

Synthesis of a ruthenium complex and preparation of an organic light emitting diode

Introduction:

Coordination compounds and complex ions of ruthenium have been of scientific interest because of interesting structural and magnetic properties. The coordination complexes have a central metal atom that is typically positively charged. The metal atom is bonded to multiple ligands, which may be a neutral molecule (e.g. H₂O or NH₃) or an anion (e.g. OH⁻), via coordinate covalent bonds in a Lewis acid-Lewis base reaction. The charged complexes form ionic bonds to other ions to form coordination compounds. The complex ion of the coordination compound is placed in brackets within the chemical formula. In this experiment you will prepare the coordination compound [Ru(bpy)₃](BF₄)₂, which has [Ru(bpy)₃]²⁺ as the coordination complex.

Complex cations adopt a range of coordination numbers from 1 to more than 12, but the two most common coordination numbers are 4 and 6.[1] Coordination numbers do not necessarily define the coordination geometry of a coordination complex. For example, a four-coordinate complex may adopt a tetrahedral or a square planar geometry. Electronic and steric factors influence the observed geometry.[1] Complex ions have diverse colors that arise from electronic absorptions. The energies of the d-orbital are no longer degenerate in a coordination complex, and the splitting depends on the geometry. In the case of a six coordinate complex in an octahedral geometry, the d-orbitals split into two sets of energies – a triply degenerate t_{2g} set at lower energy and a double degenerate e_g set at higher energy. The energy gap, or crystal field splitting, between these levels depends on several factors, two of which are the nature of the ligands and oxidation state of the metal. The crystal field splitting influences the color, with a smaller crystal field absorbing lower energy light, thus reflecting shorter wavelength light. The *d* to *d* electronic transitions, which may be spin-forbidden or Laporte-forbidden, typically have molar extinction coefficients of <1 M⁻¹ cm⁻¹ or between 1-1000 M⁻¹ cm⁻¹, respectively, depending on the centrosymmetric or non-centrosymmetric nature of the molecules. [1] For simple absorptions, a color wheel is helpful in understanding the absorbed and reflected light. Charge transfer absorptions are not restricted by the selection rules that govern *d-d*

transitions. The probability of these electronic transitions is high and the absorption bands are intense, with molar extinction coefficients typically between 1000-50,000 $\text{M}^{-1} \text{cm}^{-1}$. There are two main types of charge transfer absorptions: 1) ligand-to-metal charge transfer (LMCT) and 2) metal-to-ligand charge transfer (MLCT). A MLCT transition occurs when a ligand that is easily reduced is bound to a metal that is easily oxidized. A LMCT occurs when a ligand that is easily oxidized is bound to a metal center (typically in a high oxidation state).

The first part of this experiment involves synthesizing the coordination compound tris(2,2'-bipyridine)ruthenium(II) tetrafluoroborate. It will be used as an intermediate in the formation of a molecular diode. A trivalent ruthenium salt (RuCl_3) is a reactant that is reduced to Ru^{2+} using sodium hypophosphite (NaH_2PO_2) as a reducing agent. The Ru^{2+} reacts with 2,2'-bipyridine and sodium tetrafluoroborate to form $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$. The 2,2'-bipyridine, with two lone pairs of electrons on nitrogen atoms, acts as a bidentate ligand and forms two coordinate covalent bonds.

Procedure adapted from [2], [3], and [4].

Part I: Synthesis of tris(2,2'-bipyridine)ruthenium(II) tetrafluoroborate

Reagent preparation:

I. RuCl_3 from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$

Obtain 3 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and grind to a fine powder in a mortar and pestle. Heat the powder in a vial without a cap at 100 °C overnight, or for at least 3 hours, until the solid turns from a dark black to a dark brown. Remove from furnace, cool to room temperature, and store in a desiccator. This may be prepared ahead of time.

II. NaH_2PO_2 from H_3PO_2

In a fume hood, add 3.0 mL DI H_2O and a stirbar to a 50 mL beaker. Clamp the beaker to a ring stand over a magnetic stirrer. While stirring, add 5.0 mL of H_3PO_2 slowly and mix. Obtain 2.0 g NaOH pellets in a weigh boat. Slowly add the NaOH pellets to the mixture, testing the pH after each addition. The initial pH is acidic. Continue to add NaOH until the solution is between pH of 6-8. If too much NaOH was added, an additional drop of H_3PO_2 could be added to bring the pH into the desired range. If this solution is pre-made

by your instructor, make sure the pH at the time of the experiment still falls within the 6-8 range, and make adjustments if it does not.

Synthesis of [Ru(bpy)₃](BF₄)₂

All reactions should be performed in a fume hood. Using an analytical balance, obtain 0.083g of dried RuCl₃ (F.W. = 207.45 g/mol) and place in a 25 mL Erlenmeyer flask with a small stirbar. The RuCl₃ is hygroscopic so work swiftly. Make sure to close tightly the reaction vial if you are not actively transferring RuCl₃. Add 8.0 mL DI H₂O and place on top of a heating magnetic stirplate. Turn the heat on and warm the stirred solution. Obtain 0.188 g 2,2'-bipyridine (M.W. = 156.19 g/mol) and add to the stirring solution. Use a micropipette to add 440 μL of NaH₂PO₂ to the reaction flask. Mark the level of the solution with a marker and cover the flask with a 1" watch glass. Continue heating to gently reflux near 80°C for 30 minutes, adjusting the heat setting as necessary. For best results and in order to ensure proper uniform heating, without the risk of boiling, perform this heating step in a water bath (make sure your flask is secured), while constantly monitoring the bath temperature. Start at a low heat setting, and get a feel of the behavior of your heating plate, before cranking it up. Once the temperature reaches ~70 °C, start counting the 30 minutes heating time. Periodically check water level and add additional DI H₂O as needed to maintain the volume. Note any color changes that occur during the course of the reaction and form a hypothesis as to why the color changes.

During the 30 minute reflux period, prepare a solution of 0.333g NaBF₄ in 1.5 mL of DI H₂O, in a small vial or 10 mL flask. Swirl until the entire solid dissolves. When the reflux is complete, add the NaBF₄ solution to the reaction flask and stir for 3 minutes. Remove the watchglass, and pick up the stirbar using a stirbar retriever. Allow the solution to cool on the benchtop for about 10 minutes, then place in an ice water bath and continue to cool for 10 minutes. Note the formation of any crystals and the color.

Set up a Buchner or Hirsch funnel filtration apparatus. Ensure it is clamped to a ring stand. If needed, trim a section of filter paper to the correct size and place in the funnel. Moisten the filter paper and turn on the vacuum. Scrape the crystals from the flask into the funnel. Rinse the beaker with one pipet full (~2 mL) of cold ethanol, and let dry under suction for about 10 minutes. Preweigh a 3 dram glass vial or weighing bag and collect the

crystals. Weigh the container and crystals, and then calculate the mass of the recovered product. Collect the IR spectrum. Collect the magnetic susceptibility. Store the crystals for further use and characterization in a subsequent part of the experiment.

Part II: Assembly of a molecular (organic) light emitting diode.

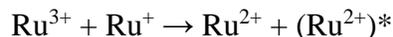
Introduction:

A light emitting diode is a combination of a p-n junction. As a current is passed through a semiconductor, electrons from the valence band can be promoted across the energy gap into the conduction band, a process which allows a semiconductor to conduct electricity. The electron that was promoted to the conduction band leaves behind a hole in the valence band. The holes can move in a material, acting as a positively charged particle and are known as p-carriers. When electrons are the charge carriers, they are referred to as n-carriers. A recombination process may occur when the electron in the conduction band loses energy and falls into the hole in the valence band. In some instances, the recombination process results in the production of photons via luminescence.

In conventional semiconductors, a doping process increases the number of p-carriers or n-carriers. When the n-type semiconductor is brought into contact with a p-type semiconductor, a p-n junction is formed. The holes on the p-side junction move towards the n-site, while the electrons on the n-site move towards the p-side. An external voltage may be applied across the p-n junction, causing it to be biased. A forward bias occurs when the magnitude of the potential difference between the n-side and p-side is reduced, whereas a reverse bias occurs when it is increased. A voltage across the p-n junction allows it to behave as a diode, which only allows current to flow in one direction. An LED is created by inducing forward bias, and light is given off when the electrons and holes recombine on both sides of the p-n junction.

The basic structure of an organic light emitting diode (OLED) consists of a thin organic layer between a transparent anode and a metallic cathode layer. The organic layer consists of (i) a hole injection layer, (ii) an electron blocking layer, (iii) an emissive layer, (iv), a hole blocking layer, and (v) an electron injection layer. The transparent layer commonly used is indium tin oxide (ITO), which is transparent to visible light and has a high work function which promotes the injection of holes into the HOMO level of the organic layer. The cathode is metallic and is a low melting gallium-indium alloy. The application of a voltage to the cell, such that the anode is positive with respect to the cathode, results in a current, consisting of electrons moving from the cathode towards the anode. The electrons hop from one ruthenium complex to another, reducing the Ru^{2+} complex to Ru^{+1} , while

injecting electrons into the LUMO. The ITO oxidizes Ru^{2+} to Ru^{3+} , which can be described as an injection of electron holes into the HOMO. The injected positive holes and negative charges recombine in the emissive layer, emitting a photon ($\lambda = 630 \text{ nm}$) via phosphorescence from an excited state Ru^{2+} formed during the recombination.[5]



The charge carrier mobility is typically low in organic materials; therefore the layers must be very thin. The typical thickness is on the order of 100-200 nm, represented in Figure 1. OLEDs can be very thin and have found use in portable devices including mobile phones, digital cameras, DVD players, PDAs, and car audio displays.

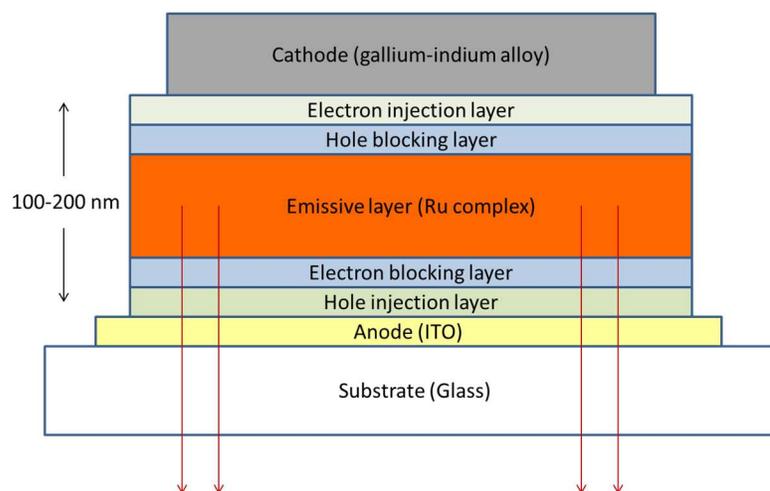


Fig. 1. Pictorial representation of the stacked layers in an OLED.

Experimental part 2:

Pre-lab preparations:

A) polyvinyl alcohol (PVA) solution:

Prepare a hot water bath with sufficient size to hold a 50 mL Erlenmeyer flask and heat at 80 - 90 °C on a hotplate magnetic stirrer. Obtain 0.15 g of polyvinyl alcohol in a small weighing dish. Add 5 mL DI H_2O and a stirbar to a 50 mL Erlenmeyer flask, clamp the flask to a ring stand and lower it into the hot water bath. Place a small watchglass over the opening to reduce evaporation. Ensure the water bath fully covers the water level in the flask, and periodically add water to the bath as needed. Turn on the stirrer and make sure effective stirring occurs. In very small increments, add the PVA to the flask. Ensure each

portion of the PVA is dissolved before adding the next portion to the flask. After all the PVA has been added, continue stirring for at least 5 minutes after all the solid has been dissolved. Remove the flask from the water bath, and pick up the stirring bar using a magnetic retriever. Cap with a stopper or parafilm. The solution can be stored in a refrigerator after use.

B) $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$

Obtain and precisely weigh on an analytical balance 0.035 g of the $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$. Dissolve it in 3 mL of the polyvinyl solution. Obtain an indium-tin-oxide (ITO) coated glass and dry for 10 minutes at 110 °C either on a watch glass in the oven, or by laying it flat on the hot plate. Carefully remove the glass using tweezers. Cool to near room temperature. Using an ohmmeter, determine which side is conducting by placing the tips of the leads at the corners. The conducting side will have a resistance of 30-50 Ω across the diagonal of the slide.

Coating method 1: Using double sided tape, secure the ITO coated slide, with the conductive side up, to the center top of a 2500 RPM fan. Dip the end of a cotton swab into the $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ -PVA solution and blot a thin layer of the solution evenly over the center region of the glass surface. Surround the sample with a splatter shield cover and spin for 30-60 seconds. Repeat for a total of 3-4 times.

Coating method 2: Using double sided tape, secure the ITO coated slide, with the conductive side up, to the benchtop. Dip the end of the cotton swab into the $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ -PVA solution and blot a thin layer of the solution evenly over the majority of the glass surface, but leave an uncoated region (~2-4 mm) around the edges.

After coating with either method, dry the coated glass slide using a hot air blower on the glass for at least 2 minutes. Monitor the evaporation and ensure the surface is completely dry before proceeding. Prepare a mask using a piece of tape (duct) in aluminum foil and punch a 1/8 inch hole. In a disposable small pipet, obtain a very small portion of the liquid gallium-indium alloy and place in a small watch glass. The liquid gallium-indium alloy is an eutectic mixture of 75.5% gallium and 25.5% indium and is a liquid above 16.5 °C. Paint, using a cotton swab, the liquid gallium-indium alloy through the template to add the active metal electrode to several locations on the coated ITO glass. Using a 4.5-6.0 Volt

power supply with leads connected to the terminals, touch the positive lead to the outside edge of the ITO glass that does not have the [Ru(bpy)₃](BF₄)₂-PVA coating. Turn off the lights and carefully touch the negative lead to the gallium-indium contact circle(s). Record your observations. Try reversing the leads and record your observations.

Collect the UV-Vis spectrum using the remaining polyvinyl alcohol solution of the complex. Dilutions will be required. Determine the wavelength of maximum absorption and the molar extinction coefficient.

References

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