ESI for:

Dithieno[2,3-d;2′,3′-d]benzo[2,1-b:3,4-b']dithiophene: Novel Building-block for a Planar Copolymer

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Contents:

Experimental Section:

1. General Methods

All reagents were purchased from commercial sources and used without further purification unless otherwise stated. Column chromatography was performed using Merck silica gel 60, 40-63 μm (230-400 mesh). Thin layer chromatography was carried out using pre-coated aluminum sheets with silica gel 60 F254 (Merck), visualization by UV light. ^{1}H-NMR and ^{13}C-NMR spectra were recorded in the listed deuterated solvents on a Bruker AVANCE 300 and 250 MHz spectrometer. Mass spectra were obtained using Field desorption mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD spectrometer. Elemental analysis was carried out using a Foss Heraeus Vario EL in the Institute of Organic Chemistry at the Johannes Gutenberg-University, Mainz. The UV-vis spectra were recorded at 298 K on a Perking-Elmer Lambda 900 spectrophotometer. CV measurements were carried out on a computer-controlled GSTAT12 in a three-electrode cell in a DCM solution of Bu_4NPF_6 (0.1 M) with a scan rate of 100 mV/s at room temperature, with using Pt disc as the working electrode, Pt wire as the counter electrode, Ag electrode as the reference electrode. HOMO and LUMO energy levels were calculated from the onsets of the first oxidation and reduction peak by empirical formulas $E_{HOMO} = - (E^{onset}_{ox1} + 4.8)$ eV, $E_{LUMO} = - (E^{onset}_{red1} + 4.8)$ eV while the potentials were determined using ferrocene (Fc) as standard. The molecular weights were determined by PSS-WinGPC (PSS) (pump: alliance GPC 2000) GPC equipped with an UV or RI detector running in tetrahydrofuran at 30 °C using a PLgel MIXED-B column (particle size: 10 mm, dimension: 0.8×30 cm) calibrated against polystyrene standards. Density functional theory (DFT) calculations were carried out at the B3LYP/6-31G (d) level using Gaussian 09[1] and molecular structures were generated using GaussView 5.0.9[2]. The X-ray crystallographic data for the molecules were collected on a Smart CCD diffractometer using a Mo-K$_\alpha$ graphite monochromator radiation source. Thermogravimetry analysis (TGA) was carried out on a Mettler 500 Thermogravimetry Analyzer with heating rates of 10 K/min. Differential scanning calormetry (DSC) were measured on a Mettler DSC 30 with heating and cooling rates of 10 K/min. Atomic force microscopy (AFM) was performed with ScanasystFluid+ probes in peak force nanomechanical mapping mode with Bruker Fastscan instrument.

2. OFET device fabrication and measurements

A bottom-gate bottom-contact OFET device was used for transistors with 50-nm-thick Au electrodes as source and drain and 300-nm-thick SiO_2 as dielectric. The dielectric was functionalized by using hexamethyldisilazane self-assembled monolayers (HMDS SAMs). The semiconducting **PDT*m*BDT-DPP** layer was drop-cast from a chloroform solution at a concentration of 2 mg/ml followed by annealing at 100 °C for 30 min. The channel length and width are 20 and 1400 μm, respectively. All electrical measurements (using Keithley 4200 SCS) were performed in a glovebox under nitrogen atmosphere.

3. Grazing incidence wide-angle X-ray scattering (GIWAXS)

GIWAXS experiments were performed by means of a solid anode X-ray tube (Siemens Kristalloflex X-ray source, copper anode X-ray tube operated at 40kV and 30mA), osmic confocal MaxFlux optics, X-ray beam with pinhole collimation (1.0, 0.5 and 0.7 mm antiscattering pinhole, Owis, Germany) and a MAR345 image plate detector. The samples were prepared as thin film with the same procedure as it was used in OFETs fabrication.

4. Synthesis:

The preparation of 3,6-Bis-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-thiophen-2-yl))-N,N'-bis(octyldodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole (**7**) was according to a literature procedure.[3] Compounds 2,5-dibromothieno[3,2-b]thiophene (**2**), (5-bromothieno[3,2-b]thiophen-2-yl)(trimethyl)silane (**3**), (3,3'-dibromo-2,2'-bithieno[3,2-b]thiene-5,5'-diyl)bis(trimethylsilane) (**4**) were synthesized according to previous reports.[4] The compound, (Z)-2,2'-(hexacos-13-ene-13,14-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**5**) was synthesized by following the reported procedures.[5, 6]

3,8-bis(trimethylsilane)-5,10-didodecyl-dithieno[2,3-d;2′,3′-d′]benzo[1,2-b;3,4-b′]dithiophene (**6**):

To a 100 mL schlenk tube, (3,3'-dibromo-2,2'-bithieno[3,2-b]thiene-5,5'-diyl)bis(trimethylsilane) (1.0 g, 1.72 mmol), (Z)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-didodecylethene (1.20 g, 1.94 mmol), 2M K_2CO_3 aq. solution (10 mL, 20 mmol) and dry THF (30 mL) were added and then degassed by bubbling argon for 30 minutes at room temperature.

The catalyst, Pd(PPh$_3$)$_4$ (200 mg, 0.17 mmol) was added and the reaction mixture was refluxed at 80 °C for 12 h and then extracted with dichloromethane and washed with brine. The organic fraction was dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The crude compound was purified by column chromatography on silica gel using hexane as an eluent to give a pale yellow solid (915 mg, yield 68 %). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$, ppm): δ 7.49 (s, 2 H), 3.22 (t, J = 7.5 Hz, 4 H), 1.77 - 1.65 (m, 8 H), 1.47 - 1.30 (m, 32 H), 0.91 (t, J = 5.75 Hz, 6 H), 0.44 (s, 18 H), ^{13}C NMR (62.5 MHz, CD$_2$Cl$_2$, ppm): δ 145.45, 140.89, 138.39, 135.70, 132.34, 131.10, 126.63, 32.60, 31.71, 31.47, 30.78, 30.37, 30.37, 30.34, 30.28, 30.08, 30.04, 23.35, 14.54, 0.18. FD-Mass: calc.: 783.45 found: 783.10. Elemental Analysis: calc.; C, 67.46; H, 9.01; S, 16.37; Si, 7.17. found; C, 67.12; H, 8.87; S, 16.51; Si, 7.50.

3,8-dibromo-5,10-didodecyl-dithieno[2,3-d;2′,3′-d′]benzo[1,2-b;3,4-b′]dithiophene (**Br$_2$-DT*m*BDT**):

Compound **6**, 3,8-bis(trimethylsilane)-5,10-didodecyl-dithieno[2,3-d;2′,3′-d′]benzo[1,2-b;3,4-b′]dithiophene (900 mg, 1.15 mmol) was added to a two-neck 250 mL flask and dissolved in dry dichloromethane (100 mL). The reaction mixture was cooled to 0 °C and N-bromosuccinimide (430 mg, 2.42 mmol) was added in small portions under argon atmosphere (reaction flask was wrapped in Al-foil to avoid the light). The reaction mixture was slowly allowed to reach room temperature and stirred overnight before quenching with water. The mixture was washed with brine and organic layer was dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The crude was recrystallized in hexane to yield needle shaped white crystals (870 mg, yield 95%). ^{1}H NMR (300 MHz, THF-d_8, ppm): δ 7.58 (s, 2 H), 3.11 (t, J = 8.7 Hz, 4 H), 1.69 - 1.67 (m, 8 H), 1.45 - 1.30 (m, 32 H), 0.89 (t, J = 6.9 Hz, 6 H). ^{13}C NMR (75 MHz, THF-d_8, ppm) δ 136.31, 135.78, 134.57, 132.35, 131.74, 124.49, 115.18, 33.07, 32.20, 32.12, 31.21, 30.86, 30.84, 30.81, 30.75, 30.60, 30.51, 23.75, 14.63. FD-Mass: calc.: 796.88 found: 796.45. Elemental Analysis: calc.; C, 57.28; H, 6.58; S, 16.09; Br, 20.05. found; C, 57.20; H, 6.66; S, 16.20; Br, 19.94.

Synthesis of **PDT*m*BDT-DPP**:

To a solution of 3,8-dibromo-5,10-didodecyl-dithieno[2,3-d;2′,3′-d′]benzo[1,2-b;3,4-b′]dithiophene (**Br$_2$-DT*m*BDT**, 100 mg 0.125 mmol), 3,6-bis-(5-(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-thiophen-2-yl))-N,N′-bis(octyldodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole (**7**, 140 mg, 0.125 mmol), tri-*tert*-butylphosphonium tetrafluoborate ((t-Bu)$_3$P·HBF$_4$, 4.86 mg, 0.00168 mmol), tris(dibenzylideneacetone)dipalladium (0) (Pd$_2$(dba)$_3$, 7.65 mg, 0.0084 mmol) and aliquat 336 (2 drops) in 10 mL of toluene was added a solution of potassium phosphate (0.186 g, 0.875 mmol) in 1.2 mL of degassed water. The mixture was vigorously stirred at 90 °C for 72 h. The polymer was end-capped with phenyl units by adding phenyl boronic acid (100 mg, 12 h, 90 °C) and bromobenzene (500 mg, 12 h, 90 °C) in sequence. After cooling to room temperature, the reaction mixture was poured into vigorously stirred methanol (100 mL). The polymer was filtered and subjected to Soxhlet extraction with acetone (6 h), hexane (6 h), and chloroform (12 h). To the chloroform fraction was added methanol and the resulting solid was collected by filtration and dried under vacuum to afford the desired polymer (0.15 g, 70%) as a dark blue solid. GPC: M_n = 149 kg/mol; M_w = 631 kg/mol; PDI = 4.2 UV-Vis: λ_{max} (solution in trichlorobenzene): 753 nm, 685 nm, and 420 nm. Elemental analysis: Calcd. for C$_{92}$H$_{138}$N$_2$O$_2$S$_6$; C, 73.84; H, 9.30; N, 1.87; O, 2.14; S, 12.85. Found; C, 72.70; H, 10.20; N, 1.79; S, 13.38.
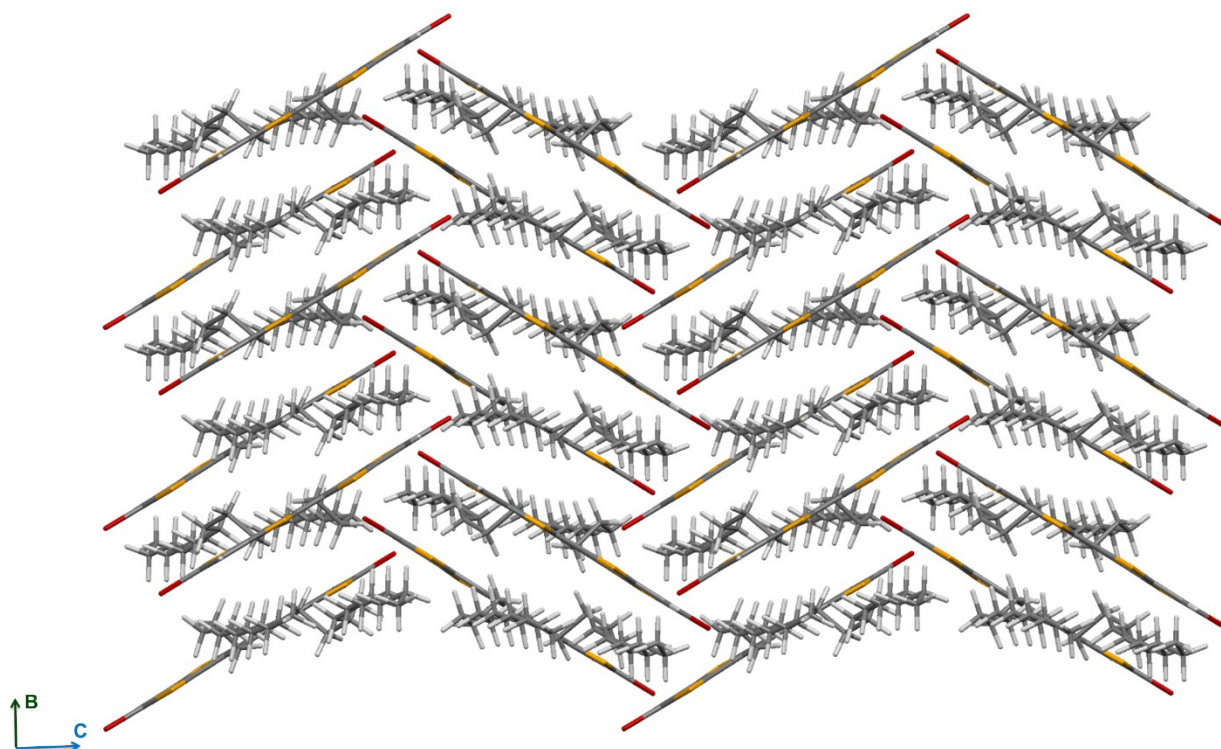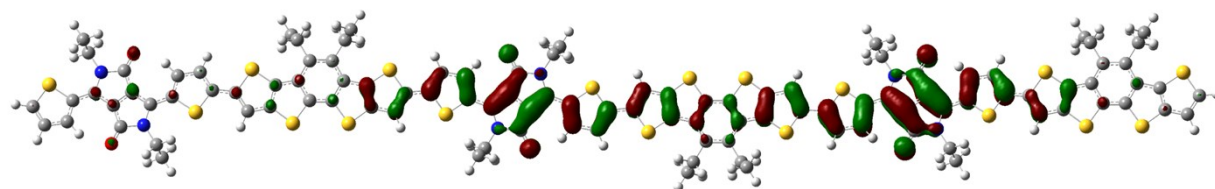

Figure S1. Crystal packing of **Br$_2$-DTmBDT**.
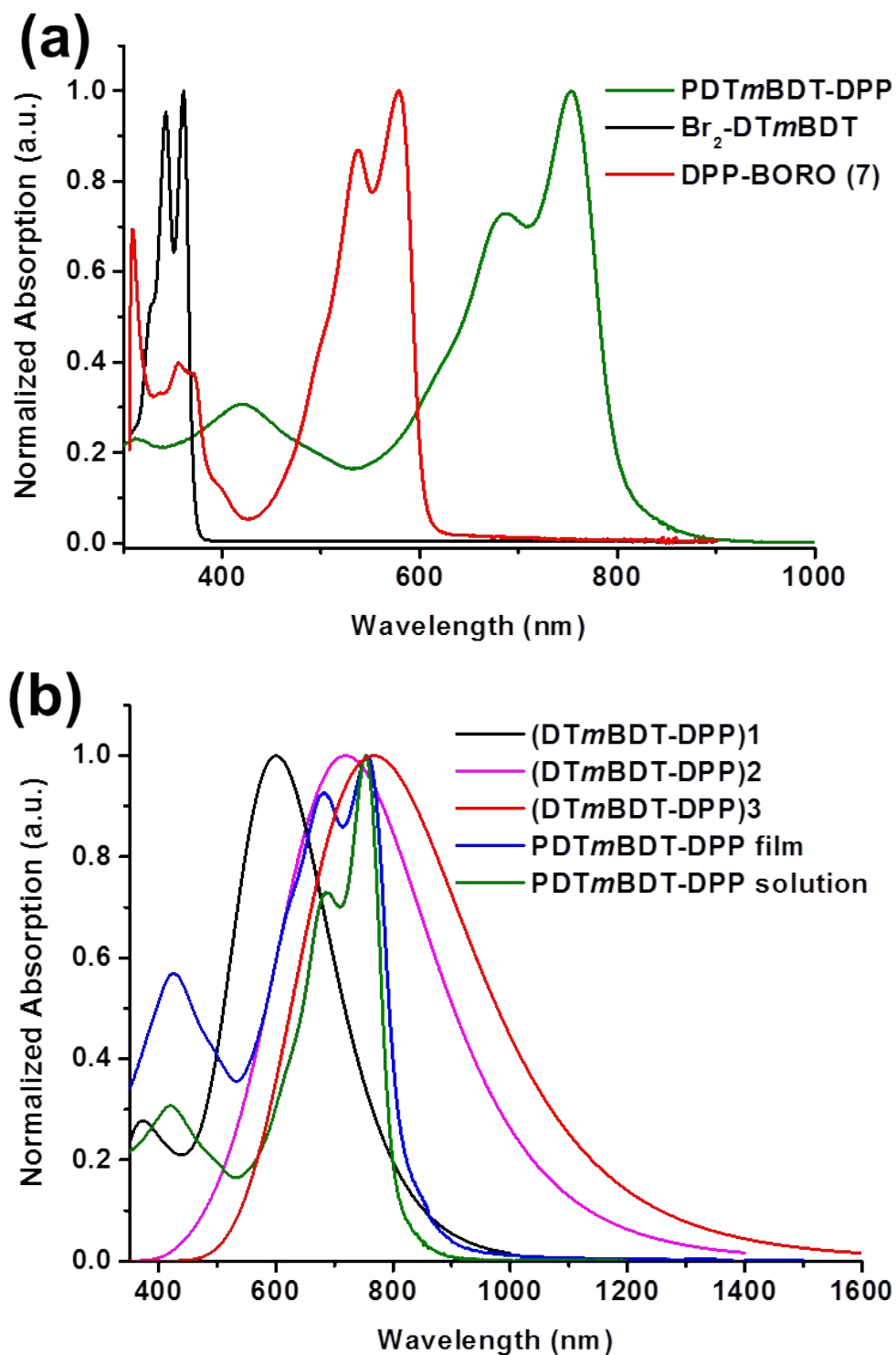
Figure S2. a). UV-vis absorption spectra of **PDT*m*BDT-DPP** and polymer precursor molecules in TCB solution. b).Calculated [using TD-SCF, B3LYP/6-31G (d)] UV-vis absorption spectra of **(DT*m*BDT-DPP)** units and experimental UV-vis absorption spectra of **PDT*m*BDT-DPP**.
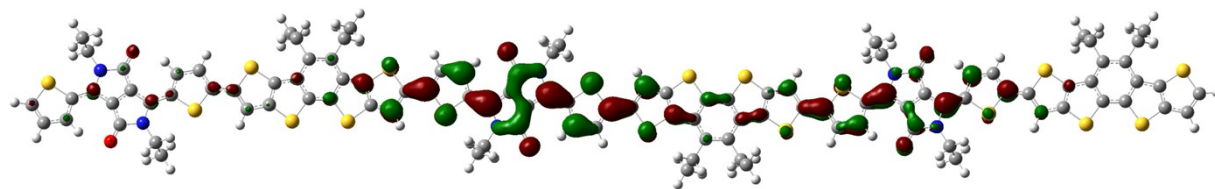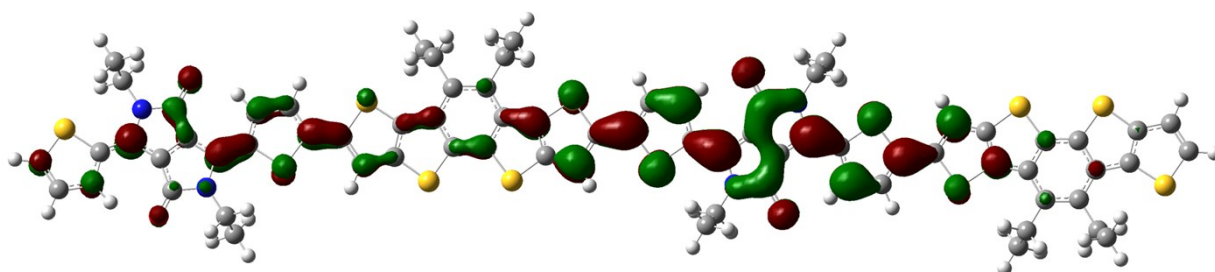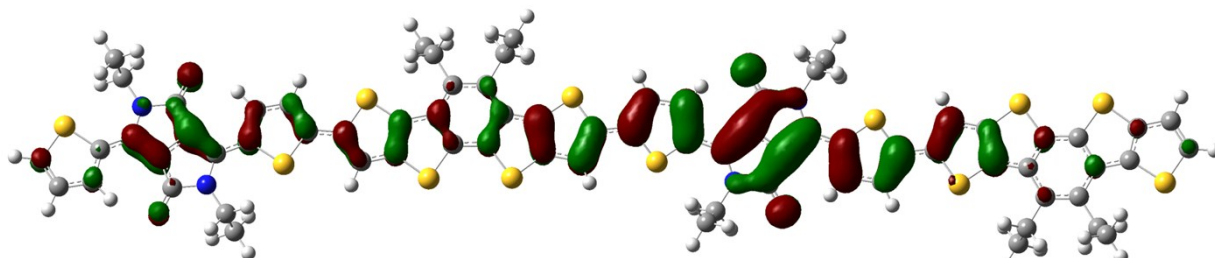
LUMO (-2.92 eV)

HOMO (-4.71 eV)
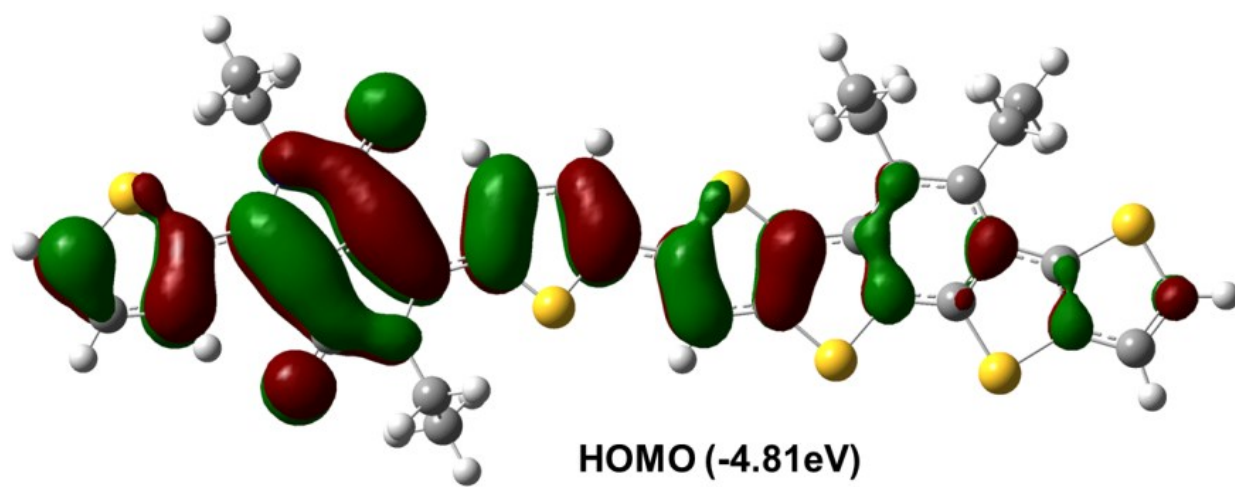
Figure S3. Calculated energy levels of (**DT*m*BDT-DPP)3**.

LUMO (-2.85 eV)

HOMO (-4.73 eV)

Figure S4. Calculated energy levels of (**DT*m*BDT-DPP)2**.

LUMO (-2.66 eV)

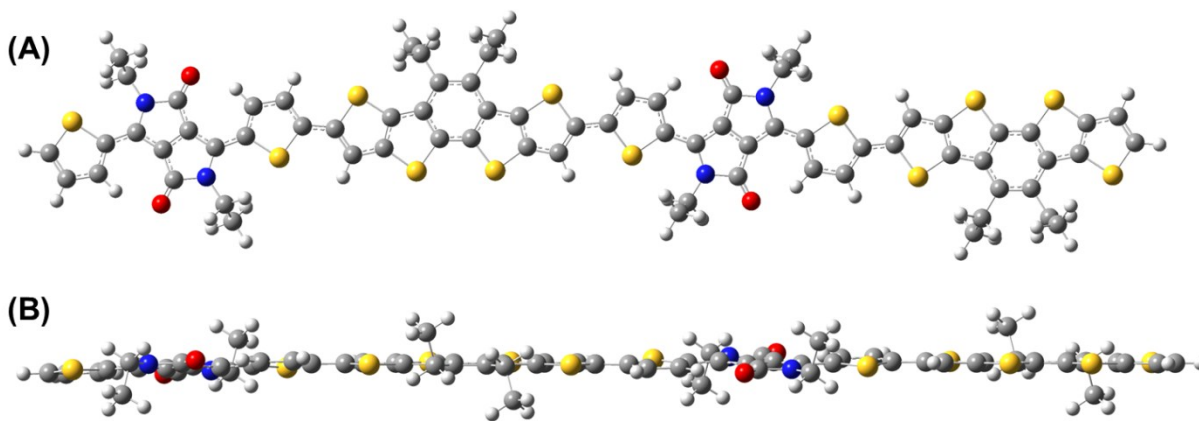HOMO (-4.81eV)
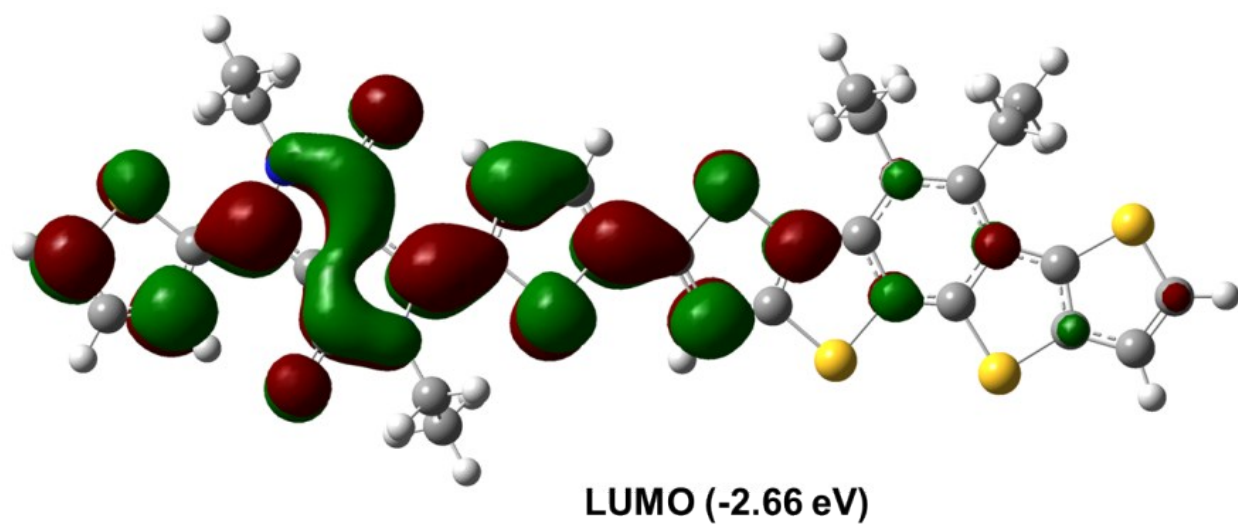
Figure S5. Calculated energy levels of (**DT*m*BDT-DPP**).
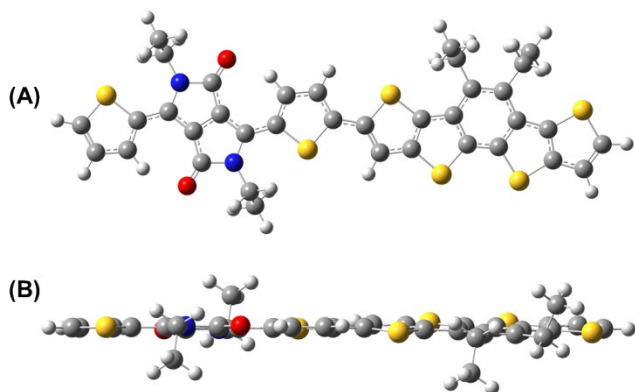
(A)

(B)
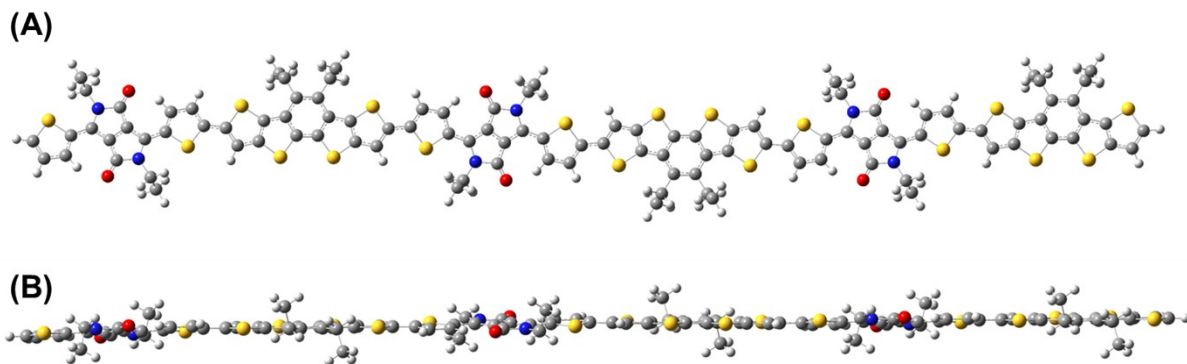
Figure S6. Geometry optimized structures of **(DT*m*BDT-DPP)3** (A) planner view and (B) side view.

(A)

(B)

Figure S7. Geometry optimized structures of **(DT*m*BDT-DPP)2** (A) planner view and (B) side view.

(A)

(B)

Figure S8. Geometry optimized structures of **DT*m*BDT-DPP** (A) planner view and (B) side view.

Table S1. Theoretically calculated energy levels of **DT*m*BDT-DPP** units.

Compound	HOMO (eV)	LUMO (eV)	E (eV)
DT*m*BDT-DPP	-4.815	-2.664	2.151
(DT*m*BDT-DPP)2	-4.730	-2.855	1.875
(DT*m*BDT-DPP)3	-4.713	-2.920	1.793
DT*m*BDT	-5.378	-1.309	4.069
DPP	-4.945	-2.496	2.449
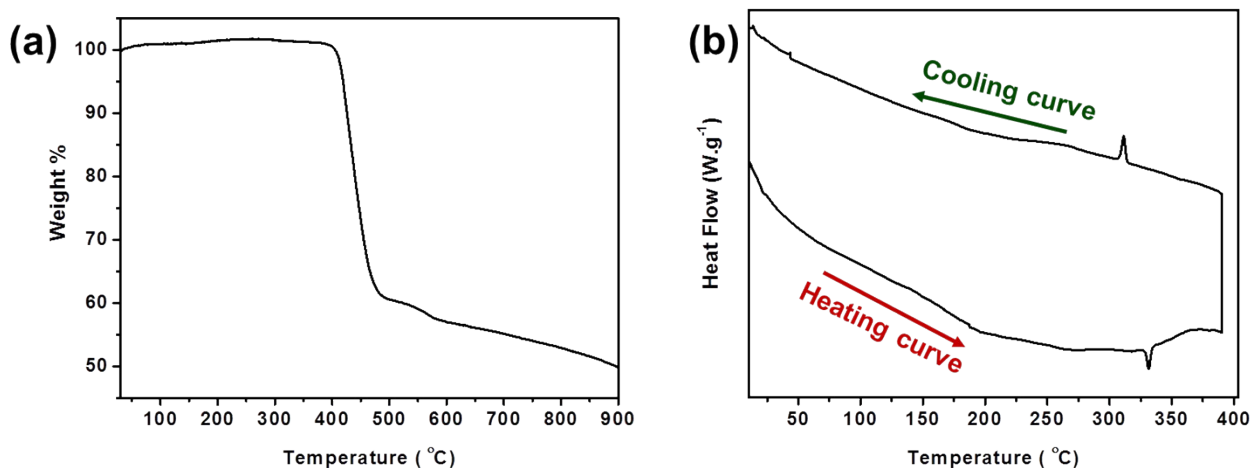
Figure S9. TGA curve (a) and DSC curve (b) of **PDT*m*BDT-DPP** measured under a nitrogen atmosphere at a heating rate of 10 ºC/min.

OFET device data:

At low gate voltage (V_G), a large drain current (I_D) offset is presented from output plots, which is defined as the I_D value at different V_G and $V_D = 0$ V.[7] This phenomenon originates from the gate-induced leakage current, but it cannot be completely eliminated in some cases.[8]
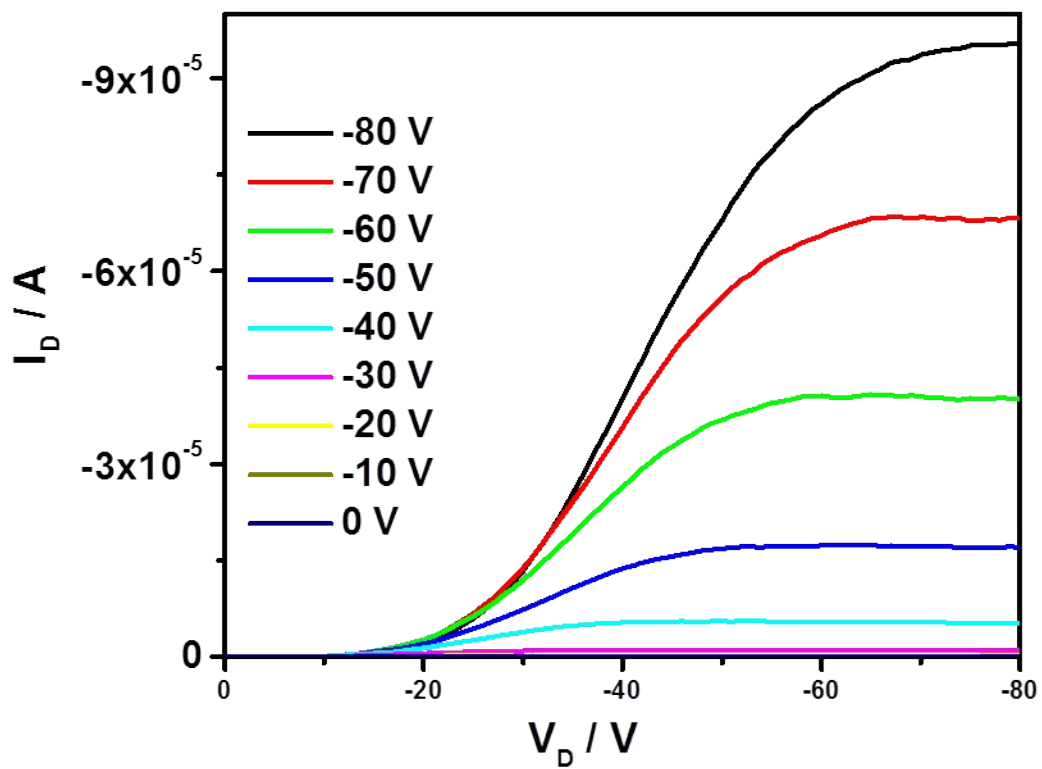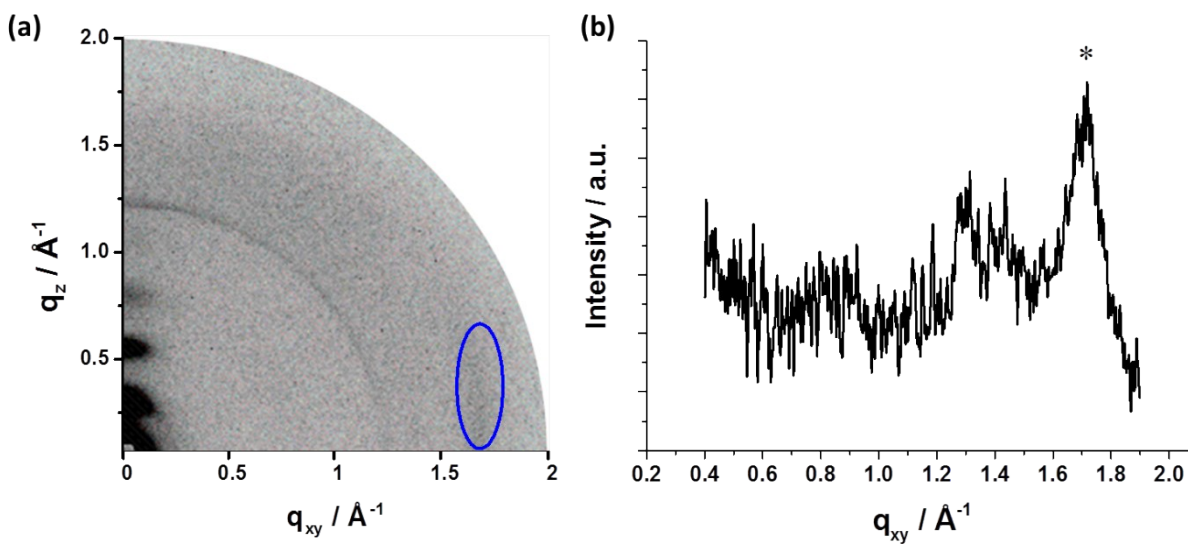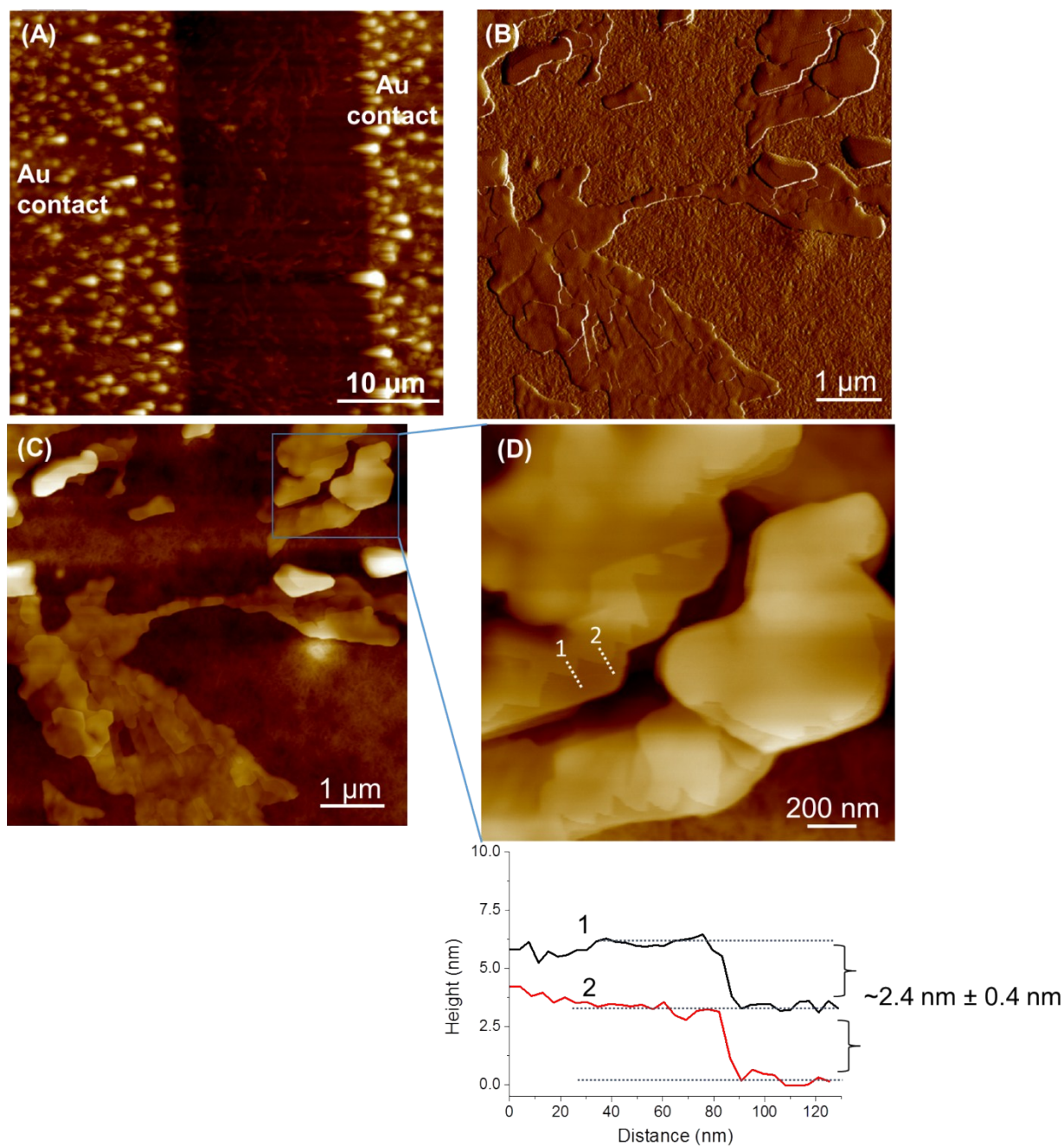
Figure S10. OFET output characteristics of **PDT*m*BDT-DPP**.

GIWAXS studies:

Figure S11. a) GIWAXS analysis of PDT*m*BDT-DPP and blue inset highlights reflection assigned to π −stacking interaction. b) equatorial integration of the GIWAXS pattern obtained for PDT*m*BDT-DPP. The indicated reflection (*) is assigned to the π −stacking interaction.

Figure S12. AFM images of (A) OFET device; (B) Peak force error and (C) Height image of polymer film in between gold electrodes; (D) Layer thickness and height analysis; average inter layer distance was 2.4 nm.
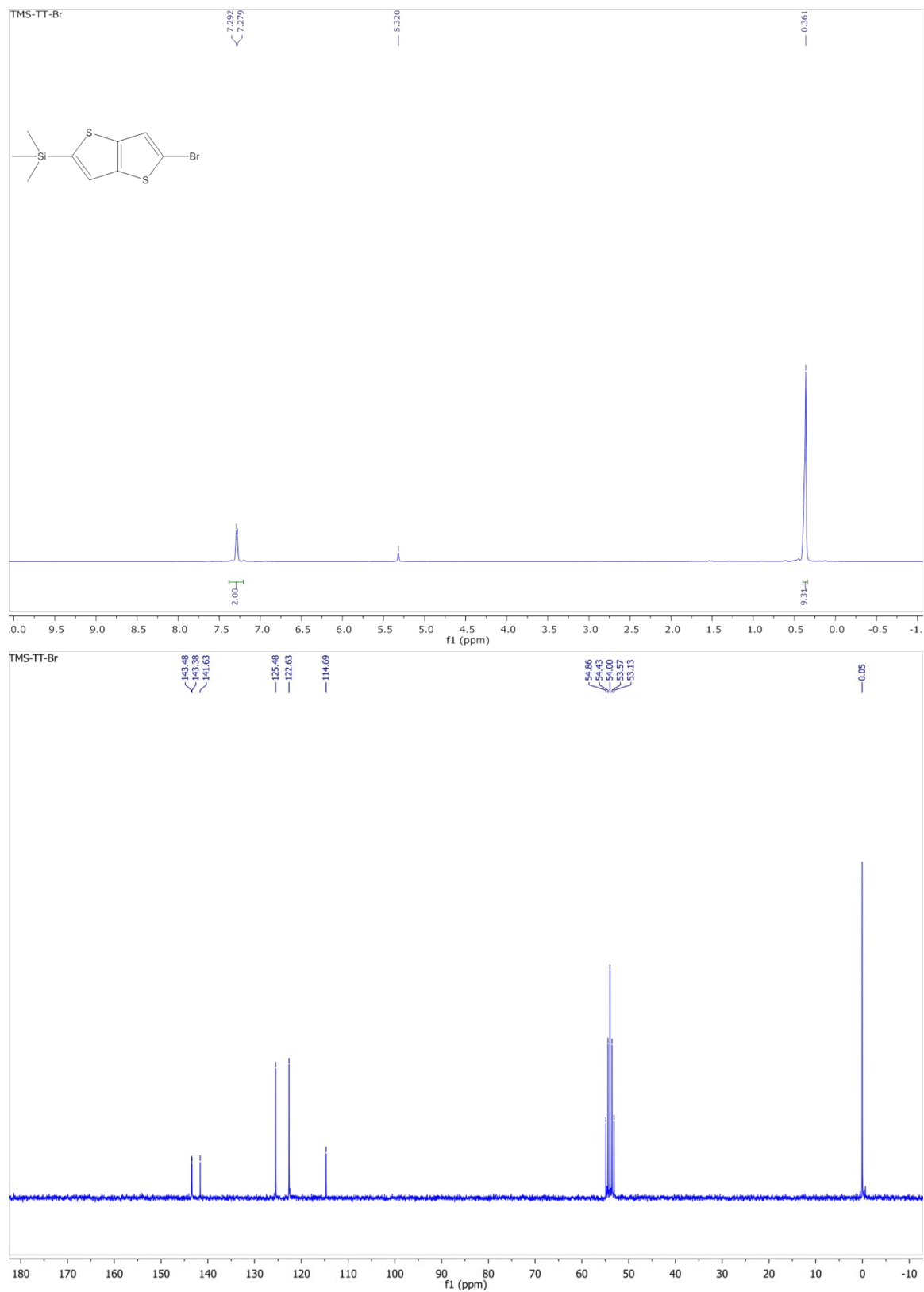
Figure S13. ^1H (above) and ^{13}C NMR (below) spectra of compound **3** in CD_2Cl_2.
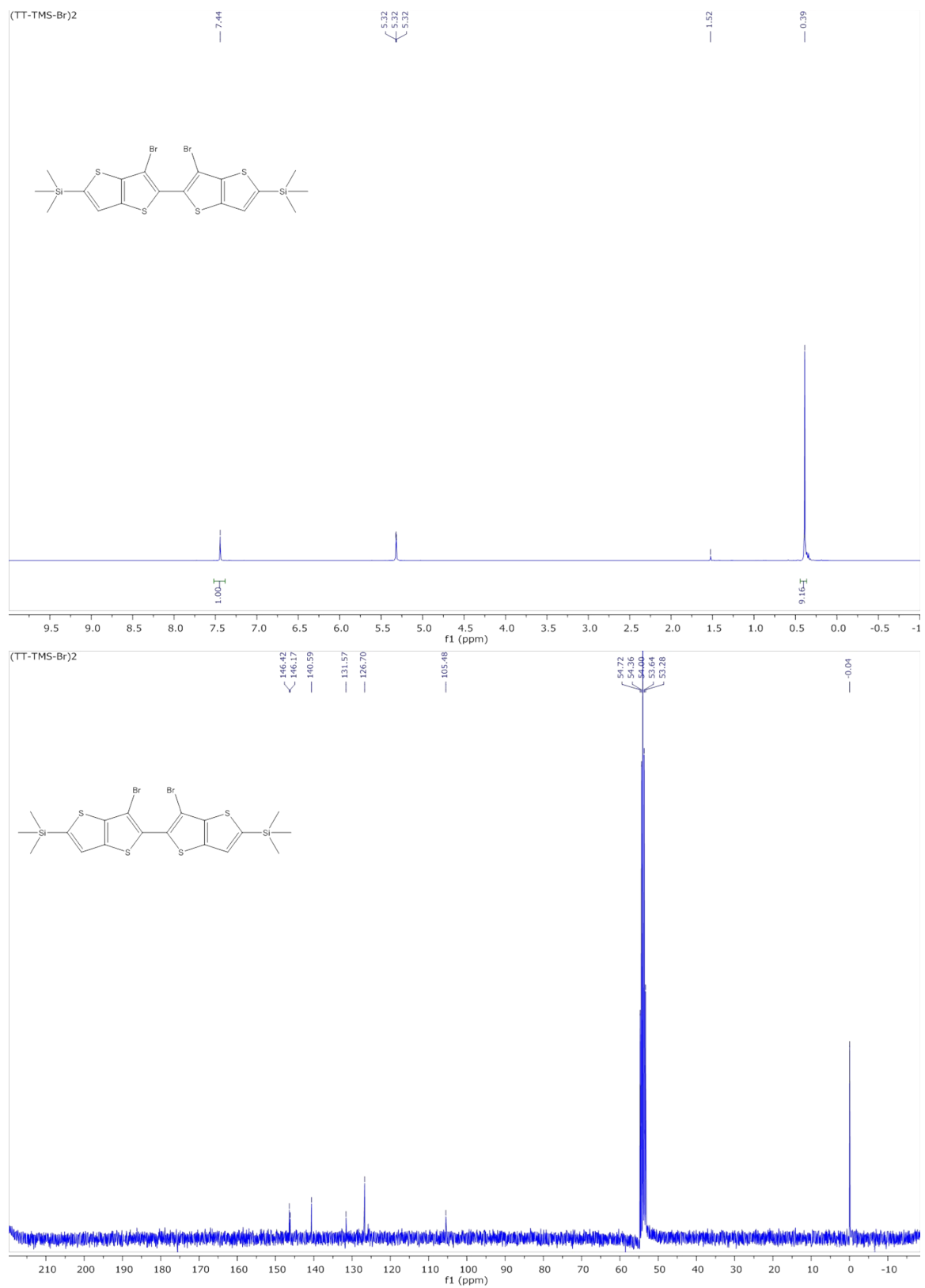
Figure S14. ^{1}H (above) and ^{13}C NMR (below) spectra of compound **4** in CD_2Cl_2.
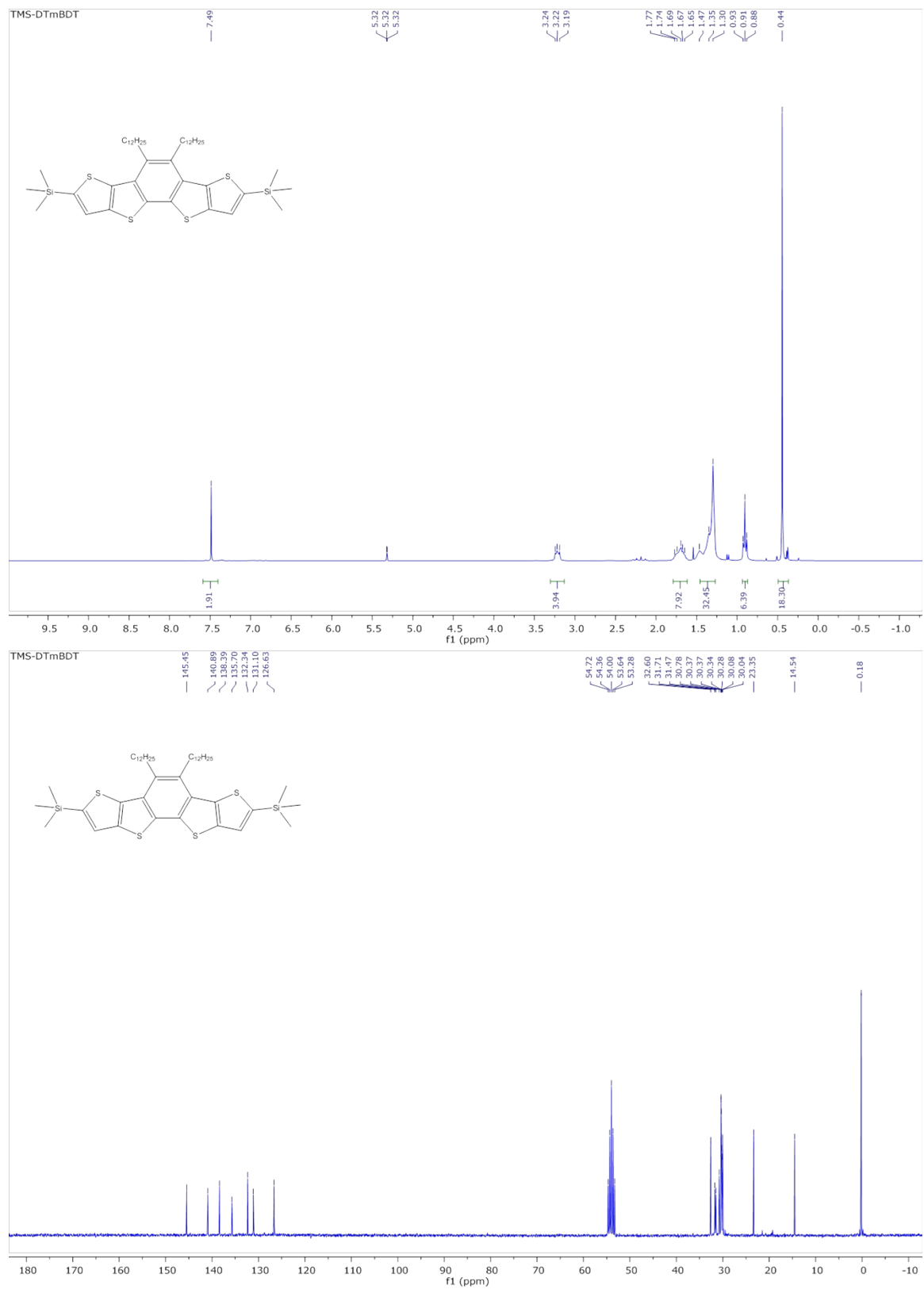
Figure S15. ^1H (above) and ^{13}C NMR (below) spectra of compound **6** in CD_2Cl_2.

Figure S16. ^1H (above) and ^{13}C NMR (below) spectra of compound **Br₂-DT*m*BDT** in THF-d_8.

Elugram:

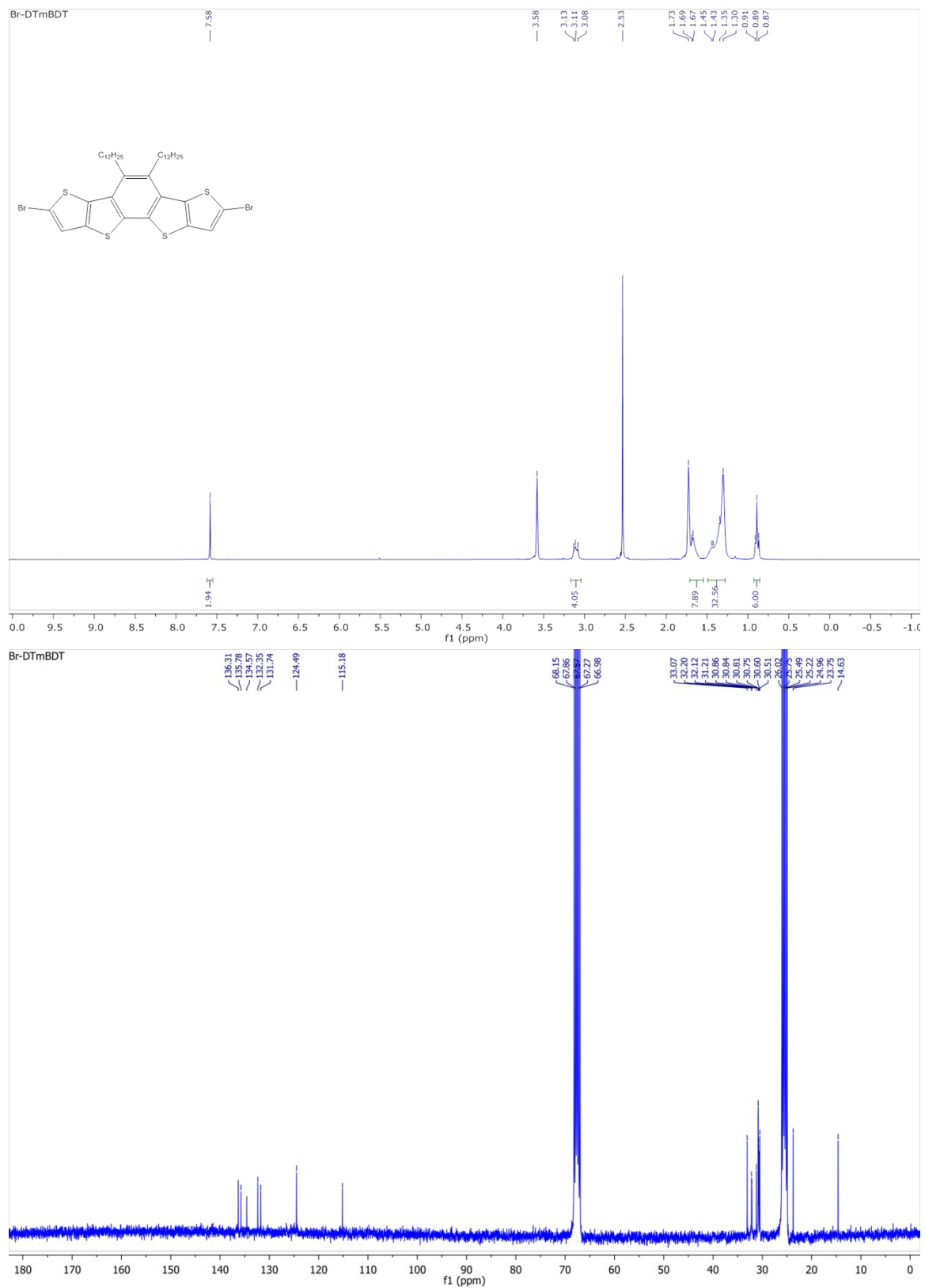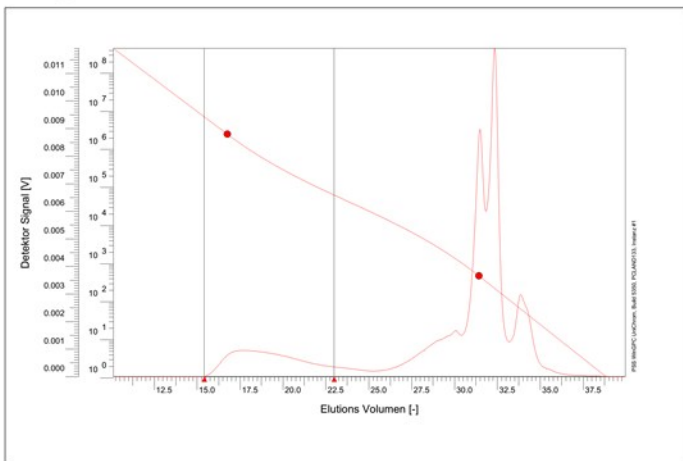|	
Calibration:	psthf11.CAL
Eluent:	THF
Flow rate:	1,0 ml/min
Pump:	PSS SECcurity
Inj.vol.:	50,00
Column1:	PSS SDV 10μm 1e6A
Column2:	SDV 10e4
Column3:	SDV 500
Temp.:	30,00 °C
Detector:	SECcurity VWD (254nm)
Detector:	SECcurity RID

Molecular weight distribution:
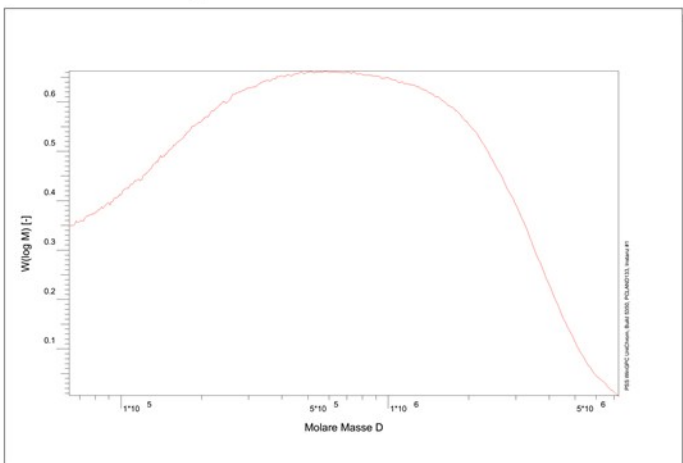
Name	Mn	Mw	D	Vp	Mp	Area
SECcurity VW	308936,00	976483,00	3,16	17,66	1300910,00	0,00
SECcurity RID	0,00	0,00	0,00	0,00	0,00	0,00
Systemdruck	0,00	0,00	0,00	0,00	0,00	0,00

Figure S17. GPC chromatogram and molecular weight distribution of synthesized co-polymer **PDT*m*BDT-DPP.**

Table S2. Single crystal data for **Br$_2$-DT*m*BDT.**

Formula	C$_{38}$H$_{52}$S$_4$Br$_2$
Molecular weight	796.8 gmol^{-1}
absorption	μ = 2.40 mm^{-1} corrected wit SADABS
Transmission	T$_{min}$ = 0.5418, T$_{max}$ = 0.7456
Crystal size	0.09 x 0.4 x 0.6 mm^3 colorless plate
Space group	P 2$_1$/c (monoclinic)
lattice parameters	a = 22.597(2)Å
(calculate from	b = 8.0328(6)Å ß = 98.073(5)°
3940 reflections with	c = 20.979(2)Å
2.3° < θ < 27.7°)	V = 3770.3(8)Å^3 z = 4 F(000) = 1656.0
Temperature	-100°C
Density	d$_{xray}$ = 1.404 gcm^{-3}

	data collection
Diffractometer	Smart CCD
radiation	Mo-K$_\alpha$ graphit monochromator
Scan type	ω-scans
Scan – width	0.5°
Scan range	2° ≤ θ < 28°
	-29 ≤ h ≤ 25 -8 ≤ k ≤ 10 -27 ≤ l ≤ 26
number of reflections:	
measured	22677
unique	8976 (R$_{int}$ = 0.0603)
observed	6215 (|F|/σ(F) > 4.0)

	data correction, structure solution and refinement
Corrections	Lorentz and polarisation correction.
Structure solution	Program: SHELXT-2014 (Direct methods)
Refinement	Program: SHELXL-2014 (full matrix). 399 refined parameters, weighting scheme: w=1/[σ^2(F$_o^2$) + (0.0391*P)^2] with (Max(F$_o^2$,0)+2*F$_c^2$)/3. H-atoms at calculated positions and refined with isotropic displacement parameters, non H- atoms refined anisotropically.
R-values	wR2 = 0.1010 (R1 = 0.0432 for observed reflections, 0.0771 for all reflections)
Goodness of fit	S = 0.987
Maximum deviation of parameters	0.001 * e.s.d
maximum peak height in diff. Fourier synthesis	0.71, -0.61 eÅ^{-3}

5. References:

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