

Supporting information for

Integrated Linker-Regulation and Ring-Fusion Engineering towards

Efficient Additive-Free Non-Fullerene Organic Solar cells

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Experimental section

Materials. Monomer FPDI-Br was synthesized according to our previous work.^{1,2} 2,5-bis(trimethylstannyl)thiophene, and 2,5-Bis(trimethylstannyl)thieno[3,2-b]thiophene were obtained from Derthon Optoelectronic Materials Science Technology Co LTD. PTB7-Th was purchased from Solarmer Materials (Beijing) Inc. All chemicals were obtained from commercial sources and used without further purification unless otherwise specified.

Synthesis of T-FPDI. A solution of FPDI-Br (400 mg, 0.27 mmol) and 2,5-bis(trimethylstannyl)thiophene (45.1 mg, 0.11 mmol) monomers in toluene (20 mL) was degassed under N₂ for three time. Then, tris(dibenzylideneacetone)dipalladium(0) (10.1 mg, 0.01 mmol) and tri(o-tolyl)phosphine (20.2 mg, 0.07 mmol) were quickly added, and the mixture solution was refluxed at 110 °C for 12 h under N₂ protection. After cooling to room temperature, the resultant solution was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel (petroleum ether/dichloromethane, 2:1 to 1:2, v/v) to yield dark brown solid T-FPDI (257 mg, 0.09 mmol, 80%). ¹H NMR (400 MHz, CDCl₃) δ 10.34 (s, 8H), 9.63 – 8.84 (m, 14H), 7.76 (s, 2H), 5.34 (dd, 8H), 2.53 – 2.22 (m, 16H), 2.02 (d, 16H), 1.31 – 1.16 (m, 98H), 0.87 (ddd, 46H). MS (MALDI-TOF): Calcd. For C₁₉₂H₂₀₈N₈O₁₆S (M⁺): 2915.55, Found: 2915.76.

Synthesis of TT-FPDI. TT-FPDI was synthesized by a similar method to the one used for T-FPDI with a yield of 78%. ¹H NMR (400 MHz, CDCl₃) δ 10.36 (s, 8H), 9.53 – 9.14 (m, 14H), 7.88 (s, 2H), 5.42 – 5.28 (m, 8H), 2.39 (s, 16H), 2.02 (d, 16H), 1.31 (dd, 98H), 0.91 – 0.80 (m, 46H). MS (MALDI-TOF): Calcd. For C₁₉₄H₂₀₈N₈O₁₆S₂ (M⁺):

2971.52, Found: 2971.75.

Synthesis of FT-FPDI. In photocyclization reaction device, T-FPDI (146 mg, 0.05 mmol) and iodine (50.0 mg) were dissolved in 360 mL toluene. Then, the mixture solution was photoirradiated using 450W mercury lamp for 36 h with minimal cooling of the inner jacketed glass tubing. The reaction mixture was terminated until the starting material could not be detected by thin-layer chromatography (TLC). Solvent was removed by rotary evaporation and the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane, 2:1 to 1:2, v/v) to yield FT-FPDI as dark red solid (118 mg, 0.04 mmol, 81 %). ^1H NMR (400 MHz, CDCl_3) δ 11.52 (s, 2H), 10.83 (d, 10H), 9.56 (d, 4H), 9.29 (s, 4H), 5.51 (d, 8H), 2.50 (d, 16H), 2.24 – 1.89 (m, 16H), 1.44 – 1.24 (m, 98H), 1.05 – 0.70 (m, 46H). MS (MALDI-TOF): Calcd. For $\text{C}_{192}\text{H}_{204}\text{N}_8\text{O}_{16}\text{S}$ (M^+): 2911.52, Found: 2913.73.

Synthesis of FTT-FPDI. FTT-FPDI was synthesized by a similar method to the one used for FTT-FPDI with a yield of 80%. ^1H NMR (400 MHz, CDCl_3) δ 10.85 (dd, $J = 135.6$, 12H), 9.51 (dd, 4H), 9.29 (s, 4H), 5.46 (t, 8H), 2.87 – 1.92 (m, 32H), 1.57 – 1.19 (m, 98H), 1.17 – 0.60 (m, 46H). MS (MALDI-TOF): Calcd. For $\text{C}_{194}\text{H}_{204}\text{N}_8\text{O}_{16}\text{S}_2$ (M^+): 2967.49, Found: 2969.74.

Characterization

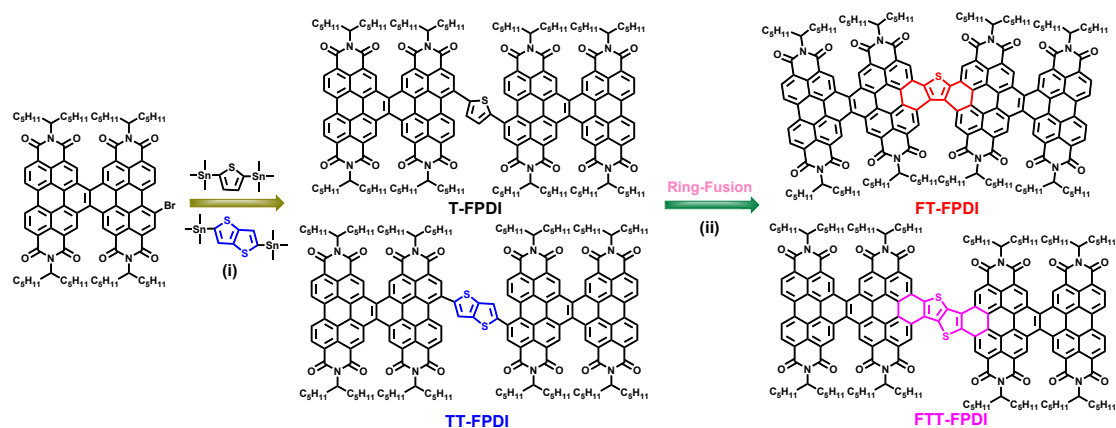
^1H NMR spectra were recorded on a Bruker AV 400 spectrometer and used tetramethylsilane (TMS) as an internal standard in CDCl_3 . MALDI-TOF-MS was performed on Bruker Daltronik GmbH (autoflex II). The UV-Vis spectra of polymers were measured on with a TU-1601 spectrophotometer by using a 1 cm glass cuvette. Cyclic voltammetry (CV) was performed in 0.1M tetrabutylammonium

hexafluorophosphate in acetonitrile at a scan rate of 100 mV/s with ITO as the working electrode, Pt wire as the counter electrode and Ag/Ag⁺ as the reference electrode. Atomic force microscopy (AFM) images were obtained using a Veeco Dimension 3100V microscope in the tapping mode. GIWAXS patterns were acquired under X-ray incident angle of 0.14° and X-ray energy of 10 keV at Beamline 7.3.3 of the Advanced Light Source, Lawrence Berkeley National Laboratory.

Device Fabrication. Prepatterned ITO-coated glasses were cleaned by sequential cycles of sonication in soap water, deionized water, ethanol, acetone, and isopropanol for 30 min, respectively. After UV/ozone treatment for 6 min, PEDOT:PSS hole transport layer was filtered and spin-coated on top of the treated-ITO at 4000 rpm for 30 s and dried over 150 °C for 15 min. The active layer solutions were prepared in CB (with a polymer concentration of 8 mg/mL and a D/A ratio at 1:1.5), and spin-coated on the PEDOT:PSS-coated substrates in a glove-box under N₂ atmosphere at 1500 rpm for 45 s to obtain a thickness of ≈ 120 nm. The blend films were then transferred to the heating platform and annealed at 100 °C for 10 min. A thin layer of PDINO (1.5 mg/mL) was spin coated on the top of active layer with 3000 rpm for 60 s. Finally, the Al (100 nm) electrode was evaporated onto the active layer under a vacuum of 10⁻⁵ Torr. Simulated solar light (100 mW cm² AM 1.5G) provided by a Newport-Oriel® Sol3A 450 W solar simulator was used to measure the photovoltaic characteristics of the devices under simulated solar light (100 mW cm² AM 1.5G). The EQE spectra were determined by a Newport-Oriel® IQE 200™ which was calibrated by a standard Si/Ge solar cell. The thickness of the active layer was investigated using a computer-

controlled Dektak 150 Veeco.

The hole-only device for the hole mobility was fabricated with a device structure of ITO/PEDOT:PSS/PTB7-Th:SMAs/MoO₃/Al. The electron-only device for the electron mobility was fabricated with a device structure of ITO/Al/PTB7-Th: SMAs/PDINO/Al. Both the hole and electron mobilities by space charge limited current (SCLC) were calculated with the following Mott-Gurney equation in the SCLC region: $J = (9/8)\epsilon_0\epsilon_r\mu(V^2/L^3)$, in which ϵ_0 is the permittivity of the vacuum, ϵ_r is the dielectric constant of the polymer and assumed to be 3, and L is the thickness of active layer.



Scheme S1 Synthetic route of T-FPDI, TT-FPDI, FT-FPDI and FTT-FPDI: (i) toluene, Pd₂(dba)₃/P(o-tol)₃, 110°C, 12h. (ii) Toluene, I₂, *hν*, 36 h.

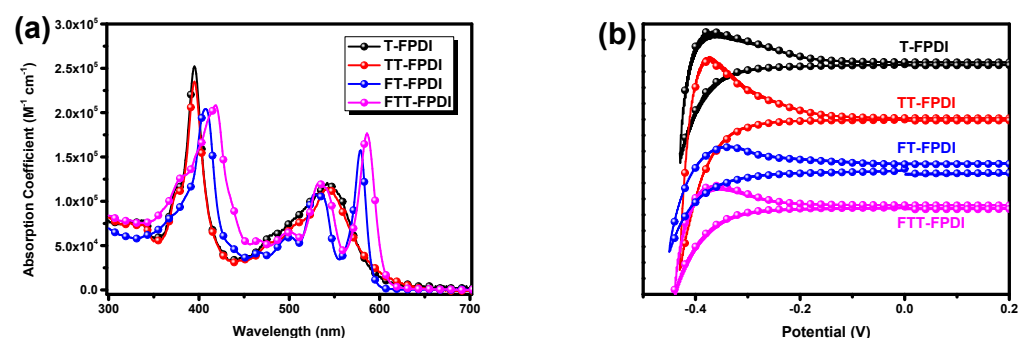


Fig. S1 (a) The absorption coefficient of four SMAs in CB solution, and (b) the cyclic voltammetry of four SMAs in solid state.

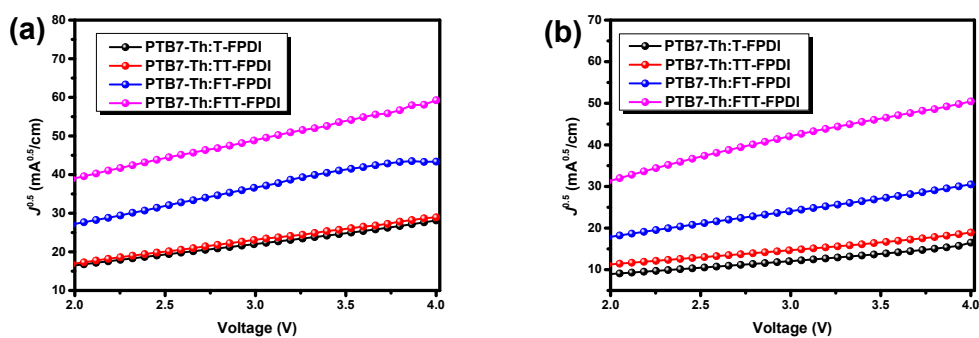


Fig. S2 $J^{0.5}$ - V plot for the optimal blend films: (a) hole-only devices; (b) electron-only devices.

Table S1 The summary devices parameters of NF-OSCs based on four electron acceptors by varying annealing temperature.

Active layer	Processing conditions	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PTB7-Th: T-FPDI	80 °C 10 min	0.779	12.0	48.7	4.57
PTB7-Th: T-FPDI	100 °C 10 min	0.780	13.4	53.0	5.52
PTB7-Th: T-FPDI	120 °C 10 min	0.782	12.3	53.9	5.18
PTB7-Th: TT-FPDI	80 °C 10 min	0.780	12.6	54.1	5.32
PTB7-Th: TT-FPDI	100 °C 10 min	0.791	14.4	62.9	7.17
PTB7-Th: TT-FPDI	120 °C 10 min	0.791	13.6	58.4	6.27
PTB7-Th: FT-FPDI	80 °C 10 min	0.808	13.2	51.6	5.50
PTB7-Th: FT-FPDI	100 °C 10 min	0.805	14.4	58.2	6.75
PTB7-Th: FT-FPDI	120 °C 10 min	0.810	14.9	55.2	6.65
PTB7-Th: FTT-FPDI	80 °C 10 min	0.817	14.7	55.9	6.73
PTB7-Th: FTT-FPDI	100 °C 10 min	0.822	16.5	56.4	7.66
PTB7-Th: FTT-FPDI	120 °C 10 min	0.813	16.7	56.1	7.60

Table S2 The summary devices parameters of NF-OSCs based on four electron acceptors under different amounts of DIO.

Active layer	Additive (volume)	Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PTB7-Th: T-FPDI	none	93	0.780	13.4	53.0	5.52
PTB7-Th: T-FPDI	0.25% DIO		0.773	13.6	51.5	5.39
PTB7-Th: T-FPDI	0.5% DIO		0.769	13.9	51.2	5.48
PTB7-Th: T-FPDI	1% DIO		0.770	13.1	50.7	5.13
PTB7-Th: T-FPDI	3% DIO		0.780	12.6	47.8	4.68
PTB7-Th: TT-FPDI	none	92	0.791	14.4	62.9	7.17
PTB7-Th: TT-FPDI	0.25% DIO		0.777	14.6	58.9	6.69
PTB7-Th: TT-FPDI	0.5% DIO		0.790	15.2	57.2	6.87
PTB7-Th: TT-FPDI	1% DIO		0.787	13.8	55.6	6.06
PTB7-Th: TT-FPDI	3% DIO		0.782	13.1	53.8	5.48
PTB7-Th: FT-PDI	none	95	0.805	14.4	58.2	6.75
PTB7-Th: FT-PDI	0.25% DIO		0.800	14.8	56.4	6.67
PTB7-Th: FT-PDI	0.5% DIO		0.808	14.4	54.4	6.34
PTB7-Th: FT-PDI	1% DIO		0.811	13.3	52.8	5.67
PTB7-Th: FT-PDI	3% DIO		0.810	12.1	53.5	5.24
PTB7-Th: FTT-PDI	none	98	0.822	16.5	56.4	7.66
PTB7-Th: FTT-PDI	0.25% DIO		0.819	17.1	54.2	7.58
PTB7-Th: FTT-PDI	0.5% DIO		0.820	15.5	58.1	7.37
PTB7-Th: FTT-PDI	1% DIO		0.811	14.0	55.7	6.33
PTB7-Th: FTT-PDI	3% DIO		0.820	13.18	54.3	5.87

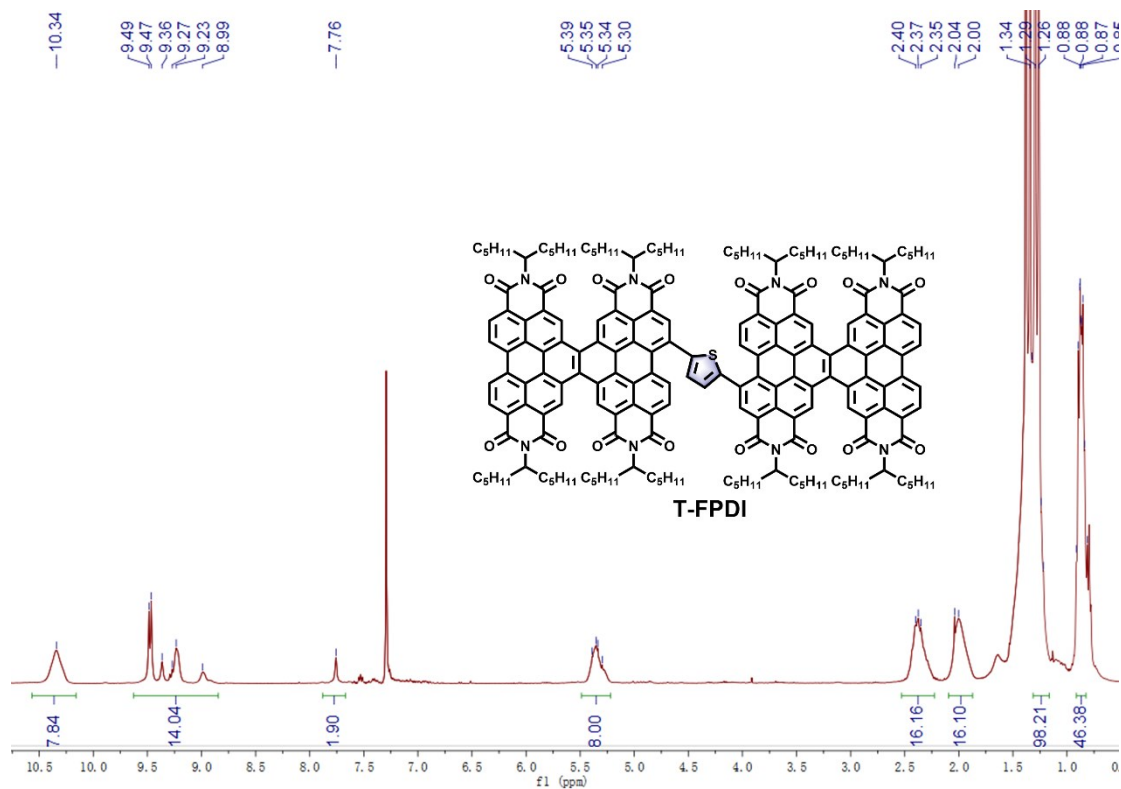


Fig. S3 The ^1H NMR spectra of T-FPDI.

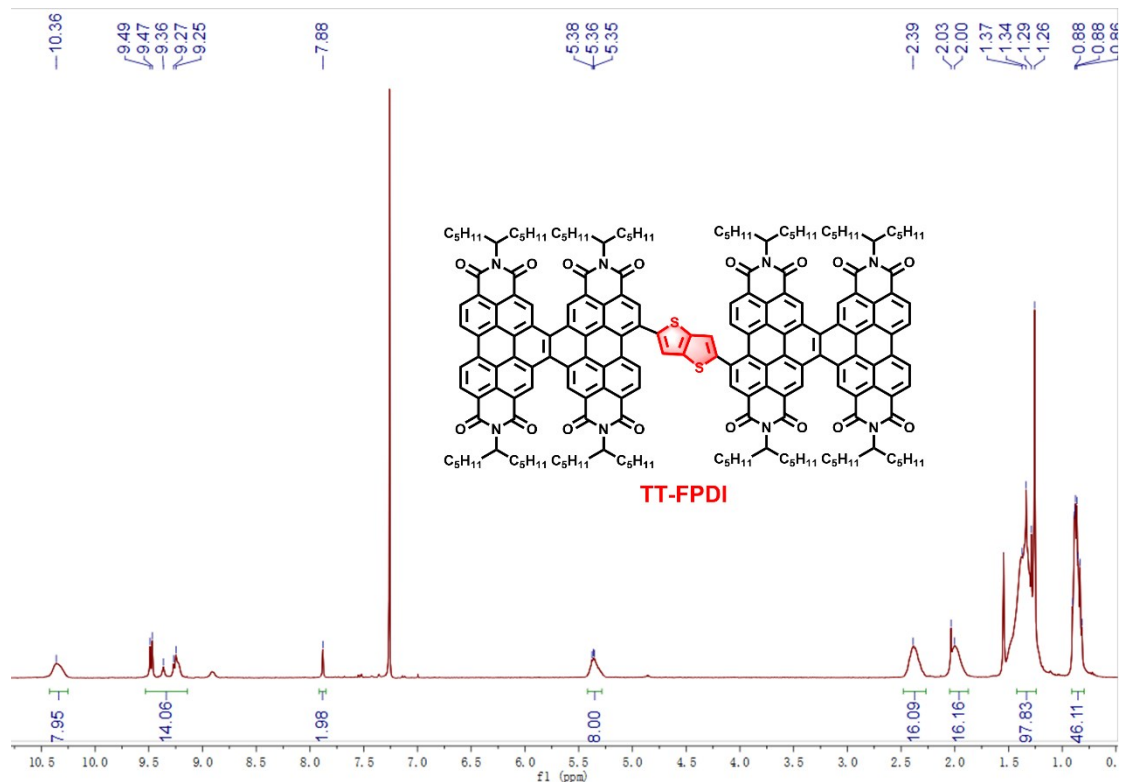


Fig. S4 The ^1H NMR spectra of TT-FPDI.

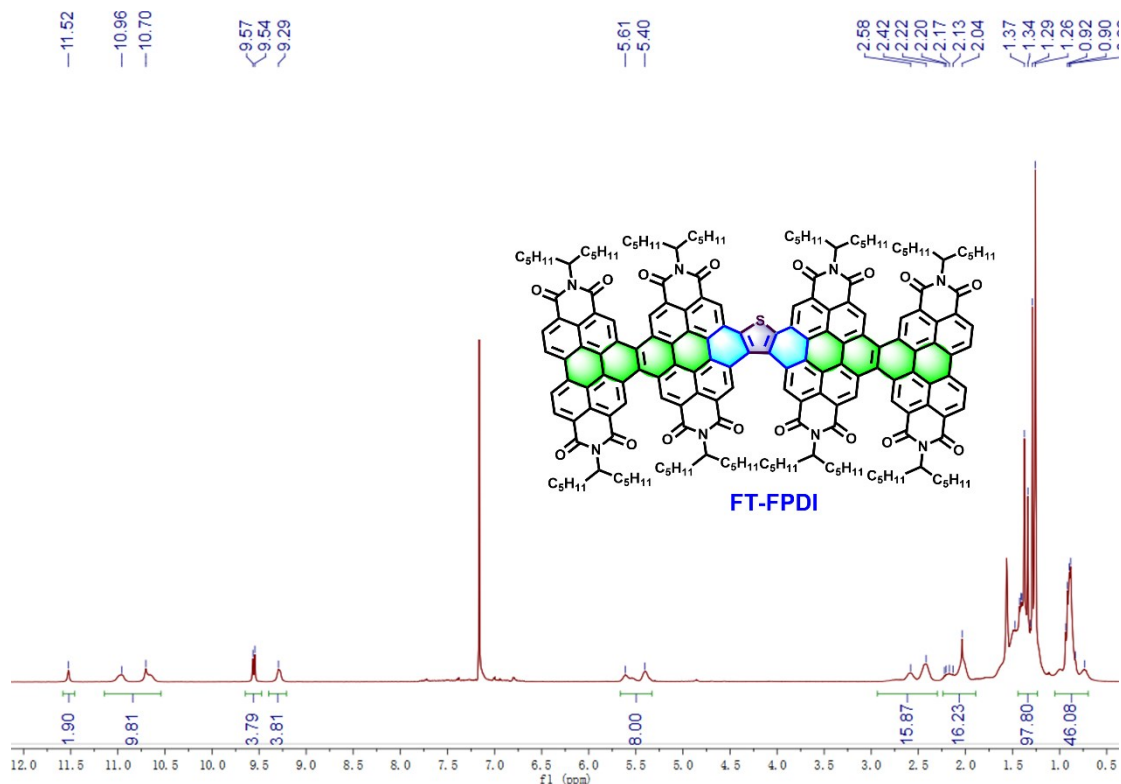


Fig. S5 The ¹H NMR spectra of FT-FPDI.

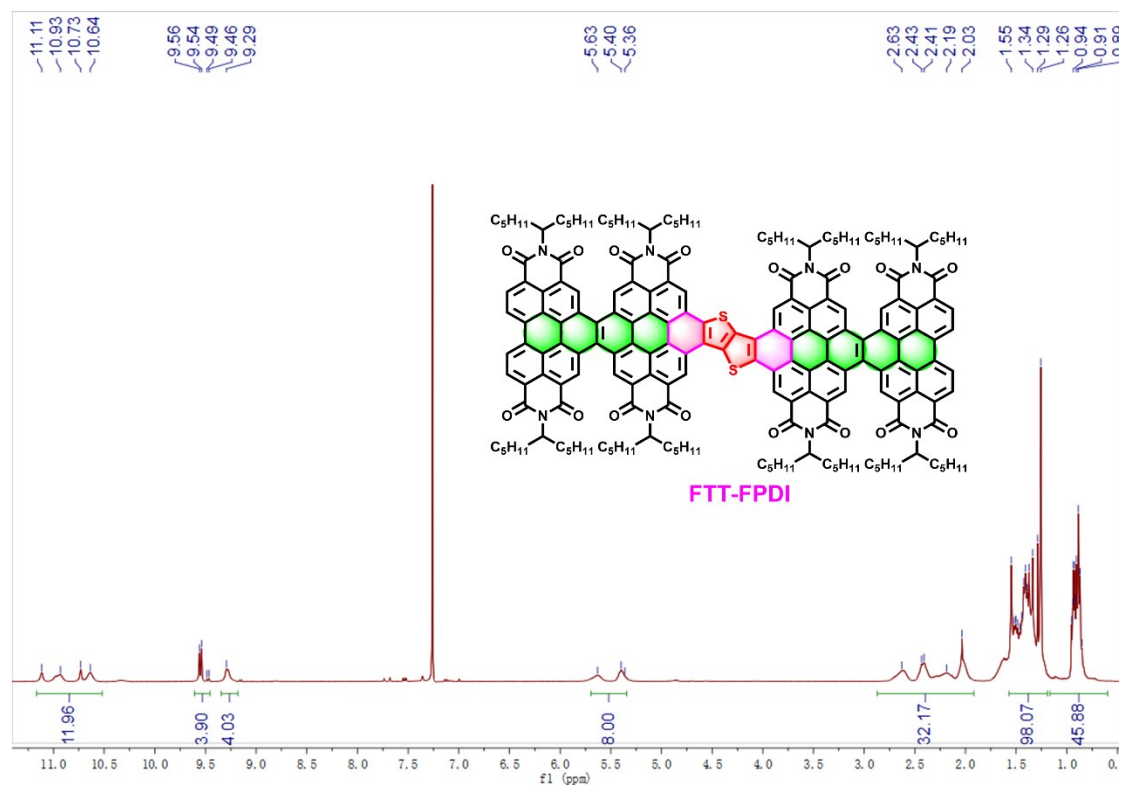


Fig. S6 The ¹H NMR spectra of FTT-FPDI.

References

1. M. Liu, J. Yang, Y. Yin, Y. Zhang, E. Zhou, F. Guo and L. Zhao, Novel Perylene Diimide-Based Polymers with Electron-Deficient Segments as the Comonomer for Efficient All-Polymer Solar Cells, *J. Mater. Chem. A*, 2018, **6**, 414-422.
2. M. Liu, J. Yang, C. Lang, Y. Zhang, E. Zhou, Z. Liu, F. Guo and L. Zhao, Fused Perylene Diimide-Based Polymeric Acceptors for Efficient All-Polymer Solar Cells, *Macromolecules*, 2017, **50**, 7559-7566.