

## Supporting information

### **Isomeric orientation of S atom in thiophene of benzodithiophene-4,8-dione to achieve high-performance electrochromic polymer**

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## **Experiment**

### **1. Materials**

The raw materials and Tetrakis(triphenylphosphine) palladium were purchased from Bide Pharmatech Co, Ltd. *N*-bromosuccinimide (NBS) was purchased from Shanghai Biochemical Co, Ltd. DMF, deuterated chloroform-*d* (CDCl<sub>3</sub>) and tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) were purchased from Shanghai McLin Biochemical Technology Co, Ltd. Toluene was purchased from Guangzhou Brand. Before the reaction, tetrahydrofuran (THF) and toluene were distilled from the sodium/benzophenone under the protection of nitrogen atmosphere.

### **2. Instruments**

<sup>1</sup>H NMR measurements were made on Bruker Avance-400 (400 MHz) using deuterated chloroform (CDCl<sub>3</sub>) as the solvent. Electrochemical studies were conducted using CHI660E electrochemical workstation. Electron absorption UV-Vis-NIR spectra of the polymeric films were obtained on a UV-1900i spectrophotometer. Scanning electron microscopy (SEM) images were obtained on a Nano SEM 430 instrument. Fluorescence data were obtained on a steady-state/transient fluorescence spectrometer (F-4600). A VER TEX 70 Bruker Fourier-transform infrared (FT-IR) spectrometer was used to record the infrared spectra of all the monomeric precursors and corresponding polymers.

### **3. Electrochemical experiments**

Electrochemical experiments were performed using a CHI660E electrochemical workstation. All measurements were performed under ambient conditions, including

the stability test. Electrochemical experiments (electropolymerization, cyclic voltammetry (CV) of monomers and polymers, and chronoamperometry) were performed in a standard three-electrode cell scheme using Ag/AgCl as the pseudo-reference electrode (RE), a platinum wire as the counter electrode (CE) and a glassy carbon electrode (d=3 mm) as the working electrode (WE). Electropolymerization of the monomers (0.01 M) was performed in DCM with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte at a scan rate of 100 mV s<sup>-1</sup> for 10 cycles under ambient conditions. The redox potential of ferrocene/ferrocene<sup>+</sup> (Fc/Fc<sup>+</sup>) under the same conditions is located at 0.44 V, which is assumed to have an absolute energy level of -4.8 eV to vacuum. Cyclic voltammograms of the polymer films were obtained using the same electrode setup in the monomer-free ACN solution containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>.

#### **4. Spectroelectrochemistry and Dynamic Switching Tests**

The spectroelectrochemical and the dynamic switching tests were measured with a three-electrode cell, which was constructed in a 1 cm cuvette, where the working electrode was an ITO glass with a surface area of 0.75×3.0 cm<sup>2</sup>, the counter electrode was a Pt wire with a diameter of 0.5 mm, and an Ag/AgCl wire (Φ 0.5 mm) was used as pseudo reference electrode. The polymer films were deposited on the ITO electrode. The medium used for the tests is the monomer free electrolyte mentioned above. The potential difference biased on the ITO electrode was actualized by the electrochemical analyzer, and the changes in absorbance intensities were recorded by the spectrophotometer mentioned above.

#### **5. Calculation of parameter**

The potentials were alternated between the reduced and oxidized states with a residence time of 5 s. The optical contrast at the specific wavelength ( $\lambda$ ) was determined by  $\Delta T\%$  values of polymer films, using the following equation:

$$\Delta T = |T_{ox} - T_{red}|$$

The coloration efficiency ( $CE$ ) is a key parameter for evaluating the energy utilization efficiency during the switching process driven by electrical power, and is defined as the change in optical density ( $\Delta OD$ ) with respect to the charge consumed per unit area of the electrode ( $\Delta Q$ ). The equations used for calculation are given below:

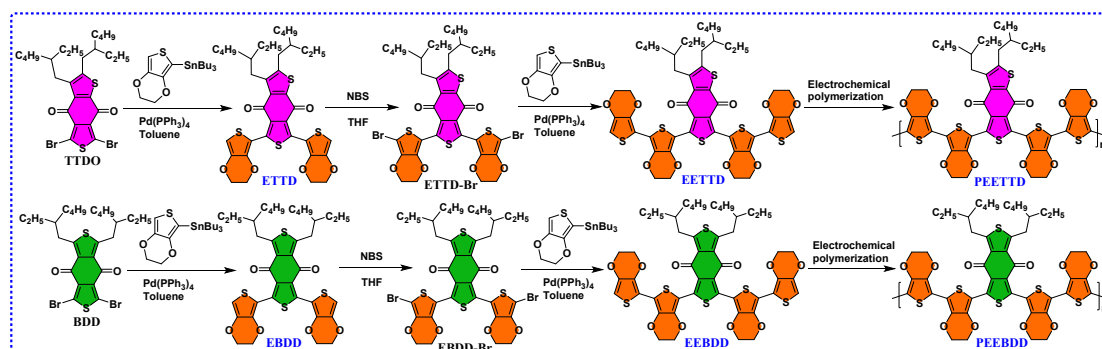
$$\Delta OD = \log \left( \frac{T_b}{T_c} \right)$$

$$\Delta Q = Q/A$$

$$CE = \Delta OD / \Delta Q$$

Where  $T_b$  and  $T_c$  represent the transmittance in the neutral and oxidized states, respectively and were used for the calculation of  $\Delta OD$ , the change in optical density at a given wavelength.  $\Delta Q$  is the amount of charge injected per unit area of the sample.  $Q$  could be determined *via* the integration of the electricity consumption during a cycle of performance in the multi-potential step curves, and  $A$  refers to the active area of the films.

## 6. Synthesis and characterization



**Tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane.** To a solution of 3,4-ethylenedioxythiophene (5.0 g, 35.16 mmol) in THF (100 ml) at -78 °C was slowly added *n*-BuLi (16.12 ml, 2.4M, 38.67 mmol). After the addition, the mixture was kept at -78 °C for 4h, tributyltin chloride (12.58 g, 38.67 mmol) was added at -78 °C. The solution was warmed naturally to room temperature and quenched with 50 ml of water and 200 ml of ethyl acetate was added, the mixture was washed with ultrapure water ten times. After drying over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed and afford the light yellow liquid (14.49 g, 96.07%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.50 (s, 1H), 4.08 (d, *J* = 1.6 Hz, 4H), 1.75-1.37 (m, 6H), 1.38-1.13 (m, 6H), 1.15-0.93 (m, 6H), 0.97=0.56 (m, 6H).

**5,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-bis(2-ethylhexyl)benzo[1,2-b:4,5-c']dithiophene-4,8-dione (ETDD).** Pd(PPh<sub>3</sub>)<sub>4</sub> (100 mg) was added to a solution of compound TTDO (1.14 g, 1.89 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (1.79 g, 4.16 mmol) in 100 mL of dry toluene. The mixture was refluxed in an argon atmosphere for 24 h. After the removal of the solvent at a reduced pressure, the residue was purified by column chromatography on a silica gel column with petroleum ether/dichloromethane (5:1 by volume) to give an red solid

(1.13 g, 83%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 6.47 (d, *J* = 12.2 Hz, 2H), 4.43 – 4.04 (m, 8H), 3.00 – 2.71 (m, 2H), 2.65 (d, *J* = 7.1 Hz, 2H), 1.73 – 1.55 (m, 2H), 1.39 – 1.06 (m, 16H), 0.95 – 0.64 (m, 12H).

**5,7-bis(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-bis(2-ethylhexyl)-benzo[1,2-b:4,5-c']dithiophene-4,8-dione (ETTD-Br).** Compound ETTD (1.1 g, 1.51 mmol) was added into THF (30 mL), after the solid dissolved completely, N-bromosuccinimide (NBS) (0.59 g, 3.33 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 4 h, water was added into the mixture, the mixture was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed at a reduced pressure, the residue was purified by column chromatography on silica gel with petroleum ether to give a red solid (2.58 g, 88%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 4.31 (d, *J* = 15.8 Hz, 8H), 2.83 (dt, *J* = 14.2, 6.7 Hz, 2H), 2.67 (d, *J* = 7.1 Hz, 2H), 1.61 (s, 2H), 1.22 (dd, *J* = 14.9, 9.4 Hz, 16H), 0.95 – 0.65 (m, 12H).

**2,3-bis(2-ethylhexyl)-5,7-bis(2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-b][1,4]dioxin]-7-yl)benzo[1,2-b:4,5-c']dithiophene-4,8-dione (EETTD).** Pd(PPh<sub>3</sub>)<sub>4</sub> (100 mg) was added to a solution of compound ETTD-Br (2.11 g, 2.09 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (1.99 g, 4.62 mmol). The mixture was refluxed in an argon atmosphere for 24 h. After the removal of the solvent at a reduced pressure, the residue was purified by column chromatography on a silica gel column with petroleum ether/dichloromethane (5:1 by volume) to give an red solid (1.91 g, 91%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 6.29 (d, *J* = 4.9 Hz, 2H), 4.48 – 4.03 (m,

16H), 2.93 (dt,  $J = 13.3, 6.8$  Hz, 1H), 2.76 (dt,  $J = 13.8, 7.1$  Hz, 1H), 2.66 (d,  $J = 7.1$  Hz, 2H), 1.61 (s, 2H), 1.21 (d,  $J = 18.5$  Hz, 16H), 0.82 (ddd,  $J = 23.6, 15.8, 7.1$  Hz, 12H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  176.76, 174.19, 150.15, 145.91, 142.02, 141.37, 141.16, 141.01, 140.40, 138.31, 137.94, 136.59, 136.18, 131.18, 129.76, 128.97, 127.90, 125.84, 114.34, 113.09, 109.76, 109.62, 107.26, 106.83, 99.49, 99.07, 65.27, 65.20, 65.15, 64.96, 64.72, 64.64, 64.60, 41.59, 40.08, 33.07, 32.63, 32.53, 31.82, 29.72, 28.92, 28.84, 25.82, 23.25, 23.00, 22.71, 14.16, 14.13, 11.10, 10.89.

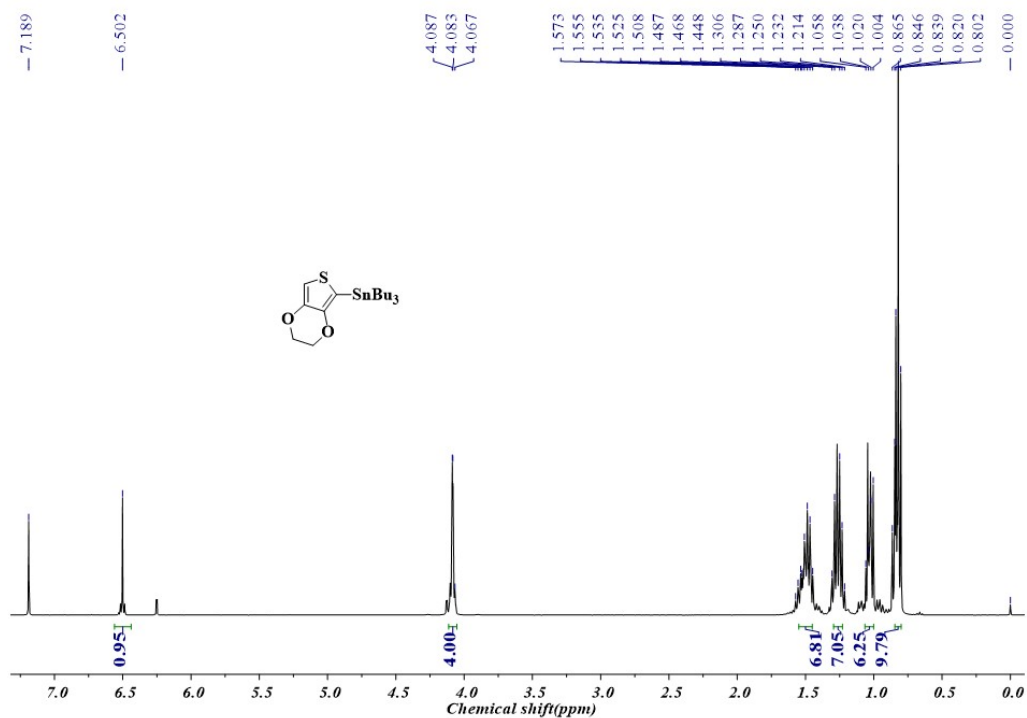
**1,3-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (EBDD).** Pd(PPh<sub>3</sub>)<sub>4</sub> (100 mg) was added to a solution of compound BDD (2.28 g, 3.78 mmol) and tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane (3.58 g, 8.32 mmol) in 100 mL of dry toluene. The mixture was refluxed in an argon atmosphere for 24 h. After the removal of the solvent at a reduced pressure, the residue was purified by column chromatography on a silica gel column with petroleum ether/dichloromethane (5:1 by volume) to give an red solid (2.26 g, 83%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  6.54 (s, 2H), 4.30 (d,  $J = 21.1$  Hz, 8H), 3.33 (dd,  $J = 15.3, 7.0$  Hz, 4H), 1.81 (s, 2H), 1.58 – 1.24 (m, 16H), 0.94 (dd,  $J = 13.1, 6.3$  Hz, 12H).

**1,3-bis(7-bromo-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (EBDD-Br).** Compound EBDD (1.1 g, 1.51 mmol) was added into THF (30 mL), after the solid dissolved completely, N-bromosuccinimide (NBS) (0.59 g, 3.33 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 4 h, water was added into the

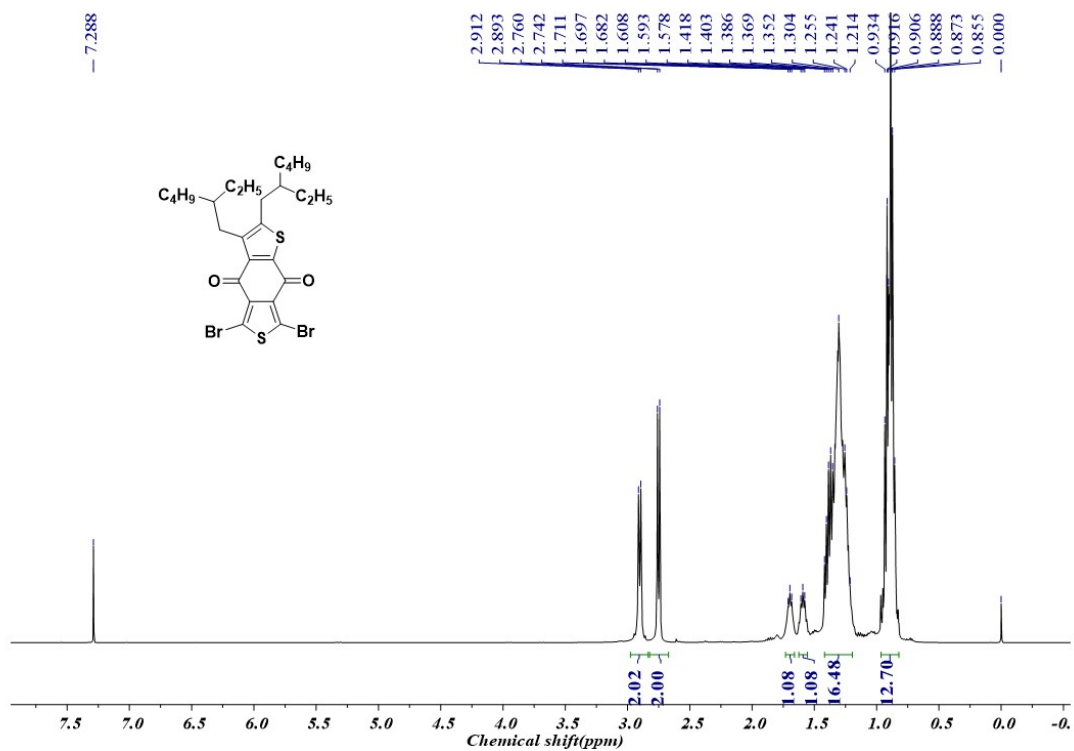
mixture, the mixture was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed at a reduced pressure, the residue was purified by column chromatography on silica gel with petroleum ether to give a red solid (2.58 g, 88%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 4.25 (s, 8H), 3.19 (d, *J* = 7.0 Hz, 4H), 1.68 (s, 2H), 1.21 (d, *J* = 39.2 Hz, 16H), 0.83 (t, *J* = 7.6 Hz, 12H).

**1,3-bis(2-ethylhexyl)-5,7-bis(2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-b][1,4]dioxin]-7-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione (EEBDD).** Pd(PPh<sub>3</sub>)<sub>4</sub> (100 mg) was added to a solution of compound EBDD-Br (2.11 g, 2.09 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (1.99 g, 4.62 mmol). The mixture was refluxed in an argon atmosphere for 24 h. After the removal of the solvent at a reduced pressure, the residue was purified by column chromatography on a silica gel column with petroleum ether/dichloromethane (5:1 by volume) to give an red solid (1.91 g, 91%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 6.27 (s, 2H), 4.31 (d, *J* = 4.7 Hz, 16H), 3.32 (dd, *J* = 14.7, 7.1 Hz, 2H), 3.15 (dd, *J* = 14.6, 9.7 Hz, 2H), 1.73 (s, 2H), 1.40 – 1.09 (m, 16H), 0.83 (dt, *J* = 26.7, 7.2 Hz, 12H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 177.24, 152.10, 141.29, 140.93, 139.49, 137.85, 136.45, 133.54, 132.68, 112.90, 109.77, 107.03, 98.92, 65.11, 64.91, 64.69, 64.62, 41.04, 33.56, 32.66, 28.73, 25.90, 23.06, 14.12, 10.84.





**Figure S1.**  $^1\text{H}$  NMR spectrum of tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane.



**Figure S2.**  $^1\text{H}$  NMR spectrum of TTDO.

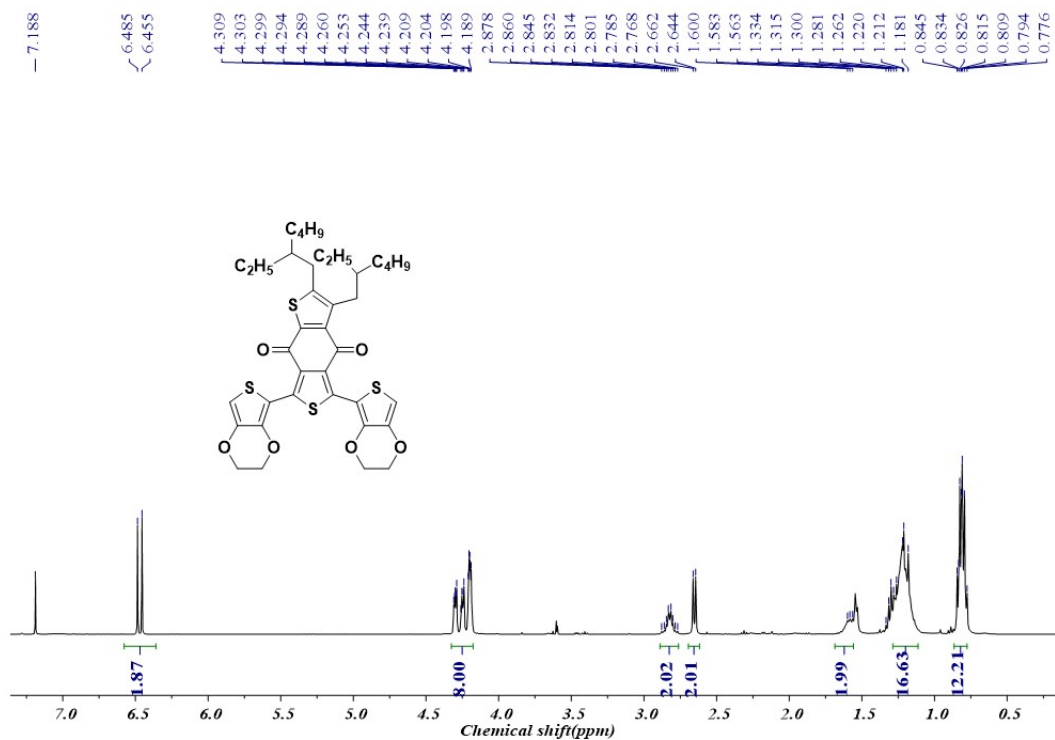


Figure S3. <sup>1</sup>H NMR spectrum of ETDD.

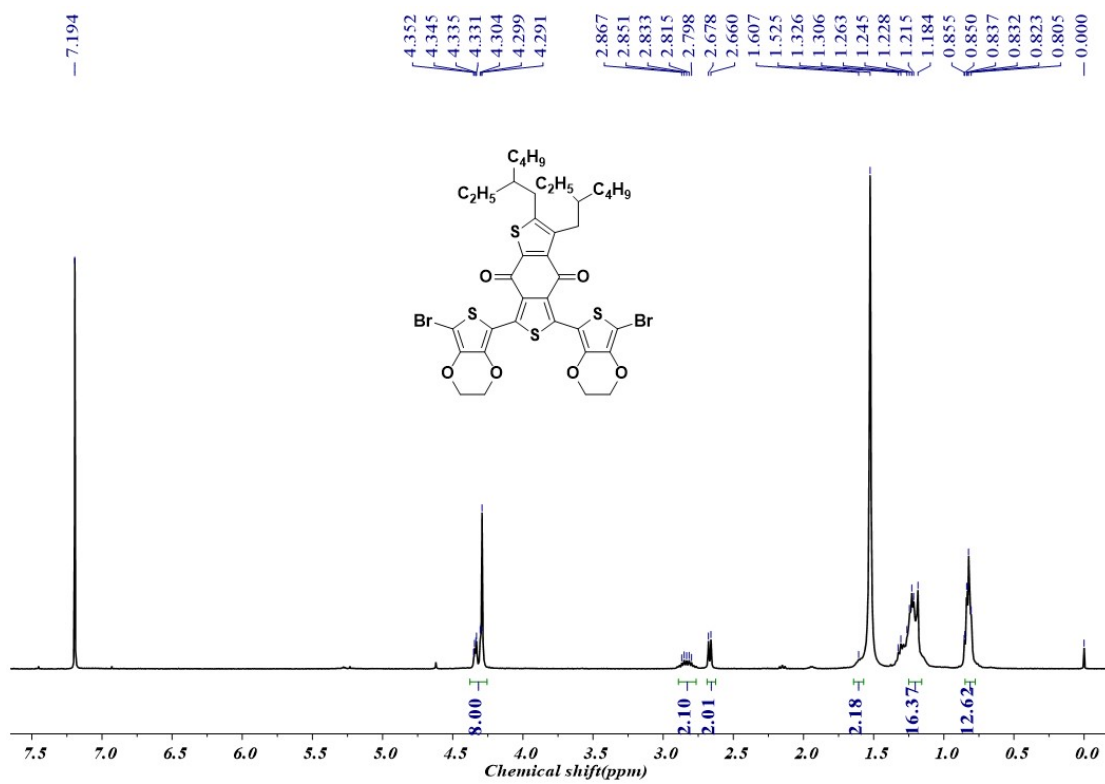


Figure S4. <sup>1</sup>H NMR spectrum of ETDD-Br.

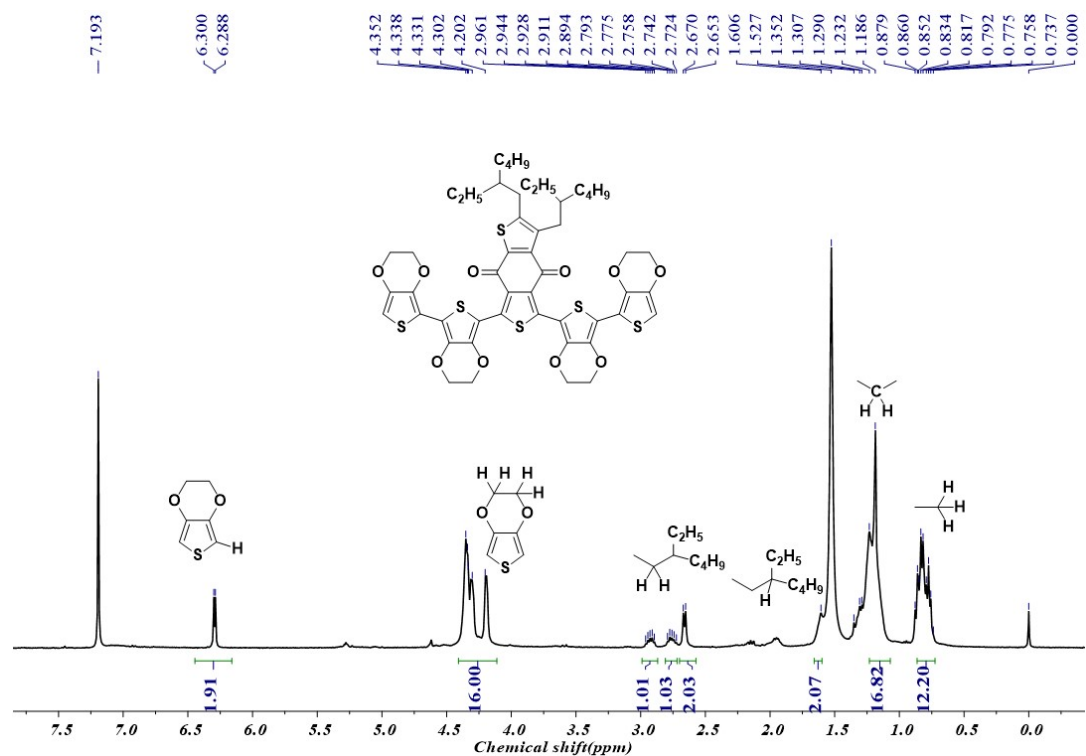


Figure S5.  $^1\text{H}$  NMR spectrum of EETTD.

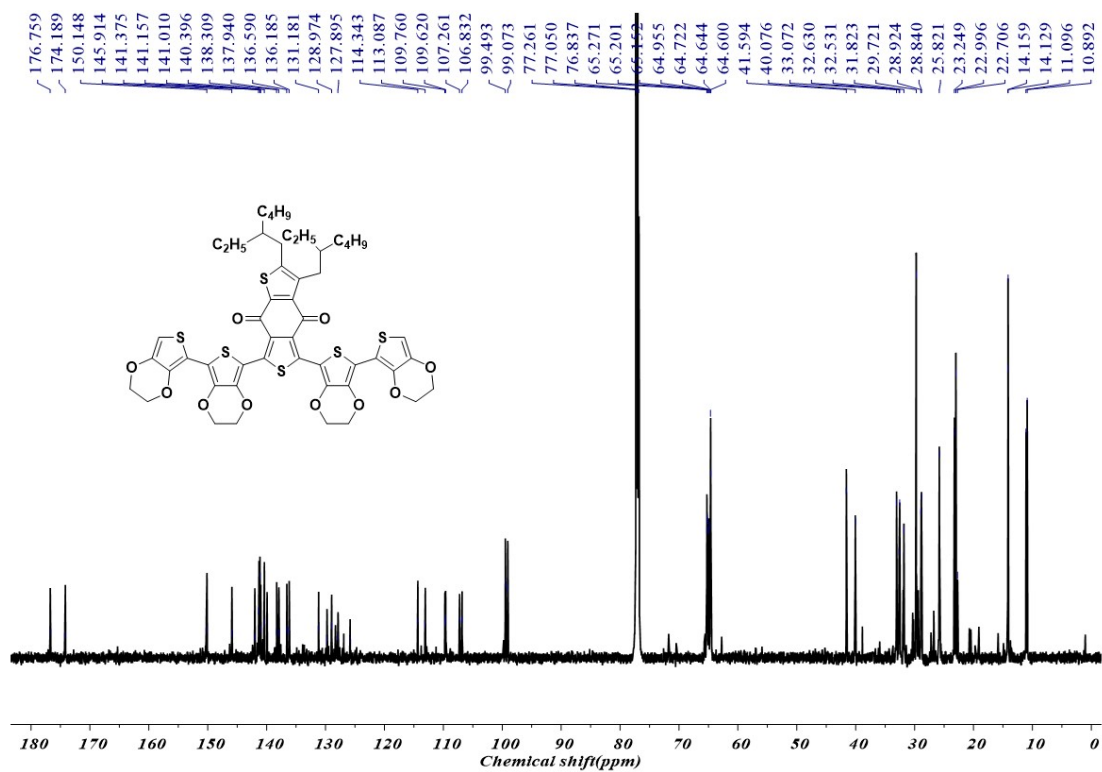
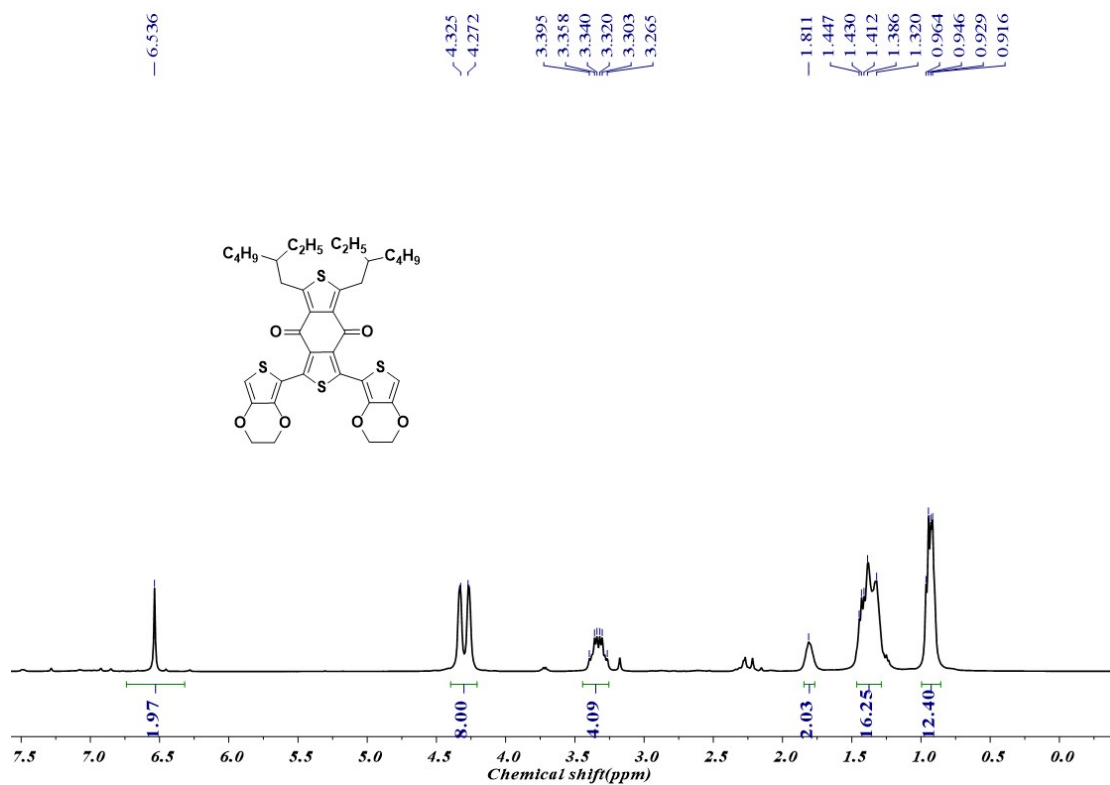
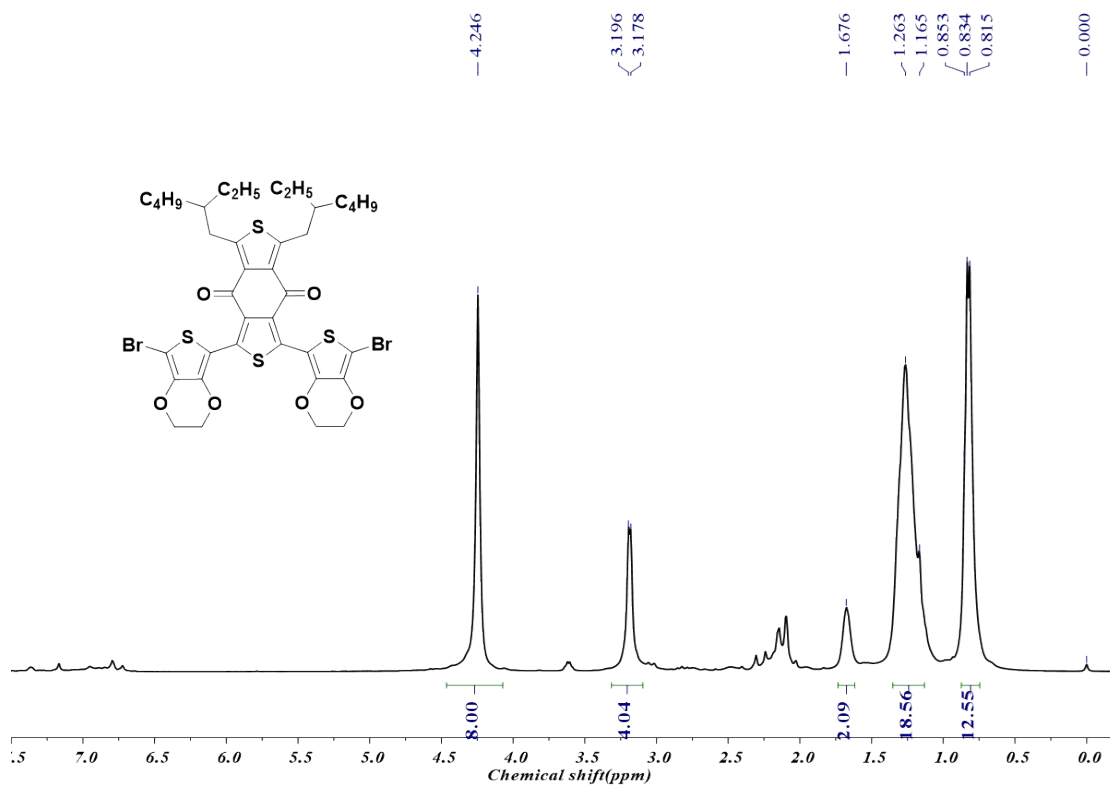


Figure S6.  $^{13}\text{C}$  NMR spectrum of EETTD.



**Figure S7.** <sup>1</sup>H NMR spectrum of compound EBDD.



**Figure S8.** <sup>1</sup>H NMR spectrum of EBDD-Br.

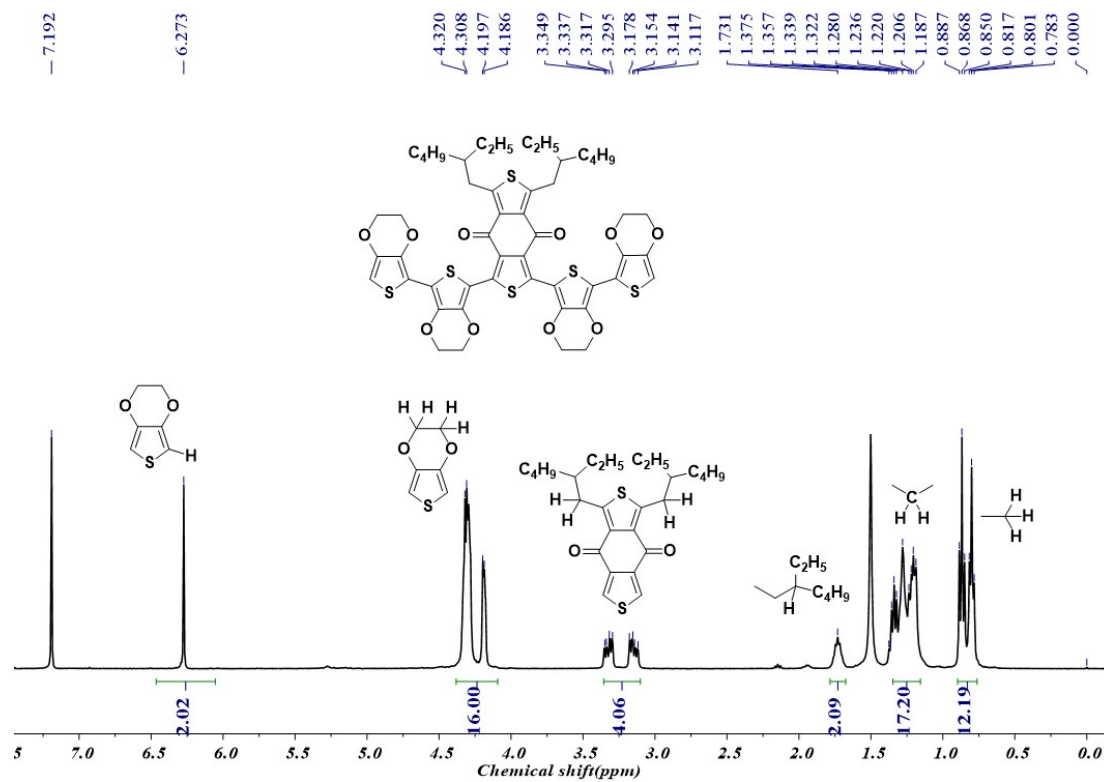


Figure S9.  $^1\text{H}$  NMR spectrum of compound EEBDD.

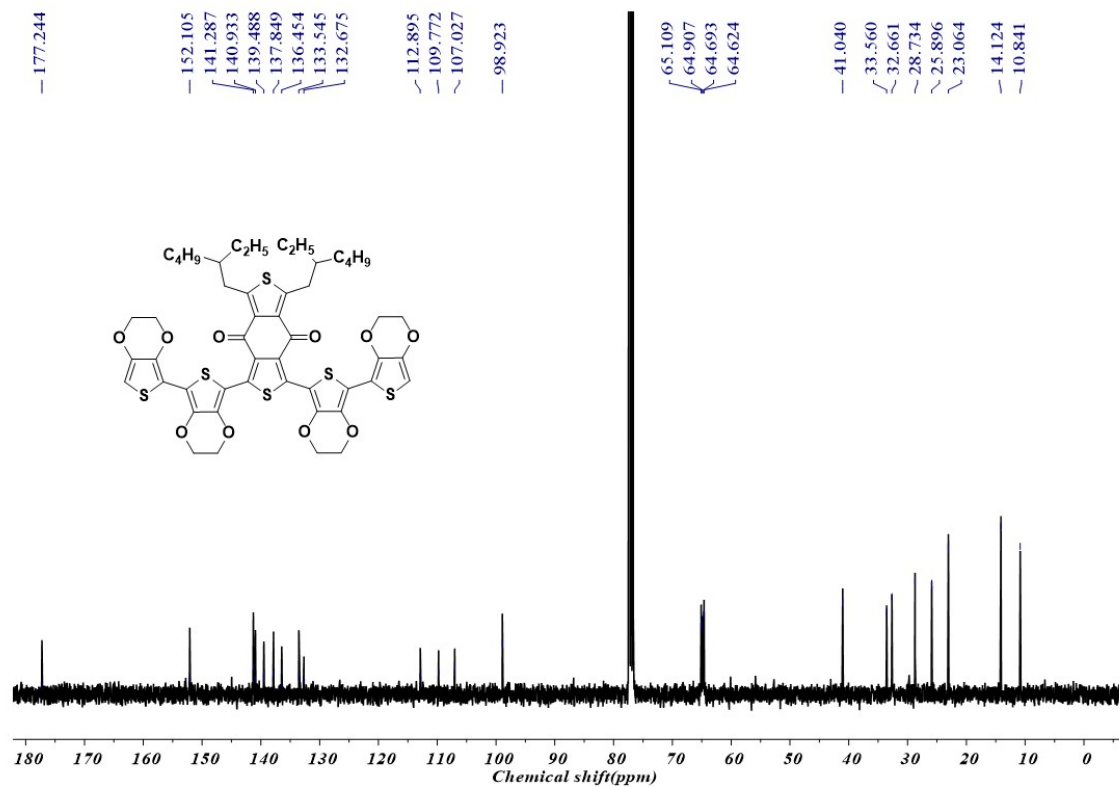
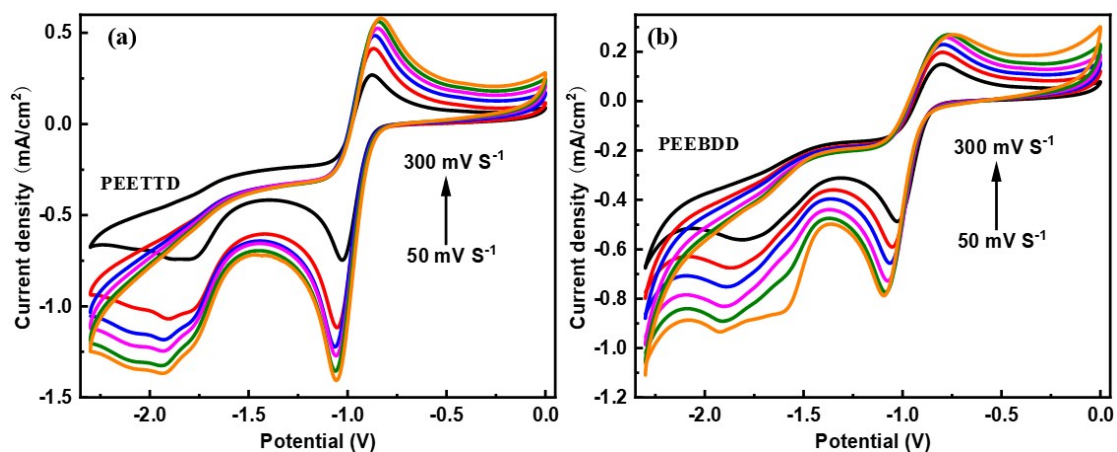
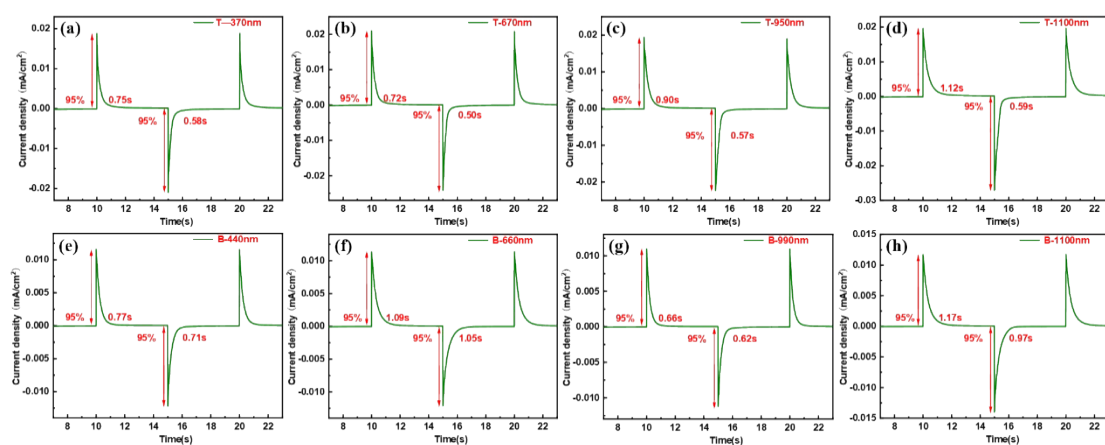


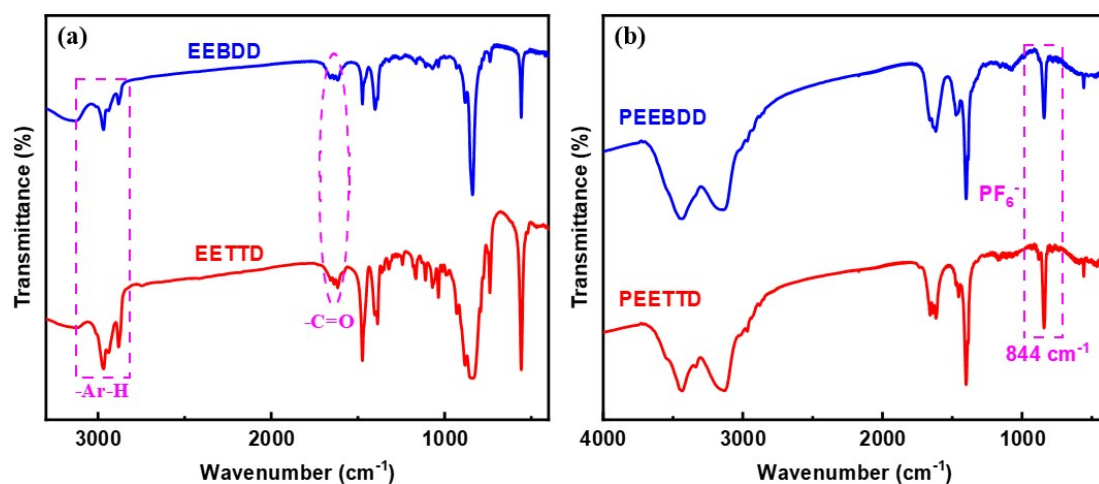
Figure S10.  $^{13}\text{C}$  NMR spectrum of EEBDD.



**Figure S11.** Cyclic voltammograms of (a) PEETTD and (b) PEEBDD in 0.1 M ACN-Bu<sub>4</sub>NPF<sub>6</sub> solution recorded at scan rates of 50, 100, 150, 200, 250 and 300 mV s<sup>-1</sup> during the n-type doping process.












**Figure S12.** Response time determined by the double-step chronoamperometry method of PEETTD (a) at 370 nm, (b) at 670 nm, (c) at 950 nm, (d) at 1100 nm; PEEBDD (e) at 440 nm, (f) at 660 nm, (g) at 990 nm, (h) at 1100 nm, respectively.












**Figure S13.** FT-IR spectra of (a) monomers EEBDD and EETTD, and (b) their corresponding polymers PEEBDD and PEETTD.

**Table S1.** Electrochromic parameters and colors of PEETTD at different voltages.

Polymer		L*	a*	b*	color
PEETTD	-0.5V	72.92	-9.37	0.00	
	-0.3V	73.24	-9.32	0.32	
	-0.1V	74.08	-8.70	1.03	
	0.1V	75.50	-8.12	2.00	
	0.3V	77.17	-7.48	3.72	
	0.5V	78.30	-7.35	4.88	
	0.7V	79.08	-7.05	5.70	
	0.9V	79.83	-6.67	6.43	
	1.1V	80.35	-6.27	7.01	

**Table S2.** Electrochromic parameters and colors of PEEBDD at different voltages.

Polymer		L*	a*	b*	color
PEEBDD	-0.5V	83.68	-9.68	-0.64	
	-0.3V	84.45	-8.92	0.08	
	-0.1V	85.27	-7.82	0.43	
	0.1V	86.12	-6.49	-0.31	
	0.3V	87.19	-5.28	0.33	
	0.5V	87.90	-4.59	0.90	
	0.7V	88.33	-4.28	1.34	
	0.9V	88.88	-3.91	1.92	
	1.1V	89.20	-3.66	2.24	

In a word, as shown in **Table S3**, both PEEBDD and PEETTD exhibited better electrochromic performance including higher optical contrast, faster response time and higher *CE* values both in the visible and near infrared regions when compared with their counterparts in the recent reports, suggesting that they have huge potential for electrochromic application in the visible and near infrared regions.

**Table S3.** Electrochromic properties of PEEBDD, PEETTD and their counterparts.

Polymers	Wavelength (nm)	$\Delta T$ (%)	Response time (s)		<i>CE</i> (cm <sup>2</sup> C <sup>-1</sup> )	References
			Reduction	Oxidation		
PEETTD	1100	23.8	0.59	1.12	125.0	This work
	950	12.9	0.57	0.90	71.6	
	670	17.7	0.50	0.72	113.7	



	370	3.70	0.58	0.75	21.2	
	1100	29.0	0.97	1.17	200.3	
PEEBDD	990	17.4	0.62	0.66	157.0	This work
	660	39.9	1.05	1.09	320.7	
	440	13.9	0.71	0.77	80.6	
PTTPA	1100	34	2.5	2.6	269.7	
	900	13	0.2	1.6	135.9	[1]
	423	4	0.2	1.5	243.4	
PDTBF-Th	644	32	1.0	1.8	165.0	
PDTBF-ThSe	670	27	1.9	4.9	81.3	[2]
PDTBF-DTh	672	48	3.1	3.4	149.3	
P(BT-Th-EDOT)	720	46	0.5	0.4	217	[3]
	467	31	0.5	0.5	197	
P(F-EDTO)	458	20.6	0.4	0.6	192	
	724	12.2	0.4	0.8	153	[4]
	900	12.7	0.2	0.4	141	
	1100	17.7	0.4	0.74	176	
PMTTPA	430	28.7	0.9	0.9	177	[5]
PMETPA	454	43.7	1.3	1.3	230	[5]
P1	420	38.6	2.50	2.50	123	[6]
	870	52.5	1.82	1.82		
P2	440	40	1.24	1.24	235	[6]
	850	50	1.20	1.20		
PTEPA	448	26.8	0.94	0.94	204	[7]
	686	17.0	1.11	1.11	277	
PTTPA	430	38	2.57	2.57		[7]
	710	53	2.10	2.10	323	
PCTTPA	420	38.6	2.50	2.50	131	[8]
	870	52.5	1.82	1.82	108	
PCEPTA	440	40	1.24	1.24	119	[8]
	850	50	1.20	1.20	91	

#### References:

- [1] S. Li, G. Liu, X. Ju, Y. Zhang and J. Zhao, in *Polymers*, 2017, **9**, 173.
- [2] S. Qi, C. Wang, Z. Liu, Y. Han, F. Bai and Z. Chen, *Dyes and Pigments*, 2022, **204**, 110432.
- [3] S. Ming, Z. Li, S. Zhen, P. Liu, F. Jiang, G. Nie and J. Xu, *Chemical Engineering Journal*, 2020, **390**, 124572.
- [4] T. Tong, D. Mo and K. Deng, *Electrochimica Acta*, 2023, **470**, 143359.

[5] J. Zhao, X. Yang, S. Wang and J. Yu, *ECS Journal of Solid State Science and Technology*, 2014, **3**, R121-R130.

[6] X. Yang, M. Wang, J. Zhao, C. Cui, S. Wang and J. Liu, *Journal of Electroanalytical Chemistry*, 2014, **714-715**, 1-10.

[7] C. Xu, J. Zhao, C. Cui, M. Wang, Y. Kong and X. Zhang, *Journal of Electroanalytical Chemistry*, 2012, **682**, 29-36.

[8] H.-y. Lin and G.-S. Liou, *Journal of Polymer Science Part A: Polymer Chemistry*, 2009, **47**, 285-294.

#### MW Averages

Mp: 5892

Mn: 3939

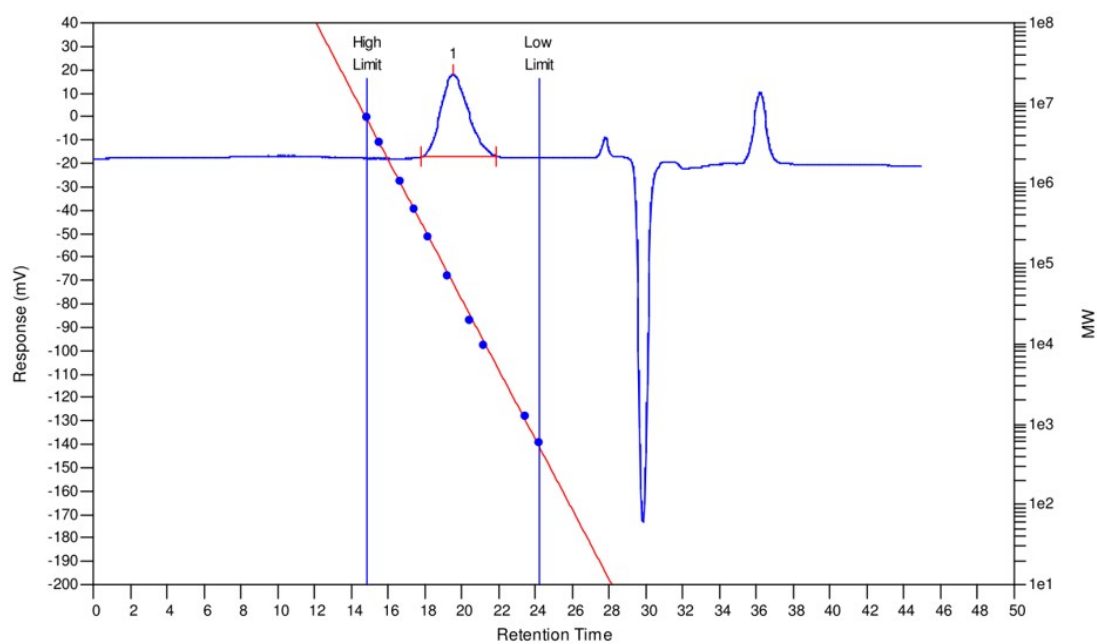
Mv: 5930

Mw: 6313

Mz: 9155

Mz+1: 12083

PD: 1.602



**Figure S14.** GPC data of polymer PEETTD.

### MW Averages

Mp: 6514

Mn: 3446

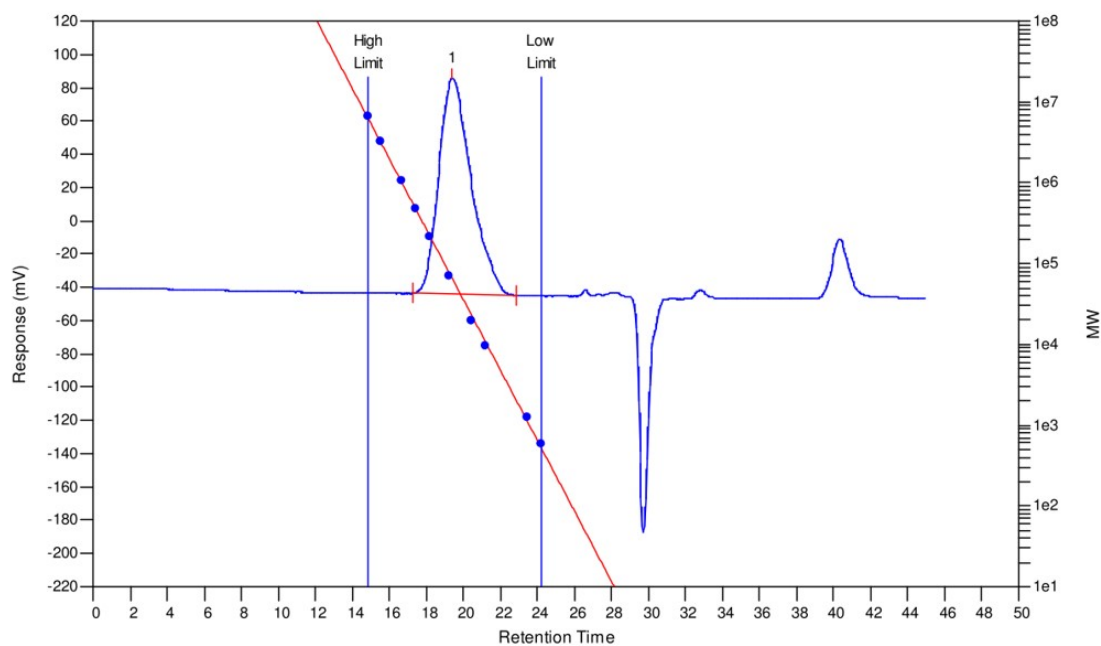
Mv: 6440

Mw: 7025

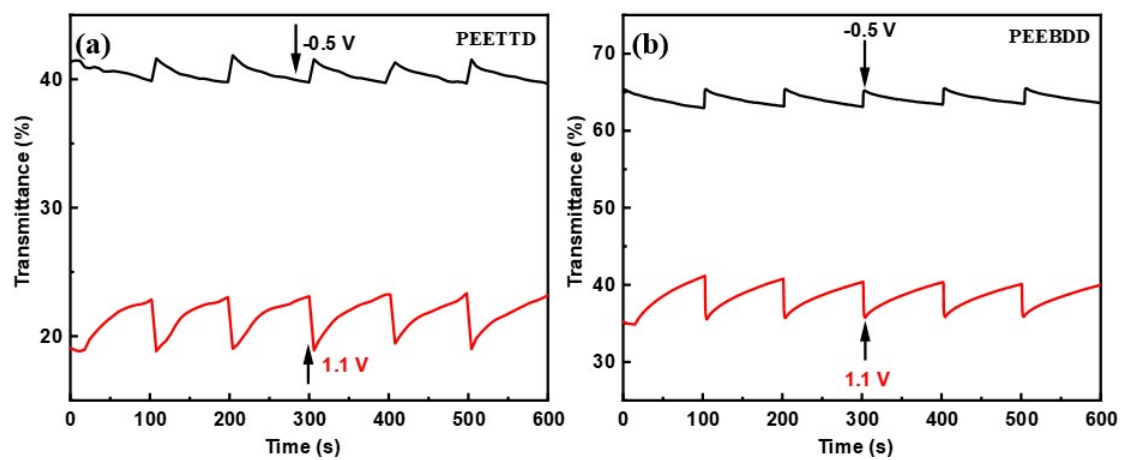
Mz: 11545

Mz+1: 16441

PD: 2.038



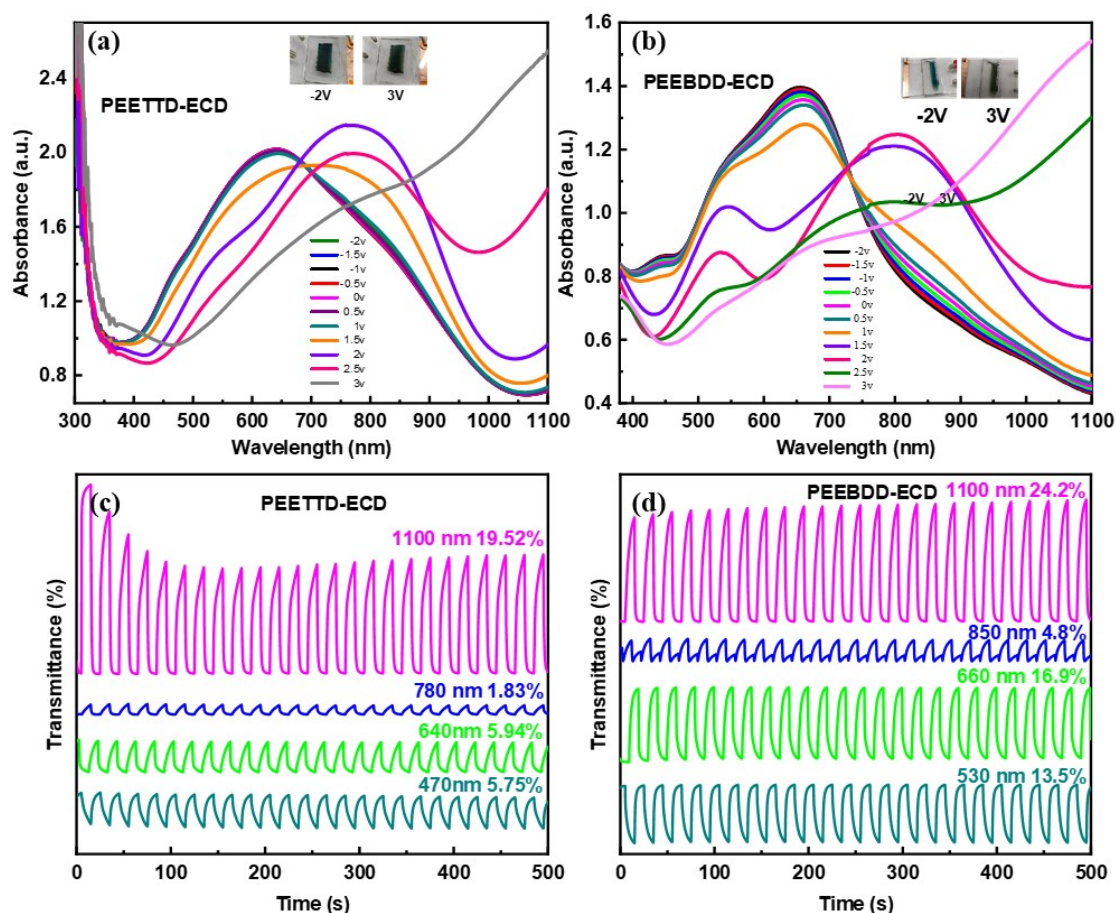
**Figure S15.** GPC data of polymer PEEBDD.



**Figure S16.** Optical memory of (a) PEETTD and (b) PEEBDD monitored at the maximum absorption wavelength.

In addition, the electrochromic devices (ECD) were fabricated using ITO glass as the electrodes, the polymer films based on triphenylamine derivatives as the active materials, and a PMMA-based gel electrolyte as the conducting medium. As shown in **Figure S17, S18** and **Table S4, S5** and **S6**,

the PEETTD-based device exhibited reversible color changes between grey ( $L^* = 18.15$ ,  $a^* = -6.28$ ,  $b^* = -9.57$ ) in the neutral state (-2.0 V) to light green ( $L^* = 17.94$ ,  $a^* = -6.19$ ,  $b^* = -9.61$ ) and then dark green ( $L^* = 37.93$ ,  $a^* = -11.35$ ,  $b^* = 2.73$ ) in the oxidized state (3.0 V). The device based on PEEBDD displayed color changes from dark green ( $L = 44.58$ ,  $a^* = -22.26$ ,  $b^* = -7.66$ ) to yellow green ( $L^* = 58.33$ ,  $a^* = -13.56$ ,  $b^* = 10.26$ ) when applying voltages of -2.0 V and 3.0 V. In addition, PEETTD-based device exhibited the optical contrast of 19.52% at 1100 nm and 5.94% at 640 nm, PEEBDD-based device exhibited the optical contrast of 24.2% at 1100 nm and 16.9% at 660 nm, respectively. All the device exhibited very fast switching time (Figure S18 and Table S4) and excellent coloration efficiency of  $334.84 \text{ cm}^2 \text{ C}^{-1}$  (PEETTD) and  $207.81 \text{ cm}^2 \text{ C}^{-1}$  (PEEBDD) at 1100 nm, indicating the promising potential in electrochromic application.

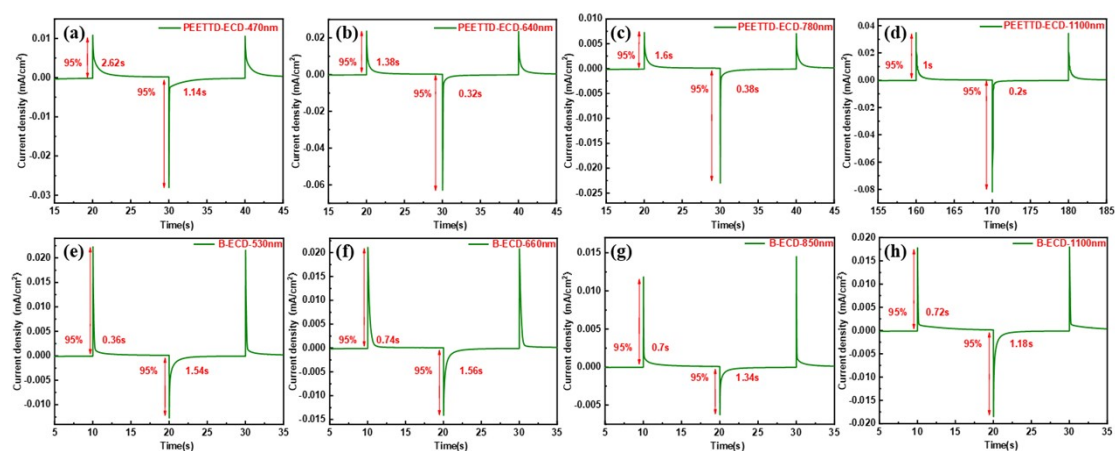


**Figure S17.** Spectroelectrochemistry spectra of electrochromic devices based on (a) PEETTD and

(b) PEEBDD. Time-transmittance curves of electrochromic devices based on (c) PEETTD and (d) PEEBDD.












**Table S4.** Electrochromic performance of electrochromic devices based on PEETTD and PEEBDD at different wavelengths.

Devices	Wavelength (nm)	$\Delta T$ (%)	Response time (s)		$CE$ (cm <sup>2</sup> C <sup>-1</sup> )
			Reduction	Oxidation	
PEETTD	1100	19.52	0.2	1	334.84
	780	1.83	0.38	1.6	278.80
	640	5.94	0.32	1.38	160.30
	470	5.75	1.14	2.62	82.08
PEEBDD	1100	24.2	1.18	0.72	207.81
	850	4.8	1.34	0.7	103.63
	530	13.5	1.54	0.36	98.95













**Figure S18.** Response time determined by the double-step chronoamperometry method of (a) PEETTD-based device at 470 nm, (b) PEETTD-based device at 640 nm, (c) PEETTD-based device at 780 nm, (d) PEETTD-based device at 1100 nm, (e) PEEBDD-based device at 530 nm, (f) PEEBDD-based device at 660 nm, (g) PEEBDD-based device at 850 nm, (h) PEEBDD-based device at 1100 nm, respectively.

**Table S5.** Electrochromic parameters and colors of PEETTD-based device at different voltages.

<b>Device</b>		<b>L*</b>	<b>a*</b>	<b>b*</b>	<b>color</b>
<b>PEETTD- ECD</b>	-2V	18.15	-6.28	-9.57	
	-1.5V	17.91	-6.22	-9.58	
	-1V	17.78	-6.18	-9.59	
	-0.5V	17.71	-6.17	-9.60	
	0V	17.67	-6.15	-9.61	
	0.5V	17.68	-6.14	-9.62	
	1V	17.94	-6.19	-9.61	
	1.5V	21.58	-6.67	-9.14	
	2V	27.89	-8.75	-6.69	
	2.5V	33.52	-10.91	-2.04	
	3V	37.93	-11.35	2.73	

**Table S6.** Electrochromic parameters and colors of PEEBDD-based device at different voltages.

<b>Device</b>		<b>L*</b>	<b>a*</b>	<b>b*</b>	<b>color</b>
<b>PEEBDD- ECD</b>	-2V	44.58	-22.26	-7.66	
	-1.5V	44.85	-22.08	-7.51	
	-1V	45.08	-21.93	-7.40	
	-0.5V	45.23	-21.83	-7.32	
	0V	45.45	-21.71	-7.21	
	0.5V	46.08	-21.33	-6.86	
	1V	46.75	-20.91	-6.44	
	1.5V	51.50	-18.20	-1.73	
	2V	55.01	-17.61	3.54	
	2.5V	57.98	-14.56	8.31	
	3V	58.33	-13.56	10.26	