# Simultaneous Electron and Proton Conduction in a Stable Metal Organic Material with Highly Selective Electrocatalytic Oxygen Reduction Reaction to Water

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# General and physicochemical characterization

All the chemicals were of analytical grade and used without further purification. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectroscopy was measured on a Nicolet Impact 410 spectrometer between 400 and 4000 cm<sup>-1</sup>, using KBr pellets. Absorption spectra were recorded on a UV/Vis/NIR Perkin Elmer Lambda 1050 spectrophotometer. The photoluminescence (PL) spectrum was recorded on a FLS1000 photoluminescence spectrometer (Edinburgh Instruments) equipped with a 450 W ozone free continuous xenon arc lamp and a photomultiplier (PMT-980) detector. Elemental mapping was carried out with AzTec INCA software. The thermal analysis was carried out using a Mettler Toledo TG-DTA 85 thermal analyzer under a flow of N<sub>2</sub> (30 mL/min). The sample was heated at a rate of 10 °C min<sup>-1</sup> with inert alumina as a reference. The powder X-ray diffraction (PXRD) data were collected using Empyrean PANalytical powder diffractometer with CuK $\alpha$  radiation ( $\lambda$  = 1.54056 Å). FESEM images were collected by using the Field Emission Scanning Electron microscope (FESEM) SCIOS 2 FIB-SEM and the corresponding EDX microanalysis was done by Oxford Ultim Max 170 Detector.

# Synthesis of single crystals of [Cu(INA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>n</sub> (1)

Single crystals of the complex were synthesized by carefully layering a 2:3  $H_2O:MeOH$  (v/v) solution (3 mL) containing sodium isonicotinate (NaINA, 292.2 mg, 2 mmol) over an aqueous solution (3 mL) of copper(II) nitrate trihydrate (240.6 mg, 1.0 mmol). Sky blue elongated prismatic single crystals, suitable for X-Ray diffraction were grown at the interface of the two layers after three days. Yield: 60 %.

# Synthesis of polycrystalline powder of $[Cu(INA)_2(H_2O)_4]_n$ (1)

Compound **1** was also prepared as a bulk polycrystalline sample by simply mixing aqueous solutions (3 mL) of sodium isonicotinate (292.2 mg, 2 mmol) with copper(II) nitrate trihydrate (240.6 mg, 1 mmol) in a 2:1 ratio. Yield 90 %. Elemental analysis: Anal. Cald.:  $C_{12}H_{16}CuN_2O_8$ : C, 37.95; H, 4.25; N, 7.38 %. Found: C, 37.79; H, 4.11; N, 7.28 %.

# **Crystallographic Data Collection and Refinement**

A blue block-shaped suitable crystal of MOM **1** with dimensions  $0.14 \times 0.08 \times 0.05$  mm<sup>3</sup> was selected and mounted on a Mylar loop with the crystal coated in a viscous hydrocarbon oil. The crystal was immediately transferred to a cold N<sub>2</sub> stream for data collection on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at a steady *T* = 119.99(10) K during data collection. The structure was solved with the ShelXT 2014/5 solution program<sup>1</sup> using iterative methods and by using Olex2 1.5 as the graphical interface.<sup>2</sup> The model was refined with ShelXL 2018/3 using full matrix least squares minimisation on *F*<sup>2</sup>.<sup>1</sup>

Data were measured using *w* scans with Cu K<sub>*a*</sub> radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro system.<sup>3</sup> The maximum resolution that was achieved was  $Q = 75.674^{\circ}$  (0.80 Å).

The unit cell was refined using CrysAlisPro 1.171.43.71a on 4790 reflections, 74 % of the observed reflections.  $^3$ 

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.43.71a.<sup>3</sup> The final completeness is 100 % out to 75.674° in *Q*. A multiscan absorption correction was performed using CrysAlisPro 1.171.43.71a.<sup>3</sup> Empirical

absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient  $\mu$  of this material is 2.680 mm<sup>-1</sup> at a wavelength  $\lambda$  = 1.54184 Å and the minimum and maximum transmissions are 0.776 and 1.000.

The structure was solved and the space group *P*-1 (# 2) was determined by the ShelXT 2014/5 structure solution program<sup>1</sup> using iterative methods and refined by full matrix least squares minimisation on  $F^2$  using version 2018/3 of ShelXL 2018/3.<sup>1</sup> All non-hydrogen atoms were refined anisotropically. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

A summary of the data collection and structure refinement for MOM **1** is given in Table S1.

## Hirshfeld surface analysis

The nature of the non-covalent interactions present within a crystal system can be visually depicted and quantified through Hirshfeld surface (HS) analysis. HS as constructed from electron distribution analysis around a molecule visualizes intermolecular interactions in molecular crystals. The two-dimensional (2D) fingerprint plots determined from the HS analysis identify each type of intermolecular interaction within supramolecular and coordination compounds and their relative contributions can be obtained from the area of the surface. For each point on the HS,  $d_i$  is the well-defined distance from the nearest nucleus internal to the surface and analogously,  $d_e$  is the distance from the nearest nucleus external to the surface. The normalized contact distance can be defined by:

$$d_{norm} = \frac{(d_i - r^{vdW})}{r^{vdW}_i} + \frac{(d_e - r^{vdW})}{r^{vdW}_e}$$
(1)

Where  $r_{i}^{vdW}$  and  $r_{e}^{vdW}$  are the van der Waals radii of the appropriate atoms internal and external to the HS. Hirshfeld surfaces and their corresponding 2D fingerprint plots were calculated over the constituent ionic and molecular geometries using CRYSTALEXPLORER 17.5 software package.<sup>4,5</sup> The properties like normalized contact distance  $d_{norm}$ , shape index, curvedness, and fragment patch were mapped over the HS and plotted with the appropriate colour scale. The 2D fingerprint plots were presented as  $d_e vs. d_i$ .

## Stability test

Microcrystalline powder samples of MOM **1** were soaked in water at different pH values (1, 3, 5, 7, 9, 11 and 14) as well as in dimethylformamide (DMF) and MeOH. After 24 h, the samples were collected by filtration and then dried. A sample was kept in boiling water for 2 h and then collected by filtration after cooling to room temperature. The PXRD and IR data confirmed the stability of the material within the pH range of 3-14 but not below pH = 3. Afterward, the samples were immersed in the respective pH solutions to make suspension for absorption spectral analysis.

#### Water adsorption study

Water sorption isotherms for pressures in the range of 0-1 bar were measured using an AutosorbiQ (Quantachorme Inc., USA) gas sorption system. 50 mg of as-synthesized material was introduced into a pre-weighed analysis tube (6 mm diameter, 6 cm<sup>3</sup> bulb), capped with a gas-tight transeal to prevent leakage of air and moisture during transfer and weighing. The samples were evacuated under dynamic vacuum (10<sup>-3</sup> torr) at 80 °C, until a constant weight was achieved. The analysis tube was then weighed again to determine the mass of the evacuated sample. For all isotherms, warm and cold free space correction measurements were performed using ultrahigh pure He gas (99.999 % purity). All gases used were of ultrapure research grade (99.999 % purity). The H<sub>2</sub>O adsorption and desorption isotherms were recorded at 298 K.

#### **Band structure calculation**

The triclinic unit cell of MOM **1** was optimized using density functional theory (DFT) methodology implemented in the CASTEP program code by Accelrys, Inc.<sup>6</sup> The crystal structure was relaxed while keeping the experimental unit cell parameters fixed. The calculations were performed employing the Generalized-Gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.<sup>7,8</sup> Additionally, Grimme's scheme<sup>9</sup> was utilized to incorporate long-range dispersion corrections.

Ultrasoft pseudopotentials from the OTFG library were employed in conjunction with the relativistic treatment proposed by Koelling-Harmon.<sup>10</sup> A plane-wave basis set with a cut-off energy of 490 eV was utilized. The Brillouin zone sampling was carried out using a Monkhorst-Pack scheme with a 3x2x2 grid.

Convergence in the self-consistent field (SCF) calculations was achieved with an energy tolerance of 2×10<sup>-6</sup> eV/atom across all computations. Band structures were computed along the k-vector of the first Brillouin zone, while Partial Density of States (PDOS) was plotted with respect to the Fermi level. The electron localization function (ELF) was calculated following the scheme DFT-ELF.<sup>11,12</sup>

Furthermore, the real and imaginary components of the dielectric function were evaluated along the xx, yy, and zz directions of the sample, employing a smearing of 0.2 eV.

## **Proton Conductivity study**

For the impedance measurement, samples of MOM **1** were heated at 60 °C for 12 h in vacuum before the measurements. All the samples were manually ground to obtain fine powders. Later, pellets were prepared by applying a pressure of 80 MPa for 3 min, which resulted in pellet thicknesses of 0.109 cm. Measurements were performed in a two-electrode assembly with stainless-steel discs as the electrodes with cross-sectional area of 0.754 cm<sup>2</sup>. The solid pellet samples were placed between the electrodes. The whole cell assembly was maintained in a humidity chamber to control the temperature and humidity. The applied frequency range for the measurement was from 0.2 MHz to 1 Hz at the open circuit potential with a sinus amplitude of 10 mV.

The proton conductivity ( $\sigma_H$ )was calculated using the equation:

$$\sigma_{\rm H} = l/A \cdot R \tag{2}$$

where, l represents the pellet thickness (0.109 cm), A is the electrode cross-sectional area (0.754 cm<sup>2</sup>) and R represents the bulk resistance of the material. The activation energy was calculated using the Arrhenius equation:

$$\log (\sigma_{\rm H} T) = \log A - E_{\rm a}/k_{\rm B} T$$
(3)

where,  $\sigma_{\rm H}$  is the conductivity,  $k_{\rm B}$  is the Boltzmann constant, A is the preexponential factor, T is the temperature and  $E_{\rm a}$  is the activation energy for proton transport.

The analysis of the influence of humidity on the proton conductivity of the samples was measured maintaining a constant temperature of 25 °C while adjusting the relative humidity (RH) between 60 % and 98 %. Subsequently, the RH was held constant at 98 % while the temperature was varied from 25 to 75 °C. The resistance for each measurement condition was determined from the semi-circular arc observed in the Nyquist plot. Alternatively, when the sample exhibited high conductivity, the semi-circular arc was less defined and the resistance was determined by its intercept with the x-axis.

## **Electron conductivity study**

The thermal dependence of the DC electrical conductivity was measured with the two contacts method on single crystals of MOM **1** in the temperature range 300-400 K. The contacts were made with Pt wires (25 mm diameter) using graphite paste. The samples were measured in a Quantum Design PPMS-9 equipment connected to an external voltage source (Keithley model 2400 source-meter) and amperemeter (Keithley model 6514 electrometer). All the quoted conductivity values were measured in the voltage range where the crystals are Ohmic conductors. The cooling and warming rates were 0.5 K/min. The samples were measured with the current along the *b*-axis of the single crystals.

#### **Rotating Ring Disk Electrode (RRDE) Analysis**

To determine the number of electrons (n) involved in the reaction and amount of  $H_2O_2$  generated during the oxygen reduction reaction (ORR), RRDE analysis was carried out with a bipotentiostat model CHI 7044E. The rotating ring disk electrode assembly is formed by a rotating Glassy Carbon (GC) disk electrode and a Platinum ring electrode (BAT SOL Equipment and Technology) with collection efficiency of 0.15. Ag/AgCl (saturated KCl) and Pt wire were used as reference and counter electrode, respectively.

# **Preparation of Deposited Electrode**

The catalyst (1 mg) was dispersed in 990  $\mu$ L of isopropyl alcohol along with 10  $\mu$ L of Nafion. The ink was sonicated for 30 minutes and 50  $\mu$ L of this ink was drop-casted on a glassy carbon disk electrode. The electrode was dried at room temperature and rinsed with chloroform, ethanol and water before use. The ORR was performed under air in 0.1 M KOH solution with a ring potential of 0.1 V (*vs.* Ag/ AgCl). The analysis was carried at rotation speeds of 300 and 600 rpm.



**Figure S1:** ORTEP diagram of MOM [Cu(INA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] (1) with the labelling scheme. Ellipsoids drawn at 80 % probability. Bond distances around the Cu<sup>II</sup> centre: Cu1-O1W = 1.9922(19) Å, Cu1-N1 = 2.007(2) Å and Cu1-O2W = 2.417(2) Å.



**Figure S2**. H-bonds (blue lines) showing the connectivity of one monomer to its six neighbours in MOM [Cu(INA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] (**1**).



Figure S3. 3D supramolecular hydrogen bonded network (blue lines) in MOM  $[Cu(INA)_2(H_2O)_4] (1). \label{eq:current}$ 



**Figure S4.** H-bonds (blue lines) formed between the carboxylate group of one monomer with the coordinated water molecules of three neighbouring monomers in MOM **1**.



Figure S5. View of the H-bonding interactions (blue lines) in the *bc* plane in MOM 1.



**Figure S6**. 2D supramolecular layers formed by intermolecular  $\pi \cdots \pi$  interactions (dashed purple lines) and anion- $\pi$  interactions (dashed green lines) within the crystallographic *bc*-plane in MOM **1**.



**Figure S7**. HS plotted over *d*<sub>norm</sub>, shape index, curvedness, and fragment patch for complex with a proper colour scale.



**Figure S8**. 2D Fingerprint plots of complex displaying the percentage contributions of the atoms within specific interacting pairs.

**Theoretical calculations**. We have calculated the formation energy of the tetrameric assembly depicted in Figure 1b to be remarkably large (-275.1 kcal/mol). Further investigations are described below with the aim to elucidate the underlying reasons for this unexpectedly high stabilization energy. We have investigated the energetic features of several dimers extracted from the solid-state architecture of MOM 1, focusing specifically on two dimers from the tetrameric assembly depicted in Figure 1b and another dimer illustrated in Figure 1c. The analysis of these dimers employed both Quantum Theory of Atoms in Molecules (QTAIM) and Non-Covalent Interaction plot (NCIplot), which are instrumental in elucidating and visualizing interactions in real space. The results are compiled in Figure 59, where the colour of the reduced density gradient (RDG) iso-surfaces represents interaction strength: green for weak interactions and blue for strong interactions.



**Figure S9**. QTAIM (BCPs in pink and bond paths as dashed bonds) and NCIPlot analysis (RDG = 0.5, ocut-off = 0.045 a.u., colour scale -0.05 a.u.  $\leq (\text{sign}\lambda_2) \leq 0.05$  a.u. of MOM **1**.

For DIMER A (Figure S9a), extracted from the tetramer, only two hydrogen bonds are formed involving the water molecules. Each O-H···O hydrogen bond features a bond critical point (BCP, marked by a pink sphere) and a bond path (illustrated with a dashed line) connecting the hydrogen to the oxygen atom, further characterized by a disk-shaped blue RDG isosurface. QTAIM/NCIplot analysis also reveals multiple BCPs and bond paths between the aromatic rings and carboxylate groups. NCIplot analysis highlights three distinct isosurfaces: one characterizing  $\pi$ -stacking (also characterized by two BCPs and bond paths interconnect two carbon atoms of the aromatic rings). The other two extended RDG regions between the carboxylate group and the pyridine indicate the presence of anion- $\pi$  interactions, supported by two symmetric BCPs and bond paths linking the oxygen atom of the carboxylate to a carbon atom of the pyridine. The dimerization energy for DIMER A is significant (-67.2 kcal/mol), consistent with the strong MEP values at the hydrogen bond donor and acceptor sites and over the centre of the pyridine ring.

In DIMER B, shown in Figure S9b, four hydrogen bonds, rather than two in DIMER A, are established, including one very strong bond denoted by a dark blue RDG isosurface, along with its corresponding BCP and bond path. This dimer features a unique and large RDG region between the rings, that extends to the -COO<sup>-</sup> groups,

indicating enhanced complementarity. Both  $\pi$ -stacking and anion- $\pi$  interactions in this dimer are defined by one BCP and bond path interconnecting two C-atoms ( $\pi$ -stacking) or connecting one O-atom of carboxylate to one C-atom of pyridine (anion- $\pi$ ). The dimerization energy in DIMER B is greater than in DIMER A (-92 kcal/mol), attributable to the presence of two additional and stronger hydrogen bonds and significant contributions from anion- $\pi$  and  $\pi$ -stacking interactions.

Finally, DIMER C (Figure S9c) connects the monomers via two hydrogen bonds and two CH···HC contacts, which are presumed to be very weak, as indicated by a minimal RDG isosurface. The interaction energy in this dimer is considerably smaller in absolute value (-36.1 kcal/mol) compared to the other dimers, due to the lack of anion- $\pi$ and  $\pi$ -stacking interactions.

The substantial dimerization energies observed in DIMERS A-C underscore the strength of the charge-assisted hydrogen bonds in this compound, which are instrumental in forming the 2D assemblies depicted in Figure 1a in cooperation with other interactions. The QTAIM/NCIplot analysis not only confirms the presence of anion- $\pi$  interactions but also shows that they are surface analysis. Additionally, the pronounced acidity of the water protons, indicated by MEP values exceeding 90 kcal/mol, corroborates the experimental observations of proton mobility in MOM **1**.



**Figure S10**. PXRD pattern of MOM **1** at different pH showing its stability over a wide pH range of 3-14. Red ellipses indicate the peaks formed when MOM **1** decomposes.



**Figure S11**. Absorption spectra of the MOM in different pH solutions in the range 14-1 showing its stability within the pH range 3-14. Note that the spectra of the bare MOM and those in the pH range 14-5 are fully coincident).



Figure S12. IR spectra of the solid MOM 1 collected from different pH solutions.



**Figure S13**. Differences in the IR spectra of MOM **1** and the sample recovered after soaking MOM **1** during 24 h in a pH = 1 solution.



**Figure S14**. PXRD patterns of MOM **1** in methanol, acetonitrile and dimethylformamide.

Electron Image 1



**Figure S15**. Electron microscopy image of a polycrystalline sample of MOM **1** showing the different regions for the Energy Dispersive X-ray spectra.



**Figure S16**. Energy Dispersive X-ray Spectroscopy analysis of a powder sample of MOM **1**. We have collected several EDXS data of the sample but accidentally we get the content of N is 0.00 for all cases even if the spectrum shows the presence of N at around 0.4 keV as also shown in the elemental mapping in Figure S17.



Figure S17. Energy Dispersive X-ray Spectroscopy elemental mapping of MOM 1.



Figure S18. Thermogravimetric analysis of MOM 1.



**Figure S19**. Powder X-ray diffractogram of MOM **1** after heating at 110 °C and then exposing it to ambient conditions for 2 h hours.



Figure S20. Water sorption profile of MOM 1 activated by heating at 80 °C for 4 h.



Figure S21. PXRD pattern of MOM 1 after water adsorption.



**Figure S22**. Thermal variation of the magnetic susceptibility times the temperature for MOM **1**. Solid line if the fit to the model (see text).



**Figure S23**. Hydrogen bonds (blue lines) and  $\pi \cdots \pi$  interactions (pink lines) along the crystallographic *b*-axis to mediate the weak interchain antiferromagnetic interaction.

## Calculation of dielectric constants of MOM 1

Figure S24 shows the real and imaginary parts of the dielectric constant of MOM **1**. The former gives information about the ability of MOM **1** to polarize in response to an electric field and the latter is associated with the loss of energy (often as heat) when an electric field is applied. The analysis was performed in the crystal's three directions (xx, yy, zz), revealing markedly different behaviours. Focusing on its imaginary part, we observe how the dielectric function begins to increase, reaching a small maximum around 2.5 eV, with a significant increase when photons with energies above approximately 3 eV are irradiated. However, although this behaviour is consistent in all crystal directions, the intensity of these values decreases significantly in the yy direction. This direction mainly houses the pyridine rings, arranged almost perpendicular to the propagation direction. Additionally, other peaks can be observed as photon energy increases, appearing in the xx and zz directions at 3.8, 4.5, 5.2, 6.2, and 6.7 eV, while in the yy direction, peaks are found at 3.4 and 5.0 eV, decreasing within the studied range of 0 to 10 eV.



**Figure S24**. Real (left) and imaginary (right) dielectric function of MOM **1** over all polarization directions.

We have utilized the Electron Localization Function (ELF) to examine the electron distribution within the unit cell. As depicted in Figure S25, the ELF values vary across different crystal planes: areas where ELF values approach one mean a high concentration of localized electrons, characteristic of covalent bonds, while areas where ELF values are close to zero indicate regions with virtually no electron presence. Through the analysis of ELF isosurfaces (refer to videos in the Supplementary Material), we identified zones with elevated ELF values that align with regions of intermolecular interactions, such as anion- $\pi$  interactions within compound **1**.



**Figure S25**. Contour plots of ELF on the 100, 010 and 001 planes of MOM **1**. (Videos showing how the contour varies along the axis of the crystal structure can be seen in the supporting information.)

Furthermore, significant electron localization is observed between molecules in the vicinity of coordinated water molecules. These areas between molecules, highlighted by significant electron probabilities, suggest regions of pronounced electron localization that do not correspond to covalent bonding. This observation likely contributes to the moderate electrical conductivity observed in this material, providing insights into the electron dynamics that influence its electrical properties.



**Figure S26**. Nyquist plots of MOM **1** at 25 °C and different relative humidity (RH) with a pellet thickness of 0.109 cm.



**Figure S27**. X-ray powder diffractogram of MOM **1** after performing the proton conductivity measurements.



**Figure S28**. Absorption spectra (a) and corresponding Tauc plot of MOM **1**. The bandgap calculated from Tauc plot is 2.87 eV.



Figure S29. Emission spectra of MOM 1.



Figure S30. Single crystals of MOM 1 used for conductivity measurements.



Figure S31. Electrical conductivity for MOM 1. (a) I-V plot at 400 K for one of the four measured single crystals. (b) Arrhenius plot for the four measured single crystals of MOM 1. Solid lines are fits to the Arrhenius law.



**Figure S32**. Rotating ring disk electrochemistry (RRDE) plots for the ORR at pH 13 for 300 (left) and 600 (right) rpm.



**Figure S33.** Chronoamperometry data of MOM in O<sub>2</sub>-saturated 0.1 M KOH at 0.56 V *vs.* RHE (blue). Comparison of blank carbon cloth under similar conditions (red).



**Figure S34.** Field emission scanning electron microscope (FESEM) images of single crystals of MOM **1**.



Figure S35. FESEM image of the bulk powder of the synthesized particles.

Compound	Structure	σ <sub>H</sub> (S cm <sup>-1</sup> )	RH/T (°C)	σ (S cm <sup>-1</sup> ) RH/T (°C)	Use	Ref.
Cu(INA) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> (1)	SupraC	10-5	n.i./25	4.8 × 10 <sup>-8</sup> n.i./25	ec-ORR	This work
[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ][In(m-TTFTB)]	3D MOF	$6.66 \times 10^{-4}$	98 %/n.i.			13
[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ][In(TTFOC)]	3D MOF	1.30 × 10 <sup>-2</sup>	98 %/n.i.	4.05 × 10 <sup>-3</sup> 90 %/30	p-C	13
Ag-MOCP (L = 1H-1,2,3-triazole)	1D CP	2.3 × 10 <sup>-7</sup>	98 %/25	3.57 × 10 <sup>-7</sup> n.i./25	ec-CO <sub>2</sub> RR	14
Ag-MOCP (L = 1H-benzotriazole)	1D CP	3.3 × 10 <sup>-9</sup>	98 %/25	2.96 × 10 <sup>-9</sup>	ec-CO <sub>2</sub> RR	14
(TTF) <sub>2</sub> [Pt <sub>2</sub> (pmdt) <sub>4</sub> ]	SupraC	$2.8 \times 10^{-6}$		1.3 × 10 <sup>-4</sup> n.i./25		15
$[Co_7(OH)_6(H_2O)_3(C_4H_4O_4)_4]$ ·7H <sub>2</sub> O	2D CP	$1.0 \times 10^{-10}$		$2.01 \times 10^{-8}$		16
$\frac{[Co_7(OH)_6(H_2O)_3(C_4H_4O_4)_4]}{\cdot 7H_2O + PBS}$	2D CP	2.02 × 10 <sup>-5</sup>		3.84 × 10 <sup>-4</sup> 99 %/100		16
Zn-HHTP-H <sub>2</sub> O	2D CP	$1.6 \times 10^{-5}$	95 %/70ª	4.4 × 10 <sup>-2</sup> 95 %/25 <sup>b</sup>		17
Zn-HHTP-H <sub>2</sub> O/Urea	2D CO	$1.6 \times 10^{-4}$	95 %/70	1.7 × 10 <sup>-2</sup> 95 %/70		17
({[Ni(bpy)(H <sub>2</sub> O) <sub>2</sub> (DMF) <sub>2</sub> ] (NO <sub>3</sub> ) <sub>2</sub> ·DMF}n)	1D CP	0.09	> 90 %/25	0.20 50 %/25	Synaptic device	18
$[La_4(H_{8-x}TTF)_6(H_2O)_3]$ -1.7EtOH-13.75H_2O (x = 0-3)	3D MOF	$4.9 \times 10^{-5}$	95 %/25	7.2 × 10 <sup>-6</sup> n.i./25		19
(ET) <sub>4</sub> [Pt <sub>2</sub> (pop) <sub>2</sub> (Hpop) <sub>2</sub> ] ·PhCN	SupraC	$2.1 \times 10^{-2}$	n.i./25	1–2 n.i./25		20
$\begin{bmatrix} Cu_{3}(\mu^{3}-OH)(C_{4}H_{2}N_{2}O_{2})_{3}(H_{3}O) \\ \cdot 2C_{2}H_{5}OH \cdot 4H_{2}O \end{bmatrix}$	3D MOF	6.39 × 10 <sup>-7</sup>	98 %/80	9.39 × 10 <sup>-9</sup> n.i./80		21
NH4[Cu3(OH)- (C4H2N2O2)3]·8H2O	3D MOF	5.3 × 10 <sup>-7</sup>	98 %/80	5.97 × 10 <sup>-6</sup> n.i./80		21
Cu <sub>3</sub> HHTT <sub>2</sub>	2D CP	2.54 × 10 <sup>-8</sup>	70 %/25	10 <sup>-7</sup> 70 %/25	Chemresistive sensing	22

**Table S1**. Proton ( $\sigma_H$ ) and electrical ( $\sigma$ ) conductivity values and applications of different dual conducting materials.

a Ea = 0.52 eV; b Ea = 0.14 eV; n.i. = not indicated; SupraC = supramolecular complex; RH = relative humidity; TTFTB = tetrathiafulvalene-tetrabenzoate; TTFOC = tetrakis(3,5-dicarboxyphenyl)tetrathiafulvalene; MOCP = metal organic coordination polymer; pmtd = phosphonomethanedithioate;  $C_4H_4O_4$  = succinate; PBS = a mixed solution of K<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>; HHTP = hexahydroxytriphenylene; ec-ORR = electrocatalytic oxygen reduction reaction; p-C = Pseudo-capacitance; ec-CO<sub>2</sub>RR = electrocatalytic CO<sub>2</sub> reduction reaction; bpy = 4,4'-bipyridine, DMF = N,N-dimethyl formamide, T: bis(ethylenedithio)tetrathiafulvalene, pop<sup>2-</sup> = P<sub>2</sub>H<sub>2</sub>O<sub>5</sub><sup>2-</sup>; H<sub>6</sub>HHTT = 2,3,7,8,12,13-hexahydroxy-4b1,5,10,15tetraazanaphtho[1,2,3-gh]- tetraphene.

CCDC Identification code	2369691
Empirical formula	$C_{12}H_{16}CuN_2O_8$
Formula weight	379.81
Temperature	120(2) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P-1
a (Å)	6.3123(3)
b (Å)	6.8085(3)
c (Å)	9.1809(4)
a (º)	98.952(4)
b (°)	105.115(4)
g (°)	108.659(4)
Volume (Å <sup>3</sup> )	348.36(3)
Z	1
Density (calculated)	1.810 Mg m <sup>-3</sup>
Absorption coefficient (m)	2.680 mm <sup>-1</sup>
F(000)	195
Crystal size	0.14 x 0.08 x 0.05 mm <sup>3</sup>
Theta range for data collection ( <sup>o</sup> )	5.170 to 75.674
Index ranges	$-7 \le h \le 7$
	$-7 \le k \le 8$
	-11 ≤ 1 ≤ 10
Reflections collected	6488
Independent reflections	1390 [R <sub>int</sub> = 0.0384]
Completeness to theta = 67.684°	99.8 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1390 / 0 / 118
Goodness-of-fit on F <sup>2</sup>	1.195
Final R indices [I > 2s(I)]	$R_1 = 0.0302, wR_2 = 0.0731$
R indices (all data)	$R_1 = 0.0350, wR_2 = 0.0946$
Extinction coefficient	n/a
Largest diff. peak and hole	0.550 and -0.684 e.Å <sup>-3</sup>

**Table S2**. Crystal data and structure refinement for MOM 1.

Atoms	Distance (Å)	Atoms	Angle (º)	Atoms	Angle (º)
Cu1-O1W	1.9922(19)	O1W-Cu1-	180.0	N1-Cu1-O2W	91.19(8)
		$O1W^1$			
Cu1-	1.9922(19)	O1W-Cu1-N1	89.61(9)	N1 <sup>1</sup> -Cu1-O2W	88.81(8)
O1W <sup>1</sup>					
Cu1-N1	2.007(2)	O1W <sup>1</sup> -Cu1-N1	90.39(9)	O1W-Cu1-O2W <sup>1</sup>	93.88(8)
Cu1-N1 <sup>1</sup>	2.007(2)	O1W-Cu1-N1 <sup>1</sup>	90.39(9)	O1W <sup>1</sup> -Cu1-	86.12(8)
				O2W <sup>1</sup>	
Cu1-O2W	2.417(2)	O1W <sup>1</sup> -Cu1-N1 <sup>1</sup>	89.61(9)	N1-Cu1-O2W <sup>1</sup>	88.81(8)
Cu1-	2.417(2)	N1-Cu1-N1 <sup>1</sup>	180.00(13)	N1 <sup>1</sup> -Cu1-O2W <sup>1</sup>	91.19(8)
O2W <sup>1</sup>					
		O1W-Cu1-O2W	86.12(8)	O2W-Cu1-O2W <sup>1</sup>	180.0
		O1W <sup>1</sup> -Cu1-	93.88(8)		
		O2W			

Table S3. Selected bond distances (Å) and angles (°) for MOM 1.

Symmetry transformations used to generate equivalent atoms: 1 = -x+2,-y+2,-z+1

Table S4. Structural para	ameters of the hydrogen	bonds observed in MOM 1.
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D-H···A	D-H (Å)	H…A (Å)	D…A (Å)	< (D-H…A)
O1W-H1W1…O1 <sup>2</sup>	0.77(4)	1.98(4)	2.743(3)	173(4)
O1W-H2W1…O2 <sup>3</sup>	0.75(4)	1.87(4)	2.612(3)	175(4)
O2W-H1W2…O1 <sup>3</sup>	0.74(4)	2.15(4)	2.887(3)	173(4)
O2W-H2W2…O2 <sup>4</sup>	0.79(4)	2.03(4)	2.827(3)	176(4)
C1-H1…O1W <sup>5</sup>	0.95	2.53	3.390(3)	151.4

Symmetry transformations used to generate equivalent atoms: 2 = -x+1, -y+1, -z; 3 = x+1, y, z+1; 4 = x, y, z+1; 5 = x-1, y, z.

**Table S5**. Structural parameters of the  $\pi$ - $\pi$  and anion- $\pi$  interactions in MOM **1**.

	π…π		
Ri…Rj	$C_g$ - $C_g$ distance (Å)	α (°)	Symmetry
R1…R1	3.9659(15)	0.00(13)	1-x, 1-y, -z
R1…R1	4.2393(15)	0.00(13)	1-x, 2-y, -z

Anion-π				
Y-X…Ri	X-C <sub>g</sub> distance (Å)	<Y-X···R <sub>i</sub> (°)	Symmetry	
C6-O1…R1	3.990(2)	56.25(15)	1-x, 2-y, -z	
C6-O2…R1	3.430(2)	80.49(16)	1-x, 1-y, -z	

\*R1: N1-C1-C2-C3-C4-C5;  $C_g$  = centroid of R1.

Sample	<b>Relative humidity (%)</b>	σ <sub>400 K</sub> (S cm <sup>-1</sup> )
1	60	$2.06 \pm 0.09 \ge 10^{-10}$
2	70	$6.10 \pm 0.26 \ge 10^{-9}$
3	80	$1.20 \pm 0.05 \ge 10^{-7}$
4	90	$1.23 \pm 0.05 \ge 10^{-6}$
5	98	$2.26 \pm 0.10 \ge 10^{-5}$

Table S6. Proton conductivity values different humidity at 25 °C of compound 1.

**Table S7**. Electrical conductivity values at 400 K and 300 K (extrapolated) and activation energies for the four crystals measured of compound **1**.

Crystal	σ <sub>300 K</sub> (S cm <sup>-1</sup> )	σ <sub>400 K</sub> (S cm <sup>-1</sup> )	E <sub>a</sub> (eV)
1	2.8(1)x10 <sup>-13</sup>	1.7(1)x10 <sup>-8</sup>	1.2(1)
2	9.2(1)x10 <sup>-13</sup>	4.0(1)x10 <sup>-8</sup>	1.1(1)
3	5.6(1)x10 <sup>-13</sup>	1.8(1)x10 <sup>-8</sup>	1.1(1)
4	1.1(1)x10 <sup>-12</sup>	1.4(1)x10 <sup>-7</sup>	1.1(1)

**Table S8**: Different onset potential for electrocatalytic ORR of MOM and other reference materials.

Catalyst	Onset Potential (V vs. RHE)
Pt	0.96
Fe PANI/C	0.85
MOM	0.70

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