

Dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]oxadiazole-based polymer donors with deep HOMO levels

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Citation: X F Li, J G Xu, Z Xiao, X Z Wang, B Zhang, and L M Ding, Dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]oxadiazole-based polymer donors with deep HOMO levels[J]. *J. Semicond.*, 2021, 42(6), 060501. <http://doi.org/10.1088/1674-4926/42/6/060501>

Star nonfullerene acceptors like ITIC^[1], IDIC^[2], O-IDTBR^[3], IT-4F^[4], CO₈DFIC^[5], Y6^[6] etc. continuously emerge and keep pushing the power conversion efficiency (PCE) of organic solar cells forward. These small molecules generally show narrow bandgaps, excellent visible to NIR light-harvesting capability, good electron mobility, suitable energy levels and miscibility with the donor materials. PCEs up to 18.56% have been achieved for the state-of-the-art nonfullerene organic solar cells^[7]. On the other hand, donor materials matching nonfullerene acceptors also received considerable interests^[8]. Owing to complementary light absorption, high hole-mobility and deep HOMO levels, wide-bandgap (WBG) conjugated copolymers are ideal donor partners for the low-bandgap nonfullerene acceptors. Hou *et al.* developed a WBG copolymer donor PM6 based on a benzo[1,2-c:4,5-c']dithiophene-4,8-dione (BDD) unit^[9]. PM6 has been widely applied in nonfullerene solar cells, delivering high PCEs up to 17.8%^[10]. Li *et al.* reported a simple-structured WBG copolymer PTQ10 based on a quinoxaline unit^[11]. Solar cells based on PTQ10 and Y6 gave a PCE of 16.53%^[12]. Huang *et al.* developed a WBG copolymer P2F-EHp by using an imide-functionalized benzotriazole (TzBI) unit^[13]. P2F-EHp:Y6 solar cells gave a 16.02% PCE. Guo *et al.* synthesized a random copolymer S1 with a fluorine and ester group functionalized thiophene (FE-T) unit^[14]. Owing to the strong electron-withdrawing property of FE-T, S1 has a deep HOMO level and delivered a high open-circuit voltage (V_{oc}) of 0.88 V and a PCE of 16.42%. Ding *et al.* developed a 2.16 eV ultra-WBG copolymer W1 by using a fluorinated 1,2-dialkoxybenzene (FAB) unit^[15]. The FAB unit offers unique S...O and F...H double-side conformation locking in the copolymer backbone, and renders W1 enhanced packing and good hole-transporting capability^[16]. W1:Y6 solar cells gave a PCE of 16.23%. Ding *et al.* also developed several high-performance WBG copolymer donors based on fused-ring acceptor units. The WBG copolymer L1 based on a fused-ring lactone unit 5H-dithieno[3,2-b:2',3'-d]pyran-5-one (DTP) delivered a 14.36% PCE^[17]. A fused-ring thiolactone copolymer D16 based on the 5H-dithieno[3,2-b:2',3'-d]thiopyran-5-

one (DTTP) unit gave a higher PCE of 16.72%^[18]. By using a dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]thiadiazole (DTBT) unit, which has a larger molecular plane than DTP and DTTP, Ding *et al.* developed a more efficient WBG copolymer donor D18^[19]. D18:Y6 solar cells gave a PCE of 18.22% (certified 17.6%). This is the first time for the PCE of OSCs surpassing 18%. Thick-film D18:Y6:PC₆₁BM ternary cells delivered 16% PCEs with an active layer thickness over 300 nm^[20]. Ding *et al.* further reported a chlorinated analogue of D18, the D18-Cl^[21]. Blending D18-Cl with a nonfullerene acceptor N3 yielded a PCE of 18.13% (certified 17.6%). Very recently, Ding *et al.* pushed the PCE to 18.56% (certified 17.9%) by blending D18 with N3, setting a new PCE record^[7]. These works demonstrated the advantages of fused-ring acceptor units in constructing WBG copolymer donors. The strong electron-withdrawing capability and extended molecular planes of these acceptor units gift copolymers deep HOMO levels, enhanced packing and high hole mobility, thus leading to improved V_{oc} , short-circuit current density (J_{sc}) and fill factor (FF) in solar cells. In this work, we report copolymers P1 and P2 based on a dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]oxadiazole (DTBO) unit (Fig. 1(a)). Compared with DTBT, DTBO has fewer synthetic steps and is more cost-effective^[22]. DFT calculations indicate that DTBO renders the copolymer a deeper HOMO level, thus yielding higher V_{oc} in solar cells. Solar cells with P1 and P2 as the donors and Y6 as the acceptor afforded high V_{oc} up to 0.91 V and decent PCEs up to 15.64%.

We built the polymer models for D18, P1 and P2 (Fig. 1(b)). Each model has two repeating units, and the alkyl chains were replaced by methyl groups for saving the calculation time. All structures were optimized at the B3LYP/6-31G(d) level. The DFT-predicted frontier molecular orbitals and energy levels for D18, P1 and P2 are shown in Fig. 1(b). From D18 to P1, DTBT being replaced by DTBO, simultaneous decrease in HOMO and LUMO energy levels was observed. The HOMO and LUMO levels for P1 are -5.05 and -2.69 eV, respectively, which are ~0.1 eV lower than that of D18. A higher V_{oc} was expected for P1-based solar cells since V_{oc} is proportional to the energy difference between donor HOMO and acceptor LUMO^[23]. Compared with P1, P2 shows higher HOMO and LUMO levels of -4.94 and -2.61 eV, respectively, due to the removal of electron-withdrawing fluorine atoms. For P1 and P2, the variation trends in DFT-predicted HOMO and LUMO levels are consistent with those from cyclic voltammetry (CV) measurements (*vide infra*).

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Received 18 MARCH 2021.

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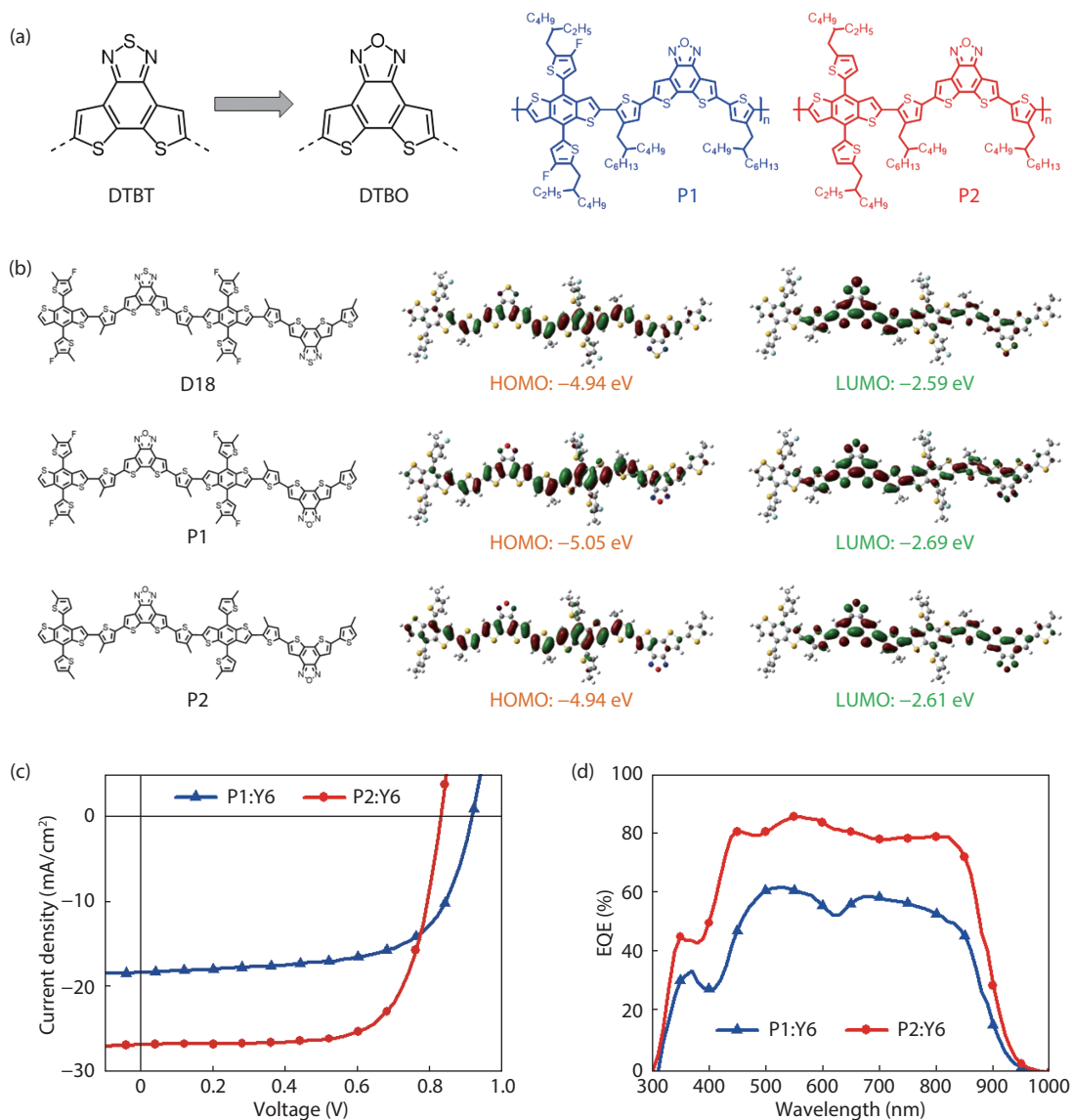


Fig. 1. (Color online) (a) DTBT and DTBO building blocks, and DTBO-based copolymers P1 and P2. (b) Molecular models and corresponding frontier molecular orbitals and energy levels for D18, P1 and P2. (c) J - V curves for P1:Y6 and P2:Y6 solar cells. (d) EQE spectra for P1:Y6 and P2:Y6 solar cells.

The synthetic routes for P1 and P2 are shown in Scheme S1. The 5,8-dibromodithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]oxadiazole (DTBO-Br) coupled with tributyl(4-(2-butyloctyl)thiophen-2-yl)stannane gave compound 1 in 62% yield. Bromination of compound 1 with NBS gave compound 2 in 80% yield. Copolymerization of compound 2 with (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (FBDT-Sn) and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT-Sn) gave P1 and P2 in 90% and 58% yield, respectively. The number-average molecular weights (M_n) for P1 and P2 are 38.0 and 47.0 kDa, respectively, with the polydispersity indexes (PDI) of 2.08 and 1.67, respectively. P1 and P2 are soluble in chloroform and chlorobenzene. The absorption spectra for P1, P2 and Y6 films are shown in Fig. S7. Both P1 and P2 show two absorption peaks, with a high-energy peak at 545 and 549 nm, respectively, and a low-energy peak at 582 and 590 nm, respectively. The absorption band for P1 and P2 lies in 400–620 nm region, which is complementary with that of Y6 (560–920 nm).

The absorption onsets for P1 and P2 films are 626 and 633 nm, respectively, corresponding to optical bandgaps (E_g^{opt}) of 1.98 and 1.96 eV, respectively. Energy levels for P1 and P2 were estimated from CV measurements (Fig. S8). The HOMO and LUMO levels for P1 and P2 were calculated from the onset potentials of oxidation ($E_{\text{on}}^{\text{ox}}$) and reduction ($E_{\text{on}}^{\text{red}}$), respectively, i.e., $\text{HOMO} = -(E_{\text{on}}^{\text{ox}} + 4.8)$ and $\text{LUMO} = -(E_{\text{on}}^{\text{red}} + 4.8)$. The energy level diagram is presented in Fig. S9. P1 and P2 show deep HOMO levels of -5.61 and -5.45 eV, respectively, which are favorable for producing high V_{oc} in solar cells. The HOMO level of P1 is 0.1 eV deeper than that of D18 (-5.51 eV)^[19], consisting with DFT calculation.

Solar cells with a structure of ITO/PEDOT:PSS/polymer:Y6/PDIN/Ag were made to evaluate the performance of P1 and P2. The D/A ratio, active layer thickness and additive (1-chloronaphthalene) content were optimized (Tables S1–S6). J - V curves and external quantum efficiency (EQE) spectra for the best cells are shown in Figs. 1(c) and 1(d), respectively. The best P1:Y6 cells gave a PCE of 10.92%, with a V_{oc} of 0.91 V, a J_{sc} of 18.22 mA cm⁻² and a FF of 65.7%. These cells

have a D/A ratio of 1 : 1.6 (w/w), an active layer thickness of 110 nm and no additive. The best P2:Y6 cells gave a PCE of 15.64%, with a V_{oc} of 0.83 V, a J_{sc} of 26.72 mA cm⁻² and a FF of 70.6%. These cells have a D/A ratio of 1 : 1.6 (w/w), an active layer thickness of 120 nm and no additive. The V_{oc} of P1:Y6 cells is 0.05 V higher than that of D18:Y6 cells^[19], suggesting the advantage of DTBO unit in enhancing V_{oc} . The P2:Y6 cells present much better performance than P1:Y6 cells due to the higher J_{sc} and FF. P2 cells afforded higher EQE than P1 cells in the whole spectrum, with the maximum EQE of 86% at 560 nm (Fig. 1(d)). The integrated current densities for P1 and P2 cells are 17.56 and 25.75 mA cm⁻², respectively, consistent with J_{sc} from J - V measurements. The exciton dissociation probabilities (P_{diss}) for P1 and P2 cells are 96.3% and 98.4%, respectively, suggesting more efficient carrier generation in the latter (Fig. S10)^[24]. Higher J_{sc} and FF for P2 cells suggest a superior charge-transporting capability of P2. Hole mobilities (μ_h) were measured for pure P1 and P2 films by using space-charge limited current (SCLC) method (Fig. S11)^[25–27]. The μ_h for P1 and P2 are 5.13×10^{-4} and 8.82×10^{-4} cm² V⁻¹ s⁻¹, respectively, confirming the better hole-transporting capability of P2. The μ_h and the electron mobilities (μ_e) were also measured for the blend films (Figs. S12 and S13). Compared with P1:Y6 film, P2:Y6 film gave a higher μ_h of 3.92×10^{-4} cm² V⁻¹ s⁻¹, a higher μ_e of 2.97×10^{-4} cm² V⁻¹ s⁻¹, and a smaller μ_h/μ_e of 1.32 (Table S7). We investigated bimolecular recombination by plotting J_{sc} against light intensity (P_{light}) (Fig. S14)^[28–31]. P2:Y6 cells showed a α value of 0.985, which is closer to 1 than that of P1:Y6 cells (0.973), suggesting less bimolecular recombination in P2:Y6 cells. The faster and more balanced charge transport as well as less charge recombination in P2:Y6 cells account for the higher FF. The morphology for P1:Y6 and P2:Y6 blend films was studied by using atomic force microscope (AFM) (Fig. S15). Both films present nanofiber structures. Compared with P1:Y6 film, P2:Y6 film has a smoother surface. The root-mean-square roughnesses for P1:Y6 and P2:Y6 films are 1.20 and 1.02 nm, respectively.

In summary, a fused-ring acceptor unit DTBO was developed. Compared with previously reported DTBT unit, DTBO can lower the HOMO level of polymer donors, thus increasing the V_{oc} of solar cells. DTBO-based copolymers delivered a maximum V_{oc} of 0.91 V and a maximum PCE of 15.64%.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2017YFA0206600, SQ2020YFE010701), the National Natural Science Foundation of China (51773045, 21772030, 51922032, 21961160720, 51473053) and the Natural Science Foundation of Hunan Province (2019JJ50603).

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at <https://doi.org/10.1088/1674-4926/42/6/060501>.

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