

Controlled Fabrication and Optoelectrical Properties of Metallosupramolecular Films Based on Ruthenium(II) Phthalocyanines and 4,4'-Bipyridine Covalently Anchored on Inorganic Substrates

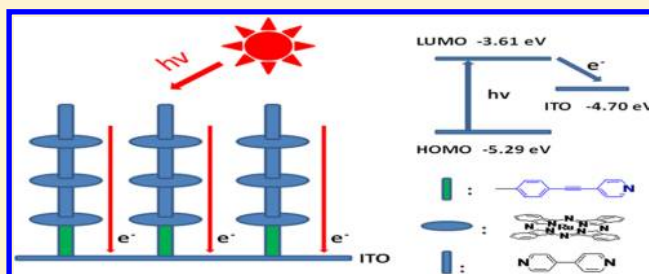
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S Supporting Information

ABSTRACT: Fully conjugated metallosupramolecular self-assembled multilayer films were controllably fabricated based on bibenzonitril-phthalocyaninato ruthenium(II) (BBPR) and 4,4'-bipyridine (BP) via axially coordination interaction between ruthenium ions and the pyridine groups on the modified substrates. The substrates were first functionalized by 4-(pyridine-4-ylethynyl)benzenic diazonium salt (PBD) through photodecomposition of diazonium group under UV irradiation. As a result, the pyridine-containing functional groups were vertically and covalently anchored onto the surface of substrate and got a stable monolayer. Soluble ruthenium phthalocyanine, axially coordinated by labile benzonitrile groups, was used to fabricate the layer-by-layer self-assembled films with BP through ligand-exchanging reaction between benzonitrile and pyridine in each self-assembled cycle. The UV-vis analysis results demonstrated the successful fabrication of bi(4,4'-bipyridine)phthalocyaninato ruthenium(II) (BPPR) metallosupramolecular ultrathin films with definite structures on PBD-modified substrate. Under illumination, the BPPR self-assembled multilayer films displayed a quick response to light. The maximum current density reached 120 nA/cm² at six bilayers. The E_g , HOMO, and LUMO of the six-bilayer were quantitatively measured to be 1.68, -5.29, and -3.61 eV, respectively. This strategy supplies a facile method to get full-conjugated metallosupramolecules and a platform for developing higher performance solar cell from the point of adjusting dye aggregate state structure.



■ INTRODUCTION

In recent years, the exploration of new organic dye systems suitable for solar energy conversion, molecular scale electronic, and photonics has attracted great attention.^{1,2} Most of this research focused on the synthesis of dyes with novel structures to increase the optoelectronic performance. However, the aggregate state of dye absorbed on inorganic semiconductor also has a great influence on the optoelectronic transfer efficiency.^{3–6} Although increasing the amount of dye can increase the light absorption,⁷ the excitation energy will be minimized and the electron injection efficiency will be decreased because of the strong intermolecular interaction between aromatic organic dye molecules, which causes the dye aggregating in π - π stacked state⁸ and further leads to the aggregation-caused quenching (ACQ) effects.^{9,10} Making the dye align in order is a good way to resolve the contradictory problem.

Since it was developed by Decher in 1991,¹¹ the layer-by-layer (LBL) self-assembled technique has attracted great

interest among researchers due to its unique advantages. Not only electrostatic interactions but also covalent bond,¹² hydrogen bond,¹³ charge transfer,¹⁴ hydrophobic,¹⁵ host-guest,¹⁶ and coordination bond¹⁷ interactions were utilized for LBL assembly. By LBL self-assembled technique, the films could be fabricated on molecular levels to get a precise arrangement of molecules into a desired structure.^{18,19} Such structures can be used to develop applications for electronics,^{20,21} photonics,^{22,23} sensors,^{24–26} and optoelectronics energy transfer devices.^{27–29}

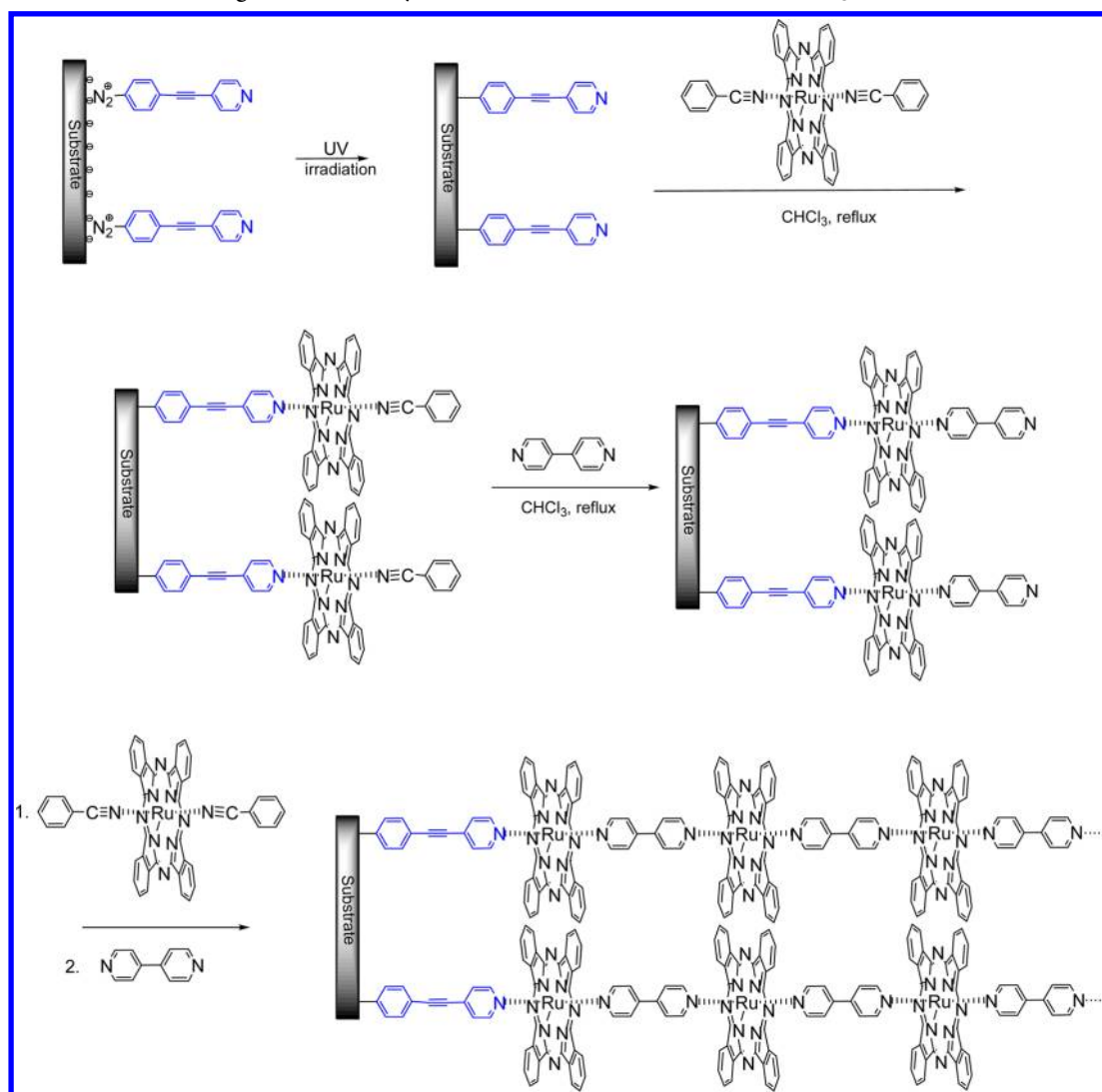
As a promising molecular component for artificial photosynthetic system, phthalocyanines (Pc) with an extended π -conjugation of 18 electrons exhibit large absorption ability in the visible region and are suitable for efficient electron-transfer

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Scheme 1. Process of Fabricating BPPR Multilayer Film Assembled on PBD-Modified Quartz



processes.^{30,31} Especially coupled to ruthenium(II), PcRu shows good electrochemical and light-responsive properties.³²

Thin films of phthalocyanines could be obtained by LBL self-assembled technique.^{33–37} Moreover, the insertion of axial groups into PcRu molecules by LBL technique avoids the formation of molecular aggregates, which minimizes ACQ effects.³⁸ Palacin et al.³⁹ obtained PcRu monolayer by self-assembly on pyridine-functionalized substrate. Because a bifunctional silane was used to modify the substrate by silanization, they could not get even and equal quantitative deposited multilayer films due to some disorder inside the silane anchoring layer. Recently, LBL films based on PcRu and triruthenium dodecacarbonyl ($\text{Ru}_3\text{CO}_{12}$) molecules bridged by bipyridine as ligand were reported.⁴⁰ Because of the uncertain fabricating process of $\text{Ru}_3\text{CO}_{12}$ coordination with pyridine, the films could, however, not grow along vertical direction to substrate, which blocks the linear transfers of electrons.

Herein, the conjugated aryl diazonium salt, 4-(2-(4-pyridinyl)ethynyl)benzenic diazonium salt (PBD), was served as anchor molecule. A stable monolayer was prepared by the decomposition of diazonium groups ($-\text{N}_2^+$) under the irradiation of UV light.⁴¹ This is helpful in allowing each self-assembled component to develop vertically along one direction

and be conducive for transmitting the electric charges from the organic layer to inorganic substrate.^{42–46} With pyridine groups as coordination sites, full-conjugated metallosupramolecular self-assembled films with definite structures were fabricated following axially coordination reactions by alternately depositing bi(benzonitril)phthalocyaninato ruthenium(II) (BBPR) and 4,4'-bipyridine (BP) onto the modified substrate. A ligand-exchanging reaction was involved, where one benzonitrile group was replaced by pyridine in each fabricated cycle. The fabrication process, electrochemical, and photoelectrochemical properties of the fabricated films were studied to investigate the relationship between properties and structures. The experimental results indicated that the metallosupramolecular chains of bi(4,4'-bipyridine)phthalocyaninato ruthenium(II) (BPPR) were vertical to the PBD-modified substrate and afford a linear transportation route for the electrons among LBL self-assembled films, which made the UV absorption red shift and decreased the energy band gap (E_g). This strategy provides a facile method to get full-conjugated metallosupramolecules and a platform for developing higher performance solar cell from the point of adjusting dye aggregate state structure.

EXPERIMENTAL SECTION

Materials. The synthesis of BBPR and PBD was according to refs 47 and 40, respectively. The BBPR yield was 37%, and the chemical structure of obtained BBPR was confirmed by ^1H NMR. Quartz and indium–tin-oxide (ITO) glass slides were used as substrates. Other reagents were purchased from Beijing Chemical Reagent and used as received without further purification.

Fabrication of the LBL Self-Assembled Films. The procedures for the pretreatment and PBD modification of quartz slide were described in ref 40. The slide covalently bonded with PBD was immersed in a refluxed solution of BBPR in CHCl_3 (1 mg/mL) at 60 °C for 20 min, then washed with CHCl_3 under ultrasonic treatment for ~ 1 min and dried under flow nitrogen. Afterward, it was immersed in a refluxed solution of BP in CHCl_3 (25.5 mM) at 60 °C for 15 min, then washed with CHCl_3 under ultrasonic treatment for ~ 1 min, dried under flow nitrogen, thus forming a bilayer film on both sides of the substrate to complete a fabrication cycle. Recycling the above procedures, multilayer films were constructed based on BPPR via coordination bonding.

Characterization. UV–vis absorption spectra were recorded on a Shimadzu 1901 UV–vis spectrophotometer. Cyclic voltammetry experiments were performed on a CHI 620A electrochemical workstation at room temperature with a conventional three-electrode configuration. The working electrode was BPPR self-assembled films with different numbers of bilayers on ITO glass slides (area 0.20 cm^2), the reference electrode was Ag/AgCl (sat. KCl), the counter electrode was a platinum sheet, and 0.1 mol/L of $[\text{NBu}_4]^+[\text{ClO}_4]^-$ in acetonitrile was used as a supporting electrolyte. Cyclic voltammograms were measured during the potential cycling ranging from -0.8 to 1.6 V at a scan rate of 0.1 V/s. Optoelectronic investigations were conducted at room temperature in a three-electrode cell using a CHF-XM-500W optoelectronic instrument. In this system, the electrodes and the supporting electrolyte were the same as those of cyclic voltammetry experiments. During photoelectrochemical measurements, a constant bias of 0 V was imposed between the reference and the counter electrodes. Steady cathode photocurrents were measured when the ITO electrodes were illuminated with xenon–mercury lamp (500 W).

RESULTS AND DISCUSSION

Fabrication of Multilayer Films. As shown in Scheme 1, the LBL self-assembled films were fabricated on the PBD-modified quartz through the coordination bonding interactions between RuPc and pyridine. A ligand-exchanging reaction was involved, where one benzonitrile group of BBPR was replaced by pyridine group of PBD in the first layer and bipyridine in the upper layers. UV–vis spectroscopy was used to monitor the formation of multilayer films prepared by the LBL self-assembled process.

The substrate was modified by PBD through the photodecomposition of diazonium groups under UV irradiation.⁴⁰ The assembling time of PBD onto the substrate was optimized. The absorbance remained constant when the substrate was immersed in PBD solution more than 15 min (Figure 1), which revealed that the depositing amount of PBD on the substrate surface reached the maximum with 15 min of immersion. The UV–vis spectra show three main peaks at the range of 300–600 nm (Figure 1). The absorption peak at ~ 448 nm belongs

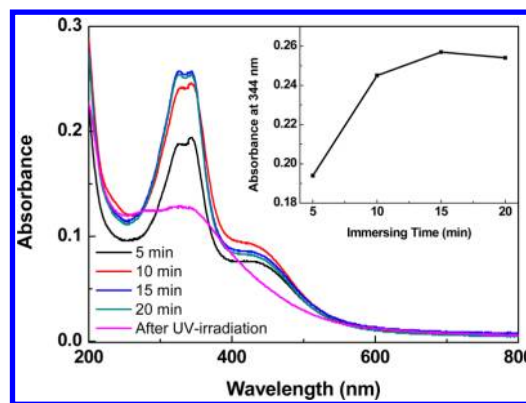


Figure 1. UV–vis absorption spectra of quartz immersed in PBD solution for different time and after UV irradiation.

to the diazonium groups in PBD, and the absorption peaks at about 343 and 326 nm are attributed to π – π^* electronic transitions of pyridine and benzene groups in PBD, respectively. After UV irradiation for 7 min and subsequently rinsing with organic solvent several times to remove physical adsorptions, the peak at 448 nm clearly disappeared, which indicated that the diazonium groups decomposed efficiently. Because of the loss of the diazonium group and the decrease in conjugation degree, the other two peaks also blue shift to 330 and 283 nm with the decrease in absorption intensities. The experimental results show the formation of covalent bonds between 4-(2-(4-pyridinyl)benzenic group and the substrate by decomposition of the diazonium group, which can ensure the PBD monolayer film stably existing on the quartz substrate in the following self-assembled reactions. As a result, the terminal pyridine group in PBD provides a coordinating site to substitute benzonitrile group in BBPR to form a coordination bond with RuPc.

One benzonitrile in BBPR was replaced by one pyridine group in PBD to form the complexes with PcRu based on coordination interaction when PBD-modified substrate was immersed into a solution of BBPR in CHCl_3 at 60 °C. When the film was subsequently immersed into BP in CHCl_3 at 60 °C, another benzonitrile in BBPR was replaced by the pyridine in BP to further achieve the complexes with PcRu based on coordination interaction. Thus, the first fabrication cycle was completed. Repeating the above process, BBPR and BP were alternately fabricated to obtain the self-assembled multilayer films. Because of the formation of coordination bonds between the two layers, the metallosupramolecule BPPR from BBPR and BP is vertically grown on the PBD-modified substrate by self-assembly method.

Because of the formation of BPPR self-assembled films based on the coordination bond, the immersion times in BBPR and BP solutions both need optimized. The experimental results revealed that the best times were 20 min for BBPR and 15 min for BP (Figures S1 and S2 in the Supporting Information), respectively. As shown in Figure 2, the absorption spectra of BPPR films from one to eight bilayers exhibit two main peaks at 314 and 645 nm, which are attributed to the B-band and Q-band of BPPR, respectively. The relationship between the absorbance of the two peaks and the number of bilayers (Figure 2b) revealed that the amounts of deposition were equal, which were similar to those in previous research.^{44–46} The results demonstrated the successful fabrication of BPPR multilayer self-assembled films on PBD-modified substrate, which was a

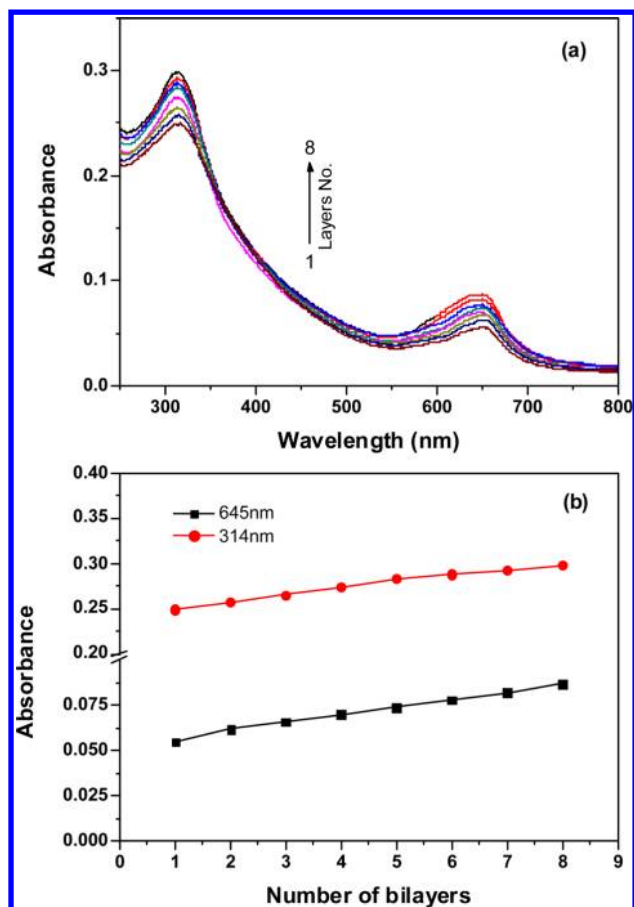


Figure 2. (a) UV-vis absorption spectra of BPPR multilayers assembled on PBD-modified quartz. (b) Plots of the maximum absorption peaks at 314 and 645 nm versus the number of bilayers.

fully conjugated linear organic metal complex with definite structures.

The BPPR multilayer films showed good stabilities in organic solvent and electrolyte solution. When five bilayers were immersed in THF or 1 M KCl solution for 30 min, the UV-vis spectra curves remained the same shapes (Figure 3). When it was immersed in THF for 1 h, the absorption slightly decreased.

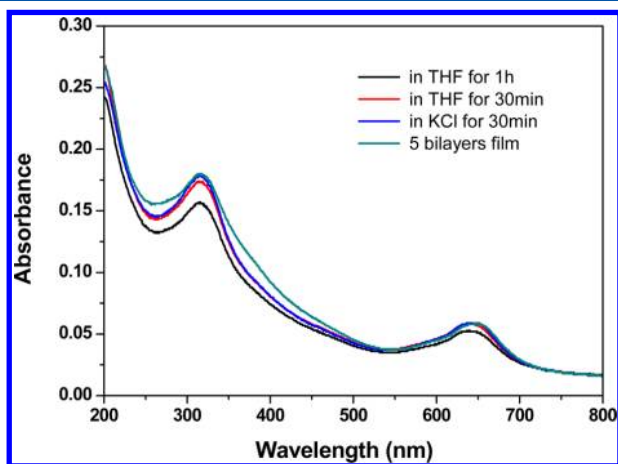


Figure 3. UV-vis absorption spectra of BPPR five bilayers films dipping in THF and KCl (1M) solution.

Electrochemical Characterization. Cyclic voltammetry of the BPPR films with different bilayer numbers in 0.1 mol/L $[\text{NBu}_4^+][\text{ClO}_4^-]$ acetonitrile solution was carried out at the scan rate of 0.1 V/s over a voltage ranging from -0.8 to 1.6 V (Figure 4). All of the multilayer films displayed chemically

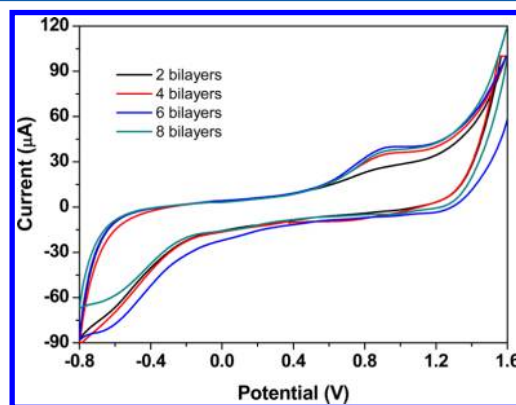


Figure 4. Cyclic voltammograms of the BPPR multilayers assembled on PBD-modified ITO films with different bilayers (2, 4, 6, 8).

irreversible Ru(II)/Ru(III) oxidation waves at 0.85 to 0.93 V corresponding to the formation of Ru(III), and the reduction wave was, however, not observed.

Figure 5 shows the relationship of the current and potential of oxidation peak versus the number of bilayers. The potentials

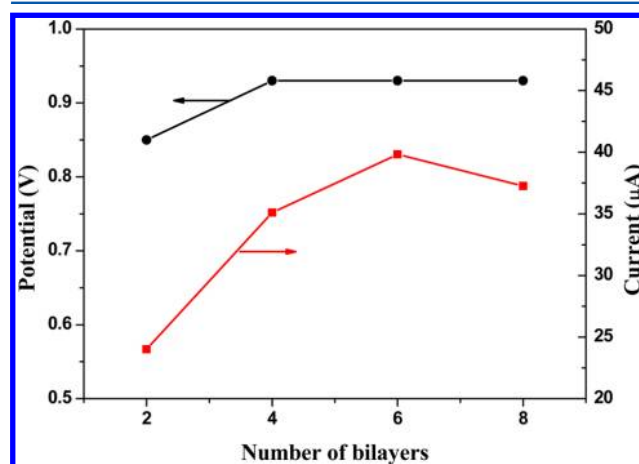


Figure 5. Fitting plot of the current and potential of oxidation peak versus the number of bilayers.

increased with increase in the bilayer number and then remained the same when the number of bilayers was increased to four. The current reached the maximum ($39.8 \mu\text{A}$) at six bilayers and then started to decrease. There were two factors influencing the electronic transportation of the fabricated films. One factor was the amount of organic-metal semiconductor RuPc. With the growing number of the bilayers, the amount of RuPc increased, which was a benefit for the oxidation current. Another factor was the internal electrical resistance, which was also increased with increasing the bilayer number. High electrical resistance blocked the electronic transportation. The converse coefficient of the RuPc amount and the internal electrical resistance with increasing bilayer numbers influenced the change of current density created by the self-assembled films.

Photoelectric Conversion Characterization. Steady-state photocurrent measurements were performed using a three-electrode electrochemical cell under the condition similar to those previously reported. The ITO substrates coated with BPPR self-assembled films comprising two, four, six, and eight bilayers were used as working electrodes (0.2 cm^2), which were illuminated with a 500 W xenon–mercury lamp. The experimental results of six bilayers film were taken as an example shown in Figure 6, which displayed a quick response to light. The current density demonstrated good stability after it was repeated many times.

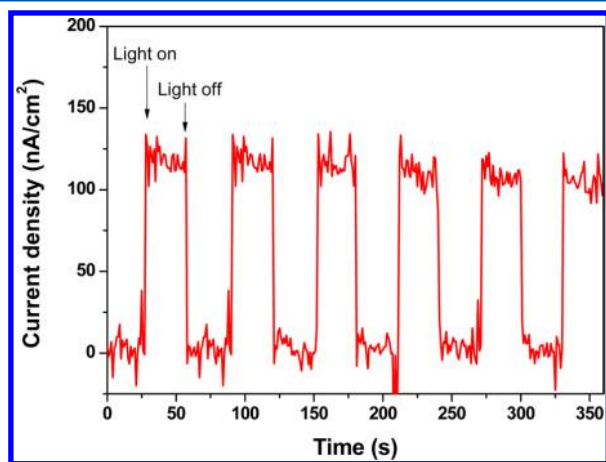


Figure 6. Current density change of self-assembled six-bilayer BPPR films on ITO modified by PBD.

The relationship of current density versus number of bilayers for the films (Figure 7) illustrated a maximum value (120 nA/

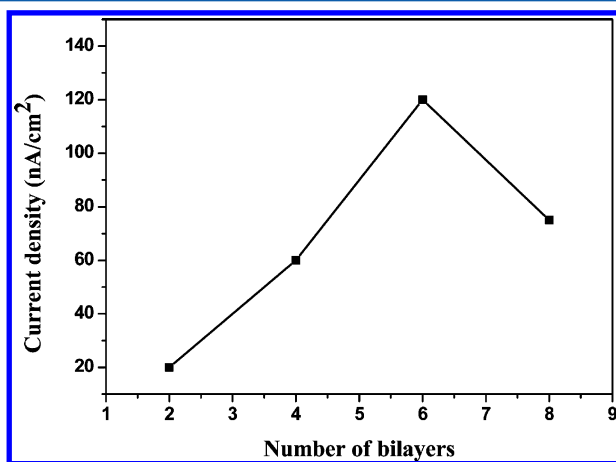


Figure 7. Fitting plot of photocurrent density versus number of bilayers for BPPR multilayer films on ITO modified by PBD.

cm^2) with the increasing number of bilayers. The converse coefficient of the RuPc amount and the internal electrical resistance with increasing bilayer numbers influenced the change of current density created by the self-assembled films under light illumination.

To illustrate the mechanism of photoinduced electron transfer, we calculated the energy band gap (E_g), the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) energy values of the multilayer films using UV–vis absorption spectra and cyclic

voltammograms (Figure 8). The E_g level for the six BPPR self-assembled films was calculated to be 1.68 eV according to the

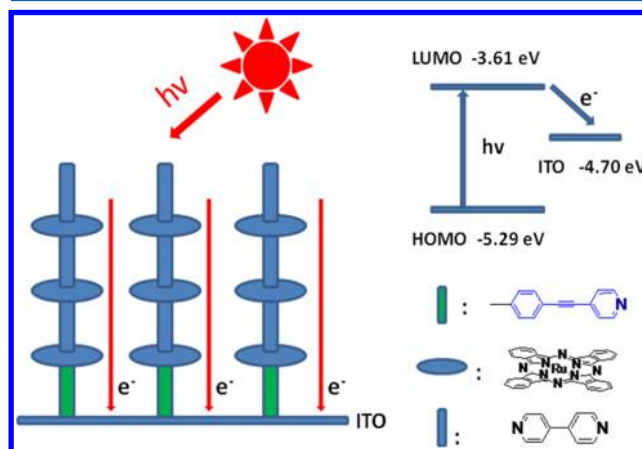


Figure 8. Schematic energy-level diagram for a self-assembled six-bilayer BPPR film on ITO modified by PBD.

equation: $E_g \text{ (eV)} = hc/\lambda$ ($\lambda = 740 \text{ nm}$, Figure 2a). The reference electrode was Ag/AgCl (sat. KCl), and the HOMO level was calculated to be -5.29 eV from the formula $E_{\text{HOMO}} = -(4.70 + eE_{\text{ox}})$ ($E_{\text{ox}} = 0.59 \text{ eV}$, Figure 4). Similarly, the LUMO level was calculated to be -3.61 eV from the formula $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$.

In the previous report, bis(4,4'-bipyridine)-(phthalocyaninato) ruthenium(II) was bridged together by $\text{Ru}_3\text{CO}_{12}$ to fabricate multilayer films. Because of the uncertainty of which CO in $\text{Ru}_3\text{CO}_{12}$ was decomposed during the coordination with Ru(II), we cannot get linearly growing multilayer films.⁴⁰ Herein, benzonitrile group in BBPR was directly substituted by pyridine, so the structures of the films were confirmative and the fabricated growing directions were vertical to the substrate. The structure benefited from the electronic transportation and increased the conjugation degree of the fabricated molecules, which red-shifted the UV absorption and led to the decreasing of E_g from 1.8 to 1.68 eV. Further research on the effect of linear structure of fabricated films on the electronic transmission rate characterized by transient absorption and the application of the fabricated films in dye-sensitized solar cell is undergoing.

CONCLUSIONS

We show the successful fabrication of BPPR self-assembled multilayer films from BBPR and BP on PBD-modified substrate, which possessed full-conjugated linear organic metal complex with well-defined structures and vertically aligned orientations. The BPPR multilayer films showed good stability in organic solvent and electrolyte solution. Under illumination, the BPPR self-assembled multilayer films displayed a quick response to light. The current density demonstrated a good stability after being repeated many times. With the increasing of bilayers numbers, the photocurrent enhanced and reached the maximum (120 nA/cm^2) at six bilayers. The E_g , HOMO, and LUMO of the six-bilayer were quantitatively measured to be 1.68, -5.29 , and -3.61 eV , respectively, which are lower than those of self-assembled films based on bis(4,4'-bipyridine)(phthalocyaninato)ruthenium(II) and triruthenium dodecacarbonyl. These experimental results revealed such kind of self-assembled structure benefits for the

electronic transportation and the light absorption. This strategy supplies a facile method to get full-conjugated metallosupramolecules and a platform for developing higher performance solar cell from the point of adjusting dye aggregate state structure.

■ ASSOCIATED CONTENT

■ Supporting Information

UV-vis absorption spectra of PBD-modified quartz dipped in BBPR CHCl_3 solution and then dipped in 4,4'-bipyridine CHCl_3 solution for different time. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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