

Letter

Rhenium(I) complex as an electron acceptor in a photovoltaic device

Sumei Yue, Bin Li^{*}, Di Fan, Ziruo Hong, Wenlian Li*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics,
Chinese Academy of Sciences, Changchun 130033, PR China*Received 9 May 2006; received in revised form 2 June 2006; accepted 2 June 2006
Available online 7 August 2006**Abstract**

An organic photovoltaic (PV) device with a structure of indium-tin-oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (20 nm)/4,4',4''-tris[3-methylphenyl (phenyl)amino]triphenylamine (*m*-MTDATA) (30 nm)/Re(CO)₃Cl-monophenanthroline (Re-Phen) (60 nm)/LiF (1 nm)/Al (100 nm) has been fabricated. When the device was irradiated by 365 nm ultraviolet (UV) light, open circuit voltage (V_{oc}) of 1.15 V, the short circuit current (I_{sc}) of 100 $\mu\text{A}/\text{cm}^2$, fill factor (FF) of 0.45 and power conversion efficiency of 4% were obtained, respectively. Spectroscopic investigation evidenced that the increase in the PV efficiency is related to the existence of a charge transfer absorption process. The generation mechanism of the PV effect was discussed.

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Keywords: Phosphorescence; Re(I) complex; Photovoltage; Optical sensor**1. Introduction**

Organic photovoltaic (PV) devices have the potential advantages of light weight and low-cost [1]. Unfortunately, their power conversion efficiency [2–9] is far from satisfactory. Most efforts made in the past decade focused on conjugated polymers [3–7] and fullerenes [7–9]. Little attention has been devoted to organic metal complexes [9–13]. Carbonyl bipyridine Re(I) complexes and their derivatives, such as Re-Phen exhibit characteristic long-lived metal-to-ligand charge transfer (MLCT) excited states [14]. They have highly desirable properties including microsecond lifetimes in solution, intense visible absorption and phosphorescence emission, good redox chemistry and high stability [14,15]. The PV devices using Re(I) complexes as electron acceptors have been demonstrated [10]. One of the most promising applications of these devices is the conversion of solar radiation into chemical energy [8]. Besides, it is possible to use them as UV detectors [13].

In this letter, Re-Phen and *m*-MTDATA were used as electron-acceptor and donor, respectively in the PV device and the photocurrent response was observed. The results indicate organic PV device based on typical triplet material, Re-Phen can be used as optical sensor.

2. Experimental

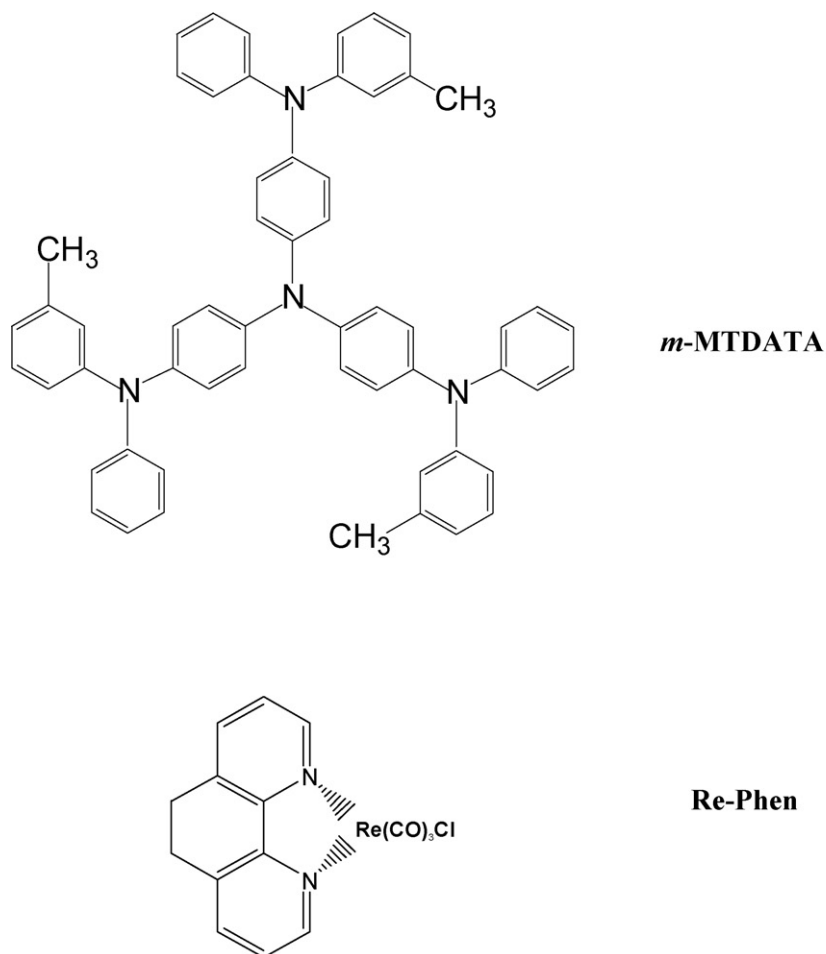
Re-Phen was prepared according to literature methods [10]. The purity and composition were confirmed by ¹H NMR, IR, positive-ion FAB-MS and elemental analyses. The configuration of the device and the chemical structure of the materials used in this study are shown in Fig. 1.

The PV device was constructed by first spin coating a 20-nm layer of PEDOT:PSS on ITO substrate. *m*-MTDATA, Re-Phen, LiF and Al cathode were sequentially deposited onto the ITO substrates by thermal evaporation at a pressure of 2×10^{-4} Pa without breaking the vacuum. The deposition rates were monitored by quartz oscillators and controlled at 0.2–0.4 nm/s for the organic layers and LiF, and 1.0 nm/s for the Al cathode, respectively. The organic films with the same thickness were also deposited on quartz substrates under same preparation condition for measuring absorption spectra with a Shimadzu UV-3101 PC spectrophotometer. The thickness measurement of the spin-coated film was performed using a variable-angle spectroscopic ellipsometer (Model 601BAM/I-Elli2000, Germanic NFT Co.). The refractive index and thickness were calculated from the simulation parameters based on Cauchy model. The light-state *I*–*V* characteristics of the PV device were measured under UV illumination at 365 nm of 1.6 mW/cm² through the glass/ITO side. All measurements were carried out under ambient atmosphere at room temperature without encapsulation.

3. Results and discussion

The absorption spectra of Re-Phen, *m*-MTDATA, *m*-MTDATA/Re-Phen films and the photocurrent response curve of the device are shown in Fig. 2. It was found that the absorption spectrum of the *m*-MTDATA/Re-Phen film is not simply the weighted sum of those of *m*-MTDATA and Re-Phen.

^{*} Corresponding author. Fax: +86 431 6176935.
E-mail address: lib020@ciomp.ac.cn (B. Li).



Al (100 nm)
LiF (1 nm)
Re-Phen (60 nm)
<i>m</i>-MTDATA (30 nm)
PEDOT:PSS (20 nm)
ITO

Fig. 1. The chemical structure of the organic materials and PV device configuration.

A new band ranging from 400 to 500 nm appeared. Such band is not observed either in *m*-MTDATA or in Re-Phen, it can be ascribed to a new transition state associated to the interaction between *m*-MTDATA and Re-Phen, most likely the charge transfer (CT) state. Despite the very weak absorption of the *m*-MTDATA/Re-Phen film from 400 to 500 nm, the photocurrent response is strong. It indicates that the CT states efficiently collect the excitons and improves the efficiency of excitons dissociation into free charge carriers. In the range of $\lambda = 300\text{--}400\text{ nm}$ the absorption of the *m*-MTDATA layer

played an important role for the generation of the photocurrent, since the absorption of *m*-MTDATA is much larger than that of Re-Phen. Although, there are strong absorptions from 250 to 350 nm for *m*-MTDATA and Re-Phen, the PV response of the device is still relative weak, which is attributed to the intense absorption of the ITO glass at the UV region shown in the inset of Fig. 2. For a single layer PV device, i.e. ITO/PEDOT:PSS/Re-Phen (60 nm)/LiF/Al, PV effects could hardly be observed. However, Re-Phen is necessary to the efficient photocurrent in the bilayer PV device. In the absence of Re-Phen layer, that

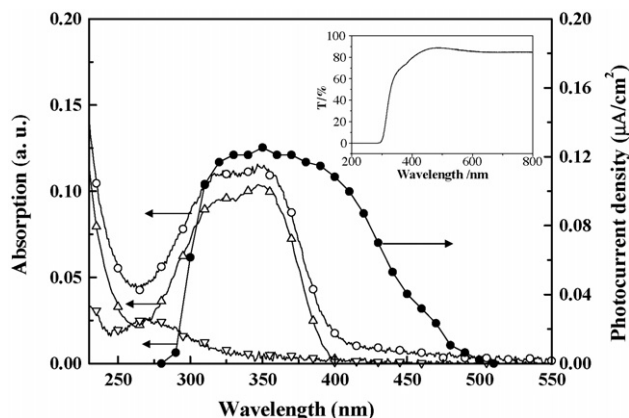


Fig. 2. The absorption spectra of Re-Phen film (down triangle), *m*-MTDATA film (up triangle), *m*-MTDATA/Re-Phen film (open circle) and photocurrent response of PV device (solid circle). Inset: The UV–vis transmission spectrum of the ITO glass.

is, for a single layer PV device ITO/PEDOT:PSS/*m*-MTDATA (30 nm)/LiF/Al, the key PV parameters, V_{oc} of 0.84 V, I_{sc} of $5.8 \mu\text{A}/\text{cm}^2$, FF of 0.3 and power conversion efficiency of 0.09% have been determined. The conversion efficiency is about 45 times smaller than that of the bilayer PV device containing both *m*-MTDATA and Re-Phen layer. So the interface between *m*-MTDATA and Re-Phen played the active site for the exciton dissociation. This is explained as following: *m*-MTDATA is a good hole-transporting and injection material [16], while Re-Phen has good electron-transporting ability [14]. According to the photocurrent response curve, first, excitons are photogenerated in the *m*-MTDATA layer near to interface of the Re-Phen and *m*-MTDATA because efficient photoabsorption mainly takes place in the *m*-MTDATA layer; second, the generated excitons diffuse to the organic interface between the materials with different electron affinities and ionization potentials, where the excitons dissociation is known to be efficient; then the electrons are accepted by Re-Phen with large electron affinity and the holes by *m*-MTDATA with the low ionization potential; last, electrons and holes travel through the Re-Phen layer and the *m*-MTDATA layer to cathode and anode, respectively.

Fig. 3 shows the I – V characteristics of the PV device under UV light (365 nm) illumination with total power density of

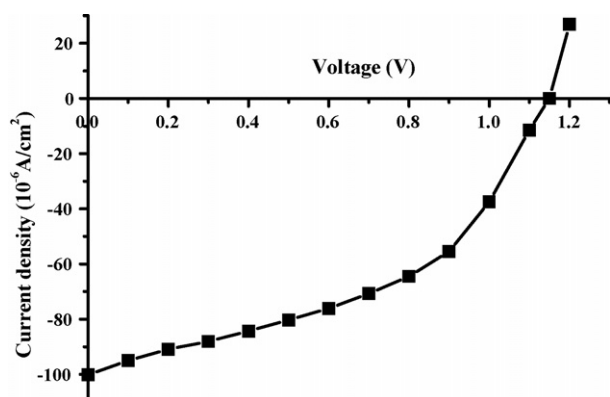


Fig. 3. I – V characteristics of the PV device under $1.6 \text{ mW}/\text{cm}^2$ UV light irradiance.

$1.6 \text{ mW}/\text{cm}^2$. I_{sc} , V_{oc} were measured to be $100 \mu\text{A}/\text{cm}^2$, 1.15 V, 0.45, 4%, respectively. FF and power conversion efficiency can be calculated by following equations, respectively.

$$FF = \frac{(IV)_{\max}}{V_{oc} \times I_{sc}}, \quad \eta = \frac{(IV)_{\max}}{P_{in} \times L} = \frac{FF \times V_{oc} \times I_{sc}}{P_{in} \times L}$$

where $(IV)_{\max}$ is the actual maximum power, L the active area and P_{in} is the incident light power per square centimeter. The most sensitive response wavelength of the device is about 300–400 nm, so it is very suitable to detect UV light.

4. Conclusions

In summary, we have shown that organic PV device based on triplet complex Re-Phen with high power conversion efficiency of 4%. This value is high comparable with the devices based other metal complexes. The existence of a CT absorption state is responsible for increasing the PV efficiency. The device is sensitive to UV light and can be used as a photodetector to UV light. It indicates that utilizing phosphorescent metal complexes is a promising way to improve PV performance, and we are in the progress of further exploring these possibilities.

Acknowledgments

The authors gratefully acknowledge the financial supports from One Hundred Talents Project from Chinese Academy of Sciences, the National Natural Science Foundation of China (Projects 20571071).

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