

THE RUTHENIUM-BIPYRIDINE PROJECT

Part 1. Synthesis and Properties of Ruthenium(II) tris-Bipyridine

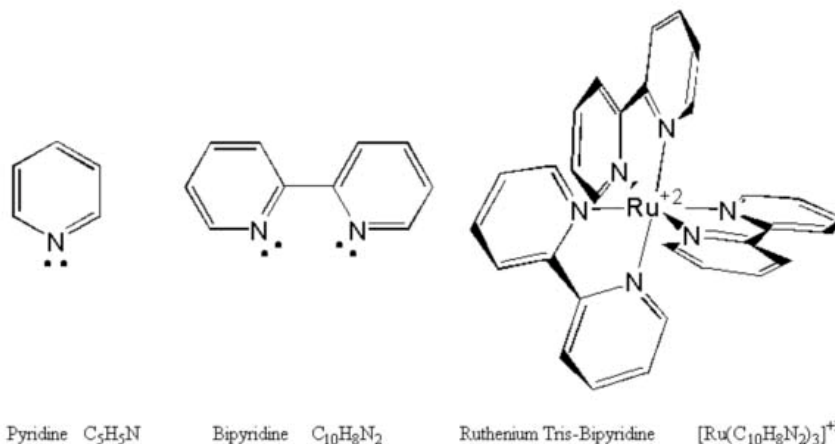
Part 2. Photoelectrochemical Energy - The Gratzel Solar Cell

Part 1. Synthesis and Properties of Ruthenium(II) tris-Bipyridine

Introduction

Transition metal complexes have been investigated as potential solar energy collectors. This research is important for our society as it could lead to the large-scale utilization of renewable energy resources. The next two experiments will focus on the ruthenium(II) tris-bipyridine complex that has been the subject of many inorganic photophysical experiments. This molecule has many favorable chemical and photochemical properties. These properties include ground and excited stability, a strong optical absorbance in the visible region of the spectrum and a long lived emissive excited state.

The ground electronic state of the ruthenium(II) tris-bipyridine complex is very stable as a result of the d^6 electron count of the metal and the chelating nature of the bipyridine ligand. The 6 d electrons completely fill the metal $d\pi^b$ orbital subshell for a maximum bonding electron count. Under octahedral symmetry the metal $d\pi$ subshell has π -bonding character with respect to orbitals of the appropriate symmetry on the ligand. The filled subshell has spherical symmetry and any incoming ligands will face electrostatic repulsion from the electrons in the filled orbitals regardless of which direction they approach the complex from.

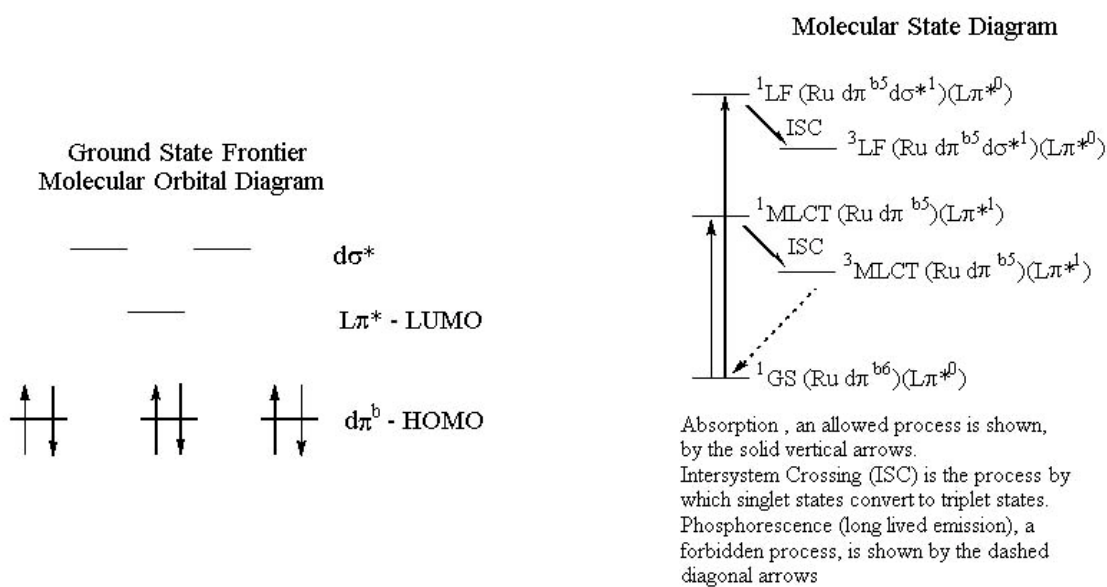


The bipyridine ligand contributes to the stability of the complex by having empty pi orbitals that can bond with the metal $d\pi^b$ orbital subshell and by being a chelating ligand. Each bipyridine bonds twice to the metal center through the donation of the lone pair electrons on both nitrogen atoms. If one of the metal-nitrogen bonds is broken, the other metal-nitrogen bond will hold the ligand in place long enough for the broken bond to re-

form. It is unlikely that the ligand will diffuse away from the metal center unless the bonds to both nitrogen atoms are broken simultaneously. This event has a low probability of occurring.

Optical transitions resulting from the absorption of photons and causing the promotion of electrons to higher energy molecular orbitals have varying degrees of quantum mechanical allowedness. The degree of allowedness depends on the symmetry and the multiplicity (or electron spin count) of the different states. Allowed transitions have no change in electron spin ($\Delta S = 0$). Forbidden transitions have a difference in electron spin between the ground and excited states. This means that only transitions from the singlet ground state, all electrons paired, to singlet excited states are allowed. Transitions from the singlet ground state to triplet excited states with two unpaired electrons, are forbidden. The allowedness of a transition can be inferred from the magnitude of the extinction coefficient, ϵ , for a given band in the optical absorbance spectrum. Allowed transitions have values of ϵ in the thousands, forbidden transitions have much smaller values of ϵ .

The lowest energy excited state of ruthenium(II) tris-bipyridine is a metal-to-ligand charge transfer state (MLCT). This state is formed by the promotion of an electron from the filled metal $d\pi^b$ HOMO (Highest Occupied Molecular Orbital) to an empty ligand π^* LUMO (Lowest Unoccupied Molecular Orbital). This transition is fully allowed by the laws of quantum mechanics (symmetry and spin selection rules) and the transition has a large extinction coefficient. The value of the extinction coefficient, ϵ , is in the thousands for MLCT transitions and much smaller for d-d or metal centered transitions. The MLCT excited state that is created is not strongly anti-bonding with respect to the metal-ligand bond. The π^* character of the LUMO is primarily with respect to internal ligand pi bonds and not metal-ligand bonds. Creation of the MLCT excited state does not lead to the decomposition or photolysis of the complex to an appreciable degree.

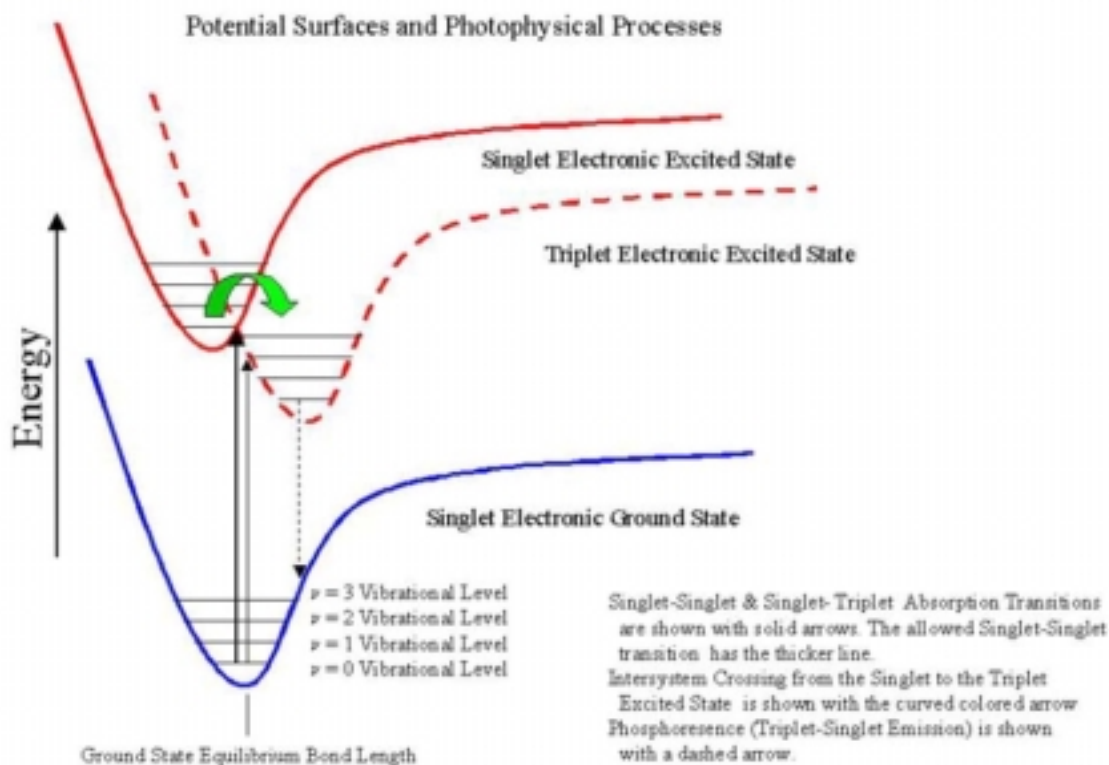


The higher energy excited state is the metal centered or ligand field (LF) excited state. This state is formed by the promotion of an electron from the filled metal $d\pi^b$ HOMO to the higher energy $d\sigma^*$ orbital. This excited state is forbidden by the symmetry selection rules of quantum mechanics and a transition of this type will have a small extinction coefficient. In this case the anti-bonding character of the orbital is with respect to the metal-ligand bond. The probability of ligand loss (photolysis of the complex) increases with the formation of the LF excited state.

After the allowed singlet ground state to singlet excited state transition that creates the excited state deactivation process occur that allow the molecule to relax to lower energy states. One of these processes is called intersystem crossing and results in the relaxation of a singlet state to a lower energy triplet state. For quantum mechanical reasons, primarily due to exchange integrals, triplet states are at lower energy than the singlet states of the same orbital parentage. On the state diagram above this is clearly seen. The singlet and triplet MLCT excited states have the same occupied orbitals, they only differ in energy due to the differences in electron spin pairings. For ruthenium tris-bipyridine it is thought that the intersystem crossing efficiency is 100%. This means that all singlet MLCT created upon absorption of a photon by the ground state become triplet MLCT states through intersystem crossing. The triplet MLCT that is created is a long lived luminescent excited state. The excited state is long-lived because relaxation to the singlet ground state is a slow process due to the difference in spin states. The relaxation process has a partially forbidden character.

Ruthenium tris-bipyridine has a quantum yield of emission of about 8%. Only a small fraction of molecules go from the triplet excited state to the singlet ground state through the radiative mechanism. The majority of molecules relax to the ground state through non-radiative, vibrational relaxation processes. Release of a photon with an accompanying spin change is called phosphorescence. Release of a photon without a spin state change is called fluorescence. Fluorescent processes occur much quicker than phosphorescent processes due to the forbidden nature of the change of spin state.

The lifetime of the triplet MLCT excited is about 800 nsec. (8.0×10^{-7} sec.) in fluid solution at room temperature. While this might seem short to us, realize that the vibrational frequency of bound atoms is about 10^{13} Hz or cycles/sec. While the molecule is in the excited state its bonds have enough time to vibrate between one to ten million times. A fluorescent molecule can have a lifetime of a few pico-seconds (10^{-12} sec) or less. The energies of the absorbed and emitted photons are not equal to the energy of the emissive excited state which is measured from the 0th vibrational level of the ground state to the 0th vibrational level of the excited state and is referred to as E_{0-0} . This is shown on the diagram below. A crude way to estimate the energy of the triplet MLCT state is by measuring the reduction potential of the ligand and the oxidation potential of the metal in the complex. The sum of these energies will approximate the value of E_{0-0} since the redox processes use the same frontier orbitals, the highest occupied metal d orbital and the lowest unoccupied ligand π^* orbital, as the photophysical process. Another way to estimate the triplet E_{0-0} is by averaging the energy of maxima of the ground state singlet to triplet absorption band and the emission band. The forbidden ground state singlet to triplet absorption band can be found in the absorption spectra of the molecule as the low energy tail of the allowed MLCT band. You will need to estimate the energy of the band maximum as it will not be clearly resolved. The energy of the triplet state has been found by more accurate methods to be at 2.1 eV or $16,940 \text{ cm}^{-1}$ above the lowest vibrational level of the ground state



Synthesis of the Complex

Place 0.4 g (1.93 mmoles) of RuCl_3 , a 10% stoichiometric excess of 2,2'-bipyridine and 40 ml of deionized water in a 100 ml round bottom flask equipped with a magnetic stir bar and a reflux condenser. Freshly prepared sodium phosphinate (see below) solution is added (2 ml) and the mixture is heated at reflux for thirty minutes. Filter the orange solution to remove undissolved material. Add 12.6 g of potassium chloride to precipitate the product. The solution and solid are then heated to a boil to give a deep red solution which on cooling to room temperature yields orange plate like crystals.

Sodium phosphinate solution is prepared by the careful addition of sodium hydroxide pellets to about 2 ml of 50% hypophosphorus acid until a slight cloudy precipitate is obtained. Hypophosphorus acid is then added dropwise until the precipitate just redissolves.

Purification of the Complex

The crude precipitate should be run on a column to separate your product from any impurities. Make up a small volume of acetonitrile solution of the crude product. Spot a silica or alumina TLC plate with a drop of your solution. Develop the plate with a solvent system. Try various mixtures of acetonitrile and toluene until you get good flow rates and separations.

Make a short (3 to 4 inches long) column. Pour a slurry of alumina or silica suspended in your solvent system into the glass tube. Let the solid settle and drain the excess solvent off the bottom. Do not let the packing go dry. Run your entire crude product through the

column at a concentration as high as possible. When the top of your solution is in the column packing add more solvent to the column. Collect the fraction with your product. Ruthenium tris-bipyridine is luminescent; you can locate your product on the column by the orange glow that appears upon irradiation with a handheld UV lamp. Rotovap the product containing fraction to dryness. Weigh and determine the yield.

Electrochemical Analysis of the Complex

Prepare 100 ml of 0.1 M tetrabutyl ammonium chloride dissolved in acetonitrile to use as electrolyte. Use distilled acetonitrile. Collect a cyclic voltammogram of your compound. You should be able to observe both reductive and oxidative processes.

Optical Analysis of the Complex

Collect a UV-Absorbance spectrum of the complex. Use a 0.5 mM acetonitrile solution for the visible region of the spectrum. This solution can be diluted by 10 to collect data in the ultraviolet region of the spectrum. Make note of the wavelength of maximum absorbance or peak positions. Calculate the extinction coefficient at each absorbance peak in your spectra.

Collect an emission spectrum of the complex. Use a 0.5 mM acetonitrile solution that has been degassed by bubbling nitrogen gas through the solution in a fluorimetry cell that has been sealed with a septa. Excite the sample at the wavelength of maximum absorbance of the lowest energy peak in your absorbance spectrum.

Measure the emission lifetime using the laser spectroscopy system. Collect data from degassed and non-degassed samples. Calculate a quantum yield of emission in both cases.

Discussion Questions for part 1.

- 1) What combination of metal and ligand properties helps make this a stable molecule?
- 2) Photophysical and electrochemical process cause changes in the electron populations of various orbitals.
Give an equation that shows the change that occurs for the photon absorption process.
Give an equation that shows the change that occurs for the photon emission process.
Give an equation that shows the change that occurs for the ligand reduction process.
Give an equation that shows the change that occurs for the metal oxidation process.
Discuss the similarities.
- 3) What does the energy difference between the absorption and emission maxima indicate?
If the energy is not emitted as visible light where does the energy go?
- 4) What is the value of the extinction coefficient at the absorption maxima? What does this indicate? What concentration of $\text{Ru}(\text{bpy})_3^{+2}$ is needed to absorb 90% of the incident light at this wavelength?
- 5) How does the energy of the greatest absorption maximum compare to the difference between the metal oxidation potential and the ligand reduction potential of the complex? to the energy of the emission maximum? Why are these values different?
- 6) How are triplet and singlet states different?

- 7) What are the values for the E_{0-0} of the emissive triplet state as estimated by electrochemical and spectroscopic methods? How do they compare with the actual value of 2.1 eV? Account for the difference.

Useful References

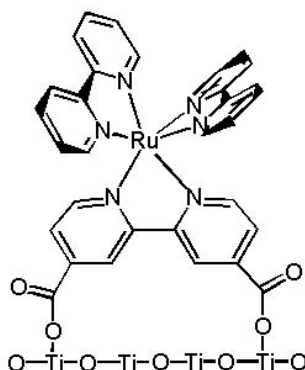
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Part 2. Photoelectrochemical Energy - The Gratzel Solar Cell

Introduction

Solar cells hold the promise of being able to help supply our energy needs and are therefore an area of research interest. We will make a type of cell developed by Michael Gratzel, of the Swiss Federal Institute of Technology, that uses dye molecules for efficient collection of light. We will use a ruthenium complex that we will synthesize as the dye. This molecule is also called the sensitizer or antenna molecule.

The cell functions (see picture and diagram below) by using dye or sensitizer molecules bound to a porous, high surface area colloidal semiconductor film of titanium dioxide (TiO_2). The high porosity of the film enables the dye molecules to collect a large fraction of the incident photons since a photon has many chances to be absorbed by the dye molecules in a pore. The dye molecules are chosen for optimal optical characteristics, they have transitions with large extinction coefficients that cover most of the utilizable spectrum and good photostability. The TiO_2 film is deposited on a transparent glass electrode in contact to an external circuit.



$[\text{Ru}(\text{bpy})_2(\text{bpy-diacid})]^{+2}$ Bound to the TiO_2 Surface

The absorption of a photon by the dye creates an excited state. For the ruthenium complex that we will use the initially created excited state is a singlet metal to ligand charge transfer state (MLCT). An electron has been promoted from a metal centered 4d orbital into a ligand centered π^* orbital. This excited state is a better reductant than the ground state of the complex as it contains a high-energy electron that can be transferred into an available lower energy orbital. The absorption of a photon has created a driving force for electron transfer. This results in rapid charge injection from the ruthenium complex into the conduction band of the semiconductor matrix to which it is bound. This happens very rapidly, on the femtosecond timescale, either directly from the singlet MLCT state or through conversion to the triplet MLCT state followed by charge injection into the semiconductor.

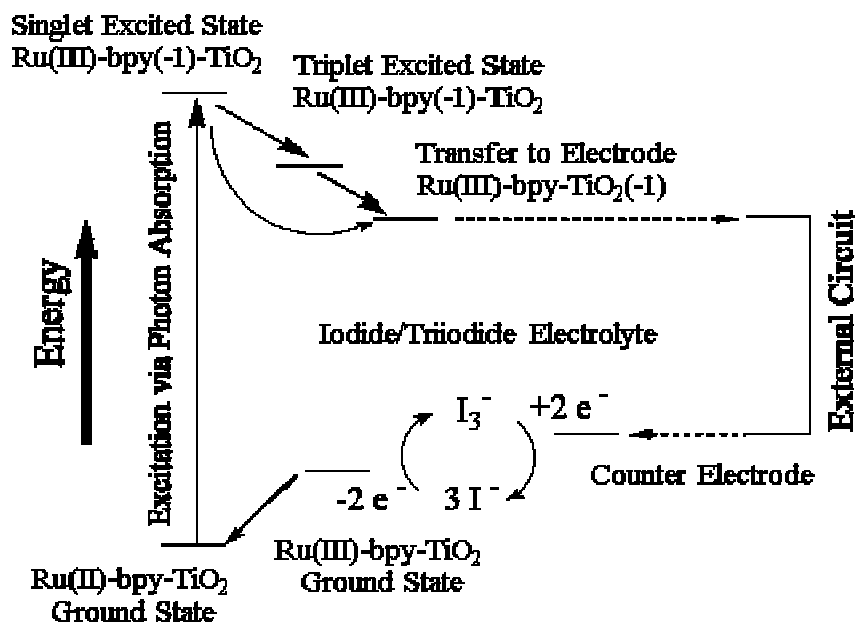
From the conduction band of the semiconductor film the electron is delivered to the transparent glass electrode and the external circuit where it can provide usable energy. The amount of work that can be extracted from an electron is the difference in potential energy or voltage between the conduction band of the semiconductor and the potential needed to reduce the electrolyte to complete the circuit.

Our cell utilizes the iodide/triiodide couple to transfer the electrons from the counter electrode to the working electrode. Triiodide is reduced at the counter electrode to iodide. Iodide is oxidized to triiodide at the working electrode as the ruthenium (III) complex is reduced back to its initial state as a ruthenium (II) complex. This regenerates the sensitizer; the cell is now ready to absorb another photon and go through the cycle again providing more energy.

The ruthenium (III) complex is reduced back to ruthenium (II) very quickly after it is photo-oxidized by the high concentration of iodide in the surrounding electrolyte solution. This is important in helping prevent the back reaction of an electron injected into the semiconductor returning to the ruthenium center directly from the semiconductor rather than going through the external circuit. The back reaction is a short circuit of the cell and produces no usable energy. The energy of the photon has been converted into unusable thermal energy or heat.

Electronic features of the ruthenium complex help accelerate charge injection and prevent the back reaction. The ligand centered p^* orbital, that injects the electron in the excited state into the TiO_2 conduction band, is directly bound to the TiO_2 . This implies good orbital overlap between the TiO_2 conduction band and the ligand p^* orbital. The singly occupied ruthenium 4d orbital that the electron returns to in the back reaction from the excited state to the ground state has little overlap with the TiO_2 conduction band. Generally large orbital overlap leads to faster rates of electron transfer while smaller orbital overlap leads to slower rates of electron transfer.

Electron Flow Through the Cell



Synthesis of bis-Bipyridine-Dichloro-Ruthenium

Ruthenium (III) trichloride (100 mg, 380 μmole), 2,2'-bipyridine (118.6 mg, 760 μmole) and LiCl (110 mg, 2.6 mmole) are dissolved in 5 ml of reagent grade N,N-dimethylformamide in a round bottom flask equipped with a magnetic stirring rod and a reflux condenser. Weigh out the ruthenium and bipyridine carefully as controlling the stoichiometry is very important in getting the maximum yield of the product. Reflux for

three hours. After the solution cools to room temperature it is poured into 25 ml of rapidly stirring acetone. The flask is washed with two 5 ml portions of acetone and the combined mixtures are allowed to stand overnight in a freezer. The resultant dark green microcrystalline material is collected on a medium porosity sintered glass filter and washed with water and diethyl ether.

Collect a UV-Vis spectrum of your sample. Make note of the wavelength of absorption maxima and calculate extinction coefficients (molar absorptivities).

Collect a cyclic voltammogram of your sample using the BAS-50 W.

Conversion to the bis-Bipyridine-(Bipyridine-diacid) Species

Dissolve 50 mg of your $\text{Ru}(\text{bpy})_2\text{Cl}_2$ in 20 ml of ethanol in a round bottom flask equipped with a magnetic stirring rod and a reflux condenser. Add a 5% stoichiometric excess of the 4,4'-diacid-2,2'-bipyridine and begin a steady reflux. The diacid will not dissolve completely. Continue refluxing until the color of the solution changes to an orange-yellow. This may involve running the reaction overnight.

Stop the reflux. Add 10 ml of a saturated aqueous NaCl solution. Evaporate off the ethanol. Collect the solid precipitate on a small sintered glass filter and dry under vacuum.

Run a TLC on alumina with acetonitrile as eluent. It may be necessary to run the material on through a short (3-4 inch) alumina column. Dissolve the material in a minimum volume of acetonitrile and run the solution through the column. Collect the appropriate fraction and evaporate to dryness.

Collect a UV-Vis spectrum of your sample. Make note of the wavelength of absorption maxima and calculate extinction coefficients.

Preparing the Titanium Dioxide

The TiO_2 solution is prepared by incremental addition of 20 ml of nitric acid solution (pH 3-4 in deionized water) to 12 grams of colloidal TiO_2 powder in a mortar while grinding with a pestle. Each 1 ml addition proceeds only after the previous mixing and grinding has produced a uniform lump free paste.

Alternatively, 0.2 ml of acetylacetone in 1 ml of water can be added to the TiO_2 powder. This is followed by addition of 19 ml of water in 1 ml increments while grinding.

Deposition of the Titanium Dioxide

During this procedure care should be taken not to touch the face of the glass electrodes. The glass plates should be held with tweezers or by the edges of the glass. Prepare two electrodes using the following procedure.

A volt-ohm meter should be used to make sure that the conductive side of the glass is face up. The correct reading should be between 10 and 30 ohms. Four pieces of scotch tape are applied to the face of the conductive glass plate to mask a 1-2 mm strip at three of the four edges, and a 4-5 mm strip is masked at the fourth side. Half of the tape extends from the glass to the table to secure the glass. This tape will form a mold or channel 40-50 mm deep into which the TiO_2 solution can flow. Three drops of water based TiO_2 solution is placed on the plate and are distributed evenly by sliding a glass

rod across the plate. The film is then allowed to dry in air. After one minute the tape is removed and the film is annealed in a furnace at 450 °C for 30 minutes. Slowly cool the furnaces back down to room temperature to avoid thermal shock to the glass.

Fabrication of the Solar Cells

Place the electrode in a concentrated aqueous solution of your complex for 10 minutes. After ten minutes check the color of your electrodes. Soak both electrodes for 10 minutes more, if there is significant changes in their color soak the electrodes again. Stop when there is no apparent change in their appearance.

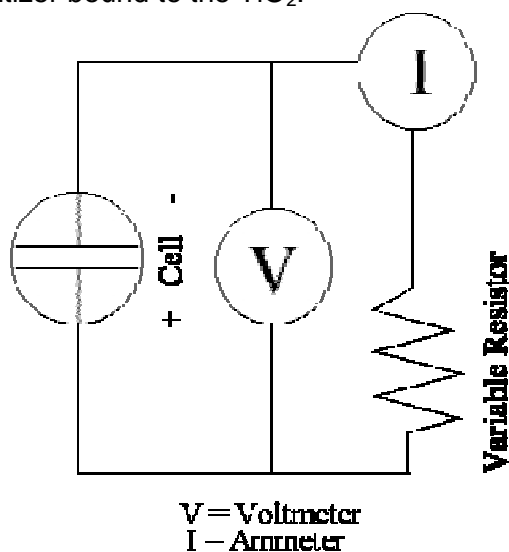
The counter electrode is prepared by rubbing a soft pencil "lead" on the conductive side of a glass plate. The thin carbon layer serves as a catalyst for the triiodide to iodide regenerative reaction. The electrode can be annealed at 450 °C for a few minutes. The counter electrode should be rinsed with ethanol and gently blotted dry before the device is assembled. Prepare two counter electrodes.

The electrolyte is prepared by mixing 0.5 M potassium iodide with 0.05 M iodine in water-free ethylene glycol.

The dye stained electrode is rinsed with water and then ethanol and gently blotted dry. The two electrodes are placed on top of each other with the conductive sides in contact. The two electrodes are offset so that the 4 mm strip of glass that is not coated with TiO₂ is exposed. This will be one of your electrical contact points. There will be another contact point on the other electrode at the opposite end. Two binder clips are placed on the other two sides. One or two drops of iodide/iodine electrolyte solution can then be placed at the edges of the plates and the two binder clips are alternatively opened and closed while in place. The liquid is drawn into the space between the two electrodes by capillary action and can be seen to wet the stained TiO₂ film.

Testing of the Solar Cells

Set up the circuit shown below using two multimeters and a variable resistor. With the variable resistor set to zero measure the voltage and current with no light. Expose to sunlight and record readings. Increase the resistance and record readings. Repeat with the cell that has no sensitizer bound to the TiO₂.



Measure the current as a function of excitation light wavelength from 350 to 750 nanometers in 20 nanometer increments using the fluorimeter as the light source. Correct the data to account for the variations in the fluorimeter lamp output as a function of wavelength over the same range.

Shine the UV lamp on your solar cell. Look for the $\text{Ru}(\text{bpy})_3^{+2}$ luminescence.

Discussion Questions

- 1) What does the change in color on going from $\text{Ru}(\text{bpy})_2\text{Cl}_2$ to $\text{Ru}(\text{bpy})_2(\text{bpy}(\text{COOH})_2)^{+2}$ tell you about the environment around the ruthenium atom? How would the replacement of two Cl^- ligands by the $\text{bpy}(\text{COOH})_2$ ligand effect the relevant properties of the metal atom.
- 2) What properties make for a good dye or sensitizer molecule? How would you evaluate the molecule used in this laboratory?
- 3) Why is the voltage output from an unbiased cell fixed? What determines the voltage?
- 4) Do you observe luminescence from the bound complex? If no, why? Where is the energy going?
- 5) What is the back reaction? Why would we want to minimize it? How do the two molecules compare in this regard? What data is significant?
- 6) How does your current vs. wavelength graph compare to the absorbance spectra of the dye?
- 7) A 1998 paper indicates that charge injection to a semiconductor occurs with iron bipyridine complexes too. Why is this surprising? What other states need to be considered with an iron complex? *J. Am. Chem. Soc.*, **120** (4), 843 -844, 1998.

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