Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Synthesis of electron-deficient polymers based on sulfur-bridged dithienylboranes as a building block

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Experimental

General

All reactions were carried out under dry argon. For the reaction solvent, toluene was distilled from calcium hydride and stored over activated molecular sieves under argon until use. All other chemicals were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. and TCI Co., Ltd. Starting materials **DPP-Br2**,[1] **^{F}DTSB-Sn2**,[2] and **DTSO$_2$B-Sn2**[3] were prepared according to the literature procedure. NMR spectra were recorded on Varian System 500 and 400MR spectrometers. Abbreviations Th, ^{F}Mes, and Tip used for the following NMR assignments stand for thiophene ring, ^{F}Mes group, and tripyl group, respectively. MALDI-TOF mass spectra were obtained on a Shimadzu MALDI-8020 instrument in positive mode, using dithranol as the matrix. UV–vis absorption spectra were measured with a Shimadzu UV-3600 Plus spectrometer. Cyclic voltammetry measurements were performed with an AMETEK VersaSTAT 4 potentiostat/galvanostat in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in acetonitrile using a three-electrode system with a Pt plate counter electrode, a Pt wire working electrode, and an Ag/Ag$^+$ reference electrode. The polymer (1 mg) and TBAPF$_6$ (10 mg) were dissolved in 1 mL of chlorobenzene, and the solution was drop-casted on the working electrode and dried under vacuum for 2 h at 50 °C. The potentials were corrected using ferrocene as the external standard.

Synthesis of ***P1-EH***

A mixture of 93.2 mg (0.137 mmol) of **DPP-Br2** (R = 2-ethylhexyl), 146 mg (0.137 mmol) of **^{F}DTSB-Sn2**, 6.9 mg (6.7 μmol, 5 mol%) of $Pd_2(dba)_3 \cdot CHCl_3$, 8.3 mg (27 μmol, 20 mol%) of P(*o*-tol)$_3$, and 5 mL of toluene was heated to 110 °C for 25 hours. The mixture was cooled to room temperature and the insoluble solids were separated. The solid was washed with ethanol then with hexane, and finally extracted with chloroform by Soxhlet extraction to give 20.5 mg (0.0203 mmol with respect to the repeating unit, 15%) of **P1-EH** as a dark purple solid. ^{1}H NMR (400 MHz, CDCl$_3$, 50 °C) δ 9.14 (br s, 2H, DPP), 8.35 (br s, 2H, Tip), 7.78–6.60 (m, 4H, Th and DPP), 4.05 (br s, 4H, 2EH), 1.84 (br s, 2H, 2EH), 1.68–1.05 (m, 16H, 2EH), 1.05–0.53 (m, 12H, 2EH). ^{13}C NMR could not be obtained due to the low solubility of the product. ^{11}B NMR (160 MHz, CDCl$_3$, 50 °C) δ 33.2. m.p. >300 °C.

Synthesis of ***P1-HD***

P1-HD was prepared from 170 mg (0.187 mmol) of **DPP-Br2** (R = 2-hexyldecyl), 201 mg (0.189 mmol) of **^{F}DTSB-Sn2**, 9.7 mg (9.4 μmol, 5 mol%) of $Pd_2(dba)_3·CHCl_3$, 11.4 mg (37.5 μmol, 20 mol%) of P(*o*-tol)$_3$, and 5 mL of toluene in a manner similar to that above. The reaction mixture was hydrolysed and extracted with chlorobenzene. The organic layer as washed with water and then with brine. After drying over anhydrous magnesium sulfate, the solvent was removed by a rotary evaporator. The resulting solid was purified by reprecipitation from chloroform/ethanol to yield 163 mg (0.132 mmol with respect to the repeating unit, 70%) of **P1-HD** as a dark purple powder. ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 9.14 (br s, 2H, DPP), 8.25 (br s, 2H, Tip), 7.82–6.50 (m, 4H, Th and DPP), 5.12–2.95 (m, 4H, 2HD), 1.93 (br s, 2H, 2HD), 1.78–1.02 (m, 48H, 2HD), 1.02–0.47 (m, 12H, 2HD). ^{13}C NMR could not be obtained due to the low solubility of the product. ^{11}B NMR (160 MHz, $CDCl_3$, 50 °C) δ 34.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.1, -66.3. m.p. >300 °C.

Synthesis of ***P2-HD***

P2-HD was prepared from 335 mg (0.369 mmol) of **DPP-Br2** (R = 2-hexyldecyl), 284 mg (0.370 mmol) of **$DTSO_2B$-Sn2**, 6.4 mg (11 μmol, 3 mol%) of $Pd(dba)_2$, 5.3 mg (11 μmol, 3 mol%) of XPhos, and 20 mL of toluene in a manner similar to that above. The reaction mixture was hydrolysed and extracted with chloroform. The organic layer as washed with water and then with brine. After drying over anhydrous magnesium sulfate, the solvent was removed by a rotary evaporator. The resulting solid was purified by reprecipitation from chloroform/ethanol to yield 297 mg (0.250 mmol with respect to the repeating unit, 68%) of **P2-HD** as a dark purple powder. ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 8.85 (br s, 2H, DPP), 7.99 (s, 2H, Th), 7.49 (br s, 2H, DPP), 7.09 (s, 2H, Tip), 4.02 (br s, 4H, 2HD), 3.10–2.80 (m, 1H, Tip), 2.63–2.35 (m, 2H, Tip), 1.93 (br s, 2H, 2HD), 1.46–0.93 (m, 66H, 2HD and Tip), 0.93–0.64 (m, 12H, 2HD). ^{13}C NMR could not be obtained due to the low solubility of the product. ^{11}B NMR (160 MHz, $CDCl_3$, 50 °C) δ 45.1. m.p. >300 °C.

OFET fabrication and measurements

To evaluate the electrical properties of the organic semiconductor film, top-contact-bottom-gate (TCBG) devices were fabricated. A heavily doped silicon wafer was used as the bottom gate electrode, and a 200 nm-thick SiO_2 film was thermally grown to serve as the gate insulator. Then the polymer was dissolved in chloroform (0.4 wt%) and spin-coated onto the substrate. Finally, gold source and drain electrodes were deposited via thermal evaporation through a shadow mask with the channel length of 100 μm and width of 1000 μm. Electrical properties were measured at room temperature using by semiconductor parameter analyzer (Keysight B1500A).

DFT calculations

The S_0 geometries were obtained by DFT calculations using a Gaussian 16 program at the B3LYP-D3BJ/6-31G(d) level of theory. The ten lowest singlet states were calculated by TD-DFT at the same level based on the S_0 geometries. Fluoride ion affinity (FIA) calculations were performed at M06-2X(D3zero)/def2-QZVPP//B3LYP-D3BJ/6-31G(d) level. FIA was value was calculated by using the experimental FIA value of Me_3Si^+ (952.5 kJ/mol) as a reference.

Figures and Tables

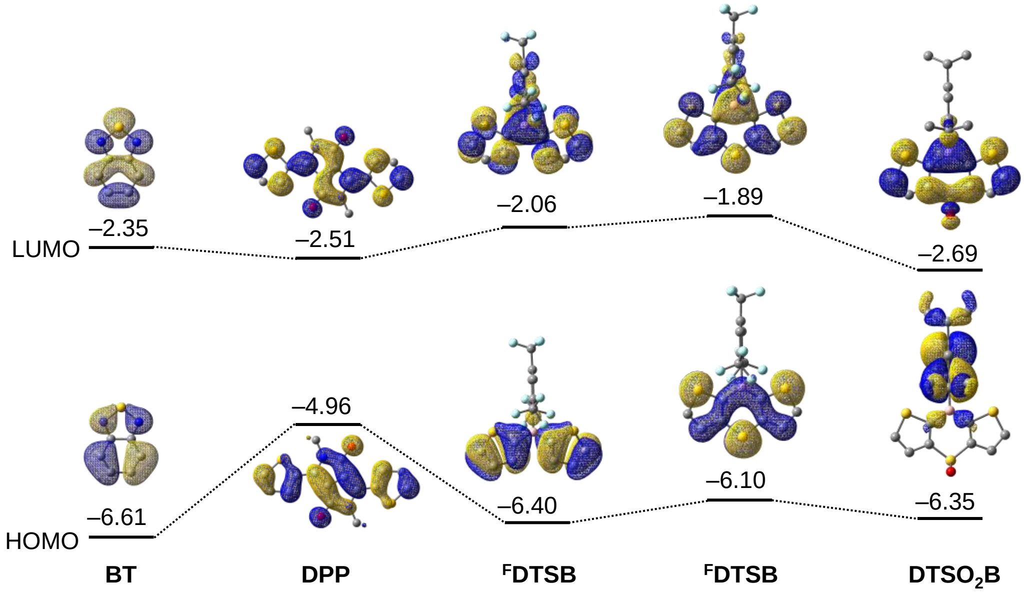


Figure S1 DFT-calculated frontier orbitals of typical acceptors and triarylborane units.

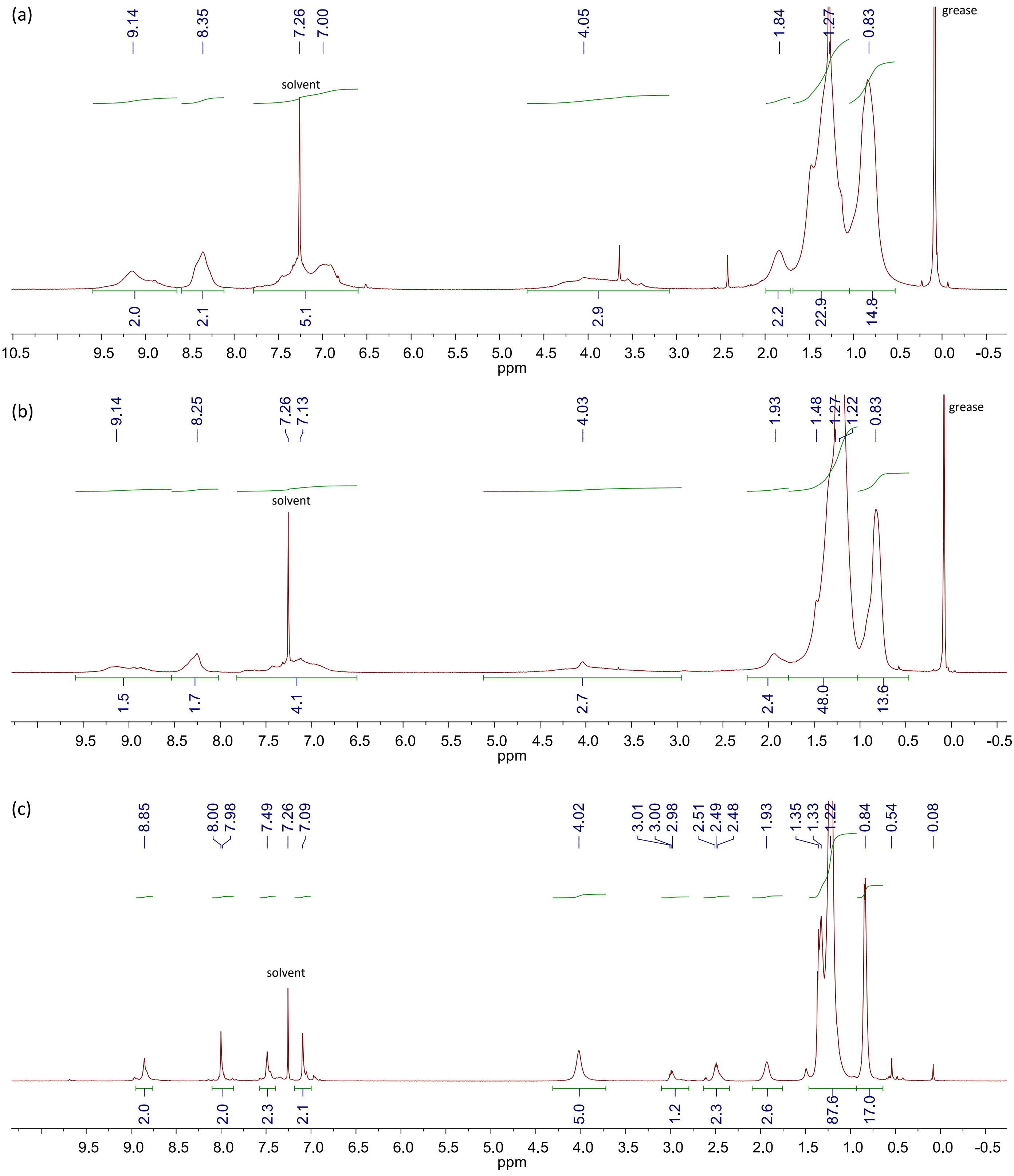


Figure S2 ^{1}H NMR spectra of **P1-EH** (a), **P1-HD** (b), and **P2-HD** (c) in $CDCl_3$ at 50 °C.

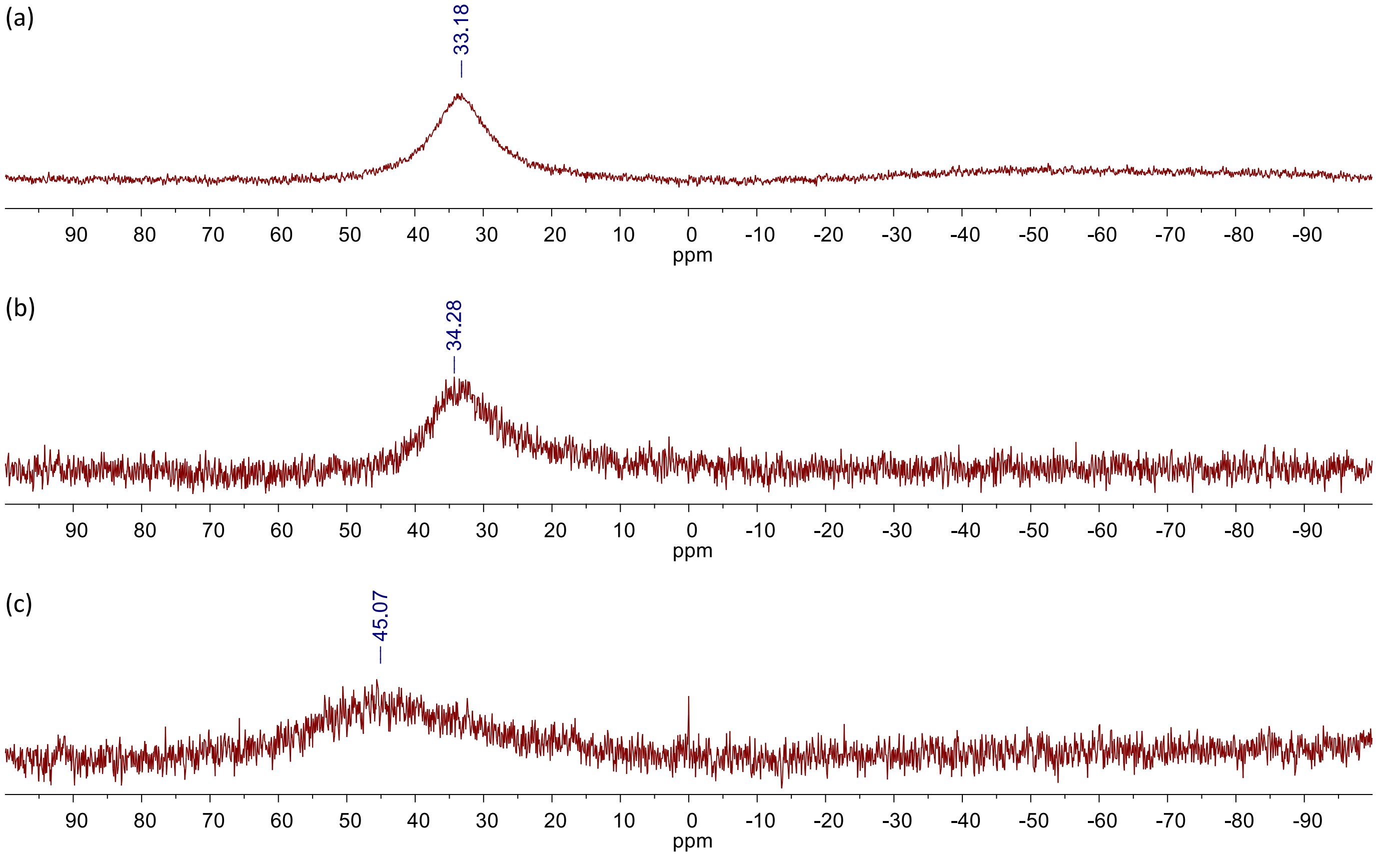


Figure S3 ^{11}B NMR spectra of **P1-EH** (a), **P1-HD** (b), and **P2-HD** (c) in $CDCl_3$ at 50 °C.

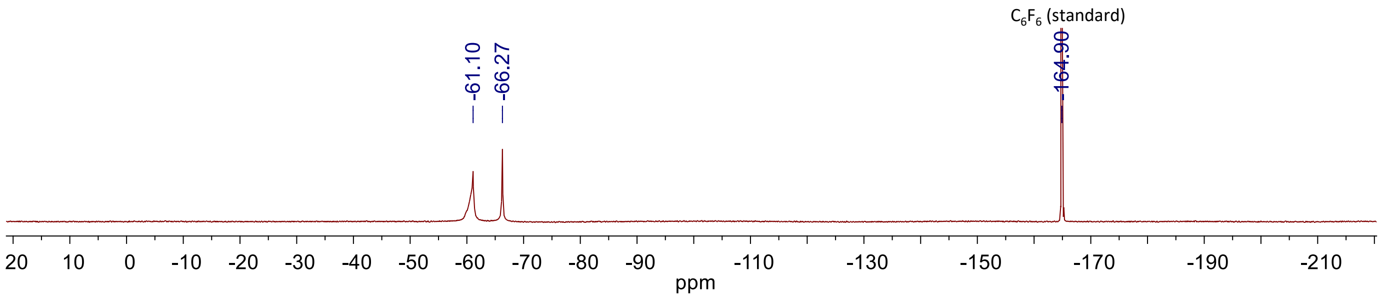


Figure S4 ^{19}F NMR spectra of **P1-HD** in $CDCl_3$.

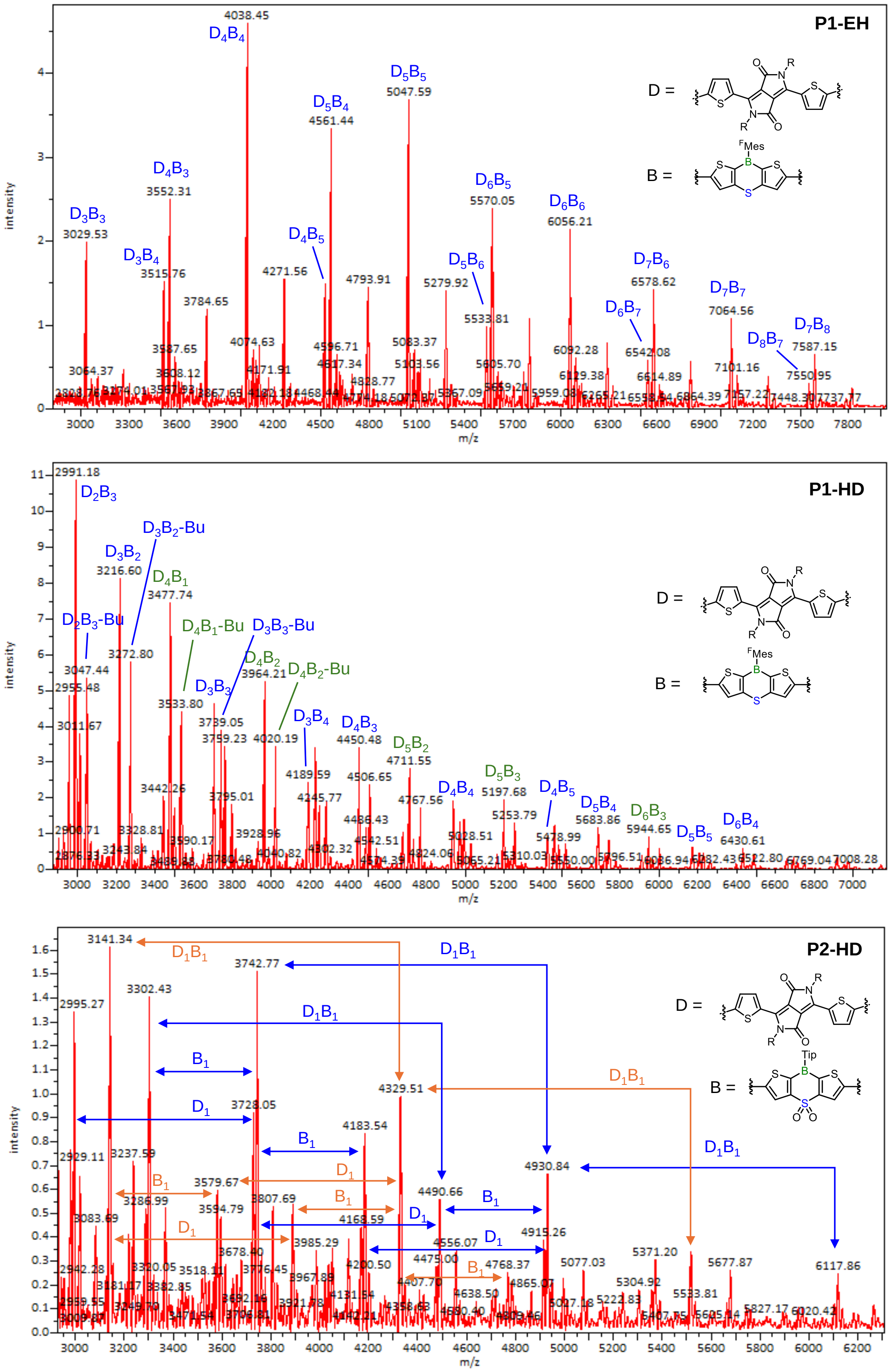


Figure S5 Positive MALDI-TOF mass spectra of DTSB/DTSO$_2$B-containing polymers mixed with dithranol as a matrix.

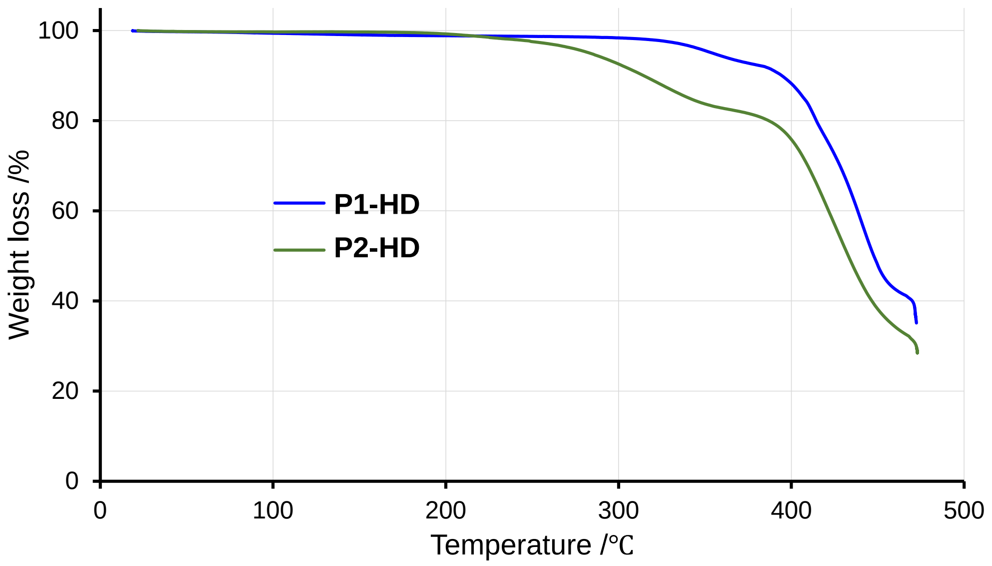


Figure S6 Thermogravimetric analysis of **P1-HD** and **P2-HD** in air.

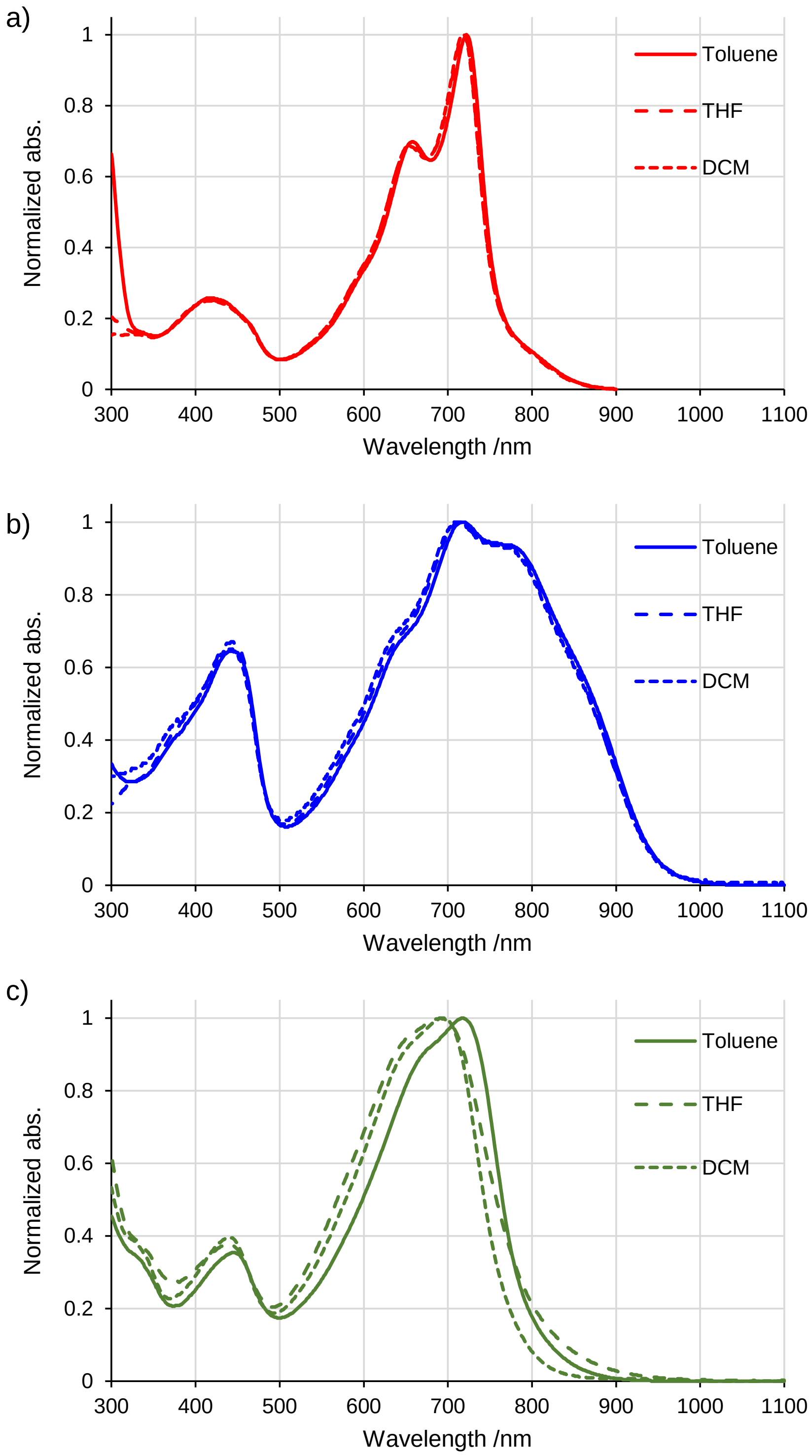


Figure S7 UV-vis absorption spectra of **P1-EH** (a), **P1-HD** (b), and **P2-HD** (c) in various solvents.

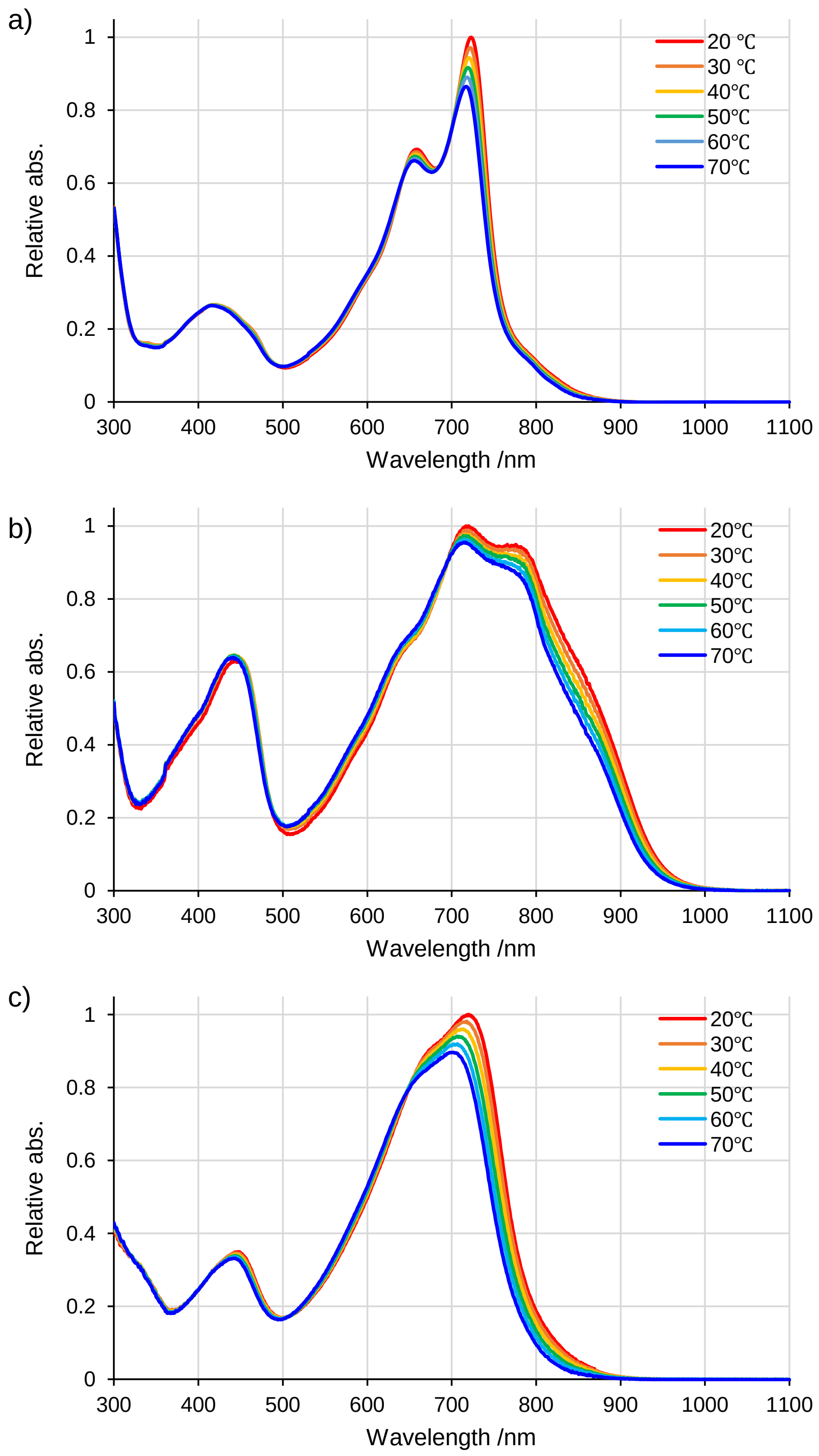


Figure S8 Temperature-dependent UV-vis absorption spectra of **P1-EH** (a), **P1-HD** (b), and **P2-HD** (c) in toluene.

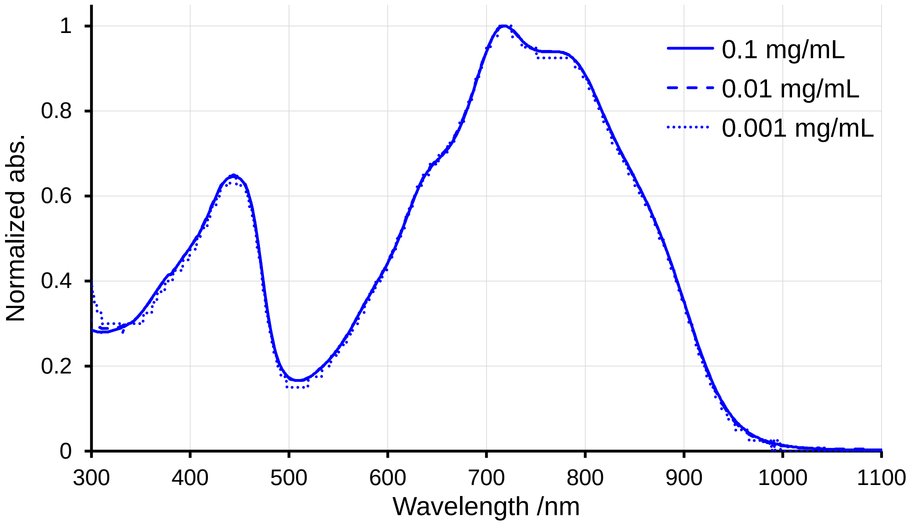


Figure S9 Concentration dependence of UV-vis absorption spectra of **P1-HD** in toluene.

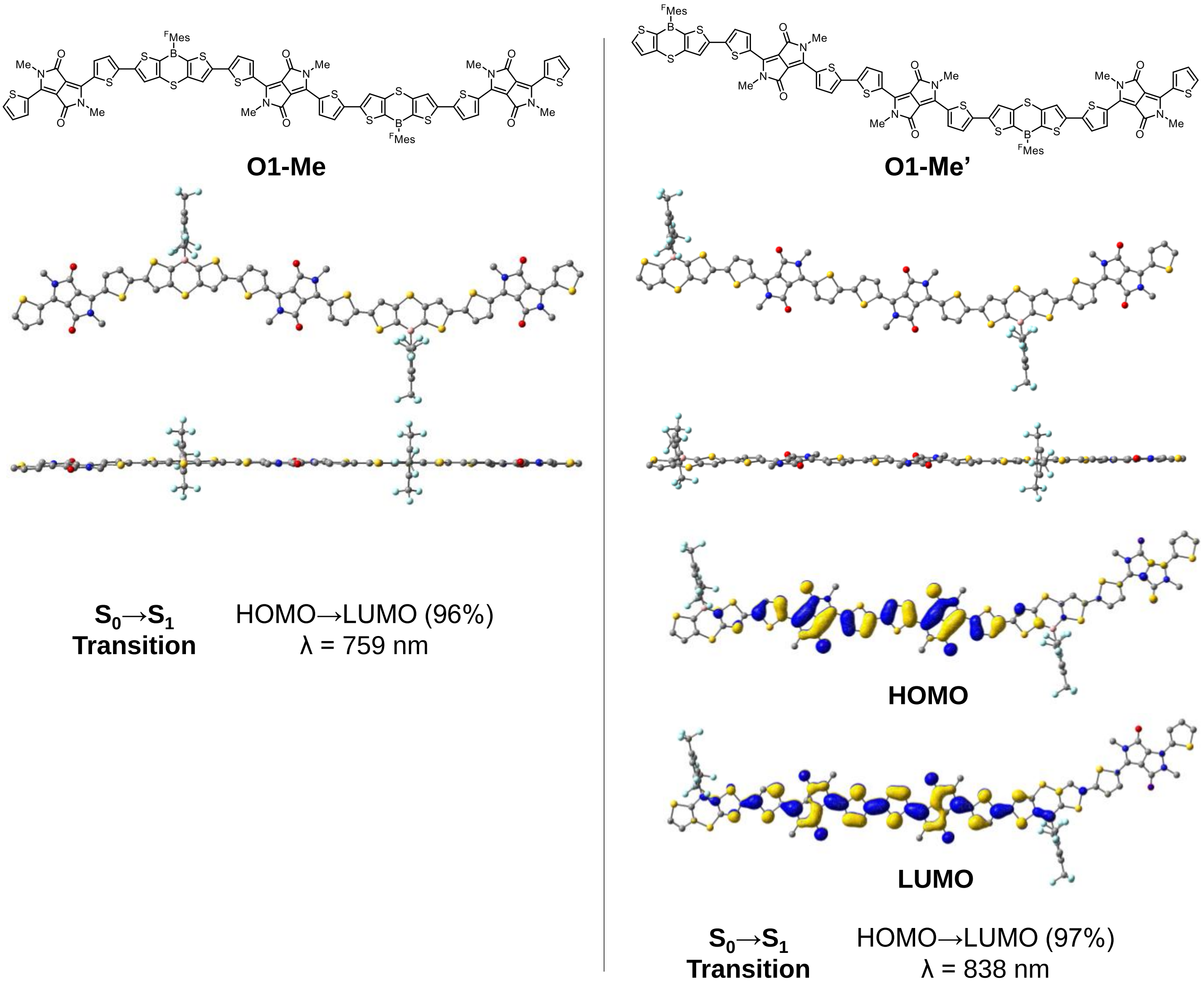


Figure S10 Optimized structures and TD-DFT results of **O1-Me** and **O1-Me'** at the B3LYP-D3BJ/6-31G(d) level.

Table S1 TD-DFT results of **O1-Me** at the B3LYP-D3BJ/6-31G(d) level. Transitions with an oscillator strength of zero were excluded from the table.

Excited State	Composition [a]	Contribution /%	Excitation energy /eV	Wavelength /nm	Oscillator strength
S0→S1	H-1→L+1	3	1.63	759	3.141
	H→L	96			
S0→S3	H-2→L	89	1.84	674	0.460
	H-1→L+1	2			
	H→L+2	7			
S0→S5	H-2→L+2	5	2.04	609	0.464
	H-1→L+1	71			
	H→L+2	21			
S0→S7	H-2→L	10	2.13	583	0.288
	H-1→L+1	21			
	H→L+2	69			
S0→S9	H-2→L+2	93	2.20	563	0.387
	H-1→L+1	3			
	H→L+2	3			

[a] H and L denote the HOMO and LUMO, respectively.

Table S2 TD-DFT results of **O1-Me’** at the B3LYP-D3BJ/6-31G(d) level.

Excited State	Composition [a]	Contribution /%	Excitation energy /eV	Wavelength /nm	Oscillator strength
S0→S1	H→L	97	1.48	838	3.712
S0→S2	H-1→L	90	1.68	737	0.016
	H→L+1	6			
S0→S3	H-2→L	40	1.77	700	0.016
	H-1→L	8			
	H→L+1	40			
	H→L+2	10			
S0→S4	H-2→L	29	1.88	661	0.014
	H→L+1	52			
	H→L+2	17			
S0→S5	H-2→L	3	1.99	622	0.551
	H-1→L+1	78			
	H→L+2	15			
S0→S6	H-2→L	24	2.13	583	0.059
	H-2→L+1	3			

	H-1→L+1	16			
	H-1→L+2	5			
	H→L+2	50			
S0→S7	H-2→L+1	56	2.19	565	0.261
	H-1→L+2	32			
	H→L+2	5			
S0→S8	H-2→L+1	35	2.22	559	0.031
	H-1→L+2	60			
S0→S9	H-2→L+2	89	2.38	522	0.151
	H→L+3	6			
S0→S10	H-6→L	3	2.43	511	0.001
	H-3→L	9			
	H-2→L+2	5			
	H→L+3	76			

[a] H and L denote the HOMO and LUMO, respectively.

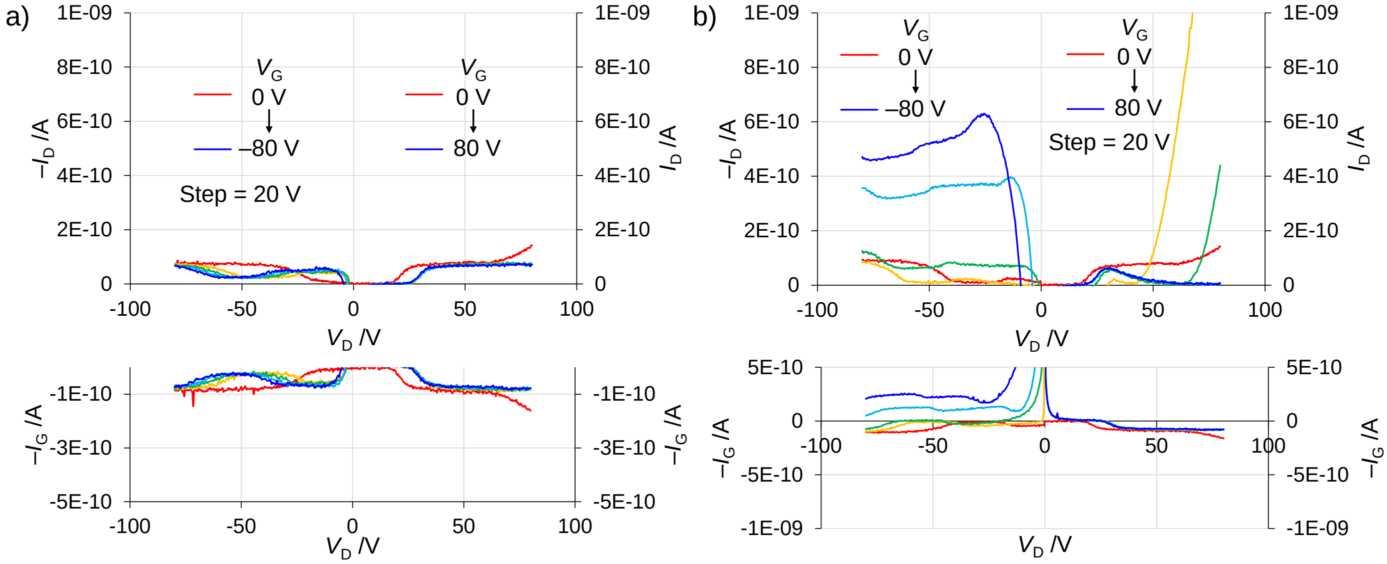


Figure S11 Gate voltage dependence of drain current–drain voltage and gate current–drain voltage characteristics of OTFT with spin-coated **P1-HD** (a) and **P2-HD** (b) films.

In the response curve of **P1-HD**, the drain current (I_D) closely matched the gate leakage current (I_G), indicating that **P1-HD** exhibits no semiconducting behavior. On the other hand, **P2-HD** exhibits weak, p-type semiconductor behavior; however, the absolute value of the drain current was negligibly small. These results indicate that field-effect-induced charge carrier generation in these polymers is minimal.

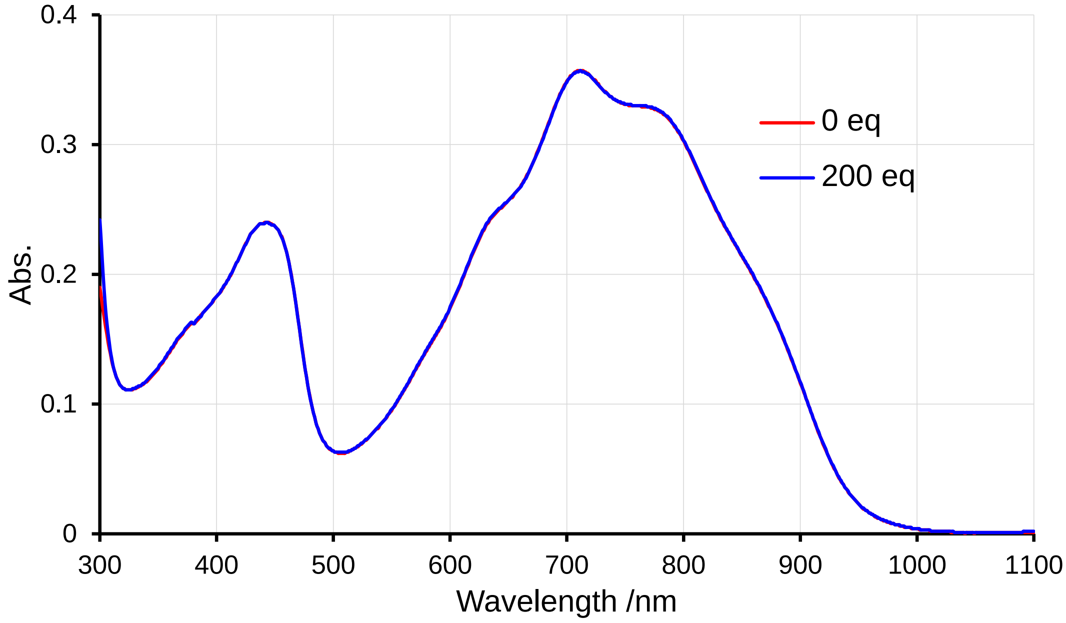
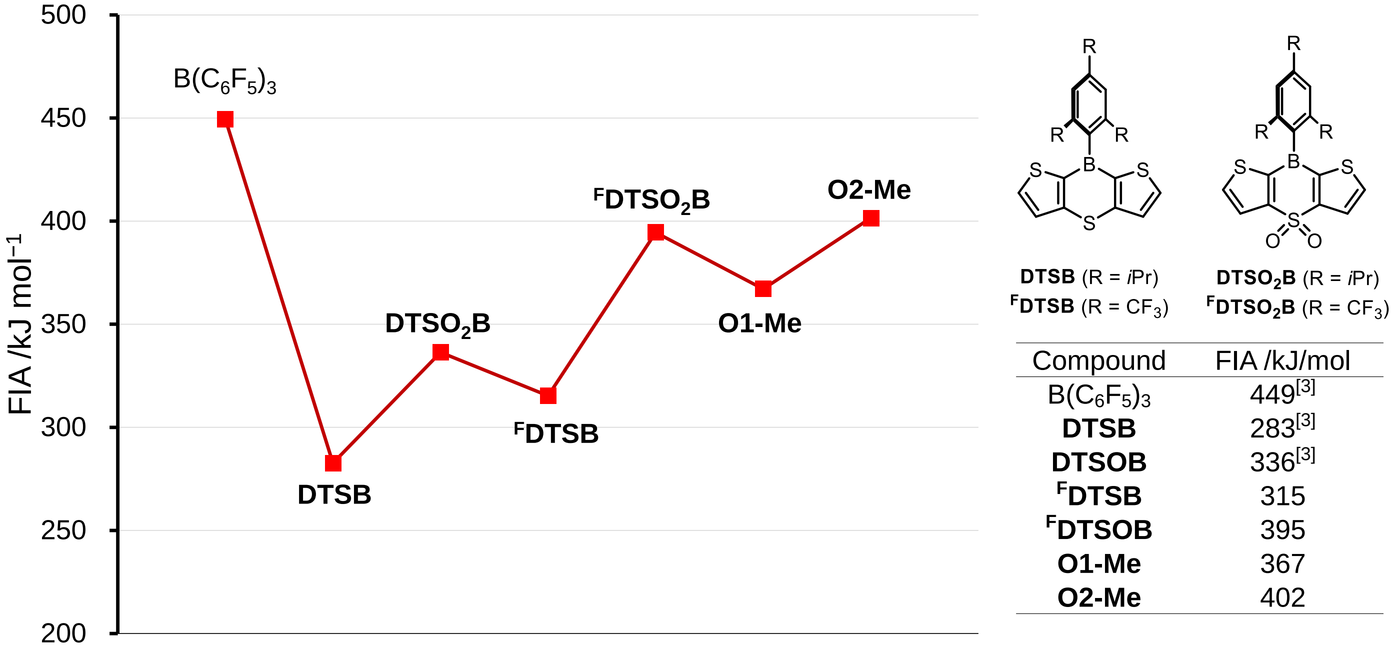


Figure S12 UV-vis absorption spectra of **P1-HD** in the presence or absence of DMAP in $CHCl_3$ at the concentration of 0.02 mM.



Compound	FIA /kJ/mol
$B(C_6F_5)_3$	449[3]
DTSB	283[3]
DTSOB	336[3]
^{F}DTSB	315
^{F}DTSOB	395
O1-Me	367
O2-Me	402

Figure S13 Evaluated Lewis acidities of the boron atom in thiaborin rings by FIA.

References

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[2] Y. Adachi, M. Sakabe, T. Nomura, J. Ohshita, *Polym. J.* **2023**, *55*, 489.

[3] Y. Adachi, R. Matsuura, J. Ohshita, *Organometallics* **2024**, *43*, 829.