

Electronic Supplementary Information

A Water-Miscible Quinone Flow Battery with High Volumetric Capacity and Energy Density

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	indicating the decomposition of the charged AQ-1,8-3E-OH is the major reason for capacity fading.
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24	Figure S17. (a) High resolution LC–MS (negative mode) spectrum of the cycled sample shows the presence of two species eluted from the LC column with retention times of 9.6 and 9.4 minutes, respectively. (b) The former has a mass/charge ratio of 549.1979, corresponding to the mass of AQ-1,8-3E-OH plus a formic acid adduct, and (c) the latter has a mass/charge ratio of 1023.4233, corresponding to the mass of 1,1',8,8'-tetrakis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)-[9,9'-bianthracene]-10,10'(9 <i>H</i> ,9' <i>H</i>)-dione plus a formic acid adduct. The existence of isotopes generates a cluster of peaks (isotope peaks); all peaks in a cluster are of the same molecular formula.
25	Scheme S1. Proposed decomposition pathways. In pathways I and II, the reduced AQ is protonated, and in pathways III and IV, it is not. In pathways I and III, the reduced AQ is directly dimerized. In pathways II and IV, PEG-anthrone forms first and then dimerizes in a second step.
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27	Figure S18. Irreversible pH change during long term cycling is explained by the hydroxide generation associated with the decomposition of charged-AQ-1,8-3E-OH. Electrolytes comprised 7 mL of 0.1 M AQ-1,8-3E-OH (negolyte) in 1 M KCl and 40 mL of 0.1 M potassium ferrocyanide and 0.04 M ferricyanide (posolyte) in 1 M KCl. The applied current density was 50 mA/cm^2 .
26-27	<u>Cost Considerations</u>

Table S1. Summary of demonstrated cell capacity and energy density of existing flow batteries in Figure 2b.

No./ Ref. in the plot	Negolyte/ electrons	Conc. of negolyte (M)	Posolyte/ electrons	Conc. of posolyte (M)	Volt. at 50% SOC (V)	Demonstrated cell capacity (Ah/L)*	Demonstrated cell energy density (Wh/L)
1/ ¹	V(acac) ₃ /1	0.1	V(acac) ₃ /1	0.1	2.1	1.34	2.81
2/ ²	FL/1	0.1	DMPZ/2	0.05	1.6	1.34	2.14
3/ ³	MVTFSI/2	0.1	FcNTFSI/1	0.2	1.2	2.68	3.22
4/ ⁴	DPPEAQ/2	0.5	K ₄ Fe(CN) ₆ /1	0.4	1.0	1.58	1.58
5/ ⁵	DBEAQ/2	0.5	K ₄ Fe(CN) ₆ /1	0.3	1.05	2.49	2.61
6/ ⁶	AQS/2	0.2	BQDS/2	0.2	0.76	5.36	4.07
7/ ⁷	MePh/1	0.3	DBMMB/1	0.3	2.3	3.2	7.36
8/ ⁸	DHPS/2	1.4	K ₄ Fe(CN) ₆ /1	0.31	1.4	6.75	9.46
9/ ⁹	DHAQ/2	0.5	K ₄ Fe(CN) ₆ /1	0.4	1.2	6.7	8.04
10/ ¹⁰	DHBQ/2	0.5	K ₄ Fe(CN) ₆ /1	0.4	1.21	4.85	5.87
11/ ¹¹	ACA/2	1	K ₄ Fe(CN) ₆ /1	0.4	1.15	6.31	7.25
12/ ¹²	methyl-Vi/1	0.5	FcNCl/1	0.5	1.05	6.70	7.04
13/ ¹³	FL/1	0.5	DBMMB/1	0.5	2.37	5.80	11.41
14/ ¹⁴	(SPr) ₂ Vi/1	0.9	NH ₄ Fe(CN) ₆ /1	0.9	0.82	12.06	9.89
15/ ¹⁵	BTMAP-Vi/1	1.3	BTMAP-Fc/1	1.3	0.7	15.20	10.64
16/ ¹⁶	AQDS/2	1	HBr/1	3	0.8	24.36	19.49
17/ ¹⁷	vanadium/1	1.5 [†]	Vanadium/1	1.5	1.25	20.10	25.13
18/ ¹⁸	methyl -Vi/1	2	TEMPTMA/1	2	1.2	22.5	27.00
19	PEGAQ/2	1.5	Na ₄ /K ₄ Fe(CN) ₆ /1	1.51	1.05	25.20	25.45
20/ ¹⁹	vanadium/1	2.5 [†]	Vanadium/1	2.5 [†]	1.25	33.50	41.88

*Demonstrated cell capacity is calculated by $(C_{CLS}/V_{tot}) \times \Phi$, where C_{CLS} is the capacity of the capacity limiting side, V_{tot} is the volume of posolyte plus the volume of negolyte, and Φ is the utilized capacity as a percentage. [†] 1.5 M solubility of vanadium species was achieved by using 2.5 M H₂SO₄ as the supporting electrolyte, while 2.5 M solubility of vanadium species was achieved by using a mixture of 2.5 M H₂SO₄ and 6 M HCl as the supporting electrolyte.

Table S2. List of chemicals and their abbreviations.

Abbreviation	Full name
(SPr) ₂ V	1,10-bis(3-sulfonatopropyl)-4,40-bipyridinium
AQDS	9,10-dioxo-9,10-dihydroanthracene-2,6-disulfonic acid
AQS	anthraquinone-2-sulfonic acid
BQDS	1,2-benzoquinone- 3,5-disulfonic acid
BTMAP-Fc	bis((3-trimethylammonio)propyl)-ferrocene dichloride
BTMAP-Vi	bis(3-trimethylammonio)propyl viologen tetrachloride
DBEAQ	4,40-((9,10-Anthraquinone-2,6-diyl)dioxy)dibutyric Acid
DBMMB	,5-di-tert-butyl-1-methoxy-4-[2' -methoxyethoxy]benzene
DHAQ	2,6-dihydroxy anthraquinone
DHBQ	2,5-dihydroxycyclohexa-2,5-diene-1,4-dione
DHPS	7,8-dihydroxyphenazine-2-sulfonic acid
DMPZ	5,10-dihydro-5,10-dimethyl phenazine
FcNCl	((ferrocenylmethyl)trimethylammonium choride
FcNTFSI	(ferrocenylmethyl)trimethylammonium bis(trifluoromethanesulfonyl)imide
FL	9-fluorenone
MePh	N-methylphthalimide
MV	methyl viologen
MViTFSI	methyl viologen bis(trifluoromethane)sulfonamide
TEMPTMA	N,N,N-2,2,6,6-heptamethylpiperidinyl oxy-4-ammonium chloride
V(acac) ₃	vanadium (III) acetylacetonate

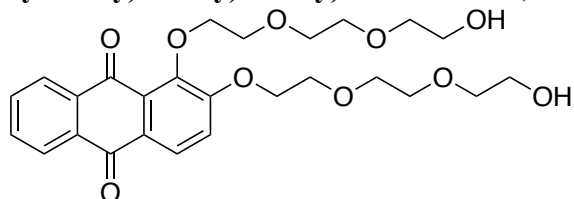
General Information

LC-MS was conducted on a Bruker microTOF-Q II mass spectrometer. All chemicals were purchased from Sigma-Aldrich unless specified otherwise. All dihydroxyanthraquinone (DHAQ) isomers, except the 2,6- and 2,7- isomers, were purchased from Alfa Aesar; 2,6-DHAQ was purchased from AK Scientific; and 2,7-DHAQ was synthesized from anthraquinone-2,7-disulfonic acid disodium salt²⁰, which was purchased from TCI America. All chemicals were used as received unless specified otherwise. Viscosity measurements were conducted on a Cambridge Viscosity VISCOLab3000 viscometer.

Synthesis and Chemical Characterization

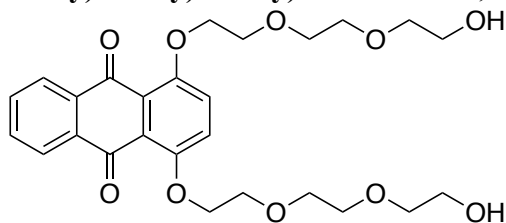
The procedure is a modification of the method described in Giguere *et al.*²¹: *n*, *m*-dihydroxyanthraquinone (DHAQ) (1 equiv.) was mixed with anhydrous K₂CO₃ (4 equiv.), NaI (0.15 equiv.), and 2-(2-(2-chloroethoxy)ethoxy)ethan-1-ol (3 equiv.) in DMF to achieve a 0.4 M DHAQ suspension in a pressure vessel. The reaction mixture was heated to 135 °C and stirred overnight. Water (2×DMF volume) was then added to the reaction mixture, which was subsequently extracted with DCM (2×DMF volume) three times. The organic layer was dried over Na₂SO₄ and then condensed under vacuum to achieve crude product. Silica gel column chromatography (eluent: 97 v/v% dichloromethane + 3 v/v% Methanol) was used to obtain the *n*, *m*-di-Pegylated-Anthraquinone.

(a) 1,2-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione



A purple solid was obtained after column chromatography. Final yield: 30.1%. ¹H NMR (500 MHz, CDCl₃) δ 8.22-8.26 (m, 2H), 8.13(d, J = 8.6 Hz, 1H), 7.73-7.76 (m, 2H), 7.26 (d, J = 8.6 Hz, 1H), 4.27-4.35 (m, 4H), 4.02-4.07 (m, 2H), 3.94-3.98 (m, 2H), 3.79-3.83 (m, 2H), 3.75-3.79 (m, 2H), 3.66-3.75 (m, 8H), 3.57-3.64 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 182.77, 182.46, 158.38, 148.97, 135.22, 133.99, 133.65, 133.06, 127.70, 127.25, 127.21, 126.80, 125.26, 117.45, 72.99, 72.83, 72.81, 71.03, 70.79, 70.69, 70.54, 70.52, 69.43, 68.79, 61.82, 61.78. MS (ESI m/z) calcd. for [C₂₆H₃₂O₁₀+Na]⁺ 527.19, found 527.19.

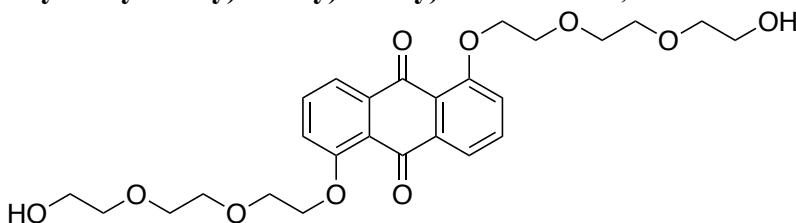
(b) 1,4-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione



A yellow-brown mud was obtained after column chromatography. Final yield: 47.6%. ¹H NMR (500 MHz, CDCl₃) δ 8.09 (m, 2H), 7.66 (m, 2H), 7.34 (s, 2H), 4.23 (t, J = 4.9 Hz, 4H), 3.94 (t, J

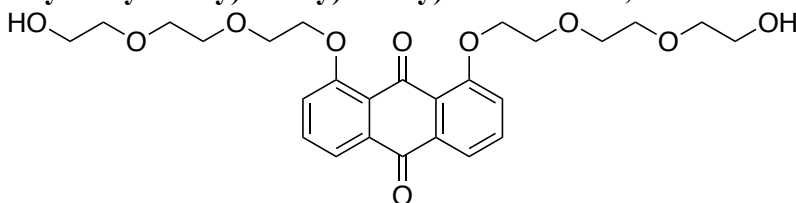
= 3.9 Hz, 4H), 3.77-3.80 (m, 4H), 3.65-3.70 (m, 8H), 3.56-3.60 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 183.18, 154.05, 134.30, 133.40, 126.50, 123.93, 123.39, 72.63, 71.14, 70.58, 70.56, 69.89, 61.88. MS (ESI m/z) calcd. for $[\text{C}_{26}\text{H}_{32}\text{O}_{10}+\text{Na}]^+$ 527.19, found 527.19.

(c) 1,5-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione



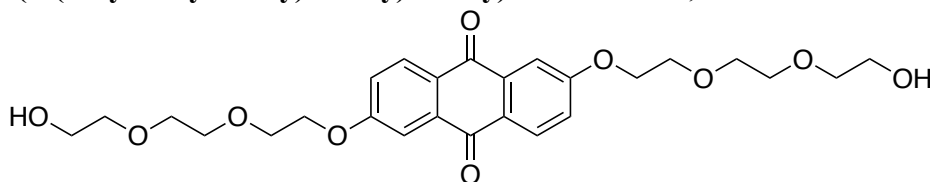
A golden solid was obtained after column chromatography. Final yield: 48.0%. ^1H NMR (500 MHz, CDCl_3) δ 7.89 (dd, J = 1.0, 7.8 Hz, 2H), 7.67 (t, J = 8.4, 2H), 7.28 (dd, J = 1.0, 8.4 Hz, 2H), 4.32 (t, J = 4.7 Hz, 4H), 4.03 (t, J = 4.7 Hz, 4H), 3.85-3.90 (m, 4H), 3.70-3.75 (m, 8H), 3.61-3.66 (m, 4H), 2.00 (broad s, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 182.55, 159.12, 137.51, 135.05, 121.47, 120.19, 118.60, 72.63, 71.29, 70.62, 69.59, 69.57, 61.95. MS (ESI m/z) calcd. for $[\text{C}_{26}\text{H}_{32}\text{O}_{10}+\text{Na}]^+$ 527.19, found 527.19.

(d) 1,8-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione



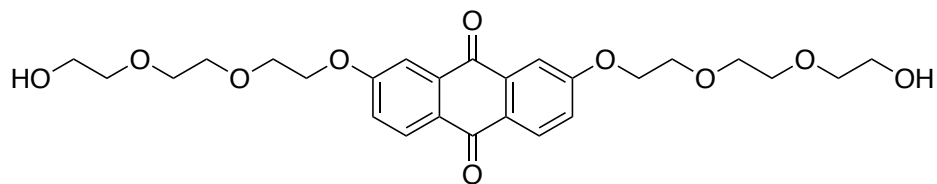
A brown-red mud was obtained after column chromatography. Final yield: 66.1%. ^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, J = 7.7 Hz, 2H), 7.61 (t, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 4.30 (t, J = 5.0 Hz, 4H), 4.01 (t, J = 5.0 Hz, 4H), 3.85-3.90 (m, 4H), 3.69-3.74 (m, 8H), 3.60-3.54 (m, 4H), 2.52 (broad s, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 183.93, 182.42, 158.59, 134.87, 124.79, 120.23, 119.63, 72.77, 71.26, 70.59, 69.91, 69.62, 61.80. MS (ESI m/z) calcd. for $[\text{C}_{26}\text{H}_{32}\text{O}_{10}+\text{Na}]^+$ 527.19, found 527.19.

(e) 2,6-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione



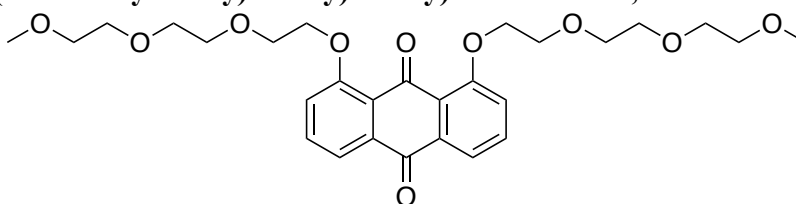
A yellow solid was obtained after column chromatography. Final yield: 75.0%. ^1H NMR (500 MHz, CDCl_3) δ 8.23 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 2.7 Hz, 2H), 7.28 (dd, J = 2.7, 8.6 Hz, 2H), 4.33 (t, J = 4.75 Hz, 4H), 3.93 (t, J = 4.75 Hz, 4H), 3.70-3.78 (m, 16H), 3.41-3.61 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 182.23, 163.71, 135.87, 129.81, 127.41, 121.29, 110.70, 72.63, 71.06, 70.52, 69.57, 68.18, 61.90. MS (ESI m/z) calcd. for $[\text{C}_{26}\text{H}_{32}\text{O}_{10}+\text{Na}]^+$ 527.19, found 527.19.

(f) 2,7-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione



A yellow solid was obtained after column chromatography. Final yield: 60.3%. ^1H NMR (500 MHz, CDCl_3) δ 8.23 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 3.0 Hz, 2H), 7.29 (dd, J = 3.0, 8.4 Hz, 2H), 4.33 (t, J = 4.8 Hz, 4H), 3.93 (t, 4.8Hz, 4H), 3.69-3.78 (m, 16H), 3.61-3.65(m, 16H), 2.33 (broad s, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 183.24, 181.29, 163.20, 135.54, 129.68, 127.38, 121.60, 110.70, 72.65, 71.00, 70.43, 69.51, 68.11, 61.81. MS (ESI m/z) calcd. for $[\text{C}_{26}\text{H}_{32}\text{O}_{10}+\text{Na}]^+$ 527.19, found 527.19.

(g) 1,8-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione



An orange oil was obtained after column chromatography. Final yield: 80.5%. ^1H NMR (600 MHz, CDCl_3) δ 7.82 (dd, J = 0.9, 7.7 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.34 (dd, J = 0.9, 8.4 Hz, 2H), 4.29 (t, J = 4.9 Hz, 4H), 3.96-3.99 (m, 4H), 3.81-3.84 (m, 4H), 3.66-3.68(m, 4H), 3.62-3.64(m, 4H), 3.51-3.53(m, 4H), 3.34 (s, 6H). ^{13}C NMR (150 MHz, CDCl_3) δ 184.06, 182.38, 158.72, 134.85, 133.84, 124.84, 120.56, 119.64, 72.00, 71.13, 70.82, 50.58, 69.81, 69.67, 59.10. MS (ESI m/z) calcd. for $[\text{C}_{28}\text{H}_{36}\text{O}_{10}+\text{Na}]^+$ 555.22, found 555.22.

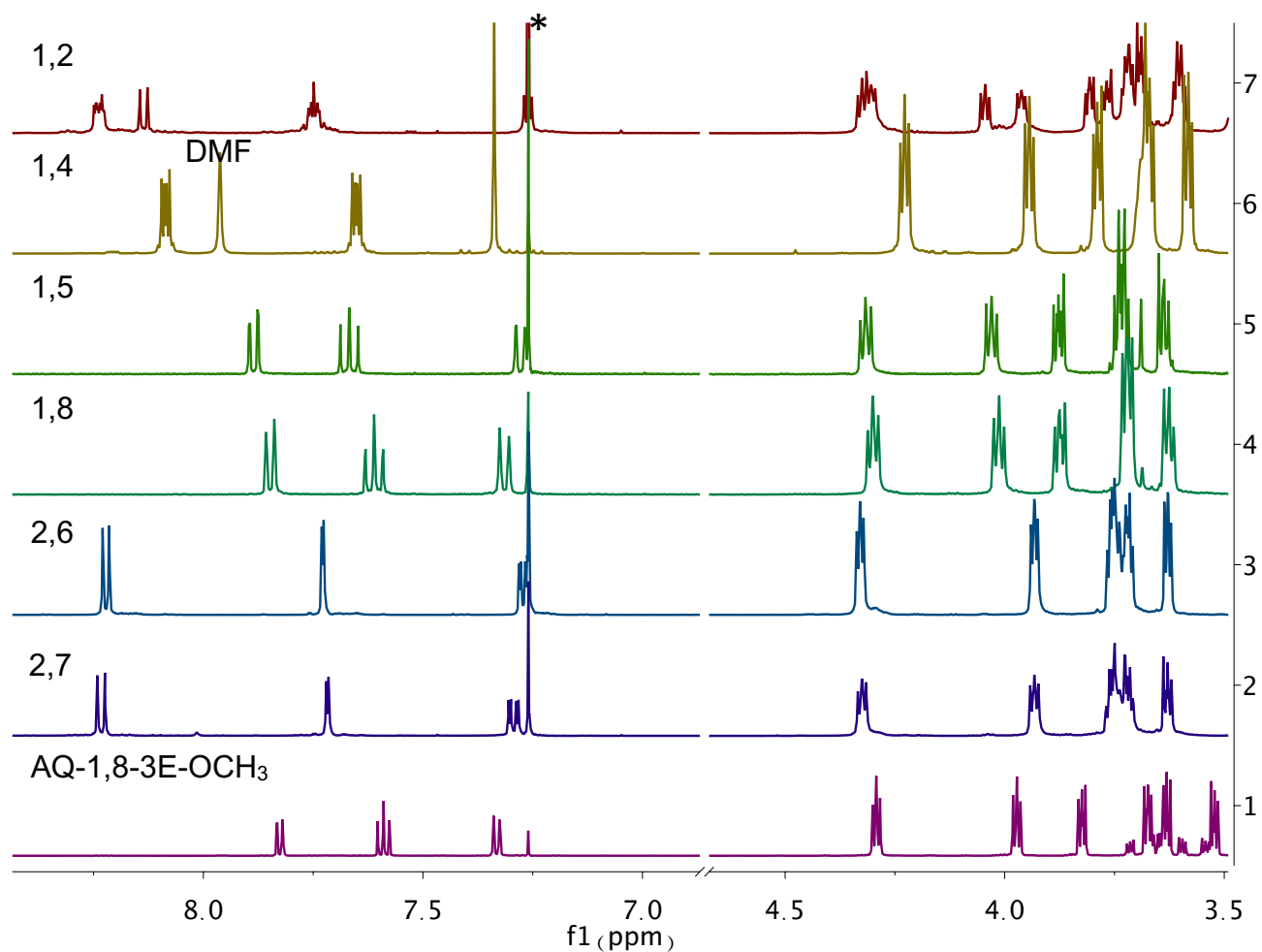


Figure S1. ^1H NMR spectra of 1,2-, 1,4-, 1,5-, 1,8-, 2,6-, 2,7-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione (AQ-*n,m*-3E-OH) and AQ-1,8-3E-OCH₃ in CDCl₃. The peak labeled with * is from a trace amount of CHCl₃ in CDCl₃ solvent at 7.26 ppm.

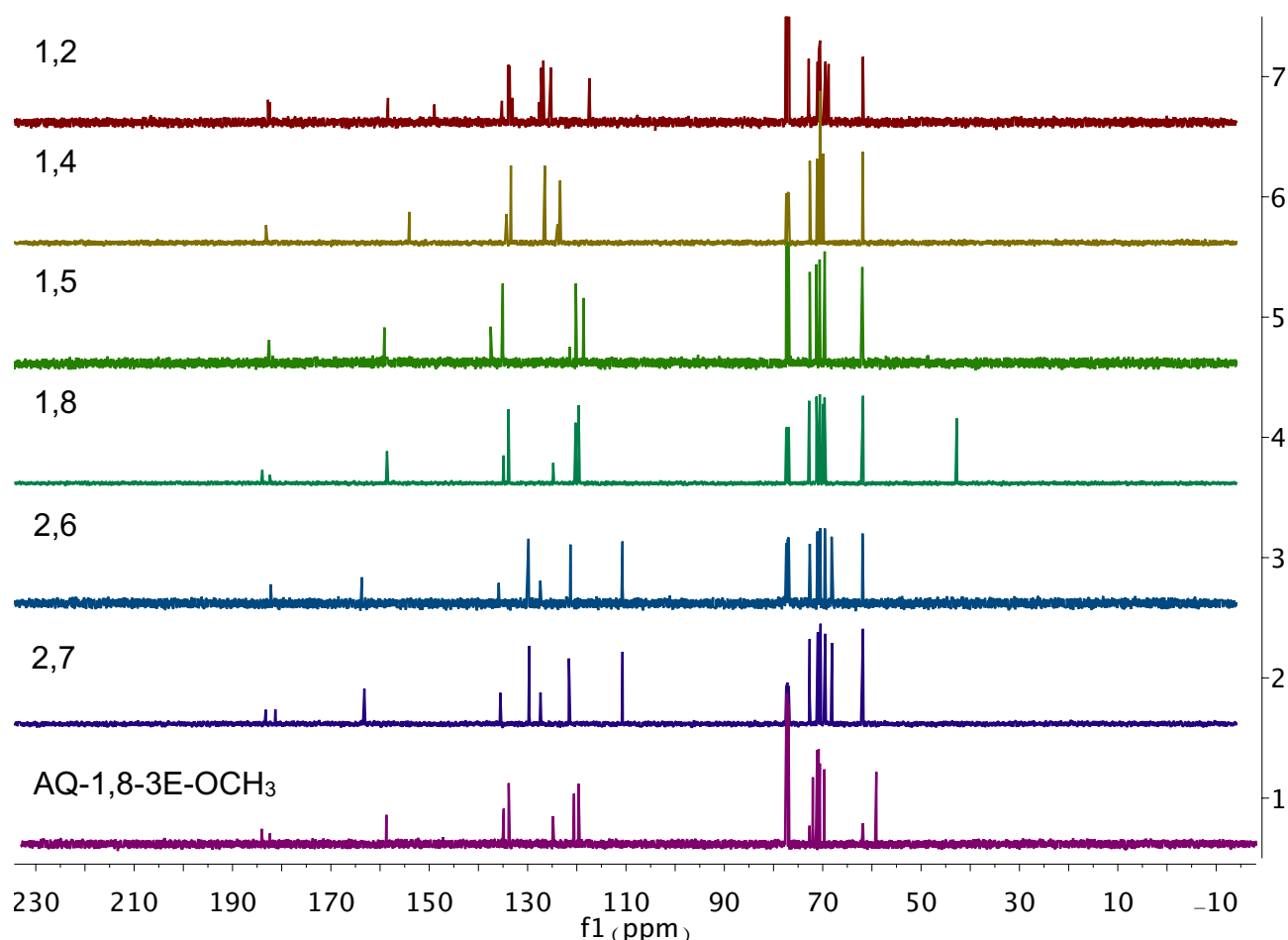


Figure S2. ^{13}C NMR spectra of 1,2-, 1,4-, 1,5-, 1,8-, 2,6-, 2,7-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione (AQ- n,m -3E-OH) and AQ-1,8-3E-OCH₃ in CDCl₃.

Solubility Measurements

The solubilities of the PEG-AQ isomers were measured by adding solids/liquids of pure AQ species into 1 M KCl solution until precipitate was observed, and the solubility was calculated using the mass of compound added and the final volume of the solution. Since the 1,8- and 1,4-isomers are miscible with water, the maximum concentration is obtained by calculating the density ($\rho = 1.13 \text{ g/mL}$) divided by the molecular weight (504.53 g/mol), which gives 2.24 M as the maximum concentration. The theoretical maximal volumetric capacity (Ah/L) can be calculated by $n \times F \times C / 3600$ (Ah/L), where n represents the number of electrons stored per AQ, F is Faraday's constant with units of Coulomb/mol, and C is the maximum concentration of AQ-1,8-3E-OH with units of M or mol/L (*e.g.*, 2.24 M). Theoretically, the maximal volumetric capacity is thus 120.1 Ah/L. Figure S4 depicts AQ-1,8-3E-OH at different concentrations.

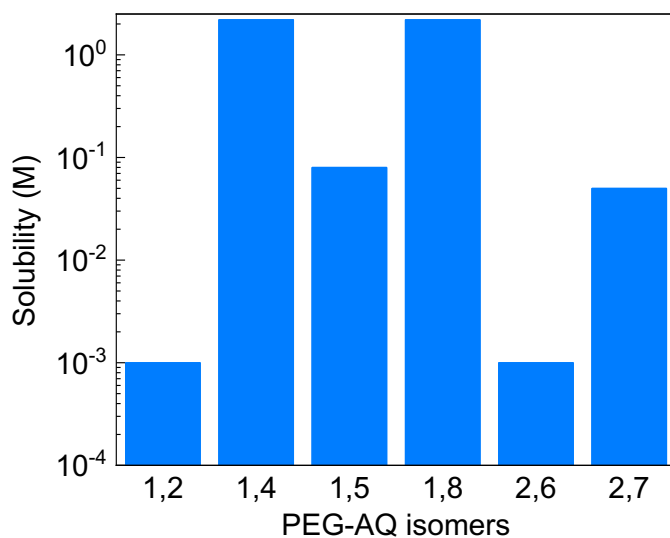


Figure S3. Measured solubility of PEGAQ isomers in 1 M KCl solution at neutral pH. The position of PEG chains tethered to AQ can influence final solubility by orders of magnitude. The 1,4- and 1,8- isomers are water-miscible; thus the bars indicate the concentrations of pure liquid PEG-AQ. The solubilities of the 1,5- and 2,7- isomers are ~ 0.1 M; and the solubilities of the 1,2- and 2,6- isomers are less than 1 mM.

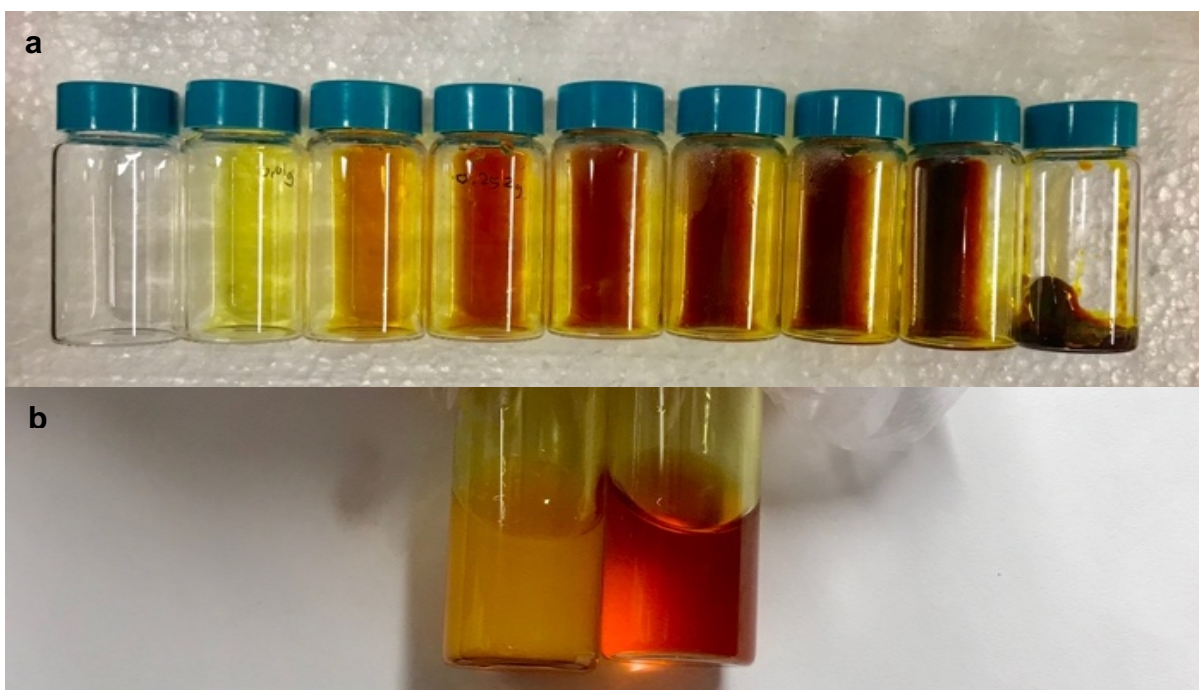


Figure S4. (a) Aqueous solutions with AQ-1,8-3E-OH at concentrations of (from left to right) 0, 0.01, 0.1, 0.25, 0.5, 0.75, 1.0, 1.5, and (pure compound) 2.24 M. Pure AQ-1,8-3E-OH melts above 35°C . The viscosity of these solutions were measured. (b) Comparison of 0.1 M AQ-1,8-3E-OCH₃ (left) and AQ-1,8-3E-OH (right) in 1 M KCl solution at 45°C . The AQ-1,8-3E-OCH₃ solution

becomes cloudy and phase-separated, while the AQ-1,8-3E-OH solution remains homogeneous and transparent.

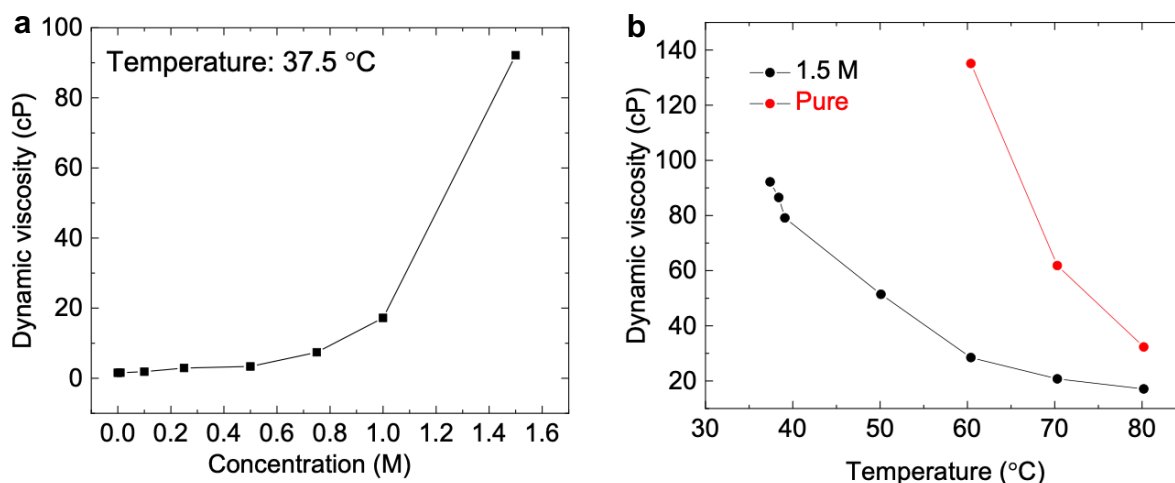


Figure S5. (a) Viscosity of AQ-1,8-3E-OH at concentrations of 0, 0.01, 0.1, 0.25, 0.5, 0.75, 1.0, and 1.5 M at 37.5 ± 0.2 °C. (b) Viscosity of 1.5 M and pure AQ-1,8-3E-OH at different temperatures.

Electrochemical Characterization

Glassy carbon was used as the working electrode for all three-electrode CV tests. Rotating Disk Electrode experiments were conducted using a Pine Instruments Modulated Speed Rotator AFMSRCE equipped with a 5 mm diameter glassy carbon working electrode, a Ag/AgCl reference electrode (BASi, pre-soaked in 3 M NaCl solution), and a graphite counter electrode. The diffusion coefficient of the oxidized form of AQ-1,8-3E-OH was calculated using the Levich equation, which relates the mass-transport-limited current to the number of electrons transferred (n), the area of the electrode (A), and the concentration of redox-active species in the electrolyte (C), by plotting the mass-transport-limited current against the square root of the rotation rate (Figure S7) with the following parameters: $n = 2$, $F = 96,485$ Coulombs/mol, $A = 0.196$ cm², $C = 5$ mM, $\nu = 1.08 \times 10^{-6}$ m²/s (the kinematic viscosity of 1 M KCl)²². The resulting value of the diffusion coefficient of AQ-1,8-3E-OH is 2.94×10^{-6} cm²/s. Koutecký–Levich analysis at low overpotentials can be extrapolated to infinite rotation rate and fitted to the Butler-Volmer equation to give the kinetic reduction rate constant $k_0 = 6.1(4) \times 10^{-3}$ cm/s.

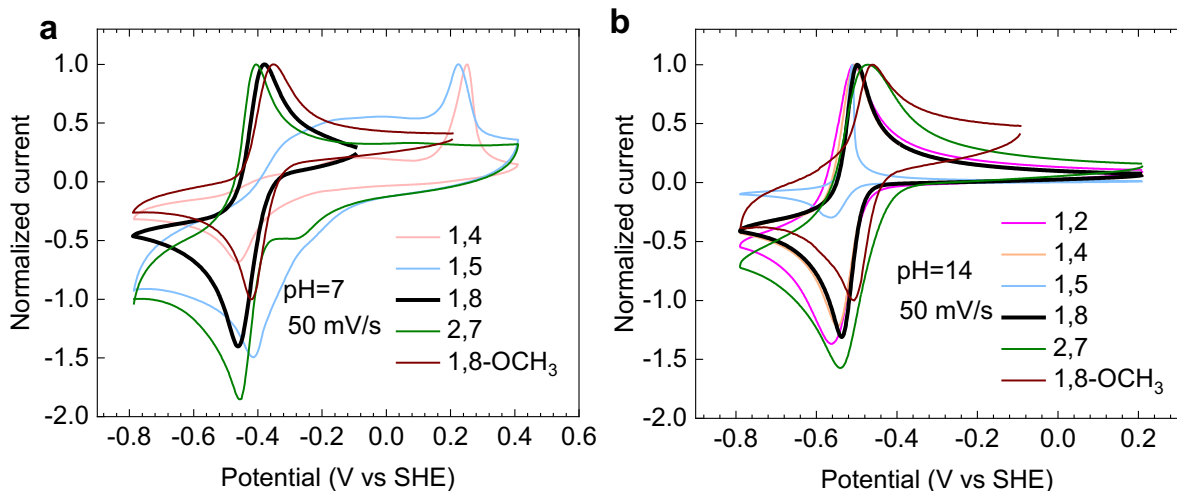


Figure S6. (a) CV of AQ- 1,4-, 1,5-, 1,8-, 2,7- 3E-OH and AQ-1,8-3E-OCH₃ in 1 M KCl measured with 50 mV/s scan rate and normalized to the height of the oxidative peak near 0.4 V. The 1,2- and 2,6- isomers were not soluble enough for CV measurements. The 1,8- and 2,7- isomers show reversible electrochemical behavior, while the 1,4- and 1,5- are irreversible. (b) CV of AQ- 1,2-, 1,4-, 1,5-, 1,8-, 2,7- 3E-OH and AQ-1,8-3E-OCH₃ in 1 M KOH measured with 50 mV/s scan rate and normalized to the height of the oxidative peak near 0.5 V. The 2,6- isomer is not soluble enough for CV measurements. All isomers except 1,5- showed reversible electrochemical behavior.

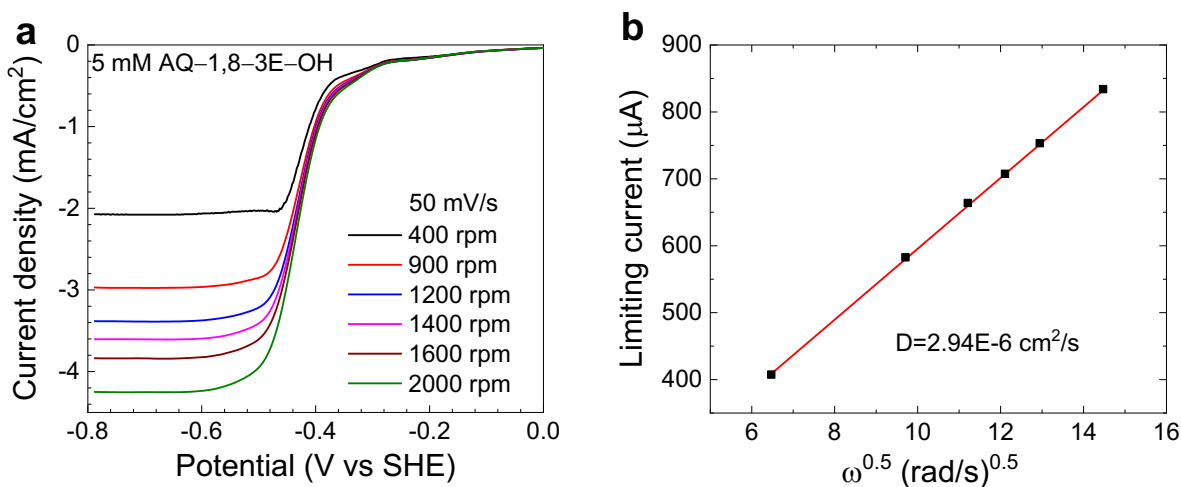


Figure S7. (a) RDE study of the reduction of 5 mM AQ-1,8-3E-OH in 1 M KCl on a glassy carbon electrode at rotation rates between 400 and 2000 rpm. (b) Levich plot (limiting current vs. square root of rotation rate in rad/s) of 5 mM AQ-1,8-3E-OH in 1 M KCl. Limiting current is taken as the current in the range -0.7 to -0.8 V in (a). The slope yields a diffusion coefficient for the oxidized form of AQ-1,8-3E-OH of $2.94 \times 10^{-6} \text{ cm}^2/\text{s}$.

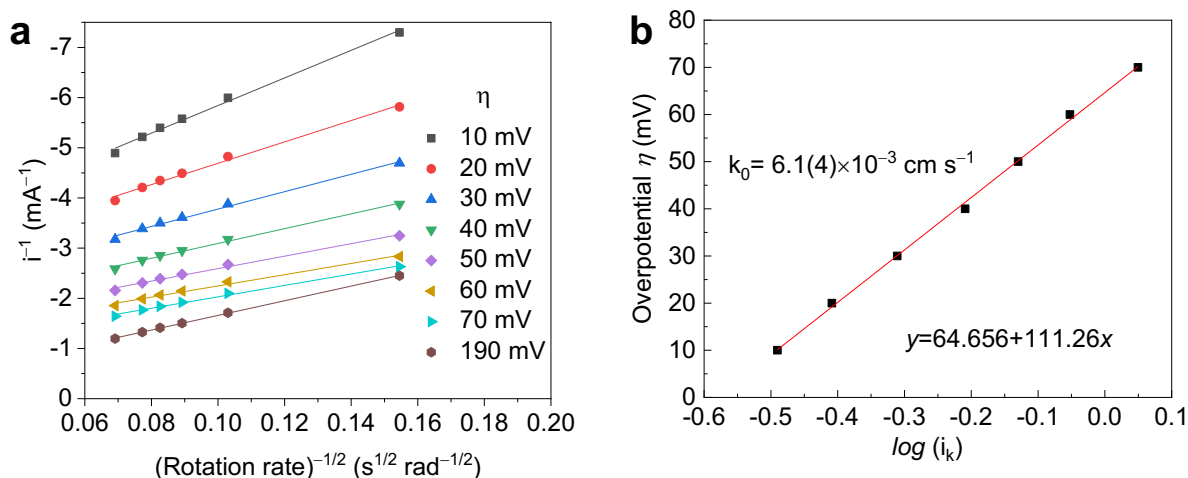


Figure S8. Koutecký–Levich analysis gives the values of mass-transport-independent currents, which result in a standard rate constant k^0 of AQ-1,8-3E-OH $6.1(4) \times 10^{-3} \text{ cm s}^{-1}$.

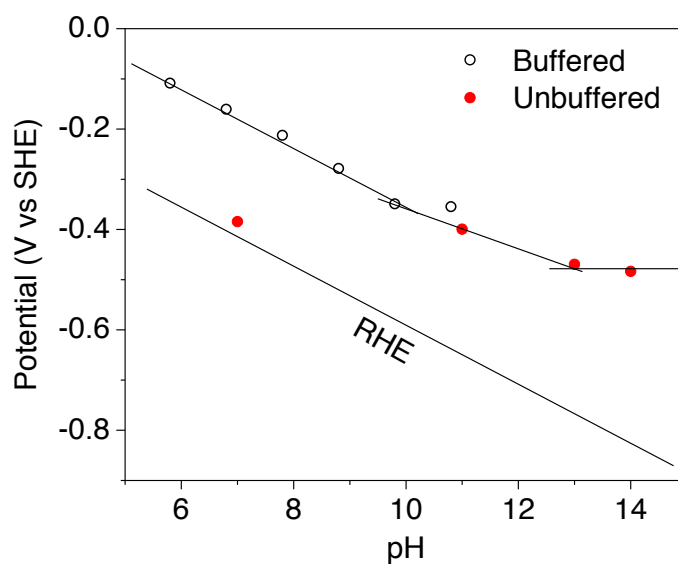


Figure S9. Pourbaix diagram of AQ-1,8-3E-OCH₃ with a slope of -59 mV/pH fit to the data from pH 6-10 and a slope of -29 mV/pH from pH 10-12.5. Above pH ~ 12.5, the potential is pH-independent, indicating that the reduced form of AQ-1,8-3E-OCH₃ is fully deprotonated. All of the potentials were determined by cyclic voltammograms of 10 mM AQ-1,8-3E-OCH₃ in buffered solutions.

Full Cell Measurements

Flow battery experiments were constructed with cell hardware from Fuel Cell Tech. (Albuquerque, NM), assembled into a zero-gap flow cell configuration, similar to a previous report⁹. Pyrosealed POCO graphite flow plates with serpentine flow patterns were used for both electrodes. Each

electrode comprised a 5 cm² geometric surface area covered by a stack of four sheets of Sigracet SGL 39AA porous carbon paper pre-baked in air for 24 h at 400 °C.

Full cell cycling was performed with a Fumasep E-620(K) membrane due to its low permeability of AQ-1,8-3E-OH and ferro/ferricyanide. To obtain the polarization curves, the cell was first charged to the desired state of charge and then polarized via linear sweep voltammetry at a rate of 100 mV/s. This method was found to yield polarization curves very close to point-by-point galvanostatic holds, yet to impose minimal perturbation to the SOC of the small-electrolyte-volume cell. Electrochemical impedance spectroscopy (EIS) was performed at SOC between 10 and 100% at open-circuit potential with a 10 mV perturbation and with frequency ranging from 1 to 300,000 Hz. Three cells with varying negolyte and posolyte concentrations were studied.

1. The negolyte of the 0.1 M cell was prepared by dissolving 0.4 g AQ-1,8-3E-OH (0.79 mmol) into 7.4 mL 1 M KCl solution. The volume of the solution expanded to achieve a 0.1 M AQ solution. The posolyte of the 0.1 M cell was prepared by dissolving 1.69 g K₄[Fe(CN)₆]·3H₂O (4 mmol) and 0.53 g K₃[Fe(CN)₆]·6H₂O (1.6 mmol) into 40 mL 1 M KCl to make a 0.1 M ferrocyanide 0.04 M ferricyanide solution.
2. The negolyte of the 1.5 M cell was prepared by dissolving 5.30 g AQ-1,8-3E-OH (0.0105 mol) into 2.4 mL 3 M KCl solution. The volume of the solution expanded to 7 mL to achieve a 1.5 M AQ solution. The posolyte of the 1.5 M cell was prepared by dissolving 19.64 g K₄[Fe(CN)₆]·3H₂O (0.0465 mol) and 15.31 g K₃[Fe(CN)₆]·6H₂O (0.0465 mol) into 150 mL 1 M KCl to make a 0.31 M ferrocyanide 0.31 M ferricyanide solution.
3. A negolyte comprising 6 mL 1.5 M AQ-1,8-3E-OH in 0.5 M KCl was paired with 12 mL of a 1.51 M ferrocyanide posolyte comprising 3.81 g K₄[Fe(CN)₆]·3H₂O (9.03 mmol), 4.37 g Na₄[Fe(CN)₆]·10H₂O (9.03 mmol) and 0.04 g K₃[Fe(CN)₆]·6H₂O (0.12 mmol). No additional KCl was added to this solution.

Using the aforementioned cell compositions, we cycled the battery using a sequential potential step method. During charging, voltage limits were set at 1.0, 1.1, and 1.3 V with 160, 100, and 16 mA/cm² cutoff current densities, respectively. During discharging, voltage limits were set at 0.8, 0.6, and 0 V with 100, 40, and 4 mA/cm² cutoff current densities, respectively. This method was applied to counter the resistance influence of the membranes, electrolytes, electrodes, *etc.* on capacity utilization; because the major purpose is to evaluate the stability of negolyte, the prerequisite is achieving almost full capacity, which was unachievable using the conventional galvanostatic cycling method in this case (**Figure S10**). If >90% of capacity cannot be accessed, the measured capacity fade rate may be underestimated.

Polarization experiments (1.06 V at 50% SOC, Figure 5a and 5b) on the 1.5 M-negolyte cell showed a higher OCV across all SOC (0.98 V at 50% SOC, Figure 4a and 4b) than with the previous 0.1 M-negolyte cell. This observation may be explained by the following considerations: 1. the higher concentration of negolyte drives the pH of the negolyte to a higher value even at a low SOC, which lowers the reduction potential of AQ-1,8-3E-OH, as a result, increasing the overall voltage of the cell; 2. the ferricyanide/ferrocyanide ratio is 1:1 in the high concentration cell as opposed to 0.4:1 in the low concentration cell, thus giving relatively higher voltage in the

1.5 M-negolyte cell at 0% SOC; 3. The capacity ratio of posolyte to negolyte is different, so that when the negolyte is at 50% SOC, the posolyte is at a higher SOC in the 1.5 M-negolyte cell than in the 0.1 M-negolyte cell.

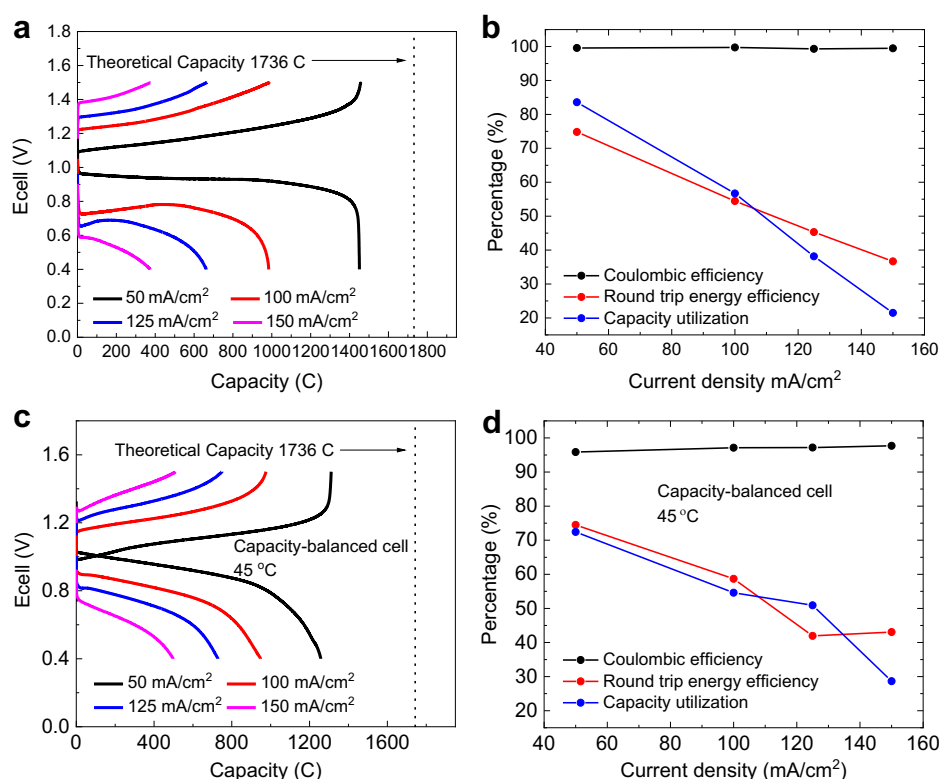


Figure S10. (a) Galvanostatic cycling of 6 mL of a 1.5 M negolyte in 1 M KCl and 40 mL of 1 M ferro/ferricyanide solution (0.5 M $\text{K}_4\text{Fe}(\text{CN})_6$ + 0.5 M $\text{Na}_4\text{Fe}(\text{CN})_6$) under 50–150 mA/cm^2 current densities at room temperature. (b) Coulombic efficiency, round trip energy efficiency, and capacity utilization of the 1.5 M negolyte cycling under current densities in (a). (c) Galvanostatic cycling of 6 mL of a 1.5 M negolyte in 0.5 M KCl and 12 mL of 1.51 M ferro/ferricyanide solution (0.755 M $\text{K}_4\text{Fe}(\text{CN})_6$ + 0.755 M $\text{Na}_4\text{Fe}(\text{CN})_6$) under 50–150 mA/cm^2 current densities at 45 °C. (d) Current efficiency, energy efficiency, and capacity utilization of the 1.5 M negolyte cycling under current densities in (c).

Decomposition Analysis of AQ-1,8-3E-OH

Although AQ-1,8-3E-OH demonstrates the highest reported capacity, the temporal fade rate is ~50 times higher than that of state-of-the-art molecules^{4, 5}. It has been demonstrated that structural stability can be significantly improved with proper molecular modification^{4, 24}. Apparently, judicious molecular design relies on a deep understanding of molecular decomposition mechanisms. We analyzed the cycled negolyte for decomposed species. Nuclear magnetic resonance (NMR) spectra of a pristine sample and cycled sample were compared (**Figure S12–13**). A D_2O sample was prepared by diluting 100 μL of a cycled 0.1 M negolyte (**Figure S11**) solution after 18% capacity loss with 700 μL D_2O solvent. A set of three new peaks with chemical shifts δ 7.14 (t), 6.91 (d) and 6.83 (d) ppm with a 1:1:1 integration ratio was observed in the aromatic region, indicating that the new species possesses similar geometry to AQ-1,8-3E-OH (**Figure S13**).

Dividing the integration of the new peaks by the total integration of the aromatic peaks (the sum of AQ-1,8-3E-OH peaks and new peaks), the new peaks correspond to 19% decomposition of AQ-1,8-3E-OH, which coincides with the amount of capacity loss observed after cycling (**Figure S11**). To determine whether any peaks were concealed by the broad water peak centered at 4.79 ppm, we also performed ^1H NMR in CDCl_3 by extracting the D_2O NMR sample with the same volume of CDCl_3 . The ratio of the integrals of the peaks corresponding to the decomposition product to those corresponding to AQ-1,8-3E-OH did not change after extraction, indicating that both AQ-1,8-3E-OH and the decomposition product have similar solubility in either solvent (**Figure S14**). A singlet peak with chemical shift δ 5.49 ppm in CDCl_3 appeared with an integration value equal to half the integral of each new peak in the aromatic region (*i.e.*, new peaks not present in the NMR spectrum of pristine AQ-1,8-3E-OH). Using this CDCl_3 sample, we further performed diffusion ordered spectroscopy (DOSY) and found two well-separated species in the diffusion dimension, except for CHCl_3 and H_2O , suggesting that the singlet peak with chemical shift δ 5.49 ppm originated from the same compound that has the three aromatic peaks with chemical shifts δ 7.46 (d), 7.26 (t), and 6.80 (d) ppm (**Figure S16**). DOSY also revealed that the new compound has a smaller diffusion coefficient and hence a larger hydrodynamic radius compared to AQ-1,8-3E-OH. High-resolution LC-MS corroborated the DOSY result by indicating that the only two species in the post-cycling sample are AQ-1,8-3E-OH with m/z 549.1979 (anion of AQ-1,8-3E-OH + formic acid adduct) and a dimer structure with m/z 1023.4233 (anion of a dimer + formic acid adduct). (**Figure S17**) The mass of the decomposition product is twice the mass that would result from subtracting one oxygen from and adding one hydrogen to the mass of AQ-1,8-3E-OH, which suggests that the dimer is a tetra-triethylene glycol-substituted dianthrone. Previous work has identified the crystal structures of two types of dianthrone formed from 1,8-dimethoxy substituted anthraquinones in a reductive environment: 1,1',8,8'-tetramethoxy dianthrone, where the methoxy substituents on the two anthrones are pointing toward each other²⁵ and 4,4',5,5'-tetramethoxy dianthrone, where the methoxy substituents on the two anthrones are pointing away from each other²⁴. The NMR peak chemical shifts in CDCl_3 solvent of the aromatic region of the 4,4',5,5'-dimer are identified as ranging from δ 8.0 to 7.16 ppm, and the methine protons have chemical shift δ 6.2 ppm. The chemical shifts of neither of these two regions match what we observed. The aromatic peaks in our case have chemical shifts δ 7.46, 7.26, and 6.80 ppm and the methine peak has chemical shift δ 5.49 ppm. On the other hand, the reported NMR peak chemical shifts for the 1,1',8,8'-tetramethoxy dianthrone have chemical shifts δ 7.42, 7.31, and 6.88 ppm for the aromatic protons and δ 5.85 ppm for the methine protons, both of which comport well with the observed peaks²³. Hence, we infer that the decomposition product is likely 1,1',8,8'-tetrakis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)-[9,9'-bianthracene]-10,10'(9*H*,9'*H*)-dione.

We then sought to determine whether the oxidized or the reduced form of AQ-1,8-3E-OH contributed more to the decomposition. Two solutions of 0.1 M AQ-1,8-3E-OH in 1 M KCl, one uncharged and the other charged, were stored in a glovebox at room temperature for two weeks. The charged sample was discharged in air after the two-week period, and both samples were extracted with CDCl_3 . The ^1H NMR spectrum of the uncharged sample showed no evidence of decomposition, whereas the spectrum of the charged sample included peaks corresponding to the dimer in the aromatic region with integration 18% that of the AQ-1,8-3E-OH aromatic peaks, representing a decomposition rate of 1.1%/day (**Figure S15**). This temporal fade rate is ~ 2 times the rate of 0.5%/day observed in long-term flow cell cycling, which is reasonable, as reduced AQ-1,8-3E-OH accounts for 50% of the total time during cycling. Therefore, we conclude that the

decomposition of the charged form of AQ-1,8-3E-OH is responsible for the observed capacity fade in flow cells.

Four decomposition pathways were proposed as described in **Scheme S1**. Structural optimization and energy calculations of the optimized structures were performed using Gaussian 16, M06/3-21G method/basis-set with Solvation Model based on Density (SMD). The computational results suggest that the dimerization is a thermodynamically favorable process. The intermediate species of routes I and III have lower energy, suggesting more favorable kinetics of these two routes (assuming that the relatively lower energies of the intermediates reflect relatively lower energy transition states as well).

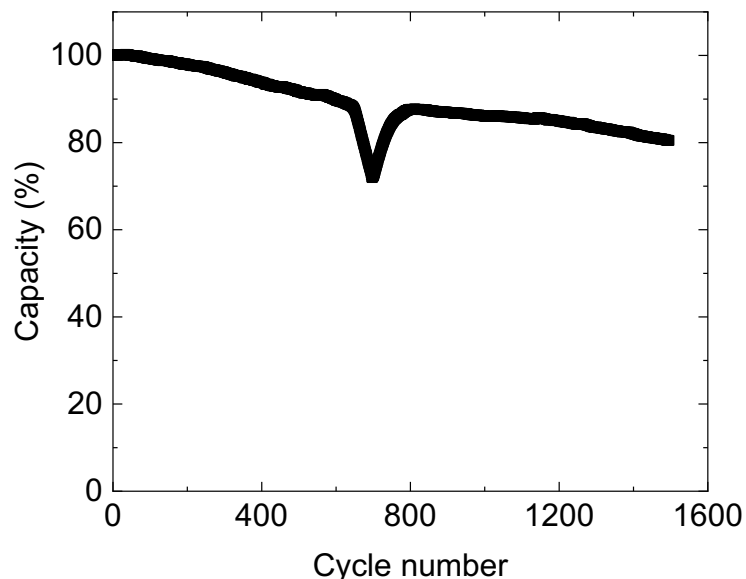


Figure S11. The discharge capacity of a full cell comprising 0.1 M AQ-1,8-3E-OH in 1 M KCl vs. 0.1 M ferrocyanide for 1500 cycles shows 18% capacity fade. The capacity drop from cycle number 600–800 was caused by depletion of nitrogen gas.

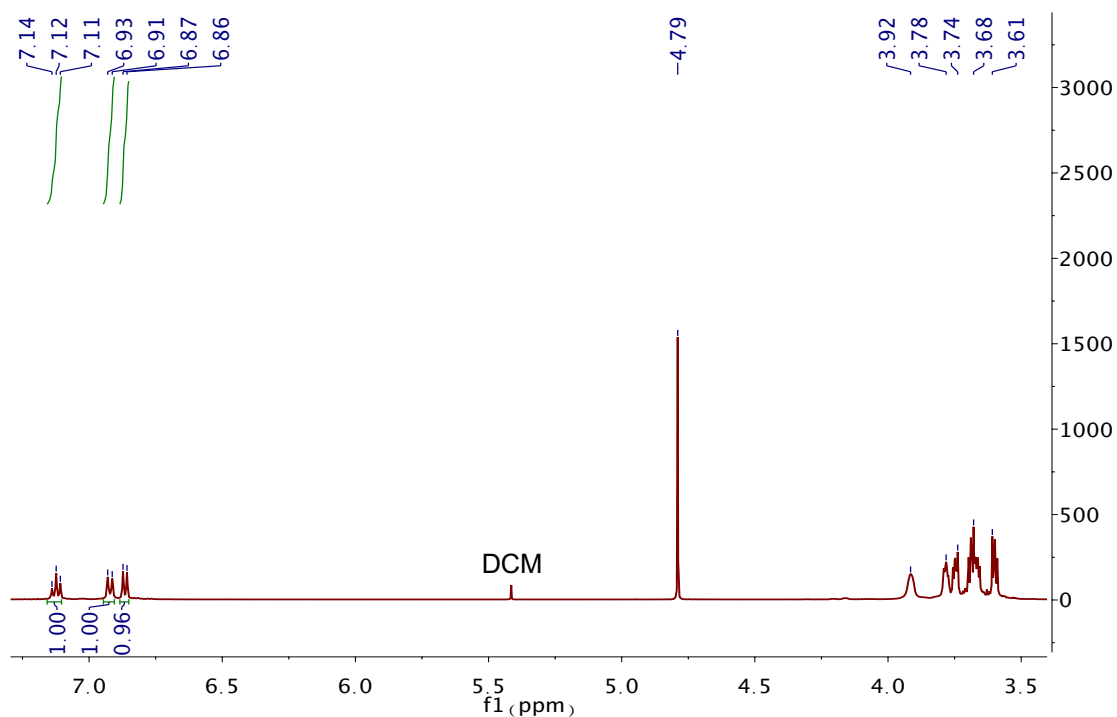


Figure S12. ^1H NMR of pristine AQ-1,8-3E-OH in D_2O . The integration of the aromatic protons of AQ-1,8-3E-OH is shown.

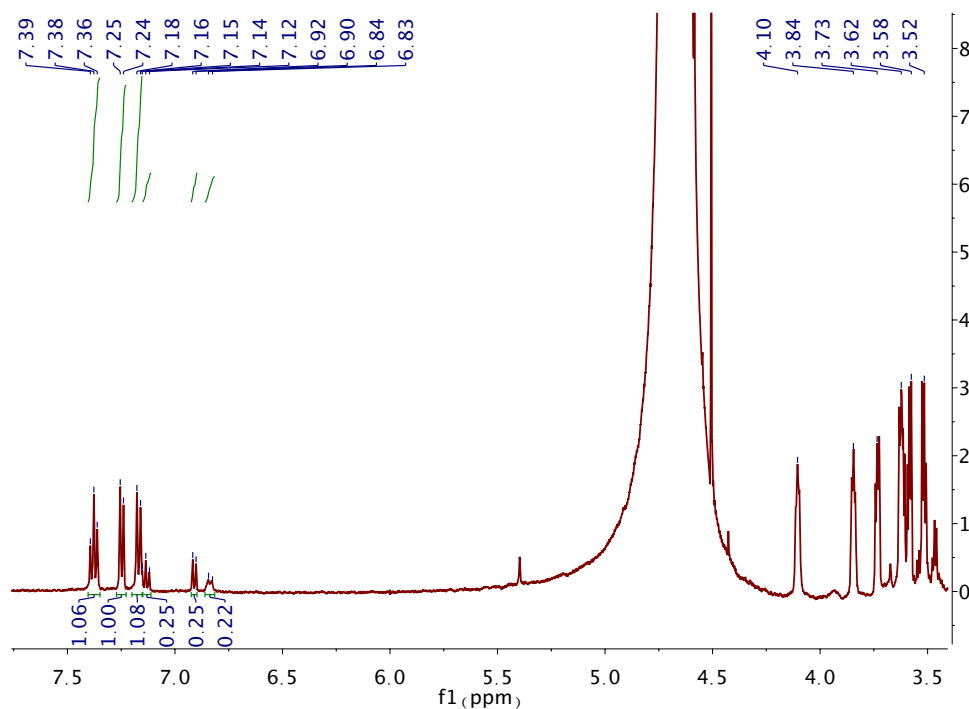


Figure S13. ^1H NMR of cycled AQ-1,8-3E-OH in D_2O . The integration of the aromatic protons of AQ-1,8-3E-OH and the decomposition product are shown, indicating 19% decomposition. The large peak corresponding to H_2O conceals some peaks corresponding to the decomposition product.

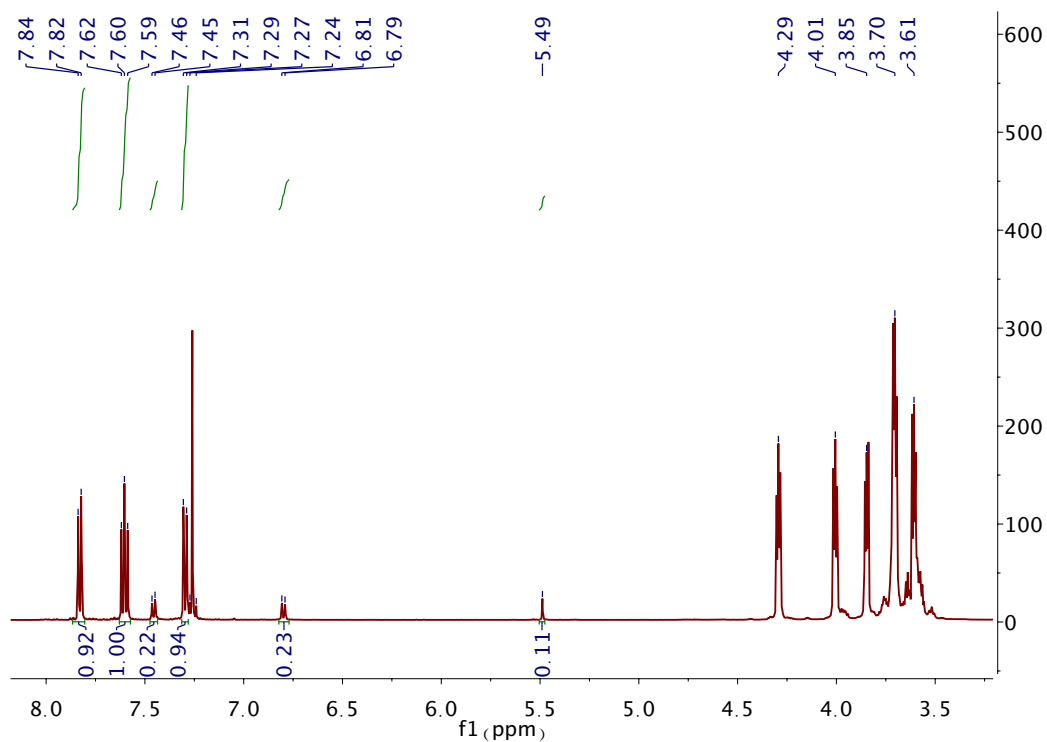


Figure S14. The ^1H NMR spectrum of cycled AQ-1,8-3E-OH in CDCl_3 . The integration and corresponding ratio are the same as the one in D_2O , suggesting that all the pristine and decomposition compounds are extracted successfully. The integration of the peak at a chemical shift of 5.49 ppm (methine proton peak) is half of the integration of one of the aromatic peaks in the decomposition compound.

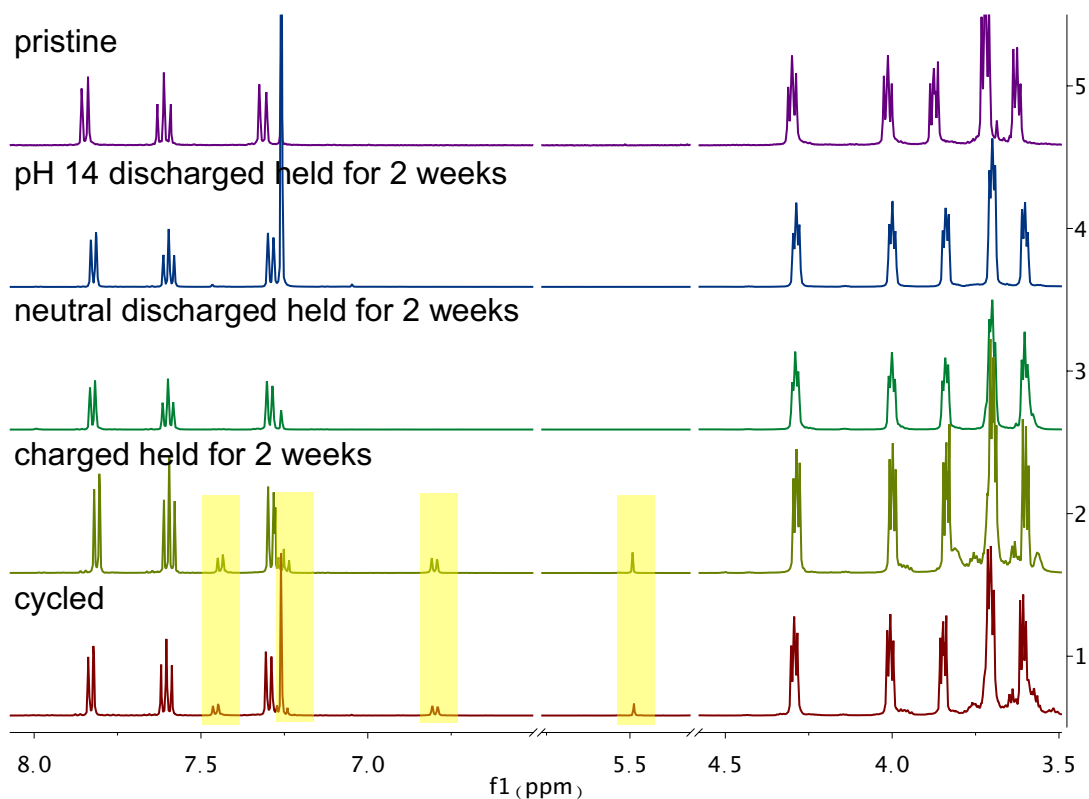


Figure S15. Comparison of ^1H NMR spectra (in CDCl_3) of pristine, discharged-held, charged-held, and cycled AQ-1,8-3E-OH. The spectrum of the charged-held sample is identical to the spectrum of the cycled sample, while the spectra from both pristine and the discharged-held samples are exactly the same, indicating the decomposition of the charged AQ-1,8-3E-OH is the major reason for capacity fading.

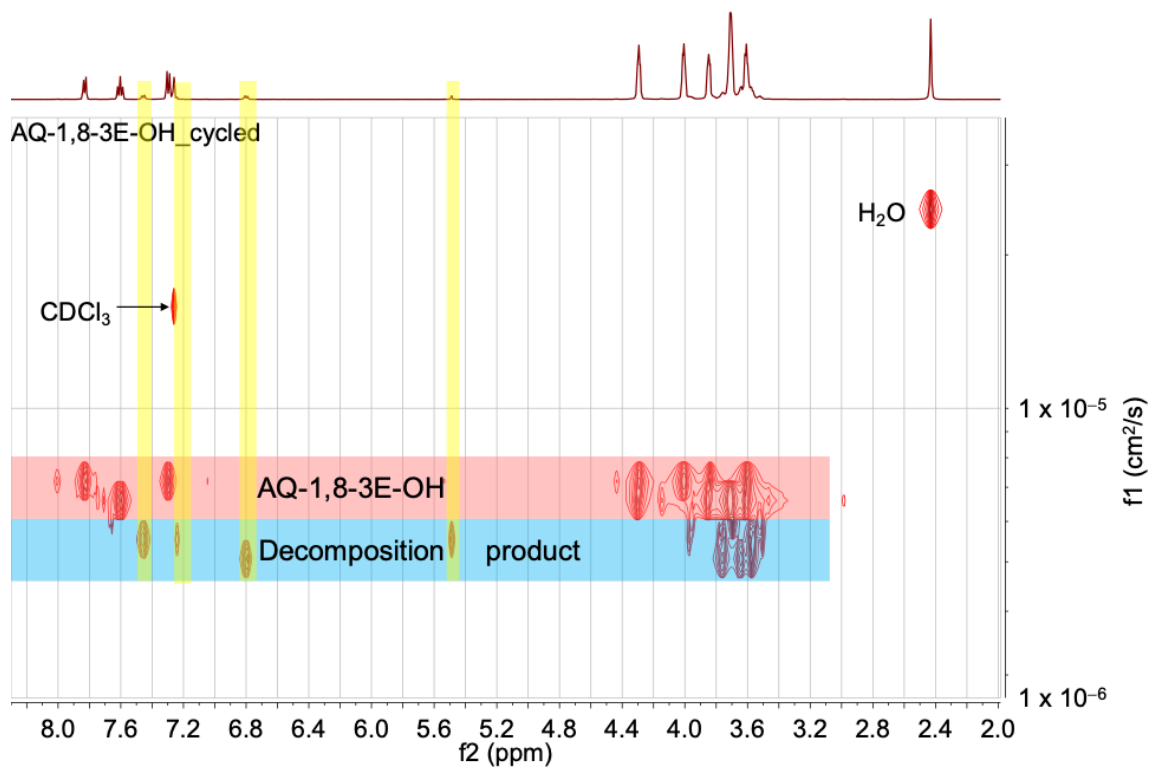


Figure S16. ^1H DOSY NMR (in CDCl_3) of cycled AQ-1,8-3E-OH. The x-axis represents the ^1H chemical shift, and the y-axis represents the relative diffusion rate. The spectrum shows two species with different diffusion coefficients. The decomposition product has a smaller diffusion coefficient compared to AQ-1,8-3E-OH, which suggests that the decomposition product has a larger hydrodynamic radius.

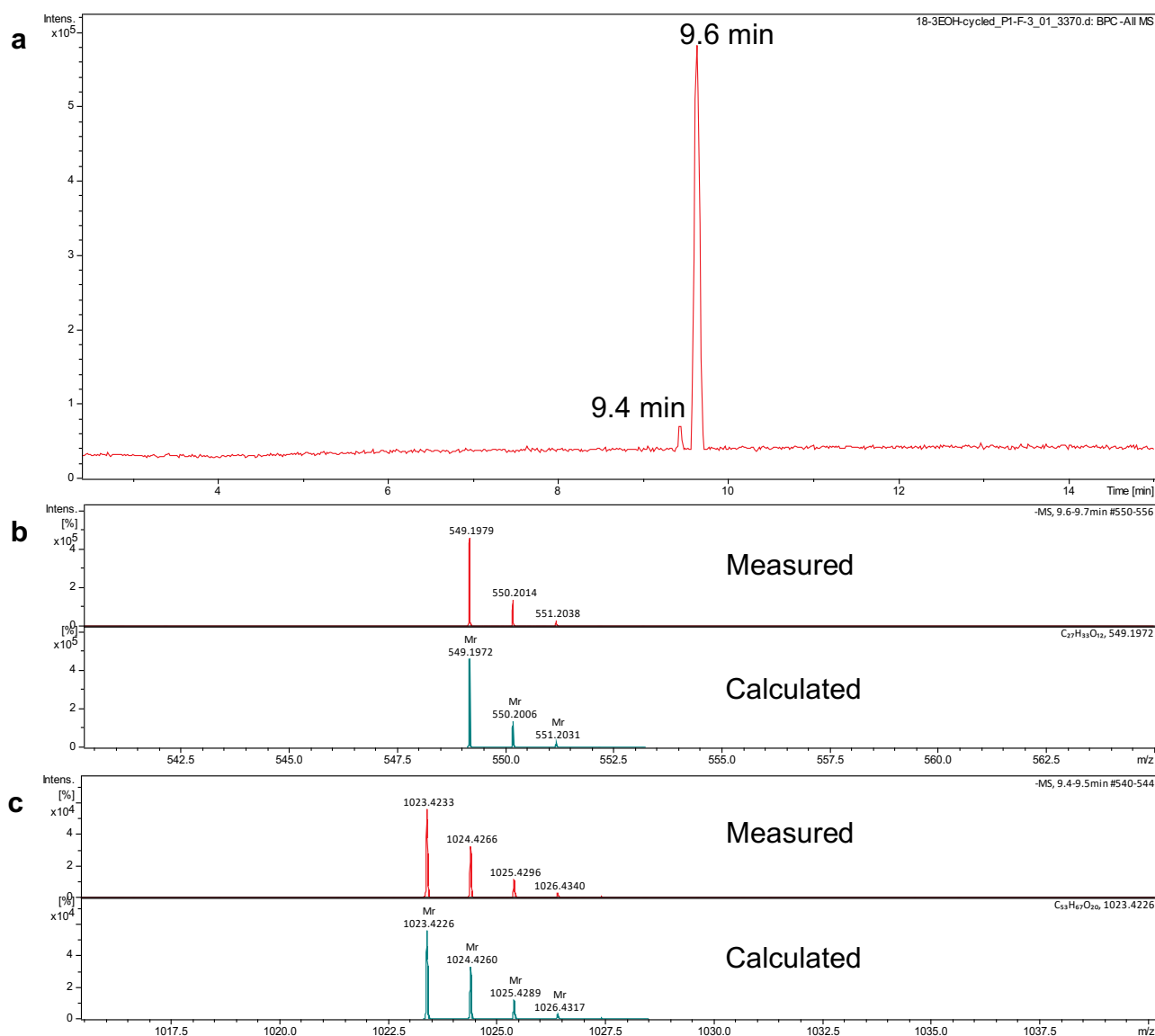
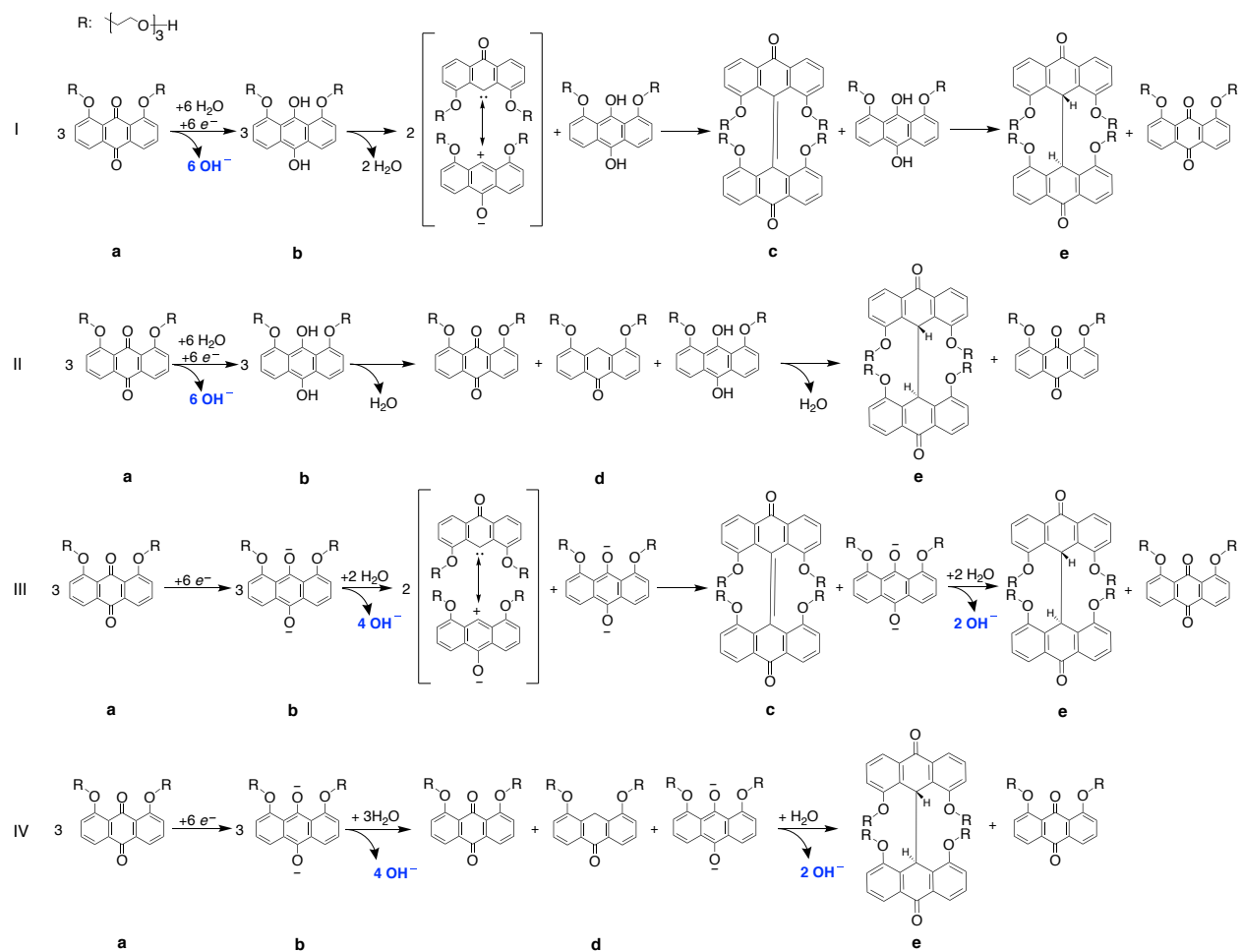


Figure S17. (a) High resolution LC-MS (negative mode) spectrum of the cycled sample shows the presence of two species eluted from the LC column with retention times of 9.6 and 9.4 minutes, respectively. (b) The former has a mass/charge ratio of 549.1979, corresponding to the mass of AQ-1,8-3E-OH plus a formic acid adduct, and (c) the latter has a mass/charge ratio of 1023.4233, corresponding to the mass of 1,1',8,8'-tetrakis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)-[9,9'-bianthracene]-10,10'(9*H*,9'*H*)-dione plus a formic acid adduct. The existence of isotopes generates a cluster of peaks (isotope peaks); all peaks in a cluster are of the same molecular formula.



Scheme S1. Proposed decomposition pathways. In pathways I and II, the reduced AQ is protonated, and in pathways III and IV, it is not. In pathways I and III, the reduced AQ is directly dimerized. In pathways II and IV, PEG-anthrone forms first and then dimerizes in a second step.

Table S3. Calculated energy, using Gaussian 16, M06/3-21G method/basis-set with SMD, for each species in the decomposition pathway as shown in **Scheme S1**. *Energy refers to electronic energy.

Name	Energy* (Hartree)
a. 1,8-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione	-1751.915
b. 1,8-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-diol	-1753.115
c. 1,1',8,8'-tetrakis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)-10H,10'H-[9,9'-bianthracenylidene]-10,10'-dione	-3354.245
d. 4,5-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracen-9(10H)-one	-1678.298
e. 1,1',8,8'-tetrakis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)-[9,9'-bianthracene]-10,10'(9H,9'H)-dione	-3355.499
H ₂ O	-75.968

Table S4. Calculated energy, using Gaussian 16, M06/3-21G method/basis-set with SMD, for the initial, intermediate, and final states. The differences in electronic energy, ΔE , compared with the initial state are listed in column 3.

State	Energy (Hartree)	ΔE (kcal/mol)
Initial: 3* b	-5259.346	0
Path A intermediate: c + b +2*H ₂ O	-5259.298	30.642
Path B intermediate: a + b + d +H ₂ O	-5259.297	31.101
Final: a + e +2*H ₂ O	-5259.351	-2.573

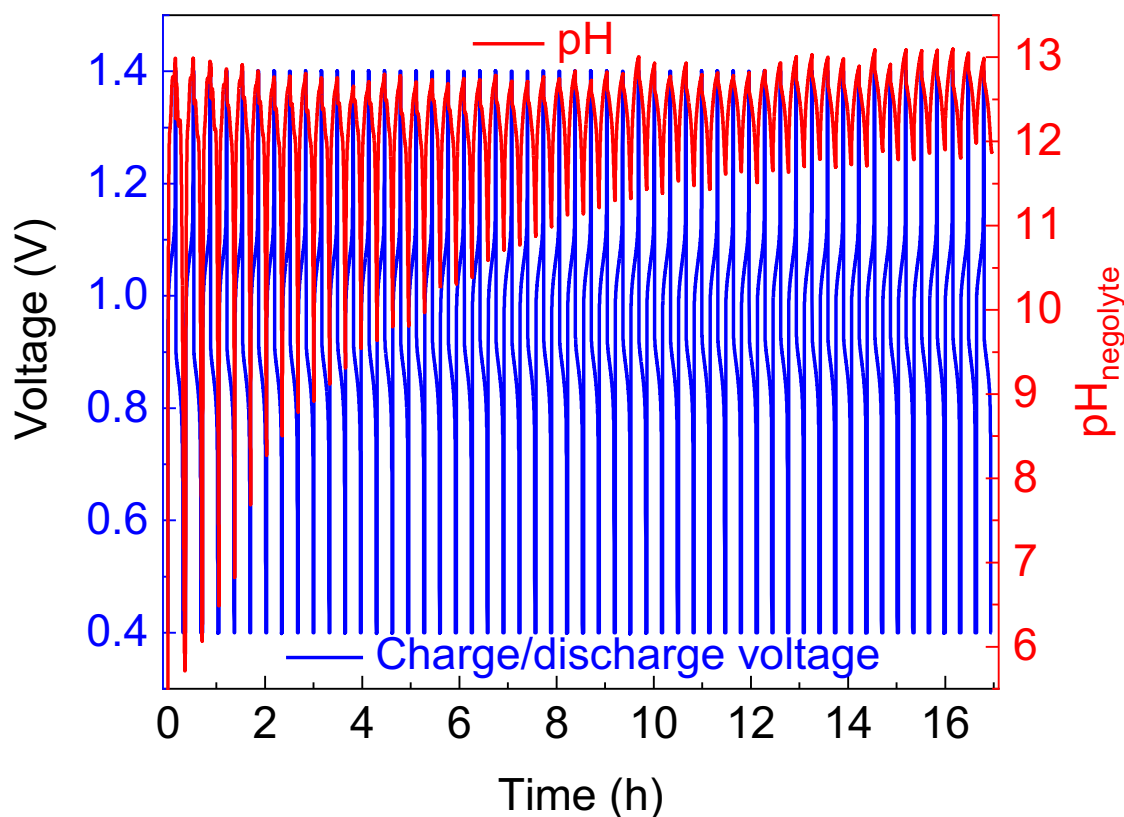


Figure S18. Irreversible pH change during long term cycling in a glovebox is explained by the hydroxide generation associated with the decomposition of charged AQ-1,8-3E-OH. Electrolytes comprised 7 mL of 0.1 M AQ-1,8-3E-OH (negolyte) in 1 M KCl and 40 mL of 0.1 M potassium ferrocyanide and 0.04 M ferricyanide (posolyte) in 1 M KCl. The applied current density was 50 mA/cm².

Cost Considerations

The mass production cost of AQ-1,8-3E-OH is presently unknown, but the expected price is similar to that of 1,8-DHAQ since the synthesis is a facile one-step Williamson etherification with cheap halogenated-ethylene-oxide as a reagent. In addition, at industrial scale, purification through column chromatography is likely unnecessary when reaction temperature and time are optimized to produce purer products in a one-pot reaction. Therefore, the cost of 1,8-DHAQ should be the dominant component in the production of AQ-1,8-3E-OH. Danthron, or 1,8-DHAQ, is found in green vegetables and widely used as precursor for dye molecules. Although the market price for mass-produced 1,8-DHAQ is unknown, current prices for lab-scale 1,8-DHAQ from Sigma Aldrich, AK Scientific, and TCI America are \$0.274/g, \$0.226/g, and \$0.814/g, respectively, which are, on average, more than fifty times cheaper than corresponding values for 2,6-DHAQ. Therefore, we expect the mass-production price for 1,8-DHAQ also to be lower than that for 2,6-DHAQ, which was projected to be \$0.92/kg–\$3.92/kg^{10, 5}. Yuan *et al.*²⁵ reported the cost of sodium ferrocyanide as \$1.07/kg; therefore, the large-scale cost of material is expected to be quite

low. Costs should be further reduced by the use of a non-fluorinated membrane and by the absence of strong base or acid in the electrolyte, enabling the use of less corrosion-resistant electrolyte-contacting materials.

Supplementary References

1. Suttill, J. A.; Kucharyson, J. F.; Escalante-Garcia, I. L.; Cabrera, P. J.; James, B. R.; Savinell, R. F.; Sanford, M. S.; Thompson, L. T. Metal Acetylacetonate Complexes for High Energy Density Non-aqueous Redox Flow Batteries. *Journal of Materials Chemistry A* **2015**, *3* (15), 7929–7938.
2. Kwon, G.; Lee, S.; Hwang, J.; Shim, H.-S.; Lee, B.; Lee, M. H.; Ko, Y.; Jung, S.-K.; Ku, K.; Hong, J.; Kang, K. Multi-redox Molecule for High-Energy Redox Flow Batteries. *Joule* **2018**, *2*, 1771–1782.
3. Hu, B.; Liu, T. L. Two Electron Utilization of Methyl Viologen Anolyte in Nonaqueous Organic Redox Flow Battery. *Journal of Energy Chemistry* **2018**, *27* (5), 1326–1332.
4. Ji, Y.; Goulet, M.-A.; Pollack, D. A.; Kwabi, D. G.; Jin, S.; De Porcellinis, D.; Kerr, E. F.; Gordon, R. G.; Aziz, M. J. A Phosphonate-Functionalized Quinone Redox Flow Battery at Near-Neutral pH with Record Capacity Retention Rate. *Adv. Energy Mater.* **2019**, *9*, 1900039.
5. Kwabi, D. G.; Lin, K.; Ji, Y.; Kerr, E. F.; Goulet, M.-A.; Porcellinis, D. D.; Tabor, D. P.; Pollack, D. A.; Aspuru-Guzik, A.; Gordon, R. G.; Aziz, M. J. Alkaline Quinone Flow Battery with Long Lifetime at pH 12. *Joule* **2018**, *2* (9), 13.
6. Yang, B.; Hooper-Burkhardt, L.; Wang, F.; Surya Prakash, G. K.; Narayanan, S. R. An Inexpensive Aqueous Flow Battery for Large-scale Electrical Energy Storage Based on Water-soluble Organic Redox Couples. *Journal of the Electrochemical Society* **2014**, *161*, A1371–A1380.
7. Wei, X.; Duan, W.; Huang, J.; Zhang, L.; Li, B.; Reed, D.; Xu, W.; Sprenkle, V.; Wang, W. A High-current, Stable Nonaqueous Organic Redox Flow Battery. *ACS Energy Letters* **2016**, *1* (4), 705–711.
8. Hollas, A.; Wei, X.; Murugesan, V.; Nie, Z.; Li, B.; Reed, D.; Liu, J.; Sprenkle, V.; Wang, W. A Biomimetic High-Capacity Phenazine-Based Anolyte for Aqueous Organic Redox Flow Batteries. *Nature Energy* **2018**, *3* (6), 508–514.
9. Lin, K.; Chen, Q.; Gerhardt, M. R.; Tong, L.; Kim, S. B.; Eisenach, L.; Valle, A. W.; Hardee, D.; Gordon, R. G.; Aziz, M. J.; Marshak, M. P. Alkaline Quinone Flow Battery. *Science* **2015**, *349* (6255), 5.
10. Yang, Z.; Tong, L.; Tabor, D. P.; Beh, E. S.; Goulet, M.-A.; Porcellinis, D. D.; Aspuru-Guzik, A.; Gordon, R. G.; Aziz, M. J. Alkaline Benzoquinone Aqueous Flow Battery for Large-Scale Storage of Electrical Energy. *Adv. Energy Mater.* **2018**, *8*, 1702056.
11. Lin, K.; Gómez-Bombarelli, R.; Beh, E. S.; Tong, L.; Chen, Q.; Valle, A.; Aspuru-Guzik, A.; Aziz, M. J.; Gordon, R. G. A Redox-flow Battery with an Alloxazine-based Organic Electrolyte. *Nature Energy* **2016**, *1* (9), 16102.
12. Hu, B.; DeBruler, C.; Rhodes, Z.; Liu, T. Leo Long-cycling Aqueous Organic Redox Flow Battery (AORFB) Toward Sustainable and Safe Energy Storage. *Journal of the American Chemical Society* **2017**, *139* (3), 1207–1214.
13. Wei, X.; Duan, W.; Huang, J.; Zhang, L.; Li, B.; Reed, D.; Xu, W.; Sprenkle, V.; Wang, W. A High-current, Stable Nonaqueous Organic Redox Flow Battery. *ACS Energy Letters* **2016**, *1* (4), 705–711.

14. Luo, J.; Hu, B.; Debruler, C.; Bi, Y.; Zhao, Y.; Bing, Y.; Hu, M.; Wu, W.; Liu, T. L. Unprecedented Capacity and Stability of Ammonium Ferrocyanide Catholyte in pH Neutral Aqueous Redox Flow Batteries. *Joule* **2019**, 3, 149–163.
15. Beh, E. S.; De Porcellinis, D.; Gracia, R. L.; Xia, K. T.; Gordon, R. G.; Aziz, M. J. A Neutral pH Aqueous Organic–Organometallic Redox Flow Battery with Extremely High Capacity Retention. *ACS Energy Lett.* **2017**, 2 (3), 639–644.
16. Huskinson, B.; Marshak, M. P.; Suh, C.; Er, S.; Gerhardt, M. R.; Galvin, C. J.; Chen, X.; Aspuru-Guzik, A.; Gordon, R. G.; Aziz, M. J. A Metal-free Organic-Inorganic Aqueous Flow Battery. *Nature* **2014**, 505 (7482), 195–8.
17. Ponce de León, C.; Frías-Ferrer, A.; González-García, J.; Szánto, D. A.; Walsh, F. C. Redox Flow Cells for Energy Conversion. *Journal of Power Sources* **2006**, 160 (1), 716–732.
18. Janoschka, T.; Martin, N.; Hager, M. D.; Schubert, U. S. An Aqueous Redox-Flow Battery with High Capacity and Power: The TEMPTMA/MV System. *Angew. Chem. Int. Ed.* **2016**, 55 (46), 14427–14430.
19. Li, L.; Kim, S.; Wang, W.; Vijayakumar, M.; Nie, Z.; Chen, B.; Zhang, J.; Xia, G.; Hu, J.; Graff, G.; Liu, J.; Yang, Z. A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage. *Adv. Energy Mater.* **2011**, 1, 7.
20. Hall, J.; Perkin, A. G., Reduction Products of the Hydroxyanthraquinones Part II. *Journal of the Chemical Society, Transactions* **1923**, 123, 2029–2037.
21. Giguere, J. B.; Morin, J. F. New Strapped Porphyrins as Hosts for Fullerenes: Synthesis and Complexation Study. *Org. Biomol. Chem.* **2012**, 10 (5), 1047–51.
22. Kestin, J.; Khalifa, H. E.; Correia, R. J. Tables of the Dynamic and Kinematic Viscosity of Aqueous KCl Solutions in the Temperature Range 25–150 °C and the Pressure Range 0.1–35 MPa. *J. Phys. Chem. Ref. Data* **1981**, 10, 15.
23. Shi, Z.; Li, Y.; Li, Y.; Lu, G.; Liu S. 1,1',8,8'-Tetramethoxy-10,10'-Bianthrone. *Acta Cryst.* **2004**, E60, 7.
24. Shyamasundar, N.; Caluwe, P.; Lithium Aluminum Hydride Reduction of peri-alkoxy-9,10-anthraquinones. *Journal of Organic Chemistry* **1981**, 46, 6.
25. Yuan, Z.; Duan, Y.; Liu, T.; Zhang, H.; Li, X. Toward a Low-Cost Alkaline Zinc-Iron Flow Battery with a Polybenzimidazole Custom Membrane for Stationary Energy Storage. *iScience* **2018**, 3, 40–49.