Supporting Information

High-Current-Density, Long-Duration Cycling of Soluble Organic Active Species for Non-Aqueous Redox Flow Batteries


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Figure S1. $^1$H NMR spectrum of MEPT in CDCl$_3$. 

1 Nuclear Magnetic Resonance Spectroscopy
Figure S2. $^{13}$C NMR spectrum of MEPT in CDCl$_3$. 
**Figure S3.** $^1$H NMR spectrum of MEEPT in CDCl$_3$. 
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Electron Paramagnetic Resonance Spectroscopy of Radical-Cation Salts

Figure S5. EPR spectra of (a) EPT-BF₄, (b) MEPT-BF₄, and (c) MEEPT-BF₄ salts in dichloromethane.
3 UV-vis Study of Radical-Cation Decay

3.1 Decay Study in Acetonitrile

Figure S6. Normalized intensity of UV-vis absorbance at 514 nm vs. time of 0.15 mM (a) EPT-BF$_4$, (b) MEPT-BF$_4$, and (c) MEEPT-BF$_4$ in ACN. Inset: data expanded between absorbance values of 0.9-1.05, recorded at 0, 1, 3, 5, and 24 h after dissolution.
### 3.2 Decay Study in Propylene Carbonate

**Figure S7.** UV-vis spectra of (a) EPT-BF$_4$, (b) MEPT-BF$_4$, and (c) MEEPT-BF$_4$ at 0.15 mM in PC, recorded at 0, 1, 3, 5, and 24 h after dissolution. Characteristic peaks appear at 317, 446, 515, 758, and 853 nm. Normalized intensity of UV-vis absorbance at 515 nm vs. time for 0.15 mM (d) EPT-BF$_4$, (e) MEPT-BF$_4$, and (f) MEEPT-BF$_4$ in PC. Insets for a-c: expansion of most intensely absorbing peak. Insets for d-f: data expanded for absorbance values between 0.8-1.05.
4 Cyclic Voltammetry

4.1 Cyclic Voltammetry with Ferrocene Reference and of the Full Potential Window

Figure S8. Cyclic voltammograms (cycle 1) of EPT (blue, top), MEPT (red, middle), and MEEPT (black, bottom) at 1 mM in 0.1 M TEABF₄ / ACN. (a) First positive couple of each active species with ~0.7 mM ferrocene internal reference. (b) Full potential window of the organic active species, indicating additional irreversible couples at 0.8 – 1.0 V vs. Fc/Fc⁺.
4.2 Cyclic-Voltammetry Scan-Rate Study

Figure S9. CV scan-rate dependence study for (a) EPT, (b) MEPT, and (c) MEEPT, and Randles-Sevcik construction (peak current vs. square root of scan rate) for the oxidative (anodic) waves of (d) EPT, (e) MEPT, and (f) MEEPT.
5 Bulk Electrolysis

5.1 Bulk-Electrolysis Cell Schematic

Figure S10. Photograph of the bulk-electrolysis cell, with relevant ports and electrodes labeled.
5.2 Potential vs. Capacity

Figure S11. Potential vs. capacity curves from bulk-electrolysis experiments showing cycles 2, 5, and 10 for each of (a) EPT, (b) MEPT, and (c) MEEPT at 5 mM in 1 M TEABF₄ / ACN. Theoretical capacities are 0.134 Ah L⁻¹ (0.469 mAh) for each experiment, and 10 cycles completed in 7 h.
5.3 Cyclic Voltammograms Before and After Cycling

**Figure S12.** Cyclic voltammograms (cycle 2) before and after 10 bulk-electrolysis cycles for (a) EPT, (b) MEPT, and (c) MEEPT at 5 mM in 1 M TEABF$_4$/ACN.
5.4 Quantitative Cyclic Voltammetry Analysis Before and After Cycling

**Table S1:** Quantitative CV characteristics of EPT, MEPT, and MEEPT before and after bulk electrolysis cycling. Tabulated values are calculated from the data available in Figure S12.

<table>
<thead>
<tr>
<th></th>
<th>Compound</th>
<th>$E_{1/2}^{0/+}$ (V vs. Fc/Fc$^+$)</th>
<th>Peak Separation (mV)</th>
<th>Peak Current Ratio</th>
<th>Peak Oxidative Current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Before Bulk Electrolysis</strong></td>
<td>EPT</td>
<td>0.284</td>
<td>65</td>
<td>1.050</td>
<td>34.7</td>
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<tr>
<td></td>
<td>MEPT</td>
<td>0.327</td>
<td>63</td>
<td>1.072</td>
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<td>MEEPT</td>
<td>0.327</td>
<td>63</td>
<td>0.991</td>
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<tr>
<td><strong>After Bulk Electrolysis</strong></td>
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<td>78</td>
<td>0.964</td>
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<tr>
<td></td>
<td>MEPT</td>
<td>0.327</td>
<td>70</td>
<td>1.005</td>
<td>33.2</td>
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<tr>
<td></td>
<td>MEEPT</td>
<td>0.324</td>
<td>76</td>
<td>1.004</td>
<td>30.5</td>
</tr>
</tbody>
</table>
6. Image of Assembled Flow Cell

Figure S13. Photograph of the assembled flow cell, connected to the pump and reservoirs.