# Electronic Supplementary Information

## The End-capped Group Effect on the Dithienosilole Trimer Based

### **Small Molecules for Efficient Organic Photovoltaics**

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#### 1. Experimental section

#### **1.1 General Information**

All reagents were used as received from commercial sources. The compounds **1**, **2**, **3**, **6** and **7** were prepared according to the literatures.<sup>1-3</sup> All the reactions were carried out under a dry argon atmosphere. Tetrahydrofuran (THF) and toluene were dried over sodium-potassium alloy. *N*,*N*-dimethylformamide (DMF) and 1,2-dichloroethane (DCE) were dried over calcium hydride. All the dry solvents were distilled just before use.

#### **1.2 Measurements and instruments**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a MERCURY-VX300 spectrometer. Elemental analysis of carbon, hydrogen and nitrogen was performed on Vario EL-III microanalyzer. EI-MS spectra were recorded on VJ-ZAB-3F-Mass spectrometer. Thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C/min. The temperature of degradation ( $T_d$ ) was correlated to a 5% weight loss. UV-vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Cyclic voltammetry (CV) measurements were carried out on a CHI voltammetric analyzer at room temperature. Tetrabutylammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode with a 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl wire reference electrode. Cyclic voltammograms were obtained at a scan rate of 100 mV/s. The potentials were determined using ferrocene as reference. The X-ray diffraction patterns were recorded on a Rigaku MiniFlex XRD 600 X-ray diffractometer.

#### **1.3 Materials**

**Preparation of 3**. To a 100 mL solution of 2.09 g (5.0 mmol) of **1** in 40 mL dry THF was added dropwise 2.2 mL (5.17 mmol) of a 2.35 M *n*-butyllithium-hexane solution. The solution was stirred at -78 °C for 1.5 h. Then, 1.7 mL (6.5 mmol) of tributyltin chloride was added. The mixture was warmed up to room temperature and stirred for an additional 12 h. Then water and ester was added and the organic layer was separated, washed with water for several times, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to give **3** as a green oil (3.45 g, yield: 97%). This compound was used for the following step without any further purification. MS (EI): calcd for (C<sub>36</sub>H<sub>64</sub>S<sub>2</sub>SiSn), 708.32; found, 708.61.

**Preparation of tDTS**. In a 100 mL two-necked flask were placed 3.45 g (4.86 mmol) of **3**, 1.27 g (2.20 mmol) of **2**, 215 mg (0.7 mmol) of Tris(o-methoxyphenyl)phosphine and 80 mg (0.088 mmol) of tris(dibenzylideneacetone)dipalladium [Pd<sub>2</sub>(dba)<sub>3</sub>] in 20 mL dry toluene. The mixture was stirred at 110 °C for 2 days. The solvent was evaporated and the residue was subjected to column chromatography on silica gel with hexane as eluent to give **tDTS** as a red oil (2.0 g, yield: 73%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.20 (d, *J* = 4.5 Hz, 2H), 7.08 (s, 4H), 7.05 (d, *J* = 4.5 Hz, 2H), 1.52-1.36 (m, 8H), 1.33-1.18 (m, 48H), 0.97 (m, 10H), 0.91-0.76 (m, 36H). <sup>13</sup>C NMR (75 MHz,

CDCl<sub>3</sub>, δ): 149.05, 147.41, 144.27, 144.04, 142.55, 138.64, 138.31, 130.15, 126.21, 125.39, 36.18, 35.91, 30.02, 29.16, 23.28, 17.91, 14.47, 11.10. MS (MALDI-TOF): calcd for (C<sub>72</sub>H<sub>110</sub>S<sub>6</sub>Si<sub>3</sub>), 1250.62; found, 1249.63.

**Preparation of 4**. To a 100 mL solution of 2.0 g (1.6 mmol) of **tDTS** in 25 mL dry THF was added dropwise 2.2 mL (3.84mmol) of a 2.35 M *n*-butyllithium-hexane solution. The solution was stirred at -78 °C for 1.5 h. Then, 1.1 mL (4.1mmol) of tributyltin chloride was added. The mixture was warmed up to room temperature and stirred for an additional 12 h. Then water and ester was added and the organic layer was separated, washed with water for several times, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to give **4** as a red oil (2.9 g, yield: 99%). This compound was used for the following step without any further purification.

**Preparation of 5.** In a 100 mL two-necked flask were placed 0.9 mL (10 mmol) phosphorus oxychloride and 10 mL of dry DMF under an ice-water bath. After stirred for 1 h, a solution of 1.25 g (1.0 mmol) of **tDTS** in 20 mL 1,2-dichloroethane (DCE) was added and then stirred at 60 °C for 12 h. After cooled to room temperature, the mixture was poured into ice-water (50 mL), neutralized with sodium carbonate, and then extracted with chloroform. The organic layer was washed with water for several times and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to and the residue was subjected to column chromatography on silica gel with hexane/chloroform (v/v, 1:1) as eluent to give **5** as a dark red oil (1.07 g, yield: 82%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.87 (s, 2H), 7.69 (s, 2H), 7.16 (d, *J* = 6.0 Hz, 4H), 1.43 (m, 8H), 1.18 (m, 48H), 1.01 (m, 10H), 0.83 (m, 36). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 163.33, 162.77, 151.36, 148.51,

145.07, 143.67, 140.28, 137.50, 133.57, 132.80, 126.94, 121.80, 113.50, 42.56, 38.35, 35.98, 35.74, 30.68, 29.00, 28.68, 24.00, 23.23, 23.14, 14.33, 10.98, 10.61. MS (MALDI-TOF): calcd for (C<sub>74</sub>H<sub>110</sub>O<sub>2</sub>S<sub>6</sub>Si<sub>3</sub>), 1306.61; found, 1306.95.

**Preparation of FBT-tDTS.** In a 50 mL two-necked flask were placed 550 mg (0.3 mmol) of **4**, 233mg (1.0 mmol) of **6**, 60 mg (0.28 mmol) of Tris(o-methoxyphenyl)phosphine and 20 mg (0.022 mmol) of Pd<sub>2</sub>(dba)<sub>3</sub> in 15 mL dry toluene. The mixture was stirred at 110 °C for 2 days. The solvent was evaporated and the residue was subjected to column chromatography on silica gel with hexane/chloroform (v/v, 3:1) as eluent to give **FBT-tDTS** as a dark red solid (220 mg, yield: 47%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.15 (s, 2H), 7.66 (t, *J* = 10.8 Hz, 2H), 7.46 (s, 2H), 7.14 (s, 4H), 1.49-1.54 (m, 8H), 1.19-1.32 (m, 48), 1.02-1.04 (m, 10), 0.80-0.84 (m, 36). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 161.84, 159.51, 148.82, 147.19, 145.86, 143.75, 139.85, 138.15, 137.76, 132.06, 126.38, 126.32, 125.97, 114.89, 114.23, 35.87, 35.60, 28.84, 22.92, 17.56, 14.08, 10.74. MS (MALDI-TOF): calcd for (C<sub>84</sub>H<sub>112</sub>F<sub>2</sub>N<sub>4</sub>S<sub>8</sub>Si<sub>3</sub>), 1554.59; found, 1555.2. Anal. calcd for (C<sub>84</sub>H<sub>112</sub>F<sub>2</sub>N<sub>4</sub>S<sub>8</sub>Si<sub>3</sub>): C 64.81, H 7.25, N 3.60; found: C 64.66, H 7.22, N 3.60.

**Preparation of DFBT-tDTS.** In a 50 mL two-necked flask were placed 550 mg (0.3 mmol) of **4**, 251 mg (1.0 mmol) of **7**, 60 mg (0.28 mmol) of Tris(o-methoxyphenyl)phosphine and 20 mg (0.022 mmol) of  $Pd_2(dba)_3$  in 15 mL dry toluene. The mixture was stirred at 110 °C for 2 days. The solvent was evaporated and the residue was subjected to column chromatography on silica gel with hexane/chloroform (v/v, 3:1) as eluent to give **DFBT-tDTS** as a dark red solid (185 mg, yield: 39%). <sup>1</sup>H

NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.32 (s, 2H), 7.59 (m, 2H), 7.18 (s, 2H), 7.15 (s, 2H), 1.50 (m, 8H), 1.21-1.32 (m, 48H), 1.05 (m, 10H), 0.82-0.84 (m, 36H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 151.10, 148.94, 148.15, 146.08, 145.74, 142.37, 142.31, 139.45, 137.62, 136.89, 126.16, 126.05, 125.67, 116.23, 115.66, 36.35, 36.10, 29.30, 23.41, 18.01, 14.54, 11.22. MS (MALDI-TOF): calcd for (C<sub>84</sub>H<sub>110</sub>F<sub>4</sub>N<sub>4</sub>S<sub>8</sub>Si<sub>3</sub>), 1590.57; found, 1591.8. Anal. calcd for (C<sub>84</sub>H<sub>110</sub>F<sub>4</sub>N<sub>4</sub>S<sub>8</sub>Si<sub>3</sub>): C 63.35, H 6.96, N 3.52; found: C 63.62, H 6.83, N 3.40.

**Preparation of RHO-tDTS**. To a solution of 800 mg (0.61 mmol) of **5** and 966 mg (1.0 mmol) 3-ethylrhodanine in 30 mL chloroform was added several drops of piperidine. The mixture was stirred at 65 °C for 24 h and then cooled down to room temperature. Then water and dichloromethane were added and the organic layer was washed with water for several times. The solvent was evaporated and the residue was subjected to column chromatography on silica gel with hexane/chloroform (v/v, 1:2) as eluent to give **RHO-tDTS** as a black solid (650 mg, yield: 67%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.90 (s, 2H), 7.35 (s, 2H), 7.17 (m, 4H), 4.20 (q, 4H), 1.42 (m, 6H), 1.30-1.67 (m, 56H), 1.01 (m, 12H), 0.82 (m, 38H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 191.68, 167.24, 156.88, 147.66, 145.77, 141.46, 139.02, 137.95, 137.59, 126.95, 126.11, 125.74, 118.27, 39.83, 35.79, 35.55, 28.78, 22.87, 17.50, 17.41, 14.04, 12.20, 10.73, 10.68. MS (MALDI-TOF): calcd for (C<sub>84</sub>H<sub>120</sub>N<sub>2</sub>O<sub>2</sub>S<sub>10</sub>Si<sub>3</sub>), 1592.59; found, 1594.7. Anal. calcd for (C<sub>84</sub>H<sub>120</sub>N<sub>2</sub>O<sub>2</sub>S<sub>10</sub>Si<sub>3</sub>): C 63.26, H 7.58, N 1.76; found: C 63.67, H 7.41, N 1.62.

#### **1.4 Fabrication and Characterization of Solar Cells.**

The device structure was ITO/PEDOT:PSS (40 nm)/donor:PC71BM (1:1) (100 nm)/PFN (5 nm)/Al. After being cleaned in ultra sonic bath by acetone, detergent, deionized water, and isopropyl alcohols equentially, the ITO-coated glass substrates were treated by oxygen plasma cleaning for 4 min. PEDOT:PSS (40 nm) was spincoated onto the ITO, and then the substrate was annealed at 150 °C for 15minunder air condition. The donor:  $PC_{71}BM$  blend layer, with a nominal thickness of ~100 nm, was prepared by spin-coating from a chloroform solution (18 mg mL<sup>-1</sup>) at 1500 rpm for 2 min. When using solvent annealing, the active layer was exposed to dichloromethane vapor for 30 s before spin coating the PFN layer. After the deposition of the thin PFN layer, Al was thermally evaporated under vacuum through a shadow mask to form the top cathode. The active area of the devices is  $0.16 \text{ cm}^2$ . The current-voltage (J-V) measurement of the devices was conducted using Keithley 2400 sourcemeter controlled by computer. And the characterization was carried out in glove box under a simulated AM 1.5G spectrum (100 mW cm<sup>-2</sup>) from a solar simulator (SAN-EI, XES-40S1 150W AAA). The incident photon-to-current conversion efficiency (IPCE) measurement was done by using quantum efficiency measurement system (QE-R, Enlitech, Taiwan) combined with a lock-in amplifier and 150 W xenon lamp. The light intensity at each wavelength was calibrated by one standard Si/Ge solar cell. Notably, the IPCE was done in ambient atmosphere at room temperature.

#### 1.5 Test of hole mobility of small molecules/PC71BM

The effective hole mobility was measured by using the space charge limited current (SCLC) method with the structure of ITO/PEDOT:PSS/donor:PC<sub>71</sub>BM/MoO<sub>3</sub>/Al. The SCLC is described as

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_\mathrm{r} \mu_\mathrm{h} \frac{V^2}{L^3}$$

(1)

Where *J* is the current density,  $\varepsilon_0$  is the permittivity of the free space,  $\varepsilon_r$  is the relative dielectric constant of the transport medium,  $\mu_h$  is the hole mobility, *V* is the internal potential in the device, and *L* is the active layer thickness. The internal potential *V* is obtained by subtracting the built-in voltage ( $V_{bi}$ ), from the applied voltage ( $V_{appl}$ ), according to  $V = V_{appl} - V_{bi}$ .

2. Thermo gravimetric analysis (TGA), cyclic voltammograms (CV) and space charge limited current (SCLC).



Fig. S1. TGA plots of FBT-tDTS, DFBT-tDTS and RHO-tDTS.



Fig. S2. Cyclic voltammograms of FBT-tDTS, DFBT-tDTS and RHO-tDTS in  $CH_2Cl_2$  solutions containing  $Bu_4NPF_6$  as the supporting electrolytes. The scan rate is 100 mV s<sup>-1</sup>.

	Pristine film			After solvent annealing		
	$\mu_{\rm h}  ({\rm cm}^2  {\rm V}^{-1}  {\rm s}^{-1})$	$\mu_{e} (cm^{2} V^{-1} s^{-1})$	$\mu_e$ : $\mu_h$	$     \mu_h (cm^2 V^{-1} s^{-1}) $	$\mu_{e} (cm^{2} V^{-1} s^{-1})$	$\mu_e:\mu_h$
FBT-tDTS	N/A	N/A	N/A	8.71×10 <sup>-5</sup>	2.86×10-4	3.28
DFBT-tDTS	N/A	N/A	N/A	3.46×10-5	1.98×10 <sup>-4</sup>	5.72
RHO-tDTS	1.03×10-5	7.37×10-5	7.15	1.08×10-4	2.95×10-4	2.73

Table S1. Hole and electron mobilities measured by SCLC.

3. X-ray diffraction (XRD) patterns.



Fig. S3 XRD patterns of FBT-tDTS film, FBT-tDTS:PC71BM (1:1) film without and with solvent annealing.



Fig. S4 XRD patterns of DFBT-tDTS film, DFBT-tDTS:PC71BM (1:1) film without and with solvent annealing.



Fig. S5 XRD patterns of RHO-tDTS film, RHO-tDTS:PC71BM (1:1) film without and with solvent annealing.

4. <sup>1</sup>H NMR spectra of compound **5**, FBT-tDTS, DFBT-tDTS and RHO-tDTS.



Fig.S6. <sup>1</sup>H NMR spectrum of Compound 5



Fig.S7. <sup>1</sup>H NMR spectrum of FBT-tDTS



Fig.S8. <sup>1</sup>H NMR spectrum of DFBT-tDTS



Fig.S9. <sup>1</sup>H NMR spectrum of RHO-tDTS

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