

BESH2025 Reversible Conversion between CO₂/H₂ and Formic Acid by Molecular Catalysts

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The Artificial Photosynthesis Group in the Chemistry Division at Brookhaven National Laboratory is carrying out fundamental research involving coordinated experimental and theoretical studies of factors that must be considered in designing artificial photosynthetic systems for the generation of fuels and oxygen from water. The work is aimed at unraveling kinetic and mechanistic details of various processes including (1) photo-initiated proton-coupled electron-transfer reactions; (2) reversible interconversion between CO₂/H₂ and formic acid using Cp*Ir complexes bearing proton responsive ligands; (3) electrochemical CO₂ reduction in organic solvents, or ionic liquids using Re, Mn, and Ru complexes as catalysts; (4) photochemical CO₂ and/or proton reduction using Ir and Co complexes as catalysts; (5) nano-structured carbide/nitride composites and oxynitrides with non-precious metals for hydrogen evolution reaction (HER) and oxygen reduction reaction/oxygen evolution reaction catalysts, respectively; and (6) water oxidation using ruthenium molecular catalysts with multifunctional ligands and at semiconductor/aqueous interfaces. At this meeting, we will report on CO₂ hydrogenation and formic acid dehydrogenation toward the use of formic acid as a sustainable H₂ storage medium.

Proton responsive ligands offer control of catalytic reactions through modulation of pH-dependent properties, second coordination sphere stabilization of transition states, or by providing a local proton source for multi-proton, multi-electron reaction pathways. Using a series of Cp*Ir complexes incorporating the proton responsive bidentate auxiliary ligands shown in Figure 1, we characterized the catalytic activity of CO₂ hydrogenation and formic acid (FA) dehydrogenation in water. Most of these complexes can act

as catalysts for both reactions by simply changing the pH of the aqueous solution. For complexes with ligands possessing *ortho*-OH group(s) we found clear experimental and theoretical evidence of the involvement of a water molecule (i.e., solvent) in the rate determining H₂ heterolysis step in CO₂ hydrogenation by forming a water bridge similar to a proton channel in proteins. While complexes with hydroxyl derivatives of bipyridine and bipyrimidine ligands show maximum reaction rates for FA dehydrogenation around pH 3.8 (i.e., an equal mixture of HCOOH and HCOO⁻), these catalysts are not stable at high temperature or low pH. However, we observed the evolution of 1 m³ of H₂/CO₂ gases from 20 mol FA without any adjustment of the solution pH (pH ~1.6) using Cp*Ir(L2), indicating complete decomposition of FA with a turnover number of

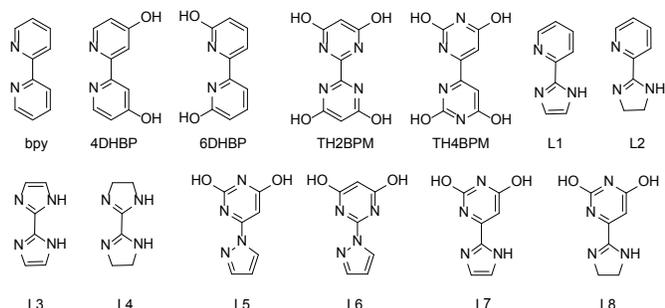


Figure 1. Proton responsive bidentate auxiliary ligands incorporated in Cp*Ir complexes are used to characterize catalytic activity of CO₂ hydrogenation and FA dehydrogenation in water.

2,000,000. This result opens future opportunities for an on-board or onsite H₂ generation system from 10 M FA or conc. FA. We are also investigating *earth-abundant HER* electrocatalysts such as nano-structured Mo or W carbide/nitride composites. These catalysts are durable and efficient catalysts in water (pH 1) and can be prepared by simple, environmentally benign methods.

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