

Supporting Information for:

Symmetric Phthalocyanine Charge Carrier for Dual Redox-Flow Battery/Capacitor Applications

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S1. Methods

Techniques and Reagents. All manipulations were performed under an atmosphere of dry, oxygen-free N₂ within an MBraun glovebox (MBRAUN UNILab Pro SP Eco equipped with a -40 °C freezer), or under an atmosphere of dry, oxygen-free Ar within a retrofitted VAC glovebox, or by standard Schlenk techniques. Pentane, C₆D₆, Et₂O, DCM and THF (inhibitor-free) were dried and degassed on an MBraun Solvent Purification System and stored over activated 4 Å molecular sieves. All other solvents were degassed by freeze-pump-thaw and stored on activated 4 Å molecular sieves prior to use. Celite® and 4 Å molecular sieves were dried at 250 °C under dynamic vacuum (< 0.1 Torr) for 24 h prior to use. Compound **1** was prepared by previously reported methods.¹ Ketjenblack® EC-600JD (KB) was purchased from a private supplier. All other reagents were obtained from Sigma-Aldrich, Fisher Scientific, or VWR and used without further purification.

Electrochemical Measurements. Cyclic voltammograms were performed on a CH Instruments 630E Electrochemical Analysis Potentiostat. All working electrodes were of 3.0 mm diameter (CH Instruments) and were cleaned prior to each experiment by sequentially polishing with a gradient of 1.0 µm, 0.3 µm, and 0.05 µm alumina (CH Instruments) on a cloth pad, followed by rinsing with distilled water and acetone. The Pt wire pseudoreference and counter electrodes were rinsed with distilled water and acetone and heated white-hot with a butane torch. All measurements were performed on recrystallized product and referenced to the Fc/Fc⁺ redox couple unless otherwise stated. Static cell cycling experiments were carried out using a Metrohm Autolab PGSTAT128N potentiostat/galvanostat, utilizing voltage cutoffs. For cycling experiments, two coiled Pt electrodes (Bio-Logic) were used and were cleaned by rinsing with distilled water and acetone and then heating white-hot with a butane torch. All electrodes were transferred into a glovebox and subsequently rinsed with the respective electrolyte solution immediately prior to use. The H-cell was custom-made by the in-house glassblower. All electrochemical measurements were performed under an inert atmosphere. For slurry measurements, solid material was first ground together using a mortar and pestle, and then combined with 5 mL of 0.2 M [Bu₄N][PF₆] in CH₃CN, and sonicated for 1 h prior to addition to the H-cell. For all cycling efficiency metrics, the first cycle was discarded.

Faradaic efficiency (*FE*) was defined by Eq. 1:

$$(1) FE = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}} * 100\%$$

Where *Q* is charge transferred. Voltage efficiency (*VE*) was defined by Eq. 2:

$$(2) VE = \frac{V(\text{mean})_{\text{discharge}}}{V(\text{mean})_{\text{charge}}} * 100\%$$

Where *V*_(mean) is the mean voltage. Energy efficiency (*EE*) was defined by Eq. 3:

$$(3) EE = \frac{(FE \times VE)}{100\%}$$

DigiSim simulations. All simulations were performed with the same concentration, starting potential, ending potential, voltage window, experimental *E*^o, and scan rate as experimental, and the assumption that T = 298 K, r = 1.5 mm. All events were assumed to have an α/λ ratio of 0.5, and the diffusion coefficient (*D*) and the heterogeneous charge transfer constant (*k*_o) were fitted to all scan rates to produce the closest fits.

Energy density calculations.

The energy density was calculated using the following assumptions:

- 1) KB provides 2.5 C when 100 mg is used (estimated from experimental charge/discharge curves; Figure S9)
- 2) **1** provides 2 e⁻ per molecule, and has a molecular weight of 934 g/mol
- 3) Experimental $V_{cell}(\text{discharge})$ values were used for each calculation

Solution-state cycling:

Using the following equation²: $\hat{E}_{RFB} = 0.5 n \cdot V_{cell} \cdot C_{active} \cdot F$

where: \hat{E}_{RFB} = energy density for RFB
 n = number of electrons transferred at the electrodes = 2
 V_{cell} = cell potential
 C_{active} = concentration of the redox active species
 F = Faraday's constant = 96,485 C/mol

with: 4.7 mg of **1** dissolved in 10 mL
 $V_{cell} = 1.40$ V

then: $\hat{E}_{RFB} = 0.5 \times 2 \times 1.4 \text{ V} \times \left(\frac{0.0047 \text{ g} / 934 \text{ g/mol}}{0.010 \text{ L}} \right) \times 96,485 \text{ C/mol} = 67.9 \text{ J/L} \approx 0.02 \text{ Wh/L}$

KB cycling:

Using the following equation: $\hat{E}_{EFC} = \frac{q \times V_{cell}}{\text{volume}}$

where: \hat{E}_{EFC} = energy density for EFC
 q = total charge transferred = 2.5 C (using 100 mg KB and following assumption 1 above)
 $\text{volume} = 0.010$ L

with: $V_{cell} = 0.84$ V

then: $\hat{E}_{EFC} = \frac{2.5 \text{ C} \times 0.84 \text{ V}}{0.010 \text{ L}} = 210 \text{ J/L} \approx 0.06 \text{ Wh/L}$

Slurry-state cycling:

Using the following equation: $\hat{E}_{total} = \hat{E}_{RFB} + \hat{E}_{EFC}$

with: 130 mg of **1**
210 mg of KB
volume = 0.010 L
 $V_{cell} = 1.04$ V

then:

$$\hat{E}_{total} = \left[0.5 \times 2 \times 1.04 V \times \frac{0.130 g / 934 g/mol}{0.010 L} \times 96,485 C/mol \right] + \left[\frac{(210 mg \times 2.5 C/100 mg) \times 1.04 V}{0.010 L} \right] = 1943 J/L \approx 0.54 Wh/L$$

S2. Electrochemistry

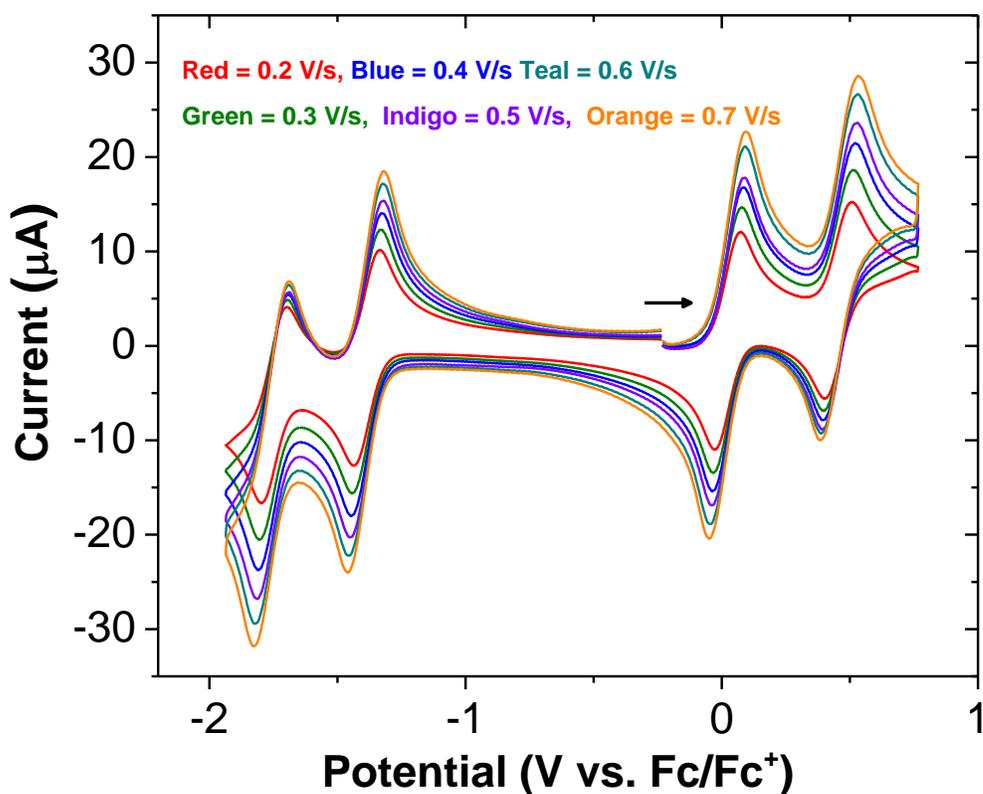


Figure S1. CV of **1** at varying scan rates (inset). Experimental conditions: Taken in DCM with 0.29 mM of **1**, 0.1 M of $[Bu_4N][PF_6]$, 3 mm diameter glassy carbon working electrode, Pt wire counter electrode, and Pt wire pseudoreference electrode.

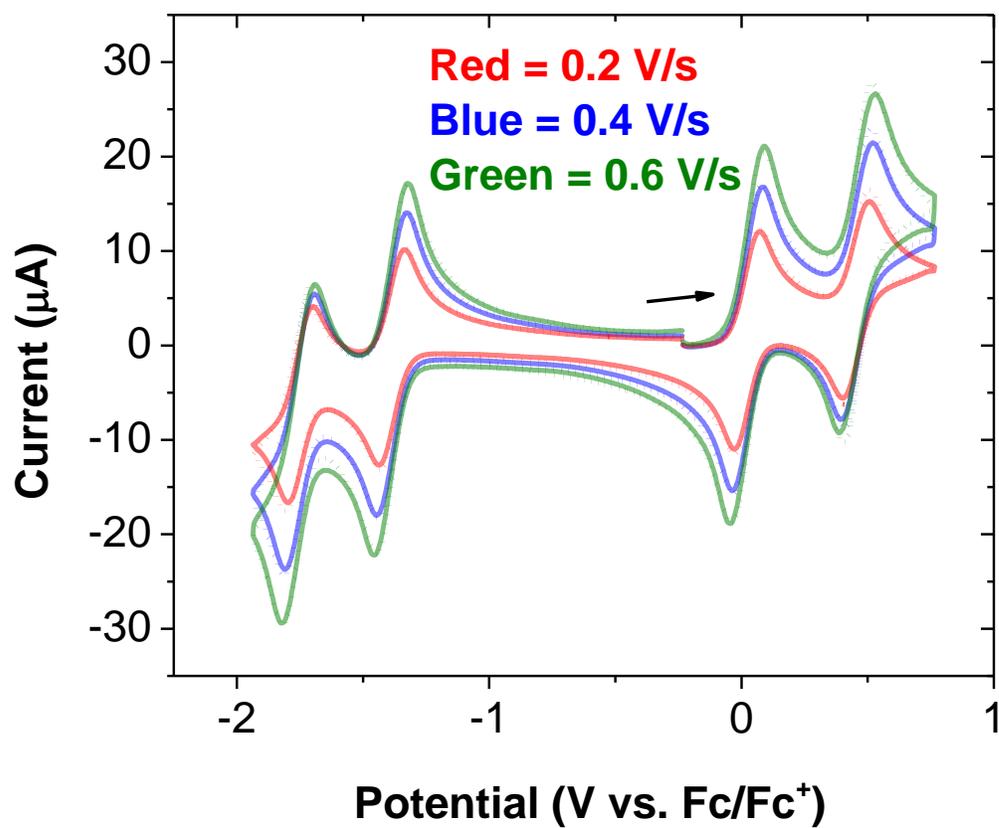


Figure S2. CV of **1** at varying scan rates (solid lines) and DigiSim fit of experimental results (dotted lines). Experimental conditions: Taken in DCM with 0.29 mM of **1**, 0.1 M of $[\text{Bu}_4\text{N}][\text{PF}_6]$, 3 mm diameter glassy carbon working electrode, Pt wire counter electrode, and Pt wire pseudoreference electrode.

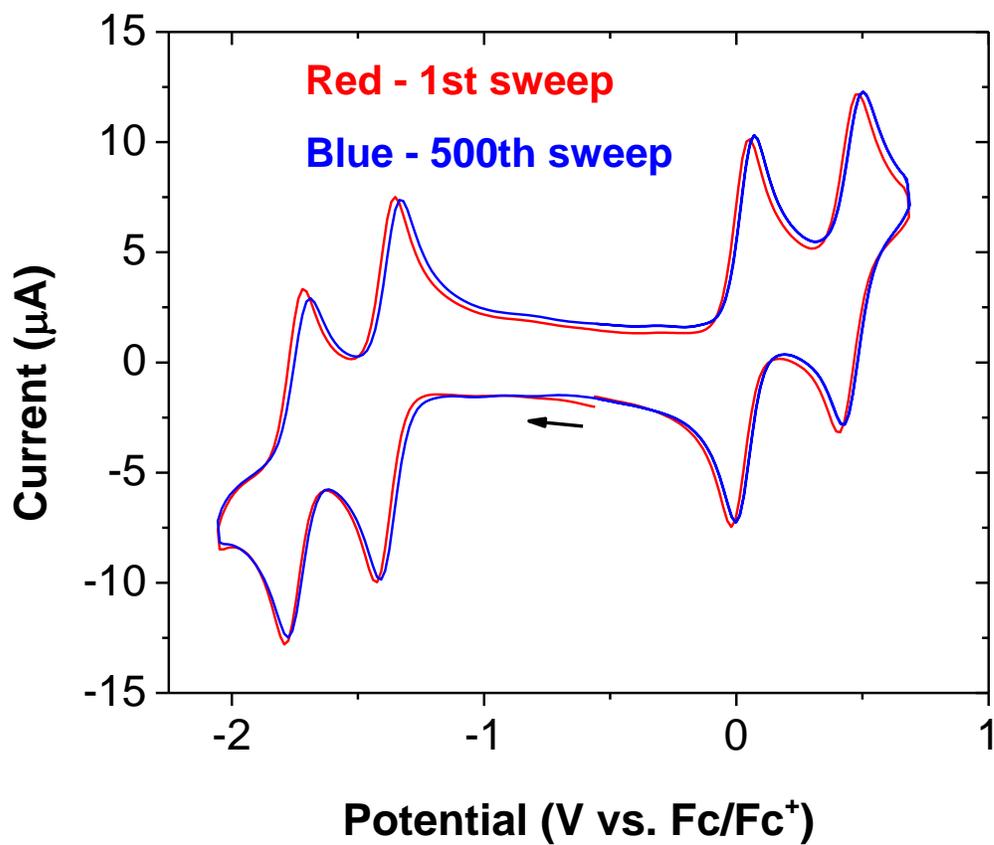


Figure S3. Multi-sweep CV of **1** displaying first scan (red) and 500th scan (blue). Experimental conditions: taken in DCM with 0.24 mM of **1**, 0.1 M of $[\text{Bu}_4\text{N}][\text{PF}_6]$, 3 mm diameter glassy carbon working electrode, Pt wire counter electrode, and Pt wire pseudoreference electrode, scan rate 500 mV/s.

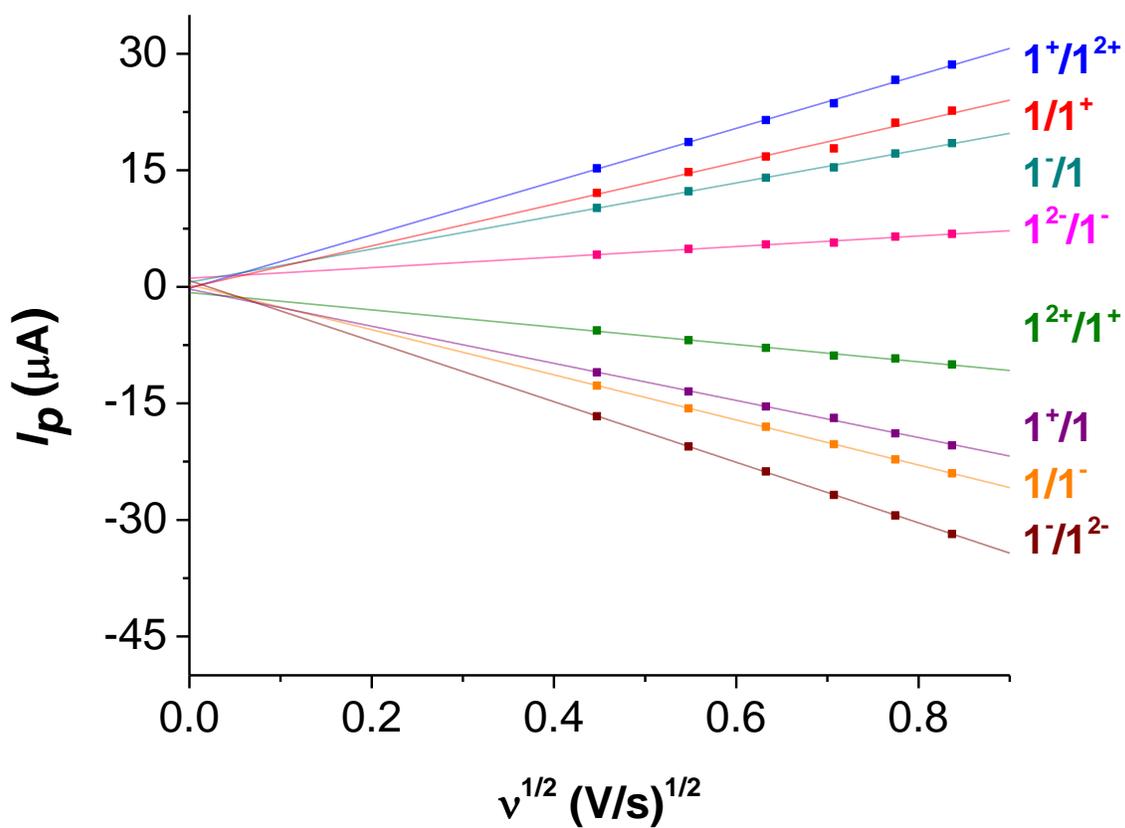


Figure S4. Randles-Ševčík plot for **1** in DCM.

Table S1. Slope and R^2 values obtained from the Randles-Ševčík analysis.

| Redox Event | Slope | R^2 |
|--------------|-----------------------|-------|
| $1/1^+$ | $2.68 \cdot 10^{-5}$ | 0.98 |
| $1^+/1^{2+}$ | $3.43 \cdot 10^{-5}$ | 0.99 |
| $1^{2+}/1^+$ | $-1.12 \cdot 10^{-5}$ | 0.99 |
| $1^+/1$ | $-2.39 \cdot 10^{-5}$ | 0.99 |
| $1/1^-$ | $-2.90 \cdot 10^{-5}$ | 0.99 |
| $1~/1^{2-}$ | $-3.90 \cdot 10^{-5}$ | 0.99 |
| $1^{2-}/1^-$ | $6.79 \cdot 10^{-6}$ | 0.98 |
| $1~/1$ | $2.13 \cdot 10^{-5}$ | 0.99 |

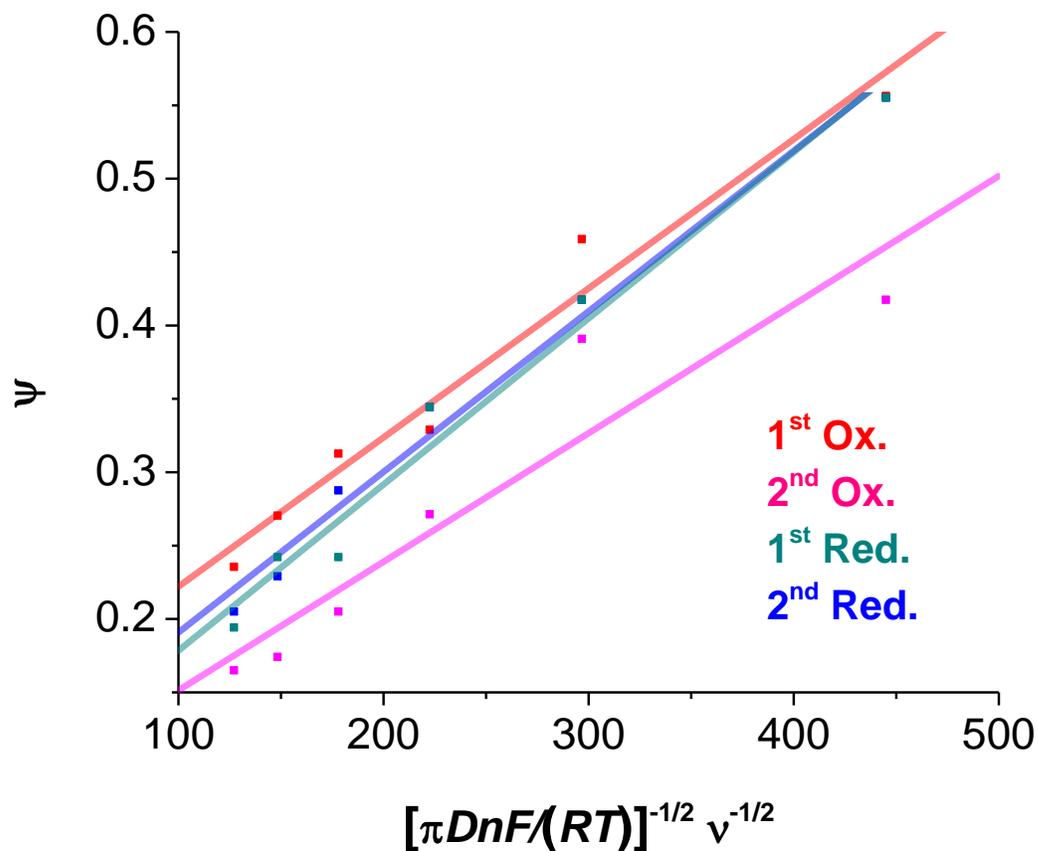


Figure S5. Nicholson plot for **1** in DCM.

Table S2. Slope and R^2 values obtained from the Nicholson analysis.

| Redox Event | Slope | R^2 |
|--------------|--------|-------|
| $1/1^+$ | 0.0010 | 0.962 |
| $1^+/1^{2+}$ | 0.0009 | 0.863 |
| $1/1^-$ | 0.0011 | 0.971 |
| $1^-/1^{2-}$ | 0.0011 | 0.981 |

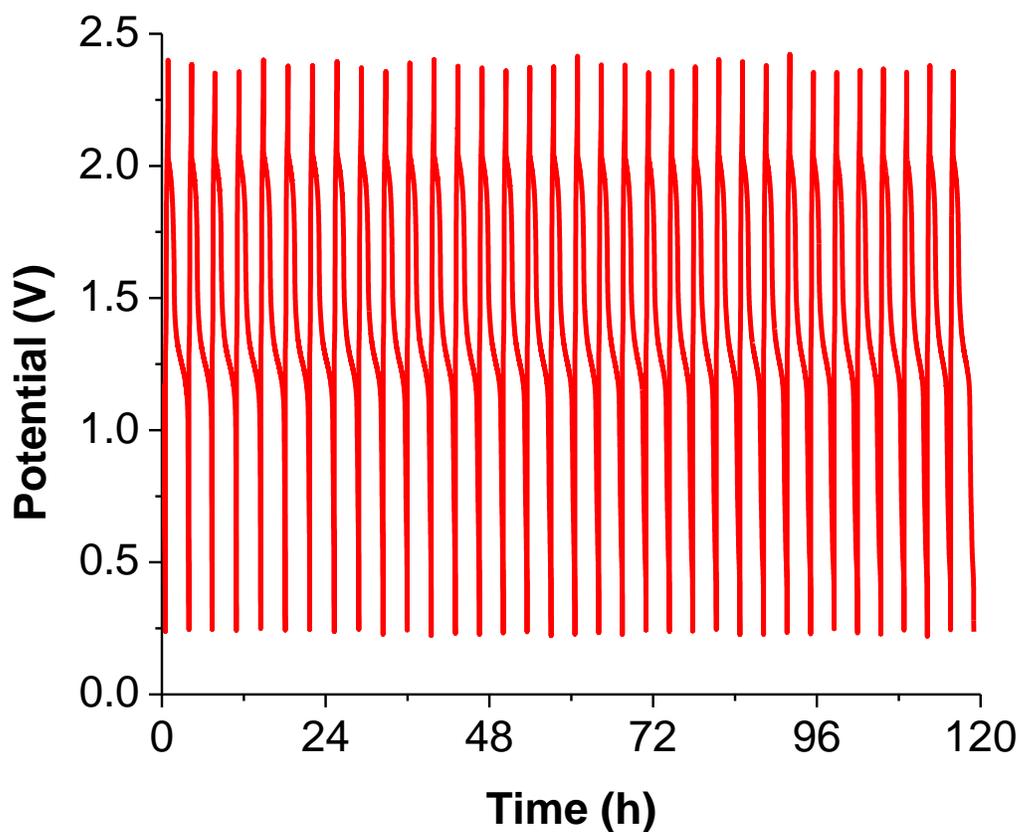


Figure S6. Galvanostatic, two-electrode charge-discharge curves of **1**. Taken in a glass-fritted H-cell in CH₃CN (5 mL per compartment; 10 mL total) with [Bu₄N][PF₆] (0.2 M) and **1** (0.50 mM). Coiled Pt working electrode, coiled Pt counter electrode. 100 μ A charge, -12.5 μ A discharge.

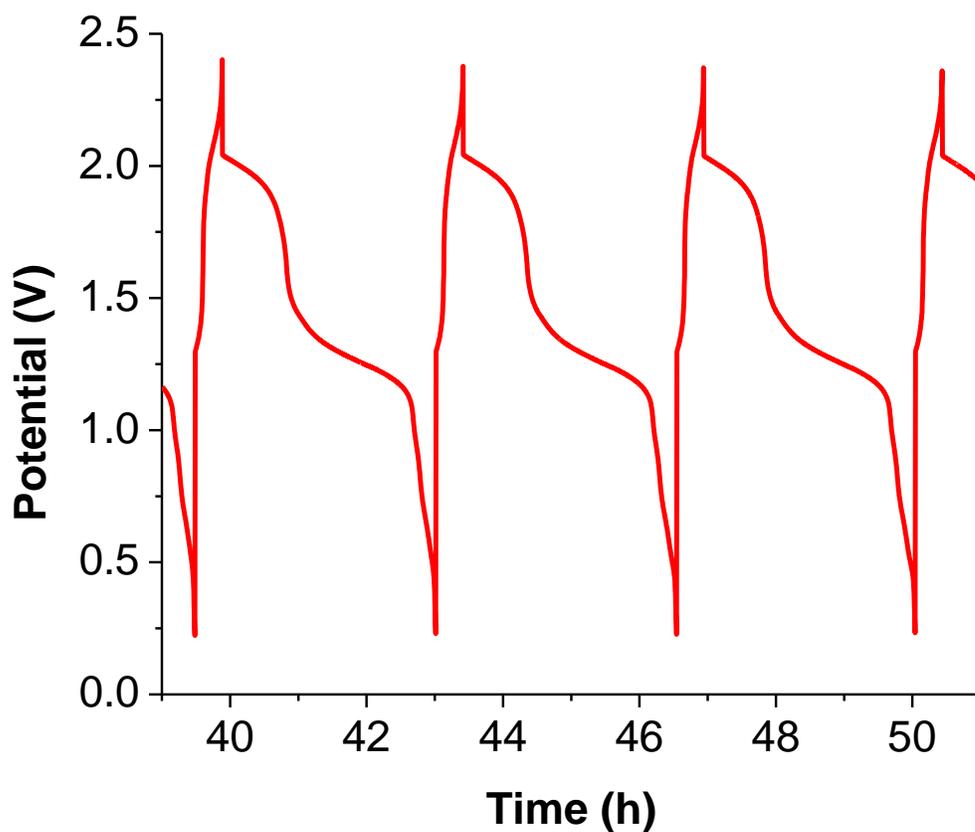


Figure S7. Selected galvanostatic charge-discharge curves for **1**. Taken in a glass-fritted H-cell in CH₃CN (5 mL per compartment; 10 mL total) with [Bu₄N][PF₆] (0.2 M) and **1** (0.50 mM). Coiled Pt working electrode, coiled Pt counter electrode. 100 μ A charge, -12.5 μ A discharge.

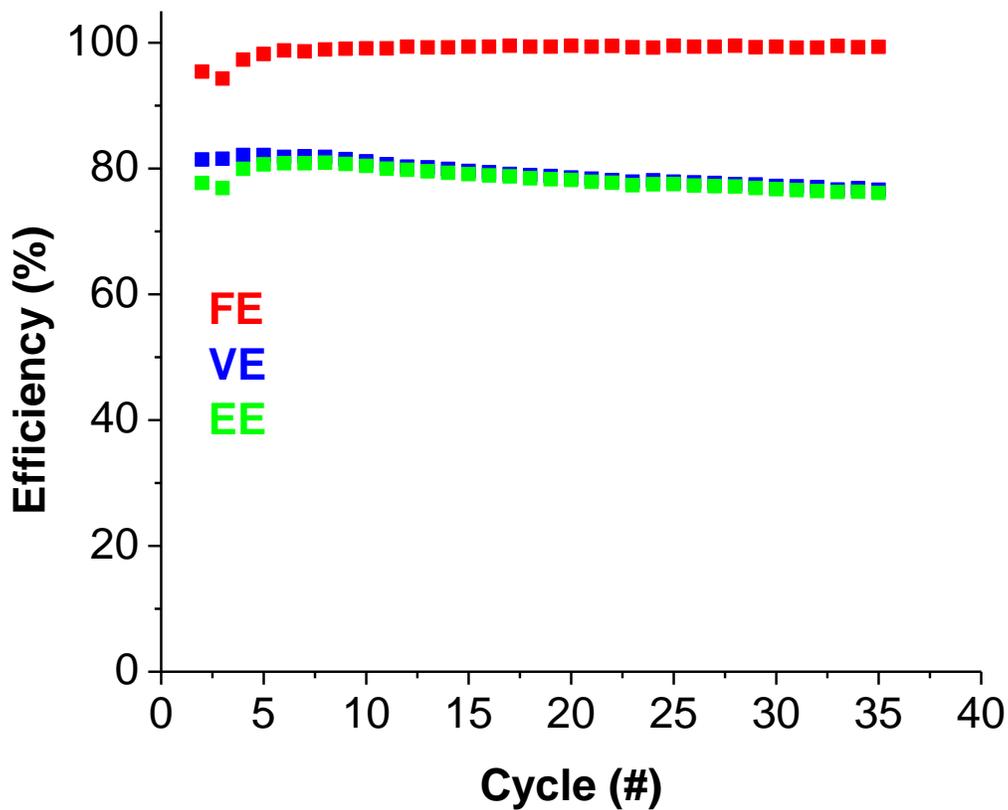


Figure S8. Efficiency values of **1** (Faradaic efficiency (FE); Voltage efficiency (VE); Energy efficiency (EE)). Taken in a glass-fritted H-cell in CH₃CN (5 mL per compartment; 10 mL total) with [Bu₄N][PF₆] (0.2 M) and **1** (0.50 mM). Coiled Pt working electrode, coiled Pt counter electrode. 100 μ A charge, -12.5 μ A discharge.

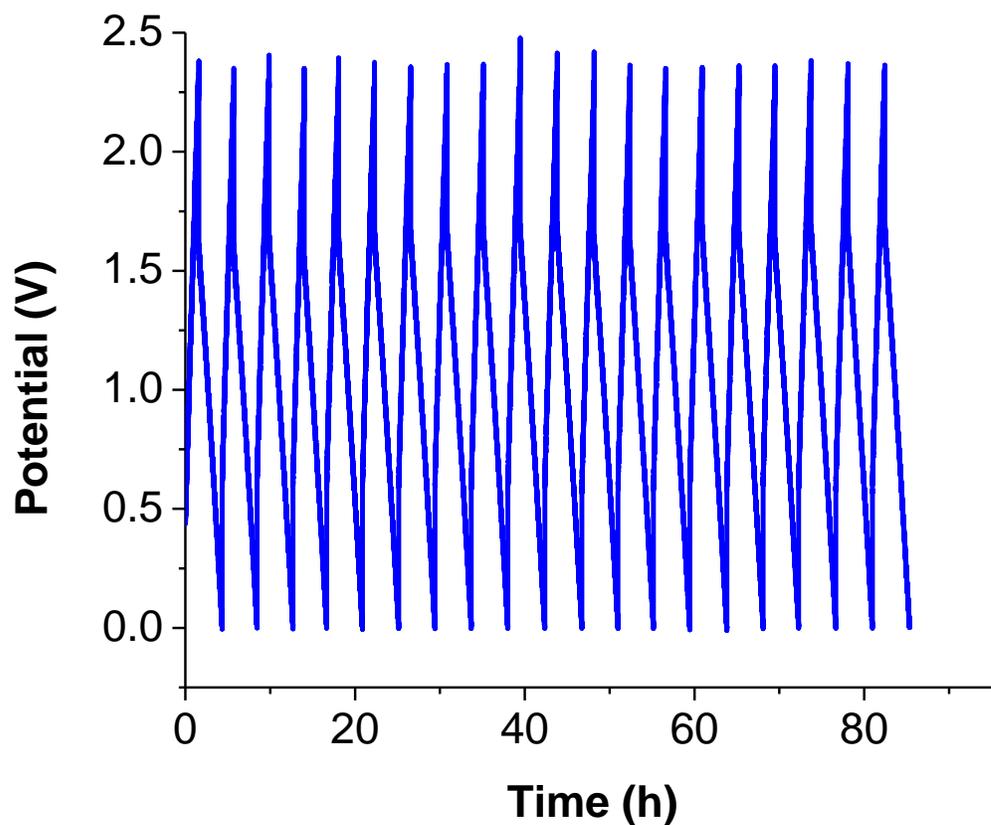


Figure S9. Galvanostatic, two-electrode charge-discharge curves of a slurry of KB. Taken in a glass-fritted H-cell with CH_3CN , 0.2 M $[\text{Bu}_4\text{N}][\text{PF}_6]$, 50 mg of KB per compartment, and 5 mL of solution per side. Coiled Pt working electrode, coiled Pt counter electrode. 500 μA charge, -250 μA discharge.

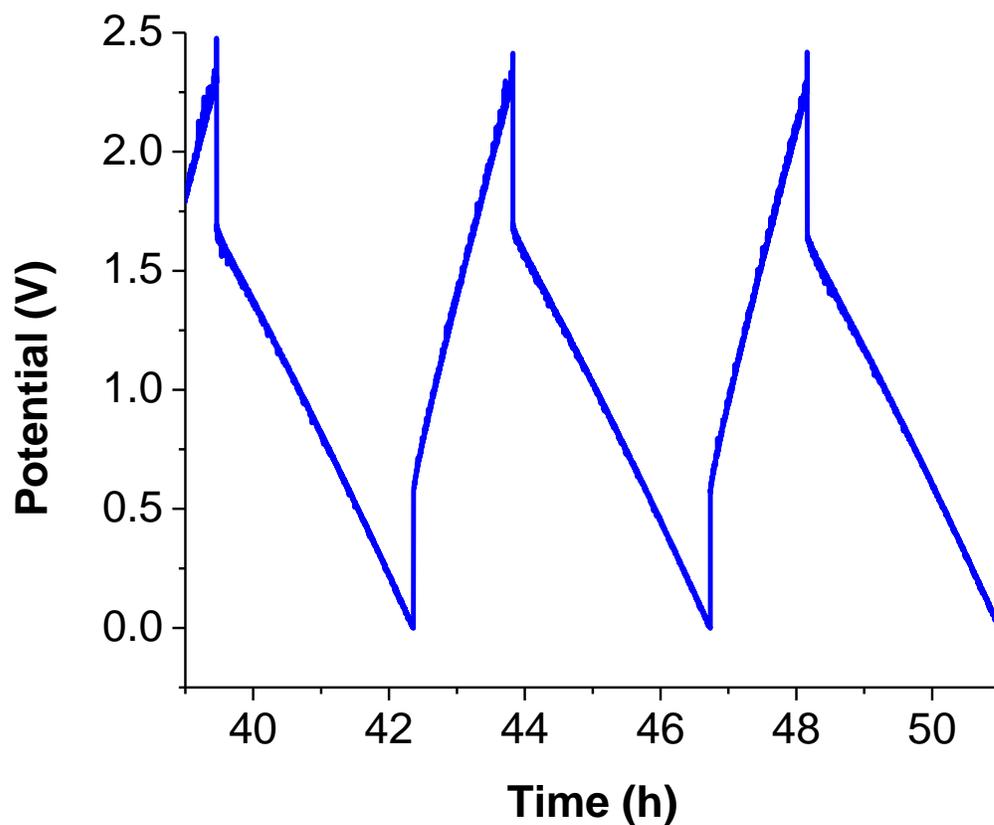


Figure S10. Galvanostatic, two-electrode charge-discharge curves of a slurry of KB. Taken in a glass-fritted H-cell with CH_3CN , 0.2 M $[\text{Bu}_4\text{N}][\text{PF}_6]$, 50 mg of KB per compartment, and 5 mL of solution per side. Coiled Pt working electrode, coiled Pt counter electrode. 500 μA charge, -250 μA discharge.

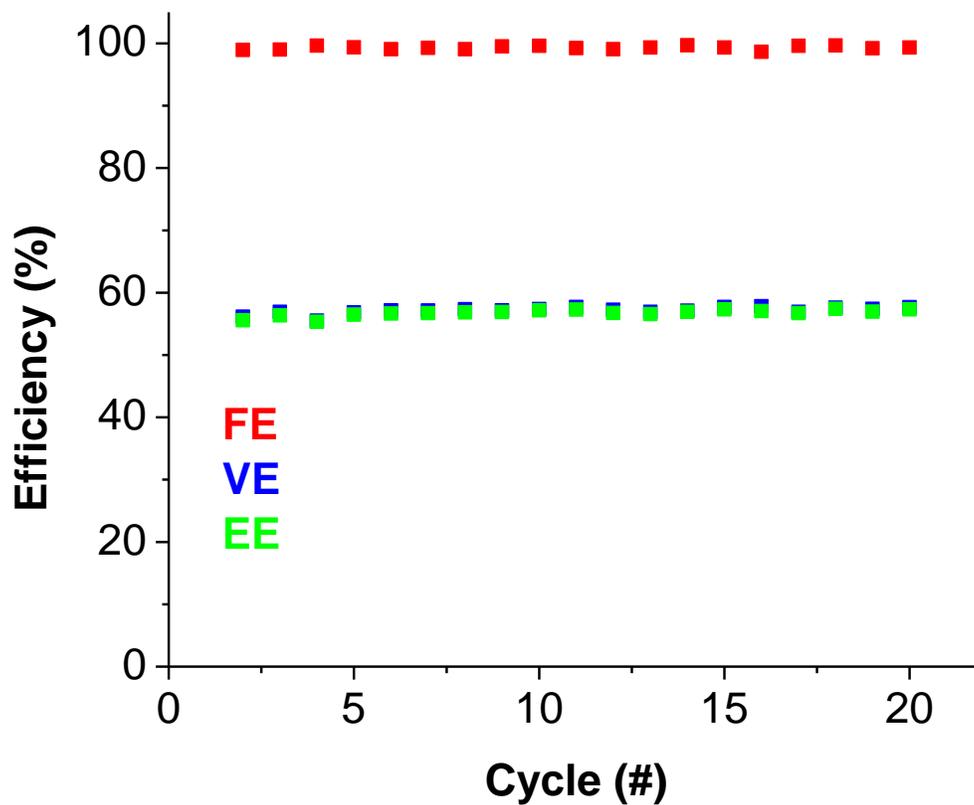


Figure S11. Efficiency values of a slurry of KB (Faradaic efficiency (FE); Voltage efficiency (VE); Energy efficiency (EE)). Taken in a glass-fritted H-cell with CH₃CN, 0.2 M [Bu₄N][PF₆], 50 mg of KB per compartment, and 5 mL of solution per side. Coiled Pt working electrode, coiled Pt counter electrode. 500 μ A charge, -250 μ A discharge.

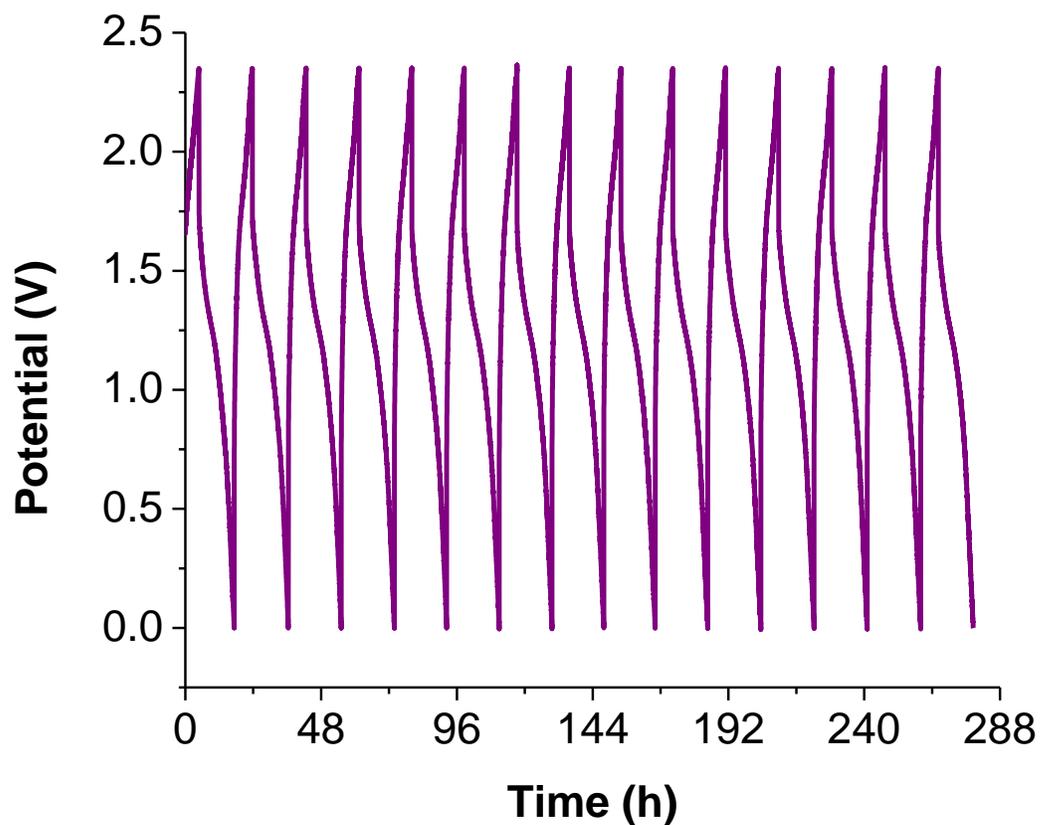


Figure S12. Galvanostatic, two-electrode charge-discharge curves of a slurry of **1**/KB. Taken in a glass-fritted H-cell with CH₃CN, 0.2 M [Bu₄N][PF₆], 65 mg of **1** and 105 mg of KB per compartment, and 5 mL of solution per side. Coiled Pt working electrode, coiled Pt counter electrode. 500 μA charge, -250 μA discharge.

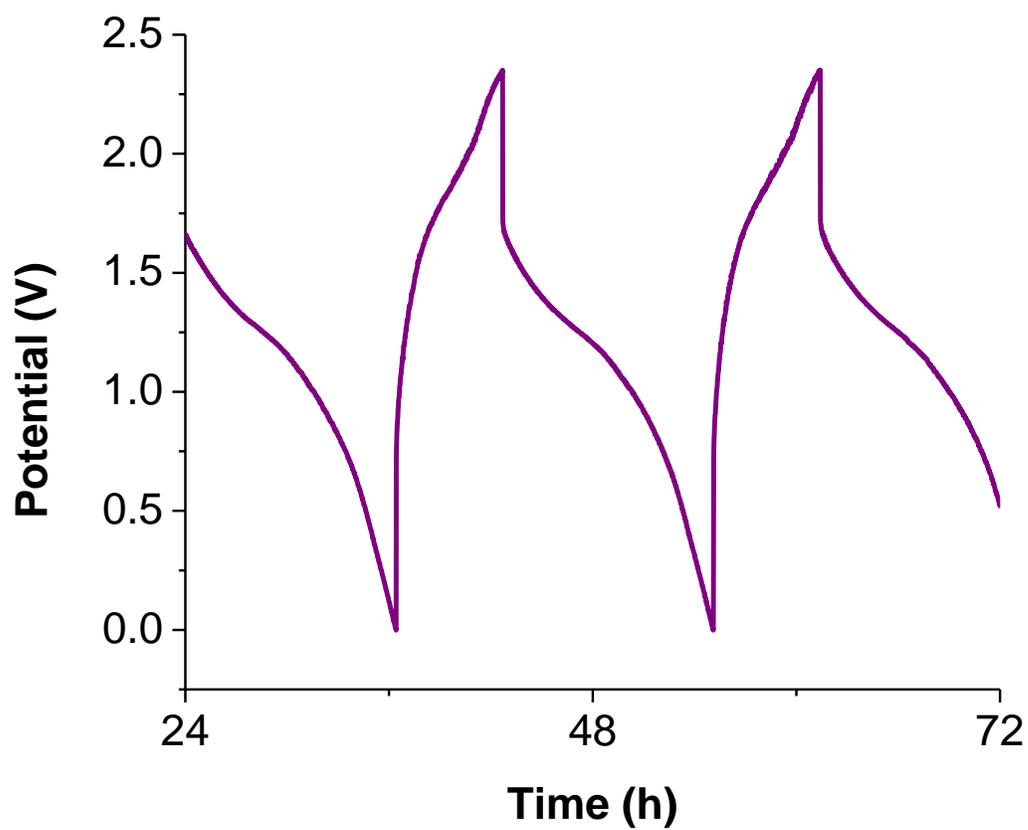


Figure S13. Galvanostatic, two-electrode charge-discharge curves of a slurry of **1**/KB. Taken in a glass-fritted H-cell with CH₃CN, 0.2 M [Bu₄N][PF₆], 65 mg of **1** and 105 mg of KB per compartment, and 5 mL of solution per side. Coiled Pt working electrode, coiled Pt counter electrode. 500 μA charge, -250 μA discharge.

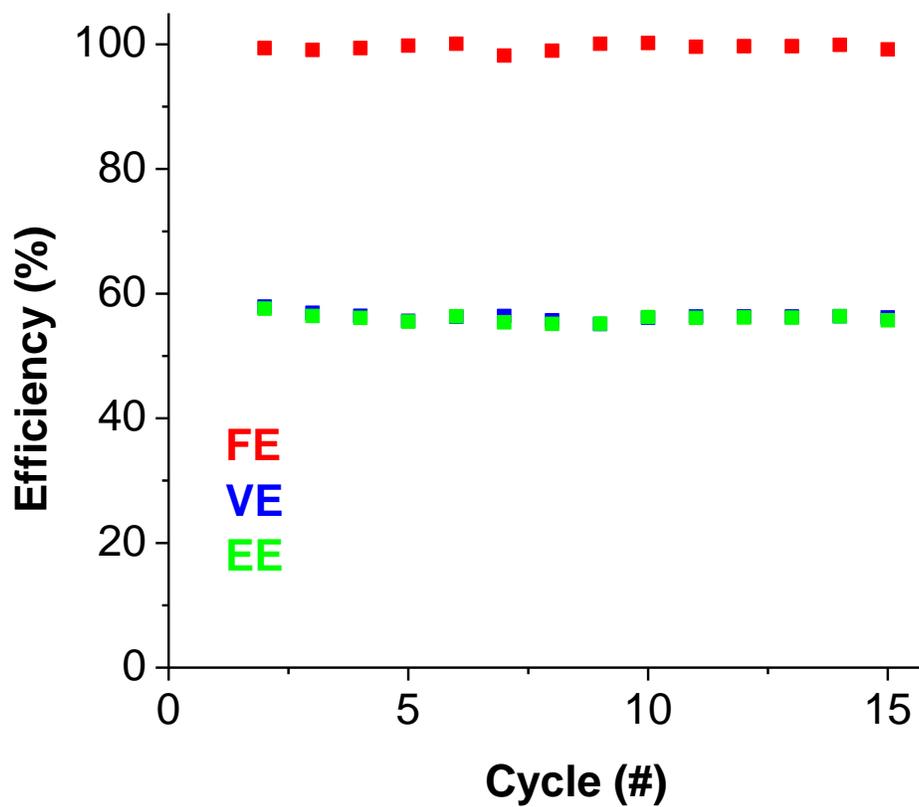


Figure S14. Efficiency values of a slurry of **1**/KB (Faradaic efficiency (FE); Voltage efficiency (VE); Energy efficiency (EE)). Taken in a glass-fritted H-cell with CH₃CN, 0.2 M [Bu₄N][PF₆], 65 mg of **1** and 105 mg of KB per compartment, and 5 mL of solution per side. Coiled Pt working electrode, coiled Pt counter electrode. 500 μ A charge, -250 μ A discharge.

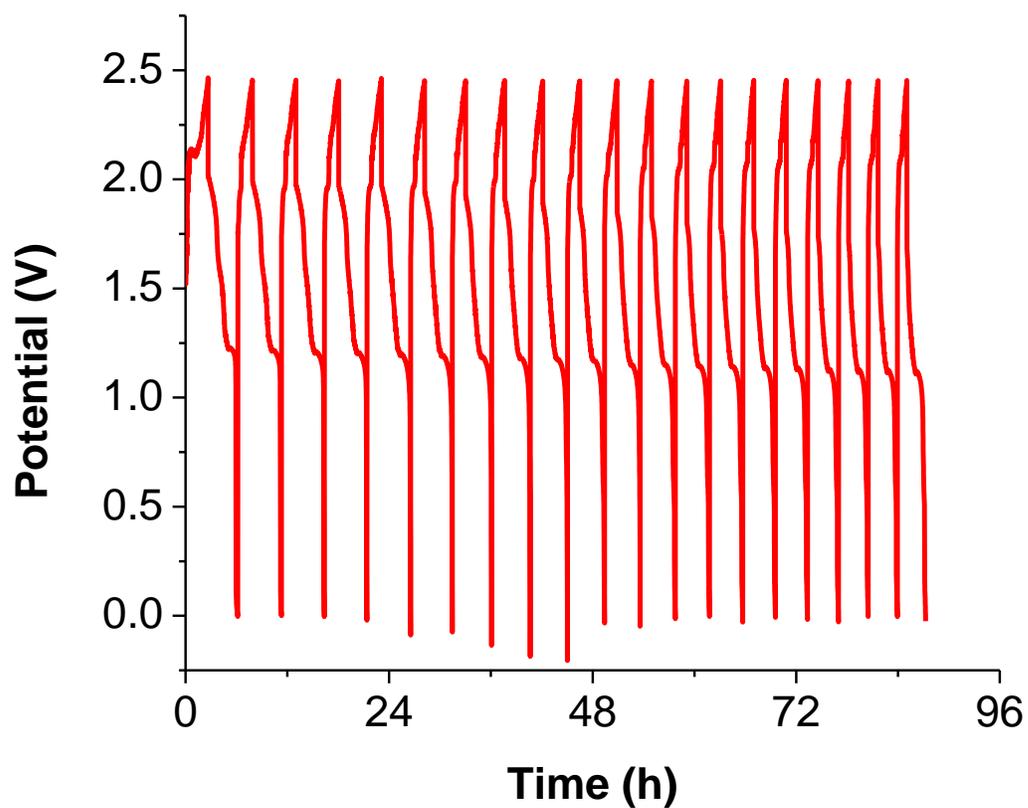


Figure S15. Galvanostatic, two-electrode charge-discharge curves of a slurry of **1**. Taken in a glass-fritted H-cell with CH₃CN, 0.2 M [Bu₄N][PF₆], 32.1 μmol of **1** per compartment, and 5 mL of solution per side. Coiled Pt working electrode, coiled Pt counter electrode. 500 μA charge, -250 μA discharge.

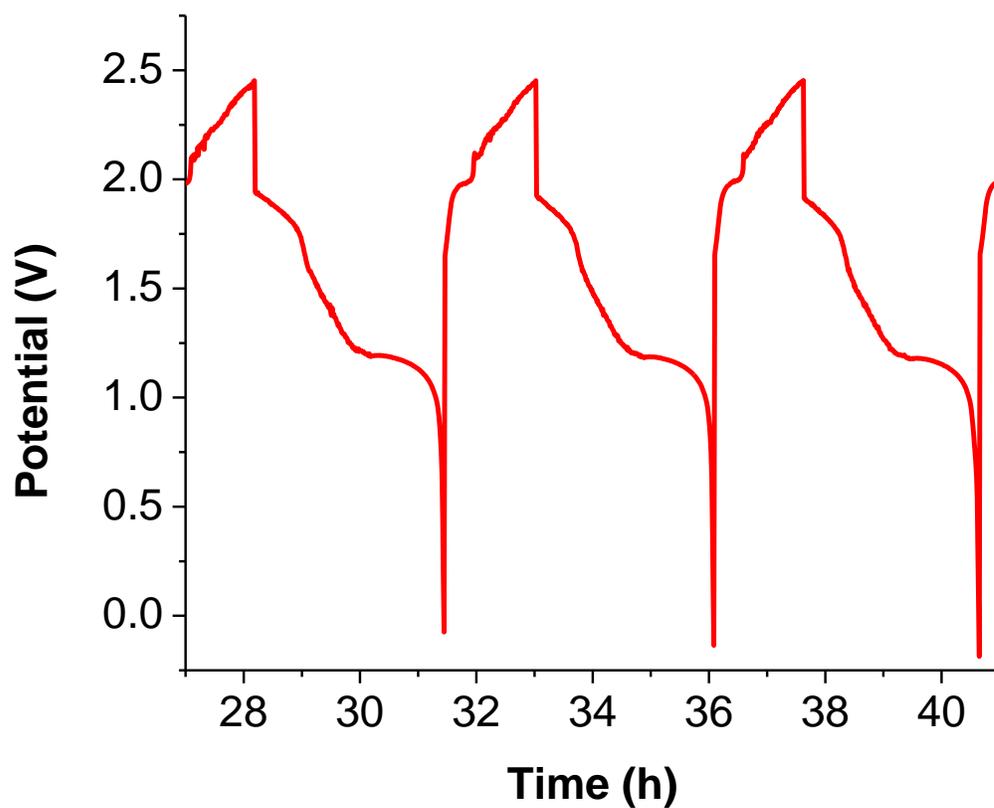


Figure S16. Galvanostatic, two-electrode charge-discharge curves of a slurry of **1**. Taken in a glass-fritted H-cell with CH₃CN, 0.2 M [Bu₄N][PF₆], 32.1 μmol of **1** per compartment, and 5 mL of solution per side. Coiled Pt working electrode, coiled Pt counter electrode. 500 μA charge, -250 μA discharge.

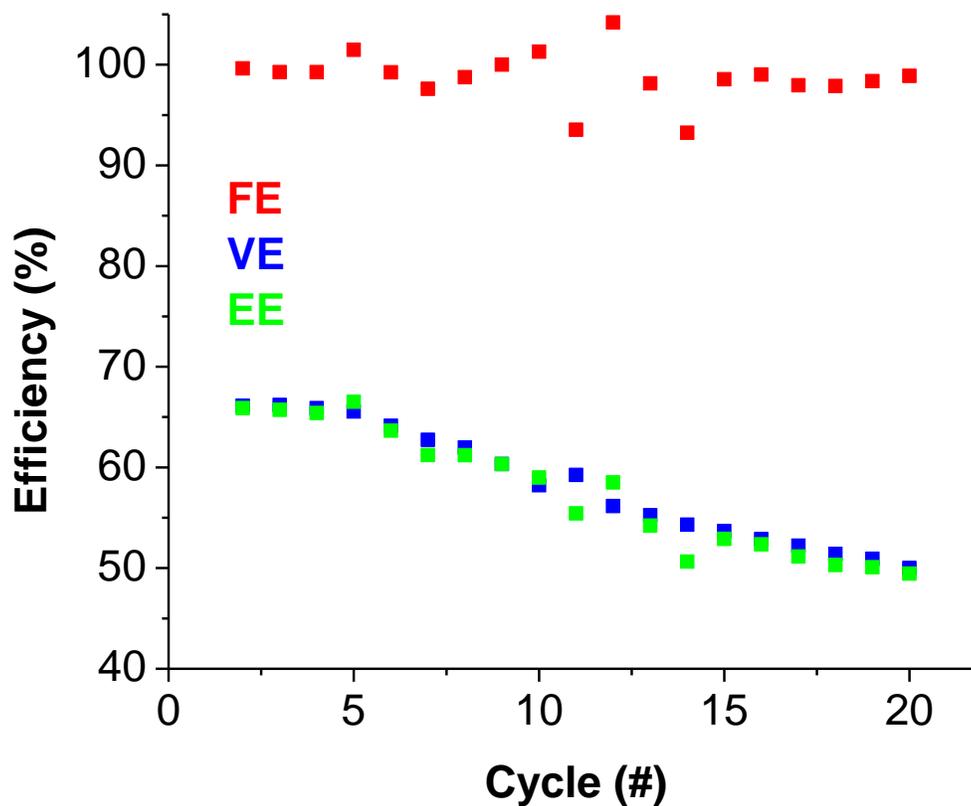


Figure S17. Efficiency values of a slurry of **1** (Faradaic efficiency (FE); Voltage efficiency (VE); Energy efficiency (EE)). Taken in a glass-fritted H-cell with CH₃CN, 0.2 M [Bu₄N][PF₆], 32.1 μmol of **1** per compartment, and 5 mL of solution per side. Coiled Pt working electrode, coiled Pt counter electrode. 500 μA charge, -250 μA discharge.

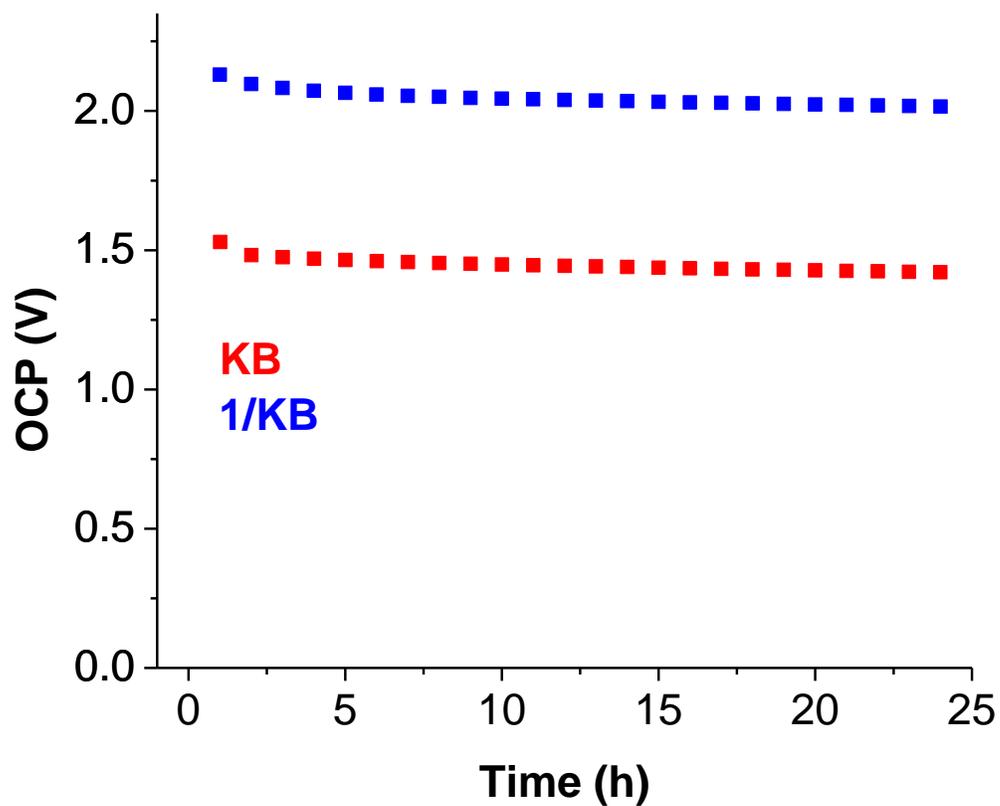


Figure S18. Slurry-state self-discharge experiments for KB (red) and 1/KB (blue), with the same experimental and charging conditions as done for galvanostatic cycling experiments. Each cell was charged using a voltage cutoff of 2.35 V, and the OCP was monitored over the course of 24 h.

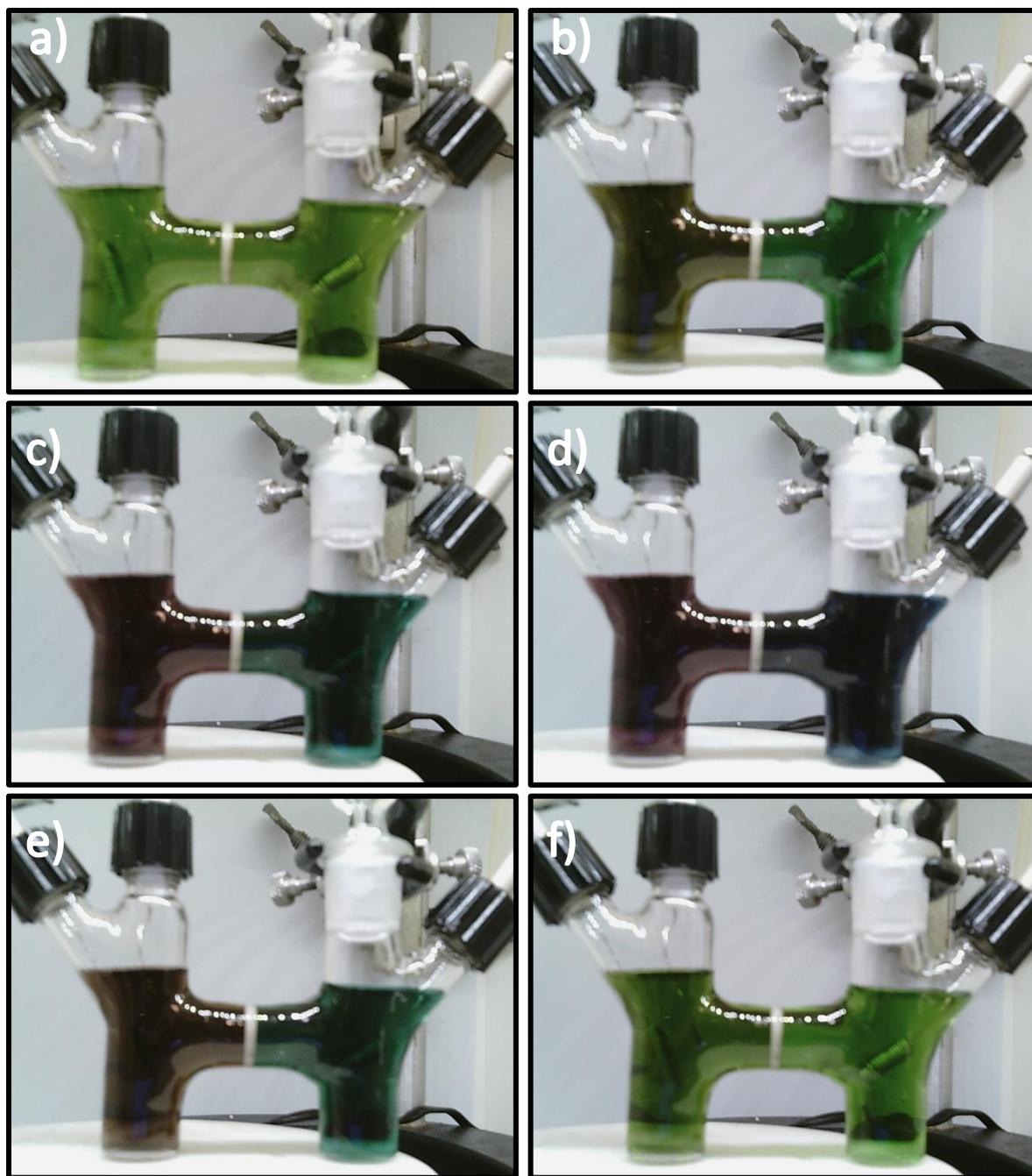


Figure S19. One full charge/discharge cycle of **1**, in CH_3CN with oxidation and reduction occurring in the left and right compartment on charging, respectively. (a-d) were taken during charging, and (e-f) were taken during discharging. (a) = ~0% state of charge (SOC), (b) = ~25% SOC, (c) = 50% SOC, (d) ~75% SOC, (e) ~35% SOC, (f) = ~0% SOC.

S3. Reference

1. Hunt, C.; Peterson, M.; Anderson, C.; Chang, T.; Wu, G.; Scheiner, S.; Ménard, G. Switchable Aromaticity in an Isostructural Mn Phthalocyanine Series Isolated in Five Separate Redox States. *J. Am. Chem. Soc.* **2019**, *141*, 2604-2613.
2. Cabrera, P. J.; Yang, X.; Suttill, J. A.; Hawthorne, K. L.; Brooner, R. E. M.; Sanford, M. S.; Thompson, L. T. Complexes Containing Redox Noninnocent Ligands for Symmetric, Multielectron Transfer Nonaqueous Redox Flow Batteries. *J. Phys. Chem. C* **2015**, *119*, 15882-15889.