Supporting Information

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

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Contents

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1 Nuclear Magnetic Resonance Spectroscopy

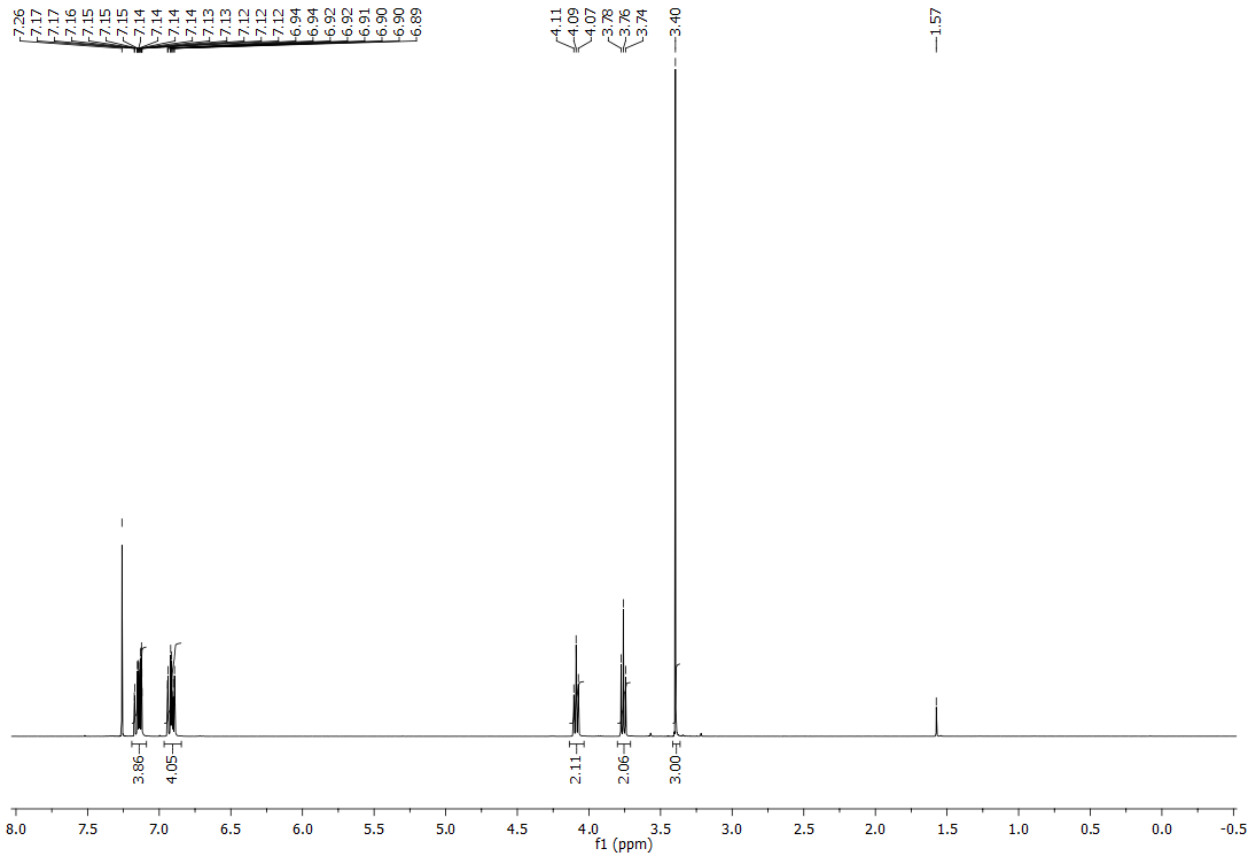

Figure S1. ^{1}H NMR spectrum of MEPT in $CDCl_3$.

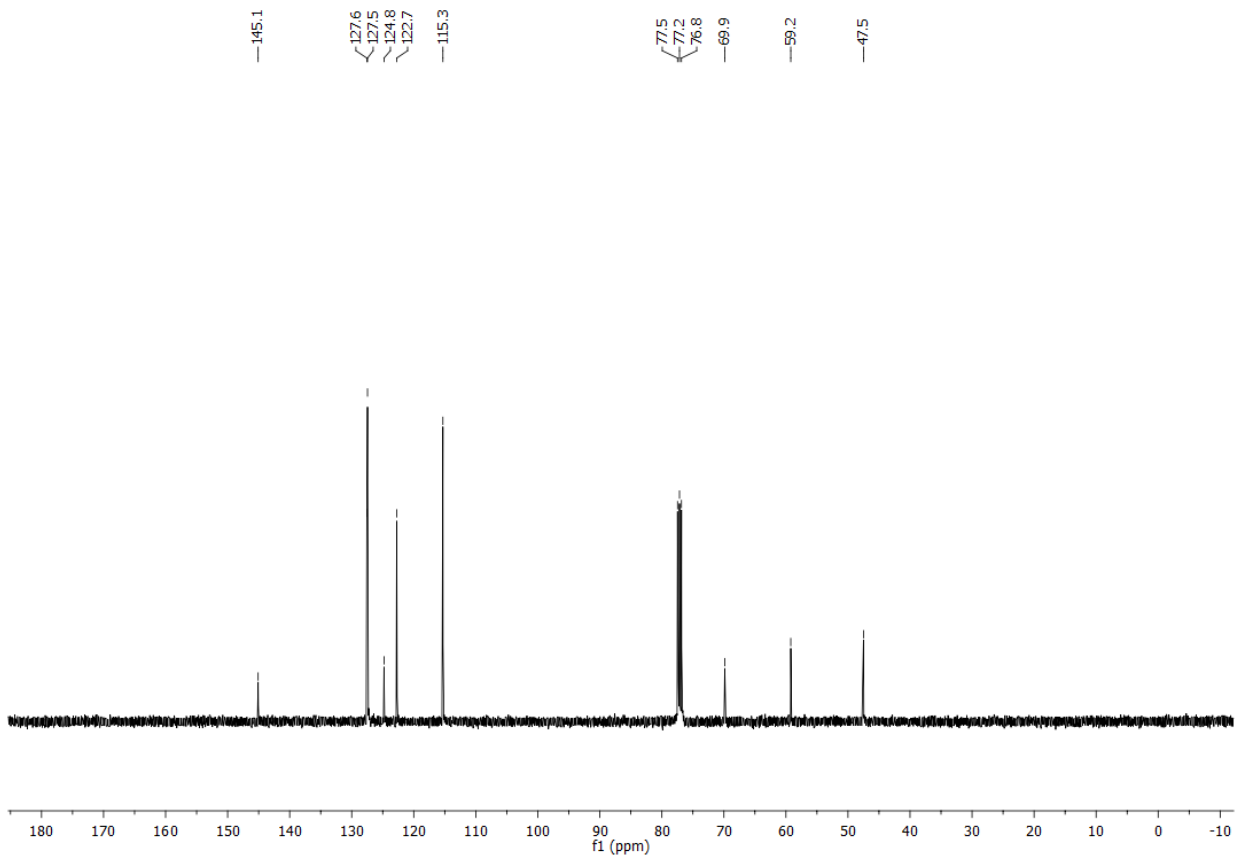

Figure S2. ^{13}C NMR spectrum of MEPT in $CDCl_3$.

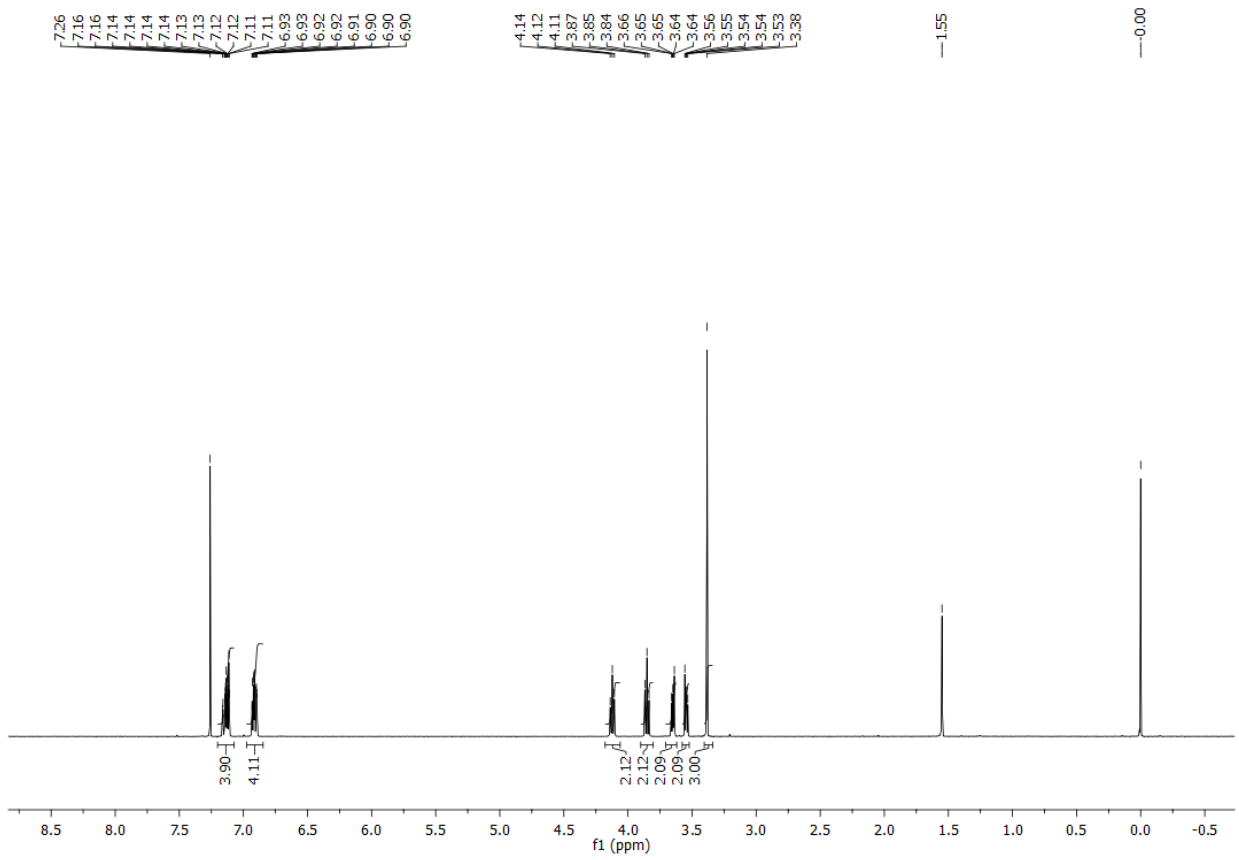

Figure S3. ^{1}H NMR spectrum of MEEPT in $CDCl_3$.

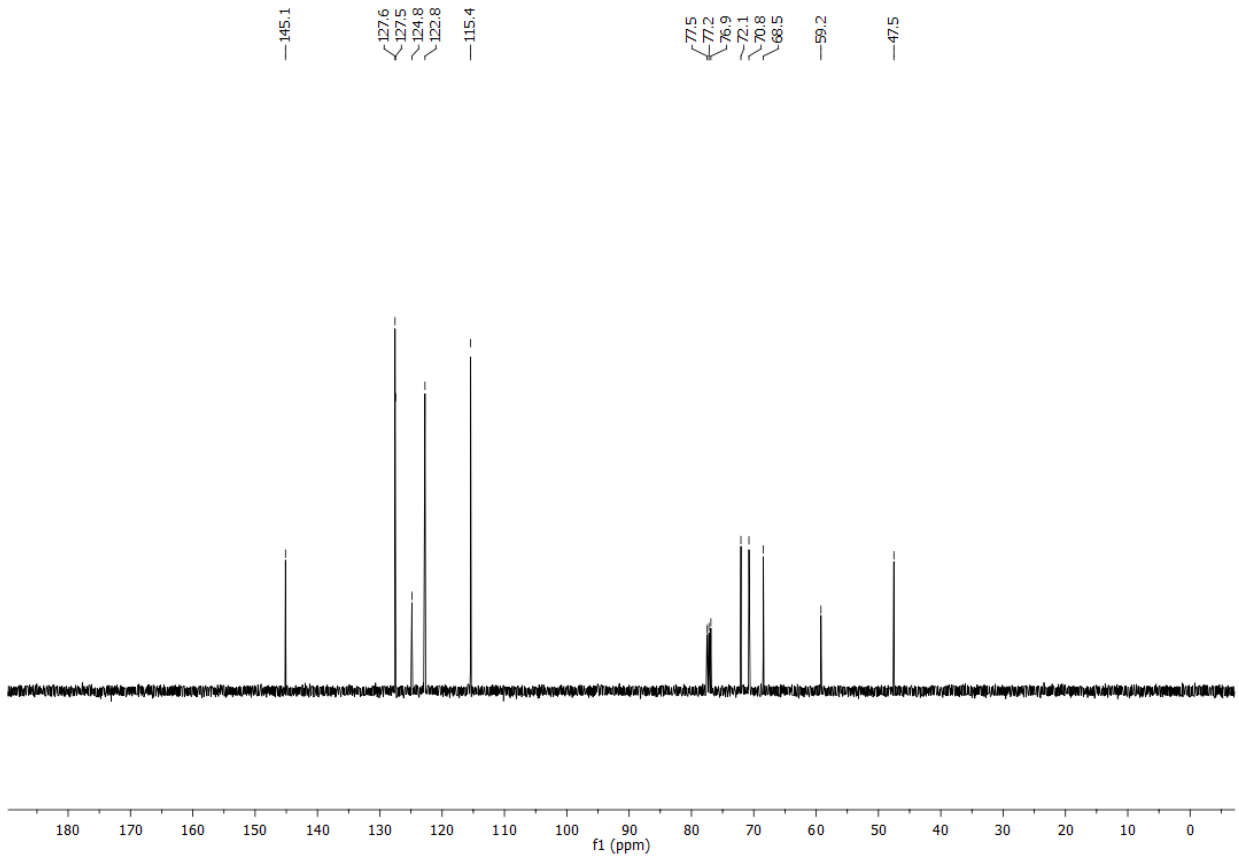

Figure S4. ^{13}C NMR spectrum of MEEPT in $CDCl_3$.

2 Electron Paramagnetic Resonance Spectroscopy of Radical-Cation Salts

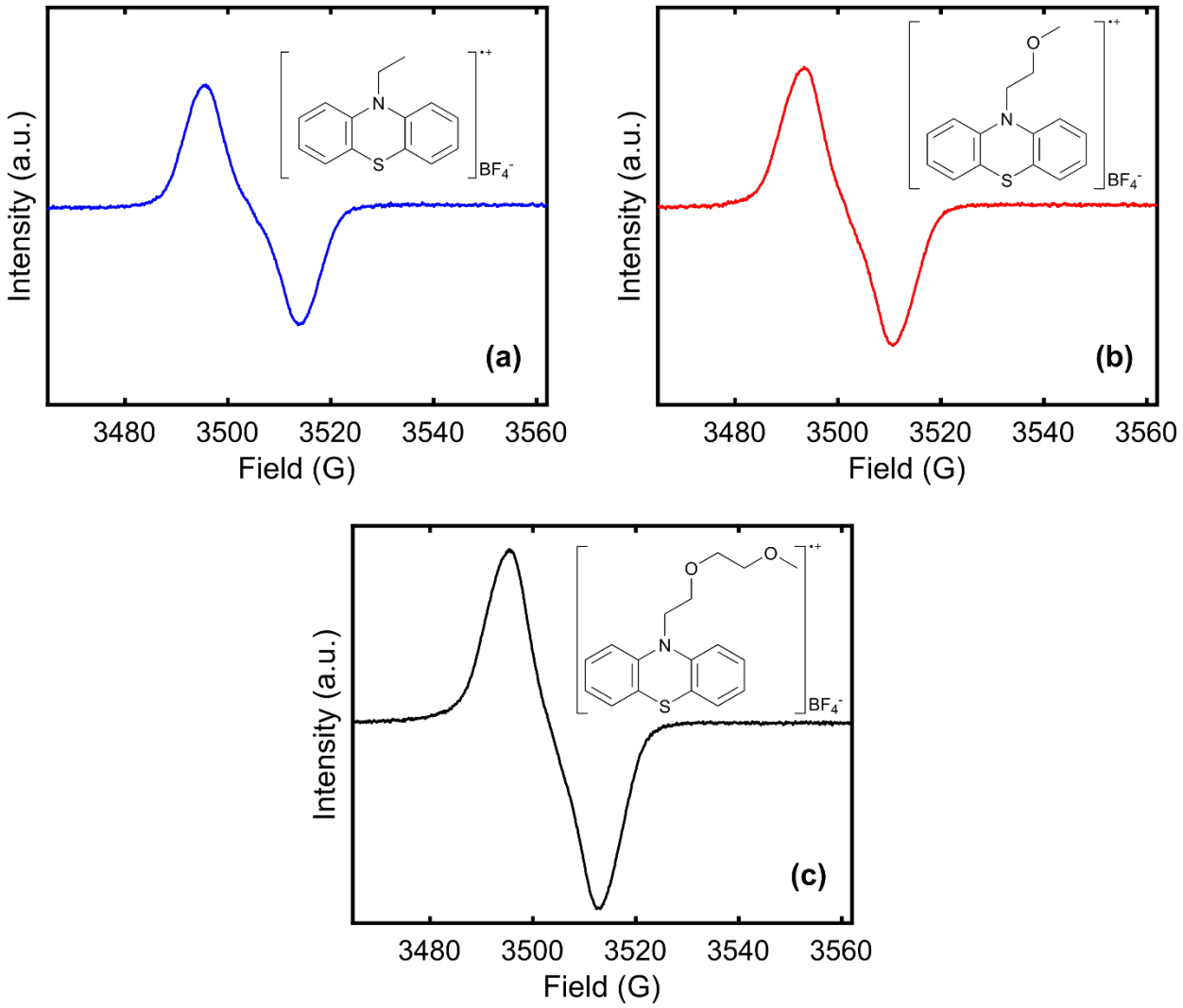

Figure S5. EPR spectra of **(a)** EPT-BF_4, **(b)** MEPT-BF_4, and **(c)** MEEPT-BF_4 salts in dichloromethane.

3 UV-vis Study of Radical-Cation Decay

3.1 Decay Study in Acetonitrile

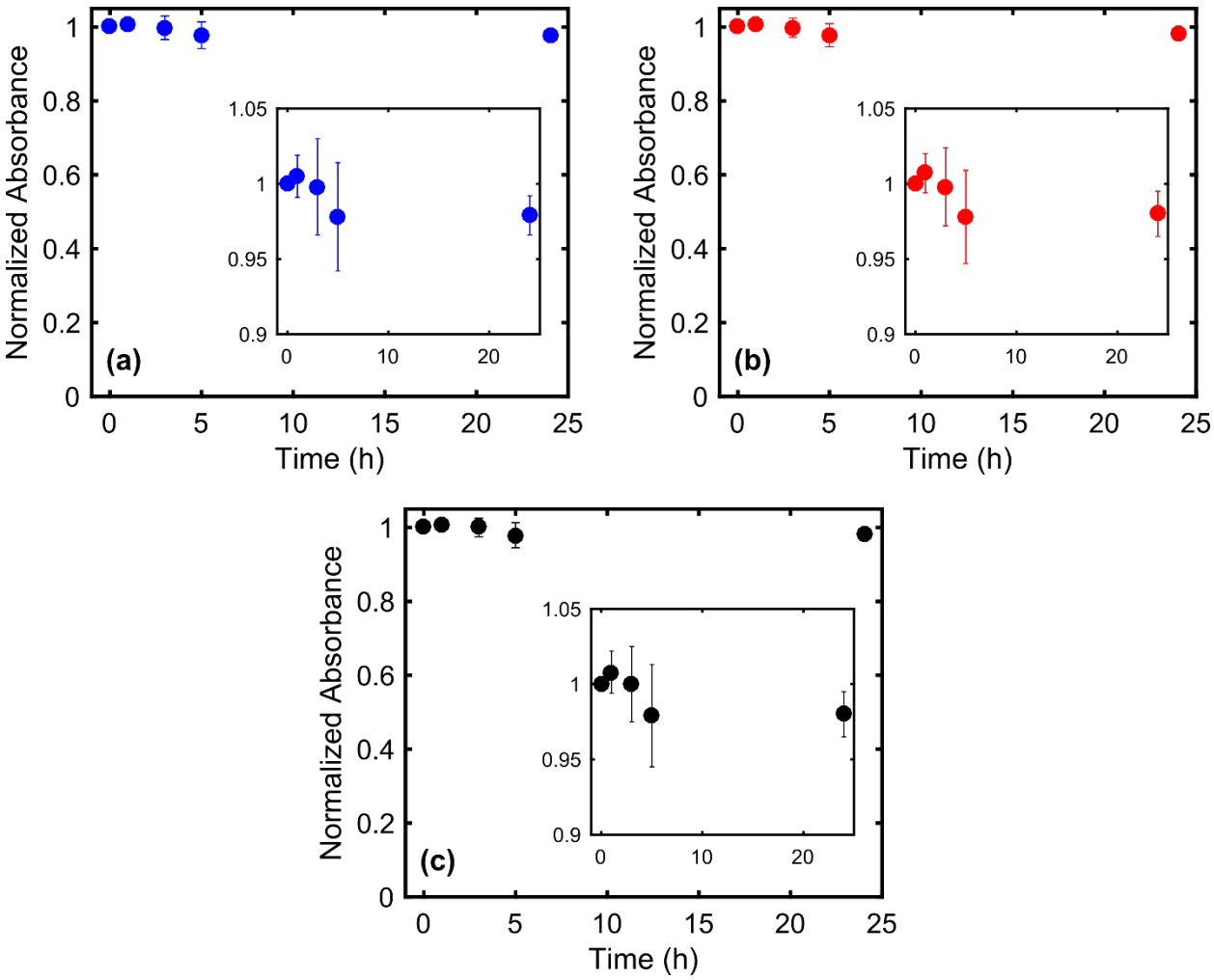

Figure S6. Normalized intensity of UV-vis absorbance at 514 nm vs. time of 0.15 mM **(a)** EPT-BF_4, **(b)** MEPT-BF_4, and **(c)** MEEPT-BF_4 in ACN. Inset: data expanded between absorbance values of 0.9-1.05, recorded at 0, 1, 3, 5, and 24 h after dissolution.

3.2 Decay Study in Propylene Carbonate

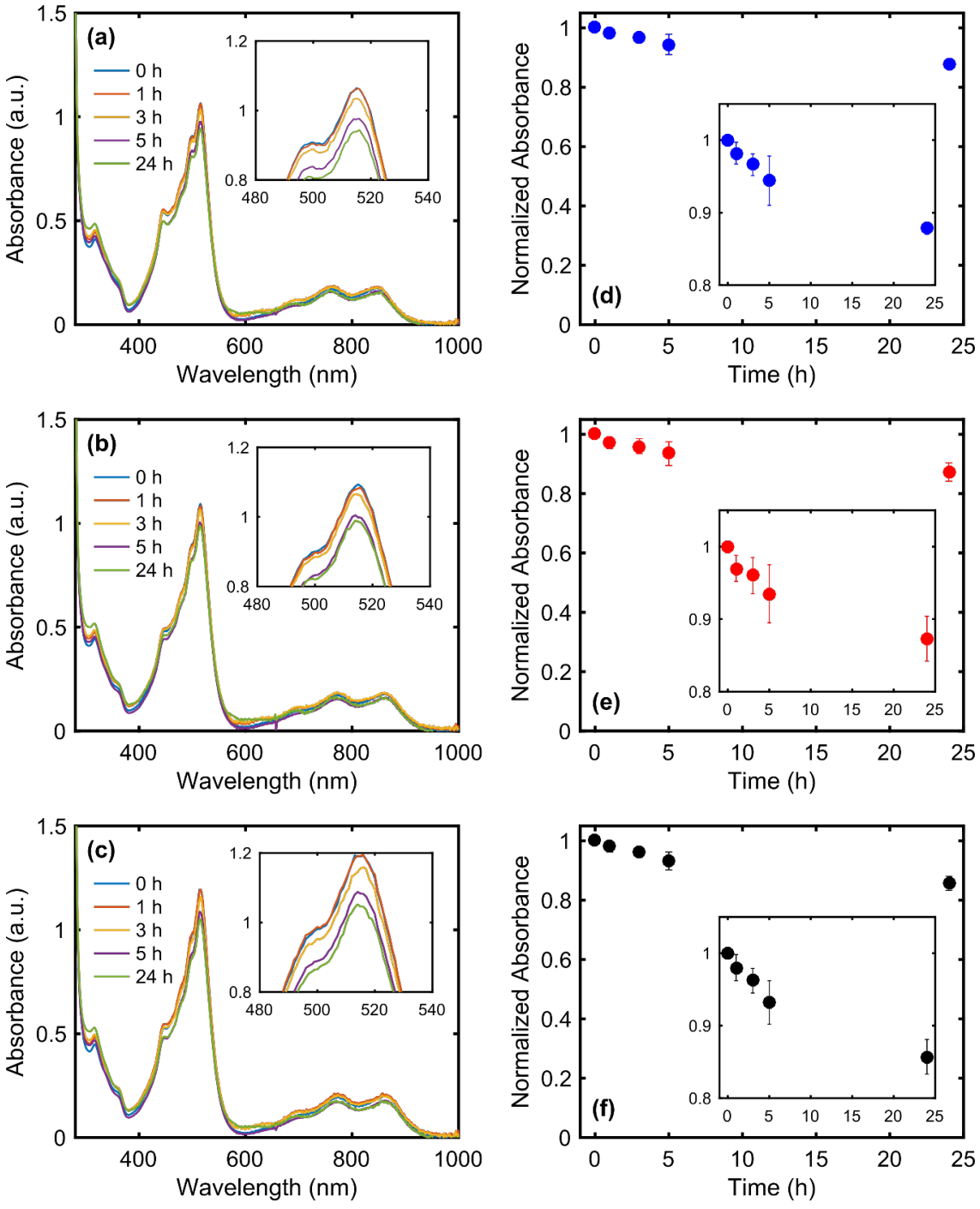

Figure S7. UV-vis spectra of **(a)** EPT-BF_4, **(b)** MEPT-BF_4, and **(c)** MEEPT-BF_4 at 0.15 mM in PC, recorded at 0, 1, 3, 5, and 24 h after dissolution. Characteristic peaks appear at 317, 446, 515, 758, and 853 nm. Normalized intensity of UV-vis absorbance at 515 nm vs. time for 0.15 mM **(d)** 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

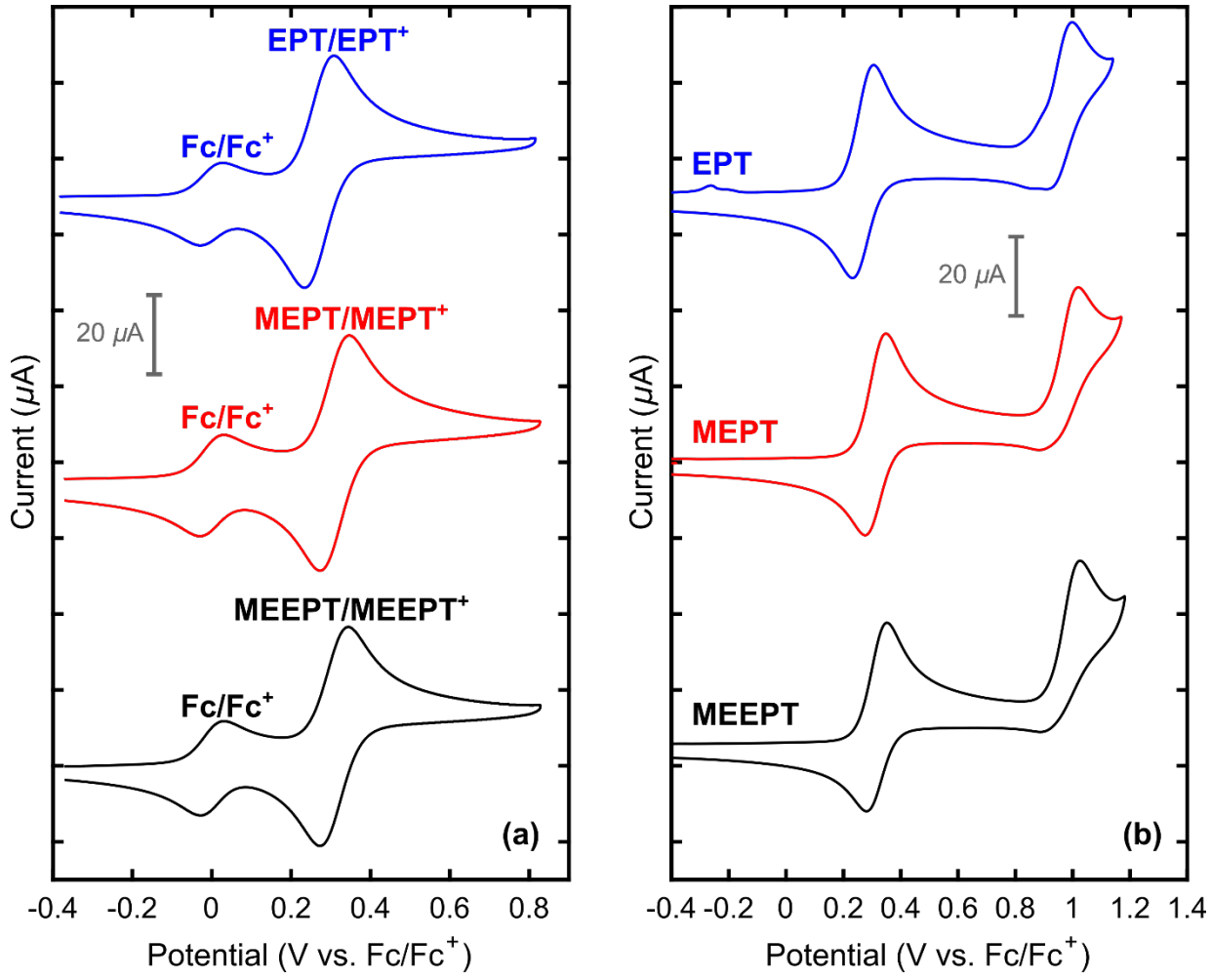

Figure S8. Cyclic voltammograms (cycle 1) of EPT (blue, top), MEPT (red, middle), and MEEPT (black, bottom) at 1 mM in 0.1 M $TEABF_4$ / ACN. **(a)** First positive couple of each active species with ~ 0.7 mM ferrocene internal reference. **(b)** Full potential window of the organic active species, indicating additional irreversible couples at 0.8 – 1.0 V vs. Fc/Fc^+.

4.2 Cyclic-Voltammetry Scan-Rate Study

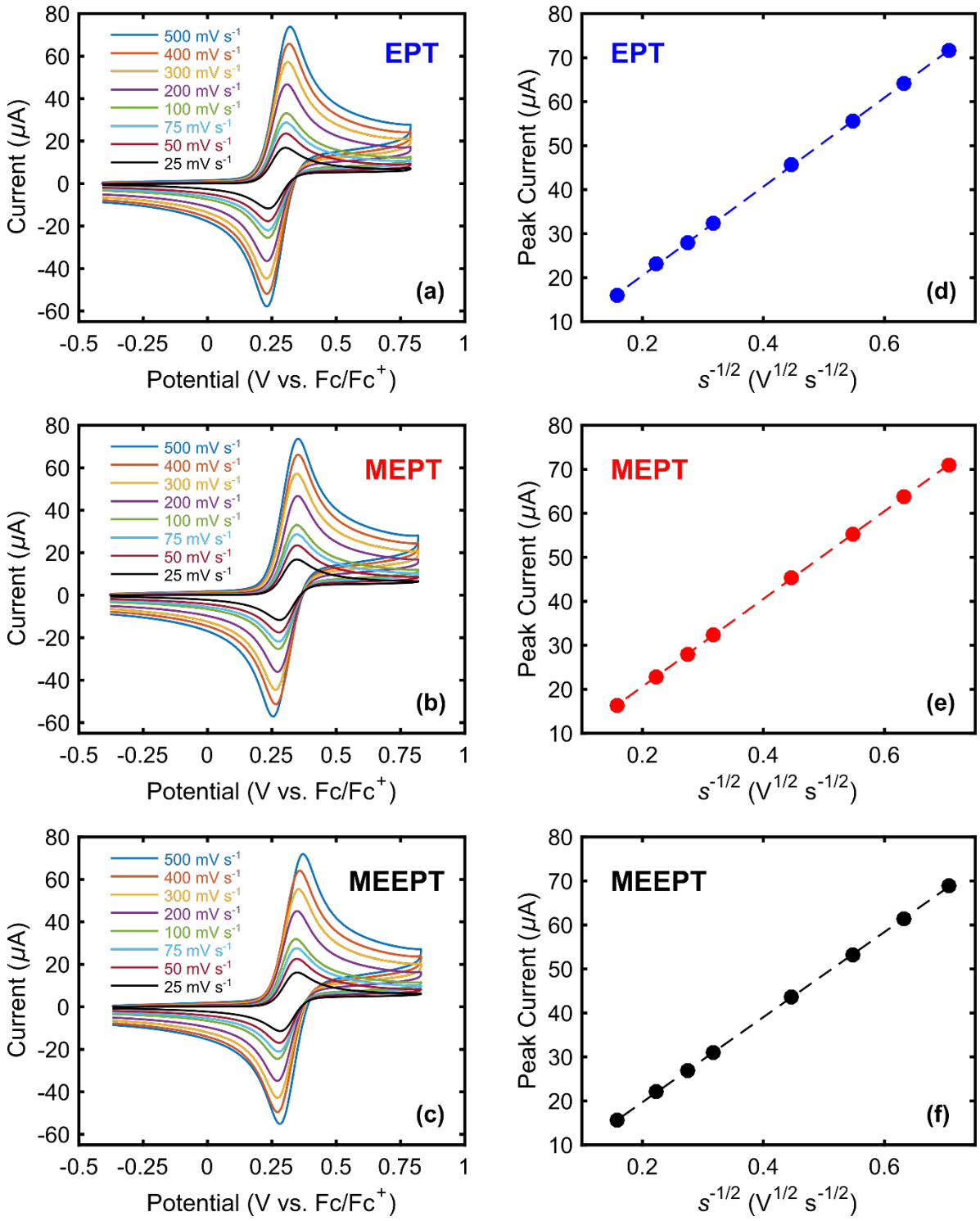

Figure S9. CV scan-rate dependence study for **(a)** EPT, **(b)** MEPT, and **(c)** MEEPT, and Randles-Sevcik construction (peak current vs. square root of scan rate) for the oxidative (anodic) waves of **(d)** EPT, **(e)** MEPT, and **(f)** MEEPT.

5 Bulk Electrolysis

5.1 Bulk-Electrolysis Cell Schematic

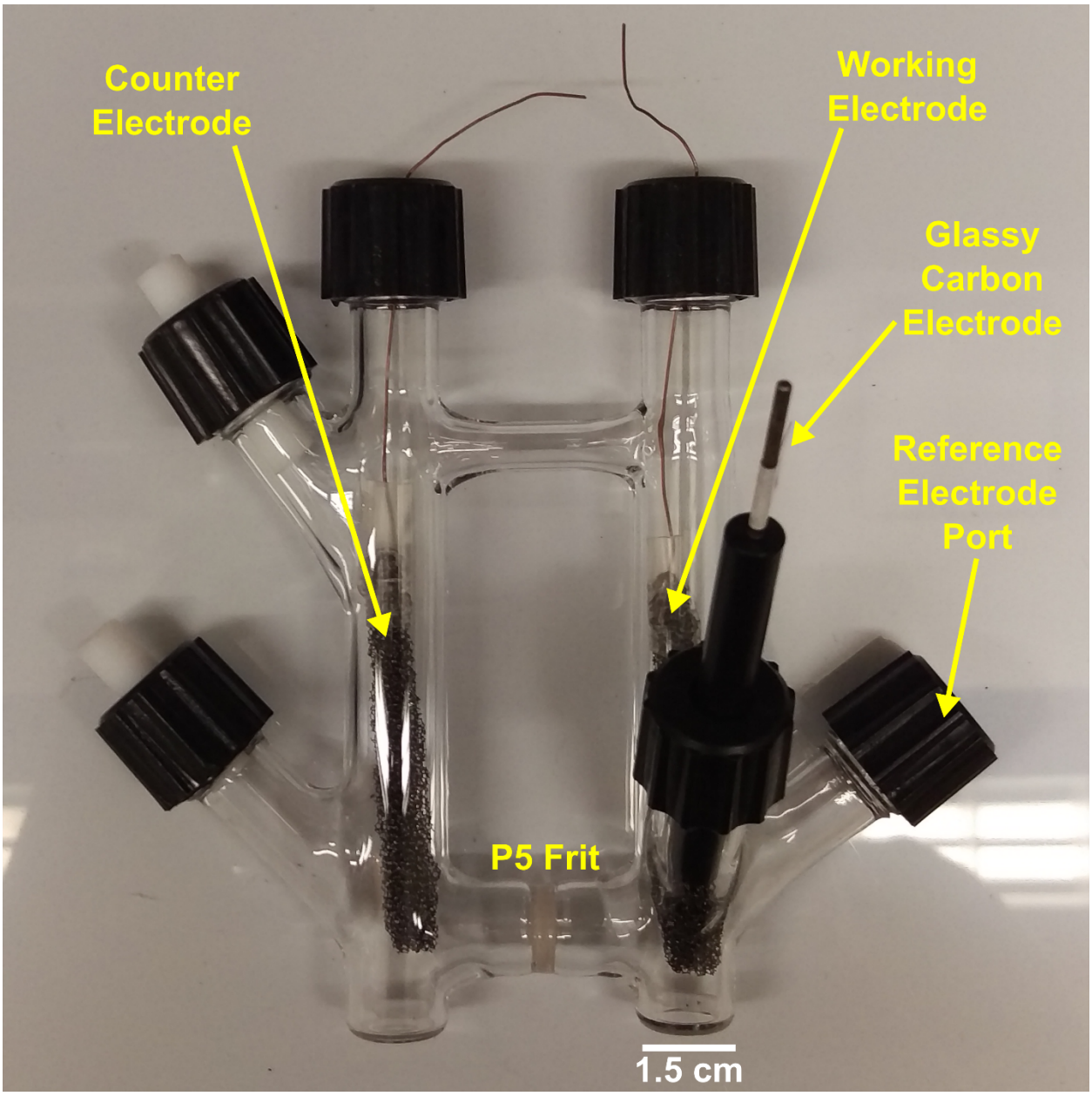

Figure S10. Photograph of the bulk-electrolysis cell, with relevant ports and electrodes labeled.

5.2 Potential vs. Capacity

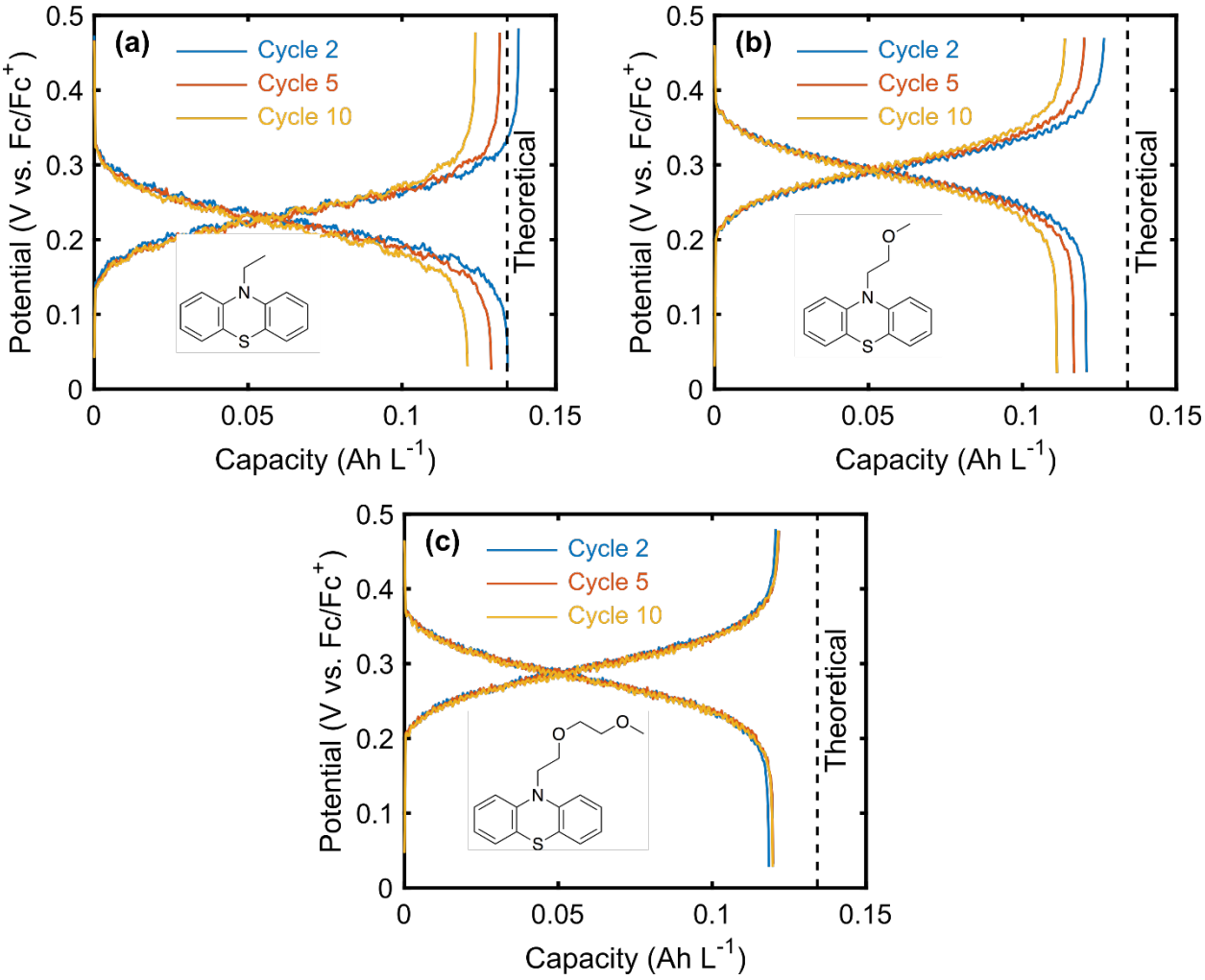

Figure S11. Potential vs. capacity curves from bulk-electrolysis experiments showing cycles 2, 5, and 10 for each of **(a)** EPT, **(b)** MEPT, and **(c)** MEEPT at 5 mM in 1 M $TEABF_4$ / ACN. Theoretical capacities are 0.134 Ah L^{-1} (0.469 mAh) for each experiment, and 10 cycles completed in 7 h.

5.3 Cyclic Voltammograms Before and After Cycling

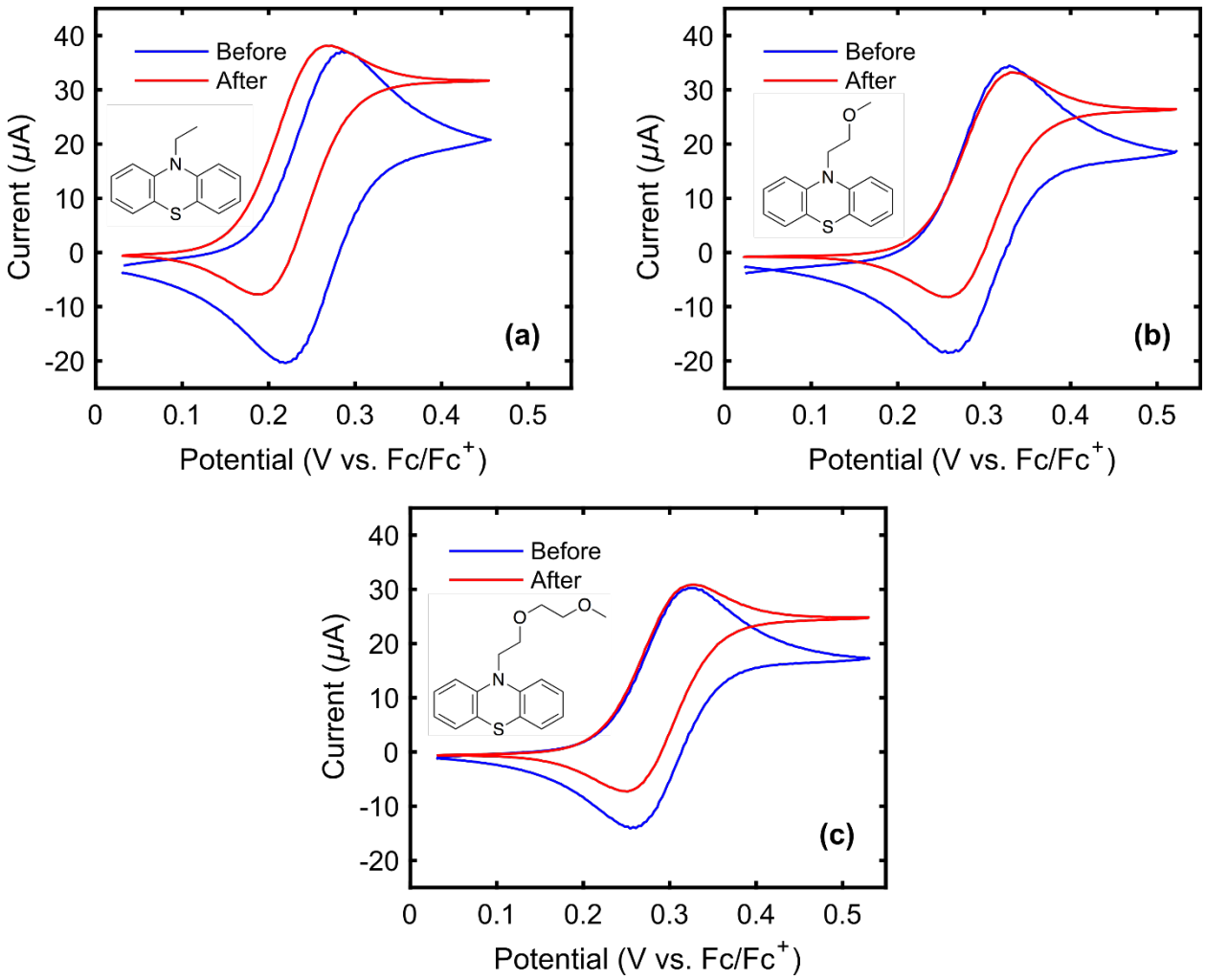

Figure S12. Cyclic voltammograms (cycle 2) before and after 10 bulk-electrolysis cycles for **(a)** EPT, **(b)** MEPT, and **(c)** MEEPT at 5 mM in 1 M $TEABF_4$ / ACN.

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.

	Compound	**$E_{1/2}^{0/+}$ (V vs. Fc/Fc^{+})**	**Peak Separation (mV)**	**Peak Current Ratio**	**Peak Oxidative Current (μA)**
Before Bulk Electrolysis	**EPT**	0.284	65	1.050	34.7
	MEPT	0.327	63	1.072	33.9
	MEEPT	0.327	63	0.991	28.7
After Bulk Electrolysis	**EPT**	0.261	78	0.964	36.8
	MEPT	0.327	70	1.005	33.2
	MEEPT	0.324	76	1.004	30.5

6. Image of Assembled Flow Cell

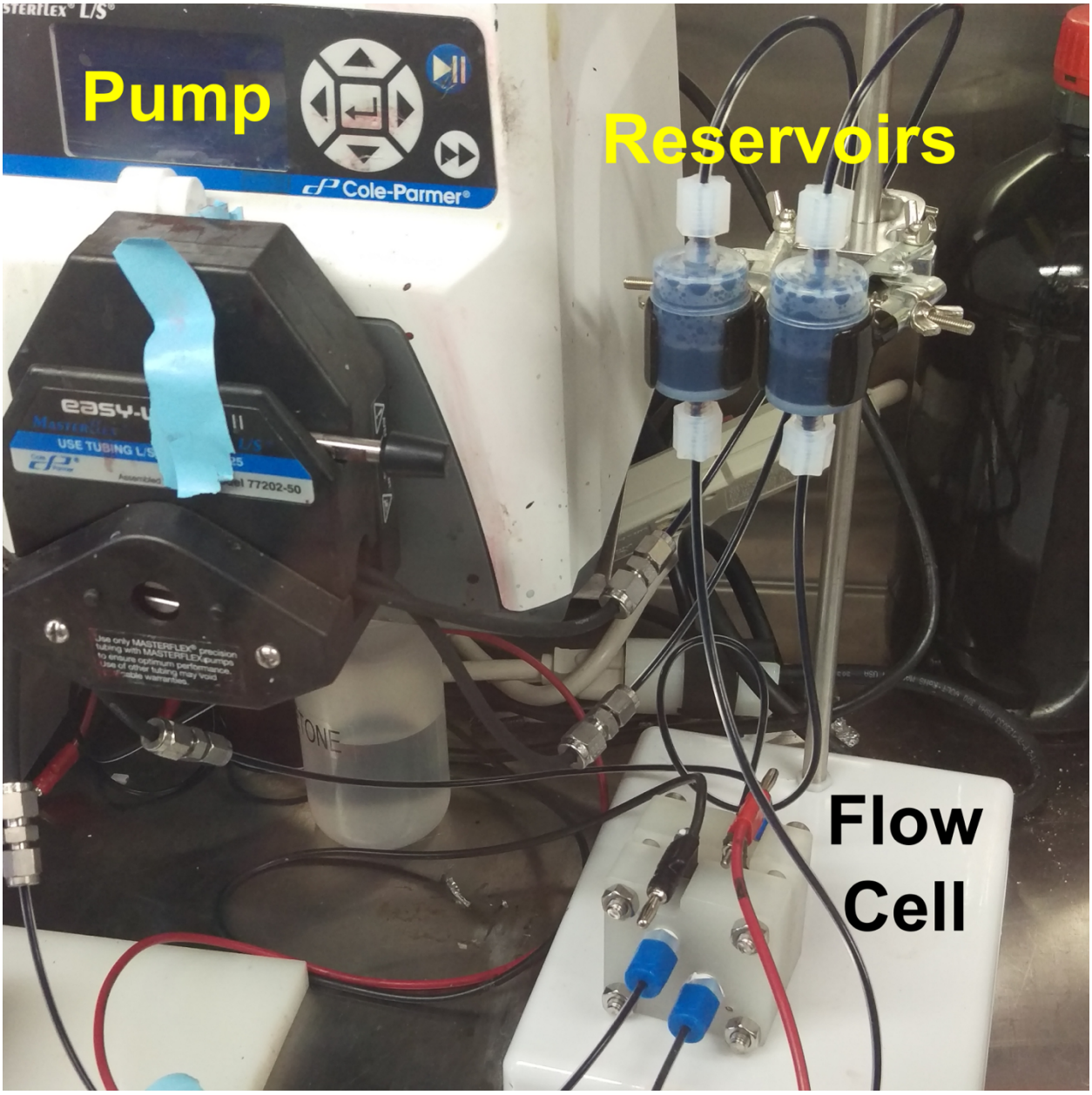

Figure S13. Photograph of the assembled flow cell, connected to the pump and reservoirs.