

## Supporting information

### **High-performance D- $\pi$ -A- $\pi$ -D type electrochromic polymers based on nitro-substituted triphenylamine derivatives with thiophene and EDOT as $\pi$ bridges**

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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:

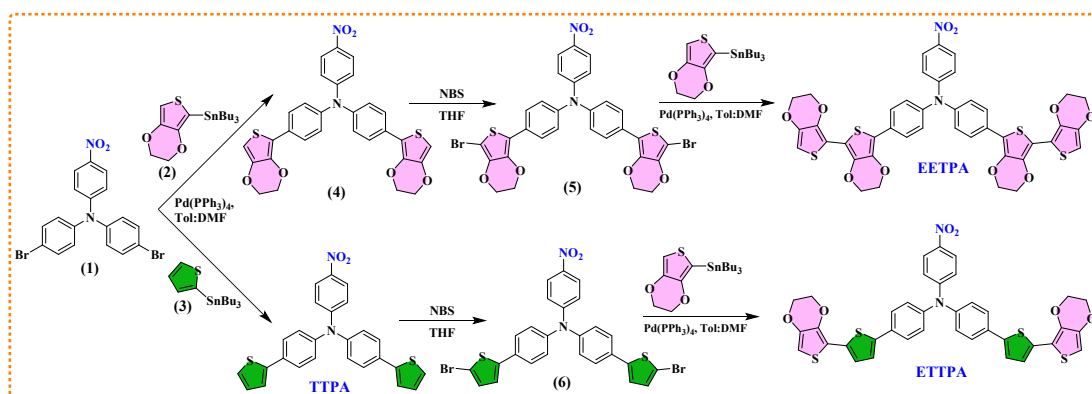
$$\Delta OD = \log \left( \frac{T_b}{T_c} \right)$$

$$\Delta Q = Q/A$$

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

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 (2).** 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).

**4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-N-(4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)phenyl)-N-(4-nitrophenyl)aniline (4).** Pd(PPh<sub>3</sub>)<sub>4</sub> (100 mg) was added to a solution of compound (1) (2 g, 4.46 mmol) and compound (2) (4.81 g, 11.15 mmol) in 100 mL of toluene. The mixture was refluxed in a nitrogen atmosphere for 12 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 obtain a solid (1.2 g, 50 %). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 9.4 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 4H), 7.16 (d, *J* = 8.8 Hz, 4H), 7.01 (d, *J* = 9.4 Hz, 2H), 6.31 (s, 2H), 4.37 – 4.19 (m, 8H).

**4-(7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-N-(4-(7-bromo-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)phenyl)-N-(4-nitrophenyl)aniline (5).**

Compound (4) (0.8 mmol, 0.50 g) was added into THF (20 mL). After the solid dissolved completely, N-bromosuccinimide (NBS) (1.9 mmol, 0.33 g) was added in one portion. The reaction mixture was stirred at room temperature for 3 h, water was added into the mixture, the mixture was extracted with CHCl<sub>3</sub>, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed at a reduced pressure; the residue was purified by column chromatography on silica gel with petroleum ether/acetic ether (30:1 by volume) to give an orange solid (0.52 g, 90 %). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 9.3 Hz, 2H), 7.54 (dd, *J* = 8.7, 1.9 Hz, 4H), 7.08 (d, *J* = 8.6 Hz, 4H), 6.94 (d, *J* = 9.1 Hz, 2H), 4.25 (s, 8H).

**4-nitro-N,N-bis(4-(2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-b][1,4]dioxin]-7-yl)phenyl)aniline (EETPA).** Pd(PPh<sub>3</sub>)<sub>4</sub> (46 mg) was added to a solution of compound (5) (0.3 g, 0.40 mmol) and compound (2) (0.38 g, 1.0 mmol) in 100 mL of toluene. The mixture was refluxed in a nitrogen atmosphere for 12 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 obtain a solid (0.23 g, 80 %). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 9.4 Hz, 2H), 7.72 (d, *J* =

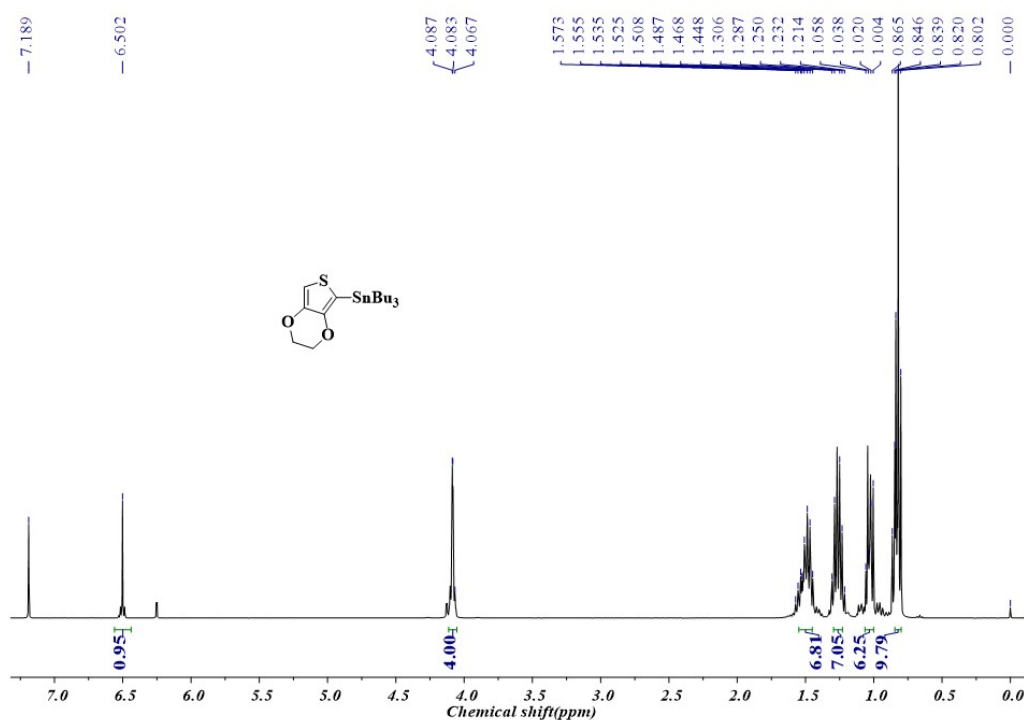
8.8 Hz, 4H), 7.15 (d,  $J = 8.8$  Hz, 4H), 7.02 (d,  $J = 9.4$  Hz, 2H),  $\delta$  6.31 (s, 1H), 4.61–4.13 (m, 16H).

**4-nitro-N,N-bis(4-(thiophen-2-yl)phenyl)aniline (TTPA).** Pd(PPh<sub>3</sub>)<sub>4</sub> (100 mg) was added to a solution of compound (1) (2.0 g, 4.46 mmol) and compound (3) (4.16 g, 11.15 mmol) in 100 mL of toluene. The mixture was refluxed in a nitrogen atmosphere for 12 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 obtain a solid (1.23 g, 50 %). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.08 (d,  $J = 9.3$  Hz, 2H), 7.61 (d,  $J = 8.1$  Hz, 4H), 7.30 (d,  $J = 7.0$  Hz, 4H), 7.19 (d,  $J = 8.6$  Hz, 2H), 7.09 (t,  $J = 4.8$  Hz, 2H), 7.04 (d,  $J = 9.3$  Hz, 2H).

**4-(5-bromothiophen-2-yl)-N-(4-(5-bromothiophen-2-yl)phenyl)-N-(4-nitrophenyl)aniline (6).** TTPA (1.1 mmol, 0.50 g) was added into THF (20 mL). After the solid dissolved completely, N-bromosuccinimide (NBS) (2.42 mmol, 0.43 g) was added in one portion. The reaction mixture was stirred at room temperature for 3 h, water was added into the mixture, the mixture was extracted with CHCl<sub>3</sub>, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed at a reduced pressure; the residue was purified by column chromatography on silica gel with petroleum ether/acetic ether (30:1 by volume) to give an orange solid (0.60 g, 90 %). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.01 (d,  $J = 9.3$  Hz, 2H), 7.43 (d,  $J = 8.8$  Hz, 4H), 7.10 (d,  $J = 8.6$  Hz, 4H), 6.98 (d,  $J = 7.1$  Hz, 6H).

**4-(5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)-N-(4-(5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)phenyl)-N-(4-nitrophenyl)aniline**

(ETTPA). Pd(PPh<sub>3</sub>)<sub>4</sub> (51 mg, 0.44 mmol) was added to a solution of compound (6) (0.3 g, 0.49 mmol) and compound (2) (0.52 g, 1.23 mmol) in 50 mL of toluene. The mixture was refluxed in a nitrogen atmosphere for 12 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 obtain a solid (0.23 g, 60 %). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 9.4 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 4H), 7.18 – 7.06 (m, 8H), 6.98 (d, *J* = 9.4 Hz, 2H), 6.18 (s, 2H), 4.25 (ddd, *J* = 41.6, 5.2, 3.3 Hz, 8H).



**Figure S1.** <sup>1</sup>H NMR spectrum of compound (2).



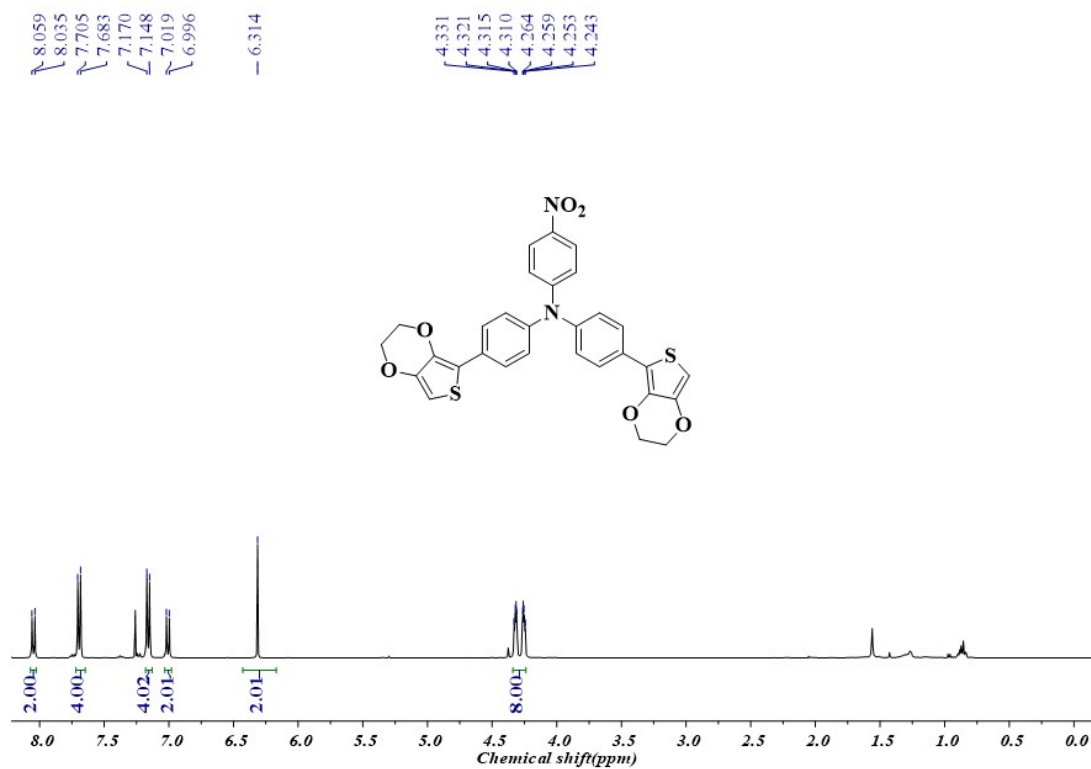


Figure S2. <sup>1</sup>H NMR spectrum of compound (4).

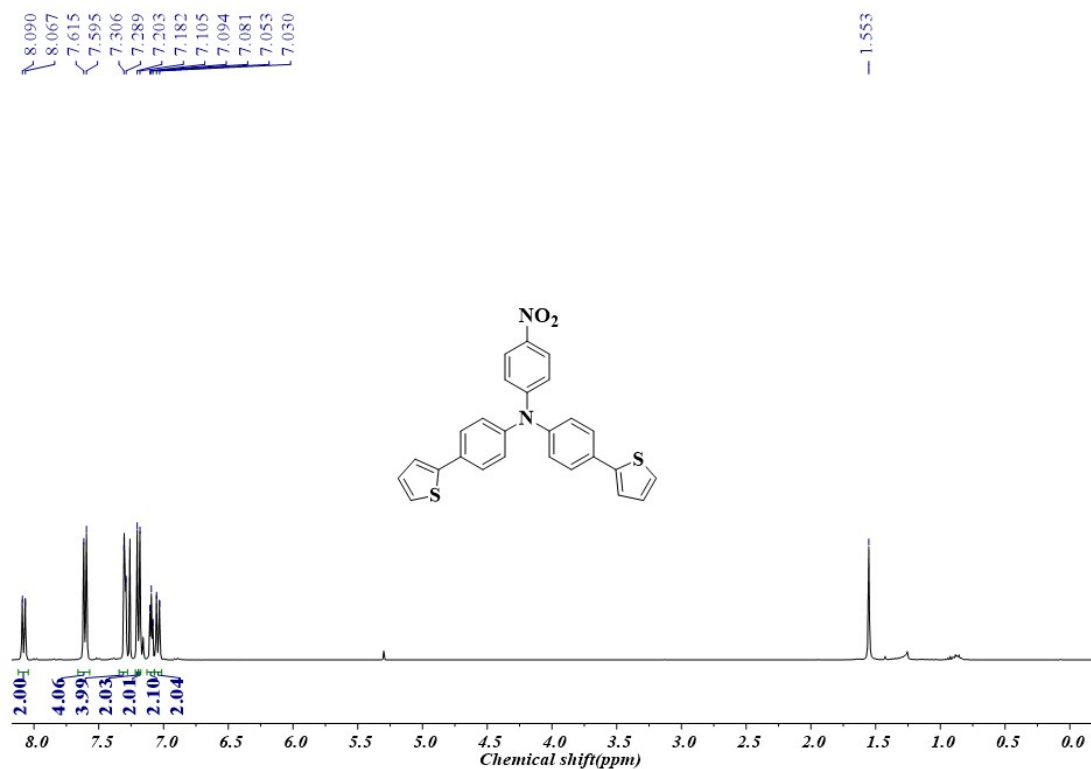


Figure S3. <sup>1</sup>H NMR spectrum of compound TPA.

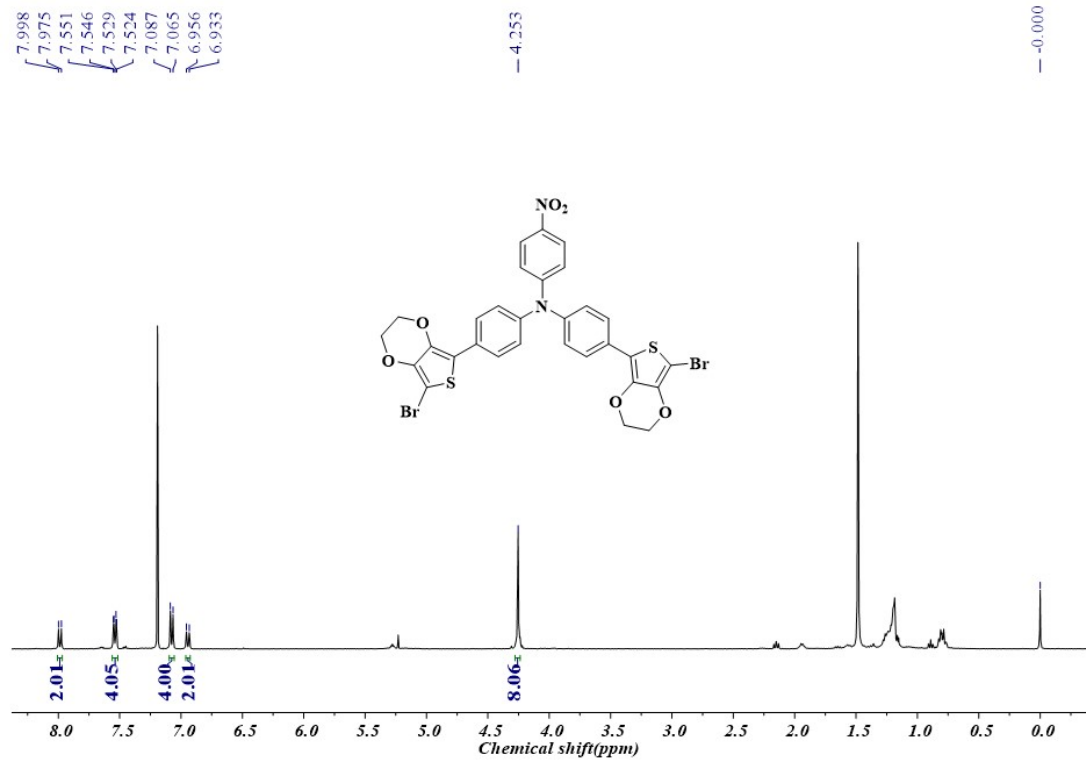


Figure S4. <sup>1</sup>H NMR spectrum of compound (5).

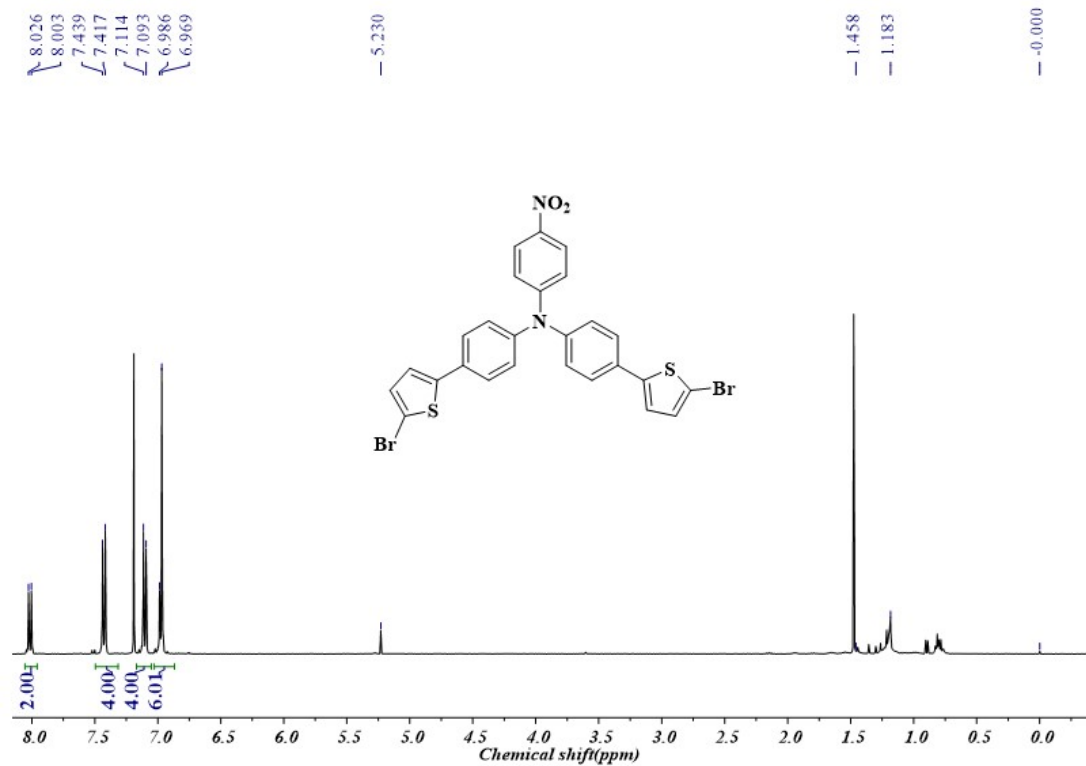
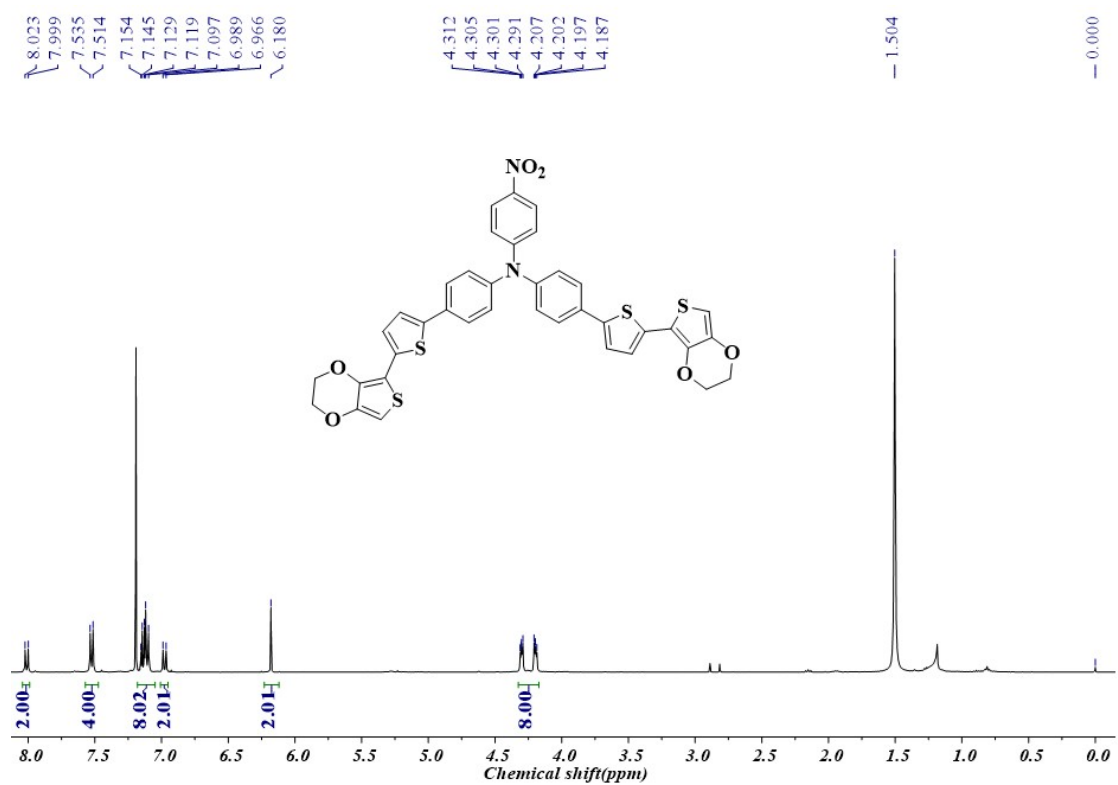
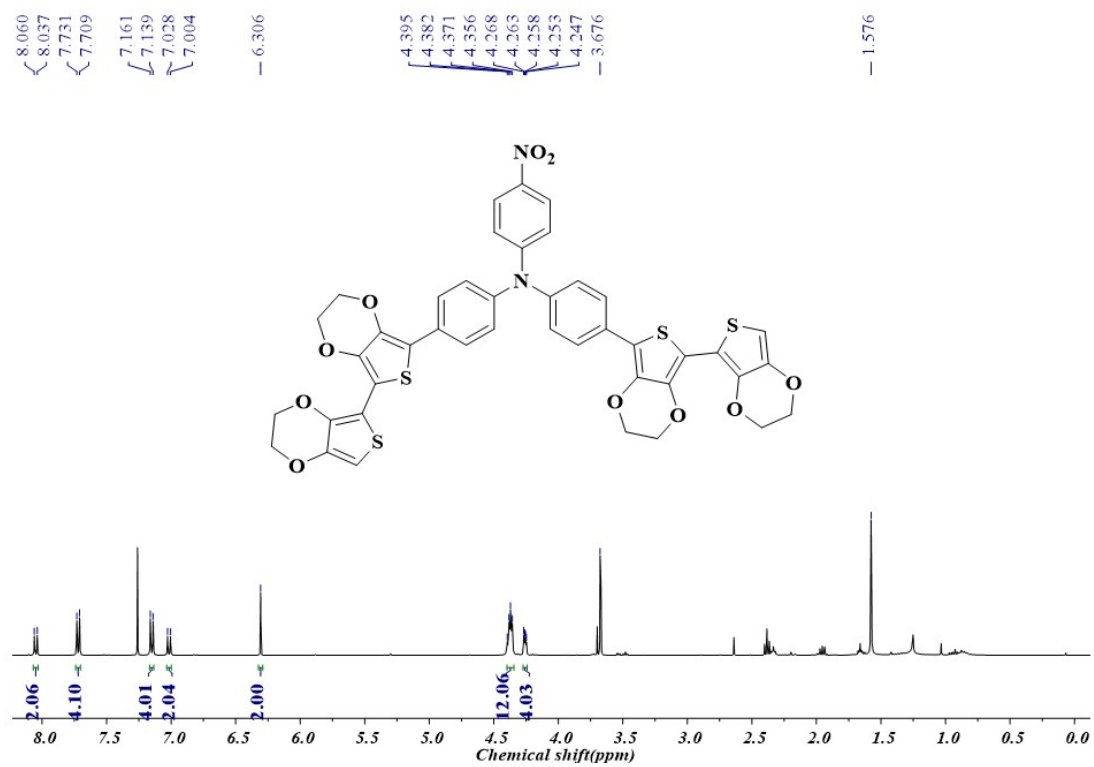


Figure S5. <sup>1</sup>H NMR spectrum of compound (6).










**Figure S6.** <sup>1</sup>H NMR spectrum of ETTPA.












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









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

Polymer		L*	a*	b*	color
PTPPA	0 V	90.95	-11.88	42.34	
	0.2 V	91.20	-11.68	43.55	
	0.4 V	91.22	-11.68	43.65	
	0.6 V	91.28	-11.65	43.75	
	0.8 V	91.32	-11.77	43.13	
	1.0 V	89.93	-10.46	36.88	
	1.2 V	87.10	-7.41	25.59	

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

Polymer		L*	a*	b*	color
PETTPA	-0.7 V	52.28	14.01	27.60	
	-0.5 V	51.87	14.59	28.07	
	-0.3 V	51.63	14.82	28.40	
	-0.1 V	51.60	14.79	28.55	
	0.1 V	51.60	14.81	27.93	
	0.3 V	51.87	13.95	27.23	
	0.5 V	52.58	8.45	24.66	
	0.7 V	54.05	-8.83	17.53	
	0.9 V	54.07	-13.78	12.05	

**Table S3.** Electrochromic parameters and colors of PEETPA at different voltages.

Compound		L*	a*	b*	color
PEETPA	-0.5 V	53.99	29.40	15.77	
	-0.3 V	54.04	29.60	16.01	
	-0.1 V	54.26	28.87	15.09	
	0.1 V	55.98	22.17	10.73	
	0.3 V	62.22	-3.02	4.36	
	0.5 V	65.91	-17.52	-5.17	
	0.7 V	69.48	-12.20	-6.07	
	0.9 V	71.92	-6.83	-5.39	
1.1 V	72.30	-6.28	-5.79	