J Mater Sci (2009) 44:1283–1286
DOI 10.1007/s10853-009-3280-7

Bulk heterojunction organic solar cell based on a novel fluorescent fluorine–boron complex

Fen Qiao · Aimin Liu · Ying Zhou ·
Yi Xiao · Ping Ou Yang

Received: 26 November 2008 / Accepted: 16 January 2009 / Published online: 7 February 2009

Abstract The photovoltaic properties of solar cells were investigated via spin coating the poly (2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) and a newly synthesized n-type difluoro [2-(2-pyridinyl)-1H-indene-1,3(2H)-dionato-N2, O1]-(T-4)-boron (PIDB) with lower LUMO level as active layers. The active layers were characterized in solid state by means of absorption and photoluminescence (PL) spectra with three mixtures ratios in weight. Compared to the pure MEH-PPV, the results showed the blend of MEH-PPV and PIDB enhanced the light intensity as well as broadened the wavelength range of absorption; the intensities of PL spectra of the blends are quenched and confirmed the electron transferred from the photoexcited MEH-PPV backbone to PIDB. Much higher power conversation efficiency was achieved when their mixtures were with a ration of 1:1 by weight. The improved performance of device is attributed to the reduction of contact resistance, which derived from the impedance analysis.

F. Qiao · A. Liu (✉)
School of Physics and Optoelectronic Technology,
Dalian University of Technology, Dalian 116024,
People's Republic of China
e-mail: pv_lab@dlut.edu.cn; PG29701612@ntu.edu.sg

Y. Zhou · Y. Xiao
The State Key Laboratory of Fine Chemicals,
Dalian University of Technology, Dalian 116012,
People's Republic of China

P. Ou Yang
Key Laboratory of Luminescence and Optical Information,
Beijing Jiaotong University, Beijing 100044,
People's Republic of China

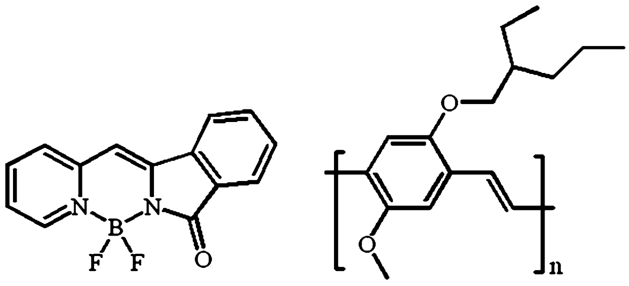
Introduction

Organic materials in solar cells are a promising alternative to inorganic ones due to their low cost as well as large scale production [1–4]. Moreover, the chemical flexibility for modifications on organic materials via chemical synthesis methods drives the researches in academia and commerce. Recently much effort has been spent in the synthesis of novel fluorine–boron complexes (FBC) and their application in photovoltaic devices; it is found that the modification of the FBC can not only adjust their optical characteristics but also improve their capabilities of electron accepting and transportation [5–7]. Although several FBC were reported to be used in organic light emitting diodes and field effect transistors, the exploration of FBC as charge transport materials in organic solar cells is still inadequate.

In this paper, a newly synthesized n-type fluorescent fluorine–boron complex which showed well-ordered molecular packing and lower LUMO level was used as electron acceptor. Since MEH-PPV is a p-type organic semiconductor with outstanding hole transport properties, it was chosen as an electron donor in this paper. The LUMO and HOMO levels of PIDB were obtained through cyclic voltammetry with 3.22 eV and 6.07 eV, respectively. Compared with those of MEH-PPV (2.7 eV and 5.1 eV), it was obvious that PIDB had good electron acceptor features, which will be suitable for fabricating cells with MEH-PPV. Photovoltaic characteristics of cells based on MEH-PPV and PIDB were studied through related measurements methods.

Experimental details

In this paper, n-type difluoro[2-(2-pyridinyl)-1H-indene-1,3(2H)-dionato-N2,O1]-(T-4)-boron (PIDB) was synthesized



(a) PIDB **(b) MEH-PPV**

Fig. 1 Chemical structure of the organic compounds studied in this work

and used as acceptor for devices; the detailed synthetic procedures for the PIDB have been described in Ref [8]. The chemical structures of the components of the blends investigated are shown in Fig. 1. The MEH-PPV and PIDB were dissolved in chlorobenzene solution; three blend solutions of active layer were prepared with proportions of PIDB (25, 50, 75%) by weight, respectively.

The solar cells were fabricated on top of indium tin oxide (ITO) coated glass substrates; the substrates were thoroughly cleaned by an ultrasonic treatment in acetone, ethanol, and de-ionized water sequentially, then was spin coated with a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) at 3000 rps for 60 s, followed by heating for 15 min at 150 °C in annealing oven. Afterward, the active layer containing a mixture of MEH-PPV and PIDB were spin-coated from chlorobenzene to the substrates, and then the aluminum (Al) top electrodes were evaporated by thermal evaporation in vacuum through a shadow mask with active areas being 0.3×0.3 cm^2.

UV–visible absorption spectra were measured through a UV-3101PC (UV-VIS-NIP Scanning, Spectrophotometer); the films of the MEH-PPV and PIDB were formed through spin coating from chlorobenzene solution on quartz substrates. The photoluminescence (PL) spectra were performed through a fluorescence spectrometer LS55, samples were illuminated by a xenon lamp, and the emission was recorded through another monochromator by a photo multiplier. The photovoltaic characteristics of cells were determined by a Source-Meter (Keithley, model 2410) under a xe lamp illumination with power density of 100 mW/cm^2 (AM1.5). Resistance was carried out through impedance measurements using a SI 1287 electrochemical interface and a SI 1260 Impedance/Gain phase Analyzer in the range from 1 MHZ to 1 HZ. Ac oscillating amplitude was set as 10 mV in order to maintain the linearity of the response. All electrical measurements were made at room temperature in air.

Results and discussions

Absorption spectra

The solid state optical absorption spectra of the MEH-PPV, PIDB, and their mixture at 1:1 weight ratio are shown in Fig. 2.

A strong peak close to 500 nm along with a weak peak at 333 nm can be found in the film of MEH-PPV, while the PIDB has one absorption peak at 455 nm. It is obvious that the spectra of their blend is much broader compared with the pure MEH-PPV and PIDB; it showed two peaks around 500 nm and 350 nm, which increases the number of photons absorbed in the visible region. It is known that an absorption spectra of conjugated polymer depends on its molecular conformation as the conjugation length of the polymer changed. As compared with the pure MEH-PPV, the maximum absorption peaks of the blend blue shifted slightly; it may be due to the decrease in the effective conjugation length of MEH-PPV after blending with PIDB [9, 10].

PL spectra

In order to check the possible application of PIDB as electron acceptors in cells, the photoluminescence (PL) spectra of the blend of MEH-PPV: PIDB in chlorobenzene solution were measured under the photo-excitation wavelength of 500 nm which is corresponding to the absorption peak wavelength of the MEH-PPV. Figure 3 shows the PL spectra of the pure MEH-PPV and their mixture with three compositions of PIDB (25, 50, and 75%) by weight, respectively.

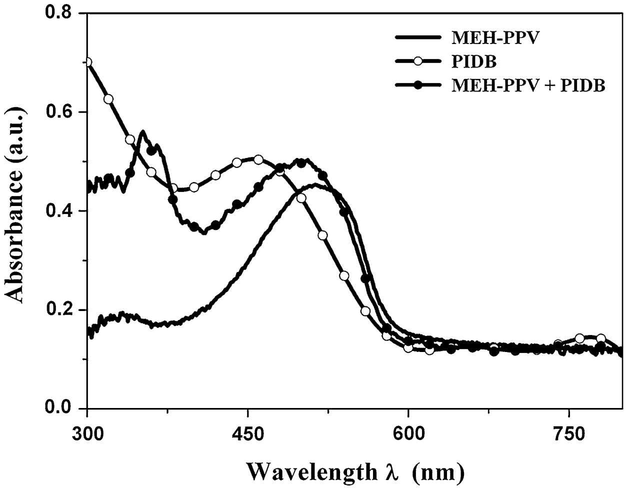


Fig. 2 Absorption spectra for MEH-PPV, PIDB and their mixture at 1:1 weight ratio

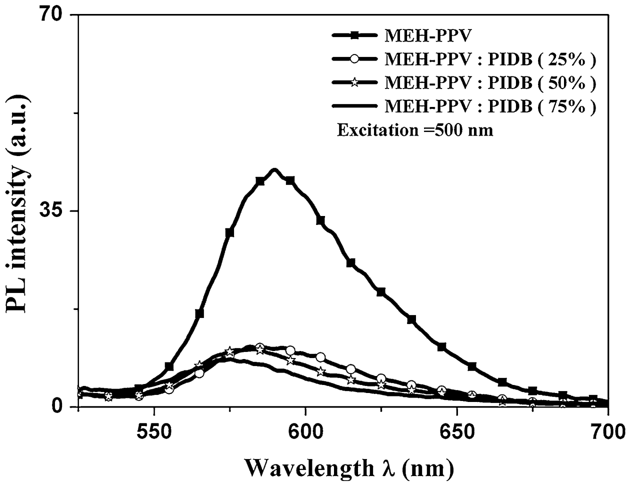


Fig. 3 The photoluminescence spectra of MH-PPV and their mixtures with PIDB

For the pure MEH-PPV, the predominant PL band with central peaks around 590 nm have been observed, but the band is significantly quenched in the MEH-PPV: PIDB blended films. It is obvious that the intensities of PL spectra of the blends are quenched to about 2% of the pure MEH-PPV layer emission indicating that 98% of the excitons are dissociated. The results indicate that electrons are transferred from the photoexcited MEH-PPV backbone to PIDB. The photoinduced charge transfer in other conjugated polymer/small molecular composites by PL quenching can be found in other literatures [11–13].

Current–voltage measurements

To further investigate the electrical characteristics of active layer based on MEH-PPV and PIDB, solar cells of ITO/PEDOT: PSS/MEH-PPV:PIDB/Al were fabricated with three compositions of the PIDB. Figure 4a and b displays the current–voltage characteristics obtained in dark and under illumination with intensity of 100 mW/cm^2.

The photovoltaic parameters are obtained from the device based on 25% of PIDB by weight with short-circuit current density (J_{SC}) of 0.077 mA/cm^2; open-circuit voltage (V_{OC}) of 0.48 V, fill factor (FF) of 0.30; and photovoltaic conversion efficiency (η) of 0.16%. It is obvious that the FF and η increase in large degree as the content of PIDB increases to 50%, with J_{SC} of 0.068 mA/cm^2, V_{OC} of 0.59 V, FF of 0.54, and η of 0.31%. However, the V_{OC}, FF, and η decrease to 0.50 V, 0.35, and 0.25%, respectively, when the content of PIDB was added to 75% in the active layer.

It is obvious that the inflection points near the open-circuit voltage in the curve occurred in the devices with 25% and 75% of PIDB from Fig. 4b, which causes a negative curvature in the fourth quadrant and induces the decrease in fill factor. This may be ascribed to poor electrical properties of top contact. The much larger FF value of cell based on 50% of PIDB is ascribed to the lower contact resistance compared to that of the other two cells.

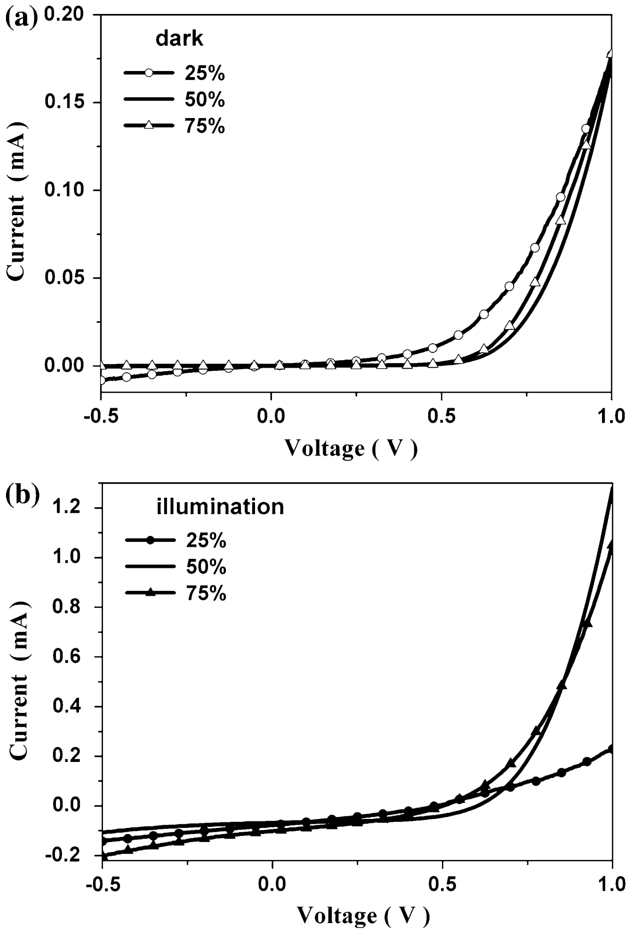


Fig. 4 The photovoltaic response of solar cells with three compositions of the PIDB in the active layers **a** in the dark and **b** under illumination

Impedance spectra

For further insight in photovoltaic parameters especially the larger difference of fill factor in three cells, electrical impedance spectra measurements were carried out. Figure 5 displays the measured electrical impedance in the complex plane for devices with three compositions of PIDB in the active layer. It can be seen that the impedance spectra are composed of a large semicircle at low frequencies together with an almost straight line in the high-frequency part (inset of Fig. 5), which is rather independent of the applied voltage.

This type of impedance pattern belongs to the responses usually encountered in systems in which carrier transport is determined by diffusion–recombination between non-absorbing contacts [14]. The impedance model consists of

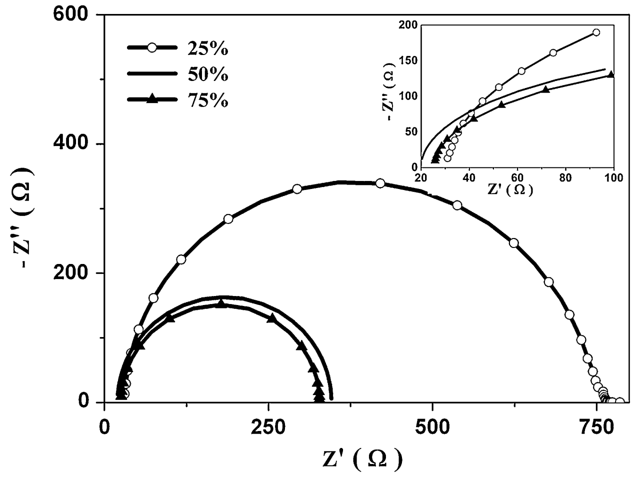


Fig. 5 Impedance spectra of devices measured in the dark

an equivalent circuit which comprises a series resistance (R_s) and is needed to model contact and wire effects. The impedance model described contains three series resistances with 31, 20.4, and 25.8 Ω, respectively, which is in agreement with the FF values assumed in I–V measurement.

Conclusion

In this work, organic solar cells were fabricated using the novel synthesized fluorine–boron complex PIDB with lower LUMO level as electron acceptor. It shows that the PIDB not only enhances the light absorption, but also improves the transport ability of electrons together with the MEH-PPV shown by the PL quenching. Although the η is not too high, this novel molecule shows its potential in photovoltaic devices with well-ordered molecular packing and low LOMO level. Further work about improving the morphology of active layer and thermal annealing treatments will be carried out to improve the photovoltaic characteristics of cells in the future.

Acknowledgements Authors thank Ying Zhou for the materials supply and Yang Ping Ou for meaningful discussion in experiments.

References

1. Forrest SR (2004) Nature 428:911
2. Gebeyehu D, Maennig B, Drechsel J, Leo K, Pfeiffe M (2003) Sol Energy Mater Sol Cells 79:81
3. Song QL, Wang ML, Obbard EG, Sun XY, Ding XM, Hou XY, Li CM (2006) Appl Phys Lett 89:2511181
4. Chen LC, Godovsky D, Inganäs O, Hummelen JC, Janssens RAJ, Svensson M et al (2000) Adv Mater 12:1367
5. Liu D, Mudadu M, Thummel R, Tao Y, Wang S (2005) Adv Funct Mater 15:143
6. Domercq B, Grasso C, Maldonado JL, Halik M, Barlow S, Marder SR, Kippelen B (2004) J Phys Chem B 108:8647
7. Sun Y, Rohde D, Liu Y, Wan L, Wang Y, Wu W, Di C, Yu G, Zhu D (2006) J Mater Chem 16:4499
8. Zhou Y, Xiao Y, Chi S, Qian X (2008) Org Lett 10:633
9. McQuade DT, Kim J, Swager TM (2000) J Am Chem Soc 122:5885
10. Diaz-Garcia MA, Hide F, Schwartz BJ, Andersson MR, Pei Q, Heeger AJ (1997) Synth Met 84:455
11. Halls JJM, Walsh CA, Greenham NC, Marseglia EA, Friend RH, Moratti SC et al (2002) Nature 376:498
12. Yang F, Shtein M, Forrest SR (2004) Nat Mater 4:37
13. Ma W, Yang C, Gong X, Lee K, Heeger AJ (2005) Adv Funct Mater 15:1617
14. Bisquert J (2002) J Phys Chem B 106:325