

Supporting Information

Hypercrosslinked phenothiazine-based polymers as high redox potential organic cathode materials for lithium-ion batteries

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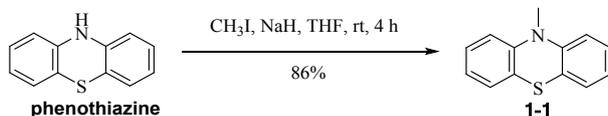
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Experimental Section

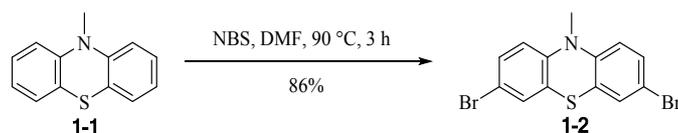
Reagents and Instrumentation: Phenothiazine (98%), iodomethane (CH₃I, 99%), sodium hydride (NaH, 60%), *N*-bromosuccinimide (NBS, 99%), *N,N*-dimethylformamide (DMF, 99.5%), bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh₃)₂Cl₂, 98%), copper(I) iodide (CuI, 99%), trimethylsilylacetylene (TMSA, 95%), triethylamine (TEA, 99%), potassium carbonate (K₂CO₃, 99%), methanol (MeOH, 99.5%), octacarbonyldicobalt (Co₂(CO)₈, 95%), 1,3,5-tribromobenzene (98%) and other solvents were purchased analytical grade. Tetrahydrofuran (THF, 99%) and 1,4-dioxane (99%) were purified by distillation prior to use. The prepared compounds were confirmed by nuclear magnetic resonance (NMR) using a 400 MHz Bruker. Fourier Transform infrared spectroscopy (FT-IR) spectra were recorded on PerkinElmer Spectrum Two. Elemental analysis (EA) was collected using a Vario EL cube. The specific surface areas were analyzed by Brunauer-Emmett-Teller (BET, Autosorb-iQ3). X-ray diffraction (XRD) was conducted on Bruker D8 Advance. Thermal gravimetric analysis (TGA) was carried out using a NETZSCH STA 409 PC/PG apparatus. Scanning electron microscopes (SEM) is measured on JEOL JSM-7810F.

Synthesis of 10-methyl-10*H*-phenothiazine (**1-1**)¹



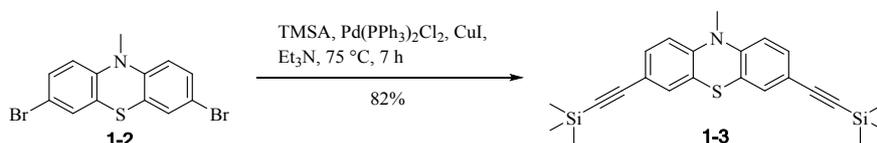
Phenothiazine (5 g, 25 mmol), anhydrous THF (125 mL) and sodium hydride (2 g, 50 mmol) were slowly added to a two-necked flask, and then the mixture was stirred for 2 h at room temperature. Afterwards methyl iodide (14 g, 0.1 mol) was added. The mixture was continued stirred for 2 h at room temperature. After cooling, the mixture was poured into water (100 mL) and extracted with dichloromethane (150 mL). The organic layer was separated and evaporated to dryness under vacuum. The crude product was recrystallized from petroleum ether to obtain compound **1-1**, white solid 4.6 g (yield: 86%). ¹H NMR (400 MHz, CDCl₃): δ 7.20 – 7.13 (m, 4H), 6.93 (dt, *J* = 7.5, 1.2 Hz, 2H), 6.82 (dd, *J* = 8.1, 1.1 Hz, 2H), 3.38 (s, 3H). The ¹H NMR data is consistent with the literature report.²

Synthesis of 3,7-dibromo-10-methyl-10H-phenothiazine (1-2)³



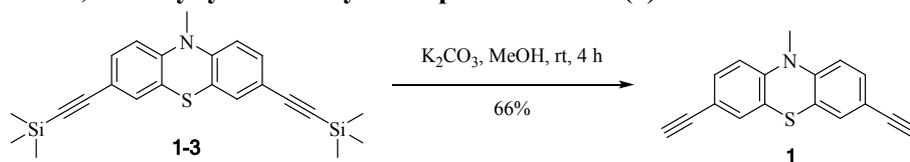
Compound **1-1** (0.2 g, 0.9 mmol), NBS (0.4 g, 2 mmol) were dissolved in DMF (1 mL). The solution was stirred in the dark for 3 h at 90 °C. After cooling, water (20 mL) was added, and the mixture was extracted with dichloromethane (3 × 20 mL). The organic layers were separated and evaporated to dryness under vacuum. The crude product was column chromatographed over silica gel (200-300 mesh, petroleum ether/dichloromethane: 10/1) afforded compound **1-2**, a white solid 0.3 g (yield: 86%). ¹H NMR (400 MHz, CDCl₃): δ 7.27 (d, *J* = 2.3 Hz, 1H), 7.25 (d, *J* = 2.3 Hz, 1H), 7.23 (d, *J* = 2.2 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 3.31 (s, 3H). The ¹H NMR data is consistent with the literature report.⁴

Synthesis of 10-methyl-3,7-bis[2-(trimethylsilyl)ethynyl]-10H-phenothiazine (1-3)^{5, 6}



Compound **1-2** (0.2 g, 0.5 mmol), Pd(PPh₃)₂Cl₂ (19 mg, 0.027 mmol) and CuI (5 mg, 0.27 mmol) were charged into a 10 mL Schlenk tube and degassed three times. Then, TMSA (122 mg, 1.24 mmol) and anhydrous Et₃N (1.5 mL) were added to this tube. The resulting mixture was stirred at 75 °C for 7 h. After cooling, the mixture was poured into dichloromethane (50 mL). The organic phase was washed twice with saturated solution of NH₄Cl, and once with brine. The organic phase was separated and evaporated to dryness under vacuum. The crude product was column chromatographed over silica gel (200-300 mesh, petroleum ether/dichloromethane: 10/1) afforded compound **1-3**, a yellow solid 0.18 g (yield: 82%). ¹H NMR (400 MHz, CDCl₃): δ 7.24 (d, *J* = 1.9 Hz, 1H), 7.20 (d, *J* = 1.9 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 3.34 (s, 3H), 0.23 (s, 18H). The ¹H NMR data is consistent with the literature report.⁴

Synthesis of 3,7-diethynyl-10-methyl-10H-phenothiazine (1)⁷



Compound **1-3** (0.3 g, 0.75 mmol), K₂CO₃ (0.6 g, 4.5 mmol), dichloromethane (4 mL) and methanol (8 mL) were charged into a round bottom flask and stirred at room temperature for 4 h. Afterwards, water (20 mL) and dichloromethane (20 mL) were added. The organic phase was separated and washed with water (2 × 20 mL) and evaporated to dryness under vacuum. The crude products were recrystallized from petroleum ether to obtain compound **1**, a pale yellow solid 0.13 g (yield: 66%). ¹H NMR (400 MHz, CDCl₃): δ 7.29 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.23 (d, *J* = 1.9 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 3.36 (s, 3H), 3.05 (s, 2H). The ¹H NMR data is consistent with the literature report.⁴

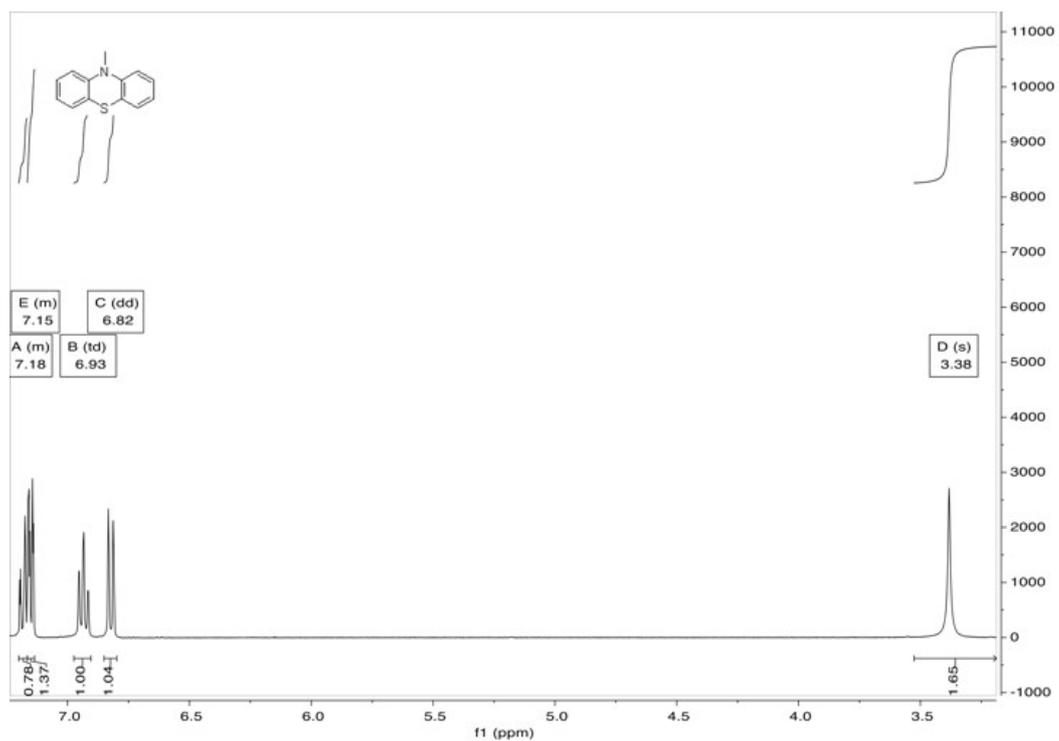


Fig. S1 400 MHz ^1H NMR spectra of compound 1-1 in CDCl_3 .

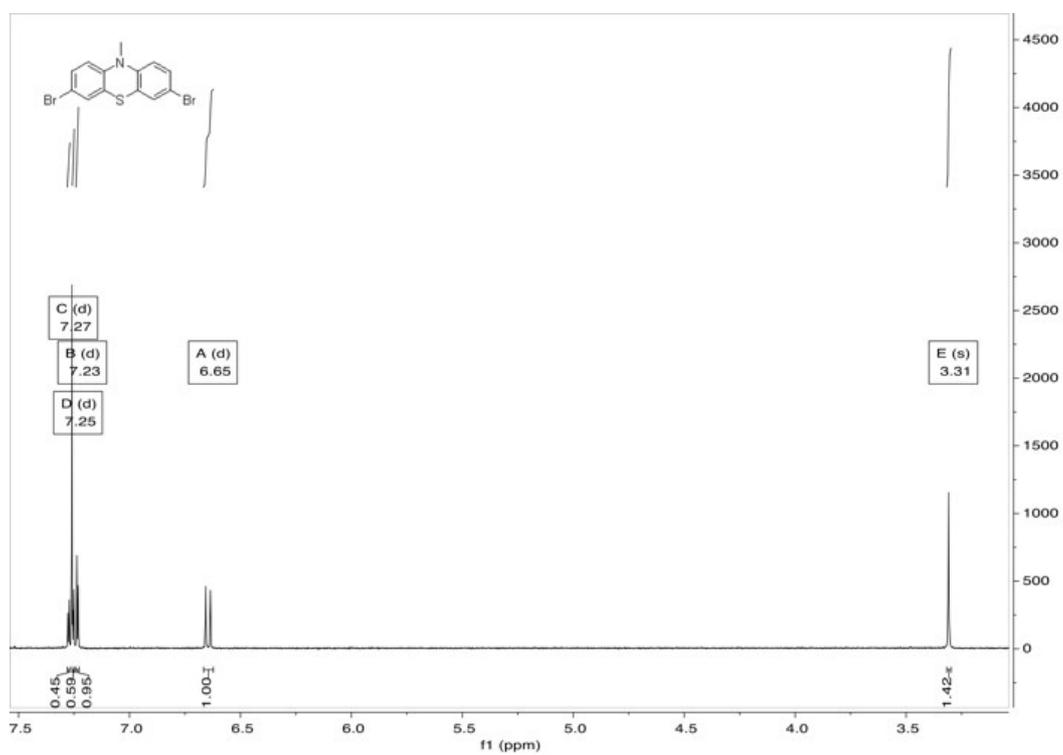


Fig. S2 400 MHz ^1H NMR spectra of compound 1-2 in CDCl_3 .

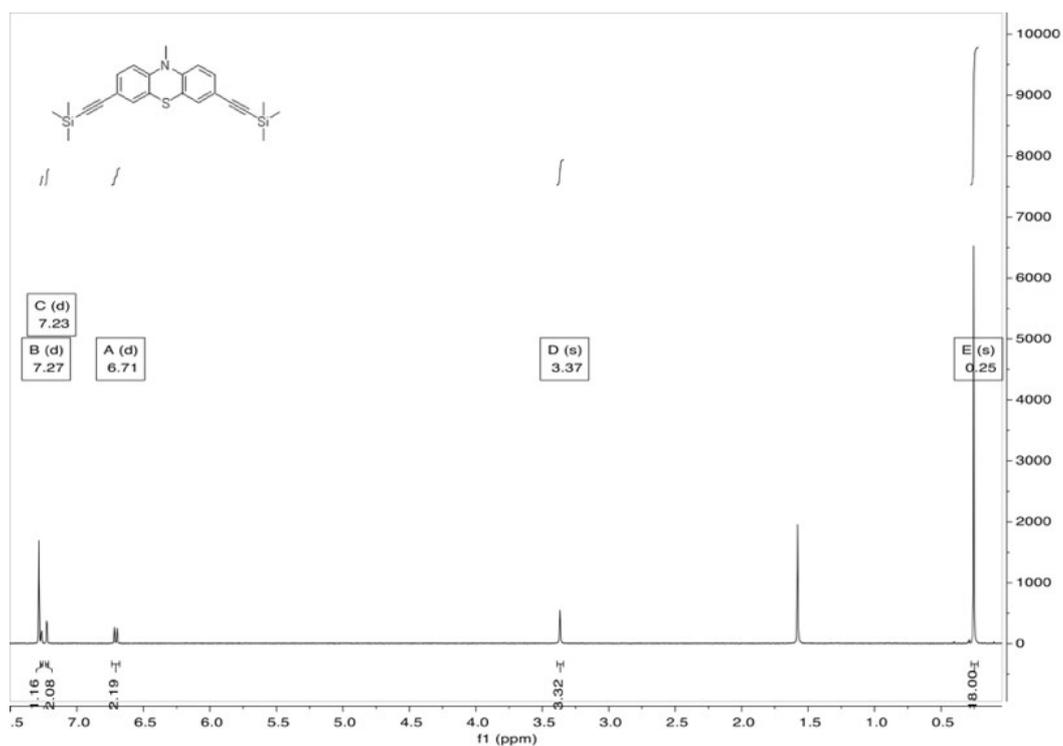


Fig. S3 400 MHz ^1H NMR spectra of compound 1-3 in CDCl_3 .

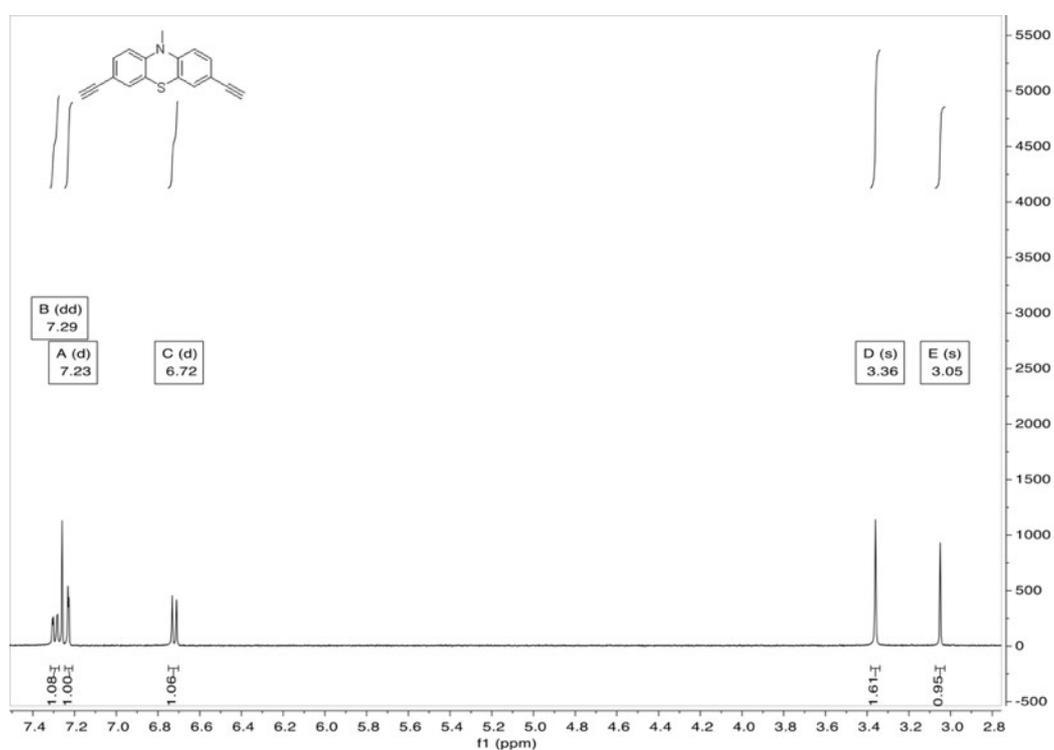


Fig. S4 400 MHz ^1H NMR spectra of compound 1 in CDCl_3 .

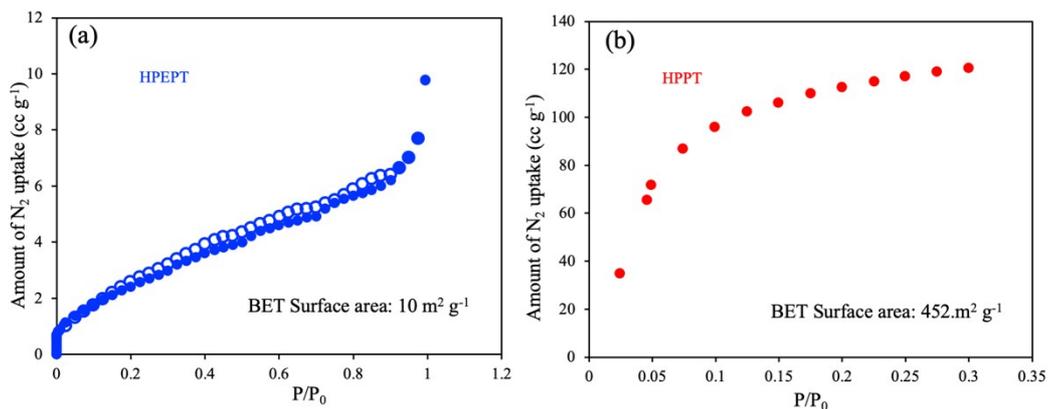


Fig. S5 (a) N₂ adsorption and desorption isotherms of HPEPT; (b) N₂ adsorption isotherm of HPPT.

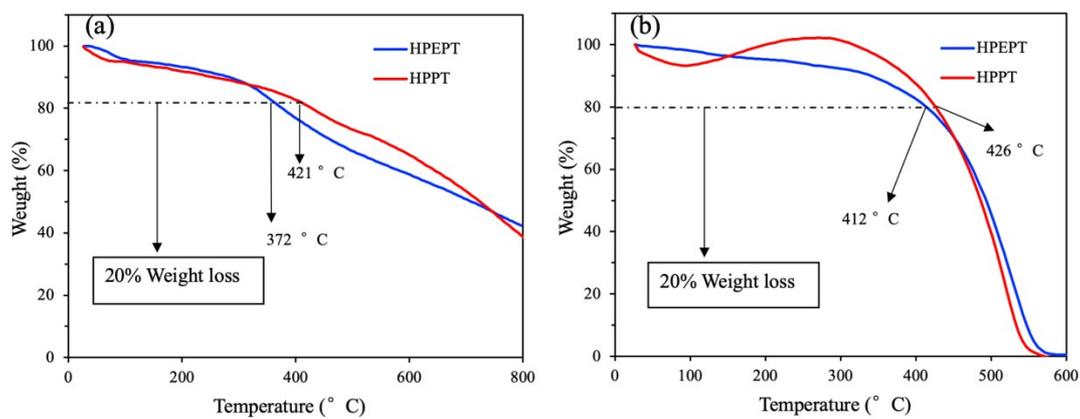


Fig. S6 (a) TGA curves of HPEPT and HPPT in N₂ atmosphere at a heating rate of 10 °C min⁻¹; (b) TGA curves of HPEPT and HPPT in air at a heating rate of 10 °C min⁻¹.

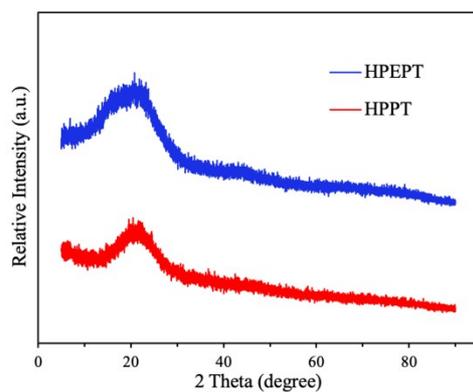


Fig. S7 XRD spectra of HPEPT and HPPT.

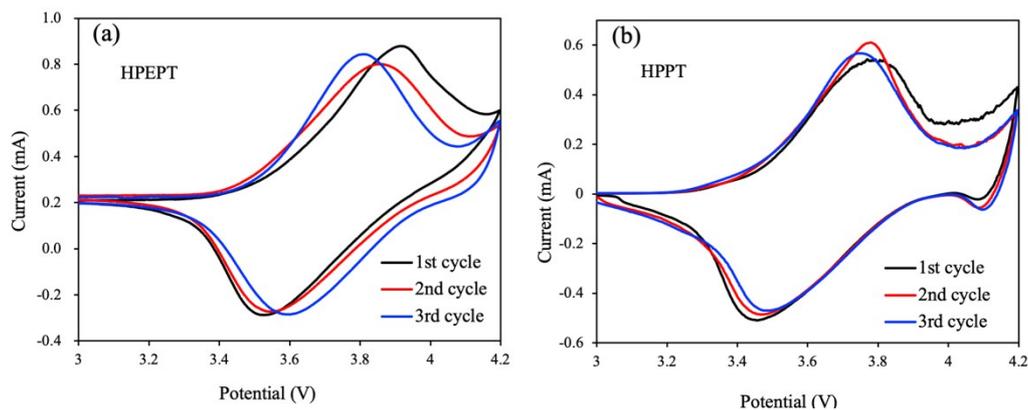


Fig. S8 (a) CV curves of **HPEPT** at a scan rate of 1 mV s^{-1} in the voltage range of 3–4.2 V vs Li/Li^+ ; (b) CV curves of **HPPT** at a scan rate of 1 mV s^{-1} in the voltage range of 3–4.2 V.

References

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