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(71) Applicant: **EMPIRE TECHNOLOGY DEVELOPMENT LLC** [US/US]; 2711 Centerville Road, Suite 400, Wilmington, Delaware 19808 (US).

(72) Inventors: **SJONG, Angele**; 601 Dahlia Way, Louisville, Colorado 80027 (US). **ADAM, Georgius Abidal**; 46A Gwandalan Road, Edensor Park, New South Wales 2176 (AU).

(74) Agent: **SRINIVAS, Harish**; Pepper Hamilton LLP, Suite 5000, 500 Grant Street, Pittsburgh, Pennsylvania 15219-2507 (US).

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(54) Title: FLUORINATED SILOXANES AND METHODS FOR THEIR PREPARATION

(57) Abstract: Fluorinated siloxane compositions, and methods of making and using the fluorinated siloxanes are disclosed. The polymers described herein may exhibit self-healing properties, a low dielectric constant, and a low refractive index. In some embodiments, a method of making a siloxane compound may involve contacting a silicon metal with a fluorinated compound to form a dichlorosilane compound, hydrolyzing the dichlorosilane compound to form a fluorinated tetrasiloxane compound, and contacting the fluorinated tetrasiloxane compound with a metal catalyst to form a fluorinated cyclic siloxane (D4) compound.

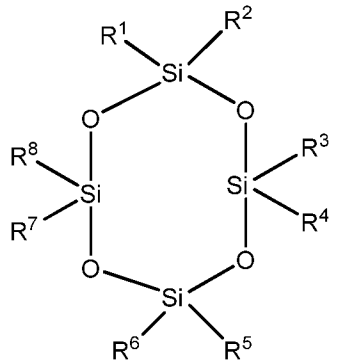
FLUORINATED SILOXANES AND METHODS FOR THEIR PREPARATION

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, and large screen and portable information display. 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 envisioned to be stable during phase transitions (for example, crystallization or melting), chemically stable, and stable in terms of optical loss, index of refraction, and density.

SUMMARY

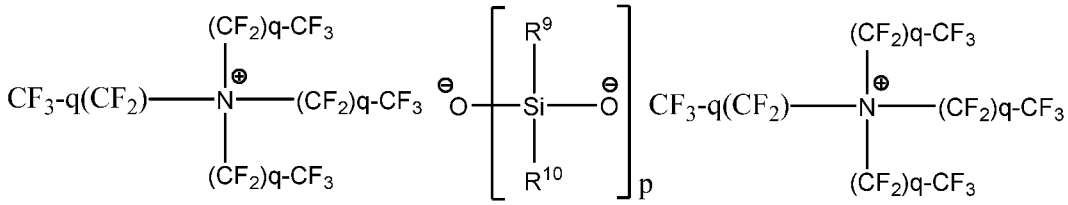
[0002] This disclosure is related to compositions of fluorinated siloxanes, and methods of making and their use. In an embodiment, a compound is of formula I:



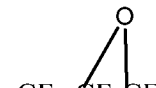
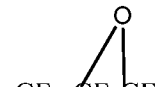
(I)

wherein each R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 is, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or .

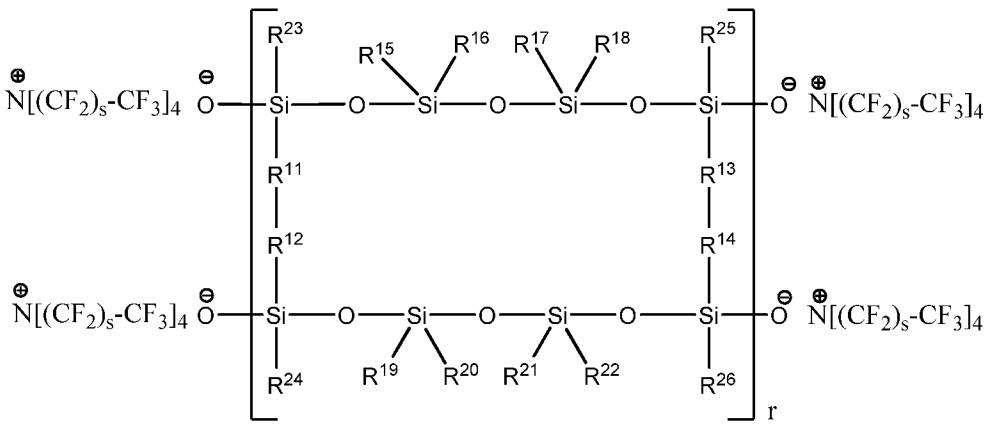
[0003] In an additional embodiment, a compound is of formula II:



(II)

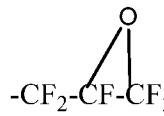
wherein each R^9 is, independently, $-CF_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ; each R^{10} is, independently, $-CF_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ; p is 1 or 2; and q is 1 or 2.

[0004] In a further embodiment, a compound is of formula III:



(III)

wherein r is an integer from 1 to 100; s is an integer from 1 to 3; R^{11}, R^{12}, R^{13}, and R^{14} are each $-CF_2-$; and each R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26}

independently are, $-CF_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, , or salts thereof.

[0005] In an additional embodiment, an article or a polymer may include one or more compounds of formula I, II or III 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, II, or III as described herein.

[0006] In a further embodiment, a method of making a siloxane compound of formula I may involve contacting a silicon metal with a fluorinated compound to form a dichlorosilane compound, hydrolyzing the dichlorosilane compound to form a fluorinated tetrasiloxane compound with hydroxyl groups, and contacting the fluorinated tetrasiloxane compound with hydroxyl groups with a metal catalyst to form a fluorinated cyclic siloxane (D4) compound.

[0007] In yet another embodiment, a method of making a compound of formula II may involve contacting a silicon metal with a fluorinated compound to form a dichlorosilane compound, hydrolyzing the dichlorosilane compound to form a fluorinated tetrasiloxane compound, contacting the fluorinated tetrasiloxane compound with a metal catalyst to form a fluorinated cyclic siloxane (D4) monomer, and contacting the fluorinated cyclic siloxane (D4) monomer with fluorinated tetramethyl-ammonium chloride.

DETAILED DESCRIPTION

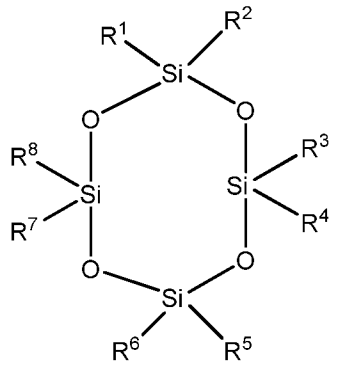
[0008] This disclosure is not limited to the particular systems, devices and methods described, as these may vary. The terminology used in the description is for the

purpose of describing the particular versions or embodiments only, and is not intended to limit the scope.

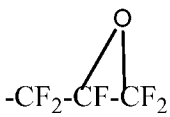
[0009] A "core material" refers to any layer of an optical waveguide that transmits light. A "cladding material" refers to any layer of an optical waveguide that confines light. In an embodiment, a core layer may be at least partially encompassed by a cladding layer.

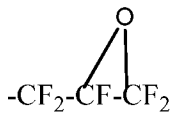
[0010] A "waveguide" refers to a system having a material that provides a path to guide an electromagnetic wave. A waveguide may have, for example and without limitation, a circular or a rectangular shape.

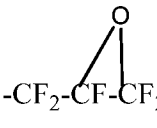
[0011] In some embodiments, a compound is of formula I:

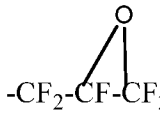


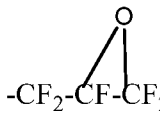
(I)

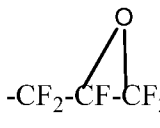
wherein each R^1 may be, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or . In some embodiments, each R^1 may be, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

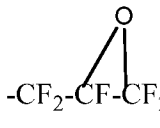
[0012] In some embodiments, each R^2 may be, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or . In some embodiments, each R^2 may be, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

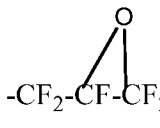
[0013] In some embodiments, each R^3 may be, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or . In some embodiments, each R^3 may be, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

[0014] In some embodiments, each R^4 may be, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or . In some embodiments, each R^4 may be, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

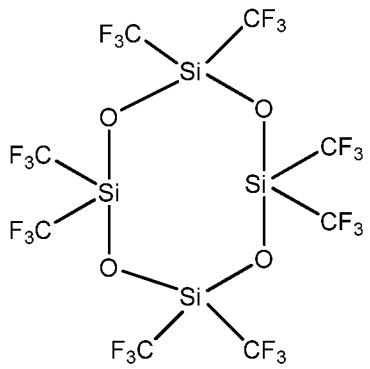
[0015] In some embodiments, each R^5 may be, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or . In some embodiments, each R^5 may be, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

[0016] In some embodiments, each R^6 may be, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or . In some embodiments, each R^6 may be, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

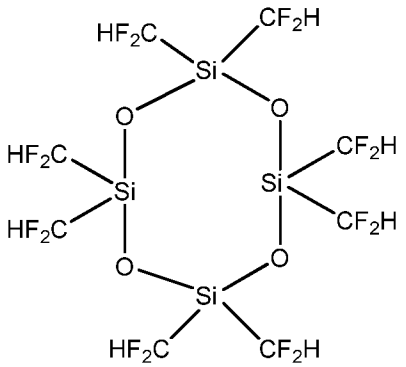
[0017] In some embodiments, each R^7 may be, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or . In some embodiments, each R^7 may be, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

[0018] In some embodiments, each R^8 may be, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or . In some embodiments, each R^8 may be, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

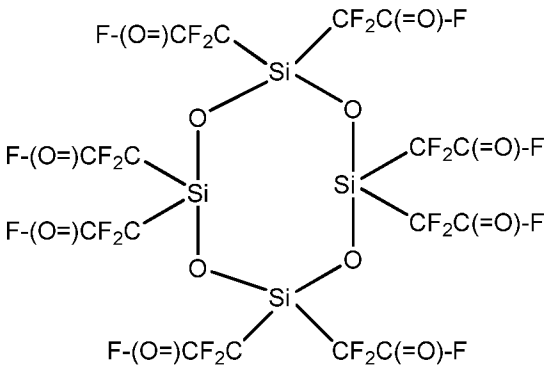
[0019] Non-limiting examples of compounds represented by formula I include, but are not limited to, the following compounds:



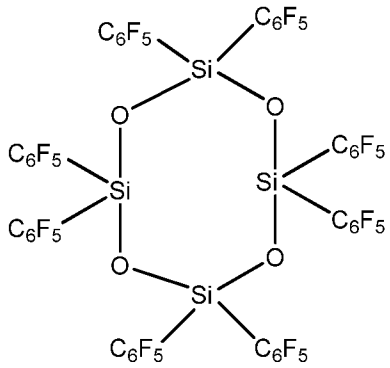
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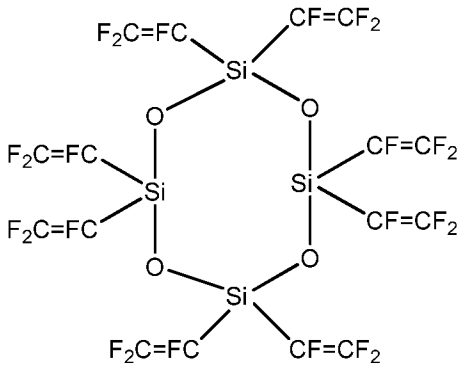
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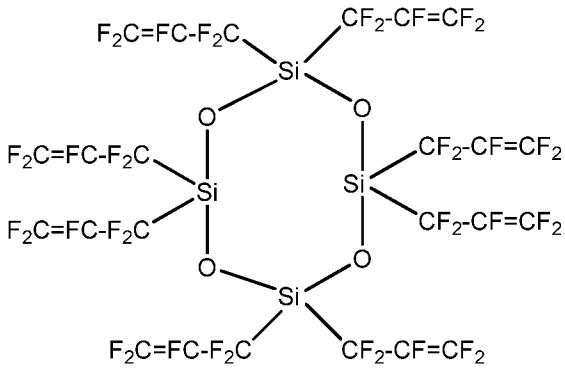
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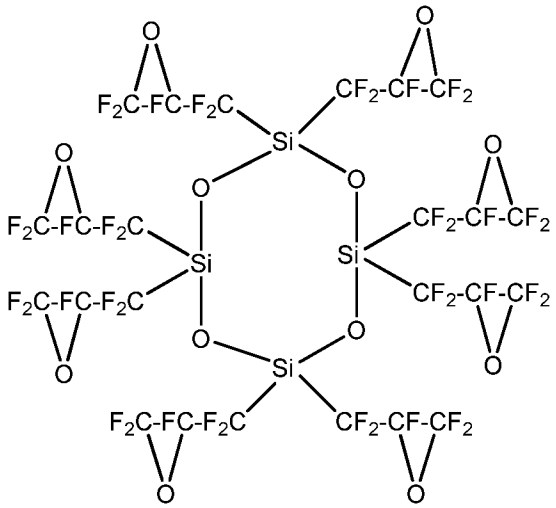
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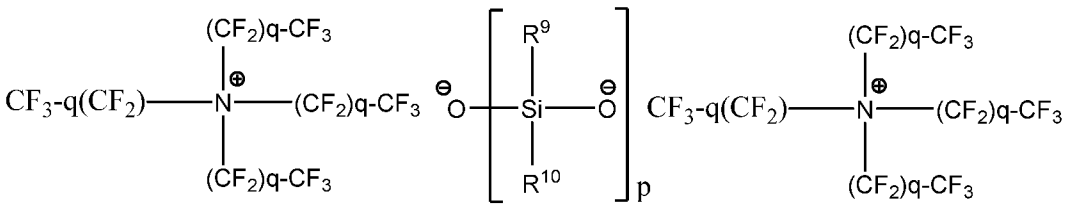


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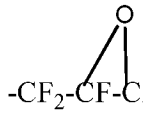
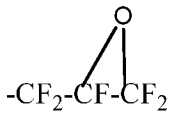
[0020] In some embodiments, a compound is of formula II:



(II)

wherein each R^9 may be, independently, $-CF_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ; each R^{10} may be, independently, $-CF_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ; p is 1 or 2; and q is 1 or 2.

[0021] In some embodiments, each R^9 may be, independently, $-CF_3$; each R^{10} may be, independently, $-CF_3$; p is 2; and q is 1.

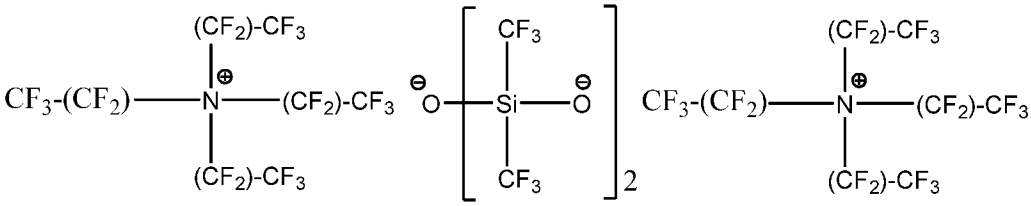
[0022] In some embodiments, each R^9 is ; each R^{10} is ; p is 2; and q is 1.

[0023] In some embodiments, each R^9 is $-CF_2-C(=O)-F$; each R^{10} is $-CF_2-C(=O)-F$; p is 2; and q is 1.

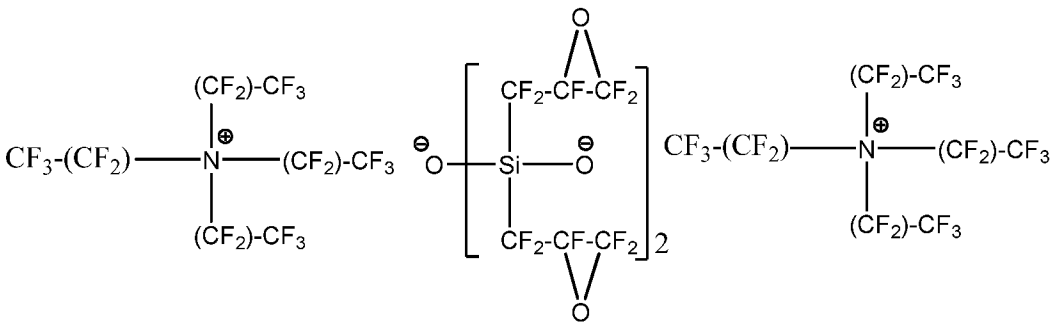
[0024] In some embodiments, each R^9 is $-C_6F_5$; each R^{10} is $-C_6F_5$; p is 2; and q is 1.

[0025] In some embodiments, each R^9 is $-CF=CF_2$; each R^{10} is $-CF=CF_2$; p is 2; and q is 1. The compounds of formula II may function as an anionic catalyst during polymerization.

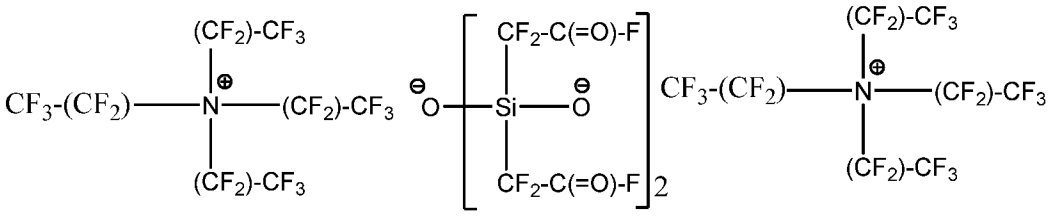
[0026] Non-limiting examples of compounds represented by formula II include, but are not limited to, the following compounds:



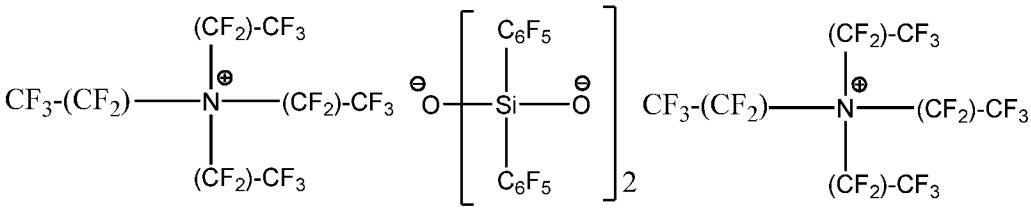
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11

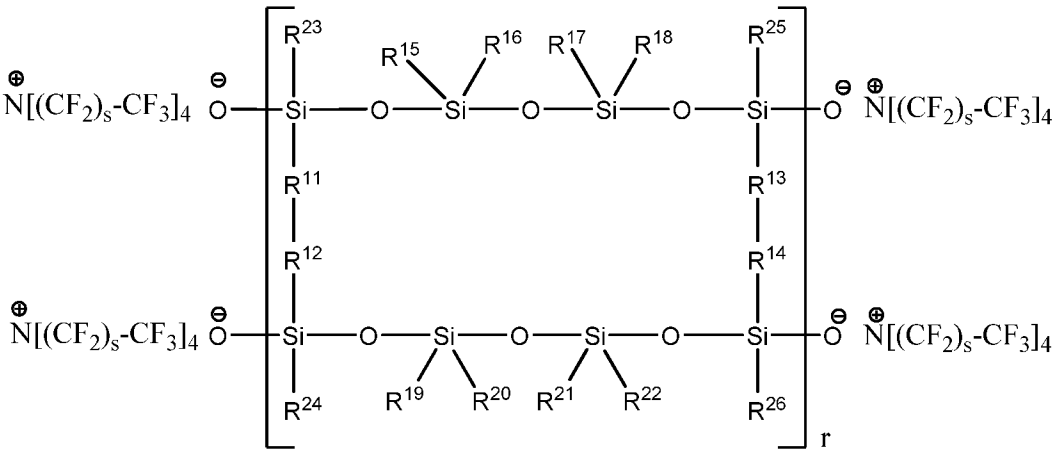


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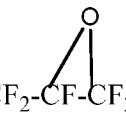
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[0027] In some embodiments, a compound is of formula III:



(III)

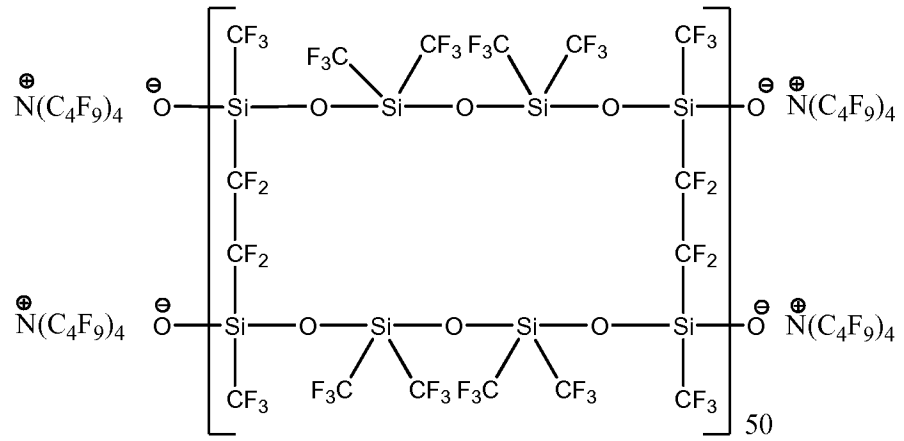
wherein r may be an integer from 1 to 100; s may be an integer from 1 to 3; R^{11}, R^{12}, R^{13}, and R^{14} are each $-CF_2-$; and each R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26} independently may be, $-CF_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$,



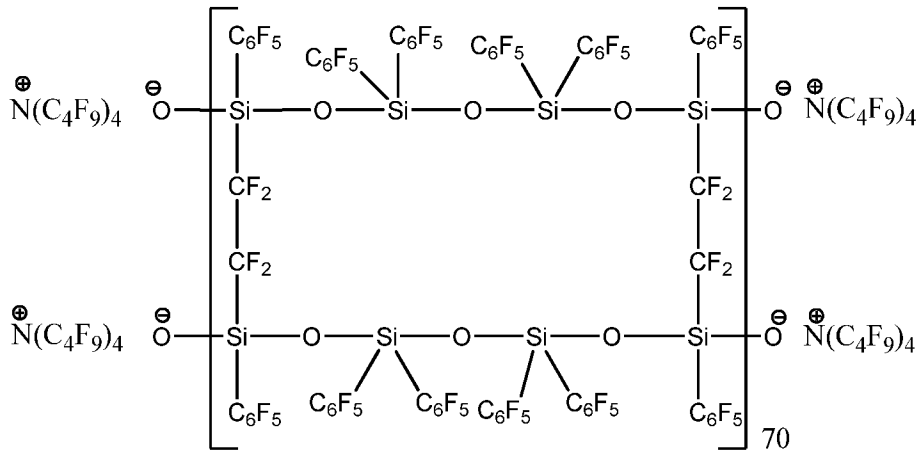
, or salts thereof. In some embodiments, each of R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20},

R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26} independently may be, $-CF_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, or $-CF=CF_2$.

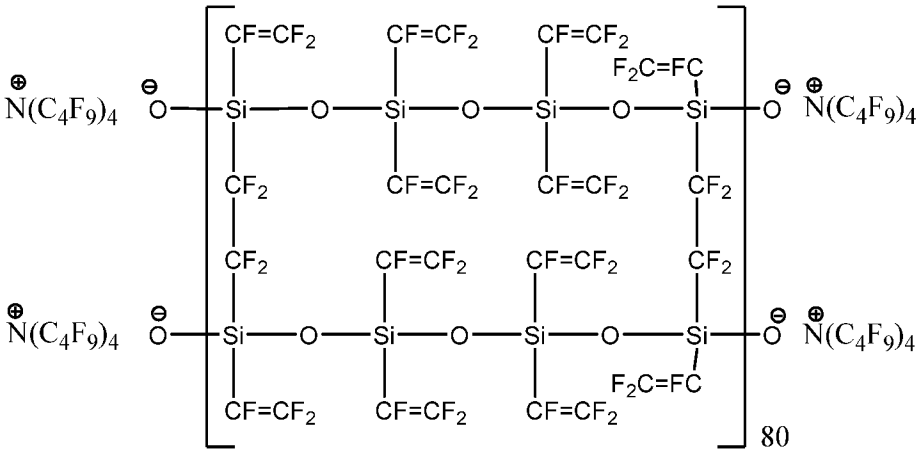
[0028] Non-limiting examples of compounds represented by formula III include, but are not limited to, the following compounds:



14



15



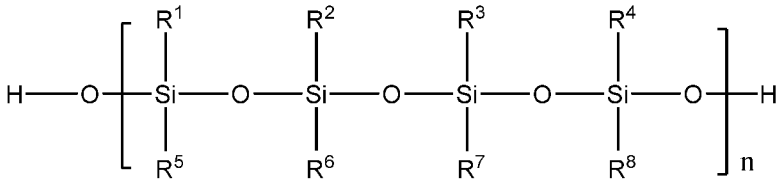
16

[0029] Compounds of formula III 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 electronegativity and electron withdrawing properties.

[0030] In some embodiments, a method of making a compound of formula I may involve contacting a silicon metal with a fluorinated compound to form a dichlorosilane compound, hydrolyzing the dichlorosilane compound to form a fluorinated tetrasiloxane compound with hydroxyl groups, and contacting the fluorinated tetrasiloxane compound with hydroxyl groups with a metal catalyst to form a fluorinated cyclic siloxane (D4) compound of formula I. Examples of fluorinated compounds that may be used are trifluorochloromethane, difluorochloromethane, fluorinated phenyldiazonium chloride, fluorinated vinylchloride,

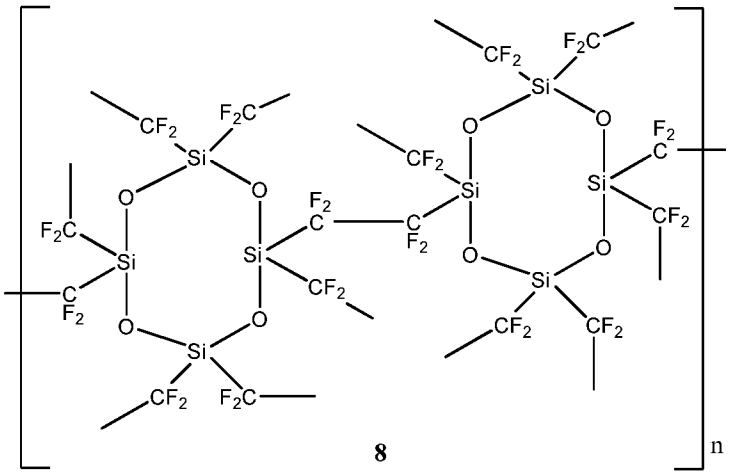
fluorinated allylchloride, and fluorinated epichlorohydrin. The dichlorosilane compound may be subjected to a controlled hydrolysis step to form fluorinated tetrasiloxane compounds. The hydroxyl terminated tetrasiloxane compound may undergo cyclization in the presence of zinc oxide to form a fluorinated cyclic siloxane (D4) compound. Other metal catalysts that may be used are oxides of Li, K, Ba, Ca, Na, Mg, Al, Mn, Zn, Cr, and any combination thereof.

[0031] In some embodiments, the cyclic siloxane (D4) monomer obtained by the methods described herein may be polymerized using a cationic catalyst, such as trifluoromethanesulphonic acid. This polymerization would cause breakage of Si-O bonds, resulting in ring opening to form polymers. The polymer may be represented by the structure below:

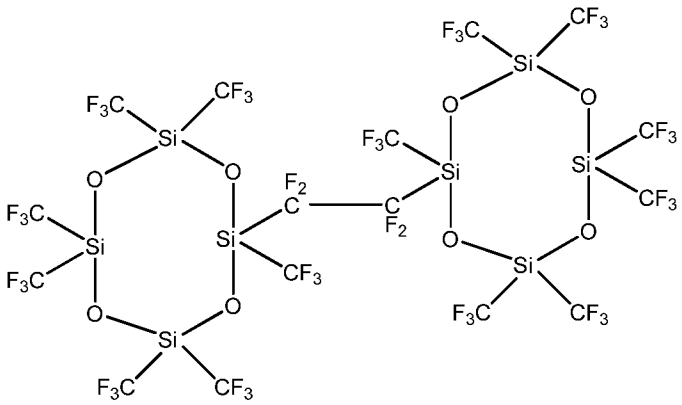


IV

[0032] In other embodiments, the cyclic siloxane (D4) monomer units may be coupled together in the presence of fluorinated benzoyl peroxide to form polymers. Examples of such polymers include compounds **8** and **9**, as shown below:



8



9

[0033] In some embodiments, a method of preparing the compound of formula II may involve contacting a silicon metal with a fluorinated compound to form a dichlorosilane compound, hydrolyzing the dichlorosilane compound to form a fluorinated tetrasiloxane compound, contacting the fluorinated tetrasiloxane compound with a metal catalyst to form a fluorinated cyclic siloxane (D4) monomer, and contacting the fluorinated cyclic siloxane (D4) monomer with fluorinated tetramethyl-ammonium chloride. During contacting the fluorinated cyclic siloxane (D4) monomer with fluorinated tetramethylammonium chloride, the reaction temperature may be below 10 °C, below 8 °C, below 6 °C, below 4 °C or below 0 °C.

[0034] The compounds and polymers disclosed herein may have 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 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 optical

waveguides, tires, mechanical parts of a vehicle, sporting goods, coupling sockets, switches, printed wiring board pins, ice skating rinks, and the like.

[0035] 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, II or III.

[0036] 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 compound 1 and its polymer

[0037] 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 obtain a fluorinated cyclic siloxane (D4) compound **1**.

[0038] About 20 grams of the compound **1** obtained above is charged into a reaction vessel along with 20 μL of the cationic catalyst trifluoromethanesulphonic acid (triflic acid). The reaction mixture is maintained at 10 °C under inert conditions, and mixed for 8-12 hours. At the end of the reaction, the polymer is separated and dissolved in chloroform, re-precipitated with methanol, and dried under vacuum to obtain a polymer of compound **1**.

EXAMPLE 2: Preparation of compound 4 and its polymer

[0039] About 0.1 mole of silicon metal is reacted with about 0.2 moles of fluorinated phenyldiazonium chloride to obtain a fluorinated diphenyl dichlorosilane compound. The fluorinated diphenyl dichlorosilane compound is 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) compound **4**.

[0040] About 20 grams of the compound **4** obtained above is charged into a reaction vessel along with 20 μL of the cationic catalyst trifluoromethanesulphonic acid (triflic acid). The reaction mixture is maintained at 10 °C under inert conditions, and mixed for 8-12 hours. At the end of the reaction, the polymer is separated and dissolved in chloroform, re-precipitated with methanol, and dried under vacuum to obtain a polymer of compound **4**.

EXAMPLE 3: Preparation of compound 5 and its polymer

[0041] About 0.1 mole of silicon metal is reacted with about 0.2 moles of fluorinated vinylchloride to obtain a fluorinated divinyl dichlorosilane compound. The fluorinated divinyl dichlorosilane compound is 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) compound **5**.

[0042] About 20 grams of the compound **5** obtained above is charged into a reaction vessel along with 20 μL of the cationic catalyst trifluoromethanesulphonic acid (triflic acid). The reaction mixture is maintained at 10 °C under inert conditions, and mixed for 8-12 hours. At the end of the reaction, the polymer is separated and dissolved in chloroform, re-precipitated with methanol, and dried under vacuum to obtain a polymer of compound **5**.

EXAMPLE 4: Preparation of compound 6 and its polymer

[0043] About 0.1 mole of silicon metal is reacted with about 0.2 moles of fluorinated allylchloride to obtain a fluorinated diallyl dichlorosilane compound. The fluorinated diallyl dichlorosilane compound is 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) compound **6**.

[0044] About 20 grams of the compound **6** obtained above is charged into a reaction vessel along with 20 μL of the cationic catalyst trifluoromethanesulphonic acid (triflic acid). The reaction mixture is maintained at 10 °C under inert conditions, and mixed for 8-12 hours. At the end of the reaction, the polymer is separated and dissolved in chloroform, re-precipitated with methanol, and dried under vacuum to obtain a polymer of compound **6**.

EXAMPLE 5: Preparation of compound 7 and its polymer

[0045] About 0.1 mole of silicon metal is reacted with about 0.2 moles of fluorinated epichlorohydrin to obtain a fluorinated bis-glycidylether dichlorosilane compound. The fluorinated bis-glycidylether dichlorosilane compound is 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) compound **7**.

[0046] About 20 grams of the compound **7** obtained above is charged into a reaction vessel along with 20 μL of the cationic catalyst trifluoromethanesulphonic acid (triflic acid). The reaction mixture is maintained at 10 °C under inert conditions, and mixed for 8-12 hours. At the end of the reaction, the polymer is separated and dissolved in chloroform, re-precipitated with methanol, and dried under vacuum to obtain a polymer of compound **7**.

EXAMPLE 6: Preparation of compound 8

[0047] About 0.1 mole of silicon metal is reacted with about 0.2 moles of difluorochloromethane to obtain bis(difluoromethyl) dichlorosilane. The bis(difluoromethyl) dichlorosilane is 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.

[0048] About 10 grams of the fluorinated cyclic siloxane (D4) monomer is mixed with 0.001 gram of fluorinated benzoyl peroxide and heated in a mold under N_2 atmosphere at 120 °C. A coupling reaction takes place resulting in a polymeric compound **8**, having fluorinated ethylene linkages between the siloxane units.

EXAMPLE 7: Preparation of compound 9

[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 the 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 forming compound **9** which can be used as a laddering agent and as ring opening polymerisation monomer

EXAMPLE 8: Preparation of anionic catalyst compound 10

[0051] The reaction vessel is charged with 0.1 mole of fully fluorinated tetrabutyl-ammonium chloride that is prepared by reacting fluorinated tributylamine with fluorinated butyl chloride. The reaction vessel is cooled to 5 ^{o}C, flushed with N_2, and about 0.05 mole of the fluorinated cyclic siloxane (D4) monomer of Example 1 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 compound **10**.

EXAMPLE 9: Preparation of compound 14

[0052] About 1 mole of compound **1** is mixed with 0.1 mole of compound **9** in the presence of the anionic catalyst compound **10**. The mixture is cooled to 0 ^{o}C for 40 minutes under a stream of nitrogen gas. The resulting polymer is a ladder type anionic living polysiloxane polymer compound **14**. The degree of laddering can be controlled by the molar ratio of compound **1** and compound **9**. The reaction can be carried out in aprotic solvents. 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 10: Preparation of a waveguide

[0053] Planar waveguides are made on 3 inch (7.62 cm) silicon wafer substrates using the siloxane polymers of compounds **4-7** 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 **4-7**) 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 11: An article prepared from siloxane polymers

[0054] 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.

[0055] 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.

[0056] 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.

[0057] 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.”

[0058] 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.

[0059] 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.

[0060] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (*for example*, bodies of the appended claims) are generally intended as “open” terms (*for 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" (*for 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 (*for 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 (*for 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 (*for 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.”

[0061] 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.

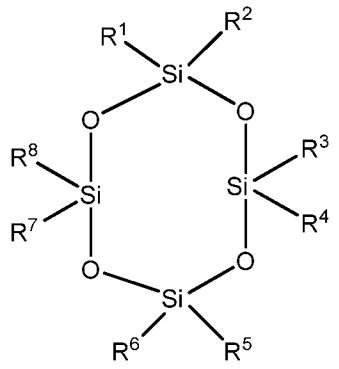
[0062] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently 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.

[0063] 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.

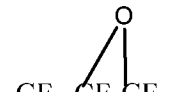
CLAIMS

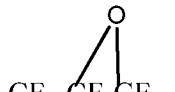
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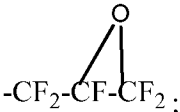
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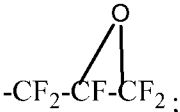


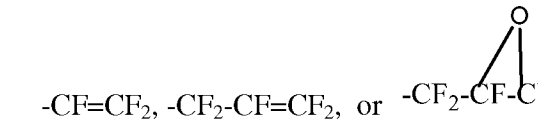
(I)

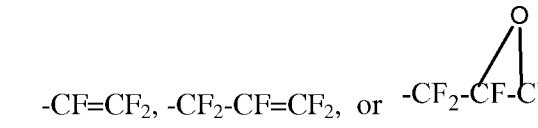
wherein each R^1 is, independently, $–CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ;

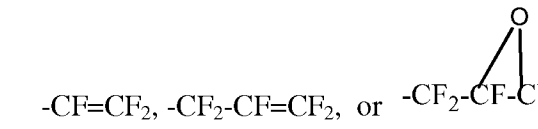
each R^2 is, independently, $–CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ;

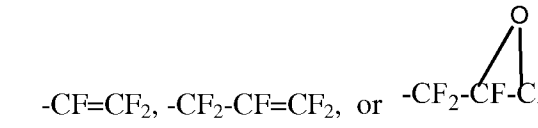
each R^3 is, independently, $–CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ;

each R^4 is, independently, $–CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ;

each R^5 is, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ;

each R^6 is, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ;

each R^7 is, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ; and

each R^8 is, independently, $-CF_3$, $-CF_2-$, $-CF_2H$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or .

2. The compound of claim 1, wherein each R^1 is, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

3. The compound of claim 1 or 2, wherein each R^2 is, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

4. The compound of any one of claims 1 to 3, wherein each R^3 is, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

5. The compound of any one of claims 1 to 4, wherein each R^4 is, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

6. The compound of any one of claims 1 to 5, wherein each R^5 is, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

7. The compound of any one of claims 1 to 6, wherein each R^2 is, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

8. The compound of any one of claims 1 to 7, wherein each R^7 is, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

9. The compound of any one of claims 1 to 8, wherein each R^8 is, independently, $-CF_3$, $-CF_2H$, or $-CF_2-C(=O)-F$.

10. The compound of claim 1, wherein:

each R^1 is $-CF_3$ or $-CF_2H$;

each R^2 is $-CF_3$ or $-CF_2H$;

each R^3 is $-CF_3$ or $-CF_2H$;

each R^4 is $-CF_3$ or $-CF_2H$;

each R^5 is $-CF_3$ or $-CF_2H$;

each R^6 is $-CF_3$ or $-CF_2H$;

each R^7 is $-CF_3$ or $-CF_2H$; and

each R^8 is $-CF_3$ or $-CF_2H$.

11. The compound of claim 1, wherein each R^1 is $-CF_3$, each R^2 is $-CF_3$, each R^3 is $-CF_3$, each R^4 is $-CF_3$, each R^5 is $-CF_3$, each R^6 is $-CF_3$, each R^7 is $-CF_3$, and each R^8 is $-CF_3$.

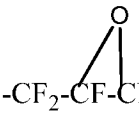
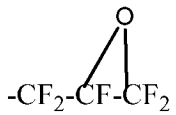
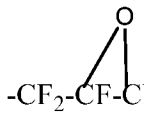
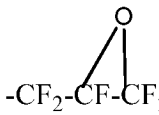
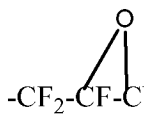
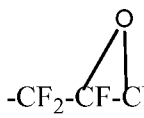
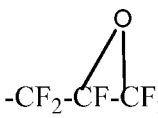
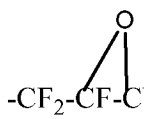
12. The compound of claim 1, wherein each R^1 is $-CF_2H$, each R^2 is $-CF_2H$, each R^3 is $-CF_2H$, each R^4 is $-CF_2H$, each R^5 is $-CF_2H$, each R^6 is $-CF_2H$, each R^7 is $-CF_2H$, and each R^8 is $-CF_2H$.

13. The compound of claim 1, wherein each R^1 is $-CF_2-C(=O)-F$, each R^2 is $-CF_2-C(=O)-F$, each R^3 is $-CF_2-C(=O)-F$, each R^4 is $-CF_2-C(=O)-F$, each R^5 is $-CF_2-C(=O)-F$, each R^6 is $-CF_2-C(=O)-F$, each R^7 is $-CF_2-C(=O)-F$, and each R^8 is $-CF_2-C(=O)-F$.

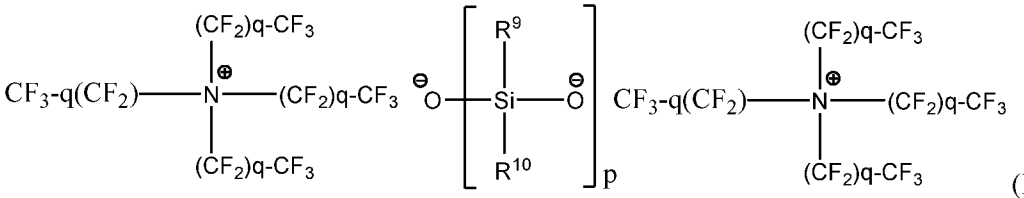
14. The compound of claim 1, wherein each R^1 is $-C_6F_5$, each R^2 is $-C_6F_5$, each R^3 is $-C_6F_5$, each R^4 is $-C_6F_5$, each R^5 is $-C_6F_5$, each R^6 is $-C_6F_5$, each R^7 is $-C_6F_5$, and each R^8 is $-C_6F_5$.

15. The compound of claim 1, wherein each R^1 is $-CF=CF_2$, each R^2 is $-CF=CF_2$, each R^3 is $-CF=CF_2$, each R^4 is $-CF=CF_2$, each R^5 is $-CF=CF_2$, each R^6 is $-CF=CF_2$, each R^7 is $-CF=CF_2$, and each R^8 is $-CF=CF_2$.

16. The compound of claim 1, wherein each R^1 is $-CF_2-CF=CF_2$, each R^2 is $-CF_2-CF=CF_2$, each R^3 is $-CF_2-CF=CF_2$, each R^4 is $-CF_2-CF=CF_2$, each R^5 is $-CF_2-CF=CF_2$, each R^6 is $-CF_2-CF=CF_2$, each R^7 is $-CF_2-CF=CF_2$, and each R^8 is $-CF_2-CF=CF_2$.

17. The compound of claim 1, wherein each R^1 is , each R^2 is , each R^3 is , each R^4 is , each R^5 is , each R^6 is , each R^7 is , and each R^8 is .

18. A compound of formula II:



(II)

wherein each R^9 is, independently, $-CF_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ;

each R^{10} is, independently, $-CF_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, or ;

p is 1 or 2; and

q is 1 or 2.

19. The compound of claim 18, wherein each R^9 is, independently, $-CF_3$, or $-CF_2-C(=O)-F$.

20. The compound of claim 18 or 19, wherein each R^{10} is, independently, $-CF_3$, or $-CF_2-C(=O)-F$.

21. The compound of claim 18, wherein each R^9 is $-CF_3$; each R^{10} is $-CF_3$; p is 2; and q is 1.

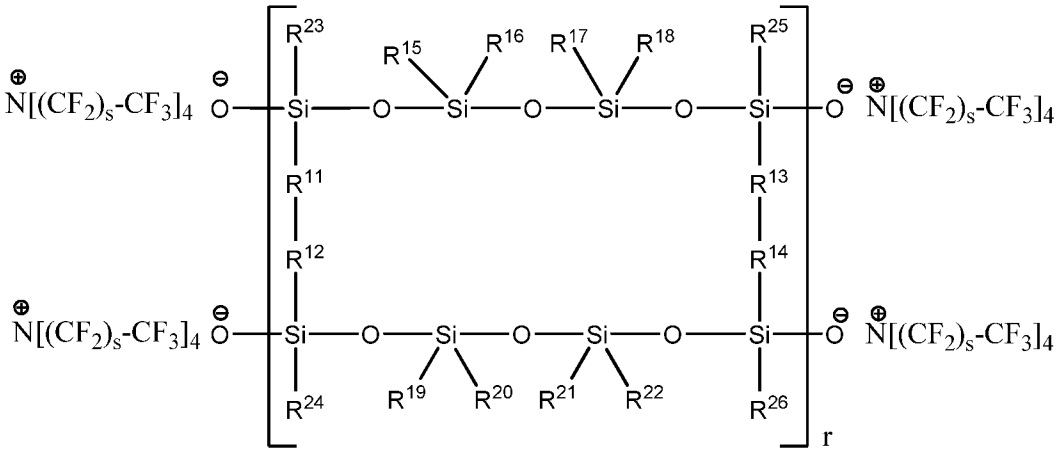
22. The compound of claim 18, wherein each R^9 is ; each R^{10} is ; p is 2; and q is 1.

23. The compound of claim 18, wherein each R^9 is $-CF_2-C(=O)-F$; each R^{10} is $-CF_2-C(=O)-F$; p is 2; and q is 1.

24. The compound of claim 18, wherein each R^9 is $-C_6F_5$; each R^{10} is $-C_6F_5$; p is 2; and q is 1.

25. The compound of claim 18, wherein each R^9 is $-CF=CF_2$; each R^{10} is $-CF=CF_2$; p is 2; and q is 1.

26. A compound of formula III:



(III)

wherein r is an integer from 1 to 100;

s is an integer from 1 to 3;

R^{11}, R^{12}, R^{13}, and R^{14} are each $-CF_2-$; and

each R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26} independently are, $-CF_3$, $-CF_2-C(=O)-F$, $-C_6F_5$, $-CF=CF_2$, $-CF_2-CF=CF_2$, , or salts thereof.

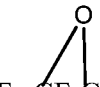
27. The compound of claim 26, wherein each R^{11}, R^{12}, R^{13}, and R^{14} are $-CF_2-$; and each R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26} independently are, $-CF_3$, $-CF_2-CF=CF_2$, or $-CF_2-C(=O)-F$.

28. The compound of claim 26, wherein each R^{11}, R^{12}, R^{13}, and R^{14} are $-CF_2-$; each R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26} independently are $-CF_3$; and s is 3.

29. The compound of claim 26, wherein each R^{11}, R^{12}, R^{13}, and R^{14} are $-CF_2-$; each R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26} are $-CF_2-CF=CF_2$; and s is 3.

30. The compound of claim 26, wherein each R^{11}, R^{12}, R^{13}, and R^{14} are $-CF_2-$; each R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26} are $-CF_2-C(=O)-F$; and s is 3.

31. The compound of claim 26, wherein each R^{11}, R^{12}, R^{13}, and R^{14} are $-CF_2-$; each R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26} independently are $-C_6F_5$; and s is 3.

32. The compound of claim 26, wherein each R^{11}, R^{12}, R^{13}, and R^{14} are $-CF_2-$; each R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26} are ; and s is 3.

33. The compound of claim 26, wherein each R^{11}, R^{12}, R^{13}, and R^{14} are $-CF_2-$; each R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, and R^{26} are $-CF=CF_2$; and s is 3.

34. An article comprising one or more compounds of any one of claims 1 to 33.

35. The article of claim 34, 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.

36. A polymer comprising one or more compounds of any one of claims 1 to 33.

37. 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 33.

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

contacting a silicon metal with a fluorinated compound to form a dichlorosilane compound;

hydrolyzing the dichlorosilane compound to form a fluorinated tetrasiloxane compound with hydroxyl groups; and

contacting the fluorinated tetrasiloxane compound with hydroxyl groups with a metal catalyst to form a fluorinated cyclic siloxane (D4) compound of formula I.

39. The method of claim 38, wherein the fluorinated compound comprises trifluorochloromethane, difluorochloromethane, fluorinated phenyldiazonium chloride, fluorinated vinylchloride, fluorinated allylchloride, fluorinated epichlorohydrin, or any combination thereof.

40. The method of claim 38, wherein hydrolyzing the dichlorosilane compound comprises controlled hydrolysis of the dichlorosilane compound.

41. The method of claim 38, wherein the metal catalyst comprises oxides of Li, K, Ba, Ca, Na, Mg, Al, Mn, Zn, Cr, or any combination thereof.

42. A method of making a compound of formula II, the method comprising:

contacting a silicon metal with a fluorinated compound to form a dichlorosilane compound;

hydrolyzing the dichlorosilane compound to form a fluorinated tetrasiloxane compound;

contacting the fluorinated tetrasiloxane compound with a metal catalyst to form a fluorinated cyclic siloxane (D4) monomer; and

contacting the fluorinated cyclic siloxane (D4) monomer with fluorinated tetramethyl-ammonium chloride.

43. The method of claim 42, wherein the fluorinated compound comprises trifluorochloromethane, difluorochloromethane, fluorinated phenyldiazonium chloride, fluorinated vinylchloride, fluorinated allylchloride, fluorinated epichlorohydrin, or any combination thereof.

44. The method of claim 42, wherein hydrolyzing the dichlorosilane compound comprises controlled hydrolysis of the dichlorosilane compound.

45. The method of claim 42, wherein the metal catalyst comprises oxides of Li, K, Ba, Ca, Na, Mg, Al, Mn, Zn, Cr, or any combination thereof.

46. The method of claim 42, wherein contacting the fluorinated cyclic siloxane (D4) monomer with fluorinated tetramethyl-ammonium chloride comprises contacting at a temperature below 10 ^{o}C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 13/69088

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C02F 5/08 (2014.01)
USPC - 507/234, 233,901; 524/588, 503
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)
USPC-507/234

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
IPC(8)-C02F 5/08 (2014.01)
USPC- 233,901; 524/588, 503

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase (PGPB, USPT, USOC, EPAB, JPAB, DWPI, TDBD), FreePatentsOnline (US Pat, PgPub, EPO, JPO, WIPO, NPL), GoogleScholar (PL, NPL); search terms: Trifluoromethane sulfonyl siloxane tetramer cyclic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,877,528 A (Friesen) 31 October 1989 (31.10.1989) col 5, ln 12-17	1-3, 10,11
X	US 3,433,765 A (Geipel) 18 March 1969 (18.03.1969) col 1, ln 48-59	1-3, 10,11
X	US 2,905,703 A (Bailey et al.) 22 September 1959 (22.09.1959) col 3, ln 1-10	1-3, 10,11
X	US 3,221,040 A (Pater et al.) 30 November 1965 (30.11.1965) col 1, ln 1-70	1-3, 10,11
X	US 3,846,462 A (Prokai et al.) 5 November 1974 (05.11.1974) abstract, col 3, ln 18-59	1-3, 10,11
X	US 3,983,148 A (Reedy et al.) 28 September 1976 (28.09.1976)	1-3, 10,11
X	US 4,003,847 A (Prokai) 18 January 1977 (18.01.1977) col 12, ln 60-61	1-3, 10,11
X	US 2008/0312365 A1 (Maton et al.) 18 December 2008 (18.12.2008) para [0031]-[0041], [0047], [0065], [0140]	1-3, 10,11
A	US 4,529,752 A (Bluestein) 16 July 1985 (16.07.1985) entire document	1-3, 10,11
A	US 2012/0100474 A1 (Hikosaka et al.)26 April 2012 (26. 04.2012) para [0013], [0028], [0032]	1-3, 10,11

☐ 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
05 May 2014 (05.05.2014)	05 JUN 2014
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young 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/US13/69088

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.: 4-9, 34-37
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:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I+, claims 1-3, and 10-17, directed to a compound formula I. Group I+ will be searched to the extent that it reads on the compound wherein R1-R8 is CF3. It is believed that claims 1-3, 10-11, (in part), read on this first named invention. Applicants must indicate, if applicable, the claims which read on the first named invention if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched/examined. An exemplary election would be on the compound wherein R1-R8 is CF2H, claims 1-3, 10, (in part), and 12.
Group II, claims 18-25, 38-46 directed to a compound formula II and a method of making compounds of formula I and II.
Group III, claims 26-33, directed to a compound formula III.
---Continued in the Supplemental Box----------

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.:
1-3, 10, (in part), and 11

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.

International application No.
PCT/US 13/69088

Continuation of Box III

The inventions listed as Groups I+ and II-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features
The special technical feature of each invention of Group I+ is the unique chemical structure of each compound, not found in any other invention of the Group I+.
Group II includes a special technical feature of method of making compounds of formulae I and II not required by Group I+ and III.
Group III includes a special technical feature of compound of formula III not required by Group I+ or II.

Common Technical Features
The inventions of Groups I+, II-III are related to siloxane derivatives broadly. Inventions of Groups I+ and Group II are related as composition (Group I+) and method making the composition (Group II) and share the common feature of the siloxane compound of formula I. However, this shared feature is not a contribution over the prior art because it is anticipated by US 4,877,528 A to Friesen et al. (hereafter 'Friesen').

Friesen discloses a siloxane compound of formula I, wherein each of R1-R8 is trifluormethyl (col 5, ln 2-30, di-(trifuoromethyl)siloxane; Tetramer I, when dimethyl group is replaced with di (trifluoromethyl) group).

Therefore, the inventions of Groups I+ and Groups II-III lack unity under PCT Rule 13.
Continuation of Item 4: Claims 4-9, 34-37 have been determined unsearchable because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).