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Original article

Tailoring the photophysical and photovoltaic properties of borondifluorodipyrromethene dimers

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Graphical abstract



The photophysical and photovoltaic properties of BODIPY based dimers can be modulated effectively by facile structural modifications.

ABSTRACT

Five boron-difluorodipyrromethene (BODIPY) dimers have been designed and synthesized successfully via acid-catalysed condensation and Pdcatalysed cross-coupling reactions. The structural modification, including verifying the structures of the π -bridges, altering the positions the bridges link (*meso-* or β - positions), and regulating the molecular planarity, can modulate the photophysical properties and the aggregation behaviors of the five dimers efficiently. Solution-processed organic solar cells were fabricated to evaluate the photovoltaic properties of these molecules further either as acceptors or donors. When using as nonfullerene acceptor and blended with the polymer donor of PTB7, an open-circuit voltaic (V_{oc}) of 1.12 and 1.08 V was achieved from the thiophene and benzodithiophene bridged BODIPY dimers, respectively. This V_{oc} is among the top values achieved from the non-fullerene organic solar cells so far.

Keywords: BODIPY Nonfullerene acceptor Small molecule donor Photovoltaic cell

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1. Introduction

The 4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes (BODIPY) dyes, known as the "little sister" of porphyrins because of the similar dipyrromethene backbone they possess [1, 2], have gained much attention in the field of labeling, liquid-crystalline materials, chemical sensors, electroluminescence, energy transfer cassettes and dye-sensitized solar cells recently [3-12]. The wide range of the applications of these dyes have a very close relationship with their excellent properties, such as facile functionalization of their backbones, outstanding spectroscopic properties with maximum molar extinction coefficient (ε_{max}) larger than 80×10^3 L mol⁻¹ cm⁻¹ and quantum yield (Φ_F) larger than 0.5, insensitive to the solvent polarity, together with excellent thermal and chemical stability [13-16]. Due to the advantages aforementioned as well as the suitable frontier energy levels of the BODIPY core, it has been regarded as promising candidate as electron-deficient group in the regime of organic photovoltaic in the past decade. By rationally tailoring the structures, such as extending the π -system by attaching or fusing electron-donating aromatic building blocks at the α and β positions, reinforcing intermolecular interaction by modifying the fragments at the meso position, power conversion efficiency (PCE) of near 5% have been realized [17-27]. Very recently, the BODIPYs have been used as the building blocks to construct non-fullerene acceptors and a moderate PCE of 1.5% has been achieved when blend with P3HT [28].

In this work, we concentrate on the structural modification of the BODIPY-based dimers with the goal of effectively modulating the energy levels, absorption as well as the optoelectronic properties in the solid. To realize this, we synthesized a series of novel BODIPY based dyes (Ph(m-BODIPY)₂, T(m-BODIPY)₂, BDT(T-m-BODIPY)₂, BDT(β -metBODIPY)₂ and BDT(β -metBODIPY)₂ (Fig. 1)), differing in the structure of the π -bridges and the positions they link to the BODIPY core as well as the substitutions on the BODIPY core. Our results imply that the π -bridges at the meso position have just slight effects on the photophysical properties of the molecules regardless of their electron-donor abilities and sizes. However, they do have significant effects on the aggregation behaviors in solid and optoelectronic properties in bulk heterojunction solar cells. Besides, variation of the positions bridges linked to the terminal BODIPY motifs and the dihedral angle between them have dramatically influences not only on the photophysical and electrochemical properties, but on the packing behaviors in the solid state, thus the optoelectronic properties of the molecules.

2. Results and discussion

Fig. 2 shows the optimal conformations of the five molecules at the ground state simulated by Guassian 09 program at the B3LYP/6-31G level. In the cases of Ph(m-BODIPY)₂, T(m-BODIPY)₂, and BDT(T-m-BODIPY)₂, the dihedral angles between the bridge units and the BODIPY planes are larger than 70°. The twisted arrangement between the bridge units and the terminal BODIPY motifs is independence of the structures of the bridges. Compared with BDT(T-m-BODIPY)₂, the dihedral angle between the BODIPY and 4,8bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b: 4,5-b']dizhiophene (BDT) plane reduce to 50° in the case of BDT(β -metBODIPY)₂, implying better planarity can be achieved when the BDT bridge is selected to link at BODIPY's β position. Moreover, the comparison between BDT(β -metBODIPY)₂ and BDT(β -BODIPY)₂ reveals that the severely steric congestion can be released further when the four methyl groups on the BODIPY plane are replaced by H atoms. Therefore, the geometries of the targeted molecules can be tuned by a series of structural evolution, thus modulating the photo-physical and optoelectronic properties consequently.

Fig. 3 depicts the absorption spectra of the five molecules both in dilute CH₂Cl₂ solution and in the solid state. The relevant data are summarized in Table 1. Obviously, the absorption spectra of the five molecules in the solution cover a wide range of the visual light region from 400 nm to 700 nm in solution. Specifically, for Ph(m-BODIPY)₂, T(m-BODIPY)₂, and BDT(T-m-BODIPY)₂, they all exhibit similar narrow Gaussian-shaped S₀ \rightarrow S₁ absorption bands with the λ_{max} at about 500 nm and ε_{max} larger than 100×10³ L mol⁻¹ cm⁻¹, besides, a pronounced shoulder peak on the high-energy side of the main peak can also be observed, which is attributed to the vibrational transition [14, 29]. Their optical phenomena are similar to those of BODIPY monomer, which implies the poor electronic communication between the π -bridges and the BODIPY planes due to their highly twisted conformations. However, in contrast, the absorption spectrum of BDT(β -metBODIPY)₂) although its λ_{max} red-shifts only a little (520 nm vs. 517 nm), this result indicates that when BDT group is selected to link the BODIPY motifs at their β positions (2, 6-positions) directly, it can conjugate with the BODIPY planes to some degree, despite that the existing of the methyl groups on the pyrrole rings deteriorate the electronic interaction between the bridge and the BODIPY cores, which is consistent with the theoretical results. Furthermore, as the steric hindrance is removed effectively when the methyl groups are removed, a broad intramolecular charge-transfer (ICT) peak which results from the strong donor-acceptor

(D-A) interaction between the BDT bridge and the BODIPY moieties, with a ε_{max} of 50×10^3 L mol⁻¹ cm⁻¹ appears at about 617 nm in BDT(β -BODIPY)₂. When spun-cast into thin films, their absorption spectra all red-shift and broaden compared with the solution counterparts due to the molecular aggregation and interaction in the solid [30, 31]. Moreover, for BDT(β -BODIPY)₂, a shoulder peak could clearly be seen at 700 nm, which is related to better π -stacking in the solid due to its more planar conformation than BDT(β -metBODIPY)₂. The optical band gaps are calculated to be 2.09, 2.11, 2.19, 1.99 and 1.54 eV for Ph(m-BODIPY)₂, T(m-BODIPY)₂, BDT(T-m-BODIPY)₂, BDT(β -metBODIPY)₂ and BDT(β -metBODIPY)₂ respectively, according the formula: $E_g^{opt} = 1240/\lambda_{edge}$ [32]. Here, λ_{edge} refers to the onset values of the absorption spectra of the molecules in the thin films.

Cyclic voltammetry (CV) was applied to investigate the electrochemical properties of the five small molecules. The corresponding CV traces are plotted in Fig. 4A. According to the onset of the oxidation and reduction potentials as well as the empirical equations: $E_{HOMO} = -e(4.4 + E_{ox})$; $E_{LUMO} = -e(4.4 + E_{red})$, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels are estimated to be -5.50 and -3.59 eV, -5.53 and -3.49 eV, -5.54 and -3.49 eV, -5.10 and-3.32 eV, and -5.10 and -3.62 eV for Ph(m-BODIPY)₂, T(m-BODIPY)₂, BDT(T-m-BODIPY)₂, BDT(β -metBODIPY)₂ and BDT(β -BODIPY)₂, respectively. The electrochemical band gaps of Ph(m-BODIPY)₂, T(m-BODIPY)₂, BDT(T-m-BODIPY)₂, BDT(β -metBODIPY)₂, are calculated to be 1.91, 2.04, 2.05, 1.78 and 1.48 eV, respectively, according to the equation: $E_g^{cv} = E_{LUMO} - E_{HOMO}$, these values are well agree with the corresponding E_g^{opt} values mentioned above. Judging from the electrochemical data, one can find that the substitutions at the meso position has very slight impact on the frontier orbital energies, thus leading to comparable bandgaps for Ph(m-BODIPY)₂, T(m-BODIPY)₂ and BDT(β -motBODIPY)₂. Therestingly, the planar BDT(β -metBODIPY)₂ possesses much lower LUMO energy (-3.62 eV) than the twisted BDT(β -metBODIPY)₂ (-3.32 eV). All the modulations of the frontier energies resulting from the structural modification leads to the decrease of the bandgap value from BDT(T-m-BODIPY)₂ (2.05 eV) to BDT(β -BODIPY)₂ (1.48 eV).

Given to the appropriate energy levels of the five small molecules (Fig. 4B), solar cells with the structure of ITO/ poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) /PTB7:Ph(m-BODIPY)2 (or T(m-BODIPY)2 and BDT(T-m-BODIPY)2)/Ca (20 nm)/Al (80 nm) and ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/PC71BM: BDT(*β*-metBODIPY)₂ (or BDT(*β*-metBODIPY)₂)/Ca (20 nm)/Al (80 nm) were constructed to evaluate Ph(m-BODIPY)₂, T(m-BODIPY)₂ and BDT(T-m-BODIPY)₂ as the acceptor materials and BDT(β -metBODIPY)₂ and BDT(β -BODIPY)₂ functioning as the donor materials. Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]]3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) was employed as the donor here not only because of its appropriate HOMO and LUMO energy but its excellent light capturing ability from 550 nm to 700 nm [33]. Unfortunately, Ph(m-BODIPY)₂ exhibits poor solubility even in dilute CHCl₃, consequently, no perfect films can be obtained from the solution mixture of PTB7: Ph(m-BODIPY)₂. Different conditions, including processing solution, donor: acceptor weight ratio, concentration, the amount of additive and thermal annealing were optimized to achieve the best performances for the others. During these procedures, we found that all the systems exhibited best performances when using o-DCB as the processing solvent with a D:A weight ratio of 1:1. Commonly used solvent additive such as DIO and 1-CN were used to optimize the performances of the devices further, however, no positive effect was observed, unfortunately. The best photovoltaic parameters for each molecule are given in Table 2. The corresponding J-V curves are displayed in Figure 5 as well. Compared with the negligible PCE of PTB7: BDT(T-m-BODIPY)₂ based system (<0.04%), PTB7: T(m-BODIPY)₂ based one exhibits higher J_{sc} (0.10 vs. 0.72 mA cm⁻²) and an extremely high V_{oc} of 1.12 V is also achieved, to the best of our knowledge, this V_{oc} is the highest value reported from PTB7 based solar cells and finally, a PCE of 0.24% is reached. The similar V_{oc} values of BDT(β metBODIPY)2: PC71BM and BDT(β -BODIPY)2: PC71BM based devices are in accordance with their close HOMO energy. However, BDT(β -metBODIPY)₂ based devices exhibit lower J_{sc} and FF than BDT(β -BODIPY)₂ based one. On the one hand, the absorption band of BDT(β -metBODIPY)₂ covers only a narrow region from 450 nm to 600 nm while that of BDT(β -metBODIPY)₂ extends even to 800 nm, which contributes to the full use of the sunlight, since about 50% of the solar photons have energies corresponding to a wavelength of 600-1000 nm, on the other, the presence of the tilt angles between the BODIPY planes and BDT plane hinders the molecules from packing orderly in the solid state. As it is known that the packing ordering of the molecules in the solid has a close correlation with the transportation of the charge carriers, thus the J_{sc} and the PCE of the solar cells [34, 35].

3. Conclusion

A series of BODIPY-based dimers have been synthesized and characterized. Our results clearly demonstrate that the modification at the meso position has only slight effect on the absorption and electrochemical properties of the dimers, their aggregation behaviors and optoelectronic behaviors can be modulated effectively, however. The thiophene π -bridge one gives superior performances to other analogues when blended with PTB7 in organic solar cells. The V_{oc} of 1.12 V is among the highest V_{oc} values in single-junction solution-processed organic solar cells. The modulation of the photophysical behaviors has also been realized by changing the positions the π -bridges link to the BODIPY cores and the dihedral angle between them. The reduction of the dihedral angle from BDT(β metBODIPY)₂ to BDT(β -BODIPY)₂ not only improves the conjugation, brings down the LUMO energy and red-shifts the absorption spectrum, but facilitates the ordered stacking of BDT(β -BODIPY)₂ in the solid, thus leading to an improvement of light-harvesting ability and charge carriers transformation behaviours, which are corresponding to the enhancement of the performance of the solar cells from 0.4% to about 1%. All the results reveal that the modulation of the photophysical properties of BODIPY dyes is achievable by

judicious structural modification, and BODIPY dyes are promising candidates for application in organic solar cells, functioning as both the donor and the acceptor materials.

4. Experimental

4.1. Materials

All the materials used were received from commercial sources (Acros, Sigma, TCI or Stream) and were used without further purification. Toluene was distilled from benzophenone ketyl under the protection of nitrogen prior to use in order to get rid of the trace amount of water. Compounds **1**, **2** and **6** were synthesized according to the reported literatures [21, 36, 37]. 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*: 4,5-*b*']dizhiophene (BDT-2Sn, compound **3**) were purchased from Suna Tech Inc and used as received.

4.2. General characterization methods

NMR spectra were measured on a Brucker AVANCE 300 MHz or 400 MHz, the samples were dissolved in chloroform-*d* or dichloromethane- $d_2 \delta = 0$ ppm

Mass spectra (MALDI-TOF-MS) were conducted on a Bruker BIFLEX III mass spectrometer (Matrix: CCA). Elemental analysis was conducted on a flash EA1112 analyser to analyse the content of C, H, and N, respectively.

UV-vis absorption spectra were recorded on Schimadzu UV 2600 absorption spectrometer. The concentration of the solutions used here was 10^{-6} mol L⁻¹, and the solid samples were prepared by spin-casting the solution on the quartzes. Cycle voltammetry (CV) was measured on a computer-controlled Zennium electrochemical workstation at a scan rate of 100 mV s⁻¹. A glassy carbon electrode, a Pt wire and a Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. The molecules were dissolved in degassed anhydrous CH₂Cl₂ to achieve a concentration of 10^{-4} mol L⁻¹ with 0.1 mol L⁻¹ tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte.

4.3. Synthetic procedures (The routines are depicted in Fig. 5)

Synthesis of Ph(m-BODIPY)₂: To a well-dried two neck round bottle with 100 mL CH₂Cl₂, 2,4-dimethylpyrrole (1.6 mL, 15.5 mmol) and terephthalaldehyde (519.9 mg, 3.88 mmol) were charged. After N₂ was purged for 1 hour, a small amount of trifluoroacetic acid (TFA) was added, and the solution turned purple quickly. After one hour, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.76 g, 7.76 mmol) was added at once. After 2 h, (i-Pr)₂EtN (15 mL) was added to the reaction mixture followed by BF₃-Et₂O (15 mL) immediately. The reaction was quenched by adding 100 mL water 1 h later. The mixture was extracted with CH₂Cl₂ and the organic phase was collected and evaporated under vacuum. Finally, the crude product was purified by column chromatography (eluent: CH₂Cl₂/petroleum = 3/2) to give a red solid as desired product (818.6 mg, yield: 37%). ¹H NMR (300MHz, CDCl₃): δ 7.52 (s, 4H), 6.01 (s, 4H), 2.58 (s, 12H), 1.55 (s, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 155.4, 143.0, 142.1, 135.1, 131.5, 128.0, 121.1, 14.6, 14.3. MS (MALDI-TOF): calculated for 570.27, found *m/z* 570.2 (M⁺). Elemental anal. calcd. for C₃₂H₃₂B₂F₄N₄ (%): C, 67.40; H, 5.66; N, 9.83. Found (%) C, 67.58; H, 5.46; N, 9.85.

Synthesis of T(m-BODIPY)₂: The procedure was similar to that of Ph(m-BODIPY)₂, except that thiophene-2,5-dicarbaldehyde (543.8 mg, 3.88 mmol) was used instead of terephthaladehyde. A reddish solid (670.7 mg, yield: 30%) was gotten after purification. ¹H NMR (300 MHz, CDCl₃): δ 7.16 (s, 2H), 6.05 (s, 4H), 2.56 (s, 12H), 1.88 (s, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 156.1, 143.4, 134.9, 133.9, 132.3, 127.4.121.6, 14.6, 13.5. MS (MALDI-TOF): calcd. for 576.23, found *m*/*z* 576.1 (M⁺). Elemental anal. calcd. for C₃₀H₃₀B₂F₄N₄S (%): C, 62.53; H, 5.25; N, 9.72. Found (%) C, 62.58; H, 5.16; N, 9.75.

Synthesis of compound **3**: *N*-Iodo-succinimid (NIS) (300 mg, 1.33 mmol) was dissolved in 30 mL anhydrous CH₂Cl₂, then the solution was added dropwise into the solution of compound **1** (429.0 mg, 1.33 mmol) in CH₂Cl₂. After the reaction was completed, water (50 mL) was added, then the organic layer was extracted by CH₂Cl₂, the organic phase was evaporated to dry under vacuum. The crude material was purified by silica gel column chromatography (eluent: CH₂Cl₂/petroleum = 1/2). A red solid was collected after purification. (419.0 mg, yield: 70%). ¹H NMR (300 MHz, CDCl₃): δ 7.49–7.51 (m, 3H), 7.25–7.27 (m, 2H, overlapped with CDCl₃), 6.04 (s, 1H), 2.64 (s, 3H), 2.57 (s, 3H), 1.38 (s, 6H).

Synthesis of compound **4**: Liquid bromine (1 mL, excess) was dissolved in 50 mL anhydrous CH₂Cl₂, then the solution was added dropwise slowly into the solution of compound **2** (804.2 mg, 3.00 mmol) in CH₂Cl₂ (100 mL). The reaction was monitored by TLC every 30 min, after all the compound **2** was consumed, the organic layer was washed with aqueous solution of sodium thiosulfate, then the organic layer was extracted with CH₂Cl₂, the organic phase was collected and evaporated to dry by a rotator evaporation equipment. Purification was conducted by silica gel column chromatography (eluent: CH₂Cl₂/petroleum = 2/5) to afford a red solid (780.7 mg, yield: 75%) as the product.¹H NMR (400 MHz, CDCl₃): δ 7.94 (s, 1H), 7.73 (s, 1H), 7.51–7.57 (m, 1H), 7.45–7.49 (m, 4H), 6.93–6.94 (d, *J* = 4 Hz, 1H), 6.82 (s, 1H), 6.53–6.54 (d, 1H, *J* = 4 Hz).

Synthesis of BDT(T-m-BODIPY)₂: Compound **5** (180.9 mg, 0.20 mmol) and compound **6** (204.5 mg, 0.50 mmol), and 10mL anhydrous toluene was added into a dry Schlenk tube. After purged with argon for 30 min, $Pd(PPh_3)_4$ (20 mg, 0.017 mmol) was charged. Then the mixture was heated at 110 °C for 12 h. After cooling to room temperature, the mixture was poured into water and

extracted with CH₂Cl₂ three times. The organic phase was collected and washed with brine and water and then dried over Na₂SO₄. The residue was then loaded on silica gel column chromatography (eluent: CH₂Cl₂/petroleum = 1/1) and recrystallized from EtOH/CHCl₂ (1/10, v/v) to produce BDT(T-m-BODIPY)₂ as a reddish powder (185.2 mg, 75%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.63 (s, 2H), 7.25–7.27 (m, 4H), 6.87–6.90 (m, 4H), 5.98 (s, 4H), 2.79–2.82 (m, 4H), 2.43 (s, 12H), 1.67 (s, 12H), 1.60–1.64 (m, 2H), 1.30–1.40 (m, 16H), 0.77–0.89 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 155.9, 145.6, 143.6, 143.3, 142.7, 138.0, 137.3, 134.4, 134.0, 132.6, 131.4, 127.5, 127.2, 125.6, 122.3, 121.1, 118.6, 116.4, 41.7, 34.4, 32.6, 29.1, 26.0, 23.2, 14.6, 14.1, 13.6, 10.9. MS (MALDI-TOF): Calcd. for 1234.42, found *m*/z 1234.0 (M⁺). Elemental anal. calcd. for C₆₈H₇₂B₂F₄N₄S₆ (%): C, 66.11; H, 5.87; N, 1.75. Found (%) C, 66.02; H, 6.00; N, 1.81.

Synthesis of BDT(β -metBODIPY)₂: The synthetic procedure was similar to that of BDT(T-m-BODIPY)₂, except that compound **3** (225.0 mg, 0.50 mmol) was used instead of compound **6**. Purification on silica gel column chromatography (eluent: CH₂Cl₂/petroleum = 2/3) following by recrystallization from a mixture of EtOH/CH₂Cl₂ (10/1, v/v) yielded BDT(β -metBODIPY)₂ as a brown-reddish powder (203.1 mg, 83%). ¹H NMR (300 MHz, CDCl₃): δ 7.46-7.48 (m, 6H), 7.35 (s, 2H), 7.28-7.31 (m, 4H, overlapped with CDCl₃), 7.24–7.28 (m, 2H, overlapped with CDCl₃), 6.83–6.84 (d, 2H, *J* = 3.3 Hz), 6.03 (s, 2H), 2.81–2.83 (d, 4H), 2.63 (s, 6H), 2.59 (s, 6H), 1.63–1.65 (m, 2H), 1.41 (s, 6H), 1.39 (s, 6H), 1.26–1.32 (m, 16H), 0.88–0.94 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 156.2, 154.1, 145.2, 143.9, 143.4, 142.9, 142.1, 140.3. 137.9, 137.4, 135.4, 132.2, 130.8, 129.4, 129.1, 128.1, 127.9, 126.6, 125.5, 122.8, 121.7, 41.7, 34.2, 32.6, 29.0, 25.8, 23.2, 14.9, 14.6, 14.0, 13.5, 12.6, 10.9. MS (MALDI-TOF): calculated for 1222.51, found *m*/*z* 1222.0 (M⁺). Elemental anal. calcd. for C₇₂H₇₆B₂F₄N₄S₆ (%): C, 70.69; H, 6.26; N, 4.58. Found (%): C, 70.62; H, 6.30; N, 4.35.

Synthesis of BDT(β -BODIPY)₂: The synthetic procedure was similar to that of BDT(T-m-BODIPY)₂, except that compound **4** (182.5 mg, 0.50 mmol) was used instead of compound **6**. Purification on silica gel column chromatography following by recrystallization from a mixture of EtOH/CH₂Cl₂ (8/1, v/v) yielded BDT(β -BODIPY)₂ as a blue-black powder (171.1 mg, 77%). ¹H NMR (300 MHz, CDCl₃): δ 8.28 (s, 2H), 7.98 (s, 2H), 7.54-7.64 (m, 12H), 7.27 (s, 2H, overlapped with CDCl₃), 6.91–6.98 (m, 6H), 6.57–6.58 (d, 2H, *J* = 2.7 Hz), 2.87–2.89 (d, 4H), 1.69–1.73 (m, 2H), 1.27–1.47 (m, 16H), 0.81–0.99 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 147.3, 146.4, 145.2, 144.3, 143.1, 142.9, 142.1, 138.1, 137.9, 135.6, 134.5, 133.8, 132.0, 131.0, 130.9, 130.6, 128.2, 127.4, 125.9, 125.3, 122.9, 120.2, 41.8, 34.2, 32.6, 29.1, 25.9, 23.3, 14.0, 11.0. MS (MALDI-TOF): Calcd. for 1111.06, found *m*/*z* 1110.9 (M⁺). Elemental anal. calcd. for C₆₄H₆₀B₂F₄N₄S₄ (%): C, 69.18; H, 5.44; N, 5.04. Found (%): C, 69.22; H, 5.36; N, 5.15.

4.4. Fabrication and characterization of the organic solar cells

Conventional organic solar cells with an architecture of: ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/active layer/Ca (20 nm)/Al (80 nm) were fabricated. The indium tin oxide (ITO) glasses were cleaned with detergent, deionized water, acetone and isopropanol and then treated in a Novascan PSD-ultraviolet-ozone chamber for 1 hour and a layer of 30 nm PEDOT: PSS (Baytron P VP AI 4083, Germany) was spin-coated subsequently. After baking at 150 °C for 15 min in the air, the glasses were transferred into a glove box. Then a blend solution (1,2-dichlorobenzene (*o*-DCB), chlorobenzene (CB) or chloroform (CF)) of PTB7:Ph(m-BODIPY)₂ (or T(m-BODIPY)₂ and BDT(T-m-BODIPY)₂) or BDT(β -metBODIPY)₂ (or BDT(β -metBODIPY)₂):PC7₁BM with various concentrations was spun-cast to form the photosensitive layer, donor/acceptor weight ratio, contents of 1,8-diiodooctance (DIO) (or 1-chloronaphthalene (1-CN)), thermal annealing temperatures were optimized to achieve the best photovoltaic responses. The solutions were stirred at 60 °C overnight prior to use. The Ca/Al cathode was deposited by vacuum evaporation onto the photosensitive layer. The effective area was measured to be 6 mm². The current–voltage (*J*–V) measurement of the devices was measured using a Keithley 2400 Source Measure Unit in the glove box under white light illumination of simulated AM 1.5 G, 100 mW cm⁻² using a xenon-lamp-based solar simulator (AAA grade, XES-70S1).

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Fig. 1. Chemical structure of five BODIPY based dyes.



Fig. 2. The optimal geometries of the five BODIPY derivatives of Ph(m-BODIPY)₂ (A), $T(m-BODIPY)_2$ (B), BDT(T-m-BODIPY)₂ (C), BDT(β -metBODIPY)₂ (D) and BDT(β -BODIPY)₂ (E) using Gaussian 09 program.



Fig. 3. Absorption spectra of the five dimers with concentration of 10⁻⁶ mol L⁻¹ in CH₂Cl₂ solution (upper) and in the thin films (lower).



Fig. 4. (A) CV curves of the five molecules in dilute CH_2Cl_2 solutions; (B) The energy diagram of the five molecules, PTB7, $PC_{71}BM$ as well as other components used in the normal solar cells for comparisons. For clarity, from 1 to 5 represent Ph(m-BODIPY)₂, T(m-BODIPY)₂, BDT(T-m-BODIPY)₂, BDT(β -metBODIPY)₂ and BDT(β -BODIPY)₂ here, respectively.



Fig. 5. Synthesis routines of the dimers. Reaction conditions: (i) TFA, DDQ, (i-Pr)₂EtN, BF₃-Et₂O, N₂, CH₂Cl₂, yield: 37% and 30% for Ph(m-BODIPY)₂ and T(m-BODIPY)₂, respectively; (ii) NIS, CH₂Cl₂, yield: 70%; (iii) Br₂, CH₂Cl₂, yield: 75%; (iv) Pd(PPh₃)₄, N₂, 120 °C, toluene, 12 h, yield: 75%, 83% and 77% for BDT(T-m-BODIPY)₂, BDT(β-metBODIPY)₂ and BDT(β-BODIPY)₂, respectively.

Table 1 A summary of the optical and electrochemical properties of the five molecules.

| Compd. | $\lambda_{abs}{}^{a}$ (nm); loge | $\lambda_{abs}{}^{b}$ (nm) | λ_{edge}^{c} (nm); $E_{g}^{opt,d}$ (eV) | HOMO (eV) | LUMO (eV) | $\mathrm{E}_{\mathrm{g}}^{\mathrm{CV},e}\left(\mathrm{eV}\right)$ |
|---------------------------------------|----------------------------------|----------------------------|----------------------------------------------------|-----------|-----------|-------------------------------------------------------------------|
| Ph(m-BODIPY) ₂ | 498; 5.11 | 545.5 | 590; 2.09 | 5.50 | 3.59 | 1.91 |
| T(m-BODIPY) ₂ | 519; 5.06 | 544 | 587; 2.11 | 5.53 | 3.49 | 2.04 |
| BDT(T-m-BODIPY)2 | 517; 5.13 | 534 | 566; 2.19 | 5.54 | 3.49 | 2.05 |
| BDT(β -metBODIPY) ₂ | 520; 5.06 | 532 | 623; 1.99 | 5.10 | 3.32 | 1.78 |
| BDT(β -BODIPY) ₂ | 617; 4.68 | 630 | 805; 1.54 | 5.10 | 3.62 | 1.48 |

^{*a*} Maximum absorption wavelength measured in dilute CH₂Cl₂. ^{*b*} Maximum absorption wavelength measured in solid. ^{*c*} Offset of the absorption spectra in solid. ^{*d*} Optical band gap, $E_g^{opt} = 1240/\lambda_{edge}$. ^{*e*} Electrochemical band gap, $E_g^{cv} = E_{LUMO} - E_{HOMO}$.

Table 2 Performances of the five molecules based solar cells under optimal conditions.

| D:A ^a | D:A (w:w) | J_{sc} (mA cm ⁻²) | V _{oc} (V) | FF (%) | PCE_{max} (%); PCE_{ave}^{d} (%) |
|------------------------------------------------------------------|-----------|---------------------------------|---------------------|--------|--------------------------------------|
| PTB7:T(m-BODIPY) ₂ ^b | 1:1 | 0.72 | 1.12 | 29.9 | 0.24; 0.20 |
| PTB7: BDT(T-m-BODIPY)2 ^c | 1:1 | 0.10 | 1.08 | 34.7 | 0.04; 0.03 |
| BDT(β-metBODIPY) ₂ : PC ₇₁ BM ^c | 1:1 | 3.72 | 0.48 | 24.0 | 0.43; 0.40 |
| BDT(β-BODIPY) ₂ : PC ₇₁ BM ^c | 1:1 | 6.17 | 0.53 | 29.1 | 0.95; 0.91 |

^{*a*} The donor materials and acceptor materials in the active layers; ^{*b*} Processing solvent: 1,2-dichlorobenzene (*o*-DCB) with a total concentration of 30 mg mL⁻¹; ^{*c*} Processing solvent: *o*-DCB with a total concentration of 40 mg mL⁻¹; ^{*d*} Average values from 12 devices.