

Supplementary Information

**Electrochemical direct air capture of CO<sub>2</sub>  
using neutral red as reversible redox active material**

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## 1. Supplementary Methods

### 1.1. General Information

#### Material

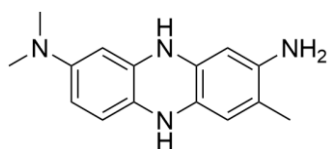
Commercially available chemicals were purchased from Sigma-Aldrich Chemical Company (Milwaukee, WI), Alfa Aesar (Ward Hill, MA), Acros Organics (Pittsburgh, PA), or TCI America (Portland, OR). All commercially available compounds were used as received. Ag/AgCl reference electrodes were purchased through BASi (West Lafayette, IN). CO<sub>2</sub> cylinders (1, 4, 15, and 100% balanced by nitrogen) were purchased from Airgas (Radnor Township, PA). Purified water was obtained using Milli-Q Direct Water Purification System.

#### Instrumentation

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra and carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were obtained on a Bruker 400 MHz NMR instrument (400 and 101 MHz, respectively). Chemical shifts for proton and carbon are reported in parts per million (ppm). The following designations are used to describe multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). The mass flow controller (GFCS-014657) and flow meter (GFMS-015835) was purchased from Aalborg Instruments & Controls, INC (Orangeburg, NY) and was calibrated for CO<sub>2</sub> by the vendor before use. The CO<sub>2</sub> FT-IR sensor (GC-0016 for 0–100%, GC-0006 for 0–20% of CO<sub>2</sub>) was purchased from CO2Meter (Ormond Beach, FL) and was calibrated for CO<sub>2</sub> before use. All cyclic voltammetry (CV) experiments were performed using PARSTAT MC (PMC-2000), from Ametek (Oak Ridge, TN). The UV-Vis Spectrophotometer (Cary 60) was purchased from Agilent (Santa Clara, CA). The experiments were carried out in a three-electrode cell configuration with a platinum working electrode and a platinum counter electrode. The potentials were measured versus Ag/AgCl in water. The pH was measured using a pH probe (Orion PerpHecT ROSS), which was calibrated prior to the experiment.

### 1.2. Procedure for extraction of reduced neutral red (NRH2)

The 4 mL aqueous solution of NRH2 was extracted with ethyl acetate (20 mL X 3 times). The combined organic layers were washed with water (20 mL X 5 times) to remove nicotinamide. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to afford NRH2 as a brown solid.



#### *N*<sup>2</sup>,*N*<sup>2</sup>,7-trimethyl-5,10-dihydrophenazine-2,8-diamine (NRH2)

<sup>1</sup>H NMR (400 MHz, DMSO) δ 7.81 (d, *J* = 9.5 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.46 (dd, *J* = 9.5, 2.8 Hz, 1H), 6.89 (s, 1H), 6.81 (d, *J* = 2.7 Hz, 1H), 5.99 (s, 2H), 3.10 (s, 6H), 2.33 (s, 3H). Minor peaks at δ 9.04, 8.69, 8.20, 8.16, 7.50 are from inseparable nicotinamide.

<sup>13</sup>C NMR (101 MHz, DMSO) δ 150.95, 150.61, 145.52, 145.22, 136.96, 135.84, 131.01, 129.98, 129.03, 119.76, 102.78, 102.55, 40.06, 18.12.

Minor peaks at δ 166.89, 152.36, 149.14, 135.60, 130.13, 123.87 are from inseparable nicotinamide

HRMS (DART+) *m/z* Calc. 255.1610 [C<sub>15</sub>H<sub>19</sub>N<sub>4</sub>]<sup>+</sup>, Found. 255.1604

### **1.3. Procedure for control experiment**

#### **Procedure for electrochemical reduction of 1 M NA solution without NR in batch**

Reactions were carried out with carbon felt (0.5 cm X 0.3 cm X 2 cm was immersed in the solution) cathode and a stainless steel wire anode in 5 mL H-cell with #9 O-ring equipped with anion exchange membrane. In the cathodic chamber, nicotinamide (488 mg, 4 mmol, 1 M) and lithium perchlorate (212 mg, 2 mmol, 0.5 M) were added into water (4.0 mL). In the anodic chamber equipped with a needle to prevent pressurization was placed lithium perchlorate solution (212 mg, 2 mmol, 0.5 M, 4.0 mL of water). The solution was bubbled with nitrogen for 10 min, after which the electrochemical potential was applied at room temperature by a constant current of  $-50$  mA for 696 s (0.36 mmol of electrons).

## 2. Supplementary Notes

### 2.1. Setup of NR/NRH2 redox system for the electrochemical CO<sub>2</sub> capture and release in batch

#### 2.1.1. General material information for electrochemical reaction setups in batch

1. 5 mL H-cell with #9 O-ring was purchased from Adams & Chittenden Scientific Glass Coop (Berkeley, CA).
2. Anion exchange membrane (Selemion AMV) was purchased from Asashi Glass (Japan).
3. Carbon felt (C100 AvCarb<sup>□</sup> Soft Carbon Felt) was purchased from Fuel Cell Earth (Stoneham, MA).
4. DC supply (SPD1168X) was purchased from Siglent (Ohio).

#### 2.1.2. Setup for the CO<sub>2</sub> release experiment in batch

We have used the identical setup as described in our previous work (see Figure S1 in supporting information).<sup>1</sup> An H-cell containing NRH2 solution that was saturated by CO<sub>2</sub> with C felt anode in the anodic chamber was connected to a DC power supply. The exiting gas stream from the anodic chamber was measured by a flow meter and FT-IR CO<sub>2</sub> sensor.

#### 2.1.3. Setup for the CO<sub>2</sub> absorption experiments in batch

We have used the identical setup as described in our previous work (see Figure S2 in supporting information).<sup>1</sup> Gas cylinder (1, 4, and 15% CO<sub>2</sub> balanced by nitrogen, Airgas<sup>®</sup>) was connected to mass flow controller and the gas stream was introduced to an 8 mL reaction vial containing an NRH2 solution. The exiting gas stream after mixing with the solution was measured by a flow meter and FT-IR CO<sub>2</sub> sensor.

### 2.2. Setup of NR/NRH2 redox system for the electrochemical CO<sub>2</sub> capture and release in continuous flow

#### 2.2.1. General material information for electrochemical reaction setups in continuous flow

1. 20 mL H-cell with #20 O-ring was purchased from Adams & Chittenden Scientific Glass Coop (Berkeley, CA).
2. Anion exchange membrane (Selemion AMV) was purchased from Asashi Glass (Japan).
3. Carbon felt (C100 AvCarb<sup>□</sup> Soft Carbon Felt) was purchased from Fuel Cell Earth (Stoneham, MA).
4. DC supply (SPD1168X) was purchased from Siglent (OH).
5. Clear Scratch- and UV-Resistant Cast Acrylic Sheet (7/16) was purchased from McMaster-Carr (Aurora, OH).
6. Titanium foil, 0.025mm (0.001in) thick, 99.94% (metals basis) was purchased from Thermo Scientific (Waltham, MA).
7. Silicone rubber sheet 0.125in thick was purchased from Rogers corporation (Chandler, AZ).
8. Peristaltic tubing (Masterflex Versilon Chemical (06475)–14) was purchased from Masterflex (Radnor, PA).
9. Tygon<sup>□</sup> tubing (ID 1/16in, OD 3/16in) was purchased from McMaster-Carr (Aurora, OH).
10. The peristaltic pump (Masterflex L/S) was purchased from Masterflex (Radnor, PA).
11. The syringe pump (Standard Infuse/Withdraw PHD ULTRA Syringe Pump) was purchased from Harvard Apparatus (Holliston, MA).

### 2.2.2. Setup for the electrochemical CO<sub>2</sub> capture and release in continuous flow

As shown in Supplementary Figure 6, a flow cell with C felt anode and cathode with an anion exchange membrane was connected to a DC power supply. The flow cell was connected to Tygon<sup>®</sup> tubing (ID 1/16in, OD 3/16in) at a liquid inlet (bottom) and outlet (top) of anodic and cathodic chambers (through hole 1/16in). A peristaltic pump was used to deliver the electrolyte solution from the catholyte and anolyte reservoirs. The distal end of the tubing system from the cathodic chamber was connected to the anolyte reservoir and the tubing from the anodic chamber to the catholyte reservoir. The 15% CO<sub>2</sub> gas cylinder was connected to tubing and its stream was metered by a mass flow controller (MFC). The 15% CO<sub>2</sub> stream was introduced to the catholyte solution. At the distal end of the outlet tubing from the headspace of the anolyte reservoir, an FT-IR CO<sub>2</sub> sensor and a flow meter were installed to monitor the output gas during continuous flow operation.

The above setup was used to direct air capture with the addition of a syringe pump to compensate for water evaporation due to vigorous bubbling of air into the catholyte solution and a pH probe to monitor the pH change in catholyte solution during the operation.

### 3. Supplementary Discussion

#### 3.1. Estimation of the hydroxide anion equivalent



$$\text{pH} = \text{pKa} + \log \frac{[\text{NR}]}{[\text{NRH}]} \quad (3)$$

$$n = \frac{2[\text{NR}] + [\text{NRH}]}{[\text{NR}] + [\text{NRH}]} = \frac{2 \cdot 10^{\text{pH} - \text{pKa}} + 1}{10^{\text{pH} - \text{pKa}} + 1} \quad (4)$$

**pKa = 6.8 for the equilibrium between NR and NRH**

**Anolyte tank pH range = 6.2 – 7.1**

$$n = 1.20 - 1.67$$

The two-electron reduction of the base form, NR, produces two equivalent of hydroxide anion (eq. 1) and the two-electron reduction of the acid form, NRH, produces one equivalent of hydroxide anion (eq. 2). The ratio of NR and NRH can be obtained from the measured pH value using the Henderson-Hasselbalch equation (eq. 3). The equivalent number ( $n$ ) of hydroxide anion to NR/NRH by the bulk electrochemical reduction can be calculated as in eq. 4. From the pH range of 6.2 – 7.1 of the anolyte tank, hydroxide anion would be 1.67 – 1.20 equivalents to NR/NRH based on the experimentally measured pH value of the oxidized solution.

#### 3.2. Energy calculation

$$E_{\text{cell}} = -E_{\text{p}}^{\text{red}} (\text{under N}_2) + E_{\text{p}}^{\text{oxi}} = 0.42 \text{ V} \quad (5)$$

1 eV = 96.49 kJ/mol, this corresponds to the Faraday constant ( $F = 96485 \text{ C/mol}$ ), where the energy in joules of  $n$  moles of particles each with energy  $E$  eV is equal to  $E \cdot F \cdot n$ .

The minimum energy requirement using 15% CO<sub>2</sub> in batch is:

$$E = E_{\text{cell}} \times 96.49 \text{ kJ/mol} \cdot \text{eV} \times (\varepsilon_{\text{CO}_2})^{-1} = 81 \text{ kJ/mole of CO}_2 \quad (6)$$

Where the average value of  $\varepsilon_{\text{CO}_2}$  for electron utilization is 0.50 in batch obtained in Figure 3b.

The minimum energy requirement using ambient air in batch is:

$$E = E_{\text{cell}} \times 96.49 \text{ kJ/mol} \cdot \text{eV} \times (\varepsilon_{\text{CO}_2})^{-1} = 123 \text{ kJ/mole of CO}_2 \quad (7)$$

Where the average value of  $\varepsilon_{\text{CO}_2}$  for electron utilization is 0.33 in batch obtained in Figure 5a.

$$E_{\text{cell}} = -E_{\text{p}}^{\text{red}} (\text{under CO}_2) + E_{\text{p}}^{\text{oxi}} = 0.26 \text{ V} \quad (8)$$

The minimum energy requirement using 15% CO<sub>2</sub> in continuous flow is:

$$E = E_{\text{cell}} \times 96.49 \text{ kJ/mol} \cdot \text{eV} \times (\varepsilon_{\text{CO}_2})^{-1} = 35 \text{ kJ/mole of CO}_2 \quad (9)$$

Where the highest value of  $\varepsilon_{\text{CO}_2}$  for electron utilization is 0.71 in continuous flow obtained in Figure 6c.

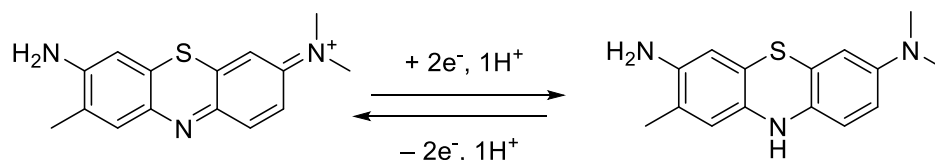
The minimum energy requirement using 15% CO<sub>2</sub> in continuous flow is:

$$E = E_{\text{cell}} \times 96.49 \text{ kJ/mol} \cdot \text{eV} \times (\epsilon_{\text{CO}_2})^{-1} = 65 \text{ kJ}_e/\text{mole of CO}_2 \quad (10)$$

Where the highest value of  $\epsilon_{\text{CO}_2}$  for electron utilization is 0.386 in continuous flow obtained in Figure 6e.

### 3.3. Evaluation of other dye molecules as redox-active compounds

#### 3.3.1. Toluidine blue



Electrochemical reduction

$$E_p^{\text{red}} = -0.233 \text{ V under N}_2 \text{ vs Ag/AgCl}$$

$$E_p^{\text{red}} = -0.202 \text{ V under CO}_2 \text{ vs Ag/AgCl}$$

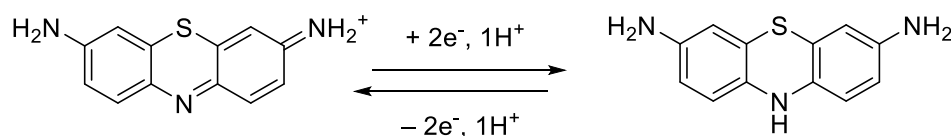
Electrochemical oxidation

$$E_p^{\text{oxi}} = -0.144 \text{ V under CO}_2 \text{ vs Ag/AgCl}$$

$$E_{\text{cell}} = -E_p^{\text{red}}(\text{under N}_2) + E_p^{\text{oxi}}(\text{under CO}_2) = 0.089 \text{ V}$$

Rapid reoxidation of the reduced form of toluidine blue when contacting air was observed.

#### 3.3.2. Thionin



Electrochemical reduction

$$E_p^{\text{red}} = -0.233 \text{ V under N}_2 \text{ vs Ag/AgCl}$$

$$E_p^{\text{red}} = -0.240 \text{ and } -0.304 \text{ V under CO}_2 \text{ vs Ag/AgCl}$$

Electrochemical oxidation

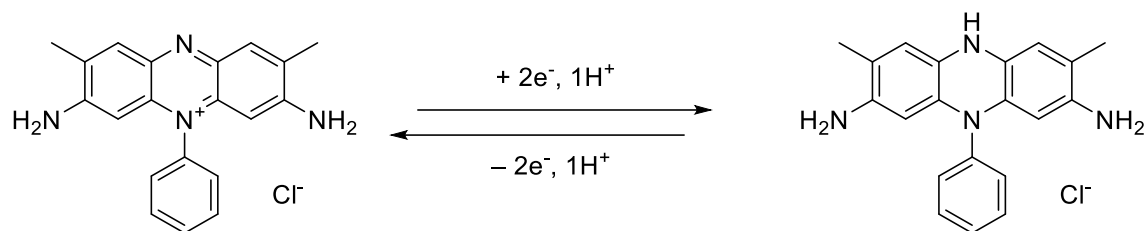
$$E_p^{\text{oxi}} = -0.072 \text{ V under CO}_2 \text{ vs Ag/AgCl}$$

$$E_{\text{cell}} = -E_p^{\text{red}}(\text{under N}_2) + E_p^{\text{oxi}}(\text{under CO}_2) = 0.232 \text{ V}$$

Rapid reoxidation of the reduced form of thionin when contacting air was observed.



### 3.3.3. Safranin O



Electrochemical reduction

$$E_p^{\text{red}} = -0.443 \text{ and } -0.552 \text{ V under } N_2 \text{ vs Ag/AgCl}$$

$$E_p^{\text{red}} = -0.369 \text{ and } -0.485 \text{ V under } CO_2 \text{ vs Ag/AgCl}$$

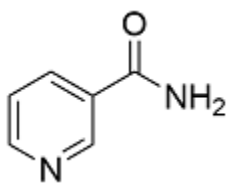
Electrochemical oxidation

$$E_p^{\text{oxi}} = -0.424 \text{ and } -0.303 \text{ V under } CO_2 \text{ vs Ag/AgCl}$$

$$E_{\text{cell}} = -E_p^{\text{red}}(\text{under } N_2) + E_p^{\text{oxi}}(\text{under } CO_2) = 0.249 \text{ V}$$

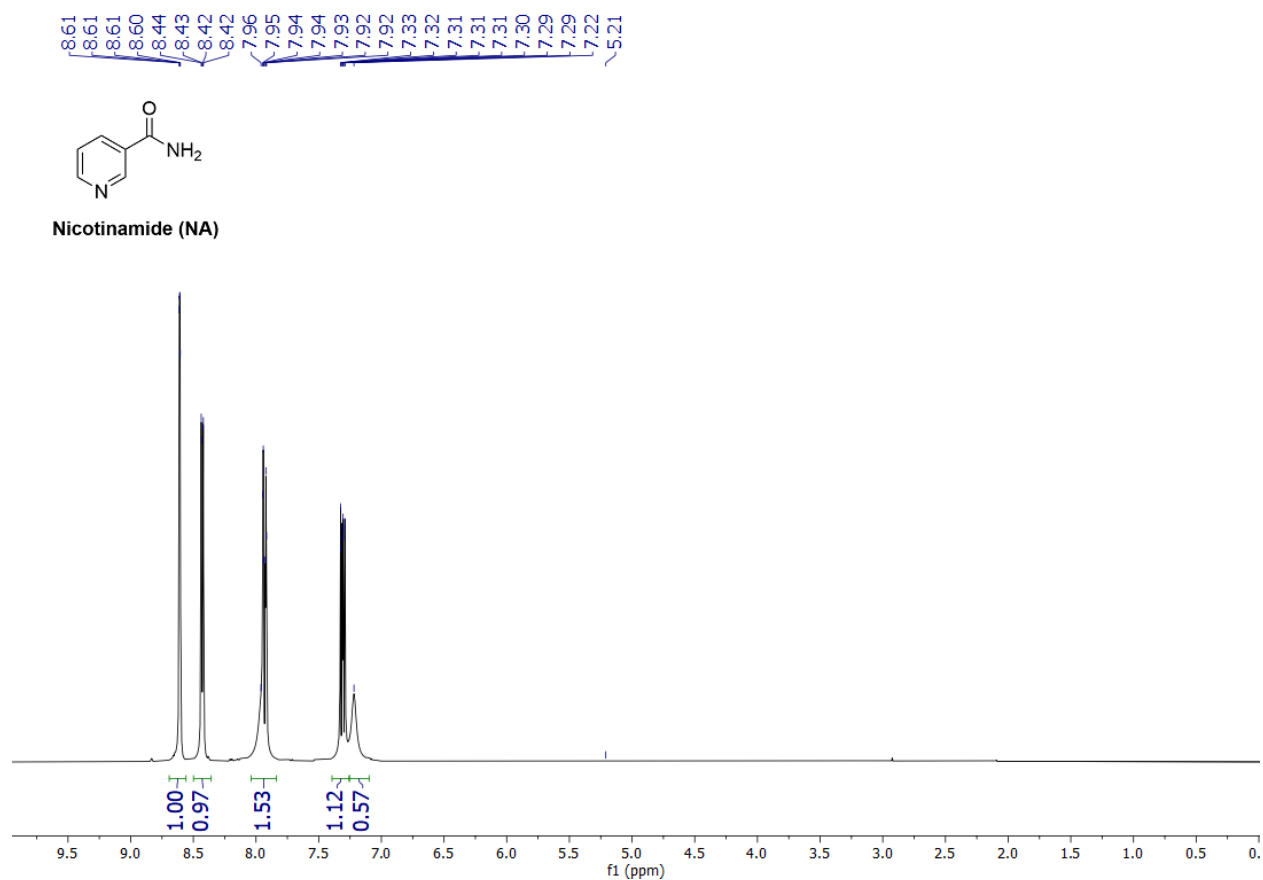
Low solubility (< 5 mM) was observed in the presence of 1 M NA as a hydrotropic agent.

#### 4. Supplementary Figures

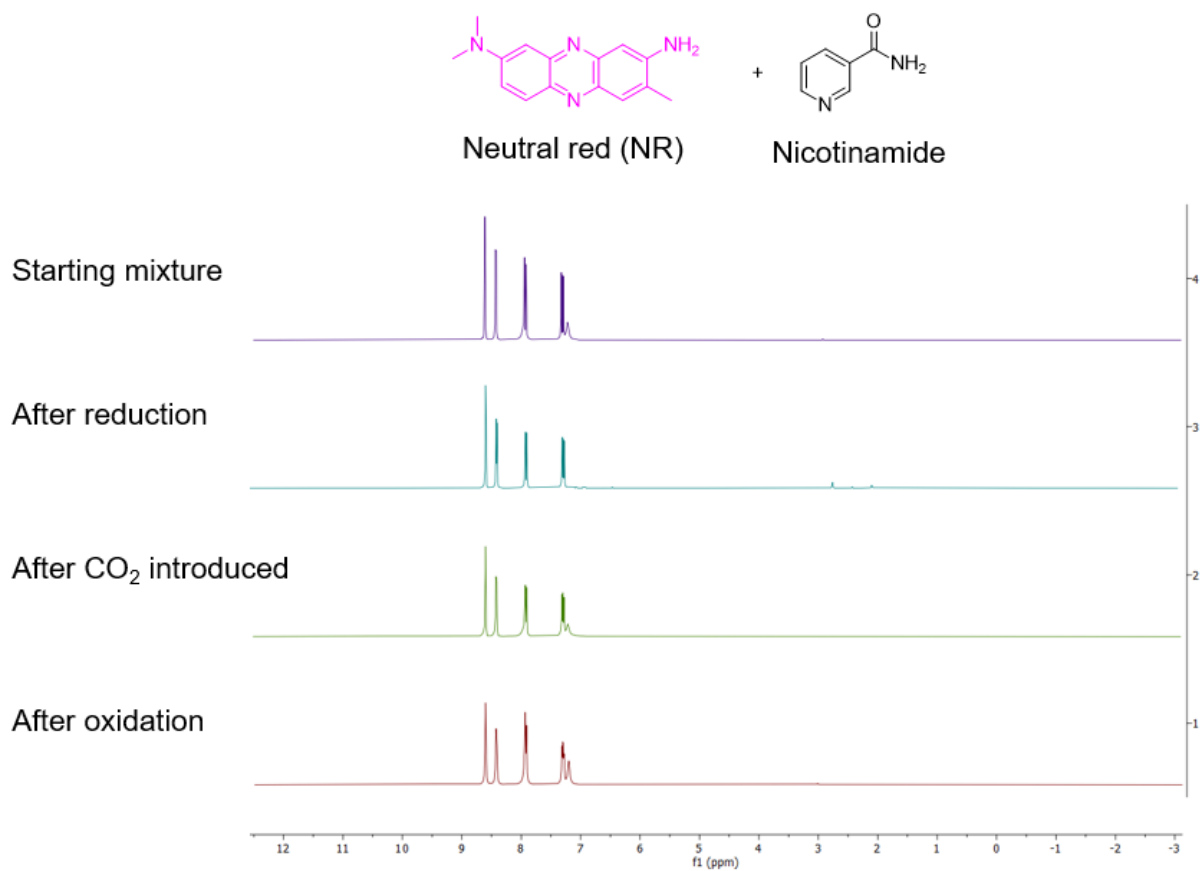


#### Nicotinamide (NA)

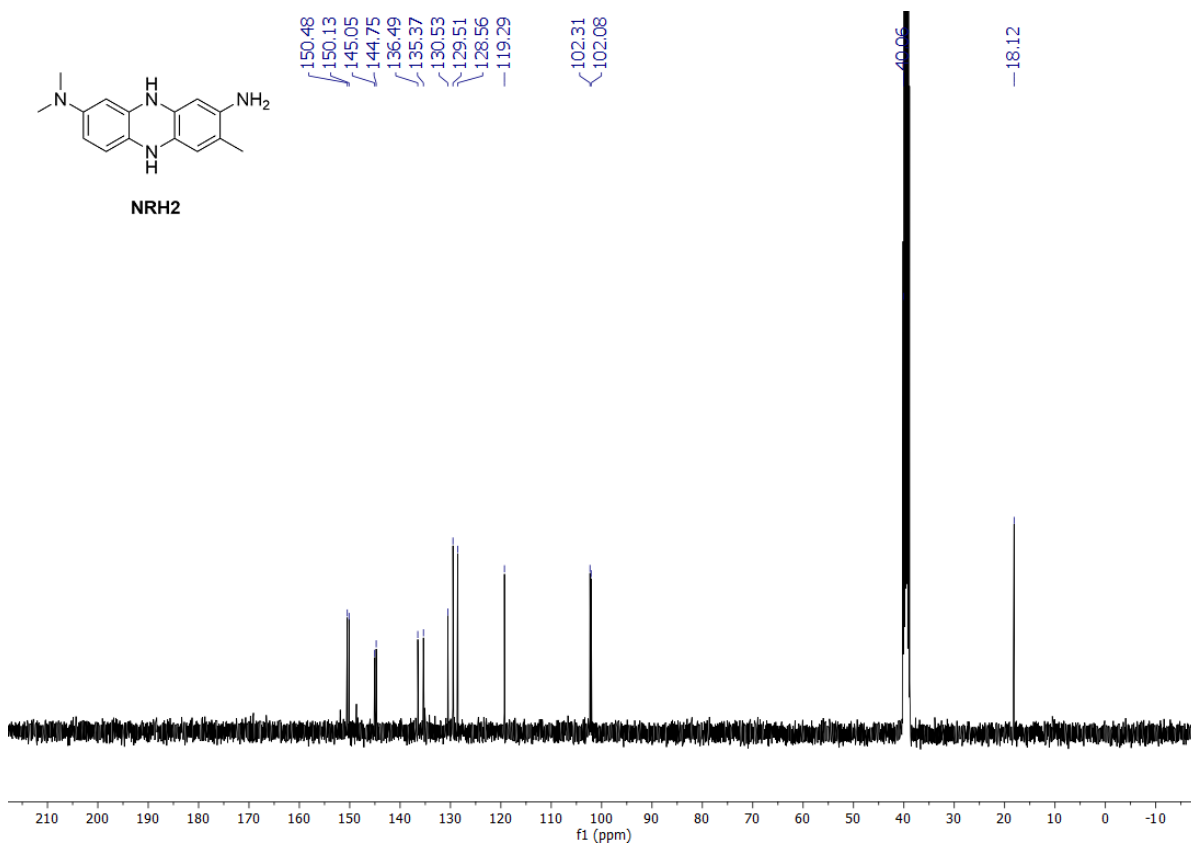
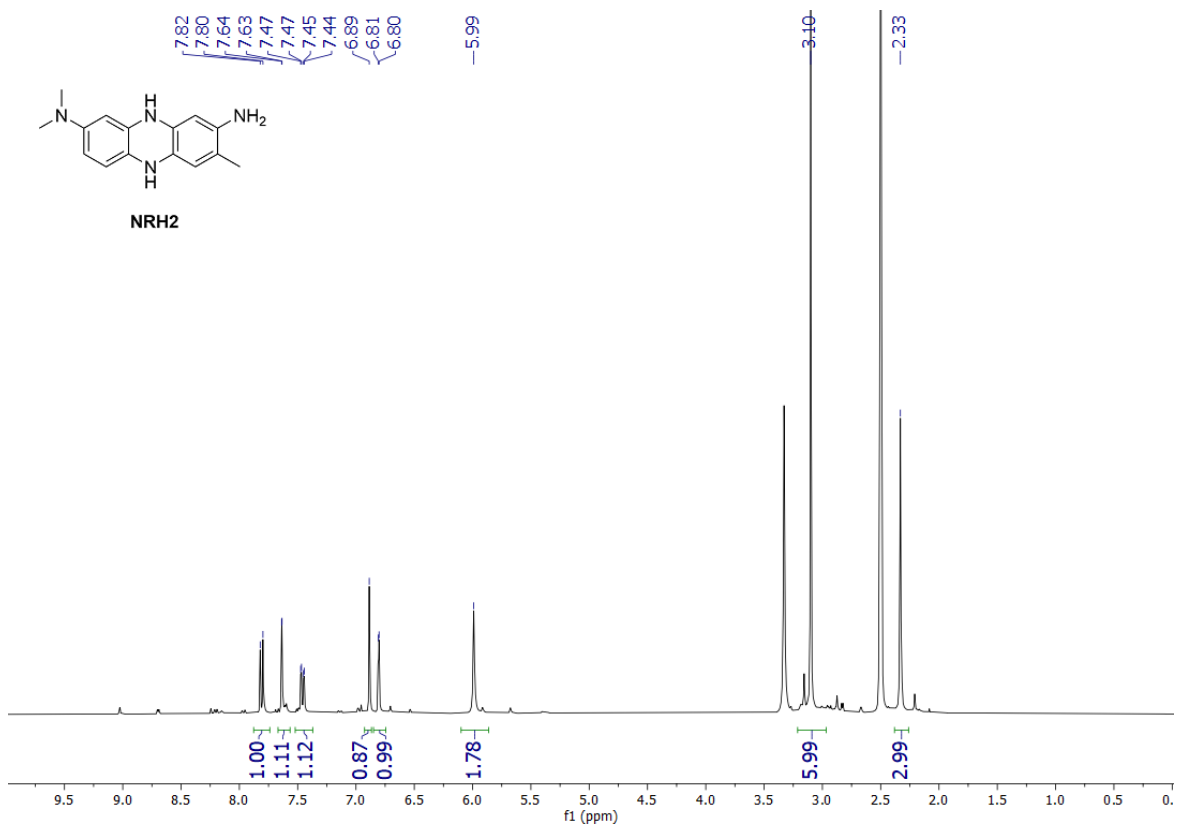
$^1\text{H}$  NMR (400 MHz,  $\text{H}_2\text{O}+\text{D}_2\text{O}$ \_salt)  $\delta$  8.61 (dd,  $J = 2.3, 0.9$  Hz, 1H), 8.43 (dd,  $J = 5.1, 1.7$  Hz, 1H), 7.97 – 7.89 (m, 1H), 7.31 (ddd,  $J = 8.1, 5.1, 0.9$  Hz, 1H), 7.22 (s, 1H).



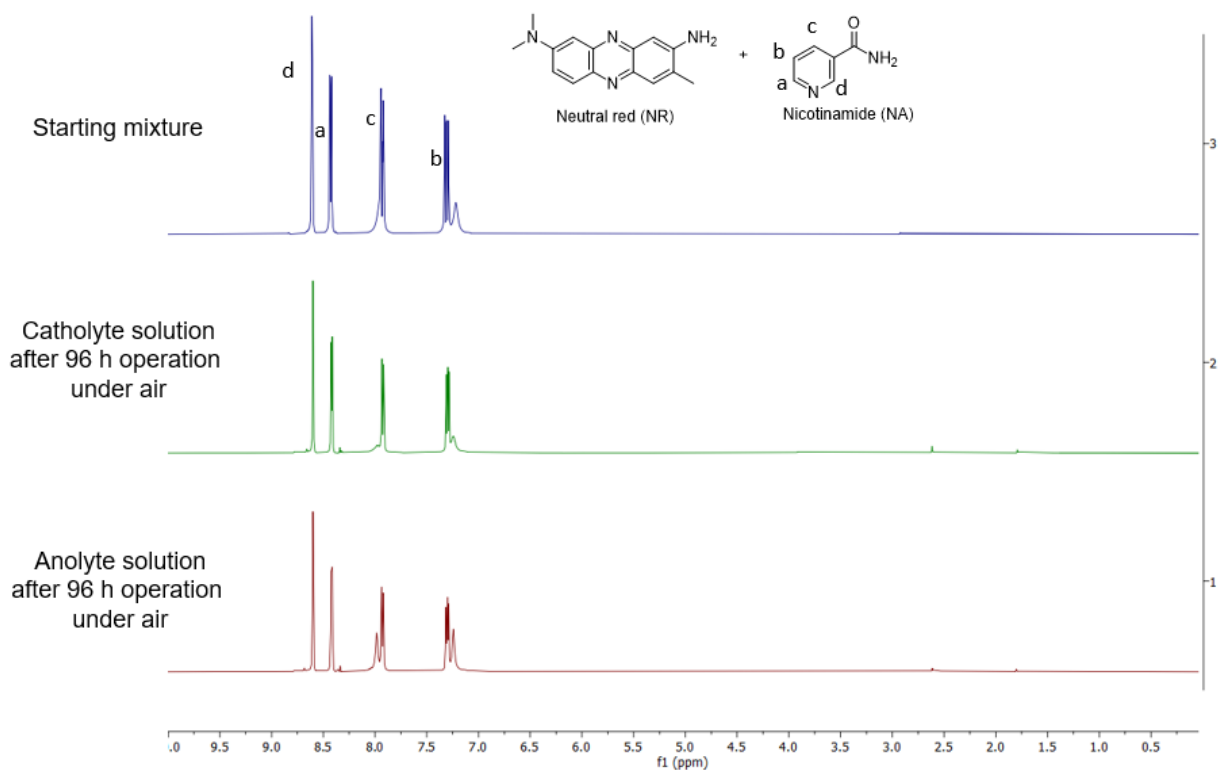
Supplementary Figure 1. H-NMR spectrum of nicotinamide in  $\text{H}_2\text{O}+\text{D}_2\text{O}$



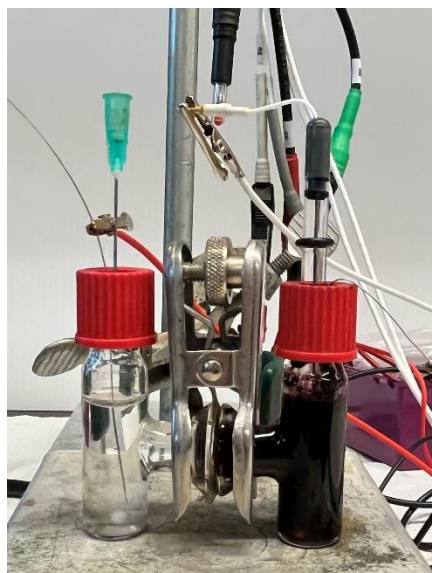
**Supplementary Figure 2.** <sup>1</sup>H-NMR spectra of the electrolyte solution of the starting material mixture, after electrochemical reduction, after CO<sub>2</sub> introduced to the solution, and after electrochemical oxidation.



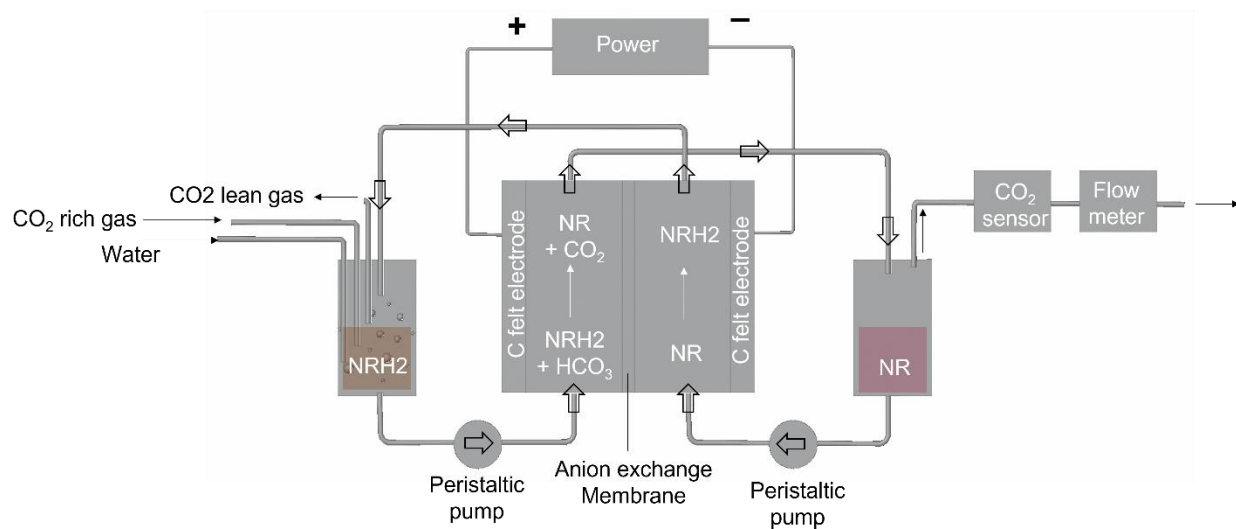
Supplementary Figure 3. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of NRH2 in DMSO



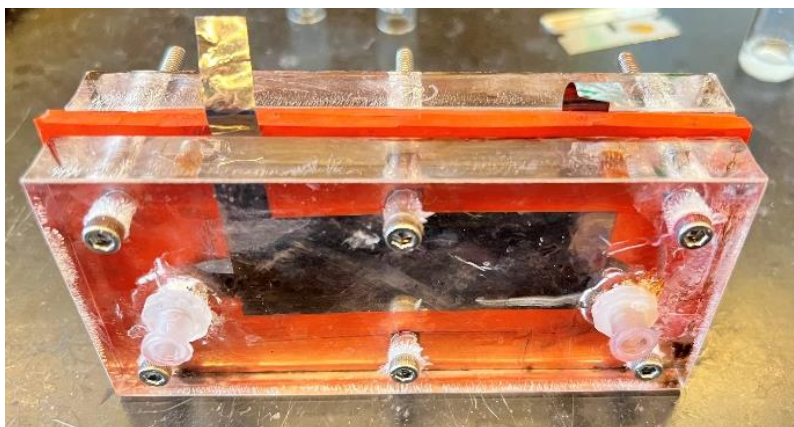
**Supplementary Figure 4.**  $^1\text{H}$  NMR spectra were collected after 96 hours of operation under air confirming redox resistance of nicotinamide under the current conditions.



**Supplementary Figure 5.** Picture of H-cell



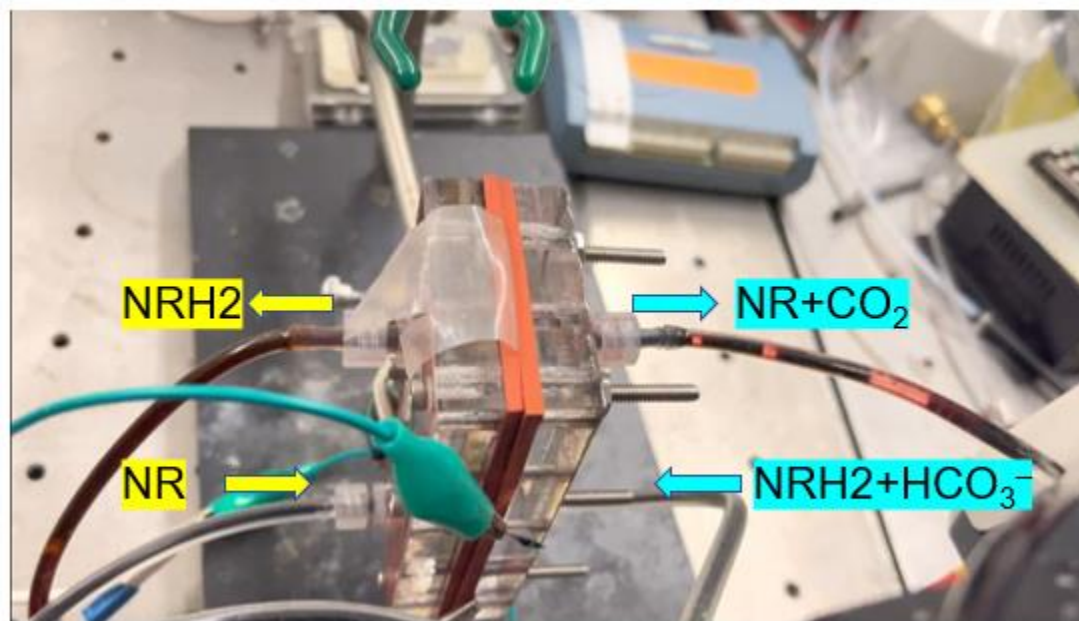
**Supplementary Figure 6.** Scheme of continuous flow electrochemical cell using NR/NRH<sub>2</sub> redox cycle for CO<sub>2</sub> capture and release experiments.



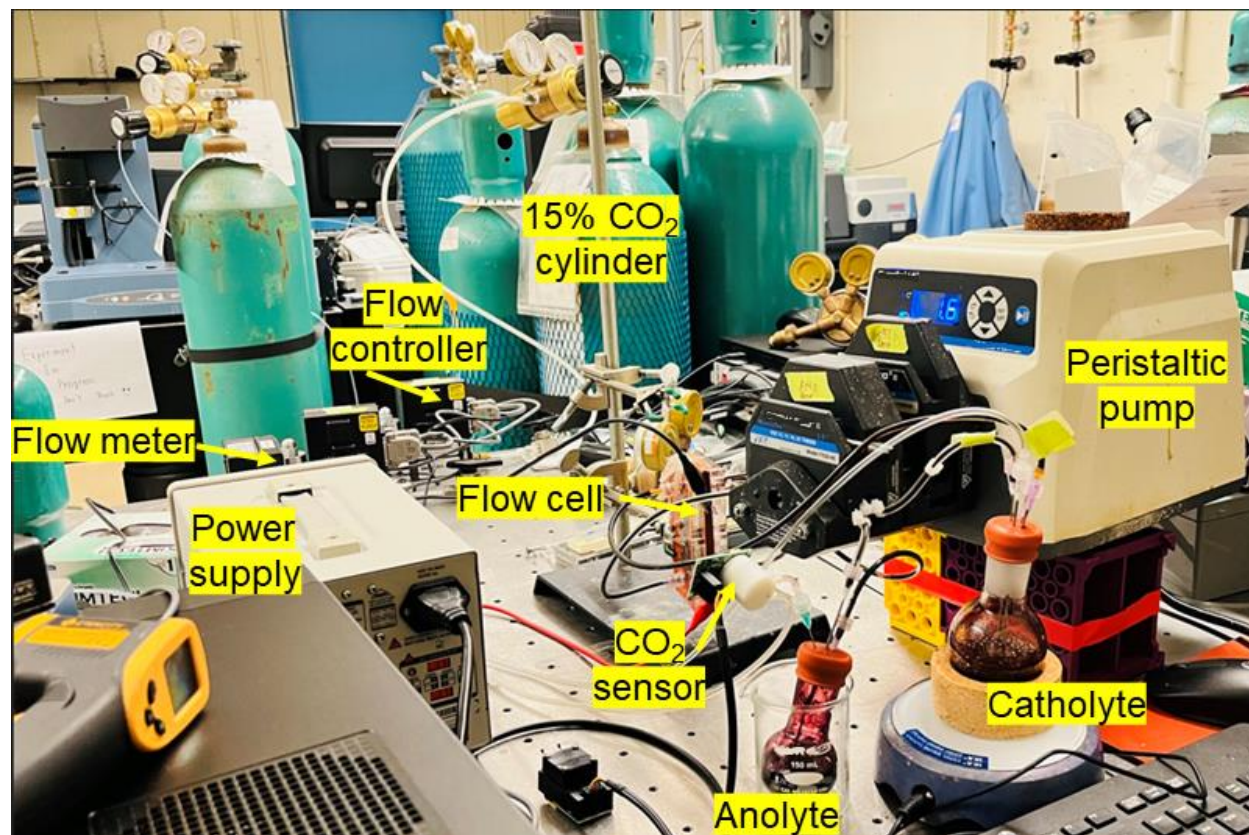
**Supplementary Figure 7.** Photograph of the assembled flow cell.



Supplementary Figure 8. Photograph of the flow cell.

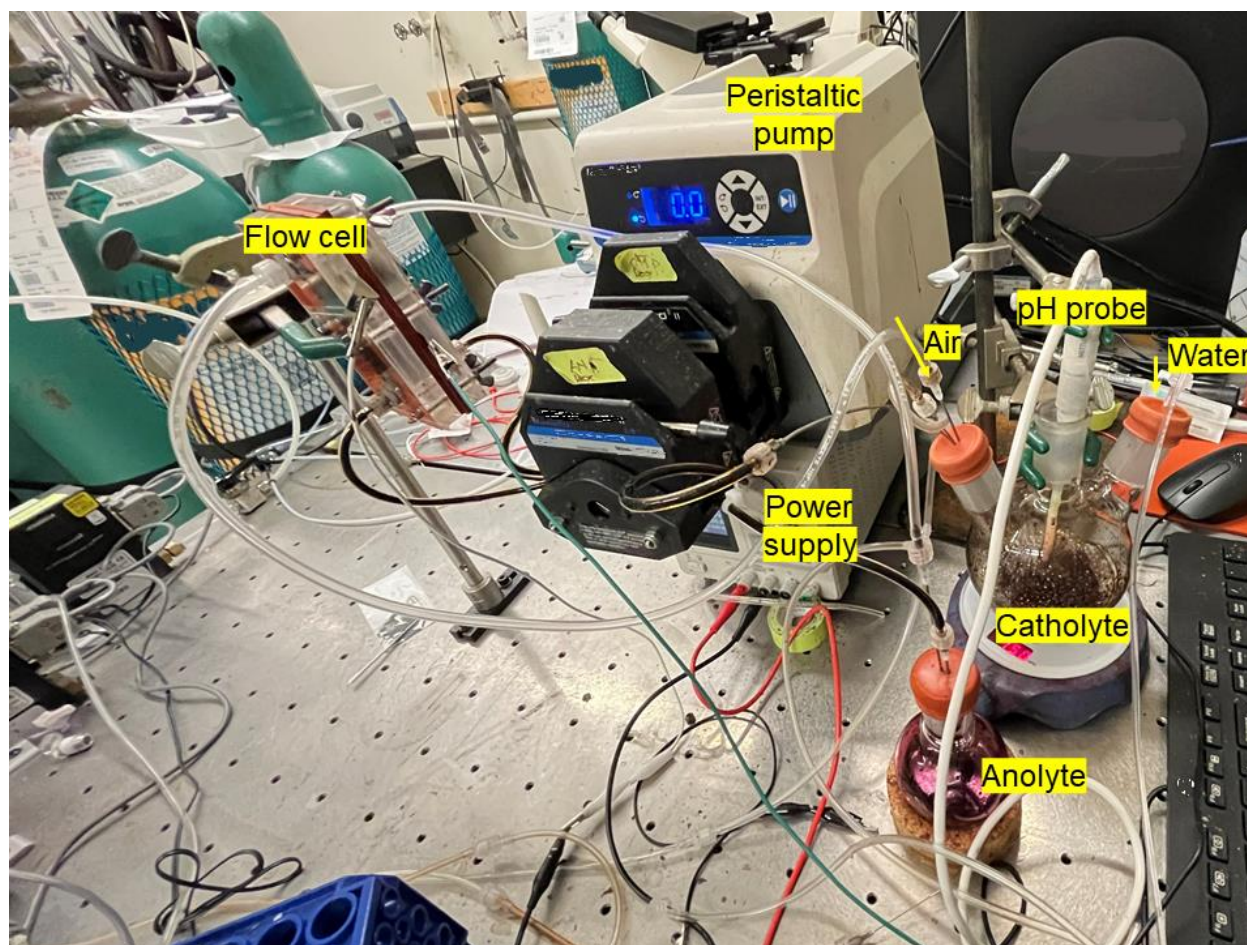


Supplementary Figure 9. Photograph of the flow cell during operation.

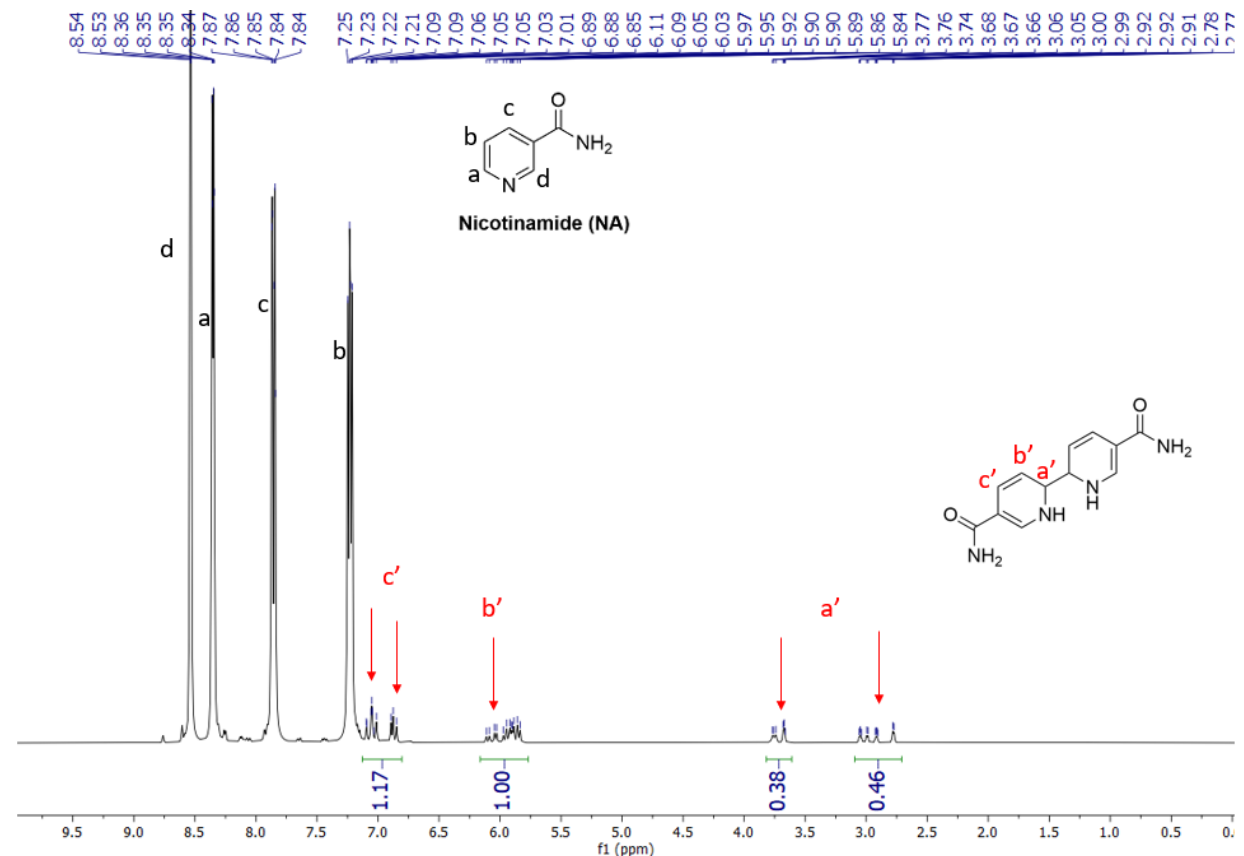


**Supplementary Figure 10.** Photograph of setup for electrochemical capture and release of CO<sub>2</sub> in continuous flow using 15% CO<sub>2</sub>.

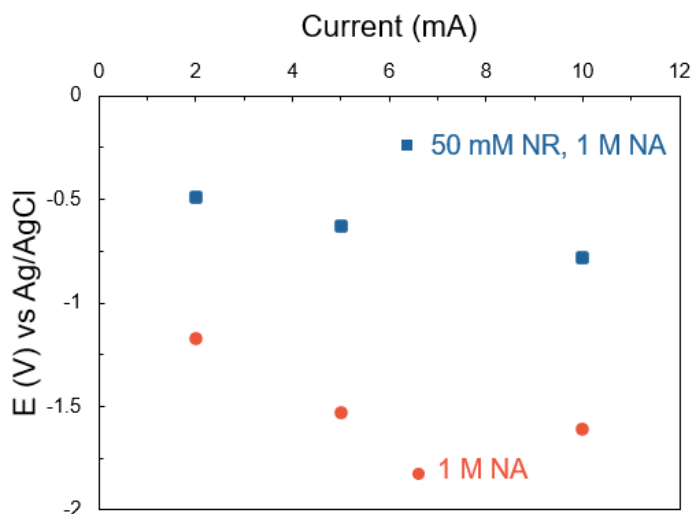




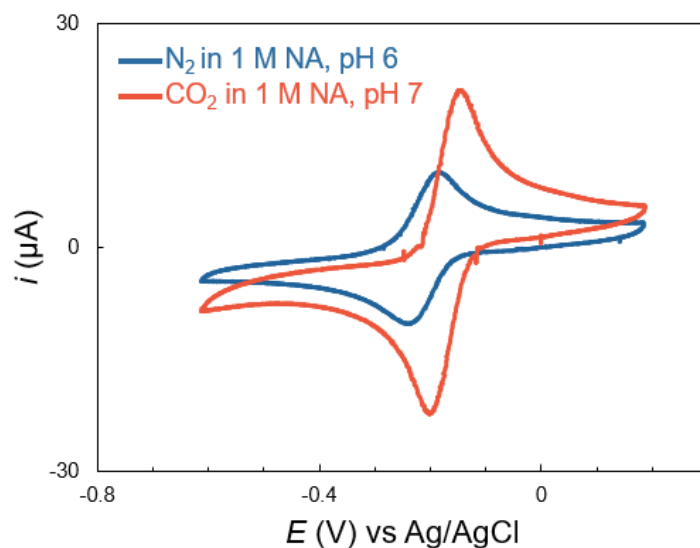
**Supplementary Figure 11.** Photograph of setup for electrochemical capture and release of CO<sub>2</sub> in continuous flow from the air.



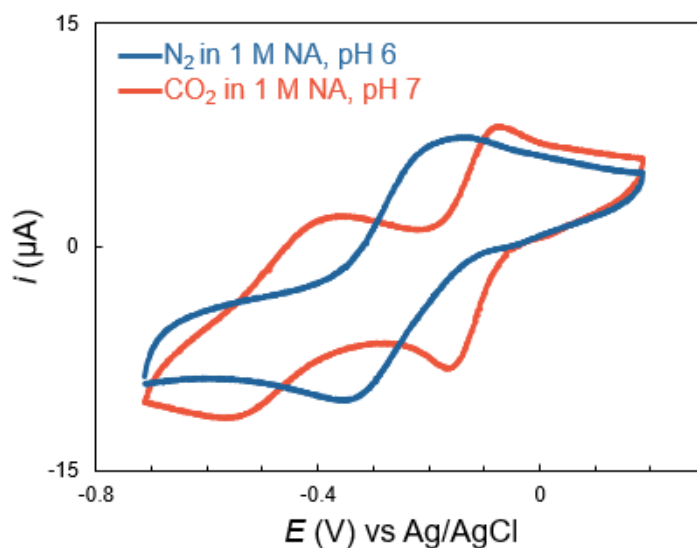
**Supplementary Figure 12.** <sup>1</sup>H-NMR spectra of the solution after reduction of the solution containing 1 M NA and 0.5 M LiClO<sub>4</sub>.



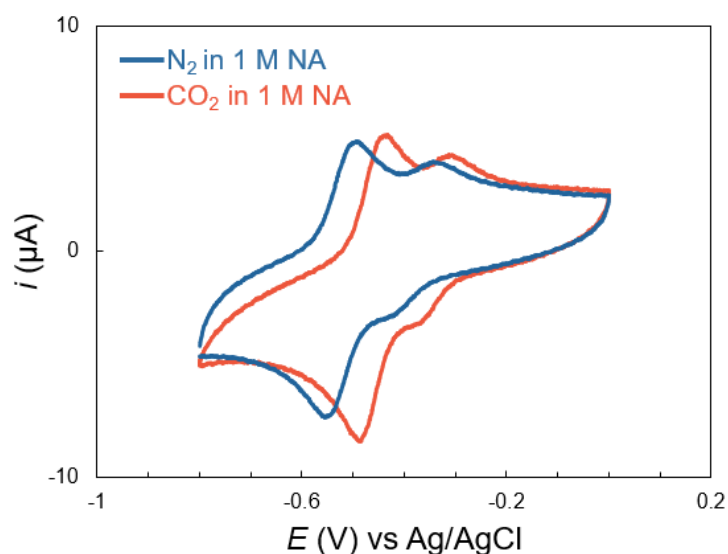
**Supplementary Figure 13.** Applied potentials vs Ag/AgCl of the solution containing 50 mM NR, 1 M NA, and 1 M KCl in water (blue squares), and 1 M NA and 1 M KCl in water (red dots) at constant currents of 2 mA, 5 mA, and 10 mA. The potential was recorded after 180 seconds of operation. Carbon felt (0.5 cm X 0.3 cm X 2 cm immersed in the solution) was used as a working electrode.



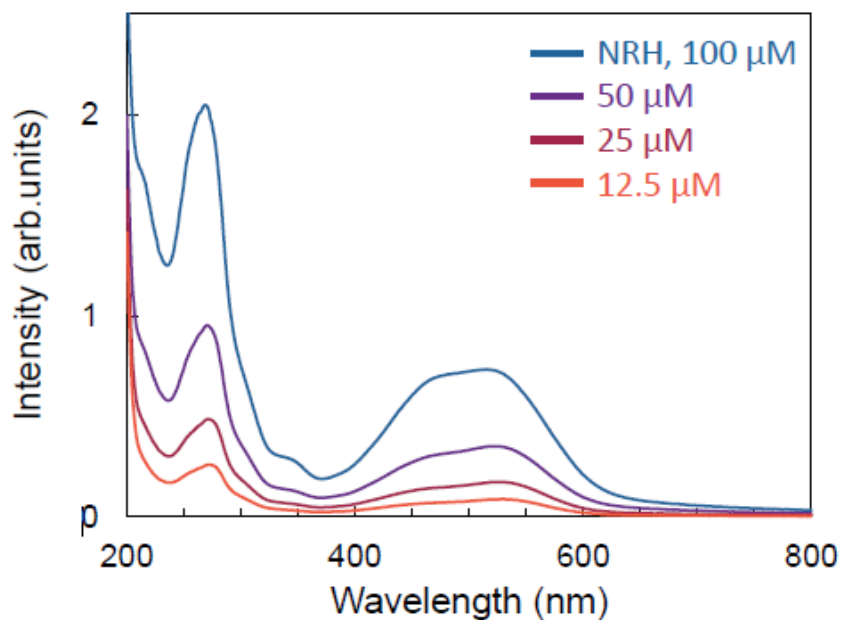
**Supplementary Figure 14.** The cyclic voltammograms of 10 mM of toluidine blue under nitrogen (blue curve) and CO<sub>2</sub> (red curve) in water with 0.1 M lithium perchlorate as a supporting electrolyte and 1 M nicotinamide as a hydrotropic agent. All CV curves were recorded at room temperature, with a glassy carbon working electrode, at a scan rate of 50 mV/s. Potentials were recorded versus Ag/AgCl as a reference electrode.



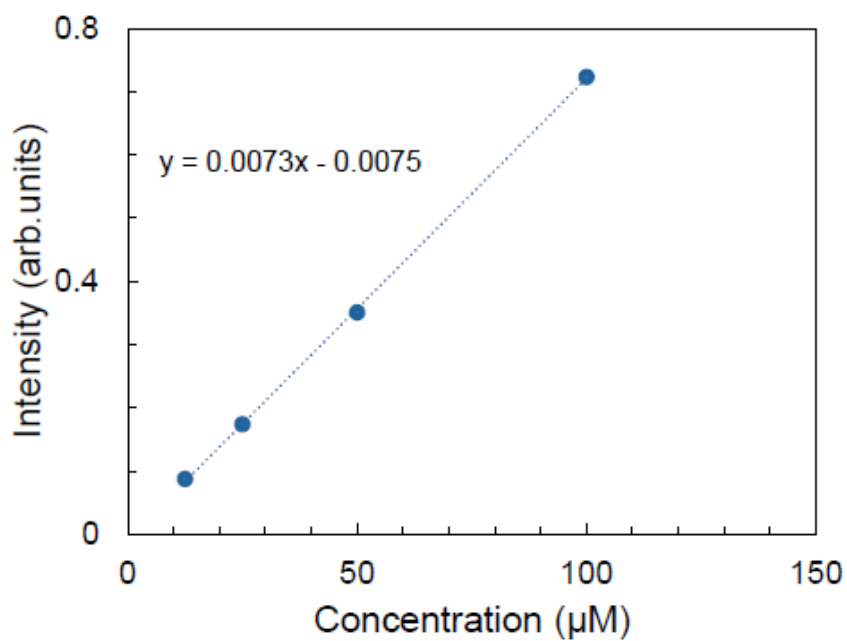
**Supplementary Figure 15.** The cyclic voltammograms of 10 mM of thionin under nitrogen (blue curve) and CO<sub>2</sub> (red curve) in water with 0.1 M lithium perchlorate as a supporting electrolyte and 1 M nicotinamide as a hydrotropic agent. All CV curves were recorded at room temperature, with a glassy carbon working electrode, at a scan rate of 50 mV/s. Potentials were recorded versus Ag/AgCl as a reference electrode.



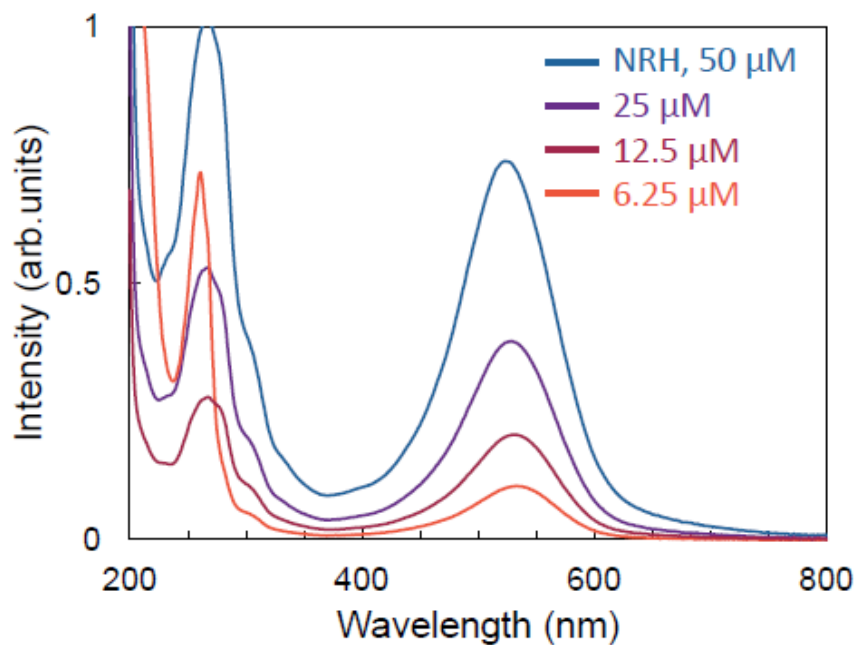
**Supplementary Figure 16.** The cyclic voltammograms of 5 mM of Safranin O under nitrogen (blue curve) and CO<sub>2</sub> (red curve) in water with 0.1 M lithium perchlorate as a supporting electrolyte and 1 M nicotinamide as a hydrotropic agent. All CV curves were recorded at room temperature, with a glassy carbon working electrode, at a scan rate of 50 mV/s. Potentials were recorded versus Ag/AgCl as a reference electrode.



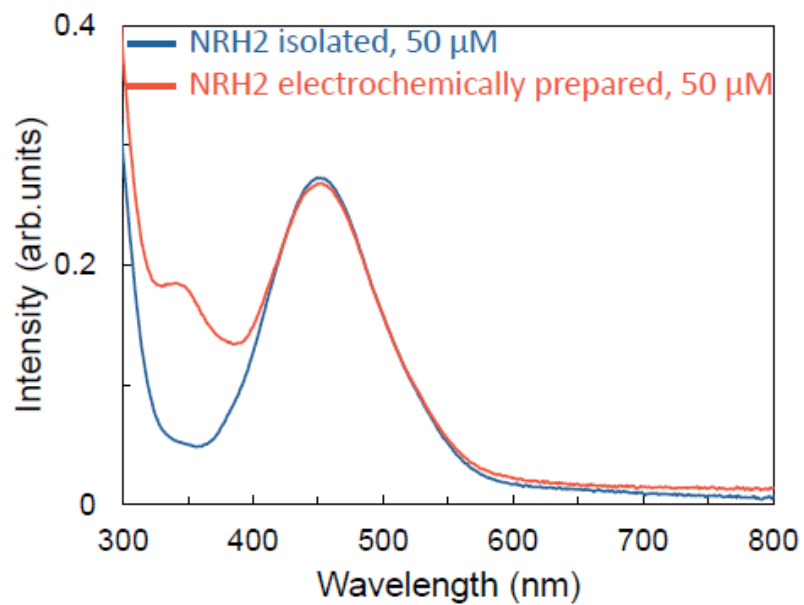
**Supplementary Figure 17.** UV-vis absorption spectroscopy of NRH aqueous solution in pH 6.6 phosphate buffer. Peaks at 525 nm are from the acid form, NRH, and peaks at 460 nm from the base form, NR.



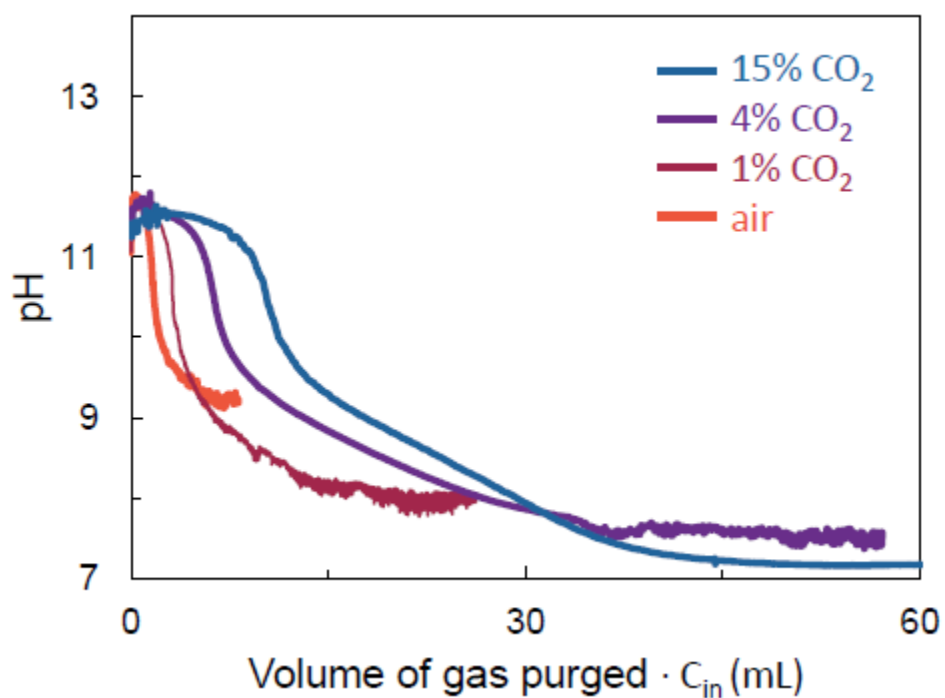
**Supplementary Figure 18.** Plot between NRH concentration and the UV-vis peak intensity at 525 nm.



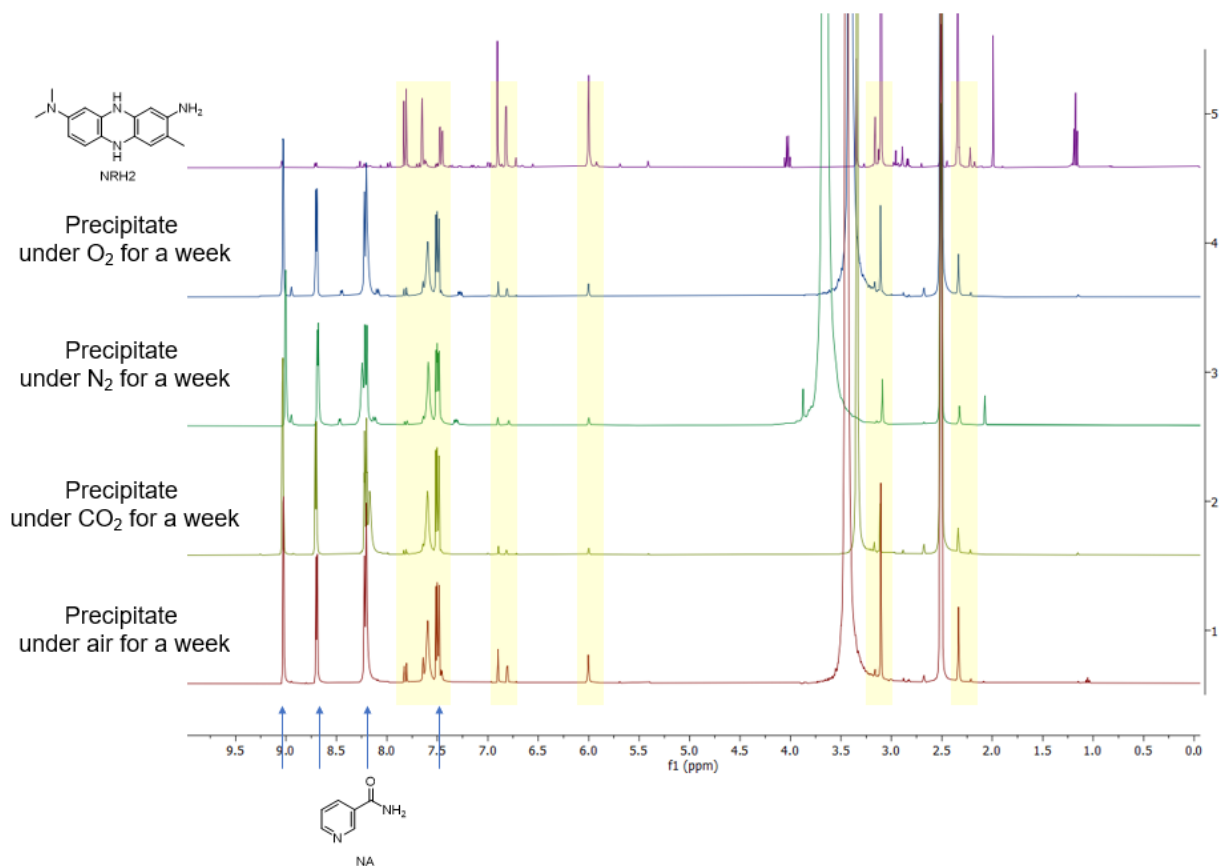
**Supplementary Figure 19.** UV-vis absorption spectroscopy of NRH aqueous solution in pH 1.3. Peaks at 525 nm show higher intensities than those measured in pH 6.6 (Supplementary Figure 17) with no peak at 460 nm.



**Supplementary Figure 20.** UV-vis absorption spectroscopy of electrochemically prepared NRH2 solution and the solution prepared using the isolated NRH2.



**Supplementary Figure 21.** Normalized pH changes while blowing gas streams of 1, 4, 15% CO<sub>2</sub>, and air.



**Supplementary Figure 22.** <sup>1</sup>H-NMR spectrum of precipitate after stability tests under O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and air for a week. Minor peaks from byproduct were observed at  $\delta$  8.94, 8.44, 8.09, 7.28 under O<sub>2</sub> and N<sub>2</sub>. Procedure for stability test using UV-vis absorption spectroscopy were followed to prepare NMR samples. The solutions after stability tests were filtered and the precipitates were analyzed by <sup>1</sup>H-NMR.

**Supplementary Table 1.** Summary of electrochemical carbon capture methods for direct air capture

Entry	Redox-active compound	Description	Min. work of separation (kJ/mol)	Remarks
1	Neutral red (This work)	pH swing in aqueous solution	Est. 35 (15% CO <sub>2</sub> ) Est. 64 (air)	O <sub>2</sub> insensitive Direct air capture demonstrated
2	DSPZ <sup>2</sup>	pH swing in aqueous solution	1.9 (46.5% CO <sub>2</sub> ) Est. 30-75 (air)	O <sub>2</sub> sensitivity limits DAC applicability
3	DHPS <sup>3</sup>	pH swing in aqueous solution	Est. 21.6 (15% CO <sub>2</sub> )	O <sub>2</sub> sensitivity limits DAC applicability
4	1-AP nitrate <sup>1</sup>	pH swing in aqueous solution	Est. 162 (air)	
5	9,10-phenanthrenequinone <sup>4</sup>		Est. 34 (0.24 M CO <sub>2</sub> in ACN)	O <sub>2</sub> sensitivity limits DAC applicability; Requires organic solvent or ionic liquid
6	2,6-di- <i>tert</i> -butyl-1,4-benzoquinone <sup>5</sup>		Est. 61 (0.5% CO <sub>2</sub> )	O <sub>2</sub> sensitivity limits DAC applicability
7	N-propyl-4,4'-bipyridinium <sup>6</sup>		Est. 19 (2.8 mM CO <sub>2</sub> in ACN)	ACN solvent
8	4,4'-bipyridine <sup>7</sup>		Est. 67 (CO <sub>2</sub> saturated solution in BMP-TFSI)	1,2-dichloroethane solvent
9	EMAR <sup>8</sup>	CO <sub>2</sub> sorbent: Ethylene diamine; Electrochemical swing between Cu(II) and Cu(I)	16 (15% CO <sub>2</sub> )	Repetitive polarity switches; Aqueous solution
10	Co(III) complex <sup>9</sup>	CO <sub>2</sub> sorbent: cyclopentadienyl indenyl Co(III) complex	Est. 34	CO <sub>2</sub> reduction; Irreversible decomposition
11	benzyldisulfide <sup>10</sup>	CO <sub>2</sub> sorbent: benzylthiolate	Est. 193 (5 mM CO <sub>2</sub> in BMP-TFSI)	Demonstrated in DMF
12	Cu(II) complex <sup>11</sup>	CO <sub>2</sub> sorbent: 1,2-dimethylimidazole; Electrochemical swing between Cu(II) and Cu(I)	Est. 27-65 (15% CO <sub>2</sub> )	Low cyclic stability due to unstable Cu(I) complexes
13	Polyanthraquinone <sup>12</sup>		113 (400 ppm CO <sub>2</sub> )	O <sub>2</sub> sensitivity limits current DAC applicability
14	PCET: MnO <sub>2</sub> <sup>13</sup>	pH swing K <sub>2</sub> CO <sub>3</sub> capture solution	33 (15% CO <sub>2</sub> )	Same benefits and downsides as traditional K <sub>2</sub> CO <sub>3</sub>

DSPZ: sodium 3,30-(phenazine-2,3-diylbis(oxy))bis(propane-1-sulfonate)

DHPS: 7,8-dihydroxyphenazine-2-sulfonic acid

ACN: acetonitrile

BMP-TFSI: 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide



## 6. Supplementary References

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