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An Extremely Stable and Soluble NH₂-Substituted Anthraquinone **Electrolyte for Aqueous Redox Flow Batteries**

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ABSTRACT: Aqueous redox flow batteries require long-term stable redox molecules for electrical energy storage. Anthraquinones, especially ether bond-decorated ones, experience two dominant decomposition pathways, including side-chain loss and anthrone formation. With the aid of DFT calculations, we designed an anthraquinone (3-NH₂-2-2PEAQ) bearing an ether substituent and a neighboring NH_2 group, which suppresses both of these decomposition mechanisms and exhibits a high solubility of 1.1 M. When paired with ferrocyanide in a full cell, this anthraquinone, at a concentration of 1.0 M, can operate at greater than 1 V with an extremely low capacity fade rate of 0.01%/day and a Coulombic efficiency above 99.8% while cycling for over a month. The synergistic effects of the ether and parent amino substituents are extremely sensitive to the precise substitution pattern of the anthraquinone. This study demonstrates the effectiveness of the judicious use of DFT-based prediction in rapidly identifying promising candidate electrolytes from a large chemical space.

KEYWORDS: quinone, redox molecule, energy storage, aqueous organic redox flow batteries, electrochemistry, density functional theory

INTRODUCTION

The inherent intermittency of wind and solar power sources can be managed by the development of large and scalable storage technologies for electrical energy.¹ Redox flow batteries (RFBs) are promising energy-storage systems that are particularly well suited for reaching the long discharge durations at rated power needed for this purpose.^{4,5} In particular, aqueous organic RFBs, in which water-soluble, redox-active small organic molecules act as energy carriers, have emerged as a potentially safe and cost-effective solution for grid-scale storage.⁶⁻¹⁰ The diversity of redox-active organic molecules and the ease with which derivatives can be prepared can, in principle, enable fine structural tunability to achieve a candidate material possessing a high energy density, robust chemical stability, and a low cost of manufacture. A molecule that satisfies all of these criteria is essential for the practical deployment of aqueous organic RFBs.

Several families of redox-active molecules including quinones,^{11–14} aza-aromatics⁹ such as phenazines,^{15–17} viol-ogens,^{18,19} and metalorganic complexes^{20,21} have been explored and investigated for RFBs. Among these, anthraquinones with ether-linked solubilizing groups^{22-24,29} stand out due to their high stability and aqueous solubility. Nevertheless, several mechanisms of decomposition remain, limiting the lifetimes of these electrolytes for practical long-term operation. Previous studies determined the dominant decomposition

pathways to be (1) nucleophilic substitution by hydroxide at the ether linkage, leading to loss of a phenoxide anion and removal of the solubilizing group,²² and (2) a redox disproportionation process in which two hydroquinone dianions produce a quinone (by oxidation) and an anthrone (by reduction)—this latter overreduction product irreversibly dimerizes to an off-cycle species with poor redox properties that lead to capacity loss. 25,26

In this study, we demonstrate the dramatically improved stability and performance of a simple derivative of a previously reported anthraquinone electrolyte species, 2-2PEAQ, in its application in aqueous RFBs. Aiming to suppress known decomposition pathways through the addition of simple substituents to the anthraquinone core, we were guided by density functional theory (DFT) calculations that predicted a significant beneficial effect of adding an electron-donating NH₂ group in the β position adjacent to the water-solubilizing ether group. Systematic in silico screening of all relevant isomers

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Figure 1. (a) Dominant decomposition mechanisms for anthraquinone-based negolytes for aqueous organic redox flow batteries. (b) This work: development of amino-substituted anthraquinones that avoid these decomposition pathways with the aid of *in silico* evaluation of candidate isomers. (c) Model isodesmic reactions used to evaluate the propensity of each candidate to undergo overreduction to anthrone or loss of the solubilizing carboxylate chain. (d) Plot of predicted thermodynamics for anthrone formation and side-chain loss for various substitution patterns. 2-2-PEAQ, a previously demonstrated molecule, is shown in black. The predicted best candidate (3-NH₂-2-2PEAQ) is indicated with a red star, and it was selected for experimental evaluation.

showed that this substitution pattern is especially effective in mitigating side-chain loss and suppressing anthrone formation, enabling a reduction of the capacity fade rate to 0.01%/day. In addition, our newly synthesized $3-NH_2-2-2PEAQ$ negolyte is highly soluble and exhibits excellent energy and power density when paired with ferri/ferrocyanide posolyte in a full cell under rigorous electrochemical cycling conditions. The discovery of this improved material addresses the major decomposition pathways limiting the lifetime of anthraquinone-based electrolytes and points out a pathway for decadal electrolyte lifetimes in aqueous organic RFBs.

EXPERIMENTAL DETAILS

Density Functional Theory (DFT) Calculations. All DFT calculations were performed with Gaussian 16. Geometry optimizations were performed with the B3LYP functional and the 6-31G(d) basis set of 6-31G(d). Grimme's D3 correction for London dispersion with Becke–Johnson damping was applied during optimization as well as an implicit SMD solvation model with water as the solvent. Singe-point energies were calculated with the B3LYP functional and a basis set of 6-311G+(d,p) with the same London dispersion and solvent corrections as those in the geometry optimization. The reported standard free energies of reaction in Figure 1 are relative to the corresponding reactions of 2-2PEAQ, the reference compound. These Gibbs free energies are composite energies calculated in the standard approach using vibrational and free energy corrections from the lower level of theory and single-point energies from the higher level of theory.

Permeability Measurements. Following published procedures,²⁷ two custom glass H-cells (Adams & Chittenden) were assembled, one with Nafion NR212 (presoaked in 1 M KOH for complete ion exchange to potassium, no further pretreatment) and the other with Fumasep E-620 (K) (used dry, as received), clamped in the center. Each H-cell had a "donating" electrolyte of 10 mL of 0.1 M 3-NH₂-2-2PEAQ in 1 M KOH and a "receiving" electrolyte of 10 mL of 0.1 M KCl in 1 M KOH. Both compartments were stirred

continuously using magnetic stir bars. Two milliliter aliquots were removed from the receiving side of each H-cell, and absorbance spectra were taken with UV–vis spectrophotometry (Agilent) to evaluate the concentration of crossed-over species. The volume removed was replaced with fresh receiving electrolyte (the resulting dilution was accounted for in evaluating permeability). The receiving electrolyte was designed to balance the pH and ion concentration of the donating electrolyte to prevent water crossover, and neither receiving electrolyte changed by more than 3% in mass over the course of the 14 day experiment.

Cyclic Voltammetry (CV) and Rotating Disk Electrode (RDE) Voltammetry. CV measurements were collected in a standard threeelectrode setup with glassy carbon as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode, 0.21 V vs SHE, and platinum wire as the counter electrode. The glassy carbon working electrode was polished with an aluminum slurry before and after each scan. All solutions were purged with nitrogen before measurements, and all experiments were blank-subtracted. The RDE tests were carried out with the use of a Pine Instruments Modulated Speed Rotator AFMSRCE outfitted with a 5 mm-diameter glassy carbon working electrode (Pine Instruments E5PK), a Ag/AgCl (3 M KCl) reference electrode, a graphite counter electrode, and a Gamry Reference 3000 potentiostat. The mass transport properties of the oxidized form of 3-NH2-2-2PEAQ were determined using the Levich equation by plotting the limiting current versus the square root of the rotation rate to yield a straight line that was fitted to extract the diffusion coefficient. Additionally, Kouteck-Levich analysis was conducted to obtain the charge transfer rate constant (k^0) for 3-NH₂-2-2PEAQ.

Galvanostatic and Polarization Testing. Room-temperature galvanostatic cycling was carried out over 20–120 mA cm⁻² with voltage limitations of 0.60 and 1.36 V. Capacity utilization, Coulombic efficiency, and energy efficiency were extracted at each current density. Polarization measurements were conducted by first charging the cell to the desired state of charge based on measured full capacity, followed by polarization via linear-sweep voltammetry with a scan rate of 100 mV s⁻¹ starting from +0.8 V vs the open-circuit voltage (OCV) to -0.8 V vs the OCV. Additionally, the OCV of the battery was measured, and potentiostatic electrochemical impedance



Figure 2. (a) Cyclic voltammetry of 10 mM 3-NH₂-2-2PEAQ (blue) and 10 mM potassium ferrocyanide (red) in 1 M KOH with a scan rate of 100 mV s⁻¹. (b) Pourbaix diagram of 3-NH₂-2-2PEAQ with least-squares fitted slope. (c) Linear sweep voltammograms of 5 mM 3-NH₂-2-2PEAQ in 1 M KOH on a rotating disk electrode at rotation rates indicated. (d) Levich plot of limiting current versus square root of rotation rate based on the data in panel (c). (e) Kouteck–Levich plot of 5 mM 3-NH₂-2-2PEAQ in 1 M KOH at various overpotentials. (f) Fitted Tafel plot of 5 mM 3-NH₂-2-2PEAQ in 1 M KOH at Various overpotentials. (f) Fitted Tafel plot of 5 mM 3-NH₂-2-2PEAQ in 1 M KOH at various overpotentials.

spectroscopy (PEIS) measurements were collected with 10 mV perturbation near OCV and with frequency ranging from 1 to 100,000 Hz to determine the high-frequency area-specific resistance (ASR). To determine the high-frequency area-specific resistance (ASR), electrochemical impedance spectroscopy (EIS) measurements were conducted at each SOC with a perturbation of 10 mV and frequencies ranging from 1 to 100,000 Hz. The battery's OCV was also measured. Additionally, the potential was swept at each SOC at a scan rate of 150 mV s⁻¹, and the current response as a result was measured to create polarization curves. The polarization ASR was computed using the linear region of the polarization curves near OCV.

Full Cell Cycling. To evaluate the performance of 3-NH₂-2-2PEAQ and 4-NH₂-1-2PEAQ, long-term battery cycling experiments, with ferro/ferricyanide as the noncapacity-limiting posolyte redox couple, were performed using the constant current followed by the constant voltage (CCCV) procedure. Low-concentration full cell cycling of 3-NH₂-2-2PEAQ was performed using a negolyte composed of 0.1 M 3-NH2-2-2PEAQ potassium salt in 1 M KOH (pH 14), with a total volume of 6.5 mL. The posolyte composition was 0.20 M potassium ferrocyanide, 0.08 M potassium ferricyanide, and 1 M KOH, with a total volume of 30 mL. A Fumasep E-620 (K) membrane was used to separate the two sides of the cell. Each electrode comprised a 5 cm^2 geometric surface area covered by a stack of three sheets of Sigracet GDL 39AA (Fuel Cell Store) per side. The outer portion of the space between the electrodes was gasketed using Viton sheets (10 mils for 161 SGL cells) with the area over the electrodes cut out. The torque applied during cell assembly was 60 lbin (6.78 N·m) on each of eight 3/8"-24 bolts; thus, the load applied per bolt is approximately 800 lb. All electrodes were baked in an oven

that was already heated at 400 °C in air for 24 h prior to use and were removed after 24 h. The cycling protocol implemented a constant current of 40 mA cm⁻², followed by constant voltage held at 1.3 V during charge and 0.65 V during discharge until the magnitude of the current density fell to 1 mA cm⁻² for charging and 0.5 mA cm⁻² for discharging. Low-concentration full cell cycling of 4-NH₂-1–2PEAQ was performed analogously using a negolyte composed of 0.1 M 4-NH₂-1-2PEAQ potassium salt in 1 M KOH (pH 14), with a total volume of 6 mL.

In addition, a high-concentration cell cycling experiment was performed for $3-NH_2-2-2PEAQ$. The negolyte was composed of 1 M $3-NH_2-2-2PEAQ$ potassium salt in 1 M KOH (pH 14), with a total volume of 4 mL. The posolyte consisted of a solution of 0.3 M potassium ferrocyanide, 0.2 M sodium ferrocyanide, and 0.3 M potassium ferricyanide in 1 M KOH, with a total volume of 100 mL. Mixed cations were used to increase the solubility of the ferrocyanide posolyte. A Nafion 212 membrane was used to separate the two sides of the cell. In each half-cell, three layers of carbon paper (SGL 39AA, baked at 400 °C overnight) were used as electrodes. The cycling protocol implemented a constant current of 40 mA cm⁻², followed by constant voltage held at 1.36 V during charge and 0.60 V during discharge until the magnitude of the current density fell to 1 mA cm⁻² for charging and 0.5 mA cm⁻² for discharging.

RESULTS AND DISCUSSION

Previously, anthraquinones bearing an ether-linked solubilizing group such as a carboxylic acid, such as 2-2PEAQ, were reported, which showed high solubility and relative stability



Figure 3. Long-term cell testing of flow batteries at pH 14 using (a) $3-NH_2-2-2PEAQ$ and (b) $4-NH_2-1-2PEAQ$ as electrolytes. The cells were cycled with a constant current (40 mA cm⁻²) followed by a constant voltage of 1.3 V (charging) and 0.65 V (discharging) at rt. Both cells were assembled with 0.1 M negolyte paired with 30 mL of 0.1 M ferrocyanide/0.02 M ferricyanide in 1 M KOH separated by a Fumasep E-620 (K) cation exchange membrane. The cell cycling tests were performed in a N₂-filled glovebox.

but remained vulnerable to (1) loss of this side chain and (2)disproportionation to form unstable overreduced anthrones.^{22-24,29} To overcome these deleterious side reactions, we explored the installation of additional substituents in anthraquinones such as 2-2PEAQ. Our attention was drawn specifically to the addition of amino (NH₂) groups for several reasons. The group is small, adding minimally to the molecular weight, and due to its polarity and hydrogen-bonding abilities, might afford favorable aqueous solubility properties. Additionally, the ability of the amino group to be a strong mesomeric electron donor in certain positions could make the phenoxide moiety a poorer leaving group in nucleophilic substitution chain-loss processes. Moreover, the lone pair of the amine could stabilize the carbonyl groups by resonance and thermodynamically disfavor anthrone formation. Finally, the parent amino group has rarely been studied as a substituent on redox-active organic molecules, and we therefore saw an opportunity for fundamental insight.

The placement of two substituents, one amino group and one solubilizing ether side chain, on anthraquinone can result in 14 different isomeric compounds. We turned to DFT thermochemical modeling to predict the effect of these various substitution patterns on the deleterious pathways of interest as a means to prioritize candidates for synthesis and further assessment. As an indicator of propensity to chain loss through nucleophilic substitution by phenoxide hydroxide, we calculated the stability of each phenoxide leaving group relative to 2-2PEAQ as a reference (x-axis of Figure 1d). To estimate the thermodynamic driving force for decomposition through anthrone formation, we computed the Gibbs free energy of reduction of each anthraquinone to the anthrone compared to the same process with 2-2PEAQ as a reference (y-axis of Figure 1d). In this calculation, both potential anthrone isomers were evaluated and the favored reduction product was used for comparison.

In these predictions, some broad trends were apparent: for example, the addition of an amino substituent anywhere on anthraquinone generally disfavors anthrone formation relative to 2-2PEAQ, likely by electron donation, although the extent varies by up to ca. 7 kcal/mol. Analysis of the leaving group ability during side-chain cleavage, however, reveals a complex interplay between the two substituents depending on their placement. Overall, the compound indicated with a red star, which we refer to as 3-NH_2 -2-2PEAQ, was chosen as the most promising candidate for experimental evaluation and confirmation. We also synthesized a compound 4-NH_2 -1-2PEAQ, indicated with a red triangle, as a comparison electrolyte because this isomer was predicted to be moderate in its susceptibility to both decomposition pathways.

We recorded the cyclic voltammograms of 3-NH₂-2-2PEAQ and potassium ferrocyanide at pH 14 (Figure 2a). The redox potential of 3-NH₂-2-2PEAQ is -0.525 V vs SHE. When paired with potassium ferrocyanide, this corresponds to an equilibrium cell voltage of 1.025 V, which is a 75 mV cell voltage enhancement over that of the 2-2-PEAQ/ferrocyanide cell. The measured Pourbaix diagram shown in Figure 2b indicates that 3-NH₂-2-2PEAQ undergoes a two-proton/twoelectron transfer below pH 11, a one-proton/two-electron transfer between pH 11 and 12.5, and a zero-proton/twoelectron transfer above pH 12.5. Rotating disk electrode studies were performed to estimate mass transport and kinetic properties of 3-NH₂-2-2PEAQ. The molecule has a diffusion coefficient of 2.61×10^{-6} cm² s⁻¹, which was obtained through Levich analysis, and a charge transfer rate constant of 2.85 \times 10^{-3} cm² s⁻¹, obtained through Koutecky-Levich analysis (Figure 2c-f). These values are well within the range of previously reported values for anthraquinone derivatives in the aqueous alkaline environment.^{22-24,29} Additionally, owing to its low symmetry and the presence of polar functional groups, 3-NH₂-2-2PEAQ displays excellent solubility that reaches 1.1 M (2.2 M transferable e^-) at pH 14, resulting in a maximum theoretical capacity of 58.9 Ah L^{-1} at room temperature (Figure S5). The molecule also shows robust thermal stability in both its oxidized and reduced forms at elevated temperature (65 °C) (Figure S6).

To verify the results of our DFT-based candidate screening summarized in Figure 1, we evaluated the long-term battery cycling of 3-NH₂-2-2PEAQ, predicted to be resistant to the two pertinent decomposition processes and 4-NH₂-1-2PEAQ (shown as the point labeled *1-OR*, *4-NH*₂), predicted to be around average in susceptibility to both mechanisms. Both negolytes were prepared as 0.1 M solutions at pH 14 and were paired, as the capacity-limiting side, with 0.1 M ferrocyanide/ 0.02 M ferricyanide as the posolyte. The cells were cycled at 40 mA cm⁻² under the standard CCCV cycling protocol to ensure access to full capacity. Figure 3a shows the results from cycling



Figure 4. Polarization and galvanostatic performance of a cell using $3-NH_2-2-2PEAQ$ in the negolyte and ferrocyanide/ferricyanide in the posolyte. (a) Galvanostatic charge–discharge curves at various current densities with 1.4 and 0.6 V cutoffs. (b) Coulombic efficiency, capacity utilization, and roundtrip energy efficiency at different applied current densities. (c) Cell voltage and power density during discharge at selected SOCs. (d) Open-circuit voltage, polarization ASR, and high-frequency ASR as a function of SOC.

of 3-NH₂-2-2PEAQ over 12 days, during which the cell maintained a high Coulombic efficiency of 99.9%. Additionally, more than 95% of the theoretical capacity (5.3 Ah L^{-1}) of the 0.1 M (6.5 mL) cell was accessed; the deficiency from the theoretical maximum can arise from measurement error or trace redox-inactive impurities. The temporal capacity fade rate over 12 days and 700 cycles was ca. 0.01%/day, which is among the lowest reported for organic electrolytes in aqueous RFBs and represents a 5-fold stability increase over 2-2PEAQ. The voltage-capacity profiles for chosen cycles are shown in Figure S7 and show no apparent change nor side reactions during the cycling of the battery. Post-mortem analysis of the electrolytes was conducted to investigate possible decomposition and crossover. ¹H NMR spectroscopy of the cycled 3-NH₂-2-2PEAQ negolyte (Figure S8) indicated no apparent decomposition based on comparison of the aromatic region to the spectrum of the initial material. However, in the aliphatic region, a small singlet peak was visible at 1.87 ppm, which was assigned previously to potassium pyruvate,²⁴ resulting from side-chain loss. High-resolution LC-MS of the cycled 3-NH₂-2-2PEAQ (Figure S9) showed no sign of anthrone dimer formation and only a trace amount of 2-amino-3-hydroxyanthraquinone, which is the result of nucleophilic cleavage of the water-solubilizing chain. Cyclic voltammetry of both negolyte and posolyte reservoirs was recorded after battery cycling, and no sign of crossover or unexpected redox events was detected

(Figure S10). The suppression of crossover was also confirmed by conducting a crossover test across Nafion NR212 and E-620 (K) cation exchange membranes in a H-cell (Figure S11). By contrast, in analogous cycling experiments, 4-NH₂-1-2PEAQ exhibited a high capacity fade rate of ca. 8.9%/day (Figure 3b). ¹H NMR spectroscopy of the cycled material showed nearly quantitative side-chain cleavage and conversion of 4-NH2-1-2PEAQ to 1-amino-4-hydroxyanthraquinone (Figure S12). This decomposition was also visually apparent during cycling in the form of rapid precipitation of the electrolyte after only a few hours of operation. In addition, LC-MS results of the postcycled 4-NH₂-1-2PEAQ (Figure S13) indicate another decomposition pathway resulting from substitution of the 1amino group by a hydroxyl group. An extremely low but detectable signal corresponding to the anthrone dimer was also observed.

Galvanostatic charge and discharge of a full cell composed of 4 mL of 0.5 M 3-NH₂-2-2PEAQ in 1 M KOH as the negolyte and ferrocyanide (0.3 M potassium ferrocyanide, 0.2 M sodium ferrocyanide, and 0.3 M potassium ferricyanide in 1 M KOH, with a total volume of 100 mL) as the posolyte separated by a Fumasep E-620 (K) membrane at pH 14 were performed (Figure 4a) to evaluate Coulombic efficiency, capacity utilization, and energy efficiency at different current densities (Figure 4b). The cell was able to hold a current density of 80 mA cm⁻² with >98% Coulombic efficiency, > 90% capacity

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Figure 5. (a) High-concentration long-term cell cycling of a flow battery composed of 1 M 3-NH₂-2-2PEAQ in 1 M KOH paired with 0.3 M potassium ferrocyanide/0.2 M sodium ferrocyanide/0.3 M potassium ferricyanide at room temperature. (b) Comparison between 3-NH₂-2-2PEAQ (this work) and previously reported anthraquinone negolytes. Only molecules with a capacity fade rate below 0.1%/day are shown here. Data obtained from refs 11,12,22-24,28, and 29.

utilization, and >70% energy efficiency (Figure 4b). Additionally, polarization experiments of the same cell were conducted in different states of charge. The cell exhibited a peak galvanic power density of 0.15 W cm⁻² at room temperature. The opencircuit voltage (OCV) (Figure 4d) increased from 1.015 V at 20% SOC to 1.08 V at 90% SOC. The high-frequency ASR through E620 (K) averaged 1.46 \pm 0.01 ohm cm² over the SOC range studied (Figure 4d), representing 78% of the average polarization ASR. In contrast, the high-frequency ASR through Nafion 212 reported in the 2-2PEAQ work²⁴ was 2.3 ohm cm², representing 77% of the polarization ASR of the cell. Cutting membrane ASR, which is typically the most important feature limiting power density in alkaline RFB chemistries without unacceptable increases in reactant crossover, remains an important research direction.

Finally, we examined the stability of $3-NH_2-2-2PEAQ$ under more realistic battery conditions by cycling under a high concentration (1.0 M, pH 14) against a ferrocyanide/ ferricyanide posolyte. At this concentration, $3-NH_2-2-2PEAQ$ showed extreme stability, decomposing at only 0.01%/day(~3.65%/year) with a high Coulombic efficiency (>99.8%) maintained over the span of the 32 day experiment (Figure 5a). The outstanding combination of stability and volumetric capacity is apparent in Figure 5b, which situates $3-NH_2-2-2PEAQ$ among all previously reported anthraquinone negolytes with a demonstrated capacity fade rate of 0.1%/day. We note, however, that in some cases,¹¹ the demonstrated volumetric capacity is well below the reported solubility and there is no apparent reason that greater volumetric capacity cannot be demonstrated.

CONCLUSIONS

In conclusion, this work demonstrates the outstanding performance of an aqueous RFB negolyte based on 3-NH_2 -2-2PEAQ, with a capacity fade rate of ~0.01%/day, an OCV vs ferro/ferricyanide >1.0 V, and a demonstrated volumetric capacity exceeding 50 Ah L⁻¹. DFT calculations revealed the synergistic effect and the remarkable sensitivity to the substitution pattern of different substituents in suppressing the two most important decomposition mechanisms. Experiments confirmed this sensitivity, where explored. This work

shows how the judicious use of DFT calculations can be effective in the design of high-performance redox-active organics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.3c01943.

Synthesis procedure, mass and ¹H NMR spectra, UVvis solubility measurement, and postbattery cycling characterization (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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Supporting Information

An Extremely Stable and Soluble NH₂-Substituted Anthraquinone Electrolyte for Aqueous Redox Flow Batteries

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1. Methods

1.1 Synthesis of 3-NH₂-2-2PEAQ

In a 250 mL round-bottom flask, 2-amino-3-hydroxyanthraquinone (3.0 g, 12.5 mmol) and potassium carbonate (5.0 g, 36 mmol, 2.9 equiv) were dissolved in DMF (35 mL). A magnetic stir bar was added, and the reaction mixture was stirred until the starting material had dissolved. Ethyl 3-bromopropionate (2.3 mL, 17.4 mmol, 1.4 equiv) was then added slowly by syringe. The flask was capped securely with a septum, and the reaction mixture was heated to 80 °C in a silicone oil bath. After stirring overnight at this temperature, the reaction mixture was cooled to rt, and 1 N aqueous HCl solution (approximately 50 mL) was added to precipitate the desired intermediate ethyl ester of 3-NH₂-2-2PEAQ, which was obtained as a yellow solid upon vacuum filtration. This solid was immediately dissolved in distilled water (20 mL) and isopropanol (20 mL) in a 100 mL round-bottom flask. Excess potassium hydroxide (8 g) and a magnetic stir bar were added, and the flask was capped securely with a septum. The reaction mixture was heated to 80 °C in a silicone oil bath. After stirring overnight at this temperature, the reaction mixture was cooled to rt, and 1 N HCl solution (approximately 50 mL) was added to precipitate the desired product 3-NH₂-2-2PEAQ as a yellow solid (2.84 g, 73% yield. ¹H NMR (400 MHz, DMSO-d6): δ 11.33 (s, 1H), 8.14 (m, 2H), 7.88 (m, 2H), 7.66 (s, 1H), 7.56 (s, 1H), 4.92 (q, J = 6.8 Hz, 1H), 1.49 (d, J = 6.8 Hz, 3H) ppm. ¹³C NMR (400 MHz, DMSO-d₆): δ 181.9, 181.7, 166.9, 148.0, 134.86, 134.84, 133.59, 133.56, 133.4, 129.7, 129.3, 127.2, 127.1, 114.4, 114.0, 73.7, 16.9 ppm. **IR** (neat, cm⁻¹): 3476, 3273, 1707, 1665, 1584, 1513, 1408, 711.

1.2 Synthesis of 4-NH₂-1-2PEAQ

In a 250 mL round-bottom flask, 1-Amino-4-hydroxyanthraquinone (3.0 g, 12.5 mmol) and potassium carbonate (5.0 g, 36 mmol, 2.9 equiv) were dissolved in DMF (35 mL). A magnetic stir bar was added, and the reaction mixture was stirred until the starting material had dissolved.

Ethyl 3-bromopropionate (2.3 mL, 17.4 mmol, 1.4 equiv) was then added slowly by syringe. The flask was capped securely with a septum, and the reaction mixture was heated to 80 °C in a silicone oil bath. After for 3 h at this temperature, the reaction mixture was cooled to rt, and 1 N aqueous HCl solution (approximately 50 mL) was added to precipitate the desired intermediate ethyl ester of 4-NH₂-1-2PEAQ, which was obtained as a dark violet solid upon vacuum filtration. This solid was immediately dissolved in distilled water (20 mL) and isopropanol (20 mL) in a 100 mL round-bottom flask. Excess potassium hydroxide (8 g) and a magnetic stir bar were added, and the flask was capped securely with a septum. The reaction mixture was heated to 80 °C in a silicone oil bath. After stirring for 2 h at this temperature, the reaction mixture was cooled to rt for another 3 h of stirring. After this, 1 N HCl solution (approximately 50 mL) was added to precipitate the desired product 4-NH₂-1-2PEAQ as a dark violet solid (2.5 g, 65% yield). ¹H NMR (400 MHz, DMSO-d₆): 8.13 (m, 2H), 7.83 (m, 2H), 7.33 (d, J = 9.4 Hz, 1H), 7.21 (d, J = 9.4 Hz, 1H), 4.77 (q, J = 6.73 Hz, 1H), 1.56 (d, J = 6.73 Hz, 3H) ppm. **IR** (neat, cm⁻¹): 3434, 3205, 1755, 1637, 1589, 1536, 1279, 726.

1.3 ESI-MS and NMR Spectroscopy

A MiniLIMS was used for high-resolution LC-MS analysis at Harvard University's Small Molecule Mass Spectrometry Facility. HPLC-grade water was used to prepare samples at 20 μ M concentration. Formic acid (0.1% v/v) in acetonitrile was used as the eluent. Positive-mode ESI was used to record the mass spectrum. All NMR spectra were obtained using a Bruker AVANCE NEO400 instrument and chemical shifts are reported in ppm relative to tetramethylsilane using residual protonated solvent as an internal reference.

2. NMR Spectra



Figure S1. ¹H NMR spectrum of 3-NH₂-2-2PEAQ in DMSO-d₆.



Figure S2. ¹³C NMR spectrum of 3-NH₂-2-2PEAQ in DMSO-d₆.



Figure S3. ¹H NMR of 4-NH₂-1-2PEAQ in DMSO-d₆.

3. UV-Vis Solubility Measurement



Figure S4. (left) UV-Vis absorbance spectra and (right) associated calibration curve for **3-NH₂-2-2PEAQ** based on absorbance at 305 nm. Measurements were made in a 1 cm path-length cuvette. The slope of the calibration curve is $0.0271 \ \mu M^{-1}$.



Figure S5. UV-Vis absorbance spectra used to determine the solubility of **3-NH₂-2-2PEAQ** at pH 14 in KOH electrolyte. A solution close to the expected solubility limit was made by dissolving **3-NH₂-2-2PEAQ** in alkaline KOH electrolyte, adjusting pH to 14 with more KOH, and subjecting to ultrasonication for 30 min. No precipitation was observed, and an aliquot of this solution was removed for UV-Vis analysis (lower solubility limit). This solution, after resting overnight, still did not form any precipitate. Additional **3-NH₂-2-2PEAQ** was added to the solution, the pH was adjusted, and the resulting solution was again subjected to ultrasonication for 30 min. After resting overnight, a small amount of solid precipitated from the solution. Therefore, a second aliquot derived from this presumably saturated solution was used to determine the "upper solubility limit." We conclude that the solubility of **3-NH₂-2-2PEAQ** in pH 14 KOH electrolyte is between 1.0 M and 1.1 M, by reference to the calibration curve (Figure S4).





Figure S6. ¹H NMR after thermal stability test of 0.1 M **3-NH₂-2-2PEAQ** solution in D_2O , during which it remained at pH 14 in the oxidized form (green trace) or reduced form (red trace) at 65 °C for 7 d. The reduced form was re-oxidized after the thermal test by agitating and exposing the solution to air prior to the NMR measurement.

5. Voltage-Capacity Profile of 3-NH₂-2-2PEAQ



Figure S7. Charge and discharge voltage–capacity profile of the 0.1 M **3-NH₂-2-2PEAQ** cell test shown for 3 representative cycles.



Figure S8. ¹H NMR of **3-NH₂-2-2PEAQ** in DMSO-d₆ before (top) and after cycling (bottom) in the cell test at 0.1 M in pH 14.

7. LC-MS of 3-NH₂-2-2PEAQ After Battery Cycling



Figure S9. Mass spectra obtained from LC-MS of **3-NH₂-2-2PEAQ** after cycling in the cell test at 0.1 M in pH 14, showing loss of side chain but no detectable anthrone dimer.

8. Post Battery Cycling Cyclic Voltammetry



Figure S10. Post-cycling cyclic voltammetry of the 0.1 M 3-NH₂-2-2PEAQ cell test at pH 14. (left) shows the expected CV of the 3-NH₂-2-2PEAQ negolyte and (right) shows the expected redox of the ferro/ferricyanide posolyte. The star indicates oxygen reduction shown in both CVs.



9. UV-Vis Permeability Measurements

Figure S11. Photographs of H-cells containing 0.1 M NH₂-2-2PEAQ in 1 M KOH as the donating electrolyte, with (a) Nafion NR212 or (b) E-620 (K), taken after 14 days-. UV-Vis absorbance spectra (c, d) of the H-cell receiving side (0.1 M KCl in 1 M KOH) after the 14-day experiment. While some absorbance is observed in the range of 200–-300 nm, there is no detectable absorbance peak at 305 nm, which would be characteristic of 3-NH₂-2-2PEAQ. Therefore, we conclude that the permeability of 3-NH₂-2-2PEAQ under these conditions cannot exceed 4×10^{-10} cm² s⁻¹ for either Nafion NR212 or E-620 (K). The Nafion has been used as -received except for soaking in 1 M KOH (at least overnight) for complete ion exchange to K⁺.

10. NMR Spectra of 4-NH₂-1-2PEAQ After Battery Cycling



Figure S12. ¹H NMR of **4-NH₂-1-2PEAQ** before (top) and after cycling (bottom) for the cell test at 0.1 M in pH 14.



Figure S13. Mass spectra obtained from LC-MS of **4-NH₂-1-2PEAQ** after cycling cell test at 0.1M in pH 14, showing several decomposition products.



12. Pourbaix Diagram Cyclic Voltammetry

Figure S14. Cyclic voltammetry of 5 mM $3-NH_2-2-2PEAQ$ at different buffered pH conditions.

13. Membrane Resistance Discussion

Figure S15. Comparison between impedance spectra of 0.1 M **3-NH₂-2-2PEAQ** as negolyte and 0.1 M ferrocyanide/0.02 M ferricyanide as posolyte at 1 M KOH pH 14 with Nafion 212 and E620 membranes.

In aqueous organic redox flow batteries (AORFBs), it is established that the energy efficiency is mainly governed by the voltage efficiency when the coulombic efficiency is extremely high, the case in this work. The major contributor to voltage efficiency loss in AORFBs is the membrane resistance as shown in several previous works.¹⁻³ Therefore, energy efficiency in AORFBs is essentially dictated by the membrane resistance. In this work, we used Fumasep E-620 (K) as cation exchange membrane for the 0.1 M cell cycling tests (Figure 3) and for polarizations and galvanostatic tests (Figure 4). For the high concentration cell, we used Nafion 212 as the cation exchange membrane because of durability with high concentration cell despite its high resistance compared to Fumasep E-620 (K) in Figure S15. Engineering better membranes for AORFBs that possess both high ionic conductivity and robust durability is still a major research challenge.

14.Additional Discussion

LC-MS results of the post-cycled 4-NH2-1-2PEAQ (Figure S13) indicate another decomposition pathway resulting from substitution of the 1-amino group by a hydroxyl group. The estimated barrier (B3LYP-D3(BJ)/6-311+G(d,p)/PCM(water)//B3LYP-D3(BJ)/6-31G(d)) for formation of the relevant Meisenheimer intermediate is 17.4 kcal/mol for 4-NH₂-1-2PEAQ and 24.7 kcal/mol for 3-NH2-2-2PEAQ. Therefore, we expect that such a decomposition reaction should be thermally accessible for the former but negligibly slow for the latter.

Anthraquinones with C-C linked sidechains such as DBAQ and DPivOHAQ are expected to be inert to side chain loss but still can undergo overreduction to anthrone. Calculations were performed and the following relative ΔG values were found for anthrone formation (relative to 2-2PEAQ):

DBAQ +0.3 kcal/mol

DPivOHAQ +1.9 kcal/mol

Therefore, DBAQ and DPivOHAQ are expected to be more prone to anthrone formation than 3-NH₂-2-2PEAQ and similarly inert to sidechain loss.

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