



Editorial: Molecular Catalysts for CO₂ Fixation/Reduction

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Editorial on the Research Topic

Molecular Catalysts for CO₂ Fixation/Reduction

Conversion of CO₂ into useful chemicals and fuels becomes more and more important as increasing CO₂ emissions continue to worsen the effects of climate change. Catalytic CO₂ reduction and fixation are important components of artificial photosynthesis (the use of renewable energy to generate useful chemicals and fuels), which is vigorously studied as part of the solution to the environmental and energy problems that arise from its continuously elevating atmospheric concentration. However, the development of chemical processes remains a significant challenge for chemists. Molecular inorganic complexes, which can be utilized as homogeneous catalysts, have several advantages: well-defined structures that are readily characterized, catalytic mechanisms that can be elucidated with high fidelity, and the opportunity to optimize catalytic activities through molecular design. In this Research Topic, we present ten original research articles and three review articles dealing with electrochemical and photochemical catalysis for CO₂ reduction or fixation.

The metal complexes, *fac*-[Mn(bpy)(CO)₃Br] and *fac*-[Re(bpy)(CO)₃Cl] (bpy = 2,2'-bipyridine), are known to be excellent catalysts for electrochemical CO₂ reduction. Rotundo et al. synthesized 14 new Mn(I) and Re(I) complexes with structurally diverse 2,2'-bipyridyl derivatives and examined their catalytic activities by using cyclic voltammetry and controlled potential electrolysis. They reported that the complexes with only electron-withdrawing groups (e.g., -CF₃, -CN) lost their catalytic activities. On the other hand, the complexes with the symmetric -NMe₂ substituted and push-pull systems (containing both -NMe₂ and -CF₃) displayed electrocatalytic current enhancement. McKinnon et al. synthesized the manganese(I) complex *fac*-[Mn(bqn)(CO)₃(CH₃CN)]⁺ with a 2,2'-biquinoline (bqn) ligand, which had unique steric and electronic properties. They examined the catalytic activities for electrochemical CO₂ reduction and further compared them to the efficiencies of the corresponding bpy, 1,10-phenanthroline (phen), and 2,9-dimethyl-1,10-phenanthroline (dmphen) derivatives. In the reaction mechanisms, the one-electron reduced species of the bpy complex dimerized, but the bqn ligand hindered the dimer formation to favorably afford two-electron reduced species. Talukdar et al. synthesized a new NNP-type pincer ligand, 8-(diphenylphosphaneyl)-2-(pyridin-2'-yl)quinolone, and the corresponding Fe, Co, Ni, and Zn complexes. Due to earth abundance, the development of molecular catalysts with first-row transition metals is desirable. They reported that the cobalt(II) complex showed the catalytic efficiency to produce CO in CO₂-saturated DMF containing 5% water; the catalytic efficiencies for CO of the active complexes in descending order were Co²⁺ >> Ni²⁺ > Fe²⁺. The Zn(II) complex did not show catalytic activity. Nichols and Machan reviewed the secondary-sphere effects in the enzymes and the molecular catalysts for electrochemical CO₂ reduction. In the CO₂-related enzymes (e.g., carbon monoxide dehydrogenase, formic acid dehydrogenase), some amino acid residues around the catalytic centers can act as the

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pendent proton donors/shuttles, charged groups, etc. They discussed standard methodologies for estimating the effective catalytic overpotential and the maximal turnover frequency, and reviewed the development of secondary-sphere strategies for the classic molecular electrocatalysts, [Fe(tetraphenylporphyrin)]⁺, [Ni(cyclam)]²⁺, Mn(bpy)(CO)₃X, and Re(bpy)(CO)₃X (X = solvent or halide). Igarashi et al. reported the surface modification of copper cathodes with ethynyl and azide monomers. Metal copper cathodes are known to be effective for electrochemical CO₂ reduction. The introduction of organic structures onto catalytically active metal surfaces has recently received attention because it often enhances activity and selectivity for specific products. They reported that an increase in ethylene production was observed for the organic molecule-modified copper electrodes in electrochemical CO₂ reduction.

Photocatalytic CO₂ reduction can be accomplished with the same molecular catalysts employed in electrochemistry by using appropriate redox photosensitizers and sacrificial electron donors instead of an electrode. The most widely used redox photosensitizer is [Ru(bpy)₃]²⁺, which exhibits strong absorption in the visible light region and has a long lifetime in the triplet metal-to-ligand charge transfer (³MLCT) excited state. Tamaki et al. synthesized a new ruthenium(II) picolinate complex, [Ru(dmb)₂(pic)]⁺ (dmb = 4,4'-dimethyl-2,2'-bipyridine; Hpic = picolinic acid), with a wider wavelength range of visible-light absorption ($\lambda_{\text{abs}} < 670 \text{ nm}$) and a strong reduction ability in the one-electron reduced state ($E_{\text{red}} = -1.86 \text{ V vs. Ag/AgNO}_3$). They demonstrated that photocatalysis using [Ru(dmb)₂(pic)]⁺ as the redox photosensitizer combined with a Re(I) catalyst reduced CO₂ to CO under red-light irradiation ($\lambda_{\text{ex}} > 600 \text{ nm}$). In contrast, [Ru(dmb)₃]²⁺, which could not absorb light at $\lambda > 560 \text{ nm}$, was not capable of working as the redox photosensitizer under the same conditions. The molar extinction coefficient is also an important factor for a redox photosensitizer. A cyclometalated iridium(III) complex having 2-(pyren-1-yl)-4-methylquinoline ligands [Ir(pyr)] has a strong absorption band in the visible region (ϵ at 444 nm = 67,000 M⁻¹ cm⁻¹) but does not act as a photosensitizer for photochemical CO₂ reduction reactions in the presence of triethylamine as an electron donor. Kuramochi and Ishitani report that the photochemical CO₂ reduction catalyzed by *trans*(Cl)-Ru(dmb)(CO)₂Cl₂ could proceed in a combination of [Ir(pyr)] as the photosensitizer and 1,3-dimethyl-2-(*o*-hydroxyphenyl)-2,3-dihydro-1*H*-benzo[d]imidazole (BI(OH)H) as the electron donor. They further synthesized a binuclear complex in which Ir(pyr) and Ru combined via an ethylene bridge. The development of efficient redox photosensitizers based on the earth-abundant metal ions as an alternative toward noble- and/or rare-metal-based photosensitizers is of continuing interest for the field. The heteroleptic Cu(I) phenanthroline complexes, such as [Cu^I(dmp)(P)₂]⁺ (dmp = 2,9-dimethyl-1,10-phenanthroline, P = phosphine ligand), are known to have long lifetimes and show strong MLCT excited state emission even in a solution at room temperature due to the Cu(I) center's d¹⁰ configuration. Yamazaki et al. synthesized heteroleptic

diimine-diphosphine Cu(I) complexes, [Cu^I(dmp)(diphos)]⁺ [dmp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; diphos = methylene chains ($n = 2-4$) linked bis(diphenyl phosphine)]. They investigated the effects of the number of methylene chains on the photocatalytic CO₂ reduction by using *fac*-[Re(bpy)(CO)₃Br] as a catalyst and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (BIH) as an electron donor. The most effective redox photosensitizer was the 1,4-bis(diphenylphosphino)butane (dppb; $n = 4$) complex. They discussed the photocatalytic results in the context of the P-Cu-P angles in the photosensitizer. Takeda et al. developed visible-light responsive Cu(I)-complex photosensitizers by introducing various aromatic substituents at the 4,7-positions of a 2,9-dimethyl-1,10-phenanthroline (dmp) ligand in a heteroleptic [Cu^I(dmp)(DPEphos)]⁺-type complexes (DPEphos = [2-(diphenylphosphino)phenyl]ether). Introduction of biphenyl groups on the dmp ligand enhanced the molar extinction coefficient of the MLCT band. They further performed the photocatalyzed CO₂ reduction by an earth-abundant metal complex, [Fe(dmp)₂(NCS)₂]. Ohtsu et al. synthesized a ruthenium(II) NAD⁺-type complex, [Ru(bpy)₂(Me-pn)]²⁺ (Me-pn = 2-Methyl-6-(pyridin-2-yl)-1,5-naphthyridine). The common photosensitizers act as a one-electron reservoir. But they demonstrated the formation of the corresponding two-electron reduced ruthenium(II) complex, [Ru(bpy)₂(Me-pnHH)]²⁺ (Me-pnHH (2-methyl-6-(pyridin-2-yl)-1,4-dihydro-1,5-naphthyridine) is the NADH-type ligand), by the photo-induced hydrogenation reaction of [Ru(bpy)₂(Me-pn)]²⁺. The complex is a two-electron reservoir and will be applicable to photocatalytic CO₂ reduction as an efficient redox photosensitizer.

Fixation of CO₂ into organic molecules is important to obtain useful and valuable chemicals. Fujihara and Tsuji reviewed the transition metal-catalyzed carboxylation reactions of organic substrates with CO₂ via allyl metal intermediates. They summarized the carboxylation reactions via transmetalation, catalytic carboxylation reactions using allyl electrophiles and suitable reducing agents, and then the catalytic carboxylation reactions via additional reactions affording allyl metal intermediates. Murata et al. reported the visible-light-driven hydrocarboxylation of alkenes with CO₂ by a Rh(I) catalyst with [Ru(bpy)₃]²⁺ (a redox photosensitizer) and BIH or BI(OH)H (an electron donor). The mechanistic study revealed that the catalysis required two photon-driven steps: the carboxylation of the hydrometalated Rh(I) complex on one hand, and the photo-induced generation of the Rh(III) dihydride complex on the other hand. The latter is an electron transfer process that requires the electron donor. The former is an energy transfer step, which would be sensitized by [Ru(bpy)₃]²⁺. Interestingly, they found that the incorporation of the cyclometalated Ir(III) complex as a second photosensitizer with [Ru(bpy)₃]²⁺ photosensitizer also resulted in the promotion of the reduction process. Fu et al. reviewed carbon capture and utilization (CCU) strategies. Although carbon capture and storage (CCS) strategies have been regarded as one of the promising options for controlling continuously elevating atmospheric CO₂ concentrations, desorption and compression

of CO₂ need extra energy input. In the CCU strategy, the CO₂ absorbents trap CO₂ to yield the CO₂ adducts, which can be reacted as transcarboxylation and transformation agents. For example, CO₂ capture and Rh- or Ru-catalyzed CO₂ adducts hydrogenation was introduced.

Conversion of CO₂ into useful chemicals by CO₂ reduction/fixation continues to attract significant interest and research effort. Through the remarkable creativity demonstrated by the authors, this collection of papers (and beyond) is clear evidence that CO₂ fixation and molecular catalysis of CO₂ reduction are and will remain very active and promising fields, promoting fundamental advances. To discover more efficient catalysts, mechanistic investigations on ligand effects, as well as the modification of the second sphere in the metal complexes, will continue to expand the impact of these efforts, with the help of many various complementary *in situ* spectroscopic techniques, such as IR, Raman, EPR, mass, and X-ray absorption spectroscopies. Developing new hybrid systems, such as those that combine the most promising molecular catalysts with semiconductor materials, will also be important developments in the near future, merging the best attributes of homogeneous and heterogeneous catalysis. We hope that this Research Topic will contribute to stimulating the next wave of research efforts in the construction of new artificial photosynthetic systems.

AUTHOR CONTRIBUTIONS

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