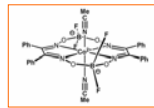
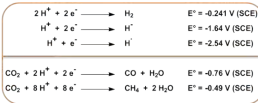
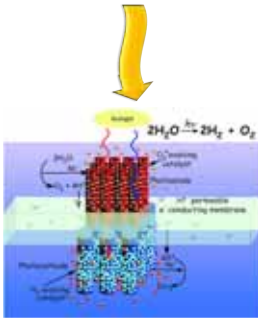
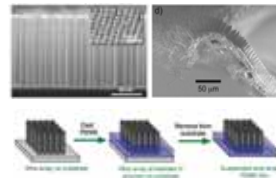




NSF Center for Chemical Innovation: CCI Solar
Interdisciplinary collaboration focused on building and understanding a self-contained water splitting system powered by the sun as a source of clean, sustainable energy



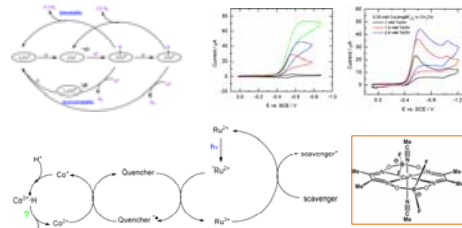
Covalently tethered or adsorbed electrocatalyst on a light-absorbing nanostructured cathode stable to (moderately) reducing conditions



Nanostructured anode or adsorbed thin film electrocatalyst stable to strongly oxidizing conditions

K. E. Plass, M. A. Filler, J. M. Spurgeon, B. M. Kayes, S. Maldonado, B. S. Brunschwig, H. A. Atwater, N. S. Lewis *Adv. Mater.* **2009**, *21*, 325-328

Selected Nonaqueous H₂ Evolution Studies



Electrocatalytic H₂ evolution occurs near Co^{2+/+} couple
Simulations and thermodynamics favor bimetallic pathway

J. L. Dempsey, J. R. Winkler, H. B. Gray *manuscript in preparation*
Hu, X.; Brunschwig, B. S.; Peters, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 8988-8998.
Connelly, F.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 2484-2486.

Thermodynamic Considerations

Bimetallic pathway strongly favored under most conditions
Strong acid and/or less positive E^o(Co^{3+/2+}) favor monometallic route
Both can be competitive under intermediate conditions

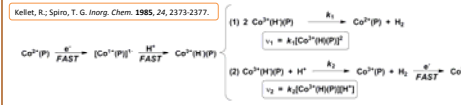
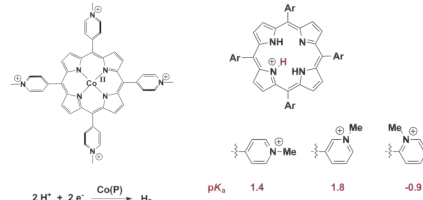
$$K_{eq} = \exp\left(\frac{2\Delta E^\circ - E^\circ(\text{Co(II)})}{k_B T}\right), \quad K_{eq} = \exp\left(\frac{\Delta E^\circ_{\text{Co(II)}} - E^\circ(\text{Co(II)})}{k_B T}\right)$$

$$= \exp\left(\frac{\Delta E^\circ_{\text{Co(II)}} - E^\circ(\text{Co(II)})}{k_B T}\right)$$

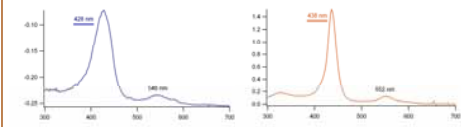
Hu, X.; Brunschwig, B. S.; Peters, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 8988-8998.
Kellert, R. M.; Spiro, T. G. *Inorg. Chem.* **1985**, *24*, 2373-2377.
Chiao, T.-H.; Espenson, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 129-133.

Aqueous Co(P) Electrocatalysts

Aqueous electrocatalysis (>90% Faradaic H₂ yield) at moderate overpotentials (<0.6 V)
Catalysis likely occurs at Co⁰/I interface (limited mechanistic details reported)
Several electronic absorptions in UV-visible region: oxidation state sensitive photoprobes

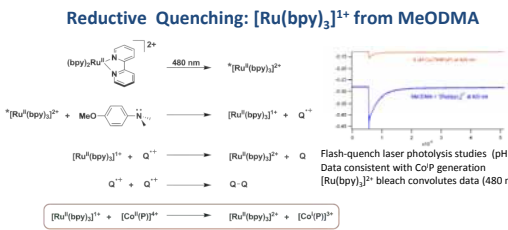
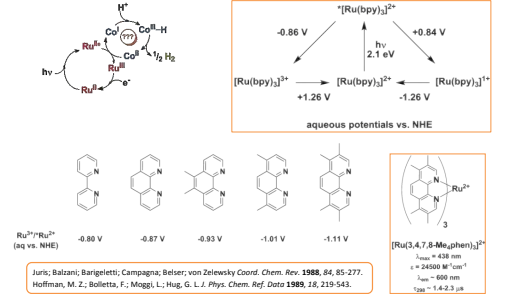


Spectroelectrochemistry: Co^I(TMPyP)³⁺ in CH₃CN



SEC-derived difference spectrum (blue; Pt mesh, 0.1 M TBAAH in MeCN)
UV-vis absorption spectrum of [Co^I(TMPyP)³⁺] in MeCN (orange)

Ongoing Flash-Quench Spectroscopic Studies



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

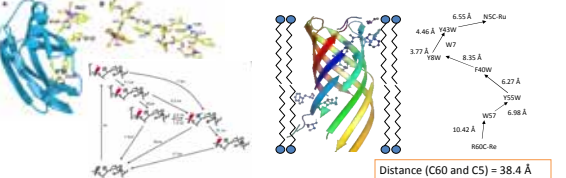
Very Long Range Membrane Electron Transfer

Goal: understand tryptophan electron transfer through OmpA as model membrane protein for PSII



Nelson, et al. *Nat. Rev. Mol. Cell Biol.* **2005**, *6*, 838.
Babin, et al. *J. Am. Chem. Soc.* **2000**, *122*, 4532.
Winkler, et al. *Pure Appl. Chem.* **1999**, *71*, 1753.
Gray, et al. *Annu. Rev. Biochem.* **1996**, *65*, 337.

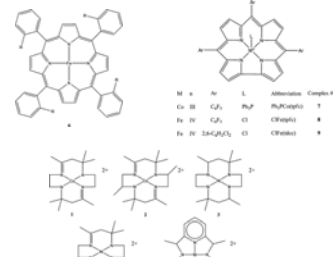
OmpA ET Pathway: Follow the Hopping Hole



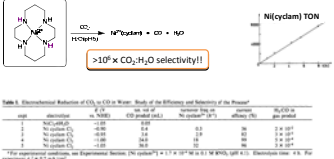
Shih, C., et al. (2008) *Science* **320**, 1760-1762.

Electron transfer rates: hopping mechanism >> tunneling mechanism
Tryptophan residues provide launch pads and landing sites
OmpA has several well-positioned residues for long range ET
ET dynamics investigated with time resolved laser flash photolysis

CO₂ Reduction Catalysts: Very High η

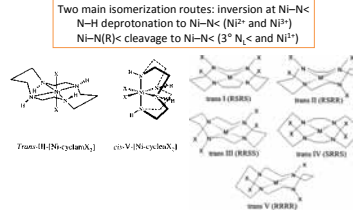


Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361.
Bhugun, L.; Lexa, D.; Savant, J.-M. *J. Am. Chem. Soc.* **1996**, *118*, 1769.
Grodzowski, J.; Neta, P.; Fujita, E.; Mohammed, A.; Simkovich, L.; Gross, Z. *J. Phys. Chem. A* **2002**, *106*, 4772.
Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. et al. *Chem. Rev.* **2009**, in press.



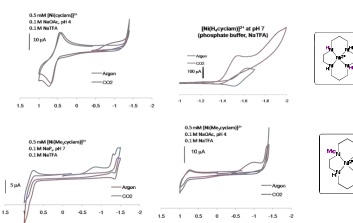
Beley, M.; Collis, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7641

Non-rigidity and Preferred Conformations



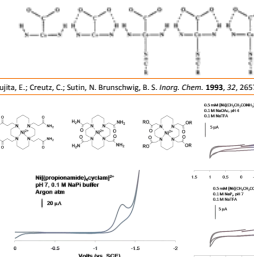
Maimon, E.; Zilbermann, I.; Cohen, H.; Kost, D.; van Eldik, R.; Meyerstein, D. *Eur. J. Inorg. Chem.* **2005**, 4597.
Sobinet, M.; Dechamps-Olivier, I.; Guillon, E.; Barbier, J.-P.; Aplincourt, M.; Chuburu, F.; Le Baccon, M.; Handel, H. *Polyhedron* **2005**, *24*, 143-150.
Neda, R.; Soneta, Y.; Miyamoto, K. *Inorg. Chem. Comm.* **2007**, *10*, 590-592.

Catalytic CO₂ Reduction: [NiL₂]²⁺



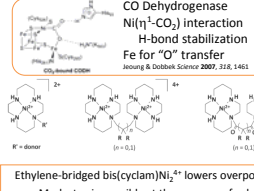
N-substitution induces conformational change: counterintuitive decrease in overpotential, but diminished reactivity

Roles of Ligand-NH-Bonding



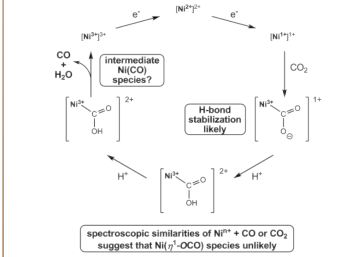
Single pendant arm donors afford similar results: diminished reactivity and minor decrease in overpotential

Targeting Cooperative C-O Cleavage



Ethylene-bridged bis(cyclam)Ni₂⁴⁺ lowers overpotential
Modest gain possibly at the expense of selectivity
Exogenous Lewis bases (e.g., pyridine) lower overpotential
Reduced pyridinium catalysis not observed

Plausible CO₂ Reduction Mechanism at Ni



Currently moving towards heterobimetallic ligands to facilitate oxygen atom or hydroxyl group transfer in a two electron process

Acknowledgements

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Jillian Dempsey & Lionel Cheruzel
Gray and Lewis research groups

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