

Cite this: *Chem. Commun.*, 2011, **47**, 8877–8879

www.rsc.org/chemcomm

COMMUNICATION

Synthesis, characterization, and photovoltaic properties of a low-bandgap copolymer based on 2,1,3-benzoxadiazole†

Jian-Ming Jiang, Po-An Yang, Hsiu-Cheng Chen and Kung-Hwa Wei*

Received 10th April 2011, Accepted 17th May 2011

DOI: 10.1039/c1cc12040a

PBDTBO, a conjugated polymer comprising benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) and 5,6-bis(octyloxy)benzo[*c*][1,2,5]-oxadiazole (BO) units, exhibits a deep HOMO energy level of -5.27 eV and excellent solubility. A device incorporating PBDTBO and [6,6]-phenyl- C_{61} -butyric acid methyl ester (1 : 1, w/w) exhibited a power conversion efficiency of 5.7%.

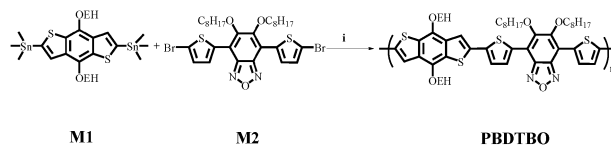
Thin film polymer solar cells (PSCs) based on bulk heterojunction (BHJ) structures, prepared through solution processing, offer an opportunity for realizing low-cost renewable energy production.¹ In recent years, several efficient polymers with donor/acceptor (D/A) units in their main² or side³ chains have exhibited promising potential for use in photovoltaic applications. For example, devices incorporating polymers featuring electron-deficient units derived from 2,1,3-benzothiadiazole (BT),^{2a} 3,6-diaryl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP),^{2b-e} thieno[3,4-*c*]pyrrole-4,6-dione (TPD),^{2f-j} and thieno[3,4-*b*]thiophene-2-carboxylate^{2k} moieties conjugated with various electron-donating units, such as fluorene, carbazole, and dithienosilole moieties, have exhibited distinguished power conversion efficiencies (PCEs) of up to 7% after systematic optimization. The PCE of a device is the product of the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) divided by the incoming light power density. Many low-bandgap polymers that absorb in the visible and near-IR regions of the solar spectrum have been developed to maximize light absorption and, thereby, increase the value of J_{sc} and the PCE. Unfortunately, because low-bandgap polymers typically exhibit low values of V_{oc} , they have limited potential for application. The value of V_{oc} of a BHJ device that features [6,6]-phenyl- C_{61} -butyric acid methyl ester (PC₆₁BM) as the n-type material and conjugated polymers as the p-type materials is linearly proportional to the difference between the highest occupied molecular orbital (HOMO) energy level of the conjugated polymer and the lowest unoccupied molecular orbital (LUMO) energy level of PC₆₁BM.⁴ Accordingly, judicious selection of suitable donor and acceptor moieties

through structural modification offers the possibility to concurrently achieve a deeper HOMO energy level and a lower bandgap, thereby enhancing the values of both V_{oc} and J_{sc} .

With its electron-deficient benzene ring fused to two flanking thiophene units, the monomer benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) features a planar and symmetrical structure—two important prerequisites for high charge carrier mobility. Several BDT-based copolymers have recently exhibited high charge carrier mobility when incorporated in organic field transistors.⁵ Strong electron-withdrawing units are necessary when choosing an acceptor unit to lower the LUMO energy level of a D/A polymer. With suitable selection of the acceptor, however, the HOMO level could be adjusted to a lower value. For instance, the thieno[3,4-*c*]pyrrole-4,6-dione (TPD) electron-withdrawing units lowered both the HOMO and LUMO energy levels.^{2f-j} Benzothiadiazole (BT) is one of the strong electron withdrawing moieties widely used in PSCs and reflects their electron accepting strength as well as their capability to adopt the quinoid structure in the polymer, resulting in a low-bandgap and coplanar polymer. Because benzoxadiazole (BO) has a lower-lying oxidation potential than BT,^{6a} it typically increases the value of V_{oc} , but provides lower PCEs, presumably a result of the low molecular weight and low solubility of its polymers.⁶ To solve this problem, we designed a soluble acceptor⁷ by introducing two octyloxy chains on the BO ring.

In this study, we prepared a new intramolecular charge transfer (ICT) conjugated polymer, PBDTBO, featuring alternating rigid, coplanar, electron-rich BDT units and soluble, electron-deficient BO units as the D and A units, respectively. We synthesized this air-stable and solution-processable polymer in high yield, anticipating that it would act as an efficient electron donor when incorporated in PSCs.

Scheme 1 displays the structures of the monomeric BDT and BO derivatives, 1,5-bis(trimethylstannyl)-4,8-di(ethylhexyloxy)-benzo[1,2-*b*:4,5-*b'*]dithiophene (M1) and 1,4-bis(5-bromothieno-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]oxadiazole (M2), respectively,



Scheme 1 Synthesis of PBDTBO. Reagents and conditions: (i) Pd₂dba₃, P(o-Tol)₃, toluene, 24 h.

Department of Materials Science and Engineering,
National Chiao Tung University, 1001 Ta Hsueh Road,
Hsihchu, Taiwan, ROC. E-mail: khwei@mail.nctu.edu.tw;
Fax: + 886-35-724-727; Tel: + 886-35-731-871

† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c1cc12040a

that we used to synthesize **PBDTBO** through Stille coupling (detailed descriptions of the syntheses of the monomers are provided in the ESI†). **PBDTBO** displayed good solubility at elevated temperature in CHCl_3 , 1,2-dichlorobenzene (DCB), 1,2,3-trichlorobenzene (TCB), and tetrahydrofuran (THF). The number-average molecular weight (M_n) of the synthesized **PBDTBO** was 62 kg mol^{-1} , with a polydispersity of 4.1, as measured using gel permeation chromatography (GPC) at 45°C with THF as the eluent (calibrated against polystyrene standards). **PBDTBO** featured a 5%-weight-loss temperature (T_d) of 330°C , as determined through thermogravimetric analysis (TGA; Fig. S1, ESI†); in addition, its differential scanning calorimetry (DSC) trace did not feature any melting point (T_m), crystallization point (T_c), or glass transition. Fig. 1 presents absorption spectra of **PBDTBO** in dilute DCB solution and as a solid film. In solution, **PBDTBO** displayed absorption signals close to 415 nm, which we assign to localized $\pi\text{-}\pi^*$ transition bands, and 575 nm, which we attribute to ICT interactions between the **BO** acceptor moieties and the **BDT** donor units. Only a very limited red-shift of the signals in the absorption spectrum occurred on passing from the solution to the solid state, indicating that the polymer was amorphous, with no obvious aggregation or long-range-ordered $\pi\text{-}\pi$ stacking in the solid state. The optical bandgap of **PBDTBO**, calculated from the absorption edges in the UV-Vis spectrum of the thin solid film, was 1.74 eV.

We used cyclic voltammetry to estimate the HOMO and LUMO energy levels of **PBDTBO** (Fig. 2). **PBDTBO** underwent irreversible p-doping and reversible n-doping processes in the positive and negative scanning range. The onset oxidation potential (E_{ox}) that was contributed by **BDT** and the onset reduction potential (E_{red}) that was contributed by **BO** were

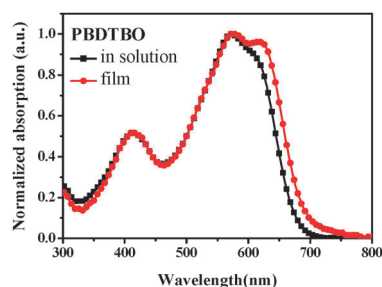


Fig. 1 UV-Vis absorption spectra of **PBDTBO** in DCB ($1 \times 10^{-5} \text{ M}$) and as a solid film.

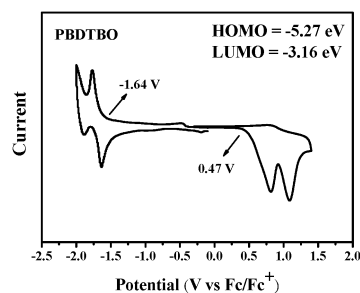


Fig. 2 Cyclic voltammograms of a solid film of the copolymer **PBDTBO**.

+0.47 and -1.64 V , respectively, *versus* ferrocene/ferrocenium (Fc/Fc^+) (detailed descriptions of the CV analysis are provided in the ESI†). The HOMO and LUMO energy levels can also be obtained relative to Fc/Fc^+ as the reference electrode (4.8 eV below the vacuum level); here, the values were -5.27 and -3.16 eV respectively. This low HOMO energy level suggested that **PBDTBO** would be stable against oxidation in air. The electrochemical bandgap of **PBDTBO**, estimated from the difference between the HOMO and LUMO energy levels, was 2.11 eV—significantly larger than its optical bandgap (1.74 eV). This discrepancy might have been caused by the presence of an energy barrier at the interface between the polymer film and the electrode surface;⁸ similar phenomena have been reported for other polymer systems.⁹ The hole mobility, measured using the space-charge-limited current (SCLC) method (Fig. S2 and Table S1, ESI†), of the pristine **PBDTBO** film was $4.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; those of **PBDTBO**/ PC_{61}BM blended films prepared at weight ratios of 1:1, 1:2, 1:3, and 1:4 were 1.7×10^{-4} , 1.1×10^{-4} , 7.7×10^{-5} , and $4.9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.

We fabricated BHJ photovoltaic devices having the typical configuration indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)/**PBDTBO**: PC_{61}BM /Ca (30 nm)/Al (100 nm); the photoactive layers, spin-coated from DCB solutions at various **PBDTBO**: PC_{61}BM blend compositions, had thicknesses in the range 125–145 nm. Fig. 3 presents the current density–voltage ($J\text{-}V$) curves of these BHJ solar cells under the illumination; Table 1 summarizes the corresponding data. We anticipated that the blends would generate high values of V_{oc} —related to the energy difference between the HOMO energy level of the polymer and the LUMO energy level of PC_{61}BM ⁴—because of the low-lying HOMO energy level of **PBDTBO**. The devices fabricated from **PBDTBO** and PC_{61}BM blends exhibited values of V_{oc} of 0.80–0.86 V. The optimal **PBDTBO**/ PC_{61}BM device, prepared at a blend weight ratio of 1:1, exhibited a value of V_{oc} of 0.86 V, a value of J_{sc} of 10.4 mA cm^{-2} , an FF of 64.4% and a resulting PCE of 5.7%. Increasing the loading weight ratio of PC_{61}BM to 1:2, the value of J_{sc} decreased to 9.7 mA cm^{-2} , presumably because of decreased hole mobility and increased phase segregation. Fig. S4 (ESI†) displays height and phase images of **PBDTBO**/ PC_{61}BM blend films probed using atomic force microscopy. Notably, the surface of the 1:1 (w/w) **PBDTBO**/ PC_{61}BM blend was more homogeneous than that of the 1:2 (w/w) **PBDTBO**/ PC_{61}BM blend.

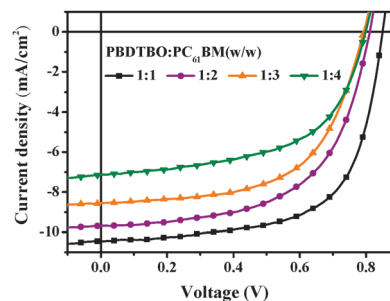


Fig. 3 Current density–voltage ($J\text{-}V$) curves of PSCs incorporating **PBDTBO**/ PC_{61}BM at weight ratios ranging from 1:1 to 1:4.

Table 1 Device characteristics of photovoltaic solar cells incorporating **PBDTBO**:PC₆₁BM blends prepared at various weight ratios

PBDTBO/PC ₆₁ BM (w/w)	Thickness/nm	V _{oc} /V	J _{sc} /mA cm ⁻²	FF (%)	PCE (%)	Rsh/Ω cm ²	Rs/Ω cm ²	Mobility/cm ² V ⁻¹ s ⁻¹
1:1	144	0.86	10.4	64.4	5.7	8695	8.2	1.7 × 10 ⁻⁴
1:2	135	0.81	9.7	57.2	4.5	1960	10.8	1.1 × 10 ⁻⁴
1:3	122	0.8	8.5	59.5	4.0	865	17.3	7.7 × 10 ⁻⁵
1:4	127	0.8	7.1	57.1	3.2	680	15.8	4.9 × 10 ⁻⁵

We measured the external quantum efficiencies (EQEs) of these devices to examine their photoresponses. The devices were first encapsulated in a N₂-filled glove box; their EQEs were measured in air. Fig. S3 (ESI†) displays EQE spectra of the **PBDTBO**/PC₆₁BM devices prepared at various blend weight ratios; each of them exhibited a broad response from 350 to 700 nm. The EQE curve of the optimal device, based on the (1:1, w/w) **PBDTBO**/PC₆₁BM blend, exhibited a maximum intensity of 60% at 570 nm. The value of J_{sc} obtained through integration of this EQE curve (9.7 mA cm⁻²) was in reasonable agreement (only 6% lower) with that measured from the *J*-*V* curve (10.4 mA cm⁻²).

In conclusion, we have used Stille coupling to prepare a low-bandgap conjugated polymer, **PBDTBO**, featuring alternating **BDT** and **BO** units in its backbone, that exhibited good thermal stability, acceptable solubility, high molecular weight (*M*_n = 62 kg mol⁻¹), and a low HOMO energy level. A PSC device incorporating **PBDTBO** and PC₆₁BM (blend weight ratio, 1:1), prepared without requiring special treatment, exhibited a high open-circuit voltage (0.86 V) and a high solar energy PCE (5.7%).

We thank the National Science Council for financial support through project NSC 98-2120-M-009-006 and Prof. Chu Chih-Wei for PSC device fabricate equipment.

Notes and references

- (a) G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789; (b) S. Günes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324; (c) M. M. Wienk, J. M. Koon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, *Angew. Chem., Int. Ed.*, 2003, **42**, 3371; (d) M. Y. Chiu, U. S. Jeng, C. H. Su, K. S. Liang and K. H. Wei, *Adv. Mater.*, 2008, **20**, 2573; (e) F. Zhang, M. Svensson, M. R. Andersson, M. Maggini, S. Bucella, E. Menna and O. Inganäs, *Adv. Mater.*, 2001, **13**, 1871; (f) J. H. Park, D. S. Chung, D. H. Lee, H. Kong, I. H. Jung, M. J. Park, N. S. Cho, C. E. Park and H. K. Shim, *Chem. Commun.*, 2010, **46**, 1863.
- (a) L. Huo, H. Y. Chen, J. Hou, T. L. Chen and Y. Yang, *Chem. Commun.*, 2009, 5570; (b) Y. Zou, D. Gendron, R. Neagu and M. Leclerc, *Macromolecules*, 2009, **42**, 6361; (c) C. H. Woo, P. M. Beaujuge, T. W. Holcombe, O. P. Lee and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2010, **132**, 15547; (d) G. Y. Chen, C. M. Chiang, D. Kekuda, S. C. Lan, C. W. Chu and K. H. Wei, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1669; (e) J. C. Bijleveld, V. S. Gevaert, D. D. Nuzzo, M. Turbiez, S. G. J. Mathijssen, D. M. de Leeuw, M. M. Wienk and R. A. J. Janssen, *Adv. Mater.*, 2010, **22**, E242; (f) Y. Zou, A. Najari, P. Berrouard, S. Beaupre, B. R. Aich, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2010, **132**, 5330; (g) Y. Zhang, S. K. Hau, H. L. Yip, Y. Sun, O. Acton and A. K. Y. Jen, *Chem. Mater.*, 2010, **22**, 2696; (h) M. C. Yuan, M. Y. Chiu, C. M. Chiang and K. H. Wei, *Macromolecules*, 2010, **43**, 6936; (i) Y. Zhang, J. Zou, H. L. Yip, Y. Sun, J. A. Davies, K. S. Chen, O. Acton and A. K. Y. Jen, *J. Mater. Chem.*, 2011, **21**, 3895; (j) G. Y. Chen, Y. H. Cheng, Y. J. Chou, M. S. Su, C. M. Chen and K. H. Wei, *Chem. Commun.*, 2011, **47**, 5064; (k) J. S. Hae, W. Wei, X. Tao, L. Yongye, W. Yue, L. Gang and L. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 1885; (l) B. Kim, B. Ma, V. R. Donuru, H. Liu and J. M. J. Fréchet, *Chem. Commun.*, 2010, **46**, 4148.
- (a) Y. T. Chang, S. L. Hsu, M. H. Su and K. H. Wei, *Adv. Mater.*, 2009, **21**, 2093; (b) Y. T. Chang, S. L. Hsu, G. Y. Chen, M. H. Su, T. A. Sing, E. W. G. Diau and K. H. Wei, *Adv. Funct. Mater.*, 2008, **18**, 2356; (c) Y. T. Chang, S. L. Hsu, M. H. Su and K. H. Wei, *Adv. Funct. Mater.*, 2007, **17**, 3326; (d) F. Huang, K. S. Chen, H. L. Yip, S. K. Hau, O. Acton, Y. Zhang, J. Luo and A. K. Y. Jen, *J. Am. Chem. Soc.*, 2009, **131**, 13886.
- (a) C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 374; (b) M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, **18**, 789.
- H. Pan, Y. Li, Y. Wu, P. Liu, B. S. Ong, S. Zhu and G. Xu, *J. Am. Chem. Soc.*, 2007, **129**, 4112.
- (a) N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. N. Plesu, M. Belletete, G. Durocher, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2008, **130**, 732; (b) J. C. Bijleveld, M. Shahid, J. Gilot, M. M. Wienk and R. A. J. Janssen, *Adv. Funct. Mater.*, 2009, **19**, 3262; (c) C. V. Hoven, X. D. Dung, R. C. Coffin, J. Peet, T. Q. Nguyen and C. C. Bazan, *Adv. Mater.*, 2010, **22**, E63.
- P. Qin, W. Li, C. Li, C. Du, C. Veit, H. F. Schleiernacher, M. Andersson, Z. Bo, Z. Liu, O. Inganäs, U. Wuerfel and F. Zhang, *J. Am. Chem. Soc.*, 2009, **131**, 14612.
- (a) D. A. M. Egbe, L. H. Nguyen, H. Hoppe, D. Mühlbacher and N. S. Sariciftci, *Macromol. Rapid Commun.*, 2005, **26**, 1389; (b) Z. K. Chen, W. Huang, L. H. Wang, E. T. Kang, B. J. Chen, C. S. Lee and S. T. Lee, *Macromolecules*, 2000, **33**, 9015.
- (a) E. Wang, M. Wang, L. Wang, C. Duanm, J. Zhang, W. Cai, C. He, H. Wu and Y. Cao, *Macromolecules*, 2009, **42**, 4410; (b) J. Hou, M. H. Park, S. Zhang, Y. Yao, L. M. Chen, J. H. Li and Y. Yang, *Macromolecules*, 2008, **41**, 6012.