Supporting Information for:

Synthesis, Characterization and OFET Performance for D-A Structures Semiconducting Small Molecular Functionalized with Perylene Diimide Groups

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1. Instrument and Methods

Instrument. UV-vis absorption spectra were recorded on an UV−Vis−NIR absorption spectrophotometer with Jasco-570 Agilent. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a thermal analysis in nitrogen at a heating rate of 10°C/min using Perkin Elmer TGA4000 and DSC6000 thermal analyzer. Cyclic voltammetry (CV) was recorded using a Zahner IM6e electrochemical workstation with Pt disk, Pt plate, as working electrode, counter electrode, and Ag/AgCl reference electrode, platinum wire as counter electrode, respectively, in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) dichloromethane solution. The CV curves were recorded versus the potential of standard calomel electrode (SCE), which was calibrated by Ag/Ag^+ redox couple. AFM were carried out with DigitalInstruments NanoscopeV. The tests of GIWAXS were conducted in Institute of High Energy Physics and the incident angle of the radiation is 0.3 °. The tests of HRMS were conducted in Institute of Chemistry Chinese Academy of Sciences by Bruker BIFLEX III MALDI-TOF. The nuclear magnetic resonance hydrogen and carbon spectrum was tested using the Bruker AVANCE NEO 400/600M instrument, with deuterated chloroform as the solvent and tetramethylsilane (TMS) as the internal standard for chemical shift.

Device fabrication and characterization. OFET devices featuring a bottom-gate/top-contact (BGTC) configurationand incorporating a dielectric layer with a thickness of 300 nm were fabricated and assembled. The silicon wafer was subjected to ultrasonic cleaning treatment with pure water, ethanol, and acetone in sequence (8 W, 5 minutes), and dried with a nitrogen and transferred to an infrared oven at 70 °C for 30 minutes. Take it into UV ozone cleaner for 20 minutes, and put it in a culture dish and add one drop of octadecyltrichlorosilane (OTS) in the middle, then heat it in a vacuum oven at 120 °C for 210 minutes. To form a thin layer of OTS, n-hexane, ethanol, and trichloromethane were treated with low-power ultrasound at 8W for 5 minutes. Through OTS modification, the orderliness of organic semiconductor thin films can be significantly improved, resulting in a smoother surface morphology and increased mobility. The synthesized molecules were dissolved in chloroform and

prepared a solution with a concentration of 10mg/mL for spin coating. The spin coating conditions are 3000 rpm for 30 seconds. Annealing treatment to further stabilize the structure and performance were conducted in glove box. The thickness of the deposited thin films was about 20-30nm. Then the source drain with 50nm thick gold electrode was prepared by vacuum evaporation, with a conductive channel width of 1400 μm and a length of 40 μm. Use Keithley 4200 semiconductor parameter analyzer was used to test and characterize the performance of the device.

2. Experimental procedures

Synthesis and characterization of S-PDI-IDT-1

N,N'-bis(2-octyldodecyl)-1-bromoperylene-3,4,9,10-tetracarboxylic diimides (721 mg, 0.7 mmol) and ((4,4,9,9-Tetrahexyl-4,9-dihydro-s-indaceno [1,2-b:5,6-b'] dithiophene-2,7-diyl)bis(trimethylstannane)(278.4mg,0.3mmol) with dimethyl formamide (DMF) 6 mL and $Pd(PPh_3)_4$ (75 mg, 0.06 mmol) as catalyzers were dissolved in 45 ml dry toluene solvent. The mixture was frozen with liquid nitrogen, followed by three times of successive vacuum and nitrogen fill cycles. Then, the mixture was refluxed at 110 ^oC for 48 hours. The molecules were dissolved in chloroform with minimum solvent. Then add methanol dropwise to the solution for precipitation. The crude product was acquired by filtering. The crude products were further refined by chromatographic column with the mixture of petroleum ether and dichloromethane (1:1-1:1.5) as the eluent, yielding a black solid: 60%. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 8.70 (dd, *J* = 12.0, 8.0 Hz, 2H), 8.62 (dd, *J* = 8.2, 7.2 Hz, 2H), 8.51 (d, *J* = 8.3 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.35 (s, 1H), 7.16 (s, 1H), 4.17 (d, *J* = 7.3 Hz, 2H), 4.10 (d, *J* = 7.3 Hz, 2H), 2.02 (dt, *J* = 17.6, 4.7 Hz, 4H), 1.94 (td, *J* = 13.2, 4.6 Hz, 2H), 1.47 – 1.32 (m, 12H), 1.29 – 1.17 (m, 64H), 1.01 (s, 2H), 0.92 (s, 2H), 0.87 – 0.80 (m, 18H). ^{13}C NMR (400 MHz, Chloroform-*d*) δ = 14.07, 14.12, 22.68, 22.71, 24.41, 26.54, 26.57, 29.31, 29.33, 29.36, 29.60, 29.66, 29.74, 30.06, 31.68, 31.78, 31.91, 31.93, 36.67, 39.18, 44.71, 44.82, 54.56, 76.71, 77.02, 77.23, 77.34, 113.67, 121.76, 122.08, 122.63, 123.01, 123.35, 123.70, 127.60, 128.14, 128.53, 129.05, 129.38, 130.14, 131.12, 133.38, 134.33, 134.54, 134.66, 134.90, 136.01, 136.74, 144.55, 145.14, 153.48, 157.00, 163.33, 163.69, 163.82, 163.88. HRMS calculated for $C_{168}H_{234}N_4O_8S_2$, m/z: 2500.75; found, m/z: 2501.75。

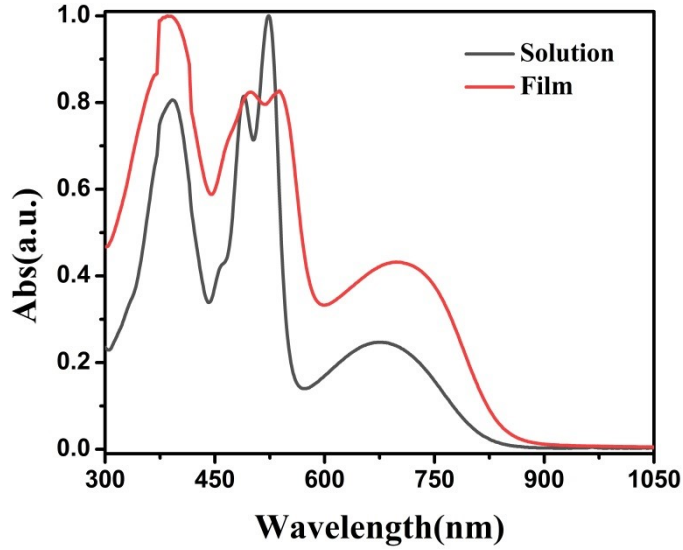

Figure S1 UV−Vis−NIR absorption spectra of S-PDI-IDT-1

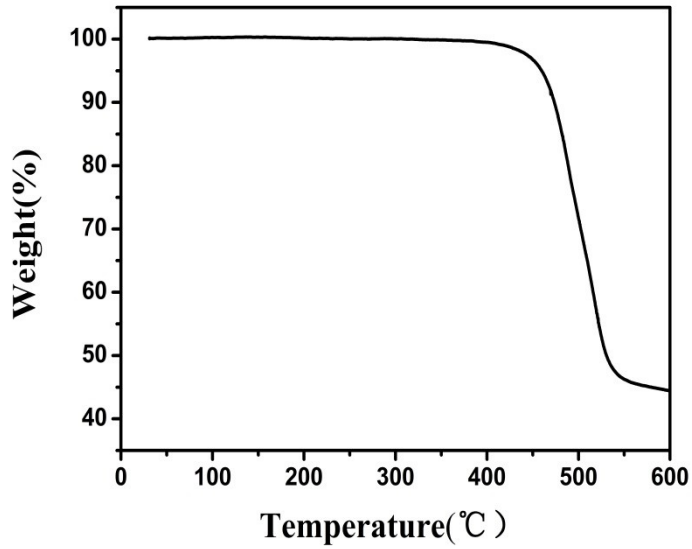

Figure S2 Thermogravimetric (TGA) analysis of S-PDI-IDT-1 measured at a heating rate of 10°C/ min in nitrogen

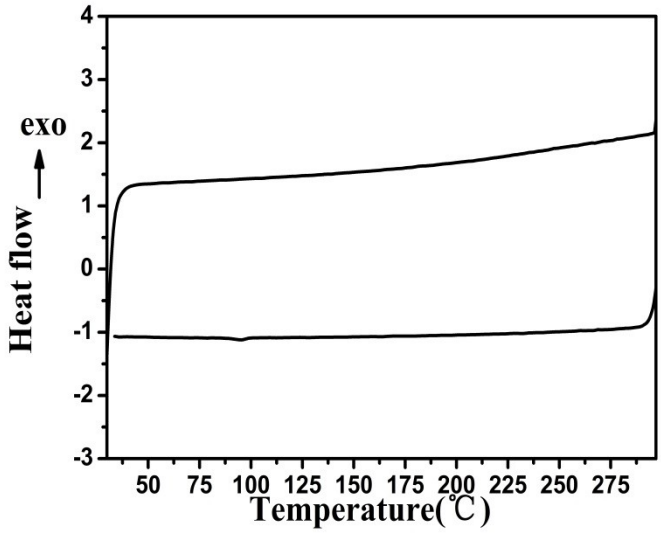

Figure S3 Differential scanning calorimetry (DSC) analysis of S-PDI-IDT-1 measured at a heating rate of 10°C/ min in nitrogen

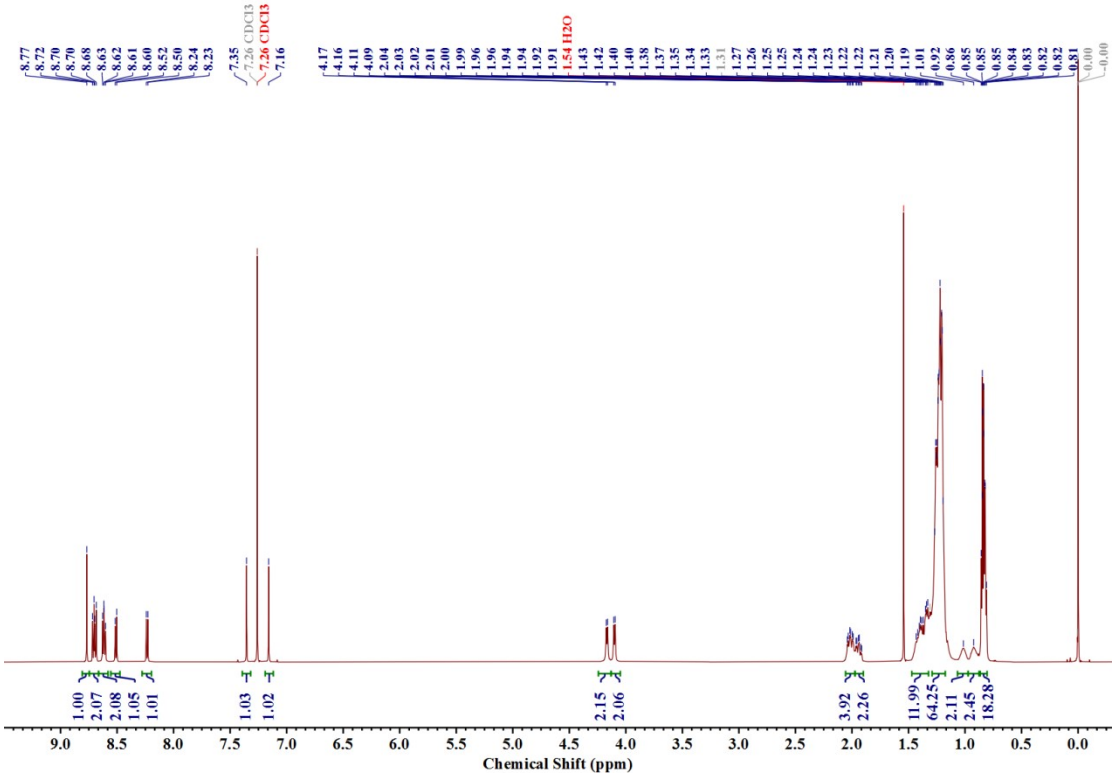

Figure S4 The ^{1}H spectrum of S-PDI-IDT-1 in $CDCl_3$

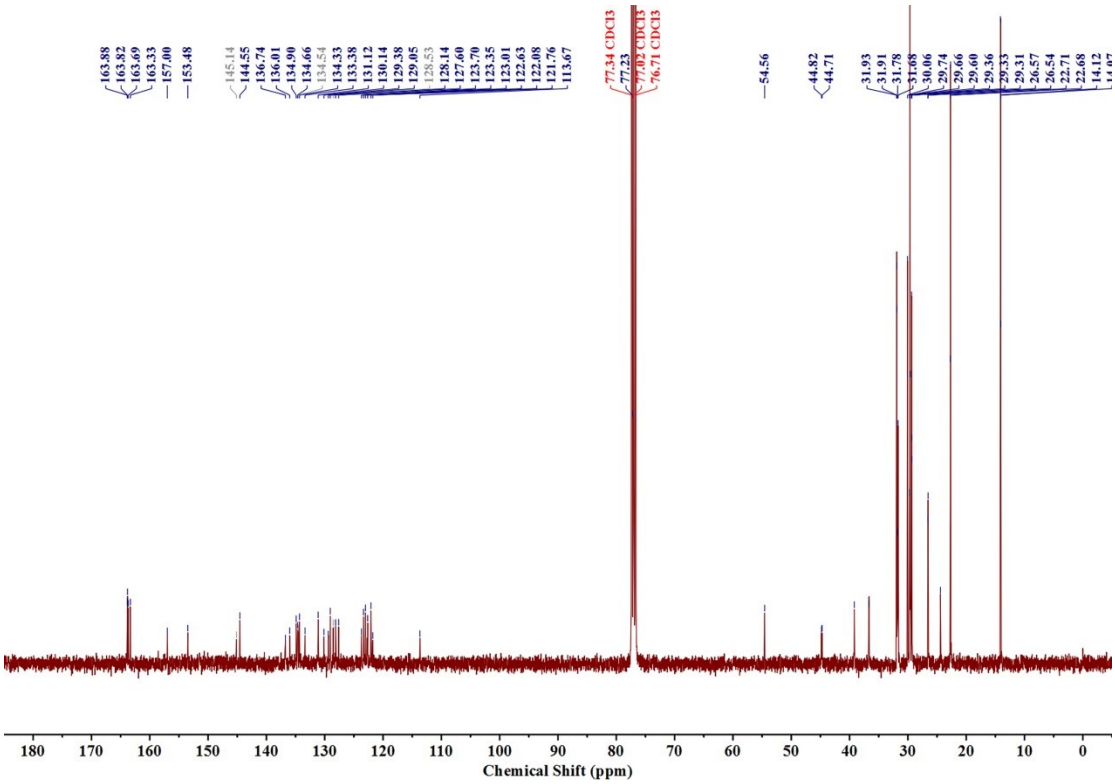

Figure S5 The ^{13}C spectrum of S-PDI-IDT-1 in $CDCl_3$

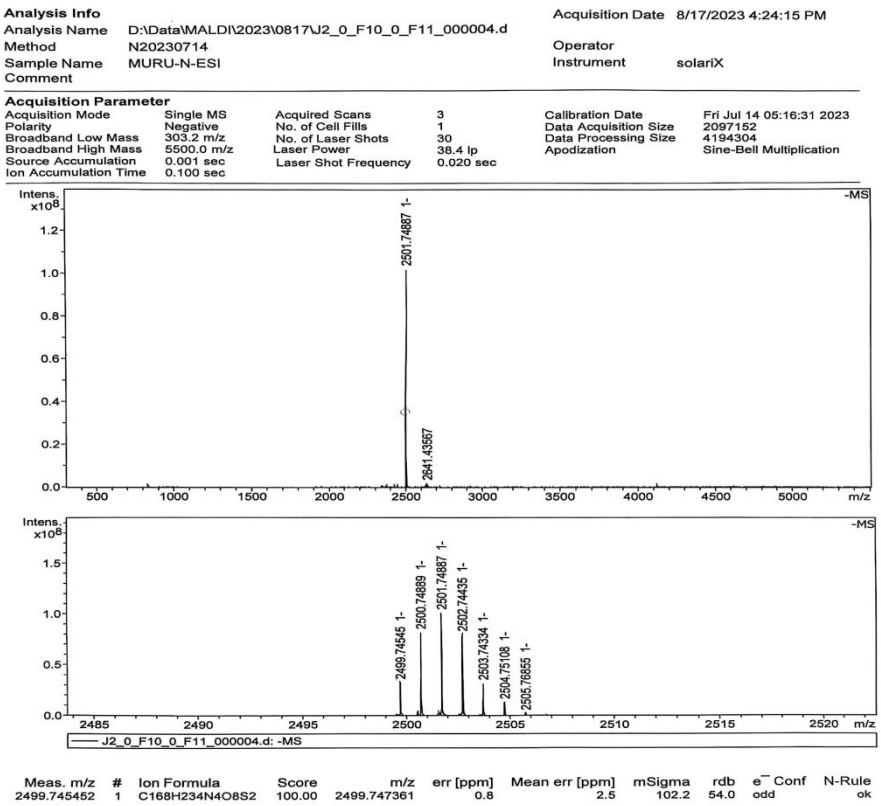

Figure S6 High resolution mass spectrometry analysis of S-PDI-IDT-1

Synthesis and characterization of S-PDI-IDT-2

N,N'-bis(2-octyldodecyl)-1-bromoperylene-3,4,9,10-tetracarboxylicdiimides (360.5 mg, 0.35 mmol) and 1,1'-[6,6,12,12-Tetrakis(4-hexylphenyl)-6,12-dihydrodithie-no [2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene-2,8-diyl]bis[1,1,1-trimethylstannane] (235.4 mg,0.175 mmol) with dimethyl formamide (DMF) 3 mL and $Pd(PPh_3)_4$ (40 mg, 0.035 mmol) as catalyzers were dissolved in 23 ml dry toluene solvent. The mixture was frozen with liquid nitrogen, followed by three times of successive vacuum and nitrogen fill cycles. Then, the mixture was refluxed at 110 °C for 48 hours. The molecules were dissolved in chloroform with minimum solvent. Then add methanol dropwise to the solution for precipitation. The crude product was acquired by filtering. The crude products were further refined by chromatographic column with the mixture of petroleum ether and dichloromethane (1:1-1:1.5) as the eluent, yielding a black solid: 43%.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 – 8.54 (m, 5H), 8.29 (t, *J* = 10.4 Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.24 (s, 2H), 7.12 (dt, *J* = 23.0, 8.1 Hz, 6H), 4.14 (d, *J* = 7.8 Hz, 4H), 2.66 – 2.47 (m, 4H), 2.02 (s, 2H), 1.32 – 1.18 (m, 68H), 0.86 (dt, *J* = 14.5, 7.2 Hz, 30H). ^{13}C NMR (400MHz, Chloroform-*d*) δ = -0.00, 14.09, 14.11, 22.62, 22.67, 26.53, 29.26, 29.30, 29.32, 29.34, 29.58, 29.61, 29.64, 30.03, 30.11, 31.34, 31.73, 31.89, 31.91, 35.57, 36.67, 44.75, 76.70, 77.01, 77.22, 77.33, 127.95, 128.62, 131.15, 139.84, 142.14, 163.79. HRMS calculated for $C_{196}H_{250}N_4O_8S_4$, m/z: 2917.82; found, m/z: 2917.80。

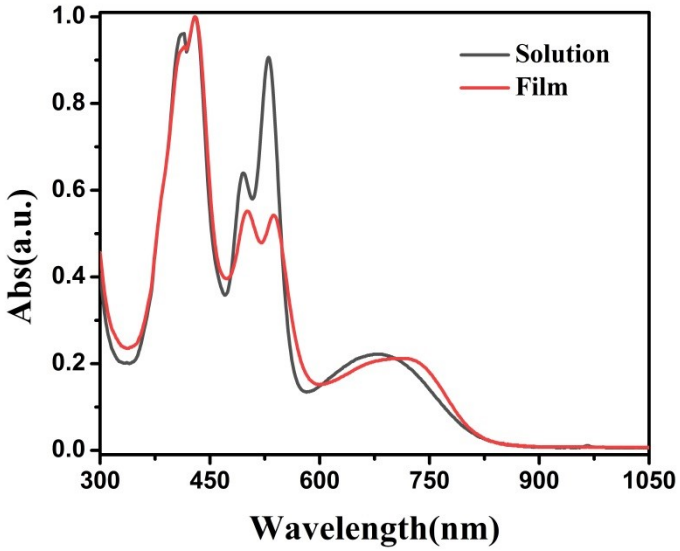

Figure S7 UV−Vis−NIR absorption spectra of S-PDI-IDT-2

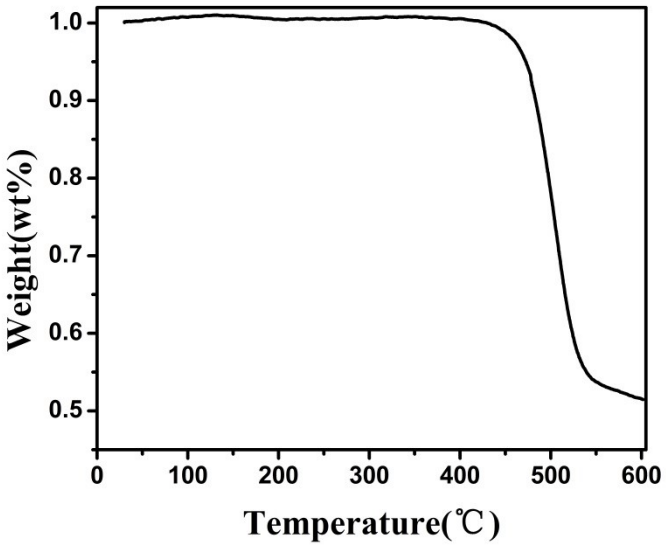

Figure S8 Thermogravimetric (TGA) analysis of S-PDI-IDT-2 measured at a heating rate of 10°C/ min in nitrogen

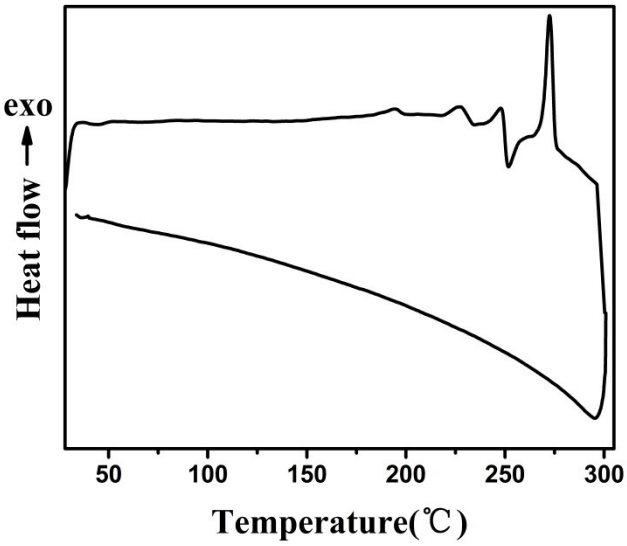

Figure S9 Differential scanning calorimetry (DSC) analysis of P-PDI-IDT-2 measured at a heating rate of 10°C/ min in nitrogen

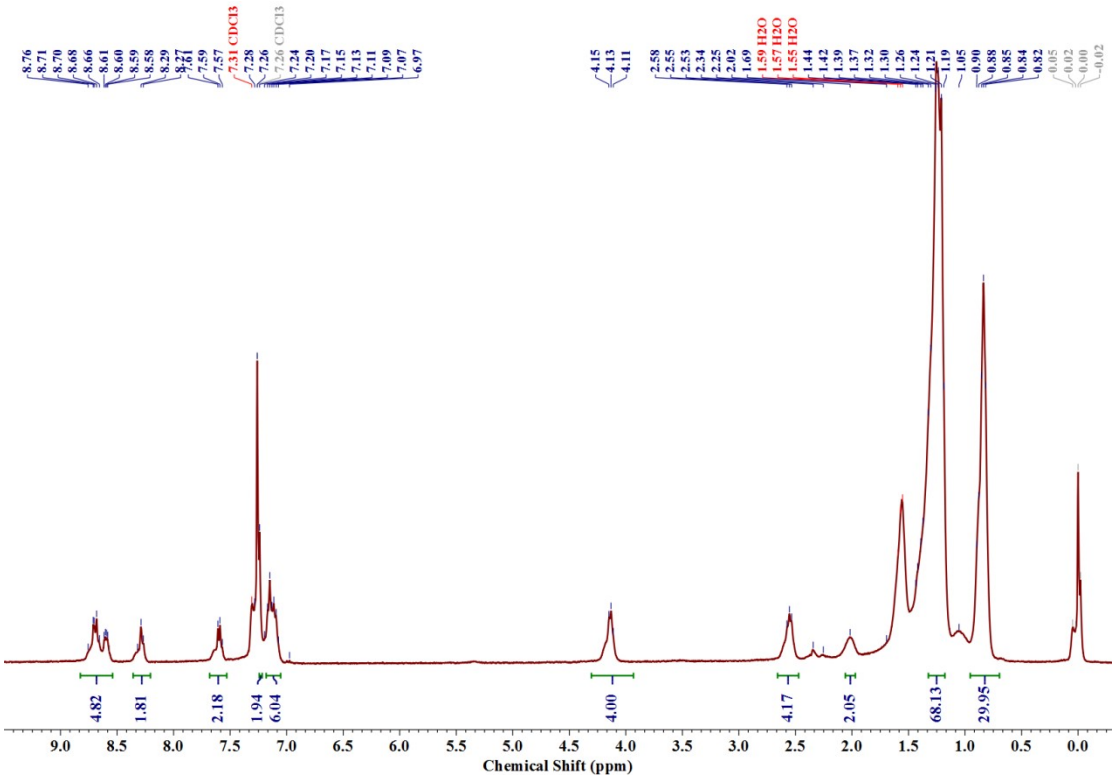

Figure S10 The ^{1}H spectrum of S-PDI-IDT-2 in $CDCl_3$

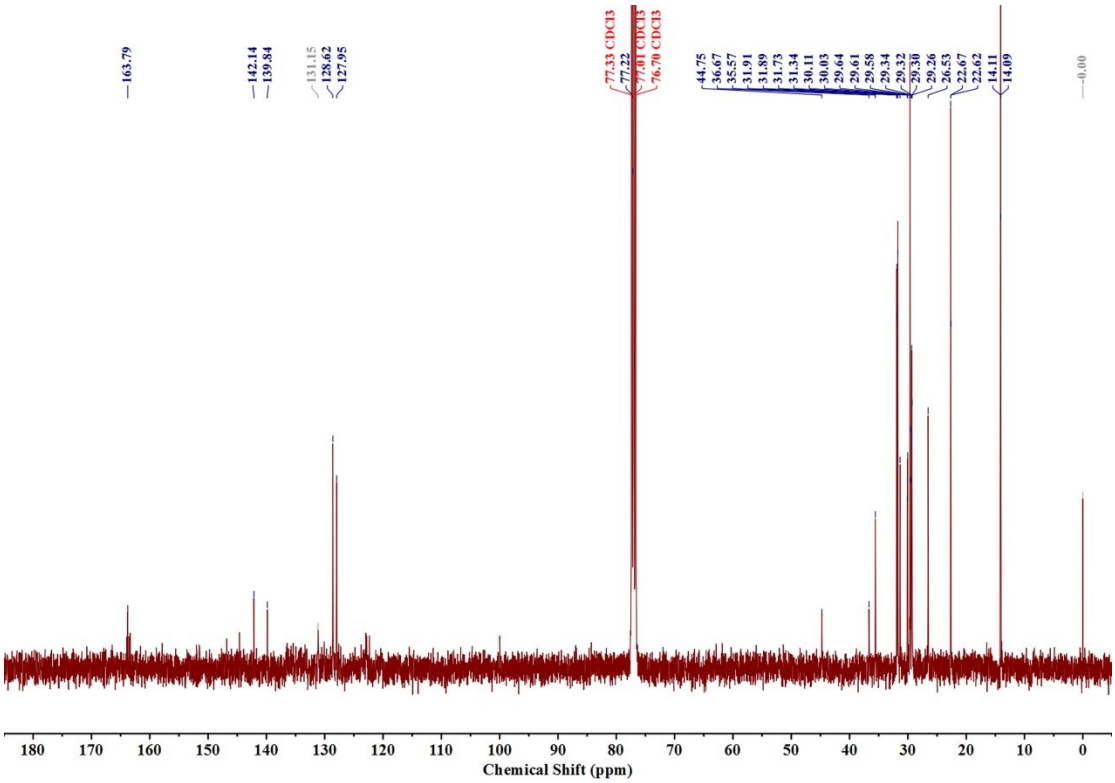

Figure S11 The ^{13}C spectrum of S-PDI-IDT-2 in $CDCl_3$

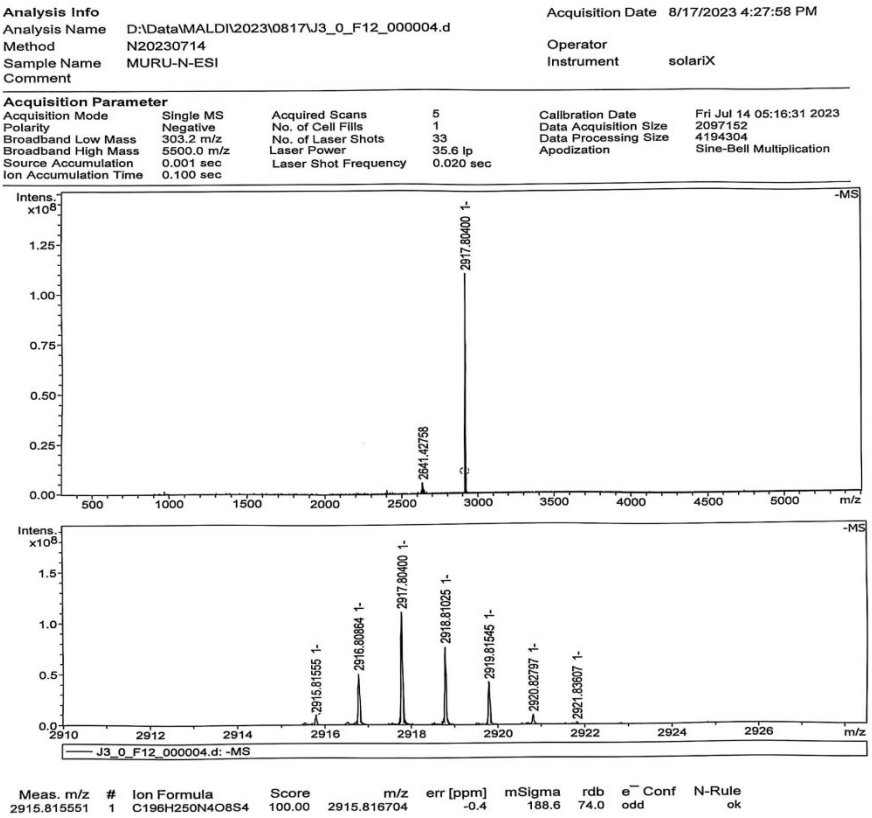

Figure S12 High resolution mass spectrometry analysis of S-PDI-IDT-2

Synthesis and characterization of S-PDI-IDT-3

N,N'-bis(2-octyldodecyl)-1-bromoperylene-3,4,9,10-tetracarboxylic diimides (360.5 mg, 0.35 mmol) and (4,4,9,9-Tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno [1,2-b:5,6-b']dithiophene-2,7-diyl)bis(trimethylstannane) (216 mg,0.175 mmol) with dimethyl formamide (DMF) 3 mL and $Pd(PPh_3)_4$ (40 mg, 0.035 mmol) as catalyzers were dissolved in 23 ml dry toluene solvent. The mixture was frozen with liquid nitrogen, followed by three times of successive vacuum and nitrogen fill cycles. Then, the mixture was refluxed at 110 ^oC for 48 hours. The molecules were dissolved in chloroform with minimum solvent. Then add methanol dropwise to the solution for precipitation. The crude product was acquired by filtering. The crude products were further refined by chromatographic column with the mixture of petroleum ether and dichloromethane (1:1-1:1.5) as the eluent, yielding a black solid: 63%.^1H NMR (400 MHz, Chloroform-*d*) δ 8.71 – 8.61 (m, 3H), 8.55 (dd, *J* = 8.0, 4.0 Hz, 3H), 8.32 (d, *J* = 8.3 Hz, 1H), 7.55 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 4H), 7.15 – 7.02 (m, 5H), 4.13 (d, *J* = 7.2 Hz, 4H), 2.57 (t, *J* = 7.9 Hz, 4H), 2.09 – 1.91 (m, 2H), 1.62 (dt, *J* = 22.5, 7.3 Hz, 8H), 1.25 (dd, *J* = 20.7, 13.2 Hz, 68H), 0.85 (dt, *J* = 9.8, 6.8 Hz, 22H). ^{13}C NMR (400MHz, Chloroform-*d*) δ = 0.01, 14.12, 22.65, 22.68, 22.71, 26.52, 26.61, 29.27, 29.31, 29.33, 29.35, 29.38, 29.59, 29.64, 29.68, 29.72, 30.04, 30.12, 31.26, 31.30, 31.72, 31.75, 31.81, 31.91, 31.94, 35.61, 36.61, 36.71, 38.16, 44.77, 59.54, 63.32, 76.71, 77.02, 77.23, 77.34, 117.92, 122.13, 122.59, 122.75, 123.01, 123.22, 123.35, 123.75, 127.60, 127.76, 128.15, 128.48, 128.52, 129.13, 129.55, 130.40, 131.13, 133.55, 134.25, 134.64, 134.86, 135.48, 136.26, 141.15, 141.97, 143.74, 146.10,

153.63, 158.11, 163.34, 163.49, 163.77, 163.90. HRMS calculated for $C_{192}H_{250}N_4O_8S_2$, m/z: 2805.88; found, m/z: 2805.87。

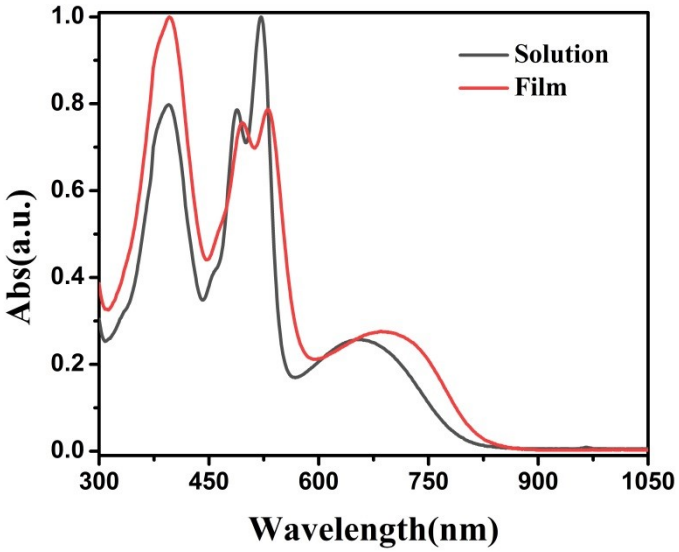

Figure S13 UV−Vis−NIR absorption spectra of S-PDI-IDT-3

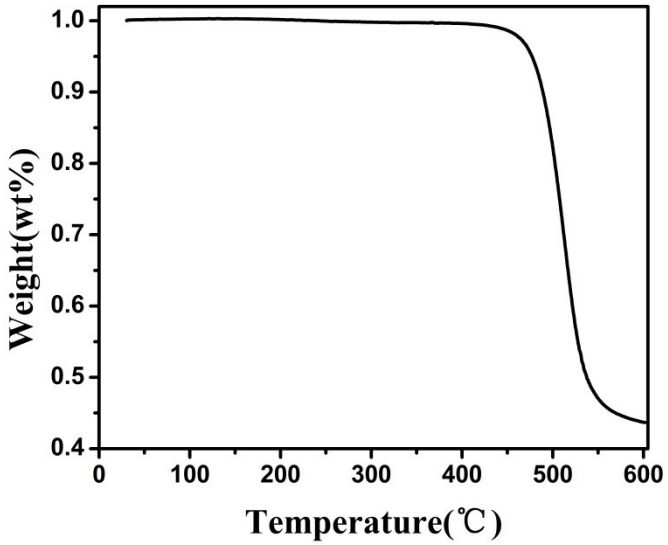

Figure S14 Thermogravimetric (TGA) analysis of S-PDI-IDT-3 measured at a heating rate of 10°C/ min in nitrogen

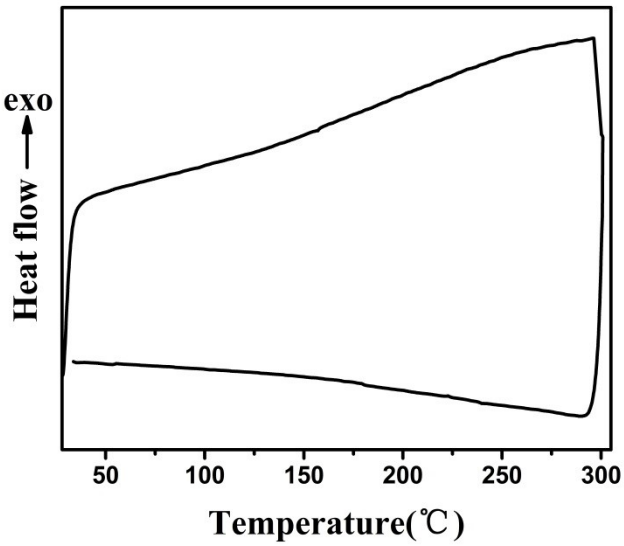

Figure S15 Differential scanning calorimetry (DSC) analysis of S-PDI-IDT-3 measured at a heating rate of 10°C/ min in nitrogen

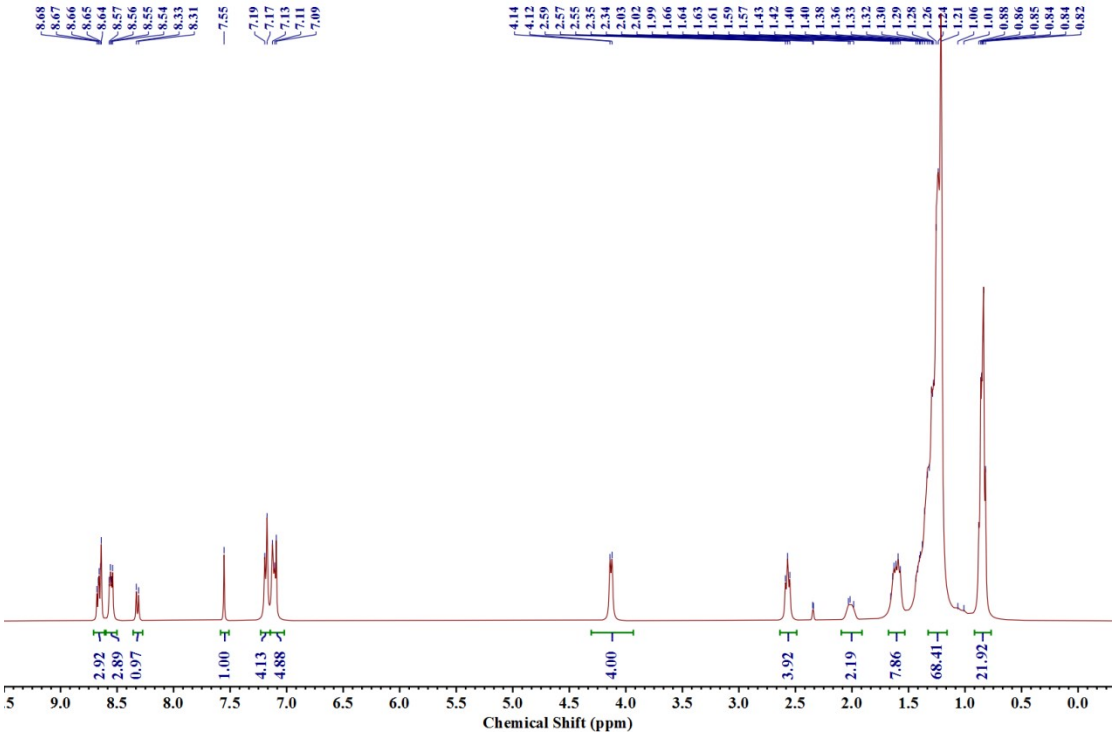

Figure S16 The ^{1}H spectrum of S-PDI-IDT-3 in $CDCl_3$

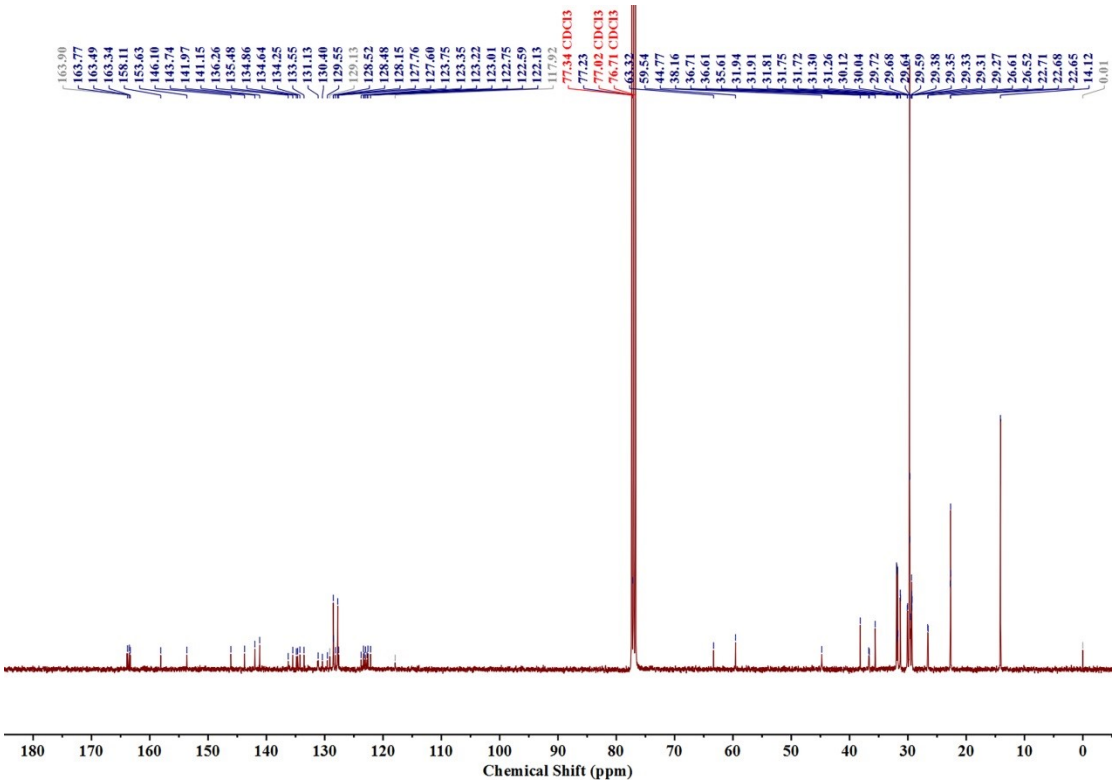

Figure S17 The ^{13}C spectrum of S-PDI-IDT-3 in $CDCl_3$

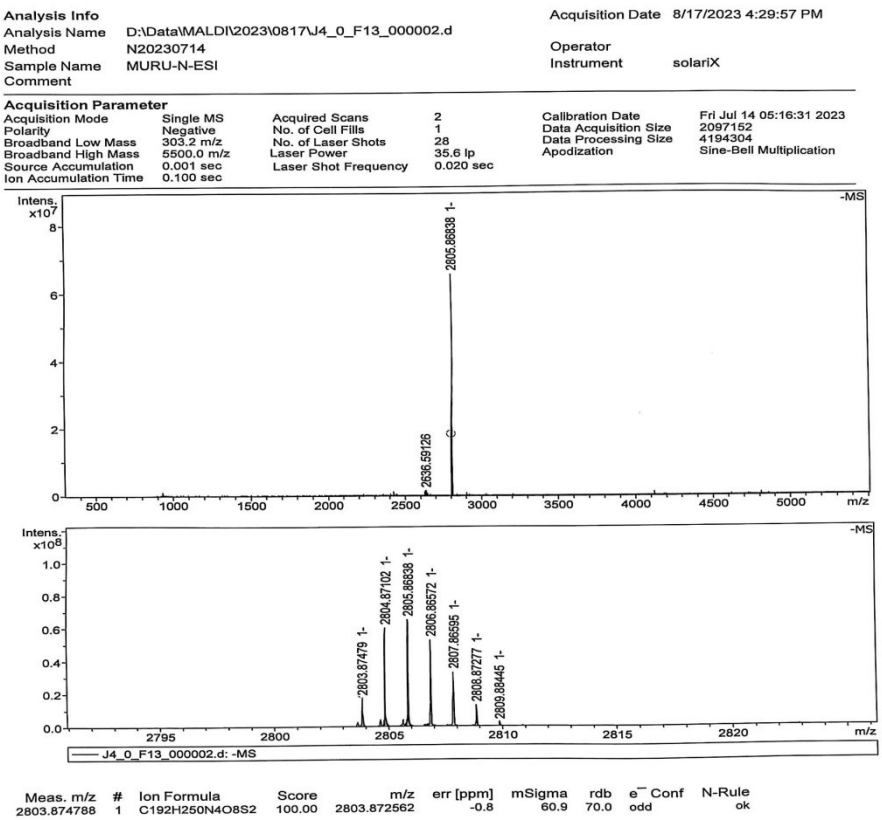

Figure S18 High resolution mass spectrometry analysis of S-PDI-IDT-3

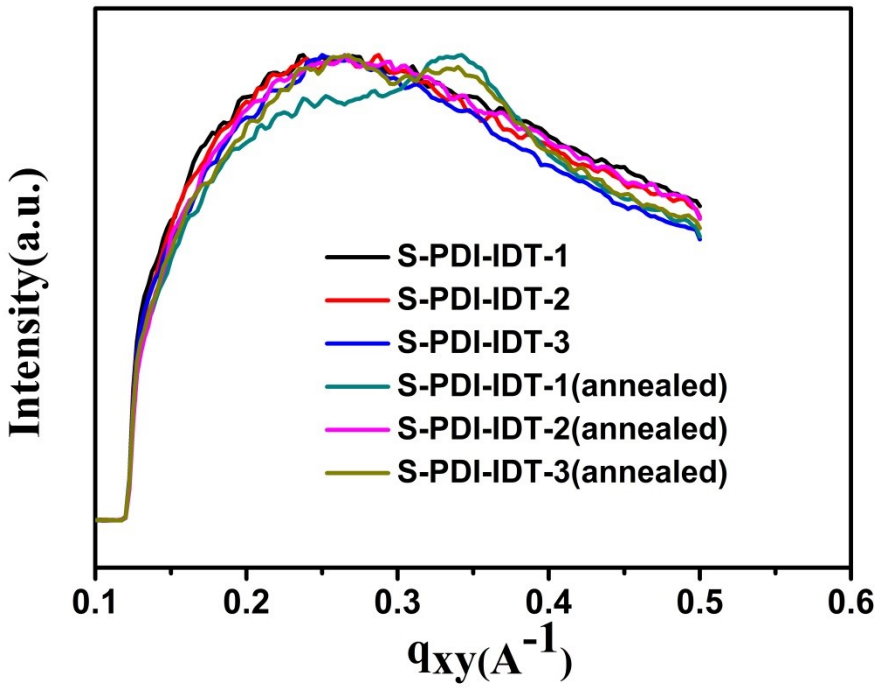

Figure S19 The GIWAXS diffraction corresponding to in plane line

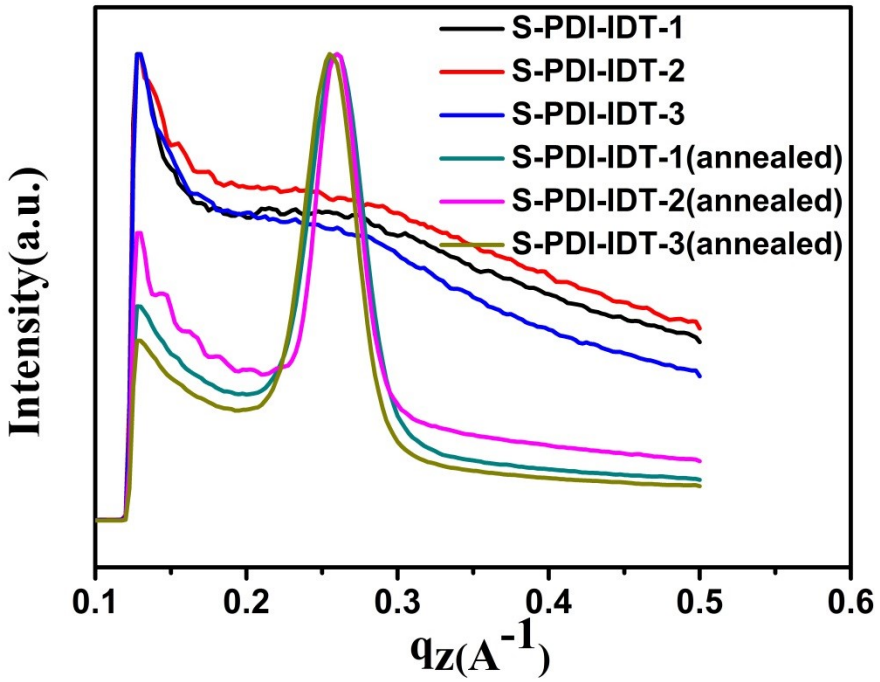

Figure S20 The GIWAXS diffraction corresponding to out of plane line