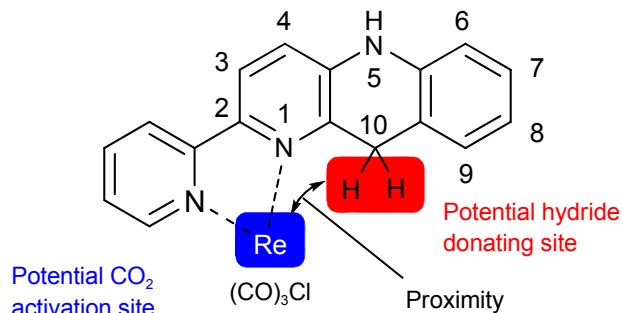


BES009 Proton-Coupled Electron Transfer in Artificial Photosynthesis

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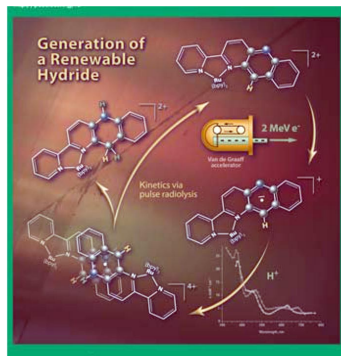
generated photochemically in high yields (quantum yield ca. 21% at 355 nm and quantitative chemical yield) and its formation in the low pH region is mainly achieved through disproportionation of a π -stacking dimer via an intermolecular PCET reaction [1,2]. The net hydride ion transfer reaction from photo-generated hydride donors was found to be controlled by steric factors around the hydride donor sites [4]. The hydride donor ability of the produced organic hydrides was not sufficient to reduce uncoordinated CO_2 , however the further photogenerated one-electron reduced form shows reactivity towards $[\text{CpRe}^I(\text{NO})(\text{CO})_2]^+$ (CO and CH_4 products were observed) [5]. We have also investigated the effect of combining both a CO_2 activation site and a hydride donating site in the same coordination sphere of *fac*- $\text{Re}(\text{pbn})(\text{CO})_3\text{Cl}$ on catalytic CO_2 reduction. It was found that the second reduction potential (-1.65 V under Ar) shifted in a positive direction to -1.44 V under CO_2 atmosphere (acetonitrile solution containing $\text{Re}(\text{pbn})(\text{CO})_3\text{Cl}$ and ~ 0.3 M water, indicating a chemical process, i.e., CO_2 binding to the complex. A 12-fold current enhancement was observed at -2.11 V with 0.26 M CO_2 in the presence of water in acetonitrile solution. The rate constant for CO_2 reduction was estimated as ~ 300 $\text{M}^{-1} \text{s}^{-1}$. Controlled potential electrolysis of $\text{Re}(\text{pbn})(\text{CO})_3\text{Cl}$ at -2.11 V produced CO with a Faradaic efficiency of ~ 70 %.[8]

Abstract

Artificial photosynthetic systems exploit a variety of photochemical transformations with the ultimate result of efficient conversion of the energy of photons into chemical bonds. The efficiency of these transformations strongly depends on how successfully PCET processes are implemented. In this part of our program we focus on mechanistic understanding of the role of PCET in reactions such as: (1) photochemical formation and reactivity of NADPH-like transition metal complexes; (2) hydrogen atom transfer (HAT) in the excited states of transition metal systems; and (3) light-driven water oxidation catalyzed by transition metal complexes.

Progress Report

Photochemical formation and reactivity of NADPH-like transition metal complexes

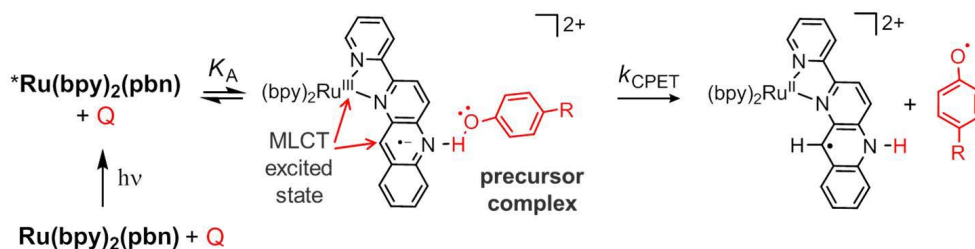


Understanding the ability of NADPH model compounds to shuttle charge in a manner that is coupled to the proton movement in reactions such as HAT or hydride ion transfer is crucial for development of efficient systems involving light-induced charge separation, charge transfer and catalytic

systems. In our early work, we found that the renewable hydride donor $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ (bpy = 2,2'-bipyridine, pbn = 2-(2-pyridyl)benzo[*b*]-1,5-naphthyridine) can be

Hydrogen atom transfer in the excited states of transition metal systems

Within the scope of this project we study light-driven CPET reactions between a series of NAD^+ model compounds, such as $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$, $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$, $[\text{Ru}(\text{bpz})_3]^{2+}$ (bpy = 2,2'-bipyridine, pbn = 2-(2-pyridyl)benzo[*b*]-1,5-naphthyridine, bpz = 2,2'-bipyrazine) and hydrogen atom donors, such as substituted hydroquinones and para-substituted phenols. We found that in solvents with high donor numbers (e.g., acetonitrile), the strong hydrogen bonding between phenol donors and solvent molecules results in significant kinetic solvent effects (KSEs). It is necessary to account for these effects if any mechanistic conclusions are based on the rate analysis.

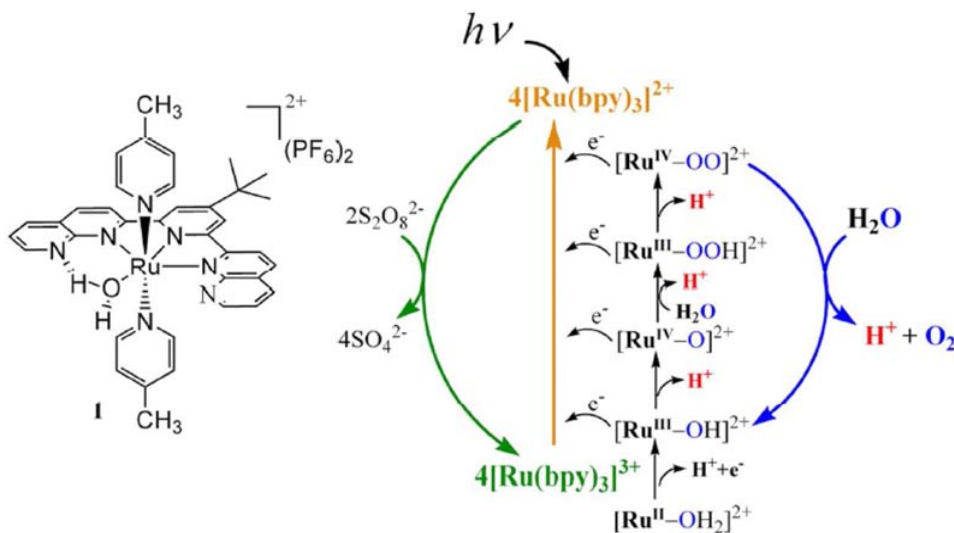


The use of low coordinating solvents such as dichloromethane enabled the measurements of CPET rate constants with minimum contribution from KSE. Based on the transient spectra and observation of substantial kinetic isotope effects (KIEs) the quenching of the excited state of all metal complexes by *para*-substituted phenols proceeds through a CPET mechanism except for the $[\text{Ru}(\text{bpz})_3]^{2+}$ / *para*-nitrophenol pair, which follows an electron-transfer (ET) mechanism. The analysis of activation parameters for CPET is indicative of zero or slightly negative activation energy, with significant negative activation entropies contributing to the overall free energy barrier. On the other hand, in the case of the ET reaction a positive activation energy and virtually zero activation entropy are observed making it distinctly different from CPET. The analysis of kinetic data using Marcus theory provides deeper insight into how the mechanism of CPET compares to ET reactions.

Light-driven water oxidation catalyzed by transition metal complexes

Another aspect of our work is related to studies of light-induced catalytic reactions. A system in which a water oxidation catalyst interacts directly in uni- or bi-molecular fashion with photoinduced charges can provide valuable mechanistic insights. In our recent work, we have

demonstrated that the mononuclear ruthenium catalyst $[\text{Ru}(\text{NPM})(\text{pic})_2]^{2+}$ (**1**) (NPM = 4-*t*-butyl-2,6-di-1',8'-naphthyrid-2'-yl)-pyridine, pic = 4-picoline) can promote light-driven water oxidation with 9% quantum efficiency in homogeneous aqueous solution in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{S}_2\text{O}_8]^{2-}$ [6]. With complex **1**, we were able to reach a TON and TOF of > 103 and 0.12 s^{-1} , respectively. These values render catalyst **1** to be one of the most active mononuclear ruthenium-based catalysts for light-driven water oxidation in a homogeneous system. According to the previously proposed mechanism for water oxidation catalyzed by **1**, a low-energy pathway for O–O bond formation via the $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ intermediate can be achieved at neutral pH [3], thus enabling the use of a mild oxidant such as photogenerated (1.26 V vs NHE) $[\text{Ru}(\text{bpy})_3]^{3+}$. Our work demonstrates that catalytic pathways for complex **1** can be tuned by a simple change of proton concentration, and that the more efficient low energy “direct pathway” enables photochemical water oxidation using $[\text{Ru}(\text{bpy})_3]^{2+}$ with persulfate. In addition, we have established a comprehensive model for the accurate description of similar reactions involving catalyst/sensitizer/quencher systems [7]. We are planning to extend this work to other catalytic systems in order to explore their advantages and limitations under photochemical conditions.



Publication list acknowledging the DOE grant or contract

1. Doherty, MD.; Grills, D. C.; Muckerman, J.T.; Polyansky, D.E.; Fujita, E. "Toward More Efficient Photochemical CO₂ Reduction: Use of scCO₂ or Photogenerated Hydrides," *Coord. Chem. Rev.* **2010**, *254*, 2472-2482.
2. Cohen, B.W.; Polyansky, D.E.; Zong, R.; Zhou, H.; Ouk, T.; Cabelli, D.; Thummel, R.P.; Fujita, E. "Differences of pH-Dependent Mechanisms on Generation of Hydride Donors using Ru(II) Complexes Containing Geometric Isomers of NAD⁺ Model Ligands: NMR and Radiolysis Studies in Aqueous Solution," *Inorg. Chem.* **2010**, *49*, 8034-8044.
3. Polyansky, D.E.; Muckerman, J.T.; Rochford, J.; Zong, R.; Thummel, R.P.; Fujita, E. "Water Oxidation by a Mononuclear Ruthenium Catalyst: Characterization of the Intermediates," *J. Am. Chem. Soc.* **2011**, *133*, 14649-14665.
4. Cohen, B.W.; Polyansky, D.E.; Achord, A.; Cabelli, D.; Muckerman, J.T.; Tanaka, K.; Thummel, R.P.; Zong, R.; Fujita, E. "Steric Effect for Proton, Hydrogen-Atom, and Hydride Transfer Reactions with Geometric Isomers of NADH-Model Ruthenium Complexes," *Faraday Discuss.* **2012**, *155*, 129-144.
5. Muckerman, J.T.; Achord, P.; Creutz, C.A.; Polyansky, D.E.; Fujita, E. "Calculation of Thermodynamic Hydricities and the Design of Hydride Donors for CO₂ Reduction," *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 15657-15662.
6. Lewandowska-Andralojc, A.; Polyansky, D.E.; Zong, R.; Thummel, R.P.; Fujita, E. Enabling Light-Driven Water Oxidation via a Low Energy Ru^{IV}=O Intermediate, *Phys. Chem. Chem. Phys.* **2013**, *15*, 14058-14068.
7. Lewandowska-Andralojc, A. and Polyansky, D.E. "Mechanism of the Quenching of the Tris(bipyridine)ruthenium(II) Emission by Persulfate: Implications for Photo-Induced Oxidation Reactions" *J. Phys. Chem. A* **2013**, *117*, 10311-10319.
8. Matsubara, Y.; Hightower, S.H.; Chen, J.; Grills, D.C.; Polyansky, D.E.; Muckerman, J.T.; Tanaka, K.; Fujita, E. "Reactivity of a *fac*-ReCl(α -diimine)(CO)₃ complex with an NAD⁺ model ligand toward CO₂ reduction" *Chem. Commun.* **2014**, *50*, 728-730.