

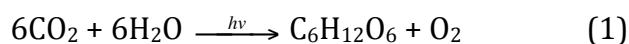
The Electronic Properties of tris-(2,2'-bipyridine)-ruthenium(II)

Jared J. Paul*† and Javier J. Concepcion‡

† Villanova University

‡ The University of North Carolina at Chapel Hill

The ability to harness light from the sun and convert it to a chemical energy source has been of intense interest for many years. Plants successfully accomplish conversion of sunlight to energy in the form of glucose in a process called photosynthesis. In photosynthesis light is absorbed by a chlorophyll reaction center and an electron is promoted down a cascade that ultimately is used to reduce carbon dioxide to glucose. Water is oxidized to molecular oxygen at a catalyst called the Oxygen Evolving Complex within the photosynthetic apparatus, ultimately transporting electrons back to the oxidized chlorophyll reaction center, enabling multiple reductive equivalents to be delivered for the reduction of carbon dioxide. The net photosynthetic reaction is thermodynamically unfavorable by +29.3 eV:



If the photosynthetic process could be mimicked in an artificial system, light energy can be coupled with a catalyst and used as a driving force for many energy rich chemicals of interest, such as hydrogen and methane.¹ The components for an artificial photosynthetic device are depicted in Figure 1. These components are: 1) a light absorbing antenna with chromophore, 2) an electron acceptor coupled to a reduction catalyst for the reaction of interest and 3) an electron donor coupled to an oxidation catalyst for another reaction of interest.

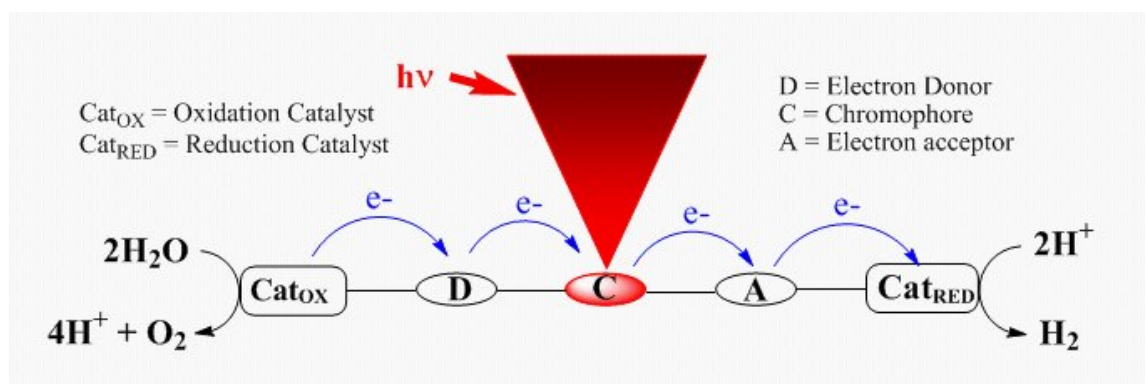


Figure 1: Assembly for artificial photosynthetic device.

Metal polypyridyl complexes have attracted a great deal of attention for both their light absorption and electron transfer properties.² Light absorption in metal polypyridyl complexes, results in metal to ligand charge transfer (MLCT) transitions, as an electron is promoted from a filled metal d orbital to a π^* orbital on the ligand. Polypyridyl complexes of Ru have been intensely studied because: 1) The ligand structures of Ru metal complexes

can be varied in many diverse ways leading to tunability of the MLCT character of these complexes.³ 2) The ligands can be altered with electron donors and acceptors to probe electron transfer.⁴ 3) Several bridging ligands can be utilized to create bimetallic and higher order multi-metallic complexes.⁵⁻⁷ *The synthetic precedence established for Ru complexes make them ideally suited for developing new complexes for the study of electron transfer in addition to gaining an understanding of the fundamental properties of these novel complexes spectroscopically and electrochemically.*

The goal of this lab will be to synthesize and study the spectroscopic and electrochemical properties of a known metal polypyridyl complex, tris-(2,2'-bipyridine)-ruthenium(II), Figure 2.

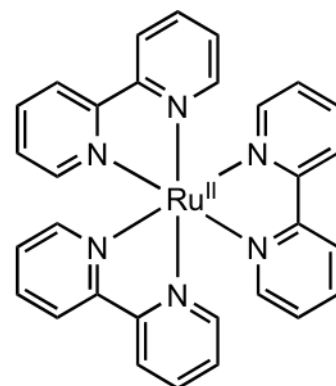


Figure 2: Chemical structure of tris-(2,2'-bipyridine)-ruthenium(II)

Synthesis of [Ru(bpy)₃][Cl]₂

The synthetic procedure has been published by Broomhead and Young.⁸ Obtain a 100 mL round bottom flask. RuCl₃•3H₂O has been dried overnight in the oven at 120°C to remove the water and yield RuCl₃. Weigh approximately 0.4 g (1.93 mmol) dried RuCl₃ and add to the round-bottom flask. Weigh approximately 0.98 g (6.27 mmol) 2,2'-bipyridine and add to the round-bottom flask. Add 40 mL distilled H₂O to round-bottom flask. Add 2 mL of a freshly prepped solution of sodium hypophosphinate to the round-bottom flask. To make the sodium hypophosphinate solution, slowly dissolve NaOH pellets (one at a time) to 2 mL of 31% phosphinic acid until a slightly cloudy solution forms. Add 31% phosphinic acid dropwise to until the solution becomes clear. When all contents are added to the reaction round-bottom flask, set up a reflux condenser. Place argon flow at the top of the condenser and heat the solution to boiling. Reflux the solution for 30 min (note the color changes that occur). After refluxing, remove the solution from heat, allow solution to cool, and filter the reaction mixture to remove unreacted ligand. Add approximately 12.6 g KCl to the filtrate to precipitate the product in a beaker. Heat the solution to a boil while stirring (the solution might not come to a complete boil). After boiling, allow solution to cool. Collect the crystals that form by filtration. Rinse crystals with a small amount of cold 10% acetone in water (2 – 5 mL portions). Rinse the crystals with approximately 30 mL acetone and allow crystals to dry. Collect an IR spectrum of the product.

Synthesis of [Ru(bpy)₃][PF₆]₂

Dissolve approximately half (up to 0.4 g) of the [Ru(bpy)₃][Cl]₂ synthesized previously in enough distilled water to completely dissolve the complex. Weigh at least a 10x mole excess of NH₄⁺PF₆⁻ and dissolve in a small amount of distilled water (make sure the salt is completely dissolved). Mix the two solutions together with stirring. Collect the precipitate via filtration. Rinse with distilled water, then ether. Allow the product to dry and then collect an IR spectrum.

Absorption and Emission

Prepare a stock solution of [Ru(bpy)₃][Cl]₂ in water by dissolving approximately 5 mg of complex in 10 mL water. From the stock solution, prepare 5 mL of a 0.02 mM

solution of $[\text{Ru}(\text{bpy})_3][\text{Cl}]_2$ in water. Collect a UV/Visible spectrum of the solution. Collect an emission spectrum of the complex. Degas the 0.02 mM $[\text{Ru}(\text{bpy})_3][\text{Cl}]_2$ solution for 20 minutes by bubbling argon or nitrogen through the solution and recollect the emission spectrum of the complex using the same settings on the emission spectrophotometer. Collect an excitation spectrum of the complex. Bubble the 0.02 mM $[\text{Ru}(\text{bpy})_3][\text{Cl}]_2$ solution for 20 minutes with air and recollect the emission spectrum with the same setting on the emission spectrophotometer.

From the stock solution of $[\text{Ru}(\text{bpy})_3][\text{Cl}]_2$ in water, prepare 1) a 5 mL solution that is 0.02 mM $[\text{Ru}(\text{bpy})_3][\text{Cl}]_2$ and 20 mM hydroquinone in water and 2) a 5 mL solution that is 0.02 mM $[\text{Ru}(\text{bpy})_3][\text{Cl}]_2$ and 10 mM ammonium cerium(IV) nitrate in water. Collect an absorption spectrum for each solution. Degas each of the solutions for 20 minutes. Collect emission spectra for each solution followed by re-collecting a second absorption spectrum of each solution.

Electrochemistry

Prepare a 10 mL solution of 2 mM of $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ and 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. This solution will be used for all of the electrochemical experiments. The instructor will demonstrate the proper setup for the electrochemical cell. Degas the solution by bubbling with argon for approximately 20 minutes. Using a scan rate of 100 mV/s, collect three scans: a) an oxidative scan from 0 to 1800 mV, b) a reductive scan from 0 to -1850 mV, c) a complete scan from 0 to 1800 mV to -1850 mV. After the scans have been collected, add a few milligrams of ferrocene to the solution and collect a complete scan from 0 to 1800 mV to -1850 mV at 100 mV/s.

Questions

1. How does exchanging the counter ion affect the properties of $[\text{Ru}(\text{bpy})_3]^{2+}$?
2. Why is the ruthenium complex degassed prior to emission studies?
3. How does the excitation spectrum compare to the absorbance spectrum for $[\text{Ru}(\text{bpy})_3][\text{Cl}]_2$?
4. How does the addition of hydroquinone affect the absorbance and emission spectra of $[\text{Ru}(\text{bpy})_3][\text{Cl}]_2$? Explain.
5. How does the addition of ammonium cerium(IV) nitrate affect the absorbance and emission spectra of $[\text{Ru}(\text{bpy})_3][\text{Cl}]_2$? Explain.
6. Why are the electrochemistry experiments done in acetonitrile instead of water?
7. Why is the ruthenium complex degassed prior to electrochemical studies?
8. Why is ferrocene added to the solution for the final CV collected?

References

- (1) Nocera, D. G. Chemistry of Personalized Solar Energy *Inorg. Chem.* **2009**, *48*, 10001-10017.
- (2) Meyer, T. J. Chemical Approaches to Artificial Photosynthesis *Acc. Chem. Res.* **1989**, *22*, 163-170.
- (3) Anderson, P. A.; Keene, F. R.; Meyer, T. J.; Moss, J. A.; Strouse, G. F.; Treadway, J. A. Manipulating the properties of MLCT excited states. *J. Chem. Soc. Dalton Trans.* **2002**, 3820-3831.

- (4) Coe, B. J.; Friesen, D. A.; Thompson, D. W.; Meyer, T. J. trans-Chromophore-quencher complexes based on ruthenium(II) *Inorg. Chem.* **1996**, *35*, 4575-4584.
- (5) Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J.-P. Stepwise syntheses of mono- and dinuclear ruthenium tpphz complexes $[(bpy)_2Ru(tpphz)]^{2-}$ and $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ {tpphz = tetrapyrido[3,2-a:2'3'-c:3",2"-h:2"',3'''-j]phenazine}. *J. Chem. Soc. Chem. Comm.* **1995**, 1799-1800.
- (6) Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J.-P. Mononuclear and binuclear tetrapyrido[3,2-a:2',3'-c:3",2"-h:2"',3'''-j]phenazine (tpphz) ruthenium and osmium complexes. *Inorg. Chem.* **1996**, *35*, 2937-2944.
- (7) D'Alessandro, D. M.; Keene, F. R. Intervalence charge transfer (IVCT) in trinuclear and tetranuclear complexes of iron, ruthenium, and osmium. *Chem. Rev.* **2006**, *106*, 2270-2298.
- (8) Broomhead, J. A.; Young, C. G. Tris(2,2'-Bipyridine)Ruthenium(II) dichloride hexahydrate *Inorg. Syn.* **1982**, *21*, 127-128.