Electronic Supporting Information for

Overcharge Performance of 3,7-Disubstituted *N*-Ethylphenothiazine Derivatives in Lithium-Ion Batteries

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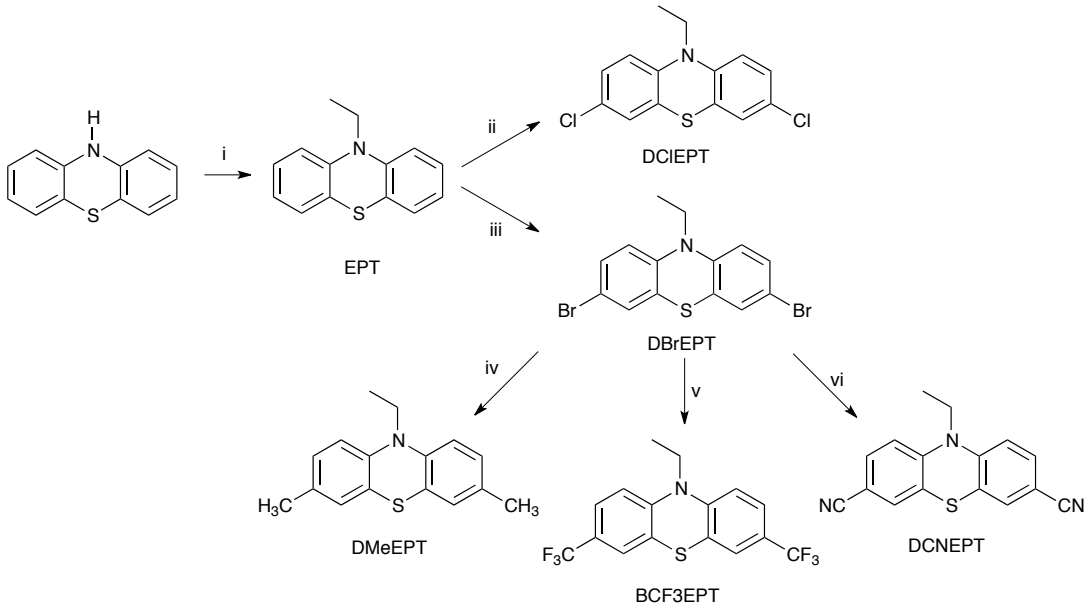
I. General Experimental Sections

Sodium hydride, *N*-chlorosuccinimide (NCS), and methyl iodide were purchased from Alfa Aesar. Antimony pentachloride was purchased from Acros Organics. Bromoethane, phenothiazine, *N*-bromosuccinimide (NBS), copper(I) cyanide, potassium trifluoroacetate, and *n*-BuLi (2.5 M in hexanes) were purchased from Sigma Aldrich. Anhydrous solvents *N*-methylpyrrolidone, *N,N*-dimethylformamide, and diethylether were purchased from Sigma Aldrich. *N*-Chlorosuccinimide and *N*-bromosuccinimide were purchased from Acros and were freshly crystallized from water prior to use. All the other reagents were used without further purification. Redox shuttle candidates 3,7-dimethyl-*N*-ethylphenothiazine (DMeEPT), 3,7-dichloro-*N*-ethylphenothiazine (DClEPT), 3,7-dibromo-*N*-ethylphenothiazine (DBrEPT), 3,7-bis(trifluoromethyl)-*N*-ethylphenothiazine (BCF3EPT), and 3,7-dicyano-*N*-ethylphenothiazine (DCNEPT) were synthesized. Their precursor *N*-ethylphenothiazine was synthesized following a reported procedure.[1] Silica gel (65×250 mesh) was purchased from Sorbent Technologies, and solvents for purification were purchased from Fisher Scientific. ^{1}H and ^{13}C NMR spectra were obtained on 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.

II. Synthesis

Disubstituted *N*-ethylphenothiazine (EPT) derivatives were synthesized from commercially available phenothiazine. First, phenothiazine was alkylated with bromoethane. *N*-chlorosuccinimide and *N*-bromosuccinimide were used to chlorinate and brominate the resultant *N*-ethylphenothiazine, affording the dichlorinated and dibrominated *N*-ethylphenothiazine, respectively. Halogen-metal exchange of the dibrominated *N*-ethylphenothiazine was followed by reaction with iodomethane afforded the dimethyl derivative. Coupling of the dibrominated derivative with potassium perfluoroacetate yielded the bis(trifluoro) product,[2] and coupling with copper cyanide the dicyano derivative.[3] The synthetic routes for the EPT derivatives are shown in Scheme S1.



Scheme S1. Synthetic routes used to synthesize *N*-ethylphenothiazine (EPT), 3,7-dimethyl-*N*-ethylphenothiazine (DMeEPT), 3,7-dichloro-*N*-ethylphenothiazine (DClEPT), 3,7-dibromo-*N*-ethylphenothiazine (DBrEPT), 3,7-bis(trifluoromethyl)-*N*-ethylphenothiazine (BCF3EPT), and 3,7-dicyano-*N*-ethylphenothiazine (DCNEPT).

Synthesis of 3,7-Dichloro-*N*-ethylphenothiazine (DClEPT)

To a solution of EPT (2.27 g, 10.0 mmol) in DMF (50 mL) in a 100 mL round-bottomed flask immersed in an ice water bath, 2.2 eq of NCS (2.94 g, 22.0 mmol) was added in portions. The reaction mixture was stirred at 0 °C for 2 h before removal from the ice water bath and let stir overnight. Water (100 mL) was added to the reaction mixture and the organic product was extracted with hexanes (2 x 100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by rotary evaporation. The crude product was purified by column chromatography with cyclohexane/ethylacetate (26:1) as the eluent and yielded an oil upon concentration by rotary evaporation. The oil was diluted with petroleum ether and chilled in dry ice / acetone bath. An off-white solid precipitated and was isolated by vacuum filtration, yielding the desired product (1.39 g, 47%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.22-7.20 (m, 4H), 6.97 (m, 2H), 3.84 (q, J = 6.8 Hz, 2H), 1.23 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm):143.44, 127.90, 126.74, 126.69, 124.83, 117.18, 41.83, 12.78. GCMS: *m/z* 297 (30%), 295 (440%), 282 (10%), 268 (72%), 266 (100%). Anal. Calcd. for $C_{14}H_{11}Cl_2SN$: C, 56.77; H, 3.74; N, 4.73. Found C, 56.68; H, 3.63; N, 4.77.

Synthesis of 3,7-Dibromo-*N*-ethylphenothiazine (DBrEPT)

To a solution of EPT (10.0 g, 44.0 mmol) in DMF (50 mL) in a 100 mL round-bottomed flask, 2.2 eq of *N*-bromosuccinimide (17.3 g, 97.0 mmol) was added in portions at rt, and the reaction mixture was stirred overnight. Water (100 mL) was added to the reaction mixture followed by saturated aqueous sodium thiosulfate (20 mL), and the organic product was extracted with hexanes (2 x 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by rotary evaporation. The crude product was crystallized from ethanol, yielding the product as a white solid (14.7 g, 87%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.36-7.34 (m, 4H), 6.94 (dd,

J = 9.1, 0.8 Hz, 2H), 3.85 (q, *J* = 7 Hz, 2H), 1.25 (t, *J* = 7 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 143.84, 130.82, 129.40, 125.22, 117.70, 114.40, 41.79, 12.74.GCMS: *m/z* 387 (23%), 385 (45%), 383 (23%), 358 (54%), 356 (100%), 354 (54%). Anal. Calcd. for $C_{14}H_{11}Br_2SN$: C, 43.66; H, 2.88; N, 3.64. Found C, 43.52; H, 2.88; N, 3.65 and C, 43.66; H, 2.88; N, 3.67.

Synthesis of 3,7-Dimethyl-*N*-ethylphenothiazine (DMeEPT)

DBrEPT (3.85 g, 10.0 mmol) in anhydrous diethylether (60 mL) was added to an oven-dried 100 mL three-necked round-bottomed flask, and the reaction flask was immersed in a dry ice / acetone bath. Then 5 eq. of *n*-butyllithium (20 mL, 50 mmol, 2.50 M in hexanes) was added dropwise, and the reaction mixture was stirred for 2 h in the dry ice / acetone bath, following which, 5.1 eq. of iodomethane (3.2 mL, 51 mmol) was added dropwise to the reaction mixture. After 2 h, the reaction flask was removed from the cold bath and stirred overnight. Water (100 mL) was added to the reaction mixture, and the organic product was extracted with hexanes (2 x 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by rotary evaporation. The crude product was purified by column chromatography with pentane as the eluent. Concentration by rotary evaporation yielded the product as a clear oil. The oil was diluted with petroleum ether and chilled in dry ice / acetone bath. A white solid precipitated and was isolated by vacuum filtration. (1.20 g, 47%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.95-6.90 (m, 4H), 6.82 (d, *J* = 8.2 Hz, 2H), 3.80 (q, *J* = 7 Hz, 2H), 2.16 (s, 6H) 1.23 (t, *J* = 7 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 142.57, 131.52, 128.38, 127.72, 123.17, 115.44, 41.34, 20.25, 13.05. GCMS: *m/z* 255(43%), 240 (8%), 226 (100%). Anal. Calcd. for $C_{16}H_{17}SN$: C, 75.25; H, 6.71; N, 5.48. Found C, 74.97; H, 6.67; N, 5.51.

Synthesis of 3,7-Bistrifluoromethyl-*N*-ethylphenothiazine (BCF3EPT).

N-Methylpyrrolidinone (150 mL) was added under nitrogen to a 250 mL round-bottomed flask containing 5.2 eq. of copper(I) iodide (9.90 g, 52.0 mmol), 5.2 eq. of potassium trifluoroacetate (7.91 g, 52.0 mmol), and DBrEPT (3.85 g, 10.0 mmol) under nitrogen atmosphere at rt. The reaction flask was immersed in an oil bath that was heated to 150 ºC and was kept at this temperature for 50 h. The reaction was allowed to cool to rt, and the crude mixture was filtered through a short pad of silica gel, eluting with hexanes (500 mL) and then with toluene (100 mL). The combined filtrate was concentrated by rotary evaporation, and the crude product was obtained as a yellow oil. The crude product mixture was purified by column chromatography with cyclohexane/diethylether (25:2) as the eluent, yielding the product as a light yellow solid (0.80 g, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41-7.39 (m, 2H), 7.33 (m, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.97 (q, *J* = 7 Hz, 2H), 1.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.88, 123.93 (q, J_{CF} = 271.2 Hz), 125.30 (q, J_{CF} = 33.0 Hz) , 124.9 (q, J_{CF} = 3.8 Hz), 124.38 (q, J_{CF} = 3.8 Hz), 124.23, 42.40, 12.70. GCMS: *m/z* 363 (44%), 348 (14%), 334 (100%), 316 (12%). Anal. Calcd. for $C_{16}H_{11}F_6SN$: C, 52.89; H, 3.05; N, 3.86. Found C, 52.63; H, 2.96; N, 3.94.

Synthesis of 3,7-Dicyano-*N*-ethylphenothiazine (DCNEPT)

Anhydrous DMF (20 mL) was added to a mixture of 5 eq. of copper(I) cyanide (1.07 g, 12.0 mmol) and DBrEPT (1.93 g, 5.00 mmol) in 100 mL round-bottomed flask under nitrogen atmosphere at rt. The reaction flask was immersed in an oil bath and heated to 150 ºC, after which the reaction mixture was stirred overnight. The reaction was allowed to cool to rt and was filtered through a short pad of silica gel, eluting with dichloromethane. After filtration, the crude mixture was purified by column chromatography with petroleum ether/ethylacetate (5:2) as the eluent, yielding the product as a bright yellow-green solid (0.72 g, 52%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.64 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.61 (d, *J* = 2.1 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 4.0 (q, *J* = 7 Hz, 2H), 1.3 (t, *J* = 7 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 147.20, 133.06,

130.73, 123.09, 118.81, 116.70, 42.43, 12.52. GCMS: *m/z* 277 (44%), 262 (16%), 248 (100%). Anal. Calcd. for $C_{16}H_{11}SN_3$: C, 69.29; H, 4.0; N, 15.15. Found: C, 69.29; H, 3.87; N, 15.04 and C, 69.16; H, 4.00; N, 14.94.

III. X-Ray Crystallographic Data

X-ray diffraction data was collected at 90K on either a Nonius Kappa CCD diffractometer or a Bruker-Nonius X8 Proteum diffractometer. Crystal indexing and data processing were performed either with DENZO-SMN (KappaCCD) or with Bruker APEX2 (X8 Proteum). The structures were solved with shelxs-97 and refined with shelxl-97 or shelxl-2013. The parameters for data collection and structure refinement for EPT, DMeEPT, and DCNEPT are shown in Table S1.

Table S1. Crystal data and structure refinement for EPT, DMeEPT, and DCNEPT.

Compound	**EPT**	**DMeEPT**	**DCNEPT**
Empirical formula	C14 H 13 N S	C16 H17 N S	C16 H 11 N3 S
Formula weight ($gmol^{-1}$)	227.31	255.36	277.34
T (K)	90.0 (2)	90.0 (2)	90.0 (2)
Wavelength (Å)	0.71073	0.71073	1.54178
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pbca	Pnma	Pnma
Unit cell dimensions			
a (Å)	7.7668 (1)	11.0824(1)	7.4009(1)
b (Å)	13.4614 (3)	13.7811(2)	18.5613 (3)
c (Å)	21.3473 (4)	8.6341(2)	9.8967 (2)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V ($Å^3$)	2231. 90 (7)	1318.67 (4)	1359.51 (4)
Z	8	4	4
*d*calc (g cm^{-3})	1.353	1.286	1.355
Absorption coefficient(mm^{-1})	0.258	0.226	2.040
Crystal size (mm)	0.37 x 0.23 x 0.21	0.30 x 0.25 x 0.18	0.20 x 0.10 x 0.08
Θ range for data collection	1.91 to 27.49	2.78 to 27.48	4.76 to 69.38
Index Ranges	-10≤h≤10 -17≤k≤17 -27≤l≤27	-14≤h≤14 -17≤k≤17 -11≤l≤11	-8≤h≤7 -22≤k≤22 -11≤l≤11
Reflections collected/ unique	4759 / 2557 [R(int)= 0.0235]	2853/1575 [R(int)= 0.0126]	18092 / 1289 [R(int)= 0.0358]
Goodness-of-fit on F^2	1.055	1.069	1.105
R [$I > 2\sigma(I)$]	0.0366	0.0382	0.0310
*wR*2 (all data)	0.1021	0.1106	0.0898

Thermal ellipsoid plots with 50% probability are shown below.

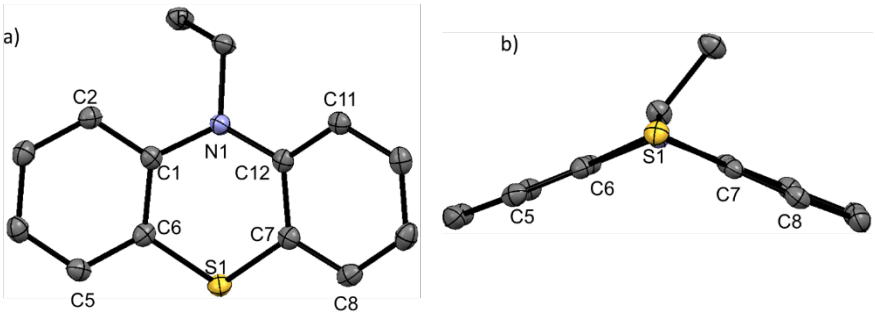


Fig. S1 Thermal ellipsoid plots for *N*-ethylphenothiazine with 50% probability top view (a) and side view (b) along the S–N line. Hydrogen atoms were omitted for clarity.

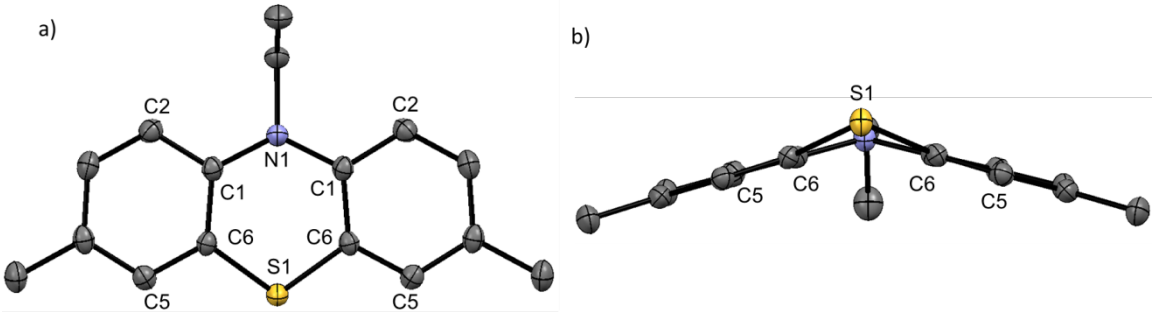


Fig. S2 Thermal ellipsoid plots for 3,7-dimethyl-*N*-ethylphenothiazine with 50% probability topview (a) and sideview (b) along the S–N line. Hydrogen atoms were omitted for clarity.

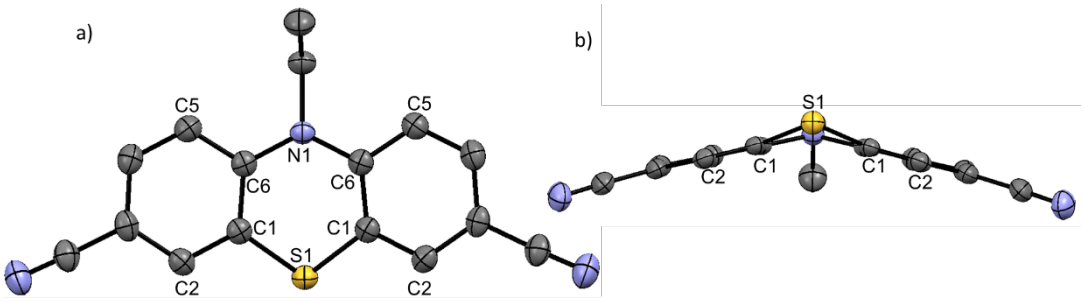


Fig. S3 Thermal ellipsoid plots for 3,7-dicyano-*N*-ethylphenothiazine with 50% probability topview (a) and sideview (b) along the S–N line. Hydrogen atoms were omitted for clarity.

Fused phenothiazine rings for EPT, DMeEPT, and DCNEPT are nonplanar and almost butterfly-like structures due to folding along S–N line. This so-called butterfly conformation is characteristic for neutral phenothiazine-based compounds.[4-8] The folded conformation of EPT has dihedral angles (Φ) of 134.60° and 143.09° whereas folded conformation of DMeEPT has Φ of 149.87° and 147.94° and DCNEPT has Φ of 153.57° and 151.39°. Substitution of EPT

increases the planarity of the center ring, which is also depicted in Table S2 by selected interatomic distances and angles.

Table S2. Selected interatomic distances and angles for EPT, DMeEPT, and DCNEPT crystals.

	EPT	**DMeEPT**	**DCNEPT**
S···N distance (Å)	2.954	3.011	3.038
Bond length (Å)	1.4188 (19) [C1-N1] 1.4163 (19) [N1-C12]	1.411 (15) [C1-N1]	1.3985 (15) [C6-N1]
Bond length (Å)	1.7649 (16) [C6-S1] 1.7654 (16) [S1-C7]	1.762 (14) [C6-S1]	1.760 (1) [C1-S1]
Bond Angle (°)	116.76 (12) [C12-N1-C1]	120.58 (15) [C1-N1-C1^{a}]	121.57 (14) [C6^{b} -N1-C6]
Bond Angle (°)	97.59 (7) [C6-S1-C7]	98.71 (9) [C6^{a} -S1-C7]	99.11 (8) [C1-S1-C1^{b}]
Torsion Angle (°)	45.30 (19) [C1-N1-C12-C7]	32.4 (2) [C1^{a} -N1-C1-C6]	28.5 (2) [C6^{b} -N1-C6-C1]
Torsion Angle (°)	40.00 (13) [C7-S1-C6-C1]	37.22 (13) [C7-S1-C6-C1]	34.16 (13) [C1-S1-C1^{b}-6^{b}]
Torsion Angle (°)	134.60 (15) [C12-N1-C1-C2]	149.87 (12) [C1-N1-C1^{a} -C2^{a}]	153.37 (10) [C6 -N1-C6^{b}-C5^{b}]
Torsion Angle (°)	143.09 (13) [C6-S1-C7-C8]	147.94 (13) [C6^{a} -S1-C6-C5]	151.39 (7) [C1^{b} -S1-C1-C2]
Torsion Angle (°)	16.9 (2) [C13-N1-C12-C11]	5.1 (2) [C8-N1-C1-C2]	10.6 (2) [C7-N1-C6-C5]

[a,b] Symmetry code : x, -y+1/2, z.

IV. Computational Methods

DFT calculations were performed with Gaussian 09.[9] Molecular geometries were optimized first by the semi-empirical quantum chemical method PM3.[10] Then density functional theory (DFT) was used for further optimization of geometry using Becke's three parameter exchange functional (B3)[11] in combination with Lee, Yang, and Parr's (LYP)[12] correlation functions on the basis set of 6-31G(dp). Calculations were performed in the gas phase for neutrals (B3LYP) and for radical cations (UB3LYP) where an unrestricted formalism was applied. Adiabatic ionization potentials (IP) were obtained in the gas phase from the total energy differences between the optimized structures of neutral and charged (radical cation) species.

V. Cyclic Voltammetry

Cyclic voltammetry (CV) experiments were performed using a CH Instruments 600D potentiostat using a three-electrode system in 0.1 M nBu$_4$NPF$_6$ in dry dichloromethane (DCM) containing ca. 3.0 x 10^{-4} M analyte. Glassy carbon was used as the working electrode, platinum wire as the

counter electrode, and freshly anodized Ag/AgCl as the reference electrode. Decamethylferrocene (Cp^*_2Fe, $E_{1/2}^{+/0}$= -0.55 V vs. $Cp_2Fe^{+/0}$ at 0 V) was added to each sample as an internal standard. CV was also performed in the battery electrolyte 1.2 M $LiPF_6$ in EC/EMC (3:7 wt.%) with glassy carbon as the working electrode, platinum as the counter electrode, and lithium as the reference electrode in an argon-filled glovebox. Cp^*_2Fe was added as an internal standard, and peaks were referenced to $Li^{+/0}$ at 0 V. All voltammograms were recorded at scan rates of 100 mV/s, and multiple scans were performed for each sample.

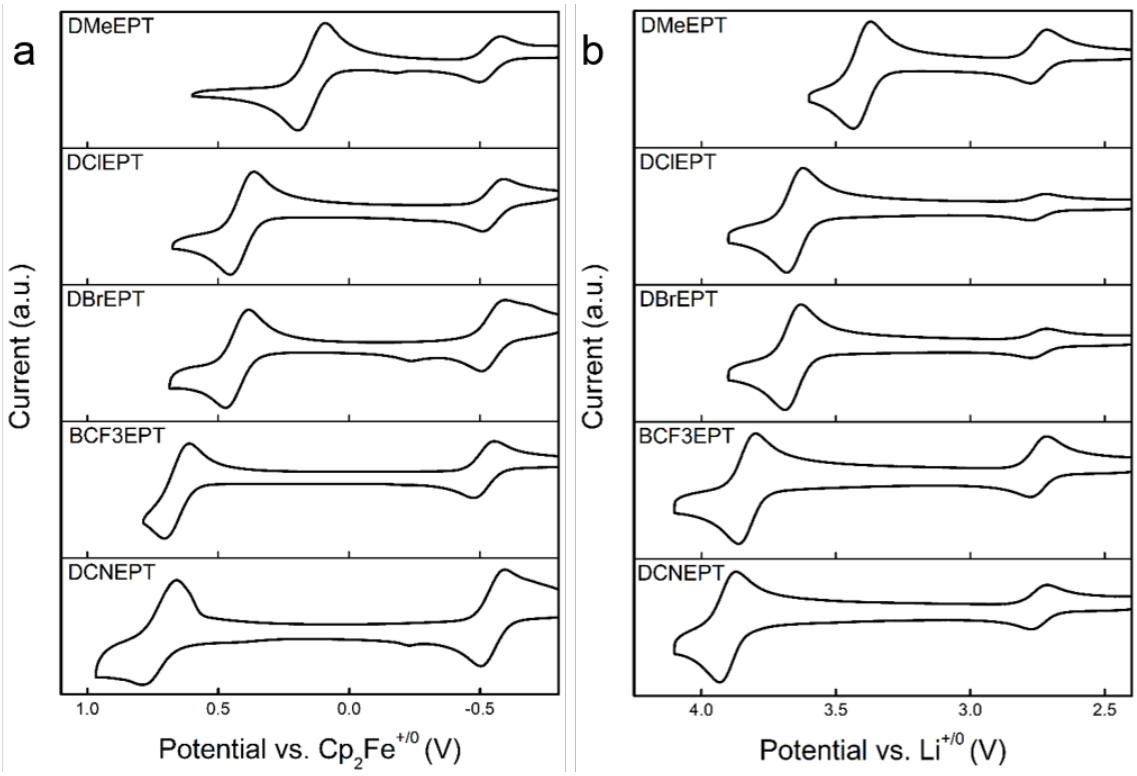


Figure S5. Cyclic voltammograms of EPT derivatives in 0.1 M nBu$_4$NPF$_6$ in dichloromethane with 100 mV/s scan rate and Cp_2*Fe as the internal standard calibrated to $Cp_2Fe^{+/0}$ at 0 V (a) and in 1.2 M $LiPF_6$ in EC/EMC (3:7 wt.%) vs. $Li^{+/0}$ at 0 V with a scan rate of 100 mV/s and Cp_2*Fe as the internal standard (b).

VI. Battery Cycling

All battery electrolyte components; ethylene carbonate, ethyl methyl carbonate, and lithium hexafluorophosphate were battery grade and were purchased from BASF Corporation (NJ, USA). Overcharge tests were conducted with 2032 coin cells using $LiFePO_4$ (Piotrek, Japan) as cathode and synthetic graphite (Gen-2, Argonne National Laboratory) as anode. Gen-2 anode is composed of 92 wt.% MAG-10 graphite (Hitachi) as the active material and 8 wt.% polyvinylidene flouride (PVDF) as the binder. The electrolyte was 1.2 M $LiPF_6$ in EC/EMC (3:7 wt.%). Coin cells were prepared in an argon-filled glovebox. A Maccor 4200 battery cycler was used for performing the cycling procedure. The coin cells were charged with constant current C/10 for 20 h (100% overcharge) or until a specific upper voltage (5.0 V) was reached. If the voltage of the coin cell does not reach 5.0 V after 20 h, the charging step was followed by a 30 s rest followed by

discharging to 3.0 V with constant current of C/10. Cycling of coin cells that reached 5.0 V was stopped. Selected cycles for 100% overcharge experiments are shown in Figure S6.

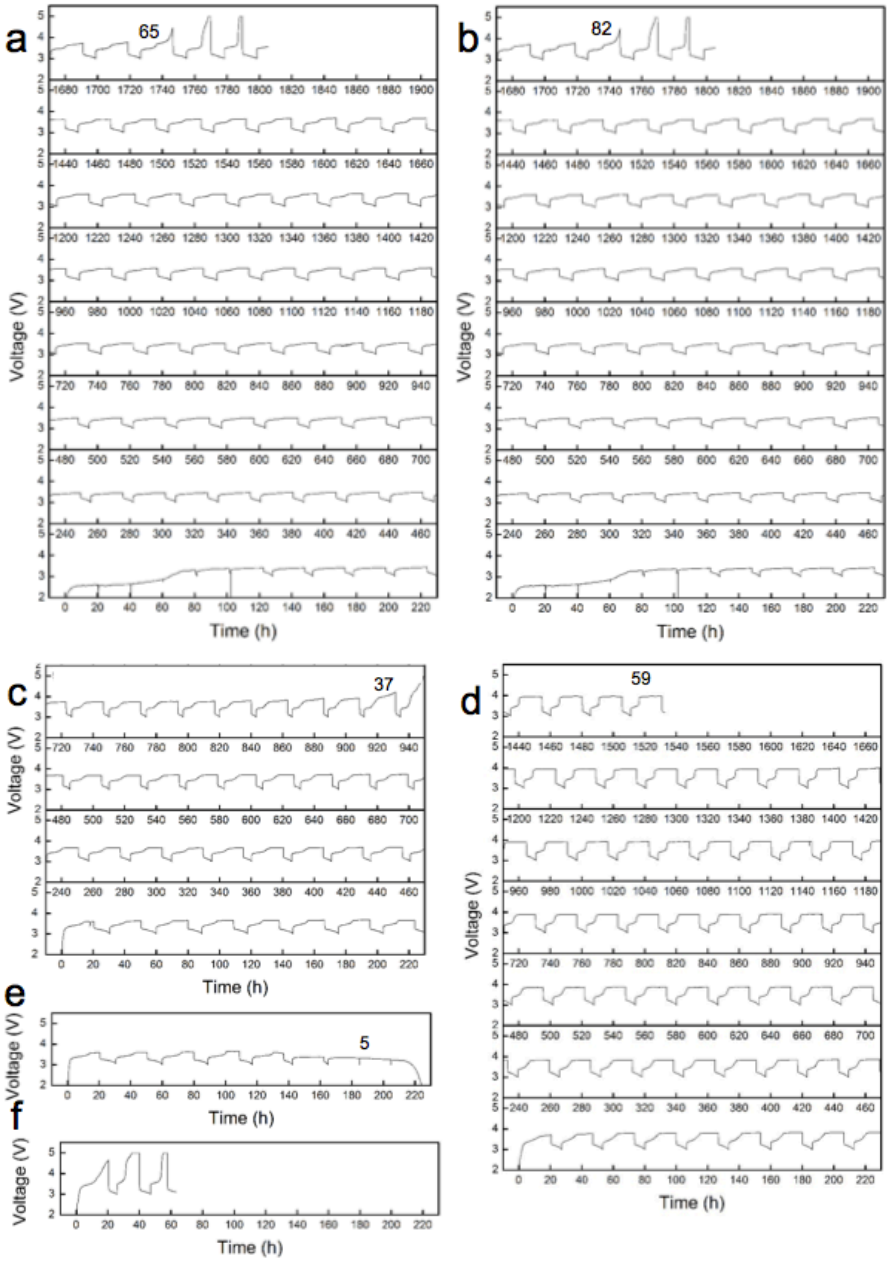


Figure S6. Overcharge cycling plots for selected batteries in potential vs. time, specifically for synthetic graphite/$LiFePO_4$ coin cells containing 0.08 M EPT (a), DMeEPT (b), DClEPT (c), DBrEPT (d), BCF3EPT* (e), and DCNEPT (f) as redox shuttle in 1.2 M $LiPF_6$ EC/EMC (3:7 wt.%). (*note: the BCF3EPT batteries are still running as of the submission date of this manuscript)

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