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(54) Title: HYBRID POLYMER WITH HIGH CLUSTER CONTENT

(57) Abstract: This deals with a luminescent salt comprising a metal cluster anion and an organic cation, wherein the metal cluster anion comprises a metal cluster with at least two metal atoms, and ligands, the metal atoms being chosen from the group consisting of molybdenum, rhenium, tungsten, thallium, niobium, and mixtures thereof, wherein the organic cation comprises a cationic head substituted by at least one substituent including a polymerisable functional group. It also deals with a polymeric material comprising a polymer matrix which has polymerised with this luminescent salt.

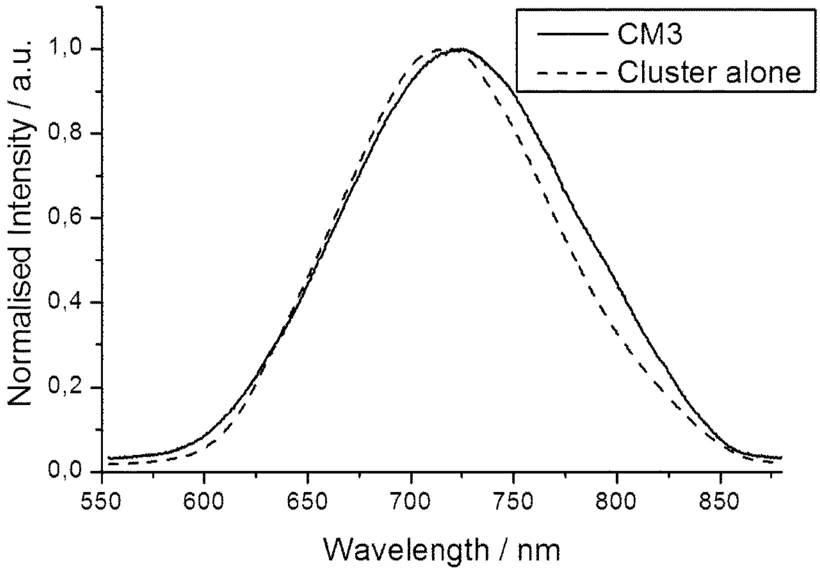

FIG. 4

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Hybrid polymer with high cluster content

Technical field

This deals with the technical field of integration of metal clusters at high or very high concentration in a polymeric matrix. More in particular, it deals with luminescent metal clusters that retain their luminescent properties and that can be integrated at high or very high concentration into a polymeric matrix.

Prior art

The integration of clusters into a host matrix, more in particular polymeric matrix, is already known. However, although the clusters are obtained by well-known solid-state chemistry techniques (solid gas or solid/solid reactions, high-temperature reactions), their ceramic like behaviour (hard, fragile, non-ductile) has until now seriously restrained their use in applicative devices in particular in optical technology.

For example, it is known to disperse octahedral metal clusters in a polymer matrix by reduction with a "monomer as solvent" approach. In this approach, six weakly bound apical triflate (OTf) ligands of an octahedral molybdenum cluster unit, namely $[Mo_6Cl_8(OTf)_6]^{2-}$, are substituted with N-vinylimidazole (NVI) monomer moieties yielding $[Mo_6Cl_8(NVI)_6].(OTf)_4$. After substitution, $[Mo_6Cl_8(NVI)_6].(OTf)_4$ is dispersed in labile NVI monomer at a concentration of 0.1 or 0.5 mol/L. Then, the modified molybdenum cluster and NVI are copolymerised by a radical process using 2,2'-azobis(isobutyronitrile) (AIBN) (Golden et al., in *Science*, 1995, 268, 1463).

This is also described in US 5,589,537, which also mentions $[Co_3(CO)_9(C_9H_7)]$ and $[Rh_{22}(CO)_{34}(NVI)_3]$ as examples of metal clusters bound to polymerisable ligands. Examples of metal cluster cations include $[Nb_6Cl_8(4\text{-vinylpyridine})_6]^{4+}$, $[Ta_6Cl_8(\text{acrylamide})_6]^{4+}$, $[Pt_{38}(CO)_{40}(4\text{-vinylpyridine})_4H_2]^{2+}$, $[Au_{13}(\text{p-dimethylphenylvinyl})_{10}Cl_2]^{3+}$ and the like. Examples of suitable anions to use with these cations include PF_6, $(BPh_4)_4^{4-}$, SO_4^{2-} and BPh_4^{4-}, wherein Ph is phenyl.

These metal cluster units can be easily dissolved and homogeneously dispersed within the polymerisable organic solvent. This is believed to be due to the polymerisable organic solvent's capacity to coordinate with or solvate the metal cluster unit.

The major drawback of these compounds is linked to the number of polymerisable ligands which are strongly coordinated to the metal cluster without possibility for spatial rearrangement. This limits the amount of metal clusters that can be incorporated into the polymer matrix. Indeed, in higher concentration, too much cross-linking reactions (reticulation) will occur, what impede processability. Further, apart from $[Mo_6Cl_8NVI_6]^{4+}$ that can be luminescent, the others are not.

Adamenko et al. (in *Doklady Physical Chemistry*, 2001, 381, 275; in *Russian Chemical Bulletin*, 2002, 51, 994; in *Inorg. Mater.*, 2004, 40, 306) used the same approach by replacing some of the six labile trifluoroacetate (CF_3COO^-) ligands of $[Mo_6Cl_8(CF_3COO)_6]^{2-}$ with acrylate moieties (CH_2CHCOO^-) to obtain $[Mo_6Cl_8(CF_3COO)_{6-n}(CH_2CHCOO)_n]^{2-}$, with n equals 1 to 3. The obtained complex is then copolymerised with methacrylic acid. However, luminescent properties of the metal cluster were lost after ageing because of some degradation induced by the lability of the CF_3COO^- ligands.

Shriver et al. (in *J. Coord. Ahem.*, 1996, 37, 119) coordinated $[Mo_6Cl_8(OTf)_6]^{2-}$ and $[Mo_6Cl_8^iCl_4^a(EtOH)_2^a]$ (i indicating inner ligands and a apical ligands) to poly(vinylpyridine) to produce cross-linked materials. Transient emission spectroscopy revealed that polymer bound hexatriflate clusters lack the luminescent properties characteristic of many $[Mo_6Cl_8]^{4+}$-based clusters while the other ones display luminescence. However, unswellable materials with no discernible glass temperature T_g are obtained with cluster/polymerisable ligand ratios of 1:5 and lower, indicating a high degree of cross-linking and, thus, the lack of processability.

The introduction of a monofunctionalised octohedral rhenium cluster (Re_6) in the side chain of polystyrene strands by copolymerisation between styrene and vinylpyridine coordinated to the cluster has been described by Zhang et al. (in *J. Cluster Sci.*, 2003, 14, 449). However, the luminescence properties of this hybrid were not reported probably because the introduction of phosphine ligands around a Re_6 cluster induces a drastic decrease in its luminescence quantum yield.

Summary

One aim of the present development is to overcome at least one of the drawbacks of the prior art presented above.

To this aim, a luminescent salt is provided. This luminescent salt comprises a metal cluster anion and an organic cation, wherein the metal cluster anion comprises a metal cluster with at least two metal atoms, the metal atoms being chosen amidst molybdenum, rhenium, tungsten, thallium and niobium,

wherein the organic cation comprises a cationic head substituted by at least one substituent including a polymerisable functional group.

It was surprisingly found that using a metal cluster anion bound to a polymerisable moiety by ionic bonds enables the metal cluster to be incorporated into an organic matrix in weight contents of 10 % and above. The resulting polymeric material stays soluble. Therefore, the resulting polymeric material remains easily processable like the polymerisable moiety alone. Furthermore, using this luminescent salt, the metal cluster is homogeneously dispersed throughout the polymer matrix without any phase segregation even at high contents (above 10% by weight) and retains its luminescence properties. These are due to the fact that the ionic bond between the metal cluster anion and the organic cation bearing the polymerisable functional group provides more flexibility for the positioning of the polymerisable function group since the organic cation can move around the metal cluster. This counters the cross linking effect resulting in a retained solubility of the material.

A polymeric material comprising a polymer matrix which has polymerised with the luminescent salt described above is also provided.

It is also provided a use of the luminescent salt described above as luminescent probes for detecting gaseous oxygen concentrations ranging from about 0.09% to 90% at 1 atm.

It is also provided a use of the luminescent salt described above as luminescent probes for medical processes such as in situ cells visualisation and monitoring drug relieves.

It is also provided a use of the luminescent salt described above in optoelectronic and photonic components such as light source, in optic amplifier, laser source, etc. or as light absorbing compound in protective glasses, for example absorbing light with wavelength below 540 nm.

It is also provided a use of the luminescent salt described above as photovoltaic improver for manufacturing converter layers suitable for solar cells and photovoltaic systems.

It is also provided a use of the luminescent salt described above as photocatylists for industrial processes.

Drawings

Figure 1 is a schematic representation of a cluster unit, the metal cluster of which comprises six metal atoms (the octahedron), surrounding by eight face-capping ligands (black beads) and six apical ligands (white beads).

Figure 2 represents the thermograms obtained by thermogravimetric analysis (ATG/TD Perkin Pyris Diamond) of CM4 (plain line), CM3 (dashed line) and CM2 (dotted line) of the examples under nitrogen atmosphere and illustrates the mass of the solid phase of CM4, CM3 and CM2 as a function of temperature, the mass being given as weight percentage of the initial mass.

Figure 3 represents the thermograms obtained by differential thermogravimetric analysis (ATG/TD Perkin Pyris Diamond at a heating rate of 10K/min) of CM4 (plain line), CM3 (dashed line) and CM2 (dotted line) of the examples under nitrogen atmosphere; these graphs are first derivates of the graphs of figure 2.

Figure 4 represents the solid state luminescence spectra of CM3 (plain line) of the examples and of $[(n\text{-}C_4H_9)_4N]_2[Mo_6Br_{14}]$ powder (dashed line) when exposed to an illumination of 405 nm at 25°C recorded with a Fluorolog-3™ fluorescence spectrometer (FL3-22, Horiba Jobin Yvon).

Figure 5 represents the ^{1}H-NMR of materials CM15 (b) and CM17 (c) of the examples, as well as the commercial PDMS material (a).

Figure 6 shows the luminescence spectra of CM24 (plain line), CM19 (dashed line), CM2 (dotted line) and CM14 (dash-dotted line) of the examples under irradiation at 400 nm.

Figure 7 shows the luminescence spectra of CM19 (dotted line), CM20 (dashed line), CM21 (dash-dotted line) and CM22 (plain line) of the examples under irradiation at 400 nm.

Figure 8 shows the luminescence spectra of CM6 (plain line) and CM16 (dashed line) of the examples under irradiation at 400 nm.

Description

Luminescent salt

Except when stated otherwise, wordings “one or more” and “one or two” should be interpreted as meaning “one or more identical or different” and “one or two identical or different”.

A luminescent salt is described hereafter.

Luminescence is emission of light by a substance not resulting from heat; this distinguishes luminescence from incandescence, which is light emitted by a substance as a result of heating. It is, thus, a form of cold body radiation. The energy of the electrons shifts upon excitation before going back to its base level. When the electrons return to their base level of energy, light is emitted. Fluorescence is luminescence wherein light emission occurs right after excitation, usually 10^{-9} to 10^{-6} s after the excitation. Phosphorescence is luminescence wherein light emission occurs after a longer lapse of time from the excitation, usually 10^{-3} to 10 s.

By “salt”, it is understood a compound composed of one or more cations and one or more anions so that the product is electrically neutral.

This luminescent salt comprises a metal cluster anion and at least one organic cation.

The metal cluster anion comprises a metal cluster with at least two metal atom.

Definition of a metal cluster is given by F.A. Cotton in *Inorg. Chem.* 1964, *3*, 1217 as: “a finite group of metal atoms that are held together mainly, or at least to a significant extent, by bonds directly between the metal atoms, even though some non-metal atoms may also be intimately associated with the cluster”.

In the following description, “metal cluster” is understood as at least two metal atoms which are covalently bound together and form metal-metal bonds. Metal-metal bonds enable delocalisation of all valence electrons on all metal atoms. The metal atoms of the metal cluster form a polyhedron. Each metal atom is considered as occupying a vertex (corner point) of the polyhedron.

The metal cluster anion may comprise at least face-capping ligands and/or edge bridging ligands, together referred as inner ligands.

A “ligand” is an ion or molecule that binds to the metal cluster to form a coordination complex. The bonding between the metal cluster and the ligand usually involves formal donation of one or more of the ligand’s electron pairs.

“Face-capping ligands” are ligands that are located normally to the centre of one face of the polyhedron, *i.e.* the virtual line passing through the ligand and the centre of the face of the polyhedron is orthogonal to that very face.

"Edge-bridging ligands" are ligands that are located normally to the middle of a metal-metal bond, *i.e.* the virtual line passing through the ligand and the middle of the metal-metal bond is perpendicular to that very metal-metal bond.

The metal cluster anion can comprise apical ligands.

"Apical ligands" are ligands located facing the vertexes of the polyhedron. The metal cluster and the inner ligands are referred together in the description as a "cluster core". The cluster core and the apical ligands are referred together as a "cluster unit".

The metal cluster has a nanometric size, preferably between about 0.5 nm to about 20 nm, more preferably between about 0.5 nm to about 2 nm.

For example, the metal cluster anion has the following formula:

$[M_aQ_bX_c]^{d-}$,

wherein M represents a metal atom of the metal cluster, *a* ranging from 2 to 20, preferably from 2 to 12, and more preferably being 6,

Q and X represent the ligands,

Q representing a face-capping ligand or an edge-bridging ligand, preferably a face-capping ligand, *b* ranging from 3 to 30, preferably from 8 to 12, and more preferably being 8,

X representing an apical ligand, *c* ranging from 2 to 50, preferably being 6, and

d ranging from 1 to 12, preferably 2 to 4.

Q may be a halogen, a chalcogen or a mixture thereof. Halogen group comprises fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At), or a mixture thereof. Among the halogens, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and a mixture thereof are preferred. The most preferred halogens are chlorine (Cl), bromine (Br), iodine (I) and a mixture thereof. More preferably, Q is bromine (Br). Chalcogen group comprises oxygen (O), sulphur (S), selenium (Se), tellurium (Te), polonium (Po), livermorium (Lv) or a mixture thereof. Among the chalcogens, oxygen (O), sulphur (S), selenium (Se), tellurium (Te) or a mixture thereof are preferred. The most preferred chalcogen is selenium (Se).

Advantageously, Q is a halogen or selenium (Se); notably is chlorine (Cl), bromine (Br), iodine (I) or selenium (Se).

X may be chosen from the group consisting of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At), carbon (C), nitrogen (N), sulphur (S), boron (B), oxygen (O), hydrogen (H), cyano (CN), carboxylate and mixtures thereof.

"Carboxylate" means, in the present invention, a group R1-COO where R1 represents a C_1-C_6 alkyl group, notably a C_1-C_3 alkyl group, in which one or several hydrogen atoms each can be replaced by a fluorine atom. It can be in particular a C_2F_5COO group.

A "C_1-C_6 alkyl", respectively "C_1-C_3 alkyl", group means a linear or branched saturated hydrocarbon chain comprising 1 to 6, respectively 1 to 3, carbon atoms.

Advantageously, X is chosen from the group consisting of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), cyano (CN) and carboxylate. Notably, X is chosen from the group consisting of chlorine (Cl), bromine (Br), cyano (CN) and carboxylate (such as C_2F_5COO).

Notably, X can be chosen from the group consisting of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At), carbon (C), nitrogen (N), sulphur (S), boron (B), oxygen (O), or hydrogen (H), or a mixture thereof. X is preferably a halogen, more preferably Br.

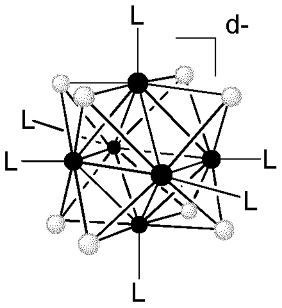
M is advantageously chosen from the group consisting of molybdenum (Mo), rhenium (Re), tungsten (W), tantalum (Ta), niobium (Nb) and a mixture thereof. Preferably the metal atoms are chosen from Mo, Re and W, more preferably, the metals atoms are Mo or Re, still more preferably, the metal atom is Mo. These metal atoms have the properties to be luminescent once integrated in a metal cluster, a cluster core or a cluster unit.

In one embodiment, the metal cluster anion comprises:

- a metal cluster with six metal atoms, which are preferably chosen from the group consisting of Mo, Re and W, more preferably Mo and Re, still more preferably Mo,
- 8 face-capping ligands, which are preferably halogens, more preferably Br, and
- six apical ligands, which are preferably halogens, more preferably Br.

According to a particular embodiment, the metal cluster anion has the formula $[M_6Q_8X_6]^{d-}$ with M, Q and X, as defined previously.

Such a metal cluster anion has the following structure:



where:

● represents M,

○ represents Q, and

L represents X.

The organic cation comprises a cationic head substituted by at least one substituent including a polymerisable functional group.

Preferably, the cationic head is chosen from the group consisting of: an imidazolium, a pyridinium, a pyrolidinium, an ammonium, a phosphonium, a hydroxyphosphonium and a sulfonium. The pyrolidinium, the ammonium, the phosphonium, the hydroxyphosphonium and the sulfonium can eventually be substituted by one or two C_1-C_3 alkyl groups. The imidazolium can also be substituted by one or two C_1-C_3 alkyl groups.

More preferably the cationic head is chosen from the group consisting of: an imidazolium, a pyridinium, a pyrolidinium, and an ammonium; and notably is an imidazolium or an ammonium, where the imidazolium can be substituted (in particular on one nitrogen atom) by one C_1-C_3 alkyl group, such as methyl, and the ammonium can be substituted by one or two C_1-C_3 alkyl groups. In particular, the cationic head is an ammonium which can be substituted by one or two C_1-C_3 alkyl groups, such as methyl groups, or an imidazolium which can be substituted (in particular on one nitrogen atom) by a C_1-C_3 alkyl group, such as methyl. Still more preferably, the cationic head is an ammonium substituted by two C_1-C_3 alkyl groups, such as methyl groups, or an imidazolium substituted (in particular on one nitrogen atom) by a C_1-C_3 alkyl group, such as methyl.

According to a particular embodiment, the cationic head is an ammonium, the ammonium can be further substituted by one or two C_1-C_3 alkyl groups. Still more preferably, the cationic head is an ammonium substituted by two methyl groups.

The substituent may comprise a terminal part and a linker. In this case, the linker has from 1 to 30 methylene groups, preferably 1 to 12, such as 8 to 12 methylene groups. Longer chains enhance mobility. The terminal part is the polymerisable functional group. The linker links the terminal part to the cationic head.

A “methylene” group means, in the present invention, a $-CH_2-$ group.

At least one of the methylene groups of the linker may be replaced by one or more atoms or groups of atoms chosen from the group consisting of aromatic rings, -O-, -CO-, -S-, -CH=CH-, -C≡C-, -COO-, -OC(O)-, -CH=N-, -CH=N-, -C(O)NH-, -N=N-, -NH-CO- and mixtures thereof. According to a particular embodiment, one methylene group can be replaced by -OC(O)-. More preferably, the methylene group that is replaced is the one closest to the terminal part. At least one hydrogen atom of the linker may further be replaced by a fluorine atom. The number of replacing fluorine atoms equals the number of the replaced hydrogen atoms.

An “aromatic ring” means, in the present invention, an aromatic hydrocarbon group comprising preferably 6 to 10 carbon atoms and comprising one or more fused rings, such as, for example, a phenyl or naphtyl group. Advantageously, it will be a phenyl group.

The polymerisable functional group may be chosen from the group consisting of: double carbon-carbon bond, triple carbon-carbon bond, an azide function ($-N_3$), a methacrylate function ($-OC(O)-C(CH_3)=CH_2$), an acrylate function ($-OC(O)-CH=CH_2$), an amine function ($-NH_2$), a carboxylic function ($-CO_2H$), an aldehyde function (-CHO), a hydroxyl function (-OH), an alkoxy function (-OR2 with R2 = C_1-C_6 alkyl), an iodine atom (-I), a bromine atom (-Br) and a chlorine atom (-Cl).

A “double carbon-carbon bond” means, in the present invention a group -CR3=CR4R5, where R3, R4 and R5 represent, independently of each other, a hydrogen atom or a C_1-C_6 alkyl group.

A “triple carbon-carbon bond” means, in the present invention a group -C≡CR6, where R6 represents a hydrogen atom or a C_1-C_6 alkyl group.

Acrylate, methacrylate, double carbon-carbon bond or triple carbon-carbon bond are preferred for radical polymerisation with the polymers or monomers of the polymer matrix. Triple carbon-carbon bond and azide function are preferred for Huisgen coupling reactions with the polymers or monomers of the polymer matrix. Amine, carboxylic functions are preferred for polyamide synthesis, *i.e.* Nylon 6-6.

Hydroxyl, alkoxy functions, bromine and chloride atoms are preferred for anionic polymerisation with the polymers or monomers of the polymer matrix.

Preferably, the polymerisable functional group is a double carbon-carbon bond (such as $-CH=CH_2$), a methacrylate function ($-OC(O)-C(CH_3)=CH_2$), an amine function ($-NH_2$) or a hydroxyl function ($-OH$).

According to a particular embodiment, the polymerisable functional group is a double carbon-carbon bond.

The cationic head may be further substituted by a second substituent containing from 1 to 30 methylene groups, preferably from 1 to 15, more preferably from 8 to 15, such as 12. At least one of the methylene group of the second substituent may be replaced by one or more atoms or groups of atoms chosen from the group consisting of aromatic rings, -O-, -CO-, -S-, -CH=CH-, -C≡C-, -COO-, -OC(O)-, -CH=N-, -CH=N-, -C(O)NH-, -N=N-, -NH-CO- and mixtures thereof. At least one hydrogen atom of the second substituent may further be replaced by a fluorine atom.

The second substituent can thus be a group of formula -A-H where A is a chain of 1 to 30 methylene groups, preferably from 1 to 15, more preferably from 8 to 15, notably 10 or 11. At least one of the methylene group of the second substituent may be replaced by one or more atoms or groups of atoms chosen from the group consisting of aromatic rings, -O-, -CO-, -S-, -CH=CH-, -C≡C-, -COO-, -OC(O)-, -CH=N-, -CH=N-, -C(O)NH-, -N=N-, -NH-CO- and mixtures thereof. At least one hydrogen atom of the second substituent may further be replaced by a fluorine atom. Preferably, no methylene group or hydrogen atom is replaced by another group or atom.

The second substituent can be a C_1-C_{30} alkyl group, such as a C_1-C_{15} alkyl group, notably a C_{10}-C_{15} alkyl group.

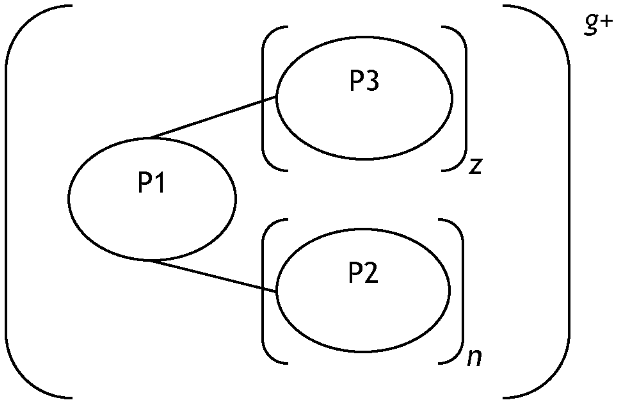
In a first particular embodiment, the organic cation comprises a head which is an ammonium, preferably substituted by one or two C_1-C_3 alkyl group, more preferably substituted by two methyl groups, a linker having 1 to 12 methylene groups, preferably 8 to 12 methylene groups, more preferably 11 methylene group, at least one of the methylene group can be further replaced by -O-CO-, preferably the one closest to the terminal part, and the terminal part is a double C-C bond, such as $-C(CH_3)=CH_2$. The ammonium can be further substituted by one C_1-C_{15} alkyl group such as a undecyl or dodecyl group.

In a second particular embodiment, the organic cation has a head which is an ammonium, preferably substituted by one or two C_1-C_3 alkyl groups such as by two methyl groups and one C_1-C_{15} alkyl group such as a undecyl or dodecyl group, a linker having 1 to 15 methylene groups, preferably 8 to 12 methylene groups, more preferably 11 methylene groups, and the terminal part is a methacrylate function ($-OC(O)-C(CH_3)=CH_2$).

In a third particular embodiment, the organic cation has a head which is an ammonium, preferably substituted by one or two C_1-C_3 alkyl group groups such as by two methyl groups and one C_1-C_{15} alkyl group such as a undecyl or dodecyl group, a linker having 1 to 15 methylene groups, preferably 1 to 10 methylene groups, more preferably 1 to 5 methylene groups, such as 3 methylene groups, and the terminal part is an amine function ($-NH_2$) or a hydroxyl function ($-OH$).

In a fourth particular embodiment, the organic cation has a head which is an imidazolium, preferably substituted by one C_1-C_3 alkyl group, more preferably substituted by one methyl group, in particular on a nitrogen atom, a linker having 1 to 15 methylene groups, preferably 8 to 12 methylene groups, such as 9 methylene groups, and the terminal part is a double C-C bond, such as $-CH=CH_2$.

More in particular, the organic cation of the luminescent salt may have the following formula:



wherein P1 represents the cationic head chosen from the group consisting of an imidazolium, a pyridinium, a pyrolidinium, an ammonium, a phosphonium, a hydroxyphosphonium or a sulfonium;

wherein P2 and P3 are substituents of P1,

z ranging from 0 to 12, preferably from 1 to 3, notably 1; *n* ranging from 1 to 12, preferably 1 or 2; and *g* ranging from 1 to 4, preferably 1;

wherein P2 comprises a terminal part and a linker having from 1 to 30 methylene groups, the terminal part being the polymerisable functional group and the linker linking the terminal part to the cationic head, wherein P3 contains from 1 to 30 methylene groups.

Preferably, at least one of the methylene groups of the linker is replaced by one or more aromatic rings, -O-, -CO-, -S-, -CH=CH-, -C≡C-, -COO-, -OC(O)-, -CH=N-, -CH=N-, -C(O)NH-, -N=N-, -NH-CO- and mixtures thereof. At least one of the hydrogen atoms of the linker may also be replaced by a fluorine atom.

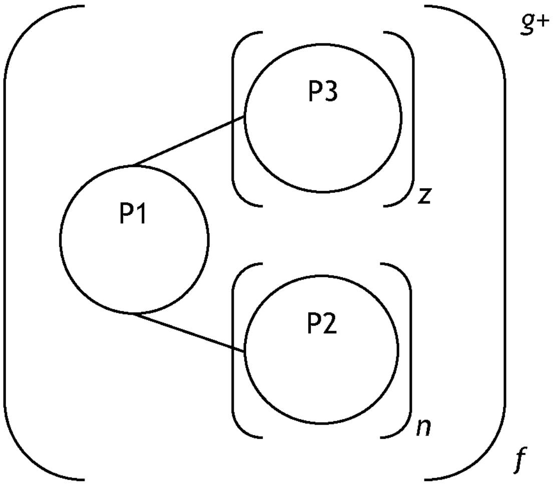
The polymerisable functional group may be chosen from the group consisting of: double carbon-carbon chemical bond, triple carbon-carbon chemical bond, an azide function, a methacrylate function, acrylate function, an amine function, a carboxylic function, an aldehyde function, a hydroxyl function, an alkoxy function, a bromine atom and a chlorine atom.

Notably, at least one of the methylene groups of P3 is replaced by one or more aromatic rings, -O-, -CO-, -S-, -CH=CH-, -C ≡ C-, -COO-, -OC(O)-, -CH=N-, -CH=N-, -C(O)NH-, -N=N-,-NHCO- and mixtures thereof.

Thus, P1 corresponds to the cationic head as defined above, P2 is a substituent of the cationic head comprising a terminal part and a linker as defined above and P3 is a second substituent of the cationic head as defined above.

The luminescent salt may thus have the following formula:

$[M_aQ_bX_c]^{d-}$



with the same definitions as stated above and where *f* ranging from 1 to 12 and equals *to d/g*.

In one particular embodiment, the metal cluster anion comprises:

- a metal cluster with six metal atoms, which are preferably chosen from the group consisting of Mo, Re and W, more preferably Mo and Re, still more preferably Mo,

- 8 face-capping ligands, which are preferably halogens, more preferably Br, and
- six apical ligands, which are preferably halogens, more preferably Br.

The organic cation of the luminescent salt of this particular embodiment can comprise a head which is an ammonium, preferably substituted by one or two C_1-C_3 alkyl group, more preferably substituted by two methyl groups, a linker having 1 to 12 methylene groups, preferably 8 to 12 methylene groups, more preferably 11 methylene group, at least one of the methylene group can be further replaced by –O-CO-, preferably the one closest to the terminal part, and the terminal part is a double C-C bond.

According to a particular embodiment, the organic cation of the luminescent salt associated to this particular metal cluster anion has:

- a head which is an ammonium, preferably substituted by one or two C_1-C_3 alkyl groups such as by two methyl groups and one C_1-C_{15} alkyl group such as a undecyl or dodecyl group, a linker having 1 to 15 methylene groups, preferably 8 to 12 methylene groups, more preferably 11 methylene groups, and the terminal part is a methacrylate function ($-OC(O)-C(CH_3)=CH_2$), or
- a head which is an ammonium, preferably substituted by one or two C_1-C_3 alkyl group such as by two methyl groups and one C_1-C_{15} alkyl group such as a undecyl or dodecyl group, a linker having 1 to 15 methylene groups, preferably 1 to 10 methylene groups, more preferably 1 to 5 methylene groups, such as 3 methylene groups, and the terminal part is an amine function ($-NH_2$) or a hydroxyl function (–OH), or
- a head which is an imidazolium, preferably substituted by one C_1-C_3 alkyl group, more preferably substituted by one methyl group, in particular on a nitrogen atom, a linker having 1 to 15 methylene groups, preferably 8 to 12 methylene groups, such as 9 methylene groups, and the terminal part is a double C-C bond, such as $-CH=CH_2$.

Depending on the nature of the cluster core/unit (metal atom used, geometry, surrounding ligands), different types of properties suitable from an applicative point of view can be expected. Many metal clusters are known to have catalytic activity towards many types of reactions.

Octahedral M_6 clusters (with M=Mo, W or Re) are highly luminescent in the red-near infrared area (form about 550nm to about 950nm). From the device perspective, the broad absorption and emission bands, large Stokes shift (about 300 nm) and long excited state lifetime of these octahedral clusters provide unique engineering advantages.

Further, the luminescence lifetime can be readily monitored using phase sensitive techniques, which can be implemented using a simple phase locked loop configuration, thereby eliminating the need for a bulky optical fluorimetre.

The upstanding luminescence properties of these luminescent salts can be used for telecommunication or biomedical applications.

The metal clusters in these luminescent salts are ideal luminescent probes for detection of gaseous oxygen concentrations ranging from about 0.09% to 90% at 1 atm, and important compositional range for medical and industrial processes.

Optoelectronic and photonic components (light source, protective glasses, optic amplifier, laser source, etc.) can also advantageously comprise these metal cluster anions.

In solar cell and photovoltaic systems, it is possible to build converter layers with these metal cluster anions to increase photovoltaic yield.

In biomedical application, use of these metal cluster anions can be advantageous for in situ cells visualisation, monitoring drug relieves, etc.

As said previously, the metal cluster anions may be used as photocatalists.

Polymeric material

A polymeric material incorporating the above luminescent salt will be described hereafter.

The polymeric material is made from two or more constituent materials with significantly different physical and/or chemical properties, which remain separate and distinct within the finished structure. In the polymeric material in question here, the polymer matrix functions as a support that can be easily shaped. The luminescent salt is used as a signal emitting element for various applications mentioned more in details here above.

The polymeric material may be obtained by mixing one or more polymers or monomers with the luminescent salt described above for subsequent polymerisation.

Polymers may be chosen from the group consisting of polyamide, polycarbonate, polyethylene, naphthalate polyethylene, terephthalate polyethylene, polyimide, polymethylmethacrylate, polystyrene, polyurethane, polycarbamate, vinylpolychloride, or a mixture thereof. The polymer can be also a hydride-terminated polydimethylsiloxane (PDMS).

Monomers may be chosen from the group consisting of amide, carbonate, ethylene, naphthalate ethylene, terephthalate ethylene, imide, methyl methacrylate, methacrylic acid, styrene, urethane, carbamate, vinyl chloride, and a mixture thereof. The monomer can be also a diol such as 1,6-butanediol, a cyanate such as hexamethylene diisocyanate (HDI), or a diamine such as hexane diamine (HAD).

According to a particular embodiment, the polymer is polymethyl methacrylate (PMMA) or the monomer is methyl methacrylate.

The polymeric material may comprise up to 100 wt.% of the luminescent salt, preferably up to 60 wt.%, more preferably up to 50 wt.%, preferably about 5 to about 50 wt.%, more preferably about 10 to about 50 wt.%. The weight percentages are given with respect to the total weight of the polymeric material.

Synthesis of a luminescent salt

A salt composed of an anion and the organic cation described above, referred to as a organic cation precursor, is mixed with a salt composed of a counter cation and the metal cluster anion described above, referred to as a metal cluster precursor. The luminescent salt described above is obtained through metathesis reaction between the organic cation precursor and the metal cluster precursor. The ratio of the organic cation precursor/metal cluster precursor may vary depending on the anionic charge of the metal cluster precursor. For example luminescent Rhenium clusters are teraanionic species of formula $[Re_6Q_8L_6]^{4-}$. Their charge is counterbalanced with Cs^+ or K^+ cations but can be replaced by a polymerisable cation.

According to a particular embodiment, the anion of the organic cation precursor is a halide such as Br^-.

According to another particular embodiment, the counter cation of metal cluster precursor is an alkali metal cation or a hydronium ion (H_3O^+).

Alkali metal comprises Li, Na, K, Rb, Cs and Fr. It can be in particular K or Cs.

Examples

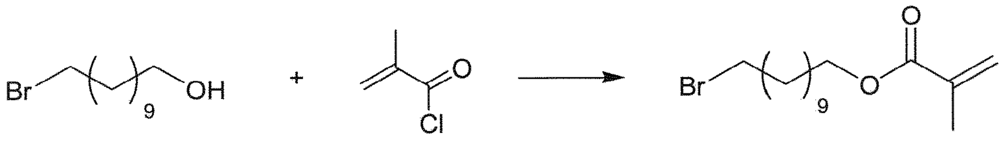
Examples of syntheses of a luminescent salt and a composite material according to the above description are given hereafter.

I - Synthesis of luminescent salts according to the invention

Compound 4

*(According to SciFinder, steps 1 and 2 were published for the first time in: M. Summers, J. Eastoe, S. Davis, Z. Du, R. M. Richardson, R. K. Heenan, D. Steytler, I. Grillo, Langmuir **2001**, 17, 5388)*

1 Esterification (step 1)

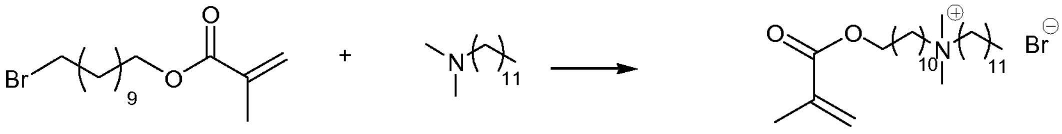


11-bromo-1-undecanol Methacryloyl chloride Compound 1

Methacryloyl chloride (0.92 g, 8.8 mmol) was dissolved in 10 mL dry tetrahydrofuran (THF) and added drop-wise to a stirred solution of 11-bromo-1-undecanol (2.0 g, 8.0 mmol) and triethylamine ($N(CH_2-CH_3)_3$)(0.87 g, 8.8 mmol) in 13 mL of dry THF. The mixture was stirred at 60°C the 2.5 hours. After cooling, the precipitated triethylamine hydrochloride ($N(CH_2-CH_3)_3 \cdot Hcl$) was filtered. The product filtrate was evaporated and purified by column chromatographic in dichloromethane (CH_2Cl_2). Compound **1** was obtained after purification as a colourless liquid (yield: 80%).

Compound **1**: ^{1}-H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.09 (d, 1H, $C\underline{H}H=C$), 5.54 (d, 1H, $C\underline{H}H=C$), 4.13 (t, 2H, $-CH_2-O$), 3.40 (t, 2H, $-CH_2-Br$), 1.94 (s, 3H, $-CH_3-C$), 1.87 - 1.84 (m, 2H, $-C\underline{H_2}CH_2-O$), 1.68 - 1.65 (m, 2H, $-C\underline{H_2}-CH_2-Br$), 1.42 - 1.39 (m, 14H, $-(CH_2)_7-$).

2. Quaternisation (step 2)

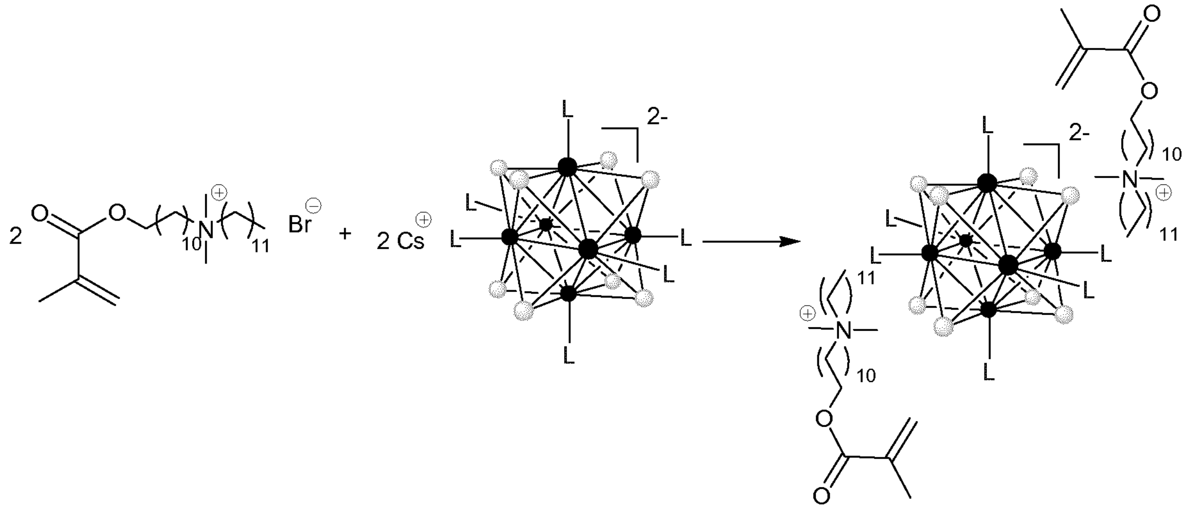


Compound 1 N, N-dimethyldodecylamine Compound **2**

The obtained compound **1** (1.3 g, 4 mmol), N,N-dimethyldodecylamine and 1 mg of 2,6-di-*tert*-butyl-4-methylmethylphenol (as inhibitor of polymerisation) were dissolved in 13 mL of chloroform and then heated at 60°C for 72 hours. On cooling the mixture was concentrated to 3-5 mL by vacuum and diethylether was added quickly. The clouded solution was kept at -18°C for three days (yield: 80%).

Compound **2**: ^{1}-H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 6.09 (d, 1H, C$\underline{\text{H}}$H=C), 5.54 (d, 1H, C$\underline{\text{H}}$H=C), 4.13 (t, 2H, -CH$_2$-O), 3.51 (t, 4H, -CH$_2$-N), 3.38 (s, 6H, CH$_3$-N), 1.94 (s, 3H, -CH$_3$-C), 1.7 – 1.67 (m, 4H, -(C$\underline{\text{H}_2}$-CH$_2$)$_2$N), 1.66 (m, 2H, -C$\underline{\text{H}_2}$-CH$_2$-O), 1.33 – 1.26 (m, 32H, -CH$_2$), 0.86 (t, 3H, -CH$_3$).

3. Metathesis with Cs$_2$Mo$_6$Br$_{14}$ (compound **3**)



Compound 2 Compound 3 Compound **4**

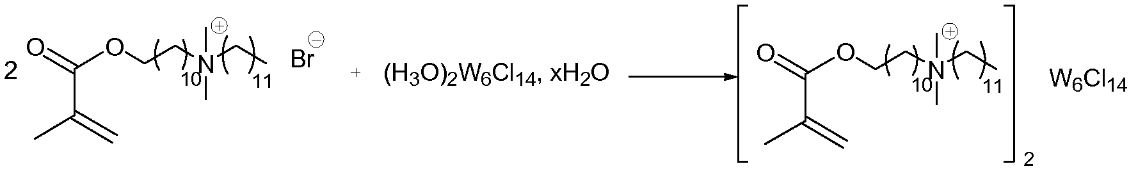
(In the reaction above, black beads represent Mo atoms, white beads and L represent Br atoms).

Compound **3** (1.97 g, 1 mmol) used as a metal cluster precursor was stirred in 20 mL of acetone until complete dissolution. A solution of compound 2 (1 g, 2.20 mmol) used as organic cation precursor was dissolved in dichloromethane and added drop wise to the previous solution of compound **3** and acetone. The mixture was heated for 2 hours. The CsBr formed was filtered off and the organic solution was dried under vacuum. Compound **4** was obtained as viscous oil after drying.

Compound **4**: ^{1}-H-NMR (400 MHz, CDCl$_3$): δ (ppm) = 6.02 (d, 2H, C$\underline{\text{H}}$H=C), 5.48 (d, 2H, C$\underline{\text{H}}$H=C), 4.06 (t, 4H, -CH$_2$-O), 3.20 (t, 8H, -CH$_2$-N), 3.09 (s, 12H, CH$_3$N-), 1.87 (s, 6H,-CH$_3$-C), 1.7 – 1.67 (m, 8H,-(CH$_2$-CH$_2$)$_2$N), 1.66 (m, 4H,-CH$_2$-CH$_2$-O), 1.24 – 1.16 (m, 64H, -CH$_2$-), 0.86 (t, 6H, -CH$_3$).

EDS: no caesium.

Compound 6

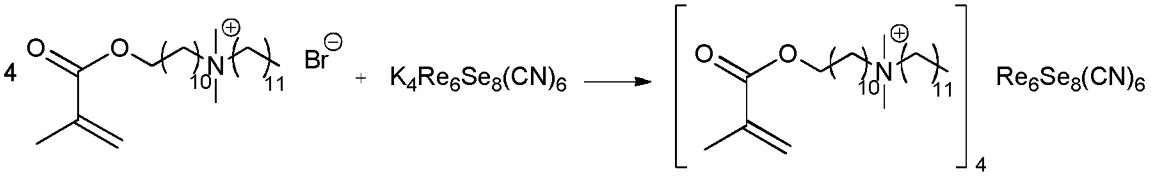


Compound **2** Compound **5** Compound **6**

Compound **5** (0.38 g, 0.23 mmol) was dissolved in 5 mL of EtOH (abs). A solution of compound **2** (0.21 g, 0.5 mmol) in 10 mL of dichloromethane was added dropwise to the cluster solution. The mixture was heated for 1 hour and the solvents evaporated under vacuum. The residue was dissolved in the minimum amount of acetone and filtered through a Celite® pad. The acetone was removed under vacuum. Compound **6** was obtained as a yellow oil. Yield 95%.

Compound **6**: ^{1}-H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 5.97 (d, 2H, C$\underline{H}$H=C), 5.48 (d, 2H, C$\underline{H}$H=C), 4.03 (t, 4H, -CH_2-O), 3.15 (t, 8H, -CH_2-N), 3.01 (s, 12H, CH_3N-), 1.84 (s, 6H,-CH_3-C), 1.7 – 1.60 (m, 8H,-(C$\underline{H_2}$-CH_2)$_2$N), 1.59 (m, 4H,-C$\underline{H_2}$-CH_2-O), 1.31 – 1.20 (m, 64H, -CH_2-), 0.80 (t, 6H, -CH_3). ^{13}-C-NMR (100 MHz, CD_2Cl_2): 167.5 (C=O), 136.7 (C(Me)=CH_2), 124.9 (CH_2=C), 65.1 (CH_2O), 64.83 (CH_2N), 51.9 (CH_3N), 31.9-22.7 (CH_2), 18.1 (CH_3 (C=CH_2), 13.9 (CH_3). Elemental analysis C58H116N2O4Cl14W6.6CH2Cl2: calc (%): C 25.50, H 4.28, N 0.93. Found: C 25.32, H 4.24, N 1.04.

Compound 8



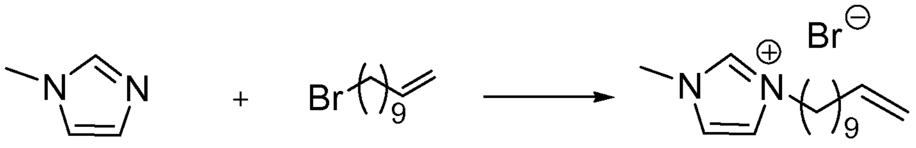
Compound **2** Compound **7** Compound **8**

Compound **7** (0.4 g, 0.19 mmol) was solubilised in 5 mL of distilled water. A solution of compound **2** in dichloromethane was added dropwise to the stirred water solution. The biphasic mixture was vigorously stirred for 1 h. After that the phases were allowed to separate and the organic phase was collected and washed three times with water. The dichloromethane was removed under vacuum to afford compound **8** as a dark red solid. Yield 95%.

Compound **8**: ^{1}-H-NMR (400 MHz, CD_2Cl_2): δ (ppm) = 5.98 (d, 4H, $C\underline{H}H{=}C$), 5.46 (d, 4H, $C\underline{H}H{=}C$), 4.03 (t, 8H, $-CH_2-O$), 3.19 (m, 20H, $-CH_2-N+CH_3-N$), 1.84 (s, 12H,-CH_3-C), 1.7 - 1.60 (m, 16H,-$(C\underline{H_2}-CH_2)_2N$), 1.59 (m, 8H,-$C\underline{H_2}-CH_2-O$), 1.31 - 1.20 (m, 128H, $-CH_2-$), 0.80 (t, 12H, $-CH_3$). ^{13}-C-NMR (100 MHz, CD_2Cl_2): 167.5 (C=O), 136.7 ($C(Me){=}CH_2$), 124.6 ($CH_2{=}C$), 64.7 (CH_2O), 64.0 (CH_2N), 52.7 (CH_3N), 31.9-22.7 (CH_2), 18.1 (CH_3 ($C{=}CH_2$), 13.9 (CH_3). EDAX: no potassium, no bromide; Re 47.45%, Se 47.34. Elemental analysis C122H232N10O8Se8Re6.2CH2Cl2: calc (%): C 38.33, H 6.12, N 3.60. Found: C 38.25, H 6.21, N 3.79.

*Compound **11***

1. Alkylation of methylimidazole (Zhang et al J. Appl. Polym. Sci., 2001, 121, 2430)

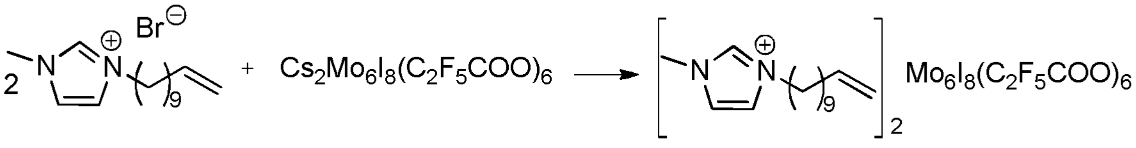


1-methylimidazole 11-bromo-1-undecene Compound **9**

11-Bromo-1-undecene (2.0 g, 8.58 mmol) and 1-methylimidazole (0.59 g, 7.17 mmol) were dissolved in 25 mL of $CHCl_3$ and the solution was stirred at 50°C for 15 h. The solvent was removed under vacuum to afford a viscous liquid. The liquid was washed 5 times with a mixture cyclohexane / ethyl acetate (1:1 v/v). Compound **9** was dried under vacuum to yield a viscous colourless oil. Yield 66%.

Compound **9**: ^{1}-H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.17 (s, 1H, $C\underline{H}{=}N$), 7.62 (s, 1H, $C\underline{H}{=}CH$), 7.44 (s, 1H, $CH{=}C\underline{H}$), 5.75 (m, 1H, $-C\underline{H}{=}CH_2$), 4.91 (dd, 2H, J = 24.4, 13.6 Hz, $-CH{=}C\underline{HH}$), 4.31 (t, 2H, J = 7.4 Hz, $-CH_2-N$), 4.28 (s, 3H, CH_3-N), 2.00 (q, 2H, J = 6.8 Hz, $-CH_2-$), 1.82 (m, 2H, $-CH_2-$) 1.24-1.17 (m, 12H,$-CH_2-$). ESI-MS (m/z): 235.21. Elemental analysis for C15H27N2Br.0.5H_2O: calc (%): C 55.55, H 8.70, N 8.64. Found: C 55.37, H 8.83, N 8.61.

2. Metathesis with $Cs_2Mo_6I_8(C_2F_5COO)_6$ (compound **10**)

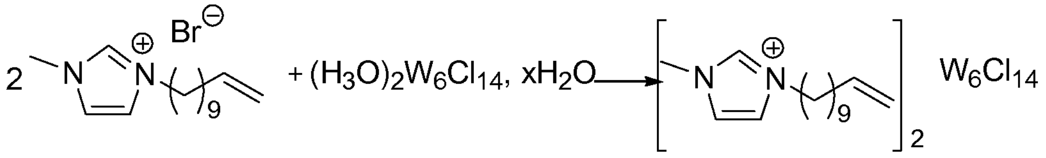


Compound **9** Compound **10** Compound **11**

The cluster precursor, compound **10**, (2 g, 0.70 mmol) was dissolved in 20 mL of dry acetone. A solution of the imidazolium salt, compound **9**, (0.45 g, 1.4 mmol) in 5 mL of dry acetone was added to the solution of cluster. The mixture was stirred at room temperature for 1 h. After that the acetone was evaporated in a rotary evaporator and the mixture was dissolved in dichloromethane. This solution was filtered through a Celite® pad. Evaporation of solvent lead to compound **11** as an orange-red viscous liquid. Yield 97%.

Compound **11**: ^{1}-H-NMR (400 MHz, acetone-d_6): δ (ppm) = 8.74 (s, 2H, C$\underline{H}$=N), 7.23 (s, 4H, C$\underline{H}$=C$\underline{H}$), 5.71(m, 2H, -C$\underline{H}$=CH$_2$), 4.88 (dd, 4H, *J* = 27.3, 13.4 Hz, -CH=C$\underline{HH}$), 4.10 (t, 4H, *J* = 7.4 Hz, -CH$_2$-N), 3.88 (s, 6H, CH$_3$-N), 1.95 (q, 4H, *J* = 7.0 Hz, -CH$_2$-), 1.80 (m, 4H, -CH$_2$-) 1.24-1.17 (m, 24H,-CH$_2$-). ^{19}F-NMR: δ (ppm) = 94.45 (3F), 56.84 (2F). EDS: no cesium, no bromide; Mo 8.30%, I 11.63 %, F 80.07% Elemental analysis for C48H54N4O12F30I8Mo6: calc (%): C 18.97, H 1.79, N 1.84. Found: C 18.71, H 1.84, N 1.62.

Compound 12



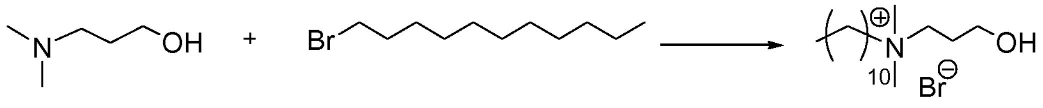
Compound **9** Compound **5** Compound **12**

Compound **5** (2 g, 1.2 mmol) were dissolved in 15 mL of EtOH (abs). A solution of compound **9** (0.77 g, 2.4 mmol) in 10 mL of dichloromethane was added drop wise to the cluster solution. The mixture was heated for 1 hour and the solvents evaporated under vacuum. The residue was dissolved in the minimum amount of dichloromethane and filtered through a Celite® pad. The dichloromethane was removed under vacuum. Compound **12** was obtained as a yellow powder. Yield 92%.

Compound **12**: ^{1}-H-NMR (400 MHz, acetone-d_6): δ (ppm) = 9.10 (s, 2H, C$\underline{H}$=N), 7.82 (s, 2H, C$\underline{H}$=CH), 7.76 (s, 2H, CH=C$\underline{H}$), 5.81 (m, 2H, -C$\underline{H}$=CH$_2$), 4.88 (dd, 4H, *J* = 28.7, 13.7 Hz, -CH=C$\underline{HH}$), 4.41 (t, 4H, *J* = 7.3 Hz, -CH$_2$-N), 4.10 (s, 6H, CH$_3$-N), 2.07-2.01 (m, 8H, -CH$_2$-), 1.38-1.13 (m, 24H,-CH$_2$-). EDS: W 29.21%, Cl 64.71%, Br 6.09 %. Elemental analysis for C30H54N4Cl14W6. HBr: calc (%): C 17.41, H 2.63, N 2.70. Found: C 17.04, H 2.57, N 2.65.

Compound 14

1. Synthesis of hydroxy-terminated ammonium salt (Progress in Organic Coatings, 72 (2011), 305-314).

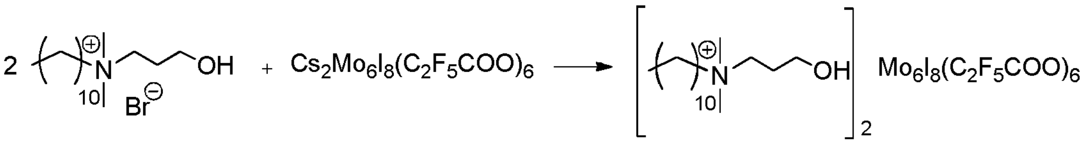


3-dimethylaminopropanol 11-bromoundecane Compound **13**

3-dimethylaminopropanol (1.55 g, 15 mmol) and 11-bromoundecane (3.06 g, 13 mmol) were mixed and refluxed at 80°C for 30 min. The reaction mixture was cooled to room temperature and 1:3 (v/v) propanol: methanol was poured into the flask. After 12 h of reaction at 80 C, the solvents were evaporated and the product was purified by washing twice with diethyl ether. Yield 82%.

Compound **13**: ^{1}-H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.52(s, 1H, OH), 3.75 (m, 4H, $C\underline{H}_2$-OH+ $C\underline{H}_2$-N), 3.42 (m, 2H, CH_2-N), 3.31 (s, 6H, -CH_3-N), 2.18 (m, 2H, $C\underline{H}_2CH_2N$), 1.78 (m, 2H, $C\underline{H}_2CH_2N$), 1.35-1.26 (m, 16H, -CH_2-), 0.88 (t, 3H, -CH_3). ^{13}-C-NMR (100 MHz, CD_2Cl_2): 63.92 (C-O), 62.01 ($\underline{C}H_2$-N), 57.96 ($\underline{C}H_2$-N), 50.55 ($\underline{C}H_3$-N), 31.76 (-CH_2-), 26.23 (-CH_2-), 25.93 (-CH_2-), 13.50 (-CH_3). ESI-MS (m/z): 258.28. Elemental analysis for C17H38NOBr.0.5H_2O: calc (%): C 55.32, H 10.74, N 4.03. Found: C 55.84, H 1.61, N 4.04.

2. Metathesis with $Cs_2Mo_6I_8(C_2F_5COO)_6$



Compound **13** Compound **10** Compound **14**

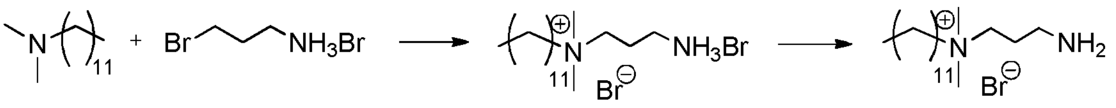
Compound **13** (1.2 g, 35 mmol) was dissolved in acetone. A solution in acetone of fluorinated cluster (0.5 g, 17.6 mmol) was added and the mixture stirred for 1h. The acetone was removed and the residue was solubilised in dichloromethane and the solution filtered through Celite®. The solvent was evaporated to yield a dark orange oil. Yield = 92%.

Compound **14**: ^{1}-H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.91 (s, 2H, OH), 3.57 (m, 4H, $C\underline{H}_2$-OH), 3.53 (m, 4H, CH_2-N), 3.42 (m, 4H, CH_2-N), 3.20 (s, 12H, -CH_3-N), 2.08-

1.70 (m, 8H, -CH2-), 1.28-1.15 (m, 32H, $-CH_2-$), 0.74 (t, 6H, $-CH_3$). ^{19}F-NMR: δ (ppm) = 94.52 (3F), 56.86 (2F).

Compound 16

1. Alkylation of the amine

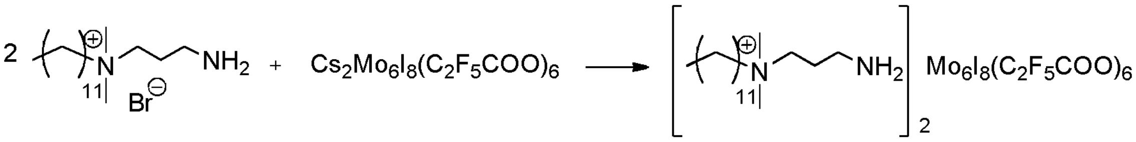


Dodecylamine bromopropylamine Compound **15**

3-Bromopropylamine (1.1 g, 5 mmol) and N,N-dimethyldodecylamine (1.1 g, 5.1 mmol) were dissolved in 12.5 mL of ethanol. The reaction was heated at reflux under Ar for 40 h. The solution was cooled down and ethylacetate was added and the compound precipitated. The white solid was filtered off and solubilised in the minimum amount of water and potassium hydroxide was added until a pH of 10. The water was evaporated and the product purified in a mixture of ethanol/THF. The solvent was evaporated and the residue solubilised in dichloromethane and precipitated in diethylether at -18°C. Yield 38%.

Compound **15**: ^{1}-H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.83 (br, 2H, NH_2), 3.40-3.26 (m, 10H, $C\underline{H}_2$-N+ $C\underline{H}_3$-N), 2.42 (m, 2H, $C\underline{H}_2-NH_2$), 1.71 (m, 2H, $C\underline{H}_2-CH_2-NH_2$), 1.30-1.20 (m, 20H, $-CH_2-$), 0.81 (t, 3H, $-CH_3$). ESI-MS (m/z): 271.3.

2. Metathesis with $Cs_2Mo_6I_8(C_2F_5COO)_6$



Compound **15** Compound **10** Compound **16**

Compound **15** (0.25 g, 70 mmol) was solubilised in ethanol and added to a solution of compound **10** (1 g, 35 mmol) in acetone. The mixture was stirred for 1 h and the solvents evaporated. The residue was solubilised in dichloromethane and filtered through a Celite® pad. The solvent was evaporated to yield an orange solid. Yield = 96 %.

Compound **16**: ^{1}-H-NMR (400 MHz, acetone-d_6): δ (ppm) = 4.05 (br, 4H, NH_2), 3.90 (m, 4H, $C\underline{H}_2-NH_2$), 3.58 (m, 4H, $C\underline{H}_2$-N), 3.38 (s, 12H, $C\underline{H}_3$-N), 2.01-1.90 (m, 8H,

$C\underline{H}_2$-NH_2 + $C\underline{H}_2$-CH_2-NH_2), 1.41 (m, 8H, -CH_2-), 1.30 (m, 32H, -CH_2-), 0.89 (t, 6H, -CH_3). EDS: no cesium, no bromide; Mo 8.30%, I 9.67 %, F 65.3%.

II - Synthesis of polymeric materials according to the invention

Synthesis of PMMA material containing Mo cluster

Compound **4** was dissolved in distilled methylmethacrylate (MMA) (from 1 wt.% to 50 wt.%). Radical initiator azobisisobutyronitrile (AIBN) (0.2 wt.%) was added. The resulting solutions were sonicated at 80°C for two hours. Then, the solutions were placed in an oven at 60°C for 48 hours. A transparent solid composite material was obtained.

Table 1 below shows measured properties of four samples. The decomposition temperatures (Td) and weight percentage of compound 4 in the material with respect to the total weight of the resulting material, are computed by Thermogravimetric analysis (TGA) using a TGA Perkin Pyris diamond at a heating rate of 10K/min. Glass transition temperatures (Tg) were measured by differential scanning calorimetry using a NETZSCH DSC 200 F3 instrument equipped with an intracooler at heating and cooling rate of 10K/min.

Sample	Compound 4 (wt.%)	MMA (mg)	Compound 4 (mg)	T_d (°C)	T_g (°C)
CM1	0	2000	0	370	107
CM2	1	1980	20	362	106
CM3	10	1800	200	365	119
CM4	50	500	500	375	113

Table 1

CM1, CM2, CM3 and CM4 were all soluble in $CHCl_3$. It was attempted to incorporate 0.36 wt.% (with respect to the total weight of the resulting material) metal cluster units comprising six covalently linked polymerisable functions (apical ligands) in a PMMA matrix, the resulting material was not soluble in $CHCl_3$.

Also, as shown in figures 2 and 3, the decomposition temperature is the same for all CM1 to CM4 samples and that 50 wt.% or 10wt.% of compound 4 were effectively introduced respectively in the CM4 and CM3 polymer matrix.

As shown in figure 4, and table 2 below (wherein xc indicates the wavelength at maximum of luminescence, w indicates the full width at half maximum of the luminescent peaks and R^2 indicates the correlation coefficient of the gaussian model of the solid state luminescence: $y=y_0+A\cdot\exp(-0.5\cdot((x-xc)/w)^2)$, the closest R^2 is to 1, the more accurate the given parameters xc and w are) the metal clusters keep their luminescence properties within the polymer matrix as compared to $Cs_2Mo_6Br_{14}$ (compound 3) powder.

	xc	w	R^2
$[(n\text{-}C_4H_9)_4N]_2[Mo_6Br_{14}]$	699	64.35	0.9998
CM3	704	79.36	0.9996

Table 2

Synthesis of PMMA material containing W cluster

Compound **6** was dissolved in acetonitrile and was added to distilled MMA (at 1 wt.% and 50 wt.%). Radical initiator AIBN (0.2 wt.%) was added. The solutions were kept for 12h in a thermostated bath at 70 °C and then placed in the oven at 60°C for 48 h. A transparent solid composite material was obtained.

Table 3 below shows measured properties of two samples. The decomposition temperatures (Td) and weight percentage of compound **6** in the material are computed by Thermogravimetric analysis (TGA). Glass transition temperatures (Tg) were measured by differential scanning calorimetry 10K/min. The weight average molecular weight (M_w) and polydispersity were mesured using a set of three columns: 2xResiPore and 1xPL gel Mixed C (Polymer Labs.). The detection system was composed of a refractometer and UV detector. Chloroform was used as eluent with flow rate of 0.8 mL min^{-1}. The elution profiles were analysed by the software Empower GPC module (Waters). Calculations were based on calibration curves obtained from polystyrene standards ranging from 200 g mol^{-1} up to 6 x 10^6 g mol^{-1}. For the analysis, samples were refluxed 30 min in chloroform. The obtained solutions were filtered prior to injection.

Sample	Compound 6 (wt.%)	MMA (mg)	Compound 6 (mg)	T_d (°C)	Inorg wt%	T_g (°C)	Mw (g.mol^{-1})	Polydispersity
CM6	1	1980	20	403	0.85	108	558000	1.1
CM7	50	500	500	402	45	90.2	-	-

Table 3

CM6 was soluble in organic solvents, i.e. $CHCl_3$ while CM7 was only partially soluble.

Synthesis of PMMA material containing Re cluster

Compound **8** was dissolved in acetonitrile and was added to distilled MMA (at 1 wt.% and 50 wt.%). Radical initiator AIBN (0.2 wt.%) was added. The solutions were kept for 12h in a thermostated bath at 70 °C and then placed in the oven at 60 °C for 48 h. A transparent solid composite material was obtained.

Table 4 below shows measured properties of two samples. The decomposition temperatures (Td) and weight percentage of compound **8** in the material are computed by Thermogravimetric analysis (TGA). Glass transition temperatures (Tg) were measured by differential scanning calorimetry 10K/min. The weight average molecular weight (M_w) and polydispersity were measured as described for examples CM6 and CM7.

Sample	Compound 8 (wt.%)	MMA (mg)	Compound 8 (mg)	T_d (°C)	Inorg wt%	T_g (°C)	Mw (g.mol^{-1})	Polydispersity
CM8	1	1980	20	383	0.64	98	627000	1.1
CM9	20	1800	200	394	40	99	583000	1.1

Table 4

CM8 and CM9 were soluble in organic solvents, i.e. $CHCl_3$.

Synthesis of Polystyrene material containing Mo cluster

Styrene is purified by an inhibitor column removal prior polymerisation. Compound **4** (in 1 and 50 wt. %) and styrene were solubilised in acetonitrile and AIBN (20 mg) as initiator was added. The polymerisation was held for 12 h in a thermostated bath at 70 °C and the 48h in an oven at 60 °C. An orange transparent composite was obtained.

Table 5 below shows the Tg, the Mw and polydispersity of three samples.

Sample	Compound 4 (wt.%)	Styrene (mg)	Compound 4 (mg)	T_d (°C)	Inorg wt%	T_g (°C)	Mw (g.mol^{-1})	Polydispersity
CM10	0	1000	0	414	0.26	91.6	242000	2.45
CM11	1	1980	20	445	0.96	93	130000	2.67
CM12	50	500	500	432	38	34.3	-	-

Table 5

CM10 and CM11 were soluble in organic solvents, i.e. $CHCl_3$ while CM12 was only partially soluble.

Synthesis of Polydimethylsiloxane (PDMS) material containing Mo cluster

Compound **11** (at 1 and 15 wt.% (maximum) was dissolved in dry dichloromethane and to that hydride-terminated PDMS (Mn = 17500) was added. Karsted's catalyst was added (20 mg) and the reaction heated at reflux for 2 days. The dichloromethane was evaporated and crude solubilised in pentane and filtered over an Acrodisc® (1μm) filter. The pentane was evaporated to afford a transparent orange oil in the case of 1% cluster and an orange solid in the case of 15% cluster.

Table 6 below shows the composition and the Mw and polydispersity of two materials.

Sample	Compound 11 (wt.%)	PDMS (mg)	Compound 11 (mg)	Mw (g.mol^{-1})	Polydispersity
CM14	1	1980	20	68000	1.4
CM15	15	1266	220	_	_

Table 6

CM14 was soluble in organic solvents, i.e. $CHCl_3$ while CM15 was only partially soluble.

Synthesis of PDMS material containing W cluster

The same procedure was followed with compound **12** (1% and 10 wt.%) as percursor. A yellow oil was obtained for 1% cluster and a yellow gel for 10% cluster.

Table 7 below shows the composition and the Mw and polydispersity of two materials.

Sample	Compound 12 (wt.%)	PDMS (mg)	Compound 12 (mg)	Mw (g.mol^{-1})	Polydispersity
CM16	1	1980	20	38000	1.1
CM17	10	1266	236	_	_

Table 7

CM16 was soluble in organic solvents, i.e. $CHCl_3$ while CM17 was only partially soluble.

Figure 5 shows the ^{1}H-NMR of materials CM15 (b) and CM17 (c) as well as the commercial PDMS material (a). The disappearance of the signal at 4.65 ppm corresponding to the proton in -Si-H groups proves the complete reaction of the cluster material with the terminal hydride functions in the commercial PDMS.

Synthesis of Polyurethane material containing Mo cluster

A mixture of 1,6-butanediol and compound **14** (from 1 to 50 wt.%) was heated to 50 °C to melt. To that the hexamethylene diisocyanate (HDI) was added under argon and the reaction was left for 4h under Ar. The polymer was purified by washing with methanol twice and filtering off. The product was dried under vacuum to yield an orange solid. All materials were insoluble in common solvents but hot DMF and DMSO.

Table 8 below shows the composition of five materials as well as the T_d, the weight percentage of inorganic cluster calculated by TGA analysis and the T_m (melting temperature) determined by DSC.

Sample	Compound 14 (wt.%)	Butanediol (mg)	Compound 14 (mg)	HDI (mg)	T_d (°C)	inorganic wt%	T_m (°C)
CM18	0	270	0	500	457	3.7	94
CM19	1	360	10	672	466	5.7	137
CM20	10	312	100	589	394	12.7	101
CM21	20	310	220	592	432	17.5	115
CM22	50	173	500	321	434	34	128

Table 8

Synthesis of nylon material containing Mo cluster

Compound **16** (1 and 50 wt.%) and hexanediamine (HDA) were dissolved in dry THF. To that a solution of adipoyl chloride in THF was added dropwise. The reaction was heated at 50°C for 12h. The precipitate formed was filtered off and washed with water and ancetone. Composites in the form of orange solid were obtained. All materials were insoluble in common solvents and water.

Table 9 below shows the composition of the materials and T_d and the calculated weight of inorganic part and the T_g and T_m that were determined by DSC.

Sample	Compound 16 (wt.%)	HDA (mg)	Compound 16 (mg)	adipoyl chloride(mg)	T_d (°C)	Inorganic wt%	T_g (°C)	T_m (°C)
CM23	0	406	0	640	473	3.2	148	173
CM24	1	490	10	500	453	9.3	135	171
CM25	50	214	500	366	382	47	106	146

Table 9

The luminescence spectra under irradiation at 400 nm:

- of CM24 (plain line), CM19 (dashed line), CM2 (dotted line) and CM14 (dash-dotted line) is represented on Figure 6;
- of CM19 (dotted line), CM20 (dashed line), CM21 (dash-dotted line) and CM22 (plain line) is represented on Figure 7; and
- of CM6 (plain line) and CM16 (dashed line) is represented on Figure 8.

Claims

1. A luminescent salt comprising a metal cluster anion and an organic cation,

wherein the metal cluster anion comprises a metal cluster with at least two metal atoms, and ligands, the metal atoms being chosen from the group consisting of molybdenum, rhenium, tungsten, thallium, niobium, and mixtures thereof,

wherein the organic cation comprises a cationic head substituted by at least one substituent including a polymerisable functional group.

2. The luminescent salt of claim 1, wherein the metal cluster anion has the following formula:

$[M_aQ_bX_c]^{d-}$,

wherein M represents the metal atoms of the metal cluster, a ranging from 2 to 20, preferably from 2 to 8, Q and X represent the ligands,

Q representing a face-capping ligand or an edge-bridging ligand, b ranging from 2 to 30, preferably from 8 to 12,

X representing an apical ligand, c ranging from 2 to 50, preferably from 2 to 6, and

d ranging from 1 to 12, preferably 2 to 4.

3. The luminescent salt of claim 2, wherein Q is either a halogen, a chalcogen, and mixtures thereof.

4. The luminescent salt of claim 2 or claim 3, wherein X comprises at least one element chosen from the group consisting of: fluorine, chlorine, bromine, iodine, carbon, nitrogen, sulphur, boron, oxygen, hydrogen and mixtures thereof.

5. The luminescent salt of one of any claim 1 to 4, wherein the cationic head is chosen from the group consisting of an imidazolium, a pyridinium, a pyrolidinium, an ammonium, a phosphonium, a hydroxyphosphonium or a sulfonium; in which said pyrolidinium, ammonium, phosphonium, hydroxyphosphonium or sulfonium can be further substituted by one or two C_{1-} C_3 alkyl groups.

6. The luminescent salt of claim 5, wherein the substituent comprises a terminal part and a linker having from 1 to 30 methylene groups, the terminal part being the polymerisable functional group and the linker linking the terminal part to the cationic head.

7. The luminescent salt of claim 6, wherein at least one of the methylene groups of the linker is replaced by one or more atoms or groups of atoms chosen from the group consisting of aromatic rings, -O-, -CO-, -S-, -CH=CH-, -C≡C-, -COO-, -OC(O)-, -CH=N-, -CH=N-, -C(O)NH-, -N=N-, -NH(CO)- and mixtures thereof.

8. The luminescent salt of claim 6 or claim 7, wherein at least one of the hydrogen atoms of the linker are replaced by fluorine atom.

9. The luminescent salt of any claim 1 to 8, wherein the polymerisable functional group is chosen from the group consisting of: double carbon-carbon chemical bond, triple carbon-carbon chemical bond, an azide function, a methacrylate function, acrylate function, an amine function, a carboxylic function, an aldehyde function, a hydroxyl function, an alkoxy function, an iodine atom, a bromine atom and a chlorine atom.

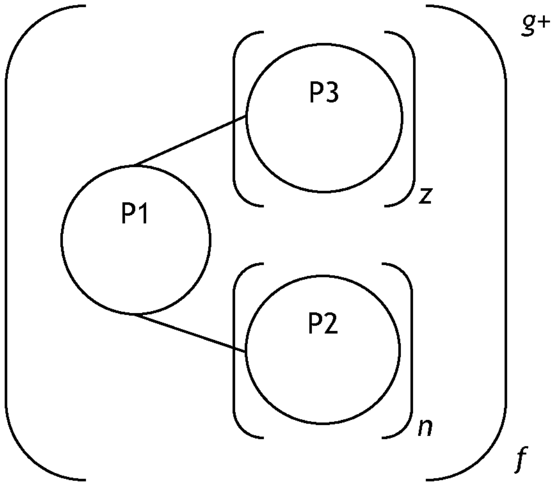
10. The luminescent salt of any claim 5 to 9, wherein the organic cation is further substituted by a second substituent containing from 1 to 30 methylene groups.

11. The luminescent salt of claim 10, wherein at least one of the methylene groups of the second substituent is replaced by one or more atoms or groups of atoms chosen from the group consisting of aromatic rings, -O-, -CO-, -S-, -CH=CH-, -C≡C-, -COO-, -OC(O)-, -CH=N-, -CH=N-, -C(O)NH-, -N=N-, -NH(CO)- and mixtures thereof.

12. The luminescent salt of claim 10 or claim 11, wherein at least one of the hydrogen atoms of the second substituent is replaced by a fluorine atom.

13. The luminescent salt of claim 2 to 4, having the following formula:

$[M_aQ_bX_c]^{d-}$



wherein P1 represents the cationic head;

wherein P2 and P3 are substituents,

z ranging from 0 to 12, preferably from 1 to 3, n ranging from 1 to 12, preferably 1 or 2, g ranging from 1 to 4, and f ranging from 1 to 12 and equals d/g;

wherein P1 is chosen from the group consisting of an imidazolium, a pyridinium, a pyrolidinium, an ammonium, a phosphonium, a hydroxyphosphonium or a sulfonium,

wherein P2 comprises a terminal part and a linker having from 1 to 30methylene groups, the terminal part being the polymerisable functional group and the linker linking the terminal part to thecationic head,

preferably, at least one of the methylene groups of the linker is replaced by one or more atoms or groups of atoms chosen from the group consisting of aromatic rings, -O-, -CO-, -S-, -CH=CH-, -C≡C-, -COO-, -OC(O)-, -CH=N-, -CH=N-, -C(O)NH-, -N=N-, -NH(CO)- and mixtures thereof,

preferably, at least one of the hydrogen atoms of the linker are replaced by a fluorine atom, and/or

preferably, the polymerisable functional group is chosen from the group consisting of: double carbon-carbon chemical bond, triple carbon-carbon chemical bond, an azide function, a methacrylate function, acrylate function, an amine function, a carboxylic function, an aldehyde function, a hydroxyl function, an alkoxy function, an iodine atom, a bromine atom and a chlorine atom;

wherein P3 contains from 1 to 30 methylene groups,

preferably, at least one of the methylene groups of P3 is replaced by one or more atoms or groups of atoms chosen from the group consisting of aromatic rings,

-O-, -CO-, -S-, -CH=CH-, -C≡C-, -COO-, -OC(O)-, -CH=N-, -CH=N-, -C(O)NH-, -N=N-, -NH(CO)- and mixtures thereof.

14. A polymeric material comprising a polymer matrix which has polymerised with the luminescent salt of any claim 1 to 13.

15. The polymeric material of claim 14, comprising up to 60wt.% of the luminescent salt, preferably up to 50wt.%, still preferably 5 to 50 wt.%, more preferably about 10 to 50 wt.%, weight percentage being given with respect to the total weight of the polymeric material.

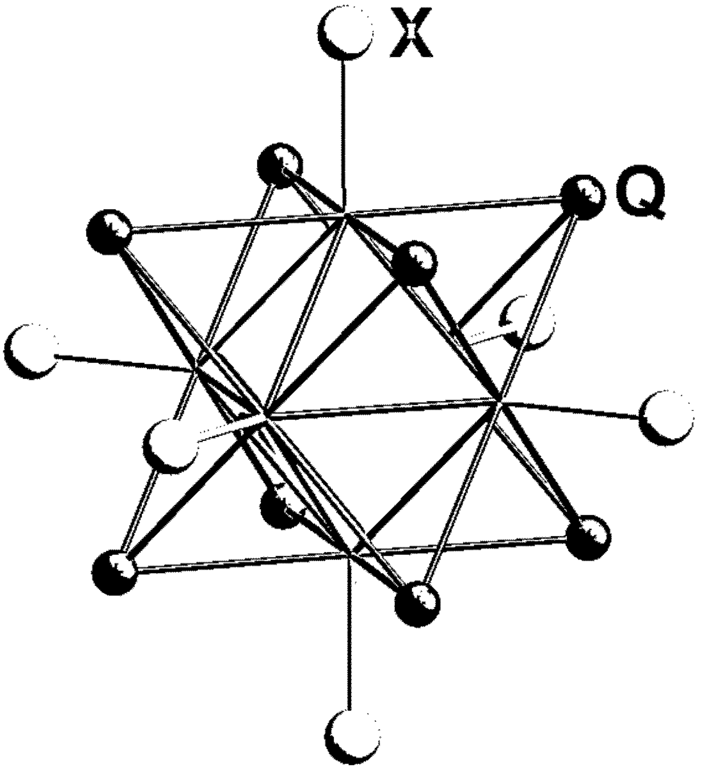

X
Q

FIG. 1

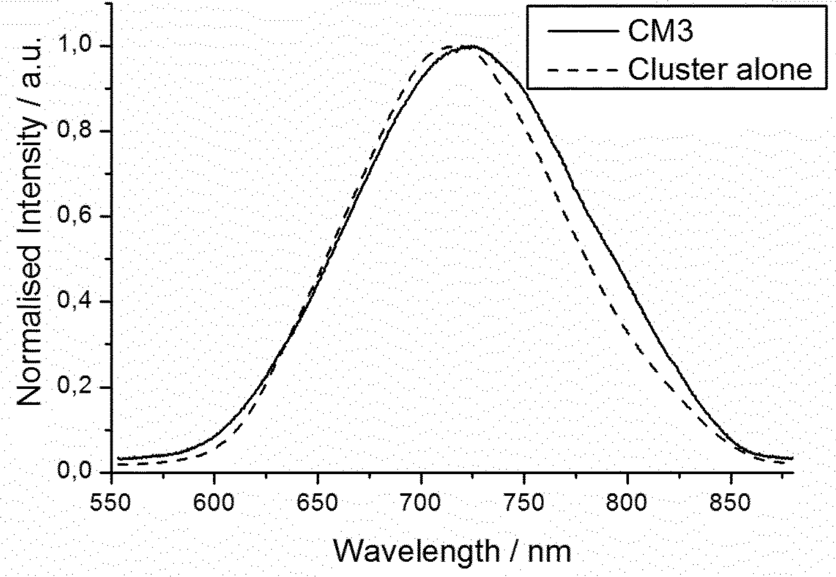

CM3
Cluster alone
Normalised Intensity / a.u.
0,0
0,2
0,4
0,6
0,8
1,0
550
600
650
700
750
800
850
Wavelength / nm

FIG. 4

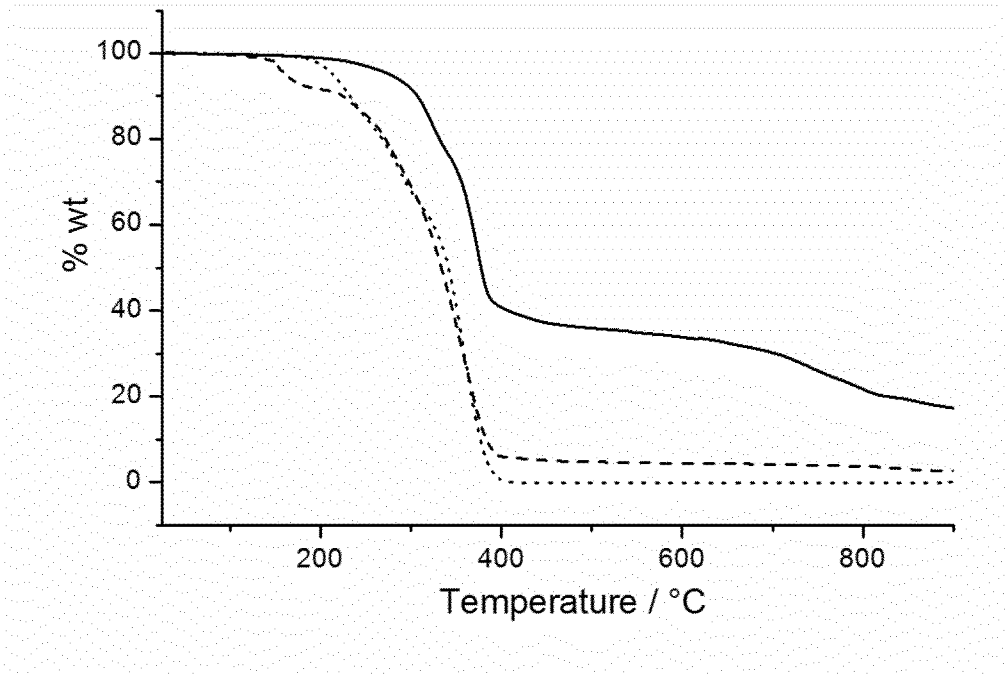

100
80
60
40
20
0
% wt
200
400
600
800
Temperature / °C

FIG. 2

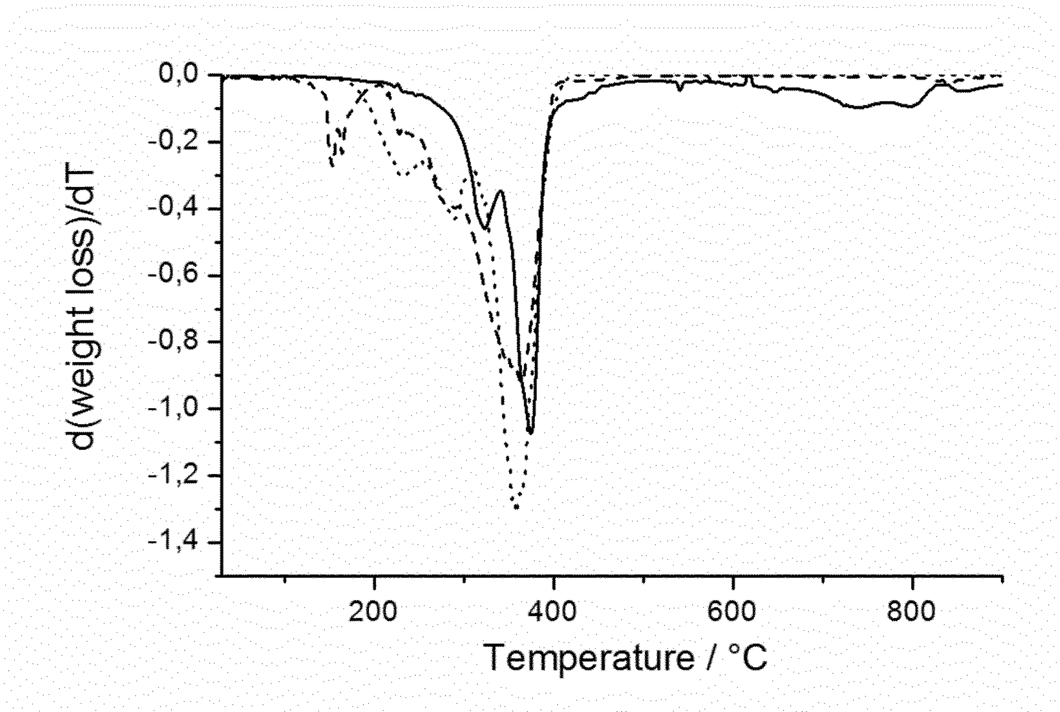

0,0
-0,2
-0,4
-0,6
-0,8
-1,0
-1,2
-1,4
d(weight loss)/dT
200
400
600
800
Temperature / °C

FIG. 3

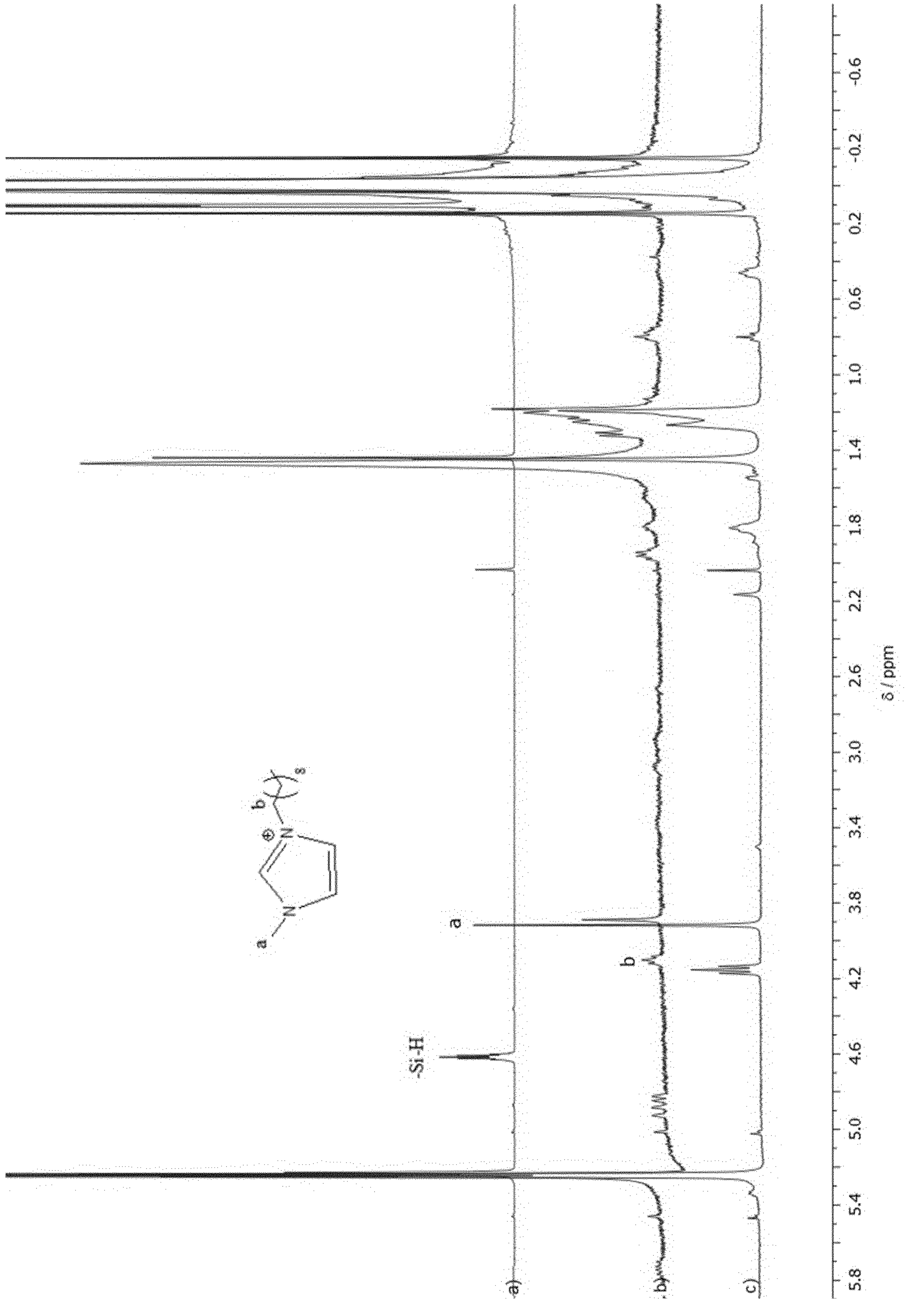

a)
b)
c)
Si-H
a
b
a
b
s
N
N
⊕
δ / ppm
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2
-0.6

FIG. 5

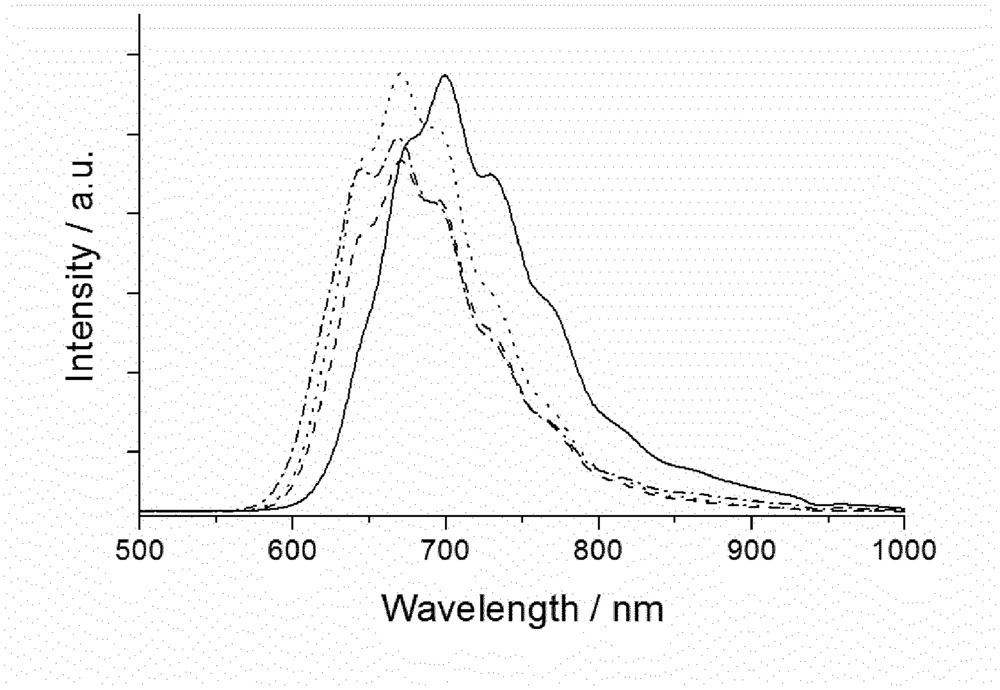

Intensity / a.u.
500
600
700
800
900
1000
Wavelength / nm

FIG. 6

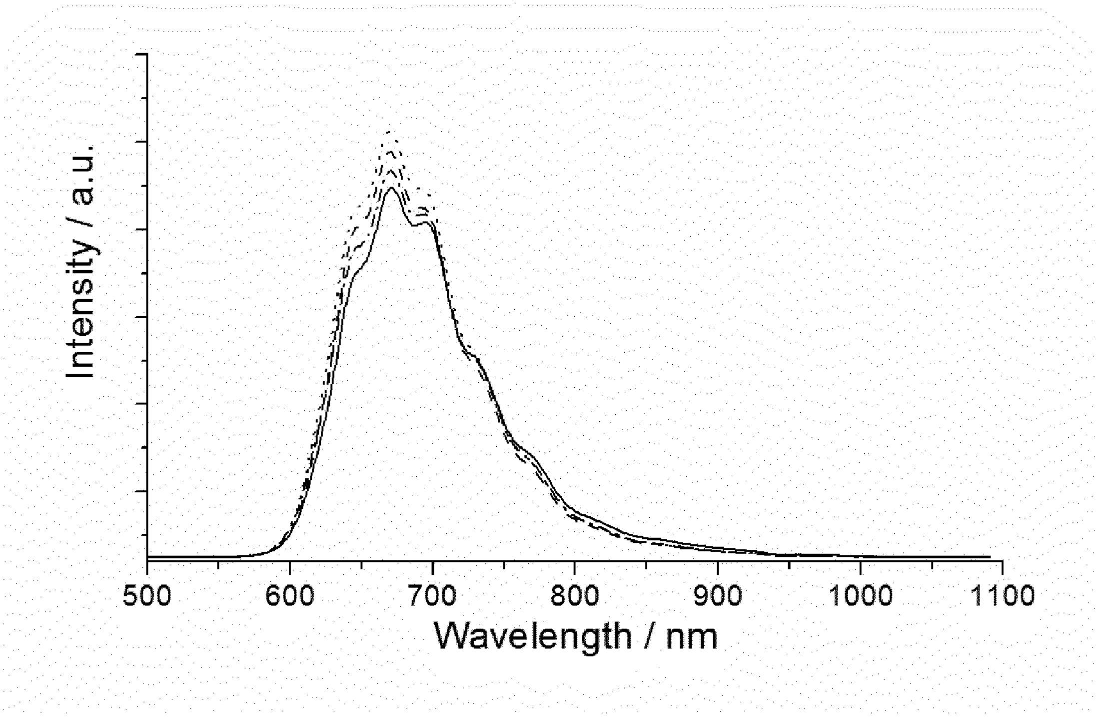

Intensity / a.u.
500
600
700
800
900
1000
1100
Wavelength / nm

FIG. 7

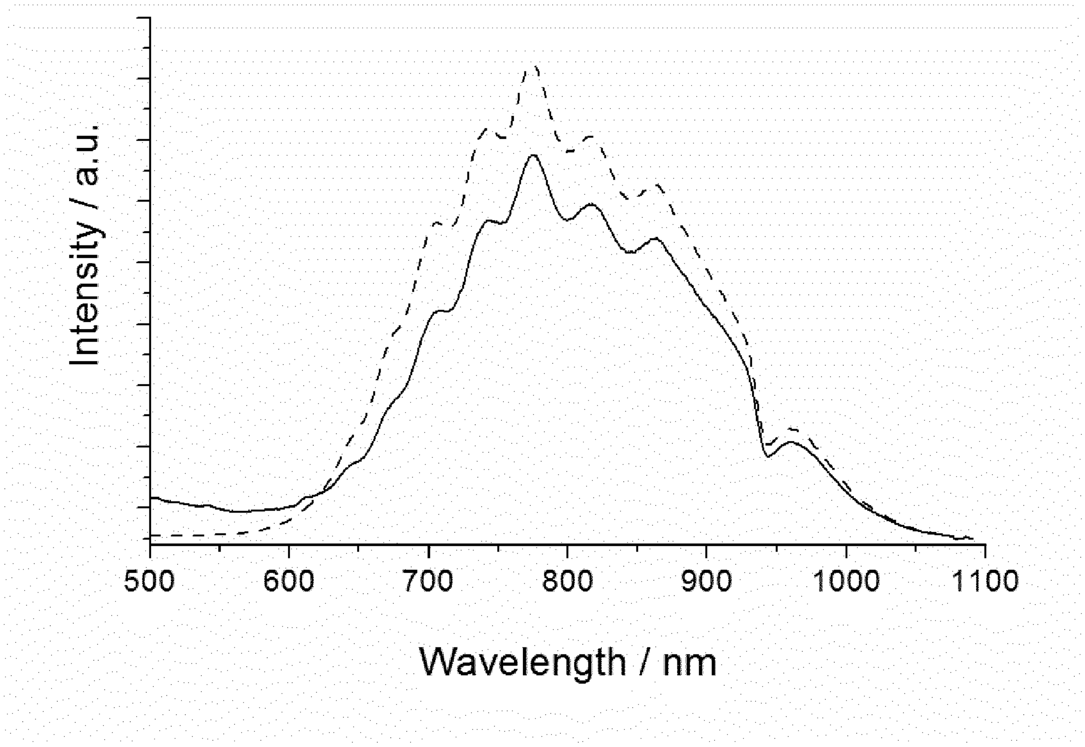


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/050739

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/06
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K

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

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

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	N. D. GOLUBEVA ET AL: "Synthesis, Structure, and Properties of New Hybrid Nanocomposites Containing the [Mo 6 (3 -Cl) 8] 4+ Cluster", INORGANIC MATERIALS, vol. 40, no. 3, 1 March 2004 (2004-03-01), pages 306-313, XP055054424, ISSN: 0020-1685, DOI: 10.1023/B:INMA.0000020534.96346.55 page 308 - page 312; figures; tables ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 12 February 2014	Date of mailing of the international search report 03/03/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Doslik, Natasa

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YU-FEI SONG ET AL: "Recent advances on polyoxometalate-based molecular and composite materials", CHEMICAL SOCIETY REVIEWS, vol. 41, no. 22, 1 January 2012 (2012-01-01), page 7384, XP055054444, ISSN: 0306-0012, DOI: 10.1039/c2cs35143a page 7385; figures page 7397 - page 7399 -----	1-15
X	ANNA PROUST ET AL: "Functionalization and post-functionalization: a step towards polyoxometalate-based materials", CHEMICAL SOCIETY REVIEWS, vol. 41, no. 22, 1 January 2012 (2012-01-01), page 7605, XP055054442, ISSN: 0306-0012, DOI: 10.1039/c2cs35119f page 7611 - page 7618; figures -----	1-15
X	JOANNA BÄCKER ET AL: "Crystalline and Liquid Crystalline Organic-Inorganic Hybrid Salts with Cation-Sensitized Hexanuclear Molybdenum Cluster Complex Anion Luminescence", EUROPEAN JOURNAL OF INORGANIC CHEMISTRY, vol. 2011, no. 26, 1 September 2011 (2011-09-01), pages 4089-4095, XP055054420, ISSN: 1434-1948, DOI: 10.1002/ejic.201100365 page 4089 - page 4093; figures -----	1-13
X	AARON R MOORE ET AL: "Organoimido-polyoxometalates as polymer pendants", CHEMICAL COMMUNICATIONS - CHEMCOM; [6015D], ROYAL SOCIETY OF CHEMISTRY, GB, 1 January 2000 (2000-01-01), pages 1793-1794, XP002469280, ISSN: 1359-7345 page 1793 - page 1794; figures -----	1-7,9