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Heterogeneous Molecular Catalysts of Metal Phthalocyanines for Electrochemical CO_2 Reduction Reactions

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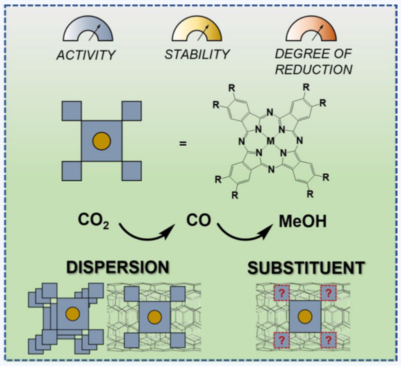

CONSPECTUS: Molecular catalysts, often deployed in homogeneous conditions, are favorable systems for structure−reactivity correlation studies of electrochemical reactions because of their well-defined active site structures and ease of mechanistic investigation. In pursuit of selective and active electrocatalysts for the CO_2 reduction reactions which are promising for converting carbon emissions to useful fuels and chemical products, it is desirable to support molecular catalysts on substrates because heterogeneous catalysts can afford the high current density and operational convenience that practical electrolyzers require. Herein, we share our understanding in the development of heterogenized metal phthalocyanine catalysts for the electrochemical reduction of CO_2. From the optimization of preparation methods and material structures for the electrocatalytic activity toward CO_2 reduction to CO, we find that molecular-level dispersion of the active material and high electrical conductivity of the support are among the most important factors controlling the activity. The molecular nature of the active site enables mechanism-based optimization. We demonstrate how electron-withdrawing and -donating ligand substituents can be utilized to modify the redox property of the molecule and improve its catalytic activity and stability. Adjusting these factors further allows us to achieve electrochemical reduction of CO_2 to methanol with appreciable activity, which has not been attainable by conventional molecular catalysts. The six-electron reduction process goes through CO as the key intermediate. Rapid and continuous electron delivery to the active site favors further reduction of CO to methanol. We also point out that, in homogeneous electrocatalysis where the catalyst molecules are dissolved in the electrolyte solution, even if the molecular structure remains intact, the actual catalysis may be dominated by molecules permanently adsorbed on the electrode surface and is thus heterogeneous in nature. This account uses our research on CO_2 electroreduction reactions catalyzed by metal phthalocyanine molecules to illustrate our understanding about heterogeneous molecular electrocatalysis, which is also applicable to other electrochemical systems.

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KEY REFERENCES

- Zhang, X.; Wu, Z.; Zhang, X.; Li, L.; Li, Y.; Xu, H.; Li, X.; Yu, X.; Zhang, Z.; Liang, Y.; Wang, H. Highly selective and active CO_2 reduction electrocatalysts based on cobalt phthalocyanine/carbon nanotube hybrid structures. *Nat. Commun.* **2017**, *8*, 14675.[1] *This study first demonstrated molecular-level dispersion of cobalt phthalocyanine on carbon nanotubes, which dramatically increases the catalytic selectivity and activity for CO_2-to-CO conversion. The catalytic performance was further enhanced by ligand modification.*
- Wu, Y.; Jiang, Z.; Lu, X.; Liang, Y.; Wang, H. Domino electroreduction of CO_2 to methanol on a molecular catalyst. *Nature* **2019**, *575*, 639−642.[2] *This study reported the first electroreduction of CO_2 to methanol in significant yield over a molecualr catalyst. Catalyst deactivation was resolved by ligand modification.*
- Wu, Y.; Hu, G.; Rooney, C. L.; Brudvig, G. W.; Wang, H. Heterogeneous Nature of Electrocatalytic CO/CO_2 Reduction by Cobalt Phthalocyanines. *ChemSusChem* **2020**, *13*, 6296−6299.[3] *The investigation into water-soluble cobalt phthalocyanine molecules dissoloved in electrolyte revealed that their catalytic reactivity for CO_2 reduction is heterogeneous in nature.*
- Zhang, X.; Wang, Y.; Gu, M.; Wang, M.; Zhang, Z.; Pan, W.; Jiang, Z.; Zheng, H.; Lucero, M.; Wang, H.; Sterbinsky, G. E.; Ma, Q.; Wang, Y.-G.; Feng, Z.; Li, J.; Dai, H.; Liang, Y. Molecular engineering of dispersed nickel phthalocyanines on carbon nanotubes for selective CO_2 reduction. *Nat. Energy* **2020**, *5*, 684−692.[4] *This work developed a nickel phthalocyanine electrocatalyst showing >99.5% selectivity and stable operation at industrially relevant current densities for CO_2-to-CO conversion.*

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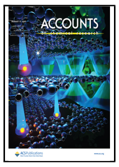

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I. INTRODUCTION

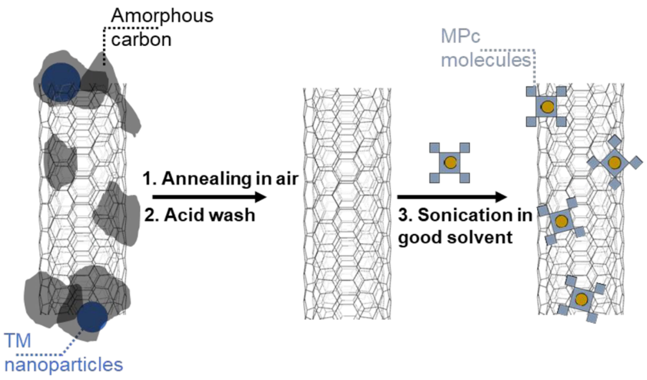
Being a promising approach to the conversion of CO_2 emissions into fuels or commodity chemicals using renewable electricity as an energy input under ambient temperature and pressure, successful electroreduction of CO_2 still necessitates the development of active and selective catalysts to improve the efficiency of the reaction.[5−9] Molecular catalysts, compared with other electrocatalytic materials (e.g., metals, metal alloys, metal oxides, and metal chalcogenides),[10] are particularly interesting systems because of their well-defined active site structures.[11,12] Molecular electrocatalysts are traditionally studied in the homogeneous electrocatalysis configuration where the catalyst molecules need to shuttle between the electrode surface to receive electrons and the bulk solution where it reacts with CO_2. This setting allows for kinetic analysis using derived physicochemical models and for characterization of reaction intermediates in the solution, which can provide valuable mechanistic insights at the molecular level. The understanding of the reaction pathway, in particular the rate-limiting step, can further guide the design of improved catalysts or identification of reaction conditions that favor the catalysis.[11−13] On the other hand, heterogenized molecular catalysts are more suitable for real-world applications. First, the heterogenization enables continuous and rapid transport of electrons to the catalytic center and can therefore afford high current density.[4,14−16] Second, heterogenized molecular catalysts can achieve a much higher spatial density that is not limited by the solubility and diffusion of the molecule.[14] Third, the localization of active material on the electrode offers much higher operational convenience that electrolyzers require (e.g., membrane electrode assembly).[17] Because of the intimate contact and interaction between the catalyst molecules and that between the catalyst molecule and electrode, the inhomogeneity at the reaction interface allows many factors to affect the catalytic reactivity of heterogenized molecules. This intrinsic complexity opens up opportunities for using interdisciplinary approaches to bridge the gap between homogeneous and heterogeneous catalysis, as has been demonstrated in recent studies of immobilized molecules achieving superior catalytic performance.[18−20]

Transition-metal phthalocyanine (MPc) complexes are a particularly suitable class of molecules to explore for heterogeneous molecular catalysts because of their generally low solubility in aqueous media,[21] their extended π-electron system that facilitates adsorption on the electrode surface (e.g., carbon substrates) through noncovalent interactions,[22] and the possibility to study the catalytic reactivity trend across different metal centers and ligand substituents.[23] Many of the early studies on heterogeneous MPc catalysts were mainly focused on performance screening with little attention paid to the various aspects that resulted in or could affect the observed catalytic performance.[24−27] In this account, we take snippets of our research on heterogeneous MPc electrocatalysts as examples to demonstrate how their molecular structures and nanoscale interactions can be tailored to achieve enhanced activity for known products and selectivity for new products in CO_2 electroreduction.[1−4,16,28−31] Given the availability of more general reviews on molecular electrocatalysts for CO_2 reduction reactions,[12,18,19,32,33] this Account focuses on the important structural parameters of heterogeneous molecular electrocatalysts, including molecule dispersion and ligand modification, that lead to distinct catalytic selectivity and activity. Experimental operations that are essential for achieving such structures and catalytic performance are emphasized. The insights gleaned from our studies should also benefit other electrochemical reactions catalyzed by heterogenized molecular complexes.

II. HETEROGENIZATION OF MOLECULAR CATALYSTS

Molecular complexes in their crystalline form are generally poor electrical conductors.[34] As a result, any aggregation of molecules on the electrode surface that resulted from a straightforward drop-casting method would likely hamper the electron transfer to the surface of the molecular solid where the catalysis takes place.[18,19] Additionally, most of the molecules in the aggregates would not be catalytically active due to the lack of exposure to the reactants (e.g., CO_2). For these reasons, the intrinsic catalytic reactivity of molecules can only be exposed when they are well-dispersed on the electrode surface and electrically wired to the current collector, ideally at the single-molecule level.[1,35] In order to increase the spatial density of the molecular catalysts while maintaining a well-dispersed state of the molecules, they can be deposited on a high-surface-area nanocarbon material. These rationales are rooted in our earlier research on growing (often electrically insulating) inorganic nanoparticles on graphene sheets or carbon nanotubes (CNTs) for electrochemical energy conversion and storage.[36,37] In our studies, multiwalled CNTs are chosen because (i) they are highly conductive ($10^{4}-10^{5}$ S m^{-1} vs 4×10^{-7} S m^{-1} for CoPc solid, for example),[38,39] (ii) they have a high specific surface area (>100 m^{2} g^{-1})[40] and can form a porous film on the electrode[41] to help achieve a high geometric loading of catalyst molecules while still maintaining the molecular level of dispersion, and (iii) they are relatively inert under electrochemical CO_2 reduction conditions. It is critical to use CNTs with low levels of defects and contaminants (e.g., transition metal catalysts used in CNT growth)[42] to minimize side reactions (e.g., H_2 evolution) during electrocatalysis. Calcining as-received CNTs in air to remove amorphous carbon followed by acid wash to remove the exposed metal impurities is therefore necessary (Scheme 1).[43,44] In order to achieve good catalyst dispersion on CNTs, it is essential to disrupt the $\pi-\pi$ interaction between the MPc molecules and promote that between MPc and CNT. Choosing a proper solvent (e.g., *N*,*N*-dimethylformamide, DMF) to disperse CNTs and dissolve MPc in combination with strong mechanical agitation to maximize the contact and interaction between MPc and CNT is therefore also necessary. Following these

Scheme 1. Procedures for Pre-treating As-Received CNTs and Assembling MPc/CNT Hybrid Catalyst Materials



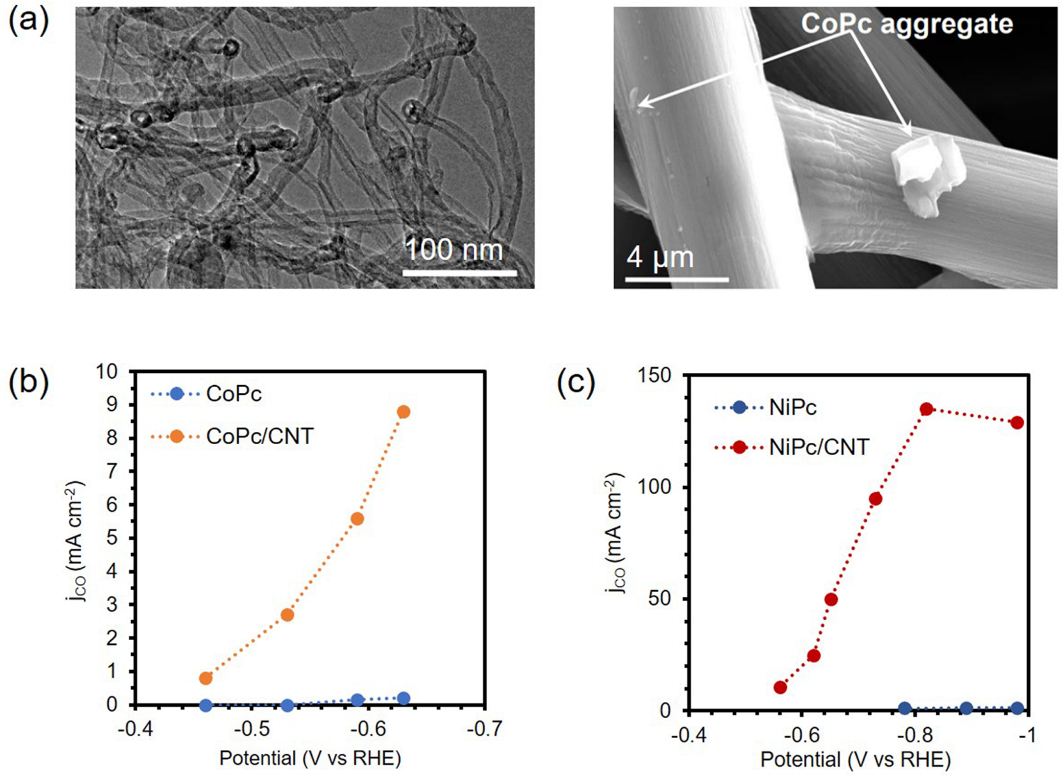


Figure 1. (a) Electron-microscopy images of CoPc/CNT (left) and bare CoPc crystals (right). (b) Comparison of CO partial current density by bare CoPc and CoPc/CNT at various cathode potentials in 0.1 M $KHCO_3$. (c) Comparison of CO partial current density by bare NiPc and NiPc/CNT on a GDE in a flow cell at various cathode potentials in 1.0 M $KHCO_3$. Panels a and b adapted with permission from ref 1. Copyright 2017 Springer Nature. Panel c adapted with permission from ref 4. Copyright 2020 Springer Nature.

considerations, we successfully developed a straightforward sonication method (Scheme 1) to uniformly deposit MPc molecules onto prepurified CNTs in DMF.[1,2,4,29] The afforded hybrid catalyst, once washed and freeze-dried, can be used to prepare catalyst ink with an ionomer binder, ready to be drop-cast onto electrode substrates (e.g., carbon fiber paper). Since this hybridization strategy does not rely on specific interactions, it is expected to generally work for other planar molecules bearing large conjugated π systems.

Boosting CO_2-to-CO Conversion

The dramatic effect of molecule dispersion on catalyst activity was demonstrated in our study of CO_2 reduction to CO catalyzed by cobalt phthalocyanine (CoPc).[1] Although the catalytic activity of CoPc for CO_2 electroreduction was first reported more than 30 years ago,[45] little attention was given to optimizing the preparation of catalyst electrodes. In most of these studies, dissolved molecules were directly loaded on the electrode without an effective attempt to enhance dispersion of the molecues.[24−26,45,46] Using the hybridization method we developed, we prepared a series of CoPc/CNT catalysts with variable CoPc loadings.[1] Good dispersion of CoPc molecules can be achieved with loadings < 5 wt %. Electron microscopy confirms the highly dispersed nature of CoPc on CNTs where no standalone CoPc chunks can be found, whereas direct deposition of CoPc on a carbon fiber paper electrode results in obvious formation of aggregates (Figure 1a). The CoPc/CNT hybrid catalysts delivers much larger catalytic current than the directly deposited CoPc catalyst. At −0.63 V vs the reversible hydrogen electrode (RHE) in CO_2-saturated 0.1 M aqueous $KHCO_3$ measured in an H-cell reactor, the partial current density of CO (j_{CO}) reaches 9.0 mA/cm^2 on CoPc/CNT (CoPc loading, 2.5 wt %), corresponding to a 43-fold increase compared to directly deposited CoPc despite the latter having twice as many CoPc molecules (Figure 1b).[1] Such a drastic increase in catalytic performance is the direct result of molecular-level dispersion of the molecular catalyst on a high-surface-area and highly conductive support. The same strategy can be applied to assemble other MPc/CNT catalysts (M = Mn, Fe, and Ni), all of which display superior reaction rates for CO_2 reduction to CO over their MPc counterparts without CNT.[4,29] We note that uniform dispersion and reasonably high geometric loading of MPc molecules are achieved simultaneously with our hybrid catalysts. Although a relatively good dispersion may also be achieved via direct drop-casting if one uses an ultradilute solution of the molecule and limit the amount of ink deposited onto the electrode, the geometric loading of the catalyst molecules would be 2 to 3 orders of magnitude smaller due to the much lower surface area of the electrode substrate compared to the CNT network, which leads to much smaller catalytic current than our hybrid catalysts.[35]

The high density of active sites on the MPc/CNT electrodes leads to large kinetic current (i.e., the kinetically limited reaction rate) which can be measured in a reactor equipped with a gas-diffusion electrode (GDE) enabling much more enhanced mass transport of CO_2 than that in a typical H cell.[17,47] In other words, the reaction rate (i.e., current) measured for these catalysts in the H cell does not fully reflect their intrinsic catalytic activity because the reaction is controlled by diffusion rather than kinetics in the high current density region. This situation demands redesign of the reactor to enhance mass transport so that the properties of the catalysts can be evaluated. It also

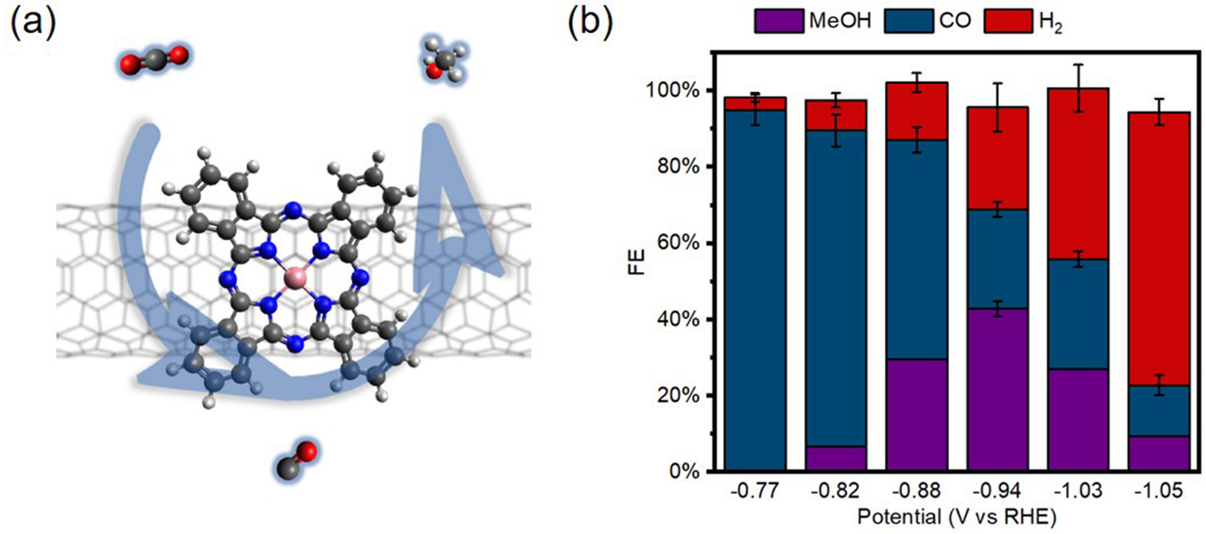


Figure 2. (a) CO_2-to-MeOH conversion catalyzed by CoPc/CNT via CO as an intermediate. (b) Product selectivity of CO_2 reduction catalyzed by CoPc/CNT at various cathode potentials in 0.1 M $KHCO_3$. Reproduced with permission from ref 2. Copyright 2019 Springer Nature.

Table 1. Comparison between Molecularly Dispersed CoPc (Entry 1) and CoPc Solids (Entries 2 and 3) as Electrocatalysts for CO_2 Reduction Reactions

entry	1	2	3
catalyst (year published)	CoPc/CNT hybrid (2019)[2]	CoPc + CNT composite (2019)[53]	CoPc (1984)[24]
purity of CNT (%)	98 (further purified in laboratory before use)	95 (used as received)	CoPc drop-cast onto glassy carbon electrodes
solvent	DMF (can dissolve CoPc)	ethylene glycol (cannot dissolve CoPc)	
CoPc/CNT assembly	30 min of sonication and 20 h of stirring	2 min of stirring after mixing	
material state	near-molecular-level dispersion of CoPc on CNT	physical mixture of CoPc aggregates and CNT	CoPc islands of different thicknesses
methanol selectivity (FE_{MeOH}; %)	44	0.3	<5
methanol formation rate (current; mA/cm^2)	10.2	0.03	<0.05

indicates the potential of these catalysts in delivering high reaction rates required for practical electrolyzers. For example, an electrolyzer with a NiPc/CNT-loaded GDE cathode can achieve j_{CO} over 130 mA cm^{-2} with CO Faradaic efficiency (FE_{CO}) of over 90%. On the contrary, the GDE loaded with bare NiPc only affords a j_{CO} smaller than 10 mA cm^{-2} (Figure 1c).[4]

The results discussed above showcase the merits of our catalyst preparation strategy in both fundamental studies and application-oriented devices. On one hand, the uniform distribution of the molecular catalysts and their hybridization with the nanocarbon support facilitates more rigorous studies of the intrinsic catalytic reactivity of the molecules because influences from variables such as morphology, size, and conductivity of molecular solids are avoided. On the other hand, the gain in catalytic performance from a higher loading of electrochemically active catalyst molecules is essential for potential real-world applications where the catalytic rate is no longer capped by the diffusion limit of dissolved CO_2.

Enabling CO_2-to-Methanol Conversion

Electroreduction of CO_2 beyond two-electron processes is desirable to access more useful products but has been difficult to achieve for molecular catalysts. Despite a number of density-functional-theory (DFT) calculations done on molecular structures bearing M−N_4 structural motifs that suggest some M−N_4 may have suitable CO binding energy for further reduction of bound CO,[48−50] the few catalysts reported active for further reduced products such as CH_4 only display very small selectivity and current.[51,52] We conjectured that dissolved (i.e., homogeneous) catalysts or poorly dispersed heterogeneous molecular catalysts are not suitable configurations for exposing this activity because the electron transfer from the electrode to the active site and further to the reactant/intermediate may not be fast or continuous enough to keep up with the multielectron transfer necessary for the deep reduction of CO_2. This issue could be solved with our MPc/CNT hybrid catalysts.

Remarkably, our CO-producing CoPc/CNT catalyst can effectively mediate further reduction of CO to methanol if more negative electrode potentials are applied, resulting in six-electron reduction catalysis of CO_2 (Figure 2a). At −0.94 V vs RHE in a CO_2-saturated 0.1 M $KHCO_3$ solution, methanol could be produced with a j_{MeOH} of more than 10 mA cm^{-2}, corresponding to a FE_{MeOH} of over 40% (Figure 2b).[2] In light of an early study where very small j_{MeOH} and FE_{MeOH} were reported for CoPc supported on glassy carbon electrodes (Table 1, entry 3),[24] the ability to reduce CO to methanol is likely an intrinsic property of CoPc molecules. Yet, significant selectivity and activity toward methanol formation is only achieved when CoPc molecules are well-dispersed on CNTs. Specifically, when the electrode is loaded with a physical mixture of CoPc and CNTs, both j_{MeOH} and FE_{MeOH} are only around 10% of the values for the CoPc/CNT hybrid catalyst, despite the fact that the physical mixture has more than 10 times the amount of CoPc in the hybrid.[2] Notably, even lower performance (j_{MeOH} of 0.03 mA

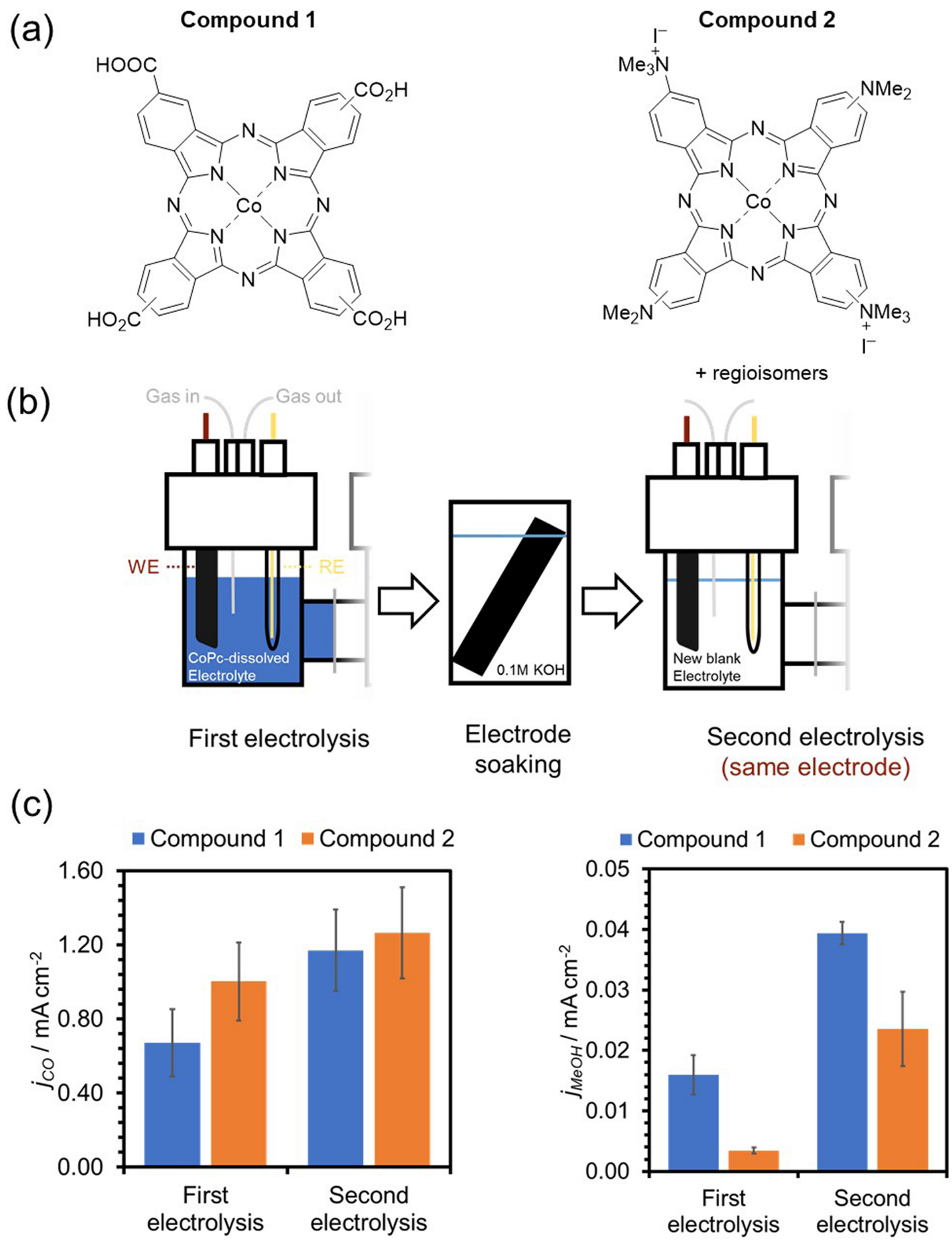


Figure 3. (a) Structures of soluble CoPc species. The floating substituent groups represent the stereoisomerism in the synthesis. (b) Control experiments to verify the nature of the observed catalysis by soluble CoPc molecules. (c) Catalytic performance during the first and second electrolyses for CO_2 and CO reduction. Adapted with permission from ref 3. Copyright 2020 Wiley.

cm^{-2} with FE_{MeOH} of 0.3%) has been reported by others for a physical mixture of CoPc and CNT,[53] which is comparable to CoPc directly drop-cast on electrodes reported more than three decades ago.[24] In this case, lower purity CNTs were used without further purification and casually mixed with CoPc solid dispersed in a poor solvent (ethylene glycol) for a very short time without sonication or extensive stirring (Table 1, entry 2).[53] On one hand, this study confirms the intrinsic catalytic reactivity for CO_2 reduction to methanol that was reported earlier.[24] On the other hand, the dramatic differences in preparation, structure, and catalytic performance between this CoPc + CNT composite (physical mixture in nature) and our CoPc/CNT hybrid (Table 1, entry 1) illustrates the critical aspects of our heterogenization strategy for molecular catalysts.[53]

While we have established that proper heterogenization of CoPc on CNTs is a critical factor in rendering high activity and selectivity for CO_2 reduction to methanol, the exact mechanism through which CNT boosts not only j_{MeOH} but also FE_{MeOH} warrants further investigation. On the basis of our current understanding, two possible mechanisms can be proposed: (i) the high surface area and porosity of the CNT network ensures a high local CO concentration necessary for the further reduction of CO to outcompete the CO_2-to-CO conversion; and (ii) the interaction between CNT and CoPc affects the binding of CO to the CoPc site, which in turn facilitates CO reduction to methanol. Future experiments are needed to study the form and magnitude of the interaction and its influences on catalysis, including, but not limited to, (1) studying the electron transfer rate from CNT to CoPc molecules, (2) detailed spectroscopic studies of CoPc molecules in dispersed vs aggregated states, (3) studying the reaction kinetics under different CO_2 and CO partial pressures, and (4) in situ vibrational spectroscopy probing the CO stretching frequency.

III. HETEROGENEOUS OR HOMOGENEOUS ELECTROCATALYSIS?

The observation that heterogenization of CoPc molecular catalysts unlocks their catalytic reactivity for electrochemical CO_2 reduction to methanol inspired us to consider whether CoPc molecules dissolved in the solution phase could catalyze the same reaction as homogeneous electrocatalysts. Considering that unsubstituted CoPc is not soluble in aqueous media, we synthesized two CoPc derivatives containing carboxylic acid or quaternary alkyl ammonium groups that can render these molecules as soluble in aqueous solutions (Figure 3a).[3] When evaluated in the homogeneous electrocatalysis setting, they are able to catalyze both CO_2 reduction to CO and CO reduction to methanol.[3] At the first glance, this appears to be a homogeneous catalysis mediated by the dissolved CoPc molecules since no catalyst decomposition is observed. However, a careful rinse test suggests otherwise. We thoroughly rinsed and soaked the used electrode from the "homogeneous" electrolysis to remove loosely bound molecules and then carried out a second electrolysis with the rinsed electrode in a blank electrolyte solution without any dissolved CoPc molecules (Figure 3b).[54] Interestingly, for both types of CoPc molecules, the second electrolysis shows even higher j_{MeOH} or j_{CO} than the first one (Figure 3c).

Qualitatively, these results, along with the cyclic voltammograms of the electrodes prior to the second electrolyses, suggest that the observed catalysis in the homogeneous reduction of CO_2 and CO mediated by dissolved CoPc molecules are predominantly catalyzed by CoPc molecules adsorbed on electrode surfaces and therefore heterogeneous in nature. In a broader context, the observation that not only catalytic activity but also catalytic selectivity of the same molecular catalyst differ in the homogeneous vs heterogeneous state is intriguing. Future studies are needed to systematically investigate the contrast between homogeneous and heterogeneous electrocatalysis in aspects such as configuration of adsorbed molecules, rate of electron transfer, mass transport of reactant, and structure of the electric double layer.

Aside from our initial intent to verify that heterogeneous electrocatalysis is much more effective for the multiple-electron reduction of CO_2 or CO to methanol, it is somewhat surprising that the CO_2-to-CO conversion catalyzed by soluble CoPc molecules in aqueous media is also a heterogeneous process.[3] While this observation for our system containing soluble CoPc complexes, aqueous electrolyte, and carbon paper electrodes is perhaps a special case, it raises the possibility that seemingly homogeneous electrocatalysis could be heterogeneous in nature. In the field of electrochemical CO_2 reduction catalyzed by molecular complexes, rinse test and cyclic voltammetry analysis are most used to distinguish homogeneous from heterogeneous processes,[54] although they are not performed in every case. Our results re-emphasize the importance of verifying the nature of catalysis in studies of homogeneously dissolved molecular electrocatalysts, especially for new catalytic systems or in cases when new reactivities are observed. In scenarios where adsorbed molecules are the active sites, in situ techniques would be useful to capture the state of these molecules under reaction-relevant conditions. Such studies could guide rational design and construction of molecularly functionalized catalytic electrodes.

IV. SUBSTITUENT EFFECTS

One major merit of molecular catalysts is their well-defined molecular structures, which makes it possible to improve catalysis via rational tuning of the molecular structure guided by reaction mechanisms. Indeed, the field of homogeneous electrocatalysis has seen formidable progress in optimizing molecular catalyst structures to achieve higher reaction rates at lower overpotentials.[12] Examples include research on iron porphyrin complexes for both two-electron reduction of CO_2 to CO[13] and four-electron reduction of O_2 to H_2O.[55] Although the less well defined electrode/catalyst/reaction layer structure in heterogeneous electrocatalysis hampers the derivation of a general analytical model with a level of detail comparable to that in the homogeneous case, the influences of molecular structure modification on catalytic reactivity in the heterogeneous case can still be observed and substantiated, provided that the catalyst molecules are properly dispersed on the electrode to render their intrinsic catalytic properties, as discussed in Section II. On the other hand, in heterogeneous electrocatalysis, the degree of utilization of catalyst molecules is much higher compared to the homogeneous catalysis case where a reservoir of molecules dissolved in the bulk solution can to some degree replenish degraded catalyst molecules, and therefore catalytic stability is a more relevant issue. The enhancement of catalytic activity, selectivity, and durability via ligand modification based on mechanistic understanding of reaction and deactivation has been successfully demonstrated in our studies of MPc/CNT catalysts for CO_2 electroreduction, where various substituents can be introduced to the Pc ligand by using substituent-bearing precursors in the synthesis of MPc.[1−4]

Electron-Withdrawing Groups

Introduction of electron-withdrawing groups to the Pc macrocycle can positively shift the reduction potential of the catalyst molecule and thus make the corresponding reduced state appear at lower overpotential. If the reduced state is the active species that directly catalyzes CO_2 reduction, the catalytic reaction rate can be increased by the appended electron-withdrawing groups at these potentials. In addition, electron-withdrawing substituents will influence the binding strength of reaction intermediates to the active site, which alters the energetics along the reaction pathway and may consequently affect the catalytic activity. In homogeneous electrocatalysis, the catalysis proceeds via (i) electrochemical reduction of catalyst molecules, (ii) diffusion of the catalyst molecules from the electrode surface to the reaction-diffusion layer, and (iii) the subsequent chemical reaction step.[11] As a result, the reaction rate at moderate or large overpotentials is often not benefited from a more positive reduction potential of the catalyst molecule.[56,57] With heterogenized molecular catalysts, however, the improvement in catalytic reaction rate from substituent effects could still be relevant at much higher current densities, especially for GDEs where mass transport of CO_2 is greatly enhanced.

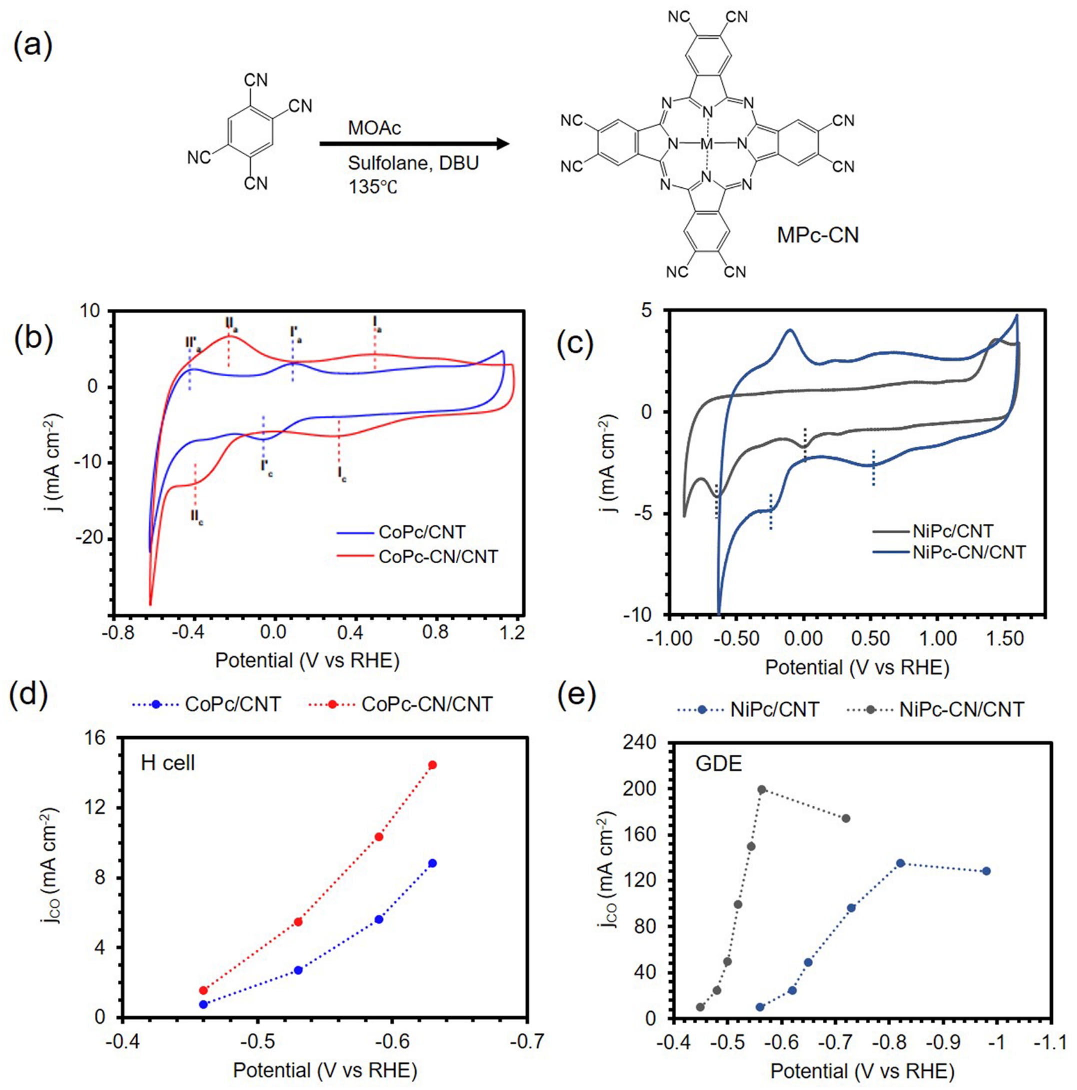


Figure 4. (a) Appending cyano substituents as electron-withdrawing groups to MPc molecules (DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene). (b) Cyclic voltammograms of CoPc/CNT and CoPc-CN/CNT in CO_2-saturated 0.1 M $KHCO_3$ (scan rate, 400 mV/s). (c) Cyclic voltammograms of NiPc/CNT and NiPc-CN/CNT in Ar-saturated 0.1 M phosphate buffer (scan rate, 400 mV/s). (d) Comparison of catalytic performance between CoPc/CNT and CoPc-CN/CNT in an H-cell reactor in a CO_2-saturated 0.1 M $KHCO_3$ solution at various cathode potentials. (e) Comparison of CO partial current density by NiPc/CNT and NiPc-CN/CNT in GDE configuration at various cathode potentials in 1.0 M $KHCO_3$. Panels b and d adapted with permission from ref 1. Copyright 2017 Springer Nature. Panels c and e adapted with permission from ref 4. Copyright 2020 Springer Nature.

We have successfully demonstrated the use of electron-withdrawing groups to enhance the CO_2 reduction catalytic performance of both CoPc and NiPc molecules heterogenized on CNTs.[1,4] Appending cyano (-CN) groups to all eight β positions of the Pc ring (Figure 4a) results in a significant positive shift of the reduction potential for both CoPc/CNT and NiPc/CNT (Figure 4b). The resulted CoPc-CN/CNT and NiPc-CN/CNT display significantly enhanced catalytic activities compared to their unsubstituted counterparts. The CoPc-CN/CNT catalyst delivers 50−100% higher activity per site for CO_2 reduction to CO in an H-cell reactor near −0.5 V vs RHE (Figure 4c).[1] An even more substantial effect is manifested in the NiPc case, where the CN substituents not only help reduce the onset potential by more than 100 mV but also boost the CO production rate (j_{CO}) by as high as a factor of 20 at the cathode potential of −0.56 V vs RHE in the GDE setting (Figure 4d).[4]

Electron-Donating Groups

Electron-donating substituents can also be utilized to improve CO_2 electroreduction catalyzed by heterogenized molecular complexes, despite the tendency to cause a more negative potential for reducing the catalyst molecule itself. Like electron-withdrawing groups, electron-donating substituents can also modify the adsorption energy of reaction intermediates on the active site and influence catalytic activity and selectivity. Furthermore, they may help solve the instability issues of heterogenized molecular catalysts in cases such as catalyst deactivation caused by irreversible reduction of the ligand[58] and catalyst poisoning by the product (e.g., CO).[59,60]

In the previous example of CoPc/CNT catalyzing CO_2 reduction to MeOH, the activity was found to drop to near zero after 4 h of continuous electrolysis. Although the deactivation mechanism was not fully revealed, we[2] and others[53] noted some correlation between the deactivation and hydro-

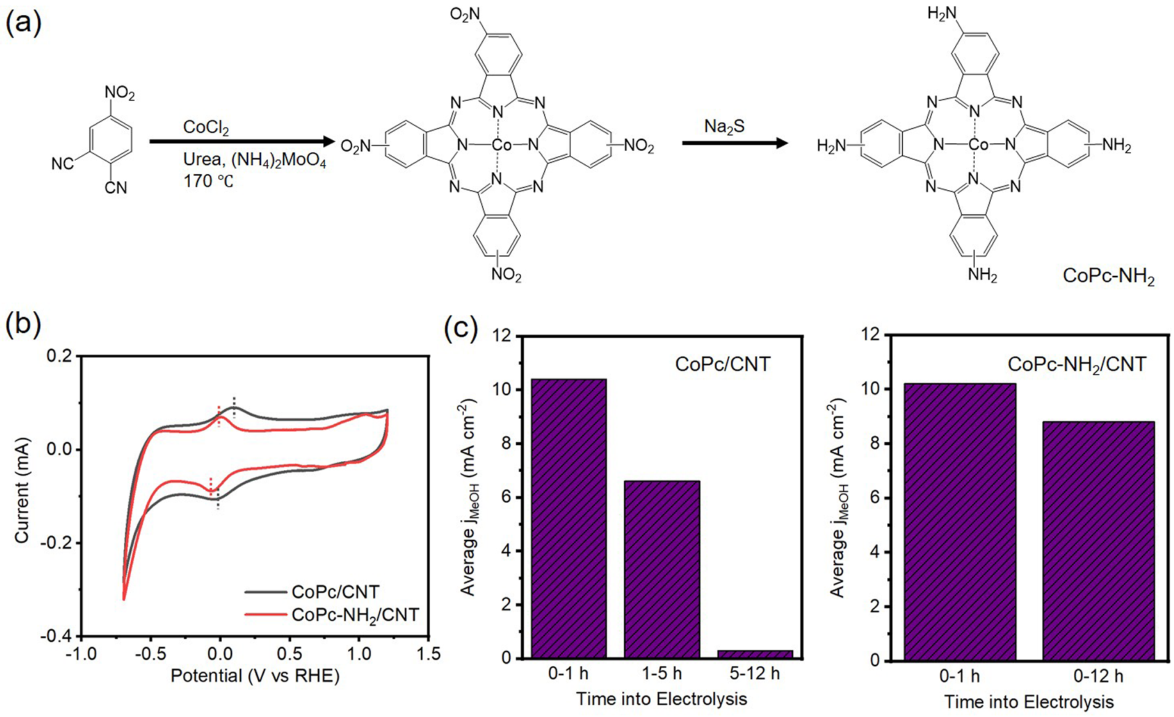


Figure 5. (a) Appending amino substituents as electron-donating groups to CoPc molecules. The floating substituent groups represent the stereoisomerism in the synthesis. (b) Cyclic voltammograms of CoPc/CNT and CoPc-NH_2/CNT in CO_2-saturated 0.1 M $KHCO_3$ (scan rate, 400 mV/s). (c) Comparison of long-term CO_2 electrolyses catalyzed by CoPc/CNT and CoPc-NH_2/CNT. Reproduced with permission from ref 2. Copyright 2019 Springer Nature.

genation of the Pc ring of CoPc under reductive conditions as documented in some earlier reports.[61] This detrimental reduction likely alters the electronic structure around the cobalt center and thus makes the catalyst inactive. On the basis of this hypothesis, we sought to make CoPc more resistant to the detrimental reduction on the ligand by appending electron-donating groups to the Pc ring. β-substituted tetraaminocobalt phthalocyanine (CoPc-NH_2, Figure 5a) was prepared and hybridized with CNTs. Expectedly, a negative shift in the redox potential is visible on the cyclic voltammogram as compared to the original CoPc/CNT (Figure 5b). Compared to the poor stability of CoPc/CNT, the CoPc-NH_2/CNT catalyst can sustain stable CO_2-to-methanol conversion for at least 12 h (Figure 5c).

More recently, we have applied a similar strategy to a different MPc system catalyzing a different CO_2 reduction reaction. We appended four methoxy (-OMe) groups on the β positions of the NiPc molecule to stabilize the catalytic performance (Figure 6a).[4] Despite the high initial activity for CO_2 reduction to CO, both NiPc/CNT and NiPc-CN/CNT suffer from significant performance decay of around 20% in merely 45 min at their respective optimal potentials for CO production (Figure 6b). The NiPc-OMe/CNT catalyst manifests much greater stability on both regular electrodes and GDEs. When operated on a GDE, the NiPc-OMe/CNT catalyst can sustain j_{CO} of 150 mA cm^{-2} with almost 100% FE_{CO} for more than 40 h (Figure 6d). DFT calculations ascribe the enhanced stability to the facilitated CO desorption as well as the largely unperturbed Ni−N bond order in the presence of an axially bound CO on NiPc-OMe as compared to NiPc and NiPc-CN (Figure 6c), which is in line with the *in situ* X-ray absorption spectroscopy (XAS) results that suggest NiPc-OMe maintains its molecular structure while NiPc-CN and NiPc-CN lose their Ni−N coordination during electrolysis.

While our studies have unambiguously demonstrated that substituent tailoring is an effective strategy to improve the catalytic performance of heterogenized molecules for electrochemical CO_2 reduction reactions, it is important to note that a substituent can sometimes have mixed influences on the catalysis. For example, electron-withdrawing groups can make the active site more electron-positive, which may, on one side, promote formation of the active reduced state at lower overpotentials, but on the other side, lower the reactivity between the active site and CO_2 because the latter is a Lewis acid. Another example is from our methanol-producing catalyst. While amino substitution greatly improves the catalytic stability of CoPc, it lowers the selectivity for methanol from ∼40% to ∼30%.[2] To understand these influences and further make use of them for improved catalysis, better understanding of the catalytic reaction mechanism is desired.

V. SUMMARY

In this Account, we have summarized our efforts in investigating various MPc molecules as heterogenized molecular catalysts or precatalysts for electrochemical CO_2 reduction reactions. We have discussed and emphasized how catalyst molecule heterogenization and ligand structure modification contribute to the various forms of catalytic reactivity observed, some of which are unprecedented for molecular systems. We have successfully demonstrated that effective heterogenization of molecular electrocatalysts, e.g., hybridization with CNTs, provides additional handles that are not available to their homogeneous counterparts to tune catalytic reactivity. These conclusions and approaches discussed here can be extended to other electrocatalytic reactions and materials. With the research

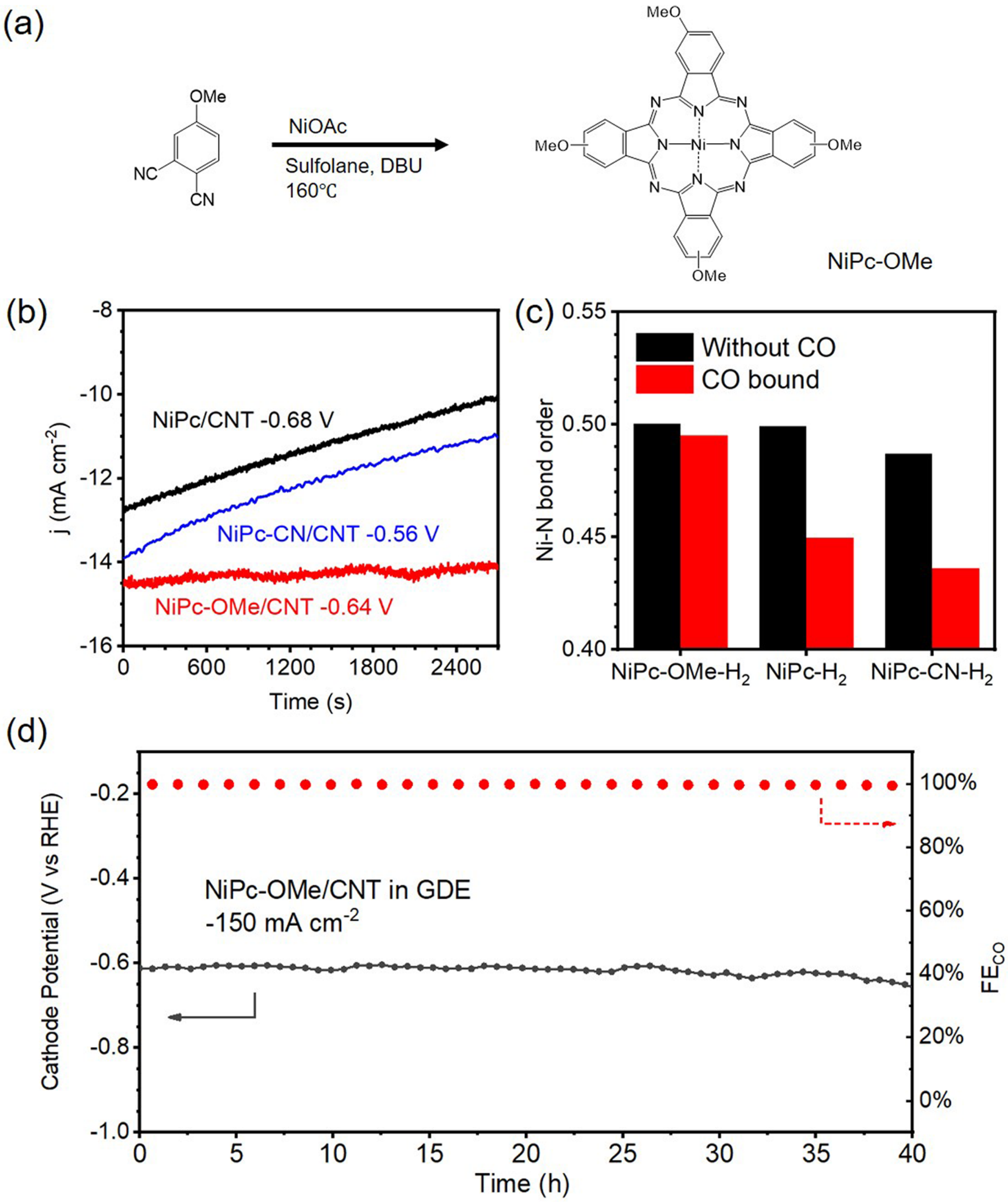


Figure 6. (a) Appending methoxy substituents as electron-donating groups to NiPc molecules. The floating substituent groups represent the stereoisomerism in the synthesis. (b) Comparison of catalytic durability between NiPc/CNT, NiPc-CN/CNT, and NiPc-OMe/CNT. (c) DFT-calculated bond order between Ni and N in the three NiPc complexes with or without CO. (d) Long-term CO_2 electrolysis by NiPc-OMe/CNT in GDE configuration at −150 mA cm^{-2} total current density in 1.0 M $KHCO_3$. Adapted with permission from ref 4. Copyright 2020 Springer Nature.

directions we have proposed in this Account, we believe future endeavors in this field will undoubtedly lead to even better heterogeneous molecular electrocatalysts and more energy-efficient systems based on such catalysts.

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■ REFERENCES

(1) Zhang, X.; Wu, Z.; Zhang, X.; Li, L.; Li, Y.; Xu, H.; Li, X.; Yu, X.; Zhang, Z.; Liang, Y.; Wang, H. Highly selective and active CO_2 reduction electrocatalysts based on cobalt phthalocyanine/carbon nanotube hybrid structures. *Nat. Commun.* **2017**, *8*, 14675.

(2) Wu, Y.; Jiang, Z.; Lu, X.; Liang, Y.; Wang, H. Domino electroreduction of CO_2 to methanol on a molecular catalyst. *Nature* **2019**, *575*, 639−642.

(3) Wu, Y.; Hu, G.; Rooney, C. L.; Brudvig, G. W.; Wang, H. Heterogeneous Nature of Electrocatalytic CO/CO_2 Reduction by Cobalt Phthalocyanines. *ChemSusChem* **2020**, *13*, 6296−6299.

(4) Zhang, X.; Wang, Y.; Gu, M.; Wang, M.; Zhang, Z.; Pan, W.; Jiang, Z.; Zheng, H.; Lucero, M.; Wang, H.; Sterbinsky, G. E.; Ma, Q.; Wang, Y.-G.; Feng, Z.; Li, J.; Dai, H.; Liang, Y. Molecular engineering of dispersed nickel phthalocyanines on carbon nanotubes for selective CO_2 reduction. *Nat. Energy* **2020**, *5*, 684−692.

(5) Chen, C.; Khosrowabadi Kotyk, J. F.; Sheehan, S. W. Progress toward Commercial Application of Electrochemical Carbon Dioxide Reduction. *Chem.* **2018**, *4*, 2571−2586.

(6) Artz, J.; Müller, T. E.; Thenert, K.; Kleinekorte, J.; Meys, R.; Sternberg, A.; Bardow, A.; Leitner, W. Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment. *Chem. Rev.* **2018**, *118*, 434−504.

(7) Zhang, W.; Hu, Y.; Ma, L.; Zhu, G.; Wang, Y.; Xue, X.; Chen, R.; Yang, S.; Jin, Z. Progress and Perspective of Electrocatalytic CO_2 Reduction for Renewable Carbonaceous Fuels and Chemicals. *Adv. Sci.* **2018**, *5*, 1700275.

(8) De Luna, P.; Hahn, C.; Higgins, D.; Jaffer, S. A.; Jaramillo, T. F.; Sargent, E. H. What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* **2019**, *364*, eaav3506.

(9) Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.; Horch, S.; Seger, B.; Stephens, I. E. L.; Chan, K.; Hahn, C.; Nørskov, J. K.; Jaramillo, T. F.; Chorkendorff, I. Progress and Perspectives of Electrochemical CO_2 Reduction on Copper in Aqueous Electrolyte. *Chem. Rev.* **2019**, *119*, 7610−7672.

(10) Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. *Chem. Soc. Rev.* **2014**, *43*, 631−675.

(11) Savéant, J.-M. Molecular catalysis of electrochemical reactions. Mechanistic aspects. *Chem. Rev.* **2008**, *108*, 2348−2378.

(12) Francke, R.; Schille, B.; Roemelt, M. Homogeneously Catalyzed Electroreduction of Carbon Dioxide-Methods, Mechanisms, and Catalysts. *Chem. Rev.* **2018**, *118*, 4631−4701.

(13) Costentin, C.; Robert, M.; Savéant, J.-M. Current Issues in Molecular Catalysis Illustrated by Iron Porphyrins as Catalysts of the CO_2-to-CO Electrochemical Conversion. *Acc. Chem. Res.* **2015**, *48*, 2996−3006.

(14) Sathrum, A. J.; Kubiak, C. P. Kinetics and Limiting Current Densities of Homogeneous and Heterogeneous Electrocatalysts. *J. Phys. Chem. Lett.* **2011**, *2*, 2372−2379.

(15) Kang, P.; Zhang, S.; Meyer, T. J.; Brookhart, M. Rapid Selective Electrocatalytic Reduction of Carbon Dioxide to Formate by an Iridium Pincer Catalyst Immobilized on Carbon Nanotube Electrodes. *Angew. Chem., Int. Ed.* **2014**, *53*, 8709−8713.

(16) Lu, X.; Wu, Y. S.; Yuan, X. L.; Huang, L.; Wu, Z. S.; Xuan, J.; Wang, Y. F.; Wang, H. L. High-Performance Electrochemical CO_2 Reduction Cells Based on Non-noble Metal Catalysts. *ACS Energy Lett.* **2018**, *3*, 2527−2532.

(17) Burdyny, T.; Smith, W. A. CO_2 reduction on gas-diffusion electrodes and why catalytic performance must be assessed at commercially-relevant conditions. *Energy Environ. Sci.* **2019**, *12*, 1442−1453.

(18) Corbin, N.; Zeng, J.; Williams, K.; Manthiram, K. Heterogeneous molecular catalysts for electrocatalytic CO_2 reduction. *Nano Res.* **2019**, *12*, 2093−2125.

(19) Sun, L.; Reddu, V.; Fisher, A. C.; Wang, X. Electrocatalytic reduction of carbon dioxide: opportunities with heterogeneous molecular catalysts. *Energy Environ. Sci.* **2020**, *13*, 374−403.

(20) Abdinejad, M.; Hossain, M. N.; Kraatz, H.-B. Homogeneous and heterogeneous molecular catalysts for electrochemical reduction of carbon dioxide. *RSC Adv.* **2020**, *10*, 38013−38023.

(21) Ghani, F.; Kristen, J.; Riegler, H. Solubility Properties of Unsubstituted Metal Phthalocyanines in Different Types of Solvents. *J. Chem. Eng. Data* **2012**, *57*, 439−449.

(22) Bottari, G.; Suanzes, J. A.; Trukhina, O.; Torres, T. Phthalocyanine−Carbon Nanostructure Materials Assembled through Supramolecular Interactions. *J. Phys. Chem. Lett.* **2011**, *2*, 905−913.

(23) Nemykin, V. N.; Lukyanets, E. A. Synthesis of substituted phthalocyanines. *ARKIVOC* **2010**, *2010*, 136−208.

(24) Kapusta, S.; Hackerman, N. Carbon dioxide reduction at a metal phthalocyanine catalyzed carbon electrode. *J. Electrochem. Soc.* **1984**, *131*, 1511−1514.

(25) Mahmood, M.; Masheder, D.; Harty, C. Use of gas-diffusion electrodes for high-rate electrochemical reduction of carbon dioxide. II. Reduction at metal phthalocyanine-impregnated electrodes. *J. Appl. Electrochem.* **1987**, *17*, 1223−1227.

(26) Furuya, N.; Matsui, K. Electroreduction of carbon dioxide on gas-diffusion electrodes modified by metal phthalocyanines. *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *271*, 181−191.

(27) Abe, T.; Taguchi, F.; Yoshida, T.; Tokita, S.; Schnurpfeil, G.; Wöhrle, D.; Kaneko, M. Electrocatalytic CO_2 reduction by cobalt octabutoxyphthalocyanine coated on graphite electrode. *J. Mol. Catal. A: Chem.* **1996**, *112*, 55−61.

(28) Lu, X.; Jiang, Z.; Yuan, X.; Wu, Y.; Malpass-Evans, R.; Zhong, Y.; Liang, Y.; McKeown, N. B.; Wang, H. A bio-inspired O_2-tolerant catalytic CO_2 reduction electrode. *Sci. Bull.* **2019**, *64*, 1890.

(29) Jiang, Z.; Wang, Y.; Zhang, X.; Zheng, H.; Wang, X.; Liang, Y. Revealing the hidden performance of metal phthalocyanines for CO_2 reduction electrocatalysis by hybridization with carbon nanotubes. *Nano Res.* **2019**, *12*, 2330−2334.

(30) Li, P.; Lu, X.; Wu, Z.; Wu, Y.; Malpass-Evans, R.; McKeown, N. B.; Sun, X.; Wang, H. Acid−Base Interaction Enhancing Oxygen Tolerance in Electrocatalytic Carbon Dioxide Reduction. *Angew. Chem., Int. Ed.* **2020**, *59*, 10918−10923.

(31) Lu, X.; Zhu, C.; Wu, Z.; Xuan, J.; Francisco, J. S.; Wang, H. In Situ Observation of the pH Gradient near the Gas Diffusion Electrode of CO_2 Reduction in Alkaline Electrolyte. *J. Am. Chem. Soc.* **2020**, *142*, 15438−15444.

(32) Costentin, C.; Savéant, J.-M. Towards an intelligent design of molecular electrocatalysts. *Nat. Rev. Chem.* **2017**, *1*, 0087.

(33) Hu, X.-M.; Pedersen, S. U.; Daasbjerg, K. Supported molecular catalysts for the heterogeneous CO_2 electroreduction. *Curr. Opin. Electrochem.* **2019**, *15*, 148−154.

(34) Schwoerer, M.; Wolf, H. C. *Organic molecular solids*; John Wiley & Sons, 2007.

(35) Zhu, M.; Ye, R.; Jin, K.; Lazouski, N.; Manthiram, K. Elucidating the Reactivity and Mechanism of CO_2 Electroreduction at Highly Dispersed Cobalt Phthalocyanine. *ACS Energy Lett.* **2018**, *3*, 1381−1386.

(36) Wang, H.; Dai, H. Strongly coupled inorganic−nano-carbon hybrid materials for energy storage. *Chem. Soc. Rev.* **2013**, *42*, 3088−3113.

(37) Liang, Y.; Li, Y.; Wang, H.; Dai, H. Strongly Coupled Inorganic/Nanocarbon Hybrid Materials for Advanced Electrocatalysis. *J. Am. Chem. Soc.* **2013**, *135*, 2013−2036.

(38) Li, Q. W.; Li, Y.; Zhang, X. F.; Chikkannanavar, S. B.; Zhao, Y. H.; Dangelewicz, A. M.; Zheng, L. X.; Doorn, S. K.; Jia, Q. X.; Peterson, D. E.; Arendt, P. N.; Zhu, Y. T. Structure-Dependent Electrical Properties of Carbon Nanotube Fibers. *Adv. Mater.* **2007**, *19*, 3358−3363.

(39) Mann, N.; Vasudevan, P.; Santosh; Sandhya; Bhushan, B.; Mathur, S. C.; Chauhan, J. P. S. *Proceedings of the 3rd International Conference on Conduction and Breakdown in Solid Dielectrics*, July 3−6, 1989.

(40) Peigney, A.; Laurent, C.; Flahaut, E.; Bacsa, R. R.; Rousset, A. Specific surface area of carbon nanotubes and bundles of carbon nanotubes. *Carbon* **2001**, *39*, 507−514.

(41) Li, J.; Cassell, A.; Delzeit, L.; Han, J.; Meyyappan, M. Novel Three-Dimensional Electrodes: Electrochemical Properties of Carbon Nanotube Ensembles. *J. Phys. Chem. B* **2002**, *106*, 9299−9305.

(42) Andrews, R.; Jacques, D.; Qian, D.; Rantell, T. Multiwall Carbon Nanotubes: Synthesis and Application. *Acc. Chem. Res.* **2002**, *35*, 1008−1017.

(43) Hou, P.-X.; Liu, C.; Cheng, H.-M. Purification of carbon nanotubes. *Carbon* **2008**, *46*, 2003−2025.

(44) Wang, H.; Liang, Y.; Gong, M.; Li, Y.; Chang, W.; Mefford, T.; Zhou, J.; Wang, J.; Regier, T.; Wei, F.; Dai, H. An ultrafast nickel−iron battery from strongly coupled inorganic nanoparticle/nanocarbon hybrid materials. *Nat. Commun.* **2012**, *3*, 917.

(45) Meshitsuka, S.; Ichikawa, M.; Tamaru, K. Electrocatalysis by metal phthalocyanines in the reduction of carbon dioxide. *J. Chem. Soc., Chem. Commun.* **1974**, 158−159.

(46) Lieber, C. M.; Lewis, N. S. Catalytic reduction of carbon dioxide at carbon electrodes modified with cobalt phthalocyanine. *J. Am. Chem. Soc.* **1984**, *106*, 5033−5034.

(47) Hansen, K. U.; Jiao, F. Hydrophobicity of CO_2 gas diffusion electrodes. *Joule* **2021**, *5*, 754−757.

(48) Tripkovic, V.; Vanin, M.; Karamad, M.; Björketun, M. E.; Jacobsen, K. W.; Thygesen, K. S.; Rossmeisl, J. Electrochemical CO_2 and CO Reduction on Metal-Functionalized Porphyrin-like Graphene. *J. Phys. Chem. C* **2013**, *117*, 9187−9195.

(49) Ju, W.; Bagger, A.; Hao, G. P.; Varela, A. S.; Sinev, I.; Bon, V.; Roldan Cuenya, B.; Kaskel, S.; Rossmeisl, J.; Strasser, P. Understanding activity and selectivity of metal-nitrogen-doped carbon catalysts for electrochemical reduction of CO_2. *Nat. Commun.* **2017**, *8*, 944.

(50) Zhang, Z.; Xiao, J.; Chen, X. J.; Yu, S.; Yu, L.; Si, R.; Wang, Y.; Wang, S.; Meng, X.; Wang, Y.; Tian, Z. Q.; Deng, D. Reaction Mechanisms of Well-Defined Metal-N_4 Sites in Electrocatalytic CO_2 Reduction. *Angew. Chem., Int. Ed.* **2018**, *57*, 16339−16342.

(51) Varela, A. S.; Ranjbar Sahraie, N.; Steinberg, J.; Ju, W.; Oh, H. S.; Strasser, P. Metal-Doped Nitrogenated Carbon as an Efficient Catalyst for Direct CO_2 Electroreduction to CO and Hydrocarbons. *Angew. Chem., Int. Ed.* **2015**, *54*, 10758−10762.

(52) Shen, J.; Kortlever, R.; Kas, R.; Birdja, Y. Y.; Diaz-Morales, O.; Kwon, Y.; Ledezma-Yanez, I.; Schouten, K. J. P.; Mul, G.; Koper, M. T. Electrocatalytic reduction of carbon dioxide to carbon monoxide and methane at an immobilized cobalt protoporphyrin. *Nat. Commun.* **2015**, *6*, 8177.

(53) Boutin, E.; Wang, M.; Lin, J. C.; Mesnage, M.; Mendoza, D.; Lassalle-Kaiser, B.; Hahn, C.; Jaramillo, T. F.; Robert, M. Aqueous Electrochemical Reduction of Carbon Dioxide and Carbon Monoxide into Methanol with Cobalt Phthalocyanine. *Angew. Chem., Int. Ed.* **2019**, *58*, 16172−16176.

(54) Lee, K. J.; McCarthy, B. D.; Dempsey, J. L. On decomposition, degradation, and voltammetric deviation: the electrochemist's field guide to identifying precatalyst transformation. *Chem. Soc. Rev.* **2019**, *48*, 2927−2945.

(55) Martin, D. J.; Wise, C. F.; Pegis, M. L.; Mayer, J. M. Developing Scaling Relationships for Molecular Electrocatalysis through Studies of Fe-Porphyrin-Catalyzed O_2 Reduction. *Acc. Chem. Res.* **2020**, *53*, 1056−1065.

(56) Pegis, M. L.; Wise, C. F.; Koronkiewicz, B.; Mayer, J. M. Identifying and Breaking Scaling Relations in Molecular Catalysis of Electrochemical Reactions. *J. Am. Chem. Soc.* **2017**, *139*, 11000−11003.

(57) Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. Turnover Numbers, Turnover Frequencies, and Overpotential in Molecular Catalysis of Electrochemical Reactions. Cyclic Voltammetry and Preparative-Scale Electrolysis. *J. Am. Chem. Soc.* **2012**, *134*, 11235−11242.

(58) Jiang, J.; Materna, K. L.; Hedström, S.; Yang, K. R.; Crabtree, R. H.; Batista, V. S.; Brudvig, G. W. Antimony Complexes for Electrocatalysis: Activity of a Main-Group Element in Proton Reduction. *Angew. Chem., Int. Ed.* **2017**, *56*, 9111−9115.

(59) Froehlich, J. D.; Kubiak, C. P. Homogeneous CO_2 reduction by Ni (cyclam) at a glassy carbon electrode. *Inorg. Chem.* **2012**, *51*, 3932−3934.

(60) Wu, Y.; Rudshteyn, B.; Zhanaidarova, A.; Froehlich, J. D.; Ding, W.; Kubiak, C. P.; Batista, V. S. Electrode-Ligand Interactions Dramatically Enhance CO_2 Conversion to CO by the [Ni(cyclam)]-$(PF_6)_2$ Catalyst. *ACS Catal.* **2017**, *7*, 5282−5288.

(61) Grodkowski, J.; Dhanasekaran, T.; Neta, P.; Hambright, P.; Brunschwig, B. S.; Shinozaki, K.; Fujita, E. Reduction of cobalt and iron phthalocyanines and the role of the reduced species in catalyzed photoreduction of CO_2. *J. Phys. Chem. A* **2000**, *104*, 11332−11339.