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(54) Title: OPTICAL GAIN MEDIA

(57) Abstract: Optical gain media and methods for making and using them are provided. An exemplary composition includes at least one suitable metal, at least one first ligand and at least one second ligand. These compositions can be used to make optical elements, components, and subsystems, including, for example, waveguides (e.g., optical fibers and films), optical amplifiers, lasers, compensated optical splitters, multiplexers, isolators, interleavers, demultiplexers, filters, photodetectors, and switches.

OPTICAL GAIN MEDIA AND METHODS FOR MAKING AND USING SAME

DESCRIPTION OF THE INVENTION

[001] This claims priority to U.S. Provisional Application No. 60/314,902, filed August 24, 2001, which is hereby incorporated by reference in its entirety.

Field of the Invention

[002] This invention relates generally to methods and apparatus for making and using optical gain media. More particularly, this invention relates to metal ligand compositions for use in optical elements, components, subsystems, and systems, including, for example, optical waveguides, amplifiers, and lasers.

Background of the Invention

[003] Optical fiber networks have been increasingly employed in long distance, metropolitan, and local access communication systems. Although these networks have substantially increased data transmissions capacity, there remains an increasing need for efficient, compact optical amplification and gain media from which various optical elements, components, and subsystems can be fabricated.

[004] Optical communication systems based on glass optical fibers (hereinafter, "GOFs") allow data to be transmitted over long distances with low attenuation at extremely high data transmission rates. These high rates result from the propagation of a single optical signal mode in low-loss windows of glass located at the near-infrared wavelengths such of 0.85 nm, 1.3 μm, and 1.55 μm. Recent developments in the fields of optical amplification and gain media include the use of erbium doped fused silica fiber.

[005] Since the introduction of the erbium-doped fiber amplifier (hereinafter, "EDFA"), the last decade has witnessed the emergence of single-mode GOF as the

standard data transmission medium for wide area networks (hereinafter, "WANs"), especially in terrestrial and transoceanic communication network backbones. In addition, the bandwidth performance of single-mode GOF has been vastly enhanced by the development of dense wavelength division multiplexing (hereinafter, "DWDM"), which can transmit up to 160 channels of different wavelengths of light through a single fiber, with each channel carrying multiple gigabits per second. Moreover, a signal transmission of 1 terabit (10^{12} bits) per second was achieved over a single fiber on a 100-channel DWDM system. Enabled by these and other technologies, the bandwidth capacity of many networks is increasing as quickly as an order of magnitude per year.

[006] The success of single-mode GOF in long-haul communication network backbones has accelerated optical networking technologies. An objective is to integrate voice, video, and data streams over all-optical systems as communication signals make their way from WANs down to smaller local area networks (hereinafter, "LANs"), fiber to the curb (hereinafter, "FTTC"), fiber to the home (hereinafter, "FTTH"), and finally to the end user by fiber to the desktop (hereinafter "FFTD"). Increased use of the Internet and the World Wide Web are demanding even higher bandwidth performance, especially in short- and medium-distance applications. Optical communication links include, however, numerous fiber connections, splices, and couplings which introduce optical loss. To compensate for this loss, relatively expensive and bulky EDFAs are used. For example, the cost of a typical commercially available EDFA can be tens of thousands of dollars and extend for lengths that are 40 meters or more. Thus, to complete the planned build-out for

FTTC and FFTD could require the purchase of millions of EDFAs at a cost of hundreds of billions of dollars.

[007] A conventional EDFA module includes a number of components. One of the most critical components in the module is the erbium-doped silica fiber (hereinafter, "EDF"). Conventional EDF performance is currently limited by a low concentration of erbium atoms (i.e., the maximum concentration is about 0.1%). Performance is also limited by clustering of the erbium atoms, which leads to a quenching of the desired photoluminescence effect, a relatively narrow emission band, a highly wavelength-dependent gain spectrum, and an inability to be fabricated in a compact, planar geometry. As a result, research efforts have been directed toward the use of other rare earth ions in fused silica glass hosts and other types of glasses, including fluoride, tellurite, and phosphate glasses.

[008] Those efforts have been limited, however, by their inability to dissolve rare earth atoms, their limited mechanical properties, their thermal instability, and a variety of other key physical limitations. For example, Mylinski et al. (IEEE Photon. Technol. Lett., Vol. 11, pp. 973-975, (Aug 1999)) disclose some of the typical limitations of glass fibers, including length limitations due to upconversion effects, low ion concentration capacity, and limited mechanical flexibility. The compositions described herein can be used to make optical materials (including optical fibers, elements, components, modules, and subsystems) that overcome these and other limitations.

SUMMARY OF THE INVENTION

[009] The invention is directed generally to compositions that include ligands and metals for use in optical materials and applications. The metals and ligands are chosen to provide appropriate optical properties for any desired optical material or device.

[010] In one illustrative embodiment consistent with this invention, a composition is disclosed. The composition can include at least one suitable metal, a first ligand, and a second ligand. The metal can be selected from aluminum (Al), chromium (Cr), scandium (Sc), yttrium (Y), lutetium (Lu), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), and ytterbium (Yb). This composition can include phosphinates or polymers. This composition can be used as an optical composition.

[011] In one embodiment, the optical composition can have a transmission window of about 1200 nm to about 2000 nm, where the wavelength range is obtained with a common host platform. In another embodiment, the transmission window can be between about 1500 nm and about 1600 nm using a common host platform. In another embodiment the optical composition can have high concentrations of metals without associated quenching and upconversion penalties, allowing use of relatively short fiber lengths (e.g., as small as a few centimeters or less). In another embodiment, the optical composition can have a low intrinsic optical loss. In still another embodiment the optical composition can be drawn into single mode optical fiber, cast into films for planar waveguide applications, or used

to make amplifiers, lasers, multiplexers, isolators, interleavers, demultiplexers, filters, switches, highly-sensitivite photodetectors and other optical devices.

[012] In another embodiment, a relatively long length of fiber (e.g., tens of meters) for efficient, compact, broadband amplification (more generally, for use as gain media) is provided. The relatively long fiber can accommodate a relatively low pumping level, a reduction of packaging complexity, and an increase in network capacity.

[013] In yet another embodiment, a method of making a complex that includes a suitable metal and an acid is provided. The method can include: (a) admixing at least one acid in at least one hydroxide salt in an inert solvent to produce a first salt, (b) optionally, recovering the first salt, (c) admixing the first salt with at least one suitable metal, (d) optionally stirring up to about 72 hours, and (e) recovering the complex.

[014] Another illustrative complex for amplification or gain media includes ligands incorporated into a cyclic or cage structure. In one embodiment, this cyclic or caged structure can allow formation of intramolecular complexing, thereby potentially reducing intermolecular bonding and potentially resulting in the formation of highly active complexes, which do not form insoluble aggregates. In another illustrative embodiment, the association tendency of the cyclic or caged structure can increase the yield of highly active complexes. The ligand could be phosphinate, phosphate, sulfate, sulfite, thiosulfite or any other ion, or any structure capable associating with metals. In another embodiment, these complexes can be mixed with or linked to a polymer matrix, where this polymer matrix could be

perhalogenated organic compounds, perfluoro, perchloro, mixed fluoro, chloro, and bromo compounds, as well as polyimides and perhalo-siloxanes.

[015] It will be appreciated that a broad range of optical devices can be made from the above-mentioned compositions consistent with this invention.

[016] In another embodiment consistent with this invention, a method is provided for making a gain medium. The method can include: (a) admixing at least one complex with at least one solvent to form a mixture, (b) heating the mixture to a temperature between about 50°C and about 150°C, (c) cooling the mixture to a temperature between about 20°C and about 30°C, (d) admixing a perfluoropolymer, and (e) forming a gain medium.

[017] Compositions consistent with this invention can be used to fabricate a variety of optical elements, including: (a) optical waveguide materials that can be processed using conventional silicon VLSI (i.e., "very large scale integration") fabrication methods and optical fiber drawing processes, (b) fiber amplifiers that incude materials having a low optical loss in short and medium distance optical communication networks, and (c) integrated optical components, such as low-loss splitters, that combine amplification/gain properties, split optical input signals, and maintain a high optical signal-to-noise ratio, (d) lasers, (e) modulators, and the like.

[018] Additional objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

[019] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

[020] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate non-limiting embodiments of the invention and together with the description, serve to explain the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[021] FIG. 1 shows an exemplary diagram showing optical fiber loss vs. wavelength of doped polymer blends for optical amplification and gain, consistent with this invention.

[022] FIG. 2a shows an energy level diagram corresponding to a lasing process consistent with this invention.

[023] FIG. 2b shows an energy level diagram for a metal-chromophore consistent with this invention.

[024] FIG. 3 shows exemplary embodiments of branched structures consistent with this invention.

[025] FIGS. 4a-4c shows exemplary embodiments of caged structures consistent with this invention.

[026] FIG. 5a shows exemplary embodiments of polymer structures, which include side chains that can be the same or different, consistent with this invention. The structures show side chain and backbone functional group locations and can be random to prevent crystallization.

[027] FIG. 5b shows another exemplary embodiment of a complex consistent with this invention. Again, the side chains can be the same or different and the structures can be random to prevent crystallization.

[028] FIG. 6 shows a perspective view, not to scale, of an exemplary embodiment of an optical fiber with cladding partially stripped away consistent with this invention.

[029] FIG. 7 shows a cross-sectional view of the exemplary embodiment shown in FIG. 6, taken along line 7-7 of FIG. 6, showing relative diameters of the core and cladding consistent with this invention.

[030] FIG. 8 shows an exemplary embodiment of a polymeric fiber fabrication technique consistent with this invention.

[031] FIG. 9a shows a cross-sectional view of an exemplary waveguide made using a composition consistent with this invention.

[032] FIG. 9b shows exemplary simplified schematic diagrams of optical devices that can be made using compositions consistent with this invention.

[033] FIG. 9c shows an exemplary optical amplifier module that can be made with compositions consistent with this invention

[034] FIG. 10a shows a simplified flow chart of in situ formation of illustrative complexes consistent with this invention.

[035] FIG. 10b shows a simplified scematic diagram of the formation of complexes shown in FIG. 10a consistent with this invention.

[036] FIG. 11 shows an experimental setup used to measure fluorescence lifetimes consistent with this invention.

DESCRIPTION OF THE EMBODIMENTS

[037] As used herein, the term "element" is understood to include ions, atoms, isotopes, and species of atoms of the Periodic Table.

[038] As used herein, the term "suitable metal" refers to one of the metals selected from aluminum (Al), chromium (Cr), scandium (Sc), yttrium (Y), lutetium (Lu), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), and ytterbium (Yb).

[039] As used herein, the term "ligand" means monomers, polymers, oligomers, chelates, adducts, or any molecule that can be used in combination with at least one suitable metal.

[040] The term "complex" means any combination of at least one ligand with at least one suitable metal. The complexes can be charged or uncharged.

[041] The term "substantially free from" for example a given bond type, means having less than the number of the bond types, such that the contribution to the absorbance in the wavelength range between about 1200 nm and about 2000 nm is less than about $5x10^{-5}$ absorbance units/cm.

[042] As used herein, the term "halide-to-hydrogen weight percent" of a molecular entity (e.g., complex, ligand or solution) is defined as (wt% of halide)/((wt% of halide)+(wt% of hydrogen)). Similarly, the term "fluoride-to-hydrogen weight percent" of a molecular entity (e.g., complex, ligand or solution) is defined as (wt% of fluoride)/((wt% of fluoride)+(wt% of hydrogen)).

[043] Also, as used herein, the term "optical gain media" includes any material that increases an optical signal transmitted from one point to another through the material, including particularly, those materials used to form amplifiers, lasers and the like.

[044] Metal waveguide amplifiers normally operate on 3 and 4 energy-level transition principles. The single pass gain of the waveguide amplifier or gain medium is, in general, the fundamental parameter to be calculated. Amplification in a suitable metal-polymer waveguide, as with most types of laser systems, can be described with a 3-level model. FIG. 1, for example, shows how the optical gain of a material can be customized to perform at various wavelengths by using different suitable metals.

[045] FIG. 2a shows an illustrative energy level diagram consistent with this invention. Within an amplifier, for example, the suitable metal ions within the gain media start out in their ground state (i.e., level 1). The electrons are then excited to level 2 by a pump beam of photons with energy $h\omega_p$ equal to the transition energy from level 1 to level 2. The ions subsequently undergo fast nonradiative decay to level 3, which is metastable state of the system. Because the lifetime of this metastable state is relatively long in comparison to level 2, which undergoes the nonradiative decay, a population inversion is created in level 3. Thus light passes by the ions in the gain medium and stimulates emission of photons with the same signal energy, $h\omega_s$. This emission corresponds to the decay from energy level 3 to energy level 1, the ground state.

[046] In one illustrative embodiment, the manifold of electronic excited states of a suitable metal ion can be altered by the presence of or encapsulation by a ligand's chromophore unit. In other embodiments, there can be one or more mechanisms to transfer energy from the ligand's chromophore unit to the suitable metal ion. In an illustrative embodiment, the excited state of the suitable metal ion can be populated by an initial selective absorption ("light harvesting") by the ligand's chromophore unit, followed by energy transfer to the suitable metal ion. Consistent with certain embodiments of this invention, this transfer can approach unit efficiency and can thus increase the absorption cross-section by 10^4-10^5 times compared to that of bare suitable metal ion.

[047] The energy level diagram corresponding to the process described above is shown in FIG. 2b. As shown, a chromophore ligand excited from its singlet state by pump light and then decays nonradiatively through intersystem crossing (IC) to its bottleneck triplet state. Radiative transitions back to the ground state are spin forbidden and, hence, the chromophore ligand can relax through energy transfer to the encapsulated suitable metal ion. This energy transfer efficiency can be increased by tuning the energy gap (e.g., through chromophore design) between the ligand triplet state and the upper level of suitable metal fluorescing transition.

[048] The optical intensity of the transmitted signal is determined in part by the optical attenuation coefficient of an optical waveguide. The various factors contributing to optical loss in optical polymers can be divided into intrinsic and extrinsic loss factors. Intrinsic loss can result from vibrational absorption of the polymer or complex materials, electronic transition absorption, and Rayleigh

scattering. Intrinsic loss is material related and cannot be reduced without changing material composition. Extrinsic loss can result from absorption due to impurities, scattering from dust and microvoids, and imperfections in fiber parameters. Extrinsic loss is usually related to material processing and fiber fabrication, and thus can be reduced by perfecting each procedure.

[049] Conventional optical polymers and complexes can be based on hydrocarbon (C-H) structures. A prototypical example is polymethylmethacrylate (PMMA), which has three principal loss windows located at about 570 nm, about 650 nm, and about 780 nm between absorption maxima arising from C-H vibrational overtone modes. In high optical quality samples, the principal window at about 650 nm exhibits a measured minimum loss of about 110 dB/km, which is close to a theoretical limit of about 106 dB/km. Molecular vibrations of aliphatic hydrocarbons in PMMA are the dominant intrinsic loss factor in optical polymeric waveguides. The fundamental C-H vibration occurs at about 3.2 μm. Although not wishing to be bound to any particular theory, the attenuation loss in the visible wavelength region is affected mainly by the 5th to 7th high harmonics of C-H absorption. At the 650 nm window, C-H absorption contributes about 90 dB/km to the total loss. In the near-infrared region, however, the minimum loss exceeds about 10^4 to about 10^5 dB/km. This loss precludes use of standard optical polymers and suitable metal chromophore structures based on these hydrocarbon structures at three commonly used telecommunications wavelengths of 850 nm, 1300 nm, and 1550 nm.

[050] When designing an optical gain medium, potential nonradiative decay pathways should be considered. In the suitable metal doped medium, the excited suitable metal should be prevented from nonradiatively returning to its ground state via coupling to vibrational modes in the surrounding medium. This can be accomplished by assuring that vibrational modes in the medium present have relatively low energies (for example, less than about 1000 cm^{-1}). A controlled microscopically engineered method for achieving this is to incorporate at least one rare earth ion in an organic or inorganic complex that has exclusively low energy vibrations. Because high vibrations are generally caused by the presence of light atoms, a method of achieving this goal is to eliminate light atoms, such as hydrogen, from the medium. This can be accomplished, for example, in rare earth doped halogenated polymers consistent with this invention. Examples of halogenated polymers include perfluoropolymers.

[051] The intensities of the harmonic absorption bands decrease significantly with each successive harmonic. If hydrogen is replaced with a more massive atom, the wavelengths of the fundamental vibration and subsequent harmonics shift to longer wavelength regions. The order of higher harmonics, which affects the near-infrared region, is higher, resulting in a significant decrease in vibrational absorption.

[052] Indeed, when the short-wavelength O-H and C-H bonds are replaced by C-F bonds having a markedly longer fundamental stretch vibration at 10 μm, the resulting fluoropolymer waveguide exhibits a reduced loss of 10 dB/km with a practically flat dispersion over the near-infrared range. The primary contributing factors to the fluoropolymer loss are wavelength-independent structural waveguide

imperfections and Rayleigh scattering (α_R = 9.5(568/λ)^4 dB/km) based on measurements of fluorinated polymer waveguides. Losses due to electronic absorption are usually negligible as are absorptions from molecular vibrations. The number of C-F vibrational overtones are practically negligable in the visible region. In the near infrared range, the strength of overtones is typically much less than 1 dB/km, even up to about 1500 nm. Consequently, the total theoretical loss of a perfluorinated polymer waveguide can approach 10 dB/km well into the near-infrared and is less than 25 dB/km over most of the visible spectrum.

[053] Varieties of fluoropolymers for passive optical waveguides have been developed for direct use, including, for example, ether-, perfluoromethyl-, and chloro-substituted polytetrafluoroethylenes, acrylates, silicones, polylimides, and co- and ter- polymers of polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF).

[054] The reduction (or elimination) of O-H bonds and the replacement of O-H and C-H bonds with C-F bonds in the polymer fiber waveguide core materials help over all radiative efficiency of the suitable metal systems. The O-H stretch (~3600 cm^{-1}) and C-H stretch (~3200 cm^{-1}) vibrations play a dominant role in phonon-assisted, nonradiative removal of electronic excitation energy from excited suitable metal ions. These nonradiative processes reduce radiative efficiency and, consequently, degrade amplifier device performance. Phonon-assisted decay decreases exponentially with increased number of phonons required to span the energy gap between the metastable state and the ground state. In suitable metal halo-complexes consistent with this invention, high-frequency O-H and C-H bonds can be replaced by C-halogen bonds that possess considerably reduced frequency

vibrations (~1000-1200 cm^{-1}), and as a consequence, the suitable metal sites exhibit long metastable(~1-10 ms) lifetimes.

[055] In one illustrative embodiment of a complex-comprising composition consistent with this invention, small amounts of molecular entities, compounds, ligands, and/or complexes that have O-H or C-H bonds can be included in the composition to enhance or at least modify desired properties of the composition, as desired.

[056] In one illustrative embodiment, the complex-comprising composition is substantially free from at least one of the following C-H, S-H, N-H, O-H, P-H, Si-H, C=O, C=N, C=S, C=C, N=O, C≡C, and C≡N. In other embodiments, the absorbance per cm is less than about $5x10^{-5}$, less than about $2.5x10^{-5}$, or less than about $1.0x10^{-5}$, where these absorbances are in a wavelength range of about 1200 nm to about 2000 nm, or about 1250 nm to about 1700 nm, or about 1250 nm to about 1350 nm, or about 1500 nm to about 1600 nm.

[057] General classes of high optical transparency suitable metal halocomplexes for optical gain media and their applications consistent with this invention are disclosed in the formula and chemical structures taught below. A basic halo-ligand structure avoids the introduction of O-H and C-H bonds and can use C-halo bonds. The Er^{3+} ion concentration in these novel complexes can be relatively high, for example, on the order of 10^{21} ions/cm^3 (~1.7 M). Also taught is the use of commercially available fluoropolymers for cladding materials with suitable metal halo-complexes. In addition to Er^{3+}, other suitable metal ions, as well as

combinations of suitable metal ions, can be encapsulated at high concentrations in a basic polymer structure.

[058] In one exemplary embodiment, the complex-comprising composition has a total concentration of suitable metals that can be greater than about 0.1% with a lifetime of the composition being greater than about 1.5 ms.

[059] In one exemplary embodiment, the complex-comprising composition has a total concentration of suitable metals that can be greater than about 5.9% with a lifetime of the composition being greater than about 5.0 ms.

[060] In another embodiment, the complex-comprising composition can have a total concentration of suitable metals greater than about 1.0% with a lifetime of the composition being greater than about 3.8 ms.

[061] The basic structure of suitable metal complexes consistent with this invention can be an isolated single suitable metal ion encapsulated by a molecular "coordination shell." In one embodiment, to create such a shell, halogenated organic phosphinate ligands can be used with coordinating donor atoms, such as oxygen, to chemically bond to the suitable metal ions. This is believed to isolate the suitable metal ion and form a physico-chemical barrier for the suitable metal ion. These suitable metal complexes are compatible with high-temperature fluorinated polymers, which are suitable as passive cladding materials. Suitable metal concentrations of ~10^{20}-10^{21} ions/cm^3 (equivalent to ~0.17-1.7 M and ~1.0-10% wt/wt) have been achieved with no undesirable effects, such as clustering and lifetime quenching. In some exemplary embodiments, the total suitable metal concentration can be in the range of about $1x10^{-3}$ M to about 3.0 M, or about 0.01 M

to about 2.0 M, or about 0.01% to about 20%, or about 0.1% to about 10%. These relatively high concentrations are to be compared to the 0.1% concentration limit common to most silica glasses and inorganic crystals.

[062] Optical gain can be achieved in rare earth doped halogenated complexes as previously described in copending, commonly owned U.S. Patent Applications Nos. 09/507,582, filed February 18, 2000, and 09/722,821 and 09/722,282, both filed November 28, 2000, which are all hereby incorporated by reference in their entireties.

[063] Some exemplary ligands that can be used to make complexes of the present invention are given below. Other halogenated phophinic acid ligands are described in commonly owned Mininni et al. U.S. Patent Application No. 10/___,___, "Processes For The Preparation of Fluorinated And Halogenated Phosphinic Acids And Their Active Metal Derivatives," filed August 26, 2002, which is hereby incorporated by reference in its entirety.

[064] Some of the ligands and complexes use the following definitions.

[065] Me is methyl.

[066] ^{t}Bu is tert-butyl.

[067] ^{n}Bu is n-butyl.

[068] An "F" inside of a cyclic structure indicates perfluorination.

[069] A_1 and A_2 can be the same or different and are selected from N, S, and O.

[070] A_3, A_4, A_5 and A_6 can be the same or different and are selected from P, and N.

[071] A_7 is selected from S and O.

[072] A_8 and A_9 can be the same or different and are selected from O, S, Se, Te, Po, and N.

[073] A_{10} is selected from B, Ge, Ga, N, P, As, Sb, Bi, S, C, and Si (wherein if A_{10} is C or Si, then $A_{11}R_1$ =nothing).

[074] A_{11} and A_{12} can be the same or different and are selected from O, S, N, and nothing.

[075] A_{20}, A_{21}, and A_{22} can be the same or different and are selected from O, S, Se, Te, and Po.

[076] A_{23} is selected from S, Se, Te, and Po.

[077] A_{25}, A_{28} can be the same or different and are selected from P, As, Sb, and Bi.

[078] A_{26} A_{27}, A_{29}, and A_{30} can be the same or different and are selected from O, S, Se, Te, and Po.

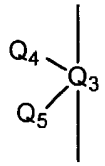
[079] A_{35} is selected from O and S.

[080] A_{36} is selected from -OH, -SH, and -OR_{80}.

[081] M, M_1, M_2, M_3, and M_4 can be the same or different and are selected from aluminum (Al), chromium (Cr), scandium (Sc), yttrium (Y), lutetium (Lu), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), and ytterbium (Yb).

[082] G is selected from nothing, p-$C_6(X)_4$, and p-$C_6(X)_4$-$C_6(X_1)_4$.

[083] G_1, G_2, G_3, G_4, G_5, G_6, G_7, G_8, G_9, G_{10}, G_{11}, G_{12}, and G_{13} can be the same or different and are



[084] Q_1 and Q_2 can be the same or different and are selected from P, As, and Sb.

[085] Q_3 is selected from N, P, As, and Sb.

[086] Q_4 and Q_5 can be the same or different and are selected from O, S, Se, and Te.

[087] Q_6 is selected from B, As, and P.

[088] Q_7 is selected from As and P.

[089] Q_8 is selected from C and Si.

[090] X, X_1, X_2, X_3, X_4, X_5, X_6, X_7, and X_8 can be the same or different and are selected from H, F, Cl, Br, and I.

[091] X_9, X_{10}, X_{11}, and X_{12} are selected from F, Cl, Br, and I.

[092] Z is $Q_2(R_3)_3$ or an oligophosphoranyl group.

[093] i, j, k, and l can be the same or different and are positive, rational numbers that are greater than zero, and less than about 1000, or less than about 100, or less than about 25, or less than about 10.

[094] n, m, and p can be the same or different and are selected from any integer of 1 to 100, or 1 to 20, or 1 to 10.

[095] R_f is selected from perflourinated alkyl, perflourinated aryl, perflourinated cyclic alkyl, perflourinated arylalkyl, and perflourinated alkylaryl.

[096] R_{f1}, and R_{f2} can be the same or different, can be branched or unbranched, can be linked to form cyclic or extended structures, and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, halogenated silazanes, halogenated olefins, fluorinated alkyl, fluorinated aryl, fluorinated cyclic alkyl, fluorinated arylalkyl, fluorinated alkylaryl, fluorinated polyether, fluorinated thioether, fluorinated ether thioether, fluorinated aklyl amino groups, fluorinated alkylene, fluorinated silylene, fluorinated siloxanes, fluorinated silazanes, fluorinated olefins, branched perfluorinated C_{1-20} alkyl, unbranched perfluorinated C_{1-20} alkyl, perfuorinated C_{1-6} alkyl C_{1-10} alkyl ethers, n-C_8F_{17}, n-C_6F_{13}, n-C_4F_9, n-C_2F_5, $(CF_3)_2CF(CF_2)_4$, n-$C_{10}F_{21}$, n-$C_{12}F_{25}$, $(CF_3)_2CF(CF_2)_6$, and $(CF_3)_2CFO(CF_2)_2$.

[097] R_1, R_2, R_3, R_4, R_5, R_6, R_7, and R_8 can be the same or different, can be linked to form cyclic or extended structures, and are selected from halide, halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, and halogenated silazanes.

[098] R_9 is selected from HO- and HS-.

[099] R_{10}, R_{11}, and R_{12} can be the same or different and are selected from R_{50}, R_{51}, R_{52}, R_{53}, R_{60}, $R_{60}O$-, $R_{60}S$-, R_{61}, $R_{61}O$-, $R_{61}S$-, HO-, and HS-.

[0100] R_{21}, R_{22}, and R_{23} can be the same or different and are selected from H, a branched or linear alkyl group having 1-50 carbon atoms, a branched or linear alkenyl group having 1-50 carbon atoms, a branched or linear halogenated alkyl group having 1-50 carbon atoms, –C(O)H, –COOH, –O–R_{30}, –O–R_{30}–OH, –R_{30}–OH, -$COOR_{30}$, $COOR_{30}$–C(O)H, –$COOR_{30}$–COOH, O–R_{30}–NH_2, –NO_2, and an amine group.

[0101] R_{24}, R_{25}, and R_{26} can be the same or different and are selected from -$(CH_2)_{0-3}COOH$, –$(CH_2)_{0-3}COOR_{29}$, –$(CH_2)_{0-3}SO_3H$, –$(CH_2)_{0-3}SO_3R_{29}$, $(CH_2)_{0-3}$–O–$P(O)(OR_{29})_2$, $(CH_2)_{0-3}$-O-$P(O)OH(OR_{29})$, –(CH_2)–O–$P(OR_{29})_3$, -$(CH_2)_{0-3}$-O-$POH(OR_{29})_2$, and –$(CH_2)_{0-3}$–O–$P(O)H(OR_{29})$.

[0102] R_{27} and R_{28} can be the same or different and are selected from -C(O)-O-R_{30}, –C(O)–COOH, –CH(O)–$COOR_{30}$, and -C(O)-$NR_{30}R_{30}$, and further may joined to form a cyclical compound selected from –CH_2–O–$(CH_2$–CH_2–O–$)_{0-3}$–CH_2–, -$(CH_2$-$N(R_{30})$-$CH_2)_{1-4}$-, –C(O)–NR_{30}-R_{31}–NR_{30}–C(O)–, and –C(O)–O–R_{31}–O–C(O).

[0103] R_{29} is a branched or linear alkyl group having 1 to 3 carbon atoms or a phenyl group.

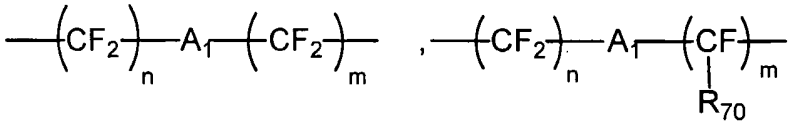
[0104] R_{30} is a branched or linear alkyl group or branched or linear alkenyl group having 1 to 50 carbon atoms.

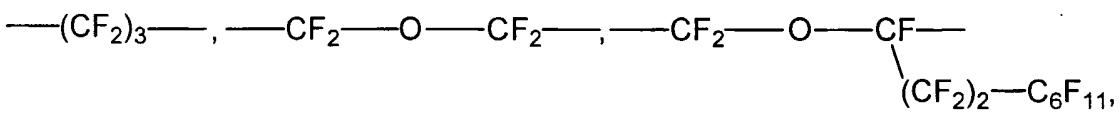
[0105] R_{31} is a branched or linear alkyl group having 2 to 8 carbon atoms.

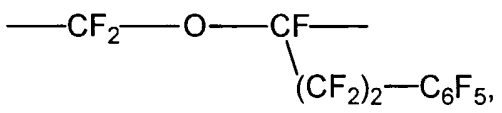
[0106] R_{40} and R_{41} can be the same or different and are selected from H, F, CH_3, C_4H_9, C_5H_{11}, C_6H_5, C_6F_5, C_6H_{13}, C_7H_{15}, C_7H_7, C_8H_{17}, $C_{14}H_{12}O$, and $CB_{10}H_{10}CCH_3$.

[0107] R_{42} and R_{43} can be the same or different and are selected from F_3C-, thenoyl C_4H_3S—, furanoyl C_4H_3O—, t-butyl, and perfluoro-n-propyl (C_3F_7).

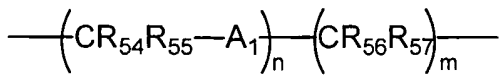
[0108] R_{50}, R_{51}, R_{52}, and R_{53} can be the same or different and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, halogenated silazanes,







$-(CR_{54}R_{55})_n-$, and



[0109] R_{54}, R_{55}, R_{56}, and R_{57} can be the same or different and selected from F, Cl, Br, I, halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes and halogenated silazanes,

halogenated polyamide, halogenated polyether, halogenated polyimide, halogenated polythioethers,

$-(CF_2)_p-CF_3$, $-(CF_2)_p-C_6F_5$, and $-(CF_2)_p-C_6F_{11}$.

[0110] R_{60}, R_{61}, and R_{62} can be the same or different and are selected from (a) substituted or unsubstituted alkyl radicals, such as amyl, isoamyl, hexyl, heptyl, octyl, the isomeric octyls, octadecyl, lauryl, dodecyl (normal or branched chain), tetradecyl, and cetyl (normal or branched chain) radicals, (b) substituted or unsubstituted aryl, such as the phenyl, diphenyl, and naphthyl, radicals, (c) substituted or unsubstituted aralkyl, such as phenyloctadecyl and similar alkyl radicals connected to the central acid-forming atom, e.g. boron or arsenic, and having an aryl group as a substituent in the alkyl chain, (d) substituted or unsubstituted alkaryl, such as octadecylphenyl, tetradecylphenyl, decylphenyl, hexylphenyl, methylphenyl, cetylphenyl, and other radicals where the aryl group is directly attached to the central acid-forming atom, e.g. boron or arsenic, and is substituted with an alkyl group, (e) substituted or unsubstituted radicals containing ether, sulfide, and ester groups, (f) substituted or unsubstituted cyclic nonbenzenoid radicals, such as cyclohexyl or other alicyclic radicals, and (g) substituted or unsubstituted oxy radicals, such as those in which the hydrogen of an hydroxyl group has been replaced by esterification, etherification, neutralization with a metal, or the like, substituted or unsubstituted radicals containing thio, amino, halogen, or other groups.

[0111] R_{75} and R_{76} can be the same or different and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl,

halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, and halogenated silazanes.

[0112] R_{80} can be branched or unbranched and is selected from C_{1-6} alkyl, C_{1-15} alkyl, C_{3-15} aryl, C_{4-15} alkylaryl, and C_{4-15} arylalkyl.

[0113] When two or more ligands are chosen to form a complex and one or more variables from each ligand has the same designation (e.g., both ligands have the variable designation R_1), these variables can be the same or different for each ligand. The ligands can be charged or uncharged. The ligands as shown can be further halogenated, further fluorinated, perhalogenated, and/or perfluorinated.

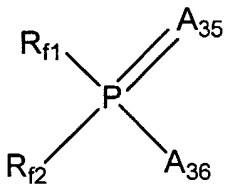
[0114] Exemplary ligands include: benzoyl acetonate ;dibenzoyl methane (dbm); 1,1,1-trifluoro-2,4-pentanedion (tfd); 1,1,1,5,5,5-hexafluoro-2,4-pentanedion (hfd); 2,2'-bipiperazine (bpip); 2,4-pentanediamine (ptdn); picolylamine (pic); 1,8-naphthyridine (napy); tris(2-pyridylmethyl)amine (tmpa); salicylidene aminate (salam); N,N'-disalicylidene ethylenediamine (salen); N-salicycildene cyclohexyl aminate (salch); 1,1,1,3,5,5,5-heptafluoro-2, 4-pentanedion (hepfd); 1,1,1,5,5,5-hexafluoro-3,3-deutero-2,4-pentanedion (hfdd); thenoyl trifluoroacetonate (ttfa); 1,1,1,5,5,6,6,6-octafluoro-2,4-hexanedion (ofhn); 1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedion (dfhn); pentafluorobenzoyl trifluoroacetonate (ofpbd); bis(pentafluorobenzoyl)methane (dfdbm); pentadecafluorooctanoic acid (pdoa); N,N'-disalicylidene-1,2-cyclohexylenediamine (dsalch); acetyl (CH_3CO, Ac); acetylacetonate ($CH_3COCHCOCH_3$, acac); 2,2'-dipyridine, or bipyridine (bpy); benzyl ($C_6H_5CH_2$, Bz); cycloocta-1,5,-diene (C_8H_{12}, cod); cyclooctatetraene (C_8H_8,

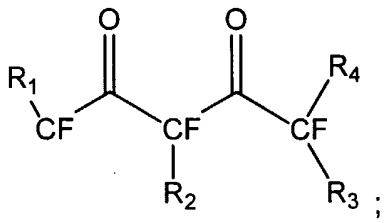
cot); cyclopentadienyl (C_5H_5, Cp); benzene; pentamethylcyclopentadienyl (Cp*); cyclohexyl (C_6H_{11}, Cy); dibenzylmethyl ($C_6H_5COCHCOC_6H_5$, dbm); dimethoxyethane ($CH_3OCH_2CH_2OCH_3$, dme); N,N'-dimethylformamide ($HCON(CH_3)_2$, dmf); 1,2-bis(dimethylphosphino)ethane ($(CH_3)_2PCH_2CH_2P(CH_3)_2$, dmpe); 1,2-bis(dimethylphosphino)methane ($(CH_3)_2PCH_2P(CH_3)_2$, dmpm); ethane-1,2-dithiolate (SCH_2CH_2S, edt); $C_6H_4(C_2H_5)COCHCOC_6H_4(C_2H_5)$ (Et2dbm); hexamethylphosphoric triamide ($OP(N(CH_3)_2)_3$, hmpa); toluene; 2,4,6-trimethylphenyl (Mes, mesityl); $NC_6H_4CH_3$ (Ntol); neopentoxide; benzoate; $CH_3C_6H_4CO_2$; oxalate (C_2O_4, ox); phenyl (C_6H_5, ph); phthalic acid ($C_6H_4(COOH)_2$); picolinate; pyridine; pyrazole ($C_3H_4N_2$); salicylaldehyde ($C_6H_4(OH)(CHO)$, sal); tolyl ($CH_3C_6H_4$, tol); triflate (CF_3SO_3); 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6); glycine; alanine; valine; leucine; isoleucine; methionine; phenylalanine; tryptophane; serine; threonine; asparagine; glutamine; aspartic acid; glutamic acid; cysteine; tyrosine; histidine; lysine; arginine; adenine; cytosine; uracil; guanine; thymine; oxygen(O); halogen; hydroxyl(OH); carbon monoxide (CO); water (H_2O); $C_6H_4O_2$; $C_6H_{12}O_2$; -OC_4H_9 ; -OC_3H_7; -OCH_3 ; -$C_7H_4O_3$; -$C_5H_7O_2$; -OOC_5H_4N; -CH_3; -C_3H_7; -C_4H_9; carbanyldicyanomethanide (cda); di(2-ethylhexyl)phosphoric acid

($(CH_3CH_2CH_2CH_2\underset{\underset{CH_2CH_3}{|}}{CH}\text{-}CH_2O)_2POOH$, dehp); 5,10,15,20-tetraphenyl porphyrin (TPP); 2,6 diaminopyridine; polymers made from $O_2CCH_2CO_2$; polymers made from diberzoylmethane; fluorescein; -$P(OCH_3)_3$; $R_1CH(SO_2R_f)_2$; fluorocarbon acid; triphenylphosphine (Ph_3P); Me_3P; $^nBu_3P$; CH_3CN; PEt_3; $P(OPh)_3$; tetramethylethyldiamine (tmen); $FSbF_5$; FBF_3^-; $OPOF_2^-$; FPF_5^-; $FAsF_5^-$; $FReF_5^-$; $OTeF_5^-$; $R_1R_2\ C(SO_2CF_3)_2$; $R_1N(SO_2CF_3)_2$; $R_1R_2P\text{-}CH_2\text{-}CH_2\text{-}PR_3R_4$;

theroyltrifluoroacetones; $(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2$ (depe); $^tBu_2P(CH_2)_2P^tBu_2$ (dbpe); $(C_6H_{11})_2P(CH_2)_3P(C_6H_2)_2$ (dcpp); $^tBu_2P(CH_2)_3P\ ^tBu_2$ (dbpp); o-$^tBu_2PCH_2C_6H_4CH_2P\ ^tBu_2$ (dbpp); $OPR_{40}R_{41}O$; 1,3-diketones such as acetylacetonate, benzoylacetonate, benzoylbenzoate, trifluoro-2-furylacetylacetone; phthalates and naphthalates such as dinaphthoylmethide; dipyridines and terpyridines such as 2,2'-bypyridine-1,1'-dioxide, 2,2',6',2''-terpyridine, 4,4'-dimethyl-2,2'-dipyridine; and phenanthrolines such as o-phenanthroline isothiocyanate and the like; trioctylphosphine oxide (TOPO); perfluorinated sulfonate polymers; phenantroline; thenoyltrifluoroacetylacetonate; beta-diketonates $R_{42}C(OH)CHCOR_{43}$; anions of aromatic carbonic acids such as benzoic acid, picolinic acid (C_5H_4NCOOH) and dipicolinic acid; pyridine and derivates thereof; trialkyl-, alkylphenyl-, and triphenyl-phosphinoxide; dialkyl-, alkylphenyl-, and diphenyl-sulfoxide, alkyl-, alkylphenyl-, and phenyl-amine; alkyl-, alkylphenyl-, and phenylphosphate; 2,2'bipyridine; 2,2',6,2''terpyridine; 1,10phenantroline; N,N,N',N'-tetramethylethylene diamine and derivatives thereof; $[C_6H_5C(O)CH_2]P(O)(OH)_2$; $[C_6H_5C(O)CH_2]_2P(O)OH$); $[C_6H_5C(O)CH_2]_2P(O)OCH_3$; $[C_6H_5C(O)CH_2]_2P(O)OC_2H_5$; $[C_6H_5C(O)CH_2]_2P(O)OC_6H_4Cl$; $(C_6H_5)_2P(O)OH$; $(C_6H_5—CH=CH)_2P(O)OH$; $(C_6H_5—C\equiv C)_2P(O)OH$; $(C_6H_5)_2P(O)OH$; $(C_6H_5)(CH_3)P(O)OH$; $(CH_3)_2P(O)OH$; $(C_6H_5)_2As(O)OH$; $(CH_3)_2As(O)OH$; $C_6H_5C(O)OH$; $NH_3CH_2P(C_6H_5)O_2$; lipids; polymers; polyamines; schiff bases; β-diketones including benzoyltrifluoroacetone, dibenzoylmethane, ditheonylmethane, furoylacetone, 2-furoylbenzoylmethane, 2-furoyltrifluoroacetone, hexafluoroacetylacetone, 1-acetyl-1-methyl acetone, β-naphthoyltrifluoroacetone, 2-theonylacetone, 2-theonyltrifluoroacetone (4,4,4-trifluoro-1,2-thienyl-1,3-

butanedione), 1,1,1-trifluoroacetylacetone, 1,3-diphenyl-1,3-propanedione and 1-phenyl-1,3-butanedione; hydroxyaldehydes including those derived from benzene and naphthalene, and their alkyl, alkoxy, and halo-substitution derivatives, such as 3-chlorosalicylal- dehyde, 5-chlorosalicylaldehyde, 4,6-dimethylsalicylaldehyde, 2-hydroxy-1-naphthaldehyde, and 2-hydroxy-3-naphthaldehyde; hydroxy acids including salicylic acid, anthraquinone carboxylic acid, and naphthoic acids; 8-hydroxyquinoline and its alkyl, aryl, and halo-substituted derivatives; -NCS; $OPPh_3$; NO_3; ethyne (acetylene); R_1-$CFCO_2^-$; $S_2CNR_1R_2$; $S_2P(C_6H_iF_j)$, where i+j=5; -$N(Si(R_1)_3)(Si(R_2)_3)$; $R_1R_2P{=}N{-}R_3$; $(n\text{-}C_8H_{17})_3P{=}O$; $(n\text{-}C_8F_{17})_2POOH$; $(n\text{-}C_6F_{13})_2POOH$; $(i\text{-}C_3F_7OC_2F_4)_2POOH$; $(n\text{-}C_4F_9)_2POOH$; $[(CF_3)_2CF(CF_2)_6]POOH$; $[(CF_3)_2CF(CF_2)_6]PSOH$; $(n\text{-}C_{10}F_{21})_2POOH$; $(CH_3)_3C\text{-}(CO)\text{-}CH_2\text{-}(CO)\text{-}CF_2CF_2CF_3]$; $[(A_8A_9)A_{10}(A_{11}R_1)(A_{12}R_2)]$; $[NR_3A_8A_{10}R_1R_2]$; $[N(R_1)R_{70}(NR_2)]$; $[(NR_1R_2)(NR_3R_4)]$; $[A_{20}A_{21}A_{22}A_{23}R_1]$; $[R_{75}R_{76}A_{25}(A_{26}A_{27})]$; $[R_{50}A_{25}(A_{26}A_{27})]$; $[R_{50}A_{25}(A_{26}A_{27})R_{51}A_{28}(A_{29}A_{30})]$;





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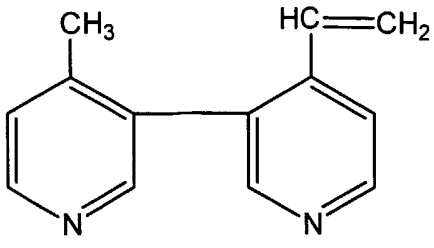

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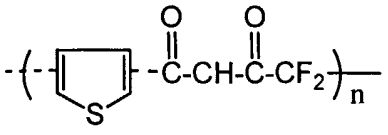

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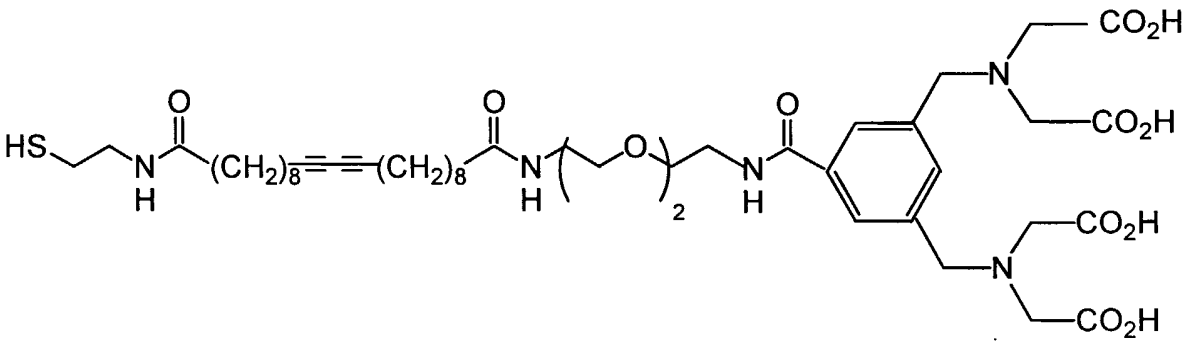

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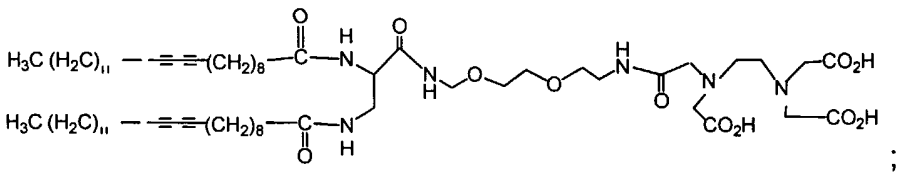

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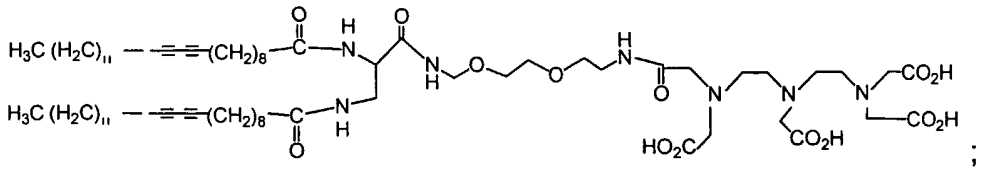

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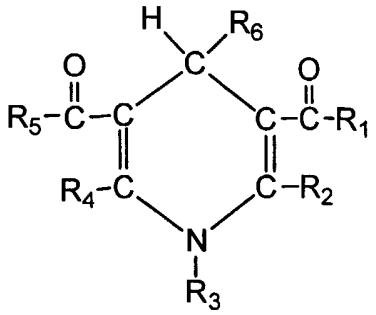

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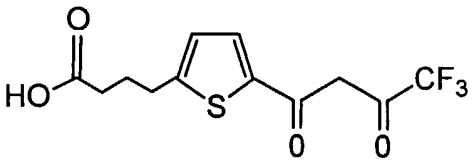

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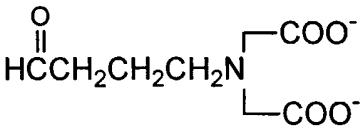

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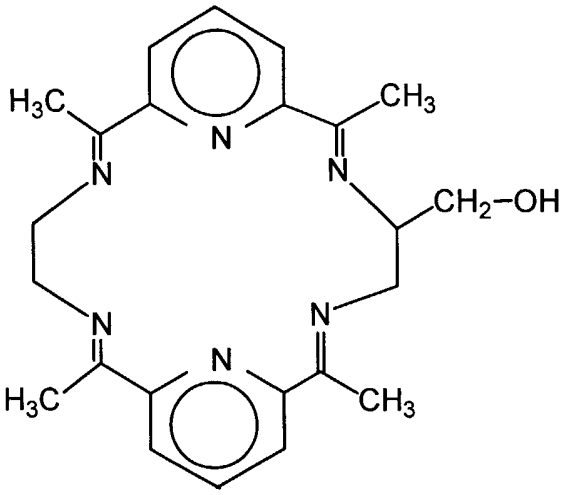

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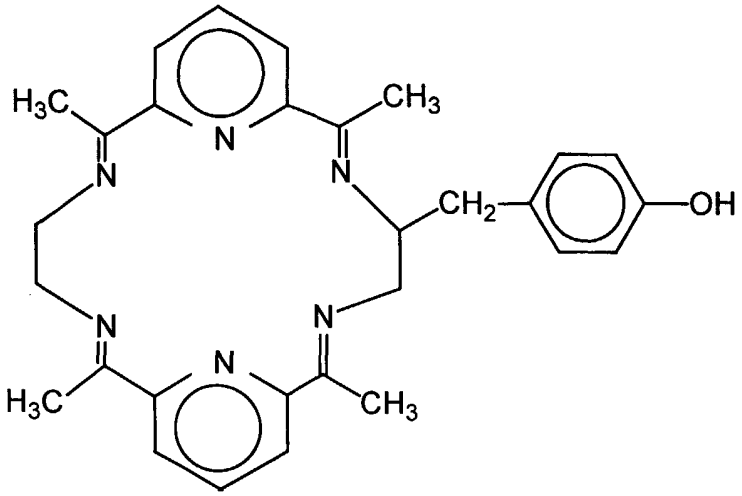

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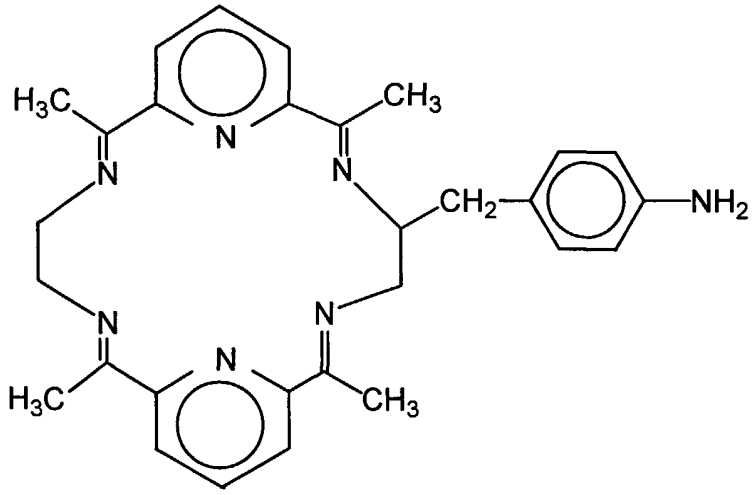

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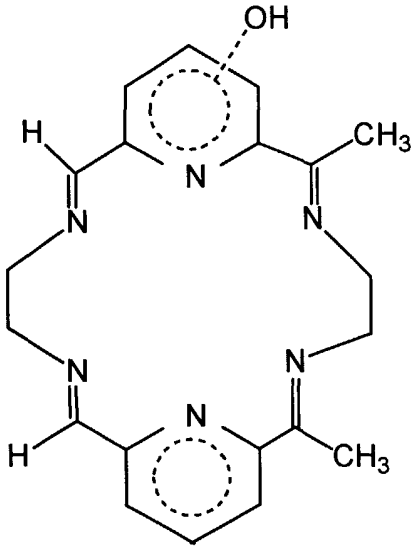

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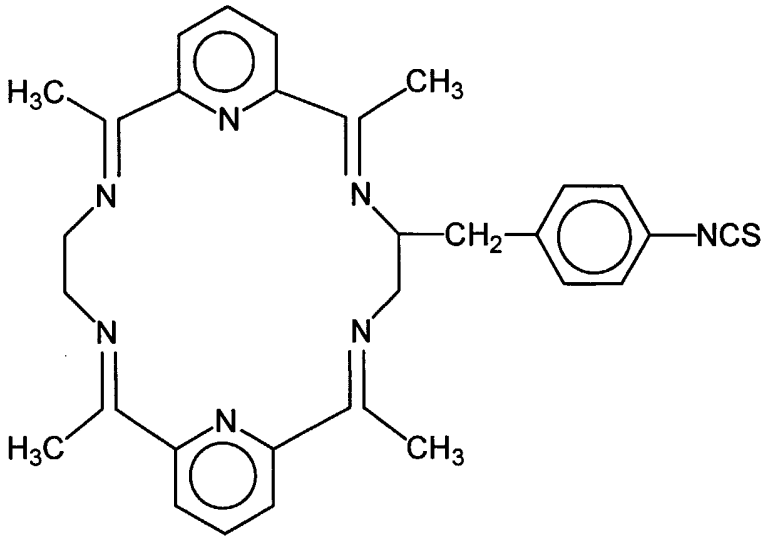

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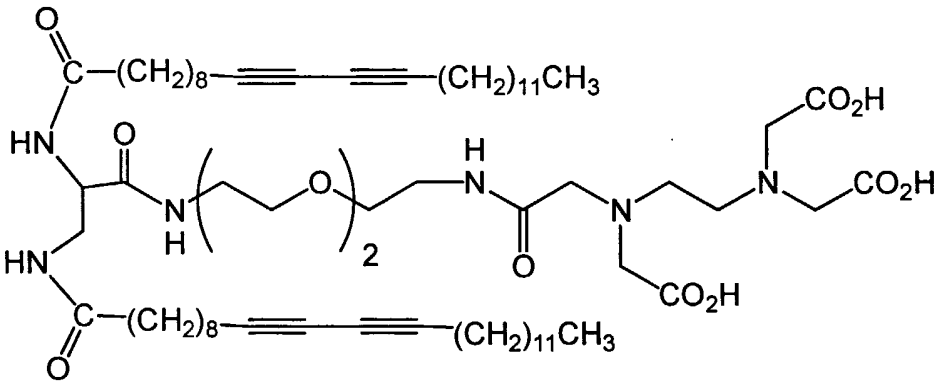

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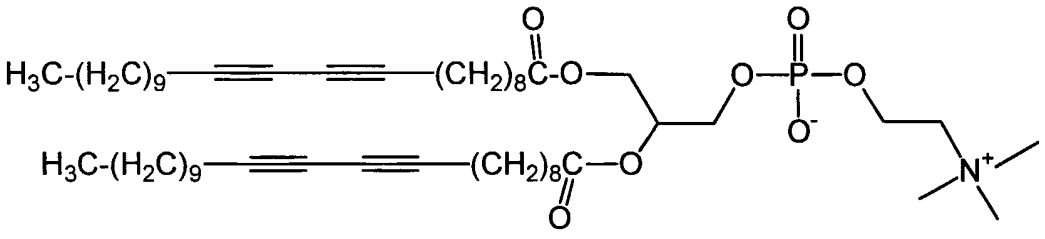

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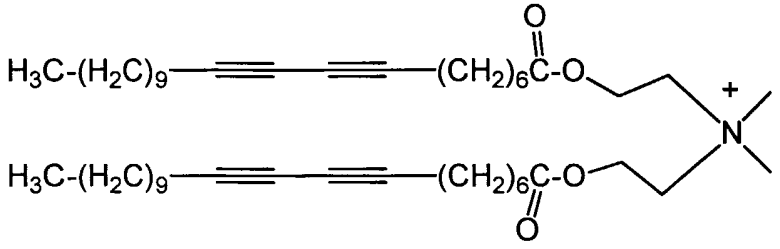

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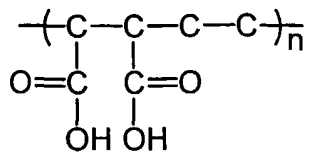

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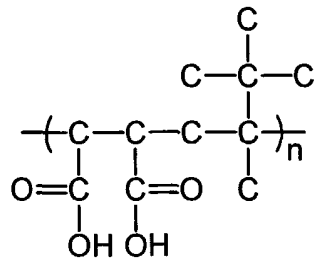

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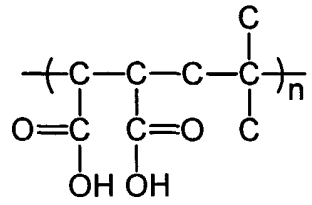

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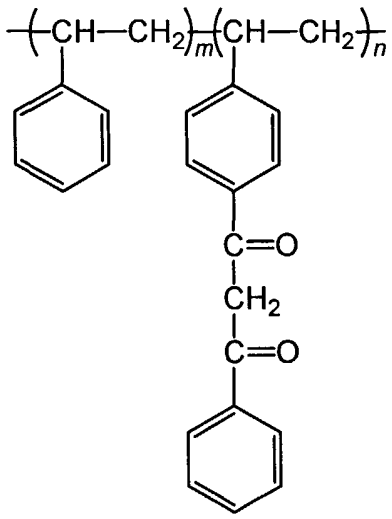

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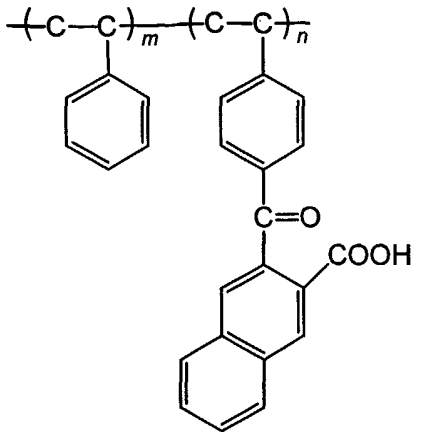

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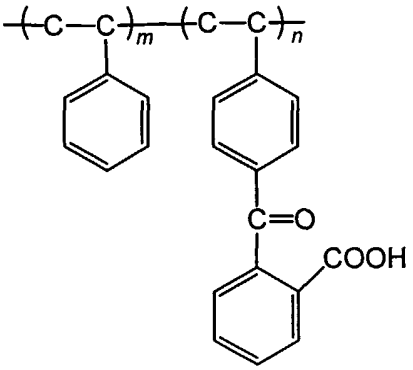

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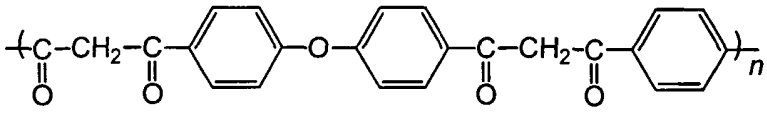

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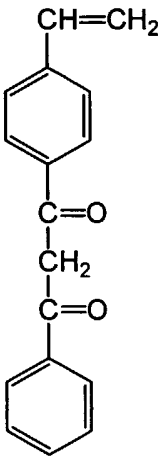
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C=O
CH2
C=O

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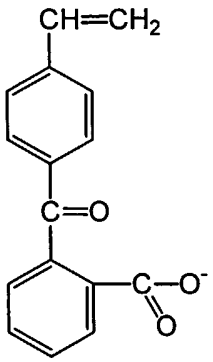
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C=O
C—O-
O

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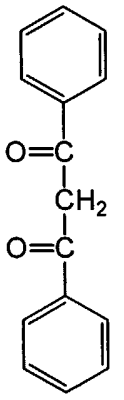
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CH2
O=C

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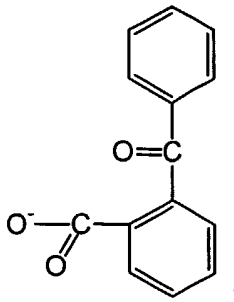

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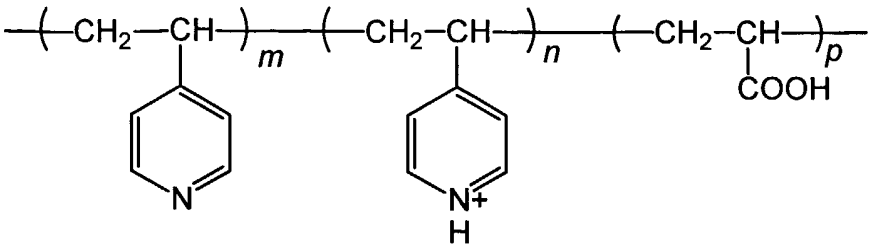

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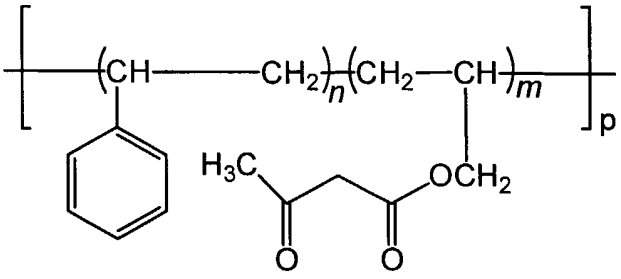

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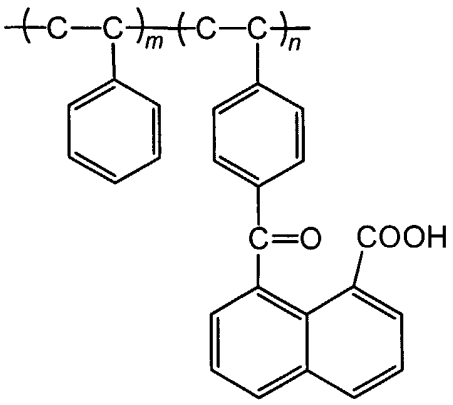

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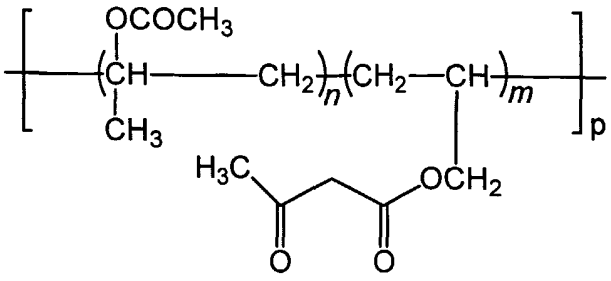

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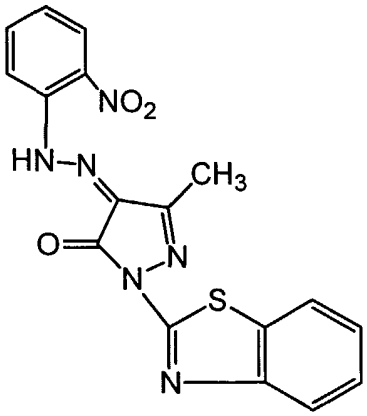

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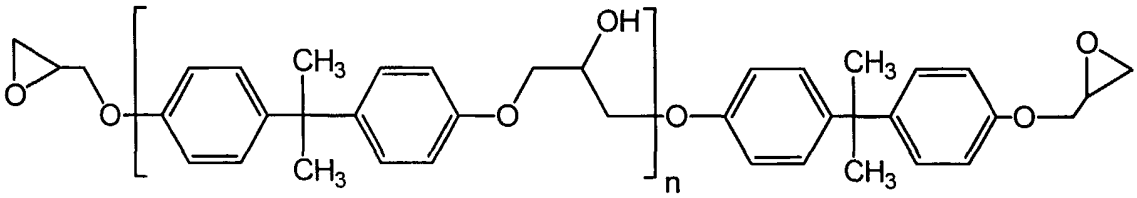

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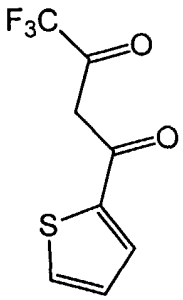

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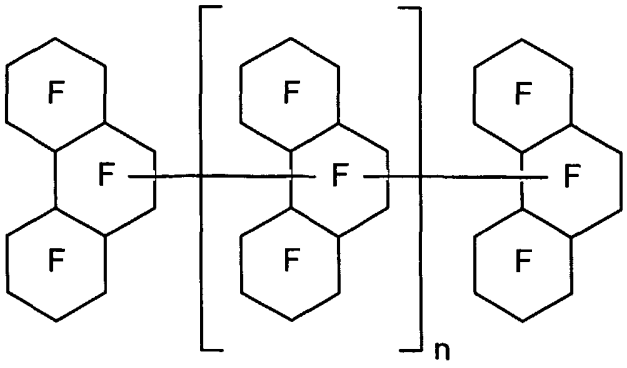
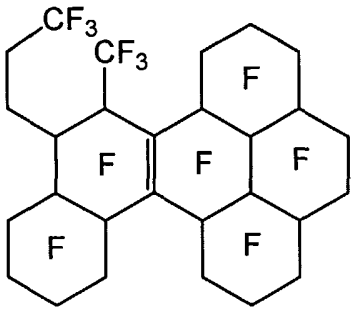

F
F
F
F
F
F
F
F
F
n

;


CF3
CF3
F
F
F
F
F
F
F

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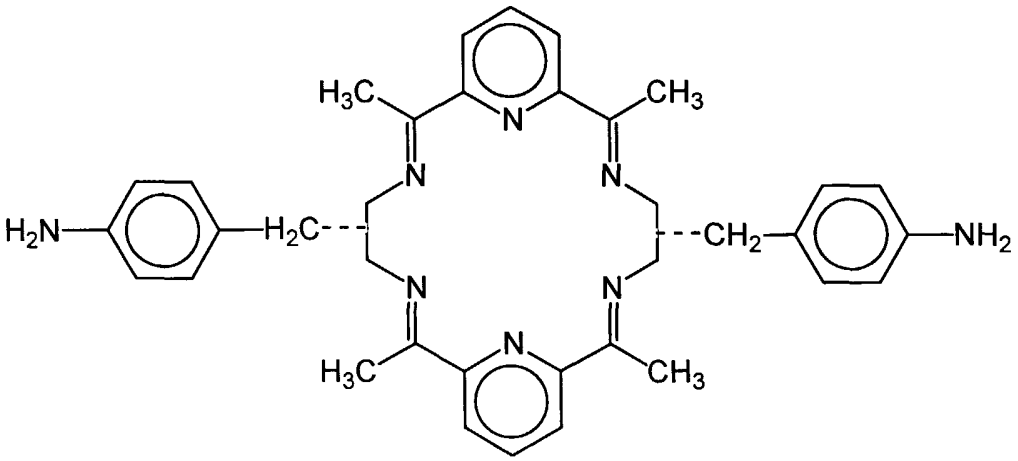
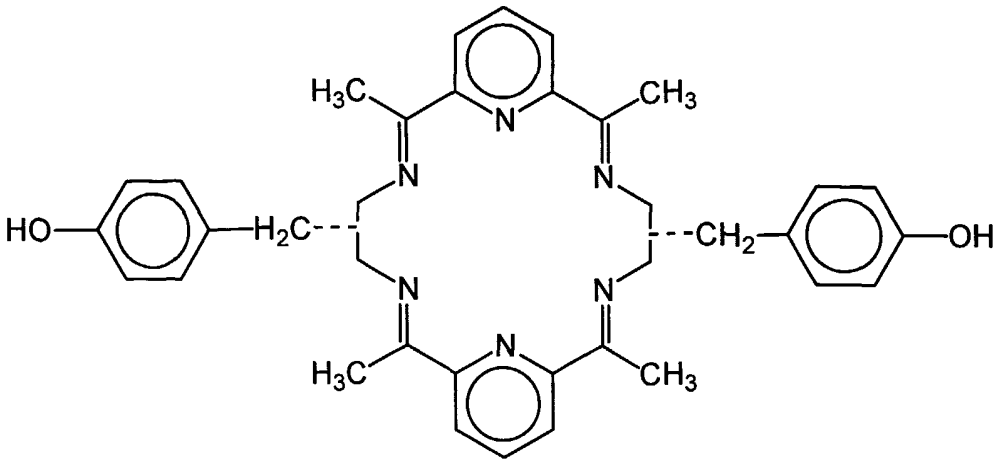

H3C
CH3
N
N
N
H2N
H2C
CH2
NH2
N
N
N
H3C
CH3

;



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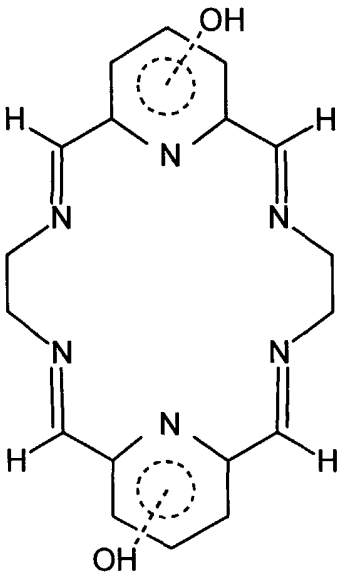

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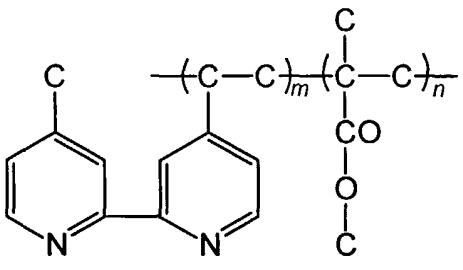

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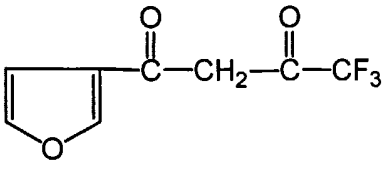
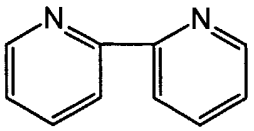

O
O
C
CH2
C
CF3
O
;


N
N
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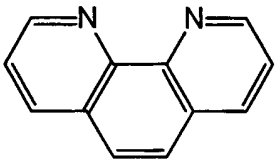
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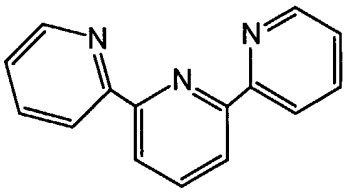
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N
N
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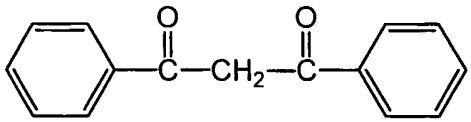
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O
C
CH2
C
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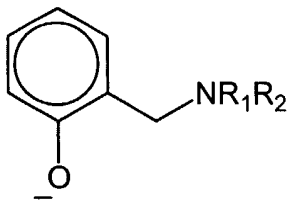
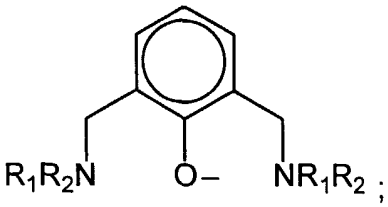
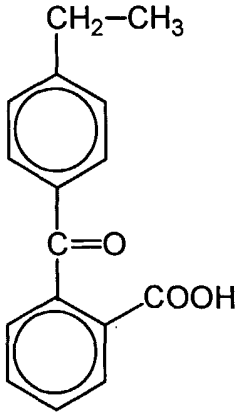

NR1R2
O
;


R1R2N
O–
NR1R2
;


CH2–CH3
C=O
COOH
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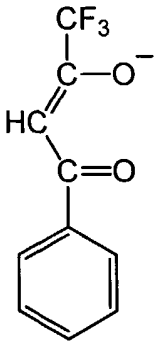
CF3
C–O–
HC
C=O
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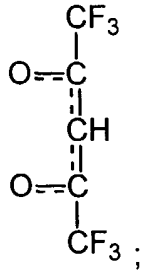
CF3
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CH
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CF3
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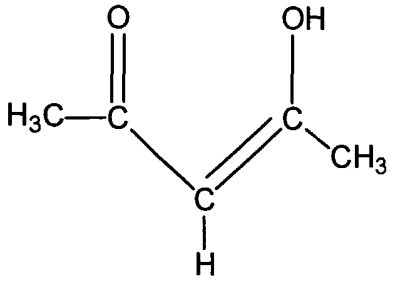

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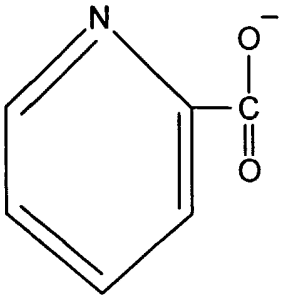

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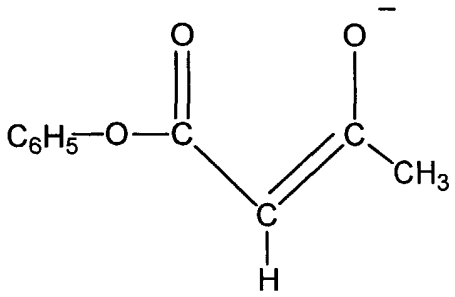

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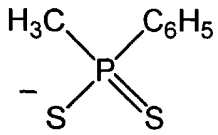

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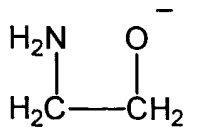

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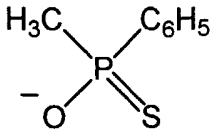
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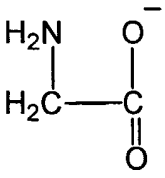
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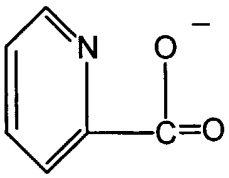
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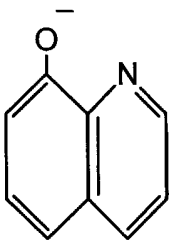
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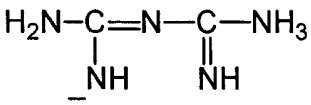
$NH_2CH_2COO^-$;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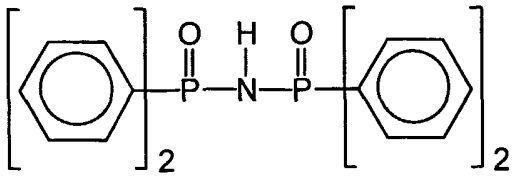

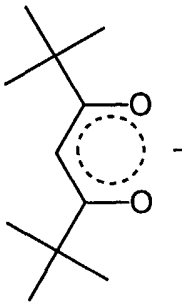

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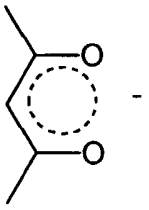

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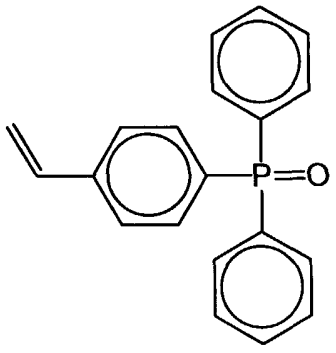

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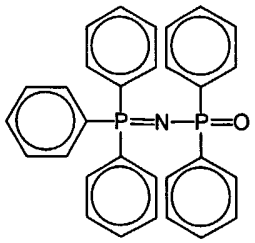
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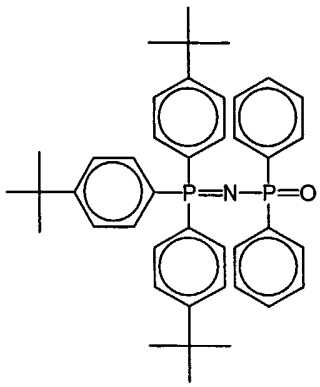
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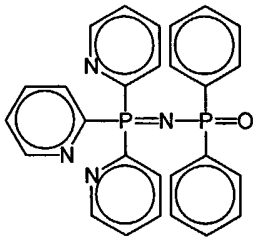
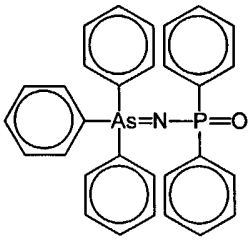

N
P=N—P=O
N
N
;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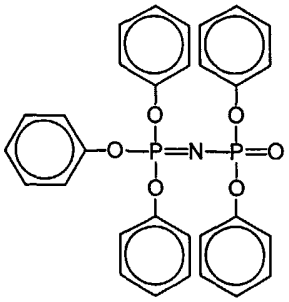
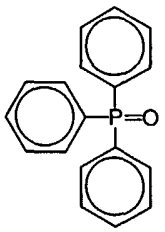

O
O
O
P=N
P=O
O
O
;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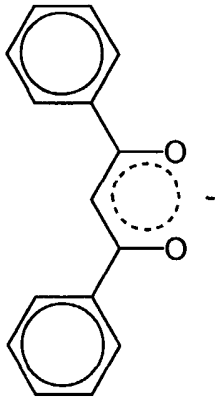
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O
-
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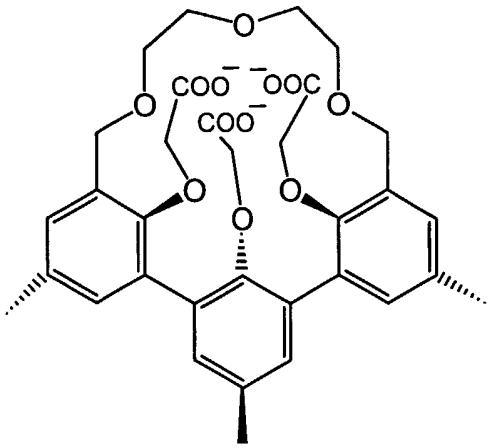

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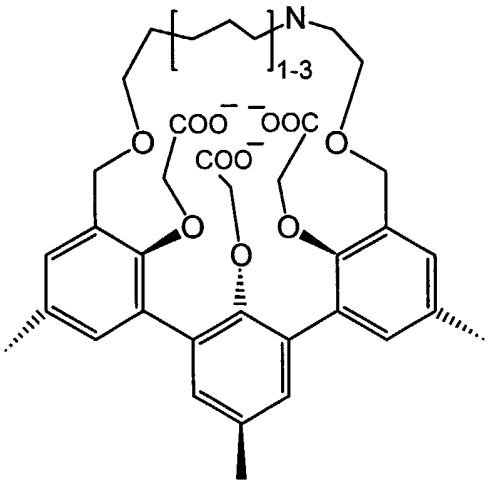

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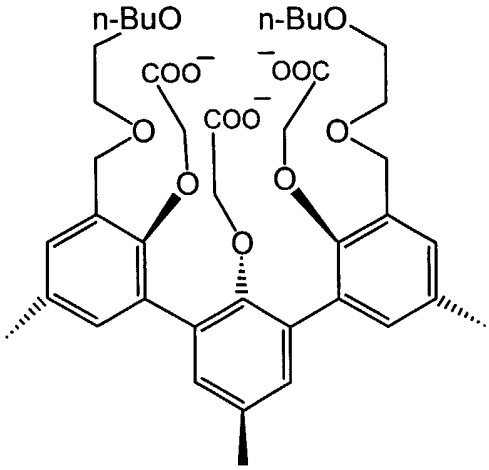

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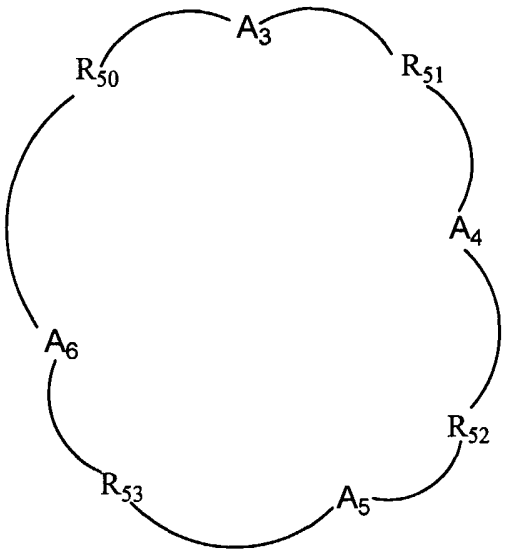
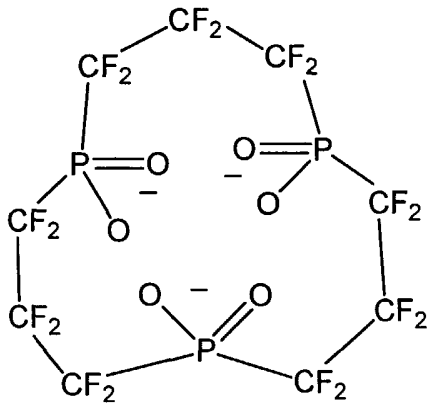

A3
R50
R51
A4
A6
R52
R53
A5

;



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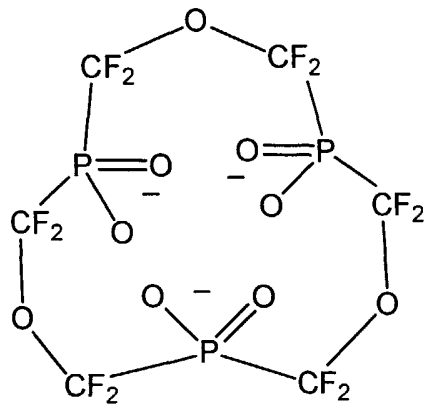

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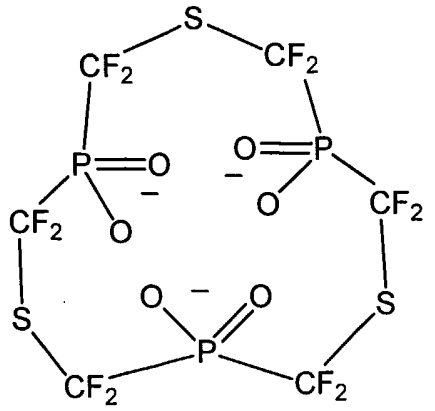

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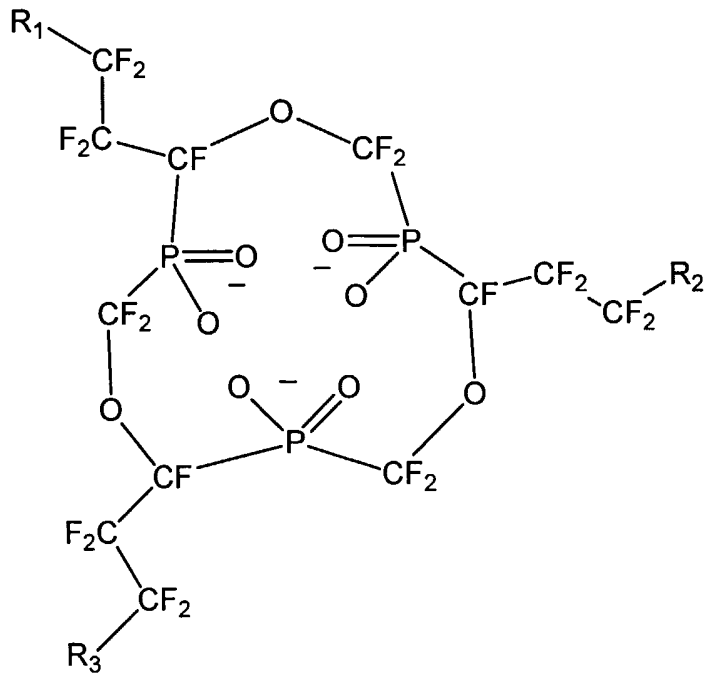

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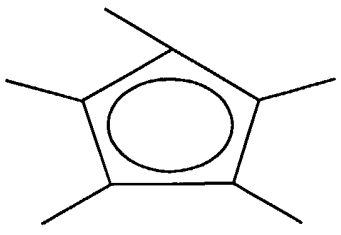

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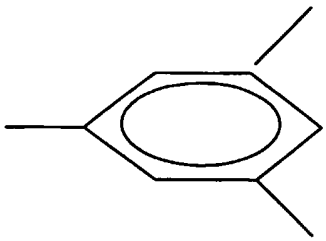
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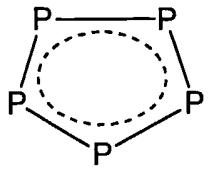
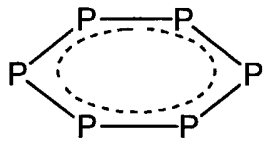
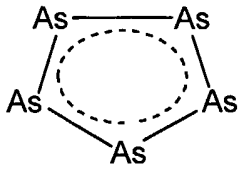
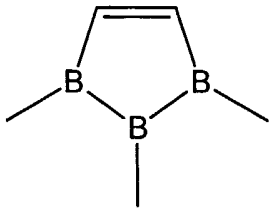
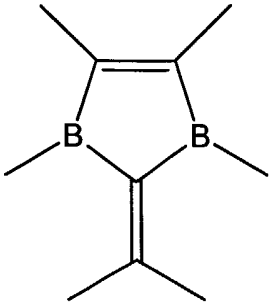
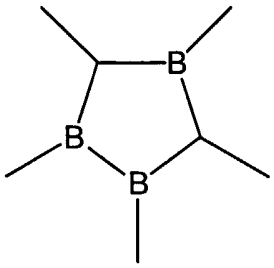

P
P
P
P
P
;

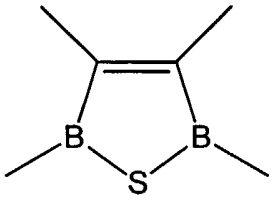

P
P
P
P
P
P
;

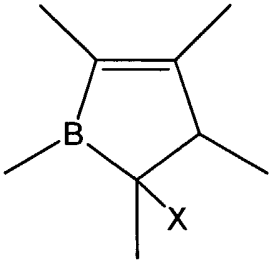

As
As
As
As
As
;

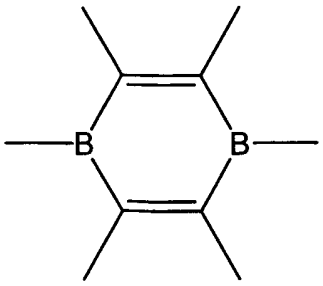

B
B
B
;


B
B
;

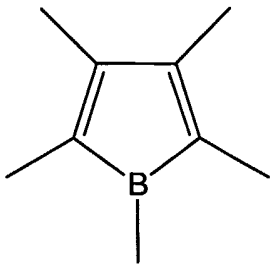

B
B
B
;


B
B
S
;

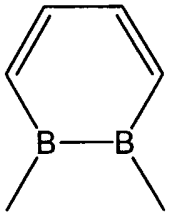

B
X
;


B
B

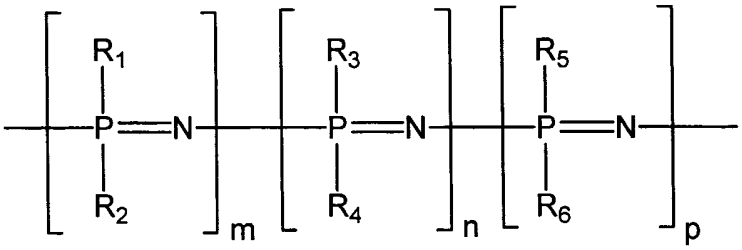
;


B

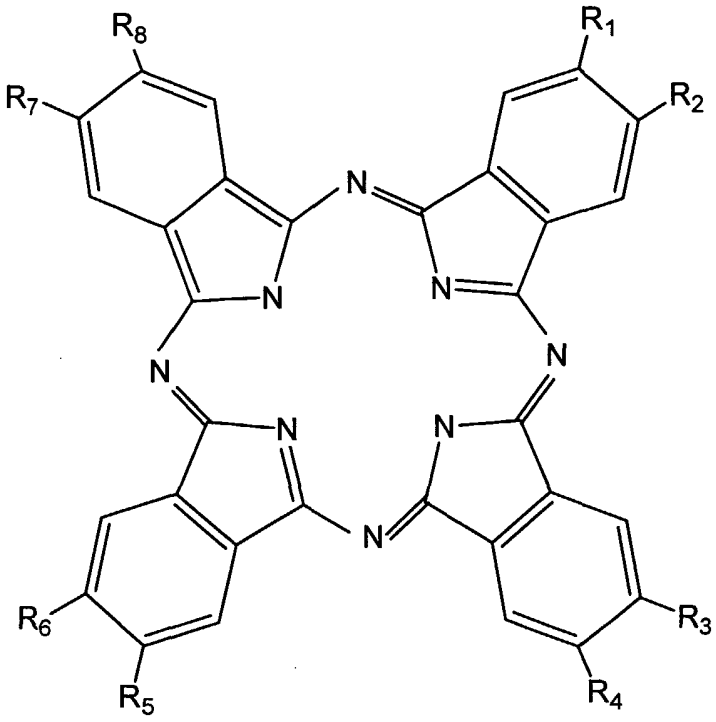
;


B
B

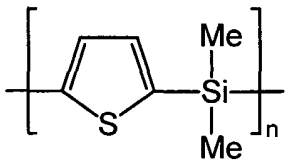
;


R1
P
N
R2
m
R3
P
N
R4
n
R5
P
N
R6
p

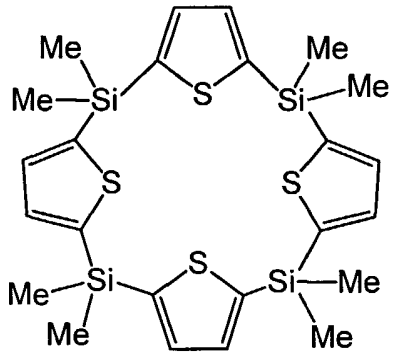
;


R8
R1
R7
R2
N
N
N
N
N
N
N
N
N
R6
R3
R5
R4

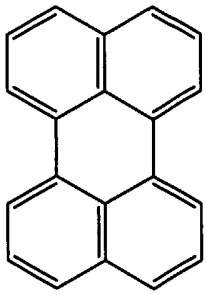
;


Me
Si
S
n
Me

;


Me
Me
Me
Si
S
Si
Me
S
S
Me
Si
S
Si
Me
Me
Me

;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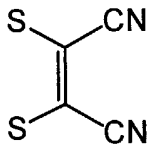
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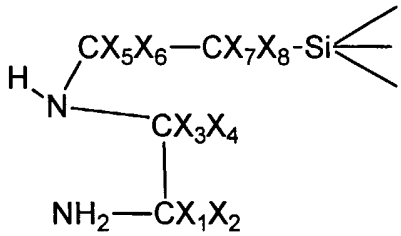
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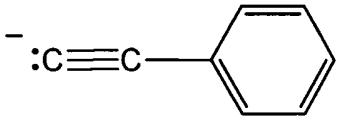
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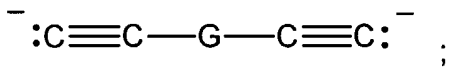
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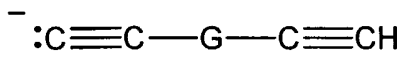
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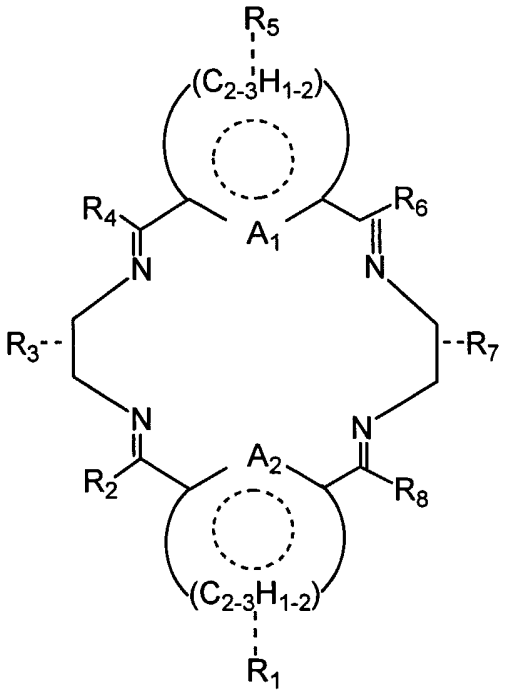
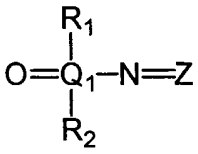
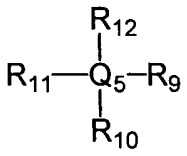

R5
(C2-3H1-2)
R4
A1
R6
N
N
R3
R7
N
N
A2
R2
R8
(C2-3H1-2)
R1

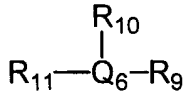
;


R1
O=Q1–N=Z
R2

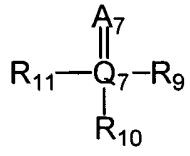
;


R12
R11—Q5—R9
R10

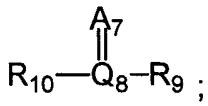
;

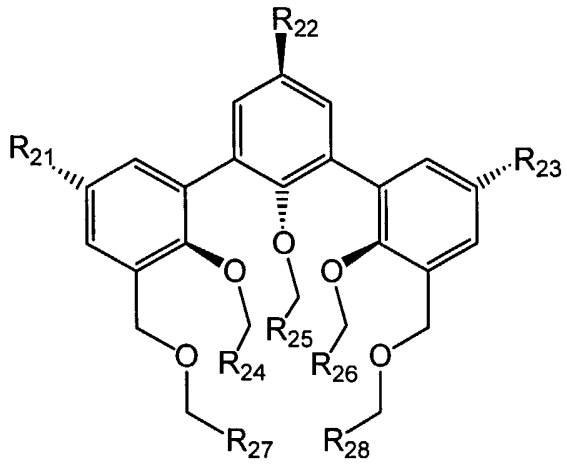

R10
R11—Q6—R9

;

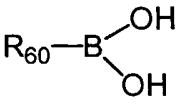

A7
R11—Q7—R9
R10

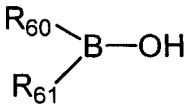
;

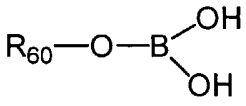


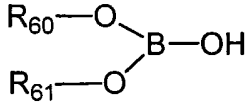


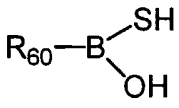
Acids of boron containing an organic substituent such as

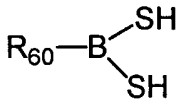
 (Organic boronic acids);

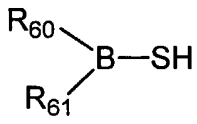
 (Organic boronic acids);

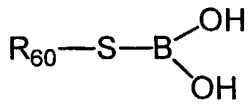
 (Monoesters of orthoboric acid);

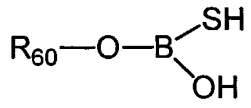
 (Diesters of orthoboric acid);

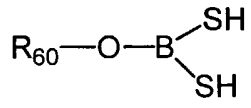

(Organic monothio-boronic acids);

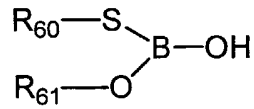

(Organic dithio-boronic acids);

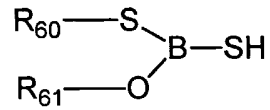

(Organic thio-boronic acids);

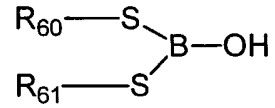

(Monoesters of monothio-organo boric acid);

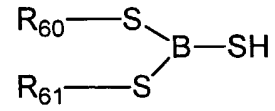

(Monoesters of organo monothio-boric acid);


(Monoesters of organo dithio-boric acid);

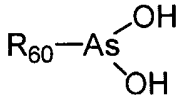

(Diesters of monothio-organo boric acid);

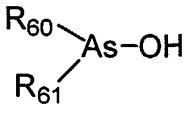

(Diesters of thio-organo thio-boric acid);

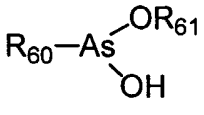

(Diesters of dithio-organo boric acid);

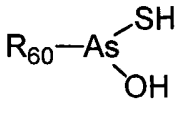

(Diesters of dithio-organo thio-boric acid);

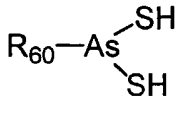
Acids of arsenic containing an organic substituent such as

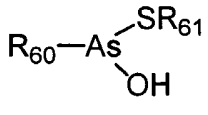

(Organo ortho-arsonous acid (arsine dihydroxides));

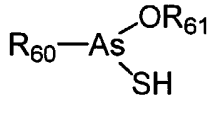

(Organo arsonous acid (diorgano substituted arsine hydroxide));

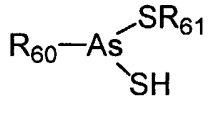

(Monoester of organo ortho-arsonous acid);

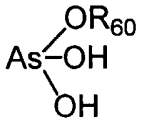

(Organo monothio-arsonous acid);

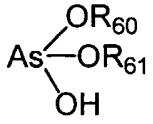

(Organo dithio-arsonous acid);

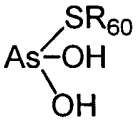

(Monothio-ester of organo arsonous acid);

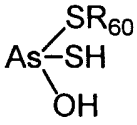

(Monoester of organo monothio-arsonous acid);

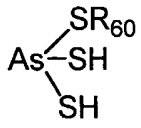

(Monoester of organo dithio-arsonous acid);

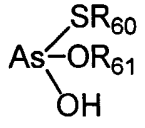

(Monoester of arsonous acid);

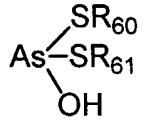

(Diester of arsonous acid);

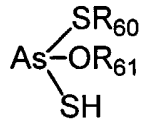

(Monothio-ester of arsonous acid);

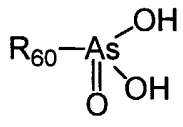

(Monothio-ester of monothio-arsonous acid);

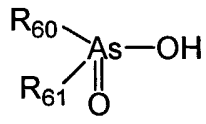

(Monoester of trithio-arsonous acid (monothio-ester of dithio-arsonous acid);

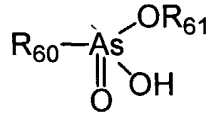

(Monothio-diester of arsonous acid);

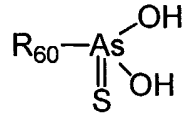

(Dithio-diester of arsonous acid);

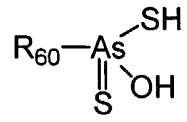

(Monothio-diester of monothio-arsonous acid);

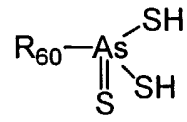

(Organo arsonic acid);

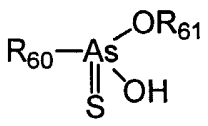

(Disubstituted organo arsinic acid);

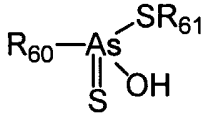

(Monoester of organo arsonic acid);

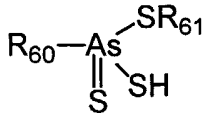

(Organo thion-arsonic acid);

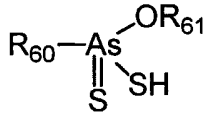

(Organo thion-monothiol-arsonic acid);

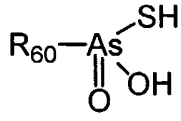

(Organo trithio-arsonic acid);

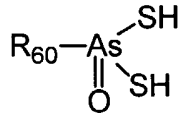

(Monoester of organo thion-arsonic acid);

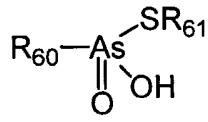

(Monothio-ester of organo thion-arsonic acid);

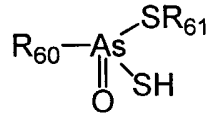

(Monoester of organo trithio-arsonic acid);

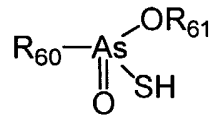

(Monoester of thion-monothiol-arsonic acid);

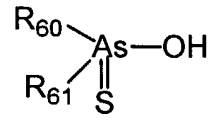

(Organo monothiol-arsonic acid);

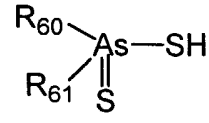

(Organo dithiol-arsonic acid);

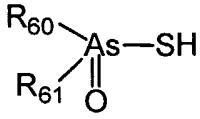

(Monothio-ester of organo arsonic acid);

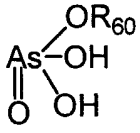

(Monothio-ester of organo thiol-arsonic acid);

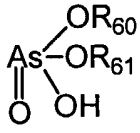

(Monoester of organo thiol-arsonic acid);

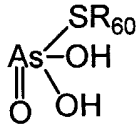

(Diorgano substituted thion-arsinic acid);

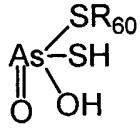

(Diorgano substituted dithio-arsinic acid);

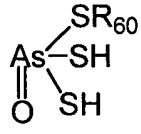

(Diorgano substituted thiol-arsinic acid);

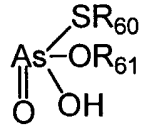

(Monoester of arsenic acid);

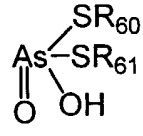

(Diester of arsenic acid);

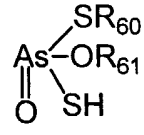

(Monothio-ester of arsenic acid);

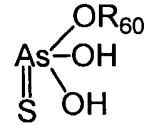

(Monothio-ester of monothiol-arsenic acid);

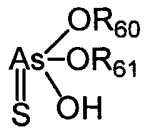

(Monothio-ester of dithiol-arsenic acid);

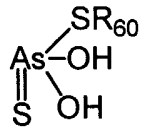

(Monothio-diester of arsenic acid);

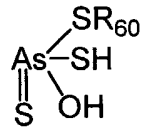

(Dithio-diester of arsenic acid);

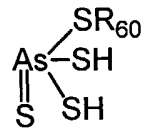

(Monothio-diester of monothiol-arsenic acid);

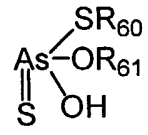

(Monoester of monothion-arsenic acid);

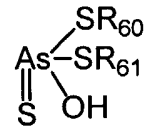

(Diester of monothion-arsenic acid);

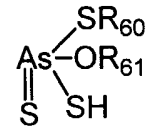

(Monothio-ester of monothion-arsenic acid);


(Monothio-ester of thion-monothiol-arsenic acid);

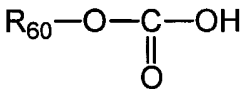

(Monothio-ester of tetrathio-arsenic acid);

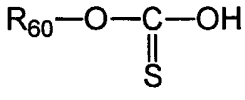

(Monothio-diester of thion-arsenic acid);

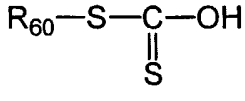

(Dithio-diester of thion-arsenic acid);

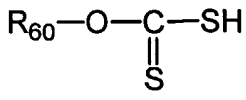

(Monothio-diester of thion-monothiol-arsenic acid);

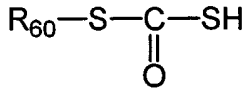
Carbonic acids containing an organic substituent, such as

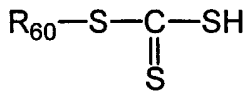

(Partial ester of carbonic acid);

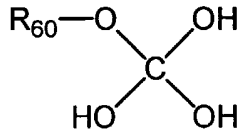

(Partial ester of thion-carbonic acid);

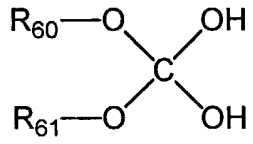

(Monothio-ester of thion-carbonic acid);

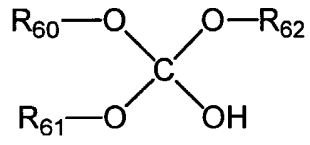

(Monoester thiol-thion of carbonic acid);


(Monothio-ester thiol of carbonic acid);

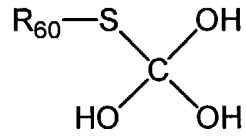

(Partial ester of trithio-carbonic acid);


(Monoester of orthocarbonic acid);


(Diester of orthocarbonic acid);


(Triester of orthocarbonic acid);

and corresponding sulfur derivatives such as—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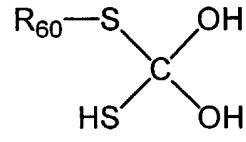
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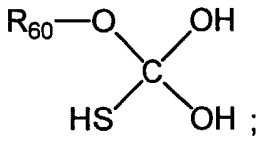
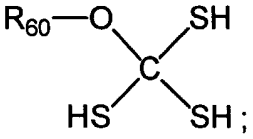
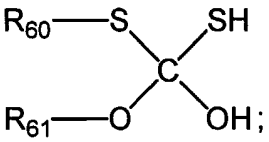
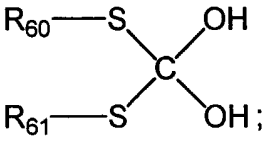
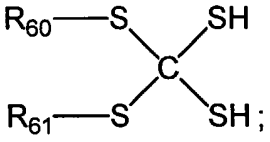
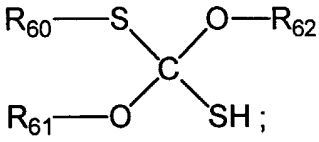


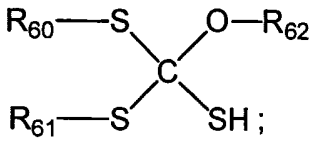


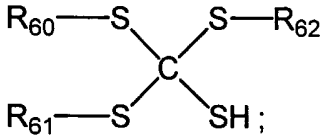


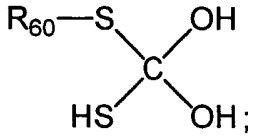


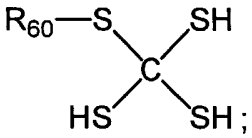


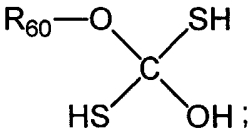


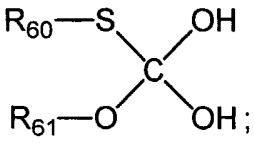


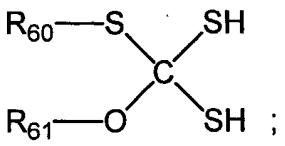


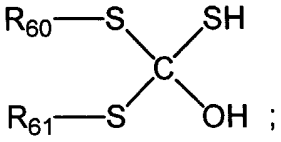


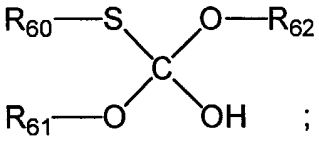


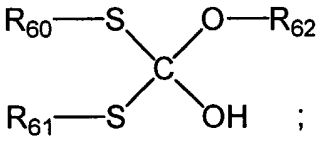


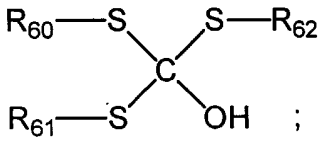




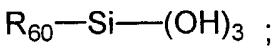


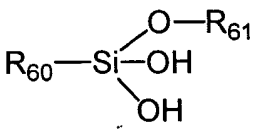


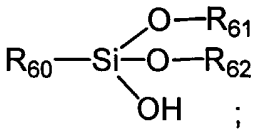




Acids of silicon containing an organic substituent, such as







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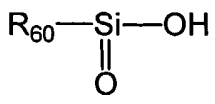

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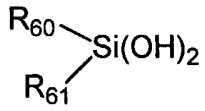

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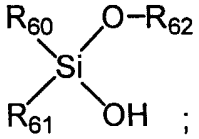

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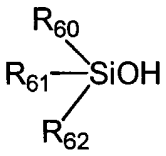


;

Partial esters of:

Mono-orthosilicic acid (H_4SiO_4) ;

Diorthosilicic acid ($H_6Si_2O_7$) ;

Triorthosilicic acid ($H_8Si_3O_{10}$);

Tetraorthosilicic acid ($H_{10}Si_4O_{13}$);

Pentaorthosilicic acid ($H_{12}Si_5O_{16}$);

Monometasilicic acid (H_2SiO_3);

Dimetasilicic acid ($H_4Si_2O_6$);

Trimetasilicic acid ($H_6Si_3O_9$);

Tetrametasilicic acid ($H_8Si_4O_{12}$);

Pentametasilicic acid ($H_{10}Si_5O_{15}$);

Dimesosilicic acid ($H_2Si_2O_5$);

Trimesosilicic acid ($H_4Si_3O_8$);

Tetramesosilicic acid ($H_6Si_4O_{11}$);

Pentamesosilicic acid ($H_8Si_5O_{14}$);

Triparasilicic acid ($H_2Si_3O_7$);

Tetraparasilicic acid ($H_4Si_4O_{10}$);

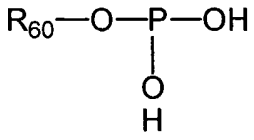
Pentaparasilicic acid ($H_6Si_5O_{13}$);

Tetratetrerosilicic acid ($H_2Si_4O_9$);

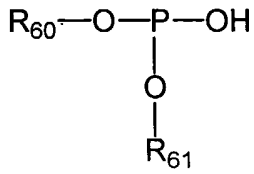
Pentatetrerosilicic acid ($H_4Si_5O_{12}$);

Penterosilicic acid ($H_2Si_5O_{11}$);

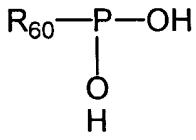
Acids of phosphorus containing an organic substituent, such as



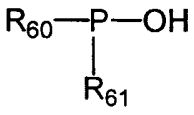
(Monoester of phosphorous acid);

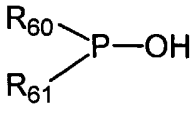


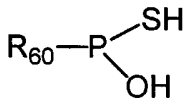
(Diester of phosphorous acid);

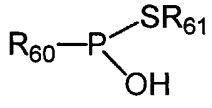


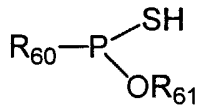
(Phosphorous acid);

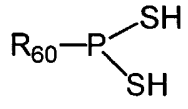

(Monoester of phosphorous acid);

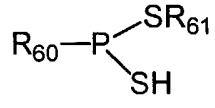

(Phosphinous acid);

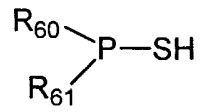

(Monothio-phosphonous acid);

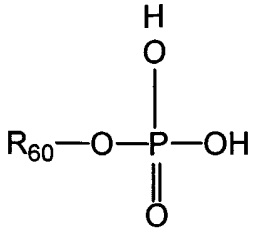

(Monothio-ester of phosphonous acid);


(Monoester of thiol-phosphonous acid);

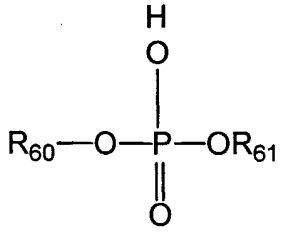

(Dithio-phosphonous acid);


(Diester of dithio-phosphonous acid);

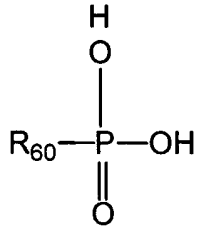

(Thio-phosphonous acid);



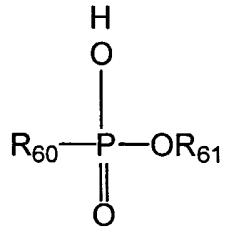
(Monoester of phosphoric acid);



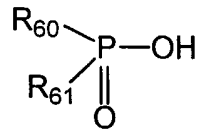
(Diester of phosphoric acid);



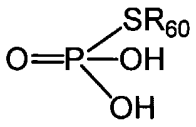
(Phosphonic acid);



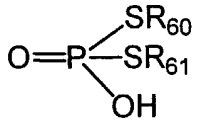
(Monoester of phosphonic acid);



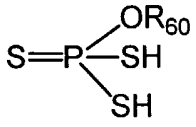
(Phosphinic acid);



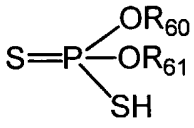
(Monothio-ester of phosphoric acid);



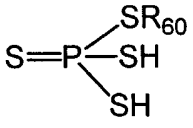
(Dithio-ester of phosphoric acid);



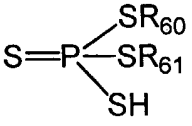
(Monoester of tetrathio-phosphoric acid);



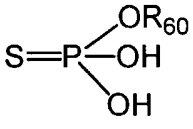
(Diester of tetrathio-phosphoric acid);



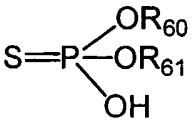
(Monothio-ester of tetrathio-phosphoric acid);

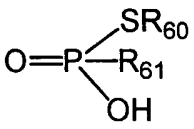


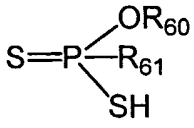
(Dithio-ester of tetrathio-phosphoric acid);

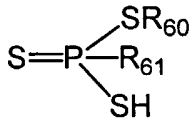


(Monoester of monothio-phosphoric acid);

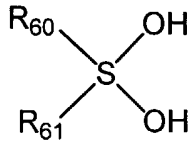

(Diester of monothio-phosphoric acid);

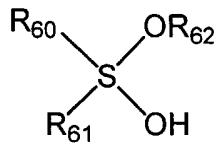

(Monothio-ester of phosphonic acid);

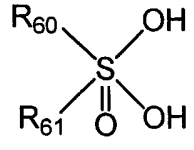

(Monoester of dithio-phosphonic acid);

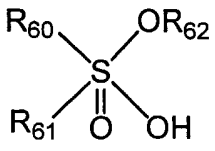

(Monothio-ester of trithio-phosphonic acid);

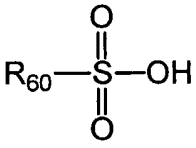
Acids of sulfur containing an organic substituent

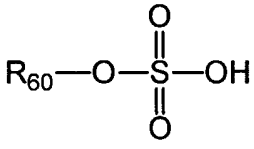

(Sulfinous acid);

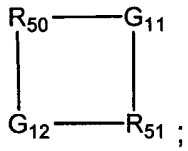

(Monoester of sulfinous acid);


(Sulfinic acid);


(Monoester of sulfinic acid);


(Sulfonic acid);


(Monoester of sulfuric acid);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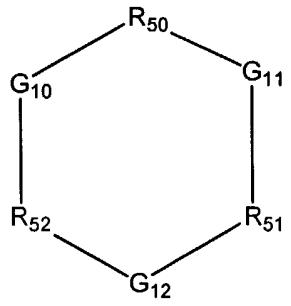
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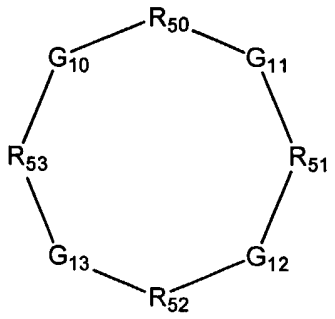
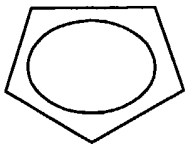


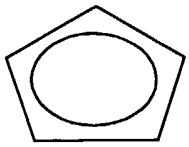
;

[0115] Some exemplary embodiments of complexes are listed below.

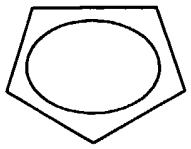
$Er[(n\text{-}C_8F_{17})_2POO]_3$; $ErYb[(n\text{-}C_8F_{17})_2POO]_6$; $ErYb_4[(n\text{-}C_8F_{17})_2POO]_{15}$; $ErYb[(n\text{-}C_6F_{13})_2POO]_6$; $ErYb_4[(i\text{-}C_3F_7OC_2F_4)_2POO]_{15}$; $ErYb[(n\text{-}C_4F_9)_2POO]_6$; $ErYb_3[((CF_3)_2CF(CF_2)_6)_2POO]_{12}$; $ErYb_3[((CF_3)_2CF(CF_2)_6)_2PSO]_{12}$; $ErYb_3[(n\text{-}C_{10}F_{23})_2POO]_{12}$; $ErYb_3[(n\text{-}C_8F_{17})(n\text{-}C_{10}F_{23})POO]_{12}$; $Er[(CH_3)_3C\text{-}(CO)\text{-}CH_2\text{-}(CO)\text{-}CF_2CF_2CF_3]_3$.; $ErYb[(n\text{-}C_8F_{17})_2POO]_6$; $ErYb_{10}[(n\text{-}C_8F_{17})_2POO]_{33}$;



M_1



M_2



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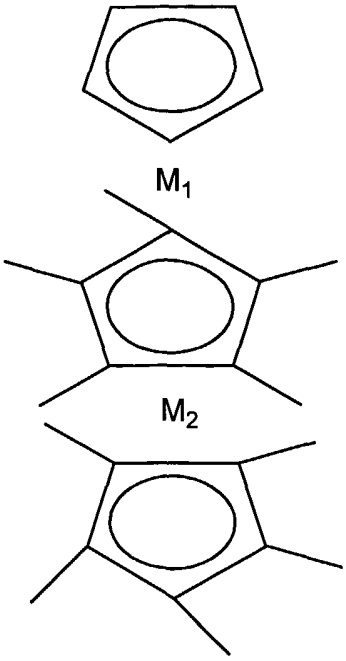
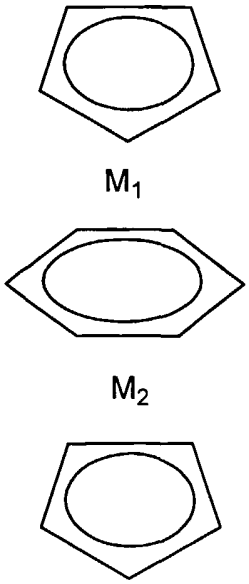
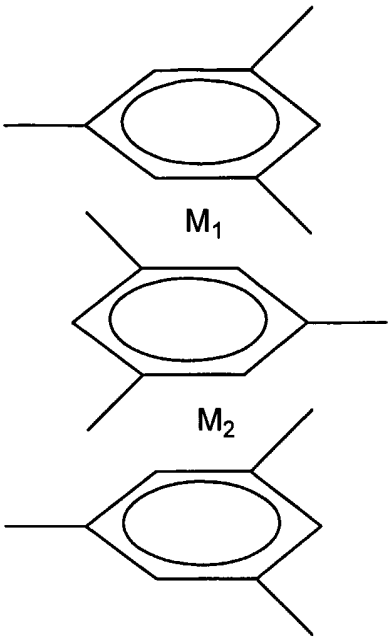

M1
M2

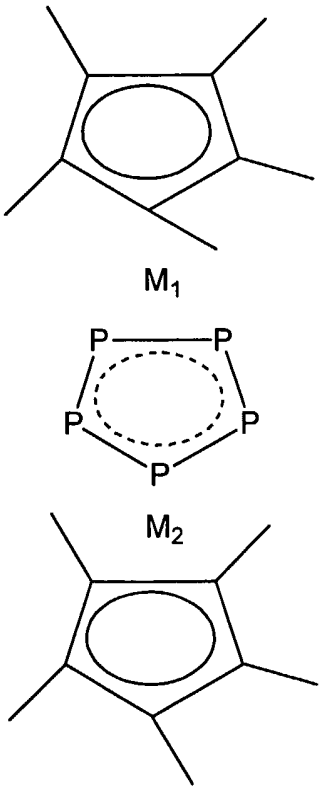
;


M1
M2

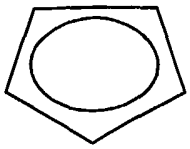
;


M1
M2

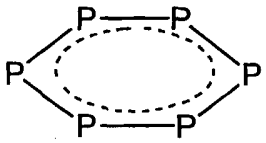
;


M1
P
P
P
P
P
M2

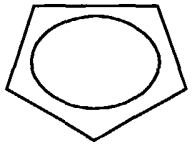
;



M_1



M_2



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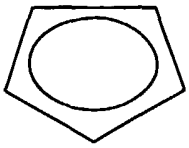
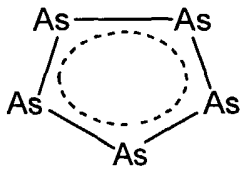
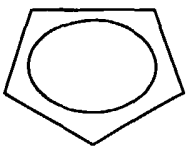


M_1



M_2



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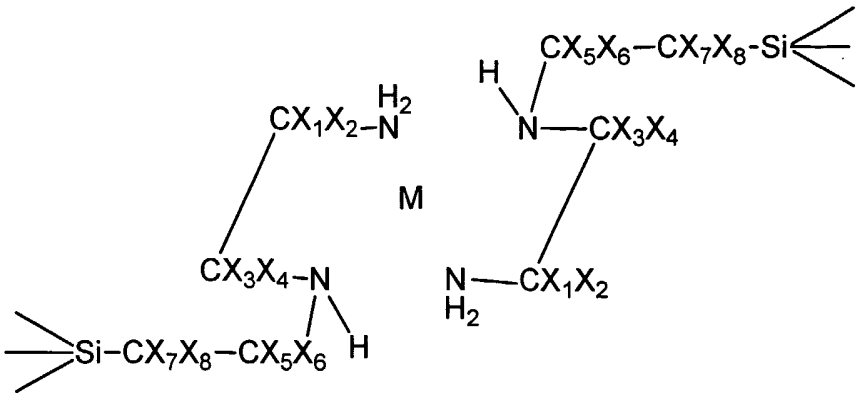

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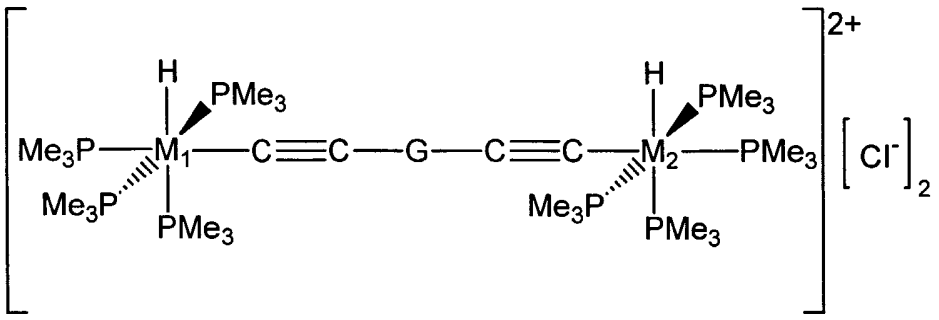

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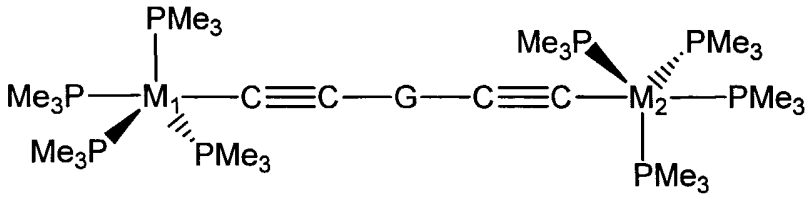

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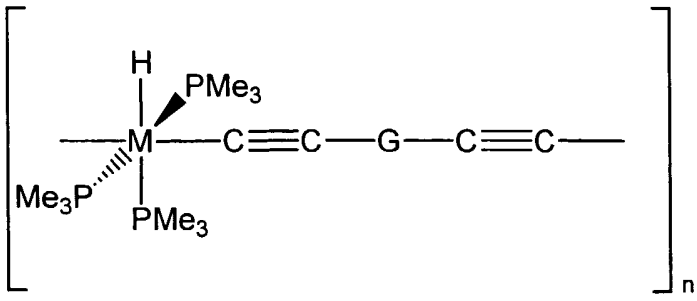

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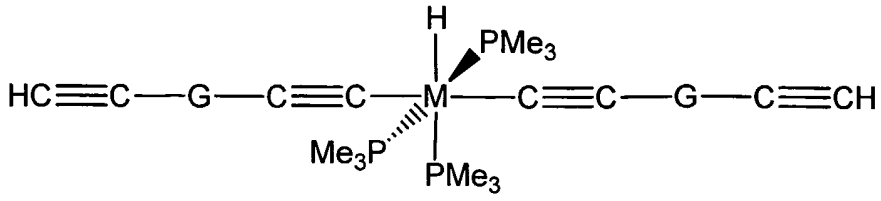

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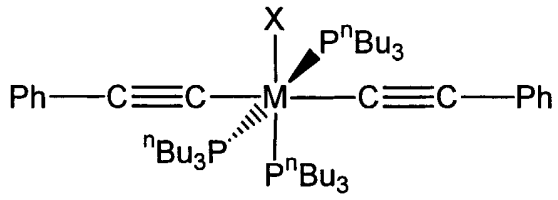

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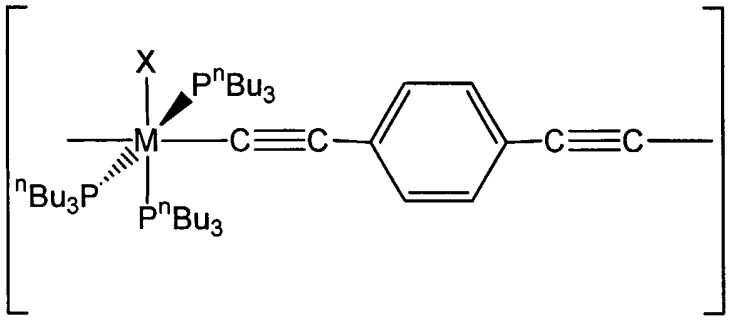

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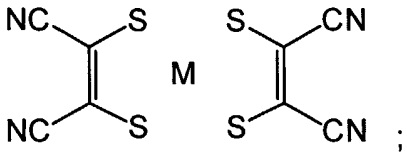


;

[0116] $[M(PMe_3)_4]Cl$;

[0117] $M[N(Si(CH_3)_3)_2]_3$;

[0118] $M[N(Si(CH_3)_3)_2]_3OPPh_3$;

[0119] $[M(CH_2Si(CH_3)_3)_4]^-$;

[0120] $[M(NCS)_6]^{3-}$;

[0121] $Na[M(S_2CN(C_2H_5)_2)_4]$;

[0122] $[M(mesityl)_4]^-$;

[0123] $M(CF_3CO_2)_3(C_4H_8SO)_2$;

[0124] $Cs[M(CF_3COCFCOCF_3)_4]$;

[0125] $M(PF\text{-}acac)_3$;

[0126] $M(HMPA)_3(X_9)_3$;

[0127] $M(OPPh_3)_3$;

[0128] $(DMSO)_nM(NO_3)_3$;

[0129] $M[N(Si(CH_3)_3)_2]_2(Al(CH_3)_3)_2$;

[0130] $(M)_3en_3(X_9)_3$;

[0131] $[Men_4CF_3SO_3]^{2+}$;

[0132] $[M(NCS)_6]^{3-}$;

[0133] $[M(S_2CNR_2)_4]^-$;

[0134] $[M(S_2P(CH_3)_2)_4]^-$;

[0135] $M[S_2P(C_6H_{11})_2]_3$;

[0136] $Cp_2MC_6F_5$;

[0137] $M(C_8H_8)$;

[0138] $[M(C_8H_8)_2]^{2-}$;

[0139] $M_1M_2M_3[(NR_1R_2)(NR_3R_4)]\ X_9$;

[0140] $M_1M_2M_3[(A_8A_9)A_{10}(A_{11}R_1)(A_{12}R_2)]_3$;

[0141] $(M_1)_i(M_2)_j(M_3)_k(M_4)_l[R_{75}R_{76}A_{25}(A_{26}A_{27})]_{3(i+j+k+l)}$;

[0142] $(M_1)_i(M_2)_j(M_3)_k(M_4)_l[R_{50}A_{25}(A_{26}A_{27})]_{3(l+j+k+l)}$; and

[0143] $(M_1)_i(M_2)_j(M_3)_k(M_4)_l[R_{50}A_{25}(A_{26}A_{27})R_{51}A_{28}(A_{29}A_{30})]_{1.5(l+j+k+l)}$, where R_{50} and R_{51} are each linked to both A_{25} and A_{28};

[0144] Other exemplary embodiments of complexes include:

[0145] $M_1M_2M_3[NR_3A_8A_{10}R_1R_2]_3$

[0146] where:

[0147] A_8, A_9, A_{10}, A_{11}, A_{12}, M_1, M_2, M_3, R_1, R_2, and R_3 are defined above but here, R_1 and R_2 can be separate groups or can be linked to form cyclic or extended structures; and

[0148] each of the three $[(A_8A_9)A_{10}(A_{11}R_1)(A_{12}R_2)]$ can be the same or different.

[0149] $M_1M_2M_3[N(R_1)R_{70}(NR_2)]X_9$

[0150] where:

[0151] M_1, M_2, M_3, R_1, R_2 and X_9 are defined above; and

[0152] R_{70} is halogenated alkylene or halogenated silylene.

[0153] $M_1M_2M_3[A_{20}A_{21}A_{22}A_{23}R_1]_3$

[0154] where:

[0155] A_8, A_9, A_{10}, A_{11}, A_{12}, A_{20}, A_{21}, A_{22}, A_{23}, M_1, M_2, M_3, and R_1 are defined above; and

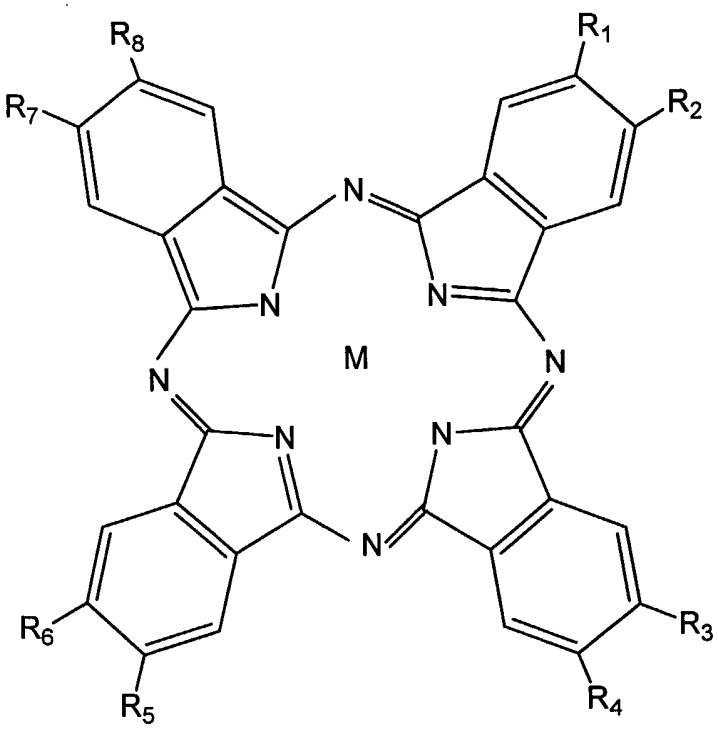
[0156] wherein each of the three $[A_{20}A_{21}A_{22}A_{23}R_1]$ can be the same or different.

[0157] The present invention also contemplates such complexes in combination with polymers having low absorption from 1200 to 1700 nanometers. These combinations can be made by blending the complex with a preform polymer or by mixing such complex with monomer(s) and then polymerizing. Alternatively, a polymer can be produced from any of the complexes (or any of the above-mentioned ligands used to make a complex) providing that the complex contains polymerizable moieties.

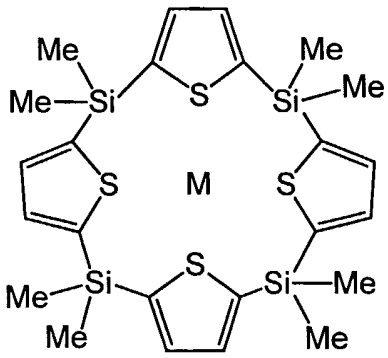
[0158] FIG. 3 discloses exemplary embodiments of branched polymers where from 2 to 10 groups (G_i) can coordinate with one or more suitable metals.

[0159] Exemplary embodiments further include cage structures wherein the suitable metal is caged within one or more of the complexes described herein. FIG. 4a discloses exemplary embodiments of cage polymers and structures where from 2 to 10 groups (G_i) can coordinate with one or more suitable metals. FIGS. 4b and 4c show additional illustrative cage structures consistent with this invention.

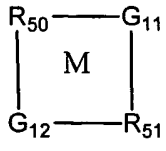
[0160] Some of the cage structures that can be used consistent with this invention include:


R8
R7
R1
R2
N
N
N
M
N
N
N
N
N
R6
R5
R3
R4

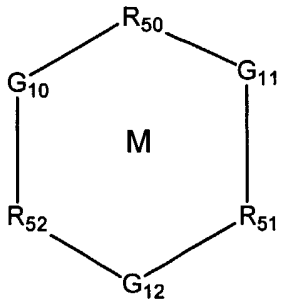
;

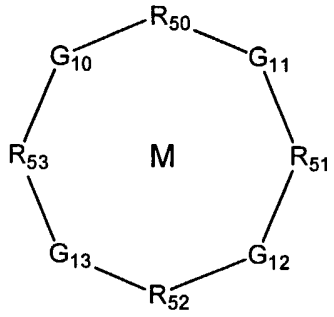

Me
Me
Si
S
Si
Me
Me
S
M
S
Me
Si
S
Si
Me
Me
Me

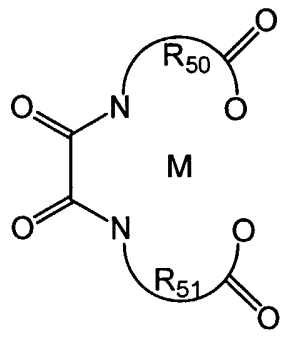
;

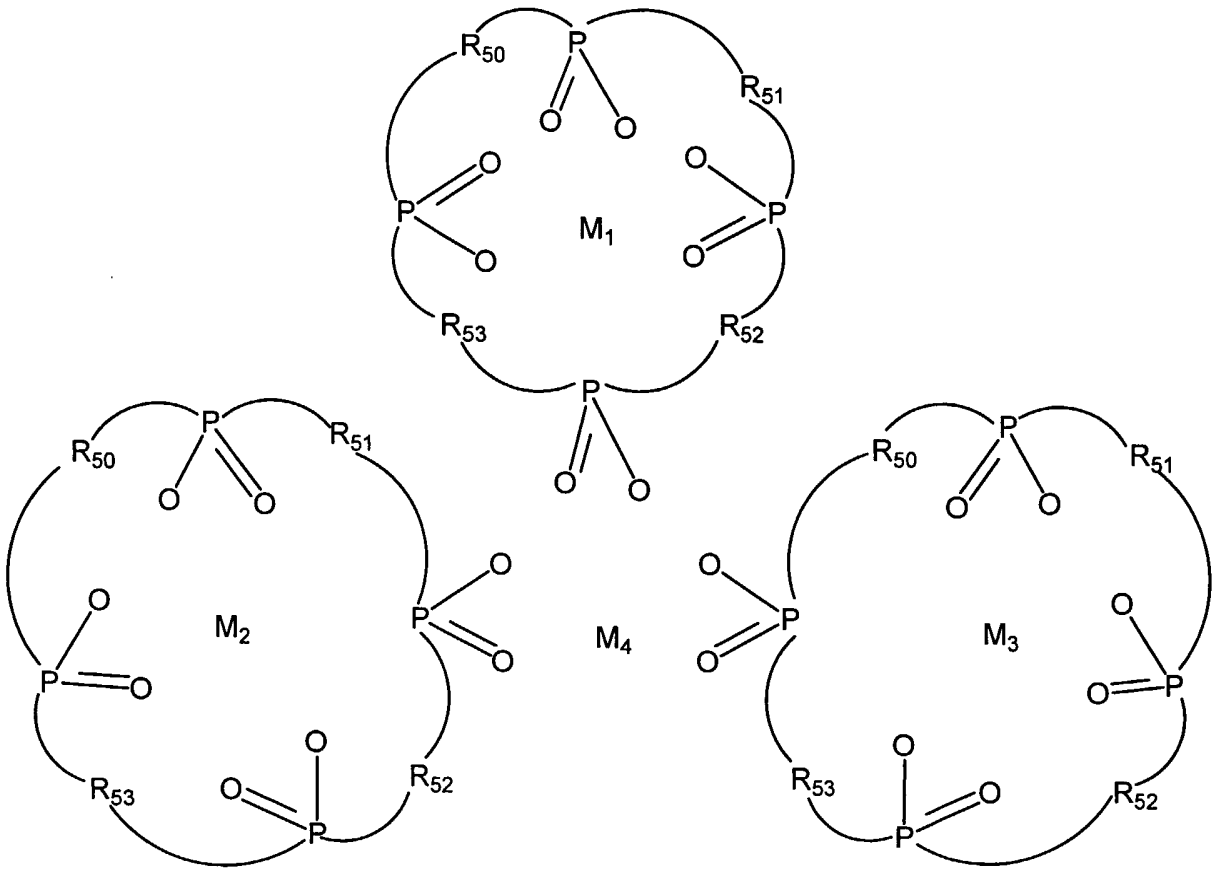

R50
G11
M
G12
R51

;

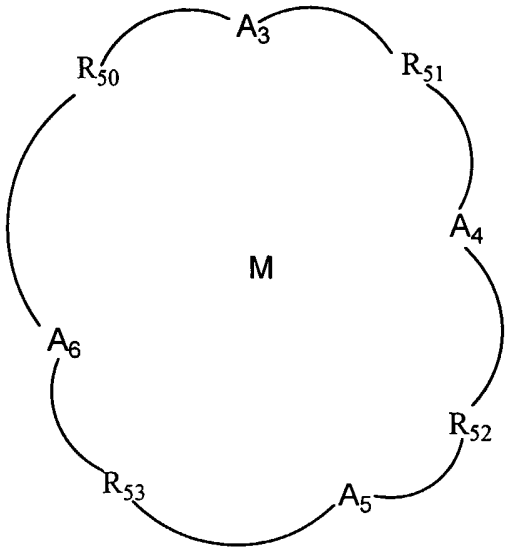

R50
G10
G11
M
R52
R51
G12
;


R50
G10
G11
R53
M
R51
G13
G12
R52
;

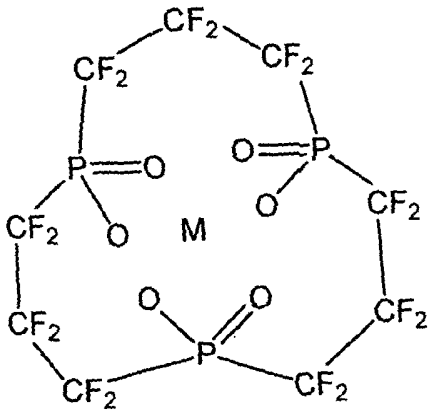

O
R50
O
N
O
M
O
N
O
R51
O
;


M1
M2
M3
M4

;


M

;



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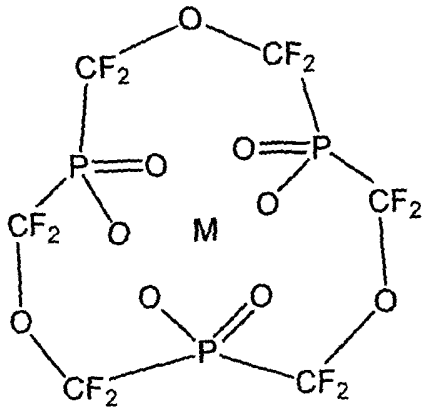

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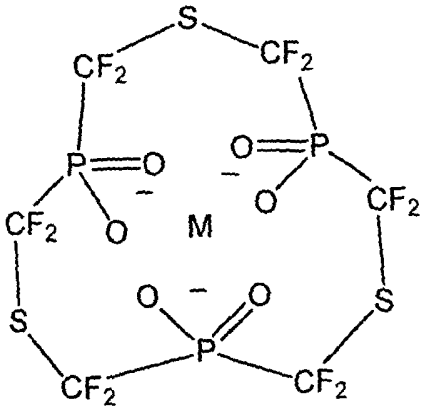
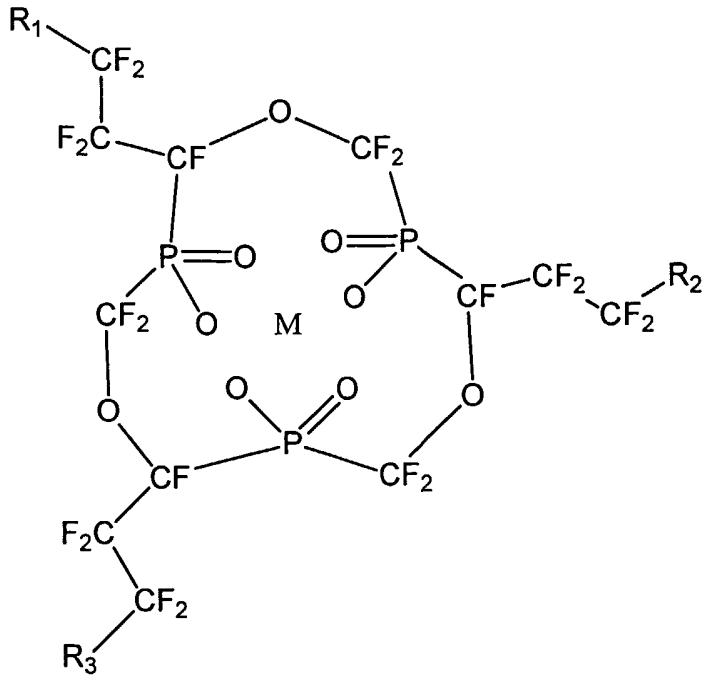


; and



[0161] Complexation tendency increases orders of magnitudes in the cage structures disclosed above, which stabilizes the compounds further. The suitable metals within the cages are isolated from each other, which also provides a higher fluorescence lifetime. Inter-complexation is reduced or even eliminated, increasing the solubility of the complex in a solvent and/or a polymer matrix.

[0162] FIGS. 5a and 5b show other illustrative polymers of the present invention. FIG. 5a shows polymers with side chain and backbone incorporation of groups (G_i) which can coordinate with one or more suitable metals. FIG. 5b shows complexes of suitable metals with polymer entities. The solid ovals represent suitable metals and the lines represent cross-linked, branched, dendritic, or amorphous polymer chains that include monomers of coordinating groups throughout. In an exemplary embodiment of FIG. 5b, the density of coordinating groups can be higher near the suitable metals.

[0163] The structures of the polymers shown in FIGS. 5a and 5b, and others, of the present invention can be random to prevent crystallization.

[0164] Any of the complexes of the present invention can be mixed with polymer matrices including perfluoropolymers, poly[2,3-(perfluoroalkenyl) perfluorotetrahydrofuran], poly[2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole-co-tetrafluoroetliylene], poly[2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole-co-tetrafluoroethylenel, fluoropolymers, tetrfluoroethylene/hexafluoropropylene/vinylidene copolymers known as THV® (3M), fluorinated polyimides, fluorinated acrylates, fluorinated methacrylates, fluorinated polyarylethers, high quality optical polymers, halogenated polymethylmethacrylate, halogenated polystyrene, halogenated polycarbonate, halogenated norbornene polymers. Perhalogenated alkoxys, perhalogenated thioalkoxys, perhalogenated aryloxys, perhalogenated polyethers, or perhalogenated polythioethers as polymers or solvents can also be mixed with complexes of the present invention.

[0165] Ionic complexes listed above can be combined with other, oppositely charged, ionic complexes described above or other oppositely charged, ionic complexes not described herein to form additional complexes. For these complexes, the suitable metal connected to the negative ionic complex can be the same as or different from the suitable metal connected to the positive ionic complex. For the above-listed ligands and complexes, where hydrogen (H) is typically present, the H can be replaced with a halogen, and in one embodiment, fluorine.

[0166] As shown in FIGS. 6 and 7, the above-identified compositions may be used, for example, to produce cores for optical fibers. The cores can be cladded with any suitable material having a lower refractive index than the core. In some cases, the core/cladding refractive index difference and core diameter can be enough to result in single optical mode propagation for optical wavelengths from about 1200 nm to about 1700 nm.

[0167] Also as shown in FIG 9a, the compositions identified may be used to produce optical amplifying film 200, which can include substrate 220, buffer film 210 disposed on substrate 220, wave guiding layer 230 disposed on buffer film 210, and upper cladding film 240 disposed on guiding layer 230. The refractive indices of buffer film 210 and upper cladding film 240 can be less than that of guiding layer film 230. In some embodiments, wave guide layer 230 can guide a single optical mode of light having a wavelength between about 1200 nm and about 1700 nm.

[0168] The suitable metal doped halogenated complexes can incorporate suitable metal atoms in a covalently bonded complex chain. In certain exemplary embodiments, deleterious effects, such as clustering and upconversion quenching, are reduced. Certain exemplary embodiments of the present invention use selected energy transfer suitable metal ion codopants that increase the overall absorption for pumping radiation and can transfer that absorbed radiation to suitable metal ions that luminescence at wavelengths of interest. These codopants can be incorporated at a continuum of desired levels, providing for more precise control over the ratio of codopant ions to luminescing ions. To obtain particular optical gain, the complex composition can be tuned to optimize absorption of the pump radiation,

luminescence efficiency, and noise level. For example, concentrations of codopant and luminescing suitable metal ions can be incorporated (up to about 5-15%) leading to a very high gain per unit length, resulting from increased pump absorption and/or efficient luminescence. In certain exemplary embodiments, the complex medium provides a broader gain spectrum than glass media, owing to nonhomogeneous broadening, thereby leading directly to a broader band amplifier or gain medium.

[0169] The codopant complexes of some embodiments consistent with this invention are made via a condensation type of polymerization in inert solvents for example, lower alkyl ketones, lower alkyl ethers, or acetone.

[0170] The salt of a perhalogenated substituted acid (and in some exemplary embodiments, phosphinic acid) may be added to a mixture of suitable metal halides, M_1X_9, M_2X_{10}, M_3X_{11}, and M_4X_{12}, where M_1, M_2, M_3, and M_4 are the same or different and are chosen from the suitable metals as defined herein, and X_9, X_{10}, X_{11}, and X_{12} can be the same or different and are halides as defined herein. Five or more suitable metals can be used. The counterion of the deprotinated acid can be Na, K, NH_4, Rb, Cs, Be, Mg, Ca, Sr, Ba, or any cation suitable for the reaction. The solid that results is stirred for up to about 72 hours (or up to about 48 hours, or up to about 2 hours, or up to about 1 minute, or any amount of time needed to make the desired suitable metal-acid salt) at about room temperature, optionally under nitrogen. Distilled water can then be added to the reaction mixture, which can be boiled to remove the halogen salt by-product, and filtered and washed with boiling water repeatedly. The washed product can then be dried in a vacuum oven. The

resultant complexes are soluble in organic solvents, such as dimethyl acetamide and are also usable in high temperature processes.

[0171] An alternate method of manufacturing the complex as described above involves mixing precursor phosphinates providing a mixed salt derivative, such as by the reaction:

$$k[R_1R_2POONa] + l[R_3R_4POONa] + m[R_5R_6POONa] + M \rightarrow$$

$$(R_1R_2POO)_k(R_3R_4POO)_l(R_5R_6POO)_mM$$

[0172] In one embodiment, k+l+m=3. The molar ratio of total phosphinate to suitable metal can be between about 2.5:1 and about 3.5:1, and in one embodiment the ratio can be about 3.0:1 to enhance solubility. Also, in another exemplary embodiment, R_1, R_2, R_3, R_4, R_5, and R_6 can be the same or different. Differences in these R-groups can produce a random structure, preventing crystallization, as shown in FIG. 5b.

[0173] In yet another exemplary embodiment, other suitable metal complexes could be made using one or more of Sc, Cr, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, or Tm. Other metals, such as Al, Sn, Zn, and other transition metals, such as Ti, Mn, etc..., can also form complexes. Any known ligands (including, but not limited to those mentioned herein) could be used to make complexes. The complex formation method could be substantially duplicated using other metal salts, such as Br, I, nitrate, acetate, and any soluble salts.

[0174] In one illustrative embodiment, a polar solvent can be used in the formation process. For example, acetone, methanol, water, ethyl ether, methanol, propanol, and acetonitrile have been used successfully in the process. In another

embodiment, complex formation with other counterions for the deprotinated acid (such as Na, K, NH_4, Rb, Cs, Be, Mg, Ca, Sr, Ba, or any cation suitable for the reaction) could be used. Although not wishing to be bound by any particular theory, it appears the phosphinic acid or its ammonium salt reacts with metals to form the complexes.

[0175] A fiber can be formed from a polymer consistent with this invention. For example, as shown in FIGS. 6-8, a polymer or a blend of the polymer with suitable polymers, such as perfluoropolymers, can be formed into cylindrical rod 100 of first diameter d_{core} and length for example, by molding or extrusion processes. In one embodiment, rod 100 can be inserted into cladding in the form of a tube 110 of a second, lower refractive index material that has a similar processing temperature. Tube 110 can include multiple cladding layers of different optical materials, if desired. Tube 110 has second diameter d_{clad} and is greater than first diameter d_{core}. Tube 110 has refractive index n_{clad} and rod 100 has a refractive index n_{core}.

[0176] In general, refractive index n_{clad} of tube 110 is less than refractive index n_{core} of rod 100. In one particular exemplary embodiment, d_{clad} can be at least two times larger than d_{core} for multimode fibers and fifteen times larger for single mode fibers. Tube 110 can be formed from a polymer similar to the polymer which forms rod 100 with a general composition as disclosed above, which may include the suitable metals disclosed as herein.

[0177] In one embodiment, insertion of rod 100 into tube 110 forms a rod and tube assembly 120. In another embodiment, resulting rod and tube assembly 120 can be, for example, a fiber preform, from which single mode optical fiber can be

drawn by standard techniques, such as by melt drawing, which is illustrated in FIG. 8. During operation perform fiber 120 is passed through furnace 130, diameter gauge 140, and coating station 150. It will be appreciated, however, that other drawing techniques can be employed, and this technique is not meant to be limiting. Fiber 122 which is formed from rod and tube assembly 120 can then be installed in an optical amplifier module. During module operation, signal light injected into the module experiences gain while propagating along fiber 122 via transfer of energy from absorbing ions to the emitting ions and subsequent stimulated emission from the emitting ion.

[0178] In certain exemplary embodiments, waveguide 200, as shown in FIG. 9 can also be formed from the complex or a blend of the complex with suitable polymers, such as perfluoropolymers. In one illustrative embodiment, the complex, or a blend of the complex with polymers, can be dissolved in a high boiling-point solvent suitable for spin coating or casting. Such a solvent is, for example, FC-40 or FC-75, although those skilled in the art will recognize that other suitable solvents can be used.

[0179] As shown in FIG. 9a, bottom cladding material 210 with a refractive index lower than the refractive index of core 230 can be originally deposited on a waveguide substrate 220. A layer of core 230 can be deposited onto bottom cladding material 210, for example by spin coating, although other methods can be used. A photoresistive layer can be deposited over the predetermined portions of core 230. The portions of the core that are not covered by the photoresist layer can be etched away from waveguide 200 by any known method. The photoresistive

layer can also be removed from waveguide 200 by any known method, such as by using a solution to form core 230.

[0180] Waveguide 200 can be overclad with top cladding material 240, which can have a refractive index lower than the refractive index of the core. In certain exemplary embodiments, the bottom cladding material can be a refractive index approximately equal to the refractive index of top cladding material 240. In one embodiment, bottom cladding material 210 and top cladding material 240 can include the same material, although different materials can be used. In an exemplary embodiment, waveguide 200 can include amplifying properties similar to that of an optical fiber and may be inserted into the optical amplifier module as described above.

[0181] FIG. 9b shows a number of simplified diagrams of illustrative embodiments of the integration of waveguide 200 with other optical components consistent with this invention including a splitter, a modulator, an arrayed waveguide grating (herein, "AWG"), and an amplifier. It will be appreciated that other components can also be constructed including, for example, switches, isolators, lasers, fibers, films, and the like.

[0182] FIG. 9c shows an optical amplifier module consistent with this invention. Signal light injected into the module will experience gain in the gain medium by transfer of energy from the absorbing chromophore in the ligand to the emitting ion and subsequent stimulated emission from the emitting ion. The gain medium can take the form of a fiber, a film, or any other type of optical waveguide or bulk optical devices. Isolators 401 and 404 prevent back reflections of the signal

and amplified signal, respectively. Wavelength division multiplexer 402 combines pump light and signal light, where pump laser 400 provides the pump light. The gain medium which is located in optical device 403, amplifies the signal. The optical amplifier module can then include (a) at least one optical isolator to prevent back reflections, (b) at least one wavelength division multiplexer to combine pump and signal light, (c) a pump laser, and optionally (d) one or more other optical components.

[0183] In situ formation of the complexes described above on a substrate to form waveguide 200 as described above provides at least one of the following advantages:

[0184] • The precursor halogenated-phosphinic acids (HPA) and its partially neutralized salts are exceedingly soluble in perfluorinated hydrocarbon solvents such as FC-75 (perfluoro n-butyl tetrahydrofuran).

[0185] • They are also very soluble in solution of halogenated polymers (HP) such as THV, poly[2,3-(perfluoroalkenyl) perfluorotetrahydrofuran], poly[2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole-co-tetrafluoroetliylene], poly[2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole-co-tetrafluoroethylenel, tetrfluoroethylene/hexafluoropropylene/vinylidene, or Kalrez.

[0186] • The composite films cast from the mixtures of the halogenated polymers and HPAs are very transparent with excellent mechanical properties.

[0187] • The composite films are allowed to come in contact with the solutions of suitable halides (or other salts such as nitrate, acetate, etc) in an organic solvent such as acetone.

[0188] • The complexes are formed after the film deposition, so there is no concern with dissolution.

[0189] • The complex formation can be further enhanced via neutralization, extraction or azotropic displacement.

[0190] • Various mixtures of HPAs can be used.

[0191] • Various mixtures of suitable metals can be utilized for making the complexes.

[0192] FIG. 10a shows a flow chart of illustrative steps for in situ formation of complexes consistent with this invention. In step 420, a ligand, a perfluoropolymer, and a solvent is admixed to form a mixture. In step 425, the solvent is removed from the mixture. This can be accomplished, for example, by casting a film to increase the surface area of the mixture. This achieves a substantially uniform distribution of ligands within the mixture with little or no aggregation. In step 430, a suitable metal solution is applied to the film. The metal solution reacts (e.g., diffuses) with the film and allows for the exchange of the metal ions with active sites within the film. The reaction thus achieves a substantially uniform distribution of metal ions within the mixture with little or no aggregation.

[0193] As shown in FIG. 10b, a mixture is formed with the active precursor HPA, HP, and the solvents as a result of step 420. In step 425, a uniform clear film can be cast on the substrate (or on the cladding surface) for removal of the solvent.

Optimization may be necessary to partially dry the solvent for improved transport/diffusion of the metal ion. In step 430, a suitable metal solution (e.g., including dry acetone), is applied to the film and allowed to equilibrate therewith, which results in metal diffusion within the mixture. When forming a film, it will be further appreciated that conventional chip processing steps, including photolithographic steps, can be performed to obtain a final optical device, including, for example, applying photo-resistive layers, masking, exposing to light, etching (e.g., reactive ion etching), etc. These steps can be followed by applying one or more cladding layers. Alternatively, ion exchange can be performed after a chip manufacturing process and before application of the cladding and packaging materials.

[0194] An Exemplary Method for Preparing an Optical Gain Medium

[0195] In an exemplary embodiment, a method for preparing a gain medium includes (a) admixing a composition comprising at least one complex with at least one suitable solvent DMAC, FC-75, CT Solv 180 (perfluorotrialkylamine, CAS No. 865-08-42-1), CT Solv 100, CT Sol 130 and any combination thereof.

[0196] In step (b), heating can occur in the range of about 50°C to about 150°C for about 5 minutes to about 2 hours. Alternately, heating can occur in the range of about 60°C to about 90°C or at about 100°C. In another embodiment, heating can be for about 10 minutes to about 30 minutes.

[0197] In step (c), cooling can occur to in the range of about 20°C to about 30°C. In other exemplary embodiments of this method, the cooling in step (c) can be to about 25°C or to about room temperature.

[0198] In step (d), admixing can occur with a perfluoropolymer to produce a mixture. The perfluoropolymer can be cyclopolymerized perfluoro-vinyl ether, copolymers of 2,2-bistrifluoromethyl-4,5-difluoro-1,3 dioxole (PDD) with other suitable monomers, cyclic polyethers prepared from cyclopolymerization of fluorine-containing dienes as described in U.S. Patent No. 4,897,457, which is hereby incorporated by reference, and polymer and copolymers of 2,2,4-trifluoro-5-trifluoromethoxy- 1,3-dioxole and other analogues as described in U.S. Patent No. 5,498,682, which is hereby incorporated by reference, with other suitable monomers.

[0199] In another embodiments the perfluoropolymer can be a 16% (wt/wt) amorphous cyclopolymerized perfluoro-vinyl ether in a perfluoroether solvent.

[0200] In step (e), the mixture can be formed into a gain medium. Forming in step (e) can include filtering using about 0.45 or about 0.2 micron filters. In another embodiment of this method, the forming can include drying for about 1 to about 50, hours or for about 5 hours to about 10 hours at a temperature of about 100°C to about 150°C or about 130°C. The forming in step (e) can also include casting, film casting, spin casting, film coating, and/or any other method for forming a gain medium into a desirable form that is known to those of ordinary skill in the art. For example, forming in step (e) can include depositing the mixture on a substrate, such as a silicon wafer.

[0201] In an exemplary embodiment, an optical device can be produced from the gain medium using methods known to those of ordinary skill in the art. Illustrative optical devices including optical fibers, waveguides, AWGs, films,

amplifiers, lasers, multiplexers, isolators, interleavers, demultiplexers, filters, photodetectors and switches.

[0202] **Example 1**

[0203] Preparation of the Na salt of $(n\text{-}C_8F_{17})_2POOH$ (dioctyl-perfluoro-phosphinic acid): Three grams (3.32 mmole) of $(n\text{-}C_8F_{17})_2POOH$ was added to 17 ml of methanol and dissolved by stirring with a magnetic stir bar. A NaOH solution was prepared by dissolving 0.133 gram (3.32 mmole) of NaOH in 17 ml of distilled water. This NaOH solution was added to the methanol-phosphinic acid mixture. The pH was adjusted to 7.00 by adding slight excess of phosphinic acid or NaOH, as needed. The solution was filtered and then dried on a warm hot plate. The Na salt of the phosphinic acid was further dried in a vacuum oven at 70°C overnight before use.

[0204] Preparation of Complex: In this example we report preparation of $Er[(n\text{-}C_8F_{17})_2POO]_3$. $Na[(n\text{-}C_8F_{17})_2POO]$ (0.447 g, 0.4838 mmole) was dissolved in 6 ml of acetone in a 30 ml vial. The $ErCl_3$ (0.04417g , 0.1613 mmole) was dissolved in 2 ml of acetone (reagent grade, Fisher). The $ErCl_3$ solution was added to the $Na[(n\text{-}C_8F_{17})_2POO]$ solution all at once while mixing with a magnetic stir bar. The container of the $ErCl_3$ was rinsed 3 times with 1.5 ml of acetone and the rinsings added to the 30 ml reaction vial. Immediately a fluffy precipitate formed which stuck to the side of the vial. The vial was heated to boil (100°C), then cooled to room temperature. The reaction vessel was left overnight and then 15 ml of distilled water was added and heated to boil for five minutes and then cooled to room temperature.

The precipitate was filtered and dried in vacuum oven at 80°C overnight. The weight of the product was 0.4247 g. The lifetime of this complex was 1.8 ms.

[0205] **Example 2**

[0206] In this example we report preparation of a complex of Er, Yb and $(n\text{-}C_8F_{17})_2POO^-$. The molar ratio of the Er to Yb in the complex is 1:1 and the ratio of the metal to the phosphinic acid is 1 metal/3 $(n\text{-}C_8F_{17})_2POO^-$. $Na[(n\text{-}C_8F_{17})_2POO]$ (1.08 g, 1.08 mmole) was dissolved in 14 ml of dry acetone and a solution of 0.049 g $ErCl_3$ and 0.050 g $YbCl_3$ in 1.4 ml dry acetone was added. The reaction mixture was stirred under N_2 for about 2 hours. The solution was boiled briefly and then filtered. The residue was washed with 50 ml of warm deionized water and dried in vacuum oven overnight. We obtained 0.80 grams of product (77% yield). The lifetime of this complex was 4.5 ms.

[0207] Example 3

[0208] In this example the complex stoichiometry of $(n\text{-}C_8F_{17})_2POO^-$ to total metal (Er+Yb) is 1.0/0.9 (i.e., 10 % excess phosphinate). The molar ratio of Er to Yb is 1:4. Ten ml of dried acetone was added to dissolve 0.9993 g (1.0815 mmole) of $Na[(n\text{-}C_8F_{17})_2POO]$. The $Na[(n\text{-}C_8F_{17})_2POO]$-acetone solution was added over 1 minute to a 2 ml solution of 17.7 mg of $ErCl_3$, 75.4 mg $YbCl_3$ in acetone. Precipitate formed immediately. The container of the metal chloride solution was rinsed twice with 1.5 ml of additional acetone and transferred to the reaction container. The reaction container was purged with N_2 overnight. Eighteen ml of hot deionized water

was admixed and heated to boil. Precipitate was filtered and washed with additional 20 ml of hot water. We obtained 0.8739 gram (84.3% yields) of product after vacuum drying at 80°C in a vacuum oven overnight. This product had a lifetime of 5.1 ms.

[0209] **Example 4**

[0210] This example describes a synthesis of a complex of $[n\text{-}C_6F_{13}]_2POOH$ with Er and Yb salt where the Er to Yb molar ratio is 1:1.

[0211] Preparation of sodium salt: $[n\text{-}C_6F_{13}]_2POOH$ (1.00 g, 1.42 mmole) was dissolved in 7.5 ml of methanol. This methanol solution was added to 0.057 g (1.42 mmole) of NaOH in 7.5 ml of deionized water. The pH was adjusted to 7.0 by addition of few drops of NaOH. The solution was filtered and dried over a warm hot plate. The powder was dried in a vacuum oven at 40°C for two days. We obtained 868 mg (84.2% yields) of white powder.

[0212] Preparation of complex: To a solution of 49 mg $ErCl_3$ and 50.9 mg $YbCl_3$ in 1 ml acetone was added 785 mg (1.08 mmole) $Na([n\text{-}C_6F_{13}]_2POO)$ in 11 ml of acetone. After 2 hours of continuous stirring under N_2, 11 ml of deionized water was added. The mixture was heated to boil, filtered and washed with 50 ml of deionized water. The residue was dried in a vacuum oven overnight at 80°C. The reaction yielded 0.56 g of product (68.3% yields). The lifetime of the product

was 4.0 ms.

[0213] **Example 5**

[0214] In this example, the phosphinic acid is $((CF_3)_2CF\text{-}O\text{-}CF_2CF_2)_2POOH$. The phosphinic acid was purified by fractional sublimation. The fraction used for this work was collected at a temperature range of 120°C to 170°C at a vacuum of >5m torr. Phosphorus-31 NMR indicated that the material was > 75% phosphinic and the remainder phosphonic acids.

[0215] Sodium salt formation and complex: $((CF_3)_2CF\text{-}O\text{-}CF_2CF_2)_2POOH$ (0.85 gram) was dissolved in 8.61 g methanol and then added to 1.161 g of 1% NaOH in methanol. Additional NaOH was added to adjust the pH to about 6. A solution of 5.6 mg $ErCl_3$ and 21.7 mg $YbCl_3$ in 1.5 ml of acetone was added dropwise over 1 minute to the solution of $Na[((CF_3)_2CF\text{-}O\text{-}CF_2CF_2)_2POO]$. Initially no precipitate was observed, but after heating at 50°C for 2 hours, some precipitate was obtained which was filtered and washed with small amount of water and then dried. We obtained 158.4 mg of product and measured a lifetime of 3.2 ms.

[0216] **Example 6**

[0217] In this example we report metal salts of the phosphinic acid, $(n\text{-}C_4F_9)_2POOH$, where the molar ratio of the Er to Yb is 1:1.

[0218] Preparation of sodium salt: After dissolving sublimed $(n\text{-}C_4F_9)_2POOH$ (2.25 g, 4.48 mmole) in 24 ml of methanol, 0.18 g (4.48 mmole) of NaOH was added

and the pH adjusted to 7.0. The solution was dried on a warm plate and left overnight in a vacuum oven. We obtained 2.28 g of solid (97% yield).

[0219] Preparation of complex: One gram (1.9 m mole) of $Na[(n\text{-}C_4F_9)_2POO]$ was dissolved in 25 ml of acetone and then added a solution of 87 mg $ErCl_3$ and 89 mg of $YbCl_3$ in 2 ml of acetone. The reaction mixture was stirred under N_2 for two days. Then it was boiled and filtered. The product was dried in a vacuum oven resulting in 800 mg of complex (75% yield). The lifetime of this product was 2.0 ms.

[0220] In the next examples, phosphinic acids and a thiophosphinic acid are converted to sodium salt and then Er/YB complexes (1:3 mole ratio) are prepared. See Table 1 for properties.

[0221] **Example 7**

[0222] $((CF_3)_2CF(CF_2)_6)_2POOH$ (1.012 gram, 0.9792 mmole) was dissolved in 6 ml of methanol, followed by the addition of 3.92 g of 1% wt/wt NaOH solution in methanol. The pH of the solution was adjusted to fall in the range of about 6.0 and about 7.0 by admixing 0.15 g of 1% NaOH in methanol. $ErCl_3$ (22.3 mg) and $YbCl_3$ (68.4 mg) were combined and dissolved in 1 ml of methanol. The solution of $ErCl_3$ and $YbCl_3$ was added over 30 seconds to the stirring $Na[((CF_3)_2CF(CF_2)_6)POO]$ solution. A white precipitate was formed immediately. The reaction mixture was heated to boiling for 5 minutes, cooled to room temperature and then kept overnight. After drying with a gentle stream of N_2, the precipitate was re-suspended in 10 ml of acetone. Ten ml of deionized water was added to remove NaCl. The crystals were filtered the next day, washed 3 times with warm deionized water and dried in a

vacuum oven at 70°C overnight to yield 0.978g of product.

[0223] Example 8

[0224] $((CF_3)_2CF(CF_2)_6)_2PSOH$ (0.5078 gram, 0.4763 mmole) was dissolved in 5 ml of methanol, followed by the addition of 1.93g of 1% wt/wt NaOH in methanol. The pH of this solution was 10.5 after the NaOH addition; the pH was not adjusted. $ErCl_3$ (10.7 mg) and $YbCl_3$ (33.3 mg) were combined and dissolved in 1 ml of methanol. The $ErCl_3$ and $YbCl_3$ solution was added over 30 seconds to the stirring $Na[((CF_3)_2CF(CF_2)_6)PSO]$ solution. An oily white residue formed and adhered to the bottom and the side of the reaction vessel. The reaction mixture was heated to boiling in 5 minutes, then cooled to room temperature and kept overnight. The solution was dried with a gentle stream of N_2. To remove NaCl, the oily residue was treated with a mixture of 10 ml of acetone and 10 ml of deionized water. The acetone/water aliquot was decanted the next day and the oily-looking residue was washed 3 times with warm deionized water and dried to yield 0.470 g of product.

[0225] Example 9

[0226] $(n\text{-}C_{10}F_{23})_2POOH$ (253.7 mg, 0.2237 mmole) was dissolved in 8 ml of methanol followed by the addition of 0.895 g 1% wt/wt NaOH in methanol. The pH of the solution was 7.0. $ErCl_3$ (5.1 mg) and $YbCl_3$ (15.6 mg) were combined and dissolved in 1 ml of methanol. The $ErCl_3$ and $YbCl_3$ solution was added over 30 seconds to the stirring $Na[(n\text{-}C_{10}F_{23})_2POO]$ solution. A white precipitate was formed immediately. The reaction mixture was heated to boiling in 5 minutes, cooled to

room temperature and kept overnight. The solution was dried with a gentle stream of N_2. To extract NaCl, the precipitate was re-suspended in a mixture of 5 ml of acetone and 5 ml of deionized water. The crystals were filtered the next day, washed 3 times with warm deionized water, and dried to yield 0.239 of product.

[0227] Example 10

[0228] (n-C_8F_{17})(n-$C_{10}F_{23}$)POOH (0.5582 gram, 0.5398 mmole) was dissolved in 8 ml of methanol, followed by the addition of 2.159 g 1% wt/wt NaOH in methanol. The pH of the solution was adjusted to fall in the range of about 6.0 and about 7.0 by adding 0.27 g of 1% NaOH in methanol. $ErCl_3$ (12.3 mg) and $YbCl_3$ (37.7 mg) were dissolved in 1 ml of methanol. The $ErCl_3$ and $YbCl_3$ solution was added over 30 seconds to the stirring Na[(n-C_8F_{17})(n-$C_{10}F_{23}$)POO] solution. A white precipitate was formed immediately. The reaction mixture was heated to boiling for 5 minutes, cooled to room temperature and kept overnight. The solution was dried with a gentle stream of N_2. To remove NaCl, the precipitate was re-suspended in 6 ml of acetone and 6 ml of deionized water. The crystals were filtered the next day, washed 3 times with warm deionized water, and dried to yield 0.535 g of product.

Table 1 - Composition and Lifetime for Various Phosphinic and Thiophosphinic Acid Complexes

Example #	Phosphinic Acid	Molar Ratio of Er/ Yb	Lifetime (ms)
1	$(n\text{-}C_8F_{17})_2POOH$	Er only	1.8
2	$(n\text{-}C_8F_{17})_2POOH$	1/1	4.5
3	$(n\text{-}C_8F_{17})_2POOH$	¼	5.1
4	$(n\text{-}C_6F_{13})_2POOH$	1/1	4.0
5	$(i\text{-}C_3F_7OC_2F_4)_2POOH$	¼	3.2
6	$(n\text{-}C_4F_9)_2POOH$	1/1	2.0
7	$((CF_3)_2CF(CF_2)_6)_2POOH$	1/3	4.6
8	$((CF_3)_2CF(CF_2)_6)_2PSOH$[a]	1/3	< 1[c]
9	$(n\text{-}C_{10}F_{23})_2POOH$	1/3	4.6
10	$(n\text{-}C_8F_{17})(n\text{-}C_{10}F_{23})POOH$[b]	1/3	< 1[c]

[a] A thiophosphonic acid
[b] Mixed fluorinated hydrocarbons on phosphinic acid
[c] Lifetime too short to measure accurately using our equipment

[0229] In examples 11-13, we demonstrate the effect of the relative concentration of phosphinic acid (e.g., R_1R_2POOH) to phosphonic acid (e.g., $R_1PO(OH)_2$) on the fluorescence life time of a 1:4 Er:Yb complex.

[0230] Examples 11, 12 and 13

[0231] The desired mixtures of phosphinic/ phosphonic acid were prepared by fractional sublimation of $(n\text{-}C_8F_{17})_2POOH$. In the fractional sublimation procedure, about 0.5 g of partially purified $(n\text{-}C_8F_{17})_2POOH$ was placed in an open container at one end of a 1 cm diameter by 50 cm long sealed glass tube. The sealed glass tube was then evacuated to about 2 mtorr and heated to produce a temperature gradient profile, wherein the temperature at the boat was 180°C and the temperature at the

end opposite the boat was room temperature. The latter end of the tube was attached to the vacuum system. After allowing sublimation for 24 hrs, the tube was removed and cut into 1 cm segments. The samples used in examples 11, 12 and 13 were collected in temperature zones corresponding to average temperature of 130°C, 115°C and 105°C, respectively. The relative amount of phosphinic and phosphonic in the samples were determined using ^{31}P NMR. The samples were converted to Er/Yb complexes in a manner similar to that described in Examples 7-10.

Table 2 - Effect of Mole Percent of Phosphinic and Phosphonic Acid on the Lifetime of Er/Yb Complexes

Example #	Mole % of Phosphinic Acid $(n\text{-}C_8F_{17})_2POOH$	Mole % of Phosphonic Acid $(n\text{-}C_8F_{17})PO(OH)_2$	Molar Ratio of Er/ Yb	Lifetime (ms)
11	100	0	1/4	4.8
12	75	25	1/4	4.0
13	20	80	1/4	<1[a]

[a] Lifetime too short to measure accurately by our equipment.

[0232] As shown in Table 2, the pure phosphinic acid has the highest lifetime (4.8 ms), the sample containing 25 mole% phosphonic acid has somewhat lower fluorescence lifetime (4.0 ms) and sample containing 80% phosphonic derivative has a lifetime too short to measure by our equipment (< 1 ms).

[0233] Comparative Example 14

[0234] In this example, the lifetime of commercial sample of ErFOD, a complex containing both fluorocarbon as well as hydrocarbon moieties was

measured. The ErFOD chemical structure is Er $[(CH_3)_3C\text{-}(CO)\text{-}CH_2\text{-}(CO)\text{-}CF_2CF_2CF_3]_3$.

[0235] This complex has a lifetime of about 1.5 ms. ErFOD has very good solubility and therefore could be compounded into many matrices including perfluoro as well as partially fluorinated resins.

[0236] Film Preparation and Evaluation

[0237] Table 3 gives two examples of composite films in a perfluoropolymer matrix. The active loadings are 20% and 34% (by wt), respectively. These examples show that we can achieve high concentrations of active materials in fluoropolymers with high fluorescent lifetimes.

[0238] Film Example 15

[0239] To 101.9 mg of the complex prepared in example 2 ($ErYb[(n\text{-}C_8F_{17})_2POO]_6$) was added 13.2 μliter of dimethylacetamide (DMAC) and 13.2 μiter of FC 75 (perfluoro n-butyl tetrahydrofuran) and 1.73 g of a CT Solv 180. The mixture was heated to 100°C with stirring until it became clear in 10-30 minutes. The solution was cooled to room temperature and 1.23 g of 16% (wt/wt) amorphous cyclopolymerized perfluoro-vinyl ether in a perfluoroether solvent was added. The resulting clear solution was filtered through a 0.45 micron filter and spin cast on a silicon wafer. After drying for 5-10 hours at 130°C, it was removed and the fluorescence lifetime was measured. Other substrates known to those of

ordinary skill in the art can be used.

[0240] Film Example 16

[0241] In this example, appropriate quantities of Er phosphinic complex and Yb phosphinic complex were dissolved in a perfluorosolvent solution containing perfluoropolymer. DMAC (16.7 μliter) and 3.24 g of the CT Solv 180 were added to 25.9 mg of $Er[(n\text{-}C_8F_{17})_2POO]_3$ and 103.5 mg of $Yb[(n\text{-}C_8F_{17})_2POO]_3$. The mixture was heated to 60-90°C with stirring. After dissolution, 3.33 g of 16% (wt/wt) amorphous cyclopolymerized perfluoro-vinyl ether in a perfluoroether solvent was added was added with stirring. The solution was filtered (0.45 Micron) and film cast on a silicon wafer. The film was dried as above and the lifetime was measured. Other substrates known to those of ordinary skill in the art can be used.

Table 3 - Lifetime of a Composition of a Perfluorofilm Containing Phosphinic Acid Complexes

Film Example #	Active Form	Concentration of Active Form(wt%) in Solid Film[a]	Lifetime (ms)
15	$ErYb[(n\text{-}C_8F_{17})_2POO]_6$ [b]	34%	2.1
16	$ErYb_4[(n\text{-}C_8F_{17})_2POO]_{15}$ [c]	20%	3.8

[a] Solution concentration is 10 wt% solid before spin coating
[b] This designates a phosphinic acid complex with Er/Yb 1/1 molar compositon using $[(n\text{-}C_8F_{17})_2POO^-]$.
[c] This was made by dissolving individual Er phosphinic acid and Yb phosphinic acid derivatives to make the solution; the phosphinic acid used was $[(n\text{-}C_8F_{17})_2POO^-]$.

[0242] Example 17 - Fluorescence lifetime measurements

[0243] The fluorescence lifetime measurements can be performed using any suitable fluorescence spectrometer using any suitable technique. The measurements reported here were performed using the experimental set-up shown in FIG. 11. Laser 310 (980 nm diode laser) was modulated by function generator 300 (WaveTek Model 275) to give a square wave pulse of amplitude 0.5 V and frequency of 10 Hz. The pump beam generated by laser 310 was expanded before being incident on sample 320, and the resulting fluorescence signal generated was expanded and collimated using lenses 330. The collimated pulsed beam was then directed toward semiconductor photo-detector 350 after passing through 1550 nm narrow band filter 340 to block reflected pump light. The signal from the photo-detector was amplified with a Model 101C Transimpedance amplifier 360, and the amplified signal was collected by a Tektronix TDS 3032 digital oscilliscope 370 upon being triggered by the trigger signal from the function generator. The metastable state lifetime (τ) was determined by fitting the averaged fluorescence signal (I(t)) to a single exponential decay, $I(t) = \alpha + \beta^*\exp(-t/\tau)$, where α and β are constant.

[0244] Example 18 - ^{31}P NMR experiments

[0245] The NMR experiments can be performed using any suitable probe, magnetic field, and NMR instrument. NMR experiments were recorded at 30°C on a Bruker DRX 500-MHz spectrometer equipped with a Broadband Observe (BBO), z-axis gradient probe. One dimension ^{1}H NMR experiments were collected with a 7.5

kHz spectral width and 32k complex data points. One dimension ^{31}P NMR experiments were collected with a 40 kHz spectral width and 32k complex data points. One dimension ^{19}F NMR experiments were collected with a 100 kHz spectral width and 128k complex data points. All NMR data were processed using XWIN NMR program (Bruker).

Other exemplary embodiments of the invention will be apparent from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

WHAT IS CLAIMED IS:

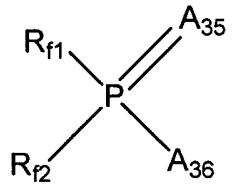
1. A composition comprising at least one suitable metal is selected from aluminum (Al), chromium (Cr), scandium (Sc), yttrium (Y), lutetium (Lu), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm) and ytterbium (Yb);

at least one first ligand; and

at least one second ligand,

wherein

the at least one first ligand is selected from



where

A_{35} is selected from O and S;

A_{36} is selected from -OH, -SH, and -OR_{80};

R_{f1}, and R_{f2} can be the same or different, can be branched or unbranched, can be linked to form cyclic or extended structures, and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated ether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, halogenated silazanes, halogenated

olefins, fluorinated alkyl, fluorinated aryl, fluorinated cyclic alkyl, fluorinated arylalkyl, fluorinated alkylaryl, fluorinated ether, fluorinated thioether, fluorinated ether thioether, fluorinated aklyl amino groups, fluorinated alkylene, fluorinated silylene, fluorinated siloxanes, fluorinated silazanes, fluorinated olefins, branched perfluorinated C_{1-20} alkyl, unbranched perfluorinated C_{1-20} alkyl, perfuorinated C_{1-6} alkyl C_{1-10} alkyl ethers, n-C_8F_{17}, n-C_6F_{13}, n-C_4F_9, n-C_2F_5, $(CF_3)_2CF(CF_2)_4$, n-$C_{10}F_{21}$, n-$C_{12}F_{25}$, $(CF_3)_2CF(CF_2)_6$, and $(CF_3)2CFO(CF_2)_2$; and

R_{80} can be branched or unbranched and is selected from C_{1-6} alkyl, C_{1-15} alkyl, C_{3-15} aryl, C_{4-15} alkylaryl, and $C_{4-}15$ arylalkyl.

2. The composition of claim 1 wherein said composition is an optical composition.

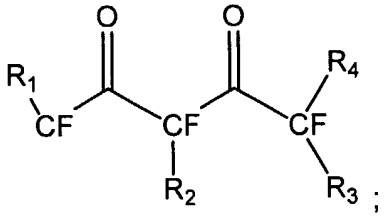
3. The composition of claim 1 wherein said at least one second ligand is selected from:

benzoyl acetonate ; dibenzoyl methane; 1,1,1-trifluoro-2,4-pentanedion; 1,1,1,5,5,5-hexafluoro-2,4-pentanedion; 2,2'-bipiperazine ; 2,4-pentanediamine ; picolylamine ; 1,8-naphthyridine ; tris(2-pyridylmethyl)amine ; salicylidene aminate ; N,N'-disalicylidene ethylenediamine ; N-salicycildene cyclohexyl aminate ; 1,1,1,3,5,5,5-heptafluoro-2, 4-pentanedion ; 1,1,1,5,5,5-hexafluoro-3,3-deutero-2,4-pentanedion ; thenoyl trifluoroacetonate ; 1,1,1,5,5,6,6,6-octafluoro-2,4-hexanedion ; 1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedion ; pentafluorobenzoyl trifluoroacetonate ; bis(pentafluorobenzoyl)methane ; pentadecafluorooctanoic acid ; N,N'-disalicylidene-1,2-cyclohexylenediamine; acetyl ; acetylacetonate

($CH_3COCHCOCH_3$); 2,2'-dipyridine; benzyl; cycloocta-1,5,-diene ; cyclooctatetraene; cyclopentadienyl; benzene; pentamethylcyclopentadienyl ; cyclohexyl; dibenzylmethyl; dimethoxyethane; N,N'-dimethylformamide; 1,2-bis(dimethylphosphino)ethane; 1,2-bis(dimethylphosphino)methane; ethane-1,2-dithiolate; $C_6H_4(C_2H_5)COCHCOC_6H_4(C_2H_5)$; hexamethylphosphoric triamide; toluene; 2,4,6-trimethylphenyl; $NC_6H_4CH_3$; neopentoxide; benzoate; $CH_3C_6H_4CO_2$; oxalate; phenyl; phthalic acid; picolinate; pyridine; pyrazole; salicylaldehyde; tolyl; triflate; 1,4,7,10,13,16-hexaoxacyclooctadecane; glycine; alanine; valine; leucine; isoleucine; methionine; phenylalanine; tryptophane; serine; threonine; asparagine; glutamine; aspartic acid; glutamic acid; cysteine; tyrosine; histidine; lysine; arginine; adenine; cytosine; uracil; guanine; thymine; oxygen; halogen; hydroxyl; carbon monoxide; water; $C_6H_4O_2$; $C_6H_{12}O_2$; $-OC_4H_9$; $-OC_3H_7$; $-OCH_3$; $-C_7H_4O_3$; $-C_5H_7O_2$; $-OOC_5H_4N$; $-CH_3$; $-C_3H_7$; $-C_4H_9$; carbanyldicyanomethanide ; $(CH_3CH_2CH_2CH_2\underset{\underset{CH_2CH_3}{|}}{CH}\text{-}CH_2O)_2POOH$; 5,10,15,20-tetraphenyl porphyrin ; 2,6 diaminopyridine; polymers made from $O_2CCH_2CO_2$; polymers made from diberzoylmethane; fluorescein; $-P(OCH_3)_3$; $R_1CH(SO_2R_f)_2$; fluorocarbon acid; triphenylphosphine; Me_3P; $^nBu_3P$; CH_3CN; PEt_3; $P(OPh)_3$; tetramethylethyldiamine; $FSbF_5$; FBF_3^-; $OPOF_2^-$; FPF_5^-; $FAsF_5^-$; $FReF_5^-$; $OTeF_5^-$; $R_1R_2C(SO_2CF_3)_2$; $R_1N(SO_2CF_3)_2$; $R_1R_2P\text{-}CH_2\text{-}CH_2\text{-}PR_3R_4$; theroyltrifluoroacetones; $(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2$; $^tBu_2P(CH_2)_2P\ ^tBu_2$; $(C_6H_{11})_2P(CH_2)_3P(C_6H_2)_2$; $^tBu_2P(CH_2)_3P\ ^tBu_2$; o-$^tBu_2PCH_2C_6H_4CH_2P\ ^tBu_2$; $OPR_{40}R_{41}O$; 1,3-diketones; benzoylbenzoate; trifluoro-2-furylacetylacetone; phthalates; naphthalates; dinaphthoylmethide; dipyridines; terpyridines; 2,2'-bypyridine-1,1'-dioxide, 2,2',6',2''-

terpyridine; 4,4'-dimethyl-2,2'-dipyridine; phenanthrolines; o-phenanthroline isothiocyanate; trioctylphosphine oxide; perfluorinated sulfonate polymers; phenantroline; thenoyltrifluoroacetylacetonate; $R_{42}C(OH)CHCOR_{43}$; anions of aromatic carbonic acids; benzoic acid; picolinic acid; dipicolinic acid; trialkyl-, alkylphenyl-, and triphenyl-phosphinoxide; dialkyl-, alkylphenyl-, and diphenyl-sulfoxide; alkyl-, alkylphenyl-, and phenyl-amine; alkyl-, alkylphenyl-, and phenylphosphate; 2,2',6,2"terpyridine; 1,10-phenantroline; N,N,N',N'-tetramethylethylene diamine; $[C_6H_5C(O)CH_2]P(O)(OH)_2$; $[C_6H_5C(O)CH_2]_2P(O)OH)$; $[C_6H_5C(O)CH_2]_2P(O)OCH_3$; $[C_6H_5C(O)CH_2]_2P(O)OC_2H_5$; $[C_6H_5C(O)CH_2]_2P(O)OC_6H_4Cl$; $(C_6H_5)_2P(O)OH$; $(C_6H_5—CH=CH)_2P(O)OH$; $(C_6H_5—C\equiv C)_2P(O)OH$; $(C_6H_5)_2P(O)OH$; $(C_6H_5)(CH_3)P(O)OH$; $(CH_3)_2P(O)OH$; $(C_6H_5)_2As(O)OH$; $(CH_3)_2As(O)OH$; $C_6H_5C(O)OH$; $NH_3CH_2P(C_6H_5)O_2$; lipids; polymers; polyamines; schiff bases; β-diketones; benzoyltrifluoroacetone; dibenzoylmethane; ditheonylmethane; furoylacetone; 2-furoylbenzoylmethane; 2-furoyltrifluoroacetone; hexafluoroacetylacetone; 1-acetyl-1-methyl acetone; β-naphthoyltrifluoroacetone; 2-theonylacetone; 2-theonyltrifluoroacetone (4,4,4-trifluoro-1,2-thienyl-1,3-butanedione); 1,1,1-trifluoroacetylacetone; 1,3-diphenyl-1,3-propanedione; 1-phenyl-1,3-butanedione; hydroxyaldehydes; 3-chlorosalicylaldehyde; 5-chlorosalicylaldehyde; 4,6-dimethylsalicylaldehyde; 2-hydroxy-1-naphthaldehyde; and 2-hydroxy-3-naphthaldehyde; hydroxy acids; salicylic acid; anthraquinone carboxylic acid; naphthoic acids; 8-hydroxyquinoline and its alkyl, aryl, and halo-substituted derivatives; -NCS; $OPPh_3$; NO_3; ethyne; $R_1\text{-}CFCO_2^-$; $S_2CNR_1R_2$; $S_2P(C_6H_iF_j)$, where i+j=5; $-N(Si(R_1)_3)(Si(R_2)_3)$; $R_1R_2P=N\text{-}R_3$;

$(n\text{-}C_8H_{17})_3P{=}O$; partial esters of mono-orthosilicic acid, diorthosilicic acid, triorthosilicic acid, tetraorthosilicic acid, pentaorthosilicic acid, monometasilicic acid, dimetasilicic acid, trimetasilicic acid, tetrametasilicic acid, pentametasilicic acid, dimesosilicic acid, trimesosilicic acid, tetramesosilicic acid, pentamesosilicic acid, triparasilicic acid, tetraparasilicic acid, pentaparasilicic acid, tetratetrerosilicic acid, pentatetrerosilicic acid, and penterosilicic acid; $(n\text{-}C_8F_{17})_2POOH$; $(n\text{-}C_6F_{13})_2POOH$; $(i\text{-}C_3F_7OC_2F_4)_2POOH$; $(n\text{-}C_4F_9)_2POOH$; $[(CF_3)_2CF(CF_2)_6]POOH$; $[(CF_3)_2CF(CF_2)_6]PSOH$; $(n\text{-}C_{10}F_{21})_2POOH$; $(CH_3)_3C\text{-}(CO)\text{-}CH_2\text{-}(CO)\text{-}CF_2CF_2CF_3$; $[NR_3A_8A_{10}R_1R_2]$; $[N(R_1)R_{70}(NR_2)]$; $[(NR_1R_2)(NR_3R_4)]$; $[R_{75}R_{76}A_{25}(A_{26}A_{27})]$; $[R_{50}A_{25}(A_{26}A_{27})]$;



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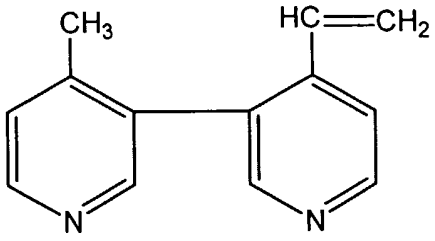

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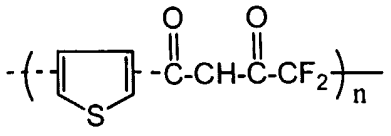

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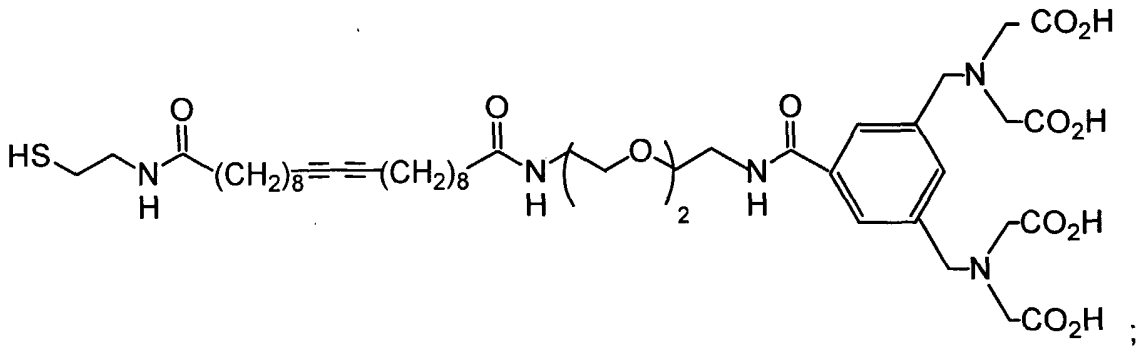

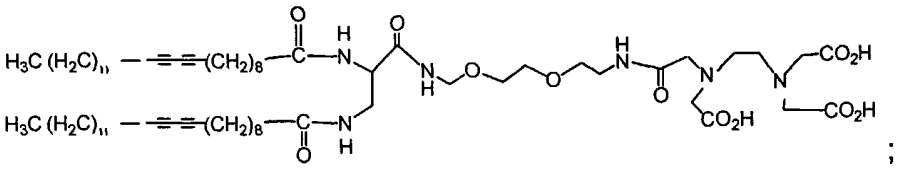

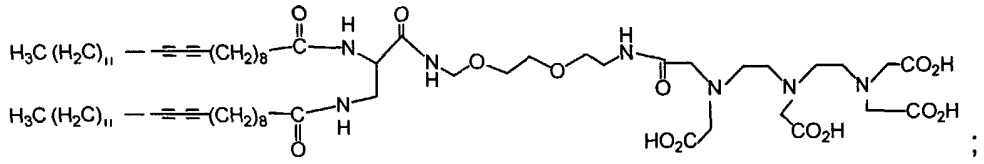

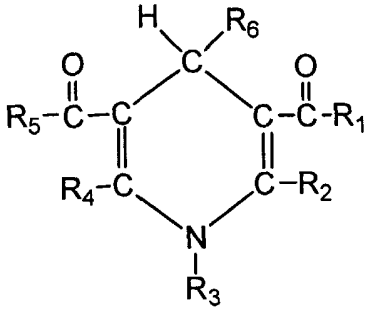

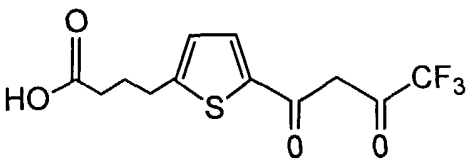

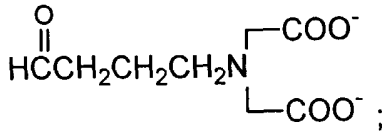

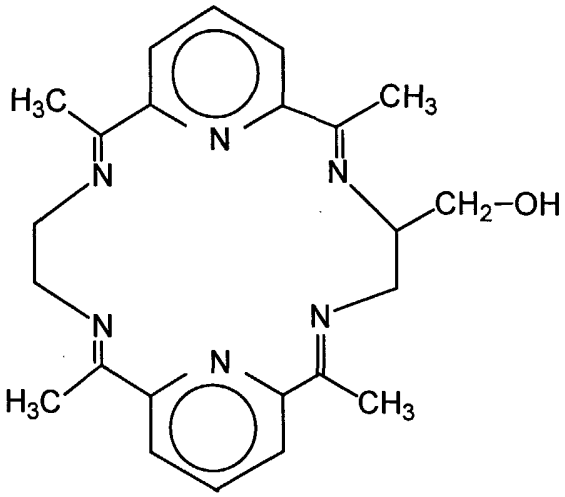
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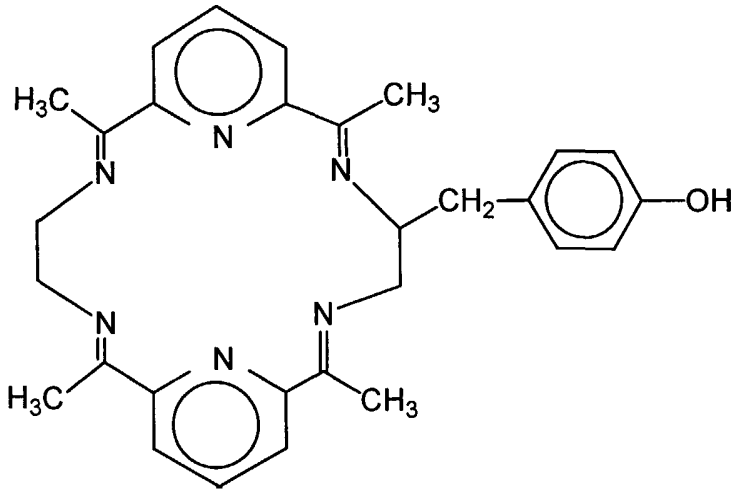
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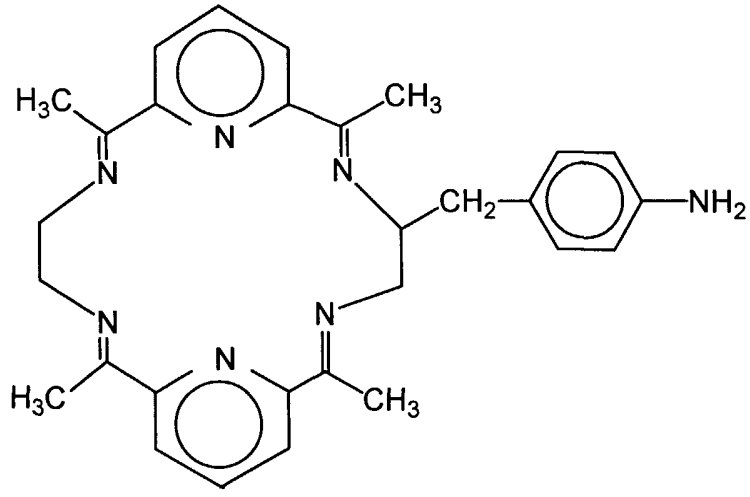
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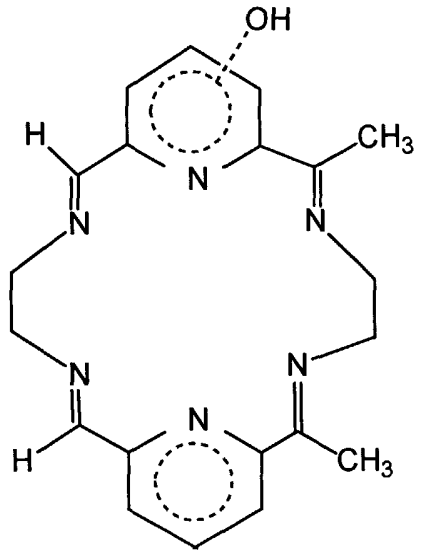

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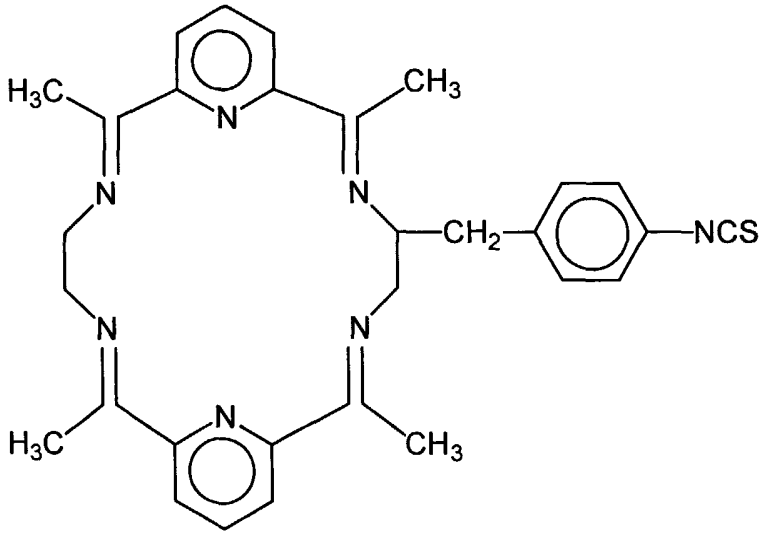

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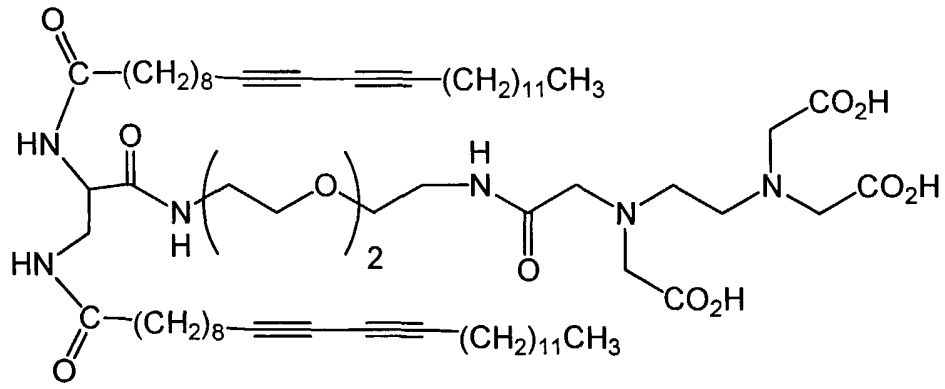

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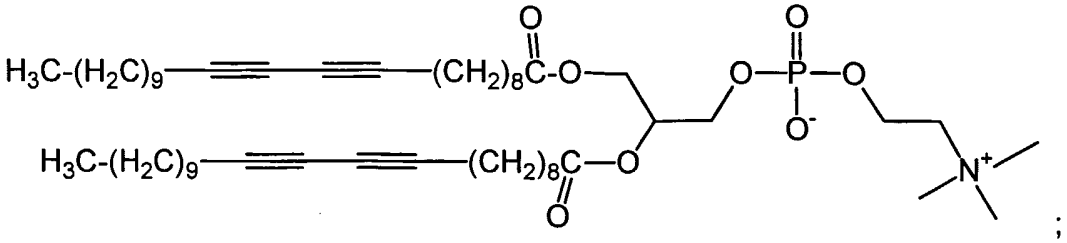

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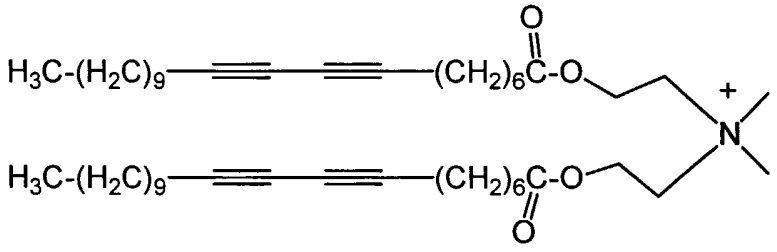

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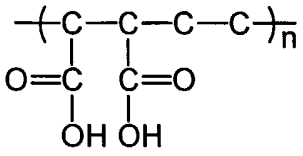

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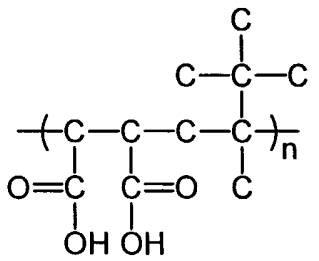

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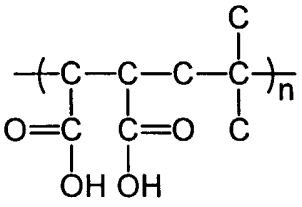

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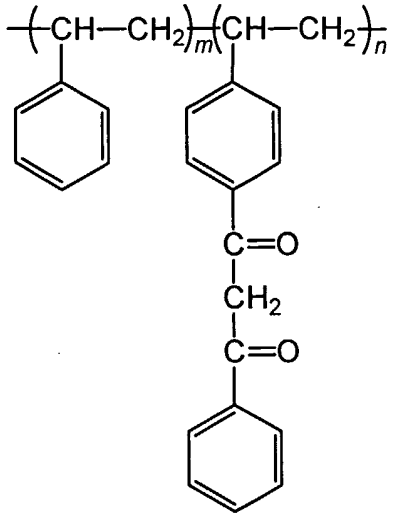

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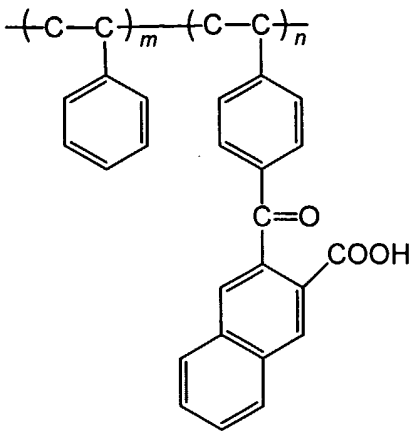

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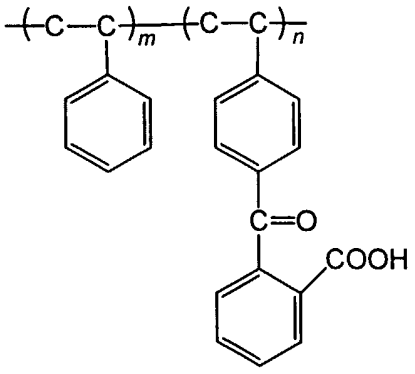

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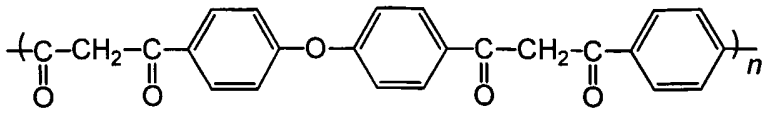

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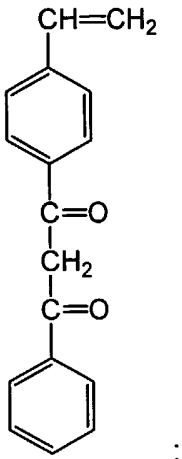

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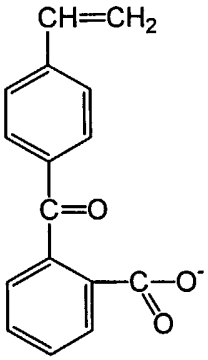

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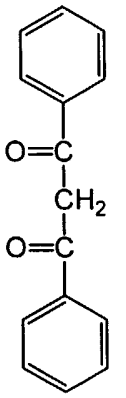

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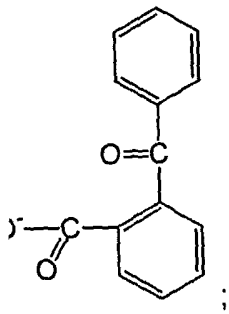

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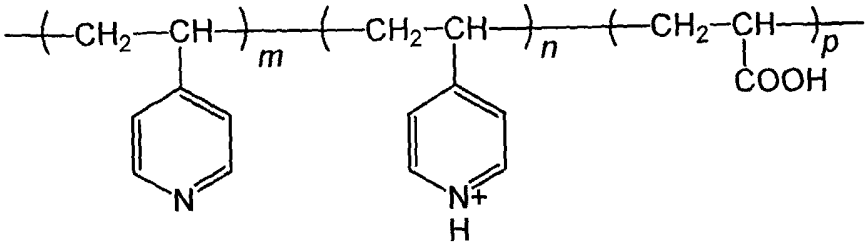

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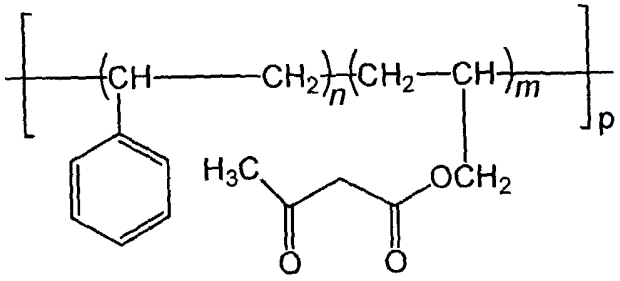

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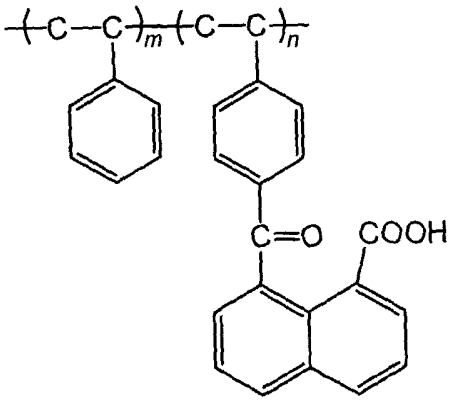

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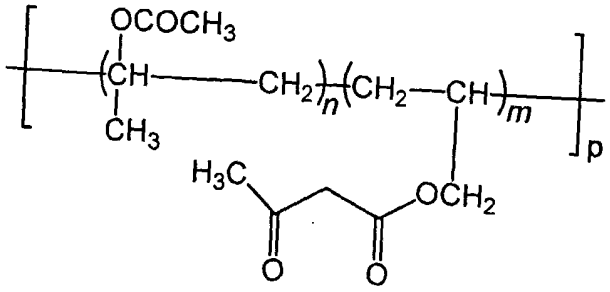

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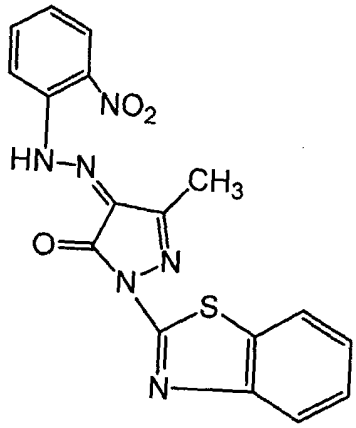

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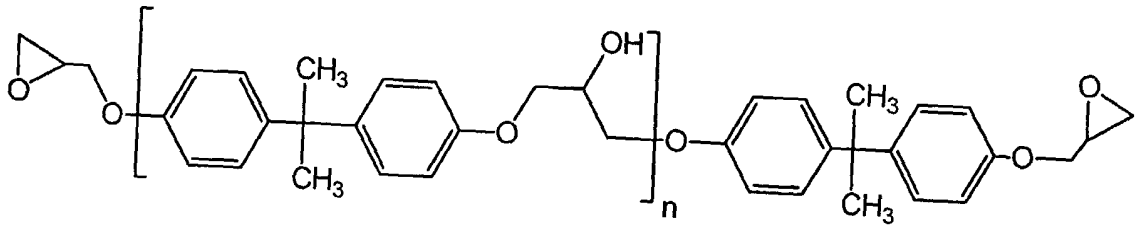

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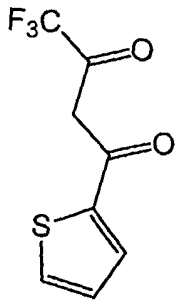

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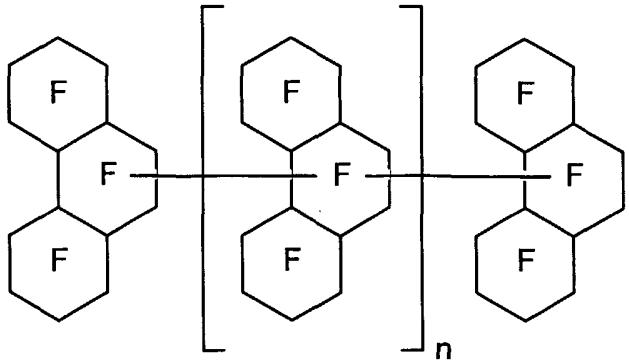
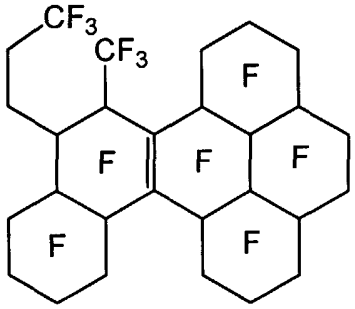

F
F
F
F
F
F
F
F
F
n

;


CF3
CF3
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F
F
F
F
F

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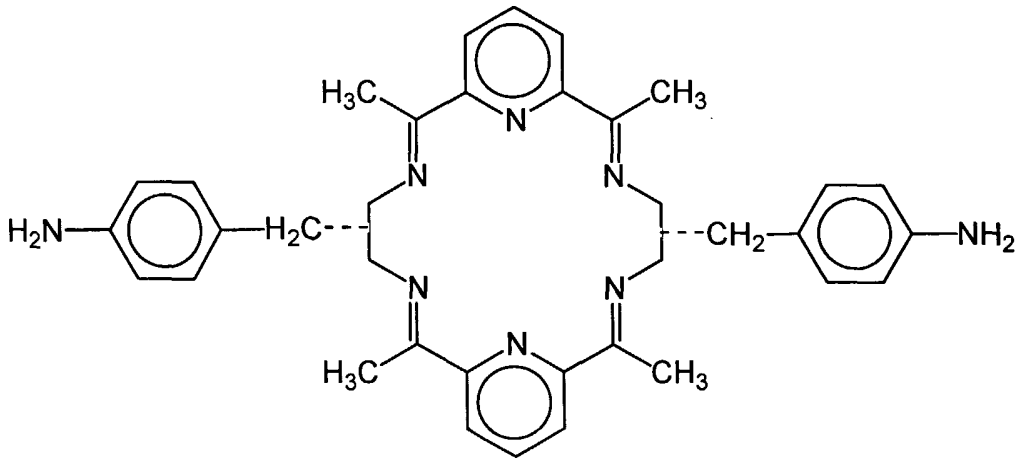
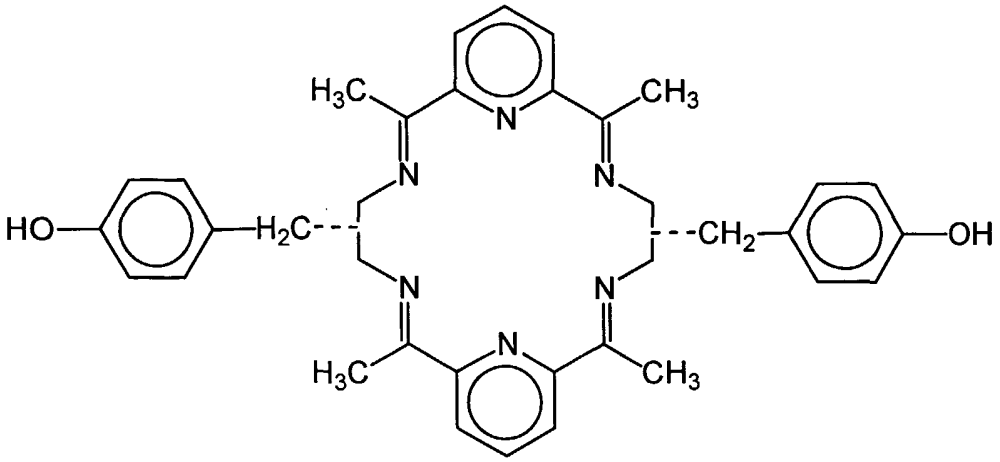

H3C
CH3
N
N
N
H2N
H2C
CH2
NH2
N
N
N
H3C
CH3

;



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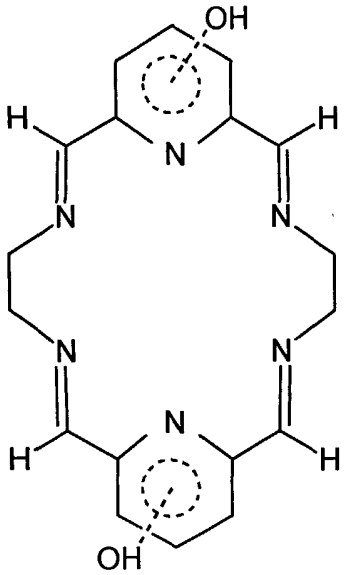

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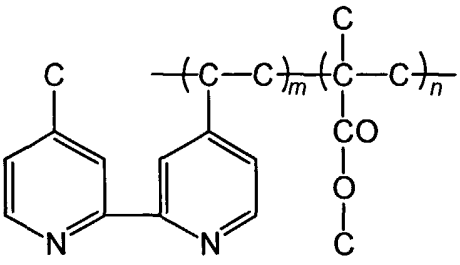

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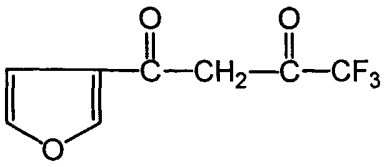
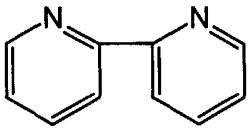
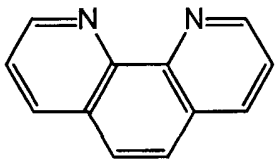

O
O
C—CH2—C—CF3
O
;


N
N
;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N
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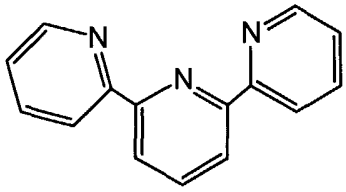
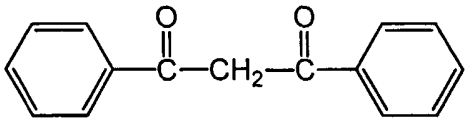
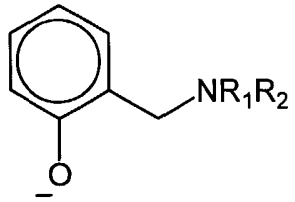
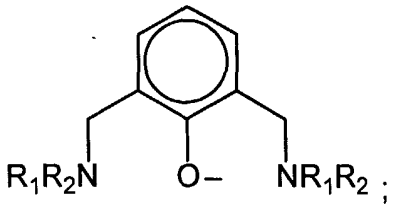
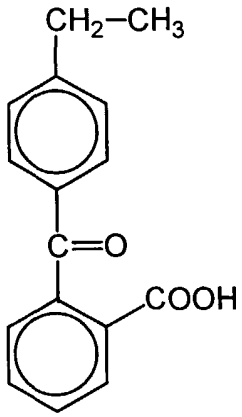
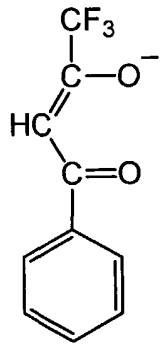

N
N
N
;

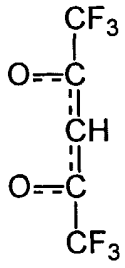

O
O
C—CH2—C
;

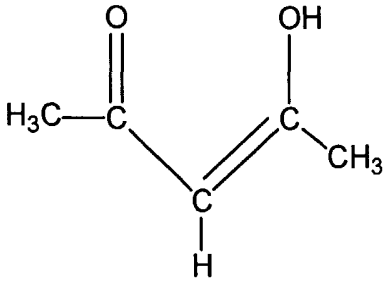

NR1R2
O
;


R1R2N
O–
NR1R2
;


CH2–CH3
C=O
COOH
;


CF3
C–O–
HC
C=O
;


CF3
O=C
CH
O=C
CF3
;



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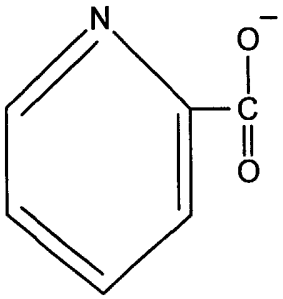

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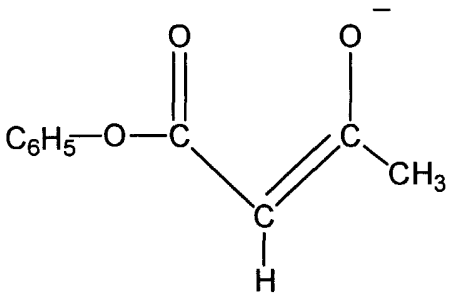

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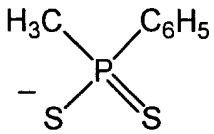

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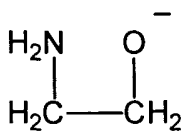

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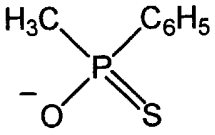
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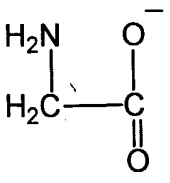
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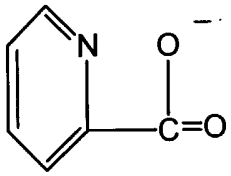
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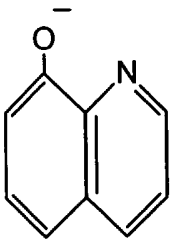
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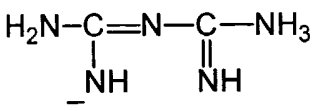
$NH_2CH_2COO^-$;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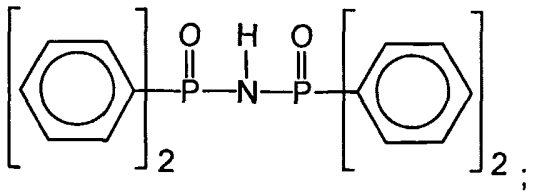

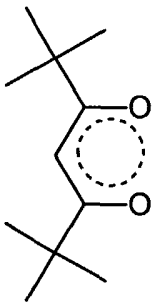

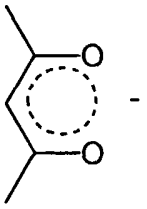

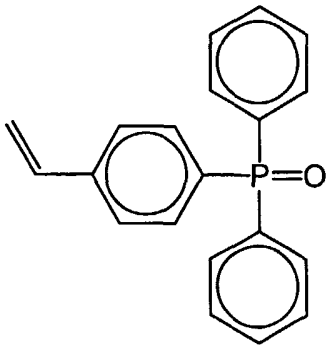

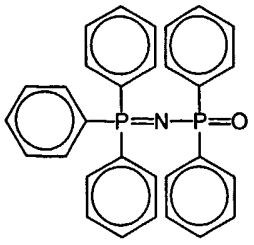
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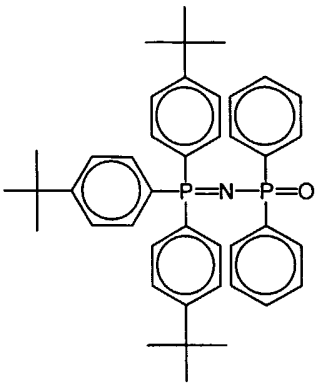
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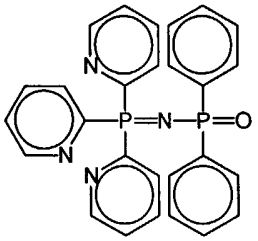
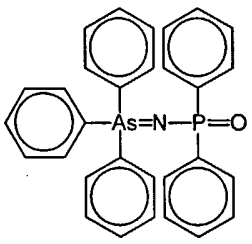

N
P=N—P=O
N
N
;


As=N—P=O
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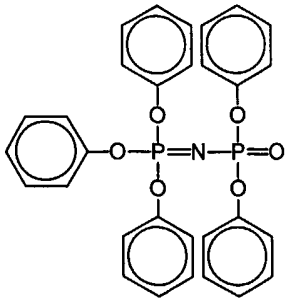
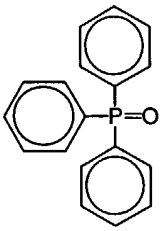

O
O
O
P=N
P=O
O
O
;


P=O
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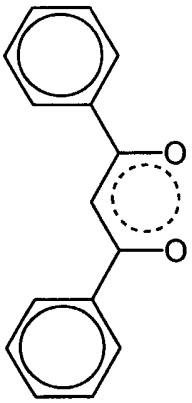
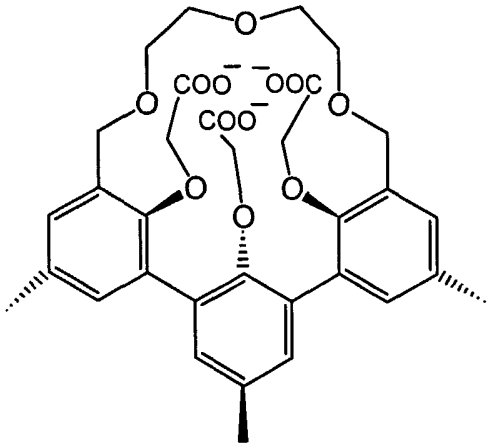
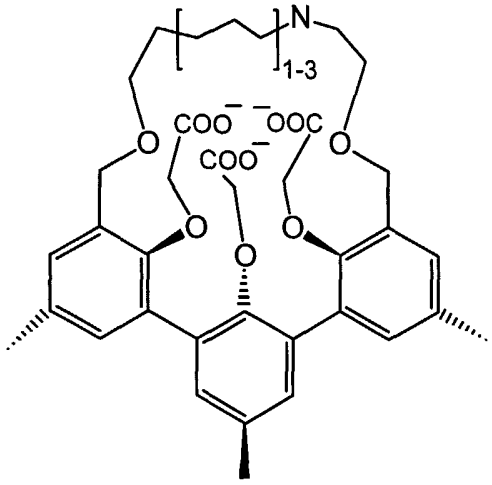
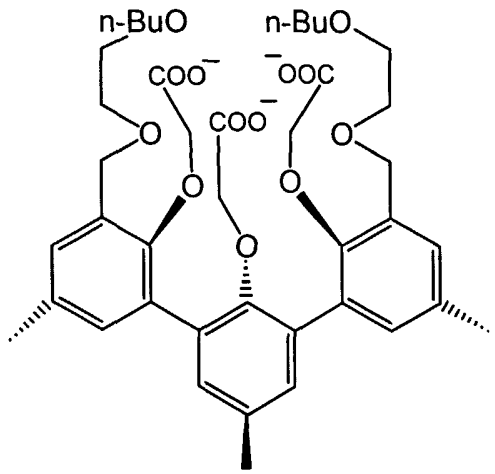

O
O
-
;


O
COO⁻ ⁻OOC
COO⁻
O
O
O
O
O

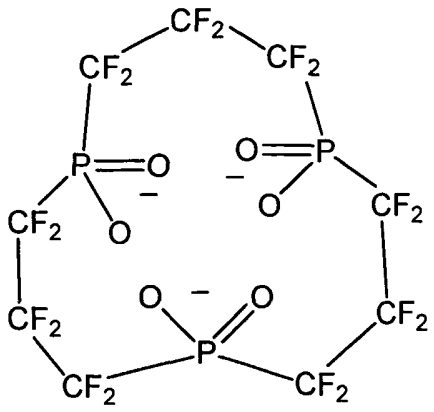
;


N
1-3
COO⁻ ⁻OOC
COO⁻
O
O
O
O
O

;


n-BuO
n-BuO
COO⁻
⁻OOC
COO⁻
O
O
O
O
O

;



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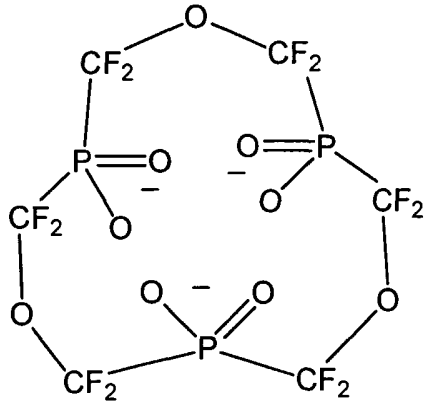

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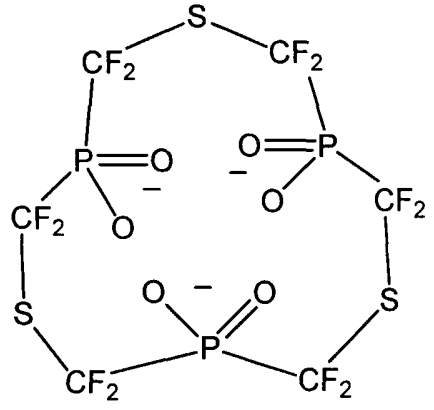

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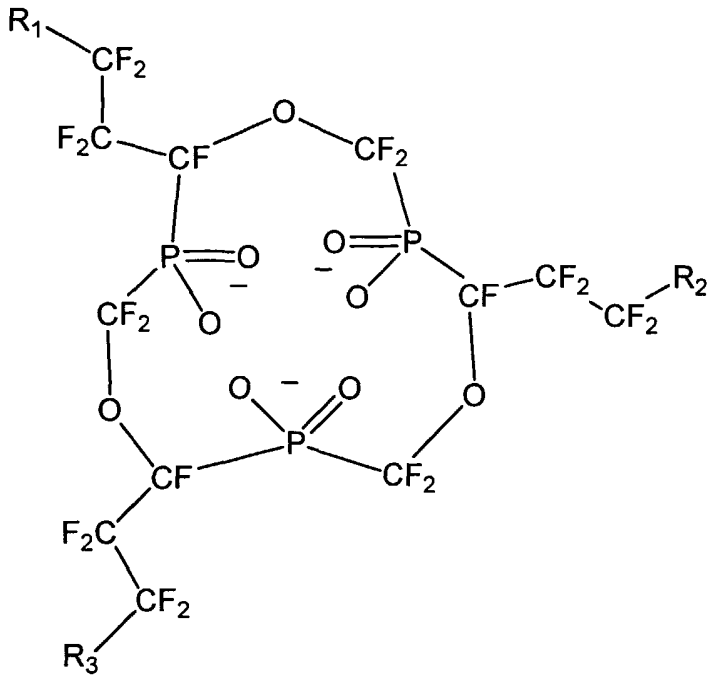
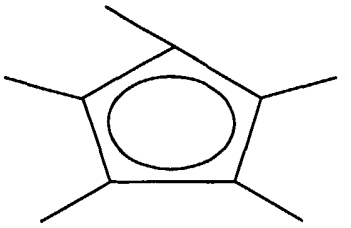

R1
CF2
F2C
CF
O
CF2
P
O
O
O
P
O
CF
CF2
CF2
R2
CF2
O
O
O
O
P
O
CF
CF2
F2C
CF2
R3

;



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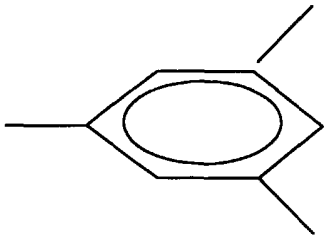

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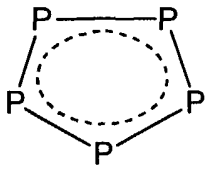
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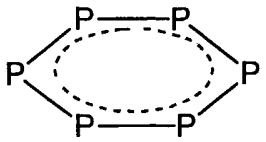
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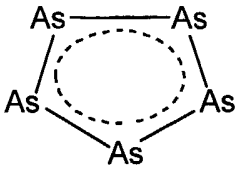
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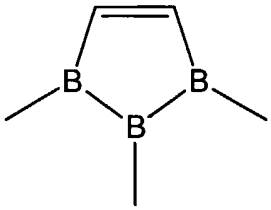
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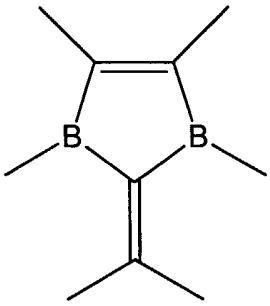
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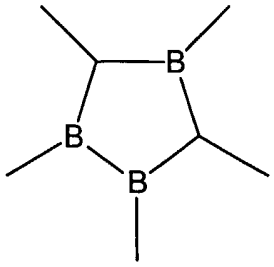
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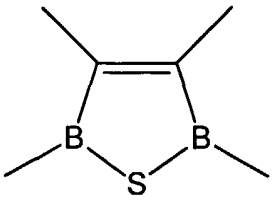
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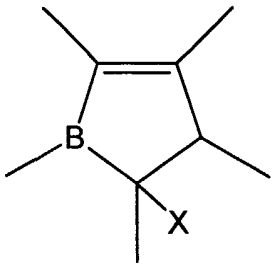
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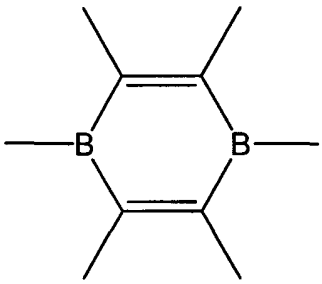
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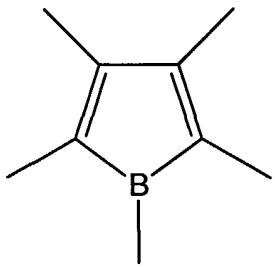
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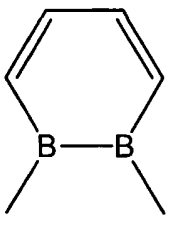
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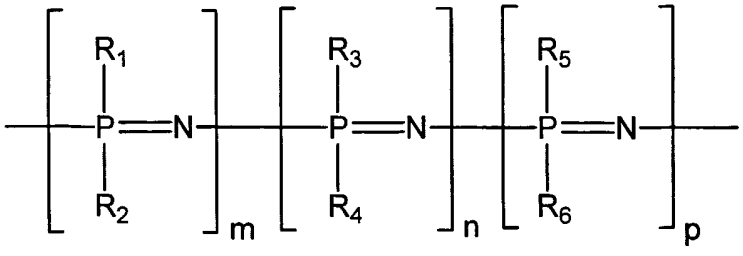

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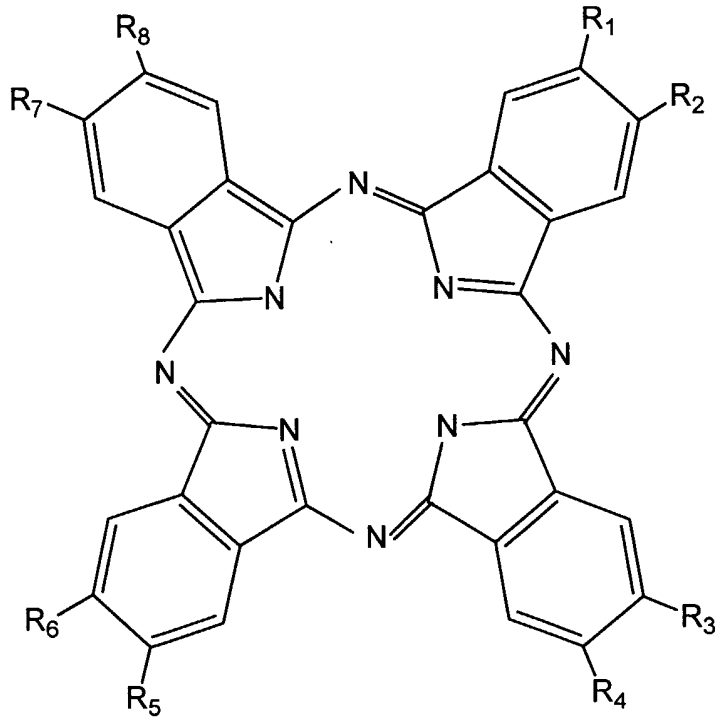

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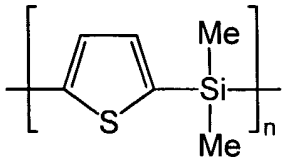

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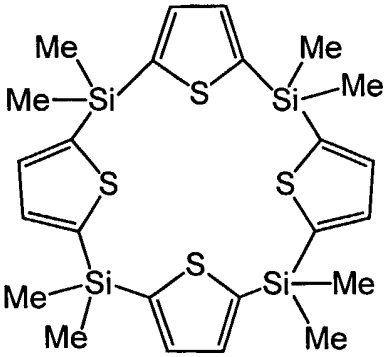
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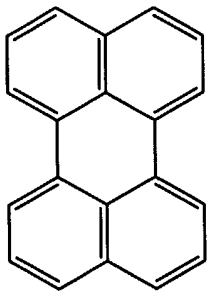
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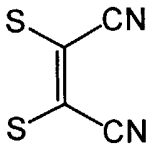
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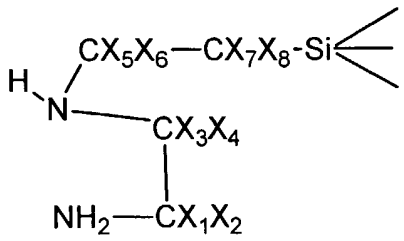
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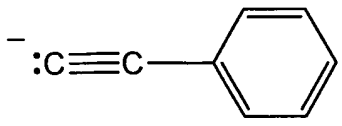
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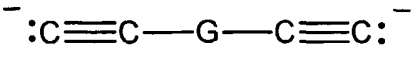

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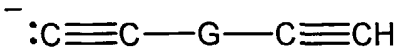

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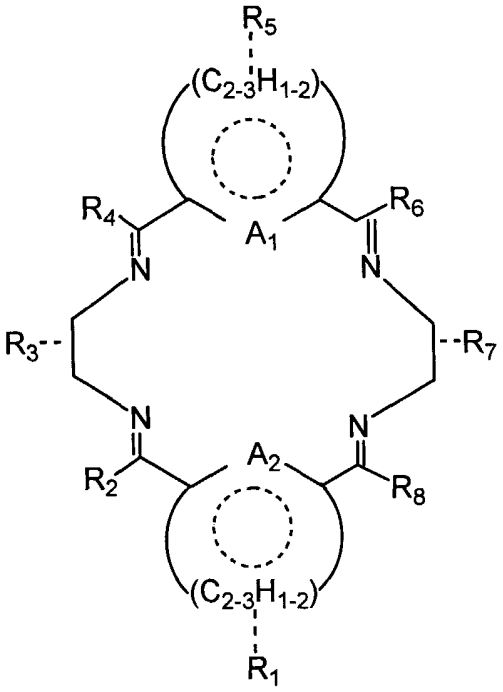

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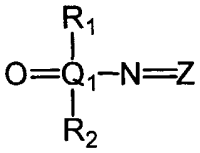

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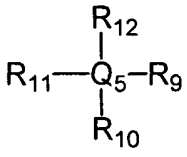

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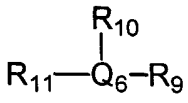

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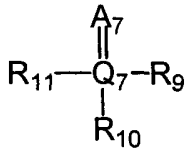

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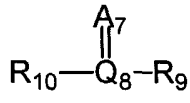

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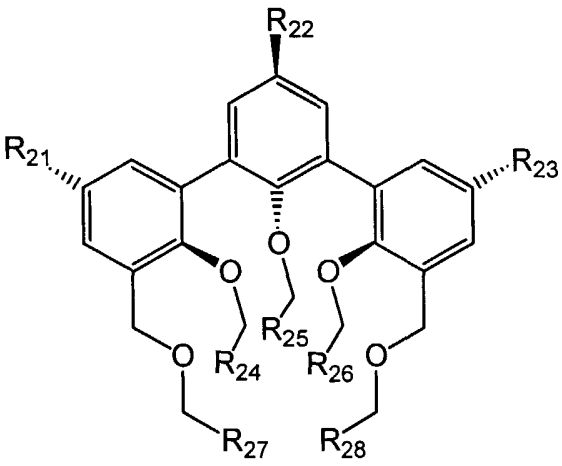

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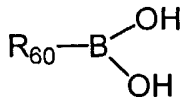

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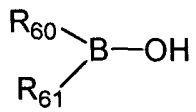

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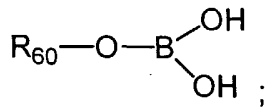

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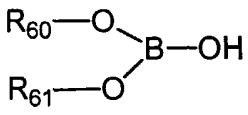
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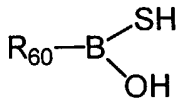
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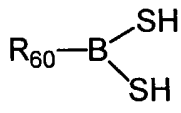
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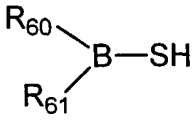
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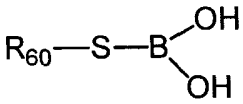
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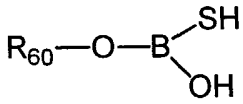
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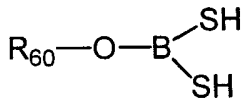
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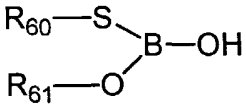
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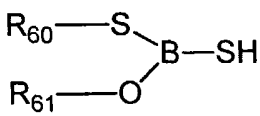
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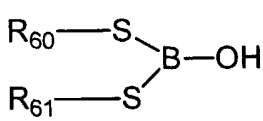
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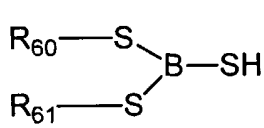
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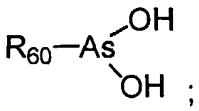
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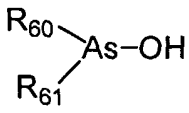
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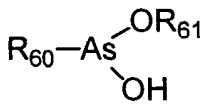
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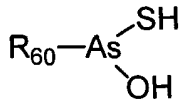
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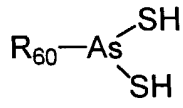
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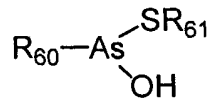
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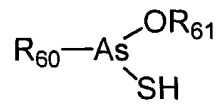
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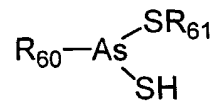
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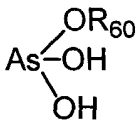
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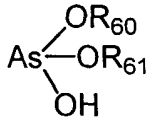
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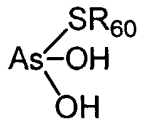
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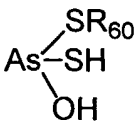
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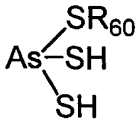
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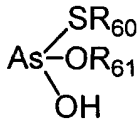
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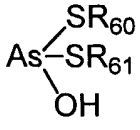
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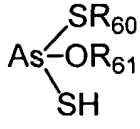
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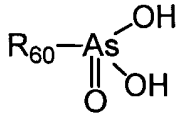
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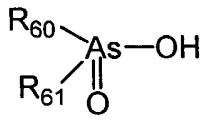
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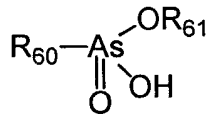
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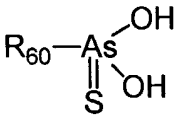
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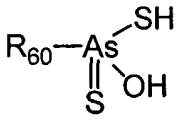
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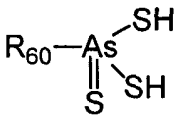
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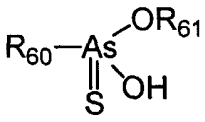
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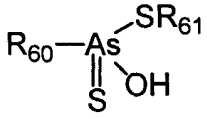
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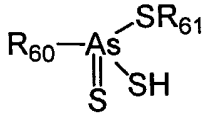
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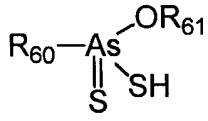
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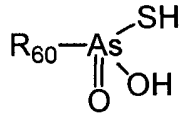
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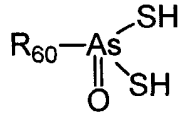
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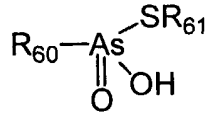
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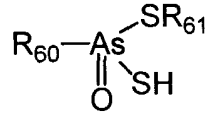
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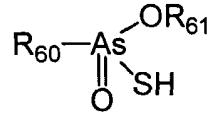
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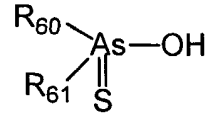
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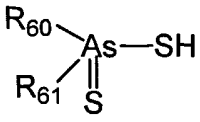
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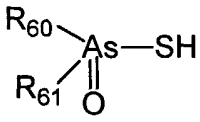
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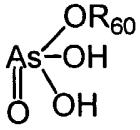
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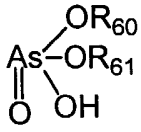
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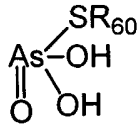
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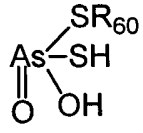
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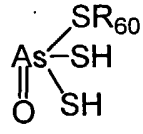
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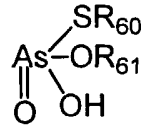
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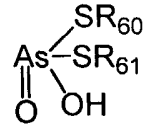
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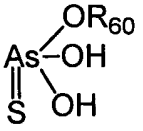
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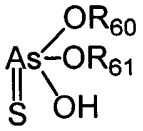
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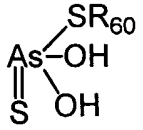
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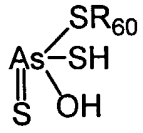
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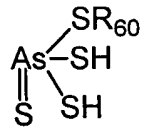
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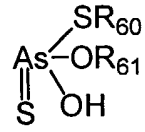
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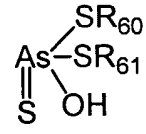
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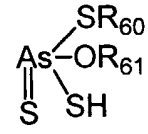
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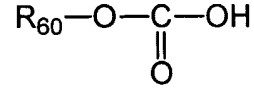
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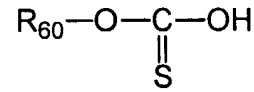
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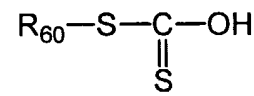
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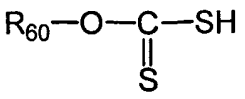
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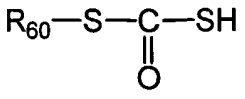
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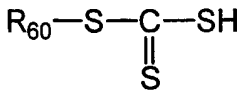
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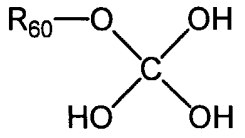
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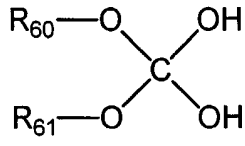
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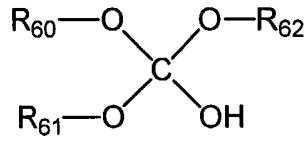
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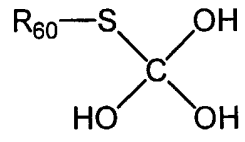
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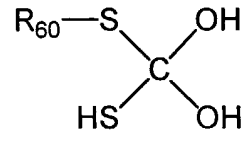
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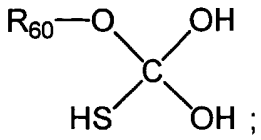

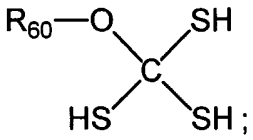

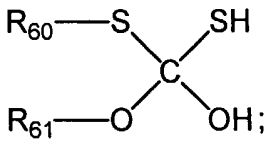

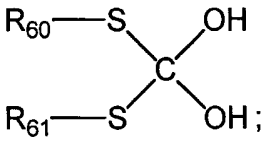

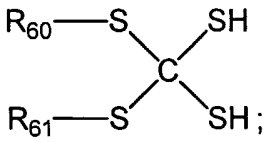

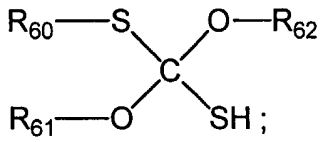

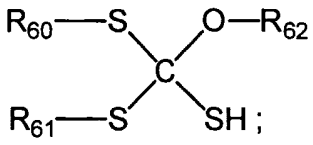

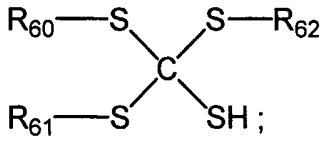

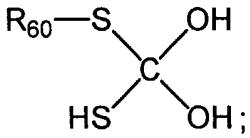

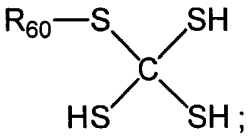

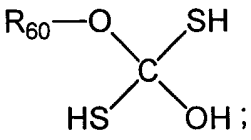

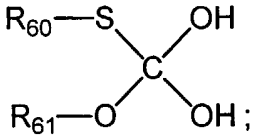

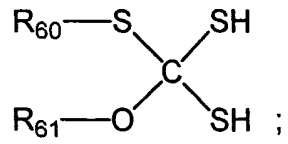

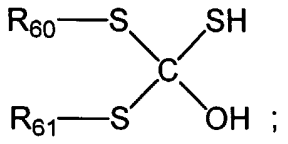

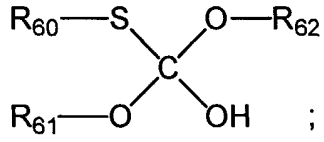

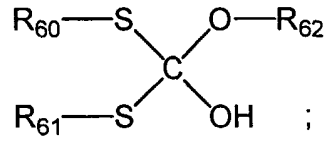

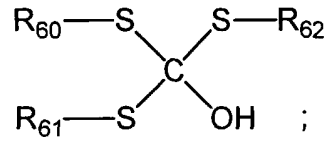

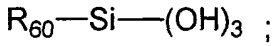

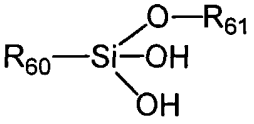

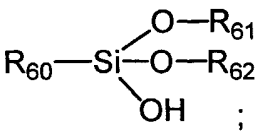
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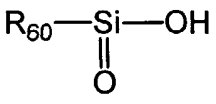
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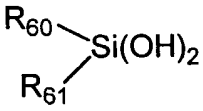
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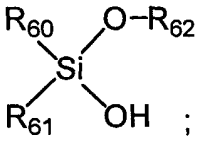
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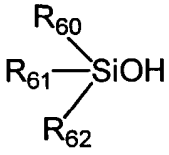
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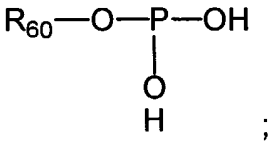
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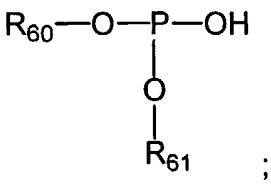
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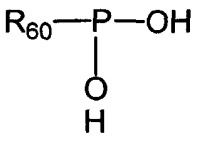
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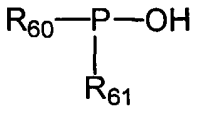
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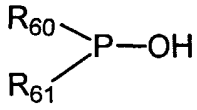
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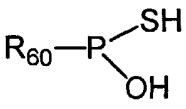
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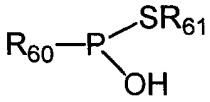
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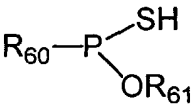
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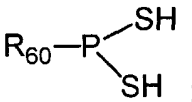
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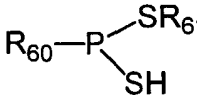
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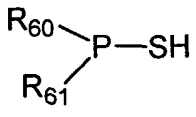
R60
P
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R61
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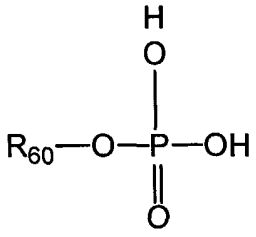
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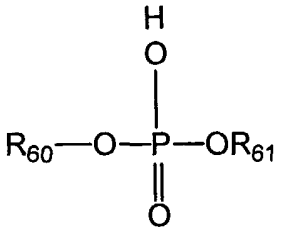
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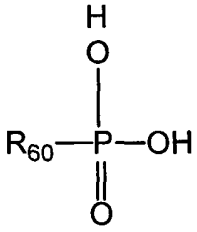
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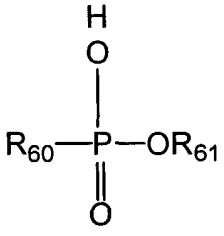
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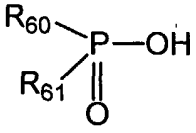
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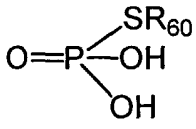
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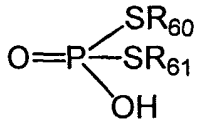
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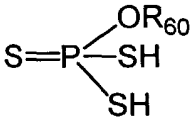
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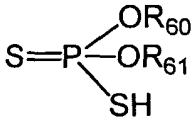
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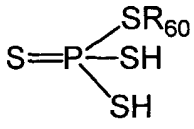
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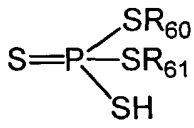
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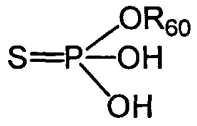
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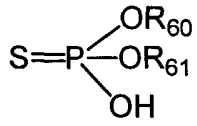
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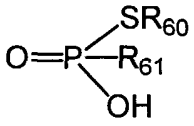
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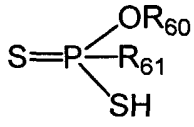
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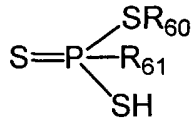
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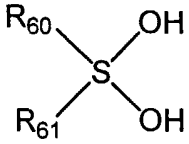
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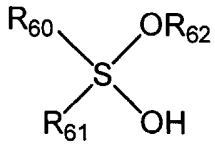
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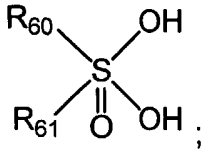
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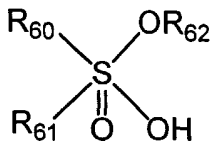
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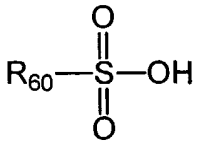
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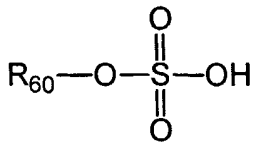
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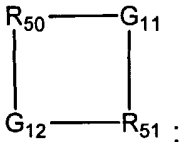
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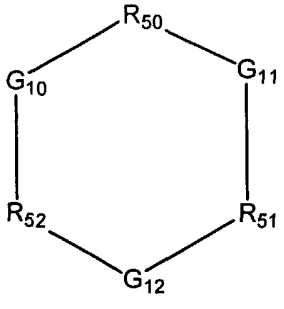
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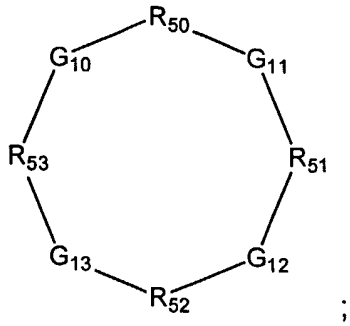


;

wherein,

A_1 and A_2 can be the same or different and are selected from N, S and O;

A_3, A_4, A_5 and A_6 can be the same or different and are selected from P and N;

A_7 is selected from S and O;

A_8 and A_9 can be the same or different and are selected from O, S, Se, Te, Po and N;

A_{10} is selected from B, Ge, Ga, N, P, As, Sb, Bi, S, C and Si, wherein if A_{10} is C or Si then $A_{11}R_1$ =nothing;

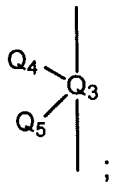
A_{11} and A_{12} can be the same or different and are selected from O, S, N, and nothing;

A_{20}, A_{21}, and A_{22} can be the same or different and are selected from O, S, Se, Te and Po;

A_{23} is selected from S, Se, Te and Po;

G is selected from nothing, p-$C_6(X)_4$, and p-$C_6(X)_4$-$C_6(X_1)_4$;

G_{10}, G_{11}, G_{12}, and G_{13} can be the same or different and are



;

Q_1 and Q_2 can be the same or different and are selected from P, As and Sb;

Q_3 is selected from N, P, As and Sb;

Q_4 and Q_5 can be the same or different and are selected from O, S, Se and Te;

Q_6 is selected from B, As, and P;

Q_7 is selected from As and P;

Q_8 is selected from C and Si;

X, X_1, X_2, X_3, X_4, X_5, X_6, X_7 and X_8 can be the same or different and are selected from H, F, Cl, Br and I;

X_9 is selected from F, Cl, Br and I;

Z is $Q_2(R_3)_3$ or an oligophosphoranyl group;

n, m and p can be the same or different and are selected from any integer in the range of 1 to 100;

R_f is selected from perflourinated alkyl, perflourinated aryl, perflourinated cyclic alkyl, perflourinated arylalkyl, and perflourinated alkylaryl;

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 can be the same or different, can be linked to form cyclic or extended structures, and are selected from halide, halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated

ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes and halogenated silazanes;

R_9 is selected from HO- and HS- ;

R_{10}, R_{11} and R_{12} can be the same or different and are selected from R_{50}, R_{51}, R_{52}, R_{53}, R_{60}, $R_{60}O$-, $R_{60}S$-. R_{61}, $R_{61}O$-, $R_{61}S$-, HO- and HS- ;

R_{21}, R_{22} and R_{23} can be the same or different and are selected from H, a branched or linear alkyl group having 1-50 carbon atoms, a branched or linear alkenyl group having 1-50 carbon atoms, a branched or linear halogenated alkyl group having 1-50 carbon atoms, –C(O)H, –COOH, –O–R_{30}, –O–R_{30}–OH, –R_{30}–OH, -$COOR_{30}$, $COOR_{30}$–C(O)H, –$COOR_{30}$–COOH, O–R_{30}–NH_2, –NO_2, and an amine group;

R_{24}, R_{25} and R_{26} can be the same or different and are selected from -$(CH_2)_{0-3}$COOH, –$(CH_2)_{0-3}COOR_{29}$, –$(CH_2)_{0-3}SO_3H$, –$(CH_2)_{0-3}SO_3R_{29}$, $(CH_2)_{0-3}$–O–$P(O)(OR_{29})_2$, $(CH_2)_{0-3}$-O-$P(O)OH(OR_{29})$, –(CH_2)–O–$P(OR_{29})_3$, –$(CH_2)_{0-3}$-O-$POH(OR_{29})_2$, and –$(CH_2)_{0-3}$–O–$P(O)H(OR_{29})$;

R_{27} and R_{28} can be the same or different and are selected from -C(O)-O-R_{30}, –C(O)–COOH, –CH(O)–$COOR_{30}$, and -C(O)-$NR_{30}R_{30}$, and further may joined to form a cyclical compound selected from –CH_2–O–$(CH_2$–CH_2–O–$)_{0-3}$–CH_2–, -$(CH_2$-$N(R_{30})$-$CH_2)_{1-4}$-, –C(O)–NR_{30}-R_{31}–NR_{30}–C(O)–, and –C(O)–O–R_{31}–O–C(O);

R_{29} is a branched or linear alkyl group having 1 to 3 carbon atoms or a phenyl group;

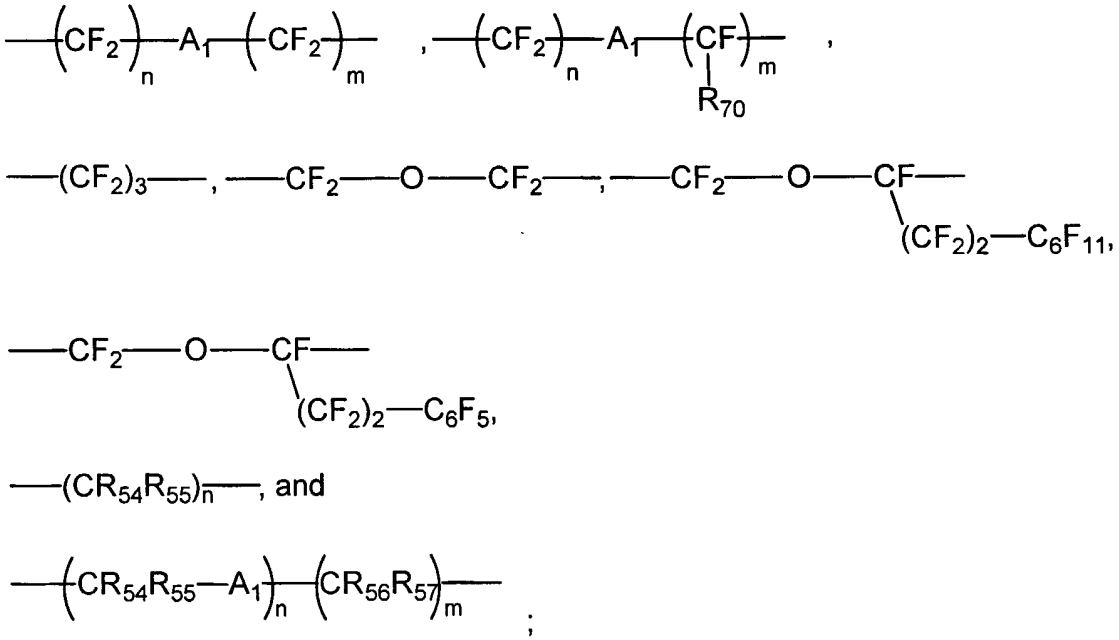
R_{30} is a branched or linear alkyl group or branched or linear alkenyl group having 1 to 50 carbon atoms;

R_{31} is a branched or linear alkyl group having 2 to 8 carbon atoms;

R_{40} and R_{41} can be the same or different and are selected from H, F, CH_3, C_4H_9, C_5H_{11}, C_6H_5, C_6F_5, C_6H_{13}, C_7H_{15}, C_7H_7, C_8H_{17}, $C_{14}H_{12}O$, and $CB_{10}H_{10}CCH_3$;

R_{42} and R_{43} can be the same or different and are selected from F_3C—, thenoyl C_4H_3S—, furanoyl C_4H_3O—, t-butyl and perfluoro-n-propyl;

R_{50}, R_{51}, R_{52}, and R_{53} can be the same or different and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, halogenated silazanes,



R_{54}, R_{55}, R_{56}, and R_{57} can be the same or different and selected from F, Cl, Br, I, halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated

thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes and halogenated silazanes, halogenated polyamide, halogenated polyether, halogenated polyimide, halogenated polythioethers, $-(CF_2)_p-CF_3$, $-(CF_2)_p-C_6F_5$, and $-(CF_2)_p-C_6F_{11}$; and

R_{60}, R_{61} and R_{62} can be the same or different and are selected from alkyl, amyl, isoamyl, hexyl, heptyl, octyl, isomeric octyls, octadecyl, lauryl, normal or branched dodecyl, normal or branched tetradecyl, normal or branched cetyl, aryl, phenyl, diphenyl, naphthyl, aralkyl, phenyloctadecyl, alkaryl, octadecylphenyl, tetradecylphenyl, decylphenyl, hexylphenyl, methylphenyl, cetylphenyl, radicals containing ether, sulfide or ester groups, cyclic nonbenzenoid radicals, cyclohexyl, alicyclic radicals, oxy radicals, radicals containing thio, amino, or halogen, (where any of the R_{60}, R_{61} and R_{62} radicals can substituted or unsubstituted);

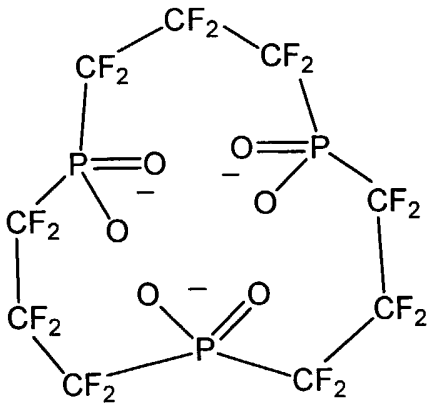
R_{75} and R_{76} can be the same or different and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes and halogenated silazanes;

wherein,

when two or more ligands are chosen and one or more variables from each ligand has the same designation, these variables can be the same or different for each ligand.

4. The composition of claim 3 wherein said at least one second ligand can be further halogenated, further fluorinated, perhalogenated or perfluorinated.

5. The composition of claim 3 wherein said at least one second ligand is selected from $[C_6H_5C(O)CH_2]P(O)(OH)_2$; $[C_6H_5C(O)CH_2]_2P(O)OH$); $[C_6H_5C(O)CH_2]_2P(O)OCH_3$; $[C_6H_5C(O)CH_2]_2P(O)OC_2H_5$; $[C_6H_5C(O)CH_2]_2P(O)OC_6H_4Cl$; $(C_6H_5)_2P(O)OH$; $(C_6H_5—CH=CH)_2P(O)OH$; $(C_6H_5—C\equiv C)_2P(O)OH$; $(C_6H_5)_2P(O)OH$; $(C_6H_5)(CH_3)P(O)OH$; $(CH_3)_2P(O)OH$; $(C_6H_5)_2As(O)OH$; $(CH_3)_2As(O)OH$; $C_6H_5C(O)OH$; $NH_3CH_2P(C_6H_5)O_2$; $(n\text{-}C_8F_{17})_2POOH$; $(n\text{-}C_6F_{13})_2POOH$; $(i\text{-}C_3F_7OC_2F_4)_2POOH$; $(n\text{-}C_4F_9)_2POOH$; $[(CF_3)_2CF(CF_2)_6]POOH$; $[(CF_3)_2CF(CF_2)_6]PSOH$; $(n\text{-}C_{10}F_{23})_2POOH$; $(CH_3)_3C\text{-}(CO)\text{-}CH_2\text{-}(CO)\text{-}CF_2CF_2CF_3$; $[NR_3A_8A_{10}R_1R_2]$; $[N(R_1)R_{70}(NR_2)]$; $[(NR_1R_2)(NR_3R_4)]$; $[R_{75}R_{76}A_{25}(A_{26}A_{27})]$; $[R_{50}A_{25}(A_{26}A_{27})]$;



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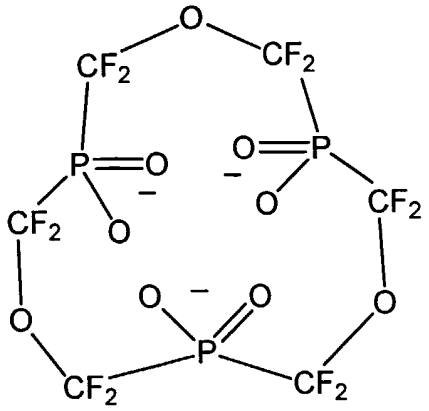

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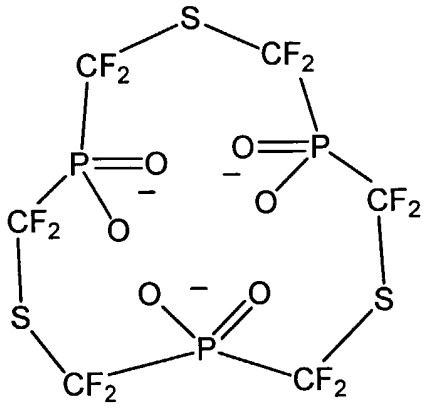

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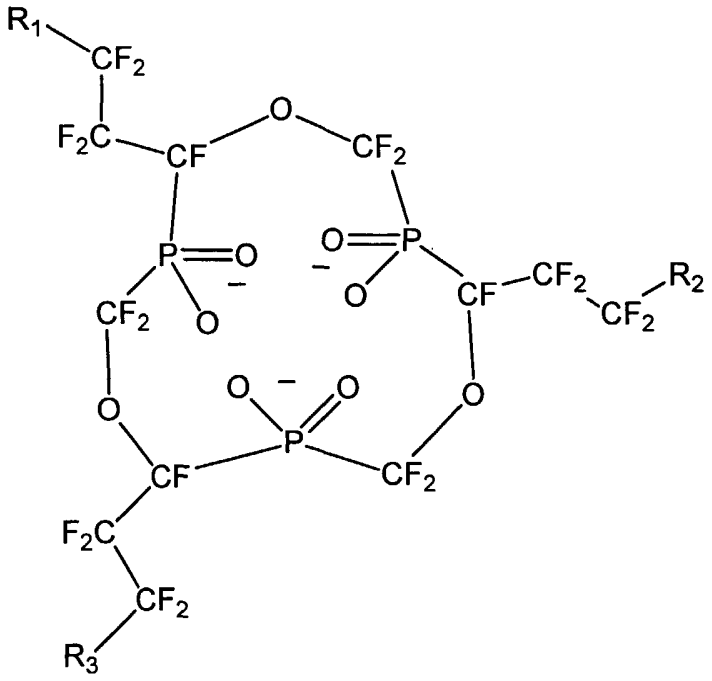

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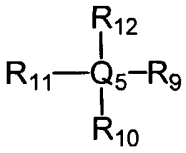

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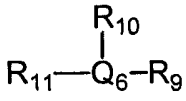

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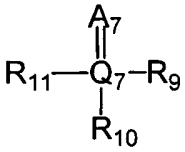

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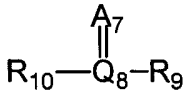

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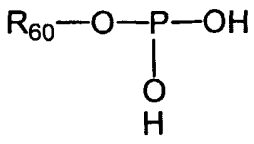
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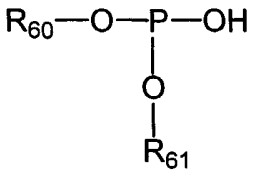
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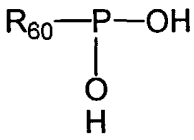
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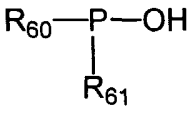
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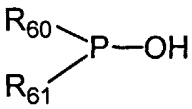
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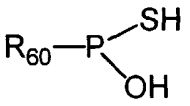
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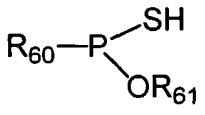

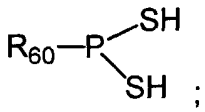

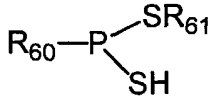

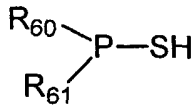

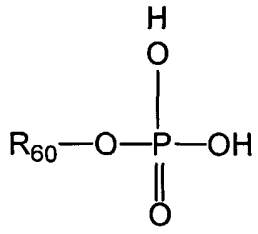

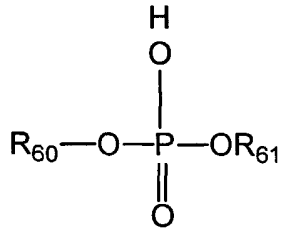

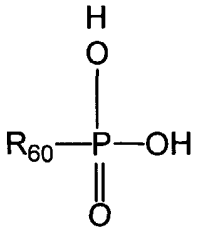
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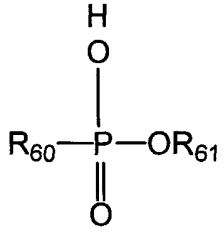
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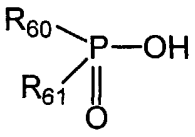
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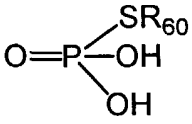
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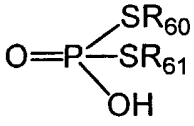
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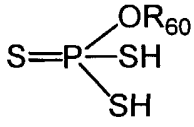
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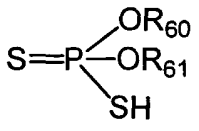
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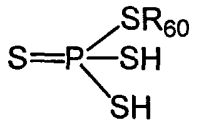
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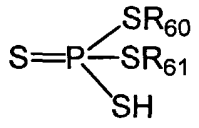
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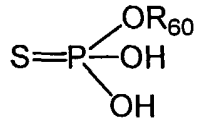
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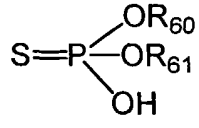
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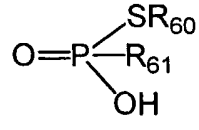
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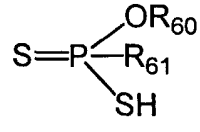
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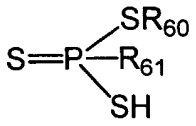

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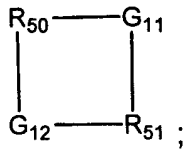

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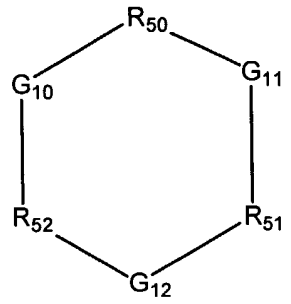

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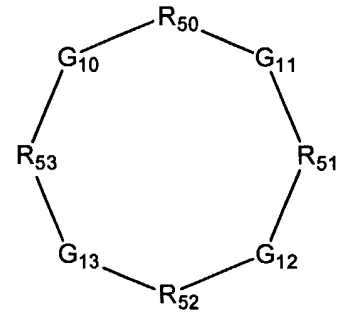

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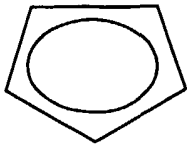
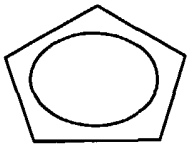
6. The composition of claim 1 wherein said composition comprises at least one complex selected from $Er[(n\text{-}C_8F_{17})_2POO]_3$; $ErYb[(n\text{-}C_8F_{17})_2POO]_6$; $ErYb_4[(n\text{-}C_8F_{17})_2POO]_{15}$; $ErYb[(n\text{-}C_6F_{13})_2POO]_6$; $ErYb_4[(i\text{-}C_3F_7OC_2F_4)_2POO]_{15}$; $ErYb[(n\text{-}C_4F_9)_2POO]_6$; $ErYb_3[((CF_3)_2CF(CF_2)_6)_2POO]_{12}$

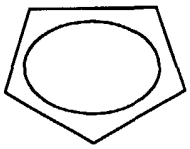
;$ErYb_3[((CF_3)_2CF(CF_2)_6)_2PSO]_{12}$; $ErYb_3[(n\text{-}C_{10}F_{23})_2POO]_{12}$;$ErYb_3[(n\text{-}C_8F_{17})(n\text{-}C_{10}F_{23})POO]_{12}$; $Er[(CH_3)_3C\text{-}(CO)\text{-}CH_2\text{-}(CO)\text{-}CF_2CF_2CF_3]_3$.; $ErYb[(n\text{-}C_8F_{17})_2POO]_6$; $ErYb_{10}[(n\text{-}C_8F_{17})_2POO]_{33}$;



M_1



M_2



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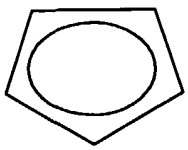

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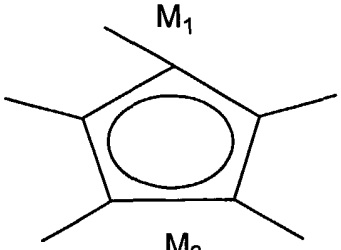

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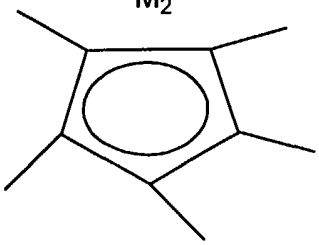

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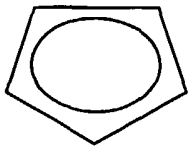

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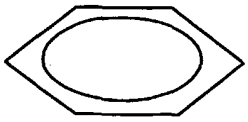

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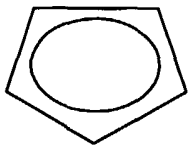

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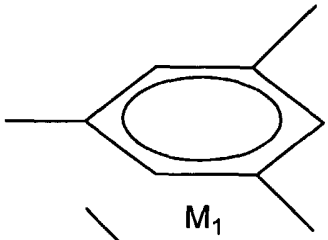

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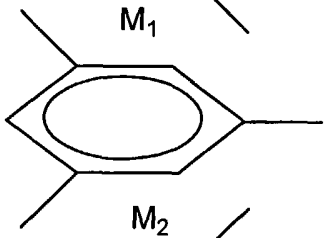

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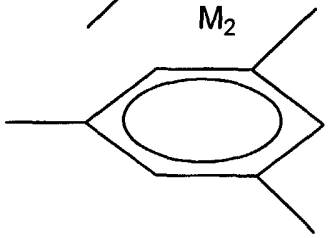

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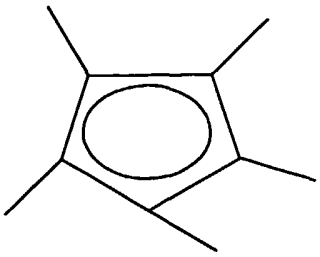
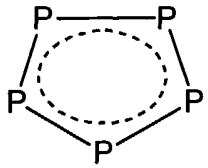
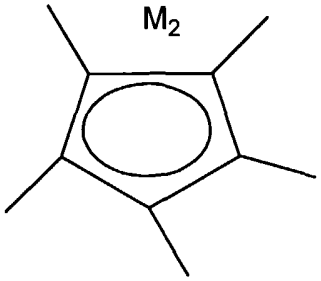


M_1



M_2



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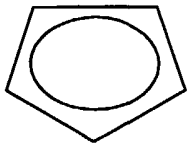
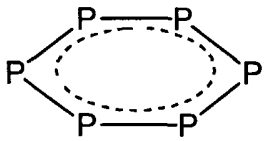
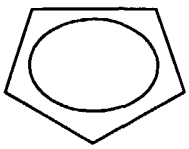


M_1



M_2



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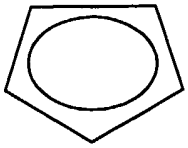
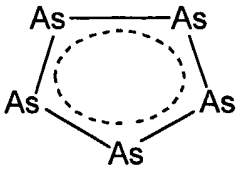
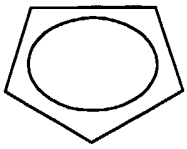


M_1


As
As
As
As
As

M_2



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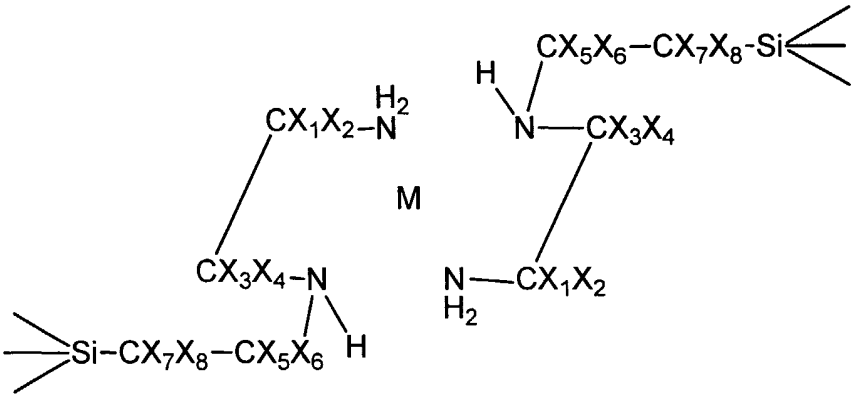
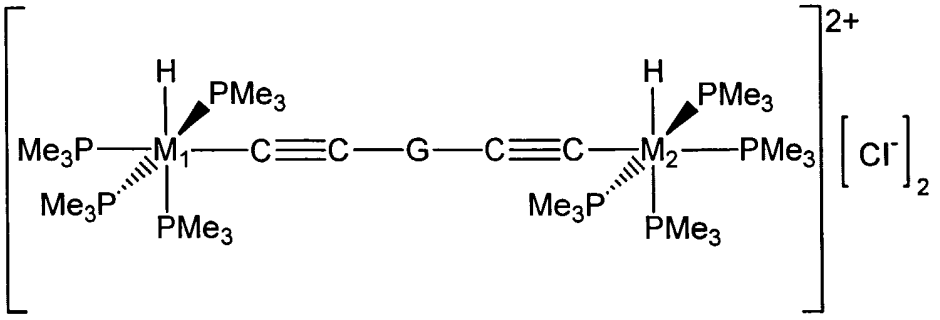
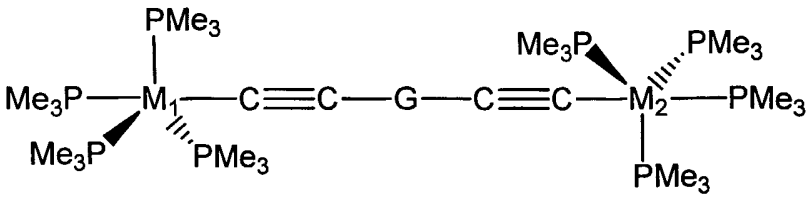

CX5X6–CX7X8-Si
H
N
CX3X4
CX1X2–N
H2
M
CX3X4–N
N
CX1X2
H2
Si–CX7X8–CX5X6
H

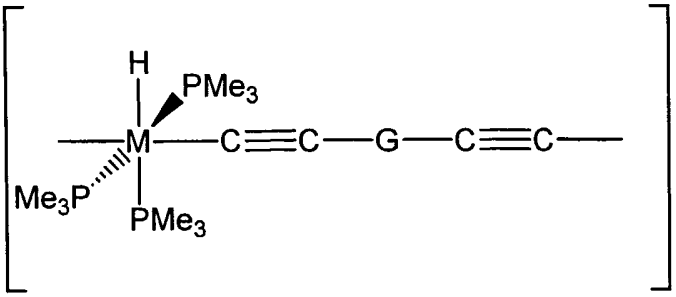
;


2+
H
PMe3
Me3P
M1
C≡C
G
C≡C
M2
PMe3
Me3P
PMe3
H
PMe3
Me3P
PMe3
[Cl-]2

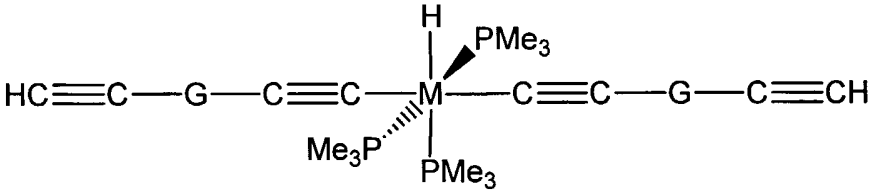
;


PMe3
Me3P
M1
C≡C
G
C≡C
Me3P
PMe3
Me3P
M2
PMe3
PMe3

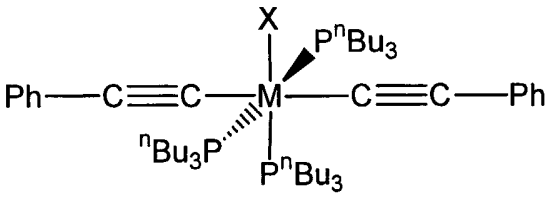
;


H
PMe3
M
C≡C
G
C≡C
Me3P
PMe3
n

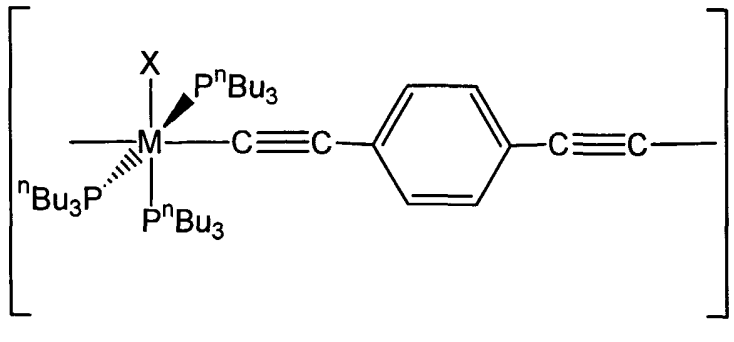
;


H
PMe3
HC≡C
G
C≡C
M
C≡C
G
C≡CH
Me3P
PMe3

;


X
PnBu3
Ph
C≡C
M
C≡C
Ph
nBu3P
PnBu3

;



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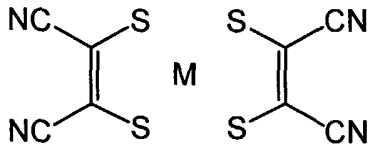

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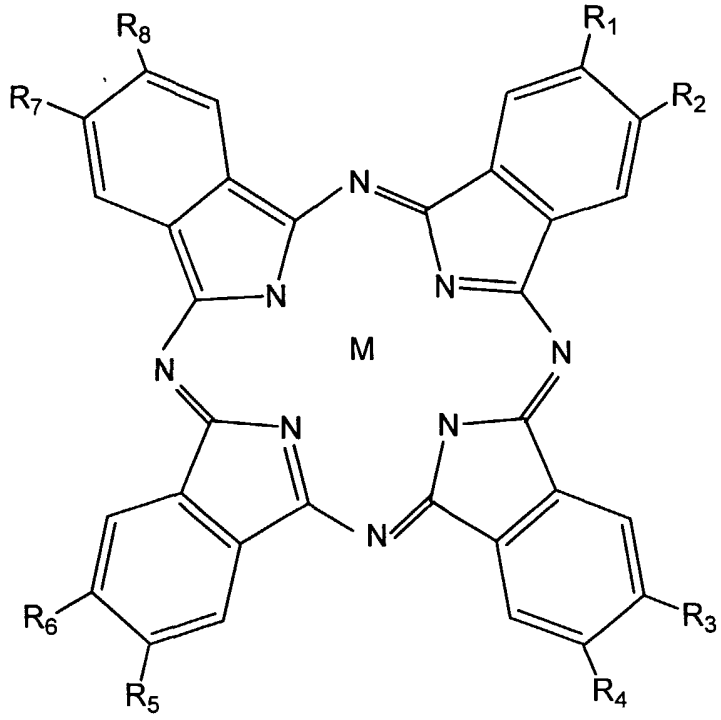

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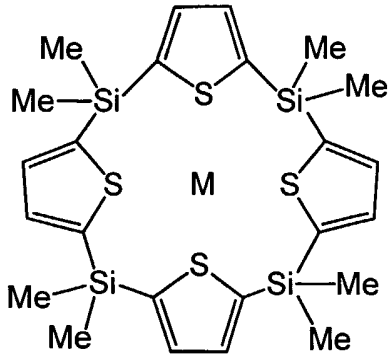
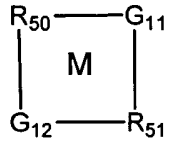
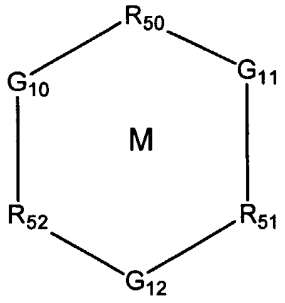
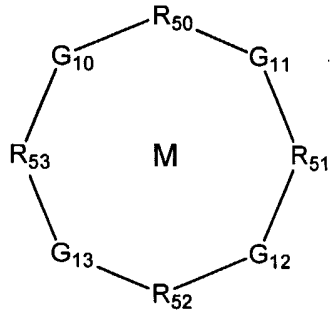
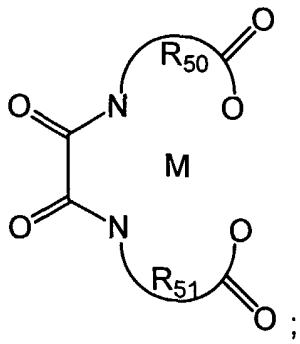

Me
Me
Si
S
Si
Me
Me
S
M
S
Me
Si
S
Si
Me
Me
Me
;

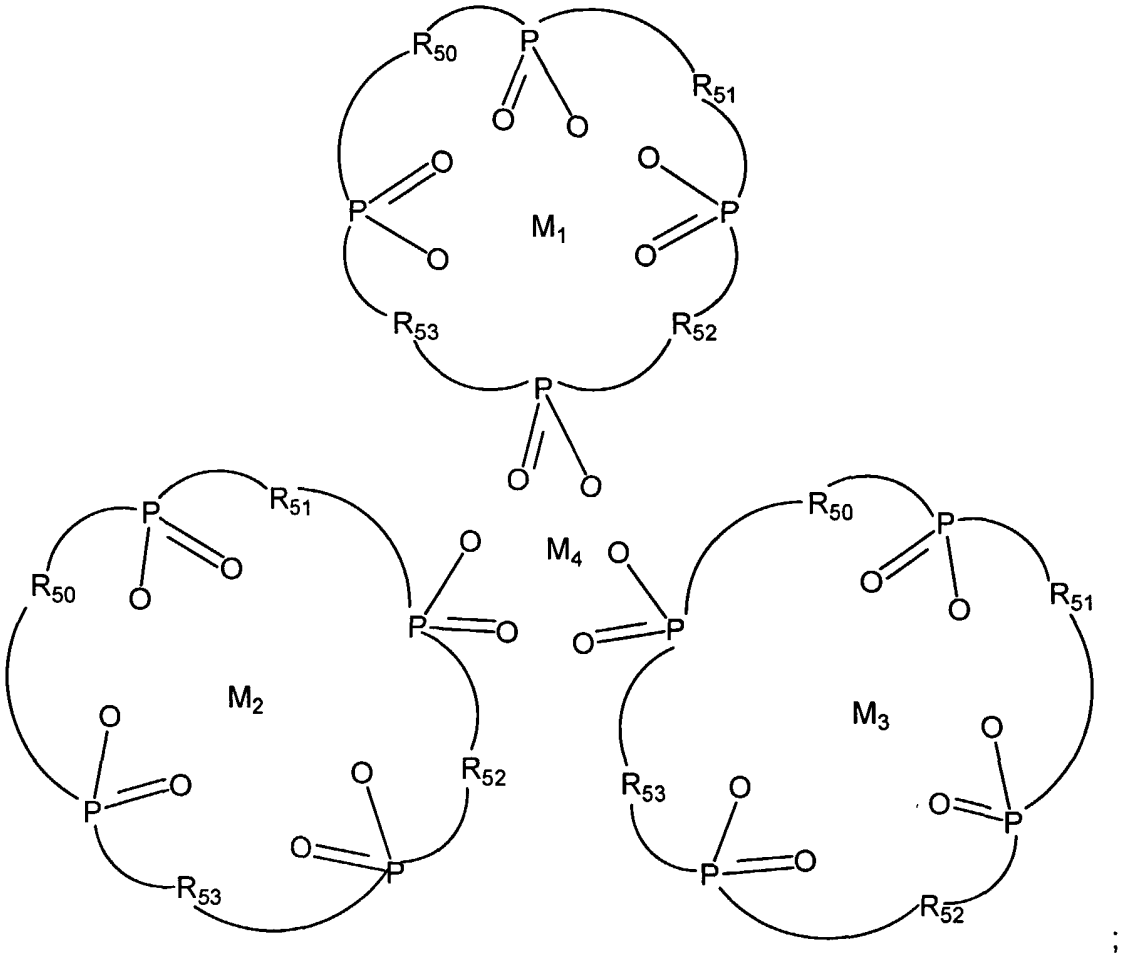

R50
G11
M
G12
R51
;


R50
G10
G11
M
R52
R51
G12
;

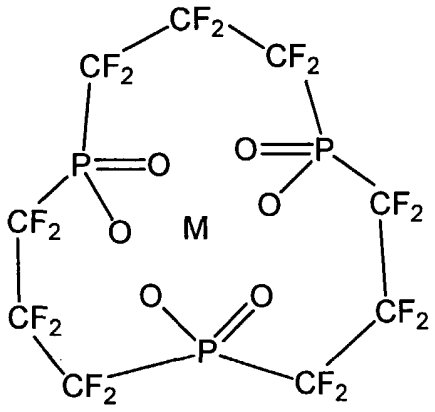

R50
G10
G11
R53
M
R51
G13
G12
R52
;


R50
O
O
N
M
O
N
O
R51
O

;


R50
P
R51
O
O
O
P
O
M1
O
P
O
R53
R52
P
O
O
R51
P
O
R50
O
M4
O
P
O
P
O
M2
O
R52
O
P
O
O
P
R53
R50
P
R51
O
O
M3
O
R53
O
O
P
P
O
R52

;



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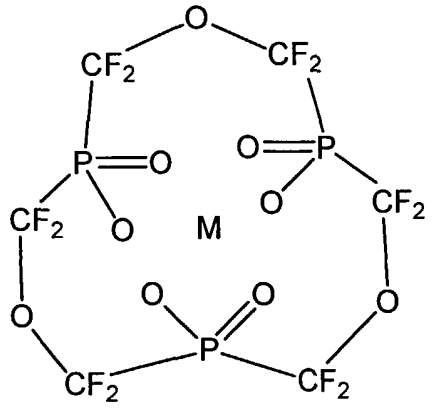

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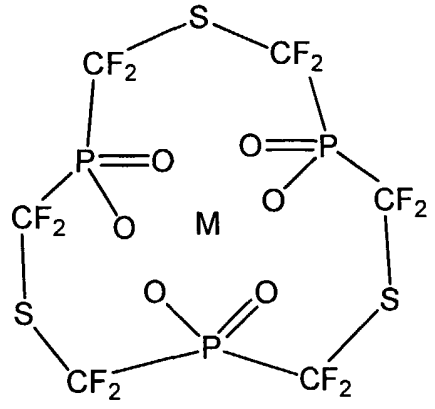

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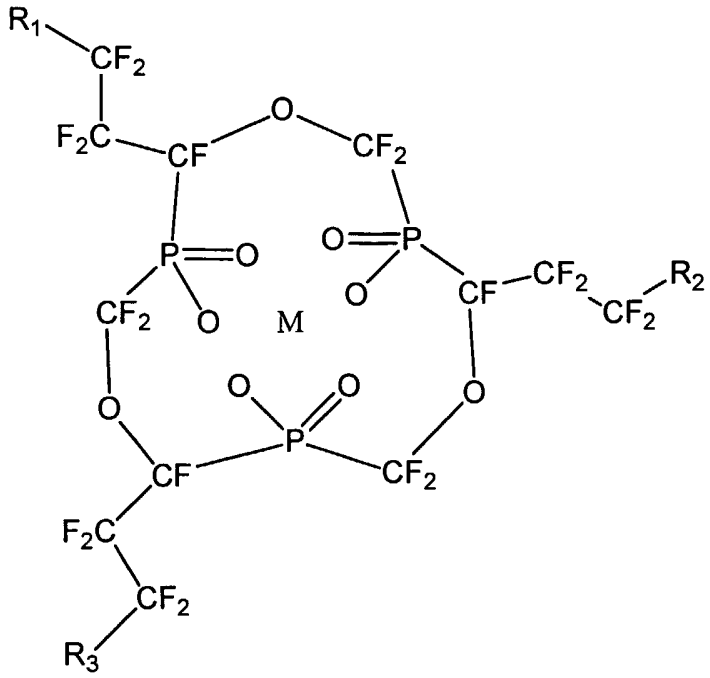


;

$[M(PMe_3)_4]Cl$;

$M[N(Si(CH_3)_3)_2]_3$;

$M[N(Si(CH_3)_3)_2]_3OPPh_3$;

$[M(CH_2Si(CH_3)_3)_4]^-$;

$[M(NCS)_6]^{3-}$;

$Na[M(S_2CN(C_2H_5)_2)_4]$;

$[M(mesityl)_4]^-$;

$M(CF_3CO_2)_3(C_4H_8SO)_2$;

$Cs[M(CF_3COCFCOCF_3)_4]$;

$M(PF\text{-}acac)_3$;

$M(HMPA)_3(X_9)_3$;

$M(OPPh_3)_3$;

$(DMSO)_nM(NO_3)_3$;

$M[N(Si(CH_3)_3)_2]_2(Al(CH_3)_3)_2$;

$(M)_3en_3(X_9)_3$;

$[Men_4CF_3SO_3]^{2+}$;

$[M[NCS)_6]^{3-}$;

$[M(S_2CNR_2)_4]^-$;

$[M(S_2P(CH_3)_2)_4]^-$;

$M[S_2P(C_6H_{11})_2]_3$;

$Cp_2MC_6F_5$;

$M(C_8H_8)$;

$[M(C_8H_8)_2]^{2-}$;

$M_1M_2M_3[(A_8A_9)A_{10}(A_{11}R_1)(A_{12}R_2)]_3$;

$M_1M_2M_3[NR_3A_8A_{10}R_1R_2]_3$;

$M_1M_2M_3[N(R_1)R_{70}(NR_2)]X_9$;

$(M_1)_i(M_2)_j(M_3)_k(M_4)_l[R_{75}R_{76}A_{25}(A_{26}A_{27})]_{3(i+j+k+l)}$;

$(M_1)_i(M_2)_j(M_3)_k(M_4)_l[R_{50}A_{25}(A_{26}A_{27})]_{3(l+j+k+l)}$;

$(M_1)_i(M_2)_j(M_3)_k(M_4)_l[R_{50}A_{25}(A_{26}A_{27})R_{51}A_{28}(A_{29}A_{30})]_{1.5(l+j+k+l)}$;

$M_1M_2M_3[(NR_1R_2)(NR_3R_4)]$ X_9 ; and

$M_1M_2M_3[A_{20}A_{21}A_{22}A_{23}R_1]_3$;

wherein ,

A_8 and A_9 can be the same or different and are selected from O, S, Se, Te, Po and N;

A_{10} is selected from B, Ge, Ga, N, P, As, Sb, Bi, S, C and Si (wherein if A_{10} is C or Si then $A_{11}R_1$ =nothing);

A_{11} and A_{12} can be the same or different and are selected from O, S, N, and nothing;

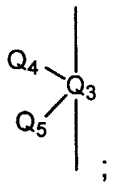
A_{20}, A_{21}, and A_{22} can be the same or different and are selected from O, S, Se, Te and Po;

A_{23} is selected from S, Se, Te and Po;

M, M_1, M_2, M_3 and M_4 can be the same or different and are selected from aluminum (Al), chromium (Cr), scandium (Sc), yttrium (Y), lutetium (Lu), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm) and ytterbium (Yb);

G is selected from nothing, p-$C_6(X)_4$, and p-$C_6(X)_4$-$C_6(X_1)_4$;

G_{10}, G_{11}, G_{12}, and G_{13} can be the same or different and are



;

Q_3 is selected from N, P, As and Sb;

Q_4 and Q_5 can be the same or different and are selected from O, S, Se and Te;

X, X_1, X_2, X_3, X_4, X_5, X_6, X_7 and X_8 can be the same or different and are selected from H, F, Cl, Br and I;

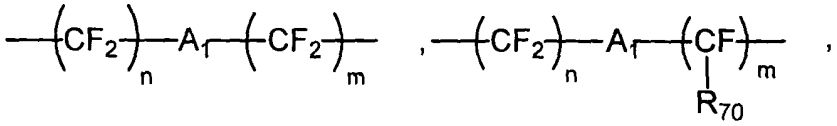
X_9 is selected from F, Cl, Br and I;

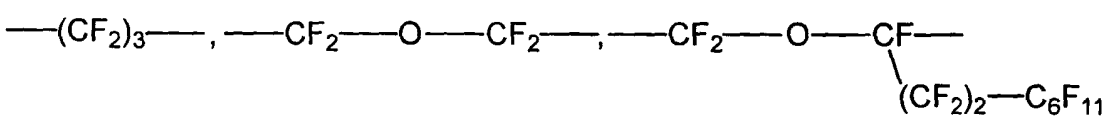
n, m and p can be the same or different and are selected from any integer in the range of 1 to 100;

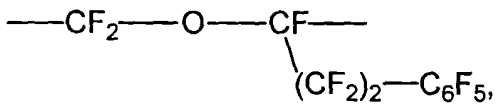
i, j, k and l can be the same or different and can be any positive, rational number from greater than zero to 1000;

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 can be the same or different, can be linked to form cyclic or extended structures, and are selected from halide, halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes and halogenated silazanes;

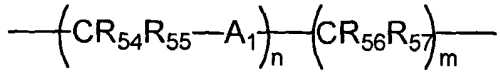
R_{50}, R_{51}, R_{52}, and R_{53} can be the same or different and are selected from halide, halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, halogenated silazanes,







$-(CR_{54}R_{55})_n-$, and



;

R_{54}, R_{55}, R_{56}, and R_{57} can be the same or different and selected from F, Cl, Br, I, halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated

:hioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes and halogenated silazanes, halogenated polyamide, halogenated polyether, halogenated polyimide, halogenated polythioethers,

$$—(CF_2)_p—CF_3,\quad —(CF_2)_p—C_6F_5,\text{ and }\quad —(CF_2)_p—C_6F_{11};$$

R_{70} is halogenated alkylene or halogenated silylene; and

R_{75} and R_{76} can be the same or different and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes and halogenated silazanes;

wherein,

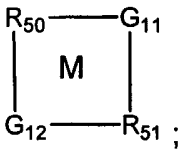
each of the $[NR_3A_8A_{10}R_1R_2]$ can be the same or different; and

when two or more ligands are part of the same complex and one or more variables from each ligand has the same designation, these variables can be the same or different for each ligand.

7. The composition of claim 6 wherein the ligands in said at least one complex can be further halogenated, further fluorinated, perhalogenated or perfluorinated.

8. The composition of claim 6 wherein said composition comprises at

$ErYb_4[(n\text{-}C_8F_{17})_2POO]_{15}$; $ErYb[(n\text{-}C_6F_{13})2POO]_6$; $ErYb_4[(i\text{-}C_3F_7OC_2F_4)_2POO]_{15}$; $ErYb[(n\text{-}C_4F_9)_2POO]_6$; $ErYb_3[((CF_3)_2CF(CF_2)_6)_2POO]_{12}$;$ErYb_3[((CF_3)_2CF(CF_2)_6)_2PSO]_{12}$; $ErYb_3[(n\text{-}C_{10}F_{23})_2POO]_{12}$;$ErYb_3[(n\text{-}C_8F_{17})(n\text{-}C_{10}F_{23})POO]_{12}$; $Er[(CH_3)_3C\text{-}(CO)\text{-}CH_2\text{-}(CO)\text{-}CF_2CF_2CF_3]_3$.; $ErYb[(n\text{-}C_8F_{17})_2POO]_6$; $ErYb_{10}[(n\text{-}C_8F_{17})_2POO]_{33}$;



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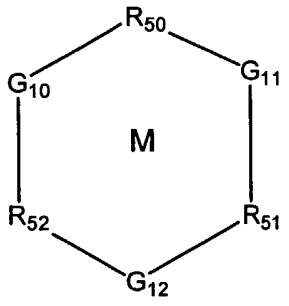

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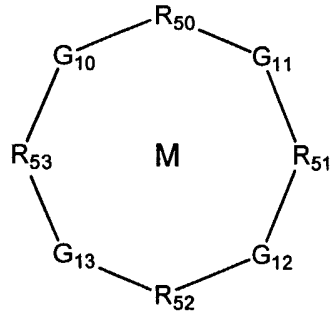

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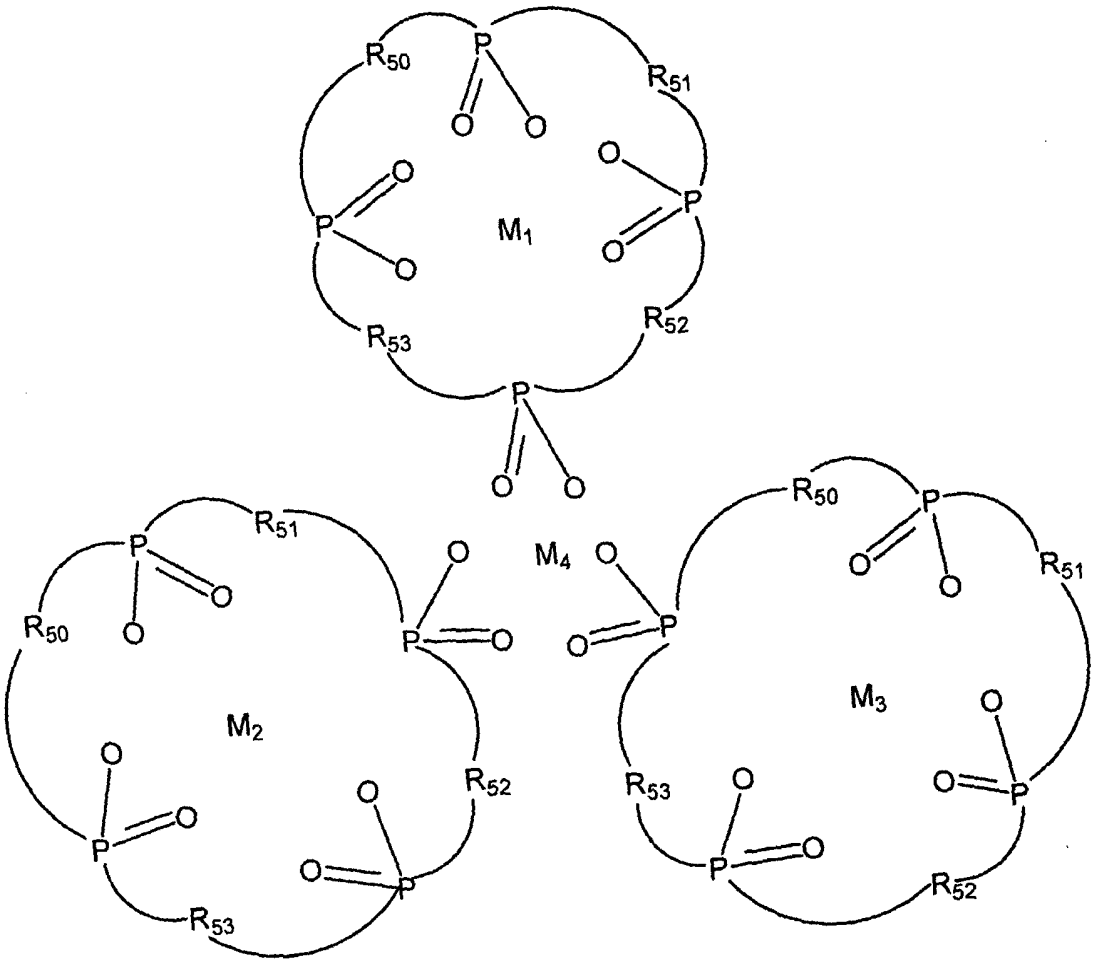
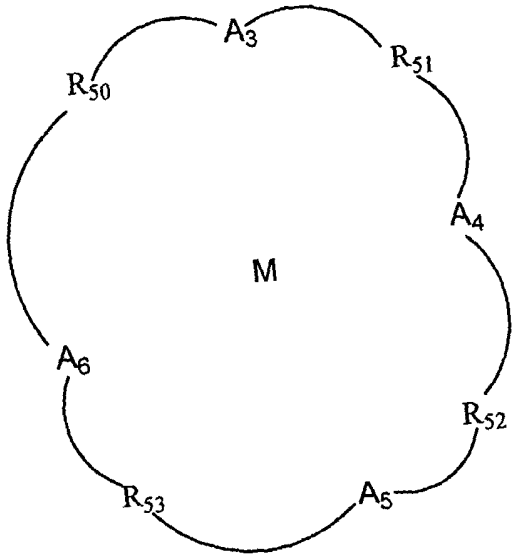
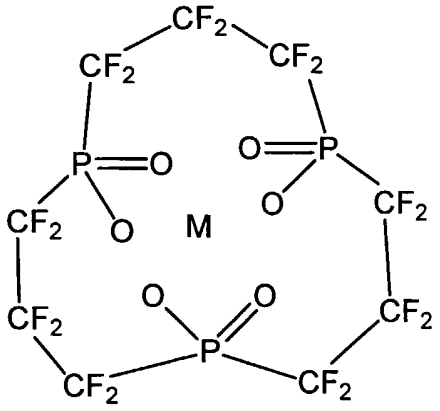

R50
P
O
O
R51
O
P
O
P
O
O
M1
O
P
O
R53
R52
P
O
O
M4
R51
P
O
R50
O
O
P
O
M2
O
P
O
O
R52
O
O
P
R53
O
P
O
R50
P
O
O
R51
M3
O
O
P
R53
O
P
O
R52

;


A3
R51
R50
A4
M
A6
R52
R53
A5

;



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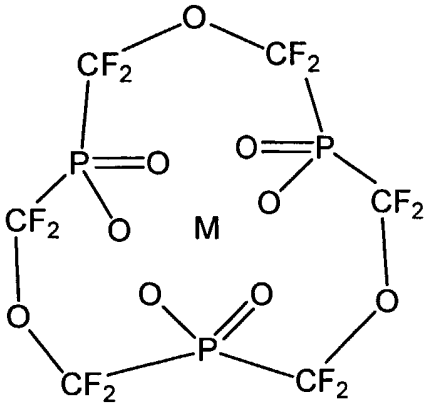

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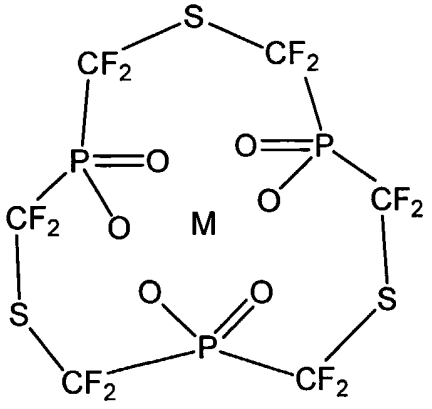
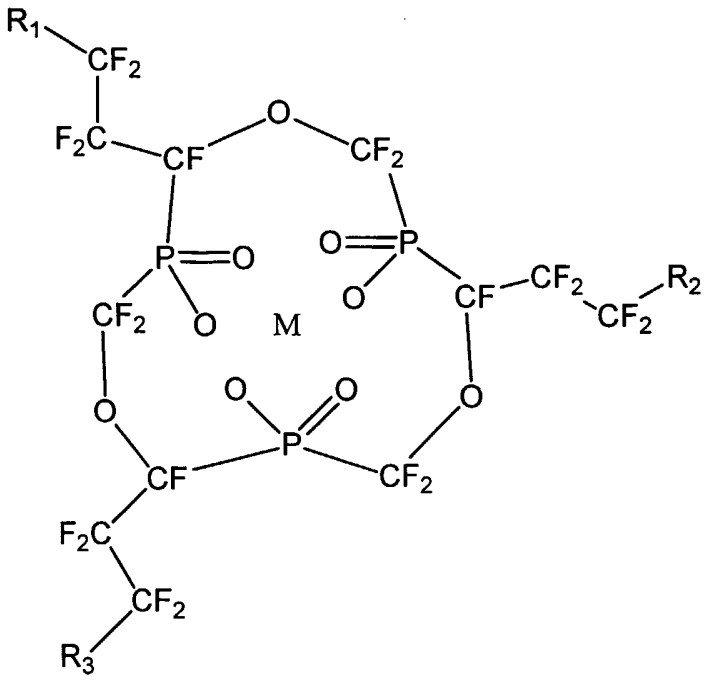


; and



9. The composition of claim 1 wherein one of the suitable metals is Er or Yb.

10. The composition of claim 1 wherein two of the suitable metals are Er and Yb.

11. The composition of claim 1 wherein the total concentration of the at least one suitable metal is in the range of about $1x10^{-3}$ M to about 3.0 M.

12. The composition of claim 1 wherein the total concentration of the at least one suitable metal is in the range of about $1x10^{-2}$ M to about 2.0 M.

13. The composition of claim 1 wherein the total concentration of the at least one suitable metal is in the range of about 0.01% (wt/wt) to about 20% (wt/wt).

14. The composition of claim 1 wherein the total concentration of the at least one suitable metal is in the range of about 0.1% (wt/wt) to 10% (wt/wt).

15. The composition of claim 1 wherein said composition has an absorbance per centimeter of less than about $5x10^{-5}$ in a wavelength range of about 1200 to about 2000 nm.

16. The composition of claim 15 wherein said wavelength range is about 1200 nm to about 1700 nm.

17. The composition of claim 15 wherein said wavelength range is about 1500 nm to about 1600 nm.

18. The composition of claim 15 wherein said wavelength range is about 1250 nm to about 1350 nm.

19. The composition of claim 15 wherein said absorbance per centimeter is less than about $2.5x10^{-5}$.

20. The composition of claim 15 wherein said absorbance per centimeter is less than about $1x10^{-5}$.

21. The composition of claim 1 wherein the total concentration of the at least one suitable metal is greater than about 0.1% and the lifetime of the composition is greater than about 1.5 ms.

22. The composition of claim 1 wherein the total concentration of the at least one suitable metal is greater than about 5.9% and the lifetime of the composition is greater than about 5.0 ms.

23. The composition of claim 1 wherein the total concentration of the at least one suitable metal is greater than about 1.0% and the lifetime of the composition is greater than about 3.8 ms.

24. A method of making a complex comprising at least one suitable metal and at least one acid, wherein said method comprises

(a) admixing at least one acid in at least one hydroxide salt in an inert solvent to produce at least one first salt;

(b) optionally, recovering said at least one first salt;

(c) admixing said at least one first salt with at least one second salt, wherein the at least one second salt comprises at least one suitable metal;

(d) optionally, stirring for up to about 72 hours; and

(e) recovering said complex.

25. The method of claim 24 wherein the cations of said at least one hydroxide salt are selected from Na, K, NH_4, Rb, Cs, Be, Mg, Ca, Sr, and Ba.

26. The method of claim 25 wherein said cations are selected from Na, K and NH_4.

27. The method of claim 24 wherein said inert solvent is selected from a polar solvent, acetone, methanol, propanol, acetonitrile and water.

28. The method of claim 24 wherein in step (b) the at least one first salt is recovered.

29. The method of claim 24 wherein in step (c) the at least one first salt is admixed with at least two second salts, wherein each said second salt, optionally comprises a different suitable metal.

30. The method of claim 24 wherein there is stirring in step (d).

31. The method of claim 24 wherein said stirring is under N_2.

32. The method of claim 24 wherein said stirring occurs for up to about 48 hours.

33. The method of claim 24 wherein said stirring occurs for up to about 2 hours.

34. The method of claim 24 wherein the said stirring occurs for up to about 1 minute.

35. The method of claim 24 wherein between step (d) and (e), there is a washing step.

36. The method of claim 24 wherein said at least one acid is a phosphorus-containing acid.

37. The method of claim 24 wherein said at least one acid is selected from phosphonic acid, $[C_6H_5C(O)CH_2]P(O)(OH)_2$; $[C_6H_5C(O)CH_2]_2P(O)OH)$; $[C_6H_5C(O)CH_2]_2P(O)OCH_3$; $[C_6H_5C(O)CH_2]_2P(O)OC_2H_5$; $[C_6H_5C(O)CH_2]_2P(O)OC_6H_4Cl$; $(C_6H_5)_2P(O)OH$; $(C_6H_5—CH=CH)_2P(O)OH$; $(C_6H_5—C\equiv C)_2P(O)OH$; $(C_6H_5)_2P(O)OH$; $(C_6H_5)(CH_3)P(O)OH$; $(CH_3)_2P(O)OH$; $(C_6H_5)_2As(O)OH$; $(CH_3)_2As(O)OH$; $C_6H_5C(O)OH$; $NH_3CH_2P(C_6H_5)O_2$; $(n\text{-}C_8F_{17})_2POOH$; $(n\text{-}C_6F_{13})_2POOH$; $(i\text{-}C_3F_7OC_2F_4)_2POOH$; $(n\text{-}C_4F_9)_2POOH$; $[(CF_3)_2CF(CF_2)_6]POOH$; $[(CF_3)_2CF(CF_2)_6]PSOH$ and $(n\text{-}C_{10}F_{23})_2POOH$.

38. The method of claim 24 wherein said at least one suitable metal is Eb, Yb, or Er and Yb.

39. The method of claim 24 wherein at least one of the anions of the said at least one second salt is selected from Cl, Br, nitrate and acetate.

40. A composition comprising at least one complex selected from

$(M_1)_i(M_2)_j(M_3)_k(M_4)_l[R_{75}R_{76}A_{25}(A_{26}A_{27})]_{3(i+j+k+l)}$;

$(M_1)_i(M_2)_j(M_3)_k(M_4)_l[R_{50}A_{25}(A_{26}A_{27})]_{3(l+j+k+l)}$; and

$(M_1)_i(M_2)_j(M_3)_k(M_4)_l[R_{50}A_{25}(A_{26}A_{27})R_{51}A_{28}(A_{29}A_{30})]_{1.5(l+j+k+l)}$, where R_{50} and R_{51} are each linked to both A_{25} and A_{28};

where:

M_1, M_2, M_3, and M_4 can be the same or different and are selected from aluminum (Al), chromium (Cr), scandium (Sc), yttrium (Y), lutetium (Lu), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm) and ytterbium (Yb);

A_1 is N, S or O;

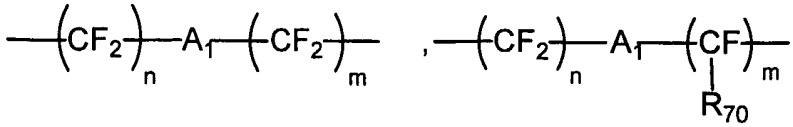
A_{25}, A_{28} can be the same or different and are selected from P, As, Sb and Bi;

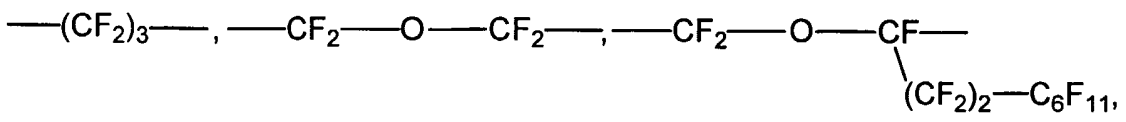
A_{26} A_{27}, A_{29} and A_{30} can be the same or different and are selected from O, S, Se, Te and Po;

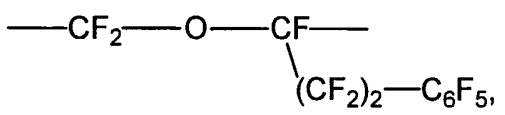
R_{75} and R_{76} can be the same or different and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes and halogenated silazanes;

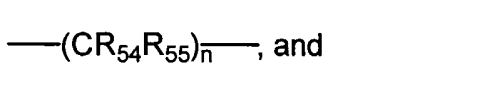
R_{50}, and R_{51} can be the same or different and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether,

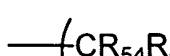
halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, halogenated silazanes,





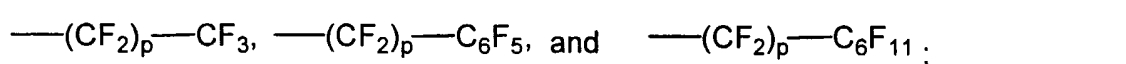




 , and

; and

R_{54}, R_{55}, R_{56}, and R_{57} can be the same or different and selected from F, Cl, Br, I, halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated polyether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes and halogenated silazanes, halogenated polyamide, halogenated polyether, halogenated polyimide, halogenated polythioethers,

 ;

n, m and p can be the same or different and can be any integer from 1 to 20;

i, j, k and l can be the same or different and can be any positive, rational number from greater than zero to 1000.

41. The composition of claim 40 wherein the number of C-halide bonds are greater than the number of C-H bonds in R_{50}, R_{51}, R_{75} and R_{76}.

42. The composition of claim 40 wherein the at least one complex has a halide-to- hydrogen weight percent equal to or greater than about 90%,

43. The composition of claim 40 wherein the number of C-halide bonds are greater than the number of C-H bonds in R_{50}, R_{51}, R_{75}, and R_{76}.

44. The composition of claim 40 wherein said at least one complex has a fluoride-to- hydrogen weight percent equal to or greater than about 90%,

45. The composition of claim 40 where i, j, k and l can be the same or different and can be any positive, rational number ranging from greater than 0 to 100.

46. The composition of 40 where i, j, k and l can be the same or different and can be any positive, rational number ranging from greater than zero to 25.

47. The composition of 40 where i, j, k and l can be the same or different and can be any positive, rational number ranging from greater than zero to 10.

48. The composition of claim 40 wherein one of M_1, M_2, M_3 or M_4 is Er or Yb.

49. The composition of claim 40 wherein two of M_1, M_2, M_3 or M_4 are Er and Yb.

50. The composition of claim 40 wherein the total concentration of the suitable metals is in the range of about $1x10^{-3}$ M to about 3.0 M.

51. The composition of claim 40 wherein the total concentration of the suitable metals is in the range of about $1x10^{-2}$ M to about 2.0 M.

52. The composition of claim 40 wherein the total concentration of the suitable metals is in the range of about 0.01% (wt/wt) to about 20% (wt/wt).

53. The composition of claim 40 wherein the total concentration of the suitable metals is in the range of about 0.1% (wt/wt) to about 10% (wt/wt).

54. The composition of claim 40 wherein said composition has an absorbance per centimeter of less than about $5x10^{-5}$ in a wavelength range of about 1200 and about 2000 nm.

55. The composition of claim 54 wherein said wavelength range is about 1200 nm to about 1700 nm.

56. The composition of claim 54 wherein said wavelength range is about 1500 nm to about 1600 nm.

57. The composition of claim 54 wherein said wavelength range is about 1250 nm to about 1350 nm.

58. The composition of claim 54 wherein said absorbance per centimeter is less than about $2.5x10^{-5}$.

59. The composition of claim 54 wherein said absorbance per centimeter is less than about $1x10^{-5}$.

60. The composition of claim 40 wherein the total concentration of suitable metals is greater than about 0.1% and the lifetime of the composition is greater than about 1.5 ms.

61. The composition of claim 40 wherein the total concentration of suitable metals is greater than about 5.9% and the lifetime of the composition is greater than about 5.0 ms.

62. The composition of claim 40 wherein the total concentration of suitable metals is greater than about 1.0% and the lifetime of the composition is greater than about 3.8 ms.

63. The composition of claim 40 wherein said composition is an optical composition.

64. A method for preparing an optical gain medium comprising:

(a) admixing at least one complex with at least one suitable solvent to form a first mixture;

(b) heating the first mixture to between about 50°C to about 150°C for about 5 minutes to about 2 hours;

(c) cooling the first mixture to between about 20°C to about 30°C;

(d) admixing a perfluoropolymer with the first mixture to produce a second mixture;

(e) forming an optical gain medium from said second mixture;

65. The method of claim 64 wherein said at least one suitable solvent in step (a) is selected from DMAC, FC-75, CT Solv, CT Sol 100, CT Sol 130 and combinations thereof.

66. The method of claim 64 wherein said at least one suitable solvent in step (a) comprises DMAC, FC-75 and CT Solv 180.

67. The method of claim 64 wherein said heating in step (b) occurs in the range of about 60°C to about 90°C.

68. The method of claim 64 wherein said heating in step (b) occurs at about 100°C.

69. The method of claim 64 wherein said heating in step (b) is for about 10 minutes to about 30 minutes.

70. The method of claim 64 wherein said cooling in step (c) is to about 25°C or to about room temperature.

71. The method of claim 64 wherein said step (d) the perfluoropolymer is selected from cyclopolymerized perfluoro-vinyl ether; copolymers of 2,2-bistrifluoromethyl-4,5-difluoro-1,3 dioxole (PDD)with other suitable monomers; cyclic polyethers prepared from cyclopolymerization of fluorine-containing dienes; and polymer and copolymers of 2,2,4-trifluoro-5-trifluoromethoxy- 1,3-dioxole with other suitable monomers.

72. The method of claim 64 wherein said step (d) the perfluoropolymer is a 16% (wt/wt) amorphous cyclopolymerized perfluoro-vinyl ether in a perfluoroether solvent.

73. The method of claim 64 wherein said forming in step (e) comprises filtering using about 0.45 microns or about 0.2 micron filters.

74. The method of claim 64 wherein said forming in step (e) comprises drying for about 1 to about 50 hours at a temperature of about 100°C to about 150°C.

75. The method of claim 74 whereby the drying is for about 5 hours to about 10 hours.

76. The method of claim 74 wherein said temperature is about 130°C.

77. The method of claim 64 wherein said forming in step (e) comprises casting, film casting, spin casting, or film coating.

78. The method of claim 64 wherein said forming in step (e) comprises depositing said mixture on a substrate.

79. The method of claim 64 wherein said forming in step (e) comprises depositing said mixture on a silicon wafer.

80. An optical device comprising the composition of claim 1 or claim 40.

81. The optical device of claim 80 wherein said optical device is selected from optical fiber, waveguide, film, amplifier, laser, multiplexer, isolator, interleaver, demultiplexer, filter, highly-sensitive photodetector and switch.

82. An optical device comprising the gain medium prepared from the method of claim 64.

83. The optical device of claim 82 wherein said optical device is selected from optical fiber, waveguide, film, amplifier, laser, multiplexer, isolator, interleaver, demultiplexer, filter, photodetector and switch.

84. The composition of claim 1 wherein said at least one first ligand is selected from $[C_6H_5C(O)CH_2]P(O)(OH)_2$, $[C_6H_5C(O)CH_2]_2P(O)OH)$, $[C_6H_5C(O)CH_2]_2P(O)OCH_3$, $[C_6H_5C(O)CH_2]_2P(O)OC_2H_5$, $[C_6H_5C(O)CH_2]_2P(O)OC_6H_4Cl$, $(C_6H_5)_2P(O)OH$, $(C_6H_5—CH=CH)_2P(O)OH$, $(C_6H_5—C\equiv C)_2P(O)OH$, $(C_6H_5)_2P(O)OH$, $(C_6H_5)(CH_3)P(O)OH$, $(CH_3)_2P(O)OH$, $(C_6H_5)_2As(O)OH$, $(CH_3)_2As(O)OH$, $C_6H_5C(O)OH$, $NH_3CH_2P(C_6H_5)O_2$, $(n\text{-}C_8F_{17})_2POOH$; $(n\text{-}C_6F_{13})_2POOH$, $(i\text{-}C_3F_7OC_2F_4)_2POOH$, $(n\text{-}C_4F_9)_2POOH$, $[(CF_3)_2CF(CF_2)_6]POOH$; $[(CF_3)_2CF(CF_2)_6]PSOH$, $(n\text{-}C_{10}F_{23})_2POOH$, and $(CH_3)_3C\text{-}(CO)\text{-}CH_2\text{-}(CO)\text{-}CF_2CF_2CF_3$.

85. An amplifier comprising:

a first substantially planar reflector having a reflectivity that is about 100%;

a second substantially planar reflector having a reflectivity that is less than about 100%; and

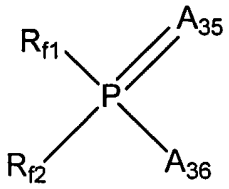
a gain medium between said reflectors, said medium comprising:

at least one suitable metal selected from aluminum (Al), chromium (Cr), scandium (Sc), yttrium (Y), lutetium (Lu), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm) and ytterbium (Yb);

at least one first ligand; and

at least one second ligand,

wherein the at least one first ligand is selected from



where

A_{35} is selected from O and S;

A_{36} is selected from -OH, -SH, and -OR_{80};

R_{f1}, and R_{f2} can be the same or different, can be branched or unbranched, can be linked to form cyclic or extended structures, and are selected

from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated ether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, halogenated silazanes, halogenated olefins, fluorinated alkyl, fluorinated aryl, fluorinated cyclic alkyl, fluorinated arylalkyl, fluorinated alkylaryl, fluorinated ether, fluorinated thioether, fluorinated ether thioether, fluorinated aklyl amino groups, fluorinated alkylene, fluorinated silylene, fluorinated siloxanes, fluorinated silazanes, fluorinated olefins, branched perfluorinated C_{1-20} alkyl, unbranched perfluorinated C_{1-20} alkyl, perfuorinated C_{1-6} alkyl C_{1-10} alkyl ethers, n-C_8F_{17}, n-C_6F_{13}, n-C_4F_9, n-C_2F_5, $(CF_3)_2CF(CF_2)_4$, n-$C_{10}F_{21}$, n-$C_{12}F_{25}$, $(CF_3)_2CF(CF_2)_6$, and $(CF_3)2CFO(CF_2)_2$; and

R_{80} can be branched or unbranched and is selected from C_{1-6} alkyl, C_{1-15} alkyl, C_{3-15} aryl, C_{4-15} alkylaryl, and C_4-15 arylalkyl.

86. An amplified splitter comprising:

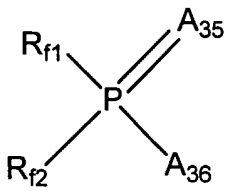
an amplifier portion comprising:

at least one suitable metal is selected from aluminum (Al), chromium (Cr), scandium (Sc), yttrium (Y), lutetium (Lu), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm) and ytterbium (Yb);

at least one first ligand; and

at least one second ligand,

wherein the at least one first ligand is selected from



where

A_{35} is selected from O and S;

A_{36} is selected from -OH, -SH, and -OR_{80};

R_{f1}, and R_{f2} can be the same or different, can be branched or unbranched, can be linked to form cyclic or extended structures, and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated ether, halogenated thioether, halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, halogenated silazanes, halogenated olefins, fluorinated alkyl, fluorinated aryl, fluorinated cyclic alkyl, fluorinated arylalkyl, fluorinated alkylaryl, fluorinated ether, fluorinated thioether, fluorinated ether thioether, fluorinated aklyl amino groups, fluorinated alkylene, fluorinated silylene, fluorinated siloxanes, fluorinated silazanes, fluorinated olefins, branched perfluorinated C_{1-20} alkyl, unbranched perfluorinated C_{1-20} alkyl, perfuorinated C_{1-6} alkyl C_{1-10} alkyl ethers, n-C_8F_{17}, n-C_6F_{13}, n-C_4F_9, n-C_2F_5, $(CF_3)_2CF(CF_2)_4$, n-$C_{10}F_{21}$, n-$C_{12}F_{25}$, $(CF_3)_2CF(CF_2)_6$, and $(CF_3)2CFO(CF_2)_2$; and

R_{80} can be branched or unbranched and is selected from C_{1-6} alkyl, C_{1-15} alkyl, C_{3-15} aryl, C_{4-15} alkylaryl, and $C_{4-}15$ arylalkyl; and

an optical splitter portion optically coupled to said amplifier portion.

87. An optical chip comprising:

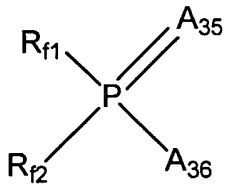
an optical amplifier comprising:

at least one suitable metal is selected from aluminum (Al), chromium (Cr), scandium (Sc), yttrium (Y), lutetium (Lu), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm) and ytterbium (Yb);

at least one first ligand; and

at least one second ligand,

wherein the at least one first ligand is selected from



where

A_{35} is selected from O and S;

A_{36} is selected from -OH, -SH, and $-OR_{80}$;

R_{f1}, and R_{f2} can be the same or different, can be branched or unbranched, can be linked to form cyclic or extended structures, and are selected from halogenated alkyl, halogenated aryl, halogenated cyclic alkyl, halogenated arylalkyl, halogenated alkylaryl, halogenated ether, halogenated thioether,

halogenated ether thioether, halogenated aklyl amino groups, halogenated alkylene, halogenated silylene, halogenated siloxanes, halogenated silazanes, halogenated olefins, fluorinated alkyl, fluorinated aryl, fluorinated cyclic alkyl, fluorinated arylalkyl, fluorinated alkylaryl, fluorinated ether, fluorinated thioether, fluorinated ether thioether, fluorinated aklyl amino groups, fluorinated alkylene, fluorinated silylene, fluorinated siloxanes, fluorinated silazanes, fluorinated olefins, branched perfluorinated C_{1-20} alkyl, unbranched perfluorinated C_{1-20} alkyl, perfuorinated C_{1-6} alkyl C_{1-10} alkyl ethers, n-C_8F_{17}, n-C_6F_{13}, n-C_4F_9, n-C_2F_5, $(CF_3)_2CF(CF_2)_4$, n-$C_{10}F_{21}$, n-$C_{12}F_{25}$, $(CF_3)_2CF(CF_2)_6$, and $(CF_3)2CFO(CF_2)_2$; and

R_{80} can be branched or unbranched and is selected from C_{1-6} alkyl, C_{1-15} alkyl, C_{3-15} aryl, C_{4-15} alkylaryl, and C_4-15 arylalkyl; and

an integrated passive component selected from a group consisting of an arrayed waveguide grating, a splitter, a coupler, a static filter, a tunable filter.

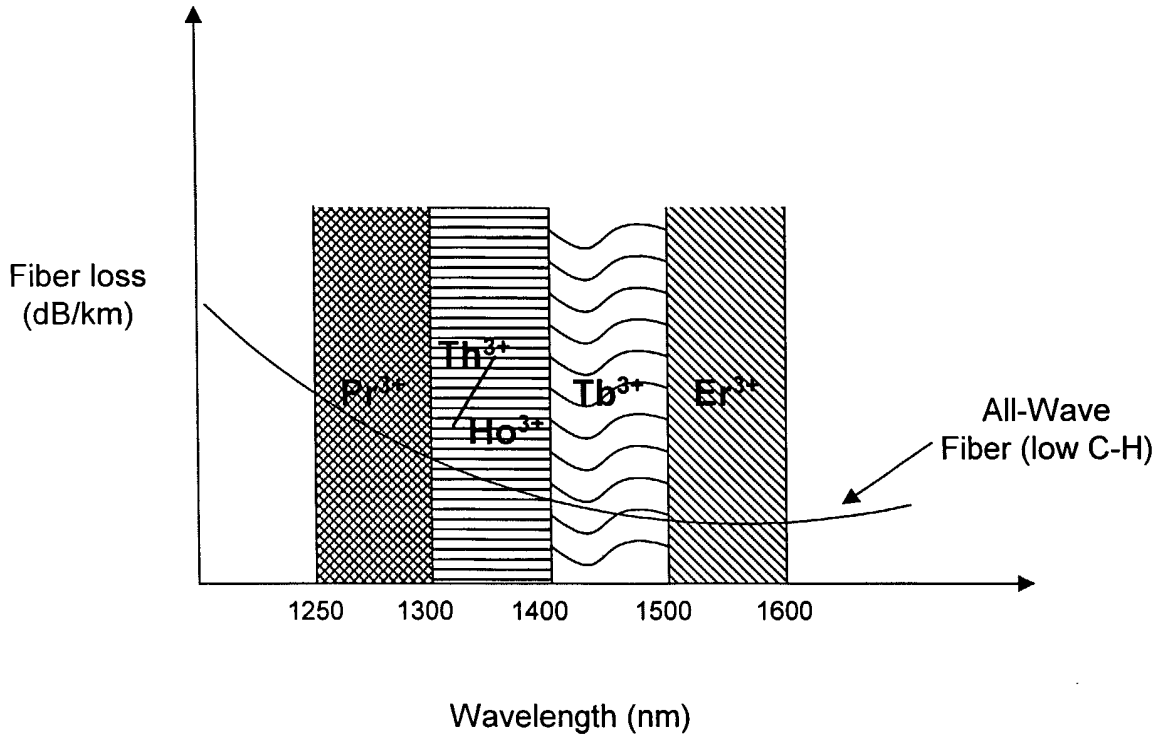

Fiber loss
(dB/km)
Pr^{3+}
Th^{3+}
Ho^{3+}
Tb^{3+}
Er^{3+}
All-Wave
Fiber (low C-H)
1250
1300
1400
1500
1600
Wavelength (nm)

FIG. 1

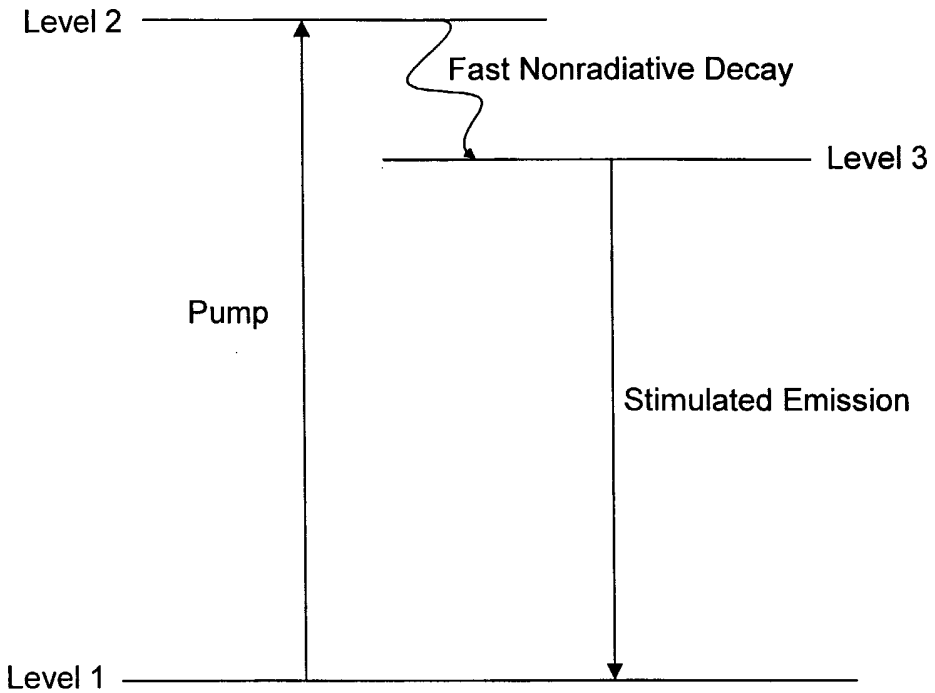

Level 2
Fast Nonradiative Decay
Level 3
Pump
Stimulated Emission
Level 1

FIG. 2a

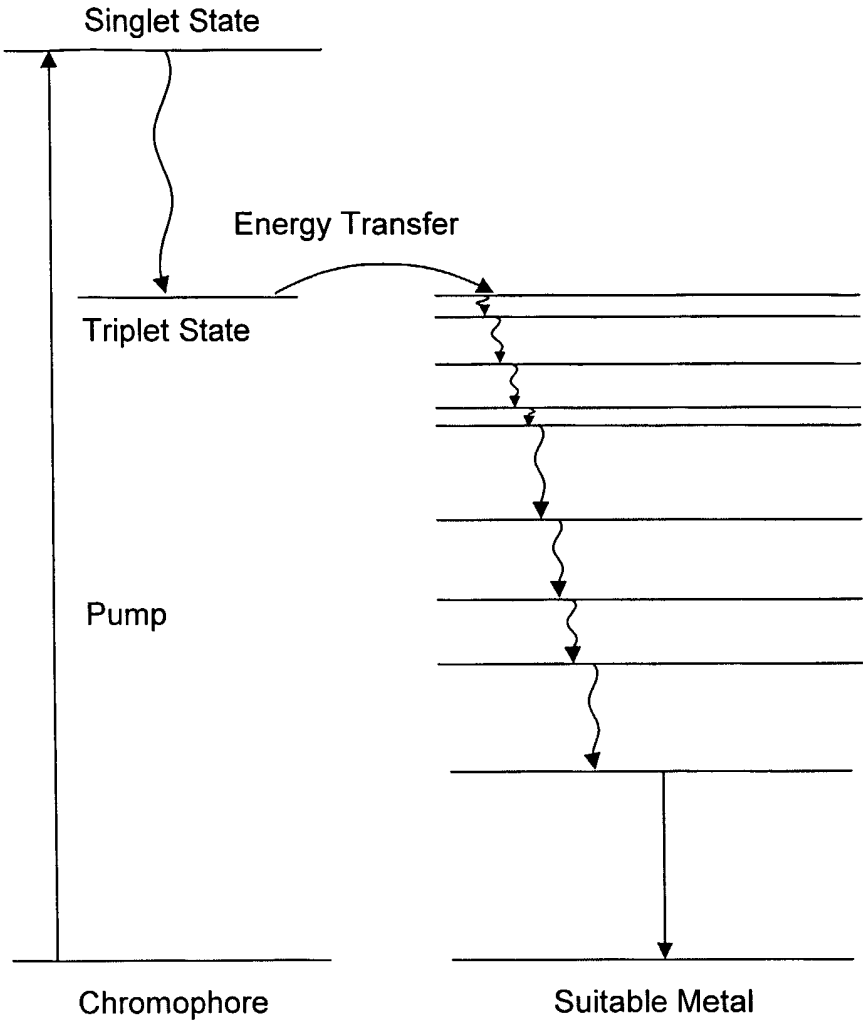

Singlet State
Energy Transfer
Triplet State
Pump
Chromophore
Suitable Metal

FIG. 2b

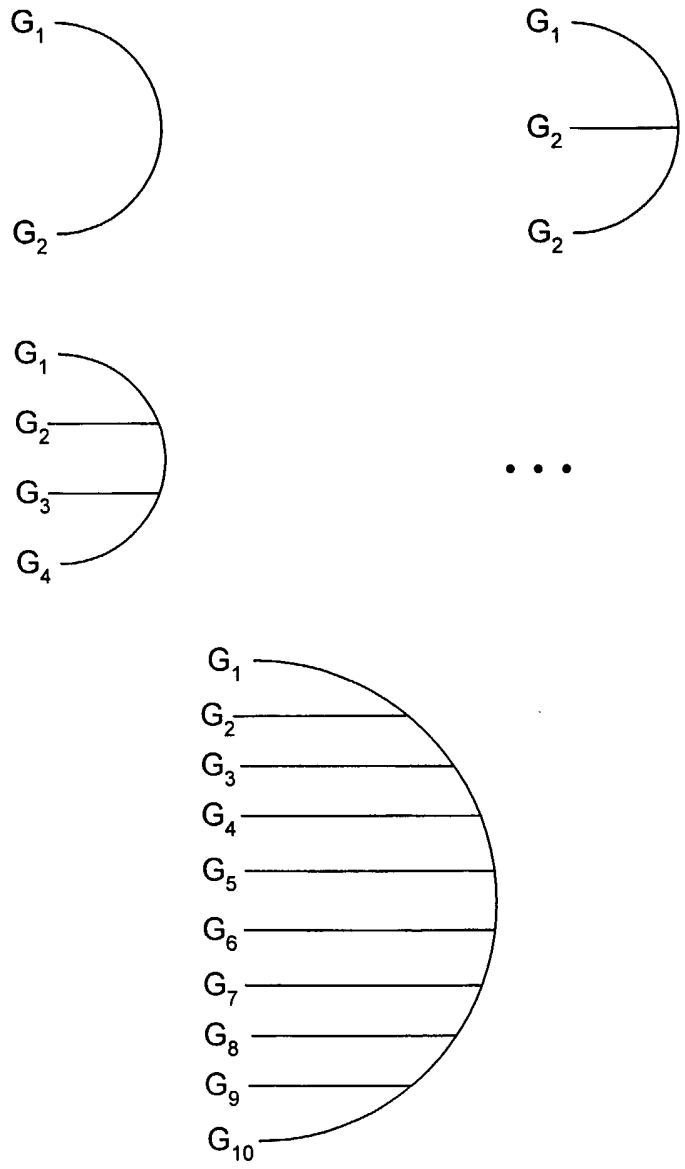


FIG. 3

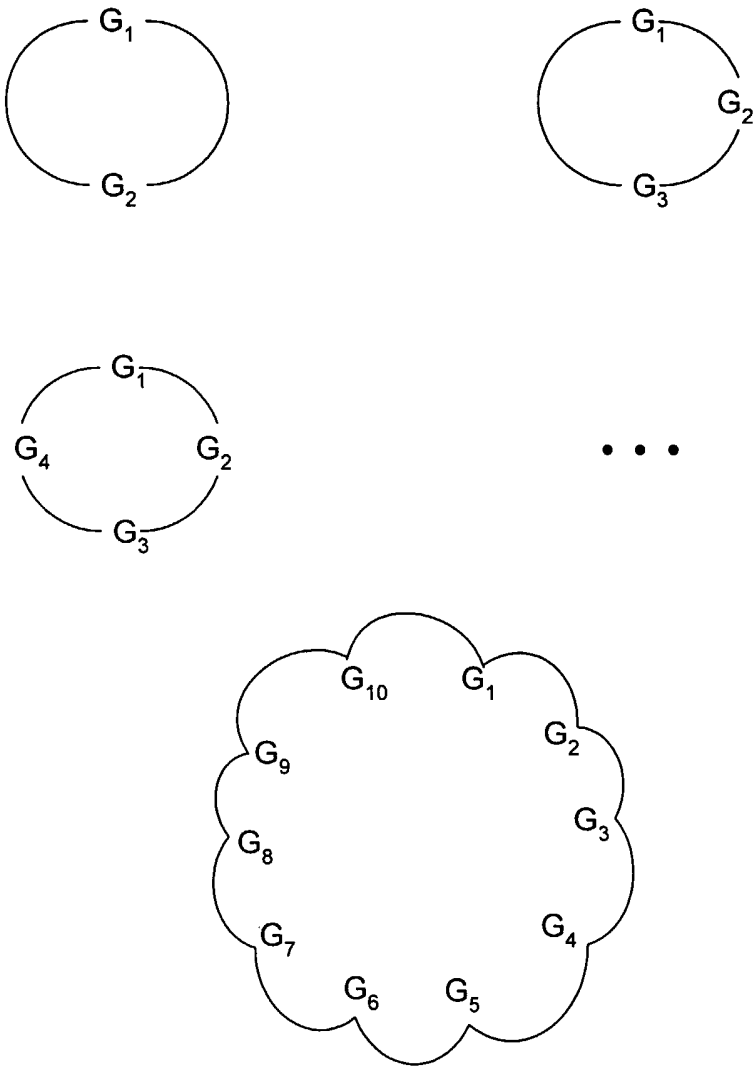


FIG. 4a

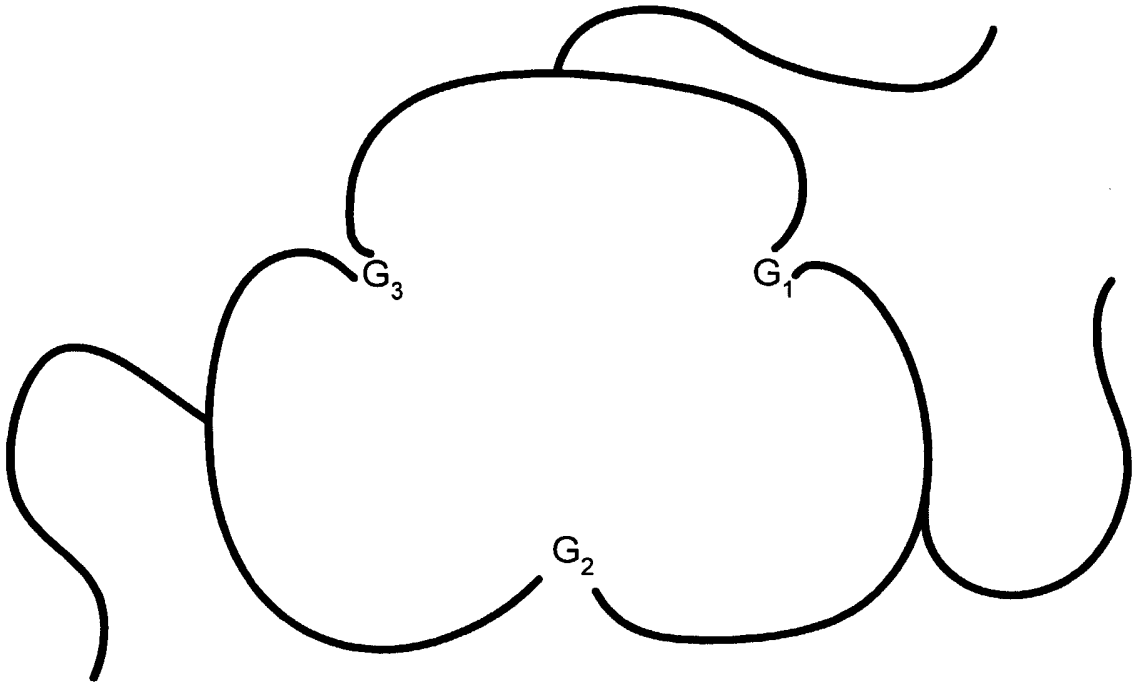


FIG. 4b

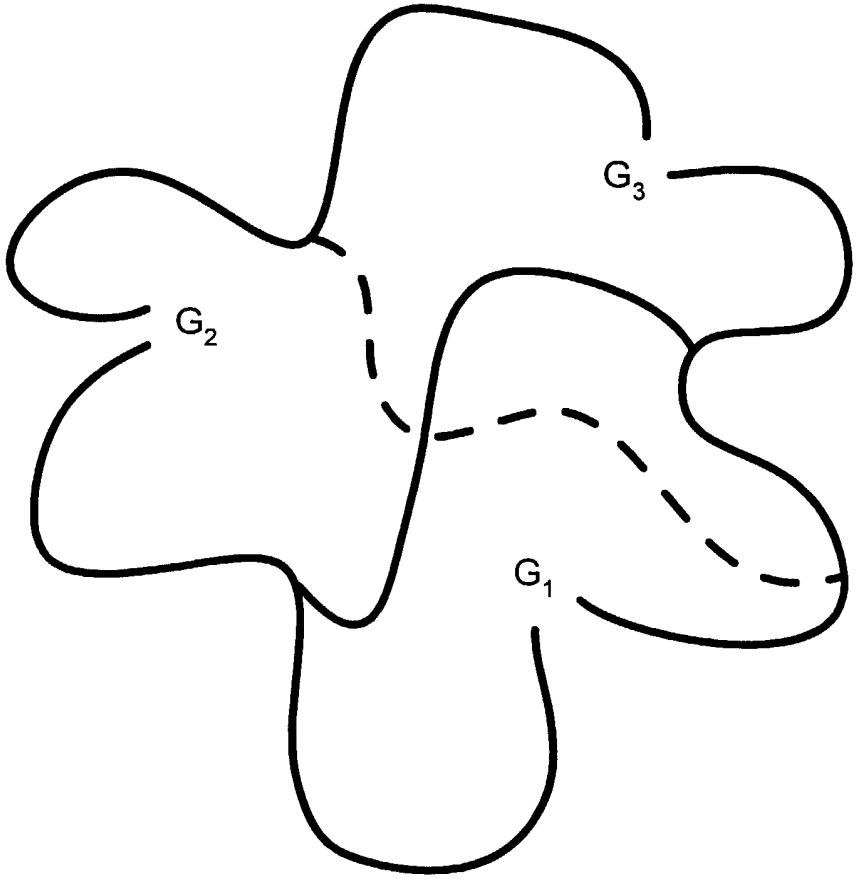


FIG. 4c

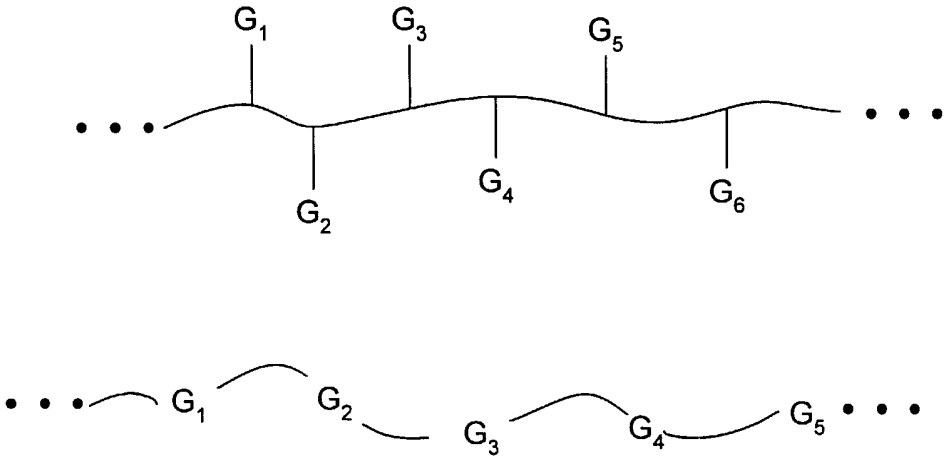


FIG. 5a

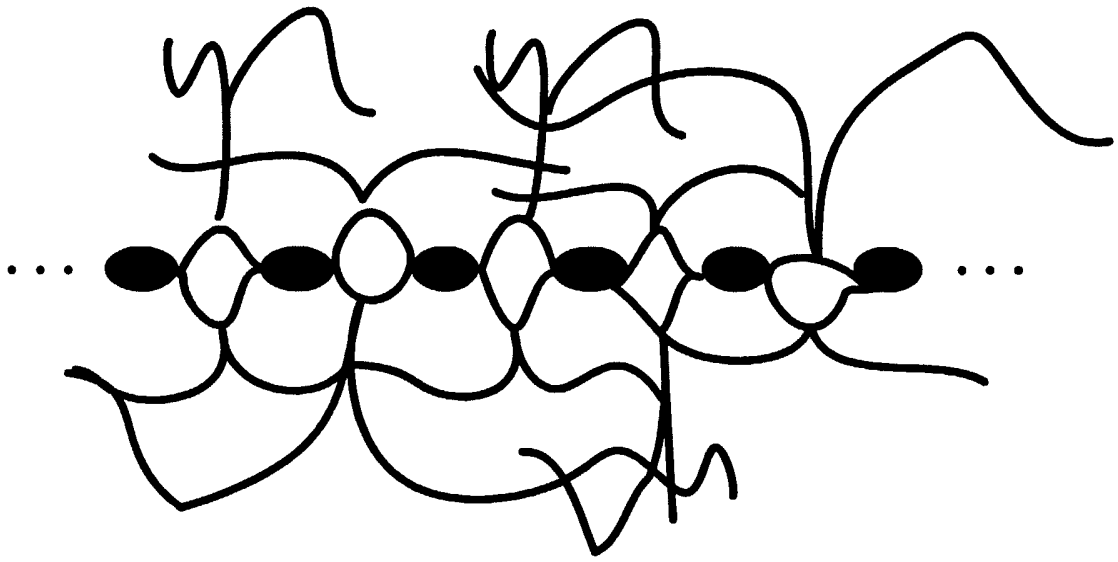


FIG. 5b

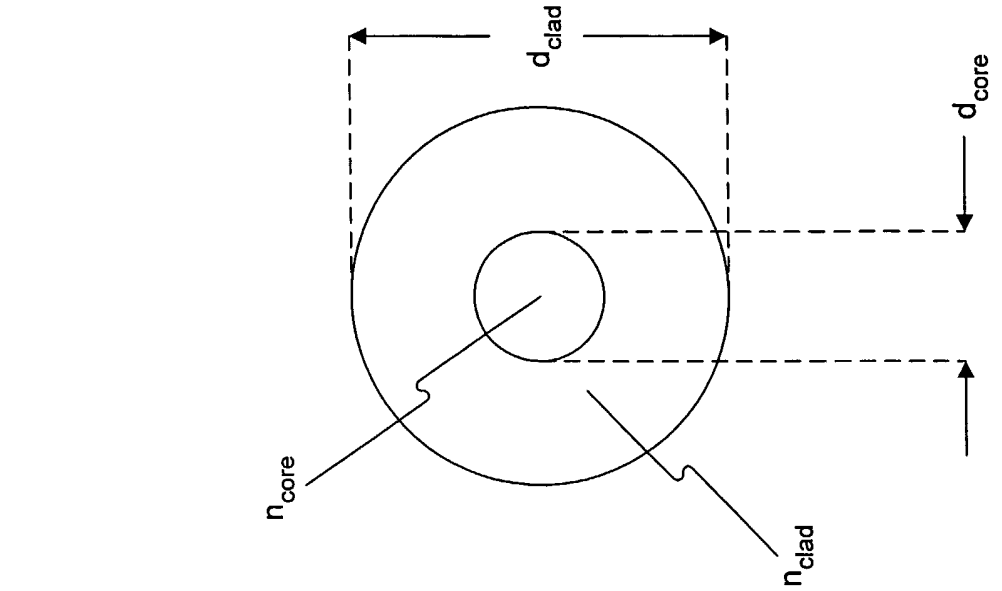


FIG. 7

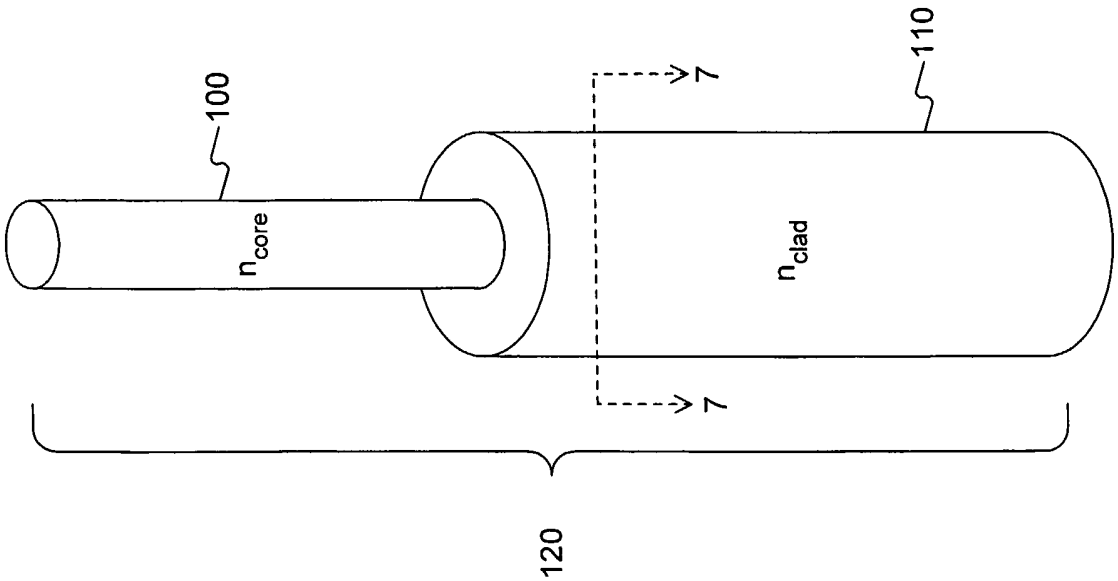
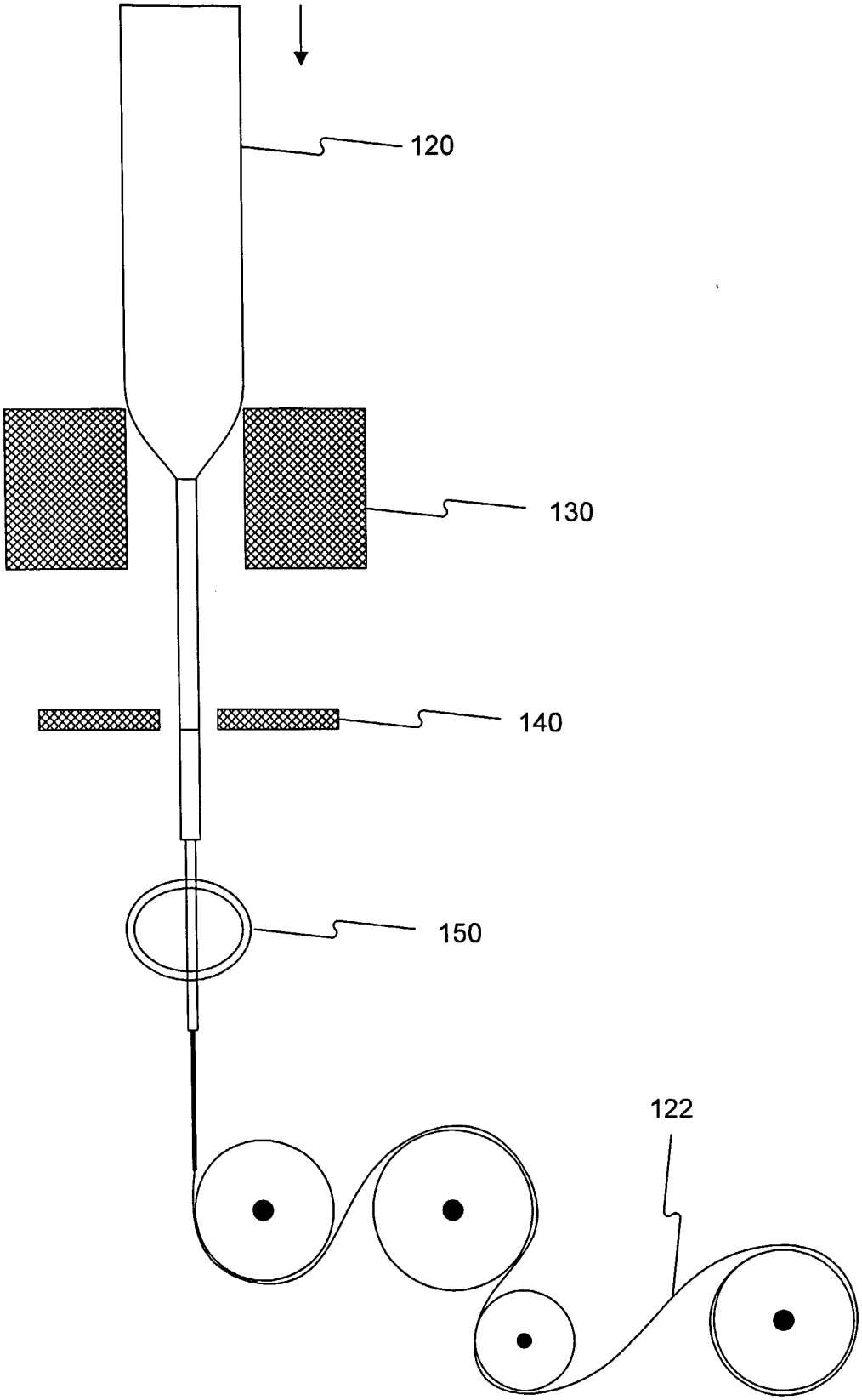


FIG. 6


120
130
140
150
122

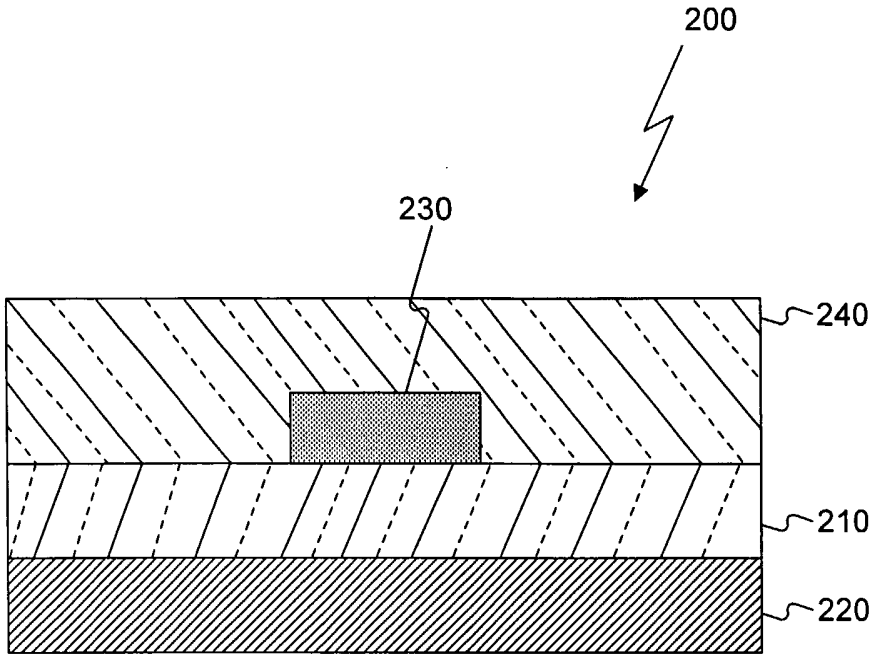


FIG. 9a

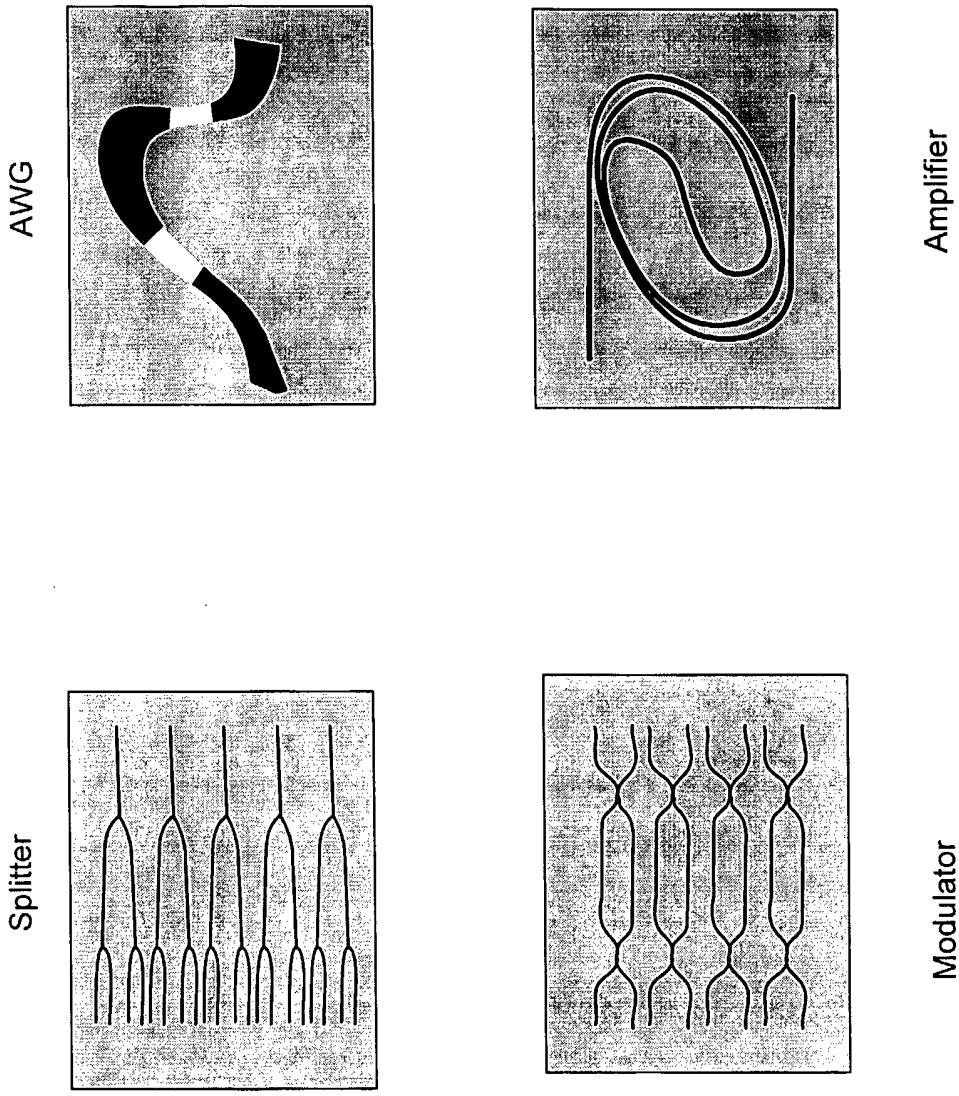


FIG. 9b

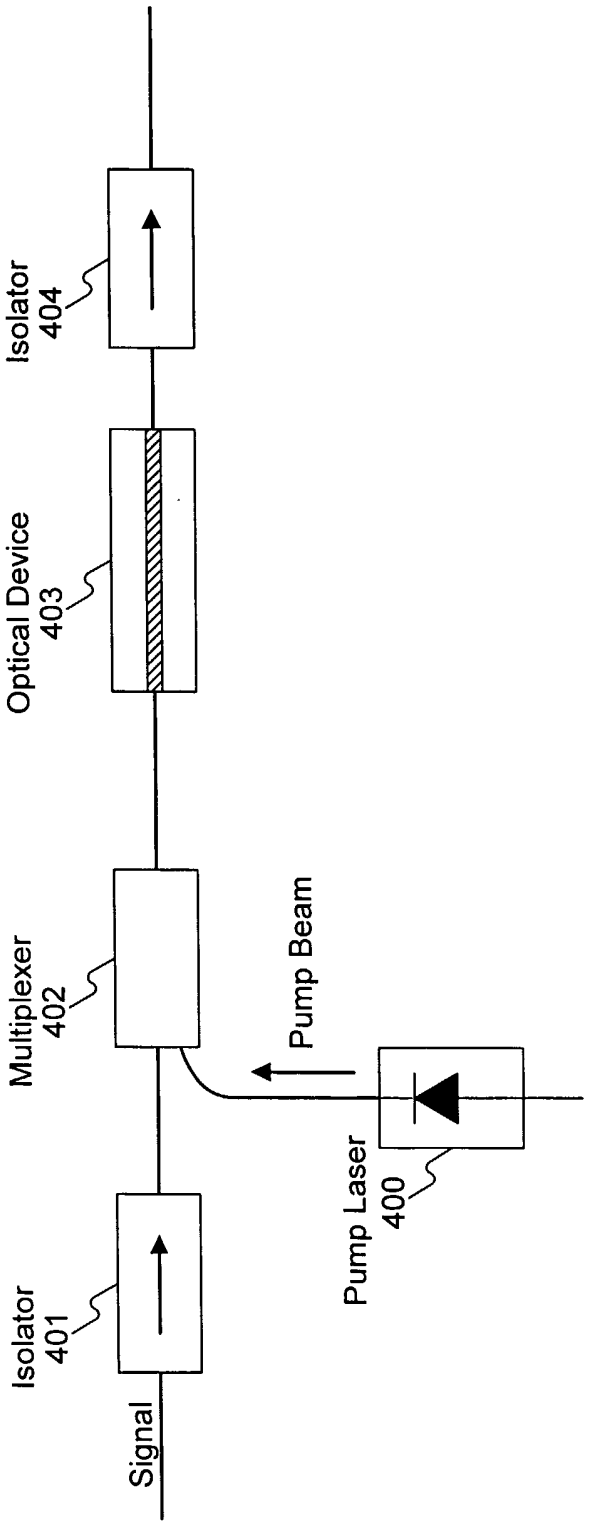

Isolator
404
Optical Device
403
Multiplexer
402
Pump Beam
Pump Laser
400
Isolator
401
Signal

FIG. 9c

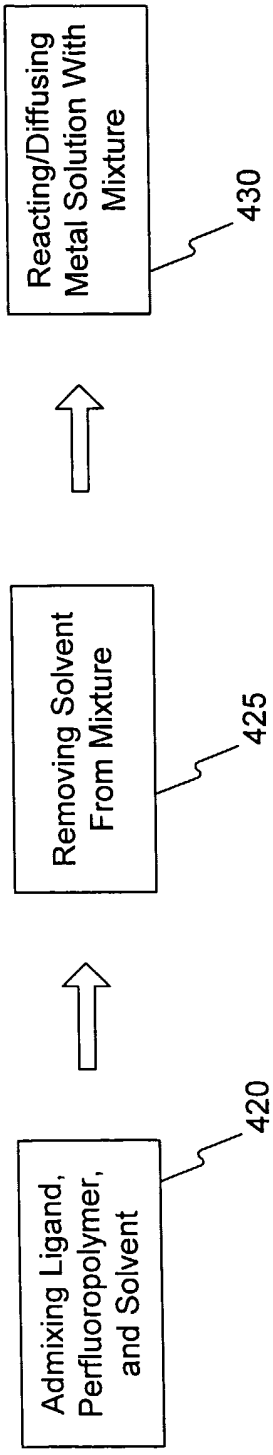

Admixing Ligand, Perfluoropolymer, and Solvent
420
Removing Solvent From Mixture
425
Reacting/Diffusing Metal Solution With Mixture
430

FIG. 10a

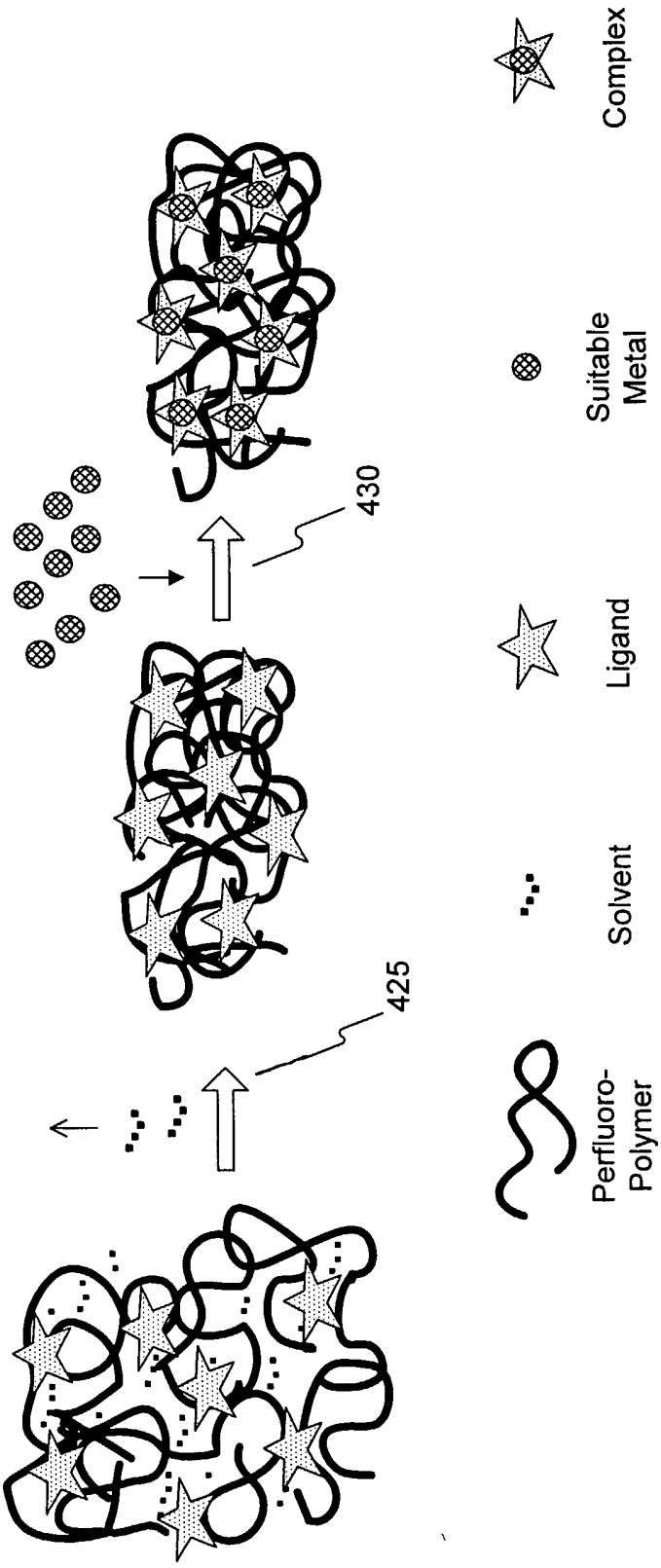

Complex
Suitable Metal
Ligand
Solvent
Perfluoro-Polymer
425
430

FIG. 10b

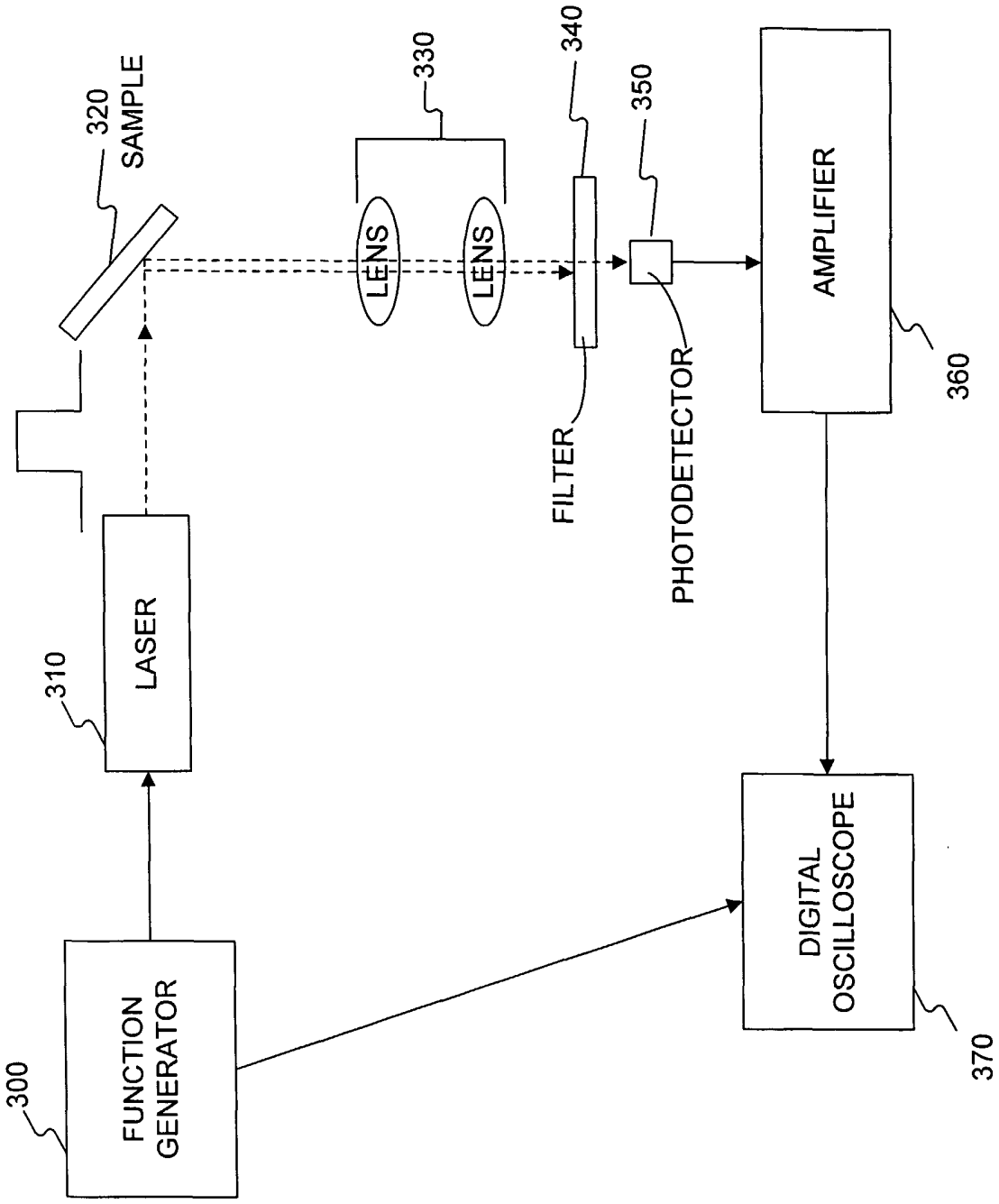

300
FUNCTION GENERATOR
310
LASER
320
SAMPLE
330
LENS
LENS
340
FILTER
350
PHOTODETECTOR
360
AMPLIFIER
370
DIGITAL OSCILLOSCOPE

FIG. 11

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/26944

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07F9/30 C07F9/38 H01S3/067

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 7 C07F H01S

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 01 61802 A (PHOTON-X, INC.) 23 August 2001 (2001-08-23) the whole document ---	1-87
Y	WO 01 61803 A (PHOTON-X, INC.) 23 August 2001 (2001-08-23) the whole document ---	1-87
Y	WO 01 61797 A (PHOTON-X, INC.) 23 August 2001 (2001-08-23) the whole document -----	1-87

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

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

"E" earlier document 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

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"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
25 November 2002	03/12/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Beslier, L

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 02/26944

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0161802 A	23-08-2001	US 6292292 B1	18-09-2001
		AU 3695000 A	27-08-2001
		AU 3832301 A	27-08-2001
		AU 3832401 A	27-08-2001
		EP 1258058 A2	20-11-2002
		WO 0161797 A1	23-08-2001
		WO 0161802 A2	23-08-2001
		WO 0161803 A2	23-08-2001
WO 0161803 A	23-08-2001	US 6292292 B1	18-09-2001
		AU 3695000 A	27-08-2001
		AU 3832301 A	27-08-2001
		AU 3832401 A	27-08-2001
		EP 1258058 A2	20-11-2002
		WO 0161797 A1	23-08-2001
		WO 0161802 A2	23-08-2001
		WO 0161803 A2	23-08-2001
WO 0161797 A	23-08-2001	US 6292292 B1	18-09-2001
		AU 3695000 A	27-08-2001
		AU 3832301 A	27-08-2001
		AU 3832401 A	27-08-2001
		EP 1258058 A2	20-11-2002
		WO 0161797 A1	23-08-2001
		WO 0161802 A2	23-08-2001
		WO 0161803 A2	23-08-2001