II.F.6 Reversible Conversion between CO_2/H_2 and Formic Acid by Molecular Catalysts

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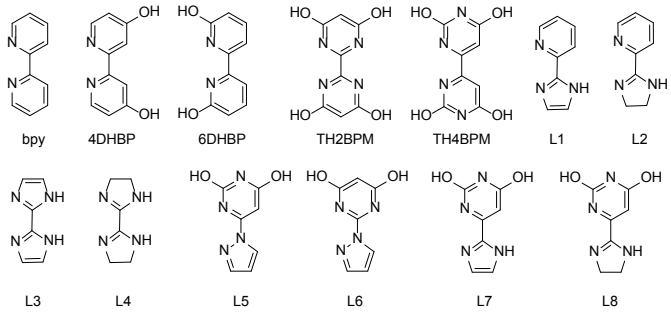

FIGURE 1. Proton responsive bidentate auxiliary ligands used in a series of Cp*Ir complexes

Abstract

The Artificial Photosynthesis Group in the Chemistry Division at Brookhaven National Laboratory (BNL) 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 CO_2/H_2 and formic acid using Cp*Ir complexes bearing proton responsive ligands; (3) electrochemical CO_2 reduction in organic solvents, or ionic liquids using Re, Mn, and Ru complexes as catalysts; (4) photochemical CO_2 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 CO_2 hydrogenation and formic acid dehydrogenation toward the use of formic acid as a sustainable H_2 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 CO_2 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 H_2 heterolysis step in CO_2 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 m^3 of H_2/CO_2 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 2,000,000. This result opens future opportunities for an onboard or on-site H_2 generation system from 10 M FA or concentrated 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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