

Domino electroreduction of CO₂ to methanol on a molecular catalyst

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Electrochemical carbon dioxide (CO₂) reduction can in principle convert carbon emissions to fuels and value-added chemicals, such as hydrocarbons and alcohols, using renewable energy, but the efficiency of the process is limited by its sluggish kinetics^{1,2}. Molecular catalysts have well defined active sites and accurately tailorable structures that allow mechanism-based performance optimization, and transition-metal complexes have been extensively explored in this regard. However, these catalysts generally lack the ability to promote CO₂ reduction beyond the two-electron process to generate more valuable products^{1,3}. Here we show that when immobilized on carbon nanotubes, cobalt phthalocyanine—used previously to reduce CO₂ to primarily CO—catalyses the six-electron reduction of CO₂ to methanol with appreciable activity and selectivity. We find that the conversion, which proceeds via a distinct domino process with CO as an intermediate, generates methanol with a Faradaic efficiency higher than 40 per cent and a partial current density greater than 10 milliamperes per square centimetre at −0.94 volts with respect to the reversible hydrogen electrode in a near-neutral electrolyte. The catalytic activity decreases over time owing to the detrimental reduction of the phthalocyanine ligand, which can be suppressed by appending electron-donating amino substituents to the phthalocyanine ring. The improved molecule-based electrocatalyst converts CO₂ to methanol with considerable activity and selectivity and with stable performance over at least 12 hours.

On the basis of the Sabatier principle, the binding energy of CO, $E_{\text{B}}(\text{CO})$, is often used as a descriptor to understand the different catalytic selectivities of metal surfaces in the electroreduction of CO₂^{4–7}. On metals that bind CO too weakly (for example, Ag and Au, which have $E_{\text{B}}(\text{CO})$ values that are relatively positive), CO easily desorbs upon formation and is thus the major product of CO₂ reduction (Fig. 1a). For metals that bind CO too strongly (for example, Ni and Pt), a very negative $E_{\text{B}}(\text{CO})$ makes further reduction of adsorbed CO (CO*) only possible at very negative potentials, where the competing H₂ evolution reaction dominates. As a result, H₂ is the major reduction product on these metal surfaces⁴ (Fig. 1a). To enable deeper CO₂ reduction to hydrocarbons or oxygenates, a moderate $E_{\text{B}}(\text{CO})$ is required, so that CO* stays bound to the catalytic site and its reduction can proceed with a reasonably low energy barrier⁶. In fact, Cu is currently the only metal that can catalyse CO₂ electroreduction to more deeply reduced products with appreciable selectivity^{6,7}. In search for an electrocatalyst other than metals that can reduce CO₂ by more than two electrons, we consider that there may be a suitable candidate molecule that (1) is capable of catalysing CO₂-to-CO conversion and (2) has a moderate binding strength for CO. Recent computational studies of M–N₄ molecular structures (a metal centre coordinated with four nitrogen atoms), which are active in catalysing the CO₂ electroreduction to CO^{8–11}, have shown that $E_{\text{B}}(\text{CO})$ on these sites can vary substantially with the identity of the metal ion^{12–14}.

For example, CO binding is strong on Fe–N₄, moderate on Co–N₄ and weak on Ni–N₄, spanning an energy range of about 1.2 eV (Fig. 1a, Extended Data Table 1). Interestingly, $E_{\text{B}}(\text{CO})$ for Co–N₄ is similar to that of Cu. Although such $E_{\text{B}}(\text{CO})$ values may not be directly put into the context of the scaling relations and reactivity trends established for metal surfaces, because the catalysts are molecular in nature and their $E_{\text{B}}(\text{CO})$ is influenced to some extent by the peripheral structure and oxidation state of the metal centre^{15,16}, this $E_{\text{B}}(\text{CO})$ trend still shows a dependence on the identity of the metal centre and is well correlated with recently published experimental results^{17,18}. This points to the exciting possibility that CO₂ may be deeply reduced beyond CO on M–N₄-based electrocatalyst materials.

To explore this possibility, we chose iron phthalocyanine (FePc), cobalt phthalocyanine (CoPc) and nickel phthalocyanine (NiPc) molecules supported on carbon nanotubes (CNTs) as catalysts for the initial screening. Our noncovalent anchoring strategy⁸ enables catalytic molecules to be highly dispersed on the surface of a highly conductive network and renders heterogenized molecular catalysts that may be able to overcome some of the limitations of homogeneous electrocatalysts: in homogeneous electrochemical CO₂ reduction, a catalyst molecule diffuses to the electrode to accept one or two electrons and then diffuses away from the surface to react with CO₂ in the solution^{1,3}, which makes it difficult to transfer multiple electrons to a CO₂ molecule to form deeply reduced products.

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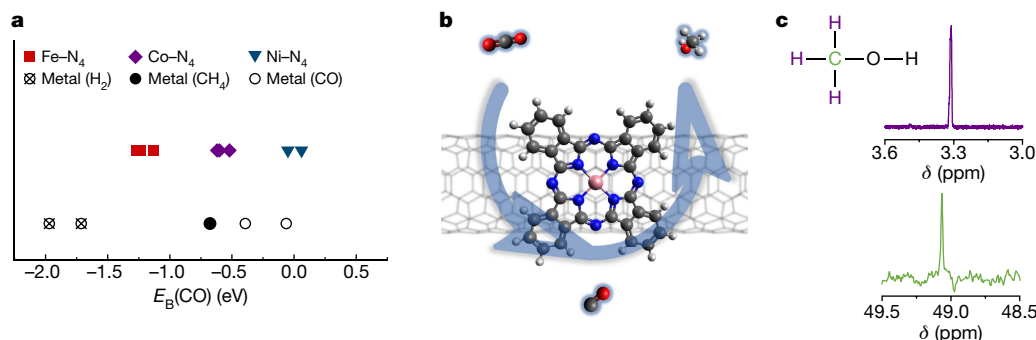


Fig. 1 | A domino electrocatalytic process of CO₂-to-MeOH conversion on CoPc/CNT, discovered through a catalyst search guided by the Sabatier principle. **a**, Computed CO binding energies on metal surfaces and on M-N₄ moieties (data from refs. ^{6,7,13,14,24}). Metals are classified according to their major product (denoted inside parentheses) for the electroreduction of CO₂.

b, Domino process of CO₂-to-MeOH conversion via CO, catalysed by CoPc supported on carbon nanotubes (CNT). Colour code: hydrogen, light grey; carbon, dark grey; nitrogen, blue; oxygen, red; cobalt, pink. **c**, Zoomed-in regions of sample ¹H NMR and ¹³C NMR spectra of the electrolyte that confirm MeOH production.

Measured in 0.1 M KHCO₃ aqueous electrolyte, all three MPC/CNT (M = Fe, Co or Ni) catalysts show a decent selectivity for CO generation in the medium overpotential range: CoPc/CNT and NiPc/CNT both achieve a maximum Faradaic efficiency (FE) of about 95% for CO production, whereas FePc/CNT exhibits a lower CO selectivity of about 80% (Extended Data Fig. 1, Fig. 2a). At more negative electrode potentials, the CO production process on both NiPc/CNT and FePc/CNT is taken over by H₂ evolution. No other gaseous products are detected (Extended Data Fig. 2a, b). Interestingly, CoPc/CNT behaves differently: it generates methanol (MeOH; Fig. 2a), which is confirmed to be the only liquid-phase product by both ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy (Fig. 1c, Extended Data Fig. 2c, d). MeOH production on CoPc/CNT onsets at about -0.82 V with respect to the reversible hydrogen electrode (RHE) and reaches its highest FE of 44% (see Extended Data Fig. 2e for the detailed quantification procedure) and largest partial current density of 10.6 mA cm⁻² (corresponding to a turnover frequency of 1.05 s⁻¹ if all the supported CoPc molecules are counted as active sites) at -0.94 V (Fig. 2a, b), as measured with a 1-h electrolysis. To the best of our knowledge, this is the first example of a transition-metal-based molecular electrocatalyst producing MeOH from CO₂ with an appreciable yield (Extended Data Table 2). A control experiment using N₂ as the feed gas produces only H₂ and a trace amount of CO (Extended Data Fig. 3), thereby confirming that the MeOH indeed comes from reduction of CO₂.

One key feature of our catalyst is the molecular-level dispersion of CoPc on CNTs, as evidenced by scanning transmission electron microscopy (STEM) images recorded with a high-angle annular dark-field (HAADF) detector and the corresponding elemental mapping obtained with energy dispersive spectroscopy (EDS). N was found to be uniformly distributed on the CNTs (Fig. 2d, e). The atomic-resolution Z-contrast image reveals the distribution of Co atoms on a CNT and directly confirms the molecular-level dispersion of CoPc (Fig. 2f). Such a high level of dispersion was found to be necessary for the selective CO₂-to-MeOH conversion. When CoPc without CNT supports was directly deposited from its solution onto a carbon fibre paper, the resulting CoPc electrode showed a much lower current density than CoPc/CNT at each measured potential and produced H₂ and CO as the only products (Extended Data Fig. 4a, b). When CoPc was physically mixed with CNTs, both the selectivity and the activity of MeOH production were considerably lower than in the case of the CoPc/CNT hybrid (Extended Data Fig. 4d), even though the content of CoPc in the mixture was ten times higher than that in the hybrid. The MeOH production rate can be inversely correlated with the charge-transfer resistance derived from electrochemical impedance spectroscopy measurements under the working conditions (Extended Data Fig. 4c). A physical mixture of CoPc and another carbon support (Vulcan XC72 or Ketjenblack) also shows much lower FE_{MeOH} and partial current density compared to

the CoPc/CNT hybrid catalyst at -0.94 V versus RHE (Extended Data Fig. 4d). Taken together, these results support that effectively dispersing CoPc molecules on highly conductive supports can expose their catalytic reactivity and enable more active and selective CO₂-to-MeOH conversion than CoPc aggregates.

Because MeOH emerges as a product at the expense of CO as the electrode potential is polarized more negatively than -0.77 V, we hypothesize that CO is an intermediate in the CO₂-to-MeOH process. To test this hypothesis, we carried out electroreduction of CO with the CoPc/CNT electrode in the same electrolyte. MeOH could be detected at potentials more negative than -0.77 V, and FE reached 28% at -0.83 V (Fig. 2c). The activity for the electroreduction of CO therefore indicates that the catalytic CO₂ reduction to MeOH on CoPc/CNT follows a domino process in which CO₂ first undergoes a two-electron reduction to CO, which continues to be reduced to MeOH through a four-electron–four-proton process (Fig. 1b). The fact that the onset potential for MeOH formation in the CO electroreduction roughly coincides with that in the CO₂ electroreduction implies that these two reactions share the same potential-limiting step. It is worth emphasizing that CoPc is currently the only catalyst other than Cu that can electrochemically reduce CO with an appreciable current density¹⁹.

The long-term electrolysis results, however, show that the electrocatalytic CO₂ reduction to MeOH on CoPc/CNT is unstable. The average FE_{MeOH} is 44% for the first 1 h and then drops to 26% over the next 4 h. After 5 h of electrolysis, FE_{MeOH} further decreases to a negligible 0.6% (Fig. 3a) while the FE for H₂ evolution increases to -80% (Extended Data Fig. 5a). This deactivation phenomenon may be another contributing factor to the scarcity of reports on CO₂-to-MeOH conversion catalysed by CoPc. Scanning electron microscopy (SEM) images of the electrode after a 12-h electrolysis excluded reductive demetallation of CoPc and formation of Co or CoO_x nanoparticles (Extended Data Fig. 5b, c). The deactivation of the catalyst was then attributed to changes within the molecular structure. Some related porphyrin complexes have been shown to undergo hydrogenation on their pyrrole rings under a protic and reductive environment and manifest a substantial change in their ultraviolet–visible (UV-Vis) absorption profile^{20,21}. We therefore speculate that the deactivation is caused by undesirable reduction of the Pc ligand. To study the degraded catalyst, the CoPc/CNT physical-mixture electrode was used because it has a CoPc content ten times higher than that of the hybrid. After a 2-h electrolysis at -0.94 V, the used CoPc molecules were dissolved by deoxygenated N,N'-dimethylformamide (DMF) and then subjected to spectroscopic characterization. Compared to the UV-Vis spectrum of a fresh CoPc/DMF solution, the used CoPc solution exhibits three new absorption peaks at 420, 460 and 700 nm (Fig. 3b). These new peaks do not pertain to the free-base phthalocyanine (H₂Pc; Extended Data Fig. 6), corroborating the absence

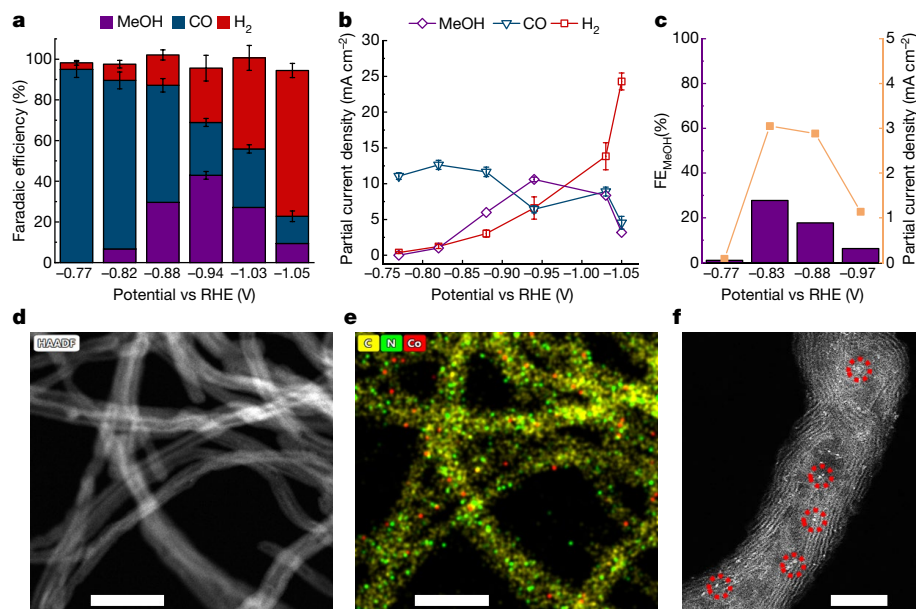


Fig. 2 | Catalytic performance of CoPc molecules supported on CNTs for CO₂ and CO reduction. **a**, Product selectivity (FE; **a**) and partial current densities (**b**) for different products versus electrode potential. Error bars represent one standard deviation from three measurements. **c**, Potential-dependent FE and partial current density for MeOH production from electroreduction of CO

catalysed by CoPc/CNT. **d**, **e**, STEM-HAADF image of CoPc/CNT (**d**) and corresponding overlaid EDS maps of Co, C and N (**e**). **f**, Atomic-resolution STEM-HAADF image of CoPc/CNT. The circled bright spots correspond to the Co centre of individual CoPc molecules. Scale bars, 50 nm (**d**, **e**) and 5 nm (**f**).

of demetallation of the complex. The same absorption peaks appear in the spectrum of CoPc molecules reacted with NaBH₄ in deoxygenated DMF. These emerging absorption features have been shown to be characteristic of singly reduced CoPc, and continuous reduction can eventually lead to hydrogenation of the Pc macrocycle²². These results support our hypothesis that the deteriorating selectivity of the CoPc/CNT catalyst for MeOH production is caused by the detrimental reduction of the ligand.

One major advantage of our heterogenized molecular catalyst system is that its structure can be tailored on the molecular level to improve its catalytic properties. To tackle the reduction-induced deactivation of CoPc/CNT, we introduced four amino groups (-NH₂) to the β positions of the Pc ligand (Fig. 4a). The electron-donating substituents successfully lowered the reduction potential of CoPc (Extended Data Fig. 7). We note that CoPc-NH₂ has a larger conjugation system than aniline, which means that the pK_a of its conjugated acid is probably lower than that of aniline (4.6). Therefore, protonation of the appended amino groups in the CO₂-saturated electrolyte (pH = 6.8) is expected to be minimal. The CoPc-NH₂/CNT catalyst exhibits a similar potential-dependent

behaviour to that of CoPc/CNT. At -1.00 V versus RHE, the conversion of CO₂ to MeOH proceeds with an FE of 32% and an average partial current density of 10.2 mA cm⁻² (Fig. 4b, c), as measured with a 1-h electrolysis. Remarkably, CoPc-NH₂/CNT shows much improved catalytic durability than its unsubstituted counterpart. The measured FE_{MeOH} for a 12-h electrolysis is 28%, comparable to the FE_{MeOH} of the 1-h electrolysis, and the total current density stays between 30 and 33 mA cm⁻² through the entire period (Fig. 4d). After a 2-h electrolysis at -1.00 V, CoPc-NH₂ molecules generate the same UV-Vis spectrum as that of pristine CoPc-NH₂ (Fig. 4e), suggesting that the catalytic structure for MeOH production remains intact under the reaction conditions. The increased durability provided by amino substitution shows the power of ligand engineering in improving the catalytic performance of our heterogenized molecular systems. Notably, the CoPc-NH₂/CNT hybrid material shows a higher selectivity (maximum FE_{MeOH} = 41%) for the electroreduction of CO than for that of CO₂ (Extended Data Figs. 2f, 8).

Several factors contribute to the efficiency of our CoPc/CNT in catalysing CO₂ electroreduction to MeOH. First, CoPc is dispersed as individual molecules on highly conductive CNTs, which is critical to fast and continuous electron delivery to the active site for multi-electron reduction of CO₂. By contrast, a simple mixture of CoPc and CNTs inevitably contains CoPc aggregates, which make it much less efficient for catalysis (Extended Data Fig. 4d). Second, the type of carbon support is important (Extended Data Fig. 4d) because the CoPc molecules are anchored on and accept electrons from the support. Third, CoPc undergoes deactivation at the reductive conditions (Fig. 3a, Extended Data Fig. 5a); it is therefore important to stabilize the active site—for instance, by modifying the Pc ligand—to ensure efficacy during longer-term electrolysis. These factors are additive and together could explain why CO₂-to-MeOH conversion was either not seen at all in other studies using CoPc and its derivatives^{23,24} or was reported to occur with very low activity and selectivity (partial current density <0.05 mA cm⁻², FE <5%)^{25,26}. Lastly, we emphasize that its molecular structure is critical and contains the active site even if support effects are important: other cobalt macrocycle complexes, such as cobalt chlorin and cobalt porphyrin^{27,28}, have not been reported to show MeOH selectivity, even when they are composited with CNTs.

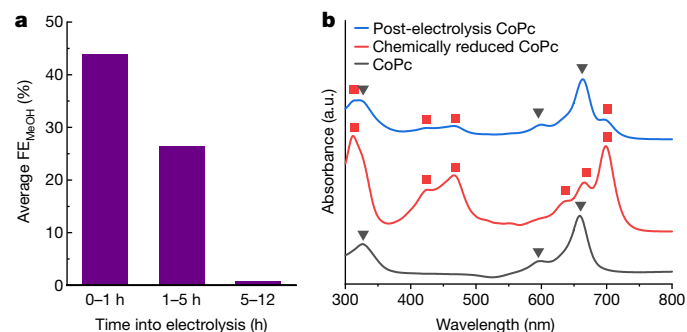


Fig. 3 | Deactivation of CoPc/CNT in long-term electrolysis. **a**, Average FE_{MeOH} of CoPc/CNT for different time intervals in a 12-h electrolysis. **b**, UV-Vis absorption profiles of CoPc, post-electrolysis CoPc and chemically reduced CoPc. Absorption peaks associated with CoPc and reduced CoPc are indicated by grey triangles and red squares, respectively. (a.u., arbitrary units.)

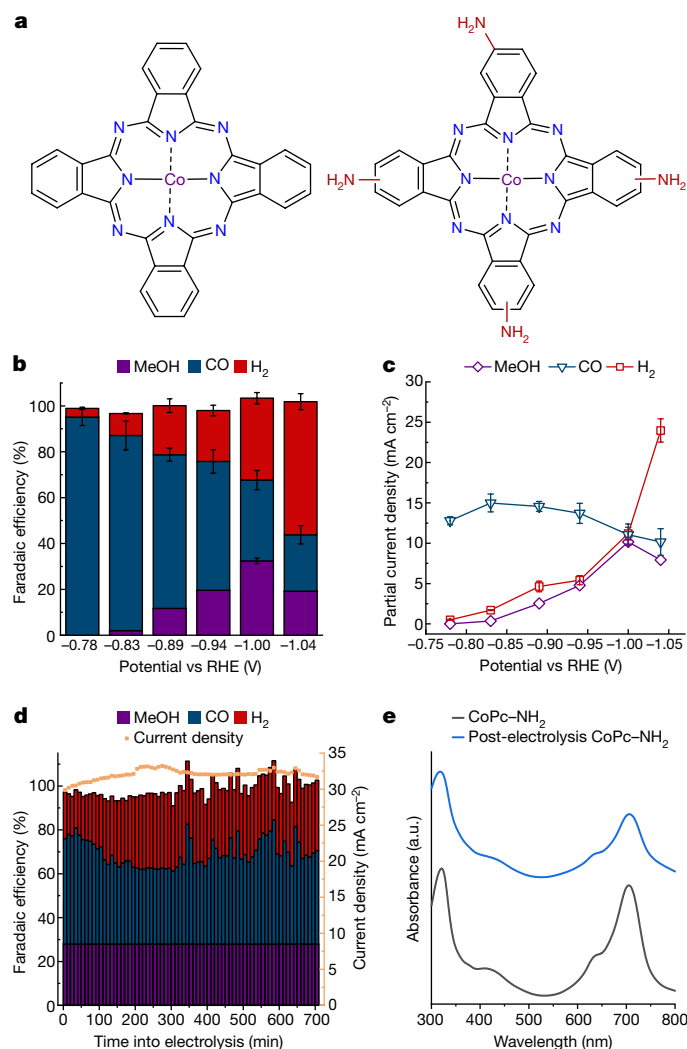


Fig. 4 | Electrochemical performance of CoPc-NH₂/CNT for CO₂ reduction to methanol. **a**, Structural comparison between CoPc and CoPc-NH₂. **b**, **c**, Potential-dependent product selectivity (FE; **b**) and partial current density (**c**) for CO₂ electroreduction catalysed by CoPc-NH₂/CNT. Error bars represent one standard deviation from three measurements. **d**, Product selectivity (FE) and total current density for a 12-h electrolysis of CO₂ reduction catalysed by CoPc-NH₂/CNT at -1.00 V versus RHE; the FE_{MeOH} value measured after the electrolysis is shown in striped violet. **e**, Comparison between UV-Vis absorption profiles of CoPc-NH₂ and post-electrolysis CoPc-NH₂.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41586-019-1760-8>.

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Methods

Materials

All chemicals were purchased and used as received without further purification unless otherwise stated. CO₂ (99.99%), CO (99.3%) and N₂ (99.999%) were purchased from Airgas. KHCO₃ (99.7%) was purchased from Sigma Aldrich. Multi-wall CNTs were purchased from C-Nano (product number FT9100). CoPc, NiPc and FePc were purchased from Alfa Aesar. Deionized water used in all experiments was purified through a Milli-Q reference water-purification system to reach a resistivity of 18.2 MΩ cm (at 25 °C).

Characterization

SEM images were taken using a Hitachi SU8230 field-emission SEM microscope. UV-Vis absorption measurements were carried out with a Shimadzu UV-2600 UV-Vis spectrophotometer. STEM imaging was performed using a double Cs-corrected FEI Themis G2 microscope at 60 kV with a Super-X EDS detector. Inductively coupled plasma mass spectrometry (ICP-MS) was performed with an Agilent Technologies 7700 series instrument. ¹H and ¹³C NMR spectra were recorded using an Agilent 400-MHz NMR instrument.

Synthesis of CoPc-NH₂

The synthesis procedure was adapted from previous publications^{29,30}. 4-Nitrophthalonitrile (10 mmol, 1.73 g), CoCl₂·6H₂O (2.5 mmol, 0.60 g), urea (80 mmol, 4.80 g) and a catalytic amount of (NH₄)₆Mo₇O₂₄·4H₂O were first well mixed by grinding in an agate mortar. Then, the mixture was reacted in the solid state at 170 °C for 5 h under Ar atmosphere. The resulting product was stirred at 90 °C for 1 h in HCl (1 M, 200 ml). The solid was filtered and then stirred at 90 °C for 1 h in NaOH (1 M, 200 ml). The crude product was filtered, washed with water, dried in vacuum and then purified by Soxhlet extraction with methanol. The resulting solid was then dissolved in DMF and filtered. The DMF solution was evaporated under vacuum to afford the CoPc-NO₂ compound as a dark-green solid (0.83 g, 44%). The synthesized CoPc-NO₂ (0.75 g, 1 mmol), Na₂S·9H₂O (4.8 g, 20 mmol), 1 ml of deionized water and 25 ml of DMF were mixed in a three-necked round-bottom flask, and the mixture was stirred at 60 °C overnight under Ar atmosphere. After that, the solution was evaporated under vacuum, and the obtained solid was washed with water and then boiled in 100 ml of 5 wt% aqueous NaOH solution. Subsequently, the precipitate was filtered and washed with water. The resulting solid was poured into 250 ml of water while stirring, and 1 M HCl was added to adjust the pH to 5. The mixture was filtered to remove the undissolved side products. The pH of the filtered solution was then adjusted to 8 by adding 1 M KOH, and the resulting solution was boiled. The precipitate was collected by filtration, washed with water and methanol and then dried in vacuum to afford the target CoPc-NH₂ compound as a dark-green solid (0.52 g, 82%). High-resolution mass spectrometry gave a mass-to-charge value of 631.12435 (Extended Data Fig. 9a). UV-Vis spectroscopy²⁹ gave wavelengths of maximum absorbance λ_{max} (in 15 M H₂SO₄) of 210 nm, 299 nm, 380 nm and 739 nm (Extended Data Fig. 9b).

Preparation of MPc/CNT hybrid materials

As-received CNTs were first calcined at 500 °C in air for 5 h. After cooling to room temperature, the CNTs were transferred into a 5 wt% HCl aqueous solution and sonicated for 30 min. The purified CNTs were collected by filtration and washed extensively with deionized water. 30 mg of the purified CNTs was subsequently dispersed in 30 ml of DMF using sonication (XM-300UHP, 600 W/10 L, 40 KHz). Then, an appropriate amount of MPc (1.5 mg CoPc, 1.2 mg CoPc-NH₂, 1.6 mg FePc or 1.1 mg NiPc) dissolved in DMF was added to the CNT suspension. The mixture was sonicated for 30 min to obtain a well mixed suspension, which was further stirred at room temperature for 20 h. Subsequently, the mixture was centrifuged and the precipitate was washed with DMF and ethanol. Finally, the precipitate was lyophilized to yield the final product. The

weight percentage of metal in the hybrid material was ~0.27% for all MPc/CNT materials, as confirmed by ICP-MS measurements.

Electrode preparation

Catalyst ink was prepared by dispersing 2 mg of hybrid materials (CoPc/CNT, CoPc-NH₂/CNT, FePc/CNT or NiPc/CNT) in 2 ml of ethanol with 6 μl of 5 wt% Nafion solution, followed by sonication for 1 h. 200 μl of the ink was then drop-casted onto a 3 × 0.5 cm² polytetrafluoroethylene-treated carbon fibre paper (Toray O30, Fuel Cell Store) to cover an area of 0.5 × 1 cm² (catalyst mass loading, 0.4 mg cm⁻²). The prepared electrodes were fully dried using an infrared lamp. The physical-mixture electrodes used for electrochemical and UV-Vis studies were prepared in the same way, except that 1 mg of CoPc (or CoPc-NH₂) was mixed with 1 mg of carbon material (purified CNTs, Vulcan XC72 or Ketjenblack) before the addition of ethanol and Nafion and that the total mass loading was 0.4 mg cm⁻² on a 1 × 1 cm² area. The free CoPc electrode was prepared by drop-casting a 0.05 mg ml⁻¹ CoPc/DMF solution onto the carbon fibre paper to cover an area of 1 × 0.5 cm² on a heating plate held at 130 °C to reach a final mass loading of 0.1 mg cm⁻². For cyclic-voltammetry measurements, 7.5 μl of CoPc/CNT or CoPc-NH₂/CNT ink was deposited on a well polished glassy carbon electrode (electrode diameter, 4 mm; mass loading, 0.06 mg cm⁻²).

Electrolyte purification

500 ml of a 0.1 M KHCO₃ aqueous solution was purified by a two-step electrolysis using two 10 × 5 cm² high-purity Ti foil (99.99%) electrodes in a two-electrode setup. The first electrolytic step was conducted at 2.5 V until the current decreased to 150 μA. The second step was performed at a constant current of 150 μA for at least 20 h. During the electrolysis, the solution was magnetically stirred. The Ti electrodes were removed from the solution before the electrolysis was terminated to avoid re-dissolution of electrodeposited impurities into the solution.

Electrochemical measurements

Electrochemical experiments were performed using a Bio-Logic VMP3 Multi Potentiostat and a custom-designed gas-tight two-compartment electrochemical cell. The graphite rod counter-electrodes were purchased from Sigma Aldrich and the Ag/AgCl reference electrodes (0.199 V versus SHE) were purchased from Pine Research Instrumentation. The cathode and anode compartments were separated by an anion-exchange membrane (Selemon DSV). Each compartment contained 12 ml of electrolyte and ~18 ml of gas headspace. For all experiments, the pre-purified 0.1 M KHCO₃ was used as the electrolyte. Before each measurement, the electrolyte was pre-saturated with CO₂, N₂ or CO by bubbling the gas for at least 15 min. Gas was continuously bubbled into the electrolyte during electrolysis (or flowed into the headspace during cyclic-voltammetry measurements) at a flow rate of 20 standard cubic centimetres per minute. Before the start of each electrolysis, the Ohmic drop between the working electrode and the reference electrode was determined using potentiostatic electrochemical impedance spectroscopy at -0.5 V versus Ag/AgCl between 200 kHz and 1 Hz with an amplitude of 10 mV. The resistance was then determined by the intersection of the curve with the real axis of the Nyquist plot. Correction for internal resistance was performed after electrolysis for all measurements except for the electrodes used for the UV-Vis studies, where the internal resistance drop was compensated during the electrochemical measurement. Current densities were calculated on the basis of the catalyst-covered geometric area of the working electrode. All potentials (V) were converted to the RHE scale using the following formula: $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + (0.199 \text{ V}) + (0.0592 \text{ V}) \times \text{pH}$.

Product quantification

The gas products of electrocatalysis were analysed using a gas chromatography system (SRI Multiple Gas Analyzer #5) equipped with a flame ionization detector and a thermal conductivity detector. High-purity

N₂ was used as the carrier gas. The peak areas of the products (H₂ and CO) were converted to gas volumes using calibration curves that were obtained using a standard gas diluted with CO₂ to different concentrations. The liquid products were quantified after electrocatalysis using ¹H NMR spectroscopy with solvent (H₂O) suppression. 400 µl of electrolyte was mixed with 100 µl of a solution of 10 mM dimethyl sulfoxide (DMSO) and 50 mM phenol in D₂O as internal standards for the ¹H NMR analysis. The concentration of MeOH was calculated using the ratio of the area of the MeOH peak (at a chemical shift of 3.31 ppm) to that of the DMSO internal standard (see Extended Data Fig. 2e, f for details). ¹³C NMR spectroscopy was performed for the samples to further verify the presence of MeOH. The FEs for the gas-phase products were average values from three measurements in a single electrolysis experiment. The FE_{MeOH} values at the optimal potentials (shown with error bars in Figs. 2 and 4) were averages from three different 1-h electrolyses, whereas the MeOH FEs at all other potentials were measured once.

UV-Vis characterization of CoPc, CoPc–NH₂ and chemically reduced CoPc

UV-Vis absorption spectra of pristine CoPc and CoPc–NH₂ were taken using their 0.1 mg ml^{−1} DMF solutions. A used CoPc/CNT or CoPc–NH₂/CNT electrode was taken out of the electrolyte solution after the electrolysis and quickly dipped into a vial containing 3 ml of deoxygenated DMF. The vial was immediately sealed, gently sonicated for 10 s and then kept still for another 60 min, after which the supernatant was used for UV-Vis measurement. The chemical reduction of CoPc was done by

mixing equal volumes of 0.1 mg ml^{−1} CoPc dissolved in deoxygenated DMF and 1 mg ml^{−1} NaBH₄ in deoxygenated DMF.

Data availability

Data supporting the findings of this study are available from the corresponding authors upon reasonable request. Source data for Figs. 2, 4 are provided with the paper.

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Author contributions Y.W. and H.W. conceived the project and designed the experiments. Z.J. and Y.L. synthesized the catalyst materials and performed the structural characterizations. Y.W. and X.L. performed the electrocatalytic studies. Y.W., Y.L. and H.W. analysed the data. Y.W. and H.W. wrote the manuscript. Y.L. and H.W. supervised the project.

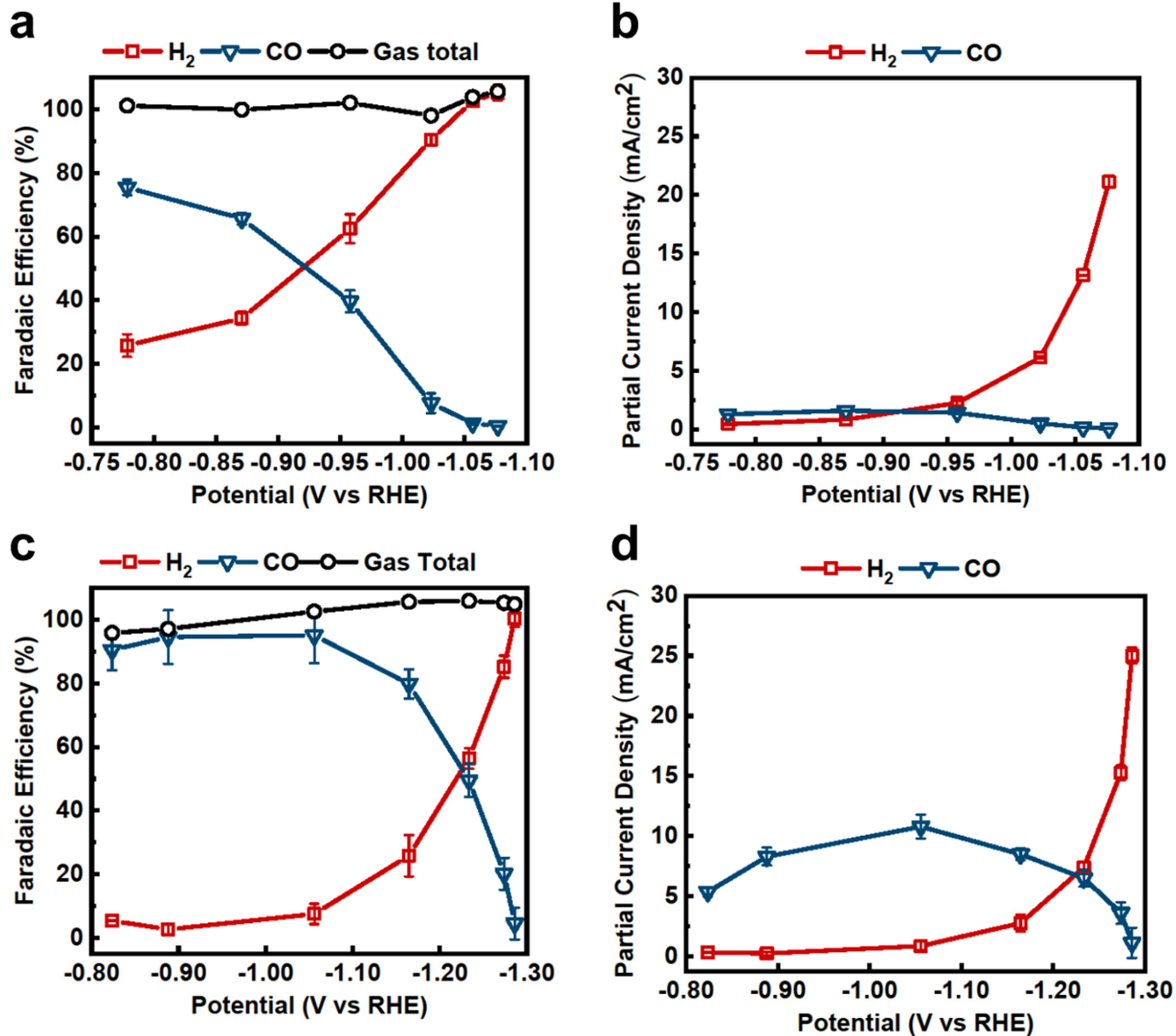
Competing interests The authors declare no competing interests.

Additional information

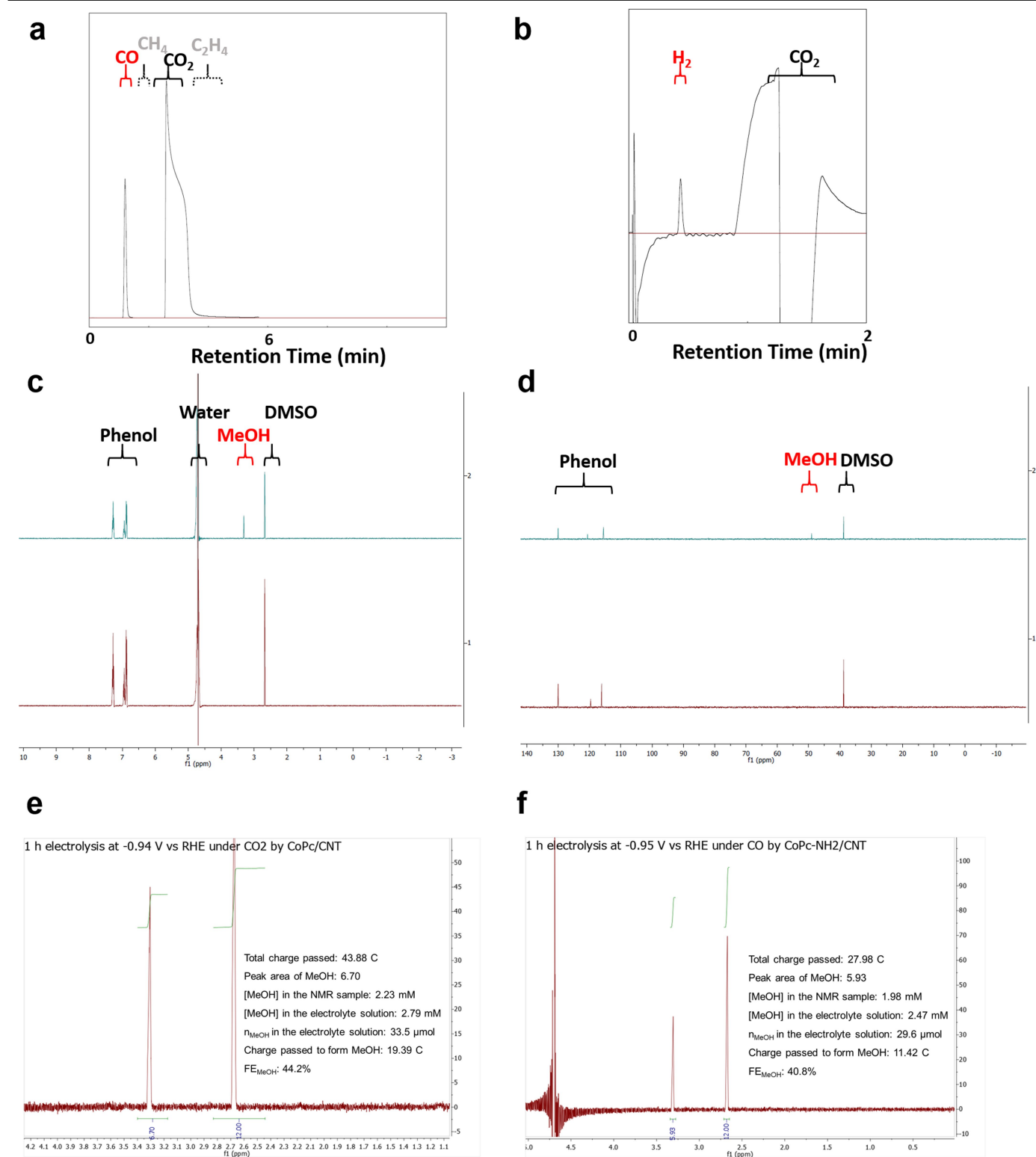
Correspondence and requests for materials should be addressed to H.W. or Y.L.

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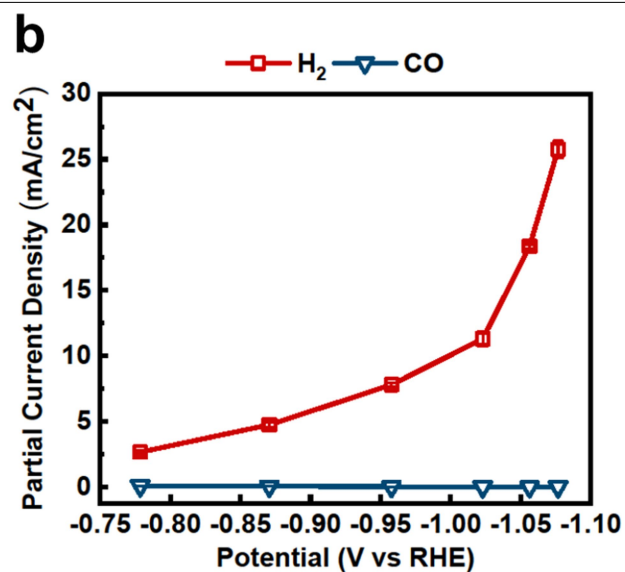
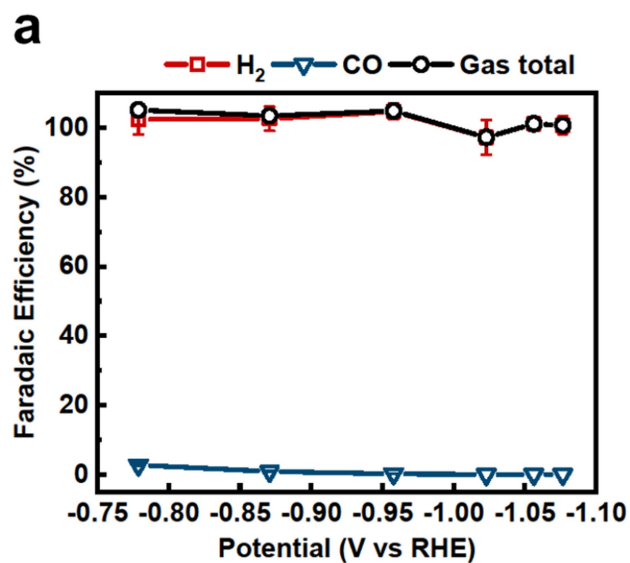
Extended Data Fig. 1 | Catalytic properties of FePc/CNT and NiPc/CNT. **a–d**, Potential-dependent catalytic performance of CO₂ electroreduction by FePc/CNT (**a, b**) and NiPc/CNT (**c, d**).



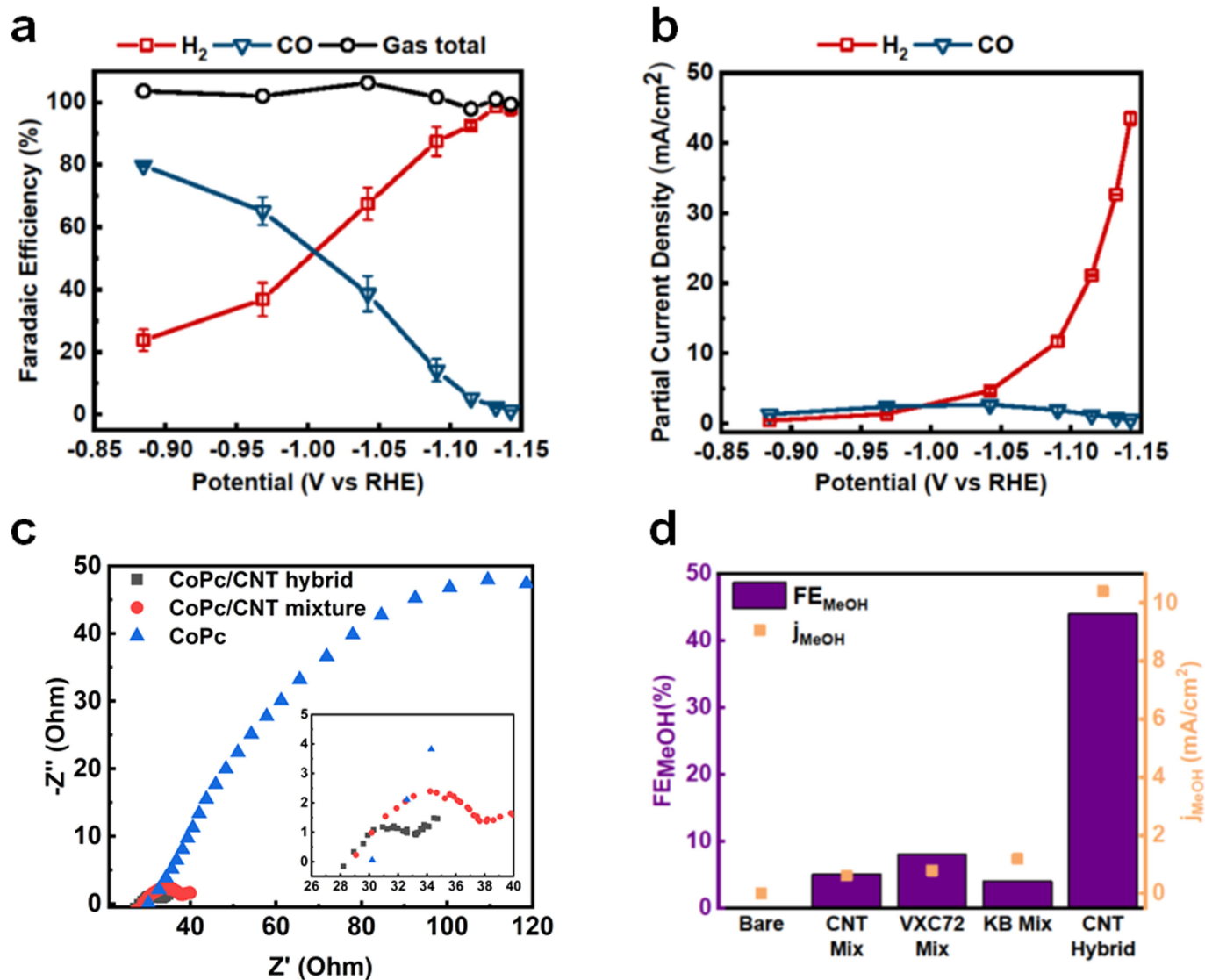
Extended Data Fig. 2 | Product identification and quantification.

a, b, Typical gas chromatography diagrams from the flame ionization detector (a) and the thermal conductivity detector (b), showing the presence of CO and H_2 (marked in red) and the absence of other common gas products (marked in grey). **c, d**, Typical ^1H NMR (c) and ^{13}C NMR (d) spectra of a liquid sample after CO_2 electroreduction electrolysis (green traces) versus a blank 0.1 M KHCO_3

solution (red traces). **e, f**, Representative ^1H NMR spectra of liquid samples after 1 h of CO_2 reduction electrolysis catalysed by CoPc/CNT at -0.94 V versus RHE (e) and 1 h of CO reduction electrolysis catalysed by $\text{CoPc-NH}_2/\text{CNT}$ at -0.95 V versus RHE (f). The detailed information used to determine the FE of MeOH production is given in the diagrams.

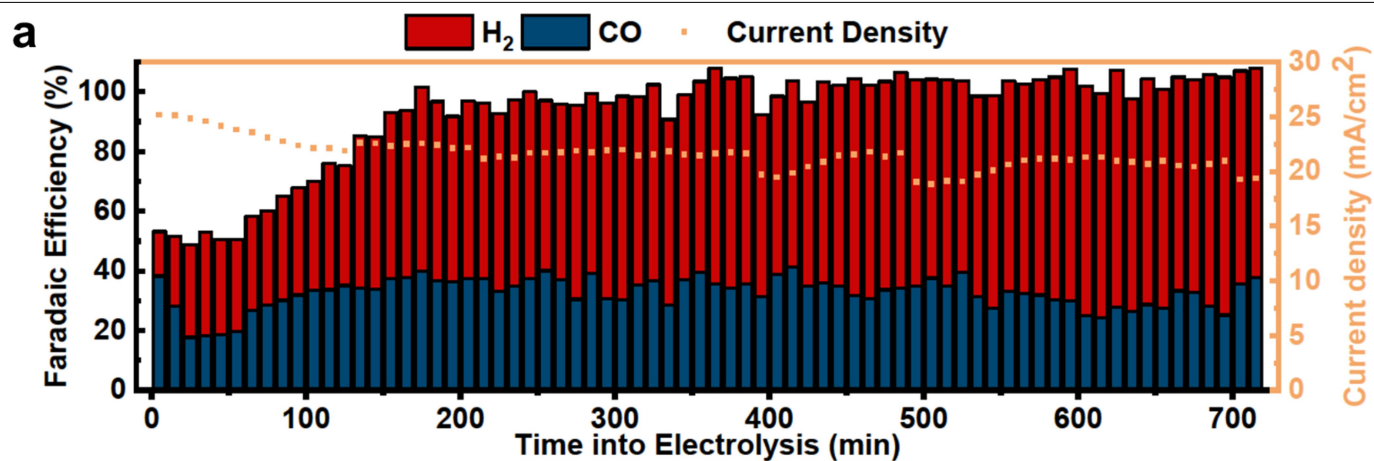


Extended Data Fig. 3 | Catalytic performance of CoPc/CNT under N_2 . a, b, Potential-dependent product selectivity (a) and partial current density (b) for CO_2 electroreduction catalysed by CoPc/CNT under N_2 .

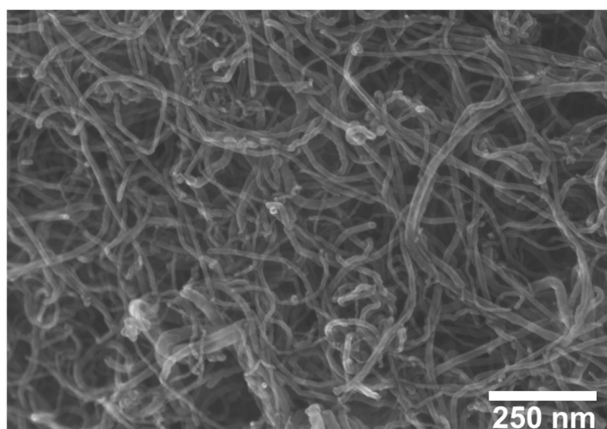


Extended Data Fig. 4 | Effects of carbon support on CO_2 -to-MeOH conversion. **a, b**, Potential-dependent product selectivity (**a**) and partial current density (**b**) for the electroreduction of CO_2 by bare CoPc aggregates on carbon paper. **c**, Nyquist plots of bare CoPc, a physical mixture of CoPc and CNTs and the CoPc/CNT hybrid, measured at -0.94 V versus RHE in a 0.1 M aqueous $KHCO_3$ solution saturated with CO_2 with a scanning frequency range from 200 kHz to 100 Hz and an a.c. amplitude of 5 mV. Z' and Z'' refer to the real

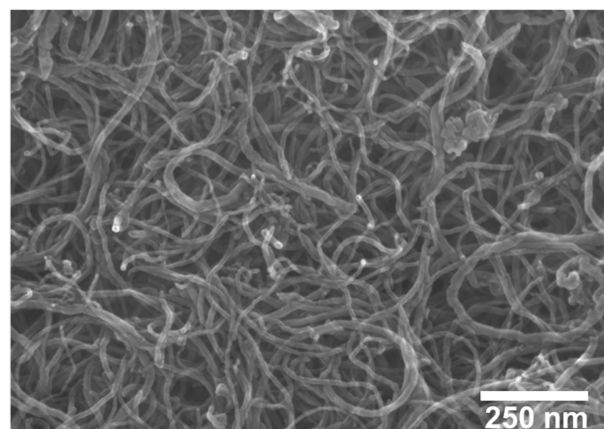
and imaginary parts of impedance, respectively. The inset shows the enlarged area where the traces for the CoPc/CNT hybrid and the mixture of CoPc and CNTs are clearer. **d**, Selectivity (FE_{MeOH}) and partial current density (j_{MeOH}) for CO_2 reduction to MeOH catalysed by bare CoPc ('Bare'), the CoPc/CNT physical mixture ('CNT Mix'), the CoPc/Vulcan XC72 mixture ('VXC72 Mix'), the CoPc/Ketjenblack mixture ('KB Mix') and the CoPc/CNT hybrid ('CNT Hybrid') at -0.94 V versus RHE.



b

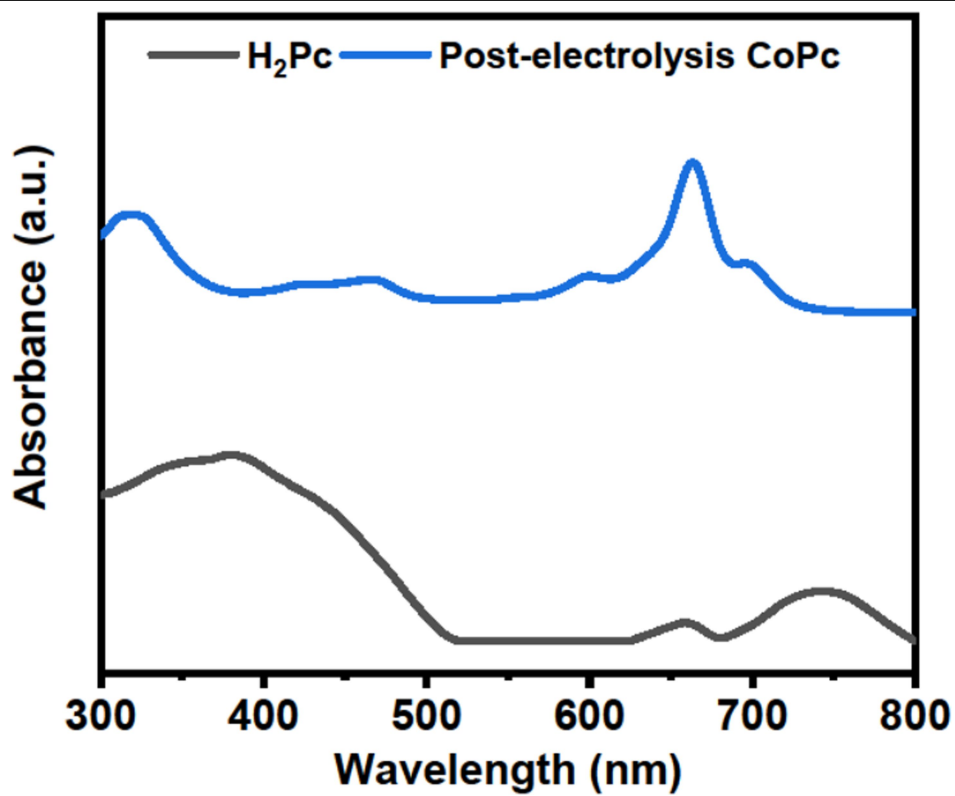


c

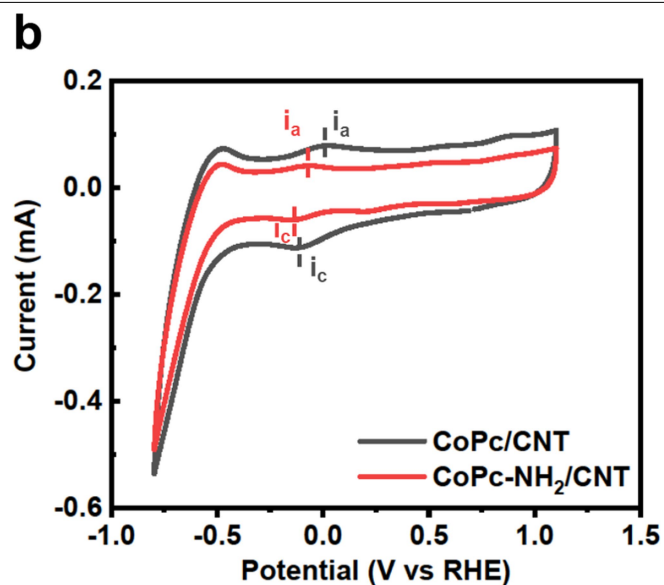
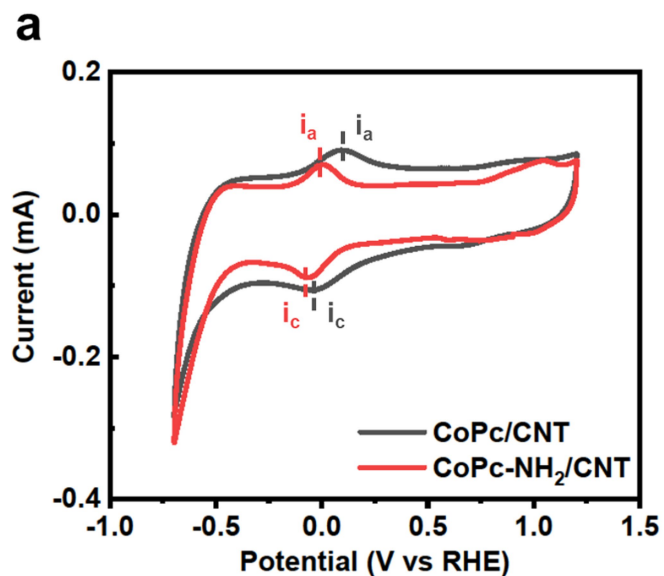


Extended Data Fig. 5 | Long-term electrocatalytic performance of CoPc/CNT. **a**, Gas product selectivity and total current density in a 12-h electrolysis of CO₂ reduction catalysed by CoPc/CNT at -0.94 V versus RHE. **b, c**, SEM images

of an as-deposited CoPc/CNT electrode before (**b**) and after (**c**) catalysing CO₂ reduction electrolysis at -0.94 V versus RHE for 12 h.

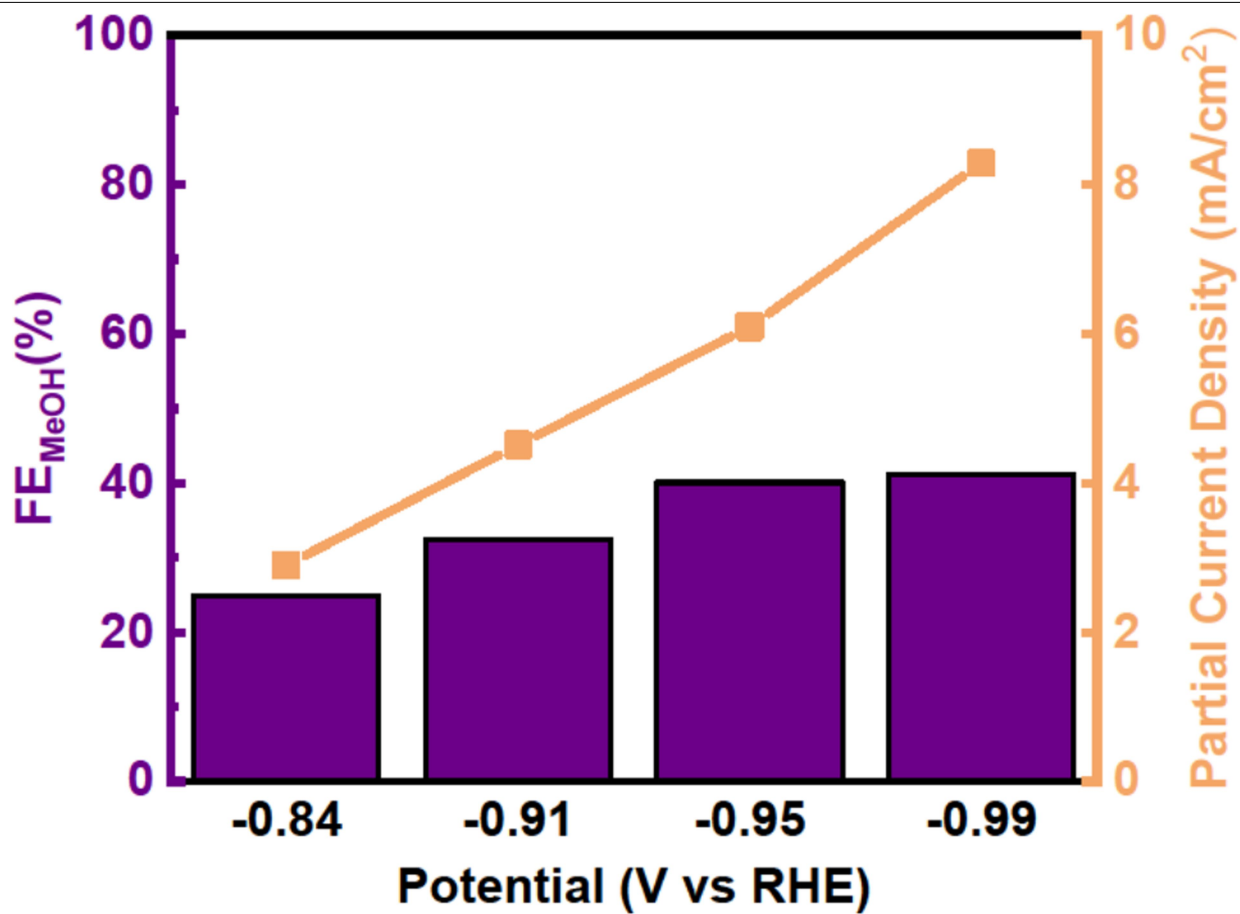


Extended Data Fig. 6 | UV-Vis spectra of post-electrolysis CoPc and free-base phthalocyanine (H₂Pc) in DMF.

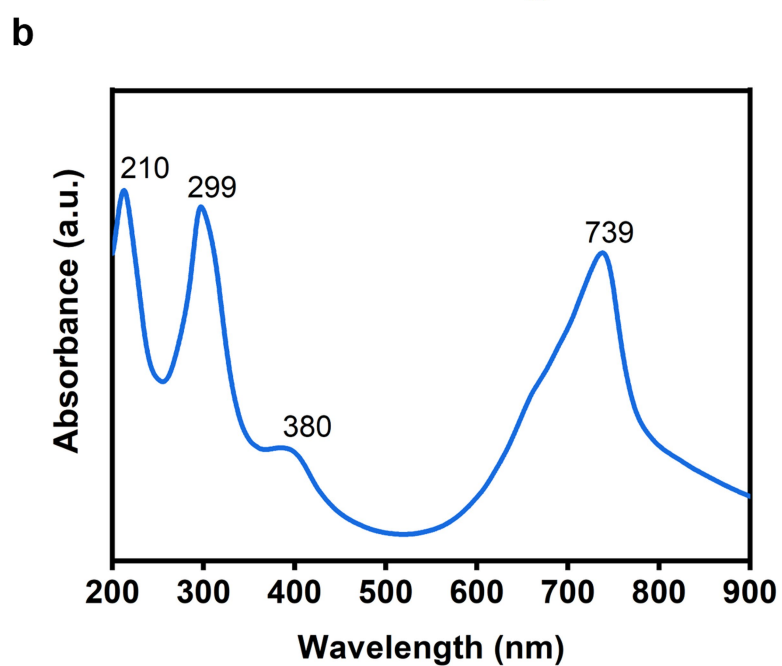
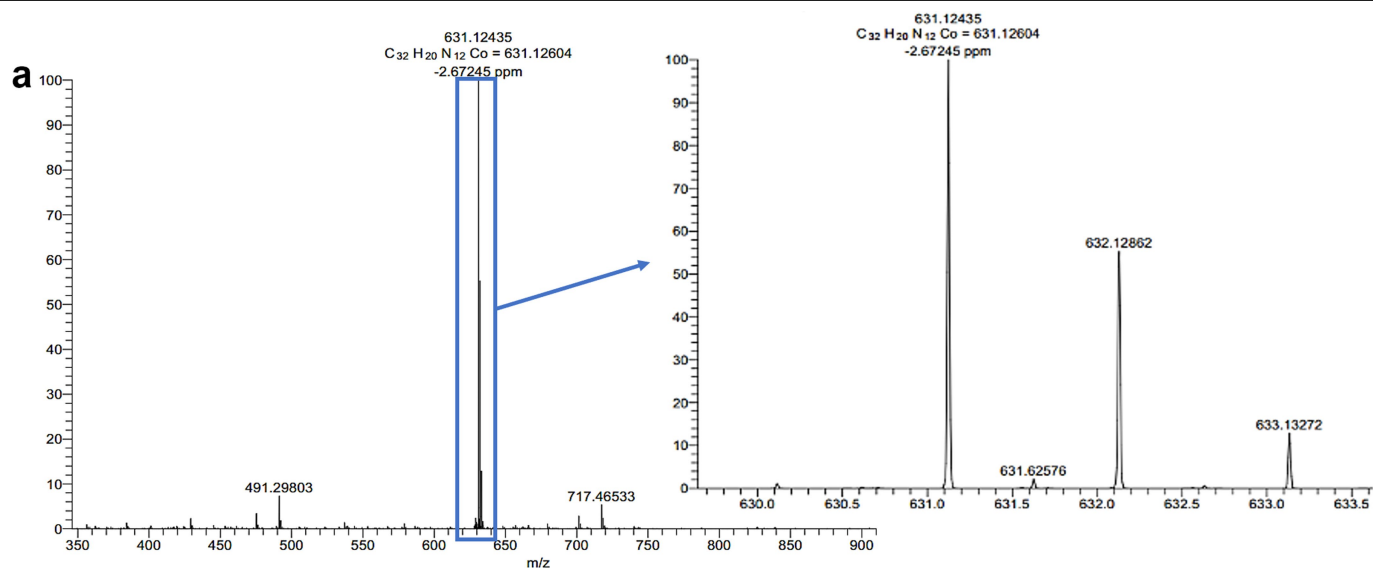


Extended Data Fig. 7 | Cyclic voltammograms of CoPc/CNT and CoPc-NH₂/CNT. a, b, The curves were recorded at a scan rate of 400 mV s⁻¹ in a 0.1 M aqueous KHCO₃ solution under N₂ (a) and CO₂ (b). The most prominent

cathodic (i_c) and anodic (i_a) features of the molecules are labelled. The redox potential of CoPc-NH₂/CNT is more negative than that of CoPc/CNT.

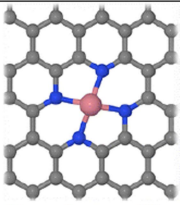
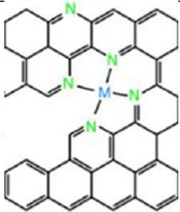
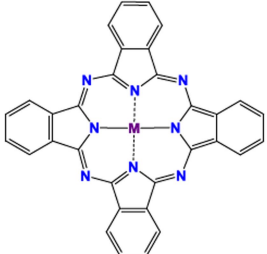


Extended Data Fig. 8 | Catalytic performance of CoPc-NH₂/CNT for electroreduction of CO to MeOH.



Extended Data Fig. 9 | Spectroscopic characterization of CoPc-NH₂. **a**, High-resolution mass spectrometry results for CoPc-NH₂. Calculated for CoC₃₂H₂₀N₁₂: 631.12604; found: 631.12435. **b**, UV-Vis spectrum of CoPc-NH₂ in 15 M H₂SO₄. λ_{max} = 210 nm, 299 nm, 380 nm and 739 nm.

Extended Data Table 1 | Electronic binding energy of CO to the metal centre of M-N₄ motifs (where M = Ni, Co or Fe)

Metal center	Oxidation state	Peripheral structure	$E_B(\text{CO})$ (eV)	Span of $E_B(\text{CO})$ from Fe to Ni	Reference
Fe	+2	 Graphene-like porphyrin	-1.13	1.19	J. Phys. Chem. C 2013, 117, 9187
Co	+2		-0.52		
Ni	+2		0.06		
Fe	+2	 Nitrogen-doped carbon scaffold	-1.27	1.23	Nat. Commun. 2017, 8, 944
Co	+2		-0.60		
Ni	+2		-0.04		
Fe	+2	 Phthalocyanine ligand	-1.24	1.19	Angew. Chem. Int. Ed. 2018, 57, 16339
Co	+2		-0.62		
Ni	+2		-0.05		

The $E_B(\text{CO})$ values were obtained by converting the corresponding DFT-computed free energies of CO binding ($G_B(\text{CO})$) reported in the literature^{13,14,24}. The conversion was done by subtracting a 0.5-eV energy term^{6,7}.

Extended Data Table 2 | Performance comparison between our catalyst system and previously reported transition-metal complex electrocatalysts for CO₂-to-MeOH conversion

Catalytic system	j _{MeOH} (mA/cm ²)	Optimal FE _{MeOH} (%)	Electrolyte solution	Potential	TOF	TON ^c	Comments	Reference
CoPc/CNT	10.6 (1 h)	44 (1 h)	0.1 M KHCO ₃	-0.94 V vs RHE	1.05	~3800		This work
CoPc-NH ₂ /CNT	10.2 (1 h)	32 (1 h)	0.1 M KHCO ₃	-1.00 V vs RHE	1.01	~3600		This work
CoPc-NH ₂ /CNT	8.9 (12 h)	28 (12 h)	0.1 M KHCO ₃	-1.00 V vs RHE	0.88	~38000		This work
Mixture of CoPc and CNT	0.03 (3 h)	0.3 (3 h)	0.5 M KHCO ₃	-0.88 V	~0.03 ^b	44		10.1002/anie.201909257
CoPc	~0.05	<5	pH = 3 acid solution	-1.2 V ~ -1.4 V vs SCE ^d	~0.005 ^b	N/A		J. Electrochem. Soc. 1984, 131, 1511-1514
[(phen) ₂ Ru(dppz)] ²⁺	~0.06 (6 h) ^a	~100 (6 h)	DMF with 0.30 mM [(phen) ₂ Ru(dppz)] ²⁺ , 0.1 M TBAPF ₆ and 1 M H ₂ O	-0.6 V vs Ag/AgCl	~4 × 10 ⁻⁴ ^b	0.92	Based on pyridine	Inorg. Chem. 2014, 53, 6544
Pt/ Polyaniline/ Prussian blue/ 2-hydroxy-1-nitronaphthalene-3,6-disulphonatocobalt(II)	~0.0006 (24 h) ^a	~0.2 (24 h)	0.5 M KCl with HCl (pH = 2.0)	-0.6 V vs SCE ^d	~3 × 10 ⁻⁶ ^b	~0.3		J. Chem. Soc., Chem. Commun., 1993, 0, 20
Pt/ metal tetraphenylporphyrin/ aquapentacyanoferrate(II) / methanol	~0.03 (5 h) ^a	15.1 (5 h)	0.1 M KCl with 15 mM 2-hydroxy-1-nitronaphthalene-3,6-disulphonatocobalt(II), 20 mM MeOH	-0.5 V vs SCE ^d	~0.001 ^b	~20	A much larger amount of MeOH added prior to electrolysis than that produced in the reaction	Journal of Molecular Catalysis, 47 (1988) 51 - 51
Pt (stainless steel)/ Quinone derivatives/ aquapentacyanoferrate(II)/ Methanol	~0.01 (2 h) ^a	70.2 (2 h)	0.1 M KCl with 10 mM aquapentacyanoferrate(II) and 15 mM MeOH	-0.34 V ~ -0.39 V vs SCE ^d	Unable to estimate	N/A		Journal of Molecular Catalysis, 41 (1987) 303 - 311
Pt/ Everitt's salt/ aquapentacyanoferrate(II)/ methanol	~0.02 (10 h) ^a	102 (10 h)	0.1 M KCl with 15 mM aquapentacyanoferrate(II) and 20 mM MeOH	-0.6 V vs SCE ^d	~1 × 10 ⁻⁴ ^b	~4		J. Electroanal. Chem., 220 (1987) 333-337
Pt/ Everitt's salt/ 1-nitroso-2-naphthol-3,6-disulfonic acid metal complex/ methanol	~0.02 (5 h) ^a	83.4 (5 h)	0.1 M KCl with 15 mM 2-naphthol-3,6-disulfonic acid Fe(II) and 20 mM MeOH	-0.6 V vs SCE ^d	~1 × 10 ⁻⁴ ^b	~2		J. Electroanal. Chem., 206 (1986) 209-216
Pt/ 1,2-dihydroxybenzene-3,5-disulphonatoferrate(III) / Ethanol	~0.04 (6 h) ^a	Not available	0.1 M KCl with 20 mM ethanol, 1 mM Fe ³⁺ and 2 mM citron	-1.0 V vs SCE ^d	Unable to estimate	N/A		Journal of Molecular Catalysis, 34 (1986) 67 - 72

^aCalculated using the reported selectivity, total charge passed (or current), duration and geometric area of the working electrode.

^bCalculated using the partial current density and catalyst loading (or amount of catalyst in the solution).

^cTurnover number (TON) in the reported catalysis, calculated on the basis of the turnover frequency (TOF) and measurement duration.

^dSaturated calomel electrode.