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(54) Title: POLYHETEROSILOXANE COMPOSITION AND SILICONE COMPOSITION INCLUDING A POLYHETEROSILOXANE

(57) Abstract: A sensitized polyheterosiloxane composition includes at least one non-lanthanide metal, siloxy units, and a photosensitizer. Each R^1 is independently a hydrocarbon or halogenated hydrocarbon group comprising 1 to 30 carbon atoms. The mole fractions of the at least one non- lanthanide metal and the siloxy units relative to each other is of the formula: $[\text{at least one non-lanthanide metal}]_a[R^1{}_3SiO_{1/2}]_m[R^1{}_2SiO_{2/2}]_d[R^1SiO_{3/2}]_t[SiO_{4/2}]_q$, wherein a is from 0.001 to 0.9, m is from zero to 0.9, d is from zero to 0.9, t is from zero to 0.9, and q is from zero to 0.9, and wherein m, d, t, and q cannot all be zero and the sum of a+m+d+t+q ≈ 1. The photosensitizer is present in an amount of less than 3 moles of photosensitizer per one mole of the at least one non-lanthanide metal. Moreover, the sensitized polyheterosiloxane composition is free of lanthanide metals. A silicone composition includes a curable silicone and the sensitized polyheterosiloxane composition. Moreover, the silicone composition is free of lanthanide metals.

POLYHETEROSILOXANE COMPOSITION AND SILICONE COMPOSITION INCLUDING A POLYHETEROSILOXANE

[0001] Various metals luminesce due to their electronic structures. However, the use of these metals in luminescent materials is typically limited by standard energetic high temperature synthesis and blending and also by quenching of luminescence at high metal concentration. Quenching can occur above a threshold metal concentration where metal ions are allowed to aggregate and subsequent coordinate changes in the electronic structure can lead to non-radiative routes to ground including cross relaxation. In some cases, excited state absorption can lead to quenching. Undetermined mechanisms, typically described as concentration quenching, may also occur. The threshold concentration for quenching can be as low as 1%, limiting the brightness of luminescent materials. Accordingly, there remains an opportunity to develop improved materials.

SUMMARY OF THE DISCLOSURE

[0002] This disclosure provides a sensitized polyheterosiloxane composition that includes at least one non-lanthanide metal and siloxy units having the formula $(R^1{}_3SiO_{1/2})$, $(R^1{}_2SiO_{2/2})$, $(R^1SiO_{3/2})$, and/or $(SiO_{4/2})$. Each R^1 is independently a hydrocarbon or halogenated hydrocarbon group comprising 1 to 30 carbon atoms. The mole fractions of the at least one non-lanthanide metal and the siloxy units relative to each other is of the formula: [at least one non-lanthanide metal]$_a[R^1{}_3SiO_{1/2}]_m[R^1{}_2SiO_{2/2}]_d[R^1SiO_{3/2}]_t[SiO_{4/2}]_q$, wherein a is from 0.001 to 0.9, m is from zero to 0.9, d is from zero to 0.9, t is from zero to 0.9, and q is from zero to 0.9, and wherein m, d, t, and q cannot all be zero and the sum of $a+m+d+t+q \approx 1$. The composition also includes a photosensitizer present in an amount of less than 3 moles of photosensitizer per one mole of the at least one non-lanthanide metal. The photosensitizer imparts a larger peak emission intensity to said composition at an excitation wavelength of from 200 to 1,000 nm as compared to a control polyheterosiloxane composition free of the photosensitizer. Moreover, the sensitized polyheterosiloxane composition is free of lanthanide metals. This disclosure also provides a silicone composition including a (sensitized) polyheterosiloxane composition and a curable silicone. The photosensitizer imparts a larger peak emission intensity to the silicone composition at an excitation wavelength of from 200 to 1,000 nm as compared to a control composition free of the photosensitizer. Moreover, the silicone composition is free of lanthanide metals. This disclosure also provides a cured product of the silicone composition and an article that includes a substrate and a coating disposed on the substrate, wherein the coating includes the cured product of the silicone composition.

BRIEF DESCRIPTION OF THE FIGURES

[0003] Figure 1A is an excitation spectrum of Example 1;

[0004] Figure 1B is an emission spectrum of Example 1;

[0005] Figure 2A is an excitation spectrum of Example 2;

[0006] Figure 2B is an emission excitation spectrum of Example 2;

[0007] Figure 3 is an excitation and emission spectrum of Example 3;

[0008] Figure 4 is an excitation and emission spectrum of Example 4;

[0009] Figure 5 is an excitation and emission spectrum of Example 5;

[0010] Figure 6 is an excitation and emission spectrum of Example 6;

[0011] Figure 7 is an excitation and emission spectrum of Example 7; and

[0012] Figure 8 is an excitation and emission spectrum of Example 8.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0013] This disclosure provides a sensitized polyheterosiloxane composition that is free of lanthanide metals, i.e., free of one or more lanthanide metals. This disclosure also describes a silicone composition that includes a (sensitized) polyheterosiloxane composition and a curable silicone (i.e., a curable silicone composition different from the silicone composition introduced immediately above). In various non-limiting embodiments, the terminology "sensitized polyheterosiloxane composition" and "polyheterosiloxane composition" may be used interchangeably. The silicone composition as a whole and/or the (sensitized) polyheterosiloxane composition is free of lanthanide metals, i.e., free of one or more lanthanide metals. For example, the terminology "free of" may describe that the silicone composition and/or the polyheterosiloxane composition includes less than 1, 0.5, 0.1, 0.05, 0.01, 0.005, 0.001, 0.0005, or 0.0001, weight percent of lanthanide metals per 100 parts by weight of the respective composition. Alternatively, the silicone composition and/or the polyheterosiloxane composition may be entirely free of lanthanide metals.

[0014] One or more of the physical properties and/or components of the polyheterosiloxane composition, as described, (e.g. emission, excitation, lifetimes, quantum yields, etc.) may also be descriptive of the physical properties and/or components of the silicone composition.

Polyheterosiloxane Composition:

[0015] The polyheterosiloxane composition includes at least one non-lanthanide metal which may be any known in the periodic table. In one embodiment, the polyheterosiloxane composition includes two or more non-lanthanide metals. The at least one non-lanthanide metal may be (M1) and/or (M2) described below.

[0016] In another embodiment, the polyheterosiloxane composition includes (A) a first non-lanthanide metal (M1), (B) a second non-lanthanide metal (M2), and (C) siloxy units having the formula $(R^1{}_3SiO_{1/2})$, $(R^1{}_2SiO_{2/2})$, $(R^1SiO_{3/2})$, and/or $(SiO_{4/2})$.

[0017] The polyheterosiloxane composition may include one (A) first non-lanthanide metal (M1), two first non-lanthanide metals (M1), or a plurality of first non-lanthanide metals (M1). In various embodiments, the first non-lanthanide metal (M1) is not particularly limited. (M1) may be chosen from Ti, Zr, Al, and Zn, or Ti, Zr, and Al, or Ti, Al, W, Ge, Zr, Hf, Mn, Nb, Y, Ta, and V, or W, Ti, Zr, Al, Zn, Hf, Ta, Y, and Nb, or Ti, Zr, Al, Ge, Ta, Nb, and Sn, and/or any single metals or combinations thereof. In various additional embodiments, (M1) is chosen from Sn, Cr, Ba, Sb, Cu, Ga, In, Mg, Mo, Te, W, Sr, and/or any single metals or combinations thereof. In various additional embodiments, (M1) is chosen from Al, Zr, and combinations thereof. In one embodiment, (M1) is Al. In another embodiment, (M1) is Zr. In still another embodiment, (M1) is a combination of Al and Zr. Any one or more of the aforementioned metals may be used singly or in combination with themselves or any one or more metals described below. Similarly, any one or more of any metals described below may be used single or in combination with themselves or any one or more of the aforementioned metals.

[0018] The oxidation state of (M1) is typically independently from 1 to 5, 1 to 4, 1 to 2, 2 to 3, 2 to 4, or any range or combination of ranges or values therebetween. If more than one (A) first non-lanthanide metal (M1) is utilized, then each (M1) may independently have the same or different oxidation states.

[0019] The polyheterosiloxane composition may include one (B) second non-lanthanide metal (M2), two second non-lanthanide metals (M2), or a plurality of second non-lanthanide metals (M2). In various embodiments, the second non-lanthanide metal (M2) is not limited. In one embodiment, each of (M1) and (M2) are independently non-lanthanide metals and are different from each other.

[0020] In various embodiments, (M2) may be one or more of those non-lanthanide metals described above or may be any other non-lanthanide metal in the periodic table. For example, (M1) and (M2) may be one of the following:

First Metal (M1)	Second Metal (M2)
Non-Lanthanide Metal	Non-Lanthanide Metal
Aluminum	Non-Lanthanide Metal
Zirconium	Non-Lanthanide Metal
Combination of Aluminum and Zirconium	Non-Lanthanide Metal
Non-Lanthanide Metal	Aluminum

Non-Lanthanide Metal	Zirconium
Non-Lanthanide Metal	Combination of Aluminum and Zirconium
Aluminum	Zirconium
Zirconium	Aluminum
Combination of Aluminum and Zirconium	Combination of Aluminum and Zirconium

In one embodiment, more than one non-lanthanide metal may be utilized. A mixture of non-lanthanide metals may be utilized.

[0021] The polyheterosiloxane composition also includes (C) siloxy units having the formula ($R^1_3SiO_{1/2}$), ($R^1_2SiO_{2/2}$), ($R^1SiO_{3/2}$), and/or ($SiO_{4/2}$). These units may be alternatively described as organopolysiloxane segments and are known in the art as M, D, T, and Q units, respectively. The polyheterosiloxane composition may include one or more M, D, T, and/or Q units, e.g. "M" and "D" units, "M" and "T" units, "M" and "Q" units, "D" and "T" units, "D" and "Q" units, or "T" and "Q" units, and/or combinations thereof. In any of the embodiments described herein above or below, it is contemplated that (M1) and/or (M2) may describe the at least one non-lanthanide metal introduced above. However, the invention, of course, is not limited to any such embodiment.

[0022] Each R^1 is typically independently a hydrocarbon or halogenated hydrocarbon group including 1 to 30, 1 to 20, 1 to 15, 1 to 12, 1 to 10, 1 to 5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, or 30, carbon atoms, or any value or range of values therebetween. Any R^1 may be the same or different from any other R^1. Non-limiting examples include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, undecyl, octadecyl, cyclohexyl, aryl, phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl, halogenated hydrocarbon, 3,3,3-trifluoropropyl, 3-chloropropyl, and dichlorophenyl, groups. At least one of R^1 may be phenyl. The number of siloxy units may vary. The number and type of siloxy units may affect the molecular weight of the organopolysiloxane segment, and hence the molecular weight of the polyheterosiloxane composition.

[0023] The (C) siloxy units may include greater than 50 mole or weight percent of $R^1SiO_{3/2}$ siloxy units where R^1 is phenyl; $R^1_2SiO_{2/2}$ siloxy units where one R^1 substituent is phenyl, and the other R^1 substituent is methyl; or $R^1_2SiO_{2/2}$ and $R^1SiO_{3/2}$ siloxy units where one R^1 substituent in the $R^1_2SiO_{2/2}$ siloxy unit is phenyl, and the other R^1 substituent is methyl, and where R^1 is phenyl in the $R^1SiO_{3/2}$ siloxy unit. One or more siloxy units may have the formula $[(C_6H_5)SiO_{3/2}]_d$, $[(C_6H_5)_2SiO_{2/2}]_d[(C_6H_5)SiO_{3/2}]_t$, or $[(CH_3)(C_6H_5)SiO_{2/2}]_d\,[(C_6H_5)SiO_{3/2}]_t$.

[0024] The polyheterosiloxane composition may include at least 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or at least 98 or 99,%, or any value or range of values

therebetween, of the at least one non-lanthanide metal (e.g. (A) and (B)) and (C) based on a total weight of the polyheterosiloxane composition. Alternatively, the polyheterosiloxane composition may include approximately 100% of the at least one non-lanthanide metal (e.g. (A) and (B)) and (C) based on a total weight of the polyheterosiloxane composition. Any range of values including those above, or any one or more values between those above, may also be utilized. Any remaining percent by weight of the polyheterosiloxane composition may include one or more solvents, one or more counterions, e.g. benzoates, naphtoates, and acetates, and/or one or more components used to form the polyheterosiloxane composition.

[0025] The varied amounts of each of the at least one non-lanthanide metal and/or (A), (B), and (C) are typically described relative to mole fractions of each to a total number of moles, e.g. of (A), (B), and (C). For example, the mole fractions of the at least one non-lanthanide metal, and the siloxy units in the polyheterosiloxane composition relative to each other may be of the formula [At least one non-Lanthanide Metal]$_a$ [$R^1_3SiO_{1/2}$]$_m$[$R^1_2SiO_{2/2}$]$_d$[$R^1SiO_{3/2}$]$_t$[$SiO_{4/2}$]$_q$. In another embodiment, (A), (B), and (C) in the polyheterosiloxane composition relative to each other is of the formula [(M1)]$_a$[(M2)]$_b$[$R^1_3SiO_{1/2}$]$_m$[$R^1_2SiO_{2/2}$]$_d$[$R^1SiO_{3/2}$]$_t$[$SiO_{4/2}$]$_q$. The subscript m denotes the mole fraction of the optional "M" unit ($R^1_3SiO_{1/2}$). The subscript d denotes the mole fraction of the optional "D" unit ($R^1_2SiO_{2/2}$). The subscript t denotes the mole fraction of the optional "T" unit ($R^1SiO_{3/2}$). The subscript q denotes the mole fraction of the optional "Q" unit ($SiO_{4/2}$).

[0026] a and/or b is each typically independently from 0.001 to 0.9, 0.010 to 0.9, 0.001 to 0.7, 0.1 to 0.7, 0.1 to 0.6, 0.2 to 0.5, 0.2 to 0.8, 0.3 to 0.7, 0.4 to 0.6, or about 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, or 0.9, or any value or range of values therebetween. Alternatively, a and/or b may be each independently from 0.001 to 0.9, 0.001 to 0.5, 0.01 to 0.3, or 0.05 to 0.25. For example, a may be from 0.1 to 0.9 and b may be from 0.001 to 0.5. The total metal content of the polyheterosiloxane composition, i.e., the sum of a+b, may be from 0.1 to 0.9, from 0.2 to 0.8, from 0.3 to 0.7, from 0.4 to 0.6, about 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, or 0.9, mole fraction, or any value or range of values therebetween.

[0027] m is typically from zero to 0.9, 0.1 to 0.6, or 0.2 to 0.5 or any value or range of values therebetween. d is typically from zero to 0.9, 0.1 to 0.5, or 0.1 to 0.3 or any value or range of values therebetween. Each of t and q is typically independently from zero to 0.9, 0.010 to 0.9, 0.001 to 0.7, 0.1 to 0.7, 0.1 to 0.6, or 0.2 to 0.5 or any value or range of values therebetween. Moreover, m, d, t, and q cannot all be zero and the sum of a+b+m+d+t+q $\approx$ 1. The terminology "$\approx$" describes that the sum of a, b, m, d, t, and q is approximately equal to 1. The sum may be 0.99, 0.98, 0.97, 0.96, 0.95, etc, or any value or range of values therebetween. If the sum does not equal 1, then the

polyheterosiloxane composition may include residual amounts of groups that are not described by the aforementioned formula. The polyheterosiloxane composition may include up to about 5 mole percent of other units, such as those that include Si-OH bonds.

[0028] The polyheterosiloxane composition may have a formula $[(M1)]_a[(M2)]_b[R^1{}_3SiO_{1/2}]_m[R^1{}_2SiO_{2/2}]_d\ [R^1SiO_{3/2}]_t[SiO_{4/2}]_q$, wherein M1 may be a combination of metals or, M1 may be a single metal, e.g. Al, wherein a is 0.54, b is 0.00, d is 0.27, and m is 0.1, or, e.g. Zr, wherein a is 0.5, b is 0.0, m is zero, d is 0.35, t is 0.155, and q is zero. In various embodiments, , a may be from 0.01 to 0.8, b may be from 0.00 to 0.5, c may be from zero to 0.8, d may be from zero to 0.8, with the provisos that c and d both cannot be zero and the sum of a+b+c+d $\approx$ 1. In various embodiments, the polyheterosiloxane composition has a formula such as $Al_{0.54}D_{0.27}T_{0.09}M_{0.1}Ligand_{0.001}$;$Al_{0.3}D_{0.525}T_{0.175}Ligand_{0.02}$;$Al_{0.6}D_{0.3}T_{0.1}Ligand_{0.005}$; $Al_{0.54}D_{0.27}T_{0.09}M_{0.1}Ligand_{0.001}$; $Zr_{0.5}D_{0.35}T_{0.15}Ligand_{0.001}$; or $Zr_{0.54}D_{0.34}T_{0.12}Ligand_{0.001}$, wherein the ligand may originate from a photosensitizer.

[0029] The number of moles of each component of the polyheterosiloxane composition may be determined using common analytical techniques. The number of moles of the siloxy units may be determined by ^{29}Si liquid or solid state NMR, ^{48}Ti NMR, ^{27}Al NMR, FT-IR, TEM EDX, ICP, XRF, GCMS, GC functionality, ICP, etc. Alternatively, the number of moles of each component may be calculated from the amounts of each used in the process to prepare the polyheterosiloxane composition, and accounting for any losses (such as removal of volatile species) that may occur.

[0030] The polyheterosiloxane composition may also include from 1 to 70, 1 to 60, 1 to 50, 1 to 40, 1 to 30, 1 to 20, from 1 to 15, from 1 to 10, or from 1 to 5, or any value or range of values therebetween, percent by weight, alkoxy groups. Residual alkoxide (-OR) groups may also be present in polyheterosiloxane structures and may be bonded to (M1) and Si, as determined using ^{29}Si and ^{13}C NMR, e.g. in an organic solvent. Residual counter ions from metal salts may also be present and may be bonded or chelated to (M1) and (M2).

[0031] One or more atoms of the at least one non-lanthanide metal, e.g. (M1) and/or (M2), may be bonded to the same or different silicon atoms, e.g. through an oxygen bond. Typically, at least one oxygen atom of the siloxy units is bonded to at least one of (M1) and/or (M2) and/or one or more (C) siloxy units. Two or more oxygen atoms of one or more siloxy units may be bonded to (M1) or (M2) or to both (M1) and (M2). Atoms of (M1) may be bonded to other atoms of (M1) or (M2). For example, atoms of (M1) may be linked via oxygen atoms to atoms of (M1) and/or (M2), e.g. M1-O-M1-O-M2 or M1-O-M2. Atoms of (M1) may also have a one or more substituents

bonded thereto such as residual or un-reacted substituents used to form the polyheterosiloxane composition.

[0032] Atoms of (M2) may be bonded to other atoms of (M2), (M1), and/or one or more (C) siloxy units. Atoms of (M2) may be linked via oxygen atoms to atoms of (M2) and/or (M1), e.g. M2-O-M2-O-M1 or M2-O-M1. Atoms of (M2) may also have a one or more substituents bonded thereto such as residual or un-reacted substituents used to form the polyheterosiloxane composition.

[0033] The polyheterosiloxane composition may include various heterosiloxane structures including, but not limited to, structures having Si-O-Si, Si-O-M1, M1-O-M1, and M1-O-M2 bonds as well as Si-O-M2 and M2-O-M2 bonds. Typically, a concentration of metal to metal bonds (e.g. M1-O-M1, M1-O-M2, M2-O-M2) is controlled so as to minimize formation of metal aggregates or particles of sufficient size to either render the polyheterosiloxane composition insoluble in organic solvents or are of insufficient size to be detected using TEM techniques.

[0034] The polyheterosiloxane composition may have "metal-rich" domains and "siloxane-rich" domains. As used herein the terminology "metal-rich" domains describes structural segments wherein a plurality of bonds include (M1) or (M2) (i.e., M1-O-M1, M1-O-M2, M2-O-M2, M1-O-Si, or M2-O-Si). As used herein, the terminology "siloxane-rich" describes structural segments wherein a plurality of bonds are siloxane (Si-O-Si) bonds. The "metal-rich" domains may be present such that the amount of metal to metal bonds (M1-O-M1, M1-O-M2, M2-O-M2) is minimized so as to minimize formation of metal aggregates or particles of sufficient size to minimize their solubility in hydrocarbons. The polyheterosiloxane composition may also include –(Si-O-M1-O-M2)- bonds. In one embodiment, Ti and/or Al can act as a bridge to M1 to bridge siloxy units with non-lanthanide-oxygen units. Use of ^{17}O NMR,^{48}Ti NMR and/or ^{27}Al NMR may increase resolution or ability to quantify Si-O and non-lanthanide-O bonds.

[0035] Alternatively, the metal rich domains may not be of sufficient size to be observed using high resolution transmission electron micrographs (TEM). Thus, the (M1) and (M2) metals may be sufficiently distributed in the polyheterosiloxane composition and have a domain size smaller than 10 nanometers, alternatively smaller than 5 nanometers, or alternatively smaller than 2 nanometers (detection limits for the TEM). Alternatively, NMR, FT-IR, and/or X-Ray PDF techniques may be utilized throughout this disclosure to determine bonding, polyheterosiloxane composition, etc.

[0036] The polyheterosiloxane composition is typically soluble in a hydrocarbon solvent, such as an aromatic hydrocarbon solvent, and may be soluble in other organic solvents as well. As used herein, "soluble" describes that the polyheterosiloxane composition dissolves in, for example toluene, to form a homogeneous solution having a concentration of at least 1, 5, 10, 15, 20, 25, 30,

35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99, or about 100, weight percent of the polyheterosiloxane composition in toluene at 23°C. The polyheterosiloxane composition may also be soluble in other organic solvents, such as chloroform, carbon tetrachloride, THF, and butyl acetate.

[0037] The polyheterosiloxane composition typically has a weight average molecular weight (M_w) from 1,000 to 1,000,000, from 2,000 to 400,000, from 2,000 to 200,000, from 5,000 to 750,000, from 10,000 to 500,000, from 20,000 to 350,000, from 30,000 to 300,000, from 40,000 to 250,000, from 50,000 to 200,000, from 60,000 to 175,000, from 70,000 to 150,000, from 80,000 to 140,000, from 90,000 to 130,000, from 100,000 to 1250,000, g/mol, or any value or range of values therebetween. The molecular weight may be determined using modified GPC techniques to minimize possible interactions between the sample and the column system. For example, the molecular weight may be determined by GPC analysis using triple detectors (light scattering, refractometer, and viscometer) with a column (PL 5u 100a 100 x 7.8mm) designed for rapid analysis or Flow Injection Polymer Analysis (FIPA).

[0038] The polyheterosiloxane composition is typically photoluminescent and may emit visible or ultraviolet light when exposed to, or excited by, visible or ultraviolet light. The polyheterosiloxane composition typically exhibits a quantum yield of at least 0.05%, as determined using the formula described in greater detail below. In various embodiments, the polyheterosiloxane composition exhibits a quantum yield of at least 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, %, or even greater, of from 5 to 75, 10 to 70, 15 to 65, 20 to 60, 25 to 55, 30 to 50, 35 to 45, 40 to 60, 40 to 50, 45 to 55, or 50 to 60, %, or any value or range of values therebetween. It is contemplated that any of the aforementioned values may be a minimum or a maximum for a range of quantum yield for the polyheterosiloxane composition and all combinations of the aforementioned values are hereby expressly contemplated. The polyheterosiloxane composition may alternatively exhibit a quantum yield of 0.5, 1, 5, or 10% or any value or range of values set forth above or between those values set forth above. In various polyheterosiloxane compositions, quantum yields may be from 35 to 55% measured, for example, using an integrating sphere attached to a Flurolog-3 fluorescence spectrometer. In other polyheterosiloxane compositions, quantum yields may be from 5.9% to 7.4%. The quantum yield may be alternatively described as any value, or range of values, both whole and fractional, within or between any one or more values described above. In various embodiments, the aforementioned quantum yield may vary by ±1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, %.

[0039] A limited size of the metal rich domains may lead to enhanced photoluminescence. For example, concentrations of non-lanthanide ions may exceed conventional concentration quenching thresholds without reduction in quantum yield. Photoluminescence may be assessed by measuring the absorption spectrum, the photoluminescent emission (PL) spectrum, or the photoluminescent excitation (PLE) spectrum of the polyheterosiloxane composition. The absorption spectrum may be measured with standard spectrometers such as a Varian Carry 5000 spectrophotometer (Agilent Technologies, Palo Alto, CA, USA). The PL excitation and emission spectra may be measured using a spectrofluorometer. Any spectrofluorometer recognized in the art, e.g. the Fluorolog-2 or -3 spectrofluorometer (FL2 or FL3) (HORIBA Jobin-Yvon Inc. Edison, NJ, USA), or any one or more described below may be utilized to determine any one or more physical properties described herein.

[0040] The efficiency in which a photoluminescent material converts light from one wavelength to another can be described as quantum yield (QY). Alternatively, Quantum Yield can be described as a percentage of overall light conversion (photons absorbed to photons emitted) of a material. While it is possible to determine the QY of a material by comparing the absorption, PL and PLE spectra of a test polyheterosiloxane composition to a reference polyheterosiloxane composition, the QY may be measured more directly using a spectrometer coupled integration sphere, where the absorption and PL spectra of a polyheterosiloxane composition are referenced against a blank reference sample. Representative equipment is an Ocean Optics USB4000 spectrometer fiber-optically coupled to an approximately 4 cm integration sphere, illuminated by a light emitting diode (LED) and run by Ocean Optics' Spectra Suite software (Ocean Optics, Dunedin, FL, USA). Alternatively, equipment such as Fluorolog-2 or -3 spectrofluorometers (FL2 or FL3) (HORIBA Jobin-Yvon Inc. Edison, NJ, USA) may be utilized with appropriate accessories. For example, a combination of a UV-Vis spectrum and a PL/PLE spectra may be utilized.

[0041] In various embodiments, the absorption and emission of a sample are measured under the illumination of an LED with a center wavelength of 395 nm. The test sample is typically placed in the approximately 4 cm integration sphere in a glass vial with an absorption cut-off less than 350 nm. Incident light is typically measured by integrating the photon count in the range 350-450 nm, and emitted light in the range 480-850 nm. A different LED light source and/or photoluminescent material may require changing the integration ranges.

[0042] The polyheterosiloxane composition may emit visible and infrared light having a wavelength in the range of 400 to 1700 nm when excited by light having a wavelength of 200 to 1000 nm, where the emitted light is a longer wavelength than the excitation wavelength, with a photon quantum yield efficiency of at least 0.1%, where photon quantum yield is determined using

the equation described above. Alternatively, the polyheterosiloxane composition may emit visible light having a wavelength of 580 to 750 nm when excited by light having a wavelength of 250 to 550 nm. Alternatively, the polyheterosiloxane composition may emit visible light having a wavelength of 610 to 620 nm when excited by ultraviolet light having a wavelength of 390 to 400 nm. The quantum yield may be at least 1%, alternatively 2%, alternatively 5%, alternatively 10%, alternatively 20%, alternatively 30%, alternatively 40%, alternatively 50%, or alternatively 60%.

[0043] The polyheterosiloxane composition may alternatively emit visible light when excited by a UV light source. The emitted light may have a wavelength ranging from 450 to 750 nm while the excitation light source may have a wavelength ranging from 250 to 520 nm. The polyheterosiloxane composition may alternatively emit visible light having a wavelength of 450 to 650 nm when excited by UV light. The polyheterosiloxane composition alternatively may emit infrared light having a wavelength of 1450 to 1650 nm when excited by a light source having a wavelength from 650 to 5,000 nm. Alternatively, the polyheterosiloxane composition may emit near IR light having a wavelength of 1000 to 1100 nm when excited by a light source having a wavelength from 650 to 5,000 nm. The polyheterosiloxane composition may alternatively emit light having a wavelength of 400 to 1700 nm when excited by a light source having a wavelength of 200 to 1000 nm. Typically, the emitted light has a longer wavelength than the excitation light source. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[0044] The human eye tends to be most sensitive at wavelengths of light from 450 to 650 nm. Typically, light having wavelengths above and below this range is of lesser value for lighting applications. In addition, when a full range of wavelengths is not present, lighting quality and color quality tends to be reduced. Red emission in the range of 600 nm to 650 nm provides for suitable color rendering with. For example, compositions that include Si+M+Ligand, e.g. $Al_{0.54}D_{0.27}T_{0.09}M_{0.1}Ligand_{0.001}$ may exhibit a CIE coordinates of x=0.61, y=0.39, a nearly saturated red, while the emitting in a visually bright range. Specific combinations of metals and ligands will provide a different emissions and subsequent CIE color values. The CIE x, y coordinates of the emitted light may independently vary x=0.1 to x=0.7 and y=0.1 to y=0.5, with the restriction that the combined x, y coordinates fall within the color space, as is known in the art. The 1931 CIE (International Commission on Illumination) color space is defined by tristimulus values, *X, Y* and *Z*. In this model, *Y* represents luminance, *Z* corresponds to the human eye's blue response, and *X* is a mix of color responses and orthogonal to *Y*. They are calculated according to the formulas:

$$X=\int_0^{\infty} I(\lambda)x'(\lambda)\,d\lambda$$
$$Y=\int_0^{\infty} I(\lambda)y'(\lambda)\,d\lambda$$
$$Z=\int_0^{\infty} I(\lambda)z'(\lambda)\,d\lambda$$

wherein $x'(\lambda)$, $y'(\lambda)$ and $z'(\lambda)$ are color matching functions with peaks at approximately 450 nm, 550 nm and 600 nm respectively, and $I(\lambda)$ is the spectra power distribution. The reported color or chromaticity coordinates x, y and z *are* cal*cu*lated $x=X/(X+Y+Z)$, $y=Y/(X+Y+Z)$, and $z=Z/(X+Y+Z)$ and by inspection $x+y+z=1$.

[0045] Steady state emission and excitation measurements are typically collected using a Horiba Jobin- Yvon Fluorolog 3 spectrofluorometer with three slit double grating excitation and emission monochromators and with dispersions of 2.1 nm/mm (1200 grooves/mm). The spectra are obtained with a 450 W xenon continuous wave lamp and detected at an angle of 90 degrees to the excitation source for solutions in 1 cm quartz cuvettes and at 30 degrees for measurements of powders in the solid state or thin films via a photomultiplier tube detector. Measured films are typically discs 3 mm thick with 5% wt resins, for example, 5% wt Si+Metal+Ligand resins, in varying silicone hosts. Samples in solution are typically measured for concentrations between 1.5% and 5% to yield optical densities below 0.10. Measurement procedures and references follow from Mavrodineau, Schultz and Menis 'Accuracy in Spectrophotometry and Luminescence Measurements', NBS Special Publications p. 378 (1973), and were updated as needed in compliance with the user manuals of cited instrumentation. In the measurement, the background thermal noise (or the dark offset) is corrected all the time. There is also a reference photodiode to collect the variations of intensities in the excitation source (Rc). An intensity standard reference material (2940-C from NIST) is used to monitor variations in the photomultiplier tube detector (PMT) signal (Rs). Then the excitation/emission spectra are typically reference corrected for both variations in intensities in the excitation source and variations in the photomultiplier tube detector by utilizing the ratio of PMT spectral response to Rc and Rs. Luminescent quantum yields are typically measured with a six (6) inch integrating sphere accessory attached via optical fibers to the spectrofluorometer. These data are typically collected in two steps, wherein a first step includes measuring the absorption of a blank reference material in the integrating sphere while avoiding saturation of the detector by using the appropriate neutral density filters for the selected bandpass. The bandpass for these measurements is typically set between 1.5 and 2 nm, and the range scanned includes both the excitation source and the emission of the material. The second step typically includes replacing the blank reference with the sample while the measurement is repeated. These datasets are then typically

analyzed in the vendor provided software, where the difference in the emission and the excitation is used to produce the resulting quantum yield for the material.

[0046] Absorption spectra are typically determined by monitoring the strongest absorption peak of the polyheterosiloxane composition and collecting data via the optically dilute method. Optical densities are typically less than 0.1 and are typically collected on a UV-Vis in 10 mm quartz cuvettes. Data is typically obtained for three different concentrations, e.g. 4 wt%, 3.2 wt% and 2.5 wt%, with targeted absorptions, e.g. of 0.100, 0.081 and 0.060. However, the concentrations may be from 1.5 to 8.0 wt %, depending on the total metal content of the polyheterosiloxane composition.

[0047] In one method, combined absorption and fluorescence data are used to calculate quantum yields relative to a standard reference. Because the optical densities can be kept below < 0.1, quantum yields could be determined via the following equation:

$$QY = [A_r(\lambda_r)/A_x(\lambda_x)][I(\lambda_r)/I(\lambda_x)][n_x^2/n_r^2][D_x/D_r]\ QY_r$$

wherein QY is the quantum yield of the sample, QY_r is the quantum yield of the reference, A is the absorbance at the excitation wavelength λ, n is the refractive index, and D is the integrated emission intensity. The subscripts r and x indicate a reference value and an experimental value, respectively. For example, quinine sulfate in 1.0 N sulfuric acid can be used as a reference with an excitation at 340 nm and will produce emission between 370 nm and 660 nm. This solution has an established quantum yield of 0.546. Other references include fluorescein (470 nm excitation, 480-700 nm emission, QY 0.91) and rhodamine (535 nm excitation, 550 – 750 nm emission, QY 1.00). These reference materials are all commonly used and referenced in the literature, e.g. in Eaton, D., *International Union of Pure and Applied Chemistry Organic Chemistry Division Commission on Photochemistry*; and/or the Journal of photochemistry and photobiology. B, Biology, 1988. 2(4): p. 523, each of which are expressly incorporated herein by reference relative to these particular materials.

[0048] FTIR spectra can be recorded between 4000 cm^{-1} and 400 cm^{-1} with a resolution of 4 cm^{-1} on a Nicolet 6700 FT-IR spectrometer. The spectra can be collected by directly measuring powder samples via attenuated total reflection (ATR) using a ZnSe or diamond cell.

[0049] The polyheterosiloxane composition may include, includes less than 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, or 0.5, weight percent of, or be free of, a curable silicone and/or an organic matrix, e.g. a curable organic composition. Curable silicone and/or organic matrices of such embodiments may be as described in one or both of U.S. Ser. Nos. 61/662,201 and 61/662,192, each of which are expressly incorporated herein by reference in one or more non-limiting embodiments.

[0050] The composition also includes a (D) photosensitizer. The (D) photosensitizer may impart a larger peak emission intensity to the polyheterosiloxane composition or the silicone composition as a whole (when the silicone composition includes a polyheterosiloxane composition and a curable silicone) at an excitation wavelength of from 200 to 1,000, 300 to 900, 400 to 800, 500 to 700, 600 to 700, 350 to 450, 320 to 480, 330 to 470, 340 to 460, 350 to 450, 360 to 440, 370 to 430, 380 to 420, 390 to 410, or about 400, nm, as compared to a control (polyheterosiloxane) composition free of the photosensitizer, i.e., an identical composition but for the (D) photosensitizer.

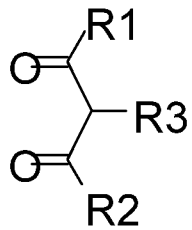
[0051] The photosensitizer may be present in the polyheterosiloxane composition in an amount of less than 3 moles of (D) photosensitizer per one mole of one or more non-lanthanide metals, e.g. (M1) and/or (M2). In other words, the (D) photosensitizer may present in an amount greater than zero but less than 3 moles of the (D) photosensitizer per one mole of one or more non-lanthanide metals, e.g. (M1) and/or (M2). In various embodiments, the (D) photosensitizer is present in amounts of less than 2.5, less than 2, less than 1.5, less than 1, less than 0.75, less than 0.5, less than 0.25, less than 0.1, less than 0.05, less than 0.01, less than 0.005, less than 0.001, less than 0.0005, less than 0.0004, etc. moles of (D) photosensitizer per one mole of the non-lanthanide metal. In other embodiments, the (D) photosensitizer is present in amounts of from 0.0001 to 0.0002, 0.0001 to 0.0003, 0.0001 to 0.0004, 0.0001 to 0.0005, 0.0001 to 0.0006, 0.0001 to 0.0007, 0.0008 to 0.0009, 0.0001 to 0.001, 0.0004 to 0.004, 0.001 to 0.1, 0.001 to 0.009, 0.001 to 0.008, 0.001 to 0.007, 0.001 to 0.006, 0.001 to 0.005, 0.001 to 0.004, 0.001 to 0.003, 0.001 to 0.002, 0.01 to 0.09, 0.01 to 0.08, 0.01 to 0.07, 0.01 to 0.06, 0.01 to 0.05, 0.01 to 0.04, 0.01 to 0.03, 0.01 to 0.02, 0.1 to 0.9, 0.1 to 0.8, 0.1 to 0.7, 0.1 to 0.6, 0.1 to 0.5, 0.1 to 0.4, 0.1 to 0.3, or 0.1 to 0.2, moles of (D) photosensitizer per one mole of the non-lanthanide metal.

[0052] The (D) photosensitizer is not particularly limited. In one embodiment, the (D) photosensitizer is chosen from (i) a β-diketone, (ii) a β-diketonate, (iii) a salicylic acid, (iv) an aromatic carboxylic acid, (v) an aromatic carboxylate, (vi) a polyaminocarboxylic acid, (vii) a polyaminocarboxylate, (viii) a N-heterocyclic aromatic compound, (ix) a Schiff base, (x) a phenol, (xi) an aryloxide, and combinations thereof. In various other embodiments, the (D) photosensitizer is (i) a β-diketone, or (ii) a β-diketonate, or (iii) a salicylic acid, or (iv) an aromatic carboxylic acid, or (v) an aromatic carboxylate, or (vi) a polyaminocarboxylic acid, or (vii) a polyaminocarboxylate, or (viii) a N-heterocyclic aromatic compound, or (ix) a Schiff base, or (x) a phenol, or (xi) an aryloxide, or a combination of one or more of the aforementioned compounds. In still other embodiments, the photosensitizer is a β-diketone or a β-diketonate. In additional embodiments, the

(D) photosensitizer is an aromatic carboxylic acid or aromatic carboxylate. Alternatively, the (D) photosensitizer may be a salicylic acid or a salicylate. The photosensitizer may be any one of the aforementioned types of compounds and/or may be further defined as a mixture of two or more of any of the aforementioned types of compounds.

[0053] Non-limiting examples of suitable (D) photosensitizers include 1,3-diphenylpropandione; 2-thenoyltrifluoroacetone, 2-dithenoylpropandione, 1-phenyl-3-(2-fluoryl)propandione; 1-(4-biphenyl)-3-(2-fluoryl)propandione; 1-(2-naphtyl)-3-(2-fluoryl)propandione; 1-(1-naphtyl)-3-(2-fluoryl)propandione; 1-(2,3,4,5-tetrafluorophenyl)-3-(2-fluoryl)propandione; 11-(2-fluoryl)-4,4,4-trifluorobutane-1,3-dione; 1-(2,3,4,5-tetrafluorophenyl)-3-(2-fluoryl)propandione; 1-(2,4,6-trifluorophenyl)-3-(2-fluoryl)propandione; 1-(3,4,5-trifluorophenyl)-3-(2-fluoryl)propandione; 1-(5-bromothiophen-2-yl)-4,4,4-trifluorobutane-1,3-dione; 1-(4'-methoxy-4-biphenyl)-4,4,4-trichlorobutane-1,3-dione; 9-hydroxyphenalen-1-one, tropolone, diethyl 2-hydroxyazulene-1,3-dicarboxylates; benzoic acid, 4-(octyloxy)benzoic acid, 4-(*t*-butyl)benzoic acid, 2-ethoxybezoic acid, 3-ethoxybezoic acid, 4-ethoxybezoic acid, 2-methoxybenzoic acid, 3-methoxybenzoic acid, 4-methoxybenzoic acid, 4-butoxybenzoic acid, 1-naphthoic acid, 2-naphthoic acid, biphenyl-2-carboxylic acid, biphenyl-4-carboxylic acid, 9-fluorenone-1-carboxylic acid, fluorene-9-carboxylic acid, fluorobenzoic acid, chlorobenzoic acid, 2-hydroxybenzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 4-methylbenzoic acid, 3,5-dimethylbenzoic acid, 4-cyanobenzoic acid; 2,2'-bipyridines, 4,4'-bipyridines, 2,2',2''-bipyridines, 1,10-phenantrolines, 1,8-naphthylridines, benzimidazole-pyridines, bis(benzimidazol)pyridines, porphyrines, macrocyclic imines, H_2Salen, 8-hydroxyquinolines; 5,7-dihalo-8-hydroxyquinolines; benzimidazole substituted 8-hydroxyquinolines, EDTA, DPTA, DOTA, and combinations thereof.

[0054] Additional non-limiting examples of suitable photosensitizers may have one or more of the structures below:

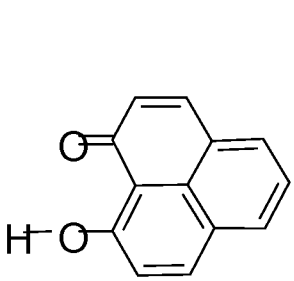
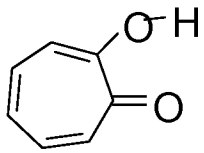
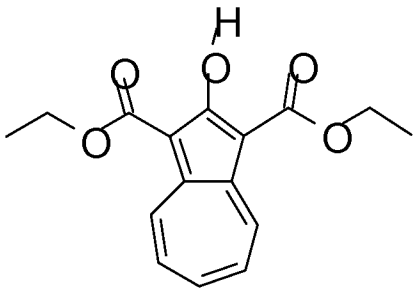
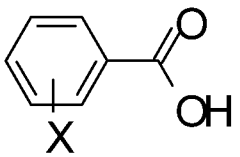
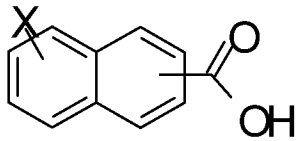
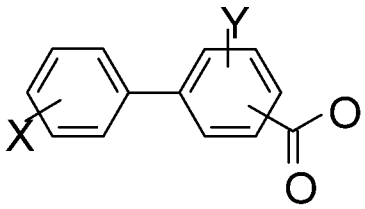


Wherein R1 = 2-fluoryl, R2 = 4-biphenyl; 1-naphthyl; 2-naphthyl; phenyl; trifluoromethyl; 2,3,4,5-tetrafluorophenyl; 2,4,6-trifluorophenyl; 3,4,5-trifluorophenyl; and R3 = H;

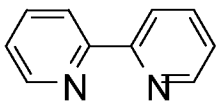
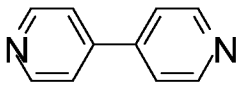
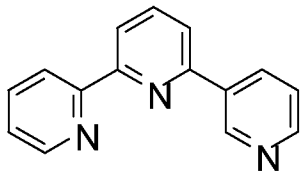
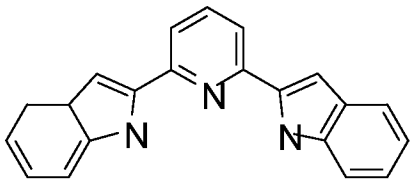
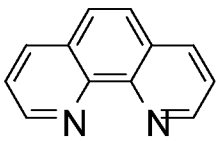
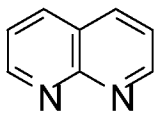
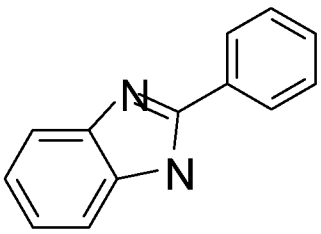
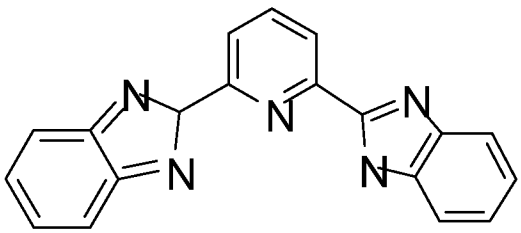
Wherein R1= trifluoromethyl; R2 = 5-bromo-2-thiophene; and R3 = H;

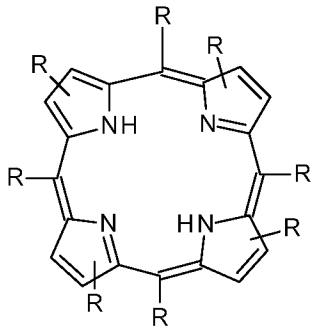
Wherein R1 = trichloromethyl; R2 = 4'-methoxy-4-biphenyl; and R3 = H; or

Wherein R1, R2 = phenyl, naphthyl, biphenyl, fluoryl, or perfluoroalkyl, and R3=H; or

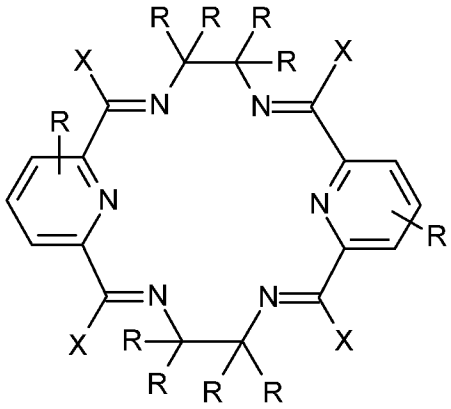







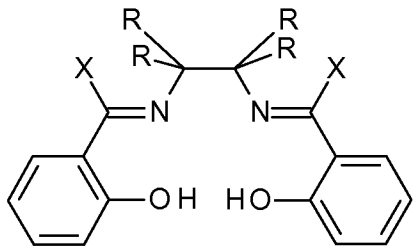
Wherein X = OH, F, Cl, Br, CN, NO_2, OR^1 (R^1 = C1 – C18), R2 (C1 – C18), R3 (branched); or any one or more of:

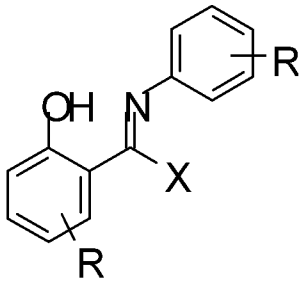









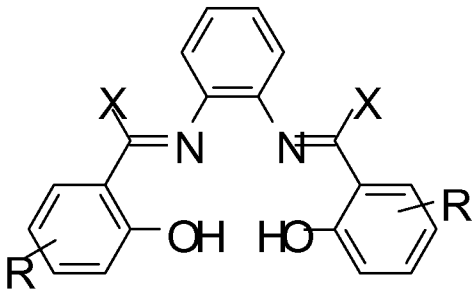


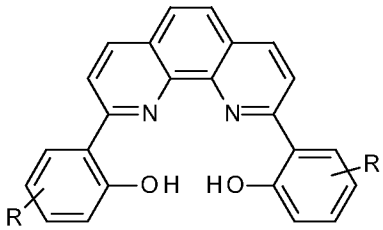
R = alkyl or aryl



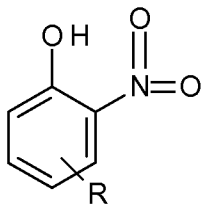




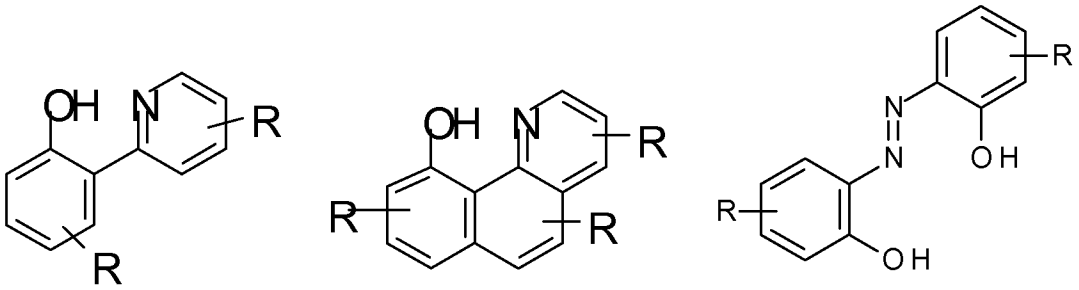




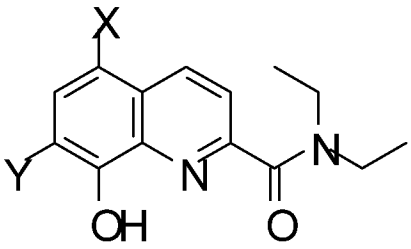
R: F, Cl, Br, I, OR1 (R1: alkyl, aryl), NO2, aryl, alkyl, NR1, OH, COOH, COOR1
X: H, alkyl, aryl, COOH, COOR1



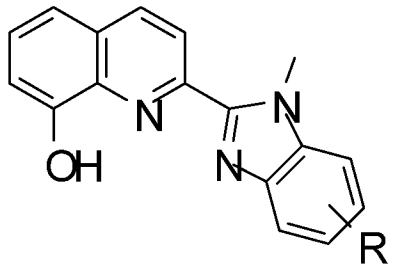
R: F, Cl, Br, I, OR1 (R1: alkyl, aryl), NO2, aryl, alkyl, NR1, OH, COOH, COOR1



R: F, Cl, Br, I, OR1 (R1: alkyl, aryl), NO2, aryl, alkyl, NR1, OH, COOH, COOR1



X, Y = H X = Br Y = H X, Y = Br



R = Me, OMe, Cl

[0055] This disclosure also provides a silicone composition including the sensitized polyheterosiloxane composition and a silicone fluid, e.g. a non-curable silicone fluid, as appreciated in the art. This disclosure also provides a silicone composition including the sensitized polyheterosiloxane composition and a curable silicone. This disclosure also provides an embodiment wherein the polyheterosiloxane composition is combined with a silicone fluid, e.g. a non-curable silicone fluid, as appreciated in the art, before, during, or after combination with the curable silicone. The silicone fluid is typically PDMS but is not limited in this way. In various embodiments, the silicone fluid has a viscosity at 25 °C of from about 0.001 to about 50 Pa·s, typically from about 0.02 to about 10 Pa·s, and more typically from about 0.05 to about 5 Pa·s. The silicone fluid can be linear, branched, cyclic, or a mixture thereof. Mixtures of the aforementioned fluids may also be used. Many of the linear, branched, and cyclic silicone fluids have melting points below about 25° C. Such materials are also commonly described as silicone liquids, silicone fluids, or silicone oils. A detailed description of non-limiting silicone fluids can be found in many references, including "Chemistry and Technology of Silicones" by W. Knoll, Academic Press, 1968, which, in one embodiment, is incorporated herein by reference relative to the silicone fluids.

[0056] Non-limiting examples of linear silicone fluids suitable for use herein include trimethylsiloxy-terminated dimethylsiloxane fluids sold by Dow Corning Corporation under the trade name "Dow Corning® 200 Fluids". These silicone fluids are manufactured to yield essentially

linear oligomers and/or polymers typically having a viscosity of from 0.001 to about 50 Pa·s at 25 °C. Such fluids are primarily linear but can include cyclic and/or branched structures. In one embodiment, the silicone fluid is a trimethylsiloxy-terminated polydimethylsiloxane having a viscosity of about 0.1 Pa·s at 25 °C.

[0057] Additional non-limiting examples of suitable cyclic silicone fluids include the cyclic polydimethylsiloxanes sold by Dow Corning Corporation under the trade names "Dow Corning® 244, 245, 344, and 345 Fluids", depending on the relative proportions of octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane. Mixtures of the straight-chain and cyclic dimethyl may also be utilized. Even additional non-limiting examples of suitable silicone fluids are $Me_3SiO[(OSiMe_3)_2SiO]SiMe_3$ and $Me_3SiO[(OSiMe_3)MeSiO]SiMe_3$.

[0058] In one additional embodiment, the sensitized polyheterosiloxane composition includes the (A) first metal (M1), the (B) second metal (M2), the (C) siloxy units having the formula $(R^1{}_3SiO_{1/2})$, $(R^1{}_2SiO_{2/2})$, $(R^1SiO_{3/2})$, and/or $(SiO_{4/2})$, wherein each R^1 is independently a hydrocarbon or halogenated hydrocarbon group comprising 1 to 30 carbon atoms, wherein the mole fractions of (A), (B), and (C) relative to each other is of the formula $[(M1)]_a[(M2)]_b[R^1{}_3SiO_{1/2}]_m[R^1{}_2SiO_{2/2}]_d[R^1SiO_{3/2}]_t[SiO_{4/2}]_q$, wherein a is from 0.001 to 0.9, b is from 0.001 to 0.9, m is from zero to 0.9, d is from zero to 0.9, t is from zero to 0.9, and q is from zero to 0.9, wherein m, d, t, and q cannot all be zero and the sum of a+b+m+d+t+q ≈ 1, and wherein one of (M1) and (M2) is a non-lanthanide metal and the other of (M1) and (M2) is aluminum (Al), zirconium (Zr), and combinations thereof, and the (D) photosensitizer is present in an amount of less than 3 moles of photosensitizer per one mole of the lanthanide metal, wherein the photosensitizer may impart a larger peak emission intensity to the sensitized polyheterosiloxane composition at an excitation wavelength of from 200 to 1,000, 300 to 900, 400 to 800, 500 to 700, 600 to 700, 350 to 450, 320 to 480, 330 to 470, 340 to 460, 350 to 450, 360 to 440, 370 to 430, 380 to 420, 390 to 410, or about 400, nm, as compared to a control polyheterosiloxane composition free of the photosensitizer.

[0059] In embodiments where a silicone composition includes the polyheterosiloxane composition and a curable silicone, the polyheterosiloxane composition is not particularly limited relative to an amount present in the silicone composition. In various embodiments, the polyheterosiloxane composition in present in the silicone composition in amounts from 50 to 1,000, from 100 to 950, from 150 to 900, from 200 to 850, from 250 to 800, from 300 to 750, from 350 to 700, from 400 to 650, from 450 to 600, or from 500 to 550, parts by weight per one million parts by weight of the silicone composition. In other embodiments, the polyheterosiloxane composition in

present in the silicone composition in amounts from 0.1 to 1, from 0.2 to 0.9, from 0.3 to 0.8, from 0.4 to 0.7, or from 0.5 to 0.6, parts by weight per 100 parts by weight of the silicone composition. In still other embodiments, the polyheterosiloxane composition in present in the silicone composition in amounts from 1 to 10, 2 to 9, 3 to 8, 4 to 7, or 5 to 6, parts by weight per 100 parts by weight of the silicone composition. In further embodiments, the polyheterosiloxane composition in present in the silicone composition in amounts from 10 to 80, from 15 to 75, from 20 to 70, from 25 to 65, from 30 to 60, from 35 to 55, from 40 to 50, or from 45 to 50, parts by weight per 100 parts by weight of the silicone composition.

Curable Silicone:

[0060] In embodiments of a silicone composition, where the silicone composition includes a polyheterosiloxane composition and a curable silicone, the silicone composition also includes a curable silicone. The curable silicone is not particularly limited and may be further defined as a curable silicone fluid, gel, etc. Examples of curable silicones include, but are not limited to, hydrosilylation-curable silicones, condensation-curable silicones, radiation-curable silicones, peroxide-curable silicones, and acid or amine cured silicones, e.g. epoxy curable silicones.

[0061] The curable silicone can be further described as curing to form a thermoset silicone polymer or a thermoplastic silicone polymer. Typically, as used herein and below, the term "thermoplastic polymer" describes a silicone polymer that has the physical property of converting to a fluid (flowable) state when heated and of becoming rigid (non-flowable) when cooled. Although thermoplastic polymers do not “cure” as that term is typically understood in the art, for purposes of this disclosure, the terminology “curable” or “cure” can describe the hardening of the thermoplastic polymer. Also, the term "thermoset polymer" may describe a cured (i.e., cross-linked) silicone polymer that does not convert to a fluid state on heating. As used herein and below, the term "thermoset polymer" typically describes a silicone polymer having the property of becoming permanently rigid (non-flowable) when cured (i.e., cross-linked).

[0062] A hydrosilylation-curable silicone typically includes an organopolysiloxane having an average of at least two silicon-bonded alkenyl groups or silicon-bonded hydrogen atoms per molecule; an organosilicon compound in an amount sufficient to cure the organopolysiloxane, wherein the organosilicon compound has an average of at least two silicon-bonded hydrogen atoms or silicon-bonded alkenyl groups per molecule capable of reacting with the silicon-bonded alkenyl groups or silicon-bonded hydrogen atoms in the organopolysiloxane; and a catalytic amount of a hydrosilylation catalyst.

[0063] A condensation-curable silicone typically includes an organopolysiloxane having an average of at least two silicon-bonded hydrogen atoms, hydroxy groups, or hydrolysable groups per molecule and, optionally, a cross-linking agent having silicon-bonded hydrolysable groups and/or a condensation catalyst. In one embodiment, the cross-linking agent has the formula $R^2_qSiX_{4-q}$, wherein R^2 is a C_1 to C_8 hydrocarbyl group or a C_1 to C_8 halogen-substituted hydrocarbyl group, X is a hydrolysable group, and q is 0 or 1.

[0064] A radiation-curable silicone typically includes an organopolysiloxane having an average of at least two silicon-bonded radiation-sensitive groups per molecule and, optionally, a cationic or free-radical photoinitiator depending on the nature of the radiation-sensitive groups in the silicone organopolysiloxane.

[0065] A peroxide-curable silicone typically includes an organopolysiloxane having silicon-bonded unsaturated aliphatic hydrocarbon groups and an organic peroxide.

[0066] An epoxy-curable silicone typically includes an organopolysiloxane having an average of at least two silicon-bonded epoxy-functional organic groups. Typically, before curing, a proton source, such as an amine, SiH, acid generator, or a cationic photo-acid generator, are utilized.

[0067] The silicone composition including the polyheterosiloxane composition and the curable silicone can be cured by exposing the silicone composition to ambient temperature, elevated temperature, moisture, or radiation, depending on the type of curable silicone.

[0068] When the curable silicone is a hydrosilylation-curable silicone, the silicone composition (which includes the polyheterosiloxane composition and the curable silicone) can be cured by exposing the silicone composition to a temperature of from room temperature (~23 ± 2 °C) to 250 °C, alternatively from room temperature to 150 °C, alternatively from room temperature to 115 °C, at atmospheric pressure. The silicone composition is generally heated for a length of time sufficient to cure (cross-link) the organopolysiloxane. For example, the film is typically heated at a temperature of from 100 to 150 °C for a time of from 0.1 to 3 h.

[0069] When the curable silicone is a condensation-curable silicone, the conditions for curing the silicone composition (which includes the polyheterosiloxane composition and the curable silicone) depend on the nature of the silicon-bonded groups in the organopolysiloxane. For example, when the organopolysiloxane contains silicon-bonded hydroxy groups, the silicone composition can be cured (i.e., cross-linked) by heating the silicone composition. The silicone composition can typically be cured by heating it at a temperature of from 50 to 250 °C, for a period of from 1 to 50 h.

When the condensation-curable silicone comprises a condensation catalyst, the silicone composition can typically be cured at a lower temperature, e.g., from room temperature (~23 ± 2 °C) to 150 °C.

[0070] When the curable silicone is a condensation-curable silicone comprising an organopolysiloxane having silicon-bonded hydrogen atoms, the silicone composition (which includes the polyheterosiloxane composition and the curable silicone) can be cured by exposing the silicone composition to moisture or oxygen at a temperature of from 100 to 450 °C for a period of from 0.1 to 20 h. When the condensation-curable silicone contains a condensation catalyst, the silicone composition can typically be cured at a lower temperature, e.g., from room temperature (~23 ± 2 °C) to 400 °C.

[0071] Further, when the curable silicone is a condensation-curable silicone comprising an organopolysiloxane having silicon-bonded hydrolysable groups, the silicone composition (which includes the polyheterosiloxane composition and the curable silicone) can be cured by exposing the silicone composition to moisture at a temperature of from room temperature (~23 ± 2 °C) to 250 °C, alternatively from 100 to 200 °C, for a period of from 1 to 100 h. For example, the silicone composition can typically be cured by exposing it to a relative humidity of 30% at a temperature of from about room temperature (~23 ± 2 °C) to 150 °C, for a period of from 0.5 to 72 h. Cure can be accelerated by application of heat, exposure to high humidity, and/or addition of a condensation catalyst to the silicone composition.

[0072] When the curable silicone is a radiation-curable silicone, the silicone composition (which includes the polyheterosiloxane composition and the curable silicone) can be cured by exposing the silicone composition to an electron beam. Typically, the accelerating voltage is from about 0.1 to 100 keV, the vacuum is from about 10 to 10-3 Pa, the electron current is from about 0.0001 to 1 ampere, and the power varies from about 0.1 watt to 1 kilowatt. The dose is typically from about 100 microcoulomb/cm^2 to 100 coulomb/cm^2, alternatively from about 1 to 10 coulombs/cm^2. Depending on the voltage, the time of exposure is typically from about 10 seconds to 1 hour.

[0073] Also, when the radiation-curable silicone further includes a cationic or free radical photoinitiator, the silicone composition(which includes the polyheterosiloxane composition and the curable silicone) can be cured by exposing it to radiation having a wavelength of from 150 to 800 nm, alternatively from 200 to 400 nm, at a dosage sufficient to cure (cross-link) the organopolysiloxane. The light source is typically a medium pressure mercury-arc lamp. The dose of radiation is typically from 30 to 1,000 mJ/cm^2, alternatively from 50 to 500 mJ/cm^2. Moreover, the

silicone composition can be externally heated during or after exposure to radiation to enhance the rate and/or extent of cure.

[0074] When the curable silicone is a peroxide-curable silicone, the silicone composition (which includes the polyheterosiloxane composition and the curable silicone) can be cured by exposing it to a temperature of from room temperature (~23 ± 2 °C) to 180 °C, for a period of from 0.05 to 1 h.

[0075] When the curable silicone is an epoxy-curable silicone, the silicone composition (which includes the polyheterosiloxane composition and the curable silicone) can be cured by exposing it to a temperature of from room temperature (~23 ± 2 °C) to 180 °C, for a period of from 0.05 to 1 h.

[0076] The curable silicone is typically present in an amount of at least about 50 weight percent based on a total weight of the silicone composition. In various embodiments, the curable silicone is present in an amount of at least 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or 99, weight percent based on a total weight of the silicone composition. In other embodiments, the curable silicone is present in an amount of from 95 to 99.9, from 90 to 95, from 85 to 90, from 80 to 85, from 75 to 80, from 70 to 75, from 65 to 70, from 60 to 65, from 55 to 60, from 50 to 55, from 90 to 99.9, from 85 to 95, from 75 to 85, from 65 to 75, from 55 to 65, from 70 to 95, from 80 to 95, from 20 to 55, 25 to 50, 30 to 45, or 35 to 40, weight percent based on a total weight of the silicone composition. All amounts, and ranges of amounts, both whole and fractional, within the ranges set forth above are herein expressly contemplated but are not described for the sake of brevity.

[0077] The curable silicone may be utilized as a single component or as a series of components, e.g. as a one part, two part, or multi-part component system. For example, various compounds in the curable silicone may be segregated into "A" and "B" portions such that when the "A" and "B" portions are combined, the curable silicone can cure.

Method of Forming the Polyheterosiloxane Composition:

[0078] This disclosure also provides a method of forming the polyheterosiloxane composition. The method includes the step of reacting (A´) a metal (M3) alkoxide, (B´) an optional hydrolyzable metal (M4) salt or metal (M4) alkoxide, (C´) a silicon-containing material having silicon-bonded hydroxy groups, and (F) an amount of water that provides between 50 and 200% necessary to hydrolyze and condense hydrolyzable groups of (A´) and optionally (B'), so long as at least one of (A') and (B') is a non-lanthanide metal and the polyheterosiloxane composition, and the composition as a whole, are free of lanthanide metals. This step forms a polyheterosiloxane composition (i.e., a

polyheterosiloxane composition that is not yet "sensitized" because the photosensitizer is not yet added/present). The method may also include one or more steps as described in WO2011/002826, which is expressly incorporated herein by reference.

[0079] It is to be understood that (A'), optionally (B'), (C'), and (F) may react together in any order to form the polyheterosiloxane composition. For example, (A'), optionally (B'), (C'), and (F) may react individually or with more of each other batch wise (e.g. simultaneously) and/or sequentially. One or more portions of (A'), optionally (B'), (C'), and (F) may react individually or with more of portions of each other batch wise (e.g. simultaneously) and/or sequentially. (B') may not be utilized and alkoxides may be utilized in the absence of a hydrolyzable metal. In another embodiment, (B') is utilized, e.g. with an alkoxide.

[0080] The (A´) metal (M3) alkoxide is not particularly limited and may be further defined as one or a mixture of alkoxides of one or more of the metals described above, so long as at least one of (A') and (B') is a non-lanthanide metal and the composition is free of lanthanide metals. One metal (M3) alkoxide, two different alkoxides of the same metal (M3), two alkoxides of different metals (M3), or a plurality of alkoxides of one or more metals (M3), may be utilized.

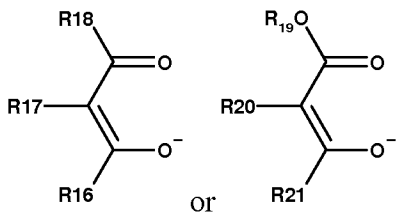
[0081] The metal (M3) is not particularly limited but is typically is the same as (M1). The metal (M3) of the metal alkoxide may be independently selected and may be the same as (M1) or (M2) or may be different, so long as at least one of (A') and (B') is a non-lanthanide metal and the composition is free of lanthanide metals.

[0082] The metal (M3) alkoxide may have the general formula (I) $R^1_kM3O_n\ X_p(OR^2)_{v1-k-p-2n}$. In Formula (I), subscript v1 is the oxidation state of metal (M3), typically from 1 to 7, 1 to 5, or 2 to 4, subscript k is typically a value from 0 to 3, alternatively 0 to 2, and alternatively 0. subscript n is typically a value from 0 to 2, alternatively 0 to 1, and alternatively 0, and subscript p is typically a value from 0 to 3, alternatively 0 to 2, and alternatively 0. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[0083] R^1 is typically a monovalent alkyl group having from 1 to 18, from 2 to 17, from 3 to 16, from 4 to 15, from 5 to 14, from 6 to 13, from 7 to 12, from 8 to 11, from 9 to 10, or from 1 to 8 carbon atoms or any value or range of values therebetween. Non-limiting examples of the alkyl group of R^1 include methyl, ethyl, propyl, isopropyl, butyl, t-butyl, hexyl, octyl, decyl, dodecyl, hexadecyl, and octadecyl groups. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[0084] Each R^2 is typically an independently selected monovalent alkyl group having from 1 to 6, 2 to 5, or 3 to 4 carbon atoms, aryl group having from 6 to 8 carbon atoms, or a polyether group having a general formula (VI) $-(R^3O)_jR^4$, where j is a value from 1 to 4 and alternatively 1 to 2. Each R^3 is typically an independently selected divalent alkylene group having from 2 to 6, 3 to 5, or 3 to 4, carbon atoms. Each R^4 is typically an independently selected hydrogen atom or monovalent alkyl group having from 1 to 6, 2 to 5, or 3 to 4 carbon atoms. Non-limiting examples of the alkyl groups of R^2 include methyl, ethyl, propyl, isopropyl, butyl, t-butyl, and hexyl groups. Non-limiting examples of the aryl groups of R^2 include phenyl and benzyl. Non-limiting examples of the divalent alkylene group include $-CH_2CH_2-$ and $-CH_2CH(CH_3)-$. Non-limiting examples of the alkyl groups having from 1 to 6 carbon atoms of R^4 are as described above for R^2. Non-limiting examples of the polyether group of Formula (VI) include methoxyethyl, methoxypropyl, methoxybutyl, ethoxyethyl, ethoxypropyl, ethoxybutyl, methoxyethoxyethyl, and ethoxyethoxyethyl groups. Alternatively, R^2 is typically an alkyl group having from 1 to 6 carbon atoms e.g. a methyl, ethyl, propyl, and butyl group, or a propyl and butyl group. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[0085] X is typically chosen from carboxylate ligands, organosulfonate ligands, organophosphate ligands, β-diketonate ligands, and chloride ligands, alternatively carboxylate ligands and β-diketonate ligands. The carboxylate ligands for X typically have a formula $R^{15}COO^-$ where R^{15} is chosen from hydrogen, alkyl groups, alkenyl groups, and aryl groups. Non-limiting examples of alkyl groups for R^{15} include alkyl groups having from 1 to 18 carbon atoms, alternatively 1 to 8 carbon atoms as described above for R^1. Non-limiting examples of alkenyl groups for R^{15} include alkenyl groups having from 2 to 18 carbon atoms, alternatively 2 to 8 carbon atoms such as vinyl, 2-propenyl, allyl, hexenyl, and octenyl groups. Non-limiting examples of aryl groups for R^{15} include aryl groups having from 6 to 18 carbon atoms, alternatively 6 to 8 carbon atoms such as phenyl and benzyl groups. Alternatively, R^{15} is methyl, 2-propenyl, allyl, and phenyl. β-diketonate ligands for X can have the following structures:



where R^{16}, R^{18}, and R^{21} are typically chosen from monovalent alkyl and aryl groups. Non-limiting examples of alkyl groups for R^{16}, R^{18}, and R^{21} include alkyl groups having from 1 to 12 carbon atoms, alternatively 1 to 4 carbon atoms such as methyl, ethyl, trifluoromethyl, and t-butyl groups. Non-limiting examples of aryl groups for R^{16}, R^{18}, and R^{21} include aryl groups having from 6 to 18 carbon atoms, alternatively 6 to 8 carbon atoms such as phenyl and tolyl groups. R^{19} is typically chosen from alkyl groups, alkenyl groups and aryl groups. Non-limiting examples of alkyl groups for R^{19} include C1 to C18 alkyl groups, alternatively C1 to C8 alkyl groups such as methyl, ethyl, propyl, hexyl and octyl groups. Non-limiting examples of alkenyl groups for R^{19} include alkenyl groups having from 2 to 18 carbon atoms, alternatively C2 to C8 carbon atoms such as allyl, hexenyl, and octenyl groups. Non-limiting examples of aryl groups for R^{19} include aryl groups having from 6 to 18 carbon atoms, alternatively 6 to 8 carbon atoms such as phenyl and tolyl groups. R^{17} and R^{20} are typically hydrogen or alkyl, alkenyl, and aryl groups. Non-limiting examples of alkyl groups for R^{17} and R^{20} include alkyl groups having from 1 to 12 carbon atoms, alternatively 1 to 8 carbon atoms such as methyl and ethyl groups. Non-limiting examples of alkenyl groups for R^{17} and R^{20} include alkenyl groups having from 2 to 18 carbon atoms, alternatively 2 to 8 carbon atoms such as vinyl, allyl, hexenyl, and octenyl groups. Non-limiting examples of aryl groups for R^{17} and R^{20} include aryl groups having from 6 to 18 carbon atoms, alternatively 6 to 8 carbon atoms such as phenyl and tolyl groups. R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, and R^{21} are each independently selected and can be the same or different from each other. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[0086] Non-limiting examples of metal alkoxides described by Formula (I) include titanium tetrapropoxides, titanium butoxide, titanium tetrabutoxides, zirconium tetrapropoxides, and zirconium tetrabutoxides from DuPont, aluminum tripropoxides, aluminum tributoxides, aluminum phenoxide, antimony (III) ethoxide, barium isopropoxide, cadmium ethoxide, cadmium methoxide, cadmium methoxyethoxide, chromium (III) isopropoxide, copper (II) ethoxide, copper (II) methoxyethoxyethoxide, gallium ethoxide, gallium isopropoxide, diethyldiethoxygermane, ethyltriethoxygermane, methyltriethoxygermane, tetra-n-butoxygermane, hafnium ethoxide, hafnium 2-ethylhexoxide, hafnium 2-methoxymethyl-2-propoxide, indium methoxyethoxide, iron (III) ethoxide, magnesium ethoxide, magnesium methoxyethoxide, magnesium n-propoxide, molybdenum (V) ethoxide, niobium (V) n-butoxide, niobium (V) ethoxide, strontium isopropoxide, strontium methoxypropoxide, tantalum (V) ethoxide, tantalum (V) methoxide, tantalum (V)

isopropoxide, tantalum tetraethoxide diemthylaminoethoxide, di-n-butyldi-n-butoxytin, di-n-butyldimethoxytin, tetra-t-butoxytin, tri-n-butylethoxytin, titanium ethoxide, titanium 2-ethylhexoxide, titanium methoxide, titanium methoxypropoxide, titanium n-nonyloxide, tungsten (V) ethoxide, tungsten (VI) ethoxide, vanadium triisobutoxide oxide, vanadium triisopropoxide oxide, vanadium tri-n-propoxide oxide, vanadium oxide tris(methoxyethoxide), zinc methoxyethoxide, zirconium ethoxide, zirconium 2-ethylhexoxide, zirconium 2-methyl-2-butoxide, and zirconium 2-methoxymethyl-2-propoxide, aluminum s-butoxide bis(ethylacetoacetate), aluminum di-s-butoxide ethylacetoacetate, aluminum diisopropoxide ethylacetoacetate, aluminum 9-octdecenylacetoacetate diisopropoxide, tantalum (V) tetraethoxide pentanedionate, titanium allylacetoacetate triisopropoxide, titanium bis(triethanolamine) diisopropoxide, titanium chloride triisopropoxide, titanium dichloride diethoxide, titanium diisopropoxy bis(2,4-pentanedionate), titanium diisopropoxide bis(tetramethylheptanedionate), titanium diisopropoxide bis(ethylacetoacetate), titanium methacrylate triisopropoxide, titanium methacryloxyethylacetoacetate triisopropoxide, titanium trimethacrylate methoxyethoxyethoxide, titanium tris(dioctylphosphato)isopropoxide, titanium tris(dodecylbenzenesulfonate)isopropoxide, zirconium (bis-2,2'-(alloxymethyl)-butoxide)tris(dioctylphosphate), zirconium diisopropoxide bis(2,2,6,6-tetramethyl-3,5-heptanedionate), zirconium dimethacrylate dibutoxide, zirconium methacryloxyethylacetoacetate tri-n-propoxide, and combinations thereof. (A´) may be chosen from titanium tetraisopropoxide, titanium butoxide, titanium tetrabutoxide, zirconium tetrabutoxide, or aluminum sec-butoxide. In various other embodiments, one or more of the aforementioned compounds, or their analogs as appreciated in the art, may be substituted with one or more metals chosen from Ti, Zr, Al, and Zn, or Ti, Zr, and Al, or Ti, Al, W, Ge, Zr, Hf, Mn, Nb, Y, Ta, and V, or W, Ti, Zr, Al, Zn, Hf, Ta, Y, and Nb, or Ti, Zr, Al, Ge, Ta, Nb, and Sn, or Sn, Cr, Ba, Sb, Cu, Ga, In, Mg, Mo, Te, W, Sr, Al, Zr, and/or any single metals or combinations thereof.

[0087] The optional (B´) hydrolyzable metal (M4) salt or metal (M4) alkoxide is not particularly limited and may be further defined as one or a mixture of salts of one or more of the metals described above. One hydrolyzable metal (M4) salt or metal (M4) alkoxide, two different salts of the same metal (M4) or metal (M4) alkoxide, two salts of different metals (M4) or metal (M4) alkoxides, or a plurality of salts of one or more metals (M4) or metal (M4) alkoxides, may be utilized. Non-limiting examples of metal (M4) alkoxides may be any of those options for the metal (M3) alkoxide or may be different.

[0088] Typically, the hydrolyzable metal (M4) is the same as the (M2). The hydrolyzable metal (M4) may be a non-lanthanide metal. The hydrolyzable metal (M4) may be the same as (M1)

or (M2) or metal (M3) or may be different. In addition, hydrolyzable metal (M4) may be independently selected and may any one of the aforementioned options for (M1) and/or (M2) and/or metal (M3). However, at least one of metal (M3) and hydrolyzable metal (M4) is typically a non-lanthanide metal.

[0089] The optional (B´) hydrolyzable metal (M4) salt may be further described as (B'1) a non-hydrated metal salt having a general formula (IV) $R^7_eM4(Z)_{(v2-e)/w}$ or (B´2) a hydrated metal salt having a general formula (V) $M4(Z)_{v2/w}\cdot xH_2O$. v2 is the oxidation state of hydrolyzable metal (M4) and w is the oxidation state of ligand Z where Z is typically independently chosen from carboxylates, β-diketonates, fluoride, chloride, bromide, iodide, organic sulfonate, nitrate, nitrite, sulphate, sulfite, cyanide, phosphites, phosphates, organic phosphites, organic phosphates, and oxalate. Each R^7 is typically an independently selected alkyl group having 1 to 18 carbon atoms, an alkenyl group having from 2 to 8 carbon atoms, or an aryl group having from 6 to 8 carbon atoms while e is typically a value from 0 to 3 and x is typically a value from 0 to 12, or from 0.5 to 12, and typically describes the average number of H_2O molecules associated with each metal salt molecule. The oxidation state of hydrolyzable metal (M4) may be as described above or may be different. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[0090] In Formulas (IV) and (V), subscript w is the oxidation state of ligand Z and typically can range from 1 to 3, alternatively from 1 to 2. The Z group in Formulas (IV) and (V) describes various counter ligands that may be attached to hydrolyzable metal (M4). Typically, each Z is independently chosen from carboxylate ligands, β-diketonate ligands, fluoride ligand, chloride ligand, bromide ligand, iodide ligand, organic sulfonate ligands, nitrate ligand, nitrite ligand, sulphate ligand, sulfite ligand, cyanide ligand, phosphate ligand, phosphite ligand, organic phosphite ligands, organic phosphate ligands, and oxalate ligand. The carboxylate ligands and β-diketonate ligands for Z may be as described above for X. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[0091] The carboxylate ligands may also be chosen from acrylate, methacrylate, butylenate, ethylhexanoate, undecanoate, undecylenate, dodecanoate, tridecanoate, pentadecanoate, hexadecanoate, heptadecanoate, octadecanoate, cis-9-octadecylenate (C18), cis-13-docoylsenoate (C22). The carboxylate ligand may be undecylenate or ethylhexanoate. Alternatively, the organic sulfonate ligands for Z may have a formula $R^{22}SO_3^-$, where R^{22} is chosen from monovalent alkyl

groups, alkenyl groups and aryl groups. Examples of alkyl groups, alkenyl groups and aryl groups are as described above for R^{15}. Alternatively R^{22} is tolyl, phenyl, or methyl.

[0092] The organic phosphate ligands for Z typically have a formula $(R^{23}O)_2\ PO_2^-$ or $R^{23}O\text{-}\ PO_3^{2-}$, where R^{23} is chosen from monovalent alkyl groups, alkenyl groups and aryl groups. Non-limiting examples of alkyl groups, alkenyl groups and aryl groups are as described above for R^{15}. Alternatively R^{23} may be phenyl, butyl, or octyl.

[0093] Organic phosphite ligands for Z may have a formula $(R^{24}O)_2\ PO^-$ or $R^{24}O\text{-}\ PO_2^{2-}$, where R^{24} is chosen from monovalent alkyl groups, alkenyl groups and aryl groups. Non-limiting examples of alkyl groups, alkenyl groups and aryl groups are as described above for R^{15}. Alternatively R^{24} may be phenyl, butyl, or octyl. Alternatively, Z in Formulas (IV) and (V) may be independently chosen from carboxylate ligands, β-diketonate ligands, nitrate ligands, sulphate ligands, and chloride ligands. Alternatively, Z may include carboxylate ligands and β-diketonate ligands.

[0094] In Formulas (IV) and (V), subscript e is typically a value from 0 to 3, alternatively from 0 to 2, and alternatively 0. In Formula (IV), R^7 may be an independently selected alkyl group having 1 to 18 carbon atoms, an alkenyl group having from 2 to 8 carbon atoms, or an aryl group having from 6 to 8 carbon atoms. Non-limiting examples of R^7 are as described above for R^5. In Formula (V), x may be a value from 0.5 to 12, and alternatively from 1 to 9. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[0095] Non-limiting examples of (B') include but are not limited to lithium acetate, sodium acetate, potassium acetate, rubidium acetate, cesium acetate, magnesium acetate, calcium acetate, strontium acetate, barium acetate, scandium acetate, yttrium acetate, hafnium acetate, vanadium acetate, niobium acetate, tantalum acetate, chromium acetate, molybdenum acetate, tungsten acetate, manganese acetate, technetium acetate, rhenium acetate, iron acetate, ruthenium acetate, osmium acetate, cobalt acetate, rhodium acetate, iridium acetate, nickel acetate, palladium acetate, platinum acetate, copper acetate, silver acetate, zinc acetate, cadmium acetate, mercury acetate, aluminum acetate, gallium acetate, indium acetate, thallium acetate, tin, lead acetate, antimony acetate, bismuth acetate, lithium acetylacetonate, sodium acetylacetonate, potassium acetylacetonate, rubidium acetylacetonate, cesium acetylacetonate, beryllium acetylacetonate, magnesium acetylacetonate, calcium acetylacetonate, strontium acetylacetonate, barium acetylacetonate, scandium acetylacetonate, yttrium acetylacetonate, titanium acetylacetonate, zirconium acetylacetonate, hafnium acetylacetonate,

vanadium acetylacetonate, niobium acetylacetonate, tantalum acetylacetonate, chromium acetylacetonate, molybdenum acetylacetonate, tungsten acetylacetonate, manganese acetylacetonate, technetium acetylacetonate, rhenium acetylacetonate, iron acetylacetonate, ruthenium acetylacetonate, osmium acetylacetonate, cobalt acetylacetonate, rhodium acetylacetonate, iridium acetylacetonate, nickel acetylacetonate, palladium acetylacetonate, platinum acetylacetonate, copper acetylacetonate, silver acetylacetonate, zinc acetylacetonate, cadmium acetylacetonate, mercury acetylacetonate, aluminum acetylacetonate, gallium acetylacetonate, indium acetylacetonate, thallium acetylacetonate, tin acetylacetonate, lead acetylacetonate, antimony acetylacetonate, aluminum acrylate, aluminum methacrylate, aluminum stearate, barium methacrylate, barium acrylate, bismuth 2- ethylhexanoate, calcium methacrylate, calcium acrylate, calcium undecylenate, copper (II) methacrylate, copper (II) 2-ethylhexanoate, hafnium 2-ethylhexanoate, iron methacrylate, iron acrylate, lead methacrylate, lead acrylate, lead 2-ethylhexanoate, lithium methacrylate, lithium acrylate, magnesium methacrylate, magnesium acrylate, potassium methacrylate, potassium acrylate, potassium sulfopropylmethacrylate, potassium sulfopropylacrylate, silver acrylate, silver methacrylate, silver neodecanoate, sodium acrylate, sodium methacrylate, sodium allylsulfonate, strontium acrylate, strontium methacrylate, bis(2-ethylhexanoate)tin, bis(neodecanoate)tin, n-butyltris(2-ethylhexanoate)tin, di-n-butylbis(2-ethylhexanoate)tin, zinc acrylate, zinc methacrylate, zinc neodecanoate, zinc undecanoate, zinc 2-ethylhexanoate, zirconium methacrylate, copper sulphate, zinc chloride, silver nitrate, iron nitrate, nickel nitrate, zinc nitrate, acryloxytri-n-butyltin, acryloxytriphenyltin, di-n-butylbis(2,4-pentanedionate)tin, di-n-butyldiacetoxytin, di-n-butyldiacrylatetin, di-n-butyldilauryltin, di-n-butyldimethacrylatetin, di-n-butyldineodecanoatetin, dimethylbis(2,4-pentanedionate)tin, dimethyldineodecanoatetin, dioctyldilauryltin, methacryloxytri-n-butyltin, tri-n-butylacetoxytin, and tri-n-butylbenzoyloxytin, zinc acetate dihydrate, nickel acetate tetrahydrate, magnesium acetate tetrahydrate, zinc nitrate hexahydrate, and copper sulphate pentahydrate, benzoates thereof, alkylbenzoates thereof, alkyloxybenzoates thereof, triphenylacetates thereof, and/or combinations thereof.

[0096] The hydrolyzable metal (M4) salt or metal (M4) alkoxide, may include one or more of the aforementioned compounds, or their analogs as appreciated in the art, substituted with one or more metals chosen from Ti, Zr, Al, and Zn, or Ti, Zr, and Al, or Ti, Al, W, Ge, Zr, Hf, Mn, Nb, Y, Ta, and V, or W, Ti, Zr, Al, Zn, Hf, Ta, Y, and Nb, or Ti, Zr, Al, Ge, Ta, Nb, and Sn, or Sn, Cr, Ba, Sb, Cu, Ga, In, Mg, Mo, Te, W, Sr, Al, Zr, and/or any single metals or combinations thereof.

[0097] In one embodiment, (B´) is chosen from (B´1) a non-hydrated metal salt having a general formula (IV) $R^7_eM4(Z)_{(v2-e)/w}$ and (B´2) a hydrated metal salt having a general formula (V) $M4(Z)_{v2/w}\cdot xH_2O$, wherein (M4) is a non-lanthanide metal, v2 is the oxidation state of M4, w is the oxidation state of Z, Z is independently chosen from alkoxides, carboxylates, β-diketonates, chlorides, organic sulfonates, nitrates, and oxalates, each R^7 is an independently selected alkyl group having 1 to 18 carbon atoms, alkenyl group having from 2 to 12 carbon atoms, or aryl group having from 6 to 18 carbon atoms, e is a value from 0 to 3 and x is a value from 0 to 12.

[0098] In another embodiment, (A´) and (B´) are reacted with water to form a mixed metal oxide solution including metal (M3)-O-(M4) oxo-bonds. This solution may then be reacted with (C´) to form the polyheterosiloxane composition, wherein the total amount of water added is between 50 and 200% of the amount theoretically necessary for the hydrolysis and condensation of all alkoxy groups and other hydrolyzable groups of (A´), and optionally (B´). The percent may be further described as mole or weight percent as a theoretical calculated stoichiometric amount.

[0099] Referring now to (C'), it is a silicon-containing material having silicon-bonded hydroxy groups. The silicon-containing material can be (C'1) a siloxane having silicon-bonded hydroxy groups, (C'2) a silane having silicon-bonded hydroxy groups, or combinations thereof.

[00100] The (C'1) siloxane can be a disiloxane, trisiloxane, or polysiloxane, or combinations thereof. Similarly, the (C'2) silane can be a monosilane, disilane, trisilane, or polysilane or combinations thereof. The structure of the (C'1) siloxane or (C'2) silane can be linear, branched, cyclic, or resinous. Cyclosilanes and cyclosiloxanes typically have from 3 to 12 silicon atoms, alternatively from 3 to 10 silicon atoms, alternatively from 3 to 4 silicon atoms. In acyclic polysilanes and polysiloxanes, the silicon-bonded hydroxy groups can be located at terminal, pendant, or at both terminal and pendant positions.

[00101] Non-limiting examples of (C'1) siloxanes having silicon-bonded hydroxy groups include MQ resins, OH-functional polydialkylsiloxanes, polydimethylsiloxane, polyalkylphenylsiloxanes polyphenylmethyldisiloxanes, polyarylalkysiloxanes, polydiphenylsiloxanes, polydiarylsiloxanes, polytrifluorumethylsiloxanes, polydiphenylsiloxane dimethylsiloxane copolymers, polyarylsiloxanes, polytrifluoropropylmethylsiloxane, and combinations thereof.

[00102] Non-limiting examples of (C'2) silanes having silicon-bonded hydroxyl groups include phenylsilanetriol, diphenylsilanediol, phenylmethylsilanediol, dimethylsilanediol, trimethylsilanol, triphenylsilanol, phenyldimethoxysilanol, phenylmethoxysilanediol, methyldimethoxysilanol,

methylmethoxysilanediol, phenyldiethoxysilanol, phenylethoxysilanediol, methyldiethoxysilanol, and methylethoxysilanediol, and combinations thereof.

[00103] In one embodiment, (C') is further defined a hydrolysis product of at least one of: (C'i) a organosiloxane, (C'ii) a silane, and combinations thereof. In this embodiment, the hydrolysis product is further defined as the product of water and at least one of (C'i), (C'ii), and combinations thereof. At least one of (C'i) and (C'ii) has a hydrolyzable group. In other words, (C'i) may have a hydrolyzable group, (C'ii) may have a hydrolyzable group, or both (C'i) and (C'ii) each have a hydrolyzable group. One or both of (C'i) and (C'ii) can have more than one hydrolyzable group.

[00104] The (C') hydrolysis product, i.e., the product formed from reaction with water, may include $R^5_g(R^6O)_f(HO)_jSiO_{(4-(f+g+j))/2}$ and/or hydrolyzed silane $R^5_h(HO)_kSiZ'_i$, wherein, for example, R^5 is hydrogen or a hydrocarbyl group. A hydrolyzed organosiloxane $R^5_g(R^6O)_f(HO)_jSiO_{(4-(f+g+j))/2}$ or hydrolyzed silane $R^5_h(HO)_kSiZ'_i$ can be used directly or diluted with aromatic solvents (toluene) and alcohol before added to a mixture of (A') and optionally (B').

[00105] One or both of (C'i) and/or (C'ii) may be treated with stoichiometric amounts of water containing catalytic amounts of a strong acid, e.g. HCl or any "strong acid", or any highly diluted aqueous acid to initiate or promote hydrolysis. Formation of a hydrolysis product may be accelerated by mixing hydrolysable (C'i) or (C'ii) with highly diluted aqueous acid or sonication of a mixture of both. For example, a silane (C'ii), e.g. having a general formula (III) $R^5_hSiZ'_i$ (wherein Z' = Cl and i = 1, 2), may be treated with stoichiometric amounts of water in the presence of a base, typically an amine such as triethylamine or pyridine, to capture resulting HCl as a hydrochloride salt. After removal of the hydrochloride salt, a hydrolyzed silane, e.g. $R^5_hSi(OH)_i$, can be isolated or used directly in solution when added to the reaction mixture of A' and B'.

[00106] In other embodiments, organosiloxane (C'i) (e.g. $R^5g(R^6O)_fSiO_{(4-(f+g))/2}$) and/or silane (C'ii) (e.g. $R^5_hSiZ'_i$) are treated with diluted aqueous acid, such as 0.1 N HCl, to form a mixture. The aqueous acid may be used in stoichiometric amounts relative to hydrolysable groups OR^6 or Z' (e.g. wherein Z' = OR^6). The mixture may be mixed or sonicated until two phases of aqueous acid and (C'i) and/or (C'ii) become one phase. A hydrolysis reaction can be monitored based on its exothermic nature. If necessary, the hydrolyzed organosiloxane and silane can be diluted with toluene and alcohol, such as ethanol or butanol, to maintain a uniform one-phase solution before being added to the reaction mixture of A' and B'.

[00107] In other embodiments, a solution of silane $R^5_hSiZ'_i$ (wherein Z' = Cl and i = 1, 2), in diethylether (1:5) is added dropwise to a stirred cooled solution of stoichiometric amounts of triethylamine or pyridine and water in a diethylether-acetone mixture (e.g. 7:1). The mixture may

then be stirred for additional time and precipitated amine or pyridine hydrochloride may be filtered off and the filtrate reduced to 1/10 volume, e.g. using a rotary evaporator at 80°C and 15 mm Hg. An excess of pentane or other suitable hydrocarbon may be added to precipitate any residual amine or pyridine hydrochloride followed by filtering and volume reduction. A resulting solid may then be collected via filtration and washed with cold pentane or hydrocarbon and re-crystallized from pentane/diethylether. The product may be isolated as white solid.

[00108] (C′i), which may be reacted to form the hydrolysis product, may be an organosiloxane having an average siloxane unit formula (II) $R^5_g(R^6O)_fSiO_{(4-(f+g))/2}$, and/or (C′ii) may be a silane having a general formula (III) $R^5_hSiZ'_i$. In these formulas, each R^5 is hydrogen or a hydrocarbyl group, each R^6 is typically an independently selected hydrogen atom or alkyl group having from 1 to 6 carbon atoms, aryl group having from 6 to 8 carbon atoms, or a polyether group having a general formula (VI) $-(R^3O)_jR^4$, where j is a value from 1 to 4, each R^3 is an independently selected divalent alkylene group having from 2 to 6 carbon atoms, R^4 is an independently selected hydrogen atom or monovalent alkyl group having from 1 to 6 carbon atoms, and the subscripts f and g are each independently any values from 0 to 3, wherein $0<f+g<3$.

[00109] In Formula (II), subscript f may be a value from 0.1 to 3 and alternatively from 1 to 3. In Formula (II), subscript g may be a value from 0.5 to 3 and alternatively from 1.5 to 2.5. In Formula (II), subscripts (f+g) may have a value from 0.6 to 3.9 and alternatively from 1.5 to 3. For example, f may be from 0.1 to 3 and g may be from 0.5 to 3. Examples of (C′i) described by Formula (II) include oligomeric and polymeric organosiloxanes, such as MQ resins.

[00110] Alternatively, Z′ may be a hydrolysable group such as acetoxy, oxime, silazane, Cl or OR^6 and/or each R^5 may be an independently selected hydrogen atom, alkyl group having 1 to 18 carbon atoms, alkenyl group having from 2 to 18 carbon atoms, aryl group having from 6 to 12 carbon atoms, epoxy group, amino group, or carbinol group. In one embodiment, at least one R^5 groups of (C′i) and/or (C′ii) silane is an R^1 group, as described above. Alternatively, at least one $R^5 = R^1$ may be as described by formula (II) or (III). Additionally, h is typically a value from 0 to 3, i is typically a value from 1 to 4 and (h+i) equals 4. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[00111] The alkyl groups having 1 to 18 carbon atoms of R^5 in Formulas (II) and (III) are typically as described above for R^1. Alternatively, the alkyl group may include 1 to 6 carbon atoms and be, for example, a methyl, ethyl, propyl, butyl, or hexyl group. The alkenyl groups having from

2 to 18 carbon atoms of R^5 in Formulas (II) and (III) may be, for example, vinyl, propenyl, butenyl, pentenyl, hexenyl, or octenyl groups. Alternatively, the alkenyl group may include 2 to 8 carbon atoms and be, for example, a vinyl, allyl, or hexenyl group. The aryl groups having 6 to 12 carbon atoms of R^5 in formulas (II) and (III) may be phenyl, naphthyl, benzyl, tolyl, xylyl, methylphenyl, 2-phenylethyl, 2-phenyl-2-methylethyl, chlorophenyl, bromophenyl and fluorophenyl groups. Alternatively, the aryl group may include 6 to 8 carbon atoms and be, for example, a phenyl group. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[00112] In Formula (III), each Z′ may be a chloro atom (Cl) or OR^6, where R^6 is as described above. Alternatively, Z′ may be OR^6. In Formula (III), subscript h may be a value from 0 to 3, from 1 to 3, or from 2 to 3. In Formula (III), subscript i is a value from 1 to 4, from 1 to 3, or from 1 to 2. In Formula (III), subscripts (h+i) may equal 4. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[00113] Examples of the silanes (C'ii), which may be reacted to form the hydrolysis product, described by Formula (III) include methyltrichlorosilane, phenyltrichlorosilane, dimethyldichlorosilane, phenylmethyldichlorosilane, methyltrimethoxysilane, phenyltrimethoxysilane, dimethyldimethoxysilane, phenylmethyldimethoxysilane, and combinations thereof.

[00114] Typically, an amount of (F) water is utilized (and/or reacted) with (A') and optionally (B') so that polyheterosiloxanes having at least two non-Si metal elements can be formed. Since water can also be incorporated via hydrated metal salts (B´2), hydrated metal salts may be utilized such that no liquid water may be utilized and the water originates from the hydrated metal salts. 0.5 mole of water may be used for hydrolysis and condensation of 1 mole of alkoxy and other hydrolyzable groups. Alternatively, the amount of water utilized may be from 50 to 200, 70 to 150, from 80 to 120, 60 to 190, 70 to 180, 80 to 170, 90 to 160, 100 to 150, 110 to 140, or 120 to 130, %, of the theoretical amount of water necessary for complete hydrolysis and condensation of alkoxy and other hydrolyzable groups, as first described above. All values and ranges of values therebetween the aforementioned values and ranges are hereby expressly contemplated.

[00115] Typically, the water is added slowly to (A') and optionally (B') in an attempt to ensure that the metal alkoxide does not react quickly with the water so as to form a precipitate. Alternatively, the water may be diluted with one or more solvents, such as those described above. Depending on the solvents used and when they are added, the water may also be added at one time

or during one or more of the method steps. Other hydrolyzable groups that may be present and need to be hydrolyzed and condensed are any found on the components used, including, but not limited to, chloro.

[00116] Each of the components (A'), optionally (B'), and/or (C') may be liquid or solid and it is typical that they are pre-mixed or dispersed. Stirring one or more of the components (A'), optionally (B'), and/or (C') in a solvent may provide a homogenous dispersion. As used herein, the terminology "dispersion" describes that the molecules of the various components (A'), (B'), and/or (C') are homogenously distributed. A solvent may not be needed if one or more components (A'), (B'), and/or (C') can be dispersed in one or more of each other. Such solvents may be as described and may be polar solvents, non-polar solvents, hydrocarbon solvents including aromatic and saturated hydrocarbons, alcohols, etc. Non-limiting examples of suitable solvents include hydrocarbonethanol, 1-propanol, isopropanol, 1-butanol, 2-butanol, methoxyethanol, methoxyethoxyethanol, butyl acetate, toluene, and xylene, alternatively isopropanol, 1-butanol, 2-butanol, and butyl acetate. The dispersing or mixing may be completed by any conventional means such as stirring.

[00117] Typically, reaction of (A') and optionally (B') with (F) water proceeds at room temperature (e.g. 20-30°C) but if desired, elevated temperatures up to about 140°C may be used. Alternatively, the temperature can range from 20°C to 120°C. Typically, the reaction may proceed from 30 minutes to 24 hours and alternatively from 10 minutes to 4 hours.

[00118] An optional method step includes removing the solvent to form the polyheterosiloxane composition. The solvent can be removed by any conventional manner such as heating to elevated temperatures or using reduced pressure. The polyheterosiloxane composition can then be redispersed in a solvent of choice such as toluene, THF, butyl acetate, chloroform, dioxane, 1-butanol, and pyridine. Since the Si-O-M may be susceptible to hydrolytic cleavage in the presence of water, to maximize shelf life it is typical to minimize the exposure of the polyheterosiloxane composition to moisture.

[00119] The method of forming the sensitized polyheterosiloxane composition may also include the step of (II) introducing a (D) photosensitizer to one or more of (A'), (B'), (C'), (E) as described below, and/or (F), prior to the step of reacting and/or introducing (D) to the polyheterosiloxane composition, to form the sensitized polyheterosiloxane composition. Said differently, until this step is completed, the polyheterosiloxane composition formed by reaction of (A'), optionally (B'), (C'), (E) and/or (F), is not yet "sensitized." Only after introduction of the (D) photosensitizer to the

"polyheterosiloxane composition" is that polyheterosiloxane composition then described as sensitized, i.e., described as the "sensitized polyheterosiloxane composition."

[00120] The (D) photosensitizer may be present in the sensitized polyheterosiloxane composition in an amount of less than 3 moles of (D) photosensitizer per one mole of the non-lanthanide metal. The step of introducing is not particularly limited and may include introducing by any method such as pouring, spraying, etc. The step of introducing may occur before, during, or after combination of one or more of (A'), (B'), (C'), (E) and/or (F), and/or before, during, or after reaction of one or more of (A'), (B'), (C'), (E) and/or (F). The step of introducing may occur more than once. For example, amounts of the (D) photosensitizer may be introduced at various points in the method. In one embodiment, the (D) photosensitizer is added to the polyheterosiloxane composition after (A'), optionally (B'), (C'), (E) and/or (F) react. Alternatively, the (D) photosensitizer can be added to a vessel in conjunction with (A') and one or more solvents. Further, the (D) photosensitizer can be added to a vessel in conjunction with (B') and/or (C') and one or more solvents. Even further, the (D) photosensitizer can be added to a vessel in conjunction with (E) and/or (F). As described above, the (D) photosensitizer may impart a larger peak emission intensity to the sensitized polyheterosiloxane composition at an excitation wavelength of from 200 to 1,000, 300 to 900, 400 to 800, 500 to 700, 600 to 700, 350 to 450, 320 to 480, 330 to 470, 340 to 460, 350 to 450, 360 to 440, 370 to 430, 380 to 420, 390 to 410, or about 400, nm, as compared to a control polyheterosiloxane composition free of the (D) photosensitizer. The method may also include one or more steps as described in PCT application No. PCT/US10/40510, which is expressly incorporated herein by reference.

[00121] The method may alternatively include the step of reacting (A'), (B'), (C'), and (E) a compatibilizing organosiloxane having at least one $[R^2_3SiO_{1/2}]$ unit and having a weight average molecular weight (M_w) of less than 10,000 g/mol.

[00122] Referring to the (E) compatibilizing organosiloxane, this organosiloxane has at least one $[R^2_3SiO_{1/2}]$ unit. However, the compatibilizing organosiloxane may have more than one $[R^2_3SiO_{1/2}]$ unit. The compatibilizing organosiloxane also has a weight average molecular weight (M_w) of less than 10,000 g/mol. In various embodiments, the M_w is less than 9,000, 8,500, 8,000, 7,500, 7,000, 6,500, 6,000, 5,500, 5,000, 4,500, 4,000, 3,500, 3,000, 2,500, 2,000, 1,500, 1,000, or 500, g/mol. Alternatively, the M_w may be any value or range of values described immediately above or between those values described immediately above.

[00123] In one embodiment, the (E) compatibilizing organosiloxane has an average formula chosen from:

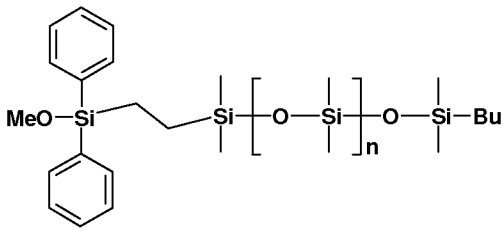
DI) $(R'O)(C_6H_5)_2SiCH_2CH_2[(CH_3)_2SiO]_nOSi(CH_3)_2(CH_2)_3CH_3$;

DII) $(R'O)(C_6H_5)_2SiCH_2CH_2\,Si(CH_3)(OSi(CH_3)_3)_2$;

DIII) $(R'O)_3SiO(CH_3)_2Si[(CH_3)_2SiO]_mOSi(CH_3)_2\,(CHCH_2)$; or

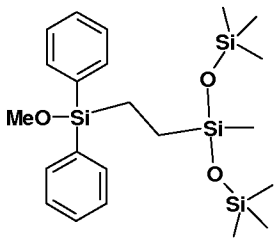
DIV) $(R'O)(C_6H_5)_2SiOSi(CH_3)_2CH_2CH_2Si(CH_3)(OSi(CH_3)_3)_2$,

wherein each n is independently from 3 to 100, alternatively from 10 to 12, each m is independently from 3 to 100, alternatively from 20 to 30, and R' is a C_1 to C_4 alkyl group. Alternatively, the (E) compatibilizing organosiloxane may have the average formula:

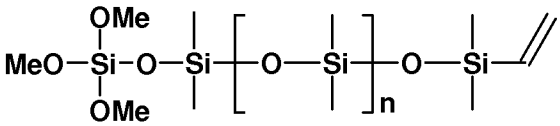


wherein n is from 3 to 100, 3 to 50, or 3 to 15.

Alternatively, the (E) compatibilizing organosiloxane may have the average formula:



Even further, the (E) compatibilizing organosiloxane may have the average formula:



wherein n is from 3 to 100, alternatively from 20 to 30.

[00124] In other embodiments, the (E) compatibilizing organosiloxane has the formula: $(Me_3SiO)_2MeSiCH_2CH_2Si(CH_3)_2OSi(C_6H_5)_2(OMe)$. Even further, the (E) compatibilizing organosiloxane may have the formula $(R^8{}_3SiO)_n(R^8)_{(3-n)}Si\text{-}R^9\text{-}Si(R^8)_2\,OSi(R^{10})_2X$, wherein n is 1 or 2. Each R^8 may be independently a monovalent C_1 to C_{20} hydrocarbyl. The hydrocarbyl group may independently be an alkyl, aryl, or alkylaryl group, including halogen substituted hydrocarbyls. Each R^8 may independently be a C_1 to C_{20} alkyl group, a C_1 to C_{18} alkyl group, a C_1 to C_6 alkyl group such as methyl, ethyl, propyl, butyl, pentyl, or hexyl. R^8 may be an aryl group, such as

phenyl, naphthyl, or an anthryl group, or any combination thereof. Alternatively, each R^8 may independently be phenyl, methyl, or a combination of both. Each R^9 may independently be a divalent hydrocarbon group including 2 to 12 carbon atoms or 2 to 6 carbon atoms and may be described as ethylene, propylene, or isobutylene. Each R^{10} may independently be a monovalent C_1 to C_{30} hydrocarbyl including at least one aryl group, an aryl group, such as phenyl, naphthyl, or an anthryl group, any combination of the aforementioned alkyl or aryl groups, or phenyl (C_6H_5). X may be a hydrolyzable group chosen from $-OR^{11}$, Cl, $-OC(O)R^9$, $-N(R^9)_2$, or $-ON=CR^9_2$ wherein each R^{11} is independently hydrogen or a C_1 to C_6 alkyl group such as a methyl, ethyl, propyl, isopropyl, butyl, pentyl, or hexyl group. Alternatively, X may be an alkoxy, hydroxyl, carboxy, amine, chloride, or oxime group, e.g. $-OCH_3$, $-OCH_2CH_3$, -OH, -Cl, or $-OC(=O)CH_3$. In one embodiment, the organosiloxane has the following formula: $(Me_3SiO)_2(Me)SiCH_2CH_2Si(CH_3)_2OSi(C_6H_5)_2(OMe)$, wherein Me is a methyl group. Alternatively, the organosiloxane has the formula $(R^8{}_3SiO)_n(R^8)_{(3-n)}Si\text{-}G\text{-}Si(R^8)_2OSi(R^{10})_2X$, wherein n is 1 or 2, R^8 is independently a monovalent C_1 to C_{20} hydrocarbyl, G is a siloxane or polysiloxane bridging group comprising at least one siloxy unit selected from a $(R^{12}{}_2SiO_{2/2})$, $(R^{12}SiO_{3/2})$, or $(SiO_{4/2})$ siloxy units, wherein R^{12} may be any organic group, R^{10} is independently a monovalent C_1 to C_{30} hydrocarbyl including at least one aryl group, X is a hydrolyzable group chosen from $-OR^9$, Cl, $-OC(O)R^9$, $-N(R^9)_2$, or $-ON=CR^9_2$ and R^{11} is hydrogen or a C_1 to C_6 alkyl group. G may also be a combination of hydrocarbyl bridging groups, such as the divalent C_2 to C_{12} hydrocarbyl groups described above, and a siloxane or polysiloxane. In various embodiments, G is a polydimethylsiloxane of the formula $-O(Me_2SiO_{2/2})_q-$ where the subscript q is from 1 to 20, alternatively from 1 to 10, or alternatively from 1 to 5. When the polysiloxane bridging group includes a $(R^{12}SiO_{3/2})$, or $(SiO_{4/2})$ siloxy unit(s), the group may further include additional M siloxy units to provide endcapping groups. Alternatively, one or more T or Q units may be silanol terminated.

Method of Forming the Silicone Composition:

[00125] This disclosure also provides a method of forming a silicone composition. The method may include forming the polyheterosiloxane composition as described above and the step of combining the polyheterosiloxane composition and the curable silicone to form a silicone composition.

[00126] The polyheterosiloxane can be added to the curable silicone or vice versa. In one embodiment, the polyheterosiloxane is present in a solvent and this combination is added to the curable silicone, or vice versa. Alternatively, the polyheterosiloxane composition (and optionally the solvent) may be added to an "A" portion, a "B" portion, or both "A" and "B" portions, of the

curable silicone, or vice versa. The polyheterosiloxane composition can also be added to the curable silicone after "A" and "B" portions are already themselves combined. Alternatively, the polyheterosiloxane composition can be added to the curable silicone, or vice versa, even if the curable silicone does not have "A" and "B" portions and is, instead, a single portion.

[00127] This disclosure also provides a cured silicone composition. Said differently, the cured silicone composition is the cured product of the aforementioned silicone composition including the polyheterosiloxane composition and the curable silicone wherein the curable silicone is cured by one or more of the aforementioned curing mechanisms. The cured silicone composition is not particularly limited and may be partially cured or completely cured. The cured silicone composition may be in any three dimensional form including a film, sheet, as a gel, as a molded form, as a cast form, etc. The level of clarity of the cured silicone composition may be predetermined by selecting and customizing the polyheterosiloxane composition and the curable silicone, as well as the methodology and conditions used to prepare the cured silicone composition.

[00128] This disclosure also provides an article which is not particularly limited and may be any three dimensional article. The article includes a substrate and a coating disposed on the substrate. The substrate is not particularly limited and may be a solid, liquid, or gel. In various embodiments, the substrate, in whole or in part, includes or is paper, plastic, a polymer, metal, wood, glass, or combinations thereof.

[00129] In one embodiment, the article is a molded article, e.g. with an overall shape or cross-section profile defined by a negative of the shape of a mold. In a non-limiting example, a mold having the shape of a hemi-spherical bowl may be utilized to produce an article having a shape of a spherical dome. Additionally, fine features or a pattern may be imparted onto the article, e.g. by utilizing a negative pattern in the mold such that vias would become pads, and vice versa. Molding techniques may include, but are not limited to, injection molding, overmolding, compression molding, casting, and imprint lithography. Feature size in any dimension may be greater than 5 nm, greater than 100 nm, greater than 1 μm, or greater than 10 um.

[00130] The coating may be disposed on and in direct contact with the substrate or disposed on and separated in space with the substrate. The coating may be disposed on one or more portions of the substrate or on the entire substrate. The coating includes the cured silicone composition, e.g. the cured polyheterosiloxane composition including the curable silicone described above. In various embodiments, the coating has an average thickness of from 1 to 10, 2 to 9, 3 to 8, 4 to 7, or 5 to 6, μm or cm. In other embodiments, the coating has an average thickness of from 10 to 100, 15 to 95, 20 to 90, 25 to 85, 30 to 80, 35 to 75, 40 to 70, 45 to 65, 50 to 60, or about 65, μm. In still other

embodiments, the coating has an average thickness of from 100 to 1000, 150 to 950, 200 to 900, 250 to 850, 300 to 800, 350 to 750, 400 to 700, 450 to 650, 500 to 600, or about 650, μm. In additional embodiments, the coating has an average thickness of from 1000 to 10000, 1500 to 9500, 2000 to 9000, 2500 to 8500, 3000 to 8000, 3500 to 7500, 4000 to 7000, 4500 to 6500, 5000 to 6000, or about 6500, μm. In further embodiments, the coating has an average thickness of from 10000 to 100000, 15000 to 95000, 20000 to 90000, 25000 to 85000, 30000 to 80000, 35000 to 75000, 40000 to 70000, 45000 to 65000, 50000 to 60000, or about 65000, μm. However, the coating is not limited to this thickness.

[00131] The coating may be disposed over a large area, on the substrate which may be rigid or flexible as recognized by those skilled in the art. The coating may also be described as a film. Non-limiting examples of coatings include bar coatings, Meyer bar coatings, gravure coatings, doctor blade coatings, slot-die coatings, spray coatings, spin coating castings, etc. The coating may be disposed on one or more portions of the substrate, or across an entirety of the substrate. The area coated may be larger than 1 mm in width or length, greater than 1 cm in width or length, greater than 20 cm in width or length, greater than 50 cm in width or length, or greater than 1 m in width or length. The coating may be disposed in such a way as to form a pattern. Methods used to form the coating include, but are not limited to, casting, ink jet printing, screen printing, stencil printing.

EXAMPLES

[00132] The following examples are included to demonstrate various embodiments of the disclosure and are not limiting. All percentages are in weight % unless indicated otherwise.

Photoluminescence

[00133] Photoluminescence of the examples is be measured using a Fluorolog-2 or Fluorolog-3 spectrofluorometer, manufactured by Jobin Yvon SPEX, and an Ocean Optics USB4000 spectrometer fiber coupled to an integrating sphere and using Ocean Optics' Spectra Suite software. The specific parameters are as described above.

Example 1: Synthesis and Preparation of Silicone Cured Polyheterosiloxane Composition $Al_x[R^1SiO_{3/2}]_d[R^1SiO_{1/2}]_t$ + 6,11-dihydroxy-5,12-naphthacenedione

[00134] 54 ml of 6:1 ratio of toluene and *sec*-butanol is charged to a 3-neck 250 ml round flask equipped with reflux condenser and temperature probe. 16.061 g of Aluminum *sec*-butoxide is charged to the flask followed by 1.051 g of $Ph_2MeSiOH$ ($R^1SiO_{1/2}$). The reaction mixture is stirred ½ hour at room temperature.

[00135] Pre-hydrolyzed $R^1SiO_{3/2}$ siloxane moieties are then formed by mixing 5.87 g of Dow Corning Z-6665 silane and 23.65 g of Dow Corning Toray RMS 757 with 0.1N HCl (1.26 g), diluted

with 70 ml of a 2:1 ratio of toluene and *sec*-butanol and added to the stirred reaction mixture. The reaction is heated to 75 °C for one hour, after which the residual amount of water (0.98 g) is added dissolved in 20 ml of a 3:1 ratio ethanol and toluene. The reaction solution and the solution are stirred for further 2 hours at 75 °C before being cooled to ambient and then filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in white solids.

[00136] To 15.8 g of the Polyheterosiloxane Composition in toluene, 0.1014 g of blue-sensitizing ligand 6,11-dihydroxy-5,12-naphthacenedione (Sigma-Aldrich) are added and filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in a highly viscous orange-red liquid.

[00137] A cured silicone sample is prepared by mixing 0.75 g of the Polyheterosiloxane Composition + 6,11-dihydroxy-5,12-naphthacenedione with 14.25 g of OE6630 Dow Corning® in a planetary mixer and degassed under vacuum. The resulting mixture is cured and molded into films in a hot press (5000 psi) for 1 h at 120 °C.

Example 2: Synthesis and Preparation of Silicone Cured Polyheterosiloxane Composition $Al_x[R^1SiO_{3/2}]_d[R^1SiO_{1/2}]_t$ + 1-(5-chloro-2-hydroxyphenyl)-3-phenyl-1,3-propandione

[00138] 54 ml of 6:1 ratio of toluene and *sec*-butanol is charged to a 3-neck 250 ml round flask equipped with reflux condenser and temperature probe. 16.061 g of Aluminum *sec*-butoxide is charged to the flask followed by 1.051 g of $Ph_2MeSiOH$ ($R^1SiO_{1/2}$). The reaction mixture is stirred ½ hour at room temperature.

[00139] Pre-hydrolyzed $R^1SiO_{3/2}$ siloxane moieties are then formed by mixing 5.87 g of Dow Corning Z-6665 silane and 23.65 g of Dow Corning Toray RMS 757 with 0.1N HCl (1.26 g), diluted with 70 ml of a 2:1 ratio of toluene and *sec*-butanol and added to the stirred reaction mixture. The reaction is heated to 75 °C for one hour, after which the residual amount of water (0.98 g) is added dissolved in 20 ml of a 3:1 ratio ethanol and toluene. The reaction solution and the solution are stirred for further 2 hours at 75 °C before being cooled to ambient and then filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in white solids.

[00140] To 13.5 g of the Polyheterosiloxane Composition in toluene, 0.0816 g of blue-sensitizing ligand 1-(5-chloro-2-hydroxyphenyl)-3-phenyl-1,3-propandione (Akros Organic) are added and filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in a highly viscous orange-red liquid.

[00141] A cured silicone sample is prepared by mixing 0.75 g of the Polyheterosiloxane Composition + 1-(5-chloro-2-hydroxyphenyl)-3-phenyl-1,3-propandione with 14.25 g of OE6630 Dow Corning® in a planetary mixer and degassed under vacuum. The resulting mixture is cured and molded into films in a hot press (5000 psi) for 1 h at 120 °C.

[00142] The excitation and emission spectra for Example 1 are set forth at Figures 1A and 1B. The excitation and emission spectra for Example 2 are set forth at Figures 2A and 2B.

Photoluminescence and Color

[00143] Photoluminescence of the examples may be measured using a Fluorolog-2 spectrofluorometer, manufactured by Jobin Yvon SPEX, and an Ocean Optics USB4000 spectrometer fiber coupled to an integrating sphere and using Ocean Optics' Spectra Suite software. The specific parameters are as described above.

[00144] Color (CIEx, CIEy, and Color) are determined as described above.

[00145] After formation of each of the following Examples 1-2, each is evaluated to determine photoluminescence. The results of these evaluations are set forth as Figures 1-4, respectively. Each of the Examples 1-2 is also evaluated to determine color. The results of the color determination are set forth immediately below.

Emission with λex=450 nm

Example	CIEx	CIEy	Color
1	0.515673	0.482542	Orange Red
2	0.35992	0.585129	Yellow

Emission with λex =393 nm

Example	CIEx	CIEy	Color
1	0.501164	0.437948	Orange Red
2	0.322788	0.527756	Yellow

[00146] This data above shows cured compositions were successfully produced of an organosiloxane host with a luminescent ligand sensitized, non-lanthanide polyheterosiloxane with a range of emission spectra and CIE color coordinates.

Photoluminescence

[00147] Again, of the examples is be measured using a Fluorolog-2 or Fluorolog-3 spectrofluorometer, manufactured by Jobin Yvon SPEX, and an Ocean Optics USB4000

spectrometer fiber coupled to an integrating sphere and using Ocean Optics' Spectra Suite software. The specific parameters are as described above.

Example 3: Synthesis of Polyheterosiloxane Composition ($Al_{0.54}D_{0.27}T_{0.09}M_{0.1}Ligand_{0.001}$)

[00148] 300 ml of 6:1 ratio of toluene and *sec*-butanol is charged to a 3-neck 500 ml round flask equipped with reflux condenser and temperature probe. 13.30 g of Aluminum *sec*-butoxide is charged to the flask followed by 2.14 g of $Ph_2MeSiOH$ ($R^1SiO_{1/2}$). The reaction mixture is stirred ½ hour at room temperature.

[00149] Pre-hydrolyzed $R^1SiO_{3/2}$ and $R^1SiO_{2/2}$ siloxane moieties are then formed by mixing 0.20 g of Dow Corning Toray RMS 757 (L), 4.92 g of $PhMeSi(OMe)_2$ (D) and 1.77 g of $PhSi(OMe)_3$ (T) with 0.1N HCl (1.47 g), diluted with 45 ml of a 2:1 ratio of toluene and *sec*-butanol and added to the stirred reaction mixture. The reaction is heated to 75 °C for one hour, after which the residual amount of water (0.64 g) is added dissolved in 20 ml of a 3:1 ratio ethanol and toluene. The reaction solution is stirred for further 2 hours at 75 °C before being cooled to ambient and then filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in white solids.

[00150] To 10 g of the polyheterosiloxane composition dissolved in toluene, 0.0548 g of sensitizing ligand 1-[2-(2-pyridinyl)diazenyl]-2-naphthalenol (Alfa Aesar) is added and filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in a yellow-orange compound.

Example 4: Synthesis of Polyheterosiloxane Composition ($Al_{0.3}D_{0.525}T_{0.175}Ligand_{0.02}$)

[00151] 300 ml of 6:1 ratio of toluene and *sec*-butanol and 7.39 g of Aluminum *sec*-butoxide are charged to a 3-neck 500 ml round flask equipped with reflux condenser and temperature probe.

[00152] Pre-hydrolyzed $R^1SiO_{3/2}$ and $R^1SiO_{2/2}$ siloxane moieties are then formed by mixing 4.00 g of Dow Corning Toray RMS 757 (L), 9.57 g of $PhMeSi(OMe)_2$ (D) and 3.47 g of $PhSi(OMe)_3$ (T) with 0.1N HCl (2.28 g), diluted with 45 ml of a 2:1 ratio of toluene and *sec*-butanol and added to the stirred reaction mixture. The reaction is heated to 75 °C for 2 hours before being cooled to ambient and then filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in white solids.

[00153] To 10 g of the polyheterosiloxane composition dissolved in toluene, 0.0471 g of sensitizing ligand 2,2'-dihydroxyazobenzene (Sigma-Aldrich) is added and filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in a yellow-orange compound.

Example 5: Synthesis of Polyheterosiloxane Composition ($Al_{0.6}D_{0.3}T_{0.1}Ligand_{0.005}$)

[00154] 300 ml of 6:1 ratio of toluene and *sec*-butanol and 14.78 g of aluminum *sec*-butoxide are charged to a 3-neck 500 ml round flask equipped with reflux condenser and temperature probe.

[00155] Pre-hydrolyzed $R^1SiO_{3/2}$ and $R^1SiO_{2/2}$ siloxane moieties are then formed by mixing 1.00 g of Dow Corning Toray RMS 757 (L), 5.47 g of $PhMeSi(OMe)_2$ (D) and 1.98 g of $PhSi(OMe)_3$ (T) with 0.1N HCl (1.62 g), diluted with 45 ml of a 2:1 ratio of toluene and *sec*-butanol and added to the stirred reaction mixture. The reaction is heated to 75 °C for one hour, after which the residual amount of water (0.82 g) is added dissolved in 20 ml of a 3:1 ratio ethanol and toluene. The reaction solution are stirred for further 2 hours at 75 °C before being cooled to ambient and then filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in white solids.

[00156] To 10 g of the polyheterosiloxane composition dissolved in toluene, 0.0469 g of sensitizing ligand 2-(2-hydroxybenzylidenamino)phenol (TCI America Fine Chemicals) is added and filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in a yellow compound.

Example 6: Synthesis of Polyheterosiloxane Composition ($Al_{0.54}D_{0.27}T_{0.09}M_{0.1}Ligand_{0.001}$)

[00157] 300 ml of 6:1 ratio of toluene and *sec*-butanol is charged to a 3-neck 500 ml round flask equipped with reflux condenser and temperature probe. 13.30 g of aluminum *sec*-butoxide is charged to the flask followed by 3.14 g of $Ph_2MeSiOH$ ($R^1SIO_{1/2}$). The reaction mixture is stirred ½ hour at room temperature.

[00158] Pre-hydrolyzed $R^1SiO_{3/2}$ and $R^1SiO_{2/2}$ siloxane moieties are then formed by mixing 0.20 g of Dow Corning Toray RMS 757 (L), 4.92 g of $PhMeSi(OMe)_2$ (D) and 1.78 g of $PhSi(OMe)_3$ (T) with 0.1N HCl (1.47 g), diluted with 45 ml of a 2:1 ratio of toluene and *sec*-butanol and added to the stirred reaction mixture. The reaction is heated to 75 °C for one hour, after which the residual amount of water (0.59 g) is added dissolved in 20 ml of a 3:1 ratio ethanol and toluene. The reaction solution are stirred for further 2 hours at 75 °C before being cooled to ambient and then filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in white solids.

[00159] To 10 g of the polyheterosiloxane composition dissolved in toluene 0.0713 g of sensitizing ligand 1,3-di-2-thienyl-propane-1,3-dione (ABI Chem Block Building Blocks) is added and filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in a yellow compound.

Example 7: Synthesis of Polyheterosiloxane Composition ($Zr_{0.5}D_{0.35}T_{0.15}Ligand_{0.001}$)

[00160] 300 ml of 6:1 ratio of toluene and *sec*-butanol and 19.18 g of zirconium *n*-butoxide are charged to a 3-neck 500 ml round flask equipped with reflux condenser and temperature probe.

[00161] Pre-hydrolyzed $R^1SiO_{3/2}$ and $R^1SiO_{2/2}$ siloxane moieties are then formed by mixing 0.20 g of Dow Corning Toray RMS 757 (L), 6.38 g of $PhMeSi(OMe)_2$ (D) and 2.97 g of $PhSi(OMe)_3$ (T) with 0.1N HCl (2.08 g), diluted with 45 ml of a 2:1 ratio of toluene and *sec*-butanol and added to the stirred reaction mixture. The reaction is heated to 75 °C for one hour, after which the residual amount of water (0.31 g) is added dissolved in 20 ml of a 3:1 ratio ethanol and toluene. The reaction solution are stirred for further 2 hours at 75 °C before being cooled to ambient and then filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in yellow solids.

[00162] To 10 g of the polyheterosiloxane composition dissolved in toluene, 0.0447 g of sensitizing ligand 5-(ethoxymethyl)-8-quinolinol (Aurora Screening Library) is added and filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in a yellow compound.

Example 8: Synthesis of Polyheterosiloxane Composition ($Zr_{0.54}D_{0.34}T_{0.12}Ligand_{0.001}$)

[00163] 300 ml of 6:1 ratio of toluene and *sec*-butanol and 20.18 g of zirconium *n*-butoxide are charged to a 3-neck 500 ml round flask equipped with reflux condenser and temperature probe.

[00164] Pre-hydrolyzed $R^1SiO_{3/2}$ and $R^1SiO_{2/2}$ siloxane moieties are then formed by mixing 0.20 g of Dow Corning Toray RMS 757 (L), 6.20 g of $PhMeSi(OMe)_2$ (D) and 2.40 g of $PhSi(OMe)_3$ (T) with 0.1N HCl (1.88 g), diluted with 45 ml of a 2:1 ratio of toluene and *sec*-butanol and added to the stirred reaction mixture. The reaction is heated to 75 °C for one hour, after which the residual amount of water (0.48 g) is added dissolved in 20 ml of a 3:1 ratio ethanol and toluene. The reaction solution are stirred for further 2 hours at 75 °C before being cooled to ambient and then filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in white solids.

[00165] To 10 g of the polyheterosiloxane composition dissolved in toluene 0.0579 g of sensitizing ligand 2-Hydroxy-3-(phenylcarbamoyl)naphthalene (Aurora Screening Library) is added and filtered through 0.45 μm PTFE filter media. Solvents and other volatiles are removed using rotary evaporation at 75°C and 15 mmHg resulting in a yellow compound.

Photoluminescence and Color

[00166] Again, photoluminescence of the examples may be measured using a Fluorolog-2 spectrofluorometer, manufactured by Jobin Yvon SPEX, and an Ocean Optics USB4000

spectrometer fiber coupled to an integrating sphere and using Ocean Optics' Spectra Suite software. The specific parameters are as described above.

[00167] After formation of each of the following Examples 3-8, each is evaluated to determine photoluminescence. The results of these evaluations are set forth as Figures 3-8, respectively. Each of the Examples 3-8 is also evaluated to determine color. The results of the color determination are set forth immediately below.

Example	Formula	CIEx	CIEy	Color
Al + 1-[2-(2-pyridinyl)diazenyl]-2-naphthalenol	$Al_{0.54}D_{0.27}T_{0.09}M_{0.1}L_{0.001}$	0.6099	0.3900	Orange Red
Al + 2,2'-dihydroxyazobenzene	$Al_{0.3}D_{0.525}T_{0.175}L_{0.02}$	0.5390	0.4592	Yellow
Al + 2-(2-hydroxybenzylidenamino)phenol	$Al_{0.6}D_{0.3}T_{0.1}L_{0.005}$	0.3181	0.5182	Green
Al + 1,3-di-2-thienyl-propane-1,3-dione	$Al_{0.54}D_{0.27}T_{0.09}M_{0.1}L_{0.001}$	0.1404	0.0753	Blue
Zr + 5-(ethoxymethyl)-8-quinolinol	$Zr_{0.5}D_{0.35}T_{0.15}L_{0.001}$	0.2744	0.4419	Bluish Green
Zr + 2-Hydroxy-3-(phenylcarbamoyl)naphthalene	$Zr_{0.54}D_{0.34}T_{0.12}L_{0.001}$	0.3153	0.4863	Green

[00168] This data above shows that ligand sensitized photoluminescent non-lanthanide polyheterosiloxane resins were successfully produces with a range of visible emission colors.

[00169] One or more of the values described above may vary by ± 5%, ± 10%, ± 15%, ± 20%, ± 25%, etc. so long as the variance remains within the scope of the disclosure. Unexpected results may be obtained from each member of a Markush group independent from all other members. Each member may be relied upon individually and or in combination and provides adequate support for specific embodiments within the scope of the appended claims. The subject matter of all combinations of independent and dependent claims, both singly and multiply dependent, is herein expressly contemplated. The disclosure is illustrative including words of description rather than of limitation. Many modifications and variations of the present disclosure are possible in light of the above teachings, and the disclosure may be practiced otherwise than as specifically described herein. In additional non-limiting embodiments, all values and ranges of values within any aforementioned range of numbers are hereby expressly contemplated

[00170] In various non-limiting embodiments, this disclosure expressly contemplates and herein affirmatively includes one or more components, articles, method steps, analytical determinations, compounds, and/or physical properties described in one or more of PCT Patent

Application Numbers PCT/US2013/046813 and PCT/US2013/046784; one or more of U.S. Provisional Patent Application Numbers 61/782230; 61/782628; 61/851990; 61/783797; and 61/784581; each of which was previously filed and is expressly incorporated herein by reference in its entirety relative to these non-limiting embodiments, or PCT application docket number DC11530PCT1/071038.01589 or Taiwanese application docket number DC11530NP1/071038.01590, which are concurrently filed and expressly incorporated herein by reference in its entirety relative to these non-limiting embodiments.

CLAIMS

What is claimed is:

1. A sensitized polyheterosiloxane composition comprising;

at least one non-lanthanide metal;

siloxy units having the formula ($R^1_3SiO_{1/2}$), ($R^1_2SiO_{2/2}$), ($R^1SiO_{3/2}$), and/or ($SiO_{4/2}$),

wherein each R^1 is independently a hydrocarbon or halogenated hydrocarbon group comprising 1 to 30 carbon atoms,

wherein the mole fractions of the at least one non-lanthanide metal and the siloxy units relative to each other is of the formula:

$$[\text{at least one non-lanthanide metal}]_a[R^1_3SiO_{1/2}]_m[R^1_2SiO_{2/2}]_d[R^1SiO_{3/2}]_t[SiO_{4/2}]_q,$$

wherein a is from 0.001 to 0.9, m is from zero to 0.9, d is from zero to 0.9, t is from zero to 0.9, and q is from zero to 0.9,

wherein m, d, t, and q cannot all be zero and the sum of $a+m+d+t+q \approx 1$, and

a photosensitizer present in an amount of less than 3 moles of photosensitizer per one mole of the at least one non-lanthanide metal,

wherein said photosensitizer imparts a larger peak emission intensity to said sensitized polyheterosiloxane composition at an excitation wavelength of from 200 to 1,000 nm as compared to a control polyheterosiloxane composition free of the photosensitizer, and

wherein said sensitized polyheterosiloxane composition is free of lanthanide metals.

2. The composition of claim 1 wherein said at least one non-lanthanide metal is further defined as comprising:

(A) a first non-lanthanide metal (M1), and

(B) a second non-lanthanide metal (M2).

3. The composition of claim 2 wherein each of (M1) and (M2) is independently chosen from Ti, Zr, Al, Zn, Hf, Ta, Y, Nb, W, and combinations thereof.

4. The composition of claim 2 or 3 wherein the mole fractions of (A), (B), and said siloxy units relative to each other is of the formula $[(M1)]_a[(M2)]_b[R^1_2SiO_{2/2}]_d[R^1SiO_{3/2}]_t$ wherein a is from 0.1 to 0.8, b is from 0.05 to 0.5, each of d and t is independently from 0.1 to 0.8. and each R^1 is independently a hydrocarbon or halogenated hydrocarbon group comprising 1 to 30 carbon atoms.

5. The composition of any one of the preceding claims comprising –(Si-O-M1-O-M2)– bonds.

6. The composition of any one of the preceding claims that:

(i) emits light having a wavelength of 400 to 1700 nm when excited by a light source having a wavelength of 200 to 1000 nm; or

(ii) emits light having a wavelength of 450 to 750 nm when excited by a light source having a wavelength of 250 to 520 nm; or

(iii) emits visible light having a wavelength of 450 to 650 nm when excited by UV light; or

(iv) emits infrared light having a wavelength of 1450 to 1650 nm when excited by light having a wavelength from 650 to 5,000 nm; or

(v) emits near IR light having a wavelength of 1000 to 1100 nm when excited by light having a wavelength from 650 to 5,000 nm,

with the proviso that the emitted light has a longer wavelength than the excitation light source.

7. The composition of any one of the preceding claims wherein said photosensitizer is present in an amount of from 0.0001 to 0.04 moles of photosensitizer per one mole of the at least one non-lanthanide metal.

8. The composition of any one of the preceding claims wherein said photosensitizer is chosen from diketonates, Schiff bases, azo dyes, polyaromatic hydrocarbons, and combinations thereof.

9. The composition of any one of the preceding claims that is soluble in a hydrocarbon solvent.

10. The composition of any one of the preceding claims further comprising a non-curable silicone fluid.

11. A method of forming a sensitized polyheterosiloxane composition, said method comprising the steps of:

(I) reacting

(A´) a metal (M3) alkoxide,

(B´) an optional hydrolyzable metal (M4) salt or metal (M4) alkoxide,

(C´) a silicon-containing material having silicon-bonded hydroxy groups, and

(F) an amount of water that provides between 50 and 200% necessary to hydrolyze and condense hydrolyzable groups of (A´) and optionally (B') to form a polyheterosiloxane composition,

wherein each of (M3) and (M4) is independently a non-lanthanide metal, and

(II) introducing a (D) photosensitizer to one or more of (A'), (B'), (C'), and (F) prior to the step of reacting and/or introducing (D) to the polyheterosiloxane composition, to form the sensitized polyheterosiloxane composition,

wherein the (D) photosensitizer is present in the sensitized polyheterosiloxane composition in an amount of less than 3 moles of (D) photosensitizer per one mole of the metals (M3) and (M4), and

wherein the (D) photosensitizer imparts a larger peak emission intensity to the sensitized polyheterosiloxane composition at an excitation wavelength of from 200 to 1,000 nm as compared to a control polyheterosiloxane composition free of the (D) photosensitizer.

12. The method of claim 11 wherein at least one of (M3) and (M4) is chosen from aluminum, zirconium, and combinations thereof.

13. The method of claim 11 or 12 wherein the (C') silicon-containing material having silicon-bonded hydroxy groups is chosen from (C'1) siloxane having silicon-bonded hydroxy groups, (C'2) a silane having silicon-bonded hydroxy groups, and combinations thereof.

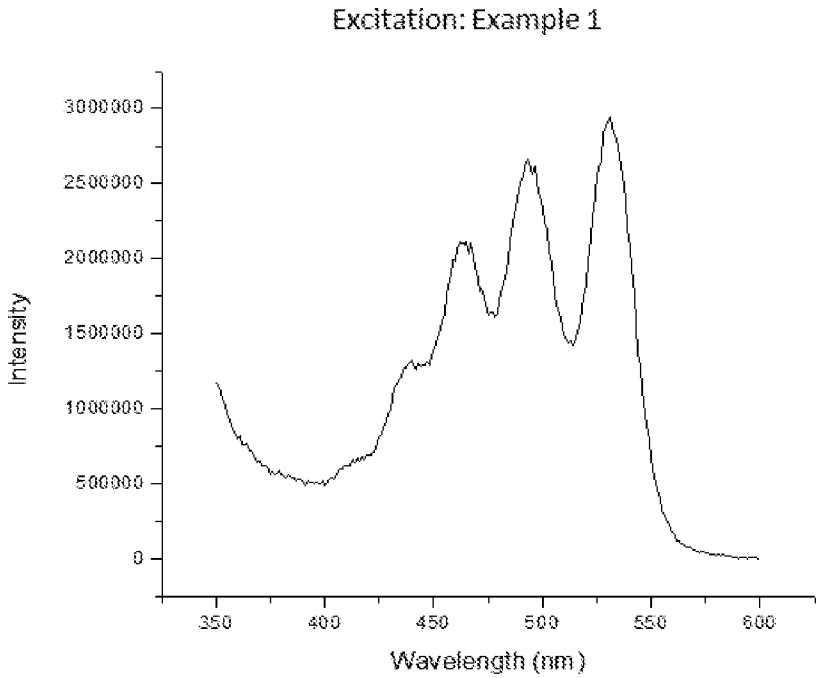
14. The method of any one of claims 11 to 13 wherein (B´) is chosen from (B´1) a non-hydrated metal salt having a general formula (IV) $R^7_eM4(Z)_{(v2-e)/w}$ and (B´2) a hydrated metal salt having a general formula (V) $M4(Z)_{v2/w}\cdot xH_2O$, (M4) is a non-lanthanide metal, v2 is the oxidation state of M4, w is the oxidation state of Z, Z is independently chosen from alkoxides, carboxylates, β-diketonates, chlorides, organic sulfonates, nitrates, and oxalates, each R^7 is an independently selected alkyl group having 1 to 18 carbon atoms, alkenyl group having from 2 to 12 carbon atoms, or aryl group having from 6 to 18 carbon atoms, e is a value from 0 to 3 and x is a value from 0 to 12.

15. A polyheterosiloxane composition formed from the method of any one of claims 11 to 14.

16. A silicone composition comprising a curable silicone and the sensitized polyheterosiloxane composition of any one of claims 1 to 10, wherein said silicone composition is free of lanthanide metals.

17. A method of forming a silicone composition comprising a curable silicone and a sensitized polyheterosiloxane composition, said method comprising the method of any one of claims 11 to 14 and further comprising the step of (III) combining the curable silicone and the sensitized polyheterosiloxane composition to form the silicone composition.

18. A silicone composition formed from the method of claim 17.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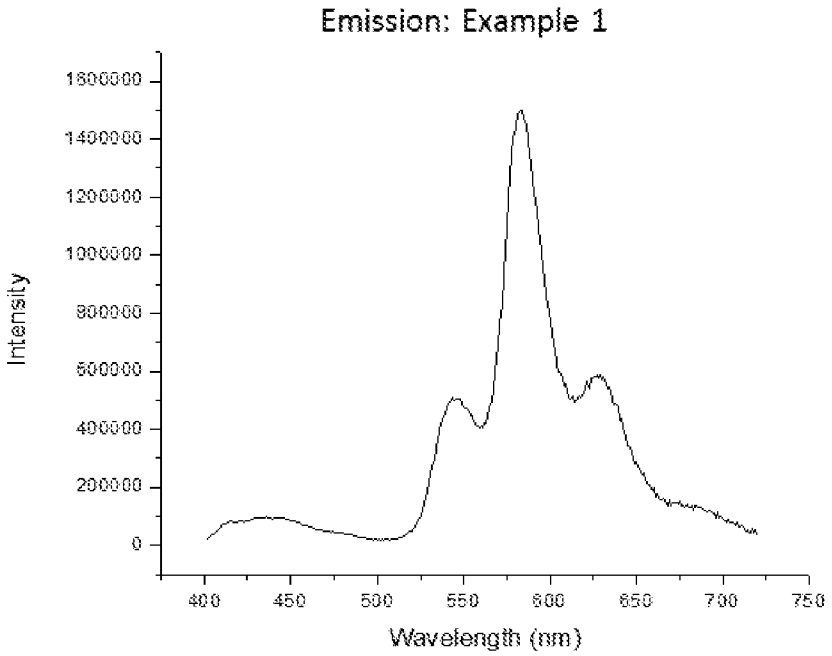
Wavelength (nm)

Figure 1A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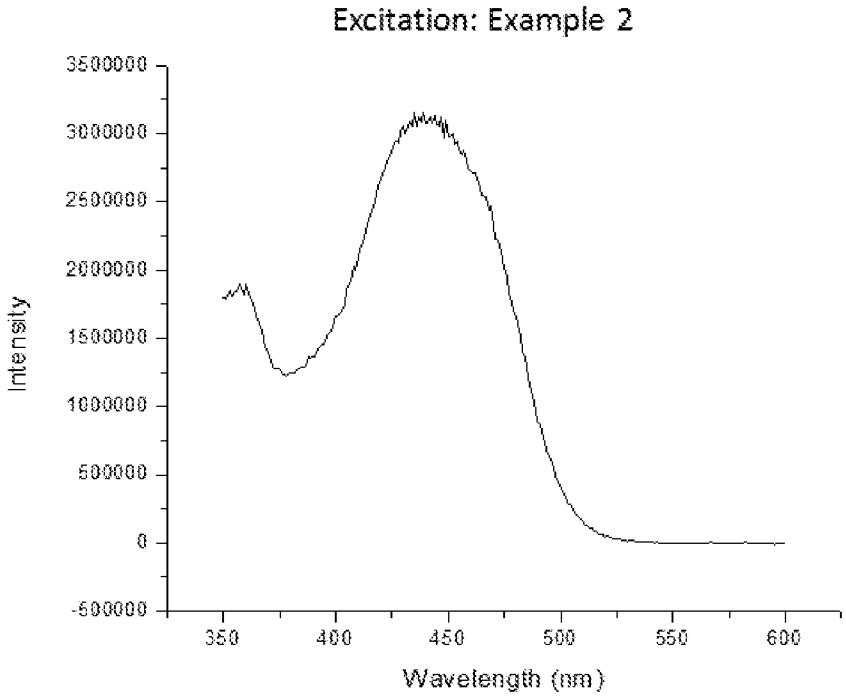
Wavelength (nm)

Figure 1B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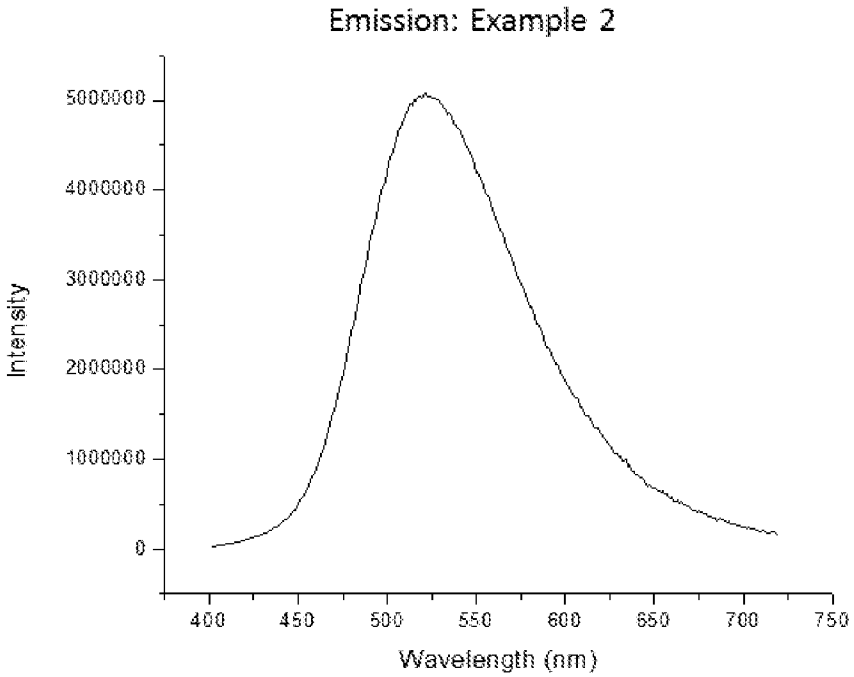
Wavelength (nm)

Figure 2A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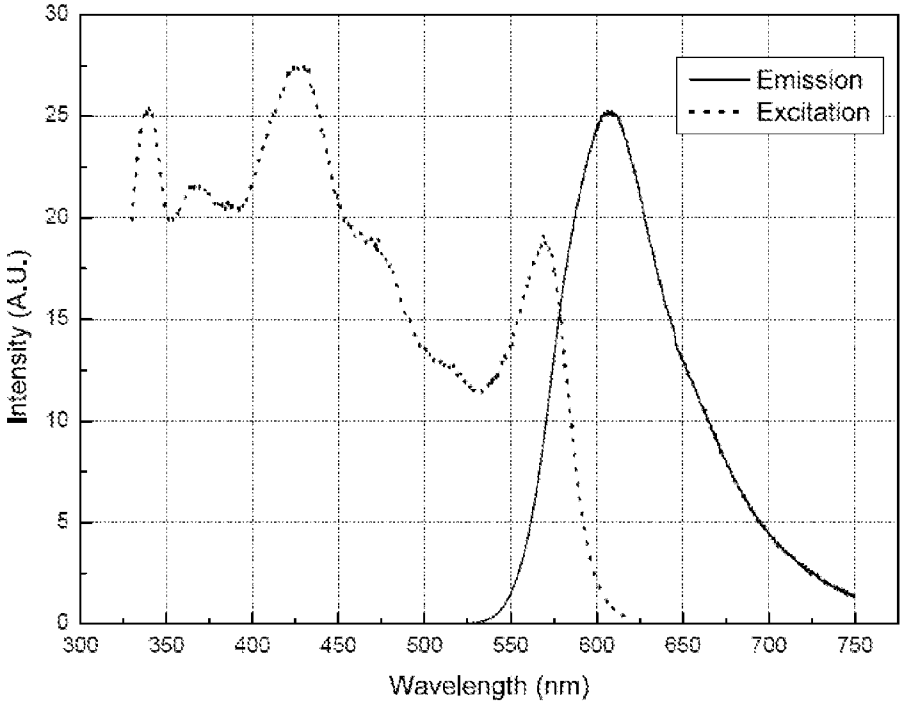
Wavelength (nm)

Figure 2B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Excitation
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Wavelength (nm)
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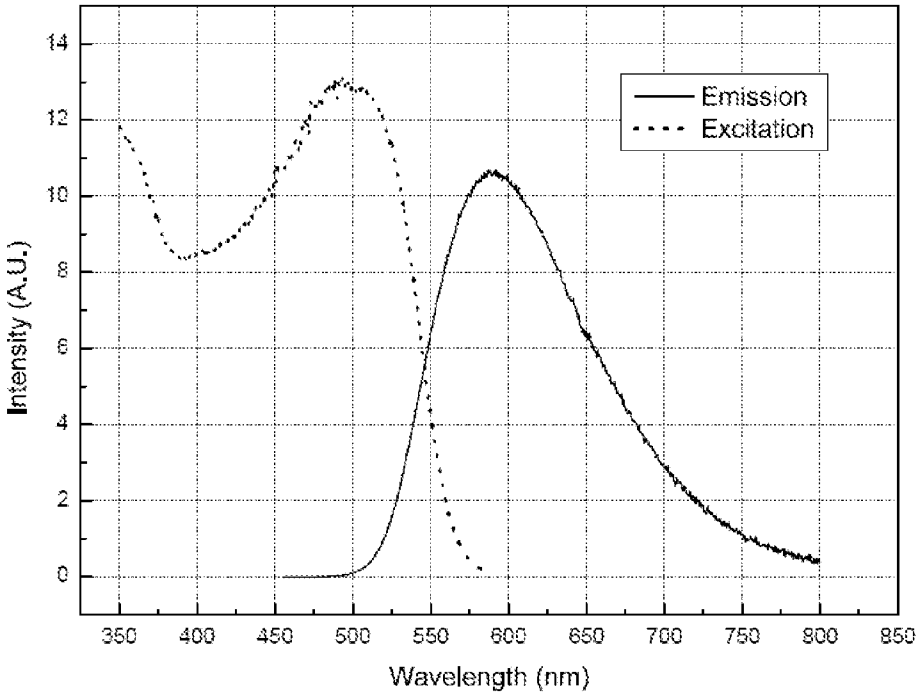
750

Figure 3


Emission
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Intensity (A.U.)
Wavelength (nm)
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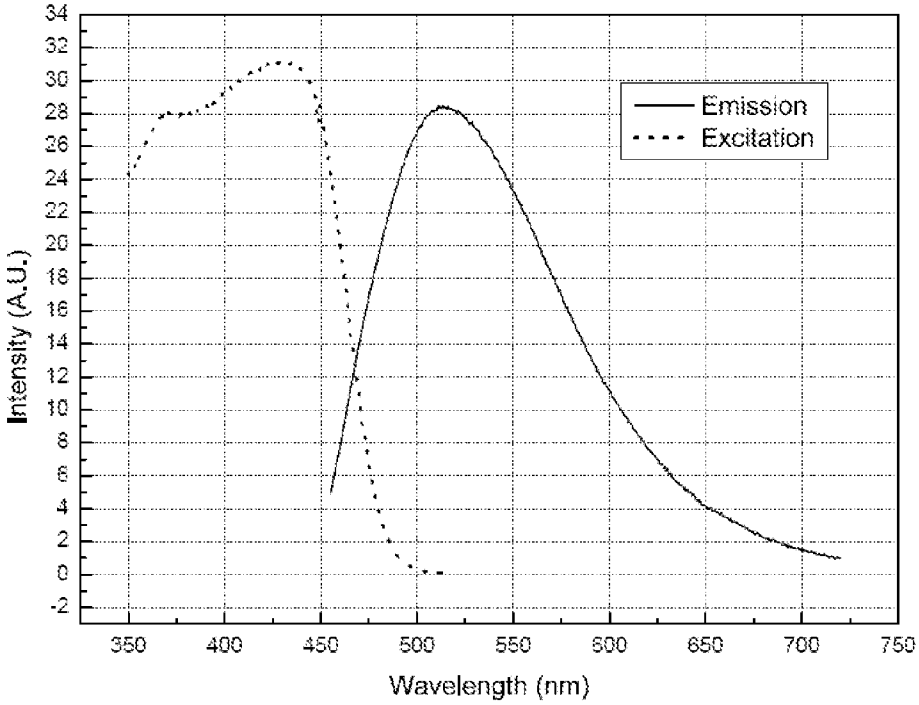
800
850

Figure 4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Excitation
Intensity (A.U.)
Wavelength (nm)
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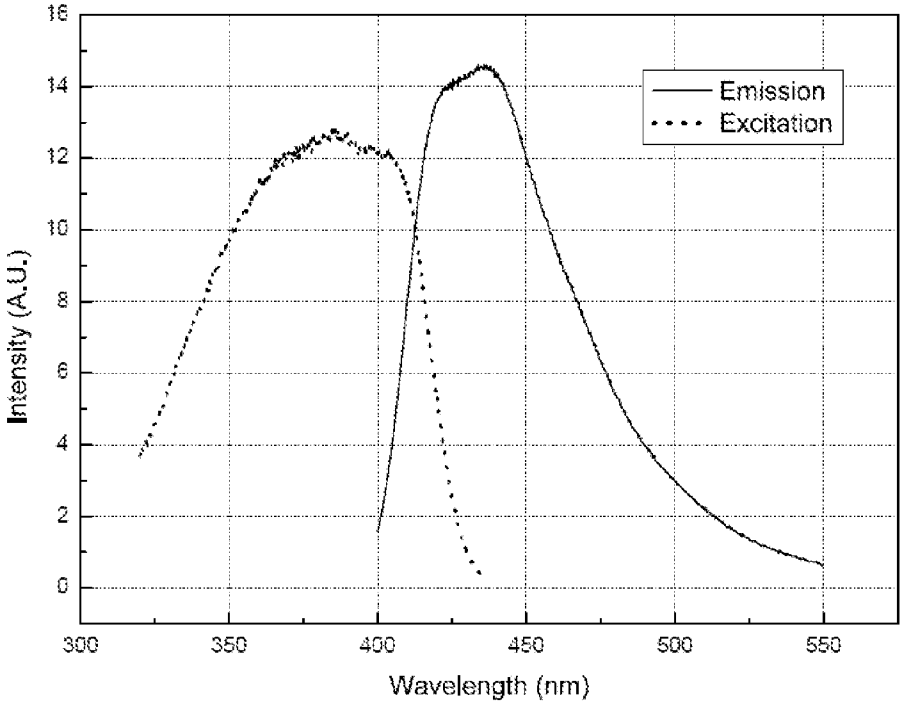
650
700
750

Figure 5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Excitation
Intensity (A.U.)
Wavelength (nm)
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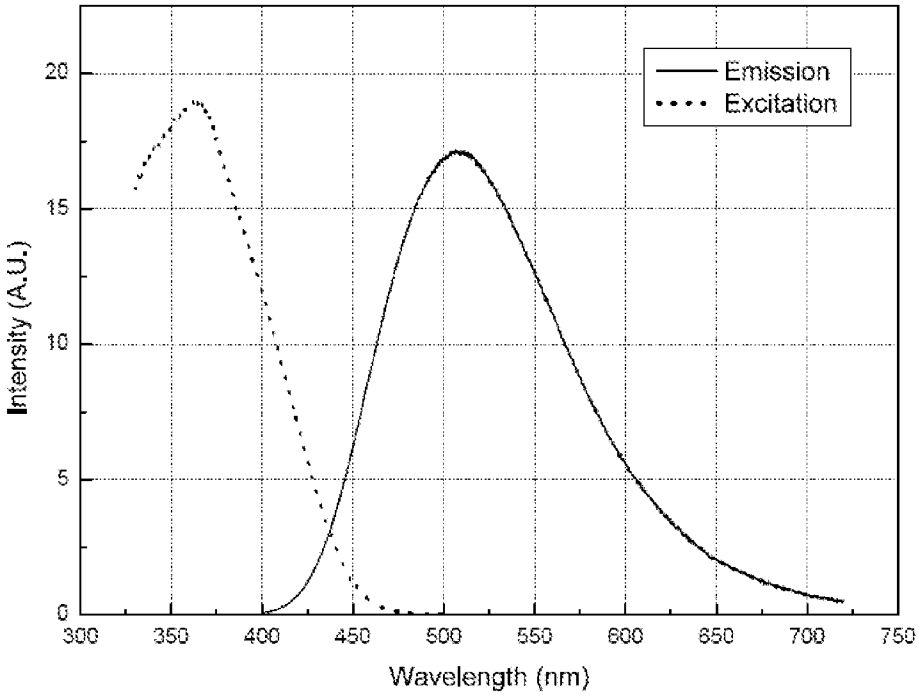
Figure 6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Wavelength (nm)
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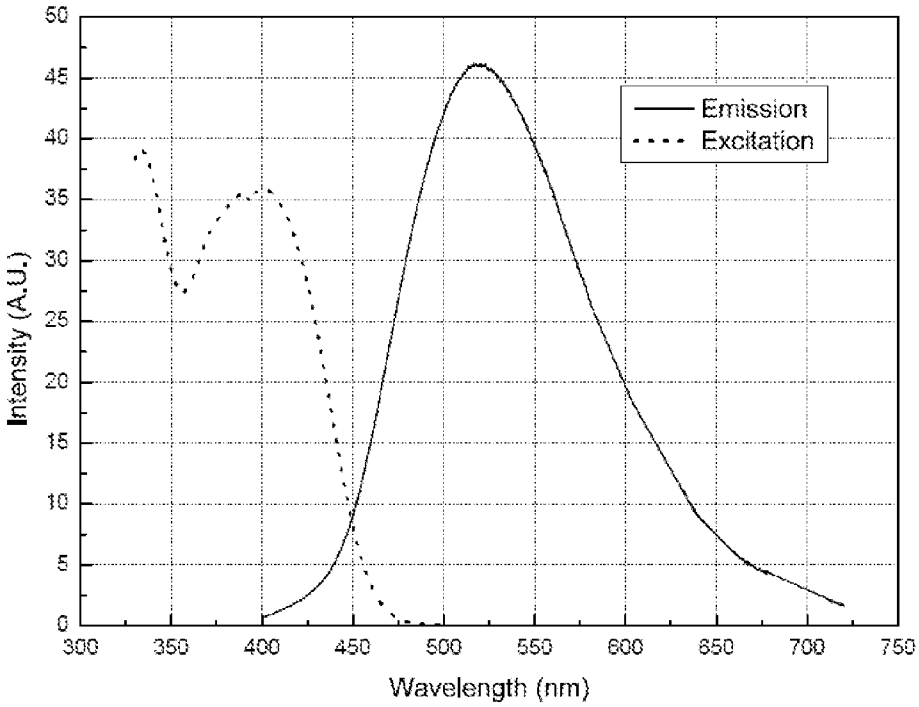
Figure 7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Excitation
Intensity (A.U.)
Wavelength (nm)
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650
700
750

Figure 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/027892

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G77/58 C08L83/14
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)
C08G C08L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/271006 A1 (SHIN JUNE-HO [KR] ET AL) 25 October 2012 (2012-10-25) claims 1,31	1-18
A	LU H ET AL: "Molecular design and photophysical properties of acylamido side functionalized polysiloxanes with lanthanide ions as luminescent centers", JOURNAL OF PHOTOCHEMISTRY AND PHOTOBIOLOGY, A: CHEMISTRY, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 215, no. 1, 5 September 2010 (2010-09-05), pages 46-51, XP027288966, ISSN: 1010-6030 [retrieved on 2010-08-14] pages 46,49-50	1-18

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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	Date of mailing of the international search report
11 August 2014	18/08/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Buestrich, Ralf

1

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.
A	WANG Q M ET AL: "Terbium/zinc luminescent hybrid siloxane-oxide materials bridged by novel ureasils linkages", JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 691, no. 4, 1 February 2006 (2006-02-01), pages 545-550, XP028047893, ISSN: 0022-328X, DOI: 10.1016/J.JORGANCHEM.2005.09.026 [retrieved on 2006-02-01] page 550 -----	1-18

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/027892

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012271006 A1	25-10-2012	CN 102686698 A	19-09-2012
		KR 100976461 B1	17-08-2010
		US 2012271006 A1	25-10-2012
		WO 2011081326 A2	07-07-2011