Electro-reduction of carbon dioxide at low over-potential at a metal-organic framework decorated cathode

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Electrochemical reduction of carbon dioxide is a clean and highly attractive strategy for the production of organic products. However, this is hindered severely by the high negative potential required to activate carbon dioxide. Here, we report the preparation of a copper-electrode onto which the porous metal–organic framework [Cu$_2$(L)] [H$_4$L = 4,4',4'',4'''-(1,4-phenylenebis(pyridine-4,2,6-triyl))tetrabenzoic acid] can be deposited by electro-synthesis templated by an ionic liquid. This decorated electrode shows a remarkable onset potential for reduction of carbon dioxide to formic acid at −1.45 V vs. Ag/Ag$^+$, representing a low value for electro-reduction of carbon dioxide in an organic electrolyte. A current density of 65.8 mA·cm$^{-2}$ at −1.8 V vs. Ag/Ag$^+$ is observed with a Faradaic efficiency to formic acid of 90.5%. Electron paramagnetic resonance spectroscopy confirms that the templated electro-synthesis affords structural defects in the metal-organic framework film comprising uncoupled Cu(II) centres homogenously distributed throughout. These active sites promote catalytic performance as confirmed by computational modelling.
increasing CO2 levels in the atmosphere present significant environmental impacts1–3. Thus, routes to carbon capture and storage, as well as development of CO2 reduction technologies to afford chemical feedstocks are being developed4–8. Reduction of CO2 is economically and environmentally desirable but technically challenging because the high energy of the C=O bond (750 kJ·mol−1) makes it an extremely stable molecule that is reluctant to transform9–9. One effective method to overcome the high activation barrier is through electrochemical catalytic reduction in which CO2 is reduced under mild conditions10–13. Copper-based electrodes have been reported as powerful catalysts for the electro-reduction of CO2 to give numerous products including CO, formic acid and, recently, C2 and other products14–18. Formic acid is heavily used in chemical industries for leather, dyeing and textiles, and can be converted directly within fuel cells19,20. It is therefore a valuable C1 product. Reduction of CO2 at Cu-based electrodes can proceed via O-bound HCOO− or C-bound –COOH intermediates that are formed from electrochemically generated CO2− radicals. The latter route can diverge to other possible products20,21, but the electro-reduction of CO2 via an O-bound HCOO− pathway may enhance the Faradaic efficiency for the formation of formic acid. In addition, the formation of formic acid requires a highly negative potential for CO2 reduction, and this often leads to decomposition of copper-based catalyst via reduction of metal sites during electrolysis. Although emerging electrocatalysts have been reported for reduction of CO2 to formic acid at low over-potentials17, more work needs to be undertaken to understand the details of this catalysis22,23.

In recent years, there has been much interest in metal–organic framework (MOF) materials as crystalline porous hosts for gas adsorption, separation and catalysis24–26. Their high surface area, potentially active metal centres, diverse pore structure and, in exceptional cases, their redox activity, promote their use as electrocatalysts for H2 and O2 evolution and reduction of O227. However, highly crystalline MOFs with fully coordinated metal centres exhibit only low charge-transfer ability and formally no active centres for electrocatalysis12. Therefore, in order to drive efficient electrocatalysis, MOFs that exhibit high capacity for charge-transfer and incorporate accessible metal sites are highly desirable.

Herein, we report the templated electrochemical growth of the Cu(II) complex [Cu2(L)]2− [H4L = 4,4′,4″,4‴-(1,4-phenylenebis(4,2,6-triyl))tetrabenzoic acid] (Supplementary Fig. 1) on a Cu-foam electrode to introduce abundant structural defects comprised of active Cu(II) sites within the deposited film. The resultant electrode, Cu2(L)-e/Cu, shows excellent activity for the reduction of CO2 to formic acid with an onset potential of −1.45 V vs. Ag/Ag+ for production of formic acid, a Faradaic efficiency (FEHCOOH) reaching 90.5% at −1.8 V vs. Ag/Ag+ and a current density of 65.8 mA·cm−2. Side reactions, such as H2 evolution and reduction of Cu(II) sites, are effectively hindered at low potentials, and the catalytic mechanism has been studied by electron paramagnetic resonance (EPR) spectroscopy and density functional theory (DFT) calculations.

Results and discussion

Electrosynthesis of Cu2(L)-e/Cu. The ligand H4L was synthesised via a three-step method from our previous report30. The electrode, Cu2(L)-e/Cu, was prepared by electro-synthesis of the MOF on Cu-foam at a potential of 8.0 V at 60 °C in the presence of the ionic liquid 1-ethyl-3-methylimidazolium acetate (Emi-AC, Supplementary Fig. 2) as supporting electrolyte (Supplementary Fig. 3). Upon completion, the porous Cu-foam was coated with green crystallites of Cu2(L)-e (Fig. 1a–d) thus limiting the further supply of Cu2+ ions from the anode for synthesis of more MOF material. SEM images confirm the spherical morphology of the complex film with an average particle size of ~50 nm (Fig. 1e, f). For comparison, the MOF was also synthesised by a conventional solvothermal reaction [denoted as Cu2(L)-t31, which crystallised in much larger octahedral-shaped crystals of several microns in size (Supplementary Fig. 4). The structure of Cu2(L) comprises of a 3D network built around binuclear [Cu2(OOCR)4] paddlewheels with four bridging carboxylate ligands (Fig. 1g, h)19.

Structural analysis and characterisation of Cu2(L). The spectra are dominated by the characteristic spin triplet spectrum of the [Cu2(OOCR)4] paddlewheel structure, which arise from strong antiferromagnetic exchange (singlet-triplet gap ca. 300 cm−1) within the binuclear moiety and the thermal population of the excited S = 1 state, which has a zero-field splitting of ca. 0.3 cm−1. The characteristic forbidden transition (mS = ±2) associated with the triplet spin state of the Cu2 entity is clearly observed (ca. 5300 G) in all Q-band spectra of Cu2(L)-e and Cu2(L)-t (Fig. 2g and Supplementary Fig. 8). In addition, features due to uncoupled Cu(II) (S = ½, gxx = 2.07, gz = 2.32, Axx = 33.6 MHz, and Azz = 450 MHz) ions are observed (ca. 3250 G at X-band; 12000 G at Q-band), and these signals are more pronounced in Cu2(L)-e than in Cu2(L)-t (Fig. 2f, g). The relative concentration of [Cu2(OOCR)4] paddlewheel units and uncoupled free Cu(II) is given by the relative intensity of the second integral of simulations of the Q-band EPR spectra, weighted by the room temperature Boltzmann populations of the spin triplet state of the [Cu2(OOCR)4] paddlewheel (Fig. 2h, i and Supplementary Table 2).34,35 Using this approach it was determined that Cu2(L)-t and Cu2(L)-e contain 1.5% and 15.3% of uncoupled Cu(II) sites, respectively, confirming that electro-synthesis generates an order of magnitude greater number of defect sites.

Analysis of porosity in Cu2(L). The porosity of these MOFs was studied by N2 isotherms at 77 K (Fig. 2) and Supplementary Table 1). Desolvated Cu2(L)-t shows a Type-I sorption profile.
consistent with the expected uniform microporosity. In contrast, desolvated Cu$_2$(L)-e exhibits a profile between Type-I and Type-IV, suggesting the presence of both mesopores and micropores. The distribution of micro- and mesopores within both materials has been analysed by Horvath-Kawazoe and Barrett–Joyner–Halenda (BJH) methods, respectively (Fig. 2k, l). The reduction in micropores in Cu$_2$(L)-e results in a low N$_2$ uptake at low pressure, while Cu$_2$(L)-t, generated by the template-effect of the ionic liquid during electro-synthesis $^{33}$, shows a total pore volume of 1.89 cm$^3$·g$^{-1}$, significantly larger than that of Cu$_2$(L)-e (0.32 cm$^3$·g$^{-1}$), reflecting the presence of mesopores in Cu$_2$(L)-e. CO$_2$ adsorption in desolvated Cu$_2$(L)-t and Cu$_2$(L)-e at 1.0 bar and 298 K are 38.5 and 44.7 cm$^3$·g$^{-1}$, respectively (Fig. 2m). Higher isosteric heats of adsorption ($Q_{st}$) were obtained for Cu$_2$(L)-e (Supplementary Figs. 9, 10), suggesting stronger interactions with CO$_2$ than in Cu$_2$(L)-t, consistent with the presence of additional active sites in the former. In summary, electro-synthesised Cu$_2$(L)-e can be grown directly onto Cu-foam to afford a decorated electrode incorporating a defect structure with active Cu(II) sites that show strong interaction with CO$_2$, a key feature for an optimal catalyst for CO$_2$ reduction $^{37}$. For comparison, the benchmark system HKUST-1 has also been electro-synthesised onto Cu-foam (denoted as HKUST-1-e/Cu) using the same method, and fully characterised by SEM, PXRD, TGA and BET (Supplementary Figs. 11–14 and Supplementary Table 1). High crystallinity and large particle sizes (~1 μm) were obtained for HKUST-1-e, consistent with its facile crystal growth.
Electrochemical reduction of CO₂. To test performance for electrochemical reduction of CO₂, Cu₂(L)-e/Cu and HKUST-1-e/Cu were used directly as electrodes, while a powder sample of Cu₂(L)-t was loaded onto carbon paper (CP) with Naflon-D521 as adhesive to fabricate a Cu₂(L)-t/CP electrode. All experiments were performed in an H-type cell with 0.5 M 1-ethyl-3-methylimidazolium tetrafluoroborate (EmimBF₄) in acetonitrile (0.5 M EmimBF₄/MeCN) as catholyte. As shown from the linear sweep voltammetry at the Cu₂(L)-e/Cu electrode, negligible current was generated in N₂-saturated electrolyte, while the current density increased dramatically in CO₂-saturated electrolyte, confirming a strong response to CO₂ (Supplementary Fig. 15). The dependence of current density on time (i-t curves) for all three electrodes is shown in Fig. 3a. Minimal current density was observed with N₂, whereas a rise in current density is observed on introduction of CO₂. The current density continuously increases in the presence of CO₂ and stabilises after 1 h for the three electrodes. The Cu₂(L)-e/Cu electrode shows the highest current density, and for all systems, formic acid was found to be the only carbon-containing product based on GC and 1H NMR.

Fig. 2 Characterisations of Cu₂(L)-t (black lines) and Cu₂(L)-e (red lines). a PXRD patterns (blue line refers to simulated PXRD pattern). The defects in Cu₂(L)-e result in broadening of peaks due to poorer crystallinity of the material. b Micrograph (top) and CFM image (bottom) of Cu₂(L)-e. c Selected FTIR spectra (full spectra are shown in Supplementary Information). d TGA curves. e X-band EPR spectra at room temperature. f Q-band EPR spectra at room temperature. g Second integrals from simulated Q-band EPR spectra for Cu₂(L)-t. h Second integrals from simulated Q-band EPR spectra for Cu₂(L)-e. i N₂ adsorption/desorption isotherms at 77 K. k Micropore size distribution. l Mesopore size distribution. m Adsorption isotherms for CO₂ at 298 K (desorption data are shown in Supplementary Information). Data for HKUST-1-e are shown in Supplementary Information. The scale bars of b and c are 20 μm.
spectroscopic analysis of gas and liquid phases, respectively, after electrolysis. No carbon-containing product was detected in the absence of CO₂ from the catholyte, confirming that the generated formic acid is derived solely from introduced CO₂ rather than decomposition of the catalyst or electrolyte. The current density and Faradaic efficiency for formation of formic acid (FEHCOOH) were recorded after 2 h of electrolysis (Fig. 3b, c) from −1.4 V to −2.2 V vs. Ag/Ag⁺. H₂ is the only bi-product within this potential range. Significantly, the Cu₂(L)-e/Cu electrode shows an onset potential of −1.45 V vs. Ag/Ag⁺ for the generation of formic acid, representing one of the lowest potentials observed in organic electrolytes for systems reported to date (Supplementary Table 3)⁶,³⁸–⁴⁰, although a recent Cu-porphyrin system shows an onset voltage as low as −1.4 V vs. Ag/Ag⁺.¹⁷ The current density increases with increasing negative potential, but FEHCOOH increases and then decreases, reaching a maximum of 90.5% at −1.8 V vs. Ag/Ag⁺ with a current density of 65.8 mA·cm⁻². The value of FEHCOOH is maintained at >80% between −1.75 V to −1.95 V vs. Ag/Ag⁺. In comparison, the Cu₂(L)-t/CP electrode exhibits a higher onset potential of −1.7 V vs. Ag/Ag⁺ for formic acid production and a lower current density across the potential range, with a maximum FEHCOOH of 77% observed at −1.9 V vs. Ag/Ag⁺. For the HKUST-1-e/Cu electrode, an even higher onset potential of −1.75 V vs. Ag/Ag⁺ was observed for production of formic acid, and FEHCOOH reaches a maximum of 62% at −2.05 V vs. Ag/Ag⁺. Thus, Cu₂(L)-e/Cu demonstrates an excellent performance for electro-reduction of CO₂ in terms of the low onset potential and high FEHCOOH with relatively low over-potentials. The current density for formic acid production increases rapidly from the onset potential to −2.0 V vs. Ag/Ag⁺, and the production of formic acid progresses slowly thereafter (Supplementary Fig. 16), reflecting the enhanced production of H₂ at potentials more negative than −2.0 V vs. Ag/Ag⁺. As potentials more negative than −2.0 V vs. Ag/Ag⁺, the HKUST-1-e/Cu electrode shows a rise in current density (Fig. 3b) with the current density of formic acid reaching a plateau (Supplementary Fig. 16). An undecorated Cu-foam electrode (Fig. 1a, b) was also tested, and a current density of 4.2 mA·cm⁻² with a FEHCOOH of 20.5% after 2 h electrolysis at −1.8 V vs. Ag/Ag⁺ were observed (Supplementary Fig. 17), demonstrating the critical role of defect Cu₂(L) on the performance of the electrode. It should be noted that a nanostructured Cu-foam has been explored previously as an electrocatalyst;¹⁶ the Cu-foam in the current study is of a different type and is much smoother.

Upon completion of reaction, HKUST-1-e turned amorphous and partially peeled off the Cu-foam as confirmed by SEM images. In contrast, Cu₂(L)-e/Cu generally maintained its morphology with a slight aggregation of particles (Supplementary Fig. 18). Thus, the thin coating with small crystallites in the Cu₂(L)-e/Cu electrode affords chemical and mechanical stability for electrolysis, although like many Cu(II) MOFs,¹⁵ the Cu₂(L)-e/Cu electrode is unstable in water.

Variations of EPR spectra of electrodes over time. To understand the mechanism of catalysis of these electrodes, EPR spectra were measured over time intervals of 15 mins during electrolysis of CO₂ at −1.8 V vs. Ag/Ag⁺. We sought to use EPR spectroscopy to probe changes in concentrations of free, uncoupled Cu(II) centres as the reaction proceeds,¹¹ and this can be monitored by the relative intensity of the second integral of the EPR spectrum (Fig. 4a). As confirmed above, as-prepared Cu₂(L)-e/Cu has a high concentration of uncoupled Cu(II) centres due to its defect structure. All three electrodes show an increase in uncoupled Cu(II) content during electrolysis: this is presumably caused by reduction of the [Cu₂(OOCR)₄] paddlewheel units under the electrolytic conditions, with subsequent structural disruption. The amount of free Cu(II) sites was maximised after electrolysis for 75, 60 and 45 mins for Cu₂(L)-e/Cu, Cu₂(L)-t/CP and HKUST-1-e/Cu, respectively, followed by a slight decrease for Cu₂(L)-t/CP and a greater decrease in Cu₂(L)-t/CP and HKUST-1-e/Cu. The quantities of uncoupled Cu(II) sites decrease after a maximum and are likely due to reduction to diamagnetic (3d¹⁰) Cu(I) over time (Supplementary Fig. 19), as confirmed by XPS and Auger spectra (Supplementary Fig. 20). These results also support the thesis that free Cu(II) defect sites are responsible for the high current density and FEHCOOH observed for Cu₂(L)-e/Cu throughout the electrolysis of CO₂ (Fig. 4b). H₂ evolution becomes more evident over time using Cu₂(L)-t/CP and HKUST-1-e/Cu electrodes also likely due to generation of Cu(I) sites over time (Supplementary Fig. 21). The reduction of [Cu₂(OOCR)₄] paddlewheel MOFs to form Cu(II), Cu(I) species has been reported previously,⁴² and is associated with tetrahedral distortion of the reduced metal centre to give an uncoupled Cu(II) centre. The current density for formation of formic acid remains constant after the uncoupled Cu(II) content reaches its maximum value, and so catalysis remains stable up to 9 h (Supplementary Figs. 22, 23). Thus, Cu₂(L)-e/Cu exhibits the best performance for long-term electrochemical stability for formic acid production. It is notable that the total Faradaic efficiency for formation of formic acid and H₂ (FEHCOOH+H₂) is lower than 100% during the first hour of electrolysis (Supplementary Fig. 24), indicating that the electrode evolves during this early period of electrolysis, consistent with the morphological changes observed at the electrode surface (Supplementary Fig. 18).

Electrochemical characteristics of electrodes. The charge-transfer ability of the electrode also plays an important role in its electrocatalytic performance. As revealed by Nyquist plots at an open circuit potential (Fig. 4d), the Cu₂(L)-e/Cu, Cu₂(L)-t/CP
and HKUST-1-e/Cu electrodes give charge-transfer resistances (Rct) of approximately 17, 114 and 408 Ω, respectively12,38. The significantly lower Rct for Cu2(L)-e/Cu is most likely due to its microscopic morphology as revealed from SEM images. Thus, nanoparticles of Cu2(L) form a compact thin coating on the Cu-foam surface with the overall porous network preserved, whereas rapid crystallisation of HKUST-1 results in bigger crystals and a thick coating of HKUST-1-e/Cu, leading to a higher overall resistance. The poorly-conductive MOF islands on the HKUST-1-e/Cu electrodes thus cause barriers for charge-transfer, in sharp contrast to Cu2(L)-e/Cu, where all MOF particles are in close contact with the highly conductive Cu-foam. The interface between Cu2(L)-t and CP results in the poor charge-transfer as observed in many other MOF-based electrodes12. The double-layer capacitance (Cdl) of the three electrodes was analysed by measuring the capacitative current associated with double-layer charging using the scan-rate dependence of cyclic voltammetric stripping to evaluate the electrochemical active surface area (Fig. 4e)43. Cu2(L)-e/Cu has the highest value for Cdl of 10.71 mF·cm⁻² with values for Cu2(L)-t/CP and HKUST-1-e/Cu of 5.31 mF·cm⁻² and 0.55 mF·cm⁻², respectively, again evidencing the high active surface area of Cu2(L)-e/Cu14,45.

**DFT calculations.** DFT calculations have been applied widely to uncover the mechanism of electro-reduction of CO₂46-48. The Gibbs free energy with respect to potential reaction steps was modelled based upon a [Cu2(OOCR)₄] paddlewheel bound to four 4-(pyridin-2-yl)benzoate groups. Pristine and defect structures representing Cu2(L)-t and Cu2(L)-e, respectively, were then analysed by DFT calculations with defect Cu2(L) modelled with one of the O-donors of one 4-(pyridin-2-yl)benzoate not bound to Cu(II) to afford a vacant site at Cu(II). The corrections for zero point energy and entropy, and the structural model and atomic coordinates of all intermediates are given in Supplementary Tables 4-12. The plausible reaction pathways via C-bound COOH and O-bound HCOO intermediates were analysed (Supplementary Figs. 25, 26) and the effects of solvation were also taken into account (Supplementary Fig. 27). In general, the formation of O-bound HCOO involved a lower Gibbs free energy than C-bound COOH or CO over both pristine and defect Cu2(L), with formation of O-bound HCOO on defect Cu2(L) the most facile pathway leading to selective production of formic acid. In the DFT calculations the free Cu(II) centres in defect Cu2(L) are generated by the rupture of one Cu–O(carboxylate) bond, which enables binding of CO₂ via an O-bound HCOO intermediates. In addition, the defect structure leads to weaker hydrogen bonding between the MOF and product, facilitating the release of HCOOH from the surface of the Cu2(L)-e/Cu electrode. The same pattern of Gibbs free energy is also observed on inclusion of solvation effects (Supplementary Fig. 27). Figure 4f shows the DFT calculated diagram of Gibbs free energy of electro-reduction of CO₂ to formic acid over pristine (black lines) and defect Cu2(L)-t (red lines) after consideration of solvation effects.

**Conclusion.** In summary, we have electrochemically prepared the Cu2(L)-e/Cu electrode through controllable growth of MOF nanoparticles onto a Cu-foam support. This integrated electrode composed of a thin compact coating of Cu2(L) on Cu-foam incorporates uncoupled Cu(II) active sites and shows high conductivity and stability. This electrode shows excellent activity for the electro-reduction of CO₂ to formic acid, with a low onset potential of −1.45 V vs. Ag/Ag⁺, and the FE_{HCOOH} reaches 90.5% at −1.80 V vs. Ag/Ag⁺ with a current density of 65.8 mA·cm⁻². Experimental (EPR spectroscopy) and theoretical (DFT) methods
confirm that the reaction is driven by defects within the structure of the decorated electrode. In Cu2(L)-e/Cu these defects favour reduction of CO2 to formic acid versus H2 evolution. The facile preparation of Cu-MOF-e/Cu electrodes offers an instructive pathway for the development of other efficient materials that catalyse CO2 reduction at less energetic potentials.

**Methods**

**Materials.** Ionic liquids (ILs), EmimOAc (>99%) and EmimBF4 (>99%) were purchased from Sigma-Aldrich Co., UK.

**Ligand synthesis.** The ligand H2L was prepared by the published procedure. 4-Methylacetophenone (13.4 g, 0.1 mol), tert-butylaldehyde (2.70 g, 0.02 mol) and NaOH powder (5.10 g, 0.128 mol) were combined and ground in a ball mill for 90 mins. The resultant solid was dissolved in EtOH (600 mL) with NH2OAc (30 g, 0.39 mol), and the solution heated under reflux for 24 h. On cooling the white solid was collected by filtration and recrystallised from toluene to yield white crystals. This product (30 g) was combined with an aqueous solution of HNO3 (2 M, 36 mL) and heated in an autoclave at 180 °C for 24 h. The reaction mixture was cooled to room temperature and the solid H2L was collected and washed with distilled water until the filtrate was pH neutral. The solid was washed further with acetone and dried in vacuo.

**Characterisations.** The morphology of the materials was characterised on a SEM Quanta 650. PXRD analysis was performed on Rigaku Model D/MAX2500 diffractometer using Cu-Kα radiation at a scan speed of 2°/min. Infrared spectra were collected on an iS5 ATR (Attenuated Total Reflection) instrument, and TGA was measured under N2 at a flow rate of 10 mL min−1. EPR spectra at X-band and Q-band were recorded using Bruker Micro spectrometers, and the intensity of the EPR signal of different samples was normalised to the sample quantity. The BET surface areas were obtained from N2 adsorption/desorption isotherms recorded on a Micromeritics 3-Flex instrument at 77 K. CO2 adsorption isotherms were obtained using Micromeritics 3-Flex at 273 K, 283 K and 298 K, and the value for Qe for CO2 adsorption was estimated by fitting these isotherms to the Brunauer–Emmett–Teller equation. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD spectrometer with a monochromated Al-Kα X-ray source (E = 1486.6 eV, 10 mA, eV). Fluorescence micrographs were recorded on an Olympus Fluoview FV-1000 instrument to measure the fluorescence generated by the oligomerisation of 1 mL furfuryl alcohol catalysed by 10 mg of MOF at 60 °C over 2 h.

**Solvothermal synthesis of Cu2(L)-t.** The solvothermal synthesis of Cu2(L)-t was conducted by following the literature method. Cu(NO3)2·3H2O (24.2 mg, 0.10 mmol), H2L (6.9 mg, 0.05 mmol) were dissolved in DMF (3 mL) with 8 M HNO3 (0.3 mL). The solution was heated at 80 °C for 48 h in a pressure tube. On cooling the white solid was collected by filtration and recrystallised from toluene to yield white crystals. The final monomer to binuclear ratio was obtained by weighting the EPR data by the relative weighting in the Eq. (2)36 using the iterative spin Hamiltonian in the Eq. (2)35,36.

**Electro-preparation of Cu2(L)-e/Cu**

Electro-preparation was performed with an initial CO2 flow rate of 20 mL min−1 prior to the experiment, which was decreased to 10 mL min−1 after the electrolysis was saturated with CO2. After electrolysis, the gaseous products were collected using a gas bag and analysed by GC and liquid products measured by 1H-NMR spectroscopy. The Faradaic efficiencies (FE) were calculated using the Eq. (1):

\[
\text{FE} = \frac{n_{\text{product}} \times n_{\text{electrons}} \times \frac{F}{Q}}{100} \quad (1)
\]

where \(n_{\text{product}}\) is the amount of product (mol) from GC (H2) or 1H NMR spectroscopy (formic acid), \(n_{\text{electrons}}\) is electron transfer number (both the production of H2 and HCOOH are two-electron processes), \(F\) is the Faraday constant (96485 C mol−1), and \(Q\) is the total charge passed during the electrolysis of CO2. The current density for a given product is calculated by multiplying the total current density with FE of the product. The Cu2(L)-t was determined by measuring CV curves at different scan rates. The potential range for the CV tests was from −0.55 V to −0.50 V vs. Ag/AgCl. The EIS spectra were recorded at open circuit potential with an amplitude of 5.0 mV (10−2 to 105 Hz), and the value for \(R_{\text{ct}}\) obtained by fitting the EIS spectra using the Zview software (Version 3.1, Scribner Associates, USA)34,35.

**EPR analysis.** EPR spectra were recorded at room temperature, in continuous-wave mode, on Bruker EMX spectrometers (X-band, ca. 9.85 GHz; Q-band, ca. 34 GHz), at mw power of ~0.63 mW and modulation amplitude 10 G; spectra reported herein were typically obtained over an average of 20 scans, and a Bruker strong pitch (q = 2.0028) reference was used as a calibrator. Theoretical modelling of the spectra was performed with the EasySpin toolbox within Matlab39. The intensity of the EPR signal of different samples was normalised to the quantity of sample.

Calculations of the spectra with EasySpin36 using the iterative spin Hamiltonian in the Eq. (2)35,36:

\[
H = gBB^* + D(S^z - 2/3) + E(S^x + S^y) \quad (2)
\]

where \(D\) and \(E\) are the axial and rhombic zero-field splitting parameters, respectively, to give \(g_{xx} = g_{yy} = 2.06–2.07\), \(g_{zz} = 2.31–2.36\), \(D = 0.33–0.35\) cm−1 and \(E = 0\) (Fig. 2g and Supplementary Figs. 5 and 6 and Supplementary Table 2). These parameters are in excellent agreement with data for binuclear copper acetate35. EPR spectra of our other Cu(II) systems with a [Cu2(OOCR)4] paddle wheel structure36,51 are in very good agreement with data for binuclear copper acetate35. The relative content of monomer [uncoupled Cu(II) centre as defect] and binuclear [within [Cu2(OOCR)4] paddlewheel] centres was calculated from the second integrals from simulated EPR Q-band spectra. At Q-band, the entire S = 1 spectrum of the binuclear unit is observed hence defining its relative weighting better than that at X-band where the zero-field splitting is comparable to the microwave frequency. The ratio of monomer to binuclear species is obtained from the weighting of the two spin systems (Supplementary Fig. 7; this is illustrated by fitting the second integrals of the simulated components in Supplementary Fig. 8)35,36. The final monomer to binuclear ratio was obtained by weighting the EPR data by the Boltzmann population of the S = 1 state of the binuclear species based upon the Bleaney-Bower equation [Eq. (3)]56,36.

\[
\frac{nT}{nS} = \frac{3exp(-\Delta E_{\text{CF}}/RT)}{1 + 3exp(-\Delta E_{\text{CF}}/RT)} \quad (3)
\]

where \(\Delta E_{\text{CF}}\) is the singlet (S)-triplet (T) energy gap (ca. 300 cm−1), \(nT\) and \(nS\) are the populations at temperature of \(T\) and \(R\) is the gas constant.

The relative content of free, uncoupled Cu(II) centres as a function of electrolysis time was measured from the second integral of the signal for this species using X-band EPR spectroscopy. EPR spectra of electrodes were collected every 15 min during electrolysis at −1.8 V vs. Ag/AgCl. The obtained EPR spectra were transformed to a second integral value, and all data normalised to the surface area of the electrodes.

**DFT calculations.** Calculations were based on spin-polarised DFT using projector augmented wave (PAW) methods, as implemented in the Vienna ab initio simulation package (VASP)35. A plane-wave basis set with a kinetic-energy cut-off of 400 eV was used to expand the wave function of valence electrons. The generalised gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was used for describing the exchange-correlation interactions35. Vacuum space of 20 Å was set to prevent the interaction between two molecules. The Brillouin-zone integration was sampled by single-point basis set.

The structure relaxations were performed by computing the Hellmann–Feynman forces within the total energy and force convergences of 10−4 eV and 0.01 eV Å, respectively. Based on computational hydrogen molecule (CHE) model34, and the Gibbs free energy of an adsorbed intermediate from reduced CO2 was calculated using \(\Delta G = \Delta E + \Delta E_{\text{EPD}} + T\Delta S_{\text{ads}}\) where \(\Delta E\), \(\Delta E_{\text{EPD}}\) and \(T\Delta S_{\text{ads}}\) are the electronic adsorption energy, charge density and entropy corrections, respectively. The corrections of zero point energy and entropy corrections in Supplementary Table 4. The Poisson–Boltzmann implicit solvation model, was used to describe the effect of solvation32, and DFT calculations were implemented via VASP with a
dielectric constant of $\varepsilon = 37.5$. The solvation energy was directly contained in the total energy.

**Data availability**

All relevant data are available from the authors, and/or are included with the manuscript. All other data supporting the findings of this study are available within the Article and its Supplementary Information, or from the corresponding author upon reasonable request.

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X.K., L.Li, X.H., J.L. and L.Liu: syntheses and characterisations of MOF samples and catalysts. L.Li, A.S., F.T. and E.J.L.M.: collection and analysis of EPR data. X.K. and R.H.: DFT calculation. R.H., S.Y. and M.S.: overall design and direction of the project. X.K., B.H., S.Y. and M.S.: preparation of the manuscript with help from all authors.

Competing interests

The authors declare no competing interests.

Additional information

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