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Sulfonyl: a new application of electron-withdrawing substituent in highly efficient photovoltaic polymer†

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A strong electron-withdrawing group, sulfonyl, was firstly introduced to a semiconducting polymer, PBDTTT-S. The PCE of the PBDTTT-S device reached 6.22% with a high open-circuit voltage of 0.76 V. The sulfonyl group is thus a promising candidate as a strong electron-withdrawing group applied to high-efficiency PSCs.

The utilization of the photovoltaic effect to generate electricity from solar energy represents an appealing solution to our growing need for clean, abundant, and renewable energy sources.[1] In the past few years, bulk-heterojunction (BHJ) polymer solar cells (PSCs) have attracted much attention because of their advantages of low cost, easy fabrication, light weight, and the capability to fabricate flexible large-area devices.[1] Meanwhile, great efforts have been devoted for developing new photovoltaic materials and novel device structures in order to enhance the photovoltaic performance of PSCs. The key photovoltaic materials in PSCs are p-type conjugated polymer donors[2–5] and soluble fullerene derivative acceptors.[6,7] A general guideline to design p-type conjugated polymers is a donor–acceptor alternating polymer structure, which leads to a low band gap for efficient light harvesting. It is important that the highest occupied molecular orbital (HOMO) energy level of the donor polymer and the lowest unoccupied molecular orbital (LUMO) energy level of acceptor match so as to achieve fast charge separation and high open circuit voltage (V_{oc}), and thus high PCE.

In order to obtain a higher V_{oc}, the HOMO energy level of the conjugated polymer donors is an important issue. There are a few ways to lower the HOMO level and therefore to improve the V_{oc}. For example, conjugated polymers with alkoxy groups as a substituent usually exhibit higher HOMO levels than their alkyl-substituted counterparts. Experimentally,

Hou et al.[8] replaced the electron-donating alkoxy group with alkyl group which results in lower HOMO and therefore higher V_{oc} in the BDT-based conjugated polymers. Since alkyl is still an electron donating group, they proposed to reduce the number of alkyl side chains by using one alkyl side chain for every three thiophene units (P3HDTTT) to replace P3HT.[9] As a result, the HOMO level of P3HDTTT (-5.3 eV) is 0.4 eV lower than that of P3HT (-4.9 eV). The difference between P3HDTTT's HOMO and PCBM's LUMO is 1.1 eV, while the difference between P3HT and PCBM's LUMO is only 0.7 eV. Therefore, V_{oc} of P3HDTTT/PCBM-based PSC is 0.82 V, which is *ca.* 0.2 V higher than that of P3HT/PCBM-based PSC.[9]

Another way to modulate the HOMO level is to introduce electron-withdrawing groups or change their position.[10] A series of new semiconducting polymers with thieno[3,4-*b*]-thiophene (TT) monomer substituted by different electron-withdrawing side groups has been widely reported in polymer solar cells.[11–14] The monomer containing the thieno[3,4-*b*]-thiophene moiety, which can support the quinoidal structure and lead to a small band gap, is crucial to efficiently harvest solar energy. Since the thieno[3,4-*b*]thiophene moiety is electron-rich, introducing an electron-withdrawing group to stabilize the resulting polymers is necessary. Liang *et al.* reported a copolymer of benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) and TT, poly(4,8-bis-alkyloxybenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl-*alt*-(alkyl thieno[3,4-*b*]thiophene-2-carbozylate)-2,6-diyl) (PBDTTT-E).[11] The PSC based on the polymer as donor exhibited very promising photovoltaic properties, including a high short circuit current density (J_{sc}) and fill factor (*FF*). However, the V_{oc} of this device was only ~0.6 V, which was the limiting factor of the device's PCE.[11] Hou *et al.* reduced the HOMO level of PBDTTT-E by removal of the oxygen atom on the ester group in the thieno[3,4-*b*]thiophene units, and obtained a ketone substituted polymer, namely PBDTTT-C. The V_{oc} of the corresponding device is 0.70 V, 0.12 V higher than that of the PBDTTT-E. The average PCE is about 6.3%.[13] It is also shown that addition of more than one electron-withdrawing group is effective in further lowering the HOMO energy level and increasing the V_{oc}. There are many examples of applying fluorinated conjugated polymers in organic photovoltaics and enhanced results have been widely reported.[12,14] As the fluorine atom is a strong electron-withdrawing substituent,

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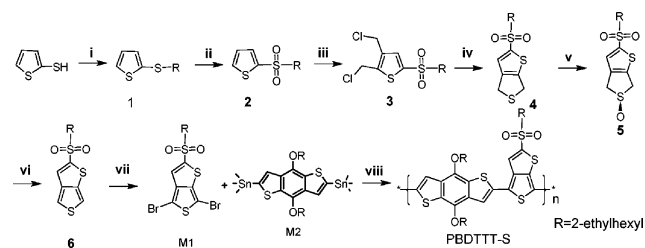‡ These authors contributed equally to this work.

the introduction of fluorine into the conjugated backbone would lower both LUMO and HOMO energy levels of the conjugated polymers. For instance, Liang *et al.* reported higher values of V_{oc} (0.74 V) when fluorine is introduced to the thieno[3,4-*b*]thiophene unit, and a PCE of 6.1% was demonstrated.[14] Hou *et al.* modified PBDTTT-C with a fluorine atom to lower its HOMO level and obtained a V_{oc} of 0.76 and a best PCE of 7.73%.[14] In a recent work, Zhou *et al.* replaced the remaining two hydrogen atoms of 2,1,3-benzothiadiazole (BT) unit with two fluorine atoms and increased the V_{oc} of the PSC based on the polymer as donor from 0.87 to 0.91 V.[15] Although the fluorine atom can effectively reduce the HOMO level of PBDTTT-based polymers, the synthesis of fluorinated monomer is quite tedious and costly.[12,14]

These results suggest that it is possible to reduce the HOMO level of polymers by introducing a stronger electron-withdrawing group to replace the existing electron-withdrawing group for improving V_{oc} of PSCs. In this work, a new strong electron-withdrawing group, sulfonyl, is used to replace the combination of ester (or ketone) and fluorinated groups to obtain a conjugated polymer with higher V_{oc}. There has been no precedent study on the photovoltaic properties of sulfonyl-containing low band gap polymers constructed using the donor–acceptor strategy.[16]

Herein we report the new copolymer of BDT and TT with sulfonyl substituent, PBDTTT-S (Scheme 1). The PBDTTT-S film shows a broad absorption with an absorption edge at 750 nm and a lower HOMO energy level at −5.12 eV. The PSC based on PBDTTT-S as donor and PC71BM as acceptor exhibits high V_{oc} of 0.76 V and PCE of 6.22%. Obviously, the sulfonyl group is a promising candidate as a strong electron-withdrawing group applied to high-efficiency PSCs.

The synthesis route of the polymer is described in Scheme 1 (see also ESI†). The polycondensation was carried out through Stille coupling reaction.[17] The weight average molecular weight (M_w) of PBDTTT-S is 18.0 K with polydispersity index (PDI) of 1.8.

Fig. 1a (inset) shows the DSC thermograms of PBDTTT-S. Interestingly, no obvious exothermic and endothermic peaks can be found over the temperature range from 25 to 250 °C by differential scanning calorimetry (DSC), indicating that the film morphology should be stable over a wide temperature range. In addition, TGA in Fig. 1a showed excellent thermal
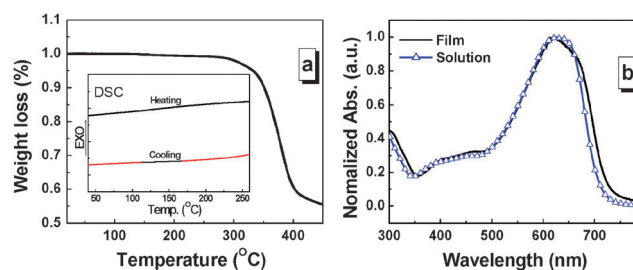

Fig. 1 (a) TGA plot of PBDTTT-S with a heating rate of 10 °C min^{-1} under the protection of nitrogen; inset: DSC thermograms of PBDTTT-S under the protection of nitrogen (heating and cooling rate: 10 °C min^{-1}); (b) normalized UV-Vis absorption spectra of PBDTTT-S in dilute CHCl$_3$ solutions and in solid films.

stability with an onset of decomposition temperature under nitrogen protection at 300 °C. There is about 40% weight loss from 290 to 400 °C. As the initial decomposition temperature of the ether group from BDT is about 290 °C, the weight loss is mainly due to the loss of the alkyl group (theoretically about 33%). Therefore, sulfonyl group is a relatively stable group in the polymer.

Absorption spectra of PBDTTT-S in the solid state and chloroform solution are shown in Fig. 1b. The absorption edges of 718 and 750 nm in solution and solid film correspond to optical band gaps of 1.73 and 1.65 eV for PBDTTT-S, respectively. The value is consistent with other PBDTTT-based polymers reported previously, which means sulfonyl almost has no influence on the band gap of this kind of polymers.

Cyclic voltammetry (CV) was used to measure oxidation and reduction potentials. PBDTTT-S presents one reversible p-doping (with onset oxidation potential $E_{ox} = 0.41$ V *vs.* Ag/Ag$^+$) and one irreversible n-doping (with onset reduction potential $E_{red} = -1.22$ V *vs.* Ag/Ag$^+$) process. The HOMO (−5.12 eV) and LUMO (−3.49 eV) energy levels (in eV) of PBDTTT-S were calculated from these electrochemical onset redox potentials according to the equations: HOMO = $-e(E_{ox} + 4.71)$ and LUMO = $-e(E_{red} + 4.71)$.[18]

Polymer solar cells were fabricated using the polymer as an electron donor material and (6,6)-phenyl-C$_{71}$-butyric acid methylester (PC$_{71}$BM) as an electron acceptor material. The device structure is ITO|PEDOT-PSS|polymer:PC$_{71}$BM|Ca|Al. The J–V curve of the fabricated PBDTTT-S/PC$_{71}$BM device under illumination of AM 1.5G (100 mW cm^{-2}) is shown in Fig. 2a The photovoltaic performance of PBDTTT-S
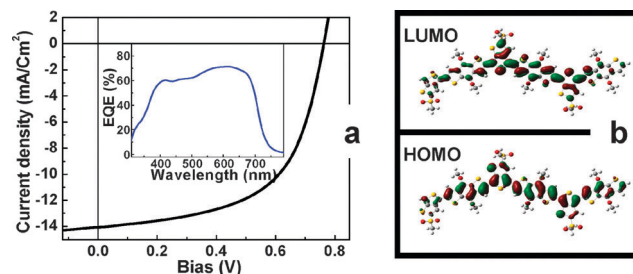

Scheme 1 Synthesis route of polymers: (i) 1-bromo-2-ethylhexane, Na$_2$CO$_3$, DMF, 110 °C, 1 h; (ii) *m*-CPBA, CHCl$_3$, ambient temp. 2 h; (iii) chloromethyl ethyl ether, SnCl$_4$, 50 °C, 0.5 h; (iv) Na$_2$S, methanol, reflux, 1 h; (v) *m*-CPBA, EtOAc, 0 °C, then ambient temp., 6 h; (vi) Ac$_2$O, reflux, 30 min; (vii) NBS, DMF, 0 °C, 5 h; (viii) Pd(PPh$_3$)$_4$, toluene, DMF, 110 °C, 18 h, argon.

Fig. 2 (a) J–V curve of the polymer solar cell based on PBDTTT-S under illumination of AM1.5, 100 mW cm^{-2} and the EQE curves of the PSC; (b) LUMO and HOMO wavefunctions of PBDTTT-S oligomer ($n = 3$) model system calculated at the B3LYP/6-31G* (d) level of theory.

exhibited a V_{oc} of 0.76 V, J_{sc} of 14.1 mA, and FF of 58%, giving a PCE of 6.22%, which is one of the highest PCEs for single active layer PSCs. It is worth noting that V_{oc} is 0.76 V, 0.16 V higher than that of the PBDTTT-E/PC$_{71}$BM-based device,[11] 0.06 V higher than that of the PBDTTT-C/PC$_{71}$BM-based device[13] and slightly higher than that of the fluorine substituted PBDTTT-E, which is 0.74 V.[19] Furthermore, the V_{oc} increases at no cost of the band gap, as a better balance of tuning band gap and energy level toward highly efficient polymer solar cell was realized. The higher V_{oc} agrees well with its low HOMO level of −5.12 eV, resulting from the stronger electron-withdrawing sulfonyl group. The external quantum efficiency (EQE) of the device is employed to reveal the photoresponse. As shown in Fig. 2a (inset), it is apparent that the device exhibits high EQE above 50% over the range 390–690 nm and the maximum EQE value reached 65% at 610 nm, which coincides with the corresponding absorption spectra and agrees well with the higher J_{sc} and better photovoltaic performance of PBDTTT-S.

To predict the electronic properties and energy levels, theoretical calculations were performed by using density functional theory (DFT) with the B3LYP/6-31G* basis set.[20] To make computation possible, we chose three repeating units as simplified models. The frontier molecular orbitals and optimized molecular geometries are illustrated in Fig. 2b. The calculated HOMO level of the oligomer is −5.12 eV. The value is almost the same as the measured one. However, the calculated LUMO level of the oligomer is about −2.81 eV, which is much higher than that of the measured value of the polymer, indicating that the LUMO level is greatly influenced by the number of repeating units. Based on the preliminary calculation, there is a general trend that the LUMO level decreases with increasing repeating units, while having little influence on the HOMO level. Compared with the reported data on fluorinated oligomers,[21] the distribution of the HOMO wave function of PBDTTT-S delocalizes over the whole π-conjugated system, while PBDTTT-S has a good delocalized LUMO wave function.

The popularity and effectiveness of fluorine is mainly originated from its strong electronegativity with Pauling electronegativity of 3.98. The Pauling electronegativity of sulfur (2.58) is lower than that of fluorine. However, after introducing two oxygen atoms with Pauling electronegativity 3.44 to the sulfur atom, the polarizability between S=O bonds should be improved to a great extent and so the electronegativity of sulfonyl is much stronger than fluorine or ester or ketone, even higher than fluorine and ester (or ketone) combined. Here it is established that the effect of sulfonyl is much better than that of fluorine or ester or ketone. As a result, our effective method to synthesize PBDTTT-S has not only reduced the synthesis process (and thus cost) and increased the yields but also resulted in a new kind of conjugated polymer with sulfonyl group which has strong electron-withdrawing ability and exhibits very promising polymer solar cell performance. The combination of a high yield and high efficiency in synthesis for a PBDTTT-based polymer and a promising solar cell performance shows a great potential for application in PSCs manufacture. From another point of view, the sulfonyl group is initially applied to polymer solar cell and provides a new way to modify and optimize the semiconducting polymer. Most importantly, it achieved a high efficiency which is not inferior to fluorine or ester or ketone substituted polymer.

In conclusion, we have reported a new strong electron-withdrawing group, sulfonyl, applied to the PBDTTT-based polymer. PBDTTT-S exhibits a PCE of up to 6.22% with a higher V_{oc} of 0.76 V under AM1.5G 100 mW cm^{-2} illumination. The higher V_{oc} from the PBDTTT-S based device originates from the strong electron-withdrawing effect of the sulfonyl group. Furthermore, the introduction of sulfonyl group to PBDTTT did not adversely affect other parameters such as J_{sc} or FF, and therefore a high PCE value can still be obtained. These results indicate that sulfonyl group is a promising candidate for application in polymer solar cells.

Notes and references

1 G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789–1791.
2 G. Dennler, M. C. Scharber and C. J. Brabec, *Adv. Mater.*, 2009, **21**, 1323–1338.
3 J. W. Chen and Y. Cao, *Acc. Chem. Res.*, 2009, **42**, 1709–1718.
4 Y. J. Cheng, S. H. Yang and C. S. Hsu, *Chem. Rev.*, 2009, **109**, 5868–5923.
5 Y. F. Li and Y. P. Zou, *Adv. Mater.*, 2008, **20**, 2952–2958.
6 Y. J. He, H. Y. Chen, J. H. Hou and Y. F. Li, *J. Am. Chem. Soc.*, 2010, **132**, 1377–1382.
7 Y. J. He and Y. F. Li, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1970–1983.
8 J. H. Hou, H. Y. Chen, S. Q. Zhang and Y. Yang, *J. Phys. Chem. C*, 2009, **113**, 21202–21207.
9 J. H. Hou, T. L. Chen, S. Q. Zhang, L. J. Huo, S. Sista and Y. Yang, *Macromolecules*, 2009, **42**, 9217–9219.
10 Y. Shu, Y. F. Lim, Z. Li, B. Purushothaman, R. Hallani, J. E. Kim, S. R. Parkin, G. G. Malliaras and J. E. Anthony, *Chem. Sci.*, 2011, **2**, 363–368.
11 L. P. Yu, Y. Y. Liang, Y. Wu, D. Q. Feng, S. T. Tsai, H. J. Son and G. Li, *J. Am. Chem. Soc.*, 2009, **131**, 56–57.
12 G. Li, Y. Y. Liang, D. Q. Feng, Y. Wu, S. T. Tsai, C. Ray and L. P. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7792–7799.
13 J. H. Hou, H. Y. Chen, S. Q. Zhang, R. I. Chen, Y. Yang, Y. Wu and G. Li, *J. Am. Chem. Soc.*, 2009, **131**, 15586–15587.
14 H. Y. Chen, J. H. Hou, S. Q. Zhang, Y. Y. Liang, G. W. Yang, Y. Yang, L. P. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649–653.
15 H. X. Zhou, L. Q. Yang, A. C. Stuart, S. C. Price, S. B. Liu and W. You, *Angew. Chem., Int. Ed.*, 2011, **50**, 2995–2998.
16 Y. F. Wang and M. D. Watson, *Macromolecules*, 2008, **41**, 8643–8647.
17 D. Milstein and J. K. Stille, *J. Am. Chem. Soc.*, 1978, **100**, 3636–3638.
18 J. H. Hou, Z. A. Tan, Y. Yan, Y. J. He, C. H. Yang and Y. F. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4911–4916.
19 Y. Y. Liang, D. Q. Feng, Y. Wu, S. T. Tsai, G. Li, C. Ray and L. P. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7792–7799.
20 R. G. Parr and Y. Weitao, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
21 H. J. Son, W. Wang, T. XU, Y. Liang, Yue Wu, L. Gang and L. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 1885–1894.