## **Electronic Supplementary Information**

for

# **BODIPY Bearing Alkylthienyl Side Chains: A New Building Block to**

# Design Conjugated Polymers with Near Infrared Absorption for

## **Organic Photovoltaics**

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#### 1. Experimental details

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of monomers were measured with a Bruker AV-500 spectrometer in CDCl<sub>3</sub> or DMSO at 25 °C, <sup>1</sup>H NMR spectra of polymers were measured with a Bruker AV-400 in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 110 °C. Elemental analysis was performed on a Vario EL elemental analyzer. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) on a PL-GPC 220-type at the temperature of 150 °C. 1,2,4-Trichlorobenzene (TCB) was used as the eluent and monodisperse polystyrene was used as the standard. UV-vis absorption spectra and fluorescence spectra were measured with a Shimadzu UV-3600 spectrometer and a Hitachi F-4500 spectrometer, respectively, in spectral grade solvents. Thermal analyses were performed on a Perkin-Elmer 7 instrument under nitrogen flow at a heating rate of 10 °C min<sup>-1</sup>. Atomic force microscopy (AFM) was performed with a SPA300HV (Seiko Instruments, Inc., Japan) in tapping mode. The thickness of various layers was measured with a Dektak 6M Stylus Profile. The grazing incidence X-ray diffraction (GI-XRD) measurement was performed using a Bruker D8 Discover reflector. Cyclic voltammetry (CV) was performed on an CHI660a electrochemical workstation using Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) in acetonitrile as electrolyte solution and ferrocene as an internal reference at a scan rate of 100 mV s<sup>-1</sup>. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a standard calomel reference electrode. The polymer was casted on the working electrode for measurements. The redox potentials were calibrated with ferrocene as an internal standard. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the materials were estimated by the equations:  $E_{\text{HOMO/LUMO}} = -(4.80 + E_{\text{onset}}^{\text{ox}}/E_{\text{onset}}^{\text{red}})$ .

All reactions were performed under argon atmosphere. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Toluene, *n*-hexane, THF and CHCl<sub>3</sub> were dried using sodium or calcium hydroxide before use.

#### 2. OSCs device and SCLC device fabrications and measurements

Indium tin oxide (ITO) glass substrates were cleaned by sequential ultrasonication

in detergent, deionized water, acetone, and isopropyl alcohol, followed by dried at 120 °C for 30 min and treated with UV-ozone for 25 min. Then PEDOT:PSS (Baytron PVP Al 4083) was spin-coated on the ITO glass substrates at 5000 rpm for 40 s to give a thickness of 40 nm, followed by baking at 120 °C for 30 min. The substrates were transferred to a nitrogen-filled glove box. The blend in o-DCB solution was spin-coated onto the PEDOT:PSS layer at 120 °C to produce the active layer (70-90 nm). The donor/acceptor ratio values of the four blends are 1:1.5 (w/w). The active layers of P-T:IEICO-4F and P-2T:IEICO-4F blends were annealed at 120 °C and 80 °C for 10 min, respectively. Finally, the active layer was transferred to a vacuum chamber, and Ca (20 nm) and Al (100 nm) were deposited by thermal evaporation at the pressure of about 2  $\times$  10<sup>-4</sup> Pa. The active area of each device was 8 mm<sup>2</sup>. The current density–voltage (*J*– V) curves of the PSC devices were measured using a computer-controlled Keithley 2400 source meter under 100 mW cm<sup>-2</sup> AM 1.5G simulated solar light illumination provided by a XES-40S2-CE Class Solar Simulator (Japan, SAN-EI Electric Co., Ltd.). The EQE spectrum was measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a calibrated monosilicon diode.

The hole mobilities of the neat films were measured using the space-chargelimited current (SCLC) method. The hole-only device structures for the pristine films of **P-T** and **P-2T** are ITO/PEDOT:PSS/**P-T** or **P-2T**/MoO<sub>3</sub>/Ag. The current–voltage curves in the range of 0–10 V were recorded using a computer-controlled Keithley 2400 source meter, and the results were fitted to a space-charge limited function:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} \exp\left(0.89\beta \left|\frac{\sqrt{V}}{\sqrt{L}}\right.\right)$$

Where J is the current density,  $\varepsilon_0$  is permittivity of free space,  $\varepsilon_r$  is the relative permittivity (assumed to be 3),  $\mu$  is the zero-field mobility, V is the potential across the device ( $V = V_{applied} - V_{bi} - V_{series}$ ), L is the thickness of active layer, and  $\beta$  is the fieldactivation factor. The series and contact resistance of the device (10–20  $\Omega$ ) were measured using blank device of ITO/PEDOT:PSS/MoO<sub>3</sub>/Ag.

#### 3. Syntheses and characterizations

#### 2-(2-decyltetradecyl)thiophene (Compound 1)

Under an argon atmosphere thiophene (6.0 g, 71.3 mmol) was solved in anhydrous THF (120 ml). A solution of *n*-butyl lithium in hexane (25.4 ml, 63.5 mmol) (2.5 M solution) was added dropwise at -78 °C. After lithiation for 2 h, the mixture was allowed to rise to room temperature, the 11-(bromomethyl)tricosane (24.8 g, 59.4 mmol) was added slowly then the mixture was heated to 60 °C and stirring for 15 h. After cooling, the solvent was evaporated in vacuo. the residue was chromatographed on silica gel using petroleum ether as an eluent. A mixture of 2-(2-decyltetradecyl)thiophene and 2,5-bis(2-decyltetradecyl)thiophene was obtained as a yellow oil.

#### 5-(2-decyltetradecyl)thiophene-2-carboxylic acid (Compound 2)

Compound **1** (23.0 g, 54.6 mmol) was solved in dry diethyl ether (200 ml) under an argon atmosphere. To this mixture was added dropwise *n*-butyl lithium in hexane (26.6 ml, 65.6 mmol) (2.5 M solution) under external ice cooling. After refluxing the reaction mixture for one hour the mixture was cooled down to room temperature and solid CO<sub>2</sub> (at least 10 fold excess) was carefully added. To complete the reaction the mixture was allowed rise to room temperature over night by stirring. The precipitated lithum salts were solved by adding water. The mixture was acidified with HCl and cooled with ice water. After an extraction with CHCl<sub>3</sub>, the organic layer being dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed in vacuo, the residue was chromatographed on silica gel using CHCl<sub>3</sub> as an eluent. Compound **2** (10.7 g) was obtained as a yellow solid in 42% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.68 (s, 1H), 6.75 (s, 1H), 2.75 (d, J = 5.2 Hz, 2H), 1.64 (d, J = 1.4 Hz, 1H), 1.34-1.18 (m, 40H), 0.88 (t, J = 6.9 Hz, 6H).

#### Methyl 5-(2-decyltetradecyl)thiophene-2-carboxylate (Compound 3)

To a stirred solution of compound **2** (12.0 g, 25.8 mmol) in MeOH (200 mL) cooled to 0  $^{\circ}$ C, SOCl<sub>2</sub> (6.9 mL, 103.1 mmol) was added and the reaction was stirred at 25  $^{\circ}$ C for 42 h. A solution of NaOH was added and volatiles were removed under

reduced pressure. The aqueous phase was extracted with  $CH_2Cl_2$  and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. the residue was chromatographed on silica gel using  $CH_2Cl_2$ /petroleum ether (1:1 v/v) as an eluent. Compound **3** (9.0 g) was obtained as a yellow solid in 80% yield. <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.63 (d, J = 3.7 Hz, 1H), 6.75 (d, J = 3.7 Hz, 1H), 3.86 (s, 3H), 2.76 (d, J = 6.7 Hz, 2H), 1.64 (d, J = 5.0 Hz, 1H), 1.36-1.15 (m, 40H), 0.88 (t, J = 6.9 Hz, 6H). <sup>13</sup>C NMR (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 162.81, 152.88, 133.61, 130.72, 126.16, 51.95, 40.03, 34.85, 33.14, 31.92, 29.89, 29.70, 29.68, 29.65, 29.37, 29.35, 26.56, 22.70, 14.13.

### 5-(2-decyltetradecyl)thiophene-2-carbohydrazide (Compound 4)

Compound **3** (9.0 g, 18.8 mmol) in EtOH (100 mL) and hydrazine monohydrate (16.0 mL, 281.9 mmol) was added dropwise into the mixture. After reflux overnight, the mixture was cooled and extracted with  $CH_2Cl_2$ , the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. Compound **4** (9.0 g) as a yellow oil was obtained in quantitative yield. <sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  (ppm) 9.62 (s, 1H), 7.51 (d, J = 3.7 Hz, 1H), 6.80 (d, J = 3.7 Hz, 1H), 2.71 (d, J = 6.7 Hz, 2H), 1.59 (d, J = 5.8 Hz, 1H), 1.33-1.11 (m, 40H), 0.85 (t, J = 6.9 Hz, 6H). <sup>13</sup>C NMR (125 MHz, DMSO):  $\delta$  (ppm) 161.73, 148.80, 136.28, 127.83, 126.71, 79.64, 60.21, 34.39, 32.87, 31.76, 29.64, 29.48, 29.35, 29.16, 26.19, 22.56, 14.55, 14.41.

# (Z)-N'-(1-(4-bromo-2-hydroxyphenyl)ethylidene)-5-(2-decyltetradecyl)thiophene-2carbohydrazide (Compound 5)

Compound **4** (3.2 g, 6.7 mmol) and 1-(4-bromo-2-hydroxyphenyl)ethan-1-one (1.8 g, 8.3 mmol) were dissolved in dry EtOH (60 mL) under Ar atmosphere. The resulting mixture was stirred for 16 h at 85 °C. After cooling in the ice bath, the resultant precipitate was washed with cooled EtOH to give Compound **5** (3.0 g) as a light-yellow solid in 69% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.58 (s, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.21 (d, *J* = 1.8 Hz, 1H), 7.02 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.82 (d, *J* = 3.0 Hz, 1H), 2.79 (d, *J* = 6.7 Hz, 2H), 2.37 (s, 3H), 1.66 (s,1H), 1.35-1.19 (m, 40H), 0.88 (t, *J* 

= 6.9 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 128.67, 126.37, 125.27, 121.98, 121.34, 118.12, 40.10, 34.83, 33.15, 31.93, 29.92, 29.69, 29.65, 29.36, 26.58, 22.69, 14.12.

# 1-(4-bromo-2-(5-(2-decyltetradecyl)thiophene-2-carbonyl)phenyl)ethan-1-one (Compound 6).

Pb(OAc)<sub>4</sub> (5.1 g, 22.8 mmol) was added into a solution of **5** (3.1 g, 9.2 mmol) in THF (60 mL)in several times under an icy condition. The mixture was stirred over night at room temperature, and then filtered using buchner funnel filled with silica gel. The filtrate was extraction with ethyl acetate, removal of solvent from the organic layer gave **6** (2.9 g) as a yellow oil in quantitative yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.72-7.66 (m, 2H), 7.64 (d, *J* = 1.5 Hz, 1H), 7.15 (d, *J* = 3.8 Hz, 1H), 6.75 (d, *J* = 3.8 Hz, 1H), 2.78 (d, *J* = 6.7 Hz, 2H), 2.50 (s, 3H), 1.66 (d, *J* = 7.3 Hz, 1H), 1.34-1.19 (m, 40H), 0.88 (t, *J* = 6.9 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 197.86, 187.48, 156.38, 141.71, 141.26, 136.64, 135.07, 132.89, 131.40, 130.48, 126.70, 126.60, 60.41, 40.00, 35.21, 33.18, 31.93, 29.91, 29.66, 29.36, 27.96, 26.56, 22.70, 14.13.

# 3,11-dibromo-5,9-bis(5-(2-decyltetradecyl)thiophen-2-yl)-7,7-difluoro-7H-6l4,7l4-[1,3,2]diazaborinino[4,3-a:6,1-a']diisoindole (Compound 8)

To a solution of **6** (1.3 g, 2.0 mmol) in EtOH (65 mL) and AcOH (13 mL) was added NH<sub>4</sub>OAc (923 mg, 12 mmol) at 65 °C. The resulting mixture was stirred for 1.5 h at 90 °C. After cooling and evaporation, the solid was partitioned between CH<sub>2</sub>Cl<sub>2</sub> and brine. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The residue was chromatographed on silica gel using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:2 v/v) as an eluent. In this way, 275 mg of benzo-fused dipyrrin was obtained in 21% yield. The product **7** (592 mg, 0.5 mmol) was dissolved in dry toluene (35 mL). Et<sub>3</sub>N (0.3 mL, 2.4 mmol) was added to the solution, followed by the addition of BF<sub>3</sub>·Et<sub>2</sub>O (1.0 mL, 4.8 mmol) at 80 °C. The mixture was stirred overnight at 100 °C. After cooling, the solution was poured into water and extracted with ethyl acetate. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, and filtrated. The filtrate was evaporated and reprecipitated with

CHCl<sub>3</sub>/MeOH. The resulting solid was chromatographed on silica gel using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:5 v/v) as an eluent. In this way, 375 mg of **8** was obtained as a green solid in 61% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.17 (s, 2H), 7.90 (d, J = 3.7 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 7.54 (s, 1H), 7.49-7.43 (m, 2H), 6.94 (d, J = 3.8 Hz, 2H), 2.87 (d, J = 6.7 Hz, 4H), 1.76 (s, 2H), 1.45-1.11 (m, 80H), 0.87 (t, J = 6.9 Hz, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 160.30, 150.66, 135.58, 131.91, 128.99, 128.92, 128.48, 128.40, 128.25, 127.01, 126.62, 125.72, 120.40, 119.41, 100.04, 40.06, 34.85, 33.36, 31.93, 30.02, 29.71, 29.67, 29.38, 26.65, 22.69, 14.12.

#### **Polymer P-T**

materials Starting of 8 (116.7)0.091 mmol), 2.5mg, bis(trimethylstannyl)thiophene (37.1 mg, 0.091 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>.CHCl<sub>3</sub> (1.8 mg, 0.0017 mmol) and P(o-Tol)<sub>3</sub> (4.4 mg, 0.014 mmol) were placed in a two-necked flask under argon, and then dried toluene (5.0 mL) was added. The mixture was stirred at 120 °C for 12 h. After cooling, the residue was dispersed in methanol and the precipitate was collected. The obtained dark solid was purified by Soxhlet extraction in acetone, hexane and CHCl<sub>3</sub>. The solid from the CHCl<sub>3</sub> solution was dispersed in methanol, then collected and dried in vacuum overnight. Yield: 92.0 mg (83%). <sup>1</sup>H NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ (ppm) 8.17 (s, 2H), 7.87 (s, 2H), 7.06-7.59 (m, 9H), 3.16 (s, 4H), 2.06 (s, 2H), 1.87-1.12 (m, 86H), 0.85 (m, 12H). Anal. Calcd for C<sub>77</sub>H<sub>111</sub>BF<sub>2</sub>N<sub>2</sub>S<sub>3</sub>: C, 76.45; H, 9.25; N, 2.32; S, 7.95. Found: C, 75.56; H, 9.08; N, 2.12; S, 7.78.

#### **Polymer P-2T**

Starting materials of **8** (123.7 mg, 0.096 mmol), 5,5'-bis(trimethylstannyl)-2,2'bithiophene (47.3 mg, 0.096 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>.CHCl<sub>3</sub> (2.0 mg, 0.0018 mmol) and P(o-Tol)<sub>3</sub> (4.7 mg, 0.015 mmol) were placed in a two-necked flask under argon, and then dried toluene (5.0 mL) was added. The mixture was stirred at 120 °C for 9 h. After cooling, the residue was dispersed in methanol and the precipitate was collected. The obtained dark solid was purified by Soxhlet extraction in acetone, hexane and CHCl<sub>3</sub>. The solid from the CHCl<sub>3</sub> solution was dispersed in methanol, then collected and dried in vacuum overnight. Yield: 107.0 mg (86%). <sup>1</sup>H NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$  (ppm) 8.09 (s, 1H), 7.77 (s, 2H), 7.64-6.89 (m, 12H), 3.16 (s, 4H), 2.06 (s, 2H), 1.49 (m, 86H),
0.92 (m, 12H). Anal. Calcd for C<sub>81</sub>H<sub>113</sub>BF<sub>2</sub>N<sub>2</sub>S<sub>4</sub>: C, 75.31; H, 8.82; N, 2.17; S, 9.93.
Found: C, 74.47; H, 8.72; N, 1.93; S, 10.00.

### 4. Thermal properties

The thermal properties of the three polymers were determined by thermogravimetric analysis (TGA) in N<sub>2</sub> flow. **P-T** and **P-2T** show good thermal stabilities with thermal decomposition temperatures ( $T_d$ ) of respective 334 °C and 384 °C.



Fig. S1 TGA plots of P-T and P-2T under  $N_2$  atmosphere.

### 5. Absorption and emission properties



Fig. S2 UV-vis absorption spectra of BOPT in o-DCB solution.



Fig. S3 Temperature-dependent UV-vis absorption spectra of P-T (a) and P-2T(b).



Fig. S4 Fluorescence spectra of P-T and P-2T in chlorobenzene solution.



Fig. S5 UV-vis absorption spectra of IEICO-4F in o-DCB solution and in film.



Fig. S6 The normalized absorption of IEICO-4F-based blend films with different donors.

### 6. Molecular packing



Fig. S7 Grazing-incidence X-ray di action patterns of P-T and P-2T.

### 7. Charge carrier mobilities



**Fig. S8** J-V curves and SCLC fittings of the hole-only device of a) **P-T** and b) **P-2T** films.



**Fig. S9** J-V curves and SCLC fittings of the a, c) hole-only device of and b, d) the electron-only device of **P-T**:IEICO-4F and **P-2T**:IEICO-4F blend films.

Active layer	$\mu_h$ (cm <sup>2</sup> v <sup>-1</sup> s <sup>-1</sup> )	$\mu_{e}$ (cm <sup>2</sup> v <sup>-1</sup> s <sup>-1</sup> )	$\mu_h  / \mu_e$
P-T:IEICO-4F	$7.7  imes 10^{-4}$	2.3 × 10 <sup>-5</sup>	33
P-2T:IEICO-4F	$2.4 \times 10^{-4}$	1.1 × 10 <sup>-5</sup>	21

Table S1. The mobility of P-T:IEICO-4F and P-2T:IEICO-4F blend films.

### 8. OSCs device performance



**Fig. S10** *J-V* curves of the OSCs based on the a) **P-T**:IEICO-4F and b) **P-2T**:IEICO-4F active layers spin-coated with different contents of 1-Chloronaphthalene (CN).

**Table S2.** Characteristics of OSCs based on the P-T:IEICO-4F and P-2T:IEICO-4F

 active layers spin-coated with different contents of CN.

Active layer	CN content (vol%)	V <sub>oc</sub> (V)	$J_{ m SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
<b>P-T</b> :IEICO-4F	0%	0.52	8.10	55.05	2.32
	0.25%	0.51	9.39	54.06	2.59
	0.5%	0.51	8.37	58.09	2.48
<b>P-2T</b> :IEICO-4F	0%	0.48	10.33	57.49	2.85
	0.5%	0.46	11.12	56.66	2.90
	1%	0.44	10.73	55.05	2.84



**Fig. S11** (a)  $J_{ph}-V_{eff}$  plot and (b) light intensity dependence of  $J_{SC}$  (solid lines are fitted results) of the photovoltaic devices based on **P-T**:IEICO-4F and **P-2T**:IEICO-4F blend film.

 Table S3. Parameters of OSCs based on the P-T:IEICO-4F and P-2T:IEICO-4F active layers.

Active layer	$J_{\rm ph,sc}$ (mA cm <sup>-2</sup> )	J <sub>ph,sat</sub> (mA cm <sup>-2</sup> )	$J_{ m ph,sc}\!/\!J_{ m ph,sat}$	α
P-T:IEICO-4F	7.56	10.90	0.69	0.95
P-2T:IEICO-4F	9.83	12.93	0.76	0.94

# 9. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra and mass spectrum



Fig. S12 <sup>1</sup>H NMR spectra of 2.



Fig. S13 <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3.



Fig. S14 <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 4.



Fig. S15  $^{1}$ H NMR and  $^{13}$ C NMR spectra of 5.



Fig. S16 <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 6.



Fig. S17 <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 8.



Fig. S18 MOLDI-TOF spectrum of 8.



Fig. S19 <sup>1</sup>H NMR spectra of P-T.



Fig. S20 <sup>1</sup>H NMR spectra of P-2T a) in  $C_2D_2Cl_4$  and b) in  $C_6D_6Cl_2$ .