

Supporting Information

Highly crystalline polycyclic aromatic lactam-based regioregular wide-bandgap polymer donors for organic solar cells

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Experimental Section

Materials and Methods

7-Bromo-5-(2-hexyldecyl)thieno[3,2-*c*]quinolin-4(5*H*)-one (TQO) and 7-bromo-4-(2-hexyldecyl)thieno[3,2-*c*]isoquinolin-5(4*H*)-one (TIQO) were synthesized using a previously reported method.^{S1} (4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (BDT) was purchased from Derthon. All other reagents were purchased from Sigma-Aldrich and were used as received without further purification. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were measured using a 300 MHz spectrometer (Varian Mercury Plus). Thermal analyses (TGA, DSC) were performed using Q600 (TA Instruments) under an inert N₂ atmosphere, with heating/cooling rates of 10 °C min⁻¹. Mass spectrometric analysis was carried out and the results were obtained using a MALDI-TOF spectrometer (Voyager-DE STR). The ultraviolet–visible spectra were recorded using a UV-Visible spectrophotometer (UV-1800). Gel permeation chromatography (GPC) was measured to check the molecular weight and confirm the polydispersity indices (PDIs) using the Polymers Lab solution at a flow rate of 1.0 mL min⁻¹ 1,2,4-trichlorobenzene solution at 150 °C with polystyrene standards. Cyclic voltammetry experiments were performed with an electrochemical analyzer (CH Instruments) in acetonitrile solutions containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) as the supporting electrolyte, with Ag/AgNO₃ as the reference electrode, a platinum wire as the counter electrode, and a platinum working electrode. Density functional theory (DFT) calculations were performed using the Gaussian 09 W package with the Becke three-parameter Lee–Yang–Parr (B3LYP) function and the 6-31G(d) basis set to elucidate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels and backbone planarity. Two-dimensional grazing-incidence wide-angle X-ray scattering (2D-GIWAXS) experiments were performed at the 9A beamlines of the Pohang Accelerator Laboratory (PAL), Korea. X-rays

with a wavelength of 1.1 Å (11.08 keV) were used. The incidence angle (0.12°) was chosen to allow for complete penetration of the X-rays into the copolymer film. The surface morphologies of the copolymer thin films were characterized using Atomic force microscopy (AFM) (Nanoscope, Bruker, Inc.) while operating in tapping mode. The performance of the organic solar cells (OSC) was confirmed using a solar simulator (Yamashita Denso) and a Keithley 2400 source measure unit (Keithley Instruments, Inc.). The current density-voltage ($J-V$) graphs of the devices were measured under AM 1.5G light conditions, and the light intensity was calibrated using a Si standard reference device (PV Measurements Inc., calibrated at the National Renewable Energy Laboratory). The external quantum efficiency (EQE) data were measured using QUANTX-300 QE measurement system (Oriel Instruments). The EQE values were obtained as a function of wavelength in the range of 300–1000 nm using a xenon short arc lamp as the light source, and the calibration was performed using a Si photodiode.

Device fabrication

Bulk heterojunction OSCs were fabricated with an inverted structure, consisting of indium tin oxide (ITO)/ZnO/active layer/MoO₃/Ag. The ZnO solution was prepared by mixing diethyl zinc with tetrahydrofuran (1:2, v/v) and coated onto pre-cleaned ITO with thickness of 30 nm and thermally annealed at 140 °C for 15 min. The active layer, which was prepared as follows: chloroform (total concentration = 14 mg mL⁻¹), was fabricated by spin-coating at various coating speeds for 30 s in a glove box filled with argon. After drying the active layer, MoO₃ (~7 nm) and Ag (~100 nm) layers were formed by thermal evaporation under a base pressure of 10⁻⁷ Torr. The effective area of the device was 9 mm².

Monomer and Copolymer syntheses.

Synthesis of 5,5'-bis(2-hexyldecyl)-[7,7'-bithieno[3,2-c]quinoline]-4,4'(5H,5'H)-dione (I).

A mixture of TQO (1.00 g, 2.00 mmol), bis(tributyltin) (0.57 g, 1.00 mmol), and dichlorobis(triphenylphosphine)palladium(II) (0.04 g, 0.06 mmol) in *N,N*-dimethylformamide were stirred under N₂ at 140 °C for overnight. The reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by silica column chromatography with eluent (dichloromethane) and recrystallized by hexane to give yellow solid (0.54 g, 65.2 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 7.94 (d, *J*=9 Hz, 2H), 7.77 (d, *J*=5.4 Hz, 2H), 7.68 (s, 2H), 7.53 (d, *J*=7.5 Hz, 2H), 7.41 (d, *J*=5.4 Hz, 2H), 4.43 (m, 4H), 2.08 (m, 2H), 1.40 (m, 48H), 0.81 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz):δ (ppm) 159.20, 144.84, 141.44, 137.55, 130.98, 126.92, 125.11, 1125.05, 121.28, 117.90, 114.50, 46.13, 36.87, 31.84, 31.70, 30.06, 29.74, 29.59, 29.27, 26.82, 22.60, 14.04.

Synthesis of 2,2'-dibromo-5,5'-bis(2-hexyldecyl)-[7,7'-bithieno[3,2-c]quinoline]-4,4'(5H,5'H)-dione (PQ). Bromine (0.22 g, 1.40 mmol) was slowly added to a mixture compound 1 (0.54 g, 0.64 mmol) and amounts of iron (III) chloride in dichloromethane. After stirring at room temperature for overnight, the mixture was extracted by dichloromethane and dried over anhydrous MgSO₄. The crude product was purified by recrystallization from hexane to obtain yellow solid (0.55 g, 85.9 %). ¹H NMR (CDCl₃, 300 MHz):δ (ppm) 7.74 (d, *J*=8.1 Hz, 2H), 7.67 (s, 2H), 7.62 (s, 2H), 7.48 (d, *J*=7.5 Hz, 2H), 4.38 (m, 4H), 2.03 (m, 2H), 1.37 (m, 48H), 0.84 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz):δ (ppm) 157.77, 145.90, 141.52, 137.51, 131.24, 129.34, 124.87, 121.41, 117.07, 114.48, 113.40, 46.18, 36.84, 31.87, 31.81, 31.67, 30.06, 29.73, 29.59, 29.28, 26.77, 22.65, 22.59, 14.04. MALDI-TOF (m/z): founded 1007.7 [M+4], calcd 1004.36 [M].

Synthesis of 4,4'-bis(2-hexyldecyl)-[7,7'-bithieno[3,2-c]isoquinoline]-5,5'(4H,4'H)-dione (2). This compound was prepared by a similar method to that of compound (1), using the TIQO (1.00 g, 1.98 mmol), bis(tributyltin) (0.57 g, 1.00 mmol), and dichlorobis(triphenylphosphine)palladium(II) (0.04 g, 0.06 mmol). The product was afforded as a yellow solid (0.66 g, 78.5 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.84 (d, *J*=1.8 Hz, 2H), 8.14 (d, *J*=8.1 Hz, 2H), 7.83 (d, *J*=8.1 Hz, 2H), 7.49 (d, *J*=6 Hz, 2H), 7.11 (d, *J*=5.4 Hz, 2H), 4.25 (d, *J*=7.2 Hz, 4H), 2.02 (m, 2H), 1.36 (m, 48H), 0.84 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 161.99, 139.85, 137.89, 131.59, 131.10, 127.24, 125.74, 124.10, 122.80, 117.75, 117.18, 49.49, 37.14, 31.84, 31.78, 31.64, 29.97, 29.65, 29.51, 29.25, 26.63, 22.64, 22.60, 14.06.

Synthesis of 2,2'-dibromo-4,4'-bis(2-hexyldecyl)-[7,7'-bithieno[3,2-c]isoquinoline]-5,5'(4H,4'H)-dione (PiQ). This compound was prepared by a similar method to that of PQ, using the compound 2 (0.66 g, 0.78 mmol), and bromine (0.27 g, 1.71 mmol). The product was afforded as a yellow solid (0.62 g, 79.2 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.79 (s, 2H), 8.09 (d, *J*=8.4 Hz, 2H), 7.68 (d, *J*=9.0 Hz, 2H), 7.07 (s, 2H), 4.15 (m, 4H), 1.97 (m, 2H), 1.34 (m, 48H), 0.86 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 161.46, 139.05, 137.80, 131.15, 130.69, 127.14, 124.01, 122.39, 120.83, 118.08, 114.45, 49.46, 37.05, 31.86, 31.80, 31.49, 29.97, 29.65, 29.53, 29.27, 26.53, 22.64, 14.07. MALDI-TOF (*m/z*): founded 1007.7 [M+4], calcd 1004.36 [M].

Synthesis of 7,7'-dibromo-5,5'-bis(2-hexyldecyl)-[2,2'-bithieno[3,2-c]quinoline]-4,4'(5H,5'H)-dione (TQ). *N*-butyllithium (2.5 M in cyclohexane, 1.03 mL, 2.58 mmol) was added dropwise to solution of diisopropylamine (0.42 mL, 2.97 mmol) in anhydrous

tetrahydrofuran at -78 °C. After stirring at -78 °C for 30 min, a solution of TQO (1.00 g, 1.98 mmol) in anhydrous tetrahydrofuran was added dropwise to the reaction mixture and stirred additionally at -78 °C for 30 min. Subsequently, the CuCl₂ (0.53 g, 3.96 mmol) was added one portion to the reaction mixture and then stirred at room temperature for overnight. The reaction mixture was quenched by 1M HCl aqueous and extracted with dichloromethane for three times. The collected organic layer was dried from anhydrous MgSO₄ and then concentrated in vacuo. The crude product was purified by silica column chromatography (dichloromethane/hexane, 5/1, v/v) to afford the product as a yellow solid (0.75, 75.1 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 7.82 (s, 2H), 7.64 (d, *J*=8.4 Hz, 2H), 7.56 (s, 2H), 7.40 (d, *J*=8.1 Hz), 4.26 (m, 4H), 1.95 (m, 2H), 1.24 (m, 48H), 0.87 (m, 12 H). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 157.88, 143.71, 137.72, 135.73, 131.21, 125.33, 123.46, 123.23, 118.54, 116.24, 45.89, 36.27, 31.89, 31.83, 31.25, 29.96, 29.67, 29.56, 29.28, 26.59, 22.68, 14.13. MALDI-TOF (m/z): founded 1007.3 [M+4], calcd 1004.36 [M].

Synthesis of 7,7'-dibromo-4,4'-bis(2-hexyldecyl)-[2,2'-bithieno[3,2-c]isoquinoline]-5,5'(4H,4'H)-dione (TiQ). This compound was prepared by a similar method to that of TQ, using TIQO (1.00 g, 1.98 mmol), *N*-butyl lithium (2.5 M in cyclohexane, 1.03 mL, 2.58 mmol), diisopropylamine (0.42 mL, 2.97 mmol), and CuCl₂ (0.53 g, 3.96 mmol). The product was afforded as a yellow solid (0.63 g, 63.1 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.63 (d, *J*=1.8 Hz, 2H), 7.79 (d, *J*=8.1 Hz, 2H), 7.55 (d, *J*=9.0 Hz, 2H), 7.20 (s, 2H), 4.20 (m, 4H), 2.00 (m, 2H), 1.37 (m, 48H), 0.84 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 160.62, 140.11, 136.20, 135.75, 132.25, 130.44, 125.31, 123.49, 120.69, 116.52, 114.42, 49.41, 37.16, 31.92, 31.60, 30.02, 29.73, 29.64, 29.34, 26.68, 22.70, 14.16. MALDI-TOF (m/z): founded 1007.6 [M+4], calcd 1004.36 [M].

General Polymerization Procedure.

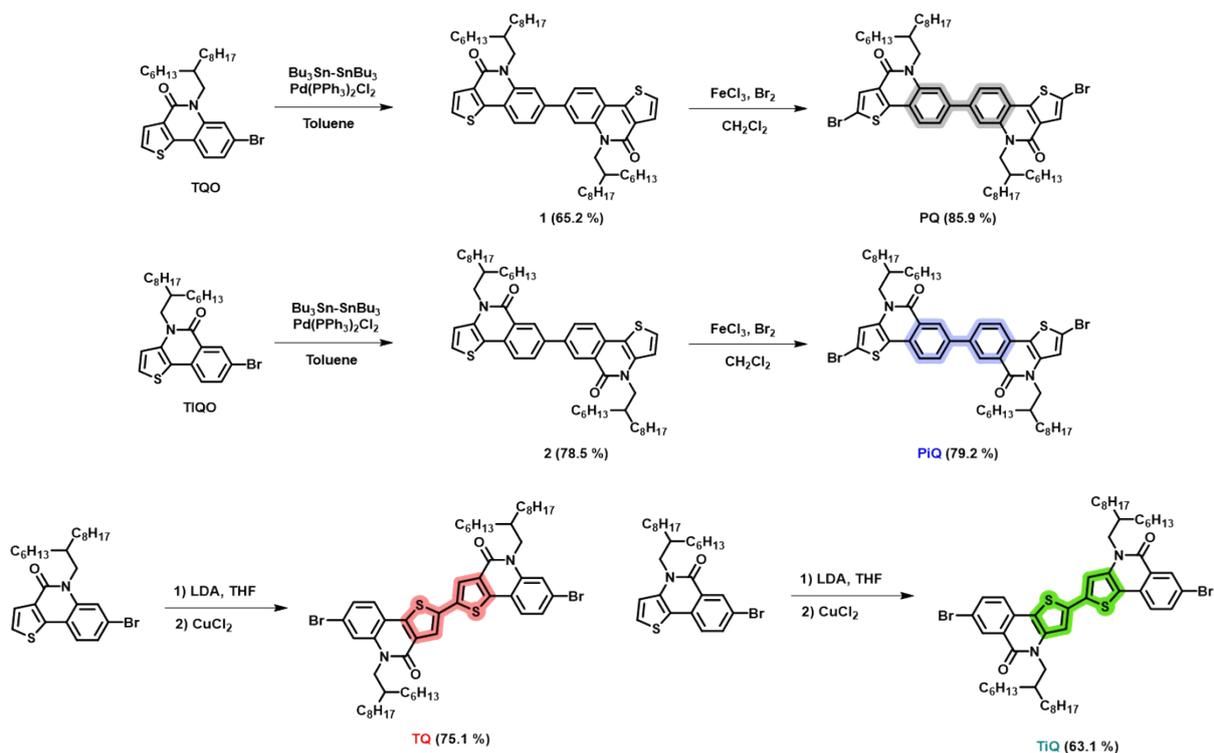
A mixture of distannylated monomer (1 equiv.), dibrominated monomer (1 equiv.), tetrakis(triphenylphosphine)palladium(0) (0.03 equiv.) was dissolved in anhydrous toluene (5 mL) and anhydrous *N,N*-dimethylformamide (1 mL). The reaction mixture was stirred at 110 °C for 16 h, and then 2-(tributylstannyl)thiophene (0.2 mL) and 2-bromothiophene (0.2 mL) as end-capper were added. After a further 2 h, the reaction mixture was poured into methanol (200 mL) and then precipitate was collected by filtration and purified by Soxhlet extraction using methanol, acetone, and hexane. The polymers were obtained by re-precipitation of the chloroform solution into methanol.

Poly(2-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-5,5'-bis(2-hexyldecyl)-[7,7'-bithieno[3,2-*c*]quinoline]-4,4'(5*H*,5'*H*)-dione) PBDT-PQ: PQ (200.00 mg, 0.20 mmol), BDT (179.60 mg, 0.20 mmol), and Pd(PPh₃)₄ (6.90 mg) were used to synthesize PBDT-PQ via the previously described method (265.00 mg, 93.6 %). GPC: $M_n = 26.0$ kDa, $PDI_s = 3.05$, $T_d = 403.42$ °C.

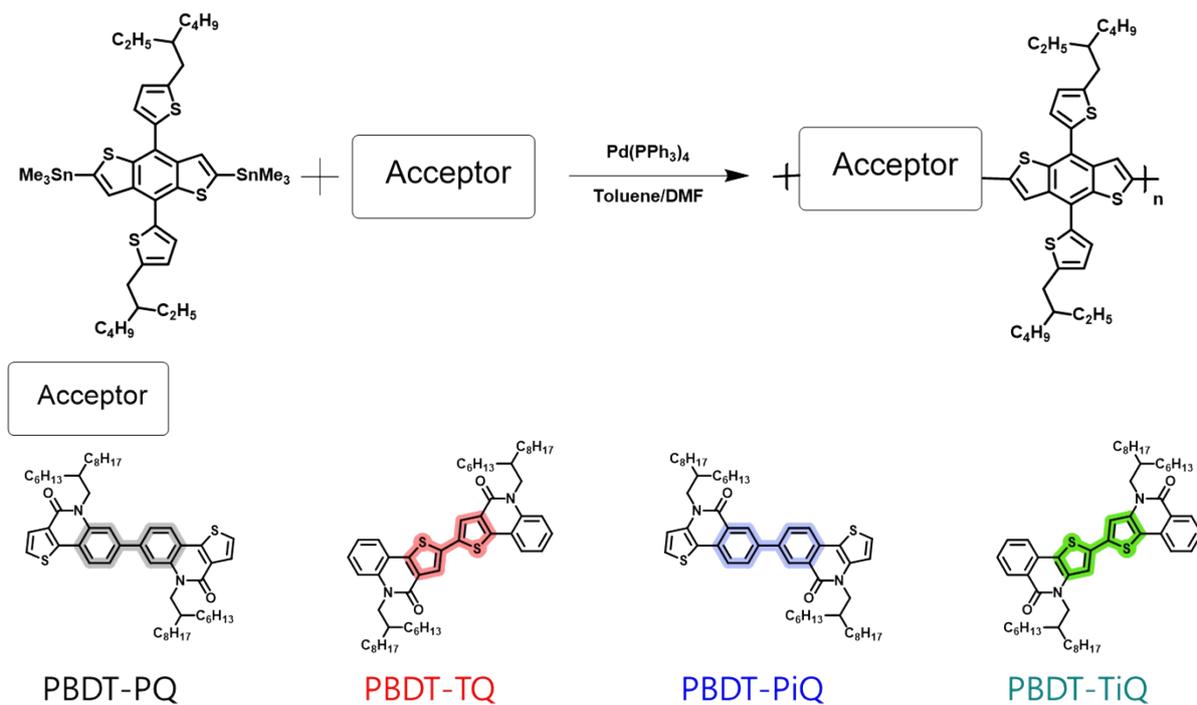
Poly(7-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-5,5'-bis(2-hexyldecyl)-[2,2'-bithieno[3,2-*c*]quinoline]-4,4'(5*H*,5'*H*)-dione) PBDT-TQ: TQ (200.00 mg, 0.20 mmol), BDT (179.60 mg, 0.20 mmol), and Pd(PPh₃)₄ (6.90 mg) were used to synthesize PBDT-TQ via the previously described method (249.00 mg, 87.9 %). GPC: $M_n = 11.0$ kDa, $PDI_s = 2.04$, $T_d = 409.38$ °C.

Poly(2-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-4,4'-bis(2-hexyldecyl)-[7,7'-bithieno[3,2-*c*]isoquinoline]-5,5'(4*H*,4'*H*)-dione) PBDT-PiQ: PiQ (215.00 mg, 0.21 mmol), BDT (193.10 mg, 0.21 mmol), and Pd(PPh₃)₄ (7.40 mg) were used to synthesize PBDT-PiQ via the previously described method (215.00 mg, 75.9 %). GPC: $M_n = 15.0$ kDa, $PDI_s = 2.51$, $T_d = 386.95$ °C.

Poly(7-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-4,4'-bis(2-hexyldecyl)-[2,2'-bithieno[3,2-*c*]isoquinoline]-5,5'(4*H*,4'*H*)-dione) PBDT-TiQ: TiQ (130.00 g, 0.13 mmol), BDT (116.80 mg, 0.13 mmol), and Pd(PPh₃)₄ (4.50 mg) were used to synthesize PBDT-TiQ via the previously described method (171.00 mg, 92.8 %). GPC: $M_n = 8.6$ kDa, $PDI_s = 2.12$, $T_d = 401.05$ °C.

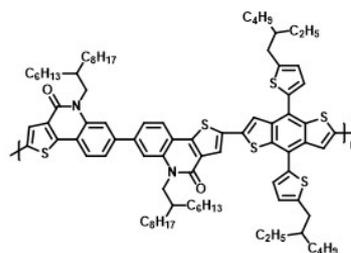


Scheme S1. Synthetic routes for symmetric electron-accepting building blocks based on TQO and TIQO.



Scheme S2. Synthetic routes for polymer donors via typically Stille-polycondensation.

Conventional GPC Summary Report



Acq. Date	Jan 16, 2019 - 23:49:49
Column	Olexis*2-Guard
Solvent	TCB
Operator (Acq)	admin : Administrator
System	System 1
Conc (mg/ml)	1.0000
Inj Vol (ul)	200.0
dn/dc (dl/g)	0.0000
Flow Rate (ml/min)	1.0000
Method	190116-2-0004.vcm

Sample	2019-01-16_23:49:49_3-1_01.vdt
Mn (Daltons)	26,937
Mw (Daltons)	82,245
Mz (Daltons)	188,688
Mw/Mn	3.053
IV (dl/g)	0.0000
Rh (nm)	0.00

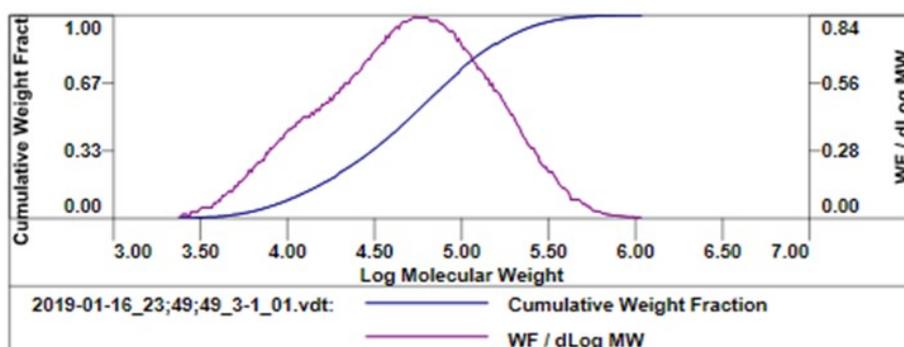
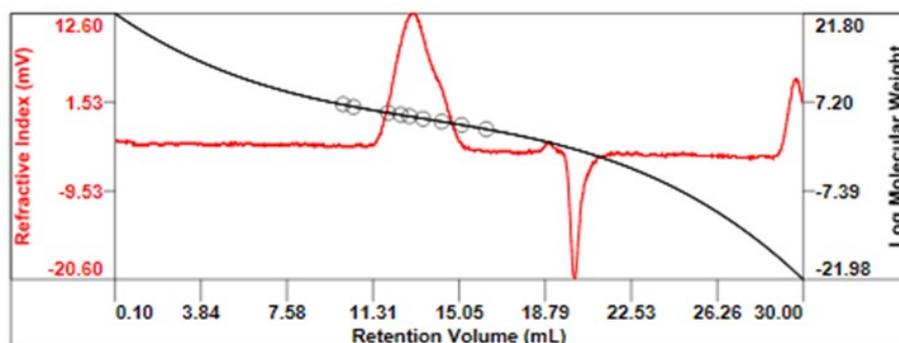
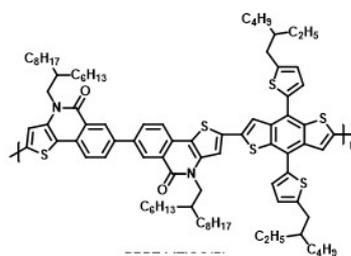


Figure S1. GPC result of PBDT-PQ.

Conventional GPC Summary Report



Acq. Date	Jan 17, 2019 - 02:01:37
Column	Olexis*2-Guard
Solvent	TCB
Operator (Acq)	admin : Administrator
System	System 1
Conc (mg/ml)	1.0000
Inj Vol (ul)	200.0
dn/dc (dl/g)	0.0000
Flow Rate (ml/min)	1.0000
Method	190116-2-0004.vcm

Sample	2019-01-17_02:01:37_5-1_01.vdt
Mn (Daltons)	14,628
Mw (Daltons)	36,767
Mz (Daltons)	77,850
Mw/Mn	2.513
IV (dl/g)	0.0000
Rh (nm)	0.00

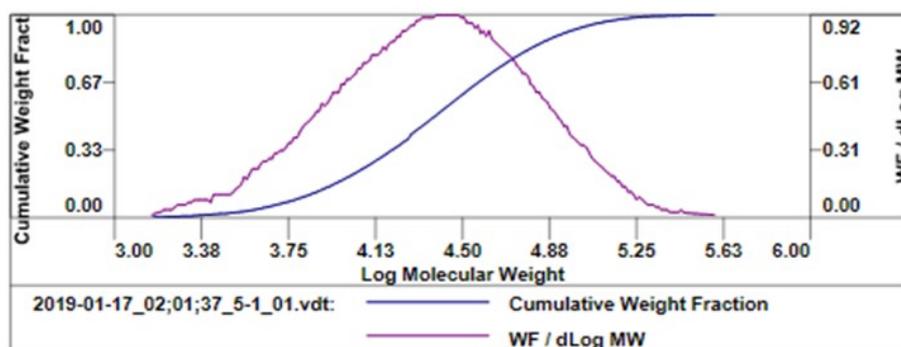
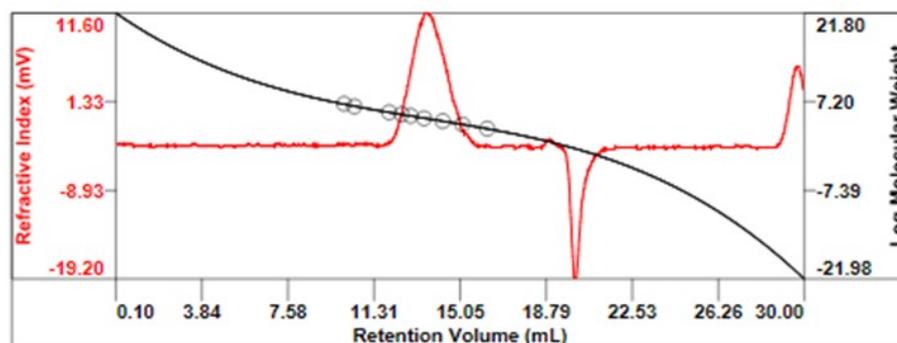
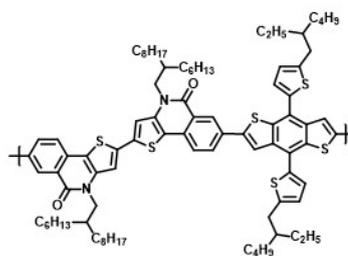


Figure S3. GPC result of PBDT-PiQ.

Conventional GPC Summary Report



Acq. Date	Jan 17, 2019 - 03:07:32	Sample	2019-01-17_03:07:32_6-1_01.vdt
Column	Olaxis*2+Guard	Mn (Daltons)	8,665
Solvent	TCB	Mw (Daltons)	18,355
Operator (Acq)	admin : Administrator	Mz (Daltons)	30,889
System	System 1	Mw/Mn	2.119
Conc (mg/ml)	1.0000	IV (dl/g)	0.0000
Inj Vol (ul)	200.0	Rh (nm)	0.00
dn/dc (dl/g)	0.0000		
Flow Rate (ml/min)	1.0000		
Method	190116-2-0004.vcm		

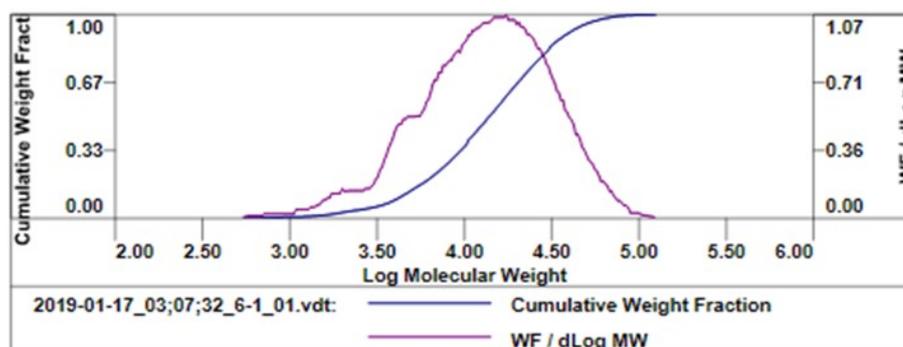
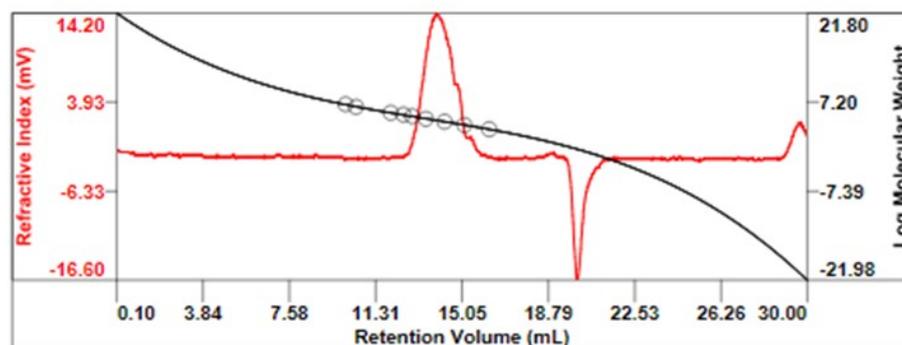


Figure S4. GPC result of PBDT-TiQ.

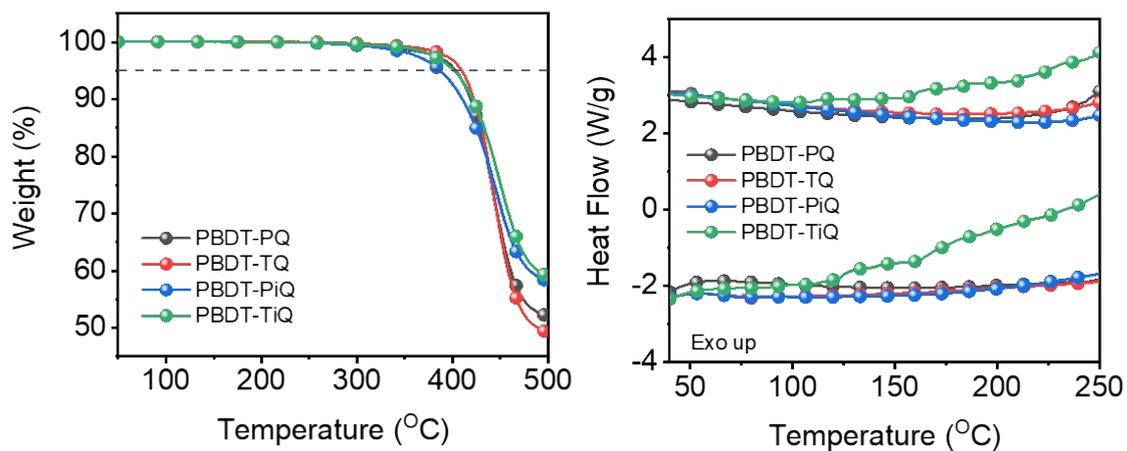


Figure S5. TGA and DSC curves of the synthesized polymers.

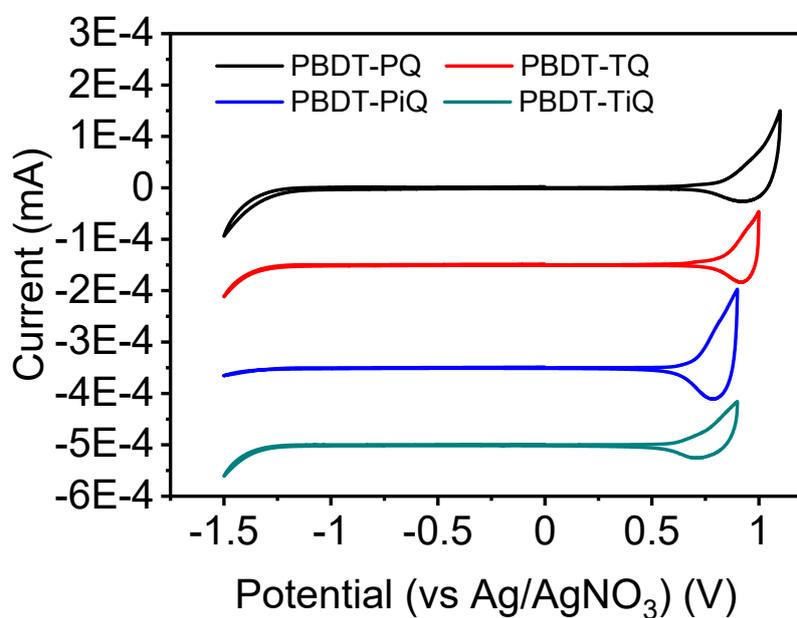


Figure S6. CV curves of the synthesized polymers.

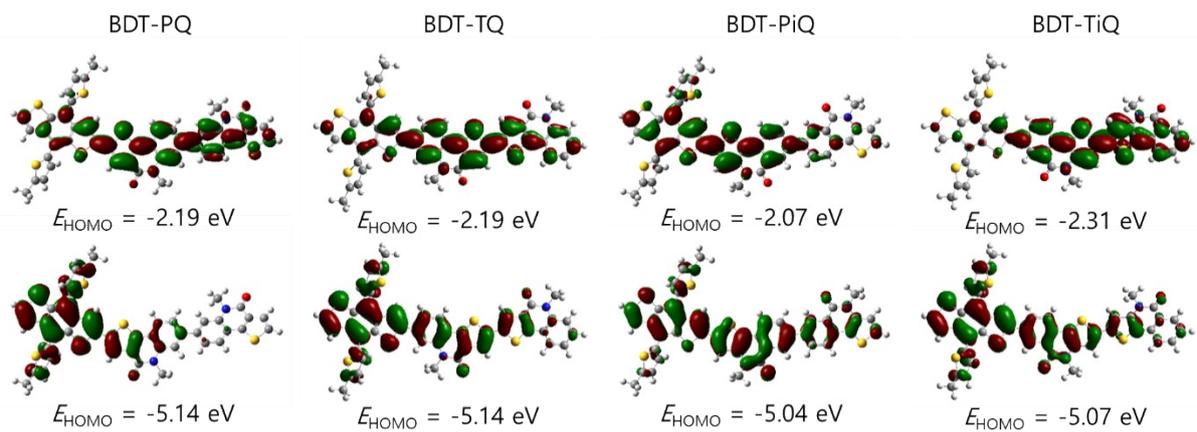


Figure S7. The simulated DFT results of the established models.

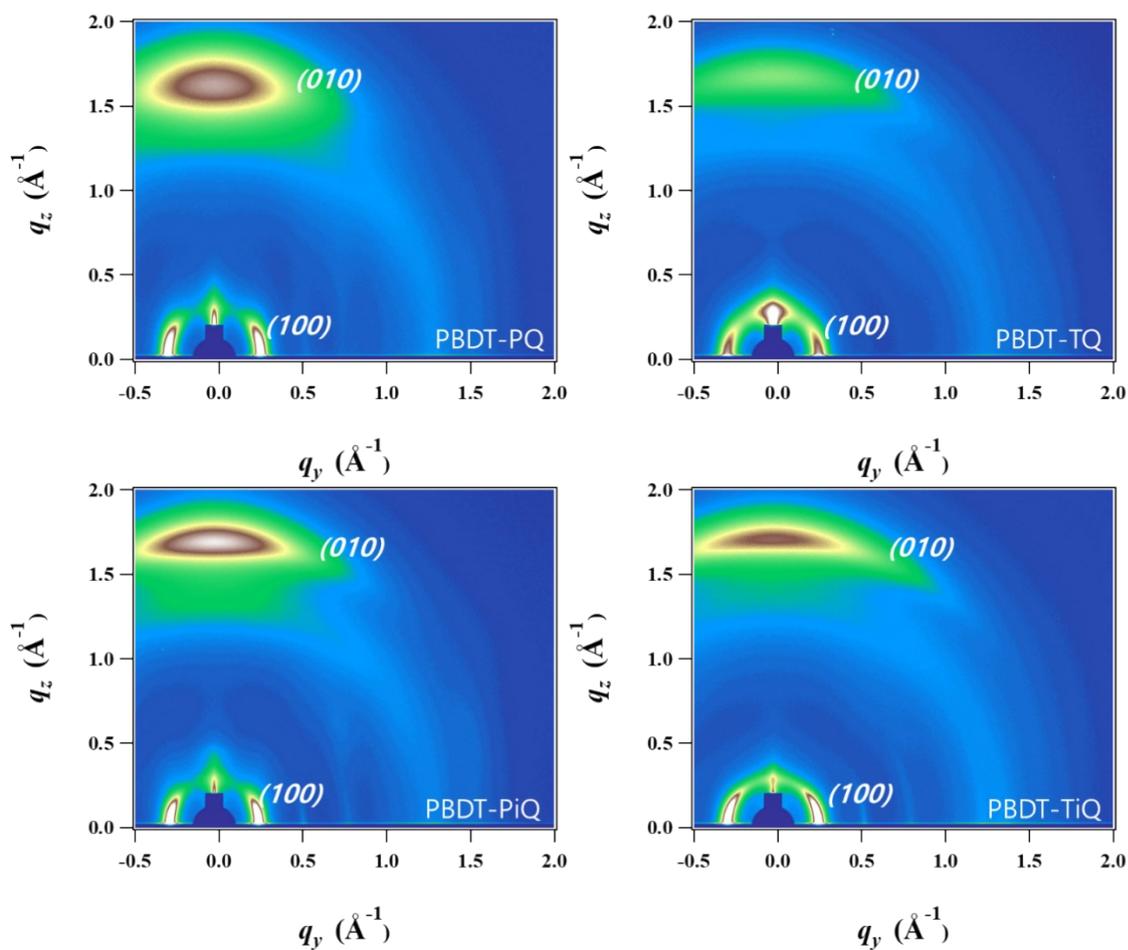


Figure S8. 2D-GIWAXS images of the neat polymer films.

Table S1. Summary of GIWAXS results of the synthesized neat polymer and reference polymer films.

	$q_{(010)}$ [\AA^{-1}]	$d_{(010)}$ [\AA] ^a	$\text{FWHM}_{(010)}$ [\AA^{-1}]	$L_{C(010)}$ [\AA] ^b
PBDT-TQO	1.68	3.74	0.32	19.63
PBDT-PQ	1.66	3.79	0.28	20.20
PBDT-TQ	1.70	3.70	0.24	23.56
PBDT-TIQO	1.67	3.76	0.27	23.27
PBDT-PiQ	1.74	3.63	0.16	35.34
PBDT-TiQ	1.75	3.61	0.16	35.34

^a $2\beta \pi / q_{(010)}$, ^b $2\beta \pi / \text{FWHM}_{(010)}$.

Table S2. Summary of the photovoltaic performances of PBDT-PiQ:Y6.

D:A	Thermal Annealing	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
	No	0.88	17.98	62.40	9.91
1.0:1.0	100 °C for 10min	0.87	18.73	64.47	10.51
	160 °C for 10min	0.84	20.53	62.97	10.89
	No	0.88	17.35	63.59	9.75
1.0:1.2	100 °C for 10min	0.86	18.86	64.78	10.56
	160 °C for 10min	0.85	20.82	63.51	11.28
	No	0.88	16.69	62.79	9.18
1.0:1.5	100 °C for 10min	0.86	17.61	62.57	9.52
	160 °C for 10min	0.85	19.99	60.83	10.28
	No	0.88	15.21	61.97	8.29
1.0:2.0	100 °C for 10min	0.87	17.74	60.89	9.40
	160 °C for 10min	0.86	19.68	60.60	10.21

D:A	Additives	Thermal Annealing	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
	DIO 0.5 vol %	160 °C for 10min	0.79	21.25	60.56	10.21
1.0:1.2	DPE 0.5 vol %	160 °C for 10min	0.80	20.97	60.74	10.17
	CN 0.5 vol %	160 °C for 10min	0.83	20.89	60.53	10.46

Table S3. Summary of the photovoltaic performances of OSCs polymer:Y6 (blend ratio = 1.0:1.2).

	Thermal Annealing	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
PBDT-PQ :Y6	No	0.90	3.36	46.88	1.42
	100 °C for 10min	0.89	4.35	46.44	1.81
	160 °C for 10min	0.87	6.26	43.16	2.35
PBDT-TQ :Y6	No	0.86	4.68	40.90	1.65
	100 °C for 10min	0.86	5.43	40.27	1.88
	160 °C for 10min	0.84	6.72	37.61	2.13
PBDT-TiQ :Y6	No	0.83	14.42	51.19	6.10
	100 °C for 10min	0.85	16.88	53.87	7.73
	160 °C for 10min	0.81	20.30	51.49	8.50

Table S4. Summary of the photo-CELIV parameters.

Photoactive Layers	T_{MAX} [μs]	Mobility [$\Delta j \ll j_0$]	Thickness
PBDT-PQ:Y6	4.90	1.93×10^5	115
PBDT-TQ:Y6	5.35	1.22×10^5	100
PBDT-PiQ:Y6	3.20	4.04×10^5	110
PBDT-TiQ:Y6	3.43	2.67×10^5	95

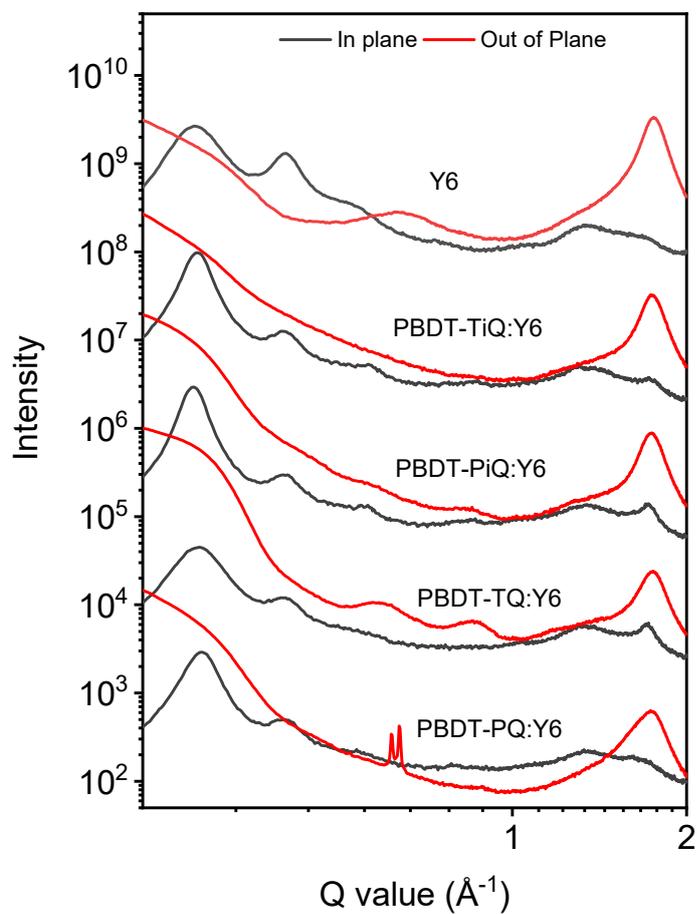


Figure S9. GIWAXS scattering line-cut profiles of the blend films and neat Y6.

Table S5. Summary of GIWAXS results of the blend films.

	$q_{(010)}$ [\AA^{-1}]	$d_{(010)}$ [\AA] ^a	$\text{FWHM}_{(010)}$ [\AA^{-1}]	$L_{C(010)}$ [\AA] ^b
PBDT-PQ:Y6	1.71	3.67	0.26	21.75
PBDT-TQ:Y6	1.74	3.61	0.22	25.70
PBDT-PiQ:Y6	1.74	3.61	0.17	33.26
PBDT-TiQ:Y6	1.75	3.59	0.17	33.26

^a $2\pi/q_{(010)}$, ^b $2\pi/\text{FWHM}_{(010)}$.

REFERENCES

(S1) J.-W. Ha, H. S. Kim, C. E. Song, H. J. Park and D.-H. Hwang, *J. Mater. Chem. C*, 2020, **8**, 12265-12271.