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(56) References cited:
CN-A- 102 627 776

- **ABHIJIT PATRA ET AL: "Fluorescent nanoparticles based on a microporous organic polymer network: fabrication and efficient energy transfer to surface-bound dyes", CHEMICAL COMMUNICATIONS, vol. 47, no. 34, 1 January 2011 (2011-01-01), pages 9612 - 9614, XP055497392, ISSN: 1359-7345, DOI: 10.1039/c1cc13420e**
- **ABHIJIT PATRA ET AL: "Fluorescent nanoparticles based on a microporous organic polymer network: fabrication and efficient energy transfer to surface-bound dyes", CHEMICAL COMMUNICATIONS (CAMBRIDGE, ENGLAND), 14 September 2011 (2011-09-14), England, pages 9612, XP055497393, Retrieved from the Internet <URL:http://www.rsc.org/suppdata/cc/c1/c1cc13420e/c1cc13420e.pdf> DOI: 10.1039/c1cc13420e**

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- **SHUANG-SHUANG ZHANG ET AL: "PREPARATION OF CHIRAL AND FLUORESCENT NANOPARTICLES OF HYPERBRANCHED CONJUGATED POLYMERS BY THE SOLVENT CHIRALITY TRANSFER TECHNOLOGY", GAOFENZI XUEBAO - ACTA POLYMERICA SINICA, KEXUE CHUBANSHE, BEIJING, CN, no. 4, 1 April 2013 (2013-04-01), pages 426 - 435, XP009507289, ISSN: 1000-3304**
- **RUI WANG ET AL: "Synthesis and characterization of highly stable blue-light-emitting hyperbranched conjugated polymers", JOURNAL OF POLYMER SCIENCE PART A: POLYMER CHEMISTRY, vol. 46, no. 3, 1 February 2008 (2008-02-01), pages 790 - 802, XP055008534, ISSN: 0887-624X, DOI: 10.1002/pola.22424**
- **VÜSALA IBRAHIMOVA ET AL: "Facile synthesis of cross-linked patchy fluorescent conjugated polymer nanoparticles by click reactions", POLYMER CHEMISTRY, vol. 2, no. 12, 12 October 2011 (2011-10-12), pages 2818, XP055213321, ISSN: 1759-9954, DOI: 10.1039/c1py00332a**

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Description

INTRODUCTION

[0001] The present invention relates to a nanoparticle composition comprising nanoparticles formed from π-conjugated cross-linked polymer, as well as to their methods of manufacture and their uses.

BACKGROUND OF THE INVENTION

[0002] Photoluminescent conjugated polymer nanoparticles (CPNs) are currently viewed as attractive alternatives to Quantum Dots (QDs) for applications ranging from biological imaging to consumer electronics.

[0003] QDs have previously shown promise in a number of *in vitro* and *in vivo* bioimaging applications, where they can be internalized by cells, allowing individual organelles to be stained. However, their potential for *in vivo* oxidative degradation, which can release toxic heavy metal species (e.g. cadmium and lead), ultimately precludes their use in humans or in long-term cell-tracking applications. Moreover, the use of such heavy metals is heavily restricted in certain territories, thereby underlining a need for less-toxic alternatives.

[0004] CPNs exhibit many of the desirable properties of QDs, including a small size (ca. 10-200 nm), photostable photoluminescence tunable across the visible spectrum, and the ability to be isolated as stable dispersions in water, whilst avoiding many of the toxicity-related drawbacks.

[0005] Behrendt et al. (Polym. Chem., 2013, 4, 1333-1336) discloses that replacing a proportion of the alkyl side chains present on polyfluorene non-cross-linked co-polymers with a more hydrophilic side chain has a significant influence on the size and optical properties of the resulting non-cross-linked CPNs.

[0006] Behrendt et al. (J. Mater. Chem. C, 2013, 1, 3297-3304) discloses hybrid inorganic-organic composite nanoparticles formed from polyfluorene having pendant triethoxysilyl side chains that are cross-linkable under basic conditions.

[0007] CN101323781A discloses nano-fluorescent microspheres having an outer shell made from a water-soluble polymer and an inner shell being a conjugated fluorescent structure, and cross-links between the inner and outer shells.

[0008] Zhang et al (Gaofenzi Xuebao (2013), (4), 426-435) discloses the preparation of chiral and fluorescent nanoparticles of hyperbranched conjugated polymers by solvent chirality transfer technology. CN102627776 also discloses a method for preparing chiral fluorescent nanoparticles based on hyperbranched conjugated polymer.

[0009] In spite of the advances made to date, it is necessary that limiting factors in the more widespread exploitation of phohotoluminescent CPNs be addressed before they can realize their full potential as a replacement for QDs. Amongst these are improved production processes, greater manufacturing control, and superior purity for use in biological applications.

[0010] The present invention was devised with the foregoing in mind.

SUMMARY OF THE INVENTION

[0011] According to a first aspect of the present invention there is provided a nanoparticle composition as claimed in claim 1.

[0012] According to a second aspect of the present invention, as claimed in claim 8, there is provided a method of forming a nanoparticle composition defined herein, the method comprising the step of forming the nanoparticles by emulsion polymerisation, miniemulsion polymerisation or dispersion polymerisation techniques to provide an aqueous suspension of nanoparticles.

[0013] According to a third aspect of the present invention, as claimed in claim 13, there is provided a use of a nanoparticle composition defined herein in one or more applications defined herein.

[0014] According to a fourth aspect of the present invention, as claimed in claim 14, there is provided a nanoparticle dispersion comprising a nanoparticle composition as defined herein dispersed throughout a dispersing medium.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0015] Unless otherwise stated, the following terms used in the specification and claims have the following meanings set out below.

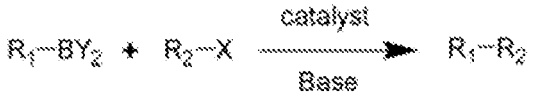
[0016] References herein to the "Stille reaction" (also known as Stille coupling) refer to a well-known chemical reaction coupling involving an organotin compound with an sp^2-hybridized organic halide catalyzed by palladium. The reaction is widely used in organic synthesis. The use of Stille polymerisation reactions for the production of conjugated polymer systems is described in, for example, Chem. Rev. 2011, 111, 1493-1528. The general reaction scheme is shown below:

$$(R)_3Sn\text{-}R_1 + X\text{-}R_2 \rightarrow R_1\text{-}R_2$$

wherein

R is a hydrocarbyl substituent group, such as (1-6C)alkyl;
R_1 and R_2 are both monomeric units to be coupled; and
X is reactive group, typically a halide, such as Cl, Br, I, or a pseudohalide, such as a triflate, $CF_3SO_3^-$.

[0017] References to the "Suzuki reaction" refer to the well-known organic reaction of an aryl- or vinyl-boronic acid with an aryl- or vinyl-halide. Suzuki reactions are typically catalyzed by a palladium(0) complex catalyst. This reaction is well known in the chemical field and follows the general reaction scheme shown below:



[0018] The reaction also works with pseudohalides, such as triflates (OTf), instead of halides. Boronic esters and organotrifluoroborate salts may be used instead of boronic acids. For polymer synthesis, R_1 and R_2 will represent monomeric units.

[0019] The term "hydrocarbyl" includes both straight and branched chain alkyl, alkenyl and alkynyl groups.

[0020] The term "alkylene" includes both straight and branched chain alkylene groups. References to individual alkylene groups such as "propylene" are specific for the straight chain version only and references to individual branched chain alkylene groups such as "isopropylene" are specific for the branched chain version only. For example, "(1-20C) alkylene" includes (1-14C)alkylene, (1-12C)alkylene, propylene, isopropylene and t-butylene. A similar convention applies to other radicals mentioned herein.

[0021] The terms "alkenylene" and "alkynylene" include both straight and branched chain alkenyl and alkynyl groups.

[0022] The term "aryl" is used herein to denote phenyl, naphthalene or anthracene ring. In an embodiment, an "aryl" is phenyl or naphthalene, and particularly is phenyl.

[0023] The term "heteroaryl" or "heteroaromatic" means an aromatic mono-, bi-, or tricyclic ring incorporating one or more (for example 1-4, particularly 1, 2 or 3) heteroatoms (for example N, O, P, S, Si, Ge, As or Se). Examples of heteroaryl groups are monocyclic, bicyclic and tricyclic groups containing from five to eighteen ring members. The heteroaryl group can be, for example, a 5- or 6-membered monocyclic ring, a 8-, 9-or 10-membered bicyclic ring or a 15-, 16-, 17- or 18-membered tricyclic ring. Suitably each ring in a bicyclic or tricyclic ring system comprises five or six ring atoms.

[0024] The term "cross-linked" used herein in relation to polymers does not encompass linear or hyperbranched polymers. The polymeric "branches" of hyperbranched polymers all emanate from a single focal point. In contrast, the polymeric strands of the cross-linked polymers forming part of the invention do not all converge to a single focal point. Rather, the strands of the cross-linked polymers forming part of the invention are randomly cross-linked to one another throughout polymer, with none of the cross-linking sites representing a single focal point in the sense of hyperbranched polymers. Furthermore, 4 or more polymeric chains emanate from a given cross-linking site within the polymers forming part of the invention, whereas the single focal point (or other branch points) within a hyperbranched polymer is only 3 coordinate. Moreover, the cross-linked polymers forming part of the invention are cross-linked to the extent that they are insoluble in all solvents (including aqueous, organic, polar and non-polar solvents), whereas hyperbranched polymers are commonly soluble.

Compositions of the invention

[0025] As discussed hereinbefore, the present invention provides a nanoparticle composition comprising a plurality of nanoparticles formed from a π-conjugated cross-linked polymer, the π-conjugated cross-linked polymer comprising

a) 80-99.9 mol.% of π-conjugated monomers, and

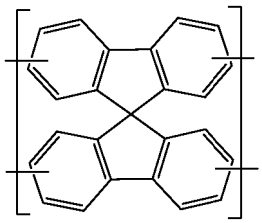
b) 0.1-20 mol.% of a cross-linker having the formula III shown below and wherein the nanoparticles forming the nanoparticle composition have a Z-average particle size of less than 30-200 nm, when measured by DLS in water.

[0026] The nanoparticle compositions of the present invention offer a number of advantages when compared with the state of the art. Principally, the nanoparticles forming the present compositions are formed from π-conjugated cross-linked polymers. The π-conjugated cross-linked polymers themselves comprise a backbone of π-conjugated monomers, with

cross-linking moieties interspersed along the π-conjugated backbone. The structure of the cross-linking moieties is such that one monomer spans two polymeric backbone chains. Therefore, during assembly of the polymer, the incorporation of the cross-linking moieties into the π-conjugated backbone chain provides a direct site for the propagation of a further π-conjugated backbone chain on both sides of the cross-linking moiety. Hence, the cross-links in the polymers forming the present nanoparticle compositions are formed *in-situ* during linking of the monomer units, meaning that the degree of cross-linking can be readily adjusted simply by varying the concentration of cross-linker. Owing to their π-conjugated structures, cross-linked polymers of this type provide good electron delocalisation properties. Such polymers also offer the possibility of electron delocalisation between adjacent backbone chain via the cross-linker. In contrast to this direct, *in-situ* formation of cross-links discussed above, prior art CPNs have focussed on the preparation of polymers formed from monomers having specially-modified pendant side chains that are amenable to cross-linking under certain conditions. Whilst being a viable method, such an approach necessarily requires the initial step of forming the polymer backbone chains prior to placing the backbone chains under suitable conditions to induce cross-linking between them. This multi-step approach is more complex than that used to prepare the polymers forming the present compositions, and the degree of cross-linking between the polymeric chains is notably more difficult to control.

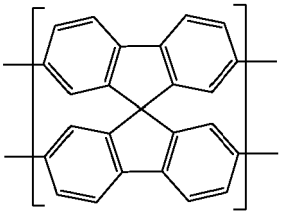
[0027] Aside from manufacturing simplicity and tuneability, the π-conjugated cross-linked polymers forming part of the invention lend themselves to obtaining nanoparticle compositions exhibiting significantly higher levels of purity. The insoluble cross-linker renders the nanoparticle composition insoluble in water and organic solvents, such that the π-conjugated cross-linked polymers exhibit swelling when brought into contact with a solvating solvent. Swelling the polymers in this manner allows impurities trapped within the polymeric network, such as catalysts and other reagents, to be easily removed by washing. Unlike prior art compositions, the resulting high purity photoluminescent nanoparticle compositions are therefore highly suitable for use in biological applications, such as bioimaging, and other *in vivo* processes.

[0028] The cross-linker has the formula III shown below:



(III)

[0029] Suitably, the cross-linker has the following structure:



[0030] The nanoparticle composition comprises 80-99.9 mol.% of one or more π-conjugated monomers. Any suitable π-conjugated monomers capable of polymerising to form nanoparticles may be used.

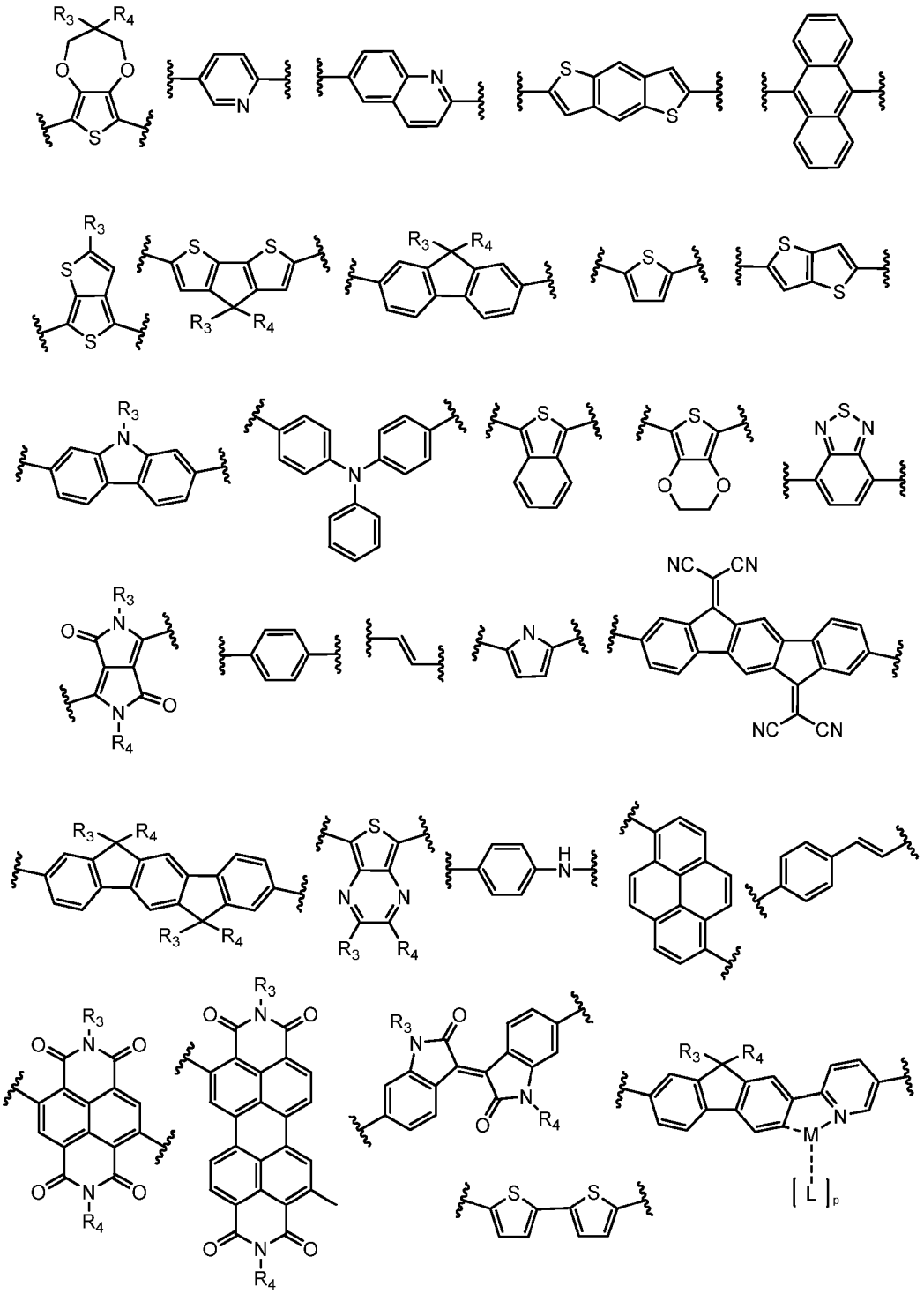
[0031] In one embodiment, the π-conjugated polymers of the present invention do not comprise any carbon-carbon triple bonds. Thus, in one aspect, the present invention relates to π-conjugated cross-linked polymers that do not comprise any carbon-carbon triple bonds. The electrons in a carbon-carbon triple bond give rise to conformations in which the π-electrons are not fully delocalised.

[0032] It will be appreciated by those skilled in the art that the monomeric units used to form the cross-linked π-conjugated polymers may comprise a selection of different chemical moieties that either alone or in combination provide a monomer having a π-conjugated ring system.

[0033] Examples of suitable π-conjugated ring systems that may be present in the monomer units, either alone or in any suitable combination, include mono-cyclic aryl groups (e.g. phenyl rings), polycyclic aryl ring systems (e.g. fluorene ring systems, naphthyl rings), mono-cyclic heteroaryl rings (e.g. thiophene rings) or polycyclic heteroaryl ring systems (e.g. benzothiazole, benzodiazathazole rings, thieno[3,2-b]thiophene, or pyrrolo[3,4-c]pyrrole) or other conjugated heterocyclic rings systems (e.g. pyrrolo-pyrrole-1,4-dione rings), and wherein each moiety is optionally substituted by one or

more organic groups, e.g. hydrocarbyl substituent groups optionally comprising 1 to 30 carbon atoms and optionally comprising one or more heteroatoms (e.g. N, O, P, S, Si, Ge, As or Se), and, where two or more of such moieties are present, they may be linked together by a bond or via an atom linkage (e.g. such as in a bi-arylamine or tri-arylamine group).

[0034] Further examples of particular moieties that may form part or all of the π-conjugated monomers include:



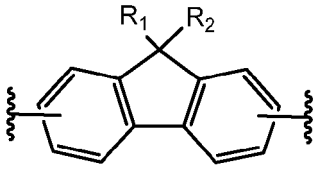
wherein R_3 and R_4 are each independently an organic substituent group (e.g. a hydrocarbyl substituent group optionally comprising 1 to 30 carbon atoms and optionally comprising one or more heteroatoms (e.g. N, O, P, S, Si, Ge, As or Se), or an aromatic or heteroaromatic group);

M is a metal (e.g. Ir, Pt, Rh, Re, Ru, Os, Cr, Cu, Pd, or Au);

L is a ligand (e.g. a halide or a hydrocarbyl substituent group optionally comprising 1 to 30 carbon atoms and optionally comprising one or more heteroatoms (e.g. N, O, S, Si, or P) or an aromatic or hetroaromatic group);

and wherein each of the above structures is optionally further substituted with one or more organic substituent groups (e.g. a hydrocarbyl substituent groups optionally comprising 1 to 30 carbon atoms and optionally comprising one or more heteroatoms (e.g. N, O, P, S, Si, Ge, As or Se) or an aromatic or heteroaromatic group).

[0035] In an embodiment, the π-conjugated monomers each independently comprise a moiety having the formula IV shown below:



(IV)

wherein

R_1 and R_2 are each independently a group:

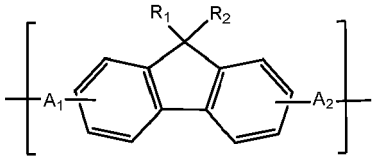
-X-Q

wherein

X is selected from the group consisting of (1-30C)alkylene, (2-30C)alkenylene, (2-30C)alkynylene, $-[(CH_2)_2-O]_n-$, $-[O-(CH_2)_2]_n-$ and $-[O-Si(R_z)_2]_n$ (wherein R_z is (1-4C)alkyl and n is 1 to 30), and
Q is a terminal group selected from hydrogen, methyl, hydroxyl, carboxy, (1-4C)alkoxycarbonyl, amino, $-C=CH_2$, -C≡CH, -SH, -biotin, -streptavidin and a polymerisable group selected from acrylates, epoxy and styrene,

or R_1 and R_2 are linked so that, together with the carbon atom to which they are attached, they form a ring.

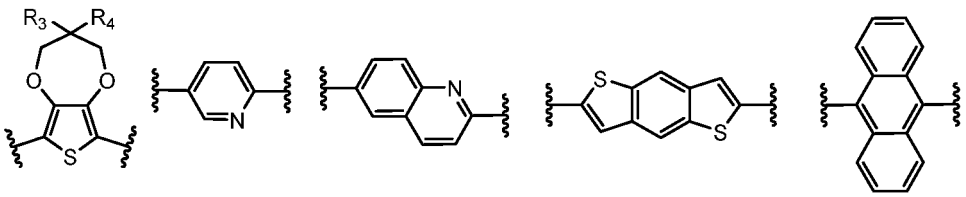
[0036] In another embodiment, π-conjugated monomers each independently have a structure defined by formula V shown below:

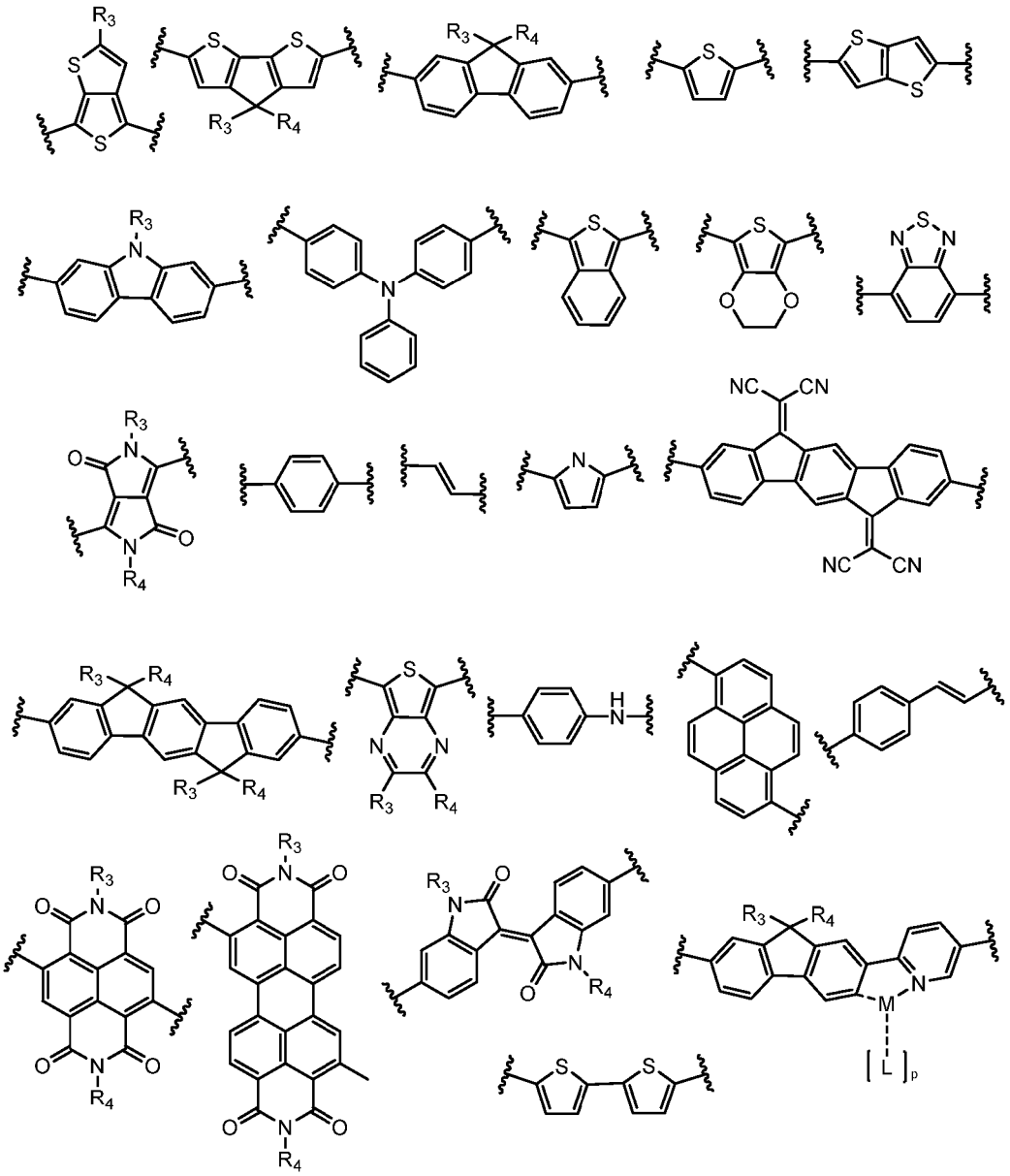


(V)

wherein

R_1 and R_2 are as defined hereinbefore;
A_1 and A_2 are independently absent or selected from any one of the following moieties:





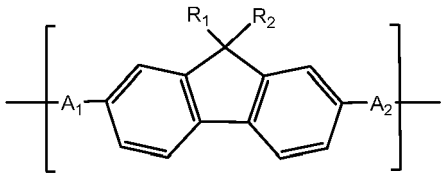
and wherein R_3 and R_4 are each independently a group:

$$-X^1-Q^1$$

wherein

X^1 is selected from the group consisting of (1-30C)alkylene, (2-30C)alkenylene, (2-30C)alkynylene, $-[(CH_2)_2-O]_n-$, $-[O-(CH_2)_2]_n-$, and $-[O-Si(R_z)_2]_n-$ (wherein R_z is (1-4C)alkyl and n is 1 to 30),
Q^1 is a terminal group selected from hydrogen, methyl, hydroxyl, carboxy, (1-4C)alkoxycarbonyl, amino, $-C=CH_2$, $-C\equiv CH$, -SH, -biotin, -streptavidin, and a polymerisable group selected from acrylates, epoxy or styrene;
M is a metal selected from Ir, Pt, Rh, Re, Ru, Os, Cr, Cu, Pd and Au;
L is a ligand independently selected from the group consisting of halo, (1-30C)hydrocarbyl optionally comprising one or more heteroatoms selected from N, O, S, Si, Ge, As or P, or an aryl or heteroaryl group optionally substituted with one or more substituents selected from (1-4C)alkyl, halo, aryl or heteroaryl; and
p is 1 to 4.

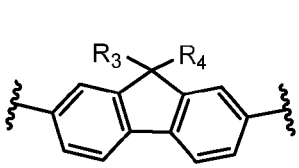
[0037] In another embodiment, the π-conjugated monomers each independently have a structure defined by formula VI below:

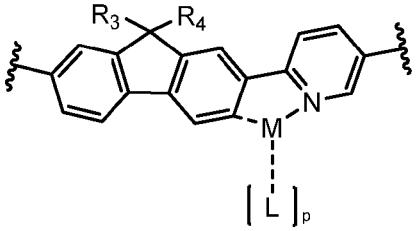


(VI)

R_1, R_2, A_1 and A_2 are as defined hereinbefore.

[0038] In another embodiment, A_1 and A_2 are independently absent or selected from any one of the following moieties:





wherein R_3, R_4, M, L and p are as defined hereinbefore.

[0039] In another embodiment both A_1 and A_2 are absent.

[0040] In another embodiment, when present:

X and X^1 are independently selected from the group consisting of (1-30C)alkylene, (2-30C)alkenylene, (2-30C) alkynylene, , $-[(CH_2)_2-O]_n-$, $-[O-(CH_2)_2]_n-$ and $-[O-Si(R_z)_2]_n-$(wherein R_z is methyl and n is 1 to 30);

Q and Q^1 are independently a terminal group selected from hydrogen, methyl, hydroxyl, carboxy, (1-4C)alkoxycarbonyl, amino, $-C=CH_2$, $-C\equiv CH$ and a polymerisable group selected from acrylates, epoxy and styrene;

M is a metal selected from Ir, Pt, Rh, Re, Ru, Os, Cr, Cu, Pd and Au;

L is a ligand independently selected from the group consisting of halo, (1-30C)hydrocarbyl optionally comprising one or more heteroatoms selected from N, O, S, Si or P, or an aryl or heteroaryl group optionally substituted with one or more substituents selected from (1-4C)alkyl, halo, aryl or heteroaryl; and

p is 1 to 4

[0041] In another embodiment, when present:

X and X^1 are independently selected from the group consisting of (1-20C)alkylene, (2-20C)alkenylene, (2-20C) alkynylene, $-[(CH_2)_2-O]_n-$ and $-[O-(CH_2)_2]_n-$ (wherein n is 1 to 20);

Q and Q^1 are independently a terminal group selected from hydrogen, methyl, hydroxyl, carboxy, (1-4C)alkoxycarbonyl, amino, $-C=CH_2$ and $-C\equiv CH$.

M is a metal selected from Ir, Pt, Cr, Cu, Pd and Au;

L is a ligand independently selected from the group consisting of halo, (1-20C)hydrocarbyl optionally comprising one or more heteroatoms selected from N, O, or S, or an aryl or heteroaryl group optionally substituted with one or more substituents selected from (1-4C)alkyl, halo, aryl or heteroaryl; and

p is 1 to 4.

[0042] In another embodiment, when present:

X and X^1 are independently selected from the group consisting of (1-20C)alkylene, $-[(CH_2)_2-O]_n-$ and $-[O-(CH_2)_2]_n-$ (wherein n is 1 to 20);

Q and Q^1 are independently a terminal group selected from hydrogen, methyl, hydroxyl, carboxy, (1-4C)alkoxycarbonyl and amino;

M is a metal selected from Ir, Pt, Cr, Cu, Pd and Au;

L is a ligand independently selected from the group consisting of aryl or heteroaryl, optionally substituted with one or more substituents selected from (1-4C)alkyl, halo, aryl or heteroaryl; and

p is 1 to 4.

[0043] In another embodiment, when present:

X and X^1 are independently selected from the group consisting of (1-20C)alkylene, - $[(CH_2)_2\text{-}O]_n$- and -$[O\text{-}(CH_2)_2]_n$- (wherein n is 1 to 20);

Q and Q^1 are independently a terminal group selected from hydrogen, methyl, (1-2C)alkoxycarbonyl and hydroxyl;

M is Ir;

L is a ligand independently selected from the group consisting of aryl or heteroaryl, optionally substituted with one or more substituents selected from aryl or heteroaryl; and

p is 1 to 2.

[0044] In another embodiment, when present:

X and X^1 are independently selected from the group consisting of (4-12C)alkylene, - $[(CH_2)_2\text{-}O]_n$- and -$[O\text{-}(CH_2)_2]_n$- (wherein n is 1 to 15);

Q and Q^1 are independently a terminal group selected from hydrogen, methyl, (1-2C)alkoxycarbonyl and hydroxyl;

M is Ir;

L is a ligand independently selected from the group consisting of phenyl or 6-membered heteroaryl, optionally substituted with one or more substituents selected from phenyl or 6-membered heteroaryl; and

p is 1 to 2.

[0045] In another embodiment, when present:

X and X^1 are independently selected from the group consisting of (4-12C)alkylene and - $[(CH_2)_2\text{-}O]_n$- (wherein n is 1 to 15);

Q and Q^1 are independently a terminal group selected from hydrogen, (1-2C)alkoxycarbonyl and methyl;

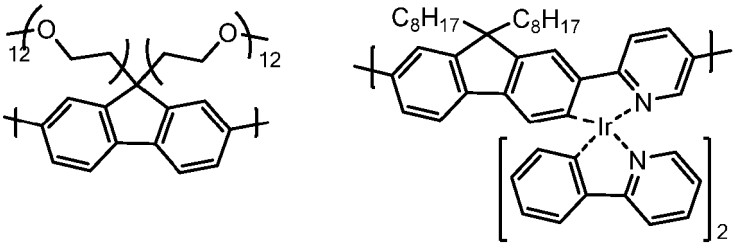
M is Ir;

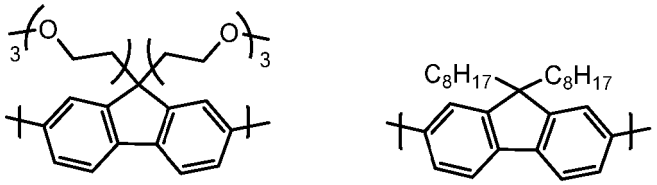
L is a ligand independently selected from the group consisting of phenyl or 6-membered heteroaryl, optionally substituted with one or more substituents selected from phenyl or 6-membered heteroaryl; and

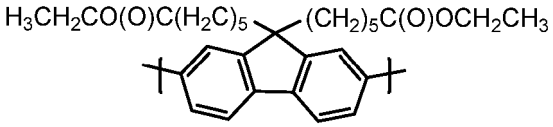
p is 1 to 2

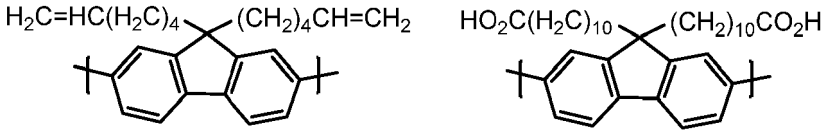
[0046] In any of the embodiments mentioned hereinbefore, X and/or X^1 may also be - $(CH_2)_m(CF_2)_n$- (wherein m is 0 to 30 and n is 1 to 30) and Q and/or Q^1 may also be $-CF_3$.

[0047] In another embodiment, the π-conjugated monomers are each independently selected from any of the following structures:

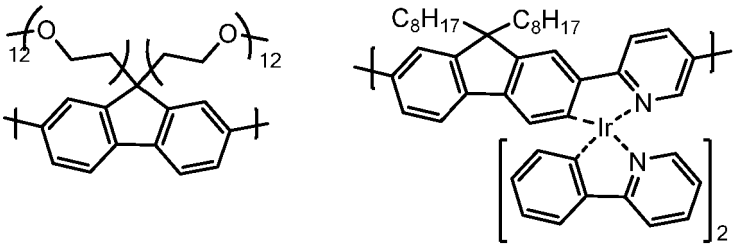


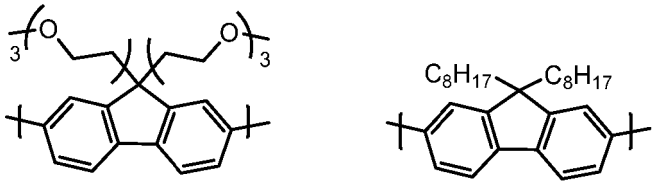


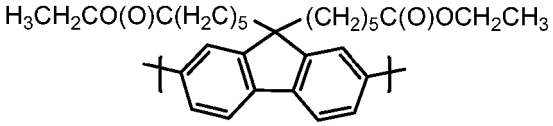




[0048] In another embodiment, the π-conjugated monomers are each independently selected from any of the following structures:







[0049] In another embodiment, the nanoparticle composition is an aqueous suspension. The aqueous medium provides a water-based vehicle in which the nanoparticles are dispersed. The medium may comprise additional components, such as dissolved materials and other water-miscible solvents. Suitably, the aqueous medium is water. More suitably, the aqueous medium is purified water.

[0050] The nanoparticles forming the nanoparticle composition have a particle size (Z-average, measured by DLS) of less than 30-200 nm. Most suitably, the nanoparticles have a particle size of less than 30-100 nm.

[0051] In another embodiment, the polymers forming part of the present invention have a degree of polymerisation of 10 to 800, more suitably 20 to 600.

[0052] In another embodiment, the nanoparticle composition comprises 1-10 mol% of the cross linker. Suitably, the nanoparticle composition comprises 2-8 mol% of the cross linker. More suitably, the nanoparticle composition comprises 3-7 mol% of the cross linker. Most suitably, the nanoparticle composition comprises 4.5-5.5 mol% of the cross linker.

[0053] In another embodiment, the nanoparticle composition of the invention may further comprise a stabiliser to maintain the particles in suspension. Any suitable stabiliser may be used such as, for example, non-ionic, cationic or anionic stabilisers known in the art. Particular examples of suitable stabilisers include non-ionic stabilisers, for example: Triton X series octylphenol ethoxylates, Tergitol series nonylphenol ethoxylates (Dow Chemical Company); Brij series poly(oxyethylene) glycol alkyl ethers, Superonic series, Tween series polysorbate surfactants (Croda); Pluronic series of block copolymers based on ethylene oxide and propylene oxide (BASF); Tetronic series tetra functional block copolymers based on ethylene oxide and propylene oxide, Lutensol series (BASF); Igepal series Rhodasurf series and Antarox series (Rhodia); and Merpol series (Stepan Co.)

[0054] In another embodiment, the nanoparticle composition further comprises an anionic stabiliser, for example sodium dodecylsulphate (SDS), and/or a cationic stabiliser, for example cetyl trimethylammonium bromide (CTAB).

Dispersions of the invention

[0055] As discussed hereinbefore, the present invention also provides a nanoparticle dispersion comprising a nanoparticle composition as defined herein dispersed throughout a dispersing medium.

[0056] In an embodiment, the dispersing medium is a liquid (e.g. water or a solution of monomers). Aqueous dispersing media may be particularly suitable where the dispersion is intended for biological applications.

[0057] Alternatively, the dispersing medium may be a solid (e.g. a polymeric matrix). Dispersions where the dispersing medium is a polymeric matrix may be particularly suitable for use as LED phosphors.

[0058] In another embodiment, the nanoparticle dispersions are prepared such that the loading of nanoparticle composition is high. Suitably, the concentration of the nanoparticles in the dispersing medium is greater than or equal to 15 mM. More suitably, the concentration of the nanoparticles in the dispersing medium is greater than or equal to 20 mM. Suitably, the concentration of the nanoparticles in the dispersing medium is greater than or equal to 25 mM. The aforementioned concentrations are based on the initial monomer concentrations used in the polymerisation reaction, and assumes 100% conversion of the monomers to the polymer.

[0059] Alternatively, depending on the application of interest, the nanoparticle dispersion may be more dilute. In an embodiment, the concentration of the nanoparticles in the dispersing medium (e.g. water) is less than or equal to 15 mg/ml. Such dispersions may be particularly useful in biological applications.

[0060] In an alternative embodiment, the concentration of the nanoparticles in the dispersing medium (e.g. a polymeric matrix) is less than or equal to 5 wt%. Suitably, the concentration of the nanoparticles in the dispersing medium is less than or equal to 3 wt%. More suitably, the concentration of the nanoparticles in the dispersing medium is less than or equal to 1 wt%. Such dispersions may find application where the nanoparticles are being used as LED phosphors.

Methods of the invention

[0061] As discussed hereinbefore, the present invention also provides a method of forming a nanoparticle composition defined herein, the method comprising the step of forming the nanoparticles by emulsion polymerisation, miniemulsion polymerisation or dispersion polymerisation techniques to provide an aqueous suspension of nanoparticles.

[0062] Emulsion polymerisation, miniemulsion polymerisation and dispersion polymerisation techniques will be known to one of skill in the art.

[0063] In the case of emulsion polymerisation, the monomeric components are dissolved in a suitable organic solvent (e.g. chlorobenzene, toluene or xylenes) along with the catalyst (e.g. $Pd(PPh_3)_4$, IPr*PdTEACl$_2$ or $Pd_2(dba)_3$/P(*o*-tol)$_3$). This solution is then added to an aqueous medium of water, tetraethylammonium hydroxide solution (40% in water) and a suitable emulsifier. Any suitable emulsifier may be used, such as, for example, SDS, Triton X102, Brij L23, and/or Tween 20. The resultant emulsion may be stirred and/or ultrasonicated to form an emulsion, suitably a mini-emulsion. The emulsion mixture may then be gently heated to a temperature of between 30 and 100 °C (for $Pd(PPh_3)_4$, $Pd_2(dba)_3$/P(*o*-tol)$_3$ suitably between 70 and 95 °C, and more suitably between 80 and 95 °C; and for IPr*PdTEACl$_2$ ideally 30°C) for period of time (e.g. from 1 hour to 2 days) to form the polymeric nanoparticles. A person skilled in the art will appreciate that the temperature of heating depends on catalyst system employed (as per the example section herein).

[0064] In an embodiment, the nanoparticles are formed by Suzuki coupling or Stille coupling reactions. Such coupling reactions are known in the art.

[0065] In another embodiment, the nanoparticles are formed by reacting π-monomeric moieties as defined herein with a pre-made cross-linking moiety as defined herein.

[0066] In another embodiment, the method further comprises the step of purifying the aqueous suspension of nanoparticles. Suitably, the aqueous suspension of nanoparticles is purified by contacting the aqueous suspension of nanoparticles with at least one organic solvent.

[0067] In another embodiment, contacting the aqueous suspension of nanoparticles with at least one suitable organic solvent causes precipitation of the nanoparticles. The precipitated nanoparticles may then be centrifuged, with the supernatant then decanted to leave the purified nanoparticles. Optionally, the purified nanoparticle may be resuspended in water, and the purification process then repeated.

[0068] In another embodiment, when the nanoparticles are lipophilic, the at least one organic solvent is a polar solvent that is miscible with water (e.g. methanol).

[0069] In another embodiment, when the nanoparticles are hydrophilic, the at least one organic solvent is a non-polar solvent.

Uses of the nanoparticle compositions

[0070] As discussed hereinbefore, the present invention also provides a use of a nanoparticle composition defined herein in one or more applications selected from the group consisting of biological or non-biological imaging or sensing, down-conversion of LED light, anti-counterfeit encoding, displays, cell-sorting/flow cytometry, long-term cell tracking, and flow visualisation.

[0071] In an embodiment, the nanoparticle composition is used in *in vivo* or *in vitro* imaging or sensing applications.

EXAMPLES

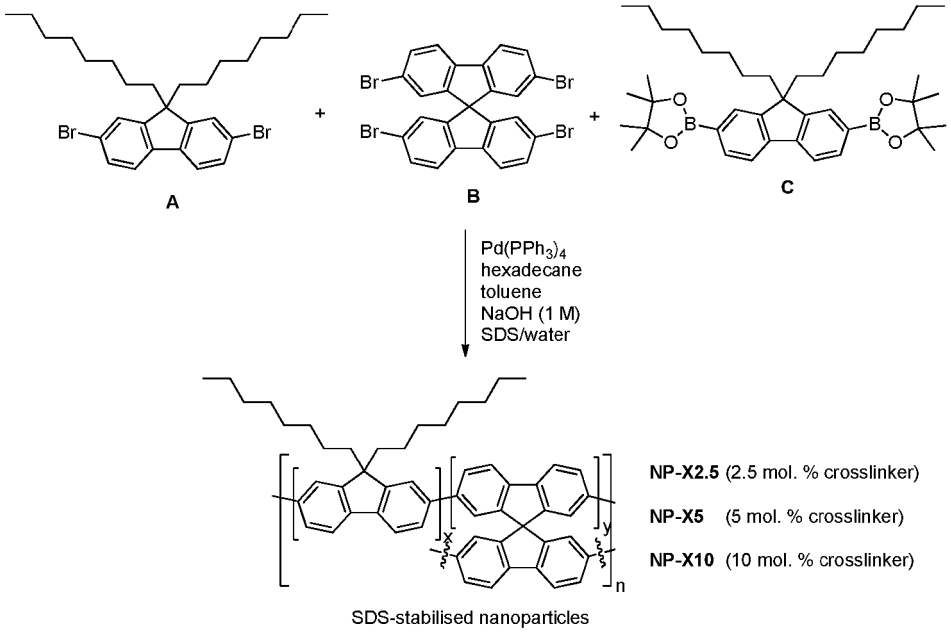
[0072] Examples of the invention will now be described, for the purpose of reference and illustration only, with reference to the accompanying figures, in which:

Fig.1 shows DLS particle size histograms of the cross-linked nanoparticles of Example 1 in water (solid line) or THF (broken line).
Fig. 2 shows UV/Vis spectra of the cross-linked nanoparticles of Example 1 in water (solid line) or THF (broken line).
Fig. 3 shows PL spectra of the cross-linked nanoparticles of Example 1 in water (solid line) or THF (broken line).
Fig. 4 shows DLS particle size histograms of the cross-linked nanoparticles of Example 2 in water (solid line) and THF (broken line) dispersants.
Fig. 5 shows UV/Vis (broken line) and PL (solid line) spectra of the cross-linked nanoparticles of Example 2.
Fig.6 shows DLS sizing histograms of cross-linked phosphorescent nanoparticles in water (solid line) or THF (broken line) of the cross-linked nanoparticles of Example 3.
Fig. 7 shows UV/Vis spectra of the cross-linked nanoparticles of Example 3 in water (solid line) or THF (broken line).
Fig, 8 shows PL spectra of the cross-linked nanoparticles of Example 3 in water (solid line) or THF (broken line).
Fig. 9 shows DLS sizing histograms of the cross-linked nanoparticles of Example 4 in water (solid line) and THF (broken line).
Fig. 10 shows DLS sizing histograms of the cross-linked nanoparticles of Example 5 in water.
Fig. 11 shows DLS sizing histograms of the cross-linked nanoparticles of Example 6 in water (broken line) and THF (solid line).
Fig. 12 shows absorption and emission spectra of the cross-linked nanoparticles of Examples 4 (Fig. 12a), 5 (Fig. 12b) and 6 (Fig. 12c).

Example 1 - **Cross-linked PFO nanoparticles**

Synthesis

[0073] Referring to Scheme 1 and Table 1 shown below, sodium dodecyl sulphate (SDS) (50.0 mg) and deionised water (10 mL) were transferred to a Schlenk tube and the resultant solution was degassed by bubbling with argon for 20 minutes. Monomer **A** (see Table 1), crosslinker B (see Table 1) and monomer **C** (58.6 mg, 9.12×10^{-2} mmol) were dissolved in toluene (1 mL), to which hexadecane (78 μL) was also added, and this solution was degassed for 5 minutes in the same manner. Tetrakis(triphenylphosphine)palladium(0) (2.2 mg, 9.13×10^{-3} mmol) was added to the monomer solution, which was then transferred to the reaction vessel. The reaction mixture was emulsified by ultrasonication (Cole Parmer 750W ultasonicator, fitted with microtip, on 22 % power) for 2 minutes while cooling with an ice bath. The Schlenk tube was resealed and the miniemulsion was heated to 72 °C, followed by addition of 1M aqueous sodium hydroxide solution (365 μL), and the reaction mixture was stirred for 16 hours. After cooling to room temperature, the cap of the reaction vessel was removed and the emulsion was stirred for 5 hours to remove the residual toluene.



Scheme 1

Table 1 - Reaction variables for synthesis of cross-linked PFO nanoparticles

Sample Name	Monomer A (mass, moles)	Crosslinker B (mass, moles)
NP-X2.5	45.0 mg 8.21×10^{-2} mmol	2.9 mg 4.6×10^{-3} mmol
NP-X5	40.0 mg 7.29×10^{-2} mmol	5.8 mg 9.1×10^{-3} mmol
NP-X10	30.0 mg 5.47×10^{-2} mmol	11.6 mg 1.82×10^{-2} mmol

Surfactant removal and DLS analysis (nanoparticles in water)

[0074] A 400 μL aliquot of the crude nanoparticle suspension was diluted with 1.6 mL of deionised water, to which Amberlite XAD-2 resin (20 mg, pre-washed with 2 × 2 mL of water) was added. The suspension was shaken at room temperature for 15 minutes before decanting off the nanoparticle suspension. This Amberlite XAD-2 purification step was repeated, after which time the suspension no longer foamed upon shaking and was filtered through glass wool prior to dynamic light scattering (DLS) analysis of particle size using a Malvern Zetasizer Nano ZS. Results are shown in Table 2 and Fig. 1.

Table 2 - DLS analysis of cross-linked PFO nanoparticles in water

Sample Name	Z-Average (d. nm)	Size by Intensity (d. nm)	St. Dev. (nm)	PdI
NP-X2.5	128	154	69	0.16
NP-X5	130	151	60	0.14
NP-X10	129	150	56	0.13

DLS analysis (nanoparticles in THF)

[0075] A 200 μL aliquot of the crude nanoparticle suspension was flocculated through addition of 1.3 mL toluene and the polymer was isolated by centrifugation (14,000 rpm, 1 minute) and decantation of the supernatant. The polymer was dried in air to remove residual methanol before dissolving in tetrahydrofuran (THF, 1 mL). The resultant suspension was measured directly using a Malvern Zetasizer Nano ZS. Results are shown in Table 3 and Fig. 1.

Table 3 - DLS analysis of cross-linked PFO nanoparticles in THF

Sample name	Z-Average (d. nm)	Size by Intensity (d. nm)	St. Dev. (nm)	PdI
NP-X2.5	-	-	-	n/a[a]
NP-X5	174	198 (99.6 %) 4827 (0.4%)[b]	74 (99.6 %) 711 (0.4%)[a]	0.13
NP-X10	147	175	73	0.15

[a] secondary peak likely to result from a small proportion of aggregated nanoparticles

UV/Vis analysis (nanoparticles in water or THF)

[0076] Following surfactant removal *via* treatment with Amberlite XAD-2, 40 μL of the nanoparticle suspension was diluted with 3 mL of water. UV-Vis absorption spectra of the nanoparticles at this concentration were recorded on a Varian Cary 55 5000UV-Vis-NIR spectrophotometer at room temperature. Fig. 2 shows UV/Vis spectra of the cross-linked PFO nanoparticles.

Photoluminescence (PL) analysis (nanoparticles in water or THF)

[0077] Following surfactant removal *via* treatment with amberlite XAD-2, 40 μL of the nanoparticle suspension was diluted with 3 mL of water. PL spectra were recorded on a Varian Cary Eclipse fluorimeter. Fig. 2 shows PL spectra of the cross-linked PFO nanoparticles

Photoluminescence (PL) analysis (nanoparticles in water)

[0078] Photoluminescencemeasurements were obtained using a Fluoromax-4 spectrofluorometer . Measurements were carried out on dilute dispersions of the nanoparticles in water (800 μL, abs > 1), using the same volume of water for background measurements. The results are provided in Table 4.

Table 4 - Optical properties of PFO nanoparticles in water

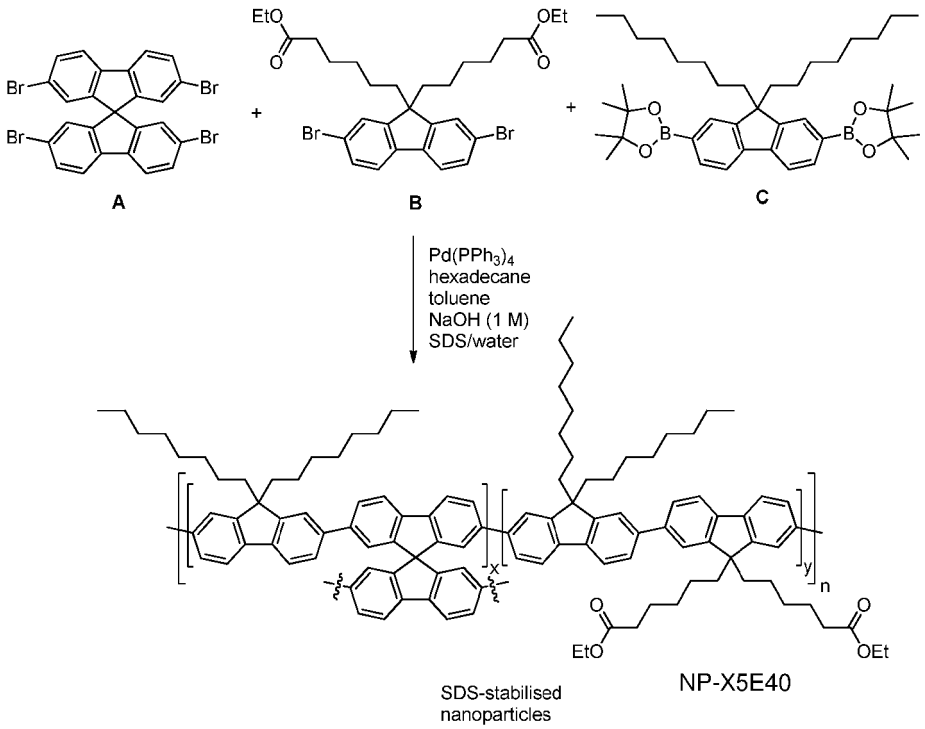
Sample Name	λ_{max}	λ_{em}[a]
NP-X2.5	390	440
NP-X5	390	438
NP-X10	390	437

[a] λ_{ex} = 380 nm

Example 2 - **Ethyl ester-functionalised Cross-linked PFO nanoparticles**

Synthesis

[0079] Referring to Scheme 2 shown below, sodium dodecyl sulfate (50.0 mg) and deionised water (10 mL) were transferred to a Schlenk tube and the resultant solution was degassed by bubbling with argon for 20 minutes. Crosslinker **A** (5.8 mg, 9.12×10^{-3} mmol), monomer **B** (44.4 mg, 7.30×10^{-2} mmol) and monomer **C** (58.6 mg, 9.12×10^{-2} mmol) were dissolved in toluene (1 mL), to which hexadecane (78 μL) was also added, and this solution was degassed for 5 minutes in the same manner. Tetrakis(triphenylphosphine)palladium(0) (2.2 mg, 9.13×10^{-3} mmol) was added to the monomer solution, which was then transferred to the reaction vessel. The reaction mixture was emulsified by ultrasonication (Cole Parmer 750W ultasonicator, fitted with microtip, on 22 % power) for 2 minutes while cooling with an ice bath. The Schlenk tube was resealed and the miniemulsion was heated to 72 °C, followed by addition of 1M aqueous sodium hydroxide solution (365 μL), and the reaction mixture was stirred for 16 hours. After cooling to room temperature, the cap of the reaction vessel was removed and the emulsion was stirred for 5 hours to remove the residual toluene.



Scheme 2

DLS analysis (nanoparticles in water or THF)

[0080] Surfactant removal was carried out using the general procedure described in Example 1. Flocculation and resuspension in THF were carried out using the general procedure described in Example 1. DLS analysis was carried out as in Example 1, using either water or THF as the dispersant. The results are provided in Table 5 and Fig. 4.

Table 5 - DLS analysis of ethyl ester-functionalised nanoparticles in water or THF

Sample Name	Dispersant	Z-Average (d. nm)	Size by Intensity (d. nm)	St. Dev (nm)	PdI
NP-X5E40	Water	118	139	56	0.14
NP-X5E40	THF	170	204	82	0.16

UV/Vis and PL analysis (nanoparticles in water)

[0081] The general UV/Vis and PL analytical_procedures described in Example 1 were used to record the UV/Vis and PL spectra of the nanoparticles in dilute aqueous dispersion. The results are provided in Fig. 5.

PLanalysis (nanoparticles in water)

[0082] PL measurements were obtained using the general method described in Example 1. The results are provided in Table 6.

Table 6 - Optical properties of ethyl ester-functionalised nanoparticles in water

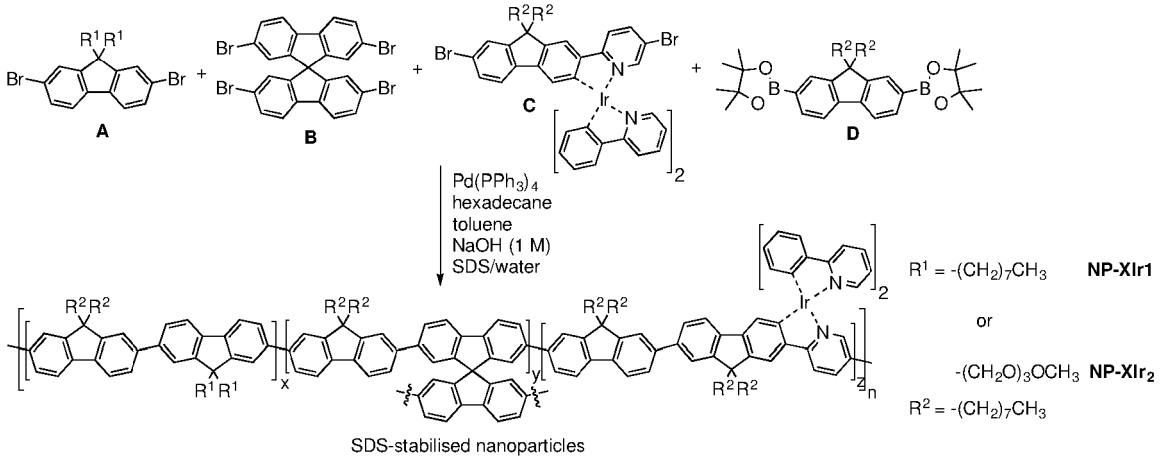
Sample Name	λ_{max}	λ_{em}[a]
NP-X5E40	391	432

[a] λ_{ex} = 380 nm

Example 3 - **Cross-linked phosphorescent nanoparticles**

Method

[0083] Referring to Scheme 3 and Table 7 shown below, sodium dodecyl sulfate (50.0 mg) and deionised water (10 mL) were transferred to a Schlenk tube and the resultant solution was degassed by bubbling with argon for 20 minutes. Monomers **A** (see Table 7), **C** (20.5 mg, 1.82×10^{-2} mmol) and **D** (58.6 mg, 9.12×10^{-2} mmol) and crosslinker **B** (5.8 mg, 9.12×10^{-3} mmol) were dissolved in toluene (1 mL), to which hexadecane (78 μL) was also added, and this solution was degassed for 5 minutes in the same manner. Tetrakis(triphenylphosphine)palladium(0) (2.2 mg, 9.13×10^{-3} mmol) was added to the monomer solution, which was then transferred to the reaction vessel. The reaction mixture was emulsified by ultrasonication (Cole Parmer 750W ultasonicator, fitted with microtip, on 22 % power) for 2 minutes while cooling with an ice bath. The Schlenk tube was resealed and the miniemulsion was heated to 72 °C, followed by addition of 1M aqueous sodium hydroxide solution (365 μL), and the reaction mixture was stirred for 16 hours. After cooling to room temperature, the cap of the reaction vessel was removed and the emulsion was stirred for 5 hours to remove the residual toluene.



Scheme 3

Table 7 - Reaction variables for synthesis of cross-linked phosphorescent nanoparticles

Sample Name	Monomer A Side Chain (R^1)	Monomer A (mass, moles)
NP-XIr1	Octyl	30.0 mg 5.47×10^{-2} mmol
NP-XIr2	MeO-PEG3	33.7 mg 5.57×10^{-2} mmol

DLS analysis (nanoparticles in water or THF)

[0084] Surfactant removal was carried out using the general procedure described in Example 1. Flocculation and resuspension in THF were carried out using the general procedure described in Example 1. DLS analysis was carried out as in Example 1, using either water or THF as the dispersant. The results are provided in Table 8 and Fig. 6.

Table 8 - DLS analysis of cross-linked phosphorescent nanoparticles in water or THF

Sample Name	Dispersant	Z-Average (d. nm)	Size by Intensity (d. nm)	St. Dev (nm)	PdI
NP-XIr1	Water	131	158	69	0.15
NP-XIr1	THF	167	210	109	0.18
NP-XIr2	Water	126	150 (99.3 %)	70 (99.3 %)	0.19
			4709 (0.7 %)[a]	774 (0.7 %)[a]	
NP-XIr2	THF	165	205	98	0.18

[a] Secondary peak likely to result from a small proportion of aggregated nanoparticles

UV/Vis and PL analysis (nanoparticles in water or THF)

[0085] The general UV/Vis and PL analytical_procedures described in Example 1 were used to record the UV/Vis (Fig. 7) and PL (Fig. 8) spectra of the nanoparticles in dilute aqueous dispersion or THF.

PL analysis (nanoparticles in water)

[0086] PLmeasurements were obtained using the general method described in Example 1. The results are provided in Table 9.

Table 9 - Optical properties of cross-linked phosphorescent nanoparticles in water

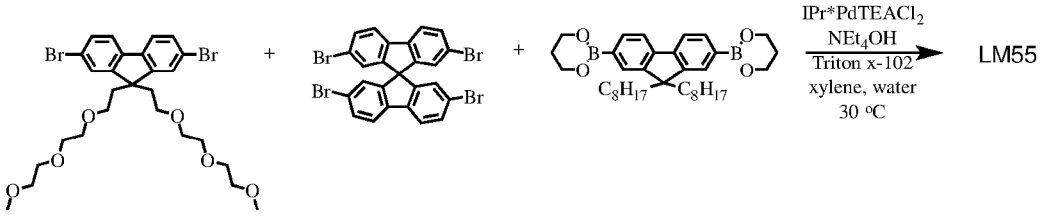
Sample Name	λ_{max}	λ_{em}[a]
NP-Ir1	392	609
NP-Ir2	392	609

[a] λ_{ex} = 390 nm

Example 4 - **PEG3 functionalised 10% cross-linked PFO nanoparticles**

Synthesis

[0087] Referring to Scheme 4 shown below, tetraethylammonium hydroxide solution (40% in water) (0.1567 g, 0.4 mmol), was added to an aqueous solution (50 ml) of non-ionic surfactant, Triton x-102 (2.5 g, 5 wt% in de-ionised water) in a 100 ml three necked round bottom flask. Then contents were then through degassed for 30 mins by bubbling nitrogen gas through the stirred solution. Then a separate 10 ml two necked round bottom flask was used to mix together the monomers in the organic solvent prior to addition to the reaction flask. 9,9-dioctylfluorene-2,7-di-boronic acid-bis(1,3-propanediol) ester (0.1151 g, 0.2 mmol), 2,7-dibromo-9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene (0.0967 g, 0.16 mmol) and 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.0126 g, 0.02 mmol) were dissolved in xylene (2 ml). The monomer solution was degassed and then the catalyst IPr*PdTEACl$_2$ (0.0095 g, 0.008 mmol) was added, followed by further degassing of the resultant solution. A syringe was used to transfer the monomer/catalyst into the stirred surfactant/base solution in the main reaction flask now maintained at 30°C with stirring and maintaining under nitrogen gas for 24h.



Scheme 4

DLS analysis (nanoparticles in water or THF)

[0088] 500 μl of sample was transferred to centrifuge vial the 1.5 ml of methanol was added. The sample vial was centrifuged at 14,000 rpm for 5 min then the liquid was decanted. Crude sample was washed with methanol 3 times and re-dispersed in THF in order to measure the size of particles. Neat products without further purification were also investigated. The results are shown in Fig. 9 and Table 10. Concentrations of polymer in water was 23 μg/ml.

Table 10 - Particle sizes of CPNs in water and THF at 25°C

Sample	Size (nm)	Dz (nm)	STD (nm)	PdI
LM55 Neat	50	44	26.81	0.244
LM55 in THF	108	218	51.80	0.217

Optical properties

[0089] Referring to Table 11 and Fig. 12, LM55 exhibited maxima band at 370 nm but no β-phase was observed.

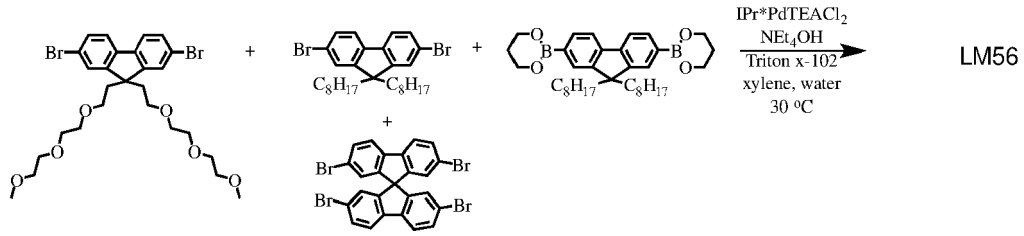
Table 11 - Summarized optical properties of cross-linked polymer in water

Sample	Final polymer conc. (mg/ml)	Size (nm)	λ_{abs} (nm)	λ_{em} (nm)	E_g*
LM55	2.5	50	370	420, 441	2.91

Example 5 - **PEG3 functionalised 5% cross-linked PFO nanoparticles**

Synthesis

[0090] Referring to Scheme 5 shown below, tetraethylammonium hydroxide solution (40% in water) (0.1567 g, 0.4 mmol), was added to an aqueous solution (50 ml) of non-ionic surfactant, Triton x-102 (2.5 g, 5 wt% in de-ionised water) in a 100 ml three necked round bottom flask. Then contents were then through degassed for 30 mins by bubbling nitrogen gas through the stirred solution. Then a separate 10 ml two necked round bottom flask was used to mix together the monomers in the organic solvent prior to addition to the reaction flask. 9,9-dioctylfluorene-2,7-di-boronic acid-bis(1,3-propanediol) ester (0.1151 g, 0.2 mmol), 2,7-dibromo-9,9-dioctylfluorene (0.0768g, 0.14 mmol), 2,7-dibromo-9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene (0.0242 g, 0.04 mmol) and 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.0063 g, 0.01 mmol) were dissolved in xylene (2 ml). The monomer solution was degassed and then the catalyst IPr*PdTEACl$_2$ (0.0095 g, 0.008 mmol) was added, followed by further degassing of the resultant solution. A syringe was used to transfer the monomer/catalyst into the stirred surfactant/base solution in the main reaction flask now maintained at 30°C with stirring and maintaining under nitrogen gas for 24h.



Scheme 5

DLS analysis (nanoparticles in water or THF)

[0091] 500 μl of sample was transferred to centrifuge vial the 1.5 ml of methanol was added. The sample vial was centrifuged at 14,000 rpm for 5 min then the liquid was decanted. Crude sample was washed with methanol 3 times and re-dispersed in THF in order to measure the size of particles. Neat products without further purification were also investigated. The results are shown in Fig. 10 and Table 12. Concentrations of polymer in water was 23 μg/ml.

Table 12 - Particle sizes of CPNs in water at 25°C

Sample	Size (nm)	Dz (nm)	STD (nm)	PdI
LM56 Neat	55	41	26.23	0.381

Optical properties

[0092] Referring to Table 13 and Fig. 12, **LM56** showed absorption peak at 378 nm.

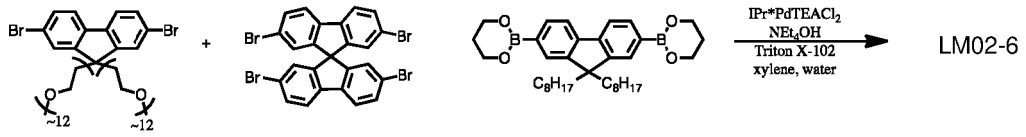
Table 13 - Summarized optical properties of cross-linked polymer in water

Sample	Final polymer conc. (mg/ml)	Size (nm)	λ_{abs} (nm)	λ_{em} (nm)	E_g*
LM56	2.5	55	378, 435	421, 436, 453	2.78

Example 6 - **PEG12 functionalised 10% cross-linked PFO nanoparticles**

Synthesis

[0093] Referring to Scheme 6 below, tetraethylammonium hydroxide solution (40% in water) (0.1567 g, 0.4 mmol), was added to an aqueous solution (50 ml) of non-ionic surfactant, Triton x-102 (2.5 g, 5 wt% in de-ionised water) in a 100 ml three necked round bottom flask. Then contents were then through degassed for 30 mins by bubbling nitrogen gas through the stirred solution. Then a separate 10 ml two necked round bottom flask was used to mix together the monomers in the organic solvent prior to addition to the reaction flask. 9,9-dioctylfluorene-2,7-di-boronic acid-bis(1,3-propanediol)ester (0.1151 g, 0.2 mmol), 2,7-dibromo-9,9-bis(polyethylene glycol monoether)fluorene (0.2255 g, 0.16 mmol) and 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.0126 g, 0.02 mmol) were dissolved in xylene (2 ml). The monomer solution was degassed and then the catalyst IPr*PdTEACl$_2$ (0.0095 g, 0.008 mmol) was added, followed by further degassing of the resultant solution. A syringe was used to transfer the monomer/catalyst into the stirred surfactant/base solution in the main reaction flask now maintained at 30°C with stirring and maintaining under nitrogen gas for 24h.



Scheme 6

DLS analysis (nanoparticles in water or THF)

[0094] 500 μl of sample was transferred to centrifuge vial the 1.5 ml of methanol was added. The sample vial was centrifuged at 14,000 rpm for 5 min then the liquid was decanted. Crude sample was washed with methanol 3 times and re-dispersed in THF in order to measure the size of particles. Neat products without further purification were also investigated. The results are shown in Fig. 11 and Table 14. Concentrations of polymer in water was 23 μg/ml.

Table 14 - Particle sizes of CPNs in water and THF at 25°C

Sample	Size (nm)	Dz (nm)	STD (nm)	PdI
LM02-6 Neat	244	13	103.2	0.359
LM02-6 in THF	74	847	10.97	0.489

Optical properties

[0095] Table 15 and Fig. 12 show summarized optical properties for LM02-6 in water.

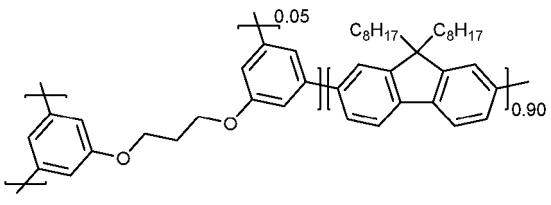
Table 15 - Summarized optical properties of cross-linked polymer in water

Sample	Final polymer conc. (mg/ml)	Size (nm)	λ_{abs} (nm)	λ_{em} (nm)	E_g*
LM02-6	2.5	244	N/A	419, 441	N/A

Example 7 - **5% 1,3-Diphenoxypropane Cross-Linked Polyfluorene Nanoparticles**

Synthesis

[0096]

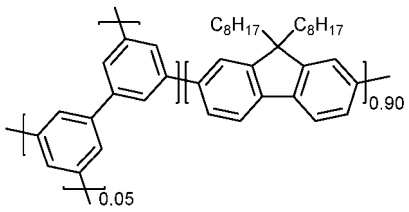


[0097] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 9,9-dioctyl-2,7-dibromofluorene (87.8 mg, 160 μmol), 1,3-bis(3,5-dibromophenoxy)propane (10.9 mg, 20 μmol), tris(dibenzylideneacetone) dipalladium(0) (4.6 mg, 5 μmol), tri(o-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 16 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL using deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky light green solution. **DLS (water):** Z-average = 110 nm, PdI = 0.156, D_n = 69 nm and SD = 21.0 nm. **UV-Vis Abs. (water):** λ_{max} = 379 nm, $\lambda_{sec.}$ = 432 nm, λ_{onset} = 455 nm. **UV-Vis PL (water):** λ_{max} = 439 nm, $\lambda_{sec.}$ = 467 nm, $\lambda_{sec.}$ = 499 nm, $\lambda_{sec.}$ = 534 nm.

Example 8 - 5% 1,1'-Biphenyl Cross-Linked Polyfluorene Nanoparticles

Synthesis

[0098]

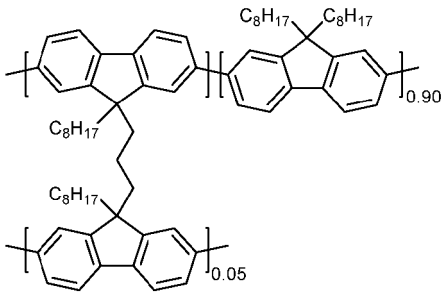


[0099] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 9,9-dioctyl-2,7-dibromofluorene (87.8 mg, 160 μmol), 3,3',5,5'-tetrabromo-1,1'-biphenyl (9.4 mg, 20 μmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 5 μmol), tri(o-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 16 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL using deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky light green solution. **DLS (water):** Z-average = 110 nm, PdI = 0.134, D_n = 61 nm and SD = 21.7 nm. **UV-Vis Abs. (water):** λ_{max} = 378 nm, $\lambda_{sec.}$ = 432 nm, λ_{onset} = 451 nm. **UV-Vis PL (water):** λ_{max} = 438 nm, $\lambda_{sec.}$ = 466 nm, $\lambda_{sec.}$ = 497 nm, $\lambda_{sec.}$ = 534 nm.

Example 9 - 5% 9,9'-(1,3-Propanediyl)bis[9-octyl-9*H*-fluorene] Cross-Linked Polyfluorene Nanoparticles

Synthesis

[0100]

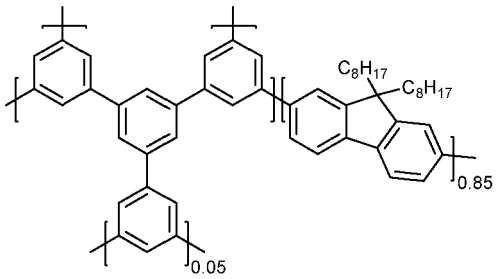


[0101] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 9,9-dioctyl-2,7-dibromofluorene (87.8 mg, 160 μmol), 9,9'-(1,3-propyldiyl)bis[2,7-dibromo-9*H*-Fluorene-9-octyl] (18.3 mg, 20 μmol), tris(dibenzylideneacetone) dipalladium(0) (4.6 mg, 5 μmol), tri(*o*-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0 °C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 16 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL using deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky light green solution. **DLS (water):** Z-average = 118 nm, PdI = 0.133, D_n = 71.7 nm and SD = 24.6 nm. **UV-Vis Abs. (water):** λ_{max} = 383 nm, $\lambda_{sec.}$ = 433 nm, λ_{onset} = 451 nm. **UV-Vis PL (water):** λ_{max} = 439 nm, $\lambda_{sec.}$ = 466 nm, $\lambda_{sec.}$ = 498 nm, $\lambda_{sec.}$ = 535 nm.

Example 10 - 5% 5'-Phenyl-1,1':3',1"-terphenyl Cross-Linked Polyfluorene Nanoparticles

Synthesis

[0102]

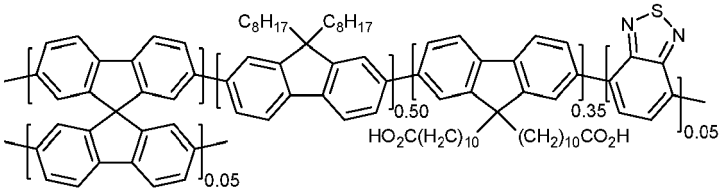


[0103] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 9,9-dioctyl-2,7-dibromofluorene (76.8 mg, 140 μmol), 3,3",5,5"-tetrabromo-5'-(3,5-dibromophenyl)-1,1':3',1"-terphenyl (15.6 mg, 20 μmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 5 μmol), tri(o-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 16 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL using deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky light green solution. **DLS (water):** Z-average = 108 nm, PdI = 0.148, D_n = 66nm and SD = 22.5 nm. **UV-Vis Abs. (water):** λ_{max} = 380 nm, $\lambda_{sec.}$ = 433 nm, λ_{onset} = 452 nm. **UV-Vis PL (water):** λ_{max} = 439 nm, $\lambda_{sec.}$ = 467 nm, $\lambda_{sec.}$ = 499 nm, $\lambda_{sec.}$ = 535 nm.

Example 11 - 5% 2,1,3-Benzothiadiazole, 35% 9,9-Di(undecanoic acid)fluorene and 5% 9,9'-Spirobifluorene Cross-Linked Polyfluorene Nanoparticles

Synthesis

[0104]

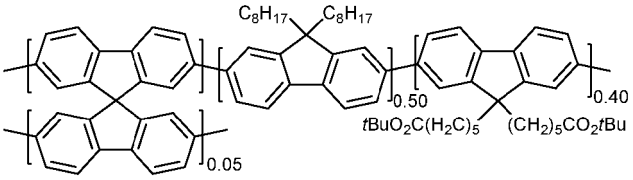


[0105] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (1080 μL, 1080 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 2,7-dibromo-9,9-di(undecanoic acid) fluorene (96.9 mg, 140 μmol), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (12.6 mg, 20 μmol), 4,7-dibromobenzo[c]-1,2,5-thiadiazole (5.9 mg, 20 μmol) tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 5 μmol), tri(*o*-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 20 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL with deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky dark green solution. **DLS (water):** *Z*-average = 79.0 nm, PdI = 0.117, D_n = 52.4 nm and SD = 15.3 nm. **UV-Vis Abs. (water):** λ_{max} = 380 nm, $\lambda_{sec.}$ = 450 nm, λ_{onset} = 520 nm. **UV-Vis PL (water):** λ_{max} = 535 nm, $\lambda_{sec.}$ = 424 nm.

Example 12 - 40% Di(t-butyl hexanoate)fluorene and 5% 9,9'-Spirobifluorene Cross-Linked Polyfluorene Nanoparticles

Synthesis

[0106]

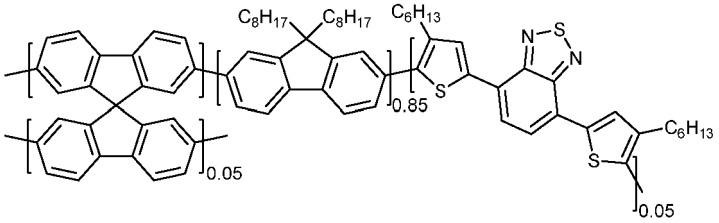


[0107] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctyl-9H-fluorene-2,7-diboronic acid bis(pinacol) ester (128.5 mg, 200 μmol), 2,7-dibromo-9,9-di(t-butyl hexanoate) fluorene (106.3 mg, 160 μmol), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (12.6 mg, 20 μmol), tetrakis (triphenylphosphine) palladium(0) (5.8 mg, 5 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 72 °C and stirred for 20 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL with deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky light green solution. **DLS (water):** *Z*-average = 129 nm, PdI = 0.226, D_n = 64 nm and SD = 23.4 nm. **UV-Vis Abs. (water):** λ_{max} = 384 nm, λ_{onset} = 441 nm. **UV-Vis PL (water):** λ_{max} = 430 nm, $\lambda_{sec.}$ = 453 nm, $\lambda_{sec.}$ = 484 nm.

Example 13 - 5% 4,7-Bis(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole and 5% 9,9'-Spirobifluorene Cross-Linked Polyfluorene Nanoparticles

Synthesis

[0108]

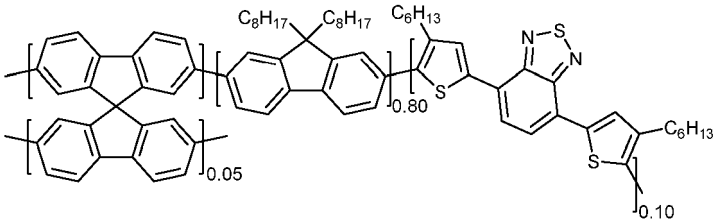


[0109] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 9,9-dioctyl-2,7-dibromofluorene (76.8 mg, 140 μmol), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (12.6 mg, 20 μmol), 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (12.5 mg, 20 μmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 5 μmol), tri(o-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 20 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL with deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky bright red solution. **DLS (water):** Z-average = 105 nm, PdI = 0.125 , D_n = 64.4 nm and SD = 20.8 nm. **UV-Vis Abs. (water):** λ_{max} = 382 nm, $\lambda_{sec.}$ = 433 nm, $\lambda_{sec.}$ = 514 nm, λ_{onset} = 620 nm. **UV-Vis PL (water):** λ_{max} = 621 nm, $\lambda_{sec.}$ = 437 nm.

Example 14 - 10% 4,7-Bis(4-hexylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole and 5% 9,9'-Spirobifluorene Cross-Linked Polyfluorene Nanoparticles

Synthesis

[0110]



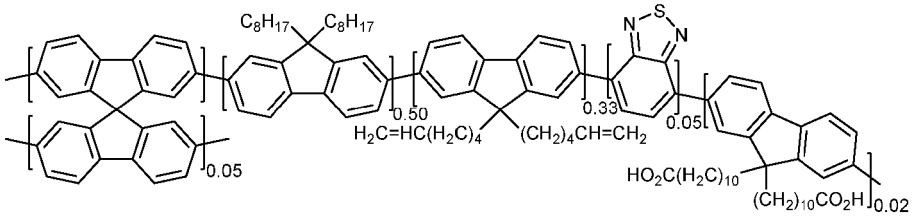
[0111] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 9,9-dioctyl-2,7-dibromofluorene (65.8 mg, 120 μmol), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (12.6 mg, 20 μmol), (25.1 mg, 40 μmol), tris(dibenzylideneacetone) dipalladium(0) (4.6 mg, 5 μmol), tri(o-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 20 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to

23.0 mL with deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky bright red solution. **DLS (water):** Z-average = 130 nm, PdI = 0.264, D_n = 58.4 nm and SD = 20.9 nm. **UV-Vis Abs. (water):** λ_{max} = 382 nm, $\lambda_{sec.}$ = 432 nm, $\lambda_{sec.}$ = 515 nm, λ_{onset} = 623 nm. **UV-Vis PL (water):** λ_{max} = 625 nm.

Example 15 - 2% 9,9-Di(undecanoic acid)fluorene, 5% 2,1,3-Benzothiadiazole, 33% Di(hex-5-en-1-yl)fluorene and 5% 9,9'-Spirobifluorene Cross-Linked Polyfluorene Nanoparticles

Synthesis

[0112]

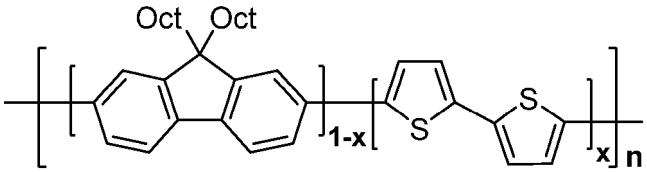


[0113] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (816 μL, 816 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 2,7-dibromo-9,9-di(undecanoic acid) fluorene (5.5 mg, 8 μmol), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (12.6 mg, 20 μmol), 4,7-dibromobenzo[c]-1,2,5-thiadiazole (5.9 mg, 20 μmol), 2,7-dibromo-9,9-di(hex-5-en-1-yl)fluorene (64.5 mg, 132 μmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 5 μmol), tri(*o*-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 20 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL with deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky dark green solution. **DLS (water):** Z-average = 101 nm, PdI = 0.166, D_n = 55.1 nm and SD = 18.1 nm. **UV-Vis Abs. (water):** λ_{max} = 381 nm, $\lambda_{sec.}$ = 453 nm, λ_{onset} = 522 nm. **UV-Vis PL (water):** λ_{max} = 530 nm.

Example 16 - CL-F8T2 CPNs

Synthesis

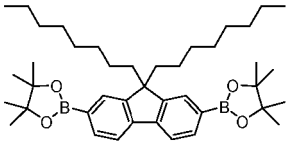
[0114]



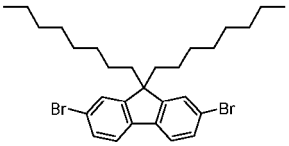
[0115] In a Schlenk tube, sodium dodecyl sulfate (50 mg) was dissolved in deionised water (10 mL) under argon. The solution was degassed by bubbling with argon for 30 minutes. In a separate vial, monomer **A** (58.6 mg, 9.12×10^{-2} mmol), monomer **B,** monomer **C** (see amounts in **Table 1),** monomer D (5.8 mg, 9.12×10^{-3} mmol), tris(dibenzylideneacetone) dipalladium(0) (0.9 mg, 0.98×10^{-3} mmol) and tri(o-tolyl)phosphine (1.2 mg, 3.9×10^{-3} mmol) were dissolved in toluene (1 mL). Hexadecane was added (78 μL) and the mixture was degassed by bubbling with argon for 5 min. After this time, the monomer mixture was then injected to the SDS solution. To promote the miniemulsion, the Schlenk tube was taken to an ice bath and the mixture was sonicated using an ultrasonicator fitted with microtip (Cole Parmer 750 W ultrasonicator, 22% amplitude) for 2 minutes. The tube was resealed and then heated up to 72 °C. Once reached this temperature, an aqueous solution of sodium hydroxide 1M (365 μL) was added and the reaction mixture was stirred for 16 h. After cooling down to room temperature, the Schlenk tube was opened and the mixture was stirred for 5 h to remove the residual toluene. To

remove SDS, 400 μL of the resulting miniemulsion was diluted with 1. 6 mL of deionised water and Amberlite XAD-2 (20 mg) previously washed with water (2 × 2 mL) was added. The mixture was stirred for 2 hours at room temperature and the Amberlite XAD-2 was removed. Treatment with Amberlite XAD-2 was repeated until the mixture was shaken and no foam formation was longer observed.

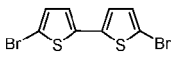
[0116] Table 15 below shows the amount of monomers B and C used. Table 16 below shows the particle size of the CL-F8T2 CPNs. Table 17 shows the optical properties of CL-F8T2 CPNs in water & THF.



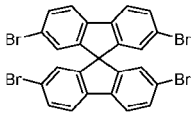
A



B



C



D

Table 15 - Initial loading of monomers **B** and **C** in CL-F8T2 CPNs

Polymer	Monomer C (% mol)	Monomer B (mass, moles)	Monomer C (mass, moles)
CL-F8T2/20	20	20 mg (3.65×10^{-2} mmol)	11.8 mg (3.65×10^{-3} mmol)
CL-F8T2/30	30	10 mg (1.82×10^{-2} mmol)	17.8 mg (5.48×10^{-2} mmol)

Table 16 - Particle size of CL-F8T2 CPNs in water & THF

	Water			THF		
Polymer	**d_z (nm)**	**PdI**	**D_{Num} (nm)**	**d_z (nm)**	**PdI**	**D_{Num} (nm)**
CL-F8T2/20	105	0.158	64	124	0.212	62
CL-F8T2/30	103	0.178	53	120	0.223	63

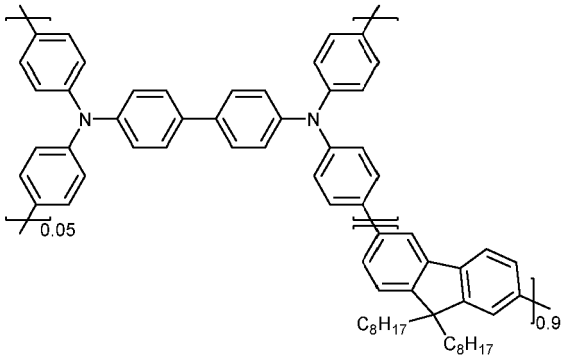
Table 17 - optical properties of CL-F8T2 CPNs in water & THF

	Water		THF	
Polymer	Absorption λ_{max} (nm)	Fluorescence λ_{max} (nm)	Absorption λ_{max} (nm)	Fluorescence λ_{max} (nm)
CL-F8T2/20	386	554	394	525
CL-F8T2/30	431	541	438	498

Example 17 - **5% *N,N,N',N'*-Tetraphenylbenzidine Cross-Linked Polyfluorene Nanoparticles**

Synthesis

[0117]

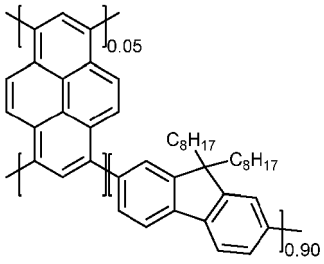


[0118] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 9,9-dioctyl-2,7-dibromofluorene (87.8 mg, 160 μmol), N^4,N^4,$N^{4'}$,$N^{4'}$-tetrakis(4-bromophenyl)-[1,1'-biphenyl]-4,4'-diamine (16.1 mg, 20 μmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 5 μmol), tri(o-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 16 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL using deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky light green solution. **DLS (water):** Z-average = 112 nm, PdI = 0.150, D_n = 72.5 nm and SD = 22.3 nm. **UV-Vis Abs. (water):** λ_{max} = 384 nm, $\lambda_{sec.}$ = 433 nm, λ_{onset} = 452 nm. **UV-Vis PL (water):** λ_{max} = 438 nm, $\lambda_{sec.}$ = 467 nm, $\lambda_{sec.}$ = 496 nm, $\lambda_{sec.}$ = 535 nm.

Example 18 - 5% **Pyrene Cross-Linked Polyfluorene Nanoparticles**

Synthesis

[0119]

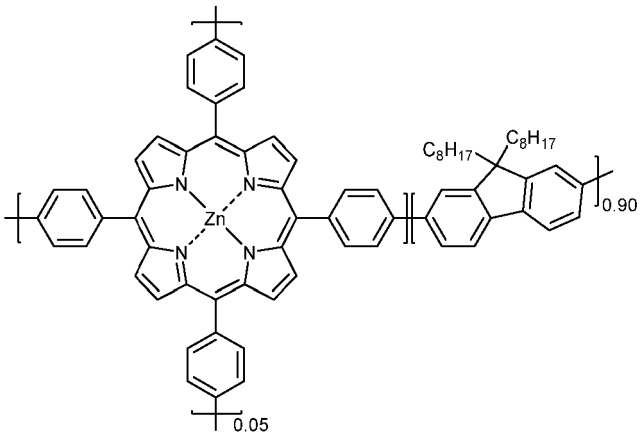


[0120] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctyl-9H-fluorene-2,7-diboronic acid bis(pinacol) ester (128.5 mg, 200 μmol), 9,9-dioctyl-2,7-dibromofluorene (87.8 mg, 160 μmol), 1,3,6,8-tetrabromopyrene (10.4 mg, 20 μmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 5 μmol), tri(*o*-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 72 °C and stirred for 20 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL with deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky light green solution. **DLS (water):** Z-average = 103 nm, PdI = 0.141, D_n = 71.5 nm and SD = 21.8 nm. **UV-Vis Abs. (water):** λ_{max} = 376 nm, $\lambda_{sec.}$ = 432 nm, λ_{onset} = 452 nm. **UV-Vis PL (water):** λ_{max} = 439 nm, $\lambda_{sec.}$ = 466 nm, $\lambda_{sec.}$ = 498 nm, $\lambda_{sec.}$ = 532 nm.

Example 19 - 5% 5,10,15,20-tetrakis(4-bromophenyl)-21*H*,23*H*-porphine (Zinc) Cross-Linked Polyfluorene Nanoparticles

Synthesis

[0121]

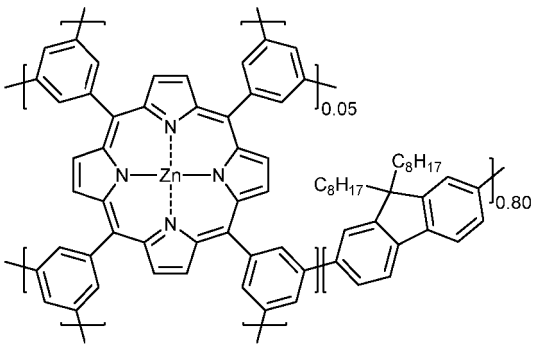


[0122] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 9,9-dioctyl-2,7-dibromofluorene (87.8 mg, 160 μmol), 5,10, 15,20-tetrakis(4-bromophenyl)-21*H*,23*H*-porphine (zinc) (19.9 mg, 20 μmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 5 μmol), tri(o-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 16 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL using deionised water and filtered through a glass wool plug. The emulsion was obtained as a dark green solution. **DLS (water):** Z-average = 95.0 nm, PdI = 0.135, D_n = 64.1 nm and SD = 19.7 nm. **UV-Vis Abs. (water):** λ_{max} = 380 nm, $\lambda_{sec.}$ = 396 nm, $\lambda_{sec.}$ = 433 nm, $\lambda_{sec.}$ = 550 nm, $\lambda_{sec.}$ = 596 nm, λ_{onset} = 625 nm. **UV-Vis PL (water):** λ_{max} = 440 nm, $\lambda_{sec.}$ = 466 nm, $\lambda_{sec.}$ = 498 nm, $\lambda_{sec.}$ = 532 nm, $\lambda_{sec.}$ = 605 nm, $\lambda_{sec.}$ = 650 nm.

Example 20 - 5% 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine (Zinc) Cross-Linked Polyfluorene Nanoparticles

Synthesis

[0123]



[0124] In a Schlenk tube was added water (22.0 mL), sodium dodecyl sulfate (110 mg, 382 μmol) and 1M aqueous sodium hydroxide (800 μL, 800 μmol). The solution was purged with argon for 2 hours. In a vial was weighed 9,9-

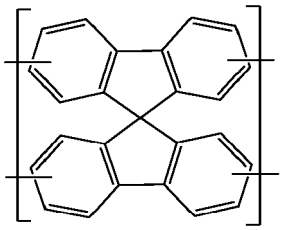
dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (111.7 mg, 200 μmol), 9,9-dioctyl-2,7-dibromofluorene (65.8 mg, 120 μmol), 5,10,15,20-tetrakis(3,5-dibromophenyl)-21*H*,23*H*-porphine (zinc) (26.2 mg, 20 μmol), tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 5 μmol), tri(o-tolyl)phosphine (9.1 mg, 30 μmol) and hexadecane (171 μL, 585 μmol). The vial was transferred to an argon filled glovebox, sealed with a rubber septum and removed. Toluene (2.19 mL) was added to the vial and the suspension sonicated until a homogenous solution was achieved. The initial aqueous solution was cooled to 0°C in an ice bath, the ultrasonic probe inserted and the toluene solution injected rapidly into the water. The solution was ultrasonicated for 1 minute, stirred for 30 seconds and ultrasonicated for 1 further minute. The Schlenk tube was sealed, placed in a preheated oil bath at 50 °C and stirred for 16 hours. The Schlenk was opened and a stream of nitrogen gas passed over the emulsion at 50 °C, with stirring. The emulsion was cooled to room temperature, the volume increased to 23.0 mL using deionised water and filtered through a glass wool plug. The emulsion was obtained as a milky dark green solution. **DLS (water):** Z-average = 98.4 nm, PdI = 0.151, D_n = 59.9 nm and SD = 19.4 nm. **UV-Vis Abs. (water):** λ_{max} = 377 nm, $\lambda_{sec.}$ = 432 nm, λ_{onset} = 451 nm. **UV-Vis PL (water):** λ_{max} = 439 nm, $\lambda_{sec.}$ = 466 nm, $\lambda_{sec.}$ = 499 nm, $\lambda_{sec.}$ = 534 nm, $\lambda_{sec.}$ = 596 nm, $\lambda_{sec.}$ = 644 nm.

[0125] While specific embodiments of the invention have been described herein for the purpose of reference and illustration, various modifications will be apparent to a person skilled in the art without departing from the scope of the invention as defined by the appended claims.

Claims

1. A nanoparticle composition comprising a plurality of nanoparticles formed from a π-conjugated cross-linked polymer, the π-conjugated cross-linked polymer comprising

   a) 80-99.9 mol.% of π-conjugated monomers, and
   b) 0.1-20 mol.% of a cross-linker having the formula III shown below:

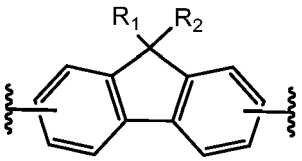


(III)

   wherein
   the nanoparticles forming the nanoparticle composition have a Z-average particle size of less than 30-200 nm, when measured by DLS in water.

2. The nanoparticle composition of claim 1, comprising 4.5-10 mol.% of the cross-linker.

3. The nanoparticle composition of any preceding claim, wherein the π-conjugated monomers each independently comprise a moiety having the formula IV shown below:



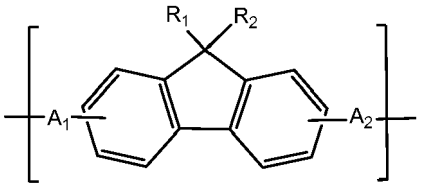
(IV)

   wherein
   R_1 and R_2 are each independently a group:

-X-Q

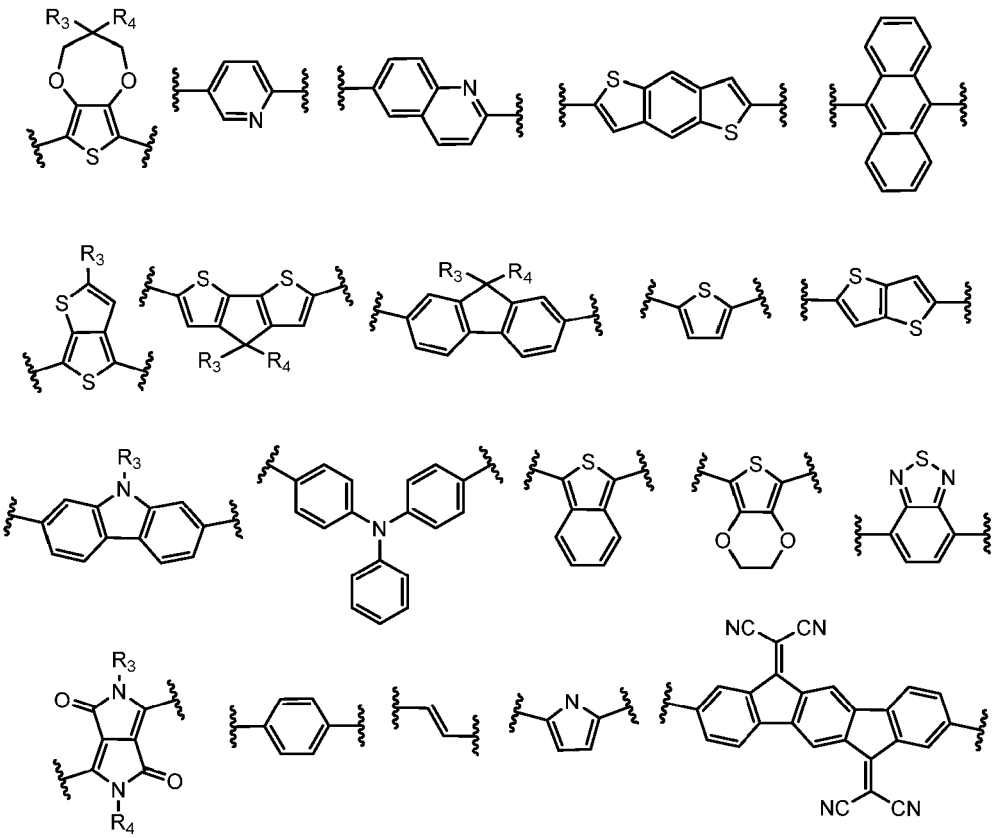
wherein

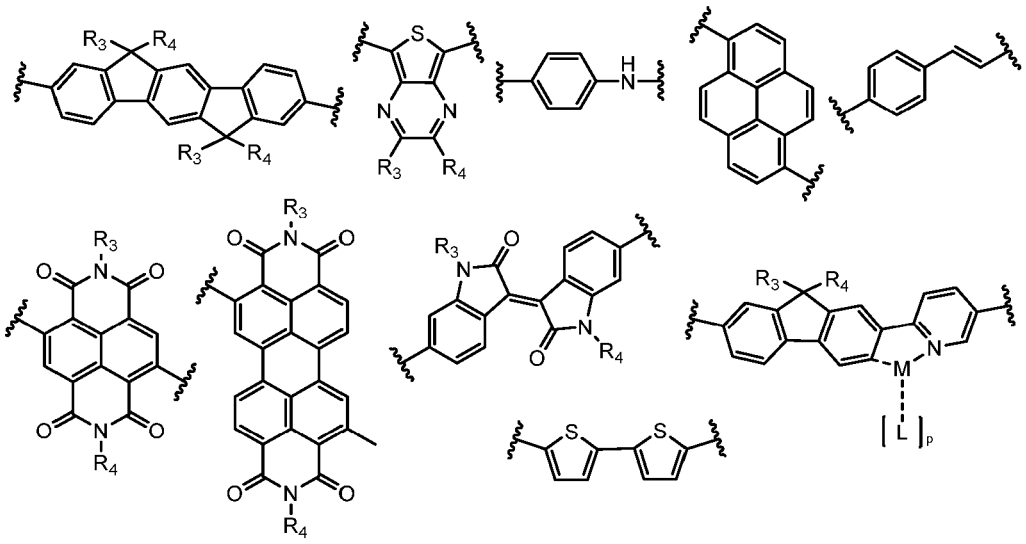
X is selected from the group consisting of (1-30C)alkylene, (2-30C)alkenylene, (2-30C)alkynylene, -[$(CH_2)_2$-O]$_n$-, -[O-$(CH_2)_2$]$_n$-, - $(CH_2)_m(CF_2)_n$-, and -[O-Si$(R_z)_2$]$_n$- (wherein R_z is (1-4C)alkyl, n is 1 to 30, and m is 0 to 30), and Q is a terminal group selected from hydrogen, methyl, hydroxyl, carboxy, (1-4C)alkoxycarbonyl, amino, -C=CH_2, -C≡CH, -SH, -biotin, -streptavidin, -CF_3 and a polymerisable group selected from acrylates, epoxy and styrene; or R_1 and R_2 are linked so that, together with the carbon atom to which they are attached, they form a ring;
or
the π-conjugated monomers each independently have a structure according to formula V shown below:



(V)

wherein
A_1 and A_2 are independently absent or selected from any one of the following moieties:





wherein

R_3 and R_4 are each independently a group:

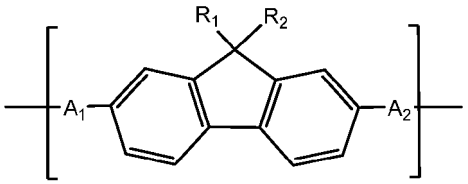
$$-X^1-Q^1$$

wherein

X^1 is selected from the group consisting of (1-30C)alkylene, (2-30C)alkenylene, (2-30C)alkynylene, $-[(CH_2)_2-O]_n-$, $-[O-(CH_2)_2]_n-$, $-(CH_2)_m(CF_2)_n-$,and $-[O-Si(R_z)_2]_n-$ (wherein R_z is (1-4C)alkyl, n is 1 to 30, and m is 0 to 30), and
Q^1 is a terminal group selected from hydrogen, methyl, hydroxyl, carboxy, (1-4C)alkoxycarbonyl, amino, $-C=CH_2$, $-C\equiv CH$, -SH, -biotin, - streptavidin, $-CF_3$, and a polymerisable group selected from acrylates, epoxy and styrene;

M is a metal selected from Ir, Pt, Rh, Re, Ru, Os, Cr, Cu, Pd and Au;
L is a ligand independently selected from the group consisting of halo, (1-30C)hydrocarbyl optionally comprising one or more heteroatoms selected from N, O, S, Si or P, or an aryl or heteroaryl group optionally substituted with one or more substituents selected from (1-4C)alkyl, halo, aryl or heteroaryl; and
p is 1 to 4;

or
the π-conjugated monomers each independently have a structure defined by formula VI below:

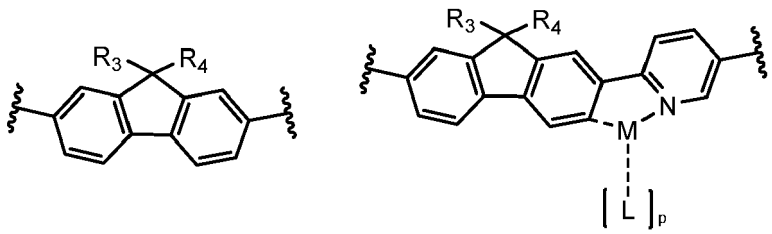


(VI)

wherein

R_1 and R_2 are as defined above; and
A_1 and A_2 are as defined above.

4. The nanoparticle composition of claim 3, wherein A_1 and A_2 are independently absent or selected from any one of the following moieties:



wherein R_3, R_4, M, L and p are as defined in claim 5;
or
A_1 or A_2 is absent;
or
A_1 and A_2 are absent.

5. The nanoparticle composition of any of claims 3 or 4, wherein R_1 and R_2 are each independently a group:

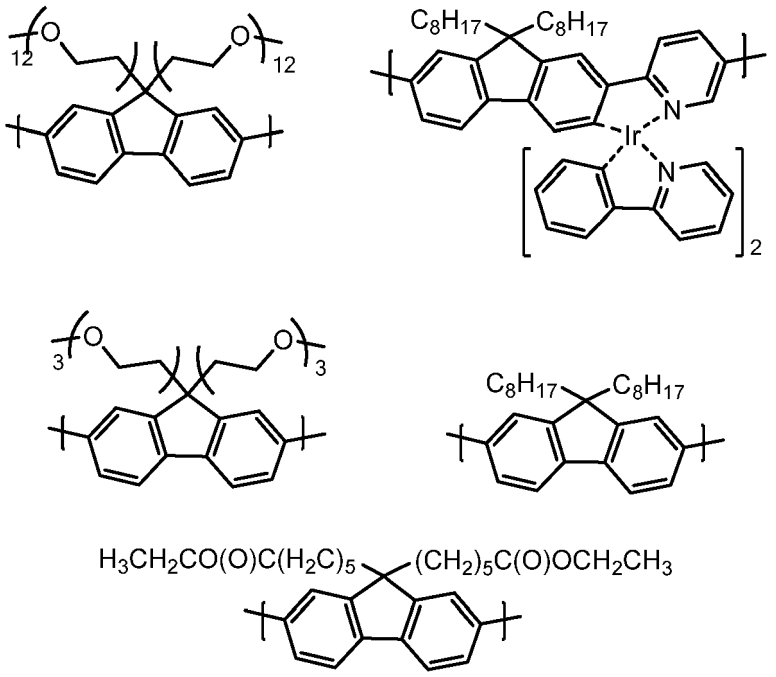
-X-Q

wherein
X and Q are as defined in claim 3.

6. The nanoparticle composition of any of claims 3 to 5, wherein when present X and X^1 are independently selected from the group consisting of (1-30C)alkylene, (2-30C)alkenylene, (2-30C)alkynylene, , $-[(CH_2)_2-O]_n-$ or $-[O-(CH_2)_2]_n-$ (wherein n is 1 to 30);

Q and Q^1 are independently a terminal group selected from hydrogen, methyl, hydroxyl, carboxy, (1-4C) alkoxycarbonyl, amino, $-C=CH_2$ or $-C\equiv CH$;
M is a metal selected from Ir, Pt, Rh, Re, Ru, Os, Cr, Cu, Pd and Au;
L is a ligand independently selected from the group consisting of halo, (1-30C)hydrocarbyl optionally comprising one or more heteroatoms selected from N, O, S, Si or P, or an aryl or heteroaryl group optionally substituted with one or more substituents selected from (1-4C)alkyl, halo, aryl or heteroaryl; and
p is 1 to 4;
or
when present X and X^1 are independently selected from the group consisting of (1-20C)alkylene, $-[(CH_2)_2-O]_n-$ or $-[O-(CH_2)_2]_n-$ (wherein n is 1 to 20);
Q and Q^1 are independently a terminal group selected from hydrogen, methyl, hydroxyl, carboxy, (1-4C) alkoxycarbonyl and amino;
M is a metal selected from Ir, Pt, Cr, Cu, Pd and Au;
L is a ligand independently selected from the group consisting of aryl or heteroaryl, optionally substituted with one or more substituents selected from (1-4C)alkyl, halo, aryl or heteroaryl; and
p is 1 to 4;
or
wherein when present X and X^1 are independently selected from the group consisting of (1-20C)alkylene, $-[(CH_2)_2-O]_n-$ or $-[O-(CH_2)_2]_n-$ (wherein n is 1 to 20);
Q and Q^1 are independently a terminal group selected from hydrogen, methyl, (1-2C)alkoxycarbonyl and hydroxyl;
M is Ir;
L is a ligand independently selected from the group consisting of aryl or heteroaryl, optionally substituted with one or more substituents selected from aryl or heteroaryl; and p is 1 to 2;
or
when present X and X^1 are independently selected from the group consisting of (4-12C)alkylene or $-[(CH_2)_2-O]_n-$ (wherein n is 1 to 15);
Q and Q^1 are independently a terminal group selected from hydrogen, (1-2C)alkoxycarbonyl and methyl;
M is Ir;
L is a ligand independently selected from the group consisting of phenyl or 6-membered heteroaryl, optionally substituted with one or more substituents selected from phenyl or 6-membered heteroaryl; and
p is 1 to 2.

7. The nanoparticle composition of claim 1 wherein the π-conjugated cross-linked polymer comprises 80-99.9 mol.% of π-conjugated monomers selected from at least one of the following structures:



8. A method of forming a nanoparticle composition as claimed in any preceding claim, the method comprising the step of forming the nanoparticles by emulsion polymerisation, miniemulsion polymerisation or dispersion polymerisation techniques to provide an aqueous suspension of nanoparticles; and
wherein the nanoparticles are optionally formed by a cross-coupling polymerisation reaction.

9. The method of claim 8, wherein the cross-coupling polymerisation reaction is a Suzuki and/or Stille reaction.

10. The method of claim 8 or claim 9, further comprising the step of purifying the aqueous suspension of nanoparticles.

11. The method of claim 10, wherein the aqueous suspension of nanoparticles is purified by contacting the aqueous suspension of nanoparticles with at least one organic solvent.

12. The method of claim 11, wherein the at least one organic solvent is selected from the group consisting of polar and non-polar solvents;
or
the at least one organic solvent is methanol.

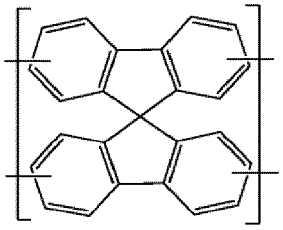
13. Use of a nanoparticle composition as defined in any of claims 1 to 7 in one or more applications selected from the group consisting of biological or non-biological imaging or sensing, down-conversion of LED light, anti-counterfeit encoding, displays, cell-sorting/flow cytometry, long-term cell tracking, and flow visualisation.

14. A nanoparticle dispersion comprising a nanoparticle composition as claimed in any one of claims 1 to 7 dispersed throughout a dispersing medium.

Patentansprüche

1. Nanopartikelzusammensetzung umfassend eine Vielzahl von Nanopartikeln, die aus einem π-konjugierten vernetzten Polymer gebildet sind, wobei das π-konjugierte vernetzte Polymer

a) 80-99,9 Mol-% π-konjugierte Monomere und
b) 0,1-20 Mol-% eines Vernetzers mit der nachstehend dargestellten Formel III

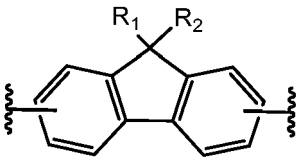


(III)

umfasst, wobei
die Nanopartikel, die die Nanopartikelzusammensetzung bilden, eine Z-durchschnittliche Partikelgröße von weniger als 30-200 nm aufweisen, wenn durch DLS in Wasser gemessen.

2. Nanopartikelzusammensetzung nach Anspruch 1, umfassend 4,5-10 Mol-% des Vernetzers.

3. Nanopartikelzusammensetzung nach einem beliebigen vorhergehenden Anspruch, wobei die π-konjugierten Monomere jeweils unabhängig eine Moietät mit der nachstehend dargestellten Formel IV:



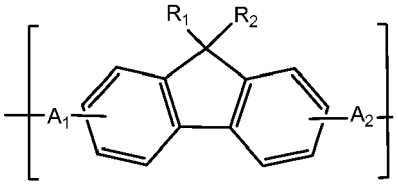
(IV)

umfassen, wobei
R_1 und R_2 jeweils unabhängig eine Gruppe:

-X-Q

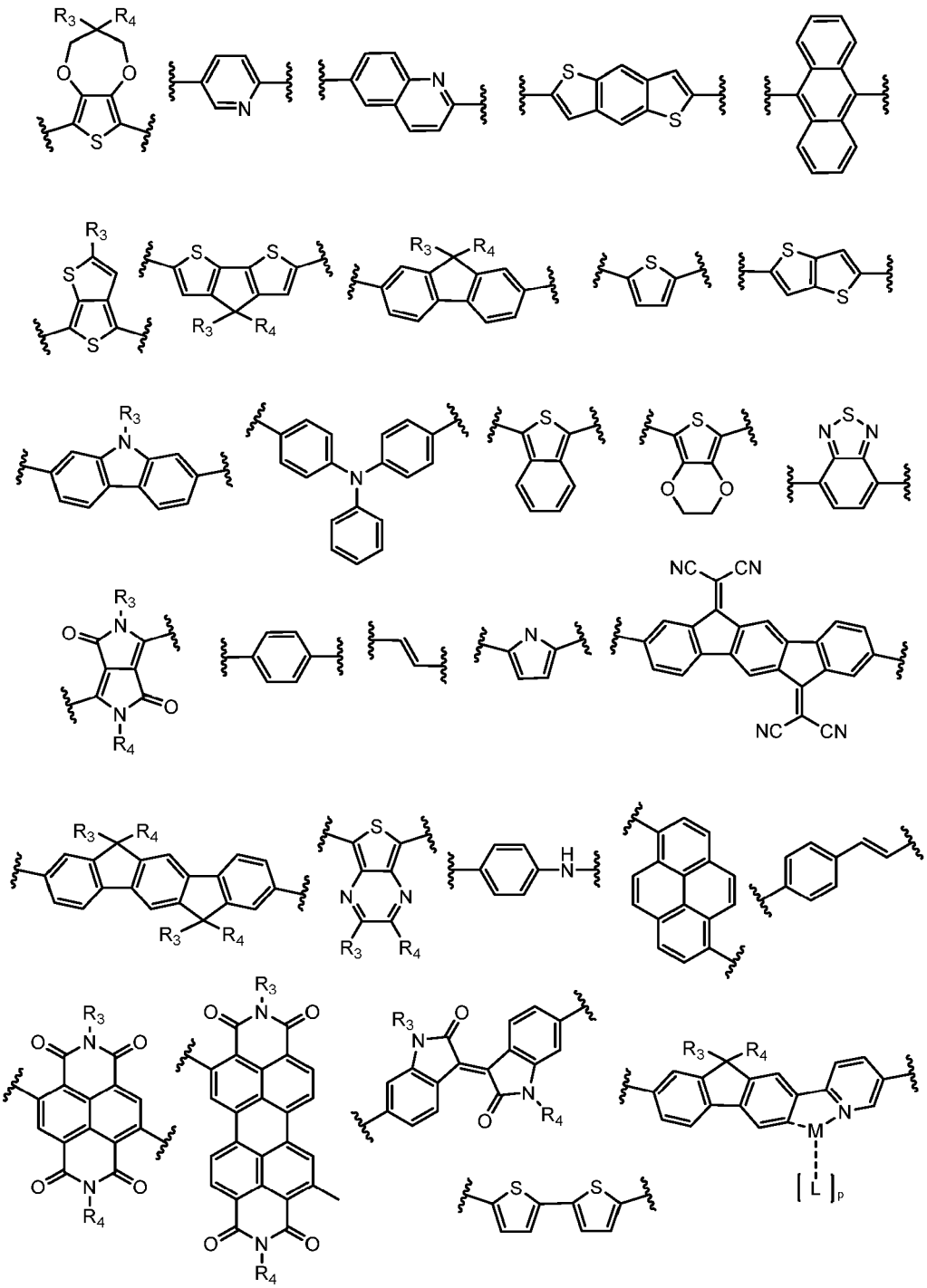
sind, wobei

X ausgewählt ist aus der Gruppe bestehend aus (1-30C)Alkylen, (2-30C)Alkenylen, (2-30C)Alkinylen, $-[(CH_2)_2-O]_n-$, $-[O-(CH_2)_2]_n-$, $-(CH_2)_m(CF_2)_n-$ und $-[O-Si(R_z)_2]_n-$ (wobei R_z (1-4C)Alkyl ist, n 1 bis 30 ist und m 0 bis 30 ist), und
Q eine terminale Gruppe ausgewählt aus Wasserstoff, Methyl, Hydroxyl, Carboxy, (1-4C)Alkoxycarbonyl, Amino, $-C=CH_2$, $-C\equiv CH$, -SH, -Biotin, -Streptavidin, $-CF_3$ und eine polymerisierbare Gruppe ausgewählt aus Acrylaten, Epoxy und Styrol ist;
oder R_1 und R_2 verknüpft sind, so dass sie zusammen mit dem Kohlenstoffatom, an das sie gebunden sind, einen Ring bilden;
oder
die π-konjugierten Monomere jeweils unabhängig eine Struktur gemäß der nachstehend dargestellten Formel V: aufweisen, wobei



(V)

A_1 und A_2 unabhängig fehlen oder ausgewählt sind aus einer beliebigen der folgenden Moietäten:



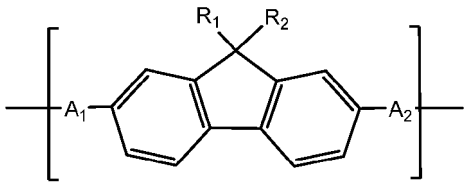
wobei
R_3 und R_4 jeweils unabhängig eine Gruppe:

$$-X^1-Q^1$$

sind, wobei

X^1 ausgewählt ist aus der Gruppe bestehend aus (1-30C)Alkylen, (2-30C)Alkenylen, (2-30C)Alkinylen, $-[(CH_2)_2-O]_n-$, $-[O-(CH_2)_2]_n-$, $-(CH_2)_m(CF_2)_n-$ und $-[O-Si(R_z)_2]_n-$ (wobei R_z (1-4C)Alkyl ist, n 1 bis 30 ist und m 0 bis 30 ist), und
Q^1 eine terminale Gruppe ausgewählt aus Wasserstoff, Methyl, Hydroxyl, Carboxy, (1-4C)Alkoxycarbonyl, Amino, $-C=CH_2$, $-C\equiv CH$, -SH, -Biotin, -Streptavidin, $-CF_3$ und eine polymerisierbare Gruppe ausgewählt aus

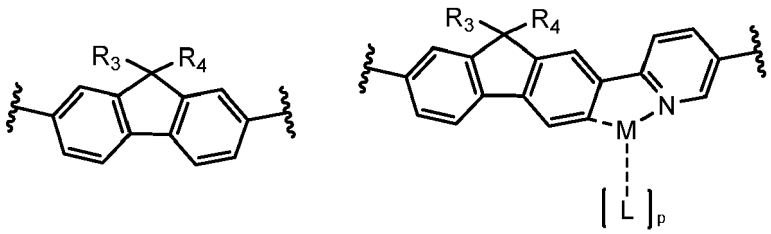
Acrylaten, Epoxy und Styrol ist;
M ein Metall ausgewählt aus Ir, Pt, Rh, Re, Ru, Os, Cr, Cu, Pd und Au ist;
L ein Ligand, unabhängig ausgewählt aus der Gruppe bestehend aus Halo, (1-30C)Hydrocarbyl, optional umfassend ein oder mehrere Heteroatome, ausgewählt aus N, O, S, Si oder P, oder einer Aryl- oder Heteroarylgruppe, optional substituiert mit einem oder mehreren Substituenten, ausgewählt aus (1-4C) Alkyl, Halo, Aryl oder Heteroaryl, ist;und p 1 bis 4 ist;
oder
die π-konjugierten Monomere jeweils unabhängig eine von der nachstehenden Formel VI definierte Struktur:



(VI)

aufweisen, wobei
R_1 und R_2 wie oben definiert sind; und
A_1 und A_2 wie oben definiert sind.

4. Nanopartikelzusammensetzung nach Anspruch 3, wobei A_1 und A_2 unabhängig fehlen oder ausgewählt sind aus einer beliebigen der folgenden Moietäten:



wobei R_3, R_4, M, L und p wie in Anspruch 5 definiert sind;
oder
A_1 oder A_2 fehlt;
oder
A_1 und A_2 fehlen.

5. Nanopartikelzusammensetzung nach einem der Ansprüche 3 oder 4, wobei R_1 und R_2 jeweils unabhängig eine Gruppe:

-X-Q

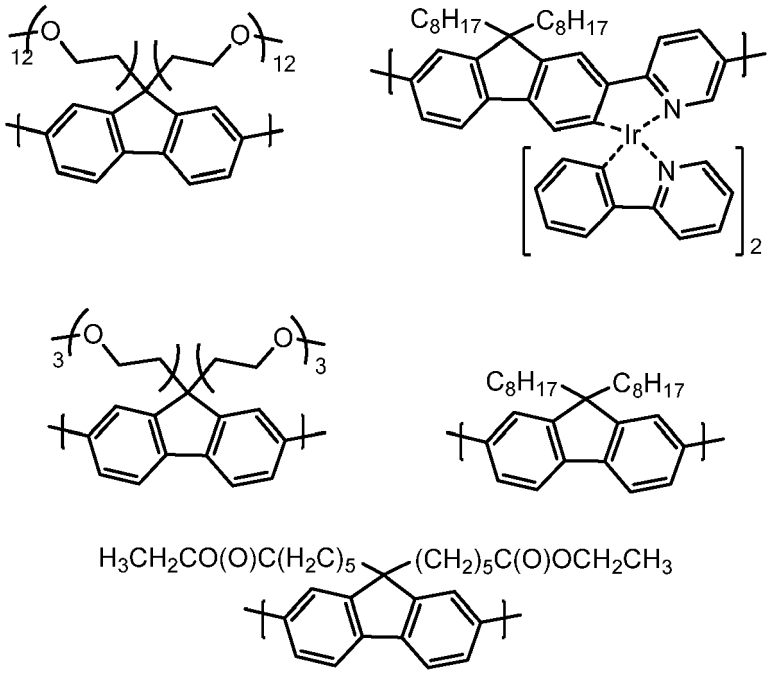
sind, wobei
X und Q wie in Anspruch 3 definiert sind.

6. Nanopartikelzusammensetzung nach einem der Ansprüche 3 bis 5, wobei, wenn vorhanden, X und X^1 unabhängig ausgewählt sind aus der Gruppe bestehend aus (1-30C)Alkylen, (2-30C)Alkenylen, (2-30C)Alkinylen, $-[(CH_2)_2-O]_n-$ oder $-[O-(CH_2)_2]_n-$ (wobei n 1 bis 30 ist);

Q und Q^1 unabhängig eine terminale Gruppe ausgewählt aus Wasserstoff, Methyl, Hydroxyl, Carboxy, (1-4C) Alkoxycarbonyl, Amino, $-C=CH_2$ oder $-C\equiv CH$ sind;
M ein Metall ausgewählt aus Ir, Pt, Rh, Re, Ru, Os, Cr, Cu, Pd und Au ist;
L ein Ligand, unabhängig ausgewählt aus der Gruppe bestehend aus Halo, (1-30C)Hydrocarbyl, optional umfassend ein oder mehrere Heteroatome, ausgewählt aus N, O, S, Si oder P, oder einer Aryl- oder Heteroarylgruppe, optional substituiert mit einem oder mehreren Substituenten, ausgewählt aus (1-4C)Alkyl, Halo, Aryl

oder Heteroaryl, ist; und p 1 bis 4 ist;
oder
wenn vorhanden, X und X^1 unabhängig ausgewählt sind aus der Gruppe bestehend aus (1-20C)Alkylen, $-[(CH_2)_2-O]_n-$ oder $-[O-(CH_2)_2]_n-$ (wobei n 1 bis 20 ist);
Q und Q^1 unabhängig eine terminale Gruppe ausgewählt aus Wasserstoff, Methyl, Hydroxyl, Carboxy, (1-4C) Alkoxycarbonyl und Amino sind;
M ein Metall ausgewählt aus Ir, Pt, Cr, Cu, Pd und Au ist;
L ein Ligand, unabhängig ausgewählt aus der Gruppe bestehend aus Aryl oder Heteroaryl, optional substituiert mit einem oder mehreren Substituenten, ausgewählt aus (1-4C)Alkyl, Halo, Aryl oder Heteroaryl, ist; und
p 1 bis 4 ist;
oder
wobei, wenn vorhanden, X und X^1 unabhängig ausgewählt sind aus der Gruppe bestehend aus (1-20C)Alkylen, $-[(CH_2)_2-O]_n-$ oder $-[O-(CH_2)_2]_n-$ (wobei n 1 bis 20 ist);
Q und Q^1 unabhängig eine terminale Gruppe ausgewählt aus Wasserstoff, Methyl, (1-2C)Alkoxycarbonyl und Hydroxyl sind;
M Ir ist,
L ein Ligand, unabhängig ausgewählt aus der Gruppe bestehend aus Aryl oder Heteroaryl, optional substituiert mit einem oder mehreren Substituenten, ausgewählt aus Aryl oder Heteroaryl, ist; und p 1 bis 2 ist;
oder
wenn vorhanden, X und X^1 unabhängig ausgewählt sind aus der Gruppe bestehend aus (4-12C)Alkylen oder $-[(CH_2)_2-O]_n-$ (wobei n 1 bis 15 ist);
Q und Q^1 unabhängig eine terminale Gruppe ausgewählt aus Wasserstoff, (1-2C)Alkoxycarbonyl und Methyl sind;
M Ir ist,
L ein Ligand, unabhängig ausgewählt aus der Gruppe bestehend aus Phenyl oder 6-gliedrigem Heteroaryl, optional substituiert mit einem oder mehreren Substituenten, ausgewählt aus Phenyl oder 6-gliedrigem Heteroaryl, ist; und p 1 bis 2 ist.

7. Nanopartikelzusammensetzung nach Anspruch 1, wobei das π-konjugierte vernetzte Polymer 80-99,9 Mol-% π-konjugierte Monomere umfasst, die aus mindestens einer der folgenden Strukturen ausgewählt sind:



8. Verfahren zum Bilden einer Nanopartikelzusammensetzung nach einem beliebigen vorhergehenden Anspruch, wobei das Verfahren den Schritt des Bildens der Nanopartikel durch Emulsionspolymerisations-, Miniemulsionspolymerisations- oder Dispersionspolymerisationstechniken umfasst, um eine wässrige Suspension aus Nanopartikeln bereitzustellen; und

wobei die Nanopartikel optional durch eine Kreuzkupplungspolymerisationsreaktion gebildet sind.

9. Verfahren nach Anspruch 8, wobei die Kreuzkupplungspolymerisationsreaktion eine Suzuki- und/oder Stille-Reaktion ist.

10. Verfahren nach Anspruch 8 oder Anspruch 9, ferner umfassend den Schritt des Reinigens der wässrigen Suspension aus Nanopartikeln.

11. Verfahren nach Anspruch 10, wobei die wässrige Suspension aus Nanopartikeln durch Inkontaktbringen der wässrigen Suspension aus Nanopartikeln mit mindestens einem organischen Lösungsmittel gereinigt wird.

12. Verfahren nach Anspruch 11, wobei das mindestens eine organische Lösungsmittel ausgewählt ist aus der Gruppe bestehend aus polaren und nicht-polaren Lösungsmitteln;
oder
das mindestens eine organische Lösungsmittel Methanol ist.

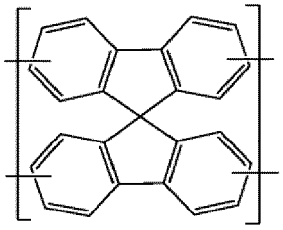
13. Verwendung einer Nanopartikelzusammensetzung wie in einem beliebigen der Ansprüche 1 bis 7 definiert in einer oder mehreren Anwendungen, die ausgewählt sind aus der Gruppe bestehend aus biologischer oder nicht-biologischer Bildgebung oder Sensorik, Herunterkonvertierung von LED-Licht, fälschungssicherer Kodierung, Displays, Zellsortierung/Durchflusszytometrie, Langzeit-Zelltracking und Strömungsvisualisierung.

14. Nanopartikeldispersion, umfassend eine Nanopartikelzusammensetzung nach einem beliebigen der Ansprüche 1 bis 7, die in einem Dispersionsmedium dispergiert ist.

Revendications

1. Composition de nanoparticules comprenant une pluralité de nanoparticules formées à partir d'un polymère réticulé π conjugué, le polymère réticulé π conjugué comprenant

a) 80-99,9 mol. % de monomères π conjugués, et
b) 0,1-20 mol. % d'un agent de réticulation comportant la formule III ci-dessous :

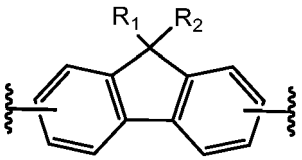


(III)

dans laquelle
les nanoparticules formant la composition de nanoparticules comportent une dimension de particule moyenne Z de moins de 30-200 nm, mesurée par DLS dans l'eau.

2. Composition de nanoparticules selon la revendication 1, comprenant 4,5-10 mol. % de l'agent de réticulation.

3. Composition de nanoparticules selon l'une quelconque des revendications précédentes, dans laquelle les monomères π conjugués comprennent chacun indépendamment une fraction comportant la formule IV ci-dessous :



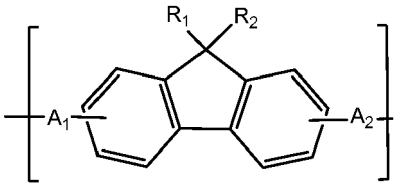
(IV)

dans laquelle
R_1 et R_2 sont chacun indépendamment un groupe :

-X-Q

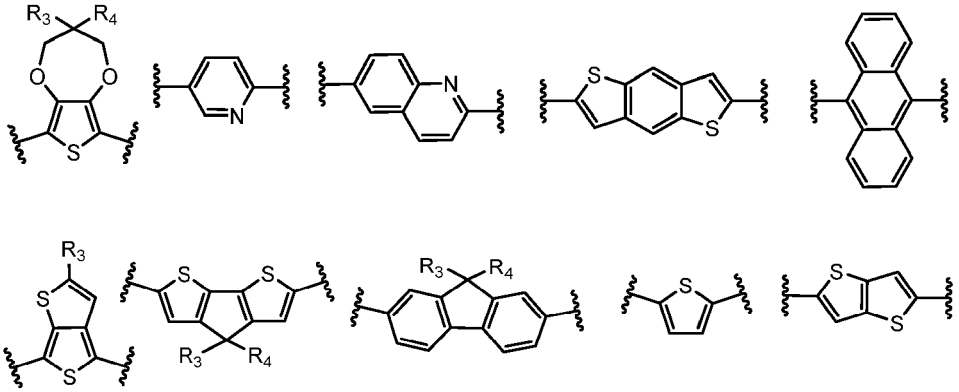
dans lequel

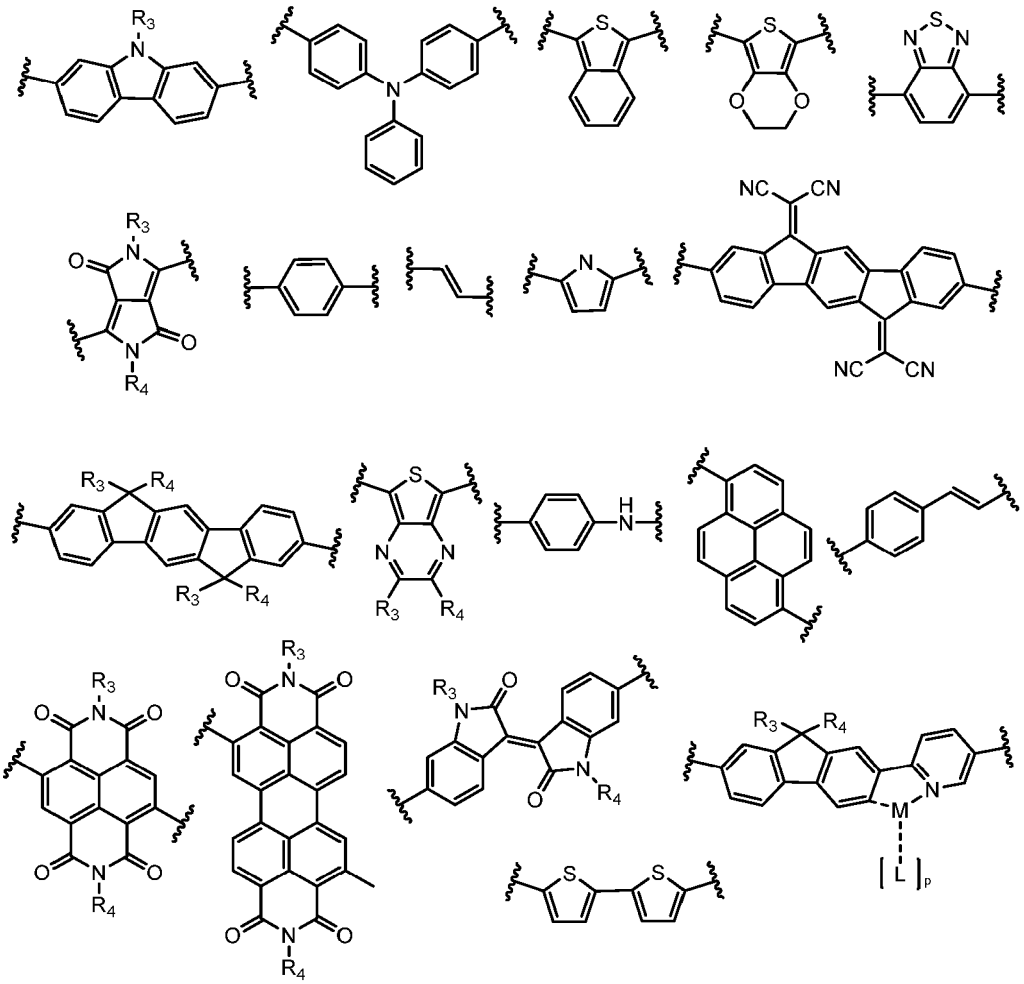
X est sélectionné dans le groupe constitué de (1-30C)alkylène, (2-30C)alkénylène, (2-30C)alkynylène, $-[(CH_2)_2-O]_n-$, $-[O-(CH_2)_2]_n-$, $-(CH_2)_m(CF_2)_n-$, et $-[O-Si(R_z)_2]_n-$ (dans lequel R_z est (1-4C)alkyle, n est 1 à 30, et m est 0 à 30), et
Q est un groupe terminal sélectionné parmi hydrogène, méthyle, hydroxyle, carboxy, (1-4C)alkoxycarbonyle, amino, $-C=CH_2$, $-C\equiv CH$, -SH, -biotine, -streptavidine, $-CF_3$ et un groupe polymérisable sélectionné parmi acrylates, époxy et styrène ;
ou R_1 et R_2 sont reliés de sorte que, conjointement avec l'atome de carbone auquel ils sont fixés, ils forment un anneau ;
ou
les monomères π conjugués comportent chacun indépendamment une structure conforme à la formule V ci-dessous :



(V)

dans laquelle
A_1 et A_2 sont indépendamment absents ou sélectionnés dans l'une quelconque des fractions suivantes :



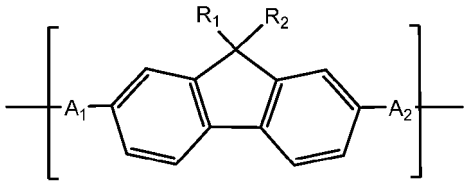


dans lesquelles
R_3 et R_4 sont chacun indépendamment un groupe :

$$-X^1-Q^1$$

dans lequel

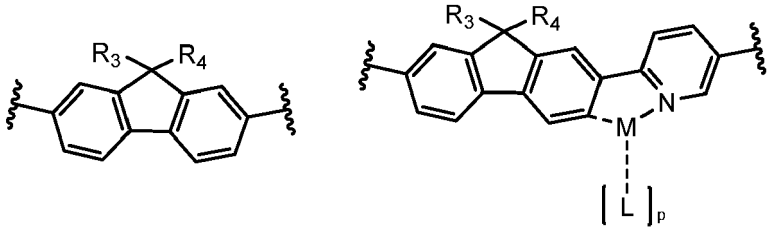
X^1 est sélectionné dans le groupe constitué de (1-30C)alkylène, (2-30C)alkénylène, (2-30C)alkynylène, $-[(CH_2)_2-O]_n-$, $-[O-(CH_2)_2]_n-$, $-(CH_2)_m(CF_2)_n-$, et $-[O-Si(R_z)_2]_n-$ (dans lequel R_z est (1-4C)alkyle, n est 1 à 30, et m est 0 à 30), et
Q^1 est un groupe terminal sélectionné parmi hydrogène, méthyle, hydroxyle, carboxy, (1-4C)alkoxycarbonyle, amino, $-C=CH_2$, $-C\equiv CH$, -SH, -biotine, - streptavidine, $-CF_3$, et un groupe polymérisable sélectionné parmi acrylates, époxy et styrène;
M est un métal sélectionné parmi Ir, Pt, Rh, Re, Ru, Os, Cr, Cu, Pd et Au ;
L est un ligand indépendamment sélectionné dans le groupe constitué de halo, (1-30C)hydrocarbyle comprenant éventuellement un ou plusieurs hétéroatomes sélectionnés parmi N, O, S, Si ou P, ou un groupe aryle ou hétéroaryle éventuellement substitué par un ou plusieurs substituants sélectionnés parmi (1-4C)alkyle, halo, aryle ou hétéroaryle ; et
p est 1 à 4 ;
ou
les monomères π conjugués comportent chacun indépendamment une structure définie par la formule VI ci-dessous :



(VI)

dans laquelle
R_1 et R_2 sont tels que définis ci-dessus ; et
A_1 et A_2 sont tels que définis ci-dessus.

4. Composition de nanoparticules selon la revendication 3, dans laquelle A_1 et A_2 sont indépendamment absents ou sélectionnés dans l'une quelconque des fractions suivantes :



dans lesquelles R_3, R_4, M, L et p sont tels que définis dans la revendication 5 ;
ou
A_1 ou A_2 est absent ;
ou
A_1 et A_2 sont absents.

5. Composition de nanoparticules selon l'une quelconque des revendications 3 ou 4, dans laquelle R_1 et R_2 sont chacun indépendamment un groupe :

-X-Q

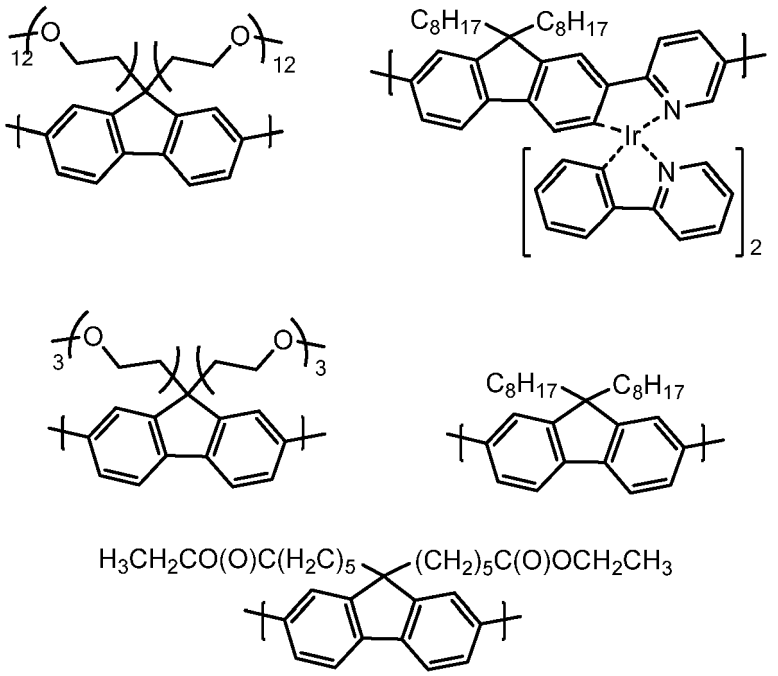
dans lequel
X et Q sont tels que définis dans la revendication 3.

6. Composition de nanoparticules selon l'une quelconque des revendications 3 à 5, dans laquelle, lorsqu'ils sont présents, X et X^1 sont indépendamment sélectionnés dans le groupe constitué de (1-30C)alkylène, (2-30C) alkénylène, (2-30C)alkynylène, $-[(CH_2)_2\text{-}O]_n-$ ou $-[O\text{-}(CH_2)_2]_n-$ (dans lequel n est 1 à 30) ;

Q et Q^1 sont indépendamment un groupe terminal sélectionné parmi hydrogène, méthyle, hydroxyle, carboxy, (1-4C)alkoxycarbonyle, amino, $-C{=}CH_2$ ou $-C{\equiv}CH$;
M est un métal sélectionné parmi Ir, Pt, Rh, Re, Ru, Os, Cr, Cu, Pd et Au ;
L est un ligand indépendamment sélectionné dans le groupe constitué de : halo, (1-30C)hydrocarbyle comprenant éventuellement un ou plusieurs hétéroatomes sélectionnés parmi N, O, S, Si et P, ou un groupe aryle ou hétéroaryle éventuellement substitué par un ou plusieurs substituants sélectionnés parmi (1-4C)alkyle, halo, aryle ou hétéroaryle ; et
p est 1 à 4 ;
ou
quand ils sont présents, X et X^1 sont indépendamment sélectionnés dans le groupe constitué de (1-20C)alkylène, $-[(CH_2)_2\text{-}O]_n-$ ou $-[O\text{-}(CH_2)_2]_n-$ (dans lequel n est 1 à 20) ;
Q et Q^1 sont indépendamment un groupe terminal sélectionné parmi hydrogène, méthyle, hydroxyle, carboxy, (1-4C)alkoxycarbonyle et amino ;
M est un métal sélectionné parmi Ir, Pt, Cr, Cu, Pd et Au ;
L est un ligand indépendamment sélectionné dans le groupe constitué d'aryle ou hétéroaryle, éventuellement

substitué par un ou plusieurs substituants sélectionnés parmi (1-4C)alkyle, halo, aryle ou hétéroaryle ; et
p est 1 à 4 ;
ou
dans laquelle, quand ils sont présents, X et X^1 sont indépendamment sélectionnés dans le groupe constitué de (1-20C)alkylène, $-[(CH_2)_2-O]_n-$ ou $-[O-(CH_2)_2]_n-$ (dans lequel n est 1 à 20) ;
Q et Q^1 sont indépendamment un groupe terminal sélectionné parmi hydrogène, méthyle, (1-2C)alkoxycarbonyle et hydroxyle ;
M est Ir ;
L est un ligand indépendamment sélectionné dans le groupe constitué d'aryle ou hétéroaryle, optionnellement substitué par un ou plusieurs substituants sélectionnés parmi aryle ou hétéroaryle ; et p est 1 à 2 ;
ou
quand ils sont présents, X et X^1 sont indépendamment sélectionnés dans le groupe constitué de (4-12C)alkylène ou $-[(CH_2)_2-O]_n-$. (dans lequel n est 1 à 15) ;
Q et Q^1 sont indépendamment un groupe terminal sélectionné parmi hydrogène, (1-2C)alkoxycarbonyle et méthyle ;
M est Ir ;
L est un ligand indépendamment sélectionné dans le groupe constitué de phényle ou hétéroaryle à 6 chaînons, éventuellement substitué par un ou plusieurs substituants sélectionnés parmi phényle ou un hétéroaryle à 6 chaînons ; et
p est 1 à 2.

7. Composition de nanoparticules selon la revendication 1, dans laquelle le polymère réticulé π conjugué comprend 80-99,9 mol.% de monomères π conjugués sélectionnés dans au moins une des structures suivantes :



8. Procédé de formation d'une composition de nanoparticules selon l'une quelconque des revendications précédentes, le procédé comprenant l'étape de formation des nanoparticules par des techniques de polymérisation en émulsion, polymérisation en mini-émulsion ou polymérisation en dispersion pour fournir une suspension aqueuse de nanoparticules ; et
dans lequel les nanoparticules sont éventuellement formées par une réaction de polymérisation par couplage croisé.

9. Procédé selon la revendication 8, dans lequel la réaction de polymérisation par couplage croisé est une réaction de Suzuki et/ou Stille.

10. Procédé selon la revendication 8 ou la revendication 9, comprenant en outre l'étape d'épuration de la suspension aqueuse de nanoparticules.

11. Procédé selon la revendication 10, dans lequel la suspension aqueuse de nanoparticules est épurée par mise en contact de la suspension aqueuse de nanoparticules avec au moins un solvant organique.

12. Procédé selon la revendication 11, dans lequel l'au moins un solvant organique est sélectionné dans le groupe constitué de solvants polaires et non polaires ;
ou
l'au moins un solvant organique est le méthanol.

13. Utilisation d'une composition de nanoparticules telle que définie dans l'une quelconque des revendications 1 à 7 dans une ou plusieurs applications sélectionnées dans le groupe constitué de : imagerie ou détection biologique ou non biologique, réduction de résolution de lumière DEL, codage anti-contrefaçon, affichages, triage de cellules/cytométrie de flux, suivi de cellules à long terme, et visualisation de flux.

14. Dispersion de nanoparticules comprenant une composition de nanoparticules selon l'une quelconque des revendications 1 à 7 dispersée dans tout le milieu de dispersion.

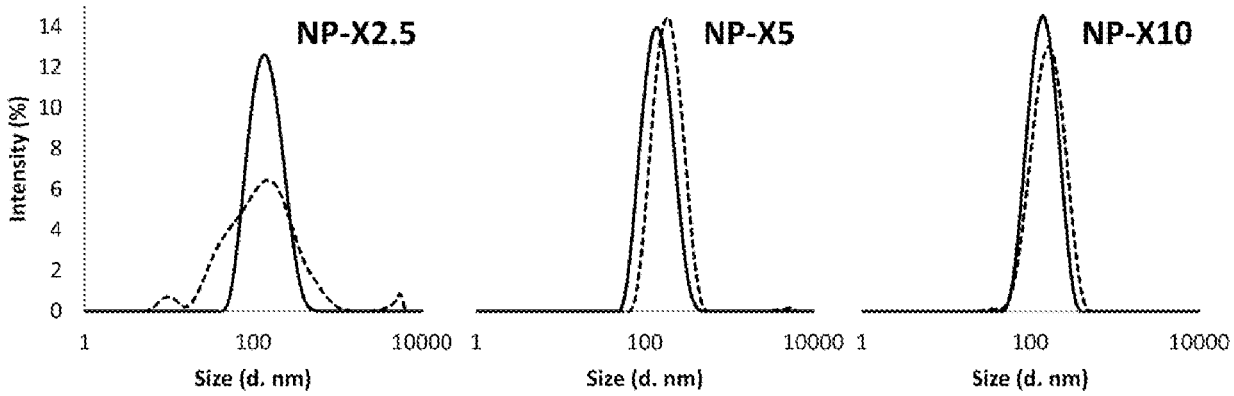

NP-X2.5
NP-X5
NP-X10
Intensity (%)
14
12
10
8
6
4
2
0
1
100
10000
Size (d. nm)

FIG. 1

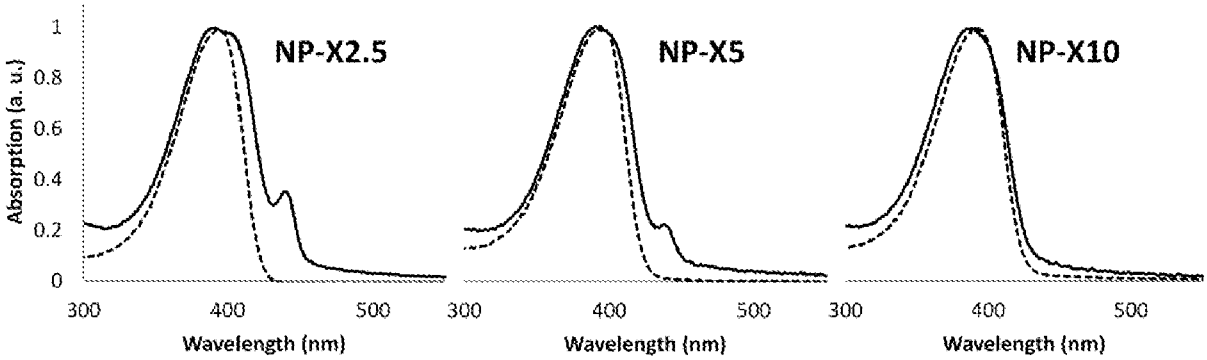

NP-X2.5
NP-X5
NP-X10
Absorption (a. u.)
1
0.8
0.6
0.4
0.2
0
300
400
500
Wavelength (nm)

FIG. 2

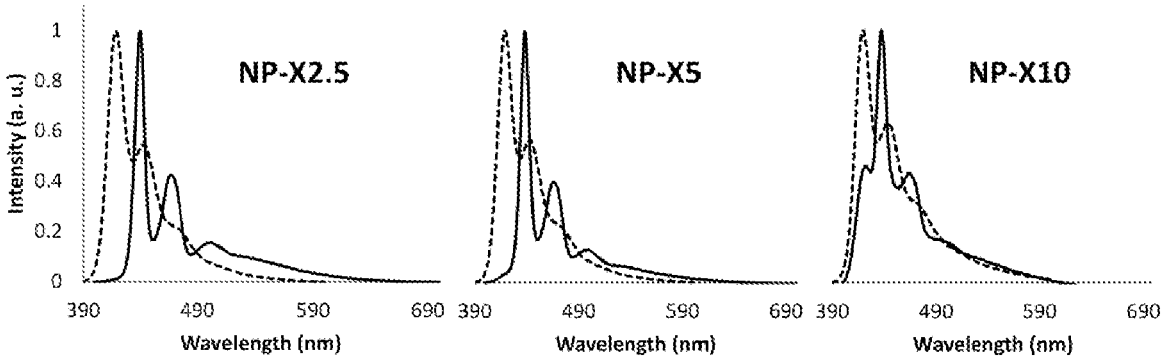

Intensity (a. u.)
1
0.8
0.6
0.4
0.2
0
NP-X2.5
NP-X5
NP-X10
390
490
590
690
Wavelength (nm)

FIG. 3

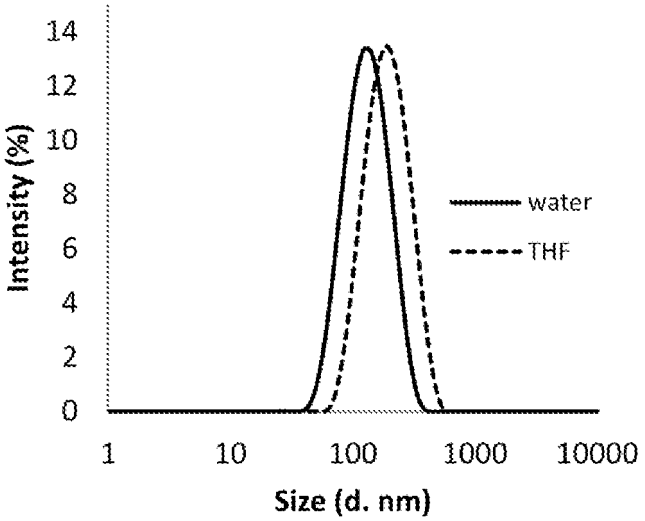

14
12
10
8
6
4
2
0
Intensity (%)
1
10
100
1000
10000
Size (d. nm)
water
THF

FIG. 4

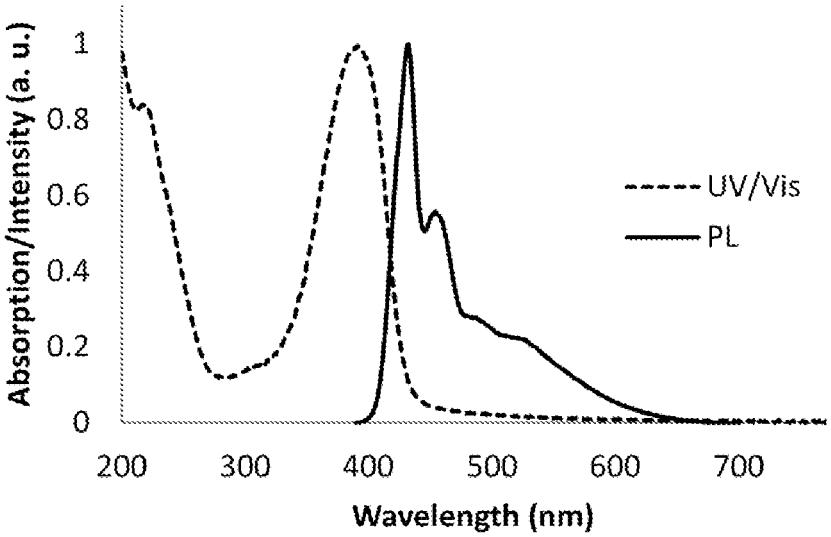

Absorption/Intensity (a. u.)
1
0.8
0.6
0.4
0.2
0
200
300
400
500
600
700
Wavelength (nm)
UV/Vis
PL

FIG. 5

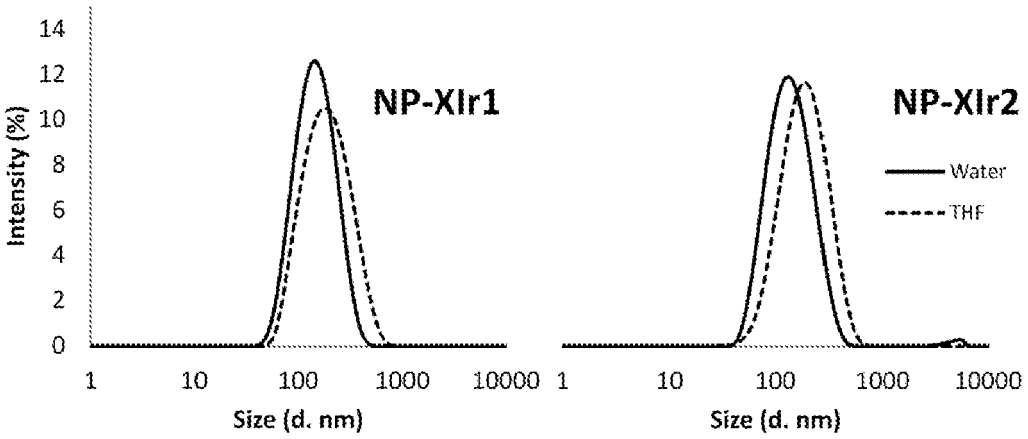

Intensity (%)
14
12
10
8
6
4
2
0
NP-XIr1
1
10
100
1000
10000
Size (d. nm)
NP-XIr2
Water
THF
1
10
100
1000
10000
Size (d. nm)

FIG. 6

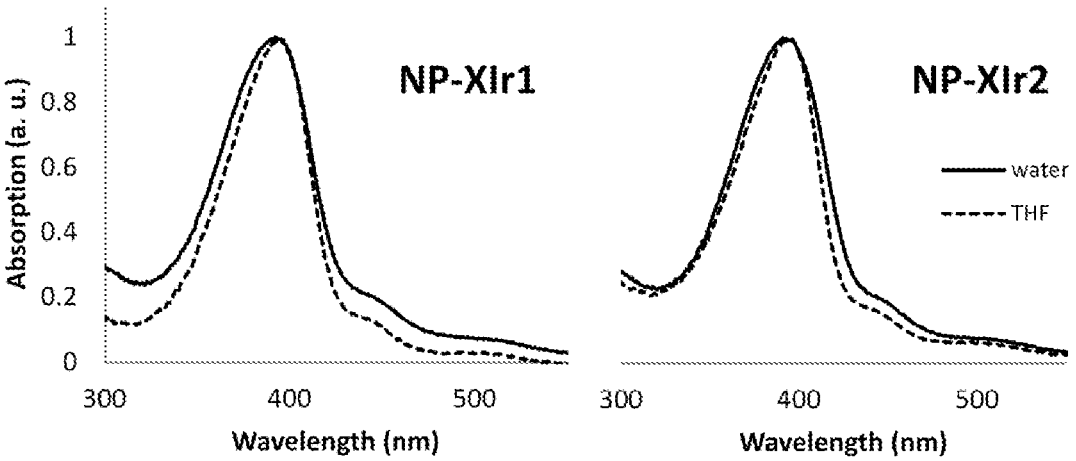

NP-Xlr1
NP-Xlr2
Absorption (a. u.)
1
0.8
0.6
0.4
0.2
0
300
400
500
Wavelength (nm)
water
THF

FIG. 7

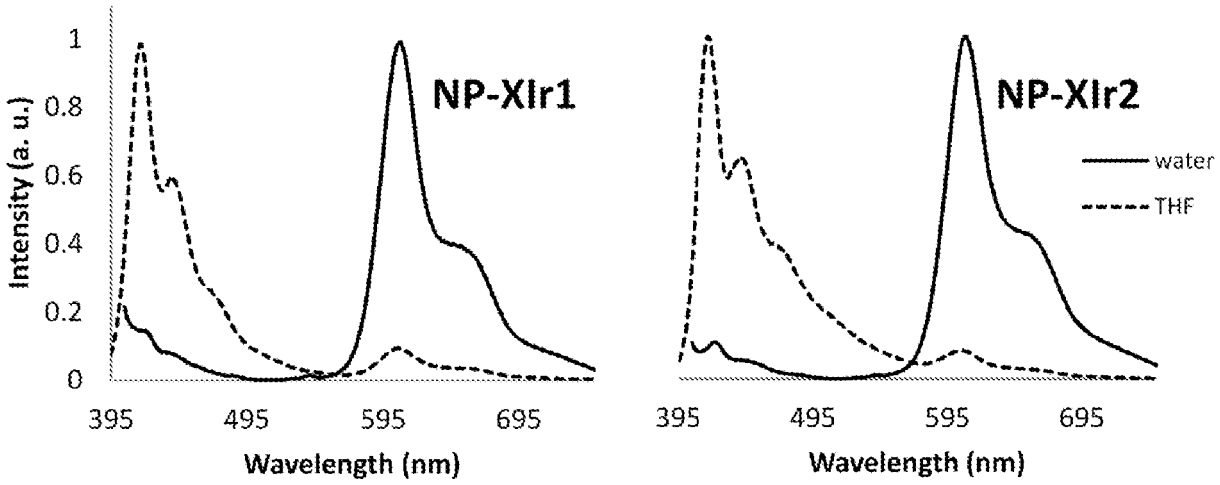

NP-XIr1
NP-XIr2
Intensity (a. u.)
1
0.8
0.6
0.4
0.2
0
395
495
595
695
Wavelength (nm)
water
THF

FIG. 8

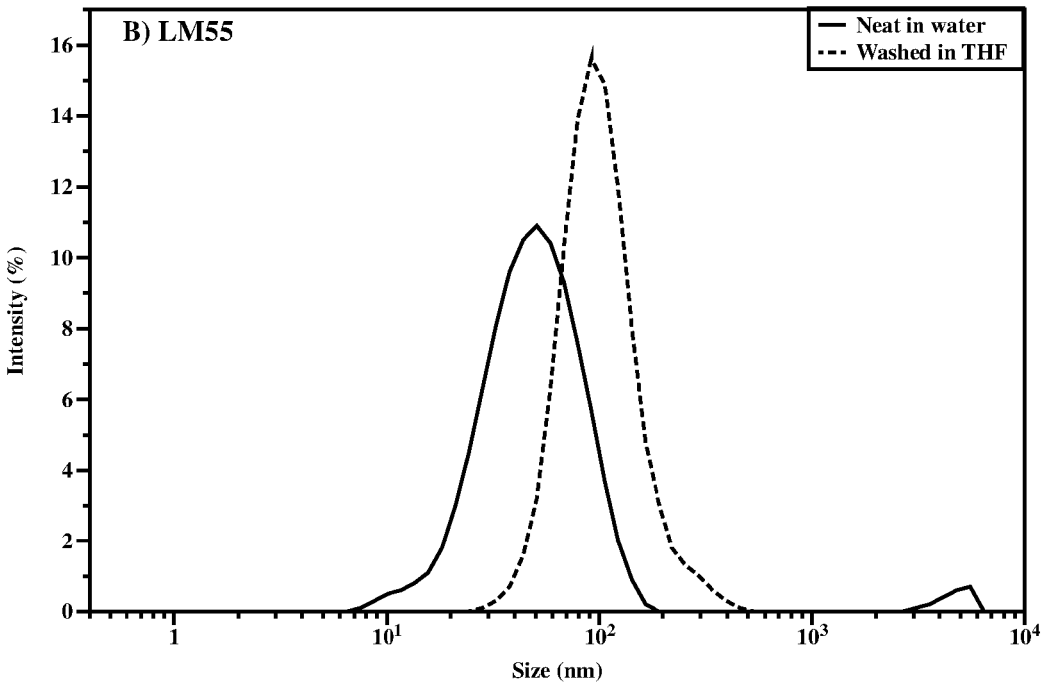

B) LM55
Neat in water
Washed in THF
Intensity (%)
Size (nm)
0
2
4
6
8
10
12
14
16
1
10^1
10^2
10^3
10^4

FIG. 9

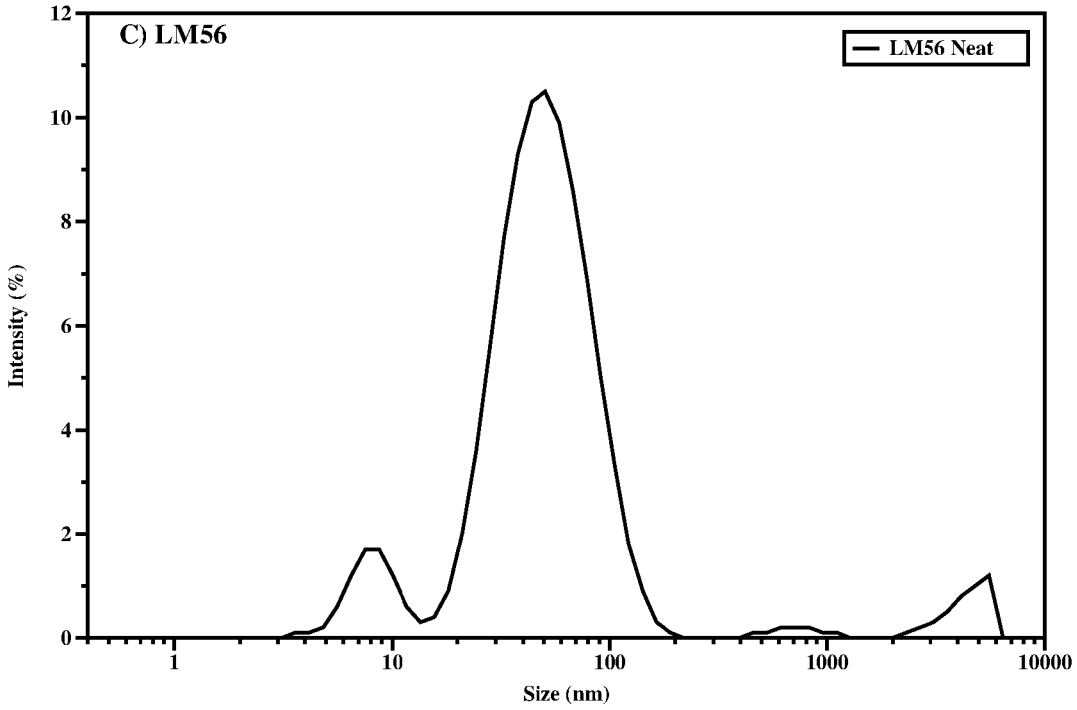

C) LM56
LM56 Neat
Intensity (%)
Size (nm)
0
2
4
6
8
10
12
1
10
100
1000
10000

FIG. 10

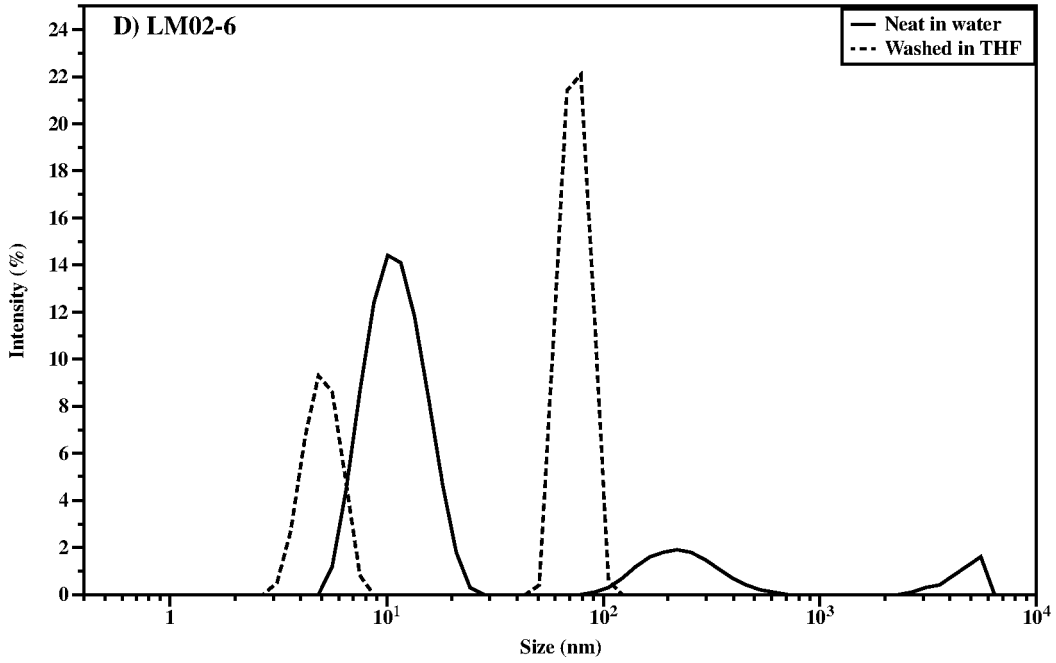
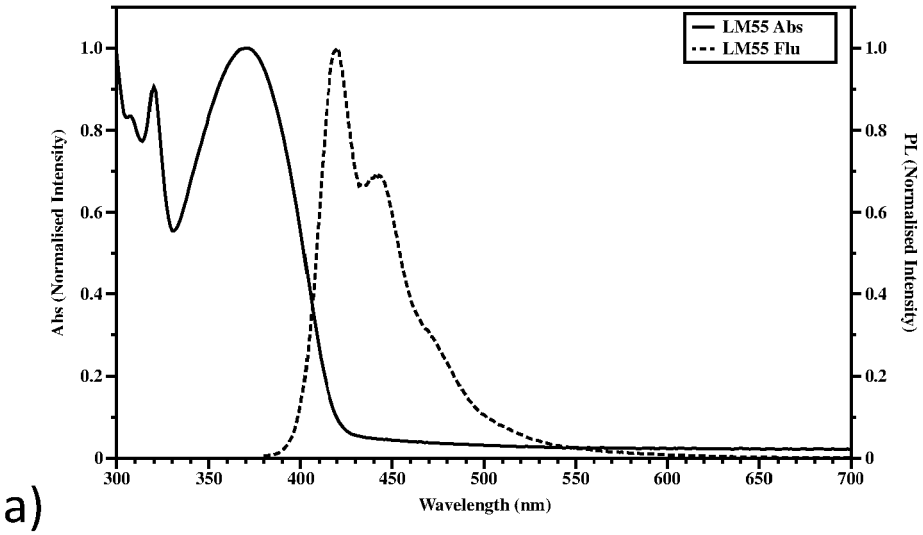
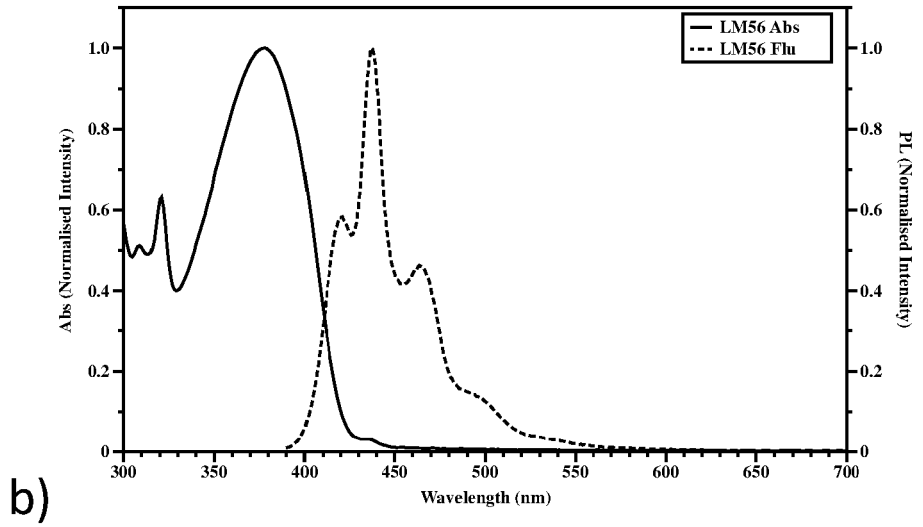

D) LM02-6
Neat in water
Washed in THF
Intensity (%)
Size (nm)
0
2
4
6
8
10
12
14
16
18
20
22
24
1
10^1
10^2
10^3
10^4

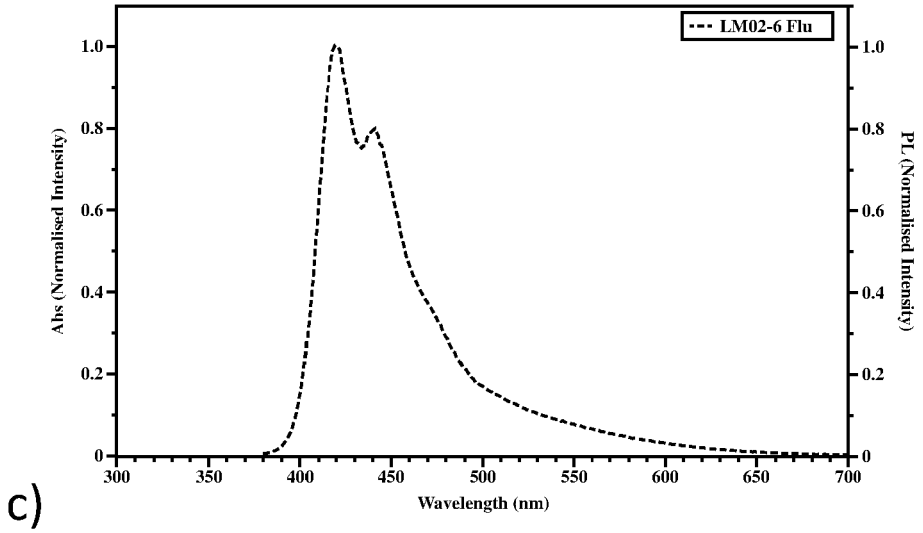
FIG. 11


LM55 Abs
LM55 Flu
Abs (Normalised Intensity)
PL (Normalised Intensity)
Wavelength (nm)
0
0.2
0.4
0.6
0.8
1.0
300
350
400
450
500
550
600
650
700

a)


LM56 Abs
LM56 Flu
Abs (Normalised Intensity)
PL (Normalised Intensity)
Wavelength (nm)
0
0.2
0.4
0.6
0.8
1.0
300
350
400
450
500
550
600
650
700

b)


LM02-6 Flu
Abs (Normalised Intensity)
PL (Normalised Intensity)
Wavelength (nm)
0
0.2
0.4
0.6
0.8
1.0
300
350
400
450
500
550
600
650
700

c)

FIG. 12

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- CN 101323781 A **[0007]**
- CN 102627776 **[0008]**

Non-patent literature cited in the description

- **BEHRENDT et al.** *Polym. Chem.*, 2013, vol. 4, 1333-1336 **[0005]**
- **BEHRENDT et al.** *J. Mater. Chem. C*, 2013, vol. 1, 3297-3304 **[0006]**
- **ZHANG et al.** *Gaofenzi Xuebao*, 2013, vol. 4, 426-435 **[0008]**
- *Chem. Rev.*, 2011, vol. 111, 1493-1528 **[0016]**