Supporting Information

Performance Enhancement of BODIPY-Dimer Based Small-Molecule Solar Cells by Using a Visible-Photons-Capturing, Diketopyrrolopyrrole π-Bridge

Wenxu Liu, Jiannian Yao and Chuanlang Zhan*

Beijing National Laboratory of Molecular Science, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China.

E-mail: clzhan@iccas.ac.cn

Table of Contents:

Materials and general methods	3
Fabrication and characterization of the organic solar cells and	hole/electron
mobility devices	4
Synthesis procedures	5
Supporting Figures	7
Supporting Tables	14
References	16
	Materials and general methods Fabrication and characterization of the organic solar cells and mobility devices Synthesis procedures Supporting Figures Supporting Tables References

1. Materials and general methods

¹H NMR and ¹³C NMR were measured in dichloromethane- d_2 ($\delta = 5.30$ ppm for ¹H NMR and 53.5 ppm for ¹³C NMR test) on a Brucker AVANCE 400 MHz $\delta = 0$ ppm

Mass spectrum (MALDI-TOF-MS) was 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 \square -vis absorption and fluorescence spectra were recorded on Schimadzu UV \square 2600 absorption spectrometer and Horiba FluoroMax-4-NIR spectrophotometer, respectively. The concentration of the solutions used here was 10⁻⁶ M⁻¹, and the solid samples were prepared by spin-casting the solution on the quartzes. When excited at 330 nm, the strong peak at about 660 nm in the fluorescence spectra was all deleted for clarity. Absolute quantum yields (Φ_{FI}) were measured on a HAMAMATSU absolute PL quantum yield spectrometer (C11347). The maximum of error was 0.01(1%) and the limit of detection (LOD) was 0.01(1%). The excitation wavelengths (λ_{ex}) were chosen according to the absorption spectra of the dimers and DPP/BDT π -bridges. For DPP segment based system, λ_{ex} was set as 580 nm, where the absorption of DPP segment is strong enough while the absorption of BODIPY is very weak; for BDT segment based one, since the absorption spectrum of BDT segment is almost covered by that of BODIPY, λ_{ex} was set as 330 nm, the maximum absorption of BDT π -bridge. The selection of the integration range of wavelength to calculate the Φ_{FL} was based on the fluorescence spectra of BODIPY, DPP and BDT segment. The ranges were determined as 750-850, 600-850 and 400-600 nm for BODIPY, DPP and BDT segment, respectively. Note that the influence of the absorption of the compounds was exclusive when Φ_{FL} was calculated. Both the concentrations of DPP and BDT segment were 1 × 10⁻⁶ M⁻¹ cm⁻¹ in the dilute chloroform solutions of one-component DPP/BDT segment, DPP/BDT to BODIPY segment (in molar) and dimers, while for the solution of one-component BODIPY monomer, the concentration was 2×10^{-6} M⁻¹ cm⁻¹ in dilute chloroform. Cycle voltammetry (CV) was measured on a computer-controlled Zennium electrochemical workstation at a scan rate of 100 mV/s. 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 CHCl₃ to achieve a concentration of 10-4 M-1with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte.

Transmission electron microscope (TEM) tests were performed on a JEM-2011F with an operated voltage of 200 kV. The specimens were prepared by transferring the spin-cast blend films to the 200 mesh copper grids. X-ray diffraction (XRD) experiments were conducted on a Rigaku D/max \Box 2500 diffractometer operated at 40 kV voltage and 200 mA current with Cu K α ($\lambda_{K\alpha} = 0.15419$ nm), the samples were prepared by drop-casting the solution in chloroform on the well cleaned silica slides.

AFM images were measured from the organic solar cells samples using a Nanoscope V AFM (Digital Instruments) in tapping mode.

The optimal conformations of the two molecules were simulated by Density Functional Theory (DFT) at the B3LYP/6-31G(d,p) level using Gaussian 03 program.¹

2. Fabrication and characterization of the organic solar cells and hole/electron mobility devices

(a) Fabrication of the organic solar cells:

Conventional organic solar cells with an architecture of: ITO/ poly(3,4-

ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) /DPP(BODIPY)2(or **BDT(BODIPY)**₂): PC₇₁BM/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 minutes in the air, the glasses were transferred into a glove box. Then a 1,2-dichlorobenzene (o-DCB) solution of **DPP(BODIPY)**₂(or **BDT(BODIPY)**₂):PC₇₁BM with a total solid concentration of 40 mg mL⁻¹ or a solution of CHCl₃ with a concentration of 10 mg mL⁻¹ was spun-cast to form the photosensitive layer (ca. 100 nm), 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 \Box -voltage ($J\Box$ -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/cm² using a xenon-lamp-based solar simulator (AAA grade, XES-70S1). EQE measurements were measured using a 250 W Quartz Tungsten Halogen (Oriel) fitted with a monochromator (Cornerstone (CS130) 1/8m) as a monochromatic light source.

(b) Measurement and calculation of the hole/electron mobility:

Hole mobility was measured using hole-only diodes devices with a configuration of ITO/PEDOT: PSS/ **DPP(BODIPY)**₂(or **BDT(BODIPY)**₂): PC₇₁BM/Au. The Au layer was deposited at the speed of 0.1 Å/ s or less to prevent the penetration of Au atoms into the active layers. Electron-only device with the architecture of ITO/TIPD/ **DPP(BODIPY)**₂(or **BDT(BODIPY)**₂): PC₇₁BM/Al was constructed to measure the electron mobility. Here, the TIPD layer was prepared by spin-casting the TIPD isopropanol solution with a concentration of 3.5 wt% at a speed of 3000 r/s for 35 s and then annealed at 150 °C for 10 min to convert TIPD into TOPD.² For both the hole-only and electron-only devices, the active layers were spin-coated under the same condition as the preparation of the best organic solar cells and the current–voltage measurement was conducted on Keithley 2400 Source Measure Unit too.

The hole and electron mobility was calculated according to the Mott–Gurney equation as followed: $\ln(JL^3V^2) = 0.89(1/E_0)^{0.5}(V/L)^{0.5} + \ln(9\varepsilon\varepsilon_0\mu_h/8)$. Herein, $\varepsilon \approx 3$, which represents the dielectric constant of the blended film, ε_0 denotes the permittivity of the vacuum (8.85419×10⁻¹² F m⁻¹), μ_h is the zero-field mobility, E_0 is the characteristic field, *J* is the current density, *L* is the thickness of the films, and $V = V_{appl} - V_{bi}$; here, V_{appl} is the applied voltage to the device, V_{bi} is the build-in voltage which arises from the difference of the work function between the two electrodes.

3. Synthesis procedures

All reagent and chemicals were purchased from commercial sources (Acros, Sigma, or Stream) and were used without further purification. Toluene and tetrahydrofuran (THF) was distilled from benzophenone ketyl under the protection of nitrogen prior to use. Monomeric BODIPY, Compound **2**, ³ DPP ⁴ and BDT ⁵ segments were synthesized according to the relevant literatures. 2,5-bis(2-ethylhexyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**DPP-2Bo**, compound **1**) and 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.

Scheme S1. The synthetic routines to DPP(BODIPY)₂ and BDT(BODIPY)₂^a



^a Conditions: (i) K₂CO₃, Pd(PPh₃)₄, H₂O/THF, N₂, 90 °C; (ii) Pd(PPh₃)₄, toluene, N₂, 110 °C.

Synthesis of DPP(BODIPY)2: To a well-dried Schlenk tube containing THF (9 mL) and 2M aqueous K₂CO₃ (3mL), compound 1 (77.7 mg, 0.1 mmol) and compound 2 (260 mg, 0.28 mmol) were added. After degassed with N2 for 30min, Pd(PPh3)4 (20 mg, 0.017 mmol) was added immediately. The tube was then sealed and heated at 90°C in an oil bath overnight. After cooling to the room temperature, the dark green mixture was poured into cold water (100 mL) and extracted with chloroform (20 mL \times 3). The organic phase was dried over Na₂SO₄, and then evaporated to dry under vacuum. The residue was loaded onto silica and purified by flash chromatography using a mixture of *n*-hexane and chloroform (from 3:1 to 1:2 gradient, v:v) as eluent. *The purification was conducted in duplicate*. Then the crude product was recrystallized in a mixture of *n*-hexane/ethanol/chloroform (2/7/1) twice to give the target molecule as a black powder (151.1 mg, 68%). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.89 (d, J = 4.0 Hz, 2H), 7.30–7.40 (m, 12H), 7.13-7.15 (m, 8H), 7.07-7.08 (d, 4H), 7.03-7.04 (d, 2H), 6.74-6.86 (d, 4H), 6.68 (s, 4H), 3.98-4.09 (m, 4H), 2.80-2.83 (t, J = 7.2 Hz, 8H), 1.88-1.93 (m, 2H), 1.82 (s, 12H), 1.65-1.72 (m, 8H), 1.25–1.39 (m, 40H), 0.85–0.92 (m, 24H). ¹³C NMR (100 MHz, CD₂Cl₂) δ161.9, 152.1, 147.0, 143.8, 141.7, 141.0, 140.1, 139.7, 138.9, 135.0, 134.9, 134.6, 134.0, 129.4, 129.2, 128.9, 128.3, 127.7, 127.3, 127.2, 125.3, 124.1, 123.7, 118.0, 117.8, 108.8, 45.0, 39.6, 31.9, 31.8, 30.7, 30.3, 29.0, 28.8, 24.2, 23.7, 22.6, 14.5, 14.3, 14.2, 10.7. MS (MALDI-TOF): calculated for 2222.83, found *m/z* 2222.2 (M⁺). Elemental anal. Calcd for C₁₂₄H₁₃₄B₂F₄N₆O₂S₁₂ (%): C, 67.00; H,

6.08; N, 3.78. Found (%) C, 66.85; H, 6.16; N, 3.75.

Synthesis of BDT(BODIPY)2: In a well-dried Schlenk tube was charged with compound 3 (99.5 mg, 0.11 mmol) and compound 2 (300 mg, 0.32mmol). After degassed with N₂ for 30min, Pd(PPh₃)₄ (25 mg, 0.021 mmol) was added immediately, then dry toluene (10 mL) was injected into the mixture. The tube was then sealed and heated at 110°C in an oil bath overnight. After cooling to the room temperature, the mixture was poured into cold water (100 mL) and extracted with chloroform (20 mL×3). The organic phase was dried over Na₂SO₄. After the solvent was removed by rotary evaporator, the residue was loaded onto silica and purified by flash chromatography using a mixture of *n*-hexane and chloroform (from 3:1 to 1:1 gradient, v:v) as eluent. The purification was conducted in duplicate too. Then the crude product was recrystallized from a mixture of *n*-hexane/ethanol/chloroform (1/8/1) twice to yield the target molecule as a black powder (205.5mg, 82%).¹H NMR (400 MHz, CD₂Cl₂) δ 7.72 (s, 2H), 7.33–7.41 (m, 12H), 7.13–7.14 (m, 8H), 7.07–7.08 (d, *J* = 4.0 Hz, 4H), 6.99–7.00 (d, *J* = 3.6 Hz, 2H), 6.94–6.95 (d, J = 3.6 Hz, 2H), 6.73–6.74 (d, J = 3.6 Hz, 4H). 6.67 (s, 4H), 2.87–2.89 (m, 4H), 2.79–2.83 (t, J = 7.6 Hz, 8H), 1.80 (s, 12H), 1.67–1.68 (m, 10H), 1.31–1.41 (m, 40H), 0.88–0.93 (m, 24H). ¹³C NMR (100 MHz, CD₂Cl₂) δ152.5, 148.3, 146.5, 145.7, 143.3, 142.7, 141.5, 140.7, 140.2, 137.9, 137.4, 136.9, 136.9, 134.5, 131.1, 130.9, 129.7, 128.9, 127.9, 125.2, 125.0, 124.3, 123.7, 122.4, 118.3, 117.9, 116.3, 114.1, 41.6, 34.1, 32.6, 31.5, 31.5, 30.2, 28.9, 28.7, 25.9, 23.2, 22.6, 13.9, 13.9, 13.8, 10.7. MS (MALDI-TOF): calculated for 2274.70, found *m/z* 2274.1 (M⁺). Elemental anal. Calcd for C₁₂₈H₁₃₆B₂F₄N₄S₁₄ (%): C, 67.52; H, 6.02; N, 2.46. Found (%) C, 67.28; H, 6.09; N, 2.55.

4. Supporting Figures

Figure S1. Optimal conformations of **DPP(BODIPY)**₂ (A) and **BDT(BODIPY)**₂ (B) calculated by Density Functional Theory (DFT). The dihedral angles between the meso position and the two BODIPY planes are denoted as θ_1 and θ_2 , respectively. All the hydrogen atoms are omitted for clarity.



Figure S2. The molecular structures of monomeric BODIPY ^{*a*}, DPP and BDT segments ^{*b*}.



^{*a*} Since the substitutions at the meso position has only slight impact on the absorption properties of the BODIPY core, so the structure drawn above was used to measure the absorption spectra both in solution and pure film for easy accessible of the material, although the "true" monomeric BODIPY should be the one that replaces the thiophene unit (colored in red) with a hydrogen atom at the meso position. ^{*b*} R = 2-ethylhexyl, here.

Figure S3. Fluorescence spectra of DPP-to-BODIPY (A) and BDT-to-BODIPY (B) mixture (1:2 in molar).



Figure S4. Fluorescence spectra of **DPP(BODIPY)**₂ (A) and **BDT(BODIPY)**₂ (B) obtained under various excitation wavelengths (λ_{ex}).



Figure S5. (A) Cycle Voltammetry (CV) traces of **DPP(BODIPY)**₂ and **BDT(BODIPY)**₂ in dilute chloroform. (B) The energy diagram of the two dimers and other components used in the normal solar cell for comparisons, **DPP(BODIPY)**₂ and **BDT(BODIPY)**₂ are denoted as D1 and D2, respectively.



Figure S6. A comparison of the EQE curves from the best cell of **DPP(BODIPY)**₂ (blue line) and from **BDT(BODIPY)**₂ based one multiplied by 1.26 (magenta line).



Figure S7. Hole (A) and electron (B) mobility of **DPP(BODIPY)**₂/ **BDT(BODIPY)**₂:PC₇₁BM blend measured by SCLC method.



Figure S8. AFM images of the blend. The height (a) and phase (b) image of **DPP(BODIPY)**₂:PC₇₁BM; height (c) and phase (d) image of **BDT(BODIPY)**₂:PC₇₁BM. Scale: $1\mu m \times 1\mu m$.



11



Figure S11. ¹H NMR spectrum of **BDT(BODIPY)**₂.





5. Supporting Table

Table	S1.	Optical	and	electro	ochem	ical 1	oroperties	of	DPP(BOD	IPY) ₂	and	
BDT(E	BODI	PY)2.				_	-			-		
		• (1					1	

Compd.	$\lambda_{abs}^{a/nm}$ (loge)	λ_{abs}^{b}/nm	$\lambda_{edge}^{c/nm}$ (E _g ^{opt,d} /eV)	HOMO/eV	LUMO/eV	Eg ^{cv,e} /e V
	453 (5.17)	465				
DPP (BODIPY) ₂	637 (4.99)	655	890 (1.39)	-5.01	-3.73	1.28
	746 (5.23)	792				
BDT	456 (5.29)	464	880	5.02	3 73	1 20
(BODIPY) ₂	742 (5.24)	788	(1.41)	-5.02	-3.75	1.27

^{*a*} Maximum absorption wavelength measured in dilute chloroform. ^{*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 S2. A collection of the absolute fluorescence quantum yield (Φ_{FL}) of different compounds and their mixture in dilute chloroform solution.

Compd. ^a	λ_{ex}^{b}/nm	$\lambda_{\rm em}^{c}/{\rm nm}$	$\Phi_{ m FL}$ /%
\mathbf{DPP}^d	580	600-850	43.6
DPP^d and	d 580 600–850		12.6
BODIPY ^e mixture	580	750-850	7.7
	580	600-850	< 0.1
	580	750-850	6.2
BDT^d	330	400-600	3.0
BDT^d and	330	400-600	0.9
BODIPY ^e mixture	330	750-850	5.5
DDT(DODIDV) d	330	400-600	0.3
$\mathbf{DD}\mathbf{I}(\mathbf{DODIF}\mathbf{I})_{2}^{*}$	330	750-850	5.3
BODIPY ^e	330	750-850	5.2
	580	750-850	< 0.1
	450	750-850	7.2

^{*a*} DPP segment, BDT segment and monomeric BODIPY are denoted as DPP, BDT and BODIPY, respectively. ^{*b*} Excitation wavelength selected. ^{*c*} Integration range of wavelength from fluorescence spectra to calculate the Φ_{FL} ^{*d*} Concentration = 10⁻⁶ M⁻¹. ^{*e*} Concentration = 2×10⁻⁶ M⁻¹.

Comnd	D:A ^a	$J_{ m sc}$	$V_{\rm oc}$	FF	$PCE_{max}(PCE_{ave}^{b})$
Compa.	(w:w)	(mA/cm^{-2})	(V)	(%)	(% (%))
	1:1.5 ^c	7.52	0.66	36.8	1.83 (1.75)
	$1:2^{c}$	8.93	0.71	37.2	2.36 (2.28)
DPP	$1:2^{d}$	10.12	0.73	36.2	2.67 (2.54)
(BODIPY) ₂	$1:2.2^{d}$	13.39	0.73	37.3	3.62 (3.40)
	$1:2.5^d$	12.29	0.73	37.0	3.32 (3.07)
	1:3 ^d	9.79	0.73	34.4	2.47 (2.28)
BDT (BODIPY)2	1:1 ^c	4.63	0.78	29.2	1.05 (0.99)
	$1:2^{c}$	6.51	0.76	36.2	1.79 (1.69)
	1:2.5 ^c	7.13	0.76	36.7	1.99 (1.87)
	1:3 ^c	6.85	0.76	36.6	1.91 (1.85)
	1:2.5 ^d	7.76	0.76	35.6	2.10 (1.98)

Table S3. Performances of solar cells with the variation of processed solvents and D:A weight ratio.

^{*a*} A = PC₇₁BM. ^{*b*} Average values estimated from 8 devices. ^{*c*} *o*-DCB. ^{*d*} chloroform.

6. References

22496.

(1) Frisch, M. J.; Trucks, G. W.;Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.;Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji,H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.;Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.;Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao,O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.;Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.;Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.;Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega,N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.;Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.;Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.;Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.;Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.;Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.
(2) Tan, Z. A.; Zhang, W. Q.; Zhang, Z. G.; Qian, D. P.; Huang, Y.; Hou, J. H.; Li, Y. F. Adv.

Mater. 2012. 24, 1476. (3) Liu, W.; Tang, A.; Chen, J.; Wu, Y.; Zhan, C.; Yao, J. ACS Appl. Mater. Interfaces, 2014, 6,

(4) Bürckstummer, H.; Weissenstein, A.; Bialas D.; Würthner, F. J. Org. Chem., 2011, 76, 2426.

(5) Huang, J.; Wang, X.; Zhang, X.; Niu, Z.; Lu, Z.; Jiang, B.; Sun, Y.; Zhan, C.; Yao, J. ACS Appl. Mater. Interfaces, 2014, 6, 3853.