

文章编号 1674-2915(2009)03-0225-05

基于磷光配合物羰基二吡啶并[3,2-a:2',3'-c]吩嗪 Re(I) 的有机光伏器件

苑冰冰^{1,2}, 刘艳红², 丛妍², 李斌²

(1. 东北师范大学 化学系, 吉林 长春 130024;

2. 中国科学院 长春光学精密机械与物理研究所 激发态物理重点实验室, 吉林 长春 130033)

摘要: 为了制备高效紫外光学传感器件, 采用真空蒸镀的方法, 分别以 4,4',4"-三(3-甲基-苯基-苯胺基)-三苯胺 (*m*-MTDATA) 为电子给体, 羰基二吡啶并[3,2-a:2',3'-c]吩嗪 Re(I) 为电子受体制成了有机光伏器件。在紫外灯 (365 nm, 1.6 mW/cm²) 从氧化铟锡膜 (ITO) 方向垂直照射下, 器件的短路电流, 开路电压, 填充因子和功率转换效率分别为 57.1 μ A/cm², 0.86 V, 0.39 和 1.2%。研究表明, 有机磷光发光材料 Re-DPPz 也具有较好的光伏性能。

关键词: 光伏器件; 光学材料; 蒸发

中图分类号: TN366; TB34 **文献标识码:** A

Organic photovoltaic device based on triplet complex Re(CO)₃ Cl-dipyrido[3,2-a:2',3'-c] phenazine

YUAN Bing-bing^{1,2}, LIU Yan-hong², CONG Yan², LI Bin²

(1. Department of Chemistry, Northeast Normal University, Changchun 130024, China;

2. Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China)

Abstract: To prepare highly efficient optical sensors for UVA light, an organic photovoltaic(PV) device, in which 4,4',4"-tris[3-methylphenyl(phenyl)amino]triphenylamine (*m*-MTDATA) and Re(CO)₃ Cl-dipyrido[3,2-a:2',3'-c]phenazine(Re-DPPz) are used as an electron donor and an acceptor, respectively, has been fabricated by a vacuum deposition method. Under illumination with UV light(365 nm, 1.6 mW/cm²), the short circuit current, open circuit voltage, fill factor and power conversion efficiency of the PV device are measured to be 57.1 μ A/cm², 0.86 V, 0.39, 1.2% respectively. These results indicate that the Re-DPPz complex, a promising triplet emitter, is characterized not only by its electroluminescence but also by good PV performance. These experiments also show that utilizing phosphorescent materials is a promising way to improve the PV performance of a device.

Key words: photovoltaic device; optical material; evaporation

收稿日期:2009-03-11;修订日期:2009-04-13

Acknowledgment: The authors gratefully thank the financial supports of the National Natural Science Foundations of China (Grant No. 50872130)

1 Introduction

Recently, organic PV devices have obtained rapidly growing attention since the report by Tang in 1986^[1] because they had many potential advantages over inorganic counterparts, such as lightweight, low cost and easy to process etc. Most of the electron accepting materials used as in organic PV devices reported to date are conjugated polymers and fullerenes, in which different kinds of functional groups are attached^[2]. Little attention has been devoted to organic metal complexes as electron acceptors^[3~6]. Carbonyl bipyridine Re (I) complexes and their derivatives are characterized by their long-lived Metal-to-ligand Charge Transfer (MLCT) excited states, which can undergo different photochemical or photophysical processes. They may serve as good electron acceptors. Several Re (I) complexes have been used in PV devices^[3,4,7]. One of the most promising potentials of these devices is the conversion of solar radiation into chemical energy^[8]. Besides, it is possible to use these materials in application for UV detectors^[6,9]. However, their power conversion efficiencies are much lower than

those based on conjugated polymers^[10]. So enhancing the electron-carrier mobility and facilitating the exciton dissociation after the photosensitization process are crucial to improve the performance of PV devices based on small molecular Re complexes. DPPz derivatives had excellent electron-transporting property reported before^[11]. Our group has studied the EL properties of Re-DPPz^[12] and the maximum brightness of 990 cd/cm² and the maximum efficiency of 6.3 cd/A were achieved from the EL device using Re-DPPz as emitter. In this article, Re-DPPz and *m*-MTDATA are used as an electron-acceptor and a donor, respectively, in an organic PV device and the photocurrent response is investigated. The results indicate that the triplet complex Re-DPPz not only possesses good electrophosphorescence performance, but also has potential applications in PV fields^[13].

2 Experiments

Re-DPPz was synthesized according to a literature procedure^[14]. The chemical structures of *m*-MTDATA and Re-DPPz are depicted in Fig. 1.

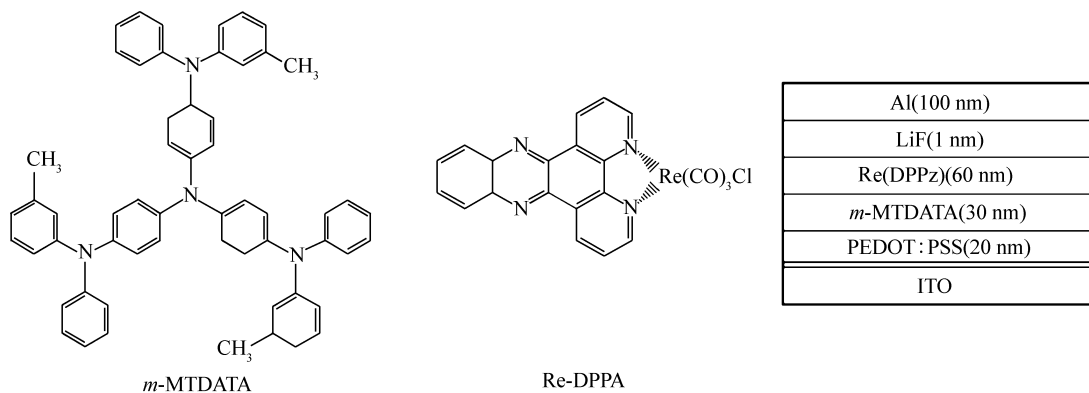


Fig. 1 Chemical structure of organic materials and PV device configuration

The PV device was constructed by spin coatings with a 20 nm layer of poly (3,4-ethylenedioxythiophene) : poly (styrenesulfonate) (PEDOT : PSS) on indium-tin-oxide (ITO) substrate firstly. *m*-MTDA-

TA, Re-DPPz, LiF and a Al cathode are sequentially deposited onto the above substrates by thermal evaporation at a pressure of 2×10^{-4} Pa without breaking the vacuum. The deposition rates are moni-

tored by a quartz oscillator and controlled at a rate of 0.2 ~ 0.4 nm/s for the organic layers and LiF, and 1.0 nm/s for the Al layer, respectively. The absorption spectra of the organic films on quartz substrates are measured with a Shimadzu UV-3101 PC spectrophotometer. The light-state PV performance device is measured under UV illumination of 365 nm with 1.6 mW/cm² through the glass/ITO side. The PL spectra are measured with a Hitachi F-4500 fluorescence spectrophotometer. All measurements are carried out under ambient atmosphere at room temperature without encapsulation.

3 Results and discussion

The PV device with structure of ITO/PEDOT:PSS/*m*-MTDATA/Re-DPPz/LiF/Al is fabricated as shown in Fig. 1. To form a smooth contact between the Re-DPPz and the Al electrode and to strengthen adsorption of Re-DPPz on the Al electrode surface, a LiF layer is introduced between the Re-DPPz and the Al electrode.

Fig. 2 shows the emission spectra of a Re-DPPz film, a *m*-MTDATA film and a *m*-MTDATA/Re-DPPz film. For the *m*-MTDATA/Re-DPPz film, the emission at 424 nm originates from *m*-MTDATA and the shoulder band from 470 nm to 650 nm is

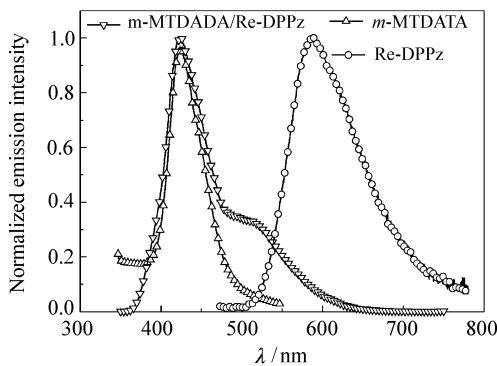


Fig. 2 Emission spectra of Re-DPPz film, *m*-MTDATA film, and *m*-MTDATA/Re-DPPz two-layer film

probably ascribed to exciplex emission. Figure 3 shows the absorption spectra of *m*-MTDATA, Re-

DPPz, *m*-MTDATA/Re-DPPz films, and the photocurrent response curve of the device. It can be found that profile of the photocurrent response curve is

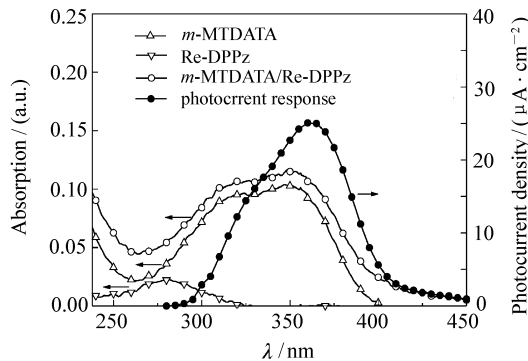


Fig. 3 Absorption spectra of Re-DPPz film, *m*-MTDATA film, *m*-MTDATA/Re-DPPz film, and photocurrent response of PV device

near to the lower energy absorption band of *m*-MTDATA film centering at 350 nm, although the two-layer film absorption spectrum also contains the contribution of Re-DPPz. These results indicate that the photocurrent is mainly based on the absorption of *m*-MTDATA because the coefficient of *m*-MTDATA is greater than that of Re-DPPz (see Fig. 3) which is different from the results reported by Tang^[1]. However, here Re-DPPz is necessary to the efficient photocurrent which originates from the PV device. In the absence of Re-DPPz layer, for an PV device with structure of ITO/PEDOT:PSS/*m*-MTDATA/LiF/Al, the typical parameters, the I_{sc} of 5.8 $\mu\text{A}/\text{cm}^2$, U_{oc} of 0.84 V, FF of 0.29 and the power conversion efficiency of 0.09% have been determined. The conversion efficiency is about thirteenth times as small as that of the PV device containing a Re-DPPz layer. So the interface between the *m*-MTDATA and the Re-DPPz plays the active site for the exciton dissociation. This is explained as following. *m*-MTDATA is a well known hole-transporting and injection material^[15] and it is easily formed a exciplex with Re-DPPz due to the excellent electron-transporting ability of DPPz^[11]. Thus, *m*-MTDATA should play a role as an electron-donor^[16], and Re-DPPz as an

electron-acceptor in our designed PV device. The exciplexes are formed in the interface of *m*-MTDA-TA/Re-DPPz. It is concluded that the PV process in the device ITO/PEDOT:PSS/*m*-MTDATA/Re-DPPz/LiF/Al is as follows. First, excitons are photogenerated in a region of *m*-MTDATA layer near to the interface between the *m*-MTDATA and the Re-DPPz films because efficient photoabsorption mainly takes place in the *m*-MTDATA layer; second, the generated excitons diffuse to the interface between the two kinds of materials with different electron affinities and ionization potentials, where exciton dissociation is known to be efficient; then the electron is accepted by the material with the large electron affinity and the hole by the material with the low ionization potential; finally, electrons and holes originating from the exciton dissociation travel through the Re-DPPz layer and the *m*-MTDATA layer to cathodes and anodes, respectively. Here, triplet Re-DPPz with long exciton lifetime may extend exciton diffusion length^[13].

Fig. 4 (a) shows the *I-V* characteristics of the PV device under UV light (365 nm) illumination with total power density of 1.5 mW/cm². *I*-c, U_{oc} , FF, and power conversion efficiency are measured to be 57.1 $\mu\text{A}/\text{cm}^2$, 0.86 V, 0.39, and 1.2%, respectively. The most sensitive response wavelength of the device is about 300 ~ 400 nm, so it is very suitable to detect UVA light.

参考文献:

- [1] TANG C W. Two-layer organic photovoltaic cell[J]. *Appl. Phys. Lett.*, 1986, 48 (2):183-185.
- [2] RIEDEL I, HAUFF E V, PARISI H, *et al.*. Diphenylmethanofullerenes; new and efficient acceptors in bulk-heterojunction solar cells[J]. *Adv. Funct. Mater.*, 2005, 15 (12):1979-1987.
- [3] CHAN W K, HUI C S, MAN K Y K K W, *et al.*. Synthesis and photosensitizing properties of conjugated polymers that contain chlorotricarbonyl bis(phenylimino)acenaphthene rhenium(I) complexes[J]. *Coord. Chem. Rev.*, 2005, 249 (13 - 14):1351-1359.
- [4] ZHANG M P, LU X M, WANG L, *et al.*. Synthesis and photophysical properties of π -conjugated polymers incorporated with phosphorescent rhenium(I) chromophores in the backbones[J]. *J. Phys. Chem. B*, 2004, 108 (35):13185-13190.
- [5] RAND B P, LI J, XUE J G, *et al.*. Organic double-heterostructure photovoltaic cells employing thick tris(acetylacetonato) ruthenium(III) exciton-blocking layers[J]. *Adv. Mater.*, 2005, 17(22):2714-2718.

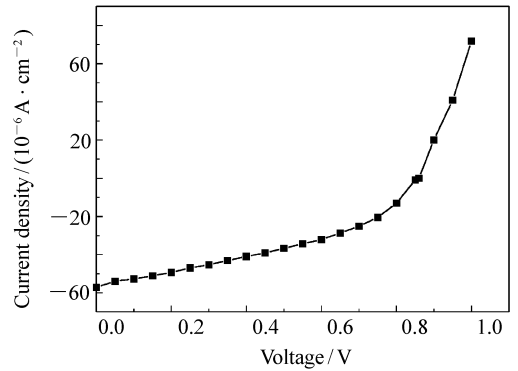


Fig. 4 *I-V* characteristics of PV device under 1.6 mW/cm² UV light irradiance

4 Conclusions

In summary, the PV device based on triplet complex Re-DPPz sensitive to UV light is fabricated. It can be used as an optical sensor to UVA light. The power conversion efficiency has achieved 1.2% in a simple multilayer heterojunction structure, which is comparable with those based on the rare-earth complexes reported by us before^[6]. It indicates that utilizing phosphorescent materials is a promising way to improve PV performance. We anticipate that the triplet materials could be further improved in power conversion efficiency by employing new materials and adopting optimal architectures of devices.

- [6] CHU B, FAN D, LI W L, *et al.* . Organic-film photovoltaic cell with electroluminescence[J]. *Appl. Phys. Lett.* ,2002,81:10-12.
- [7] WONG H L, LAM L S M, CHENG K W, *et al.* . Low-band-gap sublimable rhenium(I) diimine complex for efficient bulk heterojunction photovoltaic devices[J]. *Appl. Phys. Lett.* ,2004,84:2557-2559.
- [8] JURIS A, BALZANI V, BARIGELLETTI F, *et al.* . Ru(II) polypyridine complexes: photophysics photochemistry electrochemistry and chemiluminescence[J]. *Coord. Chem. Rev.* ,1988,84:85-277.
- [9] WEI H Z, LI W L, LI M T, *et al.* . White organic electroluminescent device with photovoltaic performances[J]. *Appl. Surf. Sci.* ,2006,252(6):2204-2208.
- [10] MA W L, YANG C Y, GONG X, *et al.* . Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology[J]. *Adv. Funct. Mater.* ,2005,15(10):1617-1622.
- [11] SUN P P, DUAN J P, SHIH H T, *et al.* . Europium complex as a highly efficient red emitter in electroluminescent devices[J]. *Appl. Phys. Lett.* ,2002,81:792-794.
- [12] FU C Y, LI M T, SU Z M, *et al.* . Improved performance of electrophosphorescent devices based on Re(CO)₃Cl-dipyrido[3.2-a;2.3-c]phenazine[J]. *Appl. Phys. Lett.* ,2006,88:093507-093509.
- [13] SHAO Y, YANG Y. Efficient organic heterojunction photovoltaic cells based on triplet[J]. *Adv. Mater.* ,2005,17(23):2841-2844.
- [14] WATERLAND M R, GORDON K C, McGARVERY J J, *et al.* . Spectroscopic and electrochemical studies of a series of copper(I) and rhenium(I) complexes with substituted dipyrido[3.2-a;2.3-c]phenazine ligands[J]. *J. Chem. Soc. Dalton Trans.* ,1998,4:609-616.
- [15] ITANO K, OGAWA H, SHIROTA Y. Exciplex formation at the organic solid-state interface: Yellow emission in organic light-emitting diodes using green-fluorescent tris(8-quinolinolato) aluminum and hole-transporting molecular materials with low ionization potentials[J]. *Appl. Phys. Lett.* ,1998,72:636-638.
- [16] COCCHI M, VIRGILI D, GIRO G, *et al.* . Efficient exciplex emitting organic electroluminescent devices[J]. *Appl. Phys. Lett.* ,2002,80:2401-2403.

作者简介:苑冰冰,女,硕士,主要从事有机电致发光材料的研究和合成。E-mail:Yuanbb263@nenu.edu.cn

李 斌(1964—),男,研究员,博士生导师,主要从事有机及无机发光材料的研究。

E-mail:lib020@ciomp.ac.cn