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High Molecular Weight Triisopropylsilylethynyl (TIPS)-benzodithiophene and Diketopyrrolopyrrole-Based Copolymer for High Performance Organic Photovoltaic Cells

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1. Experimental

1.1 Materials

Reagents were purchased from Aldrich, Alfa Aesar, or TCI Korea, and used without further purification. [6,6]-Phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) was purchased from Electronic Materials (EM) Index Co., Ltd. Solvents were dried and purified by fractional distillation over sodium/benzophenone and handled in a moisture-free atmosphere. Column chromatography was performed using silica gel (Merck, Kieselgel 60 63-200 MYM SC). 4,8-Dihydrobenzo[1,2-*b*:4,5-*b′*]dithiophen-4,8-dione and 3,6-bis-(5-bromo-thiophen-2-yl)-*N*,*N′*-bis(2-octyl-1-dodecyl)-1,4-dioxo-pyrrolo[3,4-*c*]pyrrole (DPP) were synthesized similarly to methods described in previous reports.[1]

1.2 Measurements

^1H- and ^{13}C NMR spectra were recorded using a Varian Mercury Plus 300 MHz spectrometer, and the chemical shifts were recorded in units of ppm with chloroform as an internal standard (δ 7.26 and 76.994 ppm). Elemental analysis was performed using a Vario Micro Cube at the Korea Basic Science Institute (Busan, Korea). Absorption spectra were obtained using a JASCO JP/V-570 spectrometer. The molecular weights of the polymers were determined via gel permeation chromatography (GPC) analysis relative to a polystyrene standard using a Waters high-pressure GPC assembly (model M590). Thermal analyses were performed on a Mettler Toledo TGA/SDTA 851^e under N_2 atmosphere with a heating and cooling rate of 10°C·min^{-1}. Cyclic voltammetry (CV) was performed on a CH Instruments Electrochemical Analyzer, to investigate the redox behavior of the polymer and determine its HOMO and LUMO energy levels. CV was carried out under Ar atmosphere at room temperature in a solution of tetrabutylammonium tetrafluoroborate ($TBABF_4$, 0.10 M) in acetonitrile at a scan rate of 50 mV·s^{-1}. A platinum plate, platinum wire, and $Ag/AgNO_3$ electrode were used as the working, counter, and reference electrodes, respectively. The HOMO energy level was determined by measuring the oxidation onsets (E_{ox}) of the polymer films. To obtain the oxidation potentials of the polymer films, the reference electrode was calibrated against ferrocene/ferrocenium (Fc/Fc^+), which has a redox potential with an absolute energy level of −4.80 eV in vacuum. The potential of this external standard under the experimental conditions was 0.092 eV. Accordingly, the HOMO energy values (E_{HOMO}) were calculated using the following equation: $E_{HOMO} = -(E_{ox}^{onset} + 4.70)$ eV, where E_{ox}^{onset} is the onset oxidation potential versus Ag/Ag^+. The synchrotron-based 2D GXID experiments were performed on various semiconductor films at the 3C beamline of the Pohang Accelerator Laboratory (South Korea). The incidence angle (0.13°) was chosen to allow for complete penetration of the X-rays into the polymer film. A thin layer (40–50 nm) of PEDOT:PSS was spin-coated onto Si substrates, with the polymer thin films subsequently spin-coated on top.

1.3 Synthesis of monomers and polymers

1.3.1 Synthesis of 4,8-bis(triisopropylsilylethynyl)-benzo[1,2-b:4,5-b']dithiophene.

Isopropylmagnesium chloride (2.0 M in THF, 5.5 mL, 11.0 mmol) was added dropwise to a solution of (triisopropylsilyl)acetylene (1.98 g, 10.86 mmol) in dry THF (10 mL). The solution was stirred at 60°C for 2 h and cooled to room temperature. Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (0.6 g, 2.72 mmol) was added to the solution, and the mixture was stirred at 60°C for 8 h. After cooling to room temperature, $SnCl_2 \cdot 2H_2O$ (2.0 g, 8.86 mmol) and 10% aq. HCl solution (2 mL) were added carefully to the solution. The reaction mixture was refluxed at 60°C for 5 h. After the reaction, the solution was poured into water (300 mL), and dichloromethane (300 mL) was added. The organic layer was washed with water (300 mL × 3) and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel using hexane as the eluent to afford a greenish solid. Yield: 0.86 g (57%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.61 (d, 2H), 7.56 (d, 2H), 1.23 (m, 42H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 140.86, 138.51, 128.28, 123.14, 112.18, 102.63, 101.62, 18.78, 11.33; Anal. calcd. for $C_{36}H_{46}S_2Si_2$: C 69.75, H 8.41, S 11.64; found: C 69.71, H 8.40, S 11.63.

1.3.2 Synthesis of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-4,8-bis(triisopropylsilylethynyl) -benzo[1,2-b:4,5-b']dithiophene.

A *n*-BuLi solution in hexanes (2.25 mL, 2.0 M, 4.5 mmol) was added at −70°C to a solution of 4,8-bis(triisopropylsilylethynyl)-benzo[1,2-*b*:4,5-*b*′]dithiophene (1 g, 1.8 mmol) in dry THF (50 mL). The mixture was stirred for 30 min at −70°C, and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yloxy)propan-1-ylium (0.9 mL, 4.5 mmol) was then added at −70°C. This mixture was allowed to reach room temperature overnight. The resulting mixture was extracted with methylene chloride and brine, and then dried with anhydrous $MgSO_4$. After filtration, the solvent was evaporated to provide a product yield of 56%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.69 (s, 2H), 1.35 (s, 24H), 1.23 (m, 42H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 144.68, 143.51, 139.10, 110.36, 103.33, 100.64, 84.30, 19.06, 11.39; Anal. calcd. for $C_{44}H_{68}B_2O_4S_2Si_2$: C 65.82, H 8.54, S 7.99; found: C 65.70, H 8.41, S 7.88.

1.3.3 Synthesis of poly[4,8-bis(triisopropylsilylethynyl)-benzo[1,2-b:4,5-b']dithiophene-alt-3,6-bis-(thiophen-2-yl)-N,N'-bis(2-octyl-1-dodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole] (PTIPSBDT-DPP).

To a Schlenk tube were added 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-4,8-bis(triisopropylsilylethynyl)-benzo[1,2-*b*:4,5-*b*′]dithiophene (0.400 g, 0.49 mmol), 3,6-bis-(5-bromo-thiophen-2-yl)-*N*,*N*′-bis(2-octyl-1-dodecyl)-1,4-dioxo-pyrrolo[3,4-*c*]pyrrole (0.507 g, 0.49 mmol), $Pd(PPh_3)_4$ (0.009 g, 0.004 mmol), and Bu_4NBr (0.012 g, 0.004 mmol). The tube was the n purged with N_2. Toluene (N_2 bubbled, 10 mL) was added to the Schlenk tube and the resulting solution was stirred at 110°C for 5 min. A solution of Et_4NOH (20% w/w in water, N_2 bubbled, 4 mL) was added to the tube at 110°C. After the heterogeneous mixture was stirred for 24 h at 90°C, a solution of phenylboronic acid in toluene (N_2 bubbled, 4 mL) was added. The reaction was stirred for 1 h at 110°C. Bromobenzene (the end-capper) was added to the mixture. After the reaction mixture was stirred for a further 2 h, it was allowed to cool to ambient temperature and dropped into MeOH (300 mL) with stirring. The precipitate was filtered, washed with MeOH, dried under reduced pressure, and dissolved in $CHCl_3$ (150 mL). The solution was then passed through a short plug of silica gel, flushing with copious $CHCl_3$, and concentrated under reduced pressure. The concentrated solution was again dropped into MeOH (300 mL) with stirring. The precipitated polymer was filtered, washed in a Soxhlet extraction apparatus with acetone for 48 h, and dried under reduced pressure to give PTIPSBDT-DPP as a dark green solid.

Table S1. Average molecular weights and thermal properties of the synthesized polymer.

Polymer	M_n [a] (g·mol^{-1})	M_w [a] (g·mol^{-1})	PDI[a]	T_d [b] (°C)	T_c (°C)
PTIPSBDT-DPP	76,000	190,000	2.5	400	201

[a] M_n, M_w, and PDI of the polymer were determined by gel permeation chromatography using polystyrene standards in $CHCl_3$. [b] Temperature at 5% weight loss with a heating rate of 10°C·min^{-1} under nitrogen.

Table S2. Electrical performance of PTIPSBDT-DPP OFETs.

Gate Dielectric	Casting method	T_A (for 10 min)	μ_{FET} (cm^{2}V^{-1}s^{-1})	I_{on}/I_{off}
untreated SiO_2	Spin-cast	-	0.008± 0.005	$<10^5$
PS brush-SiO_2	Spin-cast	-	0.06 ± 0.010	$>10^5$
		100°C	0.12 ± 0.020	$>10^6$
		120°C	0.05 ± 0.005	$>10^6$
		150°C	0.02 ± 0.007	$>10^5$
		200°C	0.02 ± 0.005	$>10^5$
	Drop-cast	100°C	0.05 ± 0.010	$>10^5$

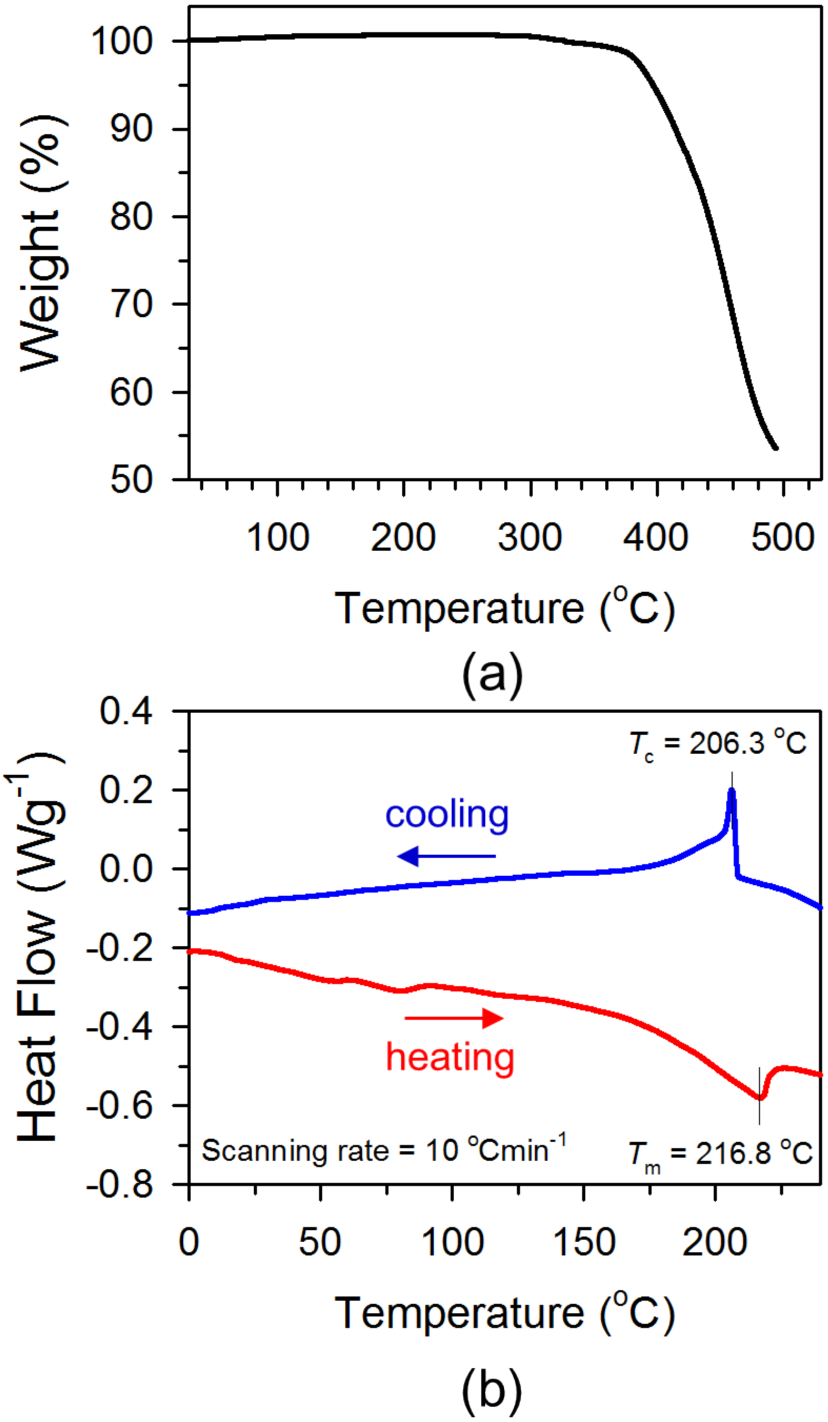

Fig S1. (a) TGA plot of PTIPSBDT-DPP with a heating rate of 10°C·min^{-1} under N_2 and (b) DSC curves of PTIPSBDT-DPP under N_2 (heating and cooling rates: 10°C·min^{-1}).

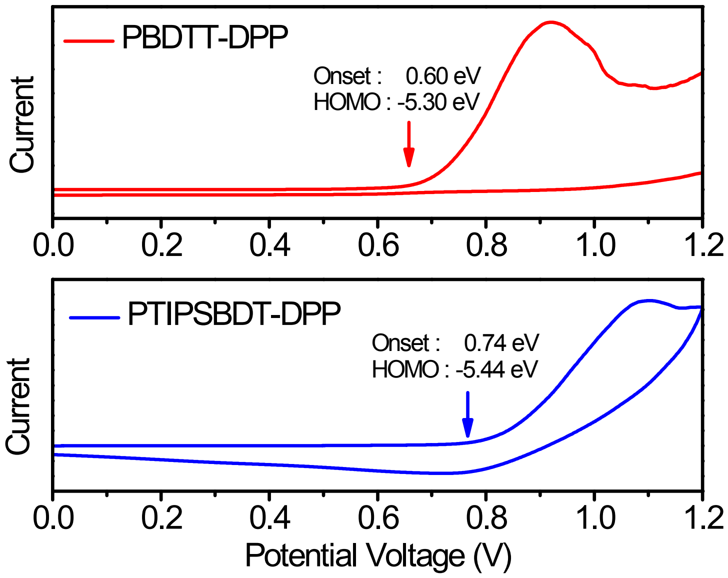

Fig S2. Cyclic voltammograms of PBDTT-DPP (above) and PTIPSBDT-DPP (below) films measured in acetonitrile containing $TBABF_4$ (0.10 M) with a scan rate of 50 mV·s^{-1}.

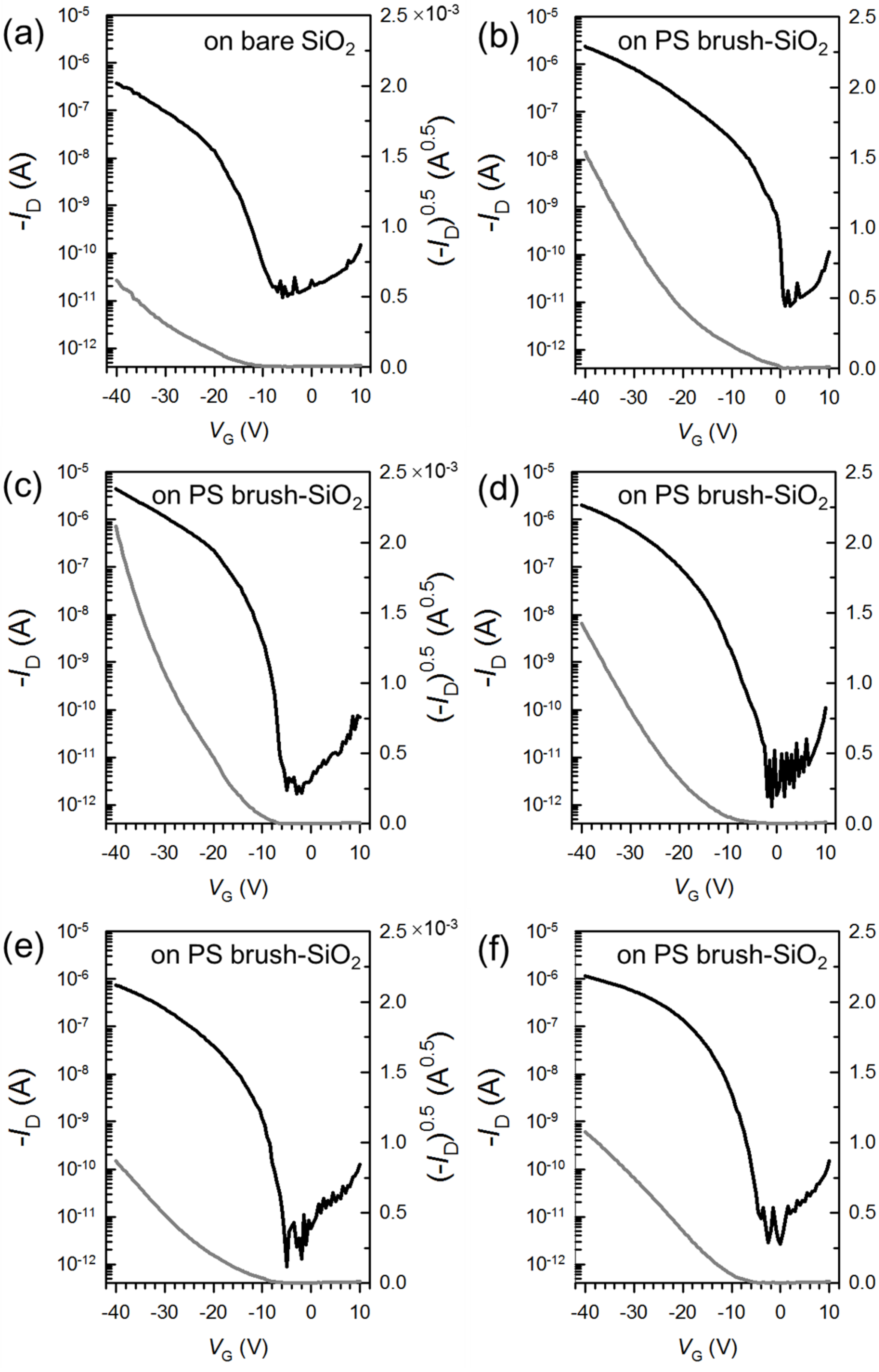

Fig S3. I_D-V_G transfer curves of PTIPSBDT-DPP OTFTs on (a) bare SiO_2 and (b–f) PS brush-SiO_2 dielectrics, before and after annealing at different T_As for 10 min: (a, b) as-spun; (c) 100°C; (d) 120°C; (e) 150°C; and (f) 200°C.

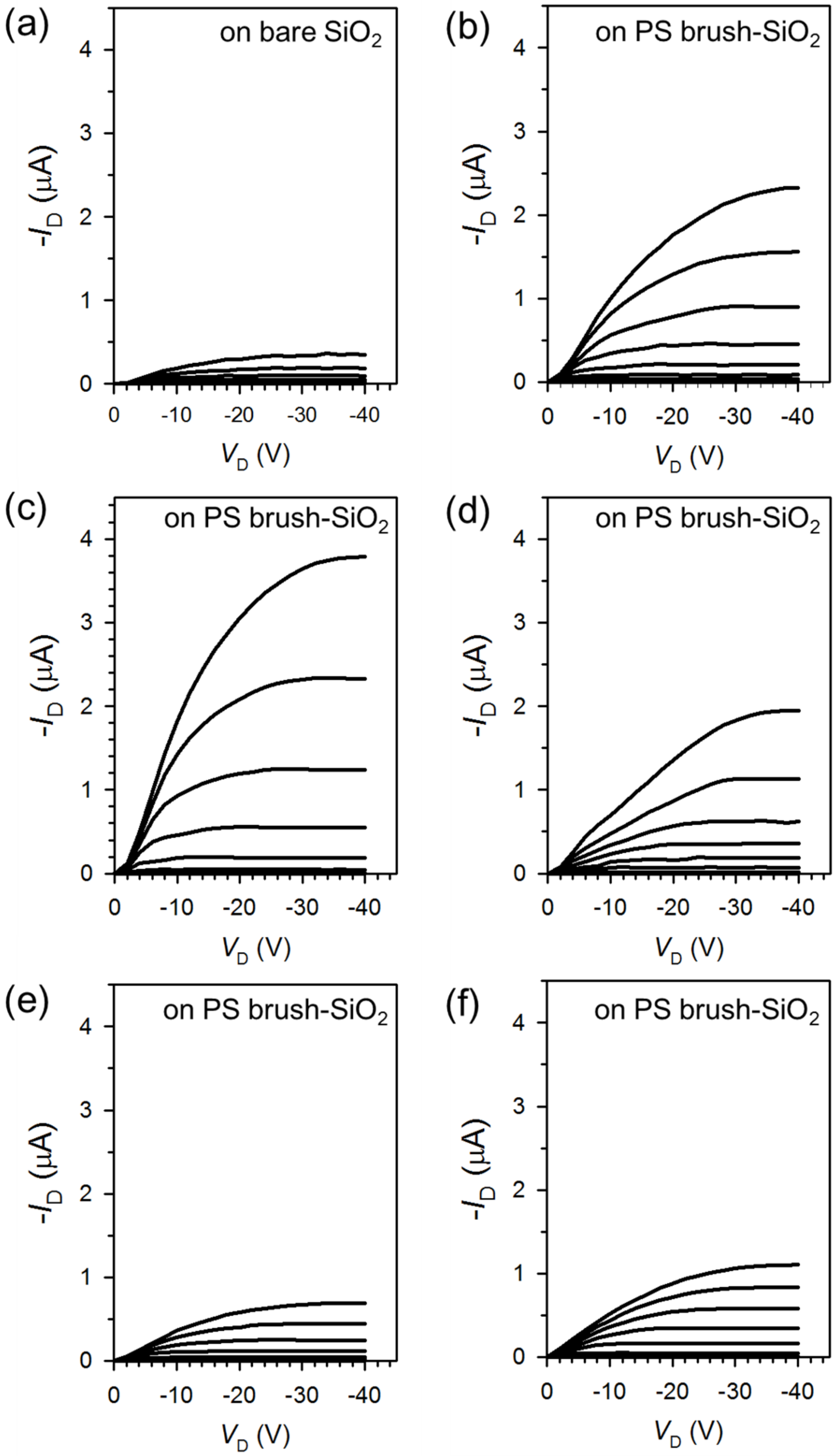

Fig S4. Output curves of PTIPSBDT-DPP OTFTs on (a) bare SiO_2 and (b–f) PS brush-SiO_2 dielectrics, before and after annealing at different T_As for 10 min: (a, b) as-spun; (c) 100°C; (d) 120°C; (e) 150°C; and (f) 200°C.

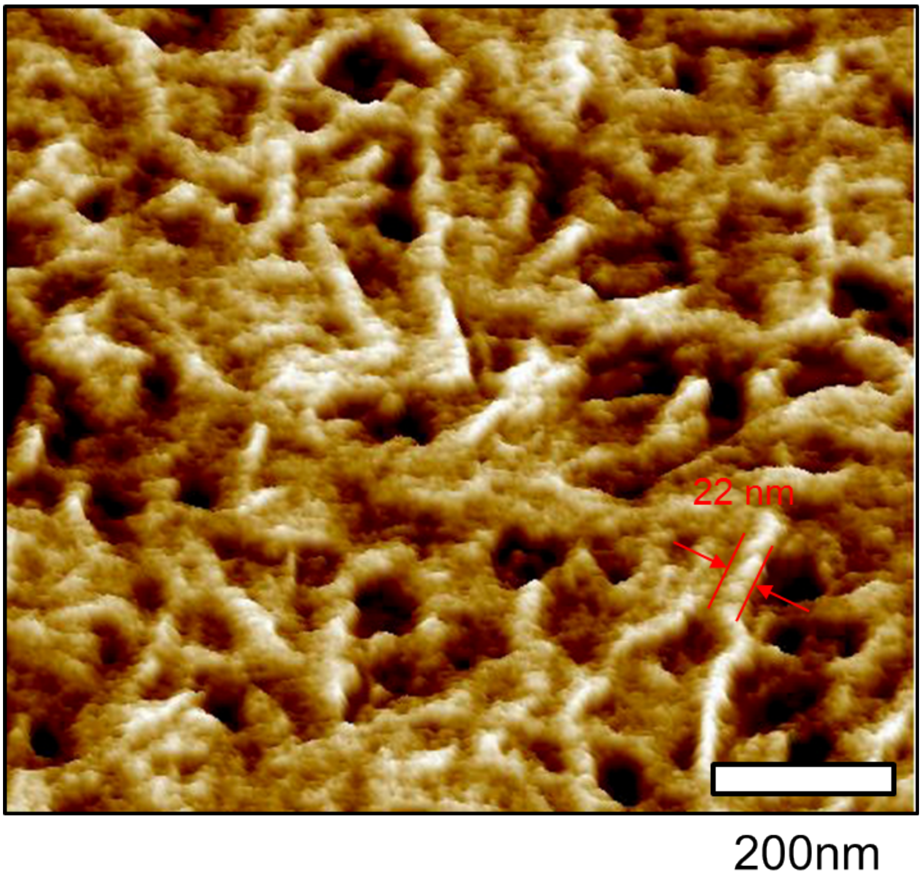

Fig S5. AFM morphology of DPP-based film spun-cast on PS-grafted SiO_2 dielectric from 0.5 vol% chloroform solution and subsequently annealed at 100°C for 100 min.

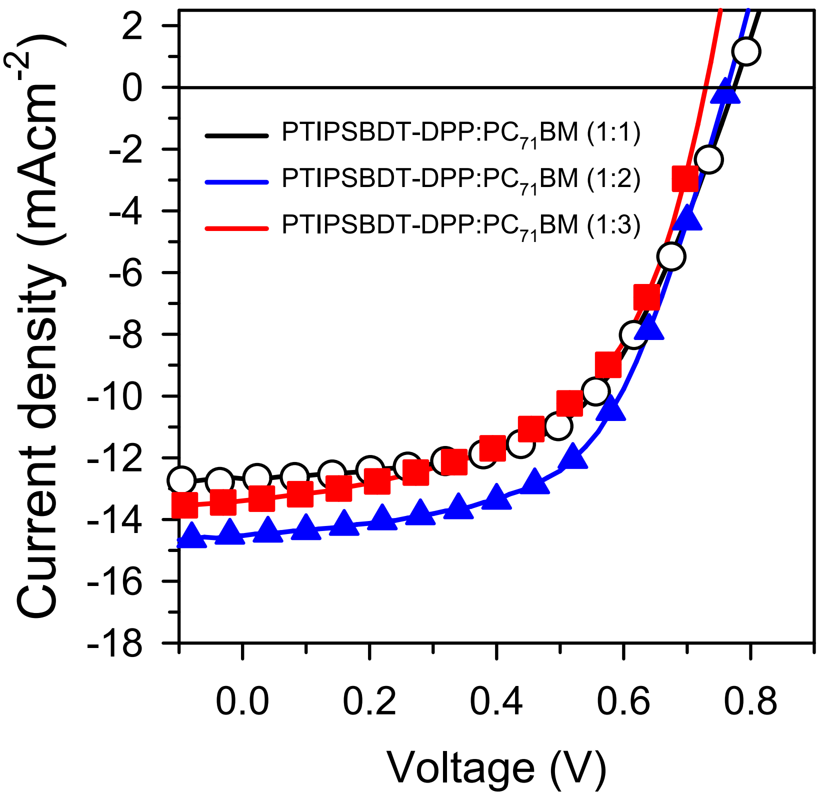

Fig S6. *J–V* curves of OPVs containing PTIPSBDT-DPP:PC$_{71}$BM films with different blending ratios (1:1, 1:2, and 1:3) spun-cast from single CB solvent.

Table S3. Photovoltaic properties of OPVs containing PTIPSBDT-DPP:PC$_{71}$BM films with different blending ratios (1:1, 1:2, and 1:3) spun-cast from single CB solvent.

PTIPSBDT-DPP:PC$_{71}$BM ratio	V_{oc} [V]	J_{sc} [mA·cm^{-2}]	*FF*	PCE [%]
1:1	0.77	12.68	0.56	5.52
1:2	0.76	14.52	0.57	6.29
1:3	0.73	13.35	0.55	5.32

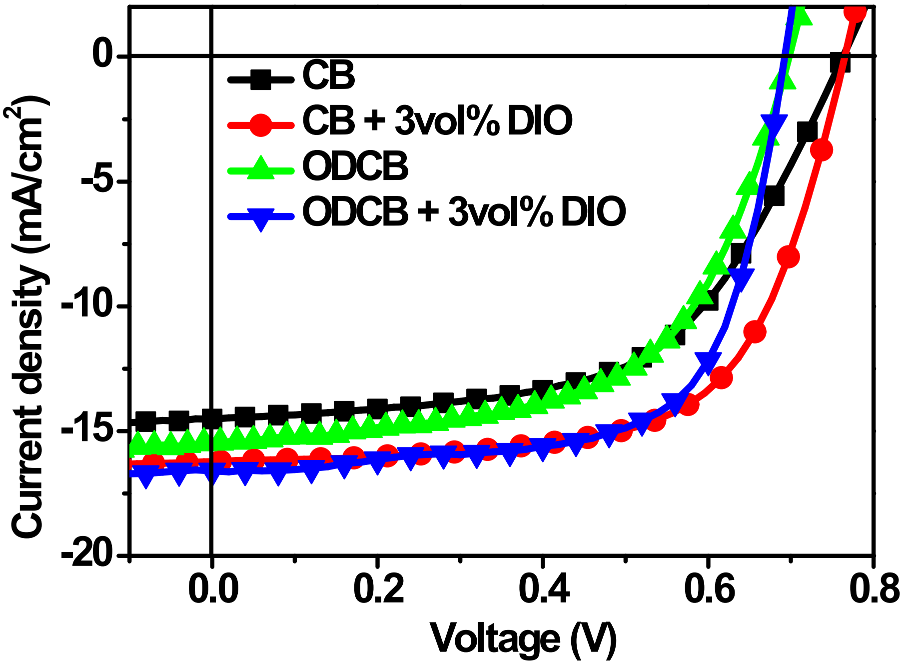

Fig S7. *J–V* curves of ITO/PEDOT:PSS/PTIPSBDT-DPP:PC$_{71}$BM (1:2)/Ca/Al configuration with different solvents under AM 1.5G illumination at 100 mW cm^{-2}.

Table S4. Comparison of the photovoltaic properties of OPVs based on PTIPSBDT-DPP:PC$_{71}$BM (1:2) with different solvents under AM 1.5G illumination at 100 mW cm^{-2}

Solvent	V_{oc} [V]	J_{sc} [mA·cm^{-2}]	*FF*	PCE [%]
CB	0.76	14.52	0.57	6.29
CB + DIO	0.76	16.21	0.65	8.00
ODCB (o-dichlorobenzene)	0.70	15.51	0.59	6.43
ODCB + DIO	0.69	16.21	0.68	7.62

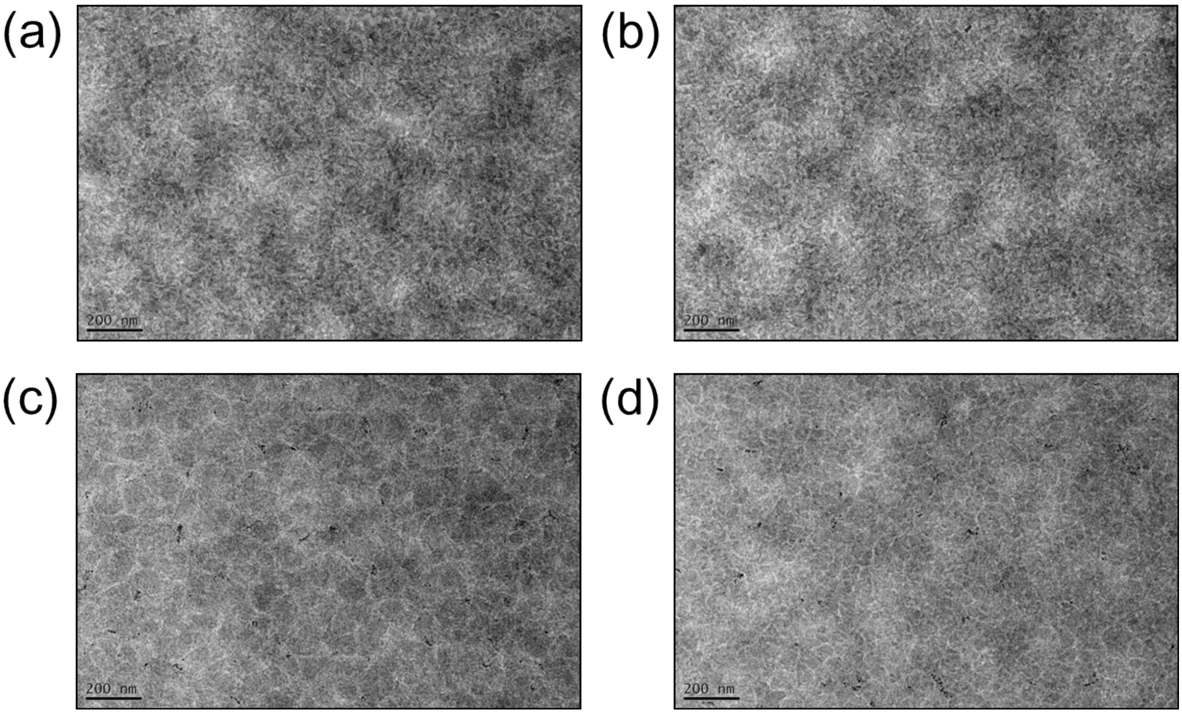

Fig S8. TEM micrographs of the PTIPSBDT-DPP:$PC_{71}BM$ (1:2, w/w) blend films spun-cast from (a) single CB solvent and (b–d) the binary CB/DIO solvents with different DIO loadings: (b) 1 vol%; (c) 3 vol%; and (d) 5 vol% DIO.

TEM

Note that $PC_{71}BM$, which contains fullerene derivatives with high electron density, can absorb many passing electrons in comparison to PTIPSBDT-DPP. As a result, the darker and brighter regions in the TEM images indicate $PC_{71}BM$- and PTIPSBDT-DPP-rich aggregates, respectively.

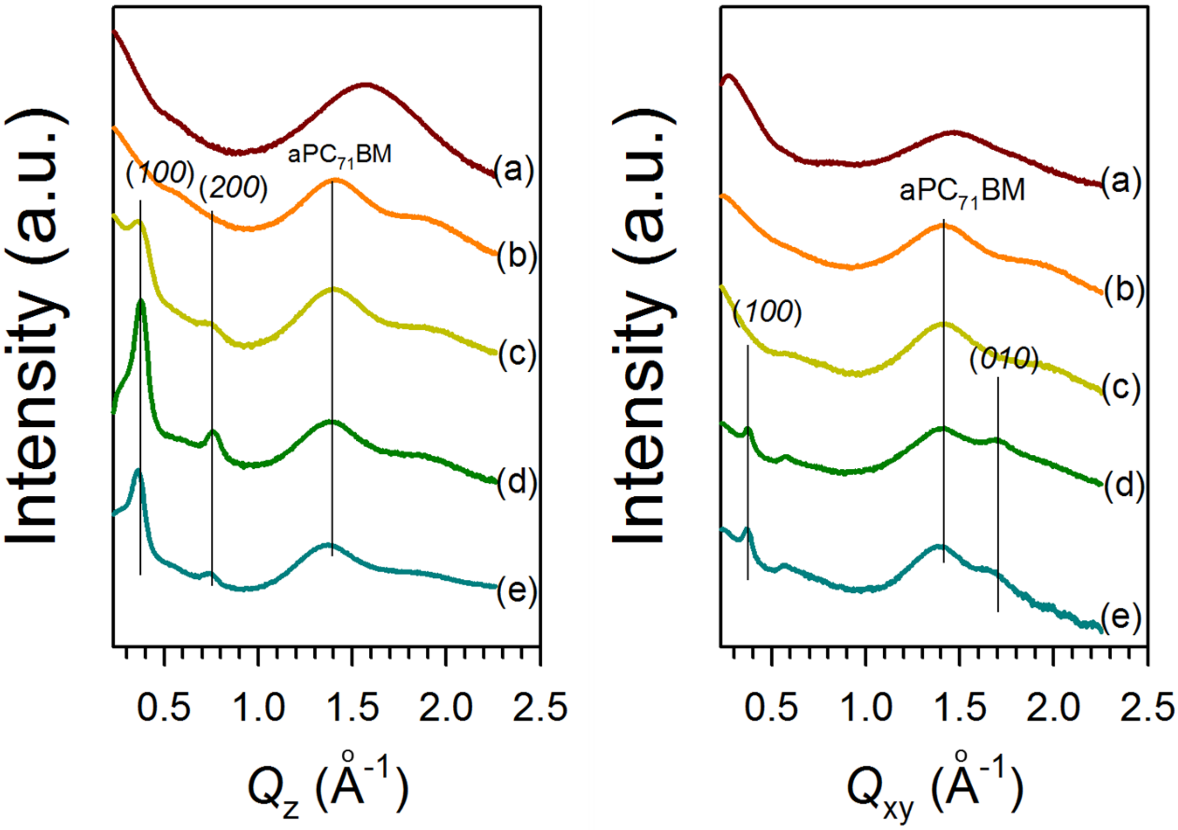

Fig S9. 1D out-of-plane (left) and in-plane (right) X-ray profiles extracted from the 2D GIXD patterns (see **Figs. 4A–4F**): (a, f) spun-cast PTIPSBDT-DPP and (b–e) PTIPSBDT-DPP:$PC_{71}BM$ (1:2 w/w) blend films with different DIO loadings: (b) 0 vol%; (c) 1 vol%; (d) 3 vol%; and (e) 5 vol% DIO.

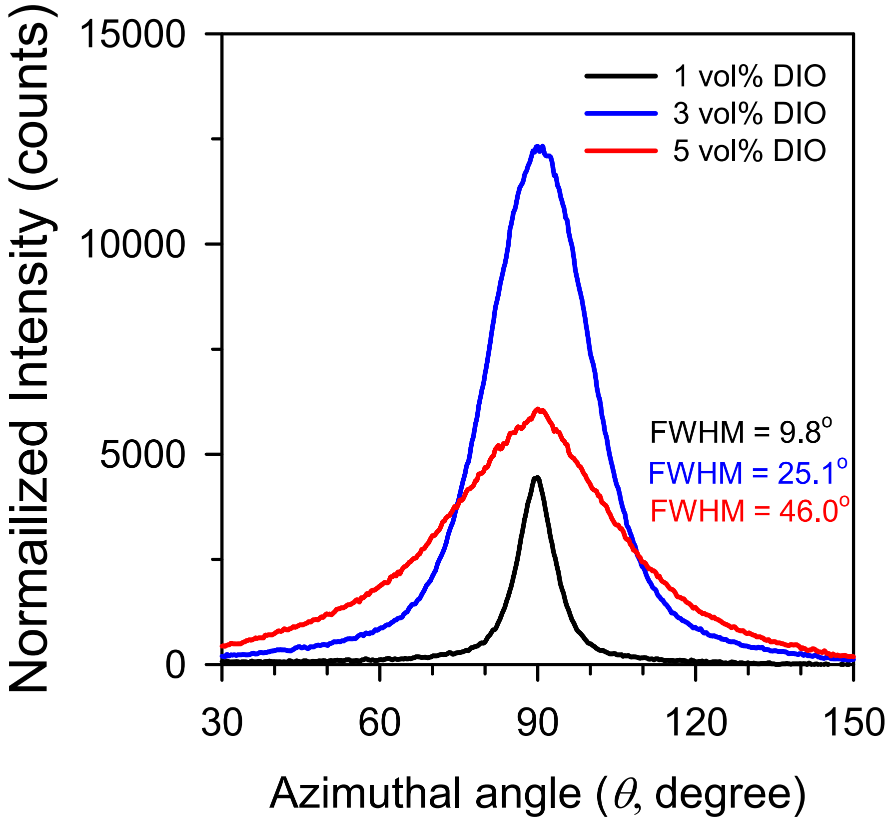

Fig S10. Azimuthal angle scans (at $Q^{(100)}$) of PTIPSBDT-DPP:$PC_{71}BM$ (1/2 w/w) spun-cast from the CB/DIO binary solvents with different DIO loadings.

[1] J. Lee, S. Cho, J. H. Seo, P. Anant, J. Jacob, C. Yang, *J. Mater. Chem.,* 2012, **22**, 1504–1510.