Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information

A Fast, Inexpensive Method for Predicting Overcharge Performance in Lithium-Ion Batteries

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I. Synthesis

Tris(2,4-dibromophenyl)amine is the compound used in the synthesis of the chemical oxidant Magic Green. A thermal ellipsoid plot of the crystal structure of this compound is shown in Figure S1.

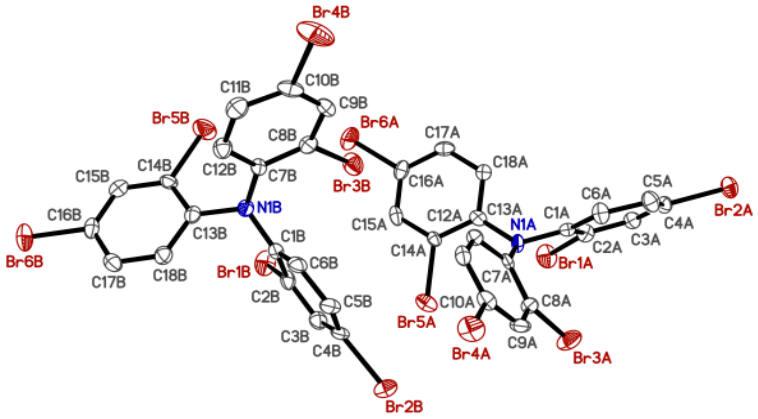

Figure S1. Thermal ellipsoid plot for tris(2,4-dibromophenyl)amine.

An EPR spectrum was recorded for Magic Green (Figure S2). The EPR spectrum indicates that a radical is present. The spectrum has no observable hyperfine coupling.

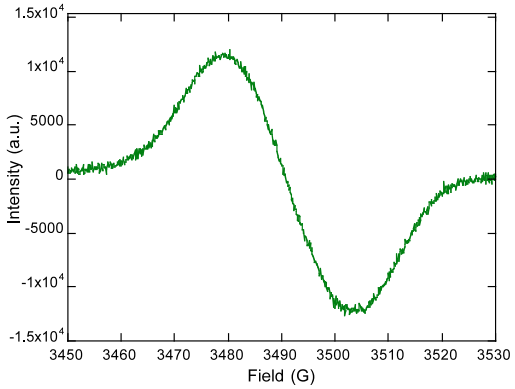

Figure S2. EPR spectrum of Magic Green in dichloromethane.

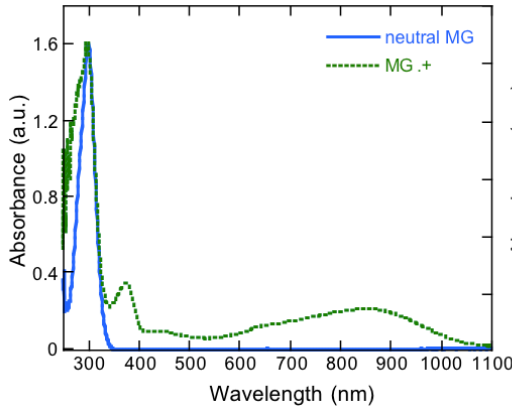

Figure S3. Absorption spectrum of the neutral (blue, solid) and radical cation (green, dotted) forms of Magic Green in dichloromethane.

II. Cyclic Voltammetry

Cyclic voltammograms shown below include decamethylferrocene (Cp^*_2Fe) as an internal reference.

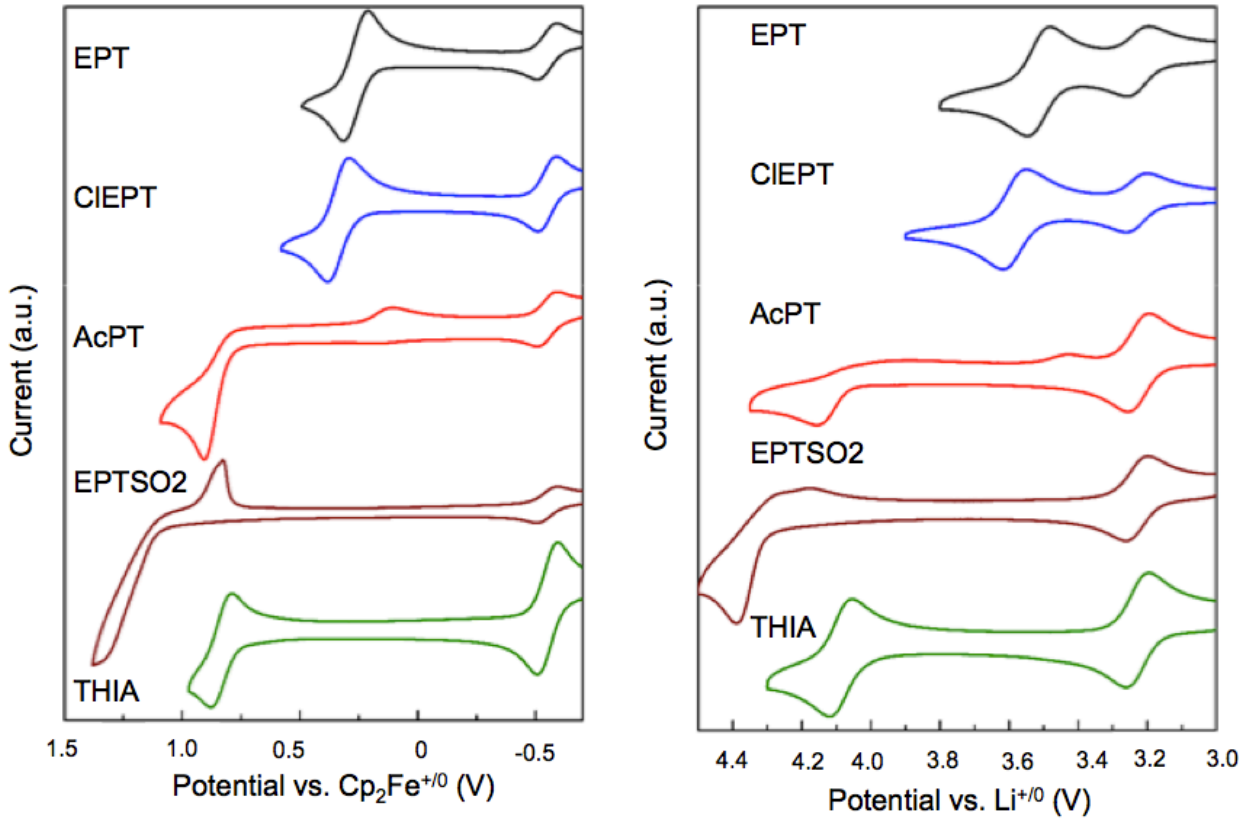

Figure S4. Cyclic voltammograms of EPT (black), ClEPT (blue), AcPT (red), EPTSO2 (maroon), and THIA (green) in 0.1 M nBu$_4$NPF$_6$ in dichloromethane (left) and 1.2 M LiPF$_6$ in EC/EMC (right) recorded at a scan rate of 100 mV/s, showing the $Cp^*_2Fe^{+/0}$ couple at -0.55 V vs $Cp_2Fe^{+/0}$ at 0 V and at 3.2 V vs $Li^{+/0}$ at 0 V.

Cyclic voltammetry of AcPT in 1.2 M $LiPF_6$ in EC/EMC (3/7) at different cycles shows a new peak that appears after the first scan. We think the compound producing this reversible oxidation is responsible in overcharge protection when AcPT is added to the electrolyte and are pursuing its identification.

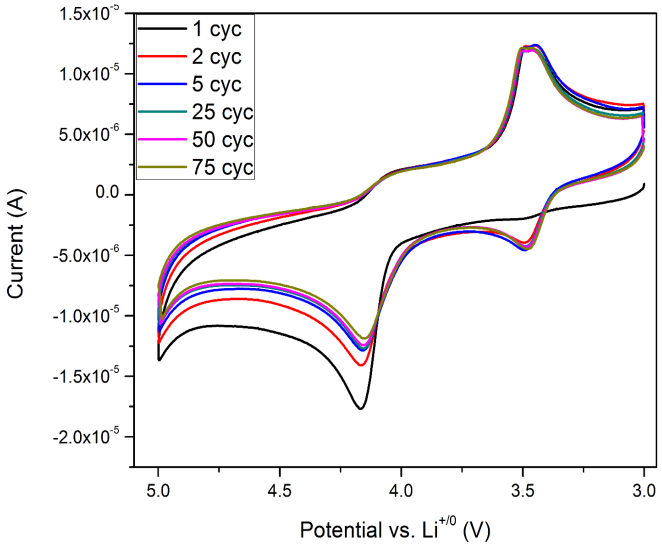

Figure S5. CV of AcPT 1.2 M $LiPF_6$ in EC/EMC (3/7) at different cycles.

III. UV-vis and EPR Spectroscopy

Table S1. The wavelength of the radical cation absorption for which decay was monitored in different solvents.

compound	λ monitored (nm)
EPT	516, 863
ClEPT	517, 860
AcPT	425, 739
EPTSO2	458, 832
THIA	550,1065

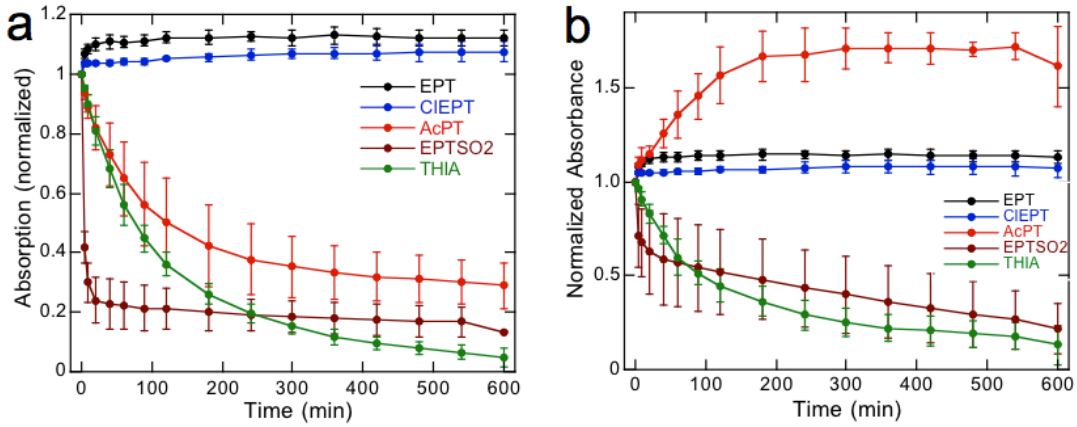

Figure S6. Normalized average absorbance of radical cations over time in the visible region (a) far-red region (b) in dichloromethane shown with error bars from three runs.

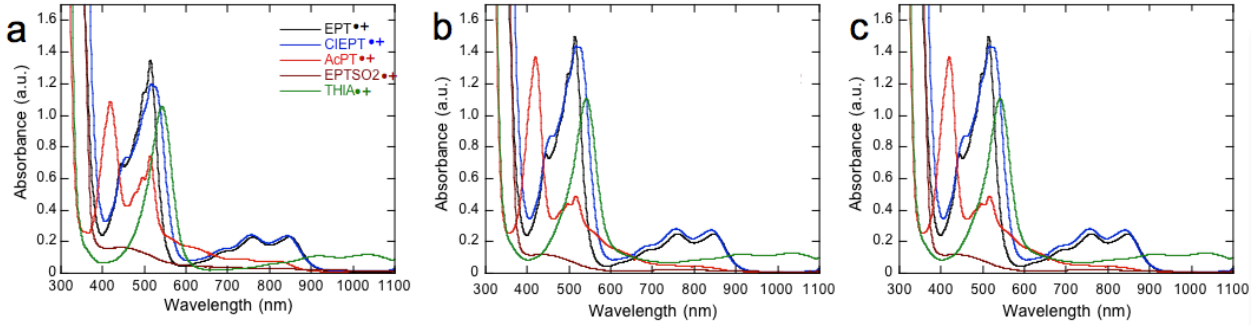

Figure S7. Absorption spectra of radical cations immediately after generation in the solvents dichloromethane (A), EC/EMC (B), and 1.2 M $LiPF_6$ in EC/EMC (C).

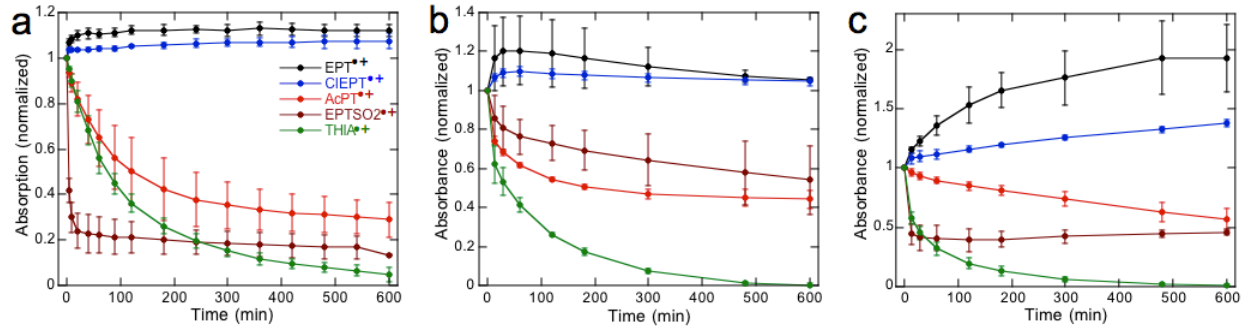

Figure S8. Average of normalized absorbance of radical cations over time in vis region with different solvents, dichloromethane (A), EC/EMC (B), and 1.2 M $LiPF_6$ in EC/EMC (C).

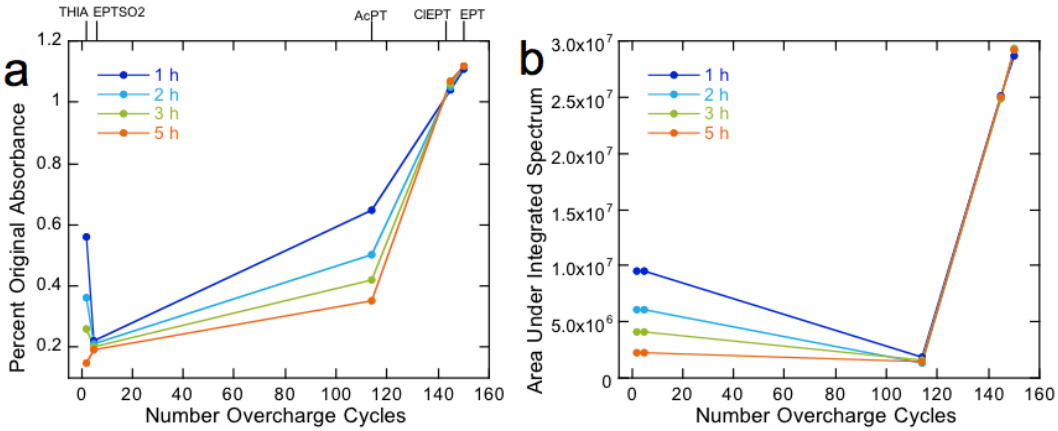

Figure S9. Plot of percent of original absorbance for the tallest peak in the UV-vis spectrum (a) and plot of area under integrated EPR spectrum (b) in DCM, each vs. the number of overcharge cycles reported for THIA, EPTSO2, AcPT, ClEPT, and EPT with $LiFePO_4$/LTO electrodes.