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# Control of evolution of porous copper-based metal–organic materials for electroreduction of CO<sub>2</sub> to multi-carbon products†

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Electrochemical reduction of CO<sub>2</sub> to multi-carbon (C<sub>2+</sub>) products is an important but challenging task. Here, we report the control of structural evolution of two porous Cu(II)-based materials (HKUST-1 and CuMOP, MOP = metal–organic polyhedra) under electrochemical conditions by adsorption of 7,7,8,8-tetracyanoquinodimethane (TCNQ) as an additional electron acceptor. The formation of Cu(I) and Cu(0) species during the structural evolution has been confirmed and analysed by powder X-ray diffraction, and by EPR, Raman, XPS, IR and UV-vis spectroscopies. An electrode decorated with evolved TCNQ@CuMOP shows a selectivity of 68% for C<sub>2+</sub> products with a total current density of 268 mA cm<sup>-2</sup> and faradaic efficiency of 37% for electrochemical reduction of CO<sub>2</sub> in 1 M aqueous KOH electrolyte at –2.27 V vs. RHE (reversible hydrogen electrode). *In situ* electron paramagnetic resonance spectroscopy reveals the presence of carbon-centred radicals as key reaction intermediates. This study demonstrates the positive impact of additional electron acceptors on the structural evolution of Cu(II)-based porous materials to promote the electroreduction of CO<sub>2</sub> to C<sub>2+</sub> products.

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## Introduction

Electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) using renewable electricity enables the sustainable synthesis of feedstock chemicals.<sup>1,2</sup> Compared with C<sub>1</sub> products (*e.g.*, CO, HCOOH), multi-carbon (C<sub>2+</sub>) products (*e.g.*, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH) are desirable because of their higher volumetric energy density and commercial value,<sup>3,4</sup> but this is a highly challenging target. Copper-based electrocatalysts can show excellent activity to convert CO<sub>2</sub> to C<sub>2+</sub> products *via* •C-based radicals which can couple to afford C<sub>2+</sub> products.<sup>5–8</sup> Porous metal–organic framework (MOF) materials have emerged as efficient catalysts for CO<sub>2</sub>RR owing to the presence of atomically dispersed metal sites, and their porous structure allows adsorptive binding of CO<sub>2</sub>.<sup>9–12</sup> Several

Cu(II)-based MOFs have been tested for electrochemical CO<sub>2</sub>RR, but they generally suffer from limited electrical conductivity and hydrolytic stability.<sup>13–15</sup> Structural evolution of Cu(II)-MOFs to active catalysts such as Cu, Cu<sub>2</sub>O, Cu@Cu<sub>x</sub>O under electrochemical conditions often results in improved conductivity and stability, and has attracted much interest.<sup>16–22</sup> In particular, evolved Cu(I) species can facilitate the coupling of •CO radical intermediates and thus promote the production of C<sub>2+</sub> products.<sup>22,23</sup> The control of the structural evolution of Cu(II)-MOFs is key to produce C<sub>2+</sub> products in CO<sub>2</sub>RR.

7,7,8,8-Tetracyanoquinodimethane (TCNQ) is an excellent electron acceptor and can be reduced readily to TCNQ<sup>•-</sup> and TCNQ<sup>2-</sup>.<sup>24,25</sup> It has been reported that adsorbed TCNQ molecules can replace the axially coordinated water molecules of the [Cu<sup>II</sup><sub>2</sub>(OOCR)<sub>4</sub>] paddlewheel in HKUST-1 to form a network of inter-connected [Cu<sup>II</sup><sub>2</sub>(OOCR)<sub>4</sub>] paddlewheels, resulting in a significant increase in electrical conductivity.<sup>26</sup> Here, we report the investigation of the impact of TCNQ on the structural evolution of Cu(II)-based porous materials during the electrochemical CO<sub>2</sub>RR process. In addition to HKUST-1, another highly porous Cu(II)-based metal–organic polyhedra material, CuMOP,<sup>27</sup> was chosen for this study because it exhibits mesopores formed from the packing of coordination cages and these might promote the capture of bulky TCNQ molecules within the structure. TCNQ was introduced as the guest species to tune the

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Fig. 2 Characterisation of adsorption of TCNQ into HKUST-1 and CuMOP. Views of (a) PXRD patterns; (b) IR spectra; (c) Raman spectra; (d) UV-vis spectra; (e) Q-band EPR spectra (feature A is due to monomeric Cu(II) monomer centers, features B are due to the intra-binuclear interaction within  $[\text{Cu}_2(\text{OOCR})_4]$  paddlewheels, and feature C is due to the inter-binuclear spin-exchange between  $[\text{Cu}_2(\text{OOCR})_4]$  paddlewheel centers; HKUST-1 and TCNQ@HKUST-1 at 100 K, CuMOP and TCNQ@CuMOP at 293 K. (f)  $\text{N}_2$  adsorption/desorption isotherms at 77 K. (HKUST-1: orange, TCNQ@HKUST-1: red, CuMOP: green, TCNQ@CuMOP: blue, TCNQ: black).

adsorption of TCNQ. Continuous-wave (CW) Q-band EPR spectroscopy was used to characterize TCNQ@HKUST-1 and TCNQ@CuMOP. In a  $[\text{Cu}^{\text{II}}_2(\text{OOCR})_4]$  paddlewheel, the two neighbouring Cu(II) ( $s = 1/2$ ) ions couple antiferromagnetically to give an  $S = 0$  ground state (EPR silent) and an excited  $S = 1$  state. To observe the EPR signal for the  $[\text{Cu}^{\text{II}}_2(\text{OOCR})_4]$  paddlewheel, variable temperature CW Q-band EPR experiments were

conducted (Fig. S2, ESI<sup>†</sup>). The EPR signal of excited  $S = 1$  triplet state of  $[\text{Cu}^{\text{II}}_2(\text{OOCR})_4]$  paddlewheels in HKUST-1 and CuMOP can be seen at 100 K and 293 K, respectively.<sup>30</sup> Therefore, the Q-band EPR spectra of TCNQ@HKUST-1 at 100 K and of TCNQ@CuMOP at 293 K were chosen to compare with the un-modified parent materials. The EPR spectrum of HKUST-1 contains three types of EPR signals:<sup>30,31</sup> (i) a sharp





signal due to monomeric,  $s = 1/2$  Cu(II) sites (feature A), which in  $[\text{Cu}^{\text{II}}_2(\text{OOCR})_4]$  paddlewheel-MOFs has been attributed to extra-framework uncoupled Cu(II) centres formed during the synthesis; (ii) excited  $S = 1$  intra-binuclear triplet state of the  $[\text{Cu}^{\text{II}}_2(\text{OOCR})_4]$  paddlewheel (feature B), spread over a wide

field range due to a zero-field splitting  $|D|$  of *ca.*  $0.325 \text{ cm}^{-1}$  (Table S1 and Fig. S3, ESI<sup>†</sup>), and (iii) a broad isotropic feature (feature C) arising from inter-dimer exchange ( $J' \approx 1 \text{ cm}^{-1}$ ; Table S1, ESI<sup>†</sup>) between neighbouring  $S = 1$  populated  $[\text{Cu}^{\text{II}}_2(\text{OOCR})_4]$  paddlewheels (Fig. 2e). Only features A and C

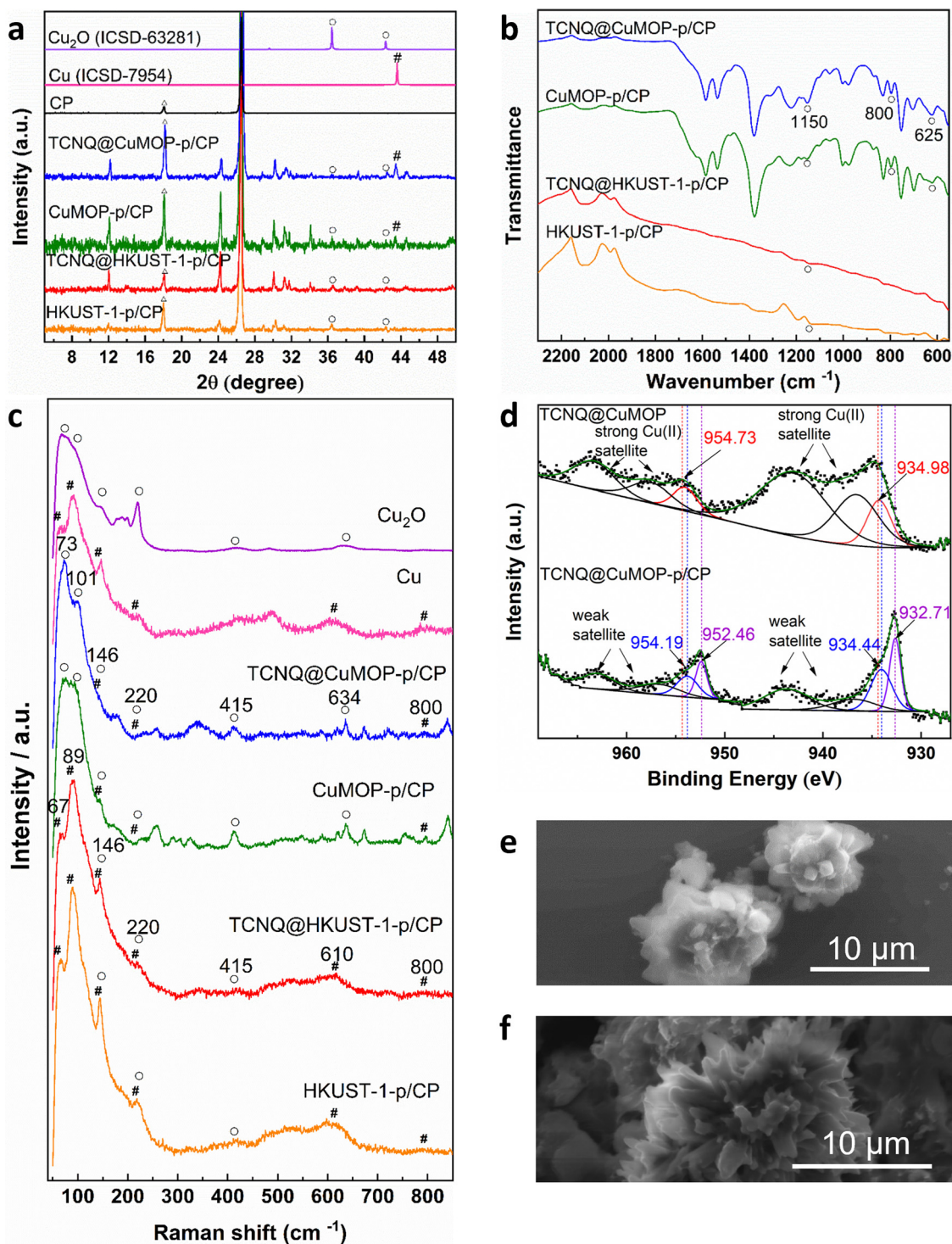


Fig. 3 Spectroscopic and morphological characterization of the evolution of working electrodes. (a) PXRD patterns; (b) IR spectra; (c) Raman spectra; (d) Cu 2p region XPS spectra; SEM images of (e) TCNQ@CuMOP and (f) TCNQ@CuMOP-p/CP ( $\Delta$  refers to CP,  $\circ$  refers to  $\text{Cu}_2\text{O}$ , # refers to Cu).



are observed in TCNQ@HKUST-1 with the latter being dominant (Fig. S3b (ESI<sup>†</sup>) and Fig. 2e). This suggests that adsorbed TCNQ molecules enhance the inter-paddlewheel exchange in TCNQ@HKUST-1. In contrast, the EPR signal of  $S = 1$  [ $\text{Cu}^{\text{II}}_2(\text{OOCR})_4$ ] paddlewheels is observed in both CuMOP and TCNQ@CuMOP (Fig. 2e and Fig. S3, ESI<sup>†</sup>), indicating that the adsorption of TCNQ in the voids has little impact on the [ $\text{Cu}^{\text{II}}_2(\text{OOCR})_4$ ] paddlewheel signature. This is consistent with the smaller shifts in the IR spectrum for TCNQ for this material compared with HKUST-1.  $\text{N}_2$  adsorption isotherms at 77 K show a reduction in the surface area of HKUST-1 (from 1449 to 1083  $\text{m}^2 \text{g}^{-1}$ ) and CuMOP (from 664 to 342  $\text{m}^2 \text{g}^{-1}$ ) upon adsorption of TCNQ (Fig. 2f) reflecting occupation of pores by TCNQ.

### Characterisation of structural evolution

Aqueous solutions of  $\text{KHCO}_3$  and  $\text{KOH}$  (0.1–1.0 M) were tested as electrolyte in a flow cell to optimise the electrochemical  $\text{CO}_2\text{RR}$  at  $-2.27 \text{ V}$  vs. RHE. A solution of 1 M  $\text{KOH}$  showed the best performance and was therefore used in this study (Fig. S4–S8, ESI<sup>†</sup>). The PXRD patterns confirm the structural evolution of both pristine and TCNQ-loaded materials upon applying a potential of  $-2.27 \text{ V}$  vs. RHE for 10 min, and the resulting working electrodes are denoted as HKUST-1-p/CP (CP = carbon paper), TCNQ@HKUST-1-p/CP, CuMOP-p/CP and TCNQ@CuMOP-p/CP. Taking TCNQ@CuMOP-p/CP as an example, the PXRD pattern confirms the formation of  $\text{Cu}_2\text{O}$  and  $\text{Cu}$  (Fig. 3a and Fig. S9). IR, Raman and XPS spectra also confirm the

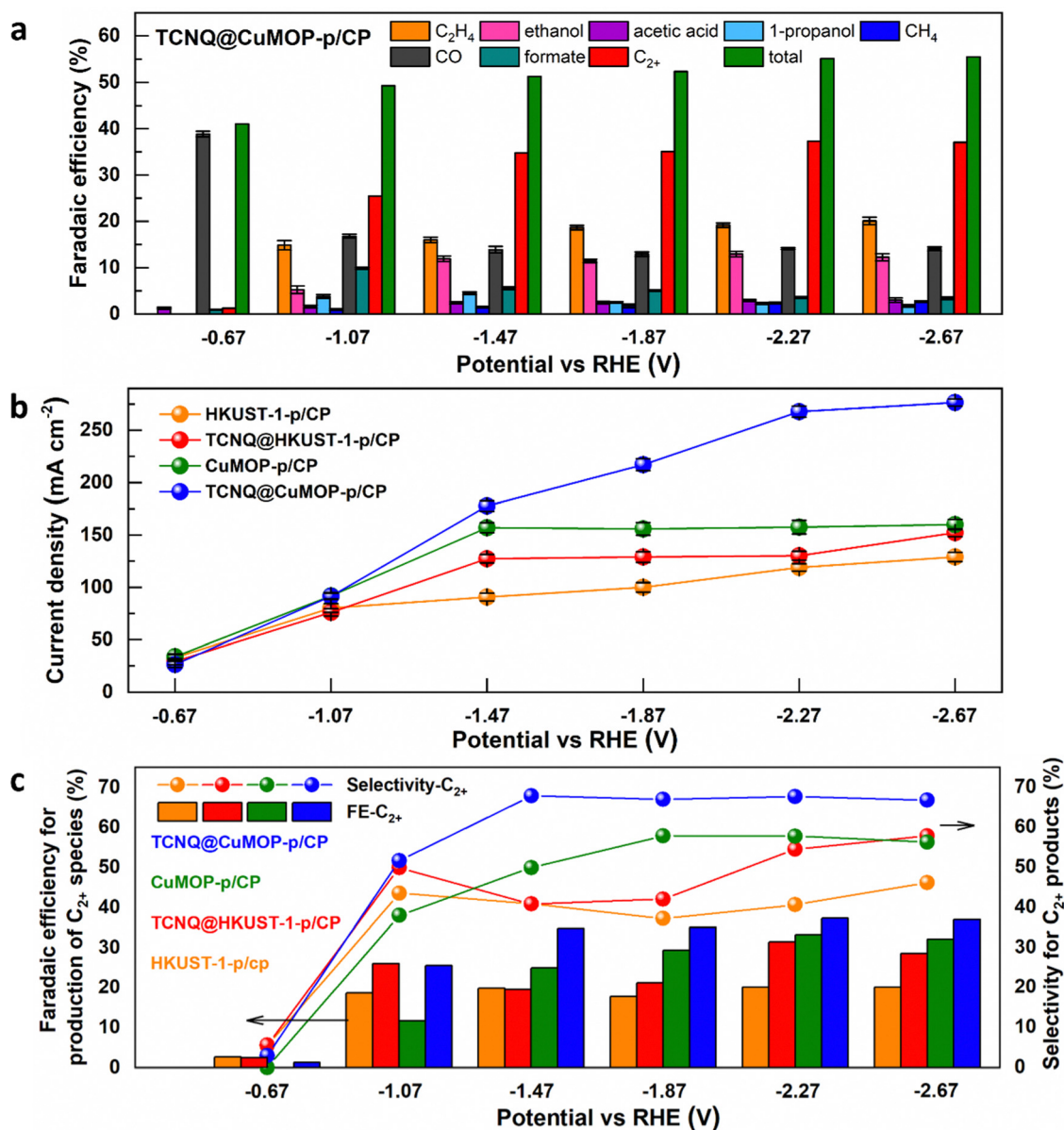


Fig. 4 (a) Catalytic performance of the TCNQ@CuMOP-p/CP electrode for  $\text{CO}_2\text{RR}$  at different potentials. (b) Comparison of the total current density over different electrodes for  $\text{CO}_2\text{RR}$  at different potentials. (c) Faradaic efficiency (FE) and selectivity to  $\text{C}_{2+}$  products over different electrodes for  $\text{CO}_2\text{RR}$  at different potentials.





formation of  $\text{Cu}_2\text{O}$  and  $\text{Cu}$  in  $\text{TCNQ@CuMOP-p}$  (Fig. 3b–d). Compared with  $\text{TCNQ@CuMOP}$ , new IR bands at 1150, 800 and  $625\text{ cm}^{-1}$  are observed for  $\text{TCNQ@CuMOP-p}$ , confirming the formation of  $\text{Cu}_2\text{O}$  (Fig. 3b and Fig. S10d, ESI†).<sup>32,33</sup> Raman spectra of  $\text{TCNQ@CuMOP-p}$  also show the characteristic peaks at 73, 101, 146, 220, 415, 634 and  $800\text{ cm}^{-1}$  assigned to  $\text{Cu}_2\text{O}$  and  $\text{Cu}$ , with the former being the main phase (Fig. 3c).<sup>34–36</sup> XPS spectra show two peaks for  $\text{Cu } 2p$  at  $\text{BE} = 954.73$  and  $934.98\text{ eV}$  in  $\text{TCNQ@CuMOP}$  corresponding to  $\text{Cu(II)}$  centers (Fig. 3d).<sup>37</sup> In  $\text{TCNQ@CuMOP-p}$ , two sets of  $\text{Cu } 2p$  peaks are observed: the peaks at  $\text{BE} = 954.19$  and  $934.44\text{ eV}$  correspond to new  $\text{Cu(II)}$  species surrounded by disordered microenvironments resulting from the structural evolution of  $\text{TCNQ@CuMOP}$ . The peaks at  $\text{BE} = 952.46$  and  $932.71\text{ eV}$  correspond to  $\text{Cu(I)}$  species with a minor amount of  $\text{Cu(0)}$ . Similar PXRD, IR and Raman results are observed for  $\text{CuMOP-p}$  (Fig. 3a–c and Fig. S9 and S10, ESI†). Interestingly, the XPS spectra of  $\text{CuMOP-p}$  show two sets of  $\text{Cu } 2p$  peaks (Fig. S11 and S12): the peaks at  $\text{BE} = 952.8$  and  $933.0\text{ eV}$  correspond to  $\text{Cu(I)}$  and the peaks at  $\text{BE} = 950.9$  and  $931.2\text{ eV}$  correspond to  $\text{Cu(0)}$ . This result confirms that adsorbed  $\text{TCNQ}$  in  $\text{CuMOP}$  may serve as an electron acceptor thus controlling the formation of  $\text{Cu(I)}$  over

$\text{Cu(0)}$  species. PXRD, IR and Raman results for  $\text{HKUST-1-p}$  and  $\text{TCNQ@HKUST-1-p}$  also confirm the formation of both  $\text{Cu}_2\text{O}$  and  $\text{Cu(0)}$ , and Raman spectra show strong signals for  $\text{Cu(0)}$  in both  $\text{HKUST-1-p}$  and  $\text{TCNQ@HKUST-1-p}$ . Overall,  $\text{TCNQ@CuMOP-p}$  shows higher selectivity for the formation of  $\text{Cu}_2\text{O}$  over  $\text{Cu(0)}$  species compared with  $\text{TCNQ@HKUST-1-p}$ , and this is likely due to (i) the large voids of  $\text{CuMOP}$  that allow better adsorption of  $\text{TCNQ}$  and (ii) the hindered charge transport in  $\text{CuMOP}$  owing to its isolated cages during evolution. SEM images confirm changes from cubic to needle-like morphology for  $\text{HKUST-1-p}$  and  $\text{TCNQ@HKUST-1-p}$  and flower-like morphology for  $\text{CuMOP-p}$  and  $\text{TCNQ@CuMOP-p}$  upon structural evolution (Fig. 3e and f and Fig. S13 and S14, ESI†).

### Electrochemical $\text{CO}_2\text{RR}$

$\text{HKUST-1-p/CP}$ ,  $\text{TCNQ@HKUST-1-p/CP}$ ,  $\text{CuMOP-p/CP}$ , and  $\text{TCNQ@CuMOP-p/CP}$  were used as working electrodes to conduct  $\text{CO}_2\text{RR}$  as a function of potential in aqueous  $1\text{ M KOH}$ . Ethylene, ethanol, acetic acid, 1-propanol, methane,  $\text{CO}$ , and formate are all detected as products (Fig. 4a and Fig. S15–S17, ESI†). In contrast, no carbon-based product was detected using  $\text{TCNQ/CP}$  as a catalyst. Of the four working electrodes,  $\text{TCNQ@CuMOP-p/CP}$  shows the best

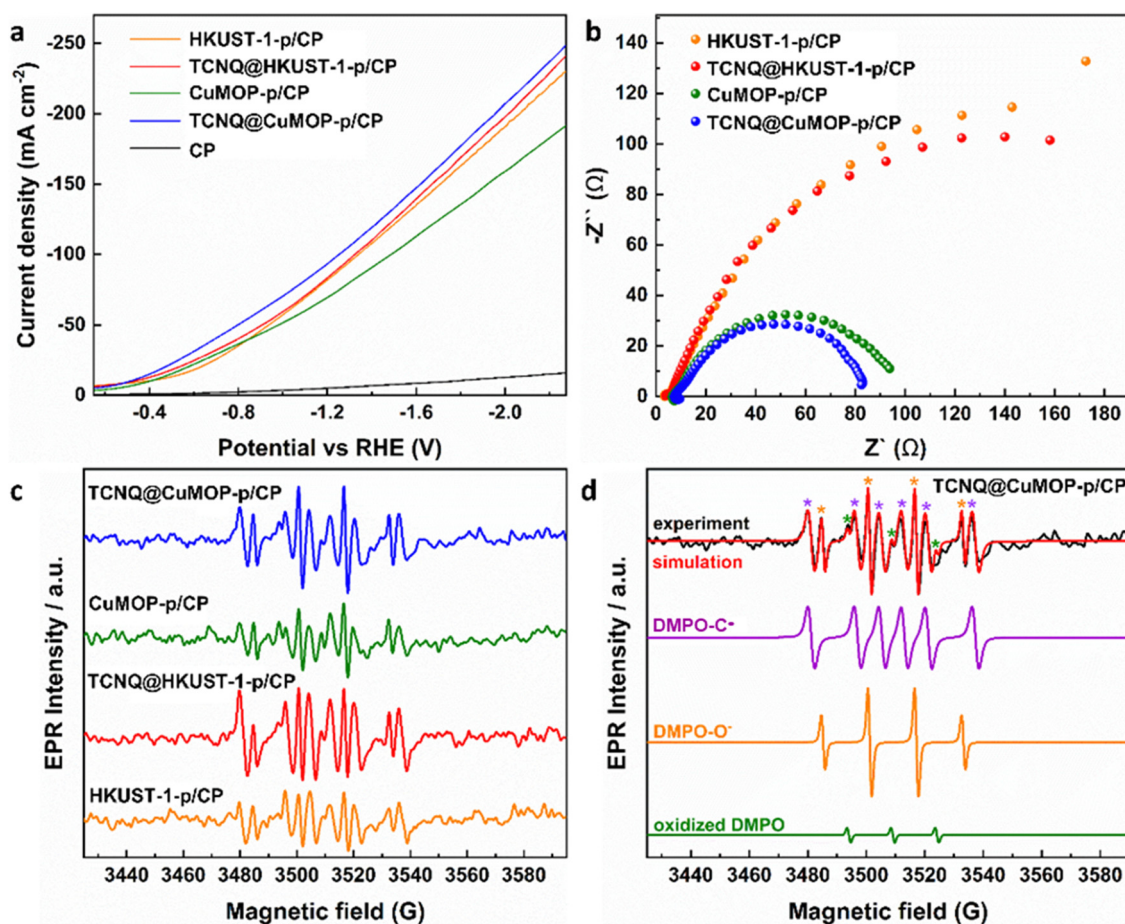


Fig. 5 (a) Linear sweep voltammetry (LSV) in  $\text{CO}_2$ -saturated electrolyte. (b) EIS spectra. (c) EPR spectra of electrolyte aliquots taken with different catalysts after electrolysis for 30 min. (d) EPR spectra of spin adducts of free radicals. The complete set of parameters for simulations are given in Tables S2 and S3 (ESI†).



catalytic performance with  $FE_{C_{2+}}$  of 37% (with a  $FE_{total}$  of 55%, thus a selectivity to  $C_{2+}$  products of 68%), a total current density of  $268 \text{ mA cm}^{-2}$ , and  $C_{2+}$  current density of  $100 \text{ mA cm}^{-2}$  at  $-2.27 \text{ V vs. RHE}$  (Fig. 4a–c). In comparison, the  $FE_{C_{2+}}$ , current density and the selectivity for  $C_{2+}$  products over CuMOP-p/CP (33%,  $52.2 \text{ mA cm}^{-2}$ , 58%), TCNQ@HKUST-1-p/CP (31%,  $40.9 \text{ mA cm}^{-2}$ , 55%) and HKUST-1-p/CP (20%,  $24.0 \text{ mA cm}^{-2}$ , 41%) electrodes are lower (Fig. 4c). Importantly, the catalytic performance of TCNQ@CuMOP-p/CP is comparable with the leading Cu(II)-MOF-derived catalysts studied for  $CO_2RR$  (Table S3, ESI†).

Linear sweep voltammetry (LSV) was used to evaluate the electrochemical response of these evolved working electrodes to reactivity with  $CO_2$  (Fig. 5a). The reductive current of all four decorated electrodes is significantly higher than that of bare CP, confirming the activity of the MOF-derived catalysts towards  $CO_2RR$ . The reductive current of TCNQ@CuMOP-p/CP is much higher than that of CuMOP/CP when the potential is more negative than  $-0.4 \text{ V vs. RHE}$ . The reductive current of TCNQ@HKUST-1-p/CP is also higher than that of HKUST-1-p/CP when the potential is more negative than  $-1.4 \text{ V vs. RHE}$ . Electrochemical impedance spectroscopy (EIS) reveals the charge-transfer resistance ( $R_{ct}$ ) of HKUST-1-p/CP ( $340 \text{ } \Omega \text{ cm}^2$ ), TCNQ@HKUST-1-p/CP ( $300 \text{ } \Omega \text{ cm}^2$ ), CuMOP-p/CP ( $100 \text{ } \Omega \text{ cm}^2$ ), and TCNQ@CuMOP-p/CP ( $87 \text{ } \Omega \text{ cm}^2$ ) in the electrolyte (Fig. 5b). These results suggest that adsorption of TCNQ has a positive impact on the conductivity of these evolved catalysts. The high conductivity of TCNQ@CuMOP-p/CP promotes its high  $FE_{C_{2+}}$  and selectivity for  $C_{2+}$  products as observed in the electrocatalysis tests.

### EPR Spectroscopy

EPR spectroscopy was employed to monitor and characterise the intermediate radicals produced during the electroreduction process. EPR spectra were measured for aliquots of electrolyte solution taken at time intervals of 10 min during reduction of  $CO_2$  at  $-2.27 \text{ V vs. RHE}$  over all four electrodes. DMPO was used as a spin trapping agent to identify the short-lived radicals during  $CO_2RR$ .<sup>38</sup> Characteristic spectra of DMPO-adduct radicals based upon O and C radicals, DMPO-O and DMPO-C, respectively, were observed for all four electrodes (Fig. 5c and d) and the signal intensity remains stable during the  $CO_2RR$  for all electrodes (Fig. S18, ESI†). However, within a given timeframe, the intensity of the EPR signal is significantly stronger for TCNQ-modified working electrodes compared with HKUST-1-p/CP and CuMOP-p/CP, consistent with their improved catalytic performance upon adsorption of TCNQ (Fig. 5c).

## Conclusion

The design and control of the structural evolution of porous materials during electrochemical  $CO_2RR$  represents an important route to new electrocatalysts. We report the control of structural evolution of HKUST-1 and CuMOP by adsorption of TCNQ as an additional electron acceptor to drive the reduction of Cu(II) sites to Cu(I) species, which promote the coupling of  $\bullet C$  radical intermediates to yield  $C_{2+}$  products. PXRD, IR, Raman,

XPS and EPR spectroscopy have been applied to investigate the evolution process and reveal the formation of Cu(I) and Cu(0) products. TCNQ@CuMOP-p/CP shows a high selectivity of 68% for  $C_{2+}$  products with  $FE_{C_{2+}}$  of 37% and a total current density of  $268 \text{ mA cm}^{-2}$  at  $-2.27 \text{ V vs. RHE}$ , comparable with the leading Cu(II)-MOF-derived catalysts studied for  $CO_2RR$ , with the remaining FE reflecting competing production of  $H_2$ . EPR spectroscopy, coupled with a spin trap experiments, confirms the formation of carbon-centred radicals as the key reaction intermediate in this system. Interestingly, oxalic acid was not observed as a product to any great extent reflecting the aqueous conditions employed in the current study. Oxalic acid generated by coupling of  $\bullet CO_2$  radicals is more frequently observed in reductions in non-aqueous media.<sup>39–43</sup> This study provides a facile pathway to control the structural evolution of porous materials by introducing additional electron acceptors to promote their activity for efficient electrochemical conversion of  $CO_2$  to multi-carbon products.

## Conflicts of interest

The authors declare no competing financial interest.

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