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SUPPORTING INFORMATION

An Organic Super-Electron-Donor as a High Energy Density Negative Electrolyte for Nonaqueous Flow Batteries

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Experimental Methods

Materials. Acetonitrile (99.8%, anhydrous) was obtained from Sigma Aldrich and stored over activated 3Å molecular sieves in a nitrogen-filled glovebox. Tetrabutylammonium hexafluorophosphate ($[NBu_4][PF_6]$, electrochemical grade) was obtained from Sigma Aldrich and was dried under high vacuum for 48 h before being transferred to a nitrogen-filled glovebox. A 0.50 M stock solution of $[NBu_4][PF_6]$ in acetonitrile was prepared in a glovebox and stored over activated 3Å molecular sieves. Neutral **M** was synthesized by the reported procedure in anhydrous ammonia,[1] while $\mathbf{M^{2+}\ 2PF_6^-}$ was prepared by deprotonation in DMF, I_2 oxidation, and ion exchange.[2]

Solubility tests. Solubility tests of $\mathbf{M^{2+}\ 2PF_6^-}$ were conducted outside the glovebox in ambient atmosphere, while solubility tests of **M** were conducted in a nitrogen-filled glovebox with air-free solvents. In each case, a saturated solution was made in the appropriate solvent, 50 µL of the saturated solution was evaporated to dryness under vacuum, and the mass of the residue measured.

Cyclic voltammetry. Cyclic voltammetry was performed in a nitrogen-filled glovebox with a Bio-Logic VSP multichannel potentiostat/galvanostat using a three electrode electrochemical cell, consisting of a glassy carbon disk working electrode (3.0 mm diameter, BASi), a Ag/Ag^+ reference electrode (Ag wire in a solution of 10 mM $AgBF_4$ in the appropriate solvent and supporting electrolyte to match the experiment), and a glassy carbon disk counter electrode identical to the working electrode. Ferrocene was added as an internal standard for the last run of any CV experiment.

Flow cell cycling. Cycling under flow conditions was performed with a zero-gap flow cell[3] comprised of graphite charge-collecting plates containing an interdigitated flow field, in combination with two layers of non-woven carbon felt electrodes (Sigracet 29 AA) on each side. PTFE gaskets were used to achieve ~20% compression of the felt. Two layers of Celgard 2500 separated the two half cells, and the exposed area of the membrane in the gasket window was 2.55 cm^2. Flow of the electrolyte solutions was established using a peristaltic pump (Cole-Parmer) with Solve-Flex and PFA (perfluoroalkoxy) tubing. After assembly, the electrolyte solutions were flowed for ~ 5 min at a rate of 10 mL/min before electrochemical cycling was started. Using the same 10 mL/min flowrate, galvanostatic charge/discharge cycling was performed using a Bio-Logic VSP galvanostat employing a charging and discharging current of 25.5 mA with voltage limits of -0.5 V and +0.5 V (with the polarity of the electrodes reversed when the system reached one of the voltage limits).

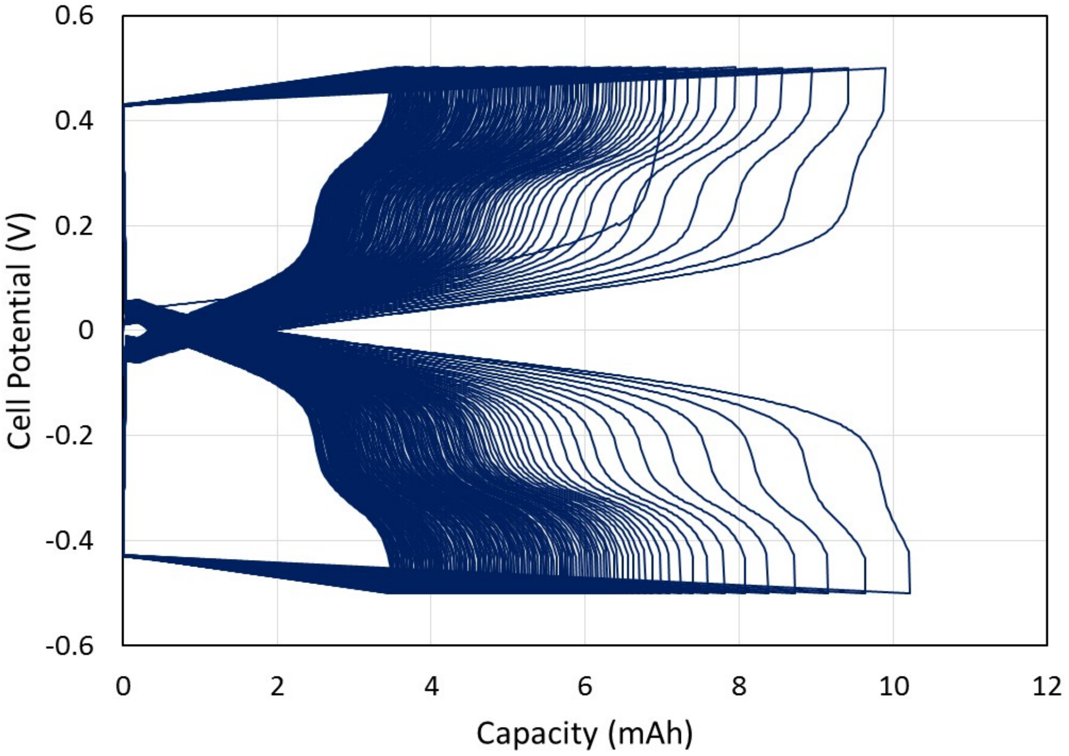

Fig. S1 Charge-discharge curves of $\mathbf{M^{2+/0}}$ over 177 cycles in the flow system.

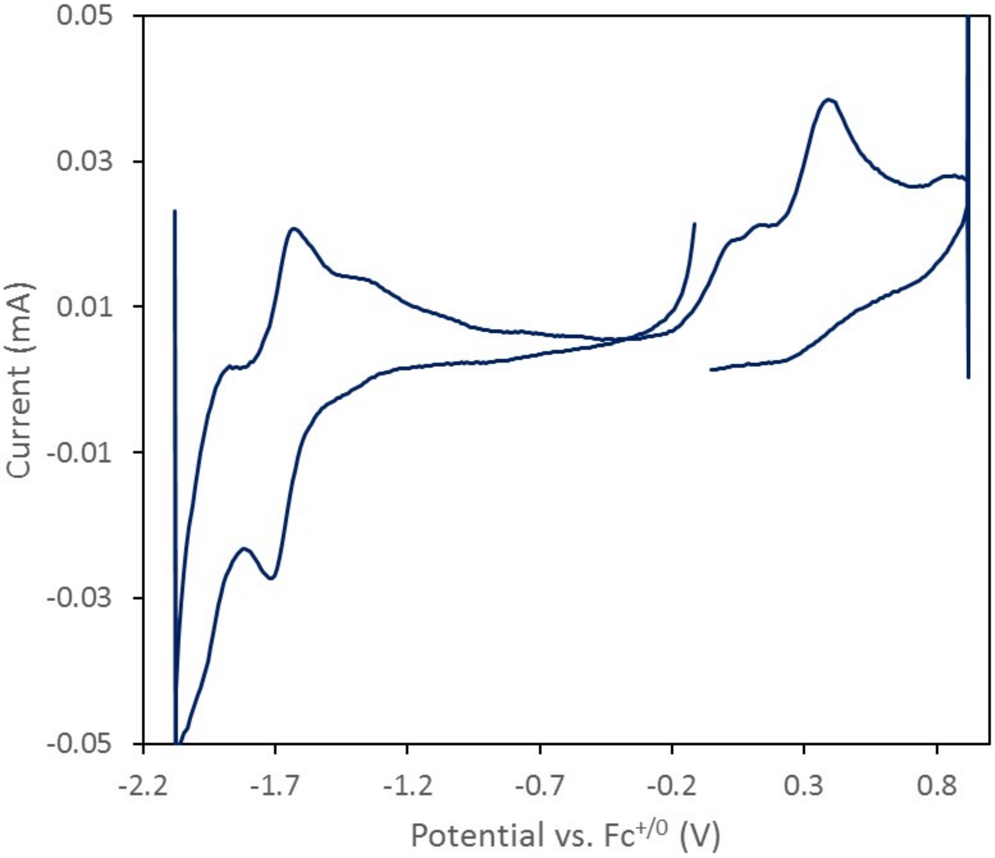

Fig. S2 Cyclic voltammetry of solution after 177 cycles of $\mathbf{M}^{2+/0}$ in the flow system.

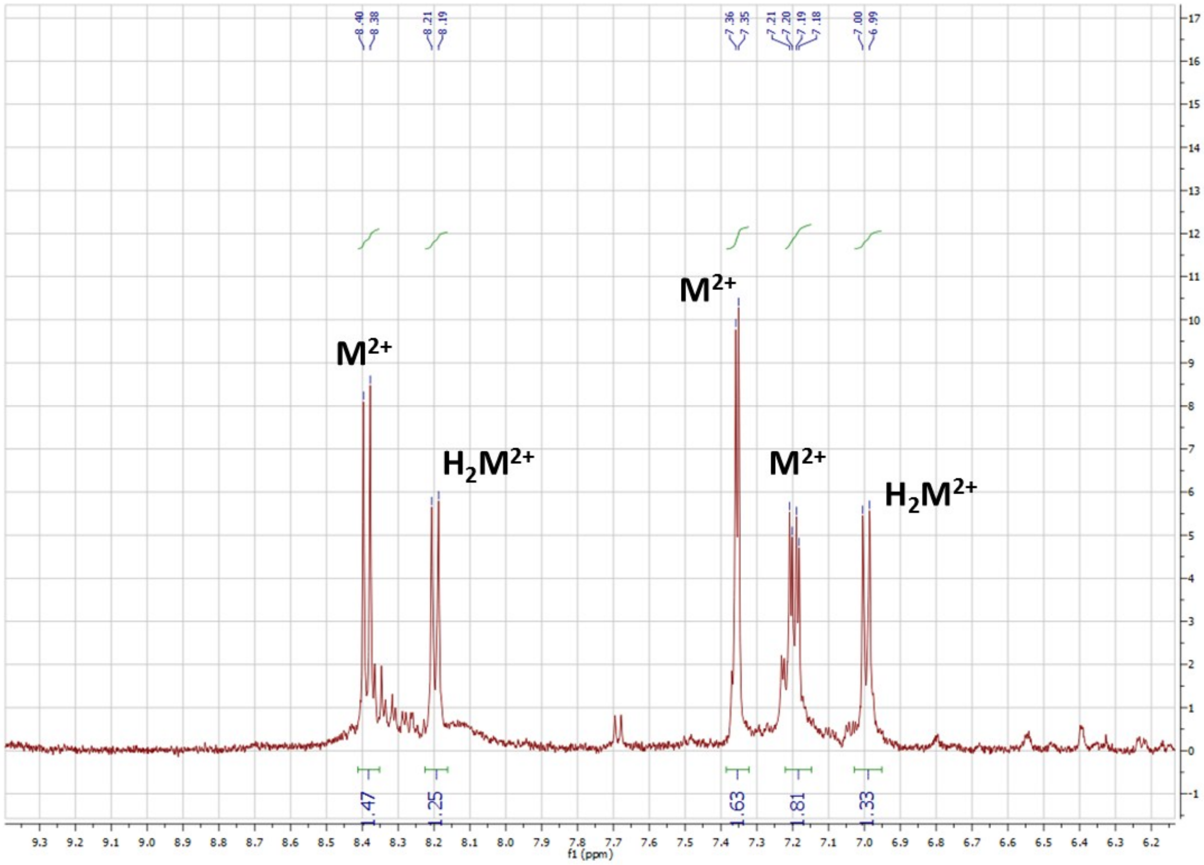

Fig. S3 ^{1}H NMR spectrum of the post-cycling solution of $\mathbf{M^{2+/0}}$, quenched with I_2.

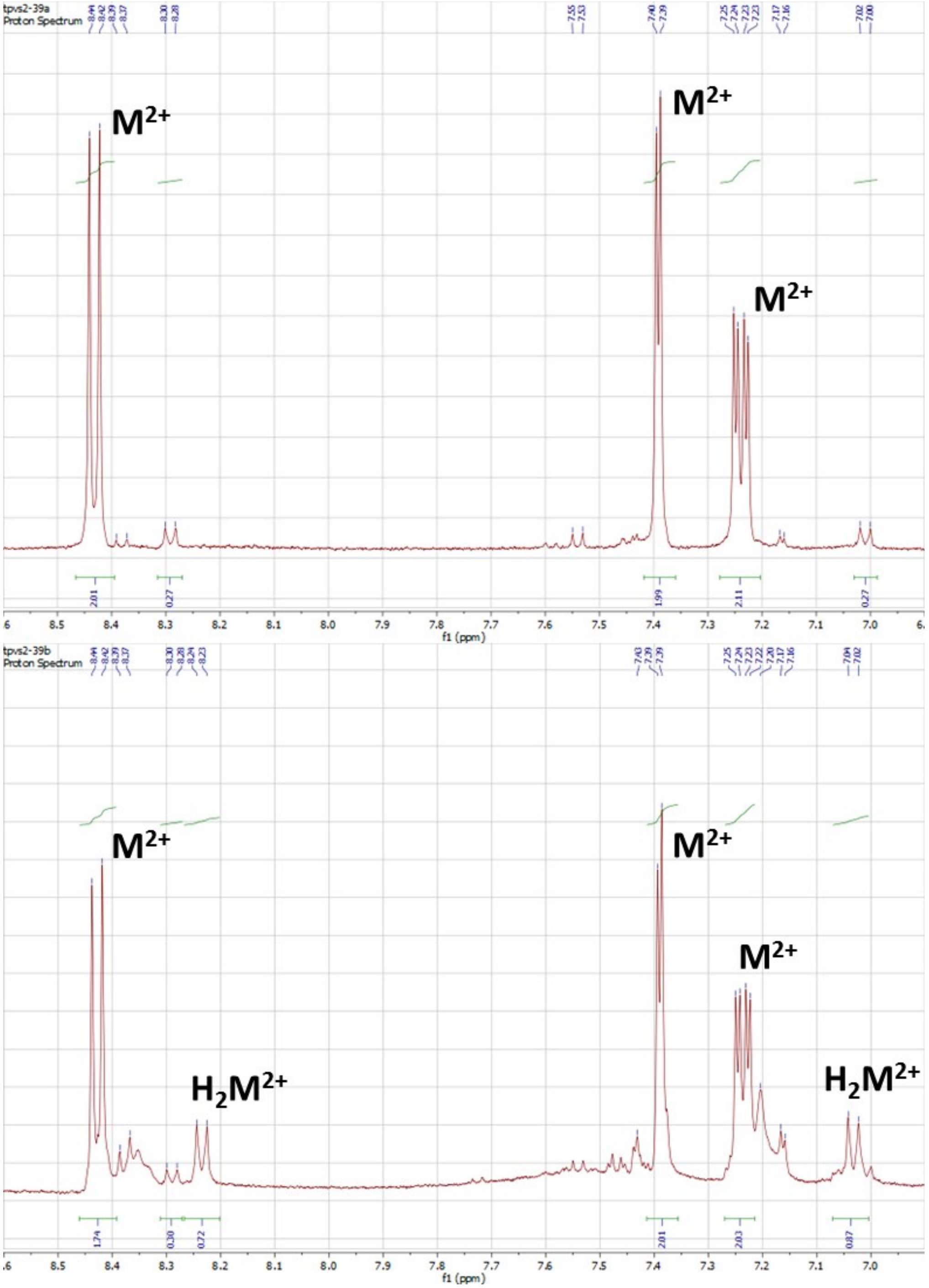

Fig. S4 ^{1}H NMR spectra of I_2-quenched solutions of **M** (top) and **M** + **M^{2+}[PF_6]$_2$** (bottom) tested for stability in dry CH_3CN (16 h at 22 °C).

References

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