

Learning About Materials Science by Making Organic Light-Emitting Electrochemical Thin Film Devices

Lab Documentation Supplementary Material for Online Publication, *Journal of Chemical Education*
H. Sevian, S. Muller, H. Rudmann, M. F. Rubner

Notes for the Instructor

The time that students require to carry out the device fabrication depends largely on advance preparation done by the Instructor. The timeframe can be shortened, for example, if the Instructor prepares the solutions ahead of time. Approximate timeframe for device fabrication procedure as written: two to three 50-minute lab periods. Investigations by students into factors affecting device performance require additional time. The instructor may wish to allow two to three additional 50-minute lab periods for this.

Hazards

The principal chemical hazards are associated with using the ruthenium (II) chloride salt and the gallium-indium eutectic. The ruthenium salt should be treated as any transition metal salt; it is not a known carcinogen or sensitizer. The gallium-indium eutectic is a liquid metal and should be handled with care so that it does not spill. There are no significant hazards reported for the liquid Ga-In eutectic. If spilled, it can be cleaned up by taking it up with a pipet and then cleaning the remainder of the spill with a cloth wet with an ammonia solution, such as glass cleaner.

CAS numbers

[Ru(bpy)₃](Cl)₂•6H₂O

50525-27-4

Ga:In eutectic

No CAS number for mixture, Ga is 7440-55-3 and In is 7440-74-6

We purchased these materials from Aldrich. Product numbers are 22,475-8 for the tris(2,2'-bipyridyl) ruthenium (II) chloride hexahydrate, and 49,542-5 for the gallium-indium eutectic.

Materials to provide at each lab station

Slides pre-coated with the transparent indium-tin-oxide anode (2)
Plastic cover slips (2)
Pipets (2)
Tweezers
Cotton swabs (4)
100-mL or larger beakers (4)
Glass vial containing [Ru(bpy)₃](Cl)₂•6H₂O
Glass vial containing polyvinyl alcohol
Empty glass vial
5-volt/200 mA DC fan
6-volt/100 mA plug transformer
Wire cutters/stripper
47-ohm resistor
Aluminum foil
Cellophane tape
Clear plastic cup
Power supply
Multimeter
Wire leads with alligator clips (2)
Lens paper or Kimwipes

Materials/Reagents to provide at a central location

Distilled water
Ammonia-based glass cleaning solution, such as Windex
Isopropyl alcohol, 99%
Gallium-indium eutectic
Hole-puncher
Carpet tape
Epoxy
Gloves
Drying oven
Hair dryers
Ultraviolet light

The following numbered notes correspond to the steps in the Procedure outlined for students in the Student Handout.

1. Glass slides pre-coated with ITO

Sheets of ITO-coated glass can be ordered from DCI, Inc., in Olathe, Kansas (tel. 913-782-5672). Use a glass cutter against a straight edge to prepare approximately 1" × 1" square pieces.

2. Use of multimeter

Make sure that the multimeter leads are not touching one another when taking the conductivity reading on the surface of the slide.

3. Components of spin coater

The specifications given make a spin coater that spins at 2500 rpm. The exact speed is not crucial, so components that differ slightly can be used. The least expensive route is to order the fans and plug transformers from surplus suppliers, such as Hosfelt or Marion-Jones. Order plenty for everyone because surplus supplies sell out. The spin speed can be measured using a strobe light and an asymmetric pattern drawn on the fan (or on a piece of tape attached to the center of the fan).

4. Solution preparation

The solutions can be prepared ahead of time to save time.

5. Operation of the spin coater

Since the spin coater operates at high speed, it is important that it be securely fastened to the work surface. The spin coaters can be cleaned using a wash bottle with distilled water. Dispose of the aluminum foil and plastic cup as with any materials containing transition metal salts.

6. Drying the slide

Alternatively, a hair dryer can be used to dry the slide. Make sure to have a good grasp on the slide with the tweezers and hold the slide far enough away from the end of a hair dryer to ensure that the polymer film does not warm up and flow. Dry for 1 to 2 minutes.

7. Film quality

Non-uniform films still work.

8. Application of Ga-In eutectic as metallic cathode

Caution students against spilling the eutectic. Wear gloves to clean any spills. If the eutectic should spill, first remove as much as possible using a pipet. Then, clean up the remainder with a cloth wet with an ammonia-based solution. Place the cloth and anything contacting the eutectic in a Ziploc baggie, label it as hazardous waste, and dispose of it according to standard/OSHA procedures of the school system.

9. Sealing with epoxy

Mix the epoxy immediately before using it. Any brand of epoxy will do.

10. Powering up the device

The room lights may need to be dimmed to see the initial glow.

Disposal Instructions

Wastes generated from this lab are of two varieties: solid and liquid. Solid wastes include any aluminum foil, plastic cups or other solids that have captured drippings of the solutions used, and used devices. Solids also include anything that has held the Ga-In eutectic (although it is a liquid eutectic, it behaves as a solid when in small quantities). For any solid wastes, place them in plastic Ziploc baggies and label as solid waste, indicating chemicals used. Then dispose of these solid wastes according to standard/OSHA procedures appropriate to the school system. Liquid wastes include leftover solutions. These should be collected, labeled, and also disposed of according to standard procedures.

Factors affecting device performance that students may wish to explore

The following list is offered to instructors, and is based on our own experiments. In this laboratory, students are encouraged to investigate the effects of varying certain factors. Here we provide the Instructor a brief summary of experimental results that can be expected and theoretical explanations.

Humidity – Even an environmental variable as mundane as moisture can have a profound effect and make the difference between the success and failure of a device. The pedagogy behind studying this effect is to point out that

the real-world environment is filled with such environmental variables, and this explains the need for clean rooms and other experimental controls in research and industry. Humidity provides competing factors that affect device performance. Moisture in the film degrades the film, causing the device to short more easily. However, allowing some moisture in the film facilitates counterion motion, which leads to a decreased response time. The device lights more quickly and also dies more quickly.

Ion Density – The ion density in the film can be controlled by varying the ratio of polymer solution to ruthenium complex solution. When the ruthenium density is low, ruthenium complex ion centers are far separated, which reduces the facility of electron hopping. However, a lower ruthenium density also reduces self-quenching. On the other hand, with less polymer solution in the spin-on mixture, the mixture is less spinnable, which contributes to more defects in the film, causing it to short more easily. The ratio we have given in the procedure represents an optimum between these two extremes.

Film Thickness – The film thickness can be controlled by varying either the solution concentrations (lower concentrations lead to thinner films) or the spin-coater speed (lower speeds lead to thicker films). Thicker films are more robust and short less easily, but the trade-off is that they require more voltage to drive the device because the potential difference drives counterion movement. The spin-speed recommended (~2500 rpm) and the concentrations specified in the procedure lead to a film thickness of 1200 Å (as measured on a profilometer). We have found this to represent an optimum that balances the trade-offs. An easy way to control the spin speed is to connect the spin-coater to a variac. Spin speed can be easily measured using a strobe light, and this measurement is an exciting spin-off of the lab for students.

Drying Time – The solutions are all water-based, so to remove the water, the temperature of the drying oven should be set above 100°C. Too far above this temperature, the polymer will flow or degrade (m.p. of polyvinyl alcohol is ~300°C). The better the film is dried, the longer the duration of the device. Control of this variable will demonstrate to students the necessity of careful laboratory procedure.

Ambient Operating Temperature – Operating temperature affects counterion mobility. Lower temperature, which can be achieved by operating the device inside a walk-in refrigerator or freezer, slows ion motion, which in turn increases the response time. Higher temperatures, which can be explored by operating the device inside a drying oven or incubator with a glass door, allow ions to move faster, but also causes the films to short more rapidly, as they are fragile.

Sealants Other Than Epoxy – We tried many other sealants, but found that most resins dissolve the thin film. Epoxy worked best for us, but silicone sealants also worked.

Contact Area Between Eutectic and Thin Film – By studying the films under a profilometer, and looking at shorted films, we found that shorts occur where there are pinhole defects in the film. Larger areas of contact between the metallic cathode and the film increase the probability of finding a pinhole defect. Students will discover this if they try to make designs in the mask for adding the eutectic; the designs will theoretically cause the light to be emitted through the ITO in designs. One possible extension related to this variable is that students can explore the pinhole density by making successively larger circles in masks to hold the eutectic.

Learning About Materials Science by Making Organic Light-Emitting Electrochemical Thin Film Devices

Lab Documentation Supplementary Material for Online Publication, *Journal of Chemical Education*
H. Sevian, S. Muller, H. Rudmann, M. F. Rubner

Student Handout

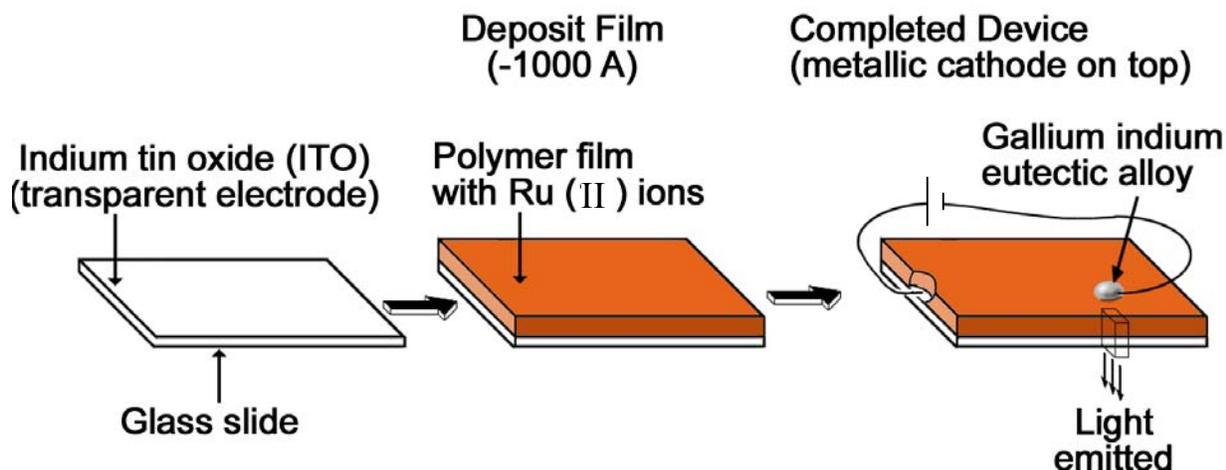
Introduction

High-tech materials are part of our everyday lives. Most of these materials are developed and improved by modifying the materials involved and processes utilized in manufacture. In the engineering design process used, materials scientists take into consideration both the operating mechanisms of devices made from high-tech materials and the microscopic structure of the materials that gives rise to its properties. The experiments on light-emitting thin organic films described here give you the opportunity to learn about electrochemistry, spectroscopy, the microscopic structure of the solid state and basic circuits.

It is only recently that organic materials have been made to efficiently emit light.^{1,2,3} Polymers and small molecules can be induced to emit light by passing an electric current through an appropriate liquid or solid solution. The resulting electroluminescence involves electrons hopping to transfer charge across the film, and light emission by phosphorescence from the excited state created in a combination reaction. Thin films of these materials only 60 to 100 molecules thick (1000 to 1500 Å)⁴ can emit light that is brighter than the equivalent area on a television screen. There are many applications for a device that does this. The advantages of producing light from thin plastic films include the flexibility of the plastic, low cost of the materials involved, and the ease of manufacture. Any flat panel display that lights up is a candidate for this technology, including such applications as display panels in automobiles, large-screen advertising displays, and backlit watch dials. Perhaps someday we may even see wallpaper television screens that utilize this technology.

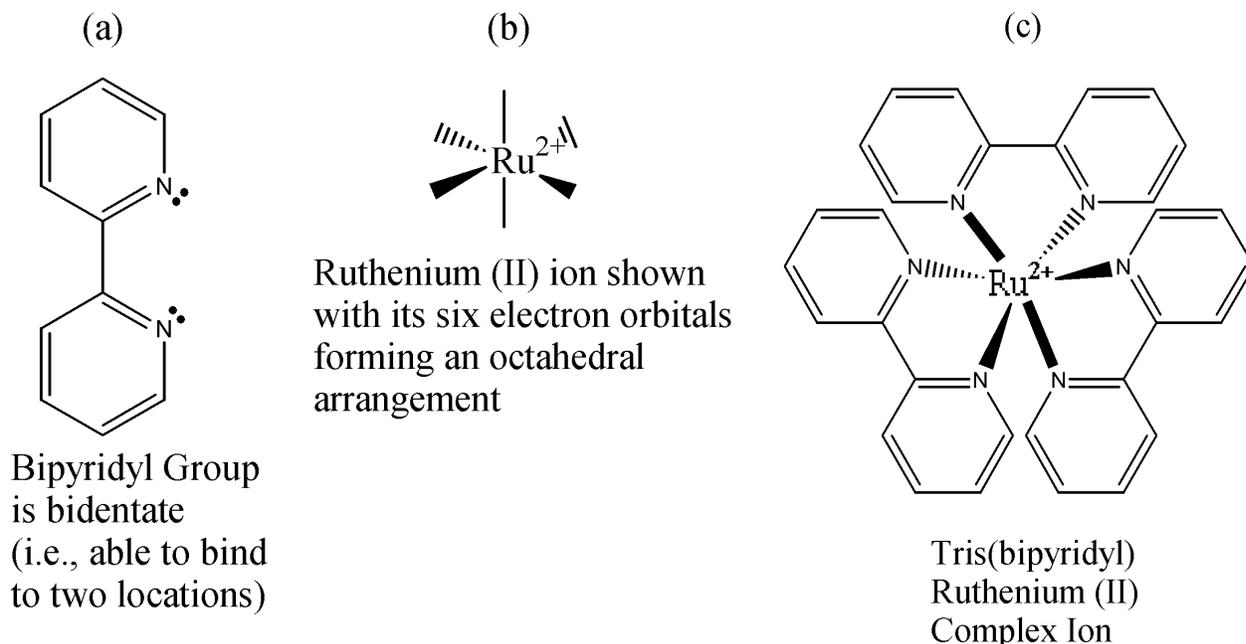
In these investigations, you are going to make light-emitting devices by spin coating a thin film containing ruthenium (II) complex ions onto a glass slide.^{5,6,7} The slide is coated with a transparent electrode on one side (see Figure 1) so that the light emitted by the film is visible through the electrode and the glass. The procedure involves

Figure 1. Device fabrication: Begin with glass slide coated with ITO. Spin-coat thin film containing $[\text{Ru}(\text{bpy})_3]^{2+}$ and Cl^- ions embedded in polymer matrix. Place metallic Ga-In cathode on top of thin film and connect Ga-In and ITO to voltage source to emit light.



making solutions of ruthenium (II) complex ions (Figure 2) and a water-soluble polymer and then spin-coating a thin layer of a mixture of these onto the slide,

Figure 2. Structures of (a) bipyridyl group (b) ruthenium ion showing octahedral symmetry (c) tris(bipyridyl) ruthenium (II) ion.



using a spin-coater you have constructed. After drying the film to form a thin layer of ruthenium (II) complex ions embedded in the polymer matrix, droplets of a gallium-indium eutectic alloy are added to the top of the film to serve as the cathode.

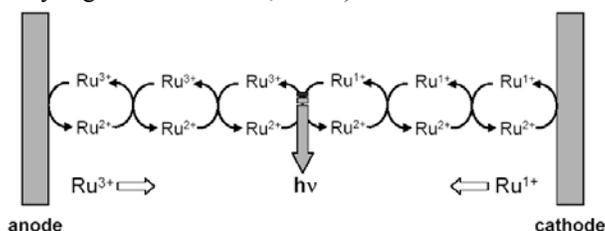
As current passes through the film, the ruthenium (II) ions oxidize to Ru^{3+} at the anode and reduce to Ru^{1+} at the cathode. Electrons are transferred toward the anode, hopping from one ruthenium ion to another. As electrons hop from ion center to ion center, the residences of the two electrochemical species Ru^{3+} and Ru^{1+} are transferred toward the center, until two unlike ions are adjacent near the middle of the film (Figure 3). At that point, Ru^{1+} and Ru^{3+} combine to form a ground state and an excited state Ru^{2+} species, the latter of which emits light as it returns to its spectroscopic ground state. Once the device is working, you can use your understandings of the chemical principles involved to investigate modifications to the process to improve the device performance.

To understand how the device works so you can modify it and explore its limitations, you must learn about the following:

- Electrochemistry occurs as current passes through the film.
- The film consists of ruthenium complex ions arranged in a polymer matrix.
- Light is emitted when Ru^{1+} and Ru^{3+} combine to form two Ru^{2+} complex ions, one of which is in an excited state. Excited ruthenium (II) complex ions emit light via phosphorescence.

In these experiments, you also practice important laboratory skills. You will make solutions of polyvinyl alcohol and the ruthenium (II) complex, and build and operate circuits in the laboratory, varying the voltage and/or current in both the spin coater and the device. You must also take into consideration environmental conditions, such as humidity. Once you have a working device, you should next establish plans for investigating the effects of modifying the device. To do this, you must keep in mind the process of how materials are developed and improved, *i.e.*, the engineering design process.

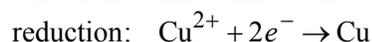
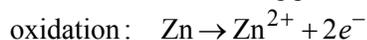
Figure 3. Electron transfer through the ruthenium film, showing oxidation occurring at the anode and reduction occurring at the cathode. Electrons hop from the cathode toward the anode, causing Ru^{1+} and Ru^{3+} centers to move toward the center of the film. Light ($h\nu$) is emitted where a Ru^{3+} ion meets a Ru^{1+} ion somewhere in the middle of the film. (Inspired by Fig. 7 from Maness, *et al.*⁸)



Background

Solid State Electrochemistry

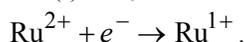
Electrochemical processes that occur in solids bear much in common with those in liquid solutions, so we will consider liquids first and then discuss the differences. In a typical electrochemical cell or battery described in textbooks, two species of ions in solution, such as zinc (II) ions (from a solution of ZnSO_4) and copper (II) ions (from a solution of CuSO_4), are separated by a salt bridge. The function of the salt bridge is to allow the migration of ions, while the cell is operating, to balance the charges in the half cells. In many textbook examples, sulfate ions (SO_4^{2-}) typically serve as counterions. While electrons are conducted through the wire from one electrode to the other, the salt bridge allows ions to migrate into or out of it to rebalance the charges in the half-cells. Current in the cell flows spontaneously in the direction in which zinc metal is oxidized to Zn^{2+} while Cu^{2+} ions are reduced to copper metal. The two half-reactions taking place are



Current (positive charge) is said to flow in the opposite direction of the electrons. The voltage produced by the battery, under zero-current conditions, can be calculated from the difference between the oxidation and reduction potentials of the two half-reactions. For example, as compared to a standard hydrogen electrode, the reduction potential for the zinc half-reaction above is -0.763 V , and for the copper half-reaction above is $+0.337 \text{ V}$. These can be used to predict the net cell potential as $0.337 \text{ V} - (-0.763 \text{ V}) = 1.100 \text{ V}$.

In the solid state, the process of electrochemistry is similar, but there are two principal differences. The two electrochemically active species, Ru^{1+} and Ru^{3+} , must first be created at the two electrodes by placing a sufficient potential difference across the film, according to the difference between the reduction potentials of the two half-reactions, just as in the traditional battery. For these species to meet and react, electrons must hop from one ruthenium complex ion center to another, while small counterions (Cl^- ions in this film) move through the film to establish charge neutrality in the film for steady state operation. Counterion movement is slow through a solid, therefore the film must be thin. The potential difference is what drives the counterions to move, so the higher the voltage the faster the counterion movement. However, the electrodes will react, causing the film to degrade and short out at high enough voltages, so there is a trade-off.

The process that occurs in the ruthenium film is electrical conduction by electron transfer through the ruthenium complex ion centers. Figure 3 is a sketch of the cross-section of a film, rotated 90° from Figure 1. As in the liquid state, electrons enter the cell through the cathode, and ruthenium (II) ions near that electrode are reduced to ruthenium (I) ions, as shown in the following half-reaction:



Meanwhile, electrons are removed from the cell through the anode as ruthenium (II) ions near that electrode are oxidized to ruthenium (III) ions:



To predict the voltage necessary to drive the device, we again turn to redox potentials. For the $\text{Ru}^{2+/1+}$ half-reaction, as compared to an Ag/Ag^+ electrode, the potential is -1.66 V , while the $\text{Ru}^{3+/2+}$ half-reaction against the Ag/Ag^+ electrode, has a potential of 0.94 V .⁸ Therefore, the voltage bias must be at least 2.60 V .

In order for electrons to complete a circuit, charges must flow. Otherwise, reduced and oxidized species would simply build up at the inside surfaces of the cathode and anode, respectively, and current would stop flowing as soon as all the inside surfaces were filled with these species. The ruthenium ions are in fixed positions, unlike in a solution in liquid state electrochemistry. Therefore, the charges must migrate toward the center of the film by the

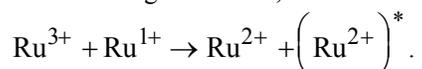
process of electron transfer (see Figure 3). In each hop, one electron is transferred from a ruthenium complex ion center to one adjacent to it. Electrons are always moving from their site of injection into the film (the cathode) to their site of removal from the film (the anode). Once a Ru^{1+} complex ion has been created at the cathode, an electron hops toward the anode by moving to a Ru^{2+} complex ion center closer to the middle of the film. The movement of the electron causes the Ru^{1+} to become a Ru^{2+} while the Ru^{2+} becomes a Ru^{1+} , effectively moving the location of the Ru^{1+} charge center toward the center of the film. Meanwhile, near the anode, Ru^{3+} charge centers move toward the center of the film as electrons hop toward the anode.

Since the electrons are moving toward the anode, counterions must move in the opposite direction to balance the charge in the film. In the films you make, the role of the counterions is filled by chloride ions (Cl^-), which are slightly mobile within the polymer matrix in which they are embedded. The reduced mobility of counterions in the solid state leads to a charging response time, however, causing a delay between when voltage is applied to the cell and when a steady light is finally emitted.

Electrochemiluminescent Films

Due to the three bipyridyl groups each binding to the Ru^{2+} ion in two places (see Figure 2), the ruthenium complex ion resembles a three-dimensional pinwheel that can be approximated as spherical, with a diameter of about 15\AA . Since each of the bipyridyl groups has two points of attachment to the ruthenium ion; bipyridyl is therefore termed bidentate. While the ruthenium ion is shown as octahedral, when it actually bonds to the three bipyridyl groups, the 90° angles become distorted, as the bipyridyl group forces the N-Ru-N angle it makes to be slightly less than 90° .

The complex ion is phosphorescent. The process involved in the light-emitting thin film that you investigate in this module is called electrochemiluminescence, since the source of the energy that excites the electron is electrochemical. After the electrons and "holes" (the lack of electrons) have traveled inward toward the center of the film via electron transfer, somewhere near the middle of the film a Ru^{3+} ion meets a Ru^{1+} ion, as shown in Figure 3. When this occurs, an electron is transferred from the Ru^{1+} ion to the Ru^{3+} ion, giving two Ru^{2+} ions. One of these is in the ground state, and the other is in an excited state:



The ruthenium (II) ion in the excited state then decays to the ground state, through phosphorescence, emitting light in the process.

The ruthenium complex ion that is employed in these films is able to emit light; this phenomenon is called luminescence. When a molecule absorbs energy, one or more electrons in the molecule are promoted to higher energy levels as the molecule accepts the energy. There are several processes that can take place inside the molecule after the absorption of energy and formation of an electronically excited species. Thermal degradation of the energy is a common fate for the excitation energy, depending on the complex, the temperature, and other factors. In this case, the energy is transferred into vibration, rotation, and translation of neighboring molecules. Thus, thermal dissipation of the energy transforms it into thermal energy of the environment. Another possible avenue for the energy is luminescence, which is the ability of a molecule to discard its excitation energy by emitting a particle of light, called a photon.

There are two mechanisms of luminescence (radiative decay that gives off light): fluorescence and phosphorescence. The difference between these two mechanisms can be ascertained by what happens when the energy source causing electronic excitation is removed. In fluorescence the light emitted by the excited molecules ceases immediately when the source is removed. In phosphorescence, the light persists afterward, and may persist for long periods of time (typically seconds or fractions of seconds, but longer times of hours and even days have been observed). Glow-in-the-dark materials contain phosphorescent species. This difference in behavior suggests that fluorescence involves an immediate conversion of the absorbed energy into light energy that is emitted, while in the process of phosphorescence the energy is stored somewhere and slowly relaxes to another state.

Figure 4. The difference between singlet and triplet electronic states is in the spins of two of the state's electrons.

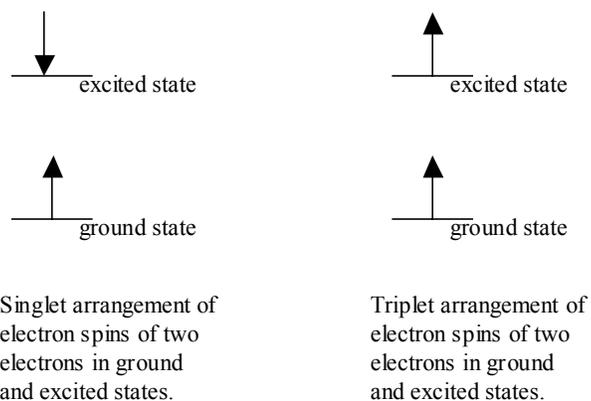
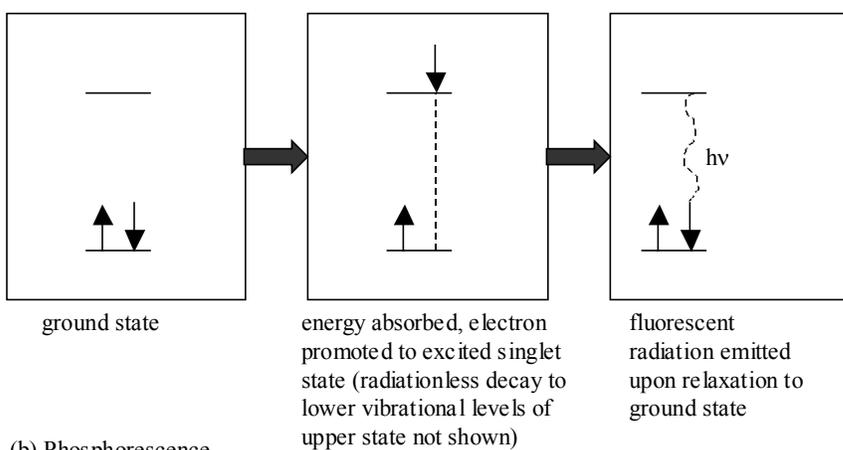
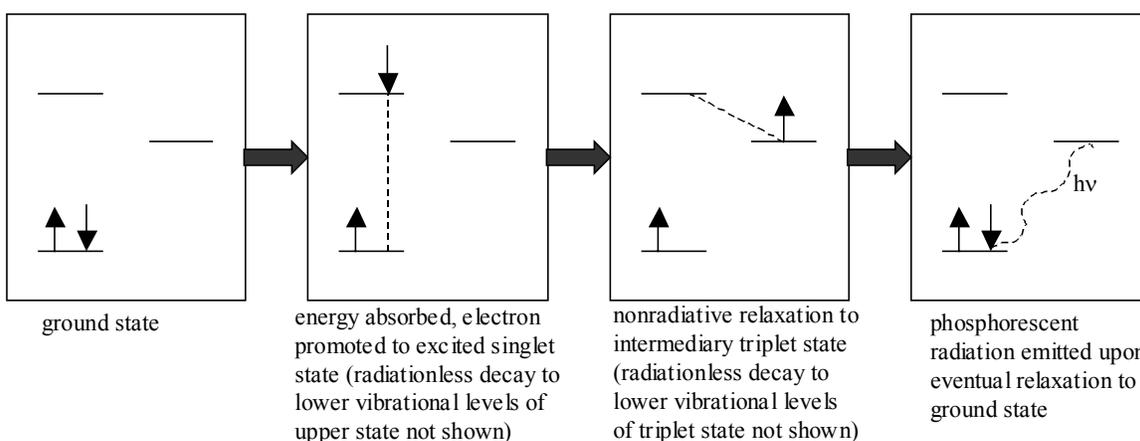


Figure 5. The difference between the processes of (a) fluorescence, and (b) phosphorescence, is in the sequence of states in the stages of the relaxation of the excited electron.

(a) Fluorescence



(b) Phosphorescence



The difference between luminescence by fluorescence and by phosphorescence is explained by what is happening inside the molecule or complex ion as energy is absorbed and re-emitted. Each process involves three electronic states: one ground state (where the electron initially resides before being excited) and two different excited states. Let us say for the sake of simplicity that there are two different kinds of electronic states, called singlet and triplet. In a singlet state, the spins of two of the state's electrons are paired (*i.e.*, aligned in opposite directions), as shown in Figure 4. In a triplet state, the spins of two of the state's electrons are similarly aligned, also shown in Figure 4.

The difference between fluorescence and phosphorescence is depicted in Figure 5. In both processes, fluorescence and phosphorescence, energy is initially absorbed by the molecule or complex ion, and an electron is promoted up to a higher excited singlet state. In the process of fluorescence, the electron initially decays down to a slightly lower singlet state by discarding some energy to the surrounding solvent. Then radiation occurs as the electron relaxes from this middle singlet state back down to the ground state. In the process of phosphorescence, the excited electron first relaxes to a middle state that is triplet. In most molecules, the singlet-triplet switching is symmetry forbidden by quantum mechanics, but in some molecules that contain heavy atoms, such as ruthenium, the process is weakly allowed by a mathematical mechanism. Once the electron is in the triplet state, it is trapped. However, in some molecules the radiative transition from the triplet state back down to the ground state is again weakly allowed, and the molecules are therefore able to emit light slowly. This is why the light emission may last long after the original excited state is formed.

Ruthenium complexes emit light by a phosphorescent process, although this is difficult to tell by the naked eye since the persistence time of the light is only 200 milliseconds. Since the luminescence is activated by an electric current, the light-emitting thin film is said to exhibit electroluminescence. The solution of ruthenium complex ions, however, also exhibits photoluminescence, that is, the ions give off light when their electrons are excited by light energy. The photoluminescence of the ruthenium (II) solution can be seen by holding an ultraviolet light source above the solution. The UV light supplies the necessary amount of energy to promote electrons to the excited state. (The absorption maximum is 450 nm, however there is a long absorption tail in the range of UV light, so UV light provides more than sufficient energy to excite the transition. The excitation could equally well be achieved by applying blue-violet visible 450 nm light.) When the ruthenium complexes finally relax to the ground state, light is emitted in the lower energy red range (wavelength 630 nm). (1 nm = 10^{-9} m, and wavelength is inversely related to energy.) The phosphorescence behavior of ruthenium complex ions is described in great detail in Juris *et al.*⁹ and references therein.

Materials

You are provided with slides pre-coated with a transparent indium-tin-oxide anode, plastic cover slips, ruthenium (II) chloride, polyvinyl alcohol, distilled water, gallium-indium eutectic, pipets, tweezers, cotton swabs, a hole-puncher, carpet tape, glass vials, epoxy, and gloves. Your lab station is supplied with beakers of solutions used for cleaning the slide: an ammonia-based glass cleaning solution, distilled water, and isopropyl alcohol. You are also provided with the components necessary for assembling a spin-coater: a 5-volt/200 mA DC fan, a 6-volt/100 mA plug transformer, a 47-ohm resistor, aluminum foil, cellophane tape, and a plastic cup. You have access to an ultraviolet light, a microwave oven, a drying oven, a power supply, a multimeter, and wire leads for connecting the device.

Hazards

The principal chemical hazards are associated with using the ruthenium (II) chloride salt and the gallium-indium eutectic. The ruthenium salt should be treated as any transition metal salt; it is not a known carcinogen or sensitizer. The gallium-indium eutectic is a liquid metal and should be handled with care so that it does not spill. There are no significant hazards reported for the liquid eutectic. If it spills, it can be cleaned up by taking it up with a pipet and then cleaning the remainder of the spill with a cloth wet with an ammonia solution, such as glass cleaner.

Procedure

1. Clean the glass slide that is pre-coated with the transparent anode

Put on gloves. Locate the two 1" × 1" slides. One side of each slide is pre-coated with the indium-tin-oxide (ITO) anode. Follow this cleaning procedure:

Using tweezers to hold the slide, dip it in succession in each of these solutions, or use a cotton swab dipped in the solutions to clean the slide.

1. An ammonia-based window cleaning solution, such as Windex.
2. Distilled water
3. Isopropyl alcohol

Then, dry the slide using a hair dryer. From now on, wear gloves and use only tweezers when handling the clean slide. While holding the clean slide with tweezers, with your other hand, wipe the slide with lens paper to dislodge any dust particles. (A second slide is provided in case you need to begin the procedure again.)

2. Find the ITO (anode) side of the slide

While holding the slide with the tweezers, use your other hand to touch both electrodes of the conductivity meter to one surface of the slide. Only one side of the slide is coated with the conducting ITO layer. Identify which side this is. Then carefully set the slide, ITO side up, on a clean surface.

3. Assemble the spin coater

The spin-coater is made from a small DC fan and a plug transformer that delivers a constant, accurate voltage to the fan. The speed of the fan depends on the voltage and current passing through it, so the speed can be controlled by placing resistors in the circuit. The fan is not a true motor; it operates only above a threshold voltage and it is like a diode in that electricity can pass in only one direction through the fan, otherwise the fan will burn out. Therefore, there is a lower limit to the speed. If you have a strobe light, you can measure the speed of the fan by drawing something asymmetric on the fan (or something that you attach to the fan blades).

To build a spin-coater that spins at a constant speed of 2500 rpm, construct the circuit shown in Figure 6 (next page). Cut off the end of the cord that comes out of the plug transformer, and separate and strip the ends of the two wires. Strip the ends of the two wires coming out of the fan. Attach one transformer wire with to one wire of the fan. Attach a 47-ohm resistor to the other wire of the fan, and then attach the other transformer wire to the other end of the resistor. If the fan does not operate in this configuration, switch the wires connected to the fan.

Tape a piece of aluminum foil firmly to the work surface to keep the surface clean. As shown in Figure 7, use loops of tape to secure the fan of the spin-coater to

Figure 7. Assembled spin-coater, showing slide attached above fan center, and dropping solution onto slide before spin-coating (protective cup omitted, so as to facilitate viewing in picture).

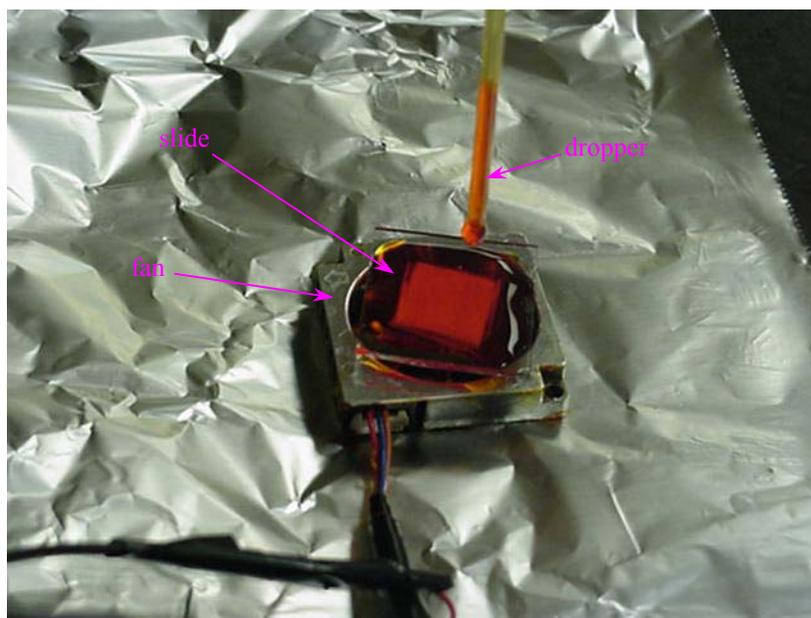
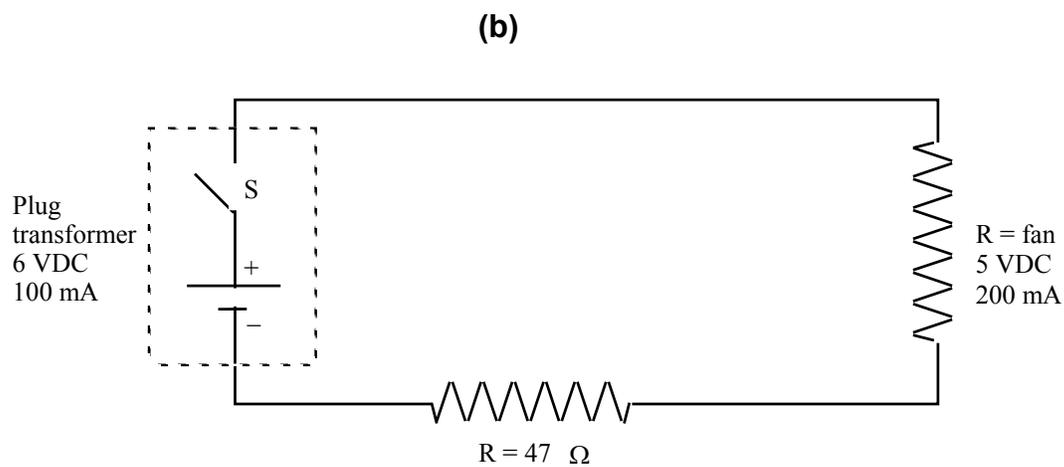
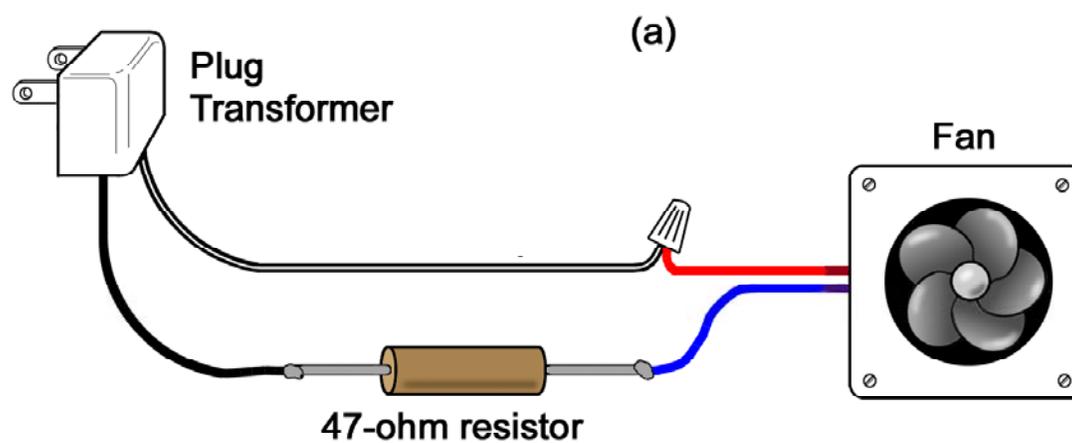


Figure 6. (a) How to connect the pieces of the spin-coater into a circuit.
(b) Circuit diagram for the spin-coater.



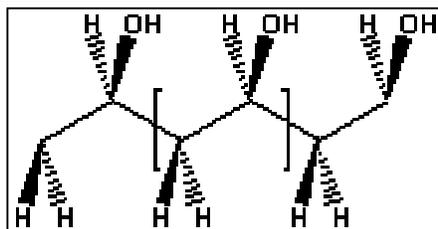
the aluminum foil, making sure that the tape does not interfere with movement of the fan blades. Test to see whether the fan blade moves freely by plugging in the transformer. Then, unplug the transformer.

Place a loop of tape symmetrically in the center of the fan blade. Using the tweezers, pick up the slide and set it down symmetrically on top of the loop of tape, ITO side up. Try to avoid touching the slide with anything other than the tweezers, but if need be, you can hold the slide by the corners with your gloves. Place the clear plastic cup upside-down over the spin-coater. Leave the transformer unplugged.

4. Prepare solutions of Ru^{2+} complex ion and water-soluble polymer, then mix them in 1:5 volume ratio

Polyvinyl alcohol (PVA, MW 44 g/mol per monomer) is a long polymer (see Figure 8) that dissolves slowly in water. The process can be accelerated to occur in about 15 minutes by heating the solution slightly in a microwave and alternately stirring it. Using distilled water, add 300 mg of PVA to 10.0 mL of water to make an aqueous solution of PVA. Cover the solution with plastic wrap, not with the vial cover, and heat in a microwave on high for 15-30 seconds. Do not allow the solution to boil. Remove the solution from the microwave and stir it. Repeat the heating and stirring procedure until the polymer is dissolved. Filter the solution by pouring it through

Figure 8. One possible structure of polyvinyl alcohol (spatial arrangement of alcohol groups may differ), showing one monomeric repeating unit in square brackets [].



Polyvinyl alcohol
 $-(CH_2CHOH)-_n$

standard lab-grade filter paper. Calculate how many moles of PVA monomers are in the solution you made.

Tris(bipyridyl) ruthenium (II) chloride salt (see Figure 2) dissolves much more easily in water than PVA. Make a solution of ruthenium (II) complex ion by mixing 53 mg of the salt into 1.0 mL of water. The formula weight of the hydrated ruthenium salt is 748.6 g/mol. Determine how many moles of ruthenium are in the solution you made.

The mixture needed is a 1:5 volume ratio of Ru (II) complex ion solution to PVA solution. Therefore, pipet 5.0 mL of the PVA solution and add it to the Ru (II) complex ion solution. About 1.0 mL of solution is necessary for spinning a single film, so you should have enough solution to make 6 slides. Determine the mole ratio of ruthenium to PVA in the mixture you made. Later you may want to experiment with changing the ratio of moles of ruthenium to moles of PVA. Since the polymer serves as a matrix to hold the ruthenium ions in place, a lower ratio causes the ruthenium centers to be farther apart, if the film is still the same thickness.

Prepare a glass Pasteur pipet by attaching a bulb. Slowly and carefully, so as not to allow any air bubbles to enter the pipet, take up one pipetful of the 1:5 solution into the pipet.

5. Spin coat thin layer onto slide

Take a clean, empty pipet and blow air across the surface of the slide to rid the slide of any dust particles that may have accumulated since placing the slide on the spin coater. Cut a small hole in the center of the bottom of the plastic cup, and then place it inverted over the spin-coater assembly. Slowly and carefully insert the filled dropper through the hole in the cup. Then, so as not to introduce any air bubbles, transfer solution from a pipet onto the surface of the slide until the solution completely covers the slide. Once the slide surface is covered, place any remaining solution back in the vial with the remainder of the solution. Set the pipet down on the table, away from the spin-coater and away from you.

Hold the cup in place from the top. Plug in the transformer to power up the spin-coater. Allow the slide to spin for 60 seconds, and then unplug the transformer or turn off the switch on a power cord to which it is connected. Remove the cup and allow the slide to air-dry for 1-2 minutes.

Dip the cotton swab into distilled water and squeeze out the excess moisture by pressing the cotton against the sides of the beaker. While the slide is still attached to the spin-coater, hold it securely in place with tweezers and use the cotton swab to wash off a small strip of the Ru film along one edge of the slide to expose the ITO underneath.

6. Dry the slide

Carefully remove the slide from the spin-coater using tweezers. Dry for one hour or overnight in a drying oven, depending on humidity.

7. Inspect thin layer visually and under UV light

Inspect the slide visually to determine the quality of the film. Bring the slide to the UV light and hold it underneath the light to observe the luminescence. A good film luminesces uniformly. A perfect film primarily waveguides out the edges. Waveguiding occurs when the light is trapped inside the film because it reflects off the inside interfaces at too shallow an angle for transmission out of the film to occur.

8. Apply mask, add metallic cathode

Create a mask to hold the metallic cathode by first attaching carpet tape to one side of a plastic cover slip and then punching a hole through the cover slip. Next, attach two parallel strips of carpet tape to either side of the hole (see Figure 9).

Remove the paper backing from the carpet tape on the side of the mask that is completely covered with carpet tape. Attach the mask to the surface of the film, making sure not to cover the small strip that you previously washed off the film, since you need to attach an electrode to the ITO along that area. Press the mask onto the film so that it adheres strongly.

Using a disposable plastic transfer pipet, carefully fill the hole in the mask with Ga-In eutectic. Agitate the slide by tapping it with your tweezers to make sure the eutectic completely contacts the Ru film. If any eutectic is spilled, notify your instructor so it can be cleaned up immediately. As with any chemical, do not allow the eutectic to contact your skin.

Set a copper wire like a bridge across the eutectic and held in place by the two parallel strips of carpet tape. Move the copper wire with the tweezers to cover it with eutectic, making electrical contact. Only one end of the copper wire will be used to connect to the power supply.

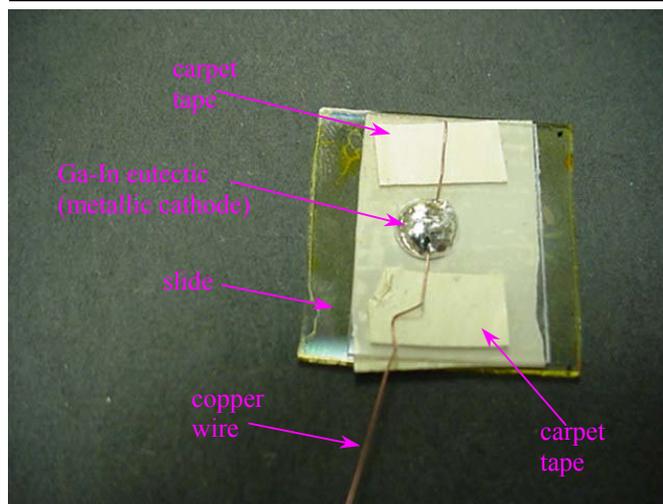
9. Seal with epoxy

Seal the device with epoxy to protect the film and eutectic from exposure to air and humidity. Cover the entire exposed surface with epoxy, except for the area of the slide that is reserved for contact to the ITO. To ensure sealing of the eutectic, carefully set a plastic cover slip on top of the epoxy before it dries. Allow the epoxy to dry for at least 5 minutes.

10. Power up the device

Turn on the power supply and set it to output 3 to 4 volts DC. Attach the negative (black) lead from the power supply to the copper wire that passes through the eutectic. Before clipping the positive (red) lead to the ITO layer, place the slide in an orientation such that you can see light emitted through the ITO and glass. Attach the positive lead to the ITO and light the device. After a brief charging time, a red-orange light should persist for several seconds to minutes. Gradually increase the voltage until light is produced uniformly. As the device eventually dims (when the ruthenium layer begins to degrade), increasing the voltage temporarily increases the light output as the light dies out. If no light is detectable, check the connection to the ITO as this is likely the faulty connection.

Figure 9. Metallic cathode in well inside mask which is adhered to film. Copper wire passes through metallic cathode and is held in place by two parallel pieces of carpet tape.



11. Clean up

Make sure the power supply is turned off and disconnected. Follow directions of the instructor to dispose of used materials.

Literature Cited

-
- ¹ Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913-915.
 - ² Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539-541.
 - ³ Pei, Q. B.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. *Science* **1995**, *269*, 1086-1088.
 - ⁴ Rillema, D. P.; Jones, D. S.; *J. Chem. Soc., Chem. Commun.* **1979**, 849.
 - ⁵ Handy, E. S.; Pal, A. J.; Rubner, M. F. *J. Am. Chem. Soc.* **1999**, *121*, 3525-3528.
 - ⁶ Rudmann, H.; Rubner, M. F. *J. Appl. Phys.* **2001**, *90*, 4338-4345.
 - ⁷ Gao, F. G.; Bard, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 7426.
 - ⁸ K. M. Maness, R. H. Terrill, T. J. Meyer, R. W. Murray, and R. M. Wightman, *J. Am. Chem. Soc.* 1996, *118*, 10609-10616.
 - ⁹ Juris, A., Balzani, V., Barigelli, F., Campagna, S., Belser, P., and von Zelewsky, A. *Coord. Chem. Rev.* 1988, *84*, 85-277.