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(54) **Title:** PHOTO-RESPONSIVE COORDINATION COMPOUNDS WITH PHOTO-CONTROLLABLE ELECTRON-TRANSPORTING AND ELECTRICAL CONDUCTING PROPERTIES, AND FABRICATION OF ORGANIC ELECTRONICS AND ORGANIC RESISTIVE MEMORY DEVICES WITH PHOTO-SWITCHABLE PERFORMANCE

(57) **Abstract:** Disclosed is a new class of photo-responsive coordination compounds with at least one photochromic unit on a coordinating ligand. The photo-responsive coordination compounds are shown to be capable of acting as electroactive materials for the fabrication of organic memory devices as well as photo-controllable electron-transporting materials.

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PHOTO-RESPONSIVE COORDINATION COMPOUNDS WITH PHOTO-CONTROLLABLE ELECTRON-TRANSPORTING AND ELECTRICAL CONDUCTING PROPERTIES, AND FABRICATION OF ORGANIC ELECTRONICS AND ORGANIC RESISTIVE MEMORY DEVICES WITH PHOTO-SWITCHABLE PERFORMANCE

TECHNICAL FIELD

Disclosed are photo-responsive coordination compounds with photo-controllable electron-transporting and electrical conducting properties that can be modulated by photo-irradiation. The photo-responsive coordination compounds can serve as a photoswitchable electron-transporting layer in organic electronics and as a photoswitchable electroactive layer in organic resistive memory devices.

BACKGROUND

Organic electronics have been of particular interest in the past several decades because of their distinct and unique properties over the conventional inorganic counterparts in view of the great flexibility, simple manufacturing process, portable size and light-weight as well as the adaptive functionalities. Specifically, attempts have been made to incorporate the photo-responsive unit to the organic electronic devices so as to modulate the device performance by light. Particularly, a photo-responsive material will show intriguing changes in its optical, magnetic, mechanical, or electrical properties as a function of light irradiation. This represents an exciting area of study in material science, where researchers are venturing into a new world of materials with properties as yet unknown but that offer the promise of beneficial applications in health, industry, agriculture, and other fields. Considerable research has been dedicated to polymers with photo-responsive units embedded due to their versatility and relative ease of synthesis in combination with the spatial and temporal control provided by using light as trigger source.

Very recently, the incorporation of photochromic molecules into the organic framework has been documented as an effective means to achieve photo-controllable behaviors. Photochromic compounds possess at least two isomeric forms, which have different physical properties, including electronic properties, refractivities, and the like, and can be transformed from one form to another by photo-irradiation at prescribed wavelengths.

Among the photo-isomerizable species, diarylethene, spiropyran and spirooxazine which undergo the pericyclic reactions to yield photochromism have been of particular interests owing to their versatility in preparing photo-responsive functional molecules. In order to fulfill the practical use in device fabrication for optical recording and other optical functioning devices, both isomeric forms must be thermally stable and possess excellent durability for reversible photochromic reactivity. Notably, diarylethenes are superior to the other photochromic moieties owing to their excellent thermal stability, high fatigue resistance, prompt photo-responsiveness and high conversion ratio between open and closed conformers. Recently, it has been shown that the incorporation of nitrogen and sulfur-containing heterocycles into the “ethene” part of the diarylethene backbone, instead of derivatizing the pendants of the bis(thienyl)perfluorocyclopentene core, can enrich the photochromic and photophysical behaviors. It has also been demonstrated that superior bistability of both open and closed isomers can be achieved through the incorporation of phosphorus- and silicon-containing heterocycles by attaching phospholes and siloles to diarylethenes.

Meanwhile, research on metal-containing and coordination motif-containing diarylethenes has been an emerging field in the past decade and has been demonstrated to be a promising molecule scaffold for tuning the photochromism. The color of the photochromic complexes and coordination compounds can be effectively tuned through the coordination of the metal centers or main group atoms and, more importantly, the use of excitation light source with much lower energy to induce photo-isomerization is feasible through the readily accessible photo-sensitization. Furthermore, this can enhance the stability of the photoswitches. At the same time, by combining both the intrinsic properties of the coordination compound and the photo-responsiveness of the photochromic moiety, multi-functional smart materials can be readily obtained.

In view of the use of metal chelates and coordination derivatives in organic electronics nowadays, the integration of the photochromic unit to the coordination motif-containing scaffold is anticipated to provide a simple and efficient approach for modulating the performance of the photoswitches by simply applying the light irradiation without any need of the reconstruction of the entire molecular framework. This approach should be a great advantage for the rapid development in organic electronics, especially in organic resistive memory devices and photoswitches, such that the time for preparation and the cost of manufacture of new materials can be effectively reduced. Different from inorganic memories of which the performances are based on the amount of charges stored in the devices, the memory effect in organic resistive memory devices are strongly dependent on the electrical bistability of conductance (resistance), where a low-conductance (OFF) state will switch to a high-conductance (ON) state during operation. With the incorporation of the photochromic motif and coordination scaffold, it is anticipated that the variability and functionality of organic resistive memory devices can be enriched.

SUMMARY

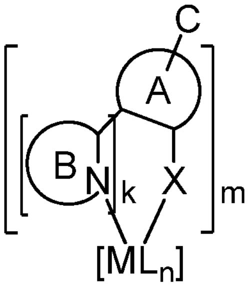
The following presents a simplified summary of the invention in order to provide a basic understanding of some aspects of the invention. This summary is not an extensive overview of the invention. It is intended to neither identify key or critical elements of the invention nor delineate the scope of the invention. Rather, the sole purpose of this summary is to present some concepts of the invention in a simplified form as a prelude to the more detailed description that is presented hereinafter.

As described herein, a novel class of photo-responsive coordination compounds with a photochromic moiety integrated into the coordinating ligand are generated. The photo-responsive coordination compounds can be utilized to serve as electroactive layer for the fabrication of organic resistive memory devices. Particularly, the photo-responsive coordination compounds exhibit high electron-transporting properties and high electrical conductivity upon light irradiation via photo-isomerization of the photochromic moiety. More importantly, the organic resistive memory devices based on the photo-switchable coordination compounds demonstrate binary memory behavior with high ON/OFF ratio of over 10^4 and long retention time.

Furthermore, this new class of photo-responsive coordination compounds demonstrates photo-switchable electron-transporting properties and electrical conductivity under photo-irradiation. Such photo-controllable properties make this class of compounds promising electroactive materials for various organic electronics. Described below in one embodiment are the design, synthesis and studies of the photo-responsive coordination compounds bearing the photochromic moiety. Such compounds exhibit high electron-transporting properties and high electrical conductivity upon light irradiation.

Described in another embodiment are photo-switchable resistive memory devices based on the photo-responsive coordination compounds that are capable of reversibly undergoing photo-isomerization of the photochromic unit when photoirradiated with light. Such organic resistive memory devices demonstrate binary memory behavior with high ON/OFF ratio of over 10^4 and long retention time. The photochromic unit can be, for example, diarylethene, spiropyran, spirooxazine or rhodamine. It is worth noting that under photo-irradiation, the electron-transporting and electrical conductivity, as indicated by the electron-transporting behavior and the memory effect of organic memory devices based on this class of compounds, can be modulated. The photo-responsive coordination compounds described herein provide a simple approach to obtain photo-responsive electron-transporting materials that can serve as active components in the fabrication of organic electronics and organic resistive memory devices. Photo-switchable memory performance can be readily achieved by photo-irradiation.

Also described herein is the preparation of photo-responsive coordination compounds having a chemical structure represented by the following general formula (I), which can be used as electroactive materials in organic electronic devices:



(I)

wherein

a) X can be oxygen, sulphur, selenium, NR or PR where R is alkyl, alkylaryl, cycloalkyl, alkoxy, benzyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group;

b) A is cyclic structure derivative of substituted or unsubstituted arene or heteroarene;

c) B, which can be fused with or singly-bonded to A, is cyclic structure derivative of substituted or unsubstituted heterocyclic group containing one or more nitrogen atoms;

d) C is a photochromic unit and preferably selected from, but not limited to, diarylethene, spiropyran, spirooxazine or rhodamine;

e) [ML$_n$] represents the coordination unit containing a metal or main group element M and L is a ligand;

f) k is the number of rings in the cyclic structure derivatives and k is integer from 0 to 2;

g) n is the number of ligands and n is an integer from 0 to 4; and

h) m is the number of the photochromic ligand and m is an integer from 1 to 4.

It is found that the incorporation of the photochromic unit into the coordination compound can effectively modulate the electrical conductivity of the compounds by photo-irradiation and induces a photo-responsive electron-transporting property in such compounds. The compounds are thermally stable, highly soluble in most of the organic solvents and can readily form a thin film by either thermal deposition or spin-coating processes.

To the accomplishment of the foregoing and related ends, the invention comprises the features hereinafter fully described and particularly pointed out in the claims. The following description and the annexed drawings set forth in detail certain illustrative aspects and implementations of the invention. These are indicative, however, of but a few of the various ways in which the principles of the invention may be employed. Other objects, advantages and novel features of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the drawings.

BRIEF SUMMARY OF THE DRAWINGS

Figure 1 shows a typical structure of an electron-only device for measuring the electrical conductivity of the photo-responsive coordination compounds.

Figure 2 shows a schematic diagram of an organic resistive memory device.

Figure 3 shows the UV-vis absorption spectral changes of compound **2** in degassed benzene upon excitation at 300 nm.

Figure 4 shows the emission spectral changes of compound **2** in degassed benzene upon excitation at 337 nm.

Figure 5 shows a plot of $\ln(A/A_o)$ versus time for the absorbance decay of compound **2** at 543 nm at various temperatures in argon-flushed toluene solution; A denotes absorbance at time t and A_o denotes the initial absorbance; solid lines represent the theoretical linear fits.

Figure 6 shows the Arrhenius plot for the thermal backward reaction of the closed form of compound **2** in argon-flushed toluene solution.

Figure 7 shows the UV-vis absorbance changes of compound **2** at 543 nm on alternate excitation at 300 and 525 nm over six cycles in degassed benzene solution at 298 K.

Figure 8 shows the current density-voltage (*J*-*V*) curves of devices with active layer doped with compound **2** and their photo-responsive behavior.

Figure 9 shows the *J*-*V* curves of devices with active layer doped with Alq_3 with or without exposure to photo-irradiation.

Figure 10 shows the current–voltage (*I*-*V*) characteristics of an indium-tin-oxide (ITO)/active layer/Al device of compound **2** after light-irradiation.

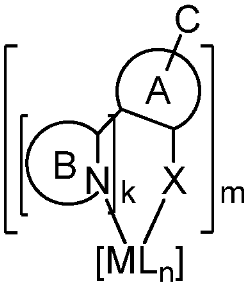
Figure 11 shows the stability of the photo-irradiated ITO/active layer/Al device of compound **2** in "OFF" and "ON" states under a constant stress (1.0 V).

Figure 12 shows the scanning electron microscopy (SEM) image of the cross-section of the photo-irradiated device of compound **2**.

DETAILED DESCRIPTION

Described herein are photo-responsive coordination compounds that enable switching from a high resistive state (OFF state) to a low resistance state (ON state) upon exposure to light irradiation. The electron-transporting properties of the photo-responsive coordination compounds can be photo-modulated and at least 2-fold increase in electrical conductivity can be obtained under photo-irradiation. In addition, the photo-responsive coordination compounds simultaneously exhibit thermal stability and fatigue resistance.

Embodiments are directed to a new class of photo-responsive coordination compounds with photo-controllable electron-transporting and electrical conducting properties. The photochromic unit can be, for example, diarylethene, spiropyran, spirooxazine or rhodamine. The photo-responsive coordination compounds have the chemical structure shown in the generic formula (I):



(I)

wherein

a) X can be oxygen, sulphur, selenium, NR or PR where R is alkyl, alkylaryl, cycloalkyl, alkoxy, benzyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group;

b) A is cyclic structure derivative of substituted or unsubstituted arene or heteroarene;

c) B, which can be fused with or singly-bonded to A, is cyclic structure derivative of substituted or unsubstituted heterocyclic group containing one or more nitrogen atoms;

d) C is a photochromic unit and preferably selected from, but not limited to, a diarylethene, a spiropyran, a spirooxazine or a rhodamine;

e) $[ML_n]$ represents the coordination unit containing a metal or main group element M and L is a ligand;

f) k is the number of rings in the cyclic structure derivatives and k is integer from 0 to 2;

g) n is the number of ligands and n is an integer from 0 to 4; and

h) m is the number of the photochromic ligand and m is an integer from 1 to 4.

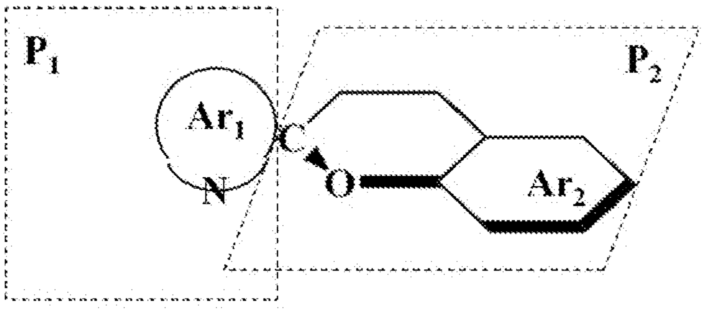
Ring A is cyclic structure derivatives where the cyclic structures are independently selected from a 5- or 6-membered arene or heteroarene. The arene can be benzene, naphthalene, anthracene, pyrene, fluorene and derivatives thereof, and the heteroarene can be pyridine, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, isoquinoline, pyrrole, pyrazine, pyridazine, pyrimidine, benzimidazole, benzothiazole, indole, triazole, tetrazole, pyran, oxadiazole, triazine, tetrazine, and derivatives thereof.

Ring B is cyclic structure derivative where the cyclic structure is independently selected from a 5- or 6-membered nitrogen-containing heteroarene or heterocycle known in the art. The heteroarene or heterocycle can be pyridine, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, isoquinoline, pyrrole, pyrazine, pyridazine, pyrimidine, benzimidazole, benzothiazole, indole, triazole, tetrazole, pyran, oxadiazole, triazine, tetrazine, and derivatives thereof.

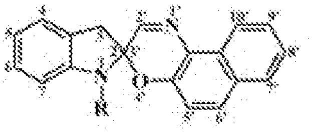
Rings A and B can be unsubstituted or substituted with one or more alkyl, alkenyl, alkynyl, aryl, cycloalkyl, OR, NR_2, SR, C(O)R, C(O)OR, $C(O)NR_2$, CN, CF_3, NO_2, SO_2, SOR, SO_3R, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or heterocyclic group, where R is independently alkyl, alkenyl, alkynyl, alkylaryl, aryl or cycloalkyl, and additionally, or alternatively, any two adjacent substituted positions of rings A and B together form, independently, a fused 5- or 6-membered cyclic group, wherein the said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein the fused 5- to 6-membered cyclic group may be substituted with one or more of alkyl, alkenyl, alkynyl, alkylaryl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, azo, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso, phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group.

C represents the photo-responsive unit. A non-limiting list of examples includes a diarylethene, a spiropyran, a spirooxazine or a rhodamine and the like. Examples of diarylethenes include dithienylethenes and stilbenes. Examples of rhodamine include rhodamine 6G, rhodamine B, rhodamine 123, carboxytetramethylrhodamine (TAMRA), tetramethylrhodamine (TMR), isothiocyanate derivative of tetramethylrhodamine (TRITC), sulforhodamine

101, and rhodamine red. Examples of spiropyrans include those having a structure:



wherein Ar$_1$ and Ar$_2$ can represent benzene, naphthalene, anthracene, indolinol, thiophenol rings, or other aromatic rings (including heterocyclic rings) including indolinospiropyran, in which Ar$_1$ represents indolinol rings. Examples of spirooxazines include the following structures 1-13: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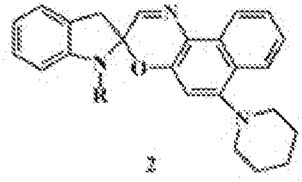
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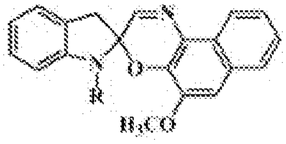
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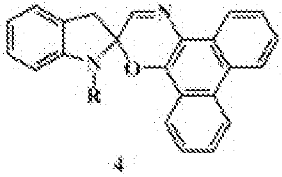
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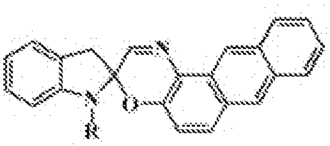
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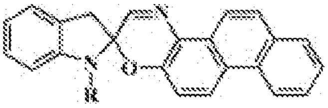
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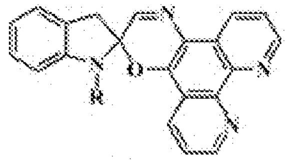
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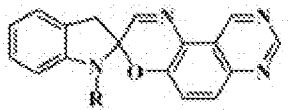
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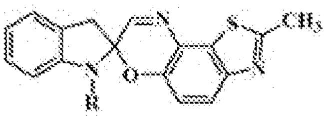
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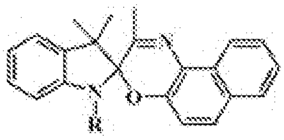
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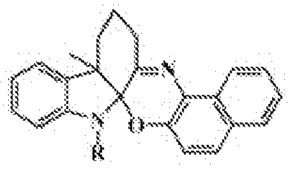
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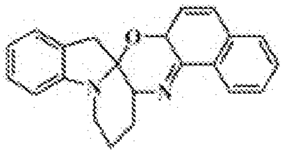
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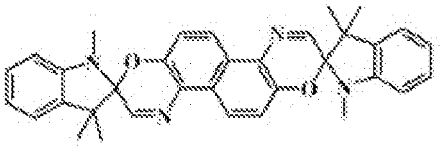
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M represents a non-limiting list of metal centers and main group elements including, but not limited to, aluminum, zinc, gallium, indium, rhodium, manganese, nickel, iron, cobalt, copper, ruthenium, platinum, palladium, tin, vanadium, chromium, iridium, gadolinium, boron, beryllium, lanthanum and the like.

L can be independently, but not limited to, alkyl, alkenyl, alkynyl, alkylaryl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso, phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group, and cyclometalating bidentate ligands which can be, but not limited to, 2-phenylpyridines, phenylisoquinolines, phenylpyrazoles, 7,8-benzoquinolines and derivatives thereof, and non-cyclometalating bidentate ligands which can be, but not limited to, diimine, diamine, diphosphine, dicarboxylate, diketonate, ketoiminate ligands and derivatives thereof, and quinolinato ligands and derivatives thereof. The cyclometalating, non-cyclometalating and quinolinato ligands can be unsubstituted or can be substituted with one or more alkyl, alkenyl, alkynyl, alkylaryl, cycloalkyl, alkoxy, carboxylate, carboxyl, nitro, sulfonyl, SOR, SO_3R, NR_2, SR, CN, CF_3, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group, where R is independently alkyl, alkynyl, alkynaryl, aryl or cycloalkyl. The cyclometalating and non-cyclometalating ligands can also be extended to tridentate and tetradentate derivatives.

In the present disclosure the following terms are used.

The term “halo” or “halogen” includes a fluorine, chlorine, bromine and iodine. The term “alkyl” as used herein includes either a straight or branched chain alkyl groups. The alkyl groups contain at least one to eighteen or more carbon atoms, including, but not limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, 3-ethylhexyl and the like. In addition, the alkyl group may be unsubstituted or substituted with one or more substituents including alkenyl, alkynyl, alkylaryl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, azo, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso, phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group.

The term “alkenyl” as used herein includes both straight and branched chain alkene radicals of two to eighteen or more carbon atoms. The alkenyl group can be unsubstituted or substituted with one or more substituents including, but not limited to, alkynyl, alkylaryl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, azo, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso, phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group.

The term “alkynyl” as used herein includes both straight and branched chain alkyne radicals of two to eighteen or more carbon atoms. The alkynyl group can be unsubstituted or substituted with one or more substituents including, but not limited to, alkyl, alkenyl, alkylaryl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, azo, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso, phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group.

The term “alkylaryl” as used herein includes an alkyl group which has an aromatic group as a substituent. The alkynyl group may be unsubstituted or substituted with one or more substituents including, but not limited to, alkyl, alkenyl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, azo, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso, phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group.

The term “cycloalkyl” as used herein includes cyclic alkyl groups. Cycloalkyl groups can contain 3 to 7 or more carbon atoms and include cyclopropyl, cyclopentyl, cyclohexyl, and the like. Cycloalkyl groups may be unsubstituted or substituted with one or more substituents including, but not limited to, alkyl, alkenyl, alkylaryl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, azo, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso, phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group.

The term “alkoxy” as used herein includes linear or branched alkoxy groups of one to eighteen or more carbon atoms, and can be unsubstituted or substituted with one or more substituents including, but not limited to, alkyl, alkenyl, alkylaryl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, azo, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso, phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group.

Aryl alone or in combination includes carbocyclic aromatic systems containing one, two or three rings, wherein each ring may be attached together in a pendant manner or may be fused and can be 5- or 6-membered rings. The aryl rings can be unsubstituted or substituted with one or more substituents including, but not limited to, alkyl, alkenyl, alkylaryl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, azo, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso, phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group.

Heteroaryl alone or in combination includes heterocyclic aromatic systems which contain one, two, three or more rings, wherein each ring may be combined in a pendant or fused manner, wherein each ring of the system is a 5- or 6-membered rings.

Heterocyclic and heterocycles refer to a 3- to 7-membered ring containing at least one heteroatom. The heterocyclic rings can be aromatic, including, but not limited to, pyridine, thiophene, furan, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, isoquinoline, pyrrole, pyrazine, pyridazine, pyrimidine, benzimidazole, benzofuran, benzothiazole, indole, naphthalene, triazole, tetrazole, pyran, thiapyran, oxadiazole, triazine, carbazole, dibenzothiophene, dibenzofuran, indole, and fluorene. The heterocyclic rings can be non-aromatic, including, but not limited to, aziridine, oxirane, thiirane, oxaziridine, dioxirane, azetidine, oxetane, thietane, diazetidine, dioxetane, dithietane, tetrahydrofurane, thiolane, borolane, phospholane, arsolane, stibolane, bismolane, silane, stannolane, piperazine, piperidine, and pyrrolidine. Heterocyclic rings can be unsubstituted or substituted, which can include, but not limited to, alkyl, alkoxy, aryl.

Cyclometalating bidentate ligand is a term well known in the art and includes, but not limited to, 2-phenylpyridine (ppy), 2-(p-tolyl)pyridine (ptpy), 4-(2-pyridyl)benzaldehyde (pba), 2-(2,4-difluorophenyl)pyridine (fppy), 4-pyridin-2-ylbenzoic acid, 3-pyridin-2-ylbenzoic acid, 2-methyl-6-phenylpyridine, 3-methyl-2-phenylpyridine, 4-methyl-2-phenylpyridine, 5-methyl-2-phenylpyridine, 2-phenylpyridine-3-carboxylic acid, 2-phenylpyridine-4-carboxylic acid, 6- phenylpyridine-3-carboxylic acid, 2,3-diphenylpyridine, 2,4-diphenylpyridine, 2,5-diphenylpyridine, phenylpyrazole (ppz), 3-methyl-1-phenyl-1H-pyrazole (mppz), 7,8-benzoquinoline (bzq), 2-phenylquinoline (pq), 1-phenylisoquinoline (piq), 2-phenylquinoline, 3-phenylisoquinoline, 3,4-diphenylisoquinoline and 2-(benzimidazol-2-yl)quinolone (biq).

Non-cyclometalating bidentate ligand is a term well known in the art and includes, but not limited to, 2,2'-bipyridine (bpy), 4-chloro-2,2'-bipyridine (4-Cl-bpy), 4-carboxy-2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine (4,4'-Me_2-bpy), 4,4'-diphenyl-2,2'-bipyridine (4,4'-Ph_2-bpy), 4,4'-dicarboxy-2,2'-bipyridine, 5,5'-bis(ethoxycarbonyl)-2,2'-bipyridine, 5-chloro-2,2'-bipyridine, 6-bromo-2,2'-bipyridine, 1,10-phenanthroline (phen), 4-chloro-1,10-phenanthroline (4-Cl-phen), 4-methyl-1,10-phenanthroline (4-Me-phen), 5-bromo-1,10-phenanthroline (5-Br-phen), 5-phenyl-1,10-phenanthroline (5-Ph-phen), 5-nitro-1,10-phenanthroline (5-NO_2-phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2-phen), 4,7-diphenyl-1,10-phenanthroline (4,7-Ph_2-phen), 5,6-dimethyl-1,10-phenanthroline (5,6-Me_2-phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-Me_4-phen), 3,8-dibromo-1,10-phenanthroline (3,8-Br_2-phen), 5,6-dibromo-1,10-phenanthroline (5,6-Br_2-phen), 2,9-dichloro-1,10-

phenanthroline (2,9-Cl_2-phen), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (2,9-Me_2-4,7-Ph_2-phen), dipyrido[3,2-a:2',3'-c]phenazine (dppz), benzo[i]dipyrido[3,2-a:2',3'-c]phenazine (dppn), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), 2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl, 2,2'-bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl, 2,2'-bis(diphenylphospino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, bis[(2-diphenylphosphino)phenyl]ether, 4,5-bis(diphenylphosphino)-9,9-dimethyl- xanthene, ethylenediamine, oxalate, acetylacetonate, hexafluoroacetylacetonate, 1,3-diphenyl-1,3-propanedionate.

Quinolinato ligand is a term well known in the art and includes, but not limited to, 8-hydroxyquinoline, 5-chloro-8-hydroxyquinoline, 7-bromo-8-hydroxyquinoline, 2-amino-8-quinolinol, 2-methyl-8-quinolinol, 5,7-dimethyl-8-quinolinol, 8-hydroxyquinoline-7-carbaldehyde, 8-hydroxy-2-quinolinecarboxylic acid 8-hydroxyquinoline-5-sulfonic acid monohydrate, 2-benzyl-8-hydroxyquinoline and 8-mercaptoquinoline.

Benzene includes substituted or unsubstituted benzene.

Pyridine includes substituted or unsubstituted pyridine.

Thiophene includes substituted or unsubstituted thiophene.

Furan includes substituted or unsubstituted furan.

Fused-thiophene includes substituted or unsubstituted fused-thiophene.

Pyrazole includes substituted or unsubstituted pyrazole.

Pyrimidine includes substituted or unsubstituted pyrimidine.

Pyrrole includes substituted or unsubstituted pyrrole.

Benzimidazole includes substituted or unsubstituted benzimidazole.

Benzofuran includes substituted or unsubstituted benzofuran.

Benzothiazole includes substituted or unsubstituted benzothiazole.

Indole includes substituted or unsubstituted indole.

Naphthalene includes substituted or unsubstituted naphthalene.

Anthracene includes substituted or unsubstituted anthracene.

Pyrene includes substituted or unsubstituted pyrene.

Thiazole includes substituted or unsubstituted thiazole.

Pyran includes substituted or unsubstituted pyran.

Thiapyran includes substituted or unsubstituted thiapyran.

Carbazole includes substituted or unsubstituted carbazole.

Dibenzothiophene includes substituted or unsubstituted dibenzothiophene.

Dibenzofuran includes substituted or unsubstituted dibenzofuran.

Fluorene includes substituted or unsubstituted fluorene.

The invention is illustrated by the following non-limiting examples. It is to be understood that changes and variations can be made therein without deviating from the scope and the spirit of the invention as hereinafter claimed. It is also understood that various theories as to why the invention works are not intended to be limiting. The compounds described herein are represented throughout by their monomeric structure. As is well known to those in the art, the compounds may also be present as dimers, trimers, larger oligomers, dendrimers, or polymers.

In some embodiments, the photo-responsive coordination compounds of formula (I) are prepared in high purity. High purity means one of at least 90 % by weight pure, at least 95 % by weight pure, at least 99 % by weight pure, or at least 99.9 % by weight pure.

The photo-responsive coordination compounds can be used to form thin films by spin-coating, spray-coating, dip-coating, layer-by-layer deposition, ink-jet printing, 3D printing, or other known suitable fabrication methods and be subjected to achieve photo-responsive electron-transporting functions and applications in organic resistive memory devices. Referring to Figure **1**, one example of a structure of a device for measuring electrical conductivity of the photo-responsive coordination compounds is shown in order: aluminum 10/LiF 11/active layer 12/LiF 13/compound 14/ITO coated glass 15, in which the active layer is formed by mixing the photo-responsive coordination compound as a dopant into a host complex. Suitable host materials should be selected to ensure an efficient energy transfer between the host material and the dopant material. Examples of desirable hosts are *m*-(*N*,*N'*-

dicarbazole)benzene (mCP), 4,4’-bis(carbazol-9-yl)-biphenyl (CBP), 4,4’,4”-tris(carbazol-9-yl)triphenylamine (TCTA), 3-(4-biphenylyl)-4-phenyl-5-*tert*-butylphenyl-1,2,butylphenyl-1,2,4-triazole (TAZ), *p*-bis(triphenylsilyl)benzene (UGH2), and PVK. LiF is deposited on the ITO coated glass or on the active layer by thermal deposition. A layer of aluminum is then thermally deposited with shadow mask on the LiF layer. In some embodiments, the electrical conductivity of the photo-responsive coordination compound dramatically increases by two-fold after light-irradiation. Unlike the conventional method by modulating electrical conductivity through the reconstruction of molecular structure of the target compound, an integration of photochromic unit into the coordination compound in the invention provides a direct and simple way to enhance the versatility of the corresponding coordination compounds for the application in organic electronics.

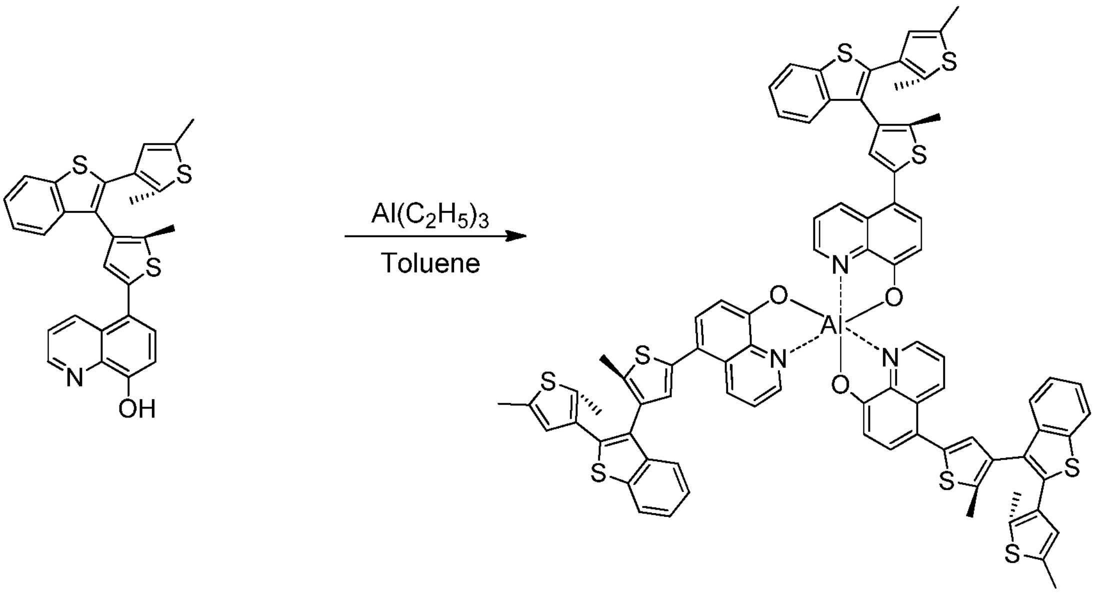
Meanwhile, the photo-responsive coordination compounds have been shown to serve as electroactive components for the applications in organic resistive memory devices. The typical structure of an organic resistive memory device is in the order shown in Figure **2**: aluminum 20/active layer 21/ITO coated glass 22, in which the photo-responsive compound serves as active layer material and is formed by spin-coating onto the ITO coated glass and covered by a layer of aluminum cathode prepared by thermal deposition with shadow mask on the former. The size of the ITO coated glass is 2 cm × 2 cm, in which 400 individual devices have been prepared simultaneously. Particularly, memory performance has been obtained after photo-irradiation onto the active layer. A high ON/OFF ratio of up to 10^4, a threshold voltage of about 3.5 V and a long retention time over 10^4 s have been achieved. Notably, the present invention represents the first example of resistive memory device based on coordination compound with photochromic motif, exhibiting unique photo-responsive memory performance reported so far.

The following examples illustrate the subject invention. Unless otherwise indicated in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, all temperatures are in degrees Centigrade, and pressure is at or near atmospheric pressure.

EXAMPLE 1

SYNTHESIS AND CHARACTERIZATION OF COMPOUNDS **1-4**

Compounds **1-4** were synthesized according to the following methodology. The desired compounds were synthesized by the coordination of the diarylethene-containing 8-hydroxyquinolines to the Al(III) center. For example, triethylaluminum in heptane was added to a solution of 5-(4-(2-(2,5-dimethylthiophen-3-yl)benzo[*b*]thiophen-3-yl)-5-methylthiophen-2-yl)quinolin-8-ol in toluene, (1 M) (0.50 mmol). The mixture was stirred overnight and the solvent was removed under vacuum afterwards. The aluminum compound was purified by recrystallization with dichloromethane-ether to afford the Al(III) compounds.



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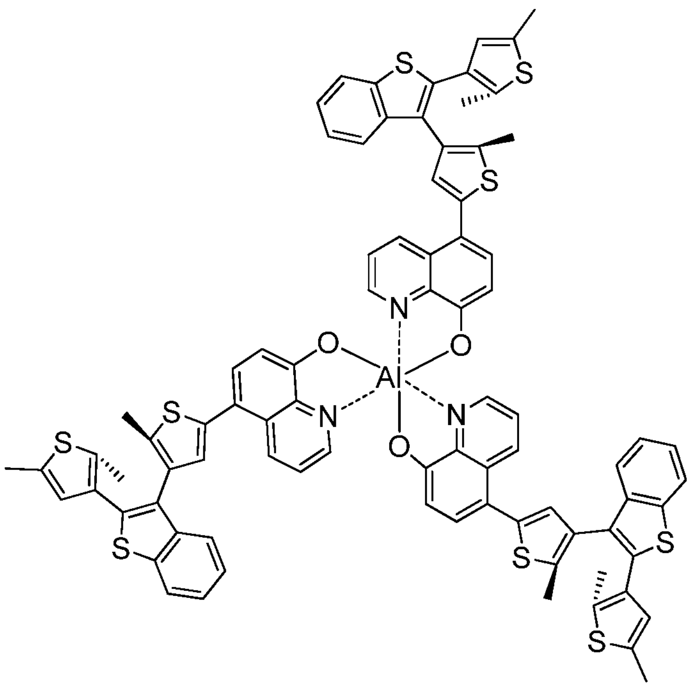

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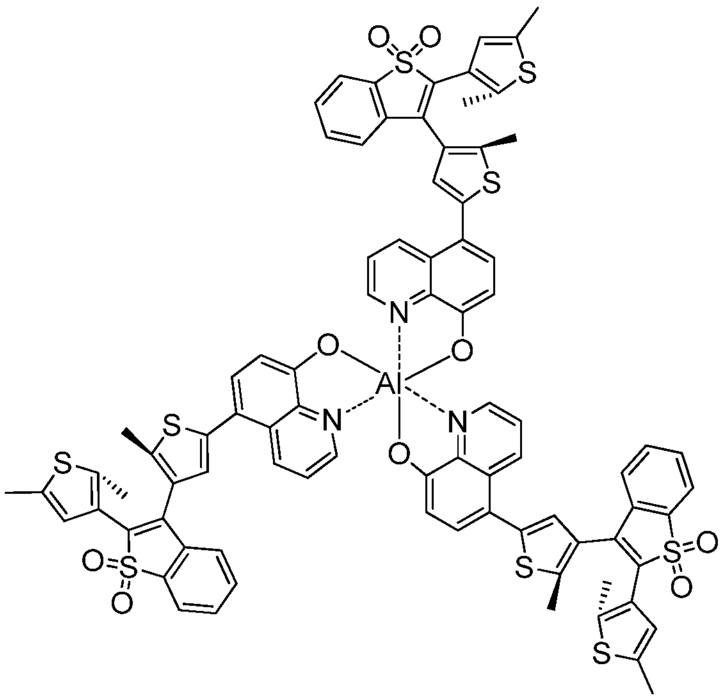

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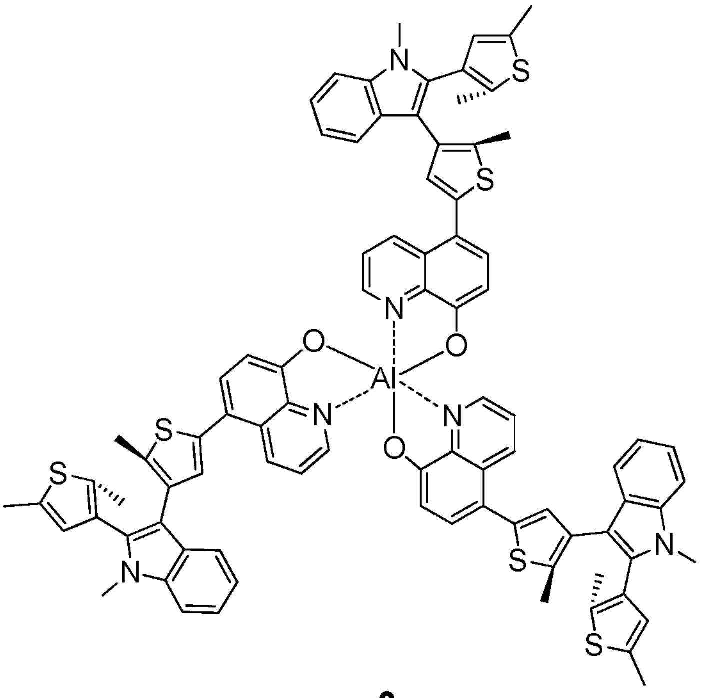

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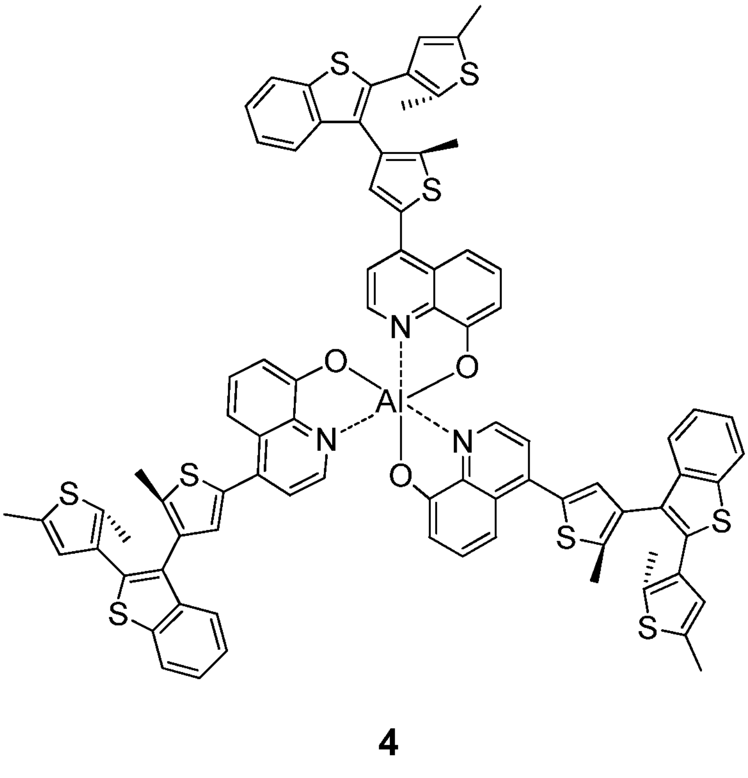

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The characteristic spectroscopic properties of compounds **1**−**4** are as follows:

Compound **1**

Yield: 0.60 g, 0.40 mmol, 81 %. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, δ /ppm): δ 2.04–2.08 (m, 9H, –CH$_3$), 2.14–2.16 (m, 9H, –CH$_3$), 2.35–2.37 (s, 9H,–CH$_3$), 6.68–6.64 (m, 3H, thienyl), 6.82–6.86 (m, 3H, quinolinyl), 6.98–7.00 (m, 3H, thienyl), 7.42–7.46 (m, 8H, phenyl and quinolinyl), 7.61–7.68 (m, 8H, phenyl and quinolinyl), 8.01 (m, 3H, phenyl), 8.35–8.43 (m, 3H, quinolinyl), 8.83 (s, 1H, quinolinyl), 8.90 (s, 1H, quinolinyl). HRMS (positive ESI) calcd. for $C_{84}H_{60}AlN_3O_3S_9$: *m*/*z* 1473.1936; found: 1473.1919 [M]$^+$. Elemental analyses, found (%): C 65.42, H 4.13, N 2.70; calcd (%) for $C_{84}H_{60}AlN_3O_3S_9$ CH_2Cl_2: C 65.45, H 4.01, N 2.69.

Compound **2**

Yield: 0.64 g, 0.41 mmol, 82 %. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, δ /ppm): δ 2.01–2.08 (m, 9H, –CH$_3$), 2.11–2.16 (m, 9H, –CH$_3$), 2.41–2.44 (s, 9H, –CH$_3$), 6.85–6.89 (m, 3H, thienyl), 7.02 (d, *J* = 8.0 Hz, 3H, quinolinyl), 7.11–7.17 (m, 3H, thienyl), 7.40–7.42 (m, 3H, phenyl), 7.56–7.74 (m, 12H, phenyl and quinolinyl), 8.01 (m, 4H, phenyl and quinolinyl), 8.44–8.57 (m, 3H, quinolinyl), 8.73 (d, *J* = 4.2 Hz, 1H, quinolinyl), 8.87 (d, *J* = 4.2 Hz, 1H, quinolinyl). HRMS (positive ESI) calcd. for $C_{84}H_{60}AlN_3O_9S_9$: *m*/*z* 1569.1631; found: 1569.1610 [M]$^+$. Elemental analyses, found (%): C 58.43, H 3.94, N 2.63; calcd (%) for $C_{84}H_{60}AlN_3O_9S_9$ 2.5CH_2Cl_2: C 58.26, H 3.67, N 2.36.

Compound **3**

Yield: 0.59 g, 0.41 mmol, 80 %. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, δ /ppm): δ 1.93–1.95 (m, 9H, –CH$_3$), 2.21–2.23 (m, 9H, –CH$_3$), 2.41–2.44 (s, 9H, –CH$_3$), 3.64 (s, 9H, –CH$_3$), 6.77–6.81 (m, 6H, phenyl and thienyl), 6.96–6.98 (m, 3H, thienyl), 7.12 (t, *J* = 6.8 Hz, 3H, phenyl), 7.23 (t, *J* = 6.8 Hz, 3H, phenyl), 7.41–7.53 (m, 12H, phenyl and quinolinyl), 7.70 (s, 1H, quinolinyl), 8.30 (s, 3H, quinolinyl), 8.69 (s, 1H, quinolinyl), 8.84 (s, 1H, quinolinyl). HRMS (positive ESI) calcd. for $C_{87}H_{69}AlN_6O_3S_6$: *m*/*z* 1464.3571; found: 1464.3437

[M]$^+$. Elemental analyses, found (%): C 69.62, H 5.11, N 5.34; calcd (%) for $C_{87}H_{69}AlN_6O_3S_6$ $2H_2O$: C 69.57, H 4.90, N 5.60.

Compound **4**

Yield: 0.60 g, 0.42 mmol, 83 %. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, δ /ppm): δ 2.00-2.04 (m, 9H, $-CH_3$), 2.14-2.19 (m, 9H, $-CH_3$), 2.34-2.36 (s, 9H, $-CH_3$), 6.65-6.81 (m, 6H, phenyl and thienyl), 6.94-6.96 (m, 3H, thienyl), 7.16-7.27 (m, 6H, phenyl), 7.31-7.58 (m, 12H, phenyl and quinolinyl), 7.68 (s, 1H, quinolinyl), 7.97-8.01 (m, 1H, quinolinyl), 8.59 (s, 1H, quinolinyl), 8.72 (s, 1H, quinolinyl). HRMS (positive ESI) calcd. for $C_{84}H_{61}AlN_3O_3S_9$: *m/z* 1474.2015; found: 1474.2005 [*M*+H]$^+$. Elemental analyses, found (%): C 66.51, H 4.40, N 2.78; calcd (%) for $C_{84}H_{60}AlN_3O_3S_9$ $2H_2O$: C 66.77, H 4.27, N 2.78.

EXAMPLE 2

PHOTOCHROMIC PROPERTIES

A solution sample of the compound was degassed on a high vacuum line in a degassing cell with a 10 cm^3 Pyrex round-bottom flask connected by a side-arm to a 1-cm quartz fluorescence cuvette and was sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. The solution sample was rigorously degassed with no fewer than four freeze-pump-thaw cycles prior to the measurements.

The solution sample was irradiated at the UV absorption band, whereby the initial pale yellow solution turned into various colors. The colored state was thermally stable. Then, it was irradiated with visible light, whereby the solution was back to the original color. The UV-vis absorbance changes of the compounds were capable of undergoing reversible cycles. Figure **3** shows the UV-vis absorption spectral changes of **2** in degassed benzene upon excitation at 300 nm. The electronic absorption data of the open forms and closed forms are summarized in Table 1. In addition to the UV-vis spectral change, the emission intensity would decrease upon photocyclization of the Alq_3 compounds (Figure **4**), rendering the compounds photo-switchable. The quantum yields for both photocyclization and photocycloreversion of the photochromic compounds are summarized in Table 2. The conversion at photostationary state is also summarized in Table 2.

Table 1

Electronic absorption data for compounds **1**-**4** in benzene solution at 298 K

Compound	Configuration	Absorption λ_{abs} / nm ($\varepsilon \times 10^{-3}$ / $dm^3mol^{-1}cm^{-1}$)
1	Open form	298 (62.8), 421 (10.5)
	Closed form	352 (113.0), 407 (33.5), 593 (57.2)
2	Open form	300 (25.2), 413 (7.7)
	Closed form	293 (17.2), 372 (38.4), 412 sh (16.5), 543 (14.1)
3	Open form	298 (53.1), 424 (7.9)
	Closed form	358 (161.2), 415 sh (34.2), 647 (54.1)
4	Open form	307 (55.3), 343 sh (24.9), 428 (12.2)
	Closed form	303 (54.2), 347 sh (27.8), 426 (12.0), 626 (4.9)

Table 2

Photochemical quantum yields and conversion at photostationary state determined in degassed benzene solution at 298 K

Compound	Photochemical Quantum Yield / ϕ[a]		Conversion at PSS (%)
	Photocyclization[b]	Photocycloreversion[c]	
1	0.012	0.005	45
2	0.107	0.035	89
3	0.006	0.004	36
4	0.009	0.005	24

[a] Data obtained with an uncertainty of ±10 %.

[b] Data obtained using 316 nm as the excitation source.

[c] Data obtained using 600 nm as the excitation source.

EXAMPLE 3

Compound **2** was used to demonstrate the thermal stability of the closed form of the photochromic compounds by measuring the absorbance decay at different temperatures in the dark (Figure **5**). By plotting the rates of thermal backward reaction at different temperature against the temperature, the Arrhenius plot (Figure **6**) could be obtained, which could be used to determine the activation energy (66.7 kJ mol^{-1}) and the pre-exponential factor (4.1×10^6 s^{-1}) of the thermal cycloreversion of compound **2**.

EXAMPLE 4

Fatigue resistance represents another important parameter that is commonly used to evaluate the performance of photochromic materials. Photochromic materials could lose their photochromic reactivities through side-reactions of the closed form. The fatigue resistance of the compound could be demonstrated by alternate excitation at the absorption bands of the open form and the closed form of the compounds and monitoring the UV-vis absorption changes at a selected wavelength. Compound **2** was used to demonstrate the fatigue resistance of the photochromic compounds, as depicted in Figure **7**.

EXAMPLE 5

ELECTROCHEMICAL PROPERTIES

To probe the electrochemical properties, cyclic voltammetry was carried out in a three-electrode cell with 0.1 M $^{n}Bu_4NPF_6$ as the supporting electrolyte in dichloromethane for compounds **1** to **4**. The ferrocenium/ferrocene couple (Fc^+/Fc) was used as the internal reference.

Compounds **1–4** show several irreversible oxidation waves at around +0.95 to +1.99 V versus standard calomel electrode (SCE). For the reduction process, one or two quasi-reversible reduction couples as well as reduction waves at about –1.57 to –1.82 V versus SCE can be observed. Upon structural modification of the 8-hydroxyquinoline ligands on the peripheral photochromic units, no considerable shifts of the first oxidation wave can be observed. As for compounds **1** and **3**, which bear no substituents on the pyridyl side of the ligands, similar reduction potential is observed. Meanwhile, a less negative reduction couple at about –1.57 V is found in compound **2**. Compound **4** also exhibits a reduction potential with less negative value, indicating that substitution of the dithienylethene unit on the pyridyl side possesses a significant influence on the electronic properties of the aluminum(III) compound. The highest occupied molecular orbital (HOMO) levels and the lowest unoccupied molecular orbital (LUMO) levels of compounds **1-4** had been determined by using ferrocene as the reference. The LUMO levels of all the compounds are found to be in the range of –2.52 to –2.77 eV, while the HOMO levels of all the compounds are found to range from –5.29 to –5.50 eV. The electrochemical data are summarized in Table 3.

Table 3

Electrochemical data in dichloromethane solution at 298 K

Compound	Oxidation[a] E_{pa} / V vs. SCE[b]	Reduction[a] $E_{1/2}$ / V[c] vs. SCE [E_{pc} / V vs. SCE][d]	HOMO[e] [eV]	LUMO[e] [eV]
1	+0.97, +1.13, +1.71	[–1.81]	–5.31	–2.53
2	+1.04, +1.25, +1.99	–1.57 (60), –1.77 (60)	–5.38	–2.77
3	+0.95, +1.39, +1.48, +1.77	[–1.82]	–5.29	–2.52
4	+1.16, +1.41, +1.79	–1.58 (80), –1.74 (60)	–5.50	–2.76

[a] 0.1 M $^{n}Bu_4NPF_6$ (TBAH) as supporting electrolyte at room temperature; scan rate 100 mV s^{-1}.

[b] Anodic peak potential for the irreversible oxidation wave.

[c] $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively.

[d] Cathodic peak potential for the irreversible reduction wave.

[e] The energy level is determined with reference to the HOMO level of ferrocene (–4.8 eV vs. vacuum level).

EXAMPLE 6

A device for measuring the electrical conductivity according to an embodiment of the invention was constructed in the following manner:

a) A transparent anode ITO coated borosilicate glass substrate (38 mm × 38 mm) with sheet resistance of 30 Ω per square was ultrasonicated in the commercial detergent Decon 90, rinsed in deionized water having a resistivity of 18.2 mega-ohm for 15 minutes, and then dried in an oven at 120 °C for an hour. The substrate was next subjected to an UV-ozone treatment in a Jelight 42-220 UVO cleaner equipped with a mercury grid lamp for 15 minutes.

b) A 5-nm thick LiF layer was deposited by thermal evaporation on the ITO coated glass substrate of step a.

c) A 60-nm thick active layer was spin-coated by using a Laurell WS-400Ez-6NPP-Lit2 single wafer spin processor at 6000 rpm for 30 seconds onto LiF layer of step b, and baked at 80 °C for 10 minutes in air, in which compound **2** was doped into the host material MCP layer at a concentration of 20 wt%.

d) A 5-nm thick LiF layer and a 100-nm thick Al layer were deposited by thermal evaporation on the active layer of step c to form an electron-injecting cathode.

LiF and Al were prepared by thermal evaporation from tantalum boats by applying current through the tantalum boats. Deposition rates were monitored with a quartz oscillation crystal together with a Sigma SQM-242 quartz crystal card and controlled at 0.1–0.2 nm s^{-1} for both organic and metal layers. *J*–*V* characteristics of the devices was measured with a programmable Keithley model 2420 source meter under ambient air conditions.

EXAMPLE 7

Figure **8** shows the *J*–*V* curves of the devices doped with compound **2**. Upon light-irradiation, a significant lowering of the driving voltage can be observed as compared to the device without any exposure to UV light. The current density at particular voltage was also found to be higher for the devices after photo-irradiation upon comparing to those without any light exposure. Notably, the extent of the lowering of the driving voltage becomes more significant upon lengthening the time of light exposure. In addition, it is found that the electrical conductivity of compound **2** has been improved to 7.8×10^{-6} mS cm^{-1} after photo-irradiation, which is a recognizable improvement from the non-irradiated conditions (i.e. 3.7×10^{-6} mS cm^{-1}). However, as shown in Figure **9**, there was no significant difference between the *J*–*V* curves obtained from the devices containing the original Alq_3 compound with or without exposure to UV light. Such two-fold increment in electrical conductivity in the diarylethene-containing Alq_3 compounds demonstrates that the coordination compounds are promising candidates for photo-responsive electron-transporting materials.

EXAMPLE 8

A memory device according to an embodiment of the invention was constructed in the following manner:

(a) A transparent anode ITO coated borosilicate glass substrate (2 cm × 2 cm) was ultrasonicated successively with deionized water having a resistivity of 18.2 mega-ohm, analytical grade acetone, analytical grade isopropanol, absolute ethanol for 15 minutes and then dried in an oven at 120 °C for an hour.

(b) A 300 μL toluene solution of compound **2** was spin-coated onto the ITO substrate of step a in a 2-step spinning mode, 500 rpm for 9 seconds followed by 2000 rpm for 30 seconds;

(c) The substrate was placed in oven at 75 °C for 30 min to remove the solvent residue;

(d) The substrate was put into a vacuum chamber, and the chamber was pumped down from 1 bar to 5×10^{-6} mbar;

(e) An aluminum layer was deposited by thermal evaporation onto the compound **2** of step b to form a cathode. *J–V* characteristics of the memory devices were measured with a programmable Keithley model 4200 power source in a four-probe station. 400 devices were fabricated on each ITO glass substrate and the active area of each cell was 0.25 mm^2.

EXAMPLE 9

The *J–V* characteristics of compound **2** of the as-fabricated memory device without and with UV exposure were investigated. For the device without any exposure to light-irradiation, there was no increase in current and a high-resistance state (OFF state) was retained under a voltage ranging from 0 to +5 V. Interestingly, after photo-irradiation, an abrupt increase in the current at the switching threshold voltage at about 3.5 V was observed as shown in Figure **10**. This process demonstrates the transition from a low-conductivity state to a high-conductivity state (ON state) with a high ON/OFF ratio of over 10^4 from 10^{-7} to 10^{-3} A. The device remained in the ON state when the voltage sweep was repeated (sweep 2), indicating that the ON state is retained and memory effect is obtained. The memory device could not be returned to the OFF state by the application of a reverse bias of the same magnitude that it had been switched ON (sweep 3). The stability of the device under a constant stress of 1 V is shown in Figure **11**. No significant degradation was observed in current for ON and OFF states for at least 10000 seconds during the measurement, suggesting that the device exhibits a precise control of the ON and OFF state with low misreading rate. The film thicknesses of compound **2** and aluminum were found to be about 77 nm and 78 nm, respectively, by using SEM to observe a cross section of the device, as shown in Figure **12**. These findings indicate the uniqueness of the diarylethene-containing Alq_3 compounds for the fabrication of organic memory devices, of which the performance is photo-controllable.

These examples should not be construed as limiting the scope of the invention, but as providing illustrations of some of the embodiments of the invention. It is being understood that changes and variations can be made therein without deviating from the scope and the spirit of the invention as hereinafter claimed.

With respect to any figure or numerical range for a given characteristic, a figure or a parameter from one range may be combined with another figure or a parameter from a different range for the same characteristic to generate a numerical range.

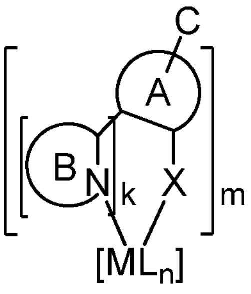
Other than in the operating examples, or where otherwise indicated, all numbers, values and/or expressions referring to quantities of ingredients, reaction conditions, etc., used in the specification and claims are to be understood as modified in all instances by the term "about".

While the invention is explained in relation to certain embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

CLAIMS

What is claimed is:

1. A photo-responsive coordination compound comprising a chemical structure represented by formula (I):



(I)

wherein

a) X is oxygen, sulphur, selenium, NR or PR where R is an alkyl, alkylaryl, cycloalkyl, alkoxy, benzyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group;

b) A is cyclic structure derivative of substituted or unsubstituted arene or heteroarene;

c) B, which is optionally fused with or singly-bonded to A, is cyclic structure derivative of substituted or unsubstituted heterocyclic group containing one or more nitrogen atoms;

d) C is a photochromic unit;

e) $[ML_n]$ represents the coordination unit containing a metal or main group element M and L is a ligand;

f) k is a number of rings in the cyclic structure derivatives and k is an integer from 0 to 2;

g) n is a number of ligands and n is an integer from 0 to 4; and

h) m is a number of the photochromic ligand and m is an integer from 1 to 4.

2. The photo-responsive compound according to claim 1, wherein ring A is cyclic structure derivative where the cyclic structure is independently selected from a 5- or 6-membered arene or heteroarene, wherein the arene is one or more of benzene, naphthalene, anthracene, pyrene, fluorene and derivatives thereof, and the heteroarene can be pyridine, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, isoquinoline, pyrrole, pyrazine, pyridazine, pyrimidine, benzimidazole, benzothiazole, indole, triazole, tetrazole, pyran, oxadiazole, triazine, tetrazine, and derivatives thereof.

3. The photo-responsive compound according to claim 1, wherein ring B is cyclic structure derivative where the cyclic structure is independently selected from a 5- or 6-membered nitrogen-containing heteroarene or heterocycle, wherein the heteroarene or heterocycle is one or more of pyridine, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, isoquioline, pyrrole, pyrazine, pyridazine, pyrimidine, benzimidazole, benzothiazole, indole, triazole, tetrazole, pyran, oxadiazole, triazine, tetrazine, and derivatives thereof.

4. The photo-responsive compound according to claim 1, wherein rings A and B can be unsubstituted or substituted with one or more alkyl, alkenyl, alkynyl, aryl, cycloalkyl, OR, NR_2, SR, C(O)R, C(O)OR, $C(O)NR_2$, CN, CF_3, NO_2, SO_2, SOR, SO_3R, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or heterocyclic group, where R is independently alkyl, alkenyl, alkynyl, alkylaryl, aryl or cycloalkyl, and additionally, or alternatively, any two adjacent substituted positions of rings A and B together form, independently, a fused 5- or 6-membered cyclic group, wherein the said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein the fused 5- to 6-membered cyclic group may be substituted with one or more of alkyl, alkenyl, alkynyl, alkylaryl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, azo, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso,

phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group.

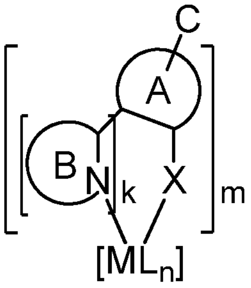
5. The photo-responsive compound according to claim 1, wherein M is a metal center selected from one or more of aluminum, zinc, gallium, indium, rhodium, manganese, nickel, iron, cobalt, copper, ruthenium, platinum, palladium, tin, vanadium, chromium, iridium, gadolinium, boron, beryllium, and lanthanum.

6. The photo-responsive compound according to claim 1, wherein L can be independently alkyl, alkenyl, alkynyl, alkylaryl, cycloalkyl, haloformyl, hydroxyl, aldehyde, carboxamide, amine, amino, alkoxy, benzyl, carbonate ester, carboxylate, carboxyl, ketamine, isocyanate, isocyanide, isothiocyanate, nitrile, nitro, nitroso, phosphine, phosphate, phosphono, pyridyl, sulfonyl, sulfo, sulfinyl, sulfhydryl, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group, and cyclometalating bidentate ligands which can be, but not limited to, 2-phenylpyridines, phenylisoquinolines, phenylpyrazoles, 7,8-benzoquinolines and derivatives thereof, and non-cyclometalating bidentate ligands which can be, but not limited to diimine, diamine, diphosphine, dicarboxylate, diketonate, ketoiminate ligands and derivatives thereof, and quinolinato ligands and derivatives thereof, the cyclometalating, non-cyclometalating and quinolinato ligands are one or more of unsubstituted or can be substituted with one or more alkyl, alkenyl, alkynyl, alkylaryl, cycloalkyl, alkoxy, carboxylate, carboxyl, nitro, sulfonyl, SOR, SO_3R, NR_2, SR, CN, CF_3, halo, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group, where R is independently alkyl, alkenyl, alkynyl, alkylaryl, aryl or cycloalkyl.

7. The photo-responsive compound according to claim 1, wherein the photochromic unit is at least one selected from the group of a diarylethene,

a spiropyran,a spirooxazine, and a rhodamine.

8. An organic memory device comprising in sequence, an anode, an active layer comprising a cathode and a photo-responsive coordination compound having formula (I):



(I)

wherein

a) X is oxygen, sulphur, selenium, NR or PR where R is an alkyl, alkylaryl, cycloalkyl, alkoxy, benzyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group;

b) A is cyclic structure derivative of substituted or unsubstituted arene or heteroarene;

c) B, which is optionally fused with or singly-bonded to A, is cyclic structure derivative of substituted or unsubstituted heterocyclic group containing one or more nitrogen atoms;

d) C is a photochromic unit;

e) $[ML_n]$ represents the coordination unit containing a metal or main group element M and L is a ligand;

f) k is a number of rings in the cyclic structure derivatives and k is an integer from 0 to 2;

g) n is a number of ligands and n is an integer from 0 to 4; and

h) m is a number of the photochromic ligand and m is an integer from 1 to 4.

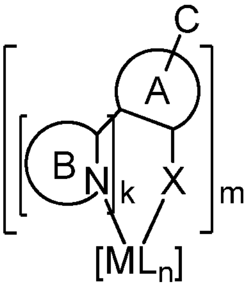
9. The organic memory device according to claim 8 in which the photo-

responsive coordination compound is thermally evaporated or spin-coated.

10. The organic memory device according to claim 8 in which the photo-responsive coordination compound is a material for an active layer in the fabrication of the organic memory device with photo-controllable performance.

11. The organic memory device according to claim 8, wherein the photochromic unit is at least one selected from the group of a diarylethene, a spiropyran,a spirooxazine, and a rhodamine.

12. A photo-responsive electron-transporting material comprising a coordination compound having a formula (I):



(I)

wherein

a) X is oxygen, sulphur, selenium, NR or PR where R is an alkyl, alkylaryl, cycloalkyl, alkoxy, benzyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl or a heterocyclic group;

b) A is cyclic structure derivative of substituted or unsubstituted arene or heteroarene;

c) B, which is optionally fused with or singly-bonded to A, is cyclic structure derivative of substituted or unsubstituted heterocyclic group containing one or more nitrogen atoms;

d) C is a photochromic unit;

e) $[ML_n]$ represents the coordination unit containing a metal or main group element M and L is a ligand;

f) k is a number of rings in the cyclic structure derivatives and k is an integer from 0 to 2;

g) n is a number of ligands and n is an integer from 0 to 4; and

h) m is a number of the photochromic ligand and m is an integer from 1 to 4.

13. The photo-responsive electron-transporting material according to claim 12, wherein ring A is cyclic structure derivative where the cyclic structure is independently selected from a 5- or 6-membered arene or heteroarene, wherein the arene is one or more of benzene, naphthalene, anthracene, pyrene, fluorene and derivatives thereof, and the heteroarene can be pyridine, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, isoquinoline, pyrrole, pyrazine, pyridazine, pyrimidine, benzimidazole, benzothiazole, indole, triazole, tetrazole, pyran, oxadiazole, triazine, tetrazine, and derivatives thereof.

14. The photo-responsive electron-transporting material according to claim 12, wherein ring B is cyclic structure derivative where the cyclic structure is independently selected from a 5- or 6-membered nitrogen-containing heteroarene or heterocycle, wherein the heteroarene or heterocycle is one or more of pyridine, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, isoquioline, pyrrole, pyrazine, pyridazine, pyrimidine, benzimidazole, benzothiazole, indole, triazole, tetrazole, pyran, oxadiazole, triazine, tetrazine, and derivatives thereof.

15. The photo-responsive electron-transporting material according to claim 12, wherein the photochromic unit is at least one selected from the group of a diarylethene, a spiropyran,a spirooxazine, and a rhodamine.

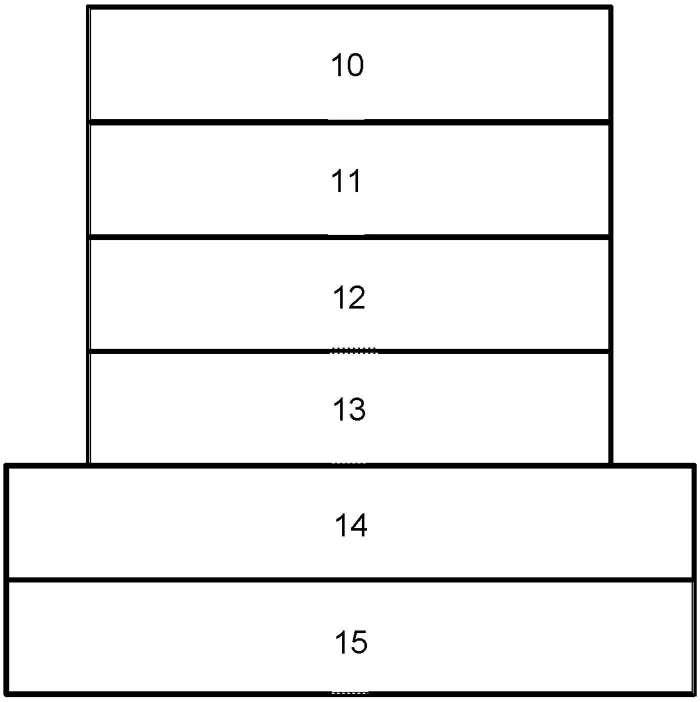


Figure 1

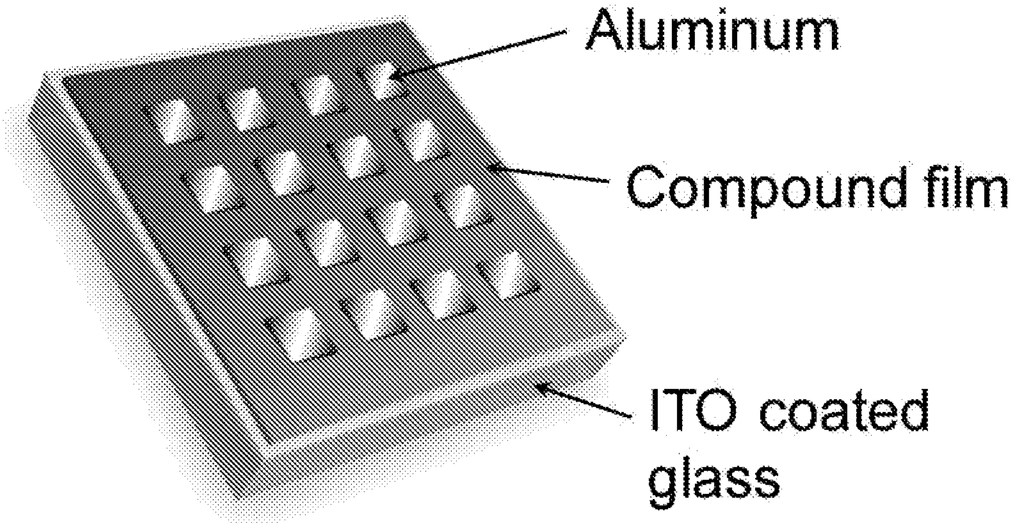


Figure 2

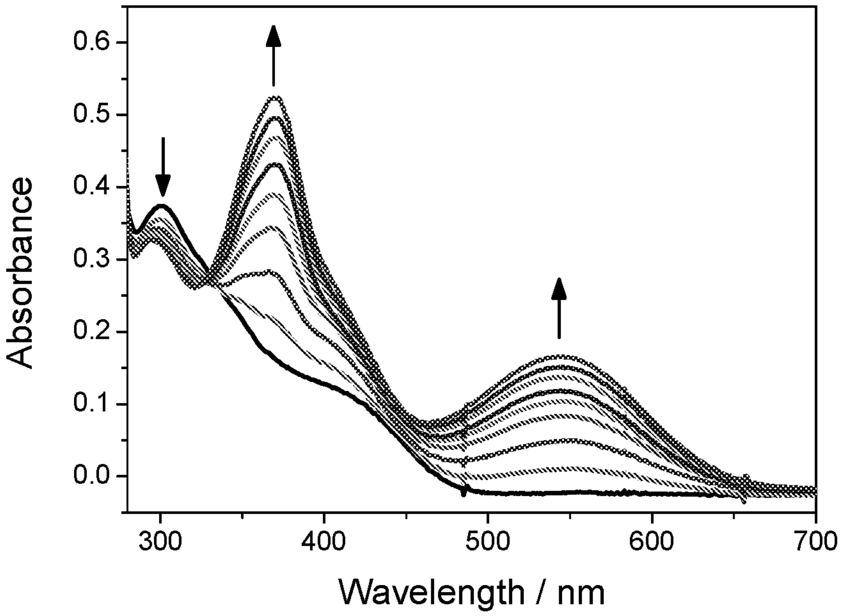


Figure 3

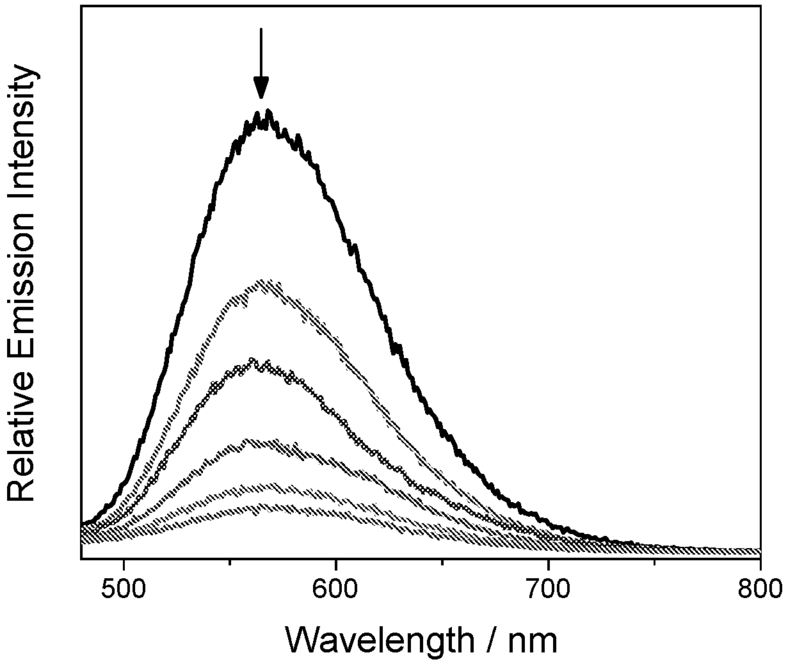


Figure 4

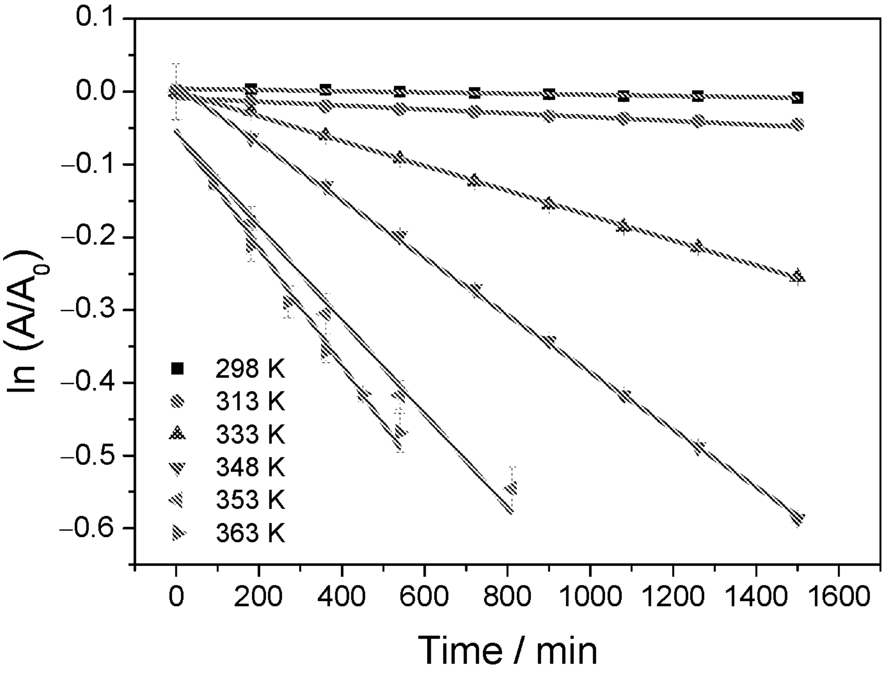


Figure 5

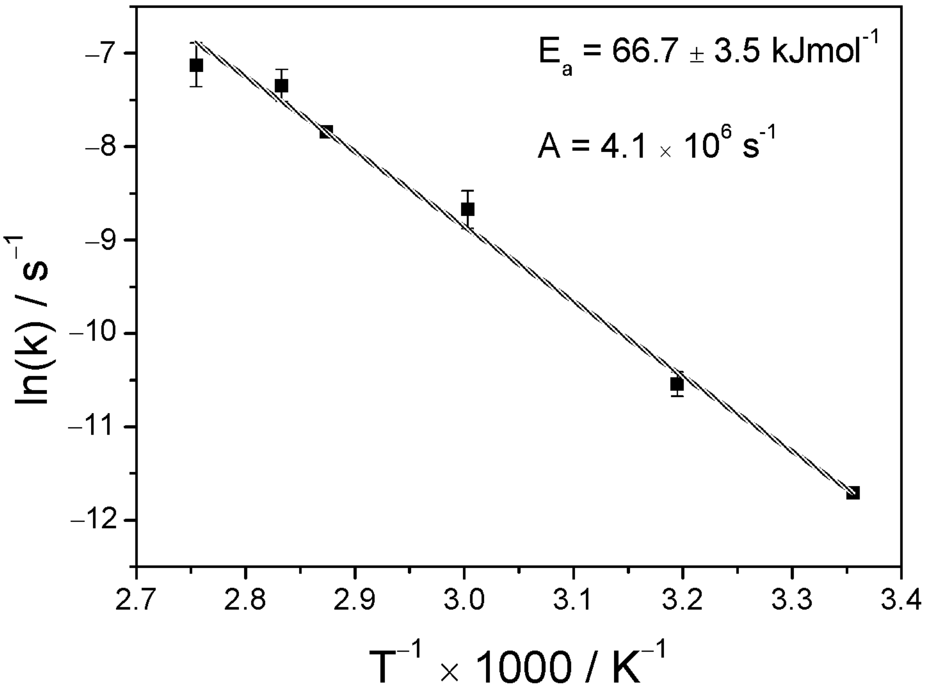


Figure 6

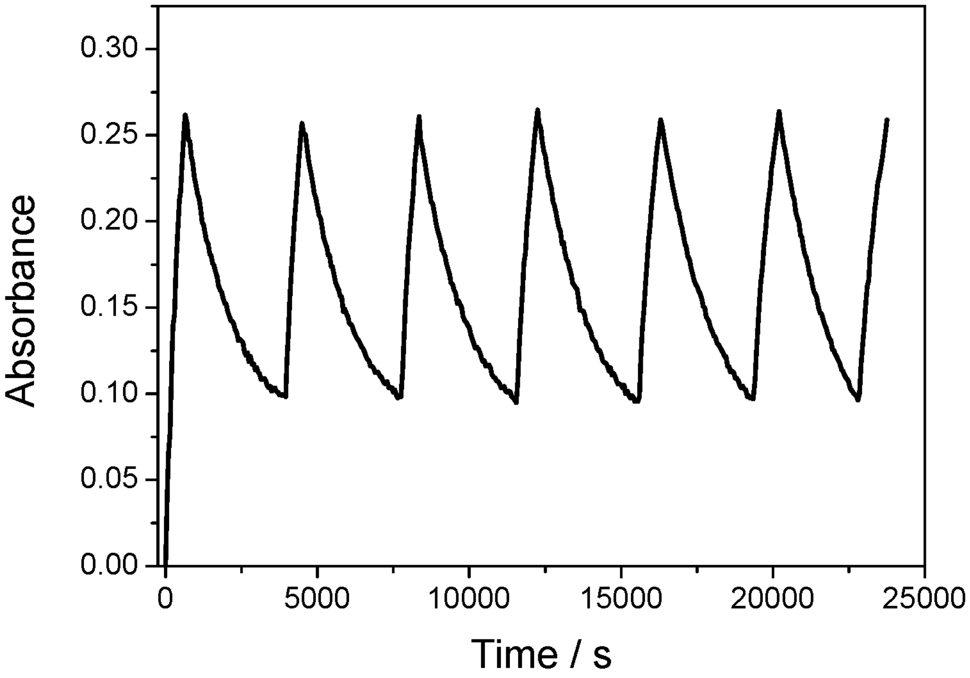


Figure 7

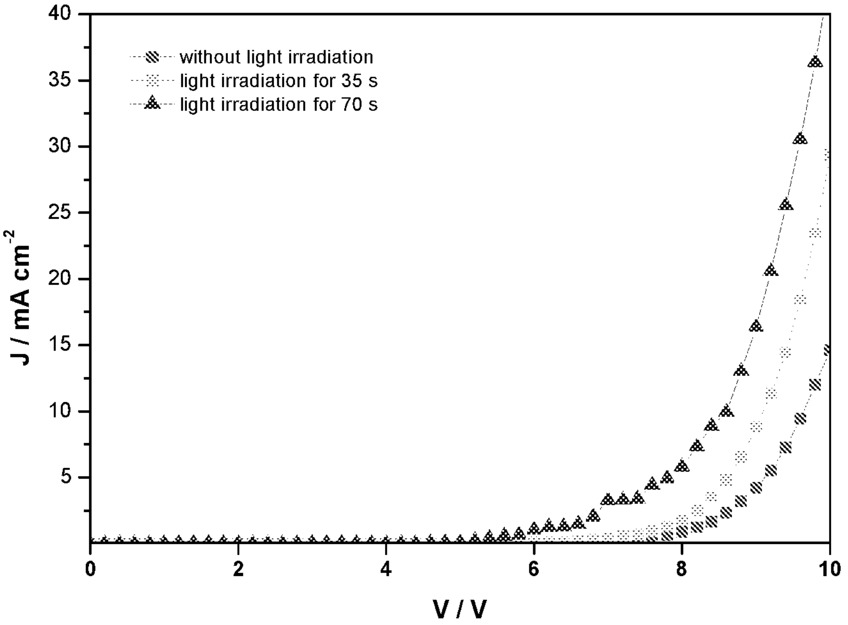


Figure 8

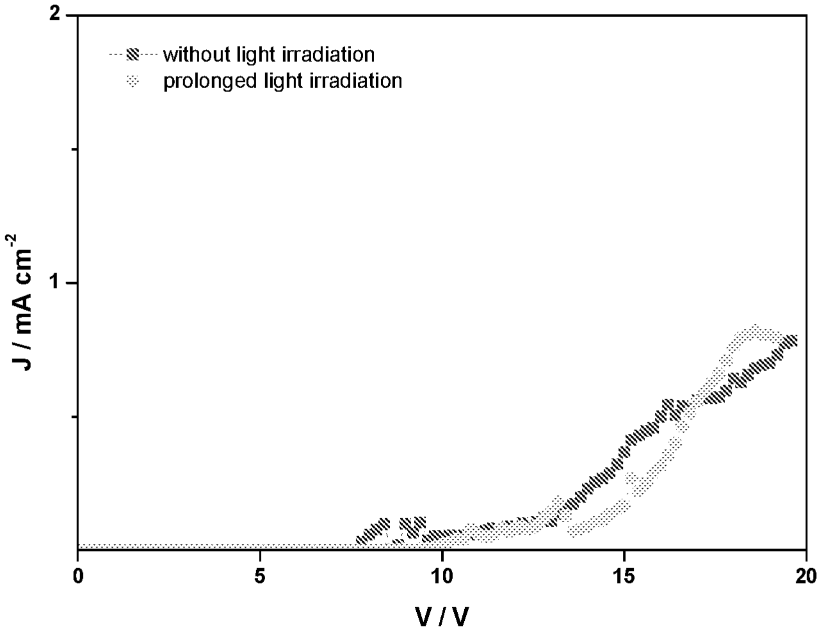


Figure 9

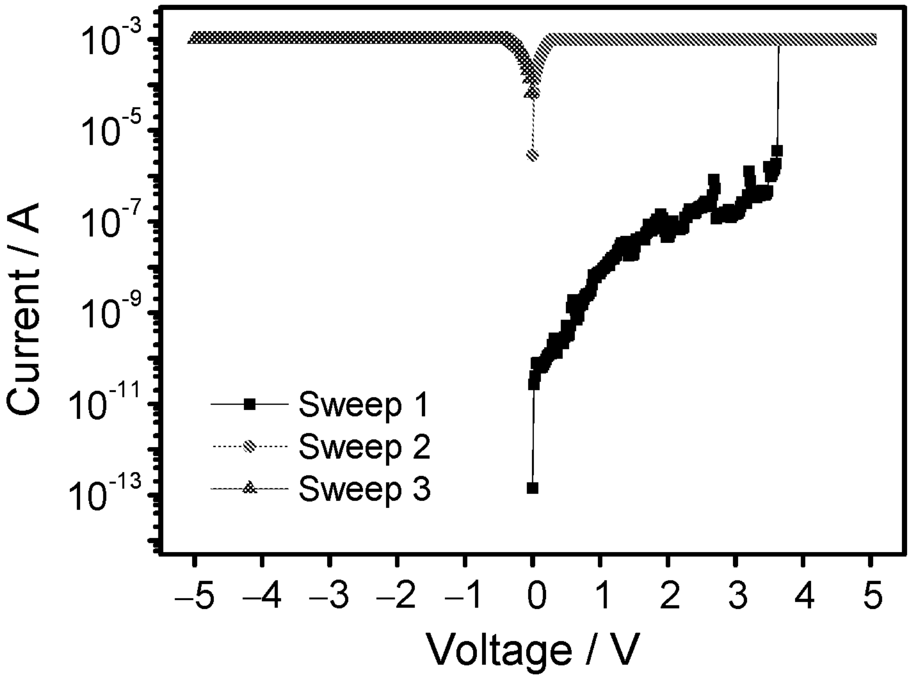


Figure 10

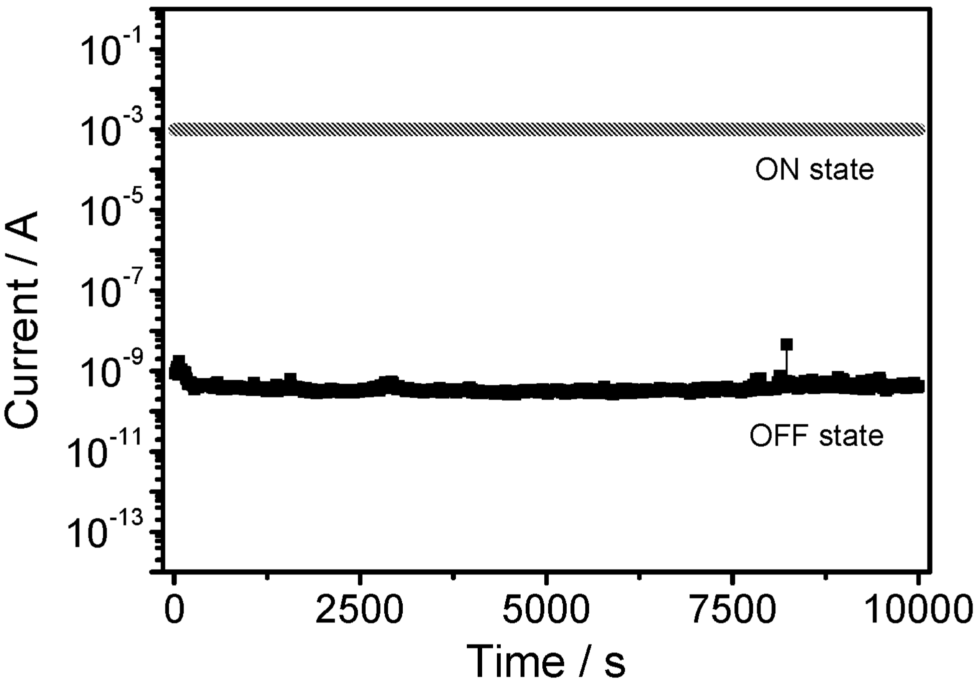


Figure 11

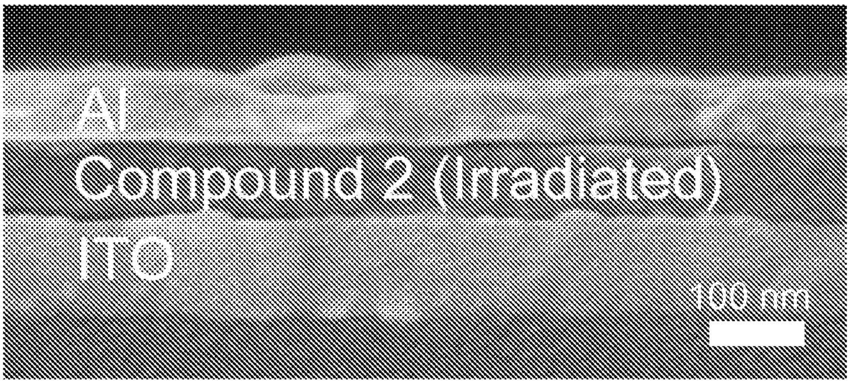


Figure 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2019/105938

A. CLASSIFICATION OF SUBJECT MATTER

C09K 9/02(2006.01)i; C07D 409/14(2006.01)i; C07D 411/14(2006.01)i; C07D 333/50(2006.01)i; G11B 7/2572(2013.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K9/-, C07D409/-, C07D411/-, C07D333/-, G11B7/-

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI,EPODOC,CNPAT,CASREACT(STN),CAPLUS(STN),CNKI: YAM Wing-Wah, Vivian, photo?responsive, coordination, complex, organic electronics, electron?transporting, metal, photo?switch, photochromic, memory device, hydoxyquinoline, diarylethene, spiropyran, rhodamine

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JAAFARI, A. et al. "Fine-tuning the optical properties of aluminium and lithium quinolates through oligothiophene substituents in 2-position" *Synthetic Metals,* Vol. 147, 22 October 2004 (2004-10-22), 175-182	1-7
A	JAAFARI, A. et al. "Fine-tuning the optical properties of aluminium and lithium quinolates through oligothiophene substituents in 2-position" *Synthetic Metals,* Vol. 147, 22 October 2004 (2004-10-22), 175-182	8-15
X	CUI, Yi et al. "Organoboron Compounds with an 8-Hydroxyquinolato Chelate and Its Derivatives: Substituent Effects on Structures and Luminescence" *Inorganic Chemistry,* Vol. 44, No. 3, 01 May 2004 (2004-05-01), 601-609	1-6
A	WO 2005003126 A1 (UNIV HONG KONG) 13 January 2005 (2005-01-13) Claims 1-4	1-15
A	WO 2011063485 A1 (UNIV FED DE OURO PRETO et al.) 03 June 2011 (2011-06-03) Page 29	1-15

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search **27 May 2020**	Date of mailing of the international search report **15 June 2020**
Name and mailing address of the ISA/CN **National Intellectual Property Administration, PRC** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088** **China**	Authorized officer **YUN,Yiming**
Facsimile No. **(86-10)62019451**	Telephone No. **86-(10)-53962157**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 20130116649 A (DAEGU GYEONGBUK INST SCIENCE) 24 October 2013 (2013-10-24) Paragraphs 32-43	1-15

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2019/105938

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
WO	2005003126	A1	13 January 2005	CN	100415739	C	03 September 2008
				US	2005033072	A1	10 February 2005
				US	7355775	B2	08 April 2008
				EP	1648864	A1	26 April 2006
				KR	101089640	B1	06 December 2011
				KR	20060117301	A	16 November 2006
				JP	2007525471	A	06 September 2007
				CN	1820005	A	16 August 2006
				EP	1648864	B1	19 August 2015
				JP	4939937	B2	30 May 2012
				EP	1648864	A4	19 August 2009
WO	2011063485	A1	03 June 2011	BR	PI0910904	A2	11 December 2012
				US	2012313268	A1	13 December 2012
KR	20130116649	A	24 October 2013	KR	101360005	B1	07 February 2014