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Supplementary information to

Post-polymerization modification towards polymer-supported metalloporphyrins for heterogeneous electrocatalysis

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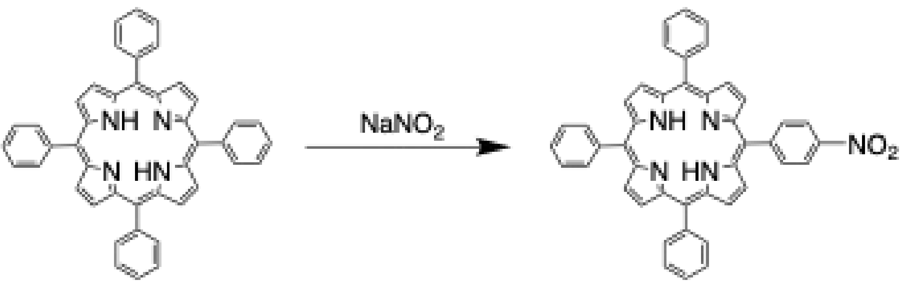
Materials

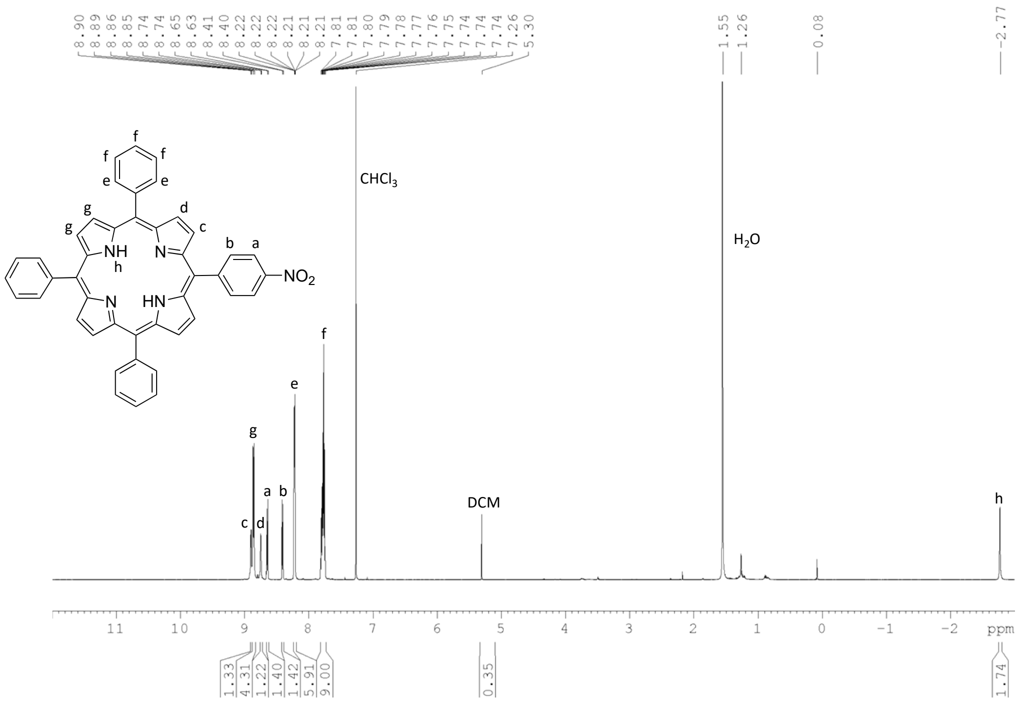
All reagents were purchased from commercial suppliers and used without any further purification. For the purification of small molecules, chromatography-grade silica was used. Tetraphenylporphyrin (TPP, 97%) was purchased from Meryer. Poly(MVE-*alt*-MA) (average Mw ~216,000, average Mn ~80,000), TFA (99%), 1-(3-aminopropyl)imidazole ($\geq$ 97%), $NaNO_2$, and $Na_2S.9H_2O$ ($\geq$ 98%) were purchased from Sigma-Aldrich. Carbon felt and MWCNTs were washed with 2.0 M HCl, deionised water, ethanol, and dried before use.

Synthesis

TPP-NO_2 synthesis



TPP (0.305 g, 0.5 mmol) was dissolved in 15 mL of TFA with sodium nitrite (0.07 g, 1.0 mmol), and the mixture was stirred for 3 minutes. The mixture was then poured into water and extracted with DCM. The organic layer was washed with 10% $NaHCO_3$ solution and then dried *in vacuo*. The residue was purified on a silica plug using DCM, and the DCM was evaporated. Yield: 270 mg (82%, m.p. >350 °C). ^1H NMR (600 MHz, $CDCl_3$): 8.89 (d, J = 4.5 Hz), 8.85 (d, J = 9.6 Hz), 8.74 (d, J = 4.5 Hz), 8.64 (d, J = 8.4 Hz), 8.40 (d, J = 8.4 Hz), 8.22-8.21 (m), 7.81-7.74 (m), -2.77 (s). ATR-FTIR (cm^{-1}): 1514 (N=O stretch), 1345 (C-N stretch), 964 (C-H bending), 795 (C-H bending).

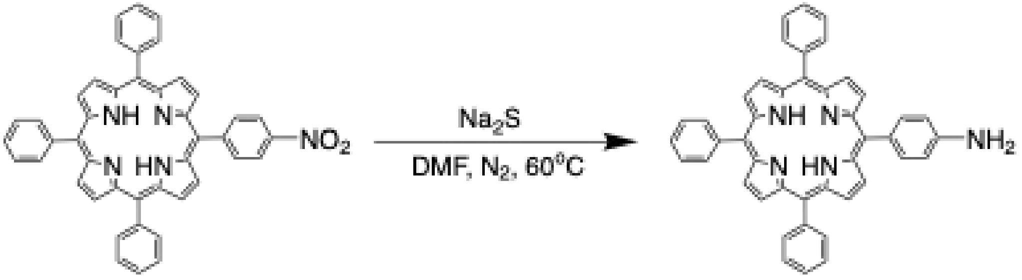


TPP-NH_2 synthesis

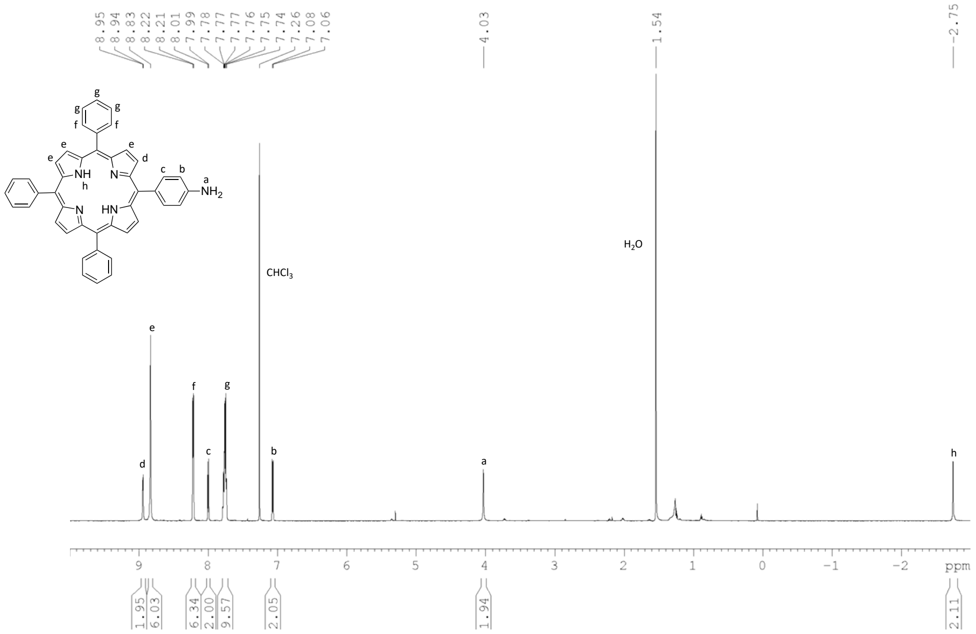
Tin(II) chloride as a reducing agent

TPP-NO_2 (0.199 g, 0.3 mmol) was dissolved in 30 mL of concentrated HCl/dioxane (85% HCl, 15% dioxane) with tin chloride ($SnCl_2$) before being heated under reflux for 1 hour under a N_2 atmosphere. The reaction mixture was quenched with cold water (100 mL) and neutralized to pH 8 using ammonium hydroxide. The organic layer was extracted with DCM until colourless, and the combined extracts were concentrated under vacuum. The residue was purified on a plug of alumina using DCM/methanol (95% DCM, 5% methanol). The final product was recrystallized from DCM/methanol, producing fine purple crystals. Yield: 107 mg (53%).

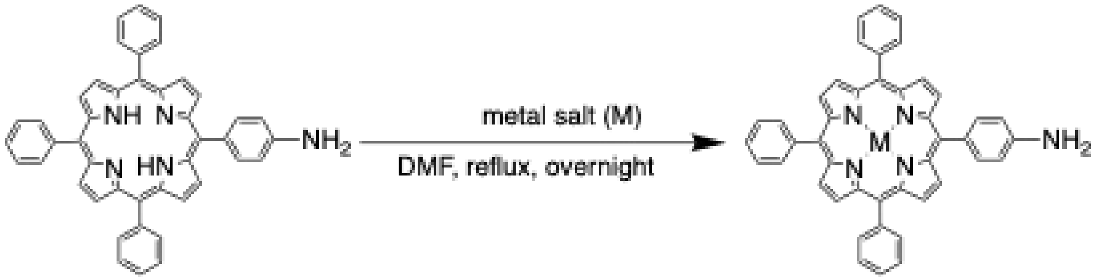
Na_2S as a reducing agent



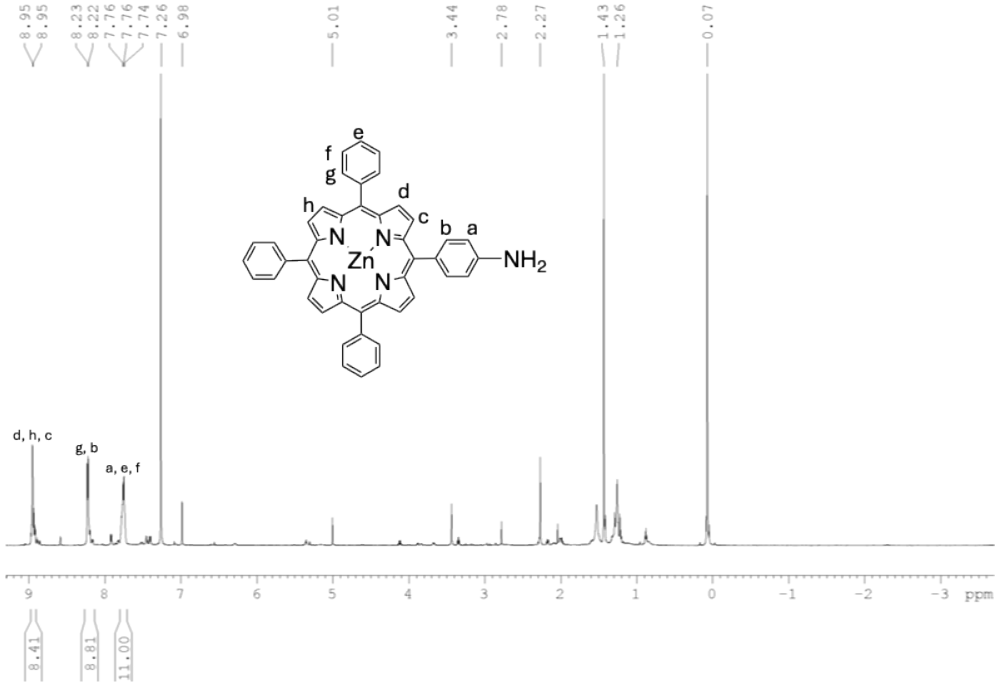
TPP-NO_2 (0.236 g, 0.4 mmol), $Na_2S.9H_2O$ (0.408 g, 5.2 mmol), 0.4 mL of deionized water, and 10 mL of DMF were heated to 60°C and stirred in a round-bottom flask overnight under N_2. DMF was evaporated under vacuum, and the dried sample was boiled in 25 mL of deionized water for 15 minutes. The residue was filtered and dried. The sample was then purified by silica gel column chromatography using DCM as the eluent (with R_f=0.5). The collected fraction was dried. Yield: 135 mg (60%, m.p. >350 °C). ATR-FTIR (cm^{-1}): 1617 (N-H bending), 1349 (C-N stretching), 1177 (C-N stretching), 965 (C-H bending), 796 (C-H bending). ^1H NMR (600 MHz, $CDCl_3$): 8.94 (d, J = 4.53 Hz), 8.83 (s), 8.22 (d, J = 7.57 Hz), 8.00 (d, J = 8.00 Hz), 7.78-7.74 (m), 7.07 (d, J = 8.05 Hz), 4.03 (s), -2.75 (s), UV-Vis in DMF: λ_{max} 417, 516, 557, 592, 652 nm.



Synthesis of M-TPP-NH_2

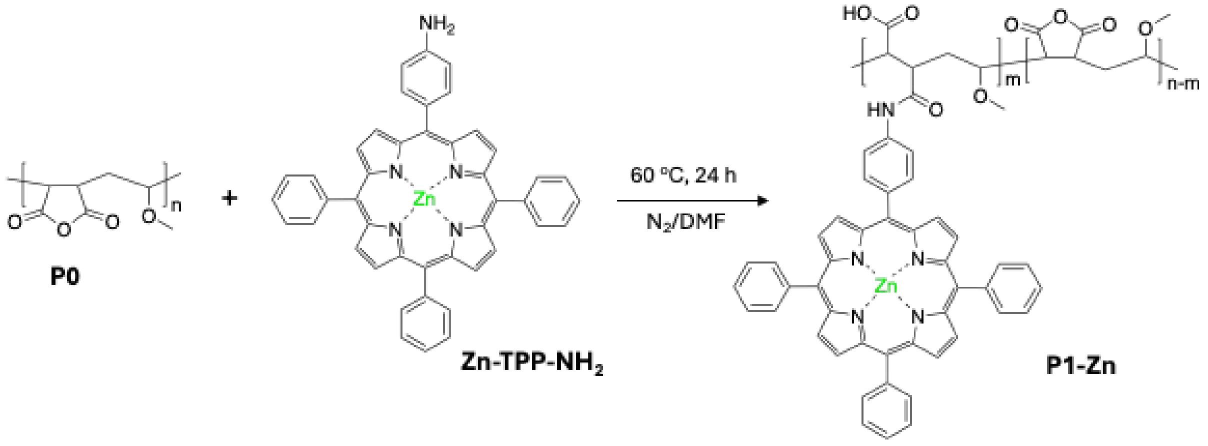


TPP-NH_2 was heated under reflux with excess metal salts (zinc acetate, cobalt chloride, copper acetate) overnight in DMF. The solution was cooled to room temperature before the solvent was removed, and the sample was washed with water and extracted using DCM. The DCM was then dried over magnesium sulphate, filtered and the DCM evaporated. The procedure was conducted in the dark. Metal insertion was determined by UV-Vis.



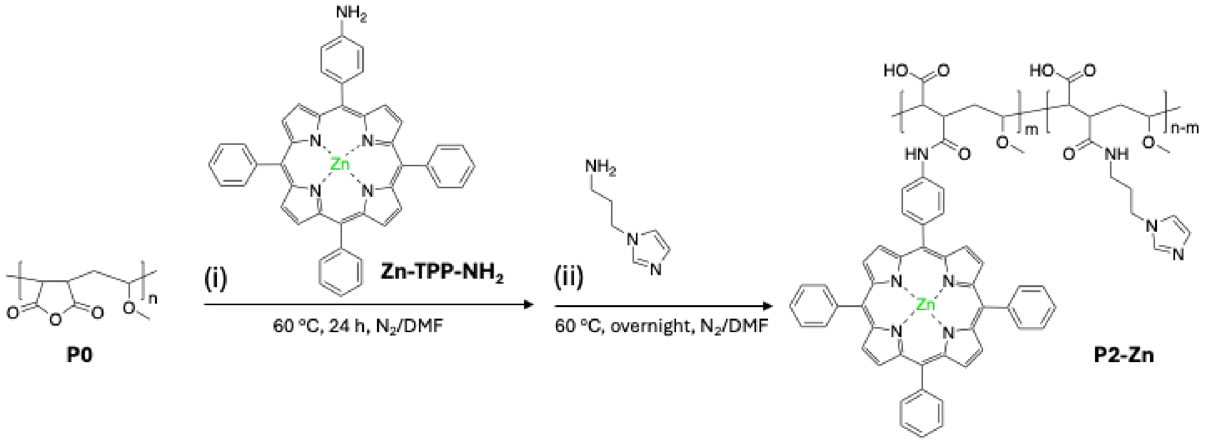
Preparation of polymer-supported metalloporphyrin catalysts

Synthesis of P1-Zn



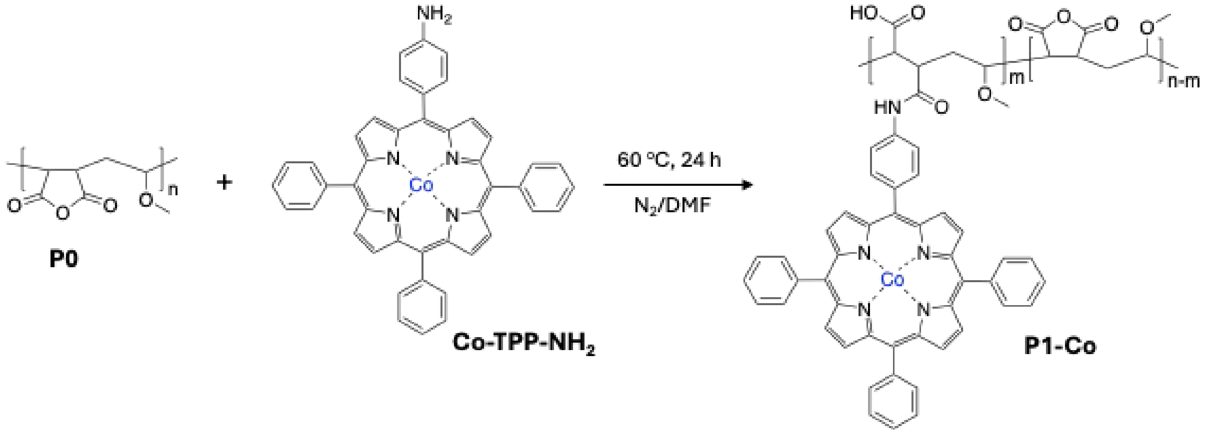
Poly(MVE-*alt*-MA) (184 mg, 1.2 x 10^{-3} mol of anhydride) was stirred in 2 mL of DMF for 30 minutes at room temperature. Zn-TPP-NH_2 (81.4 mg, 1.2 x 10^{-4} mol) was added and allowed to react under nitrogen at 60 °C for 24 hours. The DMF was evaporated, and the sample was washed with toluene because Zn-TPP-NH_2 was soluble in toluene, whereas the polymer was not. The precipitate was then dried. Yield 257 mg, UV-Vis in DMF: l_{max} 425, 559, 600 nm. Elemental analysis: Found: C, 51.03; N, 3.37.

Synthesis of P2-Zn



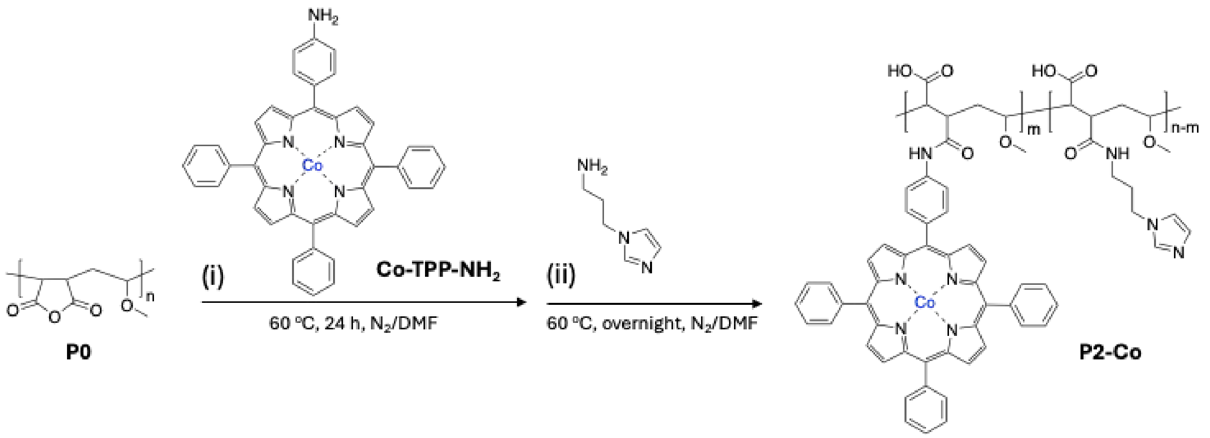
Poly(MVE-*alt*-MA) (180 mg, 1.2 x 10^{-3} mol) was stirred in 2 mL of DMF for 30 minutes at room temperature. Zn-TPP-NH_2 (82 mg, 1.3 x 10^{-4} mol) was added and left to react under nitrogen at 60 ^{o}C for 24 hrs. 1-(3-Aminopropyl)imidazole (92 µL, 7.7 × 10^{-4} mol) was then added, and the sample was left to stir under nitrogen at 60 °C overnight. The product precipitated out of solution, and the precipitate was washed with ethanol and dried. Yield 226 mg, UV-Vis in DMF: l_{max} 426, 561, 603 nm. Elemental analysis: Found: C, 51.65; N, 10.70.

Synthesis of P1-Co



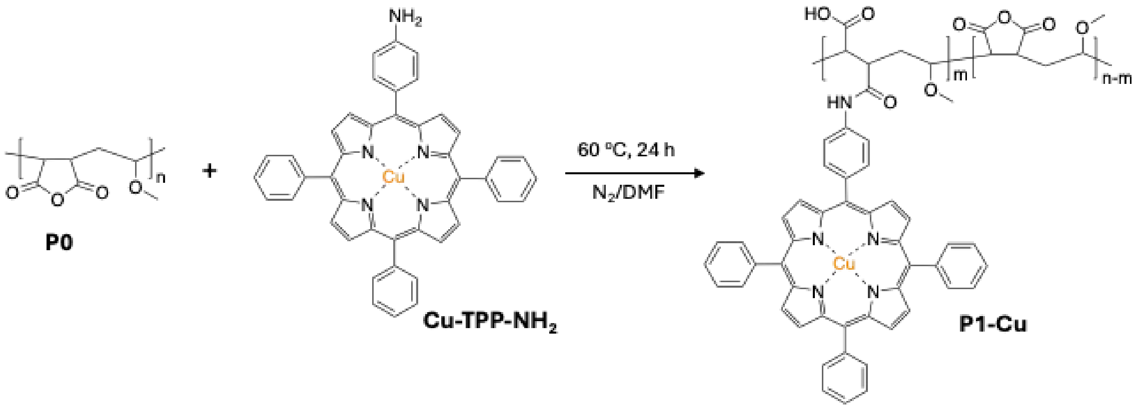
Poly(MVE-*alt*-MA) (0.150 g, 9.6 x 10^{-4} mol) was stirred in 2 mL of DMF for 30 minutes at room temperature. Co-TPP-NH_2 (0.066 g, 9.7 x 10^{-5} mol) was added and left to react under nitrogen at 60 °C for 24 hrs. To purify, the DMF was evaporated, the sample was washed with ethanol, and the precipitate was dried. Yield: 178 mg, UV-Vis in DMF: l_{max} 429, 542 nm. Elemental analysis: Found: C, 53.16; N, 2.51.

Synthesis of P2-Co



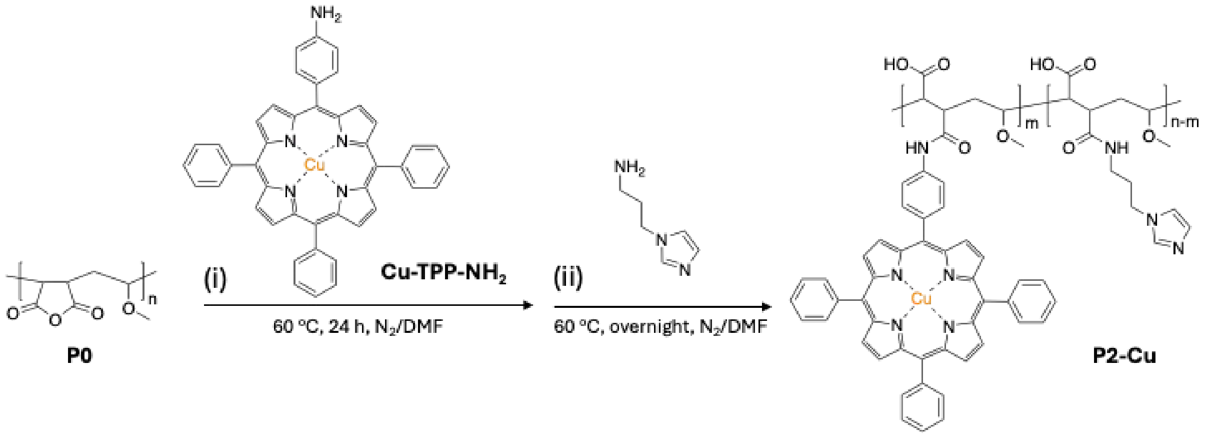
Poly(MVE-*alt*-MA) (0.151 g, 9.7 x 10^{-4} mol) was stirred in 2 mL of DMF for 30 minutes at room temperature. Co-TPP-NH$_2$ (0.066 g, 9.6 x 10^{-5} mol) was added and left to react under nitrogen at 60 °C for 24 hrs. 1-(3-aminopropyl)imidazole (0.136 mL, 1.0 x 10^{-3} mol) was then added, and the sample was left to stir under nitrogen at 60 °C overnight. The product precipitated out of solution, and the precipitate was washed with ethanol and dried. Yield 218 mg, UV-Vis in DMF: l_{max} 434, 552, 592 nm. Elemental analysis: Found: C, 57.50; N, 13.775.

Synthesis of P1-Cu



Poly(MVE-*alt*-MA) (0.184 g, 1.2 x 10^{-3} mol) was stirred in 2 mL of DMF for 30 minutes at room temperature. Cu-TPP-NH$_2$ (0.081 g, 1.2 x 10^{-4} mol) was added and left to react under nitrogen at 60 ^{o}C for 24 hrs. The sample was washed with ethanol, and the precipitate was dried. Yield: 160 mg, UV-Vis in DMF: λ_{max} 415, 540 nm. Elemental analysis: Found: C, 53.46; N, 3.07.

Synthesis of P2-Cu



Poly(MVE-*alt*-MA) (0.182 g, 1.2 x 10^{-3} mol) was stirred in 2 mL of DMF for 30 minutes at room temperature. Cu-TPP-NH_2 (0.082 g, 1.2 x 10^{-4} mol) was added and left to react under nitrogen at 60 °C for 24 hrs. 1-(3-Aminopropyl)imidazole (92 μL, 7.7 × 10^{-4}) mol) was then added, and the sample was left to stir under nitrogen at 60 °C overnight. The product precipitated out of solution, and the precipitate was washed with ethanol and dried. Yield 284 mg, UV-Vis in DMF: λ_{max} 415, 540 nm. Elemental analysis: Found: C, 52.51; N, 12.11.

Instruments and methodology

NMR

NMR spectra were measured on a Bruker 600 MHz Avance III or NEO at 25°C unless otherwise stated. The chemical shifts (δ) are given in ppm, and the coupling constants (J) are given in Hz. The ^{1}H and ^{13}C chemical shifts are referenced using the residual solvent signals (^{1}H NMR: $CDCl_3$ 7.26 ppm, DMSO-d_6 2.50 ppm; ^{13}C NMR: $CDCl_3$ 77.16 ppm, DMSO-d_6 39.52 ppm).

ATR-FTIR

ATR-FTIR analysis was conducted using a Nicolet iS50 ATR FT-IR with a resolution of 2 and 64 scans between 4000 and 400 cm^{-1}. Solid samples were analysed under atmospheric pressure and at room temperature to determine the presence/absence of specific functional groups.

Elemental Analysis

Samples were analysed on an Elementar Vario Isotope Cube with helium (He) as a carrier gas. The samples were prepared by weighing out approximately 1.5 mg of sample and combusting at 950 °C in the presence of O_2. The evolved gases were reduced in a reduction tube heated to 600 °C containing Cu wire ($NO_x \rightarrow N_2$). The water was removed from the samples using siccapent (Phosphorus pentoxide). Using a thermal conductivity detector, the C (CO_2) and N (N_2) peak areas were measured and correlated to % carbon and % nitrogen with the use of an acetanilide standard.

UV-Vis

UV-Vis analysis was used to confirm the presence of the metalloporphyrin within the polymer chain. UV-Vis analysis was conducted on an Agilent Cary 60 UV-Vis using a quartz cuvette in the wavelength range 300-800 nm. Samples were prepared by dissolving between 0.5-1 mg of solid in 5 mL of DMF. The imidazole-containing polymer samples exhibited poor solubility. As a result, the samples were stirred for 72 hours, and any undissolved material was filtered out. 10-150 mL of solution was then diluted to 5 mL in DMF for analysis.

Electrochemistry

Electrochemical characterizations, including cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectrometry (EIS), were carried out on a Gamry

Interface 1010E potentiostat (Warminster, PA, USA) using a standard three-electrode cell at 25°C. A 3 mm glassy carbon electrode was used as the working electrode, and 0.05 µm Al_2O_3 powder was used to polish after each measurement. For all analyses, Ag/AgCl (3M KCl) was the reference electrode, and a platinum wire (16 cm) was the counter electrode.

Cyclic voltammetry

CV was conducted in an undivided cell with a platinum counter electrode and an Ag/AgCl reference electrode. Analysis was conducted in a 0.5 M sodium bicarbonate electrolyte (pH=8.8) for CO_2RR/HER or a 0.1 M carbonate-bicarbonate buffer (pH=10) for OER. Ag/AgCl. Working electrodes were prepared by combining approximately 6 mg of polymer with 20 mg of carbon nanotubes, 200 µL of Nafion solution, and 1.8 mL of DMF. This mixture was sonicated to form a paste, which was then cast between a sheet of carbon felt, and the solvent evaporated. Copper-containing polymer samples P1-Cu and P2-Cu were compared to both a blank electrode and Cu-TPP. All samples were analysed under nitrogen and carbon dioxide atmospheres for CO_2RR. The samples were run under nitrogen to act as a control.

Chronoamperometry for OER

Slurries of cobalt containing polymers (P1-Co and P2-Co) were prepared by mixing with MWCNTs and Nafion. For the soluble polymer, P1-Co (6.7 mg) was dissolved in 1 mL of DMF. Nafion (200 µL) was then added to the polymer solution along with MWCNTs (20 mg), and the mixture was ground until a reflective slurry formed. For the insoluble polymer (P2-Co), the sample was ground in 0.5 mL of DMF for 10 minutes. MWCNTs were added and further ground before 200 µL of Nafion was added and ground. The sample was ground for a total of 30 minutes.

For LSV, the electrode was prepared by drop casting 2-3 µL of the sample onto the glassy carbon electrode and drying the sample under vacuum. LSV was run in a 0.1M carbonate-bicarbonate buffer (pH=10) with an Ag/AgCl reference electrode and a platinum counter electrode. LSV was run between 0.8 V and 1.6 V vs Ag/AgCl.

CA samples were prepared by loading the sample onto a titanium mesh (200). The slurry was spread onto the mesh before being dried under vacuum overnight. The mass loading for P1-Co was 1.9 mg/cm^2 and P2-Co 3.8 mg/cm^2. The current densities were normalized to µmol/cm^2 according to Co-TPP.

Coupled CA-GC for CO_2RR

CO_2RR was carried out using coupled chronoamperometry (CA) and gas chromatography (GC). CA was conducted on a CHI electrochemical station, and GC was run on an Agilent 8890 GC system. The GC system contained two detectors, a TCD detector and an FID detector. The TCD detector was set at 175 °C with a reference flow of 20 mL/min and a makeup flow (Ar) of 2 mL/min. The FID detector was set at 250 °C with an air flow of 400 mL/min, a H_2 fuel flow of 30 mL/min, and a makeup flow (Ar) of 2 mL/min. The split-splitless inlet was set to 100 °C, with a pressure of 33.6 psi and a septum purge flow of 3 mL/min. The oven was set at 80 °C.

The CA experiments were conducted in an undivided cell containing a platinum counter electrode and an Ag/AgCl reference electrode. Analysis was conducted in a 0.5 M sodium bicarbonate electrolyte (N_2: pH=8.8 and CO_2; pH= 7.2). Working electrodes were prepared by combining 6 mg of polymer with 20 mg of carbon nanotubes, 200 µL of Nafion solution, and 1.8 mL of DMF. This mixture was sonicated to form a paste, which was then spread between a sheet of carbon felt, and the solvent evaporated. P1-Cu and P2-Cu were compared to a blank carbon felt electrode and Cu-TPP. CO_2RR experiments were conducted under both N_2 and CO_2.

Before electrochemical analysis, the solutions were purged with either nitrogen or carbon dioxide for 30 minutes. CA was recorded for 2000 seconds at -1.25 V vs Ag/AgCl, with gas samples collected with a gas-tight syringe from the vial at 0, 1000, and 2000 seconds. Samples were injected directly into the GC for analysis.

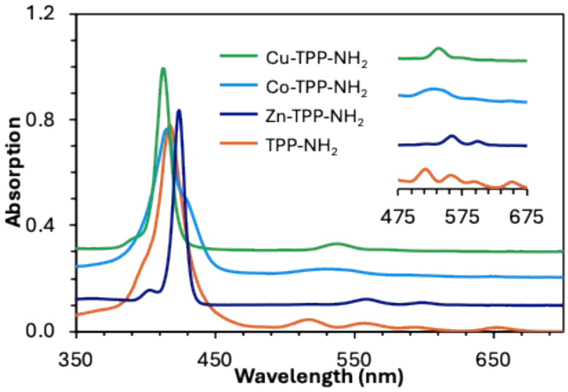


Figure S1. UV-Vis spectra of $TPP-NH_2$ and its derivatives $M-TPP-NH_2$. (The spectra were separated along the Y-axis for better presentation.)

Table S1: Spectra characteristics of metalloporphyrins and their polymer derivatives; the spectra were recorded in DMF.

	S	**Q1**	**Q2**	**Q3**	**Q4**
TPP-NH_2	417	516	557	592	652
Zn-TPP-NH_2	424	558	599		
P1-Zn	425	559	600		
P2-Zn	426	561	603		
Co-TPP-NH_2	415	530	590		
P1-Co	429	542	595		
P2-Co	434	552	600		
Cu-TPP-NH_2	413	538	578		
P1-Cu	415	540	580		
P2-Cu	415	540	582		

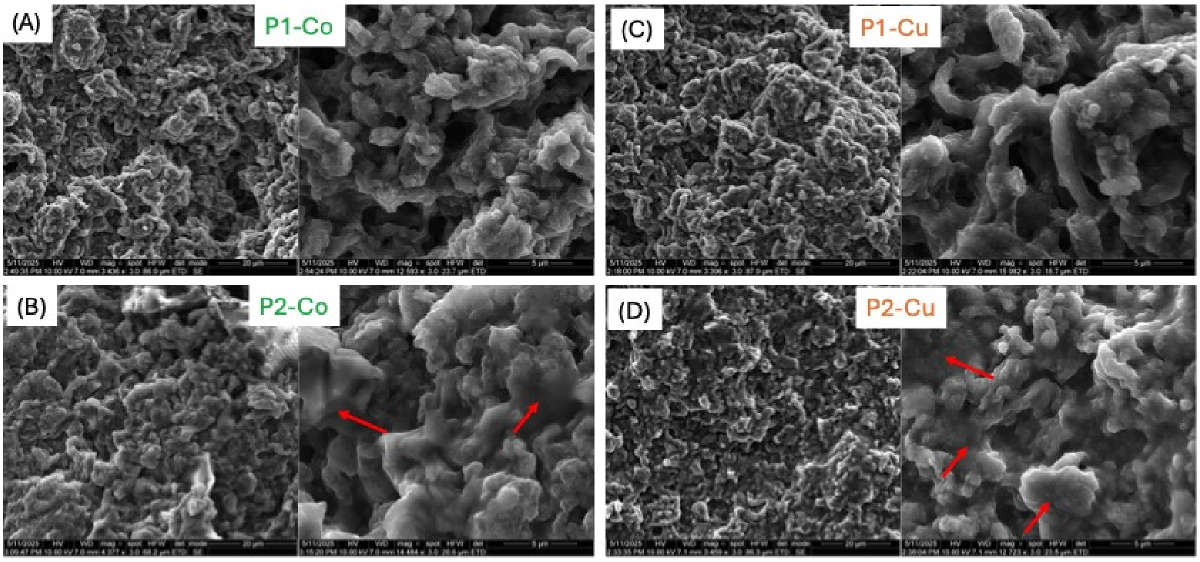


Figure S2. SEM of electrode composites for (A) P1-Co, (B) P2-Co, (C) P1-Cu, and (D) P2-Cu at the polymer/MWCNT ratio of 1/3. The red arrows indicated some polymer agglomerations.

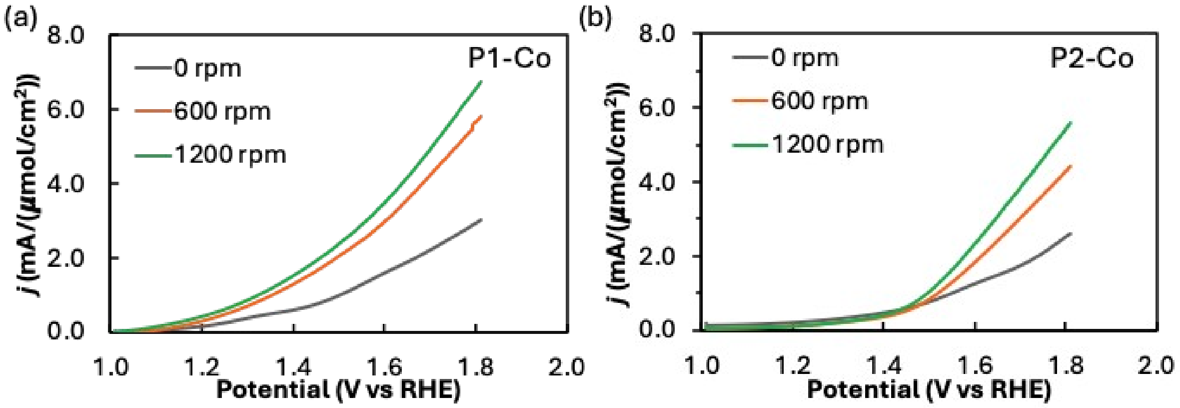


Figure S3. LSV of (a) P1-Co and (b) P2-Co for OER reaction in 0.1 M carbonate-bicarbonate buffer (pH=10).

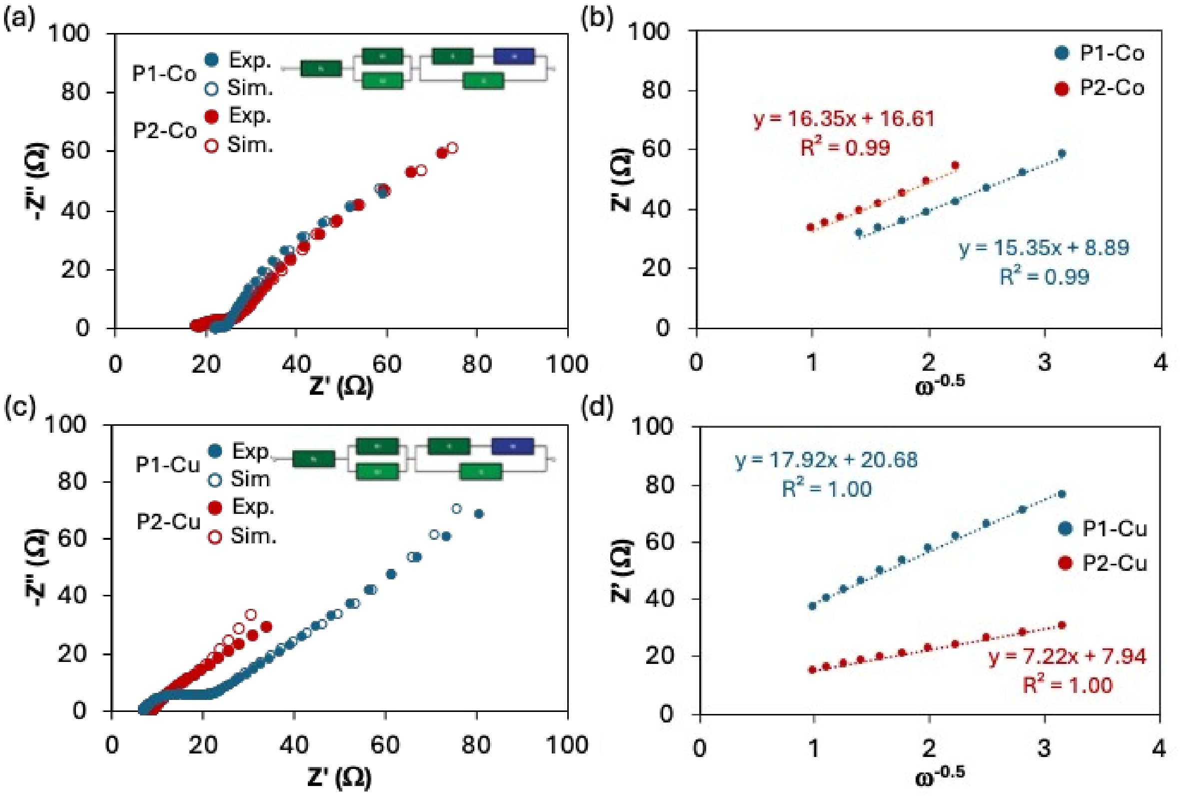


Figure S4. EIS of polymer-supported Co-TPP/MWCNT (a) and Cu-TPP/MWCNT (c) electrodes (spread on the carbon felt), and their corresponding Warburg ecoefficiencies (b and d).

Table S2: EIS parameters obtained by fitting the experimental spectra using the model in Figure S4.

	P1-Co	P2-Co	P1-Cu	P2-Cu
R_s (W)	21.82	17.69	6.96	7.66

R_{ct} (W)	143.05	64.72	99.08	2.40
W (W)	1.33E+04	1.62E-02	3.01E-04	3.14E-02
s	15.35	16.35	17.92	7.22

The Warburg resistance from fitting showed some big discrepancies; therefore, the Warburg coefficients (σ) were also calculated, which is given by the relationship of $Z' = \sigma\omega^{-1/2}$, when Z' was plotted against the reciprocal of the square root of frequency, $\omega^{-1/2}$, in the low-frequency region, such as <1 Hz. The smaller σ indicates the higher ion diffusion coefficient of the electrodes.

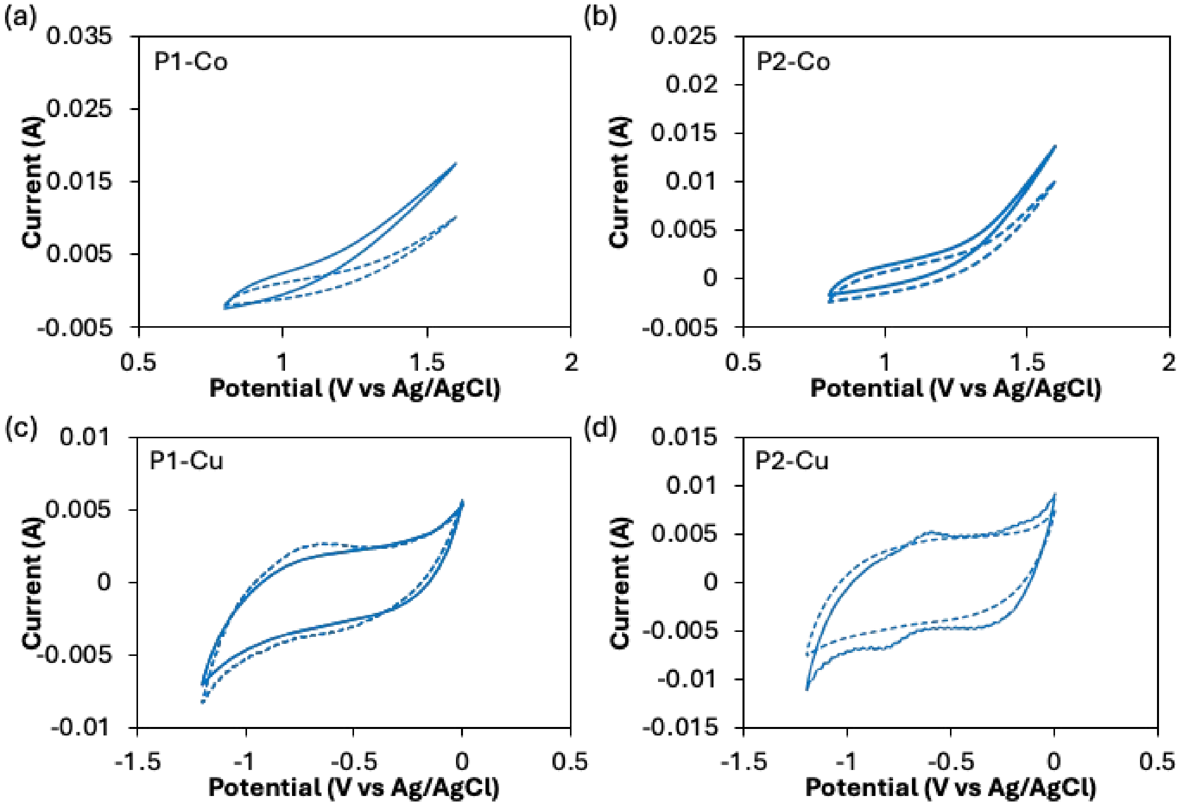


Figure S5. CV of all polymers before (solid) and after (dashed) CA (2h) measurement. (a) and (b) at pH=10, (c) and (d) at pH=7.2.

Table S3: HER performance comparison of polymer-supported M-TPP catalysts

Catalyst	1D/2D	Water soluble	Catalyst	*j* (mA/cm^2)	Solution	
Co-1	1D	+ (homogeneous)	100 (mmol/L)	5.8	0.1 M phosphate	Ref 1
Co-2	1D	+ (homogeneous)	100 (mmol/L)	3.9	0.1 M phosphate	Ref 1
Co-3	1D	+ (homogeneous)	100 (mmol/L)	1.3	0.1 M phosphate	Ref 1
2DP1-Co	2D	- (heterogeneous)	~0.3 (mmol/cm^2)	>10	0.1 M H_2SO_4	Ref 2
2DP2-Ni	2D	- (heterogeneous)	~0.3 (mmol/cm^2)	>10	0.1 M H_2SO_4	Ref 2
P1-Cu	1D	- (heterogeneous)	1 (mmol/cm^2)	2.3	0.5 M Na_2CO_3	This work
P2-Cu	1D	- (heterogeneous)	1 (mmol/cm^2)	2.6	0.5 M Na_2CO_3	This work

Ref 1: Xie et al. Angew. Chem. Int. Ed. 2020, 59, 15844 – 15848

Ref 2: Ranjeesh et al. ACS Appl. Energy Mater. 2018, 1, 11, 6442–6450