Supporting Information for

Tailoring Two-Electron Donating Phenothiazines to Enable High Concentration Redox Electrolytes for Use in Non Aqueous Redox Flow Batteries

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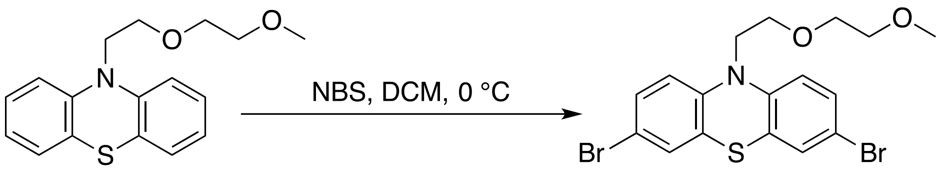
I. Synthesis

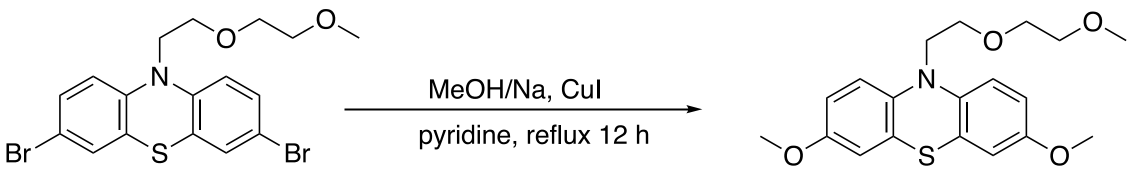
General

Phenothiazine, sodium hydride (60% dispersion in mineral oil) and copper iodide were purchased from Acros Organics. Diethylene glycol monomethyl ether and methyl formate were purchased from Tokyo Chemical Incorporated. Nitrosonium tetrafluoroborate (98%) was purchased from Alfa Aesar and was stored and weighed in an argon-filled glovebox (MBraun, $O_2 < 0.1$ ppm, $H_2O < 0.5$ ppm). Anhydrous pyridine (99.8%), *N*-bromosuccinimide (NBS), anhydrous methanol, and sodium were purchased from Sigma-Aldrich. Other solvents were purchased from VWR. Silica gel (65 x 250 mesh) was purchased from Sorbent Technologies. ^{1}H and ^{13}C NMR spectra were obtained on 400 MHz Varian spectrometers in DMSO-d_6 from Cambridge Isotope Laboratories. Mass spectra were obtained on an Agilent 5973 Network mass selective detector attached to Agilent 6890N Network GC system. Elemental analyses were performed by Atlantic Microlab, Inc. Solubility tests were performed in an argon-filled glove box.

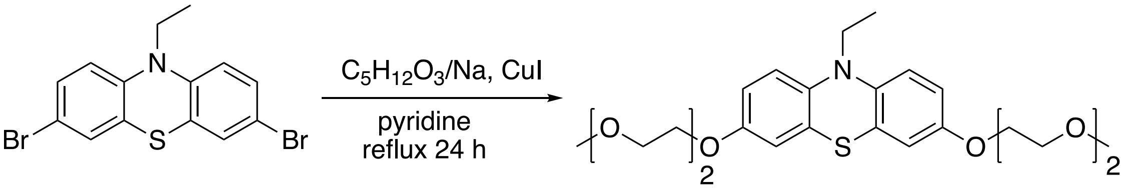
N-ethylphenothiazine (EPT),[1] *N*-((2-methoxy)ethoxy)ethylphenothiazine (MEEPT),[2] *N*-ethyl-3,7-dibromophenothiazine (DBrEPT),[3] *N*-ethyl-3,7-dimethoxyphenothiazine (DMeOEPT) and *N*-ethyl-3,7-dimethoxyphenothiazine tetrafluoroborate (DMeOEPT-BF_4),[4] were synthesized as previously reported.



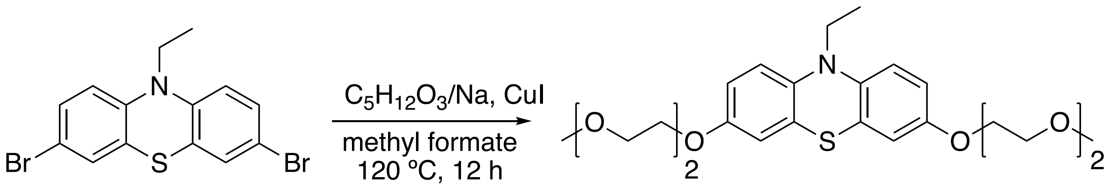
3,7-Dibromo-*N*-((2-methoxy)ethoxy)ethylphenothiazine (DBrMEEPT). *N*-((2-methoxy)ethoxy)ethylphenothiazine (1.12 g, 3.73 mmol) was dissolved in anhydrous DCM (11 mL) in a 50 mL round-bottomed flask. The reaction flask was immersed in an ice water bath, and *N*-bromosuccinimide (2.0 g, 11 mmol) was added in small portions over 10 min. The reaction was stirred at 0 °C for 30 min. Upon completion of the reaction, the reaction mixture was quenched with sodium thiosulfate, diluted with dichloromethane, and then the organic layer washed with water and brine. The organic extracts were dried over magnesium sulfate, filtered and concentrated by rotary evaporation. The organic residue was purified by silica gel chromatography using 40% ethyl acetate in hexanes as eluent to afford the product as a pale red oil (1.03 g, 60%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ 7.35 (m, 4H), 7.00 (dd, J = 6.8, 2.8 Hz, 2H), 4.00 (t, J = 5.6 Hz, 2H), 3.69 (t, J = 5.6 Hz, 2H), 3.51 (m, 2H), 3.40 (m, 2H), 3.19 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ 143.7, 130.5, 129.1, 125.4, 117.7, 114.31, 71.4, 69.8, 67.2, 58.2, 47.5. GCMS: *m/z* 457/459/461 (~1:2:1, 63%), 368/370/372 (~1:2:1, 100%), 354/356/358 (~1:2:1, 25%), 336/338/340 (~1:2:1, 16%), 289/291 (~1:1, 31%), 207 (18%), 196 (26%). Anal. calcd. for $C_{17}H_{17}Br_2NO_2S$ C, 44.47; H, 3.73; N, 3.05. Found C, 44.61; H, 3.74; N, 3.05.



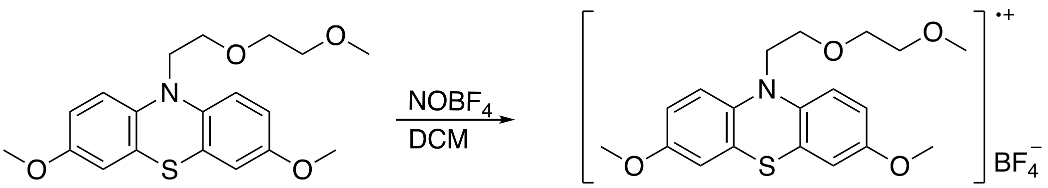
3,7-Dimethoxy-*N*-((2-methoxy)ethoxy)ethylphenothiazine (DMeOMEEPT). Sodium methoxide solution was prepared by dissolving sodium (0.50 g, 22 mmol) in 7 mL methanol. To the methoxide solution, copper(I) iodide (1.65 g, 8.68 mmol), DBrMEEPT (1.00 g, 2.17 mmol) and pyridine (10.8 mL) were added. The reaction mixture was purged with nitrogen for 15 min. A reflux condenser was attached and the reaction was refluxed for 12 h. Upon completion of the reaction, the reaction mixture was diluted with diethyl ether and washed with brine. The organic extracts were dried over magnesium sulfate, filtered and concentrated by rotary evaporation. The organic residue was purified by silica gel chromatography using 40% ethyl acetate in hexanes as the eluent to afford the product as a colorless oil (0.35 g, 45%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ 6.95 – 6.90 (m, 2H), 6.78 – 6.72 (m, 4H), 3.92 (t, *J* = 5.9 Hz, 2H), 3.68 (s, 6H), 3.66 (d, *J* = 5.9 Hz, 2H), 3.54 – 3.48 (m, 2H), 3.43 – 3.37 (m, 2H), 3.20 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ 154.7, 138.5, 124.6, 116.1, 112.9, 112.4, 71.3, 69.7, 67.5, 58.04, 55.4, 47.3. GCMS: *m/z* 361 (77%), 272 (100%), 258 (78%), 240 (60%), 215 (26%), 172 (12%). Anal. calcd. for $C_{19}H_{23}NO_4S$ C, 63.14; H, 6.41; N, 3.88. Found C, 63.16; H, 6.55; N, 3.90.



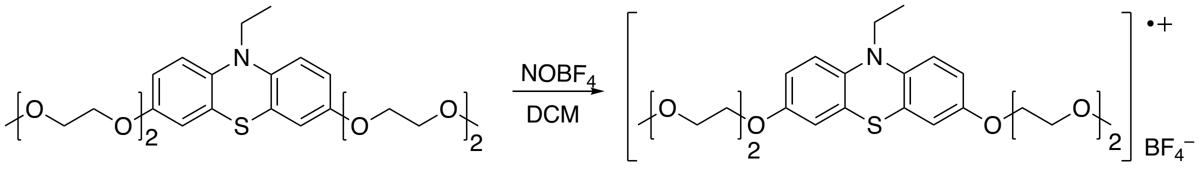
***N*-ethyl-3,7-bis(2-(2-methoxyethoxy)ethoxy)phenothiazine (B(MEEO)EPT)**, **Method I**. An oven-dried 1 L round-bottomed flask was transferred to an argon filled glove box, then diethylene glycol monomethyl ether (390 mL, 3.41 mol) was added into the round-bottomed flask, which was capped and removed from the glove box. Freshly cut sodium metal (9.56 g, 416 mmol) was dissolved in diethylene glycol monomethyl ether under nitrogen atmosphere. Then, copper(I) iodide (31.65 g, 168.2 mmol), DBrEPT (16.00 g, 41.55 mmol) and anhydrous pyridine (320 mL) were added to the resulting solution. Afterward, the reaction mixture was sparged with nitrogen about 15 min while stirring. The round-bottomed flask was immersed in an oil bath and the reaction mixture was refluxed for overnight. Upon completion of the reaction, the reaction mixture was concentrated by rotary evaporation. Then reaction mixture was diluted with ethyl acetate and washed with 1 M aq. HCl, water and brine. The combined organic extracts were dried over magnesium sulfate and concentrated by using rotary evaporation. Finally, organic residue was purified on a silica gel column using 20-50% ethyl acetate in hexanes. The silica gel was neutralized with trimethylamine (2 -3 mL) during packing the column. The product was yellow/light red viscous liquid (14.8 g, 77%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ 6.90 – 6.85 (m, 2H), 6.79 – 6.75 (m, 4H), 4.05 – 3.98 (m, 4H), 3.79 (q, *J* = 6.9 Hz, 2H), 3.71 – 3.65 (m, 4H), 3.58 – 3.52 (m, 4H), 3.47 – 3.41 (m, 4H), 3.23 (s, 6H), 1.23 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ 153.9, 138.7, 124.5, 116.0, 113.8, 113.3, 71.5, 69.9, 69.1, 67.8, 58.3, 41.3, 12.9. GCMS: *m/z* 463 (100%), 434 (30%), 360 (11%), 230 (14%), 103(18%), 59(47%). Anal. calcd. for $C_{24}H_{33}NO_6S$ C, 62.18; H, 7.18; N, 3.02. Found C, 62.40; H, 7.22; N, 3.03.



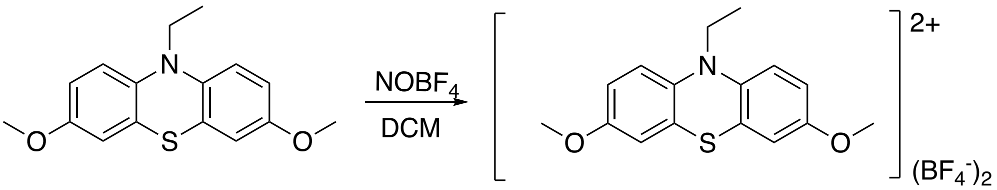
N-ethyl-3,7-bis(2-(2-methoxyethoxy)ethoxy)phenothiazine (B(MEEO)EPT), Method II. An oven-dried 350 mL pressure vessel was transferred to an argon-filled glove box. Diethylene glycol monomethyl ether (195 mL, 1.71 mol) was added into the pressure vessel, which was capped and removed from the glove box. Freshly cut sodium metal (4.78 g, 201 mmol) was dissolved in diethylene glycol monomethyl ether under nitrogen atmosphere. Then, copper(I) iodide (15.8 g, 166 mmol), DBrEPT (8.00 g, 20.8 mmol) and methyl formate (3.1 mL, 33 mmol) were added to the resultant solution. After that reaction mixture was sparged with nitrogen for 15 min while stirring. The pressure vessel was tightly capped and immersed in an oil bath and heated to 120 °C for 12 h. Upon completion of the reaction, the reaction mixture was diluted with ethyl acetate and washed with 1.6 M aq. HCl (150 mL), water, and brine. The combined organic extracts were dried over magnesium sulfate and concentrated by rotary evaporation. Finally, organic residue was purified on a silica gel column, eluting with a gradient of 20-50% ethyl acetate in hexanes. The silica gel was neutralized with trimethylamine (2 -3 mL) during packing the column. The product was light yellowish red viscous liquid (6.8 g, 71%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ 6.88 (d, J = 9.7 Hz, 2H), 6.79 – 6.75 (m, 4H), 4.05 – 3.98 (m, 4H), 3.79 (q, J = 6.9 Hz, 2H), 3.71 – 3.65 (m, 4H), 3.60 – 3.53 (m, 4H), 3.48 – 3.42 (m, 4H), 3.24 (s, 6H), 1.24 (t, J = 6.8 Hz, 3H). Anal. calcd. for $C_{24}H_{33}NO_6S$ C, 62.18; H, 7.18; N, 3.02 Found C, 62.03; H, 6.96; N, 3.09.



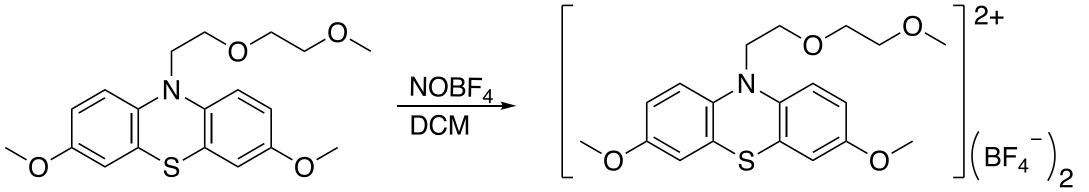
3,7-Dimethoxy-N-((2-methoxy)ethoxy)ethylphenothiazine tetrafluoroborate (DMeOMEEPT-BF$_4$). DMeOMEEPT (0.530 g, 1.38 mmol) was dissolved in anhydrous dichloromethane (15 mL) in an oven-dried 50 mL round-bottomed flask fitted with a rubber septum under nitrogen atmosphere. Then round-bottomed flask was placed in an ice water bath for 10 min after which nitrosonium tetrafluroborate (0.178 g, 1.52 mmol) was added into resultant reaction mixture and stirred 1 h. Upon completion of the reaction, anhydrous diethyl ether (25 mL) was added gradually with continued stirring, resulting in a blue precipitate. The precipitate was filtered under nitrogen, then it was redissolved in anhydrous dichloromethane (10 mL) and precipitated with anhydrous diethyl ether (20 mL). This process was repeated once more to remove unreacted starting material. The solid blue product (0.42 g, 65%) was dried under nitrogen and stored in a glove box.



N-ethyl-3,7-bis(2-(2-methoxyethoxy)ethoxy)phenothiazine tetrafluoroborate (B(MEEO)EPT-BF$_4$). B(MEEO)EPT (8.0 g, 17 mmol) was dissolved in anhydrous dichloromethane (175 mL) in an oven-dried 500 mL round-bottomed flask fitted with a rubber septum under nitrogen atmosphere. Then reaction flask was placed in an ice water bath for 10 min after which nitrosonium tetrafluroborate (2.32 g, 19.9 mmol) was added to the reaction mixture, which was stirred for 1 h. Upon completion of the reaction, anhydrous diethyl ether (260 mL) was added gradually with continued stirring, which produced a blue precipitate. The precipitate was filtered under nitrogen, then redissolved in anhydrous dichloromethane (85 mL) and precipitated with the addition of anhydrous diethyl ether (120 mL). The redissolution/reprecipitation process was repeated once more to remove unreacted starting material. Finally, the solid blue product (4.9 g, 51%) was dried under nitrogen and stored in a glove box. To grow crystals of this product, a saturated solution of D(MEEO)EPT-BF_4 salt in DCM was prepared. A small volume was transferred in a NMR tube and layered it with toluene to form two distinct layers. Finally, the NMR tube was capped and placed in a freezer set at 4 ºC, and crystals formed at the interface of the solvents.

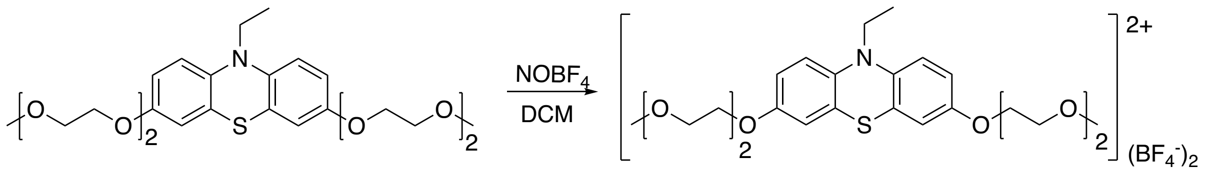


***N*-ethyl-3,7-dimethoxyphenothiazine bis(tetrafluoroborate) (DMeOEPT(BF_4)$_2$)**. DMeOEPT (0.30 g, 1.0 mmol) was dissolved in anhydrous dichloromethane (10 mL) in an oven-dried 50 mL round-bottomed flask fitted with a rubber septum under nitrogen atmosphere. Then round-bottomed flask was placed in an ice water bath for 10 min after which nitrosonium tetrafluroborate (0.32 g, 2.7 mmol) was added into resultant reaction mixture and stirred 1 h. Upon completion of the reaction, anhydrous diethyl ether (20 mL) was added gradually with continued stirring which produced a dark blue precipitate. The precipitate was filtered under nitrogen, then it was redissolved in anhydrous dichloromethane (10 mL) and precipitated with anhydrous diethyl ether (20 mL). This process was repeated once more to remove unreacted starting material. The solid dark blue product (0.34 g, 72%) was dried under nitrogen and stored in a glove box.



3,7-Dimethoxy-*N*-((2-methoxy)ethoxy)ethylphenothiazine bis(tetrafluoroborate) (DMeOMEEPT(BF_4)$_2$).

DMeOMEEPT (0.40 g, 1.1 mmol) was dissolved in anhydrous dichloromethane (15 mL) in an oven-dried 50 mL round-bottomed flask fitted with a rubber septum under nitrogen atmosphere. Then a round-bottomed flask was placed in an ice water bath for 10 min after which nitrosonium tetrafluroborate (0.344 g, 2.95 mmol) was added into resultant reaction mixture and stirred 1 h. Upon completion of the reaction, anhydrous diethyl ether (25 mL) was added gradually with continued stirring, producing a dark blue precipitate. The precipitate was filtered under nitrogen, then it was redissolved in anhydrous dichloromethane (10 mL) and precipitated with anhydrous diethyl ether (20 mL). This process was repeated once more to remove unreacted starting material. The solid dark blue product (0.47 g, 79%) was dried under nitrogen and stored in a glove box.



***N*-ethyl-3,7-bis(2-(2-methoxyethoxy)ethoxy)phenothiazine bis(tetrafluoroborate) (B(MEEO)EPT-(BF_4)$_2$)**. B(MEEO)EPT (0.40 g, 0.90 mmol) was dissolved in anhydrous dichloromethane (10 mL) in an oven-dried 50 mL round-bottomed flask fitted with a rubber septum under nitrogen atmosphere. Then reaction flask was placed in an ice water bath for 10 min after which nitrosonium tetrafluroborate (0.28 g, 2.4 mmol) was added to the reaction mixture, which was then stirred for 1 h. Anhydrous diethyl ether (20 mL) was added gradually with continued stirring, producing a dark blue precipitate. The precipitate was filtered under nitrogen, then redissolved in anhydrous dichloromethane (10 mL) and precipitated with anhydrous diethyl ether (20 mL). This process was repeated once more to ensure removal of unreacted starting material. Finally, the solid dark blue product (0.48 g, 83%) was dried under nitrogen and stored in a glove box.

II. Nuclear Magnetic Resonance Spectroscopy

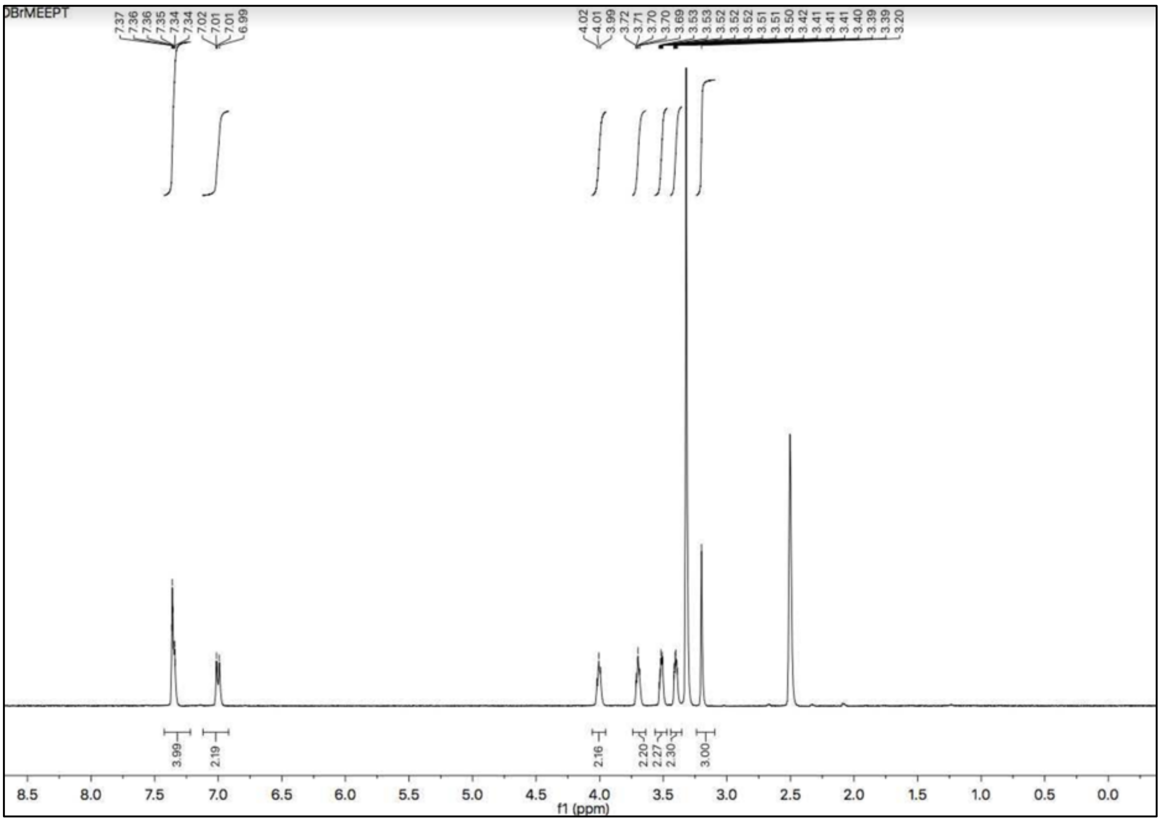


Figure S1. ^{1}H NMR spectrum of DBrMEEPT in DMSO-d_6.

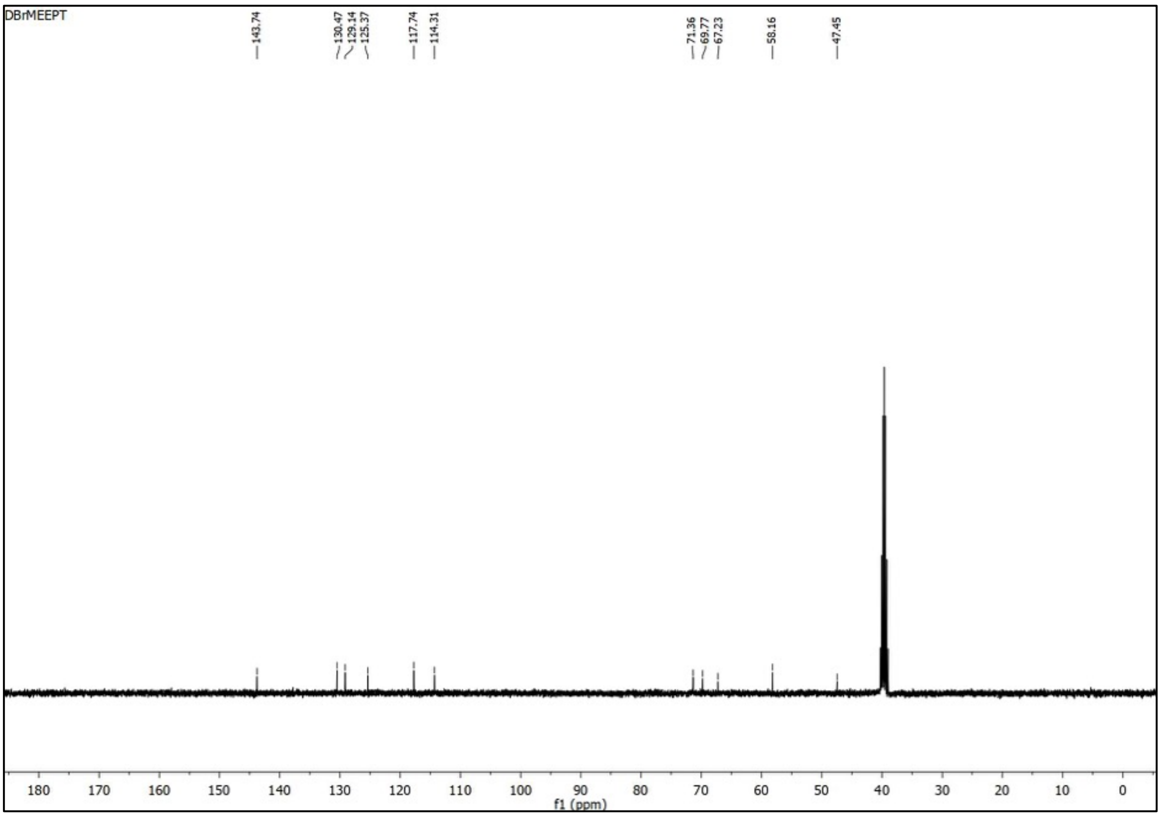


Figure S2. ^{13}C NMR spectrum of DBrMEEPT in DMSO-d_6.

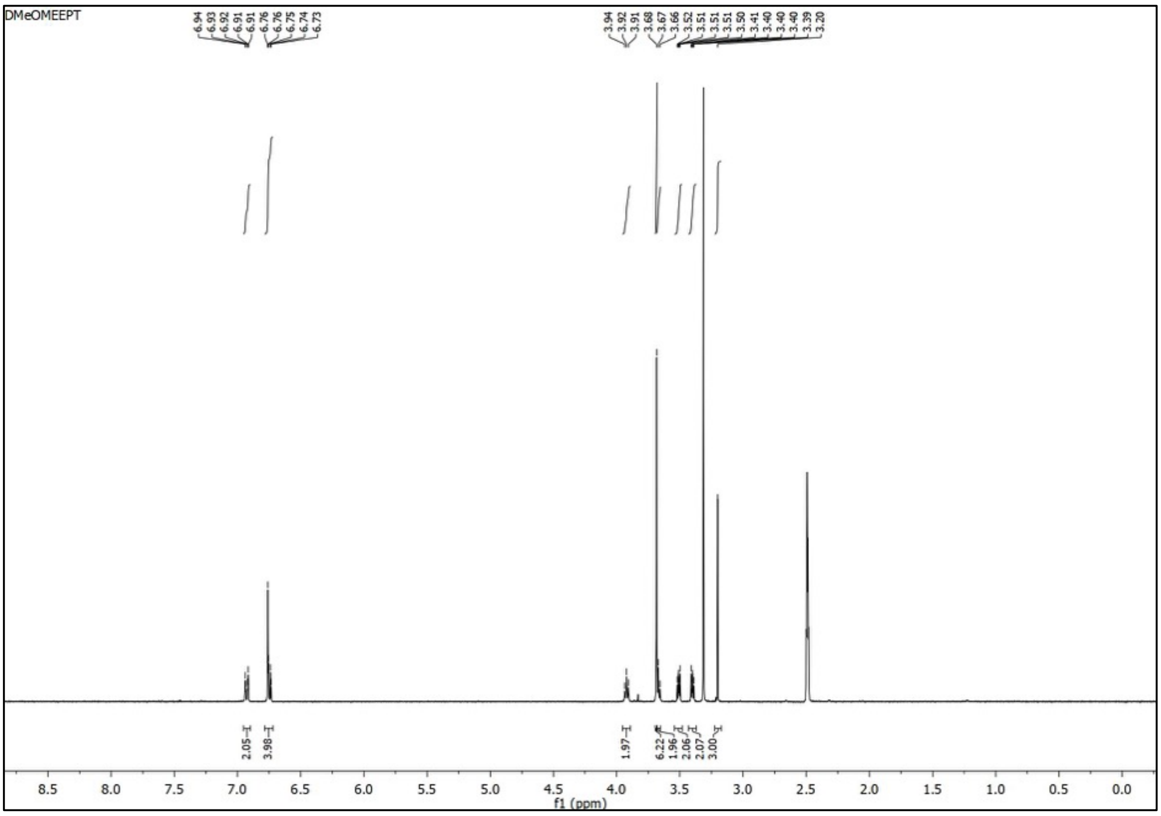


Figure S3. ^{1}H NMR spectrum of DMeOMEEPT in DMSO-d_6.

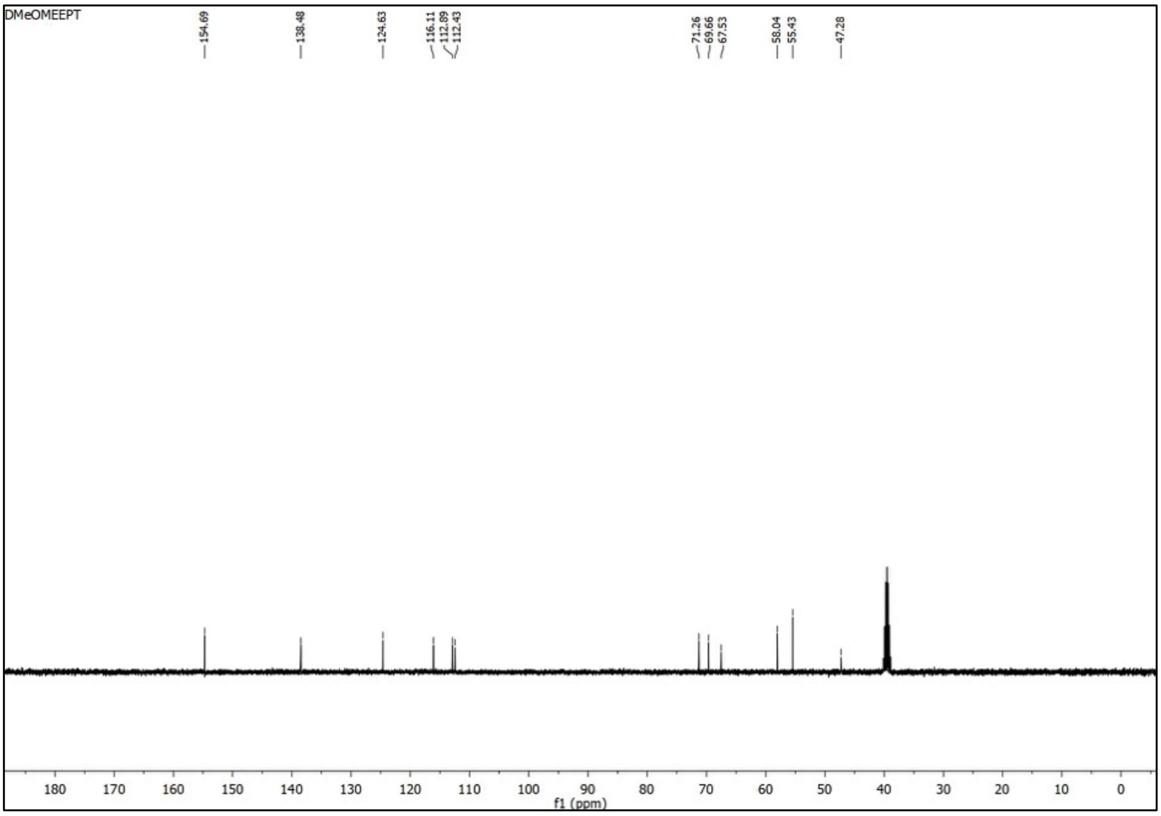


Figure S4. ^{13}C NMR spectrum of DMeOMEEPT in DMSO-d_6.

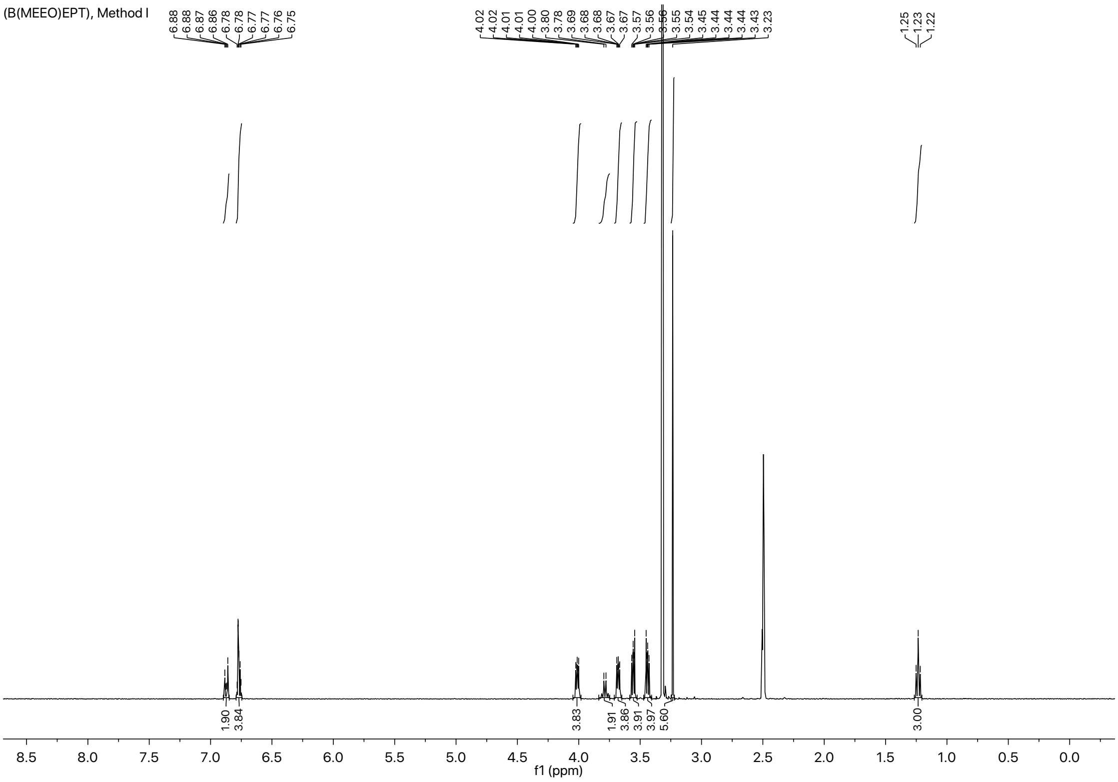


Figure S5. ^{1}H NMR spectrum of B(MEEO)EPT in DMSO-d_6, Method I.

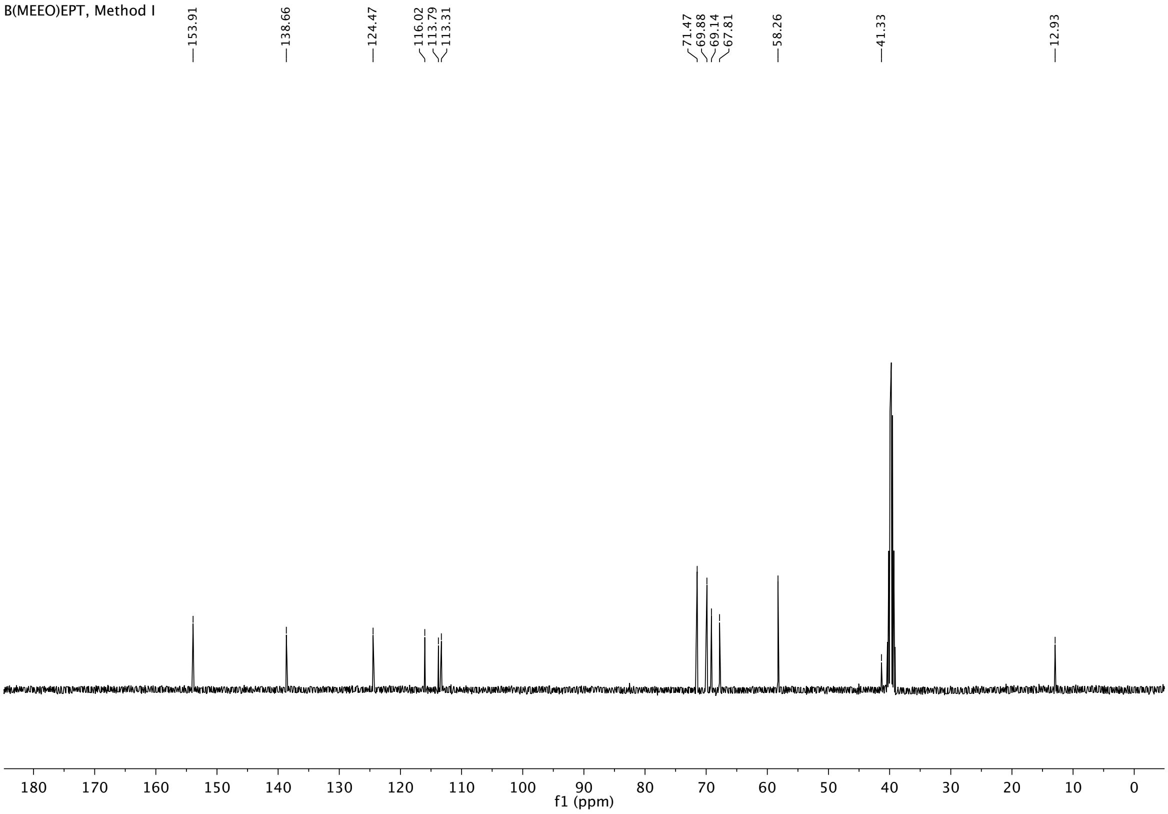


Figure S6. ^{13}C NMR spectrum of B(MEEO)EPT in DMSO-d_6, Method I.

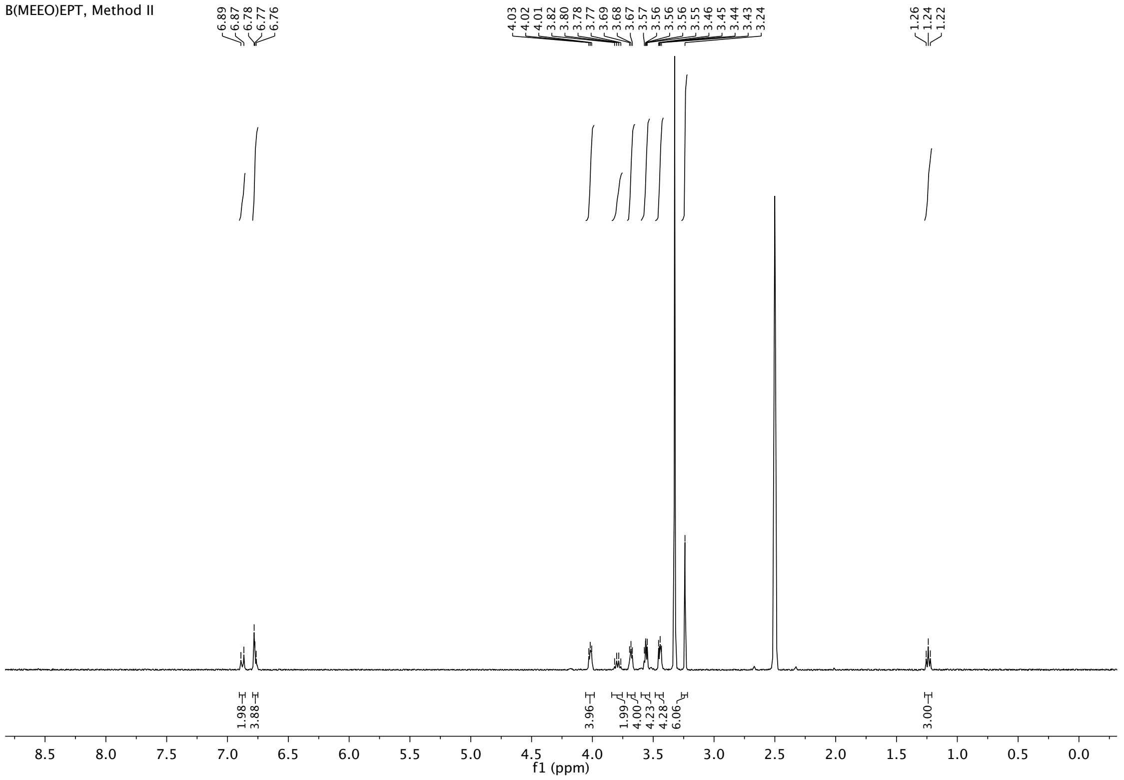


Figure S7. ^{1}H NMR spectrum of B(MEEO)EPT in DMSO-d_6, Method II

III. Additional Solubility Data

Table S1. Solubilities of the neutral molecules, their radical cation salts, and the dication salts of DMeOMEEPT and B(MEEO)EPT in 0.5 M TEABF$_4$/ACN. The radical cation salts and the dication salts had tetrafluoroborate (BF$_4$) as a counter ion. Solubility values are reported in molarity (M).

Compound	Neutral Species (M)	Radical Cation (M)	Dication (M)
DMeOMEEPT	miscible	0.10 ± 0.01	0.08 ± 0.01
B(MEEO)EPT	miscible	0.27 ± 0.01	0.24 ± 0.01

IV. UV-vis Spectroscopy

Chemical oxidation of DMeOMEEPT with one or two equivalents of $NOBF_4$ results in electron transfer from the phenothiazine core to the nitrosonium (NO^+) cation, forming one or two equivalents of the neutral NO gas and either the tetrafluoroborate salt of the radical cation or the bis(tetrafluoroborate) salt of the dication, respectively. UV-vis of the three relevant states of oxidation of DMeOMEEPT are shown in Figure S8.

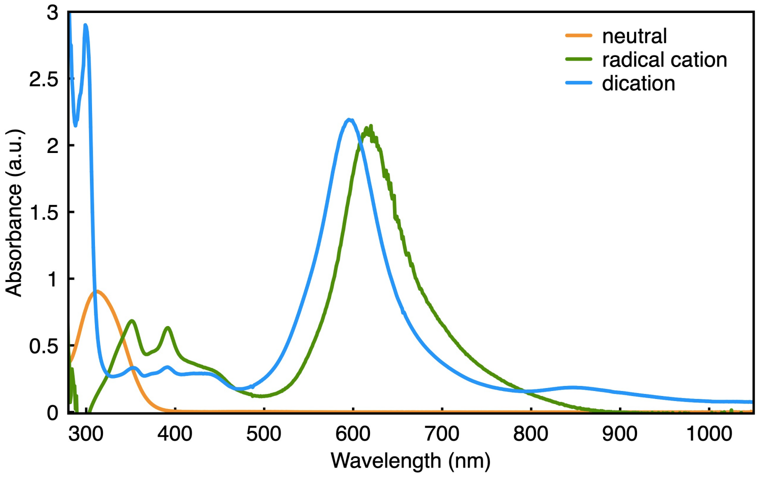


Figure S8. UV-vis absorption spectra of the neutral, radical cation, and dication forms of DMeOMEEPT in ACN.

IV. EPR Spectroscopy

EPR spectra of a 1.5 mM solution of B(MEEO)EPT-BF_4 in dichloromethane was obtained using 4mm quartz EPR tubes on an X-band Bruker EPR spectrometer.

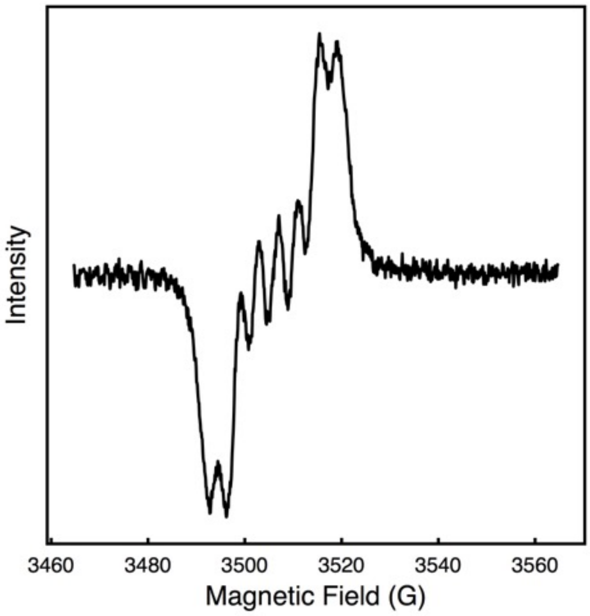


Figure S9. EPR spectrum of B(MEEO)EPT-BF_4 radical cation at 1.5 mM in dichloromethane.

V. X-Ray Crystallography

X-ray diffraction data were collected at 90.0 K on a Bruker D8 Venture kappa-axis diffractometer using MoK(alpha) X-rays. Raw data were integrated, scaled, merged and corrected for Lorentz-polarization effects using the APEX3 package.[5] Corrections for absorption were applied using SADABS.[6] The structure was solved by direct methods (SHELXT)[7] and refinement was carried out against F^2 by weighted full-matrix least-squares (SHELXL).[8] Hydrogen atoms were found in difference maps, but subsequently placed at calculated positions and refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography. [9]

VI. Electrochemical Analysis

Additional data for electrochemical analysis is provided here.

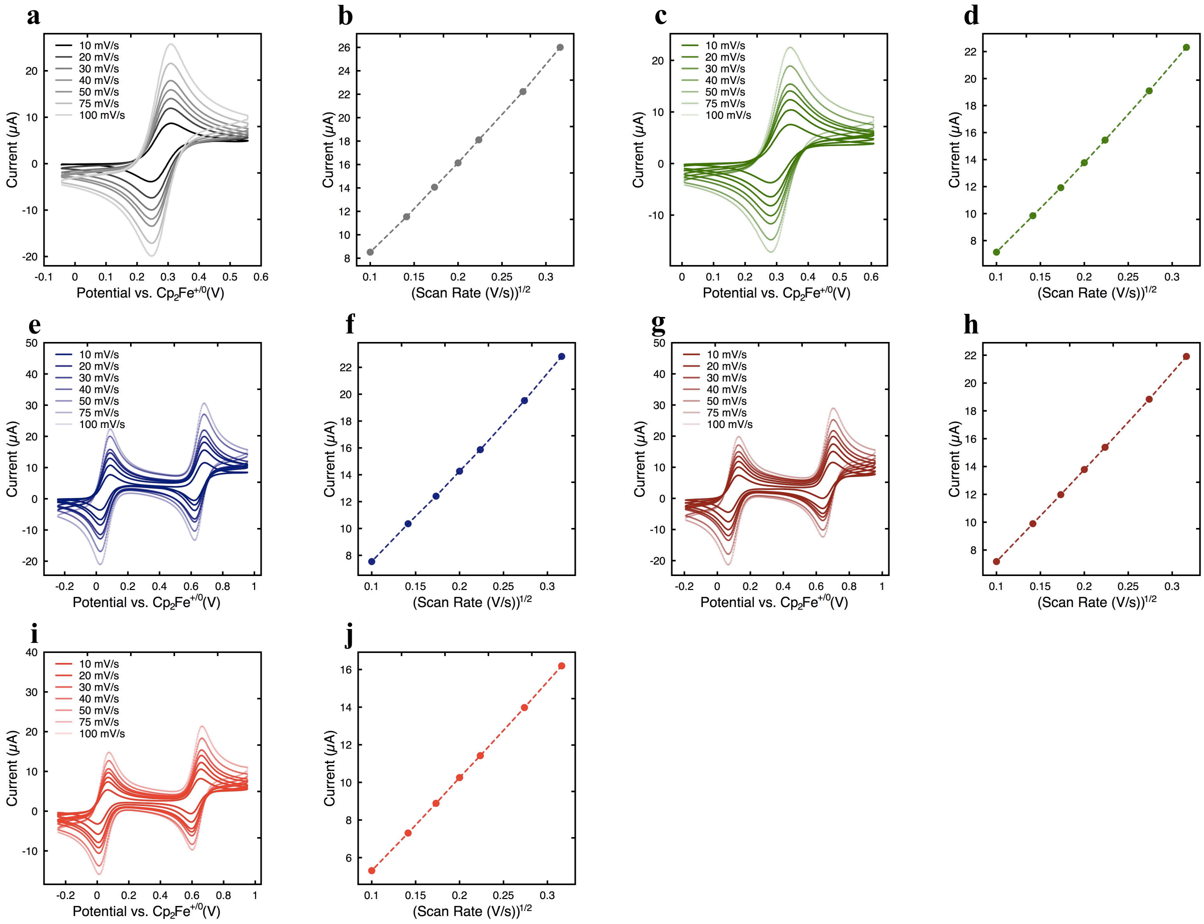


Figure S10. Cyclic voltammograms of EPT (a), MEEPT (c), DMeOEPT (e), DMeOMEEPT (g), and B(MEEO)EPT (i) at 0.001 M in 0.5 M TEATFSI/ACN at scan rates of 10, 20, 30, 40, 50, 75, and 100 mV s^{-1}. Additionally, the corresponding Randles-Sevcik plots are shown for EPT (b), MEEPT (d), DMeOEPT (f), DMeOMEEPT (h), and D(MEEO)EPT (j).

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