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Covalent structured catalytic materials containing single-atom metal sites with controllable spatial and chemical properties: concept and application

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Experimental Section

Materials and Instrumentation

Unless otherwise noted, all chemicals were purchased from either VWR chemicals, Fluorochem or Merck and used without further purification. Solvents were dried prior to reaction over 3 Å molecular sieves. Carbon Black - Vulcan XC-72R was purchased from Dols International BV. All experiments were performed under nitrogen atmosphere, unless stated otherwise. FTIR spectra (4000–400 cm^{-1}, resol. 0.5 cm^{-1}) were recorded on a Varian 660 FTIR spectrometer using ATR and the transmission technique. X-Ray diffraction (XRD) patterns were obtained with a MiniFlex II diffractometer using Ni-filtered CuKα radiation. The X-ray tube was operated at 30 kV and 15 mA, with a 0.01° step and 1s dwell time. Raman spectra were recorded using a Renishaw InVia system (532 and 632.8 nm) and a Kaiser Optical Systems RXN-4 system (785 nm) coupled with fibre optics to an immersion probe with a short focal length. ICP analysis was performed by Kolbe GmbH (Germany). The experimental values obtained were corrected for the presence of oxygen. Mass spectra were collected on two instruments: (A) AccuTOF LC, JMS-T100LP Mass spectrometer (JEOL, Japan). ESI source, positive-ion mode; needle voltage 2500V, orifice 1 voltage 120V, orifice 2 voltage 9V; ring Lens voltage 22V; orifice 1 80 °C, desolvating chamber 250 °C. The samples were measured using flow injection with a flow rate of 0.01 mL/min, and the spectra were recorded with an average duration of 0.5 min. (B) MALDI-TOF-Instrument, UltraFlextreme Company Bruker Daltonik, Bremen, Germany was used for the measurements. Matrix solution was α-cyanno-4-hydroxycinnamic-acid in 50% (0.1% TFA) and 50% MeOH (10 mgHCCA/mL). (For DHB matrix: 20 mgDHB/mL) The matrix solution was applied by pipet at the ratio of 1:1 analyte/matrix (1 µL each). The crystallisation occurred at room temperature, for a few minutes. In one spot, a standard peptide mix (Bruker) was used for the calibration of the instrument. The laser power with which the measurements were performed was adjusted per experiment, with acquisitions of 1000 or 1500 laser shots per sample. X-ray absorption spectra were collected at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF, Beijing, China) using a transmission mode. The XAS spectra and EXAFS interference functions were extracted from the raw experimental data using Athena software.[1] The radial distributions are calculated from the magnitude of the k^2-weighted interference function $X(k)$ using a Hanning window over a k range of 3.0–12.8 $Å^{-1}$.

Electrochemical Procedures:

Electrodes were prepared using a 1 wt% metal ratio on Vulcan XC-72R carbon powder. In a typical preparation, the catalyst (10–16 mg) was mixed with Vulcan XC-72R carbon powder (100 mg). THF (5 mL) was then added, and the mixture was placed in an ultrasonic bath for > 24 h. After evaporation, the impregnated polymer is isolated. The preparation of the metal oxides on Vulcan XC-72R differs from this method. Vulcan XC-72R was prepared by heating to 150 °C in a sand bath under vacuum overnight. 0.1 mL of a 1 wt% metal ratio of metal nitrate was deposited dropwise on to the Vulcan XC-72R while stirring. The catalysts were then dried overnight at 70 °C in an oven. The catalysts were then oxidised in a tubular furnace at 400 °C for 1 h.

Inks of the catalytic powders were prepared according to the following proportions: 1.0 mL EtOH, 10 µL Nafion® (D-521 dispersion 5% wt in water/isopropanol, Alfa Aesar 42117), and 1 mg catalyst powder. The inks were placed in an ultrasonic bath and stirred for several hours. The working electrode substrate was a $\Phi = 5$ mm ($A = 0.196$ cm^2) glassy carbon electrode (Gamry, USA), which was polished by diamond polishing films with 1 and 0.1 µm particles (Allied High Tech Products, USA), and rinsed well. Inks were deposited by drop-casting 5 µL portions x 6, with air drying between each drop. The total catalyst loading was 30 µg, or 153 µg/cm^2.

Electrochemical experiments were performed in a 3-electrode home-made glass cell, filled with KOH (0.1 M, 150 mL), stabilized at 25.0 ± 0.1 °C in a water bath. A Gamry Reference 600 potentiostat was employed, together with a Gamry RDE710 Rotating Electrode setup. Saturated calomel electrode (SCE, Gamry, USA) separated from the solution by a 10 cm bridge was used as a reference electrode, and a graphite rod (Gamry, USA) as a counter electrode. Potentials are reported *vs.* reversible hydrogen electrode (RHE) by adding 1.011 for pH 13. Nitrogen (99.999%) or oxygen (99.999%) were bubbled for 30 min to saturate the solution, and were flowed above the solution (so-called 'gas blanket') during the experiments. Linear scan voltammograms were measured from 0.1 to 1.0 V vs. RHE with a scan rate of 10 mV/s at rotating speeds of 400, 600, 900, 1200, 1600, 2000 and rpm. Cyclic voltammetry was measured from -0.2 to 0.2 V with a scan rate of 200 mV/s for 50 cycles, from -0.2 to 0.2 V with a scan rate of 20 mV/s with 5 cycles, and then from 0 to -0.9 V with a scan rate of 10 mV/s for 3 cycles. All cyclic voltammetry was performed without rotation.

General procedure for synthesising metal-containing tetra-amino phthalocyanines (MPc(NH$_2$)$_4$)

This is a modification of a published, analogous procedure.[2] 4-aminophthalonitrile and the corresponding metal salt were dissolved in *n*-pentanol. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added and the mixture was heated for 2 h at 140 °C, forming a black coloured solution. The mixture was cooled down to ambient temperature, after which it was vacuum filtered and washed with water (5 × 10 mL) and then with EtOH (5 × 10 mL). The residue was dried under air.

Example: **CoPc(NH$_2$)$_4$**: 4-aminophthalonitrile (286 mg, 2.0 mmol) and cobalt(II) chloride hexahydrate (0.119 g, 0.5 mmol) were dissolved in n-pentanol (2 mL) together with DBU (0.1 mL, 0.7 mmol). The mixture was heated at 140 °C for 2 h after which a black solution was formed. The mixture was allowed to cool down to room temperature, after which the product was obtained by vacuum filtration. The product was washed with water (5 × 10 mL) and EtOH (5 × 10 mL). The black powder was dried in air overnight. This gave CoPc(NH$_2$)$_4$, as a black powder, 0.14 g (45 mol% yield based on 4-aminophthalonitrile). HRMS (ESI+) *m/z* calculated $C_{32}H_{20}CoN_{12}$, 631.127, found, 631.124. FTIR (cm^{-1}): 1607, 1493, 1385, 1316, 1256, 1201, 1093, 836, 738, 426.

The synthesis of CuPc(NH$_2$)$_4$ was similarly performed, using CuCl$_2$ (68 mg, 0.5 mmol, 68 mol% yield based on 4-aminophthalonitrile) instead of the cobalt salt.

Procedure for the synthesis of CuPcC$_0$

1,2,4,5-tetracyanobenzene (100 mg, 0.6 mmol) and copper(II)chloride (75 mg, 0.6 mmol) were dissolved in *n*-pentanol (2 mL). DBU (0.1 mL, 0.7 mmol) was added and the mixture was heated for 24 h at 140 °C, forming a green solution. The reaction was cooled down to ambient temperature, filtered and washed with water (5 × 10 mL) followed by EtOH (2 × 10 mL) and finally with acetone (1 × 10 mL). The dark green precipitate was dried under a N$_2$ flow. This gave CuPcC$_0$, as a dark green product, 75.2 mg. FTIR (cm^{-1}): 3333, 2930, 2230, 1574, 1308, 1092, 748. HRMS (FD+) *m/z* calc.for three connected CuPcs: 1374.292 Da, found: 1374.105 Da.

General procedure of PMPcC$_x$ (M = Cu/Co. X= 2,6,10, TPA (teraphthaloyl chloride))

Stock solutions of MPc(NH$_2$)$_4$ and the corresponding linker were made in dimethylformamide after which the linker and MPc(NH$_2$)$_4$ and K$_2$CO$_3$ were combined at 50 °C. After 4 h, MPc(NH$_2$)$_4$ and K$_2$CO$_3$ were added to the solution and left for 16 h. To this mixture, more linker and K_2CO_3 was added and after 4 h. More $MPc(NH_2)_4$ and K_2CO_3 was added and allowed to react for 16 h. The mixture was cooled down, gravity filtrate and washed with water (5 × 10 mL), EtOH (5 × 10 mL) and dimethylformamide (2 × 10 mL). The residue was dried under air.

Example: **PolyCoPcC$_{TPA}$**: Stock solutions of 10 mg/mL of tetra-amino cobalt phthalocyanine and terephthaloyl chloride were made in dimethylformamide. Tetra-amino cobalt phthalocyanine (415 µL, 6.6 µmol) and potassium carbonate (16 mg, 1.1 mmol) were added together and heated to 50 °C. Terephthaloyl chloride (540 µL, 2.6x10^{-2} mmol) was then added, and the reaction mixture was stirred at 50 °C for 4 h. Tetra-amino cobalt phthalocyanine (1.66 mL, 2.6x10^{-2} mmol) and potassium carbonate (16 mg, 1.1 mmol) were added to the reaction mixture, and it was allowed to stir for 16 h. Terephthaloyl chloride (1.61 mL, 7.9x10^{-2} mmol) and potassium carbonate (48 mg, 3.3 mmol) were then added, and the reaction mixture was stirred at 50 °C for 4 h. Tetra-amino cobalt phthalocyanine (5.0 mL, 7.9x10^{-2} mmol) and potassium carbonate (48 mg, 3.3 mmol) were added to the reaction mixture, and it was allowed to stir for 16 h. The crude reaction mixture was then filtered and washed with water (5 × 10 mL), giving at green filtrate and black residue, followed by ethanol (5 × 10 mL), giving at green filtrate and black residue, and then dimethylformamide (2 × 10 mL), giving a dark green filtrate and black residue. This dark green filtrate was then evaporated, yielding a very dark green residue. This gave the product, yielding 0.0374 g of dark green solid. ATR-FTIR: µ(cm^{-1}) = 1658, 1606, 1522, 1495, 1471, 1437, 1408, 1385, 1352, 1319, 1259, 1192, 1132, 1097, 1061, 891, 833.

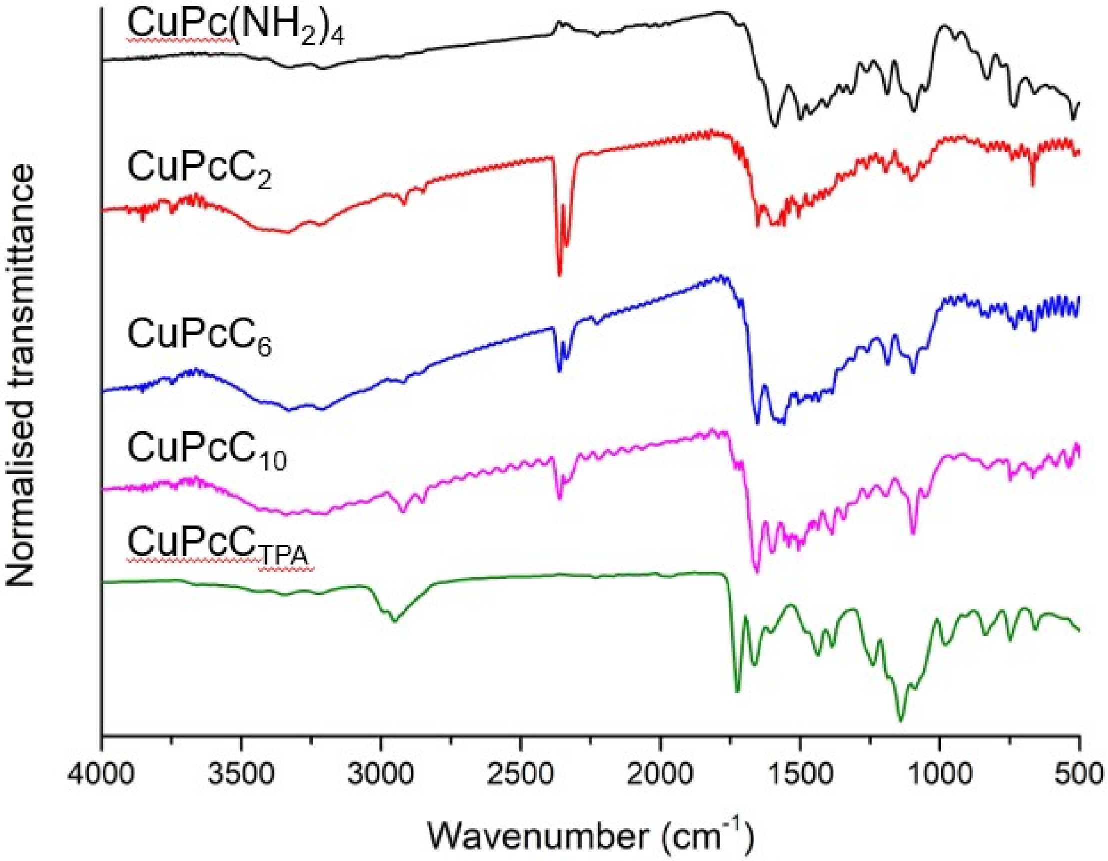

Figure S1: FTIR spectra of the $CuPc(NH_2)_4$ (black), $CuPcC_2$ (red), $CuPcC_6$ (blue), $CuPcC_{10}$(purple) and $CuPcC_{TPA}$ (green)

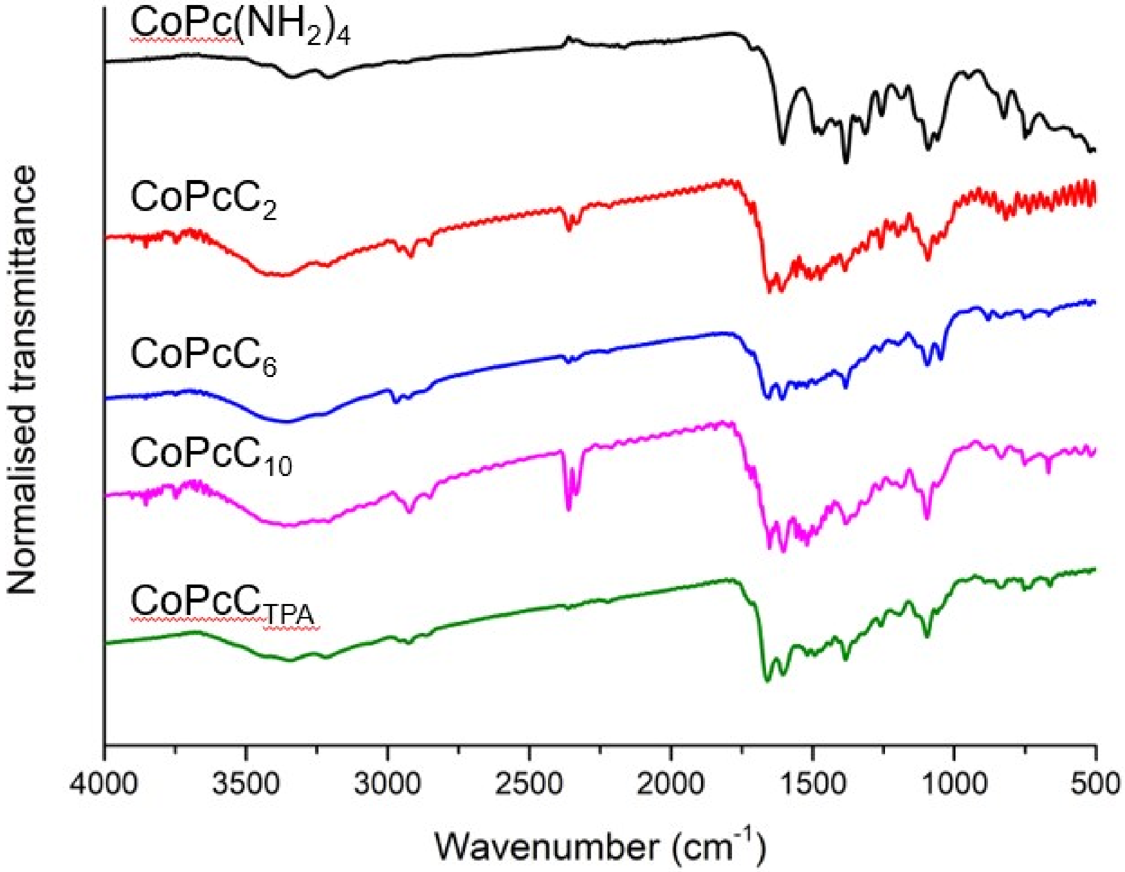

Figure S2: FTIR spectra of the $CoPc(NH_2)_4$ (black), $CoPcC_2$ (red), $CoPcC_6$ (blue), $CoPcC_{10}$(purple) and $CoPcC_{TPA}$ (green)

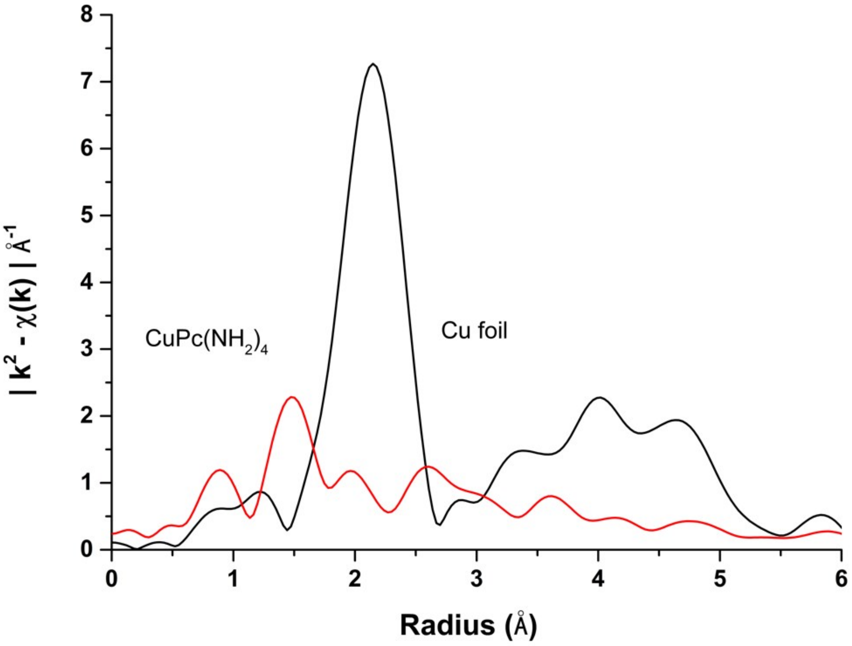

Figure S3: *k*²-weighted $\chi(k)$ EXAFS data for Cu foil (black) and $CuPc(NH_2)_4$ (red) processed with data from a *k* range of 3–13 Å^{-1}.

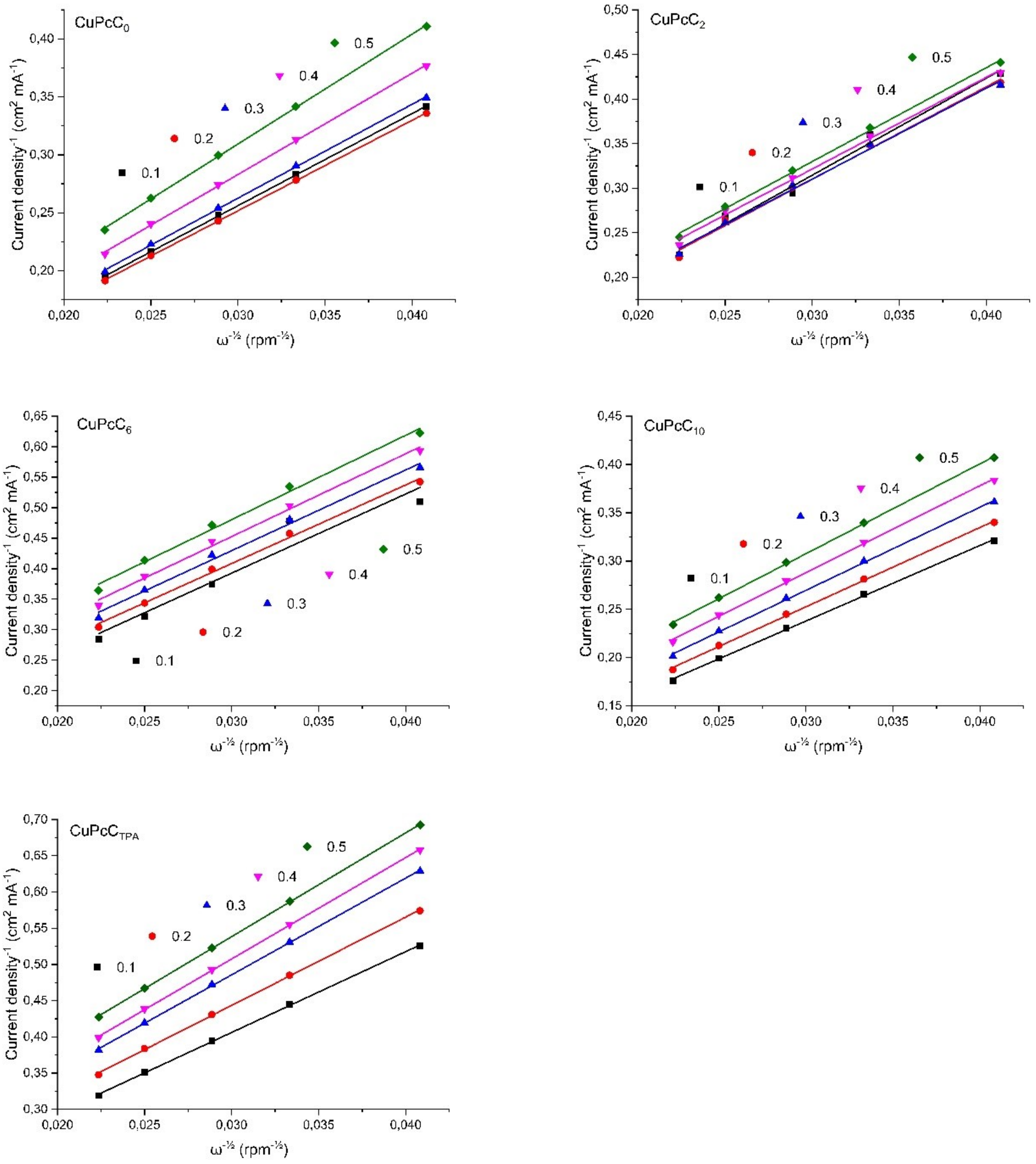

Figure S4: Koutecký–Levich plots of $CuPcC_0$, $CuPcC_2$, $CuPcC_6$, $CuPcC_{10}$, and $CuPcC_{TPA}$

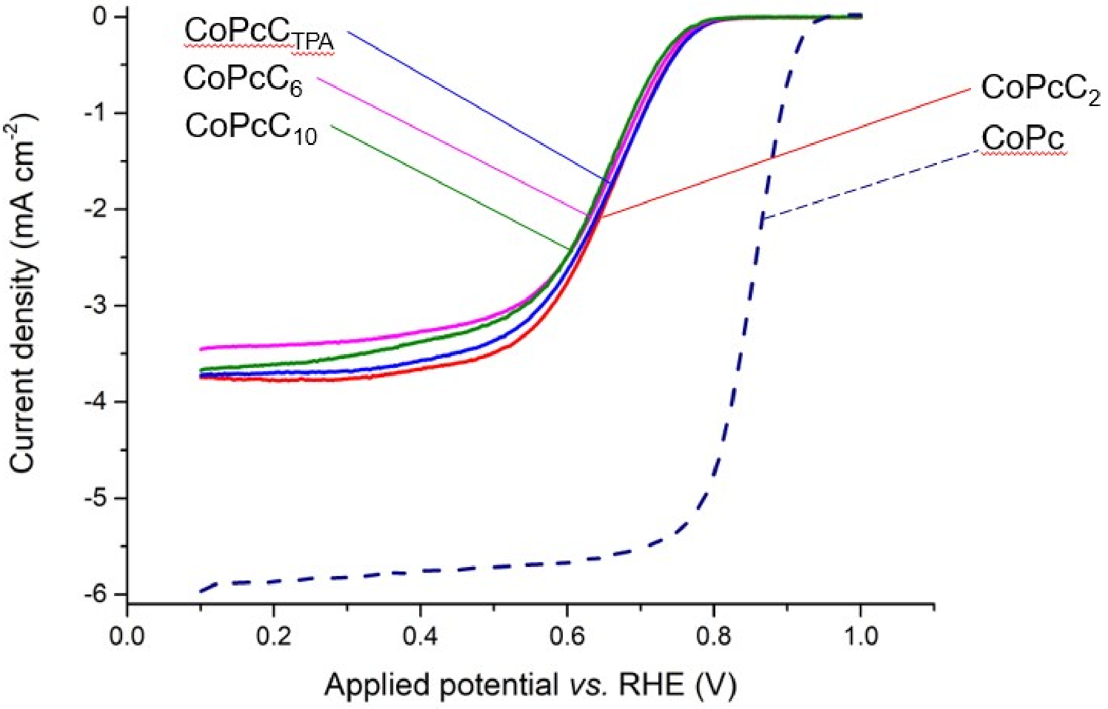

Figure S5: LSV curve of the CoPc$(NH_2)_4$ (dotted curve), CoPcC$_2$ (red), CoPcC$_6$ (purple), CoPcC$_{10}$(green) and CoPcC$_{TPA}$ (blue) obtained in 0.1 M KOH, degassed with O_2, a scan rate of 10 mVs^{-1} and a rotation speed of 1600 rpm.

Table S1. Tafel plot slope values calculated between the low current density (LCD) and the high current density (HCD).

Entry	Polymer	LCD (mVdec^{-1})	HCD (mVdec^{-1})
1	$CuPcC_0$	64	125
2	$CuPcC_2$	65	112
3	$CuPcC_6$	62	105
4	$CuPcC_{TPA}$	70	120
5	$CuPcC_{10}$	64	101
6	$CuPcH_{16}$	66	110

References:

[1] ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, B. Ravel, M. Newville, *J. Synchrotron Rad.* 2005, **12**, 537–541.

[2] I.M. Denekamp, F.L.P. Veenstra, P. Jungbacker, G. Rothenberg, *Appl. Organomet. Chem.* 2019, **33**, e4872.