

**A new electrochromic copolymer which switched between  
neutral black to oxidized transmissive**

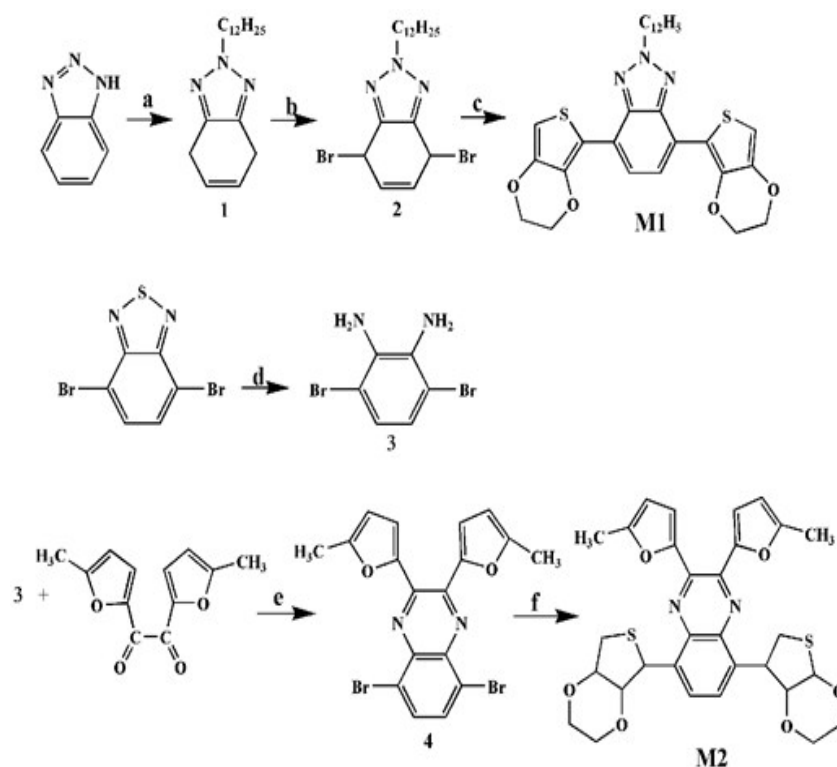
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**Scheme 1** Synthetic route of the monomers. a:  $C_{12}H_{25}Br$ , potassium *tert*-butoxide, methanol, reflux; b:  $Br_2$ ,  $HBr$  (47%), reflux; c: tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)stannane,  $Pd(PPh_3)_2Cl_2$ , toluene, reflux; d:  $NaBH_4$ , ethanol, 0 °C, 24 h; e: *p*-toluenesulfonic acid, ethanol, 85 °C, 8 h; f: the same as c.

### The synthesis of 2-dodecylbenzotriazole (1)

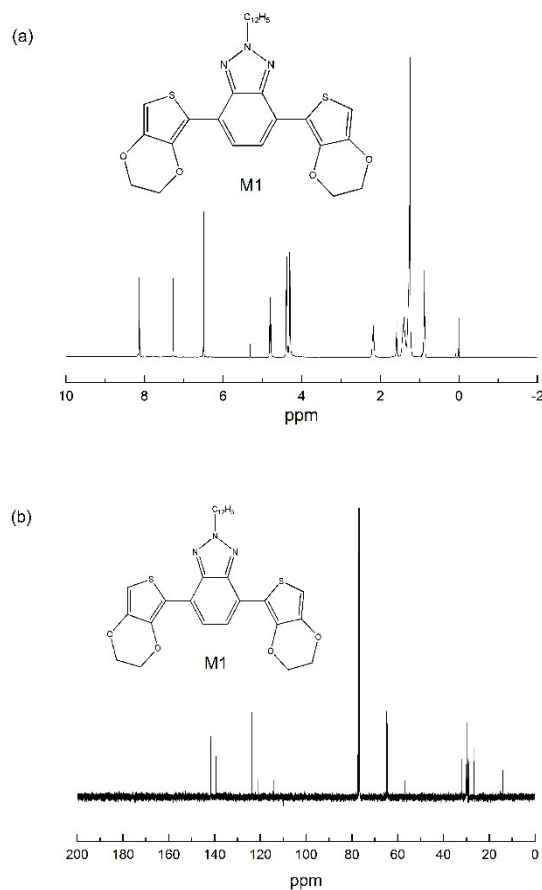
1,2,3-Benzotriazole (5.0 g, 42 mmol), potassium *tert*-butoxide (5.0 g, 44mmol), and bromododecane (12.2 g, 49 mmol) were dissolved in 5 ml of methanol. The reaction mixture was refluxed for 12 h under an argon atmosphere. After removal of the solvent by evaporation, the residue was dissolved in  $CHCl_3$  and rinsed with water for three times. The organic extract was dried over  $MgSO_4$  and the solvent was evaporated under reduced pressure. The residue was subjected to column chromatography (ethyl acetate:hexane, 1:10) to obtain 2-dodecylbenzotriazole (**1**) as a colorless oil (3.7 g, 31%).

### Synthesis of 4,7-dibromo-2-dodecylbenzotriazole (2)

3.7 g (13.1 mmol) of compound 1 and an aqueous 48% HBr solution (5.8 M, 15 mL) were added to a flask, and the mixture was stirred for 1 h at 100 °C, and then bromine (5.9 g, 36 mmol) was added dropwise, and the mixture was further stirred for 12 h at 135 °C. After the mixture was cooled to room temperature, an aqueous solution of NaHCO<sub>3</sub> was added and the product was extracted with CHCl<sub>3</sub>. The organic layer was dried over MgSO<sub>4</sub> and the solvent was evaporated under reduced pressure. The solid residue was subjected to column chromatography (ethyl acetate:hexane, 1:8) for purification. Finally, 4,7-dibromo-2-dodecylbenzotriazole (2) was obtained as light yellow oil (4.3 g, 75%).

### Synthesis of M1

Compound 2 (2 g, 4.48 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)stannane (6 mmol) were dissolved in anhydrous toluene (80 ml) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.2 g, 2.85 mmol) was added at room temperature. Raise the temperature gradually until the solution was refluxed (about 123 °C). The mixture was stirred under argon atmosphere for 24 h, cooled and toluene was distilled under reduced pressure. The residue was purified by column chromatography on silica gel using hexane-dichloromethane (4:1, vol/vol) as the eluent to obtain yellow flocculent solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ = 8.00 (s, 2H), 7.0(s,2H), 6.40(s, 2H), 4.60(t, 4H), , 4.40(m, 4H), 4.22(m, 4H), 2.10(m, 2H), 1.38 - 1.12 (m, 18H), 0.80 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, ppm): δ = 141.6, 140.7, 139.8, 122.8, 120.6, 112.3, 101.2, 64.9, 64.0, 56.1, 31.2, 29.1, 28.9, 28.8, 28.8, 28.7, 28.6, 28.2, 25.8, 22.0, 13.9. (Fig. S1)



**Fig.S1.**(a)  $^1\text{H}$ NMR spectrum of 2,3-di(5-methylfuran-2-yl)-5,8-bis(2-(3,4-ethylenedioxythiophene)) quinoxaline (**M2**) in  $\text{CDCl}_3$ . Solvent peak at  $\delta = 7.26$  ppm.(b)  $^{13}\text{C}$  NMR spectrum of **M2** in  $\text{CDCl}_3$ . Solvent peak at  $\delta = 72.50$  ppm.

### The synthesis of 3,6-dibromo-1,2-phenylenediamine (**3**)

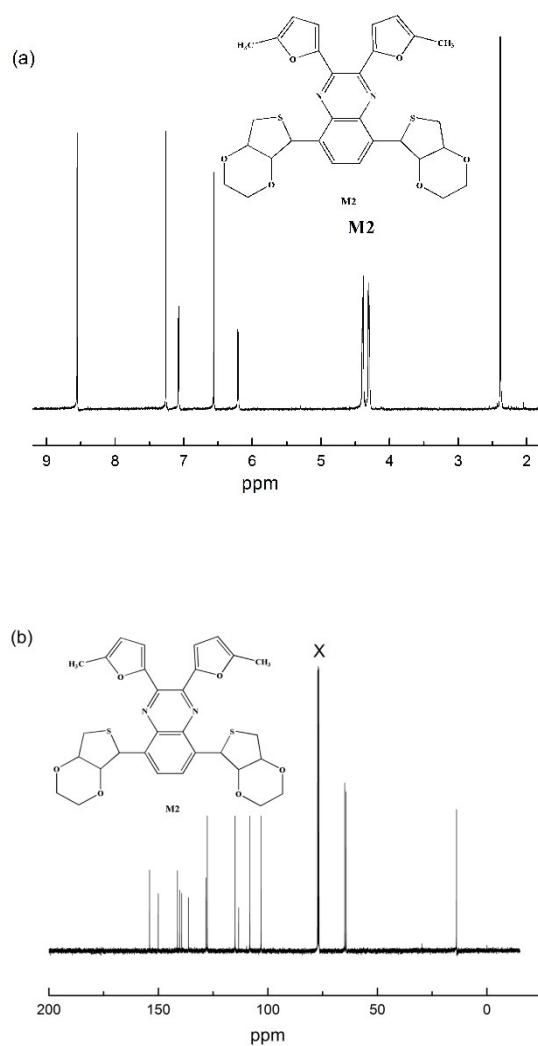
5.75 g of 4,7-dibromobenzo[c]-1,2,5-thiadiazole (19.55 mmol) was dissolved in 200 ml of EtOH. Excess  $\text{NaBH}_4$  (16 g, 0.42 mol) was added slowly to the mixture during 4 h at  $0^\circ\text{C}$  and the mixture was stirred for further 24 h at room temperature. After completion of the reaction, distilled water (about 800 ml) was added into the solution, and flocculent precipitate was observed. Then the solid product was filtered and washed by distilled water for several times to give the white solid product 3,6-dibromo-1,2-phenylenediamine (**3**) with a high productivity (about 90%).

### **The synthesis of 2,3-bis(5-methylfuran-2-yl)-5,8-dibromoquinoxaline (4)**

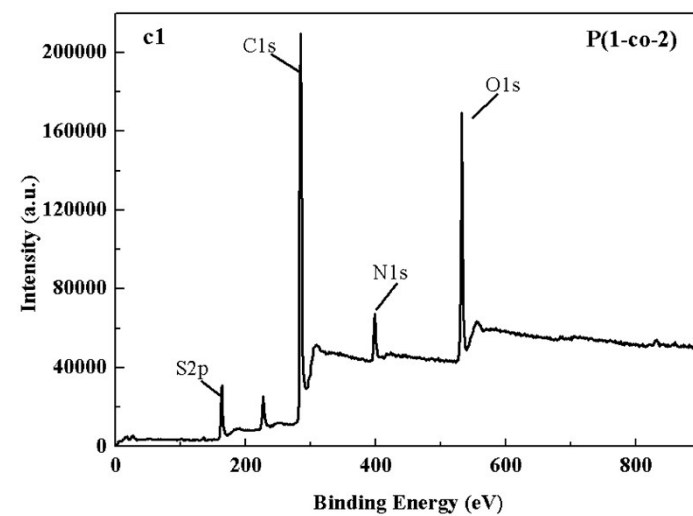
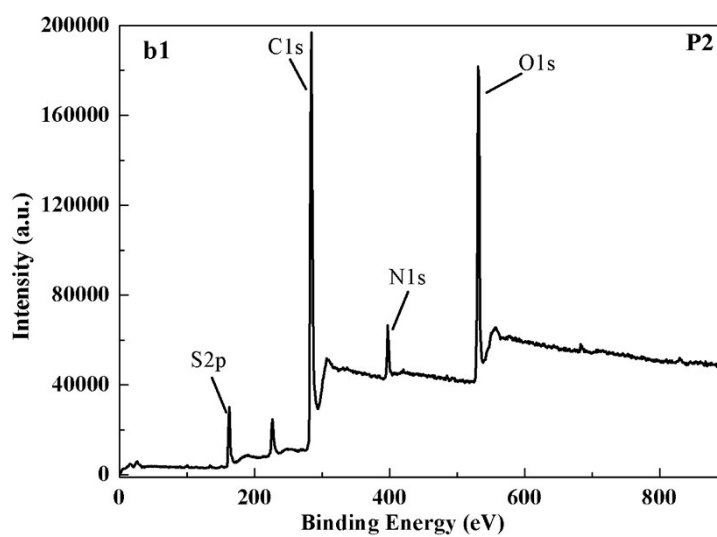
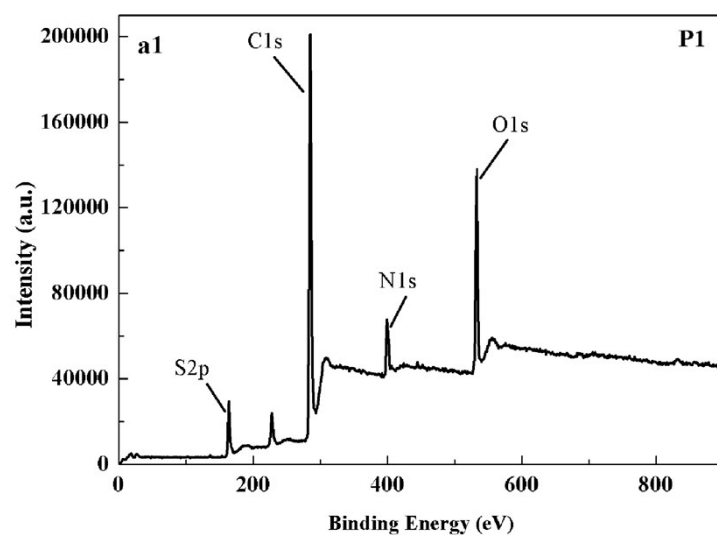
A solution of compound **3** (1.33 g, 5 mmol) and 1,2-di(2-furyl) ethanedione (0.95 g, 5 mmol) in EtOH (50 mL) was stirred magnetically and refluxed overnight by the presence of a catalytic amount of *p*-toluene sulfonic acid (PTSA). Cloudy mixture was achieved at the end of the reaction. Then the solution was cooled to 0° C and filtered. The separated solid was washed by EtOH for three times and dried under vacuum oven to give a yellow solid of 2,3-bis(5-methylfuran-2-yl)-5,8-dibromoquinoxaline (**4**) with 83% yield.

### **The synthesis of M2**

The compound **4** (2 g, 3.38 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)stannane (5.3 mmol) were dissolved in dry toluene (80 ml). Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.28 g, 0.4 mmol) used as the catalytic was also added in the solution. The solution was stirred under nitrogen atmosphere. Raising the temperature immediately until the solution was refluxed. The mixture was refluxed for 24 h under nitrogen atmosphere, and then the solution was cooled and concentrated on the rotary evaporator. The mixture was purified using column chromatography on silica gel, in which hexane-dichloromethane (3:1, vol/vol) was the eluent. The purified product is dark red solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ = 8.55 (s, 2H, ArH), 7.07 (d, 2H), 6.56(s, 2H), 6.21 (d, 2H), 4.34 (dd, 8H), 2.39 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, ppm): δ = 54.02, 150.06, 141.29, 140.29, 139.33, 136.30, 128.27, 127.68, 115.00, 113.34, 108.25, 103.12, 64.89, 64.30, 13.85 (Fig. S2).



**Fig.S2.**(a)  $^1\text{H}$ NMR spectrum of 4,7-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H-benzo [1,2,3] Triazole (**M1**) in  $\text{CDCl}_3$ . Solvent peak at  $\delta = 7.26$  ppm.(b)  $^{13}\text{C}$  NMR spectrum of **M2** in  $\text{CDCl}_3$ . Solvent peak at  $\delta = 72.50$  ppm.



**Fig. S3.** The XPS survey of P1, P2 and P(1-co-2) deposited on the ITO electrode.