

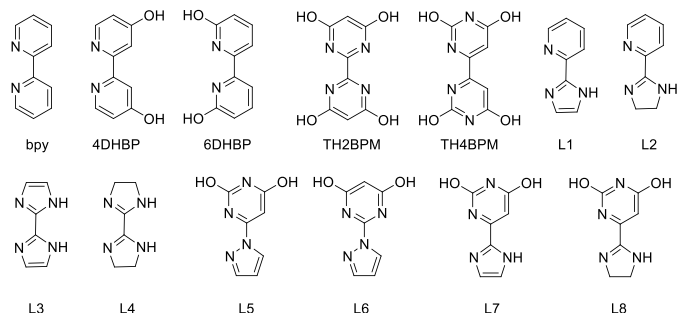
Hydrogen Production and Storage

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Hydrogen is a desirable alternative to fossil fuels for its availability from production from water using electricity from solar photovoltaics or by direct solar-to-chemical conversion. However, the storage is a problem. Formic acid (FA) has been attracted as a liquid-based hydrogen storage medium, even though the H₂ storage capacity is 4.4 wt%. Using a series of Cp*Ir (Cp* = pentamethylcyclopentadienyl) complexes incorporating

the proton responsive bidentate auxiliary ligands, we successfully carried out the reversible conversion of CO₂/H₂ and FA under mild conditions in water by simply changing solution pH without using any organic additives. Several



our catalysts can hydrogenate CO₂ at ambient conditions (i.e., 25 °C and 1 atm CO₂/H₂ mixed gas) in basic water. For FA dehydrogenation, we observed the evolution of 1 m³ of H₂/CO₂ gases from 20 mol FA without any adjustment of the solution pH using a 10 μmol Cp*Ir catalyst, indicating complete decomposition of FA with a TON of 2,000,000. This result opens future opportunities for an on-board or on-site H₂ generation system from conc. FA. While H₂ is currently produced by steam reforming of methane with forming CO₂, it is important to produce H₂ using solar energy. We prepared tetra- and heptametallic Ru(II),Rh(III) polypyridine-type supramolecules and characterized the ability for catalytic H₂ production upon visible-light irradiation using a sacrificial electron donor. We are also investigating *Earth-Abundant HER* electrocatalysts such as nano-structured Mo or W carbide/nitride composites, which are durable and efficient catalysts in water (pH 1) and can be prepared by simple, environmentally benign methods.

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