

# Mediated formic acid flow fuel cell (MFAFFC) based on bioorganic electrolytes

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## Supporting Information

### I - General information

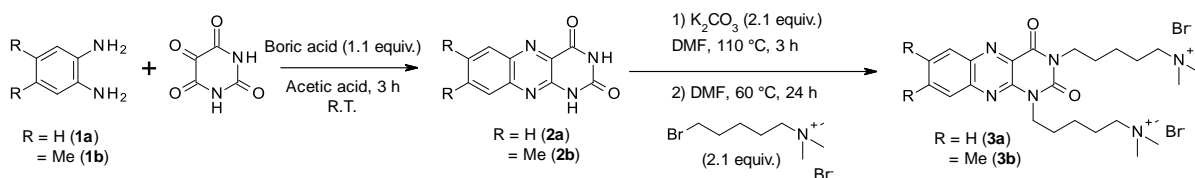
All reagents were purchased from commercial suppliers (Strem Chemicals Inc., Sigma-Aldrich or Alfa Aesar) and were used without further purification. DMF (Fisher Scientific, Illkirch, France) were stored with active molecular sieves (3 Å) for 24 hours before usage. Water used was MilliQ grade. Thin-layer chromatography (TLC) were performed on Silica gel 60 F254 plates (Merck, Fontenay-sous-Bois, France) and visualized under UV (254 nm) or by staining with potassium permanganate or phosphomolybdic acid. NMR spectra were recorded on a Bruker (Wissembourg, France) AVANCE 300 spectrometer at 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C. Chemical shifts (δ) are reported in ppm, using residual solvent as internal standard (D<sub>2</sub>O, 4.80 ppm and (CD<sub>3</sub>)<sub>2</sub>SO, 2.50 ppm). Gas emission measurements were performed with Dräger X-am® 5000 gas detector for H<sub>2</sub>, CO<sub>2</sub>, CO. UV-Vis spectra were recorded on a Perkin Elmer Lambda 25. IR spectra were recorded on a Perkin Elmer FTIR Spectrum 2.

### II - Chemical synthesis and spectroscopic characterisation.

#### A - General procedure for the synthesis of electrolytes **3a** and **3b**:

**Step 1:** To a solution of O-phenylene diamine **1a** or 4,5-dimethyl-1,2-phenylene diamine **1b** (1 equiv. 10 mmol) in acetic acid (400 mL) under inert atmosphere, Alloxane (1 equiv.) and boric acid (1,1 equiv.) are added. The solution is maintained at room temperature for 3 h. The resulting precipitate is filtered and washed with acetic acid, diethyl ether and water to yield benzo[g]ptéridine-2,4(1H,3H)-dione (**2a**) (97%) and 7,8-diméthylbenzo[g]ptéridine-2,4(1H,3H)-dione (**2b**) (96%).

**Step 2:** In a 25 mL flask, benzo[g]ptéridine **2a** or **2b** (1 equiv., 8.3 mmol) is dissolved in DMF (15 mL) and K<sub>2</sub>CO<sub>3</sub> (2.1 equiv. 17 mmol) is added. The solution is heated under inert atmosphere at 110 °C for 3 h. The resulting precipitate is filtered and washed with DMF. Next, the precipitate is added to a solution of (2-bromoalkyl)trimethylammonium bromide (2.1 equiv., 17 mmol) in DMF (15 mL) in a 25 mL flask. The resulting solution is maintained à 60 °C for 24h under inert atmosphere. The dark yellow precipitate is filtered and washed with diethyl ether and acetone to yield the 5,5'-(2,4-dioxobenzo[g]ptéridine-1,3(2H,4H)-diyl)bis(N,N,N-triméthylpentan-1-ammonium) bromide (**3a**) (80%) or 2,2'-(7,8-diméthyl-2,4-dioxobenzo[g]ptéridine-1,3(2H,4H)-diyl)bis(N,N,N-triméthylethanammonium) bromide (**3b**) (71%).



*Scheme S1. Electrolytes **3a** and **3b** synthetic pathways*

*B - Spectroscopic characterization and NMR study:*

**2a:**

$^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{SO}$ ,  $\delta$  ppm,  $J$  Hz): 7.76-7.81 (m, 1H, Ar), 7.93-7.94 (m, 2H, Ar), 8.18 (d, 1H,  $J = 8$  Hz, Ar), 11.84 (m, 2H, amide).

$^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{SO}$ ,  $\delta$  ppm): 126.9; 128.4; 130.1; 133.3; 131.6; 139.2; 142.6; 146.8; 150.1; 160.4.

UV-Vis ( $\text{H}_2\text{O}$ , pH = 14):  $\lambda_{\text{max}} = 426$  nm,  $\epsilon = 4277$   $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$

IR ( $\text{cm}^{-1}$ ): 3406, 3174, 3085, 1734, 1687, 1583, 1272

**2b:**  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{SO}$ ,  $\delta$  ppm,  $J$  Hz): 2.47 (s, 6H,  $2\times\text{CH}_3$ ), 7.76-7.81 (m, 1H, Ar), 7.71 (s, 1H, Ar), 7.92 (s, 1H, Ar), 11.73 (m, 2H, amide).

$^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{SO}$ ,  $\delta$  ppm): 20.1; 20.7; 126.3; 129.2; 130.7; 138.8; 139.4; 142.1; 145.1; 146.9; 150.6; 161.1.

UV-Vis ( $\text{H}_2\text{O}$ , pH = 14):  $\lambda_{\text{max}} = 340$  nm,  $\epsilon = 2582$   $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$

IR ( $\text{cm}^{-1}$ ): 3377, 3167, 3095, 2989, 2913, 2838, 1724, 1697, 1560, 1485, 1422.

**3a:**  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ,  $\delta$  ppm,  $J$  Hz): 1.4 - 1.48 (m, 4H,  $2\times\text{CH}_2$ ), 1.7-1.8 (m, 8H,  $4\times\text{CH}_2$ ), 3.08 (s, 9H,  $\text{N}(\text{CH}_3)_3$ ), 3.09 (s, 9H,  $\text{N}(\text{CH}_3)_3$ ), 3.26 - 3.33 (m, 4H,  $2\times\text{CH}_2$ ), 4.03 (t, 2H,  $J = 15$  Hz - 7.2 Hz,  $\text{CH}_2$ ), 4.27 (t, 2H,  $J = 15$  Hz - 9 Hz,  $\text{CH}_2$ ), 7.77 - 7.83 (m, 1H, Ar), 7.94 - 7.95 (m, 2H, Ar), 8.04 - 8.06 (m, 2H, Ar).

$^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ ,  $\delta$  ppm): 52.8; 52.9; 53.0; 21.9; 22.0; 22.8; 22.9; 26.2; 26.3; 42.2; 42.3; 66.4; 66.5; 127.5; 129.3; 130.0; 134.6; 129.2; 138.8; 143.2; 144.6; 151.1; 161.1.

UV-Vis ( $\text{H}_2\text{O}$ , pH = 1):  $\lambda_{\text{max}} = 384$  nm,  $\epsilon = 3024$   $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$

IR ( $\text{cm}^{-1}$ ): 3468, 3419, 3011, 2944, 2863, 1724, 1680, 1630, 1560, 1483, 1407.

**3b:**  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ,  $\delta$  ppm,  $J$  Hz): 1.38 - 1.48 (m, 4H,  $2\times\text{CH}_2$ ), 1.7-1.9 (m, 8H,  $4\times\text{CH}_2$ ), 2.41 (s, 3H,  $\text{CH}_3$ ), 2.43 (s, 3H,  $\text{CH}_3$ ), 3.08 (s, 9H,  $\text{N}(\text{CH}_3)_3$ ), 3.09 (s, 9H,  $\text{N}(\text{CH}_3)_3$ ), 3.27- 3.34 (m, 4H,  $2\times\text{CH}_2$ ), 4.00 (t, 2H,  $J = 15$  Hz - 8 Hz,  $\text{CH}_2$ ), 4.15 (t, 2H,  $J = 15$  Hz - 7.9 Hz,  $\text{CH}_2$ ), 7.55 (s, 1H, Ar), 7.64 (s, 1H, Ar).

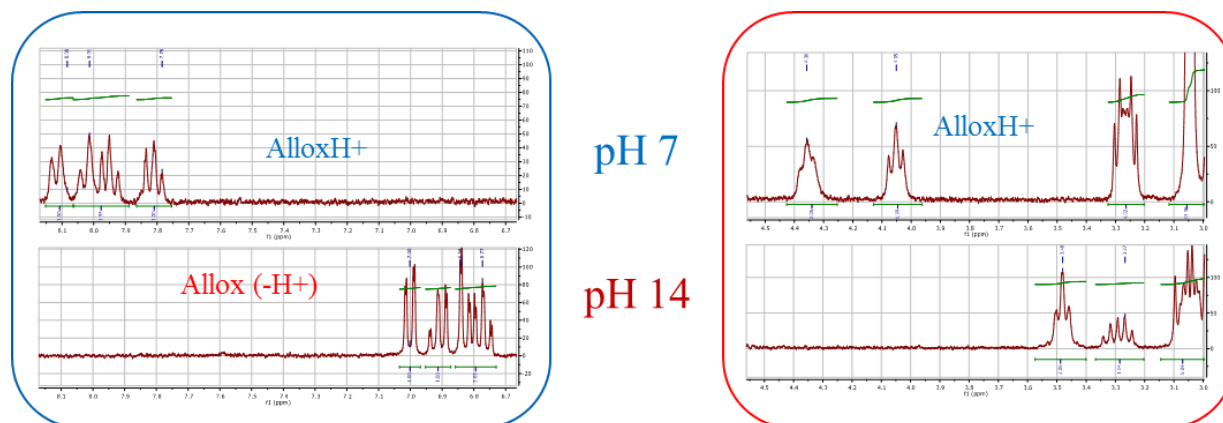
$^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ ,  $\delta$  ppm): 19.5; 20.2; 52.8; 52.9; 53.0; 22.0; 22.1; 22.8; 22.9; 26.3; 26.4; 42.2; 66.4; 66.5; 126.0; 127.5; 127.4; 137.8; 141.7; 141.9; 143.8; 147.2; 150.8; 160.7.

UV-Vis ( $\text{H}_2\text{O}$ , pH = 7):  $\lambda_{\text{max}} = 390$  nm,  $\epsilon = 1807$   $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$

IR ( $\text{cm}^{-1}$ ): 3591, 3519, 3435, 3335, 3021, 3004, 2964, 2933, 2858, 1702, 1651, 1638, 1553, 1481.

*C -  $^1\text{H}$  NMR study after addition of formic acid*

In order to choose the best conditions for fuel cell, we performed NMR study after progressive addition of formic acid to synthesized compounds in neutral and basic media. For neutral and basic condition, the samples were prepared in  $\text{D}_2\text{O}$  (by adding NaOD to adjust pH to 14 for basic one). Despite an absence of attendant proton signal of reduced form due to superposition of signals, we observed a not neglected shift of proton in both aromatic and aliphatic zone depending on pH. This can be explained by existence of protonated and deprotonated forms at pH = 7 and pH = 14 respectively that explains right shift in NMR spectra (Fig 1, 2). No full  $^1\text{H}$  NMR characterization of the reduced forms can be furnished at this stage due to strong pH dependence. Also deprotonation in basic medium is established since integrations are affected.



**Fig. S1.** Fragments of aromatic (left) and aliphatic (right) zones of NMR spectra in neutral (pH = 7, top) and basic (pH = 14) condition for Alloxazine (1).

### III - Gas measurements

*Procedure:* Nitrogen degassed solutions of **3a** or **3b** in water (0.1 M, 1 mL) at pH = 1, 7, 12 were alternatively poured into a 5 mL Schlenk tube under nitrogen atmosphere. Repeated addition of formic acid (1 eq.) to the solution followed by visual observation of gaz evolution. Measurement of the level of CO<sub>2</sub>, CO, H<sub>2</sub> in the Schlenk tube was performed by aspiration in a sensitive detector (measurement limits: CO: 0-2000 ppm; CO<sub>2</sub>: 0-5%; H<sub>2</sub>: 0-2%). A blank measurement test was performed after nitrogen degassing showing the absence of CO<sub>2</sub> into the sample.

**Table S1.** Gas measurements after formic acid addition to compounds **3a** and **3b** (data given in red are not significant probably due to bad degassing or air penetration during the experiment)

| HCOOH           | pH = 1<br>Vgas, %<br>3a                               | pH = 7<br>Vgas, %<br>3a                               | pH = 12<br>Vgas, %<br>3a                              | pH = 1<br>Vgas, %<br>3b                               | pH = 7<br>Vgas, %<br>3b                               | pH = 12<br>Vgas, %<br>3b                              |
|-----------------|---|---|---|---|---|---|
| 0 µl            | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 |
| 1.1 eq. = 4 µl  | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 |
| 2.2 eq. = 8 µl  | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.7<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 1.2<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.7<br>CO = 0 |
| 3.3 eq. = 12 µl | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.8<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.7<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.8<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.7<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 |
| 4.4 eq. = 16 µl | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 1.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.7<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 1.6<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.9<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 |
| 5.5 eq. = 20 µl | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.9<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 1.9<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.7<br>CO = 0 |
| 6.6 eq. = 28 µl | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.8<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 1.1<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 |
| 7.7 eq. = 32 µl | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 1.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 1.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.7<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 |
| 8.8 eq. = 36 µl | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 1.6<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 1.5<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.7<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.7<br>CO = 0 |

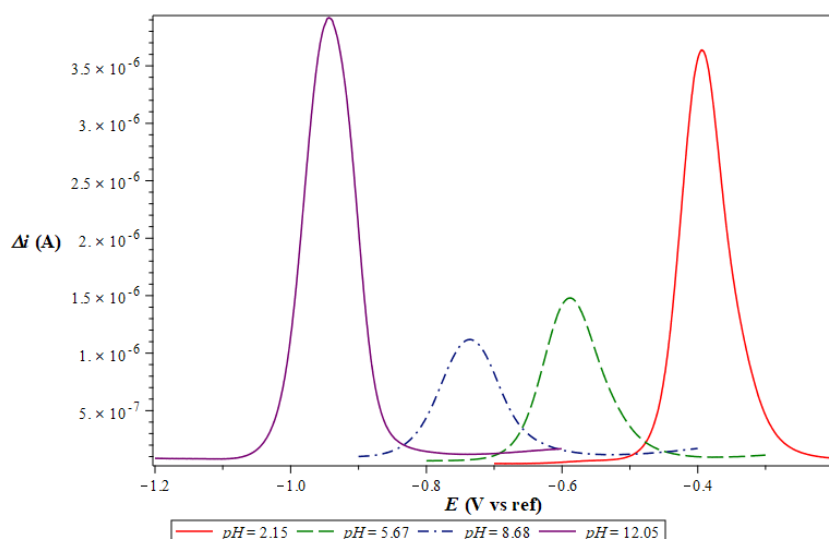
|                      |   |   |   |   |   |   |
|----------------------|---|---|---|---|---|---|
| 9.9 eq. = 40 $\mu$ l | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.4<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 2.7<br>CO = 0 | H <sub>2</sub> = 0<br>CO <sub>2</sub> = 0.6<br>CO = 0 |
|----------------------|---|---|---|---|---|---|

#### IV - Electrochemical analysis.

##### A - E-pH diagram:

For DPV as well as CV experiments, three-electrodes system including 1 mm glassy carbon Working Electrode (WE), Platinum wire Auxiliary Electrode (AE) and AgCl/Ag Reference Electrode (RE). RE potential is regularly checked.

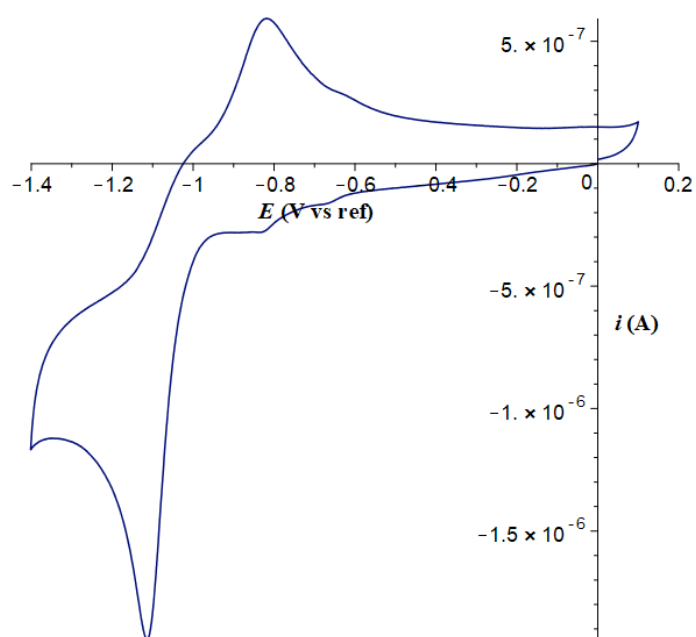
**DPV:** Inside the reactor, electroactive species' concentration is 1 mM and supporting electrolyte's concentration is 100 mM. Depending on the pH range targeted, supporting electrolyte may be Na<sub>2</sub>SO<sub>4</sub> (pH range = 1-4), AcONa (pH range = 3-6), NaH<sub>2</sub>PO<sub>4</sub> (pH range = 5-9) and Na<sub>2</sub>HPO<sub>4</sub> (pH range = 7-13) and pH variation is obtained with little additions of 1 M sodium hydroxide or sulfuric acid solutions. Potential range is chosen so that the signal gives a nice peak appearance and depends on pH, as showed on Fig. S2. Potential step is chosen to 1 mV and pulse amplitude is equal to 10 mV. After the acquisition, potential peak is reported and leads to formal redox potential.



**Fig. S2:** examples of DPV for 3b at various pH

**CV:** inside the reactor, folic acid's concentration was 1 mM with 1 M NaOH supporting electrolyte. For the CV, minimum and maximum potentials of the range are chosen to be at least 200 mV below (minimum) and above (maximum) the cathodic and anodic potentials. Potential step is set to 1 mV and scan rate to 50 mV/s. Cathodic and anodic peak potentials  $E_{pc}$  and  $E_{pa}$  are reported and lead to  $E'^0$  using:

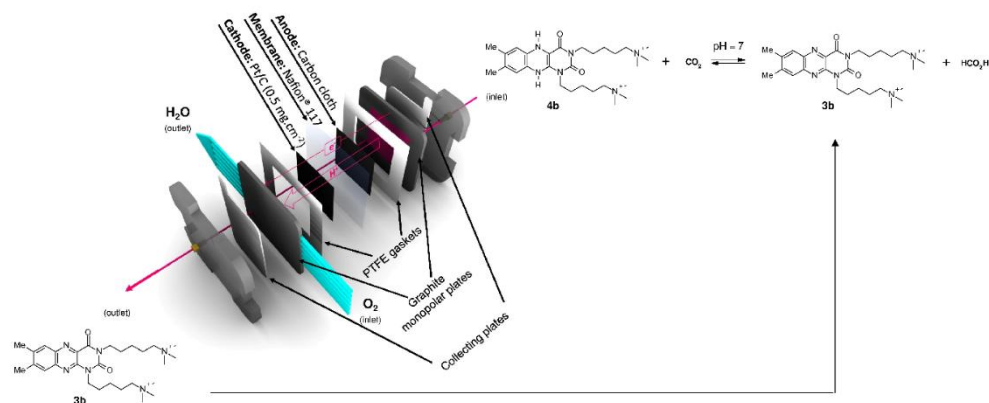
$$E'^0 = E_{pc} + \frac{E_{pa} - E_{pc}}{2}$$



**Fig S3:** CV of 1 mM folic acid in 1 M sodium hydroxide

#### *B - Mediated Formic Acid Flow Fuel Cell Experiments*

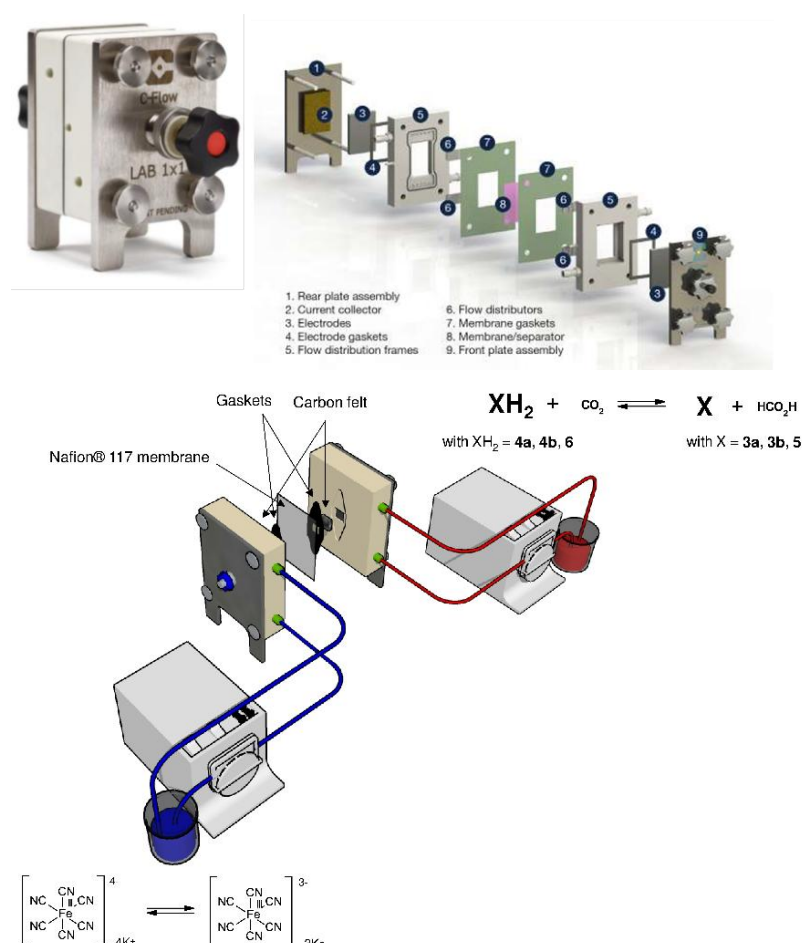
**Setup A:** The flow fuel cell is composed of a commercially available TDM® fuel cell assembled (<http://www.fuelcellstore.com/>) for which the original membrane electrode assembly (MEA) has been replaced by a custom 4 layers MEA composed of [Carbon cloth (Anode) / Nafion® 117 / Carbon gas diffusion layer / Pt-C 0.5 mg.cm<sup>-2</sup> (60%) (Cathode)] ([http:// fuelcellsetc.com/](http://fuelcellsetc.com/)) (see figure S4). This custom MEA is clamped into two PTFE gaskets, two graphite monopolar plates (serpentine design at the anode/straight channels design at the cathode), two collecting plates and two plastic plates on which are connected 1/16" tubings for the inlet and the outlet. At the anode circulate the degassed electrolyte solution resulting from addition of formic acid (50 µL) to a solution of ammonium alloxazine **3b** (0.1 M, 3 mL) and at the cathode circulate oxygen gas introduced into the straight channels by 1/16" tubings connected to a manifold, itself connected to an oxygen gas cylinder. The active surface (3.9 cm<sup>2</sup>) has been calculated as the anode serpentine/carbon cloth connection surface. The total internal volume of the fuel cell at the anode is 390 µL (depth of flow field = 1 mm). All electrochemical measurements were performed using a potentiostat/galvanostat (Metrohm Autolab®, PGSTAT128N, Villebon Courtaboeuf, France).



**Fig. S4.** Schematic representation of the experimental MFAFFC setup A based on TDM® fuel cell.

**Setup B:** Cell hardware C-Flow® Lab 1×1 was used to assemble a zero-gap flow cell configuration (Fig S5). Electrodes of 1 cm<sup>2</sup> geometric surface area were comprised of a stack with a sheet of porous carbon felt. A sheet of Nafion® 117 membrane was pre-activated in 1 M NaOH solution (boiling 8 h with stirring), served as the ion-selective membrane.

The rest of the space between the plates were flow distributor frames and gaskets. The electrolytes were fed into the cell through FEP tubing, at a flow rate of 10 ml/min controlled by ISMATEC® Reglo Analog MS-2/12 peristaltic pumps. All electrochemical measurements (Voltammetry/Polarization and Chronopotentiometry) were performed using a Potentiostat Galvanostat OrigaFlex OGF500.



**Fig. S5.** Setup B - (Top) Fuel cell C-Flow® Lab 1×1 used for flow fuel cell experiments; (bottom) fuel cell – pump and electrolytes reservoirs assembly junction used in this work.

C - Polarization curves:

Setup A:

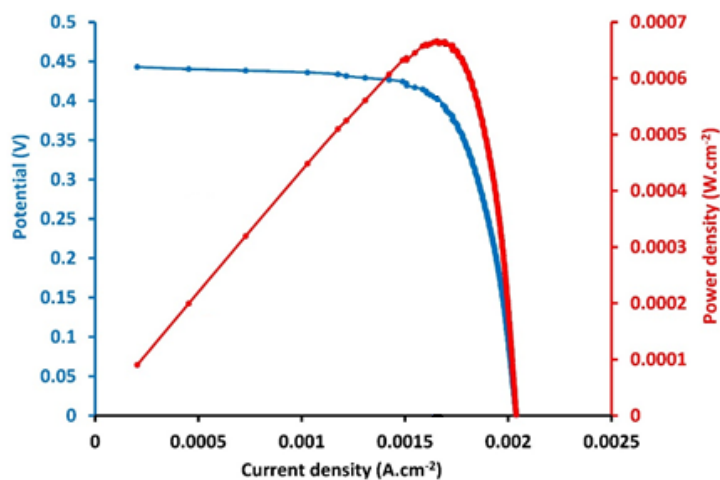


Fig. S6. Setup A – 3b (0.1 M) + HCO<sub>2</sub>H (5 equiv.) at pH = 7 and 10 mL.min<sup>-1</sup>.

Setup B:

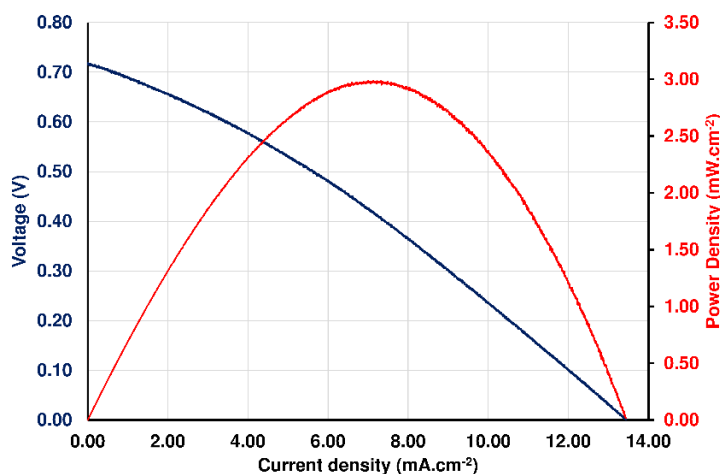


Fig. S7. Setup B – 3b (0.1 M) + HCO<sub>2</sub>H (5 equiv.) at pH = 7 and 10 mL.min<sup>-1</sup>. (Nafion® 117: 8 h water pre-activation)

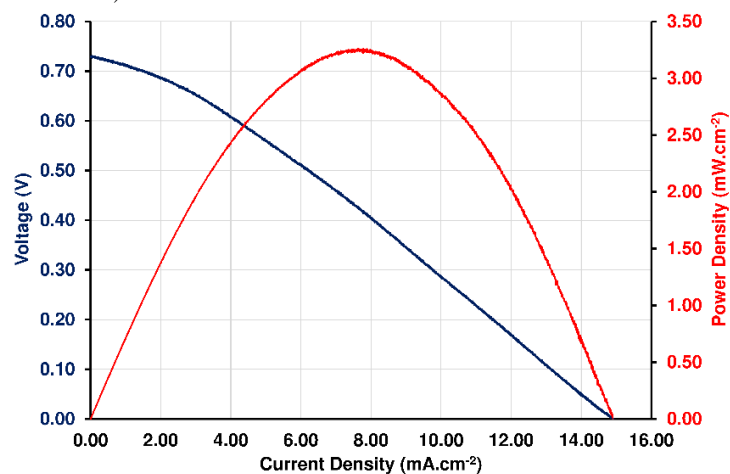
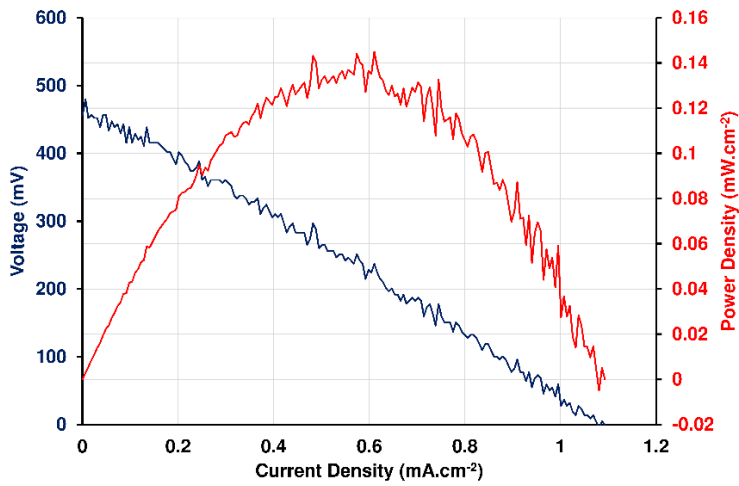
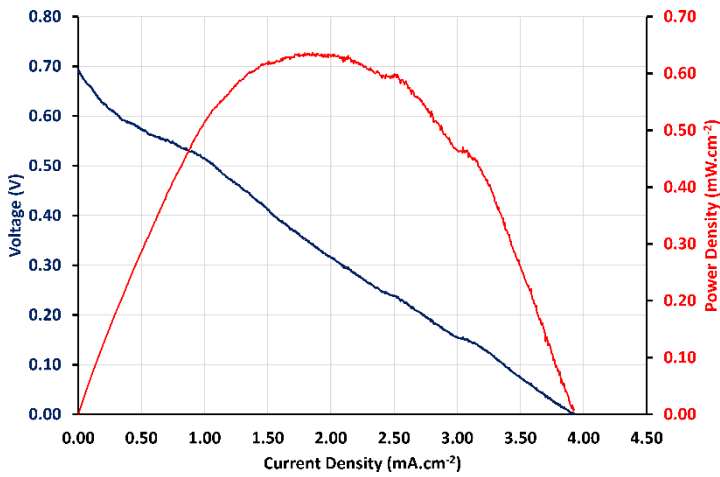


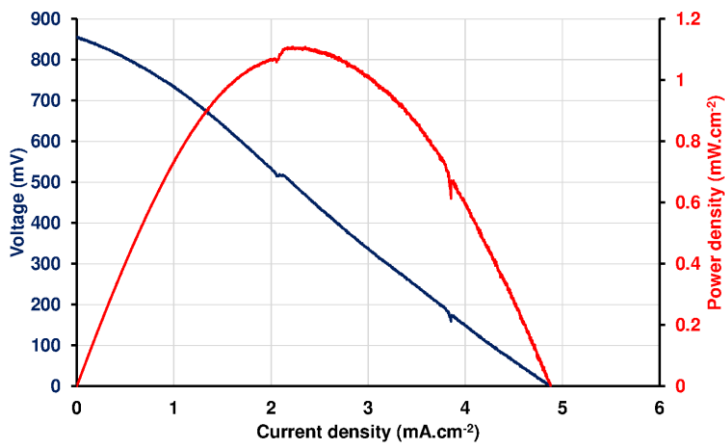
Fig. S8. Setup B – 3b (0.1 M) + HCO<sub>2</sub>H (5 equiv.) at pH = 7 and 10 mL.min<sup>-1</sup>. (Nafion® 117: 8 h NaOH (1 M) pre-activation)



**Fig. S9.** Setup B – 3b (0.46 M) + SDS (10%) + HCO<sub>2</sub>H (5 equiv.) at pH = 7 and 10 mL.min<sup>-1</sup>. (Nafion® 117: 8 h NaOH (1 M) pre-activation)

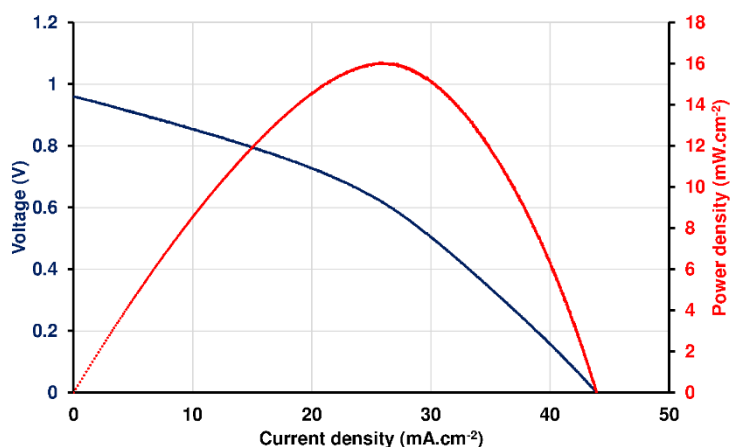


**Fig. S10.** Setup B – 3a (0.1 M) + HCO<sub>2</sub>K (3 equiv.) at pH = 7 and 10 mL.min<sup>-1</sup>. (Nafion® 117: 8 h NaOH (1 M) pre-activation)

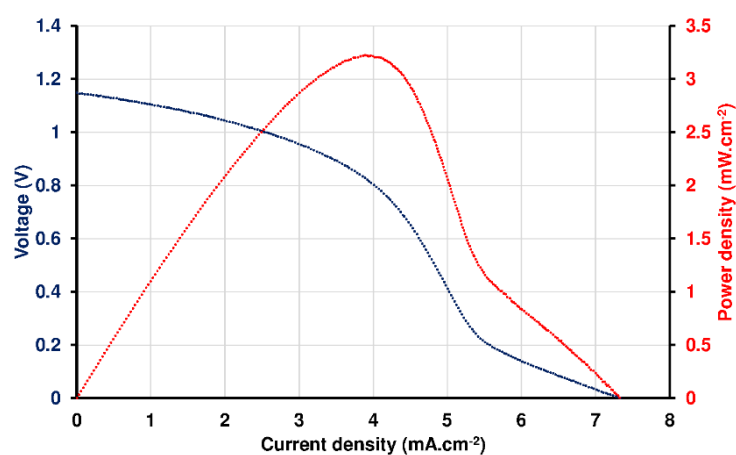


**Fig. S11.** Setup B – 3a (0.1 M) + HCO<sub>2</sub>K (3 equiv.) at pH = 12 and 10 mL.min<sup>-1</sup>. (Nafion® 117: 8 h NaOH (1 M) pre-activation)

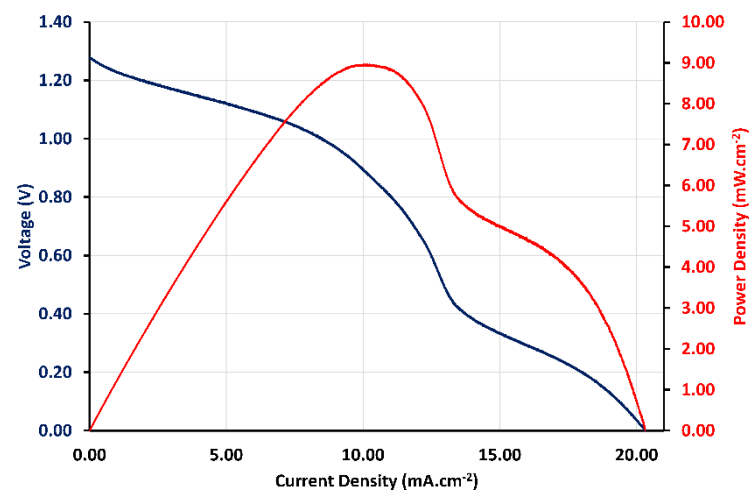




**Fig. S12.** Setup B – **3b** (0.1 M) +  $\text{HCO}_2\text{K}$  (3 equiv.) at  $\text{pH} = 7$  and  $10 \text{ mL}\cdot\text{min}^{-1}$ . (Nafion® 117: 8 h NaOH (1 M) pre-activation)



**Fig. S13.** Setup B – **3b** (0.1 M) +  $\text{HCO}_2\text{K}$  (3 equiv.) at  $\text{pH} = 12$  and  $10 \text{ mL}\cdot\text{min}^{-1}$ . (Nafion® 117: 8 h NaOH (1 M) pre-activation)



**Fig. S14.** Setup B – Folic acid (**5**) (0.5 M) +  $\text{HCO}_2\text{K}$  (5 equiv.) at  $\text{pH} = 14$  and  $10 \text{ mL}\cdot\text{min}^{-1}$ . (Nafion® 117: 8 h NaOH (1 M) pre-activation)