Electrocatalytic CO₂ Reduction by Imidazolium-Functionalized Molecular Catalysts

Siyoung Sung, † Davinder Kumar, †‡ Marcio Gil-Sepulcre, § and Michael Nipper* †‡

†Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, Texas 77843, United States
‡School of Chemistry and Biochemistry, Thapar University, Patiala, Punjab 147004, India
§Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193 Barcelona, Catalonia, Spain

Supporting Information

ABSTRACT: We present the first examples of CO₂ electro-reduction catalysts that feature charged imidazolium groups in the secondary coordination sphere. The functionalized Lehn-type catalysts display significant differences in their redox properties and improved catalytic activities as compared to the conventional reference catalyst. Our results suggest that the incorporated imidazolium moieties do not solely function as a charged tag but also alter mechanistic aspects of catalysis.

The development of selective electrocatalysts for the reduction of carbon dioxide (CO₂) to yield C₁ products such as CO (2e⁻), HCHO (4e⁻), CH₃OH (6e⁻), and CH₄ (8e⁻) or higher Cₙ products would allow for a broad utilization of CO₂ as a C₁ feedstock. However, the typically high energy barriers for the direct reduction of CO₂ on electrode or semiconductor surfaces necessitate reduction potentials significantly more negative than the corresponding thermodynamic CO₂ reduction potentials. The development of improved electrocatalysts which can lower overpotential requirements while maintaining appropriate catalytic rates and selectivity is therefore a key challenge toward future solar-driven CO₂ conversion technologies.

Molecular catalysts are an attractive option due to the high degree of tunability of electronic and geometric parameters which allows for systematic reaction studies that can lead to new catalyst design guidelines. For example, electron density at the reactive metal ion is readily tunable via incorporation of electron-withdrawing or -donating groups into the ligand backbone, which results in positively or negatively shifted redox potentials, respectively. However, lowering electron density at the reactive transition metal ion does allow for less negative reduction potentials only at the cost of significantly decreased catalytic activity.

More recently, focus has been given to tuning molecular electro-reduction catalysts via incorporation of functional groups into the secondary coordination sphere of transition metal complexes. Relevant examples include the incorporation of steric bulk and incorporation of functional groups as proton relays and/or facilitators for substrate binding via hydrogen-bonding interactions, as well as intermediate stabilization. Very recently, positively charged ammonium groups have also shown to improve electrocatalytic CO₂ reduction by metal porphyrin complexes.

Our work is inspired by reports of efficient direct CO₂ reduction in ethyl-methyl-imidazolium (EMIM)-based ionic liquids on electrode materials as well as by homogeneous catalysis. We hypothesized that the incorporation of charged, slightly acidic, and redox-active imidazolium groups into the secondary coordination sphere of molecular complexes may provide alternative routes to tune redox potentials as well as allow for synergistic intramolecular interactions between reactive metal sites, imidazolium, and CO₂ substrate molecules. To test our hypothesis we functionalized the CO₂ electro (and photo)-reduction catalyst system based on Re(bpy)(CO)₃Cl which was first discovered by Lehn et al. and has been subject of detailed mechanistic studies. Here, we present the first evaluation of imidazolium-functionalized CO₂ electro-reduction catalysts. We utilized pre-catalyst {Re[bpyMe(ImMe)](CO)₃Cl}PF₆ (1PF₆) (Figure 1) and compared its redox properties and catalytic activity to those of unfunctionalized Re(bpy)(CO)₃Cl (3). To evaluate the possible involvement of the imidazolium C₂–H bond of 1PF₆ during catalysis, we expanded our studies to include {Re[bpyMe(ImMe)](CO)₃Cl}PF₆ (2PF₆) which is devoid of aforementioned C–H bond.

The functionalized complexes 1PF₆ and 2PF₆ were obtained as described in the Supporting Information. The molecular structures of 1 and 2 (Figure 1, Tables S1 and S2) feature octahedral Re(I) ions with Re–N, Re–C₁₈, Re–C₁₉, and Re–Cl distances of 2.206[3] Å (2⁺: 2.224[6] Å), 1.916[5] Å (2⁺: 1.925[9] Å), 1.924(5) Å (2⁺: 1.993(9) Å), and 2.485(1) Å (2⁺: 2.462(2) Å), respectively, which are comparable to those reported for related Re(CO)₃Cl complexes. Importantly, the structure of 1PF₆ features close proximity between imidazolium C₂–H groups and Re-bound chloride ions of a neighboring molecule which likely indicates hydrogen-bonding like or electrostatic interactions between them in the solid state.

Binding between imidazolium moieties and anions in a C₂–H···X⁻ fashion has been broadly utilized for the sensing of anions in solution. We therefore suggest that similar C₂–H···X⁻ interactions have also to be considered in solutions of 1PF₆ and may include intramolecular C₂–H···Cl⁻ as well as C₂–H···Cl⁻ interactions.

Received: July 23, 2017
Published: September 18, 2017
Communication

The cyclic voltammograms (CVs) of 1⁺, 2⁺, and 3 recorded in CH₃CN under Ar (Figure S2) display initial redox couples at −1.65, −1.65, and −1.74 V, respectively (Table S3). The ~100 mV positive shift in $E_{1/2}$ for the initial redox couple for 1⁺ and 2⁺ as compared to 3 is a likely consequence of the positive charge introduced by the imidazolium moiety. Reversibility of the initial redox couples of 1⁺ and 2⁺ becomes more apparent at faster scan rates (Figure 2). It is well established that the first 1e⁻ reduction of 3 yields [Re(I)(bpy¹⁺)(CO)₃Cl]⁻ which features a bipyridine based radical species. Importantly, the cationic ligands employed in 1⁺ and 2⁺ feature not only a redox-active bpy moiety but also a redox-active imidazolium group which could potentially be reduced by one electron to yield a neutral radical species.¹⁵

We thought to investigate the origin of the first 1e⁻ reduction observed for 1⁺ via computational methods using density functional theory (see Supporting Information). Importantly, the highest occupied molecular orbital (HOMO) of the 1e⁻ reduced species 1(1e) (S = 1/2) is exclusively centered on the $\pi^*$ system of the bipyridine moiety (Figure 1c). No contributions from the imidazolium unit to the HOMO are observed. We therefore assign the initial reduction of 1⁺ and 2⁺ to the 1e⁻ reduction of the bipyridine moiety which parallels the initial redox behavior of unfunctionalized 3. The altered reversibility of the initial redox couples for 1⁺ and 2⁺ is therefore likely the result of accelerated Cl⁻ dissociation rates. Simulations of the CV profiles at varying scan rates according to an EC mechanism (Figure S3) suggests a ~5.4 times faster chloride dissociation rate for 1PF₆ than for 2PF₆. We suggest that intramolecular C₂—H···Cl⁻ interactions may allow for faster dissociation of Cl⁻ from the one-electron-reduced species 1(1e) (Figure 2). Electrostatic and C₄,5-H···Cl⁻ interactions may contribute to the faster Cl⁻ dissociation observed for 2PF₆ as compared to 3. It is also important to note that this stands in contrast to reports for 3 in neat EMIM-based ionic liquids for which two 1e⁻ reductions can precede Cl⁻ dissociation.¹⁶ Consequently, we argue that the intramolecular incorporation of imidazolium moieties allows for distinct chemistry as compared to intermolecular imidazolium—catalyst systems. The diffusion coefficients of 1⁺, 2⁺, and 3 are similar as judged by DOSY NMR spectroscopy (Figures S4–S6) and rotating disk electrode voltammetry (Figures S7–S9), which suggests that (i) 1⁺ is not dimeric in solution and (ii) diffusional behavior is not significantly affected by functionalization.

The activities of all complexes toward electrocatalytic reduction of CO₂ were investigated using identical conditions in CO₂ saturated CH₃CN solutions (Figure 3). Functionalized complexes 1⁺ and 2⁺ exhibit comparable reductive current enhancement following the initial 1e⁻ reduction event under CO₂. Most notably, the current enhancement occurs at significantly less negative potentials as compared to reference complex 3. Catalytic half-wave potentials (Table S3) of reductive current enhancements of 1⁺ and 2⁺ are ~170 and 140 mV less negative than that of 3. The ratios of catalytic peak currents ($i_{cat}$) and initial peak currents ($i_{ip}$ peak current of the initial 1e⁻ reduction under Ar at the same scan rate) are also given in Table S3.⁴³,¹⁷ Interestingly, for 1⁺ we find a $i_{cat}/i_{ip}$ ratio of 4.7 which is higher than the one observed for 3 (4.4), even though the corresponding catalytic potential is significantly more positive than that of 3. However, for complex 2⁺, we observe smaller $i_{cat}/i_{ip}$ (3.5) as compared to 3. We also note that the potential differences between the initial 1e⁻ reduction and onset (or half-wave) potential of catalysis is much smaller for 1⁺ ($ΔE = 100$ mV) as compared to 2⁺ (150 mV) and 3 (180 mV) at a given scan rate. The latter observation ($ΔE$) further

![Figure 1. Molecular structures of (a) 1⁺ and (b) 2⁺ and (c) HOMO of calculated neutral species 1(1e) (S = 1/2). Color code: purple = Re, green = Cl, red = oxygen, blue = nitrogen, gray = carbon). Hydrogen atoms (other than imidazolium C—H, shown in black), counteranion(s), and co-crystallized solvent molecules have been omitted for clarity.](image1)

![Figure 2. (a, b) Scan rate dependence of initial reduction of 1⁺ and 2⁺ under Ar (normalized current (1/v⁻¹/₂) shown). (c) Proposed imidazolium-promoted Cl⁻ dissociation in 1⁺ upon 1e⁻ reduction.](image2)

![Figure 3. CVs of 1.0 mM 1⁺ (red), 2⁺ (blue), and 3 (black) recorded at 100 mV s⁻¹ under CO₂ in CH₃CN (0.1 M NBu₄PF₆).](image3)
supports the hypothesis that Cl\(^-\) dissociation after 1e\(^-\) reduction is accelerated for 1\(^+\), while the former \((i_{\text{cat}}/i_p)\) may indicate synergistic effects of the C2–H group in 1\(^+\) for CO\(_2\) reduction catalysis, leading to higher current densities.

Although CO\(_2\) itself can act as an oxide acceptor during catalysis,\(^{1,6}\) the addition of a proton source can facilitate the two-electron and two-proton reduction of CO\(_2\) to CO and we decided to utilize H\(_2\)O as a proton source. CVs of 1\(^+\), 2\(^+\), and 3 were recorded under CO\(_2\) with cumulative addition of H\(_2\)O. Ratios of \(i_{\text{cat}}/i_p\) were plotted versus concentration of H\(_2\)O and are presented in insets of Figure 4. Both imidazolium-functionalized catalysts show similar current responses to the addition of H\(_2\)O. Catalytic currents of 1\(^+\) and 2\(^+\) drastically increase upon addition of a small amounts of H\(_2\)O, which results in significant increase in \(i_{\text{cat}}/i_p\) values from \(-4\) to 9 at a low H\(_2\)O concentration (0.28 M). Interestingly, the catalytic currents decrease up to \(-1\) M H\(_2\)O and increase again upon further addition of H\(_2\)O displaying the highest \(i_{\text{cat}}/i_p\) values (\(-12\) and 10 for 1\(^+\) and 2\(^+\), respectively) at 2–3 M H\(_2\)O. The catalytic currents start to decrease gradually at concentrations higher than 3 M H\(_2\)O. It should also be noted that catalytic half-wave potentials gradually shift to more positive potentials as the H\(_2\)O concentration increases. At high [H\(_2\)O], catalytic onset potentials are close to those where the initial 1e\(^-\) reduction was observed. In general, 1\(^+\) exhibits higher \(i_{\text{cat}}/i_p\) values and faster positive potential shifts than 2\(^+\) as [H\(_2\)O] increases.

The unusual \(i_{\text{cat}}/i_p\) dependence on [H\(_2\)O] observed for 1\(^+\) and 2\(^+\) contrasts the classical behavior observed for 3, which shows a linear increase of \(i_{\text{cat}}/i_p\) with increasing [H\(_2\)O]. These findings suggest that the mechanism for CO\(_2\) reduction by 1\(^+\) and 2\(^+\) is significantly altered as compared to unfunctionalized 3 and also dependent on [H\(_2\)O]. While the origins of these mechanistic changes for 1\(^+\) and 2\(^+\) are subject of ongoing studies, we highlight that similar proton source dependence of \(i_{\text{cat}}/i_p\) has been reported recently for manganese bipyridyl tricarbonyl catalysts containing pendant methoxy groups.\(^{6f}\) Here the presence of secondary coordination sphere R\(_2\)O groups was implicated in R\(_2\)O···(HO)(O)C–Mn interactions which allowed for easier C–OH bond cleavage. It is reasonable to assume that for 1\(^+\) C–H···(O)O(OC–Re and/or C–H···OH···(OH)(OC–Re interactions are also implicated during catalysis. Complex 2\(^+\) on the other hand, could only feature potential interactions involving the C4–H and C5–H groups. However, these would be expected to be weaker than hydrogen bonding via C2–H moieties in 1\(^+\).\(^{18}\) This important difference is a likely cause for the differences in catalytic activity and selectivity between 1\(^+\) and 2\(^+\) as will be discussed in detail.

In an effort to obtain rate estimates for CO\(_2\) reduction we studied the catalytic response at varying scan rates at the optimized [H\(_2\)O] of 2.8 M. The obtained \(i_{\text{cat}}/i_p\) values were used to estimate TOF\(_{\text{max}}\) values according to eq 1.\(^{19}\) We found

\[
\frac{i_{\text{cat}}}{i_p} = \frac{RT}{F} \sqrt{\text{TOF}_{\text{max}}} \times 1/2
\]

that scan rate independence is nearly reached at scan rates of 4 V s\(^{-1}\) (Figure 4d). Although scan rate independence could not completely be achieved, it is clear that complex 1\(^+\) operates at higher rates than 2\(^+\). However, 2\(^+\) shows significantly higher rates than parent complex 3.

Controlled potential electrolysis (CPE) experiments were performed for all catalysts for 1 h in the presence of 2.8 or 9.4 M H\(_2\)O (Supporting Information) and the headspace after CPE was analyzed by gas chromatography (GC). CO was the only detectable reduction product after all CPE experiments. At 2.8 M H\(_2\)O, 1\(^+\) consumes the largest charge with the highest faradaic efficiency generating the most CO among the three catalysts (Figure 5). We note that the charge consumed by 1\(^+\) in 2.8 M H\(_2\)O is nearly twice as much as the charge consumed by 3. 2\(^+\) also consumes \(-1.5\) times more charge than 3 with comparable faradaic efficiency. However, 1\(^+\) as well as 2\(^+\) show a gradual decrease in current over time (Figures S24 and S29). CVs recorded immediately after CPE experiments display the characteristic initial one-electron reductions of the complexes but a substantial decrease in the catalytic current (Figures S23 and S28). Restaration of the solutions with CO\(_2\) did not restore the high initial catalytic currents. As such, CO\(_2\) substrate depletion or deactivation of catalysts\(^{20}\) likely do not contribute to decrease in catalytic currents. These findings suggest that the

Figure 5. Results from CPE experiments at [H\(_2\)O] = 2.8 and 9.4 M for 1.0 mM 1\(^+\), 2\(^+\), and 3. Each column represents charge consumed by the respective catalyst. The shaded areas represent charge used for CO generation.
consumption of protons during electrolysis at low H$_2$O concentrations causes the decreased catalytic activity. CPE experiments were also performed at 9.4 M H$_2$O in which reference complex 3 exhibits a higher $i_{oc}/i_{pa}$ value. Interestingly, 1* shows significantly improved catalytic performance in CPE experiments while 3 does not show any noticeable improvements. In fact, not only does the higher H$_2$O concentration increase the rate for 1* but also results in improved faradic efficiency as well as longevity of the catalyst (Figures S37–S41). CVs recorded after CPE experiments show no obvious reduction in the catalytic current (Figure S38). However, 2*, devoid of the C2–H moiety, exhibits the lowest faradic efficiency (35%) among the three catalysts at 9.4 M H$_2$O although it consumes as much charge as 1*. The observed faradic efficiencies are in good agreement with previous results for Lehn-type catalyst systems in CH$_3$CN (61%,$^{21}$ 46%$^{22}$).

Taken together, our results show that the incorporation of intramolecular imidazolium groups into CO$_2$ electro-reduction catalysts results in beneficial effects for catalysis. The differences in rate and selectivity between 1* and 2* point to the potentially crucial role of the C2–H bond of the imidazolium moiety. To the best of our knowledge, this constitutes the first report of successfully utilizing intramolecular imidazolium groups to improve electrocatalysis. Computational results suggest that the redox-active imidazolium group does not interfere with the initial bipyrindine-based reduction event. Detailed studies of the catalytic mechanism and potential imidazolium substrate interactions are currently underway.

ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b07709.

Experimental and computational details, including Figures S1–S51 and Tables S1–S4 (PDF)

## X-ray crystallographic data for 1PF$_6$ ( CIF )

## X-ray crystallographic data for 2PF$_6$ ( CIF )

# AUTHOR INFORMATION

**Corresponding Author**

* nippe@chem.tamu.edu

**ORCID**

Michael Nippe: 0000-0003-1091-4677

**Notes**

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

M.N. is grateful to the TAMU Chemistry Department for startup funds and financial support by the Welch Foundation (A-1880). We thank Dr. Julien Panetier for fruitful discussions.

# REFERENCES


