Supporting Information for

Overcharge Protection of Lithium-Ion Batteries Above 4 V with a Perfluorinated Phenothiazine Derivative

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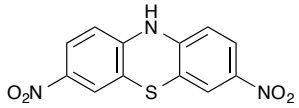
I. Synthesis and Characterization

Overall Experimental

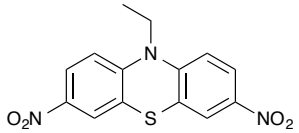
Bromoethane, copper(I) oxide, bromine, anhydrous *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), charcoal, and 1,4-dioxane were purchased from Sigma Aldrich. Phenothiazine and copper iodide were obtained from Acros Organics. Sodium hydride, sodium acetate, and acetic acid were purchased from Alfa Aesar. Pentafluorothiophenol and sodium pentafluoropropionate were purchased from Oakwood Chemical, iron powder from Mallinckrodt Pharmaceuticals, 2,3,4,5-tetrafluoroaniline from AK Scientific, potassium hydroxide and celite from Fisher Scientific, and ethanol from Decon Labs. All reagents were used without further purification.

Silica gel (65×250 mesh) was purchased from Sorbent Technologies, and solvents for purification were purchased from VWR International. ^{1}H, ^{19}F and ^{13}C NMR spectra were obtained on 400 MHz Varian NMR spectrometers in DMSO-d_6, acetone-d_6 or $CDCl_3$ purchased from Cambridge Isotope Laboratories. ^{19}F NMR spectra were recorded in $CDCl_3$ using hexafluorobenzene (Alfa Aesar) as an internal standard, and the chemical shifts are reported *vs.* $CFCl_3$ at 0 ppm by adjusting the shift of hexafluorobenzene to -164.9 ppm. 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.

Synthesis of DNO2EPT, BC2F5EPT, and OFEPT

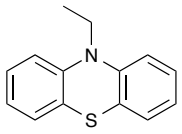


3,7-Dinitrophenothiazine. Glacial acetic acid (2 mL) was added to a suspension of phenothiazine (2.00 g, 10.1 mmol) in chloroform (10 mL) in a 100 mL round-bottomed flask containing a stir bar. Sodium nitrite (2.80 g, 40.6 mmol) was added to the reaction mixture in multiple portions over 20 min, after which more glacial acetic acid (4 mL) was added in order to maintain vigorous stirring. After 1 h, the reaction mixture was filtered to isolate the product as a red solid, which was washed with chloroform and air-dried. The isolated red solid (1.33 g) was largely insoluble in most organic solvents. ^{1}H NMR of the crude product in DMSO-d_6 is consistent with the formation of the desired dinitrated product with ca. 10% of mononitrated product. The crude product was used without purification in the next step. Major product: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (dd, J = 2.0 Hz, 8.4 Hz, 2H), 7.74 (d, J = 2.4 Hz, 2H), 6.72 (d, J = 9.2 Hz, 2H).

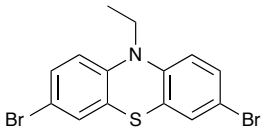


***N*-Ethyl-3,7-dinitrophenothiazine**. Crude 3,7-dinitrophenothiazine (1.33 g, 4.58 mmol) was dissolved in anhydrous DMF (50 mL) in a 250 mL round-bottomed flask containing a stir bar, which was then fitted with a rubber septum under dry N_2. Sodium hydride (60% dispersion in mineral oil, 0.301 g, 7.50 mmol)

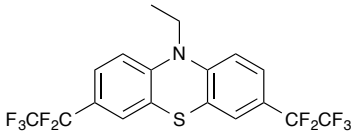
was added at rt, upon which the solution became green in color. Bromoethane (2.4 mL, 33 mmol) was added to the reaction mixture, and the reaction flask was immersed in an oil bath and heated to 60 °C. The reaction mixture was stirred for 6 h before the reaction flask was removed from the oil bath. The mixture was then allowed to cool to rt and was diluted with water to precipitate the crude product. The crude material was purified by column chromatography with silica gel, eluting with ethyl acetate/hexanes (1:4) to afford 0.296 g (9% over 2 steps) of the desired compound as a red solid. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.52-8.55 (m, 2H), 8.41 (m, 2H), 7.72-7.74 (m, 2H), 4.65 (q, J = 6.4 Hz, 2H), 1.91 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ 150.1, 145.0, 125.5, 124.6, 123.6, 117.2, 44.6, 13.3. GCMS: *m/z* 317 (100%), 302 (17%), 288 (68%), 271 (17%), 242 (35%), 225 (14%), 196 (32%). Anal. calcd. for $C_{14}H_{11}N_3O_4S$ C, 52.99; H, 3.49; N, 13.24. Found C, 52.68; H, 3.36; N, 12.77.



***N*-Ethylphenothiazine**. This compound was prepared from phenothiazine as previously described.[1]



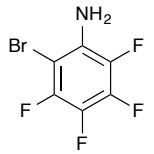
3,7-Dibromo-*N*-ethylphenothiazine. This compound was prepared from *N*-ethylphenothiazine as previously described.[1]



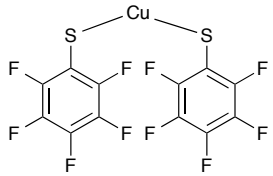
***N*-Ethyl-3,7-bis(pentafluoroethyl)phenothiazine**. 3,7-Dibromo-*N*-ethyl-phenothiazine (0.387 g, 1.00 mmol), copper (I) iodide (1.33 g, 7.01 mmol), and sodium pentafluoropropionate (0.745 g, 4.05 mmol) were dissolved in anhydrous NMP (10 mL) in a 100 mL round-bottomed flask containing a stir bar and fitted with a rubber septum. The reaction mixture was sparged with N_2 for 15 min as the reaction flask was immersed in an oil path programmed to heat to 150 °C. The reaction mixture was stirred under N_2 at 150 °C for 48 h. Upon completion, the reaction flask was removed from the oil bath and allowed to cool to rt. The reaction mixture was poured into a mixture of hexane and celite and then filtered to remove solids. The filtrate was then washed with brine, dried over $MgSO_4$, and filtered again to remove solids. The crude product concentrated by rotary evaporation and was purified by column chromatography with silica gel using 100% hexanes, which afforded 0.205 g (45%) of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, J = 1.6, 8.4 Hz, 2H), 7.28 (d, J = 1.6 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 3.96 (q, J = 6.8 Hz, 2H), 1.43 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 126.3 (t, J = 6.1 Hz), 125.6 (t, J = 6.1 Hz), 124.4, 123.5 (t, J = 25.2 Hz), 119.3 (tq, J = 39.6, 284.6 Hz), 115.2, 113.4 (qt, J = 38.2, 253.3 Hz), 42.6, 12.8. GCMS: *m/z* 463 (67%), 434 (100%), 416 (11%), 394 (11%), 365 (29%), 296 (43%). Anal. calcd. for $C_{18}H_{11}F_{10}NS$ C, 46.66; H, 2.39; N, 3.02. Found C, 46.87; H, 2.25; N, 3.06.

1,2,3,4,6,7,8,9-Octafluorophenothiazine was synthesized following a reported procedure with slight modifications in work-up conditions as described in the following sections.[2, 3]

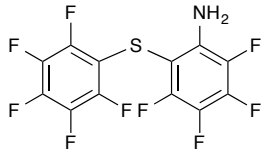
***N*-ethyl-1,2,3,4,6,7,8,9-Octafluorophenothiazine** (OFEPT) was then synthesized by *N*-ethylation of octafluorophenothiazine following a previously reported procedure.[4]



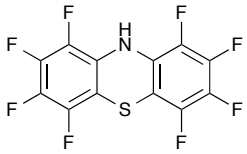
2-Bromo-3,4,5,6-tetrafluoroaniline. 2,3,4,5-tetrafluoroaniline (2.50 g, 15.1 mmol) and acetic acid (10 mL) were added under N_2 to a 100 mL round-bottomed flask containing a stir bar and fitted with a rubber septum. After dissolution of 2,3,4,5-tetrafluoroaniline, Fe powder (0.085 g, 1.5 mmol) and sodium acetate (1.37 g, 16.7 mmol) were added, and the reaction flask was immersed in an oil bath set at 50 °C. A solution of bromine (1.1 mL, 21 mmol) in acetic acid (10 mL) was added dropwise to the reaction mixture, which was stirred for 3 h under N_2 before the flask was removed from the oil bath. After the reaction mixture reached rt, the reaction was quenched by adding sodium sulfite (0.20 g, mmol) and aqueous potassium hydroxide (0.20 g in 50 mL water), after which the solution was stirred for 5 min. The product was extracted with dichloromethane, dried over $MgSO_4$, filtered to remove solids, and concentrated by rotary evaporation to obtain the desired product as reddish pink solid (3.20 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 (br s, NH_2). ^{19}F NMR (400 MHz, $CDCl_3$) δ -135.9 (m, 1 F), -161.0 (m, 1F), -162.6 (m, 1F), -174.0 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ multiple peaks in these ranges: 146.8-130.9, 91.0-91.7. GCMS: *m/z* 243 (100%), 164 (25%), 137 (46%).



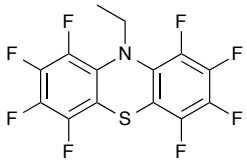
Bis(2,3,4,5,6-pentafluorothiophenolate) copper(II). Pentafluorothiophenol (2.0 mL, 3.0 g, 15 mmol) was added to a stirred suspension of Cu_2O (1.07 g, 7.50 mmol) in ethanol (22 mL) in a 50 mL round-bottomed flask containing a stir bar and equipped with a reflux condenser. The suspension was immersed in a heated oil bath and was stirred at reflux for 5 h. After removal of the reaction flask from the oil bath and cooling to rt, the reaction mixture was filtered and dried to obtain the product as an off-white solid (4.5 g, 65%). ^{19}F NMR (400 MHz, $CDCl_3$) δ -134.4 (m, 4F), -150.8 (m, 4F), -162.5 (m, 2F).



2-Amino-nonafluorodiphenyl sulfide. In an oven-dried 50 mL round-bottomed flask containing a stir bar and fitted with a rubber septum, 2-bromo-3,4,5,6-tetrafluoroaniline (3.00 g, 12.3 mmol), cuprous pentafluorothiophenolate (3.40 g, 7.38 mmol), and anhydrous DMF (12 mL) were combined under N_2. The reaction flask was equipped with a reflux condenser and immersed in a heated oil bath. The reaction mixture was stirred at reflux for 2 h under N_2. The reaction flask was then removed from the oil bath and allowed to cool to rt, after which the reaction mixture was poured into water. The aqueous mixture was extracted with diethyl ether. The organic layer was dried and concentrated by rotary evaporation to obtain the product as a dark violet solid (3.80 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (br s, NH_2). ^{19}F NMR (400 MHz, $CDCl_3$) δ -134.2 (m, 1F), -135.1 (m, 2F), -153.6 (m, 1F), -155.8 (m, 1F), -163.0 (m, 3F), -174.5 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ multiple peaks in these ranges: 150.3-131.8, 107.1-98.5. GCMS: *m/z* 363 (100%), 196 (40%).



1,2,3,4,6,7,8,9-Octafluorophenothiazine. In an oven-dried 100 mL round-bottomed flask containing a stir bar, 2-amino-nonafluorodiphenyl sulfide (3.20 g, 8.81 mmol) and 1,4-dioxane (40 mL) were combined, creating a suspension. The flask was fitted with a rubber septum, and sodium hydride (60% dispersion in mineral oil, 0.70 g, 18 mmol) was added under N_2. The reaction flask was then equipped with a reflux condenser and immersed in a heated oil bath. The reaction mixture was refluxed for 4 h under N_2, after which it was cooled to rt and filtered. The isolated precipitate was dissolved in diethyl ether, and the solution was washed with water, dried over $MgSO_4$, filtered to remove solids, and distilled under vacuum to obtain a grey solid (2.00 g, 67%). The product was crystallized from petroleum ether, obtaining white crystals suitable for analysis by single-crystal X-ray diffraction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (br s, NH). ^{19}F NMR (400 MHz, $CDCl_3$) δ -142.0 (m, 1F), -160.0 (m, 1F), -164.0 (m, 1F), -167.2 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ multiple peaks in these ranges: 145.1-135.7, 124.7 (d, J = 12.3 Hz), 101.3 (dd, J = 3.9, 16.8 Hz). GCMS: *m/z* 343 (100%), 311 (86%).



***N*-Ethyl-1,2,3,4,6,7,8,9-octafluorophenothiazine**. An oven-dried 50 mL round-bottomed flask containing a stir bar was fitted with a rubber septum and cooled to rt under N_2. Octafluorophenothiazine (0.50 g, 1.5 mmol) and anhydrous DMF (10 mL) were added under N_2 to the reaction flask, which was immersed in an oil bath set at 30 °C. After 10 min, sodium hydride (60% dispersion in mineral oil, 0.12 g, 3.0 mmol) was added to the reaction mixture. A reflux condenser was attached and the temperature of the oil bath was raised to 50 °C. After 20 min at this temperature, bromoethane (0.17 mL, 2.3 mmol) was added dropwise through the condenser. The reaction mixture was stirred under continuous heat and N_2 for 6 h. Reaction progress was monitored by GCMS and TLC with hexanes/ethyl acetate (10:1) as the eluent. Upon consumption of the starting material, the reaction flask was removed from the oil bath and allowed to cool to rt, after which the reaction mixture was poured into ice water and the organic product extracted with ethyl acetate. After drying over $MgSO_4$ and treatment with charcoal, the organic layer was filtered to remove solids and was concentrated by rotary evaporation. The crude material was purified via column chromatography with silica gel using hexanes as the eluent, yielding a white solid (0.25 g, 45%). The product was further purified by crystallization from petroleum ether, resulting in white crystals suitable for analysis by single-crystal X-ray diffraction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (q, J = 7.1 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{19}F NMR (400 MHz, $CDCl_3$) δ -142.1 (m, 1F), -151.0 (m, 1F), -159.2 (m, 1F), -163.4 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ multiple peaks in these ranges: 144.4-136.9, 129.2 (d, J = 10.7 Hz), 113.8 (d, J = 18.4 Hz), 50.1 (t, J = 5.7 Hz), 14.5. GCMS: *m/z* 371 (43%), 342 (100%), 310 (29%). Anal. calcd. for $C_{14}H_5F_8NS$ C, 45.29; H, 1.36; N, 3.77. Found C, 45.51; H, 1.30; N, 3.84.

II. Crystal Structures

X-ray diffraction data was collected at 90K on a Bruker-Nonius X8 Proteum diffractometer. Crystal indexing and data processing were performed with Bruker APEX2 software. The structures were solved with shelxt[5] and refined with shelxl-2014.[6]

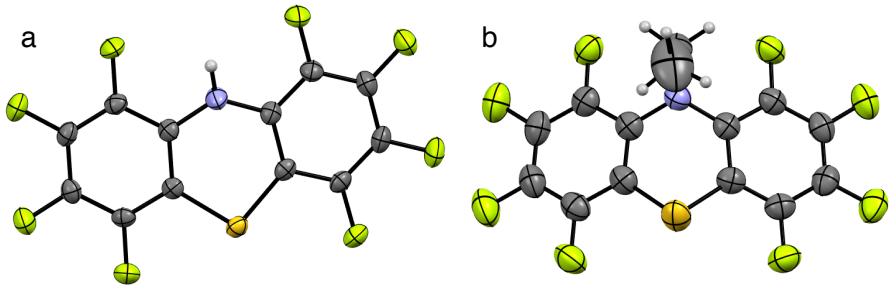


Figure S1. Thermal ellipsoid plots for the OFPT (a) and OFEPT (b) obtained by single crystal X-ray diffraction.

III. Cyclic Voltammetry

Cyclic voltammetry (CV) experiments were performed in an argon-filled glovebox using a three-electrode system with a CH Instruments 650E potentiostat. Glassy carbon was used as the working electrode, platinum wire as the counter electrode, and lithium metal as the reference electrode. Voltammograms were recorded in 1.2 M $LiPF_6$ in EC/EMC (3:7 wt. ratio) containing ca. 3.0 x 10^{-4} M analyte at a scan rate of 100 mV/s.

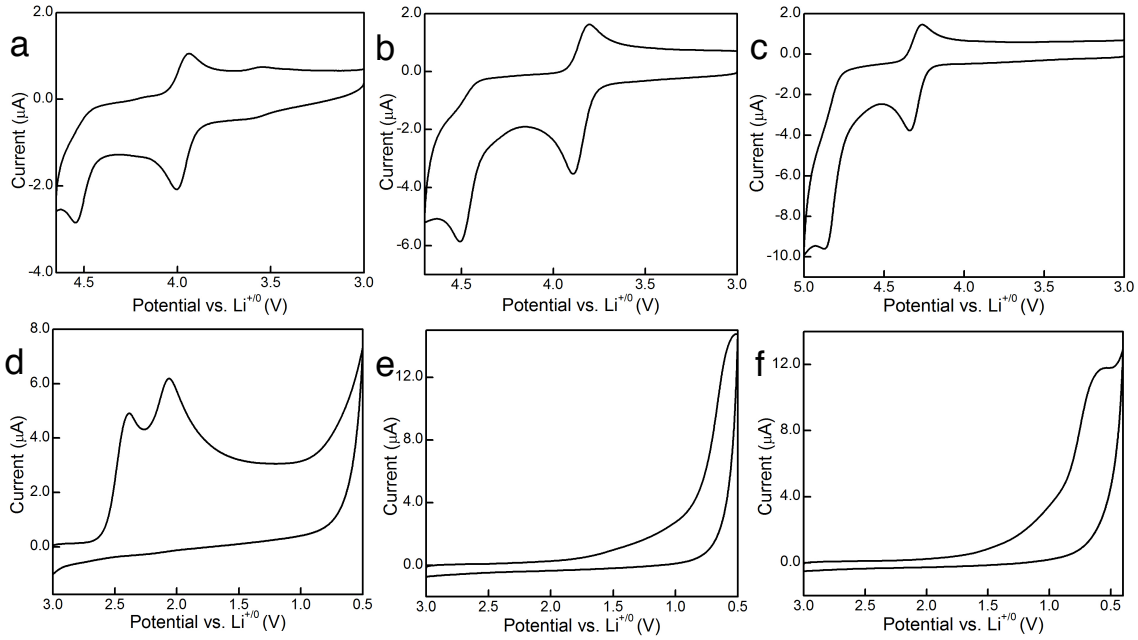


Figure S2. Cyclic voltammograms of DNO2EPT (a,d), BC2F5EPT (b,e), and OFEPT (c,f) at 0.3 mM in 1.2 M $LiPF_6$ in EC/EMC (3:7 wt. ratio) recorded at a scan rate of 100 mV/sec showing irreversible second oxidations in some cases (a, b, and c) and irreversible reductions in others (d, e, and f).

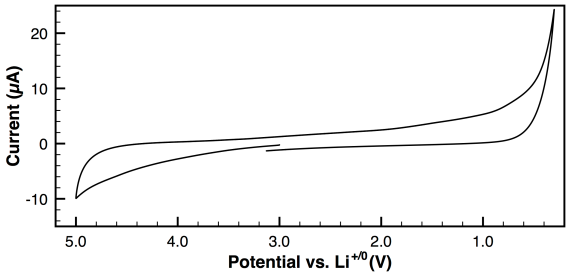


Figure S3. Cyclic voltammogram of 1.2 M $LiPF_6$ in EC/EMC (3:7 wt. ratio) recorded at a scan rate of 100 mV/sec.

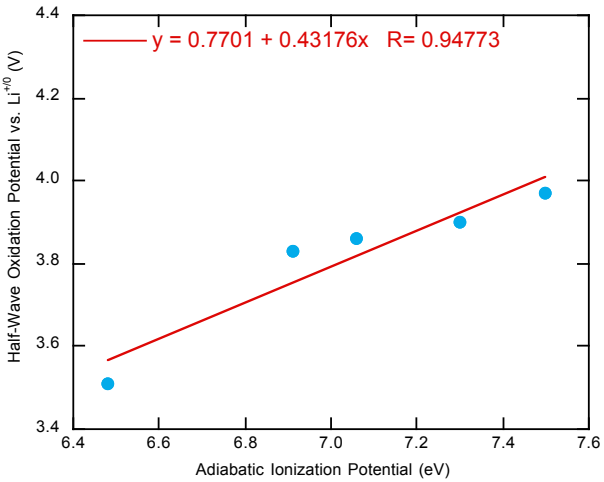


Figure S4. A plot of half-wave oxidation potentials for the first oxidation event for redox shuttle candidates EPT, BCF3EPT, BC2F5EPT, DCNEPT, and DNO2EPT in 1.2 M $LiPF_6$ in EC/EMC (3:7 wt. ratio) recorded at a scan rate of 100 mV/sec vs. the adiabatic IPs calculated at the B3LYP/6-311G(d,p) level of theory.

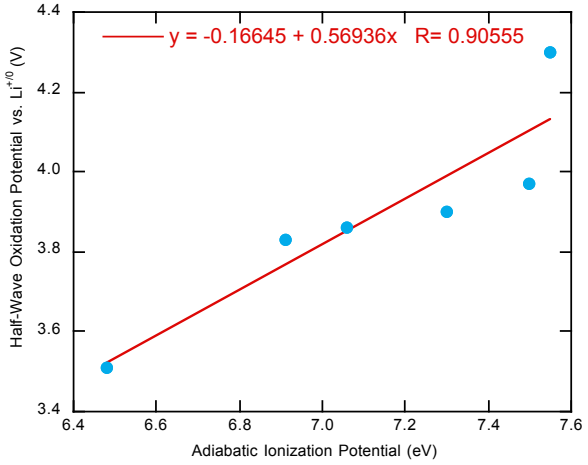


Figure S5. A plot of half-wave oxidation potentials for the first oxidation event for redox shuttle candidates EPT, BCF3EPT, BC2F5EPT, DCNEPT, DNO2EPT, and OFEPT in 1.2 M $LiPF_6$ in EC/EMC (3:7 wt. ratio) recorded at a scan rate of 100 mV/sec vs. the adiabatic IPs calculated at the B3LYP/6-311G(d,p) level of theory.

IV. Overcharge Protection

Overcharge tests were conducted by assembling 2032 coin cells in an argon-filled glovebox using $LiFePO_4$ (LFP, Piotrek or MTI) or $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA, Argonne National Laboratory's CAMP Facility) as the cathode and synthetic graphite (Gen-2 (MAG-10) or Gen-3 (MCMB), Argonne National Laboratory's CAMP Facility) as the anode. The electrodes were punched into 14 mm diameter circles and sandwiched around a 15 mm diameter microporous 2325 PP/PE/PP trilayer separator from Celgard. The electrolyte used was 1.2 M $LiPF_6$ in EC/EMC (3:7 wt. ratio), and ca. 85 µL was added to each coin cell. The coin cells were charged with a constant current of C/10 for 20 h or until 5.0 V was reached, followed by a rest of 30 s and discharging to 3.0 V (once again at C/10) using a Landt CT2001A battery cycler.

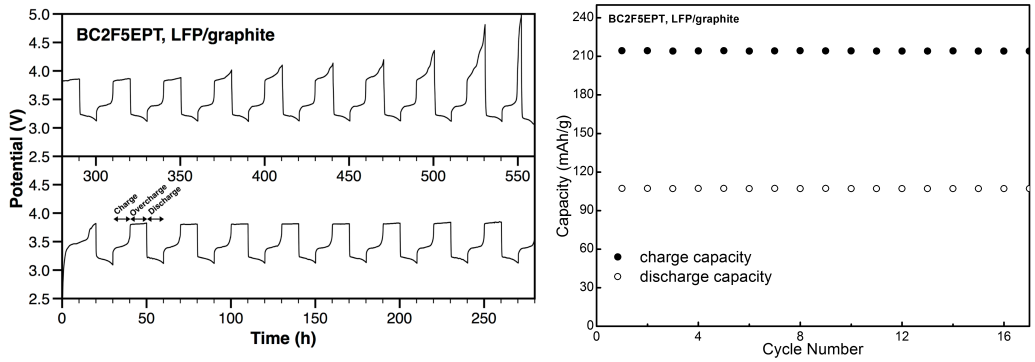


Figure S6. Potential vs. time (left) and capacity vs. cycle number (right) for 100% overcharge cycling of BC2FEPT in LFP/graphite coin cells. BC2FEPT was incorporated into 1.2 M $LiPF_6$ in EC/EMC (3:7 wt. ratio) at 0.08 M; 100% overcharge cycling was performed at a rate of C/10.

V. Density Functional Theory Calculations

All density functional theory (DFT) calculations were performed using the Gaussian09 (Revision A.02b) software suite.[7] Geometry optimizations of the neutral and radical-cation states were carried out with the B3LYP functional[8, 9] and 6-311G(d,p) basis set.[10, 11] Frequency analyses for all (fully relaxed) optimized geometries were undertaken to ensure that the geometries were energetic minima.

VI. References

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