüchen 1 und 14 und die Verbindung III) gemäß einem der Ansprüche 1 bis 13 enthält, zumindest teilweises Entfernen des Lösungsmittels und dann Überlagern des Substrats mit einer Zusammensetzung gemäß einem der Ansprüche 1 bis 14 oder mit einer Zusammensetzung, die das Lösungsmittel II) gemäß den Ansprüchen 1 und 14 und das leitfähige Polymer I) gemäß Anspruch 1 enthält;
oder
erstes Überlagern eines Substrats mit einer Zusammensetzung, die das Lösungsmittel II) gemäß den Ansprüchen 1 und 14 und das leitfähige Polymer I) gemäß Anspruch 1 enthält, zumindest teilweises Entfernen des Lösungsmittels und anschließendes Überlagern des Substrats mit der Zusammensetzung nach einem der Ansprüche 1 bis 14 oder mit einer Zusammensetzung, die das Lösungsmittel II) gemäß den Ansprüchen 1 und 14 und die Verbindung III) gemäß einem der Ansprüche 1 bis 13 enthält;
(P2) zumindest teilweise Entfernung des Lösungsmittels.

16. Leitfähige Schicht, umfassend mindestens eine Verbindung nach einem der Ansprüche 1 bis 13 und mindestens ein leitfähiges Polymer, wobei das leitfähige Polymer einen Komplex aus einem Polythiophen und einem Polyanion umfasst.

17. Elektronisches Bauelement mit einer leitfähigen Schicht, erhältlich nach dem Verfahren gemäß Anspruch 15 oder mit einer leitfähigen Schicht gemäß Anspruch 16.

18. Elektronisches Bauelement nach Anspruch 17, wobei das elektronische Bauelement eine OLED, ein Display, eine organische Solarzelle, eine Hybridsolarzelle, ein Feldeffekttransistor oder ein thermoelektrischer Generator ist.

Revendications

1. Une composition comprenant

I) au moins un polymère conducteur,
II) au moins un solvant et
III) au moins un composé ayant une formule générale Ia

$$K\text{-}[\text{-}X\text{-}A]_n \qquad \text{Ia}$$

dans laquelle

i)

K représente un groupe aromatique dans lequel au moins un atome d'hydrogène peut être substitué par un groupe fonctionnel choisi dans le groupe constitué par un groupe acide sulfonique, un groupe acide sulfurique, un groupe ammonium, un groupe aliphatique et $-CO_2M$, dans laquelle M est choisi dans le groupe constitué par H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} et Mg^{2+};
X est O ;
A représente un groupe aromatique fluoré ou perfluoré ;
n représente un nombre entier compris entre 2 et 6 ;

caractérisé en ce que le polymère conducteur comprend un complexe d'un polythiophène et d'un polyanion.

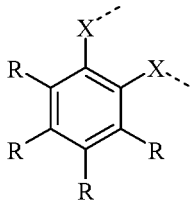
2. Composition selon la revendication 1, dans laquelle le groupe fonctionnel est choisi dans le groupe constitué par

i) $-SO_3M$, dans laquelle M est choisi dans le groupe constitué par H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} et Mg^{2+},
ii) $-OSO_3M$, dans laquelle M est choisi dans le groupe constitué par H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} et Mg^{2+},
iii) $-CO_2M$, dans laquelle M est choisi dans le groupe constitué par H^+, Na^+, K^+, Li^+, NH_4^+, Ca^{2+} et Mg^{2+},
iv) un groupe ammonium choisi dans le groupe constitué par $-N(CH_3)_4^+$, $-N(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, et-$N(C_5H_{11})_4^+$, et
v) un groupe alkyle choisi dans le groupe constitué par $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H_{21}$, $-C_{11}H_{23}$ et $-C_{12}H_{25}$.

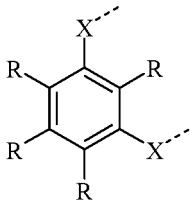
3. Composition selon l'une quelconque des revendications 1 à 2, dans laquelle K représente un groupe aromatique monocyclique et dans laquelle la sous-unité structurelle Ia' de formule Ia

$$K\text{-}[X]_n \qquad \text{Ia'}$$

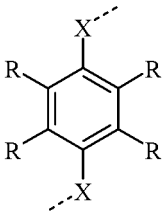
a une structure générale choisie dans le groupe constitué par les formules générales IIa à IIk :



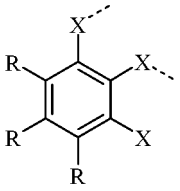
IIa



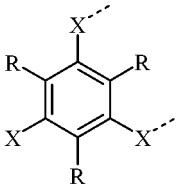
IIb



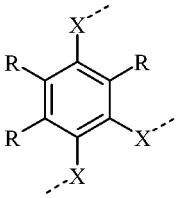
IIc



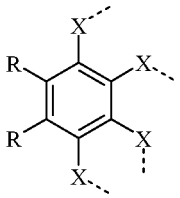
IId



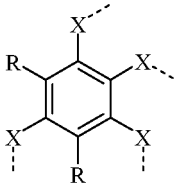
IIe



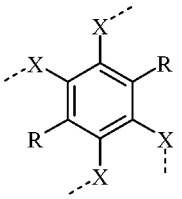
IIf



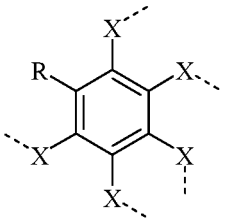
IIg



IIh



IIj



IIk

dans laquelle
-R est choisi dans le groupe constitué par H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H21$, $-C_{11}H_{23}$ et $-C_{12}H_{25}$, dans lesquels M est tel que défini dans la revendication 2 et
dans laquelle la ligne pointillée indique la liaison avec A.

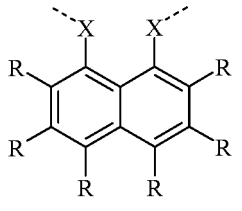
4. Composition selon la revendication 4, dans laquelle les combinaisons suivantes pour le substituant R par entité K sont remplies :

n = 2, et
R = 1 × - SO_3M et3 × H ouR = 2 × - SO_3M et 2 × H,
ou
n = 3, et
R = 3 × H ou R = 3 × $-SO_3M$,
dans laquelle M est tel que défini dans la revendication 2.

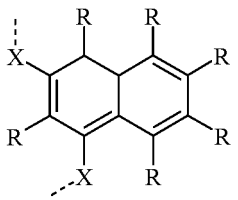
5. Composition selon l'une quelconque des revendications 1 à 2, dans laquelle K représente un groupe aromatique bicyclique, n représente 2 et dans laquelle la sous-unité structurelle Ia' de formule Ia

$$K-[X]_n \qquad Ia'$$

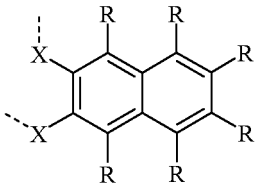
a une structure générale choisie dans le groupe constitué par les formules générales IIIa à IIIj :



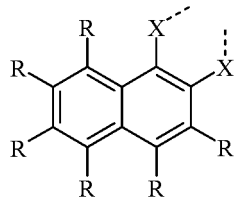
IIIa



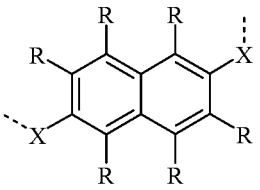
IIIb



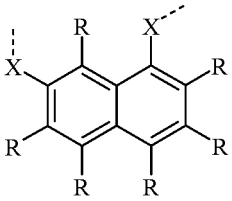
IIIc



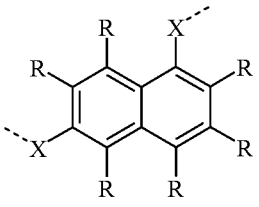
IIId



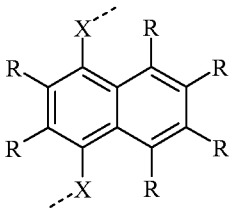
IIIe



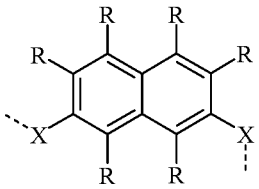
IIIf



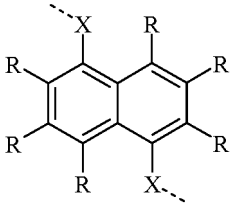
IIIg



IIIh



IIIi



IIIj

-R est choisi dans le groupe constitué par H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H_7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H21$, $-C_{11}H_{23}$ et $-C_{12}H_{25}$, dans lesquels M est tel que défini dans la revendication 2 et
dans laquelle la ligne pointillée indique la liaison avec A.

6. Composition selon la revendication 6, dans laquelle les combinaisons suivantes pour le substituant R par entité K sont remplies :

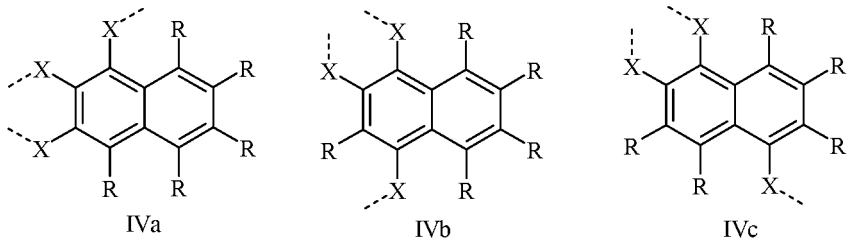
R = 2 × $-SO_3M$ et 4 × H, ou
R = 3 × $-SO_3M$ et 3 × H,

dans laquelle M est tel que défini dans la revendication 2.

7. Composition selon l'une quelconque des revendications 1 à 2, dans laquelle K représente un groupe aromatique bicyclique, n représente 3 et dans laquelle la sous-unité structurelle Ia' de formule Ia

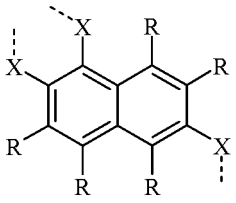
K-[X]$_n$ Ia'

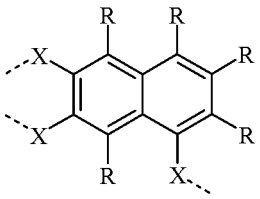
a une structure générale choisie dans le groupe constitué par les formules générales IVa à IVl :

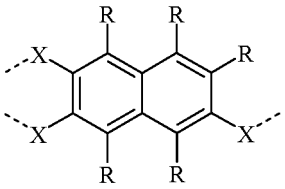

IVa

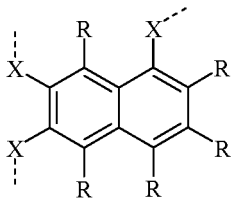
IVb

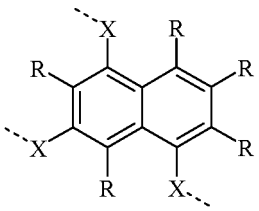
IVc

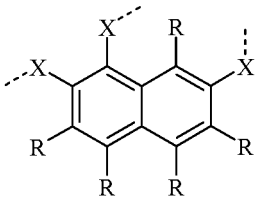

IVd

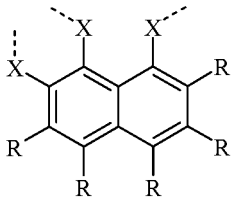

IVe

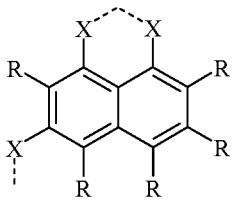

IVf

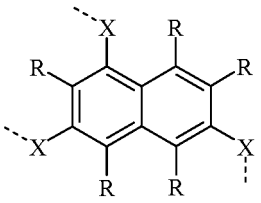

IVg


IVh


IVi


IVj


IVk

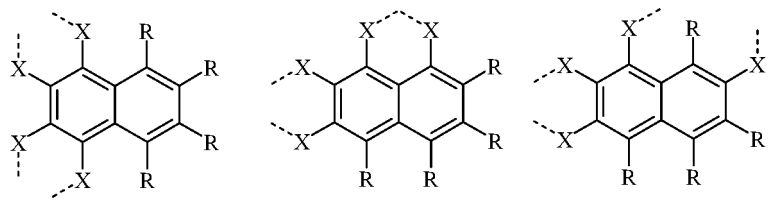

IVl

-R est choisi dans le groupe constitué par H, -SO_3M, -OSO_3M, -CO_2M, -$N(CH_3)_4^+$, -$(CH_2CH_3)_4^+$, -$N(C_3H_7)_4^+$, -$N(C_4H_9)_4^+$, -$N(C_5H_{11})_4^+$, -CH_3, -C_2H_5, -C_3H_7, -C_4H_9, -C_5H_{11}, -C_6H_{13}, -C_7H_{15}, -C_8H_{17}, -C_9H_{19}, -$C_{10}H21$, -$C_{11}H_{23}$ et -$C_{12}H_{25}$, dans lesquels M est tel que défini dans la revendication 2 et dans laquelle la ligne pointillée indique la liaison avec A.

8. Composition selon l'une quelconque des revendications 1 à 2, dans laquelle K représente un groupe aromatique bicyclique, n représente 4 et dans laquelle la sous-unité structurelle Ia' de formule Ia

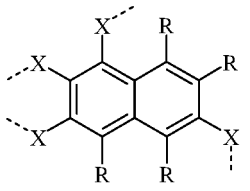
K-[X]$_n$ Ia'

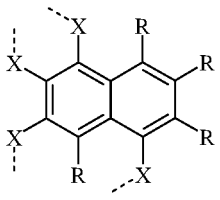
a une structure générale choisie dans le groupe constitué par les formules générales Va à Vi :

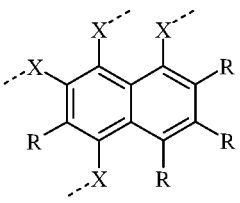

Va

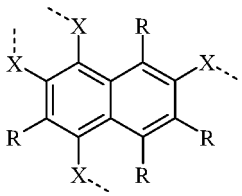
Vb

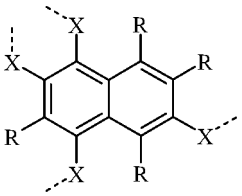
Vc

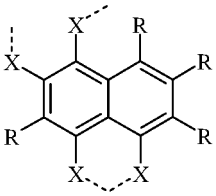

Vd


Ve


Vf


Vg


Vh

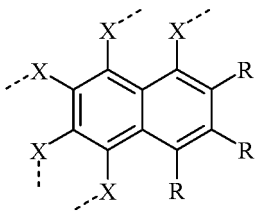

Vi

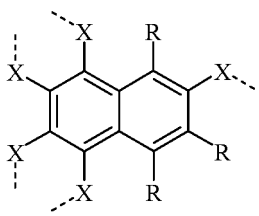
-R est choisi dans le groupe constitué par H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H21$, $-C_{11}H_{23}$ et $-C_{12}H_{25}$, dans lesquels M est tel que défini dans la revendication 2 et
dans laquelle la ligne pointillée indique la liaison avec A.

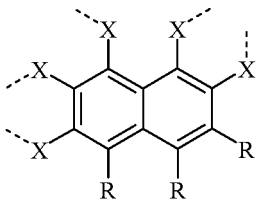
9. Composition selon l'une quelconque des revendications 1 à 2, dans laquelle K représente un groupe aromatique bicyclique, n représente 5 et dans laquelle la sous-unité structurelle Ia' de formule Ia

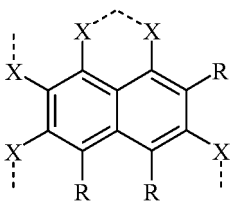
$$K\text{-}[X]_n \qquad \text{Ia'}$$

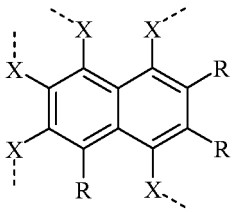
a une structure générale choisie dans le groupe constitué par les formules générales VIa à VIe :


VIa


VIb


VIc


VId


VIe

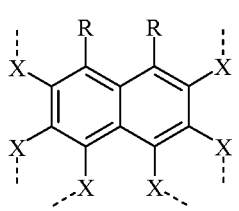
-R est choisi dans le groupe constitué par H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H7)_4^+$,

-$N(C_4H_9)_4^+$, -$N(C_5H_{11})_4^+$, -CH_3, -C_2H_5, -C_3H_7, -C_4H_9, -C_5H_{11}, -C_6H_{13}, -C_7H_{15}, -C_8H_{17}, -C_9H_{19}, -$C_{10}H21$, -$C_{11}H_{23}$ et -$C_{12}H_{25}$, dans lesquels M est tel que défini dans la revendication 2 et
dans laquelle la ligne pointillée indique la liaison avec A.

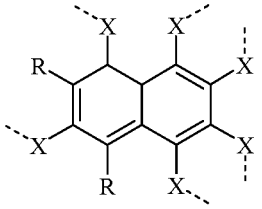
10. Composition selon l'une quelconque des revendications 1 à 2, dans laquelle K représente un groupe aromatique bicyclique, n représente 6 et dans laquelle la sous-unité structurelle Ia' de formule Ia

K-[X]$_n$ Ia'

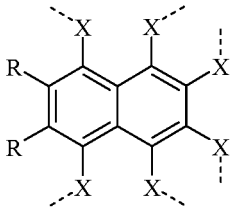
a une structure générale choisie dans le groupe constitué par les formules générales VIIa à VIIj :



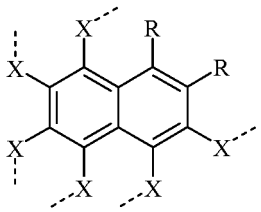
VIIa



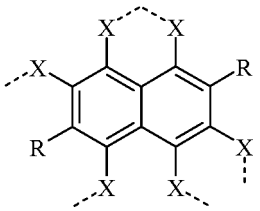
VIIb



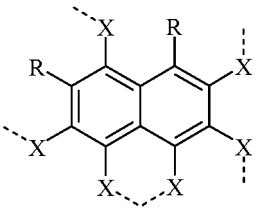
VIIc



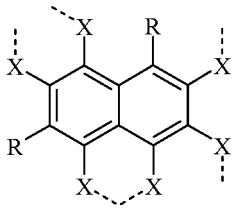
VIId



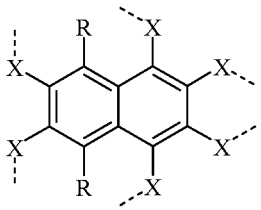
VIIe



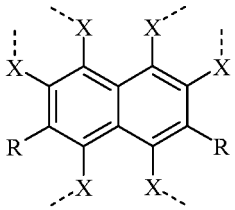
VIIf



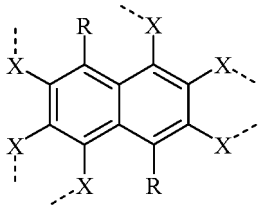
VIIg



VIIh



VIIi



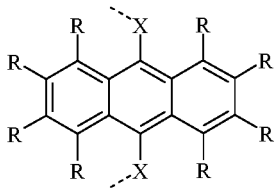
VIIj

-R est choisi dans le groupe constitué par H, -SO_3M, -OSO_3M, -CO_2M, -$N(CH_3)_4^+$, -$(CH_2CH_3)_4^+$, -$N(C_3H7)_4^+$, -$N(C_4H_9)_4^+$, -$N(C_5H_{11})_4^+$, -CH_3, -C_2H_5, -C_3H_7, -C_4H_9, -C_5H_{11}, -C_6H_{13}, -C_7H_{15}, -C_8H_{17}, -C_9H_{19}, -$C_{10}H21$, -$C_{11}H_{23}$ et -$C_{12}H_{25}$, dans lesquels M est tel que défini dans la revendication 2 et
dans laquelle la ligne pointillée indique la liaison avec A.

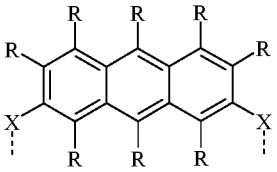
11. Composition selon l'une quelconque des revendications 1 à 2, dans laquelle K représente un groupe aromatique tricyclique et dans laquelle la sous-unité structurelle Ia' de formule Ia

$K\text{-}[X]_n$ Ia'

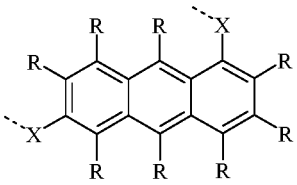
a une structure générale choisie dans le groupe constitué par les formules générales VIIIa à VIIIr :



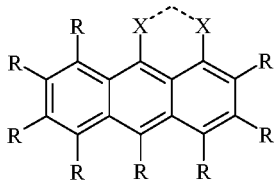
VIIIa



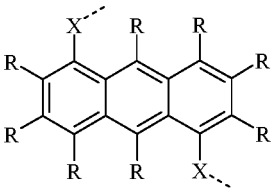
VIIIb



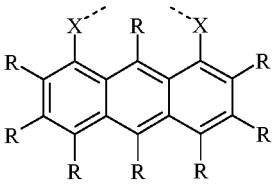
VIIIc



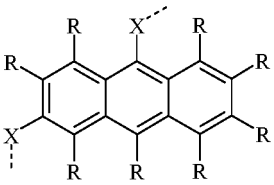
VIIId



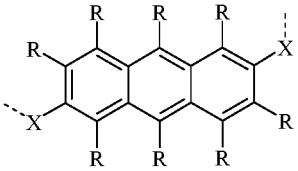
VIIIe



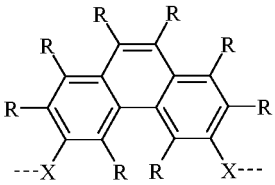
VIIIf



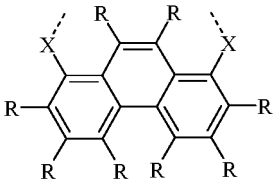
VIIIg



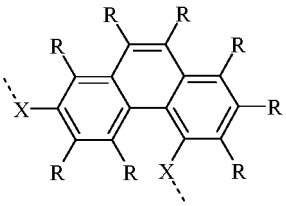
VIIIh



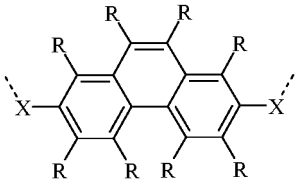
VIIIi



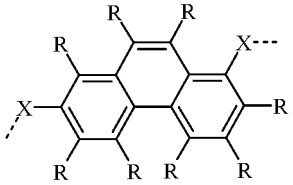
VIIIj



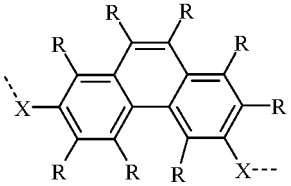
VIIIk



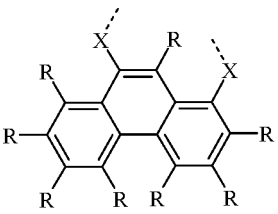
VIIIl



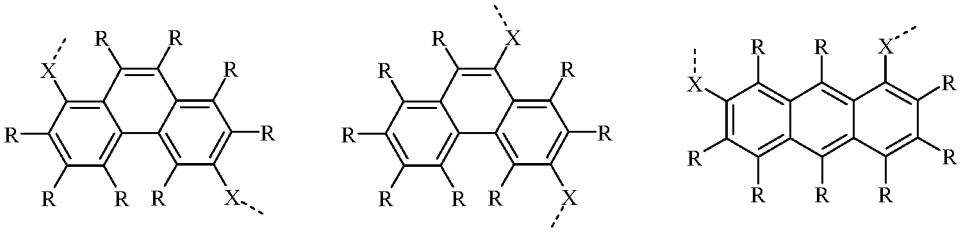
VIIIm



VIIIn



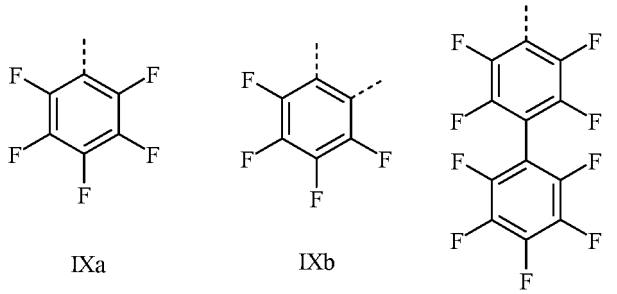
VIIIo



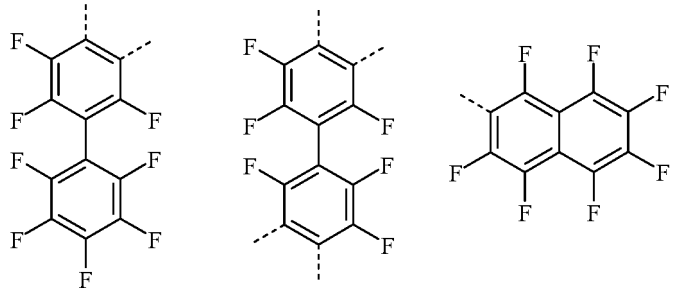
VIIIp VIIIq VIIIr

-R est choisi dans le groupe constitué par H, $-SO_3M$, $-OSO_3M$, $-CO_2M$, $-N(CH_3)_4^+$, $-(CH_2CH_3)_4^+$, $-N(C_3H7)_4^+$, $-N(C_4H_9)_4^+$, $-N(C_5H_{11})_4^+$, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_5H_{11}$, $-C_6H_{13}$, $-C_7H_{15}$, $-C_8H_{17}$, $-C_9H_{19}$, $-C_{10}H21$, $-C_{11}H_{23}$ et $-C_{12}H_{25}$, dans lesquels M est tel que défini dans la revendication 2 et
dans laquelle la ligne pointillée indique la liaison avec A.

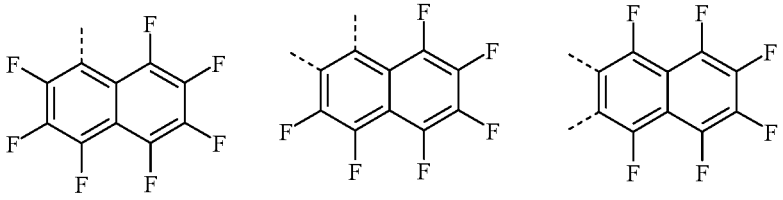
12. Composition selon l'une quelconque des revendications 1 à 11, dans laquelle A a une structure générale choisie dans le groupe constitué par les formules générales IXa à IXo :



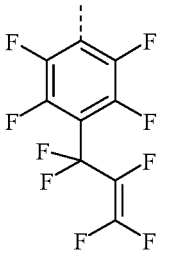
IXa IXb IXc



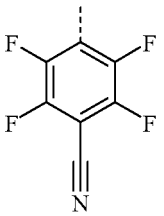
IXd IXe IXf



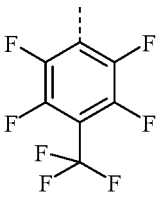
IXg IXh IXi



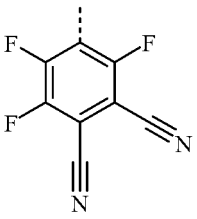
IXj



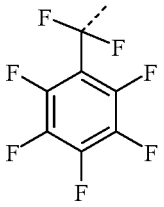
IXk



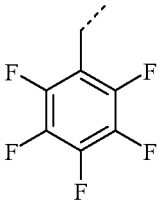
IXl



IXm



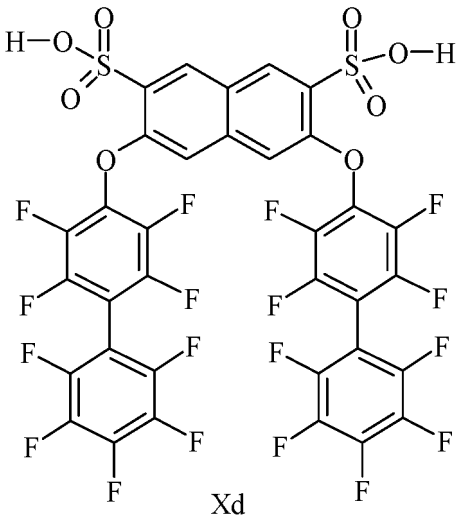
IXn



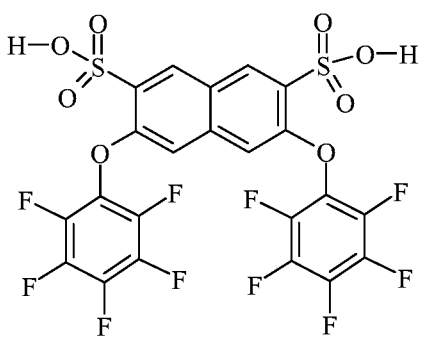
IXo

dans laquelle la ligne pointillée indique la liaison avec X.

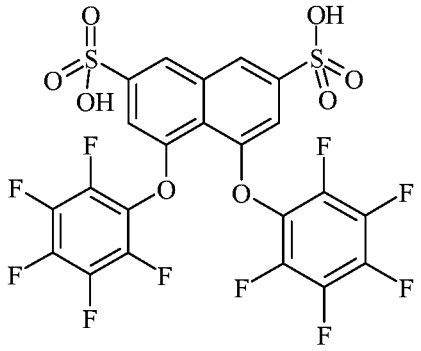
13. Composition selon l'une quelconque des revendications 1 à 12, dans laquelle le composé a une structure générale choisie dans le groupe constitué par les formules générales Xd à Xg ou leurs sels correspondants :



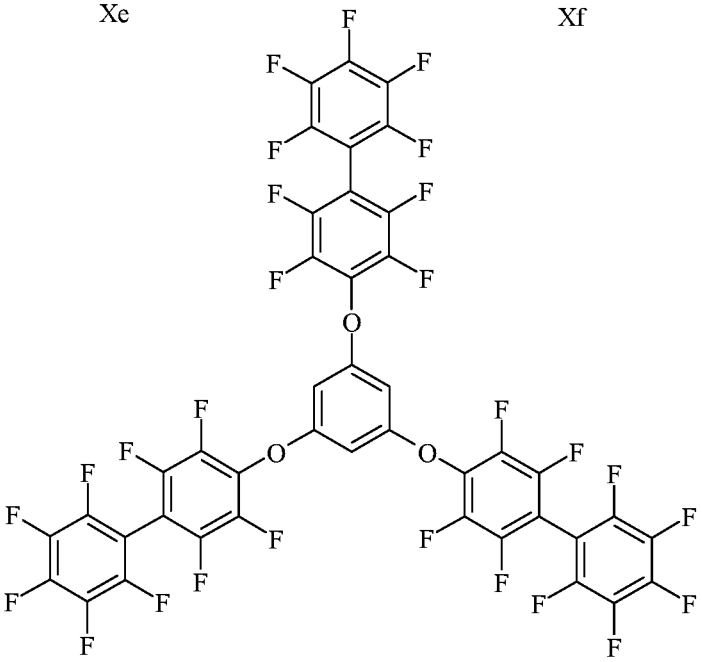
Xd



Xe



Xf



Xg

14. Composition selon l'une quelconque des revendications 1 à 13, dans laquelle le solvant II) est l'eau, un solvant organique choisi dans le groupe constitué par les alcools, les hydrocarbures aliphatiques, les hydrocarbures aromatiques, les éthers, les hydrocarbures halogénés, les nitriles aliphatiques, les acides carboxyliques aliphatiques, les acides carboxyliques aliphatiques et les cétones ou un mélange d'au moins deux de ces solvants.

15. Procédé pour la préparation d'une couche conductrice, qui comprend les étapes du procédé :

(P1) superposition d'un substrat avec la composition selon l'une quelconque des revendications 1 à 14 ;
ou
premièrement, superposition d'un substrat avec une composition comprenant le solvant II) tel que défini dans les revendications 1 et 14 et le composé III) tel que défini dans l'une quelconque des revendications 1 à 13, élimination au moins partielle du solvant et ensuite superposition du substrat avec une composition selon l'une quelconque des revendications 1 à 14 ou avec une composition comprenant le solvant II) tel que défini dans les revendications 1 et 14 et le polymère conducteur I) tel que défini dans la revendication 1 ;
ou
premièrement, superposition d'un substrat avec une composition comprenant le solvant II) tel que défini dans les revendications 1 et 14 et le polymère conducteur I) tel que défini dans la revendication 1, élimination au moins partielle du solvant et ensuite superposition du substrat avec la composition selon l'une quelconque des revendications 1 à 14 ou avec une composition comprenant le solvant II) tel que défini dans les revendications 1 et 14 et le composé III) tel que défini dans l'une quelconque des revendications 1 à 13 ;
(P2) élimination au moins partielle du solvant.

16. Couche conductrice comprenant au moins un composé tel que défini dans l'une quelconque des revendications 1

à 13 et au moins un polymère conducteur, dans laquelle le polymère conducteur comprend un complexe d'un polythiophène et d'un poly-anion.

17. Composant électronique comprenant une couche conductrice pouvant être obtenue par le procédé selon la revendication 15 ou comprenant une couche conductrice selon la revendication 16.

18. Composant électronique selon la revendication 17, dans lequel le composant électronique est un OLED, un écran, une cellule solaire organique, une cellule solaire hybride, un transistor à effet de champ, ou un générateur thermoélectrique.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 20050209388 A1 **[0006]**
- US 2004124504 A1 **[0006]**
- WO 2009096352 A1 **[0007]**
- JP 2006222010 A **[0008]**
- EP 1640372 A1 **[0009]**
- JP 2007176921 A **[0011]**
- EP 1405849 A1 **[0013]**
- US 6692662 B2 **[0049]**
- WO 9013148 A **[0059]**
- DE 19627071 A **[0059]**
- WO 20090170244 A **[0063]**

Non-patent literature cited in the description

- **YANG LIU et al.** *Journal of Membrane Science,* 2011, vol. 394, 218-229 **[0010]**
- **LIU CUIBO et al.** *Journal of Fluorine Chemistry,* 2013, vol. 156, 51-60 **[0012]**