Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2020

Desymmetrized Hexasubstituted [3]radialene Anions as Aqueous Organic Catholytes for Redox Flow Batteries

Nicholas A. Turner,[a] Matthew B. Freeman,[a] Harry D. Pratt III,[b] Austin E. Crockett,[a] Daniel S. Jones,[a] Mitchell R. Anstey,[c] Travis M. Anderson,[b] and Christopher M. Bejger*[a]

[a]Department of Chemistry, University of North Carolina at Charlotte, 9201 University City Boulevard, Charlotte North Carolina 28223, USA.

[b]Power Sources R&D Department, Sandia National Laboratories, Albuquerque, NM 87185, USA.

[c]Department of Chemistry, Davidson College, Davidson, NC 28035, USA.

Supporting Information

I. Synthetic Details S2

II. Measurements S4

III. Solubility Studies S5

IV. X-ray Diffraction S13

V. Cyclic Voltammetry S17

VI. Density Functional Theory S20

VII. H-Cell Galvanostatic Charge-Discharge Experiments S21

VIII. Flow Cell Studies S24

IX. References S25

I. Synthetic Details

General Information

All reagents were purchased commercially and used without any further purification. The following compounds were used: methyl cyanoacetate (Aldrich, 99.9%), tetrachlorocyclopropene (TCCP) (Acros Organics, 98%), concentrated hydrochloric acid (Macron), sodium iodide (Aldrich, 99.9%), triethylamine (Aldrich, 99%), malononitrile (Alfa Aesar, 99%), sodium sulfate (Aldrich, 99%), magnesium sulfate (Fisher, 99%), Celite (EMD Millipore Corp.), sodium hydride (Aldrich, 60% in oil), glyme (DME) (Aldrich, anhydrous, 99.5%), tetrabutylammonium bromide (TCI America, 99.0%), and potassium persulfate (Fisher, 99.7%). Solvents were bought from commercial suppliers and were used as is without further modification. Hexanes and dichloromethane were purified using an MBRAUN Solvent Purification System (MB-SPS).

Synthesis

The below syntheses have been previously reported by Fukunaga and coworkers.[1–3] Compounds **1**-**4** were converted to the corresponding potassium radical anion salts by addition of a concentrated aqueous solution of potassium persulfate to saturated aqueous solutions of **1**-**4**. The resulting blue solutions were cooled in ice baths and the radical solids were filtered, washed with cold water, and dried overnight.

*Synthesis of **2***

Preparation of zwitterionic 1,2-Bis(dicyanomethylene)-3-triethylammoniumcyclopropanide (**Z2**)

Tetrachlorocyclopropene (1 g, 5.6 mmol) and malononitrile (0.739 g, 11.2 mmol) were stirred in 26 mL of dry DCM. The solution was cooled to -30 ^{o}C before triethylamine (3.41 g, 33.7 mmol) was added dropwise. The yellow solution was warmed to 0 ^{o}C and treated with 8 mL of water then immediately filtered. The tan colored solid was washed with water, methanol, and DCM. The product was then recrystallized from acetonitrile and ethyl acetate. This method yielded 0.3572 g (38.4%).

Preparation of Bis(dicyanomethylene)(methoxycarbonylcyanomethylene)cyclopropandiide (Na_2•**2**)

Sodium methoxide was prepared from sodium metal (0.436 g, 18.96 mmol) and 19 mL of methanol. Methyl cyanoacetate (0.577 g, 5.83 mmol) was added to the solution and allowed to stir for 15 minutes. This reaction mixture was treated with the zwitterion (0.715 g, 2.69), made above, in acetonitrile for 1 hour at 0 °C. The solution was allowed to stir for an additional hour at 0 °C. The solution was then treated with tetrabutylammonium bromide (1.58 g, 4.92 mmol). The methanol was evaporated under reduced pressure and the brown residue was allowed to stand over night at room temperature. This was then washed with water and ethyl acetate to yield a yellow precipitate. The precipitate was collected on a medium frit using vacuum filtration. This solid was then dissolved in acetonitrile and converted to the sodium salt by adding a concentrated solution of sodium iodide in acetonitrile. The white solid was collected and dried in vacuo. This method yielded 0.5502 g (66.4%).

*Synthesis of **3***

Preparation of zwiterionic 1,2-Bis(methoxycarbonylcyanomethylene)-3-triethylammoniumcyclopropanide (**Z3**)

Tetrachlorocyclopropene (2.00 g, 11.24 mmol) and methyl cyanoacetate (2.59 g, 26.18 mmol) were stirred in 30 mL of DCM. The solution was cooled to -30 °C before triethylamine (6.99 g, 69.16 mmol) was added drop-wise. The mixture was warmed to 0 °C and washed with water three times using a separatory funnel. The organic layer was then dried with magnesium sulfate and filtered. The solvent was evaporated and the solid was recrystallized from acetonitrile. This method yielded 0.9531 g (25.6%) as a light tan solid.

1,2-Bis(methoxycarbonylcyanomethylene)-3-dicyanomethylenecyclopropandiide

(Na_2•**3**)

A solution of sodio malononitrile was prepared from sodium metal (0.358 g, 15.61 mmol) and methanol (23.83 mL). Malononitrile was added to the solution and stirred for 15 minutes. The solution was cooled to 0 °C before the zwitterion (0.953 g, 2.88 mmol) made from above, was added drop-wise in a solution of acetonitrile. The reaction mixture was warmed to room temperature and allowed to stir for 2.5 hours. The solution was then treated with tetrabutylammonium bromide. The methanol was evaporated under reduced pressure and the residual solution was diluted with water. The precipitated solid was collected by filtration on a medium glass frit. The bis(TBA)-salt was recrystallized from acetonitrile and ethyl acetate to yield crystals suitable for X-ray diffraction. These crystals were dissolved in acetonitrile and converted to the sodium salt with the addition of a concentrated solution of sodium iodide in acetonitrile.

The yellow solid was collected via vacuum filtration and rigorously washed with acetonitrile. This method yielded 0.5396 g (55.1%) of **3**.

Synthesis of ***4***

Tris(methoxycarbonylcyanomethylene)cyclopropandiide

(Na_2•**4**)

60% NaH (3.19 g, 79.69 mmol) was washed with hexanes (3x10mL) and dried under vacuum. NaH was suspended in 68 mL of anhydrous DME and then cooled to 0 °C. Methyl cyanoacetate (3.60 g, 36.42 mmol) in 8 mL of DME was added dropwise over a 35 minute period. This solution was allowed to stir for one hour at 0 °C. Tetrachlorocyclopropene (TCCP) (2 g, 11.24 mmol) in 4 mL of DME was added dropwise over a 30 minute period then allowed to stir for an additional hour. The reaction mixture was evaporated under reduced pressure to dryness. Then dissolved in water, filtered, and washed once with ether using a separatory funnel. This was treated with TBABr and allowed to sit overnight. The precipitate was filtered and then recrystallized with acetonitrile and ethyl acetate to yield a brown crystalline solid. Yield of 64%. The sodium salt variant of the product above was synthesized by dissolving the TBA salt in acetonitrile and adding a concentrated solution of NaI also in acetonitrile. The product formed was then washed with acetonitrile, vacuum filtered, and dried in a vacuum chamber to yield the disodium salt as a tan solid. This solid slowly turns blue-green over time in air, indicating the formation of the radical anion.

II. Measurements

Ultraviolet-visible Spectroscopy

UV-vis spectra were obtained on a Cary 300 UV-vis spectrophotometer with quartz cells (1 cm path length) with all solutions made using volumetric glassware and micropipettes. The samples were prepared under ambient conditions.

Electrochemical Measurements

All electrochemical measurements were obtained on a Gamry 1000E potentiostat and were recorded on Gamry Framework Software (Version 7.02). Analysis of the data was done using Gamry Echem Analyst (Version 7.02).

Static Electrochemical Measurements

For cyclic voltammetry, a three-electrode set up was used with a BASi glassy carbon working electrode, silver wire as the counter electrode, and a Ag/AgCl quasireference electrode.

Galvanostatic Half Cell Cyclic Charge Discharge

An Adam & Chittenden H cell (8 mL) was used with a Selemion CSO cation exchange membrane and sealed with a Viton rubber O-ring. Graphite felt electrodes (Fuel Cell Store) were cut and placed into an oven at 200 ^{o}C for 1 h before use. The graphite felt electrodes were submerged to have a surface area of (1 mm x 10 mm x 3mm). The half-cell was referenced versus Ag/AgCl using a quasireference electrode.

Conductivity

Conductivity measurements were collected on a Fisher Scientific AR20 pH/Conductivity Meter using saturated aqueous solutions of **1-4** as dianion and radical anion species, respectively.

III. Solubility Studies

Measurement of dianions were performed using UV/Vis spectroscopy. Calibration curves were obtained by plotting the absorbances against concentration. Supersaturated solutions were obtained by sonicating an excess of solid in 1 mL which was then allowed to sit overnight to equilibrate. An aliquot from the supersaturated solution (10 µL) was diluted to 25 mL and then diluted accordingly to reach the linear range of the calibration curve. Measurements of radical anions were determined by UV/Vis or via precipitation when exact measurements could not be obtained.

*Solubility of **1** in water*

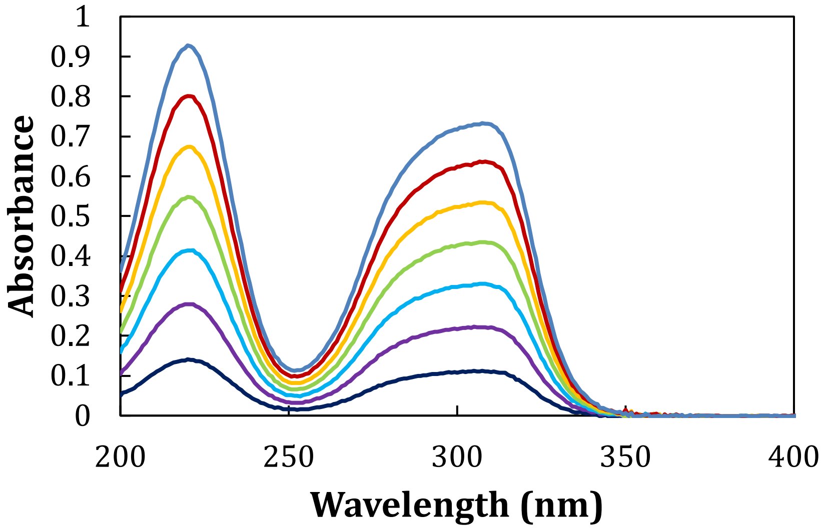


Figure S1. The overlaid absorbance spectra $\mathbf{1}^{2-}$ with absorbances at 220, and 300 nm, respectively.

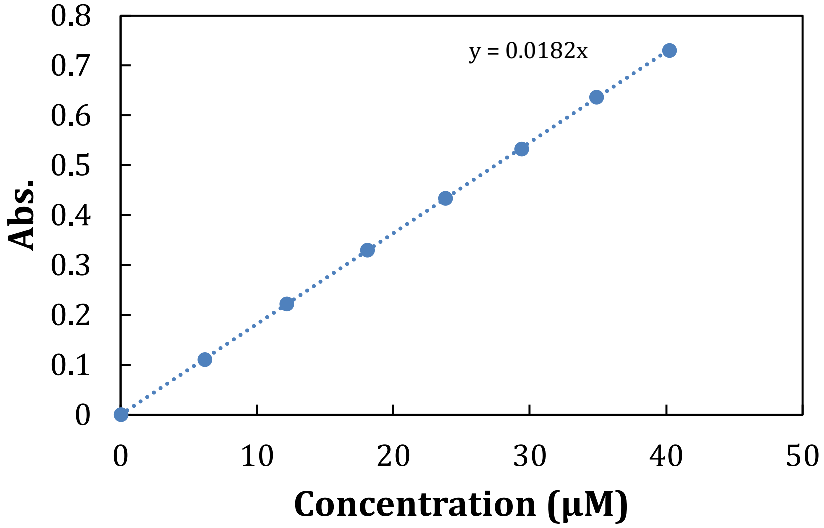


Figure S2. Beer's Law plot of absorbance at 306 nm for Na_2•**1** in water.

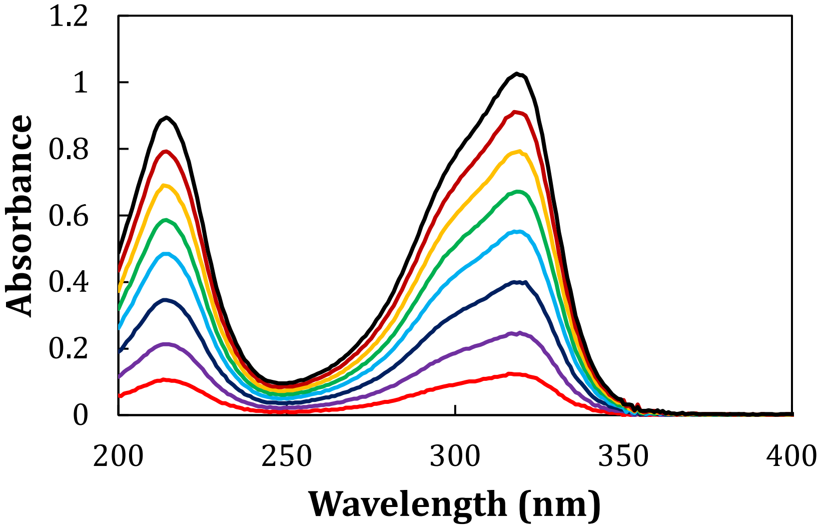


Figure S3. The overlaid absorbance spectra **1**$^{\bullet-}$ with absorbances at 220, and 300 nm, respectively.

*Solubility of **2** in water*

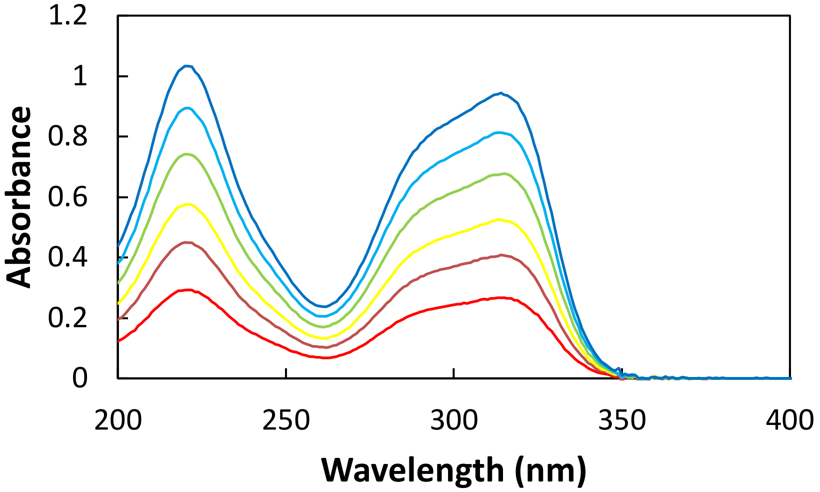


Figure S4. The overlaid absorbance spectra **2**$^{2-}$ with absorbances at 220, and 300 nm, respectively.

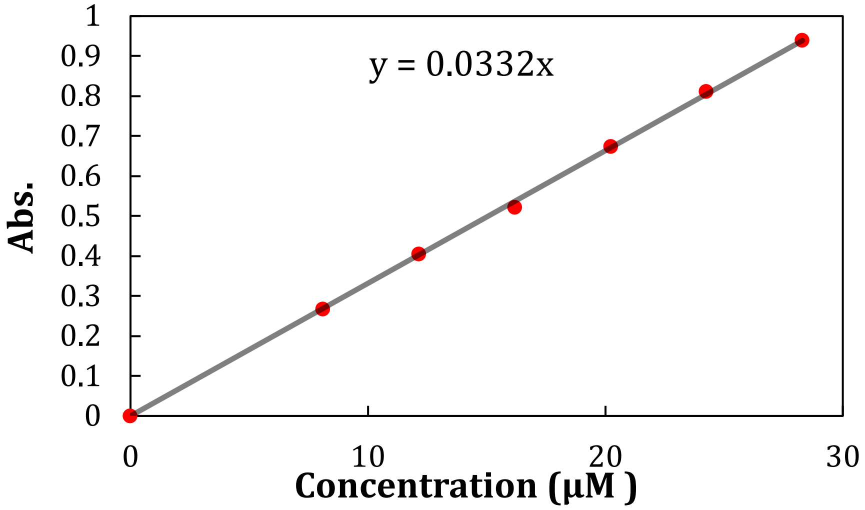
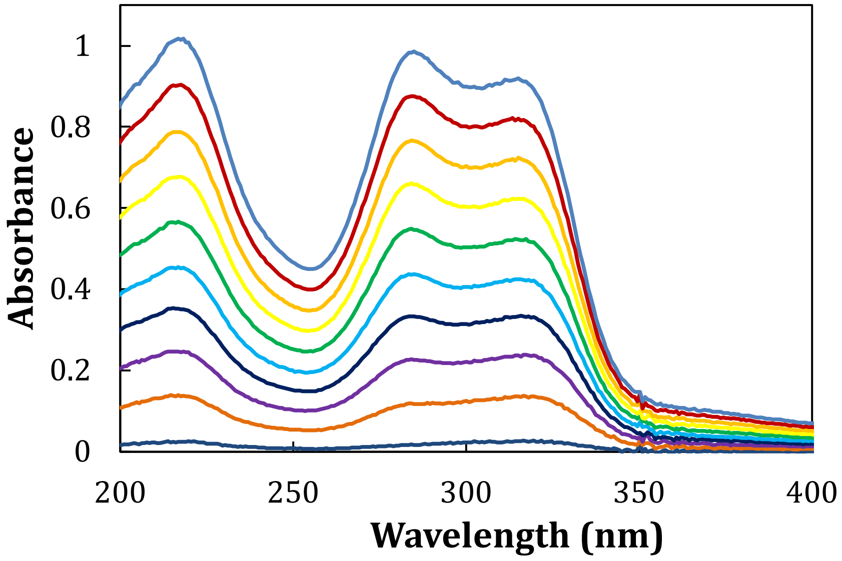


Figure S5. Beer's Law plot of absorbance at 303 nm for Na_2•**2** in water.



Figures S6. The overlaid absorbance spectra $\mathbf{2}^{\bullet-}$ in water.

*Solubility of **3** in water*

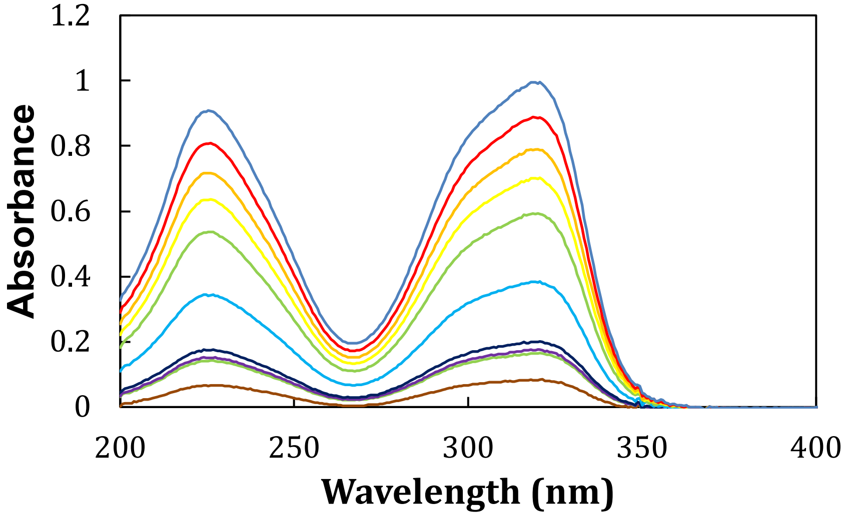


Figure S7. The overlaid absorbance spectra $\mathbf{3}^{2-}$ with absorbances at 225, and 319 nm, respectively.

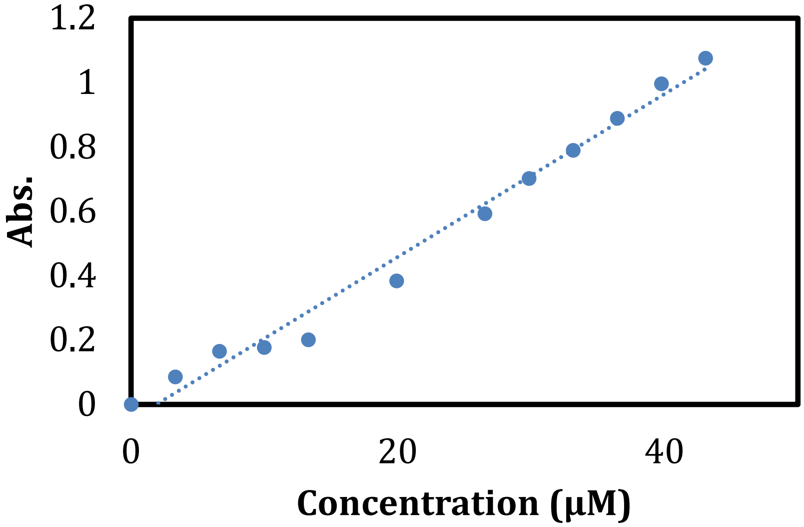


Figure S8. Beer's Law plot of absorbance at 319 nm for $\mathbf{3}^{2-}$in water.

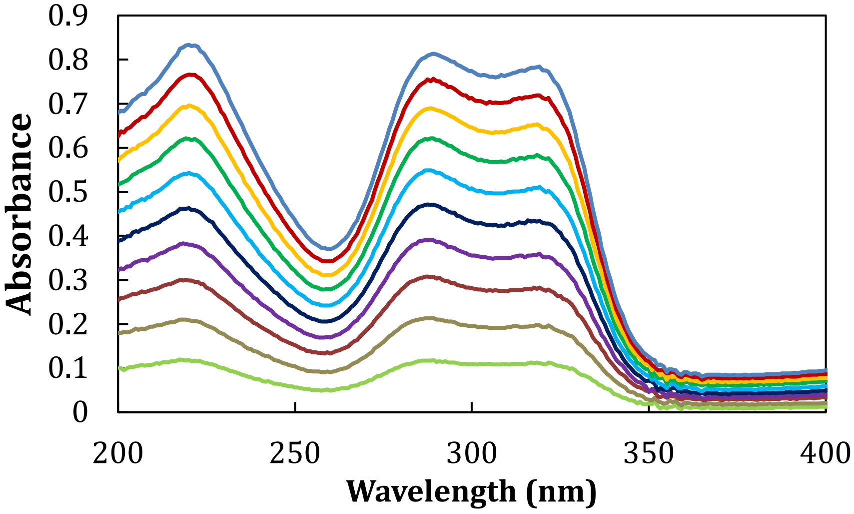


Figure S9. The overlaid absorbance spectra $\mathbf{3}^{\bullet-}$ in water.

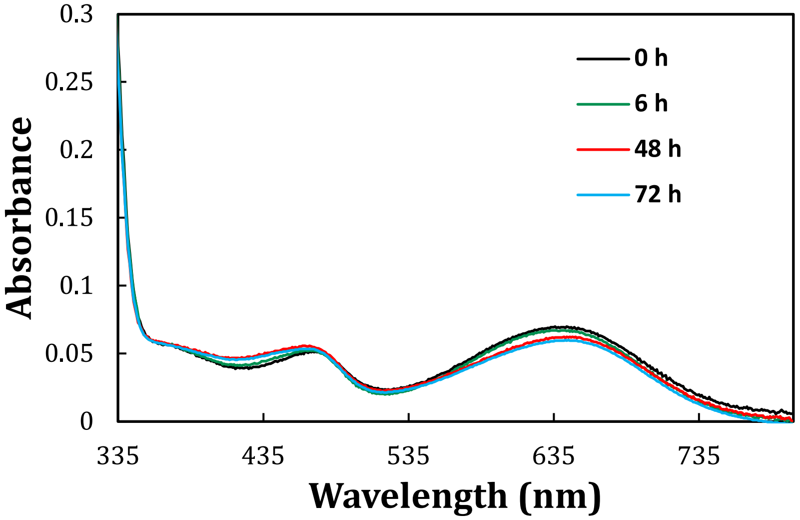


Figure S10. UV/Vis time study of $\mathbf{3}^{\bullet-}$ in water.

*Solubility of **4** in water*

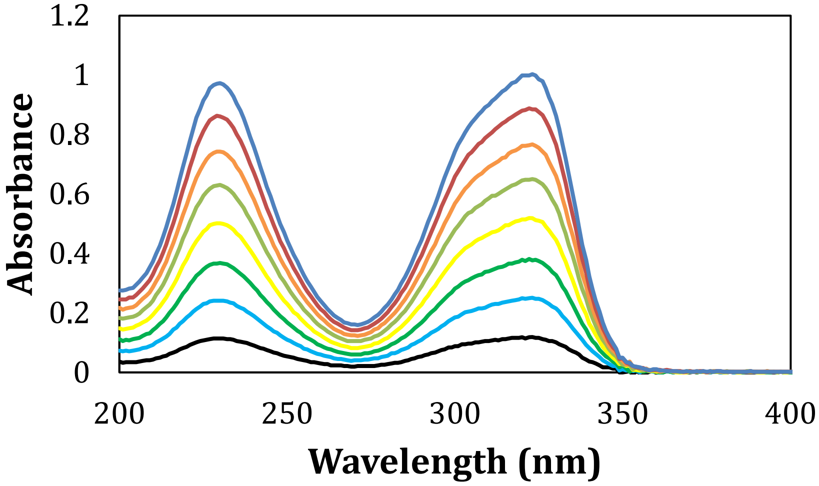


Figure S11. The overlaid absorbance spectra $\mathbf{4}^{2-}$ with absorbances at 230, and 325 nm, respectively.

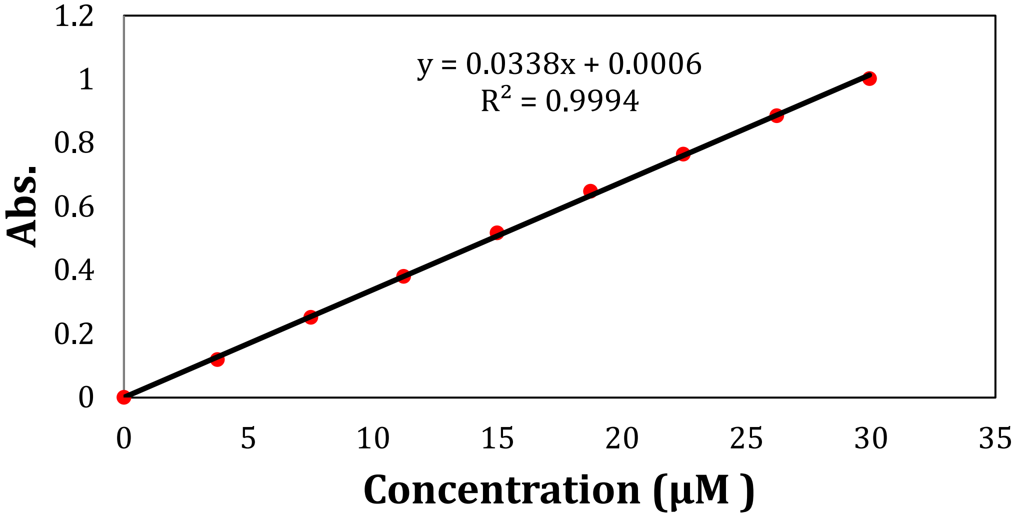


Figure S12. Beer's Law plot of absorbance at 321 nm for $\mathbf{4}^{2-}$in water.

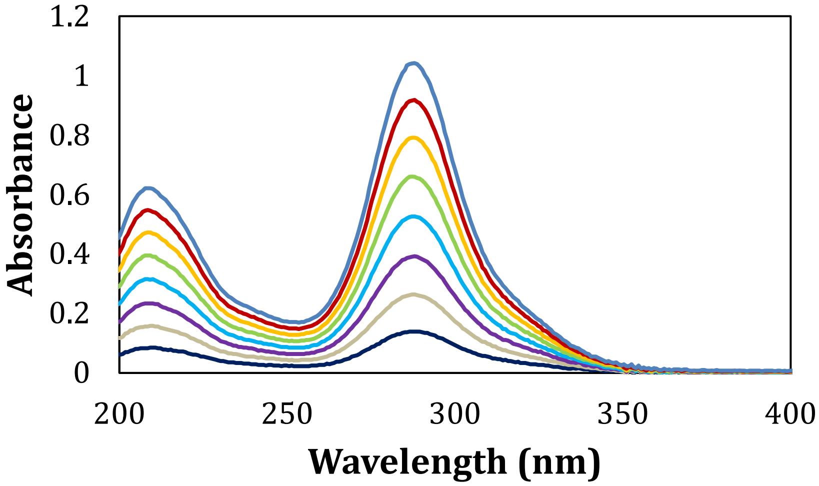


Figure S13. The overlaid absorbance spectra $\mathbf{4}^{\bullet-}$ in water.

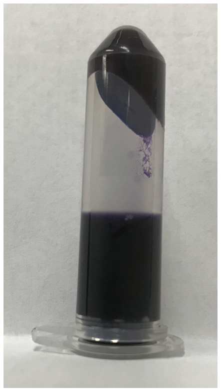


Figure S14. Image of precipitated $\mathbf{4}^{\bullet-}$ after addition of potassium persulfate to a 0.1 M solution of $\mathbf{4}^{2-}$.

IV. X-ray Diffraction

X-ray diffraction data were collected using an Agilent/Oxford Diffraction Gemini A Ultra diffractometer. The diffractometer was equipped with a sealed-tube Mo source with a graphite monochromator (λ=0.71073 Å) and a sealed-tube Cu source with graphite focusing optics (λ=1.54184 Å). In all cases data were collected to better than 0.8 Å resolution.

The CrysAlisPro diffractometer software[1] provided intensity data corrected for Lorentz, polarization, and absorption effects. Preliminary structure solutions were found with the AutoChem software package[1]. Final structures were solved with SHELXT[2] (direct methods) and refined with SHELXL[3], using the Olex2 software package[4]. Anisotropic refinement for all non-hydrogen atoms was performed. Hydrogen atoms were placed in calculated positions. Compound 2TBA•3 was refined using a solvent mask applied using BYPASS (number of electrons masked, 8, correlate to a single moiety of water).

Publication tables and graphics were generated with the WinGX suite of programs[5].

*X-ray Diffraction **3***

Table S1. Crystal Data of **3**

Identification code	ac_cb_ionpair_cu
Empirical formula	$C_{46}H_{78}N_6O_4$
Formula weight	779.14
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	P 21/n
a/Å	19.7559(3)
b/Å	12.4952(2)
c/Å	38.3843(8)
α/°	90
β/°	93.145(2)
γ/°	90
Volume/Å^3	9461.0(3)
Z	8
ρcalc g/cm^3	1.094
μ/mm^{-1}	0.545
F(000)	3424.0
Crystal size/mm^3	0.478 × 0.247 × 0.213
Radiation	Cu Kα (λ = 1.54184 Å)
2Θ range for data collection/°	7.442 to 133.75
Index ranges	$-23 \leq h \leq 21$, $-13 \leq k \leq 14$, $-45 \leq l \leq 44$
Reflections collected	54925
Independent reflections	15901 [Rint = 0.0520, Rsigma = 0.0388]
Data/restraints/parameters	15901/0/1040
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R1 = 0.0942, wR2 = 0.2573
Final R indexes [all data]	R1 = 0.1204, wR2 = 0.2878
Largest diff. peak/hole / e Å^{-3}	1.398/-0.431

*X-ray Diffraction **4***

Table S2. Crystal Data of 4

Identification code	ac_cb_newionpair2_mo
Empirical formula	$C_{47} H_{81} N_5 O_6$
Formula weight	812.17
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P\ 2_1/n$
a/Å	14.0335(7)
b/Å	19.5712(8
c/Å	38.3843(8)
α/°	90
β/°	100.406(5)
γ/°	90
Volume/Å^3	4937.5(4)
Z	4
ρcalc g/cm^3	1.093
μ/mm^{-1}	0.072
F(000)	1784.0
Crystal size/mm^3	0.526 × 0.412 × 0.14
Radiation	Mo Kα (λ = 0.71073 Å)
2Θ range for data collection/°	6.762 to 57.168
Index ranges	$-17 \leq h \leq 14$, $-21 \leq k \leq 25$, $-18 \leq l \leq 24$
Reflections collected	23673
Independent reflections	10719 [Rint = 0.0438, Rsigma = 0.0546]
Data/restraints/parameters	10719/0/546
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R1 = 0.0570, wR2 = 0.1225
Final R indexes [all data]	R1 = 0.0929, wR2 = 0.1431
Largest diff. peak/hole / e Å^{-3}	0.29/-0.24

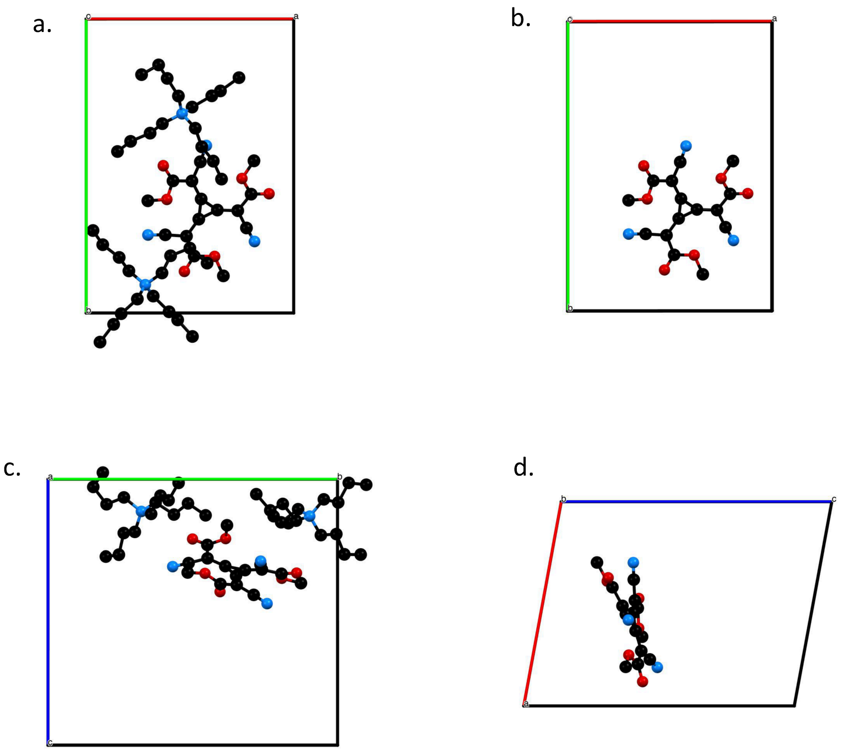


Figure S15. Single crystal-ray structure of TBA$_2$•**4** depicted as ball-and-stick and viewed down the (a) *c* axis view, (b) *c*-axis, (c) *a*-axis, and (d) *b*-axis. Hydrogen atoms were removed for clarification of the view. Tetrabutylammonium cations omitted in b-d. Carbon, black; nitrogen, blue, oxygen, red.

V. Cyclic Voltammetry

*Scan Rate Dependence for **2-3***

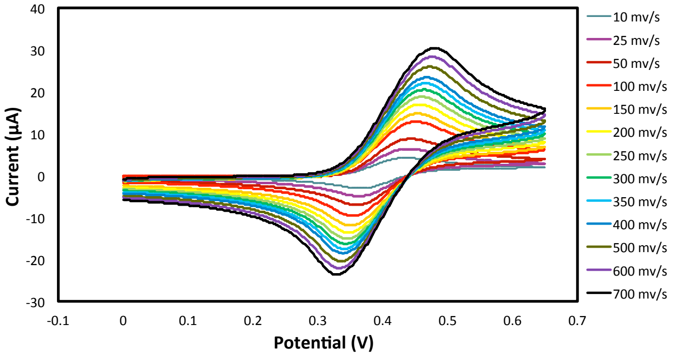


Figure S16. Cyclic voltammograms of **2** (1 mM, H_2O) at various scan rates were taken on a GC WE at 20.5 °C and referenced versus Ag/AgCl.

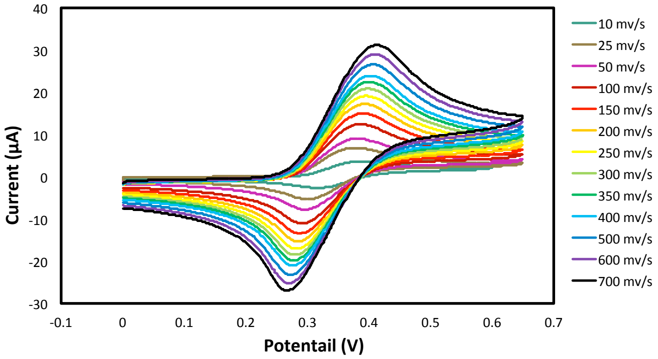


Figure S17. Cyclic voltammograms of **3** (1 mM, H_2O) at various scan rates were taken on a GC WE at 20.5 °C and referenced versus Ag/AgCl.

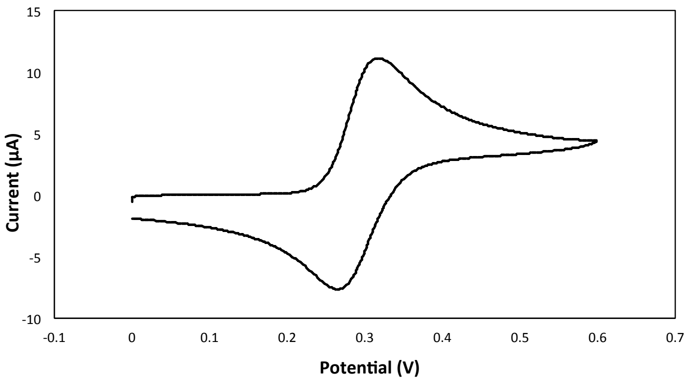


Figure S18. Cyclic voltammograms of **4** (1 mM, 0.25 M KCl, H_2O) at 100 mV/s taken on a GC WE at 20.5 °C and referenced versus Ag/AgCl.

*Time Study for **1***

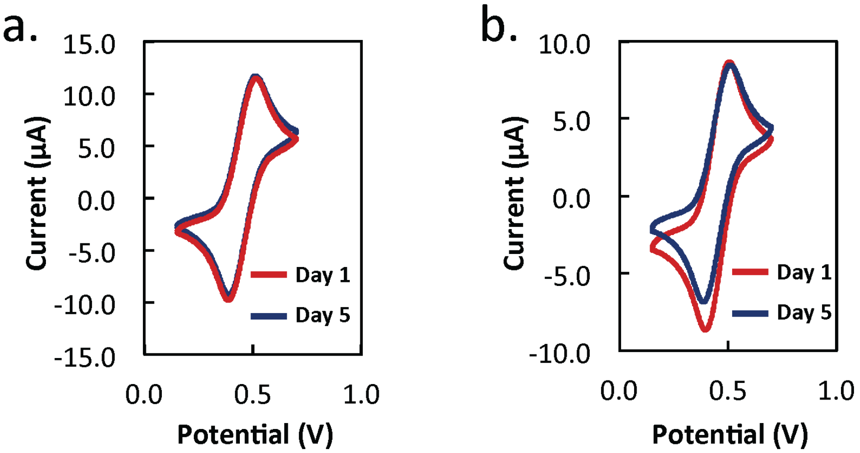


Figure S19. Cyclic voltammetry five-day time study for (a) $\mathbf{1}^{2-}$ (1 mmol) and (b) $\mathbf{1}^{\bullet-}$ (1 mmol) in water using glassy carbon working electrodes, platinum counter electrodes, and Ag/AgCl reference electrodes measured at 100 mV/s.

*Time Study for **2***

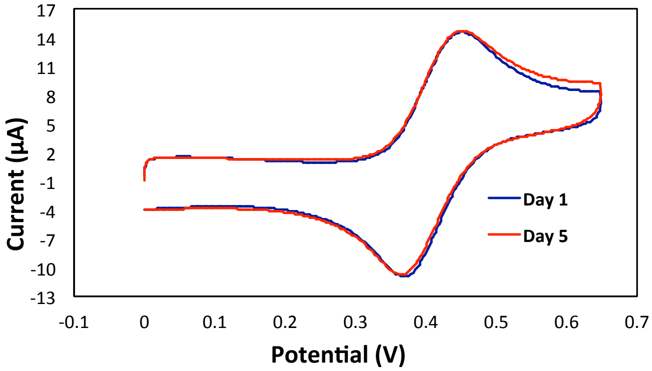


Figure S20. Cyclic voltammetry five-day time study for **2**$^{2-}$ (1 mM) and in water using glassy carbon working electrodes, platinum counter electrodes, and Ag/AgCl reference electrodes measured at 100 mV/s.

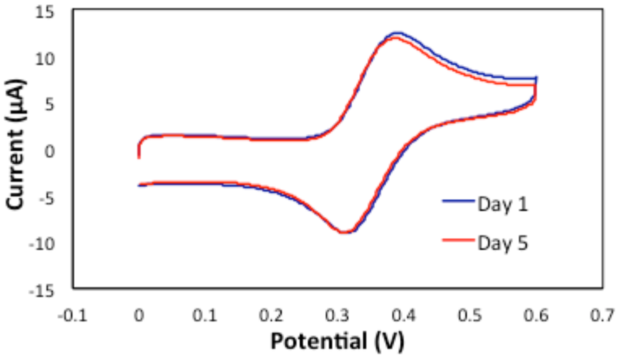


Figure S21. Cyclic voltammetry five-day time study for **3**$^{2-}$ (1 mM) and in water using glassy carbon working electrodes, platinum counter electrodes, and Ag/AgCl reference electrodes measured at 100 mV/s.

VI. Density Functional Theory

Spin density map calculations were performed on geometrical optimized radical anion species in the gas phase at the 6-31G* level of theory using SPARTAN ’16 Quantum Mechanics (1.1).[6] Cooler colors indicate areas of higher spin density while warmer colors indicate areas of lower spin density.

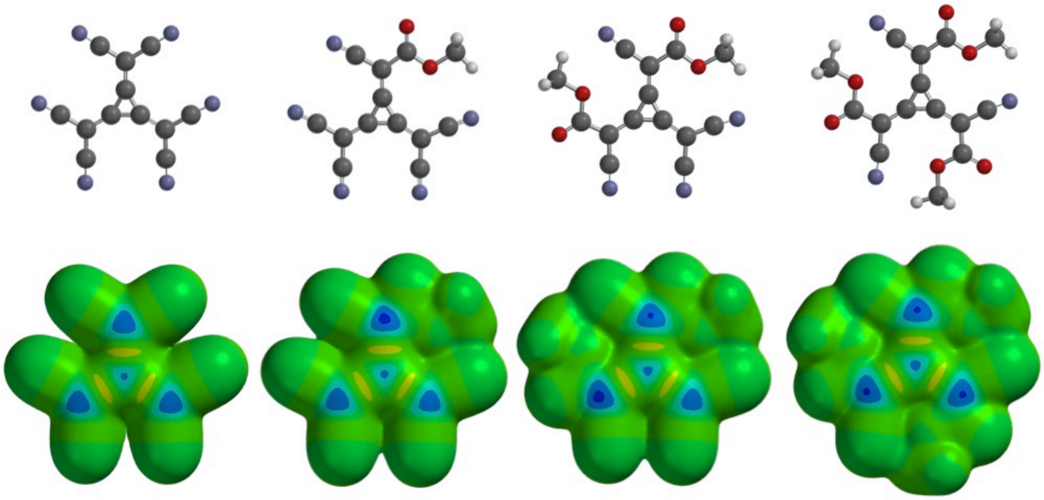


Figure S22. Spin density maps for the radical anions **1**-**4**.

VI. Galvanostatic Charge-Discharge

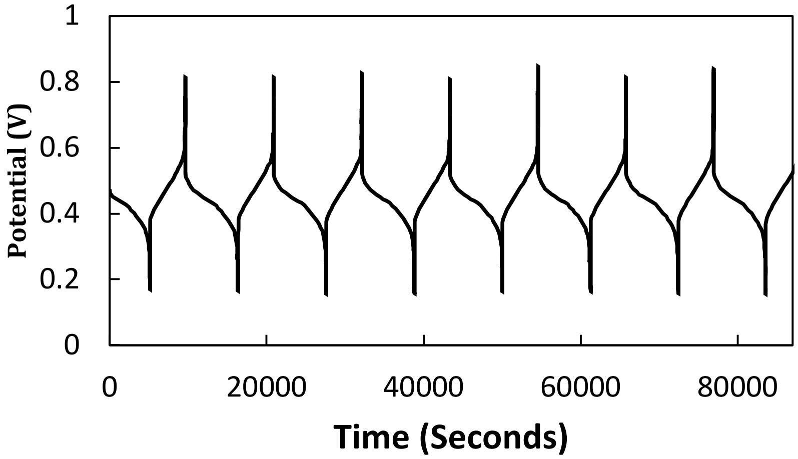


Figure S23. H- Cell charge-discharge profile for **1** (0.01M).

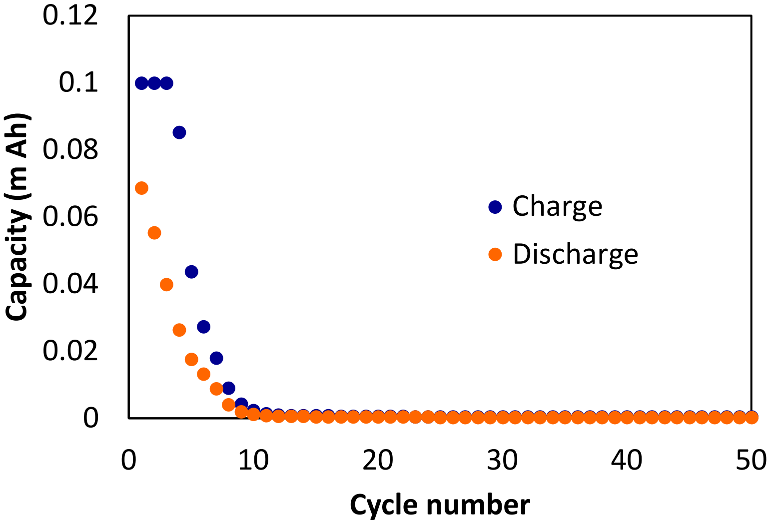


Figure S24. Plot of capacity for the 1e⁻ cycling experiment of aqueous **2** (0.1 M) in an H cell.

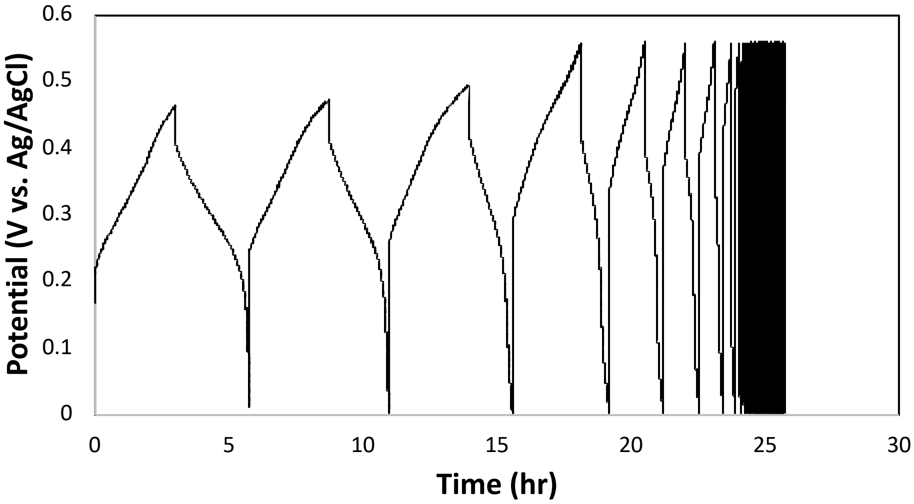


Figure S25. H- Cell charge-discharge profile for **2** (0.1M).

State of Charge Calculation for **3**

The theoretical capacity (Cp) was calculated to find the capacity at an 80% state of charge (SOC) using Equation 1 based on solution volume (V), concentration (C), number of electrons transferred (n), and Faradays constant (F).

Theoretical Capacity:

From $C_6(CN)_2(CN,COOCH_3)_2^{2-}$ to $C_6(CN)_2(CN,COOCH_3)_2^{\bullet -}$

(1) $$C_p = \frac{(1000\frac{mA}{A})*(0.004\ L)*(0.1\ M)*(1\ e^-)*(96485\ \frac{C}{mol})}{3600\ \frac{s}{h}}$$

C_p = 0.0107 Ah

80% SOC = 0.00857 Ah

Set Experimental Parameters:

Charging current was set to 0.00286 A for 3 h and the discharging current was set for 0.00214 A for 4 hours with cut off voltages at 0.475 and 0 V, respectively.

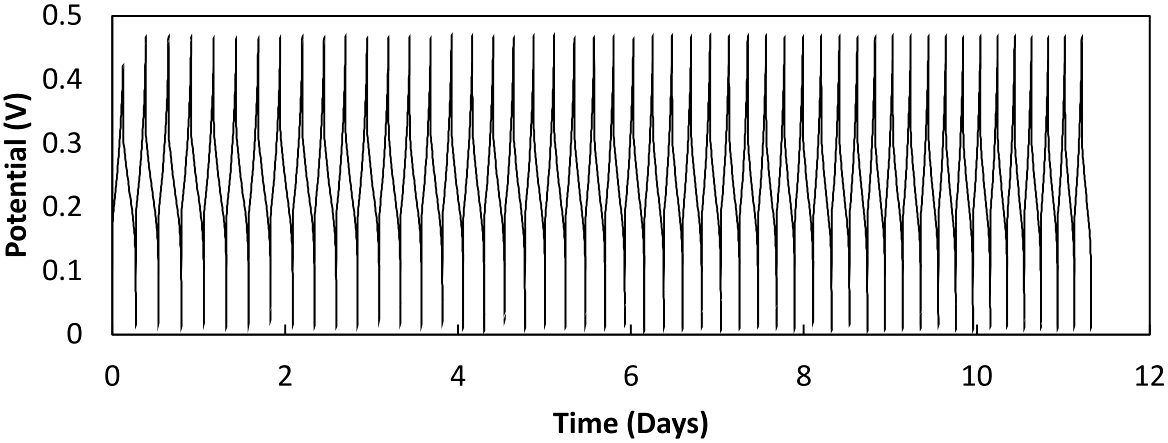


Figure S26. H- Cell charge-discharge profile for **3** (0.1 M).

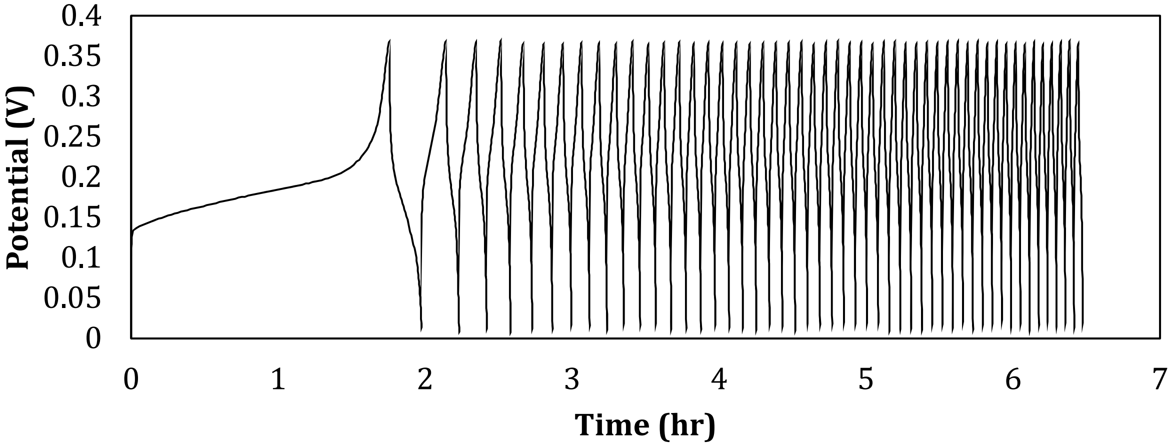


Figure S27. H- Cell charge-discharge profile for **4** (0.1 M).

VIII. Flow Cell Studies

Laboratory-scale RFBs (Fuel Cell Technologies, Albuquerque, NM, USA) were assembled using 5 mL 0.1 M radialene and methylviologen salts, in water purified to 18.2 MW·cm in a glovebox under UHP argon. The RFB was run at 25 °C, and two peristaltic pumps (Masterflex L/S) passed electrolyte at 2.5 mL min^{-1} from polypropylene reservoirs through norprene tubing into a serpentine flow field past a 5 cm^2 active membrane area. A Solartron 1287 potentiostat/galvanostat applied a 15 mA charge/discharge current across two carbon felt electrodes (SGL carbon, GFD grade, 2.5 mm nominal thickness, 5 cm^2 active area) compressed to 80% of their original thickness situated on opposing sides of Selemion CSO membrane. Voltage limits of 0.9 V and 0.1 V were applied for the experiment.

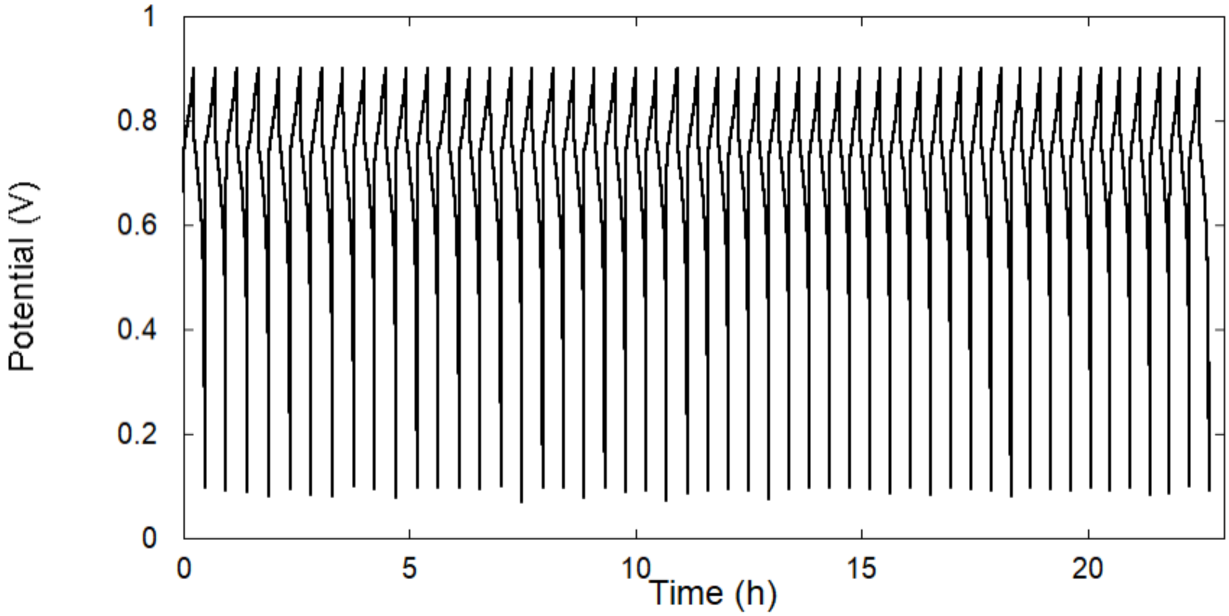


Figure S28. Galvanostatic charge-discharge cycling voltage profile for flow battery.

IX. References

1. T. Fukunaga, *J. Am. Chem. Soc.*, 1976, **98**, 610–611.
2. T. Fukunaga, M. D. Gordon and P. J. Krusic, *J. Am. Chem. Soc.*, 1976, **98**, 611–613.
3. United States Patent, US4003943A, 1976.
4. Rigaku Oxford Diffraction, CrysAlisPro Software system, version 1.171.38.46, Rigaku Corporation, Oxford, UK. (2018).
5. G. M. Sheldrick, *Acta Cryst.* **2015**, C17, 112-122.
6. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
7. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
8. L. J. Farrugia, *J. Appl. Cryst.* **2012**, *45*, 849-854.
9. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A.Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2006**, 8, 3172 .