

Electronic Supplementary Information

Molecular Engineering of Benzothienoisindigo Copolymers Allowing Highly Preferential Face-on Orientations

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Experimental Section

Synthesis

Compound (1), (2) and (3) in Scheme S1 were synthesized according to the previous report.^{S1} Synthesis procedures of other compounds are described in main text.

2-hexyldecan-1-bromine (1) was transparent liquid (yield: 69 %).

¹HNMR (400 MHz, CDCl₃), δ 0.88 (t, 6H), 1.33 (m, 24H), 1.59 (m, 1H), 3.45 (d, 2H).

2-(pentadecan-7-yl)isoindole-1,3-dione (2) was also transparent oil (yield : 89 %).

¹HNMR (400 MHz, CDCl₃), δ 0.86-0.94 (m, 6H), 1.31 (m, 8H), 1.55 (m, 1H), 2.98 (d, 2H), 3.57 (br, 1H), 5.92 (dd, *J* = 2.97, 1.62 Hz, 1H), 6.62 (dd, *J* = 5.27, 1.62 Hz, 1H), 7.14 (dd, *J* = 5.27, 3.24 Hz, 1H)

2-hexyldecylamine(3). was transparent liquid (yield: quantitative)

¹HNMR (400 MHz, CDCl₃), δ 0.88 (t, 6H), 1.27 (s, 25H), 2.60 (d, 2H)

The synthesis of N-(2-hexyldecyl)thiophen-3-amine (4) and 4-(2-hexyldecyl)thieno[3,2-b] pyrrole-5,6-dione (5) were carried out following the literature.

N-(2-hexyldecyl)thiophen-3-amine (4) is the transparent oil (yield: 74 %)^{S2}

¹HNMR (400 MHz, CDCl₃), δ 0.86-0.94 (m, 6H), 1.31 (m, 8H), 1.55 (m, 1H), 2.98 (d, 2H), 3.57 (br, 1H), 5.92 (dd, *J* = 2.97, 1.62 Hz, 1H), 6.62 (dd, *J* = 5.27, 1.62 Hz, 1H), 7.14 (dd, *J* = 5.27, 3.24 Hz, 1H)

4-(2-hexyldecyl)thieno[3,2-b]pyrrole-5,6-dione (5) is red oil (yield: 40 %)^{S2}.

¹HNMR (400 MHz, CDCl₃), δ 0.89 (m, 6H), 1.34 (m, 8H), 1.74 (m, 1H), 3.54 (d, 2H), 6.76 (d, 2H), 7.99 (d, 1H)

Compound (6) and (7) were synthesized according to the reported procedure.^{S3}

6-bromo-1-(2-hexyldecyl)indole-2,3-dione (6) is orange solid (yield: 20 %)

¹HNMR (400 MHz, CDCl₃), δ 0.88 (t, 6H), 1.26-1.38 (m, 24H), 1.84 (m, 1H), 3.58 (d, 2H), 7.03 (d, 1H), 7.27 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.46 (d, 1H)

6-bromo-1-(2-hexyldecyl)-3H-indol-2-one (7) is yellow oil (yield: 85 %)

¹HNMR (400 MHz, CDCl₃), δ 0.88 (t, 6H), 1.26-1.28 (m, 24H), 1.84 (m, 1H), 3.46 (s, 2H), 3.55 (d, 2H), 6.93 (d, 1H), 7.09 (d, 1H), 7.15 (d, *J* = 8.0, 1.6 Hz, 1H).

Polymerization of TT1, TT2, BT1, BT2.

Synthesis of copolymer TT1. Following the general polymerization procedure, bis[5-(trimethyl stannyl)-3-undecylthiophen-2-yl]-[1,3]thiazolo[5,4-d][1,3]thiazole (0.035 g, 3.6×10^{-5} mol) and compound (9) (0.035 g, 4.1×10^{-5} mol) were used in this polymerization, and the polymer was obtained as a green film like solid (0.010 g). Weight averaged molecular weight (M_w) = 32 kg mol⁻¹, polydispersity index (PDI) = 1.7.

Synthesis of copolymer TT2. Following the general polymerization procedure, bis[5-(trimethyl stannyl)-3-undecylthiophen-2-yl]-[1,3]thiazolo[5,4-d][1,3]thiazole (0.026 g, 2.7×10^{-5} mol) and compound (11) (0.038 g, 2.7×10^{-5} mol) were used in this polymerization, and the polymer was obtained as a dark purple film like solid (0.037 g). M_w = 127 kg mol⁻¹, PDI = 3.5.

Synthesis of copolymer BT1. Following the general polymerization procedure, 5,11-bis[5-(trimethyl stannyl)-3-undecylthiophen-2-yl]-4,10-dithia-6,12-diazatricyclo[7.3.0.0^{3,7}]dodeca-1,3(7),5,8,11-pentaene (0.053 g, 5.2×10^{-5} mol) and compound (9) (0.046 g, 5.2×10^{-5} mol) were used in this polymerization, and the polymer was obtained as a glass green solid (0.052 g). M_w = 142 kg mol⁻¹, PDI = 2.1.

Synthesis of copolymer BT2. Following the general polymerization procedure, 5,11-bis[5-(trimethyl stannyl)-3-undecylthiophen-2-yl]-4,10-dithia-6,12-diazatricyclo[7.3.0.0^{3,7}]dodeca-1,3(7),5,8,11-pentaene (0.029 g, 2.9×10^{-5} mol) and compound (11) (0.040 g, 2.9×10^{-5} mol) were used in this polymerization, and the polymer was obtained as a dark green film like solid (0.049 g). M_w = 231 kg mol⁻¹, PDI = 3.9.

References

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- S2. Y. Koizumi, M. Ide, A. Saeki, C. Vijayakumar, B. Balan, M. Kawamoto, S. Seki, *S. Polym. Chem.* **2013**, *4*, 484-494.
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- S4. E. Zhou, M. Nakano, S. Izawa, J. Cong, I. Osaka, K. Takimiya, K. Tajima, *ACS Macro Lett.* **2014**, *3*, 872–875.

Table S1. OPV performance of TTI:PCBM

p:n	Solvent	Additive ^a	Anneal	L / nm	PCE / %	V _{oc} / V	J _{sc} / mA cm ⁻²	FF
1:1	CB	DIO	-	80	0.60	0.56	2.83	0.38
1:2	CB	DIO	-	120	0.08	0.19	1.37	0.30
1:2	CB	DIO	-	60	0.12	0.22	1.73	0.31
1:2	CB	DIO	50 °C ^b	80	0.58	0.63	1.67	0.55
1:3	CB	DIO	-	100	0.12	0.29	1.22	0.35
1:3	CB	DIO	50 °C ^b	110	0.25	0.53	0.98	0.48

^a 1,8-Diiodooctane (DIO) was added as additive with 3 v/v % for all devices. Thermal annealing proceeded for ^b10 min. The highest performance is highlighted.

Table S2. OPV performance of TT2:PCBM

p:n	Solvent	Additive ^a	Anneal	<i>L</i> / nm	PCE / %	<i>V</i> _{oc} / V	<i>J</i> _{sc} / mA cm ⁻²	FF
1:1	CB	DIO	-	100	3.31	0.59	9.73	0.58
1:1.5	CB	DIO	-	110	2.73	0.56	9.04	0.54
1:1.5	CB	DIO	120 °C ^c	100	2.55	0.62	7.14	0.58
1:1.5	CB	DIO	160 °C ^c	100	1.26	0.60	4.07	0.52
1:2	CB	DIO	-	110	3.33	0.58	8.59	0.67
1:2	CB	DIO	-	70	2.14	0.58	5.93	0.62
1:2	CB	DIO	150 °C ^b	200	0.97	0.65	2.42	0.62
1:3	CB	DIO	-	50	2.27	0.60	5.64	0.67
1:3	CB	DIO	150 °C ^b	110	0.87	0.64	2.04	0.66

^a DIO was added with 3 v/v % for all devices. Thermal annealing proceeded for ^b10 min and ^c1 min. The highest performance is highlighted.

Table S3. OPV performance of **BTI:PCBM**.

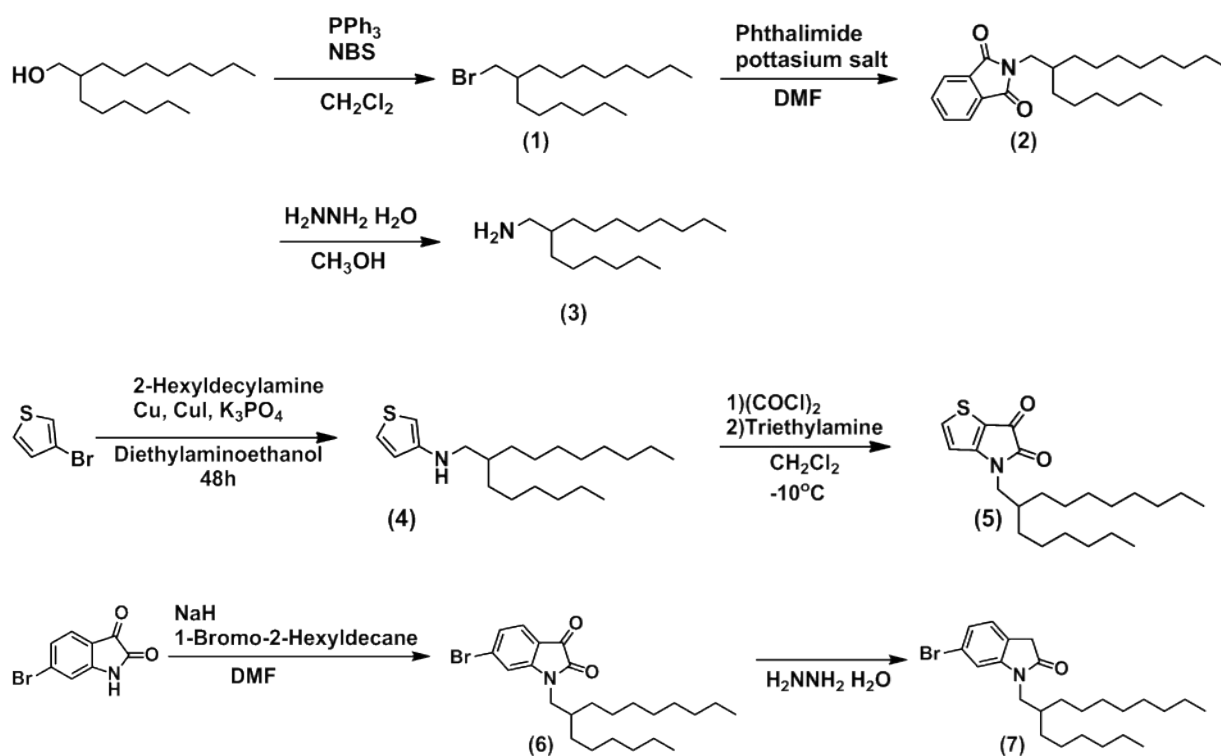
p:n	Solvent	Additive ^a	Anneal	<i>L</i> / nm	PCE / %	<i>V</i> _{oc} / V	<i>J</i> _{sc} / mA cm ⁻²	FF
1:1	CB	DIO	-	50	1.61	0.74	4.26	0.51
1:2	CB	DIO	-	120	2.96	0.72	7.38	0.56
1:3	CB	DIO	-	80	3.29	0.74	6.72	0.67
1:3	CB	DIO	50 °C ^b	80	3.03	0.75	7.31	0.55
1:3	CB	DIO	120 °C ^b	90	1.66	0.76	5.42	0.40
1:3	<i>o</i> DCB	DIO	-	100	2.71	0.72	7.00	0.54
1:3	<i>o</i> DCB	DIO	50 °C ^b	110	2.59	0.74	6.96	0.50
1:3	<i>o</i> DCB	DIO	120 °C ^b	110	1.95	0.74	5.79	0.45
1:5	CB	DIO	-	190	2.91	0.72	8.44	0.48
1:5	CB	DIO	-	120	3.25	0.73	7.35	0.61

^a DIO was added with 3 v/v % for all devices. Thermal annealing proceeded for ^b10 min. The highest performance is highlighted.

Table S4. OPV performance of **BT2:PCBM**

p:n	Solvent	Additive ^a	Anneal	L / nm	PCE / %	V_{oc} / V	J_{sc} / mA cm ⁻²	FF
1:1	CB	DIO	-	600	1.29	0.61	6.70	0.31
1:2	CB	CN	-	90	3.74	0.62	9.01	0.66
1:2	CB	CN	-	120	3.50	0.61	9.49	0.60
1:2	CB	DIO	80 °C ^c	700	2.24	0.61	9.67	0.38
1:2	CB	DIO	120 °C ^c	600	1.97	0.66	7.07	0.42
1:3	CB	DIO	-	250	3.34	0.62	12.15	0.44
1:5	CB	DIO	-	130	3.03	0.61	7.47	0.66
1:2 (PC ₇₁ BM)	CB	DIO	-	320	4.01	0.60	13.56	0.49
1:2 (PC ₇₁ BM)	CB	DIO	-	90	4.18	0.62	10.07	0.67

^a DIO or 1-chloronaphthalene(CN) was added with 3 v/v % for all devices. Thermal annealing proceeded for ^c1 min. The highest performance is highlighted.



Scheme S1. Synthesis procedure of BTIDG unit.

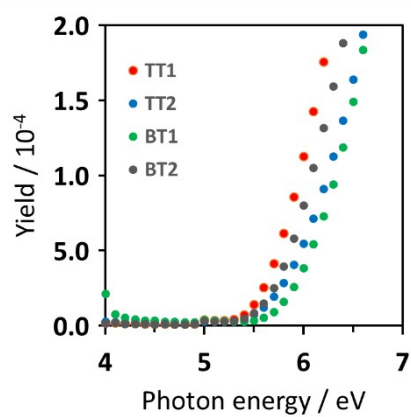


Fig. S1. Profiles of photoelectron yield spectroscopy (PYS) of drop-casted films of **TT1** (red), **TT2** (blue), **BT1** (green) and **BT2** (gray).

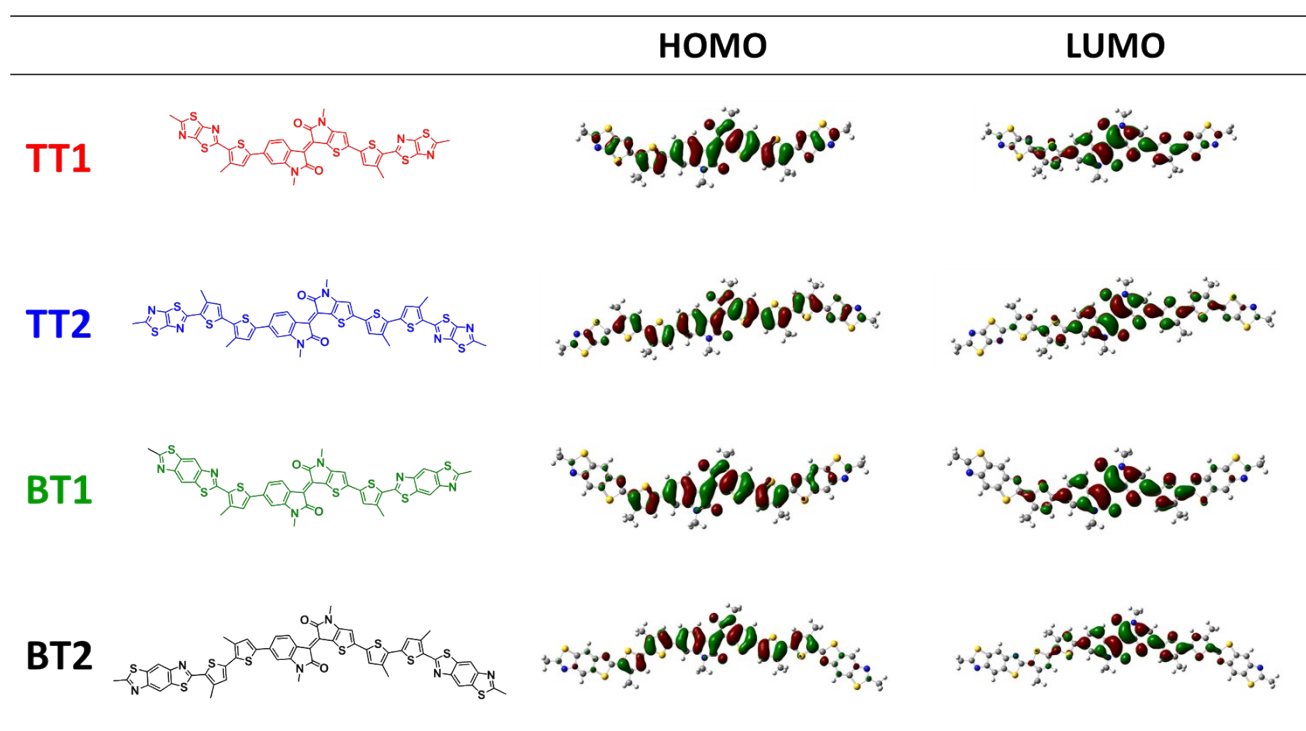


Fig. S2. Molecular orbitals of BTIDG trimers optimized by DFT B3LYP/6-31G(d). The alkyl chains are replaced with methyl groups for simplicity.

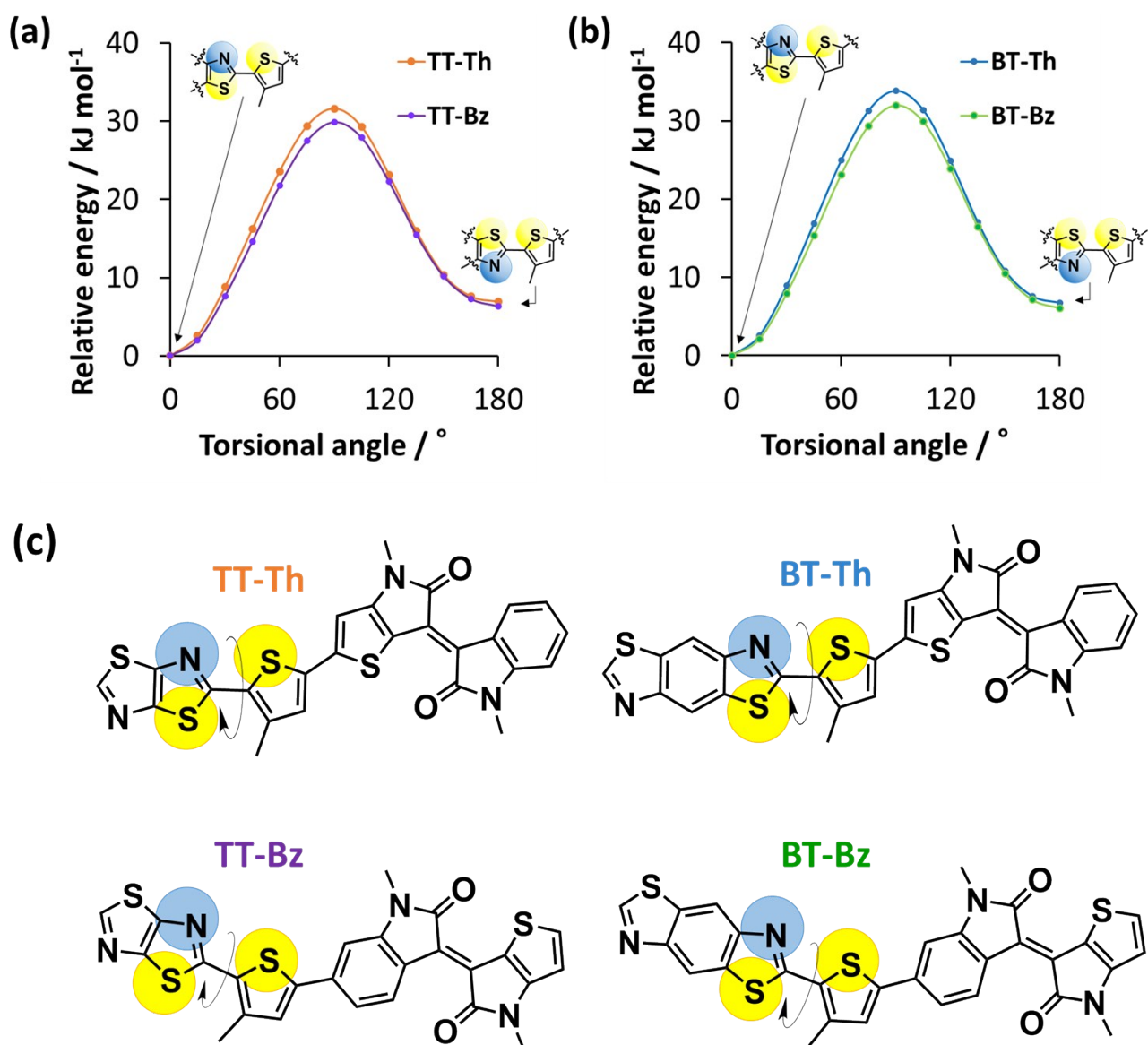


Fig. S3. Torsional energy potential profiles of neutral states of (a) TzTz-BTIDG and (b) BBTz-BTIDG dimers. Two isomers for each dimer, benzene-side or thiophene-side coupling, were examined as illustrated in (c), because BTIDG moiety is asymmetric structure. However, the difference among the isomers was negligible. The molecular geometry were optimized by DFT calculation using B3LYP/6-31G* level. The alkyl chains were replaced by methyl group for simplicity. The donor unit (TT or BT) was rotated along the arrowed bond.

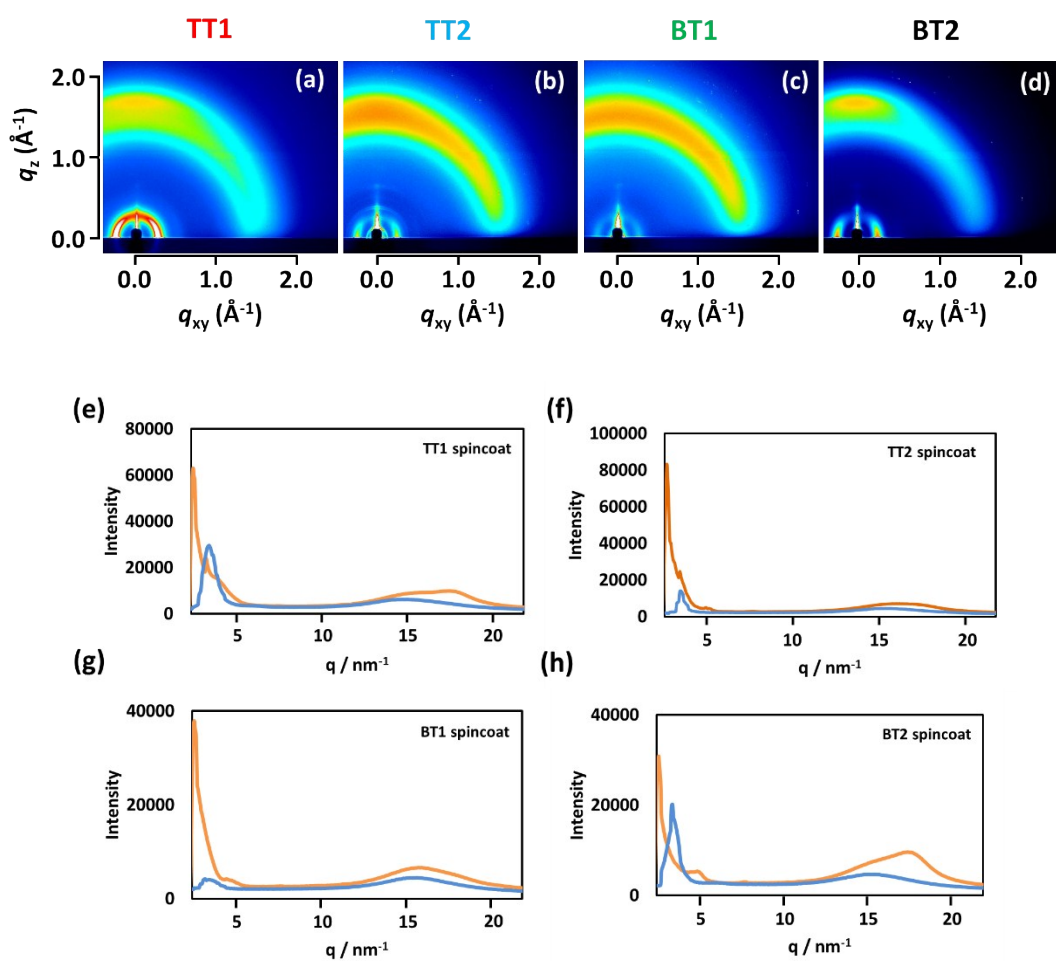


Fig. S4. 2D-GIXRD patterns (a-d) and profiles (e-h) of spun-coat pristine BTIDG polymers. Blue and orange lines are in-plane and out-of-plane diffractions, respectively.

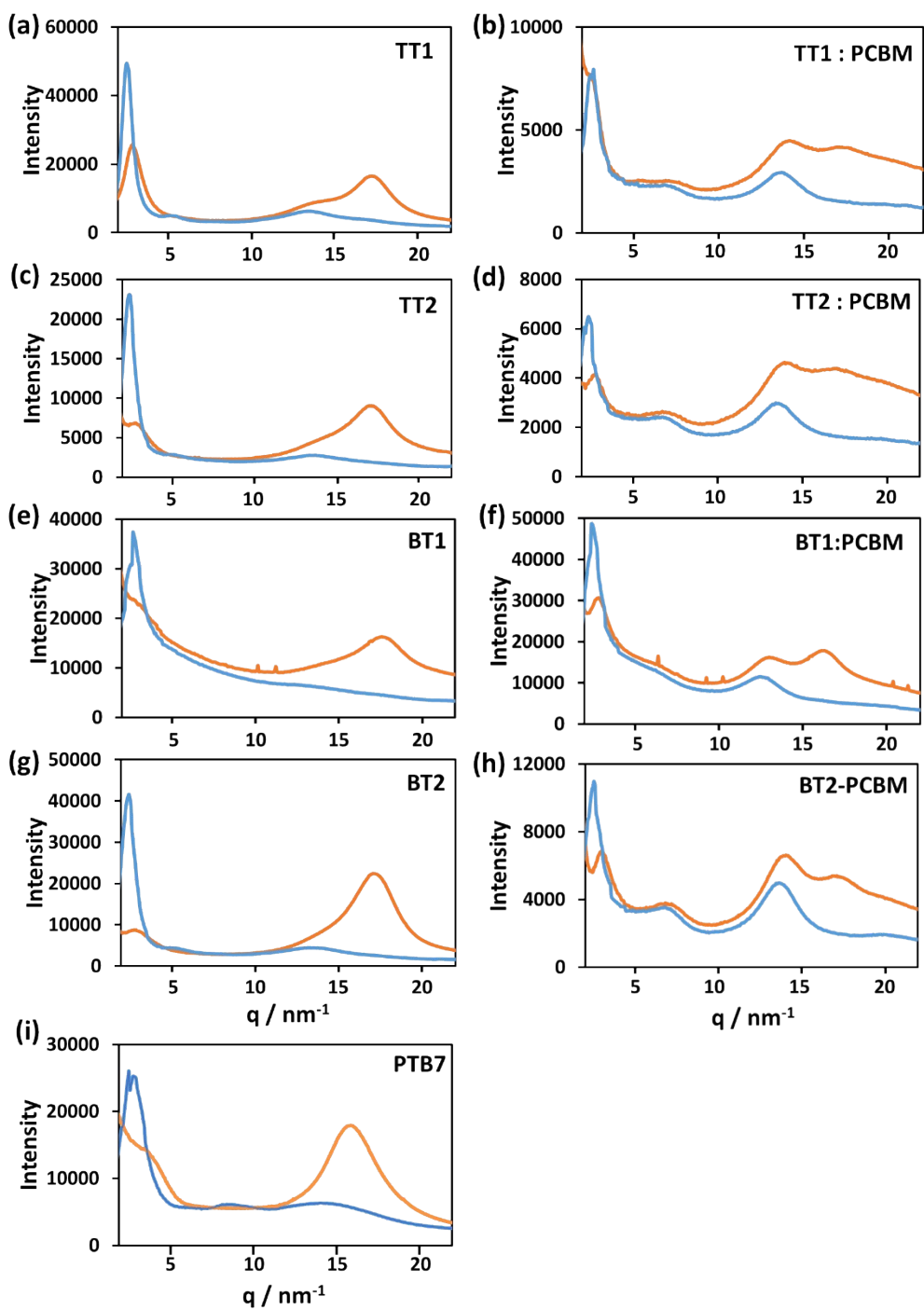


Fig. S5. 2D-GIXRD profiles of BTIDG polymers (left panel) and their blends with PC₆₁BM (right panel). Blue and orange lines are in-plane and out-of-plane diffractions, respectively. The profile of pristine PTB7 was extracted from the reference given by courtesy of Dr. K. Tajima at RIKEN, Japan.^{S4}

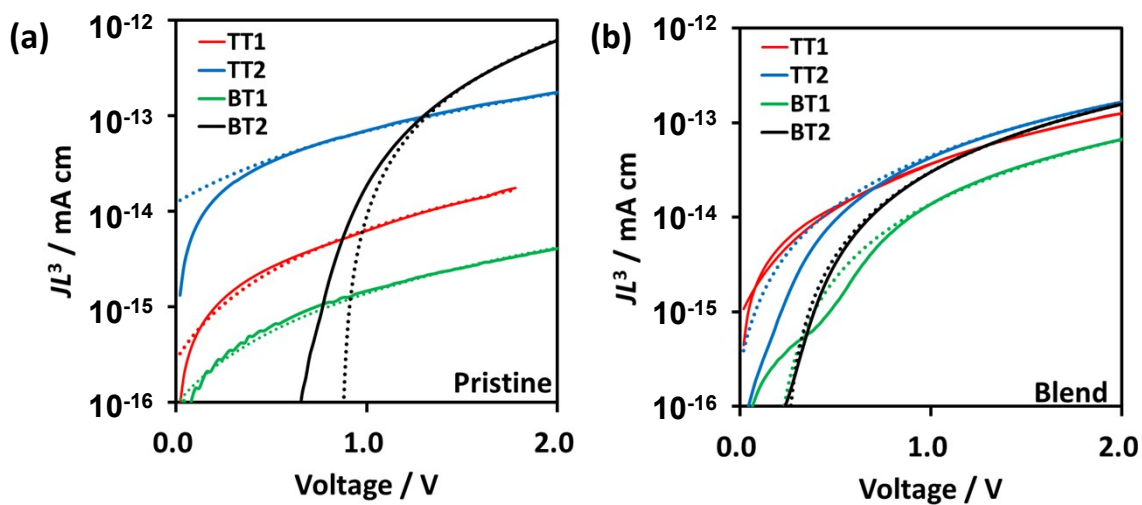


Fig. S6. J - V curves of hole only devices measured by SCLC for (a) pristine and (b) blend films. The solid and dotted lines are experimental and fitting curves, respectively. The film thicknesses are TT1 (40 nm), TT2 (70 nm), BT1 (290 nm), BT2 (350 nm), TT1:PCBM (80 nm), TT2:PCBM (130 nm), BT1:PCBM (120 nm), and BT2:PCBM (120 nm).

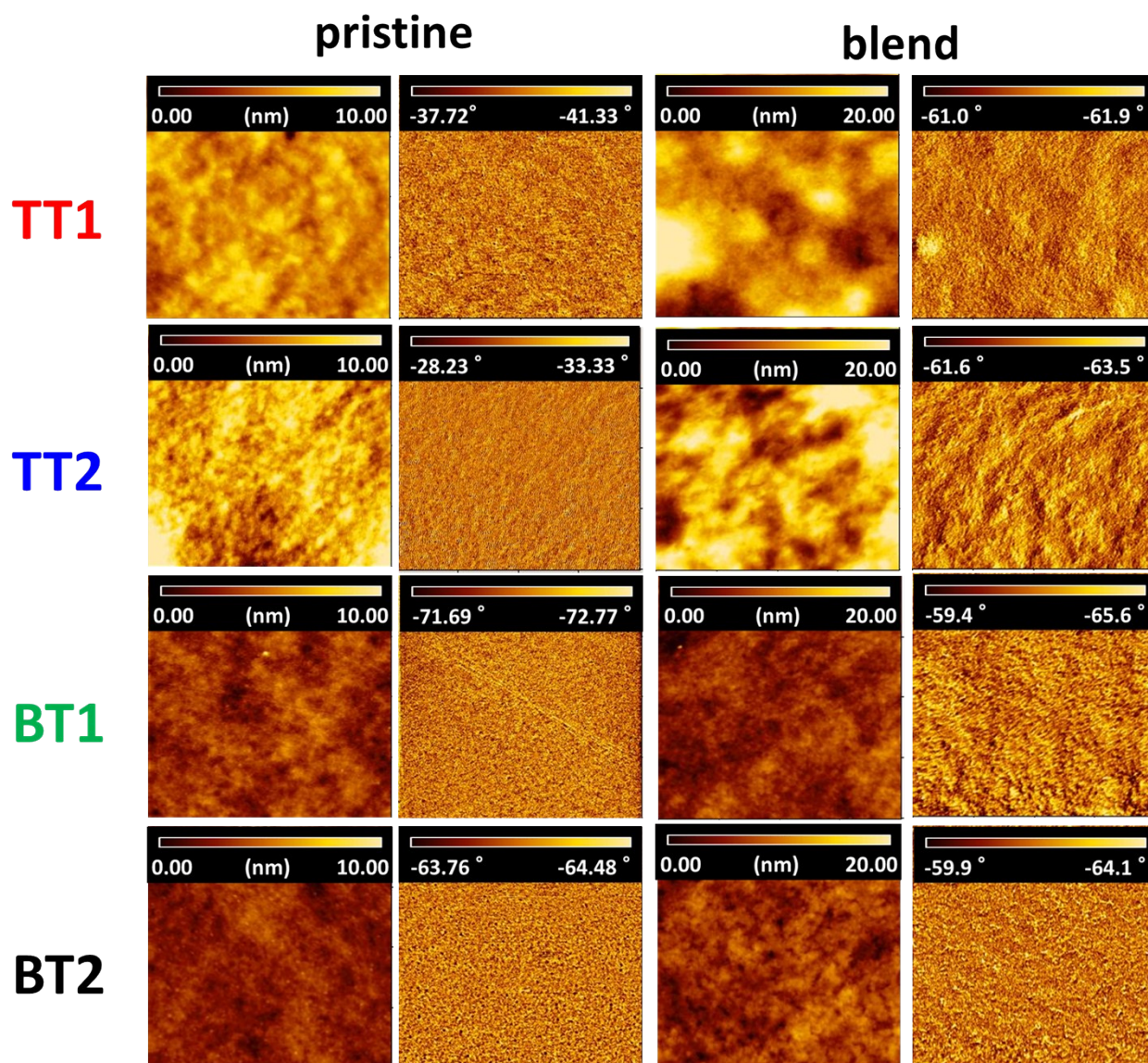


Fig. S7. AFM topology (left column) and phase (right column) images ($2 \times 2 \mu\text{m}$) of pristine films of BTIDG polymers and blend films with PC₆₁BM as photovoltaic devices. No thermal annealing proceeded and devices were fabricated with 3 % DIO additives.