

Supporting Information

Highly Transmissive Blue Electrochromic Polymers Based On Thieno[3,2-*b*]thiophene

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1. Synthetic routes

3,6-dibromothieno[3,2-*b*]thiophene (1) was synthesized according to the reported method previously¹, 85% yield. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.34 (s, 2H).

3,6-diphenylthieno[3,2-*b*]thiophene, R = phenyl (2a): A 350 mL high-pressure reaction bottle was charged with Compound **1** (1.77 g, 6 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (2.69 g, 13.2 mmol), K₂CO₃ (2 mol/L, 2.49 g, 18mmol), Aliquat 336 (1.21 g, 3mmol) and toluene (60 mL), then the solution was bubbled for 30 min via a strong nitrogen flow and the Tetrakis(triphenylphosphine)platinum (0.14g, 0.12 mmol) was added at room temperature. The whole mixture was stirred and heated to 90 °C for 2d. After cooling to room temperature, the organic layer was separated. The aqueous layer was washed twice with CH₂Cl₂ and the combined organic layers were concentrated by rotary evaporation to afford a grey powder. Column chromatographic over silica gel afforded of a white powder (1.44 g, 82 % yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.79 (d, 4H), 7.56 (s, 2H), 7.50 (t, 4H), 7.38 (t, 2H).

3,6-bis(4-hexylphenyl)thieno[3,2-*b*]thiophene, R = 4-hexylphenyl (2b): 85% yield. Compound **2b** was synthesized according to the similar method to Compound **2a**. ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.70 (d, *J* = 9.0 Hz, 4H), 7.50 (s, 2H), 7.30 (d, *J* = 9.0 Hz, 4H), 2.66 (t, 4H), 1.71-1.61 (m, 4H), 1.40-1.25 (m, 12H), 0.90 (t, 6H).

3,6-bis(5-hexylthiophen-2-yl)thieno[3,2-*b*]thiophene, R = 5-hexylthiophen-2-yl (2c): Compound **1** (1.77 g, 6 mmol) and tributyl(5-hexylthiophen-2-yl)stannane (8.98 g, 24mmol) were dissolved in dry THF (60 mL). The solution was purged with nitrogen for 30 min and Bis(triphenylphosphine)palladium(II) chloride (0.38 g, 0.54mmol) was added at room temperature. The

mixture was stirred at 100 °C under nitrogen atmosphere for 15 h, cooled and concentrated on the rotary evaporator. The residue was subjected to column chromatography to afford a white solid (2.12 g, 75% yield). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.44 (s, 2H), 7.20 (d, J = 3.0 Hz, 2H), 6.78 (d, J = 3.0 Hz, 2H), 2.84 (t, 4H), 1.75-1.60 (t, 4H), 1.42-1.30 (t, 12H), 0.92 (t, 6H).

2,5-dibromo-3,6-diphenylthieno[3,2-b]thiophene, R = phenyl (3a): In a round bottom flask, **2a** (1.4 g, 5 mmol) was dissolved in chloroform and acetic acid (30 mL: 10 mL = 3;1) at 0 °C under nitrogen atmosphere. N-bromosuccinimide (2.68 g, 15 mmol) was added and the reaction mixture was stirred for 3 h. Water was added and the mixture was extracted three times with ether, then the organic phase was washed with water and brine, dried by MgSO_4 and concentrated on the rotary evaporator. Flash column chromatographic purification on silica gel using petroleum ether as eluent to afford a white solid (2.02 g, 95% yield). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.67 (t, 4H), 7.51 (t, 4H), 7.44 (t, 2H).

2,5-dibromo-3,6-bis(4-hexylphenyl)thieno[3,2-b]thiophene, R = 4-hexylphenyl (3b). **3b** was synthesized according to the similar method to Compound **3a**: 92% yield. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.59 (d, J = 9.0 Hz, 4H), 7.58 (d, J = 9.0 Hz, 4H), 2.68 (t, 4H), 1.73-1.63 (m, 4H), 1.45-1.27 (m, 12H), 0.91 (t, 6H).

2,5-dibromo-3,6-bis(5-hexylthiophen-2-yl)thieno[3,2-b]thiophene, R = 5-hexylthiophen-2-yl (3c). **3c** was synthesized according to the similar method to Compound **3a**: 88% yield. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.40 (d, J = 3.0 Hz, 2H), 6.84 (d, J = 3.0 Hz, 2H), 2.86 (t, 4H), 1.78-1.68 (m, 4H), 1.41-1.26 (m, 12H), 0.91 (t, 6H).

tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (4). Compound **4** was synthesized according to the reported method previously²: 85% yield. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.58 (s, 1 H), 4.20-4.12 (m, 4H), 1.62-1.51 (m, 6H), 1.37-1.28 (m, 6H), 1.13-1.08 (m, 6H), 0.92-0.87 (m, 9H).

2. Fig. S1-S8 and Movie S1-S3

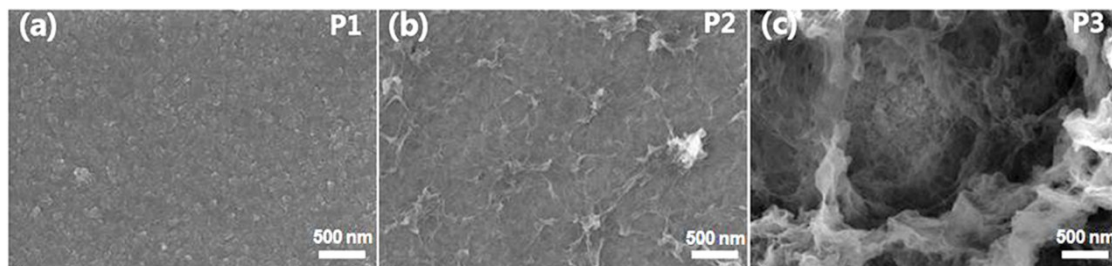


Fig. S1 (a) (b) (c) SEM topography images of polymer-coated ITO films.

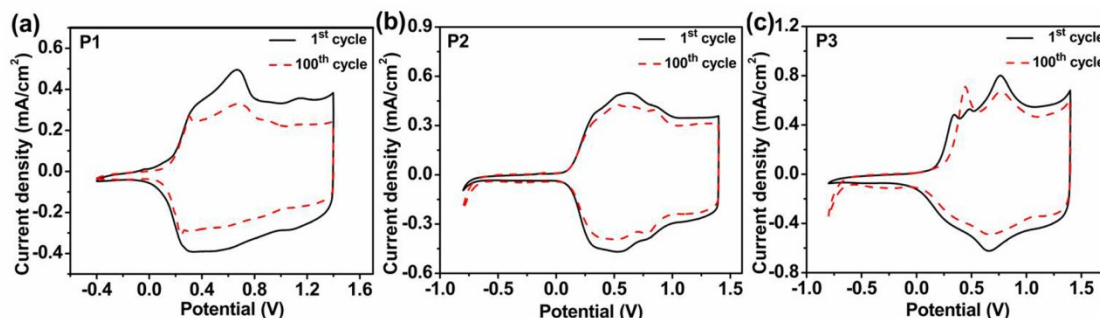


Fig. S2 Cyclic voltammetry stability test of polymer films on a Pt button electrode cycled 100 times in 0.1 M TBAPF₆/ACN system at a scan rate of 100 mV s⁻¹.

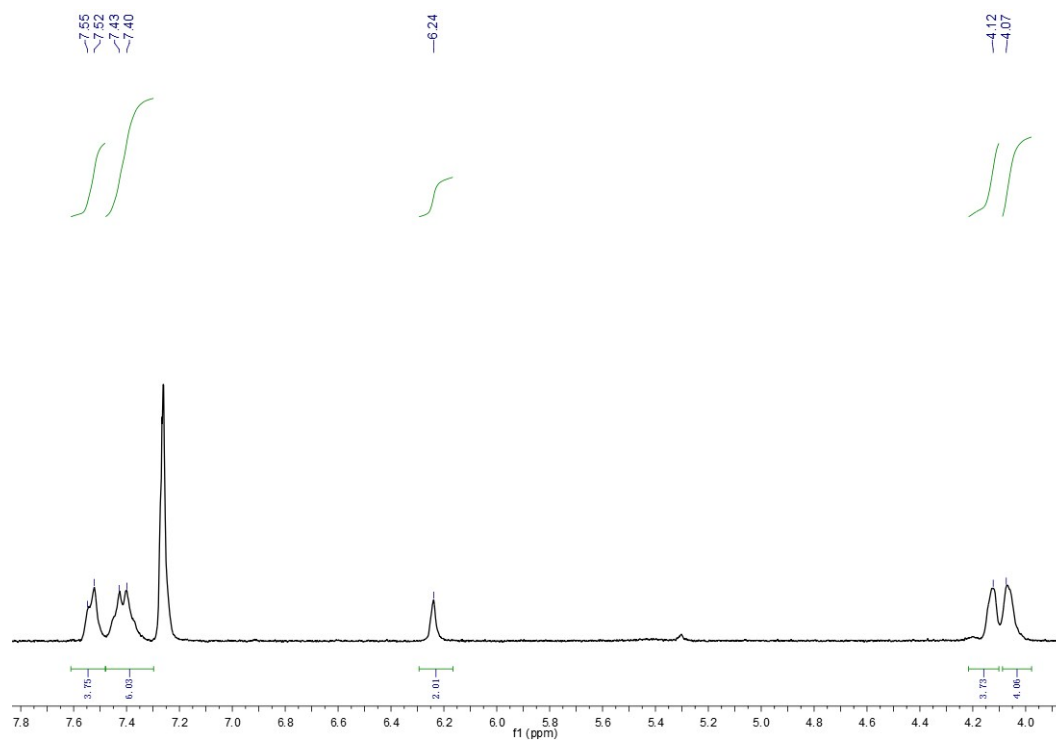


Fig. S3 ¹H NMR spectrum of M1.

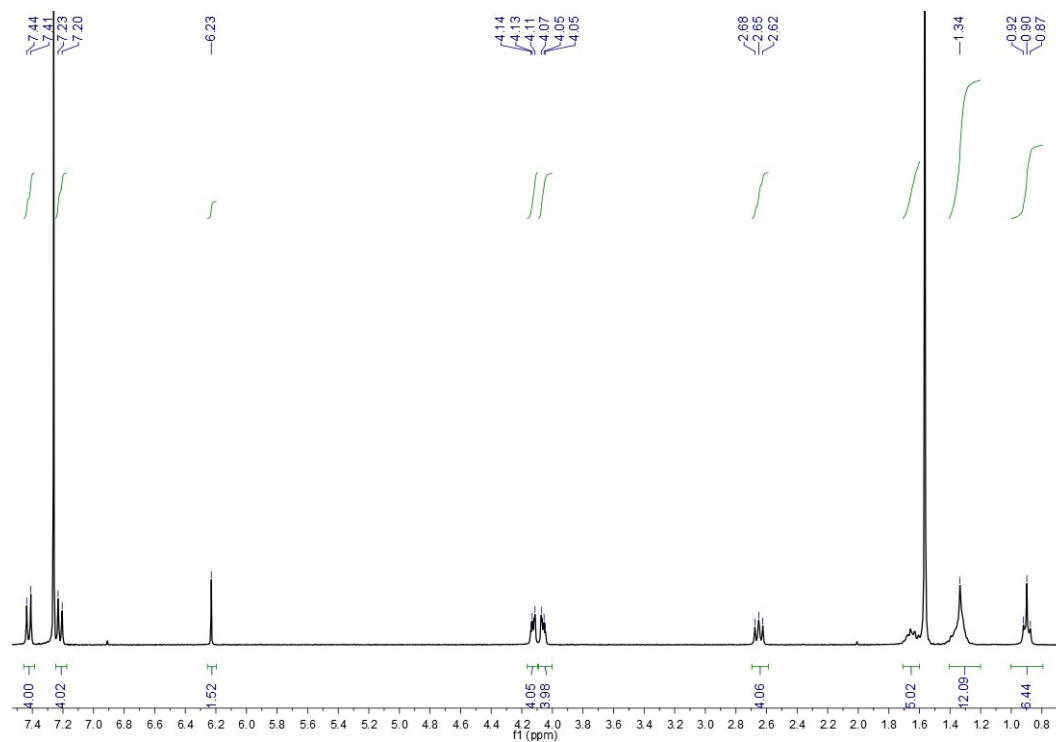


Fig. S4 ¹H NMR spectrum of M2.

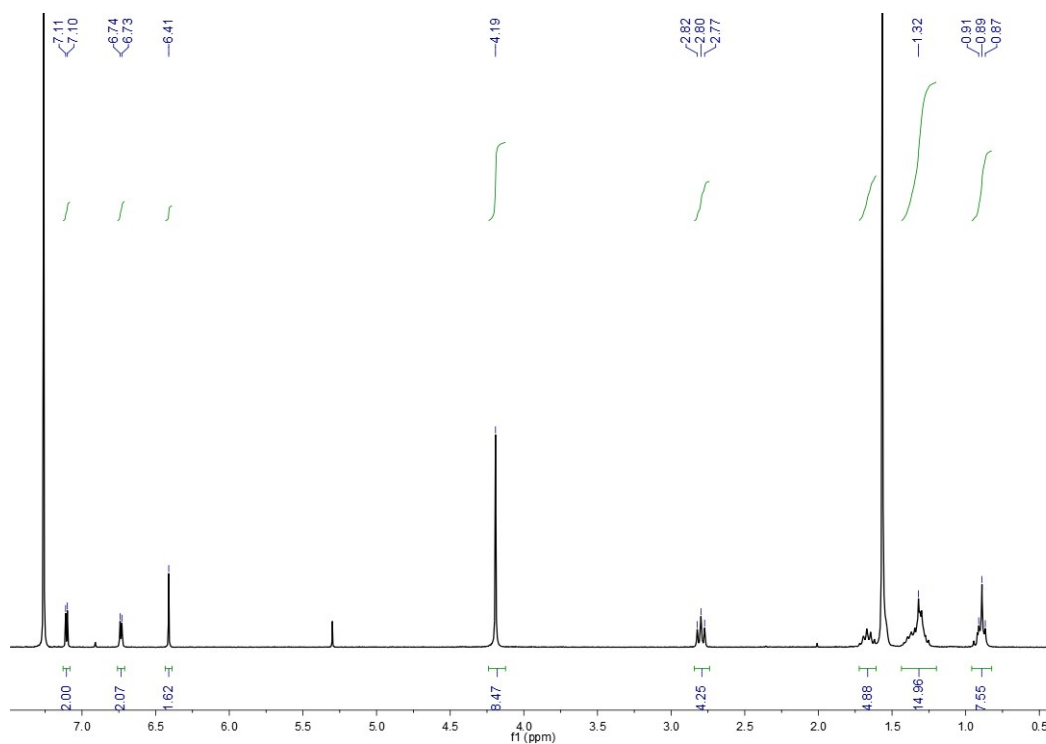


Fig. S5 ¹H NMR spectrum of M3.

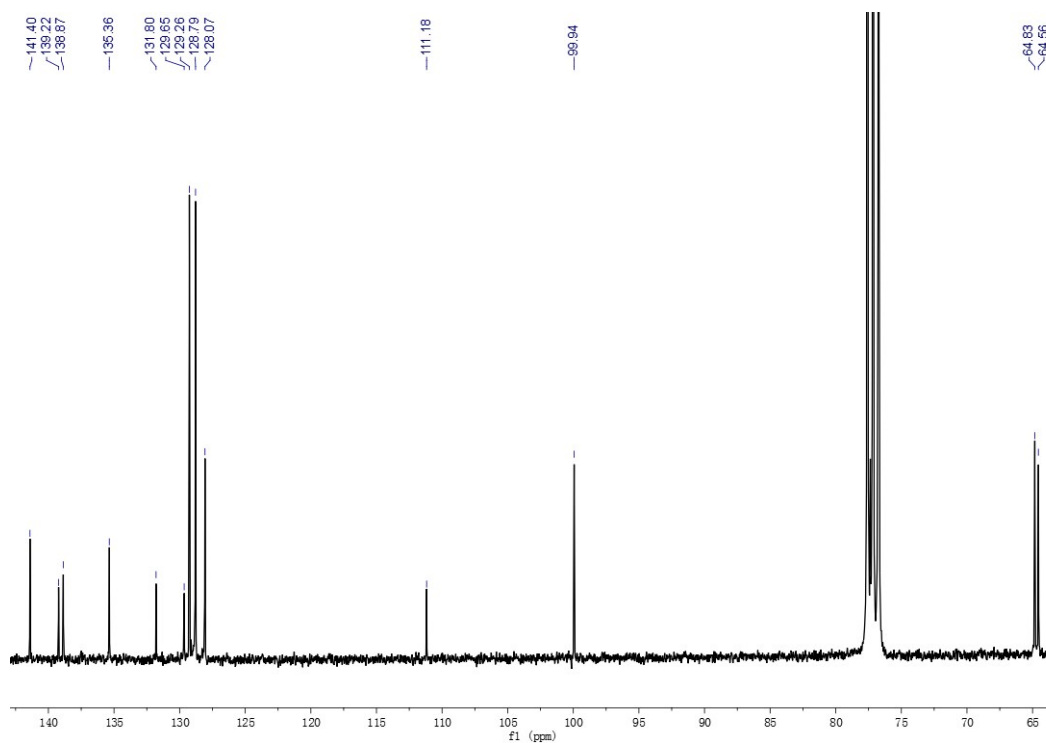


Fig. S6 ¹³C NMR spectrum of M1.

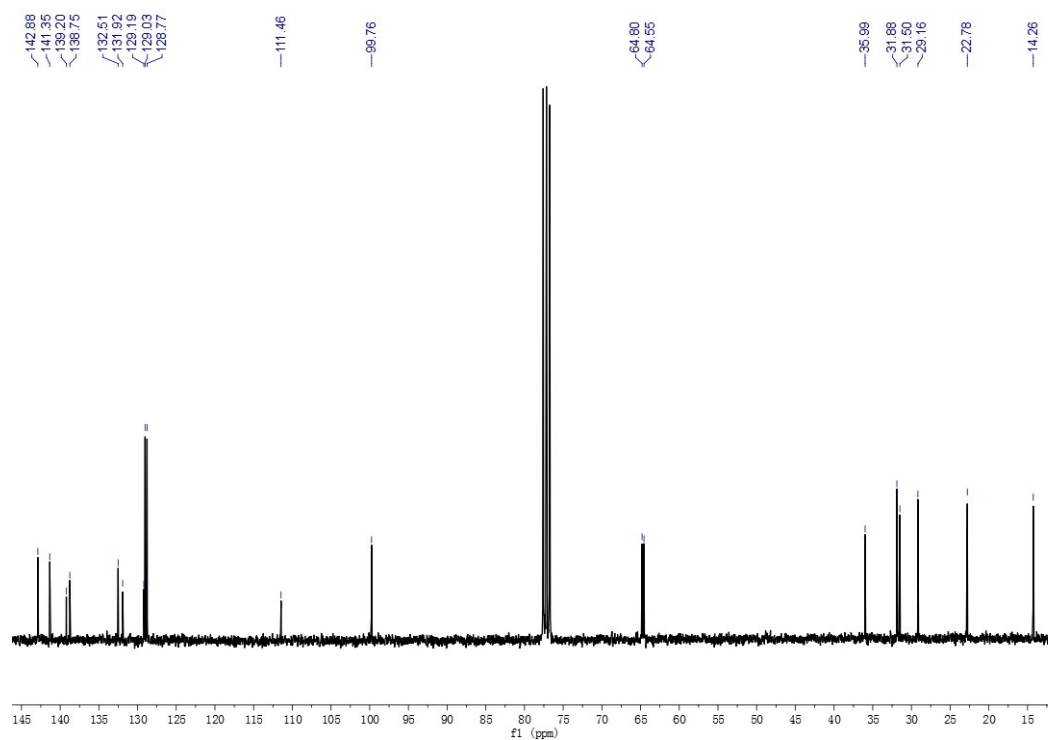


Fig. S7 ^{13}C NMR spectrum of **M2**.

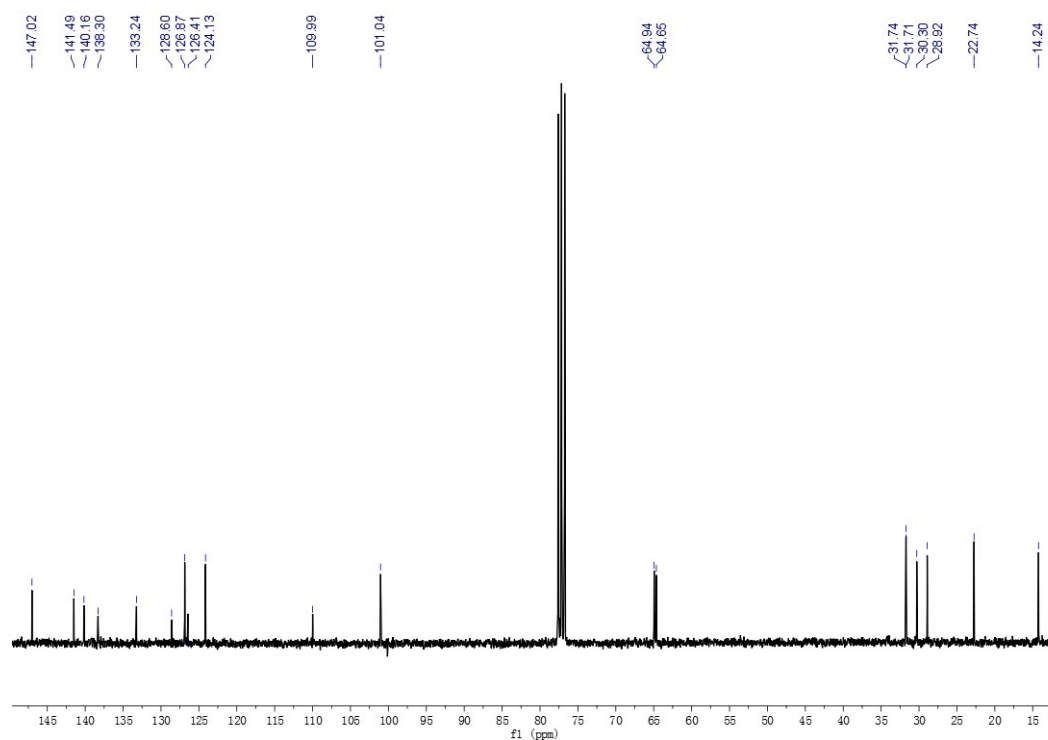


Fig. S8 ^{13}C NMR spectrum of **M3**.

Movie S1 Reversible colour change of **P1** based device from deep blue to transparency.

Movie S2 Reversible colour change of **P2** based device from deep blue to transparency.

Movie S3 Reversible colour change of **P3** based device from violet to transparency green.

- (1) Deng, P.; Wu, B.; Lei, Y.; Cao, H.; Ong, B. S. *Macromolecules* **2016**, *49*, 2541.
- (2) Taerum, T.; Lukyanova, O.; Wylie, R. G.; Perepichka, D. F. *Organic Letters* **2009**, *11*, 3230.