

# Electronic Supplementary Information

## Large Fused Rings based D-A Type Electrochromic Polymer with Magenta-Yellowish Green-Cyan Three Colors

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### 1. Instrumentation

<sup>1</sup>H NMR spectra was recorded on Advance NEO 500 MHz spectrometer, using tetramethylsilane (TMS) as the interval standard in deuterated chloroform solvent. Frontier transform infrared spectroscopy (FT-IR) curves were measured on a Nicolet 6700 FT-IR spectroscopy, using the dried potassium bromide as internal standard. X-ray photoelectron spectroscopy (XPS) measurements of the sprayed films were carried out on a thermo Escalab Xi+ with a monochromated Al X-ray resource. Thermogravimetric analysis (TG) measurements of the three copolymers were carried

out in a Netzsch STA449C DG/DSC thermal analyzer at the heating rate of 10 °C/min from 20 to 750 °C in nitrogen atmosphere. A classical three-electrode cell was fabricated using ITO glass as working electrode, Ag wire as pseudo-reference electrode and Pt wire as counter electrode. Cyclic voltammograms of polymers were tested at the scan rate of 0.1 V/s in ACN-TBAPF<sub>6</sub> (0.2 M) electrolyte solution via CHI660D electrochemical workstation at room temperature. The profiles of UV-vis-NIR spectra, colorimetric analysis and kinetics spectra were recorded in an Agilent Cary 5000 spectrophotometer. The pictures of polymer films at different redox states were recorded by a canon camera.

## **2. Materials**

Acetonitrile (ACN), chloroform (CHCl<sub>3</sub>), acetone, toluene (PhMe), anhydrous methanol (MeOH), tetrakis(triphenylphosphine)-palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>), and other chemicals were purchased from commercial resources and used directly without further purification. The precursor monomers (M<sub>1</sub>), (M<sub>2</sub>) and (M<sub>3</sub>) were purchased from Derthon Optoelectronics Materials Science Technology Co Ltd and used directly without further purification.

## **3. Synthesis of copolymers PBIT-X (X=1, 2 and 3)**

The synthetic routes of three copolymers PBIT-X (X=1, 2, 3) with different molar feeding ratios were shown in Scheme 1.

### **3.1 Synthesis of PBIT-1**

M1 (300.0 mg, 0.2584 mmol), M2 (42.9 mg, 0.0861 mmol) and M3 (213.4 mg, 0.1721 mmol) were dissolved in 40 mL toluene solution. Then

tetrakis(triphenylphosphine)palladium ( $\text{Pd}(\text{PPh}_3)_4$ , 25.0 mg) was added into round flask with a rotor. The mixture was degassed with vacuum pump and filled with argon in the reaction equipment, then the reaction equipment was heated at 120 °C for 48 hours. The reaction condition was same as the process of PBIT-1. Finally, the brown material was obtained. After reaction, the methanol (35 mL) was poured into the reaction solution. The resulting precipitate was filtered and Soxhlet washed with n-hexane, methanol and acetone, respectively. Finally, the target polymer material was obtained after the material was dry at 50 °C for 12 h. Yield: 72%. Element. Anal. Calcd. for PBIT-1: C, 75.81%; H, 8.48%; N, 1.15%; S, 12.57%; Found: C, 75.79%; H, 8.47%; N, 1.13%; S, 12.53%.

### **3.2 Synthesis of PBIT-2**

The synthesis procedure of PBIT-2 is similar with that of PBIT-1. The molar feeding ratio of M1:M2:M3 is 2:1:1. The feeding mass are 300.0 mg for M1, 64.4 mg for M2 and 160.0 mg for M3, respectively. Yield: 70%. Element. Anal. Calcd. for PBIT-2: C, 75.65%; H, 8.51%; N, 1.87%; S, 11.82%; Found: C, 75.64%; H, 8.49%; N, 1.83%; S, 11.80%.

### **3.3 Synthesis of PBIT-3**

The synthesis procedure of PBIT-3 is similar with that of PBIT-1. The molar feeding ratio of M1:M2:M3 is 3:2:1. The feeding mass are 300.0 mg for M1, 85.8 mg for M2 and 106.7 mg for M3, respectively. Yield: 74%. Element. Anal. Calcd. for PBIT-3: C, 75.46%; H, 8.54%; N, 2.73%; S, 10.94%; Found: C, 75.41%; H, 8.50%; N, 2.73%; S, 10.91%.

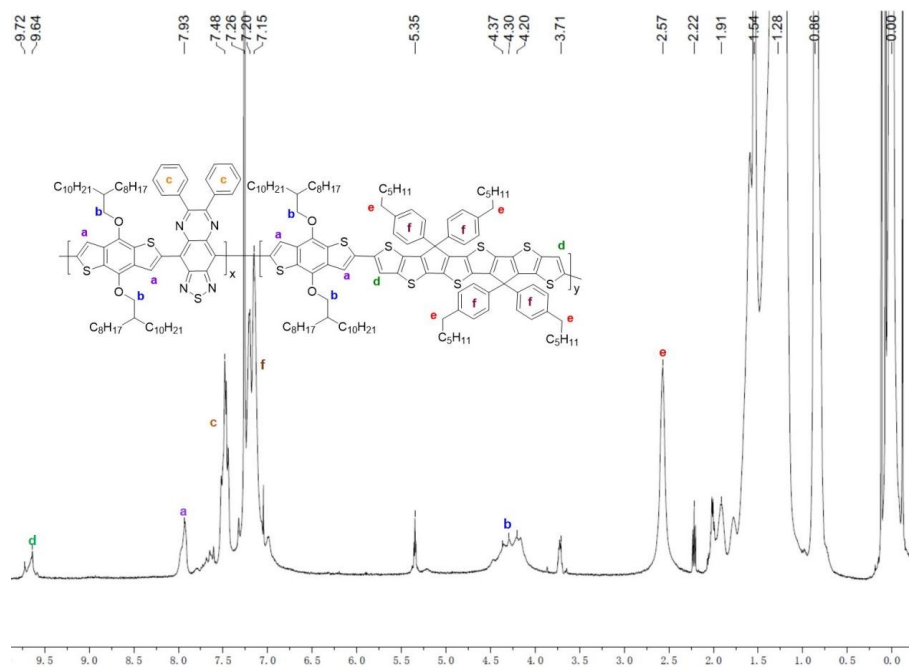


Fig. S1  $^1\text{H}$  NMR of PBIT-1 in  $\text{CDCl}_3$ .

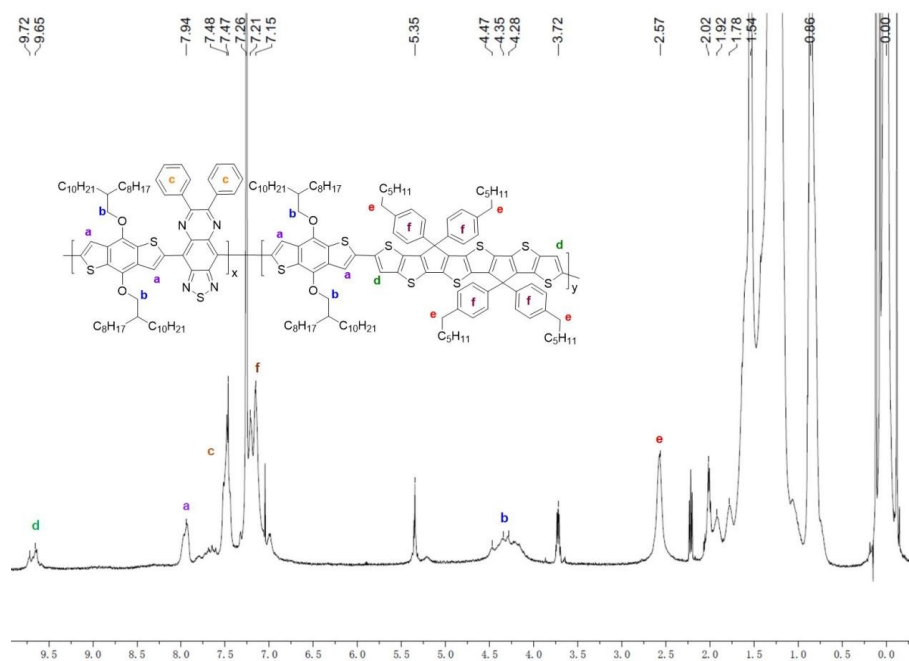


Fig. S2  $^1\text{H}$  NMR of PBIT-2 in  $\text{CDCl}_3$ .

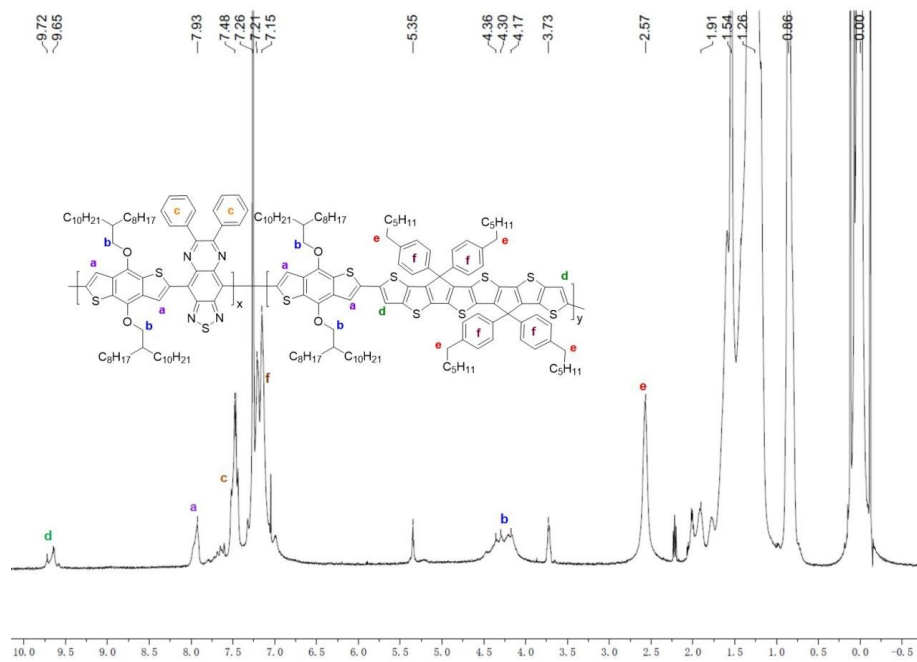


Fig. S3  $^1\text{H}$  NMR of PBIT-3 in  $\text{CDCl}_3$ .

**MW Averages**

Mp: 129876      Mn: 73325      Mv: 193965      Mw: 226032  
Mz: 527686      Mz+1: 859956      PD: 3.0826

**Distribution Plots**

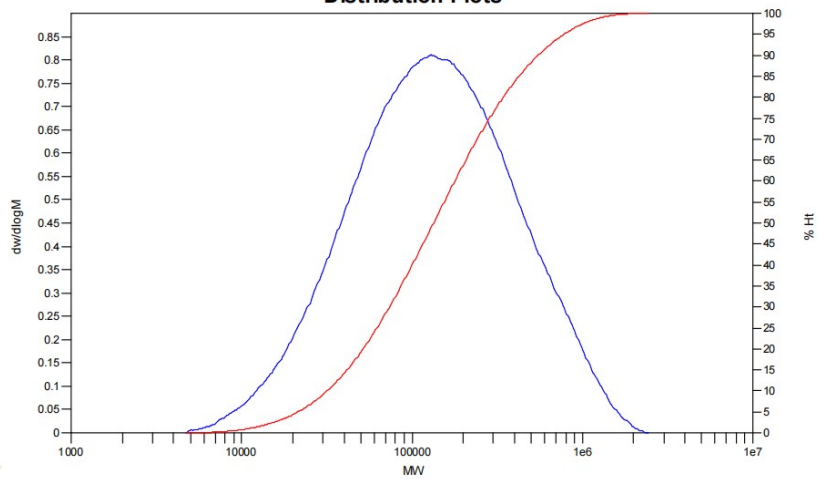


Fig. S4 GPC information of PBIT-1.

**MW Averages**

Mp: 93561      Mn: 37408      Mv: 100561      Mw: 114125  
Mz: 225263      Mz+1: 343038      PD: 3.0508

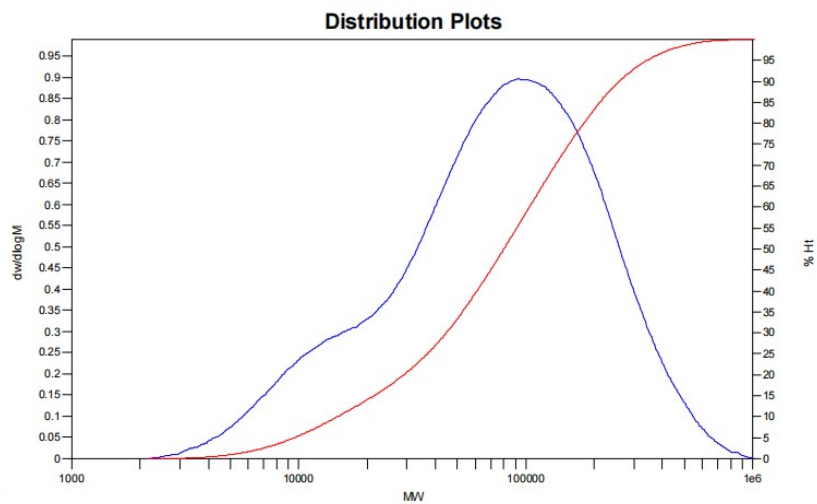


Fig. S5 GPC information of PBIT-2.

**MW Averages**

Mp: 82572      Mn: 73549      Mv: 93442      Mw: 97486  
Mz: 128572      Mz+1: 165624      PD: 1.3255

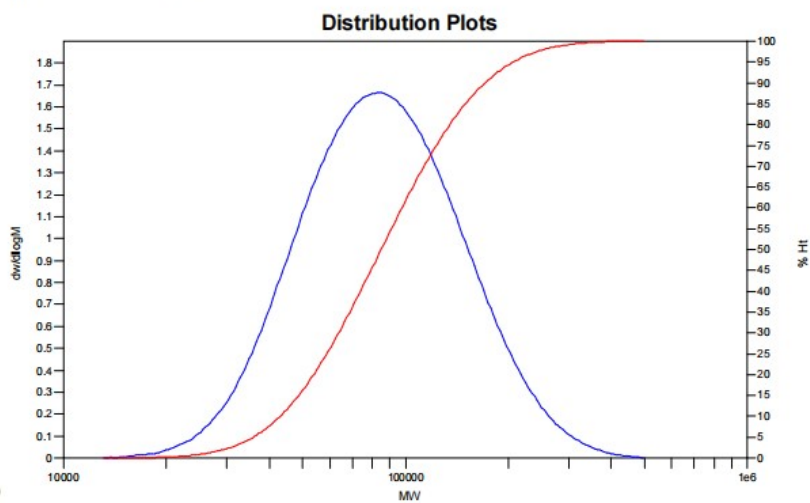


Fig. S6 GPC information of PBIT-3.

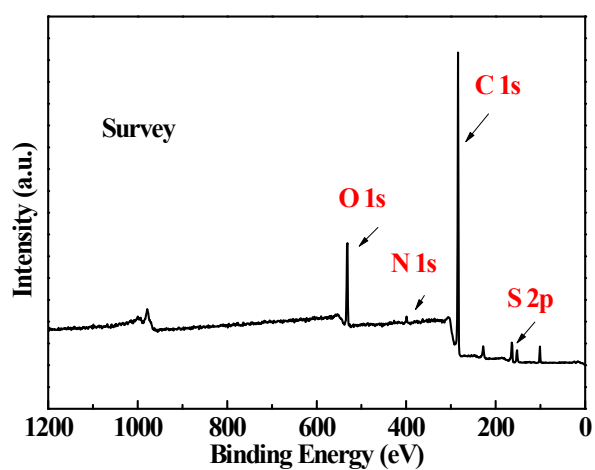


Fig. S7 XPS curves of PBIT-2.

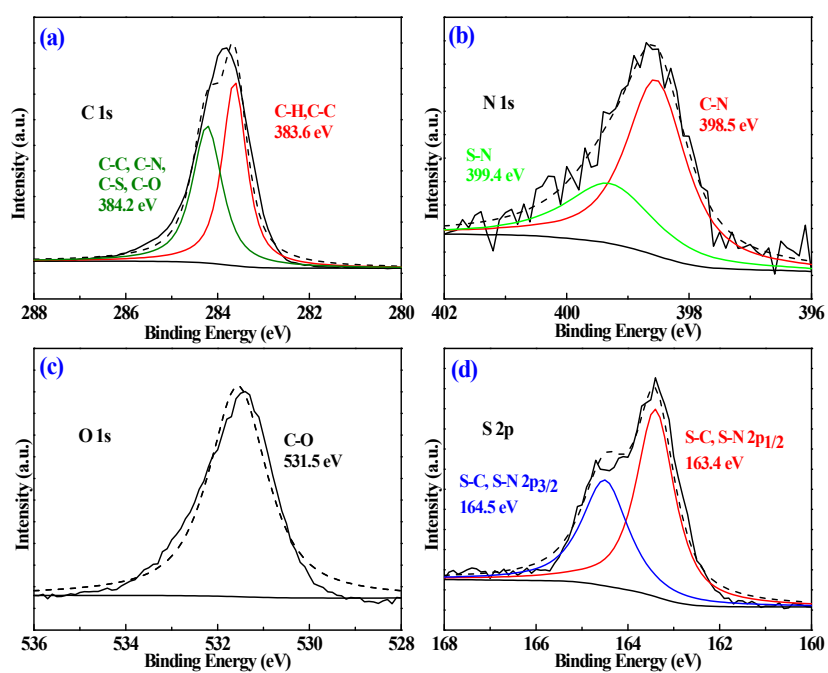
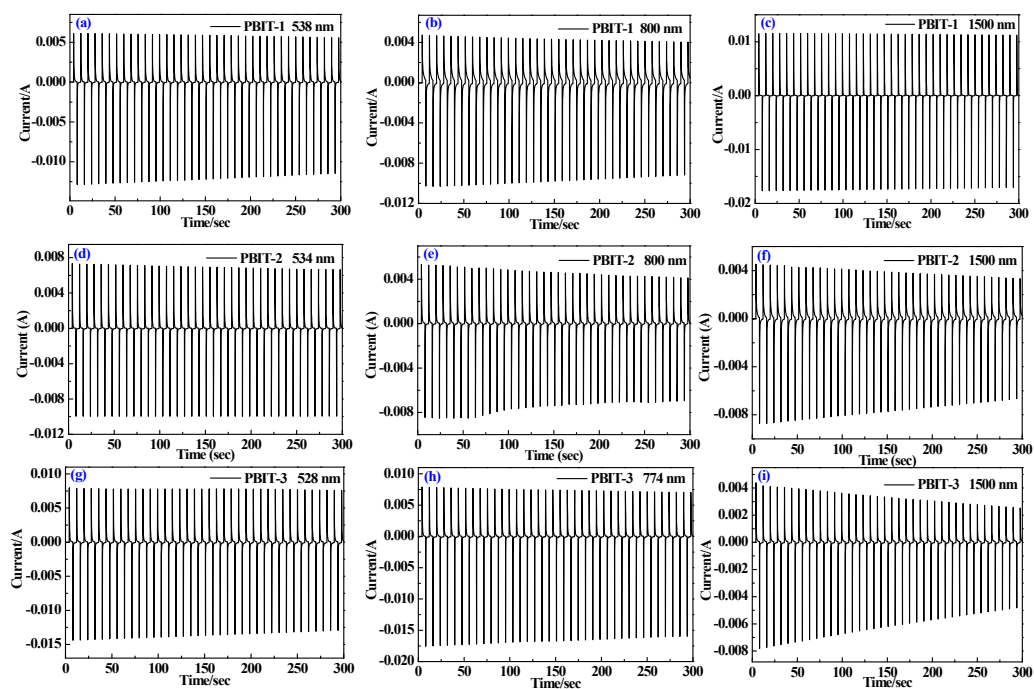


Fig. S8 High-resolution XPS curves of PBIT-2: (a) C 1s; (b) N 1s; (c) O 1s; (d) S 2p. Black solid line: experimental data; Black dotted line: fitted data.



**Fig. S9** Time-current curves of PBIT-1 (a, b, c), PBIT-2 (d, e, f) and PBIT-3 (g, h, i) in 0.2 M TBAPF<sub>6</sub>/ACN electrolyte solution.

**Table S1** GPC analysis of PBIT-1, PBIT-2, and PBIT-3

Polymer	$M_n$ / Da	$M_w$ / Da	PDI
PBIT-1	73325	226032	3.08
PBIT-2	37408	114125	3.05
PBIT-3	73549	97486	1.33