

Electronic Supplementary Information

Electrochromic polymer with multiple redox couples applied to monitor energy storage states of supercapacitor

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Material and Instruments

Unless otherwise noted, all chemicals for the synthesis of monomer were commercially available and used without further purification. For the electrochemical experiments, CH₂Cl₂ and MeCN were dried before use. Tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) as electrolyte was dried at 60 °C for 24 h before use.

NMR spectra were recorded on a Bruker AV 500. UV-visible absorption spectra were obtained on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. The scanning electron microscope (SEM) measurement was performed by JEOL JSM-6700F scanning electron microscope (JEOL Ltd., Japan). Atomic force microscopy (AFM) measurement was performed under ambient conditions using a Veeco Multimode in the tapping mode, and these test samples were heat annealed at 100 °C for 10 min before measure. The X-ray diffraction (XRD) pattern was collected using a PANalytical X'Pert PRO MPD diffractometer with Cu KR radiation. The weight of polymer film was measured by Mettler-Toledo electronic balance with the error of 0.01 mg. The thickness of the polymer film was determined by a Dektak 6 M surface profilometer.

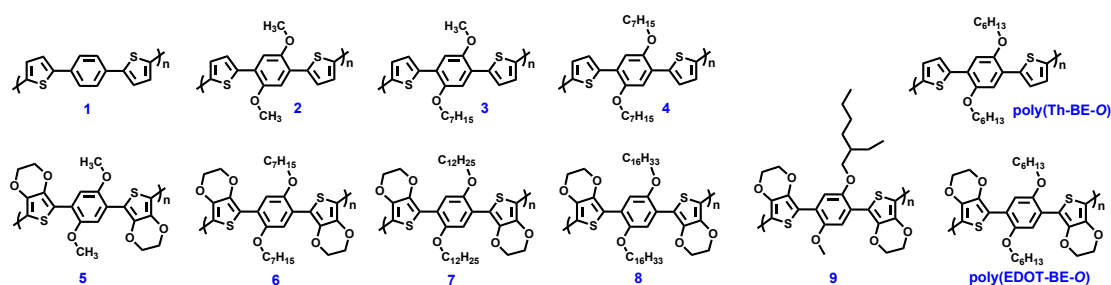


Fig. S1 Chemical structures of the thiophene-benzene derivatives based copolymers.

Table S1. Electrochemical parameters of the thiophene-benzene derivatives based copolymers.

Polymers	$E_{c,p}$ / V	$E_{a,p}$ / V	Ref
1	0.82	>1.0	
2	0.20, 0.58	0.64	
3	0.25, 0.68	0.30, 0.65	1
4	0.20, 0.61	0.40, 0.68	
5	broad	-0.20	
6	-0.36	-0.28	2
7	-0.31	-0.25	

8	-0.40	-0.30	
9	-0.55	-0.15	3
Poly(Th-BE- <i>O</i>)	0.58, 1.00	0.74, 1.13	This
Poly(EDOT-BE- <i>O</i>)	-0.05, 0.15, 0.55	0, 0.20, 0.60	work

DFT calculation

The molecular conformation is an important factor to determine film micromorphology, optical and electrical properties of conjugated polymer. Considering the steric effect of side chain and the non-covalent interaction between oxygen atom in side chain and sulfur atom in thiophene ring (the existence of non-covalent interaction has been proved in previous report⁴⁻⁶), the molecular configurations of precursors (EDOT-BE-*O* and Th-BE-*O*) have been studied by density functional theory (DFT) at B3LYP/6-31G level using the Gaussian 09 package. For simplicity, the target molecules with methoxyl groups replacing the long alkoxy chains were employed for this study. As shown in **Fig. S2**, the dihedral angles between thiophene and phenylene are 20.7° for Th-BE-*O* and 10.3° for EDOT-BE-*O*. Moreover, HOMO and LUMO of the two precursors were studied by the DFT calculations. It is found that the oxygen atom in side chain plays a role in electron delocation, which is helpful to improve the capacitance of conducting polymer.

Moreover, HOMO and LUMO of the target polymers have been calculated, as shown in **Fig. S3**. For simplicity, poly(EDOT-BE-*O*) and poly(Th-BE-*O*) were replaced with the dimers of simplified monomers. HOMO and LUMO were -4.60 eV and -1.70 eV for poly(Th-BE-*O*) and -4.10 eV and -1.36 eV for poly(EDOT-BE-*O*), respectively.

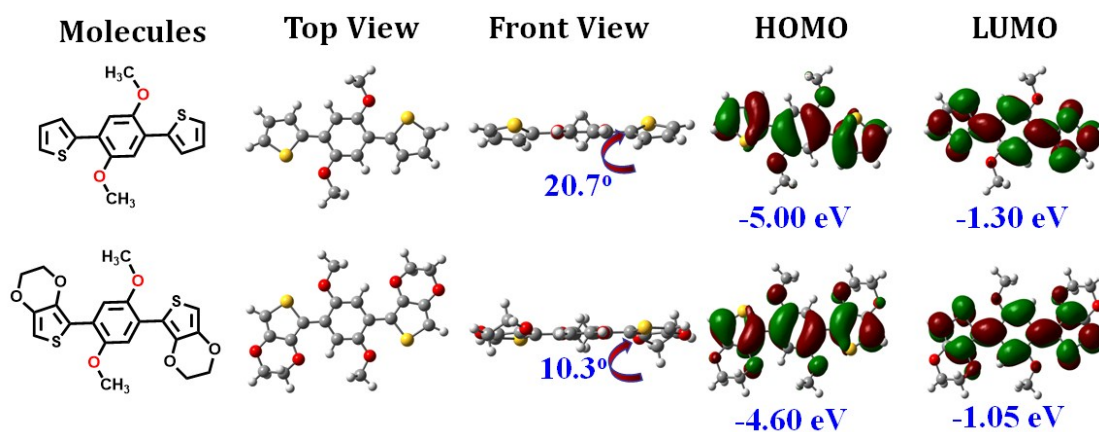


Fig. S2 Optimal configurations, HOMO and LUMO of simplified monomers.

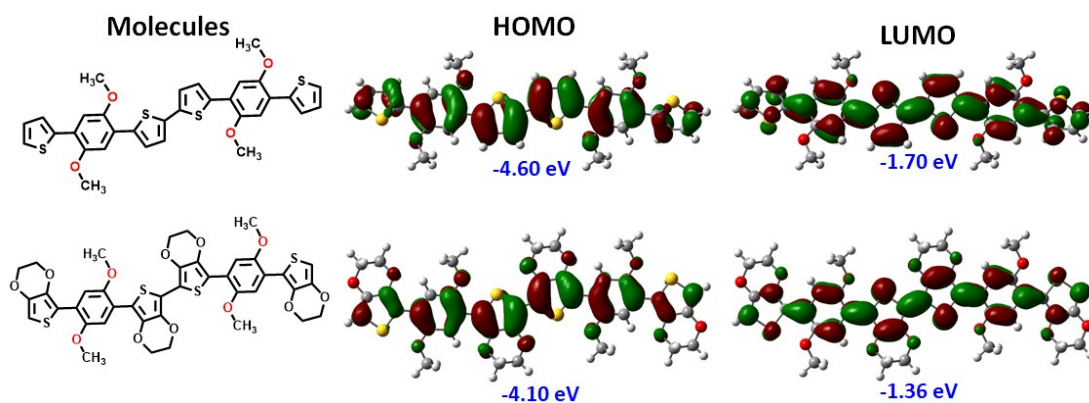


Fig. S3 Molecular structures, HOMO and LUMO of dimers.

Synthesis of monomers

Th-BE-O

A mixture of compounds **1** (1.0 g, 2.30 mmol) and **2** (2.15 g, 5.76 mmol) in DMF was degassed before Pd(PPh₃)₄ (20 mg) was added. And the mixture was stirred at 100 °C for 8 hours. After the reaction was finished, the mixed solution was poured into 100 ml water, and then extracted with CH₂Cl₂ (2 × 50 mL). The solvent was moved out with rotary evaporator. The residue was purified on silica gel column to give 0.78 g of light yellow solid. (Yield: 77%). ¹H NMR (500 MHz, CDCl₃): δ 7.54 (d, 2H), 7.34 (d, 2H), 7.26 (s, 2H), 7.11-7.09 (t, 2H), 4.08 (t, 4H), 1.93-1.87 (m, 4H),

1.56-1.51 (m, 4H), 1.38-1.35 (m, 8H), 0.93-0.90 (m, 6H).

EDOT-BE-O

The synthetic process of EDOT-BE-O is similar with Th-BE-O. EDOT-BE-O as light yellow solid was prepared by the yield of 81%. ^1H NMR (500 MHz, CDCl_3): δ 7.68 (s, 2H), 6.37 (s, 2H), 4.32-4.25 (m, 8H), 4.04 (t, 4H), 1.90-1.85 (m, 4H), 1.52-1.49 (m, 4H), 1.36-1.34 (m, 8H), 0.92-0.89 (m, 6H).

Electrochemical experiment

Unless otherwise noted, the electrochemical experiments were performed in a standard three-electrode electrolytic cell including a Pt wire working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode. The electrochemical polymerization of monomer was performed in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (v/v=1/1) mixed solvent containing $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NBF}_4$. The molar concentration of monomer is 10 mmol L^{-1} . The electrochemical behaviour of polymer was investigated in $\text{MeCN}-\text{Bu}_4\text{NBF}_4$ (0.1 mol L^{-1}).

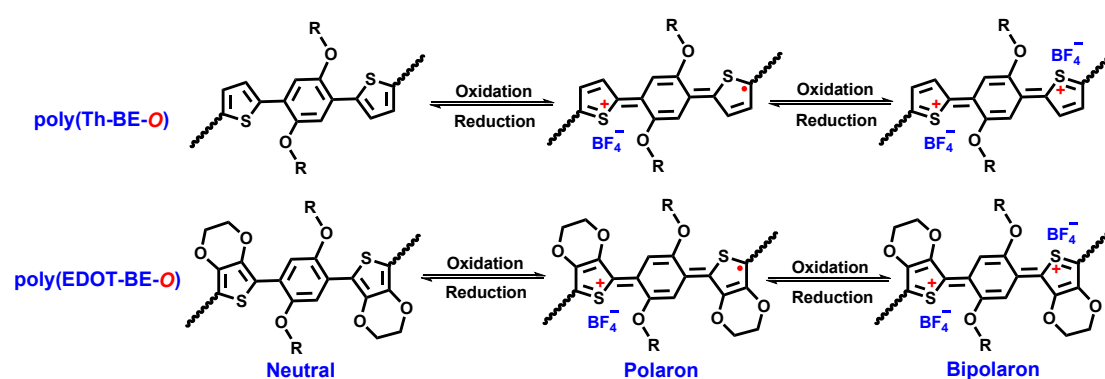


Fig. S4 Structures of polarons and bipolarons for poly(Th-BE-o) and poly(EDOT-BE-o).

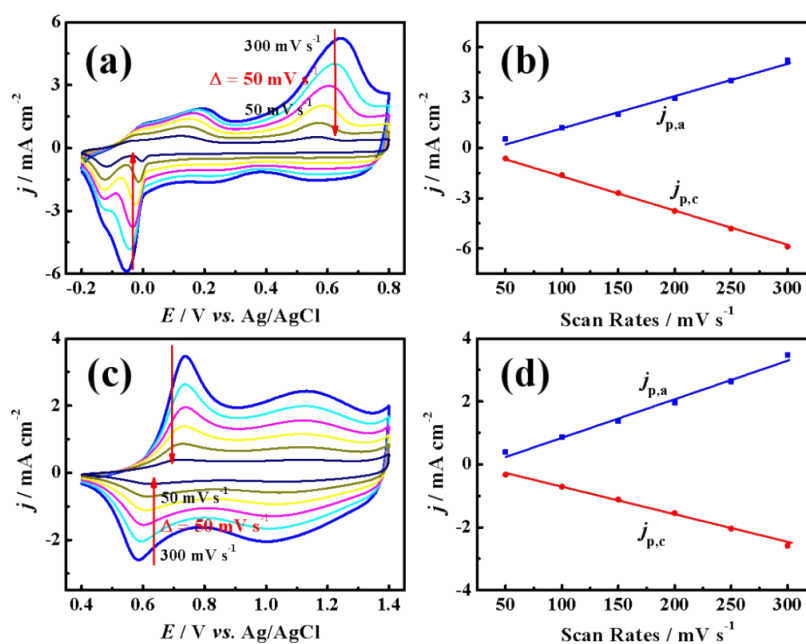


Fig. S5 (a) CVs of poly(EDOT-BE-*O*) and (b) linear relationship between scan rates and peak current densities; (c) CVs of poly(Th-BE-*O*) and (d) linear relationship between scan rates and peak current densities.

Electrochromic properties of polymers

Spectroelectrochemical property of polymer was measured in MeCN-Bu₄NBF₄ (0.1 mol L⁻¹) with a Pt wire counter electrode, an Ag/AgCl reference electrode and an ITO glass working electrode (0.8 cm × 5 cm). The thickness of polymer film is about 100 nm. During the experiment, the three-electrode electrolytic cell was fixed in UV-vis spectrometer to ensure real-time absorption monitor of polymer under different potentials.

The electrochromic performance of polymer was characterized by the time-transmittance curves. The potential windows were -0.2 V ~ 0.8 V for poly(EDOT-BE-*O*) and 0.4 V ~ 1.4 V for poly(Th-BE-*O*). The switching time is 5 s. The optical contrast (ΔT), response time and coloration efficiency (CE) of polymer were

calculated according to following formulas:

$$\Delta T = |T_{\text{ox}} - T_{\text{neut}}| \quad (1)$$

where T_{ox} and T_{neut} are the transmittances of polymer at oxidized and neutral states, respectively.

$$\Delta OD = \log(T_{\text{ox}}/T_{\text{neut}}) \quad (2)$$

$$CE = \Delta OD / Q_d \quad (3)$$

where Q_d is the density of injected/ejected charge for the change of polymer between oxidized and neutral states.

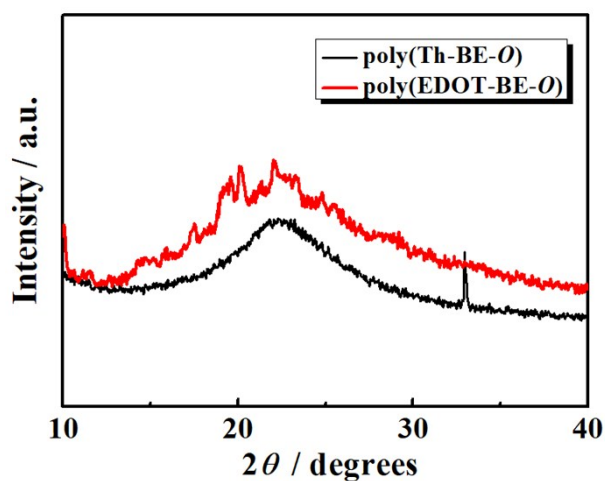


Fig. S6 X-ray diffraction curves of poly(Th-BE-O) and poly(EDOT-BE-O) films.

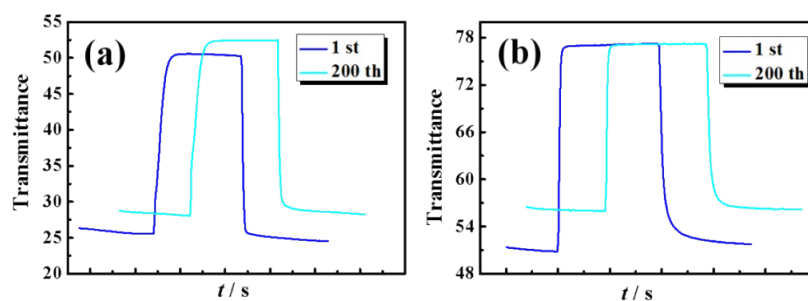


Fig. S7 Optical stability of poly(EDOT-BE-O) (a) at 530 nm and poly(Th-BE-O) (b) at 456 nm in

0.1 M MeCN-Bu₄NBF₄.

Table S2. The electrochromic parameters of poly(EDOT-BE-O) and poly(Th-BE-O).

Compound	Wavelength / nm	ΔT	Response time / s	
			Reduction	Oxidation
Poly(EDOT-BE-O)	530	27%	0.5	2.2
	705	10%	6.5	4.2
Poly(Th-BE-O)	456	25%	2.2	0.3
	647	11%	0.8	0.3

Capacitance properties of polymers

For the capacitance and impedance characterization of polymers, Pt wire working electrode is replaced with ITO glass (0.8 cm \times 5 cm). By electrochemical method, polymer was deposited on ITO glass. The thickness of polymer film is about 120 nm. According to CVs of the two polymers, the potential windows were -0.2~0.8 V for poly(EDOT-BE-O) and 0.4~1.4 V for poly(Th-BE-O), respectively. The specific capacitance (C) of polymer is calculated by the following formula:

$$C = It/Vm \quad (4)$$

where V is the charge-discharge potential range; m is the weight of polymer; I and t are the discharge current and discharge time, respectively.

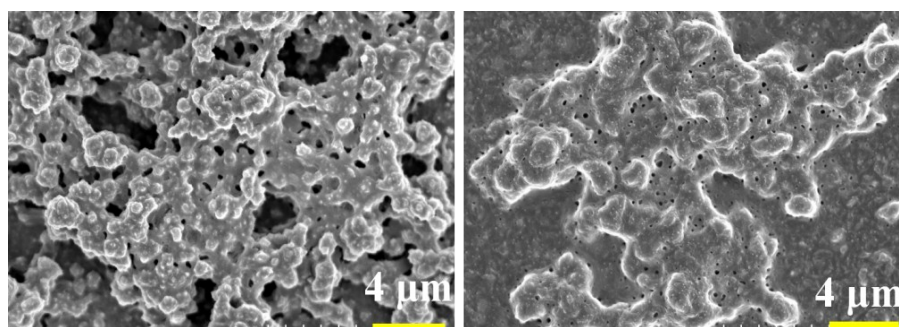


Fig. S8 SEM images of poly(EDOT-BE-O)- (a) and poly(Th-BE-O)- (b) coated ITO glasses at the magnification of 5000 \times .

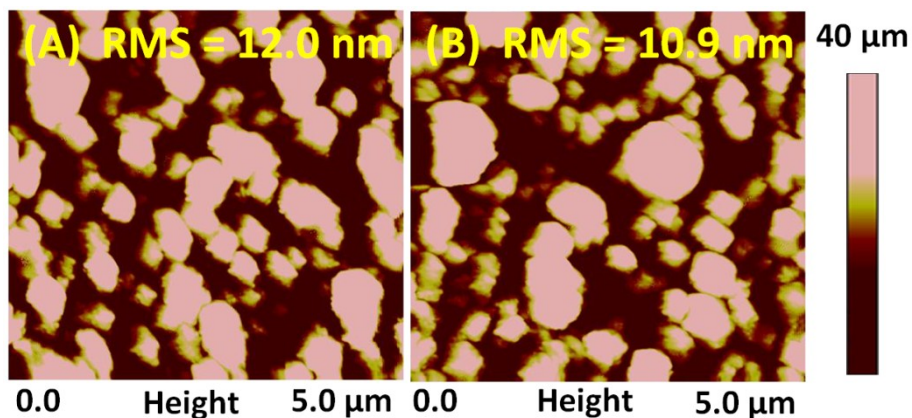


Fig. S9 AFM height images of poly(EDOT-BE-O)- (a) and poly(Th-BE-O)- (b) coated ITO glasses after heat annealing at 100 °C for 10 min.

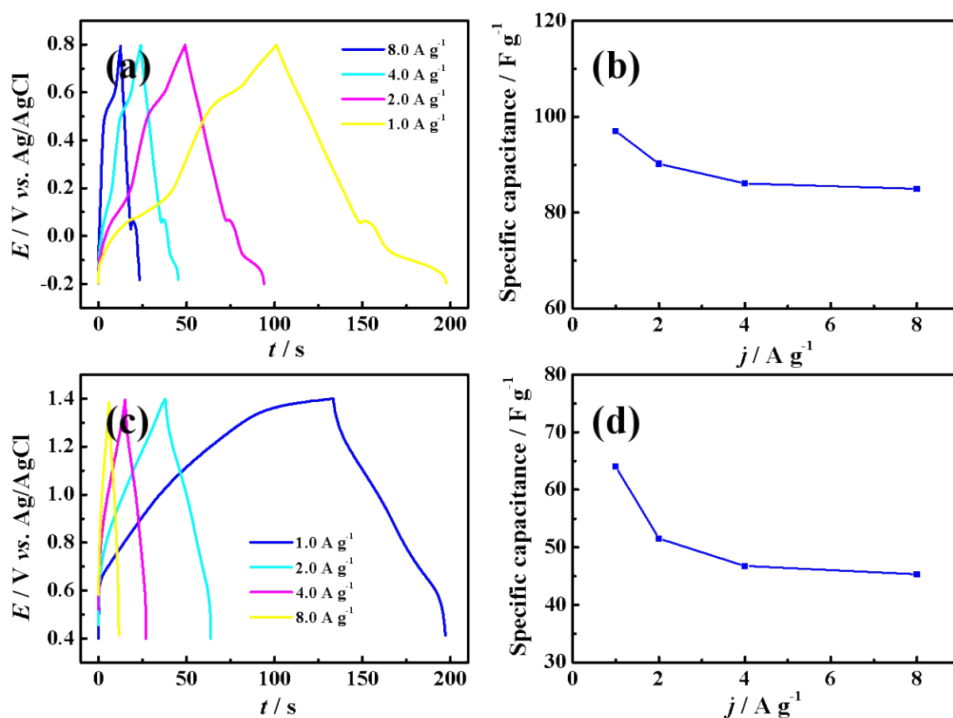


Fig. S10 (a) Galvanostatic charge-discharge curves and (b) corresponding specific capacitance of poly(EDOT-BE-O) at different current densities; (c) Galvanostatic charge-discharge curves and (d) corresponding specific capacitance of poly(Th-BE-O) at different current densities.

Preparation of solid-state device

In order to demonstrate the feasibility for the solid-state device, liquid electrolyte

was replaced with gel electrolyte. Gel electrolyte was prepared using Bu_4NBF_4 , ACN, poly(methyl methacrylate) and propylene carbonate (mass ratio of 3: 70: 7: 20), which were added together and heated at 70 °C for 30 min. Both working and counter electrodes were indium tin oxide (ITO) glasses. By electrochemical method, poly(EDOT-BE-O) film was deposited on “BUTTERFLY” ITO glass. Then the gel electrolyte and another ITO glass were put on polymer film successively. The solid-state device based on poly(EDOT-BE-O) is shown in **Fig. S11**.

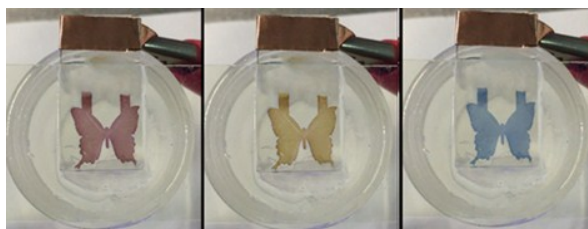


Fig. S11 Different colours of “BUTTERFLY” shaped solid-state device.

References

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