

Crystallinity modulation of donors by heteroatom side-chains engineering approaching 14.3% all-small-molecule organic solar cells

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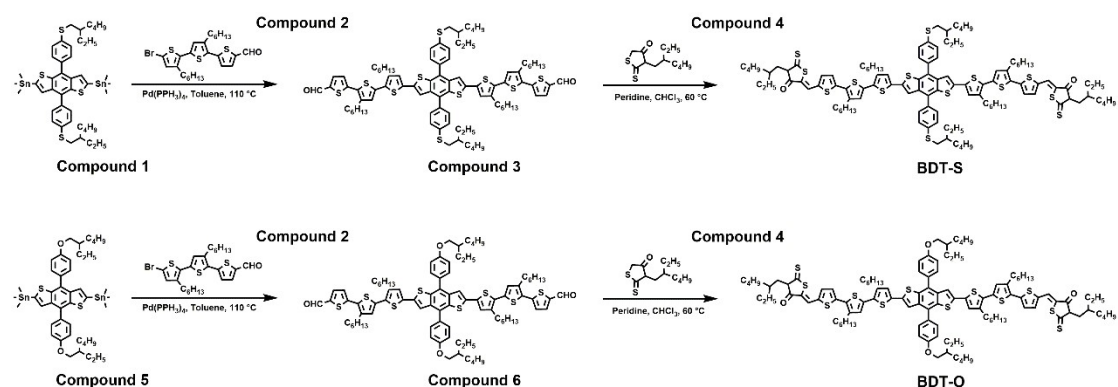
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Compound 1, 2, 4, 5, Y6-BO were purchased from Solarmer Materials Inc. Toluene, chloroform and piperidine were obtained Sinopharm Chemical Reagent Co., Ltd. Pd(PPh₃)₄ was commercially available from Energy Chemical. All the solvents, materials were used without further purification.

Synthetic route

The synthetic route for BDT-S, BDT-O were showed in scheme 1, and the detailed synthesis procedures are exhibited below.



Scheme 1. The synthetic route of BDT-S and BDT-O

Synthesis of **compound 3** (5'',5''''-(4,8-bis(4-((2-ethylhexyl)thio)phenyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3'''-dihexyl-[2,2':5',2'']-terthiophene)-5-carbaldehyde))

First the reaction device was ventilated three times by using argon gas cylinder and oil pump, and then **compound 1** ((4,8-bis(4-((2-ethylhexyl)thio)phenyl) benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane), 0.9566 g, 1.0 mmol), Pd(PPh₃)₄ (0.1156 g, 0.1 mmol), **compound 2** (5''-bromo-3',3'''-dihexyl-[2,2':5',2'']-terthiophene)-5-carbaldehyde, 1.5708 g, 3.0 mmol) and 30 mL dry toluene were sequentially added in the 100 mL round bottom flask. The mixed solution was stirred and refluxed for 12 hours in the dark at 110 °C. The reacted crude product is post-treated and purified by column chromatography, wherein the eluent ratio is petroleum ether: dichloromethane = 1: 1.5. After purification, a red solid (0.8056 g, ~53% yield) was obtained. ¹H NMR (400 MHz, Chloroform-d) δ 9.88 (s, 2H), 7.70 (d, J = 4.0 Hz, 2H), 7.62 (d, J = 8.3 Hz, 4H), 7.53 (d, J = 8.3 Hz, 4H), 7.31 (s, 2H), 7.22 (d, J = 4.0 Hz, 2H), 7.06 (s, 2H), 6.99

(s, 2H), 3.07 (d, $J = 6.3$ Hz, 4H), 2.83 – 2.72 (m, 8H), 1.69 (d, $J = 39.4$ Hz, 10H), 1.37 (d, $J = 46.5$ Hz, 40H), 0.94 (d, $J = 33.4$ Hz, 24H).

Synthesis of **BDT-S** 2,2'-(((4,8-bis(4-((2-ethylhexyl)thio)phenyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5'-diyl))bis(methanylylidene))bis(4-(2-ethylhexyl)-5-thioxodihydrothiophen-3(2H)-one) **Compound 3** (0.3032 mg, 0.2mmol) and **compound 4** (4-(2-ethylhexyl)-5-thioxodihydrothiophen-3(2H)-one, 0.4908 g, 2.0 mmol) were dissolved in dry CHCl_3 (30 mL) under an argon atmosphere. Then six drops of piperidine were added in the mixed solution. The reaction mixture was stirred and refluxed 10 hours in 65°C . After post-treated procedure, the crude product were purified by column chromatography, wherein the eluent ratio is petroleum ether: dichloromethane = 3:1. After purification, a black solid (0.2534 g, ~64% yield) was obtained. ^1H NMR (400 MHz, Chloroform- d) δ 7.83 (s, 2H), 7.63 (d, $J = 8.3$ Hz, 4H), 7.53 (d, $J = 8.3$ Hz, 4H), 7.36 (d, $J = 4.1$ Hz, 2H), 7.31 (s, 2H), 7.20 (d, $J = 4.1$ Hz, 2H), 7.06 (s, 2H), 6.99 (s, 2H), 4.03 (d, $J = 7.2$ Hz, 4H), 3.08 (d, $J = 6.3$ Hz, 4H), 2.78 (dt, $J = 23.4, 7.9$ Hz, 8H), 2.10 – 2.04 (m, 2H), 1.76 – 1.62 (m, 10H), 1.52 – 1.25 (m, 57H), 0.94 (dq, $J = 26.9, 7.1$ Hz, 36H). MALDI-TOF MS: calculated for $\text{C}_{112}\text{H}_{142}\text{O}_2\text{S}_{14}$ (M^+), 1969.2; found, 1969.7.

Synthesis of **compound 6** (5'',5''''-(4,8-bis(4-((2-ethylhexyl)oxy)phenyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'-carbaldehyde))

Compound 6 was synthesized as similar as the synthesis method of compound 3 mentioned before, and a red solid was obtained (0.2551 g, ~50 %). ^1H NMR (400 MHz, Chloroform- d) δ 9.88 (s, 2H), 7.70 (s, 2H), 7.64 (d, $J = 8.5$ Hz, 4H), 7.34 (s, 2H), 7.22 (d, $J = 4.0$ Hz, 2H), 7.14 (d, $J = 8.5$ Hz, 4H), 7.06 (s, 2H), 6.99 (s, 2H), 3.99 (d, $J = 5.7$ Hz, 4H), 2.77 (dt, $J = 26.8, 7.9$ Hz, 8H), 1.85 – 1.78 (m, 2H), 1.71 – 1.63 (m, 8H), 1.44 – 1.27 (m, 40H), 1.03 – 0.89 (m, 24H).

Synthesis of **BDT-O** (2,2'-(((4,8-bis(4-((2-ethylhexyl)oxy)phenyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl))bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5'-diyl))bis(methanylylidene))bis(4-(2-ethylhexyl)-5-thioxodihydrothiophen-3(2H)-one)) **BDT-O** was synthesized as similar as the synthesis method of BDT-S mentioned before, and a red solid was obtained (0.1432g, ~62 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.82 (s, 2H), 7.64 (d, *J* = 8.5 Hz, 4H), 7.36 – 7.31 (m, 4H), 7.19 (d, *J* = 3.9 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 4H), 7.05 (s, 2H), 6.98 (s, 2H), 4.01 (dd, *J* = 9.8, 6.6 Hz, 8H), 2.77 (dt, *J* = 24.7, 7.8 Hz, 8H), 2.07 (dt, *J* = 12.5, 5.7 Hz, 2H), 1.83 (dt, *J* = 12.1, 5.9 Hz, 2H), 1.67 (dq, *J* = 14.3, 7.4 Hz, 9H), 1.48 – 1.23 (m, 57H), 1.03 – 0.88 (m, 37H). MALDI-TOF MS: calculated for C₁₁₂H₁₄₂O₄S₁₂ (M⁺), 1937.1; found, 1938.6

Instruments and measurements

¹H NMR spectra was recorded on a Bruker AVANCE III 400MHz NMR spectrometer. Mass spectra were collected on a M-Discover100 Excellence matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The UV-vis absorption spectra were measured by Perkin-Elmer Lambda 950 spectrophotometer. Photoluminescence (PL) spectra were recorded on fluorescence spectrometer FL3-111. Cyclic voltammetry was obtained from an electrochemical workstation (CHI660C). Keithley 2440 sourcemeter with a solar simulator (Newport-Oriel® Sol3A 450W) were used to do the current-voltage (J-V) (under AM 1.5 G irradiation) and electrical conductivity test (under dark), and the simulated solar light was calibrated by a standard Si solar cell. The surface morphology of the films was investigated by a Dimension ICON microscope (AFM), Hitachi SU8230 (SEM) and Talos F200X transmission electron microscopy (TEM). The GIWAXS was measured in National Center for Nanoscience and Technology. Femtosecond transient absorption spectroscopy were measured by SOL-F-K-HP-T in 800 nm.

Device fabrication

The ASM-OSC device was fabricated by the conventional structure of ITO/PEDOT: PSS/BDT-S: Y6-BO or BDT-O: Y6-BO/PDINO/Al. ITO glass sheets were cleaned sequentially with detergent, ultrapure water, acetone and isopropanol in ultrasound. Next, the ITO glass was plasma surface treated. the ITO glass was spin coated at 3000

rpm with PEDOT: PSS aqueous solution (Clevios P VPA1 4083) for 1 min, and then annealing at 130 °C for 20min. The annealed ITO glass was transferred to a glove box filled with nitrogen. Chloroform solution containing donor and acceptor was spin-coated on the PEDOT: PSS layer at 2000 rpm for 1min. The total concentration was 20 mg/ml and D/A ratio was kept as 1:1. The DIO additive was added at a rate of 0.25% of the solvent volume. The TA treatment was performed through heating the substrate at 100° for 10 minutes. After finishing the annealing, PDINO (1.5mg/ml in ethanol solution) was spin-coated on the active layer at 3000 rpm for 1min. Finally, Al was deposited for ca. 100 nm. Photovoltaic properties of the devices were measured under simulated solar light (100 mW cm⁻² AM 1.5G) provided by a Newport-Oriel® Sol3A 450W solar simulator, and the mask area is 4 mm².

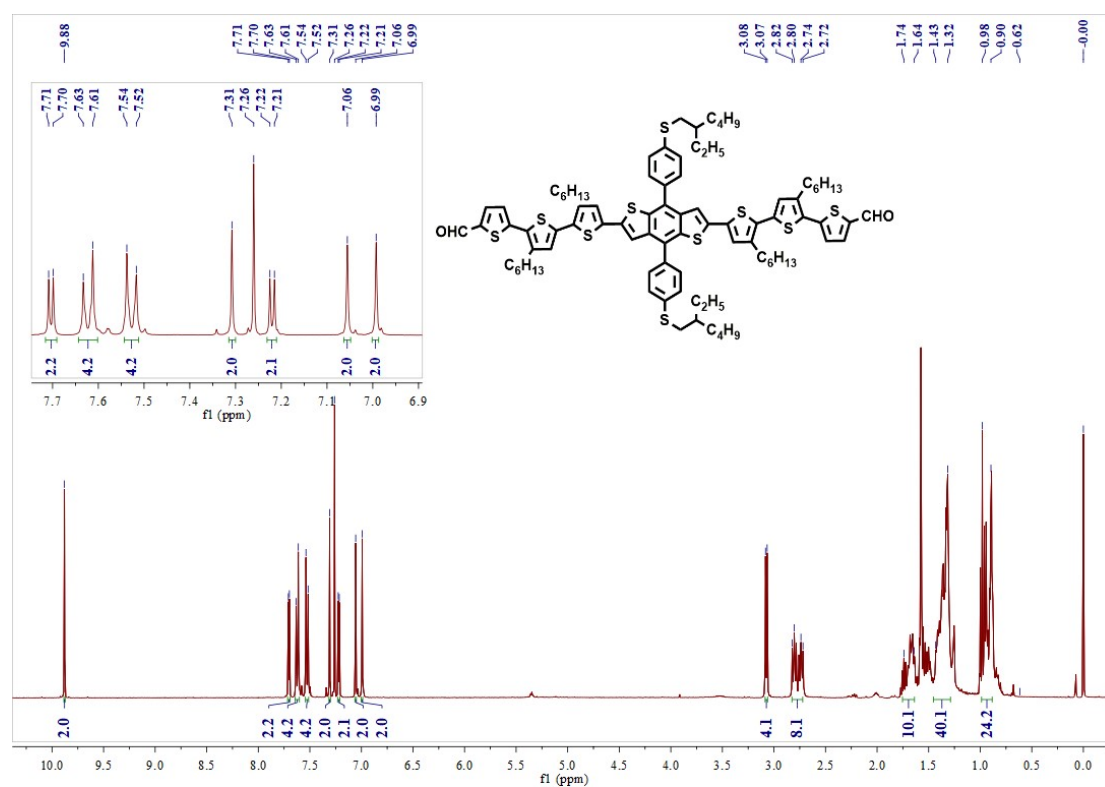


Fig. S1 ¹H NMR spectra of compound 3 in CDCl₃

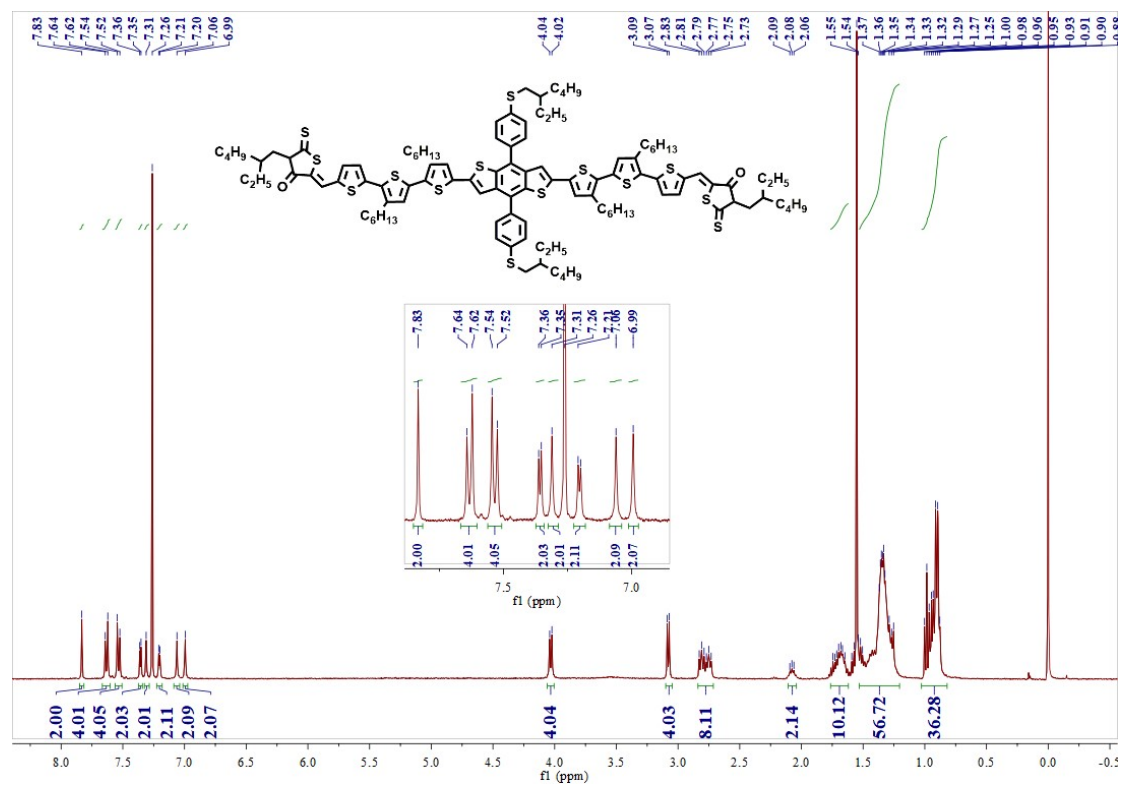


Fig. S2 ¹H NMR spectra of BDT-S in CDCl₃

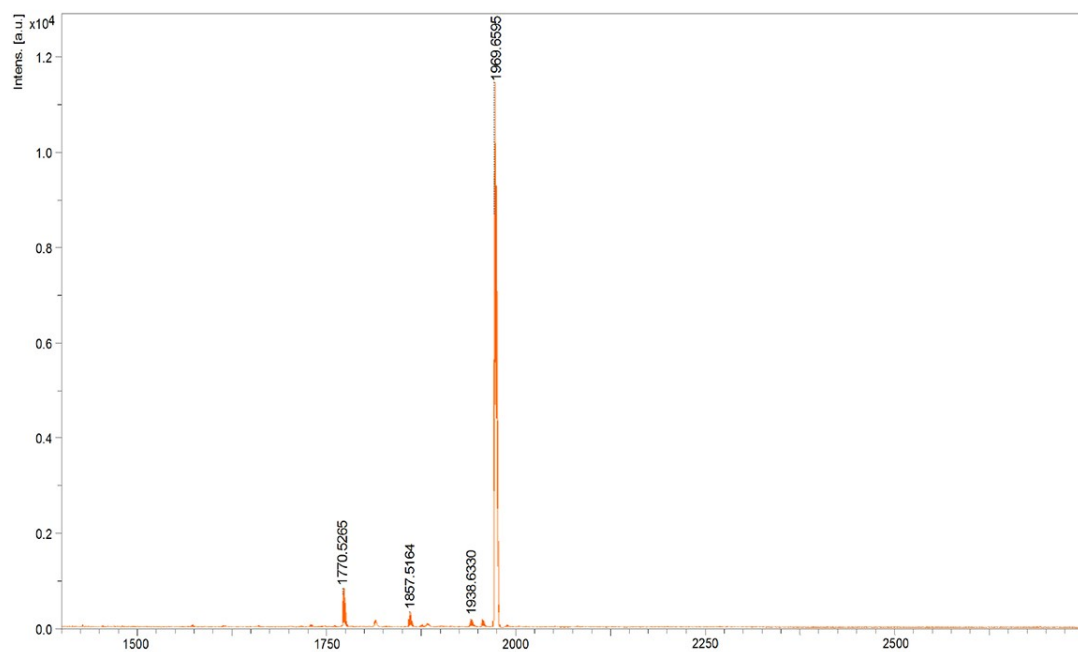


Fig. S3 MALDI-TOF-MS of BDT-S

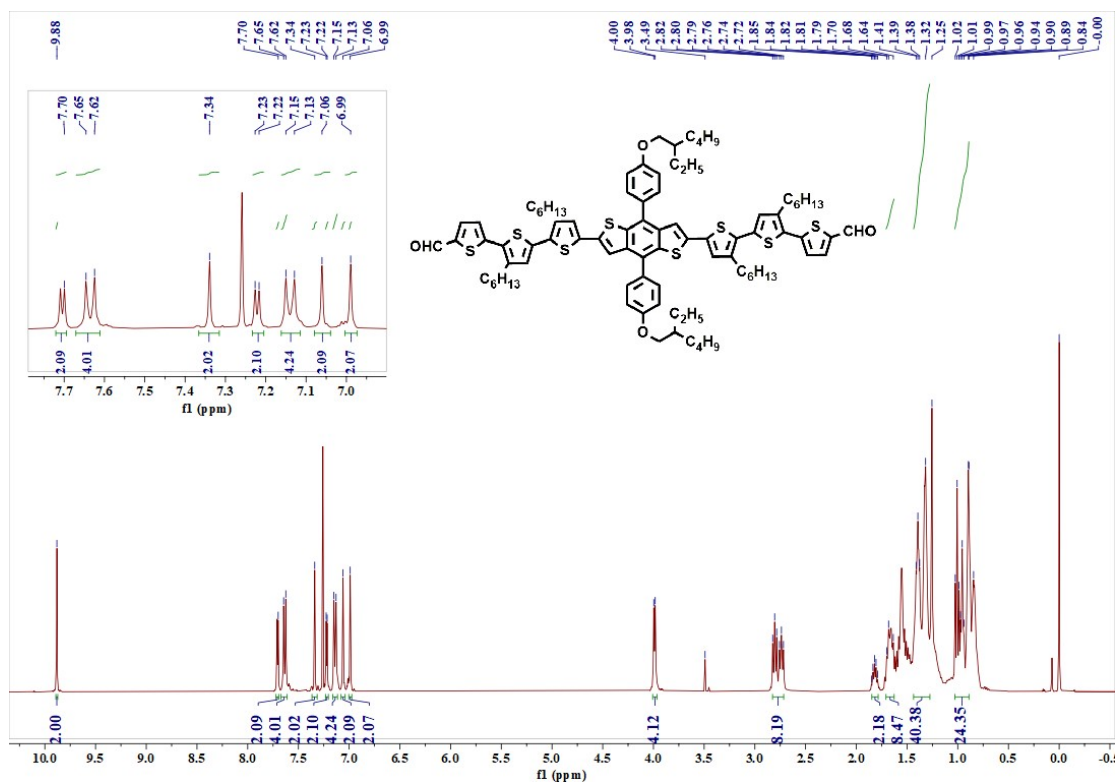


Fig.S4 ¹H NMR spectra of compound 6 in CDCl₃

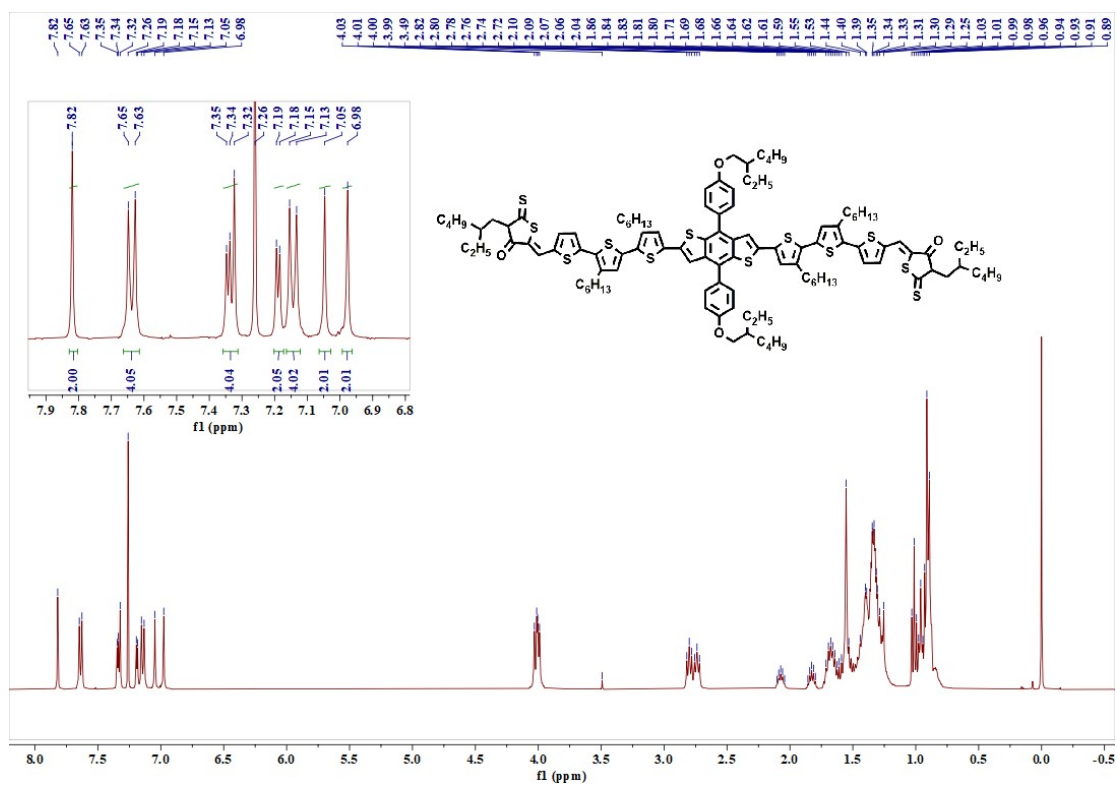


Fig.S5 ¹H NMR spectra of BDT-O in CDCl₃

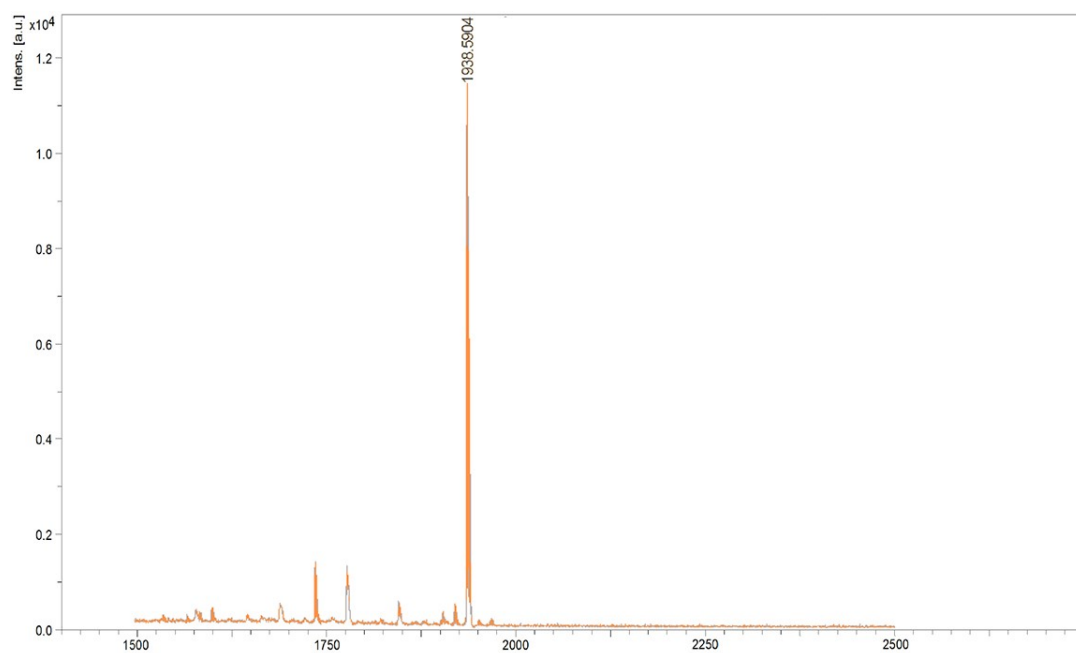


Fig.S6 MALDI-TOF-MS of BDT-O

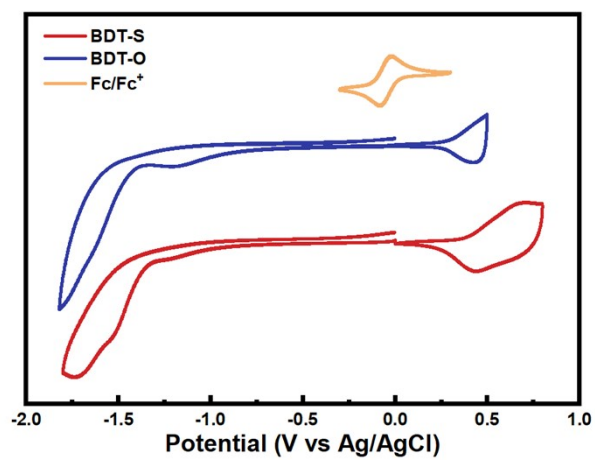


Fig. S7 Electrochemical cyclic voltammograms of BDT-S film, BDT-O film and ferrocene on the glassy carbon electrode in 0.1 mol L⁻¹ Bu₄NPF₆ acetonitrile solution

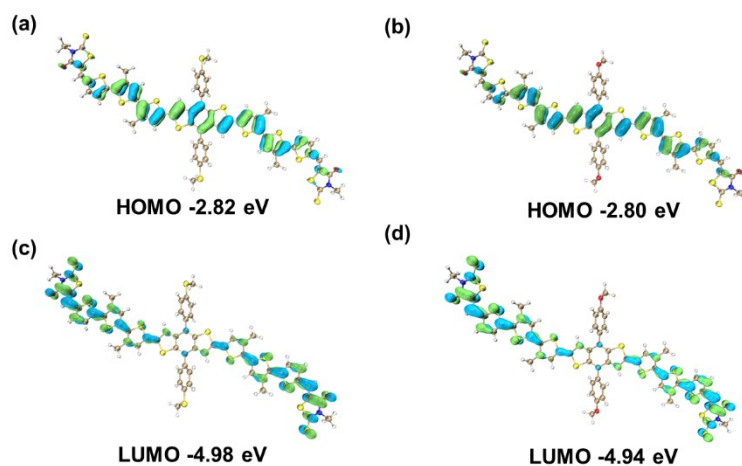


Fig. S8 DFT-optimized molecular geometries with HOMO and LUMO electron distribution of BDT-S and BDT-O.

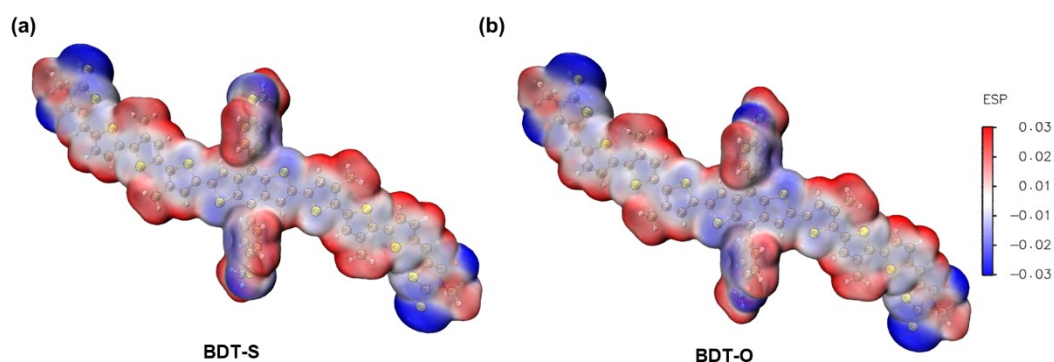


Fig. S9 The electrostatic potential distribution of (a) BDT-S and (b) BDT-O.

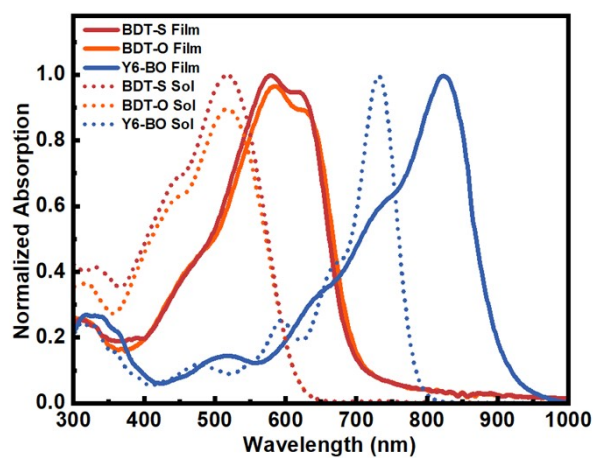


Fig. S10 The UV-visible absorption spectra of small molecule donors BDT-S and BDT-

O and non-fullerene acceptor Y6-BO in chloroform solution and solid film.

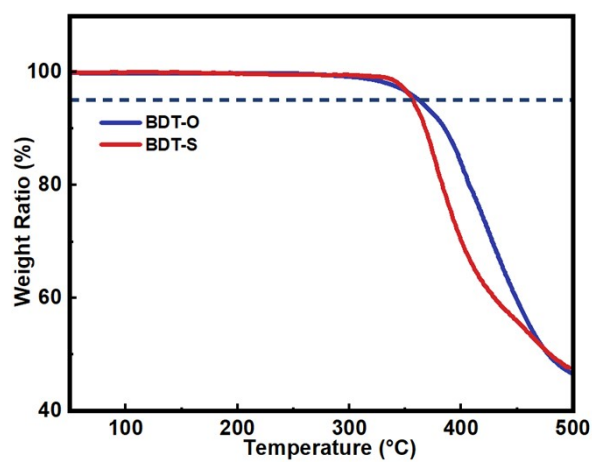


Fig. S11 The TGA curve of BDT-S and BDT-O at a scan rate of 10 °C min⁻¹ under nitrogen atmosphere.

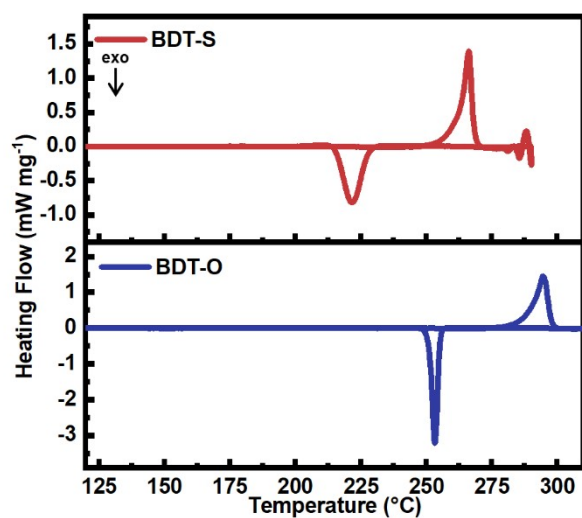


Fig. S12 DSC thermograms of BDT-S and BDT-O at a rate of 10 °C min⁻¹ under nitrogen atmosphere.

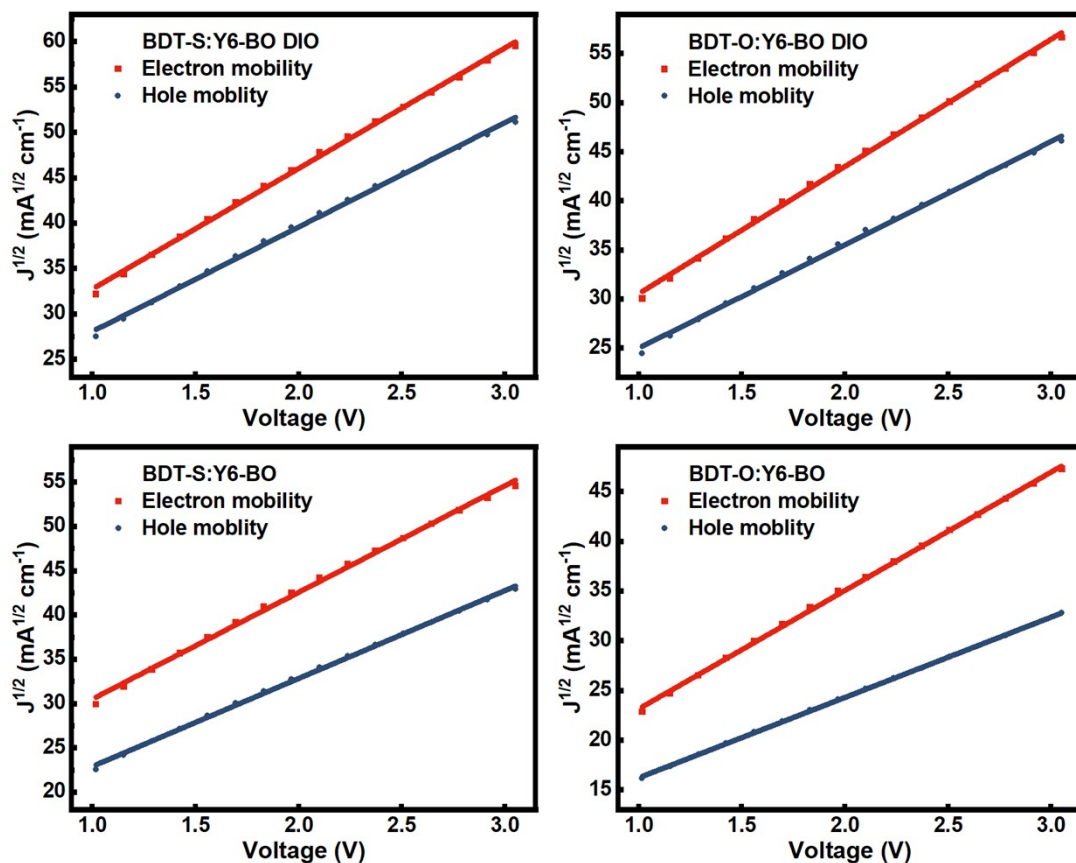


Fig. S13 $J_{1/2}$ - V characteristics for hole-only and electron-only devices.

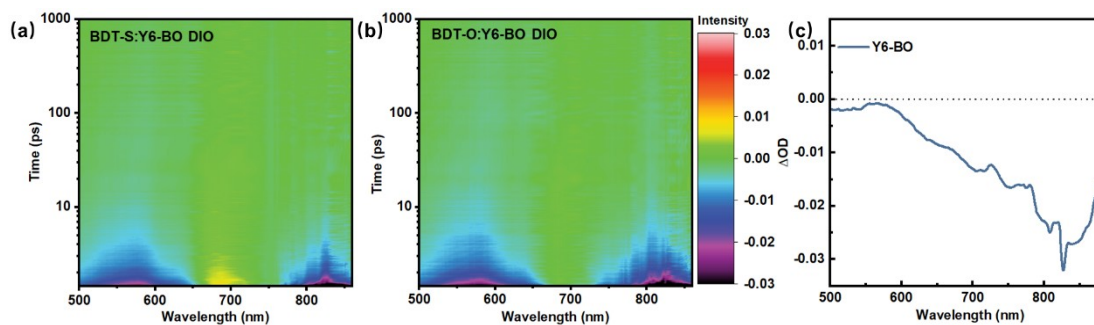


Fig. S14 2D data of the (a) BDT-S:Y6-BO and (b) BDT-O:Y6-BO blend films with the DIO additive pumped at 800 nm. (c) Corresponding TA spectra of Y6-BO at 3 ps delays.

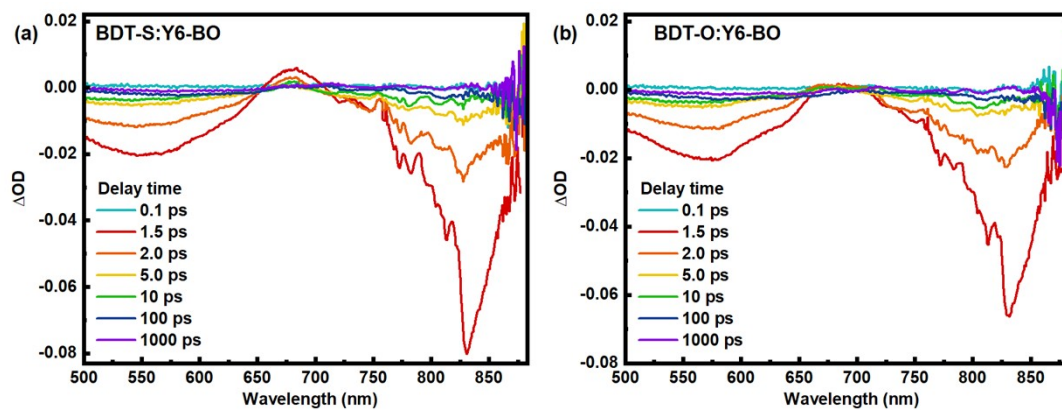


Fig. S15 Corresponding TA spectra of (a) BDT-S:Y6-BO and (b) BDT-O:Y6-BO blend films with TA treated at different delay time.

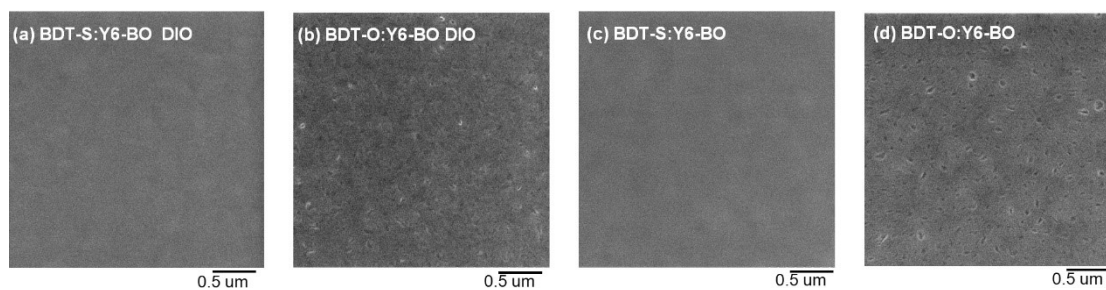


Fig. S16 SEM images of two post-treatment methods of BDT-S:Y6-BO and BDT-O:Y6-BO blend film.

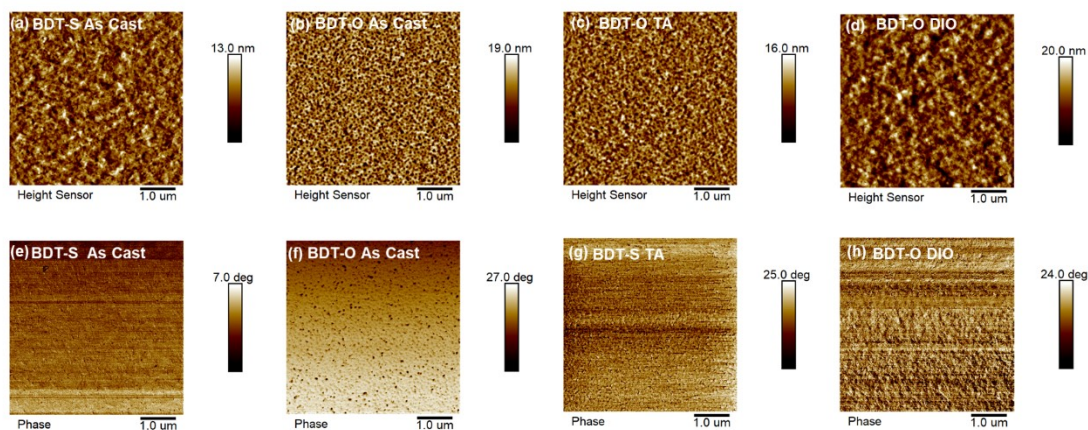


Fig. S17 AFM diagrams of (a) BDT-S As Cast, (b) BDT-O As Cast, (c) BDT-O TA and (d) BDT-O DIO.

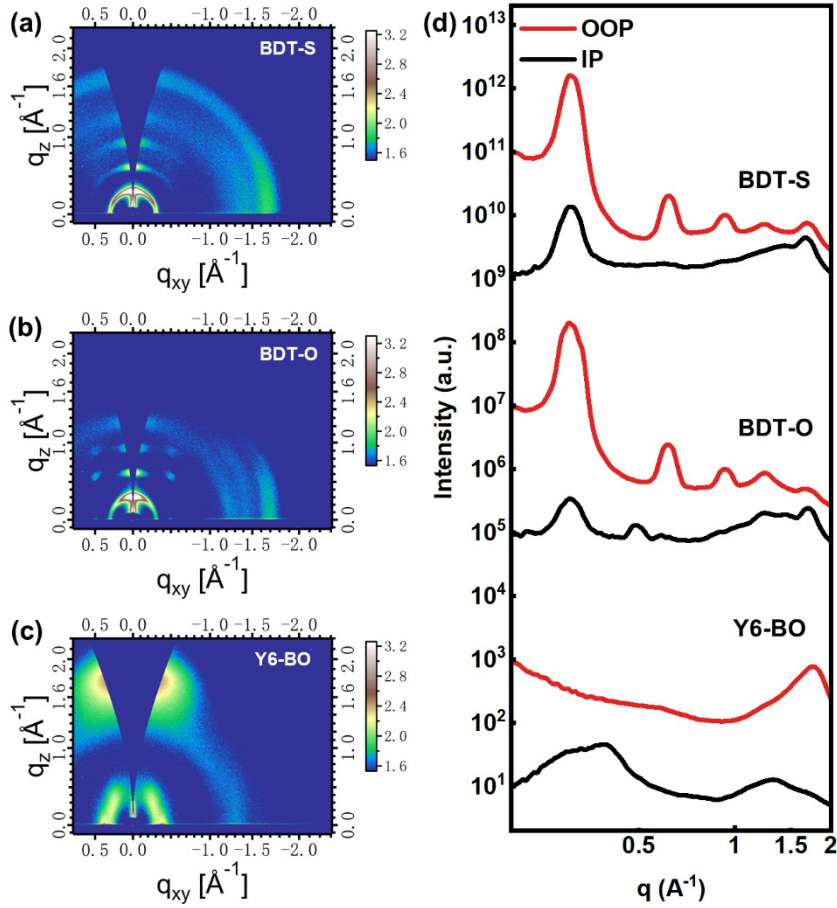


Fig. S18 2D GIWAXS patterns of (a)BDT-S and (b) BDT-O and (c) Y6-BO. (d) 1D GIWAXS of BDT-S, BDT-O and Y6-BO films under IP and OOP directions.

Table S1 The photovoltaic parameters of four devices.

Active layers	Condition	μ_e	μ_h	μ_e/μ_h	η_{diss} (%)	η_{coll} (%)	α	n
		($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)					
BDT-S:Y6-BO	DIO+TA	6.13	4.60	1.33	95.0	85.0	0.99	1.06
BDT-O:Y6-BO	DIO+TA	5.85	3.86	1.51	93.0	79.0	0.98	1.11
BDT-S:Y6-BO	TA	5.05	3.42	1.47	84.0	62.5	0.96	1.16
BDT-O:Y6-BO	TA	4.93	2.27	2.17	76.0	61.6	0.93	1.18

Table S2 The key GIWAXS data for BDT-S, BDT-O, Y6-BO, and blend films at the IP orientation.

Materials	100 (nm)	200 (nm)	300 (nm)	400 (nm)	CCLs of d-spacing (nm)
BDT-S (IP)	2.80 (0.302 Å ⁻¹)	1.00 (0.625 Å ⁻¹)	0.67 (0.935 Å ⁻¹)	0.51 (1.233 Å ⁻¹)	17.7
BDT-O (IP)	2.80 (0.302 Å ⁻¹)	1.00 (0.625 Å ⁻¹)	0.67 (0.935 Å ⁻¹)	0.51 (1.233 Å ⁻¹)	13.7
Y6-BO (IP)	1.59 (0.396 Å ⁻¹)	/	/	/	8.9
BDT-S:Y6-BO DIO (IP)	2.07 (0.304 Å ⁻¹)	/	/	/	10.7
BDT-O:Y6-BO DIO (IP)	2.09 (0.298 Å ⁻¹)	/	/	/	9.7
BDT-S:Y6-BO (IP)	2.03 (0.309 Å ⁻¹)	/	/	/	9.6
BDT-O:Y6-BO (IP)	2.09 (0.300 Å ⁻¹)	/	/	/	5.6

Table S3 The key GIWAXS data for BDT-S, BDT-O, Y6-BO, and blend films at the OOP orientation.

Materials	010 (nm)	CCLs of π - π stacking (nm)
BDT-S (OOP)	0.38 (1.661)	2.6
BDT-O (OOP)	0.37 (1.687)	2.5
Y6-BO (OOP)	0.36 (1.752)	1.7
BDT-S:Y6-BO DIO (OOP)	0.367 (1.712)	3.2
BDT-O:Y6-BO DIO (OOP)	0.371 (1.695)	2.9
BDT-S:Y6-BO (OOP)	0.364 (1.724)	3.1
BDT-O:Y6-BO (OOP)	0.374 (1.679)	2.7

