

[Supporting information]

## Bifunctional Metal-Free Porous Polyimide Networks for CO<sub>2</sub> Capture and Conversion

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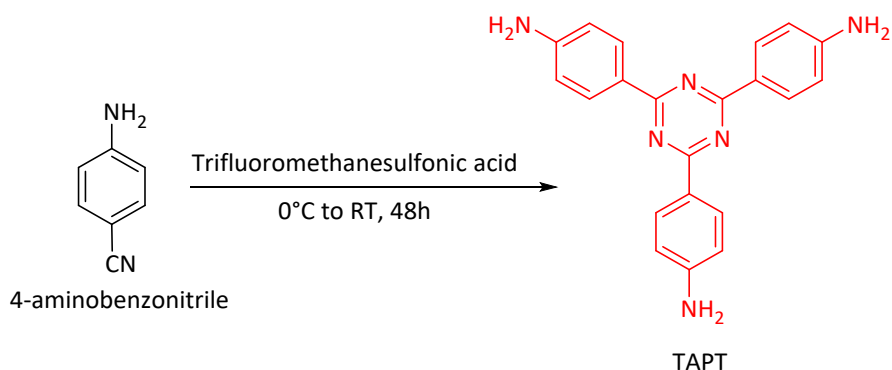
## 1. Equipment and materials:

All the chemicals used were purchased from Merck and ThermoFisher Scientific and used as received.

**Characterisation and measurements:** Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer, with samples in powder form. Thermogravimetric analyses (TGA) were carried out on a TA TGA Q500 apparatus in a nitrogen atmosphere (flow rate 30 mL/ min) in the temperature range of 30–800 °C (heating rate 20 °C/min). X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer (40 kV, 30 mA) using Cu K $\alpha$  radiation ( $2\theta = 5\text{--}50^\circ$ ). Nitrogen adsorption/desorption measurements at 77.4 K were performed after degassing the samples on a Schlenk line for 24 hours and then under high vacuum at 180 °C for at least 20 hours on a Quantachrome Quadrasorb SI-MP apparatus. The specific surface areas were calculated by applying the Brunauer–Emmett–Teller (BET) model to adsorption or desorption branches of the isotherms (N<sub>2</sub> at 77.4 K) using the QuadraWin 5.05 software package. Analysis of the isotherms by commercialized quenched solid density functional theory (QSDFT)<sup>xviii</sup> and Grand canonical Monte Carlo (GCMC)<sup>xix</sup> methodologies were also undertaken using the QuadraWin 5.05 package. The pore size distribution (PSD) profiles of the pPIs were calculated from the adsorption branch of the isotherms with the non-local density functional theory (NLDFT) approach. <sup>1</sup>H NMR experiments were performed in chloroform-d or D<sub>2</sub>O or DMSO-d<sub>6</sub> using a Bruker 400 and cryo500 MHz NMR. UV-Vis-NIR spectroscopy measurements were carried out using a Shimadzu UV-2600 spectrometer fitted with an ISR-2600 integrating sphere attachment. Measurements were recorded in 10 mm path-length quartz cuvettes.

**Electrochemical measurements:** All the electrochemical performances of pPI-1 and pPI-2 were investigated with an EG&G Princeton Applied Research Potentiostat Model 273A, using a glassy carbon working electrode (0.38 cm<sup>2</sup> contact area of electrode), platinum (Pt) counter electrode and silver chloride (Ag/AgCl) reference electrode. All potentials were converted to the reversible hydrogen electrode (RHE) using  $ERHE = E_{Ag/AgCl} + 0.059 \times pH + E^0_{Ag/AgCl}$ , where ERHE is the converted potential vs. RHE,  $E^0_{Ag/AgCl} = 0.1976$  at 25 °C, and  $E_{Ag/AgCl}$  is the experimentally measured potential against Ag/AgCl reference.

## 2. Syntheses:



Synthesis of 1,3,5-tris-(4-aminophenyl)triazine (TAPT):

A dried 100 mL two-neck round bottom flask charged with 4-aminobenzonitrile (772.0 mg, 6.5 mmol) and placed in an ice bath at 0°C under an inert atmosphere. Trifluoromethanesulfonic acid (2 mL) was added dropwise over 20 minutes, maintaining the temperature at 0°C under an inert atmosphere. The resultant mixture was stirred for 48 h at room temperature. Distilled water (20.0 mL) was added, and the reaction mixture was neutralized by 2 M NaOH solution until pH 7. Initially, with an increase in pH, an orange precipitate dissolved to give a bright orange solution, which upon the further increase in pH gave a pale-yellow precipitate. The resultant product was filtered and washed with distilled water (3 x 250 mL) and ethanol (3x 50 mL).

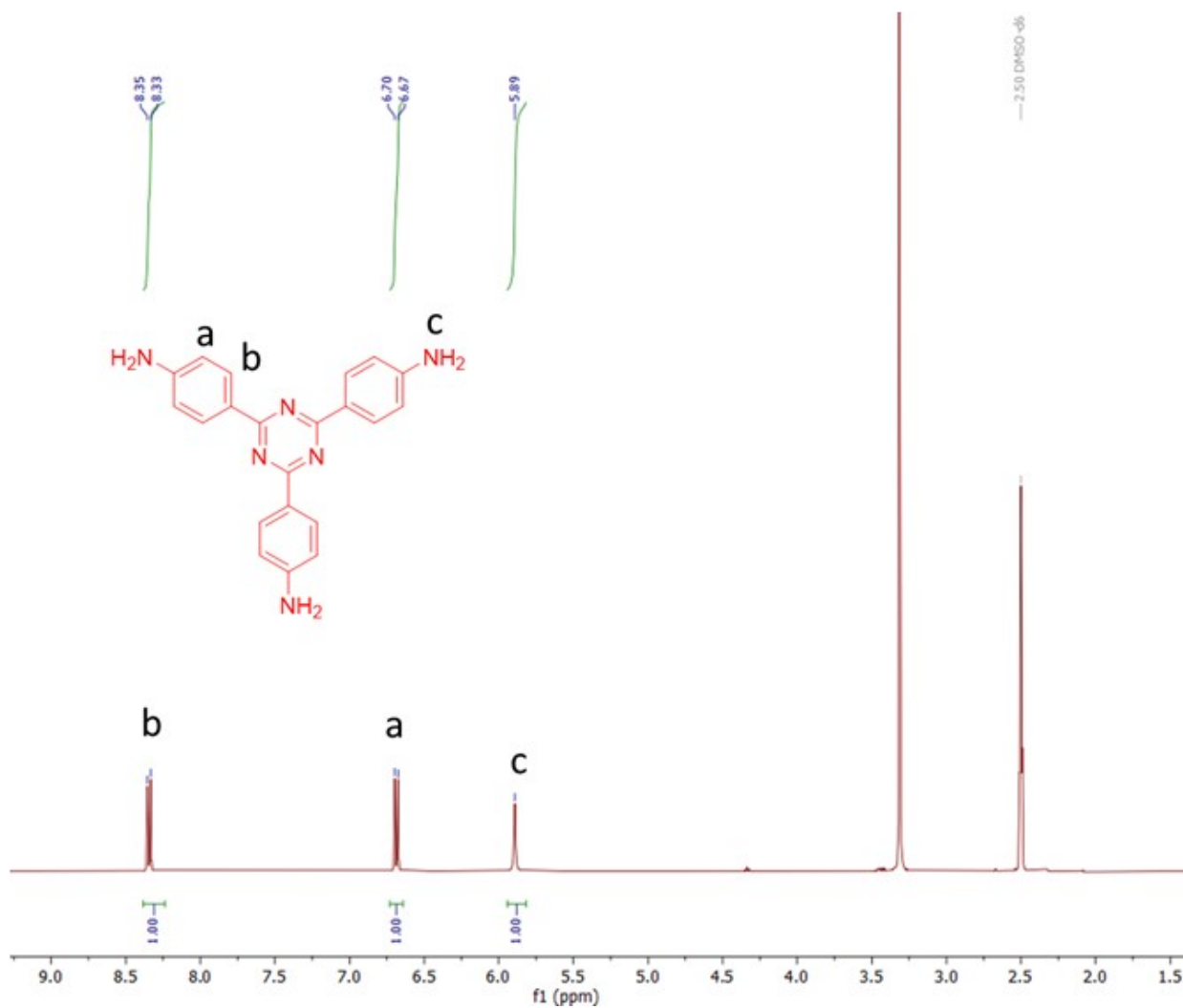
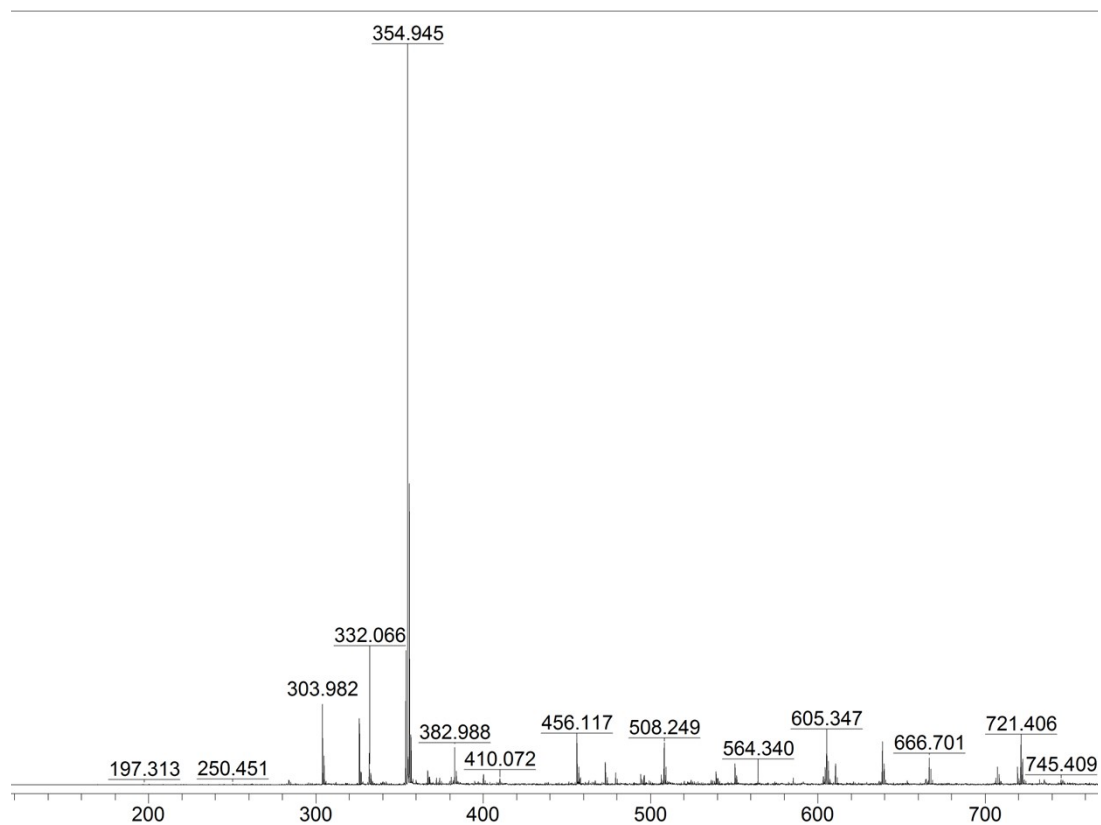


Figure S1:  $^1\text{H}$  NMR of TAPT in  $\text{DMSO-d}_6$ .



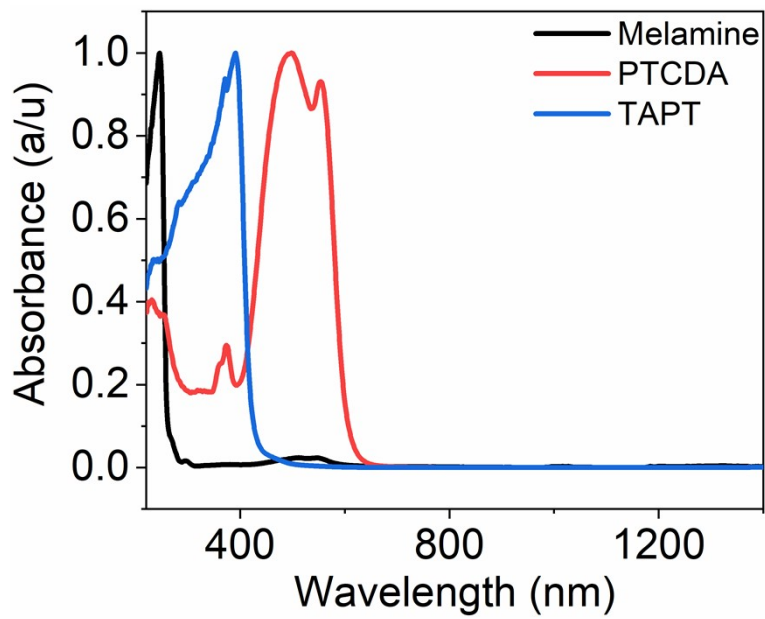
**Figure S2:** MALDI-TOF mass spectrum of TAPT.

#### Synthesis of **pPI-1**:

A dried round-bottomed flask equipped with mechanical stirring, nitrogen inlet, Dean-Stark trap and a reflux condenser was charged with 1-methyl-imidazole (40 ml), and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) (466 mg, 1.19 mmol). After 30 min of stirring at room temperature melamine (100 mg, 0.79 mmol) was added and the reaction mixture stirred at 180°C for 72 hours. After cooling to 70°C, MeOH (50 ml) was added and the precipitate was collected and washed with additional DMF and methanol, warm water and acetone (50ml x 3, each). The resulting product was dried at 80°C under vacuum for 24h.

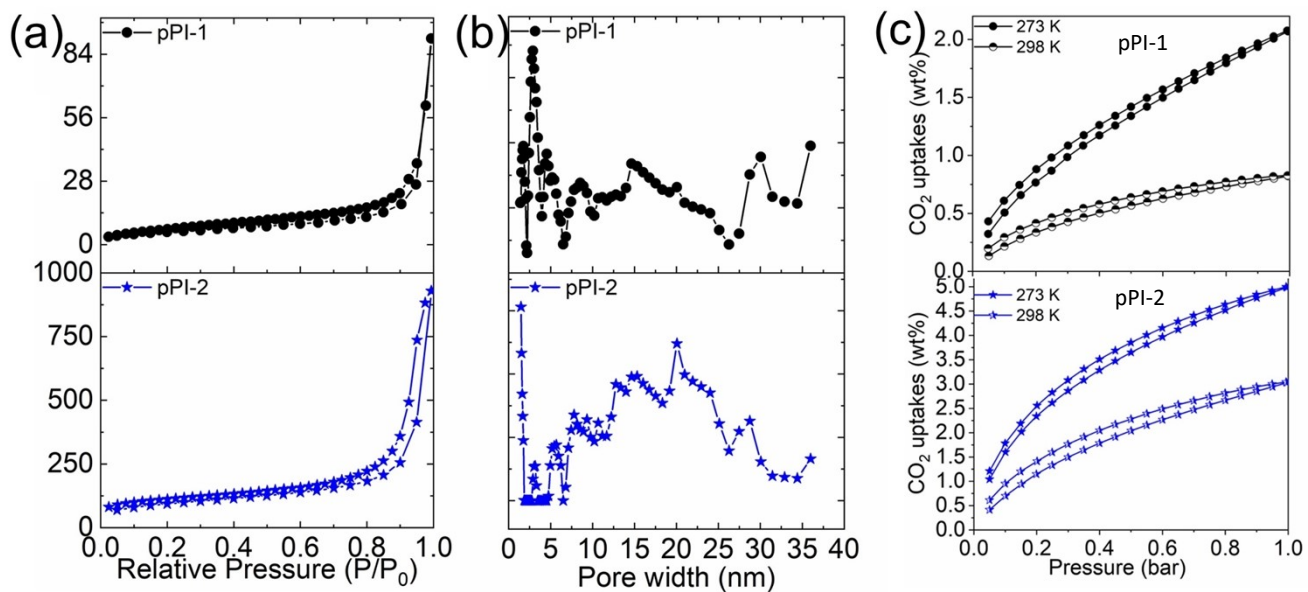
#### Synthesis of **pPI-2**:

A dried round-bottomed flask equipped with mechanical stirring, nitrogen inlet, Dean-Stark trap and a reflux condenser was charged with 1-methyl-imidazole (40 ml), and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) (297 mg, 0.76 mmol). After 30 min of stirring at room temperature TAPT (135 mg, 0.38 mmol) was added and the reaction mixture stirred at 180°C for 72 hours. After cooling to 70°C, MeOH (50 ml) was added and the precipitate was collected and washed with additional DMF and methanol, warm water and acetone (50ml x 3, each). The resulting product was dried at 80°C under vacuum for 24h.



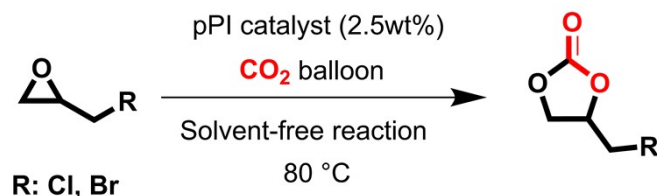
**Figure S3:** Solid-state UV-Vis-NIR spectra of melamine, PTCDA and TAPT.





**Figure S4:** (a) The  $N_2$  sorption isotherms of **pPI-1** and **pPI-2**, (b) Pore size distribution calculated from NLDFT, (c)  $CO_2$  uptake measurement at 273 K and 298 K at 1 bar.

### 3. Cyclic carbonate synthesis:

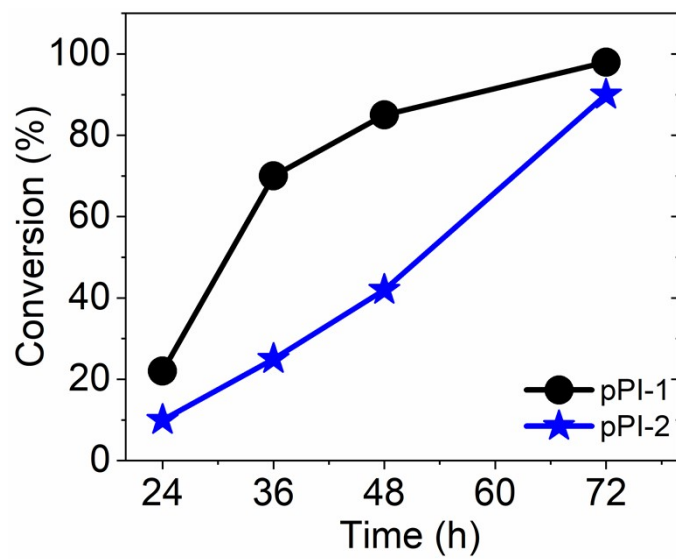


Epoxide (1.0 mL, 0.0127 mol) was loaded in a round bottom Schlenk flask. The pPI (5wt%, 30 mg) to be studied as a catalyst was added to the flask. A balloon filled with CO<sub>2</sub> (approx. 1.5–2 L) was connected to the Schlenk flask and the reaction solution flushed with CO<sub>2</sub> to replace air from the flask. Silicon grease and Parafilm were applied to the joints of the flask to prevent any leakage of CO<sub>2</sub> and the reaction stirred at 80 °C. The reaction was performed for 24 hours, 48 hours, and 72 hours, and reaction progress followed using <sup>1</sup>H NMR.

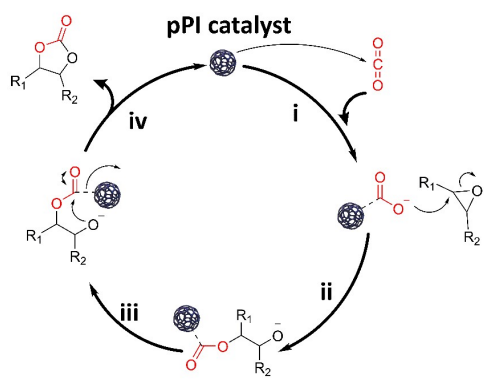
**Cyclic carbonate conversion calculated using <sup>1</sup>H NMR.**

$$\text{Conversion (\%)} = \frac{\text{Integral (b) from cyclic carbonate}}{\text{Integral (b) from cyclic carbonate} + \text{Integral (d) from epoxide}} \times 100\%$$

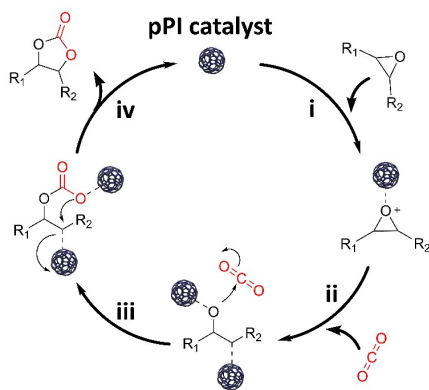
See NMR spectra below for integral **b** from cyclic carbonate and integral **d** from epoxide.



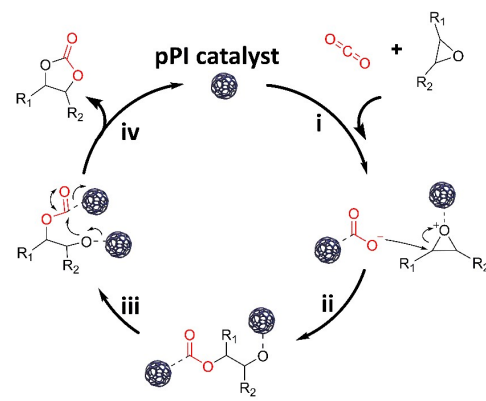
**Figure S5:** Time-dependent percentage conversion of ECH at 80 °C for **pPI-1** and **pPI-2**.



**A. CO<sub>2</sub> activation**

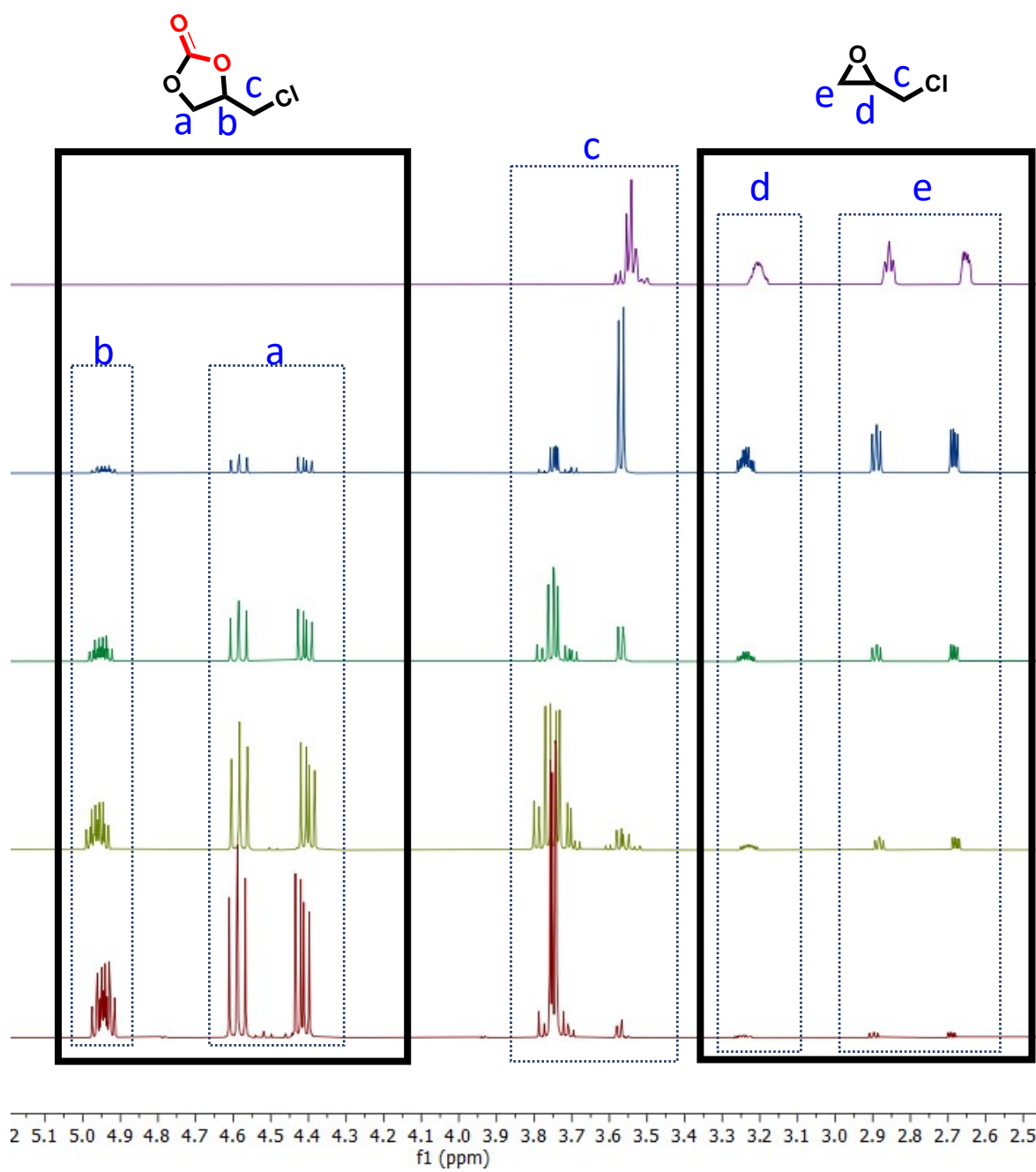


**B. Epoxide activation**

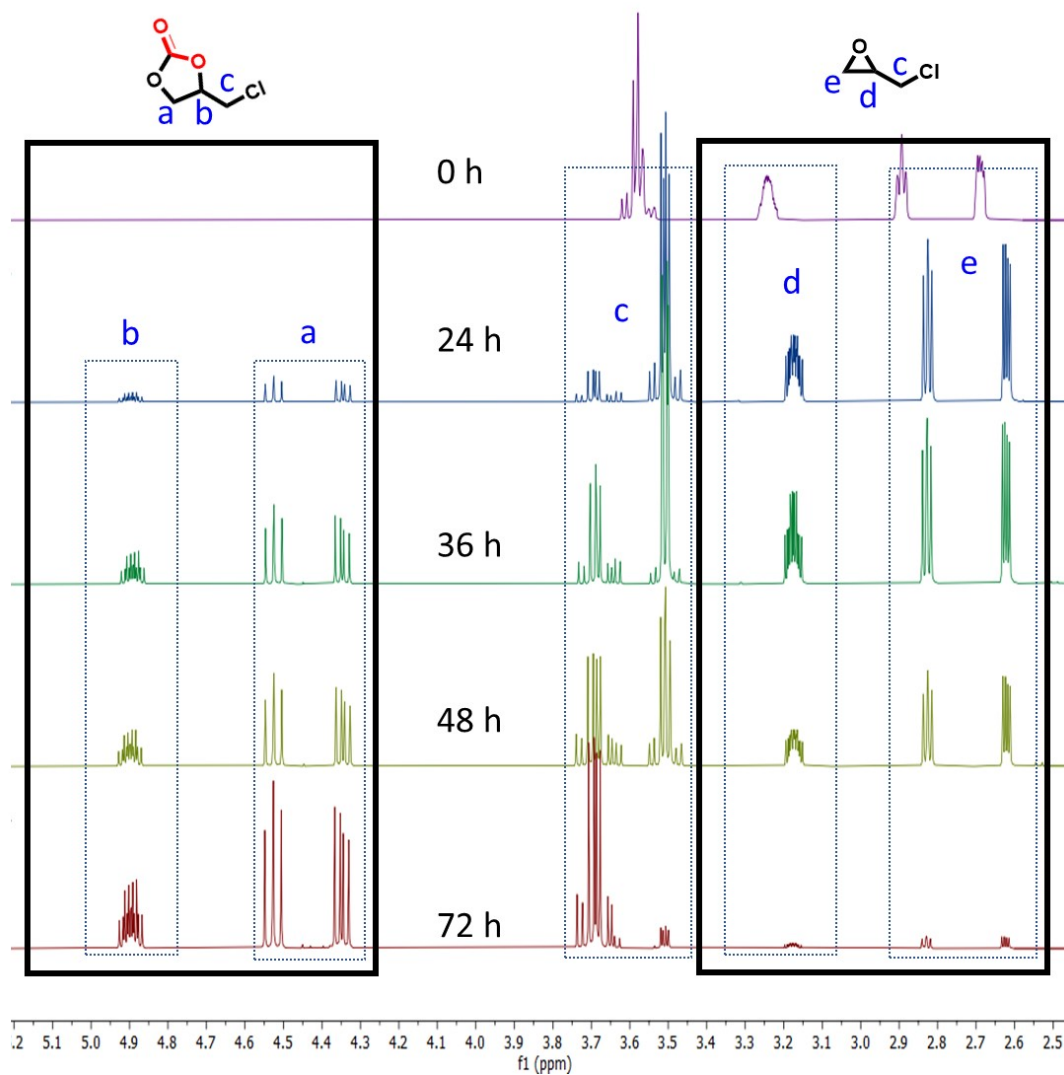


**C. CO<sub>2</sub> and epoxide activation**

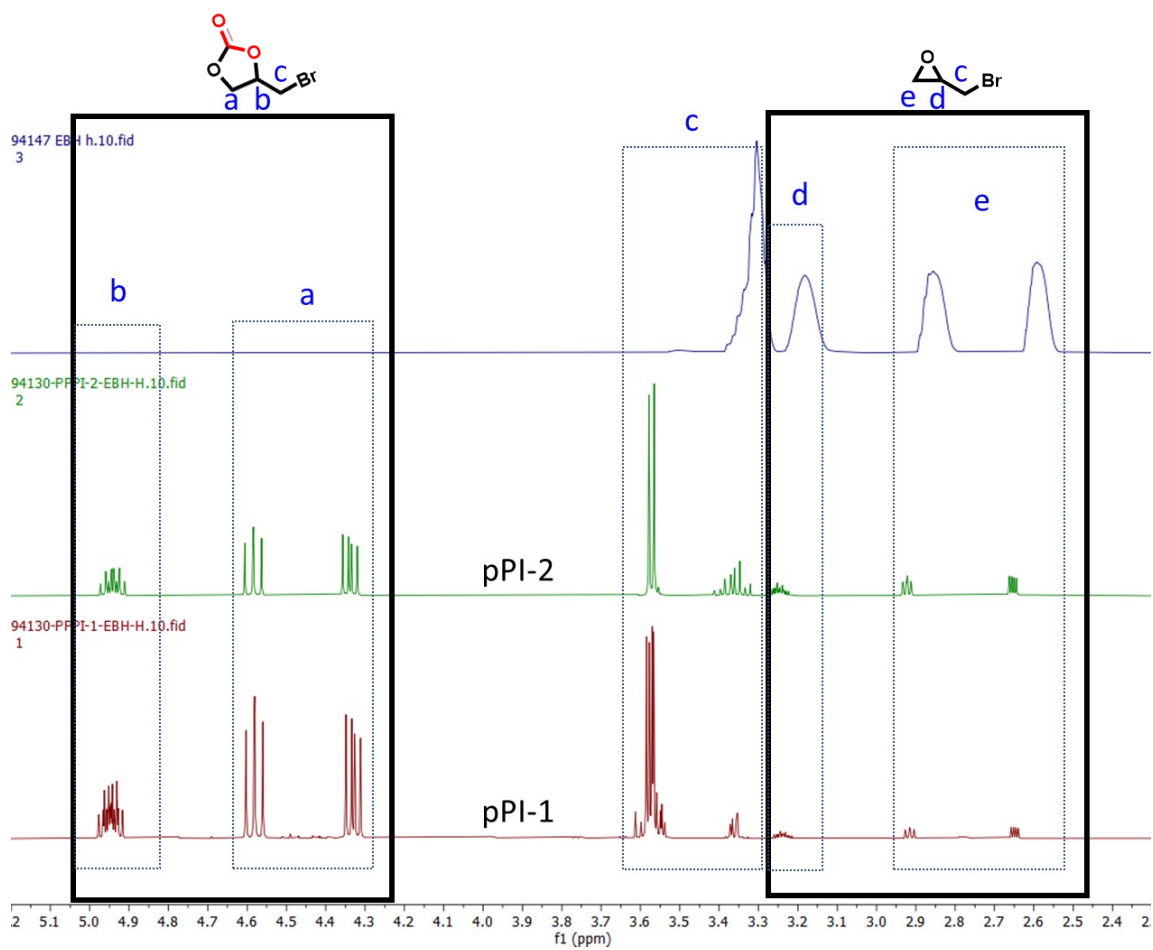
**Scheme S1:** Suggested mechanisms for cyclic carbonate synthesis using pPIs



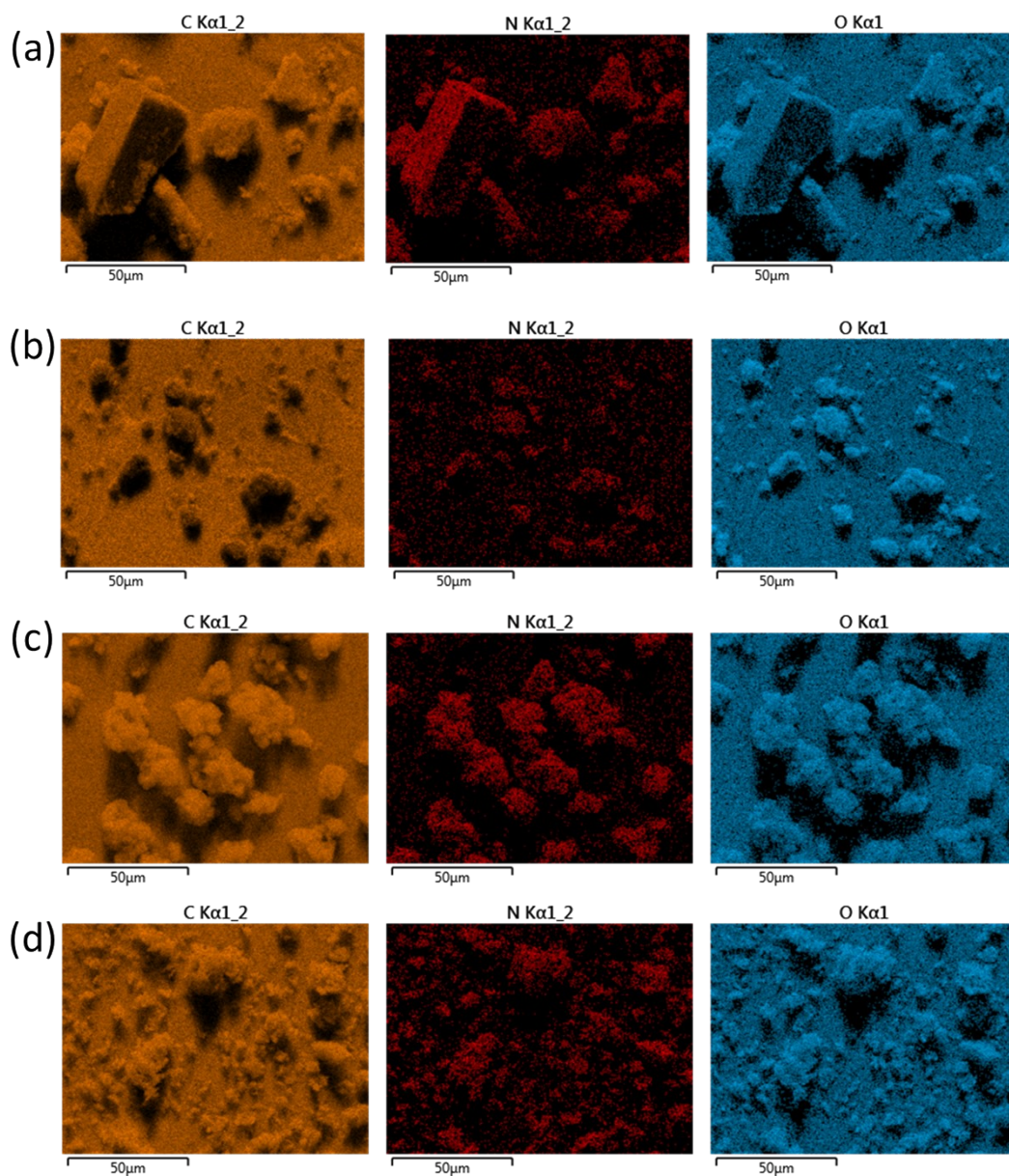
**Figure S6:** <sup>1</sup>H NMR for 4-(chloromethyl)-1,3-dioxolan-2-one using *pPI-1* from ECH.



**Figure S7:**  $^1\text{H}$  NMR for 4-(chloromethyl)-1,3-dioxolan-2-one using **pPI-2** from ECH.



**Figure S8:**  $^1\text{H}$  NMR for 4-(bromomethyl)-1,3-dioxolan-2-one using **pPI-1** and **pPI-2** from EBH (72 hours).

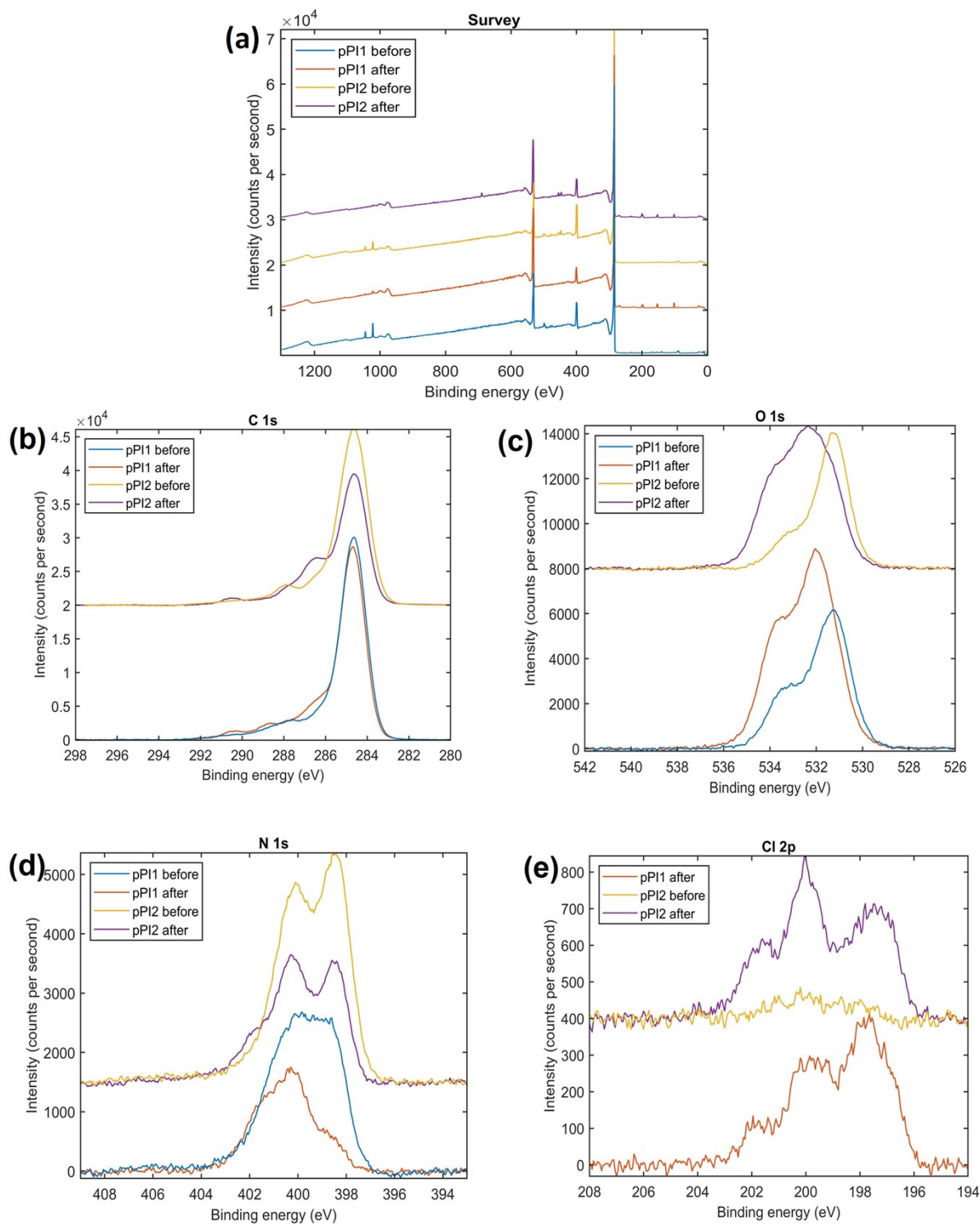


**Figure S9:** Energy-dispersive X-ray spectroscopy (EDX): (a) **pPI-1**, (b) **pPI-1** after 5 cycles, (c) **pPI-2** and (d) **pPI-2** after 1 cycle.

**Table S1:** Elemental analysis results of **pPI-1** and **pPI-2** (before and after the catalytic cycle).

Name	C%	N%	O%
<b>pPI-1</b>	79.7	6.8	13
<b>pPI-1</b> after 5 cycles	84	1.7	13.3
<b>pPI-2</b>	83	5.7	10.4
<b>pPI-2</b> after 1 cycle	82.1	5.0	12.1





**Figure S10:** X-ray photoelectron spectroscopy (XPS) spectra: (a) **pPI-1** and **pPI-2**, before and after cycle 1, (b) C 1s, (c) O 1s, (d) N 1s and (e) Cl 2p, of **pPI-1** and **pPI-2** (before and after cycle 1).

#### 4. Electrochemical CO<sub>2</sub> reduction

##### Electrode preparation:

pPIs (1.5 mg) were ground to a fine powder and sonicated in isopropanol (500 μL) for 2-3 hours. Nafion (10 μL) was added to the suspension and sonicated for 30 min. The suspension (20 μL) was drop-cast on a clean glassy carbon working electrode. The electrode was dried at room temperature vacuum oven overnight and used for electrochemical studies.

##### Electrolyte preparation for NMR analysis after electrochemical reduction of CO<sub>2</sub> experiments

After CA experiments, the electrolyte (600 μL) was collected from the cathodic side of the H-cell and product detection was undertaken using cryo500 <sup>1</sup>H NMR spectroscopy for methanol and formate, respectively. To determine the amount of methanol and formate produced, which in turn allows the determination of the FE for each product in the system, 1 mM maleic acid (10 μL) was added along with D<sub>2</sub>O (180 μL) and the mixture was analysed using <sup>1</sup>H NMR. FEs were calculated using the formula below;

$$\varepsilon_{Faradaic} = \frac{z \cdot n \cdot F}{Q}$$

*z: number of electrons required to produce a given product*

*n: number of moles of the given product*

*F: Faraday's constant (96485.33 C/mol)*

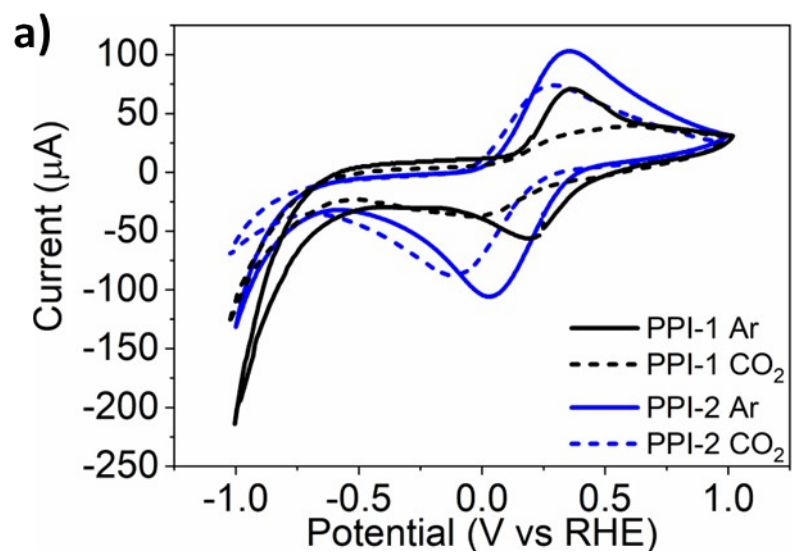
*Q: total charge passed*

*Note\**: The faradaic efficiency is calculated for each product individually, not the sum of all products formed.

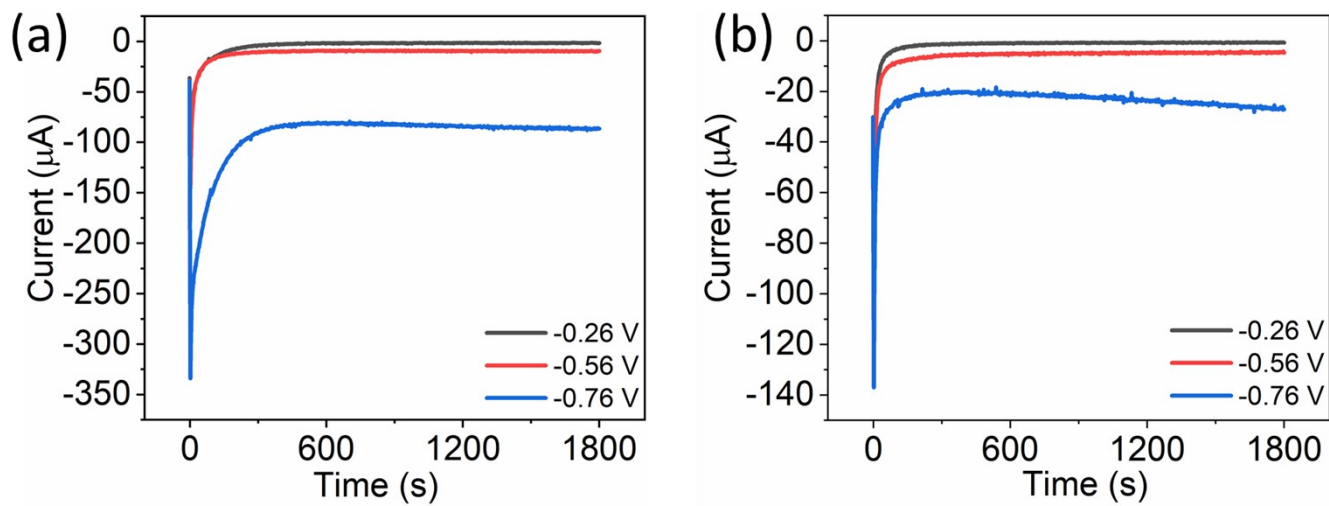
**Standard deviation (σ) was calculated using the equation:**

$$\sigma = \sqrt{\frac{\sum (xi - \mu)^2}{N}}$$

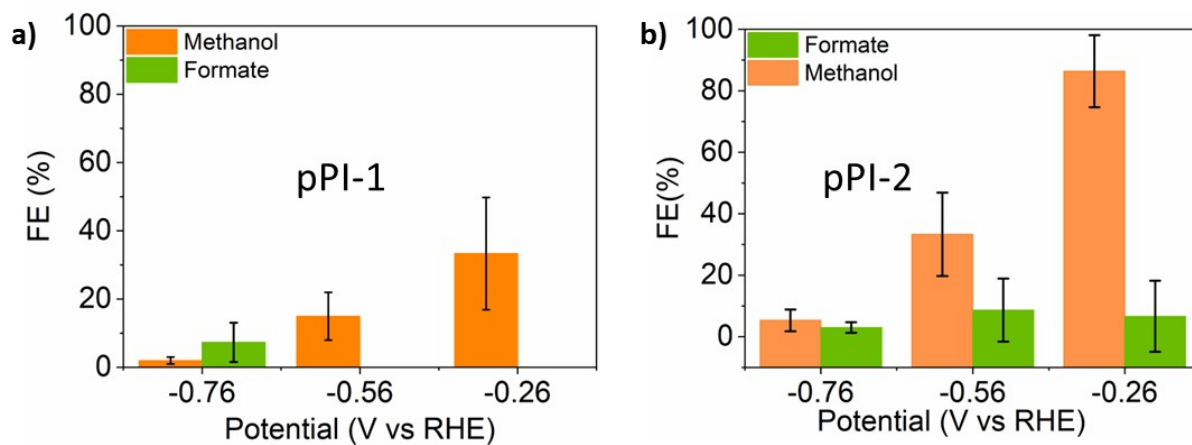
Where N=3, xi= the faradic efficiencies calculated for methanol and formate respectively and μ = the mean value of the calculated faradic efficiencies for methanol and formate respectively.



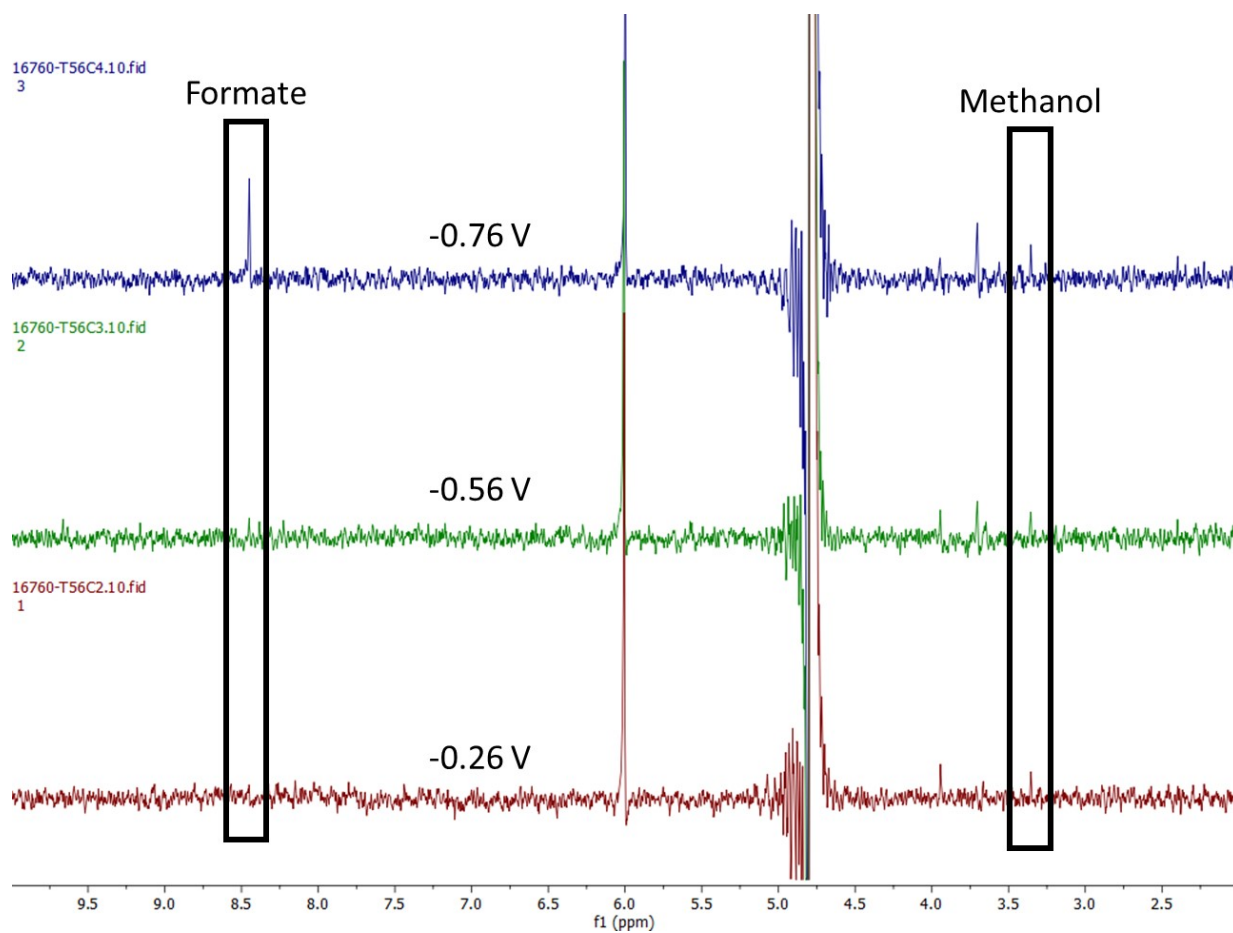
**Figure S11:** Cyclic voltammogram of **pPI-1** and **pPI-2** in the applied potential range from -1–1 V vs RHE, scan rate 20 mV/s, 20 cycles.



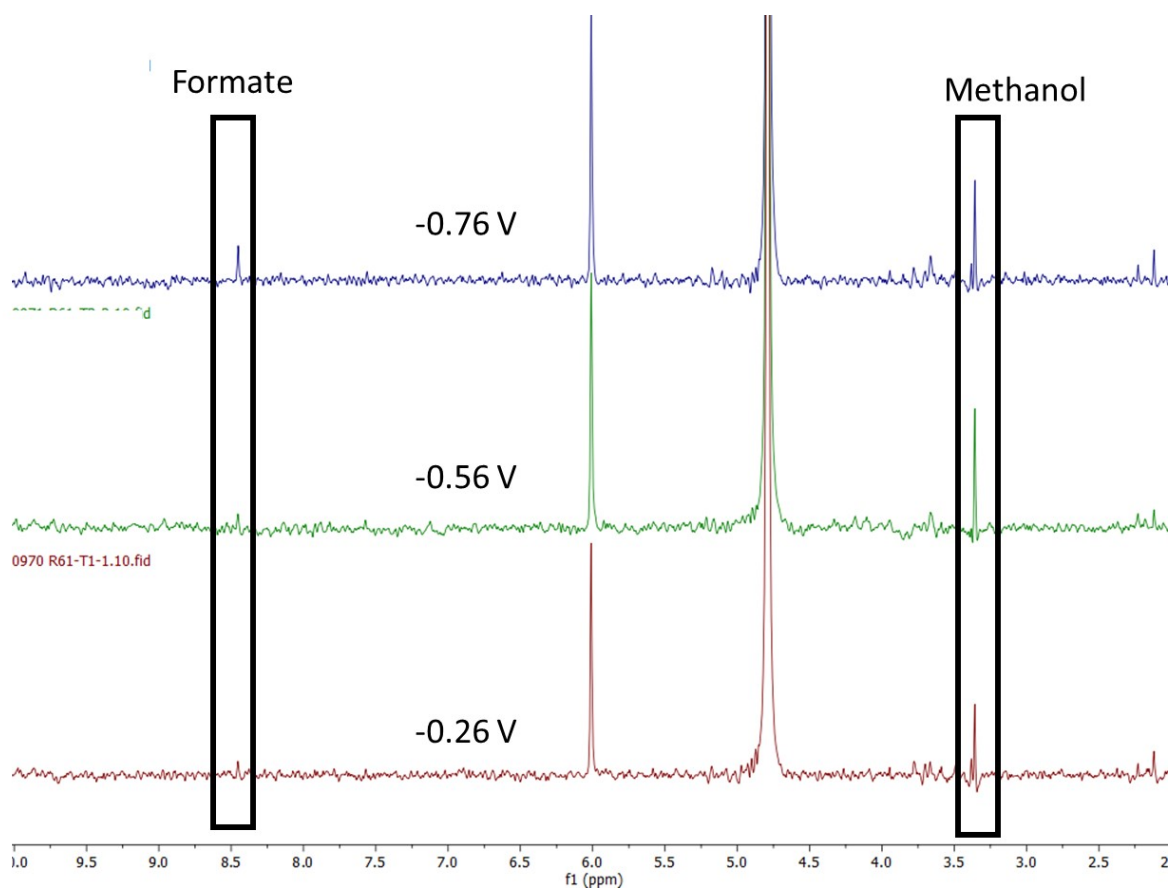
**Figure S12:** Chronoamperometry studies of (a) **pPI-1** and (b) **pPI-2**, in  $\text{CO}_2$ -saturated 0.1 M  $\text{KHCO}_3$  electrolyte for 30 min.



**Figure S13:** Graphs showing FEs, including error bars, for: (a) **pPI-1** and (b) **pPI-2**, respectively.



**Figure S14:**  $^1\text{H}$  NMR of electrolyte for **pPI-1** after CA investigations for 30 min in  $\text{CO}_2$ -saturated 0.1 M  $\text{KHCO}_3$  electrolyte.



**Figure S15:**  $^1\text{H}$  NMR of electrolyte for pPI-2 after CA investigations for 30 min in  $\text{CO}_2$ -saturated 0.1 M  $\text{KHCO}_3$  electrolyte.