

Supporting Information

Metallophthalocyanine based redox active metal-organic conjugated microporous polymers for OER catalysis

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Physical measurements:

Infrared spectra were recorded in Bruker FT-IR spectrometer. Samples were prepared for IR measurement by making KBr pellets. Thermal stability was measured using Mettler Toledo TGA 850 instrument in N₂ atmosphere in the temperature range 30-800 °C at heating rate of 5 °C/min. Thermo Scientific Flash 2000 CHN analyzer was used for elemental analysis. Powder X-ray diffraction studies for both the MO-CMPs were performed using Bruker D8 discover instrument using Cu-K α radiation. Morphological studies were performed using Lica-S440I Field Emission Scanning Electron Microscope (FESEM) by preparing the samples on silicon wafer. High vacuum with an accelerating voltage of 100 kV was used for FESEM analysis. Transmission Electron Microscopic (TEM) images were taken using JEOL JEM-3010 TEM with an accelerating voltage 300 kV. Sample was prepared for TEM by making the dispersion of material in ethanol solvent followed by drop casting on a carbon coated copper grid. Solid state ¹³C-NMR spectrum was recorded on a varian infinity plus 300WB Bruker spectrometer at a MAS rate of 5 kHz and a CP contact time of 1.4 ns. Permanent porosity was studied by CO₂ adsorption at 195 K using QUANTACHROME QUADRASORD-SI analyser. Samples were activated at 140 °C under 1x10⁻¹ Pa vacuum for 8 hrs prior to isotherm measurement. EPR study was performed using Bruker EMX 1444 EPR spectrometer.

Computational details

All DFT computations were carried out utilizing Gaussian 09 program package.¹ B3LYP/6-31G* method was used for geometry optimization of CoCMP and ZnCMP. LANL2DZ was used for basis set and ECP of cobalt and zinc.² HSEH1PBE method in conjugation with 6-

31+G* basis set was further used to evaluate molecular orbital energy from the optimized geometry.³

Electrochemical characterization

All electrochemical experiments were done in a three-electrode cell configuration with a glassy carbon (GC) electrode as the working electrode (WE), platinum as a counter electrode (CE) and Ag/AgCl as a reference electrode (RE). The working electrode was prepared by drop casting an ink containing MO-CMP, Vulcan carbon and Nafion on a glassy carbon rotating disk electrode. All the experiments were done at a rotating speed of 1600 rotations per minute (RPM) and the scan rate was 50 mV/s. The potentials are reported with respect to reversible hydrogen electrode.

Experimental Section:

1. **Materials and method:** All the reagents and chemicals used for the CMPs synthesis were purchased from Sigma-Aldrich chemical Co. Ltd and used as such. Solvents used for column chromatography were purchased from Finar Ltd, India and used after distillation. Deuterated solvent (CDCl₃) used for ¹H and ¹³C-NMR was purchased from Sigma-Aldrich chemical Co. Ltd and used as such. KBr pellets were made for recording the FTIR spectra.

2. **Synthesis:**

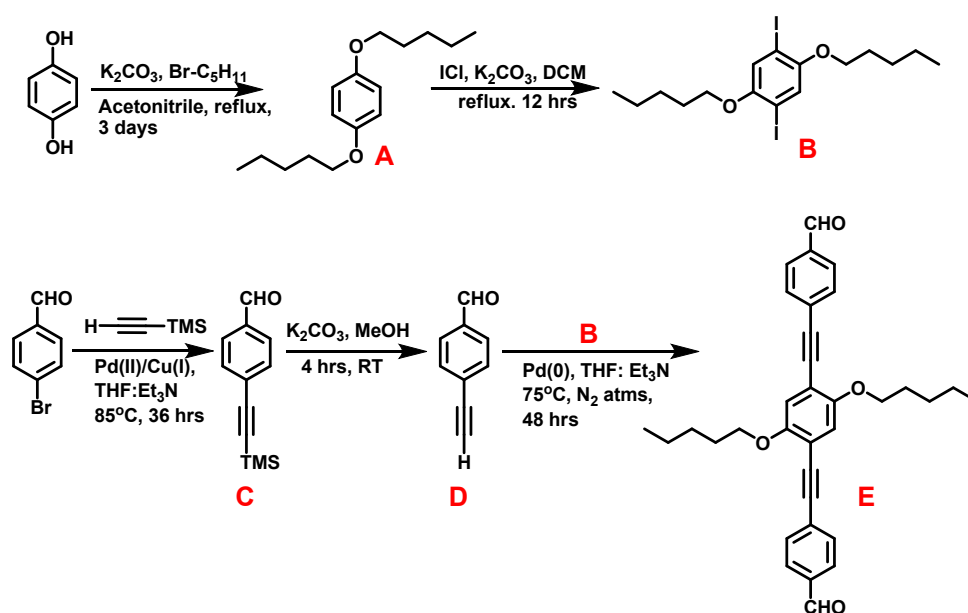
(A) OPE aldehyde synthesis:

The synthesis and characterization of 1,4-dipentoxy benzene (A) and subsequently 1,4-Diiodo-2,5-dipentoxybenzene (B) were reported by Schaate *et. al.*, in 2011.⁴ We have followed similar procedure and the compound was characterized by ¹H-NMR, IR and Mass spectrometry. The characterization data was matched with the literature report. Recently, Yin *et. al.*, has reported the synthesis and characterization of compound 4-((trimethylsilyl)ethynyl)benzaldehyde (C) and 4-ethynylbenzaldehyde (D).⁵ We were also characterized our compounds using similar experimental technique like ¹H-NMR, IR and Mass spectrometry.

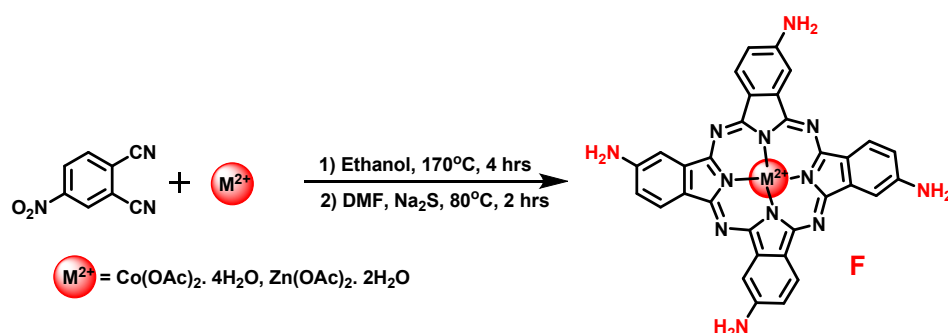
The compound 4,4'-(2,5-bis(pentyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dibenzaldehyde (E) was synthesized by the Sonogashira coupling reaction between 1,4-Diiodo-2,5-

dipentoxybenzene (B) and 4-ethynylbenzaldehyde (D). Compound B (2.3 mmol, 1 equiv.), D (4.6 mmol, 2 equiv.) and Cu(I) which acts as co-catalyst (20 mol%) were taken together in mixed of dried solvent tetrahydrofuron (THF) (40 mL) and triethylamine (20 mL). The N₂ gas was purged to the reaction mixture for 30 minutes to ensure the removal of dissolved oxygen from the solvents. In the last, 10 mol% of Palladium catalyst (Pd(0)) was added and again the reaction mixture was degassed for 20 minutes by N₂ purging. Subsequently, the reaction mixture was stirred under inert atmosphere at 75°C for 48 hrs. Reaction progress was monitored by TLC analysis. Once reactant was finished then the reaction mixture was cooled to room temperature and solvent was evaporated under reduced pressure. Solid product was dissolved in ethyl acetate and washed thrice using water, 2N HCL and saturated brine solution. Organic layer was dried over anhydrous sodium sulphate. The solvent was evaporated in rotary evaporator. Crude product was further purified by column chromatography packed in silica gel (60-120 mess size) using hexane: ethylacetate solvent system. Pure product was obtained in 5% ethyle acetate in hexane. The yield of column purified product is 65%. *R_f*: 0.5 (10% ethylacetate: hexane), IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ =3049, 2950, 2856, 2832, 2727, 2202, 1697, 1597, 1555, 1513, 1487, 1417, 1378, 1280, 1203, 1167, 1046, 988, 859, 829. ¹H NMR (CDCl₃, 400 MHz): δ 0.95 (t, 6H, 2CH₃), 1.40-1.45 (m, 4H, 2CH₂), 1.52-1.56 (m, 4H, 2CH₂), 1.85-1.89 (m, 4H, 2CH₂), 4.05 (t, 4H, 2-OCH₂), 7.03 (s, 2H, 2ArH), 7.67 (d, J= 8.4, 4H, 2ArH), 7.87 (d, J= 8.0, 4H, 2ArH), 10.02 (s, 2H, 2CHO).¹³C NMR (CDCl₃, 150 MHz): 14.0, 22.4, 28.2, 28.9, 69.5, 89.9, 94.2, 113.8, 116.7, 129.5, 129.6, 132.0, 135.4, 153.8, 191.3. ESI-MS+ *m/z* Calcd. for C₃₄H₃₅O₄: 507.2535 [M+H]⁺, found 507.2537.

(1). OPE aldehyde synthesis:



(2). Metallophthalocyanine synthesis:

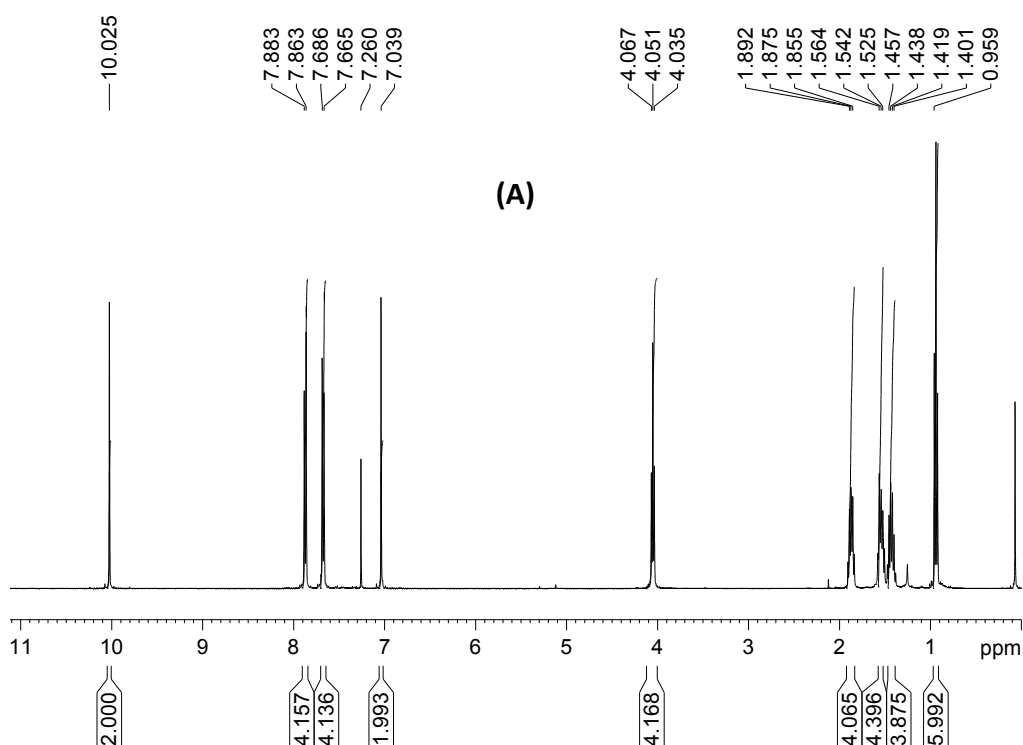


Scheme S1: Synthesis of OPE aldehyde (E) and metallophthalocyanine tetraamine (F)

(B) Metallophthalocyanine synthesis: Both cobalt phthalocyanine (CoPC) and zinc phthalocyanine (ZnPC) have been synthesized and well characterized previously in the literature.⁶ We followed the similar procedure and characterized the compounds accordingly. In brief, 4-nitrobenzodinitrile (6 mmol), metal salt ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ for cobalt phthalocyanine and ZnCl_2 for zinc phthalocyanine) (1.5 mmol) was taken together. Absolute ethanol (25 mL) was added as a solvent. The reaction mixture was heated at 170°C for 4 hrs under solvothermal condition. Then the reaction mixture was cooled to the room temperature. Bluish green compound was obtained and subsequently washed with hot ethanol and water for removing the impurity. Obtained compound was dried at 100°C under vacuum for 8-10 hrs. In the second step, the blue-green compound (1 mmol) was dissolved in DMF (15 mL) and 12 mmol of Na_2S was added into it. The reaction mixture stirred at 80°C for 2 hrs. The reaction mixture was poured in distilled water (120 mL) and the solid product was filtered off using

vacuum pump. The solid product was further treated with 1M HCL followed by 1M NaOH. The precipitate was washed with water for 4-5 times to remove the acid and base. The dark green-bluish product was dried under reduced pressure. The product was characterized by IR, CHN analysis, UV-Vis and MALDI and data was matched with literature report.

(C) Synthesis of metal-organic conjugated microporous polymers (MO-CMPs): Both the MO-CMPs (CoCMP and ZnCMP) were synthesized using literature procedure.⁷ The 4,4'-(2,5-bis(pentyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dibenzaldehyde (OPE-5) (0.079 mmol) and metallophthalocyanine (PC) (0.039 mmol) were mixed together with mesitylene (3 mL) and 1,4-dioxane solvent (2 mL). Then catalytic amount of 6 M acetic acid (200 μ l) was added into it. The reaction mixture was heated in the teflon container at 120 °C for 3 days. The reaction mixture was cooled to room temperature and subsequently washed with 1,4-dioxane and methanol three times. The resulting MO-CMPs were further Soxhlet purified in methanol for two days.



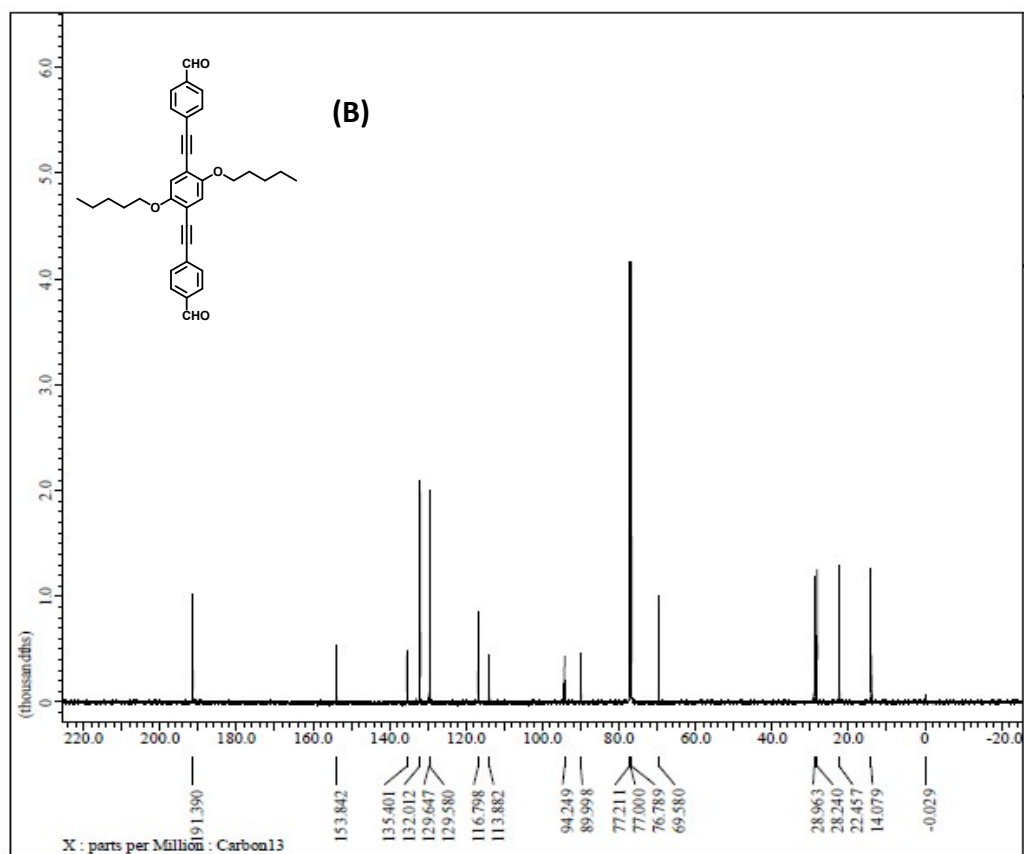


Figure S1: (A) ^1H (400 MHz) and (B) ^{13}C -NMR (150 MHz) for OPE-5 aldehyde (E) recorded in CDCl_3 solvent.

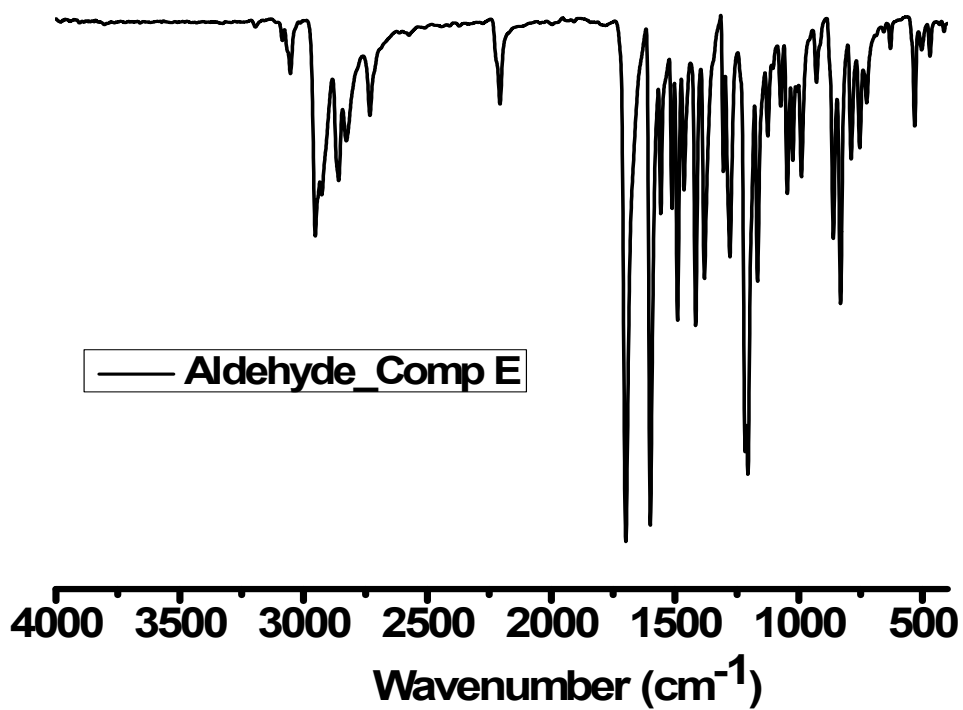


Figure S2: FT-IR spectrum for OPE-5 aldehyde (E).

Characterization of MO-CMPs:

IR spectra of MO-CMPs:

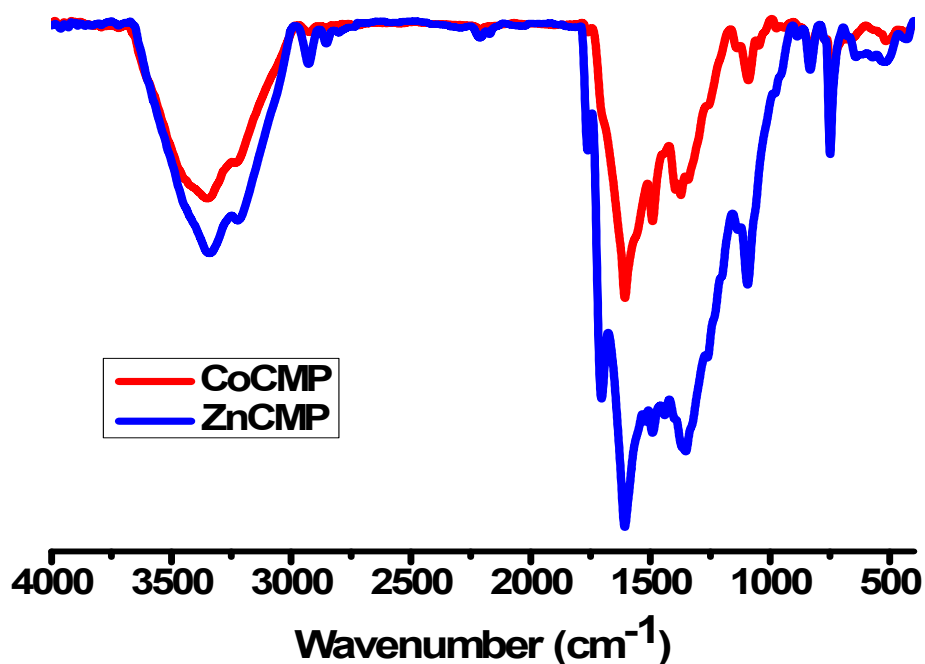


Figure S3: FT-IR spectra for CoCMP and ZnCMP.

Solid state ¹³C-NMR spectrum of ZnCMP:

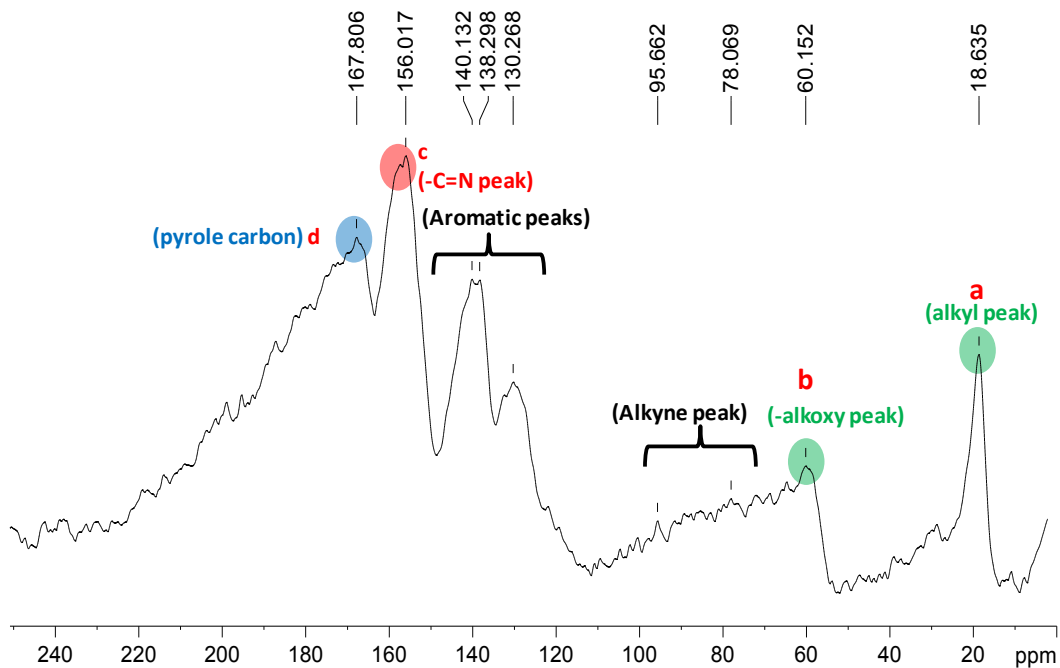


Figure S4: Solid state ¹³C-NMR spectrum for ZnCMP.

TGA Analysis:

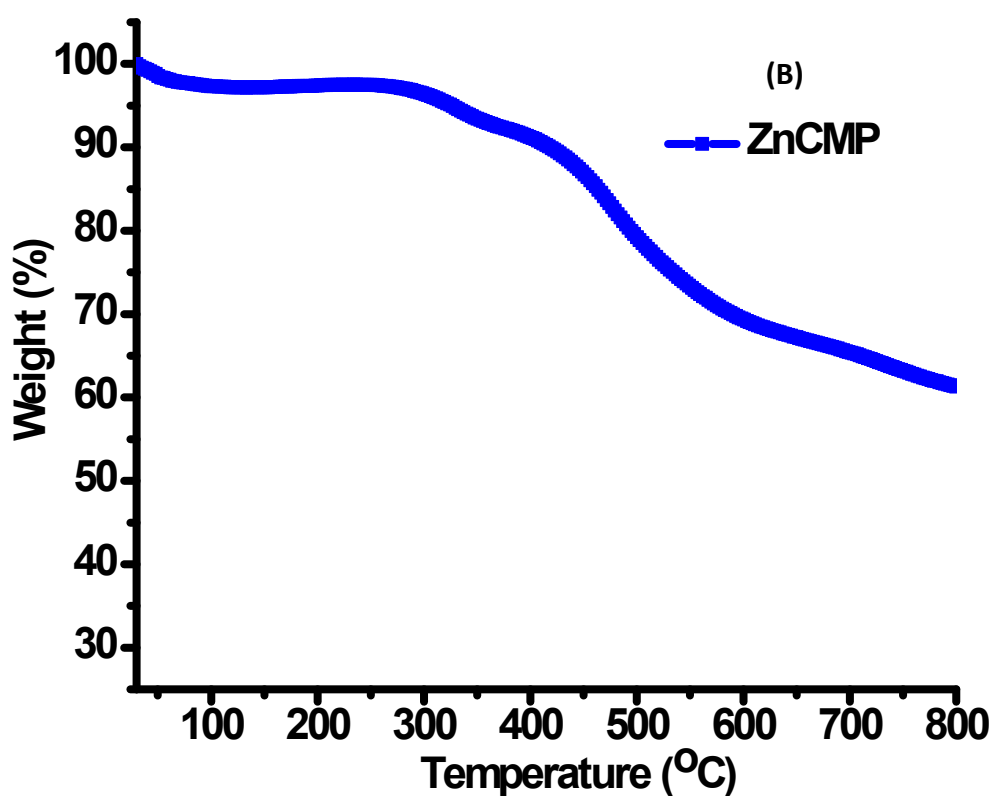
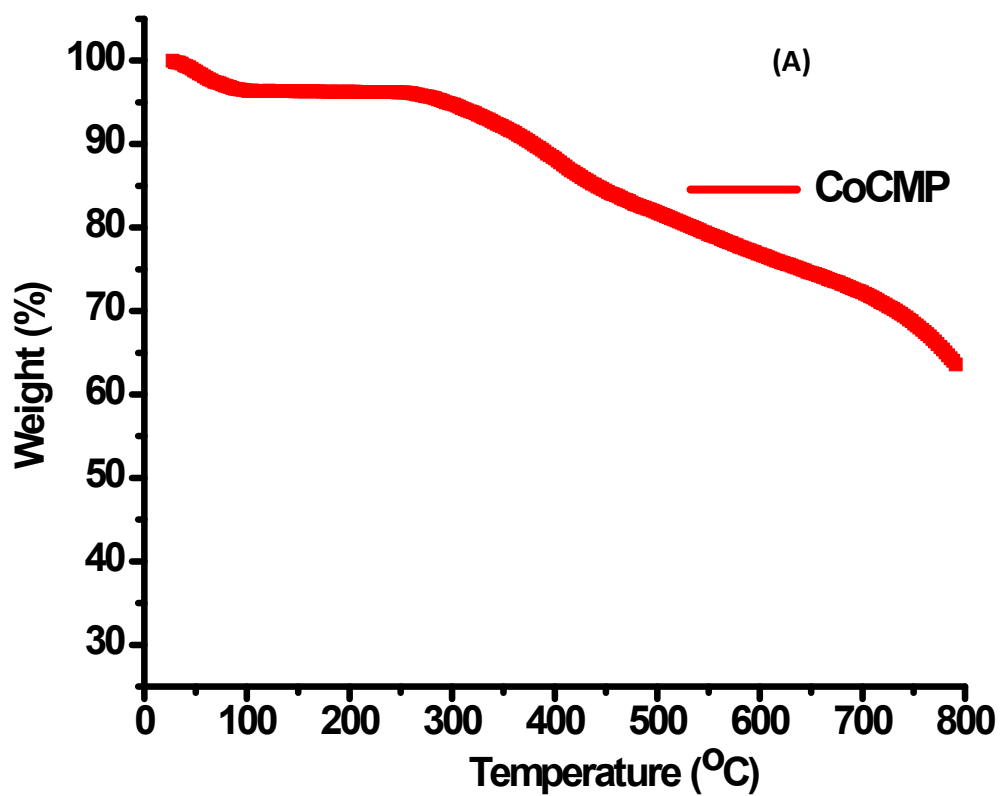


Figure S5: TGA of (A) CoCMP and (B) ZnCMP, with a heating rate of 5 °C/minutes under N₂ atmosphere.

TEM for CoCMP:

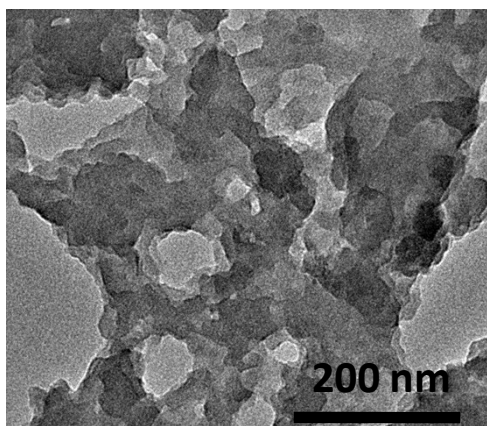
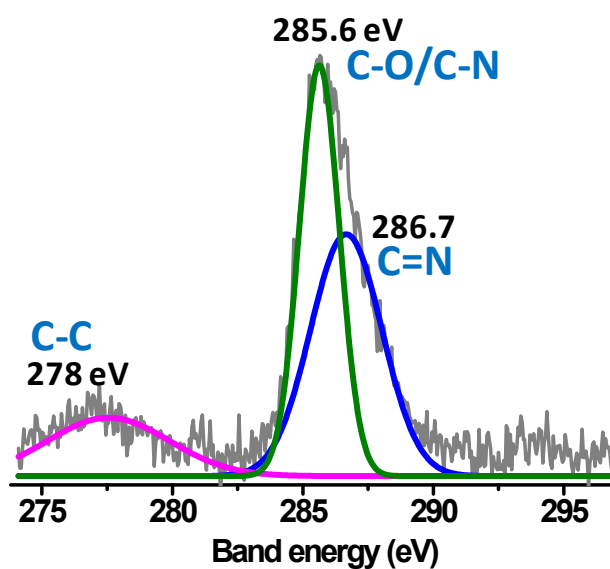


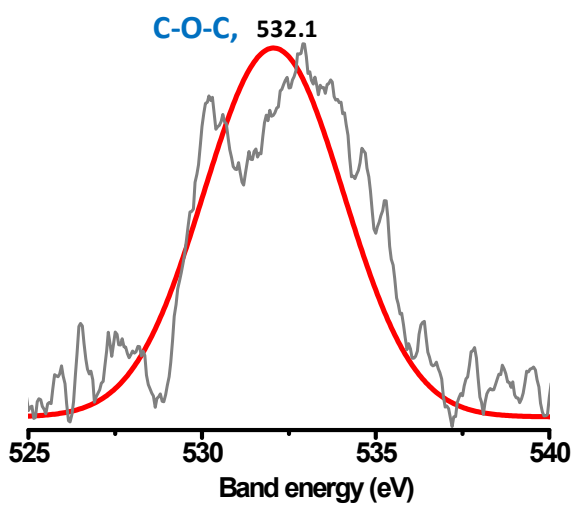
Figure S6: TEM image for CoCMP

XPS analysis for CoCMP:

a. Carbon analysis



b. Oxygen analysis:



c. Nitrogen analysis:

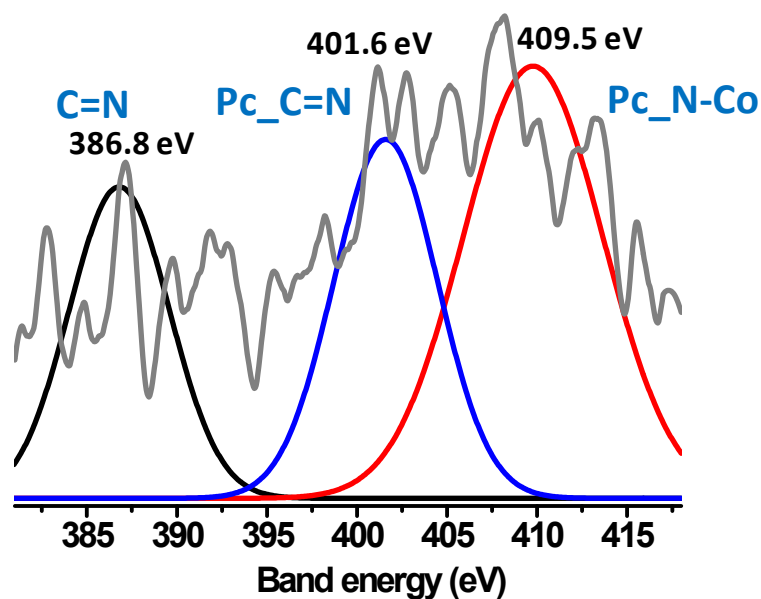


Figure S7: XPS analysis for CoCMP; (a) carbon analysis (b) oxygen analysis (c) nitrogen analysis.

N₂ Adsorption for both CMP:

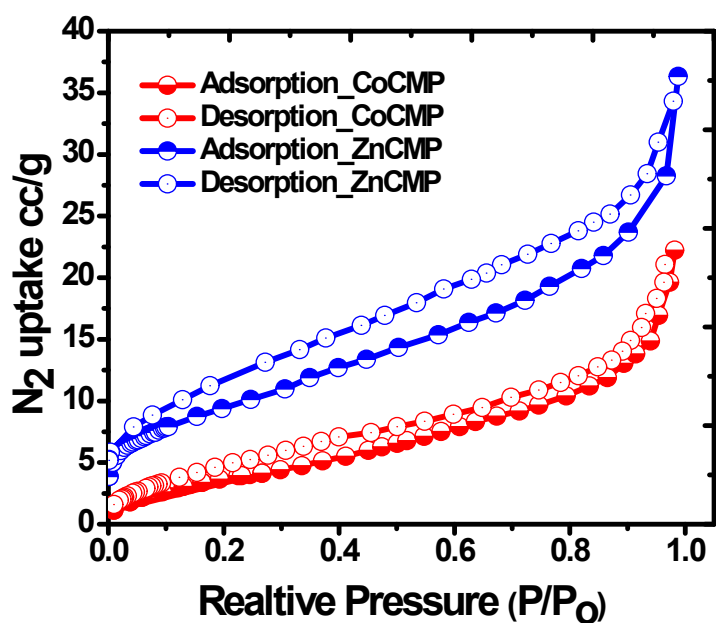


Figure S8: N₂ adsorption at 77 K

EPR spectrum for ZnCMP:

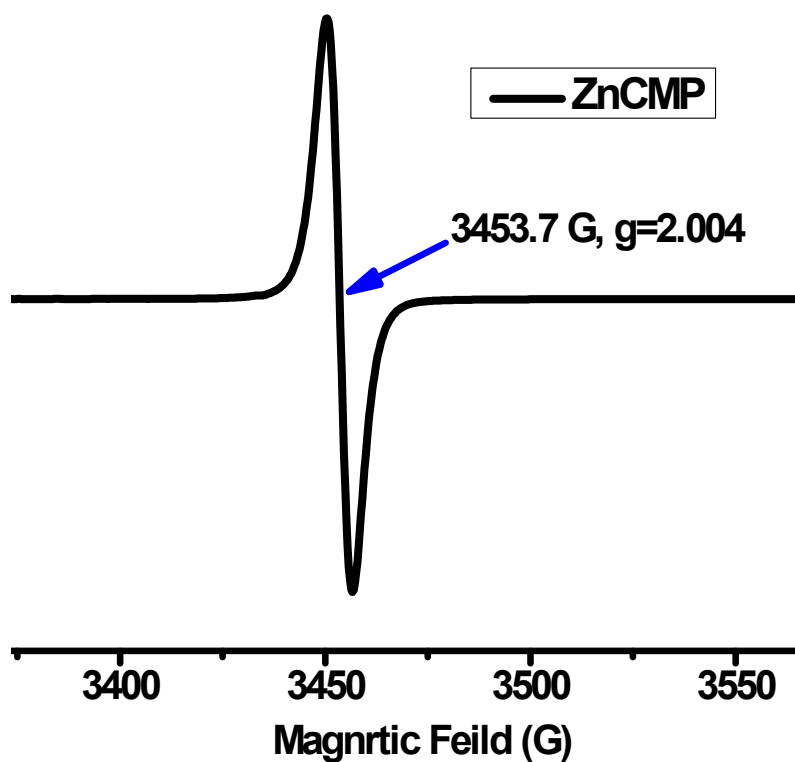


Figure S9: EPR spectrum for ZnCMP.

Theoretical calculation for band gap of ZnCMP and electron transfer from substrate to MO-CMP:

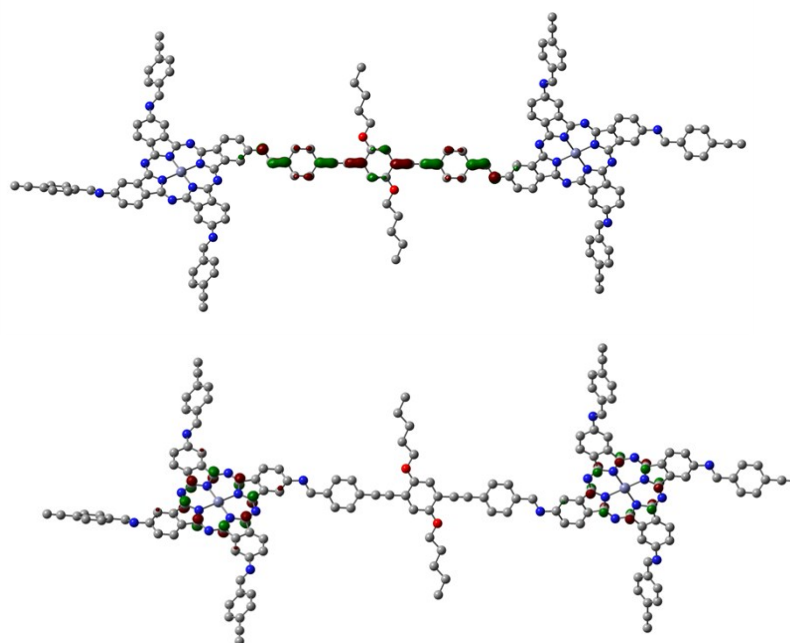


Figure S10A: HOMO on phthalocyanine (bottom) and LUMO on the OPE backbone (top) of ZnCMP.

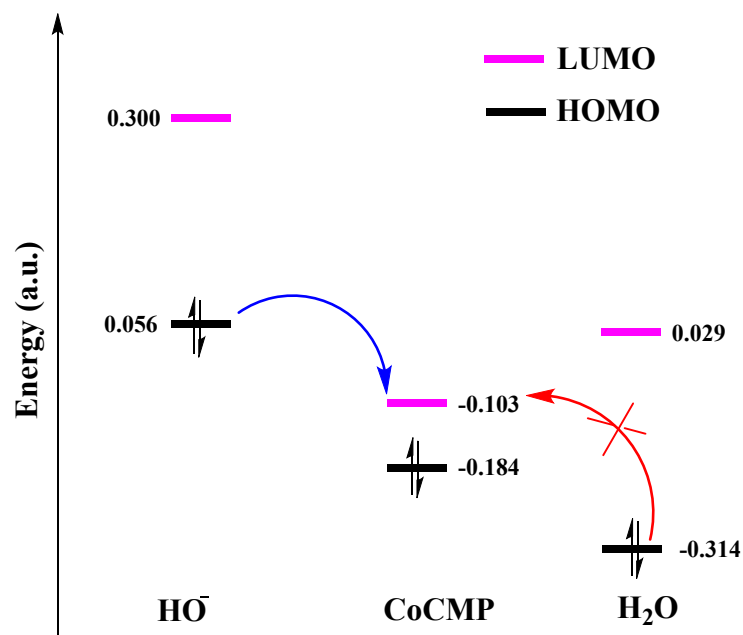


Figure S10B: Comparison of electron transfer from the HOMO of hydroxide (OH⁻) and water (H₂O) to the LUMO CoCMP.

Electrochemical calculations

a) Electrochemically active surface (ECSA)

To calculate the ECSA CV was recorded in the capacitance region at several scan rates using bare GC as well as CoCMP coated GC as WE. The slope of current density against scan rate of the CoCMP coated GC gives the double layer capacitance (C_{dl}) and that of the bare GC gives specific capacitance (C_{sp}). The ECSA was then calculated using the following relation:

$$ECSA = \frac{C_{dl}}{C_s}$$

b) Roughness Factor (RF)

It is the ratio of the ECSA and the geometrical area (GA)

$$RF = \frac{ECSA}{GA}$$

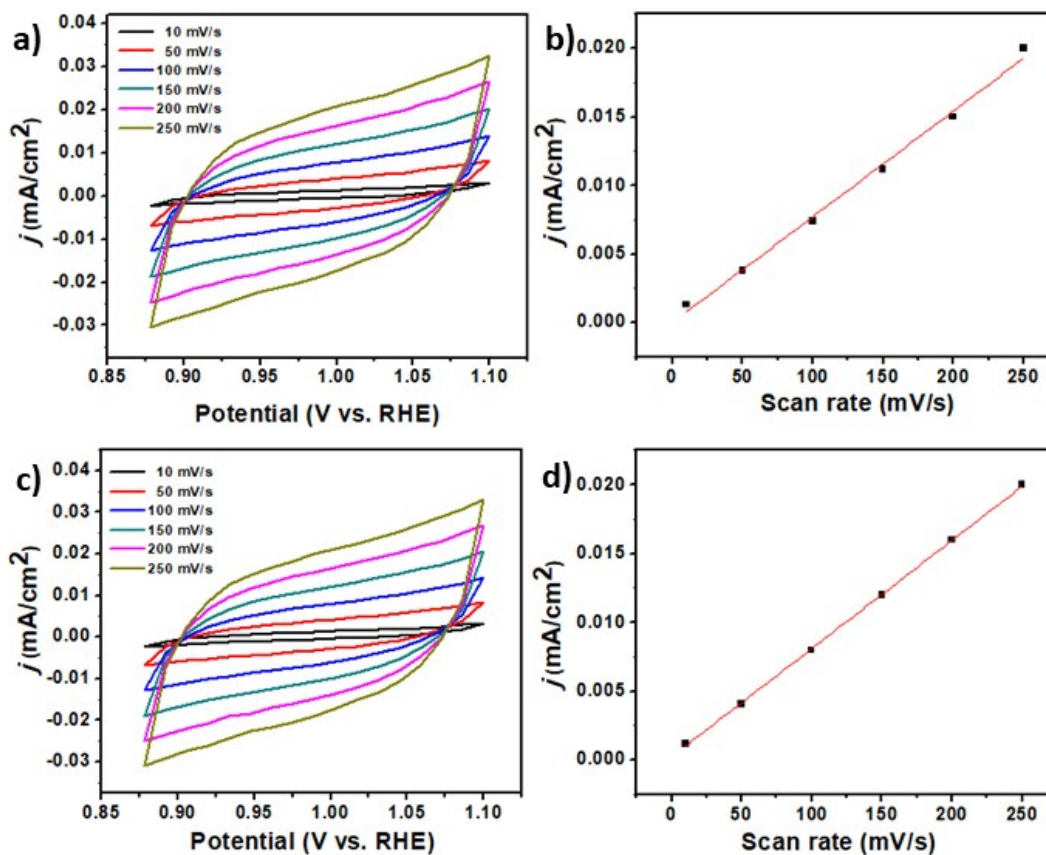


Figure S11: a,c) Capacitance CV of bare GC and CMP coated GC respectively; b,d) corresponding j vs scan rate.

c) Turnover frequency (TOF)

TOF was calculated from the following equation:

$$TOF = \frac{i}{4F \times RF \times m}$$

Where F = Faraday's constant

m = no of moles of active Co (m was calculated from ICP)

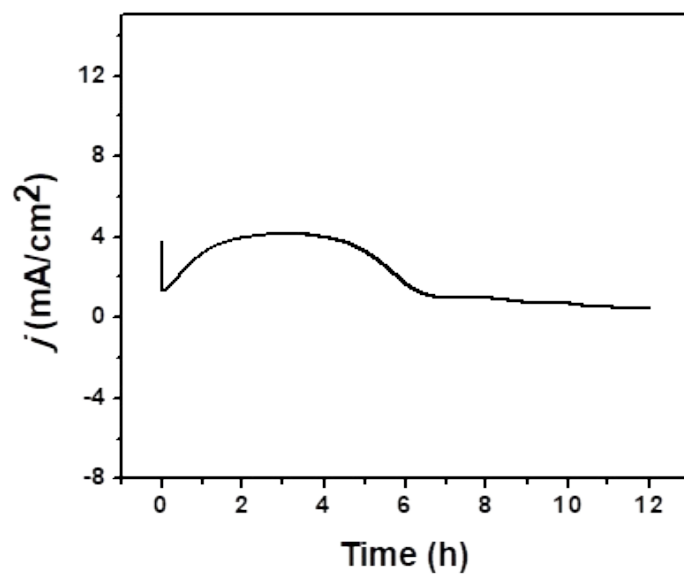


Figure S12: Chronoamperometry of CoCMP for 12 h.

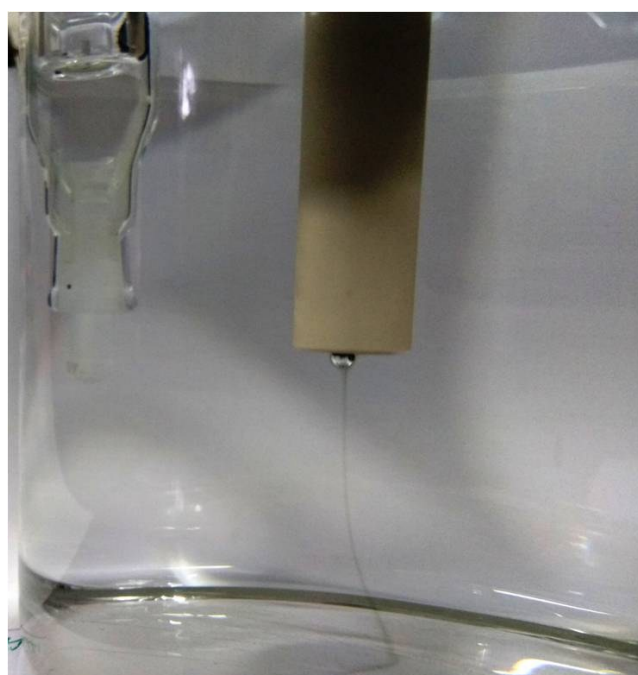


Figure S13: Leaching of the CoPC during the LSV experiment.

References:

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