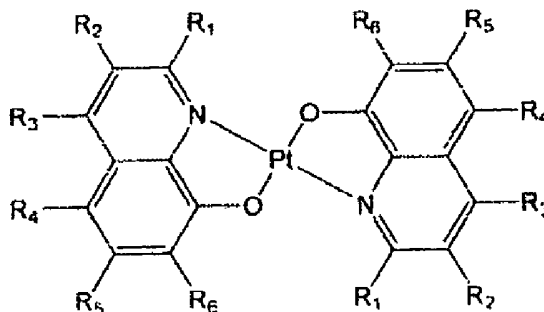




- (51) **International Patent Classification:**
H01L 51/46 (2006.01) *C07F 17/02* (2006.01)
H01L 51/42 (2006.01)
- (21) **International Application Number:**
PCT/CN2011/000176
- (22) **International Filing Date:**
31 January 2011 (31.01.2011)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/302,794 9 February 2010 (09.02.2010) US
- (71) **Applicant (for all designated States except US):** THE UNIVERSITY OF HONG KONG [CN/CN]; Pokfulam Road, Hong Kong (CN).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** CHE, Chiming [CN/CN]; Flat 5, 5th Floor, Block A, Parkway Court, 4 Park Road, Hong Kong (CN). XIANG, Haifeng [CN/CN]; 4th Floor, 36 Po Tuck Road, Shek Tong Tsui, Hong Kong (CN).
- (74) **Agent:** CHINA PATENT AGENT (H. K.) LTD.; 22/F, Great Eagle Centre, 23 Harbour Road, Wanchai, Hong Kong (CN).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report (Art. 21(3))
 - with information concerning incorporation by reference of missing parts and/or elements (Rule 20.6)

(54) **Title:** BIS-(8-QUINOLINOLATO-N,O)PLATINUM (II) BASED ORGANIC PHOTOVOLTAIC CELL



Structure I

(57) **Abstract:** Organic photovoltaic (OPV) cells and methods of forming the cells are provided. An OPV cell can include an organic photoactive layer comprising bis-(8-quinolinolato-N,O)platinum (II) (PtQ₂) having a general structure as Structure I. A method of forming an OPV cell can include forming an organic photoactive layer on a substrate, which can include a transparent electrode. The organic photoactive layer can comprise PtQ₂ having the general structure as Structure (I).

WO 2011/097948 A1

BIS-(8-QUINOLINOLATO-N,O)PLATINUM(II) BASED ORGANIC PHOTOVOLTAIC CELL

CROSS-REFERENCE TO RELATED APPLICATION

5 This application claims the benefit of U.S. provisional application Serial No. 61/302,794, filed February 9, 2010, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

10 This invention relates to organic photovoltaic (OPV) cells using bis-(8-quinolinolato-N,O) platinum (II) (PtQ_2) as an active material.

BACKGROUND OF THE INVENTION

It is widely recognized that fossil fuels, such as petroleum and
15 charcoal, will be consumed soon. In addition, the by-products generated from fossil fuels can contribute to global warming problems due to greenhouse gases such as carbon dioxide. The planet capability of natural purification has been decreased, and that is detrimental to the survival of humans. Thus, there are world-wide efforts to develop environmentally
20 friendly energy resources and devices with low energy consumption and/or driven by renewable energy such as solar energy. Solar cells or photovoltaic (PV) cells are a type of optoelectronic device which generate electricity through the absorption of electromagnetic radiation (UV, visible, and IR radiation). To date, photovoltaic cells made from inorganic
25 semiconductors, such as Si, CdTe, and $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}$, have dominated the solar cell industry. Particularly, poly-silicon (poly-Si) and single crystal silicon (SC-Si) together contributed to nearly 90% of the market share. However, the shortage of Si materials, and the high processing cost of inorganic semiconductors have posted a drawback in the development of
30 the solar cell industry.

In contrast, the potential low cost, ease of process in large scale production, and compatibility on flexible substrates of organic

semiconductors are appealing for photovoltaic applications. Organic photovoltaic (OPV) cells comprise at least one component that utilize organic or organometallic small molecules or polymeric materials for light absorption and charge processes. Harnessing the power of chemical synthesis, a large variety of organic molecules or polymers with different band gaps and absorption coefficients can be synthesized to maximize the light absorption and power generated from the photovoltaic cells. Thus, the organic photovoltaic cell has emerged as a new class of solar cell technologies. (Prog. Photovolt: Res. Appl. 2007; 15, 659).

Within the area of organic photovoltaic cells, various device architectures have been explored including the dye-sensitized solar cell (DSSC), organic/inorganic hybrid organic cells, and organic photovoltaic cells with heterojunctions. In 1986, C. W. Tang found that a bilayer heterojunction structure fabricated from copper phthalocyanine (CuPc) and perylene tetracarboxylic derivative gives a power conversion efficiency (PCE) of 0.95% at Eastman Kodak. Other small molecules such as pentacene, tetracene, and metal phthalocyanines (PCs) are among the most studied donor materials. (Appl. Phys. Lett., 2004, 85, 5427; Appl. Phys. Lett., 2004, 85, 6272; Appl., Phys. Lett., 2005, 86, 243506) Notably, a combination of fullerene (C₆₀) or perylene and organic semiconductor, which has been under development for electronic materials applications since the 1990's, is the most popular structure of organic solar cells. Starting from the 2000's, a PCE of more than 6% has been achieved (Principles of Solar Cells, Hongreung Publication).

Recently, tremendous progress has been made in the development of OPV cells based on π -conjugated semiconductors as electron donor (p-type) materials, such as regio-regular poly(3-alkylthiophene)s (P3HTs), (Adv. Mater. 2006, 18, 572; Appl. Phys. Lett. 2005, 87, 083506; Nat. Mater. 2006, 5, 197) platinum(II) polyene polymer, (Nature Mater. 2007, 6, 521), and oligothiophenes (Adv. Mater. 2006, 18, 2872). Devices with greater than 5% PCE have been achieved from nanostructures of an interpenetrating donor/acceptor polymer network, which is prepared by

limiting the solvent evaporation rate or post-fabrication thermal annealing. (Adv. Funct. Mater. 2003, 13, 85; Appl. Phys. Lett. 2005, 86, 063502; Adv. Funct. Mater. 2005, 15, 1617; Nat. Mater. 2005, 4, 864)

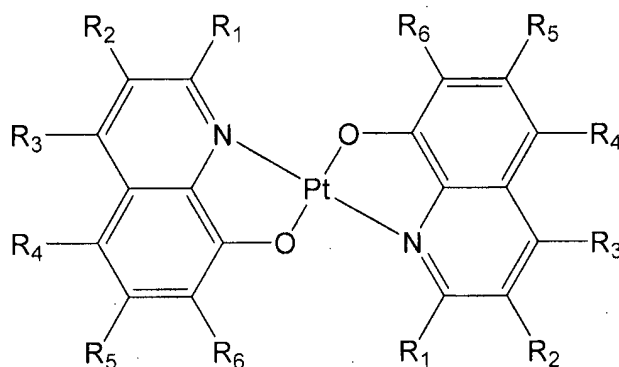
Bis-(8-quinolinolato-N,O) platinum (II) (PtQ₂) complexes were first
5 prepared by R. Ballardini et. al. in 1978 (Inorganica Chimica Acta 1978, 31, 1, L423 - L424), which show orange to red emissions in dilute solutions. However, no practical application for PtQ₂ complexes was found until 2008. In 2008, Che fabricated deep red to near infrared organic light-emitting diodes (OLEDs) from PtQ₂ complexes (Applied Physics
10 Letter 2008, 92, 16, 163305). As the device efficiency is low (up to 0.32 cd/A), no further development in OLED application has been made.

The references cited in this application are incorporated herein by reference.

15 BRIEF SUMMARY OF THE INVENTION

The present invention relates to an organic photovoltaic cell which contains at least one bis-(8-quinolinolato-N,O)platinum (II) (PtQ₂) complex and corresponding derivatives as a light absorption and charge-transporting material in an organic photoactive layer. The disclosed
20 bis-(8-quinolinolato-N,O)platinum (II) (PtQ₂) complexes and their derivatives have photocurrent/power generation properties. This invention relates the organometallic quinacridone bis-(8-quinolinolato-N,O)platinum (II) (PtQ₂) complex derivative-based photovoltaic cells for potential applications in batteries, energy storage, and powering up electronics.

25 This invention relates organic photovoltaic (OPV) cells using bis-(8-quinolinolato-N,O)platinum (II) (PtQ₂) with structure I as an active material:



Structure I

wherein R_1 - R_6 are independently hydrogen, halogen, hydroxyl, an
 5 unsubstituted alkyl, a substituted alkyl, cycloalkyl, an unsubstituted aryl, a
 substituted aryl, acyl, alkoxy, acyloxy, amino, nitro, acylamino, aralkyl,
 cyano, carboxyl, thio, styryl, aminocarbonyl, carbamoyl, aryloxycarbonyl,
 phenoxycarbonyl, or an alkoxycarbonyl group.

The OPV cell can be single layer, multi-layer, tandem structured,
 10 and/or a dispersed heterojunction OPV cell.

In an embodiment, an organic photovoltaic (OPV) cell can include an
 organic photoactive layer comprising bis-(8-quinolinolato-N,O)platinum
 (II) (PtQ_2) having structure I, wherein R_1 - R_6 are independently hydrogen,
 halogen, hydroxyl, an unsubstituted alkyl, a substituted alkyl, cycloalkyl,
 15 an unsubstituted aryl, a substituted aryl, acyl, alkoxy, acyloxy, amino,
 nitro, acylamino, aralkyl, cyano, carboxyl, thio, styryl, aminocarbonyl,
 carbamoyl, aryloxycarbonyl, phenoxycarbonyl, or an alkoxycarbonyl
 group.

In another embodiment, an OPV cell can include one of Complexes
 20 1-5 as the active layer therein.

In another embodiment, a method of forming an organic photovoltaic
 (OPV) cell can include the step of forming an organic photoactive layer on
 a substrate (which can include a transparent electrode), wherein the
 organic photoactive layer comprises bis-(8-quinolinolato-N,O)platinum (II)
 25 (PtQ_2) having structure I, wherein R_1 - R_6 are independently hydrogen,
 halogen, hydroxyl, an unsubstituted alkyl, a substituted alkyl, cycloalkyl,

an unsubstituted aryl, a substituted aryl, acyl, alkoxy, acyloxy, amino, nitro, acylamino, aralkyl, cyano, carboxyl, thio, styryl, aminocarbonyl, carbamoyl, aryloxycarbonyl, phenoxycarbonyl, or an alkoxycarbonyl group.

5

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of an organic photovoltaic cell incorporating the present invention;

Figure 2 shows current-density vs. voltage (J-V) curves of an organic photovoltaic cell fabricated with complex 5 in the dark and under illumination;

Figure 3 is a scanning electron micrograph image of complex 1 on a silicon dioxide surface;

Figure 4 is a scanning electron micrograph image of complex 2 on a silicon dioxide surface;

Figure 5 is a scanning electron micrograph image of complex 3 on a silicon dioxide surface;

Figure 6 is a scanning electron micrograph image of complex 4 on a silicon dioxide surface;

Figure 7 is a scanning electron micrograph image of complex 5 on a silicon dioxide surface; and

Figure 8 is a power X-ray diffraction pattern of a thin film 5 (50 nm) after annealing at different temperatures: (a) 25°C; (b) 80°C ; and (c) 100°C.

25

DETAILED DISCLOSURE OF THE INVENTION

The preferred embodiments of the present invention will now be described with reference to the accompanying drawings. These embodiments will be presented only by way of example for implementing the invention and not by way of limitation.

When the terms “on” or “over” or “above” are used herein, when referring to layers, regions, patterns, or structures, it is understood that the

layer, region, pattern, or structure can be directly on (and in contact with) another layer or structure, or intervening layers, regions, patterns, or structures may also be present. When the terms “under” or “below” are used herein, when referring to layers, regions, patterns, or structures, it is understood that the layer, region, pattern, or structure can be directly under (and in contact with) the other layer or structure, or intervening layers, regions, patterns, or structures may also be present.

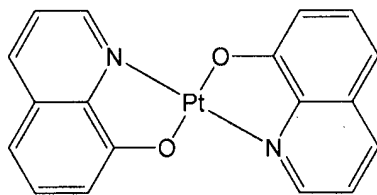
Figure 1 shows a cross section through a photovoltaic cell incorporating an organic photoactive layer according to an embodiment of the present invention. The organic photoactive layer can be on a transparent electrode or carrier material on a substrate. The substrate is not specifically limited as long as it is transparent, and it can be made of, for example, glass, plastic, polymer foils, crystal, or similar materials. The electrode 2 of the present invention may be made from any transparent conducting materials. Electrode 2 (anode) may include, for example, indium-tin-oxide (ITO), other transparent metal oxides, carbon nanotubes, conducting polymers such as polyethylenedioxythiophene, poly(3,4-ethylenedioxythiophene)poly(styrene-sulfonate) (PEDOT:PSS), polyacetylene, polypyrrole, polythiophene, polyaniline, and composite polymers with carbon nanotubes, among other examples. After the organic photoactive layer is deposited, electrode 1 is then deposited. Electrode 1 is not specifically limited and examples may include Al, Ag, Mg, Cu, Au, In, Zn, an alkali metal (group 1 metal), an alkali earth metal (group 2 metal), a transition metal, rare earth metal, or alloys. In an embodiment, the thickness of electrode 1 (cathode) can be from 20 nm to 1000 nm.

The organic photoactive layer can include at least an organometallic PtQ_2 semiconductor having the chemical structure of structure I; or an organic semiconductor having chemical structure of structure I that acts as an electron donor and electron acceptor layer (donor-acceptor heterojunction). The donor-acceptor heterojunction in an embodiment of the present invention could be bulk heterojunction, blended heterojunction, or connected in series as stacked or tandem cell. In an embodiment, the

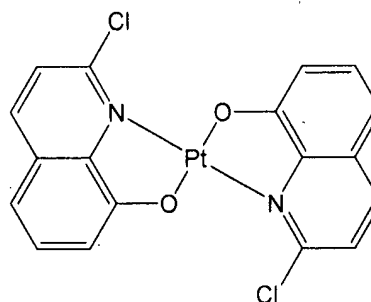
thickness of the PtQ₂ layer can be from 20 nm to 40 nm.

The electron acceptor layer in the organic photoactive layer of the present invention can be any organic semiconductor which exhibits electron accepting properties or electron transport properties. Examples of
5 electron acceptor layer may include, but not limited to, perylene derivatives, 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI), quinoxaline derivatives, poly(phenylquinoxaline) (PPQ), C₆₀, and composite polymers containing C₆₀. In an embodiment, the thickness of the electron accepting layer can be from 20 nm to 80 nm.

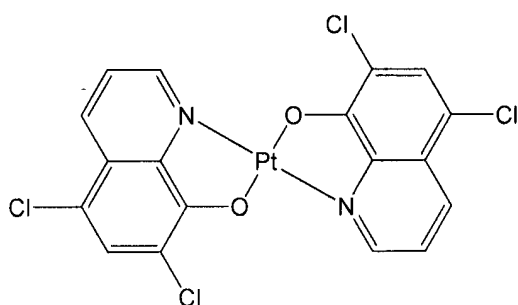
10 The PtQ₂ complexes with chemical structure of Structure I can be referred to as cyclometallated complexes. The platinum center in Structure I is in a +2 oxidation state and has a square planar geometry. The coordination sites of the platinum center are occupied by two deprotonated 8-hydroxquinoline units through one nitrogen atom and one oxygen atom.
15 Representative examples of PtQ₂ complexes (Complexes 1-5) based on Structure I are shown below:



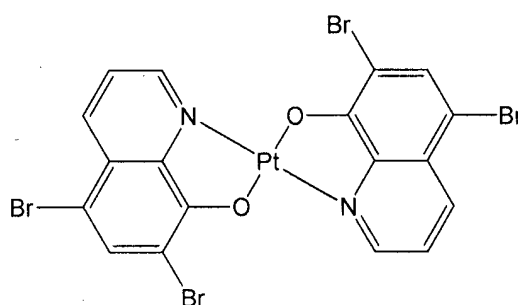
Complex 1



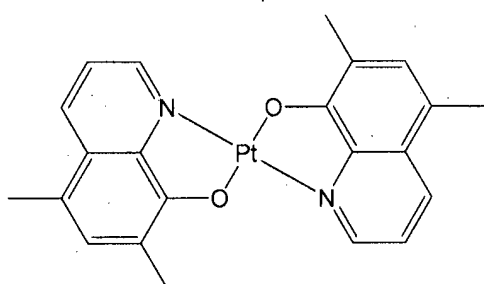
Complex 2



Complex 3

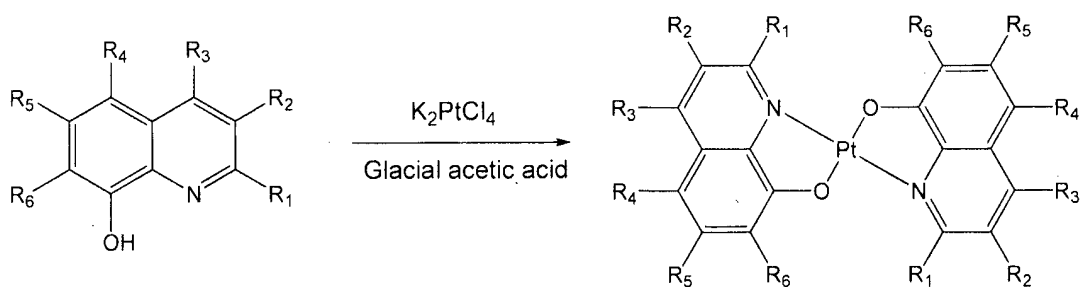


Complex 4



Complex 5

In preferred embodiments, there is a general method for preparing PtQ₂ complexes with the corresponding 8-hydroxyquinoline in the representative examples. To prepare these PtQ₂ complexes, a mixture of potassium tetrachloroplatinate (K₂PtCl₄) and 8-hydroxyquinoline in glacial acetic acid was refluxed for 24 hours, and gave a red suspension. The red solid was washed with water and acetone, and recrystallized in CH₂Cl₂ or DMF. Reaction I below illustrates the preferred use of acetic acid as a solvent in forming neutral platinum complexes.



Reaction I

In an embodiment, an exciton blocking layer can be introduced
 5 between the organic photoactive layer and electrode 1 (cathode) as a
 double heterostructure. Examples of the exciton blocking layer may
 include, but are not limited to, bathocuproine derivatives,
 bathophenanthroline derivatives, tris-8-hydroxy-quinolinato aluminum
 derivatives, and 2,9-Bis(naphthalen-2-yl)-4,7-diphenyl-1,10-phenanthroline
 10 derivatives. In an embodiment, the thickness of the photoactive layer can
 be from 20 nm to 120 nm. In an embodiment, the thickness of the exciton
 blocking layer can be from 7.5 nm to 10 nm.

In one embodiment, the organic photoactive layer, including the PtQ₂
 complex and electron acceptor layer, can be fabricated by vacuum
 15 deposition, electron beam deposition, sputtering, spray coating, spin
 coating, drop casting, and dip coating. The exciton blocking layer and
 electrode(s) can be fabricated by vacuum deposition, electron beam
 deposition, and sputtering.

In another preferred embodiment, the organic photoactive layer,
 20 exciton blocking layer, and electrode(s) can be deposited onto the
 transparent electrode substrate sequentially by vacuum deposition without
 breaking the vacuum during the fabrication process.

More preferably, the PtQ₂ complexes used in the organic photovoltaic
 cell should form a crystalline or polycrystalline thin film on the substrate.

25 The PtQ₂ complexes used in the organic photovoltaic cell should
 have high absorption coefficients of, for example, $\alpha > 10^5 \text{ cm}^{-1}$, and large
 spectral coverage within the solar spectrum.

In one embodiment, the electrode 2 (anode) is transparent and is directly on and in contact with the substrate. The organic photoactive layer is directly on and in contact with the electrode 2, and the electrode 1 (cathode) is metal and is directly on and in contact with the organic photoactive layer. In an alternative embodiment, an exciton blocking layer can be present between the organic photoactive layer and electrode 1, such that the exciton blocking layer is in contact with both the organic photoactive layer and electrode 1.

The following examples are illustrative of the practice of the present invention, but should not be considered in any way as limiting the scope thereof.

MATERIALS AND METHODS

All patents, patent applications, provisional applications, and publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

Following are examples that illustrate procedures for practicing the invention. These examples should not be construed as limiting. All percentages are by weight and all solvent mixture proportions are by volume unless otherwise noted.

EXAMPLE 1—

The configuration of bis-(8-quinolinolato-N,O)platinum (II) (PtQ_2) based organic photovoltaic cell in the present invention is schematically shown in Figure 1. The organic photovoltaic cell has multiple layers as shown. The transparent electrode substrate is preferably indium-tin oxide on glass (ITO-glass substrate). An organic photoactive layer containing at least one PtQ_2 complex is deposited onto the ITO glass by vacuum deposition. An electron donor layer, preferably comprising C_{60} can be deposited onto the PtQ_2 complex(es) or co-deposited with the PtQ_2 complex(es). An exciton blocking layer preferably comprising

bathocuproine (BCP) is then deposited onto the organic photoactive layer without breaking the vacuum. The metal electrode, preferably comprising Al, is then placed on top of the exciton blocking layer and organic photoactive layer.

5

EXAMPLE 2—

Thermal stabilities of the PtQ₂ complexes were characterized by thermogravimetric analysis (TGA) before vacuum deposition. The decomposition temperature (T_d) was measured with a scanning rate of 15 °C/min under a nitrogen atmosphere. The decomposition temperature of
10 Complexes 1 and 5 are 477°C and 461°C respectively.

EXAMPLE 3—

The film morphologies (Figures 3-7) of PtQ₂ complexes 1-5 on a
15 silicon dioxide surface were characterized by scanning electron microscopy (SEM). Figure 3 shows complex 1, Figure 4 shows complex 2, Figure 5 shows complex 3, Figure 6 shows complex 4, and Figure 7 shows complex 5. All films were deposited with a deposition rate of 2 Å s⁻¹. As shown in Figure 3, complex 1 exhibits a thin film with micrometer-sized
20 crystal grains and complexes 2-5 exhibit continuous thin film with nano-sized crystal grains (Figures 4-7). To confirm the crystalline nature of the thin film, power X-ray diffraction experiments were performed on vacuum deposited thin film 5. Thin film of complex 5 shows a sharp power X-ray diffraction peak at $2\theta = 9.2^\circ$, which indicates the thin film is
25 crystalline and the molecules are arranged with a d spacing of 9.60 Å. The thin film 5 becomes more crystalline upon annealing at 80°C and 100°C as indicated by the enhancement in diffraction intensity (Figure 8).

EXAMPLE 4—

30 The power conversion efficiency (η), fill factor (FF), open-current voltage (V_{OC}), and short-circuit current density (J_{SC}) of the organic photovoltaic cell fabricated with PtQ₂ complexes were measured

respectively and their performances are listed in Table 1. The PtQ₂ based photovoltaic devices were fabricated by vacuum deposition. The photovoltaic device generates direct current upon illumination and the power conversion efficiency and fill factor are comparable to other organic photovoltaic devices. A maximum power conversion efficiency of 2.03% is achieved using a bulk heterojunction device configuration with C₆₀ and BCP as an electron donor layer and an exciton blocking layer respectively.

EXAMPLE 5—

10 An example of using organoplatinum (II) (PtQ₂) complexes as organic photovoltaic cell described by the current invention were prepared with the following device structure:

ITO/PtQ₂ complexes (X nm)/C₆₀ (Y nm)/BCP (7.5nm)/Al(100 nm).

Device A was fabricated using complex 1 as an electron donor in the photoactive layer. Complex 1 was deposited onto the prefabricated transparent ITO glass by vacuum deposition at a rate of 2 Å s⁻¹. The thickness of thin film 1 is 30 nm. C₆₀ (40 nm) and BCP layers (7.5 nm) were deposited subsequently onto the PtQ₂ layer without breaking the vacuum. A 100 nm aluminum layer was deposited as metal electrode.

20 Device A gives a power conversion efficiency $\eta=0.17\%$, fill factor FF = 30%, open-current voltage $V_{OC} = 0.25$ V, and short-circuit current density $J_{SC} = 2.25$ mA cm⁻².

EXAMPLE 6—

25 An example of an embodiment of the present invention was fabricated using complex 5 as electron donor in the photoactive layer of an organic photovoltaic cell. Device B was fabricated with the same device configuration and fabrication procedure as Device A described in Example 5. Device B gives a power conversion efficiency $\eta=1.70\%$, fill factor FF = 40%, open-current voltage $V_{OC} = 0.32$ V, and short-circuit current density $J_{SC} = 13.3$ mA cm⁻².

30

EXAMPLE 7—

The effect of the thickness of an electron accepting layer on the performance of an organic photovoltaic cell was studied. Devices B, C, and D were fabricated using complex 5 (30 nm) as an electron donor and C₆₀ as an electron-accepting layer in the photoactive layer described by the current invention. The thickness of the C₆₀ (electron-accepting layer) of devices B, C, and D are 40, 50, and 60 nm, respectively. Device B gives a power conversion efficiency $\eta=1.70\%$, fill factor $FF = 40\%$, open-current voltage $V_{OC} = 0.32$ V, and short-circuit current density $J_{SC} = 13.3$ mA cm⁻², while the power conversion efficiency of devices C and D are slightly lowered to 1.45 % and 1.13%, respectively.

EXAMPLE 8—

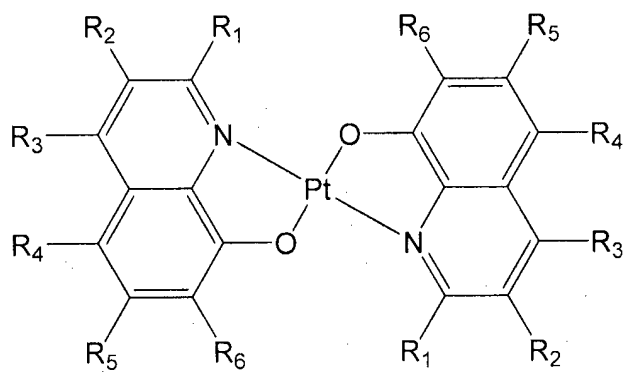
The effect of post-fabrication annealing on the performance of an organic photovoltaic cell was studied. Device E was fabricated using complex 5 following the procedure described in Example 5 with the device structure of ITO/Complex 5 (30 nm)/C₆₀ (50 nm)/BCP (7.5nm)/Al(100 nm). Device E was then annealed at 80°C under nitrogen atmosphere for 1 hour. Device E gives a power conversion efficiency $\eta=1.93\%$, fill factor $FF = 38\%$, open-current voltage $V_{OC} = 0.47$ V, and short-circuit current density $J_{SC} = 10.7$ mA cm⁻². Power X-ray diffraction study (Figure 8) of annealed thin film 5 showed an increase in intensity upon annealing at 80 °C, suggesting that the thin film becomes more crystalline after an annealing process. Device F fabricated with the same device configuration and procedure resulted in an increase in the power conversion efficiency (2.07%) and fill factor (42.9%) after annealing at 80°C for 2 hours.

Table 1

Device	Complex	Annealing Condition	C ₆₀ Thickness	J _{sc} (mA/cm ²)	VOC (V)	FF (%)	η (%)
A	1	n/a	40	2.25	0.25	30	0.17
B	5	n/a	40	13.3	0.32	40	1.70
C	5	n/a	50	8.08	0.57	31	1.45
D	5	n/a	60	5.65	0.44	46	1.13
E	5	80°C, 1 hour	50	10.7	0.47	38	1.93
F	5	80°C, 2 hour	50	8.14	0.58	43	2.03

CLAIMS

1. An organic photovoltaic cell comprising
 a substrate;
 5 a transparent electrode;
 an organic photoactive layer; and
 a metal electrode;
 wherein the organic photoactive layer comprises
 bis-(8-quinolinolato-N,O)platinum (II) (PtQ₂) compounds having structure
 10 I:

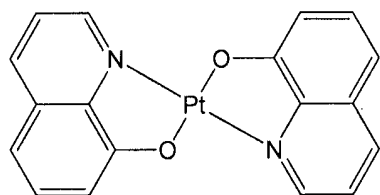


Structure I

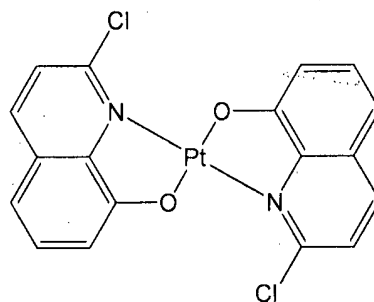
- 15 wherein R₁-R₆ are independently selected from hydrogen, halogen, hydroxyl, an unsubstituted alkyl, a substituted alkyl, cycloalkyl, an unsubstituted aryl, a substituted aryl, acyl, alkoxy, acyloxy, amino, nitro, acylamino, aralkyl, cyano, carboxyl, thio, styryl, aminocarbonyl, carbamoyl, aryloxycarbonyl, phenoxycarbonyl, or an alkoxycarbonyl
 20 group.

2. The organic photovoltaic cell according to claim 1, wherein R₁-R₆ are independently selected from hydrogen, fluorine, chlorine, bromine, iodine, a C₁-C₆ alkyl, a C₃-C₆ cycloalkyl or a C₆-C₁₂ aryl group.

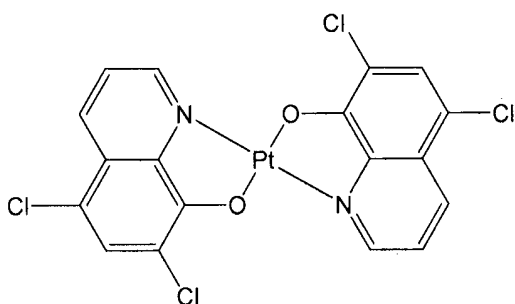
3. The organic photovoltaic cell according to claim 1 or 2, wherein
 25 the bis-(8-quinolinolato-N,O)platinum (II) compounds are selected from the following compounds:



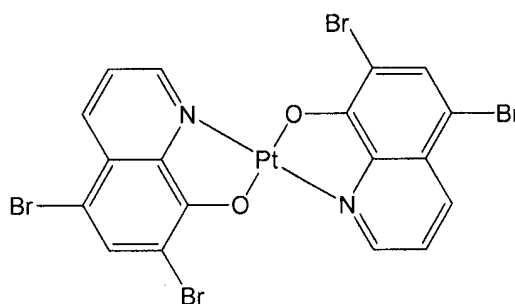
Complex 1



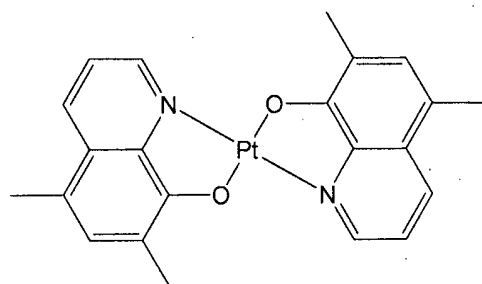
Complex 2



Complex 3



Complex 4



Complex 5

4. The organic photovoltaic cell according to claim 1, wherein the organic photovoltaic cell is a single layer cell, a multilayer cell, a tandem cell or a dispersed heterojunction cell.

5. The organic photovoltaic cell according to claim 1, wherein the transparent electrode is on and in contact with the substrate, and wherein the organic photoactive layer is on and in contact with the transparent electrode, and wherein the metal electrode is on the organic photoactive layer.

6. The organic photovoltaic cell according to claim 5, further comprising an exciton blocking layer on and in contact with the organic photoactive layer, wherein the metal electrode is on and in contact with the

exciton blocking layer.

7. The organic photovoltaic cell according to claim 6, wherein the exciton blocking layer comprises a bathocuproine derivative, a bathophenanthroline derivative, a tris-8-hydroxy-quinolinato aluminum
5 derivative, or a 2,9-Bis(naphthalen-2-yl)-4,7-diphenyl-1,10-phenanthroline derivative.

8. The organic photovoltaic cell according to claim 6, wherein a thickness of the exciton blocking layer is from 7.5 nm to 10 nm.

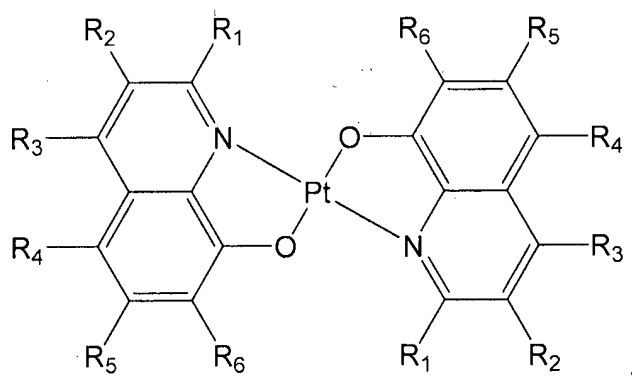
9. The organic photovoltaic cell according to claim 1, wherein a
10 thickness of the organic photoactive layer is from 20 nm to 120 nm.

10. The organic photovoltaic cell according to claim 1, wherein the organic photoactive layer further comprises an electron acceptor layer.

11. The organic photovoltaic cell according to claim 13, wherein the electron acceptor layer comprises a perylene derivative,
15 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI), a quinoxaline derivative, poly(phenylquinoxaline) (PPQ), C₆₀, or a composite polymer containing C₆₀.

12. The organic photovoltaic cell according to claim 1, wherein the transparent electrode is on and in contact with the substrate; and
20 the metal electrode is on the active layer,
wherein the active layer is on and in contact with the transparent electrode.

13. A method of forming an organic photovoltaic cell, comprising:
forming an organic photoactive layer on a substrate, wherein the
25 organic photoactive layer comprises bis-(8-quinolinolato-N,O)platinum (II) (PtQ₂) having structure I:



Structure I

wherein R_1 - R_6 are independently hydrogen, halogen, hydroxyl, an
 5 unsubstituted alkyl, a substituted alkyl, cycloalkyl, an unsubstituted aryl, a
 substituted aryl, acyl, alkoxy, acyloxy, amino, nitro, acylamino, aralkyl,
 cyano, carboxyl, thio, styryl, aminocarbonyl, carbamoyl, aryloxycarbonyl,
 phenoxy carbonyl, or an alkoxy carbonyl group.

14. The method according to claim 13, further comprising:

10 forming a transparent electrode on and in contact with the substrate
 before forming the organic photoactive layer, such that the organic
 photoactive layer is formed on and in contact with the transparent
 electrode; and

forming a metal electrode on the organic photoactive layer.

15 15. The method according to claim 14, wherein the organic
 photoactive layer and the metal electrode are formed sequentially by
 vacuum deposition without breaking vacuum.

16. The method according to claim 13, wherein forming the organic
 photoactive layer comprises:

20 refluxing a mixture of potassium tetrachloroplatinate (K_2PtCl_4) and
 8-hydroxyquinoline in glacial acetic acid to give a suspension;

washing the suspension with water and acetone; and

recrystallizing the suspension in CH_2Cl_2 or DMF to give the PtQ_2
 having structure I.

25

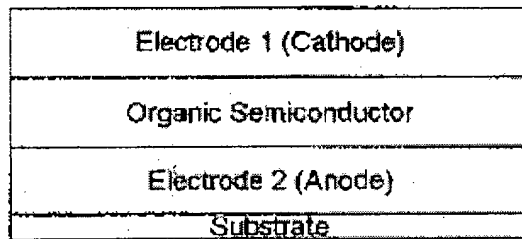


FIG. 1

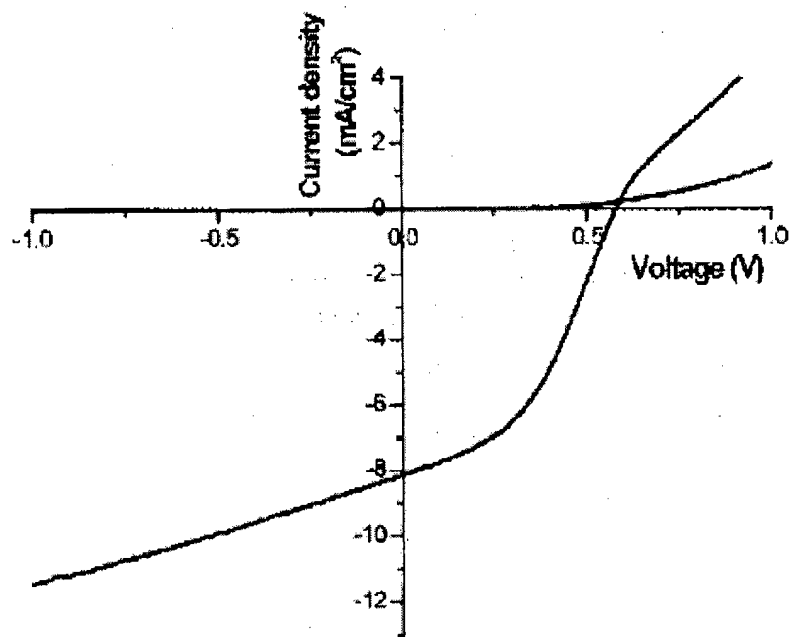


FIG. 2

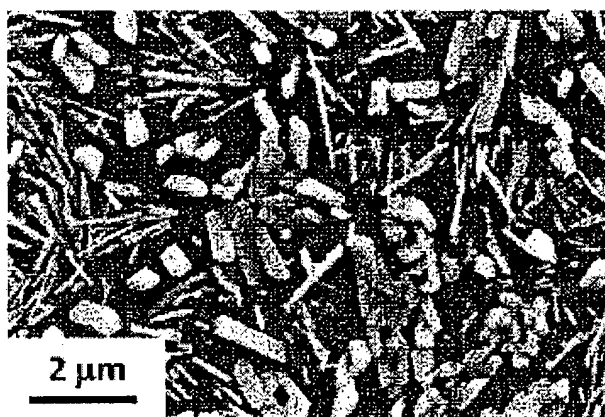


FIG. 3



FIG. 4



FIG. 5

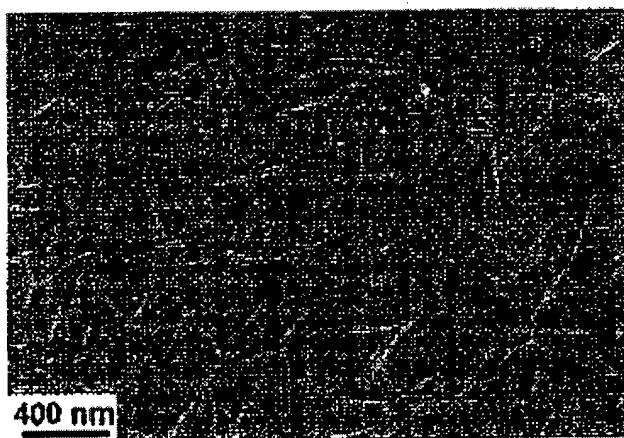


FIG. 6

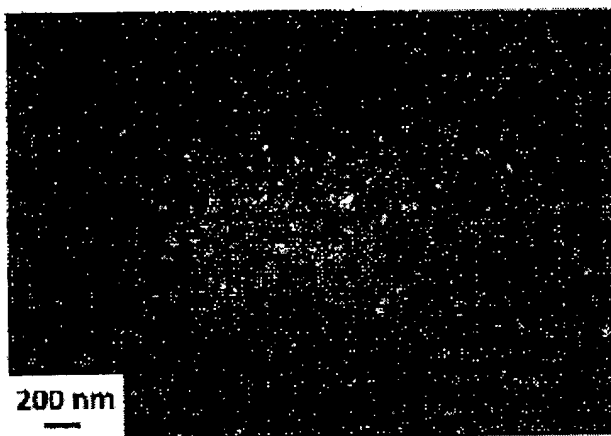


FIG. 7

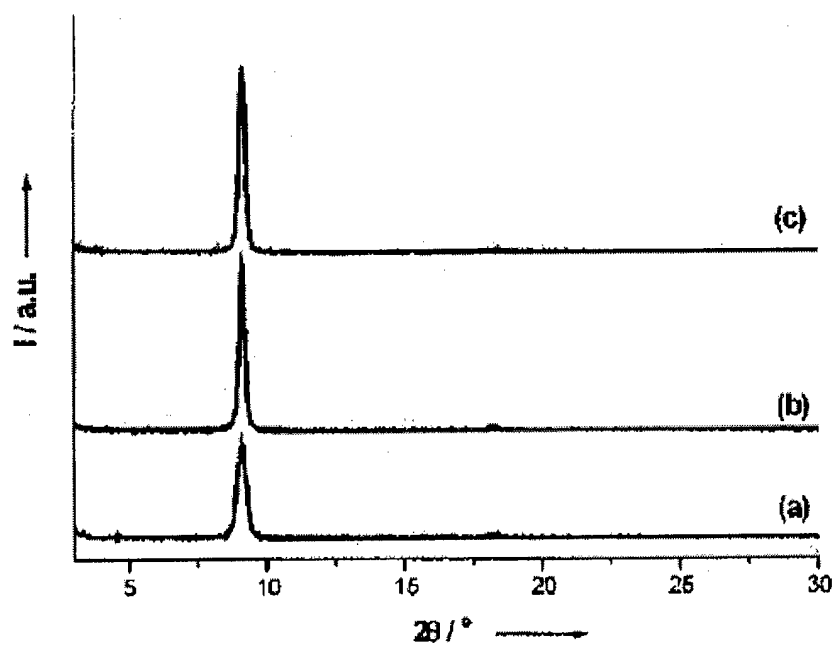


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2011/000176

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: H01L 51/-; C07F 17/-

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; CPRS; CNKI; CA

quinolinolato platinum Pt cell photoactive photovoltaic electrode

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	XIANG, Haifeng et al. Deep-red to near-infrared electrophosphorescence based on bis(8-hydroxyquinolato) platinum(II) complexes. Appl. Phys. Lett. 22 April 2008. Vol.92, No.16, 163305 (2008)	1-16
A	MASAKO Kato et al. Bis(8-quinolinolato-N,O)platinum(II) and its synthetic intermediate, 8-hydroxyquinolinium dichloro(8-quinolinolato-N,O)platinat(II) tetrahydrate. ACTA CRYSTALLOGRAPHICA SECTION C CRYSTAL STRUCTURE COMMUNICATIONS, March 2002, Vol. 58, Issue 3, Pages m147-m149, ISSN 0108-2701	1-12
A	CN 101562230A(CHANG CHUN INSTITUTE OF APPLIED CHEMISTRY CHINESE ACADEMY OF SCIENCES) 21 Oct. 2009(21.10.2009) the whole document	13-16

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

<p>* Special categories of cited documents:</p> <p>“A” document defining the general state of the art which is not considered to be of particular relevance</p> <p>“E” earlier application or patent but published on or after the international filing date</p> <p>“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)</p> <p>“O” document referring to an oral disclosure, use, exhibition or other means</p> <p>“P” document published prior to the international filing date but later than the priority date claimed</p>	<p>“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</p> <p>“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</p> <p>“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</p> <p>“&” document member of the same patent family</p>
--	---

Date of the actual completion of the international search 03 May 2011(03.05.2011)	Date of mailing of the international search report 02 Jun. 2011 (02.06.2011)
--	--

Name and mailing address of the ISA/CN
The State Intellectual Property Office, the P.R.China
6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China
100088
Facsimile No. 86-10-62019451

Authorized officer
WANG, Qingeng
Telephone No. (86-10)82245406

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2011/000176

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN 101562230A	21.10.2009	CN 101562230B	08.12.2010

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/000176

A. CLASSIFICATION OF SUBJECT MATTER

H01L 51/46(2006.01)i

H01L 51/42(2006.01)i

C07F 17/02(2006.01)i