

Preparation of an Organic Light Emitting Diode

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Purpose:

Create a circuit using a complex ion between two metal electrodes to form an organic light emitting diode when a current is passed through it.

Learning Objectives:

1. Identify the components and geometry of a complex ion.
2. Predict if a complex ion has a large or small crystal field splitting energy.
3. Distinguish between n-type and p-type semiconductors.
4. Differentiate between phosphorescence and fluorescence.
5. Analyze the components that make up a diode.

Introduction:

Complex ions are charged molecules in which a central metal atom is bonded to two or more ligands, which can be any molecule and/or anion with an unshared pair of electrons. The central metal atom is normally positively charged, while as mentioned above the ligands can be neutral (i.e. H_2O or NH_3) or negative (i.e. OH^-). All the bonds to the central metal atom are coordinate covalent bonds, in that the ligands donate a pair of electrons which the central atom accepts. In this manner, all ligands can be thought of as Lewis bases, while the central metal atom acts as a Lewis acid. Charged complex ions can form ionic bonds to other ions, forming coordination compounds. To designate which part of the coordination compound is the complex ion, the complex ion is placed in brackets within the chemical formula.

The coordination number of a complex ion is the number of bonds that are formed to the central metal atom. The most common coordination numbers are 2, 4 and 6 although other formations do exist. The coordination number of a complex ion determines the shape, or geometry, of the molecule. If the coordination number is 2, then the molecule is said to have a linear geometry. A complex ion with a coordination number of 4 can either be tetrahedral or square planar. A complex ion with a coordination number of 6 has an octahedral geometry.

Complex ions are known for their bright and vivid colors created by the transitional metal cations. The five d-orbitals of a metal cation with octahedral geometry can be split into two sets of different energies, known as crystal-field splitting energy. The size of the energy gap between the two levels of d-orbitals in the crystal-field splitting energy depends on the particular ligands that are bonded to the metal atom. In relation to the color of the complexes, the smaller the crystal-field splitting for a

molecule, the longer the wavelength of light absorbed by that molecule or the shorter the wavelength of light that is reflected.

In this experiment the coordination compound tris(2,2'-bipyridine)ruthenium(II) tetrafluoroborate is used as an intermediate in the formation of an organic diode. To synthesize the complex ion, Ru^{3+} found in the form of RuCl_3 is first reduced to Ru^{2+} using sodium hypophosphite (NaH_2PO_2) as a reducing agent. The Ru^{2+} is then systematically introduced to 2,2'-dipyridyl and sodium tetrafluoroborate to form $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$. The 2,2'-dipyridyl is a bidentate ligand (aka chelating agent) in that one molecule has two pairs of electrons it can donate to the central atom, therefore forming two coordinate covalent bonds (Figure 1).

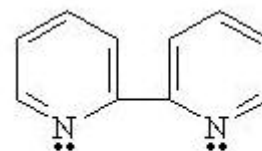


Fig. 1

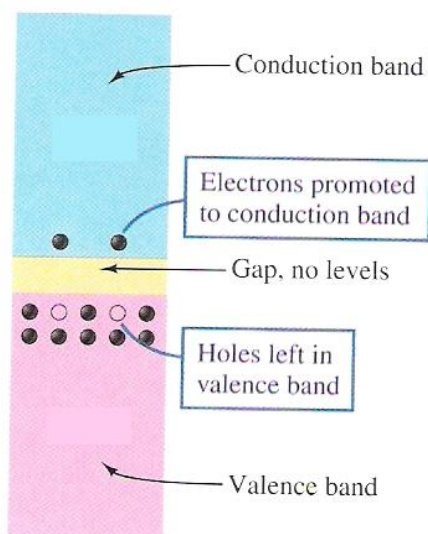


Fig. 2

When a current is passed through a semiconductor, electrons from the valence band can be promoted across the energy gap into the conduction band, which allows the semiconductor to conduct electricity. When an electron is promoted into the conduction band, it is said to leave behind a hole in the valence band (Figure 2). As with electrons, holes can move in the substance, and they act as a positively charged particle. Holes are known as p-carriers for carrying a positive charge, while electrons are known as n-carriers for carrying a negative charge. When an electron in the conduction band loses energy and falls back into a hole it is said to recombine. This electron-hole recombination can produce photons and give off energy in the form of light through a process called photoluminescence.

Semiconductors can be doped to increase the number of p-carriers or n-carriers. A p-type semiconductor is one that has had additional p-carriers added, while an n-type semiconductor has had additional n-carriers added. When an n-type semiconductor is brought into contact with a p-type semiconductor of the same material, a p-n junction is formed. The holes on the p-side of the junction move toward the n-side, while the electrons on the n-side move toward the p-side due to the attraction between the positive and negative charges.

An external voltage can be applied across a p-n junction, causing it to be biased. If the magnitude of the potential difference between the n-side and p-side is reduced, it is called forward bias, and if it is increased it is called reverse biased. Applying a voltage across the p-n junction allows it to behave as a diode. A diode is a device that allows current to only travel in one direction. A light-emitting diode (LED) is created by inducing forward bias, and when the electrons and holes recombined on both sides of the p-n junction light is given off.

The tris (2,2'-bipyridine) ruthenium (II) tetrafluoroborate coordination compound is placed in between two electrodes on a glass plate. These electrodes act as

semiconductors in the reaction. The gallium-indium alloy is a cathode, and the tin oxide coating on the glass acts as an anode. The gallium-indium alloy reduces the adjacent ground state Ru^{2+} in the complex ion to Ru^{1+} , while the tin oxide oxidizes adjacent Ru^{2+} to Ru^{3+} .

Electrons are transferred through the substance from “hopping” on one ruthenium complex ion to another. As electrons travel, Ru^{1+} and Ru^{3+} ions start to move toward the center. When a Ru^{1+} ion is adjacent to a Ru^{3+} ion, they combine to form Ru^{2+} ions. However, some of these ions are in an excited state species. When these ions relax to the ground

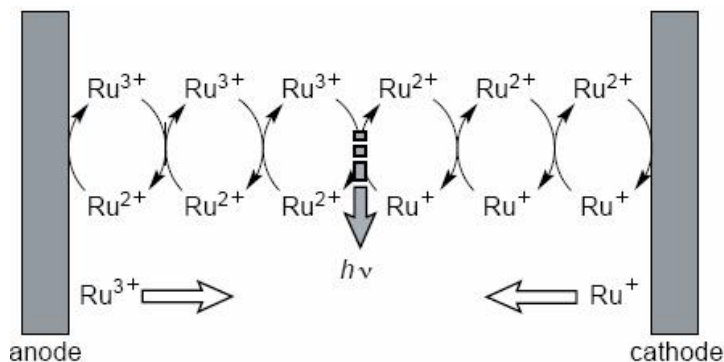


Fig. 3

state, photoluminescence occurs (Figure 3). Photoluminescence can happen rapidly (fluorescence) in as little as 10^{-8} seconds, or slowly (phosphorescence) in that it could take seconds or minutes to occur. Photoluminescence in this reaction was a result of electroluminescence, in that an electrical current was used to excite the electrons to let recombination occur.

Materials:

- *polyvinylalcohol (PVA) solution
- *dried ruthenium(III) chloride
- *sodium hypophosphite (NaH_2PO_2)
- cold ethanol
- 2,2'-dipyridyl
- sodium tetrafluoroborate (NaBF_4)
- gallium-indium alloy aka GaIn Eutectic
- ohmmeter
- masking tape or double sided tape
- hot air blower
- 4.5-volt power supply
- tin oxide conductive glass (1" x 1" x 2.3 mm)

*prepared beforehand

Procedure:

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

Prepare in a fume hood:

1. Measure 0.083 g (to the nearest 0.001 g) of the dried RuCl_3 (MM = 207.45 g) in a 30-mL beaker and place a stirbar in it.
2. Add 8 mL of water to the beaker, clamp it to a ring stand, and place beaker on top of a heater/magnetic stirrer. Turn the heat on ~ 5 and start mixing the solution.
3. In a weigh boat, measure 0.188 g (to the nearest 0.001 g) of 2,2'-dipyridyl (MM = 156.19 g) and add to the beaker.
4. Use a micropipette to measure out 440 μL of NaH_2PO_2 into the beaker. Cover with a watch glass to prevent evaporation, and mark the initial water level on the outside of the beaker with a permanent marker.
5. Reflux the solution for 30 minutes. If the solution starts to bubble too rapidly, turn down the variac. During this time, check the water level every 5 minutes or so, and add additional water to maintain volume if necessary.

What color change is occurring? What is this the result of (hint: what is being formed)?

6. Measure out 0.333 g of NaBF_4 in small glass vial and add 1.5 mL of water, swirling mixture so all the solid dissolves.
7. After refluxing is complete, add the NaBF_4 solution to the beaker, and allow it to stir for an additional 3 minutes. After the 3 minutes, remove the watchglass and stirbar from the beaker.
8. Remove beaker from heat and stirrer and allow it to cool on counter for ~ 10 minutes until solution is about room temperature. Then place beaker into an ice water bath and continue to let it cool for another 10 minutes. Bright orange crystals should be forming.
9. Set up a suction filtration apparatus using a Hirsch funnel and filter flask clamped to a ring stand. Place filter paper in funnel and moisten it with water, and turn on suction.
10. Scrape as much of the crystals as possible from the beaker into the funnel using a spoonula.
11. Rinse the beaker out with one pipet full of cold ethanol and pour into funnel. Rinse the contents of funnel with one pipet full of cold ethanol, and let it suction dry for about 10 minutes.
12. Preweigh a small glass container. When suction drying is complete, scrape the crystals from the funnel into this vial. Reweigh the vial and calculate the mass of product recovered. Record all masses below.

Mass container + product	
Mass container	
Mass product	

II. Creating an Organic Light Emitting Diode

1. In a small glass vial, measure out 0.035 g (nearest 0.001 g) of the $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ and dissolve it in 3 mL of the PVA solution.
2. Obtain a tin oxide-coated piece of glass, and using an ohmmeter, determine which side is the conducting side. The conducting side will have a resistance of 20-30 ohms when contacts are placed at diagonal corners of the glass.
3. Use double-sided tape or roll a small piece of masking tape to produce a double sticky side, and tape the tin oxide glass with the conductive-side up to the bench top.
4. Dip the end of a cotton swab in the PVA solution, and blot a thin layer of the $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ polyvinylalcohol solution **evenly** over the majority of the surface of the glass. **It is important** to leave some uncoated regions around the edges.
5. Use a hot air blower on the glass for at least 2 minutes. Evaporation is readily visible, but make sure surface is completely dry before proceeding.
6. In a pipet, suck up a very small portion of the liquid gallium-indium alloy into the tip. In the center of the glass, place one small drop of the alloy, and dispense the rest of it back into the original container. With the same pipet, suck up most of the drop that was dispensed on the glass surface, and return this to the original container. All that should be left is a small, flat, silver-colored circle on the slide.
7. Using a 4.5-Volt power source connect positive and negative leads to the terminals. Touch the positive lead to the outer edge of the tin oxide glass that does not have the $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ coating on it. Gently touch the negative lead to the gallium-indium spot to complete the circuit. Turn off the lights.

What do you observe on the underside of the glass? Reverse the positive and negative lead on the glass—now what do you observe?

Questions

1. Calculate the percent yield of $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ (MM = 743.29 g) recovered. Use the RuCl_3 as the limiting reactant.
2. Does the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex exhibit a small or large crystal-field splitting energy? Explain. (Hint: think about the color of the pure compound)
3. Identify the central atom, ligand(s), and coordination number in the coordination compound $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$. Draw a sketch of the complex ion.
4. In what direction is the current flowing in the circuit (anode \rightarrow cathode or cathode \rightarrow anode)? How do you know this?
5. Identify which electrode was the n-type semiconductor and which was the p-type semiconductor.

Pre-lab materials

Ruthenium(III) chloride trihydrate ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$)
Polyvinylalcohol (PVA) with average MW 124,000-186,000
Hypophosphorous acid 50 wt % in water (H_3PO_2)
Sodium hydroxide pellets (NaOH)
Mortar and pestle
pH strips

Pre-lab Preparations for Individual

A. Drying $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ to form anhydrous RuCl_3

1. Grind about 0.2 grams of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in a mortar and pestle until it is a fine powder.
2. Place powder in a small beaker and heat in 100°C oven until solid turns from dark black to dark brown (~ 3 hours).

B. Polyvinylalcohol solution

1. Set up hot water bath on a magnetic stirrer and heat water to a temperature between 80°C and 90°C .
2. Measure 0.15 grams of polyvinylalcohol (PVA) in a weighboat and put aside.
3. In a 50-mL 14/20 Erlenmeyer flask add 5 mL of water and a stir bar. Clamp flask to a ring stand and lower it into the water bath. Make sure there is enough water in the bath to completely cover the water level in the flask.
4. Turn on the magnetic stirrer. In very small increments, add the PVA to the flask. Make sure each portion of PVA is fully dissolved before adding the next portion. When you are not adding the PVA to the flask, cover it with a watch glass to prevent evaporation.
5. After all the PVA has been added, let the solution mix for at least an additional 5 minutes. Remove it from the water bath and make sure all the solid has dissolved. If it has, let that cool and mix for an additional 5 minutes.
6. Remove the stir bar from the flask, and the solution can be stored capped in a refrigerator.

C. Preparation of NaH_2PO_2 from H_3PO_2

This is to be done in a fume hood:

1. In a 5-mL Wheaton vial add 600 μL of water and a stirbar, and clamp vial to ring stand over a magnetic stirrer.
2. Turn stirrer on. Add 1000 μL of H_3PO_2 slowly and let it mix.
3. In a weigh boat measure out around 0.40 grams of NaOH pellets. Using your spoonula, crush the pellets to form a powder.
4. Slowly add NaOH to this mixture, and using the pH strips, test the pH after each addition. The pH is initially very acidic, but you want to add enough NaOH so

that the solution is between a pH of 6-8. It will take ~ 0.39 g or around 4 of the NaOH pellets for this to occur. If the solution becomes too basic, additional drops of H_3PO_2 can be added to bring the pH in the correct range.

Pre-lab preparations for 25 Students

A. Drying $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ to form anhydrous RuCl_3

1. Grind about 3 grams of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in a mortar and pestle until it is a fine powder.
2. Place powder in a small beaker and heat in 100°C oven until solid turns from dark black to dark brown (~ 3 hours).

B. Polyvinylalcohol solution

1. Set up hot water bath on a magnetic stirrer and heat water to a temperature between 80°C and 90°C .
2. Measure 3.0 grams of polyvinylalcohol (PVA) in a weighboat and put aside.
3. In a 250-mL 14/20 Erlenmeyer flask add 100 mL of water and a stir bar. Clamp flask to a ring stand and lower it into the water bath. Make sure there is enough water in the bath to completely cover the water level in the flask.
4. Turn on the magnetic stirrer. In very small increments, add the PVA to the flask. Make sure each portion of PVA is fully dissolved before adding the next portion. When you are not adding the PVA to the flask, cover it with a watch glass to prevent evaporation.
5. After all the PVA has been added, let the solution mix for at least an additional 5 minutes. Remove it from the water bath and make sure all the solid has dissolved. If it has, let that cool and mix for an additional 5 minutes.
6. Remove the stir bar from the flask, and the solution can be stored capped in a refrigerator.

C. Preparation of NaH_2PO_2 from H_3PO_2

This is to be done in a fume hood:

1. In a 100-mL beaker add 15.0 mL of water and a stirbar, and clamp the beaker to ring stand over a magnetic stirrer.
2. Turn stirrer on. Add 25.0 mL of H_3PO_2 slowly and let it mix.
3. In a weigh boat measure out around 10.0 grams of NaOH pellets.
4. Slowly add NaOH pellets to this mixture, and using the pH strips, test the pH after each addition. The pH is initially very acidic, but you want to add enough NaOH so that the solution is between a pH of 6-8. If the solution becomes too basic, additional drops of H_3PO_2 can be added to bring the pH in the correct range.

Supplies for 10 students

2.0 g $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$

1.5 g of polyvinylalcohol solid

10.0 mL of H_3PO_2

5.0 g of NaOH pellets

1.0 g of the dried RuCl_3

2.0 g of 2,2'-dipyridyl

5.0 mL of NaH_2PO_2

25.0 mL of cold ethanol

30.0 mL of the PVA solution (premade)

10 mortar and pestles

10 tin oxide glass slides

10 cotton swabs

very small portion liquid gallium-indium alloy

pH strips

alligator clips

4.5-Volt power sources

Ohmmeters

} can be shared among students

Suggestions for placement:

With the techniques used to synthesize the complex ion, this lab is best suited for an organic chemistry lab. However, if the polyvinylalcohol and tris (2,2'-bipyridine) ruthenium (II) tetrafluoroborate were made ahead of time, preparing the organic light emitting diode portion of the lab would be well suited for a general physics lab.

Answer Key

1. Calculate the percent yield of $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ (MM = 743.29 g) recovered. Use the RuCl_3 as the limiting reactant.

Theoretical Yield

$$0.083 \text{ g RuCl}_3 \left(\frac{1 \text{ mol RuCl}_3}{207.45 \text{ g RuCl}_3} \right) \left(\frac{1 \text{ mol ion}}{1 \text{ mol RuCl}_3} \right) \left(\frac{743.29 \text{ g ion}}{1 \text{ mol ion}} \right) = 0.30 \text{ g ion}$$

Actual yield = 0.23 g (for example)

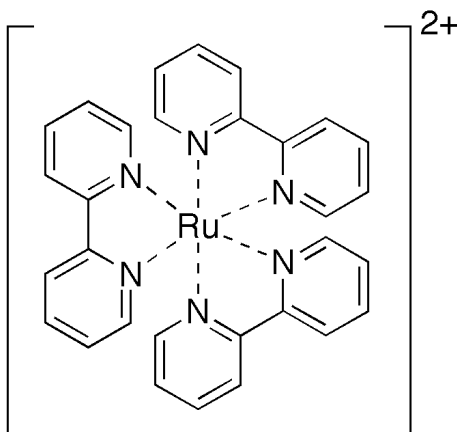
% Yield

$$\left(\frac{\text{Actual}}{\text{Theoretical}} \right) \times 100 = \left(\frac{0.23 \text{ g}}{0.30 \text{ g}} \right) \times 100 = 77\%$$

2. Does the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex exhibit a small or large crystal-field splitting energy? Explain. (Hint: think about the color of the pure compound)

It has a large crystal field splitting energy. The color of a compound is the wavelength of light that an object reflects. Since it is orange, the compound reflects a relatively longer wavelength of light. The longer the wavelength reflected, the shorter the wavelength absorbed, or the larger the crystal field splitting energy.

3. Identify the central atom, ligand(s), and coordination number in the coordination compound $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$. Draw a sketch of the complex ion.



Central atom = Ru^{2+} Ligand = bpy coordination # = 6

4. In what direction is the current flowing in the circuit (anode → cathode or cathode → anode)? How do you know this?

If flows from cathode to anode because 1) the negative lead was connected to the cathode and the positive lead was connected to the anode (electrons travel negative to positive) and/or 2) it's at the cathode the reduced ruthenium ions are formed, which move toward the anode with an extra electron (carry the current).

5. Identify which electrode was the n-type semiconductor and which was the p-type semiconductor.

**Cathode and/or gallium-indium alloy = n-type
Anode and/or tin oxide = p-type**

6. Would the photoluminescence in this reaction be classified as fluorescence or phosphorescence? Why?

It is phosphorescence because it took several seconds for the light to appear where as if it were fluorescence it would happen almost instantly.

7. When the negative and positive leads were switched no light is emitted. Why is this and what does this prove?

This shows that the circuit only allows current to flow one way, and proves that the device is a diode.

Citations

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