**Electronic Supplementary Information (ESI)** 

# A new multi-functional conjugated polymer towards high performance bulk heterojunction solar cells

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### Materials

All solvents and reagents were purchased from Aldrich, Alfa Aesar, and TCI. Catalysts used by coupling reactions were purchased from Umicore. The other materials were common commercial level and used as received. All solvents were further purified prior to use.

## **Synthesis**

Synthesis of (3,3'-dibromo-4,4'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylsilane)

(1). (3,3'-Dibromo-4,4'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylsilane) (1) was prepared according to literature procedure<sup>1</sup>. Yield: 9.8 g (90%). <sup>1</sup>H NMR (300 MHz,  $CD_2Cl_2)$ [ppm]  $\delta = 2.72$  (t, 4H), 1.64–1.60 (m, 4H), 1.47–1.30 (br, 36H), 0.92 (t, 6H), 0.41 (s, 18H).

*Synthesis of 3,5-didodecyl-4-phenyl-2,6-bis(trimethylsilyl)phospholo[3,2-b:4,5-b']dithiophene 4-oxide* (2). To solution of (3,3'-dibromo-4,4'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylsilane) (1) (9.8 g, 0.012 mol) in dry diethyl ether (280 mL), n-butyllithium in hexane (2.5 M) (9.7 mL, 0.024 mol) was added to dropwise at -78 °C. After complete addition, dichlorophenylphosphine (2.2 g, 0.012 mol) in dry diethyl ether (20 mL) was added dropwise slowly. The reaction mixture was stirred at room temperature for 2 h, and hydrogen peroxide (20 mL) in dichloromethane (100 mL) was added to the solution. The reaction mixture was stirred for 4 h. The organic layer was extracted with dichloromethane and the combined organic layer was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, obtained sticky oil. The crude product was taken to the next reaction without further purification.

*Synthesis of 2,6-dibromo-3,5-didodecyl-4-phenylphospholo[3,2-b:4,5-b']dithiophene 4-oxide* (3). To solution of crude 3,5-didodecyl-4-phenyl-2,6-bis(trimethylsilyl)phospholo[3,2-b:4,5-b']dithiophene 4-oxide (2) (4.6 g, 0.006 mol) in chloroform:acetic acid (200 mL, 1:1

[v/v]), n-bromosuccinimide (2.2 g, 0.012 mol) was added to one portion at room temperature, and the reaction mixture was stirred under dark for 6 h. The organic layer was extracted with dichloromethane, and the combined organic layer was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the resulting residue was purified by silica gel chromatography using hexane:ethyl acetate (10:1 [v/v]) as the eluent. The product was further purified by recrystallization from ethanol to give yellow powder. Yield: 1.2 g (25%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)[ppm] δ = 7.74 (m, 2H), 7.56 (m, 1H), 7.45 (m, 2H), 2.57 (m, 2H), 2.37 (m, 2H), 1.43–1.10 (br, 40H), 0.92–0.87 (m, 6H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)[ppm] δ = 144.26, 144.08, 143.20, 143.09, 137.98, 137.12, 133.00, 131.22, 131.13, 129.52, 129.42, 128.71, 111.92, 111.78, 32.32, 30.02, 29.82, 29.74, 29.69, 29.57, 29.04, 23.08, 14,49. MS (EI) m/z = 782 (M+). FT-IR (cm<sup>-1</sup>, neat): 3087, 3053, 3021, 2917, 2852, 1673, 1603, 1469, 1437, 1272, 1197, 1092, 787, 749, 713, 693.

*Synthesis of 2,7-bis(trimethylstannyl)-5,10-bis(4,5-didecylthiophen-2-yl)benzo[1,2-b:4,5-b']dithieno[3,2-b]thiophene* (4). 2,7-Bis(trimethylstannyl)-5,10-bis(4,5-didecylthiophen-2-yl)benzo[1,2-b:4,5-b']dithieno[3,2-b]thiophene (4) was prepared according to literature procedure<sup>2</sup>. Yield: 0.8 g (61%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)[ppm]  $\delta$  = 7.32 (s, 2H), 7.13 (s, 2H), 2.96–2.67 (m, 8H), 1.83–1.73 (m, 8 H), 1.49–1.31 (m, 56H), 0.92–0.88 (m, 12H), 0.50–0.31 (m, 18H).

*Polymerization of PDTP-DTBDT.* The polymer was synthesized via Stille coupling under a nitrogen. 2,6-Dibromo-3,5-didodecyl-4-phenylphospholo[3,2-b:4,5-b']dithiophene 4-oxide (3) (0.162 g 0.207 mmol) and 2,7-bis(trimethylstannyl)-5,10-bis(4,5-didecylthiophen-2yl)benzo[1,2-b:4,5-b']dithieno[3,2-b]thiophene (4) (0.280 g 0.207 mmol) were dissolved in chlorobenzene (7.5 mL). After Pd<sub>2</sub>(dba)<sub>3</sub> (0.004 g, 2 mol%) and P(*o*-tol)<sub>3</sub> (0.005 g, 8 mol%) were added to mixture, The reaction mixture was heated at 110°C and stirred for 48 h. 2-Bromothiophene (0.2 mL) was added with a small amount of catalysts for end capping, and the reaction mixture was further refluxed for 6 h. Tributyl-thiophen-2-yl-stannane (0.2 mL) was then added. After another 6 h, the reaction mixture was poured into methanol (200 mL) and filtered over a glass filter. The polymer was further purified by Soxhlet extraction with methanol, acetone, hexane, and toluene. The toluene solution containing the polymer was reprecipitated in methanol and filtered out. Yield: 0.22 g (65%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)[ppm]  $\delta$  = 7.85 (br, 2H), 7.57 (br, 1H), 7.49 (br, 2H), 7.24 (br, 2H), 7.09 (br, 2H), 2.88 (br, 4H), 2.73 (br, 2H), 2.65 (br, 4H), 2.54 (br, 2H), 1.77 (br, 4H), 1.70 (br, 4H), 1.48–1.03 (br, 96H), 0.88 (br, 18H). FT-IR (cm<sup>-1</sup>, neat): 3074, 3055, 2920, 2848, 1462, 1387, 1327, 1283, 1209, 1109, 996, 958, 806, 750, 713, 689.

## **General Instruments**

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded using a BrukerAM-200 spectrometer. <sup>13</sup>C-NMR spectra were recorded with a Bruker Advance-300 spectrometer. HRMS (EI) spectra were performed on a high resolution GC mass spectrometer with LabRAM HR800 UV. Mass spectrum was determined using a high-resolution 4800 Tof/Tof mass spectrometer with Voyager DE-STR. The molecular weight and polydispersity of the copolymer were determined by gel permeation chromatography (GPC) using a polystyrene standard. GPC was conducted using water as the moving phase in a high-pressure GPC assembly using a Model M515 pump with u-Styragel columns of HR4, HR4E, HR5E, which yielded 500 and 100 Å resolutions. Thermal gravimetric analysis (TGA) were performed on a TA TGA 2100 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 10 °C/min. UV-Vis absorption spectra were determined using a Carry 5000 UV-vis-near-IR double beam spectrophotometer. Cyclic voltammetry (CV) was performed using a PowerLab/AD instrument model system in 0.1 M solution of tetrabutylammonium hexafluorophospate (Bu<sub>4</sub>NPF<sub>6</sub>) in anhydrous acetonitrile as supporting electrolyte at a scan rate of 50 mVs<sup>-1</sup>. A

glassy carbon disk (~0.05 cm<sup>2</sup>) coated with a thin polymer film, an Ag/AgNO<sub>3</sub> electrode, and a platinum wire were used as working electrode, reference electrode, and counter electrode, respectively. Density functional theory (DFT) calculations were carried out at the B3LYP/6-31G\* level of theory using the Spartan 08 computational programs. The atomic force microscope (AFM) (Multimode IIIa, Digital Instruments) was operated in tapping mode to obtain surface images (surface area:  $5 \times 5 \ \mu m^2$ ) of the polymer:PC<sub>71</sub>BM blend films without and with CN additive under ambient conditions. The X-ray diffraction (XRD) was performed at the 5A beamline (wavelength = 1.071 Å) at the Pohang Accelerator Laboratory (PAL) in Korea. Samples for the X-ray measurements were prepared by spin-coating the polymer:PC<sub>71</sub>BM solutions without or with CN additive onto PEDOT:PSS spin-coated ITO glass.

#### Fabrication and Characterizations of Solar cell devices

The devices were fabricated with a conventional structure of glass/ITO/PEDOT:PSS/active layer (**PDTP-DTBDT**:PC<sub>71</sub>BM)/Ca/Al using a solution process. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 20 min each and subsequently dried by a nitrogen blow. A thin layer (~40 nm) of PEDOT:PSS (Clevios P VP AI 4083, filtered at 0.45µm PVDF) was spin-coated at 4000 rpm onto the ITO surface. After being baked at 120 °C for 20 min, the substrates were transferred into a nitrogen-filled glovebox. Subsequently, the active layer was spin-coated from donor-acceptor blend solutions with different ratios, total concentrations, active layer thickness or additive 1-chloronaphthalene (1 vol%). Finally, a 2 nm Ca and 80 nm Al layer were deposited on the active layer under high vacuum (2 × 10<sup>-6</sup> torr). The effective area of each cell was 9 mm<sup>2</sup> defined by the mask. The current density-voltage (*J-V*) characteristics of photovoltaic devices were measured under ambient conditions,

using a Keithley Model 2400 source-measurement unit. An Oriel xenon lamp (450 W) with an AM 1.5 G filter was used as the solar simulator. The light intensity was calibrated to 100 mW/cm<sup>2</sup>, using a calibrated silicon cell with a KG5 filter, which is traced to the National Renewable Energy Laboratory (LREL). The external quantum efficiency (EQE) spectra were obtained by using a photomodulation spectroscopic set-up (model Merlin, Oriel), a calibrated Si UV detector, and a SR570 low noise current amplifier.

#### Charge carrier mobility measurement

The hole only devices were fabricated with configuration of ITO/PEDOT:PSS/**PDTP-DTBDT**:PC<sub>71</sub>BM/Au. The Au layer was deposited under a low speed (1 /s) to avoid the penetration of Au atoms into the active layer. The active layers were spin-coated without or with additive CN (1 vol%). Mobilities were extracted by fitting the current-voltage curves using the Mott-Curney relationship (space charge limited current).

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{L^3}$$

Where *J* is the current density, *L* is the film thickness of active layer,  $\mu_h$  is the hole mobility,  $\varepsilon_r$  is the relative dielectric constant of the transport medium,  $\varepsilon_0$  is the permittivity of free space, *V* is the internal voltage in the device and  $V = V_{appl} - V_r - V_{bi}$ , where  $V_{appl}$  is the applied voltage to the device,  $V_r$  is the voltage drop due to contact resistance and series resistance across the electrodes, and  $V_{bi}$  is the built-in voltage due to the relative work function difference of the two electrodes. The  $V_{bi}$  can be determined from the transition between the ohmic region and the SCLC region.

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2 H. J. Yun, Y. J. Lee, S. J. Yoo, D. S. Chung, Y. H. Kim and S. K. Kwon, *Chem. Eur. J.* 2013, **19**, 13242.



Scheme S1. Synthetic route of PDTP-DTBDT



**Fig. S1.** Dipole structural calculations for a dithienophosphole oxide unit (a) and a DTP-DTBDT unit (b). The axes (green lines) shows the center of mass axes in the X, Y and Z directions and the vector of the dipole exhibits the direction of electron flow in these directions.



Fig. S2. HOMO and LUMO wave functions of the dimer models of PDTP-DTBDT.



**Fig. S3**. *J-V* curves for **PDTP-DTBDT**:PC<sub>71</sub>BM devices at various ratios in chlorobenzene under an illumination of AM 1.5G, 100mW/cm<sup>2</sup>.



Fig. S4. *J-V* characteristics of the PDTP-DTBDT based solar cells with different solvents (1,2-dichlorobenzne (DCB), chlorobenzene (CB) or chloroform (CF)) (PDTP-DTBDT:PC<sub>71</sub>BM = 1:4 w/w).



Fig. S5. Photocurrent-voltage (*J-V*) curves (AM 1.5G, 100mW cm<sup>-2</sup>) of the PDTP-DTBDT:PC<sub>71</sub>BM (1:4 w/w) blend photovoltaic cells as a function of the active layer thickness.



Fig. S6. Out-of plane (a) and in-plane (b) X-ray profiles extracted from 2D-GIXD.



**Fig. S7**. Current-voltage (*J-V*) characteristics of hole only devices for pure **PDTP-DTBDT** and **PDTP-DTBDT**:  $PC_{71}BM$  blends in the dark.

| Polymer : PCBM                          | Blend<br>ratios | Voc<br>(V) | Jsc (mA / cm <sup>2</sup> ) | FF<br>(%) | PCE <sup>max</sup><br>(%) | PCE <sup>avg</sup><br>(%) |
|---|-----------------|------------|-----------------------------|-----------|---------------------------|---------------------------|
| <b>PDTP-DTBDT</b> : PC <sub>71</sub> BM | 1:1             | 0.72       | 3.0                         | 39.7      | 0.87                      | 0.62                      |
|   | 1:2             | 0.78       | 5.1                         | 42.0      | 1.67                      | 1.48                      |
|   | 1:3             | 0.79       | 6.7                         | 41.9      | 2.21                      | 2.10                      |
|   | 1:4             | 0.79       | 8.8                         | 45.1      | 3.14                      | 2.89                      |

**Table S1**. Summary of device parameters at various **PDTP-DTBDT**/PC<sub>71</sub>BM compositions blended in chlorobenzene.

PCE<sup>avg</sup> : data obtained from 8 devices.

**Table S2**. Photovoltaic data of the **PDTP-DTBDT**/PC71BM (1:4 w/w) at various conditionsbased on several solvents.

| Polymer : PCBM                          | Thickness<br>(nm) | Voc<br>(V) | Jsc (mA / cm <sup>2</sup> ) | FF<br>(%) | PCE <sup>max</sup><br>(%) | PCE <sup>avg</sup><br>(%) |
|---|-------------------|------------|-----------------------------|-----------|---------------------------|---------------------------|
| <b>PDTP-DTBDT</b> : PC <sub>71</sub> BM | DCB               | 0.81       | 11.2                        | 52.0      | 4.71                      | 4.43                      |
|   | CB                | 0.79       | 8.8                         | 45.1      | 3.14                      | 2.89                      |
|   | CF                | 0.73       | 7.4                         | 30.6      | 1.64                      | 1.43                      |

PCE<sup>avg</sup> : data obtained from 8 devices.

1,2-dichlorobenzne (DCB), chlorobenzene (CB) or chloroform (CF)

**Table S3**. Summary of the photovoltaic properties of **PDTP-DTBDT**:  $PC_{71}BM$  BHJ solarcells as a function of active layer thickness.

| Polymer : PCBM                          | Thickness<br>(nm) | Voc<br>(V) | Jsc (mA / cm <sup>2</sup> ) | FF<br>(%) | PCE <sup>max</sup><br>(%) | PCE <sup>avg</sup><br>(%) |
|---|-------------------|------------|-----------------------------|-----------|---------------------------|---------------------------|
| <b>PDTP-DTBDT</b> : PC <sub>71</sub> BM | 82                | 0.79       | 8.3                         | 49.9      | 3.30                      | 3.14                      |
|   | 95                | 0.82       | 13.4                        | 55.1      | 6.05                      | 5.92                      |
|   | 120               | 0.81       | 11.2                        | 52.0      | 4.71                      | 4.43                      |
|   | 138               | 0.81       | 7.5                         | 48.8      | 3.00                      | 2.89                      |

PCE<sup>avg</sup> : data obtained from 8 devices.