Accordingly, there is a need in this field of technique of improved fluorescent nano-structured materials.

Summary of the invention

The present invention addresses the problems above, and in particular provides a method for the preparation of nano-structured material(s). The nano-structured material prepared from the method of the present invention may be used for applications such as in bio-imaging and bio-detection of biomolecules.

According to a first aspect, the present invention provides a method of preparing at least one nano-structured material of formula $M_1M_2X_t$ comprising the step of treating:

- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$; and
- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$;

wherein

each X is the same or different and is selected from the group consisting of: halogens, O, S, Se, Te, N, P and As;

t is $0 \leq t \leq 10$;

each n is the same or different and is $0 \leq n \leq 10$;

each m is the same or different and is $0 \leq m \leq 10$;

each p is the same or different and is $1 \leq p \leq 5$;

each M_1 is the same or different and is selected from the group consisting of: Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra and NH_4;

each M_2 is the same or different and is a metal ion.

According to a particular aspect, the present invention provides a method for preparing at least one nano-structured material of formula $M_1M_2X_{n}:M_q$ comprising the step of treating:

- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$;
- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$; and
- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$,

wherein

each M_q is the same or different and is selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu;

t, n, m, p, X, M_1 and M_2 are as defined above; and

each q is the same or different and is $0 \leq q \leq 10$.

According to a further aspect, the treating in the method may be carried out in the presence of at least one source of energy. Any suitable source of energy may be used. For example, the source of energy may be, but not limited to, any one of the following: light source, electric source, thermal source, magnetic source, or a combination thereof. In particular, the source of energy is a thermal source. The treating may be carried out at a temperature of up to about 1000°C. For example, the treating may be carried out at a temperature of 200°C - 400°C. In particular, the treating is carried out at a temperature of 300°C - 350°C. Even more in particular, the treating is carried out at a temperature of 330°C.

According to another aspect, the present invention provides a method of preparing at least one nano-structured material of formula M_2X_{n} comprising the step of treating at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$, in the presence of at least one source of energy,

wherein

each X is the same or different and is selected from the group consisting of: halogens, O, S, Se, Te, N, P and As;

t is $0 \leq t \leq 10$;

each n is the same or different and is $0 \leq n \leq 10$;

each m is the same or different and is $0 \leq m \leq 10$;

each p is the same or different and is $1 \leq p \leq 5$; and

each M_2 is the same or different and is a metal ion.

According to another particular aspect, the present invention provides a method for preparing at least one nano-structured material of formula $M_2X_{nt}:M_q$ comprising the step of treating:

- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$; and
- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$;

in the presence of at least one source of energy, wherein

each M_q is the same or different and is selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu;

t, n, m, p, X and M_2 are as defined above; and

each q is the same or different and is $0 \leq q \leq 10$.

Any suitable source of energy may be used. For example, the source of energy may be, but not limited to, any one of the following: light source, electric source, thermal source, magnetic source or a combination thereof. In particular, the source of energy is a thermal source. The treating may be carried out at a temperature of up to about 1000°C. For example, the treating may be carried

out at a temperature of 200°C - 400°C. In particular, the treating is carried out at a temperature of 300°C - 350°C. Even more in particular, the treating is carried out at a temperature of 330°C.

M_2, according to any aspect of the present invention, may be the same or different and may be selected from the group consisting of: transition metal ions, inner transition metal ions, and Group I to Group VI metal ions. In particular, each M_2 may be the same or different and may be Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu.

The nano-structured material according to any aspect of the present invention may be selected from the group consisting of: NaM_2F_4, LiM_2F_4, KM_2F_4, RbM_2F_4, CsM_2F_4, BeM_2F_5, ~~$Be(M_2)_2F8$~~$Be(M_2)_2F_8$, MgM_2F_5, $Mg(M_2)_2F_8$, CaM_2F_5, $Ca(M_2)_2F_8$, SrM_2F_5, $Sr(M_2)_2F_8$, $BaLnF_5$, $Ba(M_2)_2F_8M_2F_3$, M_2F_3, M_2Cl_3, M_2Br_3, M_2I_3, M_2FClBr, M_2OF, M_2OCl, M_2OBr, M_2OS, $(M_2)_2S_3$, wherein each M_2 is as defined above. In particular, the nano-structured material is $NaYF_4$, $LiYF_4$, $BaYF_5$, $NaLaF_4$, LaF_3, YF_3, BaY_2F_8, $NaGdF_4$ or GdF_3. Even more in particular, the nano-structured material is $NaYF_4$.

The at least one compound of formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$ may be selected from the group consisting of: CF_3COONa and CF_3COOLi. The at least one compound of formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$ may be selected from the group consisting of: $(CF_3COO)_3Y$ and $(CF_3COO)_3La$. For example, the at least one compound of formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$ may be selected from the group consisting of: $(CF_3COO)_3Yb$, $(CF_3COO)_3Er$, $(CF_3COO)_3Tm$ and $(CF_3COO)_3Ho$.

The at least one nano-structured material prepared according to any method of the present invention may be selected from the group consisting of: $NaM_2F_4:M_q$, $LiM_2F_4:M_q$, $KM_2F_4:M_q$, $RbM_2F_4:M_q$, $CsM_2F_4:M_q$, $BeM_2F_5:M_q$, $Be(M_2)_2F_8:M_q$, $MgM_2F_5:M_q$, $Mg(M_2)_2F_8:M_q$, $CaM_2F_5:M_q$, $Ca(M_2)_2F_8:M_q$, $SrM_2F_5:M_q$, $Sr(M_2)_2F_8:M_q$, $BaM_2F_5:M_q$, $Ba(M_2)_2F_8:M_q$, $M_2F_3:M_q$, $M_2Cl_3:M_q$, $M_2Br_3:M_q$, $M_2I_3:M_q$,

$M_2FClBr:M_q$, $M_2OF:M_q$, $M_2OCl:M_q$, $M_2OBr:M_q$, $M_2OS:M_q$, $(M_2)_2S_3:M_q$, wherein each M_2 and M_q are as defined above. In particular, each M_q is the same or different and is selected from the group consisting of: Yb, Er, Tm and Ho. In particular, the at least one nano-structured material of formula $M_1M_2X_{n1}:M_q$ is $NaYF_4$:Yb,Er; $NaYF_4$:Yb,Tm; $NaYF_4$:Yb,Ho; LiYF4:Yb,Er; $BaYF_5$:Yb,Er; $NaLaF_4$:Yb,Er; or YOF:Yb,Er. Even more in particular, the nano-structured material is $NaYF_4$:Yb,Er, $NaYF_4$:Yb,Tm or $NaYF_4$:Yb,Ho.

According to a further aspect, the mixing or treating in the method according to any aspect of the present invention may be carried out in the presence of at least one polar or non-polar solvent, or a mixture thereof. Any suitable polar or non-polar solvent may be used. For example, the polar solvent may be water, methanol, ethanol, propyl alcohol, butanol, pentanol, hexanol, ketone, ethylene glycol, glycerol, propylene glycol, polyethylene glycol, ethyl acetate and a combination thereof. The non-polar solvent may be oleylamine, octadecene, oleic acid, alkyl amine, dialkyl amine, trialkyl amine, alkenyl amine, dialkenyl amine, trialkenyl amine, alkyl acid, alkenyl acid, trialkyl phosphine, trialkyl phosphine oxide, trialkylphosphate, alkane, alkene, alkyl ether, alkenyl ether or a combination thereof.

The at least one nano-structured material prepared by the method according to any aspect of the present invention may have a structure selected from one of the following: hexagonal, cubic, tetragonal, rhombohedral, orthorhombic, monoclinic, triclinic and a combination thereof. For example, the nano-structured material prepared from the method according to any aspect of the present invention may have a lattice structure selected from the group consisting of: hexagonal, cubic, tetragonal, rhombohedral, orthorhombic, monoclinic, triclinic and a combination thereof. In particular, the nano-structured material has a hexagonal lattice structure. Even more in particular, the nano-structured material is hexagonal phase $NaYF_4$, hexagonal phase $NaYF_4$:Yb,Er, hexagonal phase $NaYF_4$:Yb,Tm or hexagonal phase $NaYF_4$:Yb,Ho.

The nano-structured material prepared by the method according to any aspect of the present invention may comprise at least one dimension having size ≤1000 nm. For example, ≤100 nm, in particular, less than 50 nm. In particular, the nano-structured material comprises at least one dimension of size ≤25 nm. Even more in particular, the at least one dimension is of size ≤10 nm.

The nano-structured material prepared by the method according to any aspect of the present invention may be in the form of: nanoparticle(s), nanofilm or monolith. In particular, the at least one nano-structured material may be at least one nanoparticle and the average diameter of the nanoparticle is ≤1000 nm. For example, ≤100 nm, in particular, less than 50 nm. Even more in particular, the average diameter of the nanoparticle is ≤10 nm. The nanoparticle(s) may comprise a core nanoparticle(s) or a core-shell nanoparticle(s).

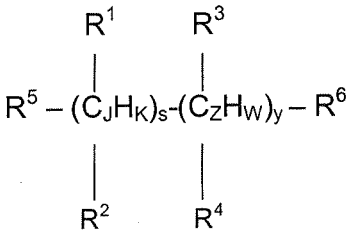
According to a further aspect, the present invention provides a method of preparing a nano-structured material as described above, wherein the nanoparticle is in the form of a core nanoparticle, and the method further comprises applying at least one organic and/or inorganic material (shell) on the core, to obtain a core-shell nanoparticle(s). According to another further aspect, the present invention provides a method of preparing a nano-structured material as described above, wherein the nanoparticle is in the form of a core nanoparticle, and the nanoparticle further comprises at least one organic and/or inorganic material (shell) applied on the core, to obtain a core-shell nanoparticle(s). The shell may be applied continuously or discontinuously on the core.

The shell of the core-shell nanoparticle may comprise an organic shell material or an inorganic shell material. The shell may comprise a material of the formula $M_1M_2X_{nt}$ or $M_1M_2X_{nt}:M_q$, wherein each M_1, M_2, X, nt and M_q are as defined above. For example, the organic shell material may comprise at least one polymer, a

surfactant or a lipid, or a combination thereof. Any suitable polymer, surfactant or lipid may be used for the purposes of the present invention.

The inorganic shell material may comprise NaM_2F_4, LiM_2F_4, KM_2F_4, RbM_2F_4, CsM_2F_4, BeM_2F_5, ~~$Be(M_2)_2F8$~~$Be(M_2)_2F_8$, MgM_2F_5, $Mg(M_2)_2F_8$, CaM_2F_5, $Ca(M_2)_2F_8$, SrM_2F_5, $Sr(M_2)_2F_8$, $BaLnF_5$, $Ba(M_2)_2F_8M_2F_3$, M_2F_3, M_2Cl_3, M_2Br_3, M_2I_3, M_2FClBr, M_2OF, M_2OCl, M_2OBr, M_2OS, $(M_2)_2S_3$, wherein each M_2 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; SiO_2; TiO_2; ZnS; or a combination thereof.

According to a further aspect, the surface of the nano-structured material may be modified by adding at least one surfactant, lipid, polymer, inorganic material, or a mixture thereof. Any suitable surfactant, lipid, polymer, inorganic material may be used. For example, the surfactant may have Formula (I):



(Formula I)

wherein

each J is the same or different, and $1 \leq J \leq 9$;

each K is the same or different, and $0 \leq K \leq 9$;

each s is the same or different, and $0 \leq s \leq 9$;

each Z is the same or different, and $1 \leq Z \leq 9$;

each W is the same or different, and $0 \leq W \leq 9$;

each y is the same or different, and $0 \leq y \leq 9$;

each R^1, R^2, R^3, R^4 and R^5 is the same or different, and is independently selected from the group consisting of: H, substituted or unsubstituted C_1-C_6 alkyl, substituted or unsubstituted C_1-C_6 aryl, HS, COOH, NH_2 and OH;

each R_6 is the same or different, and is selected from the group consisting of: COOH, NH_2, OH, P=0 and P;

with the proviso that s + y < 10.

The surfactant may be hydrophilic, hydrophobic and/or amphiphilic.

According to a further aspect, the present invention provides a method of preparing a nano-structured material as described above, wherein a biomolecule is attached to the nano-structured material. The biomolecule may be any suitable biomolecule. For example, the biomolecule is selected from the group consisting of: protein, nucleic acid, nucleosides, nucleotides, DNA, hormone, amino acid, peptide, peptidomimetic, RNA, lipid, albumin, antibody, phospholipids, glycolipid, sterol, vitamins, neurotransmitter, carbohydrate, sugar, disaccharide, monosaccharide, oligopeptide, polypeptide, oligosaccharide, polysaccharide and a mixture thereof.

The present invention also provides a nano-structured material obtainable by the method according to any aspect described above.

According to another aspect, the present invention provides a nano-structured material of formula $M_1M_2X_{nt}:M_q$, wherein M_1, M_2, X, nt and M_q are as defined above. The nano-structured material may have a hexagonal lattice structure and may comprise at least one dimension of < 50 nm. In particular, the at least one dimension is ≤ 10 nm.

According to a particular aspect, the present invention provides a nano-structured material of formula $M_1M_2X_{nt}:M_q$, wherein M_1, M_2, X, nt and M_q are as defined above, and wherein the nano-structured material has a hexagonal

size distribution of the nano-structured material. A narrow size distribution would be preferred. For example, the nano-structured material may be used in the bio-imaging and bio-detection of biomolecules.

According to a first aspect, the present invention provides a method of preparing at least one nano-structured material of formula $M_1M_2X_t$ comprising the step of treating (mixing):

- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$; and
- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$;

wherein

each X is the same or different and is selected from the group consisting of: halogens, O, S, Se, Te, N, P and As;

t is $0 \leq t \leq 10$;

each n is the same or different and is $0 \leq n \leq 10$;

each m is the same or different and is $0 \leq m \leq 10$;

each p is the same or different and is $1 \leq p \leq 5$;

each M_1 is the same or different and is selected from the group consisting of: Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra and NH_4;

each M_2 is the same or different and is a metal ion.

In particular, the step of treating comprises reacting at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$ and at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$.

According to a further aspect, the present invention provides a method for preparing at least one nano-structured material of formula $M_1M_2X_n:M_q$ comprising the step of treating (mixing):

- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$;
- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$; and
- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$,

wherein

each M_q is the same or different and is selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu;

t, n, m, p, X, M_1 and M_2 are as defined above; and

each q is the same or different and is $0 \leq q \leq 10$.

In particular, the step of treating comprises reacting at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$; at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$ and at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$.

The treating in the method according to any aspect of the present invention may be carried out in the presence of at least one source of energy. Accordingly, the method may also be referred to as a method according to any aspect of the invention wherein the method comprises treating the compounds (or the mixing) in the presence of at least one source of energy. For example, the source of energy may be light source, electric source, thermal source, magnetic source, heat source, or a combination thereof. The at least one source of energy may also comprise microwave assisted heating, NIR assisted heating, IR assisted heating, laser heating, X-ray heating. According to a particular aspect, the at

least one source of energy is thermal source. The treating may be carried out at a temperature up to 1000°C. In particular, the treating is carried out at a temperature 200°C - 400°C, even more in particular, at a temperature 300°C - 350°C. For example, the treating is carried out at a temperature of 330°C.

According to another aspect, the present invention provides a method of preparing at least one nano-structured material of formula M_2X_{nt} comprising the step of treating (mixing) at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$, optionally with at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$, in the presence of at least one source of energy,

wherein

each X is the same or different and is selected from the group consisting of: halogens, O, S, Se, Te, N, P and As;

t is $0 \leq t \leq 10$;

each n is the same or different and is $0 \leq n \leq 10$;

each m is the same or different and is $0 \leq m \leq 10$;

each p is the same or different and is $1 \leq p \leq 5$;

each M_2 is the same or different and is a metal ion; and

each M_q is as defined as below.

According to another further aspect, the present invention provides a method for preparing at least one nano-structured material of formula $M_2X_{nt}:M_q$ comprising the step of treating (mixing):

- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$; and
- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$,

in the presence of at least one source of energy, wherein

each M_q is the same or different and is selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu;

t, n, m, p, X, M_1 and M_2 are as defined above; and

each q is the same or different and is $0 \leq q \leq 10$.

In particular, the step of treating comprises reacting at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$ and at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$.

Each M_2, according to any aspect of the present invention, may be the same or different, and may be any suitable metal ion. For example, each M_2 may be the same or different and may be a transition metal ion, inner transition metal ion, or any one of Group I to Group VI metal ion. In particular, each M_2 may be selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

According to another aspect, the present invention provides a method which comprises the steps as shown:

$[CX_3(CX_2)_{n1}(CH_2)_{m1}COO]_pM_1 + [CX_3(CX_2)_{n2}(CH_2)_{m2}COO]_pM_2 + \ldots\ldots + [CX_3(CX_2)_{nq}(CH_2)_{mq}COO]_pM_q$ + Surfactant (optionally)

$\xrightarrow[\text{Solvent}]{\text{Energy source}}$

$M_1M_2\ldots M_{m-1}MX_{nt}:M_q$ nano-structured material

wherein each X may be the same or different and refers to halogen, such as F, Cl, Br and I; each M_1 may be the same or different and refers to ions which may be selected from the group consisting of: NH_4, Group I and Group II metal ions such as Li, Na, K, Rb, Cs, Be, Mg, Ba, Ca, Sr; M_2 to M_q each may be the same or different metal ion and may be selected from the group consisting of rare

earth metal ions such as Y, La, Ce Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

Further, $0 \leq t \leq 10$, $0 \leq n \leq 10$, $0 \leq m \leq 10$, $1 \leq p \leq 5$, $0 \leq q \leq 10$. The surfactant is optional in the method described. Any suitable surfactant, energy source and solvent may be used for the present invention, as will be described below.

According to another aspect, the present invention also provides a method comprising the following reaction:

$$CF_3COOM_1 + CF_3COOM_2 + CF_3COOM_q + \text{Surfactant} \xrightarrow[\text{High-boiling organic solvent}]{\text{Heating in}} M_1M_2F_{nt}:M_q \text{ nano-structured material}$$

M_1, M_2, nt and M_q may be as described above. For example, each M_1 may be the same or different and is selected from the group consisting of: Na, K, Ba, Li and NH_4. each M_2 may be the same or different and is selected from the group consisting of: Y, La, Gd, Lu. Each M_q may be the same or different and is selected from the group consisting of: Yb, Er, Ho, Tm and a combination thereof, such as Yb-Er, Yb-Ho and Yb-Tm.

M_q according to any aspect of the present invention may act as the dopant. A dopant may be an impurity which is added to a compound in low concentrations to alter some properties of the compound. For example, a dopant may be added in a concentration ranging from one part in a thousand to one part in ten million. It would be understood that a dopant does not alter the crystal structure of the compound it is added to. For example, a dopant may be added to a nano-structured material prepared according to the method of any aspect of the present invention so that the nano-structured material can have additional or enhanced properties. The properties include, but are not limited to, optical properties, magnetic properties, electrical properties and fluorescence.

temperature 200°C - 400°C, even more in particular, at a temperature 300°C - 350°C. For example, the treating is carried out at a temperature of 330°C.

The treating in the method according to any aspect of the present invention may be carried out in the presence of at least one solvent. Solvent may be defined as being a fluid phase (such as liquid, gas or plasma) that dissolves a solid, liquid or gaseous compound, resulting in a solution. The at least one solvent may be a polar solvent, a non-polar solvent, or a mixture thereof. Any suitable polar solvent and non-polar solvent may be used for the present invention.

For example, the polar solvent may be selected from the group consisting of: water, methanol, ethanol, propyl alcohol, butanol, pentanol, hexanol, ketone, ethylene glycol, glycerol, propylene glycol, polyethylene glycol, ethyl acetate, esters and a combination thereof.

The non-polar solvent may be selected from the group consisting of: oleylamine, octadecene, oleic acid, alkyl amine, dialkyl amine, trialkyl amine, alkenyl amine, dialkenyl amine, trialkenyl amine, alkyl acid, alkenyl acid, trialkyl phosphine, trialkyl phosphine oxide, trialkylphosphate, alkane, alkene, alkyl ether, alkenyl ether and a combination thereof.

The at least one solvent may be an organic solvent, inorganic solvent or a mixture thereof. Examples of organic solvent include solvents which contain carbon atom(s), such as acetone, alcohol, benzene, benzol, carbon disulphide, carbon tetrachloride, chloroform, ether, ethyl acetate, furfural, gasoline, toluene, turpentine, xylene, xylol, octadecane, tetracosane, oleylamine or oleic acid. Inorganic solvents are solvents which do not contain carbon atom(s), such as water.

The nano-structured material prepared from the method according to any aspect of the present invention may be selected from the group consisting of: NaM_2F_4, LiM_2F_4, KM_2F_4, RbM_2F_4, CsM_2F_4, BeM_2F_5, ~~$Be(M_2)_2F_8$~~$Be(M_2)_2F_8$, MgM_2F_5,

illustration of the core nanoparticle and core-shell nanoparticle is shown in Figures 1(a) and 1(b) respectively Figure 1(a) shows a core nanoparticle with at least one kind of surfactant on its surface. Figure 1(b) shows a core-shell nanoparticle with at least one kind of surfactant on the shell. Figure 2 shows a nano-structured material where the core and the shell are of the same material, $NaYF_4$. For example, the nanoparticle may be a core nanoparticle and the nanoparticle further comprises at least one organic and/or inorganic material (shell) applied on the core, to obtain a core-shell nanoparticle(s). Accordingly, the method according to any aspect of the present invention may comprise a further step of applying at least one organic and/or inorganic material (shell) on the core to obtain a core-shell nanoparticle(s).

As mentioned above, the nanoparticle may comprise an organic and/or inorganic material (shell). The organic and/or inorganic material (shell) may be applied continuously or discontinuously on the core. According to a particular aspect, the shell material has the formula $M_1M_2X_{nt}$ or $M_1M_2X_{nt}:M_q$, wherein M_1, M_2, X, nt and M_q are as defined above. For example, the shell material may comprise a material selected from the group consisting of: NaM_2F_4, LiM_2F_4, KM_2F_4, RbM_2F_4, CsM_2F_4, BeM_2F_5, ~~$Be(M_2)_2F8$~~$Be(M_2)_2F_8$, MgM_2F_5, $Mg(M_2)_2F_8$, CaM_2F_5, $Ca(M_2)_2F_8$, SrM_2F_5, $Sr(M_2)_2F_8$, $BaLnF_5$, $Ba(M_2)_2F_8M_2F_3$, M_2F_3, M_2Cl_3, M_2Br_3, M_2I_3, M_2FClBr, M_2OF, M_2OCl, M_2OBr, M_2OS, $(M_2)_2S_3$, wherein M_2 is as defined above. In particular, each M_2 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

According to another particular aspect, the organic shell material may comprise at least one polymer, a surfactant, a lipid, or a combination thereof. For example, the polymer may be selected from the group consisting of: polystyrene (PS), polyethylene (PE), polymethyl methacrylate (PMMA), polylactic acid (PLA) and a combination thereof. For the purposes of the present invention, a surfactant will be understood to be on which is a surface active agent that

lowers the surface tension. The surfactant may contain both hydrophilic and hydrophobic components and may be semi-soluble in both organic and aqueous solvents. For example, surfactants tend to clump up when in solution, forming a surface between fluid and air with hydrophobic tails in the air and the hydrophilic heads in the fluid.

The inorganic shell material may comprise any one of the following: NaM_2F_4, LiM_2F_4, KM_2F_4, RbM_2F_4, CsM_2F_4, BeM_2F_5, ~~$Be(M_2)_2F8$~~$Be(M_2)_2F_8$, MgM_2F_5, $Mg(M_2)_2F_8$, CaM_2F_5, $Ca(M_2)_2F_8$, SrM_2F_5, $Sr(M_2)_2F_8$, $BaLnF_5$, $Ba(M_2)_2F_8M_2F_3$, M_2F_3, M_2Cl_3, M_2Br_3, M_2I_3, M_2FClBr, M_2OF, M_2OCl, M_2OBr, M_2OS, $(M_2)_2S_3$, wherein each M_2 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; SiO_2; TiO_2; ZnS; or a combination thereof.

The shell material may confer certain properties onto the nano-structured material. For example, the shell may make the nano-structured material more hydrophilic, hydrophilic or amphiphilic. In particular, the nano-structured material may be made hydrophilic in order to better attach the nano-structured materials to biomolecules such as proteins and DNA.

According to a further aspect, the nano-structured material prepared from the method according to any aspect of the present invention may have its surface modified. The surface of the nano-structured material may be modified by adding at least one surfactant, lipid, polymer, inorganic material, or a mixture thereof. The surface of the nano-structured material may be modified to confer certain properties onto the nano-structured material. For example, the surface of the nano-structured material may be modified to make the nano-structured material more hydrophilic, hydrophilic or amphiphilic. In particular, the nano-structured material may be made hydrophilic in order to better attach the nano-structured materials to biomolecules such as proteins and DNA. The nano-

According to yet another aspect, the present invention provides a nano-structured material of formula $M_1M_2X_{nt}:M_q$, wherein each of M_1, M_2, M_q, X and nt are as defined above, and wherein the nano-structured material has a hexagonal (lattice) structure and comprises at least one dimension of size ≤1000 nm, ≤100 nm, ≤ 50 nm, < 50 nm, ≤25 nm, ≤10 nm or ≤ 5 nm. In particular, the nano-structured material comprises at least one dimension of ≤ 10 nm.

In particular, the present invention provides a nano-structured material of formula $M_1M_2X_{nt}:M_q$, wherein M_1, M_2, X, nt and M_q are as defined above, and wherein the nano-structured material has a hexagonal lattice structure, comprising at least one dimension of < 50 nm, with the proviso that the nano-structured material is not LaF_3:Yb,Er, LaF_3:Yb,Ho or LaF_3:Yb,Tm. Even more in particular, the nano-structured material is hexagonal phase $NaYF_4:M_q$. For example, $NaYF_4:M_q$ is $NaYF_4$:Yb,Er, $NaYF_4$:Yb,Ho or $NaYF_4$:Yb,Tm. The nano-structured material may have a hexagonal (lattice) structure and comprise at least one dimension of size ≤1000 nm, ≤100 nm, ≤ 50 nm, < 50 nm, ≤25 nm, ≤10 nm or ≤5 nm. In particular, the nano-structured material comprises at least one dimension of ≤ 10 nm.

The present invention also provides an article of manufacture comprising the any nano-structured material as described above. For example, the article of manufacture may be at least one of the following: a display device, a solar cell, an optical data storage, a bio-probe, a carrier for drug delivery, a lamp, a LED, a LCD, a wear resistance, a laser, optical amplifier, low density IR imaging, mercury-free fluorescent lamps, plasma display panel (PDP) and/or a device for bio-imaging. For example, nano-structured material such as $BaYF_5$, BaY_2F_8, $LiYF_4$, NaM_2F_4 and M_2F_3, wherein each M_2 is the same or different and is as described above, are efficient hosts for near-infrared emission ions such as Nd^{3+}, Er^{3+}, Ho^{3+} and Pr^{3+}. Because the emissions fall in the telecommunication

Claims

1. A method of preparing at least one nano-structured material of formula ~~$M_1M_2X_n$~~-$M_1M_2X_t$, comprising the step of ~~treating~~heating:

- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$; and

- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$;

wherein

each X is the same or different and is selected from the group consisting of: halogens, O, S, Se, Te, N, P and As;

$0<t\leq10$;

each n is the same or different and is $0\leq n\leq10$;

each m is the same or different and is $0\leq m\leq10$;

each p is the same or different and is $1\leq p\leq5$;

each M_1 is the same or different and is selected from the group consisting of: Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra and NH_4;

each M_2 is the same or different and is ~~a metal ion~~selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

~~2. The method according to claim 1, wherein M_2 is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.~~

3.2. The method according to claim 1 ~~or claim 2~~, wherein the method ~~is for preparing~~further comprises heating at least one compound having a formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$ with the at least one compound having a formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$ and the at least one compound having a formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$ to prepare at least one nano-structured material of formula $M_1M_2X_{n1}:M_{q1}$ ~~comprising the step of treating:~~wherein

~~at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$;~~

~~at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$; and~~

~~at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$, wherein~~

each M_q is the same or different and is selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu;

~~n, m, p, X, M_1 and M_2 are as defined in claim 1 or claim 2;~~ and

each q is the same or different and is $0 \leq q \leq 10$.

4.3. The method according to ~~any one of the preceding~~ claims 1, wherein M_2 is selected from the group consisting of: transition metal ions, inner transition metal ions, and Group I to Group VI metal ions.

~~5. The method according to any one of the preceding claims, wherein the treating is carried out in the presence of at least one source of energy.~~

~~6. The method according to claim 5, wherein the source of energy is selected from at least one of the following: light source, electric source, thermal source and magnetic source.~~

~~7. The method according to at least one of the preceding claims, wherein the treating is carried out at a temperature up to 1000ºC.~~

~~8. The method according to any one of the preceding claims, wherein the treating is carried out at a temperature of 200°C - 400°C.~~

~~9. The method according to claim 8, wherein the treating is carried out at a temperature of 300°C - 350°C.~~

~~10. The method according to claim 8 or claim 9, wherein the treating is carried out at a temperature of 330°C.~~

~~11.~~4. The method according to claim ~~any one of the preceding claims~~ 1, wherein the ~~treating~~heating is carried out in the presence of at least one polar or non-polar solvent, or a mixture thereof.

~~12. The method according to claim 11, wherein the polar solvent is selected from the group consisting of: water, methanol, ethanol, propyl alcohol, butanol, pentanol, hexanol, ketone, ethylene glycol, glycerol, propylene glycol, polyethylene glycol, ethyl acetate and a combination thereof.~~

~~13. The method according to claim 11, wherein the non-polar solvent is selected from the group consisting of: oleylamine, octadecene, oleic acid, alkyl amine, dialkyl amine, trialkyl amine, alkenyl amine, dialkenyl amine, trialkenyl amine, alkyl acid, alkenyl acid, trialkyl phosphine, trialkyl phosphine oxide, trialkylphosphate, alkane, alkene, alkyl ether, alkenyl ether.~~

~~14.~~5. The method according to ~~any one of the preceding~~ claims 1, wherein the nano-structured material is selected from the group consisting of: NaM_2F_4, LiM_2F_4, KM_2F_4, RbM_2F_4, CsM_2F_4, BeM_2F_5, $Be(M_2)_2F_8$, MgM_2F_5, $Mg(M_2)_2F_8$, CaM_2F_5, $Ca(M_2)_2F_8$, SrM_2F_5, $Sr(M_2)_2F_8$, $BaLnF_5$, $Ba(M_2)_2F_8M_2F_3$, wherein

each M_2 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

~~15.~~6. The method according to claim ~~14~~5, wherein the nano-structured material is $NaYF_4$.

~~16.~~7. The method according to ~~any one of~~ claim~~s 3 to 15~~ 2, wherein the nano-structured material is selected from the group consisting of: $NaM_2F_4:M_q$, $LiM_2F_4:M_q$, $KM_2F_4:M_q$, $RbM_2F_4:M_q$, $CsM_2F_4:M_q$, $BeM_2F_5:M_q$, $Be(M_2)_2F_8:M_q$, $MgM_2F_5:M_q$, $Mg(M_2)_2F_8:M_q$, $CaM_2F_5:M_q$, $Ca(M_2)_2F_8:M_q$, $SrM_2F_5:M_q$, $Sr(M_2)_2F_8:M_q$, ~~$BaM_2F_5:M_q$~~$BaLnF_5:M_q$, and $Ba(M_2)_2F_8$~~M_2F_3~~$:M_q$, wherein each M_2 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and each M_q is the same or different and is selected from the group consisting of: Yb, Er, Tm and Ho.

~~17.~~8. The method according to claim ~~16~~7, wherein the nano-structured material is ~~$NaYF_4:Yb,Er,$~~ $NaYF_4$:Yb,Tm or $NaYF_4$:Yb,Ho.

~~18.~~9. The method according to ~~any one of the preceding~~ claim~~s~~ 2, wherein the at least one compound of formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_1$ is selected from the group consisting of: CF_3COONa and CF_3COOLi~~;~~.

~~19. The method according to any one of the preceding claims, wherein~~ the at least one compound of formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$ is selected from the group consisting of: $(CF_3COO)_3Y$ and $(CF_3COO)_3La$; and~~.~~

~~20. The method according to any one of claims 3 to 19, wherein~~ the at least one compound of formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$ is selected from the group consisting of: $(CF_3COO)_3Yb$, $(CF_3COO)_3Er$, $(CF_3COO)_3Tm$ and $(CF_3COO)_3Ho$.

~~21.~~10. The method according to ~~any one of the preceding~~ claim~~s~~ 1, wherein the nano-structured material has a structure selected from the group consisting of: hexagonal, cubic, tetragonal, rhombohedral, orthorhombic, monoclinic, triclinic and a combination thereof.

~~22. The method according to claim 21, wherein the nano-structured material has a hexagonal structure.~~

~~23.~~11. The method according to ~~any one of the preceding~~ claim~~s~~ 1, wherein the nano-structured material comprises at least one dimension of size < 50 nm.

~~24. The method according to any one of the preceding claims, wherein the nano-structured material comprises at least one dimension of size ≤ 25 nm.~~

~~25. The method according to any one of the preceding claims, wherein the nano-structured material comprises at least one dimension of size ≤ 10 nm.~~

~~26. The method according to any one of the preceding claims, wherein the nano-structured material comprises at least one dimension of size ≤ 5 nm.~~

~~27. The method according to any one of the preceding claims, wherein the nano-structured material is in the form of: nanoparticle(s), nanofilm or monolith.~~

~~28. The method according to claim 27, wherein the nanoparticle(s) comprise core nanoparticle(s) and/or core-shell nanoparticle(s).~~

~~29.~~12. The method according to claim ~~27 or claim 28~~1, wherein the nano-structured material is in the form of nanoparticles, and the nanoparticle is in the form of a core nanoparticle, and the method further comprises applying at least one organic and/or inorganic material ~~(shell)~~ on the core, to obtain a core-shell nanoparticle(s).

~~30. The method according to claim 27 or claim 28, wherein the nanoparticle is in the form of a core nanoparticle, and the nanoparticle further comprises at least one organic and/or inorganic material (shell) applied on the core, to obtain a core-shell nanoparticle(s).~~

~~31.~~13. The method according to claim ~~29 or claim 30~~12, wherein the shell material has the formula $M_1M_2X_{nt}$ or $M_1M_2X_{nt}:M_q$, wherein each X is the same or different and is selected from the group consisting of: halogens, O, S, Se, Te, N, P and As; each M_1 is selected from the group consisting of: Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra and NH_4; each M_2 is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; each M_q is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; $0<t\leq10$; and $1\leq q\leq10$ ~~M_1, M_2, X, n and M_q are as defined in any one of claims 1 to 3~~.

~~32. The method according to claim 29 or claim 30, wherein the organic shell material comprises at least one polymer, a surfactant or a lipid, or a combination thereof.~~

~~33. The method according to claim 32, wherein the at least one polymer is selected from the group consisting of: polystyrene (PS), polyethylene (PE), polymethyl methacrylate (PMMA) and polylactic acid (PLA).~~

~~34. The method according to any one of claims 29 to 31, wherein the inorganic shell material comprises: NaM_2F_4, LiM_2F_4, KM_2F_4, RbM_2F_4, CsM_2F_4, BeM_2F_5, $Be(M_2)_2F8$, MgM_2F_5, $Mg(M_2)_2F_8$, CaM_2F_5, $Ca(M_2)_2F_8$, SrM_2F_5, $Sr(M_2)_2F_8$, $BaLnF_5$, $Ba(M_2)_2F_8M_2F_3$, M_2F_3, M_2Cl_3, M_2Br_3, M_2I_3, M_2FClBr, M_2OF, M_2OCl, M_2OBr, M_2OS, $(M_2)_2S_3$, wherein each M_2 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; SiO_2; TiO_2; ZnS; or a combination thereof.~~

~~35. The method according to any one of claims 28 to 34, wherein the shell is applied continuously or discontinuously on the core.~~

~~36. The method according to any one of the preceding claims, wherein the at least one nano-structured material is at least one nanoparticle and the average diameter of the nanoparticle(s) is < 50 nm.~~

~~37. The method according to any one of the preceding claims, wherein the at least one nano-structured material is at least one nanoparticle and the average diameter of the nanoparticle(s) is ≤ 10 nm.~~

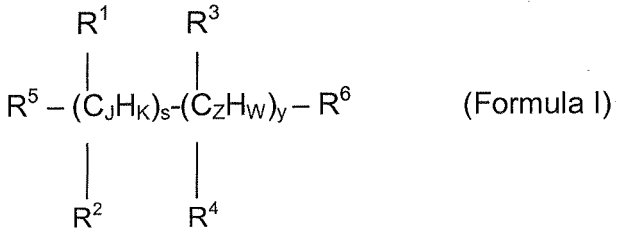
~~38.~~14. The method according to ~~any one of the preceding~~ claim~~s~~ 1, wherein the nano-structured material is hexagonal phase $NaYF_4$.

~~39.~~15. The method according to ~~any one of the preceding~~ claim~~s~~ 2, wherein the nano-structured material is hexagonal phase $NaYF_4$:Yb,Er, hexagonal phase $NaYF_4$:Yb,Tm or hexagonal phase $NaYF_4$:Yb,Ho.

~~40.~~16. The method according to ~~any one of the preceding~~ claim~~s~~ 1, wherein the surface of the nano-structured material is modified by adding at least one surfactant, lipid, polymer, inorganic material, or a mixture thereof.

~~41. The method according to any one of the preceding claims, wherein the surface of the nano-structured material is modified by adding at least one surfactant.~~

~~42.~~17. The method according to claim ~~41~~16, wherein the at least one surfactant has Formula (I):



(Formula I)

wherein

each J is the same or different, and $1 \leq J \leq 9$;

each K is the same or different, and $0 \leq K \leq 9$;

each s is the same or different, and $0 \leq s \leq 9$;

each Z is the same or different, and $1 \leq Z \leq 9$;

each W is the same or different, and $0 \leq W \leq 9$;

each y is the same or different, and $0 \leq y \leq 9$;

each R^1, R^2, R^3, R^4 and R^5 is the same or different, and is independently selected from the group consisting of: H, substituted or unsubstituted C_1-C_6 alkyl, substituted or unsubstituted C_1-C_6 aryl, HS, COOH, NH_2 and OH;

each R_6 is the same or different, and is selected from the group consisting of: COOH, NH_2, OH, P=0 and P;

with the proviso that s + y < 10.

~~43. The method according to claim 41 or claim 42, wherein the surfactant is hydrophilic, hydrophobic and/or amphiphilic.~~

~~44. The method according to any one of the preceding claims, wherein a biomolecule is attached to the nano-structured material.~~

~~45. The method according to claim 44, wherein the biomolecule is selected from the group consisting of: protein, nucleic acid, nucleosides, nucleotides, DNA, hormone, amino acid, peptide, peptidomimetic, RNA, lipid, albumin, antibody, phospholipids, glycolipid, sterol, vitamins, neurotransmitter,~~

carbohydrate, sugar, disaccharide, monosaccharide, oligopeptide, polypeptide, oligosaccharide, polysaccharide and a mixture thereof.

46. A nano-structured material obtainable by the method according to any one of claims 1 to 45.

47. A nano-structured material of formula $M_1M_2X_n:M_q$ as defined in any one of claims 1 to 3, wherein the nano-structured material has a hexagonal lattice structure and comprises at least one dimension of size < 50 nm, with the proviso that the nano-structured material is not LaF_3:Yb,Er, LaF_3:Yb,Ho or LaF_3:Yb,Tm.

48. The nano-structured material according to claim 47, wherein the at least one dimension is of size ≤ 10 nm.

49. The nano-structured material according to claim 48, wherein the at least one dimension is of size ≤ 5 nm.

50. The nano-structured material according to any one of claims 47 to 49, wherein the nano-structured material is hexagonal phase $NaYF_4:M_q$.

51. The nano-structured material according to claim 50, wherein $NaYF_4:M_q$ is $NaYF_4$:Yb,Er, $NaYF_4$:Yb,Ho or $NaYF_4$:Yb,Tm.

52. An article of manufacture comprising the nano-structured material according to any one of claims 46 to 51.

53. The article of manufacture according to claim 52, wherein the article of manufacture is at least one of the following: a display device, a solar cell, an optical data storage, a bio-probe, a carrier for drug delivery, a lamp, a LED, a LCD, a wear resistance, a laser, optical amplifier, and/or a device for bio-imaging.

54. A kit comprising at least one nano-structured material according to any one of claims 46 to 51 and at least one biomolecule.

55. The kit according to claim 54, wherein the biomolecule is selected from the group consisting of: protein, nucleic acid, nucleosides, nucleotides, DNA, hormone, amino acid, peptide, peptidomimetic, RNA, lipid, albumin, antibody, phospholipids, glycolipid, sterol, vitamins, neurotransmitter, carbohydrate, sugar, disaccharide, monosaccharide, oligopeptide, polypeptide, oligosaccharide, polysaccharide and a mixture thereof.

56. A bio-imaging and/or bio-detection system comprising:

- at least one nano-structured material prepared from the method according to any one of claims 1 to 45;

- at least one biomolecule;

- at least one source of excitation; and

- at least one means for delivery of the source of excitation to the system.

57. The system according to claim 56, wherein the biomolecule is selected from the group consisting of: protein, nucleic acid, nucleosides, nucleotides, DNA, hormone, amino acid, peptide, peptidomimetic, RNA, lipid, albumin, antibody, phospholipids, glycolipid, sterol, vitamins, neurotransmitter, carbohydrate, sugar, disaccharide, monosaccharide, oligopeptide, polypeptide, oligosaccharide, polysaccharide and a mixture thereof.

58. The system according to claim 56 or claim 57, wherein the source of excitation is NIR.

59. The system according to claim 58, wherein the NIR is at 980 nm.

60. The system according to any one of claims 56 to 59, wherein the means for delivery of the source of excitation to the system is selected from the group consisting of: optical fibres, endoscopes, external light and external laser.

61. A method of modifying at least one hydrophobic structure to make it hydrophilic, comprising applying at least one modifier on the structure surface to make a structure-modifier complex, and wherein the modifier is a surfactant, lipid, polymer and/or inorganic material.

62. The method according to claim 61, comprising applying at least one first modifier on the structure surface, and further a second hydrophilic modifier to make a structure-first modifier-second modifier complex, and wherein the first and/or second modifier is a surfactant, lipid, polymer and/or inorganic material.

63. The method according to claim 61 or claim 62, comprising applying at least one hydrophilic surfactant on the structure to make a structure-surfactant complex.

64. The method according to any one of claims 61 to 63, wherein the structure is the nano-structured material according to any one of claims 46 to 51.

65. A method of preparing at least one nano-structured material of formula M_2X_n comprising the step of treating at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$ in the presence of at least one source of energy,

wherein

each X is the same or different and is selected from the group consisting of: halogens, O, S, Se, Te, N, P and As;

each n is the same or different and is $0 \leq n \leq 10$;

each m is the same or different and is $0 \leq m \leq 10$;

each p is the same or different and is $1 \leq p \leq 5$; and

each M_2 is the same or different and is a metal ion.

66. The method according to claim 65, wherein each M_2 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

67. The method according to claim 65 or claim 66, wherein the method is for preparing at least one nano-structured material of formula $M_2X_n:M_q$ comprising the step of treating:

- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$; and

- at least one compound having the formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$;

in the presence of at least one source of energy and wherein

each M_q is the same or different and is selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu;

n, m, p, X and M_2 are as defined in claim 65 or claim 66;

each q is the same or different and is $0 \leq q \leq 10$.

68. The method according to any one of claims 65 to 67, wherein each M_2 is the same or different and is selected from the group consisting of: transition metal ions, inner transition metal ions, and Group I to Group VI metal ions.

~~69. The method according to any one of claims 65 to 68, wherein the at least one source of energy is selected from at least one of the following: light source, electric source, thermal source and magnetic source.~~

~~70. The method according to any one of claims 65 to 69, wherein the treating is carried out at a temperature up to 1000ºC.~~

~~71. The method according to claim 70, wherein the treating is carried out at a temperature of 200°C - 400°C.~~

~~72. The method according to claim 71, wherein the treating is carried out at a temperature of 300°C - 350°C.~~

~~73. The method according to claim 72, wherein the treating is carried out at a temperature of 330°C.~~

~~74. The method according to claim any one of claims 65 to 73, wherein the treating is carried out in the presence of at least one polar or non-polar solvent, or a mixture thereof.~~

~~75. The method according to claim 74, wherein the polar solvent is selected from the group consisting of: water, methanol, ethanol, propyl alcohol, butanol, pentanol, hexanol, ketone, ethylene glycol, glycerol, propylene glycol, polyethylene glycol, ethyl acetate and a combination thereof.~~

~~76. The method according to claim 74, wherein the non-polar solvent is selected from the group consisting of: oleylamine, octadecene, oleic acid, alkyl amine, dialkyl amine, trialkyl amine, alkenyl amine, dialkenyl amine, trialkenyl amine, alkyl acid, alkenyl acid, trialkyl phosphine, trialkyl phosphine oxide, trialkylphosphate, alkane, alkene, alkyl ether, alkenyl ether and a combination thereof.~~

77. The method according to any one of claims 65 to 76, wherein the nano-structured material is selected from the group consisting of: M_2F_3, M_2Cl_3, M_2Br_3, M_2I_3, M_2FClBr, M_2OF, M_2OCl, M_2OBr, M_2OS, $(M_2)_2S_3$, wherein each M_2 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

78. The method according to claim 77, wherein the nano-structured material is LaF_3, CeF_3, GdF_3, YF_3 or YOF.

79. The method according to any one of claims 67 to 78, wherein the nano-structured material is selected from the group consisting of: M_2F_3:M_q, M_2Cl_3:M_q, M_2Br_3:M_q, M_2I_3:M_q, M_2FClBr:M_q, M_2OF:M_q, M_2OCl:M_q, M_2OBr:M_q, M_2OS:M_q, $(M_2)_2S_3$:M_q, wherein each M_2 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and M_q is selected from the group consisting of: Yb, Er, Tm and Ho.

80. The method according to claim 79, wherein the nano-structured material is YOF:Yb,Er, LaF_3:Yb,Er, CeF_3:Yb,Er, GdF_3:Yb,Er, YF_3:Yb,Er, YOF:Yb,Tm, LaF_3:Yb,Tm, CeF_3:Yb,Tm, GdF_3:Yb,Tm or YF_3:Yb,Tm.

81. The method according to any one of claims 65 to 80, wherein the at least one compound of formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_2$ is selected from the group consisting of: $(CF_3COO)_3Y$ and $(CF_3COO)_3La$.

82. The method according to any one of claims 67 to 81, wherein the at least one compound of formula $[CX_3(CX_2)_n(CH_2)_mCOO]_pM_q$ is selected from the group consisting of: $(CF_3COO)_3Yb$ and $(CF_3COO)_3Er$.

83. The method according to any one of claims 65 to 82, wherein the nano-structured material has a structure selected from the group consisting of: hexagonal, cubic, tetragonal, rhombohedral, orthorhombic, monoclinic, triclinic and a combination thereof.

~~84.The method according to any one of claims 65 to 83, wherein the nano-structured material comprises at least one dimension of size < 50 nm.~~

~~85.The method according to any one of claims 65 to 84, wherein the nano-structured material comprises at least one dimension of size ≤ 25 nm.~~

~~86.The method according to any one of claims 65 to 85, wherein the nano-structured material comprises at least one dimension of size ≤ 10 nm.~~

~~87.The method according to any one of claims 65 to 86, wherein the nano-structured material is in the form of: nanoparticle(s), nanofilm or monolith.~~

~~88.The method according to claim 87, wherein the nanoparticle(s) comprise core nanoparticle(s) and/or core-shell nanoparticle(s).~~

~~89.The method according to claim 87 or claim 88, wherein the nanoparticle is in the form of a core nanoparticle, and the method further comprises applying at least one organic and/or inorganic material (shell) on the core, to obtain a core-shell nanoparticle(s).~~

~~90.The method according to claim 87 or claim 88, wherein the nanoparticle is in the form of a core nanoparticle, and the nanoparticle further comprises at least one organic and/or inorganic material (shell) applied on the core, to obtain a core-shell nanoparticle(s).~~

~~91.The method according to any one of claims 88 to 90, wherein the shell material has the formula $M_1M_2X_n$ or $M_1M_2X_n:M_q$, wherein M_1, M_2, X, n and M_q are as defined in any one of claims 1 to 3 or claims 65 to 67.~~

~~92.The method according to claim 89 or claim 90, wherein the organic shell material comprises at least one polymer, a surfactant or a lipid, or a combination thereof.~~

93.The method according to claim 92, wherein the at least one polymer is selected from the group consisting of: polystyrene (PS), polyethylene (PE), polymethyl methacrylate (PMMA) and polylactic acid (PLA).

94.The method according to any one of claims 89 to 91, wherein the inorganic shell material comprises: NaM_2F_4, LiM_2F_4, KM_2F_4, RbM_2F_4, CsM_2F_4, BeM_2F_5, $Be(M_2)_2F8$, MgM_2F_5, $Mg(M_2)_2F_8$, CaM_2F_5, $Ca(M_2)_2F_8$, SrM_2F_5, $Sr(M_2)_2F_8$, $BaLnF_5$, $Ba(M_2)_2F_8M_2F_3$, M_2F_3, M_2Cl_3, M_2Br_3, M_2I_3, M_2FClBr, M_2OF, M_2OCl, M_2OBr, M_2OS, $(M_2)_2S_3$, wherein each M_2 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; SiO_2; TiO_2; ZnS; or a combination thereof.

95.The method according to any one of claims 88 to 94, wherein the shell is applied continuously or discontinuously on the core.

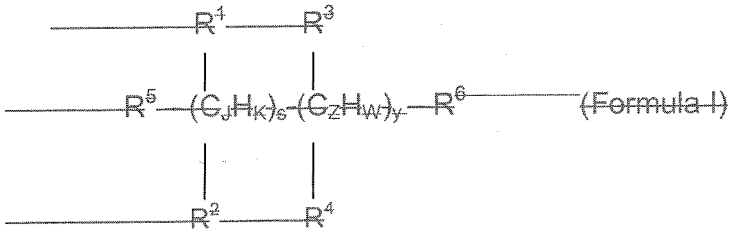
96.The method according to any one of claims 65 to 95, wherein the at least one nano-structured material is at least one nanoparticle and the average diameter of the nanoparticle(s) is < 50 nm.

97.The method according to any one of claims 65 to 96, wherein the at least one nano-structured material is at least one nanoparticle and the average diameter of the nanoparticle(s) is ≤ 10 nm.

98.The method according to any one of claims 65 to 97, wherein the surface of the nano-structured material is modified by adding at least one surfactant, lipid, polymer, inorganic material, or a mixture thereof.

99.The method according to any one of claims 65 to 98, wherein the surface of the nano-structured material is modified by adding at least one surfactant.

100. The method according to claim 99, wherein the at least one surfactant has Formula (I):



(Formula I)

wherein

each J is the same or different, and $1 \leq J \leq 9$;

each K is the same or different, and $0 \leq K \leq 9$;

each s is the same or different, and $0 \leq s \leq 9$;

each Z is the same or different, and $1 \leq Z \leq 9$;

each W is the same or different, and $0 \leq W \leq 9$;

each y is the same or different, and $0 \leq y \leq 9$;

each R^1, R^2, R^3, R^4 and R^5 is the same or different, and is independently selected from the group consisting of: H, substituted or unsubstituted C_1-C_6 alkyl, substituted or unsubstituted C_1-C_6 aryl, HS, COOH, NH_2 and OH;

each R_6 is the same or different, and is selected from the group consisting of: COOH, NH_2, OH, P=O and P;

with the proviso that $s + y < 10$.

101. The method according to claim 99 or claim 100, wherein the surfactant is hydrophilic, hydrophobic and/or amphiphilic.

102. The method according to any one of claims 65 to 101, wherein a biomolecule is attached to the nano-structured material.

~~103. The method according to claim 102, wherein the biomolecule is selected from the group consisting of: protein, nucleic acid, nucleosides, nucleotides, DNA, hormone, amino acid, peptide, peptidomimetic, RNA, lipid, albumin, antibody, phospholipids, glycolipid, sterol, vitamins, neurotransmitter, carbohydrate, sugar, disaccharide, monosaccharide, oligopeptide, polypeptide, oligosaccharide, polysaccharide and a mixture thereof.~~

~~104. A nano-structured material obtainable by the method according to any one of claims 65 to 103.~~

~~105. An article of manufacture comprising the nano-structured material according to claim 104.~~

~~106. The article of manufacture according to claim 105, wherein the article of manufacture is at least one of the following: a display device, a solar cell, an optical data storage, a bio-probe, a carrier for drug delivery, a lamp, a LED, a LCD, a wear-resistance, a laser, optical amplifier, and/or a device for bio-imaging.~~

~~107. A kit comprising at least one nano-structured material according to claim 104 and at least one biomolecule.~~

~~108. The kit according to claim 107, wherein the biomolecule is selected from the group consisting of: protein, nucleic acid, nucleosides, nucleotides, DNA, hormone, amino acid, peptide, peptidomimetic, RNA, lipid, albumin, antibody, phospholipids, glycolipid, sterol, vitamins, neurotransmitter, carbohydrate, sugar, disaccharide, monosaccharide, oligopeptide, polypeptide, oligosaccharide, polysaccharide and a mixture thereof.~~

~~109. A bio-imaging and/or bio-detection system comprising:~~

~~at least one nano-structured material prepared from the method according to any one of claims 65 to 103;~~

~~at least one biomolecule;~~

~~at least one source of excitation; and~~

~~at least one means for delivery of the source of excitation to the system.~~

~~110. The system according to claim 109, wherein the biomolecule is selected from the group consisting of: protein, nucleic acid, nucleosides, nucleotides, DNA, hormone, amino acid, peptide, peptidomimetic, RNA, lipid, albumin, antibody, phospholipids, glycolipid, sterol, vitamins, neurotransmitter, carbohydrate, sugar, disaccharide, monosaccharide, oligopeptide, polypeptide, oligosaccharide, polysaccharide and a mixture thereof.~~

~~111. The system according to claim 109 or claim 110, wherein the source of excitation is NIR.~~

~~112. The system according to claim 111, wherein the NIR is at 980 nm.~~

~~113. The system according to any one of claims 109 to 112, wherein the means for delivery of the source of excitation to the system is selected from the group consisting of: optical fibres, endoscopes, external light and external laser.~~