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# Supplementary Information

# *In situ* Electrosynthesis of Anthraquinone Electrolytes in Aqueous Flow Batteries

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Table of Contents

## General information for synthesis and characterization

All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received unless otherwise stated. All reactions sensitive to moisture or oxygen were carried out in oven-dried or flame-dried and nitrogen-charged glassware. All anhydrous solvents were saturated with argon and passed through a column of activated alumina immediately prior to use.

$^{1}$H NMR spectra were recorded on Varian INOVA 500 spectrometers at 500 MHz. NMR spectra were recorded in solutions of deuterated dimethyl sulfoxide (DMSO-*d*$_6$) with the residual dimethyl sulfoxide ($\delta$ 2.25 ppm for $^{1}$H NMR), or deuterated water ($D_2O$) with the residual $H_2O$ ($\delta$ 4.79 ppm for $^{1}$H NMR).

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 (~20μM) before LC–MS measurements.

## Electrochemical characterization

*Cyclic voltammetry measurements*

Glassy carbon was used as the working electrode for all three-electrode CV tests with a 5 mm diameter glassy carbon working electrode, an Ag/AgCl reference electrode (BASi, pre-soaked in 3 M NaCl solution), and a graphite counter electrode.

All electrochemical oxidation and flow cell cycling was conducted with Biologic equipment and corresponding software.

*Flow cell setup*

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 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 is pre-soaked (1 M KOH for 24 hours) Nafion 212.

## Brief description of electrosynthesis

*Undivided electrolytic cell setup*

Working electrode: carbon felt, where **DPivOHAC(COO$^-$)** was oxidized to **DPivOHAQ(COO$^-$)**; counter electrode: carbon rod, where water was reduced to hydrogen gas.

*Divided electrolytic cell setup vs. the ORR*

Anode: Commercial AvCarb HCBA (woven carbon cloth), where **DPivOHAC(COO$^-$)** was oxidized to **DPivOHAQ(COO$^-$)**; cathode: platinum coated carbon paper (SGL 39AA), where humidified air/oxygen was reduced to hydroxide.

*Divided electrolytic cell setup 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.

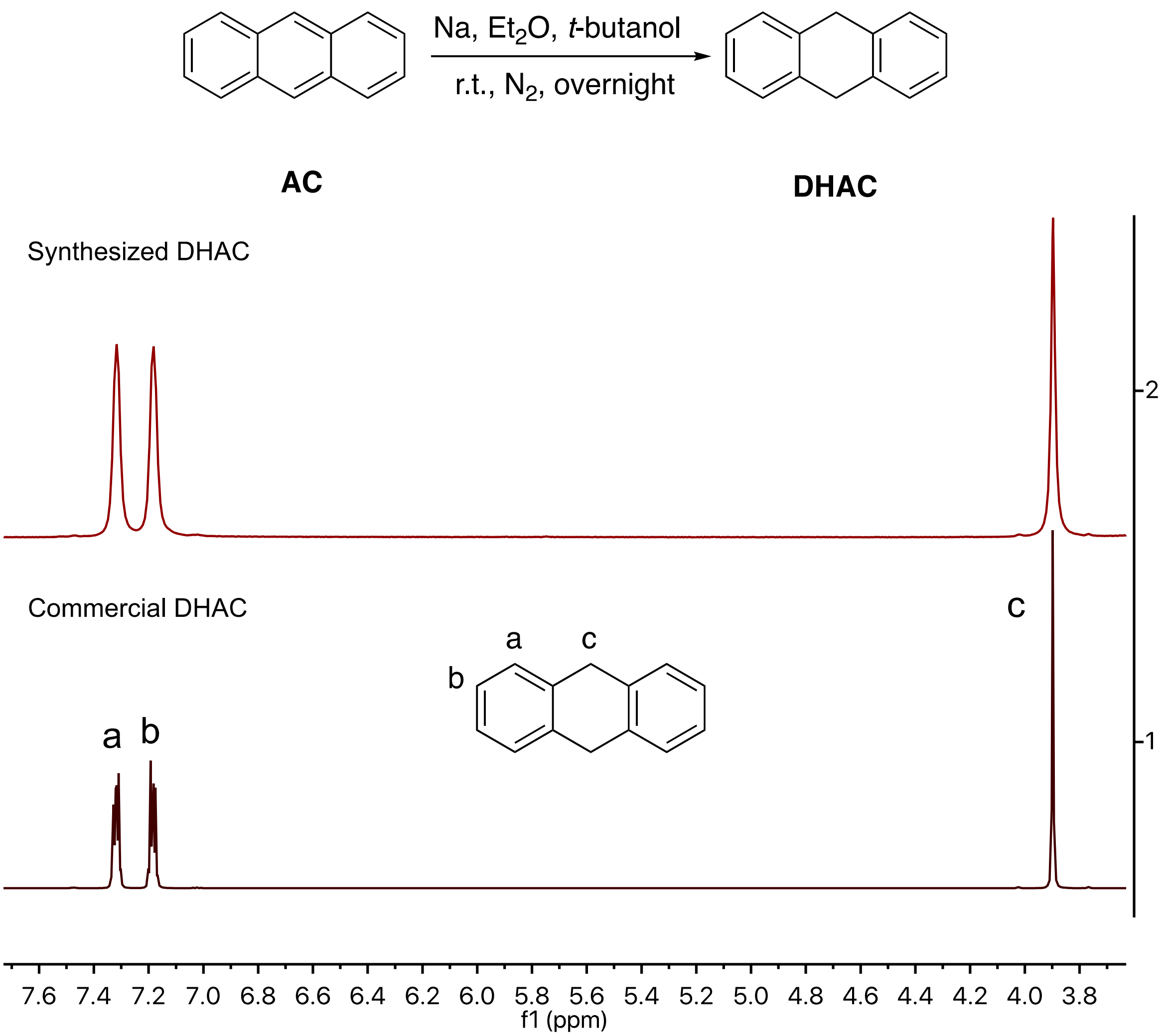


**Figure S1.** $^1$H NMR spectra of commercial and synthesized 9,10-dihydroanthracene (**DHAC**) in DMSO-*d*$_6$.

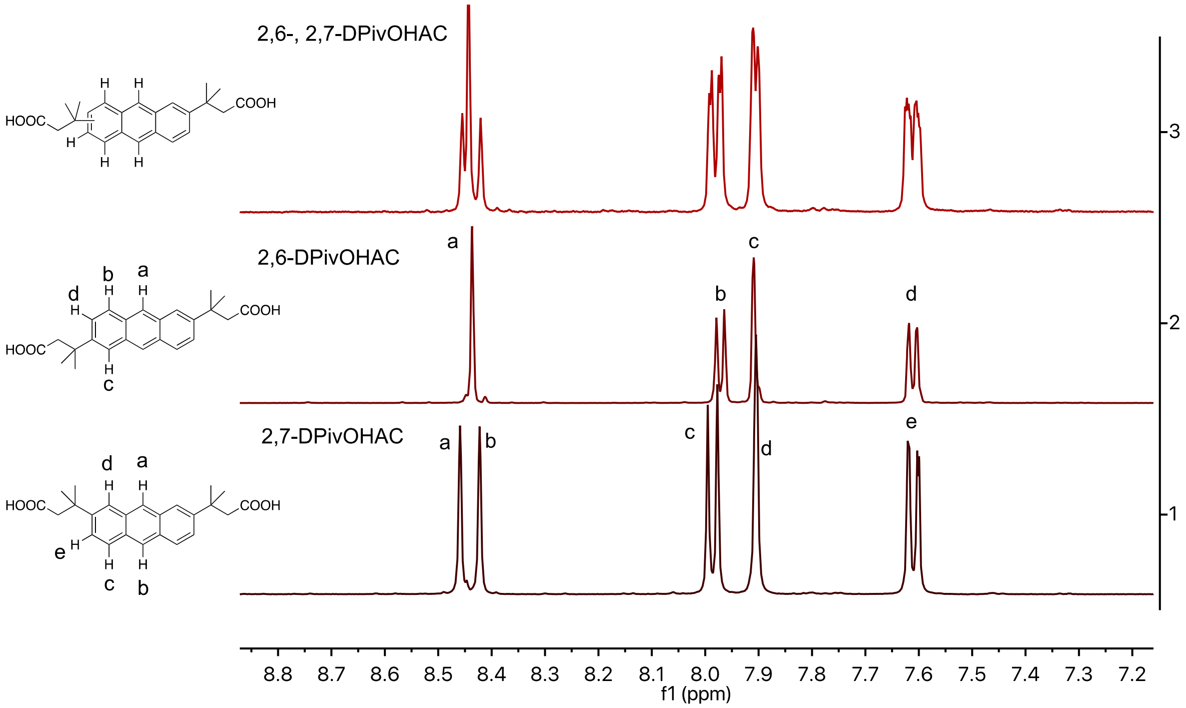


**Figure S2.** $^1$H NMR spectra of 2,7-, 2,6-**DPivOHAC** isomers and their mixture (aromatic region) in DMSO-$d_6$.

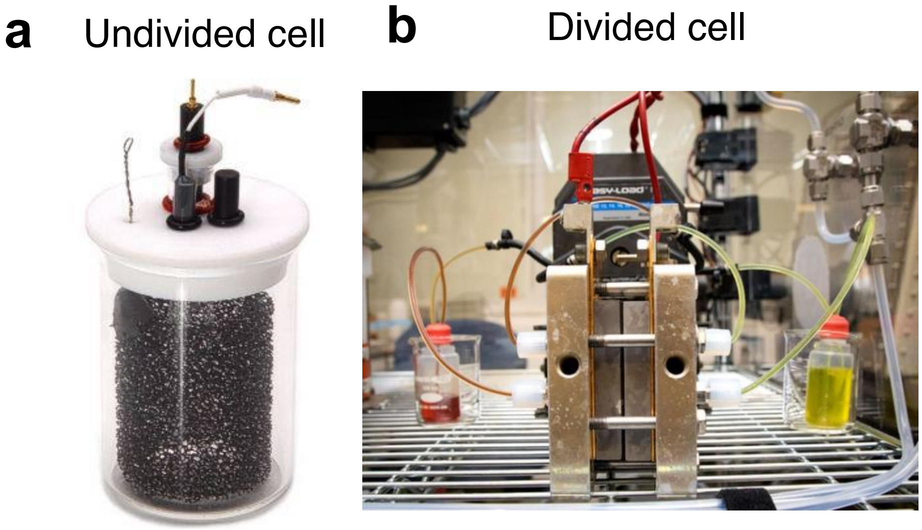


**Figure S3.** Photos of undivided cell (a) and divided cell (b).

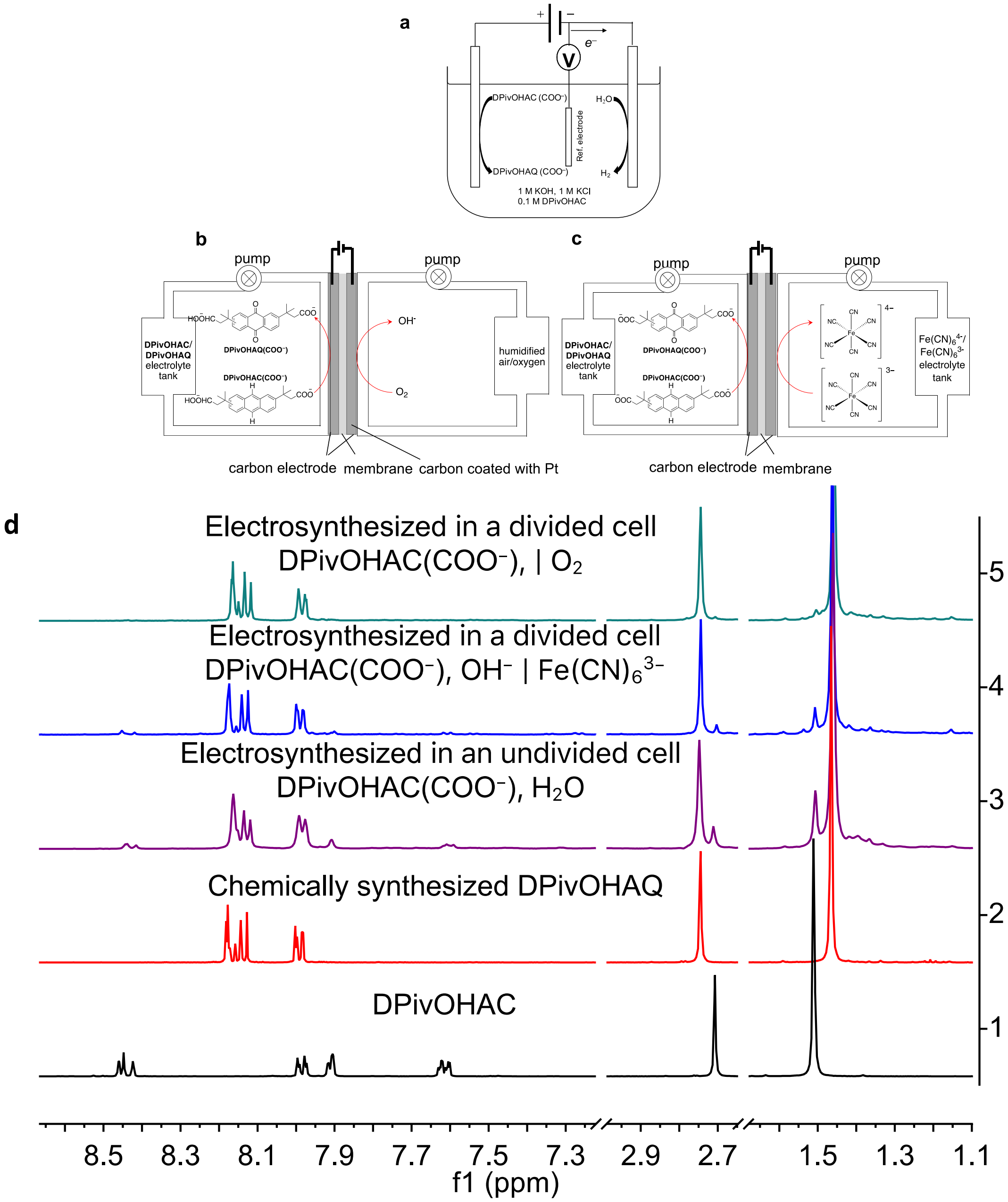
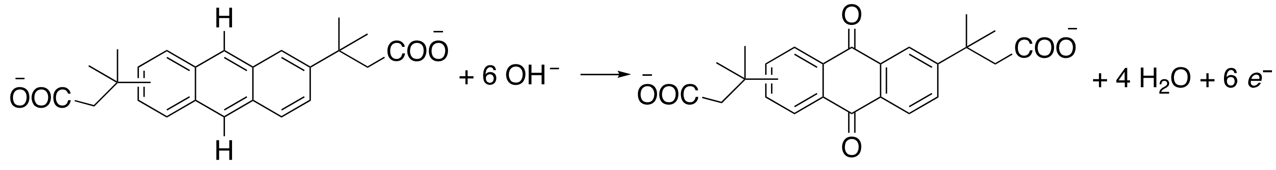


**Figure S4.** Schematics of (a) undivided cell against the HER and divided cells against (b) the ORR and (c) ferricyanide to ferrocyanide, respectively. (d) $^1H$ NMR spectra of (bottom to top): chemically synthesized **DPivOHAC** (black); chemically synthesized **DPivOHAQ** (red); electrosynthesized **DPivOHAQ** in an undivided cell (purple), 17.3% of **DPivOHAC** remained unreacted according to the integration, yield: 82.7%; electro-synthesized **DPivOHAQ** in a divided cell against $Fe(CN)_6^{3-}$ (blue), 7.0% of **DPivOHAC** remained unreacted according to the integration, yield: 93.0%; electrosynthesized **DPivOHAQ** in a divided cell against $O_2$ (green), 0 % of **DPivOHAC** remained unreacted according to the integration, yield: 100%. The deuterated solvent is DMSO-$d_6$, and the solvent peaks (DMSO and $H_2O$) were removed to better display the peaks of interest. The electrosynthetic details are described under the headings **Electrosynthesis I, II,** and **III**.

No ion-selective membrane is needed in the undivided cell (against the HER), nor are hydroxides 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 either if all generated hydroxides from the ORR can immediately crossover to the **DPivOHAC** anolyte side. The divided cell against ferri- to ferrocyanide reduction needs six equivalents of hydroxide for electrosynthesis, the advantage of which is incorporating the electrosynthesis and flow battery in one setup, and electrosynthesis becomes a part of the on-site setup and takes as long as the energy/power ratio of the battery.

**Electrosynthesis I**. Electrochemical synthesis of **DPivOHAQ(COO$_-$)** in an undivided cell at 0.1 M concentration, against the hydrogen evolution reaction (HER).



DPivOHAC (COO⁻) DPivOHAQ (COO⁻)

$$6\,H_2O + 6\,e^- \longrightarrow 3\,H_2 + 6\,OH^-$$

An undivided 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 NaCl) as the reference electrode.

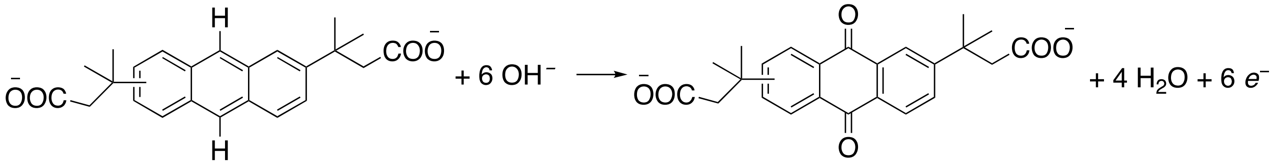
Electrolyte preparation: 0.378 g **DPivOHAC**, 0.745 g KCl, and 0.561 g KOH were dissolved in deionized water to obtain a 10 mL solution containing 0.1 M **DPivOHAC**, 1.0 M KCl, and 1.0 M KOH.

On the working electrode: **DPivOHAC(COO$_-$)** was oxidized to **DPivOHAQ(COO$_-$)**; on the counter electrode: water was reduced to hydrogen gas.

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

Characterization of anolyte: an aliquot (~250 µL) 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 $_1$H NMR measurement. According to the integration of the $_1$H NMR spectrum (Figure 3d), the yield is 82.7%. The faradaic efficiency (%) = [yield (%) / 1.2] = 68.9%.

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



$$1.5\ O_2 + 6\ e^- + 3\ H_2O \longrightarrow 6\ OH^-$$

In a flow cell setup (divided electrolytic cell), where unbaked AvCarb HCBA was used on the anode side, carbon paper was used on the cathode side with coated platinum particles to catalyze the ORR; Nafion® 212 was used as the membrane. The high-frequency area specific resistance (HF−ASR) was maintained in the range of 1.48−1.54 Ω cm$_2$ before and after electrosynthesis.

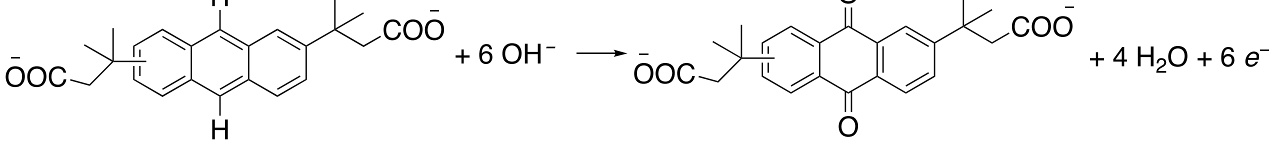
Anolyte preparation: 0.378 g **DPivOHAC**, 0.745 g KCl, and 0.561 g KOH were dissolved in deionized water to obtain a 10 mL solution containing 0.1 M **DPivOHAC**, 1.0 M KCl, and 1.0 M KOH.

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

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/cm$_2$. The number of extracted electrons was ~1.2 times higher than the theoretical value.

Characterization of anolyte: an aliquot (~250 µL) was transferred from the as-prepared anolyte to an Eppendorf® tube (capacity: 1.5 mL) and acidified by concentrated HCl to obtain **DPivOHAQ** precipitate. The final **DPivOHAQ** precipitate was re-dissolved in DMSO-*d*$_6$ for $_1$H NMR measurement. According to the integration of the $_1$H NMR spectrum (Figure 3d), the yield is 100%. The faradaic efficiency (%) = [yield (%) / 1.2] = 83.3%.

**Electrosynthesis III.** Electrochemical synthesis of **DPivOHAQ(COO$_-$)** in a divided cell at 0.1 M concentration, against the reduction of ferricyanide.



$$6\ Fe(CN)_6^{3-} + 6\ e^- \longrightarrow 6\ Fe(CN)_6^{4-}$$

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 ~1.12 Ω $cm^2$ 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.

Catholyte preparation: 3.292 g $K_3Fe(CN)_6$, 7.445 g KCl, and 2.805 g KOH were dissolved in deionized water to obtain a 100 mL solution containing 0.1 M $K_3Fe(CN)_6$, 1.0 M KCl, and 0.5 M KOH.

The reason for which 0.5 M KOH was added to the catholyte is to counterbalance the added $OH^-$ in the anolyte, which is required for the electrosynthesis, thereby suppressing the loss of $OH^-$ from the anolyte to the catholyte due to crossover.

Electrochemical oxidation of **DPivOHAC(COO$^-$)**: 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/$cm^2$. The number of extracted electrons was ~1.2 times higher than the theoretical value.

Characterization of anolyte: an aliquot (~250 µL) 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 $^1$H NMR measurement. According to the integration of the $^1$H NMR spectrum (Figure 3d), the yield is 93.0%. The faradaic efficiency (%) = [yield (%) / 1.2] = 77.5%.

Because a few aliquots were transferred and the volume of as-prepared **DPivOHAQ** changed, 5 mL of the **DPivOHAQ** solution was used as the negolyte and 100 mL of the ferro-/ferricyanide solution [~0.06 M $K_4Fe(CN)_6$ and ~0.04 M $K_3Fe(CN)_6$] generated from **Electrosynthesis III** was used as the posolyte for charge–discharge cycling. Due to leakage, 4.5 mL of **DPivOHAQ** remained for subsequent cycling.

**Electrosynthesis IV.** Electrochemical synthesis of **DPivOHAQ(COO$^-$)** in a divided cell at 0.5 M concentration with excess 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 ~1.1 Ω $cm^2$ before and after electrosynthesis.

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 1.0 M KOH. Although the **DPivOHAC** electrochemical oxidation requires $OH^-$ ions, we observed that 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.

Catholyte preparation: 16.46 g $K_3Fe(CN)_6$, 7.445 g KCl, and 2.805 g KOH were dissolved in deionized water to obtain a 100 mL solution containing 0.5 M $K_3Fe(CN)_6$, 1.0 M KCl, and 0.5 M KOH.

Electrochemical oxidation of **DPivOHAC(COO$^-$)**: a constant current density (100 mA/cm$^2$) 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/cm$^2$. The number of extracted electrons was ~1.2 times higher than the theoretical value.

Characterization of anolyte: an aliquot (~250 µL) 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 $^1$H NMR measurement; the yield is 89.0%. The faradaic efficiency (%) = [yield (%) / 1.2] = 74.2%.

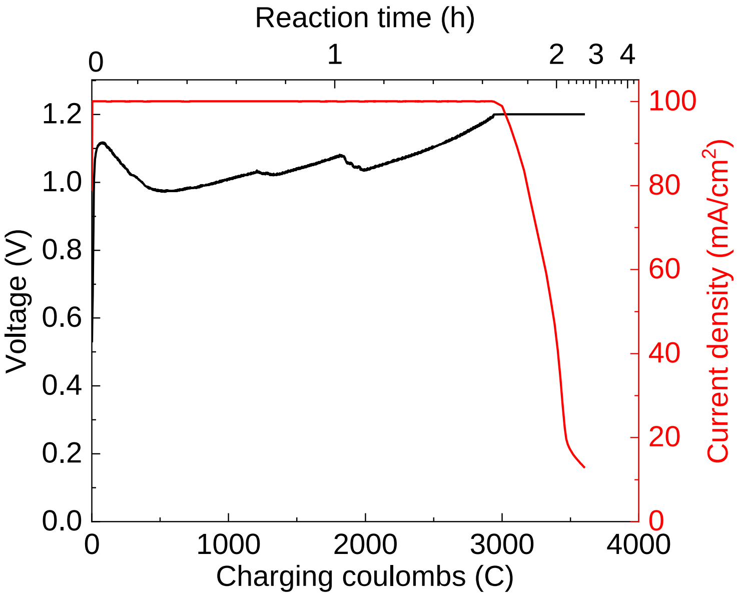


**Figure S5.** The electrochemical oxidation of 0.5 M **DPivOHAC(COO$^-$)** (**Electrosynthesis IV**).

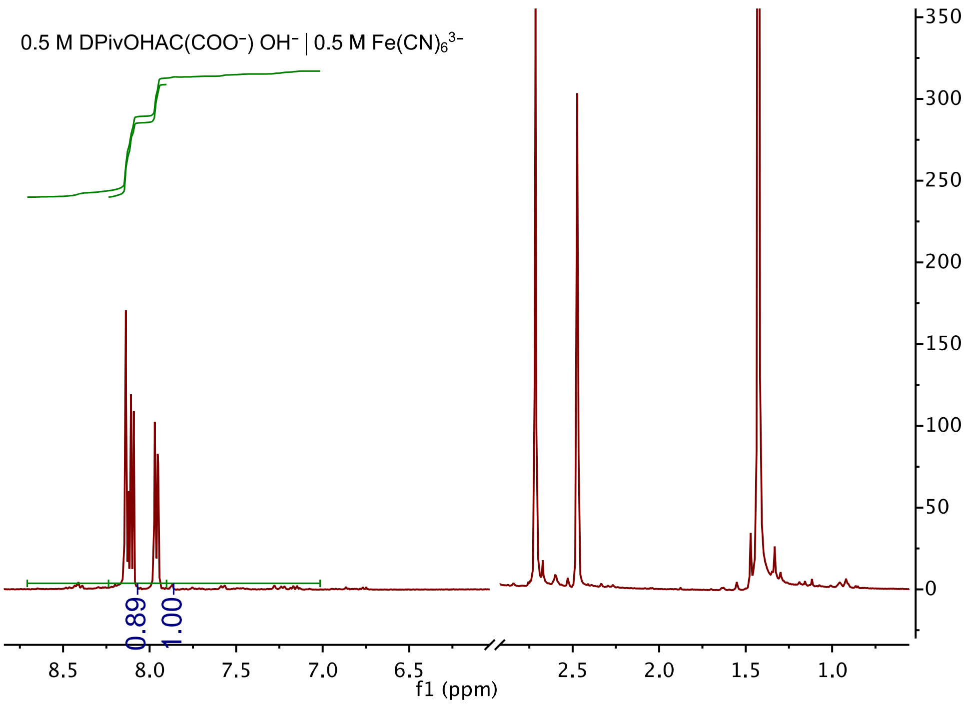


**Figure S6.** $^1$H NMR spectrum of **DPivOHAQ** in DMSO-$d_6$ synthesized via the procedure described in **Electrosynthesis IV**. From the aromatic peak integrations, we found that 89.0% **DPivOHAQ** was generated (when the two sets of peaks at chemical shifts of 7.95 and 8.10 ppm were integrated), 11.0% **DPivOHAC** was remaining.

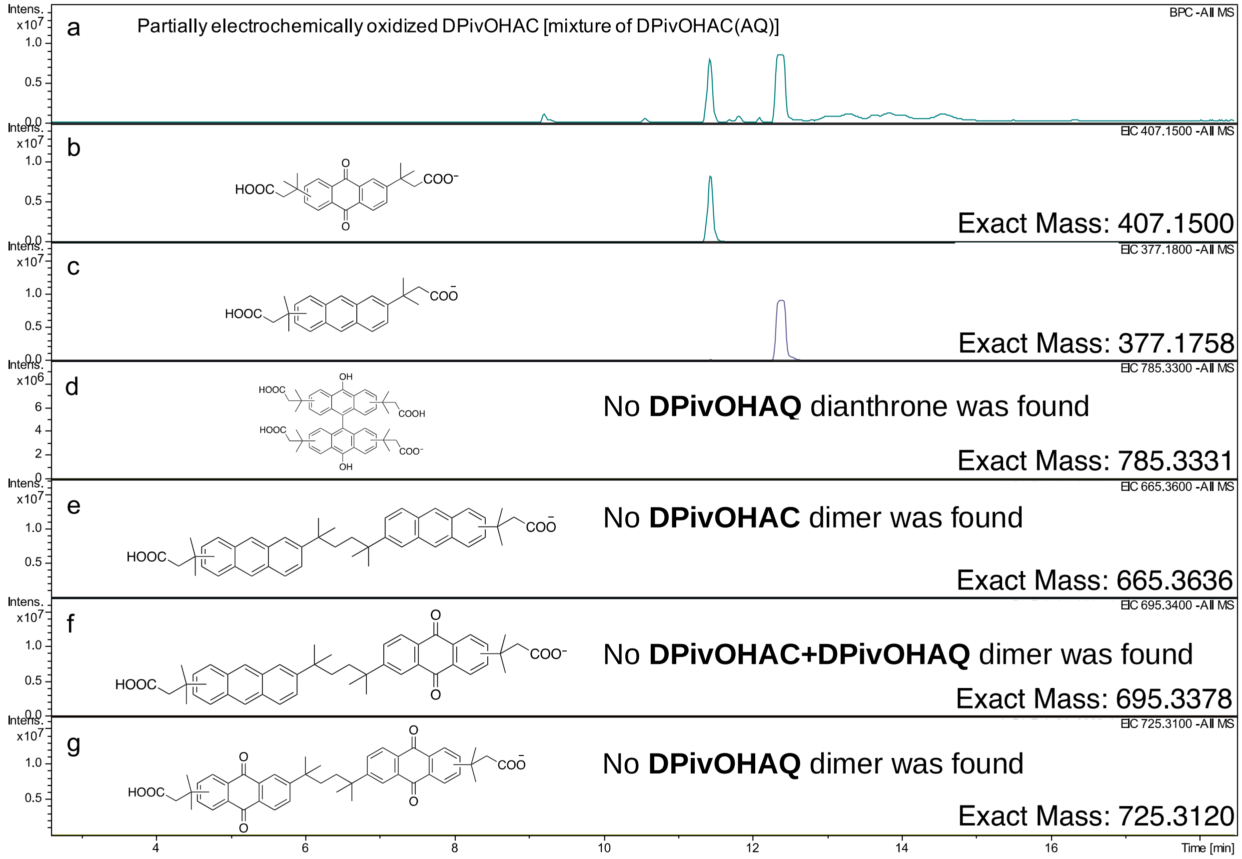
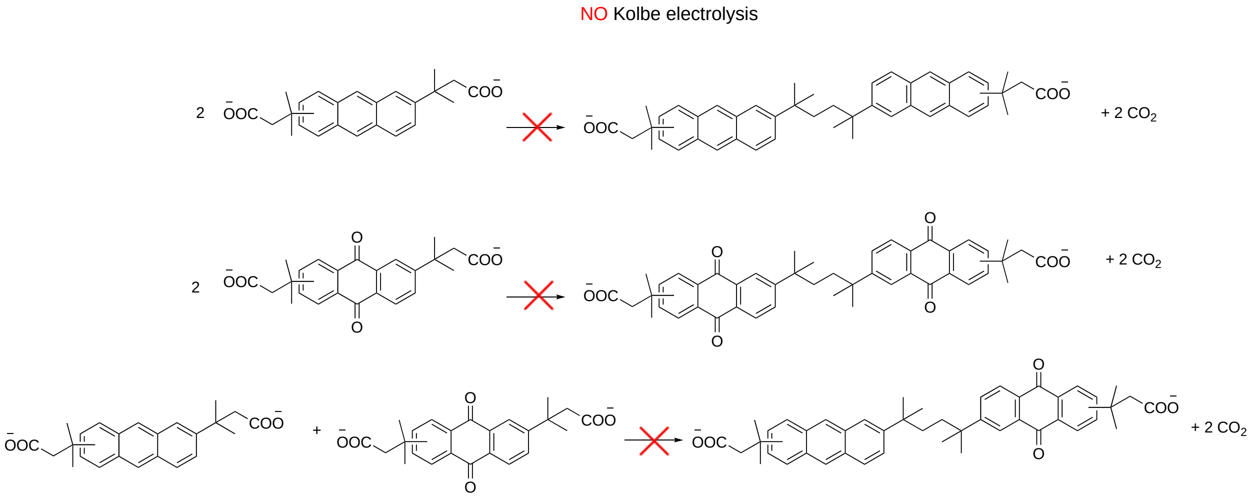


**Figure S7.** Mass spectra of partially electrosynthesized **DPivOHAQ** (from **Electrosynthesis IV**) measured by liquid chromatography–mass spectrometry (LC–MS). (a) The peak intensity and retention time of partially electrosynthesized **DPivOHAQ** under negative mode. (b) The peak intensity and retention time of **DPivOHAQ** under negative mode. (c) The peak intensity and retention time of **DPivOHAC** under negative mode. (d) The peak intensity and retention time of the **DPivOHAQ** dianthrone under negative mode. No peak was found in the given retention time region, which, in combination with the absence of impurities in the $_1$H NMR spectra in Figures 3d and S6, indicates that no observable **DPivOHAQ** dianthrone was generated during the electrosynthesis. (e)-(g) 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 $_1$H NMR spectra in Figures 3d and S6, indicates that no observable **DPivOHAQ(AC)**-related Kolbe electrolysis byproducts were generated during the electrosynthesis.



**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.

**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 cm$^2$ before and after electrosynthesis.

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.

Catholyte preparation: 16.46 g $K_3Fe(CN)_6$, 7.445 g KCl, and 2.805 g KOH were dissolved in deionized water to obtain a 100 mL solution containing 0.5 M $K_3Fe(CN)_6$, 1.0 M KCl, and 0.5 M KOH.

Electrochemical oxidation of **DPivOHAC(COO$^-$)**: a constant current density (100 mA/cm$^2$) 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/cm$^2$. The number of extracted electrons was ~1.2 times higher than the theoretical value.

Characterization of anolyte: an aliquot (~250 µL) 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 $^1$H NMR measurement; the yield is 81.8%. The faradaic efficiency (%) = [yield (%) / 1.2] = 68.2%.

## Formation of dianthrone during electrosynthesis

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

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 **$AQ^{2-}$**.

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.

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.

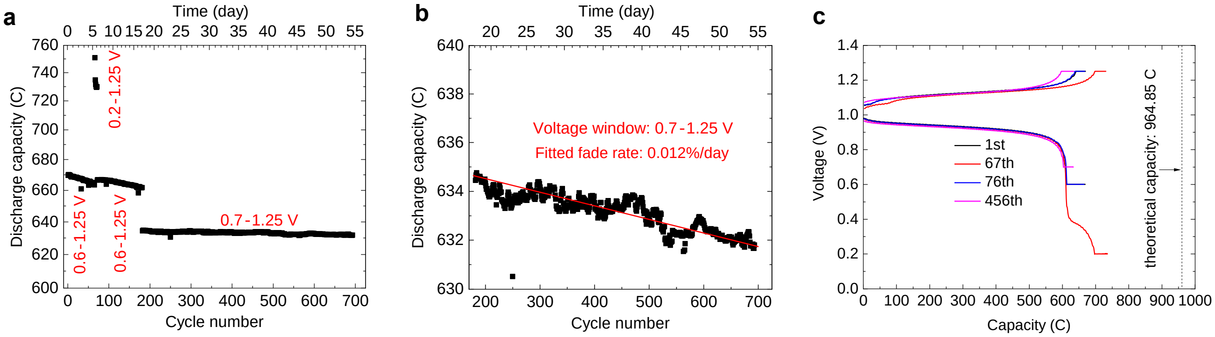


**Figure S8.** Cell performance of 0.5 M electrosynthesized **DPivOHAQ** when a stoichiometric quantity of hydroxide was added into the **DPivOHAC(COO$^-$)** solution (**Electrosynthesis V**). (a) The long-term cycling performance with adjusted lower voltage cutoffs. (b) The zoomed in discharge capacity 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.

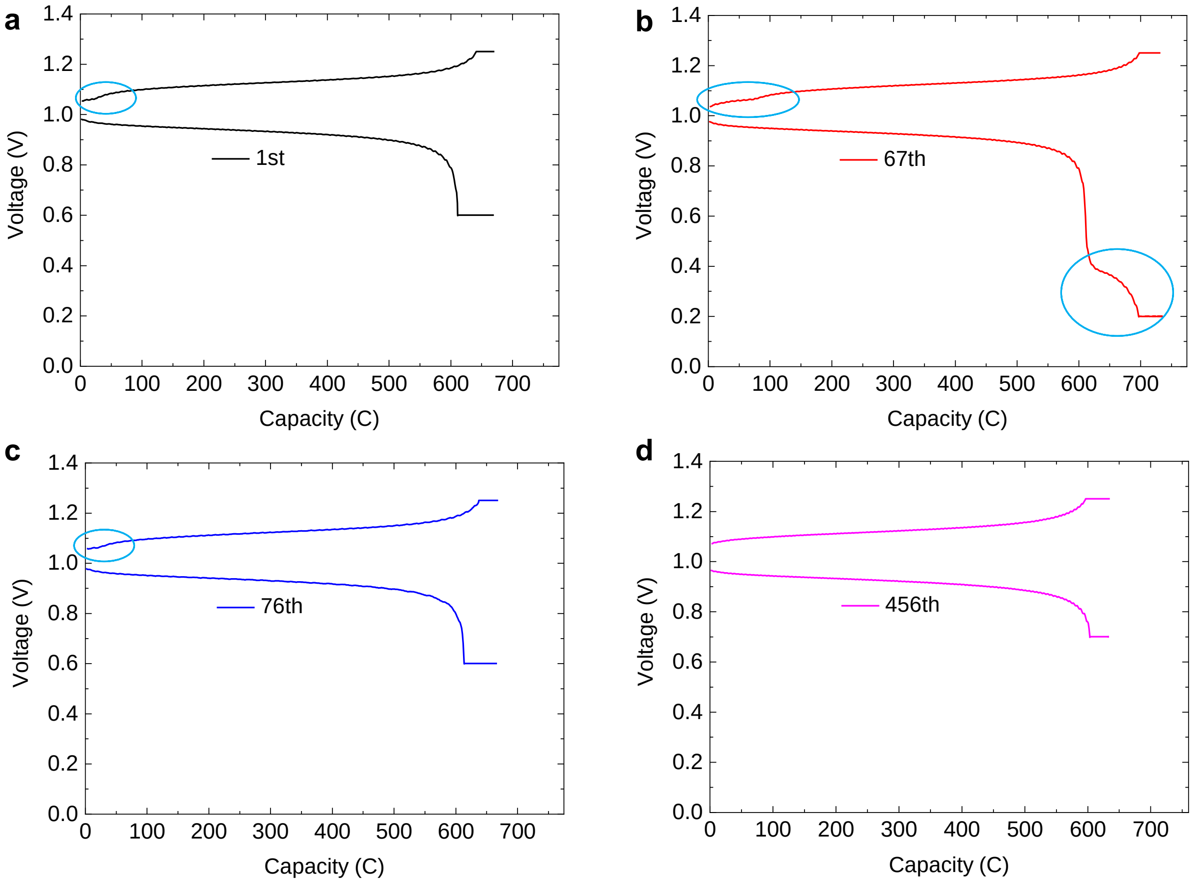


**Figure S9.** Voltage profiles of 0.5 M electrosynthesized **DPivOHAQ** when a stoichiometric quantity of hydroxide was added into the **DPivOHAC** solution (**Electrosynthesis V**) with different lower voltage cutoffs [(a) 0.6, (b) 0.2, (c) 0.6, and (d) 0.7 V]. The upper voltage cutoff is kept constant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

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

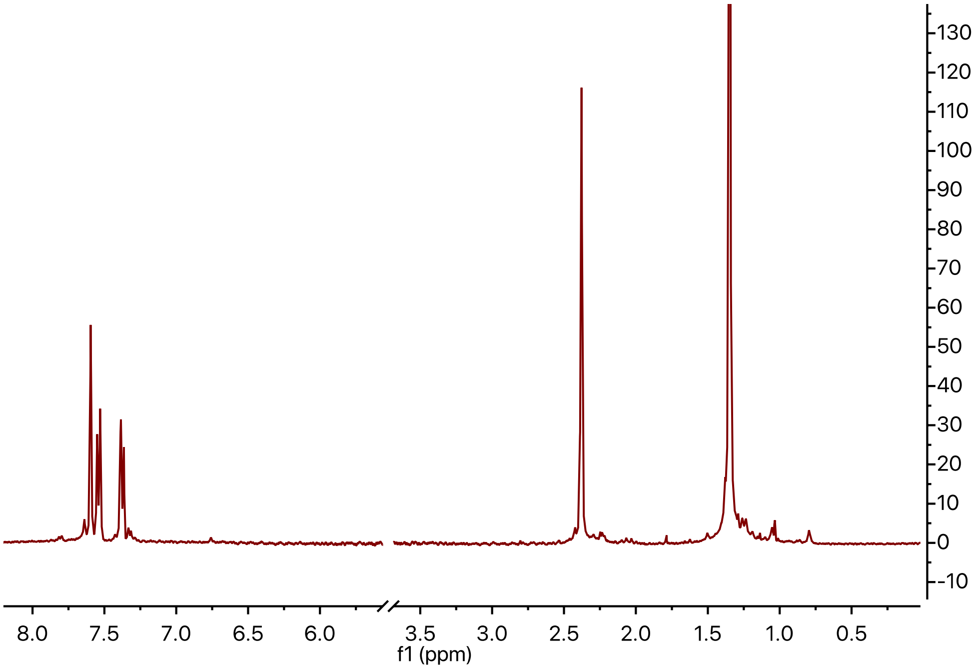


**Figure S10.** $^1$H NMR spectrum of cycled 0.5 M electrosynthesized **DPivOHAQ** when a stoichiometric quantity of hydroxide was added into the **DPivOHAC(COO$^-$)** solution (**Electrosynthesis V**). The solvent peak was removed to clearly show both aromatic and aliphatic regions of the cycled **DPivOHAQ** solution. The deuterated solvent is $D_2O$. The dominant 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 $^1$H NMR instrument.

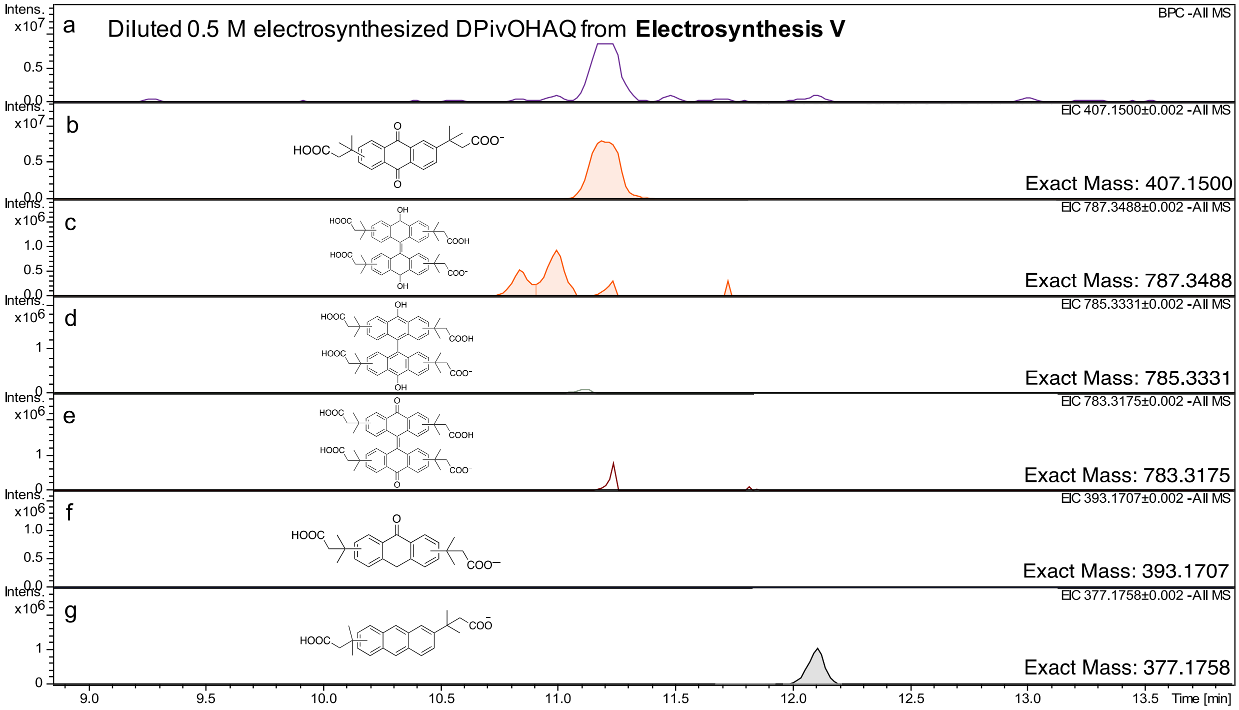
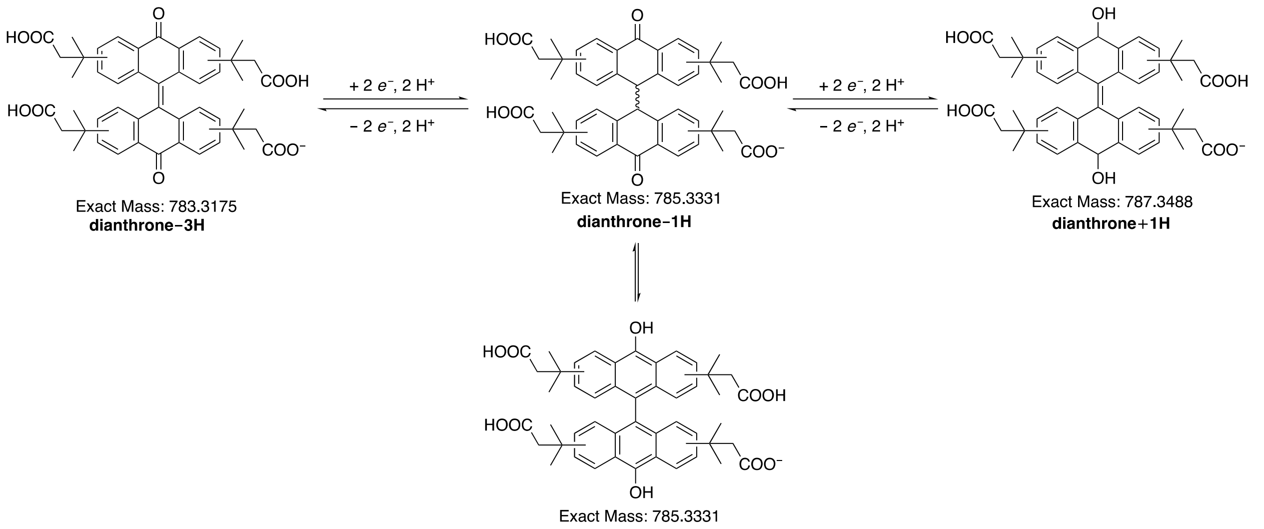
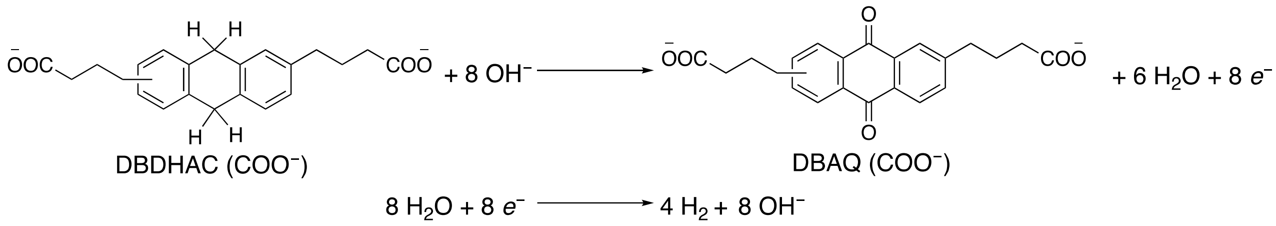


**Figure S11.** LC–MS results of cycled 0.5 M electrosynthesized **DPivOHAQ** when a stoichiometric quantity of hydroxide was added into the **DPivOHAC** solution (**Electrosynthesis V**). (a) The base peak chromatogram of the sample, showing all peaks observed by mass spectrometry under negative mode. (b) The peak intensity and retention time of **DPivOHAQ–1H** under negative mode. (c) The peak intensity and retention time of **dianthrone+1H** under negative mode. (d) The peak intensity and retention time of **dianthrone–1H** under negative mode. (e) The peak intensity and retention time of **dianthrone–3H** under negative mode. (f) The peak intensity 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), (c), (d), (e), (f) and (g), we found the percentages of **DPivOHAQ** (81.8%), **dianthrone+1H** (10.2%), **dianthrone–1H** (0.4%), **dianthrone–3H** (1.3%), and **DPivOHAC** (6.3%).



**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.

**Electrosynthesis VI.** Electrochemical synthesis of **DBAQ(COO$_{-}$)** in an undivided electrolytic cell at 0.1 M concentration, against the HER.



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 NaCl) as the reference electrode.

Electrolyte preparation: 0.35 g **DBDHAC**,[S2] 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.

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

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 coulombs were extracted from the working electrode. [0.1 M * 0.01 L * 96485 C/mol * 8 * 1.2 = 926.3 C; 8 electrons need to be extracted from every **DBDHAC** molecule].

Characterization of anolyte: an aliquot (250 µL) 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 **DBAQ** precipitate. The final **DBAQ** precipitate was re-dissolved in DMSO-$d_6$ for $^1$H NMR measurement. According to the integration of the $^1$H NMR spectrum in the Figure S12, the yield is 70%. The faradaic efficiency (%) = [yield (%) / 1.2] = 58.3%.

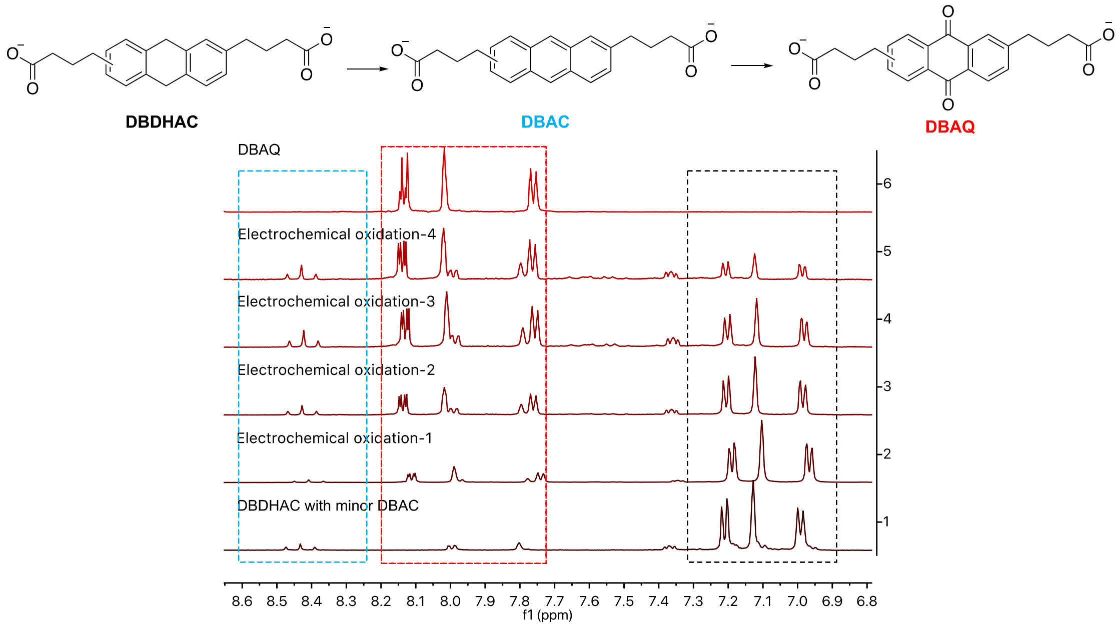


**Figure S12.** $^1$H NMR spectra of **DBDHAC** (bottom), chemically synthesized **DBAQ** (top), and electrochemically synthesized **DBAQ** in an undivided cell after varying extents of reaction. **DBDHAC**: 4,4'-(9,10-dihydroanthracene-diyl)dibutanoic acid; **DBAC:** 4,4'-(anthracene-diyl)dibutanoic 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-$d_6$.

## Light sensitivity experiments

It has been reported that quinones and related compounds can decompose in the presence of light.[S3-S7] In order to determine the light sensitivity of **DPivOHAQ** and **DBAQ**, we compared solutions of each compound held in the presence of and in the absence of light for 1 week. Two samples of **DPivOHAQ** (0.1 M, pH 12 in water with 1 M KCl, 1.5 mL each) and two samples of **DBAQ** (0.1 M, pH 12 in water, 1.5 mL each) were prepared in separate FEP bottles (VWR Catalog No. 16071-008). For each compound, one sample was wrapped in aluminum foil and stored in a 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 QL 1000Bulb). The samples exposed to light were allowed to float at the top of a water bath containing approximately 16 L of water to dissipate excess heat produced by the lamp (the liquid level decreased gradually due to evaporation and was replenished daily). The liquid level was maintained at a distance of approximately 20 cm from the light source.

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

**DPivOHAQ** sample exposed to light. $^1$H NMR spectra of each sample demonstrate decomposition of both compounds stored in the presence of light (Figures S14 and S15).

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

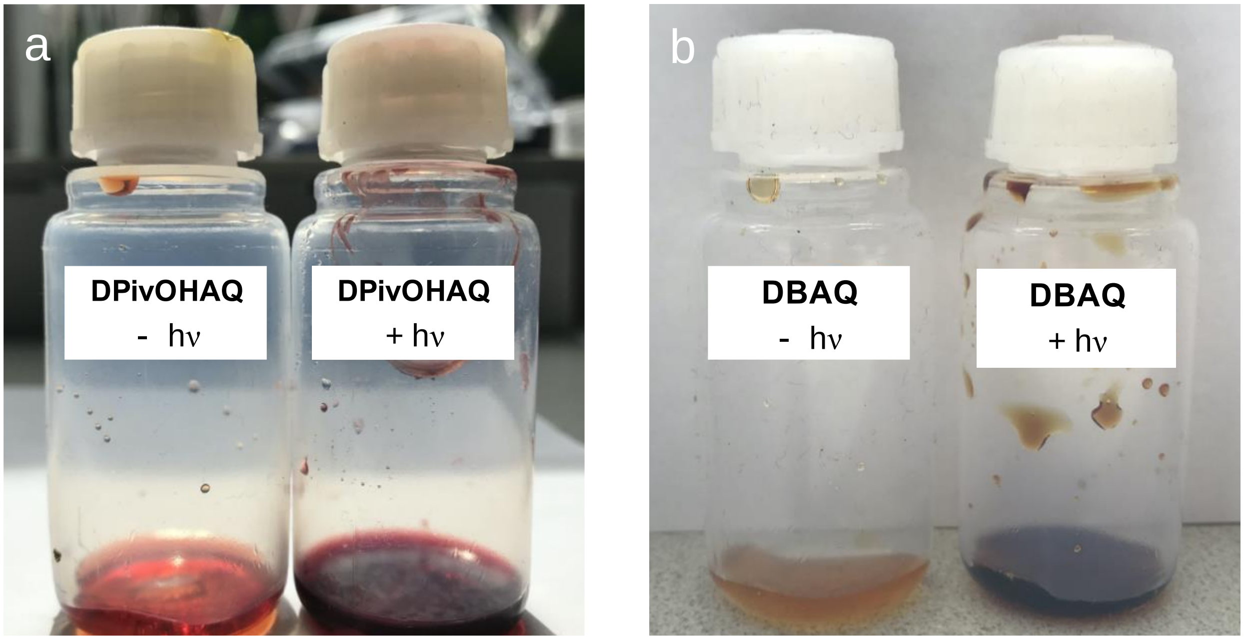


**Figure S13.** Samples of (a) **DPivOHAQ** (0.1 M, pH 12) stored for 1 week in the absence of light (– hν) and under a 500 W lamp (+ hν) and of (b) **DBAQ** (0.1 M, pH 12) stored for 1 week in the absence of light (– hν) and under a 500 W lamp (+ hν). Differences in color were observed between the two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

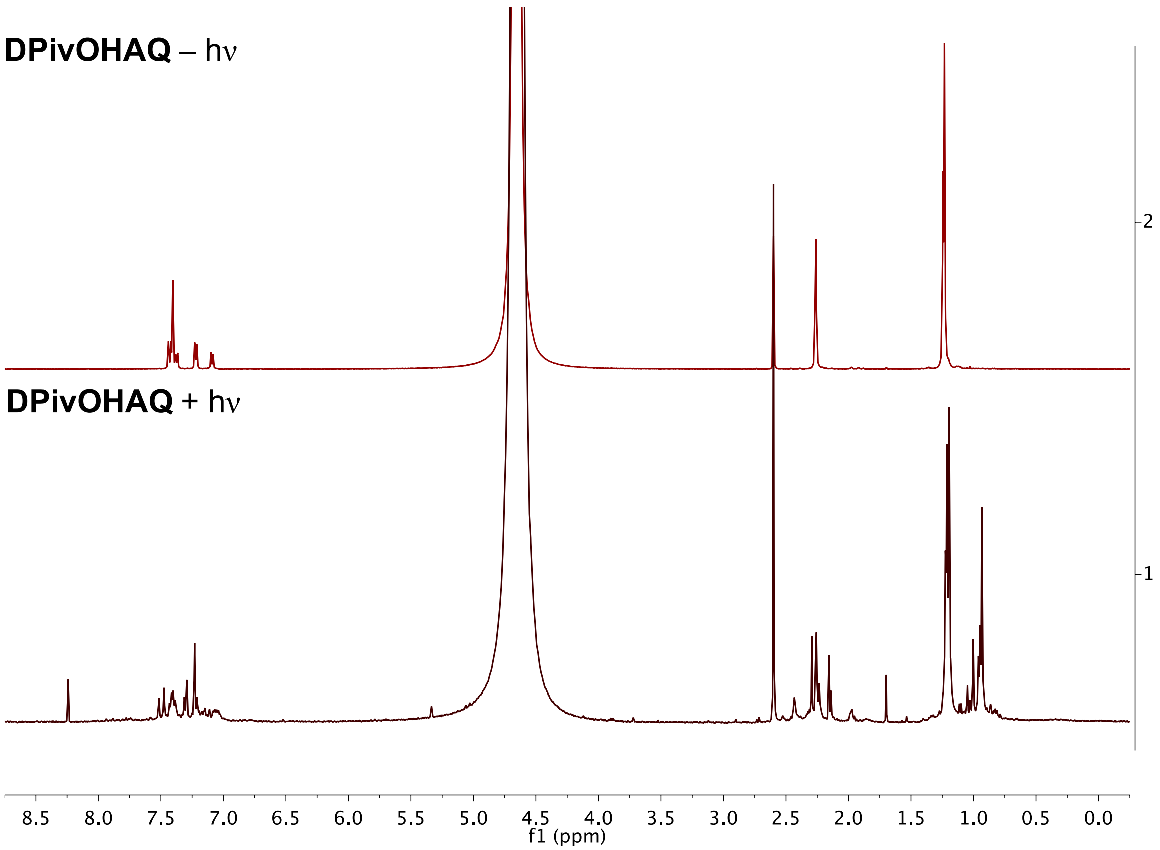


**Figure S14.** $^1$H NMR spectra of samples of **DPivOHAQ** (0.1 M, pH 12) stored for 1 week in the absence of light (– hν) and under a 500 W lamp (+ hν), each diluted (1:5.5) in pH 14 $D_2O$ (1 M KOD) containing a 9 mM $NaCH_3SO_3$ internal standard ($\delta$ 2.6 ppm).

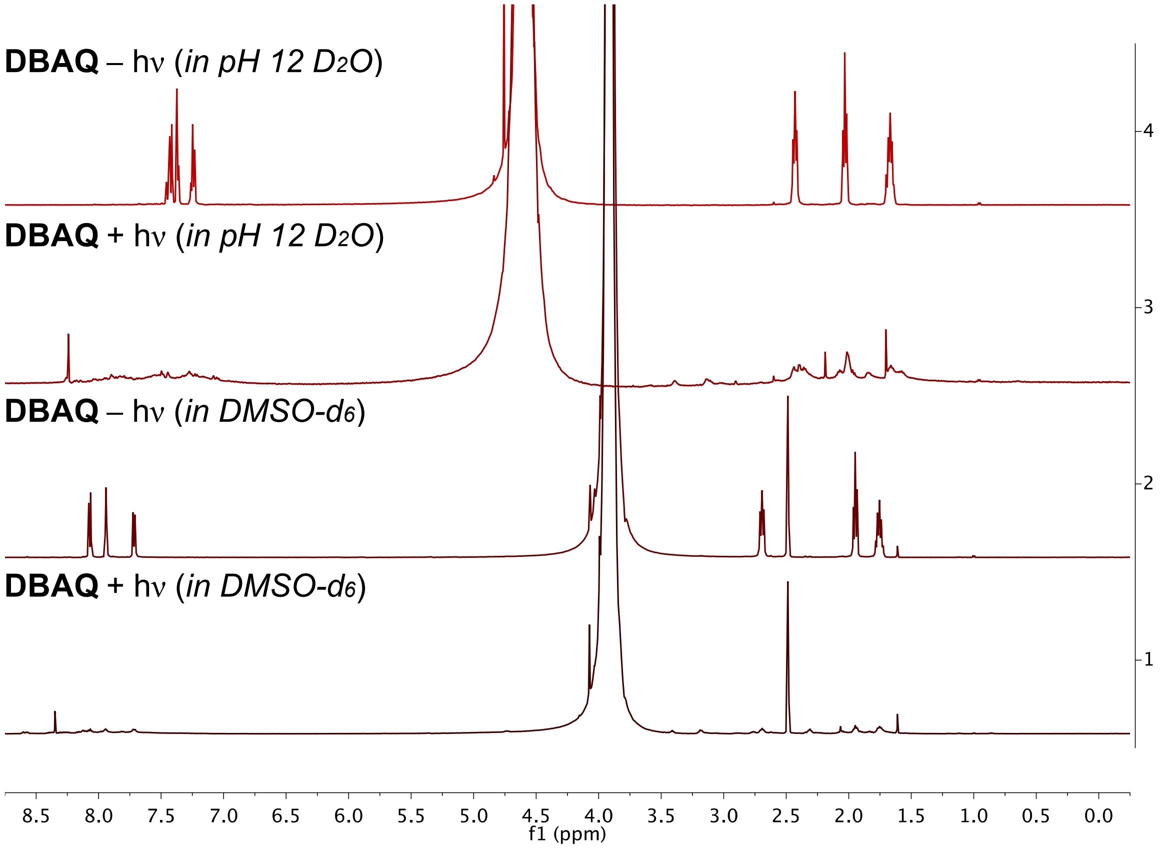
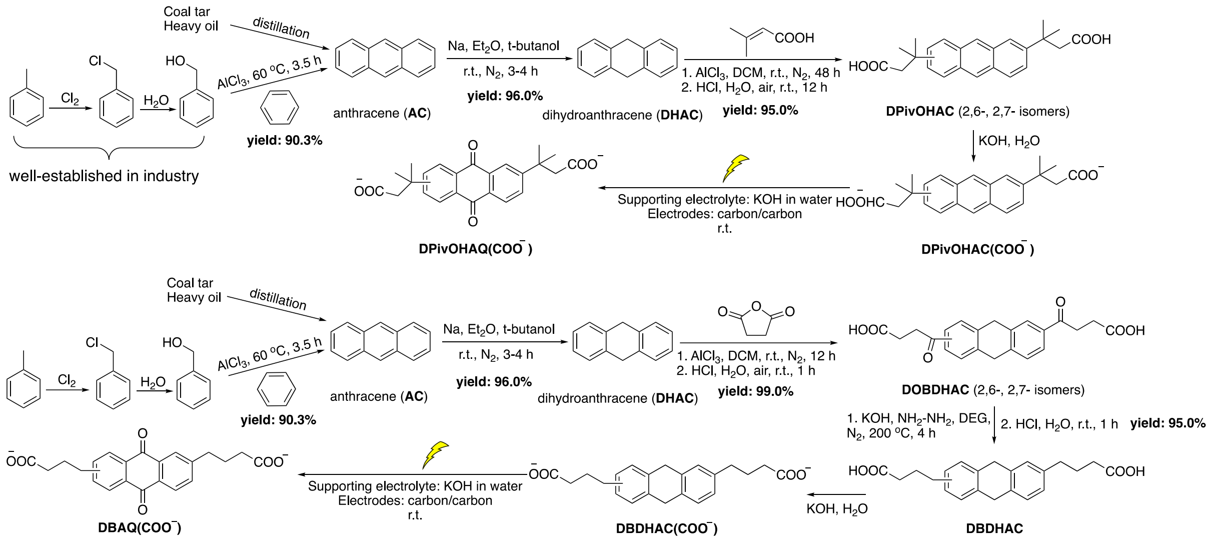


**Figure S15.** $^1$H NMR spectra of samples of **DBAQ** (0.1 M, pH 12) stored for 1 week in the absence of light (– h*ν*) and under a 500 W lamp (+ h*ν*), each diluted (1:5) in pH 12 $D_2O$ or in DMSO-$d_6$.

## Complete synthesis



**Scheme S3.** Complete synthetic routes, conditions, and yields of **DPivOHAQ** and **DBAQ** when commercially available commodity chemicals are used as starting materials.

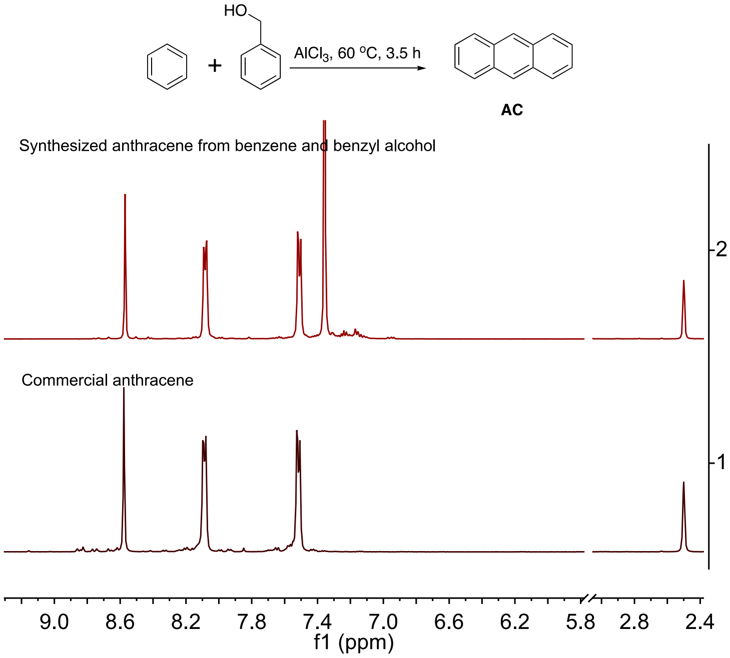


**Figure S16**. $_1$H NMR spectra of commercial and synthesized anthracene (**AC**) in DMSO-*d*6. The peak at 7.37 ppm in the synthesized **AC** spectrum is from benzene.

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