



(43) International Publication Date
23 April 2015 (23.04.2015)

(10) International Publication Number
WO 2015/055280 A1

(51) International Patent Classification:

C09C 3/12 (2006.01) *C09C 1/30* (2006.01)
C09K 11/02 (2006.01)

(21) International Application Number:

PCT/EP2014/002641

(22) International Filing Date:

29 September 2014 (29.09.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13004937.2 15 October 2013 (15.10.2013) EP
13005469.5 21 November 2013 (21.11.2013) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: COATED SILICA PARTICLES FOR INK-JET PRINTING OF ORGANIC ELECTRONIC DEVICES, A METHOD FOR THEIR PRODUCTION AND DEVICES PRODUCED THEREWITH

(57) Abstract: The present invention relates to coated silica particles, said silica particles comprising a first coating and a second coating. The present coated silica particles are particularly useful for ink-jet printing of organic electronic devices. Furthermore, the present invention relates to a method for producing such coated particles and also to devices produced with such coated silica particles.



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COATED SILICA PARTICLES FOR INK-JET PRINTING OF ORGANIC ELECTRONIC DEVICES, A METHOD FOR THEIR PRODUCTION AND DEVICES PRODUCED THEREWITH

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Technical Field

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The present invention relates to coated silica particles, said coated silica particles comprising a first surface modifying group and a second surface modifying group. The present coated silica particles are particularly useful for ink-jet printing of organic electronic devices. Furthermore, the present invention relates to a method for producing such coated particles and also to devices produced with such coated silica particles.

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Background and description of the prior art

20

Organic electronic devices have attracted a lot of research interest in recent years as they allow for good processability in combination with improved final properties such as for example reduced weight. The particular combination of properties renders organic electronic devices extremely suitable for example for portable devices, such as for example tablet computers. A particular example of organic electronic devices, which have been and continue to be a focus of development efforts, are organic light emitting diodes (OLEDs). As further examples of organic electronic devices mention may be made of organic photovoltaic cells, organic thin film transistors or organic field effect transistors, to only name a few.

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OLEDs in general as well as their structure are for example disclosed in US 4539507, US 5151629, EP 0676461 and WO 98/27136. The term "organic light emitting diodes" is generally used for electronic devices which comprise at least one organic material and emit light when an electric current is applied.

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In the production of organic electronic devices vapor deposition techniques have been successfully used. These techniques are, however, limited with regards to the size of the possible substrate as well as with regards to throughput.

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In consequence, there is an interest in facilitating mass production of organic electronic devices, for example by printing methods.

It is therefore an object of the present invention to provide means for improving the production of organic electronic devices.

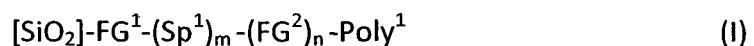
It is also an object of the present invention to provide for a dispersion of coated silica particles, said dispersion being suitable for use in printing of organic electronic devices. In addition it is an object to provide for such a dispersion with high stability, preferably in the absence of an emulsifier.

Further objects and advantages of the present invention may become evident from the following description.

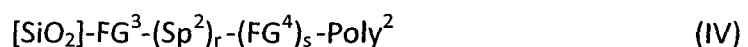
Summary of the invention

The present inventors have now surprisingly found that the above objects may be attained either individually or in any combination by the present coated silica particles as well as by further aspects of the present application.

The present application therefore provides for coated silica particles comprising a first surface modifying group or a second surface modifying group or both, wherein the first surface modifying group is of general formula (I)



and the second surface modifying group is of general formula (IV)



wherein $[\text{SiO}_2]$ denotes the silica particle, which either essentially consists of silica or which is a core/shell particle the shell of which essentially consists of silica, FG^1 is a first functional group, FG^2 is a second functional group, FG^1 and FG^2 being different from one another, FG^3 is a third functional group, FG^4 is a fourth functional group, FG^3 and FG^4 being different from one another, Sp^1 and Sp^2 are

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spacers, m is 0 or 1, n is 0 or 1, r is 0 or 1, s is 0 or 1, and Poly¹ and Poly² are polymers.

The present application also provides for a dispersion comprising such coated silica particles.

Further, the present application provides for a method for producing coated silica particles, said method comprising the step of

(A) providing an alcoholic dispersion of silica particles, said silica particles either essentially consisting of silica or being core/shell particles the shell of which essentially consists of silica;

and at least one of the following steps (B) and (C) being

(B) a first functionalization step comprising the steps of

(B-1) treating the surface of the silica particles with a first surface modifying agent of general formula (I')



and

(B-2) subsequently polymerizing a polar olefinic compound;

and

(C) a second functionalization step comprising the steps of

(C-1) treating the surface of said intermediate coated particles with a second surface modifying agent of general formula (IV')



and

(C-2) subsequently radically polymerizing thereon at least a first and a second monomer, wherein said first monomer comprises a light emitter, and wherein the second surface modifying agent acts as a radical transfer agent,

to obtain coated silica particles, wherein the steps can be performed in either order, wherein [SiO₂] denotes the silica particle, FG^{1'} is a first functional group, FG^{2'} is a second functional group, FG^{1'} and FG^{2'} being different from one another, FG^{3'} is a third functional group, FG^{4'} is a fourth functional group, FG^{3'} and FG^{4'}

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being different from one another, Sp^1 and Sp^2 are spacers, m is 0 or 1, and r is 0 or 1, and wherein $FG^{1'}$ and $FG^{3'}$ are capable of reacting with hydroxyl groups on the surface of said silica particles.

- 5 In addition, the present application provides for organic electronic devices, particularly for organic light emitting diodes (OLEDs), comprising said coated silica particles.

10 Detailed description of the invention

For the purposes of the present application, the abbreviation "Me" may be used to denote methyl, and "Et" may be used to denote ethyl.

- 15 For the purposes of the present application, the solids content of a dispersion is given in wt%, indicating weight percent of solids with respect to the total weight of the dispersion.

- 20 For the purposes of the present application, an asterisk ("*") is used to indicate covalent bonding to chemical groups on the surface of the silica particles.

COATED SILICA PARTICLES

- 25 Generally stated, the present coated silica particles comprise a first surface modifying group or a second surface modifying group or, preferably, both. It is, however, to be understood that the terms "first surface modifying group" and "second surface modifying group" do not necessarily imply that one or the other covers the respective other. It is also noted that in addition to the first surface modifying group and the second modifying group said coated silica particles may
- 30 further comprise other layers, such as layers comprising additional functional compounds as defined below.

FIRST SURFACE MODIFYING GROUP

- 35 The coated silica particles of the present application comprise a first surface modifying group, which preferably can be represented by the following formula (I)

- 5 -



wherein $[\text{SiO}_2]$ denotes the silica particle, FG^1 is a first functional group as defined below, FG^2 is a second functional group as defined below, FG^1 and FG^2 being different from one another, Sp^1 is a spacer as defined below, $m = 0$ or 1 , $n = 0$ or 1 , and Poly^1 is a polymer chain as defined below. As indicated by m being 0 or 1 , said spacer is optional, i.e. it is not present for $m = 0$. However, it is preferred that $m = 1$. As indicated by n being 0 or 1 , said functional group FG^2 is optional, i.e. it is not present for $n = 0$. It is noted that FG^1 is bound to the silica particle by means of one or more groups -O- , resulting from abstraction of the proton of a hydroxyl group -OH on the surface of said silica particle.

For the purposes of the present application silica particles comprising only the first surface modifying group or only the second surface modifying group may also be referred to as "intermediate coated silica particles".

The type of functional group FG^1 is not particularly limited. Examples of suitable functional groups FG^1 are alkoxysilanedyl groups, silyl groups and acid groups of phosphoric acid and phosphonic acid and their esters. Particularly well suited examples of such functional groups are alkoxysilanedyl groups of general formula (II)



wherein R^2 and R^3 are independently of each other alkyl having from 1 to 10 carbon atoms. Other particularly well suited examples of such functional groups are of general formula (IIa)



wherein R^2 is as defined above. This can for example occur if one functional group FG^1 is bound to two groups -O- resulting from the abstraction of the protons from

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two hydroxyl groups on the surface of said silica particle. Alternatively, said functional group FG^1 may be



which is bound to three groups -O- resulting from the abstraction of the protons from three hydroxyl groups on the surface of said silica particle.

Suitable alkyls for R^2 and R^3 may be branched or straight and have from 1 to 10 carbon atoms. Preferred examples of such alkyls are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl. Of these methyl, ethyl, n-propyl, iso-propyl, n-butyl and pentyl are more preferred. Even more preferred are methyl, ethyl and n-propyl. Most preferred is ethyl.

Without wishing to be bound by theory it is believed that the chemical nature of the spacer Sp^1 aids in controlling the stability of the dispersion of the silica particles in the alcohol. To this end, without wishing to be bound by theory, the polarity of the spacer Sp^1 is thought to play an important role. Without wishing to be bound by theory it is believed that the stability of the dispersion of silica particles can be improved for example by changing the length of the spacer Sp^1 or by changing the coverage of the surface of the silica particles with surface modifying groups.

A preferred example of a spacer Sp^1 is one of general formula $(-CH_2-CH_2-X^1-)_p$, wherein X^1 is O or NR^5 , preferably X^1 being O, with R^5 defined in the following and p may be an integer of from 1 to 20. Alternatively p may be at least 5 (for example at least 4 or at least 3 or at least 2 or at least 1) and/or at most 20 (for example at most 19, or at most 18, or at most 17, or at most 16, or at most 15, or at most 14, or at most 13, or at most 12, or at most 11, or at most 10).

Suitable groups R^5 may be selected from the group consisting of hydrogen and alkyl groups having from 1 to 10 carbon atoms. Suitable examples of such alkyls are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl. Of these methyl and ethyl are particularly suited.

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A preferred example of FG^2 is $-C(=O)-C(CH_3)_2-$. Another preferred example of FG^2 is $-C(=O)-CR^1(CH_3)-CH_2-$.

Optionally the $*-FG^1-(Sp^1)_m-(FG^2)_n-Poly^1$ group of formula (I) may comprise one or more further functional groups, which may be the same or different from FG^1 and FG^2 as defined above. In addition to what is defined for FG^1 and FG^2 such further functional groups may also be chosen from the group consisting of acrylate, methacrylate, vinyl, amino, cyano, isocyanate, epoxy, carboxy and hydroxyl groups. The one or more further functional groups may for example be bound to or comprised in FG^1 , FG^2 and/or the spacer Sp^1 .

In one aspect preferably at least 5 %, more preferably at least 7 %, even more preferably at least 9 %, still even more preferably at least 11 % and most preferably at least 13 % of the surface of the silica particle is covered by the groups $*-FG^1-(Sp^1)_m-(FG^2)_n-Poly^1$ of formula (I). Preferably at most 50 %, more preferably at most 40 %, even more preferably at most 30 %, still even more preferably at most 25 % and most preferably at most 20 % of the surface of the silica particles is covered by the groups $*-FG^1-(Sp^1)_m-(FG^2)_n-Poly^1$ of formula (I).

In another aspect preferably at least 0.1, more preferably at least 0.2, even more preferably at least 0.3 and most preferably at least 0.4 of the groups $*-FG^1-(Sp^1)_m-(FG^2)_n-Poly^1$ of formula (I) are covalently bound per 1 nm² of the surface of the silica particles. Preferably at most 2.0, more preferably at most 1.6, even more preferably at most 1.4, still even more preferably at most 1.3 and most preferably at most 1.2 of the groups $*-FG^1-(Sp^1)_m-(FG^2)_n-Poly^1$ of formula (I) are covalently bound per 1 nm² of the surface of the silica particles.

The percentage of coverage and the number of compounds bound per surface area of the silica particles can be determined with thermogravimetric analysis (TGA), wherein a sample is gradually heated and the evolution of its weight recorded. A more detailed description is given in the test methods. Using TGA it has also been determined that the reaction between the one or more compounds of formula (I') as defined below and hydroxyl groups of the silica surface is in fact quantitative, meaning that the entire amount of the compound of formula (I') reacts with said hydroxyl groups.

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Poly¹ is a polymer of a polar olefinic compound. A suitable polar olefinic compound may for example be selected from the group consisting of acrylates, methacrylate, vinyl alcohol, vinyl acetate, acrylamide and blends thereof.

5 Preferably Poly¹ is a polymer represented by the following general formula (III)

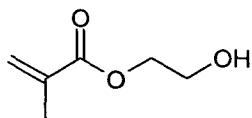


10 wherein v is an integer from 1 to 100, R⁶ is hydrogen or methyl; and R⁷ is selected from the group consisting of -OH, -C(=O)-NH₂, -C(=O)-CH₃, and -C(=O)-(X²-(CH₂)₂)_q-OR⁸ with q being an integer of from 1 to 10, X² being O or NR⁵ with R⁵ as defined above, and R⁸ being hydrogen or an alkyl group having from 1 to 10 carbon atoms. Suitable examples of such alkyl groups are those mentioned above in respect to R⁵. Optionally, the polar olefinic compound is polymerized in presence of one or
15 more comonomers. An exemplary comonomer is ethylene.

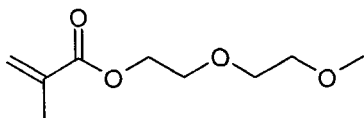
Preferred R⁶ is methyl.

20 Specific preferred examples of R⁷ are -C(=O)-(O-(CH₂)₂)_q-OR⁸ with q and R⁸ as defined above. Particularly preferred are compounds wherein q is 1, 2, 3, 4 or 5. Good results have been obtained with q being 1 or 2.

25 Specific examples of suitable polar organic compounds of formula (III) are 2-hydroxyethylmethacrylate (HEMA) and di(ethyleneglycol)methylether-methacrylate (MEO2MA).



(HEMA)



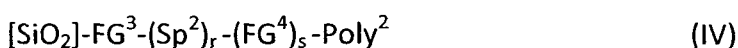
(MEO2MA)

35 The present silica particles comprising a first surface modifying group as defined above have been found to exhibit surprisingly good dispersion stability and can be

stored for significant periods of time without any noticeable signs of gelling or agglomeration.

SECOND SURFACE MODIFYING GROUP

The coated silica particles of the present application comprise a second surface modifying group which preferably can be represented by the following formula (IV)



wherein $[\text{SiO}_2]$ denotes the silica particle, FG^3 is a third functional group as defined below, FG^4 is a fourth functional group as defined below, FG^3 and FG^4 being different from one another, Sp^2 is a spacer as defined below, $r = 0$ or 1 , $s = 0$ or 1 , and Poly^2 is a polymer as defined below. As indicated by r being 0 or 1 , said spacer is optional, i.e. it is not present for $r = 0$. However, it is preferred that $r = 1$. As indicated by s being 0 or 1 , said functional group FG^4 is optional, i.e. it is not present for $s = 0$. It is noted that FG^3 is bound to the silica particle by means of one or more groups -O- , resulting from abstraction of the proton of a hydroxyl group -OH on the surface of said silica particle.

The type of functional group FG^3 is not particularly limited as long as it is capable of chemically reacting with hydroxyl groups on the surface of said silica particles.

Examples of suitable functional groups FG^3 are alkoxysilanedyl groups, silyl groups and acid groups of phosphoric acid and phosphonic acid and their esters. Particularly well suited examples of such functional groups are alkoxysilanedyl groups of general formula (V)



wherein R^9 and R^{10} are independently of each other alkyl having from 1 to 10 carbon atoms. Another particularly well suited example of such functional groups are of general formula (IIa)

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wherein R^2 is as defined above. This can for example occur is one functional group FG^1 is bound to two groups -O- resulting from the abstraction of the protons from two hydroxyl groups on the surface of said silica particle. Alternatively, said functional group FG^1 may be



which is bound to three groups -O- resulting from the abstraction of the protons from three hydroxyl groups on the surface of said silica particle.

It is noted that FG^1 and FG^3 are selected independently of each other.

Suitable alkyls for R^9 and R^{10} may be branched or straight and have from 1 to 10 carbon atoms. Suitable examples of such alkyls are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl. Of these methyl, ethyl, n-propyl, iso-propyl, n-butyl and pentyl are more preferred. Even more preferred are methyl, ethyl and n-propyl. Most preferred is ethyl.

Said functional group FG^4 is selected preferably from the group consisting of thiol, sulfide, disulfide, polysulfide and the reaction products of the azo compounds defined in respect to $\text{FG}^{4'}$. Of these thiol and the reaction products of the azo compounds defined in respect to $\text{FG}^{4'}$ are preferred.

With regards to FG^4 , sulfide may be represented as -S-. with regards to FG^4 , disulfide may be represented as -S-S-. With regards to FG^4 , polysulfide may be represented as $-\text{S}_w-$, with w being an integer of from 2 to 20.

Said reaction products of the azo compounds defined in respect to $\text{FG}^{4'}$ may for example correspond to R^{16} as defined in respect to $\text{FG}^{4'}$.

Said second surface modifying agent may also comprise a spacer Sp^2 , which may for example be of general formula $(-\text{CH}_2-\text{CH}_2-\text{X}^2-)_t$ or of general formula $(-\text{CH}_2-)_t$ or

a combination of these, wherein X^2 is selected from the group consisting of O, $CR^{12}R^{13}$ and NR^{14} , with R^{12} , R^{13} and R^{14} independently of each other defined as R^5 above, t may be an integer of from 0 to 20, and t' may be an integer of from 0 to 60. Alternatively t may be at least 5 (for example at least 4 or at least 3 or at least 2 or at least 1) and/or at most 20 (for example at most 19, or at most 18, or at most 17, or at most 16, or at most 15, or at most 14, or at most 13, or at most 12, or at most 11). Alternatively t' may be at least 1 (for example at least 2, or at least 3, or at least 4, or at least 5, or at least 6, or at least 7, or at least 8, or at least 9 or at least 10) and/or at most 50 (for example at most 45, or at most 40, or at most 35, or at most 30, or at most 29, or at most 28, or at most 27, or at most 26, or at most 25, or at most 24, or at most 23, or at most 22, or at most 21, or at most 20).

It is preferred that X^2 is O or $CR^{12}R^{13}$, and more preferably X^2 is $CR^{12}R^{13}$ with R^{12} and R^{13} defined as R^5 above. Most preferably X^2 is CH_2 .

Optionally the second surface modifying agent may comprise one or more further functional groups, which may be the same or different from FG^3 and FG^4 as defined above. In addition to what is defined for FG^3 and FG^4 such further functional groups may also be chosen from the group consisting of acrylate, methacrylate, vinyl, amino, cyano, isocyanate, epoxy, carboxy and hydroxyl groups. The one or more further functional groups may for example be bound to or comprised in FG^3 , FG^4 and/or the spacer Sp^2 .

$Poly^2$ is a polymer comprising a first monomer and a second monomer, wherein said first monomer comprises a functional compound. It is possible to use a single monomer comprising a functional compound. However, two or more monomers comprising a functional compound may also be used. Alternatively, a monomer may also comprise two or more functional compounds, which are different from each other. It is also possible to use a blend of two or more monomers, each monomer comprising different functional compounds. Preferably said functional compounds are covalently bound to the polymerizable unit of the monomer. The term "functional compound" is used to denote compounds that fulfill a function. Examples of such "functional compounds" are - in an illustrative non-limiting way - light emitting compounds, dielectric compounds, semiconducting compounds, photoactive compounds, hole blocking compounds, electron blocking compounds,

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hole transporting compounds, electron transporting compounds, colorants, antistatic compounds etc.

5 In the following the present invention will mainly be illustrated by example of the functional compound being a light emitting compound. It is clear, however, that the skilled person can easily substitute the light emitting compound with any other suitable functional compound.

10 The type of light emitting compound to be used herein is not particularly limited. It can be selected amongst the compounds known to the skilled person for this purpose and described in the literature. The light emitting compounds used herein are preferably organic light emitting compounds. With regards to the properties of the emitted light, it is preferred that the light emitting compounds are chosen such that they emit light in the visible region, i.e. having a wavelength
15 in the range from about 400 nm to about 700 nm. Examples of light emitting compounds, such as for example phosphorescent compounds, that may be used in the present invention are given below.

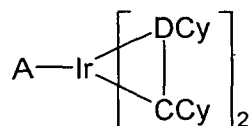
20 Suitable phosphorescent compounds are, in particular, compounds which emit light, preferably in the visible region, on suitable excitation and in addition contain at least one atom having an atomic number greater than 20, preferably greater than 38 and less than 84, more preferably greater than 56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

Particularly preferred organic phosphorescent compounds are compounds of formulae (1) to (4):

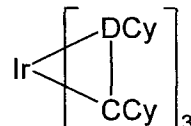
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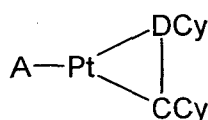
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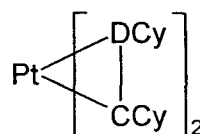
formula (1)



formula (2)



formula (3)



formula (4)

wherein

DCy is, identically or differently on each occurrence, a cyclic group which contains at least one donor atom, preferably nitrogen, carbon in the form of a carbene or phosphorus, via which the cyclic group is bonded to the metal, and which may in turn carry one or more substituents R^{18} ; the groups DCy and CCy are connected to one another via a covalent bond;

CCy is, identically or differently on each occurrence, a cyclic group which contains a carbon atom via which the cyclic group is bonded to the metal and which may in turn carry one or more substituents R^{18} ;

A is, identically or differently on each occurrence, a monoanionic, bidentate chelating ligand, preferably a diketonate ligand;

R^{18} are identically or differently at each instance, and are F, Cl, Br, I, NO_2 , CN, a straight-chain, branched or cyclic alkyl or alkoxy group having from 1 to 20 carbon atoms, in which one or more nonadjacent CH_2 groups may be replaced by $-\text{O}-$, $-\text{S}-$, $-\text{NR}^{19}-$, $-\text{CONR}^{19}-$, $-\text{CO}-\text{O}-$, $-\text{C}=\text{O}-$, $-\text{CH}=\text{CH}-$ or $-\text{C}\equiv\text{C}-$, and in which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group which has from 4 to 14 carbon atoms and may be substituted by one or more nonaromatic R^{18} radicals, and a plurality of substituents R^{18} , either on the same ring or on two different rings, may together in turn form a mono- or polycyclic, aliphatic or aromatic ring system; and

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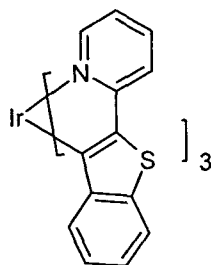
R^{19} are identically or differently at each instance, and are a straight-chain, branched or cyclic alkyl or alkoxy group having from 1 to 20 carbon atoms, in which one or more nonadjacent CH_2 groups may be replaced by $-O-$, $-S-$, $-CO-O-$, $-C=O-$, $-CH=CH-$ or $-C\equiv C-$, and in which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group which has from 4 to 14 carbon atoms and may be substituted by one or more nonaromatic R^{18} radicals.

Formation of ring systems between a plurality of radicals R^{18} means that a bridge may also be present between the groups DCy and CCy.

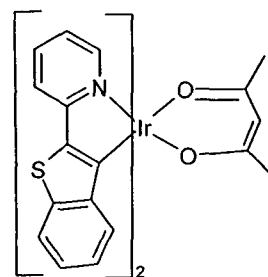
Furthermore, formation of ring systems between a plurality of radicals R^{18} means that a bridge may also be present between two or three ligands CCy-DCy or between one or two ligands CCy-DCy and the ligand A, giving a polydentate or polypodal ligand system.

Examples of the emitters described above are revealed by the applications WO 00/70655, WO 01/41512, WO 02/02714, WO 02/15645, EP 1191613, EP 1191612, EP 1191614, WO 04/081017, WO 05/033244, WO 05/042550, WO 05/113563, WO 06/008069, WO 06/061182, WO 06/081973 and DE 102008027005. In general, all phosphorescent complexes as are used in accordance with the prior art for phosphorescent OLEDs and as are known to the person skilled in the art in the area of organic electroluminescence are suitable, and the person skilled in the art will be able to use further phosphorescent compounds without inventive step. In particular, it is known to the person skilled in the art which phosphorescent complexes emit with which emission colour.

Examples of preferred phosphorescent compounds are shown in the following.



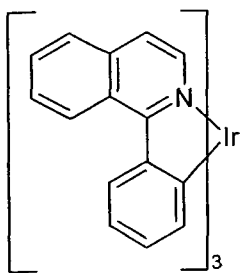
(1)



(2)

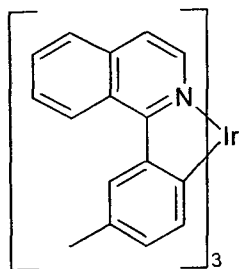
- 15 -

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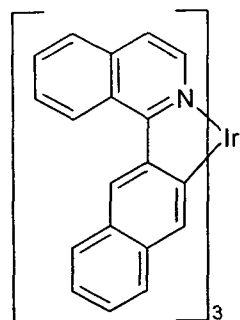
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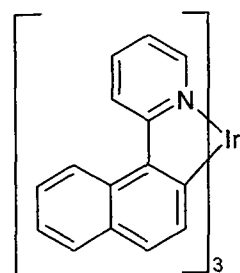
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(7)

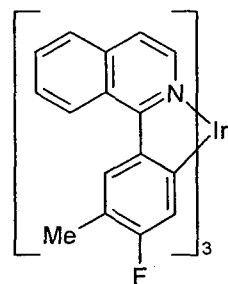
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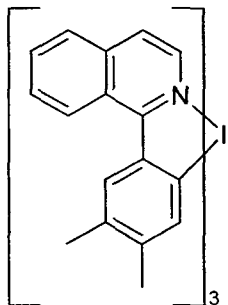
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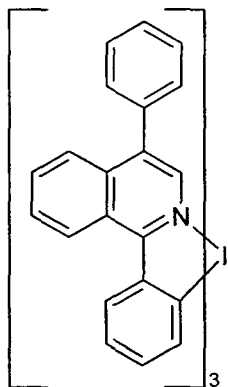
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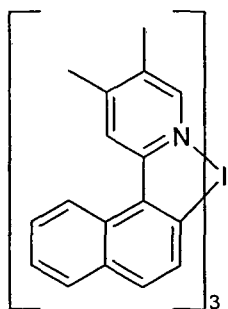
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(6)

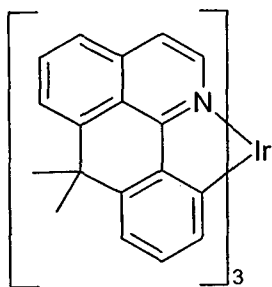


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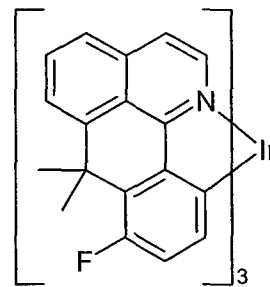


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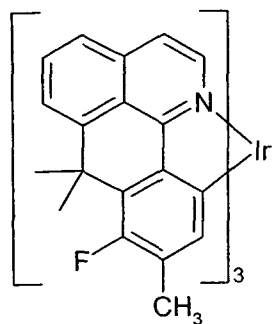


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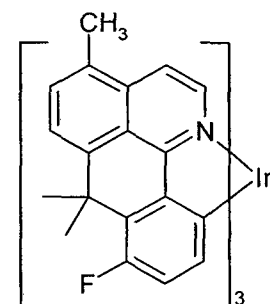


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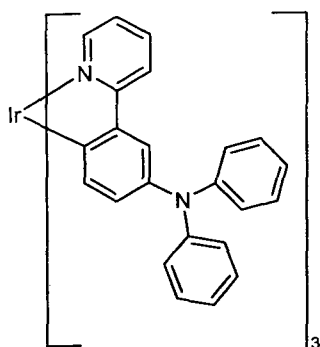


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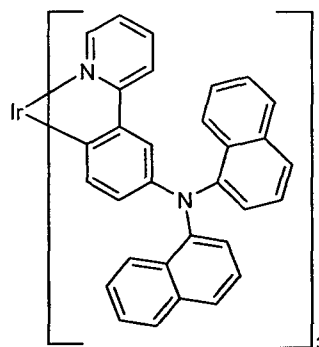
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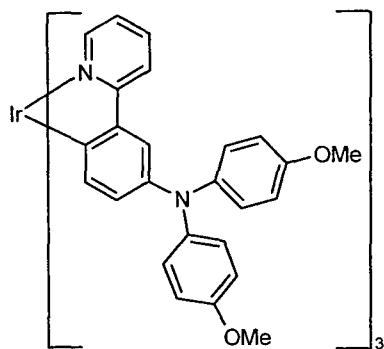
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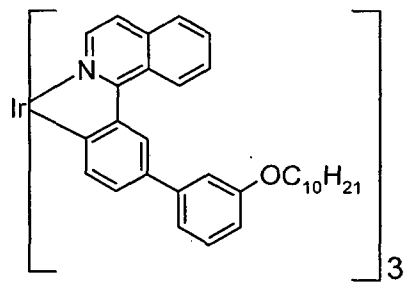
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(17)

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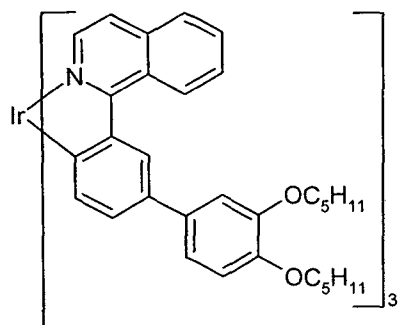


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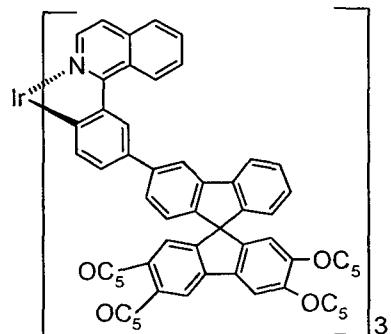
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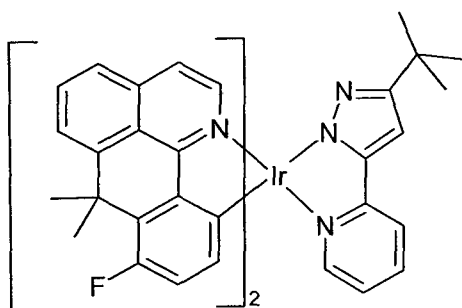


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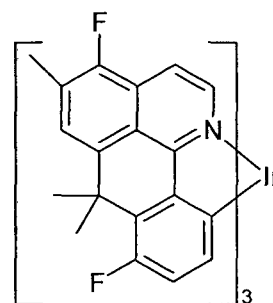
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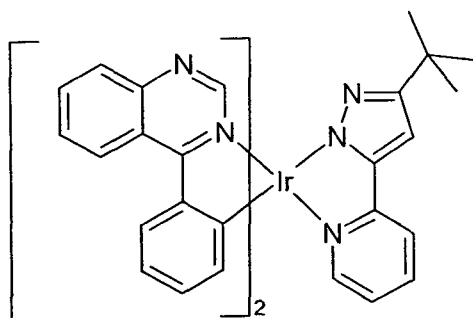
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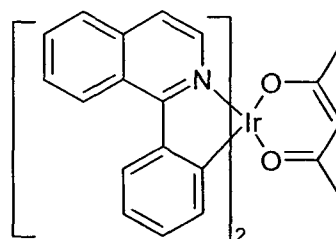
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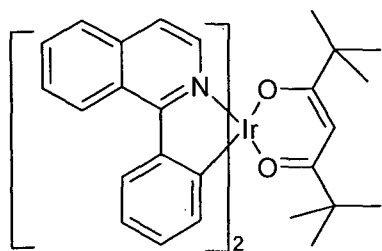
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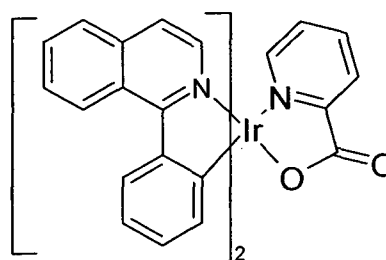


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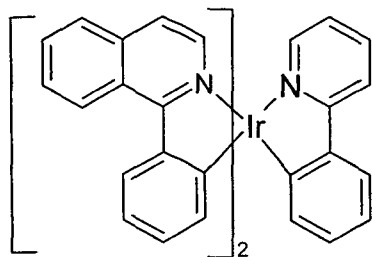
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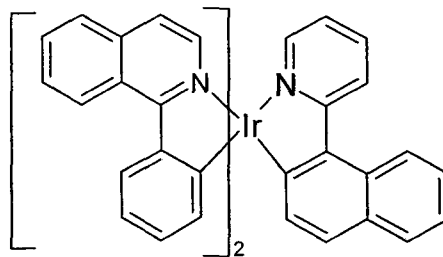
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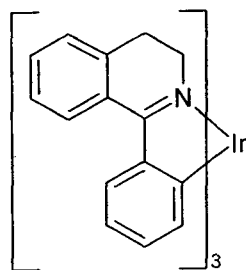


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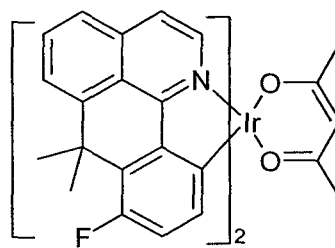


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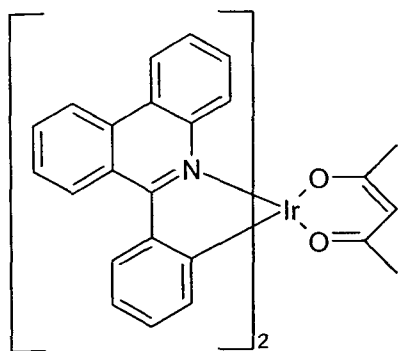


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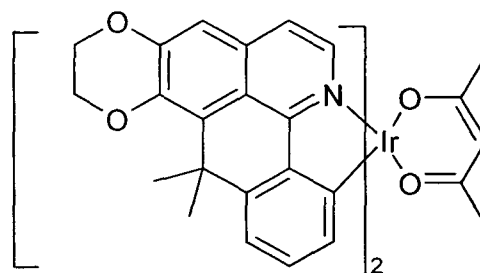


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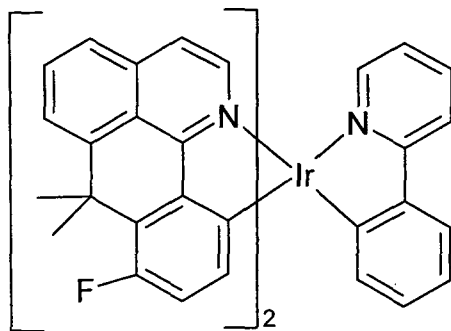
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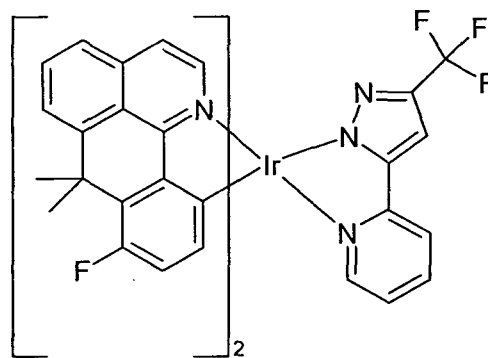
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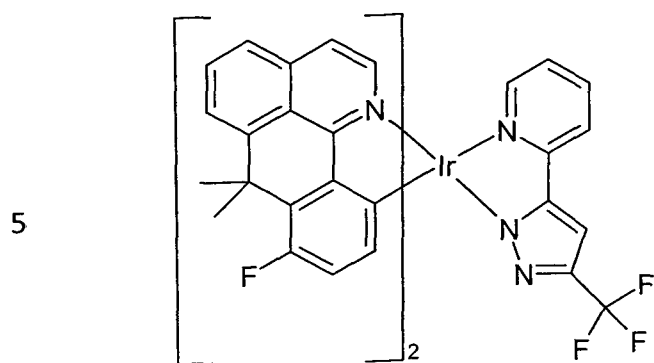
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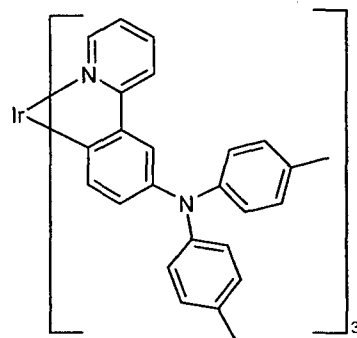
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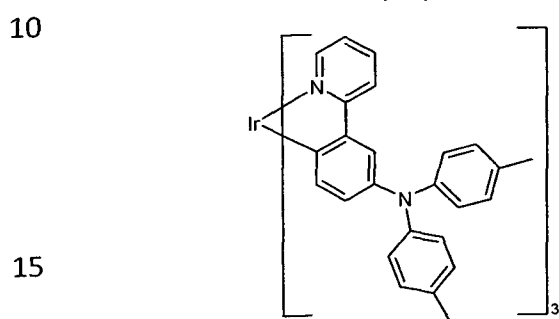
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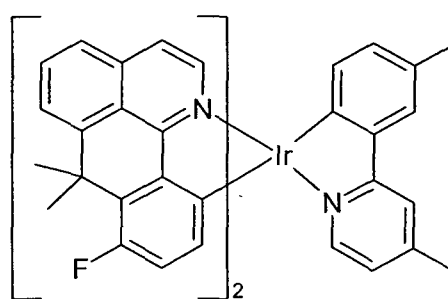
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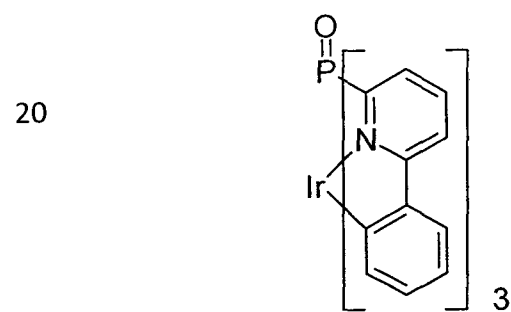
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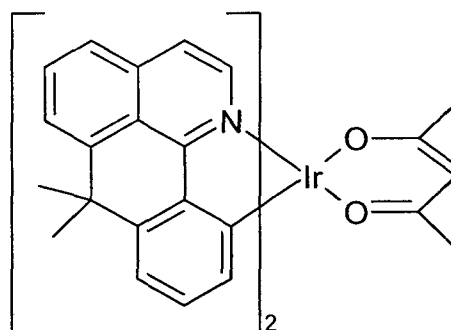
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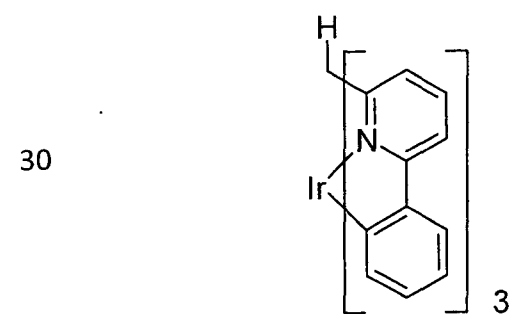
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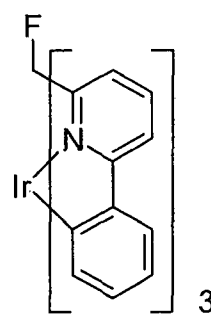
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(40)



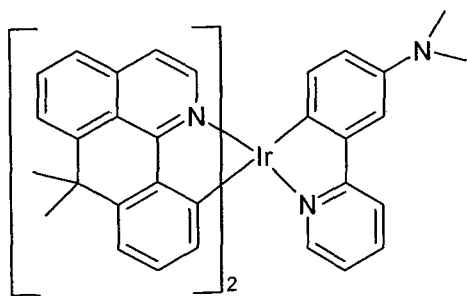
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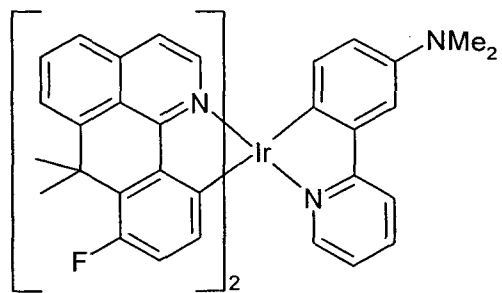
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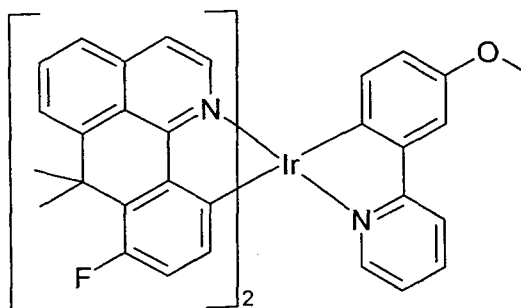


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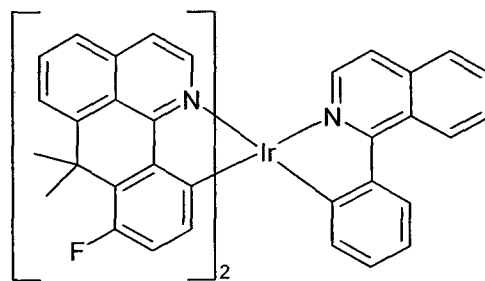


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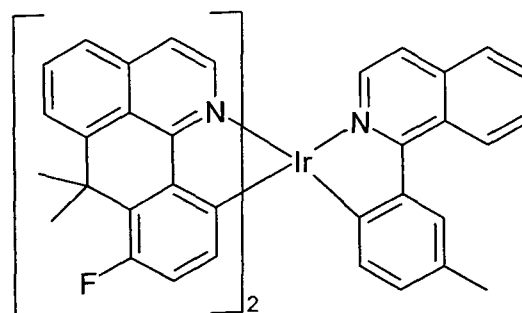
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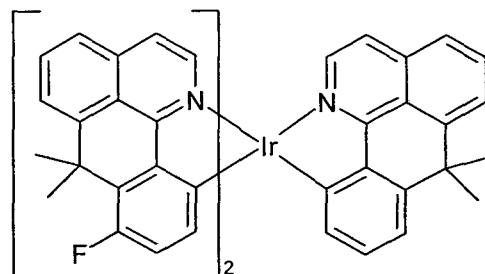
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(47)



(48)

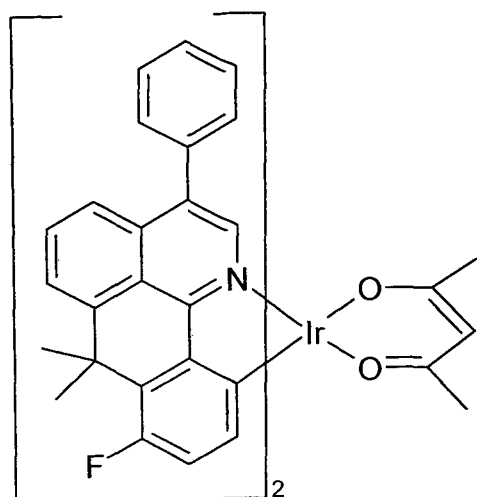
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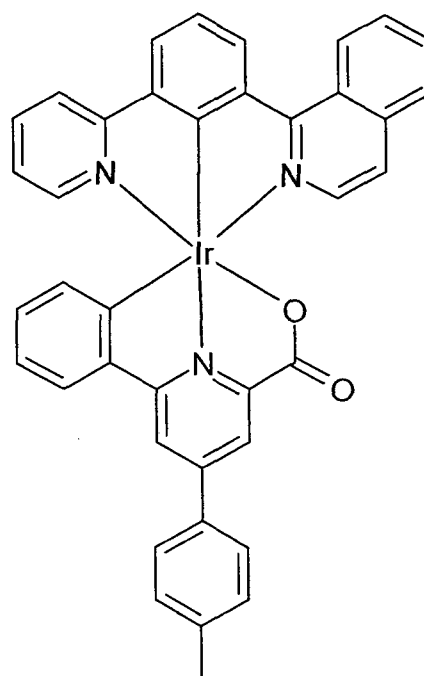
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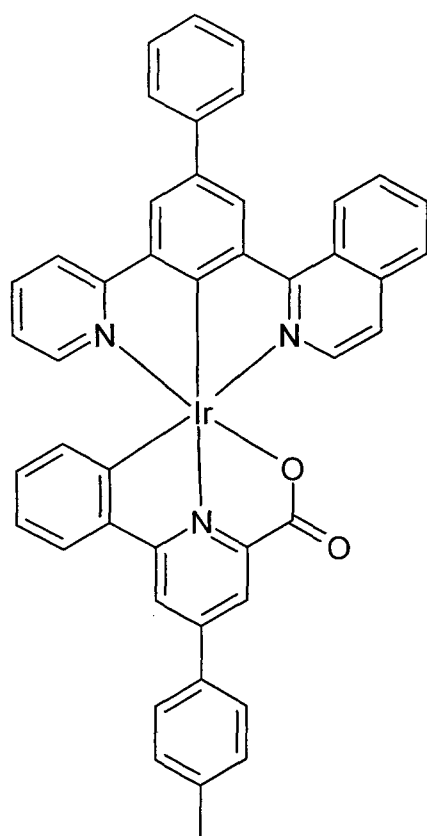


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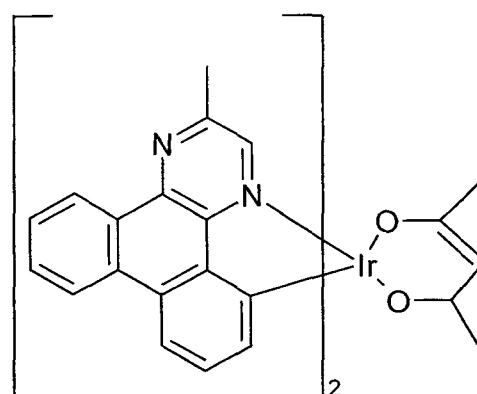
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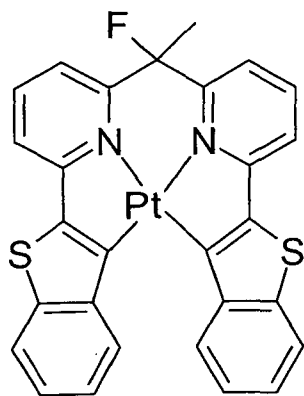
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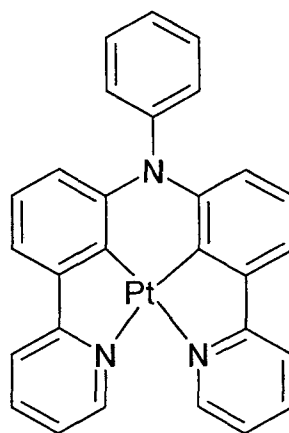
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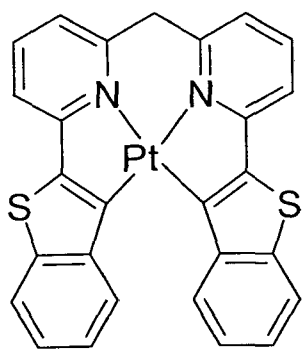
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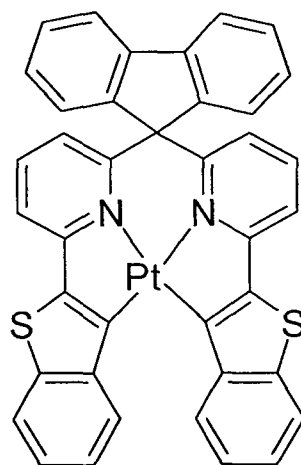
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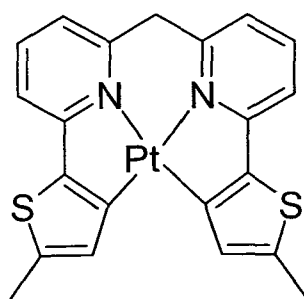
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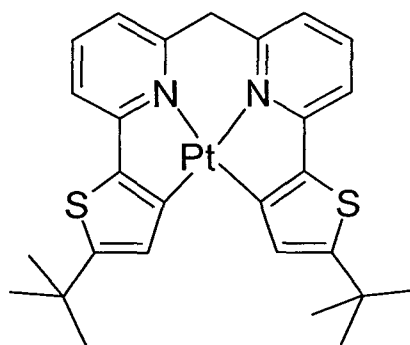
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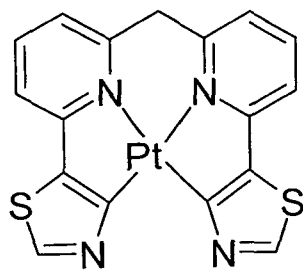
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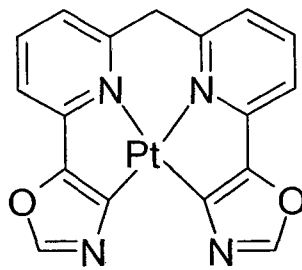
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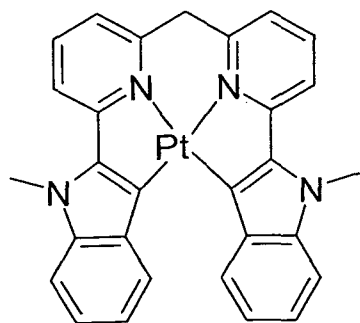
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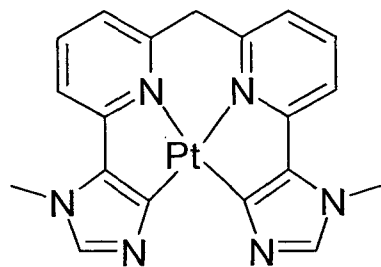
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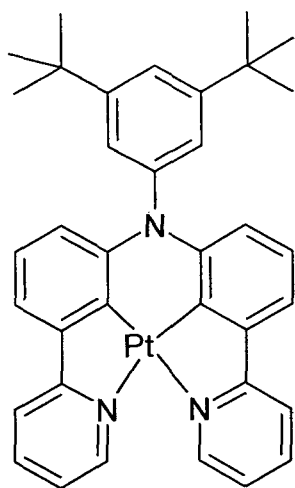
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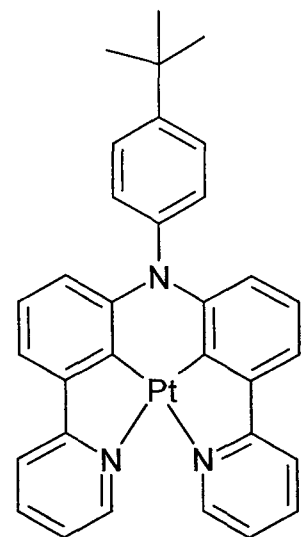
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(62)

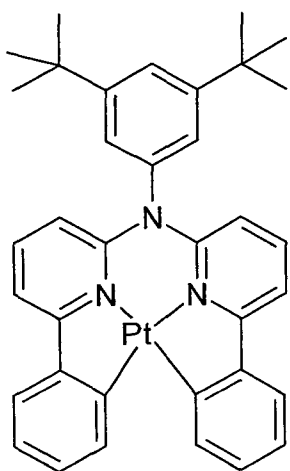


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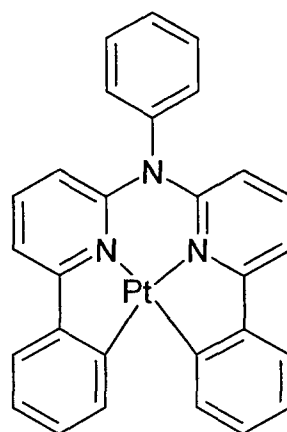
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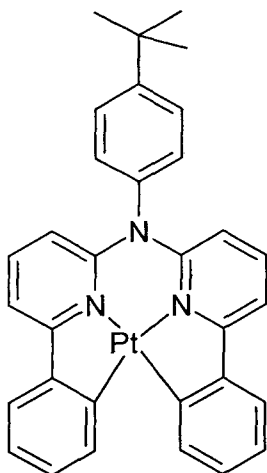
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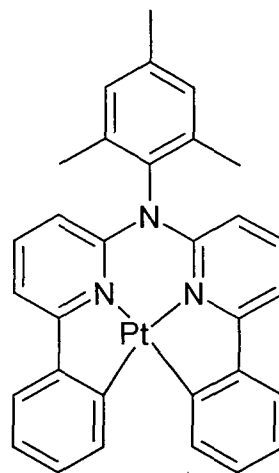
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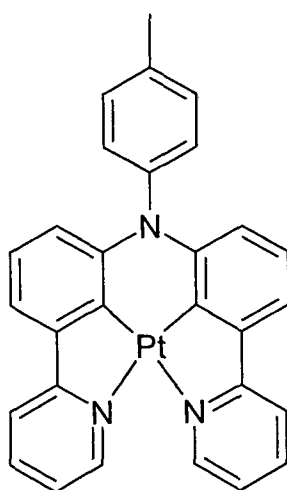
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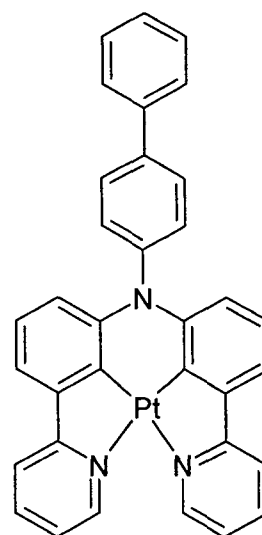
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(69)

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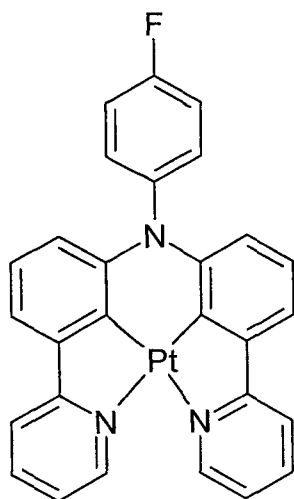


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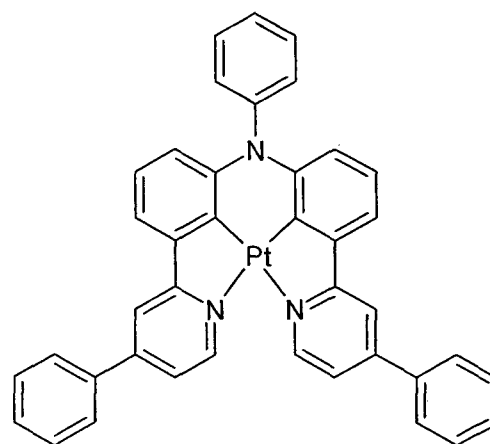
- 25 -

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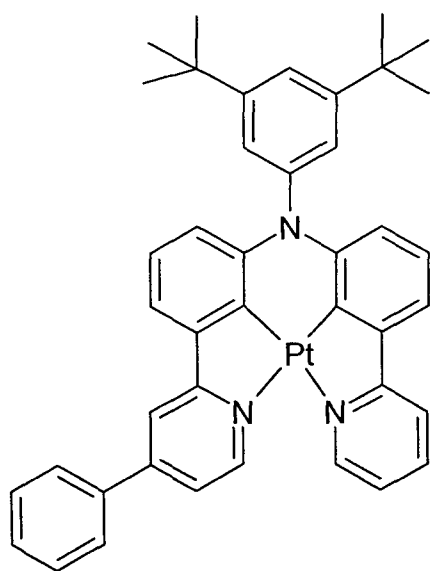
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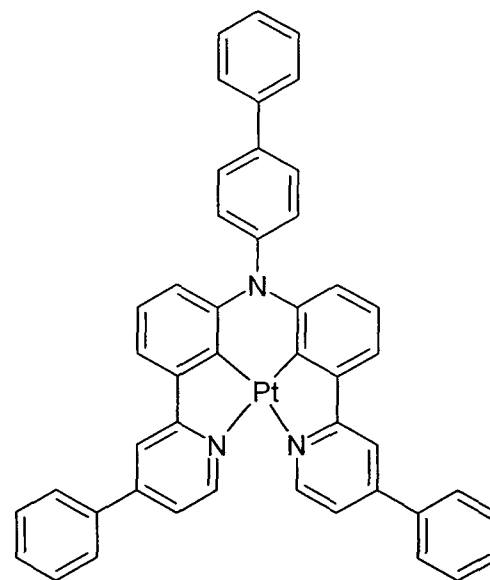
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(73)



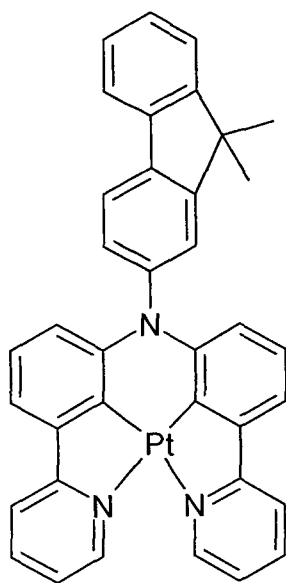
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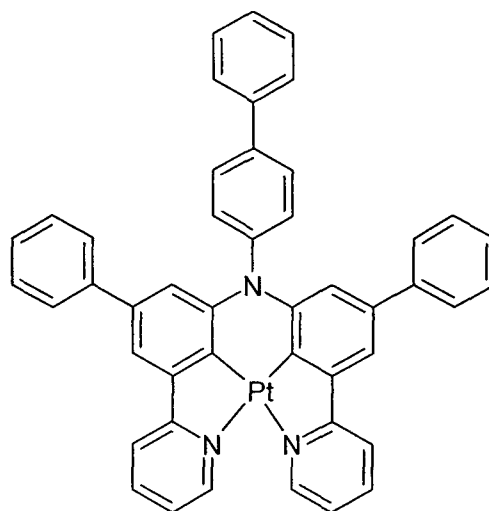
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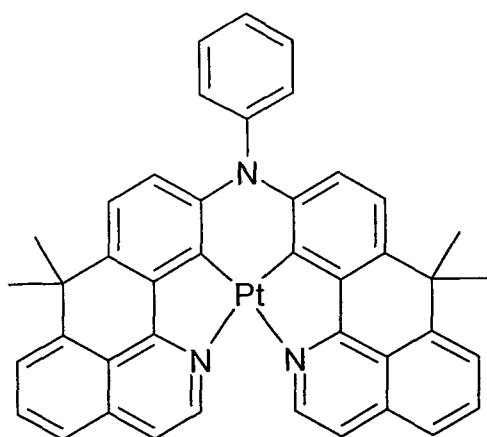
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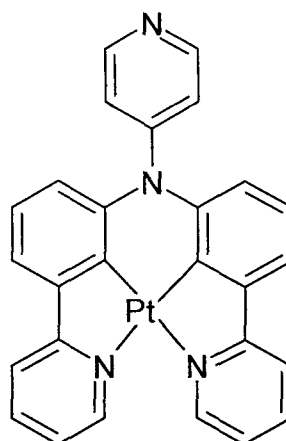
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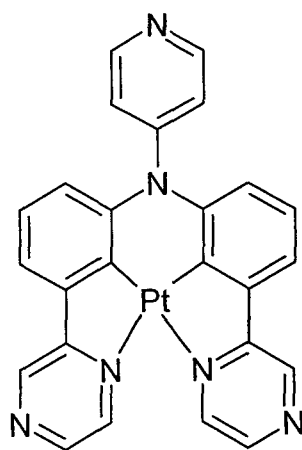
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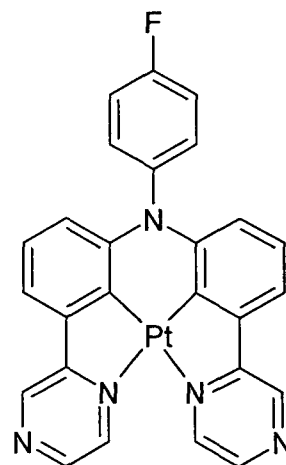
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(79)

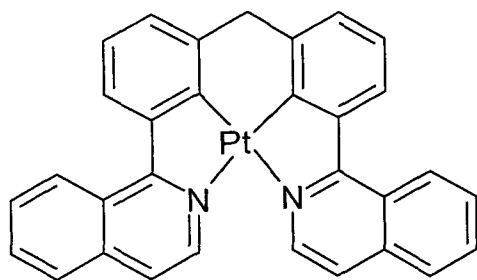
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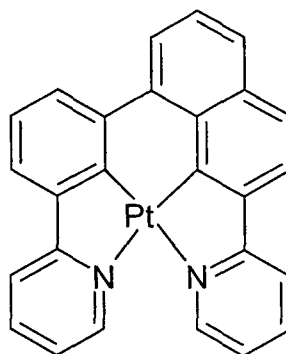
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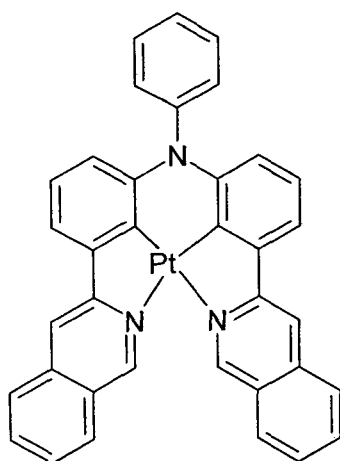
- 27 -



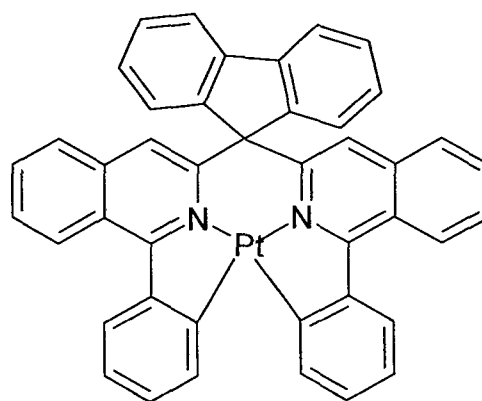
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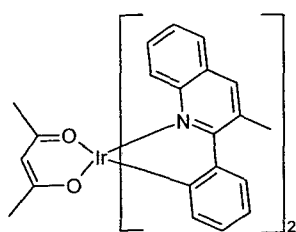
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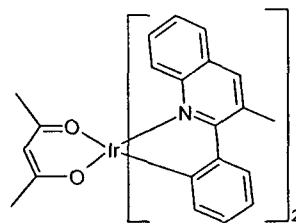
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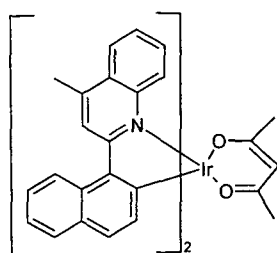
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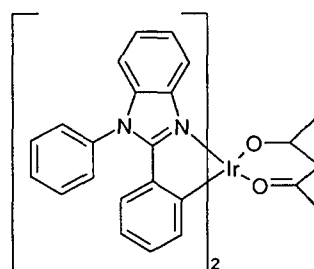
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(86)

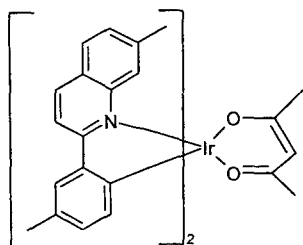


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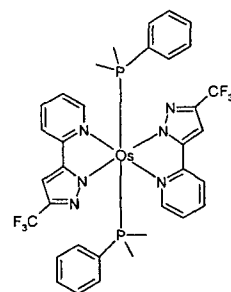


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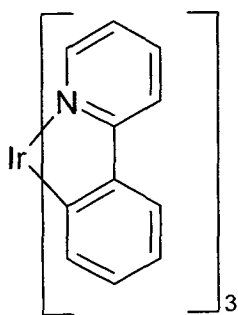
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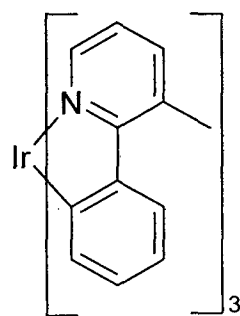
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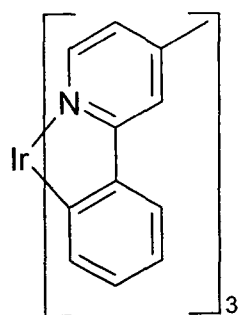
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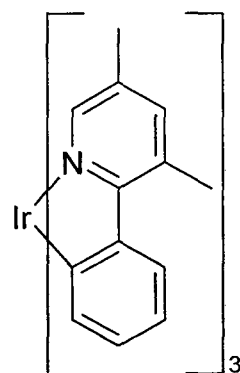
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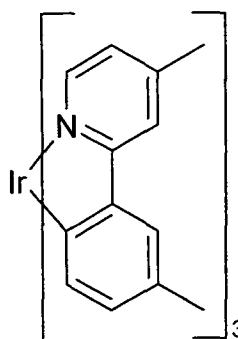
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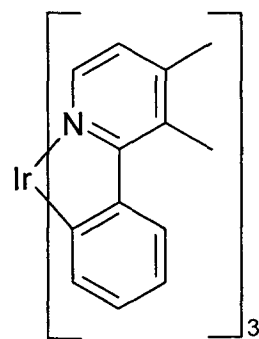
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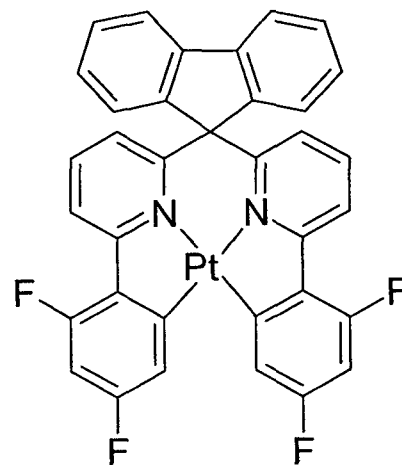
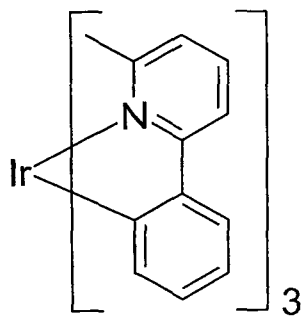
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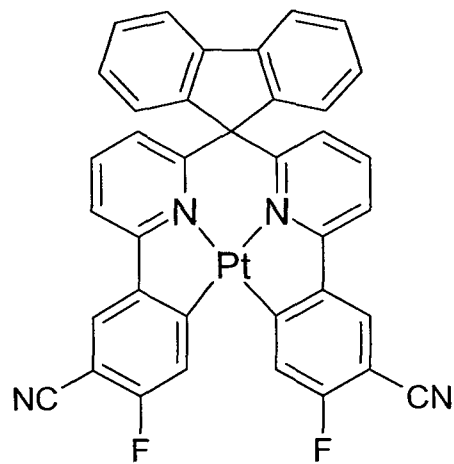
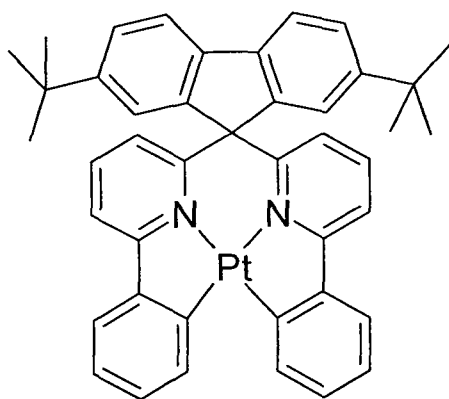


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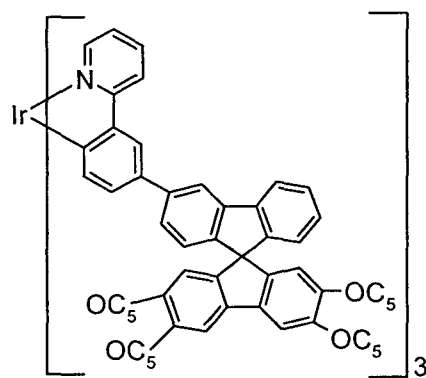
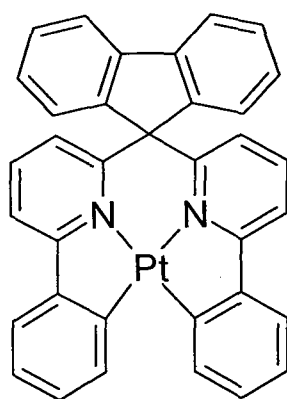
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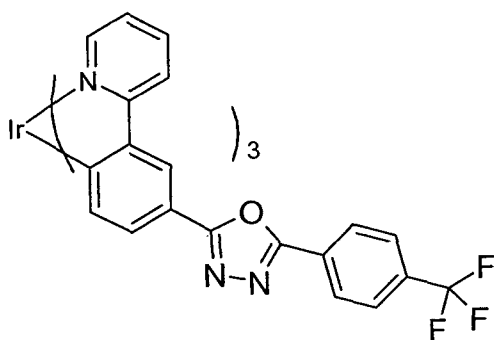
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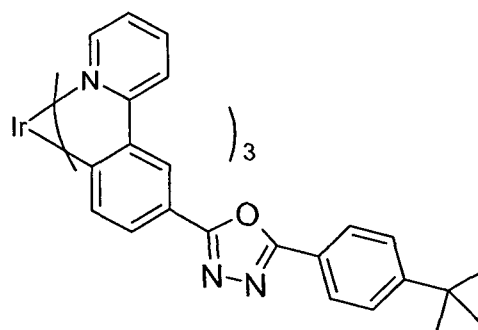
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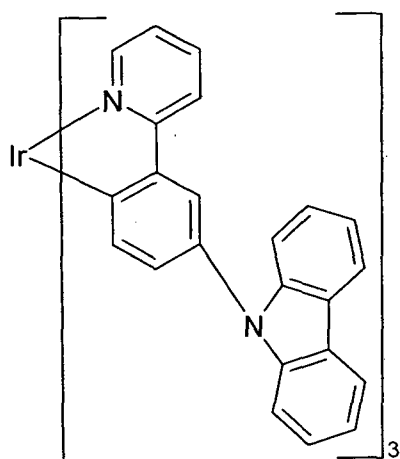
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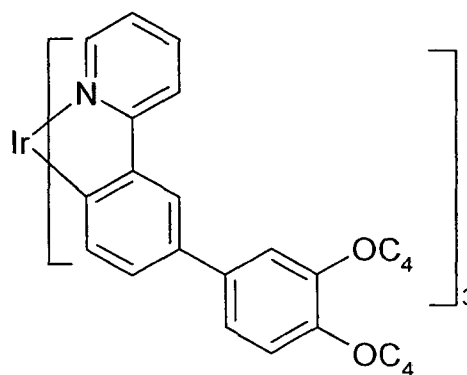
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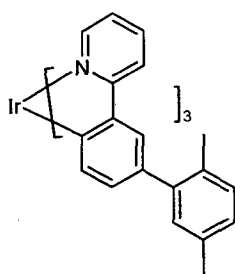
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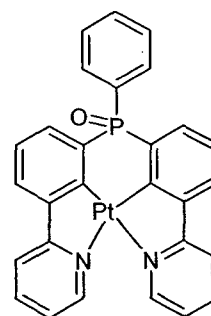
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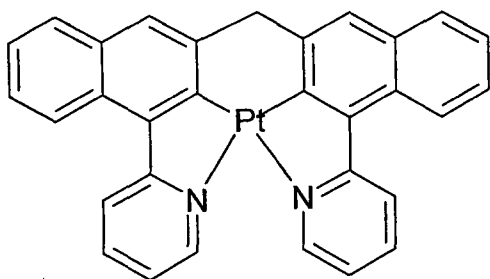


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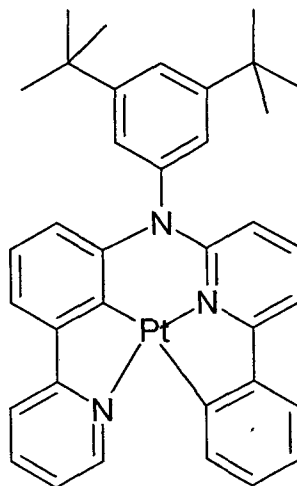


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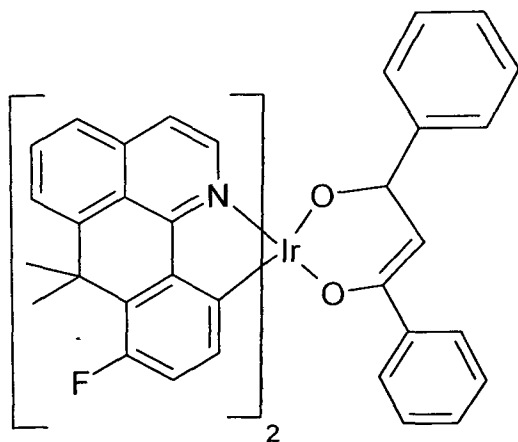
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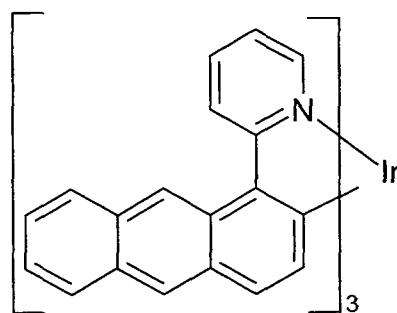
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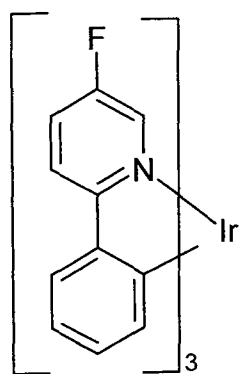
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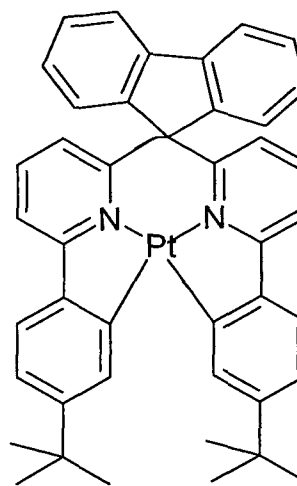
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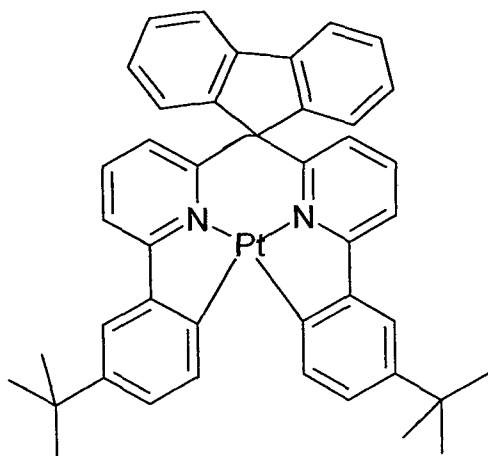


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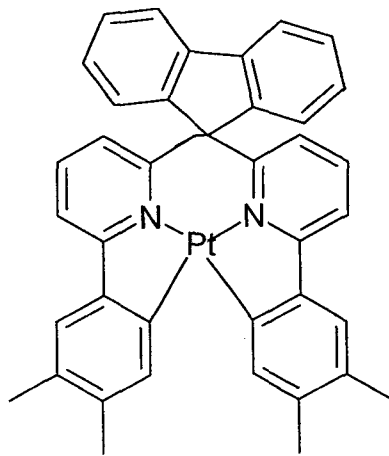
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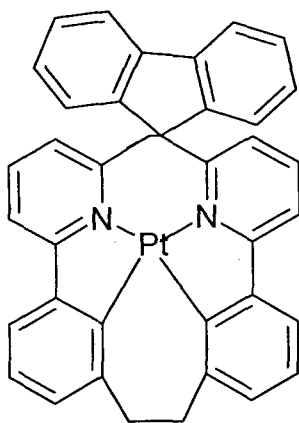
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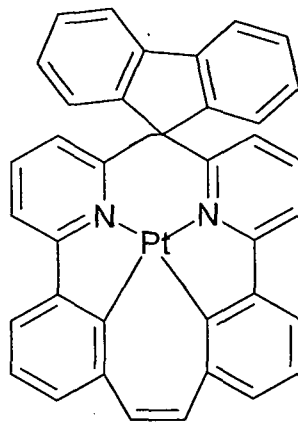
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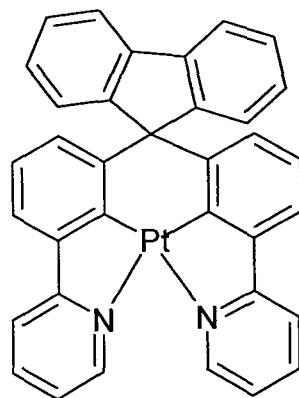
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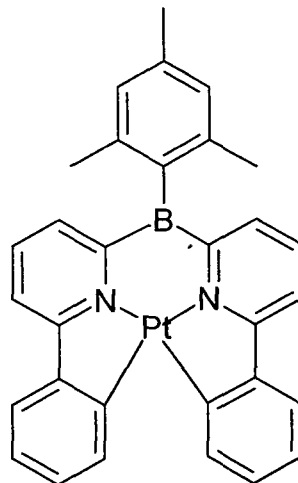
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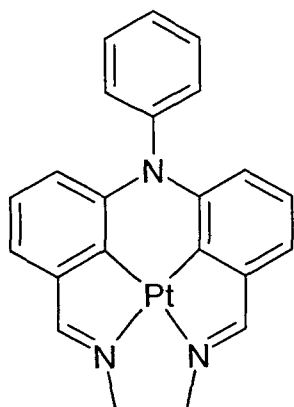
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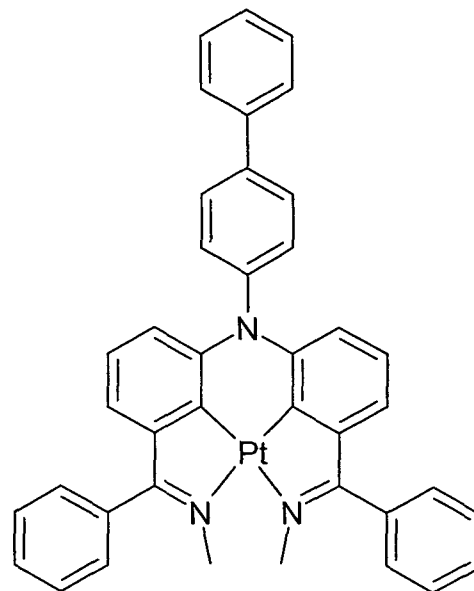
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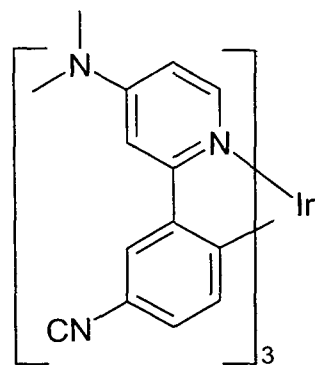
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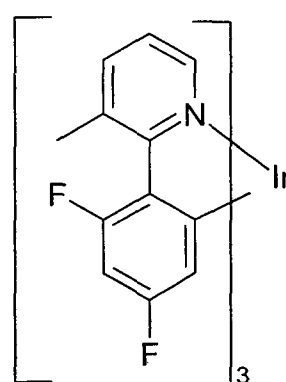
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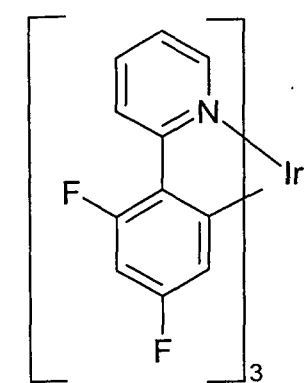
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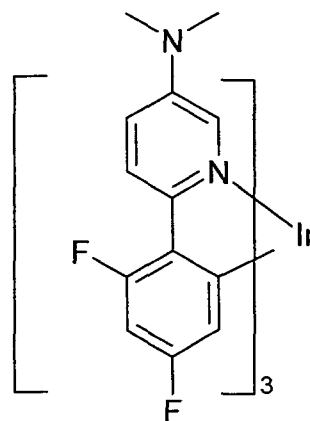
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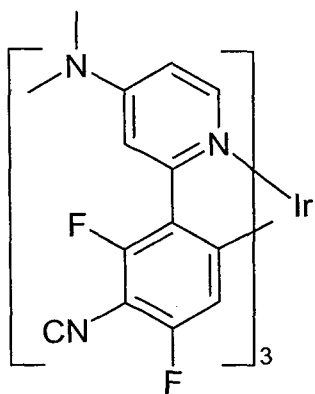


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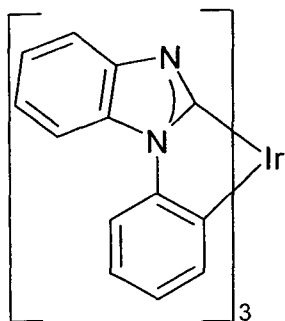
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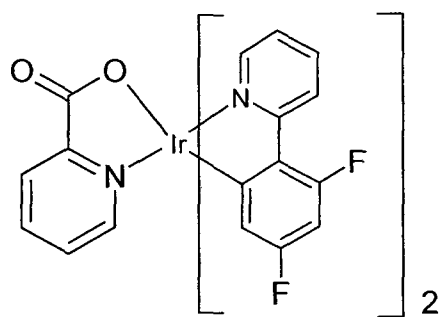
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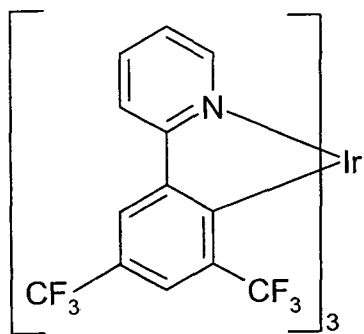
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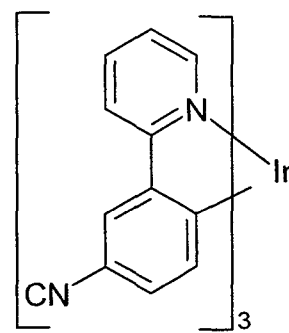
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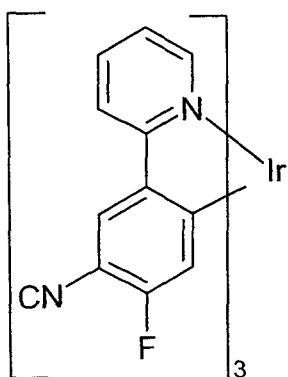
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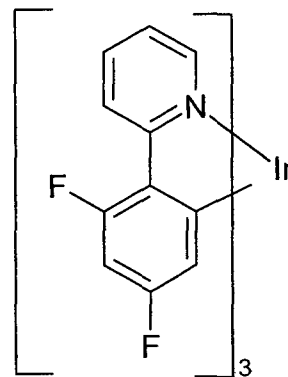
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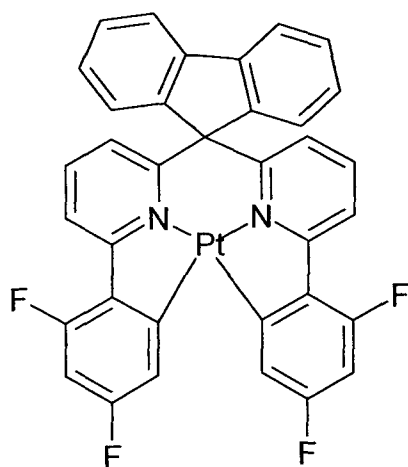


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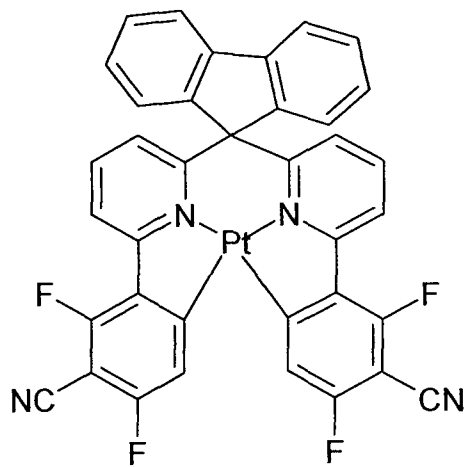


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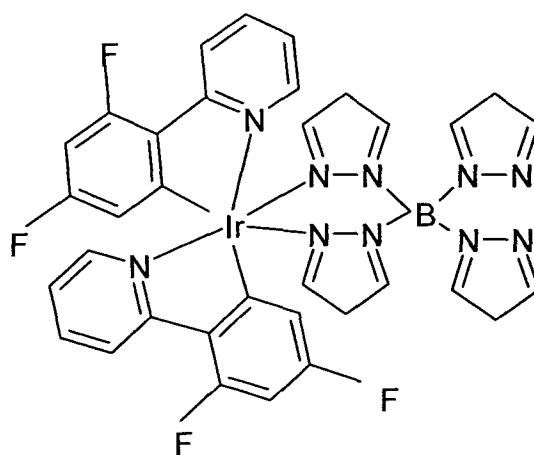


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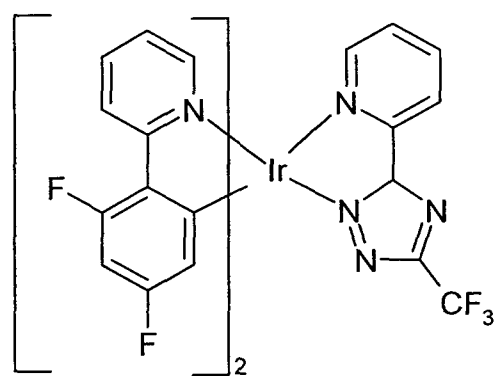


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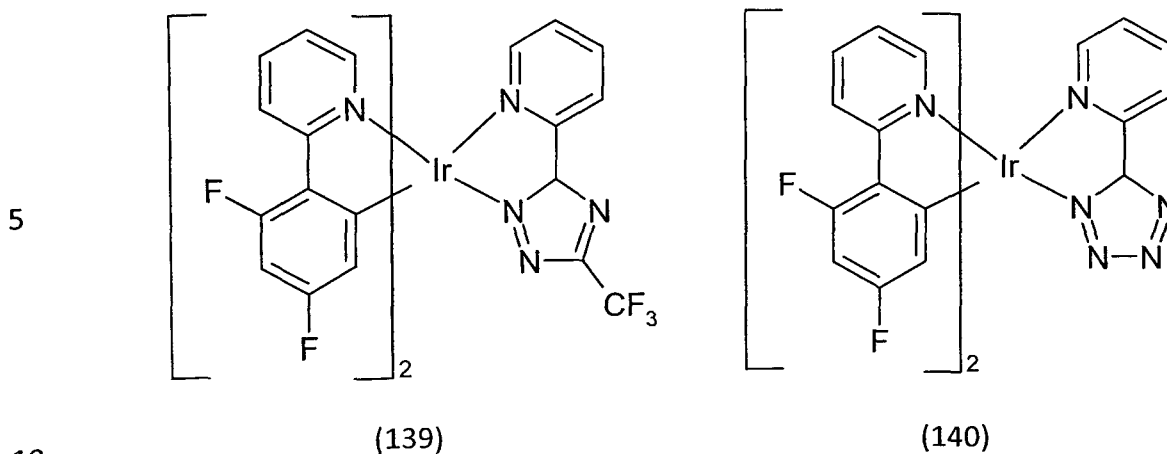
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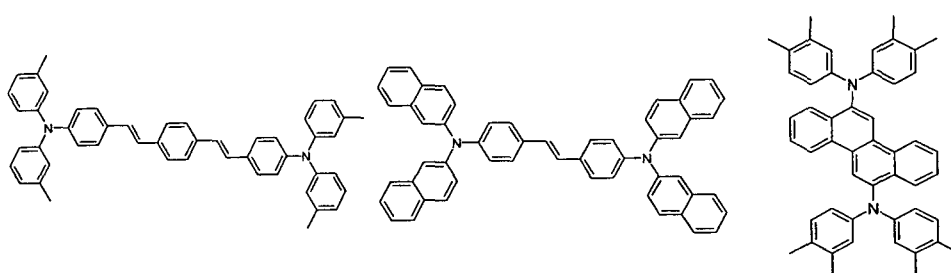
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Preferred dopants are selected from the class of the monostyrylamines, the distyrylamines, the tristyrylamines, the tetrastyrylamines, the styrylphosphines, the styryl ethers and the arylamines. A monostyrylamine is taken to mean a compound which contains one substituted or unsubstituted styryl group and at least one, preferably aromatic, amine. A distyrylamine is taken to mean a compound which contains two substituted or unsubstituted styryl groups and at least one, preferably aromatic, amine. A tristyrylamine is taken to mean a compound which contains three substituted or unsubstituted styryl groups and at least one, preferably aromatic, amine. A tetrastyrylamine is taken to mean a compound which contains four substituted or unsubstituted styryl groups and at least one, preferably aromatic, amine. The styryl groups are particularly preferably stilbenes, which may also be further substituted. Corresponding phosphines and ethers are defined analogously to the amines. For the purposes of the present invention, an arylamine or an aromatic amine is taken to mean a compound which contains three substituted or unsubstituted aromatic or heteroaromatic ring systems bonded directly to the nitrogen. At least one of these aromatic or heteroaromatic ring systems is preferably a condensed ring system, particularly preferably having at least 14 aromatic ring atoms. Preferred examples thereof are aromatic anthraceneamines, aromatic anthracenediamines, aromatic pyreneamines, aromatic pyrenediamines, aromatic chryseneamines or aromatic chrysenediamines. An aromatic anthraceneamine is taken to mean a compound in which one diarylamino group is bonded directly to an anthracene group, preferably in the 9-position. An aromatic anthracenediamine is taken to mean a compound in which two diarylamino groups are bonded directly to an anthracene group, preferably in the 9,10-position. Aromatic pyreneamines, pyrenediamines,

chryseneamines and chrysenediamines are defined analogously thereto, where the diarylamino groups are preferably bonded to the pyrene in the 1-position or in the 1,6-position. Further preferred dopants are selected from indeno-
 fluoreneamines or indenofluorenediamines, for example in accordance with
 5 WO 06/122630, benzoindenofluoreneamines or benzoindenofluorenediamines, for example in accordance with WO 08/006449, and dibenzoindenofluorene-
 amines or dibenzoindenofluorenediamines, for example in accordance with
 WO 07/140847. Examples of dopants from the class of the styrylamines are
 substituted or unsubstituted tristilbeneamines or the dopants described in
 10 WO 06/000388, WO 06/058737, WO 06/000389, WO 07/065549 and
 WO 07/115610. Preference is furthermore given to the condensed hydrocarbons
 disclosed in DE 102008035413.

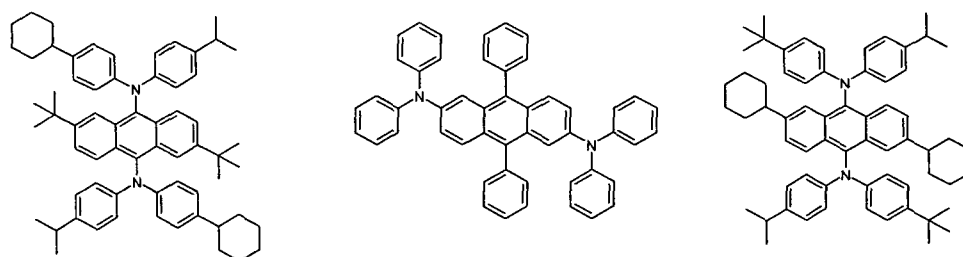
Suitable dopants are furthermore the structures depicted in the following table,
 15 and the derivatives of these structures disclosed in JP 06/001973, WO 04/047499,
 WO 06/098080, WO 07/065678, US 2005/0260442 and WO 04/092111.



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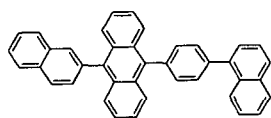
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35 The proportion of the dopant in the mixture of the emitting layer is between 0.1
 and 50.0 % by vol., preferably between 0.5 and 20.0 % by vol., particularly

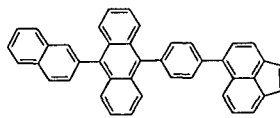
preferably between 1.0 and 10.0 % by vol. Correspondingly, the proportion of the host material is between 50.0 and 99.9 % by vol., preferably between 80.0 and 99.5 % by vol., particularly preferably between 90.0 and 99.0 % by vol.

- 5 Suitable host materials for this purpose are materials from various classes of substance. Preferred host materials are selected from the classes of the oligoarylenes (for example 2,2',7,7'-tetraphenylspirobifluorene in accordance with EP 676461 or dinaphthylanthracene), in particular the oligoarylenes containing condensed aromatic groups, the oligoarylenevinylenes (for example DPVBi or
- 10 spiro-DPVBi in accordance with EP 676461), the polypodal metal complexes (for example in accordance with WO 04/081017), the hole-conducting compounds (for example in accordance with WO 04/058911), the electron-conducting compounds, in particular ketones, phosphine oxides, sulfoxides, etc. (for example in accordance with WO 05/084081 and WO 05/084082), the atropisomers (for
- 15 example in accordance with WO 06/048268), the boronic acid derivatives (for example in accordance with WO 06/117052) or the benzantracenes (for example in accordance with WO 08/145239). Suitable host materials are furthermore also the benzo[c]phenanthrene compounds according to the invention which are described above. Apart from the compounds according to the invention,
- 20 particularly preferred host materials are selected from the classes of the oligoarylenes containing naphthalene, anthracene, benzantracene and/or pyrene or atropisomers of these compounds, the oligoarylenevinylenes, the ketones, the phosphine oxides and the sulfoxides. Apart from the benzo[c]phenanthrene compounds according to the invention, very particularly preferred host materials
- 25 are selected from the classes of the oligoarylenes containing anthracene, benzantracene and/or pyrene or atropisomers of these compounds. For the purposes of this invention, an oligoarylene is intended to be taken to mean a compound in which at least three aryl or arylene groups are bonded to one another.
- 30 Suitable host materials are furthermore, for example, the materials depicted in the following table, and derivatives of these materials, as disclosed in WO 04/018587, WO 08/006449, US 5935721, US 2005/0181232, JP 2000/273056, EP 681019, US 2004/0247937 and US 2005/0211958.

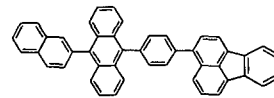
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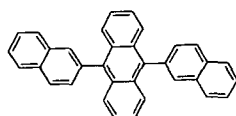
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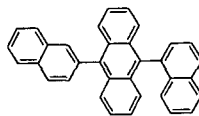
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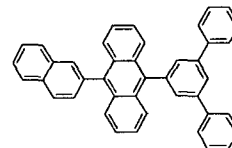
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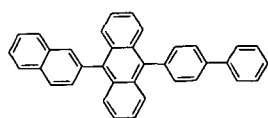
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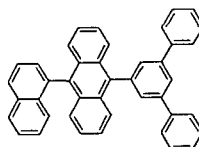
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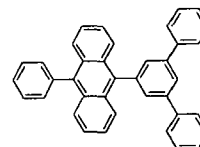
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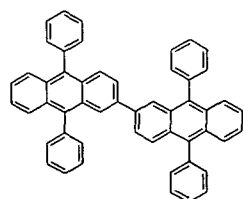
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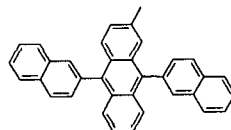
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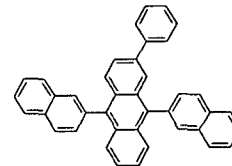
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Suitable materials having charge transport properties, for example hole transport properties or electron transport properties, are for example disclosed in Y. Shirota et al., Chemical Reviews 2007, 107(4), 953-1010. Suitable examples are aluminum complexes, zirconium complexes, benzimidazole, triazine, pyridine, pyrimidine, pyrazine, chinoxaline, chinoline, oxadiazole, aromatic ketones, lactame, borane, diazaphosphole, phosphin oxide and their derivatives as for example disclosed in JP 2000/053957, WO 2003/060956, WO 2004/028217, WO 2004/080975 or WO 2010/072300.

Preferred examples of hole transport materials, which may be used in a hole transport, hole injection or electron blocking layer, are derivatives of indenofluorene amine (e.g. disclosed in WO 06/122630 or WO 06/100896), amines (e.g. the amines disclosed in EP 1661888 or those disclosed in

5 WO 95/09147), derivatives of hexaazatriphenylene (e.g. disclosed in WO 01/049806), derivatives of amines with annealed aryls (e.g. as disclosed in US 5,061,569), monobenzoindenofluorenamines (for example as disclosed in WO 08/006449), dibenzoindenofluorenamines (for example as disclosed in WO 07/140847), spirobifluorene-amines (for example as disclosed in WO 2012/034627), fluorene-amines, spiro-dibenzopyrane-amines and derivatives of acridine.

10 The monomer comprising a light emitting compound and more generally a functional compound is preferably an olefinic compound, which is substituted with a light emitting compound and more generally with a functional compound. A specific example of such a compound and an exemplary synthesis is illustrated below in this application.

15 Suitable monomer(s) comprising a light emitting compound or more general a functional compound may be synthesized as described below.

20 In case of copolymerization the type of the at least one further monomer is not particularly limited as long as they can be polymerized by radical polymerization. Preferred monomers are those comprising an olefinic group. Examples of such monomers are styrene, acrylates, methacrylate, vinyl alcohol, vinyl acetate, acrylamide and blends thereof. A particularly well suited example of such a monomer is styrene.

25 If a mixture of monomers with and without light emitting compound is used the respective ratio of monomers with to monomers without light emitting compounds can be controlled depending upon the desired properties of the final light emitting diode to be produced. For example, the light emitting compound can be present in up to 50 wt%, relative to the weight of monomers without light emitting compound. However, the light emitting compound may also be present
30 in as low as 0.5 wt%, relative to the weight of monomers without light emitting compound.

DISPERSIONS

The dispersion according to the present invention comprises the present coated silica particles as defined above and an alcohol.

5

Exemplary preferred alcohols for use in the present invention are of general formula $R^1\text{-OH}$ with R^1 being an alkyl having from 1 to 10 carbon atoms. Examples of suitable alkyl are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl. Of these methyl, ethyl, n-propyl, iso-propyl, n-butyl and pentyl are more preferred. Even more preferred are methyl, ethyl and iso-propyl. Most preferred is ethyl.

10

While the above has been described for "an alcohol", for the purposes of the present application this term might also indicate a blend of two or more alcohols.

15

Very surprisingly the alcoholic dispersions of the present invention have been found to be extremely stable, with regards to concentration as well as with regards to long term stability of the dispersion. Even more surprisingly it is possible to achieve this stability in the absence of emulsifiers. Thus, in a preferred aspect the present application also provides for an emulsifier-free dispersion of the coated silica particles as defined in the present application.

20

It has for example been found that the alcoholic dispersion may be concentrated up to very high weight fractions of silica in the dispersion without any noticeable agglomeration of the silica particles. Thus, in one preferred aspect the present invention discloses an alcoholic dispersion of silica particles with at least 20 wt%, more preferably with at least 30 wt%, even more preferably of at least 40 wt%, even more preferably of at least 50 wt% of silica, relative to the total weight of the dispersion. In a further aspect the present invention discloses an alcoholic dispersion of silica particles with at most 60 wt% of silica, relative to the total weight of the dispersion.

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It has for example also been found that the alcoholic dispersions of the present invention show long term stability of the dispersion. In a preferred aspect, the present alcoholic dispersions are stable for a period of at least 6 months, more preferably of at least 9 months, and most preferably of at least 12 months for a

35

dispersion having a silica content of 10 wt%, relative to the total weight of the dispersion.

5 In addition to the alcohol as defined above the present dispersion may also comprise one or more organic solvents different from alcohols. Examples of such organic solvents are alkanes and aromatic solvents. Examples of suitable alkanes are pentane, hexane, heptane and octane. Examples of suitable aromatic solvents are toluene, o-xylene, m-xylene and p-xylene. If such organic solvent different from alcohols is present it is preferred that such organic solvent comprises at
10 most 50 vol% relative to the total volume of solvent in the dispersion.

METHOD FOR PRODUCING THE COATED SILICA PARTICLES

15 Generally stated, the present method for producing coated silica particles comprises the step of

(A) providing an alcoholic dispersion of silica particles.

The process further comprises at least one of the following steps (B) and (C):

(B) a first functionalization step to produce intermediate coated silica particles;
20 and

(C) a second functionalization step to produce the coated silica particles.

The order of steps (A), (B) and (C) is not particularly important. For example they may be performed in sequence (A), (B) and (C), or in sequence (A), (C) and (B), or
25 in sequence (B), (A) and (C), or in sequence (B), (C) and (A), or in sequence (C), (A) and (B), or in sequence (C), (B) and (A).

While steps (B) and (C) can be performed in either order, it is preferred to first perform step (B) and then step (C). However, depending upon the intended use of
30 the coated silica particles, it is also possible to only apply either step (B) or step (C).

It is also possible to perform two or even three steps simultaneously. It is for example possible to perform steps (A) and (B) simultaneously and then perform
35 step (C). It is for example also possible to perform steps (A) and (C) simultaneously and then perform step (B). Or it is for example possible to perform step (A) and

then simultaneously steps (B) and (C). The possibility of simultaneously performing two or three steps allows for easier production of the coated silica particles of the present invention.

5 A - PROVIDING THE ALCOHOLIC DISPERSION OF SILICA PARTICLES

The type of silica particles to be used in the present invention is not particularly limited. Said silica particles may for example essentially consist of silica, i.e. have uniform composition and essentially consist of silica, throughout the particle. Said
10 silica particles may for example also have a non-uniform composition throughout the particles. An example of such a non-uniform composition is a core/shell silica particle, wherein the shell essentially consists of silica and the core may essentially consist of a different composition. Said different composition may be selected for specific properties. As examples of such specific properties mention
15 may be made of magnetic properties, electrical properties, optical properties, antistatic properties, catalytic properties, photoactive properties, dielectric properties, semiconducting properties, hole or electron blocking properties and hole or electron conducting properties.

20 With respect to the present silica particles the term "essentially consisting of" is used to denote a content of at least 90 wt%, for example at least 91 wt% or 92 wt% or 93 wt% or 94 wt% or 95 wt% or 96 wt% or 97 wt% or 98 wt% or 99 wt%, respective to the total weight of said particle or the shell in case of a core/shell particle.

25 It is, however, preferred that they have a diameter of at least 1 nm, more preferably of at least 3 nm, even more preferably of at least 5 nm and most preferably of at least 7 nm. Preferably they have a diameter of at most 200 nm, more preferably of at most 150 nm or 100 nm, even more preferably of at most
30 90 nm or 80 nm, still even more preferably of at most 70 nm or 60 nm, and most preferably of at most 50 nm. The diameter of the silica particles can for example be determined as disclosed in the test methods.

35 Silica particles useful in the present invention can for example be bought as an aqueous dispersion. Such dispersions are for example commercially available under the Levasil tradename from Kurt Obermeier GmbH & Co KG. A suitable

grade is for example Levasil® 300/30, which is a 30 wt% dispersion of silica particles having an active surface area of $300 \text{ m}^2 \text{ g}^{-1}$.

5 In case the silica particles are bought in form of an aqueous dispersion, it is advantageous to exchange the water for an alcohol so that the resulting alcoholic dispersion preferably comprises at most 20 vol%, more preferably at most 10 vol%, even more preferably at most 5 vol%, still even more preferably at most 3 vol% and most preferably at most 1 vol% of water, relative to the combined
10 volumes of water and alcohol. Starting with an aqueous dispersion of silica particles the water can be exchanged for an alcohol for example by azeotropic distillation under acidic conditions. Under acidic conditions it is meant that the pH of the aqueous dispersion preferably is at most 4.0, more preferably at most 3.5, even more preferably at most 3.0, and most preferably at most 2.5. A detailed example of such an azeotropic distillation is given in the examples.

15 Preferably, once an alcoholic dispersion of the silica particles has been obtained, said dispersion is reduced in volume by evaporation of a part of the alcohol.

20 Exemplary preferred alcohols for use in the present invention are of general formula $\text{R}^1\text{-OH}$ as defined previously.

While the above has been described for "an alcohol", for the purposes of the present application this term might also indicate a blend of two or more alcohols.

25 In addition to the alcohol as defined above the present dispersion may also comprise one or more organic solvents different from alcohols. Examples of such organic solvents include alkanes and aromatic solvents. Examples of suitable alkanes are pentane, hexane, heptane and octane. Examples of suitable aromatic solvents are toluene, o-xylene, m-xylene and p-xylene. If such organic solvent
30 different from alcohols is present it is preferred that such organic solvent comprises at most 50 vol% relative to the total volume of solvent in the dispersion.

B - FIRST FUNCTIONALIZATION STEP

35 The first functionalization step comprises the steps of

(B-1) treating the surface of the dispersed silica particles with a first surface modifying agent, and

(B-2) subsequently polymerizing a polar olefinic compound, to produce intermediate coated silica particles.

5

Said first surface modifying agent comprises at least two functional groups, $FG^{1'}$ and $FG^{2'}$, and can for example be described by the following general formula (I')



10

wherein $FG^{1'}$ is a first functional group as defined in the following, $FG^{2'}$ is a second functional group as defined in the following, $FG^{1'}$ and $FG^{2'}$ being different from one another, Sp^1 is a spacer as defined above, and m is as defined above,.

15

The type of functional group $FG^{1'}$ is not particularly limited as long as it is capable of chemically reacting with hydroxyl groups on the surface of said silica particles.

Examples of suitable functional groups $FG^{1'}$ are alkoxyisilanyl groups, halogen silanes and acid groups of phosphoric acid and phosphonic acid and their esters. Particularly well suited examples of such functional groups are alkoxyisilanyl groups of general formula (II')

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wherein R^2 , R^3 and R^4 are independently of each other selected as defined for R^2 and R^3 in respect to formula (II).

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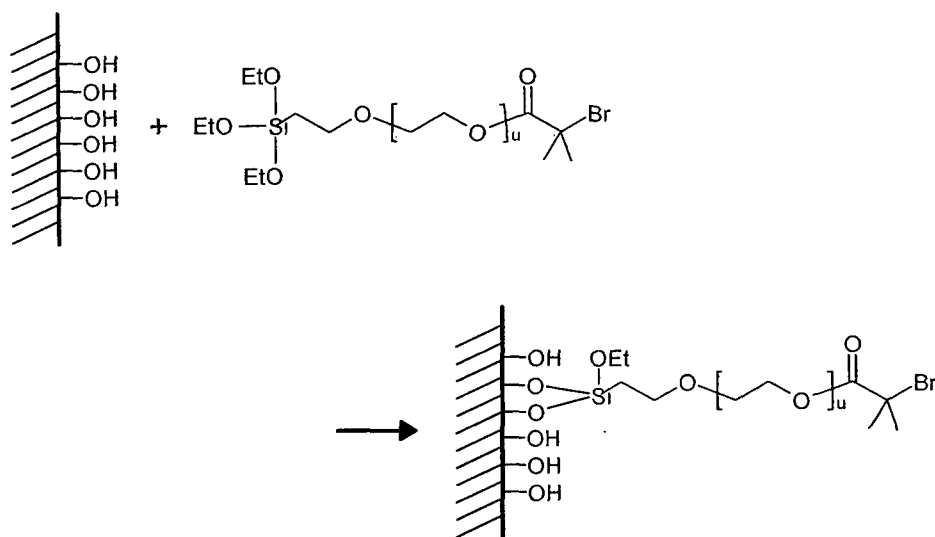
Suitable examples of said second functional group $FG^{2'}$ comprise a group selected from C=C double bond, Cl, Br and I, with C=C double bond and Br being preferred, and Br being most preferred. A particularly suitable example of $FG^{2'}$ is $-C(=O)-C(CH_3)_2-Br$. An example of $FG^{2'}$ with a C=C double bond is $-C(=O)-C(CH_3)=CH_2$.

35

Optionally the first surface modifying agent may comprise one or more further functional groups, which may be the same or different from $FG^{1'}$ and $FG^{2'}$ as

defined above. In addition to what is defined for $FG^{1'}$ and $FG^{2'}$ such further functional groups may also be chosen from the group consisting of acrylate, methacrylate, vinyl, amino, cyano, isocyanate, epoxy, carboxy and hydroxyl groups. The one or more further functional groups may for example be bound to or comprised in $FG^{1'}$, $FG^{2'}$ and/or the spacer Sp^1 .

An exemplary embodiment of the reaction of a silica and a first surface modifying agent of general formula (I') is illustrated in the following Scheme 1 with u being an integer of from 0 to 20.

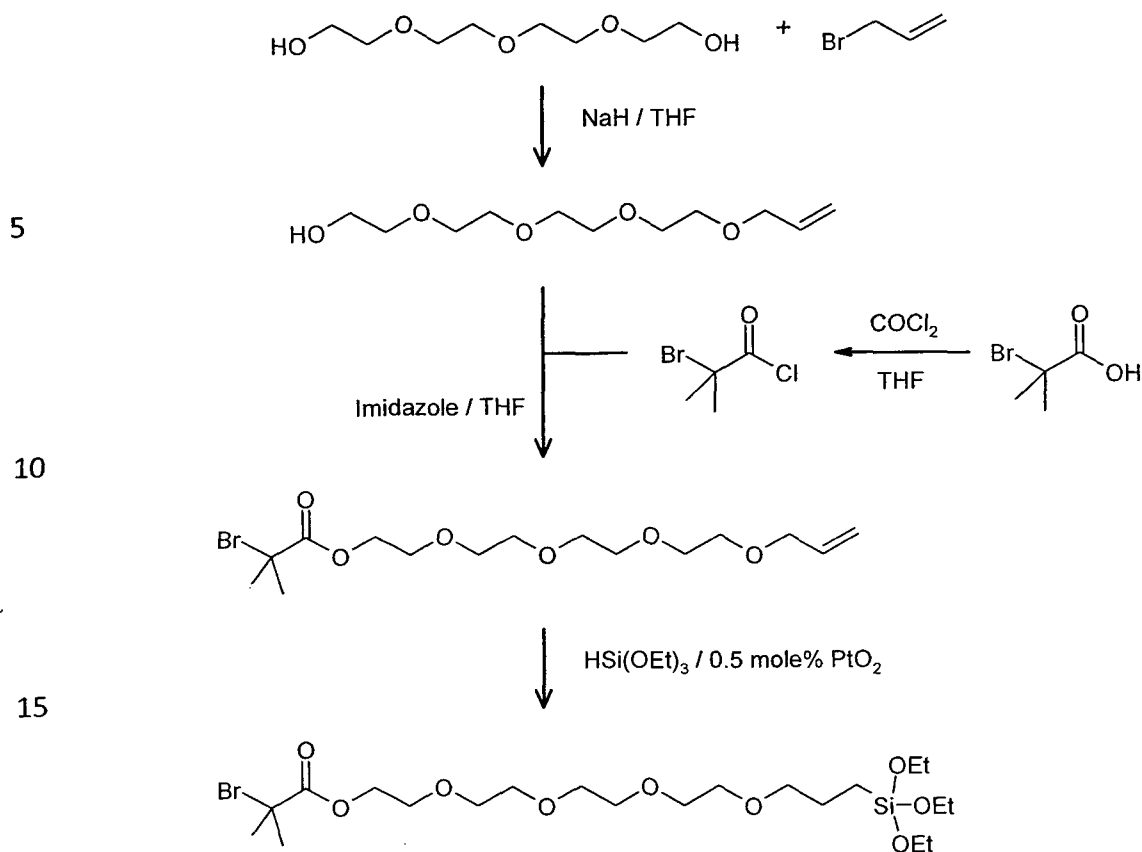


Scheme 1

Compounds of formula (I') can be synthesized by commonly known chemical reactions. Scheme 2 depicts an exemplary reaction sequence starting with the reaction of a di-alcohol and 3-bromopropene (commonly also referred to as "allylbromide"), the reaction product of which is further first reacted with $Br-C(CH_3)_2-C(=O)-Cl$ and subsequently subjected to a hydrosilylation in presence of a PtO_2 -catalyst to yield a compound according to formula (I').

Scheme 2 is intended to give an exemplary and schematic synthetic reaction sequence leading to an exemplary compound of formula (I'). The synthesis of further compounds corresponding to general formula (I') can be found in the examples. It is noted that all the chemical reactions used herein are commonly known to the skilled person.

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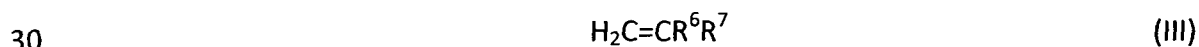


Scheme 2

20 Following the introduction of the first surface modifying agent, a polar olefinic compound is polymerized to obtain the intermediate coated silica particles.

25 A suitable polar olefinic compound may for example be selected from the group consisting of acrylates, methacrylate, vinyl alcohol, vinyl acetate, acrylamide and blends thereof.

Preferably said polar olefinic compound is of following general formula (III)

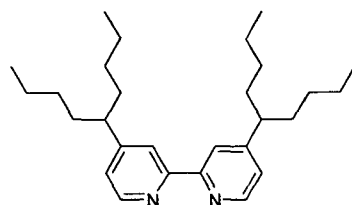


with R^6 and R^7 as defined previously.

35 The method of polymerizing the polar olefinic compound is not particularly limited. It may for example be done by radical polymerization. It may also for example be performed by atom transfer radical polymerization (ATRP). The

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polymerization may be started with any suitable chemical compound. It is, however, preferred to use azobisisobutyronitrile ($\text{NC-C(CH}_3)_2\text{-N}\equiv\text{N-C(CH}_3)_2\text{-CN}$) as initiator. Instead of using a separate starter for the polymerization reaction, said starter, such as for example an azo compound, may for example also be comprised in the second surface modifying agent as described below. For the present invention it may be particularly advantageous to use as initiator a mixture of a Cu(I) compound and 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy).

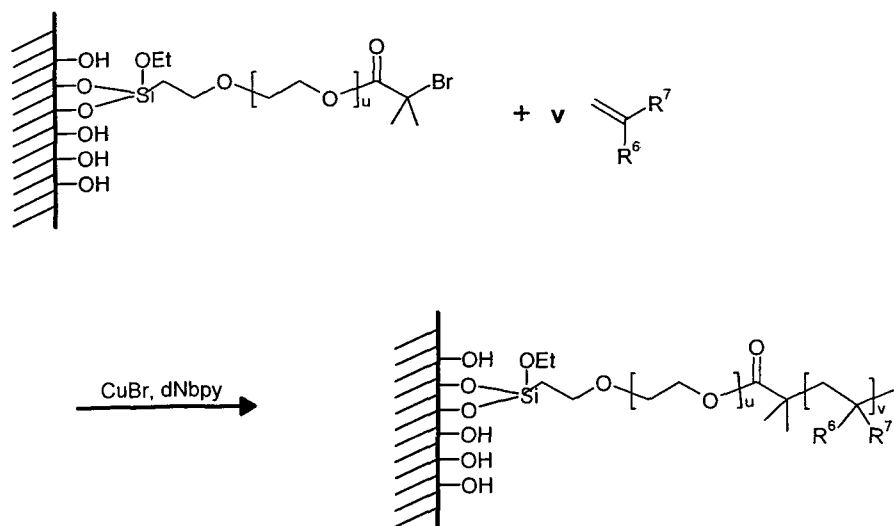


(dNbpy)

Said Cu(I) compound is preferably selected from the group consisting of CuCl, CuBr and CuI. Most preferably it is CuBr.

The ratio of Cu(I) compound to dNbpy is preferably in the range from 5 : 1 to 1 : 10. More preferably, said ratio is in the range from 2 : 1 to 1 : 5. And most preferably, said ratio is in the range from 1 : 1 to 1 : 3.

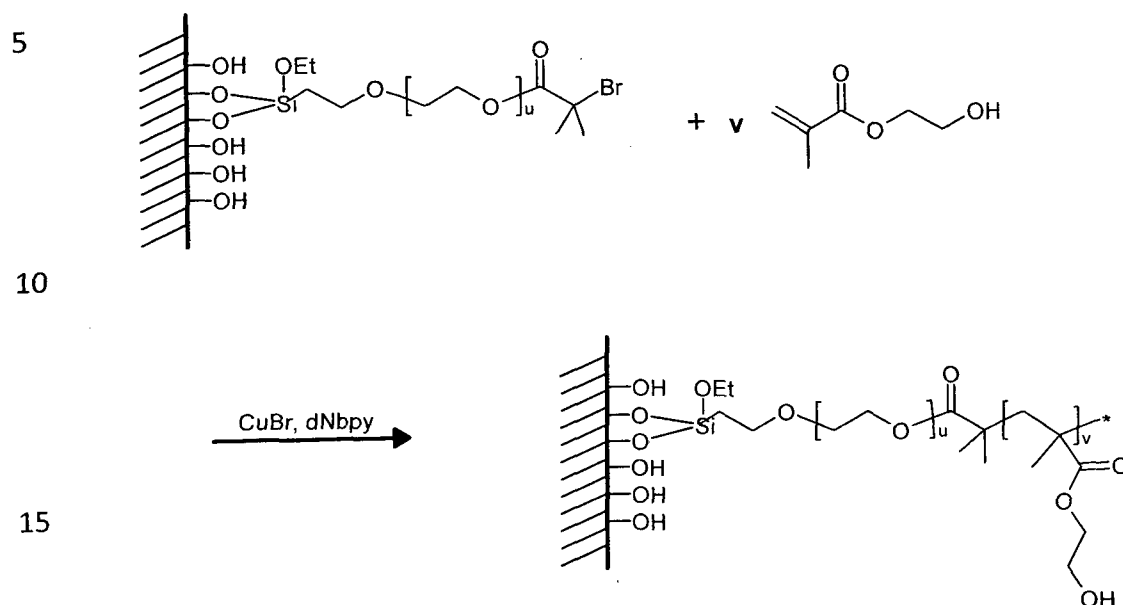
An exemplary general polymerization reaction is shown in Scheme 3a with u being an integer of from 0 to 20 and v being an integer of from 1 to 100.



Scheme 3a

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A more specific exemplary polymerization reaction is shown in Scheme 3b, with u being an integer of from 0 to 20, v being an integer of from 1 to 100, R^6 being methyl and R^7 being $-C(=O)O-(CH_2)_2-OH$.



Scheme 3b

The so-obtained intermediate silica particles may be precipitated from solution by the addition of an alkane. Examples of suitable alkanes are pentane, hexane, heptane and octane, of which hexane is particularly well suited. The obtained precipitated silica particles can easily be re-dispersed in an alcohol as defined above.

C - SECOND FUNCTIONALIZATION STEP

The second functionalization step comprises the steps of

- (C-1) treating the surface of said intermediate coated silica particles with a second surface modifying agent, and
- (C-2) subsequently radically polymerizing thereon at least a first and a second monomer, wherein said first monomer comprises a light emitter, and wherein the second surface modifying agent acts as a radical transfer agent, to obtain the coated silica particles.

Said second surface modifying agent comprises at least two functional groups $FG^{3'}$ and $FG^{4'}$, and can for example be described by the following general formula (IV')



wherein $FG^{3'}$ is a third functional group as defined in the following, $FG^{4'}$ is a fourth functional group as defined in the following. $FG^{3'}$ and $FG^{4'}$ being different from one another, Sp^2 is a spacer as defined above, and r is as defined above.

The type of functional group $FG^{3'}$ is not particularly limited as long as it is capable of chemically reacting with hydroxyl groups on the surface of said silica particles.

Examples of suitable functional groups $FG^{3'}$ are alkoxysilanyl groups, halogen silanes and acid groups of phosphoric acid and phosphonic acid and their esters. Particularly well suited examples of such functional groups are alkoxysilanyl groups of general formula (V')



wherein R^9 , R^{10} and R^{11} are independently of each other selected as defined for R^9 and R^{10} in respect to formula (V) earlier in this application.

Said functional group $FG^{4'}$ is preferably selected from the group consisting of thiol, sulfide, disulfide, polysulfide and azo compounds. Of these thiol and azo compounds are the preferred examples.

With regards to $FG^{4'}$, thiol may be represented as $-SH$. With regards to $FG^{4'}$, sulfide may be represented as $-S-R^{15}$, with R^{15} as defined below. With regards to $FG^{4'}$, disulfide may be represented as $-S-S-R^{15}$, with R^{15} as defined below. With regards to $FG^{4'}$, polysulfide may be represented as $-S_w-R^{15}$, with R^{15} as defined below and with w being an integer of from 2 to 20. R^{15} may be a straight-chain, branched or cyclic alkyl or alkoxy group having from 1 to 20 carbon atoms, in which one or more nonadjacent CH_2 groups may be replaced by $-O-$, $-S-$, $-CO-O-$, $-C=O-$, $-CH=CH-$ or $-C\equiv C-$, and in which one or more hydrogen atoms may be replaced by F , or an

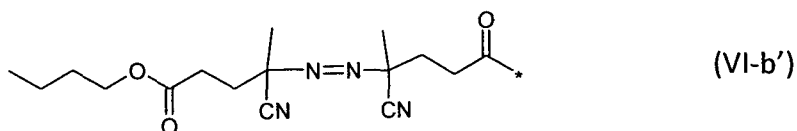
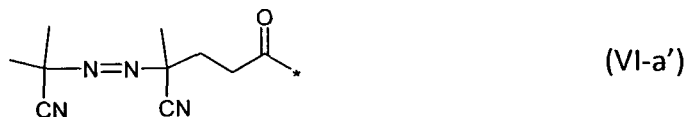
aryl or heteroaryl group which has from 4 to 14 carbon atoms and may be substituted by one or more groups R^5 . Preferably R^{15} is as defined for R^5 above.

Exemplary azo compounds suitable as $FG^{4'}$ may be represented by $-R^{16}-N=N-R^{17}$, with R^{16} and R^{17} as defined in the following.

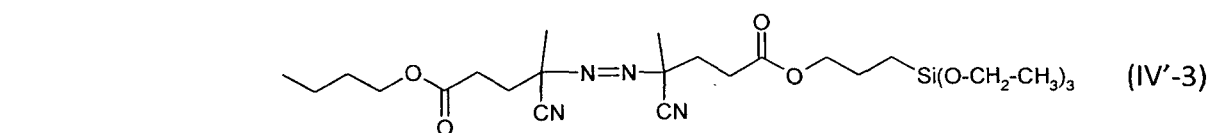
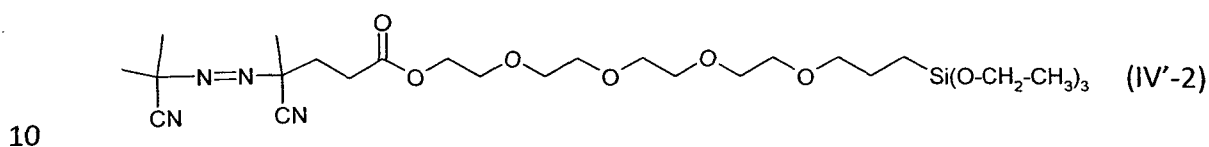
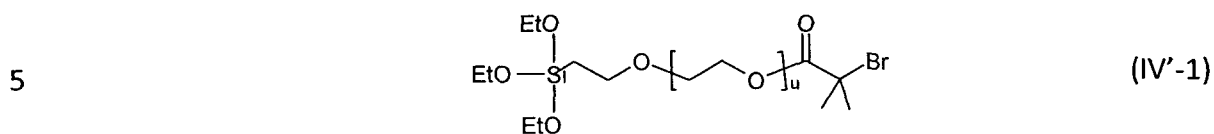
R^{16} may for example be selected from the group consisting of straight-chain, branched or cyclic alkanediyl groups having from 1 to 20 carbon atoms, in which one or more nonadjacent CH_2 groups may be replaced by $-O-$, $-S-$, $-CO-O-$, $-C=O-$, $-CH=CH-$ or $-C\equiv C-$, and in which one or more hydrogen atoms may be replaced by F or CN, or an arylene or heteroarylene group which has from 4 to 14 carbon atoms and may be substituted by one or more groups R^5 . Preferably R^{16} may be selected from straight-chain, branched or cyclic alkanediyl group having from 1 to 10 carbon atoms, in which one or more nonadjacent CH_2 groups may be replaced by $-O-$, $-CO-O-$ or $-C=O-$, and in which one or more hydrogen atoms may be replaced by CN,

R^{17} may for example be selected from the group consisting of straight-chain, branched or cyclic alkyl groups having from 1 to 20 carbon atoms, in which one or more nonadjacent CH_2 groups may be replaced by $-O-$, $-S-$, $-CO-O-$, $-C=O-$, $-CH=CH-$ or $-C\equiv C-$, and in which one or more hydrogen atoms may be replaced by F or CN, or an aryl or heteroaryl group which has from 4 to 14 carbon atoms and may be substituted by one or more groups R^5 . Preferably R^{17} may be selected from straight-chain, branched or cyclic alkyl group having from 1 to 20 carbon atoms, in which one or more nonadjacent CH_2 groups may be replaced by $-O-$, $-CO-O-$ or $-C=O-$, and in which one or more hydrogen atoms may be replaced by CN,

Examples of such azo compounds suitable as $FG^{4'}$ may be selected from the following formulae (VI-a') and (VI-b')

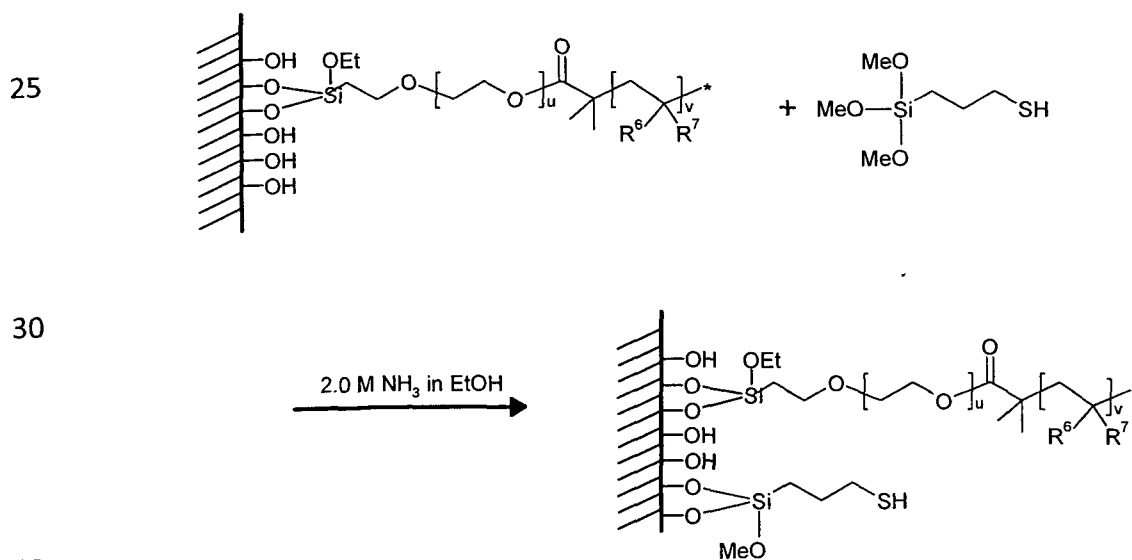


Particular examples of the second surface modifying agent may be selected from the group consisting of the following formula (IV'-1) to (IV'-3)



A general method for introducing the second surface modifying agent is disclosed for example in WO 2007/107222, which is hereby incorporated by reference.

20 An exemplary embodiment of the reaction between the hydroxyl groups on the surface of the intermediate coated silica particle with the second surface modifying agent is illustrated in Scheme 4, with u being an integer of from 0 to 20, and v being an integer of from 1 to 100.



Scheme 4

In the subsequent radical polymerization, wherein the second surface modifying agent acts as a radical transfer agent, one or more monomers are polymerized onto the silica particles obtained in the previous step.

5

The type of monomers used in this step is not particularly limited as long as they can be polymerized by radical polymerization. Preferred monomers are those comprising an olefinic group. Examples of such monomers are acrylates, methacrylate, vinyl alcohol, vinyl acetate, acrylamide and blends thereof. A particularly well suited example of such a monomer is styrene.

10

At least one of the monomers comprises a functional compound, for example a light emitting compound, as defined above. However, two or more monomers comprising a functional compound, for example a light emitting compound, may also be used. Alternatively, a monomer may also comprise two or more functional compounds, for example two or more light emitting compounds, which are different from each other. It is also possible to use a blend of two or more monomers, each monomer comprising different functional compounds, for example light emitting compounds. Preferably said functional compounds are covalently bound to the polymerizable unit of the monomer.

15

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If a mixture of monomers with and without functional compounds, for example light emitting compounds, is used the respective ratio of monomers with to monomers without functional compounds can be controlled depending upon the desired properties of the final electronic device, for example a light emitting diode in the case the functional compound(s) is/are light emitting compounds, to be produced. For example, the functional compound can be present in up to 50 wt%, relative to the weight of monomers without functional compound. However, the functional compound may also be present in as low as 0.5 wt%, relative to the weight of monomers without functional compound.

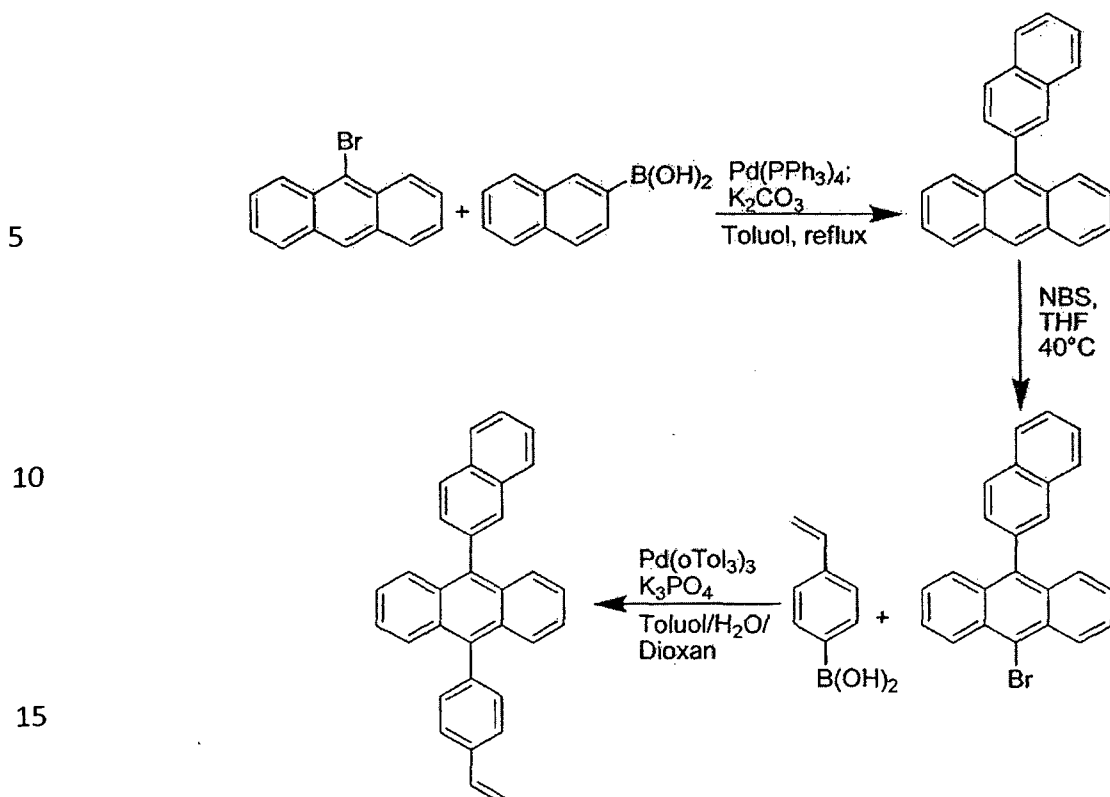
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Suitable monomers comprising a functional compound may be synthesized by known reactions. An example of such a synthesis with the functional compound being a light emitting compound is shown in Scheme 5, wherein "NBS" denotes N-bromosuccinimide and "THF" tetrahydrofuran.

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Scheme 5

20 The radical polymerization may be initiated by any of the initiators known to the skilled person. An example of a suitable initiator is azobisisobutyronitrile ($\text{NC-C(CH}_3)_2\text{-N}\equiv\text{N-(H}_3\text{C)}_2\text{C-CN}$). Other initiators, such as various organic peroxides, can be used as well.

25 The present application provides for organic electronic devices comprising the above defined coated silica particles. The present organic electronic devices include, without limitation, optical, electrooptical, electronic, electroluminescent and photoluminescent devices. Examples thereof include, without limitation, organic field effect transistors (OFETs), organic thin film transistors (OTFTs), organic light emitting diodes (OLEDs), organic light emitting transistors (OLETs), organic photovoltaic devices (OPVs), organic photodetectors (OPDs), organic solar cells, laser diodes, Schottky diodes, photoconductors, and photodiodes. Preferably, the present devices are selected from the group consisting of organic light emitting diodes, and organic light emitting transistors. Most preferably the present devices are organic light emitting diodes.

35

The present application also provides for a component or device comprising such compound, said component or device being selected from the group consisting of organic field effect transistors (OFET), thin film transistors (TFT), integrated circuits (IC), logic circuits, capacitors, radio frequency identification (RFID) tags, devices or components, organic light emitting diodes (OLED), organic light emitting transistors (OLET), flat panel displays, backlights of displays, organic photovoltaic devices (OPV), organic solar cells (OSC), photodiodes, laser diodes, photoconductors, organic photodetectors (OPD), electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, charge injection layers, charge transport layers or interlayers in polymer light emitting diodes (PLEDs), Schottky diodes, planarising layers, antistatic films, polymer electrolyte membranes (PEM), conducting substrates, conducting patterns, electrode materials in batteries, alignment layers, biosensors, biochips, security markings, security devices, and components or devices for detecting and discriminating DNA sequences.

It is preferred that the present organic electronic devices comprise an anode, a cathode and a light emitting layer, wherein said light emitting layer comprises the above defined coated silica particles. Preferably, said organic electronic device may further comprise at least one layer selected from the group consisting of electron transport layer, hole transport layer, hole injection layer, electron injection layer, exciton blocking layer, interlayers, and charge generation layer.

The present organic electronic devices may also have more than one light emitting layer, each layer in turn comprising the silica particles of the present invention. In such a case it is preferred that the different light emitting layers have different emission maxima between 380 nm and 750 nm, thereby allowing the emission of light of different colors, and resulting for example in the emission of white light.

Alternatively, the light emitting layer may comprise coated silica particles in accordance with the present invention, whereby such coated silica particles comprise more than one light emitting compound. It is also possible to use a blend of at least a first type of coated silica particles of the present invention and a second type of coated silica particles of the present invention, wherein the at least two types of silica particles differ in the nature of the light emitting compound.

Preferably, the sequence of layers is as follows:

- anode,
- optional hole injection layer,
- 5 - optional one or more hole transport layer,
- light emitting layer,
- optional electron transport layer,
- optional electron injection layer, and
- cathode.

10 It is noted that any layer indicated as "optional" may either be present or absent.

The anode is generally formed of an electrically conductive material. Exemplary electrically conductive materials include electrically conductive metals, electrically conductive alloys, electrically conductive polymers, and electrically conductive metal oxides. Exemplary electrically conductive metals include gold, silver, copper, aluminum, nickel, palladium, platinum, and titanium. Exemplary electrically conductive alloys include stainless steel (e.g., 332 stainless steel, 316 stainless steel), alloys of gold, alloys of silver, alloys of copper, alloys of aluminum, alloys of nickel, alloys of palladium, alloys of platinum, and alloys of titanium. Exemplary electrically conducting polymers include polythiophenes (e.g., doped poly(3,4-ethylenedioxythiophene)), polyanilines (e.g., doped polyanilines), polypyrroles (e.g., doped polypyrroles). Exemplary electrically conducting metal oxides include indium tin oxide, indium zinc oxide, fluorinated tin oxide, tin oxide and zinc oxide. It is preferred that the anode is formed of a material with high work function, for example with a work function of at least 4.5 eV versus vacuum. In some embodiments, blends or combinations of electrically conductive materials are used. In some embodiment, it may be advantageous to form the anode of transparent material, such as for example indium tin oxide or indium zinc oxide. Alternatively the anode may comprise more than one layer, for example it may comprise an inner layer of indium tin oxide and an outer layer of tungsten oxide, molybdenum oxide or vanadium oxide.

The cathode is generally formed of an electrically conductive material, preferably one with a low work function. Exemplary materials suitable are metals such as earth alkaline metal, main group metals or lanthanide. Particular examples of such metals are Ca, Ba, Mg, Al, In, Yb, Sm and Eu as well as alloys thereof. It is also

possible to use alloys of silver and an alkaline or alkaline earth metal, such as for example an alloy of silver and magnesium. The cathode may also be formed of more than one layer, in which case metals or alloys having a higher work function may be present. Examples of such metals or alloys having a higher work function are Ag, Al, Ca/Ag alloy, Mg/Ag alloy and Ba/Ag alloy.

In some embodiments the cathode may also comprise a layer of material having a high dielectric constant. Examples of suitable materials are metal fluorides, oxides or carbonates with the metal selected from the alkaline and alkaline earth metals. Specific examples of such materials are LiF, Li₂O, BaF₂, MgO, NaF, CsF, Cs₂CO₃ or CaF₂. Lithium chinolate may also be used.

Suitable materials for a charge transport layer are already described earlier in this application.

Preferred examples of hole transport materials, which may be used in a hole transport, hole injection or electron blocking layer, have already been described earlier in this application.

The OPV device can for example be of any type known from the literature (see e.g. Waldauf *et al.*, *Appl. Phys. Lett.*, **2006**, *89*, 233517).

A first preferred OPV device according to the invention comprises the following layers (in the sequence from bottom to top):

- optionally a substrate,
- a high work function electrode, preferably comprising a metal oxide, like for example ITO, serving as anode,
- an optional conducting polymer layer or hole transport layer, preferably comprising an organic polymer or polymer blend, for example of PEDOT:PSS (poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate), or TBD (N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine) or NBD (N,N'-diphenyl-N,N'-bis(1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine),
- a layer, also referred to as "active layer", comprising a p-type and an n-type organic semiconductor, which can exist for example as a p-type/n-type bilayer or as distinct p-type and n-type layers, or as blend or p-type and n-type semiconductor, forming a BHJ,

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- optionally a layer having electron transport properties, for example comprising LiF,
- a low work function electrode, preferably comprising a metal like for example aluminum, serving as cathode,

5 wherein at least one of the electrodes, preferably the anode, is transparent to visible light, and

wherein the p-type semiconductor is a polymer according to the present invention.

10 A second preferred OPV device according to the invention is an inverted OPV device and comprises the following layers (in the sequence from bottom to top):

- optionally a substrate,
- a high work function metal or metal oxide electrode, comprising for example ITO, serving as cathode,
- 15 - a layer having hole blocking properties, preferably comprising a metal oxide like TiO_x or Zn_x ,
- an active layer comprising a p-type and an n-type organic semiconductor, situated between the electrodes, which can exist for example as a p-type/n-type bilayer or as distinct p-type and n-type layers, or as blend or p-type and
- 20 n-type semiconductor, forming a BHJ,
- an optional conducting polymer layer or hole transport layer, preferably comprising an organic polymer or polymer blend, for example of PEDOT:PSS or TBD or NBD,
- an electrode comprising a high work function metal like for example silver,
- 25 serving as anode,

wherein at least one of the electrodes, preferably the cathode, is transparent to visible light, and

wherein the p-type semiconductor is a polymer according to the present invention.

30

The coated silica particles of the present invention may also be suitable for use in an OFET as the semiconducting channel. Accordingly, the invention also provides an OFET comprising a gate electrode, an insulating (or gate insulator) layer, a source electrode, a drain electrode and an organic semiconducting channel connecting the source and drain electrodes, wherein the organic semiconducting

35 channel comprises a compound, polymer, polymer blend, formulation or organic

semiconducting layer according to the present invention. Other features of the OFET are well known to those skilled in the art.

OFETs where an OSC material is arranged as a thin film between a gate dielectric and a drain and a source electrode, are generally known, and are described for example in US 5,892,244, US 5,998,804, US 6,723,394 and in the references cited in the background section. Due to the advantages, like low cost production using the solubility properties of the compounds according to the invention and thus the processibility of large surfaces, preferred applications of these FETs are such as integrated circuitry, TFT displays and security applications.

The gate, source and drain electrodes and the insulating and semiconducting layer in the OFET device may be arranged in any sequence, provided that the source and drain electrodes are separated from the gate electrode by the insulating layer, the gate electrode and the semiconductor layer both contact the insulating layer, and the source electrode and the drain electrode both contact the semiconducting layer.

An OFET device according to the present invention preferably comprises:

- a source electrode,
- a drain electrode,
- a gate electrode,
- a semiconducting layer,
- one or more gate insulator layers, and
- optionally a substrate,

wherein the semiconductor layer preferably comprises a compound, polymer, polymer blend or formulation as described above and below.

The OFET device can be a top gate device or a bottom gate device. Suitable structures and manufacturing methods of an OFET device are known to the skilled in the art and are described in the literature, for example in US 2007/0102696 A1.

The coated silica particles as defined above, or alternatively the dispersions as defined above, may be used in the production of organic electronic devices, particularly organic light emitting diodes (OLEDs). In particular, said coated silica

- 60 -

particles and said dispersions are useful in the production of the light emitting layer of an organic light emitting diode.

Hence, the present application also discloses a process for the production of organic electronic devices, preferably of organic light emitting diodes, said process comprising the steps of

- (i) providing either coated silica particles as defined above or a dispersion of the above defined coated silica particles; and
- (ii) solution-processing said dispersion to obtain the light emitting layer of an organic light emitting diode.

Solution processing may for example be done using a liquid-based coating process, chosen for example from a range of well-known printing techniques, such as for example screen-printing or ink-jet printing. Of these ink jet printing is preferred.

Ink jet printing is particularly preferred when high resolution layers and devices need to be prepared. Selected formulations of the present invention may be applied to prefabricated device substrates by ink jet printing or microdispensing. Preferably industrial piezoelectric print heads such as but not limited to those supplied by Aprion, Hitachi-Koki, InkJet Technology, On Target Technology, Picojet, Spectra, Trident, Xaar may be used to apply the organic semiconductor layer to a substrate. Additionally semi-industrial heads such as those manufactured by Brother, Epson, Konica, Seiko Instruments Toshiba TEC or single nozzle microdispensers such as those produced by Microdrop and Microfab may be used.

Test methods

TGA-spectra were obtained on a TGA Q 500 (TA Instruments) under airflow of 60 ml/min and a heater rate of 10 K/min from room temperature up to 700°C using the TA Instruments Universal Analysis.

TEM-pictures were obtained on a LEO-TEM Type 902 with an accelerating voltage of 80 kV and a Slow-Scan-digital camera (1024x1024 pixel).

NMR-spectra were obtained on a Bruker ARX 300 or DRX 500 using the Bruker Topspin software (version 2.1). Chemical shifts are indicated in ppm relative to tetramethylsilane (TMS) as internal standard with $\delta_{\text{TMS}} = 0$ ppm.

Examples

The advantages of the present invention are further illustrated by the following non-limitative examples.

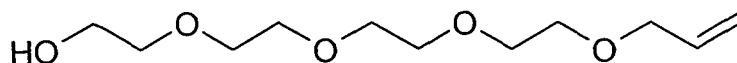
All chemicals used in the present examples were purchased from commercial suppliers such as for example Sigma-Aldrich, ACROS, Fluka or ABCR.

Tetrahydrofuran (THF), toluene and n-hexane were dried over sodium/benzophenone and distilled before use. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were purchased on molecular sieve and had a water content of < 50 ppm.

MEO2MA and HEMA were cleaned of stabilizing agent by filtration through basic aluminum oxide, stored at -20°C, and degassed before each polymerization.

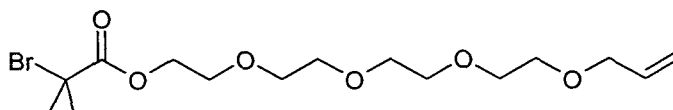
Example 1 - Preparation of an alcoholic dispersion of silica particles

125 g Levasil® 300/30 were mixed with 250 g absolute ethanol. Under stirring a strongly acidic cation exchange resin (Amberlite® IR 120) was added (ca. 6 g) until the pH was constant between 2 and 3. Keeping the volume constant a total of 2.5 l of absolute ethanol was added at the same rate as the ethanol-water-azeotrope was removed at a temperature of 50-55 °C and a pressure of 250-300 mbar. Subsequently the cation exchange resin is removed by filtration and a slightly yellow dispersion, which was stable over a longer period of time, with a solids content of 8 wt% was obtained. Removal of the solvent by distillation allowed an increase in the solids content up to 56 wt%.

Example 2 - Synthesis of 3,6,9,12-tetraoxopentadec-14-en-1-ol (Allyl-PEG4)

5 In a 1000 ml Schlenk flask 2.74 g (114.00 mmol) of NaH were suspended in 360 ml THF and cooled to 0°C. 22.04 g (114.00 mmol) of tetraethyleneglycol were dissolved in 20 ml of THF and slowly added to the suspension. The reaction mixture was stirred at 0°C until no further gas formation was observed. Subsequently, at room temperature 21.00 g (114.00 mmol, 15 ml) allyl bromide in 20 ml THF was added, and the reaction mixture was stirred for a further 5 hours. The resulting solids were removed by filtration and the solvent removed under vacuum. 26.80 g of a yellow raw product were obtained. The raw product was further purified by chromatography first with 1 l of ethyl acetate, then with 2.5 l of a 9:1 mixture of ethyl acetate and methanol. 12 g Allyl-PEG4 was obtained as a colorless oil.

10 ¹H-NMR (300 MHz; CDCl₃): 6.10 - 5.59 (m, 1H), 5.34 - 4.89 (m, 2H), 3.96 (d, J = 5.6, 2H), 3.76 - 3.36 (m, 18H), 2.96 (s, 1H).

Example 3 - Synthesis of 3,6,9,12-tetraoxopentadec-14-enyl-2-bromo-2-methylpropanoate (B-PEG4)

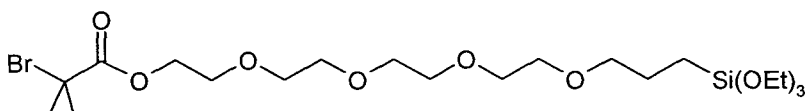
25 in a 100 ml Schlenk flask 5.49 g (32.3 mmol) α-bromobutyric acid, 4.09 g (32.3 mmol, 2.77 ml) oxalyl chloride and a drop of DMF were stirred at room temperature until no further gas evolution could be observed and were subsequently transferred to a 250 ml Schlenk flask containing 7.56 g (32.20 mmol) of Allyl-PEG4 dissolved in 40 ml dry THF. Stirring was continued at room temperature for 5 hours. Resulting solids were removed by filtration. Solvent was subsequently removed under vacuum. The resulting raw product was purified by chromatography with ethyl acetate. 10.4 g of B-PEG4 were obtained as a colorless oil.

30 ¹H-NMR (300 MHz; CDCl₃): 6.05 - 5.69 (m, 1H), 5.35 - 4.99 (m, 2H), 4.42 - 4.18 (m, 2H), 4.12 - 3.90 (m, 2H), 3.88 - 3.85 (m, 16H), 1.93 - 1.86 (m, 6H).

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¹³C-NMR (75 MHz; CDCl₃): 171.56, 134.76, 117.00, 72.18, 70.70, 70.61, 69.41, 68.72, 65.11, 55.68, 30.74.

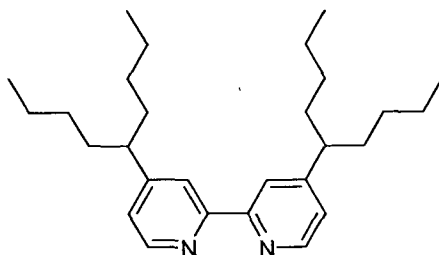
Example 4 - Synthesis of 4,4-diethoxy-3,8,11,14,17-pentaoxa-4-silanonadecan-19-yl-2-bromo-2-methylpropanoat (B-PEG4-a)



To ca. 10 mg (0.5 mol%) PtO₂ in an argon-filled 50 ml Schlenk flask 1.70 g (10.40 mmol, 1.90 ml) of triethoxysilane and 3.80 g (10.00 mmol) of B-PEG4 were added and stirred for 30 hours at 70°C. The reaction mixture was then cooled to 50°C and remaining triethoxysilane was removed under high vacuum. The Pt-catalyst was removed by filtration over 2 cm of Celite and washed out with THF. The solvent and still remaining triethoxysilane were then removed under high vacuum yielding an amber-colored product.

¹H-NMR (300 MHz; CDCl₃): 4.36 - 4.21 (m, 1H), 4.19 - 4.07 (m, 1H), 3.92 - 3.46 (m, 19H), 3.43 - 3.24 (m, 2H), 1.87 (s, 4H), 1.72 - 1.45 (m, 2H), 1.28 - 1.04 (m, 9H), 0.62 - 0.48 (m, 1H).

Example 5 - Synthesis of 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy)



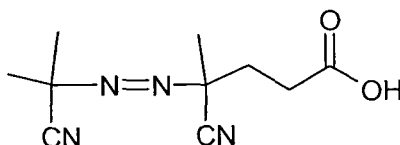
In a 250 ml argon-filled Schlenk flask 40 ml dry THF and 5.76 g (56.0 mmol, 8.00 ml) diisopropylamine (dried over KOH and freshly distilled) were cooled to -78°C. Then 25 ml of n-butyllithium (2.5 M in hexane; ca. 63 mmol) were slowly added. The yellow dispersion was stirred for another 15 min at -78°C. Then 2.45 g (13.30 mmol) of 4,4'-dimethyl-2,2'-dipyridine dissolved in 65 ml dry THF was slowly added. Stirring was continued for 15-20 min at -78°C before 10.98 g (80.00 mmol, 8.58 ml) of 1-bromobutane were added. The yellow reaction mixture was allowed

to warm to room temperature overnight and then poured into 170 ml of cold NaCl-solution. The aqueous phase was extracted three times with 20 ml of ethyl acetate. The combined organic phases were dried over magnesium sulfate. The solvent was removed under vacuum. The slightly yellow oily residue was stored at
5 -20°C for two weeks to allow it to crystallize. It was then re-crystallized from methanol. 3.67 g of dNbpy were obtained.

¹H NMR (300 MHz, CDCl₃): δ = 8.56 (d, *J*=5.1, 2H), 8.23 (s, 2H), 9.13 (s, 2H), 2.70 – 2.47 (m, 2H), 1.76 – 1.49 (m, 8H), 1.32 – 0.93 (m, 16H), 0.88 – 0.61 (m, 12H).

¹³C NMR (75 MHz, CDCl₃): δ= 158.3, 155.7, 149.6, 122.7, 122.6, 46.4, 36.0, 29.2, 23.3,
10 14.1.

Example 6 - Synthesis of 2',4-azo(2'-cyanopropyl)-(4-cyanovaleric acid) (AIBN-a-OH)



56 g (0.86 mol) potassium cyanide and 56 g (0.43 mol) hydrazine sulfate were suspended in 600 ml water in a 500 ml three-necked flask and warmed to 50°C. 50
20 g (0.43 mol) levulinic acid, dissolved in 100 ml water and neutralised with NaHCO₃, and 25 g acetone were added by means of a dropping funnel. The reaction mixture was stirred at 50°C for 3 h and then cooled with an ice bath to 0°C. Using concentrated hydrochloric acid the pH was slowly brought to 4, during which the precipitation of a white solid was observed. In the following an excess of bromine
25 (ca. 45 ml) was slowly added, followed by stirring overnight. The remaining bromine was reacted with sodium hydrosulfite and the obtained precipitate collected by filtration. The collected solid was stirred in 250 ml of 1 N aqueous NaOH at room temperature for 30 min. Insoluble components (AIBN 13.8 g) were separated off. The pH of the solution was adjusted to 2 with about 25 ml concentrated hydrochloric acid, whereby the product separated out as a yellow oil. A second fraction of the product was obtained by extracting the original reaction mixture 4 times with 100 ml dichloromethane each. The solvent was removed in vacuo. The combined product fractions were re-crystallized from a mixture of water and methanol (5:1 volumic ratio; ca. 20 ml per g of product).
30 14.9 g (0.11 mol; 16.3%) of AIBN-a-OH were obtained as white solid.
35

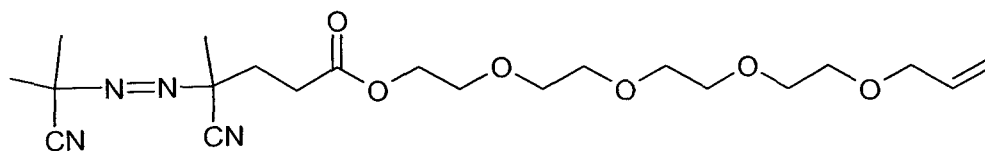
¹H NMR (300 MHz, CDCl₃): δ = 2.65 – 2.49 (m, 2H), 2.48 – 2.37 (m, 2H), 1.78 (s, 3H), 1.74 (s, 3H), 1.72 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ = 179.07, 118.93, 119.66, 71.57, 68.72, 33.03, 28.99, 25.38, 25.03, 23.89.

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Example 7 - Synthesis of 3,6,9,12-tetraoxapentadec-14-enyl-4-cyano-4-((2-cyanopropan-2-yl)diazenyl)propanoate) (AIBN-a-Allyl)

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In a 50 ml Schlenk vessel 3.55 g (16.1 mmol) AIBN-a-OH (see Example 6) and 2.05 g (16.1 mmol) oxalyl chloride were dissolved in 10 ml dry THF and a drop of DMF was added. The reaction mixture was stirred until gas evolution stopped and then added to a 100 ml Schlenk vessel containing a solution of 3.78 g (16.1 mmol) Ally-PEG4 (see Example 2) and 3.0 g (44.0 mmol) imidazole in 20 ml dry THF. The resulting reaction mixture was stirred for 5 h at room temperature. After separating from the solids the solvent was removed in vacuo and the crude product chromatographically purified with ethyl acetate. 6.35 g (14.5 mmol, 90%) of AIBN-a-Allyl was obtained as colorless solid of low melting point.

20

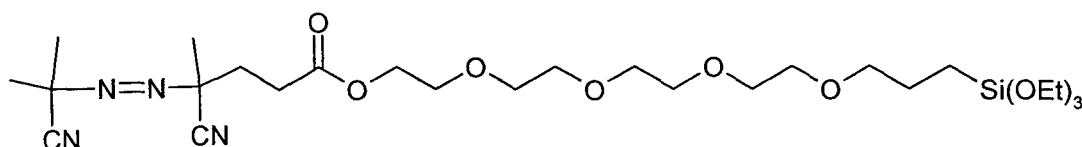
¹H NMR (300 MHz, CDCl₃): δ = 5.93 – 5.74 (m, 1H), 5.32 (dd, J = 19.3, 1.5 Hz, 1H), 5.15 (dd, J = 10.4, 1.5 Hz, 1H), 4.43 – 4.31 (m, 2H), 4.00 (dt, J = 5.7, 1.5 Hz, 2H), 3.78 – 3.69 (m, 2H), 3.68 – 3.56 (m, 10H), 3.56 – 3.50 (m, 2H), 2.53 – 2.41 (m, 1H), 2.39 – 2.27 (m, 1H), 1.69 (s, 3H), 1.66 (s, 3H), 1.64 (s, 2H).

25

¹³C NMR (75 MHz, CDCl₃): δ = 171.82, 135.03, 119.51, 119.93, 119.30, 72.36, 71.58, 70.87, 70.44, 69.51, 69.06, 68.65, 68.44, 66.04, 64.23, 33.30, 29.24, 25.29, 25.18, 23.93.

Example 8 - Synthesis of AIBN-a-Si(OEt)₃

30

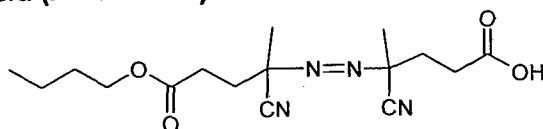


35

The hydrosilylation was performed using an iron-based catalyst, denoted $[(\text{MePDI})\text{Fe}(\text{N}_2)]_2(\mu^2\text{-N}_2)$, described by A.M. Tondreau et al., Science **335**, 567 (2012).

5.0 mmol of AIBN-a-Allyl in 10 ml dry THF and 0.04 mol% (relative to AIBN-a-Allyl) of $[(\text{MePDI})\text{Fe}(\text{N}_2)]_2(\mu^2\text{-N}_2)$ were introduced into a well-dried Schlenk tube. Then 11 mmol of $\text{HSi}(\text{OEt})_3$ was added and the reaction mixture was stirred for 3 h at 30°C. AIBN-a-Si(OEt)₃ could be isolated in 45 % yield.

Example 9 - Synthesis of (5-butoxy-2-cyano-5-oxopentan-2-yl)diazenyl)-4-cyanovaleric acid (AIBN-b-OH)

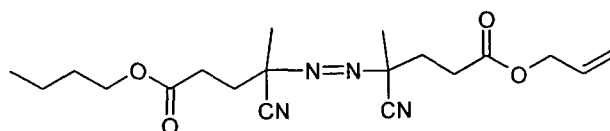


To a solution of 5.60 g (20.0 mmol) 4,4'-azobis(4-cyanovaleric acid), 75 mg 4-dimethylamino)pyridine (DMAP) and 1.48 g (20.0 mmol; 1.83 ml) n-butanol in 40 ml dry THF, which was cooled to 0°C in an ice bath, 4.12 g (20.0 mmol) 1,3-dicyclohexylcarbodiimide (DCC) in 15 ml dry THF were added dropwise. The reaction mixture was stirred for 5 h at room temperature and the resulting urea separated off by filtration. Most of the solvent was removed in vacuo at below 40°C. The residue was added to water and extracted 4 times with dichloromethane 50 ml each. The organic phase was then washed twice with brine 50 ml each and dried over magnesium sulfate. The solvent was removed in vacuo at below 40°C and the product dried in vacuo. 6.8 g (94 %) of AIBN-b-OH was obtained as a colorless solid of low melting temperature.

¹H NMR (300 MHz, CDCl₃): δ = 4.11 (t, 2H, 6.6 Hz), 2.47 (m, 8H), 1.74 (s, 3H), 1.68 (s, 3H), 1.62 (m, 2H), 1.37 (m, 2H), 0.94 (t, 3H, 9.3Hz).

¹³C NMR (75 MHz, CDCl₃): δ = 178.4, 173.1, 114.5, 64.9, 56.5, 31.1, 30.5, 30.2, 29.4, 25.2, 23.9, 18.9, 13.8.

Example 10 - Synthesis of (allyl-4-(5-Butoxy-2-cyano-5-oxopentan-2-yl)diazenyl)-4-cyanopentanoate (AIBN-b-Allyl)

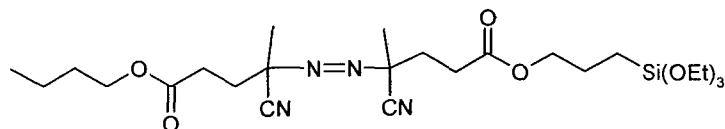


6.8 g (18.7 mmol) AIBN-b-OH (see Example 9), 75 mg 4-dimethylamino)pyridine (DMAP) and 1.16 g (20.0 mmol, 1.36 ml) allyl alcohol in 40 ml dry THF was cooled to 0°C in an ice bath. Then 4.12 g (20.0 mmol) 1,3-dicyclohexylcarbodiimide (DCC) in 15 ml dry THF was added dropwise. The reaction mixture was stirred for 5 h at room temperature and the resulting urea separated off by filtration. Most of the solvent was removed in vacuo at below 40°C. The residue was taken up in water and extracted 4 times with dichloromethane 50 ml each. The organic phase was then washed twice with brine 50 ml each and dried over magnesium sulfate. The solvent was removed in vacuo at below 40°C and the product dried in vacuo. 7.09 g (100 %) of AIBN-b-Allyl was obtained as a colorless solid of low melting temperature

¹H NMR (300 MHz, CDCl₃): δ = 5.88 (m, 1H), 5.25 (dd, 2H, 9.3Hz), 4.6 (d, 2H, 6.1Hz), 4.11 (t, 2H, 6.6Hz), 2.47 (m, 8H), 1.74 (s, 3H), 1.68 (s, 3H), 1.62 (m, 2H), 1.37 (m, 2H), 0.94 (t, 3H, 9.3Hz).

¹³C NMR (75 MHz, CDCl₃): δ = 173.1, 132.1, 118.2, 114.5, 65.9, 64.9, 56.5, 31.1, 30.5, 25.3, 25.2, 23.9, 18.9, 13.8.

Example 11 - Synthesis of AIBN-b-Si(OEt)₃



The hydrosilylation was performed using an iron-based catalyst, denoted [(MePDI)Fe(N₂)]₂(μ²-N₂), described by A.M. Tondreau et al., Science **335**, 567 (2012).

5.0 mmol of AIBN-b-Allyl in 10 ml dry THF and 0.04 mol% (relative to AIBN-b-Allyl) of [(MePDI)Fe(N₂)]₂(μ²-N₂) were introduced into a well-dried Schlenk tube. Then 11 mmol of HSi(OEt)₃ was added and the reaction mixture was stirred for 3 h at 30°C. AIBN-a-Si(OEt)₃ could be isolated in 75 % yield.

Example 12 - First functionalization step (General procedure)

The alcoholic dispersion of silica particles is degassed in a Schlenk flask closed with a septum by introducing argon while continuously stirring the dispersion. Subsequently the first surface modifying agent is added in an amount so as to

arrive at the desired percentage of coverage, and the reaction mixture is stirred overnight at room temperature yielding the intermediate coated silica particles.

Example 13 - First functionalization step (with 10 wt% ethanolic dispersion)

81 g of ethanolic silica particle dispersion having a 10 wt% solids content was degassed with argon for 30 min in a 250 ml Schlenk flask closed with a septum. 1.10 g of B-PEG4-a were added, and the reaction mixture was stirred overnight at room temperature. The resulting intermediate coated silica particles had a percentage of coverage of 15.5 %, corresponding to about 0.5 surface modifying agent per nm².

Example 14 - First functionalization step (with 5 wt% ethanolic dispersion)

15 g of ethanolic silica particle dispersion having a 5 wt% solids content was degassed with argon for 30 min in a 100 ml Schlenk flask closed with a septum. 0.102 g of B-PEG4-a were added and the reaction mixture was stirred overnight at room temperature. The resulting intermediate coated silica particles had a percentage of coverage of 15.5 %, corresponding to about 0.5 surface modifying agent per nm².

Example 15 - Atom transfer radical polymerization (ATRP) with 2-hydroxyethylmethacrylate (HEMA) (General procedure)

A defined amount m_{Disp} of the alcoholic dispersion of a solids content of 25, 10, 5 or 1 % of the intermediate coated silica particles having a percentage of coverage d is degassed with argon for 30 min in a Schlenk flask closed with a septum by introducing argon while continuously stirring the dispersion. Then the required amount m_{Cat} of catalyst dissolved in ethanol is added at room temperature under stirring. Then 2-hydroxyethylmethacrylate (HEMA) is added in a specific monomer/initiator ratio and the reaction is discontinued after time t by introducing oxygen. The resulting particles are precipitated in the 10 fold amount of n-hexane, centrifuged and re-dispersed in water. The process is repeated until all copper has been removed. A milky dispersion with a solids content of 1 % is obtained.

Example 16 - ATRP of HEMA/SiO₂ with monomer/initiator ratio of 50/1 and solids content of 1 %

5 50 ml of a dispersion having a solids content of 1 % of intermediate coated silica particles with 15.5 % coverage were degassed with argon for 30 min in a Schlenk flask closed with a septum.

13,6 mg (0,100 mmol) of CuBr and 77,5 mg (0,200 mmol) 4,4'-Di-(5nonyl)-2,2'-bipyridin (dNbpy) in 0.95 ml ethanol were added at room temperature under stirring. The reaction was started by the introduction of 0,62 g (4,75 mmol, 0,575 ml) 2-hydroxyethylmethacrylat (HEMA), corresponding to a monomer/initiator ratio of 50/1. The reaction was stopped after 24 hours by the introduction of oxygen. The resulting particles were precipitated with 500 ml n-hexane, centrifuged and re-dispersed in water. The process was repeated until all copper had been removed. A milky dispersion with a solids content of 1 % was obtained.

Example 17 - ATRP of HEMA/SiO₂ with monomer/initiator ratio of 100/1 and solids content of 10 %

10 ml of a dispersion having a solids content of 10 % of intermediate coated silica particles with 15.5 % coverage were degassed with argon for 30 min in a Schlenk flask closed with a septum.

13,6 mg (0,100 mmol) of CuBr and 77,5 mg (0,200 mmol) of 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy) in 0,95 ml ethanol were added at room temperature under stirring. The reaction was started by the introduction of 1.24 g (9.50 mmol, 1.15 ml) of 2-hydroxyethylmethacrylate (HEMA), corresponding to a monomer/initiator ratio of 100/1. The reaction mixture became gelled and cloudy after ca. 45 minutes.

Example 18 - ATRP of HEMA/SiO₂ with monomer/initiator ratio of 100/1 and solids content of 5 %

10 ml of a dispersion having a solids content of 5 % of intermediate coated silica particles with 15.5 % coverage were degassed with argon for 30 min in a Schlenk flask closed with a septum.

13.6 mg (0.100 mmol) of CuBr and 77.5 mg (0.200 mmol) of 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy) in 0.95 ml ethanol were added at room temperature under

stirring. The reaction was started by the introduction of 1.30 g (10.0 mmol, 1.21 ml) of 2-hydroxyethylmethacrylate (HEMA), corresponding to a monomer/initiator ratio of 100/1. After 45 min the reaction mixture had become slightly viscous and after 75 min became gelled and cloudy.

5

Example 19 - ATRP of HEMA/SiO₂ with monomer/initiator ratio of 100/1 and solids content of 1 %

10

50 ml of a dispersion having a solids content of 1 % of intermediate coated silica particles with 15.5 % coverage were degassed with argon for 30 min in a Schlenk flask closed with a septum.

15

13.6 mg (0.100 mmol) of CuBr and 77.5 mg (0.200 mmol) of 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy) in 0.95 ml ethanol were added at room temperature under stirring. The reaction was started by the introduction of 1.24 g (9.50 mmol, 1.15 ml) of 2-hydroxyethylmethacrylate (HEMA), corresponding to a monomer/initiator ratio of 100/1. After 24 h the reaction mixture had become slightly viscous and the reaction was stopped by the introduction of oxygen. The resulting particles were precipitated with 500 ml n-hexane, centrifuged and re-dispersed in water. The process was repeated until all copper was removed. A milky dispersion with a solids content of 1 % was obtained.

20

Example 20 - ATRP of HEMA/SiO₂ with monomer/initiator ratio of 200/1 and solids content of 1 %

25

50 ml of a dispersion having a solids content of 1 % of intermediate coated silica particles with 15.5 % coverage were degassed with argon for 30 min in a Schlenk flask closed with a septum.

30

13.6 mg (0.100 mmol) of CuBr and 77.5 mg (0.200 mmol) of 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy) in 0.95 ml ethanol were added at room temperature under stirring. The reaction was started by the introduction of 4.48 g (19.0 mmol, 2.30 ml) of 2-hydroxyethylmethacrylate (HEMA), corresponding to a monomer/initiator ratio of 200/1. After 15 h the reaction mixture had become slightly viscous and the reaction was stopped by the introduction of oxygen. The resulting particles were precipitated with 500 ml n-hexane, centrifuged and re-dispersed in water.

35

The process was repeated until all copper was removed. A milky dispersion with a solids content of 1 % was obtained.

Example 21 - Atom transfer radical polymerization (ATRP) with di(ethyleneglycol)methylethermethacrylate (MEO₂MA) (General procedure)

5 A defined amount m_{Disp} of the alcoholic dispersion of a solids content of 5 % of the intermediate coated silica particles having a percentage of coverage d is degassed with argon for 30 min in a Schlenk flask closed with a septum by introducing argon while continuously stirring the dispersion. Then the required amount m_{Cat} of catalyst dissolved in ethanol is added at room temperature under stirring.
10 Subsequently di(ethyleneglycol)methylethermethacrylate (MEO₂MA) is added in a specific monomer/initiator ratio and the reaction is discontinued after time t by introducing oxygen. The resulting particles are precipitated in the 10 fold amount of *n*-hexane, centrifuged and re-dispersed in water. The process is repeated until
15 all copper has been removed. A clear dispersion, which is stable at room temperature and has a solids content of 1 wt%, is obtained. The solids content can in the following be increased to 5 % by removal of part of the solvent by distillation; one obtains a dispersion, which is milky at room temperature and clear at 40°C.

20 **Example 22 - ATRP of MEO₂MA/SiO₂ with monomer/initiator ratio of 50/1 and solids content of 5 %**

10 ml of a dispersion having a solids content of 5 % of intermediate coated silica particles with 15.5 % coverage were degassed with argon for 30 min in a Schlenk
25 flask closed with a septum.
13.6 mg (0.100 mmol) of CuBr and 77.5 mg (0.200 mmol) of 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy) in 0.95 ml ethanol were added at room temperature under stirring. The reaction was started by the introduction of 0.94 g (5.0 mmol, 0.92 ml) of di(ethyleneglycol)methylethermethacrylate (MEO₂MA), corresponding to a
30 monomer/initiator ratio of 50/1. After 28 h at room temperature the reaction was stopped by the introduction of oxygen. The resulting particles were precipitated with 100 ml *n*-hexane and dried, thus obtaining 1,57 g of MEO₂MA-grafted particles as colorless gel. The particles were re-dispersed in 160 ml ethanol, leading to a clear solution with a solids content of 1 %.

35

Example 23 - ATRP of MEO2MA/SiO₂ with monomer/initiator ratio of 100/1 and solids content of 5 %

10 ml of a dispersion having a solids content of 5 % of intermediate coated silica particles with 15.5 % coverage were degassed with argon for 30 min in a Schlenk flask closed with a septum.

13.6 mg (0.100 mmol) of CuBr and 77.5 mg (0.200 mmol) of 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy) in 0.95 ml ethanol were added at room temperature under stirring. The reaction was started by the introduction of 1.88 g (10.0 mmol, 1.84 ml) of di(ethyleneglycol)methylethermethacrylate (MEO2MA), corresponding to a monomer/initiator ratio of 100/1. After 28 h at room temperature the reaction was stopped by the introduction of oxygen. The resulting particles were precipitated with 100 ml n-hexane and dried, thus obtaining 2.04 g of MEO2MA-grafted particles as colorless gel. The particles were re-dispersed in 230 ml ethanol, leading to a clear solution with a solids content of 1 %.

Example 24 - ATRP of MEO2MA/SiO₂ with monomer/initiator ratio of 200/1 and solids content of 5 %

10 ml of a dispersion having a solids content of 5 % of intermediate coated silica particles with 15.5 % coverage were degassed with argon for 30 min in a Schlenk flask closed with a septum.

13.6 mg (0.100 mmol) of CuBr and 77.5 mg (0.200 mmol) of 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy) in 0.95 ml ethanol were added at room temperature under stirring. The reaction was started by the introduction of 3.76 g (20.0 mmol, 3.68 ml) of di(ethyleneglycol)methylethermethacrylate (MEO2MA), corresponding to a monomer/initiator ratio of 200/1. After 28 h at room temperature the reaction was stopped by the introduction of oxygen. The resulting particles were precipitated with 100 ml n-hexane and dried, thus obtaining 3.34 g of MEO2MA-grafted particles as colorless gel. The particles were re-dispersed in 420 ml ethanol, leading to a clear solution with a solids content of 1 %. Removal of a part of the solvent by distillation led to a dispersion with a solids content of 5 %, which was milky at room temperature and clear at 40°C.

Example 25 - First and second functionalization simultaneously

246 ml of a dispersion having a content of 5 % of silica particles were degassed under continuous stirring with argon for 2 h in a 500 ml Schlenk flask closed with a septum. Then 1.74 g B-PEG4-a (see Example 4) and 1.61 g AIBN-b-Si(OEt)₃ (see Example 11) were added and the reaction mixture stirred overnight at room temperature, resulting in coverage of about 15.5 % (ca. 0.5 groups nm⁻²) each, i.e. a total coverage of about 31 %, as indicated by a weight loss of 17.23 % in TGA-analysis.

Example 26 - Organic light emitting diode

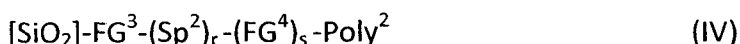
An organic light emitting diode with an anode, a cathode and a light emitting layer between the two may be produced using standard methods. The light emitting layer may be deposited by ink-jet printing the dispersions of coated silica particles as obtained in Examples 15 to 24. The present dispersions are expected to show good processing behavior. Furthermore, the so-produced organic light emitting diodes are expected to have properties comparable to organic light emitting diodes having a light emitting layer deposited by other methods.

Claims

1. Coated silica particles comprising a first surface modifying group or a second surface modifying group or both, wherein the first surface modifying group is of general formula (I)

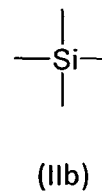
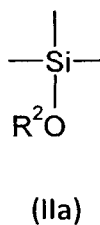
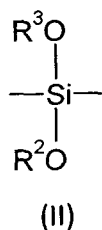


and the second surface modifying group is of general formula (IV)



wherein $[\text{SiO}_2]$ denotes the silica particle, which either essentially consists of silica or which is a core/shell particle the shell of which essentially consists of silica, FG^1 is a first functional group, FG^2 is a second functional group, FG^1 and FG^2 being different from one another, FG^3 is a third functional group, FG^4 is a fourth functional group, FG^3 and FG^4 being different from one another, Sp^1 and Sp^2 are spacers, m is 0 or 1, n is 0 or 1, r is 0 or 1, s is 0 or 1, and Poly^1 and Poly^2 are polymers.

2. Coated silica particles according to claim 1, wherein FG^1 is selected from the group consisting of formulae (II), (IIa) and (IIb)



wherein R^2 and R^3 are independently of each other alkyl having from 1 to 10 carbon atoms.

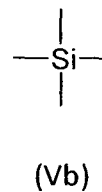
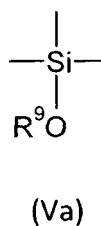
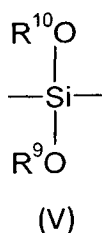
3. Coated silica particles according to any one or more of the preceding claims, wherein Sp^1 is of general formula $(\text{-CH}_2\text{-CH}_2\text{-X}^1\text{-})_p$, wherein X^1 is O or NR^5 , and p may be an integer of from 0 to 20, with R^5 being selected from the

group consisting of hydrogen and alkyl groups having from 1 to 10 carbon atoms.

4. Coated silica particles according to any one or more of the preceding claims, wherein FG^2 is $-C(=O)-C(CH_3)_2-$ or $-C(=O)-CR^1(CH_3)-CH_2-$.

5. Coated silica particles according to any one or more of the preceding claims, wherein $Poly^1$ is obtained by polymerization of a polar olefinic compound.

6. Coated silica particles according to any one or more of the preceding claims, wherein FG^3 is selected from the group consisting of the following formulae (V), (Va) and (Vb)



wherein R^9 and R^{10} are independently of each other alkyl having from 1 to 10 carbon atoms.

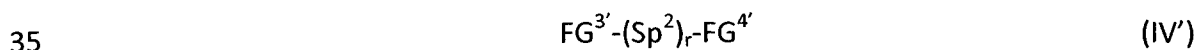
7. Coated silica particles according to any one or more of the preceding claims, wherein Sp^2 is of general formula $(-CH_2-CH_2-X^2-)_{t'}$ or of general formula $(-CH_2-)_{t'}$ or of a combination of these, wherein X^2 is selected from the group consisting of O, $CR^{12}R^{13}$ and NR^{14} , with R^{12} , R^{13} and R^{14} independently of each other defined as R^5 in claim 3, and t is an integer of from 0 to 20, and t' may be an integer of from 0 to 60.

8. Coated silica particles according to any one or more of the preceding claims, wherein FG^4 is selected from the group consisting of thiol, sulfide, disulfide, polysulfide and R^{16} , with R^{16} may for example be selected from the group consisting of straight-chain, branched or cyclic alkanediyl groups having from 1 to 20 carbon atoms, in which one or more nonadjacent CH_2 groups may be replaced by $-O-$, $-S-$, $-CO-O-$, $-C=O-$, $-CH=CH-$ or $-C\equiv C-$, and in which one or more hydrogen atoms may be replaced by F or CN, or an arylene or

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heteroarylene group which has from 4 to 14 carbon atoms and may be substituted by one or more groups R^5 , with R^5 being selected from the group consisting of hydrogen and alkyl groups having from 1 to 10 carbon atoms

- 5 9. Coated silica particles according to any one or more of the preceding claims, wherein Poly² is obtained by polymerization or copolymerization of a monomer comprising a functional compound, preferably a light emitting compound.
- 10 10. A dispersion comprising the coated silica particles of any one or more of claims 1 to 9.
11. Dispersion according to claim 10, wherein the dispersion comprises an alcohol.
- 15 12. A method for producing coated silica particles, said method comprising the step of
- (A) providing an alcoholic dispersion of silica particles, said silica particles either essentially consisting of silica or being core/shell particles the shell of which essentially consists of silica;
- 20 and at least one of the following steps (B) and (C) being
- (B) a first functionalization step comprising the steps of
- (B-1) treating the surface of the silica particles with a first surface modifying agent of general formula (I')
- 25
$$FG^{1'}-(Sp^1)_m-FG^{2'} \quad (I')$$
- and
- (B-2) subsequently polymerizing a polar olefinic compound;
- 30 and
- (C) a second functionalization step comprising the steps of
- (C-1) treating the surface of said intermediate coated particles with a second surface modifying agent of general formula (IV')



and

(C-2) subsequently radically polymerizing thereon at least a first and a second monomer, wherein said first monomer comprises a light emitter, and wherein the second surface modifying agent acts as a radical transfer agent,

to obtain coated silica particles, wherein the steps can be performed in either order, wherein $[\text{SiO}_2]$ denotes the silica particle, $\text{FG}^{1'}$ is a first functional group, $\text{FG}^{2'}$ is a second functional group, $\text{FG}^{1'}$ and $\text{FG}^{2'}$ being different from one another, $\text{FG}^{3'}$ is a third functional group, $\text{FG}^{4'}$ is a fourth functional group, $\text{FG}^{3'}$ and $\text{FG}^{4'}$ being different from one another, Sp^1 and Sp^2 are spacers, m is 0 or 1, and r is 0 or 1, and wherein $\text{FG}^{1'}$ and $\text{FG}^{3'}$ are capable of reacting with hydroxyl groups on the surface of said silica particles.

13. A method for producing coated silica particles, said method comprising the step of

(A) providing an alcoholic dispersion of silica particles, said silica particles either essentially consisting of silica or being core/shell particles the shell of which essentially consists of silica;

(B) a first functionalization step comprising the steps of

(B-1) treating the surface of the dispersed silica particles with a first surface modifying agent of general formula (I')



and

(B-2) subsequently polymerizing a polar olefinic compound to produce intermediate coated silica particles;

and

(C) a second functionalization step comprising the steps of

(C-1) treating the surface of said intermediate coated particles with a second surface modifying agent of general formula (IV')



and

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(C-2) subsequently radically polymerizing thereon at least a first and a second monomer, wherein said first monomer comprises a light emitter, and wherein the second surface modifying agent acts as a radical transfer agent,

to obtain coated silica particles, wherein $[\text{SiO}_2]$, $\text{FG}^{1'}$, $\text{FG}^{2'}$, $\text{FG}^{3'}$, $\text{FG}^{4'}$, Sp^1 , Sp^2 , m and r are as defined in claim 12.

14. The method according to claim 12 or claim 13, wherein the first and third functional groups $\text{FG}^{1'}$ and $\text{FG}^{3'}$ are selected independently of each other from the group consisting of alkoxysilanyl groups, halogen silanes, phosphoric acid, phosphoric acid esters, phosphonic acid, phosphonic acid esters and blends of any of these.

15. The method according to any one of claims 12 to 14, wherein Sp^1 is as defined in claim 3.

16. The method according to any one or more of claims 12 to 15, wherein the second functional group $\text{FG}^{2'}$ is selected from the group consisting of C=C double bond, Cl, Br and I.

17. The method according to any one or more of claims 12 to 16, wherein Sp^2 is as defined in claim 7.

18. The method according to any one or more of claims 12 to 17, wherein the fourth functional group $\text{FG}^{4'}$ is selected from the group consisting of thiol, sulfide, disulfide, polysulfide and azo compounds.

19. The method according to any one or more of claims 12 to 18, wherein the first and second monomer comprise an olefinic group.

20. The method according to any one or more of claims 12 to 19, wherein the second monomer is selected from the group consisting of acrylates, methacrylate, vinyl alcohol, vinyl acetate, acrylamide and a blend of any of these.

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21. An organoelectronic device comprising the coated silica particles of any one or more of claims 1 to 11.

5 22. The organoelectronic device according to claim 21, wherein the organoelectronic device is selected from the group consisting of organic field effect transistors (OFET), thin film transistors (TFT), integrated circuits (IC), logic circuits, capacitors, radio frequency identification (RFID) tags, devices or components, organic light emitting diodes (OLED), organic light emitting transistors (OLET), flat panel displays, backlights of displays, organic photovoltaic devices (OPV), organic solar cells (O-SC), photodiodes, laser diodes, photoconductors, organic photodetectors (OPD), electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, charge injection layers, charge transport layers or interlayers in polymer light emitting diodes (PLEDs), Schottky diodes, planarising layers, antistatic films, polymer electrolyte membranes (PEM), conducting substrates, conducting patterns, electrode materials in batteries, alignment layers, biosensors, biochips, security markings, security devices, and components or devices for detecting and discriminating DNA sequences.

20 23. A method for producing the organoelectronic device of claim 21 or claim 22, said method comprising the steps of

(i) providing either coated silica particles as defined above or a dispersion of the above defined coated silica particles; and

25 (ii) solution-processing said dispersion to obtain a light emitting layer.

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/002641

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09C3/12 C09K11/02 C09C1/30
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09C C09K

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 967 924 A1 (SEB SA [FR]; ECOLE NALE SUP ARTES METIERS [FR]; SPECIFIC POLYMERS [FR]) 1 June 2012 (2012-06-01)	1-20
A	claims 1-10 examples 1a, 1b	21-23
X	WO 2004/024811 A2 (FRAUNHOFER GES FORSCHUNG [DE]; HARTWIG ANDREAS [DE]; SEBALD MONIKA [DE]) 25 March 2004 (2004-03-25)	1-20
A	claims 1-20	21-23
X	EP 2 298 822 A1 (SHOWA DENKO KK [JP]) 23 March 2011 (2011-03-23)	1-23
	claims 1-3,5 paragraphs [0010] - [0012], [0014] - [0021], [0114] - [0123]	



Further documents are listed in the continuation of Box C.



See patent family annex.

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

"&" document member of the same patent family

Date of the actual completion of the international search

12 January 2015

Date of mailing of the international search report

19/01/2015

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/002641

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2967924	A1	01-06-2012	CN 103370379 A 23-10-2013
			CO 6781479 A2 31-10-2013
			EP 2646513 A1 09-10-2013
			FR 2967924 A1 01-06-2012
			JP 2014503622 A 13-02-2014
			KR 20140000701 A 03-01-2014
			US 2014034651 A1 06-02-2014
			WO 2012072953 A1 07-06-2012
WO 2004024811	A2	25-03-2004	AU 2003266194 A1 30-04-2004
			DE 10241510 A1 18-03-2004
			DE 10393704 D2 21-07-2005
			EP 1525227 A2 27-04-2005
			JP 2005538228 A 15-12-2005
			US 2006084723 A1 20-04-2006
			WO 2004024811 A2 25-03-2004
EP 2298822	A1	23-03-2011	CN 102076723 A 25-05-2011
			EP 2298822 A1 23-03-2011
			JP 5466640 B2 09-04-2014
			KR 20110038107 A 13-04-2011
			TW 201014870 A 16-04-2010
			US 2011098411 A1 28-04-2011
			WO 2010001875 A1 07-01-2010