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# Small molecule BODIPY dyes as non-fullerene acceptors in bulk heterojunction organic photovoltaics†

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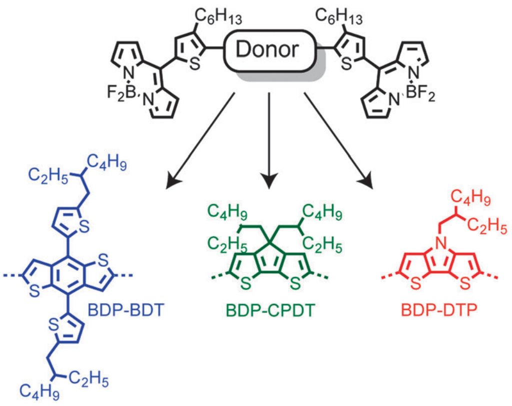
**A series of acceptor–donor–acceptor molecules containing terminal BODIPY moieties conjugated through the *meso* position were synthesized. Deep LUMO energy levels and good visible absorption led to their use as acceptors in bulk heterojunction solar cells. Inverted devices were fabricated, reaching efficiencies as high as 1.51%.**

The field of organic photovoltaics (OPV) has advanced in recent years through extensive investigation into various conjugated polymer and small molecule structures. Most of these accomplishments have been focused on optimizing donors in bulk heterojunction (BHJ) organic solar cells, where the acceptor is primarily based on fullerenes.[1] While fullerene derivatives have several obviously attractive features for BHJ OPV devices,[2] the search for non-fullerene acceptors has gained significant attention in recent years, mainly driven by the possibility that the new acceptors could exhibit stronger absorption in the visible region of the electromagnetic spectrum.[3] Concurrently, there has also been a surge in the development of small molecules as active materials for OPVs, because of the reproducibility and the potential for frontier orbital energy level controls that they offer.[1c,3c] The combination of these two interests has triggered the search for small molecule non-fullerene acceptors for BHJ OPV.[1b,3b,4]

Considering that 4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (BODIPY) based molecules exhibit a strong absorption in the visible region (>500 nm) and variable redox chemistry, we conceived the use of these molecules as acceptors in BHJ OPV devices.[5,6] Specifically, we hypothesized that acceptor–donor–acceptor (A–D–A) type molecules with BODIPY as the acceptor moiety will provide convenient access to low band-gap small molecules that could be tested as acceptors in BHJ devices. Herein, we report three such molecules, in which BODIPY is conjugated through its *meso* position using a 3-hexylthiophene linker to 4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)benzo[1,2-*b*:4,5-*b*′]dithiophene, 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta-[2,1-*b*:3,4-*b*]dithiophene or *N*-(2-ethylhexyl)-dithieno [3,2-*b*:2′,3′-*d*]pyrrole to afford **BDP-BDT**, **BDP-CPDT**, and **BDP-DTP** respectively (Scheme 1). These molecules show strong visible absorption with low lying LUMO levels, making them electronically suitable as acceptors for many donor materials. To examine their potential as acceptors in BHJ OPVs, devices were fabricated using P3HT as the donor.

Syntheses of the molecules include the formation of a terminal unit composed of a BODIPY core substituted at the *meso* position with a brominated hexylthiophene, providing an additional solubilizing group and a functional handle on the α-position of the thiophene for subsequent palladium catalyzed cross coupling reactions. The lack of β-substituents on the BODIPY moiety is expected to greatly benefit the overall planarity of the molecule due to the limited steric interactions that often force a twist between the thiophene and the BODIPY cap.[7] This molecule is synthesized through Liebeskind–Srogl coupling between 8-(thiomethyl)-BODIPY and 2-bromo-3-hexylthiophene-5-boronic acid.[8] Stille coupling between the bistannylated donors and the previously synthesized terminal unit afforded the targeted molecules in good yields. For detailed syntheses and characterization, refer to the ESI.†



Scheme 1 Molecular structures of the BODIPY-based A–D–A molecules.

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† Electronic supplementary information (ESI) available: Detailed synthetic procedures, NMR spectra, cyclic voltammograms, OFET device preparation procedure and output and transfer characteristics, photovoltaic device preparation procedure and related data. See DOI: 10.1039/c3cc49648a

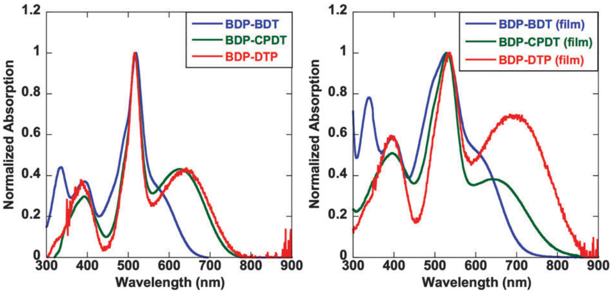

Fig. 1 Solution (left) and thin film (right) absorption spectra of **BDP-BDT**, **BDP-CPDT** and **BDP-DTP**.

Donor incorporation through the α and β positions of the BODIPY core is known to extend conjugation and, in turn, red shift the absorption and reduce the band gap of the resulting system. However, conjugation through the *meso* position does not typically provide the same dramatic shift in absorption due to minimal communication between the core and terminal BODIPY in the ground state.[9] Consequently, through selective tuning of the core, a system possessing a predictable and well-defined absorption profile with significant absorbance within the visible region of the solar spectrum can be synthesized with ease. This feature is important for tuning the absorption properties of the acceptor to complement the donor material with which it is paired in BHJ devices.

Fig. 1 shows the UV-visible absorption spectra of chlorobenzene solutions and thin films spun from dichloromethane solutions; the optical properties are summarized in Table 1. The three molecules exhibit an absorption maximum that is characteristic of the π–π* transition in the BODIPY moiety,[10] with an extinction coefficient on the order of $10^4$ $M^{-1}$ $cm^{-1}$ (Table 1). This absorption slightly red shifts in thin films. All molecules also exhibit a lower energy shoulder that is attributed to an intramolecular charge transfer process, as its position in both the solution and solid states varies with the donor strength of the core moiety. While this band exists as a shoulder in **BDP-BDT**, both **BDP-CPDT** and **BDP-DTP** possess significantly red shifted peaks with absorption onsets at 805 and 845 nm respectively. The significant shift in the latter two molecules is attributed to the enhanced donor strength of the core moiety.[11] The optical band gaps for these molecules were estimated from the absorption onset in thin films (Table 1).

Next, the electrochemical properties of the molecules were examined using cyclic voltammetry.[12] Each molecule shows amphoteric behavior, exhibiting two reversible oxidations and at least one reduction (Fig. S1, ESI†). The onset of the first oxidation potential for **BDP-CPDT** and **BDP-DTP** are very similar, leading to comparable HOMO energy levels (Table 1). Decreasing the donor strength of the core moiety stabilized the HOMO energy level, as the weakest donor (**BDP-BDT**) possesses the most stable HOMO (−5.40 eV). $E^{red}$ values are similar throughout the series, indicating that the reduction of the BODIPY moiety within the molecule is relatively unaffected by the donor strength of the core moiety. Since each of these molecules possesses a LUMO significantly lower than that of P3HT, exciton dissociation is thermodynamically possible, allowing them to be considered as candidates for acceptors in BHJ devices.

To investigate the charge transport properties of these molecules, bottom contact organic field effect transistors (OFET) were fabricated. Output and transfer characteristics are displayed and summarized in the ESI.† All molecules exhibit only n-type characteristics with mobilities on the order of $10^{-5}$ $cm^2$ $V^{-1}$ $s^{-1}$ (Table S1, ESI†). Of the devices, **BDP-CPDT** exhibited the highest electron mobility ($5.77 \times 10^{-5}$ $cm^2$ $V^{-1}$ $s^{-1}$), while that of **BDP-BDT** was the lowest ($3.30 \times 10^{-5}$ $cm^2$ $V^{-1}$ $s^{-1}$). Although the directionality of charge transport in OPV devices and OFET devices is orthogonal, the consistent n-type transport in these BODIPY-capped molecules does suggest that this functionality could be a promising building block of low band gap, small molecule acceptors for OPVs.

Inverted OPV devices were fabricated with the architecture ITO/ZnO/P3HT:acceptor (40 nm)/$MoO_3$ (7 nm)/Ag (100 nm). The active layer was spun cast from 15 mg $ml^{-1}$ solutions in *o*-dichlorobenzene (*o*-DCB). An optimal D : A ratio was determined to be 1 : 1.5 for each acceptor (ESI†) with **BDP-BDT**, **BDP-CPDT** and **BDP-DTP** yielding efficiencies of 1.21%, 1.02% and 0.84%, respectively. To assess whether the light absorption characteristics at wavelengths complementary to that of P3HT contribute to the overall efficiency, we obtained the external quantum efficiency (EQE) for these devices (Fig. 2). EQE measurements show that the devices containing acceptors with red shifted charge transfer bands (**BDP-CPDT**, **BDP-DTP**) significantly benefit from the

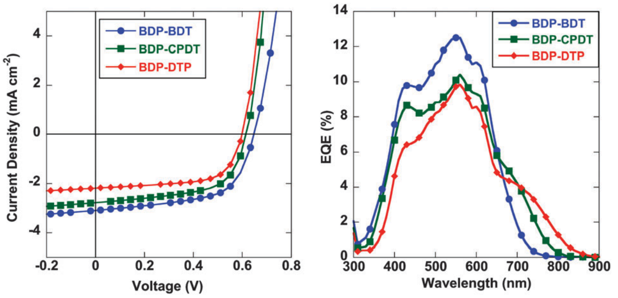

Fig. 2 *J–V* curves (left) and EQE spectra (right) of devices with various acceptors where the P3HT : acceptor ratio is 1 : 1.5.

Table 1 Optical and electrochemical properties of synthesized molecules

| | $\lambda_{max}^{solution}$ (nm) ($\varepsilon$ ($\times 10^4$ $M^{-1}$ $cm^{-1}$))[a] | $\lambda_{max}^{film}$ (nm) ($\lambda_{onset}^{film}$ (nm))[b] | $E_g^{optc}$ (eV) | $E^{ox\,d}$ (V) | HOMO[e] (eV) | $E^{red\,d}$ (V) | LUMO[f] (eV) |
|---|---|---|---|---|---|---|---|
| **BDP-BDT** | 518 (6.2) | 532 (717) | 1.73 | 0.60 | −5.40 | −0.91 | −3.79 |
| **BDP-CPDT** | 516 (7.6) | 530 (805) | 1.54 | 0.36 | −5.16 | −0.98 | −3.82 |
| **BDP-DTP** | 516 (2.5) | 532 (845) | 1.47 | 0.34 | −5.14 | −1.06 | −3.74 |

[a] Measured in chlorobenzene solutions. [b] Determined from thin films spun cast from dichloromethane solutions and annealed at 150 °C. [c] $E_g^{opt} = 1240/\lambda_{onset}^{film}$. [d] Determined from the onset of oxidation and reduction extracted from cyclic voltammograms measured in anhydrous dichloromethane with 0.1 M $Bu_4NPF_6$ as the supporting electrolyte and corrected with respect to the $Fc/Fc^+$ redox couple. [e] HOMO = $-(E^{ox} + 4.8)$. [f] LUMO = $-(E^{red} + 4.8)$.

Table 2 Photovoltaic cell performance (ITO/ZnO/P3HT : acceptor (1 : 1.5)/$MoO_3$/Ag) with various amounts of the CN solvent additive

| Acceptor | CN (vol%) | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF | PCE (%) |
|---|---|---|---|---|---|
| **BDP-BDT** | 0 | 0.65 | 3.09 | 0.60 | 1.21 |
| | 1 | 0.39 | 2.73 | 0.30 | 0.33 |
| | 3 | 0.57 | 3.20 | 0.56 | 1.01 |
| | 5 | 0.14 | 3.03 | 0.26 | 0.11 |
| **BDP-CPDT** | 0 | 0.60 | 3.28 | 0.61 | 1.20 |
| | 1 | 0.60 | 3.04 | 0.61 | 1.11 |
| | 3 | 0.62 | 3.90 | 0.63 | 1.51 |
| | 5 | 0.61 | 3.67 | 0.63 | 1.41 |
| **BDP-DTP** | 0 | 0.60 | 2.18 | 0.65 | 0.84 |
| | 1 | 0.56 | 2.64 | 0.62 | 0.92 |
| | 3 | 0.57 | 3.28 | 0.63 | 1.18 |
| | 5 | 0.57 | 1.60 | 0.62 | 0.56 |

Active layers spun cast from 1,2-dichlorobenzene solutions (15 mg ml$^{-1}$) at 1500 RPM for 60 s and annealed at 150 °C for 2 min.

acceptor absorption above 650 nm. The weaker performance of the **BDP-DTP** molecule is due to the relatively low $J_{SC}$ (2.18 mA cm$^{-2}$), which is likely due to non-optimal active layer morphology. Use of solvent additives has improved the efficiency of PCBM-based BHJ devices, which has been attributed to the ability of certain solvents to promote PCBM aggregation by selectively solubilizing the acceptor.[13] Since these acceptors have good solubility in most organic solvents, we decided to use 1-chloronaphthalene (CN) as a solvent additive. The *J–V* curves and EQE spectra are shown in the ESI;† the device characteristics are listed in Table 2.

The use of CN as a solvent additive had positive effects on the **BDP-CPDT** and **BDP-DTP** devices, as the device efficiency increased to 1.51% and 1.18%, respectively, when 3% CN was added. However, CN had a detrimental effect on **BDP-BDT** devices, yielding decreased $V_{OC}$ and FF values (Table 2). To examine the effect of CN on the morphology of the P3HT:**BDP-CPDT** devices, atomic force microscopy (AFM) was used. AFM height and phase images of the P3HT:**BDP-CPDT** active layer are shown in Fig. S9 (ESI†). Addition of 3% CN increased the surface roughness from 5.9 nm to 7.2 nm; the additive-based device also shows a much more uniform and well-ordered network, which is desired for efficient charge transport.

In summary, a series of n-type small molecules consisting of a thiophene-based donor core conjugated to a BODIPY cap through the *meso* position were synthesized. These molecules exhibited good visible absorption with a common peak between 530 and 532 nm in thin films, independent of the donor core. Introduction of a stronger donor (CPDT, DTP) to the core of the molecule led to a significant red shift in the charge transfer band, resulting in an optical band gap as low as 1.47 eV. Each of the molecules possessed a low-lying LUMO, between −3.7 eV and −3.9 eV, and a decent electron mobility, $\sim 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, making them potential acceptors for many donor materials. Inverted bulk heterojunction photovoltaic devices were successfully fabricated, combining these molecules with P3HT as the donor. The P3HT:**BDP-BDT** active layer yielded an efficiency of 1.21%. The use of 1-chloronaphthalene as a solvent additive improved the device performance in **BDP-CPDT** and **BDP-DTP** based devices, with the best performing cell yielding a PCE of 1.51% (P3HT:**BDP-CPDT** + 3% CN). Further device optimization and morphological studies of the blends are currently underway. Also, we are further investigating the effect of both core and cap modifications on the electronic properties of the resulting materials for optimal pairing with donors other than P3HT. Through fine-tuning of the molecular structure *vs.* device performance and morphological characteristics, we hope to achieve a library of BODIPY based electron acceptors with robust electronic properties for OPV applications.

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## Notes and references

1 (*a*) Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photonics*, 2012, **6**, 593; (*b*) C. L. Chochos and S. A. Choulis, *Prog. Polym. Sci.*, 2011, **36**, 1326; (*c*) Y. Lin, Y. Li and X. Zhan, *Chem. Soc. Rev.*, 2012, **41**, 4245; (*d*) Y. Li, *Acc. Chem. Res.*, 2012, **45**, 723; (*e*) L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li and J. Hou, *Angew. Chem., Int. Ed.*, 2011, **50**, 9697; (*f*) H. Zhou, L. Yang and W. You, *Macromolecules*, 2012, **45**, 607.

2 (*a*) B. C. Thompson and J. M. Frechet, *Angew. Chem., Int. Ed.*, 2008, **47**, 58; (*b*) T. Liu and A. Troisi, *Adv. Mater.*, 2013, **25**, 1038.

3 (*a*) Y. Zhou, Y. Z. Dai, Y. Q. Zheng, X. Y. Wang, J. Y. Wang and J. Pei, *Chem. Commun.*, 2013, **49**, 5802; (*b*) J. T. Bloking, X. Han, A. T. Higgs, J. P. Kastrop, L. Pandey, J. E. Norton, C. Risko, C. E. Chen, J.-L. Brédas, M. D. McGehee and A. Sellinger, *Chem. Mater.*, 2011, **23**, 5484; (*c*) C. L. Chochos, N. Tagmatarchis and V. G. Gregoriou, *RSC Adv.*, 2013, **3**, 7160.

4 (*a*) Y. Zhou, L. Ding, K. Shi, Y. Z. Dai, N. Ai, J. Wang and J. Pei, *Adv. Mater.*, 2012, **24**, 957; (*b*) Y. Lin, P. Cheng, Y. Li and X. Zhan, *Chem. Commun.*, 2012, **48**, 4773; (*c*) J. E. Anthony, *Chem. Mater.*, 2011, **23**, 583; (*d*) A. F. Eftaiha, J.-P. Sun, I. G. Hill and G. C. Welch, *J. Mater. Chem. A*, 2014, **2**, 1201.

5 A. C. Benniston and G. Copley, *Phys. Chem. Chem. Phys.*, 2009, **11**, 4124.

6 Y. Hayashi, N. Obata, M. Tamaru, S. Yamaguchi, Y. Matsuo, A. Saeki, S. Seki, Y. Kureishi, S. Saito, S. Yamaguchi and H. Shinokubo, *Org. Lett.*, 2012, **14**, 866.

7 (*a*) A. C. Benniston, G. Copley, A. Harriman, D. B. Rewinska, R. W. Harrington and W. Clegg, *J. Am. Chem. Soc.*, 2008, **130**, 7174; (*b*) C.-C. Chi, Y.-J. Huang and C.-T. Chen, *J. Chin. Chem. Soc.*, 2012, **59**, 305.

8 (*a*) E. Lager, J. Liu, A. Aguilar-Aguilar, B. Z. Tang and E. Pena-Cabrera, *J. Org. Chem.*, 2009, **74**, 2053; (*b*) E. Pena-Cabrera, A. Aguilar-Aguilar, M. Gonzalez-Dominguez, E. Lager, R. Zamudio-Vazquez, J. Godoy-Vargas and F. Villanueva-Garcia, *Org. Lett.*, 2007, **9**, 3985.

9 (*a*) J. C. Forgie, P. J. Skabara, I. Stibor, F. Vilela and Z. Vobecka, *Chem. Mater.*, 2009, **21**, 1784; (*b*) B. C. Popere, A. M. Della Pelle, A. Poe, G. Balaji and S. Thayumanavan, *Chem. Sci.*, 2012, **3**, 3093; (*c*) E. H. A. Beckers, P. A. van Hal, A. Dhanabalan, S. C. J. Meskers, J. Knol, J. C. Hummelen and R. A. J. Janssen, *J. Phys. Chem. A*, 2003, **107**, 6218.

10 (*a*) H. Y. Lin, W. C. Huang, Y. C. Chen, H. H. Chou, C. Y. Hsu, J. T. Lin and H. W. Lin, *Chem. Commun.*, 2012, **48**, 8913; (*b*) S. Yin, V. Leen, C. Jackers, D. Beljonne, B. Van Averbeke, M. Van der Auweraer, N. Boens and W. Dehaen, *Chem.–Eur. J.*, 2011, **17**, 13247.

11 D. Collado, J. Casado, S. Rodriguez Gonzalez, J. T. Lopez Navarrete, R. Suau, E. Perez-Inestrosa, T. M. Pappenfus and M. M. Raposo, *Chem.–Eur. J.*, 2011, **17**, 498.

12 C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367.

13 (*a*) M. T. Dang, L. Hirsch and G. Wantz, *Adv. Mater.*, 2011, **23**, 3597; (*b*) J. Peet, A. J. Heeger and G. C. Bazan, *Acc. Chem. Res.*, 2009, **42**, 1700; (*c*) A. Facchetti, *Chem. Mater.*, 2011, **23**, 733.