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Electronic Supplementary Information (ESI)

Fused polycyclic lactam-based π-conjugated polymers for efficient nonfullerene organic solar cells

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Instrumentation and Measurements

NMR spectra were recorded on an Avance III 400 spectrometer (Bruker) using tetramethylsilane (δ = 0.00) as an internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on an Autoflex III spectrometer (Bruker Daltonics) using dithranol as a matrix. Elemental analysis was carried out using an MT-5 CHN corder (Yanaco). The molecular weights of polymers were determined using gel permeation chromatography (GPC) performed on an HLC-8420GPC (Tosoh), with chloroform as an eluent and polystyrene as a standard. Film thickness was measured using a Surfcorder ET150 profilometer (Kosaka Laboratory). UV−vis absorption spectra were measured with a V-670 spectrometer (Jasco). The HOMO energy levels were determined using an AC-2 ultraviolet photoelectron yield spectrometer (Riken Keiki). The LUMO energy levels were estimated by subtracting the optical energy gap (E_g) from the measured HOMO energy levels. Grazing-incidence X-ray diffraction (GIXD) measurements were carried out at the SPring-8 synchrotron radiation facility using the BL49B2 and BL05XU beamlines. The samples were prepared on Si substrates in the same way as OPV devices and then irradiated with an X-ray energy of 12.39 keV (λ = 1.0 Å) at a fixed incidence angle of 0.1°. Transmission electron microscopy (TEM) images were obtained using a JEM-2010 transmission electron microscope (JEOL) at an accelerating voltage of 120 kV. The spin-coated thin films on mica were peeled from the substrates by soaking in water and then transferred onto copper grids for the TEM observations. Geometry optimization was carried out using the B3LYP functional with the 6-31G(d,p) basis set. The lowest excited singlet states were computed using the optimized structures with time-dependent DFT (TD-DFT) at the same level.

Device Fabrication and Evaluation

Prepatterned ITO-coated grass substrates were cleaned sequentially by sonicating in detergent solution, deionized water, acetone, and isopropyl alcohol for 10 min each, and then subjected to UV/ozone treatment for 30 min. A thin layer (~30 nm) of ZnO was prepared by spin-coating (at 5000 rpm for 60 s) a precursor solution of zinc acetate (1.00 g) and ethanolamine (0.28 g) in 2-methoxyethanol (10 mL) through a 0.20 µm polyethylene membrane filter, followed by baking at 200 °C for 10 min under air. The active layer was then deposited by spin-coating from a chloroform (or chlorobenzene) solution containing a polymer donor and IT-4F acceptor after passing through a 0.45 µm poly(tetrafluoroethylene) membrane filter. The samples were then loaded into an E-200 vacuum evaporation system (ALS Technology). Finally, 10-nm-thick MoO_3 and 100-nm-thick Ag layers were sequentially vacuum-deposited on top of the photoactive layer under high vacuum ($<5.0 \times 10^{-4}$ Pa) through a shadow mask, defining an active area of 0.04 cm^2 for each device. The current density–voltage (J–V) characteristics and EQE spectra of OSCs were measured with a computer-controlled Keithley 2400 source measure unit in air, under simulated AM 1.5G solar illumination at 100 mW cm^{-2} (1 sun) conditions, using a Xe lamp-based SRO-25GD solar simulator and IPCE measurement system (Bunko Keiki). The light intensity was calibrated using a certified silicon photovoltaic reference cell.

Synthesis and Characterization

All chemical reactions were performed under a dry N_2 atmosphere using anhydrous solvents unless otherwise noted.

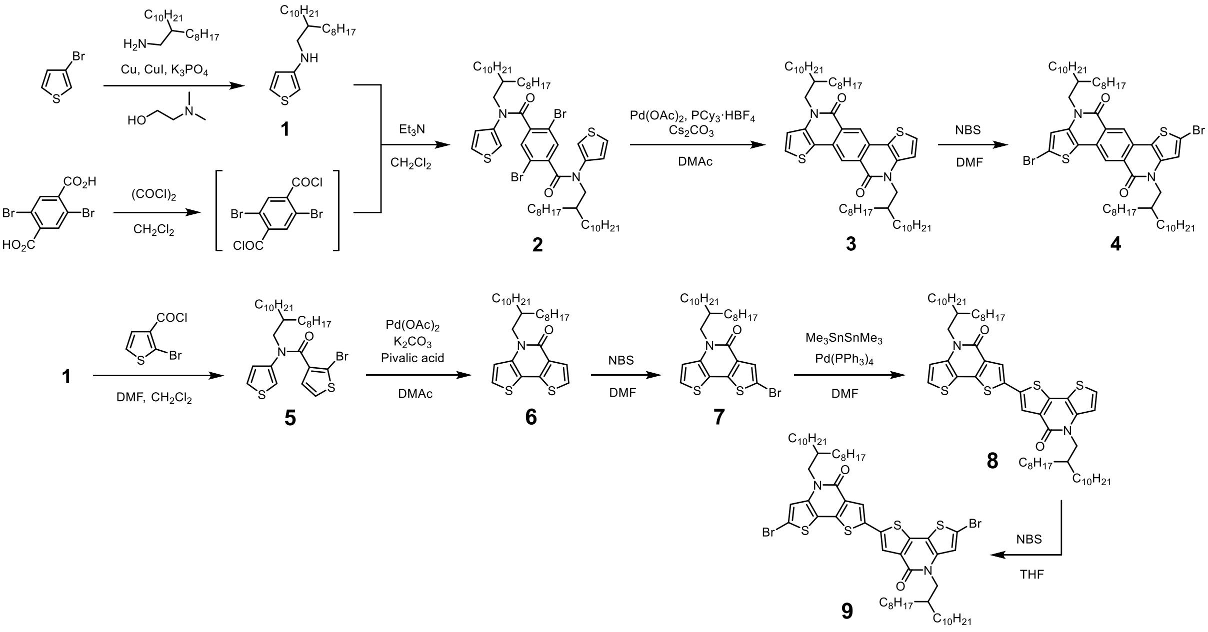

Fig. S1 Synthesis of monomers.

***N*-(2-octyldodecyl)thiophen-3-amine (1):** A mixture of 3-bromothiophene (24.4 g, 150 mmol), 2-octyldodecan-1-amine (53.5 g, 180 mmol), Cu powder (0.94 g, 15 mmol), CuI (I) (2.86 g, 15 mmol) and K_3PO_4 (63.38 g, 300 mmol) in 2-dimethylaminoethanol (150 mL) was stirred for 45 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into water, and the product was extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane) and dried under vacuum to afford **1** as a brown oil (yield = 52.2 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (dd, J = 5.2, 2.8 Hz, 1H), 6.61 (dd, J = 5.2, 1.6 Hz, 1H), 5.91 (dd, J = 2.8, 1.6 Hz, 1H), 3.57 (br, 1H), 2.96 (d, J = 6.0 Hz, 2H), 1.62-1.55 (m, 1H), 1.35-1.20 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H).

2,5-Dibromo-*N*,*N*-bis(2-octyldodecyl)-*N*,*N*-di(thiophen-3-yl)terephthalamide (2): To a stirred solution of 2,5-dibromoterephthalic acid (5.18 g, 16.0 mmol) in CH_2Cl_2 (27 mL) were added oxalyl chloride (4.6 mL, 48.0 mmol) and DMF (few drops) at 0 °C. The mixture was stirred for 20 h at room temperature. Then, the solvent and excess oxalyl chloride were removed under vacuum to obtain 2,5-dibromoterephthaloyl dichloride, which was used in next step without further purification. To a solution of 2,5-dibromoterephthaloyl dichloride in CH_2Cl_2 (27 mL) was slowly added a solution of **1** (13.4 g, 35.2 mmol) and Et_3N (3 mL) in CH_2Cl_2 (27 mL) at 0 °C. The mixture was stirred overnight at room temperature. Then, the mixture was poured into water and extracted with hexane. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2) and dried under vacuum to afford **2** as a brown oil (yield =14.5 g, 87%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (dd, J = 5.1, 3.1 Hz, 2H), 7.08 (s, 2H), 6.84 (dd, J = 2.0 Hz, 2H), 6.76 (dd, J = 5.1, 1.4 Hz, 2H), 3.88-3.62 (m, 4H), 1.60-1.49 (m, 2H), 1.36-1.15 (m, 64H), 0.88 (td, J = 7.0, 1.4 Hz, 12H). MS (MALDI-TOF): *m/z* 1046.48 $[M]^+$; found 1047.23.

4,10-Bis(2-octyldodecyl)thieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11-dione (3): A mixture of **2** (23.0 g, 22.0 mmol), Cs_2CO_3 (88.9 g, 273 mmol), $Pd(OAc)_2$ (3.16 g, 14.1 mmol), and $PCy_3{\cdot}HBF_4$ (7.03 g, 19.1 mmol) in DMAc (880 mL) was stirred at 120 °C overnight. After cooling to room temperature, the reaction mixture was filtered through Celite (eluent: chloroform) and the solvent was removed under vacuum. The product was extracted with $CHCl_3$ and the organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by silica gel column chromatography (eluent: chloroform/hexane = 1:1, v/v) and dried under vacuum to afford **3** as a yellow solid (yield =14.1 g, 72%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 2H), 7.49 (d, J = 5.5 Hz, 2H), 7.10 (d, J = 5.3 Hz, 2H), 4.32-4.16 (m, 4H), 2.08-1.98 (m, 2H), 1.44-1.22 (m, 64H), 0.85 (q, J = 6.7 Hz, 12H). MS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd 884.63; found 884.66.

2,8-Dibromo-4,10-bis(2-octyldodecyl)thieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11-dione (4): To a stirred solution of **3** (8.50 g, 9.6 mmol) in a mixed solvent of CH_2Cl_2 (420 mL) and DMF (220 mL) was slowly added NBS (4.27 g, 24 mmol) at 0 °C. The mixture was stirred for 24 h at room temperature. Then, CH_2Cl_2 was removed under reduced pressure. The formed precipitate was collected by filtration. The product was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 5:4, v/v), followed by recycling preparative GPC (eluent: $CHCl_3$), to afford **4** as a yellow solid (yield = 8.92 g, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 2H), 7.08 (s, 2H), 4.26-4.05 (m, 4H), 2.06-1.92 (m, 2H), 1.42-1.16 (m, 64H), 0.88-0.83 (m, 12H). MS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd 1042.45; found 1042.19.

2-Bromo-*N*-(2-octyldodecyl)-*N*-(thiophen-3-yl)thiophene-3-carboxamide (5): To a solution of 2-bromothiophene-3-carboxylic acid (20.7 g, 100 mmol) in dry CH_2Cl_2 (150 mL) and dimethylformamide (few drops) was added oxalyl chloride (19.0 g, 150 mmol) slowly. The mixture was stirred for 20 h at room temperature. Then, the solvent and excessive oxalyl chloride were removed under reduced pressure to obtain 2-bromothiophene-3-carbonyl chloride. To a solution of 2-bromothiophene-3-carbonyl chloride in dry THF was added slowly a solution of **1** (41.7 g, 110 mmol) in triethylamine (20 mL) and dry THF (150mL) at 0 °C. The mixture was stirred overnight at room temperature. The resulting mixture was poured into water and extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane/chloroform = 3:1, v/v) and dried under vacuum to afford **5** as a brown oil (yield = 37.4 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (s, 1H), 7.00 (dd, J = 3.2, 2.0 Hz, 1H), 6.85 (s, 1H), 6.78 (s, 1H), 6.57 (d, J = 4.4 Hz, 1H), 3.80 (d, J = 6.4 Hz, 2H), 1.62-1.55 (m, 1H), 1.35-1.20 (m, 32H), 0.90-0.85 (m, 6H). MS (MALDI-TOF): *m/z* 567.22 $[M]^+$; found 568.02.

4-(2-Octyldodecyl)dithieno[3,2-b:2',3'-d]pyridin-5(4H)-one (6): A mixture of **2** (33.0 g, 60 mmol), $Pd(OAc)_2$ (II) (1.35 g, 6.0 mmol), K_2CO_3 (12.44 g, 90 mmol), and pivalic acid (2.04 g, 20 mmol) in dry DMF (300 mL) was stirred for 18 h at 110°C. After cooling to room temperature, the reaction mixture was poured into water, and the product was extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane) and dried under vacuum to afford **6** as a brown oil (yield = 22.0 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 5.2 Hz, 1H), 7.43 (d, J = 5.2 Hz, 1H), 7.23 (d, J = 5.2 Hz, 1H), 7.08 (d, J = 5.2 Hz, 1H), 4.21 (d, J = 6.0 Hz, 2H), 2.03-1.95 (m, 1H), 1.40-1.15 (m, 32H), 0.90-0.84 (m, 6H). MS (MALDI-TOF): *m/z* 487.29 $[M]^+$; found 488.04.

2-Bromo-4-(2-octyldodecyl)dithieno[3,2-b:2',3'-d]pyridin-5(4H)-one (7): To a stirred solution of **6** (10.26 g, 21 mmol) in THF (100 mL) was added slowly NBS (2.62 g, 14.7 mmol) at 0°C. The mixture was stirred overnight at 0°C and then for 7 h at room temperature. The reaction mixture was poured into water and extracted with hexane. The combined organic layer was washed with water and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 97:3, v/v) and dried under vacuum to afford **7** as a yellow oil (yield = 6.50 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.46 (d, J = 5.5 Hz, 1H), 7.07 (d, J = 5.3 Hz, 1H), 4.25-4.14 (m, 2H), 2.03-1.91 (m, 1H), 1.60-1.56 (m, 4H), 1.42-1.18 (m, 32H), 0.92-0.86 (m, 6H). MS (MALDI-TOF): *m/z* 565.20 $[M]^+$; found 565.94.

4,4'-Bis(2-octyldodecyl)-[7,7'-bidithieno[3,2-*b*:2',3'-*d*]pyridine]-5,5'(4*H*,4'*H*)-dione (8): A mixture of **7** (6.40 g, 11.3 mmol), hexamethylditin (1.87 g, 5.7 mmol), and $Pd(PPh_3)_4$ in DMF (10 mL) was stirred for 24 h at 100 °C. After cooling to room temperature, the reaction mixture was poured into methanol. The formed precipitate was collected by filtration and washed with methanol. Then, the product was purified by silica gel column chromatography (eluent: chloroform/hexane = 1:1, v/v) and dried under vacuum to afford **8** as a yellow solid (yield = 4.18 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 2H), 7.48 (d, J = 5.3 Hz, 2H), 7.08 (d, J = 5.5 Hz, 2H), 4.30-4.14 (m, 4H), 2.07-1.91 (m, 2H), 1.48-1.16 (m, 64H), 0.89-0.83 (m, 12H). MS (MALDI-TOF): *m/z* 972.57 $[M]^+$; found 973.25.

2,2'-Dibromo-4,4'-bis(2-octyldodecyl)-[7,7'-bidithieno[3,2-*b*:2',3'-*d*]pyridine]-5,5'(4*H*,4'*H*)-dione (9): To a stirred solution of **8** (4.08 g, 4.19 mmol) in THF (70 mL) was slowly added NBS (1.53 g, 8.59 mmol) at 0 °C. The mixture was allowed to warm up to room temperature and stirred for 24 h. The reaction mixture was poured into methanol, and the formed precipitate was collected by filtration. The product was purified by recycling preparative GPC (eluent: chloroform) to afford **9** as an orange solid (yield = 4.57, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 2H), 7.07 (s, 2H), 4.26-4.04 (m, 4H), 2.01-1.91 (m, 2H), 1.44-1.18 (m, 64H), 0.89-0.83 (m, 12H). MS (MALDI-TOF): *m/z* 1130.39 $[M]^+$; found 1130.97.

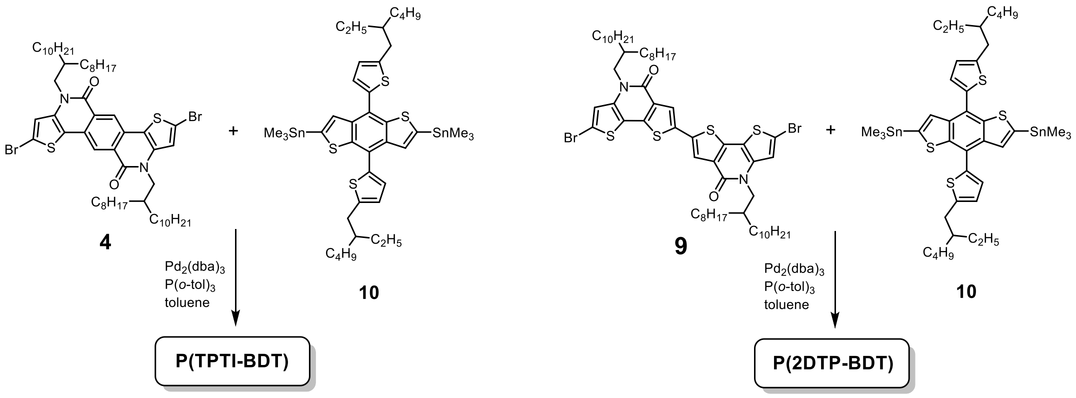

Fig. S2 Synthesis of polymers.

P(TPTI-BDT): To a solution of **4** (1.15 g, 1.10 mmol) and **10** (0.995 g, 1.10 mmol) in toluene (70 mL) were added $Pd_2(dba)_3$ (0.03 g, 0.033 mmol) and P(*o*-tol)$_3$ (0.05 g, 0.17 mmol). The mixture was stirred for 48 h at 100 °C. After cooling to room temperature, the reaction mixture was added dropwise into methanol (300 mL), and the formed precipitate was collected by filtration. The product was purified by sequential Soxhlet extraction using methanol, acetone, hexane, and chloroform. The chloroform fraction was concentrated and reprecipitated into methanol. The product was collected by filtration and dried under vacuum to afford **P(TPTI-BDT)** as a dark reddish purple solid (yield = 1.06 g, 66%). GPC (THF): M_n = 125 kDa, PDI = 4.4. Anal. calcd (%) for $C_{90}H_{126}N_2O_2S_6$: C 74.02, H 8.70, N 1.92; found: C 73.93, H 8.70, N 1.93.

P(2DTP-BDT): To a solution of **9** (0.566 g, 0.50 mmol) and **10** (0.452 g, 0.50 mmol) in toluene (30 mL) were added $Pd_2(dba)_3$ (0.014 g, 0.015 mmol) and P(*o*-tol)$_3$ (0.023 g, 0.075 mmol). The mixture was stirred for 24 h at 100 °C. After cooling to room temperature, the reaction mixture was added dropwise into methanol (300 mL), and the formed precipitate was collected by filtration. The product was purified by sequential Soxhlet extraction using methanol, acetone, hexane, and chloroform. The chloroform fraction was concentrated and reprecipitated into methanol. The product was collected by filtration and dried under vacuum to afford **P(2DTP-BDT)** as a dark reddish purple solid (yield = 0.43 g, 55%). GPC (THF): M_n = 42 kDa, PDI = 4.4. Anal. calcd (%) for $C_{92}H_{126}N_2O_2S_8$: C 71.36, H 8.20, N 1.81; found: C 71.12, H 8.20, N 1.76.

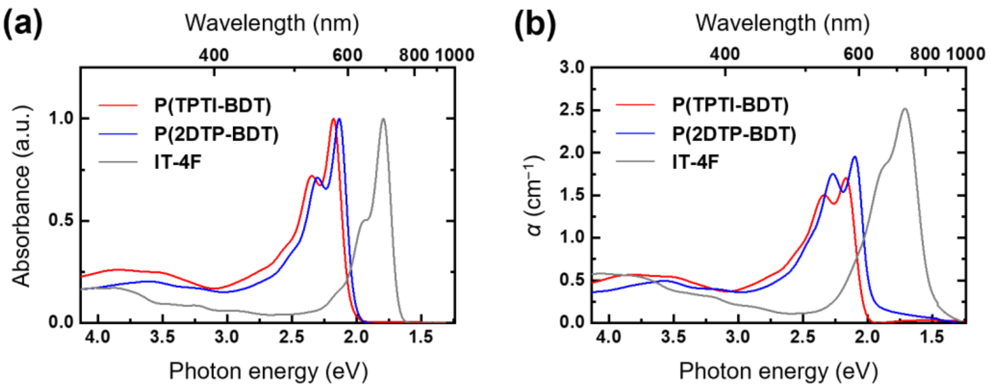

Fig. S3 UV–vis absorption spectra of **P(TPTI-BDT)**, **P(2DTP-BDT)**, and **IT-4F** in (a) chloroform solution and (b) as-spun thin films.

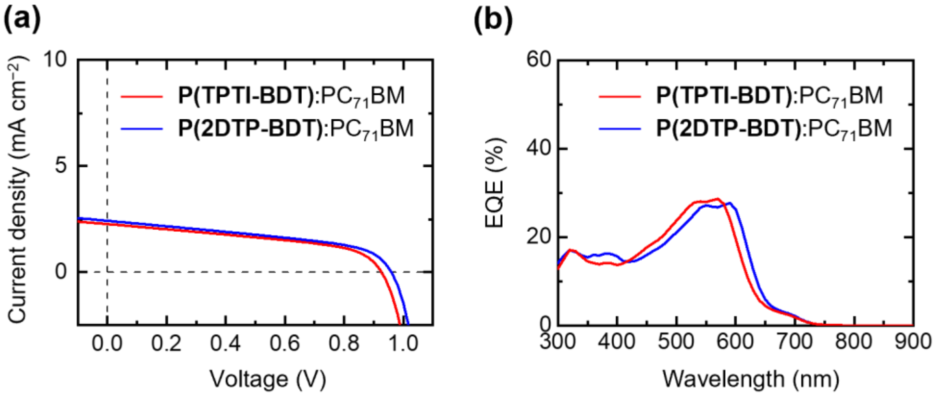

Fig. S4 *J*–*V* curves and EQE spectra for OSCs based on **P(TPTI-BDT)**:PC$_{71}$BM and **P(2DTP-BDT)**:PC$_{71}$BM (1:1, w/w).

Table S1 Photovoltaic parameters for fullerene-based OSCs (cf. Fig. S4)

Active layer	t (nm)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
P(TPTI-BDT):PC$_{71}$BM (1:1, w/w)	79	2.3	0.93	45	1.0
P(2DTP-BDT):PC$_{71}$BM (1:1, w/w)	85	2.4	0.96	45	1.1

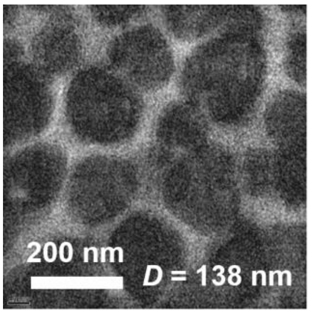

Fig. S5 TEM image of **P(TPTI-BDT)**:PC$_{71}$BM (1:1, w/w) blend film.