Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Conjugated Molecular Dyads with Diketopyrrolopyrrole-based Conjugated Backbone for Single-Component Organic Solar Cells

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1. Materials and measurements

The synthetic procedures were performed under argon atmosphere. Commercial chemicals (from sigma-Aldrich, JK Chemical and TCI) were used as received. Compound (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**M2**), Compound (4,8-bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**M3**) and (4,8-bis(5-((2-ethylhexyl)thio)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**M4**) were purchased from Suna Tech Inc. Compound 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**S1**) and compound 9,9'-((1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-2,5(1H,4H)-diyl)bis(dodecane-12,1-diyl))bis(2-(tricosan-12-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone) (**S2**) were synthesized according to our previous work.[1]

^{1}H-NMR spectra of intermedia products and monomers were recorded at 400 MHz on a Bruker AVANCE spectrometer. ^{1}H-NMR spectra of the “double-cable” small molecules were recorded on a Bruker AVIII 500WB NMR Spectrometer at 100 °C with 1,1,2,2-tetrachloroethane-d_2 as the solvent and tetramethylsilane (TMS) as the internal standard. Optical absorption spectra were recorded on a JASCO V-570 spectrometer with a slit width of 2.0 nm and a scan speed of 1000 nm min^{-1}. Cyclic voltammetry was performed under an inert atmosphere at a scan rate of 0.1 V s^{-1} and 1 M tetrabutylammonium hexafluorophosphate in o-DCB as the electrolyte. The working, counter and reference electrodes were glassy carbon, Pt wire and Ag/AgCl, respectively. The concentration of the sample in the electrolyte was approximately 0.8 mg/mL. All potentials were corrected against Fc/Fc$^+$. Thermogravimetric analysis data were obtained from a TGA8000 Thermogravimetric Analyzer (PerkinElmer), DSC measurement was performed on a DSC-250 apparatus. Melting point was measured by Melting-point Apparatus (WRS-3) in visual model with the heating rate of 1 °C/min.

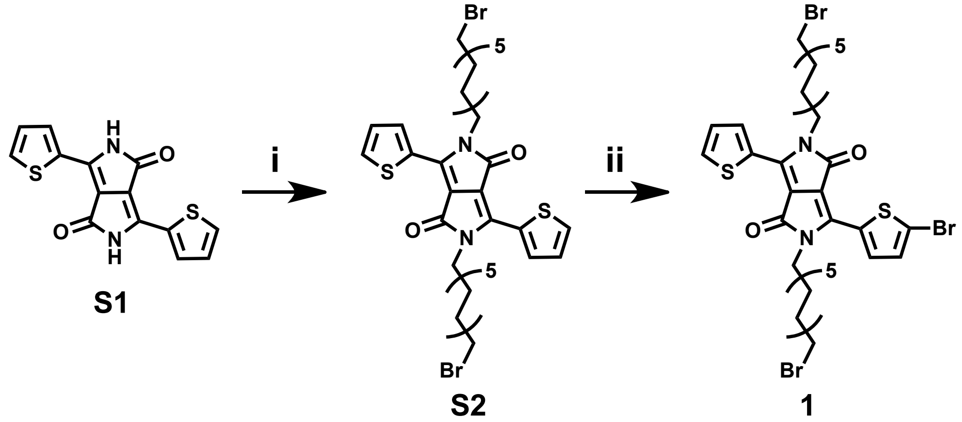
Photovoltaic devices with inverted configuration were made by spin-coating a ZnO sol-gel at 4000 rpm for 60 s onto pre-cleaned, patterned ITO substrates. The photoactive layer was deposited by spin coatingsolution containing double-cable small molecules within 60 s in N_2-filled glove box, after that let the solution evaporative dry. The thin films were then transferred into the N_2-filled glove box. MoO_3 (10 nm) and Ag (100 nm) were deposited by vacuum evaporation at ca. 4×10^{-5} Pa as the back electrode. The thickness of the active layer is about 50 nm.

The active area of the cells was 0.040 cm^2. The *J–V* curves were measured under AM1.5G illumination at 100 mW cm^{-2} using an AAA solar simulator (XES-70S1, SAN-EI Electric Co., Ltd) calibrated with a standard photovoltaic cell equipped with a KG5 filter (certificated by the National Institute of Metrology) and a Keithley 2400 source-measure unit. The EQE data were obtained using a solar cell spectral response measurement system (QE-R3011, Enli Technology Co. Ltd). The film thickness data were obtained via a surface profilometer (Dektak XT, Bruker).

Atomic force microscopy (AFM) images were recorded using a Digital Instruments Nano scope IIIa multimode atomic force microscope in tapping mode under ambient conditions.

The two-dimensional (2D) GI-WAXS/MAXS experiments were carried out on a GANESHA 300XL+ system from JJ X-ray in the X-ray lab at DSM Materials Sciences Center (DMSC). The instrument is equipped with a Pilatus 300K detector, with pixel size of 172 μm × 172 μm. The X-ray source is a Genix 3D Microfocus Sealed Tube X-Ray Cu-source with integrated Monochromator (multilayer optic "3D version" optimized for SAXS) (30 W). The wavelength used is $\lambda = 1.5418$ Å. The detector moves in a vacuum chamber with sample-to-detector distance varied between 0.115 m and 1.47 m depending on the configuration used, as calibrated using silver behenate ($d_{001} = 58.380$ Å). The minimized background scattering plus high-performance detector, allows for a detectable q-range varying from 3 E^{-3} to 3 $Å^{-1}$ (0.2 to 210 nm). The sample was placed vertically on the goniometer and tilted to a glancing angle of 0.2° with respect to the incoming beam. A small beam was used to gain a good resolution. The primary slits have a size of 0.3 × 0.5 mm (horizontal × vertical), and the guard slits have a size of 0.1 × 0.3 mm (horizontal × vertical). The accumulation time was 6 h for each measurement. The line cuts were conducted using SAXSGUI program.

2. Synthesis



Scheme S1. The chemical structures of the monomers. (i) K_2CO_3 in DMF at 120 °C, 18 h; (ii) NBS in $CHCl_3$.

Compound **1:** To a solution of **S2** (0.30 g, 0.38 mmol) in $CHCl_3$ (25 mL) was added NBS (0.067 g, 0.38 mmol) with portions in dark at room temperature. The reaction mixture was stirred at room temperature for 4 h. 20 mL H_2O was added and the mixture was extracted by $CHCl_3$. The crude product was purified by silica gel chromatography (dichloromethane : petroleum ether, v/v = 1:3 as eluent) to obtain **1** as a black solid. (0.16 g, yield 49%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.94-8.93 (d, 1H), 8.67-8.66 (d, 1H), 3.99 (t, 4H), 7.66-7.65 (d, 1H), 7.30-7.28 (t, 1H), 7.25-7.24 (d, 1H), 4.08-4.04 (t, 2H), 4.01-3.97 (t, 2H), 3.42-3.38 (t, 4H), 1.88-1.81 (m, 4H), 1.77-1.70 (m, 4H), 1.54-1.43 (m, 8H), 1.41-1.38 (m, 24H).

M1: To a solution of compound **1** (81.3 mg, 0.093 mmol), potassium carbonate (257.2 mg, 1.86 mmol) in DMF (15 mL) was added compound **2** (165.9 mg, 0.23 mmol). The reaction mixture was stirred at 80 °C for 36 h and then cooled to room temperature. Chloroform (100 mL) and water (100 mL) were added and the organic layer was separated and washed with brine and the solvent evaporated. The resulting solid was purified by silica gel chromatography (dichloromethane : ethyl acetate, v/v = 100:1 as eluent) to afford **M1** as a black solid (100 mg, 51%). ^1H NMR ($CDCl_2CDCl_2$, 400 MHz): δ (ppm) 8.86-8.86 (d, 1H), 8.62-8.52 (m, 17H), 7.69-7.68 (d, 1H), 7.28-7.26 (t, 1H), 7.21-7.20 (d, 1H), 5.15 (br, 2H), 4.13 (br, 4H), 3.93 (br, 2H), 3.84 (br, 2H). 2.22-2.20 (br,4H), 1.89 (br, 4H), 1.73-1.69 (m, 8H), 1.28-1.20 (m, 104H), 0.85-0.82 (t, 12H).

SMDPP: To a degassed solution of monomer **M1** (122 mg, 0.057 mmol), **M2** (23.46 mg, 0.026 mmol) in toluene (5 mL), $Pd(PPh_3)_4$ (1.50 mg, 0.0013 mmol) was added. The mixture was stirred at 120 °C for 8 h. The mixture was precipitated in methanol, after filtration, the crude product was dissolved and purified by silica gel chromatography (chloroform : tetrahydrofuran, v/v = 5:1 as eluent) to obtain **SMDPP** (83 mg, yield 68%) as dark purple solid. ^{1}H NMR ($CD_2Cl_2CD_2Cl_2$, 500 MHz, 373K): δ (ppm) 8.83 (d, 2H), 8.79-8.78 (d, 2H), 8.68-8.50 (m, 32H), 7.84 (s, 2H), 7.69-7.68 (d, 2H), 7.44-7.43 (d, 4H), 7.31 (s, 2H), 7.04-7.03 (d, 2H), 5.20-5.19 (m, 4H), 4.24-4.21 (t, 4H), 4.14-4.13 (t, 4H), 4.04 (br, 8H), 2.99-2.97 (d, 4H), 2.27-2.26 (m, 8H), 1.97-1.96 (m, 8H), 1.83-1.82 (m,16H), 1.80-1.77 (m, 6H), 1.36-1.28 (m, 216H), 1.07-1.04 (t, 6H), 1.01-0.98 (t, 6H), 0.92-0.89 (t, 24H). HR-MS (MALDI-TOF): m/z (%): 4692.5941. (calcd for $C_{298}H_{366}N_{12}O_{20}S_8$: 4692.7500)

S-SMDPP: To a degassed solution of monomer **M1** (100 mg, 0.047 mmol), **M3** (20.59 mg, 0.021 mmol) in toluene (5 mL), $Pd(PPh_3)_4$ (2.46 mg, 0.0021 mmol) was added. The mixture was stirred at 120 °C for 8 h. The mixture was precipitated in methanol, after filtration, the crude product was dissolved and purified by silica gel chromatography (chloroform : tetrahydrofuran, v/v = 5:1 as eluent) to obtain **S-SMDPP** (81 mg, yield 80%) as dark purple solid. ^{1}H NMR ($CD_2Cl_2CD_2Cl_2$, 500 MHz, 373K): δ (ppm) 8.84-8.83 (d, 2H), 8.77-8.76 (d, 2H), 8.68-8.50 (m, 32H), 7.80 (s, 2H), 7.69-7.69 (d, 2H), 7.47-7.44 (d, 4H), 7.33-7.32 (d, 4H), 5.20-5.19 (m, 4H), 4.24-4.21 (t, 4H), 4.15-4.12 (t, 4H), 4.04 (br, 8H), 3.08-3.07 (d, 4H), 2.28-2.27 (m, 8H), 1.97-1.96 (m, 8H), 1.78-1.77 (m,16H), 1.75-1.58 (m, 6H), 1.34-1.28 (m, 216H), 1.03-0.97 (t, 12H), 0.92-0.89 (t, 24H). HR-MS (MALDI-TOF): m/z (%): 4756.5474. (calcd for $C_{298}H_{366}N_{12}O_{20}S_{10}$: 4756.8700)

SF-SMDPP: To a degassed solution of monomer **M1** (63 mg, 0.029 mmol), **M4** (13.46 mg, 0.013 mmol) in toluene (5 mL), $Pd(PPh_3)_4$ (2.46 mg, 0.0013 mmol) was added. The mixture was stirred at 120 °C for 8 h. The mixture was precipitated in methanol, after filtration, the crude product was dissolved and purified by silica gel chromatography (chloroform : tetrahydrofuran, v/v = 5:1 as eluent) to obtain **SF-SMDPP** (50 mg, yield 64%) as dark purple solid. ^{1}H NMR ($CD_2Cl_2CD_2Cl_2$, 500 MHz, 373K): δ (ppm) 8.85 (d, 2H), 8.75-8.75 (d, 2H), 8.68-8.50 (m, 32H), 7.78 (s, 2H), 7.70-7.69 (d, 2H), 7.46 (d, 2H), 7.35-7.33 (d, 2H), 7.32-7.31 (d, 2H), 5.19 (m, 4H), 4.24-4.21 (t, 4H), 4.14-4.11 (t, 4H), 4.04 (br, 8H), 3.03-3.02 (d, 4H), 2.28-2.26 (m, 8H), 1.96 (m, 8H), 1.78-1.77 (m,16H), 1.58 (m, 6H), 1.33-1.28 (m, 216H), 1.03-1.00 (t, 12H), 0.97-0.90 (t, 24H). HR-MS (MALDI-TOF): m/z (%): 4792.5353. (calcd for $C_{298}H_{364}F_2N_{12}O_{20}S_{10}$: 4792.8508)

3. CV

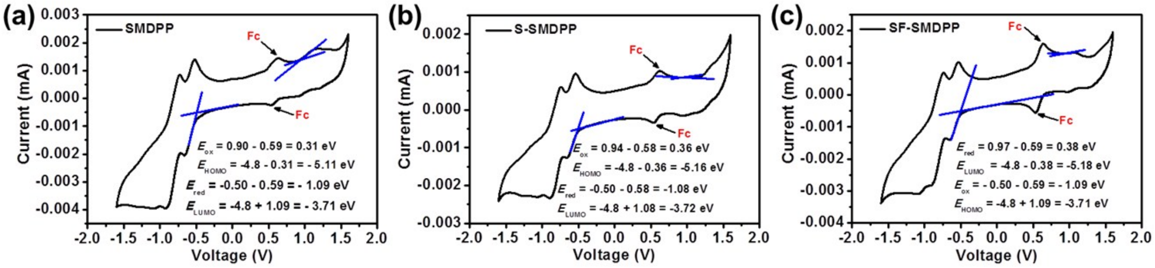


Figure S1. Cyclic voltammogram of (a) SMDPP, (b) S-SMDPP and (c) SF-SMDPP in *o*-DCB solution with concentration of 0.8 mg/ml. The ferrocene (Fc) peaks are also included. Potential vs. Fc/Fc^{+}.

4. DSC of 2DPP-BDT and PBI

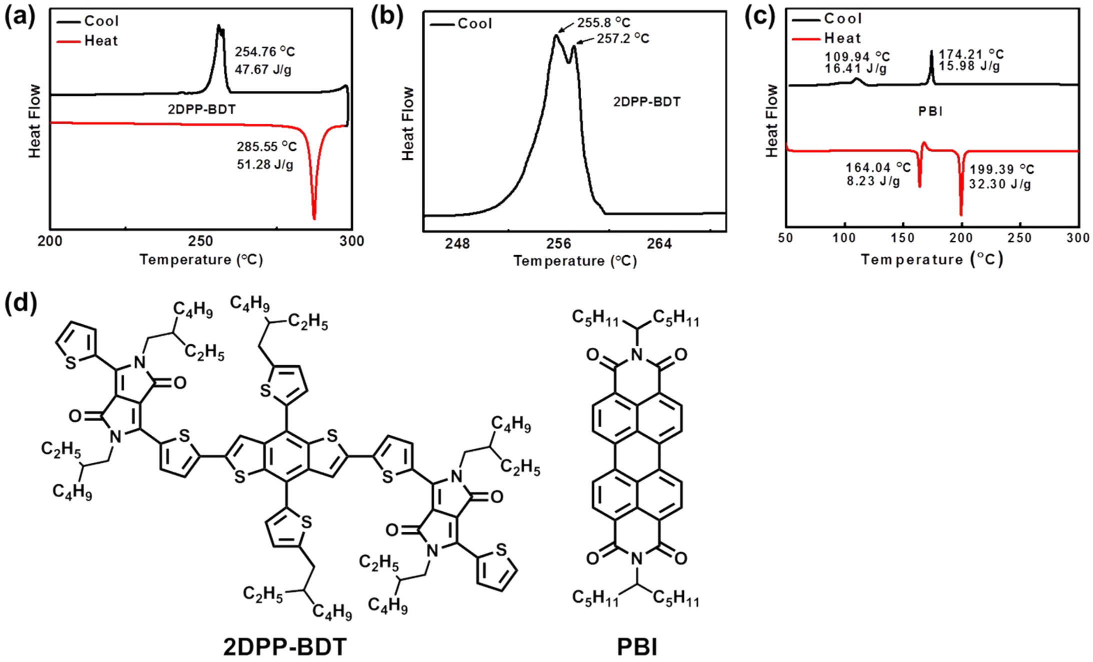


Figure S2. (a-c) DSC curves and (d) the chemical structures of **2DPP-BDT** and **PBI**. (a) **2DPP-BDT** and (b) its enlarged region to show the two peaks. (c) **PBI**.

5. Solar cells performance

Table S1. Photovoltaic performances of devices based on SMDPP fabricated from *o*-DCB with different content of additive and annealed at different temperature.

No.	TA (°C)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)

o-DCB	RT	5.62	0.68	0.45	1.73
o-DCB/DIO (0.2%)	RT	5.30	0.68	0.43	1.55
o-DCB/DIO (0.5%)	RT	5.46	0.68	0.40	1.49
o-DCB/DIO (1%)	RT	5.51	0.68	0.40	1.48
o-DCB	RT	5.62	0.68	0.45	1.73
o-DCB	100	5.49	0.69	0.43	1.61
o-DCB	150	4.34	0.65	0.47	1.32

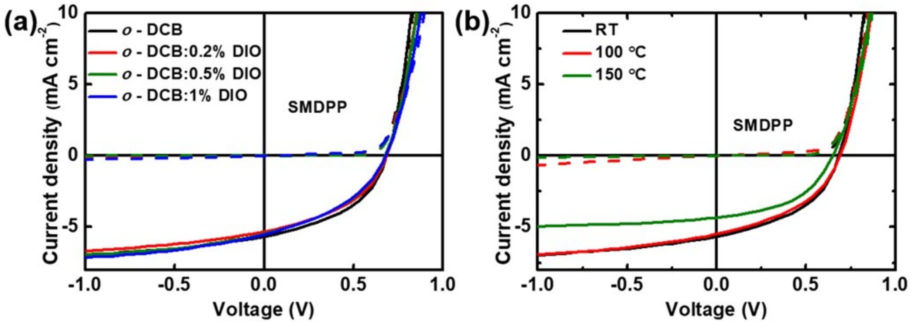


Figure S3. IV curves of SMDPP, (a) *o*-DCB with different content of additive and (b) annealed at different temperature.

Table S2. Photovoltaic performances of devices based on S-SMDPP fabricated from *o*-DCB with different content of additive and annealed at different temperature.

No.	TA (°C)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
o-DCB	RT	8.03	0.73	0.43	2.52
o-DCB/DIO (0.2%)	RT	8.02	0.72	0.44	2.54
o-DCB/DIO (0.5%)	RT	7.84	0.72	0.42	2.40
o-DCB/DIO (1%)	RT	7.68	0.72	0.39	2.28
o-DCB	RT	8.03	0.73	0.43	2.52
o-DCB	100	6.86	0.72	0.47	2.33
o-DCB	150	6.82	0.70	0.54	2.57

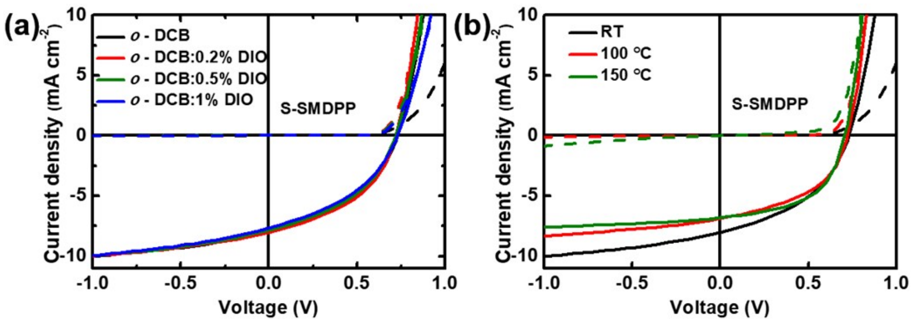


Figure S4. IV curves of S-SMDPP, (a) *o*-DCB with different content of additive and (b) annealed at different temperature.

Table S3. Photovoltaic performances of devices based on SF-SMDPP fabricated from *o*-DCB with different content of additive and annealed at different temperature.

No.		J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
o-DCB	RT	6.08	0.83	0.40	2.04
o-DCB/DIO (0.2%)	RT	5.73	0.82	0.41	1.90
o-DCB/DIO (0.5%)	RT	5.99	0.81	0.40	1.93
o-DCB/DIO (1%)	RT	5.06	0.82	0.37	1.53
o-DCB	RT	6.08	0.83	0.40	2.04
o-DCB	100	5.44	0.82	0.43	1.93
o-DCB	150	4.97	0.81	0.48	1.92

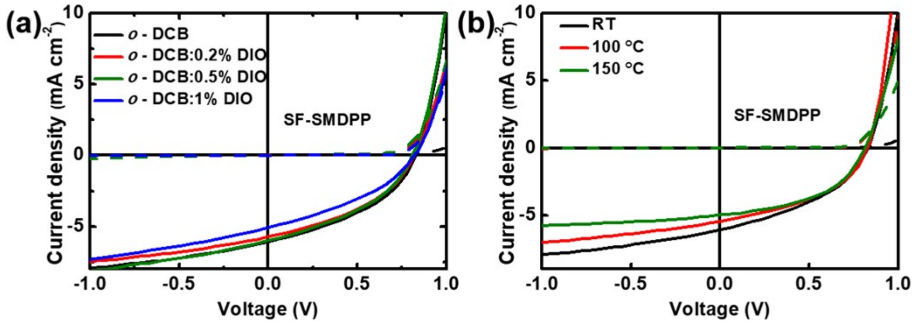


Figure S5. IV curves of SF-SMDPP, (a) *o*-DCB with different content of additive and (b) annealed at different temperature.

Table S4. Photovoltaic performances of 6 devices based on SMDPP fabricated from *o*-DCB at room temperature.

No.	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
1	5.65	0.68	0.45	1.73
2	5.49	0.68	0.45	1.70
3	5.37	0.69	0.45	1.66
4	5.87	0.67	0.42	1.68

5	5.99	0.68	0.41	1.65
6	5.70	0.69	0.41	1.62
average	5.68±0.21	0.68±0.007	0.43±0.018	1.67±0.035

Table S5. Photovoltaic performances of 6 devices based on S-SMDPP fabricated from *o*-DCB at room temperature.

No.	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
1	8.32	0.73	0.41	2.48
2	8.03	0.73	0.43	2.52
3	8.14	0.73	0.42	2.51
4	7.98	0.73	0.42	2.47
5	8.26	0.73	0.42	2.50
6	8.06	0.72	0.43	2.49
average	8.13±0.12	0.73±0.0037	0.42±0.0068	2.49±0.017

Table S6. Photovoltaic performances of 6 devices based on SF-SMDPP fabricated from *o*-DCB at room temperature.

No.	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
1	6.08	0.83	0.40	2.04
2	5.82	0.83	0.42	2.03
3	5.88	0.81	0.40	1.91
4	5.99	0.83	0.39	1.96
5	6.00	0.83	0.40	1.98
6	5.83	0.83	0.41	2.00
average	5.93±0.096	0.83±0.0074	0.40±0.0094	1.99±0.044

6. AFM

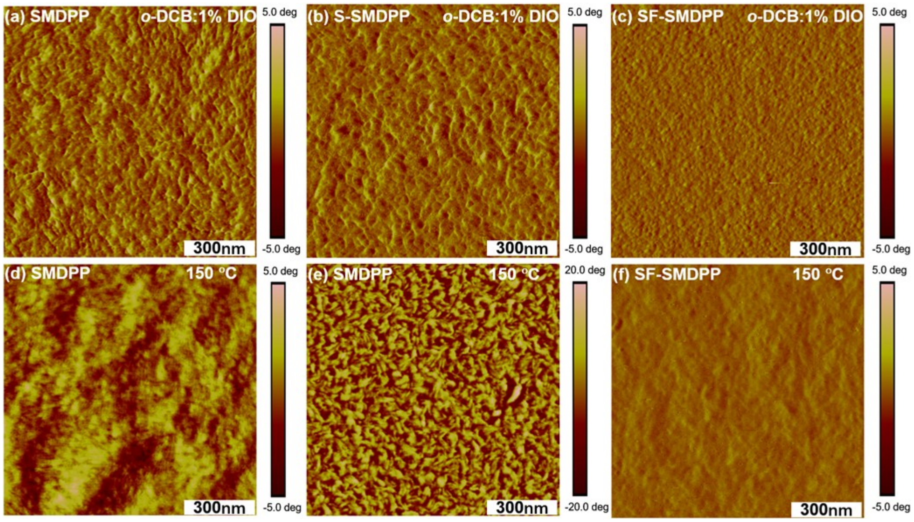


Figure S6. AFM phase images of (a, d) SMDPP, (b, e) S-SMDPP and (c, f) SF-SMDPP . (a, b, c) thin films were fabricated from *o*-DCB solution with 1% DIO as additive. (d, e, f) thin films were fabricated from *o*-DCB and annealed at 150 °C for 10 mins. (a-f) 1.0 × 1.0 μm^2.

7. NMR of the compounds

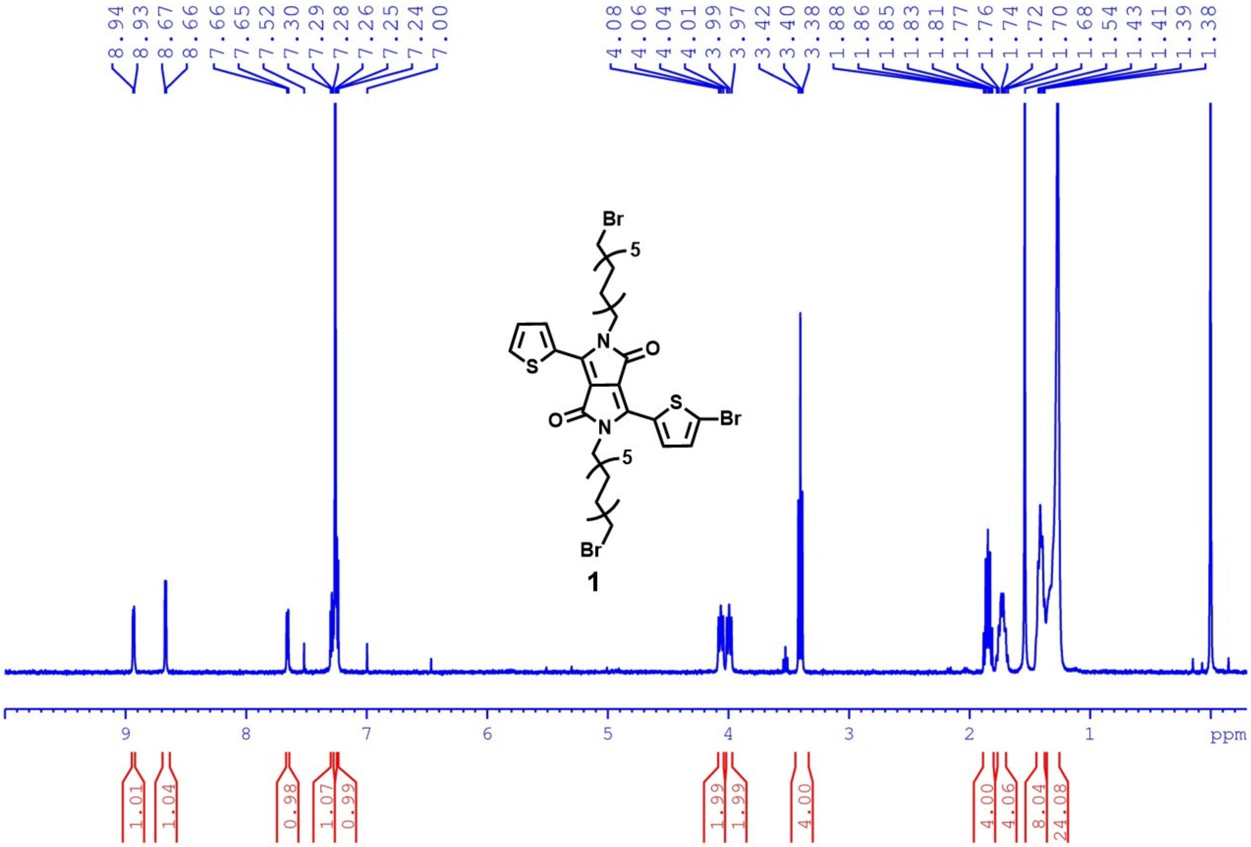


Figure S7. ^{1}H-NMR of compound **1** recorded in CDCl$_3$

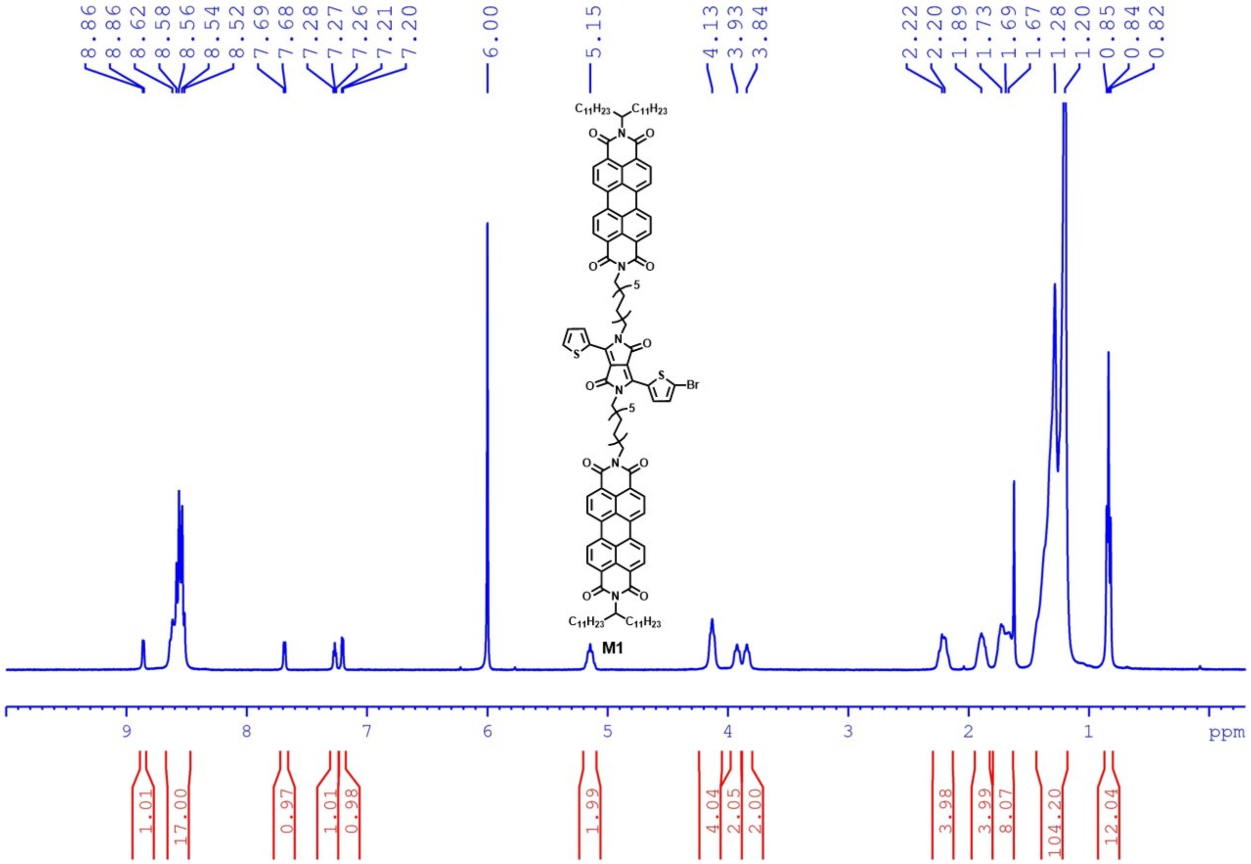


Figure S8. ^{1}H-NMR of **M1** recorded in $CDCl_2CDCl_2$

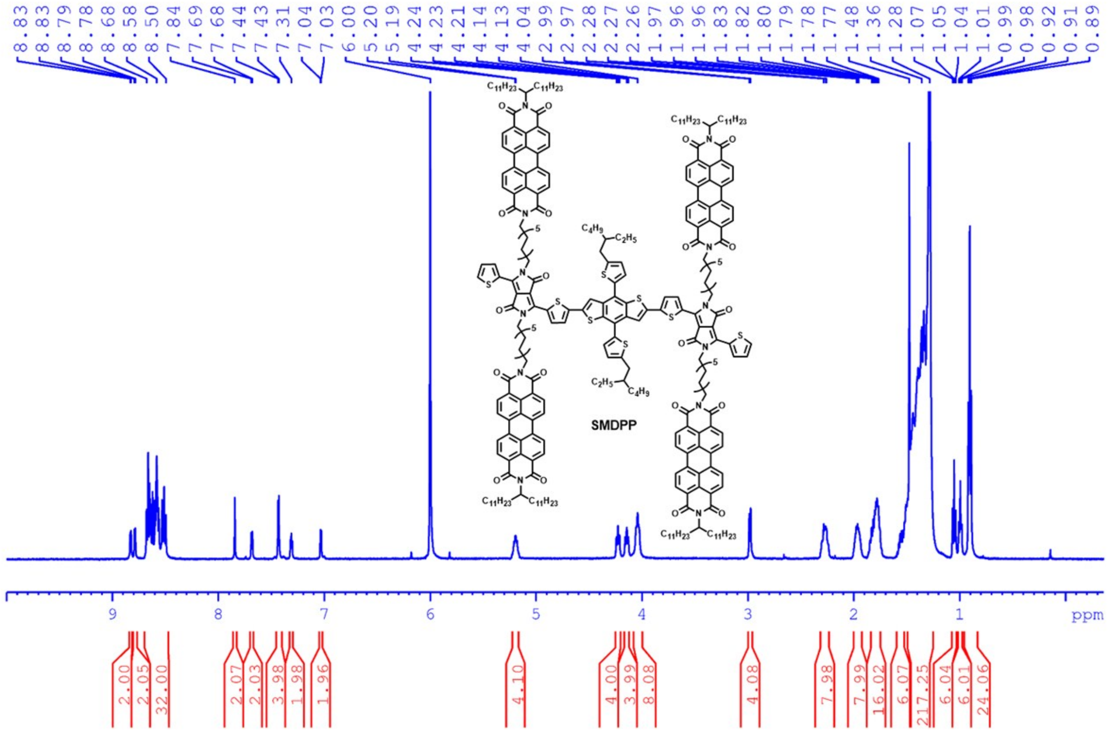


Figure S9. ^{1}H-NMR of **SMDPP** recorded at 100 ºC with 1,1,2,2-tetrachloroethane-d_2 as the solvent.

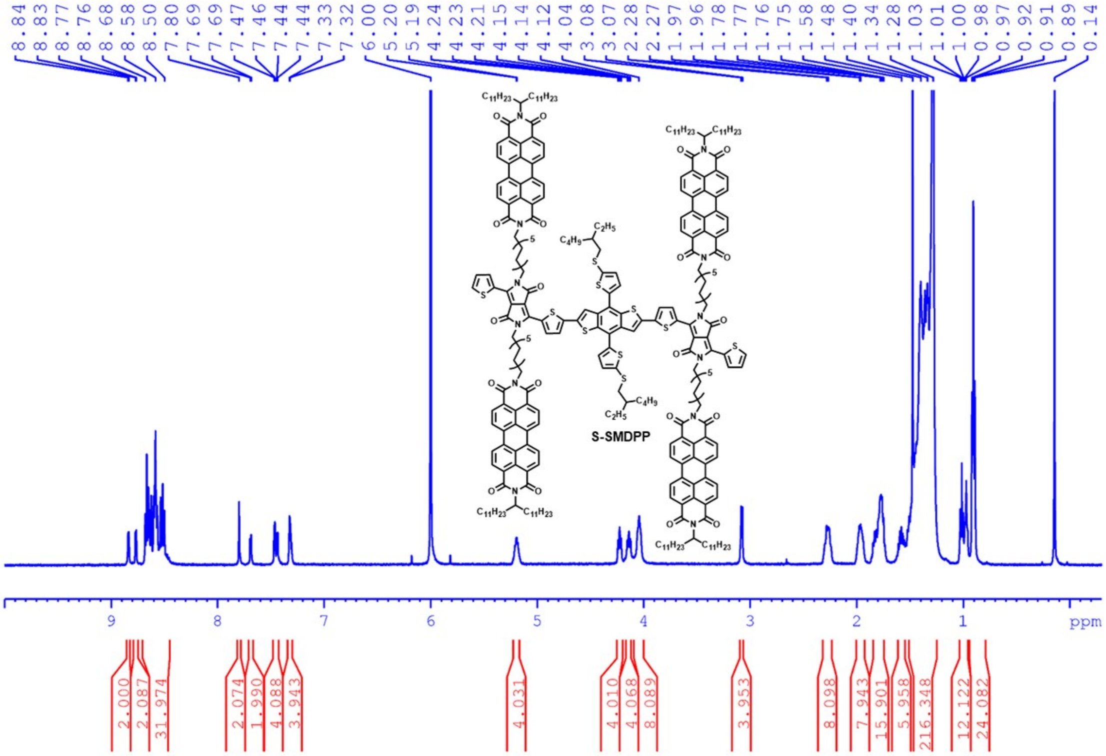


Figure S10. ^{1}H-NMR of **S-SMDPP** recorded at 100 ºC with 1,1,2,2-tetrachloroethane-d$_2$ as the solvent.

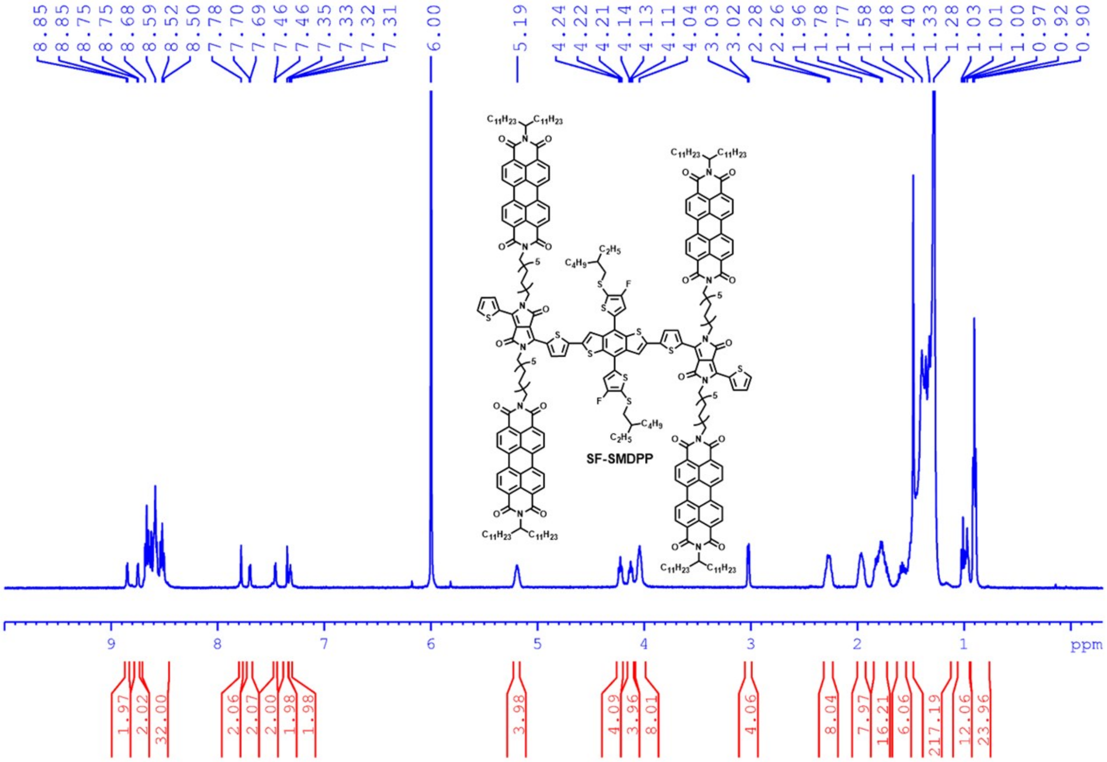


Figure S11. ^{1}H-NMR of **SF-SMDPP** recorded at 100 ºC with 1,1,2,2-tetrachloroethane-d_2 as the solvent..

8. References

1. W. Lai, C. Li, J. Zhang, F. Yang, F. J. M. Colberts, B. Guo, Q. M. Wang, M. Li, A. Zhang, R. A. J. Janssen, M. Zhang and W. Li, *Chem. Mater.*, 2017, **29**, 7073-7077.