Catalysts for Solar Fuels
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NSF Center for Chemical Innovation: CO2 Capture and Conversion Institute
Building and understanding a self-contained water splitting system powered by the sun as a source of clean, sustainable energy

Selected Nonaqueous H2 Evolution Studies
Electrocatalysts: H2 evolution occurs near CoII/CoI couple Simulations and thermodynamics favor bimetallic pathway

Thermodynamic Considerations
Bimetallic pathway strongly favored under most conditions Strong and/or less positive 2° (CoII+CoI) favor monometallic route Both can be competitive under intermediate conditions

Aqueous Co(P) Electrocatalysts
Aqueous electrocatalysis (<100 mV Faraday H2 yield) at moderate overpotentials (<0.5 V)
Catalysis likely occurs at CoII/CIII interface (limited mechanistic details reported)
Several electronic absorptions in UV-visible region: oxidations sensitive photospectroscopy

Spectroelectrochemistry: Co(TMPyP)3+ in CH3CN
SEC-derived difference spectrum (blue): Pt mesh, 0.3 H2/THF in NaNO3 UV-vis absorption spectrum of [Co(TMPyP)3]2+ in NaNO3 (orange)

Ongoing Flash-Quench Spectroscopic Studies

Reductive Quenching: [Ru(bpy)3]2+ from MeODMA
Flash-quench laser photolysis studies (pH 7) Data consistent with CoII generation [Ru(bpy)3]2+ bleach correlates data (460 nm)

Currently investigating timescale to confirm reduction at CoII site in [Co(TMPyP)3]2+ Reductive quenching of [Ru(bpy)3]2+ promising for CoII generation in situ Efforts to expand range of conditions to pH 5–8 continue Bulk photocatalysis experiments ongoing to confirm H2 evolution via homogeneous catalytic

Very Long Range Membrane Electron Transfer
Goal: understand tryptophan electron transfer through OmpA as model membrane protein for PSI

CO2 Reduction Catalysts: Very High η
Non-rigidity and Preferred Conformations
Two main nomenclature routes: inversion at Ni–N< to Ni–N> or Ni–N< cleavage to Ni–N> (2° Pyr and Ni–N<)

Roles of Ligand–N–H Bonding
OmpA ET Pathway: Follow the Hopping Hole

Plausible CO2 Reduction Mechanism at Ni
Catalytic CO2 Reduction: [NiL]2+

Targeting Cooperative C–O Cleavage
Ethylene bridged bis(pyridyl)Pt2+ lowers overpotential Monotonic gain possible at the expense of selectivity Emergency Lewis bases (e.g., pyridine) lower overpotential Reduced pyridinium catalysis not observed

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