

Supporting Information

Inside-fused Perylenediimide Dimers with Planar Structures for High-performance Fullerene-free Organic Solar Cells

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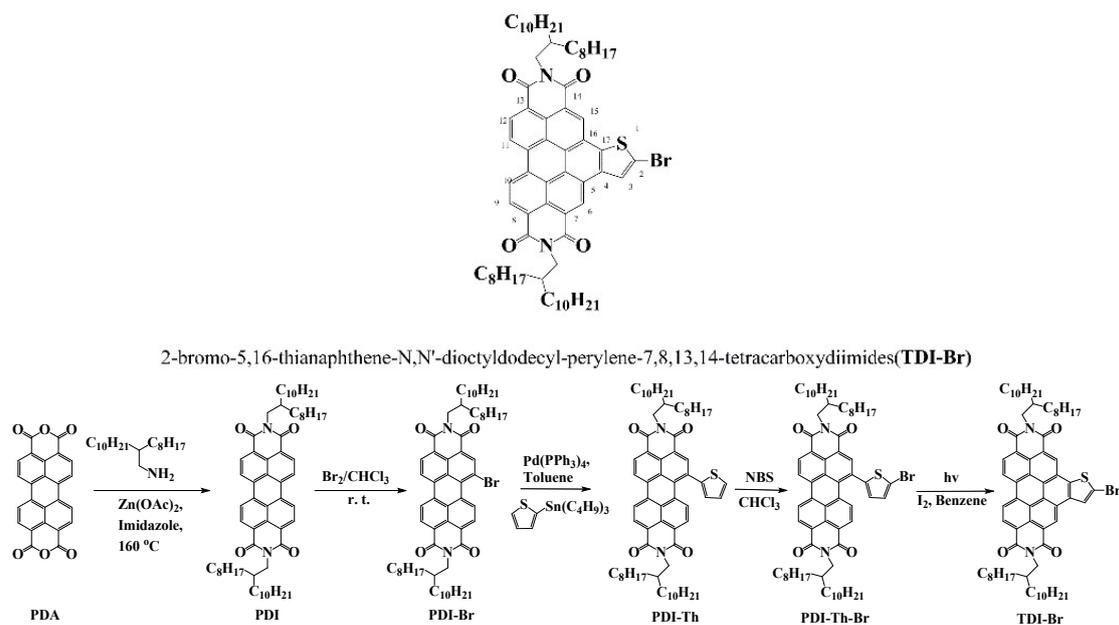
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Methods

All the chemicals were purchased from commercial suppliers and used as received without further treatment. Toluene was freshly distilled from sodium/benzophenoneketyl prior to use. ¹H NMR spectra was obtained using a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope in CDCl₃ with TMS as an internal standard. Chemical shifts for protons are referenced to tetramethylsilane (TMS, ¹H NMR: 0.00 ppm). UV-vis absorption measurements were carried out on Lambda950 UV-vis spectrophotometer (Perkin Elmer Instruments Co. Ltd, USA). Cyclic voltammetric (CV) measurements were carried out in a conventional three-electrode cell using a platinum plate as the working electrode, a platinum wire as the counter electrode, and an Ag/Ag⁺ electrode as the reference electrode on a electrochemical workstation (Mode CHI 600E) in a tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) acetonitrile solution at a scan rate of 100 mV s⁻¹. The height and phase images of blend films were obtained on a Veeco Dimension 3100 atomic force microscopy (AFM) in the tapping-mode

using an etched silicon cantilever. 2D GIWAXS measurements were conducted at the SPring-8 on beamline BL46XU with an X-ray energy of 12.39 keV ($\lambda = 1 \text{ \AA}$). The sample was irradiated at a fixed incident angle of 0.12° through a diffractometer (Huber), and the GIXD pattern was recorded with Pilatus 300 K 2D image detectors (Dectris).

Experimental section:



Scheme S1: The molecular structure of TDI-Br and the synthetic method.

Synthesis of PDI

PDI was synthesized according to literature methods [1]. Perylene-3,4,9,10-tetracarboxy dianhydride (PDA) (19.6 g, 50 mmol), 2-octyldodecan-1-amine (60.0 g, 150 mmol), zinc acetate (9.2 g, 50 mmol) and imidazole (120.0 g) were heated to 160 °C for 12 hours. The reaction mixture was cooled to room temperature and 10 % HCl was added. After being washed with methanol and water adequately, the filtrate was extracted with chloroform, dried with MgSO_4 . The product PDI was purified by recrystallization with chloroform and methanol as solvents (44.7 g, 94.0 %). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.56-8.50 (m, 4H), 8.41-8.37 (m, 4H), 4.11 (d, $J = 8.0$, 4H), 1.99 (m, 2H), 1.39-1.21 (m, 64H), 0.86-0.82 (m, 12H).

Synthesis of PDI-Br

PDI-Br was synthesized according to a modified previously reported method [2]. To a Schlenk tube charged with a solution of PDI (9.51 g, 10.0 mmol) in CH_2Cl_2 (700 mL), bromine (122 g) was added slowly in 2 h. After the reaction mixture was stirred at room temperature for 10 days, the organic mixture was dealt with Na_2SO_3 (aq.) and water sequentially. The organic phase was collected and dried over anhydrous Na_2SO_4 . After the solvents was removed under reduced pressure, the product was purified with

column chromatography over silica gel, eluted with chloroform to afford PDI-Br (4.33 g, 4.20 mmol, 42.0 %). ¹H NMR (400 MHz, CDCl₃): δ 9.77-9.75 (d, 1H), 8.88 (s, 1H), 8.68-8.66 (m, 3H), 8.56-8.54 (d, 2H), 4.15-4.11 (m, 4H), 2.00 (s, 2H), 1.39-1.22 (m, 64H), 0.86-0.83 (m, 12H).

Synthesis of PDI-Th

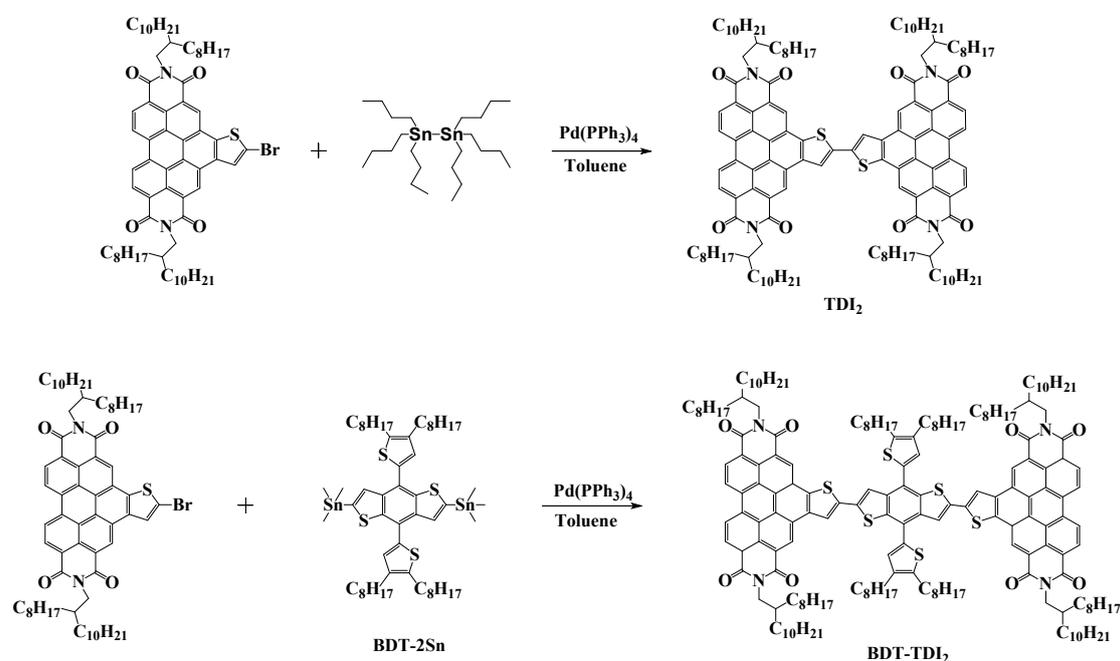
In an inert nitrogen atmosphere, PDI-Br (4.0 g, 3.9 mmol) and 2-(Tributylstanny)thiophene (1.53 g, 4.1 mmol) in dry toluene (150 ml) were added to Pd(PPh₃)₄ (300 mg) in a sealed flask. The mixture was stirred vigorously for 24 h at 110 °C. After cooling to room temperature, the reaction mixture was washed with saturated potassium fluoride and brine, dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated under reduced pressure, the crude product was purified by column chromatographically with DCM/petroleum ether (1:1), recrystallized from DCM /methanol, and dried under vacuum to afford PDI-Th (3.71 g, 92.0 %). ¹H NMR (400 MHz, CDCl₃): δ 8.54-8.46 (m, 3H), 8.37-8.32 (m, 2H), 8.13-8.11 (d, *J* = 8.0, 1H), 7.90-7.88 (d, *J* = 8.0, 1H), 7.51-7.49 (m, 1H), 7.21-7.19 (m, 2H), 4.10-4.06 (m, 4H), 1.96-1.95 (d, 2H), 1.36-1.21 (m, 64H), 0.94-0.82 (m, 12H).

Synthesis of PDI-Th-Br

A mixture of PDI-Th (3.40 g, 3.3 mmol), N-bromosuccinimide (NBS) (0.588 g, 3.3 mmol), chloroform (200 mL) and acetic acid (one drop) was stirred at room temperature in dark overnight. Then the reaction mixture was poured into water (200 mL) and extracted with chloroform (3x100 ml). The organic phases were combined and washed with brine and water, then dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica, eluting with petroleum ether/chloroform (1:2), and dried under vacuum to afford PDI-Th-Br (3.52 g, 96.0 %). ¹H NMR (400 MHz, CDCl₃): δ 8.65-8.48 (m, 5H), 8.30-8.27 (m, 1H), 8.21-8.15 (m, 1H), 7.19-7.18 (d, *J* = 4.0, 1H), 7.05-7.04 (d, *J* = 4.0, 1H), 4.11-4.08 (m, 4H), 1.98 (s, 2H), 1.41-1.21 (m, 64H), 0.86-0.83 (m, 12H).

Synthesis of TDI-Br

A mixture of compound PDI-Th-Br (3.45 g, 3.11 mmol) and iodine (0.790 g, 3.11 mmol) in benzene (200 mL) was exposed to light for 48 h. The reaction mixture was washed by water and brine successively. The combine organic layer crude was evaporated under reduced pressure, the crude product was purified by column chromatographically with DCM/petroleum ether, recrystallized from DCM /methanol, and dried under vacuum to afford TDI-Br (3.27 g, 94.8 %). ^1H NMR (400 MHz, CDCl_3): δ 8.60-8.56 (t, 2H), 8.49-8.45 (t, 2H), 8.39 (s, 1H), 8.13 (s, 1H), 7.46 (s, 1H), 4.20-4.15 (m, 4H), 2.02 (s, 2H), 1.41-1.21 (m, 64H), 0.86-0.81 (m, 12H). MS (MALDI-TOF-MS): Calculated for $\text{C}_{68}\text{H}_{89}\text{BrN}_2\text{O}_4\text{S}$, 1110.4, found[M+H]: 1111.5.



Scheme S2: The synthesis of two TDI-based molecules via stille coupling reaction.

Synthesis of TDI_2

In an inert nitrogen atmosphere, TDI-Br (0.40 g, 0.36 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (30 mg) were added to in a sealed flask. Anhydrous toluene (50 ml) was added from a syringe, followed by hexa-n-butyl-distannane (0.21 g, 0.36 mmol). The mixture was stirred vigorously for 36 h at 110°C . After cooling to room temperature, the reaction mixture was washed with saturated potassium fluoride and brine, dried over anhydrous Na_2SO_4 . After filtration, the solvent was evaporated under reduced pressure, the crude

product was purified by column chromatographically with DCM, recrystallized from DCM /methanol, and dried under vacuum to afford TDI₂ (0.32 g, 85.0 %). MS (MALDI-TOF-MS): Calculated for C₁₃₆H₁₇₈N₄O₈S₂, 2059.3, found: 2060.0.

Synthesis of BDT-TDI₂

In an inert nitrogen atmosphere, TDI-Br (0.50 g, 0.45 mmol) and BDT-Sn (0.226 g, 0.20 mmol) in dry toluene (50 ml) were added Pd(PPh₃)₄(30 mg) in a sealed flask. The mixture was stirred vigorously for 24 h at 110 °C. After cooling to room temperature, the reaction mixture was washed with saturated potassium fluoride and brine, dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated under reduced pressure, the crude product was purified by column chromatographically with DCM/petroleum ether (3:1), recrystallized from DCM /methanol, and dried under vacuum to afford BDT-TDI₂ (0.43 g, 75.0 %). ¹H NMR (400 MHz, CDCl₃): δ 9.31-8.11 (m, 12H), 7.73-7.69 (m, 2H), 7.45-7.36 (m, 4H), 4.43 (s, 8H), 3.16-2.95 (m, 8H), 2.06-1.99 (m, 10H), 1.73-1.64 (m, 14H), 1.42-1.17 (m, 136H), 0.94-0.81 (m, 36H). MS (MALDI-TOF-MS): Calculated for C₁₈₆H₂₅₄N₄O₈S₆, 2863.8, found: 2862.6.

Fabrication and characterization of photovoltaic cells

Organic solar cells were fabricated with the structure of ITO/PEDOT:PSS/active layer/Ca/Al. The patterned indium tin oxide (ITO) glass with a sheet resistance of 10 Ω sq⁻¹ was pre-cleaned in an ultrasonic bath of acetone and isopropanol, and treated in an ultravioletozone chamber (Ultraviolet Ozone cleaner, Jelight Company, USA) for 15 min. A thin layer of poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) was spin-coated onto the ITO glass and baked at 100 °C for 10 min. The BDDT:TDIs mixture (10/20 mg·mL⁻¹ in total in different solvents) was spin-coated on the PEDOT:PSS layer to form a photosensitive layer. The calcium layer (ca.20 nm) and the aluminum layer (ca. 80 nm) were then evaporated onto the surface

of the photosensitive layer under vacuum (ca 4×10^{-6} torr) to form the negative electrode. The active area of the device was 4 mm^2 . The thicknesses of the active layer were detected by Alpha-atepD-120 stylus profilometer, Kla-Tencor. Grazing-incidence wide-angle X-ray scattering (GIWAXS) samples of pristine films were prepared by drop-casting of solutions on silica slides and BDDT/TDI₂ blending films were spin-coated using the same conditions of the best devices on a PEDOT:PSS pre-coated Si substrate.

The J-V curve was measured using a Keithley 2400 source-measure unit. Photocurrent was measured under AM 1.5 G illumination at $100 \text{ mW}\cdot\text{cm}^2$ using a Newport Thermal Oriel 91159A solar simulator. Light intensity is calibrated with a Newport oriel PN 91150V Si-based solar cell. The EQE spectrum was measured using an Oriel Newport system (Model 66902).

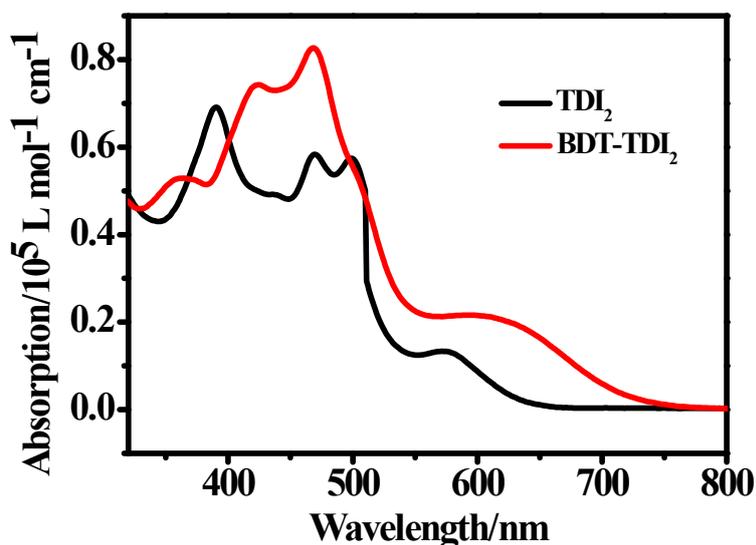


Figure S1. UV-vis absorption spectra of TDI₂ and BDT-TDI₂ in CH₂Cl₂.

Table S1 Electrochemical properties of TDIs acceptors

TDI _s	HOMO (eV) ^a	LUMO (eV) ^a	<i>E_g</i> (eV) ^a	HOMO (eV) ^b	LUMO (eV) ^b	<i>E_g</i> (eV) ^b
TDI ₂	-5.95	-3.57	2.38	-6.11	-3.62	2.49
BDT-TDI ₂	-5.59	-3.59	2.00	-5.54	-3.49	2.05

^a Measured in thin films obtained in CH₃CN/0.1 M [n-Bu₄N]⁺[PF₆]⁻ solution, ^b Theoretical calculation values through DFT at the B3LYP/6-31G level.

Table S2 Photovoltaic performance of the optimized devices based on BDDT:TDI₂ under the illumination of AM 1.5 G, 100 mW cm⁻²

Solvent	Additive	Concentration (mg/mL, w/w)	Rpm	<i>V_{oc}</i> (V)	<i>J_{sc}</i> (mA cm ⁻²)	FF (%)	PCE (%)
CF	-	10 mg, 1:1	2000	0.93	3.45	31.09	1.01
CB	-	10 mg, 1:1	2000	0.97	8.01	48.22	3.80
ODCB	-	10 mg, 1:1	2000	1.00	6.26	59.17	3.75
			1800	0.99	6.91	57.37	4.07
ODCB	-	10 mg, 1:1.5	1800	0.94	6.86	59.77	4.20
ODCB	-	10 mg, 1.5:1	1500	0.99	6.55	50.24	3.34
ODCB	-	10 mg, 1:2	2500	0.99	5.82	59.42	3.51
ODCB	-	25 mg, 1:1	2000	1.0	6.88	56.05	3.96
			2500	1.0	7.18	55.83	4.12
ODCB	-	12.5 mg, 1:1	2500	0.99	6.70	58.31	4.01
ODCB	0.5%DIO	12.5 mg, 1:1	2500	0.99	6.37	52.89	3.48
ODCB	0.5%CN	12.5 mg, 1:1	2000	0.99	7.18	62.54	4.63

ODCB	0.5%DPE	12.5 mg, 1:1	2500	0.99	7.41	59.74	4.54
ODCB	0.2%CN	12.5 mg, 1:1	2000	1.0	6.69	63.30	4.45
ODCB	0.8%CN	12.5 mg, 1:1	2000	0.99	6.95	64.59	4.68
ODCB	1%CN	12.5 mg, 1:1	2000	0.99	7.22	64.32	4.85
ODCB	2%CN	12.5 mg, 1:1	2000	0.99	6.69	63.11	4.41
ODCB	1%DPE	12.5 mg, 1:1	2000	0.98	7.73	60.93	4.90
ODCB	2%DPE	12.5 mg, 1:1	2000	0.99	7.85	63.83	5.28
				0.98	7.98	66.01	5.52 ^a
ODCB	3%DPE	12.5 mg, 1:1	2000	0.99	7.95	63.10	5.29
				0.98	7.93	65.57	5.44 ^a
				0.98	8.08	65.75	5.57 ^b
ODCB	4%DPE	12.5 mg, 1:1	2000	0.99	7.71	64.16	5.20
				0.99	7.82	66.33	5.45 ^a
				0.98	7.95	64.42	5.32 ^b
CB	3%DPE	10 mg, 1:1	2000	0.96	8.51	62.34	5.40
				0.96	8.78	65.01	5.80^a
CB	4%DPE	10 mg, 1:1	2000	0.96	8.16	59.88	5.02
CB	3%DPE	20 mg, 1:1	2500	0.96	8.51	64.78	5.67 ^a
				0.95	8.49	65.56	5.70 ^b
CB	3%DPE	20 mg, 1:1	2500	0.96	8.83	60.47	5.50 ^c
CB	3%DPE	20 mg, 1:1	2500	0.95	8.74	63.35	5.66 ^d

^a Annealed 80°C 5 minutes; ^b Annealed 90°C 5 minutes; ^c Washed with methanol without annealed; ^d Washed with methanol before annealed 80°C 5 minutes.

Table S3 Photovoltaic performance of the optimized devices based on BDDT:BDT-TDI₂ under the illumination of AM 1.5 G, 100 mW cm⁻²

Solvent	Additive	Concentration (mg/mL, w/w)	Rpm	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
CB	-	20 mg, 1:1	2500	1.03	7.29	51.66	4.12
CB	-	20 mg, 1:1.5	2000	1.02	6.68	50.55	3.67
CB	-	20 mg, 1:2	2500	0.97	5.45	40.46	2.28
CB	-	20 mg, 1.5:1	3000	1.02	7.04	49.78	3.81
ODCB	-	25 mg, 1:1	1500	1.01	4.93	47.09	2.50
			1800	1.02	4.73	47.33	2.44
			2000	1.03	4.66	49.49	2.54
CB	-	20 mg, 1:1	2500	1.03	7.23	53.70	4.26
				1.03	7.25	55.27	4.39 ^a
CB	-	20 mg, 1:1.5	2500	1.01	6.76	49.93	3.65
			3000	1.01	6.90	50.41	3.76
CB	0.5%DIO	20 mg, 1:1	2000	1.02	5.23	43.50	2.48
CB	0.5%DIO	20mg, 1:1	2500	1.02	5.51	45.36	2.72
				1.01	6.05	45.19	2.95 ^a
CB	0.5%CN	20 mg, 1:1	2000	1.02	6.96	50.80	3.86
			2500	1.03	7.16	52.44	4.12
			3000	1.03	7.10	52.63	4.09
CB	1%DPE	20 mg, 1:1	2000	1.03	6.36	46.71	3.26

			2500	1.03	6.79	48.43	3.60
			3000	1.03	6.78	49.04	3.65
CB	-	20 mg, 1:1	2500	1.03	7.64	52.64	4.44
				0.98	7.32	53.83	4.15 ^b
				0.93	7.32	53.07	3.90 ^c
				1.03	7.21	55.83	4.44 ^d
CB	0.2%CN	20 mg, 1:1	2500	1.02	7.16	52.59	4.16
				1.02	7.55	54.67	4.52^b
				1.02	7.23	55.88	4.44 ^d
CB	0.5%DPE	20 mg, 1:1	2500	1.02	7.08	50.51	3.90
				0.98	6.96	51.50	3.76 ^b
				1.02	7.06	50.18	3.87 ^d

^a Washed with methanol without annealed; ^b Annealed 80°C 5 minutes; ^c Annealed 90°C 5 minutes; ^d Washed with methanol without annealed.

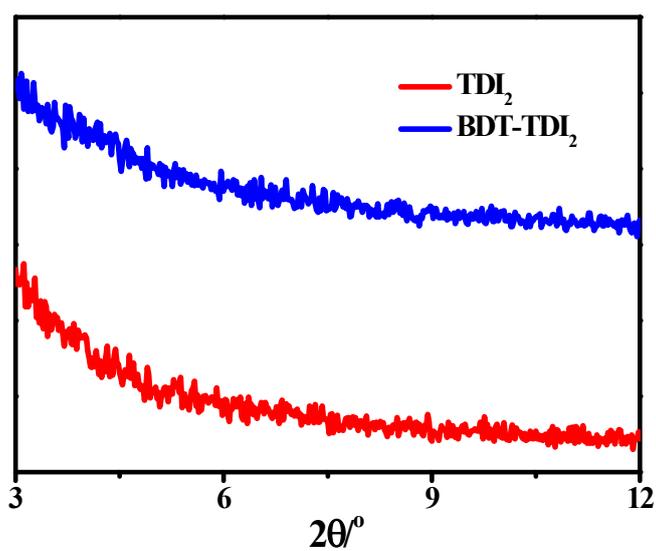
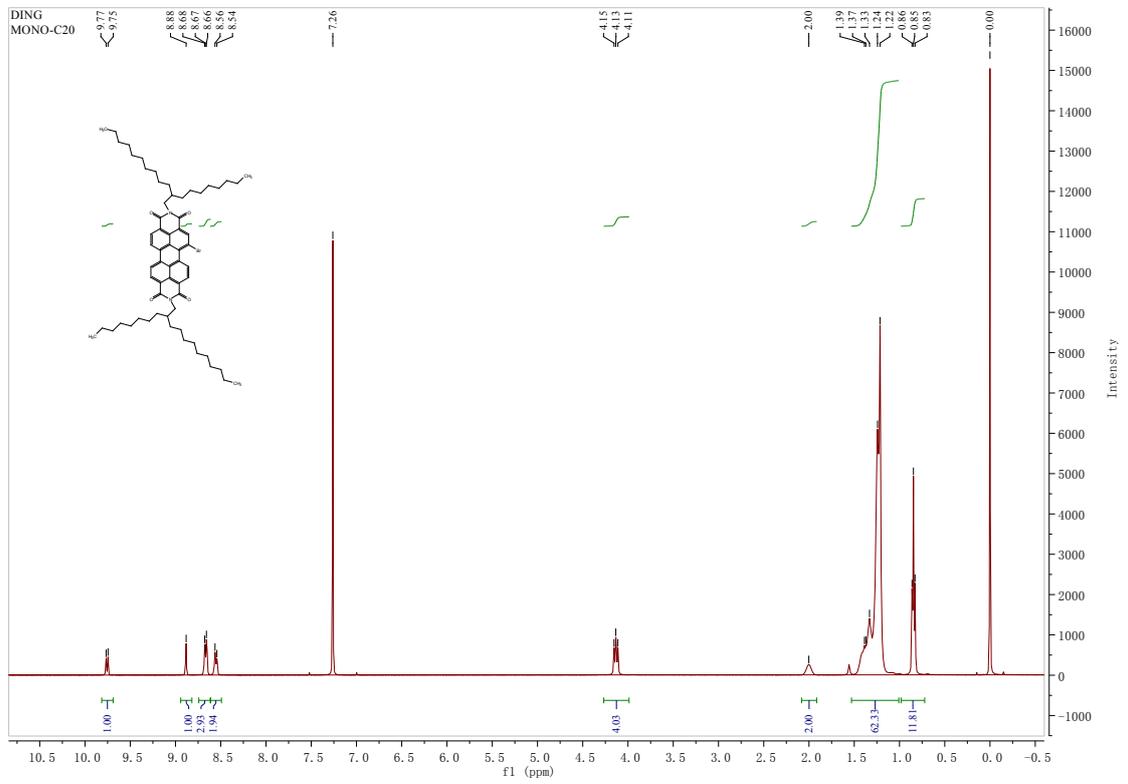
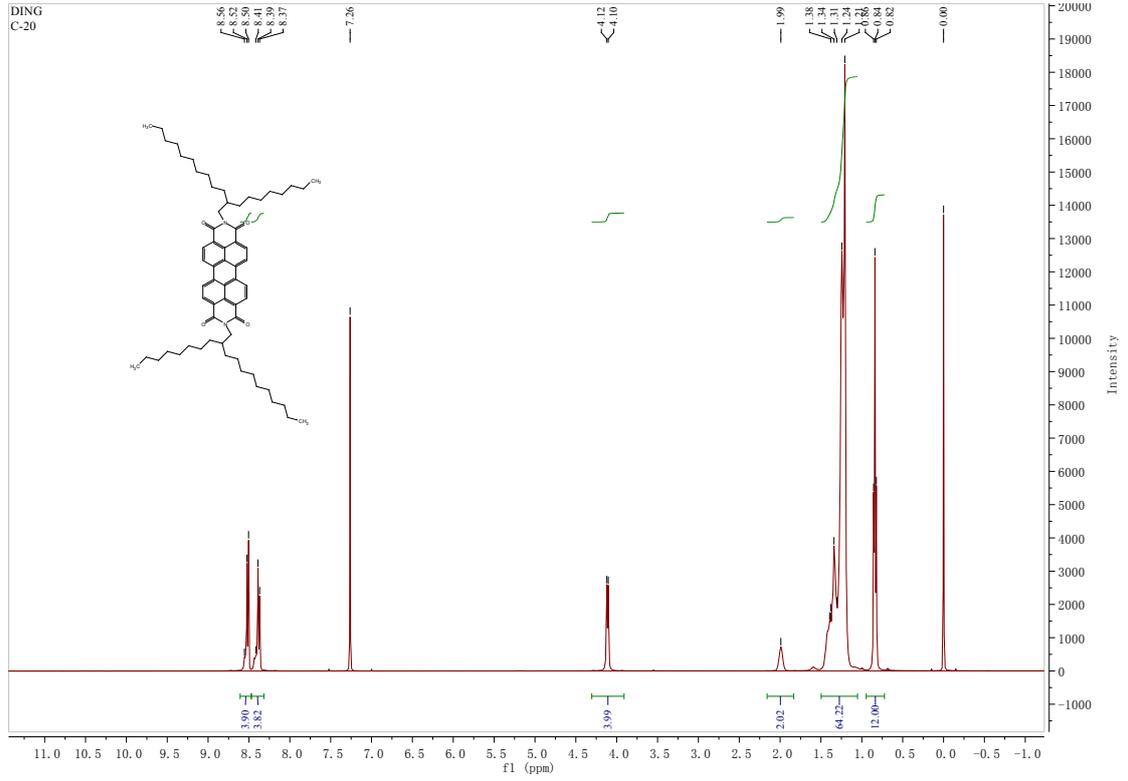
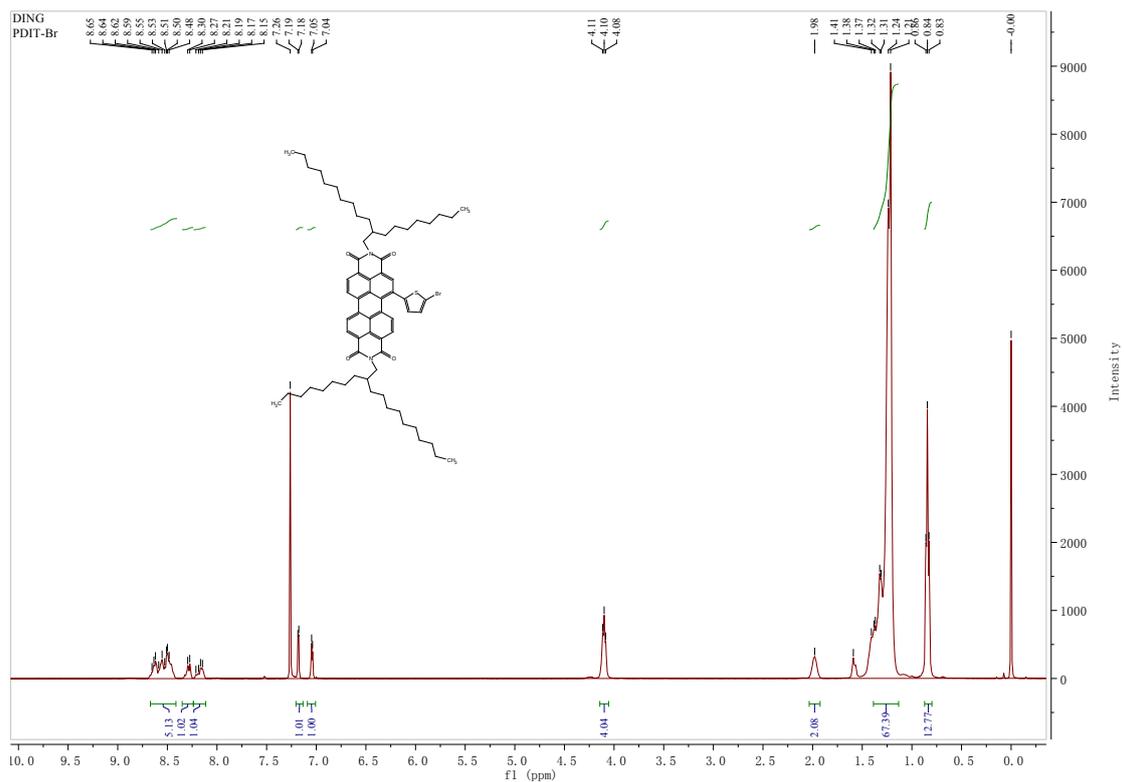
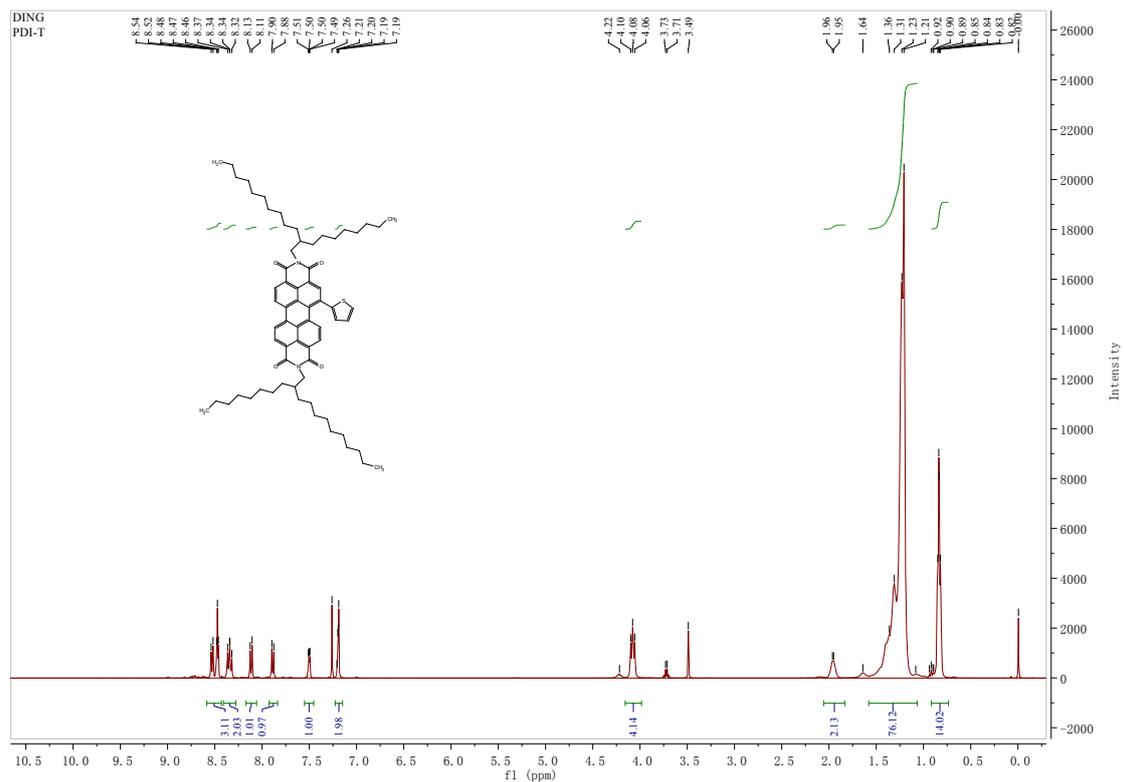
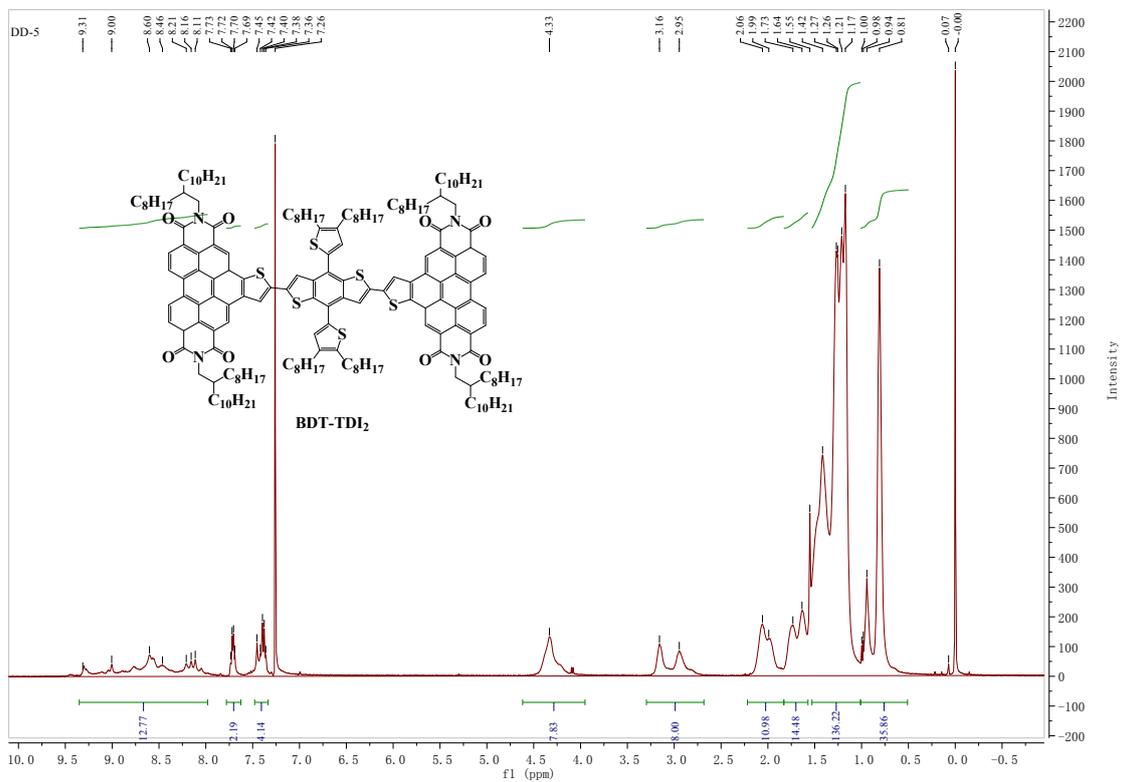
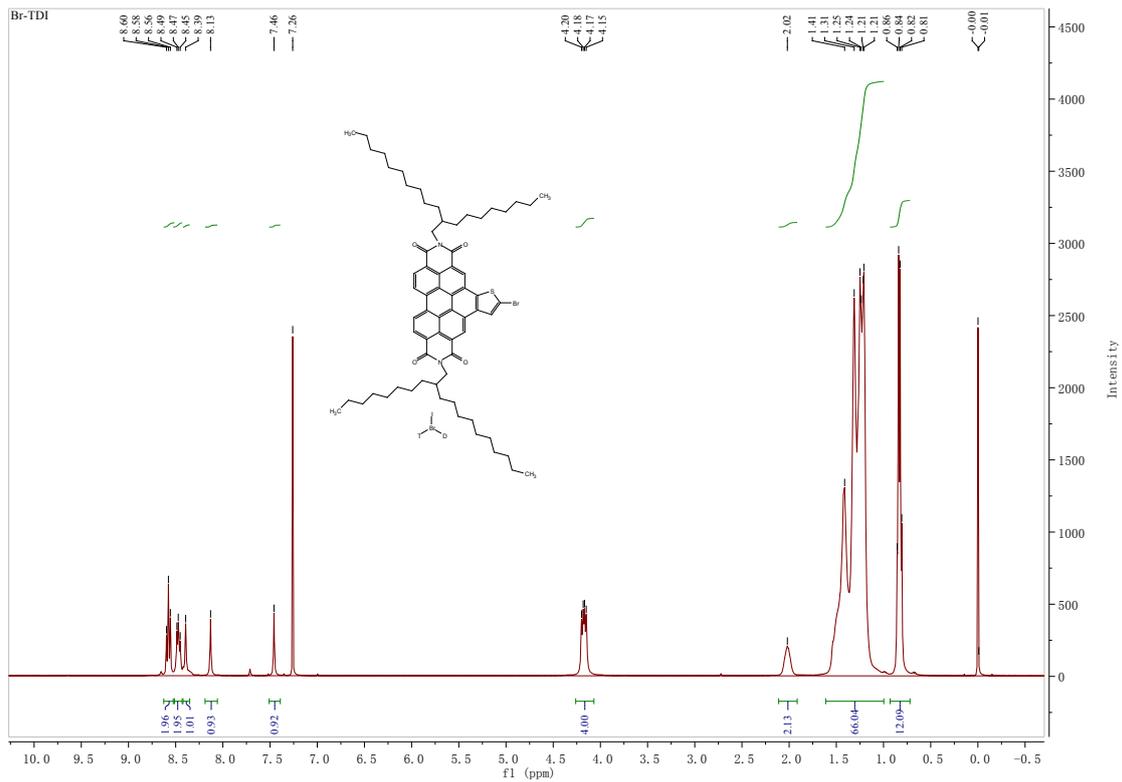


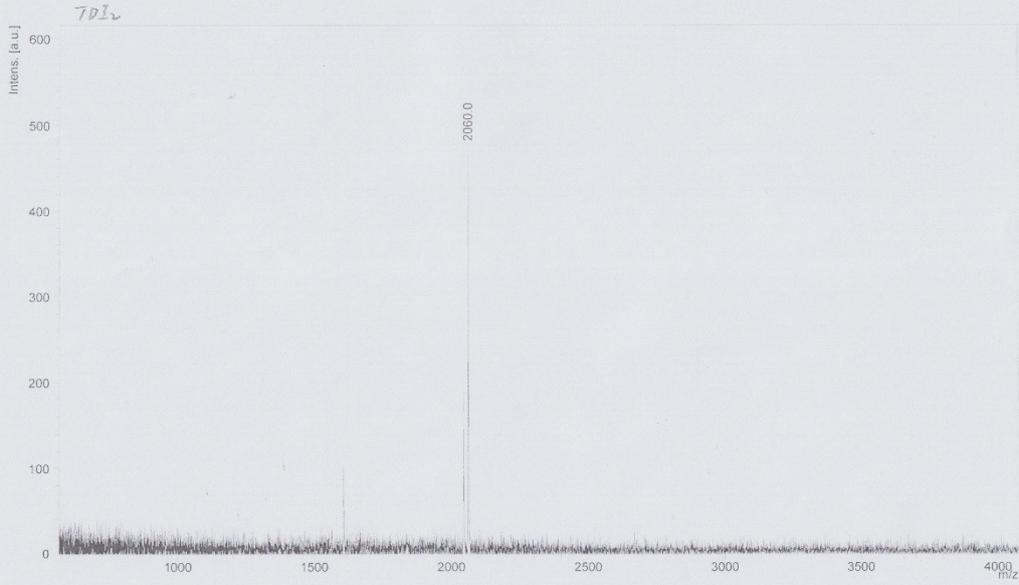
Figure S2. XRD patterns of the TDI_2 and BDT-TDI_2 films.







MALDI-TOF MS, CCA, 3, 20170113



MALDI-TOF,CCA,2,2016,10,11



Figure S4. MALDI-TOF-MS of TDI₂ and BDT-TDI₂.

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