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Tandem electrocatalytic CO₂ reduction with Feporphyrins and Cu nanocubes enhances ethylene production†

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Copper-based tandem schemes have emerged as promising strategies to promote the formation of multicarbon products in the electrocatalytic CO₂ reduction reaction. In such approaches, the CO-generating component of the tandem catalyst increases the local concentration of CO and thereby enhances the intrinsic carbon-carbon (C-C) coupling on copper. However, the optimal characteristics of the COgenerating catalyst for maximizing the C2 production are currently unknown. In this work, we developed tunable tandem catalysts comprising iron porphyrin (Fe-Por), as the CO-generating component, and Cu nanocubes (Cucub) to understand how the turnover frequency for CO (TOF_{CO}) of the molecular catalysts impacts the C-C coupling on the Cu surface. First, we tuned the TOF_{CO} of the Fe-Por by varying the number of orbitals involved in the π -system. Then, we coupled these molecular catalysts with the Cucub and assessed the current densities and faradaic efficiencies. We discovered that all of the designed Fe-Por boost ethylene production. The most efficient Cu_{cub}/Fe-Por tandem catalyst was the one including the Fe-Por with the highest TOF_{CO} and exhibited a nearly 22-fold increase in the ethylene selectivity and 100 mV positive shift of the onset potential with respect to the pristine Cucub. These results reveal that coupling the TOF_{CO} tunability of molecular catalysts with copper nanocatalysts opens up new possibilities towards the development of Cu-based catalysts with enhanced selectivity for multicarbon product generation at low overpotential.

Introduction

The electrochemical CO_2 reduction reaction (CO_2RR) offers the opportunity to convert CO_2 into fuels and chemical feedstocks, while mitigating anthropogenic CO_2 emissions and storing renewable energy. Multi-carbon (C_{2+}) compounds (e.g., ethylene, ethanol, propanol) are among the most attractive CO_2RR products owing to their commercial value and high energy densities. However, optimizing the activity of CO_2RR electrocatalysts towards one particular product remains a crucial challenge that is not trivial to address because multiple

intermediates are involved in the CO_2 to C_{2+} conversion pathway.³⁻⁵ Cu-based materials have been widely employed as CO_2RR

catalysts due to their unique ability to facilitate the electroreduction of CO₂ beyond two electron reduction products.^{5,6} Numerous studies on catalyst development and mechanistic investigations have demonstrated that the surface coverage of the adsorbed CO (indicated as *CO) regulates the activation barrier of the C-C coupling step and, thus, the formation of C₂₊ products.⁷⁻⁹ An attractive approach to realize this high *CO surface coverage is via tandem catalysis, wherein Cu is coupled with a CO-producing component to realize the sequential CO₂to-CO and CO-to-C2+ product conversion on complementary active sites that are coupled at the nanometer scale. 10-21 However, the correlation between the intrinsic catalytic properties of the CO-generating component (e.g. turnover frequency, TOF, and overpotential) and its impact on the outcome of tandem catalysis (e.g. C-C coupling efficiency) is still critically missing. Thus, the fundamental design principles required to rationally promote C2+ production while decreasing the overpotential in tandem catalysis remain to be elucidated.

Bimetallic systems comprising Cu and another metal (Au, Ag, or Zn) as the CO-producing component have been extensively investigated as electrocatalysts in tandem CO₂

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reduction. ^{15–21} One drawback of these catalysts is that composition (*e.g.* alloying) and morphology can change during operation. ^{15–18} These changes affect both the physical and electronic structure, thus complicating the interpretation of the catalytic behavior and delaying the establishment of design principles required to further improve the catalytic activity of these systems. ^{18–22} Additionally, tuning the intrinsic activity and efficiency of metals is difficult and requires their coupling with organic modifiers. ^{23,24} Consequently, these systems are not ideal for guiding the understanding of the performance-determining factors in tandem catalysis.

Recent studies have suggested that CO-producing molecular catalysts are alternative candidates to metals in tandem schemes.²⁵⁻²⁷ Molecular components offer additional versatility compared to metals because their electronic and structural features can be tuned via synthetic modifications. 28-31 While the examples are still limited, studies in the literature on tandem catalysts including CO-producing molecular catalysts and Cu are encouraging. 25-27 For example, the addition of either an iron porphyrin or a cobalt phthalocyanine to sputtered Cu resulted in enhanced C₂₊ product yields.^{25,26} Specifically, the coupling of iron porphyrin with sputtered Cu resulted in increased faradaic efficiency for ethanol from 29% to 41% and in a shift the detection potential of this product from -0.84 to -0.82 V vs. RHE.25 The cobalt phthalocyanine/Cu catalyst enhanced the faradaic efficiency for C₂₊ products from 45% to 82% in a highly basic electrolyte.26 Instead, the combination of a cobalt phthalocyanine with a Zn-N-C catalyst promoted formation of methane with a total faradaic efficiency of 18%, a product not observed on the pristine Zn-N-C, again in a highly basic electrolyte.27 However, these studies have so far focused only on the integration of commercial molecular catalysts in tandem CO₂RR, thus not profiting from the chemical tunability of these systems. Furthermore, they remain a few isolated examples each utilizing a different electrocatalyst and with testing performed under different conditions, which make any comparison among them difficult to make.

Herein, we exploit the intrinsic tunability of molecular catalysts (in terms of TOFCO and overpotential) to understand the impact of the CO-generating component on subsequent C-C coupling on Cu surfaces during tandem catalysis. Iron porphyrin (F-Por) molecular catalysts are selected as the COproducing entity because of their high efficiency for CO2 to CO conversion at neutral pH when immobilized on conductive substrates.32-34 Furthermore, their versatile chemistry enables facile tuning of their redox behaviors via modification of the π system.35-37 To this end, we synthesized three Fe-Por with different numbers of orbitals involved in the π -system. Colloidally dispersible Cu nanocubes (Cucub) were chosen as Cu catalysts. Their intrinsic selectivity towards C-C coupling, and ethylene production in particular, as well as the demonstrated possibility to integrate them in different electrochemical cell designs, justifies this choice.38-41 Furthermore, the fact that both Fe-Por and Cucub catalysts can be employed as inks is beneficial for catalyst processability, scalability, and device integration. By studying the designed series of Fe-Por molecules in tandem CO₂RR, we investigate how their TOF_{CO} impacts the

C–C coupling on Cu_{cub} . Importantly, we discover that the most active **Fe-Por** generates an optimal local environment that boosts the intrinsic activity of Cu_{cub} towards ethylene while also increasing energy efficiency by anodically shifting the potential at which this product is detected.

Results and discussion

A series of Fe-Por complexes with a varying number of orbitals involved in the π -system of the porphyrin ligand were synthesized and tested as molecular catalysts for CO2RR (Fig. 1). These complexes are iron(III)-chlorido-tetrabicyclo[2.2.2]octadienetetraphenyl porphyrin (Fe-TbcTPP), iron(III)-chloridotetraphenyl porphyrin (Fe-TPP), and an iron(III)-chloridotetrabenzo-tetraphenyl porphyrin (Fe-TBTPP). The synthesis of Fe-TPP was carried out following a procedure reported in the literature,42 whereas Fe-TbcTPP and Fe-TBTPP were prepared according to the synthetic approach described in detail in the ESI and illustrated in Scheme S1†. In brief, the initial step corresponds to the synthesis of the free base porphyrin H₂-TbcTPP via a "Lindsey condensation reaction". 43 Refluxing H2-**TbcTPP** in a tetrahydrofuran (THF) solution containing FeBr₂ and 2,6-lutidine generates the desired Fe-TbcTPP. The last step is a retro-Diels-Alder reaction achieved by heating the Fe-TbcTPP complex at 200 °C under vacuum to produce Fe-TBTPP. The ¹H and ¹³C-NMR spectra of H₂TbcTPP are presented in Fig. S1 and S2,† while the MALDI-TOF spectra of the ironderivatives (Fe-TbcTPP and Fe-TBTPP) are provided in Fig. S3

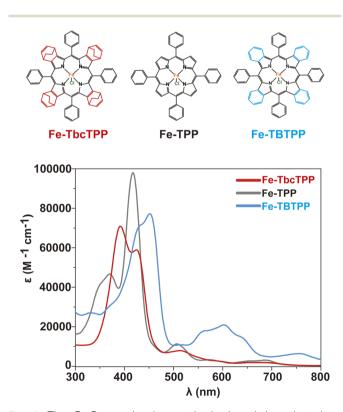


Fig. 1 The Fe-Por molecules synthesized and investigated as molecular catalysts in this study (top) along with the UV-vis spectra of the same in THF (bottom).

and S4.† The aromatic delocalization effect in **Fe-Por** is revealed by optical absorption spectroscopy (Fig. 1 and Table S1†). According to expectation, as the number of π -orbitals contributing to the system increases, the respective Soret band redshifts, following the peak wavelength (λ_{max}) order λ_{max} (**Fe-TBTPP**) > λ_{max} (**Fe-TBTPP**).

To understand the impact of the different porphyrin ligands on the electrocatalytic properties, we performed cyclic voltammetry (CV) experiments in homogeneous conditions (Fig. 2 and ESI† for details). A very similar behavior was observed for all **Fe-Por**, with each characterized by three redox processes that

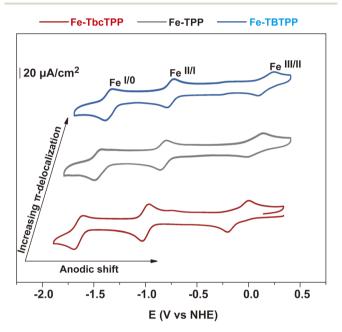


Fig. 2 Cyclic voltammetry of 0.25 mM Fe-Por dissolved in DMF containing 0.1 M TBAPF $_6$ as the supporting electrolyte, carried out at a scan rate of 100 mV s $^{-1}$. Fe-TbcTPP (red), Fe-TPP (gray), and Fe-TBTPP (blue).

are assigned to Fe^{III}/Fe^{II} , Fe^{II}/Fe^{II} , and Fe^{I}/Fe^{0} , as depicted in Fig. 2 and Table S1.† The second and third reduction waves are associated with two consecutive one electron reductions that are mainly ligand-based. 44,45 As expected, the different degree of π -delocalization of the **Fe-Por** results in a significant shift of the respective redox potentials. More specifically, the **Fe-TbcTPP** containing the more σ -donating and less π -accepting bicyclo [2.2.2]octadiene groups has the lowest potentials. On the other hand, the **Fe-TBTPP** containing benzo groups and phenyl substitution at the meso positions has more anodic values. The **Fe-TPP** with no additional functionalization onto the pyrrole moieties has redox potentials between those of **Fe-TbcTPP** and **Fe-TBTPP**.

We then investigated the CO₂RR catalytic properties of the Fe-Por in an H-cell using CO₂ saturated 0.1 M KHCO₃ as the electrolyte (see ESI† for details). Results of these experiments are presented in Fig. 3. Linear sweep voltammetry (LSV) (Fig. 3a) reveals an anodic shift of the onset potential (i.e. the potential at which the current starts to be detectable from the background) for CO₂ reduction from -0.57 V (Fe-TbcTPP) to -0.50 V (Fe-TPP) and to -0.40 V (Fe-TBTPP) vs. RHE (Reversible Hydrogen Electrode). This anodic shift follows the π -delocalization trend of the Fe-Por reported above. 46-48 Furthermore, the faradaic efficiency for CO (FECO) is higher for Fe-TBTPP than for either Fe-TPP or Fe-TbcTPP across the entire potential range (Fig. 3b and S5†), with a maximum of 91% at -0.55 V vs. RHE. The TOF_{CO} (see ESI† for details) follows the same trend, with TOF_{CO} (Fe-TBTPP) > TOF_{CO} (Fe-TPP) > TOF_{CO} (Fe-TbcTPP) (Fig. 3c). Specifically, Fe-TBTPP exhibits the highest TOF_{CO} (0.26 s⁻¹) compared to Fe-TPP (0.11 s⁻¹) and Fe-TbcTPP (0.02 s⁻¹) at -0.95 V vs. RHE.

Following the analysis of the **Fe-Por**, we prepared the Cu_{cub} /**Fe-Por** by mixing the **Fe-Por** and the Cu_{cub} (Fig. S6†) (see ESI† for details). The inks were then drop cast onto glassy carbon electrodes and the activities of the tandem catalysts were tested from -0.45 V to -1.05 V vs. RHE. Fig. 4 and S7† provide an overview of the obtained data. At low potentials (-0.45 V and

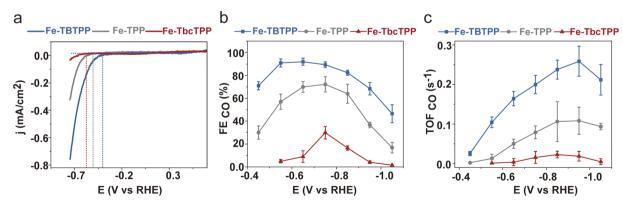


Fig. 3 (a) LSV curves of the Fe-Por catalysts measured at a scan rate of 10 mV s⁻¹, with the vertical dashed lines representing the onset potentials for each catalyst; (b) FE_{CO} and (c) TOF_{CO} as a function of applied potential. These measurements were performed at Fe-Por loadings of 16 nmol cm⁻² on carbon nanotubes deposited onto glassy carbon electrodes (S = 1.33 cm²) using an H-cell with CO₂ saturated 0.1 M KHCO₃ electrolyte. The carbon nanotubes were chosen as commonly used as a conductive support to homogeneously disperse the molecular catalysts *via* noncovalent interactions.³²⁻³⁴ The reported FE and TOF values are the average of three independent experiments with error bars indicating the standard deviations.

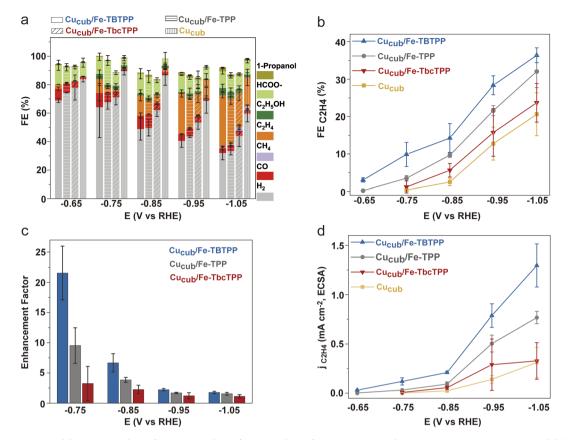


Fig. 4 (a) Total FEs and (b) $FE_{C_2H_2}$ for $Cu_{cub}/Fe-TBTPP$, $Cu_{cub}/Fe-TPP$, $Cu_{cub}/Fe-TbcTPP$ and Cu_{cub} as a function of potential; (c) C_2H_4 product enhancement factor of the $Cu_{cub}/Fe-Por$ compared to the pristine Cu_{cub} (enhancement factor = $(FE_{C_2H_4}$ of $Cu_{cub}/Fe-Por)/(FE_{C_2H_4}$ of $Cu_{cub}/Fe-Por)/(FE_{C_2H_4}$ of $Cu_{cub}/Fe-Por)/(FE_{C_2H_4})$ of $Cu_{cub}/Fe-Por)/(FE_{C_2H_4})$ a function of potential; (d) $j_{C,H,/ECSA}$ for $Cu_{cub}/Fe-TBTPP$, $Cu_{cub}/Fe-TPP$, $Cu_{cub}/Fe-TbcTPP$ and Cu_{cub} as a function of potential. The electrodes for these experiments were prepared by loading 3.12×10^2 nmol cm⁻² of Cu_{cub} and 8 nmol cm⁻² of the Fe-Por onto glassy carbon electrodes. The reported values are an average of three independent experiments with error bars indicating the standard deviations.

-0.55 V vs. RHE), the addition of the **Fe-Por** to Cu_{cub} suppresses the hydrogen evolution reaction (HER) and enhances the production of CO and formate. However, no evidence of C-C coupling reactions is observed at these potentials (Fig. S7†). The HER suppression and CO₂RR promotion induced by the Fe-Por become more pronounced at more negative potentials (-0.65 Vto -1.05 V vs. RHE, Fig. 4a). Indeed, the enhancement of C_2H_4 faradaic efficiency from $Cu_{cub}/Fe-Por$ relative to Cu_{cub} is clearly observed for all tandem-catalysts (Fig. 4b). Interestingly, C₂H₄ is produced at a potential as low as -0.65 V vs. RHE for the Cu_{cub} **Fe-TBTPP**, which maintains the highest FE_{C,H_a} across the entire potential range (Fig. 4b), reaching a $FE_{C_9H_4}$ of 36% at -1.05 V vs. RHE. By comparison, the Cucub in the absence of Fe-Por only achieved a FE_{C,H} of 19% at the same potential. At more negative potential, CH₄ is favored over C₂H₄ (Fig. S8†). Thus, while Fe-TBTPP still promotes C-C coupling, the FE_{C,H_a} decreases (\sim 25% at -1.15 V). The FE_{C,H₄} was much lower also for Cu_{sphere}/ Fe-TBTPP (\sim 15% at -1.05 V), which highlights the importance of the Cu morphology to maximize ethylene production (Fig. S9†).

To quantify the impact of the Fe-Por on C-C coupling, we define an enhancement factor for C2H4 production as the ratio of $FE_{C_2H_4}$ of $Cu_{cub}/Fe-Por$ to the $FE_{C_2H_4}$ of Cu_{cub} at a given

potential. The corresponding enhancement factors for Cu/Fe-TBTPP, Cu/Fe-TPP and Cu/Fe-TbcPP are 21.5, 9.5 and 3.2 at -0.75 V vs. RHE, respectively (Fig. 4c). Analysis of the electrochemically active surface area (ECSA) of Cucub/Fe-Por reveals a decreased solid/liquid contact area compared to the Cucub, which is likely a consequence of the blocking of Cu active sites by the molecules (Fig. S10†). However, the ECSA-normalized current density $(j_{\text{C}_2\text{H}_4/\text{ECSA}})$ indicates an increase in the intrinsic activity of the unpassivated sites in the presence of the Fe-Por, with a trend that is consistent with the FE and the enhancement factor (Fig. 4d).

To exclude the contribution of C₁ product suppression on the observed trends and to provide further evidence for the tandem mechanism, we analyzed the C1 products in greater detail (Fig. 5). The FE_{C_1} and the $j_{C_1,ECSA}$ of the $Cu_{cub}/Fe-Por$ catalysts are generally higher than those for the pristine Cucub across the entire potential range (Fig. 5a, b and S11†). Furthermore, the trend of ${
m FE_{C_1}}$ and $j_{{
m C_1/ECSA}}$ among the ${
m Cu_{cub}/Fe-}$ **Por** follows that of the FE_{C,H,}, which are higher values measured for higher molecular TOFCO. The improved capacity of Cucub to catalyze C-C coupling at more negative potentials results in an increase of FE_{Co.}/FE_{Co.} for all catalysts at higher overpotentials (Fig. 5c). The decrease of FE $_{CO}$ (Fig. 5d) and the saturation of j_{CO}

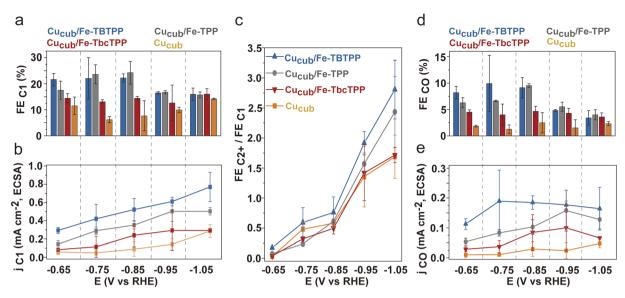
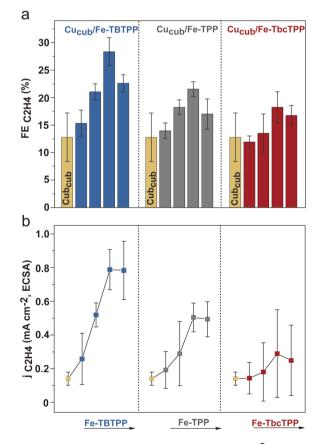


Fig. 5 (a) FE $_{C_1}$ and (b) partial current density for the C_1 products (j_{C_1}) normalized by ECSA, (c) FE ratio of C_{2+} to C_1 products, (d) FEs and (e) partial current density for CO (j_{CO}) normalized by ECSA of $Cu_{cub}/Fe-TBTPP$, $Cu_{cub}/Fe-TDFPP$, $Cu_{cub}/Fe-TDFPP$ and Cu_{cub} at different potentials. The reported values are an average of three independent experiments with error bars indicating the standard deviations.

(Fig. 5e) with increasing overpotential is consistent with the increased consumption of CO as more ethylene is generated via the tandem catalytic mechanism. In contrast, FE $_{\rm CO}$ and $j_{\rm CO}$ remain approximately constant for pure Cu $_{\rm cub}$ across all potentials, reflecting the unmodified native activity of the nanocubes in the absence of tandem CO generation.

To investigate possible changes of electronic and chemical properties of Cu_{cub} due to interactions with the molecular constituents, which could influence the overall catalytic properties of the $Cu_{cub}/Fe-Por$, we performed X-ray photoelectron spectroscopy (XPS) (Fig. S12†). The analysis of the Cu 2p peaks and Cu LMM spectra indicated that Cu is present in its metallic form in all systems. Furthermore, the absence of any peak shifts in spectra from $Cu_{cub}/Fe-Por$ compared to Cu_{cub} indicated that there are no changes in surface composition and/or charge transfer effects. This lack of a specific chemical or electronic change of the Cu surface, together with the systematic correlations between C–C coupling efficiency of $Cu_{cub}/Fe-Por$ with the TOF_{CO} trends among Fe-Por, indicates that overall selectivity and activity is governed by the tandem catalytic process.

Having established that a tandem mechanism is dominant in defining activity and selectivity of $\mathbf{Cu_{cub}}/\mathbf{Fe-Por}$, optimization of ethylene production requires understanding of the relationship between the loading of the CO-generating component and the CO conversion rate of the Cu catalyst. With this aim, we tested the impact of $\mathbf{Fe-Por}$ loading on enhancing C–C coupling in $\mathbf{Cu_{cub}}/\mathbf{Fe-Por}$ tandem catalysts (Fig. 6). We observe that the $\mathbf{FE_{C_2H_4}}$ increases with the $\mathbf{Fe-Por}$ loading until reaching its maximum value at 8 nmol cm⁻² (Fig. 6a). This trend suggests that addition of more $\mathbf{Fe-Por}$ results in the local accumulation of CO in the vicinity of $\mathbf{Cu_{cub}}$, which promotes C–C coupling. However, a further increase of the $\mathbf{Fe-Por}$ coverage leads to decreased $\mathbf{C_2H_4}$ selectivity. Concomitantly, the $\mathbf{FE_{CO}}$ increases



Fe-Por: 2, 4, 8 and 16 nmol cm⁻²

Fig. 6 (a) ${\rm FE_{C_2H_4}}$ and (b) $j_{{\rm C_2H_4/ECSA}}$ of ${\rm Cu_{cub}/Fe-TBTPP}$, ${\rm Cu_{cub}/Fe-TbcTPP}$ and ${\rm Cu_{cub}}$ at different loadings of the Fe-Por (2, 4, 8 and 16 nmol cm $^{-2}$) at -0.95 V vs. RHE in ${\rm CO_2}$ saturated 0.1 M KHCO $_3$ H-cell. The reported values are an average of three independent experiments with error bars indicating the standard deviations.

(Fig. S13†), which indicates that the additionally generated CO escapes the system.

As discussed above, the **Fe-Por** molecules also block Cu active sites. Consistent with this conclusion, we observe a continuous decrease of the ECSA with increased loading (Fig. S14†). The enhancement in intrinsic activity of the unpassivated sites on the $\mathbf{Cu_{cub}}$ compensates the decreasing concentration of sites, but only up to a certain loading. Above that point, the C_2H_4 selectivity is suppressed, which is also reflected in the $j_{C_2H_4,ECSA}$ (Fig. 6b). In particular, the $j_{C_2H_4,ECSA}$ in $\mathbf{Cu_{cub}}/\mathbf{Fe-Por}$ increases up to 8 nmol cm⁻² and thereafter saturates.

The comparison of different **Fe-Por** at the same loadings reveals more efficient C_2H_4 production for the $Cu_{cub}/Fe-TBTPP$. Furthermore, we note that lower loadings of the **Fe-TBTPP** generate higher $FE_{C_2H_4}$ and $j_{C_2H_4/ECSA}$ compared to higher loadings of the **Fe-TbcTPP** (e.g. 4 nmol cm⁻² of **Fe-TBTPP** $\nu s.$ 8 nmol cm⁻² of **Fe-TbcTPP**). As the **Fe-TBTPP** possesses the highest TOF_{CO} , these data prove that the CO production rate plays a crucial role in achieving optimal C–C coupling in the tandem catalysts.

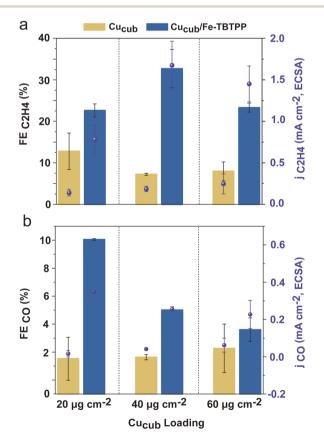


Fig. 7 (a) FE and partial current density for the C_2H_4 product normalized by ECSA ($j_{C_2H_4,ECSA}$) and (b) FE and partial current density for the CO product normalized by ECSA ($j_{CO,ECSA}$) for Cu_{cub} /Fe-TBTPP at different loading of Cu_{cub} (3.12 \times 10², 6.24 \times 10² and 9.36 \times 10² nmol cm⁻²) with the same Fe-TBTPP loading (16 nmol cm⁻²) at -0.95 V vs. RHE in the CO₂ saturated 0.1 M KHCO₃ H-cell. The reported values are an average of three independent experiments with error bars indicating the standard deviations.

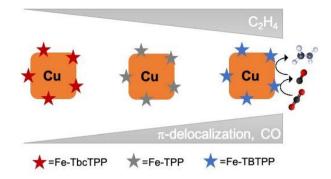


Fig. 8 Schematic representation of the proposed mechanism for C_2H_4 promotion in $Cu_{cub}/Fe-Por$ tandem catalysts. The C–C coupling enhancement and C_2H_4 promotion correlate with the Fe-Por selectivity and conversion rate for CO.

To test whether the bottleneck for further improving C_2H_4 generation with the highest Fe–Por loading is the CO consumption, we tested increased Cu-cube loadings for the best performing $\mathbf{Cu_{cub}}/\mathbf{Fe-TBTPP}$ (Fig. 7 and S15†). The Fe-TBTPP loading was kept at 16 nmol cm $^{-2}$ for comparison with Fig. 6. An increase in $\mathbf{Cu_{cub}}$ loading from 3.12×10^2 to 6.24×10^2 nmol cm $^{-2}$ does improve the $\mathbf{C_2H_4}$ production, with both the $\mathbf{FE_{C_2H_4}}$ and $\mathbf{j_{C_2H_4, ECSA}}$ increasing (Fig. 7a). A $\mathbf{FE_{C_2H_4}}$ of 33% is thus measured at -0.95 V ν s. RHE. The concomitant decrease $\mathbf{FE_{CO}}$ and $\mathbf{j_{CO,ECSA}}$ (Fig. 7b) indicates that the CO produced by Fe-TBTPP is indeed further consumed by the increased $\mathbf{Cu_{cub}}$ loading.

For higher $\mathbf{Cu_{cub}}$ loading (9.36 \times 10² nmol cm⁻²), the $\mathbf{FE_{C_2H_4}}$ and $j_{\mathbf{C_2H_4},\mathbf{ECSA}}$ decrease and the $\mathbf{FE_{CO}}$ and $j_{\mathbf{CO,ECSA}}$ don't change further. In a similar manner to the **Fe-Por** loading experiments, the ratio between the CO-generating component and the CO conversion rate of the Cu catalyst must be balanced for optimal performance.

Finally, we characterized the **Fe-Por** by Fourier-transform infrared spectroscopy (FT-IR) and ultraviolet-visible spectroscopy (UV-vis) (Fig. S16 and S17†), and the Cu_{cub} morphology by TEM (Fig. S18†), which proved the intact structure of **Fe-Por** and cubic shape of Cu_{cub} after 1.5 hours of electrolysis. Furthermore, the best performing tandem catalyst in terms of C_2H_4 production, which is Cu_{cub} /Fe-TBTPP, displayed an excellent stability and selectivity over 10 hours of electrolysis (Fig. S19†). Altogether, these data indicate that the addition of the **Fe-Por** has a stabilizing effect on the morphology of the Cu cubes. While a dedicated study is needed, we speculatively attribute the origin of this observation to the formation of the CO intermediate on a different surface than Cu.

Conclusions

In summary, we built tandem catalysts including **Fe-Por** with tunable CO_2 to CO selectivity (**Fe-TBTPP** > **Fe-TPP** > **Fe-TbcTPP**) and $C\mathbf{u_{cub}}$. We discovered that the C–C coupling enhancement in these tandem catalysts correlates directly with the **Fe-Por** selectivity and conversion rates for CO, with the $C\mathbf{u_{cub}}$ /**Fe-TBTPP** being the best performing one.

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We found a 100 mV anodic potential shift for C₂H₄ detection, a 22 times enhancement of C_2H_4 production at -0.75 V vs. RHE and a doubled $FE_{C.H.}$ of 36% at -1.05 V vs. RHE in the Cu_{cub}/Fe -**TBTPP** compared to the Cu_{cub}. This performance is comparable to the state-of-the-art in this class of catalysts. 25-27 Going beyond it, these results demonstrate that the rate and potential at which CO is generated plays a defining role for the selectivity and overpotential of multiple-carbon products in tandem schemes (Fig. 8).

Overall, this study encourages further investigations on the design of the homogenous catalyst as a promising strategy to further optimize molecular-based tandem systems.

Data availability

Data for this paper, including UV-vis and electrochemical characterization, are available at Zenodo at https://doi.org/ 10.5281/zenodo.7229402.

Author contributions

M. W. carried out the synthesis of the tandem catalysts and all electrocatalytic testing for CO₂RR. V. N. synthesized and characterized the molecular catalysts. A. L. performed X-ray photoelectron spectroscopy and contributed to daily discussions. A. L. supervised the work on the molecular catalysts. I. S. contributed to discussions. R. B. supervised the work on the tandem catalysts and CO₂RR and coordinated the project. All the authors contributed to the writing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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