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[Continued on next page]

(54) Title: INORGANIC SILOXANE LADDER COMPOSITES AND METHODS OF THEIR PREPARATION

(57) Abstract: Inorganic siloxane ladder polymers with metal-aza/thio crown complexes, and methods of making and using such siloxane ladder polymers are disclosed. The polymers described herein may exhibit self-healing properties, a low dielectric constant, and a low refractive index. These siloxane ladder polymers are anchored to transparent, high-refractive index (RI) metal nanoparticles, such as ZrO_2, via aza/thio crown macromolecules. The siloxane ladder polymers may be considered as "living polymer network" since the polymer active chain ends may further undergo anionic polymerization.

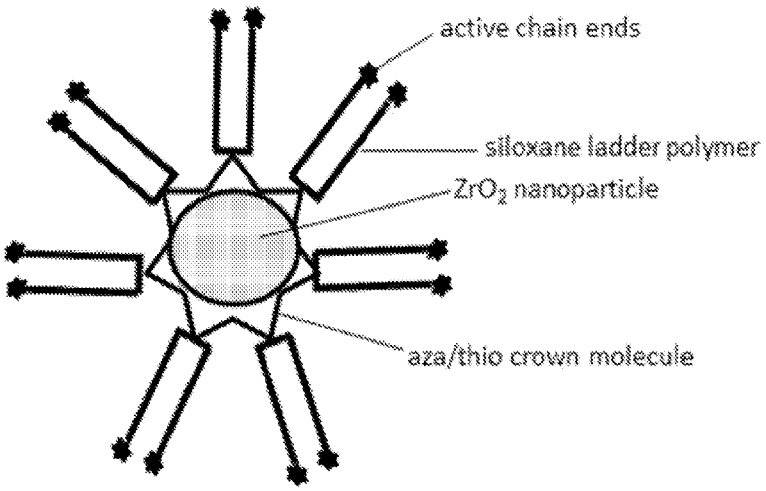


FIG. 1

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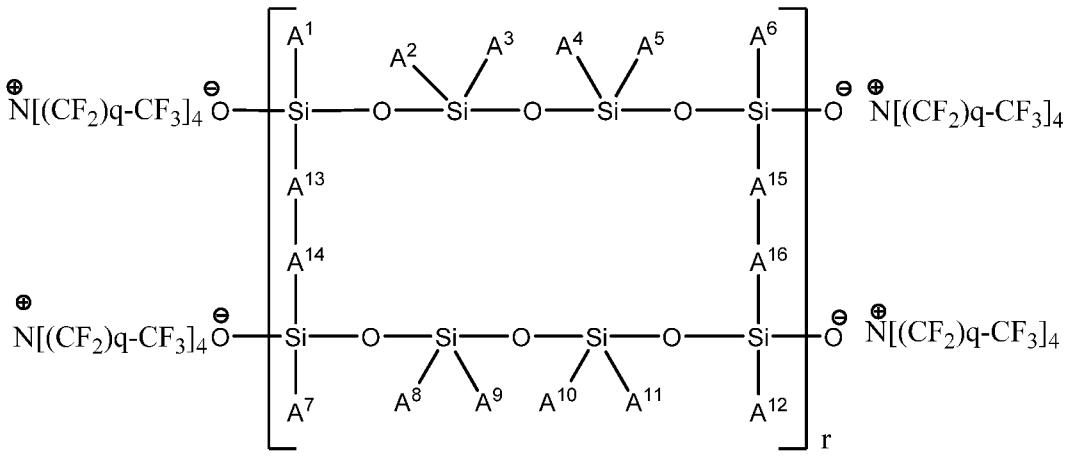
INORGANIC SILOXANE LADDER COMPOSITES AND METHODS OF THEIR PREPARATION

BACKGROUND

[0001] The demand for a continuous increase in transmission speed, data capacity and data density in integrated optical and optoelectronic circuits has been the motivating force behind numerous innovations in areas of broadband communications, high-capacity information storage, large screen and portable information display, and other areas. Although glass optical fibers are routinely used for high-speed data transfer over long distances, they are inconvenient for complex high-density circuitry because of their high density, poor durability, and high cost of fabrication for complex photonic circuits. Thus, there is a need to develop alternative materials that can at least ameliorate or address the aforementioned problems. Such materials can be any one or more of stable during phase transitions (for example, crystallization or melting), chemically stable, and stable in terms of optical loss, index of refraction, and/or density.

SUMMARY

[0002] This disclosure is related to compositions of fluorinated siloxanes with metal-aza crown and/or metal-thio crown complexes, and methods of making and their use. One embodiment provides a compound of formula I:



(I)

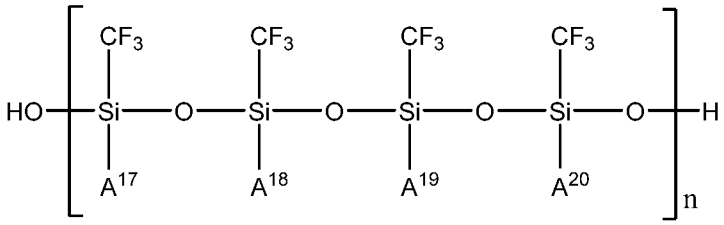
wherein q is an integer from 1 to 3;

r is an integer from 1 to 10000;

each A^1 , A^2, A^3, A^4, A^5, A^6, A^7, A^8, A^9, A^{10}, A^{11}, and A^{12} independently is, $-CF_3$, $-CH_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, a metal-aza crown complex, a metal-thio crown complex, or a metal-acrylic acid complex, and wherein at least one of A^1 , A^2, A^3, A^4, A^5, A^6, A^7, A^8, A^9, A^{10}, A^{11}, and A^{12} is a metal-aza crown complex or a metal-thio crown complex; and

each A^{13}, A^{14}, A^{15}, and A^{16} independently is $-CH_2-$ or $-CF_2-$.

[0003] Another embodiment provides a compound of formula IV:



(IV)

wherein n is an integer from 1 to 100;

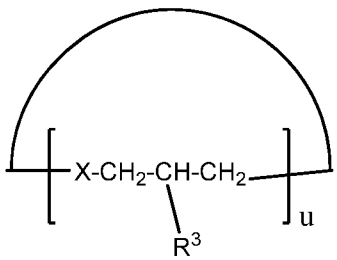
A^{17} is a metal-aza crown complex or a metal-thio crown complex;

A^{18} is a metal-aza crown complex or a metal-thio crown complex;

A^{19} is a metal-aza crown complex or a metal-thio crown complex; and

A^{20} is a metal-aza crown complex or a metal-thio crown complex.

[0004] Another embodiment provides a compound of formula V:



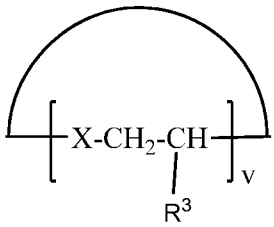
(V),

wherein X is -NH- or -S-;

u is an integer from 4 to 12; and

each R^3 is, independently, -H, -F, -Cl, $-CF_3$, -OH, $-CF_2Cl$, $-CH_2Cl$, -COCl, or $-NH_2$.

[0005] A further embodiment provides a compound of formula VI:



(VI)

wherein X is -NH- or -S-;

v is an integer from 4 to 12; and

each R^3 is, independently, -H, -F, -Cl, $-CF_3$, -OH, $-CF_2Cl$, $-CH_2Cl$, -COCl, or $-NH_2$.

[0006] In an additional embodiment, an article or a polymer may include one or more compounds of formulae I, IV, V, or VI as described herein. In another embodiment, an optical waveguide structure may include a light transmitting core material having a first refractive index, and a cladding material contacting partially or entirely surrounding the core material, wherein the cladding material has a second refractive index lower than the first refractive index of the core material, and wherein the core material may include one or more compounds of formulae I, IV, V, or VI as described herein.

[0007] In a further embodiment, a method of making a siloxane compound of formula I may involve contacting a metal-crown complex with trifluorochloromethane and a silicon metal to form a dichlorosilane-metal-crown complex, hydrolyzing the dichlorosilane-metal-crown complex to form a fluorinated siloxane polymer compound of formula IV, and contacting the polymer compound of formula IV with a bis-siloxane D4 compound and an anionic catalyst to form the siloxane compound of formula I.

BRIEF DESCRIPTION OF THE FIGURES

[0008] FIG. 1 depicts a string of siloxane ladder polymers attached to a metal-crown complex according to an embodiment.

DETAILED DESCRIPTION

[0009] This disclosure is not limited to the particular systems, devices and methods described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope.

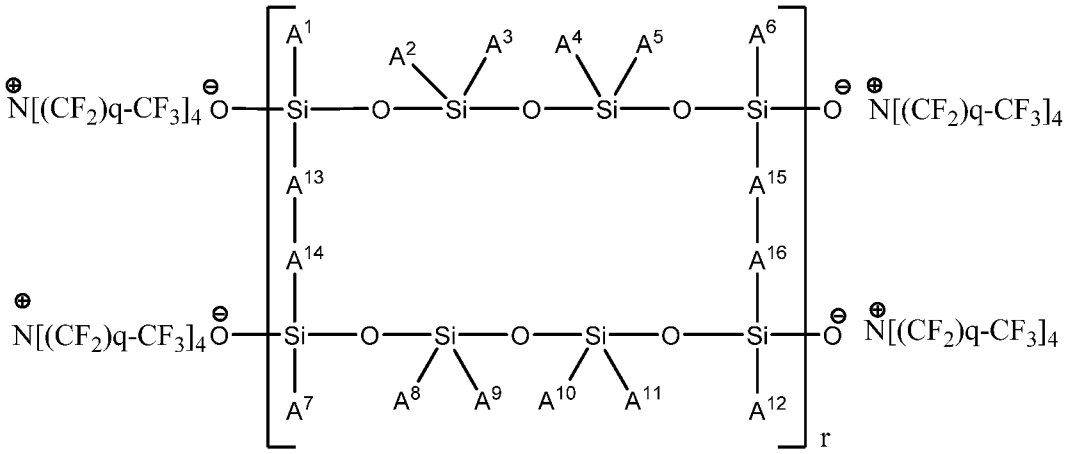
[0010] A "core material" refers to any layer of an optical waveguide that transmits light. A "cladding material" refers to any layer of an optical waveguide that confines light. In an embodiment, a core layer may be at least partially encompassed by a cladding layer.

[0011] A "waveguide" refers to a system having a material that provides a path to guide an electromagnetic wave. A waveguide may have, for example and without limitation, a circular or a rectangular shape.

[0012] A "substituted" moiety indicates that any hydrogen on the designated moiety can be replaced with a fluorine group. For example, substituted $-CH_3$ may refer to $-CH_2F$, $-CHF_2$, $-CF_3$, and the like. Similarly, substituted $-CH_2-C(=O)-H$ may refer to $-CH_2-C(=O)-F$, $-CF_2-C(=O)-H$, $-CF_2-C(=O)-F$, and the like.

[0013] Disclosed herein are inorganic siloxane ladder composites that include metal-aza crown and/or metal-thio crown complexes. These inorganic siloxane ladder polymers are anchored to transparent, high-refractive index (RI) metal nanoparticles, such as ZrO_2, via aza/thio crown macromolecules. The siloxane ladder polymers, for example as shown in FIG. 1, may be considered as a "living polymer network" since the polymer active chain ends may further undergo anionic polymerization.

[0014] In some embodiments, a compound is of formula I:



(I),

wherein q is an integer from 1 to 3;

r is an integer from 1 to 10,000;

each A^1 , A^2, A^3, A^4, A^5, A^6, A^7, A^8, A^9, A^{10}, A^{11}, and A^{12} independently is, $-CH_3$, substituted $-CH_3$, $-CH_2-C(=O)-H$, substituted $-CH_2-C(=O)-H$, $-C_6H_5$, substituted $-C_6H_5$, $-CH=CH_2$, substituted $-CH=CH_2$, $-CH_2-CH=CH_2$, substituted $-CH_2-CH=CH_2$, a metal-aza crown complex, a metal-thio crown complex, or a metal-acrylic acid complex, and wherein at least one of A^1, A^2, A^3, A^4, A^5, A^6, A^7, A^8, A^9, A^{10}, A^{11}, and A^{12} is a metal-aza crown complex or a metal-thio crown complex; and each A^{13}, A^{14}, A^{15}, and A^{16} independently is $-CH_2-$ or $-CF_2-$.

[0015] In some embodiments, each A^1 , A^2, A^3, A^4, A^5, A^6, A^7, A^8, A^9, A^{10}, A^{11}, and A^{12} independently may be, $-CH_3$, $-CF_3$, $-CH_2-C(=O)-H$, $-CF_2-C(=O)-F$, $-C_6H_5$, $-C_6F_5$, $-CH=CH_2$, $-CF=CF_2$, $-CH_2-CH=CH_2$, $-CF_2-CF=CF_2$, a metal-aza crown complex, a metal-thio crown complex, or a metal- acrylic acid complex, and wherein at least one of A^1, A^2, A^3, A^4, A^5, A^6, A^7, A^8, A^9, A^{10}, A^{11}, and A^{12} is a metal-aza crown complex or a metal-thio crown complex; and each A^{13}, A^{14}, A^{15}, and A^{16} independently may be $-CH_2-$ or $-CF_2-$.

[0016] In some embodiments, each A^1 , A^2, A^3, A^4, A^5, A^6, A^7, A^8, A^9, A^{10}, A^{11}, and A^{12} independently may be, $-CHF_2$, $-CH_2-C(=O)-F$, $-C_6H_4F$, $-CH=CF_2$, $-CH_2-CH=CF_2$, a metal-aza crown complex, a metal-thio crown complex, or a metal-acrylic acid complex, and

wherein at least one of A^1, A^2, A^3, A^4, A^5, A^6, A^7, A^8, A^9, A^{10}, A^{11}, and A^{12} is a metal-aza crown complex or a metal-thio crown complex; and each A^{13}, A^{14}, A^{15}, and A^{16} independently may be $-CH_2-$ or $-CF_2-$.

[0017] In some embodiments, the compound of formula I may include at least one metal-aza crown complex, at least 10 metal-aza crown complexes, at least 50 metal-aza crown complexes, at least 100 metal-aza crown complexes, at least 500 metal-aza crown complexes, at least 1000 metal-aza crown complexes, at least 5000 metal-aza crown complexes, or at least 10,000 metal-aza crown complexes.

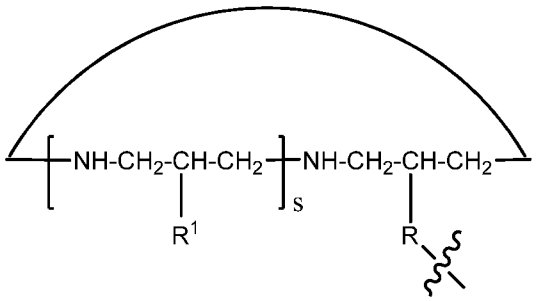
[0018] In some embodiments, the compound of formula I may include at least one metal-thio crown complex, at least 10 metal-thio crown complexes, at least 50 metal-thio crown complexes, at least 100 metal-thio crown complexes, at least 500 metal-thio crown complexes, at least 1000 metal-thio crown complexes, at least 5000 metal-thio crown complexes, or at least 10,000 metal-thio crown complexes.

[0019] In some embodiments, the compound of formula I may include a combination of numerous metal-thio crown complexes and numerous metal-aza crown complexes.

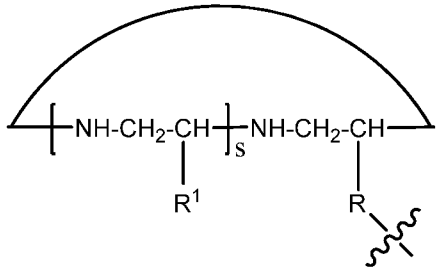
[0020] In some embodiments, the compound of formula I may include at least one metal- acrylic acid complex, at least 10 metal- acrylic acid complexes, at least 50 metal-acrylic acid complexes, at least 100 metal-acrylic acid complexes, at least 500 metal-acrylic acid complexes, at least 1000 metal-acrylic acid complexes, at least 5000 metal-acrylic acid complexes, or at least 10,000 metal-acrylic acid complexes. These acrylic acid groups may co-ordinate with metal nanoparticles and help to anchor them with siloxane ladder polymers.

[0021] The metal-aza crown complex disclosed herein may include a metallic nanoparticle in contact with the aza crown molecule. Non-limiting examples of metallic nanoparticle include a ZrO_2 nanoparticle, a TiO_2 nanoparticle, a ZnS nanoparticle, a ZnO

nanoparticle, or any combination thereof. The aza crown molecule may be represented by formula IIa or IIb:



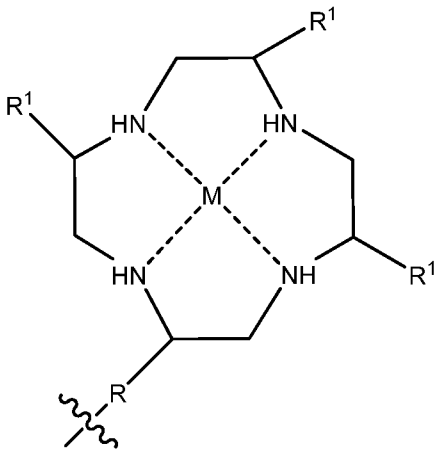
(IIa)

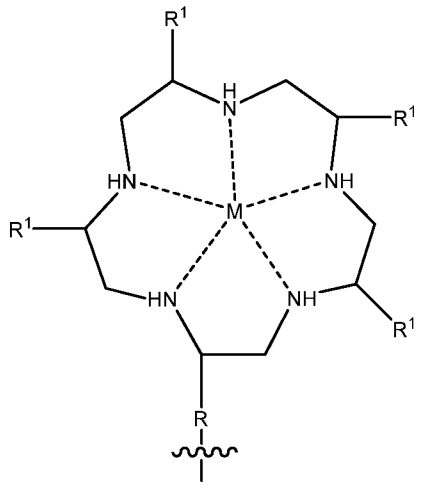


(IIb),

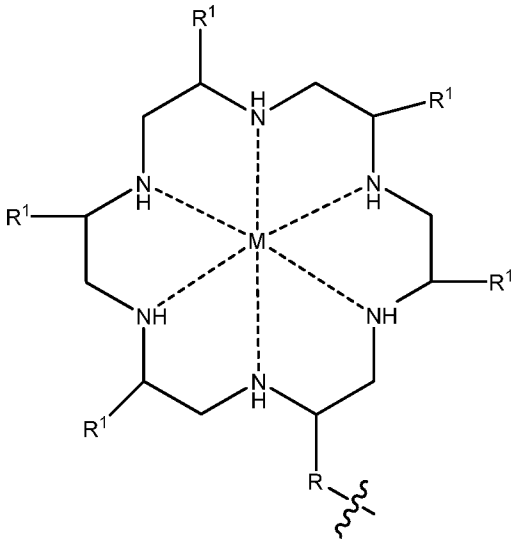
wherein s is an integer from 3 to 12; each R is independently, -O-, $-CF_2-$, -C(=O)-O-, -C(=O)-NH-, or -NH- ; and each R^1 is independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, $-NH_2$. In some embodiments, each R^1 may cross-link to another siloxane backbone of formula I, and can be a bivalent -O- linked to the siloxane polymer of formula I, a bivalent $-CF_2-$ linked to the siloxane polymer of formula I, or a bivalent -NH- linked to the siloxane polymer of formula I.

[0022] In some embodiments, the metal-aza crown complex of formula IIa or IIb may be:

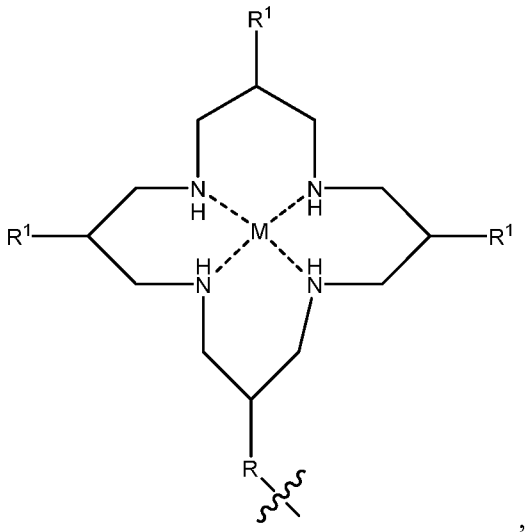




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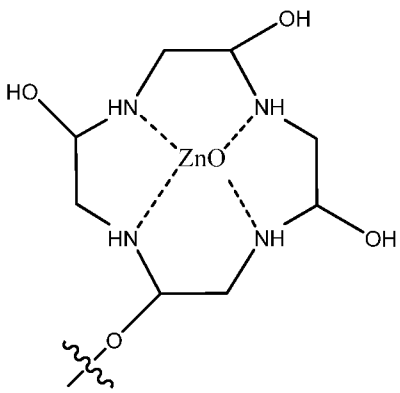
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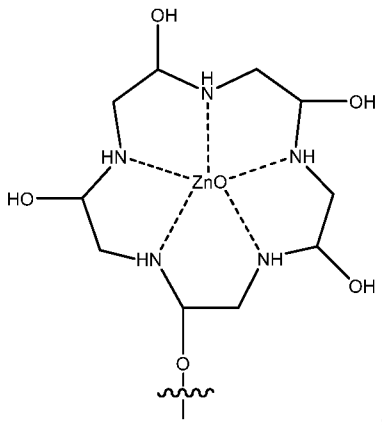
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wherein M is ZrO_2 nanoparticle, TiO_2 nanoparticle, ZnS nanoparticle, or ZnO nanoparticle; R is -O-, $-CF_2-$, -C(=O)-O-, -C(=O)-NH-, or -NH-; and each R^1 is independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, $-NH_2$, a bivalent -O- linked to the siloxane polymer of formula I, a bivalent $-CF_2-$ linked to the siloxane polymer of formula I, or a bivalent -NH- linked to the siloxane polymer of formula I.

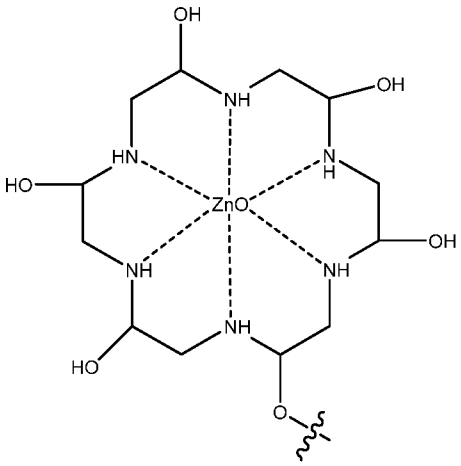
[0023] Non-limiting examples of the metal-aza crown complex molecules attached to the siloxane polymer of formula I are shown below:



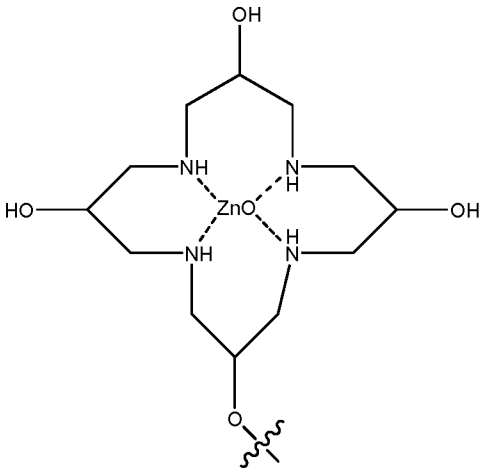
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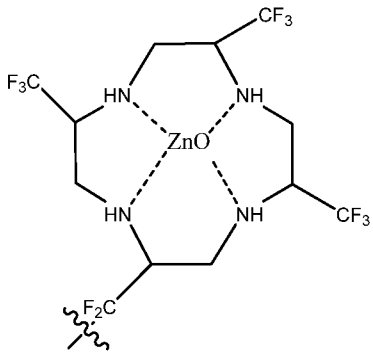
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OH
NH
OH
HN
N
H
HO
ZnO
OH
NH
NH
NH
HO
O

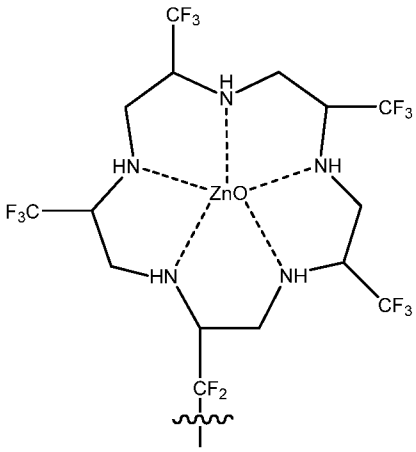
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OH
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H
HO
ZnO
OH
H
NH
N
O

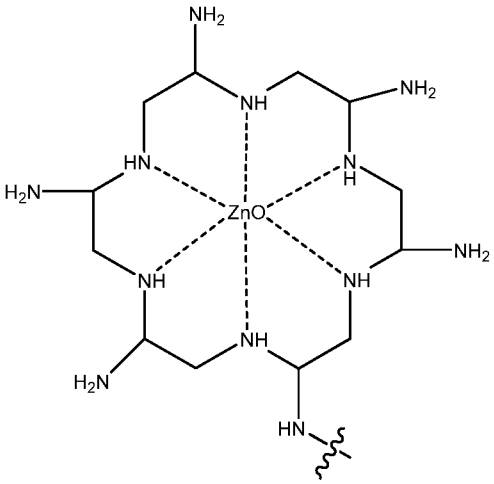
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CF3
F3C
HN
NH
ZnO
HN
NH
CF3
F2C

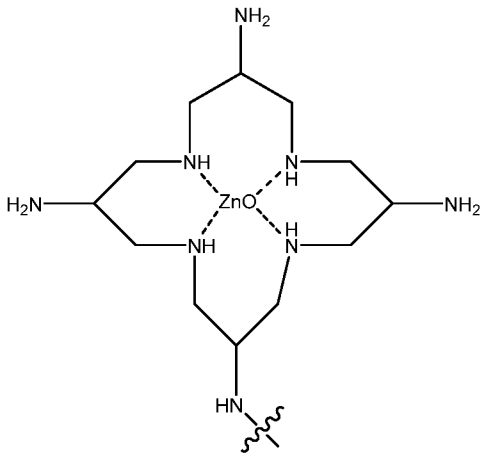
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CF3
H
N
CF3
HN
NH
ZnO
F3C
HN
NH
CF3
CF2

,

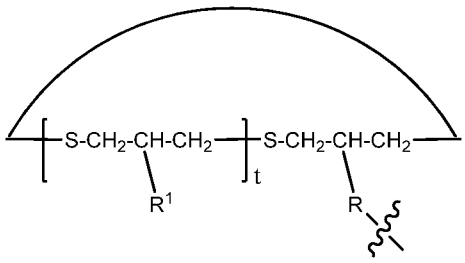

NH2
NH
NH2
HN
N
H
H2N
ZnO
NH2
NH
NH
NH
H2N
HN

,

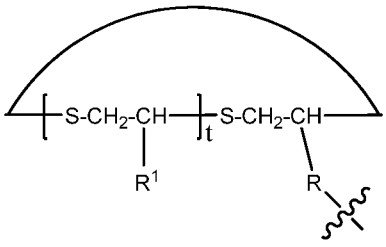

NH2
NH
N
H
H2N
ZnO
NH2
H
NH
N
HN

.

[0024] In some embodiments, the metal-thio crown complex disclosed herein may include a metallic nanoparticle in contact with the thio crown molecule. Non-limiting examples of metallic nanoparticle include a ZrO_2 nanoparticle, a TiO_2 nanoparticle, a ZnS nanoparticle, a ZnO nanoparticle, or any combination thereof. The thio crown molecule may be represented by formula IIIa or IIIb:



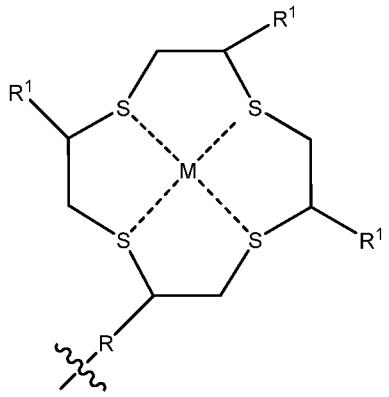
(IIIa)



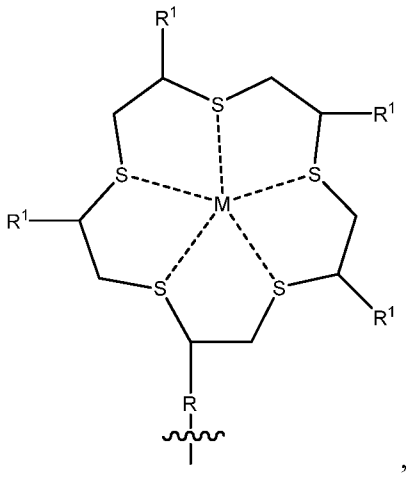
(IIIb)

wherein t is an integer from 3 to 12; each R is, independently, -O-, $-CF_2-$, -C(=O)-O-, -C(=O)-NH-, or -NH-; and each R^1 is independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, $-NH_2$, a bivalent -O- linked to the siloxane polymer of formula I, a bivalent $-CF_2-$ linked to the siloxane polymer of formula I, or a bivalent -NH- linked to the siloxane polymer of formula I.

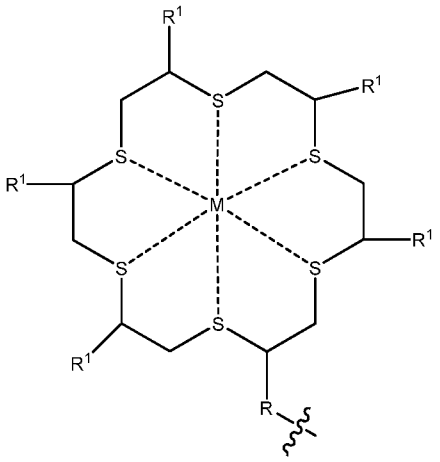
[0025] In some embodiments, the metal-thio crown complex of formula IIIa or IIIb may be:



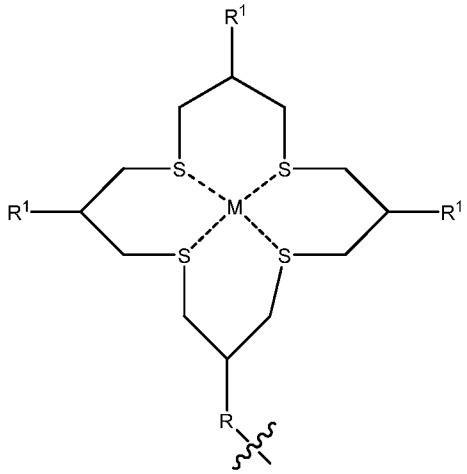
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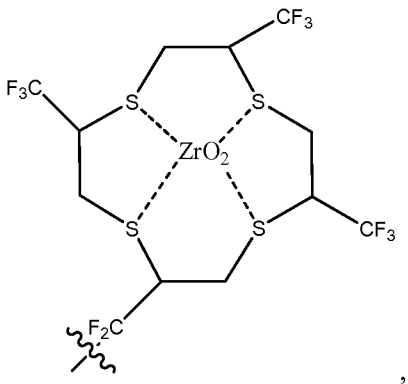
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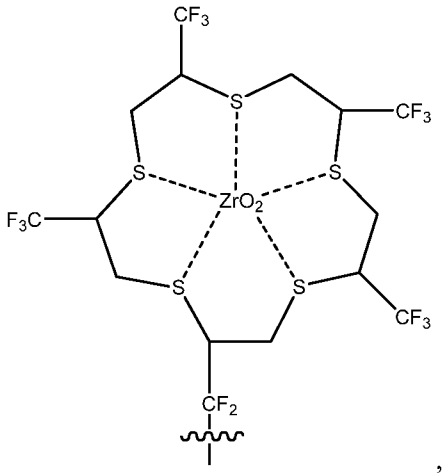
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wherein M is ZrO_2 nanoparticle, TiO_2 nanoparticle, ZnS nanoparticle, or ZnO nanoparticle; R is, independently, -O-, $-CF_2-$, -C(=O)-O-, -C(=O)-NH-, or -NH-; and each R^1 is independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, $-NH_2$, a bivalent -O- linked to the siloxane polymer of formula I, a bivalent $-CF_2-$ linked to the siloxane polymer of formula I, or a bivalent -NH- linked to the siloxane polymer of formula I.

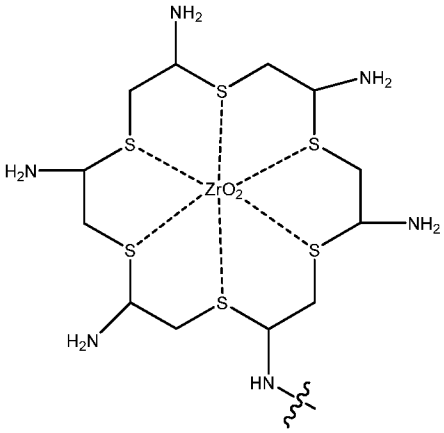
[0026] Non-limiting examples of the metal-thio crown complex molecules attached to the siloxane polymer of formula I are shown below:



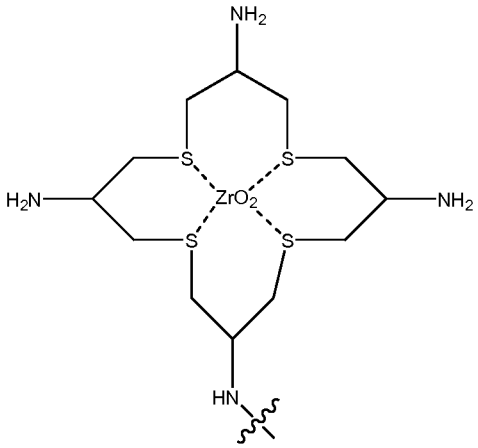
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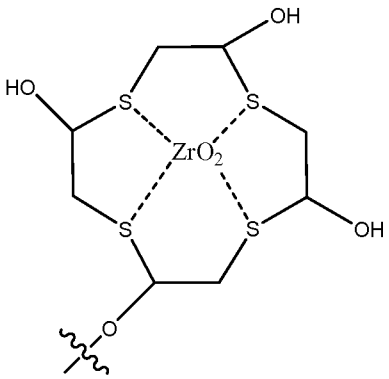
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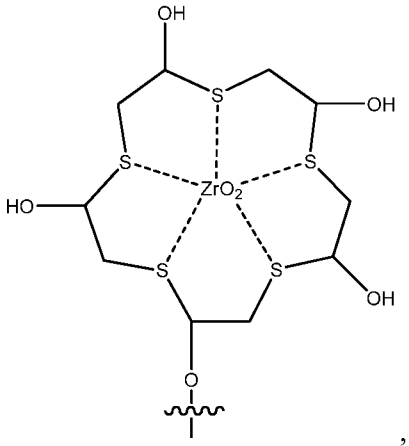
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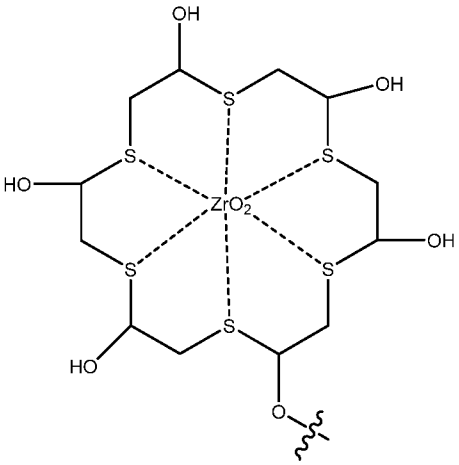
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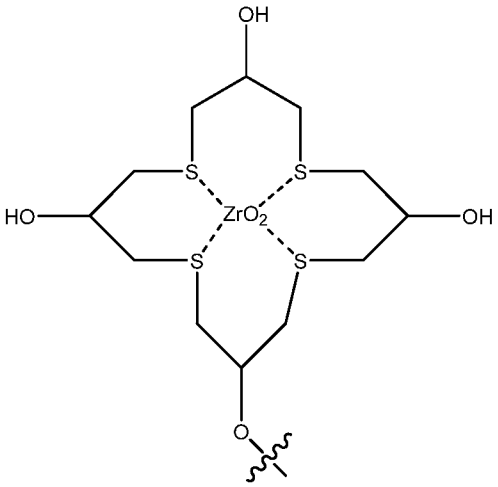
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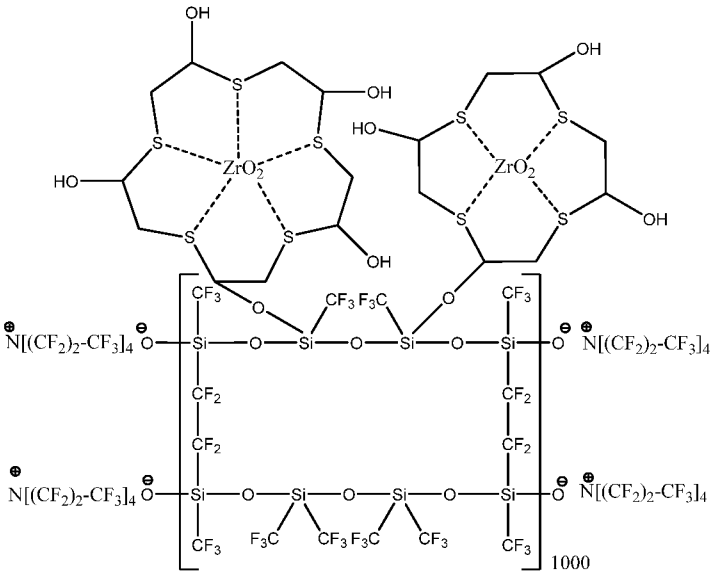


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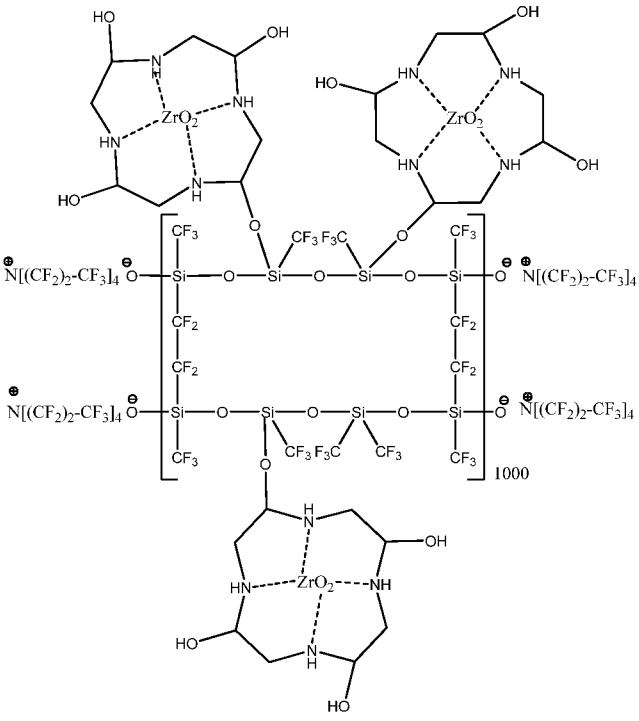


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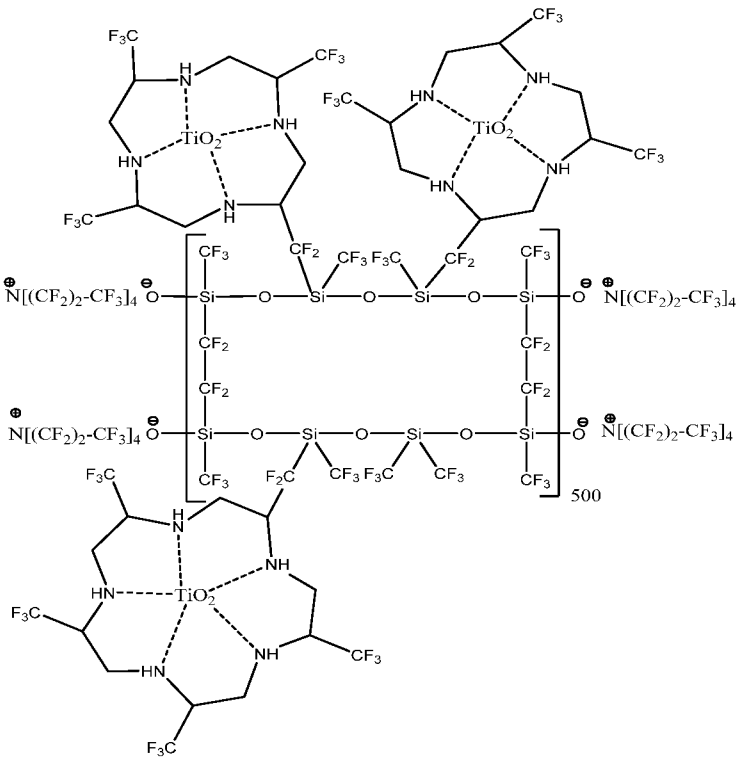
[0027] Non-limiting examples of compound of formula I are shown below:



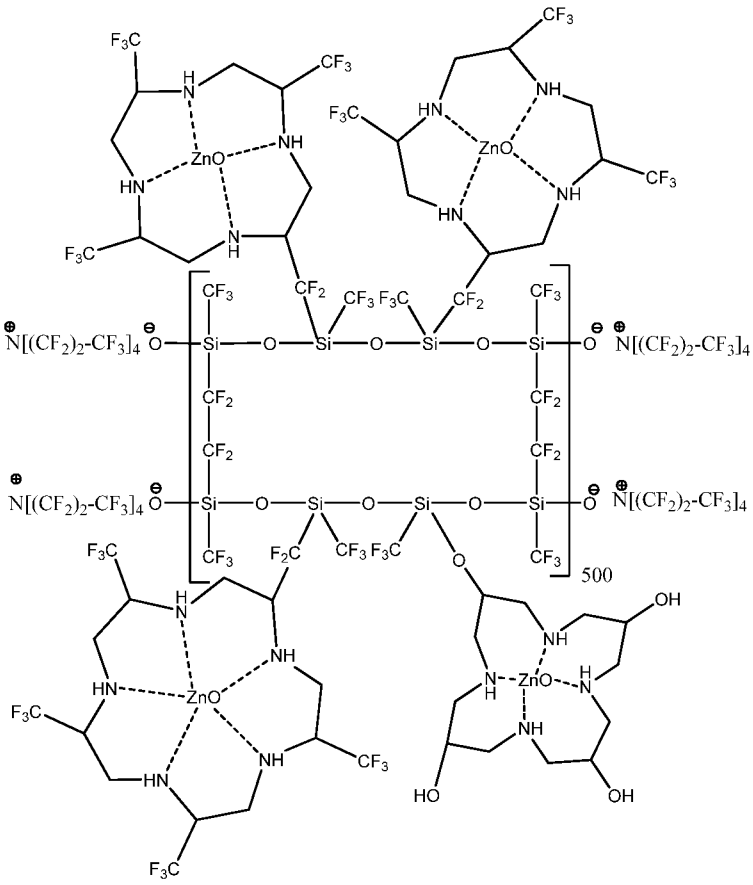
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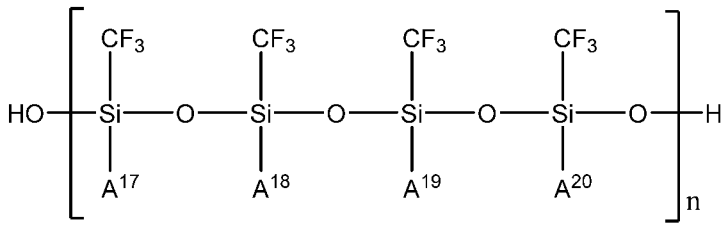


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[0028] In some embodiments, a compound is of formula IV:

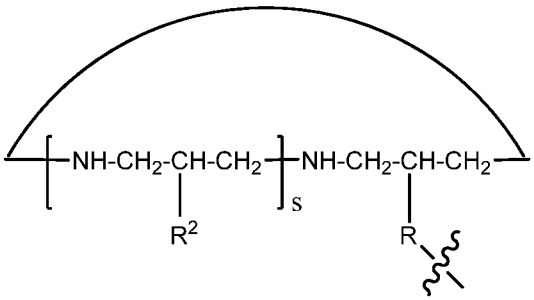


(IV)

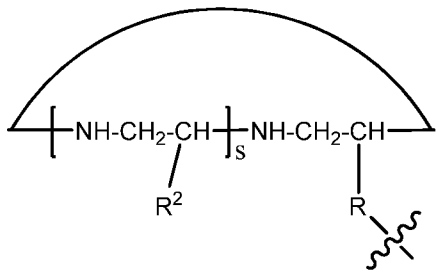
wherein n is an integer from 1 to 100; A^{17} is a metal-aza crown complex or a metal-thio crown complex; A^{18} is a metal-aza crown complex or a metal-thio crown complex; A^{19} is a metal-aza crown complex or a metal-thio crown complex; and A^{20} is a metal-aza crown complex or a metal-thio crown complex.

[0029] In some embodiments, each one of A^{17}-A^{20} independently is a metal-thio crown complex. In some embodiments, each A^{17}-A^{20} independently is a metal-aza crown complex. In some embodiments, A^{17} and A^{18} are metal-aza crown complexes, and A^{19} and A^{20} are metal-thio crown complexes.

[0030] In some embodiments, the metal-aza crown complex attached to compound of formula IV can be represented by:



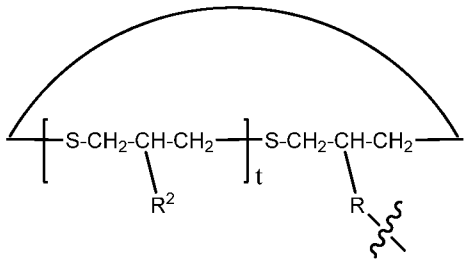
(IIc)



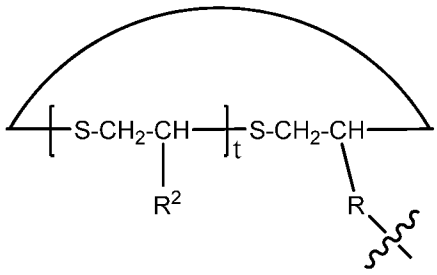
(IId)

wherein s is an integer from 3 to 12; each R is independently, -O-, $-CF_2-$, -C(=O)-O-, -C(=O)-NH-, or -NH-; and each R^2 is independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$. The metallic nanoparticle of the metal-aza crown complex may be a ZrO_2 nanoparticle, a TiO_2 nanoparticle, a ZnS nanoparticle, a ZnO nanoparticle, or any combination thereof.

[0031] In some embodiments, the metal-thio crown complex attached to compound of formula IV can be represented by:



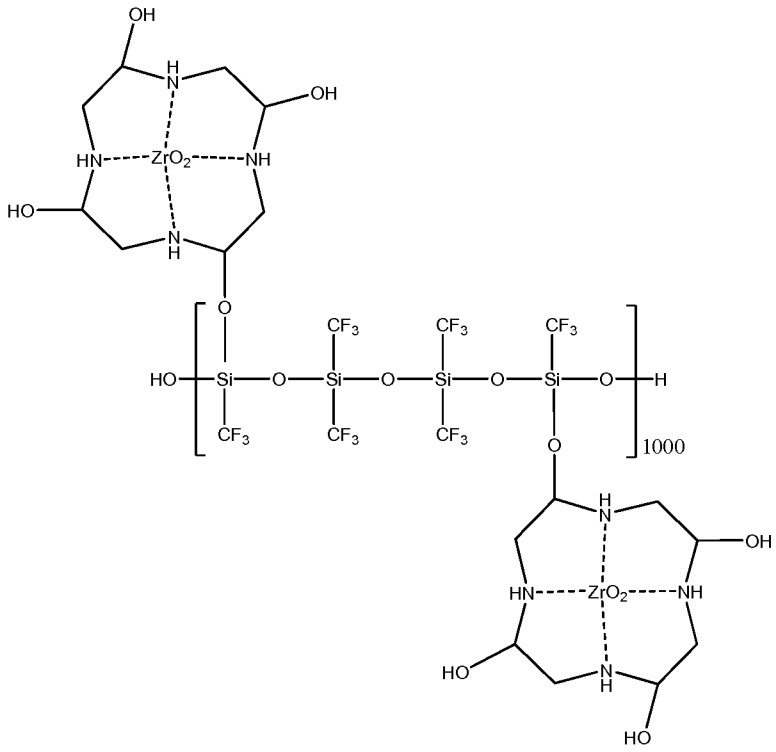
(IIIc)



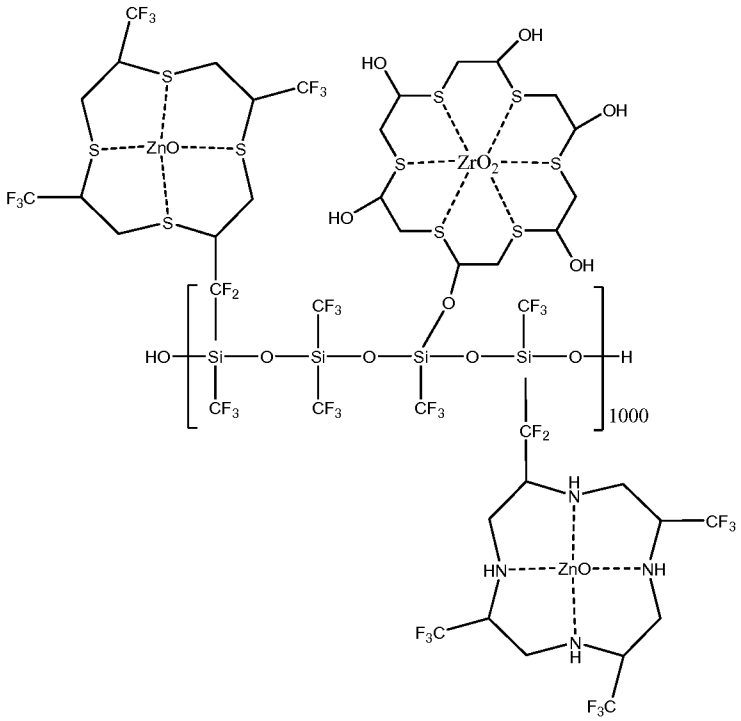
(IIId)

wherein t is an integer from 3 to 12; each R is, independently, -O-, $-CF_2-$, -C(=O)-O-, -C(=O)-NH-, or -NH-; and each R^2 is independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$. The metallic nanoparticle of the metal-thio crown complex may be a ZrO_2 nanoparticle, a TiO_2 nanoparticle, a ZnS nanoparticle, a ZnO nanoparticle, or any combination thereof.

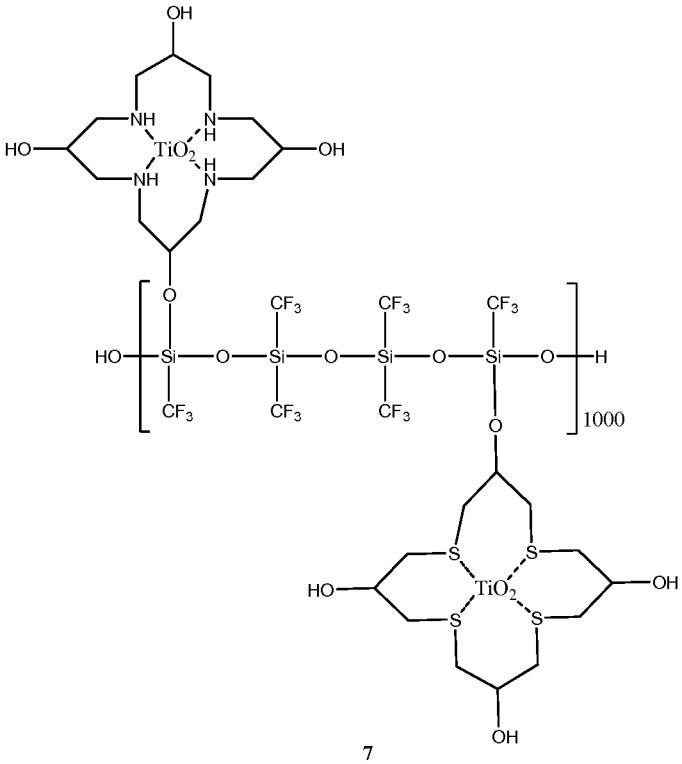
[0032] Non-limiting examples of compound of formula IV are shown below:



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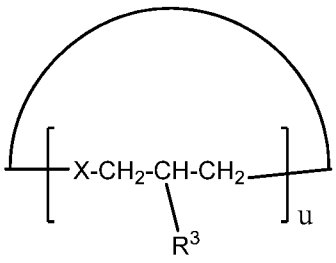


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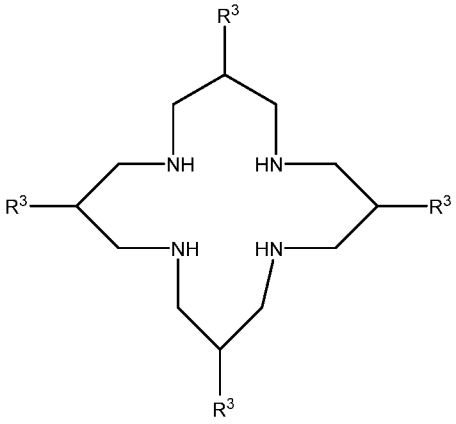
[0033] Also disclosed herein are novel aza-crown and thio-crown macromolecules. In some embodiments, a compound is of formula V:



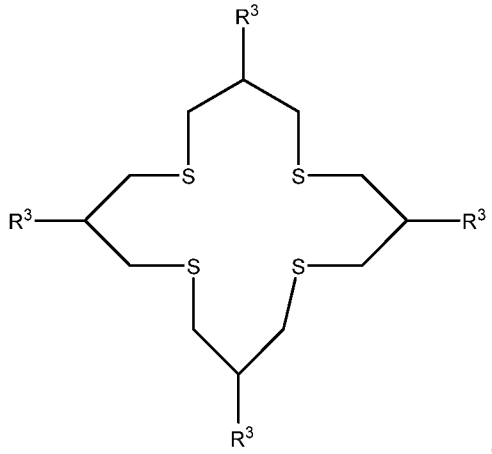
(V)

wherein X is -NH- or -S-; u is an integer from 4 to 12; and each R^3 is, independently, -H, -F, -Cl, $-CF_3$, -OH, $-CF_2Cl$, $-CH_2Cl$, -COCl, or $-NH_2$. In some embodiments, X is -NH-, and R^3 is, independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$. In some embodiments, X is -S-, and R^3 is, independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$.

[0034] Non-limiting examples of compound of formula V are shown below:



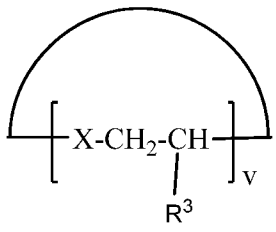
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,

wherein each R^3 is, independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$.

[0035] In some embodiments, a compound is of formula VI:

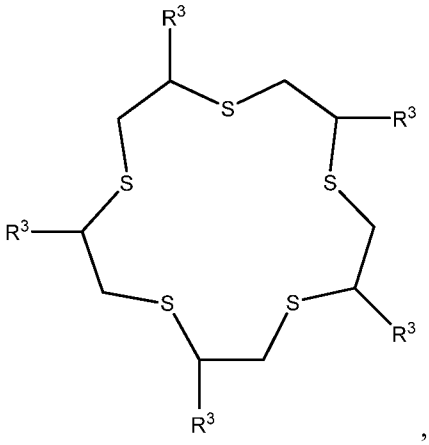


(VI)

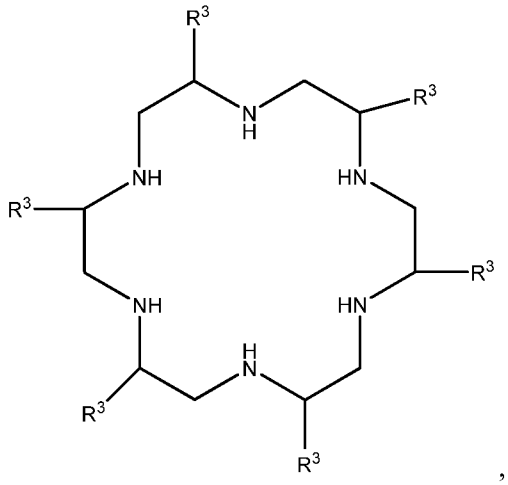
wherein X is -NH- or -S-; v is an integer from 4 to 12; and each R^3 is, independently, -H, -F, -Cl, $-CF_3$, -OH, $-CF_2Cl$, $-CH_2Cl$, -COCl, or $-NH_2$. In some embodiments, X is -NH-,

and R^3 is, independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$. In some embodiments, X is -S-, and R^3 is, independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$.

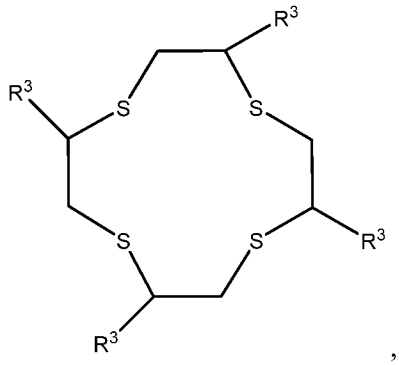
[0036] Non-limiting examples of compound of formula VI are shown below:



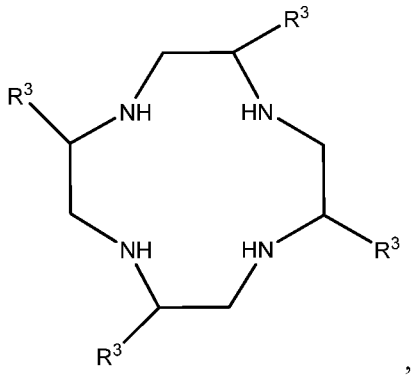
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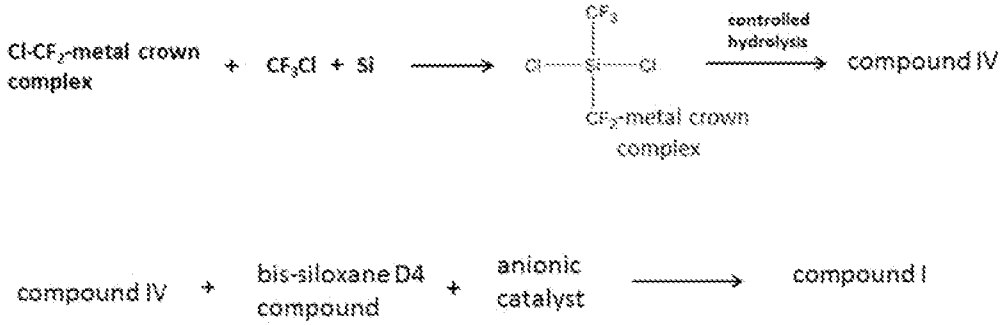


,

wherein each R^3 is, independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$.

[0037] Also disclosed herein are methods to make compounds of formula I. In some embodiments, a method of making a siloxane compound of formula I may involve contacting a metal-crown complex with trifluorochloromethane and a silicon metal to form a dichlorosilane- trifluoromethyl-metal-crown complex, and hydrolyzing the dichlorosilane-trifluoromethyl-metal-crown complex to form a fluorinated siloxane polymer compound of formula IV, and contacting the polymer compound of formula IV with a bis-siloxane D4 compound and an anionic catalyst to form the siloxane compound of formula I.

[0038] An exemplary reaction is outlined below:

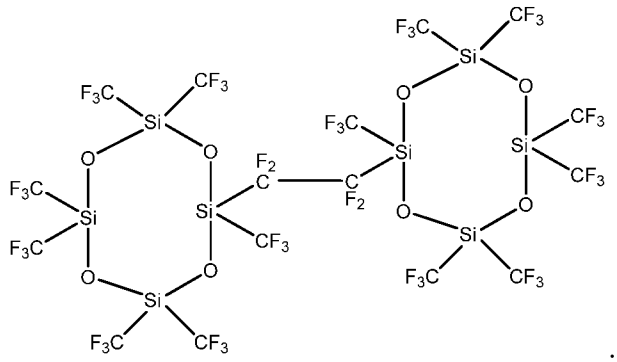


[0039] The metal-crown complex may be formed by contacting a crown macromolecule with a metallic nanoparticle, to form metal-aza crown complex or metal-thio crown complex. The metallic nanoparticle may be any metallic nanoparticle disclosed herein, such as a ZrO_2 nanoparticle, a TiO_2 nanoparticle, a ZnS nanoparticle, a ZnO nanoparticle, or any combination thereof. The crown macromolecule may be any aza-crown macromolecule or a thio-crown macromolecule described herein, and are represented by formulae V and VI.

[0040] In some embodiments, the metal-crown complex and the trifluoro-chloromethane may be contacted in a molar ratio of about 1:1 to about 1:4, about 1:1 to about 1:3, or about 1:1 to about 1:2. Specific examples include about 1:1, about 1:1.5, about 1:2.5, about 1:4, and ranges between any two of these values.

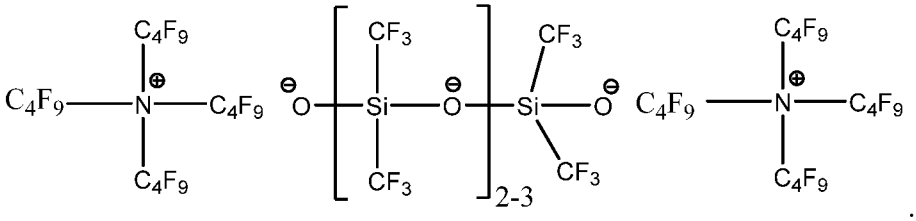
[0041] In some embodiments, the dichlorosilane-trifluoromethyl-metal-crown complex is subjected to a controlled hydrolysis step, resulting in the fluorinated siloxane polymer compound of formula IV. For example, hydrolysis may be controlled by varying the molar ratio of cyclic monomer to water.

[0042] In some embodiments, the bis-siloxane D4 compound may be represented by the structure:



8

[0043] The anionic catalyst may be represented by the structure:



9

[0044] In some embodiments, the compound of formula IV and the bis-siloxane D4 compound are contacted in a molar ratio of about 1:0.1 to about 1:0.5, about 1:0.1 to about 1:0.4, or about 1:0.1 to about 1:0.2. Specific examples include about 1:0.1, about 1:0.2, about 1:0.3, about 1:0.4, about 1:0.5, and ranges between any two of these values.

[0045] Compounds of formula I may be considered to be a "living polymer network" because the tetrafluoroalkyl ammonium end groups may react with the network chains to restructure the crosslinks in the network. For example, when the polymer is subjected to temperatures above 300 °C, the polymer active chain ends are transferred to Si-O–C_4F_9, and the catalyst is transferred to $N(C_4F_9)_3$ and siloxane oligomer, which is available at any time for further polymerization. While self-alignment occurs at such high temperatures via anionic polymerization, neither thermal degradation nor melting occurs. The presence of fluorine substituent groups in the catalyst and siloxane backbone increases the anionic initiation activity of both the catalyst and the monomer due to the high electro-negativity and electron withdrawing properties.

[0046] The compounds and polymers disclosed herein may have any or all of high thermal stability, good mechanical properties, self-healing properties, a low dielectric constant, and a low refractive index. Due to their high thermal stability, thermal degradation may not occur, or may be reduced compared to other compounds and polymers, during high temperature processing, for example, a solder reflow process in the manufacturing of optical circuits. Since the compounds and polymers are prepared by anionic living polymerization, they maintain the active catalyst, active polymerizable chain end, and cyclic structure in the system thereby meeting the fundamental requirements of being printable waveguide materials. Such compounds and polymers may be used in a wide variety of uses, including optical waveguides, tires, mechanical parts of a vehicle, sporting goods, coupling sockets, switches, printed wiring board pins, ice skating rinks, and the like.

[0047] The compounds and polymers disclosed herein may be used for preparing optical waveguides. An optical waveguide structure may have a light transmitting core material having a first refractive index, and a cladding material partially contacting or entirely surrounding the core material, wherein the cladding material has a second refractive index lower than the first refractive index of the core material, and wherein the core material includes one or more compounds of formula I, IV, V or VI.

[0048] The optical waveguides may be synthesized using any method known in the art. Briefly, a layer of cladding material is formed over a suitable substrate. The substrate may be any material upon which it is desired to establish a waveguide, such as a semiconductor material (silicon, silicon oxide, silicon oxide/silicon, gallium arsenide, silicon nitride, silica on silicon, or the like), glass, plastics, quartz, ceramics, or crystalline materials. The cladding material may be formed on the substrate by any known method, such as spin casting, dip coating, roller coating, doctor blading, or evaporating. Suitable cladding materials include silica xerogels, silicon oxide, metal oxides, air, silicon dioxide,

benzocyclobutene, plasma oxides, acrylates, fluorinated acrylates, polyimides, and other polymers having a lower refractive index than the core. The siloxane core material can then be deposited into a thin film on top of the cladding. Before or after curing, the core siloxane material can optionally be patterned using known methods, such as photolithography, wet etching, reactive-ion etching (RIE), photoablation, and the like.

EXAMPLES

EXAMPLE 1: Preparation of bis-siloxane D4 compound

[0049] About 3 moles of hexafluorodimethyl dichlorosilane and 2 moles of trifluoromethyl-difluoromethyl dichlorosilane are mixed and subjected to controlled hydrolysis to obtain a fluorinated tetrasiloxane compound. The tetrasiloxane compound undergoes cyclization in the presence of zinc oxide to obtain a fluorinated cyclic siloxane (D4) monomer.

[0050] About 20 grams of above obtained cyclic siloxane (D4) monomer is mixed with 0.001 grams of the fully fluorinated benzoyl peroxide and heated at 120 ^{o}C for 30 minutes. The free radical coupling reaction takes place to form the bis-siloxane D4 compound.

EXAMPLE 2: Preparation of anionic catalyst

[0051] About 0.1 mole of silicon metal is reacted with about 0.2 moles of trifluorochloromethane to obtain hexafluorodimethyl dichlorosilane. The hexafluorodimethyl dichlorosilane is subjected to controlled hydrolysis to obtain a hydroxyl terminated fluorinated tetrasiloxane compound. The tetrasiloxane compound undergoes cyclization in the presence of zinc oxide to form a fluorinated cyclic siloxane (D4) compound.

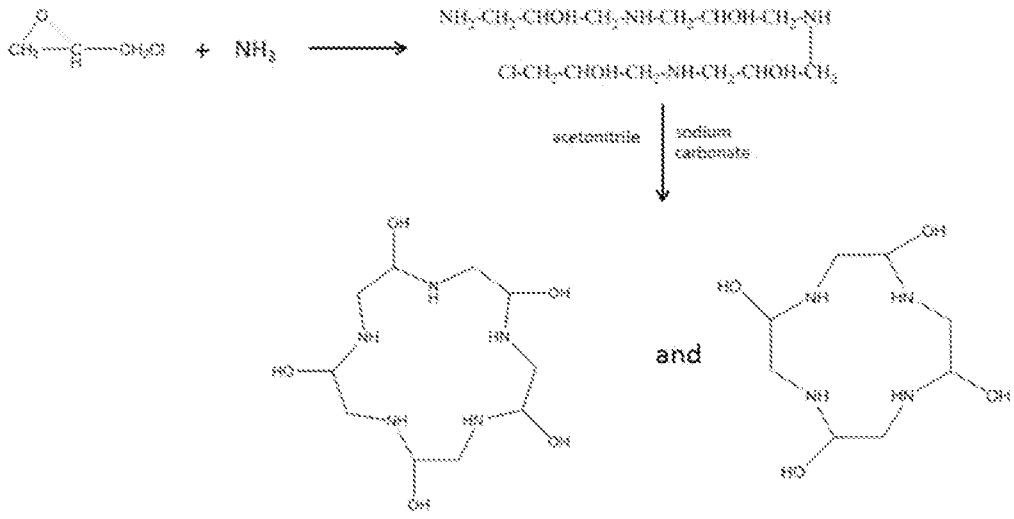
[0052] A reaction vessel is charged with 0.1 mole of fluorinated tetrabutyl-ammonium chloride that is prepared by reacting fluorinated tributylamine with fluorinated

butyl chloride. The reaction vessel is cooled to 5 °C, flushed with N_2, and about 0.05 mole of above obtained fluorinated cyclic siloxane (D4) monomer is added. The reaction is continued for one hour under N_2 atmosphere, and the product is purified and dried to obtain an anionic catalyst.

EXAMPLE 3: Preparation of metal-aza crown complex

[0053] About 1 mole of epichlorohydrin is mixed with 1 mole of ammonia in the presence of 0.01 mole of sodium carbonate (catalyst) and 750 mL of acetonitrile (solvent). The mixture is heated to 25 °C for 180 minutes in an autoclave. Fractions are taken out every 30 minutes until the condensation reaction reaches the required molecular weight (degree of polymerization =4).The resulting product poly(2-hydroxy-3-iminopropylene) undergoes cyclisation reaction to form 12-crown-4 and 15-crown-5 aza-crown molecules. The aza-crown molecules are further incubated with ZrO_2 nanoparticles to obtain a metal-aza crown complexes.

The reaction is outlined below:



EXAMPLE 4: Preparation of compound 5

[0054] About 1 mole of metal-aza crown complex of Example 3 is mixed with 1 mole of trifluorochloromethane and 1 mole of silicon metal to form the methylated

dichlorosilane-metal-crown complex. The methylated dichlorosilane-metal-crown complex is subjected to partial hydrolysis with a predetermined molar ratio of water at room temperature according to the chain length required to obtain compound **5.**

EXAMPLE 5: Preparation of compound 2

[0055] About 1 mole of compound **5** is mixed with 0.1 mole of compound **8** in the presence of the anionic catalyst compound **9**. The mixture is cooled to 0 °C for 40 minutes under a stream of nitrogen gas. The resulting polymer is a ladder type anionic living polysiloxane polymer compound **2**. The degree of laddering can be controlled by the molar ratio of compound **1** and compound **8**. The reaction can be carried out in aprotic solvents. It is to be noted that various polymeric compounds within the scope of formula I can be made by varying the starting material. For example compound **6** or compound **7** may be used in place of compound **5**.

[0056] The polymer that is formed can be considered as a "living polymer network" as the active polymerizable chain end groups can react with the network chains to restructure the crosslinks in the network, giving the polymer its self-aligning property. In addition, the polymer may have high thermal stability, good mechanical properties, self-healing properties, a low dielectric constant, and a low refractive index.

EXAMPLE 6: Preparation of a waveguide

[0057] Planar waveguides are made on 3 inch (7.62 cm) silicon wafer substrates using the siloxane polymers of compounds **1-4** as the high refractive index core material, and silicon oxide as the cladding. The silicon oxide is spin-coated on a wafer to a thickness of about 1 μm. The core material (compounds **1-4**) is then spun-onto the cladding film to a thickness of about 2 μm (6000 rpm for 100 seconds). Next, the samples are baked at 100 °C for 20 minutes and annealed at 150 °C. As the siloxane polymers are expected to have high

thermal stability, thermal degradation may not occur during subsequent high temperature processing, for example, a solder reflow process in the manufacturing of optical circuits containing the planar waveguides. The waveguide may also have good mechanical properties, self-healing properties, a low dielectric constant, and a low refractive index.

EXAMPLE 7: An article prepared from siloxane polymers

[0058] The siloxane polymer pellets of compound **1** are heated in an injection molding machine and fed into a mold cavity and allowed to cool. The cooled polymer obtains the shape according to the contour of the cavity, and articles such as coupling sockets, switches, tennis rackets, and brake pads may be manufactured using appropriate molds. It will be expected that the articles manufactured from the siloxane polymer may have high thermal stability, good mechanical properties, self-healing properties, a low dielectric constant, and a low refractive index.

[0059] In the above detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be used, and other changes may be made, without departing from the spirit or scope of the subject matter presented herein. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the Figures, can be arranged, substituted, combined, separated, and designed in a wide variety of different configurations, all of which are explicitly contemplated herein.

[0060] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Many modifications and variations can be made without departing from its spirit and

scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, compositions or biological systems, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0061] As used in this document, the singular forms “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term “comprising” means “including, but not limited to.”

[0062] While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0063] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0064] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (example, bodies of the appended claims) are generally intended as "open" terms (example, the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (example, "a" and/or "an" should be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (example, the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (example, " a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention

analogous to "at least one of A, B, or C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (example, " a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[0065] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

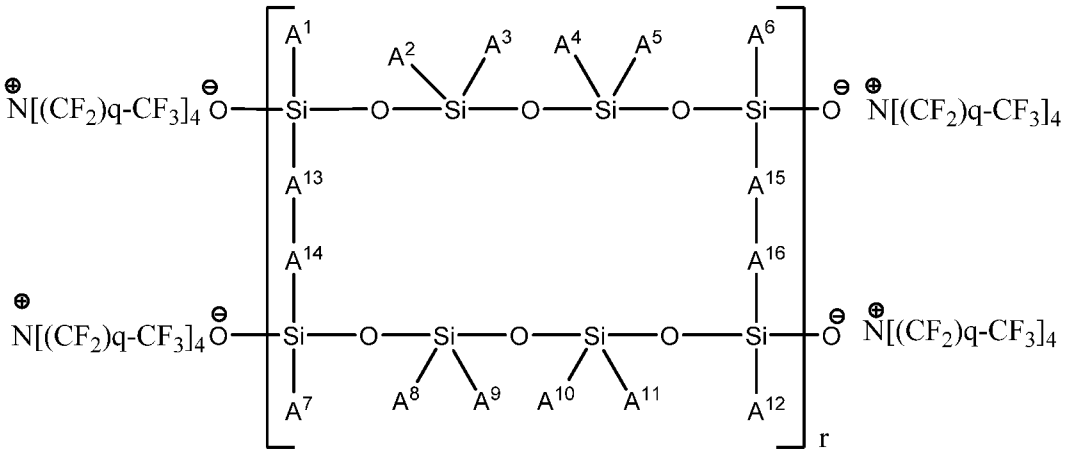
[0066] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells. Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.

[0067] Various of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, each of which is also intended to be encompassed by the disclosed embodiments.

CLAIMS

What is Claimed is:

1. A compound of formula I:



(I)

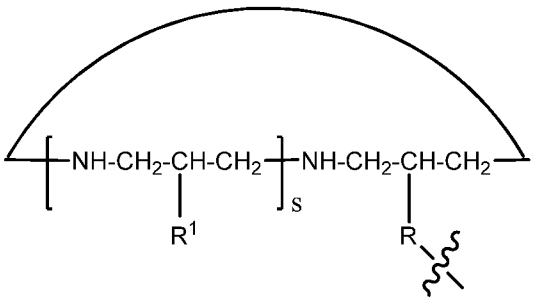
wherein q is an integer from 1 to 3;

r is an integer from 1 to 10000;

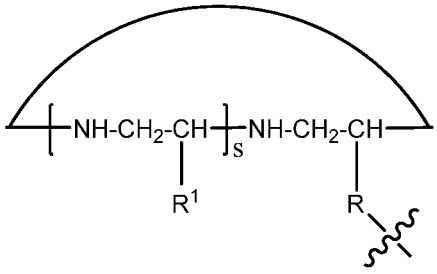
each A^1, A^2, A^3, A^4, A^5, A^6, A^7, A^8, A^9, A^{10}, A^{11}, and A^{12} independently is, $-CH_3$, substituted $-CH_3$, $-CH_2-C(=O)-H$, substituted $-CH_2-C(=O)-H$,$-C_6H_5$, substituted $-C_6H_5$, $-CH=CH_2$, substituted $-CH=CH_2$, $-CH_2-CH=CH_2$, substituted $-CH_2-CH=CH_2$, a metal-aza crown complex, a metal-thio crown complex, or a metal-acrylic acid complex, and wherein at least one of A^1, A^2, A^3, A^4, A^5, A^6, A^7, A^8, A^9, A^{10}, A^{11}, and A^{12} is a metal-aza crown complex or a metal-thio crown complex; and

each A^{13}, A^{14}, A^{15}, and A^{16} independently is $-CH_2-$ or $-CF_2-$.

2. The compound of claim 1, wherein when any one of A^1 to A^{12} is a metal-aza crown complex, the metal-aza crown complex comprises a metallic nanoparticle in contact with an aza crown molecule, and the aza crown molecule is selected from formula IIa or IIb:



(IIa)



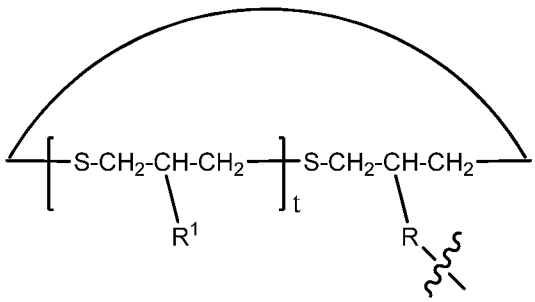
(IIb)

wherein s is an integer from 3 to 12;

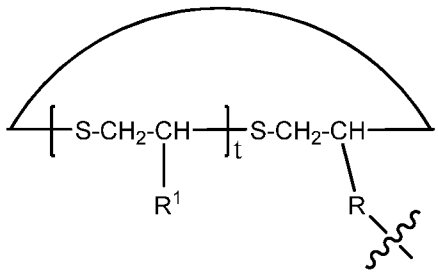
each R is independently, -O-, -CF_2-, -C(=O)-O-, -C(=O)-NH-, or -NH- ; and

each R^1 is independently, -H, -F, -CF_3, -OH, -CF_2Cl, -NH_2, a bivalent -O- linked to the siloxane polymer of formula I, a bivalent -CF_2- linked to the siloxane polymer of formula I, or a bivalent -NH- linked to the siloxane polymer of formula I.

3. The compound of claim 1, wherein when any one of A^1 to A^{12} is a metal-thio crown complex, the metal-thio crown complex comprises a metallic nanoparticle in contact with a thio-crown molecule, and the thio-crown molecule is selected from formula IIIa or IIIb:



(IIIa)



(IIIb),

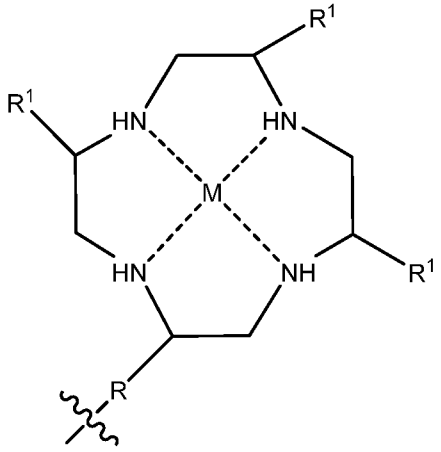
wherein t is an integer from 3 to 12;

each R is, independently, -O-, -CF_2-, -C(=O)-O-, -C(=O)-NH-, or -NH-; and

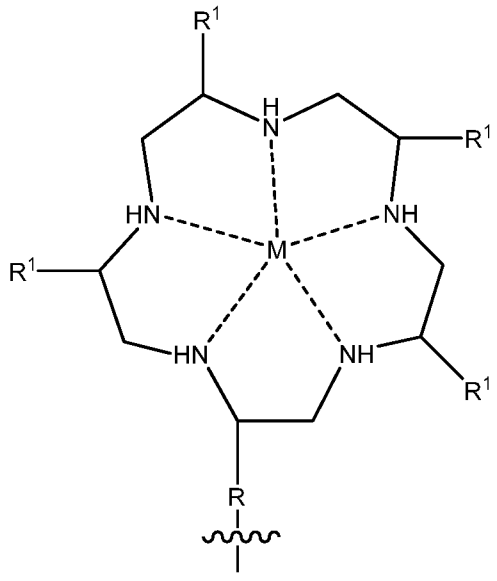
each R^1 is independently, -H, -F, -CF_3, -OH, -CF_2Cl, -NH_2, a bivalent -O- linked to the siloxane polymer of formula I, a bivalent -CF_2- linked to the siloxane polymer of formula I, or a bivalent -NH- linked to the siloxane polymer of formula I.

4. The compound of claim 2 or 3, wherein the metallic nanoparticle is a ZrO_2 nanoparticle, a TiO_2 nanoparticle, a ZnS nanoparticle, a ZnO nanoparticle, or any combination thereof.

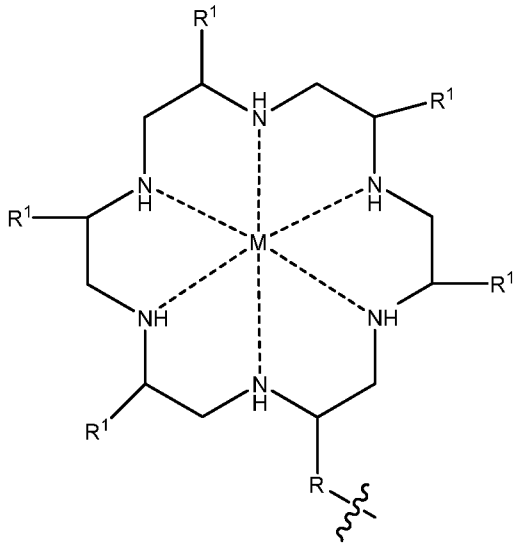
5. The compound of claim 1, wherein the metal-aza crown complex is selected from:



,

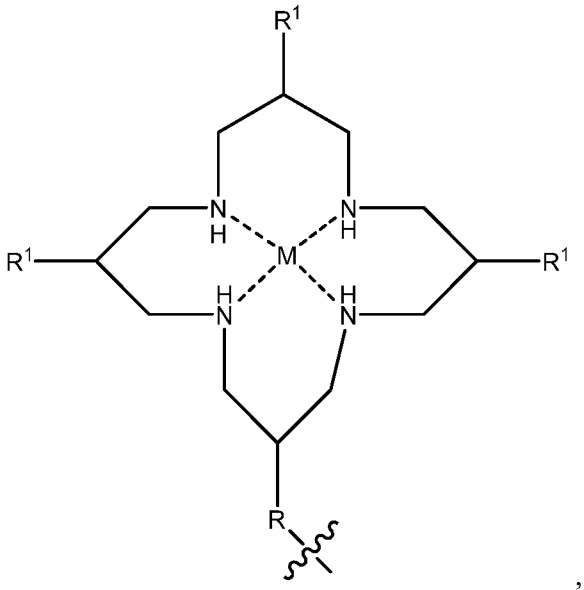


,



,

and



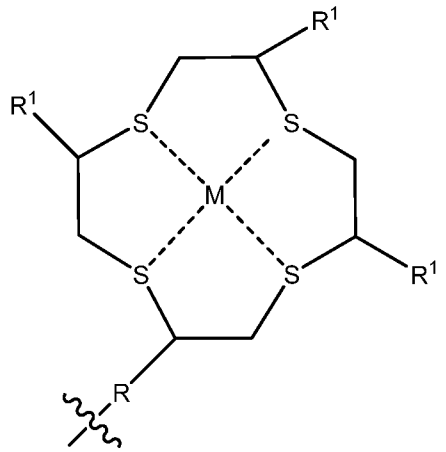
,

wherein M is ZrO_2 nanoparticle, TiO_2 nanoparticle, ZnS nanoparticle, or ZnO nanoparticle;

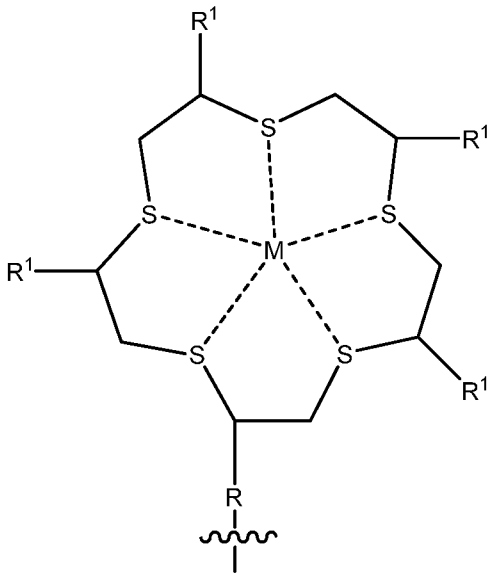
R is -O-, $-CF_2-$, -C(=O)-O-, -C(=O)-NH-, or -NH-; and

each R^1 is independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, $-NH_2$, a bivalent -O- linked to the siloxane polymer of formula I, a bivalent $-CF_2-$ linked to the siloxane polymer of formula I, or a bivalent -NH- linked to the siloxane polymer of formula I.

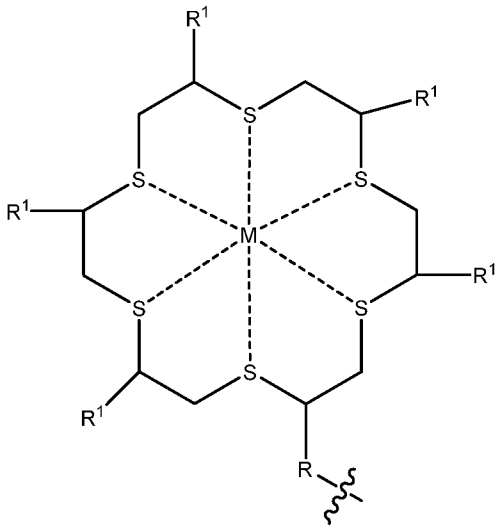
6. The compound of claim 1, wherein the metal-thio crown complex is selected from:



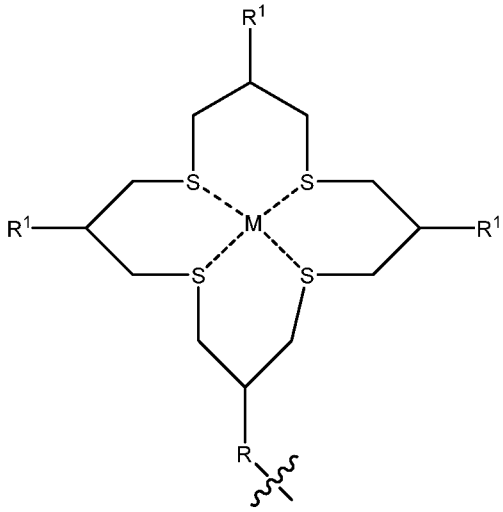
,



,



,



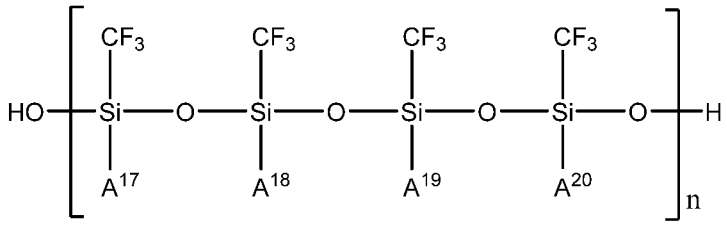
, and ,

wherein M is ZrO_2 nanoparticle, TiO_2 nanoparticle, ZnS nanoparticle, or ZnO nanoparticle;

R is, independently, -O-, $-CF_2-$, -C(=O)-O-, -C(=O)-NH-, or -NH-; and

each R^1 is independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, $-NH_2$, a bivalent -O- linked to the siloxane polymer of formula I, a bivalent $-CF_2-$ linked to the siloxane polymer of formula I, or a bivalent -NH- linked to the siloxane polymer of formula I.

7. A compound of formula IV:



(IV),

wherein n is an integer from 1 to 100;

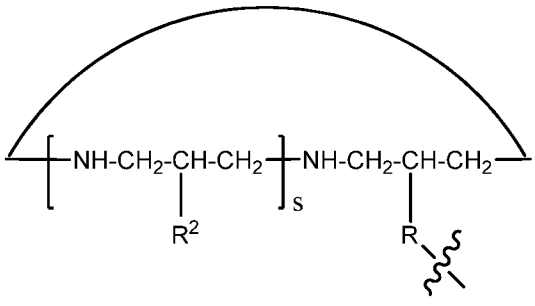
A^{17} is a metal-aza crown complex or a metal-thio crown complex;

A^{18} is a metal-aza crown complex or a metal-thio crown complex;

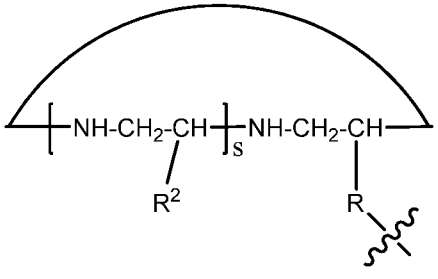
A^{19} is a metal-aza crown complex or a metal-thio crown complex; and

A^{20} is a metal-aza crown complex or a metal-thio crown complex.

8. The compound of claim 7, wherein when any one of A^{17}, A^{18}, A^{19}, or A^{20} is a metal-aza crown complex, the metal-aza crown complex comprises a metallic nanoparticle in contact with an aza crown molecule, and the aza crown molecule is selected from formula IIc or IId:



(IIc)



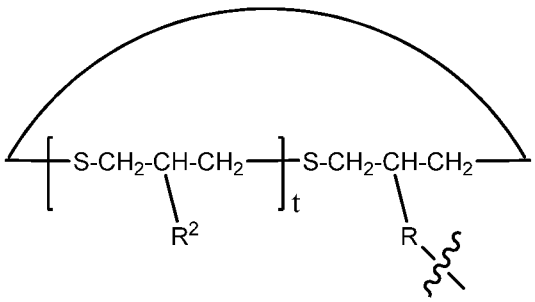
(IId)

wherein s is an integer from 3 to 12;

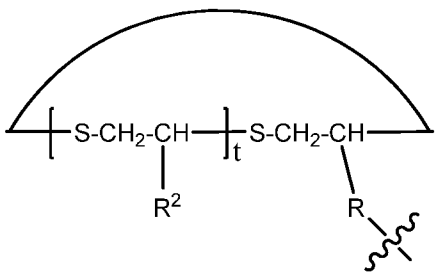
each R is independently, -O-, -CF_2-, -C(=O)-O-, -C(=O)-NH-, or -NH-; and

each R^2 is independently, -H, -F, -CF_3, -OH, -CF_2Cl, or -NH_2.

9. The compound of claim 7, wherein when any one of A^{17}, A^{18}, A^{19}, or A^{20} is a metal-thio crown complex, the metal-thio crown complex comprises a metallic nanoparticle in contact with a thio-crown molecule, and the thio-crown molecule is selected from formula IIIc or IIId:



(IIIc)



(IIId),

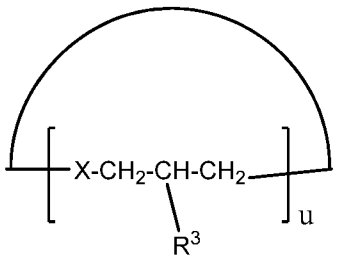
wherein t is an integer from 3 to 12;

each R is, independently, -O-, -CF_2-, -C(=O)-O-, -C(=O)-NH-, or -NH-; and

each R^2 is independently, -H, -F, -CF_3, -OH, -CF_2Cl, or -NH_2.

10. The compound of claim 8 or 9, wherein the metallic nanoparticle is a ZrO_2 nanoparticle, a TiO_2 nanoparticle, a ZnS nanoparticle, a ZnO nanoparticle, or any combination thereof.

11. A compound of formula V:



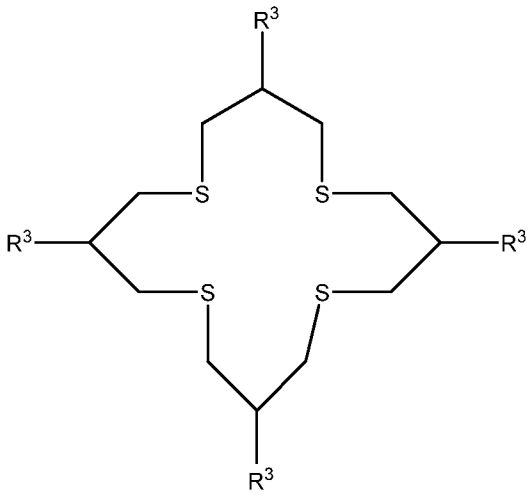
(V)

wherein X is -NH- or -S-;

u is an integer from 4 to 12; and

each R^3 is, independently, -H, -F, -Cl, $-CF_3$, -OH, $-CF_2Cl$, $-CH_2Cl$, -COCl, or $-NH_2$.

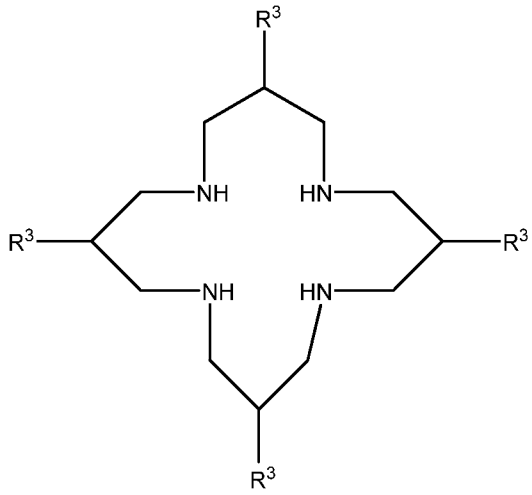
12. The compound of claim 11, wherein the compound is



,

and each R^3 is, independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$.

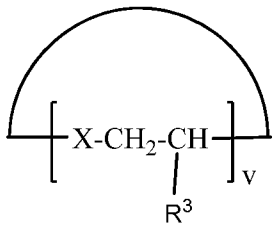
13. The compound of claim 11, wherein the compound is



,

and each R^3 is, independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$.

14. A compound of formula VI:



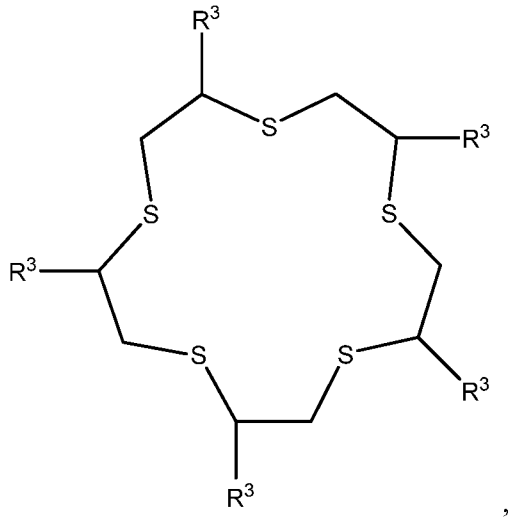
(VI),

wherein X is -NH- or -S-;

v is an integer from 4 to 12; and

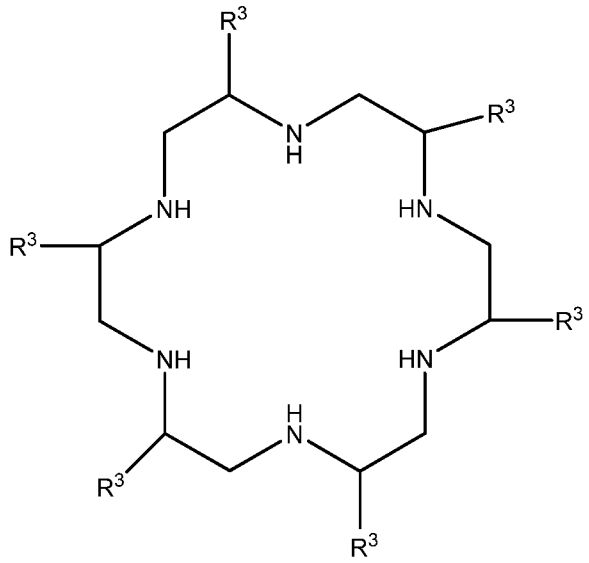
each R^3 is, independently, -H, -F, -Cl, $-CF_3$, -OH, $-CF_2Cl$, CH_2Cl, -COCl, or $-NH_2$.

15. The compound of claim 14, wherein the compound is



and each R^3 is, independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$.

16. The compound of claim 14, wherein the compound is



and each R^3 is, independently, -H, -F, $-CF_3$, -OH, $-CF_2Cl$, or $-NH_2$.

17. An article comprising one or more compounds of any one of claims 1 to 16.

18. The article of claim 17, wherein the article is an optical waveguide, a tire, a mechanical part of a vehicle, a coupling socket, a switch, or a printed wiring board pin.

19. A polymer comprising one or more compounds of any one of claims 1 to 16.

20. An optical waveguide structure comprising a light transmitting core material having a first refractive index, and a cladding material partially contacting or entirely surrounding the core material, wherein the cladding material has a second refractive index lower than the first refractive index of the core material, and wherein the core material comprises one or more compounds of any one of claims 1 to 16.

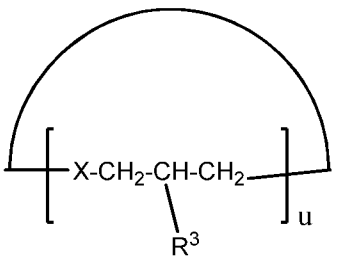
21. A method of making a siloxane compound of formula I, the method comprising:

contacting a metal- crown complex with trifluorochloromethane and a silicon metal to form a dichlorosilane- trifluoromethyl-metal-crown complex;

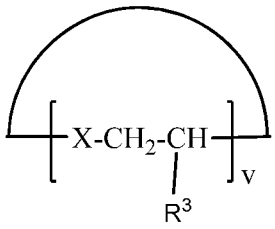
hydrolyzing the dichlorosilane- trifluoromethyl-metal-crown complex to form a fluorinated siloxane polymer compound of formula IV; and

contacting the polymer compound of formula IV with a bis-siloxane D4 compound and an anionic catalyst to form the siloxane compound of formula I.

22. The method of claim 21, wherein the metal-crown complex is formed by contacting a crown macromolecule with a metallic nanoparticle, the crown macromolecule represented by the formula V or VI:



(V) or



(VI)

wherein each X is -NH- or -S-;

u is an integer from 4 to 12;

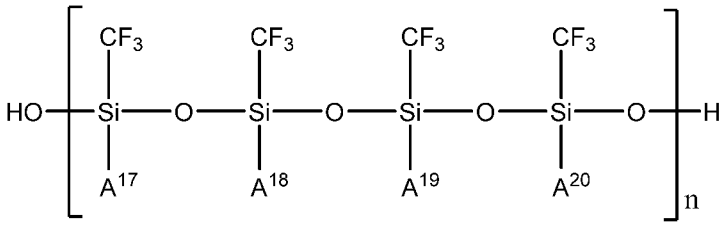
v is an integer from 4 to 12; and

each R^3 is, independently, -F, -Cl, $-CF_3$, -OH, $-CF_2Cl$, $-CH_2Cl$, -COCl, or $-NH_2$.

23. The method of claim 22, wherein the metallic nanoparticle is a ZrO_2 nanoparticle, a TiO_2 nanoparticle, a ZnS nanoparticle, a ZnO nanoparticle, or any combination thereof.

24. The method of claim 21, wherein hydrolyzing the dichlorosilane-trifluoromethyl-crown compound comprises controlled hydrolysis of the dichlorosilane-trifluoromethyl-crown compound.

25. The method of claim 21, wherein the compound of formula IV is



(IV)

wherein n is an integer from 1 to 100;

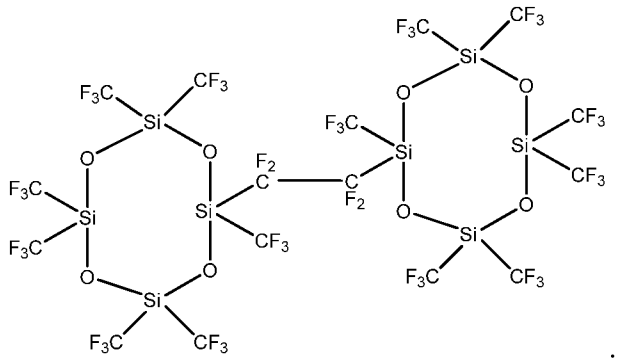
A^{17} is a metal-aza crown complex or a metal-thio crown complex;

A^{18} is a metal-aza crown complex or a metal-thio crown complex;

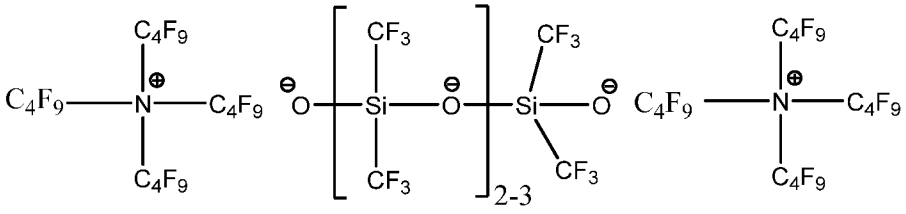
A^{19} is a metal-aza crown complex or a metal-thio crown complex and

A^{20} is a metal-aza crown complex or a metal-thio crown complex.

26. The method of claim 21, wherein the bis-siloxane D4 compound is



27. The method of claim 21, wherein the anionic catalyst is



28. The method of claim 21, wherein the metal-crown complex and the trifluoro-chloromethane are contacted in a molar ratio of about 1:1 to about 1:4.

29. The method of claim 21, wherein the compound of formula IV and the bis-siloxane D4 compound are contacted in a molar ratio of about 1:0.1 to about 1:0.5.

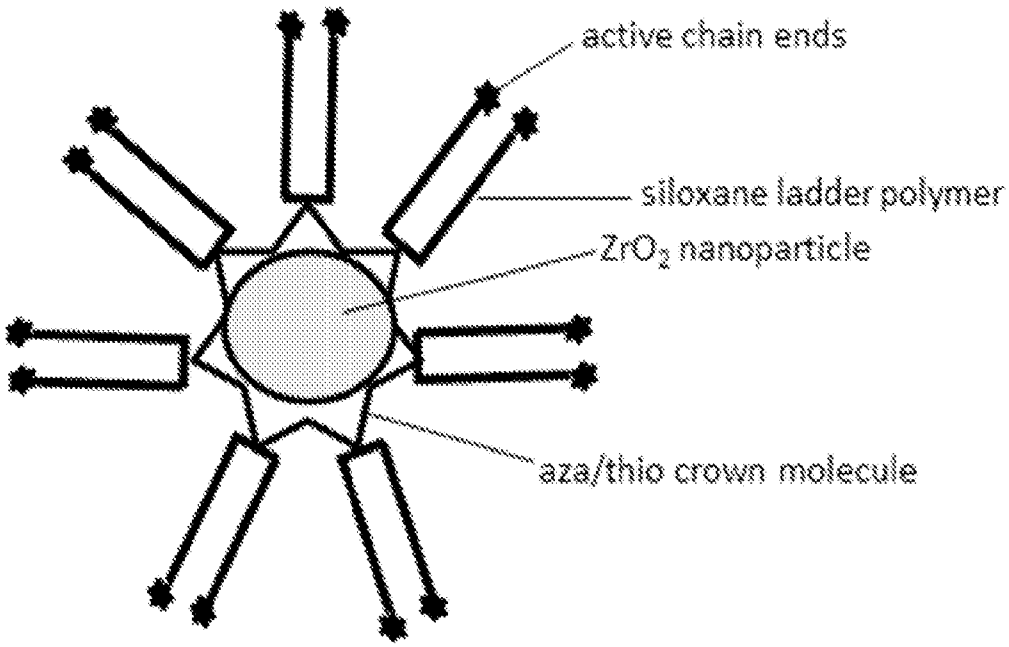

active chain ends
siloxane ladder polymer
ZrO_2 nanoparticle
aza/thio crown molecule

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/035316

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C07F 7/18 (2014.01)
USPC - 524/588
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)
IPC(8) - C07F 7/12, 7/18; C08F 8/12, 8/44 (2014.01)
USPC - 106/287.1; 524/588; 528/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - B29C 33/64; C08F 8/12, 8/42 (2014.06)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Patents, Google Scholar, Google, PubChem

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,922,527 A (BARLOW et al) 13 July 1999 (13.07.1999) entire document	11, 12
X	US 2007/0248537 A1 (YANG et al) 25 October 2007 (25.10.2007) entire document	11, 13
X	US 2011/0165459 A1 (HALALAY et al) 07 July 2011 (07.07.2011) entire document	14, 16
X	US 7,288,144 B2 (UOZUMI et al) 30 October 2007 (30.10.2007) entire document	14-16
A	US 5,230,962 A (STEPHENSON) 27 July 1993 (27.07.1993) entire document	1-29
A	US 6,737,370 B2 (ESPE) 18 May 2004 (18.05.2004) entire document	1-29

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

* 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
13 August 2014	28 AUG 2014

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/035316

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 17-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.