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Low Band-Gap Weak Donor-Strong Acceptor Conjugated Polymer for Organic Solar Cell

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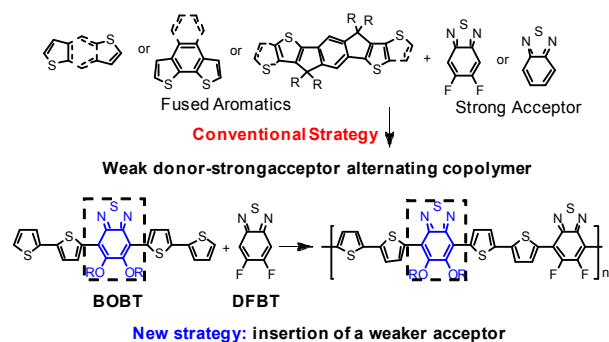
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By insertion of an additional weak acceptor into a donor-acceptor conjugated polymer backbone, a new weak donor-strong acceptor alternating copolymer PTTBOBT-DFBT was synthesized and it showed a low band-gap of 1.64 eV with a deep HOMO energy level (-5.44 eV). The bulk heterojunction (BHJ) solar cell fabricated from polymer PTTBOBT-DFBT displayed a remarkable power conversion efficiency (PCE) of 5.36% ($J_{sc} = 11.04 \text{ mA/cm}^2$, FF = 63.65%, $V_{oc} = 0.76 \text{ V}$).

The cost-effective solution processability and good compatibility with flexible substrate and high PCE have made organic photovoltaic (OPV) an intriguing research field over decades. However, the efficiency of OPV is still far behind its inorganic counterpart, silicon solar cell. Thus tremendous efforts have been dedicated to improve its efficiency by either sophisticated material design or device structure optimization.¹⁻⁶ Among them, fine tuning of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of materials has recorded significant progress.⁷⁻²¹ Recently, the weak donor-strong acceptor strategy demonstrated great potential for high performance OPV materials.²²⁻²⁶ The typical methodology for construction of weak donor could be readily achieved by decreasing electron-richness of thiophene unit by fusing with a relatively electron-deficient aryl unit *via* multiple steps synthesis, and it has been demonstrated that this strategy is effective to lower down the HOMO energy level, yielding high open circuit voltages (V_{oc}) in related BHJ devices (Scheme 1). Herein, we report a simple alternative weak donor-strong acceptor approach. Generally, the donor-acceptor conjugated polymers are constructed by linking electron-rich aromatics as donors, such as oligothiophenes, and electron-deficient

counterparts as acceptors, such as 2, 1, 3-benzothiadiazole. Our hypothesis is to introduce a relatively weak acceptor into



Scheme 1 Design of low band-gap polymers by weak donor-strong acceptor strategy.

donor part,^{27,28} and meanwhile incorporate 5, 6-difluoro-2, 1, 3-benzothiadiazole (**DFBT**) as a strong acceptor to ensure an appropriate LUMO level (Scheme 1).²⁹⁻³⁵ Owing to the presence of two electron-donating alkoxy side chains, 5, 6-bis(octyloxy)-2,1,3-benzothiadiazole (**BOBT**) is defined as a weak acceptor in this case. The two side chains could significantly improve the solubility of resultant polymers. Additionally, it is believed that the noncovalent Coulomb interactions $S \cdots O$ and weak hydrogen bonding $C-H \cdots N$ would minimize the polymer backbone torsional angle, thus improving backbone coplanarity.³⁶⁻³⁹ Based on these hypotheses, a unique copolymer **PTTBOBT-DFBT** was designed and synthesized to examine this concept. As depicted in Scheme 2, **BOBT** was inserted into a bithiophene building block to form a weak donor unit, which then underwent Stille coupling with strong acceptor **DFBT**. As expected, the polymer **PTTBOBT-DFBT** exhibited a deep HOMO (-5.44 eV) level, together with narrow band-gap (1.64 eV), indicating that it would be a promising candidate for OPV application. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on **PTTBOBT-DFBT**. It exhibited excellent thermal stability with 5% weight loss temperature (T_d) up to 343 °C (Fig S2). DSC revealed no clear

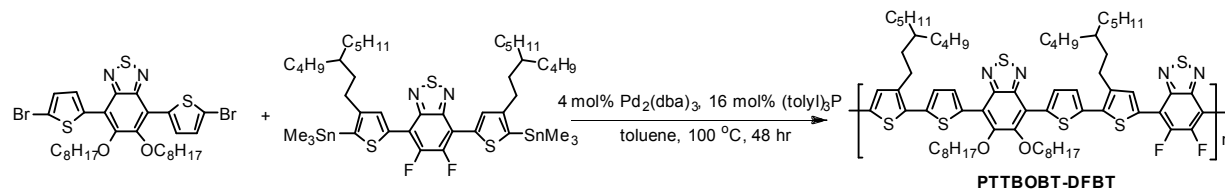
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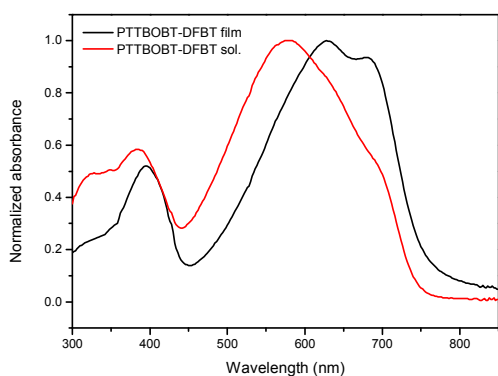
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**Scheme 2** Synthesis of weak donor-strong acceptor copolymer **PTTBOBT-DFBT**.

thermal transitions from room temperature to 300 °C (Fig S3). The optical properties of **PTTBOBT-DFBT** were studied by UV-Vis-NIR absorption spectra. The solution and thin film absorption spectra are shown in Figure 1, and the corresponding photophysical data are summarized in Table S1. In solution, it showed two absorption bands, attributable to π - π^* transition at short wavelength region and intramolecular charge transfer at long wavelength region. A small shoulder peak at ~700 nm was observed in solution, suggesting that a low degree of inter-chain aggregation existed. In its thin film spectrum, the absorption was red-shifted compared to solution (from 576 nm to 632 nm), implying stronger aggregation and higher ordering in the solid state. A significant shoulder peak at ~688 nm was observed in the absorption of thin film, indicating strong intermolecular interactions (inter-chain packing or aggregation). From the absorption onset of the polymer thin film, its optical band-gap was calculated to be 1.64 eV.

**Fig. 1** UV-Vis-NIR spectra of **PTTBOBT-DFBT** in chlorobenzene and as thin film.

The cyclic voltammetric property of **PTTBOBT-DFBT** thin film is shown in Figure S4. The HOMO level was estimated from the onsets of its corresponding oxidative peak. The LUMO level was then calculated based on the difference between the HOMO energy level and optical band-gap. **PTTBOBT-DFBT** demonstrated a deep HOMO energy level of -5.44 eV, which is

lower than these of documented analogous polymers containing either **DFBT** or **BOBT** as a single acceptor, namely **FBT-Th₄(1,4)** (-5.36 eV)^{32, 40} and **PQT12oBT** (-5.18 eV)⁴¹ (Scheme S2). Accordingly, a high V_{oc} could be expected for its bulk heterojunction OPV device. The calculated LUMO levels for **PTTBOBT-DFBT** is -3.80 eV, matching the energy difference (> 0.3 eV) with PCBM (-4.2 eV), thus ensuring efficient charge separation.

Table 1 Photovoltaic properties of **PTTBOBT-DFBT**.

Ratio ^a	T ^b	PCE (%)	J_{sc} (mA/cm ²)	FF (%)	V_{oc} (V)
1:1	25 °C	3.86	10.95	54.30	0.65
1:1	90 °C	4.65	10.63	56.48	0.77
1:1.5	90 °C	5.36	11.04	63.65	0.76
1:2	90 °C	4.72	10.36	60.10	0.76
1:2.5	90 °C	3.99	9.40	56.33	0.75

a **PTTBOBT-DFBT**:PC₇₁BM weight ratio, b T = Annealing temperature.

BHJ polymer solar cells were fabricated with a general device structure of ITO/PEDOT:PSS/copolymer:PC₇₁BM/Al and the performance was measured under 100 mW/cm² AM 1.5 G illumination. Figure 2 shows the typical current-voltage and external quantum efficiency (EQE) curves. The BHJ polymer solar cell device made from **PTTBOBT-DFBT** with weight ratio to PC₇₁BM (1:1) resulted in 3.86% PCE, and J_{sc} of 10.95 mA/cm², V_{oc} of 0.65 V and FF of 54.30%, without thermal treatment. As shown in table 1, the efficiency of **PTTBOBT-DFBT**:PC₇₁BM was significantly improved to 4.65% after annealing at 90 °C. The improvement was attributed to higher open circuit voltages and fill factor (V_{oc} = 0.77 V, FF = 56.48%), which should be stemmed from better film morphologies after thermal annealing. The effect of different polymer/PC₇₁BM ratio was then systematically investigated. When the weight ratio of **PTTBOBT-DFBT**:PC₇₁BM = 1:1.5, the highest efficiency was observed. The improvement could be attributed to higher J_{sc} and fill factor (J_{sc} , from 10.63 mA/cm² to 11.04 mA/cm²; fill factor, from 56.48% to 63.65%), while V_{oc} remained. When more acceptor materials were blended (polymer: PC₇₁BM = 1:2.0 or 1:2.5), J_{sc} and FF were decreased, although V_{oc} remained.

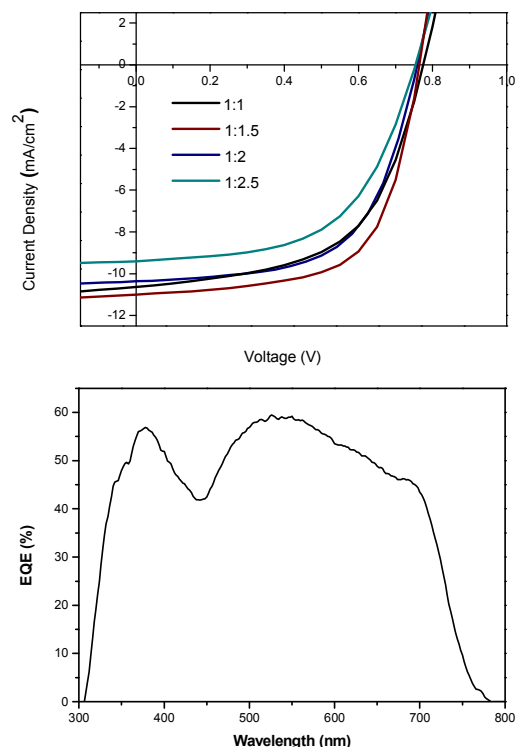


Fig. 2 Current density-voltage of photovoltaic devices using blends of PTTBOBT-DFBT/PC₇₁BM (1:1, 1:1.5, 1:2, 1:2.5) as active layers and EQE curve of photovoltaic device using blend of PTTBOBT-DFBT/PC₇₁BM (1:1.5).

As aforementioned, **FBT-Th₄(1,4)** is the analogous polymer with 5,6-difluoro-2,1,3-benzothiadiazole as a single acceptor, having a higher HOMO energy level (-5.36 eV) compared to **PTTBOBT-DFBT** (-5.44 eV). Generally, the open circuit voltage (V_{oc}) is correlated with the energy difference between the HOMO of the donor polymer and the LUMO of the acceptor (PCBM), and thus a higher V_{oc} could be expected by **PTTBOBT-DFBT**. Gratifyingly, with the same device structure, similar fabrication and test conditions, indeed a higher V_{oc} (0.77eV) was observed for **PTTBOBT-DFBT**, while **FBT-Th₄(1,4)** gave a lower V_{oc} (0.74eV).⁴⁰ This result demonstrated the additional weak acceptor **BOBT** unit could improve the open circuit voltage. However, the overall performance of **FBT-Th₄(1,4)** (PCE= 6.63%) is better than **PTTBOBT-DFBT**, which is attributed to its high short circuit current and fill factor ($J_{sc} = 12.56$, $FF = 71.30$). The higher molecular weight of **FBT-Th₄(1,4)** ($M_n = 25$ kDa) than **PTTBOBT-DFBT** ($M_n = 12.2$ kDa) and better blend film morphology may account for these interesting results. It also suggests that improvement of OPV efficiency be sophisticated, systematic considerations and optimizations are prerequisite.

The morphology of polymer:PC₇₁BM blend films has significant influence on exciton separation, charge carrier mobility and photovoltaic performance. As shown in Fig. 3, the transmission electron microscopy (TEM) image of **PTTBOBT-DFBT/PC₇₁BM** (1:1.5) blend film annealed at 90 °C possess uniform and fine features, suggesting nanoscale phase separation. Clear fibrous networks are believed to lead to large polymer-PC₇₁BM interface area for exciton dissociation, contributing to higher

FF and J_{sc} , respectively. The fibres could also be observed in phase images obtained from atomic force microscopy (Fig. S6).

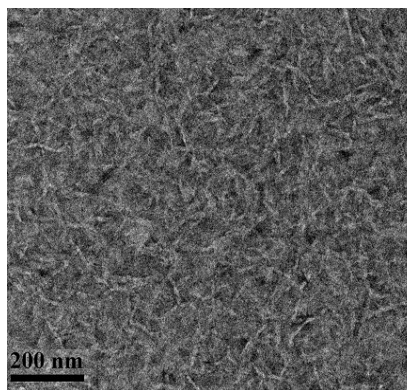


Fig. 3 TEM image of PTTBOBT-DFBT/PC₇₁BM (1:1.5) blend film.

In conclusion, by insertion of a weak acceptor moiety (**BOBT**) into a classic donor unit (tetrathiophenes), a new weak donor was formed; it then underwent coupling with a strong acceptor (**DFBT**), generating a novel weak donor-strong acceptor alternating copolymer with remarkable PCE. Comparing with reported weak donor-strong acceptor design strategy that mainly relies on fusing different aromatics into polycyclic conjugated π -systems through complicated organic synthesis, the present work would offer an alternative feasible approach to achieve low band-gap conjugated polymers with high PCE for solar cell application. More investigations to further explore the potential of this approach are in progress in our group.

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Notes and references

- 1 Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.* 2009, **109**, 5868.
- 2 X. Zhao and X. Zhan, *Chem. Soc. Rev.* 2011, **40**, 3728.
- 3 Y. Jiang, L. Lu, M. Yang, C. Zhan, Z. Xie, F. Verpoort and S. Xiao, *Polym. Chem.*, 2013, **4**, 5612.
- 4 Z. Xiao, K. Sun, J. Subbiah, T. Qin, S. Lu, B. Purushothaman, D. J. Jones, A. B. Holmes and W. W. H. Wong, *Polym. Chem.*, 2015, **6**, 2312.
- 5 M. L. Keshotov, D. V. Marochkin, V. S. Kochurov, A. R. Khokhlov, E. N. Koukaras and G. D. Sharma, *Polym. Chem.*, 2013, **4**, 4033.
- 6 C. Du, W. Li, Y. Duan, C. Li, H. Dong, J. Zhu, W. Hu and Z. Bo, *Polym. Chem.*, 2013, **4**, 2773.
- 7 J. Peet, J.-Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. C. Bazan, *Nat. Mater.* 2007, **6**, 497.
- 8 J. Hou, H.-Y. Chen, S. Zhang, G. Li and Y. Yang, *J. Am. Chem. Soc.* 2008, **130**, 16144.
- 9 M. M. Wienk, M. Turbiez, J. Gilot and R. A. J. Janssen, *Adv. Mater.* 2008, **20**, 2556.

- 10 S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, **3**, 297.
- 11 Y. Liang, D. Feng, Y. Wu, S. T. Tsai, G. Li, C. Ray and L. Yu, *J. Am. Chem. Soc.* 2009, **131**, 7792.
- 12 Y. J. He, H. Y. Chen, J. H. Hou, Y. F. Li, *J. Am. Chem. Soc.* 2010, **132**, 1377.
- 13 P. P. Khlybich, B. C. Burkhardt and B. C. Thompson, *J. Am. Chem. Soc.* 2011, **133**, 14534.
- 14 S. C. Price, A. C. Stuart, L. Q. Yang, H. X. Zhou and W. You, *J. Am. Chem. Soc.* 2011, **133**, 4625.
- 15 C. E. Small, S. Chen, J. Subbiah, C. M. Amb, S. W. Tsang, T. H. Lai, J. R. Reynolds and F. So, *Nat. Photonics* 2012, **6**, 115.
- 16 H. Xin, S. Subramanian, W. T. Kwon, S. Shoaee, J. R. Durrant and S. A. Jenekhe, *Chem. Mater.* 2012, **24**, 1995.
- 17 Y. Zhang, S. C. Chien, K. S. Chen, H. L. Yip, Y. Sun, J. A. Davies, F. C. Chen and K. Y. Jen, *Chem. Commun.* 2011, **47**, 11026.
- 18 S. Albrecht, S. Janietz, W. Schindler, J. Frisch, J. Kurpiers, J. Kniepert, S. Inal, P. Pingel, K. Fostiropoulos, N. Koch and D. Neher, *J. Am. Chem. Soc.* 2012, **134**, 14932.
- 19 H. C. Chen, Y. H. Chen, C. C. Liu, Y. C. Chien, S. W. Chou and P. T. Chou, *Chem. Mater.* 2012, **24**, 4766.
- 20 A. C. Stuart, J. R. Tumbleston, H. X. Zhou, W. T. Li, S. B. Liu and H. Ade, W. You, *J. Am. Chem. Soc.* 2013, **135**, 1806.
- 21 M. Zhang, X. Guo, S. Zhang and J. Hou, *Adv. Mater.* 2014, **26**, 1118.
- 22 F. Zhang, K. G. Jespersen, C. Björström, M. Svensson, M. R. Andersson, V. Sundström, K. Magnusson, E. Moons, A. Yartsev and O. Inganäs, *Adv. Funct. Mater.* 2006, **16**, 667.
- 23 H. Zhou, L. Yang, S. Stoneking and W. You, *Applied Materials & Interfaces*, 2010, **2**, 1377.
- 24 S. C. Price, A. C. Stuart and W. You, *Macromolecules* 2010, **43**, 797.
- 25 H.-H. Chang, C.-E. Tsai, Y.-Y. Lai, D.-Y. Chiou, S.-L. Hsu, C.-S. Hsu and Y.-J. Cheng, *Macromolecules* 2012, **45**, 9282.
- 26 H. Bronstain, J. M. Frost, A. Hadipour, Y. Kim, C. B. Nielsen, R. S. Ashraf, B. P. Rand, S. Watkins and I. McCulloch, *Chem. Mater.* 2013, **25**, 277.
- 27 B. Burkhardt, P. P. Khlyabich and B. C. Thompson, *ACS Macro Lett.* 2012, **1**, 660.
- 28 B. Burkhardt, P. P. Khlyabich and B. C. Thompson, *Macromol. Chem. Phys.* 2013, **214**, 681.
- 29 H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, *Angew. Chem. Int. Ed.* 2011, **50**, 2995.
- 30 Z. Li, J. Lu, S.-C. Tse, J. Zhou, X. Du, Y. Tao and J. Ding, *J. Mater. Chem.* 2011, **21**, 3226.
- 31 G. Li, C. Kang, X. Gong, J. Zhang, W. Li, C. Li, H. Dong, W. Hu and Z. Bo, *J. Mater. Chem. C*, 2014, **2**, 5116.
- 32 Z. Chen, P. Cai, J. Chen, X. Liu, L. Zhang, L. Lan, J. Peng, Y. Ma and Y. Cao, *Adv. Mater.* 2014, **26**, 2586.
- 33 N. Wang, Z. Chen, W. Wei and Z. Jiang, *J. Am. Chem. Soc.* 2013, **135**, 17060.
- 34 J.-F. Jheng, Y.-Y. Lai, J.-S. Wu, Y.-H. Chao, C.-L. Wang and C.-S. Hsu, *Adv. Mater.* 2013, **25**, 2445.
- 35 Y. Wang, X. Xin, Y. Lu, T. Xiao, X. Xu, N. Zhao, X. Hu, B. S. Ong and S. C. Ng, *Macromolecules* 2013, **46**, 9587.
- 36 W. Lee, G.-H. Kim, S.-J. Ko, S. Yum, S. Hwang, S. Cho, Y.-H. Shin, J. Y. Kim and H. Y. Woo, *Macromolecules* 2014, **47**, 1604.
- 37 G. Zuo, Z. Li, M. Zhang, X. Guo, Y. Wu, S. Zhang, B. Peng, W. Wei and J. Hou, *Polym. Chem.* 2014, **5**, 1976.
- 38 G. Zotti, M. C. Gallazzi, G. Zerbi and S. V. Meille, *Synth. Met.* 1995, **73**, 217.
- 39 S. V. Meille, A. Farina, F. Bezziccheri and M. C. Gallazzi, *Adv. Mater.* 1994, **6**, 848.
- 40 J. Chen, Z. Chen, P. Cai, Y. Cao, CN103030790.
- 41 K. W. Song, M. H. Choi, J. H. Song, S. W. Heo, J. Y. Lee and D. Y. Moon, *Sol. Energy Mater. Sol. Cells* 2014, **120**, 303.

