

Molecular engineering of D-A-D type thiophen-based polymers consisting of quinoline moieties for electrochromism and energy storage

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Preparation of Compound 1: To a stirred suspension of catechol (11 g, 0.1 mol) and K_2CO_3 (69 g, 0.5 mol) in anhydrous N, N-Dimethylformamide (150 ml), bromohexane (82.5 g, 0.5 mol). The reaction mixture was stirred at 60 °C for 12 h. Then the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 . The organic layers were combined and washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. Evaporation of the solvent under reduced pressure to afford the compound **1** (25 g, yield: 90%). The compound **1** was directly used for the next step without further purification.

Preparation of Compound 2: To a stirred solution of Compound **2** (14 g, 0.05 mol) in 80 ml acetic acid was added HNO_3 (40 ml) dropwise at 0 °C. The reaction mixture was stirred at 0°C for half an hour, then heated to 60°C. The reaction mixture was further stirred at 60°C for 8 h. After completion, the reaction mixture was cooled to 10°C, then the crystalline product was filtered, washed with *n*-hexane, and dried under vacuum at 60 °C to get compound **2** (12 g, yield: 65%). 1H NMR (600 MHz, $CDCl_3$) δ 7.29 (s, 2H), 4.10 (t, $J = 6.5$ Hz, 4H), 1.89 – 1.84 (m, 4H), 1.51 – 1.46 (m, 4H), 1.35 (dd, $J = 8.7, 5.3$ Hz, 8H), 0.91 (t, $J = 6.8$ Hz, 6H).

Preparation of Compound 3: Iron powder (2.2 g, 40 mmol) was added to the acetic acid (50 ml) solution of compound **2** (1.84 g, 5 mmol). The resulting mixture was stirred at 60 °C under N_2 atmosphere for 5 h. After completion, filtering off the solid impurities. Evaporate the filtrate under reduced pressure to remove the solvent, yielding crude product compound **3**, which is then transferred directly to the subsequent step.

Preparation of Compound 4: To a stirred solution of Compound **3** (1.54 g, 5 mmol) in 30 ml acetic acid was added butane-2,3-dione (430 mg, 5 mmol). The resulting mixture was stirred at 100 °C overnight under N_2 atmosphere. Evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using a petroleum ether/EA (30/1, v/v) eluent to afford Compound **4** (502 mg, yield: 28%). 1H NMR (600 MHz, $CDCl_3$) δ 7.24 (s, 2H), 4.13 (t, $J = 6.6$ Hz, 4H), 2.66 (s, 6H), 1.92 – 1.87 (m, 4H), 1.53 – 1.48 (m, 4H), 1.35 (dd, $J = 7.1, 3.5$ Hz, 8H), 0.91 (t, $J = 6.9$ Hz, 6H).

Preparation of Compound 5: To a stirred solution of Compound **3** (1.54 g, 5 mmol) in

30 ml acetic acid was added benzil (1.05 g, 5 mmol). The resulting mixture was stirred at 100 °C overnight under N₂ atmosphere. Evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using a petroleum ether/EA (25/1, v/v) eluent to afford Compound **5** (580 mg, yield: 24%). ¹H NMR (600 MHz, CDCl₃) δ 7.50 – 7.46 (m, 4H), 7.42 (s, 2H), 7.34 – 7.29 (m, 6H), 4.19 (t, *J* = 6.6 Hz, 4H), 1.96 – 1.91 (m, 4H), 1.56 – 1.51 (m, 4H), 1.41 – 1.35 (m, 8H), 0.92 (t, *J* = 6.9 Hz, 6H).

Preparation of Compound 6: To a stirred solution of Compound **3** (1.54 g, 5 mmol) in 30 ml acetic acid was added 9,10-phenanthraquinone (1.04 g, 5 mmol). The resulting mixture was stirred at 100 °C overnight under N₂ atmosphere. Evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using a petroleum ether/EA (20/1, v/v) eluent to afford Compound **6** (702 mg, yield: 22%). ¹H NMR (600 MHz, CDCl₃) δ 9.35 (d, *J* = 7.8 Hz, 2H), 8.59 (d, *J* = 7.8 Hz, 2H), 7.78 – 7.71 (m, 4H), 7.52 (s, 2H), 4.27 (t, *J* = 6.6 Hz, 4H), 2.02 – 1.96 (m, 4H), 1.61 – 1.56 (m, 4H), 1.45 – 1.38 (m, 8H), 0.95 (t, *J* = 6.9 Hz, 6H).

Preparation of Compound 7. To a stirred suspension of Compound **4** (300 mg, 0.837 mmol) and NaHCO₃ (282 mg, 3.35 mmol) in 30 ml dichloromethane was added dichloromethane containing liquid bromine (535 mg, 3.35 mmol) dropwise at 0 °C. The resulting mixture was stirred at 25 °C for 12 h under N₂ atmosphere. Evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using a petroleum ether/EA (30/1, v/v) eluent to afford Compound **7** (237 mg, yield: 55%). ¹H NMR (600 MHz, CDCl₃) δ 4.16 (t, *J* = 6.7 Hz, 4H), 2.78 (s, 6H), 1.91 – 1.85 (m, 4H), 1.57 – 1.51 (m, 4H), 1.37 (dd, *J* = 8.8, 5.4 Hz, 8H), 0.92 (t, *J* = 6.9 Hz, 6H).

Preparation of Compound 8: To a stirred suspension of Compound **5** (300 mg, 0.622 mmol) and NaHCO₃ (209 mg, 2.48 mmol) in 30 ml dichloromethane was added dichloromethane containing liquid bromine (397 mg, 2.48 mmol) dropwise at 0 °C. The resulting mixture was stirred at 25 °C for 12 h under N₂ atmosphere. Evaporation of the solvent under reduced pressure, the crude product was purified by column

chromatography on silica gel using a petroleum ether/EA (25/1, v/v) eluent to afford Compound **8** (200 mg, yield: 50%). ^1H NMR (600 MHz, CDCl_3) δ 7.63 (d, $J = 7.1$ Hz, 4H), 7.36 (dt, $J = 24.3, 7.2$ Hz, 6H), 4.21 (t, $J = 6.7$ Hz, 4H), 1.94 – 1.89 (m, 4H), 1.57 – 1.54 (m, 4H), 1.39 (dd, $J = 8.9, 5.4$ Hz, 8H), 0.93 (t, $J = 6.9$ Hz, 6H).

Preparation of Compound 9: To a stirred suspension of Compound **6** (300 mg, 0.624 mmol) and NaHCO_3 (210 mg, 2.50 mmol) in 30 ml dichloromethane was added dichloromethane containing liquid bromine (400 mg, 2.50 mmol) dropwise at 0 °C. The resulting mixture was stirred at 25 °C for 12 h under N_2 atmosphere. Evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using a petroleum ether/EA (20/1, v/v) eluent to afford Compound **9** (180 mg, yield: 45%). ^1H NMR (600 MHz, CDCl_3) δ 9.43 (d, $J = 7.1$ Hz, 2H), 8.54 (d, $J = 7.7$ Hz, 2H), 7.77 (dt, $J = 29.2, 7.2$ Hz, 4H), 4.28 (t, $J = 6.3$ Hz, 4H), 1.97 (dd, $J = 17.9, 13.1$ Hz, 5H), 1.59 (d, $J = 7.7$ Hz, 4H), 1.41 (d, $J = 2.5$ Hz, 9H), 0.97 – 0.89 (m, 6H).

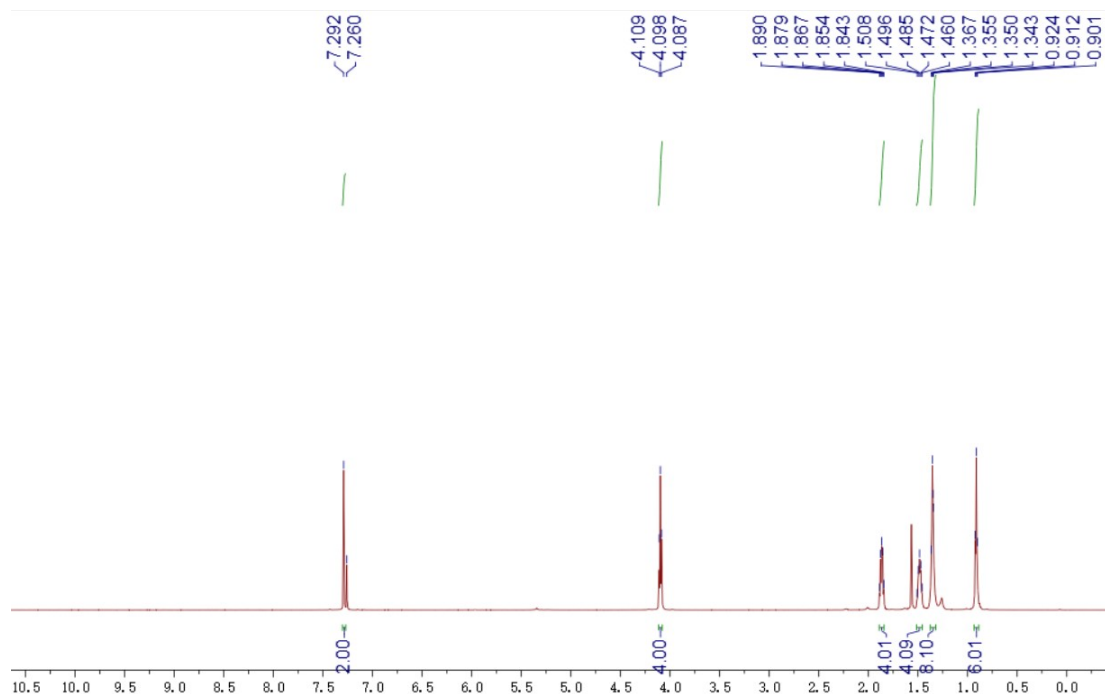


Fig. S1. ^1H -NMR spectra of compound **2** in CDCl_3 .

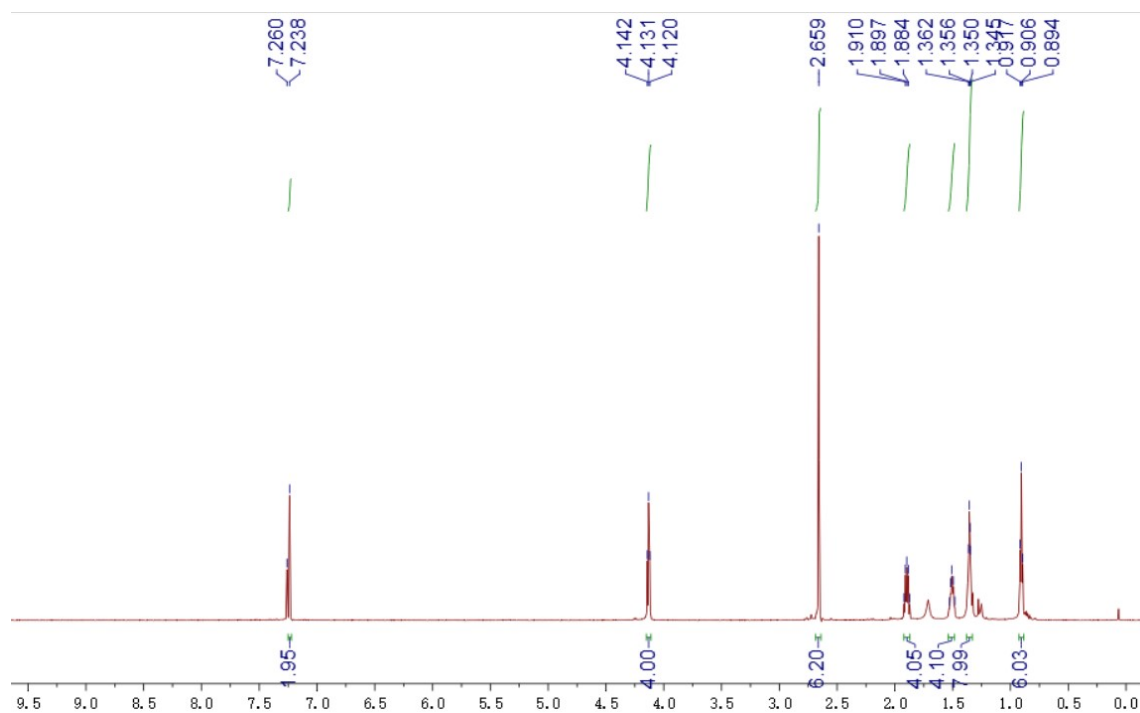


Fig. S2. $^1\text{H-NMR}$ spectra of compound **4** in CDCl_3 .

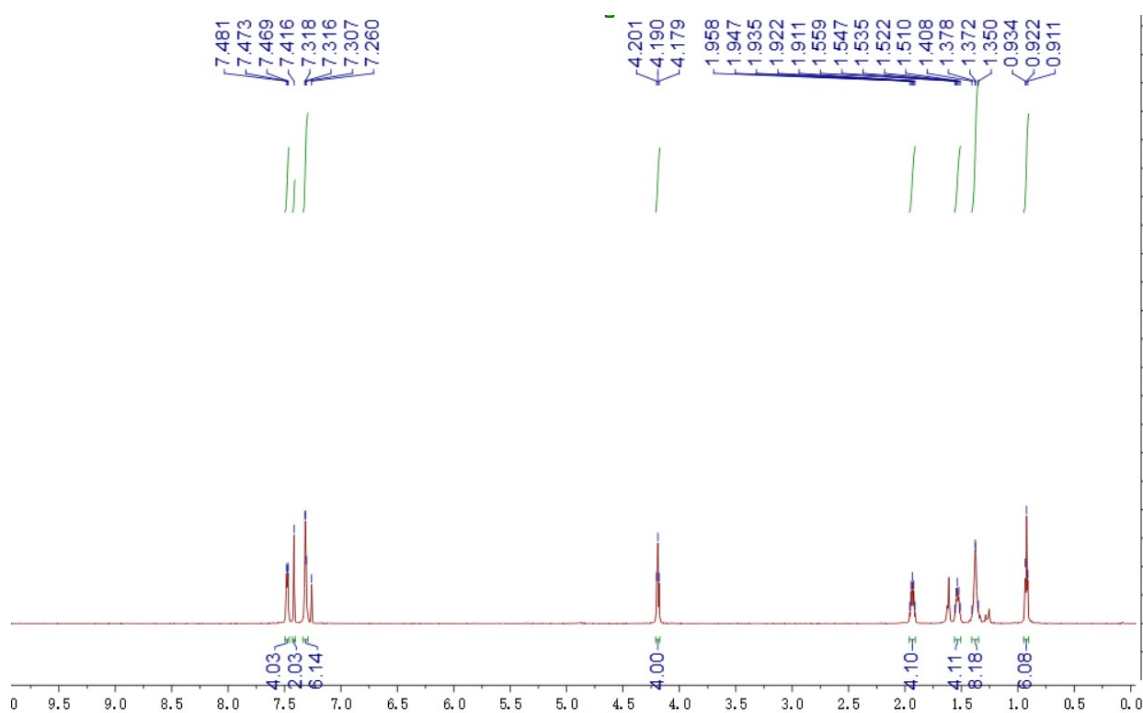


Fig. S3. $^1\text{H-NMR}$ spectra of compound **5** in CDCl_3 .

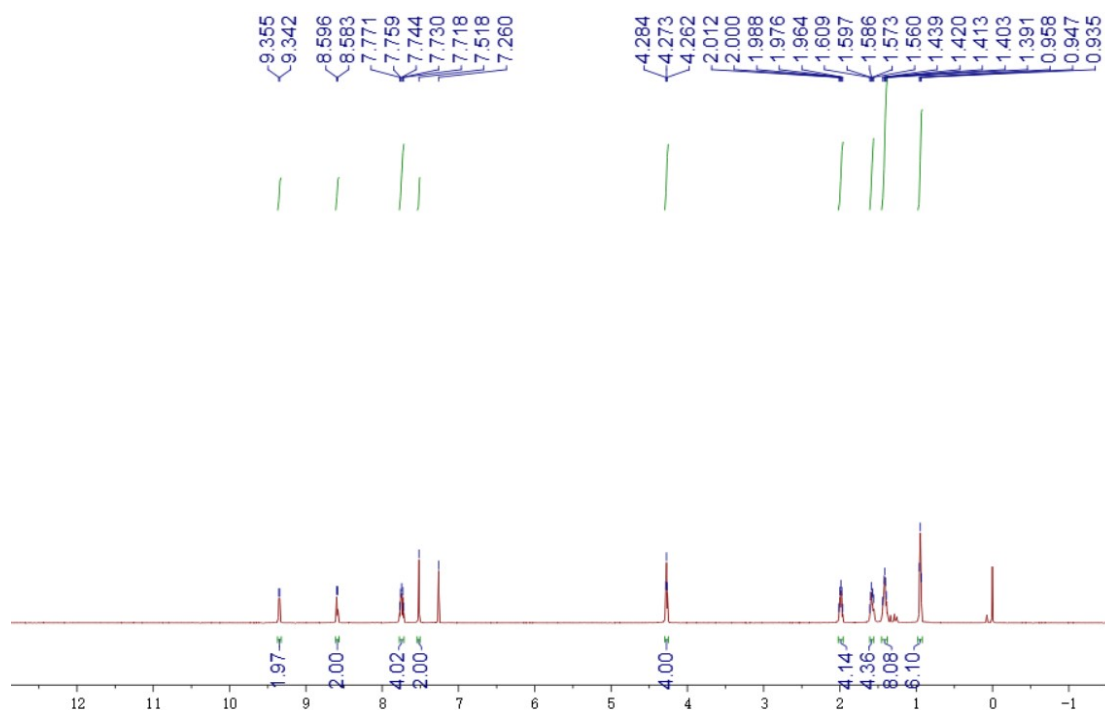


Fig. S4. ^1H -NMR spectra of compound **6** in CDCl_3 .

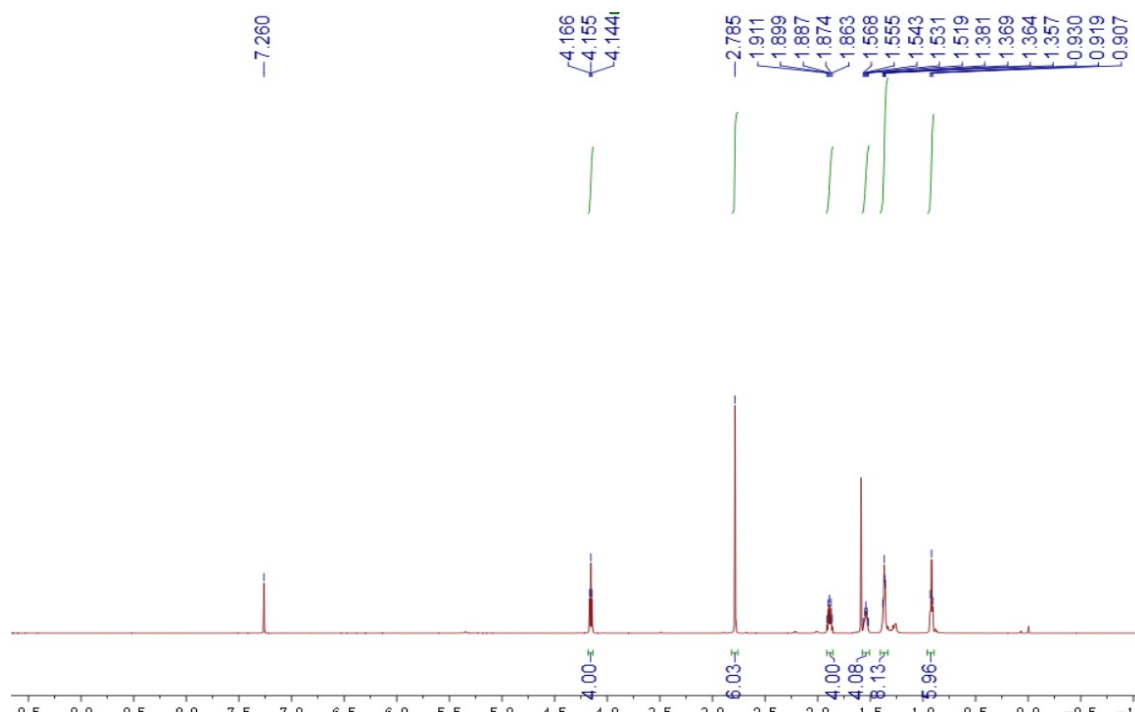


Fig. S5. ^1H -NMR spectra of compound **7** in CDCl_3 .

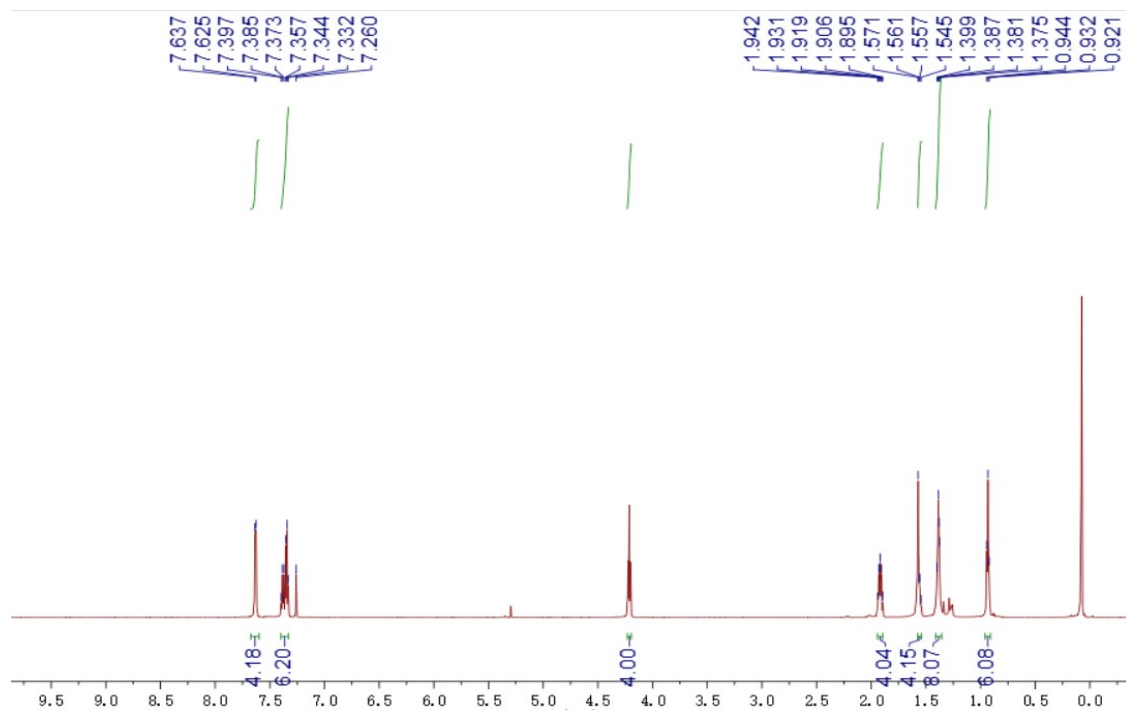


Fig. S6. ^1H -NMR spectra of compound **8** in CDCl_3 .

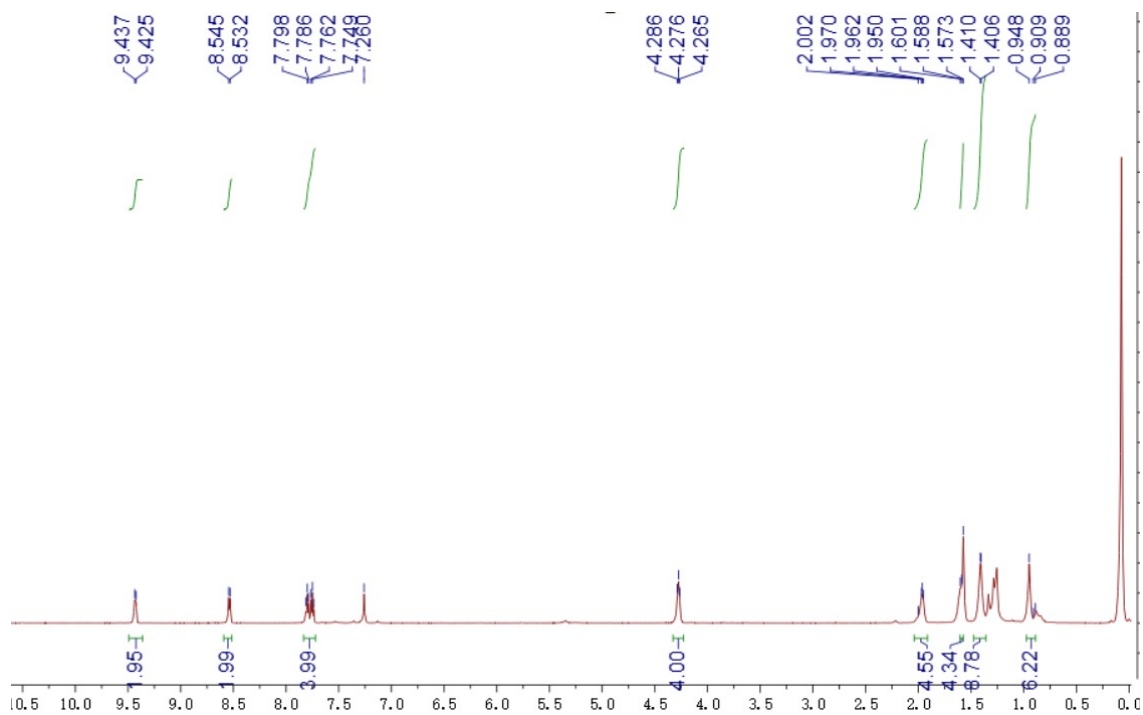


Fig. S7. ^1H -NMR spectra of compound **9** in CDCl_3 .

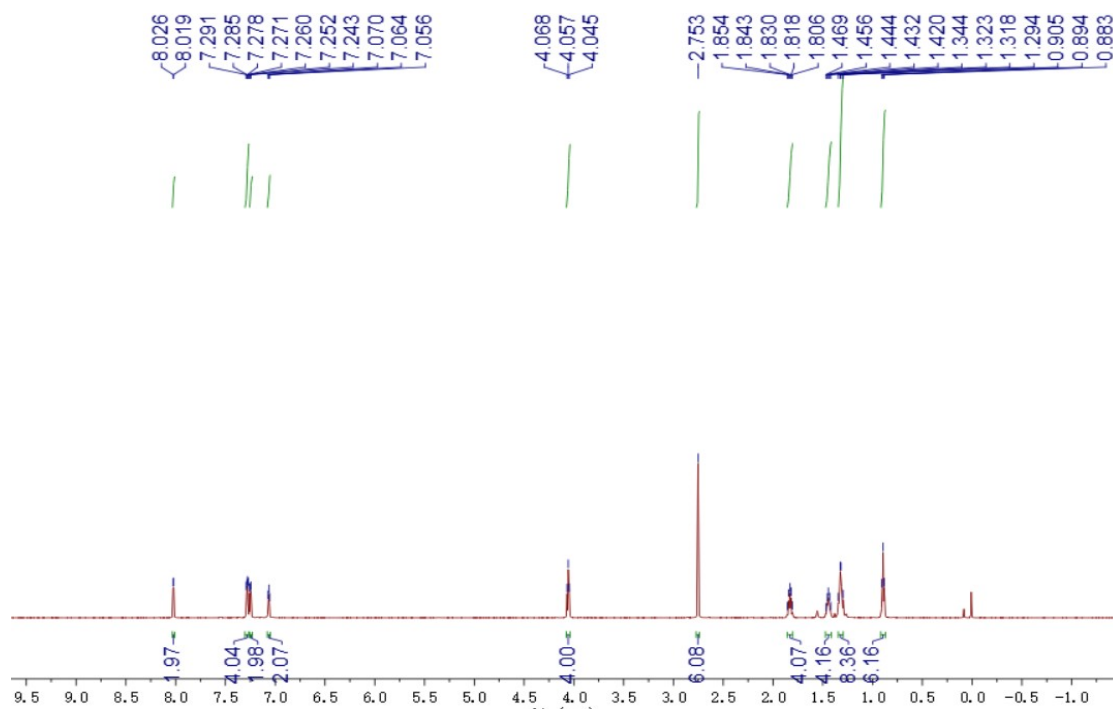


Fig. S8. ^1H -NMR spectra of the monomer **HDMQT** in CDCl_3 .

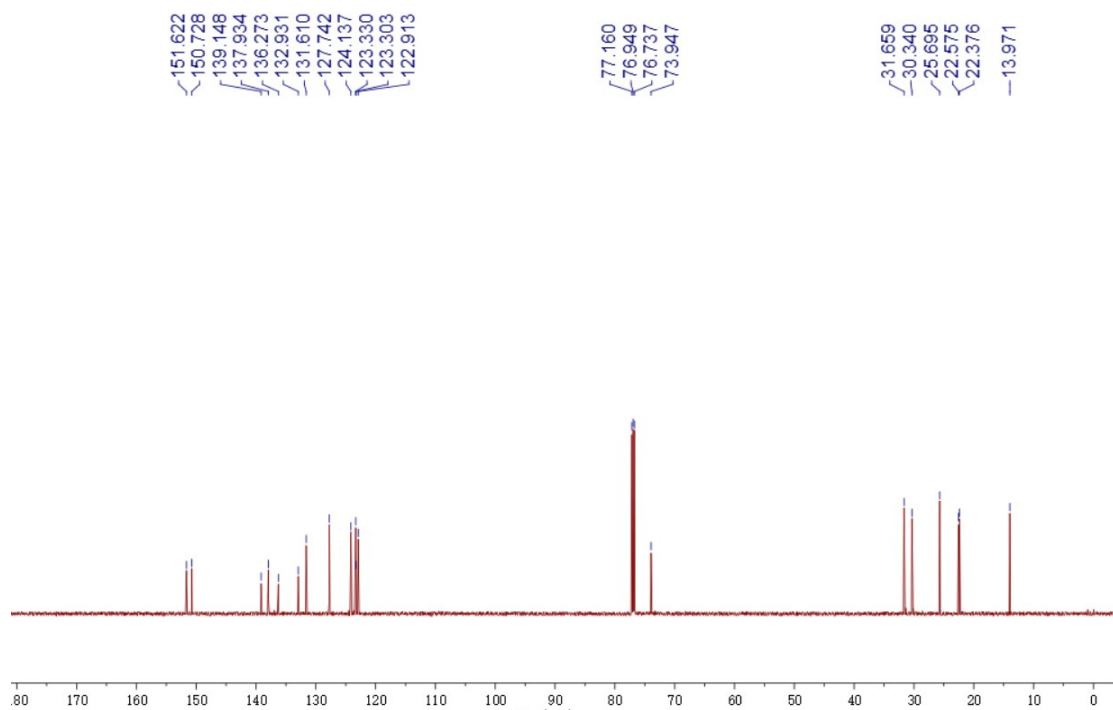


Fig. S9. ^{13}C NMR spectra of the monomer **HDMQT** in CDCl_3 .

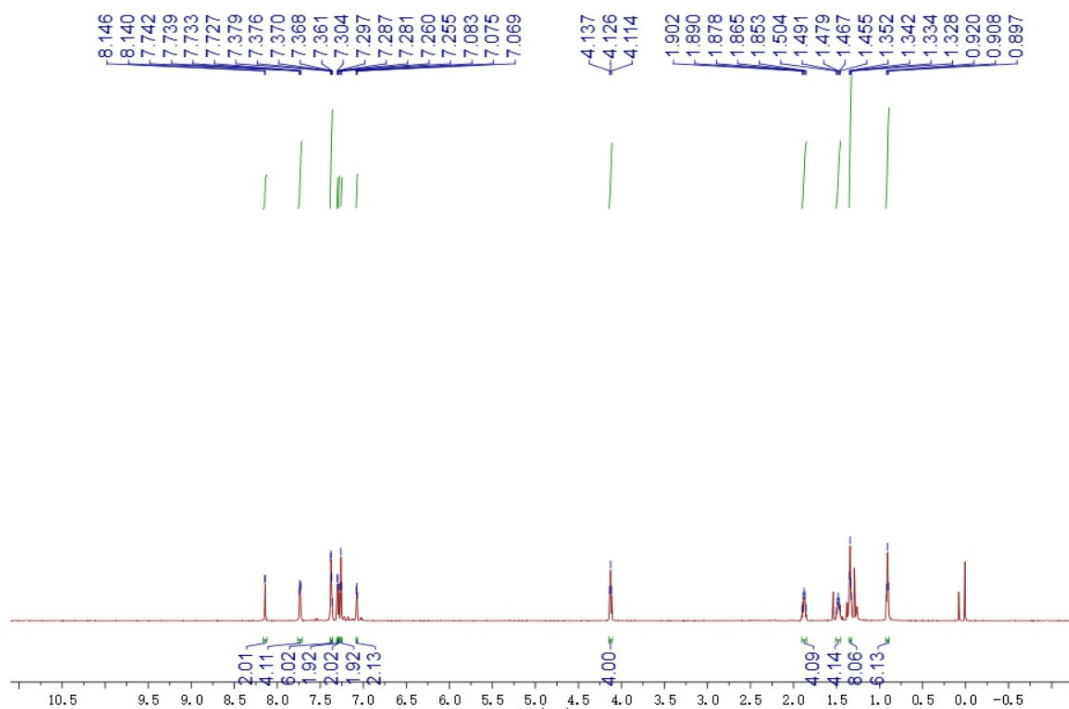


Fig. S10. $^1\text{H-NMR}$ spectra of the monomer **HDPQT** in CDCl_3 .

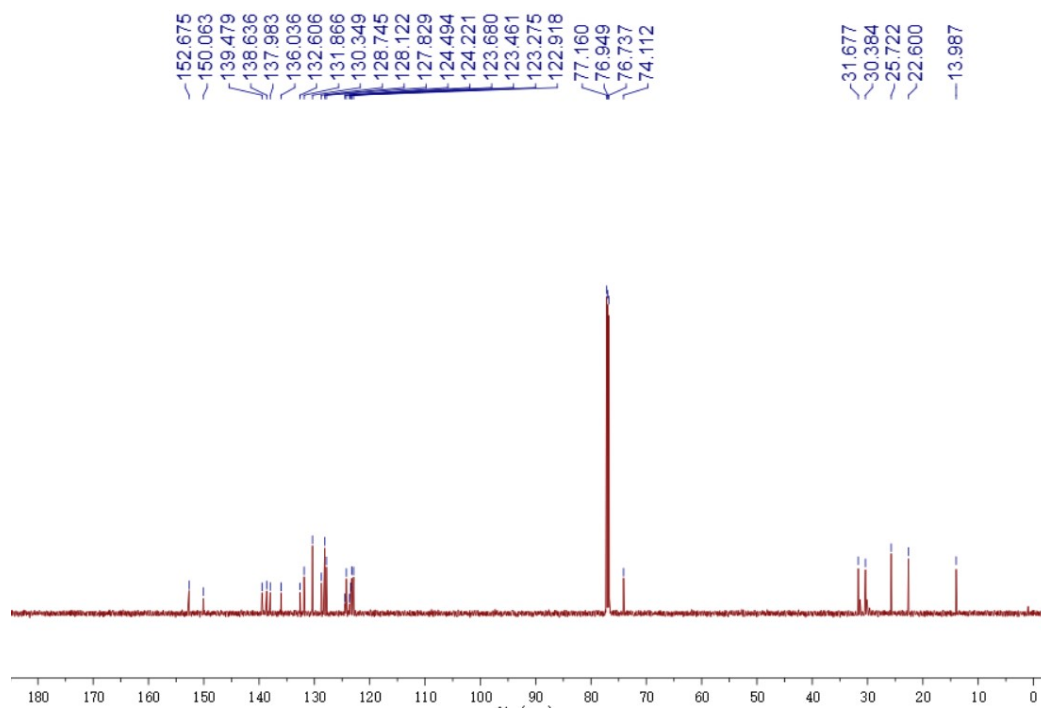


Fig. S11. $^{13}\text{C-NMR}$ spectra of the monomer **HDPQT** in CDCl_3 .

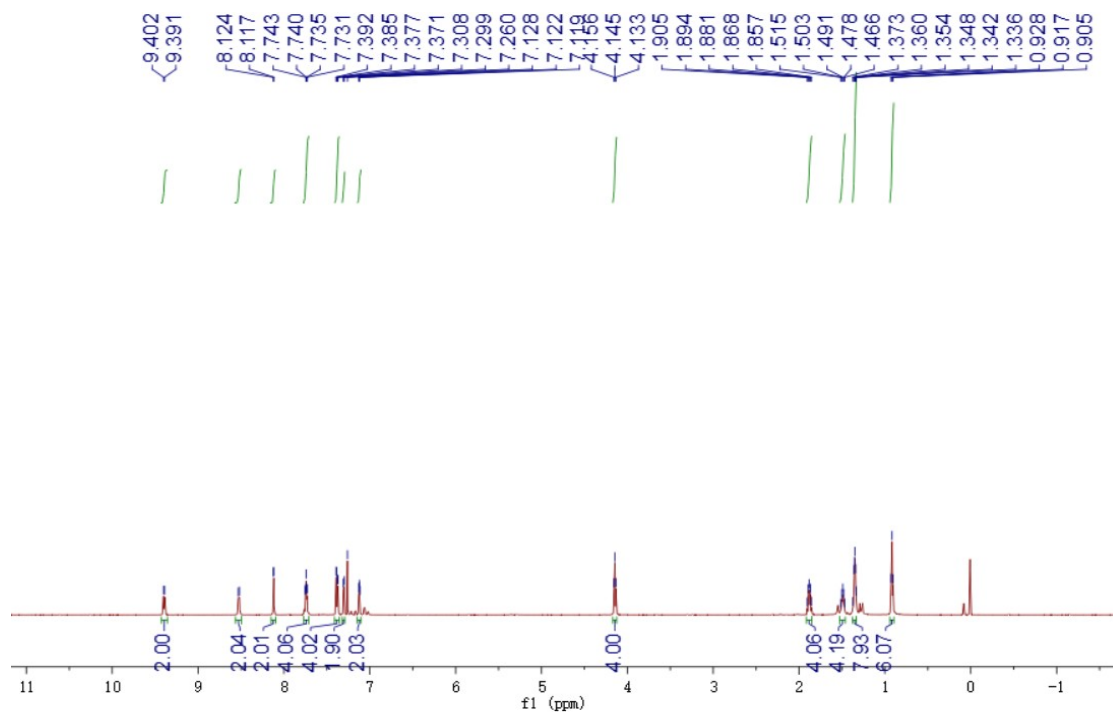


Fig. S12. ^1H -NMR spectra of the monomer HPAQT in CDCl_3 .

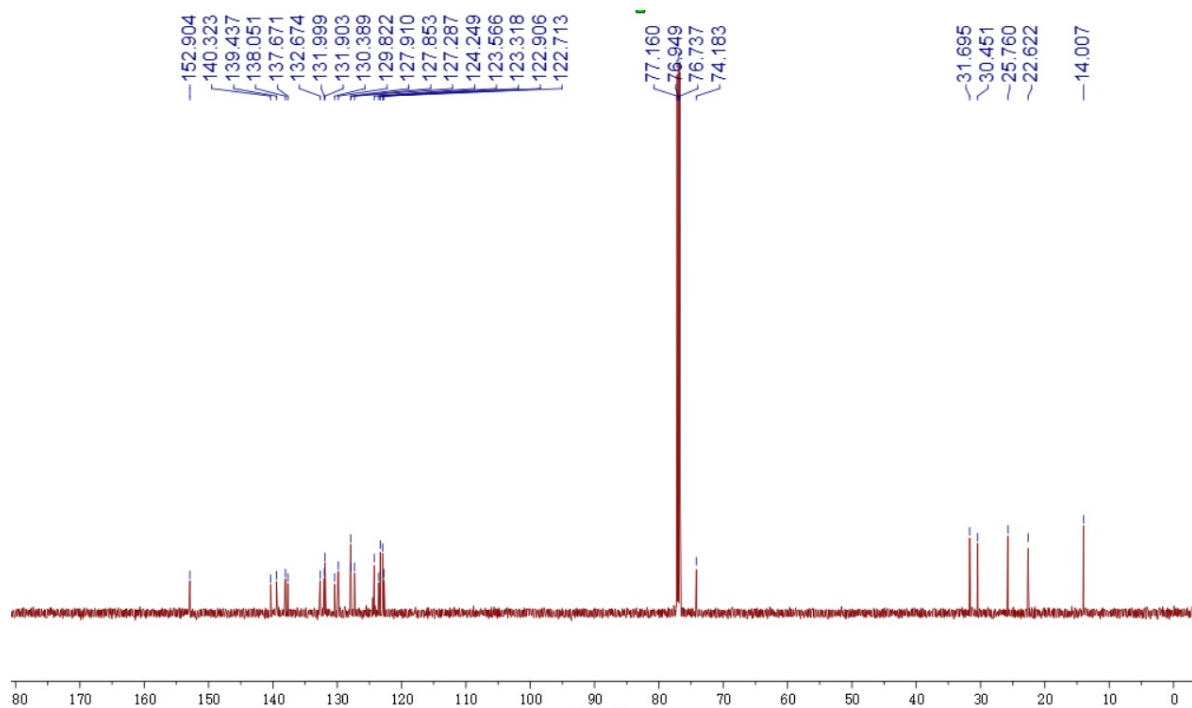


Fig. S13. ^{13}C -NMR spectra of the monomer HPAQT in CDCl_3 .

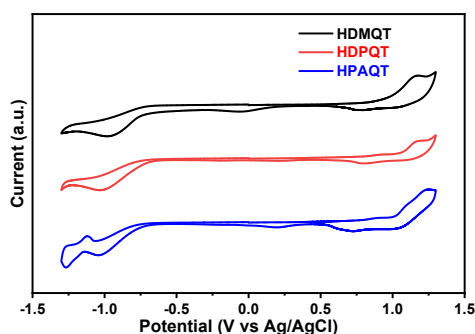


Fig. S14. CV curves of three monomers in CH_2Cl_2 containing 0.1 M TBAP at a scan rate of 100 mV/s within a potential window of -1.3 to 1.3 V.

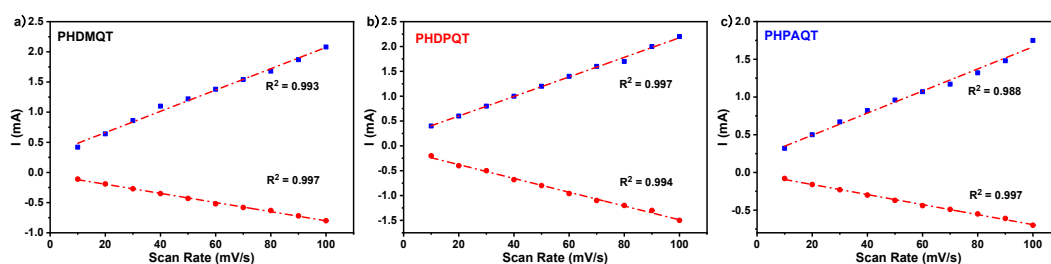


Fig. S15. The relationship of (a) PHDMQT, (b) PHDPQT, and (c) PHPAQT thin films between scan rate and oxidation/reduction peak current obtained from the CV curves at different scan rates in 0.1 M TBAP/ACN at different scan rates.

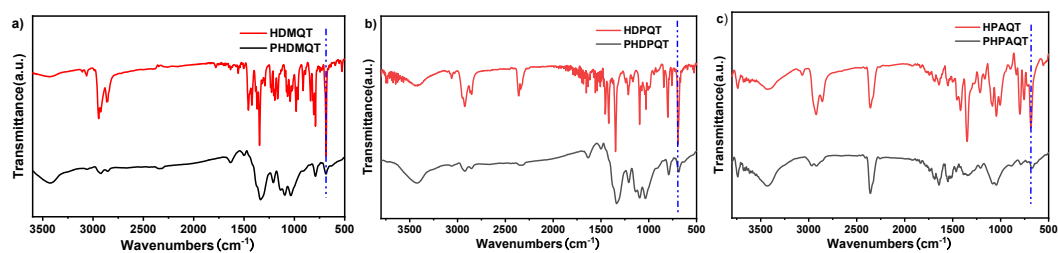


Fig. S16. FT-IR spectra of (a) HDMQT and PHDMQT, (b) HDPQT and PHDPQT, (c) HPAQT and PHPAQT.

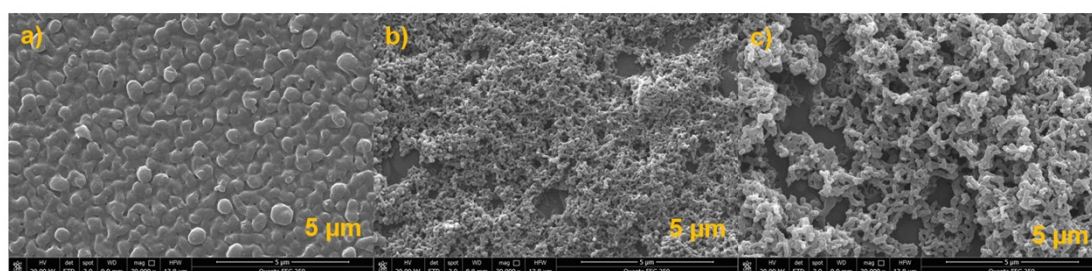


Fig. S17. SEM images of polymer thin films (a) PHDMQT, (b) PHDPQT, and (c) PHPAQT.

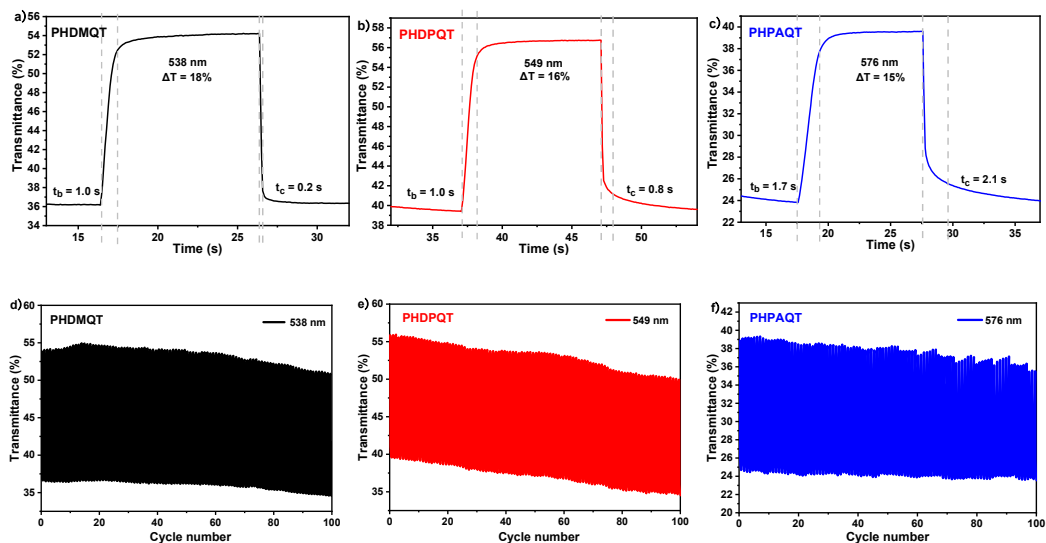


Fig. S18. Optical contrast and response time of the electrochromic polymer thin films (a) **PHDMQT** at 538 nm, (b) **PHDPQT** at 549 nm, and (c) **PHPAQT** at 576 nm, respectively; Electrochromic cycling stability of polymer thin films (d) **PHDMQT** at 538 nm, (e) **PHDPQT** at 549 nm, and (f) **PHPAQT** at 576 nm, respectively.

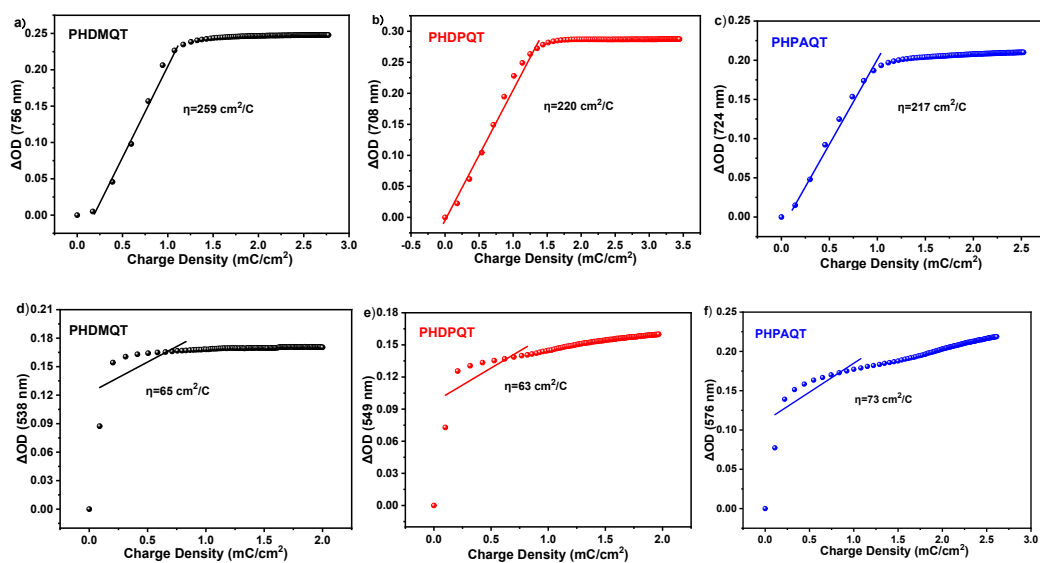


Fig. S19. The coloration efficiency curves of **PHDMQT** at (a) 756 nm and at (d) 538 nm, **PHDPQT** at (b) 708 nm and (e) 549 nm, and **PHPAQT** at (c) 724 nm and (f) 576 nm, respectively.

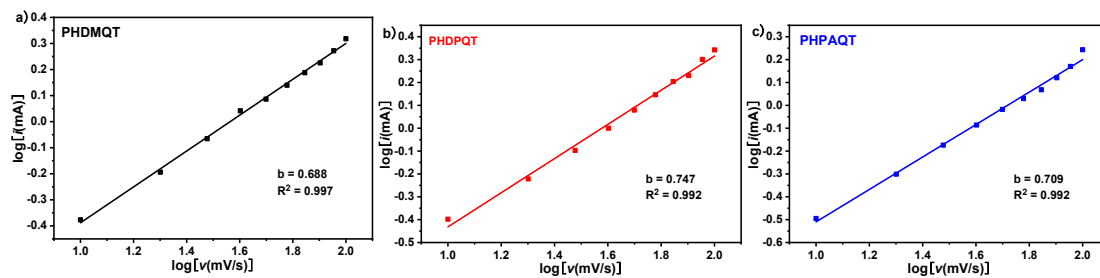
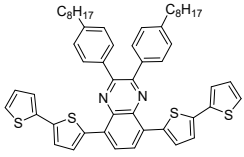
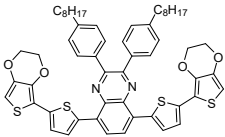
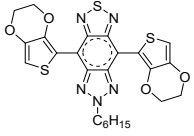
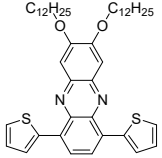
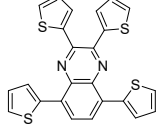
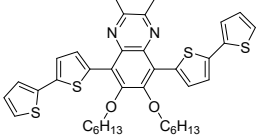
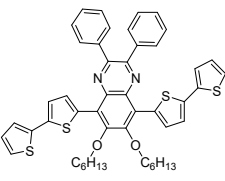
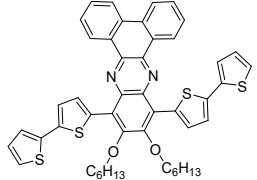


Fig. S20. log–log plot of peak current versus sweep rate of (a) **PHDMQT**, (b) **PHDPQT**, and (c) **PHPAQT** thin films in 0.1 M TBAP/ACN.

Table S1. Comparison of electrochromic properties of structurally similar polymers prepared by electrochemical polymerization reported in the existing literatures

Polymers ^[Ref]	Structures of monomers	λ (nm)	ΔT (%)	t_b/t_c (s)	CE (cm ² /C)
Q-T-T [2]		622	30	0.83/1.35	174.5
Q-T-E [2]		681	14	0.82/1.02	83
pCDB-EDOT [3]		790	26	1.7/1.0	158
P2 [4]		653	25.3	3.05/1.53	132.6
PThQ-Th [5]		627	30.2	0.9/0.5	217.8
PHDMQT		756	39	0.3/0.5	259
PHDPQT		708	34	0.5/0.6	220
PHPAQT		724	27	2.1/0.7	217

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