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Electronic Supplementary Information

Naphthalene Substituent via β-Position Linkage: An Effective Extended Conjugated Moiety Can Make a Decent Trade-Off between Optical Band Gap and Open Circuit Voltage in Symmetry-Breaking Benzodithiophene

Based Polymer Solar Cells

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1. Materials and Methods

All reagents and starting materials were obtained commercially as analytical grade and used directly without any purification. Toluene and THF were distilled over sodium/benzophenone and calcium hydride under N₂ prior to use. 4,8-Dihydrobenzo[1,2b:4,5-b']dithiophen-4,8-dione¹ and 4,7-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)-5,6difluorobenzo [c] [1,2,5] thiadiazole² were synthesized as reported in the literatures. ¹H NMR and ¹³C NMR spectra were taken on a Bruker AVANCE-III 600 Spectrometer. Thermal gravimetric analysis (TGA) measurement was performed on STA-409 at a heating rate of 10 °C min⁻¹. UV-Vis absorption spectrum was measured with a Hitachi U-4100 spectrophotometer. The organic molecule films on quartz used for absorption spectral measurement were prepared by spin-coating their *o*-dichlorobenzene solutions. Cyclic voltammetry (CV) was performed using a CHI660D electrochemical workstation with a glassy carbon working electrode, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode at a scan rate of 100 mV s⁻¹. Tetrabutylammonium phosphorus hexafluoride (Bu₄NPF₆, 0.1 M) in acetonitrile was used as the supporting electrolyte. Polymer film was prepared by drop-casting onto the glassy carbon working electrode from o-dichlorobenzene solution and dried before measurements. The redox potential of the Fc/Fc⁺ internal reference is 0.39 V vs. SCE. The highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energy levels, were determined by calculating the empirical formulas³ of $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.8 - E_{1/2}(\text{Fc/Fc+})), E_{\text{LUMO}} =$ $-e(E_{red}+4.8-E_{1/2}(Fc/Fc+))$, where E_{ox} and E_{red} were the onset oxidation potential and the onset reduction potential, respectively. Density functional theory (DFT) calculations were carried out by the Gaussian 09 program suite at the B3LYP/6-31G(d,p) level.⁴ Atomic force microscopy (AFM) images were acquired with Agilent 5400 scanning probe microscope with a Nanodrive controller in tapping mode with MikroMasch NSC-15 AFM tips with resonant frequencies ~300 kHz. Transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV. Grazing incidence wide-angle X-ray scattering (GIWAXS) patterns were acquired at beamline BL16B1 (Shanghai Synchrotron Radiation Facility).

2. Device Fabrication and Testing

Photovoltaic devices were fabricated on pre-patterned indium tin oxide (ITO) coated glass substrates with a layered structure of ITO/PEDOT:PSS/polymer:PC71BM (ITIC)/Ca (10 nm)/Al (100 nm). The ITO coated glass substrates were cleaned sequentially with detergent, de-ionized water, acetone and isopropanol, followed by drying with N₂ flow. And then, oxygen plasma treatment was made for 20 min, then spin-coated with PEDOT:PSS at 5000 rpm, and dried under argon for 20 min at 120 °C. Subsequently, the active layer was spincoated from different blend weight ratios of donor and PC71BM/ITIC in odichlorobenzene/chlorobenzene solution with or without DIO solvent on the ITO/PEDOT:PSS substrate. Before spin-coating the active layer, the blend solution was stirred overnight at room temperature. The thickness of the active layer was controlled by changing the spin speed during the spin-coating process and measured using Veeco Dektak 150 surface profiler in our laboratory. Finally, Ca (10 nm) and aluminum (100 nm) were thermally evaporated at a vacuum of $\sim 2 \times 10^{-4}$ Pa on top of active layer. The effective area of the device was measured to be 0.1 cm^2 . The current density-voltage (J-V) characteristics were measured with a Keithley 2420 source measurement unit under simulated 100 mW cm⁻² (AM 1.5 G) irradiation from a Newport solar simulator. Light intensity was calibrated with a standard silicon solar cell. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system. Hole mobility was measured using the space charge limited current (SCLC) model, using a device configuration of ITO/PEDOT:PSS/polymer:PC71BM(ITIC)/Au by taking current-voltage in the range of 0-5 V and fitting the results to a space charge limited form, where the SCLC is described by:

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$$J = (9/8)\varepsilon\mu(V^2/L^3)$$

where ε is the static dielectric constant of the medium and μ is the carrier mobility, V is the voltage drop across the device ($V = V_{appl} - V_{bi} - V_{rs}$, where V_{appl} is the applied voltage to the device, V_{bi} is the built-in voltage due to the difference in work function of the two electrodes, and V_{rs} is the voltage drop due to series resistance across the electrodes), and L is the active layer thickness.



3. Synthesis and Characterization

Scheme S1. Synthetic routes of the monomers and polymers.

8-hydroxy-8-naphthalen-1-yl-benzo[1,2-b:4,5-b']dithiophen-4-one (1)

To a mixture of magnesium turnings (0.43 g, 18 mmol) and a grain of I_2 in dry THF (15 mL) was added dropwise 1-bromonaphthalene (3.11 g, 15 mmol) in THF (10 mL) at a rate sufficient to maintain reflux under nitrogen. After addition, the reflux was maintained for 3 h. The Grignard reagent was then added dropwise to a solution of 4,8-dihydrobenzo[1,2-*b*:4,5-*b*']dithiophen-4,8-dione (2.20 g, 10 mmol) in toluene (200 mL) under an ice-water bath. Finally, the mixture was stirred for 40 h at room temperature under nitrogen. Then, the

mixture was hydrolyzed by careful addition of water followed by 38% aqueous HCl and extracted with diethyl ether. The organic phase was dried over Na₂SO₄. After removing the solvent under vacuum, residue (2.61 g, 75%) was used for next step without further purification.

8-hydroxy-8-naphthalen-2-yl-benzo[1,2-b:4,5-b']dithiophen-4-one (2)

To a mixture of magnesium turnings (0.43 g, 18 mmol) and a grain of I_2 in dry THF (10 mL) was added dropwise 2-bromonaphthalene (3.11 g, 15 mmol) in THF (10 mL) at a rate sufficient to maintain reflux under nitrogen. After addition, the reflux was maintained for 3 h. The Grignard reagent was then added dropwise to a solution of 4,8-dihydrobenzo[1,2-*b*:4,5-*b*']dithiophen-4,8-dione (2.20 g, 10 mmol) in toluene (200 mL) under an ice-water bath. Finally, the mixture was stirred for 40 h at room temperature under nitrogen. Then, the mixture was hydrolyzed by careful addition of water followed by 38% aqueous HCl and extracted with diethyl ether. The organic phase was dried over Na₂SO₄. After removing the solvent under vacuum, residue (2.71 g, 78%) was used for next step without further purification.

4-octyldodecyloxy-8-naphthalen-1-yl-benzo[1,2-b:4,5-b']dithiophene (3)

Compound **1** (2.09 g, 6 mmol) and zinc powder (0.98 g, 15 mmol) were put into a 100 mL flask under nitrogen, then 4 g of NaOH in water (50 mL) was added into the mixture. The mixture was well stirred and heated to reflux for 3 h. Then, 1-bromo-2-octyl-dodecane (5.42 g, 15 mmol) and a catalytic amount of tetrabutylammonium bromide were added into the flask. After being refluxed overnight, the reactant was poured into cold water and extracted by petroleum ether. The organic phase was dried over Na₂SO₄. After removing the solvent under vacuum, residue was purified by silica column chromatography with petroleum ether to give compound **3** as pale yellow oil (2.39 g, 65%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.99-7.95 (m, 2H), 7.65-7.60 (m, 2H), 7.58 (d, *J*=5.6 Hz, 1H), 7.50-7.47 (m, 1H), 7.39 (d, *J*=8.5 Hz, 1H), 7.33-7.28 (m, 3H), 6.80 (d, *J*=5.5 Hz, 1H), 4.35 (d, *J*=5.4 Hz, 2H), 1.97-1.92 (m, 1H), 1.72-

1.67 (m, 2H), 1.46-1.27 (m, 30H), 0.90-0.87 (m, 6H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 148.48, 140.81, 139.24, 136.65, 133.98, 131.59, 129.77, 128.67, 128.39, 128.18, 127.87, 126.88, 126.31, 126.19, 126.07, 126.05, 125.66, 124.59, 123.37, 119.98, 76.42, 39.32, 31.96, 31.39, 30.13, 29.74, 29.72, 29.70, 29.69, 29.40, 27.05, 26.94, 22.73, 14.15.

4-octyldodecyloxy-8-naphthalen-2-yl-benzo[1,2-b:4,5-b']dithiophene (4)

Compound **2** (2.09 g, 6 mmol) and zinc powder (0.98 g, 15 mmol) were put into a 100 mL flask under nitrogen, then 4 g of NaOH in water (50 mL) was added into the mixture. The mixture was well stirred and heated to reflux for 3 h. Then, 1-bromo-2-octyl-dodecane (5.42 g, 15 mmol) and a catalytic amount of tetrabutylammonium bromide were added into the flask. After being refluxed overnight, the reactant was poured into cold water and extracted by petroleum ether. The organic phase was dried over Na₂SO₄. After removing the solvent under vacuum, residue was purified by silica column chromatography with petroleum ether to give compound **4** as pale yellow oil (2.32 g, 63%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.13 (s, 1H), 8.00 (d, *J*=8.4 Hz, 1H), 7.96-7.89 (m, 2H), 7.77-7.74 (m, 1H), 7.59-7.54 (m, 3H), 7.41-7.36 (m, 2H), 7.30 (d, *J*=5.5 Hz, 1H), 4.30 (d, *J*=5.4 Hz, 2H), 1.94-1.90 (m, 1H), 1.70-1.65 (m, 2H), 1.51-1.28 (m, 30H), 0.90-0.87 (m, 6H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 148.31, 139.77, 138.24, 136.80, 133.59, 132.95, 130.04, 128.79, 128.46, 128.21, 127.84, 127.56, 127.02, 126.46, 126.38, 126.32, 126.25, 123.07, 120.15, 39.31, 31.96, 31.95, 31.35, 30.11, 29.73, 29.71, 29.69, 29.67, 29.40, 29.39, 27.02, 26.94, 22.73, 14.15.

2,6-bis(trimethyltin)-4-octyldodecyloxy-8-naphthalen-1-yl-benzo[1,2-*b*:4,5*b*']dithiophene (5)

To a solution of compound **3** (1.84 g, 3 mmol) in THF (60 mL) at -78 °C was added dropwise *n*-BuLi (4.69 mL, 7.5 mmol, 1.6 M in hexane) under nitrogen. The mixture was stirred at -78 °C for 1 h and then warmed to room temperature for 0.5 h. After cooling back to -78 °C again, trimethyltin chloride (9 mL, 9 mmol, 1 M in hexane) was added in one portion. The mixture was brought to room temperature and stirred overnight. Water was subsequently added to the reaction mixture and extracted by diethyl ether. The combined organic extracts were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was recrystallized by ethanol two times. Compound **5** was obtained as a white solid (2.20 g, 78%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.00-7.95 (m, 2H), 7.65-7.62 (m, 3H), 7.50-7.47 (m, 1H), 7.42 (d, *J*=8.4 Hz, 1H), 7.30-7.27 (m, 1H), 6.85 (s, 1H), 4.36 (d, *J*=5.4 Hz, 2H), 1.97-1.93 (m, 1H), 1.75-1.69 (m, 2H), 1.51-1.27 (m, 30H), 0.90-0.87 (m, 6H), 0.37-0.26 (m, 18H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 137.40, 133.93, 132.06, 131.72, 131.05, 128.39, 128.27, 127.90, 127.76, 126.40, 126.07, 126.01, 125.70, 122.99, 76.01, 39.33, 32.00, 31.98, 31.50, 30.25, 29.83, 29.81, 29.78, 29.74, 29.46, 29.42, 27.14, 22.75, 22.73, 14.18, 14.16, - 8.29, -8.38.

2,6-bis(trimethyltin)-4-octyldodecyloxy-8-naphthalen-2-yl-benzo[1,2-b:4,5-

b']dithiophene (6)

To a solution of compound **4** (1.84 g, 3 mmol) in THF (60 mL) at -78 °C was added dropwise *n*-BuLi (4.69 mL, 7.5 mmol, 1.6 M in hexane) under nitrogen. The mixture was stirred at -78 °C for 1 h and then warmed to room temperature for 0.5 h. After cooling back to -78 °C again, trimethyltin chloride (9 mL, 9 mmol, 1 M in hexane) was added in one portion. The mixture was brought to room temperature and stirred overnight. Water was subsequently added to the reaction mixture and extracted by diethyl ether. The combined organic extracts were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was recrystallized by ethanol two times. Compound **6** was obtained as a white solid (1.83 g, 65%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.15 (s, 1H), 8.02 (d, *J*=8.4 Hz, 1H), 7.96-7.91 (m, 2H), 7.79-7.76 (m, 1H), 7.62 (s, 1H), 7.56-7.53 (m, 2H), 7.32 (s, 1H), 4.31 (d, *J*=5.3 Hz, 2H), 1.94-1.90 (m, 1H), 1.73-1.67 (m, 2H), 1.51-1.27 (m, 30H), 0.90-0.87 (m, 6H), 0.44-0.33 (m, 18H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 146.93, 144.24, 141.74, 140.85, 139.46, 137.55, 133.66, 132.88, 132.65, 131.15, 130.68, 128.45, 128.33, 128.28, 127.94, 127.88,

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127.85, 126.26, 126.17, 124.91, 76.00, 39.32, 31.99, 31.97, 31.46, 30.23, 29.82, 29.80, 29.77, 29.73, 29.45, 29.42, 27.13, 22.74, 22.73, 14.17, 14.15, -8.29, -8.38.

Synthesis of PBDTaNPFBT

To a 25 mL flask, compound **5** (140.79 mg, 0.15 mmol), 5,6-difluoro-4,7-bis(5-bromo-4-(2-ethylhexyl)-2-thienyl)-2,1,3-benzothiadiazole (107.8 mg, 0.15 mmol), Pd₂(dba)₃ (4.2 mg, 0.0045 mmol), and tri(*o*-tolyl)phosphine (8.4 mg, 0.027 mmol) were added under nitrogen. After the addition of toluene (5 mL), the mixture was heated to 115 °C and maintained at the same temperature for 24 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected and purified by column chromatography over silica using heated *o*-dichlorobenzene as the eluant. Then, the solution was poured into methanol again. The product was collected and dried overnight under vacuum at 40 °C with the yield 58% for **PBDT***a***NPFBT** as a black solid. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.22-6.89 (m, 11H), 4.48-4.10 (br, 2H), 2.99-2.38 (br, 4H), 1.69-0.84 (m, 69H). GPC: *M*_n=76.3 KDa, PDI=1.68. *T*_d=335 °C.

Synthesis of PBDT BNPFBT

To a 25 mL flask, compound 6 (140.79 mg, 0.15 mmol), 5,6-difluoro-4,7-bis(5-bromo-4-(2-ethylhexyl)-2-thienyl)-2,1,3-benzothiadiazole (107.8 mg, 0.15 mmol), Pd₂(dba)₃ (4.2 mg, 0.0045 mmol), and tri(*o*-tolyl)phosphine (8.4 mg, 0.027 mmol) were added under nitrogen. After the addition of toluene (5 mL), the mixture was heated to 115 °C and maintained at the same temperature for 24 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected and purified by column chromatography over silica using heated *o*-dichlorobenzene as the eluant. Then, the solution was poured into methanol again. The product was collected and dried overnight under vacuum at 40 °C with the yield 65% for **PBDT/**/**NPFBT** as a black solid. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.24-7.38 (m, 11H), 4.45-3.91 (br, 2H), 3.01-2.32 (br, 4H), 1.71-0.84 (m, 69H). GPC: M_n =78.5 KDa, PDI=1.57. T_d =353 °C.

4. TGA Curves



Figure S1. Thermogravimertic analysis (TGA) of the polymers.

5. The Detailed Optimized Device Parameters and *J-V* Curves

Table S1. The o	ptimized detai	ls and the corro	esponding phot	tovoltaic paran	neters of the PSCs
	1				

Polymer	Acceptor	D/A	DIO	Voc	J _{SC}	FF	PCE ^[a]
		(w/w)	(v%)	(V)	(mA cm ⁻²)		(%)
	PC ₇₁ BM	1:1	3	0.92	9.62	0.678	6.00 (5.89)
	PC ₇₁ BM	1:1.5	3	0.91	12.61	0.699	8.02 (7.87)
	PC ₇₁ BM	1:2	3	0.91	10.38	0.687	6.49 (6.27)
	PC ₇₁ BM	1:2.5	3	0.92	8.53	0.670	5.26 (5.12)
	PC ₇₁ BM	1:1.5	0	1.02	8.52	0.432	3.75 (3.52)
	PC ₇₁ BM	1:1.5	1	0.94	10.54	0.696	6.90 (6.82)
ΡΒΟΤ <i>α</i> ΝΡΕΒΤ	PC ₇₁ BM	1:1.5	2	0.92	11.42	0.690	7.25 (7.12)
	PC ₇₁ BM	1:1.5	4	0.86	6.30	0.619	3.90 (3.78)
	ITIC	1:0.8	0	1.00	8.46	0.403	3.41 (3.38)
	ITIC	1:1	0	0.99	10.20	0.497	5.02 (4.84)
	ITIC	1:1.2	0	0.99	7.57	0.422	3.16 (3.08)
	ITIC	1:1	0.5	1.02	7.75	0.549	4.34 (4.16)
ΡΒDΤ <i>β</i> ΝΡΓΒΤ	PC ₇₁ BM	1:1	0	0.90	13.23	0.676	8.05 (7.93)
	PC ₇₁ BM	1:1.5	0	0.88	13.78	0.707	8.57 (8.45)
	PC ₇₁ BM	1:2	0	0.89	15.53	0.709	9.80 (9.61)
	PC ₇₁ BM	1:2.5	0	0.87	11.13	0.721	6.98 (6.89)
	PC ₇₁ BM	1:2	3	0.85	13.63	0.691	8.01 (7.83)
	ITIC	1:0.8	0	0.91	11.13	0.565	5.72 (5.59)
	ITIC	1:1	0	0.90	14.67	0.555	7.33 (7.15)
	ITIC	1:1.2	0	0.90	14.75	0.476	6.32 (6.18)
	ITIC	1:1	0.5	0.90	13.76	0.548	6.78 (6.65)

[a] Average PCE in brackets (15 devices).



Figure S2. *J-V* curves for the PSCs based on (a) PBDT α NPFBT/PC₇₁BM, (b) PBDT β NPFBT/PC₇₁BM, (c) PBDT α NPFBT/ITIC and (d) PBDT β NPFBT/ITIC with different D/A ratios and DIO volume under the illumination of AM 1.5G (100 mW cm⁻²).

6. Hole Mobility Measurements



Figure S3. *J-V* plots for the devices ITO/PEDOT:PSS/polymer:PC₇₁BM (ITIC)/Au. (a) PBDT α NPFBT/PC₇₁BM with 3% DIO, (b) PBDT β NPFBT/PC₇₁BM without DIO, (c) P PBDT α NPFBT/ITIC and (d) PBDT β NPFBT/ITIC (The symbols are experimental data for transport of hole, and the red lines are fitted according to the space-charge-limited-current model).

7. AFM and 2D-GIWAXS Measurements



Figure S4. AFM height (3×3 µm, a-1, b-1, c-1, d-1, e-1, f-1), and phase (3×3 µm, a-2, b-2, c-2, d-2, e-2, f-2) images of the active layers containing PBDT α NPFBT/PC₇₁BM (1:1.5, w/w) without DIO (a), PBDT β NPFBT/PC₇₁BM (1:2, w/w) without DIO (b), PBDT α NPFBT/PC₇₁BM (1:1.5, w/w) with 3% DIO (c), PBDT β NPFBT/PC₇₁BM (1:2, w/w) with 3% DIO (d), PBDT α NPFBT/ITIC (1:1, w/w) (e) and PBDT β NPFBT/ITIC (1:1, w/w) (f).



Figure S5. 2D-GIWAXS patterns for the blend films (a) PBDTαNPFBT/PC₇₁BM (1:1.5, w/w) without DIO, (b) PBDTβNPFBT/PC₇₁BM (1:2, w/w) without DIO, (c)
PBDTαNPFBT/PC₇₁BM (1:1.5, w/w) with 3% DIO, (d) PBDTβNPFBT/PC₇₁BM (1:2, w/w) with 3% DIO, (e) PBDTαNPFBT/ITIC (1:1, w/w) and (f) PBDTβNPFBT/ITIC (1:1, w/w). (g)
Out-of-plane line cuts and (h) in-plane line cuts of the 2D-GIWAXS patterns for the blend

films.

8. NMR Spectra



Figure S6. ¹H NMR spectrum of compound 3.



Figure S7. ¹³C NMR spectrum of compound 3.



Figure S8. ¹H NMR spectrum of compound 4.



Figure S9. ¹³C NMR spectrum of compound 4.



Figure S10. ¹H NMR spectrum of compound 5.



Figure S11. ¹³C NMR spectrum of compound 5.



Figure S12. ¹H NMR spectrum of compound 6.



Figure S13. ¹³C NMR spectrum of compound 6.



Figure S14. ¹H NMR spectrum of PBDTaNPFBT.



Figure S15. ¹H NMR spectrum of PBDTβNPFBT.

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