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1 In situ Electrosynthesis of Anthraquinone Electrolytes in Aqueous Flow Batteries

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11 Abstract

We demonstrate the electrochemical oxidation of an anthracene derivative to a redox-active anthraquinone at room temperature in a flow cell without the use of hazardous oxidants or noble metal catalysts. The anthraquinone, generated *in situ*, was used as the active species in a flow battery electrolyte without further modification or purification. This potentially scalable, safe, green, and economical electrosynthetic method is also applied to another anthracene-based derivative and may be extended to other redox-active aromatics.

18 Introduction

Aqueous redox flow batteries (ARFBs) represent a class of devices for storing electrical energy that are especially well suited for large-scale stationary deployment.^{1, 2} Vanadium redox flow batteries, the most developed ARFB technology, have been limited by the high and fluctuating price of vanadium.³

Anthraquinone-based aqueous redox flow batteries are considered as one class of the most promising alternatives to vanadium redox flow batteries because they can be composed of earthabundant elements such as C, H, O, and N while providing comparable electrochemical performance.⁴⁻⁹ However, reducing the production cost of anthraquinone-based electrolytes and

improving their chemical stability are two major challenges preventing them from being cost-27 competitive.⁹⁻¹⁴ Many factors can influence the synthesis cost of an organic molecule, including 28 the number, duration, complexity, and yields of the reaction steps, the reaction conditions (time, 29 temperature, and pressure), solvent and precursor costs, the cost of waste disposal, and economies 30 of scale. Likewise, a host of factors contributes to the stability, and by extension the long-term 31 32 viability, of redox-active organics including the chemical structure, solvent conditions, applied potentials, and state of charge. Only through careful consideration of all of these factors can 33 commercial-scale organic ARFBs be viable storage solutions. Therefore, not only is the 34 35 development of a stable anthraquinone important, but the design of a potentially economical, scalable, and green synthetic route toward targeted molecules is equally significant.^{11, 15} 36

Electrochemically-mediated synthesis (electrosynthesis) enables the replacement of hazardous 37 oxidizing and reducing agents by electric current, or "clean" electrons, through an electrode and 38 has attracted considerable attention for both laboratory and industrial applications in multiple 39 fields of research.¹⁶⁻²¹ Compared to traditional thermochemical synthesis, electrosynthesis can be 40 significantly more environmentally benign due to reduced waste production and alternative 41 chemicals consumed.^{22, 23} However, the necessity of using specific solvents combined with 42 43 supporting electrolytes, along with their subsequent separations, are some of the primary hurdles limiting the feasibility of electrosynthesis compared to thermochemical processes in many cases.¹⁶ 44 As an example, anthraquinone is typically produced from anthracene, an inexpensive and 45 abundant component of coal tar and petroleum.²⁴ Typically, hazardous oxidants such as 46 cerium(IV), chromium(VI), and vanadium(V) compounds dissolved in strong acids, sometimes at 47 elevated temperatures, are used to facilitate this thermochemical conversion.²⁵ To minimize the 48 49 use of hazardous materials, often these consumed oxidants are electrochemically regenerated and

reused for chemical oxidations,²⁵⁻³⁰ that is, a mediated or indirect electrochemical oxidation. However, in both thermochemical conversion and mediated (indirect) electrochemical conversion, isolating anthraquinone from these hazardous solutions can be time- and capital-intensive. Electrooxidations of anthracene and its derivatives at \sim 1 mM concentration have been performed previously; however, the low concentrations of anthracene substrates and poor selectivity of the reactions have prevented the method from being synthetically useful.³¹⁻³⁶

Using a scalable flow cell setup,³⁷ we demonstrate the capability to electrochemically oxidize 56 water-soluble anthracenes directly to anthraquinones in electrolytes without the use of strong 57 58 oxidants or catalysts, producing the desired negolyte (negative electrolyte) and ferrocyanide posolyte (positive electrolyte) in situ. Compared to conventional thermochemical and 59 electrochemical methods, the new method is safe and potentially inexpensive because it eliminates 60 both the use of hazardous oxidants and the necessity of post-synthesis isolation of the products 61 from the supporting electrolytes. Taking advantage of a flow cell and bulk electrolysis setup, the 62 demonstrated electrosynthetic method is amenable to both continuous and batch processing. 63 Furthermore, we confirmed that the electrosynthetic method can also be extended to other 64 anthracene derivatives. 65

3,3'-(9,10-anthraquinone-diyl)bis(3-methylbutanoic acid) (DPivOHAQ) was recently reported
as an extremely stable and potentially inexpensive negolyte active species for organic ARFBs.³⁸
However, the use of CrO₃ in the synthesis can be highly toxic and explosive if produced in large
scale. Figure 1a shows the synthetic route for DPivOHAQ in three steps: 1) Through Birch
reduction, anthracene (AC) is converted to 9,10-dihydroanthracene (DHAC) at room temperature
(Figure S1). 2) After a Friedel–Crafts reaction and subsequent oxidation by air in one pot, two
water-soluble groups are introduced and DHAC is re-oxidized to an AC derivative (Figure S2),

forming 3,3'-(anthracene-diyl)bis(3-methylbutanoic acid) (**DPivOHAC**). The **DPivOHAC** powder was then dissolved in water by adding KOH to deprotonate the carboxylic acid groups. 3) Lastly, **DPivOHAQ** negolyte active species is produced by electrochemical oxidation in an aqueous electrolyte without the need for further purification. Figure 1b illustrates how **DPivOHAQ** and ferrocyanide active species can be produced *in situ* in the flow cell's electrosynthesis mode. These materials can directly serve as the active species in the negolyte and the posolyte, respectively, of a flow battery in the same cell as illustrated in Figure 1c.



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Figure 1. Preparation of DPivOHAQ and the corresponding flow battery. (a) The
DPivOHAQ synthetic route and conditions starting from anthracene. (b) The setup for
electrosynthesis of DPivOHAQ and ferrocyanide. (c) The flow battery setup with DPivOHAQ
negolyte (generated *in situ*) and ferrocyanide posolyte (generated *in situ*). DPivOHAC: 3,3'(anthracene-diyl)bis(3-methylbutanoic acid); DPivOHAC(COO⁻) is deprotonated DPivOHAC.
DPivOHAQ: 3,3'-(9,10-anthraquinone-diyl)bis(3-methylbutanoic acid); DPivOHAQ(COO⁻) is
deprotonated DPivOHAQ.

Figure 2a lists three different oxidation methods for **DPivOHAQ** synthesis. Conventionally,

89 anthracene derivatives can be chemically oxidized to their anthraquinone forms by oxidants such

as chromium oxide (CrO₃) in strong acidic media at elevated temperature.³⁸ To minimize the use

of hazardous oxidants, the strategy of mediated electrochemical oxidation can be performed by regenerating oxidants such as cerium(IV) compounds.^{26, 29} However, in both of these thermochemical and indirect electrochemical oxidation processes, tedious and expensive isolation of anthraquinone-based products from oxidants and acids is required. Taking advantage of the high solubility of **DPivOHAC** in base, we demonstrate a synthetic route via direct electrochemical oxidation in alkaline electrolyte with a flow cell. This method allows the complete elimination of hazardous oxidants and costly separation processes.



Figure 2. Comparison of DPivOHAQ synthetic methods. (a) Thermochemical, mediated
 (indirect) electrochemical, and direct electrochemical oxidation reactions to synthesize
 DPivOHAQ. (b) Advantages of direct electrochemical oxidation *in situ*.

103 Experimental

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105 Glassy carbon was used as the working electrode for all three-electrode cyclic voltammetry (CV)

tests with a 5 mm diameter glassy carbon working electrode, an Ag/AgCl reference electrode

- 107 (BASi, pre-soaked in 3 M NaCl solution), and a graphite counter electrode. Both undivided cell
- and divided cell were built for electrosynthesis. Flow battery experiments were constructed with
- 109 cell hardware from Fuel Cell Tech (Albuquerque, NM) assembled into a zero-gap flow cell
- 110 configuration. Pyrosealed POCO graphite flow plates with serpentine flow patterns were used for

¹⁰⁴ *Cell hardware*

- both electrodes. Each electrode comprised a 5 cm^2 geometric surface area covered by AvCarb
- 112 HCBA woven carbon fiber without pretreatment, or Pt-coated Toray carbon paper without
- 113 pretreatment. The membrane is pre-soaked (1 M KOH for 24 hours) Nafion 212.
- 114 *Undivided electrolytic cell setup (electrochemical oxidation vs. the HER)*
- 115 Working electrode: carbon felt, where **DPivOHAC(COO⁻)** was oxidized to **DPivOHAQ(COO⁻)**;
- 116 counter electrode: carbon rod, where water was reduced to hydrogen gas. While the electrolyte
- 117 was stirred, a constant potential (1.1 V vs. Ag/AgCl) was applied to the divided electrolytic cell
- 118 until 120% of the required coulombs were extracted from the working electrode.
- 119 *Divided electrolytic cell setup (electrochemical oxidation vs. the ORR)*

Anode: Commercial AvCarb HCBA (woven carbon cloth), where **DPivOHAC(COO⁻)** was oxidized to **DPivOHAQ(COO⁻)**; cathode: platinum coated Toray carbon paper, where humidified air/oxygen was reduced to hydroxide. A constant voltage (1.8 V) was applied to the divided electrolytic cell until the current decreased to 2 mA/cm². The number of extracted electrons was

- $124 \sim 1.2$ times higher than the theoretical value.
- 125 Divided electrolytic cell setup (electrochemical oxidation vs. the reduction of ferricyanide)

Anode: AvCarb HCBA (woven carbon cloth), where **DPivOHAC(COO⁻)** was oxidized to **DPivOHAQ(COO⁻)**; cathode: AvCarb HCBA (woven carbon cloth), where potassium ferricyanide was reduced to potassium ferrocyanide. A constant current density (20 mA/cm^2) was applied to the divided cell for at most 1.5 hours with a 1.2 V voltage cutoff; when either time or voltage reached the limit, the potential was held (1.2 V vs. ferro-/ferricyanide) until the current decreased to 2 mA/cm². The number of extracted electrons was ~1.2 times higher than the theoretical value. An aliquot (~250 μ L) was transferred from the as-prepared anolyte to an Eppendorf® tube (capacity: 1.5 mL) and acidified by a drop of concentrated HCl to obtain **DPivOHAQ** precipitate. The final **DPivOHAQ** precipitate was re-dissolved in DMSO-*d*₆ for ¹H NMR measurement. The yield was determined by peak integrations of spectrum. Faradaic efficiency (%) = yield (%) / 1.2. More detailed information can be found in the Supplementary information.

138 Results and Discussion

In an electrolytic cell, an anodic oxidation half reaction must be accompanied by a cathodic reduction half reaction. As shown in Table 1, we devise three different reduction half reactions to be coupled with direct **DPivOHAC** electrochemical oxidation, *i.e.*, the hydrogen evolution reaction (HER), the oxygen reduction reaction (ORR), and the $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ reduction reaction. The corresponding oxidation or reduction potentials for these reactions are listed in Table 1.

For the electrochemical oxidation of **DPivOHAC** to **DPivOHAQ**, two cell types are used, as diagramed and described in Figures S3 and S4. A divided cell uses an ion exchange membrane to separate the two half reactions, resembling the architecture of traditional fuel cells and ARFBs. An undivided cell employs two electrodes suspended in electrolyte without the use of a membrane, reflecting a bulk electrolysis cell.

150 Comparing these three overall reactions, the first one paired with the HER requires the highest 151 voltage; the second one paired with the ORR is known to have slow reaction kinetics and a high 152 overpotential;³⁹ the third one paired with $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ reduction exhibits the lowest 153 overall reaction cell voltage, suggesting the least amount of energy will be required for 154 electrosynthesis. Another merit of the third reaction is the *in situ* generation of the desired negolyte 155 active species (**DPivOHAQ**) and posolyte active species $Fe(CN)_6^{4-}$ simultaneously. The

disadvantage is that at least six equivalents of ferricyanide and hydroxide are used. Given the 156 similar reduction potentials of the ORR and of ferricyanide to ferrocyanide, an important direction 157 for future research is the concurrent reduction of oxygen and ferricyanide in order to achieve high 158 yields as well as lower ferricyanide usage. By using the same full cell configuration without 159 changing electrolyte reservoirs, carbon-based electrodes, or ion-exchange membranes, we can 160 161 immediately switch from electrosynthesis mode to flow battery mode for electrochemical energy storage. In this configuration, neither hazardous oxidants nor purification steps are needed, nor is 162 waste generated. Furthermore, the reaction may proceed at room temperature with high atom 163 efficiency. The new synthesis is therefore potentially safe, green, economical, and scalable. 164

Reactions		Potential at pH 14 (V vs SHE) / Cell voltage (V)
Anodic	DPivOHAC(COO ⁻) + 6 OH ⁻ → DPivOHAQ(COO ⁻) + 4 H ₂ O + 6 <i>e</i> ⁻	1.14*
	$6 H_2O + 6 e^- \longrightarrow 3 H_2 + 6 OH^-$ (divided or undivided cell)	-0.83
Cathodic	1.5 O_2 + 6 e^- + 3 $H_2O \longrightarrow 6 OH^-$ (divided or undivided cell)	0.40
	$6 \operatorname{Fe}(\operatorname{CN})_6^{3^-} + 6 e^- \longrightarrow 6 \operatorname{Fe}(\operatorname{CN})_6^{4^-} \qquad \text{(divided cell)}$	0.44
Overall	DPivOHAC(COO⁻) + 2 $H_2O \longrightarrow$ DPivOHAQ(COO⁻) + 3 H_2	1.97
	DPivOHAC(COO⁻) + 1.5 $O_2 \longrightarrow DPivOHAQ(COO-) + H_2O$	0.74
	DPivOHAC(COO⁻) + 6 OH ⁻ + 6 Fe(CN) ₆ ³⁻ \longrightarrow DPivOHAQ(COO⁻) + 6 Fe(CN) ₆ ⁴⁻ + 4 H ₂ O	0.70

 Table 1. Anodic, cathodic, and overall reactions for direct electrochemical oxidation.

*: The electro-oxidation potential at peak current

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The cyclic voltammogram (CV) of **DPivOHAC** at pH 14 (Figure 3a) indicates a peak oxidation
current at 1.14 V vs. SHE. This value is more positive than the standard redox potential of 0.40 V
vs. SHE for the oxygen evolution reaction (OER), and we expect that the OER will be a major side
reaction of electrosynthesis.

171 We then assembled a flow cell with **DPivOHAC** as the analyte and $K_3Fe(CN)_6$ as the catholyte.

172 Galvanostatic electrolysis with a potentiostatic hold after reaching a potential limit of 1.2 V was

173 performed for ~4.5 hours to complete the electrosynthesis. The OER side reaction, evidenced by

the observation of bubbles generated in the anolyte, precludes a faradaic efficiency of 100%. Thus, the number of electrons extracted from the anolyte was ~1.2 times higher than the theoretical number for complete conversion. A plateau appears at ~0.8 V against $K_3Fe(CN)_6$ (0.44 V vs. SHE) in the voltage profile (Figure 3b).



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Figure 3. Electrosynthesis and characterization of DPivOHAO. (a) The cyclic voltammogram 179 (CV) of 0.1 M **DPivOHAC** in 1.0 M KCl + 1.0 M KOH aqueous solution. Scan rate: 0.1 V/s. (b) 180 The electrochemical oxidation was conducted by using a constant current (20 mA/cm²) with a 181 subsequent potential hold (1.2 V) until the current density decreased to 2 mA/cm². (c) CV of 182 10 mM electrosynthesized **DPivOHAQ** (against Fe(CN)₆³⁻) without purification and 10 mM 183 chemically synthesized **DPivOHAQ** with purification in 1 M KOH aqueous solutions, 184 respectively. Scan rate: 0.1 V/s. (d) ¹H NMR spectra of (bottom to top): chemically synthesized 185 **DPivOHAC** (black); chemically synthesized **DPivOHAQ** (red); electrosynthesized **DPivOHAQ** 186 in an undivided cell (purple), 17.3% of DPivOHAC remained unreacted according to the 187 integration, vield: 82.7%; electro-synthesized **DPivOHAO** in a divided cell against $Fe(CN)_{6}^{3-1}$ 188 (blue), 7.0% of **DPivOHAC** remained unreacted according to the integration, yield: 93.0%; 189 electrosynthesized **DPivOHAQ** in a divided cell against O₂ (green), 0 % of **DPivOHAC** remained 190 unreacted according to the integration, yield: 100%. The deuterated solvent is DMSO- d_6 , and the 191 solvent peaks (DMSO and H₂O) were removed to better display the peaks of interest. The 192

electrosynthetic details are described under the headings Electrosynthesis I, II, and III in the
Supporting Information.

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We compared the CV of **DPivOHAQ** produced by electrosynthesis against the reduction of 196 $Fe(CN)_{6}^{3-}$ to that of the chemically synthesized product at the same concentration to verify that 197 198 the reaction products are the same regardless of the synthetic procedure employed (Figure 3c). The 199 two CV curves show identical redox peaks and similar peak currents, indicating a high-yield 200 electrosynthesis process. ¹H nuclear magnetic resonance (NMR) spectroscopy was used to further 201 examine the structure of electrosynthesized DPivOHAQ when using either a divided or undivided 202 cell (Figure S3) and to compare the spectra with those of the starting material, **DPivOHAC**, and the chemically synthesized **DPivOHAQ**. The top three spectra in Figure 3d are the ¹H NMR 203 spectra from electrosynthesized **DPivOHAQ**, in which the dominating peaks have the same 204 205 chemical shifts as those in the spectrum of chemically synthesized **DPivOHAQ**, further suggesting the desired product was achieved. 206

Slightly different yields of DPivOHAQ were obtained when paired with the HER in an 207 undivided cell or with $Fe(CN)_{6}^{3-}$ reduction or the ORR in a divided cell (Figure S4). The 82.7% 208 yield when paired with the HER in an undivided cell could be explained by a molecular shuttling 209 effect; *i.e.*, the electrosynthesized **DPivOHAQ** can first migrate to the cathode where it is reduced, 210 then diffuse back to the anode for re-oxidation. As a result, double counting of electrons can occur. 211 When paired with the $Fe(CN)_6^{3-}$ reduction half reaction, a yield of 93.0% was obtained. The 212 incomplete yield is likely due to the consumption and therefore decreased concentration of both 213 214 **DPivOHAC** and OH⁻ as the electrosynthesis continues, making further oxidation increasingly difficult. 215

The use of the ORR half reaction achieved almost 100.0% yield. This exceptional yield may be attributed to the as-formed OH⁻ ions on the cathode (ORR) side crossing over to the anolyte and compensating for any loss of OH⁻ ions on the anode side. Overall yields in excess of 80.0% for all three conditions exceed many conventional reactions and are acceptable for direct flow battery use without purification or separation.



Figure 4. Full cell performance evaluation from Electrosynthesis III and IV. (a) A 222 representative charge-discharge profile with 0.1 M DPivOHAO. Negolyte: 5 mL of 0.1 M 223 **DPivOHAQ** pH = \sim 13.5. Posolyte: 100 mL of 0.1 M potassium ferro-/ferricyanide solution [\sim 0.06 224 M K₄Fe(CN)₆ and ~0.04 M K₃Fe(CN)₆] pH = ~13.6. (b) Discharge capacity (C) and coulombic 225 efficiency (%) vs. cycle number and time (days). Negolyte: 4.5 mL of 0.1 M DPivOHAQ. Posolyte: 226 100 mL of 0.1 M ferro-/ferricyanide solution [~0.06 M K₄Fe(CN)₆ and ~0.04 M K₃Fe(CN)₆]. 227 Current density: 30 mA/cm² with potential hold (cutoffs: 0.6 V, 1.2 V) until current decreased to 228 2 mA/cm². (c) A representative charge–discharge profile with 0.5 M **DPivOHAO**. Negolyte: 6 229 230 mL of 0.5 M DPivOHAQ. Posolyte: 100 mL of 0.5 M potassium ferro-/ferricyanide solution [~0.3

M K₄Fe(CN)₆ and ~0.2 M K₃Fe(CN)₆]. Current density: 100 mA/cm² with potential hold (cutoff: 0.4 V, 1.4 V) until current decreased to 2 mA/cm². (d) Polarization curves of the 0.5 M **DPivOHAQ** at the SOC of 20%, 40%, 60%, 80%, and ~100% respectively. Descriptions of **Electrosynthesis III** and **IV** can be found in the Supporting Information.

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To demonstrate the feasibility of switching from the electrosynthesis mode (when paired with 236 $Fe(CN)_{6}^{3-}$ reduction) to flow battery mode, we began charge-discharge cycling immediately upon 237 completion of the electrosynthesis, without performing any purification. Because other research 238 has reported that guinones and related compounds can decompose in the presence of light, ⁴⁰⁻⁴² we 239 wrapped the electrolyte reservoirs with aluminum foil to avoid light-induced decomposition during 240 241 cell cycling (Figures S13–S15). Figure 4a shows the charge–discharge profile of a single cycle with an open circuit voltage of ~1.0 V and a capacity of 84.0 coulombs. Given the 93.0% yield 242 found from the ¹H NMR, the capacity utilization is 93.6%. Long-term cycling was then performed 243 to determine a temporal capacity fade rate of the full cell. Figure 4b demonstrates the discharge 244 capacity and coulombic efficiency over 33.2 days and 2271 cycles with a fitted fade rate of 245 246 0.014%/day and an average coulombic efficiency of 99.53%. This is consistent with the fade rate of chemically synthesized **DPivOHAQ**.³⁸ The extremely low capacity fade rate is attributed to the 247 chemical stability of the molecular structure. The C-C covalent bond between the anthraquinone 248 core and the functionalizing chains is more robust in strong base and at elevated temperature than 249 the C–O bond demonstrated in previous work.^{4, 5, 38} Furthermore, the two branched methyl groups 250 on the carbon connected to the anthraquinone (AQ) core may increase the stability of the 251 solubilizing chain even when exposed to harsh conditions.¹⁵ 252

To examine the feasibility of this method for potential industry use, we further conducted electrosynthesis with a higher concentration (0.5 M) of **DPivOHAC** at a higher current density (100 mA/cm²) (See Figure S5). Figure 4c shows that 0.5 M electrosynthesized negolyte can deliver 72.9% of the theoretical capacity. We attribute the discrepancy between the delivered capacity and the theoretical capacity primarily to incomplete conversion (Figure S6). The capacity utilization is
81.9% if we consider that there is 11.0% unreacted DPivOHAC(COO⁻) in the negolyte.
Additionally, the mass transport of active species at 0.5 M concentration may be another issue
limiting the full capacity utilization. The corresponding polarization curve at different states of
charge (SOC) is shown in Figure 4d. The peak power density exceeds 0.2 W/cm² when at ~100 %
of SOC.

263 Given the total transfer of six electrons during the electrosynthesis of **DPivOHAC** to 264 **DPivOHAQ**, the high yields achieved in this work might be surprising. We hypothesize a threestep successive two-electron transfer mechanism^{34, 35}: first, when a potential is applied, anthracene 265 (AC) may react with three OH⁻ ions and donate two electrons to produce two water molecules and 266 267 the anthrone anion (A^-); second, A^- may further react with another three OH⁻ ions and donate another two electrons to generate two water molecules and the deprotonated anthrahydroquinone 268 dianion (AQ^{2-}) ; third, AQ^{2-} may further release two electrons to afford the anthraquinone species 269 (AQ). Complete electrochemical conversion in the third step has been well-documented at 270 negative potentials vs. ferro-/ferricyanide^{1, 2, 43} and should therefore be rapid at positive potentials 271 vs. ferro-/ferricyanide. The reverse reaction of the second step has recently been identified as a 272 side reaction in ARFBs, and the forward reaction is chemically feasible when exposed to O₂ or 273 air.^{14, 38} Given the high voltage applied to the cell, it is thus plausible that the forward reactions 274 (AC to A^- to AQ^{2-}/AQ) can electrochemically proceed completely and swiftly. 275

Our group has also previously proposed a side reaction pathway for anthraquinones,^{14,44} where the anthrone anion (A⁻) can be oxidatively dimerized to dianthrone (DA) chemically and/or electrochemically. According to ¹H NMR spectra (Figure 3d) and liquid chromatography–mass spectrometry (LC–MS) results (Figure S7), neither DA nor Kolbe electrolysis-related byproducts⁴⁵

were detected (Scheme S1), suggesting that AC/AQ-related side reactions can be negligible when 280 a sufficient OH⁻ concentration is present to prevent dianthrone formation and a sufficiently low 281 voltage cutoff is chosen to prevent Kolbe electrolysis dimer formation. The major competing side 282 reaction is the OER, which, along with the reactions of AC to A⁻ to AQ²⁻, will consume OH⁻ and 283 may lead to the formation of **DA** as a result of insufficient OH⁻ ions in the **DPivOHAC** solution 284 (see Electrosynthesis V in the SI). Interestingly, the dianthrones (Scheme S2), detected by 285 LC-MS (Figure S11), are surprisingly redox-active when a broad voltage window is applied 286 (Figures S8 and S9 and Scheme S2). On the one hand, the OER can reduce faradaic efficiency; on 287 288 the other hand, the generated oxygen can serve as a mediator and chemically oxidize intermediates (*i.e.*, A⁻, AQ²⁻) to the final AQ form, *i.e.*, mediated (indirect) electrochemical oxidation. Because 289 290 the entire process involves not only electrochemical oxidations, but also chemical oxidations, it is more appropriate to call it an electrochemical-chemical oxidation process.⁴⁶ 291

In the proposed mechanism, the anthrone derivative is an intermediate in the electrochemical oxidation. Anthrone formation has been identified as the major side reaction causing capacity fade in previous work;^{14, 38} therefore, it is plausible that lost capacity of anthraquinone flow battery systems may be recovered and anthraquinone lifetime extended by electrochemically oxidizing anthrone to redox-active anthraquinone derivatives.



Scheme 1. Proposed electrochemical oxidation mechanism. Three-step successive two-electron transfer process from AC to A^- , A^- to AQ^{2-} , and AQ^{2-} to AQ. The generated oxygen from the OER side reaction may incur chemical oxidation processes including A^- to AQ^{2-} , AQ^{2-} to AQ, and oxidative dimerization (A^- to DA).

To demonstrate that the electrochemical oxidation can be applied to other anthracene derivatives, we performed electrochemical oxidation of 4,4'-(9,10-dihydroanthracenediyl)dibutanoic acid (**DBDHAC**), where the molecular core is 9,10-dihydroanthracene.³⁸ The ¹HNMR results indicate that**DBDHAC**can, like**DPivOHAC**, be electrochemically oxidized to thefinal anthraquinone (Figure S12),**DBAQ**(4,4'-(9,10-anthraquinone-diyl)dibutanoic acid), whichhas also been shown to be extremely stable.³⁸

The shared precursor of **DPivOHAQ** and **DBAQ**, anthracene, is abundant in crude petroleum and coal tar, and can be synthesized from benzene and benzyl alcohol (Scheme S3).⁴⁷ The precursor of **DPivOHAQ**, 3,3'-dimethyl acrylic acid, can be industrially produced from malonic acid, a food acid; the precursor of **DBAQ**, succinic anhydride, can be industrially hydrogenated from maleic anhydride and used as an important intermediate on an industrial scale. Thus, both **DPivOHAQ** and **DBAQ** can be readily synthesized from commodity chemicals. Although the synthetic cost of **DPivOHAQ** or **DBAQ** should be somewhat higher than that of 2,6dihydroxyanthraquinone (DHAQ) due to more steps and more chemicals involved, the capital cost
of AORFBs that utilize finite-lifetime electrolytes can be viewed as including the total active cost,
which is the sum of the initial cost of redox-active materials and the present value of the future
costs of periodic electrolyte replacement.¹³ This can lead to an initial cost—lifetime trade-off in
the choice of electrolytes. Over an extended operational lifetime, the total active cost of
DPivOHAQ or DBAQ may be less than that of DHAQ due to their much longer lifetimes.¹⁴

322

323 Conclusion

This work demonstrates a potentially scalable, safe, green, and economical in situ 324 electrosynthetic method for anthraquinone electrolytes in a flow cell without the use of hazardous 325 oxidants or precious metal catalysts. The as-generated electrolytes, which are extremely stable, 326 can be immediately used in a redox flow battery without separation or purification. Other low-cost 327 compounds may also be amenable to this approach, providing a pathway to lower the cost of 328 electrochemical grid storage systems, thereby accelerating the development of a renewable energy 329 330 economy. The technique extends the opportunities for direct aqueous electrosynthesis to replace thermochemical synthesis of value-added organics. 331

- 332 Supplementary Information
- 333 Supplementary Information can be found with this article online at

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339 Declaration of Interests

Harvard University has filed a patent application on the materials and the electrosynthetic methodsdescribed in this paper.

343		REFERENCES
344	1.	B. Huskinson, M. P. Marshak, C. Suh, S. Er, M. R. Gerhardt, C. J. Galvin, X. Chen, A. Aspuru-
345	2	Guzik, R. G. Gordon and M. J. Aziz, <i>Nature</i> , 2014, 505 , 195–198. K. Lin, O. Chen, M. R. Gerhardt, I. Tong, S. R. Kim, L. Eisenach, A. W. Valle, D. Hardee, R. G.
340	Ζ.	Gordon M I Aziz and M P Marshak Science 2015 349 1529–1532
348	3.	M. Moore, R. Counce, J. Watson and T. Zawodzinski, <i>Journal of Advanced Chemical</i>
349		<i>Engineering</i> , 2015, 5 , doi:10.4172/2090-4568.1000140.
350	4.	D. G. Kwabi, K. Lin, Y. Ji, E. F. Kerr, MA. Goulet, D. De Porcellinis, D. P. Tabor, D. A.
351		Pollack, A. Aspuru-Guzik, R. G. Gordon and M. J. Aziz, <i>Joule</i> , 2018, 2, 1894–1906.
352	5.	Y. Ji, MA. Goulet, D. A. Pollack, D. G. Kwabi, S. Jin, D. De Porcellinis, E. F. Kerr, R. G.
353	_	Gordon and M. J. Aziz, <i>Adv. Energy Mater.</i> , 2019, 9 , 1900039.
354	6.	A. Hollas, X. Wei, V. Murugesan, Z. Nie, B. Li, D. Reed, J. Liu, V. Sprenkle and W. Wang,
355	_	Nature Energy, 2018, 3 , 508–514.
356	7.	C. Wang, X. Li, B. Yu, Y. Wang, Z. Yang, H. Wang, H. Lin, J. Ma, G. Li and Z. Jin, ACS Energy
357	0	Letters, 2020, 5, 411–417.
328	о.	J. D. Hollinahili, F. L. Flanschilling, N. Klawczyk, F. Geigle, L. Holig, S. Schillansch, H. A. Wegner, D. Mellenhauer, I. Janek and D. Schröder, <i>Chemistry of Materials</i> , 2018, 20 , 762, 774
360	9	D G Kwabi V Ji and M I Aziz Chem Rev 2020 120 doi org/10.1021/acs chemrev 9b00599
361	J. 10	Z Yang L Tong D P Tabor F S Beh M -A Goulet D De Porcellinis A Aspuru-Guzik R
362	10.	G. Gordon and M. J. Aziz. Adv. Energy Mater., 2018. 8. 1702056.
363	11.	V. Dieterich, J. D. Milshtein, J. L. Barton, T. J. Carney, R. M. Darling, F. R. Brushett,
364		Translational Materials Research, 2018, 5, 034001.
365	12.	S. Jin, E. M. Fell, L. Vina-Lopez, Y. Jing, P. W. Michalak, R. G. Gordon and M. J. Aziz, Adv.
366		Energy Mater., 2020, 10, doi.org/10.1002/aenm.202000100.
367	13.	F. R. Brushett, M. J. Aziz and K. E. Rodby, ACS Energy Letters, 2020, 5, 879–884.
368	14.	MA. Goulet, L. Tong, D. A. Pollack, D. P. Tabor, S. A. Odom, A. Aspuru-Guzik, E. E. Kwan,
369	. –	R. G. Gordon and M. J. Aziz, <i>J. Am. Chem. Soc.</i> , 2019, 141 , 8014–8019.
370	15.	P. Anastas, N. Eghbali, <i>Chem. Soc. Rev.</i> , 2010, 39 , $301-312$.
3/1	16.	D. S. P. Cardoso, B. Sljukic, D. M. F. Santos, C. A. C. Sequeira, Organic Process Research &
372	17	Development, 2017, 21, 1213–1226.
3/3	17. 10	M. Yan, Y. Kawamata, P. S. Baran, Chem. Rev., 2017, 117, 15250–15519.
374	10.	D. K. Felels, K. A. Rounguez, S. H. Reisberg, S. B. Den, D. F. Hickey, T. Rawaniata, M. Collins, J. Starr, J. Chen, S. Udvavara, K. Klunder, T. J. Gorev, S. L. Anderson, M. Neurock, S.
376		D Minteer and P S Baran Science 2019 363 838–845
377	19.	E. J. Horn, B. R. Rosen, Y. Chen, J. Tang, K. Chen, M. D. Eastgate, P. S. Baran, <i>Nature</i> , 2016.
378		533 , 77–81.
379	20.	A. Badalyan, S. S. Stahl, <i>Nature</i> , 2016, 535 , 406–410.
380	21.	G. G. Botte, The Electrochemical Society Interface, 2014, 23, 49–55.
381	22.	P. M. Bersier, L. Carlsson and J. Bersier, Topics in Current Chemistry, 1994, 170, 116–136.
382	23.	C. Xia, Y. Xia, P. Zhu, L. Fan and H. Wang, Science, 2019, 366, 226–231.
383	24.	M. Granda, C. Blanco, P. Alvarez, J. W. Patrick and R. Menendez, Chem. Rev., 2014, 114, 1608-
384		1636.
385	25.	R. S. Tipson, in National Bureau of Standards Monograph 87, 1965, 1-49.
386	26.	R. P. Kreh, R. M. Spotnitz and J. T. Lundquist, J. Org. Chem., 1989, 54, 1531-1535.
387	27.	E. Oppermann, US Pat., US823,435A, 1906.
388	28.	E. Steckhan, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH &
389		Co. KGaA, Weinheim, 2011, 12 , DOI: 10.1002/14356007.009_004.

390	29.	R. M. Spotnitz, R. P. Kreh, J. T. Lundquist and P. J. Press, Journal of Applied Electrochemistry,
391		1990, 20 , 209–215.
392	30.	R. P. Kreh, R. M. Spotnitz and J. T. Lundquist, <i>Tetrahedron Letters</i> , 1987, 28, 1067–1068.
393	31.	E. J. Majeski, J. D. Stuart and W. E. Ohnesorge, J. Am. Chem. Soc., 1968, 90, 633-636.
394	32.	L. R. Faulkner, A. J. Bard, J. Am. Chem. Soc., 1968, 90, 6284-6290.
395	33.	C. Amatore and A. R. Brown, J. Am. Chem. Soc., 1996, 118, 1482-1486.
396	34.	O. Tovide, N. Jahed, C. E. Sunday, K. Pokpas, R. F. Ajayi, H. R. Makelane, K. M. Molapo, S. V.
397		John, P. G. Baker and E. I. Iwuoha, Sensors and Actuators B: Chemical, 2014, 205, 184–192.
398	35.	C. A. Paddon, C. E. Banks, I. G. Davies and R. G. Compton, Ultrason. Sonochem., 2006, 13,
399		126–132.
400	36.	V. D. Parker, Acta Chemica Scandinavica, 1970, 24, 2757–2767.
401	37.	T. Noel, Y. Cao and G. Laudadio, Acc. Chem. Res., 2019, 52, 2858–2869.
402	38.	M. Wu, Y. Jing, A. A. Wong, E. M. Fell, S. Jin, Z. Tang, R. G. Gordon and M. J. Aziz, Chem,
403		2020, 6, 1432–1442.
404	39.	R. W. Zurilla, R. K. Sen and E. Yeager, J. Electrochem. Soc., 1978, 125, 1103–1109.
405	40.	G. Maier, L. H. Franz, HG. Hartan, K. Lanz and H. P. Reisenauer, Chemische Berichte, 1985,
406		118 , 3196–3204.
407	41.	S. A. Carlson and D. M. Hercules, Analytical Chemistry, 1973, 45, 1794–1799.
408	42.	B. E. Hulme, E. J. Land and G. O. Phillips, J. Chem. Soc. Faraday Trans. 1, 1972, 68, 1992-
409		2002.
410	43.	M. Quan, D. Sanchez, M. F. Wasylkiw and D. K. Smith, J. Am. Chem. Soc., 2007, 129, 12847-
411		12856.
412	44.	S. Jin, Y. Jing, D. G. Kwabi, Y. Ji, L. Tong, D. De Porcellinis, M. A. Goulet, D. A. Pollack, R. G.
413		Gordon and M. J. Aziz, ACS Energy Letters, 2019, 4, 1342–1348.
414	45.	HJ. Schäfer, Topics in Current Chemistry, 1990, 152, 91–151.
415	46.	C. Costentin and JM. Savéant, Proc. Natl. Acad. Sci. USA, 2019, 116, 11147–11152.
416	47.	H. E. Ungnade and E. W. Crandall, J. Am. Chem. Soc., 1949, 71, 3009-3010.

1 2	Supplementary Information
3	In situ Electrosynthesis of Anthraquinone Electrolytes in Aqueous Flow Batteries
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14	Table of Contents
15	General information for synthesis and characterization3
16	Electrochemical characterization3
17	Brief description of electrosynthesis3
18 19	Figure S1. ¹ H NMR spectra of commercial and synthesized 9,10-dihydroanthracene (DHAC) in DMSO- <i>d</i> ₆
20 21	Figure S2. ¹ H NMR spectra of 2,7-, 2,6-DPivOHAC isomers and their mixture (aromatic region) in DMSO- <i>d</i> ₆
22	Figure S3. Photos of undivided cell (a) and divided cell (b)5
23 24	Figure S4. Schematics of (a) undivided cell against the HER and divided cells against (b) the ORR and (c) ferricyanide to ferrocyanide, respectively
25 26	Electrosynthesis I. Electrochemical synthesis of DPivOHAQ(COO ⁻) in an undivided cell at 0.1 M concentration, against the hydrogen evolution reaction (HER)7
27 28	Electrosynthesis II. Electrochemical synthesis of DPivOHAQ(COO ⁻) in a divided cell at 0.1 M concentration, against the oxygen reduction reaction (ORR)
29 30	Electrosynthesis III. Electrochemical synthesis of DPivOHAQ(COO ⁻) in a divided cell at 0.1 M concentration, against the reduction of ferricyanide
31 32	Electrosynthesis IV. Electrochemical synthesis of DPivOHAQ(COO ⁻) in a divided cell at 0.5 M concentration with excess hydroxide, against the reduction of ferricyanide
33	Figure S5. The electrochemical oxidation of 0.5 M DPivOHAC(COO ⁻) (Electrosynthesis IV) 10

34 35 36 37	Figure S6. ¹ H NMR spectrum of DPivOHAQ in DMSO- <i>d</i> ₆ synthesized via the procedure described in Electrosynthesis IV. From the aromatic peak integrations, we found that 89.0% DPivOHAQ was generated (when the two set of peaks at chemical shifts of 7.95 and 8.10 ppm were integrated), 11.0% DPivOHAC was remaining
38 39	Figure S7. Mass spectra of partially electrosynthesized DPivOHAQ (from Electrosynthesis IV) measured by liquid chromatography–mass spectrometry (LC–MS)
40	Scheme S1. Kolbe electrolysis
41 42 43	Electrosynthesis V. Electrochemical synthesis of DPivOHAQ(COO ⁻) in a divided cell at 0.5 M concentration with a stoichiometric quantity of hydroxide, against the reduction of ferricyanide.
44	Formation of dianthrone during electrosynthesis14
45 46	Figure S8. Cell performance of 0.5 M electrosynthesized DPivOHAQ when a stoichiometric quantity of hydroxide was added into the DPivOHAC(COO ⁻) solution (Electrosynthesis V) 14
47 48 49	Figure S9. Voltage profiles of 0.5 M electrosynthesized DPivOHAQ when a stoichiometric quantity of hydroxide was added into the DPivOHAC solution (Electrosynthesis V) with different lower voltage cutoffs [(a) 0.6, (b) 0.2, (c) 0.6, and (d) 0.7 V]
50 51 52	Figure S10. ¹ H NMR spectrum of cycled 0.5 M electrosynthesized DPivOHAQ when a stoichiometric quantity of hydroxide was added into the DPivOHAC(COO ⁻) solution (Electrosynthesis V)
53 54	Figure S11. LC–MS results of cycled 0.5 M electrosynthesized DPivOHAQ when a stoichiometric quantity of hydroxide was added into the DPivOHAC solution (Electrosynthesis V)
55 56	Electrosynthesis VI. Electrochemical synthesis of DBAQ(COO ⁻) in an undivided electrolytic cell at 0.1 M concentration, against the HER
57 58	Figure S12. ¹ H NMR spectra of DBDHAC (bottom), chemically synthesized DBAQ (top), and electrochemically synthesized DBAQ in an undivided cell after varying extents of reaction 19
59	Light sensitivity experiments 19
60 61 62 63 64	Figure S13. Samples of (a) DPivOHAQ (0.1 M, pH 12) stored for 1 week in the absence of light (– hv) and under a 500 W lamp (+ hv) and of (b) DBAQ (0.1 M, pH 12) stored for 1 week in the absence of light (– hv) and under a 500 W lamp (+ hv). Differences in color were observed between the two samples of each compound. The formation of a film was also observed in the DPivOHAQ sample exposed to light
65 66 67	Figure S14. ¹ H NMR spectra of samples of DPivOHAQ (0.1 M, pH 12) stored for 1 week in the absence of light (– hv) and under a 500 W lamp (+ hv), each diluted (1:5.5) in pH 14 D ₂ O (1 M KOD) containing a 9 mM NaCH ₃ SO ₃ internal standard (δ 2.6 ppm)
68 69	Figure S15. ¹ H NMR spectra of samples of DBAQ (0.1 M, pH 12) stored for 1 week in the absence of light (– hv) and under a 500 W lamp (+ hv), each diluted (1:5) in pH 12 D ₂ O or in DMSO- <i>d</i> ₆ . 22
70	Complete synthesis 22

- 71 Scheme S3. Complete synthetic routes, conditions, and yields of DPivOHAQ and DBAQ when 72 73 Figure S16. ¹H NMR spectra of commercial and synthesized anthracene (AC) in DMSO-d₆. The 74 75 76 General information for synthesis and characterization All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received unless 77 otherwise stated. All reactions sensitive to moisture or oxygen were carried out in oven-dried or 78 flame-dried and nitrogen-charged glassware. All anhydrous solvents were saturated with argon 79 and passed through a column of activated alumina immediately prior to use. 80 81 ¹H NMR spectra were recorded on Varian INOVA 500 spectrometers at 500 MHz. NMR spectra 82 were recorded in solutions of deuterated dimethyl sulfoxide (DMSO-*d*₆) with the residual dimethyl 83
- sulfoxide (δ 2.25 ppm for ¹H NMR), or deuterated water (D₂O) with the residual H₂O (δ 4.79 ppm
- 84 for ¹H NMR). 85
- 86

87 LC-MS was conducted on a Bruker microTOF-Q II mass spectrometer. The sample was diluted by water/acetonitrile (V/V = 1:1) to the desired concentration (~ 20μ M) before LC-MS 88 89 measurements.

90

Electrochemical characterization 91

- Cyclic voltammetry measurements 92
- Glassy carbon was used as the working electrode for all three-electrode CV tests with a 5 mm 93
- diameter glassy carbon working electrode, an Ag/AgCl reference electrode (BASi, pre-soaked in 94
- 3 M NaCl solution), and a graphite counter electrode. 95
- All electrochemical oxidation and flow cell cycling was conducted with Biologic equipment and 96 97 corresponding software.
- 98
- Flow cell setup 99
- 100 Flow battery experiments were constructed with cell hardware from Fuel Cell Tech (Albuquerque,
- NM) assembled into a zero-gap flow cell configuration. Pyrosealed POCO graphite flow plates 101
- 102 with serpentine flow patterns were used for both electrodes. Each electrode comprised a 5 cm^2
- geometric surface area covered by a piece of AvCarb HCBA woven carbon fiber. The membrane 103
- is pre-soaked (1 M KOH for 24 hours) Nafion 212. 104
- 105

106 **Brief description of electrosynthesis**

- Undivided electrolytic cell setup 107
- Working electrode: carbon felt, where **DPivOHAC(COO⁻)** was oxidized to **DPivOHAQ(COO⁻)**; 108
- 109 counter electrode: carbon rod, where water was reduced to hydrogen gas.
- 110
- Divided electrolytic cell setup vs. the ORR 111
- Anode: Commercial AvCarb HCBA (woven carbon cloth), where DPivOHAC(COO⁻) was 112
- oxidized to DPivOHAQ(COO⁻); cathode: platinum coated carbon paper (SGL 39AA), where 113 humidified air/oxygen was reduced to hydroxide. 114
- 115

- 116 *Divided electrolytic cell setup vs. the reduction of ferricyanide*
- 117 Anode: AvCarb HCBA (woven carbon cloth), where **DPivOHAC(COO⁻)** was oxidized to 118 **DPivOHAQ(COO⁻)**; cathode: AvCarb HCBA (woven carbon cloth), where potassium 119 ferricyanide was reduced to potassium ferrocyanide.
- 120



Figure S1. ¹H NMR spectra of commercial and synthesized 9,10-dihydroanthracene (DHAC) in DMSO-*d*₆.



Figure S2. ¹H NMR spectra of 2,7-, 2,6-DPivOHAC isomers and their mixture (aromatic region)
 in DMSO-*d*6.

b

128

a Undivided cell





- 129
- 130 Figure S3. Photos of undivided cell (a) and divided cell (b).



134 Figure S4. Schematics of (a) undivided cell against the HER and divided cells against (b) the ORR and (c) ferricyanide to ferrocyanide, respectively. (d) ¹H NMR spectra of (bottom to top): 135 chemically synthesized **DPivOHAC** (black); chemically synthesized **DPivOHAQ** (red); 136 electrosynthesized DPivOHAQ in an undivided cell (purple), 17.3% of DPivOHAC remained 137 unreacted according to the integration, yield: 82.7%; electro-synthesized **DPivOHAQ** in a divided 138 cell against Fe(CN)6³⁻ (blue), 7.0% of **DPivOHAC** remained unreacted according to the 139 integration, yield: 93.0%; electrosynthesized **DPivOHAQ** in a divided cell against O₂ (green), 0 % 140 of DPivOHAC remained unreacted according to the integration, yield: 100%. The deuterated 141 solvent is DMSO-d₆, and the solvent peaks (DMSO and H₂O) were removed to better display the 142 peaks of interest. The electrosynthetic details are described under the headings Electrosynthesis 143 I, II, and III. 144 145

No ion-selective membrane is needed in the undivided cell (against the HER), nor are hydroxides 146 147 required theoretically because the HER generates the required number of hydroxides for DPivOHAQ electrosynthesis. Ideally, the divided cell against the ORR will not require hydroxides 148 either if all generated hydroxides from the ORR can immediately crossover to the DPivOHAC 149 anolyte side. The divided cell against ferri- to ferrocyanide reduction needs six equivalents of 150 hydroxide for electrosynthesis, the advantage of which is incorporating the electrosynthesis and 151 flow battery in one setup, and electrosynthesis becomes a part of the on-site setup and takes as 152 long as the energy/power ratio of the battery. 153

154

Electrosynthesis I. Electrochemical synthesis of DPivOHAQ(COO⁻) in an undivided cell at 0.1 155

M concentration, against the hydrogen evolution reaction (HER). 156

DPivOHAC (COO⁻)

 $6 \text{ H}_2\text{O} + 6 e^- \longrightarrow 3 \text{ H}_2 + 6 \text{ OH}^-$

157



DPivOHAQ (COO⁻)

158

159

160 An undivided cell was prepared with carbon felt (XF30A, Toyobo Co., volumetric porosity: 95%) 161 as the working electrode, a carbon rod as the counter electrode, and Ag/AgCl (3 M NaCl) as the 162 reference electrode.

163

164

Electrolyte preparation: 0.378 g DPivOHAC, 0.745 g KCl, and 0.561 g KOH were dissolved in 165 166 deionized water to obtain a 10 mL solution containing 0.1 M DPivOHAC, 1.0 M KCl, and 1.0 M KOH. 167

168

On the working electrode: DPivOHAC(COO⁻) was oxidized to DPivOHAQ(COO⁻); on the 169 counter electrode: water was reduced to hydrogen gas. 170

171

176

Characterization of anolyte: an aliquot (~250 µL) was transferred from the as-prepared anolyte to 177 an Eppendorf® tube (capacity: 1.5 mL) and acidified by a drop of concentrated HCl to obtain 178 **DPivOHAQ** precipitate. The final **DPivOHAQ** precipitate was re-dissolved in DMSO-*d*₆ for ¹H 179 NMR measurement. According to the integration of the ¹H NMR spectrum (Figure 3d), the yield 180 is 82.7%. The faradaic efficiency (%) = [yield (%) / 1.2] = 68.9%. 181 182

Electrochemical oxidation of **DPivOHAC(COO⁻)**: while the electrolyte was stirred, a constant 172 potential (1.1 V vs. Ag/AgCl) was applied to the divided electrolytic cell until 120% of the required 173 coulombs were extracted from the working electrode. [0.1 M * 0.01 L * 96485 C/mol * 6 *1.2 = 174 694.7 C, 6 electrons need to be extracted from every **DPivOHAC** molecule]. 175

Electrosynthesis II. Electrochemical synthesis of DPivOHAQ(COO⁻) in a divided cell at 0.1 M
 concentration, against the oxygen reduction reaction (ORR).

186



188 189

In a flow cell setup (divided electrolytic cell), where unbaked AvCarb HCBA was used on the anode side, the carbon paper was used on the cathode side with coated platinum particles to catalyze the ORR; Nafion® 212 was used as membrane. The high-frequency area specific resistance (HF-ASR) was maintained in the range of $1.48-1.54 \ \Omega \ cm^2$ before and after electrosynthesis.

- Anolyte preparation: 0.378 g DPivOHAC, 0.745 g KCl, and 0.561 g KOH were dissolved in
 deionized water to obtain a 10 mL solution containing 0.1 M DPivOHAC, 1.0 M KCl, and 1.0 M
 KOH.
- 199

195

Catholyte preparation: humidified oxygen or air was pumped into the flow cell to participate inthe electrochemical reaction.

202

Electrochemical oxidation of DPivOHAC(COO⁻): a constant voltage (1.8 V) was applied to the
 divided electrolytic cell until the current decreased to 2 mA/cm². The number of extracted electrons
 was ~1.2 times higher than the theoretical value.

206

207 Characterization of anolyte: an aliquot (~250 μ L) was transferred from the as-prepared anolyte to 208 an Eppendorf® tube (capacity: 1.5 mL) and acidified by concentrated HCl to obtain **DPivOHAQ** 209 precipitate. The final **DPivOHAQ** precipitate was re-dissolved in DMSO-*d*₆ for ¹H NMR 210 measurement. According to the integration of the ¹H NMR spectrum (Figure 3d), the yield is 100%. 211 The faradaic efficiency (%) = [yield (%) / 1.2] = 83.3%.

212

Electrosynthesis III. Electrochemical synthesis of **DPivOHAQ(COO⁻)** in a divided cell at 0.1 M

- concentration, against the reduction of ferricyanide.
- 215



In a flow cell setup (divided electrolytic cell), unbaked AvCarb HCBA (woven carbon cloth) was 219 used as electrodes for both sides; Nafion® 212 was used as the membrane. The high-frequency 220 area specific resistance (HF-ASR) was maintained at ~1.12 Ω cm² before and after 221 electrosynthesis. 222 223 Anolyte preparation: 0.378 g DPivOHAC, 0.745 g KCl, and 0.561 g KOH were dissolved in 224 deionized water to obtain a 10 mL solution containing 0.1 M DPivOHAC, 1.0 M KCl, and 1.0 M 225 226 KOH. 227 Catholyte preparation: 3.292 g K₃Fe(CN)₆, 7.445 g KCl, and 2.805 g KOH were dissolved in 228 deionized water to obtain a 100 mL solution containing 0.1 M K₃Fe(CN)₆, 1.0 M KCl, and 0.5 M 229 KOH. 230 231 The reason for which 0.5 M KOH was added to the catholyte is to counterbalance the added OH⁻ in 232 the anolyte, which is required for the electrosynthesis, thereby suppressing the loss of OH⁻ from 233 234 the anolyte to the catholyte due to crossover. 235 Electrochemical oxidation of **DPivOHAC(COO⁻)**: a constant current density (20 mA/cm²) was 236 applied to the divided cell for at most 1.5 hours with a 1.2 V voltage cutoff; when either time or 237 voltage reached the limit, the potential was held (1.2 V vs. ferro-/ferricyanide) until the current 238 decreased to 2 mA/cm². The number of extracted electrons was ~1.2 times higher than the 239 theoretical value. 240 241 Characterization of anolyte: an aliquot (~250 µL) was transferred from the as-prepared anolyte to 242 an Eppendorf® tube (capacity: 1.5 mL) and acidified by a drop of concentrated HCl to obtain 243 **DPivOHAQ** precipitate. The final **DPivOHAQ** precipitate was re-dissolved in DMSO-*d*₆ for ¹H 244 NMR measurement. According to the integration of the ¹H NMR spectrum (Figure 3d), the yield 245 is 93.0%. The faradaic efficiency (%) = [yield (%) / 1.2] = 77.5%. 246 247 Because a few aliquots were transferred and the volume of as-prepared **DPivOHAO** changed, 5 248 mL of the DPivOHAQ solution was used as the negolyte and 100 mL of the ferro-/ferricyanide 249 250 solution [~0.06 M K₄Fe(CN)₆ and ~0.04 M K₃Fe(CN)₆] generated from Electrosynthesis III was used as the posolyte for charge-discharge cycling. Due to leakage, 4.5 mL of DPivOHAO 251 remained for subsequent cycling. 252 253 Electrosynthesis IV. Electrochemical synthesis of DPivOHAQ(COO⁻) in a divided cell at 0.5 M 254 255 concentration with excess hydroxide, against the reduction of ferricyanide. 256 257 In a flow cell setup (divided electrolytic cell), unbaked AvCarb HCBA (woven carbon cloth) was used as electrodes for both sides; Nafion® 212 was used as the membrane. The high-frequency 258 area specific resistance (HF-ASR) was maintained at ~1.1 Ω cm² before and after electrosynthesis. 259 260 Anolyte preparation: 1.89 g DPivOHAC, 0.745 g KCl, and 0.567 g KOH were dissolved in 261 deionized water to obtain a 10 mL solution containing 0.5 M DPivOHAC, 1.0 M KCl, and 1.0 M 262 KOH. Although the **DPivOHAC** electrochemical oxidation requires OH⁻ions, we observed that 263

- 0.5 M DPivOHAC tends to crash out of solution when the concentration of KOH exceeds 1.5 M.
 To circumvent this precipitation issue, we added 1.5 times the required amount of KOH pellets
 (2.52 g) (*i.e.*, 1.5 times 6 equivalents relative to DPivOHAC) into the anolyte over the course of
 constant current charging. According to the Nernst equation, the cell voltage is a function of [OH⁻];
 thus, the voltage fluctuation reflects the addition of KOH in Figure S5.
- 269

270 Catholyte preparation: 16.46 g K₃Fe(CN)₆, 7.445 g KCl, and 2.805 g KOH were dissolved in 271 deionized water to obtain a 100 mL solution containing 0.5 M K₃Fe(CN)₆, 1.0 M KCl, and 0.5 M

- 272 KOH.
- 273

Electrochemical oxidation of **DPivOHAC(COO⁻)**: a constant current density (100 mA/cm²) was applied to the divided cell for at most 1.7 hours with a 1.2 V voltage cutoff; when either time or voltage reached the limit, the potential was held (1.2 V vs. ferro-/ferricyanide) until the current decreased to 12 mA/cm². The number of extracted electrons was ~1.2 times higher than the theoretical value.

279

280 Characterization of anolyte: an aliquot (~250 μ L) was transferred from the as-prepared anolyte to

an Eppendorf® tube (capacity: 1.5 mL) and acidified by a drop of concentrated HCl to obtain

282 **DPivOHAQ** precipitate. The final **DPivOHAQ** precipitate was re-dissolved in DMSO-*d*₆ for ¹H

NMR measurement; the yield is 89.0%. The faradaic efficiency (%) = [yield (%) / 1.2] = 74.2%.



Figure S5. The electrochemical oxidation of 0.5 M DPivOHAC(COO⁻) (Electrosynthesis IV).



Figure S6. ¹H NMR spectrum of DPivOHAQ in DMSO-*d*₆ synthesized via the procedure described in Electrosynthesis IV. From the aromatic peak integrations, we found that 89.0%
DPivOHAQ was generated (when the two set of peaks at chemical shifts of 7.95 and 8.10 ppm were integrated), 11.0% DPivOHAC was remaining.



and S6, indicates that no observable **DPivOHAQ** dianthrone was generated during the electrosynthesis. (e)-(f) The peak intensity and retention time of **DPivOHAQ**(AC)-related Kolbe electrolysis byproducts under negative mode. No peak was found in the given retention time region, which, in combination with the absence of impurities in the ¹H NMR spectra in Figures 3d and S6, indicates that no observable **DPivOHAQ**(AC)-related Kolbe electrolysis byproducts were generated during the electrosynthesis.

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NO Kolbe electrolysis



Scheme S1. Kolbe electrolysis. Kolbe electrolysis-related byproducts are not expected in our cell,
 as the decarboxylation and dimerization reactions usually require much higher voltages and
 precious-metal-based electrodes.^{S1} In our cell, we use carbon electrodes and an applied potential
 of 1.2 V. Additionally, we did not detect any dimer formation from LC–MS measurements.

311

306

Electrosynthesis V. Electrochemical synthesis of DPivOHAQ(COO⁻) in a divided cell at 0.5 M
 concentration with a stoichiometric quantity of hydroxide, against the reduction of ferricyanide.

In a flow cell setup (divided electrolytic cell), unbaked AvCarb HCBA (woven carbon cloth) was used as electrodes for both sides; Nafion® 212 was used as the membrane. The high-frequency area specific resistance (HF-ASR) was maintained at ~1.45 Ω cm² before and after electrosynthesis.

319

Anolyte preparation: 1.89 g **DPivOHAC**, 0.745 g KCl, and 0.567 g KOH were dissolved in deionized water to obtain a 10 mL solution containing 0.5 M **DPivOHAC**, 1.0 M KCl, and 1.01 M KOH. We added the stoichiometric quantity of KOH pellets (1.68 g) (*i.e.*, 6 equivalents relative to **DPivOHAC**) into the anolyte over the course of constant current charging.

324

Catholyte preparation: 16.46 g K₃Fe(CN)₆, 7.445 g KCl, and 2.805 g KOH were dissolved in
deionized water to obtain a 100 mL solution containing 0.5 M K₃Fe(CN)₆, 1.0 M KCl, and 0.5 M
KOH.

328

Electrochemical oxidation of **DPivOHAC(COO⁻)**: a constant current density (100 mA/cm²) was applied to the divided electrolytic cell for at most 1.7 hours with a 1.2 V voltage cutoff; when either time or voltage reached the limit, the potential was held (1.2 V vs. ferro-/ferricyanide) until the current decreased to 12 mA/cm². The number of extracted electrons was ~1.2 times higher than the theoretical value.

334

Characterization of anolyte: an aliquot (~250 μ L) was transferred from the as-prepared anolyte to an Eppendorf® tube (capacity: 1.5 mL) and acidified by a drop of concentrated HCl to obtain **DPivOHAQ** precipitate. The final **DPivOHAQ** precipitate was re-dissolved in DMSO-*d*₆ for ¹H NMR measurement; the yield is 81.8%. The faradaic efficiency (%) = [yield (%) / 1.2] = 68.2%.

340 Formation of dianthrone during electrosynthesis

- Anthrone dimers can be produced during the electrosynthesis when insufficient hydroxide is present.
- 343

When there is excess hydroxide in the solution, although some OH^- ions will be electrochemically oxidized to oxygen via the OER, the remaining OH^- ions are sufficient for the conversion of A^- to AO^{2-} .

346 347

When there is no excess hydroxide, given that the OER side reaction is an inevitable competing reaction, there will be insufficient OH^- ions for the conversion of A^- to AQ^{2-} ; instead, the anthrone anion A^- may be oxidatively dimerized to the dianthrone **DA**. The following figures and scheme illustrate how **DA** was identified and propose its corresponding electrochemistry.

352

During the electrochemical oxidation of the 10 mL 0.5 M **DPivOHAC(COO⁻)** at pH 12, only 1.68 g of KOH (10*0.001 L*0.5 M*6*56.1056 g/mol =1.68 g) were added to the solution. Although there is some additional KOH added to the potassium ferricyanide side, hydroxide cannot cross

over to the **DPivOHAC** side of the cell sufficiently rapidly to offset its consumption by **DPivOHAC** oxidation and the OER.

358



359

360 Figure S8. Cell performance of 0.5 M electrosynthesized DPivOHAQ when a stoichiometric

quantity of hydroxide was added into the **DPivOHAC(COO⁻)** solution (**Electrosynthesis V**). (a)

The long-term cycling performance with adjusted lower voltage cutoffs. (b) The zoomed in discharge capacity when 0.7–1.25 V voltage cutoffs were applied; the fitted temporal fade rate was 0.01%/day. (c) The voltage profiles at varying cycle numbers with different lower voltage cutoffs.



Figure S9. Voltage profiles of 0.5 M electrosynthesized **DPivOHAQ** when a stoichiometric quantity of hydroxide was added into the **DPivOHAC** solution (**Electrosynthesis V**) with different lower voltage cutoffs [(a) 0.6, (b) 0.2, (c) 0.6, and (d) 0.7 V]. The upper voltage cutoff is kept constant at 1.25 V for the duration of cell cycling.

371

372 In the 1st cycle, the region in (a) circled in cyan shows a small plateau, indicating some redoxactive byproducts were produced during the electrosynthesis. In the 67th cycle, after lowering the 373 lower cutoff from 0.6 to 0.2 V, we can clearly see the discharge plateau (in the region of 0.2–0.4 374 V) attributed to byproducts, and the charge plateau attributed to byproducts is also becoming 375 longer. In the 76th cycle, after elevating the lower cutoff back to 0.6 V, the shape of the charge 376 profile becomes nearly the same as the one in the 1st cycle. After the lower voltage cutoff was 377 further increased to 0.7 V, in the 456th cycle, the small plateau attributed to the byproducts 378 disappeared. 379



Figure S10. ¹H NMR spectrum of cycled 0.5 M electrosynthesized **DPivOHAQ** when a stoichiometric quantity of hydroxide was added into the **DPivOHAC(COO⁻)** solution (**Electrosynthesis V**). The solvent peak was removed to clearly show both aromatic and aliphatic regions of the cycled **DPivOHAQ** solution. The deuterated solvent is D₂O. The dominating peaks can be assigned to **DPivOHAQ**. Some small impurity peaks were observed, but they are difficult to identify. The percentages of side products are very close to the detection limit of the ¹H NMR instrument.



Figure S11. LC-MS results of cycled 0.5 M electrosynthesized DPivOHAQ when a 392 stoichiometric quantity of hydroxide was added into the DPivOHAC solution (Electrosynthesis 393 V). (a) The base peak chromatogram of the sample, showing all peaks observed by mass 394 spectrometry under negative mode. (b) The peak intensity and retention time of **DPivOHAO-1H** 395 under negative mode. (c) The peak intensity and retention time of dianthrone+1H under negative 396 mode. (d) The peak intensity and retention time of dianthrone-1H under negative mode. (e) The 397 peak intensity and retention time of dianthrone-3H under negative mode. (f) The peak intensity 398 399 and retention time of anthrone-1H under negative mode (none observed). (g) The peak intensity and retention time of **DPivOHAC-1H** under negative mode. By integrating the peak areas in (b), 400 (c), (d), (e), (f) and (g), we found the percentages of DPivOHAQ (81.8%), dianthrone+1H 401 (10.2%), dianthrone–1H (0.4%), dianthrone–3H (1.3%), and DPivOHAC (6.3%). 402 403



Scheme S2. Proposed possible redox reactions of dianthrones. Because the dianthrone+1H (exact mass: 787.3488) and dianthrone-3H (exact mass: 783.3175) were detected and plateaus were observed from the voltage profiles, we propose that there are three redox-active states for the dianthrones.

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Electrosynthesis VI. Electrochemical synthesis of DBAQ(COO⁻) in an undivided electrolytic
 cell at 0.1 M concentration, against the HER.

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An undivided electrolytic cell was prepared with carbon felt (XF30A, Toyobo Co., volumetric porosity: 95%) as the working electrode, a carbon rod as the counter electrode, and Ag/AgCl (3 M

- 416 porosity: 95%) as the working ele417 NaCl) as the reference electrode.
- 418

Electrolyte preparation: 0.35 g DBDHAC (synthesized by following our previous work), 0.745 g
KCl, and 0.561 g KOH were dissolved in deionized water to obtain a 10 mL solution containing
0.1 M DBDHAC, 1.0 M KCl, and 1.0 M KOH.

422

423 On the working electrode: DBDHAC was oxidized to DBAQ; on the counter electrode: water was
424 reduced to hydrogen gas.

- 425
- Electrochemical oxidation of **DBDHAC(COO⁻)**: while the electrolyte was stirring, a constant potential (1.1 V vs. Ag/AgCl) was applied to the divided electrolytic cell until 120% of the required
- 428 coulombs were extracted from the working electrode. [0.1 M * 0.01 L * 96485 C/mol * 8 * 1.2 =
- 429 926.3 C; 8 electrons need to be extracted from every **DBDHAC** molecule].
- 430

431 Characterization of anolyte: an aliquot (250 μ L) was transferred from the as-prepared anolyte to 432 an Eppendorf® tube (capacity: 1.5 mL) and acidified by a drop of concentrated HCl to obtain 433 **DBAQ** precipitate. The final **DBAQ** precipitate was re-dissolved in DMSO-*d*₆ for ¹H NMR 434 measurement. According to the integration of the ¹H NMR spectrum in the Figure S12, the yield 435 is 70%. The faradaic efficiency (%) = [yield (%) / 1.2] = 58.3%.

436



Figure S12. ¹H NMR spectra of DBDHAC (bottom), chemically synthesized DBAQ (top), and electrochemically synthesized DBAQ in an undivided cell after varying extents of reaction. DBDHAC: 4,4'-(9,10-dihydroanthracene-diyl)dibutanoic acid; DBAC: 4,4'-(anthracenediyl)dibutanoic acid; DBAQ: 4,4'-(9,10-anthraquinone-diyl)dibutanoic acid. The time interval between successive measurements labeled electrochemical oxidation-1, 2, 3, and 4 is approximately one hour. The deuterated solvent is DMSO-*d*₆.

444

445 Light sensitivity experiments

It has been reported that quinones and related compounds can decompose in the presence of 446 light.^{S2-S6} In order to determine the light sensitivity of **DPivOHAQ** and **DBAQ**, we compared 447 solutions of each compound held in the presence of and in the absence of light for 1 week. Two 448 samples of DPivOHAQ (0.1 M, pH 12 in water with 1 M KCl, 1.5 mL each) and two samples of 449 **DBAQ** (0.1 M, pH 12 in water, 1.5 mL each) were prepared in separate FEP bottles (VWR Catalog 450 No. 16071-008). For each compound, one sample was wrapped in aluminum foil and stored in a 451 452 dark drawer for 1 week. The other sample was held for 1 week under a quartz halogen lamp with a controllable output of 50-1000 W set to 500 W (CowboyStudio QL-1000 W HEAD; ePhotoInc 453 OL 1000Bulb). The samples exposed to light were allowed to float at the top of a water bath 454 containing approximately 16 L of water to dissipate excess heat produced by the lamp (the liquid 455 456 level decreased gradually due to evaporation and was replenished daily). The liquid level was 457 maintained at a distance of approximately 20 cm from the light source.

458

After 1 week, differences in color were observed between the samples of each compound stored in the dark and exposed to light (Figure S13). The formation of a film was also observed in the 461 **DPivOHAQ** sample exposed to light. ¹H NMR spectra of each sample demonstrate decomposition
 462 of both compounds stored in the presence of light (Figures S14 and S15).

463

464 We therefore wrapped the electrolyte reservoirs with aluminum foil to avoid decomposition due 465 to light exposure during cell cycling.

466



467 468

Figure S13. Samples of (a) **DPivOHAQ** (0.1 M, pH 12) stored for 1 week in the absence of light (-hv) and under a 500 W lamp (+hv) and of (b) **DBAQ** (0.1 M, pH 12) stored for 1 week in the absence of light (-hv) and under a 500 W lamp (+hv). Differences in color were observed between the two samples of each compound. The formation of a film was also observed in the **DPivOHAQ** sample exposed to light.



475

Figure S14. ¹H NMR spectra of samples of **DPivOHAQ** (0.1 M, pH 12) stored for 1 week in the

477 absence of light (– hv) and under a 500 W lamp (+ hv), each diluted (1:5.5) in pH 14 D₂O (1 M KOD) containing a 9 mM NaCH₃SO₃ internal standard (δ 2.6 ppm).



480 Figure S15. ¹H NMR spectra of samples of DBAQ (0.1 M, pH 12) stored for 1 week in the

481 absence of light (-hv) and under a 500 W lamp (+hv), each diluted (1:5) in pH 12 D₂O or in 482 DMSO- d_6 .

483

484 Complete synthesis

485



488 Scheme S3. Complete synthetic routes, conditions, and yields of DPivOHAQ and DBAQ when

489 commercially available commodity chemicals are used as starting materials.



Figure S16. ¹H NMR spectra of commercial and synthesized anthracene (AC) in DMSO-*d*₆. The
 peak at 7.37 ppm in the synthesized AC spectrum is from benzene.

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REFERENCES

- 495 S1 H.-J. Schäfer, *Topics in Current Chemistry*, 1990, **152**, 91–151.
- 496 S2. G. Maier, L. H. Franz, H.-G. Hartan, K. Lanz and H. P. Reisenauer, *Chemische Berichte*, 1985,
 497 118, 3196–3204.
- 498 S3. B. E. Hulme, E. J. Land and G. O. Phillips, J. Chem. Soc. Faraday Trans. 1, 1972, 68, 1992–2002.
- 499 S4. S. A. Carlson and D. M. Hercules, *Analytical Chemistry*, 1973, **45**, 1794–1799.
- 500 S5. D. M. Hercules, S. A. Carlson, Analytical Chemistry 1974, 46, 674–678.
- 501 S6. A. D. Broadbent, R. P. Newton, *Canadian Journal of Chemistry* 1972, 50, 381–387.