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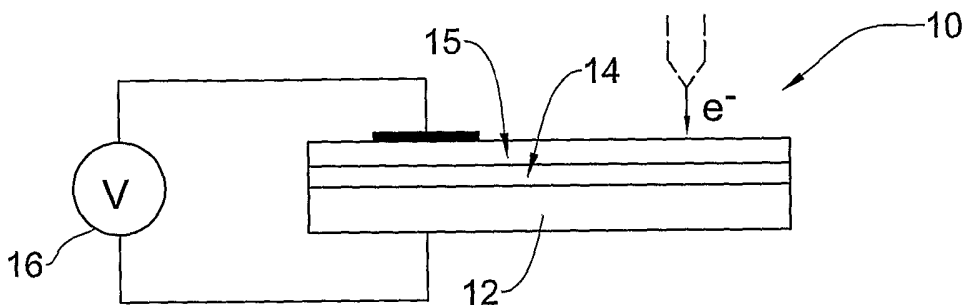
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(54) Title: REDOX-ACTIVE STRUCTURES AND DEVICES UTILIZING THE SAME



(57) Abstract: A device is presented having reversibly changeable and optically readable optical properties. The device comprises a substrate having an electrically conductive surface and carrying a redox-active layer structure. The redox-active layer structure may be a monolayer or a multi-layer structure and is configured to have at least one predetermined electronic property including at least one of electrodensity and oxidation state. The electronic property of the layer structure defines an optical property of the structure thereby determining an optical response of the structure to certain incident light. This at least one electronic property is changeable by subjecting the redox-active layer structure to an electric field or to a redox-active material. The device thus enables effecting a change in said electronic property that results in a detectable change in the optical response of the layer structure.

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REDOX-ACTIVE STRUCTURES AND DEVICES UTILIZING THE SAME

FIELD OF THE INVENTION

This invention is in the field of devices utilizing redox-active structures.

LIST OF REFERENCES

5 The following references are considered to be pertinent for the purpose of understanding the background of the present invention:

1. Li, Q. et al, *Appl. Phys. Lett.* **2002**, 81, 1495.
2. Liu, Z.; Yasseri et al, *Science* **2003**, 302, 1543.
3. Yasutomi, S. et al, *Science* **2004**, 304, 1944.
- 10 4. Collier, C. P. et al, *Science*, **2000**, 289, 1172.
5. Sortino, S. et al; *J. Am. Chem. Soc.* **2004**, 122, 1122.
6. Lahann, J. et al, *Science* **2003**, 299, 271.
7. US 6,728,129
8. WO 01/03126
- 15 9. WO 03/038886
10. Lee, J.-K. et al., *Chem. Comm.* **2003**, 1602-1603, and reference cited therein.

The above references will be acknowledged in the text below by indicating their numbers [in brackets] from the above list.

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BACKGROUND OF THE INVENTION

Thin film chemistry and surface engineering, in particular, the generation of new molecular electronic and photonic materials is attracting considerable interest. Development of a fundamental understanding of molecular interactions, orientation, and function is essential for the formation of device-quality organic mono- and multi-layers. Direct control of thin film properties led to a wide range of applications in molecular-based optics and electronics. For instance, low-voltage redox-active molecules were found useful in the design of new charge-storage memory devices [1, 2]. These molecular-based memories, bound to Si(100), withstand operation and device processing temperatures [2]. Much effort has been devoted to the development of molecular switches in solution, whereas such system immobilized on substrate surfaces is a rapidly developing field [1, 2-6]. Recently, an example of a redox-switch self-assembled structure on an optically transparent Pt electrode has been reported [5].

Molecular memory applications based on porphyrin-based elements and methods of forming electrically addressable data storage devices based on such elements are described for example in references [7-9].

SUMMARY OF THE INVENTION

There is a need in the art for patterned structures with small-size features of the pattern, which can be read by optical means, and which can be easily fabricated by the available equipment. It is also a need in the art to provide a memory device having a non-binary data pattern, which can be easily produced (written) and read.

The inventors have found that electrochemically varying the oxidation state and/or electrodensity of a redox-active layer structure causes a change (in a reversible manner) in the optical properties of the structure. This change can be effected in ambient conditions and monitored with a standard UV-vis spectrophotometer. Furthermore, varying the oxidation state and/or

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electrodensity of a redox-active layer structure causes a change (reversible) in the dipole moment of the structure, which can be detected by optical means as different optical responses of regions of the redox-active layer structure having different dipole moments. The device may be configured to enable reading of a light response thereof, namely reflection, absorption, second-harmonic generation, third-harmonic generation or transmission of the incident light, or emission of light excited by the exciting incident light.

According to one broad aspect of the invention there is provided a device having reversibly changeable and optically readable optical properties, the device comprising a substrate having an electrically conductive surface and carrying a redox-active layer structure configured to have at least one predetermined electronic property including at least one of electrodensity and oxidation state, said at least one electronic property being changeable by subjecting the layer structure to an electric field, wherein the electronic property of the layer structure defines an optical property of the structure thereby determining an optical response of the structure to certain incident light, the device enabling to effect a change in said electronic property that results in a detectable change in the optical response of the layer structure.

The term "*redox-active*" refers herein to a molecule or component of a molecule that is capable of being oxidized or reduced or undergoing a change in the electrodensity, by the application of a suitable electric field. Such an electric field may be created as a potential difference between the electrically conductive surface of the substrate and the redox-active layer structure; or by irradiating the redox-active layer structure with an electron beam. The term "*redox-active layer structure*" refers to a monolayer structure or multilayered structure containing redox-active molecules.

The term "*oxidation state*" refers to the electrically neutral state or to the state produced by the gain or loss of electrons to an element, compound, or chemical substituent/subunit. In a preferred embodiment, the term "*oxidation*

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state" refers to states including the neutral state and any state other than a neutral state caused by the gain or loss of electrons (reduction or oxidation).

The change in the electronic property is caused electrochemically by addition or withdrawal of one or more electrons to or from the at least one
5 compound in the layer structure. The electric field can be created via the electrically-conductive substrate (or electrically conductive surface of the non-conductive substrate) and one or more electrodes coupled to the layer structure. Alternatively, the electric field can be created by irradiating the redox-active layer structure by an electron beam.

10 It should be noted that the term "*electrically-conductive substrate*" will be used herein to refer to an electrically-conductive surface of a substrate which carries the redox-active layer structure. Such a surface may be a surface of an electrically conductive substrate layer or a layer/coating on a non-conductive substrate. It should be noted that the electrically conductive surface regions may
15 or may not be located directly below the redox-active layer structure. For example, the redox-active layer structure can be patterned to define spaced-apart regions of redox-active regions, and the electrically-conductive surface regions are located in the spaces between the redox-active regions.

Preferably, the redox-active layer structure is a metal based layer
20 structure, metal complex, or a structure utilizing redox-active organic molecules (non-polymer molecules) such as quinones or thiophenes, or a structure utilizing a mixture of such materials. The metal based redox-active layer structure may include one or more transition metal, which is selected from Os, Ru, Fe, Ni, Ir, Rh, Co, Cu, Re, Tc, Mn, V, Nb, Ta, Hf, Zr, Cr, Mo, W, Ti, Zn, Pt, Pd. The metal-
25 based redox-active layer structure is preferably configured as a ruthenium-based redox-active monolayer. This may be a ruthenium(II)- or ruthenium(III)-based redox-active monolayer. The ruthenium monolayer consists for example of a charged trisbipyridyl ruthenium unit bound to a linker unit designed to covalently bind to the conductive surface of the substrate of the device.

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The device may be configured to define in the redox-active layer structure a predetermined pattern of the electronic property regions. This pattern may be in the form of an array (one-, two- or three-dimensional array) of the regions of the structure having different and distinguishable electrical properties. The pattern
5 may be the array of the spaced-apart regions having the certain electronic property.

As indicated above, the device may include an electrode arrangement for applying the electric field to the redox-active layer structure. The electrode arrangement may be formed by the electrically-conductive surface of the
10 substrate (constituting a first electrode arrangement) and a second electrode arrangement coupled to the layer structure. The second electrode arrangement may be coupled directly to the redox-active layer structure, or indirectly via an electrolyte or another electrically conductive (including also semi-conductive) material.

15 The electrically-conductive surface of the substrate may be patterned to form an array of electrically-conductive regions (electrodes) spaced by non-conductive regions of the substrate, thereby defining the first electrodes array and thus defining an array of regions of the layer structure carried thereby to be selectively addressed to affect the electronic property of the regions. The second
20 electrode arrangement may include an array of the electrodes coupled to the layer structure, thereby defining an array of regions of the layer structure to be selectively addressed to affect the electronic property thereof.

The present invention also provides for creating the electronic property pattern, as well as reading the pattern, in the redox-active layer structure by
25 means of scanning the structure with an Atomic Force Microscope (AFM), where the microscope tip acts as an electrode. The use of an AFM for the pattern creation allows for applying an appropriate voltage to the structure region resulting in a partial oxidation of this region, thus allowing for fabricating a non-binary memory device.

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The redox-active layer structure may include one or more layer formed by one or more metal based redox-active material or redox-active organic molecules (e.g., quinones, thiophenes) or a mixture thereof. The redox-active layer structure may have the following configurations: a monolayer of a metal based redox-active material or a mixture of metal based redox-active materials; a monolayer of metal based redox-active complexes of one metal, complexes of different metals, or complexes with identical metals. The redox-active layer structure may also have the following configurations: a monolayer of a metal based redox-active material and organic material or a monolayer of organic redox-active materials.

The redox-active layer structure may include a plurality of identical layers (each formed by a metal based redox-active material or organic molecules or a mixture thereof); or a plurality of different layers. In the latter case, each of the layers may be formed by a metal based redox-active material or redox-active organic molecules or a mixture thereof; a layer of a metal based redox-active material or a mixture of metal based redox-active materials; or a monolayer of metal based redox-active complexes. As indicated above, the metal based redox-active complexes may include at least one metal; different metals; or identical metals.

In some embodiments of the invention, the electrically-conductive substrate is hydrophilic or bears a surface carrying a functional group capable to attach (e.g., covalently or via coordination) to said redox-active layer structure. As indicated above, the substrate is either made of an electrically-conductive material (metal, metal oxide, metal alloy or semiconductor), or has an electrically conductive surface (metal, metal oxide, metal alloy or semiconductor). The substrate may for example be made of glass, group IV elements, quartz, mica, mixtures of metal and metal oxides, polymers, plastics, mixtures of materials including alloys, organic materials, inorganic materials, etc., bearing when necessary electrically conductive surface (layer or coating) made of metal, metal

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oxide, metal alloy or semiconductor. The substrate may be optically transparent to incident light of UV, visual, IR range or near IR spectral range.

The substrate may be configured to carry a functional group capable to attach to the redox-active layer structure in one step. Alternatively, the substrate
5 may be configured to carry a functional group capable to attach to the redox-active layer structure in a stepwise procedure.

The device may be configured and operable as a display device, e.g., electroluminescent display device, e.g., dynamic or static display device.

The display device may be configured to provide multiple colors. This can
10 be achieved by making the layer structure from the mixed metal-based film of different chromophores modules and variation of the periodic table position of the metal.

The redox-active layer structure may be formed from one or more layers each including a plurality of ink particles. The ink particle is made of a core
15 which is made of an electrically conductive (e.g., metal or semiconductor) or dielectric material, and is at least partially coated with the redox-active (e.g. metal based) material. The particle core may be configured to be highly scattering, thereby creating multiple reflections and increasing pathlength of light within the ink-particles layer(s). To this end, the particles are made from at least
20 one metal; or from at least one material with a relatively high index of refraction (e.g., Titanium dioxide). The use of such a configuration of the redox-active structure (i.e., ink particles formed by core coated with redox-active material) increases the amount of light passing in the redox-active layer structure, thereby improving the image contrast. In the case the redox-active layer structure (formed
25 by multiple layers or a stack of ink particles) is located on the electrode(s), then either the particles' core or the redox-active coating is configured to support an electric current passage between the particles. The ink-particles layer(s) may include different chromophores thereby providing a multicolor ink. To selectively activate the different color components, different voltages may be
30 used as required for an electrochemical reaction of each chromophore; or

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different inks can be selectively applied (each containing a different chromophore) to different locations each determining a different pixel for each color. The electrode arrangement may be configured to define an array of electrochemical cells. An electrolyte for the electrochemical cell may be solid electrolyte, e.g., mixed with a solvent and the ink particles to create a liquid ink mixture and then applied to the surface of the substrate; evaporation of the solvent results in the particle layers in the solid electrolyte matrix.

The device of the present invention may be operable as an optically readable memory device, which may include a mixed metal-based film having different metal centers. The electrode arrangement may be configured to address the different metal centers by the different electrical field values. The memory device may be configured as a multi-layer optically readable memory, in which case the layer structure includes the multiple metal based redox-active layers.

The device of the present invention may also be operable as a readable memory device, based on variation of the dipole moment of the molecules and/or variation of the dipole moment of the layers, where molecules/layers may include a mixed metal-based film having different metal centers. The electrode arrangement may be configured to address the different metal centers by the different electrical field values. The memory device may be configured as a multi-layer readable memory, in which case the layer structure includes the multiple metal based redox-active layers.

The present invention also provides for writing/reading of data in a non-binary fashion in a memory device, based on the redox-active layer structure as described above. This is achieved by scanning the layer structure with the tip of an AFM.

The device may be operable as an optical sensor. The sensor may be tunable by varying the electronic property of at least a selected region of the layer structure via the variation of the electric field.

The device may be operable as a spectral filter, in which the electronic property of at least a region of redox-active layer structure determines a spectral

range of the incident light to which the region of the structure is optically responsive. The spectral filter may similarly be tunable.

The device may be operable as an optical switch; or a light emitting device. The light emitting device may be optically pumped by the incident light.

5 The light emitting device may be tunable by varying the electronic property, and consequently the spectral range of the optical response, via the variation of the electric field. The light emitting device may be configured to produce multiple colors of the emitted light, which can be achieved by providing the layer structure in the form of a mixed metal-based film of different chromophores
10 modules and variation of the periodic table position of the metal.

The layer structure may be configured such that variation of the electronic property of at least a region of the structure effects a change in an index of refraction of this region. The device may thus be operable as a non-linear medium (carrying out frequency doubling, optical switching, light modulation,
15 etc.). The layer structure may be operable by the electric field to define a predetermined pattern of spaced-apart regions of different refraction indices. The device may be operable as a data transfer device, a data storage device, a pulse shaper, and an optical processor.

The electronic property of a selected region of said layer structure may be
20 defined by a single-molecule metal region. The layer structure may be patterned to define an array of the single-molecule metal regions arranged in a spaced-apart relationship. The device may thus be operable as a molecular-electronic device. The metal-based chromophores layer structure may possess switching properties providing for the formation of semiconductor devices. The layer structure may be
25 configured and operable for storing a charge. The layer structure may be configured and operable for dipole moment variation. The device can thus be operable as a switch device, a memory device, a transistor, a diode, or a conductor of a microelectronic circuitry, or a single electron tunneling device. The device may be a nano-scale electro-optical device.

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The device may be configured and operable as a diode, e.g., photodiode, e.g., with the layer structure including the metal-based film prepared with different metals and/or chromophores. The device may be configured such that irradiating the layer structure with the incident light of a certain frequency range results in an anodic photocurrent, controllable changeable in a reversible manner by electrochemically addressing of the electronic property of the layer structure.

The device can be configured and operable as a photovoltaic cell or solar cell. The layer structure may include at least one metal-based film on the substrate formed of one or more conductive (mesoporous) metal oxide.

The device can be configured and operable as a controllable metal-semiconductor junction. The layer structure is operable by the electric field to effect variation of the metal-based film dipole moment resulting in creation of diodes with an effective barrier height tunable by the dipole moment of the film.

The device can also be configured and operable as a battery assembly; or can be operable by the application of an electric field for energy conversion, for photochemical cleavage of water resulting in formation of O_2 and H_2 or H^+ .

The device can be operable as a DNA analyzer. To this end, the metal within at least one region of the layer structure is selected for binding to a selected DNA.

The device of the present invention, when subjected to an external magnetic field, possesses magnetic susceptibility caused by a change in a magnetic dipole of at least a region of the device resulting from the oxidation and reduction of the metal center in this region. This can be used to construct a memory device; or a molecular-based magnet.

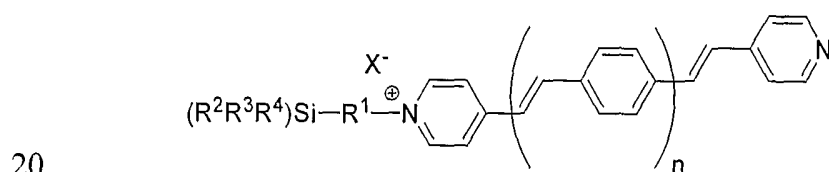
According to another aspect of the invention, there is provided a method for fabricating an electro-optical device, the method comprising chemically binding a metal based redox-active layer structure to an electrically conductive surface of a substrate, said structure comprising at least one metal selected in accordance with the device intended operation, said layer structure being configured to have at least one predetermined electronic property defined by at

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least one of electrodensity and oxidation state changeable by subjecting the structure to an electric field, the electronic property of the structure defining a certain optical property of the structure thereby determining a certain optical response of the layer structure to certain incident light, effecting a change in the electronic property resulting in a reversible change in the optical response of the layer structure.

According to yet another broad aspect of the invention, there is provided a method for writing/reading non-binary data in a memory device, which comprises a substrate having an electrically-conductive surface and carrying a redox-active layer structure configured to have at least one predetermined electronic property, including at least one of electrodensity and oxidation state, changeable by subjecting the layer structure to an electric field, the method comprising scanning the redox-active layer structure by a tip of an atomic force microscope operable to apply to respective locations of the structure voltages corresponding to various conditions of said at least one electronic property thereby creating/detecting a non-binary data pattern in the layer structure.

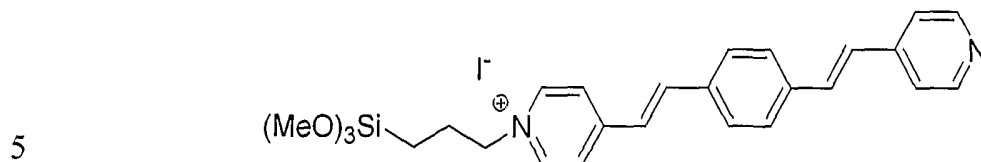
According to yet other broad aspects of the invention, there are provided new compounds for use in a redox-active layer structure:



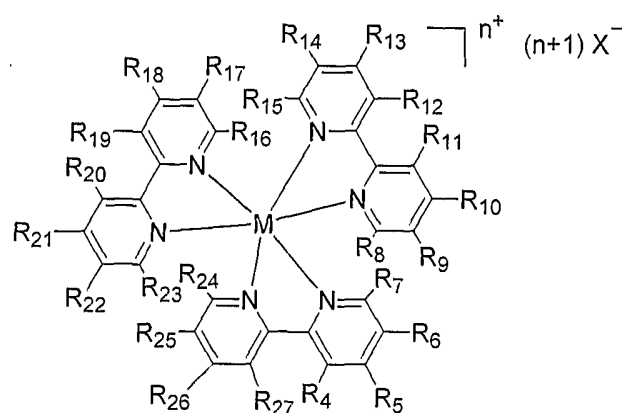
wherein $n = 0-6$, $R^1 =$ alkyl, aryl, benzyl, alkene, O-alkyl, N-alkyl, S-alkyl, peptide, aminoacid, alkyl-O-alkyl, C=N, N=C and R^2, R^3, R^4 are independently or together selected from Cl, I, F, Br, alkoxy, alkyl, aryl, fluoroaromatic, fluoroalkyl, hydrogen, hydroxyl, amine, triflate, aryloxy, acetate, and X is a counter ion selected from Br, Cl, F, I, PF_6 , BF_4 , OH, ClO_4 , CH_3COO , SO_3^- and CF_3COO , CN, AlkylCOO, ArylCOO.

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In a preferred embodiment, the invention provides a new compound having the following structure:



According to yet another embodiment of the invention, there is provided a compound of the general formula I, for use in a redox-active layer structure:



10 wherein

M is selected from Os, Ru, Fe, Cu, and Co:

n is the formal oxidation state of the metal, $n = 0 - 4$:

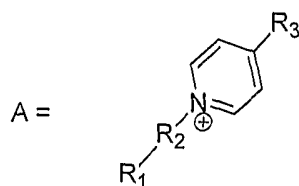
X is a counter anion selected from Br, Cl, F, I, PF_6^- , BF_4^- , OH, ClO_4^- , CH_3COO^- , SO_3^- and CF_3COO^- , CN, AlkylCOO, ArylCOO, or any combination thereof:

15

R_4 to R_{27} are each independently selected from hydrogen, halogen, hydroxyl, azide, nitro, cyano, amine, thiol, C_1 - C_{10} alkyl, cycloalkyl, heterocycloalkyl, haloalkyl, aryl, heteroaryl, alkoxy, alkene, alkyne, amide, carboxylic acid, protected carboxylic acid, protected amine, sulfonyl, substituted aryl, substituted cycloalkyl, and substituted heterocycloalkyl; wherein at least one of said R_4 to R_{27} being group A:

20

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wherein

A is linked to the ring structure of the compound of general formula I via
 5 R₃; said R₃ is selected from *cis/trans* C=C, C≡C, N=N, C=N, N=C, C-N, N-C, alkylene, arylene, or any combination thereof;

R₂ is selected from hydrogen, alkyl, alkylene, aryl, arylene, or any combination thereof, or R₂ may be absent;

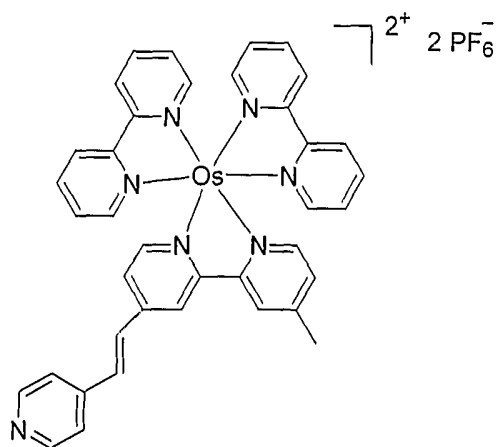
R₁ is selected from hydrogen, trialkoxysilane, trihalidesilane, thiol,
 10 carboxylate, COOH, COO⁻, Si(OH)₃, and phosphonate, or R₁ may be absent;

any two vicinal R₄-R₂₇ substituents, together with the carbon atoms to which they are attached, may form a fused ring system selected from cycloalkyl, heterocycloalkyl, heteroaryl, and aryl; said fused system may be substituted by one or more groups selected from C₁-C₁₀ alkyl, aryl, azide, cycloalkyl, halogen,
 15 heterocycloalkyl, alkoxy, hydroxyl, haloalkyl, heteroaryl ring, alkene, alkyne, nitro, cyano, hydrogen, amine, amide, carboxylic acid, protected carboxylic acid, protected amine, thiol, sulfonyl, and substituted aryl; said fused system may also contain at least one heteroatom selected from N, O and S.

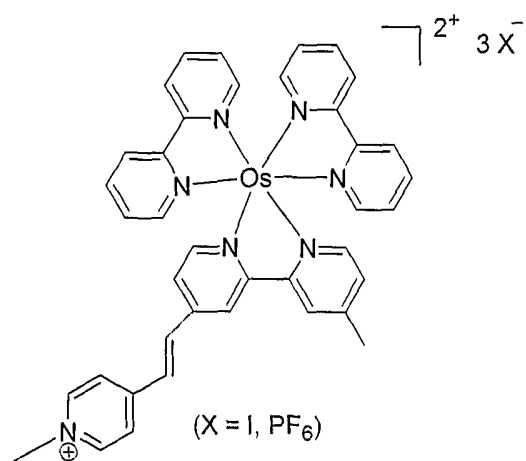
In one embodiment, the compound of the general formula I is one in
 20 which M is Os and two substituents of R₄-R₂₇ are non hydrogen. In another embodiment, one of said two substituents of R₄-R₂₇ which are non-hydrogen is a methyl group and the second of said two substituents of R₄-R₂₇ which are non-hydrogen is A wherein R₃ is a *cis* or *trans* C=C, and R₂ and R₁ are absent. In yet another embodiment, in the compound of general formula I, R₂ is an alkylene and
 25 R₁ is selected from hydrogen and a trimethoxysilane.

In another preferred embodiment, the compounds of general formula I are the compound herein referred to as **Compounds 1, 2 and 3**.

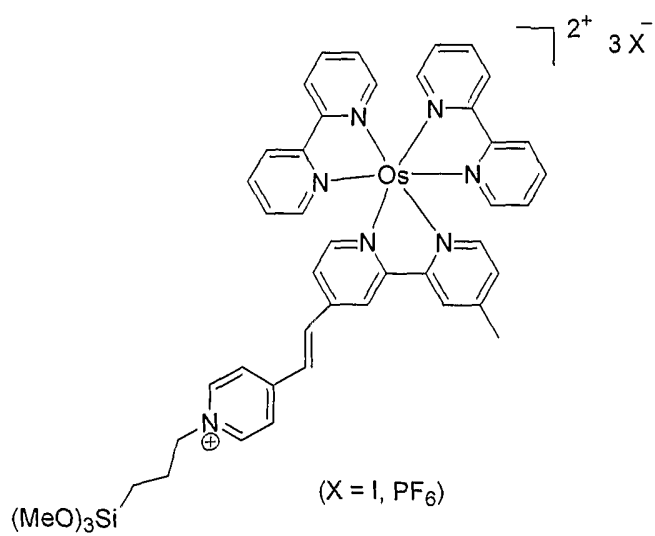
- 14 -



Compound 1



Compound 2



Compound 3

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The term "*halogen*" refers to one or more of the following atoms: Br, Cl, I, or F. The term "*haloalkyl*" refers to an alkyl, as defined hereinbelow, substituted by at least one halogen.

The term "*hydroxyl*" refers to $-OH$ and the term "*thiol*" refers to $-SH$. The term "*alkoxy*" refers to the group $-OR$, wherein R is an alkyl group. The term "*azide*" refers to $-N_2$. The term "*nitro*" refers to $-NO_2$ and the term "*cyano*" refers to $-CN$. The term "*amine*" refers to the group $-NH_2$ or to any substitution thereof, namely secondary, tertiary and quaternary substitutions. The term "protected amine" refers to such groups which may be converted to the amine, for example, the amide. An "*amide*" is the group $-CONH_2$ or to the group in which each of the hydrogens are replaced by an alkyl group.

The term "*sulfonyl*" refers to the group $-SO_2-$.

The term "*carboxylic acid*" refers to the group $-COOH$.

The term "*protected carboxylic acid*" refers to such groups which may be converted into the carboxylic acid group. Such groups may be esters (e.g. $-COOR$, wherein the R is an alkyl group or an equivalent thereof), and amide group as defined, and others which may be known to a person versed in the art of organic chemistry.

The term "*alkyl*" as used herein refers to a saturated aliphatic hydrocarbon having preferably between 1 to 10 carbon atoms, inclusive. The alkyl may be a straight or a branched alkyl and may or may not be further substituted. Examples of said C_1-C_{10} alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, sec-butyl, amyl, pentyl, isopentyl, hexyl, nonyl, decyl and others.

The term "*cycloalkyl*" refers similarly to a saturated aliphatic hydrocarbon in a cyclic form (ring) and preferably having between 1 and 10 carbon atoms, in total. Such ring systems may be cyclopropyl, cyclobutyl, cyclopentyl, cyclodecyl and the like. Such cycloalkyl ring systems may be fused to other cycloalkyls, such in the case of cis/trans decalin.

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The term "*heterocycloalkyl*" refers to a cycloalkyl as defined, being substituted by at least one heteroatom, preferably and heteroatom selected from N, O and S.

The term "*alkene*" refers to a carbon chain having preferably between 2
5 and 10 carbon atoms and containing at least one double bond. Examples of such alkenes are vinyl, 1-propylene, 1-butylene, 2-butylene, 3-hexylene and others.

The term "*alkyne*" refers to a carbon chain preferably having between 2 and 10 carbon atoms and containing at least one triple bond.

The term "*AlkylCOO*" refers to an alkyl group as defined, being
10 substituted by a carboxyl group (-COO-) on any one of its carbon atoms. Preferably, the alkyl has between 1 and 10 carbon atoms.

The term "*aryl*" refers to any aromatic group as may be known to a person skilled in the art. Preferably, the term refers to a neutral aromatic group such as benzene. The aryl group may be substituted by any known substituents.

15 The group "*ArylCOO*" refers, for example, to such a substituted aryl, in this case being substituted by a carboxylate group.

The term "*heteroaryl*" refers to an aromatic ring system in which one or more of the carbon atoms are replaced by heteroatoms selected from N, O or S. One example of a heteroaryl group is pyridyl.

20 The term "*trialkoxysilane*" refers to a group of the general formula – Si(OR)₃, wherein each of the three R groups is an alkyl group, as defined, and may be the same or different. Similarly, the term "*trihalidesilane*" refers to – SiX₃, wherein X is a halogen, each X may be same or different.

The expression "*any two vicinal R₄-R₂₇ substituents*" refers to any two
25 substituents on the benzene rings, being ortho to one another. The expression "*fused ring system*" refers to at least two rings sharing one bond, such as in the case of naphthalene, phenanthrene, benzindole, benzpyridine and others. The fused ring system contains at least one benzene ring, being the ring of the compound of general formula I and another ring being formed by the ring closure

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of said any two vicinal R₄-R₂₇ substituents. The said another ring may be saturated or unsaturated, substituted or unsubstituted and may be heterocyclic.

The expression "*non-hydrogen substituents*" or any lingual variation thereof, refers to any substituent which is not hydrogen.

5 According to yet another broad aspect of the invention, there is provided a sensor device configured an operable for sensing at least one predetermined liquid (e.g. a compound dissolved in a solvent) or gas substance, the device comprising a redox-active layer structure selected to be capable of changing its oxidation state in response to a reaction with said at least one substance thereby
10 causing a change in optical properties of said structure, said change being reversible and being optically readable.

The substance(s) detectable by the device of the present invention is of the kind capable of effecting a change in the oxidation state of a redox-active layer structure (i.e. oxidize or reduce the redox-active layer structure). The
15 substance(s) include at least one of the following: water, anions, gas, alcohols, ketones, aldehydes, carboxyles, phenols, halogenated substances, sulfides, phosphonates, nitro-containing substances, peroxides, cations, ozone, sugars, carbohydrates, SO₂, NO⁺, NO₂, NO_x, CO, CO₂, fluorocarbons, heterocyclic compounds, mustard gas, sulfur mustards, TNT, insecticides, malathion, sarin,
20 chemical warfare reagents, greenhouse gases, phosphines, vesicants, incapacitating agents, tear gases, vomiting gases, lung toxicants, adamsite, phosponates, phosgene, diphosgene, nerve agent VX, nerve agent Tabun, nerve agent Soman, nerve agent GF, or blister agent HD, acids, bases, cyanides, hydrogen cyanide, cyanogen chloride, ethyl N,N-dimethyl-
25 phosphoramidocyanidate, isopropyl-methylphosphonofluoridate, 1,2,2-trimethyl-propyl methylphosphonofluoridate, cyclohexyl-methylphosphonofluoridate, o-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothiolate, carbonyl chloride, trichloromethyl chloroformate, bis -2-chloroethyl sulfide, 2-chlorovinyl dichloroarsine, mustard-lewisite mixture, 3-quinuclidinyl benzilate (QNB), 2-
30 chloro-1-phenylethanone, 2-chlorobenzalmalononitrile, 10-chloro-5,10-dihydro-

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phenarsazine, DNA, RNA, peptides, amino acids, proteins, steroids, anabolic-
androgenic steroids, anabolic steroids, hormones, narcotics, heroin,
amphetamine, methamphetamine, ecstasy, LSD, codeine, concentrate of poppy
straw, methadone, morphine, medicinal opium, opium, acetic anhydride, acetyl
5 chloride, ethylidin diacetate, chlorpseudophedrine, ergometrine, ergotamine,
isosafrole, lysergic acid, piperonal, safrole, azide explosives, HMTD,
hexamethylenetriperoxidodiamine, nitrate explosive mixtures, picrate explosives,
TATP, triacetone triperoxide, DIPAM, dipicramide, diaminohexanitrobiphenyl,
EDNA, ethylenedinitramine, PBX, RDX, plastic bonded explosives, water-
10 bearing explosives having salts of oxidizing acids and nitrogen bases, sulfates, or
sulfamates, trinitrotoluene, trotyl, trilitite, triton, acetylides of heavy metals,
aluminum containing polymeric propellant, a luminum ophorite explosive,
amatex, amatol, ammonal, ammonium perchlorate composite
propellant, ammonium perchlorate explosive mixtures, ammonium picrate, picrate
15 of ammonia, ammonium salt lattice with isomorphously substituted inorganic
salts, ANFO, ammonium nitrate-fuel oil, aromatic nitro-compound explosive
mixtures, azide explosives, baranol, baratol, BEAF, 1, 2-bis (2, 2-difluoro-2-
nitroacetoxyethane), black powder, black powder based explosive mixtures,
blasting agents, nitro-carbo-nitrates, including non-cap sensitive slurry and water
20 gel explosives, blasting caps, blasting gelatin, blasting powder, BTNEC, bis
(trinitroethyl) carbonate, BTNEN, bis (trinitroethyl) nitramine, BTTN, 1,2,4
butanetriol trinitrate, bulk salutes, butyl tetryl, calcium nitrate explosive mixture,
cellulose hexanitrate explosive mixture, chlorate explosive mixtures, copper
acetylides, cyanuric triazide, cyclonite, RDX, cyclotetramethylenetetranitramine,
25 HMX, cyclotol, cyclotrimethylenetrinitramine, DATB, diaminotrinitrobenzene,
DDNP, diazodinitrophenol, DEGDN, diethyleneglycol dinitrate, dimethylol
dimethyl methane, dinitrate composition, dinitroethyleneurea, dinitroglycerine,
glycerol dinitrate, dinitrophenol, dinitrophenolates, dinitrophenyl hydrazine,
dinitroresorcinol, dinitrotoluene-sodium nitrate explosive mixtures, DIPAM,
30 dipicramide; diaminohexanitrobiphenyl, dipicryl sulfone, dipicrylamine, display

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fireworks, DNPA, 2,2-dinitropropyl acrylate, DNPD, dinitropentano nitrile, dynamite, EDDN, ethylene diamine dinitrate, EDNA, ethylenedinitramine, ednatol.EDNP, ethyl 4,4-dinitro-pentanoate, EGDN, ethylene glycol dinitrate, erythritol tetranitrate explosives, esters of nitro-substituted alcohols, ethyl-tetryl, explosive conitrates, explosive gelatins, explosive liquids, explosive mixtures containing oxygen-releasing inorganic salts and hydrocarbons, explosive mixtures containing oxygen-releasing inorganic salts and nitro bodies, explosive mixtures containing oxygen-releasing inorganic salts and water insoluble fuels, explosive mixtures containing oxygen-releasing inorganic salts and water soluble fuels, explosive mixtures containing sensitized nitromethane, explosive mixtures containing tetranitromethane (nitroform), explosive nitro compounds of aromatic hydrocarbons, explosive organic nitrate mixtures, explosive powders, flash powder, fulminate of mercury, fulminate of silver, fulminating gold, fulminating mercury, fulminating platinum, fulminating silver, gelatinized nitro-cellulose, gem-dinitro aliphatic explosive mixtures, guanyl nitrosamino guanyl tetrazene, guanyl nitrosamino guanylidene hydrazine, guncotton, heavy metal azides, hexanite, hexanitrodiphenylamine, hexanitrostilbene, hexogen, hexogene, octogene, nitrated N-methylaniline, hexolites, HMTD, hexamethylenetriperoxidediamine, HMX, cyclo-1,3,5,7-tetramethylene 2,4,6,8-tetranitramine, Octogen, hydrazinium nitrate/hydrazine/aluminum explosive system, hydrazoic acid, KDNBF, potassium dinitrobenzo-furoxane, lead azide, lead mannite, lead mononitroresorcinate, lead picrate, lead salts, explosive, lead styphnate, styphnate of lead, lead trinitroresorcinate, liquid nitrated polyol, trimethylolethane, liquid oxygen explosives, magnesium ophorite explosives, mannitol hexanitate, MDNP, methyl 4,4-dinitropentanoate, MEAN, monoethanolamine nitrate, mercuric fulminate, mercury oxalate, mercury tartrate, metriol trinitrate, minol-2, MMAN, monomethylamine nitrate, methylamine nitrate, mononitrotoluene-nitroglycerin mixture, monopropellants, NIBTN, nitroisobutametriol trinitrate, nitrate explosive mixtures, nitrate sensitized with gelled nitroparaffin, nitrated carbohydrate explosive, nitrated

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glucoside explosiv, nitrated polyhydric alcohol explosives, nitric acid and a nitro aromatic compound explosive, nitric acid and carboxylic fuel explosive, nitric acid explosive mixtures, nitro aromatic explosive mixtures, nitro compounds of furane explosive mixtures, nitrocellulose explosive, nitroderivative of urea
5 explosive mixture, nitrogelatin explosive, nitrogen trichloride, nitrogen tri-iodide, nitroglycerine, NG, RNG, nitro, glyceryl trinitrate, trinitroglycerine, nitroglycide, nitroglycol, ethylene glycol dinitrate, EGDN, nitroguanidine explosives, nitronium perchlorate propellant mixtures, nitroparaffins explosive Grade and ammonium nitrate mixtures, nitrostarch, nitro-substituted carboxylic acids,
10 nitrourea, octogen, HMX, octol, organic amine nitrates, organic nitramines, PBX, plastic bonded explosives, pellet powder, penthrinite composition, pentolite, perchlorate explosive mixtures, peroxide based explosive mixtures, PETN, nitropentaerythrite, pentaerythrite, tetranitrate, pentaerythritol, tetranitrate, picramic acid and its salts, picramide, picrate explosives, picrate of potassium explosive mixtures, picratol, picric acid, picryl chloride, picryl fluoride, PLX,
15 nitromethane, ethylenediamine, polynitro aliphatic compounds, polyolpolynitrate-nitrocellulose explosive gels, potassium chlorate and lead sulfocyanate explosive, potassium nitrate explosive mixtures, potassium nitroaminotetrazole, pyrotechnic compositions, PYX, 2,6-bis(picrylamino)]-3,5-dinitropyridine, RDX, cyclonite, hexogen, T4, cyclo-1,3,5,-trimethylene-2,4,6,-
20 trinitramine; hexahydro-1,3,5-trinitro-S-triazine, salts of organic amino sulfonic acid explosive mixture, salutes (bulk), silver acetylide, silver azide, silver fulminate, silver oxalate explosive mixtures, silver styphnate, silver tartrate explosive mixtures, silver tetrazene, slurried explosive mixtures of water,
25 inorganic oxidizing salt, gelling agent, fuel, sensitizer, smokeless powder, sodatol, sodium amatol, sodium azide explosive mixture, sodium dinitro-ortho-cresolate, sodium nitrate explosive mixtures, sodium nitrate-potassium nitrate explosive mixture, sodium picramate, special fireworks, squibs, styphnic acid explosives, tacot, tetranitro-2,3,5,6-dibenzo- 1,3a,4,6a tetraza-pentalene, TATB,
30 triaminotrinitrobenzene, TATP, triacetoneperoxide, TEGDN, triethylene glycol

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dinitrate, tetranitrocarbazole, tetrazene tetracene, tetrazine, 1(5-tetrazolyl)-4-guanyl tetrazene hydrate, tetryl [2,4,6 tetranitro-N-methylaniline], tetrytol, thickened inorganic oxidizer salt slurried explosive mixture, TMETN, trimethylolethane trinitrate, TNEF, trinitroethyl formal, TNEOC, trinitroethyl-
5 orthocarbonate, TNEOF trinitroethylorthoformate, torpex, tridite, trimethylol ethyl methane trinitrate composition, trimethylolthane trinitrate-nitrocellulose, trimonite, trinitroanisole, trinitrobenzene, trinitrobenzoic acid, trinitrocresol, trinitro-meta-cresol, trinitronaphthalene, trinitrophenetol, trinitrophenol, trinitrophenol, trinitroresorcinol, tritonal, urea nitrate, water-bearing explosives having salts of
10 oxidizing acids and nitrogen bases, sulfates, or sulfamates, water-in-oil emulsion explosive compositions, xanthamons hydrophilic colloid explosive mixture. Also, any other carbon-containing organic substances, or any combination of the above-mentioned substances, can be used. The basic redox-active layer structure is thus suitable both for the formation of memory and sensing devices.

15 BRIEF DESCRIPTION OF THE DRAWINGS

In order to understand the invention and to see how it may be carried out in practice, preferred embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Fig. 1 schematically illustrates a device of the present invention having
20 reversibly changeable and optically readable optical properties;

Fig. 2 schematically shows the formation of ruthenium-based monolayer on a substrate surface functionalized with a chlorobenzyl-based coupling layer (CL).

Figs. 3A-3C exemplify the features of a device of the present invention;
25 **Fig. 3A** shows an experimental set for measuring electronic and optical properties of the device; **Fig. 3B** is a graph showing the cyclic voltammetric responses at different scan rates of the ruthenium-based monolayer on ITO substrate, which operates as the working electrode. Pt wires were used as reference and counter electrodes; **Fig. 3C** is a graph showing the linear

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correlation ($R^2 = 0.988$) of the anodic peak current, I_{pa} , vs. the square root of the scan rate, $v^{1/2}$.

Fig. 4 is a graph showing the electrochemical redox-switching as a function of redox cycles. The CV experiments were conducted at a sweep rate of 1000 mVs^{-1} . The lines are drawn as a guide to the eye.

Fig. 5 is an absorption spectra showing the optical switching of the ruthenium-based monolayer on ITO at $\lambda = 314$ nm for a 10 min. time interval: (a) graph G_1 : Ru^{2+} , (b) graph G_2 : Ru^{3+} , (c) graph G_3 : Ru^{2+} (d) graph G_4 : baseline. The inset shows the electrochemical ON/OFF switching of the intensity change of the absorbance band at $\lambda = 314$ nm, ΔA , vs. the number of $\text{Ru}^{2+}/\text{Ru}^{3+}$ cycles. The lines are drawn as a guide to the eye. Electrochemical oxidation was carried out with bulk-electrolysis at 1.4 V, while reduction was performed at -0.1 V (20 min. each). UV-vis spectra were recorded in situ on a Cary 100 spectrophotometer after each oxidation state change.

Fig. 6 schematically shows a layer-by-layer approach for the formation of a metal-organic multi layer arrangement.

Fig. 7A shows the experimental results for representative absorption spectral changes using 10 ppm water in THF and resetting with 0.1 mM solution of ammonium hexanitratocerate(IV) in acetonitrile of the osmium-based monolayer on glass, for Os^{3+} , Os^{2+} , and Os^{3+} ; and further increase/decrease of absorbance vs immersion time of monolayer in 10 ppm of water in THF.

Fig. 7B illustrates the transmission UV-Vis data of a multilayer arrangement with K_2PdCl_2 for 12 Layers.

Fig. 8 is a graph showing max. absorbance at 387 nm vs. layers number

Fig. 9 shows the transmission UV-Vis data of a multilayer arrangement with $\text{PdCl}_2(\text{PhCN})_2$ for seven layers 1, 3, 5, 7, 9, 11 and 13, respectively.

Fig. 10 exemplifies a device of the present invention having a patterned redox-active layer structure is in the form of an array of regions having different and distinguishable electrical properties, which may be operable as a display device or an optically readable memory device.

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Figs. 11A and 11B exemplify a device of the present invention utilizing an electrochemically addressed ink, based on conductive thin film containing chromophores, operable as a display or sign device.

Fig. 12 shows how the present invention is used for writing on the same spot with different voltages applied to the tip of an Atomic Force Microscope (AFM), where reversible changing the oxidation states by the AFM voltage results in an observable and readable change in the dipole of the system.

Fig. 13 shows that reversible changing the oxidation state by the AFM voltage results in a readable dipole moment change, which is depended on the applied voltage for a given area.

Fig. 14A exemplifies a device of the present invention, operating as a (tunable) spectral filter or optical sensor, or optically pumped light emitter.

Fig. 14B exemplifies a device of the present invention configured and operable as a sensor for sensing at least one predetermined gas or liquid (e.g. a compound dissolved in a solvent).

DETAILED DESCRIPTION OF THE INVENTION

The present invention, according to its one aspect, is based on the understanding that electrochemically varying the oxidation state and/or electrodensity of a redox-active layer structure causes a reversible change in the optical properties of the structure as well as a change in the dipole moment of the structure. The change can be carried out in ambient conditions and monitored with a standard UV-VIS spectrophotometer. According to another aspect, the invention provides for changing the electronic property of the redox-active layer structure and thus creating a non-binary pattern of multiple electronic property conditions, as well as identifying (detecting) these multiple different conditions, by applying to the structure the AFM tip.

Referring to **Fig. 1**, there is schematically illustrated a device, generally denoted **10**, of the present invention configured to possess reversibly changeable and optically readable optical properties. The device **10** includes a substrate **12**

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having an electrically conductive surface (which in the present example is implemented by providing the electrically conductive substrate **12**) and carrying a redox-active layer structure **14**, i.e., a single-layer or multi-layer structure formed by redox-active thin film(s). This may for example be ruthenium-based
5 monolayer on a hydrophilic substrate. The redox-active layer structure **14** carries an electrode **15**, which may be solid, gel-type, polymer, silver paste, metallic, alloyed, carbon, conducting tape, silver, gold, platinum, semiconductor, conductor, indium, tin-oxide, tin, indium-tin-oxide, transparent conducting oxide, gallium, gallium arsenide, or a liquid electrode, or a combination thereof.

10 It should be understood that the redox-active layer structure **14** may include metals other than ruthenium or more than one type of metal, as well as redox-active organic molecules (e.g., quinones, thiophenes) or a mixture of such materials. The redox-active layer structure **14** may be formed by a monolayer of redox-active material (metal or organic molecules or a mixture thereof), or a
15 monolayer of metal based redox-active complexes of one metal, multiple different or identical metals. The redox-active layer structure **14** may include a plurality of identical layers (each formed by a metal based redox-active material or organic molecules or a mixture thereof); or a plurality of different layers. Each layer may be formed by a metal based redox-active material or organic molecules
20 or a mixture thereof; a layer of a metal based redox-active material or a mixture of metal based redox-active materials; or a monolayer of metal based redox-active complexes. As indicated above, the metal based redox-active complexes may include at least one metal, or multiple different or identical metals.

Also, as indicated above, the substrate **12** may be non-conductive and
25 having an electrically-conductive surface layer. The term "*electrically-conductive substrate*" will be used here as referring to both such options.

The layer structure **14** is configured to have at least one predetermined electronic property, including electrodensity and/or oxidation state, changeable by subjecting the structure **14** to an electric field (e.g., irradiating the structure **14**
30 by an electron beam or applying a potential difference between the substrate **12**

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and the electrode 15) to thereby cause a change in the electronic property (e.g., oxidation state). To this end, the device 10 is associated with an electric field source 16, which may include a voltage supply unit associated with an electrode arrangement, or may include an electron beam source/column (as shown in the figure in dashed lines). In the present example, the voltage supply unit 16 supplies voltages to the substrate 12 and to the electrode 15 on the redox-active layer structure 14. It should, however, be understood that the same effect (change of electronic property of the redox-active layer structure) can be achieved by supplying appropriate voltage only to the metal-based redox-active layer structure thus causing electron transfer via tunneling or hopping or another mechanism from the electrically conductive substrate 12 to the layer structure 14. In addition, the same effect (change of electronic property of the redox-active layer structure) can be achieved when the voltage supply unit 16 supplies voltages to the substrate 12 and to the redox-active layer structure 14.

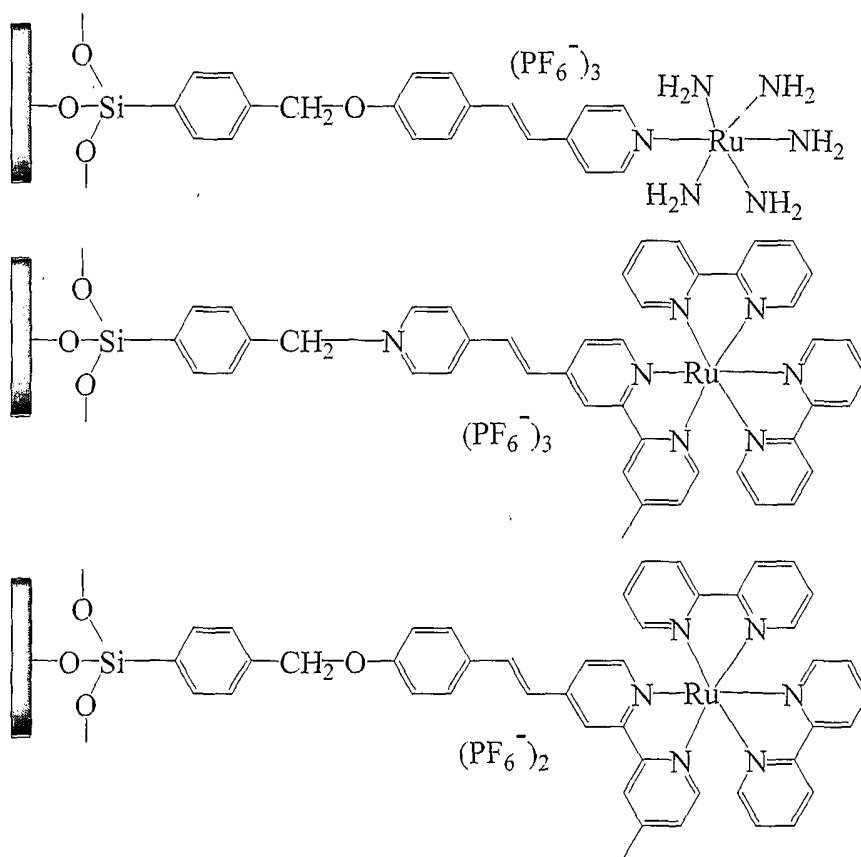
The inventors have found that the electronic property (e.g., oxidation state) of a region of the structure 14 defines certain optical properties of the structure 14 (absorption spectrum), and therefore determines the optical response of the region of the layer structure to incident light of a certain frequency range which can be read by a light detector. Effecting a change in the electronic property of the structure (or one or more selected regions thereof) results in a reversible change in the optical response of the layer structure (or selected region(s)). Hence, the device 10 has reversibly changeable and optically readable optical properties.

Various applications of such a device will be exemplified further below. To facilitate understanding, the same reference numbers will be used for identifying components that are common in all the examples.

The following is a specific but not limiting example of the formation and characterization of a redox-active monolayer on an electrically conductive surface, where the redox-active layer coordinates or forms covalent or noncovalent bonding to a functionalized substrate. The substrate, which may or

may not be a hydrophilic substrate, carries a functional group capable to attach to the redox-active layer structure (e.g., monolayer).

More specifically, the redox-active layer consists of a metal complex bound to a vinylphenol, vinylthiol or vinylpyridine moiety that is covalently attached, through the phenolic hydroxyl, or the sulfur, or the nitrogen of pyridine, to the substrate through a functional linker, e.g. siloxane-based aromatic or aliphatic molecule. Alternatively, metal complexes can also be attached directly to the substrate if the substrate surface bears chemical groups that may attach to the metal complex. The following structures exemplify some redox-active monolayer systems bound to a substrate through siloxane-based aromatic linker and suitable to be used in the present invention:



Suitable hydrophilic substrates are for example glass with electrically conductive coating, e.g. Si(100) and Indium-Tin-Oxide (ITO) coated glass. A wide range of electrically-conductive materials (any metal, metal alloy or semiconductor) can be used in the substrate, as well as a wide range of non-conductive materials (e.g., glass, metal oxide, etc.) provided they have an electrically-conductive surface layer. Generally, various materials combinations can be used, including silicon, indium-tin-oxide (ITO) coated glass, gold, platinum, GaAs (beads, wafers, slides), nanoparticles, polymers, dendrimers, mesoporous materials.

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Examples of redox-active metal complexes include but are not limited to organic complexes of transition metals such as ruthenium, palladium, osmium, iron, cobalt, platinum, and the like. Transition metal complexes have numerous advantages due to the fact that they exhibit excellent stability in multiple redox states. Ruthenium tris-bipyridine, $[\text{Ru}(\text{bpy})_3]^{2+}$, which is a model compound for this class of materials, also features ionic conductivity. It carries a net +2 charge, which is compensated by two counter ions such as Br^- , I^- , Cl^- , BF_4^- , PF_6^- or ClO_4^- or mixtures thereof. Bivalent or higher valent counter ions may be used as well.

In a more specific but not limiting example, schematically showed in **Fig. 2**, a redox-active layer structure consists of a tris-bipyridyl ruthenium complex bound to a vinyl-phenol unit that is covalently attached to a hydrophilic substrate through a siloxane-based aromatic molecule. The substrates, e.g. freshly cleaned float glass, Si(100) or Indium-Tin-Oxide (ITO) coated glass, were treated with a dry pentane solution of p-chloromethylphenyl-trichlorosilane (1:100 v/v) at room temperature for 30 min under N_2 . The substrates were then thoroughly washed with copious amounts of dry pentane and dried at 115 °C for about 15 min. Subsequently, the colorless chlorobenzyl-functionalized substrates were immersed into a 2.0 mM toluene/ CH_2Cl_2 (6:4 v/v) solution of the ruthenium complex, and heated for 48 h at 80 °C under N_2 using glass pressure tubes. The resulting films were washed and sonicated (1 min) with copious amounts of CH_2Cl_2 , acetone, and iso-propanol, and dried under a gentle stream of N_2 . The new monolayers strongly adhere to the glass and silicon substrates, are insoluble in common organic solvents, and can be removed neither by the "Scotch tape decohesion" test nor by CO_2 snowjet cleaning.

Freshly prepared samples were characterized by a combination of noncontact atomic force microscopy (NC-AFM), optical transmission (UV-vis) spectroscopy, X-ray photoelectron spectroscopy (XPS), electrochemistry and spectroelectrochemistry. The latter technique was used to vary and to read the optical properties of the system. XPS measurements of the Ru(II)-based film on ITO-coated glass reveal a Si/N ratio of ~1:2.1, indicating that about 35% of the

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CL molecules reacted. NC-AFM measurements on films grown on Si(100) substrates show an essentially smooth film surface without pinholes or cracks. The root mean square (rms) surface roughness is ~ 0.2 nm for $1 \times 1 \mu\text{m}^2$ scan areas. The film thickness as derived from angle-resolved XPS is estimated to be
5 $13 \pm 2 \text{ \AA}$.

Electrochemical measurements were performed to evaluate the redox activity of the monolayers. **Fig. 3A** shows, in a self-explanatory manner, an example of an experimental setup for measuring electronic and optical properties of a device of the present invention (monolayer on ITO), which in the present
10 example is placed in an electrolyte solution. The ITO substrate surface thus served as the working electrode; Pt wires were used as reference and counter electrodes. **Fig. 3B** shows the cyclic voltammetry (CV) of the monolayer on ITO at different voltage scan rates (v). The half-wave redox potential, $E_{1/2}$, remains constant within $v = 100$ - 1000 mVs $^{-1}$. The peak to peak separation, ΔE , is about
15 64 mV for $v = 500$ mVs $^{-1}$. **Fig. 3C** shows the linear correlation of the anodic peak current, I_{pa} , vs. $v^{1/2}$. Apparently, a reversible redox process occurs involving a one electron transfer. ΔE is expected to be ~ 60 mV for a Ru(II)/Ru(III) couple. The potential of the Ru(II)/Ru(III) couple, $E^{1/2}$, is 0.95 V with respect to the ferrocene/ferrocenium standard.

20 Continuous cyclic voltammetry (CV) measurements show, after the initial conditioning scans, a repetitive redox behavior for at least 45 cycles. The magnitude of the ruthenium-centered oxidation current decreases slightly with the first 6 successive sweeps possibly as a result of deactivation or reordering of the molecular components (**Fig. 4**).

25 Referring to **Fig. 5**, UV-vis optical absorbance measurements show the optical switching of the Ru(II)-based films on glass or on ITO-coated glass substrates: a ligand-based π - π^* transition band at $\lambda = 314$ nm. Here, graphs G_1 - G_4 correspond to, respectively, Ru^{2+} , Ru^{3+} , Ru^{2+} and baseline. The inset shows the electrochemical ON/OFF switching of the intensity change of the absorbance
30 band at $\lambda = 314$ nm, ΔA , vs. the number of $\text{Ru}^{2+}/\text{Ru}^{3+}$ cycles. The lines are drawn

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as a guide to the eye. Electrochemical oxidation was carried out with bulk-electrolysis at 1.4 V, while reduction was performed at -0.1 V (20 minute each). UV-vis spectra were recorded in situ on a Cary 100 spectrophotometer after each oxidation state change. The low energy metal-to-ligand charge-transfer (MLCT) band appears at $\lambda=462$ nm. In situ spectroelectrochemistry performed in air displayed a significant reversible change in the intensity of the absorbance band at $\lambda_{\max} = 314$ nm upon alternation of the metal oxidation state, $\text{Ru}^{2+}/\text{Ru}^{3+}$. Nine repetitions of the phenomenon shown in the inset demonstrate the possibility of optical read-out of the charge storage.

The above results show that electrochemically varying the metal oxidation state of the covalently surface bound molecular building blocks causes a reversible change in the optical properties of the ligand module. The processes of oxidation state variation (writing a pattern) and identification of the oxidation state pattern (reading) can be carried out conveniently in air and monitored with a standard UV-vis spectrophotometer. The low-voltage operation and the stability of the film allow for using the film in non-volatile memory devices.

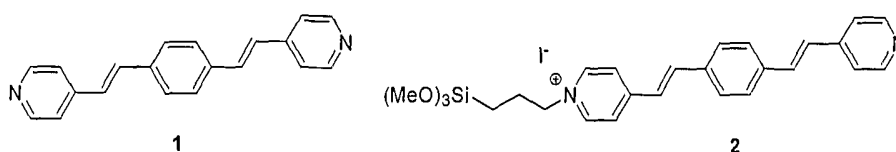
According to the present invention, the redox-active layer system may comprise more than one active layer bound to the conductive surface. A multilayer arrangement, as schematically shown in **Fig. 6**, is obtained using a layer-by-layer construction approach from the bottom (i.e. the substrate) up. In step (i) of this specific but non-limiting example, chromophore **2** binds covalently to a surface, exposing free pyridine groups to the surface. In step (ii) the resulting product is reacted with a metal complex, e.g. Pd(II) complex, such as $(\text{PhCN})_2\text{PdCl}_2$, K_2PdCl_4 etc, or ruthenium complex, such as *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{OH}_2)_2](\text{PF}_6)_2$ followed by reaction with chromophore **1** in step (iii) to yield a bi-layered product.

The films have been characterized by transmission UV-vis, contact angle measurements, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS).

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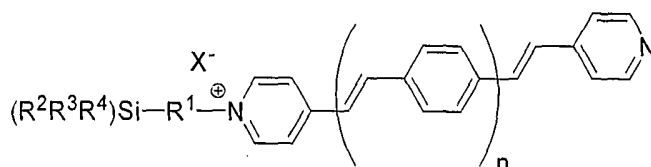
The chromophore **1** has been prepared by reaction of 1,4-diiodo-benzene with 4-vinyl-pyridine in triethylamine using palladium(II) acetate as catalyst stabilized by triphenylphosphine. Treatment of **1** with iodo-*n*-propyl-trimethoxysilane results in the quantitative formation of the new chromophore **2**.

5



Chromophore **2** was prepared as follows: an excess of 3-iodo-*n*-propyl-1-trimethoxysilane (0.741 g, 2.56 mmol) was added to a dry THF solution (20 mL) of chromophore **1** (0.060 g, 0.331 mmol) under N₂ in a pressure vessel. The reaction mixture was stirred and heated for 48 hours at 77°C. Subsequently, the volume was reduced to about 3 mL. Addition of dry pentane (10 mL) at -25°C to the reaction mixture resulted in the precipitation of the desired product. The precipitate was washed repeatedly with dry pentane and isolated by filtration and dried under high vacuum yielding chromophore **2** (yield >90%). ¹H NMR (250 MHz, CDCl₃) δ 0.53 (t, ³J = 8.0 Hz, 2H; CH₂Si), 2.0 (m, 2H; CH₂), 3.43 (s, 9H; Si(OCH₃)₃), 4.59 (t, ³J = 8.0 Hz, 2H; N-CH₂), 6.95 (d, ³J = 16.0 Hz, 2H; CH=CH), 7.09 (d, ³J = 10.0 Hz, 2H; ArH), 7.22 (m, 2H; ArH), 7.42 (d, ³J = 8.0 Hz, 2H; ArH), 7.48 (d, ³J = 8.0 Hz, 2H; Pyridine), 7.58 (d, ³J = 16.0 Hz, 2H; CH=CH) 7.90 (d, ³J = 6.5 Hz, 2H; Pyridine), 8.44 (d, ³J = 6.3 Hz, 2H; pyridine), 8.87 (d, ³J = 6.5 Hz, 2H; pyridine).

Similarly, additional new compounds have been prepared, having the following general formula:



25

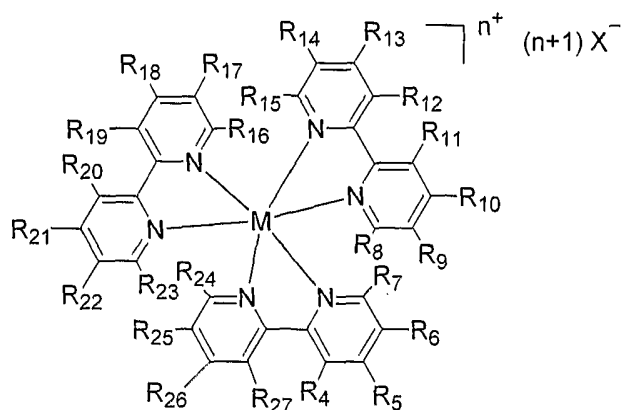
wherein $n = 0-6$, $R^1 =$ alkyl, aryl, benzyl, alkene, O-alkyl, N-alkyl, S-alkyl, peptide, aminoacid, alkyl-O-alkyl, C=N, N=C and R^2, R^3, R^4 are independently or together selected from Cl, I, F, Br, alkoxy, alkyl, aryl, fluoroaromatic,

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fluoroalkyl, hydrogen, hydroxyl, amine, triflate, aryloxy, acetate, and X is an counter ion selected from Br, Cl, F, I, PF₆, BF₄, OH, ClO₄, CH₃COO, SO₃⁻ and CF₃COO, CN, AlkylCOO, ArylCOO.

Monolayer Formation. Under N₂, freshly cleaned quartz glass, and silicon substrates were loaded into a Teflon sample holder and immersed in a dry THF solution (1.0 mM) and heated at 77 °C for 16 h in a sealed pressure vessel with the exclusion of light. The substrates functionalized with the monolayers were then rinsed repeatedly THF, sonicated twice in THF followed by acetone and ethanol for 6 min each. The substrates were dried under a stream of N₂ and stored under N₂ with the exclusion of light. The assembly process was carried out in a single reaction vessel using standard cannula techniques to transfer the solutions.

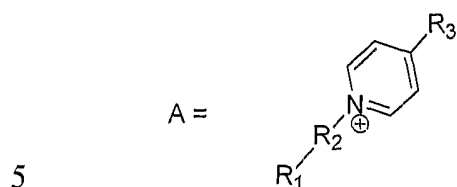
The inventors have obtained a new compound of the general formula I, for use in a redox-active layer structure:



Here, M is selected from Os, Ru, Fe, Cu, and Co; n is the formal oxidation state of the metal, n = 0 – 4; X is a counter anion selected from Br, Cl, F, I, PF₆, BF₄, OH, ClO₄, CH₃COO, SO₃⁻ and CF₃COO, CN, AlkylCOO, ArylCOO, or any combination thereof; R₄ to R₂₇ are each independently selected from hydrogen, halogen, hydroxyl, azide, nitro, cyano, amine, thiol, C₁-C₁₀ alkyl, cycloalkyl, heterocycloalkyl, haloalkyl, aryl, heteroaryl, alkoxy, alkene, alkyne, amide, carboxylic acid, protected carboxylic acid, protected amine, sulfonyl, substituted

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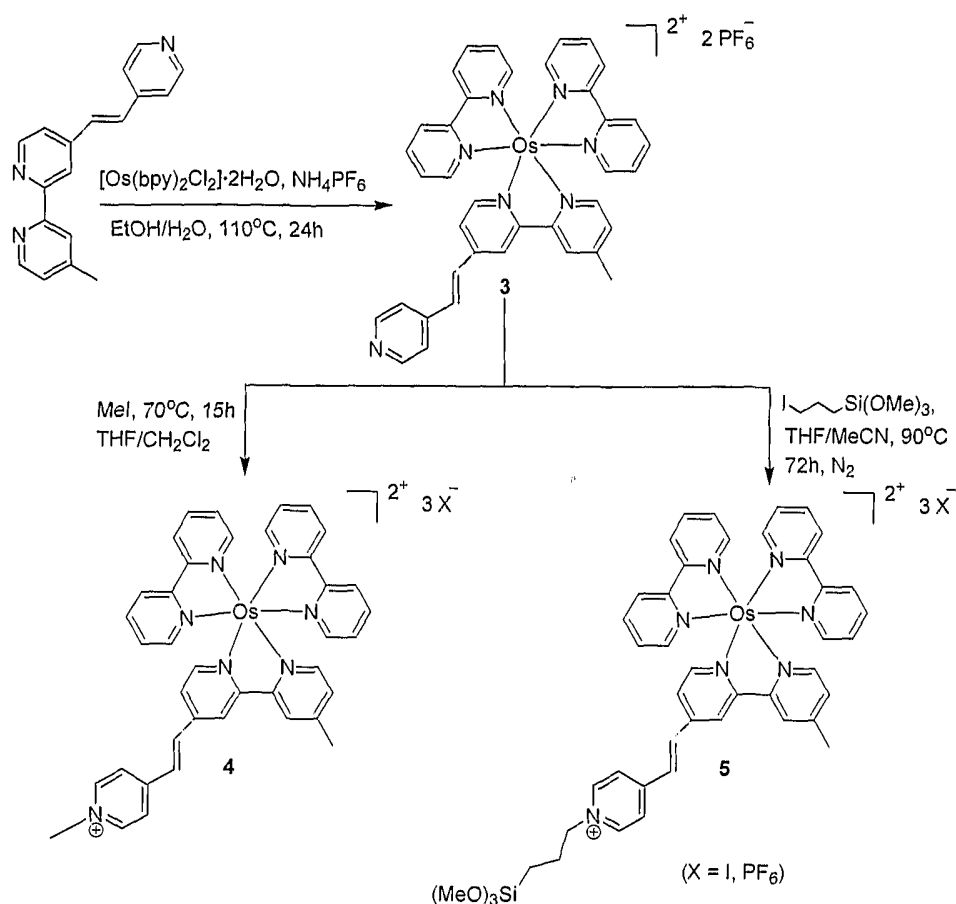
aryl, substituted cycloalkyl, and substituted heterocycloalkyl; wherein at least one of said R_4 to R_{27} being group A:



wherein A is linked to the ring structure of the compound of general formula I via R_3 ; said R_3 is selected from cis/trans C=C, C≡C, N=N, C=N, N=C, C-N, N-C, alkylene, arylene, or any combination thereof; R_2 is selected from hydrogen, 10 alkyl, alkylene, aryl, arylene, or any combination thereof, or R_2 may be absent; R_1 is selected from hydrogen, trialkoxysilane, trihalidesilane, thiol, carboxylate, COOH, COO⁻, Si(OH)₃, and phosphonate, or R_1 may be absent; any two vicinal R_4 - R_{27} substituents, together with the carbon atoms to which they are attached, may form a fused ring system selected from cycloalkyl, heterocycloalkyl, 15 heteroaryl, and aryl; said fused system may be substituted by one or more groups selected from C₁-C₁₀ alkyl, aryl, azide, cycloalkyl, halogen, heterocycloalkyl, alkoxy, hydroxyl, haloalkyl, heteroaryl ring, alkene, alkyne, nitro, cyano, hydrogen, amine, amide, carboxylic acid, protected carboxylic acid, protected amine, thiol, sulfonyl, and substituted aryl; said fused system may also contain at 20 least one heteroatom selected from N, O and S.

The compounds of the general formula are preferably chromophore complexes denoted **3**, from which their pyridinium salts, denoted chromophores **4** and **5**, were then obtained

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In the present example, the osmium-based complexes are shown. It should, however, be understood that other transition metal may be used as well.

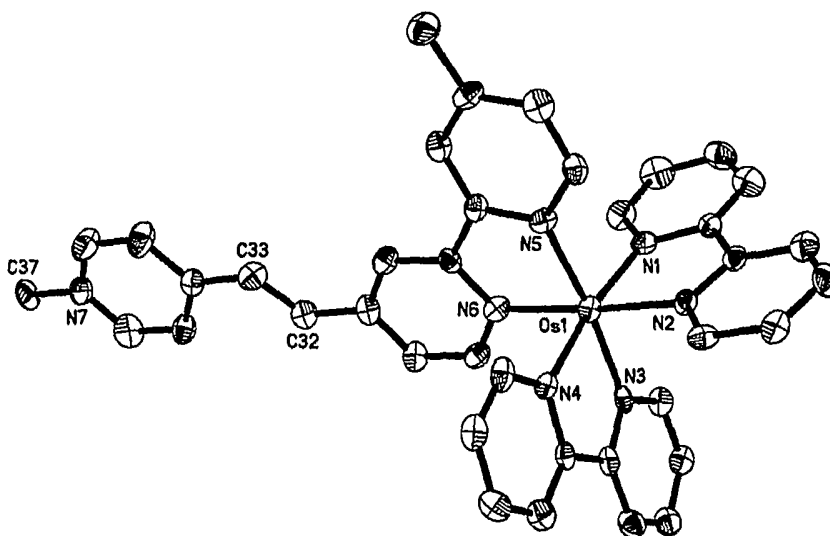
- 5 Chromophore **3** was prepared as follows: Reaction of $\text{Os}(\text{bipyridine})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (200 mg; 0.328 mmol) with 4'-methyl-4-(2-pyridin-4-yl-vinyl)-[2,2']bipyridinyl (107 mg; 0.39 mmol) under reflux in 50 mL ethanol-water (1:1, v/v) for 24 hours resulted in a dark green solution, which was concentrated to ~10 mL under vacuum. Subsequently, complex **3** was
- 10 precipitated by addition of an excess of a saturated aqueous solution of NH_4PF_6 (150 mg in 3 mL) and filtered off. The residue was washed with an excess of water (100 mL), then with diethyl-ether (50 mL), and purified by column chromatography (neutral alumina, G-III) using toluene-acetonitrile (80:20 v/v) as eluent. The second green fraction was collected and dried under vacuum to afford
- 15 complex **3**. Yield: 220 mg (63%). Anal. Found (%): C, 43.06; H, 3.08, Calc. (%) for $\text{OsC}_{38}\text{H}_{31}\text{F}_{12}\text{N}_7\text{P}_2$: C, 42.82; H, 2.93. ^1H NMR (500 MHz, CD_3CN): δ 8.65

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(3H, m), 8.49 (5H, d) 7.873 (4H, m), 7.72-7.2 (14H, m) 7.63 (1H, d; $J = 16.4\text{Hz}$), 7.5 (1H, d; $J = 16.4\text{Hz}$), 2.66 (3H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CD_3CN): 21.07 (1 CH_3), 122.2-130.04 (14CH), 134.67 (2CH), 138.24-138.31 (4CH), 143.71 (1C), 145.76 (2C), 151.47-152.0 (8CH), 160.04-160.52 (6C). ES MS: m/z : 922 (M^+-PF_6); 776 ($\text{M}^{++}-2\text{PF}_6$). UV/Vis (CH_3CN), λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 676 (6.0×10^3), 487 (20×10^3), 293 (81×10^3), 256 (30×10^3), 202 (43×10^3).

Chromophore 4 was prepared as follows: An excess of methyl iodide (35 mg, 0.25 mmol) was added to a THF/ CH_2Cl_2 (9:1 v/v) solution (20mL) of complex 3 (50 mg, 0.047mmol) in a pressure vessel. The reaction mixture was stirred and heated at 70°C for 15 hours. Subsequently, the content was dried under vacuum and in a desiccator with P_2O_5 to afford complex 4. Yield: 52 mg (92 %). Anal. Found (%): C, 40.08; H, 3.06, Calc. (%) for $\text{OsC}_{39}\text{H}_{34}\text{I}_3\text{N}_7$: C, 39.98; H, 2.92. ^1H NMR (500.13 MHz, CD_3CN): 8.78-7.17 (26H, ArH), 8.12 (1H, d, $-\text{CH}=\text{; } J=16.4\text{Hz}$), 7.45 (1H, d, $=\text{CH}-\text{; } J=16.4\text{Hz}$), 4.26 (3H, s), 2.67 (3H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CD_3CN): 21.1 (1 CH_3), 48.6 (1 CH_3), 122.63-130.43 (14CH), 136.28 (2CH), 138.0-138.29 (4CH), 143.62 (1C), 146.18 (2C), 151.02-152.82 (8CH), 159.08-160.85 (6C). ES MS m/z : 1045 (M^+-I). UV/Vis (CH_3CN), λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 694 (9.0×10^3), 510 (22×10^3), 294 (84×10^3), 246 (35×10^3), 200 (65×10^3).

Moreover, the inventors have obtained the crystalline form complex 4:



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This example presents ORTEP diagram of complex **4** (thermal ellipsoids set at 50% probability; counterions are omitted for clarity). Selected bond lengths [Å] and angles [°] are as follows: Os(1)–N(1), 2.063(6); Os(1)–N(2), 2.061(6); Os(1)–N(3), 2.048(6); Os(1)–N(4), 2.052(6); Os(1)–N(5), 2.052(6); Os(1)–N(6), 2.047(6); C(37)–N(7), 1.484(9); C(32)–C(33), 1.328(11); N(6)–Os(1)–N(3), 96.3(2); N(6)–Os(1)–N(4), 86.5(2); N(3)–Os(1)–N(4), 78.2(2); N(6)–Os(1)–N(5), 78.1(2); N(3)–Os(1)–N(5), 173.9(2); N(4)–Os(1)–N(5), 98.8(2); N(6)–Os(1)–N(2), 174.7(2); N(3)–Os(1)–N(2), 89.0(2); N(4)–Os(1)–N(2), 94.2(2); N(5)–Os(1)–N(2), 96.6(2); N(6)–Os(1)–N(1), 101.2(2); N(3)–Os(1)–N(1), 97.7(2); N(4)–Os(1)–N(1), 171.6(2); N(5)–Os(1)–N(1), 86.0(2); N(2)–Os(1)–N(1), 78.4(2).

Single crystals of complex **4** were obtained by a diffusion technique at room temperature in which an acetonitrile solution of the complex was layered with diethyl ether. It should be noted that complex **4** crystallized with three iodine anions. The unit cell parameters and the intensity data of a crystal mounted on a glass fiber using epoxy cement were obtained using a Nonius Kappa CCD diffractometer, equipped with sealed tube Mo- K_{α} ($\lambda = 0.71073$) graphite monochromator, with increasing ω (width 0.5 deg frame⁻¹) at a scan speed of 1.0 deg per 125 sec. The data were processed with Denzo-scalepack and corrected for absorption. Structure solution and refinement were done using SHELXS system of programs using direct methods. Hydrogen atoms were placed at their calculated positions and refined using a riding model. The non-hydrogen atoms were refined anisotropically. Selected crystallographic data and structure refinement parameters for complex **4** are given in the following Table:

25

Empirical formula	C ₃₉ H ₃₈ I ₃ N ₇ O ₂ Os
Formula weight/g mol ⁻¹	1207.66
Temperature/K	120(2)
λ /Å (Mo- K_{α})	0.71073
Crystal system	Triclinic

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Space group	<i>P</i> -1
<i>a</i> /Å	8.8930(18)
<i>b</i> /Å	13.165(3)
<i>c</i> /Å	19.115(4)
α /deg	104.89(3)
β /deg	98.89(3)
γ /deg	105.97(3)
<i>V</i> /Å ³	2017.3(7)
<i>Z</i>	2
ρ_{calc} /mg m ³	1.988
μ (Mo- <i>K</i> _α)/mm ⁻¹	5.499
Crystal size/mm	1.00 × 0.20 × 0.05
<i>F</i> (000)	1144
Theta range for data collection	2.32 to 21.96°
Index ranges	-9 ≤ <i>h</i> ≤ 9, -13 ≤ <i>k</i> ≤ 13, 0 ≤ <i>l</i> ≤ 20
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4923/0/487
Goodness-of-fit on <i>F</i> ²	1.057
<i>R</i> 1 ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0323
<i>R</i> 1 [all data]	0.0398
<i>wR</i> 2 ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0704
<i>wR</i> 2 [all data]	0.0734

Here, ^a*R*1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$; ^b*wR*2 = $\{\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2 (F_o^2) + (AP)^2 + BP]$ where $P = [\max (F_o^2, 0) + 2F_c^2]/3$.

Chromophore **5** was prepared as follows: An excess of 3-iodo-*n*-propyl-1-trimethoxysilane (67 mg, 0.23 mmol) was added to a dry THF/acetonitrile (9:1
5 v/v) solution (20 mL) of complex **3** (50 mg, 0.047 mmol) under N₂ in a pressure vessel. The reaction mixture was stirred and heated at 90°C for 72 hours. Subsequently, the volume was reduced to ~2mL. The addition of dry pentane (15mL) to the reaction mixture resulted in the precipitation of the desired product
10 at room temperature. The solvent was decanted and the precipitate was washed with dry pentane (3×60 mL) then dried under vacuum to afford complex **5**.

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Yield: 56 mg (88%). Anal. Found: C, 38.95; H, 3.24, Calc. for $C_{44}H_{46}F_{12}I$
 $N_7O_3OsP_2Si$: C, 38.97; H, 3.42. 1H NMR (500.13 MHz, CD_3CN): 9.0- 7.22 (26H,
ArH), 8.13 (1H, d, -CH=; $J=16.4$ Hz), 7.45 (1H, d, =CH-; $J=16.4$ Hz), 4.46 (2H,
t), 3.55(9H, s), 2.72 (3H, s), 2.04(2H, m), 0.66 (2H, t). $^{13}C\{^1H\}$ NMR (125.77
5 MHz, CD_3CN): 19.3 (1 CH_2), 20.7 (1 CH_3), 25.1 (1 CH_2), 49.6 (3 CH_3), 62.3
(1 CH_2), 121-127 (14CH), 128.8 (2CH), 134.8-137.8 (4CH), 142.6-145.2 (3C),
149.4-151.5 (8CH), 158.2-159.8 (6C). ES-MS: m/z : 1212 (M^+-PF_6). UV/Vis
(CH_3CN), λ , nm (ϵ , $M^{-1}cm^{-1}$): 690 (6.7×10^3), 505 (23×10^3), 291 (87×10^3), 247
(42×10^3), 208 (68×10^3).

10 **Monolayer Formation.** Robust siloxane-based monolayers are formed by
covalent assembly of complex **4** from solution on glass and Si(100) substrates
(similar to the Ru-based example of Fig. 2). Freshly cleaned glass and silicon
substrates were fully immersed in a dry acetonitrile/toluene (3:7 v/v) solution of
complex **5** (0.5 mM) under N_2 and heated for 52 h at $85^\circ C$ using glass pressure
15 vessels with the exclusion of light. Subsequently, the functionalized substrates
were rinsed with dichloromethane, acetonitrile in a glovebox and sonicated for 6
minutes each in acetonitrile and isopropanol. The samples were then carefully
wiped with a task wipe and dried under a stream of N_2 . The samples were
cleaned with a CO_2 snowjet and stored in the dark. UV/Vis measurements on the
20 functionalized glass substrates show that the new monolayers strongly adhere to
the substrate surface as they cannot be removed by either the "Scotch-tape
decohesion" test or by a stream of critical carbon dioxide (snow jet). The
robustness of the monolayers is also illustrated by the thermal stability. Heating
the monolayers assembled on glass substrates at $200^\circ C$ for 50 hours in air with
25 the exclusion of light showed no significant effect on the optical absorbance of
the system, indicating that the molecular integrity and monolayer function are
maintained even at these very high temperatures.

The new monolayers were characterized by a combination of aqueous
contact angle measurements, semicontact atomic force microscopy (AFM),
30 optical transmission (UV/Vis) and ellipsometry. Aqueous contact angle

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measurements reveal that θ_a changes from $<20^\circ$ for freshly cleaned silicon substrate to $65\pm 4^\circ$ for the monolayer surface. Semicontact AFM measurements on monolayers grown on Si(100) substrates show an essentially smooth film surface. The root-mean-square surface roughness, R_q is ~ 0.12 nm for 500 nm \times 500 nm scan areas. Horizontal polymerization was not observed. The UV/Vis optical absorbance measurements of the monolayer on glass show the characteristic $^1\text{MLCT}$ and the triplet state of the metal-ligand charge transfer ($^3\text{MLCT}$) bands at $\lambda_{\text{max}} = 516$ nm and 692 nm, respectively. These results are comparable to the solution UV/Vis spectra of complex **5** with red shifts of $\Delta\lambda = +11$ nm and $\Delta\lambda = +2$ nm for the $^1\text{MLCT}$ and $^3\text{MLCT}$ bands, respectively. Increasing the reaction time from 52 to 96 hours does not affect the intensity and peak position of the MLCT bands, indicating the formation of a fully formed monolayer. Shortening the monolayer deposition time to 40 hours decreases the intensity of both $^1\text{MLCT}$ and $^3\text{MLCT}$ bands. The average chromophore footprint of the covalent assembled monolayer on glass has been roughly estimated by UV/Vis measurements to be about $60\text{-}70$ \AA^2 /chromophore, which is as expected for this kind of molecular building blocks. The ellipsometry-derived monolayer thickness is about 1.7 nm. The estimated molecular length of complex **5** is about 2.1 nm, indicating an average molecular tilt angle of about 17° with respect to the surface normal. The packing density of chromophore **5** on the surface, $V = 1.0\text{-}1.2$ nm^3 , is approximately the packing density of the model complex **4** in the unit cell of the crystal structure ($V = 2.0$ nm^3 with two chromophores in one unit cell, as shown in the Table above).

The inventors have found that thermally robust siloxane-based monolayer of each of the above chromophores **3-5** is characterized by the reversibly changeable optical properties (absorbance) in the entire visible region ($400\text{-}750$ nm) as a function of the metal oxidation state (obtained either chemically or electrochemically) of the dipolar osmium-based chromophore.

Fig. 7A shows the representative absorption spectral changes observed during sensing experiment with 10 ppm water in THF and resetting with 0.1 mM

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solution of ammonium hexanitratocerate(IV) in acetonitrile of the osmium-based monolayer on glass. Here curves **a**, **b**, **c** and **d** correspond to, respectively, Os^{3+} , Os^{2+} , Os^{3+} and baseline. The inset shows follow-up measurements of the increase/decrease of absorbance vs immersion time of monolayer in 10 ppm of water in THF.

Formation of multilayer structure with K_2PdCl_2 . Functionalized quartz or Si substrates were loaded onto a Teflon holder and immersed for 30 minutes, at room temperature, in a 0.3 mMol solution of K_2PdCl_2 in DI water (Millipore, $<18\mu\text{ohm}$) which was mixed for 1 minute prior to immersion. The samples were then rinse in DI water and dried under a stream of N_2 . Subsequently, the samples were (2) immersed for 30 minutes in a 1 mMol solution of chromophore 1 THF at room temperature. The solution was stirred for at least 15 minutes before immersion. The samples were then sonicated twice in THF and once in acetone for 5 minutes each. They were then rinsed ethanol and dried under an N_2 stream. Steps (1) and (2) were repeated each time in a freshly prepared solution. **Fig. 7B** shows graphs L_1 - L_5 and L_7 - L_{12} for the transmission UV-VIS data of a multilayer arrangement with K_2PdCl_2 for different layers of the structure.

Fig. 8 shows the maximal absorbance at 387 nm vs. layers number indicating the linear growth of a multilayered structure.

Formation of a multilayer with $\text{PdCl}_2(\text{PhCN})_2$. Functionalized quartz and Si substrates were loaded onto a Teflon holder and immersed for 15 minutes, at room temperature, in a 1 mMol solution of $\text{PdCl}_2(\text{PhCN})_2$ in THF. The samples were then sonicated twice in THF and once in acetone for 3 minutes each. Subsequently, the samples were dipped in THF and immersed for 15 minutes in a 1 mMol solution of **1** in THF at room temperature. The solution was stirred for at least 15 minutes before immersion. The samples were then sonicated twice in THF and once in acetone for 5 minutes each. They were then dipped in THF and the deposition steps were repeated. Finally, samples were rinsed in ethanol and dried under a stream of N_2 . **Fig. 9** shows seven graphs of the transmission UV-

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Vis data of a multilayer arrangement with $\text{PdCl}_2(\text{PhCN})_2$ for Layers 1, 3, 5, 7, 9, 11 and 13, respectively.

As can be seen from **Figs. 7B and 9**, the colloid-based system has a UV-vis absorption maximum several times stronger than that of the PdCl_2 based multilayer.

General experimental data

Single-crystal silicon $\langle 100 \rangle$ substrates were cleaned by sonication in acetone followed by ethanol and dried under an N_2 stream. Subsequently, they were cleaned in for 20 minutes with UV and ozone in a UVOCS cleaning system (Montgomery, PA). Quartz slides were cleaned by immersion in a hot (ca. 70°C) "piranha" solution (7:3 (v/v) $\text{H}_2\text{SO}_4/30\% \text{H}_2\text{O}_2$) at room temperature for 1 h. Subsequently, the substrates were rinsed with deionized water followed by the RCA cleaning protocol: 1:5:1 (v/v) $\text{NH}_3\cdot\text{H}_2\text{O}/\text{H}_2\text{O}/30\% \text{H}_2\text{O}_2$ at room temperature, 45 min. The substrates were subsequently washed with deionized water, dried under an N_2 stream and then in an oven (130°C) for 2 hours.

The monolayer formation was carried out under an inert atmosphere using either standard Schlenk/cannula techniques. Advancing contact angles (CAs) were measured on a Rame-Hart goniometer. UV-vis spectra were recorded with a Cary 100 spectrophotometer. The ^1H NMR spectrum was recorded at 250.17 and 62.9 on a Bruker DPX 250 NMR spectrometer. All chemical shifts (δ) are reported in ppm and coupling constants (J) are in Hz. The ^1H NMR chemical shifts are relative to tetramethylsilane; the resonance of the residual protons of the solvent was used as an internal standard for ^1H . All measurements were carried out at 298 K, unless otherwise stated.

Turning back to **Fig. 1**, the device **10** of the present invention can be used in various applications. The following are some specific but non-limiting examples of designing/using the device of the present invention.

For example, the device of the present invention can be used in displays or signs (either of the kind requiring electronic change of a displayed picture or the so-called "static" displays/signs), or in lighting systems. An array (one- or two-

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dimensional array) of pixels is provided by configuring the redox-active layer structure to define a predetermined pattern of the electronic property regions.

Fig. 10 shows a device **100** having a patterned redox-active layer structure **140** on a substrate **12** having electrically-conductive surface (the electrically conductive substrate in the present example). The pattern is in the form of an array of regions having different and distinguishable electrical properties. In the present example, the pattern is formed in a continuous layer structure **14** by creating in this structure spaced-apart regions of certain electronic property (oxidation state and/or electrodensity) R_1 spaced by regions R_2 of the structure **140** having a different value of this electronic property.

The device **100** includes an electrode arrangement formed by the electrically-conductive substrate **12** (constituting a first electrode, or a first electrode arrangement in the case the electrically conductive surface is patterned to form an array of electrode elements), and a second electrode arrangement coupled to the layer structure. It should be noted, although not specifically shown that in the example of **Fig. 10** (i.e., the patterned redox-active layer structure), the second electrode arrangement may be formed by regions of the metal-based redox-active layer structure, or by an array of electrode elements associated with respective regions of the pattern, to enable activation of selected pixels by appropriately controlling the application of electric field to selected regions of the pattern.

Alternatively or additionally, the pixel arrangement can be defined by patterning the electrically-conductive substrate to form an array of electrically-conductive regions spaced by non-conductive regions (thereby defining the first electrodes array).

The device of the present invention may be used in electrogenerated chemiluminescence (ECL) systems (displays) and sensors. Variation of the metal oxidation state of the layer structure provides for controlling the electroluminescence of the device. Sensor systems might be applied in analytical

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equipment (e.g., HPLC) as detection devices. Sensing of various analytes with Ru(bpy)₃²⁺-based complexes is known [10].

Optoelectronics, photochromic and electrochromic display devices are of much current interest. Electroluminescence with the Ru(bpy)₃²⁺-based complexes might be in applied in thin films and polymer-based displays and/or organic light emitting diodes (OLEDs). The availability of multiple colors can be achieved by using mixed films with different chromophores modules and variation of the periodic table position of the metal (e.g., Os and Ru couples).

The device of the present invention can utilize an electrochemically addressed ink, based on redox-active thin film containing chromophores. According to the invention, thin film containing chromophores deposited on particles, such as spheres, can be electrochemically addressed and thus can be used as a component in electronic ink, which can be useful for displays, signs, and other applications (e.g., spatial light modulator in projectors) requiring that information including text and pictures be changed electronically. This electronic ink has the distinct advantage of being non-volatile. Once an image (pattern) is stored in the ink by the electrochemical reaction it remains visible without further electronic excitation.

Figs. 11A and 11B schematically illustrate two examples of a device **200** (that can be operable as a display/sign device) utilizing such an electronic ink. The device **200** includes an electrically conductive substrate **12** carrying a layer structure **240**. The layer structure **240** is in the form of a single layer or multiple layers (as shown in Fig. 11A in dashed curves) of ink particles, generally at **242**, each particle **242** having a core part **244A** and a thin film coating **244B** of a redox-active material. In the example of **Fig. 11A**, the layer structure **140** is a continuous (non-patterned structure), and a pattern defining an array of pixels is created by appropriate voltage supply to an array of spaced-apart regions of the structure **140** (as described above with reference to Fig. 10) As shown in **Fig. 11B**, the ink particles are deposited on spaced-apart regions of a substrate **12** so as to define an array of pixels **P**. It should be understood that the electrically

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conductive substrate **12** may be patterned to define an array of electrode elements, each carrying the ink particles of the layer structure. The electronic ink regions are addressed selectively by applying an activation current selectively to the desired pixels, namely regions on which the ink particles are deposited.

5 In order to achieve high levels of absorption, it is desirable to adjust the cross-sectional dimension (diameter) of the ink particles so that many layers of particles are deposited on the surface of the substrate. The particle layers need to maintain intimate contact in order to insure a conducting path from the electrode on which they are deposited.

10 The light absorption effect can be further improved by making the particles core **244A** strong scatterers of light. This creates multiple reflections and increases the pathlength of light within the ink layer. This can be accomplished by using suitable metals or materials with a large index of refraction such as Titanium dioxide for the particle core.

15 In the case where the particles are made from materials such as dielectrics or semiconductors, the thin film layer coating have to support the current transported between the particles. This is because image creation by the ink particles based layer structure requires electric current passage through the layer structure; if the core of the ink particle is not conductive, then the electric current
20 needs to flow on the outside of the particle.

The image created by the ink particles can be changed electronically by flowing an electric current through the layer structure. The image, once stored, does not require continued electrical power supply until replacing of the image with a new one is required. Such a device can thus be used for applications where
25 the "static" image is to be created, or image needs to be erased and replaced electronically from time to time, like advertisements, e.g., outdoor signs.

By use of different chromophores, a multicolor ink can be obtained. Activation of the different color components can be achieved by applying different voltages as required for the electrochemical reaction of each

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chromophore, or by selectively applying different inks, each one containing a different chromophore (e.g., by screen printing) to pixel locations for each color.

5 Pixels containing deposited ink can be selectively activated electrochemically by use of electrodes to make an electrochemical cell (as shown in **Fig. 11B**). The conductive ink particles (semiconductor or dielectric core with redox-active coating) sit on the active pixel electrode (surface region of the substrate **12**) adjacent to which counterelectrode is located, one electrode serving for oxidation reaction (oxidation state change) and the other for reduction.

10 It should be understood, although not specifically shown in the figures, that the electrodes can be arrayed in well known configurations such as a crossbar array to enable selective activation of each pixel cell. The electrode array (electrode arrangement associated with the electrically conductive substrate) could also be possibly screen printed on a supporting surface as is commonly done in the electronics and display industry.

15 An electrolyte that may be used in the above-described electrochemical cell could be a solid electrolyte. This can be achieved by mixing the solid electrolyte with a solvent and the ink particles to create a liquid ink mixture, which can then be applied to the surface of the substrate. The solvent would then evaporate, leaving the particles' layers in the solid electrolyte matrix. For many applications the image to be stored can be written slowly so that resistance of the electrolyte and cell can be tolerated allowing greater flexibility in the choice of the electrolyte and the electrode architecture.

20 The device of the present invention can be configured and operable as a memory device, including Read-Only-Memory (ROM), Rewritable Memory, and Write-Once-Read-Many Memory. The memory device can be operated as a binary or non-binary system or a combination thereof. The data pattern is created as a pattern of different electronic property conditions of the redox-active layer structure. The data pattern can be read optically as described above, as the regions of the structure having different electronic properties provide different optical response to certain incident light.

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Most existing memory devices utilize charge storage as the mechanism of information storage, including dynamic random access memory (DRAM), FLASH RAM, and one-transistor static RAM. According to the present invention, writing of data in the redox-active layer structure based device is carried out by affecting the electronic property of one or more region of the redox-active layer structure, and reading of data is carried out by applying incident light to successive regions of the structure and identifying variations of the optical response corresponding to different Boolean values.

Reference is made to **Figs. 12 and 13** demonstrating the principles of present invention for creating a non-binary memory device that can be electronically read. In the figures, the areas of a monolayer have a Ru metal addressed with different potentials and read-out electronically.

In this connection, the inventors have demonstrated that atomic force microscopy (AFM) allows nanometric manipulation and addressing of molecular assemblies. **Fig. 12** shows how the present invention is used for writing on the same spot with different voltages applied to the AFM tip. Reversible changing the oxidation states by the AFM voltage results in an observable change in the dipole of the system.

The Ru-based films on conducting or semiconducting substrate surface (e.g., ITO, doped silicon, Au, Pt, Ag, metal-oxides, etc.) can be addressed (patterned) in multiple reversible ways by variation of the applied voltage. **Fig. 13** shows that reversible changing of the oxidation state by the AFM voltage results in a dipole moment change, which depends on the applied voltage for a given area. This implies that the technique of the present invention can be used for developing memory elements having two (e.g., ON/OFF) or more than two states for a given area. Mixed films, having different metal centers, may be addressed at different voltages. Applications include but are not limited to, game consoles, cellular phones, phone-cards, identification devices, mobile products, chip-cards, computers, electronic labels, disk-on-key, etc.

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The present invention can also be used as an electrooptic (EO) or photonic, or optical, or nonlinear optical (NLO) device. This is based on the following: Variation of the metal oxidation state results in a change of the index of refraction, EO, second and third NLO properties of the film. This is demonstrated by the AFM induced dipole variation and spectroelectrochemistry. The latter showed a reversible change in the optical properties of the system. The films might be integrated into a wide range of EO and NLO devices, including frequency doubling devices, optical switches, modulator, and spatial light modulators. Applications include data transfer and storage, ultrafast pulse shaping, and, radars, telecommunication devices, television, optical computing.

Turning back to **Fig. 10**, it should be understood that such a device configuration can be operable as spatial light modulator (SLM), where the array of regions with different oxidation states presents an active matrix (pixel arrangement) of the SLM; or active phase mask.

It should be noted that the optical response of the device of the present invention includes reflection of incident light; or emission of light excited by the exciting incident light.

The effect of changing the refraction index of the redox-active layer structure also allows for using the present invention as an optical sensor, which may tunable optical sensor: variation of the electronic property of at least a selected region of the structure (via the variation of the external electric field) results in at least local change of the refraction index.

The device of the present invention can also be configured and operated as a spectral filter, which may similarly be tunable: The electronic property of the structure determines a spectral range of incident light to which the structure is optically responsive.

The above is illustrated in **Fig. 14A** showing a device **300A** of the present invention, including a redox-active layer structure **14** on an electrically-conductive substrate **12**, which is associated with an electric field source **16**, a light source **18** and a light detector **20**. A control unit **22** operates the electric

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field source to affect the oxidation state of the layer structure **14** to change it from the first state OS_1 , in which the structure **14** is responsive to incident light of the first frequency F_1 to provide a first light response LR_1 , to the second oxidation state OS_2 at which the structure **14** response either to the same incident light F_1 or to a second different frequency F_2 is different – second light response LR_2 . In the present example, the substrate **12** is transparent, and the light response of the structure is measured as light transmitted through the device, but it should be understood that the present invention is not limited to this specific configuration.

Fig. 14B shows another example of a sensor device **300B** of the present invention. The device **300B** is configured as a chemical sensor for sensing predetermined environmental condition(s) such as the presence of predetermined gas or liquid, e.g. a compound dissolved in a solvent. As indicated above, the substances detectable by the device of the invention may include at least one of the following: water, anions, gas, alcohols, ketones, aldehydes, carboxyles, phenols, halogenated substances, sulfides, phosphonates, nitro-containing substances, peroxides, cations, ozone, sugars, carbohydrates, SO_2 , NO^+ , NO_2 , NO_x , CO, CO_2 , fluorocarbons, heterocyclic compounds, mustard gas, sulfur mustards, TNT, insecticides, malathion, sarin, chemical warfare reagents, greenhouse gases, phosphines, vesicants, incapacitating agents, tear gases, vomiting gases, lung toxicants, adamsite, phosphonates, phosgene, diphosgene, nerve agent VX, nerve agent Tabun, nerve agent Soman, nerve agent GF, or blister agent HD, acids, bases, cyanides, hydrogen cyanide, cyanogen chloride, ethyl N,N-dimethyl-phosphoramidocyanidate, isopropyl-methylphosphonofluoridate, 1,2,2-trimethylpropyl methylphosphonofluoridate, cyclohexyl-methylphosphonofluoridate, o-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothiolate, carbonyl chloride, trichloromethyl chloroformate, bis -2-chloroethyl sulfide, 2-chlorovinyl dichloroarsine, mustard-lewisite mixture, 3-quinuclidinyl benzilate (QNB), 2-chloro-1-phenylethanone, 2-chloro-

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benzalmalononitrile, 10-chloro-5,10-dihydrophenarsazine, any other redox-active carbon-containing organic substances, or any combination thereof.

This device **300B** may be formed solely by a redox-active layer structure **14**, which may be monolayer (e.g. crystal) or multi-layer. Practically, such structure **14** is carried on a substrate **12** which may or may not be electrically
5 conductive, and/or has a supporting layer **20** at its upper surface. The substrate **12** and layer **20** may both be substantially optically transparent at least for a specific wavelength range used for reading a change in the absorption of the structure **14** considering the transmission mode operation of the sensor (as exemplified in the
10 figure), or either one of substrate **12** and layer **20** only is transparent considering the reflection mode operation of the sensor. The material of the redox-active layer structure **14** is selected such that when this structure is exposed to the environment, its oxidation state can be changed (e.g. locally changed) by reacting with one or more substances that are to be detected. The substance when reaches
15 the structure **14** causes a change in the oxidation state of the metal center, thus causing a change in the optical properties of the structure **14**. Considering the use of layer **20** on that side of the structure **14** with which it is exposed to environment, this layer **20** is also transparent for said one or more substances to be detected, e.g. layer **20** is porous. The structure **14** may for example be the
20 monolayer of the above-described compound (chromophore) **5** enabling sensing of water (in ppm and sub-ppm levels in organic solvents and in air) and NO^+ (in ppm and sub-ppm levels). Generally, the structure **14** may include mono- or multi-layer based on Fe, Ru, Os, Co.

Thus, the device of the present invention may be operable as an optical
25 sensor for sensing various analytes, liquid and/or gas.

The device of the present invention can be used as light emitter of a changeable spectral range of emitted light. Such a light emitting device can be optically pumped. The device may be configured to produce multiple colors of the emitted light. To this end, the redox-active layer structure includes a mixed

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metal-based film of different chromophore modules and variation of the periodic table position of the metal.

The device of the present invention can be operable as a non-linear medium. Such a medium is formed by varying the electronic property of at least
5 a selected region of the layers structure (**14** in **Fig. 1**), thereby effecting a change in the index of refraction of this at least selected region.

The device of the present invention can also be used in molecular electronics (or moletronics). This area seeks to use (individual) molecules to perform functions in electronic circuitry now performed by semiconductor
10 devices. Semiconductor switch device is crucial in modern electronics. The metal-based chromophores films exhibit the classical switching properties necessary for the formation of semiconductor devices. The films exhibit semiconductive properties that give them the ability to storage a charge or behave like switches or memory, meaning that these systems could replace transistors,
15 diodes, and conductors of conventional microelectronic circuitry, e.g., Single Electron Tunnelling (SET). The electronic property of a selected region of the layer structure is defined by a single-molecular metal region. The layer structure can be patterned to form an array of the single-molecular metal regions arranged in a spaced-apart relationship. A pattern of the nano-scale features can be
20 provided.

The present invention can be used as a photodiode. As indicated above. mixed films can be prepared with different metals and/or chromophores. Excitement with light of a certain wavelength may result in an anodic photocurrent. This photocurrent can be controlled (reversed) by
25 electrochemically addressing the oxidation state. Due to the possibility to vary the dipole moment of the metal complexes they could be used as modulators. The invention can be used in photovoltaics, namely in photovoltaic cells (solar cells) that produce electricity directly from light. The metal-based films on conductive (mesoporous) metal oxides may be used for the efficient generation
30 of photoelectric currents.

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The present invention can also be used to control over electrical characteristics of metal-semiconductor junctions. This is because variation of the film dipole moment may result in diodes with an effective barrier height that is tuned by the dipole moment of the films.

5 The invention can be used in batteries (e.g., polymer-based batteries), and other charge storage applications. Additionally, the device of the present invention may be used for energy conversion, including photochemical cleavage of water resulting in the formation of O_2 and H_2 or H^+ . Yet another possible application of the device of the present invention is in DNA analysis. This can be
10 implemented by bonding the metal within at least one region of the metal-based redox-active layer structure to a selected DNA, thus enabling selective DNA cleavage and analysis.

The technique of the present invention provides for magnetic susceptibility. Oxidation and reduction of the metal center results in a change of
15 the magnetic dipole (e.g., diamagnetic/paramagnetic). When a substance is placed in an external magnetic field, the substance produces its own magnetic field. If the substance is paramagnetic, this field adds to the applied field; if the substance is diamagnetic, this field subtracts from the main field. This contribution to the external magnetic field is known as the magnetic
20 susceptibility of the substance. Applications include memory devices, molecular-based magnets, etc.

Those skilled in the art will readily appreciate that various modifications and changes can be applied to the embodiments of the invention as hereinbefore described, without departing from its scope defined in and by the appended
25 claims.

CLAIMS:

1. A device having reversibly changeable and optically readable optical properties, the device comprising a substrate having an electrically conductive surface and carrying a redox-active layer structure configured to have at least one
5 predetermined electronic property including at least one of electrodensity and oxidation state, said at least one electronic property being changeable by subjecting the layer structure to an electric field, wherein the electronic property of the layer structure defines an optical property of the structure thereby determining an optical response of the structure to certain incident light, the
10 device enabling to effect a change in said electronic property that results in a detectable change in the optical response of the layer structure.
2. The device of Claim 1, wherein the redox-active layer structure is metal-based structure including one or more metals.
3. The device of Claim 2, wherein the metal based redox-active layer
15 includes a transition metal.
4. The device of Claim 3, wherein said transition metal is selected from Os, Ru, Fe, Pt, Pd, Ni, Ir, Rh, Co, Cu, Re, Tc, Mn, V, Nb, Ta, Hf, Zr, Cr, Mo, W, Ti and Zn.
5. The device of Claim 3, wherein the metal-based redox-active layer
20 structure is configured as a ruthenium-based redox-active monolayer.
6. The device of Claim 5 comprising a ruthenium(II)- or ruthenium(III)-based redox-active monolayer.
7. The device of Claim 5 wherein said ruthenium monolayer consists of a charged trisbipyridyl ruthenium unit bound to a linker unit designed to covalently
25 bind to the surface of the electrically conductive substrate of the device.
8. The device of Claim 1, wherein the redox-active layer structure comprises redox-active organic molecules.
9. The device of Claim 8, wherein said organic molecules include thiophenes or quinones or a combination thereof.

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10. The device of Claim 2, wherein said redox-active layer structure further comprises redox-active organic molecules.
11. The device of Claim 1, wherein said change in the electronic property is caused electrochemically by addition or withdrawal of one or more electrons to
5 or from said redox-active layer structure, via the electrically-conductive surface and one or more electrodes coupled to the layer structure.
12. The device of Claim 1, wherein said redox-active layer structure is configured to define a predetermined pattern of the electronic property regions.
13. The device of Claim 12, wherein said pattern is in the form of an array of
10 the regions of said structure having different and distinguishable electronic properties.
14. The device of Claim 12, wherein said pattern is in the form of an array of the space-apart regions having the certain electronic property.
15. The device of Claim 12, wherein said pattern includes a one-dimensional, two-dimensional or three-dimensional array of said regions.
16. The device of Claim 1, comprising an electrode arrangement for applying the electric field to the structure.
17. The device of Claim 16, wherein said electrode arrangement comprises at least one first electrode arrangement formed by the electrically-conductive
20 surface, and at least one second electrode associated with said redox-active layer structure.
18. The device of Claim 17, wherein the electrically-conductive surface is in the form of a pattern including an array of electrically-conductive regions spaced by non-conductive regions of the substrate, thereby defining the first electrodes
25 array defining an array of regions of the layer structure carried thereby to be selectively addressed to affect the electronic property of the regions of the layer structure.
19. The device of Claim 17, wherein the second electrodes is formed as an array of the electrodes coupled to said layer structure, thereby defining an array

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of regions of the layer structure to be selectively addressed to affect the electronic property thereof.

20. The device of Claim 1, wherein said redox-active layer structure comprises a monolayer of a metal based redox-active material or organic molecules or a mixture thereof.

21. The device of Claim 1, wherein said redox-active layer structure comprises a monolayer of a metal based redox-active material or a mixture of metal based redox-active materials.

22. The device of Claim 1, wherein said redox-active layer structure comprises a monolayer of metal based redox-active complexes having at least one metal.

23. The device of Claim 1, wherein said redox-active layer structure comprises a monolayer of metal based redox-active complexes having different metals.

24. The device of Claim 1, wherein said redox-active layer structure comprises a monolayer of metal based redox-active complexes having identical metals.

25. The device of Claim 1, wherein said redox-active layer structure comprises a plurality of layers each formed by a metal based redox-active material or organic molecules or a mixture thereof.

26. The device of Claim 1, wherein said redox-active layer structure comprises a plurality of identical layers each formed by a metal based redox-active material or redox-active organic molecules or a mixture thereof.

27. The device of Claim 1, wherein said redox-active layer structure comprises a plurality of different layers each formed by a metal based redox-active material or redox-active organic molecules or a mixture thereof.

28. The device of Claim 1, wherein said redox-active layer structure comprises a plurality of different layers each comprising a layer of a metal based redox-active material or a mixture of metal based redox-active materials.

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29. The device of Claim 1, wherein said redox-active layer structure comprises a plurality of different layers each comprising a monolayer of metal based redox-active complexes having at least one metal.
30. The device of Claim 1, wherein said redox-active layer structure
5 comprises a plurality of different layers each comprising a layer of metal based redox-active complexes having different metals.
31. The device of Claim 1, wherein said redox-active layer structure comprises a plurality of different layers each comprising a layer of metal based redox-active complexes having identical metals.
- 10 32. The device of Claim 1, wherein said redox-active layer structure comprises more than one metal.
33. The device of Claim 1, wherein the electrically-conductive surface carries a functional group capable to coordinate, or to covalently, non-covalently or by a combination thereof attach to said redox-active layer structure.
- 15 34. The device of Claim 15, wherein the substrate is a hydrophilic, hydrophobic substrate or a combination thereof.
35. The device of Claim 1, wherein the substrate is made of an electrically-conductive material.
36. The device of Claim 1, wherein the substrate is made of a non-
20 conductive material and has an electrically conductive surface coating.
37. The device of Claim 36, wherein the substrate includes a material selected from glass, metal oxide, group IV elements, quartz, mica, mixtures of metal and metal oxides, polymers, plastics, mixtures of materials including alloys, organic materials, inorganic materials; and bears electrically-conductive
25 surface made of metal, metal oxide, group IV elements, mixtures of metal and metal oxides, polymers, plastics, mixtures of materials including alloys, organic materials, inorganic materials, or semiconductor.
38. The device of Claim 1, wherein said substrate is optically transparent.
39. The device of Claim 38, wherein said substrate is transparent to at least
30 one of the following spectral ranges: UV, visual, IR and near IR spectral range.

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40. The device of Claim 1, configured to define an array of spaced-apart regions of the changeable electronic property, and comprising an electrodes arrangement for applying said electric field, the electrodes arrangement including a first electrode arrangement formed by the electrically-conductive substrate surface, and a second electrode arrangement coupled to said layer structure.
- 5
41. The device of Claim 40, wherein the electrodes arrangement is configured as an array of electrode elements defining said array of the changeable electronic property regions.
42. The device of Claim 41, wherein the substrate is patterned to define an array of spaced-apart electrically-conductive regions spaced by non-conductive regions.
- 10
43. The device of Claim 42, wherein the substrate is patterned to define an array of spaced-apart electrically-conductive regions spaced by non-conductive regions.
- 15
44. The device of Claim 41, operable as a display device.
45. The device of Claim 44, operable as an electroluminescent display device.
46. The device of Claim 44 operable as a static display.
47. The device of Claim 44, configured to provide multiple colors of the display device.
- 20
48. The device of Claim 47, wherein said redox-active layer structure comprises the mixed metal-based film of different chromophores modules and variation of the periodic table position of the metal.
49. The device of Claim 44, wherein the redox-active layer structure is formed by at least one layer including ink particles each formed by a core coated with the redox-active material.
- 25
50. The device of Claim 49, wherein the particles are configured to be highly scattering, thereby creating multiple reflections and increasing pathlength of light within said at least one ink-particles layer.

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51. The device of Claim 50, wherein the particles core are made from at least one metal.
52. The device of Claim 49, wherein the particles core are made from at least one material with a relatively high index of refraction.
- 5 53. The device of Claim 49, wherein the particles core are made from Titanium dioxide.
54. The device of Claim 49, wherein the particle core is made from at least one material including at least one of dielectric and semiconductor materials.
55. The device of Claim 49, wherein said at least one ink-particles layer
10 includes different chromophores thereby providing a multicolor ink.
56. The device of Claim 49, wherein the ink particles are different in at least one of the following: size, core composition, index of refraction and redox-active composition.
57. The device of Claim 49, configured and operable to allow activation of
15 the different color components.
58. The device of Claim 57, wherein the different color components are activatable by different voltages required for an electrochemical reaction of each chromophore.
59. The device of Claim 57, wherein the different color components are
20 provided by selectively applying the different ink particles, each one containing a different chromophore, to different locations each determining a different pixel for each color.
60. The device of Claim 49, wherein the electrode arrangement is configured to define an array of electrochemical cells.
- 25 61. The device of Claim 60, wherein an electrolyte for the electrochemical cell is a solid or liquid electrolyte or a combination thereof.
62. The device of Claim 61, wherein the solid or liquid electrolyte is mixed with a solvent and the ink particles to create a liquid ink mixture applied to the surface of the substrate, evaporation of the solvent resulting in creation of the
30 particle layers in the solid or liquid electrolyte matrix.

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63. The device of Claim 40, operable as an optically readable memory device.
64. The device of Claim 63, operable as one of the following memory devices: rewritable memory, read-only-memory and write-once-read-many
5 memory; data writing being carried out by affecting the electronic property of one or more of said regions and data reading being carried out by applying the incident light to one or more of said regions.
65. The device of Claim 64, wherein said layer structure comprises a mixed metal-based film, having different metal centers.
- 10 66. The device of Claim 65, comprising an electrode arrangement configured to address said different metal centers by the different electrical field values.
67. The device of Claim 64, operable as the readable memory device based on variations of a dipole moment of molecules of the redox-active layer structure or layers of the multilayer structure.
- 15 68. The device of Claim 64, configured as a multilayer optically readable memory device, said layer structure comprising the multiple metal based redox-active layers.
69. The device of Claim 1, wherein said optical response includes reflection of the incident light or emission of light excited by the exciting incident light.
- 20 70. The device of Claim 1 operable as an optical sensor.
71. The device of Claim 70, wherein said optical sensor is tunable by varying the electronic property of at least a selected region of the layer structure via the variation of the electric field.
72. The device of Claim 1, operable as a spectral filter, the electronic
25 property of at least a region of said layer structure determining a spectral range of the incident light to which said at least region of the structure is optically responsive.
73. The device of Claim 1, operable as an optical switch.
74. The device of Claim 1, operable as a light emitting device.

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75. The device of Claim 74, wherein said light emitting device is optically pumped by the incident light.

76. The device of Claim 74, wherein said light emitting device is tunable by varying the electronic property, and consequently a spectral range of the optical response, via the variation of the electric field.

77. The device of Claim 74, configured to produce multiple colors of the emitted light.

78. The device of Claim 77, wherein said structure comprises a mixed metal-based film of different chromophores modules and variation of the periodic table position of the metal.

79. The device of Claim 1, wherein said layer structure is configured such that variation of the electronic property of at least a region of said structure effects a change in an index of refraction of said at least region of the structure.

80. The device of Claim 79, wherein said structure is operable as a non-linear medium.

81. The device of Claim 79, operable as at least one of the following: a frequency doubling device, an optical switch, a modulator, a spatial light modulator, and a phase mask.

82. The device of Claim 1, operable as at least one of the following: a data transfer device, a data storage device, a pulse shaper, and an optical processor.

83. The device of Claim 82, wherein said structure is operable by the electric field to define a predetermined pattern of spaced-apart regions of different refraction indices.

84. The device of Claim 1, wherein the electronic property of a selected region of said layer structure is defined by a single-molecule metal region.

85. The device of Claim 84, wherein said layer structure is patterned to define an array of the single-molecule metal regions arranged in a spaced-apart relationship.

86. The device of Claim 84, operable as a molecular-electronic device.

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87. The device of Claim 86, wherein the metal-based chromophores layer structure has switching properties providing for the formation of semiconductor devices.
88. The device of Claim 87, wherein said layer structure is configured and operable for storing a charge.
89. The device of Claim 88, configured and operable as at least one of the following: a switch device, a memory device, a transistor, a diode, a conductor of a microelectronic circuitry.
90. The device of Claim 88, configured and operable as a single electron tunneling device.
91. The device of Claim 84, configured and operable as a nano-scale electro-optical device.
92. The device of Claim 1 configured and operable as a diode.
93. The device of Claim 92, configured and operable as the photodiode.
94. The device of Claim 92, wherein said layer structure comprises the metal-based film prepared with different metals and/or chromophores, irradiating the layer structure with the incident light of a certain frequency range resulting in an anodic photocurrent, controllably changeable in a reversible manner by electrochemically addressing said electronic property of the structure.
95. The device of Claim 1, configured and operable as a photovoltaic cell or solar cell.
96. The device of Claim 95, wherein said layer structure comprises at least one metal-based film on the substrate formed of one or more conductive (mesoporous) metal oxide.
97. The device of Claim 1, configured and operable as a controllable metal-semiconductor junction.
98. The device of Claim 97, wherein said layer structure is operable by the electric field to effect variation of the metal-based film dipole moment resulting in creation of diodes with an effective barrier height tunable by the dipole moment of the film.

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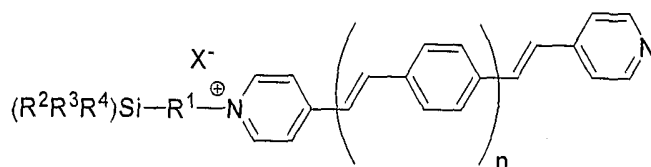
99. The device of Claim 1, wherein said layer structure is configured and operable by the electric field for storing a charge or charge pattern.
100. The device of Claim 1, configured and operable as a battery assembly.
101. The device of Claim 1, wherein said structure is configured and operable
5 by the application of the electric field for energy conversion.
102. The device of Claim 101, operable for photochemical cleavage of water resulting in formation of O₂ and H₂ or H⁺.
103. The device of Claim 1, wherein the metal within at least one region of the layer structure is selected for binding to a selected DNA, the device being
10 therefore operable for selective DNA cleavage and analysis.
104. The device of Claim 1, characterized in that, when subjected to an external magnetic field, it possesses magnetic susceptibility, caused by a change in a magnetic dipole of at least a region of the device resulting from the oxidation and reduction of a metal center in said at least one region.
- 15 105. The device of Claim 104, operable as a memory device.
106. The device of Claim 104, operable as a binary memory device.
107. The device of Claim 104, operable as a non-binary memory device.
108. The device of Claim 104, operable as a memory device capable of storing information as function of the applied field.
- 20 109. The device of Claim 104, operable as a molecular-based magnet.
110. A display device comprising a substrate carrying a redox-active layer structure, the redox-active layer structure comprising at least one layer including ink particles, each particle having a core coated with a redox-active material which is configured to have at least one predetermined electronic property
25 including at least one of electrodensity and oxidation state, said at least one electronic property being changeable by subjecting the layer structure to an electric field, said at least one electronic property of the layer structure defining a certain optical property of the structure thereby determining an optical response of the structure to certain incident light, the device thereby enabling to effect a

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change in said electronic property that results in a change in the optical response of the layer structure.

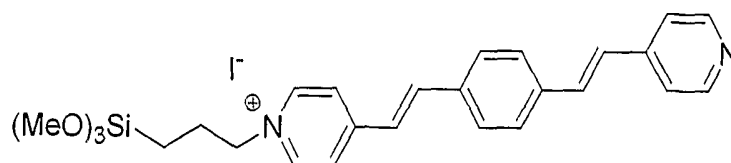
111. A method for fabricating an electro-optical device, the method comprising chemically binding a metal based redox-active layer structure to an electrically conductive surface of a substrate, said structure comprising at least one metal selected in accordance with the device intended operation, said layer structure being configured to have at least one predetermined electronic property defined by at least one of electrodensity and oxidation state changeable by subjecting the structure to an electric field, the electronic property of the structure defining a certain optical property of the structure thereby determining a certain optical response of the layer structure to certain incident light, effecting a change in the electronic property resulting in a reversible change in the optical response of the layer structure.

112. As a new compound:



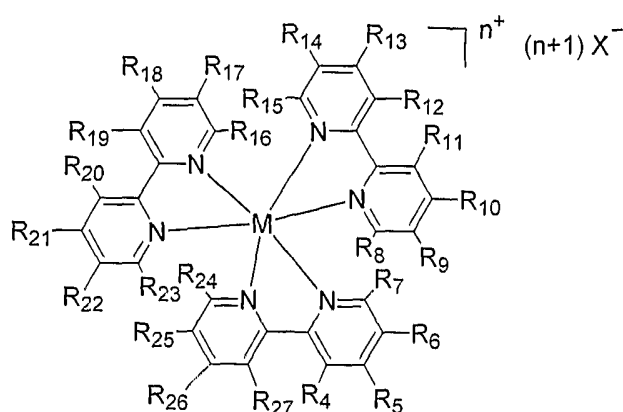
wherein $n = 0-6$, $R^1 =$ alkyl, aryl, benzyl, alkene, O-alkyl, N-alkyl, S-alkyl, peptide, aminoacid, alkyl-O-alkyl, C=N, N=C and R^2, R^3, R^4 are independently or together selected from Cl, I, F, Br, alkoxy, alkyl, aryl, fluoroaromatic, fluoroalkyl, hydrogen, hydroxyl, amine, triflate, aryloxy, acetate, and X is a counter ion selected from Br, Cl, F, I, PF_6 , BF_4 , OH, ClO_4 , CH_3COO , SO_3^- and CF_3COO , CN, AlkylCOO, ArylCOO.

113. As a new compound:



- 62 -

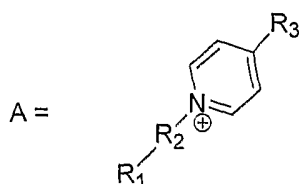
114. As a new compound of general formula I, for use in a redox-active layer structure:



wherein M is selected from Os, Ru, Fe, Cu, and Co; n is the formal oxidation state of the metal, $n = 0 - 4$; X is a counter anion selected from Br, Cl, F, I, PF_6 , BF_4 , OH, ClO_4 , CH_3COO , SO_3^- and CF_3COO , CN, AlkylCOO, ArylCOO, or any combination thereof; R_4 to R_{27} are each independently selected from hydrogen, halogen, hydroxyl, azide, nitro, cyano, amine, thiol, C_1-C_{10} alkyl, cycloalkyl, heterocycloalkyl, haloalkyl, aryl, heteroaryl, alkoxy, alkene, alkyne, amide, carboxylic acid, protected carboxylic acid, protected amine, sulfonyl, substituted aryl, substituted cycloalkyl, and substituted heterocycloalkyl; wherein at least one of said R_4 to R_{27} being group A:

10

15

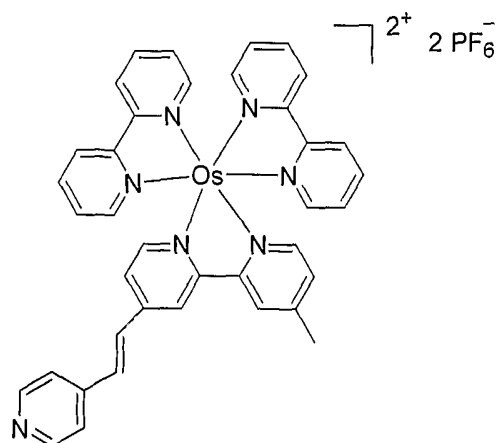


20 wherein A is linked to the ring structure of the compound of general formula I via R_3 ; said R_3 is selected from cis/trans $C=C$, $C\equiv C$, $N=N$, $C=N$, $N=C$, $C-N$, $N-C$, alkylene, arylene, or any combination thereof; R_2 is selected from hydrogen,

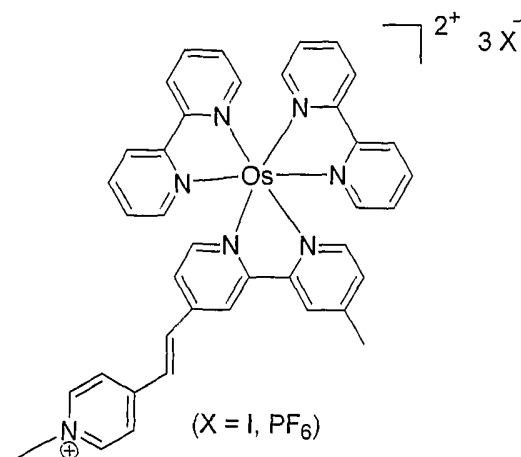
- 63 -

alkyl, alkylene, aryl, arylene, or any combination thereof, or R_2 may be absent; R_1 is selected from hydrogen, trialkoxysilane, trihalidesilane, thiol, carboxylate, COOH, COO^- , $\text{Si}(\text{OH})_3$, and phosphonate, or R_1 may be absent; any two vicinal R_4 - R_{27} substituents, together with the carbon atoms to which they are attached, may form a fused ring system selected from cycloalkyl, heterocycloalkyl, heteroaryl, and aryl; said fused system may be substituted by one or more groups selected from C_1 - C_{10} alkyl, aryl, azide, cycloalkyl, halogen, heterocycloalkyl, alkoxy, hydroxyl, haloalkyl, heteroaryl ring, alkene, alkyne, nitro, cyano, hydrogen, amine, amide, carboxylic acid, protected carboxylic acid, protected amine, thiol, sulfonyl, and substituted aryl; said fused system may also contain at least one heteroatom selected from N, O and S;

115. As a new redox-active compound:

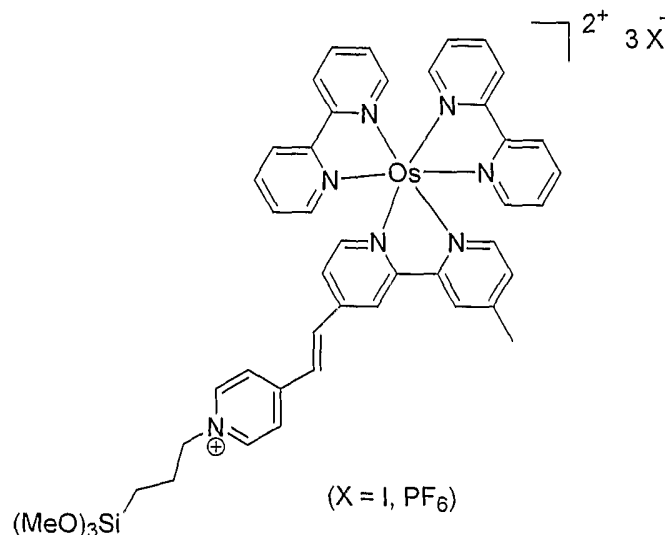


116. As a new redox-active compound:



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117. As a new redox-active compound:



5 **118.** A sensor device configured an operable for sensing at least one predetermined liquid or gas substance, the device comprising a redox-active layer structure selected to be capable of changing its oxidation state in response to a reaction with said at least one substance thereby causing a change in optical properties of said structure, said change being reversible and being optically
10 readable.

119. The device of Claim 118, wherein said at least one predetermined substance includes at least one of the following: water, anions, gas, alcohols, ketones, aldehydes, carboxyles, phenols, halogenated substances, sulfides, phosphonates, nitro-containing substances, peroxides, cations, ozone, sugars,
15 carbohydrates, SO₂, NO⁺, NO₂, NO_x, CO, CO₂, fluorocarbons, heterocyclic compounds, mustard gas, sulfur mustards, TNT, insecticides, malathion, sarin, chemical warfare reagents, gasses, phosphines, vesicants, incapacitating agents, tear gases, vomiting gases, lung toxicants, adamsite, phosponates, phosgene, diphosgene, nerve agent VX, nerve agent Tabun, nerve agent Soman, nerve agent
20 GF, or blister agent HD, acids, bases, cyanides, hydrogen cyanide, cyanogen chloride, ethyl N,N-dimethyl-phosphoramidocyanidate, isopropyl-methylphosphonofluoridate, 1,2,2-trimethylpropyl methylphosphonofluoridate,

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cyclohexyl-methylphosphono-fluoridate, o-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothiolate, carbonyl chloride, trichloromethyl chloroformate, bis - 2-chloroethyl sulfide, 2-chlorovinyl dichloroarsine, mustard-lewisite mixture, 3-quinuclidinyl benzilate (QNB), 2-chloro-1-phenylethanone, 2-
5 chlorobenzalmalononitrile, 10-chloro-5,10-dihydrophenarsazine, DNA, RNA, peptides, amino acids, proteins, steroids, anabolic-androgenic steroids, anabolic steroids, hormones, narcotics, heroin, amphetamine, methamphetamine, ecstasy, LSD, codeine, concentrate of poppy straw, methadone, morphine, medicinal opium, opium, acetic anhydride, acetyl chloride, ethylidin diacetate,
10 chlorpseudoephedrine, ergometrine, ergotamine, isosafrole, lysergic acid, piperonal, safrole, azide explosives, HMTD, hexamethylenetriperoxidediamine, nitrate explosive mixtures, picrate explosives, TATP, triacetone triperoxide, DIPAM, dipicramide, diamino hexanitro biphenyl, EDNA, ethylenedinitramine, PBX, RDX, plastic bonded explosives, water-bearing explosives having salts of
15 oxidizing acids and nitrogen bases, sulfates, or sulfamates, trinitrotoluene, trotyl, trilitite, triton, acetylides of heavy metals, aluminum containing polymeric propellant, a luminum ophorite explosive, amatex, amatol, ammonal, ammonium perchlorate composite propellant, ammonium perchlorate explosive mixtures, ammonium picrate, picrate of ammonia, ammonium salt lattice with
20 isomorphously substituted inorganic salts, ANFO, ammonium nitrate-fuel oil, aromatic nitro-compound explosive mixtures, azide explosives, baranol, baratol, BEAF, 1, 2-bis (2, 2-difluoro-2-nitroacetoxyethane), black powder, black powder based explosive mixtures, blasting agents, nitro-carbo-nitrates, including non-cap sensitive slurry and water gel explosives, blasting caps, blasting gelatin, blasting
25 powder, BTNEC, bis (trinitroethyl) carbonate, BTNEN, bis (trinitroethyl) nitramine, BTTN, 1,2,4 butanetriol trinitrate, bulk salutes, butyl tetryl, calcium nitrate explosive mixture, cellulose hexanitrate explosive mixture, chlorate explosive mixtures, copper acetylide, cyanuric triazide, cyclonite, RDX, cyclotetramethylenetetranitramine, HMX, cyclotol,
30 cyclotrimethylenetrinitramine, DATB, diaminotrinitrobenzene, DDNP,

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diazodinitrophenol, DEGDN, diethyleneglycol dinitrate, dimethylol dimethyl methane, dinitrate composition, dinitroethyleneurea, dinitroglycerine, glycerol dinitrate, dinitrophenol, dinitrophenolates, dinitrophenyl hydrazine, dinitroresorcinol, dinitrotoluene-sodium nitrate explosive mixtures, DIPAM, 5 dipicramide; diaminohexanitrobiphenyl, dipicryl sulfone, dipicrylamine, display fireworks, DNPA, 2,2-dinitropropyl acrylate, DNPD, dinitropentano nitrile, dynamite, EDDN, ethylene diamine dinitrate, EDNA, ethylenedinitramine, ednatol.EDNP, ethyl 4,4-dinitro-pentanoate, EGDN, ethylene glycol dinitrate, erythritol tetranitrate explosives, esters of nitro-substituted alcohols, ethyl-tetryl, 10 explosive conitrates, explosive gelatins, explosive liquids, explosive mixtures containing oxygen-releasing inorganic salts and hydrocarbons, explosive mixtures containing oxygen-releasing inorganic salts and nitro bodies, explosive mixtures containing oxygen-releasing inorganic salts and water insoluble fuels, explosive mixtures containing oxygen-releasing inorganic salts and water soluble 15 fuels, explosive mixtures containing sensitized nitromethane, explosive mixtures containing tetranitromethane (nitroform), explosive nitro compounds of aromatic hydrocarbons, explosive organic nitrate mixtures, explosive powders, flash powder, fulminate of mercury, fulminate of silver, fulminating gold, fulminating mercury, fulminating platinum, fulminating silver, gelatinized nitro-cellulose, 20 gem-dinitro aliphatic explosive mixtures, guanyl nitrosamino guanyl tetrazene, guanyl nitrosamino guanylidene hydrazine, guncotton, heavy metal azides, hexanite, hexanitrodiphenylamine, hexanitrostilbene, hexogen, hexogene, octogene, nitrated N-methylaniline, hexolites, HMTD, hexamethylenetriperoxidediamine, HMX, cyclo-1,3,5,7-tetramethylene 2,4,6,8- 25 tetranitramine, Octogen, hydrazinium nitrate/hydrazine/aluminum explosive system, hydrazoic acid, KDNEF, potassium dinitrobenzo-furoxane, lead azide, lead mannite, lead mononitroresorcinate, lead picrate, lead salts, explosive, lead styphnate, styphnate of lead, lead trinitroresorcinate, liquid nitrated polyol, trimethylolethane, liquid oxygen explosives, magnesium ophorite explosives, 30 mannitol hexanitate, MDNP, methyl 4,4-dinitropentanoate, MEAN,

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monoethanolamine nitrate, mercuric fulminate, mercury oxalate, mercury tartrate, metriol trinitrate, minol-2, MMAN, monomethylamine nitrate, methylamine nitrate, mononitrotoluene-nitroglycerin mixture, monopropellants, NIBTN, nitroisobutametriol trinitrate, nitrate explosive mixtures, nitrate
5 sensitized with gelled nitroparaffin, nitrated carbohydrate explosive, nitrated glucoside explosiv, nitrated polyhydric alcohol explosives, nitric acid and a nitro aromatic compound explosive, nitric acid and carboxylic fuel explosive, nitric acid explosive mixtures, nitro aromatic explosive mixtures, nitro compounds of furane explosive mixtures, nitrocellulose explosive, nitroderivative of urea
10 explosive mixture, nitrogelatin explosive, nitrogen trichloride, nitrogen tri-iodide, nitroglycerine, NG, RNG, nitro, glyceryl trinitrate, trinitroglycerine, nitroglycide, nitroglycol, ethylene glycol dinitrate, EGDN, nitroguanidine explosives, nitronium perchlorate propellant mixtures, nitroparaffins explosive Grade and ammonium nitrate mixtures, nitrostarch, nitro-substituted carboxylic acids,
15 nitrourea, octogen, HMX, octol, organic amine nitrates, organic nitramines, PBX, plastic bonded explosives, pellet powder, penthrinite composition, pentolite, perchlorate explosive mixtures, peroxide based explosive mixtures, PETN, nitropentaerythrite, pentaerythrite, tetranitrate, pentaerythritol, tetranitrate, picramic acid and its salts, picramide, picrate explosives, picrate of potassium
20 explosive mixtures, picratol, picric acid, picryl chloride, picryl fluoride, PLX, nitromethane, ethylenediamine, polynitro aliphatic compounds, polyolpolynitrate-nitrocellulose explosive gels, potassium chlorate and lead sulfocyanate explosive, potassium nitrate explosive mixtures, potassium nitroaminotetrazole, pyrotechnic compositions, PYX, 2,6-bis(picrylamino)]-3,5-
25 dinitropyridine, RDX, cyclonite, hexogen, T4, cyclo-1,3,5,-trimethylene-2,4,6,-trinitramine; hexahydro-1,3,5-trinitro-S-triazine, salts of organic amino sulfonic acid explosive mixture, salutes (bulk), silver acetylde, silver azide, silver fulminate, silver oxalate explosive mixtures, silver styphnate, silver tartrate explosive mixtures, silver tetrazene, slurried explosive mixtures of water,
30 inorganic oxidizing salt, gelling agent, fuel, sensitizer, smokeless powder,

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sodatol, sodium amatol, sodium azide explosive mixture, sodium dinitro-ortho-cresolate, sodium nitrate explosive mixtures, sodium nitrate-potassium nitrate explosive mixture, sodium picramate, special fireworks, squibs, styphnic acid explosives, tacot, tetranitro-2,3,5,6-dibenzo- 1,3a,4,6a tetraza-pentalene, TATB, 5 triaminotrinitrobenzene, TATP, triacetonetriperoxide, TEGDN, triethylene glycol dinitrate, tetranitrocarbazole, tetrazene tetracene, tetrazine, 1(5-tetrazolyl)-4-guanyl tetrazene hydrate, tetryl [2,4,6 tetranitro-N-methylaniline], tetrytol, thickened inorganic oxidizer salt slurried explosive mixture, TMETN, trimethylolethane trinitrate, TNEF, trinitroethyl formal, TNEOC, trinitroethyl- 10 orthocarbonate, TNEOF trinitroethylorthoformate, torpex, tridite, trimethylol ethyl methane trinitrate composition, trimethylolthane trinitrate-nitrocellulose, trimonite, trinitroanisole, trinitrobenzene, trinitrobenzoic acid, trinitrocresol, trinitro-meta-cresol, trinitronaphthalene, trinitrophenetol, trinitrophenol, trinitroresorcinol, trinitroresorcinol, tritonal, urea nitrate, water-bearing explosives having salts of 15 oxidizing acids and nitrogen bases, sulfates, or sulfamates, water-in-oil emulsion explosive compositions, xanthamomas hydrophilic colloid explosive mixture, any other carbon-containing organic substances.

120. The sensor device of claim 118, wherein said structure comprises the compound of Claim 114.

20 **121.** A method for writing/reading non-binary data in a memory device, which comprises a substrate having an electrically-conductive surface and carrying a redox-active layer structure configured to have at least one predetermined electronic property, including at least one of electrodensity and oxidation state, changeable by subjecting the layer structure to an electric field, 25 the method comprising scanning the redox-active layer structure by a tip of an atomic force microscope operable to apply to respective locations of the structure voltages corresponding to various conditions of said at least one electronic property thereby creating/detecting a non-binary data pattern in the layer structure.

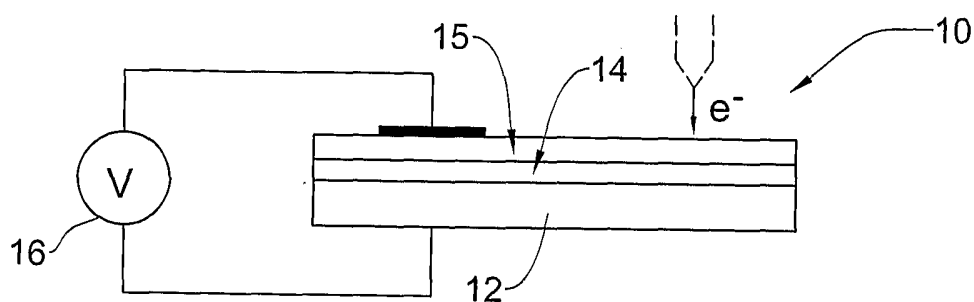


FIG. 1

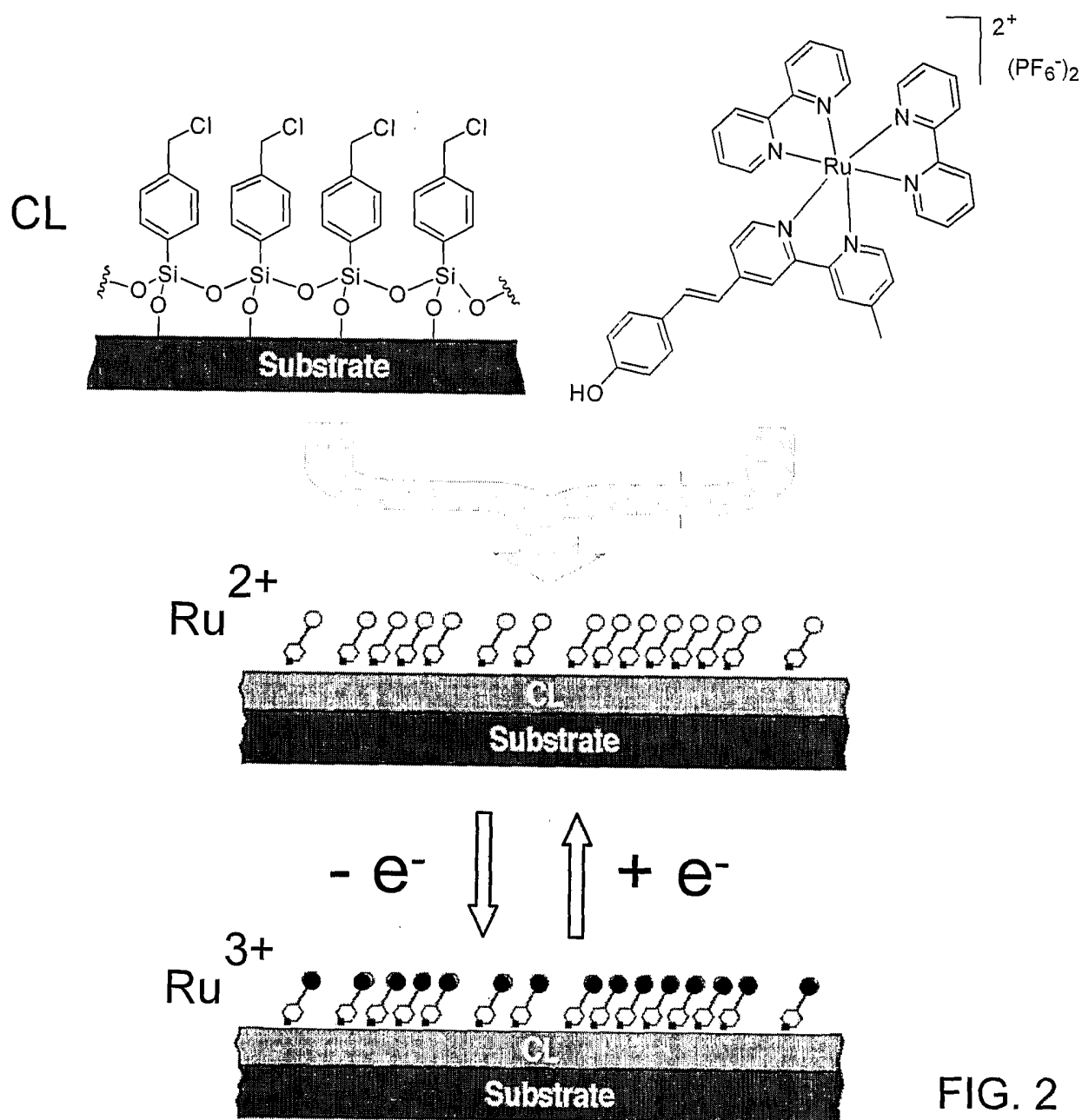


FIG. 2

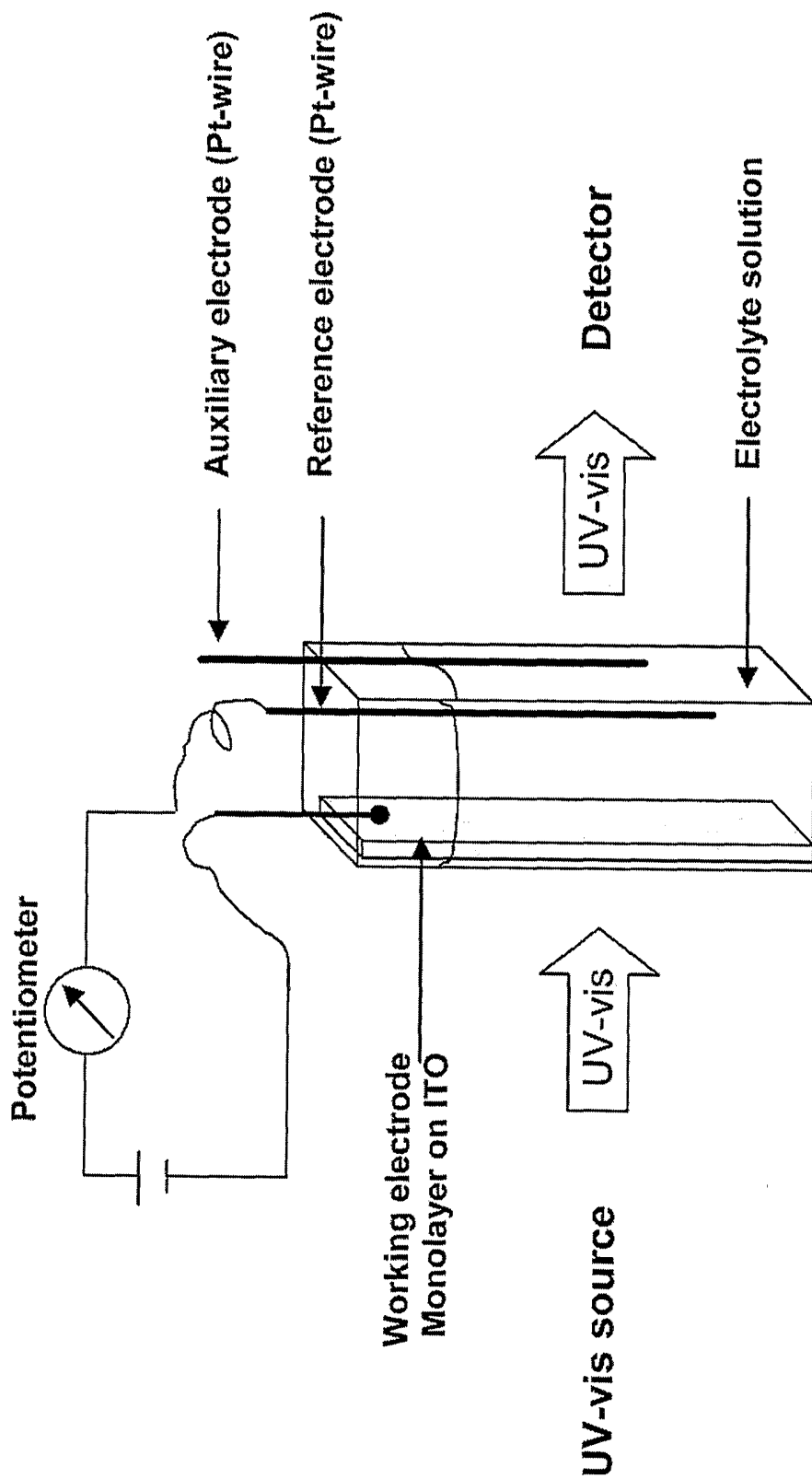


FIG. 3A

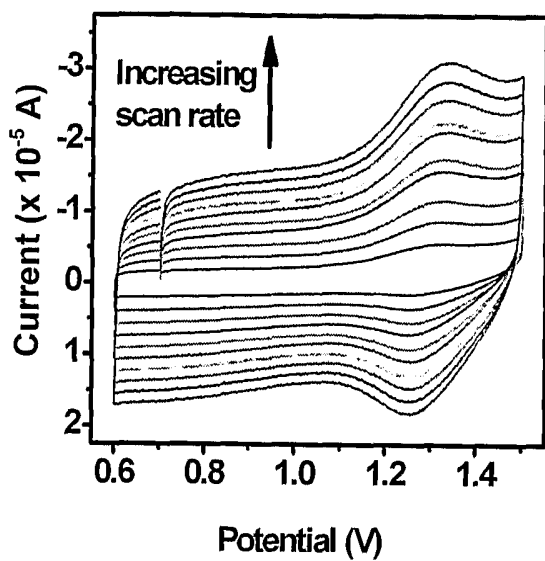


FIG. 3B

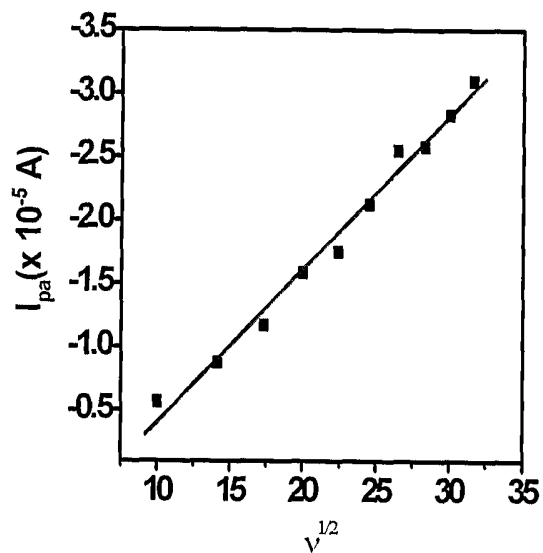


FIG. 3C

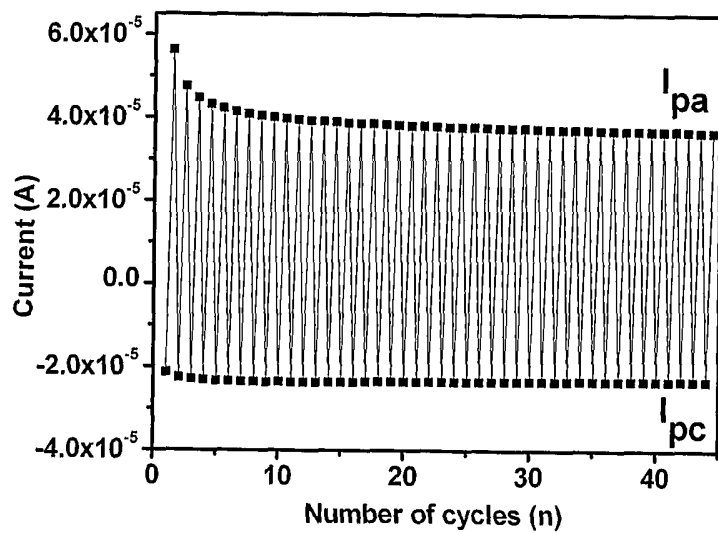


FIG. 4

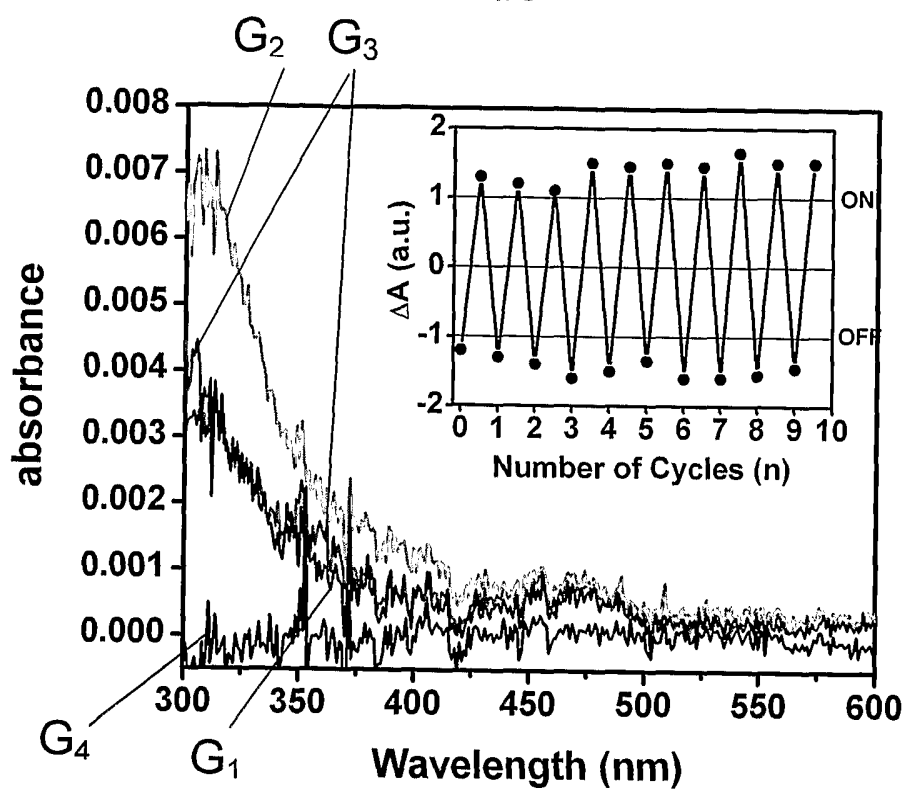


FIG. 5

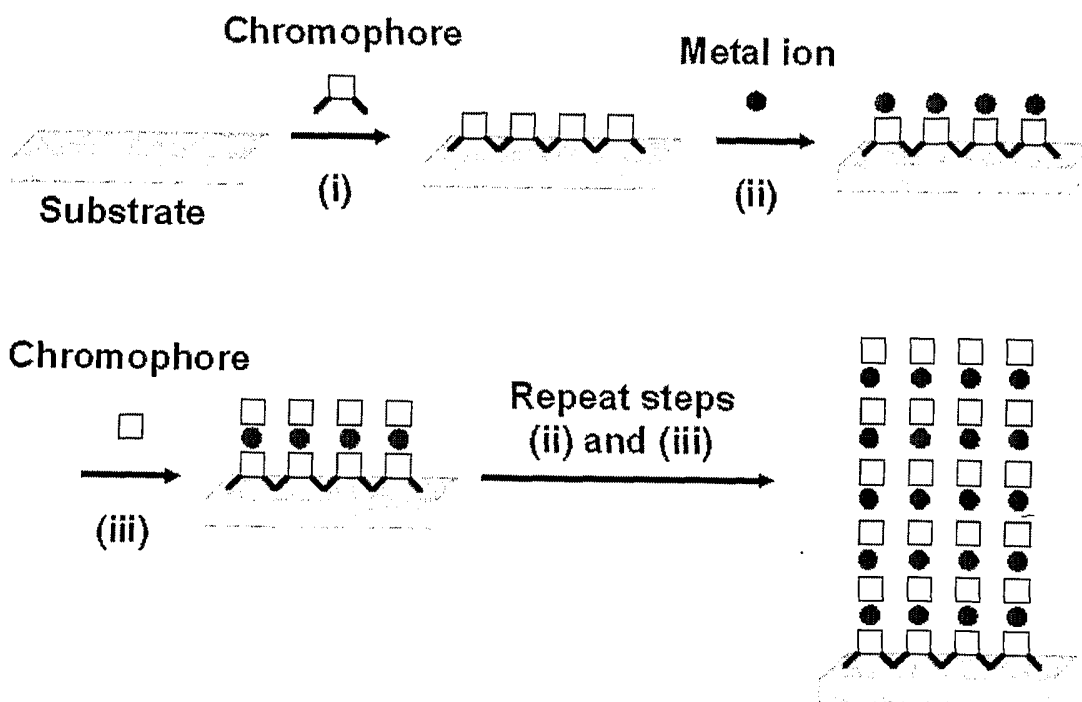


FIG. 6

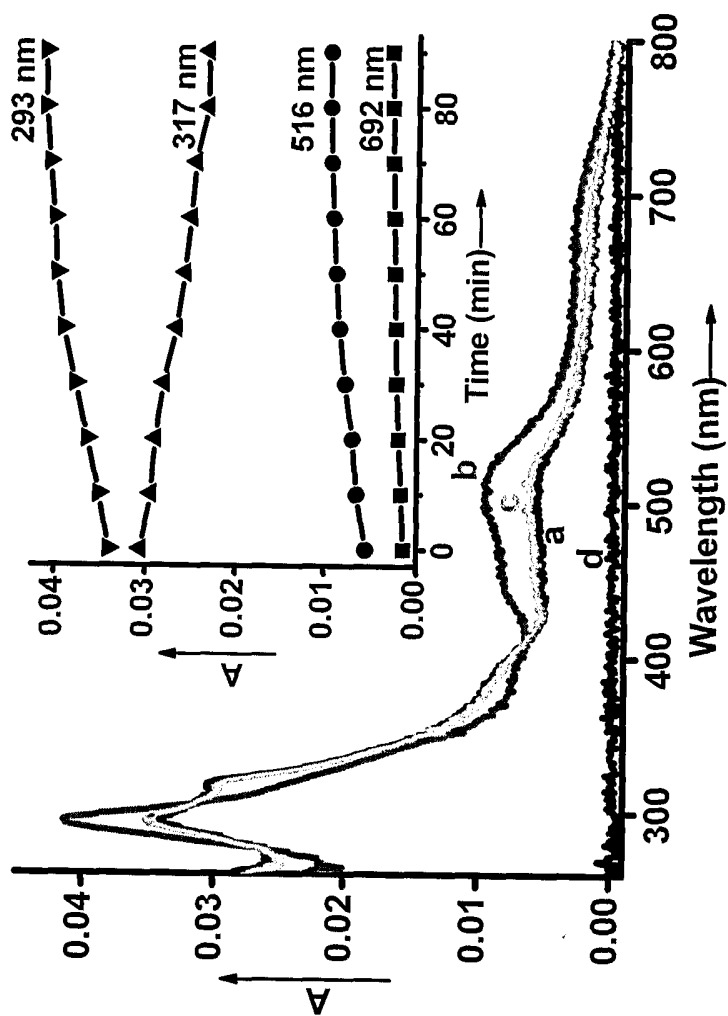


FIG.7A

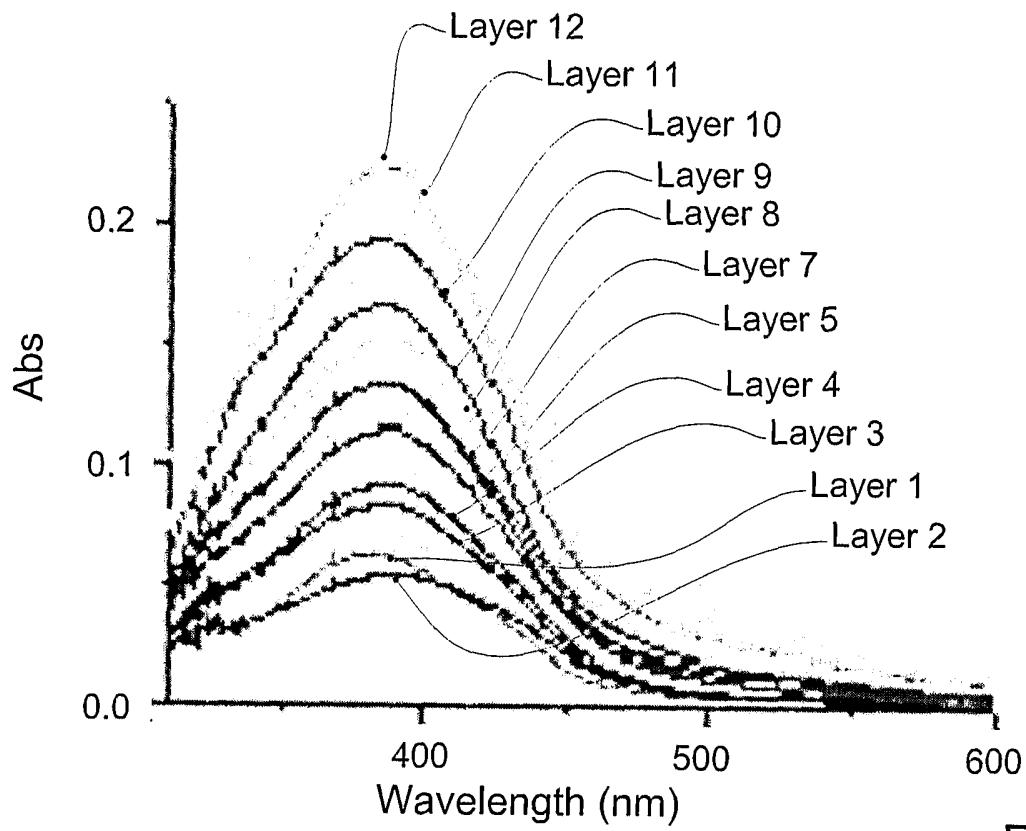


FIG. 7B

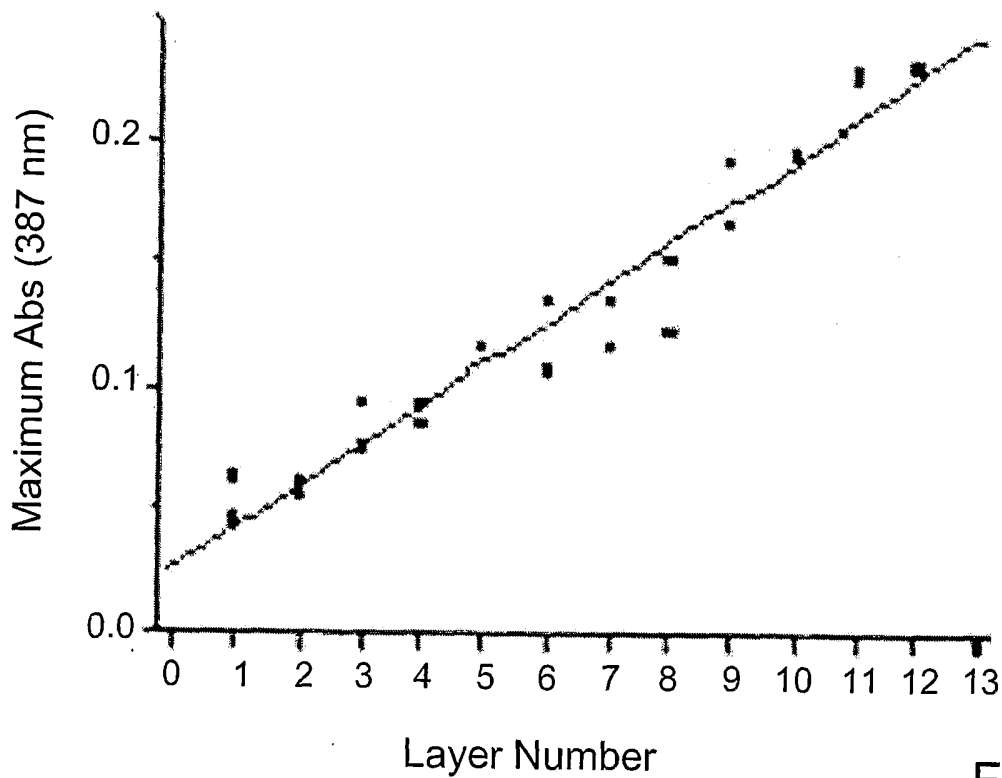


FIG. 8

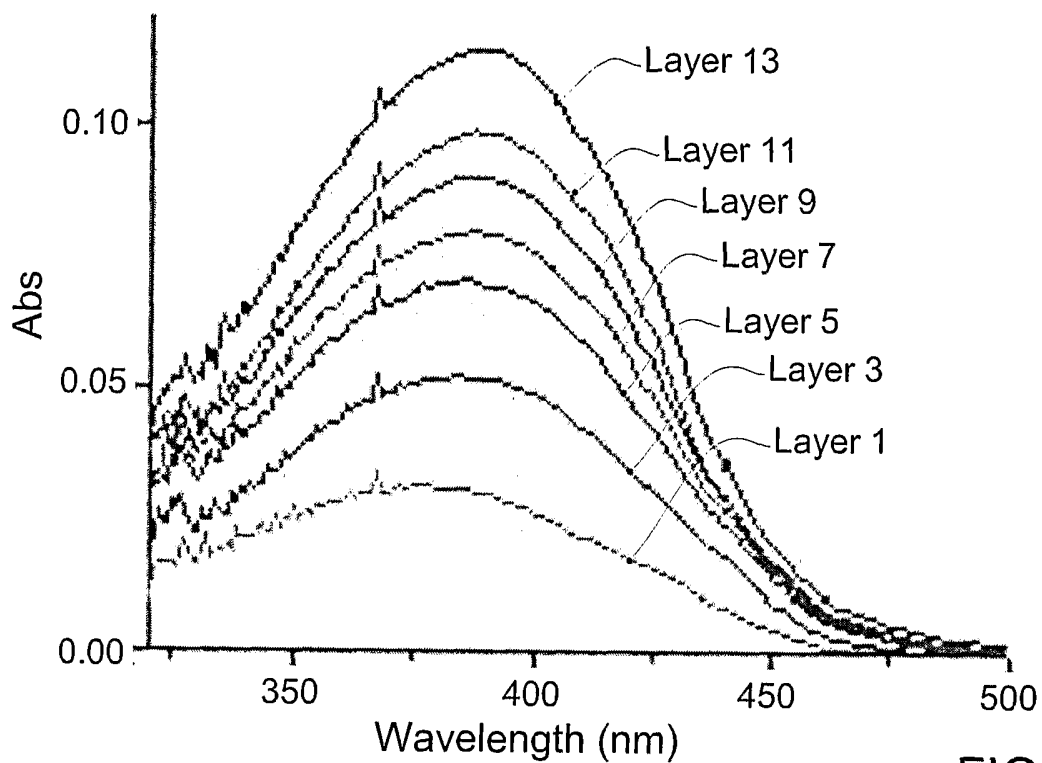


FIG. 9

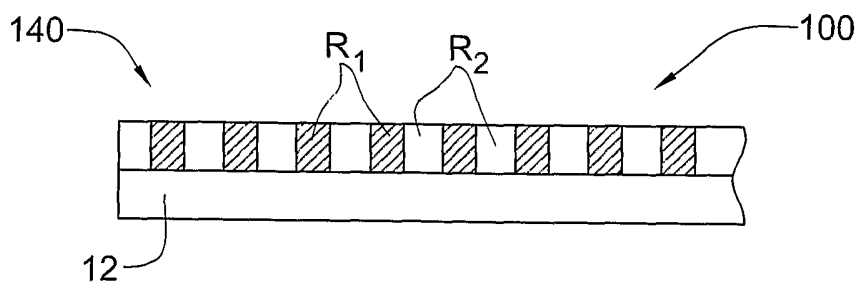


FIG. 10

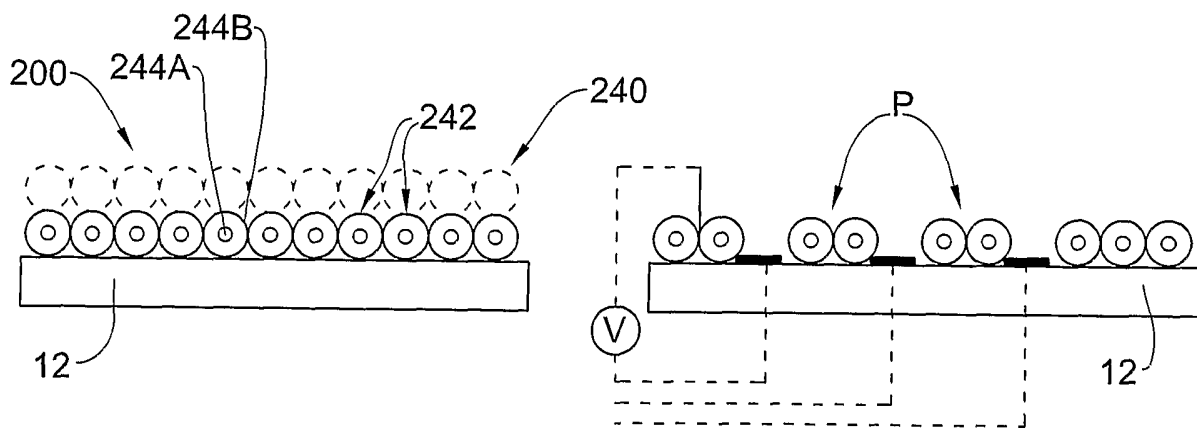
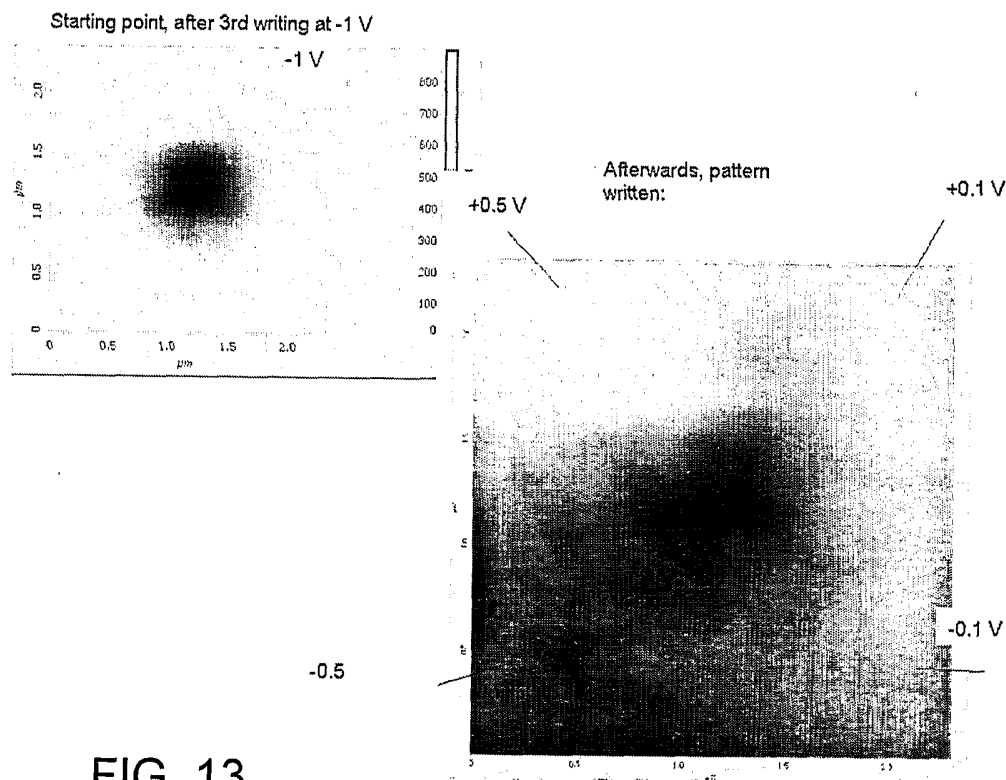
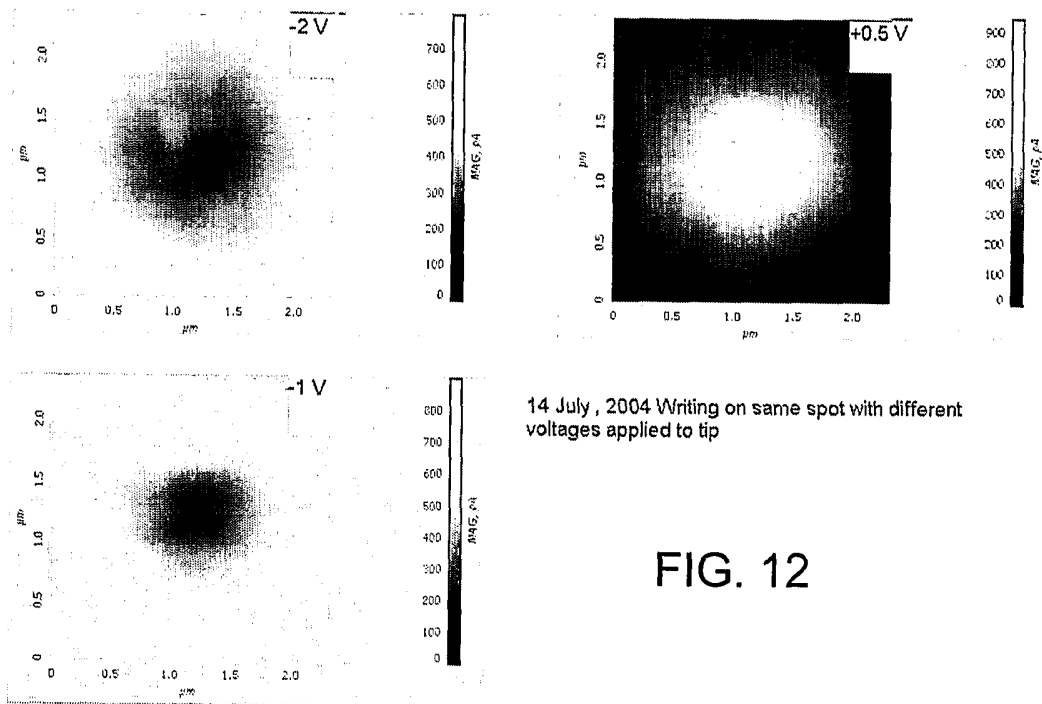


FIG. 11A

FIG. 11B



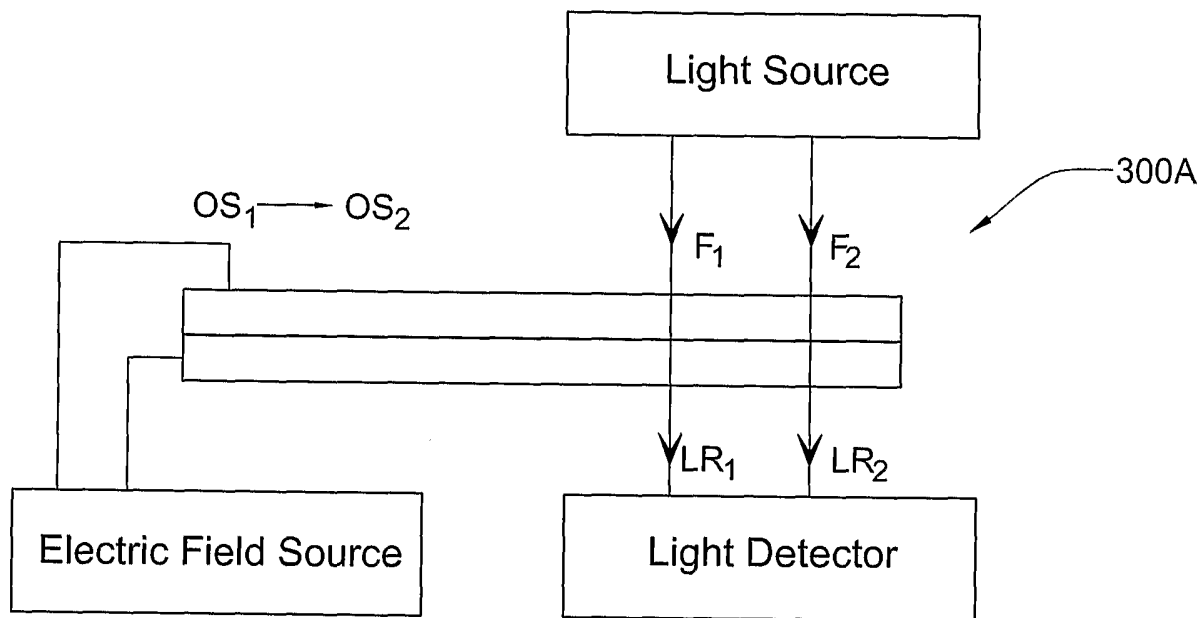


FIG. 14A

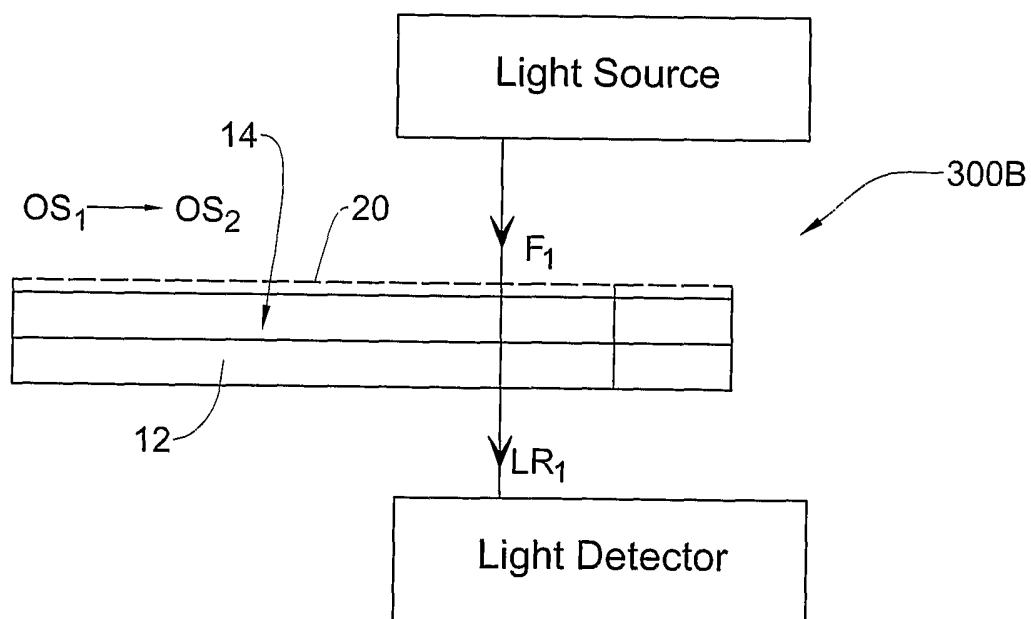


FIG. 14B