

Observation of Metal-Organic Interphase in Cu-based Electrochemical CO₂-to-Ethanol Conversion

Corresponding Author: Professor Cheng Wang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this manuscript, Shen et al. systematically investigated the influence of metal-organic-interphase on the selectivity of C₂+ product on the CuOx surface. The authors constructed an automatic electrocatalysis platform to study the CO₂RR performance using 180 nitrogen/oxygen/sulfur-terminated or water-insoluble molecular modifiers on the oxide-derived Cu. This instrument not only increased the experimental efficiency, but also enhanced the precision and repeatability of evaluation results. From the automatic electrochemical experiments, data collection, machine learning, in situ experimental characteristics, and DFT simulation, they found that the interphase crucially modulates Cu surface coordination, CO₂RR intermediates, and interfacial water configuration, markedly altering the catalyst's electrochemical properties. Due to my research interest on the DFT and machine learning, I think it is an interesting job to investigate the effect of metal-organic interphase on C₂+ products. Please considering the following questions.

1. For the machine learning part, the author just selected the S-terminal modifiers as the database, except for the N-/O-terminal modifiers, please giving the rational explanations. What's more, have you utilized the whole features including MFFs and molecule physicochemical properties to train machine learning model, not just for important features by SVR method, please showcasing these results for all the ML methods.

2. In the results and discussion part of the manuscript, I think Figure 2 should be placed back in Figure 3. Figure 3 is about the data analysis from the automatic electrocatalysis platform in Figure 1 and following machine learning analysis, which is significantly natural to understand the content, not directly focusing on the S-based modifiers analysis.

3. About the adsorption of 1,8-octanedithiol on the Cu (100) and Cu (110) surface, the difference between their adsorption energies is a little small with the DFT errors, did you consider the solvent effect to the adsorption energy? This result may affect the Cu surface coordination by the interphase.

4. Please completing the full name of the abbreviations in the manuscript and SI for the kind reading, such as ECFP fingerprints, PEOE Charge, MOE.

5. The pictures in the Figure S21-S23 are quite fuzzy, please rewriting again.

6. In Figure 6(d, e), it missed the figure lettering.

Reviewer #2

(Remarks to the Author)

Referee Report

Shen et al. investigated the impact of molecular modifiers with N/S/O terminal groups on CuOx surfaces and their effects on electrochemical CO₂ reduction performance. The authors claim that sulfur-terminal modifiers enhance selectivity towards C₂ products, correlating these effects with changes in the hydrophobicity of the modified electrodes. Additionally, they observed improved ethanol selectivity in some cases, suggesting the formation of a metal-organic interphase at the electrode surface. While the study explores an interesting approach, the conclusions appear premature and somewhat speculative, especially when considering the correlation between product selectivity and the physico-chemical properties of the modified

electrodes. Given the complexity of the system, with numerous variables at play, the explanations provided are not sufficiently supported by the data, making the key findings less convincing. In comparison, recent work has shown that molecular catalysts coated on Ni electrodes can achieve ethanol faradaic efficiencies (FE) of up to 70%, attributed to strong coupling between the catalyst and metal surface (<https://doi.org/10.1038/s41929-024-01225-1>). In contrast, the selectivity changes in Shen et al.'s work are attributed to interphase formation, yet the evidence supporting this is not comprehensive or clearly articulated. Although the authors performed an extensive screening of 180 molecular modifiers and conducted significant product characterization, the study involves too many variables (e.g., chemical structures, morphology of the metal-organic interphase, choice of CuOx or Cd@CuOx substrates), which complicates the interpretation of results and weakens the clarity of the discussion. The conclusions about the relationship between selectivity and electrode properties thus remain tentative and unsubstantiated.

Given the above concerns, I cannot recommend the manuscript for publication in its current form. However, I hope the following points will aid the authors in revising the manuscript for potential submission to other journals.

Major Concerns:

1. The study introduces too many variables, and the inconsistency in their discussion throughout the manuscript makes it difficult for the reader to follow the correlations. For example, Figure 2 (a-e) presents Faradaic efficiencies (FEs) for 1,8-Octanedithiol on CuOx, while Figure 2 (f-g) presents FEs for 1,8-Octanedithiol on Cd@CuOx and Eu@CuOx, showing the best ethanol selectivity. However, these promising results are not discussed further in subsequent sections, leading to incomplete coverage of key data.
2. The reported current densities vary significantly across samples, from 96 to 1300 mA cm⁻², raising concerns about the consistency of the fabrication methods used, particularly the loading amount of CuOx catalysts. This large variation undermines the reliability of the comparisons between samples, as it suggests significant differences in catalyst preparation that are not adequately controlled for.
3. The total FEs listed in Table S23 range from 65% to 78%, whereas the FEs presented in Figure 2 exceed 90%. This discrepancy requires an explanation, as it suggests potential inconsistencies in the reported data or issues with measurement accuracy that must be addressed.
4. The discussion surrounding the metal-organic interphase is limited to hypotheses or speculative correlations. Several key points need further clarification:
 - o The authors correlate molecular hydrophobicity with the formation of stacked layers, but this relationship is not clearly explained.
 - o No clear evidence is provided to support the existence of a continuous metal-organic interphase.
 - o The attribution of improved ethanol selectivity to changes in electrode morphology is based on observations, but there is insufficient evidence to substantiate the underlying cause of this morphology.
5. The observed thickness of the organic layer seems more dependent on intermolecular stacking than on the terminal groups. Given the interplay between multiple variables (i.e., organic layer thickness, the presence of a metal-organic interphase, and the molecular structure of the modifiers), the study lacks a convincing comparison of results. To draw meaningful conclusions, the authors should focus on isolating and analyzing one variable at a time.
6. The manuscript discusses the potential role of hydrogen bonding in stabilizing *CO on CuOx, but it is unclear whether the observed selectivity variations are attributed to adsorption on the CuOx facets or on the metal-organic interphase. This distinction is critical and requires further clarification.
7. There is missing text at line 145, which appears as "Error!..." in the manuscript. This needs to be corrected for clarity.

Reviewer #3

(Remarks to the Author)

The paper presents an interesting result of metal-organic interphases in CO₂ electroreduction processes, particularly focusing on their role in enhancing ethanol production on Cu-based catalysts, challenging the traditional view of surface modifications as monolayers. This discovery is essential for understanding the factors that modulate CO₂RR selectivity towards ethanol and C₂+ products.

1. The use of 1080 CO₂RR experiments and the systematic investigation of 180 different modifiers is commendable. The extensive dataset and the use of an automatic electrocatalysis platform add credibility to the findings. However, it would be beneficial to include more details regarding the reproducibility of results for modifiers that showed moderate changes in selectivity.
2. The in-depth characterization of the interphase using techniques such as TEM, EDX, XPS, and in situ Raman spectroscopy is thorough and provides clear mechanistic insights. The discussion on the effect of hydrophobicity and hydrophilicity, as well as the involvement of Cu facets, could be enhanced by addressing potential limitations of these characterizations, especially regarding surface dynamics during the catalytic process.
3. The paper's findings on how certain sulfur-containing modifiers enhance ethanol production while others promote formate or suppress C₂+ products are intriguing. Further discussion on the balance between hydrophobic interactions, surface coordination, and interfacial water structure, particularly in relation to hydrogen transfer, would provide more clarity.
4. The figures effectively illustrate key experimental results. However, the interpretation of certain violin plots (e.g., relative FEEtOH for different molecular categories) would benefit from clearer labeling and a more detailed explanation in the text to help readers quickly grasp the significance of these distributions.

5. The role of electrochemical conditions, such as electrolyte composition and temperature, should be discussed more comprehensively, as these could also influence the formation and stability of metal-organic interphases.

Overall, this paper is a valuable addition to the field of electrocatalysis, and the findings could impact the design of future CO₂ reduction catalysts.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have properly addressed my concerns and I suggested it for publications.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

I appreciate the efforts made by the authors to address my comments and improve their manuscript. The authors have carefully considered the suggestions and provided substantial updates. They have clarified that the discrepancies in current densities arise from the use of different platforms during measurements. Additionally, they have included more characterizations, such as HRTEM, for the Eu@CuOx catalysts, ensuring consistency in comparisons with other CuOx catalysts.

For the previously missing Faraday efficiencies (FEs), the authors have addressed this by comparing their findings with published literature, highlighting that certain products may be undetectable or missed. For the reactions occurring at the interface, the authors have strengthened their argument by presenting additional evidence, including Au ion addition and subsequent deposition at the interface after electrochemical operations.

Minor comments:

Platform Distinctions: It is essential to clearly distinguish the different experimental platforms used in the study early in the manuscript. Figure 1 focuses entirely on the automated platform, which may mislead readers into assuming that all experiments were conducted using the same platform. For clarity, consider including some representative data from the automated platform in Figure 1, followed by a subtitle or explicit transition to emphasize that subsequent discussions focus on the manual platform. This will provide a clearer performance comparison for a broader audience. Avoid burying this clarification mid-paragraph (e.g., "We validated the accuracy of the data collected by the automated electrocatalytic platform by manually checking the performance of 1,8-octanedithiol, one of the best ethanol promoters, on the commercial flow cell").

Hydrophobicity: The hydrophobicity has been mentioned several times through the manuscript, especially as a potential factor in the ML models. However, I was a bit lost in the connection to the next part of discussion for the interphase effect. For instance, the statement at line 166 ("This complexity challenges the simplistic understanding of hydrophobicity-promoted ethanol production") raises questions. Please clarify how hydrophobicity influences ethanol production in the context of your findings.

Lastly, I noticed a formatting issue in Figure 1 (a partial box appears at the top of the figure, likely due to PDF conversion). Ensuring the figure is visually clear and free from such issues will further aid readability.

I fully recognize the value of this work, not only for demonstrating a promising catalyst for CO₂RR but also for providing a comprehensive dataset that could serve as a valuable resource for future research. However, as the manuscript is very heavy in terms of data presented, I feel that the manuscript would still benefit from a clearer and more cohesive storyline. I still want to emphasize that I have no doubt on the quality of this work, regarding the data and their interpretations. Therefore, I recommend this paper to be published in Nature Communication.

(Remarks on code availability)

Reviewer #3

(Remarks to the Author)

The authors have addressed my comments well.

(Remarks on code availability)

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The authors have addressed all my comments.

(Remarks on code availability)

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Reviewer #1 (Remarks to the Author):

In this manuscript, Shen et al. systematically investigated the influence of metal-organic-interphase on the selectivity of C_{2+} product on the CuO_x surface. The authors constructed an automatic electrocatalysis platform to study the CO_2RR performance using 180 nitrogen/oxygen/sulfur-terminated or water-insoluble molecular modifiers on the oxide-derived Cu. This instrument not only increased the experimental efficiency, but also enhanced the precision and repeatability of evaluation results. From the automatic electrochemical experiments, data collection, machine learning, in situ experimental characteristics, and DFT simulation, they found that the interphase crucially modulates Cu surface coordination, CO_2RR intermediates, and interfacial water configuration, markedly altering the catalyst's electrochemical properties. Due to my research interest on the DFT and machine learning, I think it is an interesting job to investigate the effect of metal-organic interphase on C_{2+} products. Please considering the following questions.

Reply and actions taken: We thank the reviewer for the positive evaluation of our manuscript. We also appreciate the constructive comments raised by this reviewer to help further improve the quality of our manuscript. Our responses to the detailed comments raised by this reviewer and the corresponding revisions are described as follows.

1. For the machine learning part, the author just selected the S-terminal modifiers as the database, except for the N-/O-terminal modifiers, please giving the rational explanations. What's more, have you utilized the whole features including MFFs and molecule physicochemical properties to train machine learning model, not just for important features by SVR method, please showcasing these results for all the ML methods.

Reply and actions taken: We thank the reviewer for the comment.

First, based on the experimental data of N/O/S type molecular modifiers, we found that S type molecules have the most significant selective regulation effect on single products, e. g., only changing the different substituents at the S terminal can regulate the selectivity of ethanol/formate. We thus chose to do machine learning study on the S-molecules in hope to find something interesting.

Second, we had a small dataset. It is quite challenging to do machine learning in a vast molecular space with data scarcity. It is easier to focus on a category of molecules for the analysis. In the machine learning section of this work, aside from the Rdkit and MFF

descriptors, the calculations for other descriptors are based on the physicochemical properties of the sulfur (S) atomic center (<https://github.com/sym823808458/Surfacia>), so we only focused on the S-group. We have added the link of the program to the Supporting Information (*please see the revised Supporting Information, Page 4, Paragraph 8, Line 8*).

Third, among the 180 modifiers, the modifier with the highest single selectivity for ethanol/C₂₊ product falls within the 'S terminal + Hydrophobic FGs' category (*Please see Figures 3c-3d in the revised manuscript*). Ethanol is one of the most important C₂₊ products, and we hope to explore the CO₂-to-EtOH conversion.

We have tried to use all MFF and physicochemical related features as input instead of using SVR stepwise regression to select features for MLP model training. The MLP model metrics are shown in the following Table R1 and Figure R1, which are also added in the revised Supporting Information as Table S4 and Figure S13.

Table R1. Classification performance on MLP model calculated from 10-fold average results for individual CO₂RR product FE target based on all 307 features without SVR feature selection.

Target label	Accuracy	Precision	Recall	F1 Score	AUC-ROC
FE _{H₂}	0.57	0.60	0.47	0.51	0.65±0.17
FE _{CO}	0.58	0.67	0.64	0.57	0.66±0.13
FE _{CH₄}	0.50	0.46	0.49	0.45	0.49±0.29
FE _{C₂H₄}	0.64	0.64	0.59	0.60	0.69±0.13
FE _{formate}	0.59	0.63	0.55	0.54	0.59±0.28
FE _{acetate}	0.61	0.60	0.71	0.63	0.65±0.13
FE _{EtOH}	0.61	0.66	0.64	0.61	0.63±0.18
FE _{n-PrOH}	0.72	0.63	0.37	0.35	0.63±0.22
FE _{C₂+}	0.57	0.50	0.47	0.48	0.67±0.11

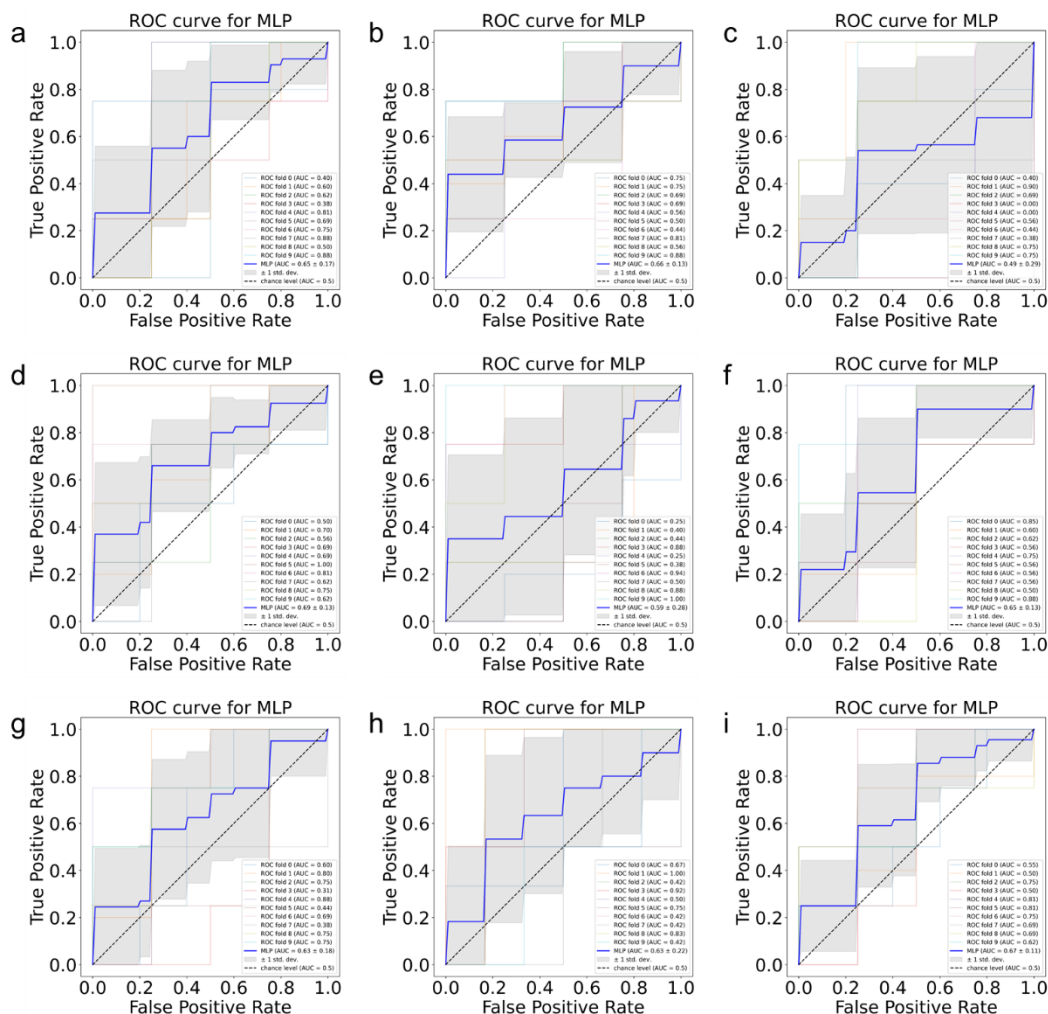


Figure R1. ROC response in 10-fold cross validation of (a) H₂, (b) CO, (c) CH₄, (d) C₂H₄, (e) formate, (f) acetate, (g) EtOH, (h) *n*-PrOH and (i) C₂⁺ products based on all 307 features.

Compared with the MLP model metrics based on selected features, the accuracy, precision, recall, F1 score and area under the receiver operating characteristic curve (AUC-ROC) of MLP model for individual CO₂RR product of the test set based on all 307 features decreased to varying degrees. Without feature selection, the risk of model overfitting increases. The feature importance is also difficult to interpret, and there may be strong correlations between multiple features. It is difficult to distinguish the independent contribution of each feature to the model output, resulting in a decrease in the interpretability of the model.

We have added the following sentences to describe these details in the revised Supporting Information: “Without SVR features selection, the MLP model trained directly with 307 features performs worse than the MLP model trained with the selected features (Figure S13 and Table S4).” (please see the revised Supporting Information, Page 21, Paragraph 3, Lines 8-9)

2. In the results and discussion part of the manuscript, I think Figure 2 should be placed back in Figure 3. Figure 3 is about the data analysis from the automatic electrocatalysis platform in Figure 1 and following machine learning analysis, which is significantly natural to understand the content, not directly focusing on the S-based modifiers analysis.

Reply and actions taken: We thank the reviewer for the comment. We appreciate your insight and following your valuable suggestions, we have rearranged the layout and order of the figures and related content in the revised manuscript. After adjustment, Figure 2 shows the reliability verification of the data screened by the automation platform, and Figure 3 further analyzes the data collected from the automation platform that has been verified. *(please see the revised manuscript, Pages 2-4)*

3. About the adsorption of 1,8-octanedithiol on the Cu (100) and Cu (110) surface, the difference between their adsorption energies is a little small with the DFT errors, did you consider the solvent effect to the adsorption energy? This result may affect the Cu surface coordination by the interphase.

Reply and actions taken: We thank the reviewer for the comment. In our manuscript, the DFT calculations were primarily based on the material's intrinsic structure, which better represents the state of the material before or at the early stage of CO₂RR. Following your suggestion, we incorporated water molecules into the Cu (100) and Cu (110) model and recalculated the system to better reflect the material's state during the electrolysis. Due to the hydrophobicity of alkyl chains, the water molecules we added were distributed outside the alkyl chain layer after model optimization. The calculation results show that the introduction of the solvent layer does not change the coordination mode of S and Cu on Cu (110) and Cu(100), and has almost no effect on the binding energy of 1,8-octanedithiol. The updated results are shown in Figure R2. Furthermore, the average adsorption energies of 1,8-octanedithiol on Cu (100) and Cu (110) change from -3.66 eV and -3.36 eV (without considering the solvent effect) to -3.08 eV and -3.50 eV (with the solvent effect considered), respectively. This difference between their adsorption energies is also small considering the DFT errors. We agree that such a small difference in adsorption energy is not significant. Accordingly, we have made the necessary corrections to the text: *“Moreover, the average adsorption energies of 1,8-octanedithiol on Cu(100) and Cu(110) are -3.66 eV and -3.36 eV, respectively. Such a small difference in adsorption energy is within the DFT calculation error.” (please see the revised manuscript, Page 9, Paragraph 2, Lines 11-13)*

We have also added the following sentences to describe these details in the revised manuscript: “We also considered solvent effect on catalyst state during electrolysis (Figure S69). Water molecules outside the alkyl chain did not influence the coordination of 1,8-octanedithiol on Cu(100) and Cu(110) but change the average adsorption energies to -3.08 eV and -3.50 eV for Cu (100) and Cu (110), respectively, with the difference being minimal and within the margin of DFT error.” (please see the revised manuscript, Page 9, Paragraph 2, Lines 13-17)

The Figure R2 was added to the revised Supporting Information as Figure S69.

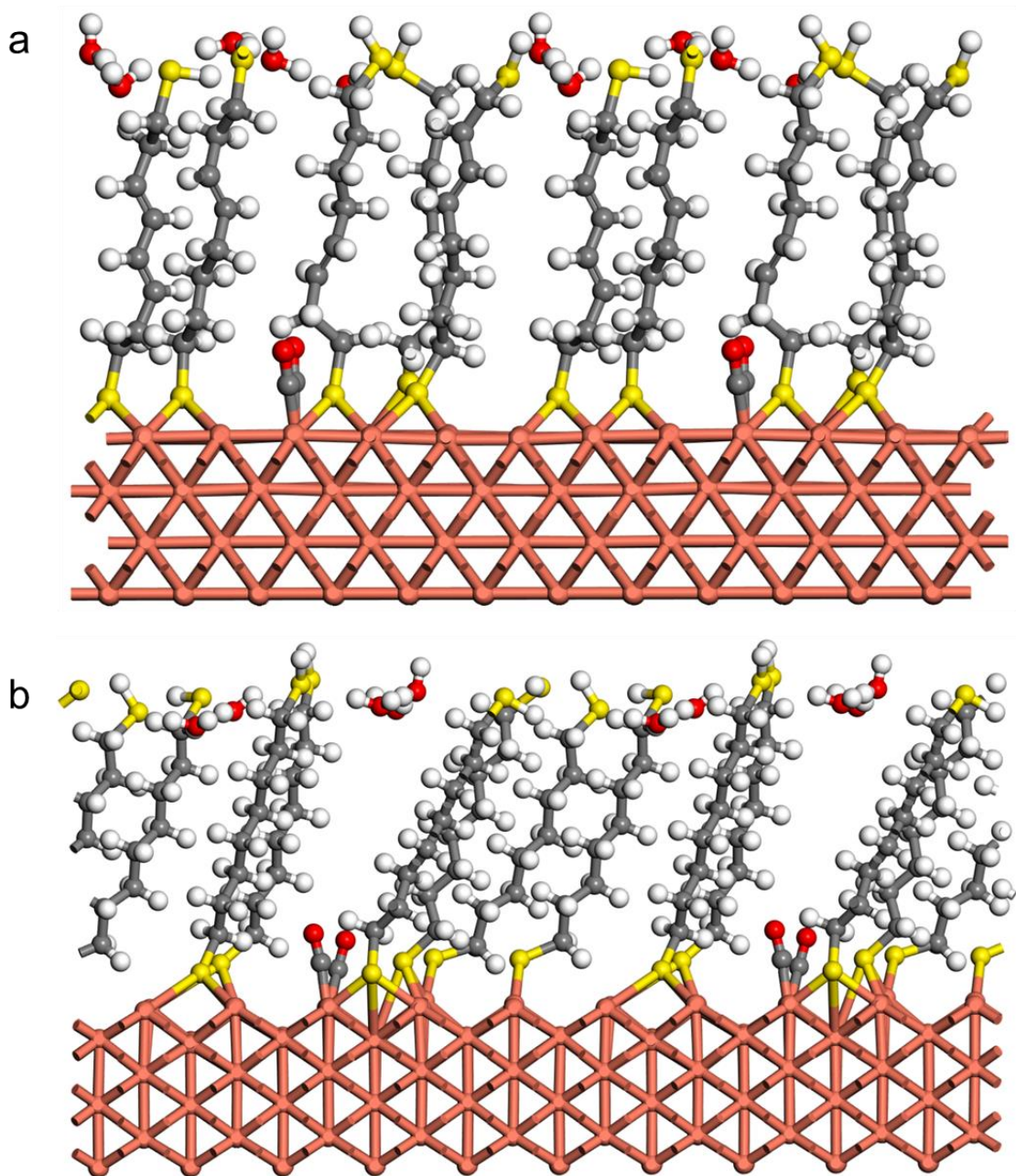


Figure R2. The side views of the 1,8-octanedithiol coordinated on (a) Cu(100) and (b) Cu(110) with H₂O molecules. Atomic color

codes: Cu (brown), S (yellow), C (grey), O (red) and H (white).

4. Please completing the full name of the abbreviations in the manuscript and SI for the kind reading, such as ECFP fingerprints, PEOE Charge, MOE.

Reply and actions taken: We thank the reviewer for the comment and apologize for the difficulty this may have caused in your reading. We have added the full name of the abbreviations in the revised manuscript and Supporting Information, such as 'Extended-Connectivity Fingerprints (ECFP) fingerprints', 'Partial Equalization of Orbital Electronegativities (PEOE) Charge' and 'Molecular operating environment (MOE)'. *(please see the revised manuscript, Page 4, Paragraph 2, Lines 5-6, please see the revised Supporting Information, Pages 2-3)*

5. The pictures in the Figure S21–S23 are quite fuzzy, please rewriting again.

Reply and actions taken: We thank the reviewer for the comment. This is because the image was compressed when converting word to pdf format. We have re-uploaded clearer images in an attachment PDF.

6. In Figure 6(d, e), it missed the figure lettering.

Reply and actions taken: We thank the reviewer for the comment. We have added the figure lettering and updated Figure 6 (d, e) lettering in the revised manuscript. The Figure 6 (d, e) lettering was updated as 'CO stripping of CuO_x, 1,8-octanedithiol-CuO_x and 2-pyridinemethanethiol-CuO_x catalysts' and 'Correlation coefficients and hierarchical clustering results between FE of each CO₂RR product', respectively. *(please see the revised manuscript, Page 11, Figure 6)*

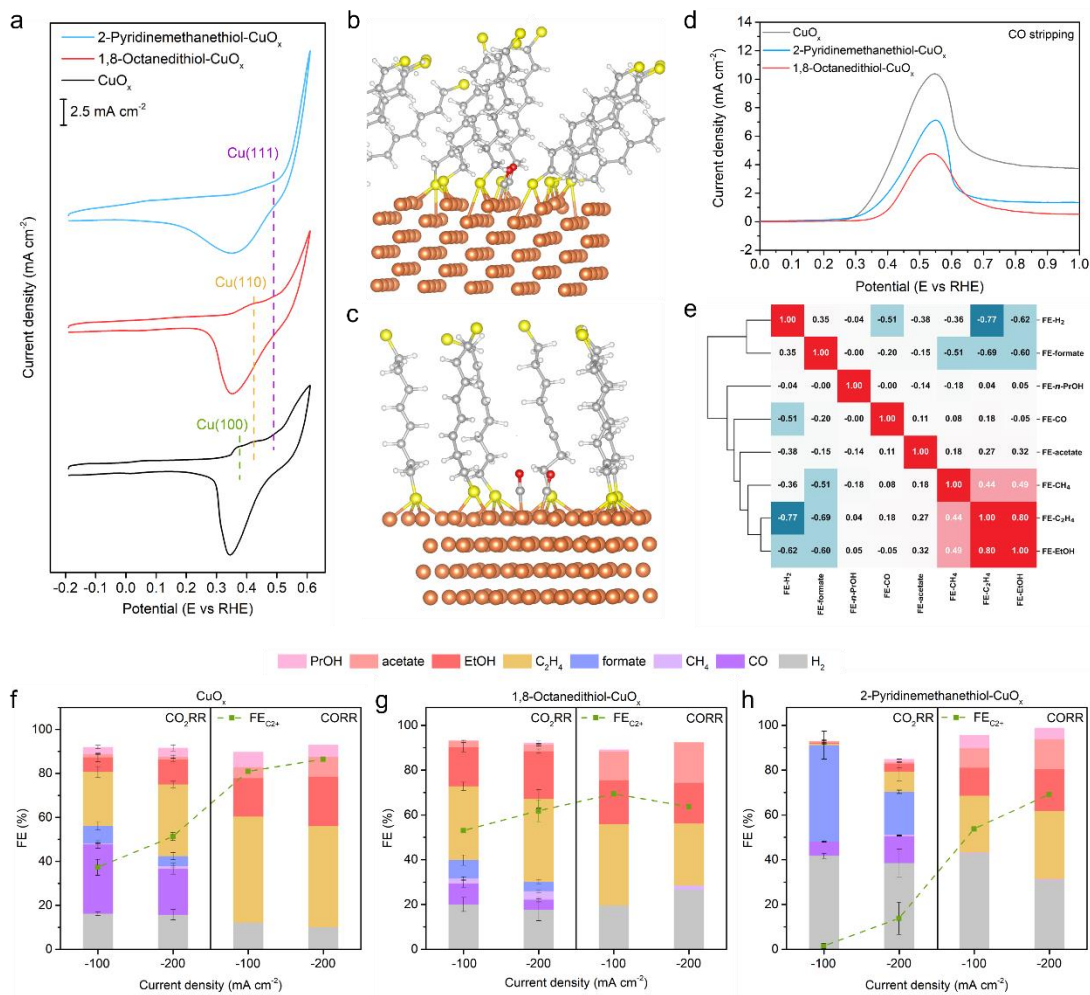


Figure 6. (a) OH⁻ electro-adsorption measurements of CuO_x, 1,8-octanedithiol-CuO_x (current density was magnified 1.5 times) and 2-pyridinemethanethiol-CuO_x catalysts in Ar-saturated 1.0 M KOH after 200 s reduction at -0.69 V vs RHE. (b) The side view of the 1,8-octanedithiol coordinated on Cu(111). (c) The side view of the 1,8-octanedithiol coordinated on Cu(100). Atomic color codes: Cu (brown), S (yellow), C (grey), O (red) and H (white). (d) CO stripping of CuO_x, 1,8-octanedithiol-CuO_x and 2-pyridinemethanethiol-CuO_x catalysts. (e) Correlation coefficients and hierarchical clustering results between FE of each CO₂RR product. Comparison of CO₂RR and CORR product distributions on (f) CuO_x, (g) 1,8-octanedithiol-CuO_x and (h) 2-pyridinemethanethiol-CuO_x catalysts at applied current density of 100 mA cm⁻² and 200 mA cm⁻², respectively.

Reviewer #2 (Remarks to the Author):

Referee Report

Shen et al. investigated the impact of molecular modifiers with N/S/O terminal groups on CuO_x surfaces and their effects on electrochemical CO₂ reduction performance. The authors claim that sulfur-terminal modifiers enhance selectivity towards C₂ products, correlating these effects with changes in the hydrophobicity of the modified electrodes. Additionally, they observed improved ethanol selectivity in some cases, suggesting the formation of a

metal–organic interphase at the electrode surface.

While the study explores an interesting approach, the conclusions appear premature and somewhat speculative, especially when considering the correlation between product selectivity and the physico-chemical properties of the modified electrodes. Given the complexity of the system, with numerous variables at play, the explanations provided are not sufficiently supported by the data, making the key findings less convincing.

In comparison, recent work has shown that molecular catalysts coated on Ni electrodes can achieve ethanol faradaic efficiencies (FE) of up to 70%, attributed to strong coupling between the catalyst and metal surface (<https://doi.org/10.1038/s41929-024-01225-1>). In contrast, the selectivity changes in Shen et al.'s work are attributed to interphase formation, yet the evidence supporting this is not comprehensive or clearly articulated.

Although the authors performed an extensive screening of 180 molecular modifiers and conducted significant product characterization, the study involves too many variables (e.g., chemical structures, morphology of the metal–organic interphase, choice of CuO_x or Cd@CuO_x substrates), which complicates the interpretation of results and weakens the clarity of the discussion. The conclusions about the relationship between selectivity and electrode properties thus remain tentative and unsubstantiated.

Given the above concerns, I cannot recommend the manuscript for publication in its current form. However, I hope the following points will aid the authors in revising the manuscript for potential submission to other journals.

Reply and actions taken: We sincerely thank the reviewer for the valuable feedback provided. We appreciated the opportunity to clarify and expand the contributions of our work. There may be some misunderstanding due to certain unclear expressions in our previous manuscript. We would like to clarify these points:

1. We focus to explore the relationship between different molecular modifiers and product selectivity and search for high performance CO₂-to-EtOH catalysts. Therefore, we did not just focus on the two best ethanol selective catalysts.
2. We have tried to reduce the introduction of multiple variables as much as possible during catalyst preparation, but the complexity of the chemical system is inevitable. Due to the nonlinear and multi-variable interactions in complex systems that are difficult to describe with traditional models, machine learning excels in handling high-dimensional data and uncovering hidden patterns directly from the data, making it highly effective for identifying underlying principles in such systems. We believe that reporting results showing its full complexity is better than only focusing on a specific region of the data that seems to be clearer. Nevertheless,

among this complexity, we discovered the formation of interphase to be critical, which we believe would be a significant contribution to the community.

3. Regarding the issue about the lack of clarity on the causes of interphase formation, we have supplemented a series of experiments, such as spherical aberration electron microscopy, and combined with the results reported in previous literature to further elaborate on our points. Please see below for our detailed responses to the questions.

4. The calculated overall Faradaic efficiency range is 72%-117% with the majority of the samples within the 86%-108% range instead of 65%-78%, which is similar to the previously reported range of 50%-110% (*Angew. Chem. Int. Ed.* **2022**, 61, e202110657, *Nat. Catal.* **2021**, 4, 20-27).

5. The current density for 11 different 1,8-octanedithiol-modified CuO_x catalysts varies from 96-1300 mA cm⁻² because these catalysts were tested on different platforms (AEP and CFC reactors) under different conditions (fixed current or fixed potential) to validate the universality of the modification strategies. These 11 CuO_x substrates were partially sourced from literature and we did not focus on the further optimization of these catalysts in the paper.

Major Concerns:

1. The study introduces too many variables, and the inconsistency in their discussion throughout the manuscript makes it difficult for the reader to follow the correlations. For example, Figure 2 (a-e) presents Faradaic efficiencies (FEs) for 1,8-Octanedithiol on CuO_x, while Figure 2 (f-g) presents FEs for 1,8-Octanedithiol on Cd@CuO_x and Eu@CuO_x, showing the best ethanol selectivity. However, these promising results are not discussed further in subsequent sections, leading to incomplete coverage of key data.

Reply and actions taken: We thank the reviewer for this insightful comment. While developing a catalyst with superior CO₂RR performance is valuable, our main focus in this paper is to investigate the effect of different molecular modifiers. As a result, we selected CuO_x, which is the simplest substrate, for the majority of the study.

Interestingly, the promoting modifier 1,8-octanedithiol found on CuO_x can also promote CO₂-to-EtOH activity of another 11 Cu-based substrates including the Cd@CuO_x and Eu@CuO_x, which showed the best ethanol selectivity. This is what is presented in Figure 2f, and we think this is a significant strength of our paper. This shows that the promoting effect of S-containing modifiers is an intrinsic effect. For Figure 2g, we are comparing the performance of our catalysts to literature reports. We have modified the figures to make them clearer to

avoid the misunderstanding by the reviewer. The original Figure 2 is split into Figure 2 and Figure 7 in the revised manuscript, which illustrate the reliability of the automated platform test data (Figure 2) and the universality of the modification strategy together with the comparison of the optimization results of catalyst performance (Figure 7), respectively.

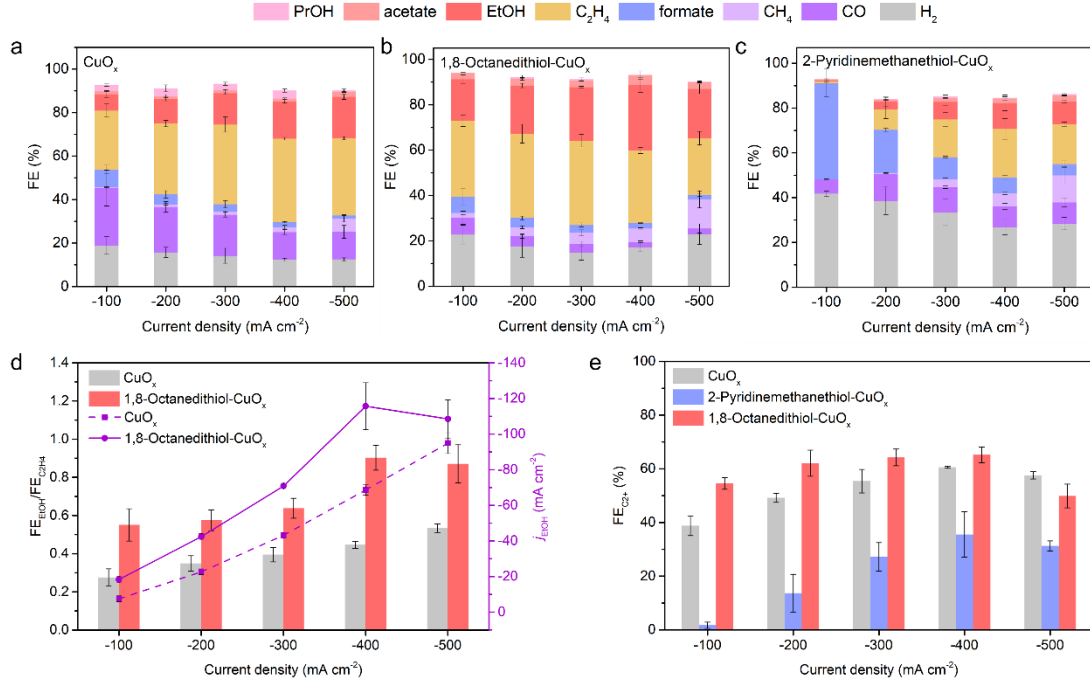


Figure 2. FEs for all products over (a) CuO_x catalyst, (b) 1,8-octanedithiol-CuO_x catalyst, and (c) 2-pyridinemethanethiol-CuO_x catalyst. (d) The ratio of faradaic efficiencies of ethanol and ethylene (FE_{EtOH}/FE_{C₂H₄}) and partial ethanol current density of CuO_x and 1,8-octanedithiol-CuO_x. (e) The C₂+ FE plots of CuO_x, 1,8-octanedithiol-CuO_x, and 2-pyridinemethanethiol-CuO_x catalysts. The experiments at all the applied current density were performed at least three times and the results were displayed as mean ± standard deviation.

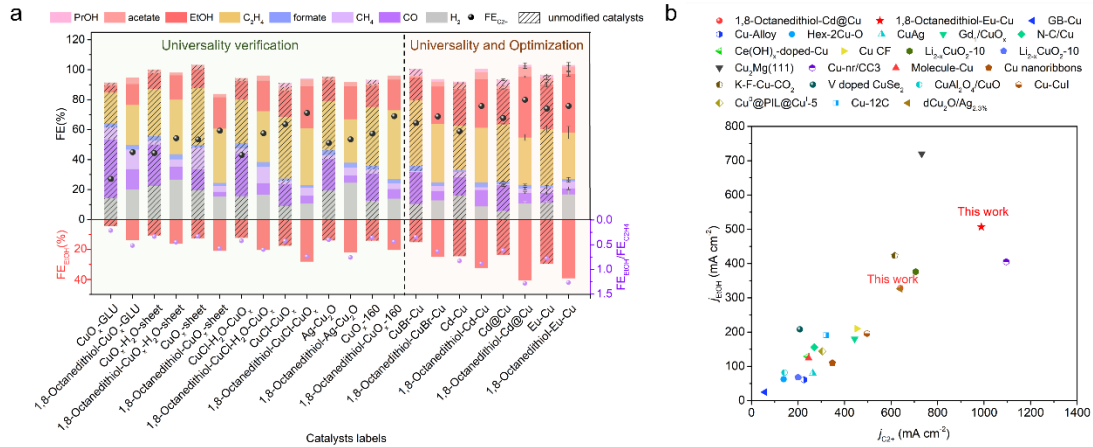


Figure 7. (a) The 1,8-octanedithiol functionalization approach verified on diverse oxide derived Cu substrates synthesized by 11 methods and the optimized CO₂-to-EtOH/C₂+ performance. (b) Comparison of CO₂RR-to-EtOH/C₂+ with state-of-the-art Cu-based catalysts reported recently in 1.0 M KOH flow cell.

It is worth noting that when examining the CO₂RR product distribution in Figures 2(a-e) and 7(a-b), we find that regardless of the CuO_x substrate, a similar pattern for 1,8-octanedithiol modification emerges: reduced FE_{CO}, enhanced ethanol selectivity, and slight increase in FE_{H₂} and FE_{CH₄}. This consistency across substrates with different structures suggests a likely shared reaction pathway. We therefore believe that the CO₂-to-EtOH mechanism proposed in this work is commonly applicable to these different catalysts listed in Figure 7.

The reviewers suggested us to perform more analysis on the modified Cd@CuO_x and Eu@CuO_x catalysts. We agree that further exploration of these catalysts would be highly valuable. Following the suggestion, we analyzed the contact angle, XRD, TEM, EDX mapping, OH⁻ adsorption and XPS data of Cd@CuO_x and Eu@CuO_x with or without 1,8-octanedithiol.

The XRD patterns (Figure R3) demonstrated that the Cd@CuO_x catalysts mainly consisted of CuO and the Eu@CuO_x catalysts consisted of CuO and Cu₂O. The modification of 1,8-octanedithiol on both Cd@CuO_x and Eu@CuO_x catalysts did not change the phase, which was consistent with the results of 1,8-octanedithiol-modified CuO_x in this work.

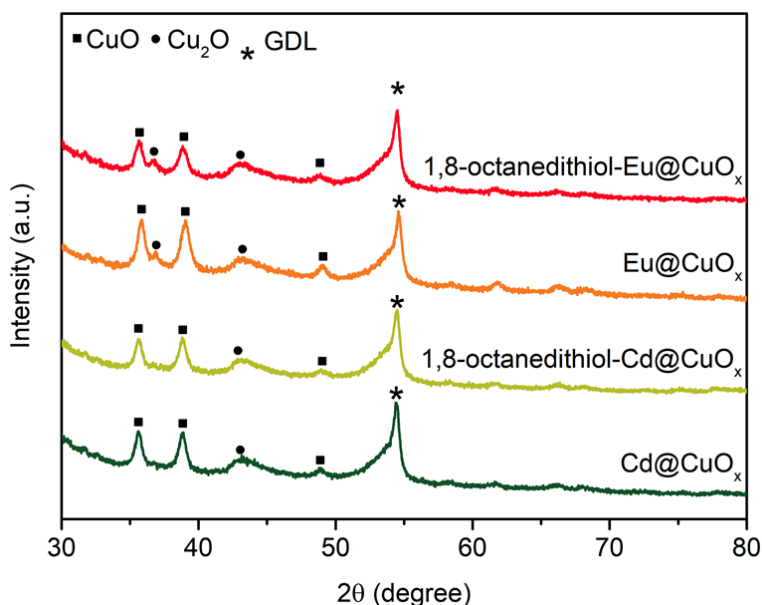


Figure R3. XRD patterns of as prepared Cd@CuO_x, 1,8-octanedithiol-Cd@CuO_x, Eu@CuO_x and 1,8-octanedithiol-Eu@CuO_x catalysts.

The contact angle measurement shown in Figure R4 indicated that the functionalization of 1,8-octanedithiol on both Cd@CuO_x and Eu@CuO_x catalysts did not change the hydrophobicity / hydrophilicity of electrodes, which was also consistent with the contact angle results of 1,8-octanedithiol-modified CuO_x in this work.

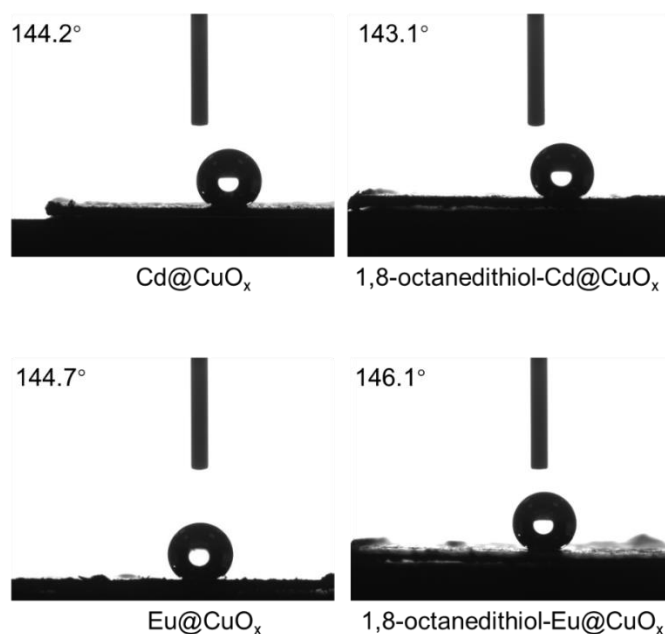


Figure R4. Contact angles of as prepared Cd@CuO_x, 1,8-octanedithiol-Cd@CuO_x, Eu@CuO_x and 1,8-octanedithiol-Eu@CuO_x catalysts.

Similar to the OH⁻ electro-adsorption measurements results of 1,8-octanedithiol-CuO_x, 1,8-octanedithiol on Eu@CuO_x catalysts and Cd@CuO_x catalysts also selectively exposed the Cu(110) as main electrochemical facet and inhibited the Cu(100) facets, although the electrochemical facets compositions of Eu@CuO_x and Cd@CuO_x catalysts are slightly different (Figure R5).

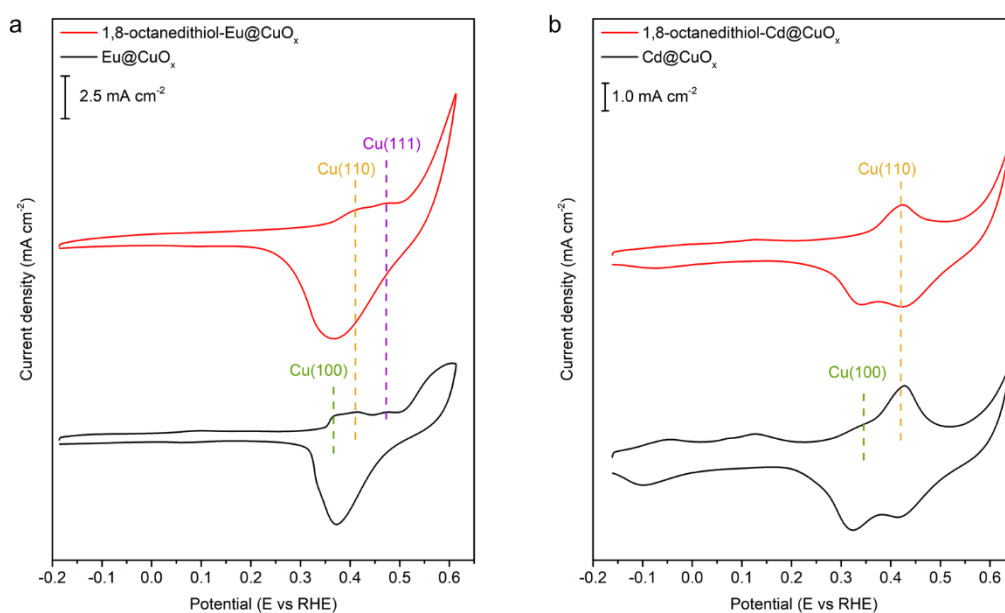


Figure R5. OH^- electro-adsorption measurements of (a) Eu@CuO_x and 1,8-octanedithiol- Eu@CuO_x catalysts, (b) Cd@CuO_x and 1,8-octanedithiol- Cd@CuO_x catalysts in Ar-saturated 1.0 M KOH after 200 s reduction at -0.69 V vs RHE.

The TEM image and EDX mapping results of Cd@CuO_x catalyst (Figure R6) indicated that Cd species distributed throughout the catalysts.

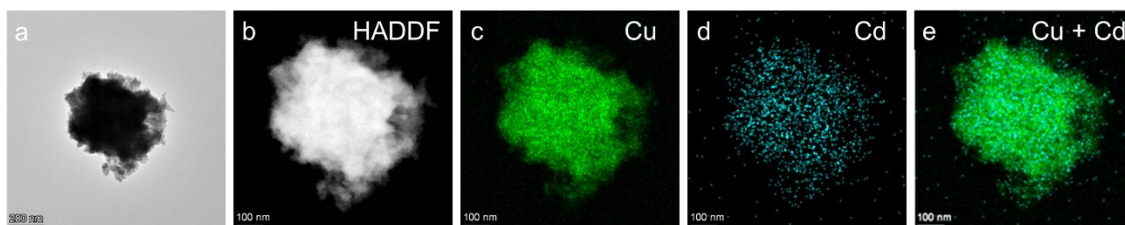


Figure R6. (a) TEM image of Cd@CuO_x catalyst. (b) HAADF image of Cd@CuO_x catalyst and corresponding EDX mapping elements images of (c) Cu, (d) Cd and (e) Cu and Cd overlapping.

The TEM image and EDX mapping results of Eu@CuO_x catalyst (Figure R7) indicated that Eu species distributed on the surface of Cu. The Eu@CuO_x catalyst is spindle-shaped.

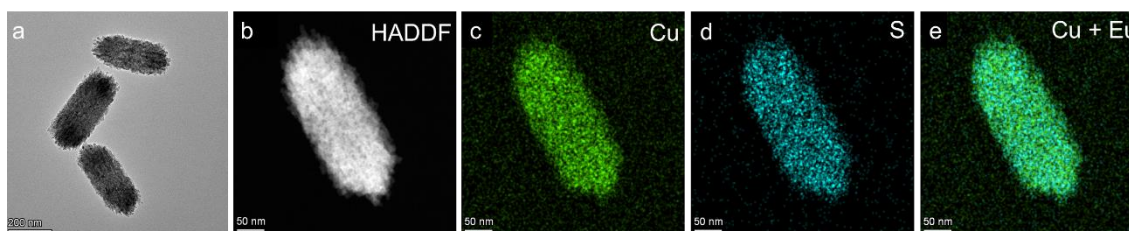


Figure R7. (a) TEM image of Eu@CuO_x catalyst. (b) HAADF image of Eu@CuO_x catalyst and corresponding EDX mapping elements images of (c) Cu, (d) Eu and (e) Cu and Eu overlapping.

The TEM images and EDX mapping results of 1,8-octanedithiol- Cd@CuO_x catalyst (Figure R8) demonstrated that the modification of 1,8-octanedithiol on Cd@CuO_x does not affect the existence of Cd species. Similar to the 1,8-octanedithiol modification on CuO_x , a metal-organic interphase of > 10 nm is also formed.

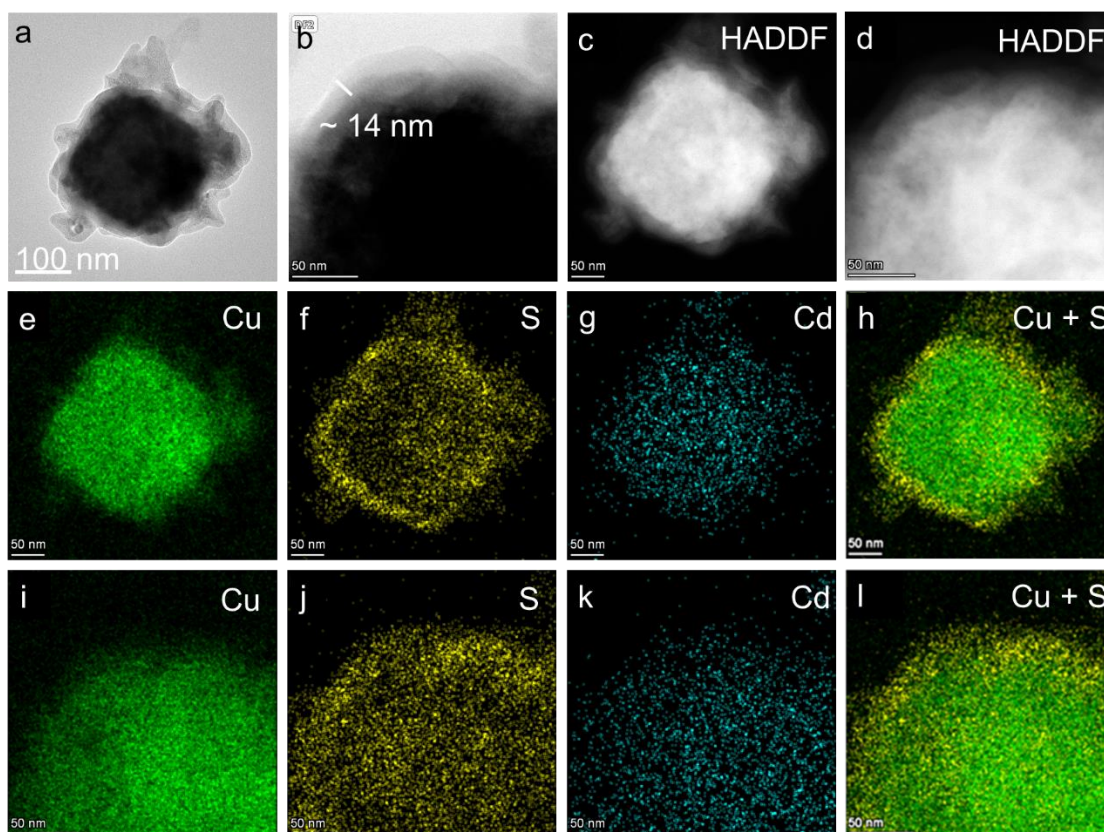


Figure R8. (a-b) TEM images of 1,8-Octanedithiol-Cd@CuO_x catalyst. (c-d) HAADF image of 1,8-octanedithiol-Cd@CuO_x catalyst. Corresponding EDX mapping elements images of (d) Cu, (e) S, (f) Cd and (g) Cu and S overlapping on (c). Corresponding EDX mapping elements images of (i) Cu, (j) S, (k) Cd and (l) Cu and S overlapping on (d).

The TEM images and EDX mapping results of 1,8-octanedithiol-Eu@CuO_x catalyst (Figure R9) demonstrated that the modification of 1,8-octanedithiol on Eu@CuO_x would reduce the signal intensity of marginal Eu species compared with that of Eu@CuO_x catalysts. Similar to the 1,8-octanedithiol modification on CuO_x, a metal-organic interphase of > 10 nm is also formed (Figure R9b).

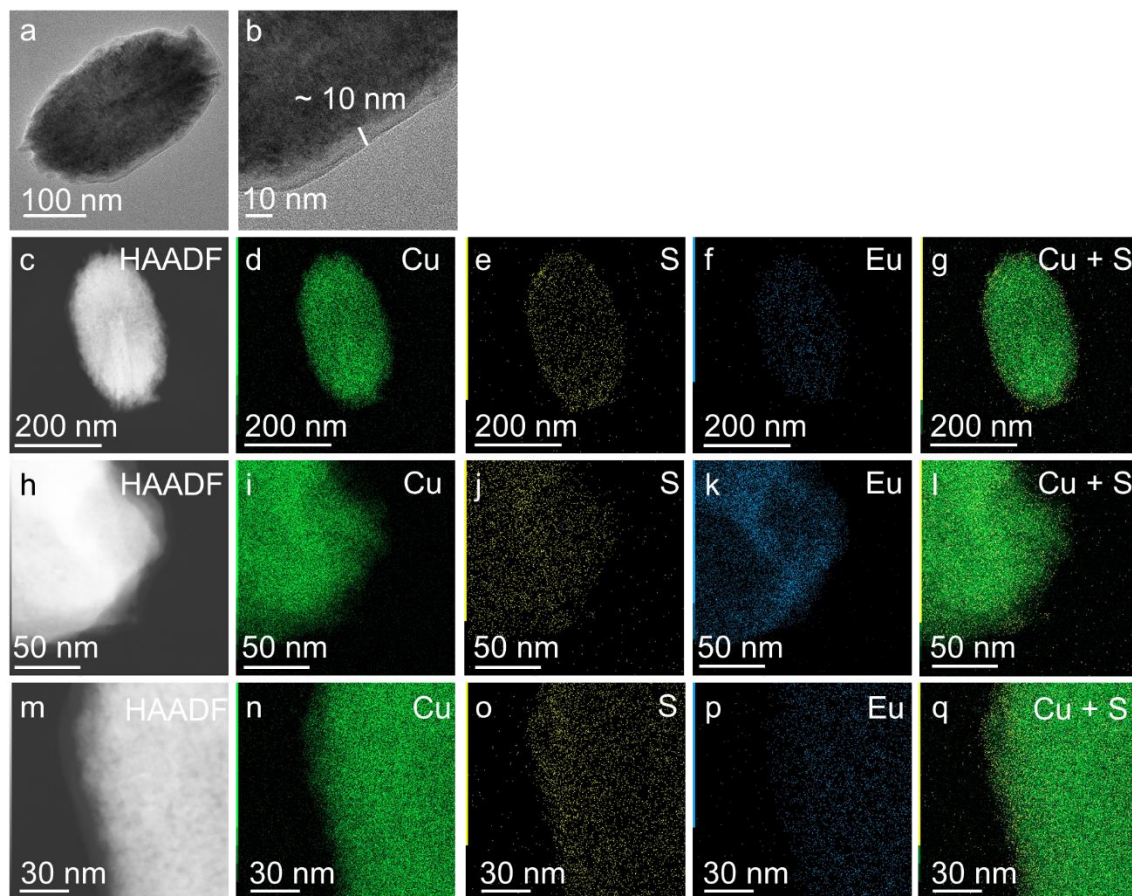


Figure R9. (a-b) TEM images of 1,8-Octanedithiol-Eu@CuO_x catalyst. (c) HAADF image of 1,8-octanedithiol-Eu@CuO_x catalyst and corresponding EDX mapping elements images of (d) Cu, (e) S, (f) Eu and (g) Cu and S overlapping. (h) HAADF image of 1,8-octanedithiol-Eu@CuO_x catalyst and corresponding EDX mapping elements images of (i) Cu, (j) S, (k) Eu and (l) Cu and S overlapping. (m) HAADF image of 1,8-octanedithiol-Eu@CuO_x catalyst and corresponding EDX mapping elements images of (n) Cu, (o) S, (p) Eu and (q) Cu and S overlapping.

As shown in Figures R10-R11, X-ray photoelectron spectroscopy (XPS) measurements showed that modification with 1,8-octanedithiol converted most Cu^{II} (Cu 2p_{3/2} at 933.9 eV, Cu LMM at 568.9 eV) in Cd@CuO_x catalyst to Cu^I on 1,8-octanedithiol-Cd@CuO_x catalyst (Cu 2p_{3/2} at 932.7 eV, Cu LMM at 570.5 eV). The Cd species are mainly distributed on the Cd@CuO_x catalyst surface in divalent form with or without 1,8-octanedithiol modification. Additionally, S 2p spectra (Figure R11d) confirmed the presence of metal-bound (Cu^I-S bonds) thiol (S 2p_{3/2} at 162.4 eV), unbound thiol (S 2p_{3/2} at ~164 eV) and oxidized sulfur (S 2p_{3/2} at ~168-169 eV) on 1,8-octanedithiol-Cd@CuO_x catalyst.

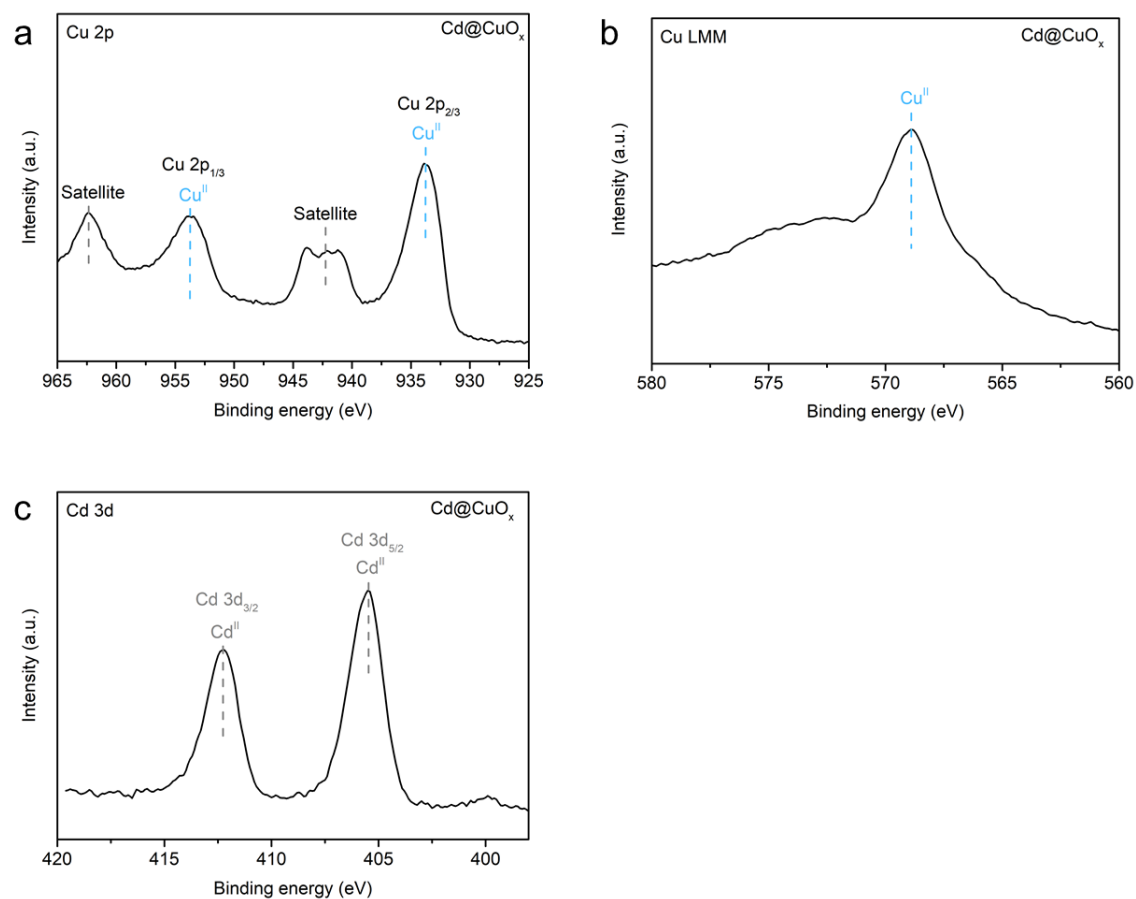


Figure R10. (a) XPS spectra of Cu 2p of as prepared Cd@CuO_x catalysts. (b) XPS spectra of Cu LMM of as prepared Cd@CuO_x catalysts. (c) XPS spectra of Cd 3d of as prepared Cd@CuO_x catalysts.

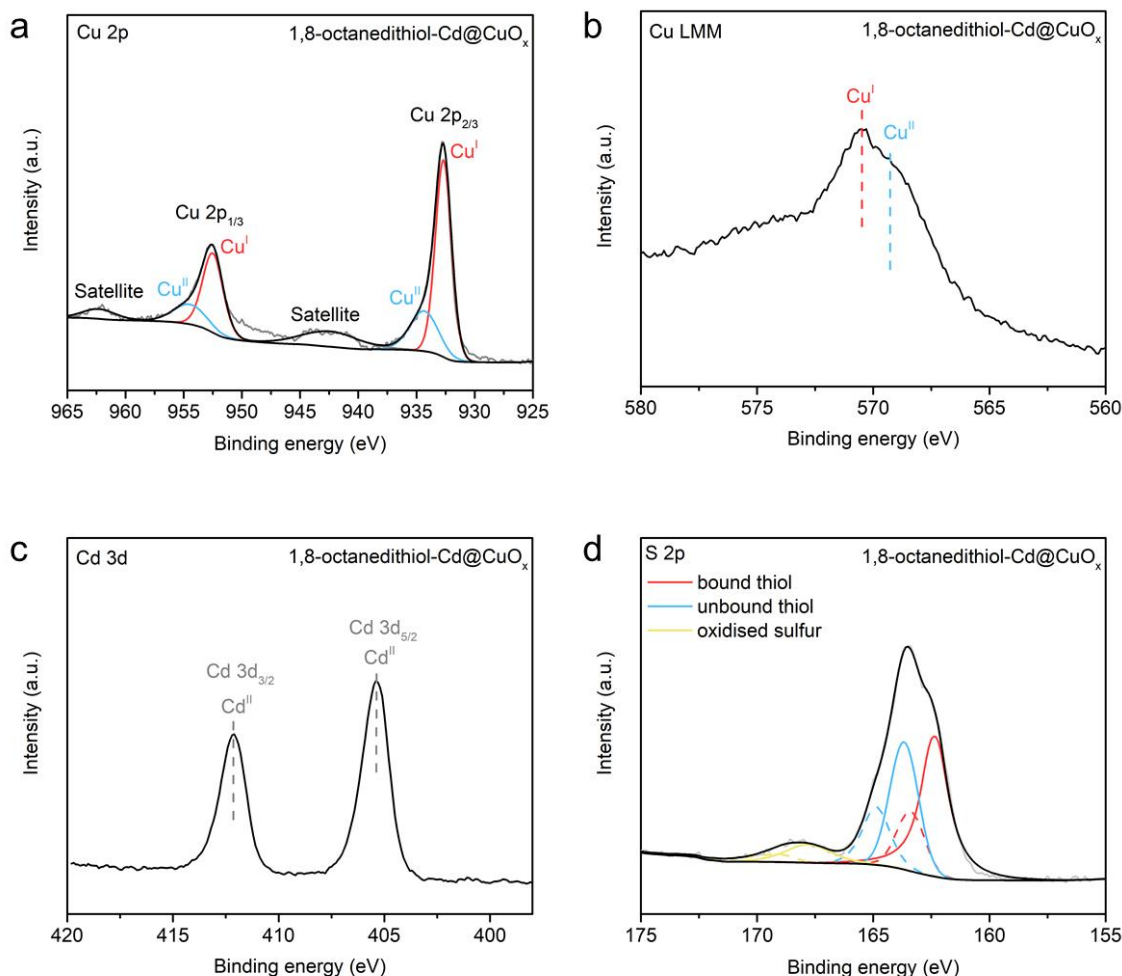


Figure R11. (a) XPS spectra of Cu 2p of as prepared 1,8-octanedithiol-Cd@CuO_x catalysts. (b) XPS spectra of Cu LMM of as prepared 1,8-octanedithiol-Cd@CuO_x catalysts. (c) XPS spectra of Cd 3d of as prepared 1,8-octanedithiol-Cd@CuO_x catalysts. (d) XPS spectra of S 2p (The solid line represents S 2p_{3/2}, the dashed line represents S 2p_{1/2}) of as prepared 1,8-octanedithiol-Cd@CuO_x catalysts.

As shown in Figures R12-R13, X-ray photoelectron spectroscopy (XPS) measurements showed that modification with 1,8-octanedithiol converted Cu^{II} (Cu 2p_{3/2} at 933.7 eV, Cu LMM at 568.6 eV) in Eu@CuO_x catalyst to Cu^I on 1,8-octanedithiol-Eu@CuO_x catalyst (Cu 2p_{3/2} at 932.6 eV, Cu LMM at 570.4 eV). The Eu species are in trivalent form with or without 1,8-octanedithiol modification. Additionally, S 2p spectra (Figure R13d) confirmed the presence of metal-bound (Cu^I-S bonds) thiol (S 2p_{3/2} at 162.2 eV), unbound thiol (S 2p_{3/2} at ~164 eV) and oxidized sulfur (S 2p_{3/2} at ~168-169 eV) on 1,8-octanedithiol-Eu@CuO_x catalyst. It can also be observed that the modification of 1,8-octanedithiol reduces the signal-to-noise ratio of the Eu 3d XPS spectrum (Figure R12c and Figure R13c), which is consistent with the result that the Eu element signal in EDX becomes weaker after 1,8-octanedithiol modification on Eu@CuO_x catalyst (Figure R9).

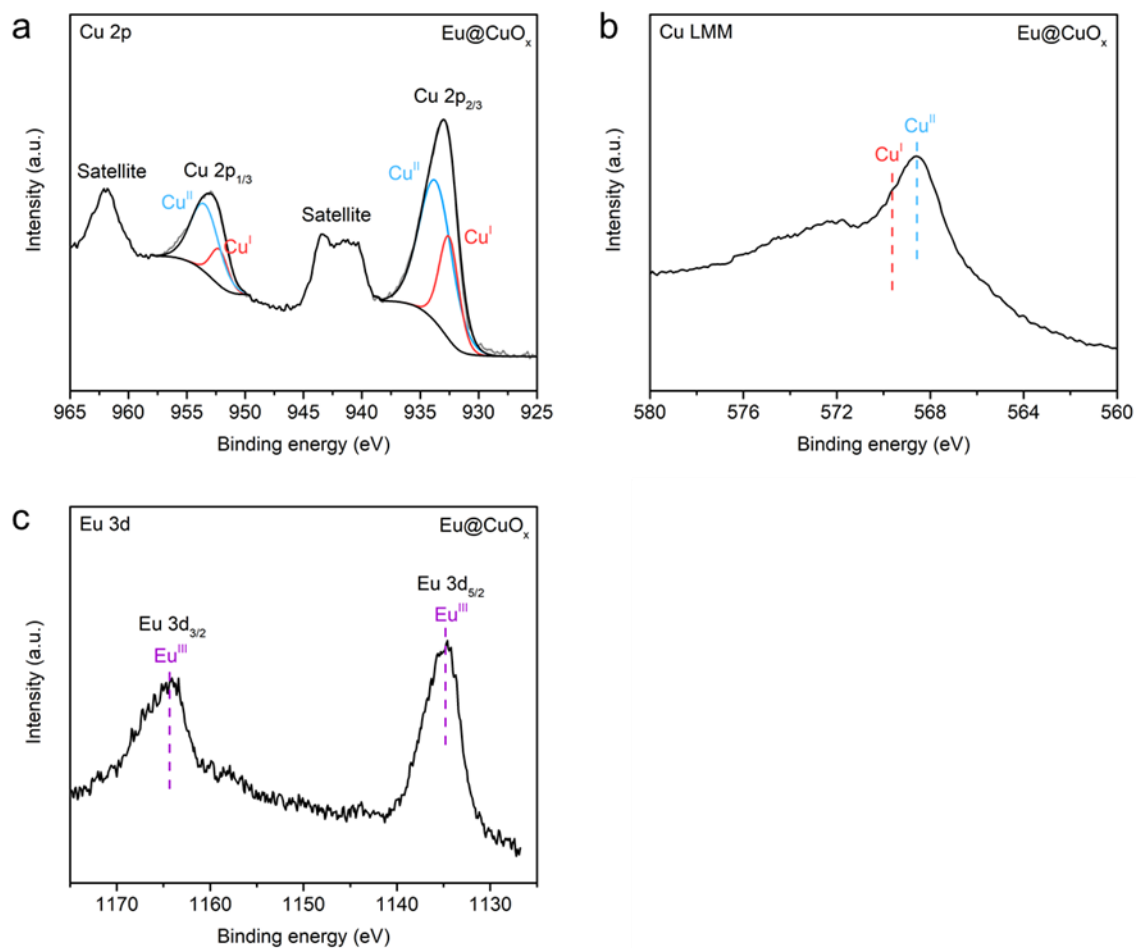


Figure R12. (a) XPS spectra of Cu 2p of as prepared Eu@CuO_x catalysts. (b) XPS spectra of Cu LMM of as prepared Eu@CuO_x catalysts. (c) XPS spectra of Eu 3d of as prepared Eu@CuO_x catalysts.

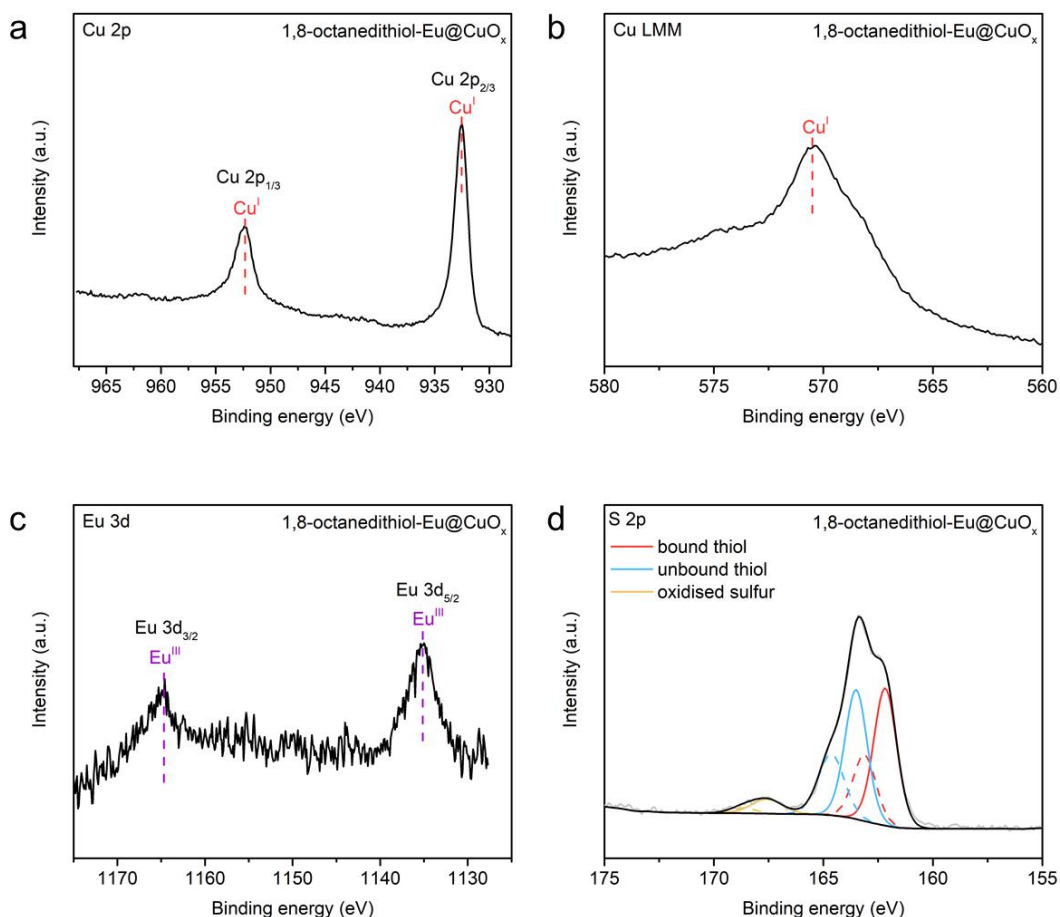


Figure R13. (a) XPS spectra of Cu 2p of as prepared 1,8-octanedithiol-Eu@CuO_x catalysts. (b) XPS spectra of Cu LMM of as prepared 1,8-octanedithiol-Eu@CuO_x catalysts. (c) XPS spectra of Eu 3d of as prepared 1,8-octanedithiol-Eu@CuO_x catalysts. (d) XPS spectra of S 2p (The solid line represents S 2p_{3/2}, the dashed line represents S 2p_{1/2}) of as prepared 1,8-octanedithiol-Eu@CuO_x catalysts.

We have modified the relevant sentences and added the following content in the revised manuscript: “

Applying 1,8-octanedithiol to Other CuO_x-based Catalysts

We further used the discovered 1,8-octanedithiol modifier to treat 11 different CuO_x-based CO₂RR catalysts to boost ethanol production on these catalysts. Some of these CuO_x-based catalysts were synthesized according to literature reports,^{25,72-75} while others were synthesized using our own methods (detailed synthesis methods are listed in the Supporting Information). Interestingly, the 1,8-octanedithiol modifier enhanced FE_{EIOH} and FE_{C2+}, as well as the FE_{C2H4}/FE_{EIOH} ratio, in all of them, indicating a general promoting effect (Figure 7a, Table S22). Notably, the promotion of Cd-modified CuO_x (Cd@Cu) and Eu-modified CuO_x (Eu-Cu) achieved 80% FE_{C2+} (j_{C2+} = 640 mA cm⁻²) with j_{EIOH} of 328 mA cm⁻² at -0.77 V vs RHE and 76% FE_{C2+} (j_{C2+} = 988 mA cm⁻²) with j_{EIOH} of 507 mA cm⁻² at -0.85 V vs RHE, respectively, which

are comparable or better than recently reported state-of-the-art performance of CO₂-to-EtOH/C₂₊ conversion using Cu-based electrocatalysts (Figure 7b and Table S23).

We also conducted characterizations on Cd@CuO_x and Eu@CuO_x catalysts with or without 1,8-octanedithiol modification. The modification of 1,8-octanedithiol did not change the phase structure (Figure S73) or electrode surface hydrophilicity/hydrophobicity (Figure S74) of Cd@CuO_x and Eu@CuO_x catalysts. Although the electrochemical facets compositions of Eu@CuO_x and Cd@CuO_x catalysts are slightly different, the selectively exposed Cu(110) electrochemical facet on 1,8-octanedithiol-Eu@CuO_x and 1,8-octanedithiol-Cd@CuO_x can be clearly observed in the OH electro-adsorption measurement (Figure S75). Importantly, the modification also formed > 10 nm metal-organic interphase (Figures S76-S79). The XPS results of these two optimal CO₂-to-EtOH catalysts demonstrated the conversion of Cu^{II} to Cu^I after 1,8-octanedithiol modification and the presence of Cu^I-S bonds (Figures S80-S83).” ***(please see the revised manuscript, Pages 11-12, Paragraphs 1-2)***

We have also added the Figures R3-R13 as Figures S73-S83 in the revised Supporting Information. ***(please see the revised Supporting Information, Pages 84-97)***

2. The reported current densities vary significantly across samples, from 96 to 1300 mA cm⁻², raising concerns about the consistency of the fabrication methods used, particularly the loading amount of CuO_x catalysts. This large variation undermines the reliability of the comparisons between samples, as it suggests significant differences in catalyst preparation that are not adequately controlled for.

Reply and actions taken: We thank the reviewer for the insightful comment. The issues raised are based on the experimental results in Table S1. However, the current density ranging from 96 to 1300 mA cm⁻² is not an issue at all, as they were obtained from different catalysts tested at various negative potentials. Each catalyst has its own optimal CO₂ reduction reaction (CO₂RR) potential window and corresponding current density. Data obtained on our automated platform (referred to as the AEP reactor) and manually on a commercial flow cell (referred to as the CFC reactor) may also be slightly different. Besides that, some of the data were obtained using a fixed current density approach, while others were obtained using a fixed potential.

The reason for such diversity is because some catalysts were obtained based on literature reports and we modified them with 1,8-octanedithiol to test the universal ability for the modifier to promote ethanol production. As a result, we basically followed the different testing condition reported in literature. In the revised paper, we added the referred literature source and whether the test was using fixed current densities or fixed voltages with their ranges in the updated

Table S22 (originally Table S1) in the revised Supporting Information. *(please see the revised Supporting Information, Page 148, Table S22)* To reduce the concern from the reviewer, we also added some measurements of these catalysts on different platforms in the updated Table S22. These data are quite reproducible. We did not focus on the further optimization of these catalysts in the paper.

Table S22. CO₂RR test conditions of catalysts used in universality verification of 1,8-octanedithiol functionalization and product distribution information. The abbreviation 'AEP' stands for being tested on 'Automated Electrolysis Platform' and the abbreviation 'CFC' stands for being tested on 'Commercial Flow Cell' in 'Reactor' column. The data of CuO_x-H₂O-sheet and 1,8-Octanedithiol-CuO_x-H₂O-sheet tested on CFC, Cd-Cu and 1,8-Octanedithiol-Cd-Cu tested on AEP was not presented in Figure 7a.

Cat.	E (V vs RHE)	j_{total} (mA cm ⁻²)	FE (%)										Reactor	Ref.	Test conditions in ref.
			H ₂	CO	CH ₄	formate	C ₂ H ₄	EtOH	acetate	PrOH	C ₂				
CuO _x -GLU	-0.62	100	14	39	8	3	21	4	2	0	27	AEP	Nat Commun 2023, 14, 501.	Fixed applied potentials ranging from -0.45 V to -0.78 V vs RHE	
1,8-Octanedithiol-CuO _x -GLU	-0.62	102	20	14	13	3	27	14	4	0	45	AEP			
CuO _x -H ₂ O-sheet	-0.62	118	22	28	3	3	32	11	2	0	44	AEP			
1,8-Octanedithiol-CuO _x -H ₂ O-sheet	-0.62	105	27	9	5	3	36	16	2	0	54	AEP	Adv. Funct. Mater. 33, 2214946 (2023)	Fixed applied potentials ranging from -0.4 V to -1.6 V vs RHE	
CuO _x -H ₂ O-sheet	-1.0	500	17	12	5	2	34	15	4	1	54	CFC			
1,8-Octanedithiol-CuO _x -H ₂ O-sheet	-1.0	400	12	5	4	2	35	21	2	2	60	CFC			
CuO _x -sheet	-0.69	150	19	14	14	2	38	13	3	0	53	AEP	Cryst. Res. Technol. 44, 721- 724 (2009).	None	
1,8-Octanedithiol- CuO _x -sheet	-0.69	138	15	3	4	2	36	21	2	0	59	AEP			
CuCl-H ₂ O-CuO _x	-0.69	165	16	29	3	4	29	12	2	0	43	AEP			
1,8-Octanedithiol- CuCl-H ₂ O-CuO _x	-0.69	138	17	8	11	3	34	20	3	0	58	AEP			
CuCl-CuO _x	-0.95	800	9	15	2	2	41	18	2	2	64	CFC			
1,8-Octanedithiol-CuCl-CuO _x	-1.17	800	11	5	5	2	38	28	5	1	71	CFC	Nat. Commun. 13, 3754 (2022).	Fixed current density ranging from ~200 to ~800 mA cm ⁻² with applied potentials ranging from ~-0.6 V to -0.9 V vs RHE	
Ag-Cu ₂ O	-0.62	114	19	21	3	3	33	14	2	0	49	AEP			
1,8-Octanedithiol-Ag-Cu ₂ O	-0.62	96	25	5	5	3	29	22	3	0	54	AEP			
CuO _x -160	-0.69	156	13	18	3	2	39	14	1	2	57	AEP	Angew. Chem. Int. Ed. 2022, 61, e202213423.	Fixed current density ranging from ~100 to ~800 mA cm ⁻² with applied potentials ranging from -0.54 V to -1.1 V vs RHE	
1,8-Octanedithiol-CuO _x -160	-0.69	144	14	6	4	3	46	20	3	0	69	AEP			
CuBr-Cu	-1.47	800	10	21	1	4	44	15	1	5	65	CFC	None	None	
1,8-Octanedithiol-CuBr-Cu	-1.31	800	13	6	3	2	39	25	3	2	69	CFC			
Cd-Cu	-0.69	800	16	12	4	1	30	24	4	1	59	CFC			
1,8-Octanedithiol- Cd-Cu	-0.66	800	9	11	2	3	37	32	5	2	76	CFC			
Cd-Cu	-0.58	116	17	32	1	3	34	10	4	0	46	AEP			
1,8-Octanedithiol-Cd-Cu	-0.58	100	21	12	5	4	33	21	5	0	57	AEP			
Cd@Cu	-0.77	800	6	18	0	2	38	24	2	4	68	CFC			
1,8-Octanedithiol-Cd@Cu	-0.77	800	11	7	3	2	32	41	6	1	80	CFC			
Eu-Cu	-0.87	1300	11	7	4	1	38	30	4	2	74	CFC			
1,8-Octanedithiol-Eu-Cu	-0.85	1300	17	4	5	2	31	39	5	1	76	CFC			

3. The total FEs listed in Table S23 range from 65% to 78%, whereas the FEs presented in Figure 2 exceed 90%. This discrepancy requires an explanation, as it suggests potential inconsistencies in the reported data or issues with measurement accuracy that must be addressed.

Reply and actions taken: There must be some misunderstanding regarding Table S23. We did not have a column of total FEs in Table S23 in the previous version of the paper but only provided FEs of different products. The summation of the FEs different products did not fall into the 65% to 78% region either. Now we added the FE_{total} column as a sum of the FEs of different products and presented the updated table as Table S24 in the revised Supporting Information. The FE_{total} ranges from 72% to 117% with the majority of the samples within the 86%-108% range (Figure R14). We think this is an acceptable range. It is not uncommon for total Faradaic efficiency to deviate from 100%. Certain CO_2RR products may not be detectable via the GC or NMR setups (for example, oxalate), and intense H_2 production may divert some gas products at the liquid outlet of the flow cell. In the literature currently reported, the total Faradaic efficiency ranges from ~110% to ~50%, (summarized from reports of '*Angew. Chem. Int. Ed.* **2022**, 61, e202110657, *Nat. Catal.* **2021**, 4, 20-27.' papers), which is similar to our reported range.

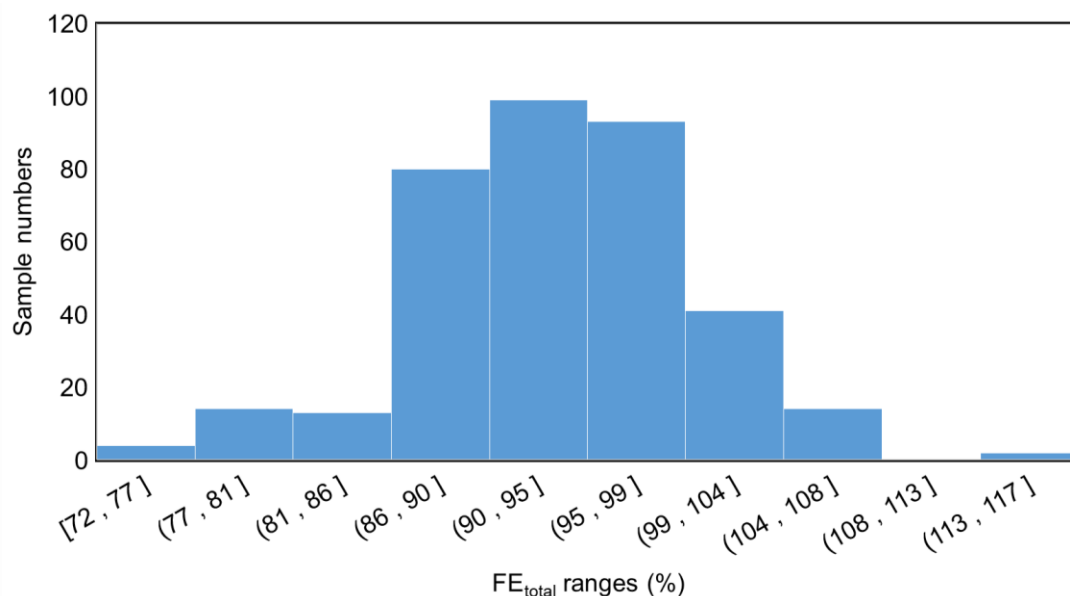


Figure R14. Histogram of the total Faradaic efficiency data in Table S23.

Table S24. The high-throughput screening data of 180 molecules modifying CuO_x electrocatalysts measured on the automatic platform.

*Individual test FE

**Average FE of three individual test

Molecules modifiers	E (V vs RHE)	j (mA cm ⁻²)		FE _{H2} (%)		FE _{CO} (%)		FE _{CH4} (%)		FE _{C2H4} (%)		FE (%)						total
		i*	a**	i*	a**	i*	a**	i*	a**	i*	a**	acet ate	form ate	EtO H	n- PrO H	C ₂ .		
Glyphosate	-0.56	56		15		29		0		13								
		63	61	19	18	27	28	0	0	12	12	5	2	6	0	20	72	
		63		20		29		1		12								
	-0.62	92		20		25		3		17								
		91	91	18	19	21	24	3	3	14	16	4	2	10	0	27	78	
		89		19		24		3		15								
2,2'-Bipyridine- 4,4'-dicarboxylic acid	-0.56	66		23		20		2		16								
		67	67	23	23	21	21	2	2	15	15	6	1	13	0	29	81	
		67		23		21		2		14								
	-0.62	89		22		19		6		18								
		87	87	21	21	19	19	5	6	18	16	3	1	11	2	29	72	
		84		21		19		6		10								
Dimethylglyoxime	-0.56	54		21		36		0		9								
		57	56	20	21	42	40	0	0	10	10	5	3	2	0	15	78	
		57		21		42		0		10								
	-0.62	82		21		31		1		13								
		82	83	22	21	34	32	1	1	13	13	8	2	3	0	18	81	
		85		21		32		2		13								
2,2'-Bipyridine	-0.56	68		28		25		0		11								
		70	70	31	29	28	27	0	0	10	10	7	2	3	5	20	83	
		72		30		28		0		10								
	-0.62	99		28		23		1		15								
		98	98	27	27	25	23	1	1	15	14	4	1	8	0	23	78	
		98		25		20		1		13								
Risedronic acid	-0.56	69		15		24		0		18								
		74	73	18	17	30	28	0	0	14	15	5	2	6	0	22	73	
		75		18		30		0		13								
	-0.62	105		21		20		2		19								
		105	105	20	20	19	19	2	2	17	17	4	2	13	3	34	78	
		104		19		18		2		15								
4,5- Imidazoledicarbox ylic acid	-0.56	77		10		32		0		19								
		85	83	12	13	34	34	0	0	13	15	5	1	6	0	23	75	
		86		16		35		1		14								
	-0.62	110		24		22		2		19								
		120	116	20	21	23	23	3	3	21	20	3	2	6	0	28	78	
		119		20		23		3		21								
4- (Diphenylamino)p henylboronic acid	-0.56	55		12		22		0		23								
		60	59	16	15	24	24	0	0	19	19	5	2	7	0	28	72	
		62		18		25		0		17								
	-0.62	93		18		18		1		24								
		94	93	19	19	18	18	2	2	22	23	4	2	10	3	37	80	
		93		19		18		2		22								
[4-(4- phosphonophenyl)phenyl]phosphoni c acid	-0.56	79		33		6		0		21								
		76	76	36	35	7	6	0	0	20	20	8	2	8	0	29	80	
		73		38		7		1		19								
	-0.62	120		30		9		1		24								
		116	116	28	29	8	8	1	1	25	25	8	1	9	2	37	84	
		112		28		8		2		26								
Pyromellitic acid	-0.56	86		13		32		0		25								
		90	89	15	14	34	34	1	0	22	22	3	1	5	0	28	79	
		90		15		35		0		20								
	-0.62	125		17		28		1		29								
		123	119	17	17	28	29	2	2	28	27	2	1	9	0	37	86	
		108		18		29		2		25								
4- Pyridinecarboxald ehyde	-0.56	84		11		25		0		30								
		91	89	13	13	30	29	0	0	26	27	4	2	11	2	43	90	
		91		13		31		0		25								
	-0.62	104		15		26		1		32								
		105	105	15	15	27	26	1	1	32	31	3	1	11	1	44	89	
		106		15		25		1		29								
Methyl 4- bromobenzoate	-0.56	87		12		29		1		32								
		88	87	14	14	30	30	1	1	30	31	5	2	9	2	44	93	
	-0.62	87		15		29		1		29								
		119	117	15	16	23	22	2	3	32	32	4	2	11	2	47	91	

			<u>117</u>		<u>16</u>		<u>22</u>		<u>2</u>		<u>32</u>							
			<u>116</u>		<u>16</u>		<u>22</u>		<u>3</u>		<u>31</u>							
4-Hydroxyphenylboronic acid	-0.56		<u>78</u>	80	<u>18</u>	19	<u>29</u>	28	<u>1</u>	1	<u>28</u>	25	5	2	10	0	37	90
		<u>82</u>	<u>19</u>		<u>29</u>		<u>1</u>		<u>24</u>									
		<u>81</u>	<u>20</u>		<u>27</u>		<u>1</u>		<u>24</u>									
	-0.62	<u>112</u>	112	<u>20</u>	20	<u>22</u>	22	<u>2</u>	2	<u>27</u>	29	2	2	12	0	42	90	
		<u>113</u>		<u>20</u>		<u>22</u>		<u>2</u>		<u>28</u>								
<u>111</u>		<u>21</u>		<u>23</u>		<u>3</u>		<u>31</u>										
Poly(4-vinylpyridine)	-0.56		<u>85</u>	90	<u>13</u>	16	<u>37</u>	39	<u>1</u>	1	<u>12</u>	13	4	1	5	0	19	79
		<u>92</u>	<u>17</u>		<u>40</u>		<u>1</u>		<u>13</u>									
		<u>92</u>	<u>18</u>		<u>38</u>		<u>2</u>		<u>13</u>									
	-0.62	<u>131</u>	128	<u>21</u>	21	<u>20</u>	22	<u>6</u>	6	<u>19</u>	22	3	3	6	0	31	84	
		<u>126</u>		<u>22</u>		<u>20</u>		<u>7</u>		<u>22</u>								
<u>128</u>		<u>20</u>		<u>26</u>		<u>5</u>		<u>23</u>										
5-Bromo-2-pyridinecarbonitrile	-0.56		<u>90</u>	91	<u>21</u>	22	<u>26</u>	27	<u>2</u>	3	<u>31</u>	29	3	1	9	0	39	94
		<u>92</u>	<u>22</u>		<u>27</u>		<u>3</u>		<u>29</u>									
		<u>92</u>	<u>23</u>		<u>27</u>		<u>3</u>		<u>28</u>									
	-0.62	<u>133</u>	133	<u>25</u>	25	<u>20</u>	20	<u>6</u>	6	<u>32</u>	31	1	1	10	0	42	96	
		<u>133</u>		<u>26</u>		<u>20</u>		<u>7</u>		<u>31</u>								
<u>132</u>		<u>26</u>		<u>21</u>		<u>7</u>		<u>30</u>										
2-(1H-Pyrazol-3-YL)Pyridine	-0.56		<u>94</u>	97	<u>10</u>	11	<u>19</u>	21	<u>0</u>	1	<u>39</u>	35	3	1	12	0	47	84
		<u>99</u>	<u>11</u>		<u>21</u>		<u>0</u>		<u>34</u>									
		<u>99</u>	<u>13</u>		<u>24</u>		<u>1</u>		<u>32</u>									
	-0.62	<u>144</u>	143	<u>12</u>	14	<u>21</u>	22	<u>1</u>	1	<u>33</u>	31	3	2	16	0	49	90	
		<u>143</u>		<u>14</u>		<u>22</u>		<u>1</u>		<u>31</u>								
<u>141</u>		<u>16</u>		<u>24</u>		<u>1</u>		<u>30</u>										
5-Methyl-3-(pyridin-2-yl)-1H-1,2,4-triazole	-0.56		<u>100</u>	103	<u>21</u>	28	<u>16</u>	18	<u>0</u>	0	<u>31</u>	26	4	2	11	2	41	92
		<u>105</u>	<u>29</u>		<u>18</u>		<u>0</u>		<u>25</u>									
		<u>105</u>	<u>35</u>		<u>20</u>		<u>0</u>		<u>23</u>									
	-0.62	<u>138</u>	138	<u>30</u>	32	<u>20</u>	20	<u>1</u>	1	<u>26</u>	25	2	1	10	0	36	91	
		<u>137</u>		<u>31</u>		<u>20</u>		<u>1</u>		<u>24</u>								
<u>138</u>		<u>34</u>		<u>21</u>		<u>1</u>		<u>24</u>										
4-Ethylbenzoic acid	-0.56		<u>96</u>	98	<u>13</u>	15	<u>30</u>	32	<u>1</u>	1	<u>23</u>	22	4	1	9	1	33	84
		<u>99</u>	<u>15</u>		<u>32</u>		<u>1</u>		<u>20</u>									
		<u>99</u>	<u>16</u>		<u>33</u>		<u>2</u>		<u>24</u>									
	-0.62	<u>140</u>	137	<u>16</u>	16	<u>21</u>	21	<u>3</u>	3	<u>21</u>	22	2	2	11	2	37	80	
		<u>137</u>		<u>16</u>		<u>22</u>		<u>3</u>		<u>21</u>								
<u>134</u>		<u>17</u>		<u>21</u>		<u>4</u>		<u>23</u>										
1,2,4-Triazole	-0.56		<u>102</u>	104	<u>14</u>	16	<u>27</u>	29	<u>1</u>	1	<u>28</u>	25	4	2	9	0	36	86
		<u>105</u>	<u>17</u>		<u>30</u>		<u>1</u>		<u>25</u>									
		<u>105</u>	<u>18</u>		<u>29</u>		<u>1</u>		<u>23</u>									
	-0.62	<u>155</u>	154	<u>18</u>	19	<u>26</u>	26	<u>2</u>	2	<u>26</u>	26	4	2	10	1	39	90	
		<u>155</u>		<u>19</u>		<u>26</u>		<u>2</u>		<u>26</u>								
<u>152</u>		<u>19</u>		<u>26</u>		<u>2</u>		<u>26</u>										
[4,2':6',4"-Terpyridine]-4'-carboxylic acid	-0.56		<u>85</u>	88	<u>21</u>	22	<u>15</u>	18	<u>2</u>	2	<u>28</u>	26	7	1	9	0	36	85
		<u>89</u>	<u>23</u>		<u>18</u>		<u>2</u>		<u>24</u>									
		<u>89</u>	<u>21</u>		<u>21</u>		<u>2</u>		<u>26</u>									
	-0.62	<u>133</u>	131	<u>15</u>	16	<u>19</u>	21	<u>3</u>	3	<u>32</u>	34	4	2	13	0	49	92	
		<u>131</u>		<u>16</u>		<u>21</u>		<u>3</u>		<u>34</u>								
<u>129</u>		<u>16</u>		<u>22</u>		<u>4</u>		<u>36</u>										
Mono-methyl isophthalate	-0.56		<u>100</u>	102	<u>13</u>	15	<u>25</u>	28	<u>1</u>	1	<u>29</u>	27	5	1	9	5	42	92
		<u>102</u>	<u>15</u>		<u>28</u>		<u>1</u>		<u>26</u>									
		<u>103</u>	<u>16</u>		<u>30</u>		<u>1</u>		<u>26</u>									
	-0.62	<u>140</u>	139	<u>17</u>	17	<u>24</u>	26	<u>2</u>	2	<u>30</u>	32	5	1	13	3	49	100	
		<u>139</u>		<u>17</u>		<u>26</u>		<u>2</u>		<u>32</u>								
<u>138</u>		<u>17</u>		<u>27</u>		<u>3</u>		<u>34</u>										
4-Pyridinylphosphonic acid	-0.56		<u>92</u>	91	<u>20</u>	21	<u>21</u>	24	<u>4</u>	5	<u>22</u>	21	5	1	11	0	33	88
		<u>91</u>	<u>22</u>		<u>24</u>		<u>5</u>		<u>21</u>									
		<u>91</u>	<u>22</u>		<u>25</u>		<u>6</u>		<u>20</u>									
	-0.62	<u>141</u>	139	<u>23</u>	23	<u>22</u>	23	<u>12</u>	14	<u>24</u>	26	3	1	9	0	36	99	
		<u>139</u>		<u>23</u>		<u>23</u>		<u>14</u>		<u>25</u>								
<u>137</u>		<u>23</u>		<u>24</u>		<u>16</u>		<u>29</u>										
5-Hydroxy-1,4-naphthalenedione	-0.56		<u>89</u>	89	<u>15</u>	16	<u>21</u>	23	<u>5</u>	6	<u>24</u>	25	4	2	12	2	40	89
		<u>89</u>	<u>16</u>		<u>22</u>		<u>5</u>		<u>24</u>									
		<u>88</u>	<u>18</u>		<u>27</u>		<u>7</u>		<u>27</u>									
	-0.62	<u>130</u>	128	<u>16</u>	16	<u>17</u>	18	<u>9</u>	10	<u>30</u>	31	2	2	14	1	48	94	
		<u>127</u>		<u>16</u>		<u>17</u>		<u>10</u>		<u>29</u>								
<u>127</u>		<u>16</u>		<u>19</u>		<u>11</u>		<u>33</u>										
	-0.56		<u>79</u>	81	<u>20</u>	23	<u>20</u>	22	<u>3</u>	3	<u>25</u>	25	5	3	9	0	37	89
		<u>81</u>	<u>24</u>		<u>22</u>		<u>3</u>		<u>24</u>									

1,4-Benzenedimethanol		82		24		24		4		25							
		118		22		19		8		30							
	-0.62	121	120	21	21	20	20	9	9	31	31	3	2	12	0	45	98
		121		21		21		10		33							
		95		13		25		1		33							
	-0.56	98	97	16	16	30	29	2	2	29	30	6	3	10	0	43	95
Tetrahydroxyquinone		98		17		31		2		28							
		128		17		26		3		31							
	-0.62	127	127	17	17	27	26	3	3	31	31	5	2	7	0	39	91
		126		17		27		4		31							
		81		16		17		7		29							
	-0.56	83	82	20	19	18	18	7	7	27	27	4	3	16	0	46	94
4-Chlorobenzyl alcohol		83		21		19		7		26							
		128		18		13		10		28							
	-0.62	125	125	18	18	13	13	11	11	28	28	4	3	17	0	49	95
		123		18		13		12		28							
		81		15		20		7		34							
	-0.56	87	85	19	18	21	21	7	7	29	30	4	3	15	0	48	98
5-Aminovaleric acid		87		19		22		7		28							
		120		16		19		7		33							
	-0.62	122	121	20	19	19	19	8	8	30	31	4	2	15	0	48	98
		122		21		20		9		31							
		80		17		19		4		32							
	-0.56	85	83	20	19	20	20	4	4	28	29	7	2	8	0	40	90
4-Aminobutyric acid		85		21		21		4		27							
		122		20		17		8		31							
	-0.62	120	120	21	20	17	17	8	8	31	31	3	2	11	0	44	93
		119		21		17		9		31							
		87		19		17		3		30							
	-0.56	89	88	22	21	19	19	3	3	27	28	5	2	12	0	42	90
2,6-Dichloro-1,4-benzoquinone		89		23		20		4		27							
		126		23		16		6		31							
	-0.62	123	124	23	23	17	17	7	7	32	32	3	2	15	0	49	99
		123		23		18		7		33							
		82		15		20		4		30							
	-0.56	83	82	19	18	21	21	4	4	28	28	3	3	9	0	40	87
5,10,15,20-Tetra(4-pyridyl)-21H,23H-porphine		82		20		21		5		27							
		103		19		16		7		32							
	-0.62	103	101	19	19	16	16	8	8	34	34	3	2	14	0	50	97
		98		20		17		9		37							
		91		13		16		2		30							
	-0.56	92	92	17	16	18	18	2	2	27	28	2	1	13	0	43	81
Pyrrole		93		18		19		3		27							
		131		18		15		4		29							
	-0.62	129	129	19	18	16	15	5	5	30	30	4	2	12	2	46	88
		128		19		16		5		31							
		78		14		21		4		30							
	-0.56	83	81	19	18	22	22	4	4	27	28	4	3	13	3	47	96
L-Phenylalanine		83		21		23		5		26							
		119		20		17		8		29							
	-0.62	118	118	20	20	17	17	8	8	29	29	4	3	15	4	50	99
		117		20		17		9		29							
		79		14		22		3		33							
	-0.56	82	81	16	16	23	24	4	4	31	33	4	3	12	3	51	98
L-Serine		82		19		26		5		35							
		114		17		18		7		34							
	-0.62	113	113	17	18	17	18	7	8	32	35	3	2	12	4	52	99
		111		19		19		9		38							
		83		10		22		3		39							
	-0.56	86	85	14	14	25	24	4	4	34	35	3	2	12	3	52	98
L-Alanine		86		17		26		5		32							
		119		15		20		8		35							
	-0.62	118	118	16	15	20	20	8	8	35	35	3	3	13	2	53	99
		117		15		20		9		34							
		77		14		21		4		30							
	-0.56	78	78	17	16	23	22	4	4	29	29	4	2	13	4	48	95
D(+)-Tryptophan		78		18		23		5		29							
		115		18		17		9		31							
	-0.62	112	113	17	18	17	17	9	9	31	31	4	2	16	2	51	98
		111		17		17		10		31							

L(+)-Ascorbic acid	-0.56	<u>77</u>	79	<u>9</u>	12	<u>24</u>	26	<u>3</u>	4	<u>34</u>	31	4	4	13	0	48	94
		<u>80</u>		<u>13</u>		<u>27</u>		<u>4</u>		<u>30</u>							
		<u>80</u>		<u>15</u>		<u>29</u>		<u>4</u>		<u>28</u>							
	-0.62	<u>119</u>	118	<u>14</u>	14	<u>23</u>	24	<u>6</u>	7	<u>31</u>	31	4	2	11	2	45	94
		<u>118</u>		<u>14</u>		<u>25</u>		<u>7</u>		<u>32</u>							
		<u>117</u>		<u>15</u>		<u>24</u>		<u>7</u>		<u>30</u>							
D-Tyrosine	-0.56	<u>84</u>	87	<u>14</u>	15	<u>22</u>	25	<u>3</u>	4	<u>33</u>	30	5	1	12	0	43	91
		<u>89</u>		<u>15</u>		<u>25</u>		<u>4</u>		<u>29</u>							
		<u>89</u>		<u>16</u>		<u>26</u>		<u>4</u>		<u>28</u>							
	-0.62	<u>124</u>	123	<u>15</u>	15	<u>22</u>	22	<u>6</u>	7	<u>30</u>	30	5	2	10	1	43	92
		<u>123</u>		<u>15</u>		<u>22</u>		<u>7</u>		<u>29</u>							
		<u>121</u>		<u>15</u>		<u>22</u>		<u>8</u>		<u>29</u>							
D-Alanine	-0.56	<u>74</u>	75	<u>10</u>	12	<u>21</u>	22	<u>4</u>	4	<u>35</u>	31	5	2	13	0	46	90
		<u>76</u>		<u>13</u>		<u>22</u>		<u>4</u>		<u>31</u>							
		<u>76</u>		<u>14</u>		<u>23</u>		<u>5</u>		<u>29</u>							
	-0.62	<u>118</u>	117	<u>11</u>	13	<u>16</u>	16	<u>8</u>	8	<u>32</u>	32	3	2	16	0	50	90
		<u>116</u>		<u>13</u>		<u>16</u>		<u>8</u>		<u>32</u>							
		<u>116</u>		<u>13</u>		<u>16</u>		<u>9</u>		<u>32</u>							
D-Cystine	-0.56	<u>76</u>	78	<u>22</u>	21	<u>19</u>	23	<u>3</u>	4	<u>31</u>	30	6	3	12	0	44	97
		<u>80</u>		<u>21</u>		<u>22</u>		<u>3</u>		<u>28</u>							
		<u>79</u>		<u>20</u>		<u>26</u>		<u>5</u>		<u>30</u>							
	-0.62	<u>116</u>	116	<u>23</u>	22	<u>19</u>	19	<u>8</u>	9	<u>34</u>	34	3	2	12	0	48	101
		<u>116</u>		<u>22</u>		<u>19</u>		<u>8</u>		<u>32</u>							
		<u>115</u>		<u>22</u>		<u>20</u>		<u>10</u>		<u>34</u>							
D-2-Aminobutyric acid	-0.56	<u>55</u>	57	<u>11</u>	15	<u>21</u>	25	<u>4</u>	5	<u>36</u>	31	4	3	10	0	44	93
		<u>58</u>		<u>16</u>		<u>26</u>		<u>5</u>		<u>30</u>							
		<u>59</u>		<u>18</u>		<u>28</u>		<u>5</u>		<u>28</u>							
	-0.62	<u>86</u>	86	<u>20</u>	20	<u>21</u>	21	<u>11</u>	12	<u>28</u>	28	3	2	10	0	41	97
		<u>87</u>		<u>19</u>		<u>22</u>		<u>12</u>		<u>29</u>							
		<u>85</u>		<u>22</u>		<u>21</u>		<u>13</u>		<u>28</u>							
L(+)-2-Aminobutyric acid	-0.56	<u>65</u>	67	<u>11</u>	14	<u>22</u>	24	<u>4</u>	4	<u>28</u>	26	3	3	12	0	41	86
		<u>67</u>		<u>15</u>		<u>24</u>		<u>4</u>		<u>26</u>							
		<u>68</u>		<u>16</u>		<u>25</u>		<u>5</u>		<u>25</u>							
	-0.62	<u>101</u>	100	<u>16</u>	17	<u>21</u>	22	<u>9</u>	10	<u>31</u>	32	3	4	11	0	47	98
		<u>100</u>		<u>17</u>		<u>23</u>		<u>10</u>		<u>33</u>							
		<u>98</u>		<u>18</u>		<u>23</u>		<u>10</u>		<u>32</u>							
2-(1H-1,2,3,4-tetraazol-5-yl)pyridine	-0.56	<u>61</u>	65	<u>7</u>	10	<u>23</u>	27	<u>3</u>	3	<u>33</u>	29	5	4	13	0	46	91
		<u>66</u>		<u>10</u>		<u>28</u>		<u>3</u>		<u>27</u>							
		<u>67</u>		<u>12</u>		<u>30</u>		<u>4</u>		<u>26</u>							
	-0.62	<u>121</u>	120	<u>17</u>	17	<u>21</u>	21	<u>6</u>	7	<u>30</u>	31	3	3	12	0	45	94
		<u>120</u>		<u>17</u>		<u>21</u>		<u>7</u>		<u>32</u>							
		<u>120</u>		<u>17</u>		<u>21</u>		<u>8</u>		<u>31</u>							
3-Hydroxyphenylboronic acid	-0.56	<u>48</u>	48	<u>15</u>	19	<u>17</u>	20	<u>5</u>	6	<u>37</u>	34	4	4	12	0	50	99
		<u>47</u>		<u>19</u>		<u>20</u>		<u>6</u>		<u>33</u>							
		<u>50</u>		<u>22</u>		<u>22</u>		<u>7</u>		<u>32</u>							
	-0.62	<u>98</u>	97	<u>15</u>	15	<u>14</u>	15	<u>10</u>	11	<u>32</u>	31	3	2	14	0	48	91
		<u>97</u>		<u>16</u>		<u>15</u>		<u>11</u>		<u>32</u>							
		<u>96</u>		<u>15</u>		<u>15</u>		<u>11</u>		<u>30</u>							
Methylphosphonic acid	-0.56	<u>63</u>	65	<u>10</u>	12	<u>21</u>	25	<u>3</u>	4	<u>31</u>	30	3	2	14	0	46	90
		<u>66</u>		<u>11</u>		<u>26</u>		<u>4</u>		<u>30</u>							
		<u>65</u>		<u>14</u>		<u>27</u>		<u>5</u>		<u>28</u>							
	-0.62	<u>97</u>	96	<u>14</u>	14	<u>19</u>	20	<u>8</u>	8	<u>29</u>	29	3	2	13	0	44	90
		<u>96</u>		<u>14</u>		<u>20</u>		<u>8</u>		<u>29</u>							
		<u>94</u>		<u>15</u>		<u>21</u>		<u>9</u>		<u>29</u>							
Erythorbic Acid	-0.56	<u>65</u>	67	<u>12</u>	16	<u>32</u>	35	<u>6</u>	7	<u>29</u>	25	3	2	10	0	36	98
		<u>67</u>		<u>16</u>		<u>36</u>		<u>7</u>		<u>24</u>							
		<u>68</u>		<u>19</u>		<u>38</u>		<u>7</u>		<u>23</u>							
	-0.62	<u>96</u>	95	<u>15</u>	16	<u>26</u>	27	<u>12</u>	13	<u>26</u>	26	4	2	12	0	40	99
		<u>95</u>		<u>16</u>		<u>27</u>		<u>13</u>		<u>27</u>							
		<u>94</u>		<u>16</u>		<u>27</u>		<u>14</u>		<u>26</u>							
Pyridine-4-boronic acid	-0.56	<u>66</u>	68	<u>10</u>	13	<u>19</u>	24	<u>2</u>	3	<u>39</u>	35	4	3	11	0	49	92
		<u>69</u>		<u>13</u>		<u>25</u>		<u>3</u>		<u>34</u>							
		<u>70</u>		<u>15</u>		<u>27</u>		<u>4</u>		<u>32</u>							
	-0.62	<u>105</u>	104	<u>15</u>	16	<u>21</u>	21	<u>6</u>	7	<u>35</u>	35	3	2	15	0	52	99
		<u>104</u>		<u>16</u>		<u>21</u>		<u>7</u>		<u>35</u>							
		<u>104</u>		<u>17</u>		<u>22</u>		<u>7</u>		<u>35</u>							
N-tert-ButylacetaMide	-0.56	<u>61</u>	64	<u>8</u>	12	<u>22</u>	26	<u>4</u>	5	<u>37</u>	32	3	3	12	0	48	94
		<u>65</u>		<u>12</u>		<u>28</u>		<u>5</u>		<u>31</u>							
		<u>66</u>		<u>14</u>		<u>29</u>		<u>6</u>		<u>28</u>							
-0.62	<u>96</u>	95	<u>14</u>	17	<u>23</u>	25	<u>9</u>	11	<u>31</u>	33	3	2	12	0	47	103	

		95		18		27		13		35						
		95		18		26		12		34						
		66		10		26		3		41						
	-0.56	70	69	14	14	30	29	3	3	31	33	4	2	11	0	46
		70		17		32		4		27						
		101		15		24		6		30						
	-0.62	99	100	16	16	25	25	7	7	31	31	3	2	13	1	47
		99		18		26		8		31						
		47		24		16		9		32						
	-0.56	49	48	29	29	15	16	7	8	28	29	3	3	13	0	45
		49		32		16		7		27						
		82		31		12		14		28						
	-0.62	79	80	33	33	11	11	15	14	29	28	2	3	12	0	42
		78		33		10		14		26						
		58		20		16		2		38						
	-0.56	59	62	26	24	18	18	2	2	37	38	4	1	11	0	49
		70		26		19		2		38						
		108		26		12		5		32						
	-0.62	107	107	25	26	14	14	6	5	36	36	3	2	12	0	50
		106		25		15		6		41						
		72		12		19		2		36						
	-0.56	74	73	15	14	20	20	3	3	30	32	5	3	12	4	50
		74		16		21		3		29						
		110		15		17		5		30						
	-0.62	109	109	15	15	17	18	5	5	31	31	4	2	15	2	50
		107		16		19		5		31						
		67		11		25		1		30						
	-0.56	70	69	13	13	31	29	1	1	27	27	5	2	11	0	40
		71		14		32		2		25						
		109		13		25		3		30						
	-0.62	107	108	14	14	27	26	4	3	32	30	4	1	12	4	46
		107		14		26		3		28						
		74		17		20		2		33						
	-0.56	74	74	16	16	19	20	1	2	32	32	5	4	9	0	45
		75		16		20		2		32						
		107		15		16		3		35						
	-0.62	106	106	15	15	17	17	3	3	37	37	4	2	14	2	55
		105		16		17		4		38						
		68		10		19		2		34						
	-0.56	71	70	13	12	22	21	3	2	31	31	5	3	12	3	49
		71		14		22		3		27						
		107		15		15		6		32						
	-0.62	106	106	15	15	15	17	7	7	31	32	2	2	17	0	51
		105		16		20		7		32						
		61		13		25		5		29						
	-0.56	66	65	15	15	29	28	5	5	25	26	4	3	10	2	40
		67		16		30		5		24						
		101		14		24		9		28						
	-0.62	100	100	15	15	25	26	10	10	29	29	3	3	11	0	42
		99		16		28		11		31						
		59		11		23		5		29						
	-0.56	63	62	15	14	28	27	5	5	25	26	3	3	12	0	40
		64		16		29		6		24						
		96		15		23		10		26						
	-0.62	94	94	17	16	26	25	12	11	30	28	3	2	11	1	43
		92		16		25		11		28						
		67		14		25		2		30						
	-0.56	71	70	15	15	28	28	2	2	26	27	5	2	10	0	40
		71		16		31		2		26						
		105		16		23		4		30						
	-0.62	104	104	17	17	25	25	5	5	33	33	3	3	12	0	48
		104		18		28		6		36						
		74		15		24		5		22						
	-0.56	74	74	15	16	24	24	5	5	21	21	4	2	12	1	36
		74		16		25		5		21						
		105		16		18		9		23						
	-0.62	103	103	16	16	19	19	9	9	23	23	3	3	14	0	40
		101		16		19		10		24						
		74		17		16		3		37						
	-0.56	76	76	20	19	19	18	4	4	35	36	4	3	13	0	52

4-Carboxy-p-terphenyl		77		19		20		5		34							
		114		17		17		8		36							
	-0.62	113	113	18	17	18	17	9	9	39	38	3	2	14	0	54	100
		112		18		18		9		38							
		65		13		23		6		28							
	-0.56	67	66	16	15	27	26	6	6	25	26	4	3	14	0	42	94
		67		17		28		7		25							
		97		16		18		11		29							
	-0.62	96	96	17	17	19	19	12	12	29	29	2	3	14	0	46	96
		95		17		21		12		30							
1-[(tert-butoxy)carbonyl]pyrrolidine-2-carboxylic acid		70		11		21		2		30							
	-0.56	74	73	13	12	24	24	2	2	27	28	5	3	13	0	44	87
		75		14		26		2		27							
		105		13		21		4		30							
	-0.62	106	105	15	15	23	23	5	5	34	33	2	2	13	2	51	96
Acetohydroxamic acid		105		16		26		6		37							
	-0.56	59		13		21		11		25							
		63	62	17	16	24	23	11	11	22	23	5	2	10	0	36	91
		64		18		25		12		22							
	-0.62	94		18		16		18		23							
4-(Phenylazo)benzoic acid		92	92	19	18	16	16	19	19	24	23	3	3	11	0	37	93
		91		19		15		19		22							
	-0.56	59		11		21		10		26							
		60	60	15	14	23	22	7	9	24	24	4	4	11	0	40	89
		61		17		24		8		24							
2-Phenylpyridine		95		16		19		12		24							
	-0.62	92	92	18	17	20	20	14	13	25	25	3	4	10	0	38	91
		90		18		20		14		25							
	-0.56	68		11		21		2		30							
		71	70	14	14	24	24	3	3	26	27	4	3	14	0	44	88
4-(2-Aminoethyl)pyridine		70		16		26		3		25							
	-0.62	105	103	14	15	20	22	6	7	33	34	3	2	13	1	50	95
		103		15		22		7		33							
		102		15		23		7		35							
	-0.56	64		11		21		5		31							
2-Bromo-5-(trifluoromethyl)pyridine		67	66	13	13	24	23	4	4	29	30	4	3	11	0	44	88
		67		14		25		4		29							
	-0.62	101	100	13	13	22	22	7	8	31	32	3	3	12	0	48	94
		99		13		22		8		33							
		99		14		23		8		34							
2,5-Dibromopyridine		80		10		22		2		40							
	-0.56	82	81	13	12	25	25	3	3	36	37	4	2	14	0	53	97
		82		14		27		3		35							
	-0.62	118	116	13	13	20	21	5	6	37	39	4	2	14	0	55	100
		117		14		21		6		39							
4-Cyanopyridine		113		14		22		7		42							
	-0.56	80		10		16		2		36							
		82	81	13	12	18	17	2	2	33	34	6	2	16	0	52	89
		82		14		19		3		32							
	-0.62	119	118	16	16	15	16	4	5	32	33	6	2	14	3	52	94
2-Bromo-5-methylpyridine		116		16		17		6		35							
	-0.56	79		11		20		2		34							
		83	82	15	14	24	23	3	3	29	30	5	2	14	2	47	93
		83		17		24		3		28							
	-0.62	118	116	17	18	17	18	8	8	33	35	2	1	14	1	51	97
3-Iodopyridine		115		18		19		8		36							
	-0.56	79		10		21		2		32							
		79	79	12	12	23	22	2	2	28	28	5	2	13	2	45	86
		79		13		23		3		26							
	-0.62	104	94	14	14	19	19	4	5	28	29	4	2	17	0	48	90
4-Cyanopyridine		86		15		18		5		29							
		91		15		19		5		30							
	-0.56	69		10		23		4		28							
		71	70	13	13	24	24	5	5	25	26	3	3	14	0	42	87
		71		15		24		5		24							
3-Iodopyridine	-0.62	98		17		19		11		30							
		98	98	17	17	18	19	11	12	28	29	2	2	17	0	48	98
		97		18		19		13		30							

2-Anilinopyridine	-0.56	<u>75</u>	76	<u>9</u>	11	<u>14</u>	16	<u>2</u>	2	<u>38</u>	35	4	4	17	0	56	89
		<u>77</u>		<u>11</u>		<u>16</u>		<u>2</u>		<u>35</u>							
		<u>75</u>		<u>13</u>		<u>18</u>		<u>2</u>		<u>33</u>							
	-0.62	<u>109</u>	108	<u>13</u>	13	<u>15</u>	16	<u>4</u>	4	<u>33</u>	34	3	3	18	0	54	91
		<u>108</u>		<u>14</u>		<u>16</u>		<u>4</u>		<u>34</u>							
		<u>107</u>		<u>14</u>		<u>17</u>		<u>5</u>		<u>35</u>							
4-Nitrobenzyl alcohol	-0.56	<u>72</u>	72	<u>14</u>	17	<u>22</u>	24	<u>5</u>	5	<u>37</u>	34	3	2	12	0	49	98
		<u>73</u>		<u>17</u>		<u>24</u>		<u>5</u>		<u>34</u>							
		<u>72</u>		<u>19</u>		<u>25</u>		<u>6</u>		<u>33</u>							
	-0.62	<u>88</u>	94	<u>19</u>	19	<u>22</u>	21	<u>9</u>	10	<u>33</u>	35	3	2	11	0	48	102
		<u>87</u>		<u>20</u>		<u>22</u>		<u>10</u>		<u>34</u>							
		<u>107</u>		<u>19</u>		<u>20</u>		<u>11</u>		<u>36</u>							
2,5-Dihydroxybenzaldehyde	-0.56	<u>75</u>	77	<u>13</u>	16	<u>16</u>	18	<u>4</u>	4	<u>29</u>	27	4	3	15	0	45	86
		<u>78</u>		<u>16</u>		<u>19</u>		<u>4</u>		<u>26</u>							
		<u>79</u>		<u>18</u>		<u>19</u>		<u>5</u>		<u>25</u>							
	-0.62	<u>116</u>	115	<u>19</u>	19	<u>15</u>	15	<u>9</u>	9	<u>29</u>	27	3	3	14	2	46	93
		<u>115</u>		<u>19</u>		<u>15</u>		<u>9</u>		<u>26</u>							
		<u>114</u>		<u>20</u>		<u>15</u>		<u>10</u>		<u>28</u>							
1,4-Benzoquinone	-0.56	<u>72</u>	73	<u>11</u>	13	<u>17</u>	18	<u>5</u>	5	<u>31</u>	29	2	3	16	2	49	88
		<u>74</u>		<u>14</u>		<u>18</u>		<u>5</u>		<u>28</u>							
		<u>74</u>		<u>15</u>		<u>19</u>		<u>5</u>		<u>27</u>							
	-0.62	<u>80</u>	84	<u>14</u>	15	<u>12</u>	14	<u>10</u>	10	<u>29</u>	28	3	3	17	0	48	90
		<u>93</u>		<u>15</u>		<u>14</u>		<u>10</u>		<u>28</u>							
		<u>78</u>		<u>17</u>		<u>15</u>		<u>11</u>		<u>29</u>							
Trimethylhydroquinone	-0.56	<u>68</u>	67	<u>18</u>	20	<u>26</u>	27	<u>6</u>	6	<u>21</u>	21	4	2	9	0	31	88
		<u>68</u>		<u>20</u>		<u>27</u>		<u>6</u>		<u>20</u>							
		<u>66</u>		<u>20</u>		<u>28</u>		<u>7</u>		<u>20</u>							
	-0.62	<u>86</u>	84	<u>18</u>	19	<u>19</u>	18	<u>14</u>	14	<u>24</u>	24	2	3	12	0	38	91
		<u>84</u>		<u>19</u>		<u>16</u>		<u>14</u>		<u>24</u>							
		<u>83</u>		<u>21</u>		<u>19</u>		<u>15</u>		<u>24</u>							
Chloranil	-0.56	<u>76</u>	79	<u>12</u>	13	<u>25</u>	24	<u>3</u>	3	<u>38</u>	31	4	3	10	0	44	88
		<u>80</u>		<u>13</u>		<u>24</u>		<u>3</u>		<u>29</u>							
		<u>80</u>		<u>14</u>		<u>24</u>		<u>3</u>		<u>27</u>							
	-0.62	<u>118</u>	116	<u>14</u>	14	<u>19</u>	19	<u>5</u>	5	<u>29</u>	28	3	2	17	2	49	90
		<u>116</u>		<u>14</u>		<u>18</u>		<u>5</u>		<u>27</u>							
		<u>115</u>		<u>14</u>		<u>18</u>		<u>5</u>		<u>27</u>							
4-Methoxybenzyl alcohol	-0.56	<u>69</u>	72	<u>13</u>	16	<u>22</u>	23	<u>5</u>	5	<u>28</u>	24	3	3	11	0	38	85
		<u>73</u>		<u>17</u>		<u>24</u>		<u>5</u>		<u>24</u>							
		<u>74</u>		<u>18</u>		<u>22</u>		<u>5</u>		<u>21</u>							
	-0.62	<u>102</u>	101	<u>17</u>	17	<u>18</u>	17	<u>8</u>	8	<u>21</u>	20	3	2	12	0	34	78
		<u>101</u>		<u>17</u>		<u>16</u>		<u>8</u>		<u>19</u>							
		<u>99</u>		<u>17</u>		<u>16</u>		<u>8</u>		<u>19</u>							
Bromanilic Acid	-0.56	<u>71</u>	73	<u>13</u>	15	<u>29</u>	31	<u>2</u>	2	<u>31</u>	29	4	3	8	0	40	92
		<u>74</u>		<u>16</u>		<u>31</u>		<u>2</u>		<u>28</u>							
		<u>74</u>		<u>17</u>		<u>33</u>		<u>3</u>		<u>29</u>							
	-0.62	<u>105</u>	104	<u>17</u>	18	<u>26</u>	27	<u>5</u>	5	<u>33</u>	34	4	2	11	2	49	103
		<u>104</u>		<u>18</u>		<u>27</u>		<u>5</u>		<u>33</u>							
		<u>103</u>		<u>19</u>		<u>28</u>		<u>6</u>		<u>35</u>							
2',5'-Dihydroxyacetophenone	-0.56	<u>75</u>	77	<u>17</u>	19	<u>26</u>	29	<u>4</u>	5	<u>34</u>	32	3	2	10	0	44	100
		<u>77</u>		<u>19</u>		<u>30</u>		<u>5</u>		<u>32</u>							
		<u>78</u>		<u>20</u>		<u>32</u>		<u>6</u>		<u>31</u>							
	-0.62	<u>101</u>	104	<u>20</u>	20	<u>24</u>	24	<u>10</u>	11	<u>34</u>	34	3	3	12	0	48	106
		<u>105</u>		<u>20</u>		<u>24</u>		<u>10</u>		<u>32</u>							
		<u>106</u>		<u>20</u>		<u>26</u>		<u>12</u>		<u>35</u>							
4-Bromobenzaldehyde	-0.56	<u>74</u>	75	<u>13</u>	17	<u>29</u>	32	<u>3</u>	4	<u>33</u>	31	3	3	11	0	45	100
		<u>75</u>		<u>18</u>		<u>33</u>		<u>4</u>		<u>30</u>							
		<u>75</u>		<u>19</u>		<u>34</u>		<u>4</u>		<u>29</u>							
	-0.62	<u>108</u>	107	<u>19</u>	19	<u>26</u>	27	<u>7</u>	8	<u>33</u>	35	3	1	11	1	48	105
		<u>107</u>		<u>20</u>		<u>27</u>		<u>8</u>		<u>35</u>							
		<u>106</u>		<u>19</u>		<u>28</u>		<u>9</u>		<u>36</u>							
2-Chlorobenzyl alcohol	-0.56	<u>74</u>	75	<u>9</u>	12	<u>30</u>	33	<u>3</u>	4	<u>33</u>	30	5	2	11	0	43	97
		<u>76</u>		<u>13</u>		<u>34</u>		<u>4</u>		<u>29</u>							
		<u>76</u>		<u>14</u>		<u>36</u>		<u>5</u>		<u>28</u>							
	-0.62	<u>107</u>	105	<u>15</u>	15	<u>28</u>	29	<u>7</u>	8	<u>31</u>	32	3	2	6	0	41	96
		<u>105</u>		<u>15</u>		<u>30</u>		<u>8</u>		<u>32</u>							
		<u>103</u>		<u>16</u>		<u>30</u>		<u>9</u>		<u>33</u>							
3-Chloro-1-propanol	-0.56	<u>75</u>	77	<u>11</u>	14	<u>23</u>	26	<u>2</u>	3	<u>34</u>	32	4	3	12	0	48	95
		<u>78</u>		<u>15</u>		<u>26</u>		<u>3</u>		<u>31</u>							
		<u>78</u>		<u>16</u>		<u>29</u>		<u>4</u>		<u>31</u>							
-0.62	<u>112</u>	110	<u>15</u>	16	<u>20</u>	21	<u>5</u>	6	<u>34</u>	36	3	4	16	0	56	102	

		<u>111</u>		<u>16</u>		<u>21</u>		<u>6</u>		<u>37</u>							
		<u>108</u>		<u>16</u>		<u>22</u>		<u>7</u>		<u>39</u>							
1-Octene	-0.56	<u>72</u>	74	<u>10</u>	13	<u>21</u>	23	<u>4</u>	5	<u>35</u>	31	3	5	14	0	50	94
		<u>75</u>		<u>14</u>		<u>24</u>		<u>5</u>		<u>30</u>							
		<u>75</u>		<u>15</u>		<u>25</u>		<u>5</u>		<u>29</u>							
	-0.62	<u>106</u>	104	<u>16</u>	17	<u>17</u>	18	<u>9</u>	10	<u>31</u>	31	4	3	16	0	50	99
		<u>103</u>		<u>17</u>		<u>18</u>		<u>10</u>		<u>32</u>							
		<u>102</u>		<u>17</u>		<u>18</u>		<u>11</u>		<u>32</u>							
Triphenylamine	-0.56	<u>72</u>	73	<u>12</u>	16	<u>25</u>	28	<u>4</u>	5	<u>35</u>	32	4	3	8	0	43	94
		<u>74</u>		<u>17</u>		<u>28</u>		<u>5</u>		<u>31</u>							
		<u>74</u>		<u>19</u>		<u>30</u>		<u>5</u>		<u>30</u>							
	-0.62	<u>104</u>	103	<u>18</u>	19	<u>21</u>	22	<u>9</u>	10	<u>33</u>	34	3	2	13	0	49	103
		<u>103</u>		<u>19</u>		<u>22</u>		<u>10</u>		<u>34</u>							
		<u>101</u>		<u>20</u>		<u>23</u>		<u>11</u>		<u>35</u>							
Adamantane	-0.56	<u>72</u>	72	<u>11</u>	15	<u>21</u>	23	<u>4</u>	5	<u>39</u>	34	4	3	11	0	48	95
		<u>72</u>		<u>16</u>		<u>24</u>		<u>5</u>		<u>33</u>							
		<u>72</u>		<u>19</u>		<u>25</u>		<u>6</u>		<u>31</u>							
	-0.62	<u>104</u>	103	<u>17</u>	18	<u>19</u>	20	<u>9</u>	10	<u>34</u>	34	3	3	15	0	52	104
		<u>103</u>		<u>18</u>		<u>20</u>		<u>11</u>		<u>35</u>							
		<u>102</u>		<u>19</u>		<u>20</u>		<u>11</u>		<u>35</u>							
cis-Cyclooctene	-0.56	<u>76</u>	77	<u>12</u>	16	<u>19</u>	21	<u>3</u>	4	<u>33</u>	29	3	2	12	0	43	86
		<u>78</u>		<u>16</u>		<u>21</u>		<u>4</u>		<u>28</u>							
		<u>78</u>		<u>18</u>		<u>21</u>		<u>4</u>		<u>27</u>							
	-0.62	<u>115</u>	113	<u>17</u>	19	<u>16</u>	17	<u>6</u>	7	<u>29</u>	30	2	2	12	0	44	90
		<u>113</u>		<u>19</u>		<u>18</u>		<u>7</u>		<u>31</u>							
		<u>111</u>		<u>20</u>		<u>18</u>		<u>8</u>		<u>31</u>							
Glyoxal	-0.56	<u>71</u>	73	<u>12</u>	15	<u>24</u>	27	<u>3</u>	4	<u>36</u>	32	4	1	13	0	47	96
		<u>74</u>		<u>16</u>		<u>27</u>		<u>4</u>		<u>31</u>							
		<u>75</u>		<u>17</u>		<u>29</u>		<u>4</u>		<u>29</u>							
	-0.62	<u>108</u>	108	<u>16</u>	16	<u>21</u>	22	<u>6</u>	7	<u>29</u>	32	6	4	14	0	49	100
		<u>108</u>		<u>16</u>		<u>23</u>		<u>7</u>		<u>33</u>							
		<u>108</u>		<u>16</u>		<u>23</u>		<u>8</u>		<u>33</u>							
2-Ethylhexyl bromide	-0.56	<u>69</u>	70	<u>10</u>	13	<u>24</u>	27	<u>4</u>	5	<u>36</u>	32	4	0	11	0	44	93
		<u>71</u>		<u>14</u>		<u>28</u>		<u>6</u>		<u>31</u>							
		<u>71</u>		<u>16</u>		<u>29</u>		<u>6</u>		<u>29</u>							
	-0.62	<u>94</u>	91	<u>17</u>	17	<u>21</u>	22	<u>9</u>	11	<u>29</u>	30	5	2	13	0	45	100
		<u>90</u>		<u>18</u>		<u>22</u>		<u>11</u>		<u>29</u>							
		<u>89</u>		<u>18</u>		<u>23</u>		<u>13</u>		<u>32</u>							
Agarose	-0.56	<u>58</u>	57	<u>13</u>	16	<u>24</u>	25	<u>6</u>	6	<u>30</u>	28	5	4	10	0	42	94
		<u>57</u>		<u>16</u>		<u>26</u>		<u>6</u>		<u>28</u>							
		<u>56</u>		<u>18</u>		<u>26</u>		<u>6</u>		<u>26</u>							
	-0.62	<u>104</u>	102	<u>15</u>	16	<u>19</u>	19	<u>9</u>	10	<u>29</u>	29	1	3	13	0	45	91
		<u>103</u>		<u>16</u>		<u>19</u>		<u>10</u>		<u>29</u>							
		<u>100</u>		<u>16</u>		<u>19</u>		<u>11</u>		<u>29</u>							
4-Bromotoluene	-0.56	<u>67</u>	67	<u>13</u>	15	<u>24</u>	26	<u>6</u>	7	<u>34</u>	33	4	3	13	0	50	101
		<u>67</u>		<u>15</u>		<u>25</u>		<u>7</u>		<u>33</u>							
		<u>66</u>		<u>16</u>		<u>27</u>		<u>7</u>		<u>32</u>							
	-0.62	<u>101</u>	100	<u>15</u>	16	<u>21</u>	21	<u>10</u>	11	<u>35</u>	34	3	3	14	0	51	102
		<u>100</u>		<u>17</u>		<u>21</u>		<u>12</u>		<u>33</u>							
		<u>99</u>		<u>17</u>		<u>20</u>		<u>12</u>		<u>33</u>							
4-Chlorobenzonitrile	-0.56	<u>64</u>	65	<u>11</u>	14	<u>26</u>	29	<u>3</u>	3	<u>32</u>	28	5	3	11	0	43	94
		<u>66</u>		<u>15</u>		<u>29</u>		<u>3</u>		<u>27</u>							
		<u>65</u>		<u>17</u>		<u>31</u>		<u>3</u>		<u>26</u>							
	-0.62	<u>101</u>	100	<u>16</u>	16	<u>24</u>	25	<u>5</u>	6	<u>27</u>	28	2	2	15	0	45	93
		<u>100</u>		<u>17</u>		<u>25</u>		<u>6</u>		<u>28</u>							
		<u>98</u>		<u>17</u>		<u>25</u>		<u>6</u>		<u>28</u>							
1,4-Phenylenediaceto nitrile	-0.56	<u>62</u>	63	<u>12</u>	15	<u>24</u>	26	<u>2</u>	3	<u>34</u>	30	5	2	12	0	45	93
		<u>63</u>		<u>15</u>		<u>27</u>		<u>3</u>		<u>29</u>							
		<u>64</u>		<u>17</u>		<u>27</u>		<u>3</u>		<u>27</u>							
	-0.62	<u>99</u>	97	<u>14</u>	15	<u>19</u>	19	<u>5</u>	5	<u>28</u>	28	4	2	15	0	46	90
		<u>97</u>		<u>15</u>		<u>19</u>		<u>5</u>		<u>28</u>							
		<u>94</u>		<u>16</u>		<u>19</u>		<u>6</u>		<u>28</u>							
D-Phenylalanine	-0.56	<u>69</u>	67	<u>14</u>	16	<u>37</u>	38	<u>4</u>	4	<u>32</u>	28	6	3	7	0	38	102
		<u>68</u>		<u>18</u>		<u>43</u>		<u>5</u>		<u>31</u>							
		<u>65</u>		<u>20</u>		<u>35</u>		<u>3</u>		<u>20</u>							
	-0.62	<u>100</u>	100	<u>17</u>	17	<u>30</u>	30	<u>7</u>	8	<u>35</u>	34	2	1	11	0	46	103
		<u>100</u>		<u>17</u>		<u>30</u>		<u>8</u>		<u>34</u>							
		<u>100</u>		<u>17</u>		<u>30</u>		<u>8</u>		<u>32</u>							
N-Acetyl-D- Glucosamine	-0.56	<u>54</u>	54	<u>22</u>	22	<u>25</u>	25	<u>3</u>	3	<u>39</u>	27	5	1	8	0	37	91
		<u>55</u>		<u>21</u>		<u>24</u>		<u>3</u>		<u>27</u>							

	-0.62	53	88	22	19	25	19	4	7	26	27	4	3	13	0	43	92
		85		18		19		6		26							
		89		19		20		8		27							
		89		18		20		8		28							
L-Threonine	-0.56	68	68	13	16	32	36	3	3	30	26	3	2	8	0	36	94
		67		18		37		3		25							
		70		18		38		4		23							
		101		14		29		6		27							
	-0.62	96	98	15	15	28	29	6	6	25	27	3	3	11	0	41	95
		97		17		31		7		28							
		67		13		33		4		30							
		71		17		37		5		27							
L-Aspartic acid	-0.56	68	69	18	16	36	35	5	4	23	27	4	2	10	0	39	98
		95		17		29		7		25							
		97		18		28		8		26							
		99		16		27		8		25							
cis-4-Hydroxy-D-proline	-0.56	68	71	11	14	29	33	3	3	35	30	4	1	14	0	45	100
		72		15		35		2		30							
		74		15		35		4		26							
		108		14		28		7		32							
	-0.62	107	107	16	16	29	28	8	8	32	32	3	1	12	0	45	100
		105		16		29		8		31							
		65		14		28		3		27							
		70		17		32		4		24							
L-Glutamic acid	-0.56	70	68	20	17	32	31	4	4	21	24	4	3	10	0	38	93
		108		17		26		8		28							
		107		17		27		8		29							
		105		18		27		8		28							
DL-Phenylalanine	-0.56	70	71	17	19	38	41	4	5	28	29	4	1	8	0	37	107
		70		19		41		5		28							
		72		20		44		6		30							
		92		19		32		6		26							
	-0.62	108	103	20	19	31	31	8	7	28	28	3	2	10	1	41	103
		110		19		31		8		30							
		61		10		8		1		44							
		60		15		8		2		39							
1-Mercaptooctane	-0.56	60	60	18	14	6	7	2	2	38	40	5	2	15	0	56	85
		97		18		5		4		34							
		98		19		6		3		34							
		97		19		7		3		35							
2,2'-Dithiodipyridine	-0.56	91	89	54	45	3	6	0	0	2	7	25	2	5	0	14	90
		89		41		7		0		9							
		88		39		9		1		11							
		135		34		10		3		18							
	-0.62	133	133	33	33	12	12	3	3	17	18	13	2	8	3	30	91
		132		32		13		4		18							
		87		40		6		1		7							
		91		36		9		1		13							
3-Pyridinemethanethiol	-0.56	90	89	34	37	10	8	1	1	15	12	24	2	7	0	21	91
		121		28		14		3		24							
		118		28		15		3		26							
		117		28		18		4		31							
4-Mercaptopyridine	-0.56	92	86	66	59	6	9	0	0	7	12	11	1	4	0	17	97
		84		59		9		0		13							
		82		53		12		0		16							
		138		39		12		2		23							
	-0.62	133	134	34	35	13	13	2	2	25	25	7	1	11	0	36	94
		131		32		14		3		26							
		100		18		17		1		29							
		102		23		22		2		25							
Thiophene	-0.56	101	101	24	22	21	20	2	2	25	26	4	2	8	1	37	84
		156		25		17		3		27							
		154		26		18		3		28							
		153		28		19		4		30							
2,2':5',2''-Terthiophene	-0.56	94	91	28	32	12	10	1	2	31	26	10	2	12	3	44	97
		92		33		10		2		23							
		88		34		8		3		24							
		130		36		6		4		26							
	-0.62	123	125	38	37	6	6	5	5	28	27	9	2	13	2	43	100
		123		37		6		5		27							

7-Diethylamino-3-thenoylcoumarin	-0.56	96	97	22	26	12	14	1	2	28	25	9	2	10	0	37	88
		97		27		16		2		24							
		98		28		15		2		24							
	-0.62	145	144	27	27	12	13	3	3	27	27	7	2	12	3	44	95
		144		27		14		3		27							
		142		28		14		4		28							
1,2-Ethanedithiol	-0.56	80	85	37	32	5	8	3	3	29	31	8	2	13	2	48	98
		86		31		7		2		31							
		88		28		11		2		33							
	-0.62	133	130	29	27	9	9	3	3	36	38	5	2	16	2	58	102
		129		26		9		4		39							
		127		27		8		4		38							
Mercaptoacetic acid	-0.56	97	98	38	36	11	15	0	1	7	10	24	2	4	0	16	93
		98		35		16		1		11							
		99		36		19		1		12							
	-0.62	136	135	31	30	18	21	3	3	18	21	12	1	7	2	30	97
		135		30		20		3		20							
		133		30		24		4		25							
L-Cysteine	-0.56	94	96	43	42	11	14	1	2	21	19	6	1	8	3	31	95
		97		43		14		2		18							
		96		39		17		2		18							
	-0.62	141	136	30	30	17	16	6	7	23	23	3	2	9	0	34	90
		137		30		17		7		24							
		131		30		13		9		21							
4-Thiazolecarboxylic acid	-0.56	98	99	38	37	12	16	1	1	13	14	15	3	7	3	27	97
		100		37		18		1		15							
		99		37		20		2		15							
	-0.62	150	147	33	32	17	18	3	4	18	21	9	2	9	3	35	98
		147		32		17		4		21							
		145		33		19		5		24							
1,4-Benzenedithiol	-0.56	79	74	61	58	3	3	2	2	11	13	8	2	10	0	25	95
		73		58		3		2		13							
		71		54		3		2		14							
	-0.62	105	104	51	50	3	4	6	10	16	14	5	2	8	0	25	94
		105		50		5		14		11							
		102		49		4		9		17							
2-Thiopheneacetic acid	-0.56	90	94	23	25	20	22	1	1	27	24	5	1	8	2	35	88
		96		25		22		2		23							
		96		26		23		2		21							
	-0.62	154	150	31	32	16	18	3	4	19	21	5	1	8	1	32	90
		150		32		18		4		21							
		147		32		20		4		22							
10-Methylphenothiazine	-0.56	101	102	27	31	12	14	1	1	26	24	7	3	10	3	40	94
		103		33		14		1		23							
		102		34		16		2		23							
	-0.62	148	146	33	33	15	15	3	4	27	27	4	1	9	2	39	94
		146		33		15		4		28							
		144		33		15		4		27							
2-Chlorophenothiazine	-0.56	101	103	19	22	17	18	2	2	32	30	5	2	14	2	48	96
		104		23		18		2		28							
		104		25		19		2		30							
	-0.62	149	147	24	25	17	18	4	5	33	34	2	1	13	1	49	98
		147		24		17		4		32							
		145		26		19		5		36							
Benzothiazole	-0.56	105	106	30	33	14	18	1	1	25	23	8	2	9	0	34	94
		107		34		18		1		22							
		106		36		22		1		23							
	-0.62	151	149	30	31	21	22	2	3	25	27	7	1	8	0	36	98
		150		30		21		3		26							
		147		31		23		4		29							
3-(Carboxymethyl)benzothiazolium Bromide	-0.56	100	103	16	21	23	25	1	2	22	22	6	2	8	1	33	87
		104		23		26		2		22							
		104		25		26		2		22							
	-0.62	134	132	23	23	20	20	5	5	30	29	4	2	10	2	43	96
		132		23		20		5		28							
		129		24		20		6		30							
5-(2-Hydroxyethyl)-4-methylthiazole	-0.56	92	92	44	42	11	15	0	1	8	10	22	1	4	2	17	96
		93		42		14		1		10							
		92		39		18		1		11							
-0.62	150	148	36	34	15	17	2	3	18	19	10	1	7	1	29	93	

3,3'-dimercapto- [1,1'-biphenyl]- 4,4'-dicarboxylic acid	-0.56	147	67	34	32	17	36	3	3	19	13	5	2	3	0	19	95
		147		33		18		3		20							
		65		33		39		3		13							
	-0.62	68	33	36	3	13	19	4	2	7	0	28	89				
		69	31	33	3	13											
		102	27	24	7	19											
5-Acetyl-2- thiopheneboronic acid	-0.56	102	102	27	26	25	24	7	7	19	15	10	2	5	0	21	87
		102		27		25		7		19							
		103		25		23		7		18							
	-0.62	99	36	13	2	15	18	7	2	8	0	27	91				
		100	39	16	3	15											
		100	39	17	3	15											
Thiourea	-0.56	148	83	36	43	14	7	6	0	1	3	33	3	0	0	6	90
		84		43		7		0		3							
		84		42		11		0		5							
	-0.62	126	38	14	2	12	13	16	1	5	0	18	90				
		126	36	20	2	13											
		125	36	17	3	13											
Thioacetamide	-0.56	80	81	49	46	6	11	1	1	3	5	24	2	0	0	7	89
		81		46		12		1		6							
		82		44		15		1		7							
	-0.62	131	40	16	3	11	12	21	1	4	0	17	97				
		130	38	19	3	12											
		130	37	20	3	12											
2- Bromothiophene	-0.56	86	89	12	18	15	18	2	3	28	27	5	3	9	0	38	82
		90		19		18		3		25							
		91		22		22		4		28							
	-0.62	134	21	18	7	31	32	2	2	10	0	43	94				
		133	22	19	9	33											
		132	22	18	10	31											
2-Bromo-5- methylthiophene	-0.56	95	95	24	28	20	20	2	2	22	20	7	3	8	0	31	88
		96		29		20		2		20							
		95		32		20		2		19							
	-0.62	133	33	16	4	20	21	6	1	10	0	32	90				
		127	33	16	5	21											
		121	33	16	6	21											
N- Fluorobenzenesul fonimide	-0.56	96	100	25	26	20	23	2	2	27	24	5	2	8	3	37	92
		102		26		23		2		23							
		101		27		24		2		21							
	-0.62	133	28	20	3	27	27	4	1	9	0	38	91				
		130	29	21	3	27											
		126	29	11	3	28											
L-Cystine	-0.56	80	81	21	23	12	13	3	4	33	32	4	2	12	0	45	89
		81		24		13		4		31							
		81		23		14		5		30							
	-0.62	118	19	11	8	29	31	3	3	16	0	50	97				
		113	21	14	10	32											
		110	21	14	12	32											
Glutathione	-0.56	86	87	20	22	22	23	3	3	27	25	9	3	13	0	40	97
		88		23		23		3		24							
		88		24		24		3		23							
	-0.62	132	22	20	6	26	29	7	2	11	2	43	100				
		129	23	20	6	28											
		127	24	24	7	32											
2- Mercaptopyridine	-0.56	100	96	48	46	4	11	0	0	2	4	23	2	2	0	8	89
		94		46		13		1		5							
		95		45		15		1		5							
	-0.62	141	39	18	2	10	11	15	1	4	0	17	92				
		138	37	20	3	12											
		136	35	22	3	12											
4,4'-Dipyridine disulfide	-0.56	85	88	96	99	0	1	0	0	0	0	6	0	0	0	0	107
		94		101		2		0		0							
		84		101		2		0		1							
	-0.62	120	82	7	1	5	8	6	2	3	0	14	108				
		110	74	10	3	9											
		104	68	12	5	12											
	-0.56	86	87	49	43	2	7	0	0	1	6	29	1	1	0	8	87
		88		40		9		1		7							

2-Pyridinemethanethiol		87		40		11		1		9							
		130		32		15		3		18							
	-0.62	130	129	31	32	15	15	4	4	19	19	16	2	8	3	32	99
Ethanethiol		128		31		16		5		21							
		93		25		15		3		24							
	-0.56	94	93	28	28	16	16	3	3	23	23	7	1	9	0	33	86
2-Amino-1-ethanethiol		93		30		16		4		22							
		131		30		14		7		25							
	-0.62	127	127	29	30	14	15	8	8	26	27	3	1	10	0	38	94
2-Amino-1-ethanethiol		123		31		15		10		29							
		90		60		5		1		8							
	-0.56	88	89	47	50	9	9	1	1	14	13	15	1	4	0	18	92
Thiazole		88		42		11		1		17							
		134		31		12		4		24							
	-0.62	132	133	28	28	13	13	4	4	26	26	8	1	9	0	36	90
Methanethiole		132		26		14		5		27							
		74		14		22		7		25							
	-0.56	80	78	19	18	23	23	6	6	21	22	4	2	11	0	35	87
Methanethiole		80		21		25		6		20							
		116		19		16		11		23							
	-0.62	115	115	19	19	16	17	12	12	22	23	4	3	15	0	41	92
1,5-Pentanedithiol		113		20		17		13		23							
		82		19		12		3		27							
	-0.56	83	83	28	25	14	14	3	3	21	22	7	2	13	0	38	87
1,5-Pentanedithiol		85		28		17		3		20							
		118		25		12		8		26							
	-0.62	116	117	24	24	13	13	11	10	27	27	4	4	16	0	47	97
2,3-Butanedithiol		116		23		14		10		27							
		51		41		1		5		28							
	-0.56	53	53	42	41	5	4	4	4	30	30	4	3	12	0	44	96
2,3-Butanedithiol		55		39		5		3		31							
		83		28		2		7		35							
	-0.62	84	84	27	27	2	2	7	7	36	36	3	3	17	0	56	95
1,8-Octanedithiol		84		26		2		7		36							
		46		44		1		13		23							
	-0.56	56	54	39	38	1	1	8	9	25	26	2	3	10	0	39	90
1,8-Octanedithiol		59		32		2		7		29							
		98		32		1		13		26							
	-0.62	96	96	30	30	2	2	14	13	26	26	2	2	15	0	44	90
1,2-Benzenedithiol		94		28		2		14		27							
		60		23		3		6		38							
	-0.56	66	65	27	25	3	3	5	5	35	36	4	3	17	0	56	93
1,2-Benzenedithiol		68		26		3		5		35							
		109		20		3		6		35							
	-0.62	108	108	18	18	3	3	6	6	36	36	3	3	22	1	62	93
1,10-Decanedithiol		108		17		3		6		37							
		64		20		15		4		26							
	-0.56	66	65	21	21	20	19	5	5	25	25	8	4	12	0	40	94
1,10-Decanedithiol		65		22		23		5		24							
		101		22		17		12		24							
	-0.62	99	100	23	23	18	18	14	13	24	24	4	3	14	0	41	99
1,4-Butanedithiol		99		24		19		15		24							
		46		23		10		6		31							
	-0.56	46	46	23	23	10	10	6	6	29	29	5	5	16	0	51	95
1,4-Butanedithiol		46		23		9		5		28							
		86		24		6		9		31							
	-0.62	85	85	25	25	6	6	9	9	30	31	2	2	18	0	51	93
1,3-Benzenedithiol		85		25		6		9		32							
		64		29		9		3		30							
	-0.56	65	65	31	30	10	10	3	3	30	30	4	3	17	0	50	98
1,3-Benzenedithiol		65		31		12		3		31							
		102		30		10		7		30							
	-0.62	101	101	31	31	10	10	8	8	32	32	2	2	16	0	50	102
1,4-Butanedithiol		99		31		11		9		34							
		58		21		18		5		26							
	-0.56	62	61	26	25	22	21	6	6	25	25	4	1	10	0	36	91
1,4-Butanedithiol		63		28		23		6		24							
		98		24		18		11		29							
	-0.62	98	98	25	25	19	19	11	11	29	29	4	3	13	0	44	104
1,4-Butanedithiol		97		26		20		11		28							
		97		26		20		11		28							
		97		26		20		11		28							

4-Mercaptobenzoic acid	-0.56	55	20	25	2	28	25	6	2	8	0	34	96
		59	26	28	2	24							
		60	29	30	2	22							
	-0.62	82	24	24	4	26	28	5	3	11	0	42	104
		80	26	28	5	28							
		79	27	26	6	29							
6,6'-Dithiodinitrocinic Acid	-0.56	64	53	8	1	7	10	22	2	3	0	14	99
		64	43	17	2	10							
		64	41	22	2	12							
	-0.62	96	30	22	7	17	18	10	3	8	0	29	101
		95	30	26	7	18							
		94	29	27	8	20							
p-Tolyl disulfide	-0.56	67	14	15	3	36	33	3	2	13	0	49	91
		70	18	19	3	34							
		74	19	21	3	31							
	-0.62	104	19	17	7	34	34	2	2	13	0	50	98
		103	20	19	8	35							
		102	21	20	9	34							
2-Chlorobenzyl Mercaptan	-0.56	58	26	6	2	31	31	10	2	13	0	46	91
		58	26	6	2	31							
		60	25	6	2	32							
	-0.62	88	22	5	6	34	35	5	3	16	0	54	92
		84	23	5	6	36							
		80	23	5	6	36							
Tetrahydrothiopyran-4-one	-0.56	68	18	24	4	30	30	3	3	6	0	40	93
		69	20	28	3	30							
		69	21	30	4	30							
	-0.62	99	19	18	6	34	36	3	2	12	0	50	100
		98	20	21	7	37							
		96	20	22	8	37							
4-(Methylsulfanyl)benzaldehyde	-0.56	83	19	21	3	25	30	4	2	11	0	43	102
		85	24	29	4	32							
		86	25	32	5	33							
	-0.62	111	23	21	8	34	33	3	2	13	1	50	107
		109	23	21	8	33							
		106	24	23	9	33							
2-Amino-4-chlorothiophenol	-0.56	82	50	13	2	26	22	12	0	0	0	22	100
		83	47	15	2	21							
		82	47	18	2	20							
	-0.62	122	39	14	7	28	28	6	2	10	0	40	104
		118	36	16	7	29							
		111	34	16	7	27							
4,4'-Diaminodiphenylsulfone	-0.56	67	11	19	3	33	31	6	4	15	0	50	94
		67	14	22	4	30							
		65	16	23	4	30							
	-0.62	98	14	17	7	34	36	3	2	15	0	52	97
		97	15	18	8	35							
		96	16	19	9	37							
1-Methyl-2-imidazolidinethione	-0.56	60	25	20	2	22	19	13	3	4	0	26	90
		63	25	25	1	19							
		65	26	29	2	17							
	-0.62	92	22	23	5	25	24	8	3	5	0	32	92
		91	21	27	5	24							
		90	20	29	5	24							
2-Mercaptophenol	-0.56	91	102	0	0	0	0	8	1	2	0	2	114
		86	103	0	0	0							
		81	105	0	0	0							
	-0.62	114	102	1	0	0	0	9	0	4	0	4	117
		106	102	1	0	0							
		100	104	1	0	0							
4-Chlorothiophenol	-0.56	68	18	14	3	39	33	4	1	11	0	45	90
		67	23	17	3	32							
		67	23	18	3	29							
	-0.62	96	20	15	6	31	30	5	3	15	0	48	95
		97	20	15	6	29							
		96	20	18	7	31							
1,3-Diphenyl-2-thiourea	-0.56	66	26	12	4	27	23	17	2	12	0	38	99
		67	28	13	4	23							
		66	32	13	3	20							
	-0.62	98	32	11	9	21	20	14	2	12	0	34	101

				95	34	11	8	20											
				93	37	12	7	19											
				56	26	18	3	21											
				53	25	22	3	22											
Tetrahydrothiazol yl thione	-0.56	53	53	26	26	22	22	3	3	22	21	4	1	7	0	29	84		
		51		26		25		4		21									
		94	94	22	22	20	20	11	11	31	30	29	4	3	7	0	39	96	
				93		22		20		11		27							
				61		37		20		4		24							
				64	63	43	42	22	22	4	4	19	20	6	2	5	0	27	101
				64		46		24		4		17							
4- (Methylthio)pheno l				90		44		16		10		19							
				90	90	41	41	18	18	11	11	21	21	5	2	6	0	28	103
				90		39		20		12		22							
				59		34		10		2		27							
2-Amino-6- bromobenzothiaz ole				61	61	43	41	11	11	2	2	21	23	13	3	10	0	35	103
				62		45		12		2		20							
				89		38		14		5		23							
				87	87	37	37	16	16	5	5	23	22	9	1	9	0	32	100
				85		37		17		5		21							
				62		25		13		2		31							
				64	63	33	32	14	15	2	2	22	24	13	2	7	0	34	95
				64		36		16		2		20							
2-Amino-6- fluorobenzothiazol e				96		31		15		4		20							
				95	95	31	31	17	17	4	4	20	20	6	3	7	0	31	89
				93		31		19		4		21							
				60		17		23		3		22							
Diphenyl sulfone				64	62	22	22	30	29	4	4	19	21	5	6	15	0	41	101
				62		26		34		5		21							
				85		22		21		10		26							
				84	83	22	21	21	21	10	10	26	25	4	3	19	0	47	103
				81		21		22		10		24							
				53		31		18		6		23							
				56	55	31	32	21	21	6	6	22	23	9	4	13	0	39	106
				56		32		25		6		22							
2,2'- Diaminodiphenyl disulphide				86		25		17		13		27							
				85	86	26	25	19	18	14	14	29	28	5	1	11	0	40	103
				86		25		20		15		29							
				61		23		21		4		31							
Bis(2-nitrophenyl) disulfide				65	63	28	27	22	23	4	4	24	26	5	3	12	0	41	100
				64		31		25		4		24							
				96		24		19		8		27							
				95	95	26	25	20	20	9	9	28	28	6	3	13	0	44	105
				93		26		22		10		29							
				63		37		16		2		23							
				66	66	41	39	19	18	2	2	20	20	8	3	8	0	31	99
				68		40		20		2		18							
Phenyl Disulfide				98		33		15		4		21							
				96	96	34	34	16	16	5	5	22	21	5	6	8	0	36	96
				94		34		18		5		21							
				64		15		31		2		35							
Glycol sulfite				64	64	18	18	34	35	2	2	31	33	5	1	8	0	43	102
				65		19		39		2		34							
				95		17		28		4		39							
				95	95	17	17	28	28	4	4	38	38	5	1	10	0	50	105
				94		18		29		5		39							
				64		16		11		4		33							
				64	64	22	20	13	13	4	4	31	32	8	1	12	0	45	90
				64		22		14		5		31							
Di(thiophen-2- yl)methanone				96		18		10		8		33							
				94	94	19	19	11	11	9	9	37	36	5	2	13	0	52	96
				93		19		12		9		38							
				71		21		26		5		22							
p- Toluenesulfonami de				72	72	23	23	28	27	5	5	21	21	4	2	7	0	31	91
				72		24		29		6		21							
				104		20		18		9		25							
				103	103	20	20	19	19	10	10	28	27	3	2	11	0	40	93
				101		21		21		11		29							
				48	53	18	21	22	24	2	2	21	16	19	3	8	0	27	92
				54		22		21		2		16							

2-Amino-5-methyl-1,3,4-thiadiazole		57		23		29		1		13							
		92		22		21		3		15							
	-0.62	92	92	21	21	24	25	3	3	16	16	13	2	9	0	28	90
		92		21		30		3		18							
2,3,5,6-Tetrafluorothiophenol		63		21		14		4		26							
	-0.56	64	64	22	21	21	19	4	4	25	25	7	1	14	0	40	92
		65		21		22		4		25							
	-0.62	97	96	18	18	15	15	9	9	31	33	4	2	18	0	53	99
Triphenylmethane thiol		96		18		16		10		34							
	-0.56	56	58	49	50	6	7	1	1	8	6	28	3	0	0	9	94
		59		50		6		1		6							
	-0.62	60	85	45	44	7	10	1	4	6	14	20	2	3	0	18	96
Cyclohexyl mercaptan		86		43		8		4		12							
	-0.56	85	63	42	13	10	12	4	2	14	38	4	2	19	0	58	90
		84		42		12		4		15							
	-0.62	89	89	14	14	11	11	3	3	36	37	3	3	20	2	61	93
Di-tert-butyl disulfide		88		14		10		3		37							
	-0.56	54	56	11	15	17	21	1	1	36	31	9	3	9	1	44	90
		56		16		22		1		30							
	-0.62	57	80	19	21	23	18	2	4	27	30	6	5	9	0	44	92
1-Adamantanethiol		80	80	20	21	17	18	4	4	31							
	-0.56	80	59	21	15	4	14	4	5	30	33	3	5	12	0	50	87
		80		21		19		4		30							
	-0.62	83	87	19	19	11	11	7	9	37	38	2	2	16	0	56	97
2-Phenyl-1,3-dithiane		88		19		10		9		39							
	-0.56	44	46	34	40	4	4	4	3	26	25	12	2	12	0	39	98
		46		43		5		2		23							
	-0.62	48	79	42	33	4	8	2	4	25	32	8	2	8	0	43	96
Dimethylthioacetamid		78		35		6		4		31							
	-0.56	80	59	33	30	7	12	4	1	32	32	8	2	8	0	43	96
		80		31		10		4		34							
	-0.62	58	59	29	30	7	12	1	1	10	12	32	3	5	0	21	95
Diallyl sulfide		59	59	30	30	12	12	1	1	13							
	-0.56	60	90	29	24	17	23	1	3	14	20	17	3	3	0	26	93
		90		25		17		3		20							
	-0.62	91	62	24	16	26	23	3	2	20	29	8	4	9	0	41	90
DL-Dithiothreitol		88		24		25		4		21							
	-0.56	62	62	14	16	19	21	2	5	32	30	5	2	13	0	45	91
		62		17		24		2		29							
	-0.62	63	88	18	16	26	21	2	5	26	30	5	2	13	0	45	91
Benzyl mercaptan		88		16		22		5		29							
	-0.56	61	64	28	28	10	15	4	4	26	24	9	3	10	0	37	93
		65		27		16		4		24							
	-0.62	67	94	28	27	20	20	3	7	22	29	6	1	11	0	41	102
1H,1H,2H,2H-Perfluorooctyl mercaptan		95		26		18		7		27							
	-0.56	94	70	27	15	21	18	7	4	27	29	7	3	15	0	47	91
		94		27		22		8		30							
	-0.62	62	64	26	27	9	11	3	3	23	24	13	4	11	0	39	92

1-Octadecanethiol	-0.56	60	63	11	17	19	2	3	36	32	5	4	11	1	47	90
		64		18			3		30							
		65		21			3		29							
	-0.62	93	92	22	23	15	4	5	31	31	3	1	15	0	47	94
		92		24			5		31							
		92		24			6		32							
D-Cystine	-0.56	69	73	17	20	19	2	2	35	31	3	3	12	1	47	92
		74		22			2		30							
		75		22			2		28							
	-0.62	108	107	18	19	20	6	7	32	33	3	2	12	0	47	96
		107		19			7		34							
		107		19			8		33							
2,2'-dithiobis(ethylamine)	-0.56	72	72	77	69	3	0	0	3	6	11	2	0	0	8	92
		73		75			0		4							
		72		56			0		10							
	-0.62	91	84	78	64	3	0	1	4	8	9	2	3	1	13	90
		83		61			1		8							
		79		50			2		13							
DL-Cystine	-0.56	58	61	22	21	21	2	2	32	29	4	5	9	0	43	91
		62		21			2		29							
		63		19			2		27							
	-0.62	112	113	16	16	18	7	8	30	30	2	2	15	2	49	93
		113		16			8		30							
		113		16			8		30							
tert-dodecylthiol	-0.56	62	63	17	20	11	3	2	34	30	8	3	11	0	43	86
		63		21			3		29							
		64		23			2		27							
	-0.62	92	93	22	22	14	6	5	29	29	8	2	10	0	40	89
		93		22			5		29							
		93		22			5		28							
CuOx	-0.56	108	113	15	19	17	0	0	36	32	9	2	8	4	46	91
		115		20			0		30							
		115		22			0		30							
	-0.62	146	143	22	22	17	1	1	35	35	6	1	9	3	49	96
		143		22			1		36							
		139		23			1		36							

4. The discussion surrounding the metal–organic interphase is limited to hypotheses or speculative correlations. Several key points need further clarification:

o The authors correlate molecular hydrophobicity with the formation of stacked layers, but this relationship is not clearly explained.

Reply and actions taken: We thank the reviewer for this comment. However, we did not suggest that hydrophobic molecular modifiers lead to the formation of a metal-organic interphase. Instead, we proposed that the molecules need to have a coordination site to coordinate to Cu or Cu nanoparticles. After that, if the molecule has a hydrophobicity part, they may induce the stacking of the modifier-Cu complex or modified Cu nanostructure and possibly also the modifier molecule itself. We obtained this hint from machine learning analysis, but such a stacking can be driven by several interactions, based on basic chemical principles:

1. **Hydrophobic Effect:** Hydrophobic groups aggregate to reduce their exposure to water, minimizing the free energy of the whole system.
2. **Van der Waals Forces:** Weak attractive forces between hydrophobic groups encourage stacking.
3. **Conjugation (π - π Stacking):** Aromatic rings can form π - π interactions, promoting

further aggregation.

These interactions collectively lead to stable molecular arrangements, which are widely applied in areas such as self-assembly, nanotechnology, and biomolecular aggregation. (*Nature*, 437(7058), 640-647. *Science*, 295(5564), 2418-2421.)

We have added the reference mentioned above in the revised manuscript to address your concern: “*First, the hydrophobicity may encourage the stacking of the modifier-Cu complex or nanostructure in water, helping in the formation of the metal-organic interphase.*^{40,41}” (**please see the revised manuscript, Page 7, Paragraph 5, Lines 2-3**)

o No clear evidence is provided to support the existence of a continuous metal-organic interphase.

Reply and actions taken: The existence of a continuous metal-organic interphase was carefully tested and analyzed in the ‘**Characterization of Interphase vs. Monolayer Modification**’ and ‘***In situ* Raman Spectroscopy**’ sections in our original manuscript. In general, TEM and EDX images demonstrated the presence of multi-layer Cu-thiol phase (Figures 4a-4f). The Cu^I-S bonds shown in S 2p XPS spectra validated the metal-thiol coordination (Figure 4u). The Raman shifts of $\nu(\text{C-S})_{\text{G}}$, $\nu(\text{C-S})_{\text{T}}$, $\nu(\text{C-C})_{\text{G}}$, $\nu(\text{C-C})_{\text{T}}$, $\nu_{\text{s}}(-\text{CH}_2)$ and $\nu_{\text{as}}(-\text{CH}_2)$ for pure 1,8-octanedithiol shifted after being modified on CuO_x catalysts also proved the coordination of thiol on Cu (Figures S57 and S58).

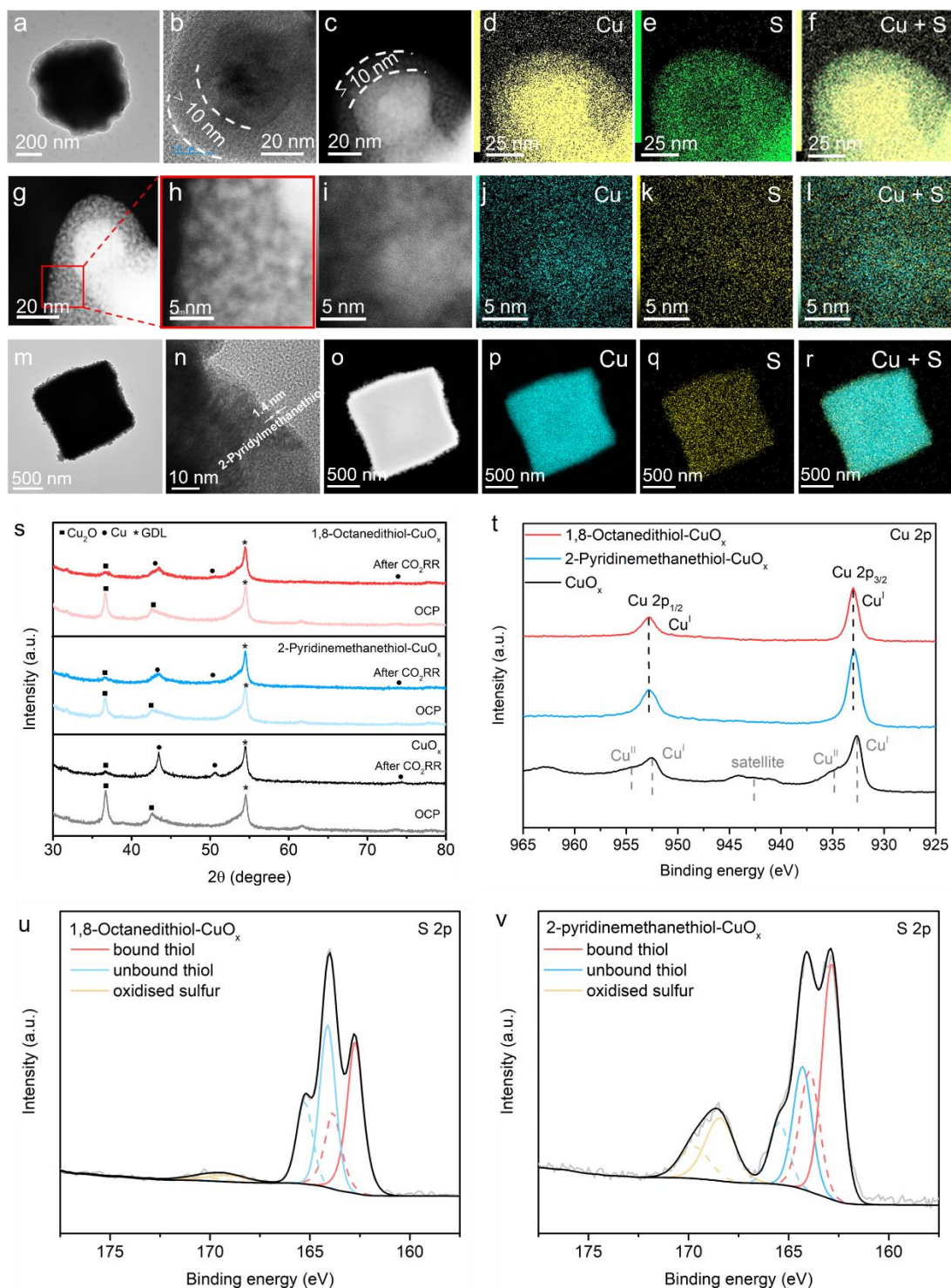


Figure 4. (a-b) TEM image of as prepared 1,8-octanedithiol-CuO_x catalyst, (c) HADDF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping results of (d) Cu, (e) S elements and (f) overlapping plot of Cu and S elements. (g) DF-STEM image. (h) The enlarged BF-STEM image of 1,8-octanedithiol-CuO_x of the red frame in (g). (i) Magnified DF-STEM image of a localized region within the interphase for 1,8-octanedithiol-CuO_x and its corresponding EDX mapping of (j) Cu, (k) S and (l) Cu and S overlapping. (m-n) TEM image of as prepared 2-pyridinemethanethiol-CuO_x catalyst, (o) HADDF image of 2-pyridinemethanethiol-CuO_x catalyst and corresponding EDX mapping results of (p) Cu, (q) S elements and (r) overlapping plot of Cu and S elements. (s)

XRD patterns of CuO_x , 1,8-octanedithiol- CuO_x , and 2-pyridinemethanethiol- CuO_x catalysts at open circuit potential (OCP) and after CO_2RR . (t) XPS spectra of Cu 2p of as prepared CuO_x , 1,8-octanedithiol- CuO_x , and 2-pyridinemethanethiol- CuO_x catalysts. XPS spectra of S 2p (The solid line represents S 2p_{3/2}, the dashed line represents S 2p_{1/2}) of as prepared (u) 1,8-octanedithiol- CuO_x catalyst and (v) 2-pyridinemethanethiol- CuO_x catalyst.

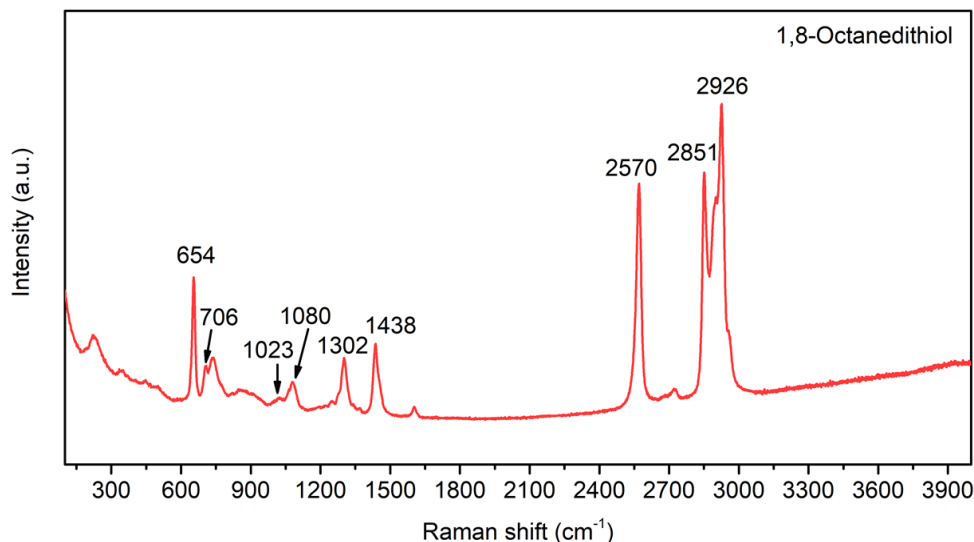


Figure S57. *Ex situ* Raman spectrum of standard 1,8-octanedithiol.

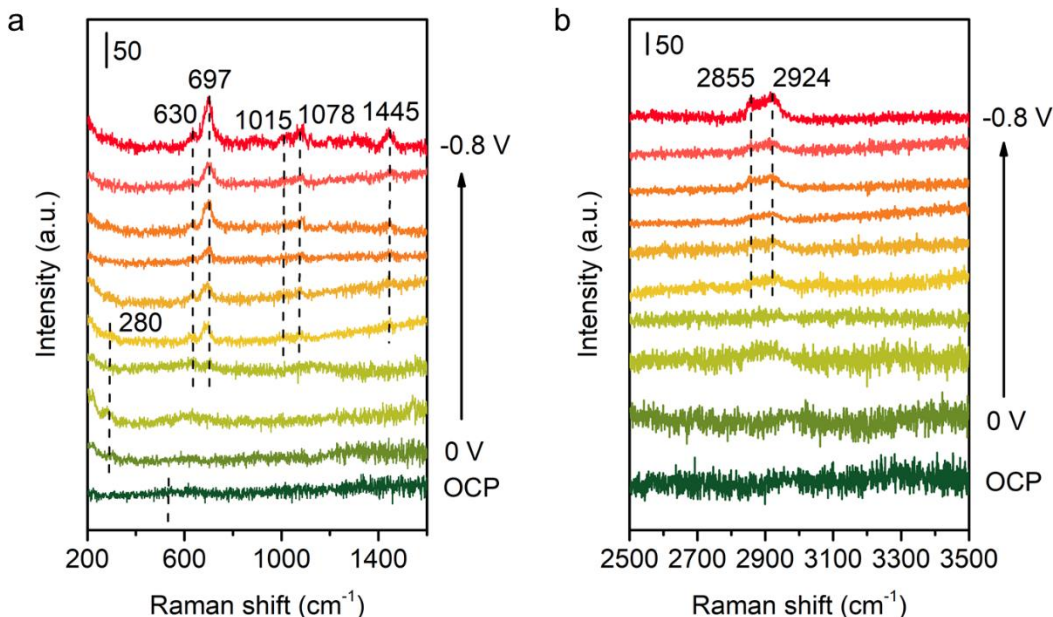


Figure S58. *In situ* Raman spectra of 1,8-octanedithiol- CuO_x in the region of (a) 200~1600 cm^{-1} and (b) 2500~4000 cm^{-1} . The peak at 1445 cm^{-1} could be assigned to the absorbed carbon species CH_x or the vibration of SC-H_2 .

To provide clearer evidence, we used spherical aberration electron microscopy to take images of the metal-organic interphase in higher resolution in the revised paper.

As shown in Figure R15 for the 1,8-octanedithiol- CuO_x catalyst, within the interphase, there were regions rich in Cu and regions of a few nanometers in size, intercalated with regions deficient in Cu. This is consistent with a picture of Cu nanoparticles coordinated by 1,8-

octanedithiol aggregated together.

We also tried to perform EELS tests (Figure R16) in the interphase region to explore the valence distribution of Cu and S, but due to the limitations of the instrument's optical path and the thickness of the interphase, only very weak signals could be observed, which could not serve as a strong evidence.

By the way, when we re-examine some published results in literature, we also found substantial evidence supporting formation of an interphase for alkylthiol modified Cu or CuO, as revealed by XPS, TEM and Raman characterization (*Langmuir* **2016**, 32, 3848-3857, *Thin Solid Films* **1994**, 244, 799-805.).

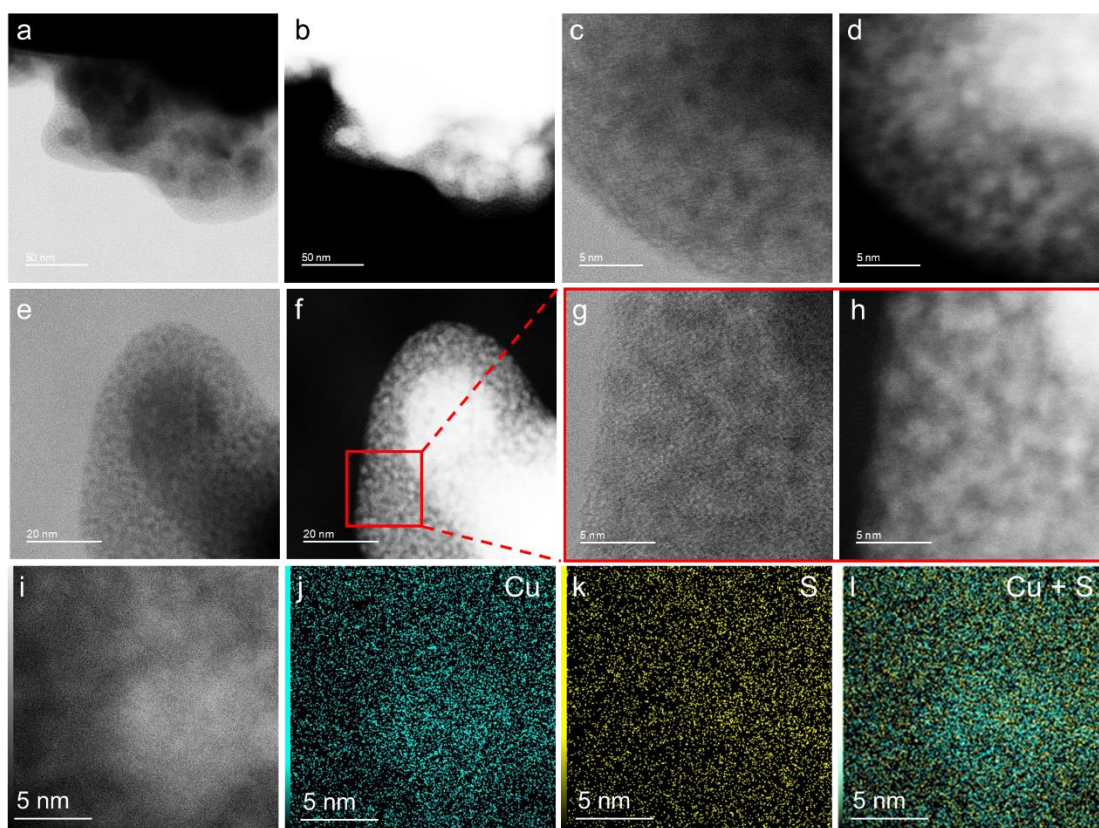


Figure R15. Spherical aberration corrected electron microscopy characterization. (a) BF-STEM image of 1,8-octanedithiol-CuO_x and its corresponding (b) DF-STEM image. (c) BF-STEM image of 1,8-octanedithiol-CuO_x and its corresponding (d) DF-STEM image. (e) BF-STEM image of 1,8-octanedithiol-CuO_x and its corresponding (f) DF-STEM image. (g) The enlarged BF-STEM image of 1,8-octanedithiol-CuO_x of the red frame in (f) and its corresponding (h) DF-STEM image. (i) Magnified DF-STEM image of a localized region within the interphase for 1,8-octanedithiol-CuO_x and its corresponding EDX mapping of (j) Cu, (k) S and (l) Cu and S overlapping.

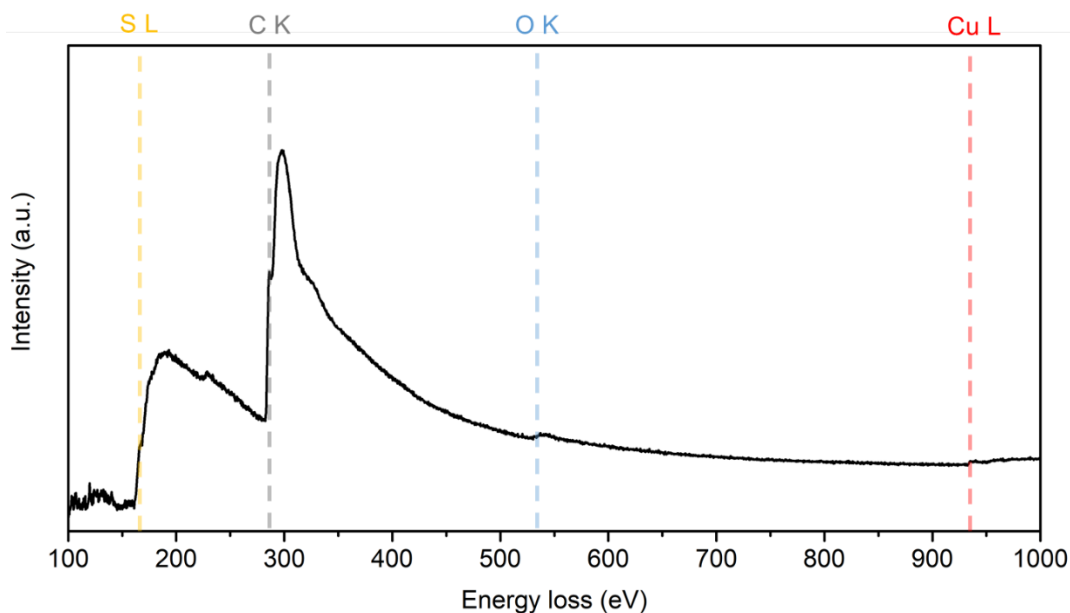


Figure R16. Electron energy loss spectroscopy (EELS) obtained by scanning the interphase local area of 1,8-octanedithiol-CuO_x on spherical aberration corrected electron microscopy. The annotated elements correspond to the following characteristic peaks: ~165 eV for sulfur (S L-edge), ~290 eV for carbon (C K-edge), ~530 eV for oxygen (O K-edge), and ~930 eV for copper (Cu L-edge). Due to the limitations of the instrument and the thickness of the interphase, the signals of these characteristic peaks are weak.

We have modified the relevant content of the text in the revised manuscript: *“Scanning transmission electron microscopy (STEM) by spherical aberration corrected electron microscopy (Figure 4g-4l and Figure S27) further revealed Cu-rich areas of a few nanometers intercalated with regions deficient in Cu. The distribution of S was more uniform. This is consistent with a picture of very small Cu-based nanoparticles or nanoclusters, coordinated by the 1,8-octanedithiol-CuO_x catalyst, aggregated into an interphase of > 10 nm thickness.” (please see the revised manuscript, Page 6, Paragraph 1, Lines 7-11)*

The Figure R15 was added to the updated Figure 4 in the revised manuscript and Figure S27 in the Supporting Information, respectively. *(please see the revised manuscript, Page 5 and the revised Supporting Information, Page 67)*

o The attribution of improved ethanol selectivity to changes in electrode morphology is based on observations, but there is insufficient evidence to substantiate the underlying cause of this morphology.

Reply and actions taken: We thank the reviewer for this insightful comment. The reason you might feel confused about the underlying cause of this morphology could be that we did not provide a detailed explanation of the growth process of the material.

First, DMF is hydrolyzed to produce formic acid and dimethylamine, and dimethylamine

reacts with Cu^{2+} and H_2O to form CuO . Then CuO is reduced by formic acid to form Cu_2O . In the above chemical reaction process, the growth steps of CuO_x can be summarized: (i) formation of CuO nanocrystallites; (ii) spherical aggregation of primary CuO crystallites; (ii) reductive conversion of CuO nanospheres to Cu_2O . The specific growth mechanism of CuO_x can be found in *Langmuir* **2005**, 21, 1074-1079. Therefore, you can see that in Figure S25, the SEM image of CuO_x shows that there are many rough particles distributed on the surface of CuO_x . These are the reduced and unreduced CuO nanocrystallites from step (i) during the catalyst synthesis process.

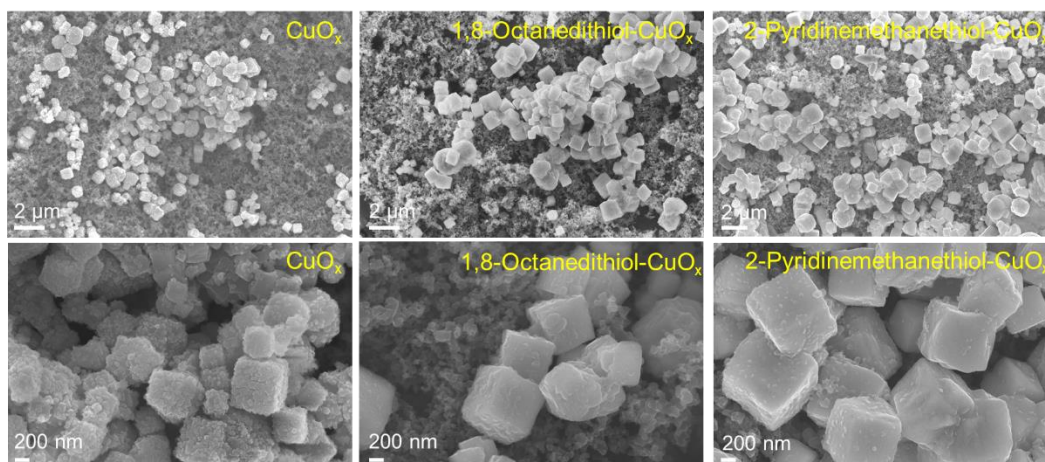


Figure S25. SEM images of as prepared CuO_x , 1,8-octanedithiol- CuO_x and 2-pyridinemethanethiol- CuO_x catalysts.

When CuO_x was modified with the thiol molecules containing the reducing terminal $-\text{SH}$, CuO can undergo a redox reaction with $-\text{SH}$ to generate Cu^{I} species. These generated Cu^{I} species and Cu^{I} from Cu_2O can further form a $\text{Cu}^{\text{I}}-\text{S}$ coordination bond with the S terminal of the thiol molecule that contains a lone pair of electrons and has coordination ability. These phenomena can be validated through the observation of peak due to bonded-thiol in the S 2p XPS spectrum (Figure 4u and 4v) and the disappearance of the Cu^{2+} signal in the Cu 2p XPS spectrum, as well as significant shift towards higher binding energy of the Cu^{I} signal compared to Cu 2p XPS spectra of pristine CuO_x (Figure 4t). The coordination ability of thiols with metals and relevant characterization evidence has been widely reported in literature (*Angew. Chem. Int. Ed.* **61**, e202206279 (2022), *Langmuir* **1996**, 12, 5083-5086). In addition, the reasons and phenomena that alkylthiol can form multilayer Cu-thiol compounds on CuO_x have also been confirmed in the literature, which proposed that Cu^{2+} is reduced to Cu^{1+} by alkylthiol, and thiol (RSH) is oxidized to disulfide (RS-SR), and the excess thiol molecules on the surface further form multilayer Cu-thiol coordination complexes with Cu^{1+} . (*Langmuir* **2016**, 32, 3848-3857, *Thin Solid Films* **1994**, 244, 799-805.). The S 2p XPS spectra also confirmed the presence of disulfide as unbound thiol (Figure 4u and 4v). This also demonstrated that the length of the

alkyl chain is related to the thickness of the interphase produced on the alkylthiol-modified CuO_x .

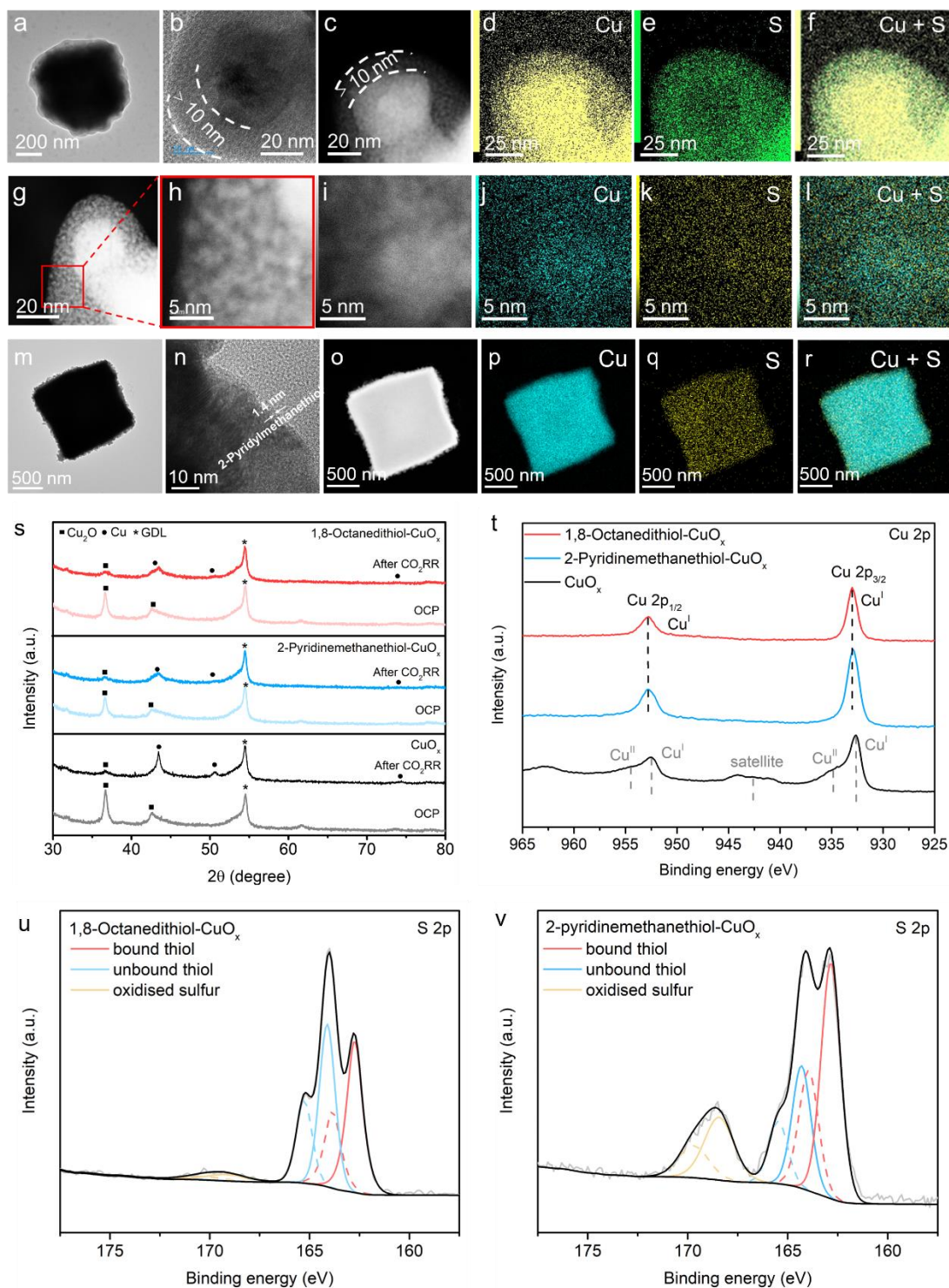


Figure 4. (a-b) TEM image of as prepared 1,8-octanedithiol- CuO_x catalyst, (c) HADDF image of 1,8-octanedithiol- CuO_x catalyst and corresponding EDX mapping results of (d) Cu, (e) S elements and (f) overlapping plot of Cu and S elements. (g) DF-STEM image. (h) The enlarged BF-STEM image of 1,8-octanedithiol- CuO_x of the red frame in (g). (i) Magnified DF-STEM image of a localized region within the interphase for 1,8-octanedithiol- CuO_x and its corresponding EDX mapping of (j) Cu, (k) S and (l) Cu and

S overlapping. (m-n) TEM image of as prepared 2-pyridinemethylthiol-CuO_x catalyst, (o) HADDF image of 2-pyridinemethylthiol-CuO_x catalyst and corresponding EDX mapping results of (p) Cu, (q) S elements and (r) overlapping plot of Cu and S elements. (s) XRD patterns of CuO_x, 1,8-octanedithiol-CuO_x, and 2-pyridinemethanethiol-CuO_x catalysts at open circuit potential (OCP) and after CO₂RR. (t) XPS spectra of Cu 2p of as prepared CuO_x, 1,8-octanedithiol-CuO_x, and 2-pyridinemethanethiol-CuO_x catalysts. XPS spectra of S 2p (The solid line represents S 2p_{3/2}, the dashed line represents S 2p_{1/2}) of as prepared (u) 1,8-octanedithiol-CuO_x catalyst and (v) 2-pyridinemethanethiol-CuO_x catalyst.

Besides, the reducing ability and coordination ability can be modulated by the connected functional groups. For example, pyridinethiol is less reducible because of the electron-withdrawing effect of the pyridine ring, reducing the electron density of the sulfur atom. This makes its ability to reduce Cu²⁺ weaker and unable to form a thick interphase similar to CuO_x modified by alkylthiol. For molecular modifiers that do not contain S but contain other terminals with certain coordination/reducing abilities, the same chemical reaction process can be achieved.

The underlying reason for the formation of the metal-organic interphase is the presence of CuO on the surface of the CuO_x we synthesized. CuO can undergo redox reactions with molecules containing reducing terminal groups, leading to the formation of multilayer metal-organic coordination compounds. Moreover, the terminal groups of these molecular modifiers contain lone pairs of electrons and possess coordination ability, allowing them to form coordination compounds with Cu in different oxidation states.

Some of the above contents are described in our text, but it may be that our statement in the manuscript was not clear enough, which caused confusion. Therefore, we have added the reference mentioned above and modified the relevant parts of the text to solve this problem in the revised manuscript:

1. *“The unbound thiol in Figure 4u and 4v refers to disulfide.^{36” (please see the revised manuscript, Page 7, Paragraph 3, Line 6)}*
2. *“Based on previous literature reports,³⁷⁻³⁹ the CuO on the surface of CuO_x first undergoes a redox reaction with the reducing -SH terminal of alkylthiols (RSH), resulting in the formation of Cu^I and disulfide (RS-SR), which became the disordered stacking of the organic part in the interphase. Subsequently, the Cu^I species, originating both from Cu₂O and reduced CuO, further coordinate with excess alkylthiol molecules on the CuO_x surface, leading to the formation of multilayer metal-thiol (Cu^I-S) compounds, which is the metal coordination layers in the interphase. The reducing and coordinating abilities of the S terminals can be modulated by the attached functional groups. For instance, pyridinethiol is less reducible due to the electron-withdrawing effect of the pyridine ring. Other molecular modifiers with terminal groups that possess reducing and coordinating capabilities can also form metal-organic interphases, as*

discussed in the 'Observation of Metal-Organic Interphase' section." (please see the revised manuscript, Page 7, Paragraph 3, Lines 11-20)

3. The underlying reason that the presence of 10 nm interphase can promote ethanol selectivity has been explored through *in situ* Raman, *in situ* IR spectroscopy, OH⁻ electro-adsorption measurements and DFT calculations in the sections of '***In situ* Raman Spectroscopy**', '***In situ* IR Spectroscopy**', '**Exploring Exposed Cu Facets via OH Electro-Adsorption**' and '**Possible Consequences of Forming a Metal-Organic Interphase**' in the manuscript.

The existence of this morphology changes the configuration ratio of the important intermediate *CO. The presence of > 10 nm interphase inhibits the formation of inert *CO_{bridge} and led to higher *CO_{HFB}/*CO_{LFB} ratio for 1,8-octanedithiol-CuO_x, reflecting that *CO_{LFB} is consumed more rapidly in downstream conversion processes than *CO_{HFB} (Figure 5a-5e). The *CO_{LFB} is associated with terrace sites, which favor further *CO reduction and C–C coupling. The > 10 nm interphase also decreased oxygen affinity on catalyst surfaces, since the ratio of C-absorbed *COOH: O-absorbed CO(*)O(*)⁻ increased on 1,8-octanedithiol-CuO_x catalyst (Figures S61 and S63). The Cu surfaces of weaker oxygen affinity promote C₂H₅OH formation by preserving the C–O bond. Besides, this morphology regulates the configuration of interfacial water, which increased the percentage of isolated water, facilitating the transfer of H from water to the Cu surface. It also reduced the Stark slopes of three configurations of interfacial water by decreasing the electrode's Electrical Double-Layer (EDL) capacitance, thus leading to a longer distance from the metal surface and / or a more restricted water molecule with a slower reorientation (Figures 5g-5i and Figures S64, S65 and S67). Therefore, an interphase with moderate thickness can achieve a good balance between *CO hydrogenation and C–C coupling rates to enhances ethanol selectivity.

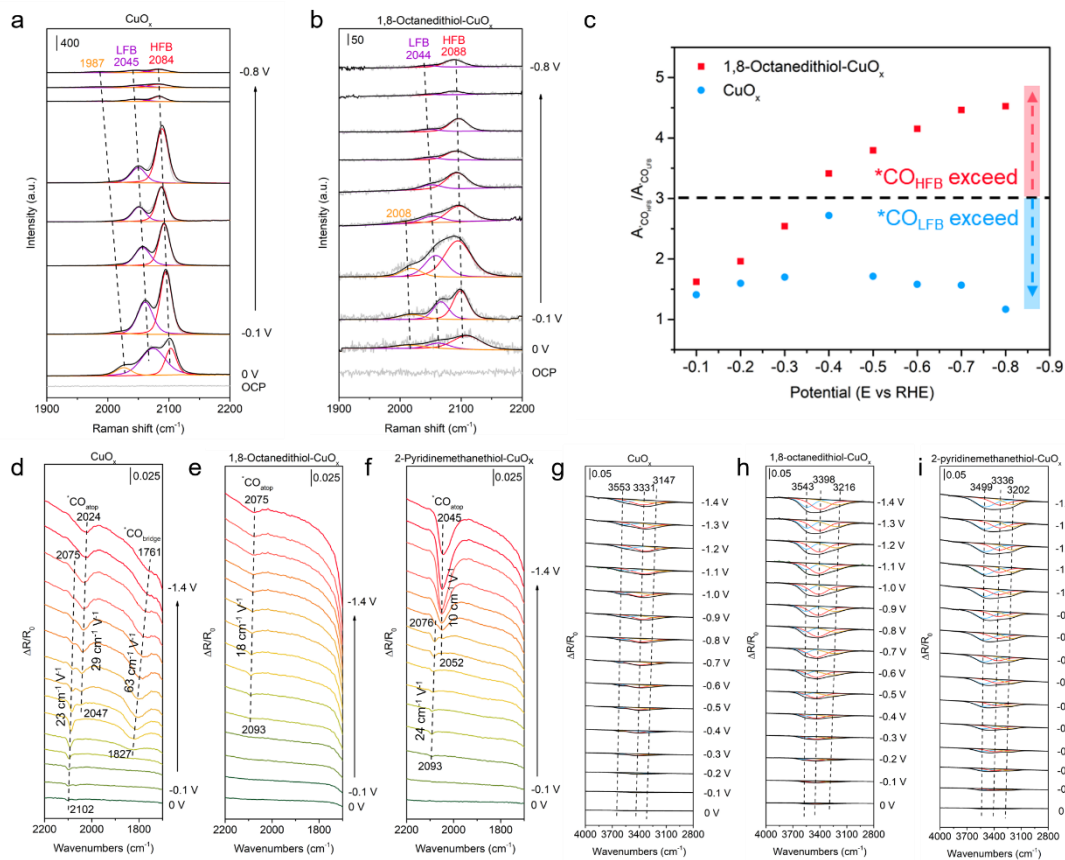


Figure 5. *In situ* Raman spectroscopy in the region from 1900 to 2200 cm⁻¹ for (a) CuO_x and (b) 1,8-octanedithiol-CuO_x catalyst in flow cell with continuously pumped CO₂ and 1.0 M KOH from open circuit potential (OCP) to -0.8 V vs RHE. Although there is some debate on whether the nature of the *CO band at ~2000 cm⁻¹ is attributed to *CO_{bridge}, this does not affect our analysis. (c) Area ratio of *CO_{HFB} to *CO_{LFB} over applied potential window calculated from *in situ* Raman spectroscopy. *In situ* ATR-SEIRAS spectra in the region of 2200 to 1700 cm⁻¹ for (d) CuO_x, (e) 1,8-octanedithiol-CuO_x catalyst and (f) 2-pyridinemethanethiol-CuO_x catalyst from 0 to -1.4 V vs RHE in CO₂-saturated 0.5 M KHCO₃. *In situ* ATR-SEIRAS spectra in the region of 3800 to 2800 cm⁻¹ for (g) CuO_x, (h) 1,8-octanedithiol-CuO_x catalyst and (i) 2-pyridinemethanethiol-CuO_x catalyst from 0 to -1.4 V vs RHE in CO₂-saturated 0.5 M KHCO₃.

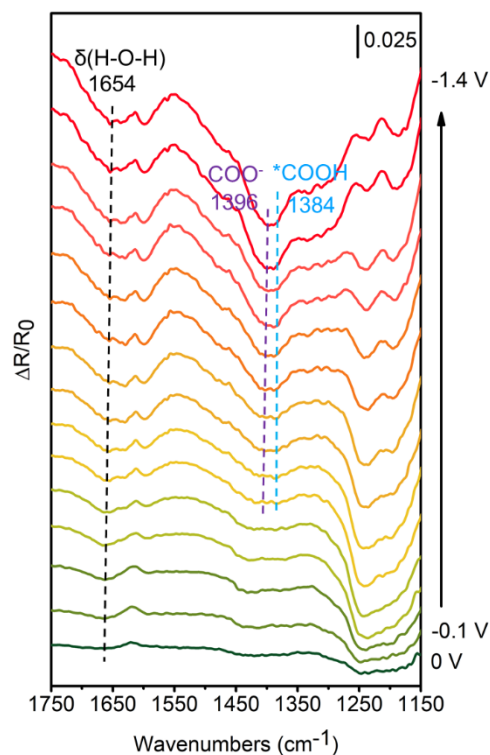


Figure S61. *In situ* ATR-SEIRAS spectra for CuO_x catalyst in the region of $1750\sim1150\text{ cm}^{-1}$ from 0 to -1.4 V vs RHE in CO_2 -saturated 0.5 M KHCO_3 .

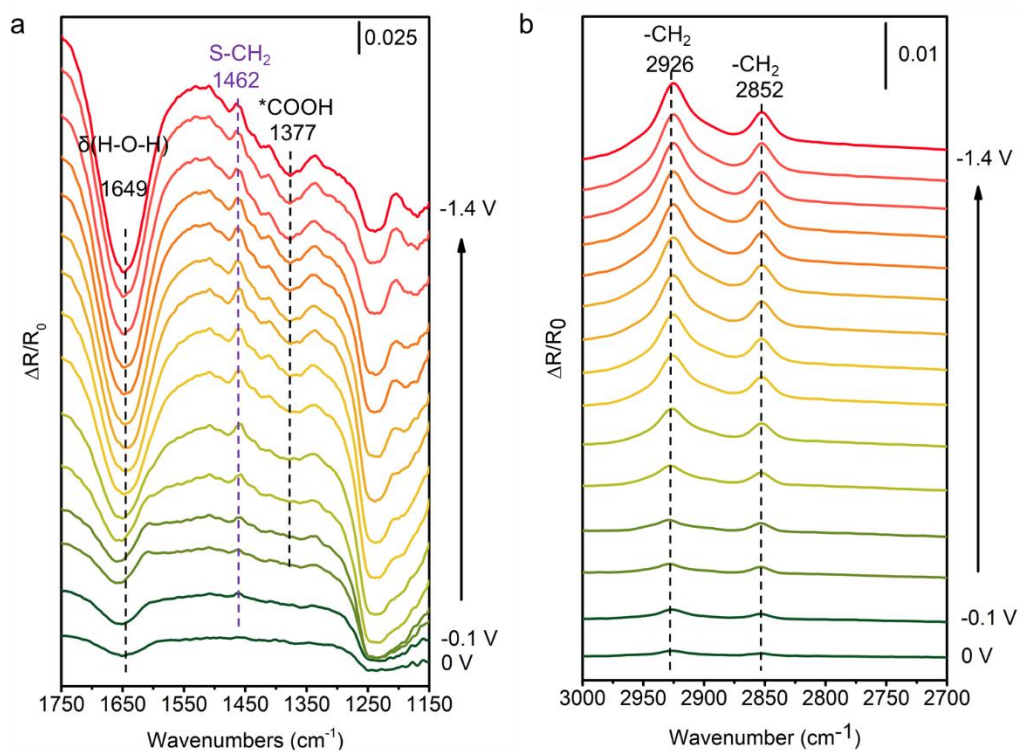


Figure S63. *In situ* ATR-SEIRAS spectra for 1,8-octanedithiol- CuO_x catalyst in the region of (a) $1750\sim1150\text{ cm}^{-1}$ and (b) $3000\sim2700\text{ cm}^{-1}$ from 0 to -1.4 V vs RHE in CO_2 -saturated 0.5 M KHCO_3 . The peak at 1462 cm^{-1} is assigned to vibration of S-CH_2 , and 2926 and 2852 cm^{-1} are assigned to C-H stretches of $-\text{CH}_2$.

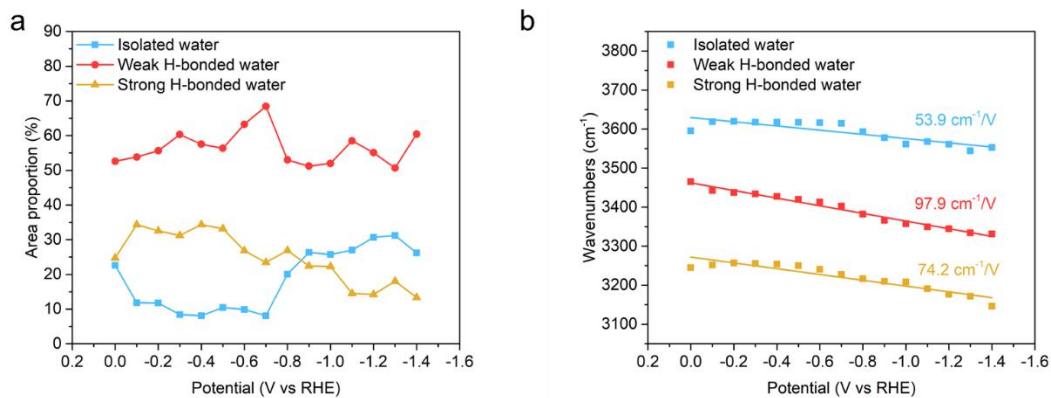


Figure S64. (a) Area proportion of three peaks at $\sim 3250\text{ cm}^{-1}$, $\sim 3450\text{ cm}^{-1}$, and $\sim 3550\text{ cm}^{-1}$ on CuO_x. (b) Peak frequencies of the O-H stretching mode of interfacial water on CuO_x as a function of the applied potential.

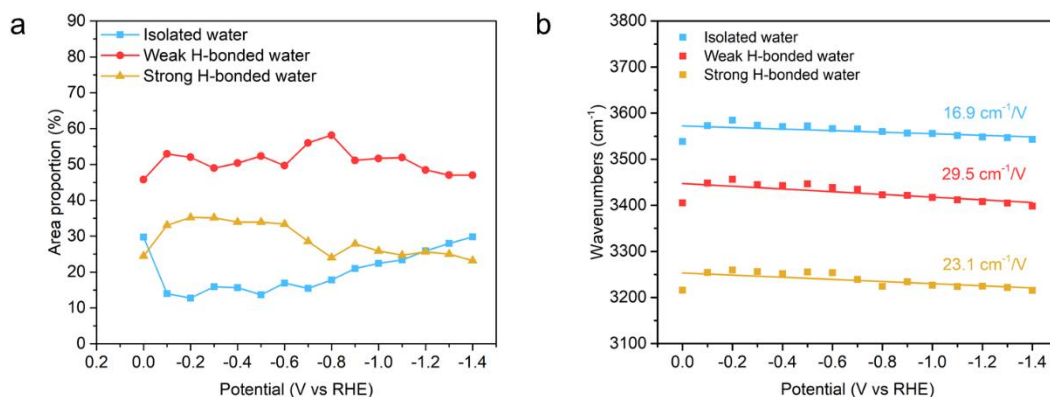


Figure S65. (a) Area proportion of three peaks at $\sim 3250\text{ cm}^{-1}$, $\sim 3450\text{ cm}^{-1}$ and $\sim 3550\text{ cm}^{-1}$ on 1,8-octanedithiol-CuO_x. (b) Peak frequencies of the O-H stretching mode of interfacial water on 1,8-octanedithiol-CuO_x as a function of the applied potential.

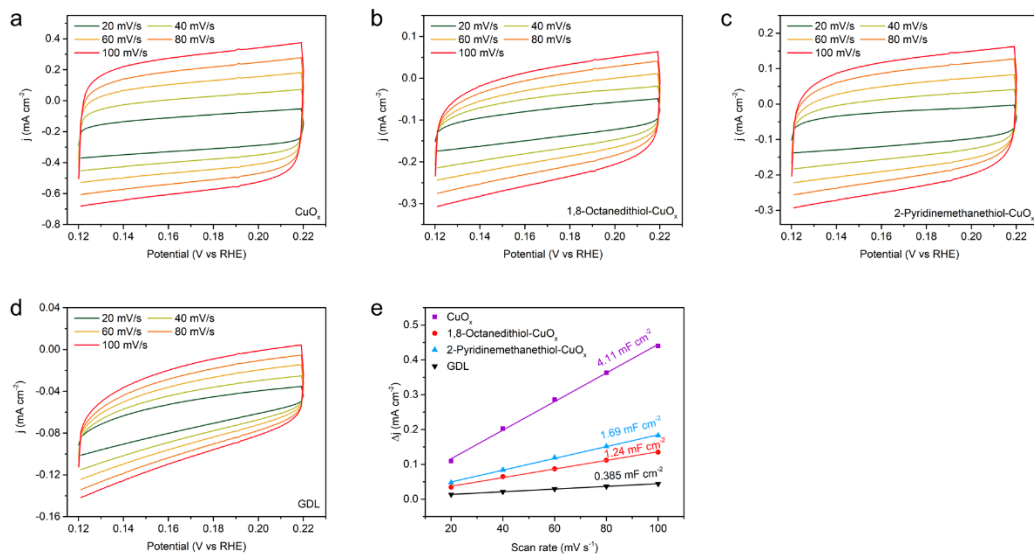


Figure S67. Electrical double-layer (EDL) capacitance determined by double-layer capacitance over a range of scan rates in 1.0 M KOH saturated with Ar. CVs for (a) CuO_x catalysts, (b) 1,8-octanedithiol-CuO_x catalysts, (c) 2-pyridinemethanethiol-CuO_x catalysts and (d) GDL. Capacitance values for (e) CuO_x, 1,8-octanedithiol-CuO_x, 2-pyridinemethanethiol-CuO_x catalysts and GDL.

The generation of this morphology is also accompanied by the selective exposure of the Cu(110) electrochemical facet (Figure 6a), which is caused by the different coordination mode of thiol molecules on Cu(110) and Cu(100) (Figures 6b and 6c). The Cu(110) has been reported to benefit the generation of oxygenated multi-carbon products such as ethanol and acetate. Moreover, the modifiers occupying and blocking certain facets by the modifiers decreased the amount of adsorbed *CO (Figure 6d). The high *CO occupation does not lead to high FE_{EtOH} or FE_{C₂H₄} for 1,8-octanedithiol-CuO_x according to the CORR products distribution results (Figures 6f and 6g), which is consistent with the limited H-to-*CO transfer rate in the interphase of 1,8-octanedithiol-CuO_x. As the *CO occupation is high, the H-to-*CO transfer is not fast enough to generate highly hydrogenated products like ethanol and ethylene but the less hydrogenated acetate.

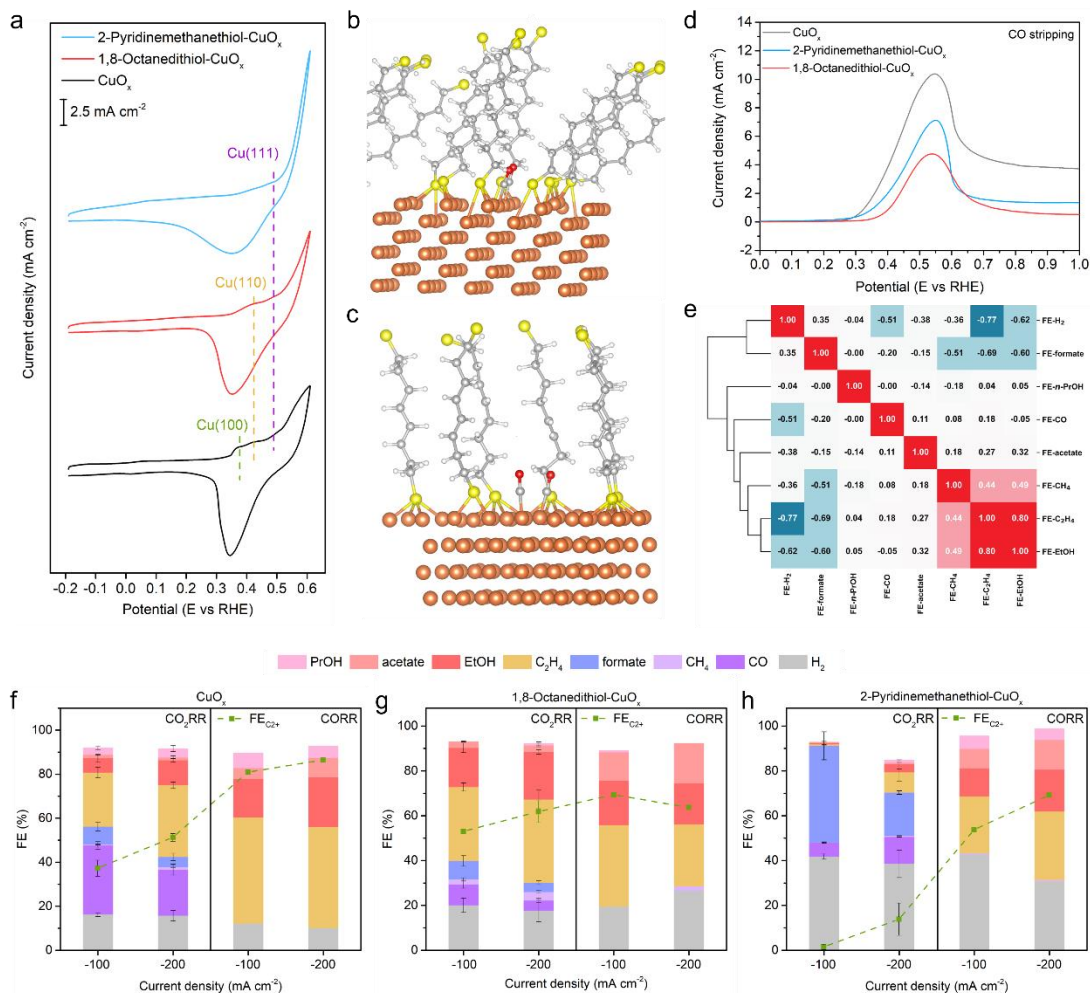


Figure 6. (a) OH⁻ electro-adsorption measurements of CuO_x, 1,8-octanedithiol-CuO_x (current density was magnified 1.5 times) and 2-pyridinemethanethiol-CuO_x catalysts in Ar-saturated 1.0 M KOH after 200 s reduction at -0.69 V vs RHE. (b) The side view of the 1,8-octanedithiol coordinated on Cu(110). (c) The side view of the 1,8-octanedithiol coordinated on Cu(100). Atomic color codes: Cu (brown), S (yellow), C (grey), O (red) and H (white). Comparison of CO₂RR and CORR product distributions on (f) CuO_x, (g) 1,8-octanedithiol-CuO_x and (h) 2-pyridinemethanethiol-CuO_x catalysts at applied current density of 100 mA cm⁻² and 200 mA cm⁻², respectively.

5. The observed thickness of the organic layer seems more dependent on intermolecular stacking than on the terminal groups. Given the interplay between multiple variables (i.e., organic layer thickness, the presence of a metal-organic interphase, and the molecular structure of the modifiers), the study lacks a convincing comparison of results. To draw meaningful conclusions, the authors should focus on isolating and analyzing one variable at a time.

Reply and actions taken: We thank the reviewer for this insightful comment. When designing the experiments, we tried our best to control the variables. As shown in our catalyst modification procedure, we standardized the feeding amount of these modifiers, without

initially anticipating that they would form metal-organic interphases or not. This discovery of the formation of metal-organic interphase, which emerged through characterization, is a surprise to us, which highlights the unpredictability and serendipity in scientific research and data science. Nevertheless, we greatly appreciate the valuable suggestions of the reviewers to make the comparison more controllable after the initial discovery. In the revision, we have made the following efforts in this direction.

First, regarding the function of the terminal groups, we have added modifiers of 1,8-diaminooctane and 1,8-octanediol, as controls to 1,8-octanedithiol. They all share the same aliphatic chains and only differ in the terminal anchoring groups. We performed TEM and EDX analyses on these two catalysts. As shown in Figures R17 and R18, for 1,8-octanediol-CuO_x catalyst, we cannot tell the difference between untreated CuO_x and 1,8-octanediol-treated CuO_x. For 1,8-diaminooctane, although the EDX mapping of N can confirm surface modification, we did not positively observe a complete interphase over the CuO_x particle. The modification of 1,8-octanediol on CuO_x mainly increased FE_{CO} and decreased $FE_{C_2H_4}$ and FE_{EtOH} at the applied current density of 100 mA cm⁻² (Figure R20). On the other hand, the 1,8-diaminooctane-treated CuO_x can only achieve an FE_{EtOH} of 11%, as compared to 7.5% for bare CuO_x and 18% for 1,8-octanedithiol-treated CuO_x at the applied current density of 100 mA cm⁻² (Figure R20).

The above results show that the coordination ability of terminal groups is crucial to the formation of metal-organic interphase, which determines the morphology, thickness and composition of the interphase. We have added the following sentences in the revised manuscript:

“For a more controlled comparison to 1,8-octanedithiol, we prepared CuO_x modified by 1,8-octanediol and 1,8-diaminooctane. TEM and EDX mapping showed that none of them formed a complete interphase around the CuO_x particles (Figures S49-S51). The modification of 1,8-octanediol on CuO_x mainly increased FE_{CO} and decreased $FE_{C_2H_4}$ and FE_{EtOH} at the applied current density of 100 mA cm⁻² (Figure S52). On the other hand, the 1,8-diaminooctane-treated CuO_x can only achieve a relative FE_{EtOH} of 44%, as compared to 144% for 1,8-octanedithiol-treated CuO_x at the applied current density of -100 mA cm⁻² (Figure S52). This shows the importance of the coordination group in forming the metal-organic interphase and tuning the CO₂RR activity and selectivity.” (please see the revised manuscript, Pages 6-7, Paragraph 6)

The Figures R17-R20 were also added in the revised Supporting Information as Figures S49-S52. **(please see the revised Supporting Information, Pages 60-63)**

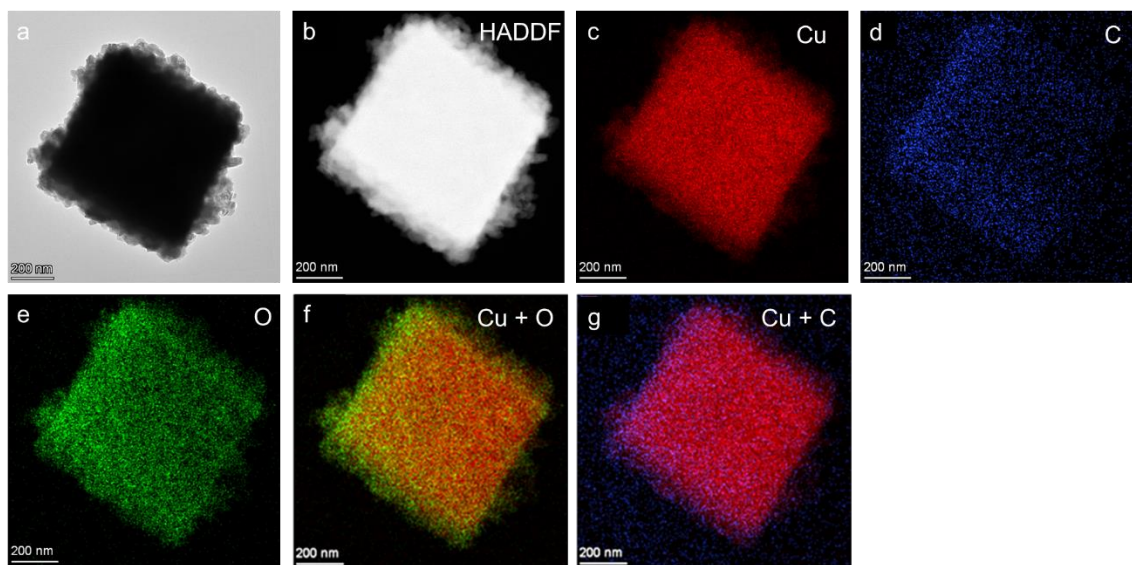


Figure R17. (a) TEM image of CuO_x catalyst. (b) HAADF image of CuO_x catalyst and the corresponding EDX mapping of (c) Cu, (d) C, (e) O, (f) Cu and O overlapping, and (g) Cu and C overlapping.

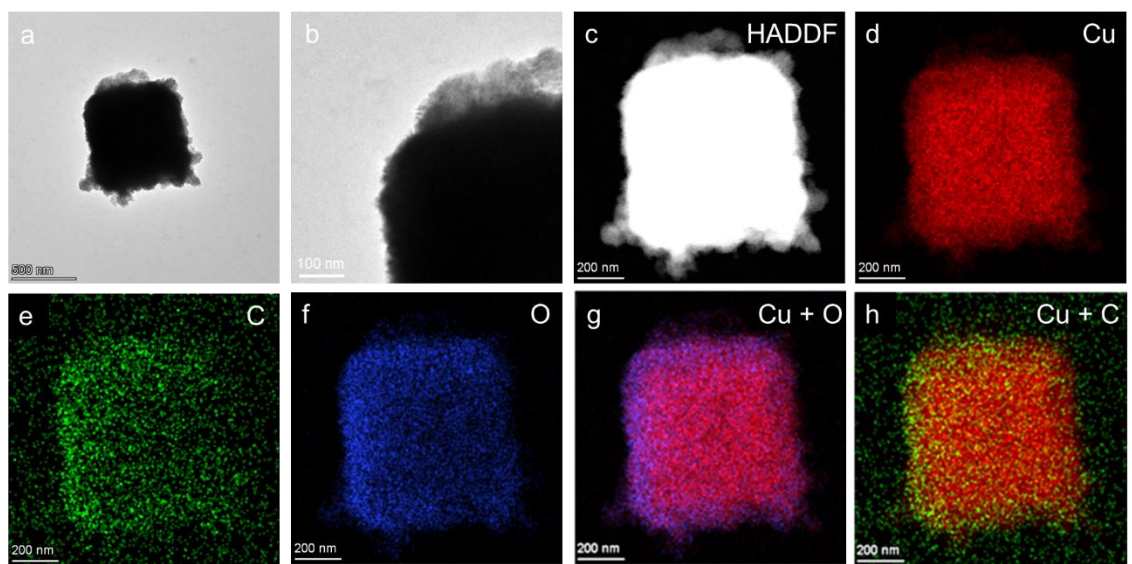


Figure R18. (a) TEM image of 1,8-octanediol- CuO_x catalyst. (b) HAADF image of 1,8-octanediol- CuO_x catalyst and the corresponding EDX mapping of (c) Cu, (d) C, (e) O, (f) Cu and O overlapping, and (g) Cu and C overlapping.

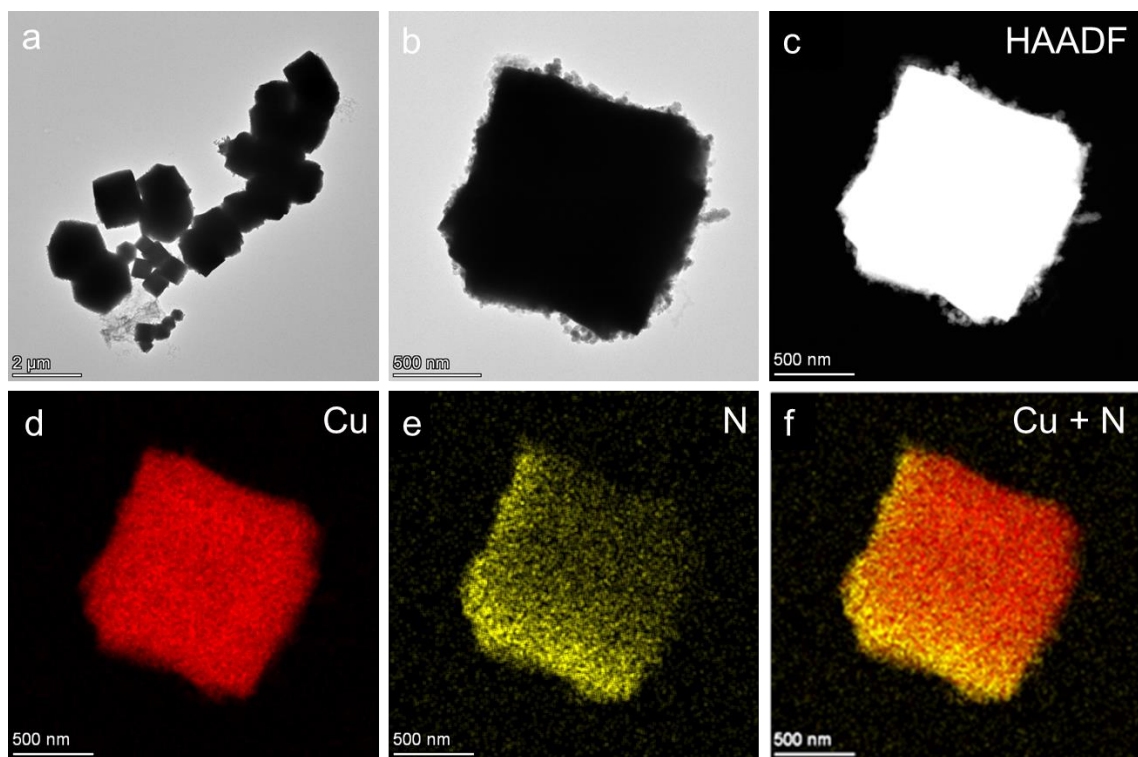


Figure R19. (a-b) TEM image of 1,8-diaminooctane-CuO_x catalyst. (c) HAADF image of 1,8-diaminooctane-CuO_x catalyst and the corresponding EDX mapping of (d) Cu, (e) N and (f) Cu and O overlapping.

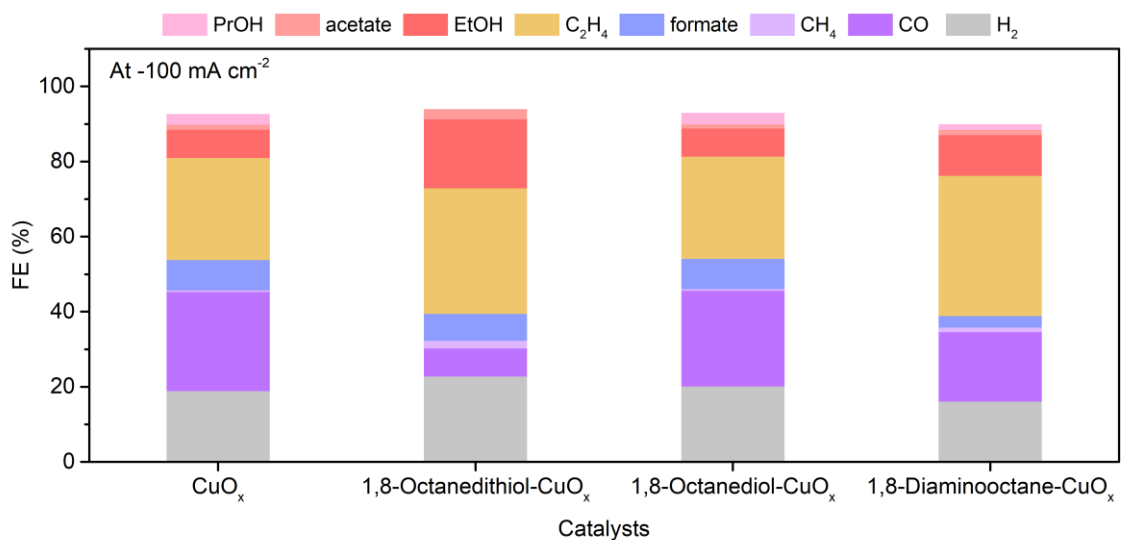


Figure R20. CO₂RR products distributions of CuO_x, 1,8-octanedithiol-CuO_x, 1,8-octanediol-CuO_x and 1,8-diaminooctane-CuO_x catalysts at -100 mA cm⁻².

In an additional effort to better control the experimental parameters, we tried to regulate the interphase thickness of 1-octadecanethiol-CuO_x catalyst, which is not a good FE_{EtOH} promoter with a > 100 nm metal-organic interphase. We reduced the amount of 1-octadecanethiol to 15% or 50% of the original feeding amount in the catalyst preparation

procedure. These catalysts were denoted as 15%-1-octadecanethiol-CuO_x and 50%-1-octadecanethiol-CuO_x catalysts, respectively. The TEM, EDX mapping of these two catalysts showed that the 15%-1-octadecanethiol-CuO_x and 50%-1-octadecanethiol-CuO_x catalysts have similar interphase thickness of ~50 nm and ~60 nm, respectively (Figures R21 and R22). In addition, reducing the feed amount of 1-octadecanethiol to 15% would result in incomplete interphase coverage on the CuO_x, i.e., some of the particles had ~50 nm interphase, while the others did not have interphase at all (Figure R21d-R21h and R21i-R21m). It is not easy to systematically tune the thickness of the interphase by simply changing the feed amount of the molecules. Similarly, we also reduced the feeding amount of 1,8-octanedithiol to prepare the 15%-1-octadecanethiol-CuO_x catalyst, but the metal-organic interphase thickness was still ~10 nm (Figure R23).

Nevertheless, the CO₂RR product distribution of 1-octadecanethiol-CuO_x catalysts with different interphase thicknesses was also tested. The 15%-1-octadecanethiol-CuO_x (~50 nm or 0 nm interphase), 50%-1-octadecanethiol-CuO_x catalysts (~60 nm interphase), and 100%-1-octadecanethiol-CuO_x (> 100 nm interphase) catalysts achieved FE_{EtOH} of 12%, 15% and 11%, respectively, at the applied current density of -100 mA cm⁻² (Figure R24). This result further indicates that the thickness of the interphase plays an important role in FE_{EtOH} regulation.

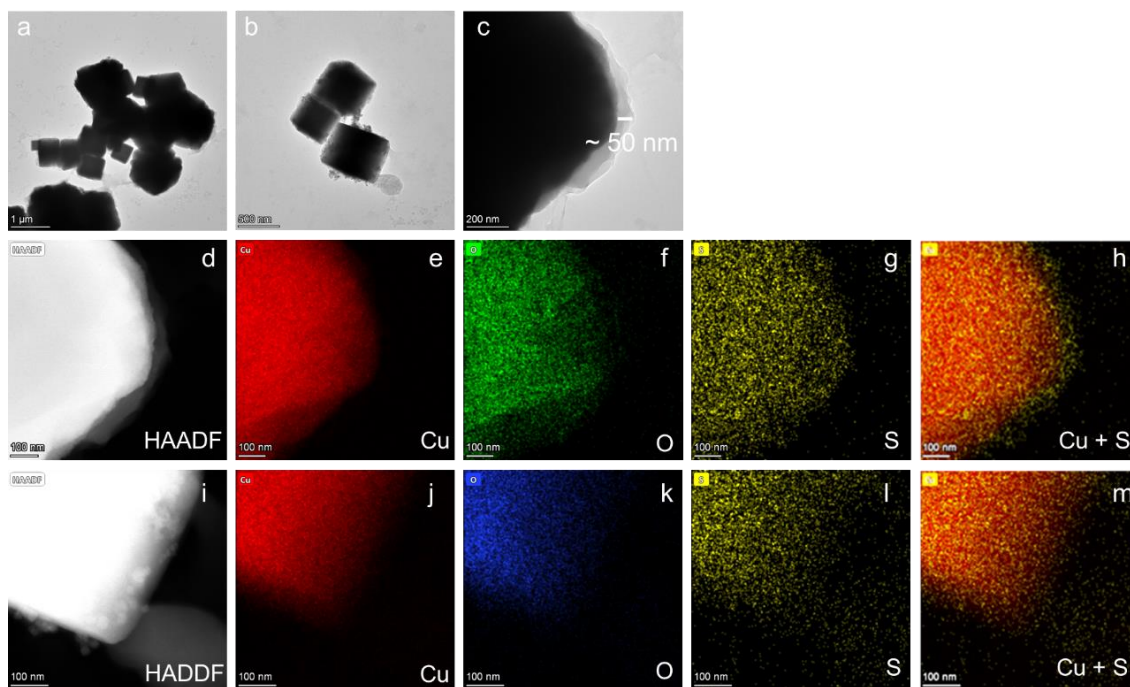


Figure R21. (a-c) TEM images of 15%-1-octadecanethiol-CuO_x catalyst. (d) HAADF image of 15%-1-octadecanethiol-CuO_x catalyst and the corresponding EDX mapping images of (e) Cu, (f) O, (g) S, and (h) Cu and S overlapping. (i) HAADF image of 15%-1-

octadecanethiol-CuO_x catalyst and the corresponding EDX mapping images of (j) Cu, (k) O, (l) S, and (m) Cu and S overlapping. The 15% in the catalyst label means that the feed amount is 15% of the original feed amount.

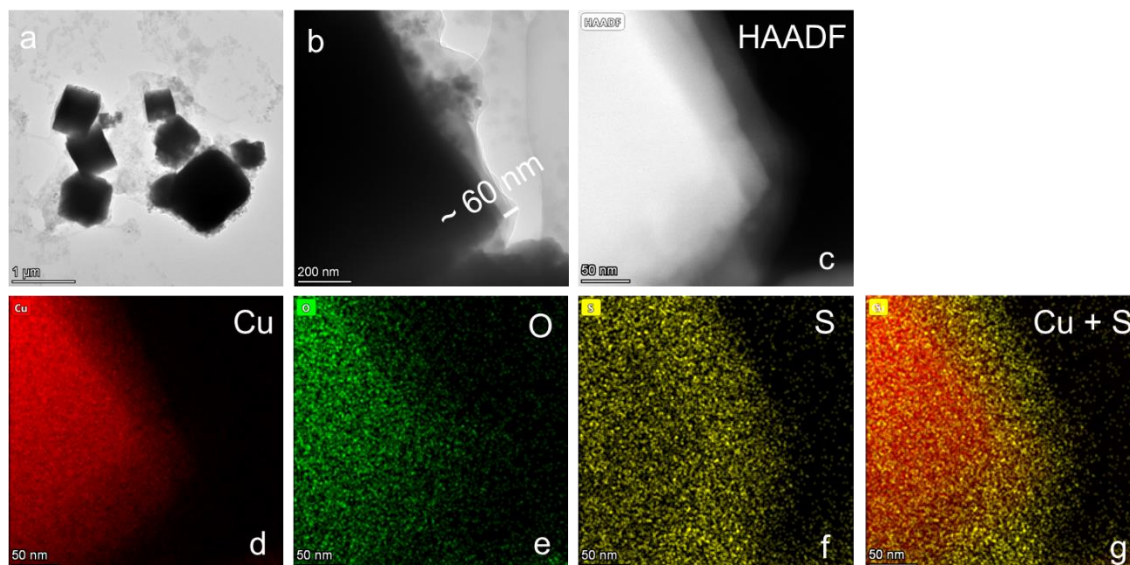


Figure R22. (a-b) TEM images of 50%-1-octadecanethiol-CuO_x catalyst. (c) HAADF image of 50%-1-octadecanethiol-CuO_x catalyst and the corresponding EDX mapping images of (d) Cu, (e) O, (f) S, and (g) Cu and S overlapping. The 50% in the catalyst label means that the feed amount is 50% of the original feed amount.

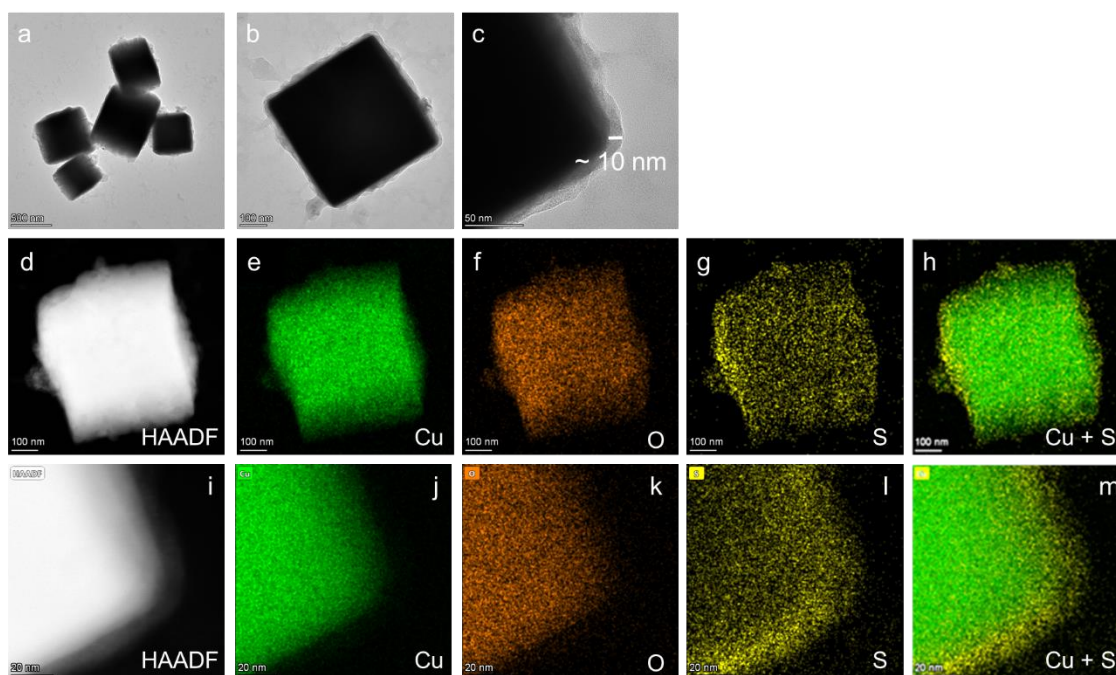


Figure R23. (a-c) TEM images of 15%-1,8-octanedithiol-CuO_x catalyst. (d) HAADF image of 15%-1,8-octanedithiol-CuO_x catalyst and the corresponding EDX mapping images of (e) Cu, (f) O, (g) S, and (h) Cu and S overlapping. (i) HAADF image of 15%-1,8-octanedithiol-CuO_x catalyst and the corresponding EDX mapping images of (j) Cu, (k) O, (l) S, and (m) Cu and S overlapping. The 15% in the catalyst label means that the feed amount is 15% of the original feed amount.

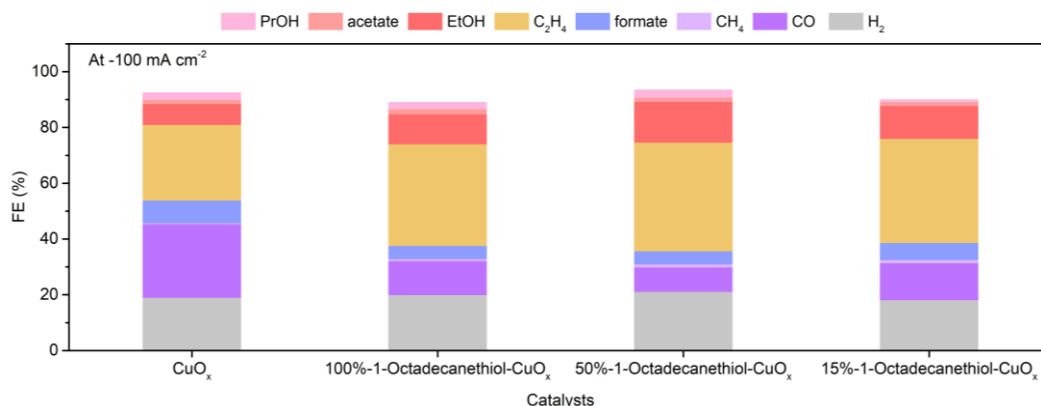


Figure R24. CO₂RR products distributions of CuO_x, 15%-1-octadecanethiol-CuO_x, 50%-1-octadecanethiol-CuO_x, 100%-1-octadecanethiol-CuO_x at -100 mA cm⁻². The 15%, 50% and 100% in the catalyst labels mean that the feed amount is 15%, 50 and the same feed amount of the original feed amount, respectively.

We have added the following sentences in the revised manuscript: “We further changed the amount of 1-octadecanethiol to tune the interphase thickness (Figures S39-S40). When adding only 50% of the initial amount of 1-octadecanethiol, we observed the interphase thickness decreases to 60 nm, and the relative FE_{EtOH} increased to +94% (Figure S41). When further decreasing the 1-octadecanethiol to 15% of its initial value, an incomplete interphase coverage of the 15%-1-octadecanethiol-CuO_x was observed, and the relative FE_{EtOH} decreased to 57% (Figure S41). This shows that the thickness of the interphase is also critical to the performance.” (please see the revised manuscript, Page 6, Paragraph 4, Lines 4-10)

The Figures R21-R24 were also added in the revised Supporting Information as Figures S39-S41. (please see the revised Supporting Information, Pages 50-52)

6. The manuscript discusses the potential role of hydrogen bonding in stabilizing *CO on CuO_x, but it is unclear whether the observed selectivity variations are attributed to adsorption on the CuO_x facets or on the metal–organic interphase. This distinction is critical and requires further clarification.

Reply and actions taken: We thank the reviewer for this insightful comment. It is challenging to figure out whether the CO₂RR took place within the interphase or on the particle buried below the interphase. The peak positions of *CO adsorption on CuO_x with or without 1,8-octanedithiol during electrolysis, show no significant differences in *in-situ* Raman or *in-situ* IR spectra (Figure 5a-5f). Furthermore, the coordination of 1,8-octanedithiol on Cu different facets made the vibrational frequencies of *CO intermediates highly complex, making it difficult to determine the specific adsorption sites of the intermediates based on *in-situ* spectroscopic data. However, we tried our best to figure out two related points: whether the interphase is

porous and whether the interphase is electrochemically active.

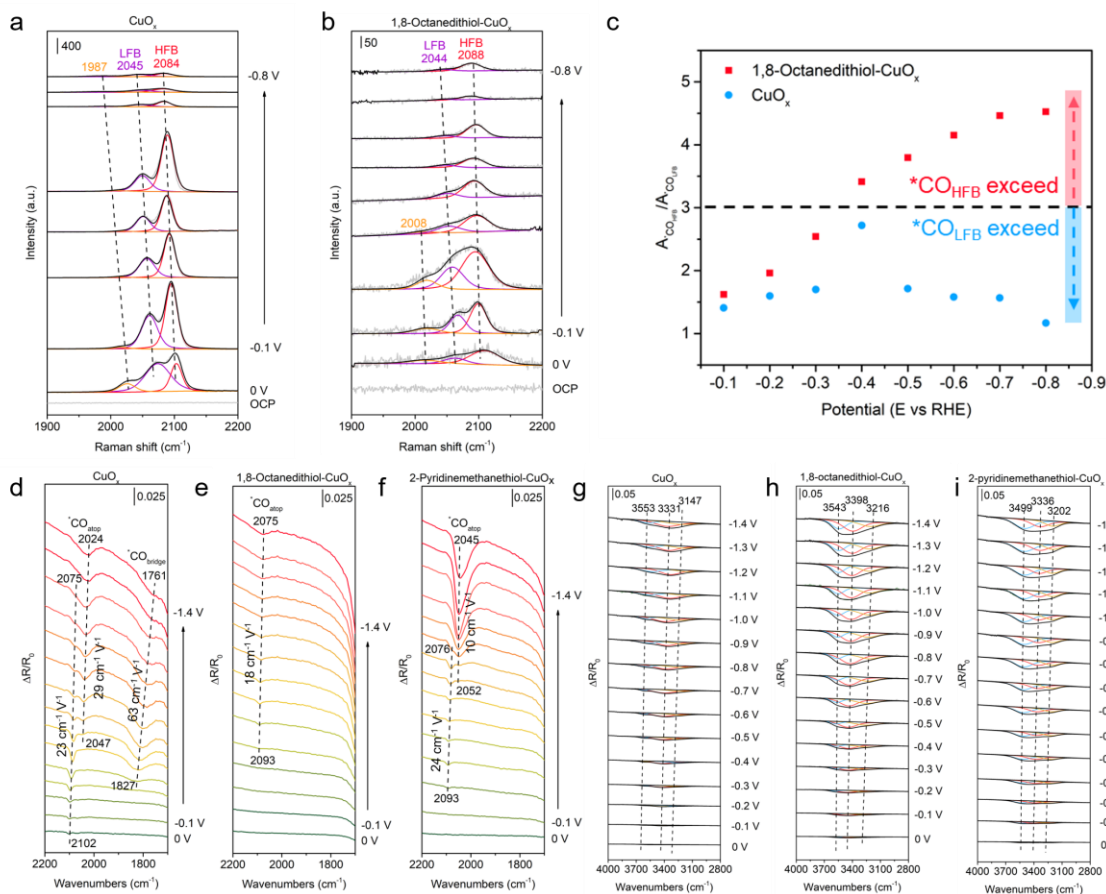


Figure 5. *In situ* Raman spectroscopy in the region from 1900 to 2200 cm⁻¹ for (a) CuO_x and (b) 1,8-octanedithiol-CuO_x catalyst in flow cell with continuously pumped CO₂ and 1.0 M KOH from open circuit potential (OCP) to -0.8 V vs RHE. Although there is some debate on whether the nature of the *CO band at ~2000 cm⁻¹ is attributed to *CO_{bridge}, this does not affect our analysis. (c) Area ratio of *CO_{HFB} to *CO_{LFB} over applied potential window calculated from *in situ* Raman spectroscopy. *In situ* ATR-SEIRAS spectra in the region of 2200 to 1700 cm⁻¹ for (d) CuO_x, (e) 1,8-octanedithiol-CuO_x catalyst and (f) 2-pyridinemethanethiol-CuO_x catalyst from 0 to -1.4 V vs RHE in CO₂-saturated 0.5 M KHCO₃. *In situ* ATR-SEIRAS spectra in the region of 3800 to 2800 cm⁻¹ for (g) CuO_x, (h) 1,8-octanedithiol-CuO_x catalyst and (i) 2-pyridinemethanethiol-CuO_x catalyst from 0 to -1.4 V vs RHE in CO₂-saturated 0.5 M KHCO₃.

We added HAuCl₄ into KOH to prepare an electrolyte of 1 mM AuCl₄⁻ in 1.0 M KOH. The 1,8-octanedithiol-CuO_x catalyst was then tested in such electrolyte for CO₂RR. The AuCl₄⁻ would be reduced to Au at negative potential and can be used as probe to explore the conductivity and porosity of interphase. We rinsed the electrode after the reaction with water and then ultrasonically stripped the 1,8-octanedithiol-CuO_x catalyst from the carbon black layer on the GDE surface. As shown in Figures R25 and R26, the interphase > 10 nm thickness was kept after electrolysis in 1 mM AuCl₄⁻ in 1.0 M KOH. Interestingly, there are obvious signals of interspersed Cu nanoparticles and Au electrodeposition on Cu in the > 10 nm interphase on 1,8-octanedithiol-CuO_x catalyst after CO₂RR. Since the interphase has a certain thickness,

the Cu nanoparticles in the interphase vary in depth, resulting in different strengths of the Cu or Au signals. Besides, the signal of K for KOH can also be detected both in the interphase and on the Cu particle buried below the interphase. These evidences illustrate that the Cu within interphase is electrochemically active and the interphase is porous thus the AuCl_4^- and KOH can penetrate in.

Regarding the active form of the catalyst, we believed that most of the CuO_x was reduced to metallic Cu under negative potentials, as *in situ Raman* spectroscopy revealed no Cu^{I} or Cu^{II} signals under the electrolysis condition (Figure S58). As a result, the $^*\text{CO}$ adsorption took place on metallic Cu.

We have added the Figures R25 and R26 in the revised Supporting Information and the following sentences in the revised manuscript to address this issue: *“To probe whether this interphase is porous and electrochemically active, we added HAuCl_4 to the KOH electrolyte during the electrolysis using 1,8-octanedithiol- CuO_x catalyst. The Au reduced from AuCl_4^- at the negative potential on the electrode can serve as a probe for EDX mapping to explore the accessibility of the interphase during CO_2RR . We observed significant Au electrodeposition on Cu in the interphase and on the Cu surface buried under the interphase after CO_2RR (Figures S29 and S30), together with K distribution in the interphase. These observations suggested that the interphase is porous and the Cu within the interphase and buried below the interphase are both electrochemically active.”* **(please see the revised manuscript, Page 6, Paragraph 1, Lines 11-18)**

The Figures R25-R26 were also added in the revised Supporting Information as Figures S29-S30. **(please see the revised Supporting Information, Pages 40-41)**

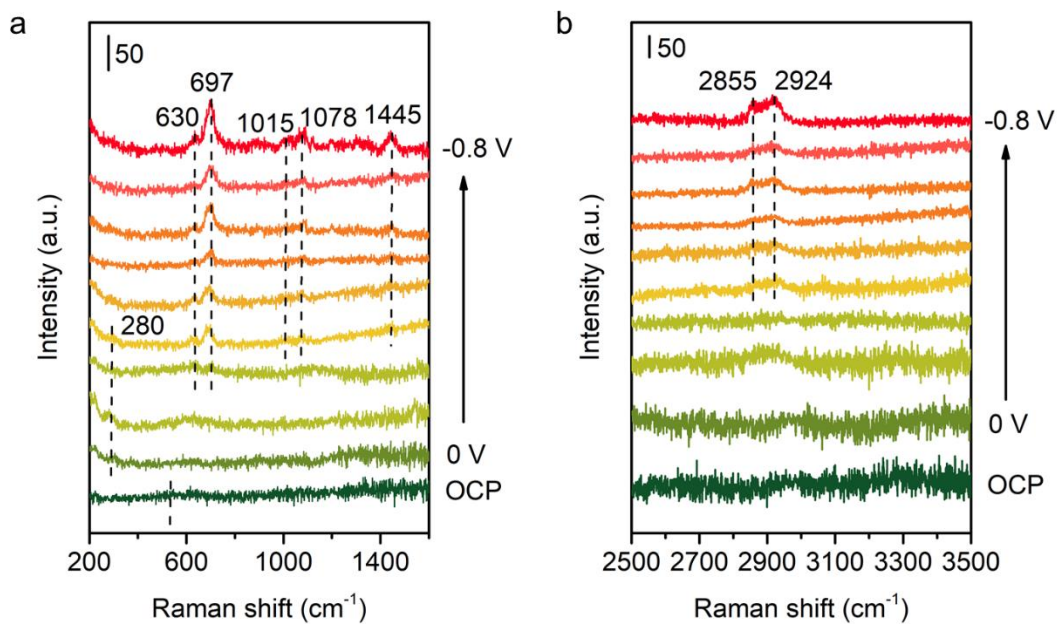


Figure S58. *In situ* Raman spectra of 1,8-octanedithiol-CuO_x in the region of (a) 200~1600 cm⁻¹ and (b) 2500~4000 cm⁻¹. The peak at 1445 cm⁻¹ could be assigned to the absorbed carbon species CH_x or the vibration of SC-H₂.

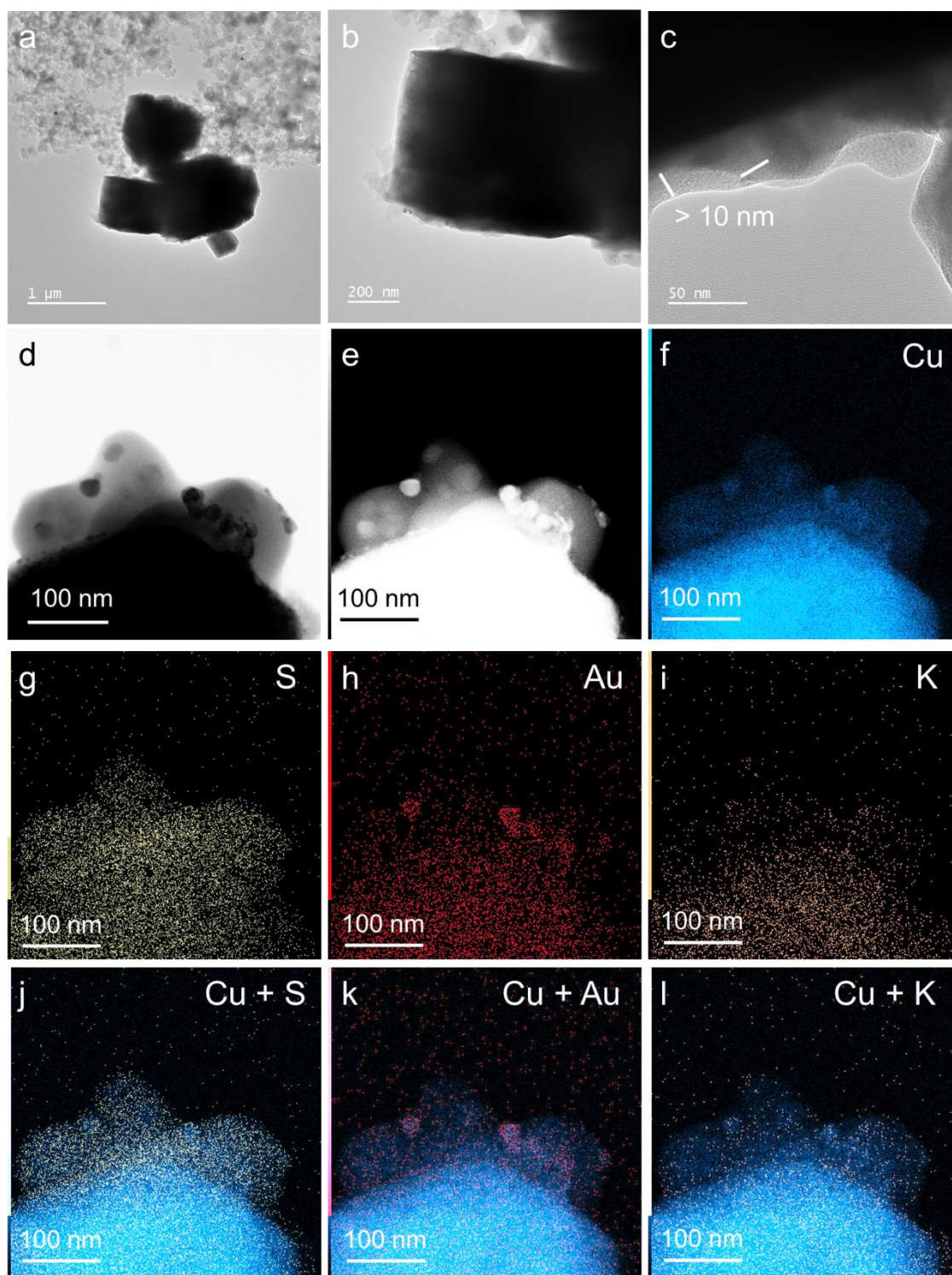


Figure R25. (a-c) TEM images of 1,8-octanedithiol-CuO_x catalyst after CO₂RR in the 1 mM AuCl₄⁻ in 1.0 M KOH. (d) Bright-field (BF) STEM image of 1,8-octanedithiol-CuO_x after CO₂RR in the 1 mM AuCl₄⁻ in 1.0 M KOH. (e) HAADF image of 1,8-octanedithiol-CuO_x and its corresponding EDX mapping images of (f) Cu, (g) S, (h) Au, (i) K, (j) Cu and S overlapping, (k) Cu and Au overlapping and (l) Cu and K overlapping after CO₂RR in the 1 mM AuCl₄⁻ in 1.0 M KOH.

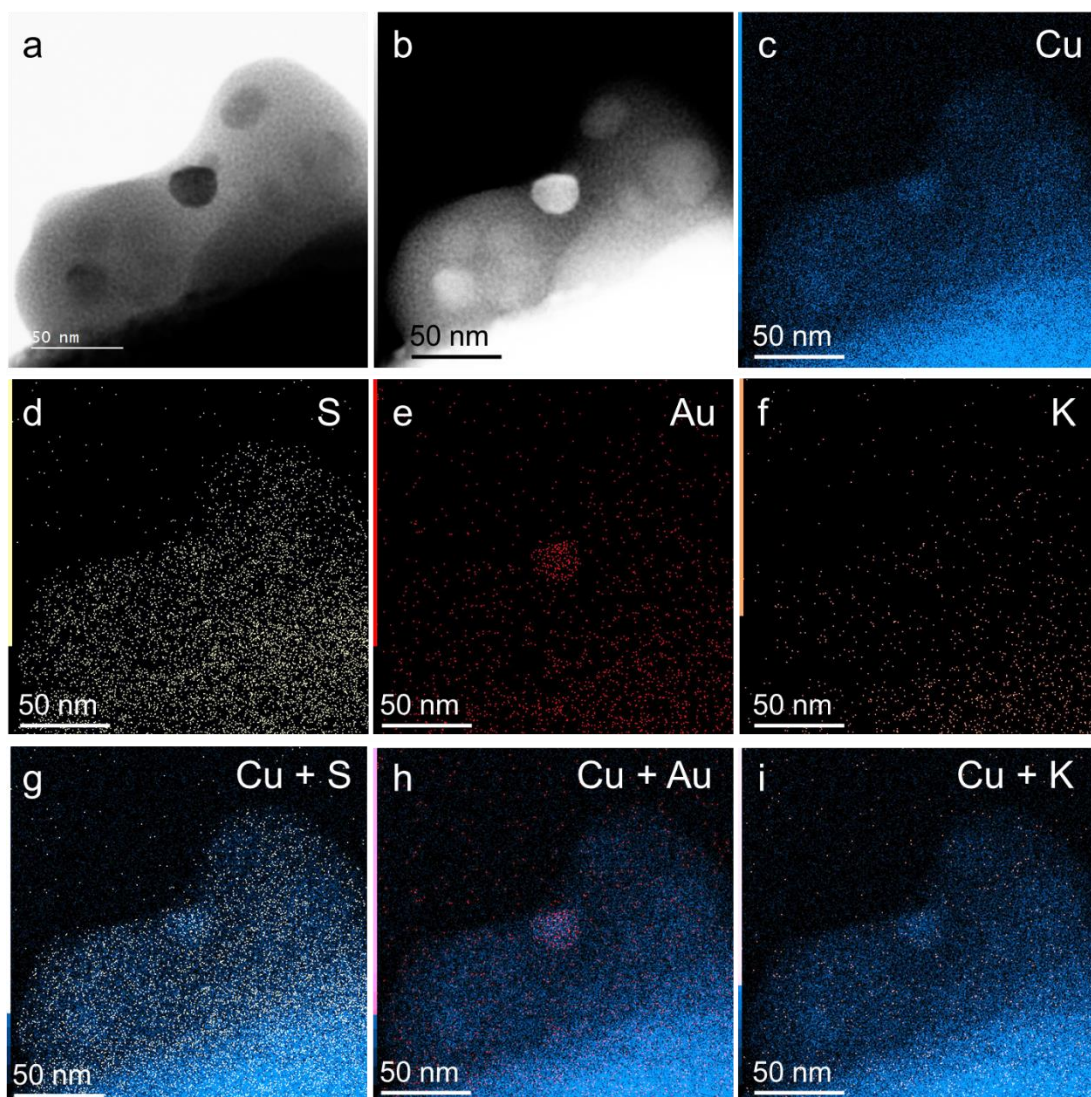


Figure R26. (a) Bright-field (BF) STEM image of 1,8-octanedithiol-CuO_x after CO₂RR in the 1 mM AuCl₄⁻ in 1.0 M KOH. (b) HAADF image of 1,8-octanedithiol-CuO_x and its corresponding EDX mapping images of HAADF image of 1,8-octanedithiol-CuO_x and its corresponding EDX mapping images of (c) Cu, (d) S, (e) Au, (f) K, (g) Cu and S overlapping, (h) Cu and Au overlapping and (i) Cu and K overlapping after CO₂RR in the 1 mM AuCl₄⁻ in 1.0 M KOH.

7. There is missing text at line 145, which appears as "Error!..." in the manuscript. This needs to be corrected for clarity.

Reply and actions taken: We thank the reviewer for the comment and sincerely apologize for the difficulty this may have caused in your reading. This is because an unexpected error occurred when converting word to pdf. The 'Error! Reference source not found' actually is the word 'Figure'. We have reconverted the file to avoid such errors.

Reviewer #3 (Remarks to the Author):

The paper presents an interesting result of metal–organic interphases in CO₂ electroreduction processes, particularly focusing on their role in enhancing ethanol production on Cu–based catalysts, challenging the traditional view of surface modifications as monolayers. This discovery is essential for understanding the factors that modulate CO₂RR selectivity towards ethanol and C₂₊ products.

Reply and actions taken: We thank the reviewer for the positive evaluation of our manuscript. We also appreciate the constructive comments raised by this reviewer to help further improve the quality of our manuscript. Our responses to the detailed comments raised by this reviewer and the corresponding revisions are described as follows.

1. The use of 1080 CO₂RR experiments and the systematic investigation of 180 different modifiers is commendable. The extensive dataset and the use of an automatic electrocatalysis platform add credibility to the findings. However, it would be beneficial to include more details regarding the reproducibility of results for modifiers that showed moderate changes in selectivity.

Reply and actions taken: We thank the reviewer for the comment. Following the suggestion, we selected some molecules modified-CuO_x catalysts and repeated the CO₂RR data for 2-3 times at different potentials on the automatic platform and listed them in Table S25 in the revised Supporting Information, which is a strong proof of the reproducibility of our platform.

Table S25. Repeated CO₂RR product distribution test of some molecule-modified CuO_x catalysts under different potentials on the automated electrocatalysis platform.

*Individual test FE

**Average FE of three individual test

Molecules modifiers	E vs RHE	<i>j</i> (mA cm ⁻²)		FE _{H₂} (%)		FE _{CO} (%)		FE _{CH₄} (%)		FE _{C₂H₄} (%)		FE (%)					
		i*	a**	i*	a**	i*	a**	i*	a**	i*	a**	acetate	formate	EtOH	<i>n</i> -PrOH	C ₂₊	Total
1,8-Octanedithiol	-0.62	107		20		6		7		34							
		108	108	25	24	4	5	6	7	32	33	4	4	21	0	58	97
		108		25		3		6		32							
1,8-Octanedithiol	-0.62	103		18		3		6		36							
		102	102	18	18	3	4	6	6	37	37	3	3	21	2	62	92
		101		17		4		6		38							

1,8-Octanedithiol	−0.62	<u>109</u>		<u>20</u>		<u>3</u>		<u>6</u>		<u>35</u>							
		<u>108</u>	108	<u>18</u>	18	<u>3</u>	3	<u>6</u>	6	<u>36</u>	36	3	3	22	1	62	93
		<u>108</u>		<u>17</u>		<u>3</u>		<u>6</u>		<u>37</u>							
L-Cystine	−0.56	<u>66</u>		<u>14</u>		<u>11</u>		<u>3</u>		<u>36</u>							
		<u>70</u>	69	<u>19</u>	18	<u>17</u>	16	<u>3</u>	3	<u>35</u>	35	4	2	11	0	48	89
		<u>70</u>		<u>20</u>		<u>20</u>		<u>4</u>		<u>34</u>							
L-Cystine	−0.56	<u>80</u>		<u>21</u>		<u>12</u>		<u>3</u>		<u>33</u>							
		<u>81</u>	81	<u>24</u>	23	<u>13</u>	13	<u>4</u>	4	<u>31</u>	32	4	2	12	0	45	89
		<u>81</u>		<u>23</u>		<u>14</u>		<u>5</u>		<u>30</u>							
L-Cystine	−0.56	<u>92</u>		<u>29</u>		<u>13</u>		<u>2</u>		<u>30</u>							
		<u>94</u>	93	<u>25</u>	26	<u>17</u>	16	<u>3</u>	2	<u>30</u>	30	3	3	14	0	47	93
		<u>93</u>		<u>23</u>		<u>18</u>		<u>2</u>		<u>31</u>							
4-Bromobenzaldehyde	−0.56	<u>70</u>		<u>13</u>		<u>19</u>		<u>4</u>		<u>30</u>							
		<u>69</u>	70	<u>17</u>	17	<u>21</u>	21	<u>5</u>	5	<u>28</u>	28	4	2	13	0	43	89
		<u>70</u>		<u>19</u>		<u>21</u>		<u>5</u>		<u>26</u>							
4-Bromobenzaldehyde	−0.56	<u>74</u>		<u>13</u>		<u>29</u>		<u>3</u>		<u>33</u>							
		<u>75</u>	75	<u>18</u>	17	<u>33</u>	32	<u>4</u>	4	<u>30</u>	31	3	3	11	0	45	100
		<u>75</u>		<u>19</u>		<u>34</u>		<u>4</u>		<u>29</u>							
2,2'-Dithiodipyridine	−0.56	<u>89</u>		<u>44</u>		<u>3</u>		<u>0</u>		<u>0</u>							
		<u>87</u>	87	<u>34</u>	37	<u>5</u>	5	<u>0</u>	0	<u>2</u>	2	28	1	3	0	6	75
		<u>86</u>		<u>32</u>		<u>8</u>		<u>0</u>		<u>4</u>							
2,2'-Dithiodipyridine	−0.56	<u>75</u>		<u>62</u>		<u>0</u>		<u>0</u>		<u>0</u>							
		<u>74</u>	75	<u>45</u>	50	<u>5</u>	4	<u>0</u>	0	<u>2</u>	2	28	0	0	0	2	84
		<u>75</u>		<u>41</u>		<u>8</u>		<u>0</u>		<u>5</u>							
2,2'-Dithiodipyridine	−0.56	<u>59</u>		<u>48</u>		<u>1</u>		<u>0</u>		<u>0</u>							
		<u>63</u>	62	<u>35</u>	37	<u>5</u>	3	<u>0</u>	0	<u>0</u>	0	28	2	0	0	2	71
		<u>65</u>		<u>30</u>		<u>4</u>		<u>0</u>		<u>1</u>							
Anthracene-9-carboxylic acid	−0.62	<u>120</u>		<u>17</u>		<u>19</u>		<u>0</u>		<u>31</u>							
		<u>118</u>	118	<u>16</u>	16	<u>20</u>	20	<u>0</u>	1	<u>31</u>	30	3	1	10	3	45	84
		<u>115</u>		<u>15</u>		<u>19</u>		<u>1</u>		<u>30</u>							
Anthracene-9-carboxylic acid	−0.62	<u>108</u>		<u>24</u>		<u>11</u>		<u>4</u>		<u>30</u>							
		<u>107</u>	107	<u>24</u>	24	<u>13</u>	13	<u>5</u>	5	<u>34</u>	34	3	2	12	0	48	93
		<u>106</u>		<u>24</u>		<u>14</u>		<u>6</u>		<u>38</u>							
1,4-Butanedithiol	−0.56	<u>58</u>		<u>21</u>		<u>18</u>		<u>5</u>		<u>26</u>							
		<u>62</u>	61	<u>26</u>	25	<u>22</u>	21	<u>6</u>	6	<u>25</u>	25	4	2	11	0	38	94
		<u>63</u>		<u>28</u>		<u>23</u>		<u>6</u>		<u>24</u>							
1,4-Butanedithiol	−0.56	<u>67</u>		<u>22</u>		<u>14</u>		<u>5</u>		<u>28</u>							
		<u>69</u>	68	<u>25</u>	25	<u>17</u>	17	<u>4</u>	5	<u>25</u>	26	8	2	13	0	41	95
		<u>68</u>		<u>28</u>		<u>19</u>		<u>5</u>		<u>25</u>							
1,5-Pentanedithiol	−0.56	<u>51</u>		<u>41</u>		<u>1</u>		<u>5</u>		<u>28</u>							
		<u>53</u>	53	<u>42</u>	41	<u>5</u>	4	<u>4</u>	4	<u>30</u>	30	4	3	12	0	44	96

		55		39		5		3		31							
		64		36		2		5		25							
1,5-Pentanedithiol	-0.56	68	67	40	38	2	2	3	4	27	27	5	3	13	0	43	92
		70		39		2		3		29							
		64		37		5		6		24							
1,5-Pentanedithiol	-0.56	68	67	38	37	6	6	4	5	24	25	8	4	14	0	43	99
		69		35		8		4		26							
		80		17		20		4		33							
	-0.56	85	83	20	20	21	21	4	4	28	30	7	2	9	0	41	93
4-Aminobutyric acid		85		21		22		5		28							
		122		21		18		8		32							
	-0.62	120	120	21	21	17	17	9	9	32	32	3	3	13	0	47	98
		119		21		17		9		31							
		85		15		16		4		36							
	-0.56	90	88	18	17	17	17	4	4	33	33	4	2	12	0	47	89
4-Aminobutyric acid		90		19		18		4		32							
		103		19		15		7		32							
	-0.62	130	120	18	18	15	15	7	7	30	31	4	2	13	4	49	93
		128		18		15		7		31							
		86		12		15		4		30							
	-0.56	90	88	16	15	17	16	4	4	28	29	3	2	11	0	42	80
4-Aminobutyric acid		89		17		17		4		28							
		128		16		13		7		30							
	-0.62	126	126	16	17	13	13	7	7	30	30	4	3	16	0	49	90
		124		17		13		8		30							
		46		44		1		13		23							
	-0.56	56	54	39	38	1	1	8	9	25	26	2	3	10	0	39	90
2,3-Butanedithiol		59		32		2		7		29							
		98		32		1		13		26							
	-0.62	96	96	30	30	2	2	14	13	26	26	2	2	15	0	44	90
		94		28		2		14		27							
		47		41		1		9		24							
	-0.56	55	54	38	38	1	1	6	6	26	26	3	5	8	0	39	87
2,3-Butanedithiol		59		35		2		5		29							
		99		32		1		9		26							
	-0.62	99	99	30	30	2	2	10	9	30	29	2	2	17	0	47	90
		99		27		2		9		31							
		126		17		17		7		30							
4-Chlorobenzyl alcohol	-0.62	125	125	17	17	17	17	7	7	30	31	4	2	13	1	47	93
		123		18		17		8		31							
4-Chlorobenzyl alcohol	-0.62	128	125	18	18	13	13	10	11	28	28	4	3	17	0	49	95

			125	18	13	11	28										
			123	18	13	12	28										
			99	9	14	5	30										
4-Chlorobenzyl alcohol	-0.62	100	101	10	9	14	6	6	32	32	3	3	16	0	50	82	
			101	10	15	7	33										
			131	15	21	1	34										
CuO _x	-0.62	131	131	16	16	22	1	1	33	33	4	1	10	0	45	87	
			130	16	23	1	33										
			153	21	19	1	33										
CuO _x	-0.62	146	147	22	22	16	1	1	34	33	5	1	11	4	49	94	
			143	23	16	1	33										
			146	22	18	1	35										
CuO _x	-0.62	143	143	22	22	17	1	1	36	35	6	1	9	3	49	96	
			139	23	17	1	36										

We also added the following sentences in the revised manuscript: *“The reproducibility of the collected CO₂RR product dataset on autonomous electrocatalytic platform is supported by repeated experimental data for several selected molecular modifiers-CuO_x catalysts (Table S25).” (please see the revised manuscript, Page 12, Paragraph 4, Lines 3-5)*

2. The in-depth characterization of the interphase using techniques such as TEM, EDX, XPS, and in situ Raman spectroscopy is thorough and provides clear mechanistic insights. The discussion on the effect of hydrophobicity and hydrophilicity, as well as the involvement of Cu facets, could be enhanced by addressing potential limitations of these characterizations, especially regarding surface dynamics during the catalytic process.

Reply and actions taken: We thank the reviewer for the insightful comment. We agree that discussing the potential limitations of TEM, EDX, XPS, and in situ Raman spectroscopy will strengthen the understanding of hydrophobicity/hydrophilicity effects and the involvement of Cu facets. Below, we address the limitations of each technique and their impact on capturing dynamic surface changes during CO₂RR:

1. TEM and EDX:

TEM imaging captures the catalyst structure before and after electrolysis but cannot reflect dynamic interphase changes during CO₂RR. For EDX, the limited spatial resolution challenges accurate elemental distribution mapping in thin or uneven interphases, such as the 2-pyridinemethylthiol-CuO_x system. Additionally, organic materials are sensitive to high-energy electron beams, leading to potential decomposition or damage. These factors may distort structural integrity and

compromise elemental accuracy, particularly in thin modification layers.

In the revised paper, we have added aberration-corrected TEM images. As shown in updated Figure 4 and Figure S27 for the 1,8-octanedithiol-CuO_x catalyst, within the interphase, there were regions rich in Cu and regions of a few nanometers in size, intercalated with regions deficient in Cu. This is consistent with a picture of Cu nanoparticles coordinated by 1,8-octanedithiol aggregated together.

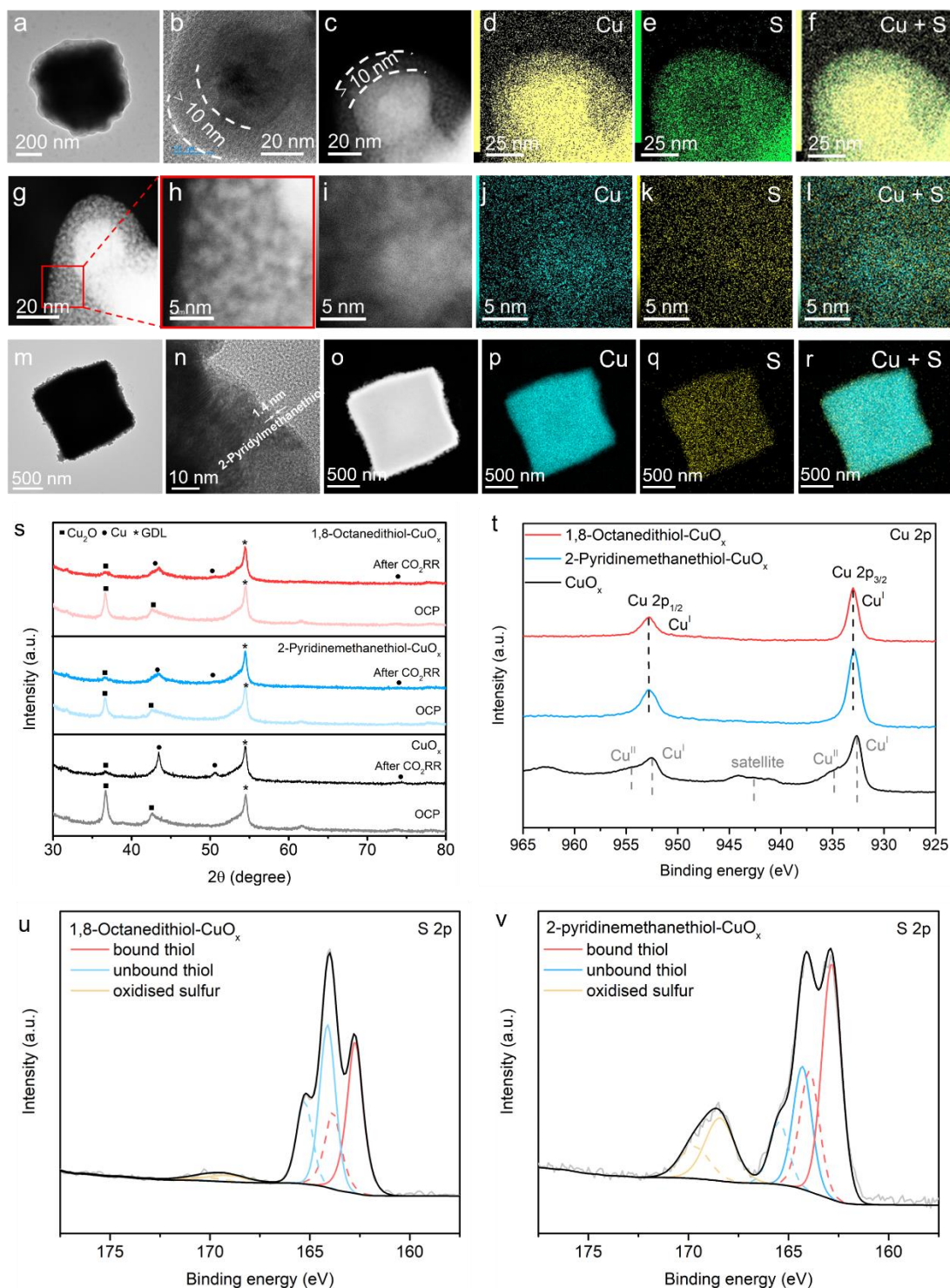


Figure 4. (a-b) TEM image of as prepared 1,8-octanedithiol-CuO_x catalyst, (c) HADDF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping results of (d) Cu, (e) S elements and (f) overlapping plot of Cu and S elements. (g) DF-STEM image. (h) The enlarged BF-STEM image of 1,8-octanedithiol-CuO_x of the red frame in (g). (i) Magnified DF-STEM image of a localized region within the interphase for 1,8-octanedithiol-CuO_x and its corresponding EDX mapping of (j) Cu, (k) S and (l) Cu and S overlapping. (m-n) TEM image of as prepared 2-pyridinemethanethiol-CuO_x catalyst, (o) HADDF image of 2-pyridinemethanethiol-CuO_x catalyst and corresponding EDX mapping results of (p) Cu, (q) S elements and (r) overlapping plot of Cu and S elements. (s)

XRD patterns of CuO_x, 1,8-octanedithiol-CuO_x, and 2-pyridinemethanethiol-CuO_x catalysts at open circuit potential (OCP) and after CO₂RR. (t) XPS spectra of Cu 2p of as prepared CuO_x, 1,8-octanedithiol-CuO_x, and 2-pyridinemethanethiol-CuO_x catalysts. XPS spectra of S 2p (The solid line represents S 2p_{3/2}, the dashed line represents S 2p_{1/2}) of as prepared (u) 1,8-octanedithiol-CuO_x catalyst and (v) 2-pyridinemethanethiol-CuO_x catalyst.

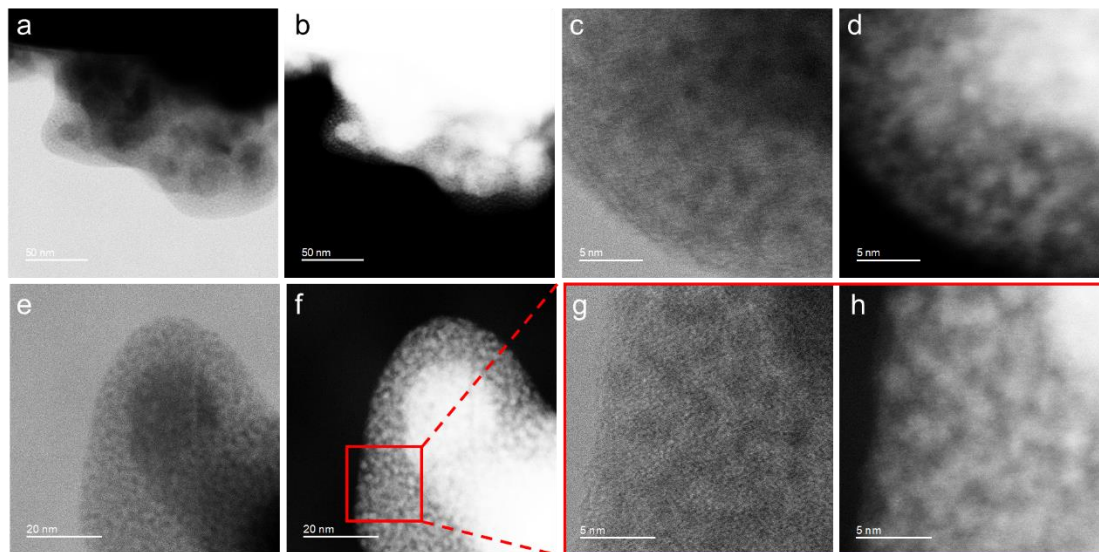


Figure S27. Spherical aberration corrected electron microscopy characterization. (a) BF-STEM image of 1,8-octanedithiol-CuO_x and its corresponding (b) DF-STEM image. (c) BF-STEM image of 1,8-octanedithiol-CuO_x and its corresponding (d) DF-STEM image. (e) BF-STEM image of 1,8-octanedithiol-CuO_x and its corresponding (f) DF-STEM image. (g) The enlarged BF-STEM image of 1,8-octanedithiol-CuO_x of the red frame in (f) and its corresponding (h) DF-STEM image.

2. XPS:

As a non-in-situ characterization technique, XPS may be affected by unavoidable oxidation of the electrode surface during sample transfer, influencing the determination of Cu valence states and the forms of thiol molecules (e.g., metal-coordinated, non-coordinated, or oxidized thiols). To mitigate this, we transferred the electrochemical cell to a glove box and disassembled the electrode immediately after reaction termination, which we believe minimizes oxidation-induced errors.

3. In-situ Raman Spectroscopy:

While the Raman flow cell attempts to replicate real conditions, structural differences between the Raman flow cell and the commercial flow cell used for performance evaluation result in lower current densities during Raman measurements. This discrepancy limits the ability to capture catalyst surface dynamics under high-current conditions. Additionally, while Raman shifts can indicate intermediates on specific Cu facets, the presence of organic ligands complicates facet identification, requiring further theoretical calculations or advanced techniques for precise determination.

We have added the following sentences in the 'The limitations of TEM, EDX, XPS, and in

situ Raman spectroscopy' section in the revised Supporting Information to address these limitations:

1. *"Although the interphase structure of 1,8-octanedithiol-CuO_x shows no difference before and after CO₂RR, ex situ TEM cannot determine its dynamic changes during electrolysis. EDX mapping faces limitations in accurately obtaining elemental distribution in thin, uneven organic layers due to limited spatial resolution and potential damage from high-energy electron beams, particularly impacting the analysis of thin interphases, such as interphase on 2-pyridinemethylthiol-CuO_x."*

2. *"Although the XPS characterization is ex-situ and unavoidable surface oxidation may affect the determination of the valence states and forms of Cu and thiol molecules, our approach of rapidly transferring the flow cell to a glove box immediately after the reaction for electrode disassembly helps preserve the catalyst surface conditions as closely as possible to those during the reaction."*

3. *"Structural differences between the Raman flow cell and the commercial flow cell used for performance evaluation result in lower current densities during in situ Raman measurements, which limits the observation of surface dynamics at high catalytic rates. Besides, the complexity of the organic coordination Cu surface also makes it difficult to identify specific Cu facets through the Raman shift of adsorbed intermediates, which requires further theoretical calculations or advanced techniques for precise determination."*

(please see the revised Supporting Information, Page 10, Paragraph 3)

3. The paper's findings on how certain sulfur-containing modifiers enhance ethanol production while others promote formate or suppress C₂⁺ products are intriguing. Further discussion on the balance between hydrophobic interactions, surface coordination, and interfacial water structure, particularly in relation to hydrogen transfer, would provide more clarity.

Reply and actions taken: We thank the reviewer for the comment. We agree that further discussing the balance between hydrophobic interactions, surface coordination, and interfacial water structure, particularly in relation to hydrogen transfer, will enhance the clarity of our findings.

The balance between hydrophobic interactions, surface coordination, and interfacial water structure is critical for enhancing ethanol selectivity. First, based on statistical analysis of the experimental data (Figure 3c), molecular modifiers with hydrophobic functional groups are more favorable for ethanol production. Second, these modifiers not only require hydrophobic functional groups but should also include terminal groups capable of surface coordination (with S-terminal groups being the most effective). By adjusting the coordination with different Cu

facets, these modifiers selectively expose electrochemically active Cu(110) facets, making them the primary sites for intermediate adsorption and conversion. Finally, these modifiers form a hydrophobic metal-organic interphase with an appropriate thickness, which significantly disrupts the interfacial water structure. On the one hand, this increases the proportion of isolated water, promoting H₂O dissociation to generate more H. On the other hand, the formation of a metal-organic interphase presents some restrictions on the interfacial water and pushing them further away from the Cu surface, which hinders the H-to-Cu transfer (to generate *H) and also decreases H-to-*CO transfer rate. The size of the hydrophobic functional group affects the thickness of the formed interphase, thus affecting the degree of reduction in the H transfer rate. This balance between *CO hydrogenation and C–C coupling rates ultimately enhances ethanol selectivity.

These conclusions have been discussed in the section of **‘Possible Consequences of Forming a Metal-Organic Interphase’** in the manuscript. We have slightly modified the relevant content to make this statement clearer as follows:

Change in Interfacial Water Structure and H Transfer. The presence of the interphase likely disrupts the interfacial water structure. As revealed by the water O–H stretching band in the *in situ* Raman and IR measurements, water molecules may be further away from the Cu surface in the interphase. Moreover, upon thiol group modification, the percentage of isolated water increased, promoting H transfer from H₂O to Cu or species on Cu surface. This explains why the majority of S-containing modifiers, especially pyridinethiols, promoted H₂ evolution (up to FE_{H₂} ~ 100%) (Figure S70). Consistent with this, the pyridinethiols enhanced formate formation, which also requires H addition (Figures S71 and S72). We noticed a correlation between FE_{formate} and FE_{H₂} among the different modifiers (Pearson correlation coefficient of 0.35) (Figure 6e), indicating H-transfer is part of the rate-determining step of formate formation. There is also a correlation between FE_{CH₄} and FEs of C₂H₄ and EtOH (Pearson correlation coefficients of 0.44~0.49). The formation of CH₄, C₂H₄, and EtOH all require the addition of H onto *CO as a common step. Their correlation suggests that the H-to-*CO transfer is a critical step in these systems.

These arguments converge into a coherent picture regarding interfacial water: the modifiers on Cu surface in general disrupts the regular hydrogen-bonded interfacial water structure and increases the percentage of isolated water. These water molecules are prone to provide H to the Cu surface to increase surface *H occupation as well as H addition to surface species, leading to increased H₂ generation. On the other hand, the formation of a metal-organic interphase presents some restrictions on the interfacial water and pushing them further away from the Cu surface. This hinders the H-to-Cu transfer (to generate *H) and also

decreases H-to-*CO transfer rate but to a less degree, balancing *CO hydrogenation and C–C coupling rates to enhance EtOH formation.

CO Adsorption and C–C Coupling. To explore the effect of *CO coverage, we switched the reactant from CO₂ to CO to increase CO adsorption (Figures 6f-h). For both bare CuO_x and 2-pyridylmethanethiol-CuO_x, FEs of all C₂ compounds (ethylene, ethanol and acetate) increased with no specific selectivity for a single C₂ product. However, abundant *CO on 1,8-octanedithiol-CuO_x primarily enhanced FE_{acetate} with only slight promotion or even inhibition for other C₂ products at 100-200 mA cm⁻², which is consistent with several literature results of promoted FE_{acetate} in CORR.⁶³⁻⁶⁶

This indicates that high *CO occupation does not lead to high FE_{EtOH} or FE_{C₂H₄} for 1,8-octanedithiol-CuO_x. This would be consistent with the limited H-to-*CO transfer rate in the interphase of 1,8-octanedithiol-CuO_x. As the *CO occupation is high, the H-to-*CO transfer is not fast enough to generate highly hydrogenated products like CH₃CH₂OH and C₂H₄ and thus promotes the less hydrogenated CH₃CO₂⁻ as the product.

However, under CO₂RR condition, 1,8-octanedithiol modification induces faster *CO_{LFB} conversion than *CO_{HFB} conversion upon scanning to negative potential as shown in the Raman spectra. The Raman peak position of the CO stretching modes did not change as compared to bare CuO_x, suggesting unaltered adsorption strengths and back-bonding to the *CO. The *CO_{LFB} / *CO_{HFB} conversion rate difference is likely due to different rate of H-transfer to *CO. Notably, OH electro-adsorption measurement showed that the interphase in 1,8-octanedithiol-CuO_x left the Cu (110) facet accessible and blocked the other facets, which can be responsible for this *CO_{LFB} vs *CO_{HFB} difference as well as the EtOH selectivity.

FE_{EtOH} and FE_{C₂H₄} among different modifiers are strongly correlated (Pearson correlation coefficient of 0.80 for S-modifiers) (Figure 6e), suggesting that ethylene and ethanol likely share a common formation pathway and only diverge at the end of the electrochemical process.⁶⁷⁻⁶⁹ C₂H₄ formation can occur on multiple pathways, the most referenced being through H₂C=CHO* + H⁺ + e⁻ → H₂C=CH₂ + O*, which is associated with the formation of surface-bound O*.^{67,70} In contrast, the Cu surfaces of weaker oxygen affinity promote C₂H₅OH formation by preserving the C–O bond.⁷¹ Based on the different ratios of C-absorbed *COOH and O-absorbed CO(*)O(*)⁻ on CuO_x and that modified by 1,8-octanedithiol and 2-pyridinemethylthiol (Figure S61-S63), the order of oxygen affinity on their surfaces can be inferred: 1,8-octanedithiol-CuO_x < CuO_x < 2-pyridinemethylthiol-CuO_x. The surface modification, change of interfacial water structure, preservation of a certain facet may interfere with the O* formation, responsible for the general modification effect on CH₃CH₂OH / C₂H₄ ratio as compared to bare CuO_x.

In addition, the similar position of electrochemical CO stripping peaks of CuO_x with or without modification indicate that the Cu–CO adsorption strengths on the three catalyst surfaces are similar.

(please see the revised manuscript, Pages 11-12)

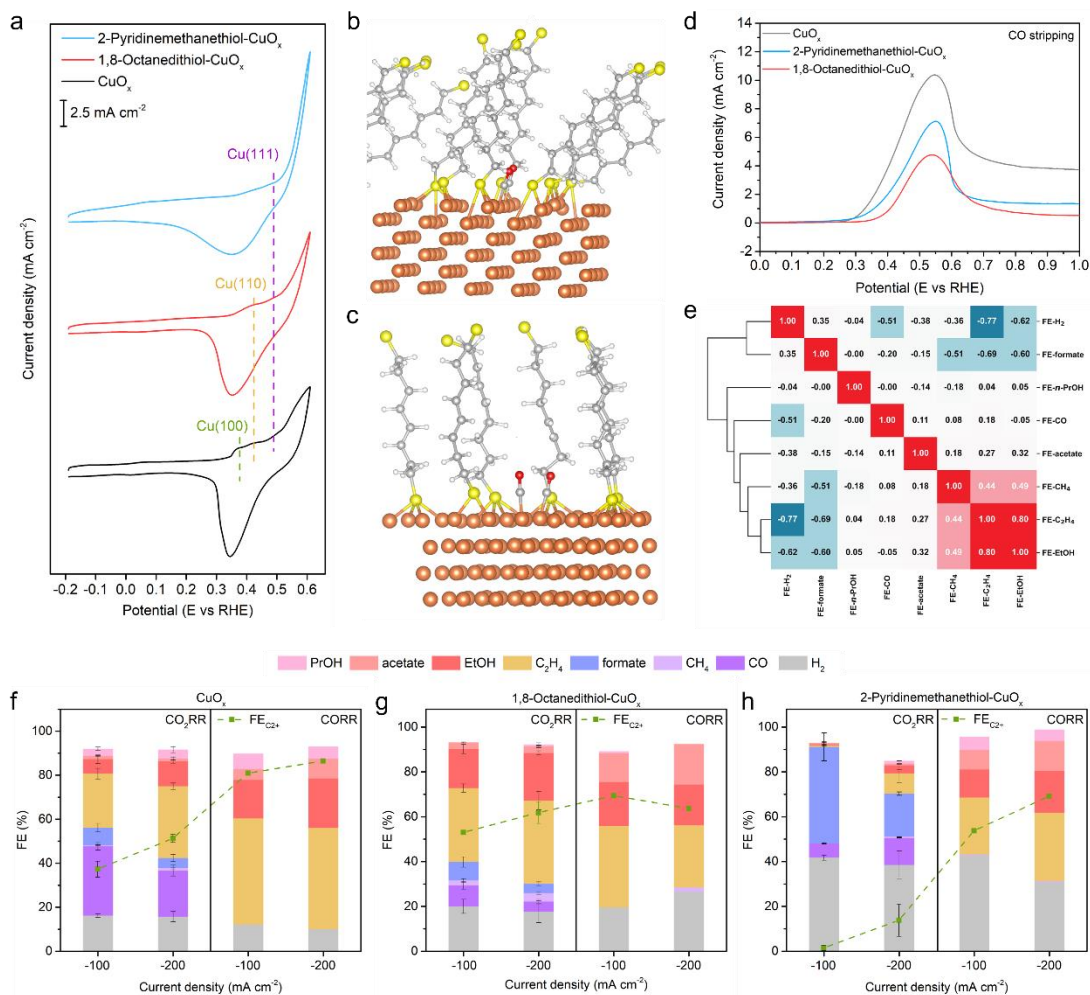


Figure 6. (a) OH⁻ electro-adsorption measurements of CuO_x, 1,8-octanedithiol-CuO_x (current density was magnified 1.5 times) and 2-pyridinemethanethiol-CuO_x catalysts in Ar-saturated 1.0 M KOH after 200 s reduction at -0.69 V vs RHE. (b) The side view of the 1,8-octanedithiol coordinated on Cu(110). (c) The side view of the 1,8-octanedithiol coordinated on Cu(100). Atomic color codes: Cu (brown), S (yellow), C (grey), O (red) and H (white). (d) CO stripping of CuO_x, 1,8-octanedithiol-CuO_x and 2-pyridinemethanethiol-CuO_x catalysts. (e) Correlation coefficients and hierarchical clustering results between FE of each CO₂RR product. Comparison of CO₂RR and CORR product distributions on (f) CuO_x, (g) 1,8-octanedithiol-CuO_x and (h) 2-pyridinemethanethiol-CuO_x catalysts at applied current density of 100 mA cm⁻² and 200 mA cm⁻², respectively.

4. The figures effectively illustrate key experimental results. However, the interpretation of certain violin plots (e.g., relative FE_{EtOH} for different molecular categories) would benefit from clearer labeling and a more detailed explanation in the text to help readers quickly grasp the

significance of these distributions.

Reply and actions taken: We thank the reviewer for the comment. The violin plot reflects the distribution shape, central tendency, and variability of the collected data. We re-plotted the figures based on the suggestion so that readers can quickly grasp the significance of these distributions. We added a row of example molecular structures to the violin plot in Figure 3, randomly selecting a representative molecule from each category as an example. The updated Figure 3 was added to the revised manuscript. (*please see the revised manuscript, Page 4, Figure 3*)

We have also added the following sentences in the revised manuscript to help readers quickly grasp the significance of these distributions: “*The violin plot reflects data distribution, central tendency, and variability. Plotting the relative/absolute FE of CO₂RR products for each molecular category highlights their regulatory effects on product selectivity.*” (*please see the revised manuscript, Page 3, Paragraph 2, Lines 2-4*)

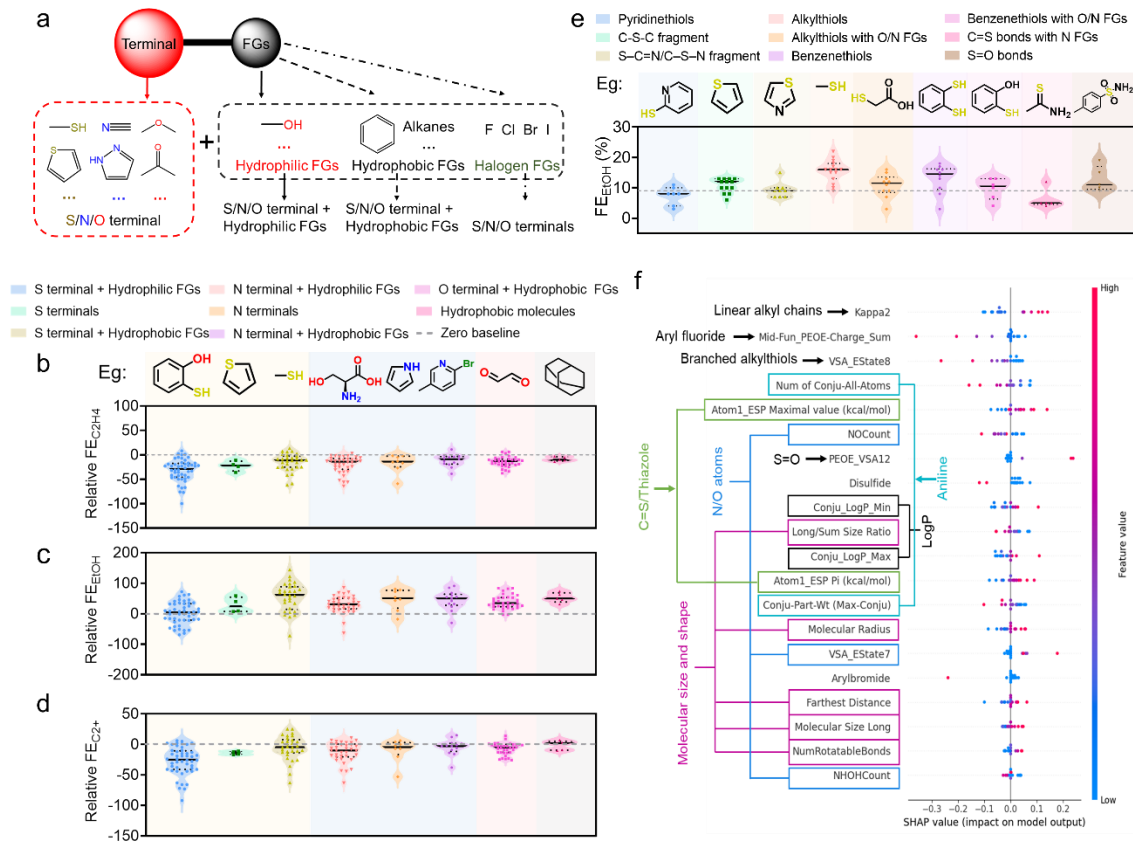


Figure 3. (a) Schematic illustration for the division rules of molecules tested according to types of coordination terminals and the hydrophilicity and hydrophobicity of functional groups. (b) Violin plot of relative FE_{C₂H₄} for each molecular category with a row of example molecular structures for each category (N/O/S terminals are plotted in blue, red, and yellow, respectively, hydrophobic groups in black, hydrophilic groups in red, and halogen atoms in green). (c) Violin plot of relative FE_{EtOH} for each molecular category.

(d) Violin plot of relative FE_{C2+} for each molecular category. (e) Violin plot of highest FE_{EtOH} on tested S-molecules in different categories with a row of example molecular structures for each category. The gray dashed line represents the highest FE_{EtOH} of the pristine CuO_x catalyst. The embedded dashed black lines within each violin plot indicates the 25th and 75th percentiles with the median represented by the center solid black line. (f) SHAP analysis diagram based on the optimal combination of selected features in EtOH Faradaic efficiency using MLP model. The annotations connected by arrows in the figure are factor categories related to physicochemical property descriptors, and the remaining annotations connected by solid lines are related physicochemical property categories.

5. The role of electrochemical conditions, such as electrolyte composition and temperature, should be discussed more comprehensively, as these could also influence the formation and stability of metal–organic interphases.

Reply and actions taken: We thank the reviewer for the comment. 0.1 M $KHCO_3$, 1.0 M KCl, 1.0 M KOH electrolyte at room temperature and 80 °C are used to explore the influence on metal-organic interphases. The TEM images, EDX mapping results and CO_2RR data at the applied current density of 100 $mA\ cm^{-2}$ under these conditions are presented in Figure S28 and Figures R28-R32. Different electrolytes and reaction temperatures do affect the composition of the metal-organic interphase and product selectivity.

As shown in Figure R28, after electrolysis in 1.0 M KOH at 80 °C, the interphase with ~10 nm thickness on 1,8-octanedithiol- CuO_x catalyst can also be observed. Interestingly, different from the TEM and EDX mapping results of the 1,8-octanedithiol- CuO_x catalyst after CO_2RR at room temperature in 1.0 M KOH (Figure S28), the composition of the interphase has changed, mainly in that O also occupies the interphase. The EDX signal of S elements becomes weaker. Furthermore, this change of the metal-organic interphase in 1.0 M KOH at 80 °C reduced the FE_{EtOH} of the 1,8-octanedithiol- CuO_x catalyst in 1.0 M KOH at room temperature, but still achieved a FE_{EtOH} of 11% compared with FE_{EtOH} of 6% for CuO_x catalyst tested in 1.0 M KOH at 80 °C at the applied current density of 100 $mA\ cm^{-2}$ (Figures R33 and R34).

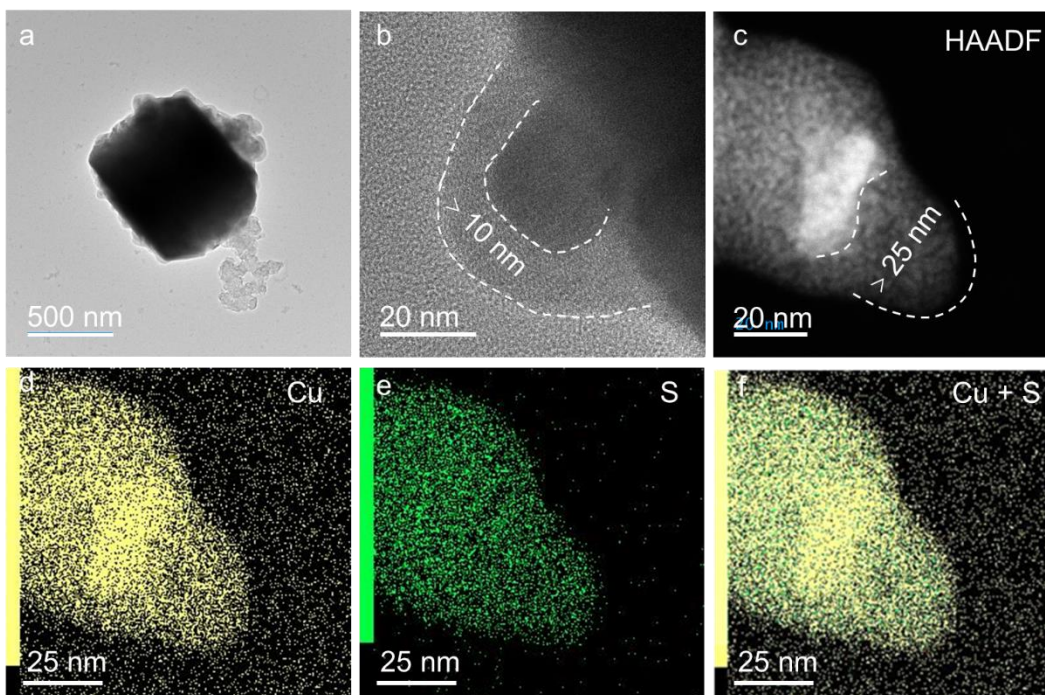


Figure S28. Characterization after CO₂RR in 1.0 M KOH at room temperature: (a-b) TEM images of 1,8-octanedithiol-CuO_x catalyst, (c) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping results of (d) Cu, (e) S elements and (f) overlapping image of Cu and S elements.

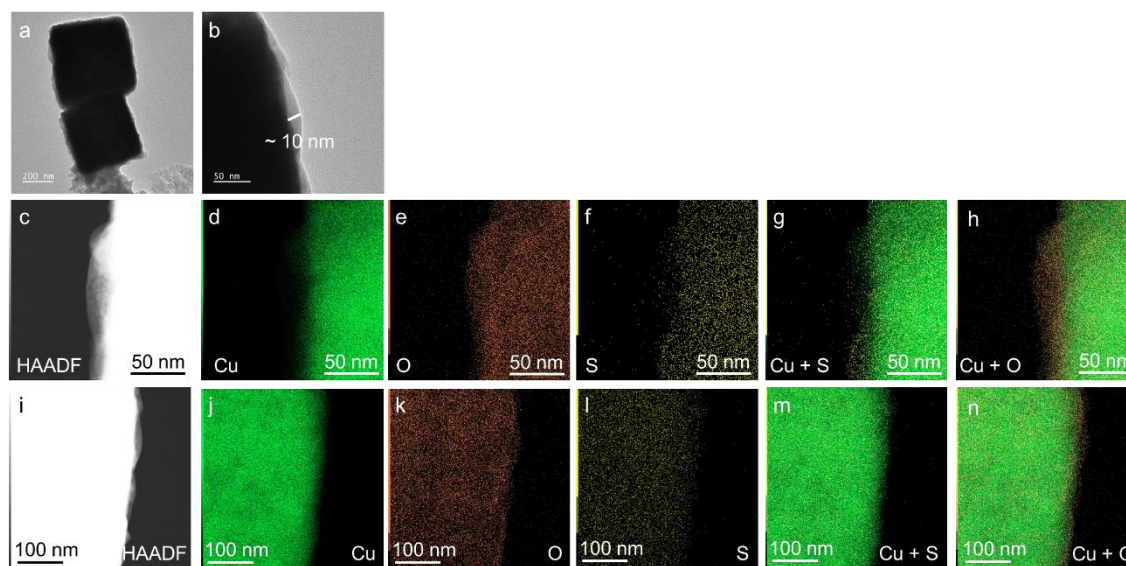


Figure R28. (a-b) TEM images of 1,8-Octanedithiol-CuO_x catalyst in 1.0 M KOH at 80 °C after CO₂RR. (c) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (d) Cu, (e) O, (f) S, (g) Cu and S overlapping, and (h) Cu and O overlapping in 1.0 M KOH at 80 °C after CO₂RR. (i) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (j) Cu, (k) O, (l) S, (m) Cu and S overlapping, and (n) Cu and O overlapping in 1.0 M KOH at 80 °C after CO₂RR.

As shown in Figure R29, the interphase with a thickness of ~10 nm on the 1,8-

octanedithiol-CuO_x catalyst after electrolysis in 0.1 M KHCO₃ at room temperature, is basically identical in composition and thickness to the interphase formed after CO₂RR in 1.0 M KOH at room temperature (Figures S28). The 1,8-octanedithiol-CuO_x catalyst achieved a FE_{EtOH} of 10% , as compared with 5% for CuO_x catalyst tested in 0.1 M KHCO₃ at room temperature at the applied current density of 100 mA cm⁻² (Figures R33 and R34).

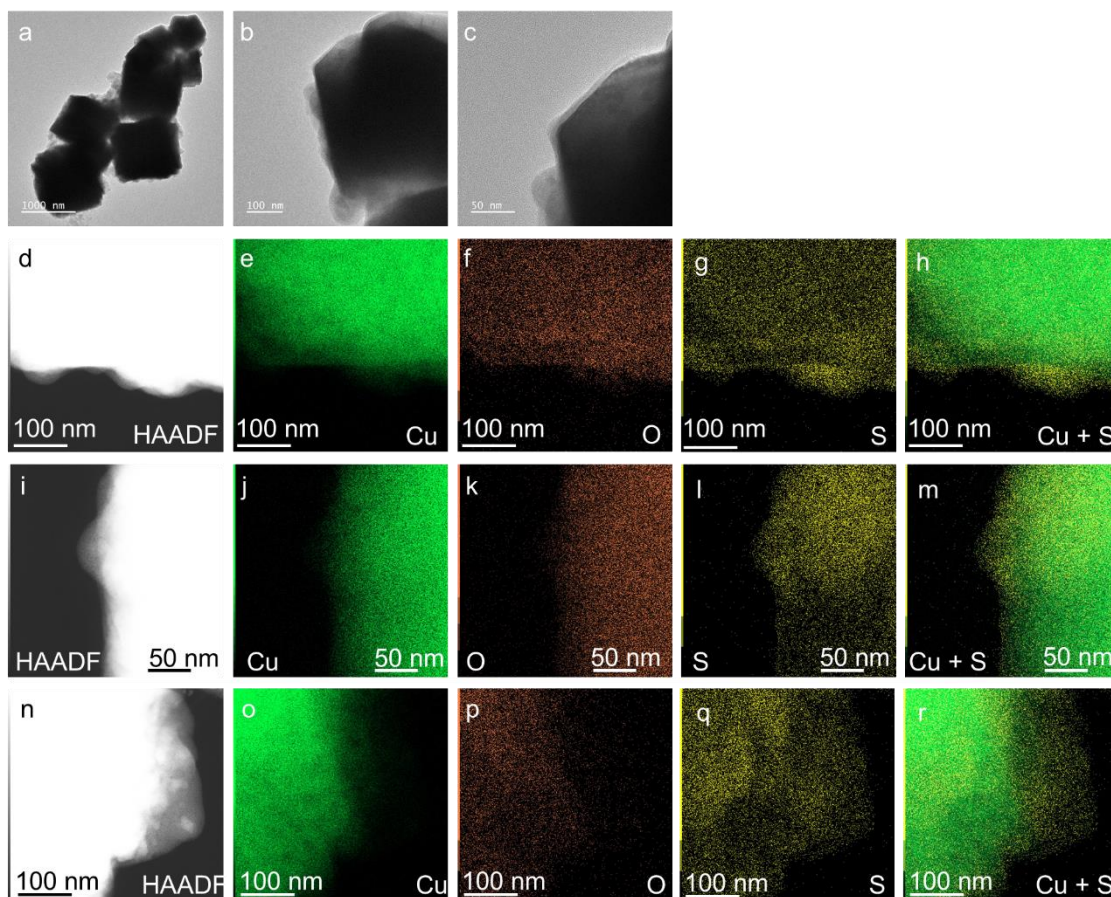


Figure R29. (a-c) TEM images of 1,8-Octanedithiol-CuO_x catalyst in 0.1 M KHCO₃ at room temperature after CO₂RR. (d) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (e) Cu, (f) O, (g) S, (h) Cu and S overlapping in 0.1 M KHCO₃ at room temperature after CO₂RR. (i) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (j) Cu, (k) O, (l) S, and (m) Cu and S overlapping in 0.1 M KHCO₃ at room temperature after CO₂RR. (n) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (o) Cu, (p) O, (q) S, and (r) Cu and S overlapping in 0.1 M KHCO₃ at room temperature after CO₂RR.

As shown in Figure R30, there is no obvious interphase on the 1,8-octanedithiol-CuO_x catalyst after electrolysis in 0.1 M KHCO₃ at 80 °C. The 1,8-octanedithiol-CuO_x catalyst only achieved a FE_{EtOH} of 7%, as compared to 4% for CuO_x catalyst tested in 0.1 M KHCO₃ at 80 °C at the applied current density of 100 mA cm⁻² (Figures R33 and R34).

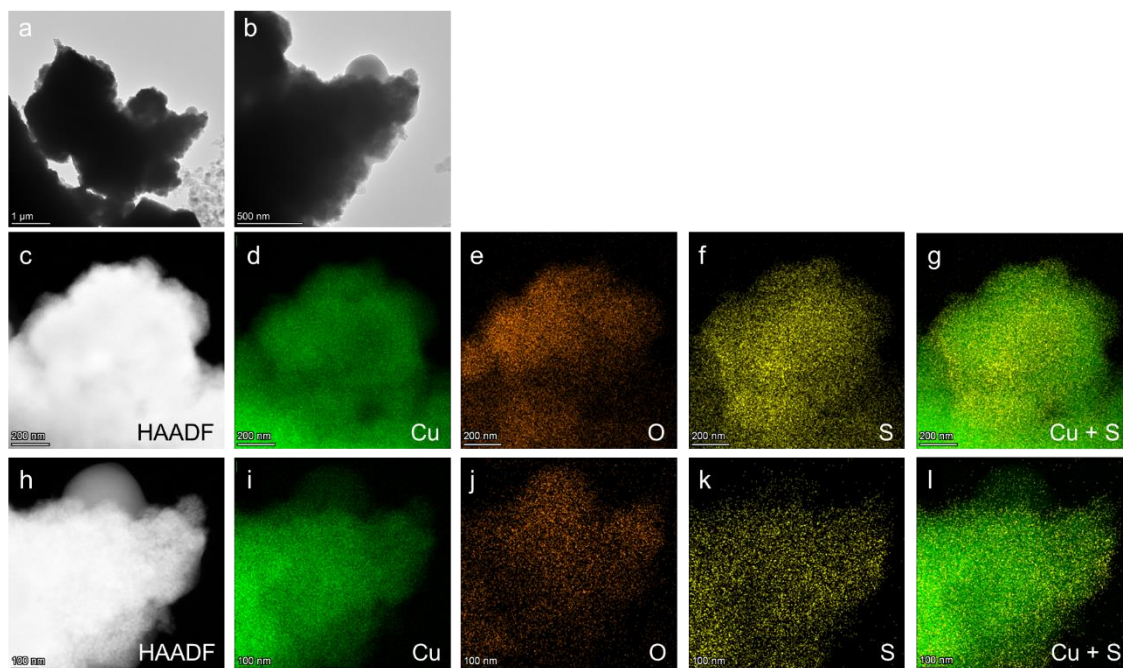


Figure R30. (a-b) TEM images of 1,8-Octanedithiol-CuO_x catalyst in 0.1 M KHCO₃ at 80 °C after CO₂RR. (c) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (d) Cu, (e) O, (f) S, and (g) Cu and S overlapping in 0.1 M KHCO₃ at 80 °C after CO₂RR. (h) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (i) Cu, (j) O, (k) S, and (l) Cu and S overlapping in 0.1 M KHCO₃ at 80 °C after CO₂RR.

As shown in Figure R31, there is no obvious interphase on the 1,8-octanedithiol-CuO_x catalyst after electrolysis in 1.0 M KCl at room temperature. The 1,8-octanedithiol-CuO_x catalyst only achieved a FE_{EtOH} of 9%, as compared with 5% for CuO_x catalyst tested in 1.0 M KCl at room temperature at the applied current density of 100 mA cm⁻² (Figures R33 and R34).

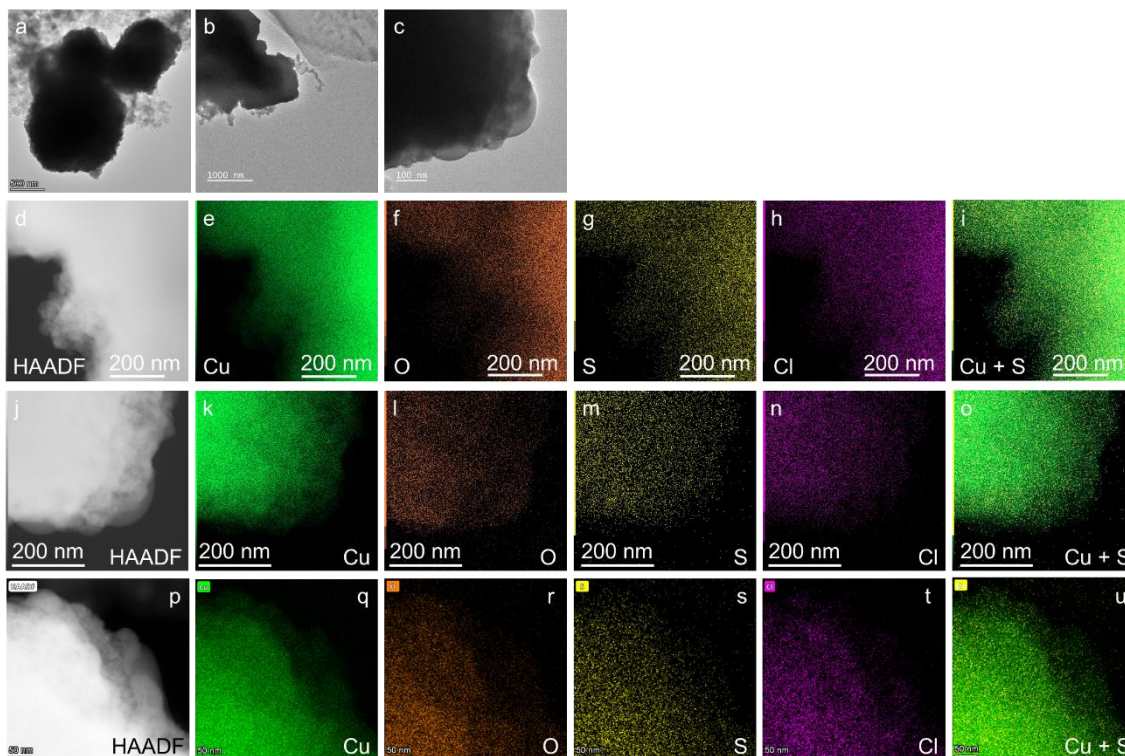


Figure R31. (a-c) TEM images of 1,8-Octanedithiol-CuO_x catalyst in 1.0 M KCl at room temperature after CO₂RR. (d) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (e) Cu, (f) O, (g) S, (h) Cl, and (i) Cu and S overlapping in 1.0 M KCl at room temperature after CO₂RR. (j) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (k) Cu, (l) O, (m) S, (n) Cl, and (o) Cu and S overlapping in 1.0 M KCl at room temperature after CO₂RR. (p) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (q) Cu, (r) O, (s) S, (t) Cl, and (u) Cu and S overlapping in 1.0 M KCl at room temperature after CO₂RR.

As shown in Figure R32, there is no obvious interphase in most areas on the 1,8-octanedithiol-CuO_x catalyst after electrolysis in 1.0 M KCl at 80 °C. The 1,8-octanedithiol-CuO_x catalyst only achieved a FE_{EIOH} of 8%, as compared with 6% for CuO_x catalyst tested in 1.0 M KCl at 80 °C at the applied current density of 100 mA cm⁻² (Figures R33 and R34).

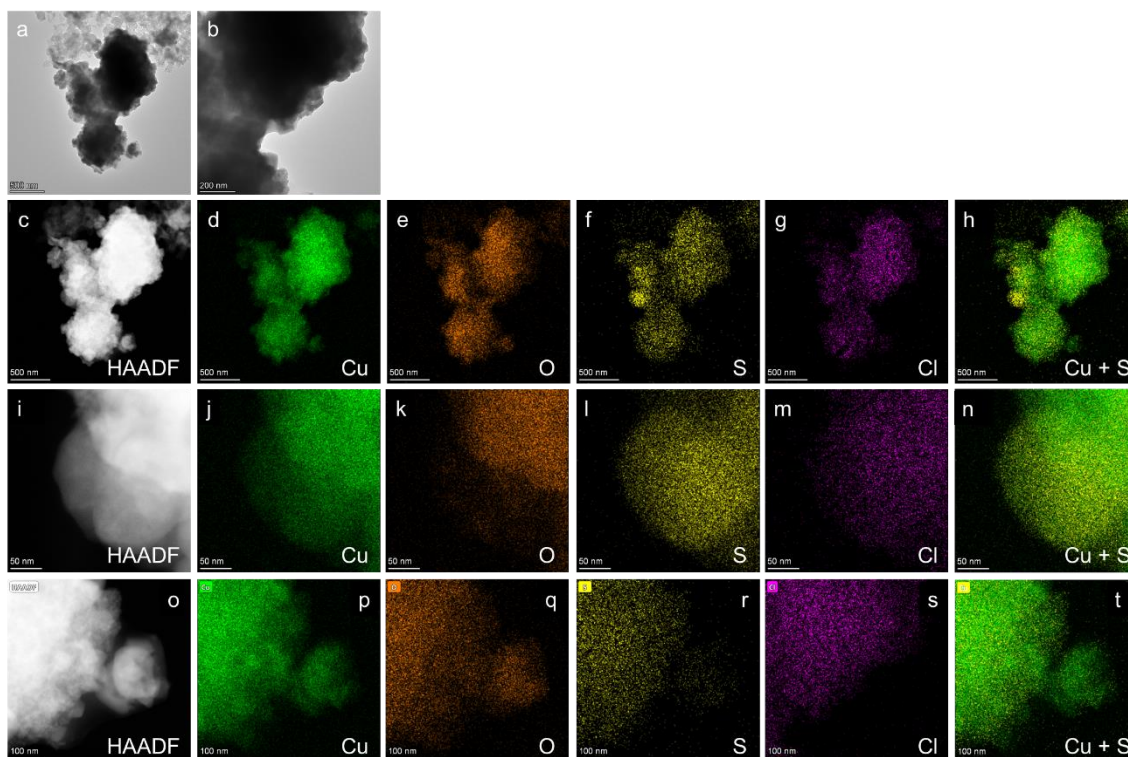


Figure R32. (a-b) TEM images of 1,8-Octanedithiol-CuO_x catalyst in 1.0 M KCl at 80 °C after CO₂RR. (c) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (d) Cu, (e) O, (f) S, (g) Cl, and (h) Cu and S overlapping in 1.0 M KCl at 80 °C after CO₂RR. (i) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (j) Cu, (k) O, (l) S, (m) Cl, and (n) Cu and S overlapping in 1.0 M KCl at 80 °C after CO₂RR. (o) HAADF image of 1,8-octanedithiol-CuO_x catalyst and corresponding EDX mapping elements images of (p) Cu, (q) O, (r) S, (s) Cl, and (t) Cu and S overlapping in 1.0 M KCl at 80 °C after CO₂RR.

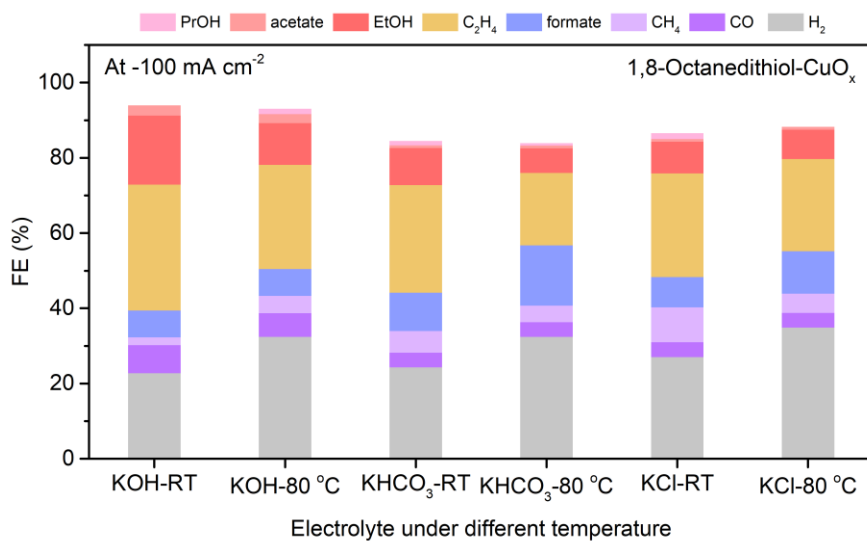


Figure R33. CO₂RR products distributions of CuO_x catalysts at 100 mA cm⁻² in different electrolyte under different temperatures. The abbreviation 'RT' refers to room temperature.

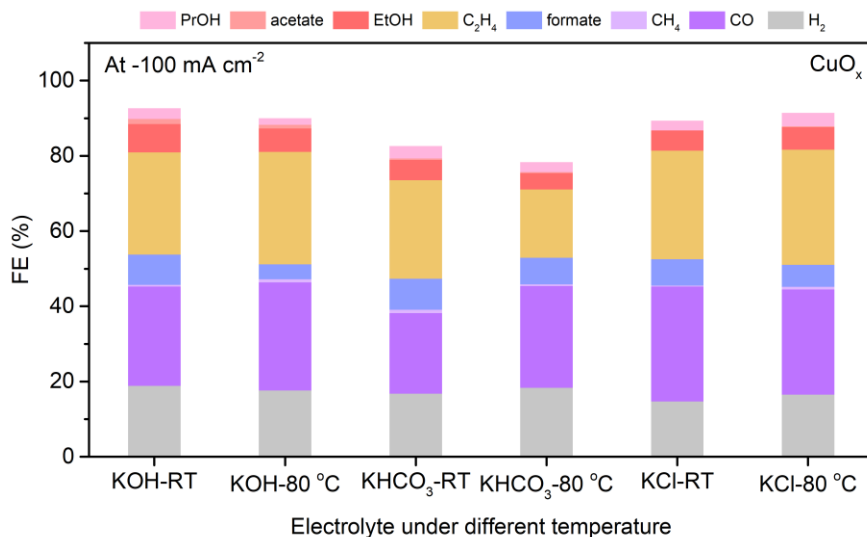


Figure R34. CO₂RR products distributions of 1,8-octanedithiol-CuO_x catalysts at 100 mA cm⁻² in different electrolyte under different temperatures. The abbreviation 'RT' refers to room temperature.

Based on above evidence, it can be concluded that electrolyte composition and temperature would influence the thickness and composition of interphase on 1,8-octanedithiol-CuO_x catalyst. The relative ethanol FEs (relative FE = (FE_{Molecule-Cu}-FE_{CuO_x})/ FE_{CuO_x}×100%) of 1,8-octanedithiol-CuO_x catalysts in 1.0 M KOH at room temperature (~10 nm interphase consisting of Cu and S), 1.0 M KOH at 80 °C (~10 nm interphase consisting of Cu and O), 0.1 M KHCO₃ at room temperature (~10 nm interphase consisting of Cu and S), 0.1 M KHCO₃ at 80 °C (no obvious interphase), 1.0 M KCl at room temperature (no obvious interphase) and 1.0 M KCl at 80 °C (no obvious interphase) were +144%, +79%, +91%, +52%, +55% and +30%, respectively. It can be concluded that the increasing temperature of the selected electrolyte and 1.0 M KCl is not conducive to the stable existence of the interphase on 1,8-octanedithiol-CuO_x catalysts. These results further demonstrated that the presence of ~10 nm interphase consisting of Cu and S elements on 1,8-octanedithiol-CuO_x catalyst play an important role in the enhancement of FE_{EtOH}.

To address the concerns, we have added the following sentences in the revised manuscript: “*The thickness and composition of interphase on 1,8-octanedithiol-CuO_x catalyst would be affected by electrolyte and temperature. We used TEM and EDX mapping to examine 1,8-octanedithiol-CuO_x catalysts after CO₂RR in 1.0 M KOH, 0.1 M KHCO₃ and 1.0 M KCl at room temperature and 80 °C, respectively (Figures S31-S34). Decreasing the pH or increasing temperature in electrolysis destabilized the interphase on 1,8-octanedithiol-CuO_x catalysts. Related to this, the relative ethanol FEs of 1,8-octanedithiol-CuO_x catalysts in 1.0 M KOH at room temperature (~10 nm interphase consisting of Cu and S), 1.0 M KOH at 80 °C (~10 nm*

*interphase consisting of Cu and O), 0.1 M KHCO₃ at room temperature (~10 nm interphase consisting of Cu and S), 0.1 M KHCO₃ at 80 °C (no obvious interphase), 1.0 M KCl at room temperature (no obvious interphase), and 1.0 M KCl at 80 °C (no obvious interphase) were +144%, +79%, +91%, +52%, +55% and +30%, respectively, at the applied current density of 100 mA cm⁻² (Figures S35-S36). These results are consistent with the notion that the presence of ~10 nm interphase consisting of Cu and S elements on 1,8-octanedithiol-CuO_x catalyst correlated with the enhancement of FE_{EtOH}.” **(please see the revised manuscript, Page 6, Paragraph 2)***

The Figures R28-R34 were also added in the revised Supporting Information as Figures S31-S36. **(please see the revised Supporting Information, Pages 41-47)**

Overall, this paper is a valuable addition to the field of electrocatalysis, and the findings could impact the design of future CO₂ reduction catalysts.

Reviewer #1 (Remarks to the Author):

The authors have properly addressed my concerns and I suggested it for publications.

Reply: We thank the reviewer for the positive evaluation of our manuscript.

Reviewer #2 (Remarks to the Author):

I appreciate the efforts made by the authors to address my comments and improve their manuscript. The authors have carefully considered the suggestions and provided substantial updates. They have clarified that the discrepancies in current densities arise from the use of different platforms during measurements. Additionally, they have included more characterizations, such as HRTEM, for the Eu@CuO_x catalysts, ensuring consistency in comparisons with other CuO_x catalysts.

For the previously missing Faraday efficiencies (FEs), the authors have addressed this by comparing their findings with published literature, highlighting that certain products may be undetectable or missed. For the reactions occurring at the interface, the authors have strengthened their argument by presenting additional evidence, including Au ion addition and subsequent deposition at the interface after electrochemical operations.

Reply: We thank the reviewer for the positive evaluation of our manuscript.

Minor comments:

Platform Distinctions: It is essential to clearly distinguish the different experimental platforms used in the study early in the manuscript. Figure 1 focuses entirely on the automated platform, which may mislead readers into assuming that all experiments were conducted using the same platform. For clarity, consider including some representative data from the automated platform in Figure 1, followed by a subtitle or explicit transition to emphasize that subsequent discussions focus on the manual platform. This will provide a clearer performance comparison for a broader audience. Avoid burying this clarification mid-paragraph (e.g., “We validated the accuracy of the data collected by the automated electrocatalytic platform by manually checking the performance of 1,8-octanedithiol, one of the best ethanol promoters, on the commercial flow cell”).

Reply and actions taken: We thank the reviewer for the comment. Following your suggestion, we have revised the relevant content and figure legends to clearly distinguish the different experimental platforms used in the manuscript. We have modified the relevant content in the sections of ‘Automated Electrocatalysis Experiments for Screening Organic Modifiers on CuO_x’ and ‘Modifiers Promoting EtOH Production’ in the revised manuscript to make this statement clearer as follows:

Automated Electrocatalysis Experiments for Screening Organic Modifiers on CuO_x

The automatic electrocatalysis platform used in this work has undergone iterative

optimization and updates since our previous publication.^{25,27} The major updates include the installation of a catalyst replacement and positioning module (Figure S1) and a catholyte collection unit (Figure S2) for collecting CO₂RR liquid products during the measurements. The system now features an automatic electrolysis unit with an automatically assembled flow cell, a catalyst replacement module, a compliant peristaltic pump for transporting 1.0 M KOH, a catholyte collection unit, and an online micro-fast chromatography (GC) for gas products analysis (Figure 1a). The platform reduces assembly and testing time by nearly 10 times compared to commercial flow cells while simultaneously enhancing the precision and repeatability of evaluation results.

We selected CuO_x catalysts synthesized by a facile solvothermal method as the substrate for molecular modification due to the superior CO₂-to-C₂⁺ performance of oxide-derived Cu (OD-Cu) compared to pure Cu in alkaline environments.²⁸⁻³¹ To modify the catalysts, we chose molecules containing N/S/O terminals that can coordinate to the CuO_x surface through lone pair electrons or water-insoluble organics that bind via non-bonding interactions.

Most modifications led to a decrease of the total current density during electrolysis compared to bare CuO_x, possibly due to a decreased area of exposed Cu and slightly increased charge-transfer resistance (R_{ct}) (Figure S3), but the decreases in current density ranging from 11% to 18% over 0 to -1.2 V vs reversible hydrogen electrode (RHE) were mostly less than 20%, keeping the activity acceptable (Figure 1b).

We calculated relative Faradaic efficiencies (FEs) by comparing the optimized FE of a molecule-modified CuO_x with that of the unmodified CuO_x catalyst:

$$\text{Relative FE}_i = (\text{FE}_{\text{Molecule-Cu}} - \text{FE}_{\text{CuO}_x}) / \text{FE}_{\text{CuO}_x} \times 100\%$$

where i represents different products like C₂H₄, EtOH and C₂⁺ products.

The accuracy of the data collected by the automated platform (Figure 1) was manually validated on a commercial flow electrolysis cell platform by selecting 1,8-octanedithiol-CuO_x for ethanol selectivity, 2-pyridinemethanethiol-CuO_x for formate selectivity, and CuO_x catalyst (Figure 2).

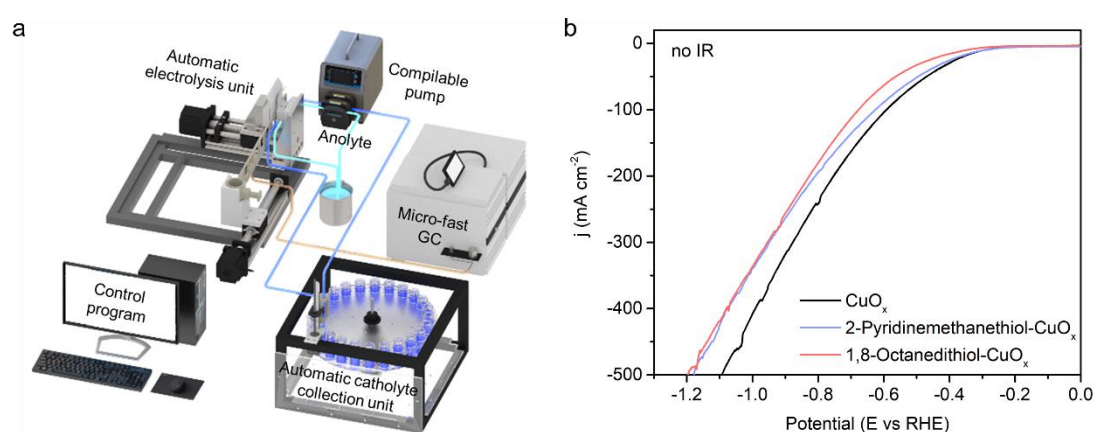


Figure 1. (a) Schematic illustration of automatic electrocatalysis platform for CO₂RR. (b) Linear Sweep Voltammetry (LSV) curves without IR compensation of CuO_x, 1,8-octanedithiol-CuO_x and 2-pyridinemethanethiol-CuO_x catalysts. Figure 1 focuses on data from the automated platform.

Modifiers Promoting EtOH Production: Manual Verification

From the data collected by the automation platform (Figure 1), it is worth noting that 15 S-terminal modifiers exhibited significantly enhanced selectivity for ethanol with relative FE above +70%. Among these, 1,8-octanedithiol achieved a maximum Faradaic efficiency for ethanol that was 2.4 times that of the CuO_x catalyst at -0.62 V vs RHE (Figure S4). These 15 S-molecules maintained $\text{FE}_{\text{C}_2\text{H}_4}$ while reducing FE_{CO} , suggesting a common catalytic pathway directing more $^*\text{CO}$ coupling towards ethanol. Notably, the CO_2RR results manually verified on commercial flow cell platform confirmed the enhancement of FE_{EtOH} from 17% on CuO_x to 29% on 1,8-octanedithiol- CuO_x at applied current density of 400 mA cm^{-2} , with a $\text{FE}_{\text{EtOH}}/\text{FE}_{\text{C}_2\text{H}_4}$ ratio of ~ 0.9 , which is 2.3-fold higher than that over the pristine CuO_x (~ 0.4). FE_{CO} was suppressed (31% $\sim$ 13% of CuO_x vs 9% $\sim$ 2% of 1,8-octanedithiol- CuO_x), and the $\text{FE}_{\text{C}_2^+}$ was also enhanced from 36% $\sim$ 61% (CuO_x) to 53% $\sim$ 65% (1,8-octanedithiol- CuO_x) at applied current density ranging from 100 to 400 mA cm^{-2} (Figures 2a-2b and Figures 2d-2e). In contrast, the automatic electrocatalysis platform showed that another thiol-containing compound which inhibited $\text{FE}_{\text{C}_2^+}$, 2-pyridinemethanethiol, increased $\text{FE}_{\text{formate}}$, which was also confirmed on the commercial flow cell (from 8% on CuO_x to 43% on 2-pyridinemethanethiol- CuO_x) (Figures 2c and 2e).

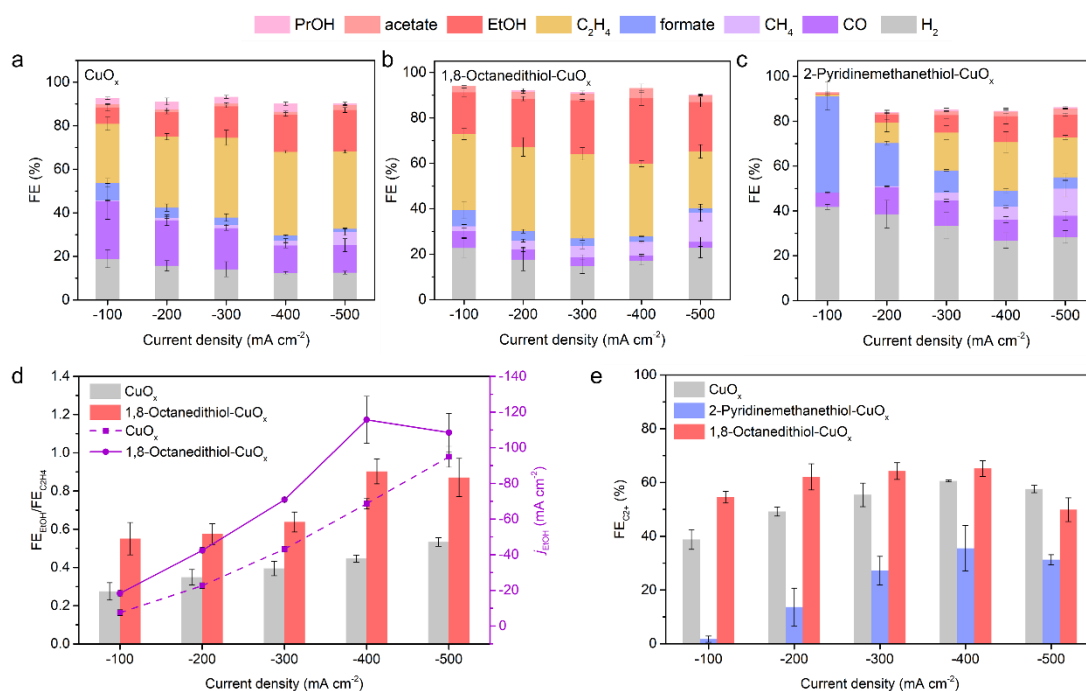


Figure 2. FEs for all products over (a) CuO_x catalyst, (b) 1,8-octanedithiol- CuO_x catalyst, and (c) 2-pyridinemethanethiol- CuO_x catalyst. (d) The ratio of faradaic efficiencies of ethanol and ethylene ($\text{FE}_{\text{EtOH}}/\text{FE}_{\text{C}_2\text{H}_4}$) and partial ethanol current density of CuO_x and 1,8-octanedithiol- CuO_x . (e) The C_2^+ FE plots of CuO_x , 1,8-octanedithiol- CuO_x , and 2-pyridinemethanethiol- CuO_x catalysts. The experiments at all the applied current density were performed at least three times and the results were displayed as mean $\pm$ standard deviation. The data in Figure 2 were collected manually on the commercial flow cell platform.

Hydrophobicity: The hydrophobicity has been mentioned several times through the manuscript, especially as a potential factor in the ML models. However, I was a bit lost in the connection to the next part of discussion for the interphase effect. For instance, the statement at line 166 ("This complexity challenges the simplistic understanding of

hydrophobicity-promoted ethanol production”) raises questions. Please clarify how hydrophobicity influences ethanol production in the context of your findings.

Reply and actions taken: We thank the reviewer for the comment. After considering this comment, we realized that there are two levels of meanings of “hydrophobicity / hydrophilicity”. One level is on the molecular level: hydrophobic vs. hydrophilic functional groups, while the other level is on the device level: a hydrophobic vs. hydrophilic electrode surface. These two levels are expected to correlate. However, our experimental evidences point to the lack of correlation between the two.

Although the machine learning and statistical analysis showed that molecular hydrophobicity is a critical factor for the modifier, the measurement of the contact angle of the water droplet on the electrode did not show much effect of hydrophobic modifiers on the hydrophobicity of the electrode. This is possibly due to other components on the gas-diffusion electrode contribute and dominate the hydrophobicity on the electrode level. This showed that the contribution of molecular hydrophobicity of the modifier to the overall catalytic performance must be due to affecting other aspects than adjusting the electrode level hydrophobicity. We think the finding of the metal-organic interphase provides a possible explanation of this contribution, as the formation of the interphase is also favored if the modifiers are hydrophobic for integrating to a phase insoluble to water.

We revised the following sections as highlighted in yellow accordingly:

Hydrophobicity / Hydrophilicity of the Modifiers

Previous reports suggested hydrophobicity of the modifier can affect the hydrophobicity of the electrode for preserving water/gas interface, which is beneficial for generating C₂₊ products.^{15,22-24} In search for such relationship, we measured the contact angle of a water droplet on various modified electrodes using alkylthiols with various alkyl chain lengths, pyridinethiols, and aromatic thiols. However, we did not observe a correlation between the FEs with the contact angles either before or after the reaction (Figures S5-S6). For example, bare CuO_x has a contact angle of 145.9° before reaction and 98.7° after reaction, while the 1,8-octanedithiol modified electrode has a contact angle of 146.1° before reaction and 103.2° after reaction. Similarly, 2-pyridinethiol, which leads to high FE for formate and low FE for C₂₊ products, has a contact angle of ~ 142.4° before reaction and 100.1° after reaction.

We categorized all modifiers into eight groups based on the type of N/O/S coordination terminals and the hydrophilicity/hydrophobicity of the connected functional groups (FGs) (Figure 3a and Table S1). The violin plot reflects data distribution, central tendency, and variability. Plotting the relative/absolute FE of CO₂RR products for each molecular category highlights their regulatory effects on product selectivity. Statistical analysis of data of all the modifiers showed that hydrophobic FGs were more likely to promote ethylene/ethanol/C₂₊ production for molecules with similar coordination terminals (Figures 3b-3d). The ‘S terminal + hydrophobic FGs’ displayed the best promotion effect, but there were significant variations within each category. Some molecules with hydrophilic functional groups still promoted ethanol production, such as 4-nitrobenzaldehyde with relative FE_{EtOH} of +86%

and L-Cystine with relative FE_{EtOH} of +72%. Only a few modifiers could increase FE_{EtOH} while maintaining $FE_{C_2H_4}$ at levels similar to bare CuO_x . This indicates that factors other than hydrophobicity / hydrophilicity may influence the performance.

These data showed that the hydrophobicity of the functional groups in the modifier promotes ethanol but does not directly correlate with the hydrophobicity on the electrode level.

Machine Learning Analysis Revealing Factors Influencing EtOH Production

First focusing on sulfur-containing modifiers including 82 tested samples, we found that most S-modifiers enhanced FE_{CH_4} , FE_{EtOH} and $FE_{acetate}$ but decreased $FE_{C_2H_4}$ and $FE_{n-propanol}$ (Figure 3e and Figures S7-S10, Table S2). We then used machine learning to analyze the dataset. The featurization was achieved using a combination of molecular fragment fingerprints (MFFs) and descriptors of molecular physicochemical properties (RDkit and LoFFi/LoFFi-MOE³²). Using various machine learning models, a pipeline of stepwise forward feature selection, cross validation, and SHAP analysis was established for analysis. To predict the FEs of each CO_2RR product to be low or high, the best performance was achieved using a multi-layer perceptron (MLP) model with test set accuracy ranging from 60% to 79% (Figures S11-S13, Tables S3-S7) and area under the receiver operating characteristic curve (AUC-ROC) ranging from 62% to 81%. The FE_{EtOH} prediction by this model was 64% in accuracy and 70% in AUC-ROC for the test set.

The important features for each CO_2RR product were identified by a SHAP analysis (Figure 3f and Figures S14-S21), and the interpretation of many of the physicochemical descriptors were achieved by correlating them to structural features of the molecules in the dataset using factor analysis (Figures S22-S24 and Tables S8-S17), a new interpretation method tailor-designed for this work (see 'Feature Selection via Regression Model and Feature Interpretability' and 'Classification Models and Shapley Value Analysis' sections in the Supporting Information for more details). Using this method, we found several of the descriptors surprisingly represent something in the small dataset totally different from their intended general definition, an issue that was overlooked in previous works. For example, the size of the conjugation part of the molecules accidentally correlates with the presence of aniline in this small dataset, which can otherwise give misleading interpretation. A bunch of structural features beyond hydrophobicity (represented by LogP)^{15,22} were identified to promote EtOH production (Figure 3f, Figures S22-S24 and Table S15):

- (1) Linear alkyl chains (represented by 'Kappa2') promoted ethanol production, while branched alkylthiols ('VSA_EState8') disfavored EtOH production, indicating critical steric effect around the thiol group.
- (2) Larger and round-shaped modifiers favored EtOH production (represented by 'Long/Sum size ratio', 'Molecular Radius', 'Farthest Distance', 'Molecular Size Long', 'Num_Rotatable_Bonds').
- (3) Disulfide, 'Aryl bromide' and 'Aryl fluoride' (represented by 'Mid-Fun_Partial Equalization of Orbital Electronegativities (PEOE)-Charge_Sum') disfavored EtOH production as compared to thiol-groups, possibly due to poor coordination capability of them.
- (4) The presence of N/O atoms ('NO count', 'NHOH count', 'VSA_EState7'),

C=S/thiazole (negatively correlated to 'Atom1_ESP Maximal value' and 'Atom1_ESP Pi'³³⁻³⁵), or aniline (related to 'Num of Conju-All-Atoms' and 'Conju-Part Wt (Max Conju)'), all related to hydrophilicity, reduces ethanol production.

- (5) The presence of S=O ('PEOE_VSA12') that is also hydrophilic positively impact the FE_{EtOH} , violating the hydrophobicity requirement.

The hydrophobicity of the functional groups at the microscopic level of the S-modifier is an important but not the only factor affecting the selectivity for ethanol. This complexity challenges the simplistic understanding of hydrophobicity-promoted ethanol production. The role of the hydrophobicity of functional groups in S-modifiers in enhancing ethanol selectivity is discussed in the following sections.

Lastly, I noticed a formatting issue in Figure 1 (a partial box appears at the top of the figure, likely due to PDF conversion). Ensuring the figure is visually clear and free from such issues will further aid readability.

Reply and actions taken: We thank the reviewer for the comment. We checked the format of Figure 1 in the document. It may be a problem during the PDF conversion. We re-inserted Figure 1 to avoid this problem from happening again.

I fully recognize the value of this work, not only for demonstrating a promising catalyst for CO₂RR but also for providing a comprehensive dataset that could serve as a valuable resource for future research. However, as the manuscript is very heavy in terms of data presented, I feel that the manuscript would still benefit from a clearer and more cohesive storyline. I still want to emphasize that I have no doubt on the quality of this work, regarding the data and their interpretations. Therefore, I recommend this paper to be published in Nature Communication.

Reviewer #3 (Remarks to the Author):

The authors have addressed my comments well.

Reply: We thank the reviewer for the positive evaluation of our manuscript.