Chemistry 123
Inorganic Chemistry
Laboratory

UCSD Department of Chemistry and Biochemistry

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Location: 4108 York Hall

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CONTENTS

Safety

Safety is our biggest concern in this course! You must read and know the section on Safety before starting your first experiment. If you are ever unsure of a procedure, make sure you ask the instructor or the TA.

General Information. A chemistry laboratory is a dangerous place. One must be aware of the dangers and exercise extreme caution at all times. Before beginning work in the laboratory, review the following rules. If you are in violation of any of the following rules, you will be asked to leave the laboratory and will possibly be removed from the course.

Eating, drinking, and smoking are strictly forbidden in the laboratory.

Eye Protection. Approved eye protection (safety glasses with side shields or goggles) must be worn **at all times** in the laboratory. Contact lens must never be worn because they can trap corrosive, volatile materials which may damage the eye.

Lab Attire. A lab coat is recommended. Protective gloves should be worn whenever the potential exists for contact with toxic chemicals. Shorts and sandals are not safe lab attire, since they provide no protection from splashed or spilled materials. Bare feet are absolutely forbidden in the laboratory. To avoid entanglement with laboratory equipment, necklaces and bracelets should not be worn, and long hair should be tied back.

Fume Hoods. All reactions using or evolving noxious or combustible chemicals must be performed in the fume hoods.

Chemical Spills. Clean up chemical and water spills immediately. If the spill involves dangerous chemicals, inform the instructor or the TA. Water on the floor can cause slips and falls, and should therefore be cleaned up as soon as possible.

Check Glassware. Small cracks or "star-cracks" can cause glassware to break, explode, or implode. Broken glassware should be turned over to the instructor or TA immediately.

Liquid Nitrogen Traps. Never isolate a cold trap cooled by liquid nitrogen from the vacuum pump to which it is attached.   Also, any operation involving liquid nitrogen should be conducted carefully to ensure that liquid oxygen (which has a slightly higher boiling point than nitrogen) is not condensed into the apparatus. Upon warming, liquid oxygen will rapidly vaporize and, particularly if organic material is present, cause a violent explosion.

Working with Chemicals. If you are unfamiliar with the properties, safe handling procedures, or disposal requirements of any chemical, consult with your instructor or TA before you attempt to use it**.**   Dispose of all chemical waste in the appropriate containers that are supplied.

Prior to coming to lab, you may want to look up the Material Safety Data Sheets (MSDS) for any chemicals that are unfamiliar to you. The following web page will allow you to access a large number of MSDS: http://chem-courses.ucsd.edu/CoursePages/Uglabs/Instruc/index.html

Inappropriate Conduct. Disruptive behavior will lead to your immediate dismissal from the laboratory.

Be Prepared. **Be familiar with the locations for the shower, the eye wash fountain, and the fire extinguishers.   Note emergency exit routes.**

Keeping Your Laboratory Notebook

A bound laboratory notebook, with numbered pages, is required for this course.   Your lab notebook is the primary record of all data and observations generated during the experiment. It is regarded as proof of exactly what you observed, and when the experiments were performed. All calculations (including, for example, gross, tare, and final weights) should be recorded in your notebook - **do not make these on scratch paper**. All entries should be in ink, and no erasing or white-out should be employed. If an entry is to be disregarded, it should be deleted with a single line drawn through it, such that it can still be read. Record any important observations that you think would help someone else repeat your work (color changes, gas evolution, etc.).   Procedures should describe what was done and observed, not what you expected to do or observe.

The notebooks will be graded in class.

Before you perform each experiment, your laboratory notebook should contain a **pre-lab write-up**. This should include a title, a purpose, a list of reactants involved with molecular weights, formulas, amounts in grams and moles to be used, and a list of balanced equations including molecular structures that describe the reactions that you will be carrying out.

After the pre-lab section, the **procedure section** in your lab notebook should record what actually happens.   Here is where you make your observations about the details of the experiments, including the entries of the weights of materials used and their physical appearance, and all of the data recorded. Once prepared, products will be weighed, and the yields calculated in this section of the lab notebook.

Preparation of Laboratory Reports

For each of the seven experiments, you are required to complete a laboratory report sheet that is given at the end of each experiment in this lab manual. This report is to be completed by you and your lab partner and you will share the grade for the report sheet with that person. The report sheets contain questions that relate to experimental observations and background information relevant to the experiment. In some cases, it will be appropriate to include some background from the literature. If you use information from the literature, be sure to include the citation.

Each report sheet will be due ~two weeks after the experiment is finished. It must be sent to the TA by email attachment (copy Prof. Sailor, msailor@ucsd.edu). Due to the size restriction on attachments of certain email providers (Yahoo, Hotmail etc.) and the UCSD spam filters, it is recommended that use your UCSD email account when sending in your reports.

Grading

Each of the seven labs as well as your lab techniques (including safety aspects, cleanliness, preparation, written notebook, and conduct), and the lab report will be critically reviewed and graded.

Reports	7 x 10	70 pts
Notebook[a]	7 x 20	140 pts
Technique[b]	7 x 20	140 pts
	TOTAL:	350 pts

[a]Includes preparation (pre-lab reading)
[b]Includes knowledge of subject matter, safety, cleanliness, conduct

Submission of Lab Reports

Each lab report will be due approximately two weeks after it is finished. The details of what is required in each report can be found in the section on Lab Reports. Each team of 2 students will submit only one lab report. The students on the team will share the grade for the written report.

Laboratory Knowledge

The knowledge and preparation of each individual student will be checked in class throughout the course. Students are expected to be able to answer questions on the techniques, procedures, motivations, and expected outcomes of the current experiment.

Reference Texts

In addition to your Chem 120A text (Chem 120A is a pre-requisite for this course), references that are directly related to the lab experiment are listed below. These are available in the S&E library.

M. J. Sailor "Porous Silicon in Practice: Preparation, Characterization, and Applications" Wiley-VCH: Weinheim, Germany, 2012.

R. J. Angelici "Synthesis and Technique in Inorganic Chemistry" 2nd Ed.; Saunders: 1977.

D. Shriver and M. A. Drezdzon "The Manipulation of Air-Sensitive Compounds" 2nd Ed.; Wiley-Interscience: 1986.

R. B. King "Organometallic Syntheses" Vol 1; Academic Press: 1965.

F. A. Cotton and G. Wilkinson "Advanced Inorganic Chemistry" 5th Ed: Wiley-Interscience: 1988.

J. P. Collman. L. S. Hegedus, J. R. Norton, and R. G. Finke "Principles and Applications of Organotransition Metal Chemistry" 2nd Ed: University Science Books: 1987.

Experiment 1: Bioinorganic Chemistry: Synthesis and Study of an Oxygen-Carrying Cobalt Complex Which Models Hemoglobin.

Objective: In this experiment, you will synthesize a coordination complex of cobalt, and demonstrate how it displays chemistry similar to that of metal-containing biological systems. A simple apparatus will be used to quantitatively monitor the gas-uptake/ release reaction.

Background: Bioinorganic chemistry is a growing field of inorganic chemistry that addresses a number of significant biological issues.   Much of the work in this area involves attempts to model the activity of a complicated, or ill-characterized, metal-containing system with more simple coordination complexes that can be prepared in the laboratory.   The coordination chemistry relevant to biological systems is reviewed in most inorganic textbooks, for example Chapter 30 in Cotton and Wilkinson (5th Ed) and Chapter 18 in Huheey (3rd Ed).

This experiment involves use of a cobalt(II) complex, which serves as a model for oxygen-transport systems.   Oxygen transport and storage are accomplished in higher animals by the iron-containing materials hemoglobin and myoglobin.   The challenge in developing suitable model systems to study this chemistry is in designing appropriate metal coordination complexes which react with dioxygen simply by binding it intact, rather than by much more commonly encountered redox processes, which can result in $L_nM=O$ (with a terminal oxo ligand) or $L_nM-O-ML_n$ (with a bridging μ-oxo ligand). Complexes of the latter type are usually inactive toward release of O_2.   Cobalt(II) complexes are known to form two types of adducts with dioxygen: a 1:1 adduct L_nCo-O_2, and a 2:1 peroxo structure $L_nCo-O-O-CoL_n$.

Biologically active metal centers are very often found in a coordination environment that includes *multidentate* ligands. Therefore the synthesis of bioinorganic "model complexes" often makes use of multidentate ligands that resemble those found in nature (e.g., as part of a peptide chain).   The multidentate ligand used in this experiment is tetradentate N,N'-bis(salicylaldehyde)ethylenediimine (abbreviated $salenH_2$). It is obtained by the condensation reaction shown below:
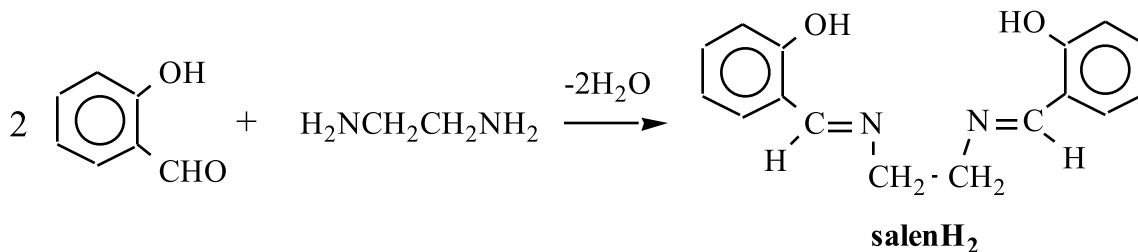
Addition of a Co(II) salt to salenH$_2$ results in formation of the Co(II) salen complex:
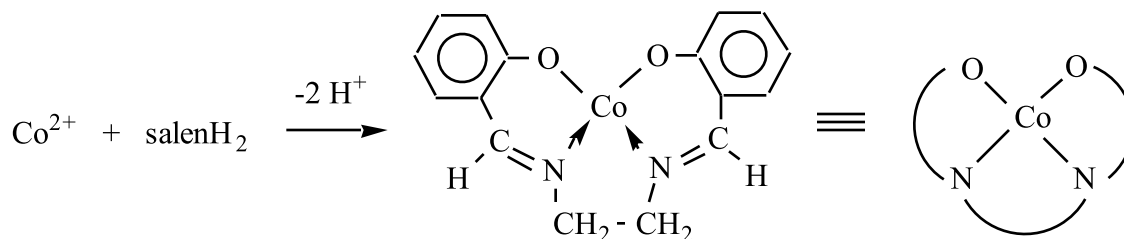
This four-coordinate Co(salen) complex is reactive toward addition of donor ligands in forming five- or six-coordinate complexes.   In the solid state it exists in two different forms (**I**, a dark red isomer inactive toward oxygen binding, and **II**, the active isomer).
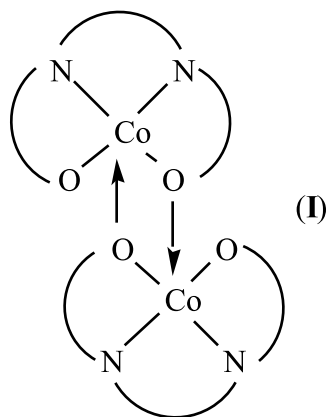
The experiments below will be conducted in chloroform and dimethyl sulfoxide, Me$_2$S=O (DMSO) solvents.   Chloroform (CHCl$_3$) is not a good ligand for transition metals, whereas DMSO is.

Briefly, we will prepare salenH$_2$, and its complex with Co(II), Co(salen), as a mixture of the brown and dark red forms.   This mixture is heated to accomplish complete conversion to the dark red form. This material is dissolved in DMSO in a closed system containing pure oxygen to generate an active form. The oxygen uptake is quantitatively measured at constant temperature and pressure. The oxygen adduct is then dissolved in chloroform to release the O$_2$.

Additional literature references:
E. I. Ochiai, *J. Inorg. Nucl. Chem.* **1973**, *35,* 1727, 3375.
C. F. Floriani and F. Calderazzo *J. Chem. Soc. (A)* **1969**, 946-953.
R. H. Bailes and M. Calvin *J. Am. Chem. Soc.* **1947**, *69,* 1886-1893.
W. L. Jolly, *The Synthesis and Characterization of Inorganic Compounds,* p. 466.
H. Diehl and C. C. Hach *Inorg. Synth.* **1950**, *3,* 196.
Experiment taken from: Appleton, T. G. *J. Chem. Educ.* **1977**, 443.

Safety precautions: Co(salen) is reported to be toxic, therefore avoid inhalation of particles of this material. While DMSO is not itself very toxic, it can transport dissolved compounds through your skin. Therefore avoid skin contact with DMSO.

Equipment and Materials:

salicylaldehyde	Buchner funnel
melting point apparatus	95% ethanol
100 mL 3-necked flask (24/40)	ethylenediamine
magnetic stir-bar	$Co(O_2CMe)_2 \cdot 4H_2O$
addition funnel (w/ 24/40 joint)	diethyl ether
vacuum desiccator with $CaCl_2$	O_2 tank with regulater and hose
O_2-uptake apparatus	DMSO
$CHCl_3$	test tube (1 x 7.5 cm)

Procedure (2 periods):   Preparation of salenH$_2$.   To a solution of 3.9 g (3.4 mL) of salicylaldehyde in 40 mL of boiling 95% ethanol (in an Erlenmeyer flask) add 1.0 g (1.08 mL) of ethylenediamine *in portions* with a pipette (otherwise, the reaction mixture may froth out of the flask).   Stir the reaction mixture for 3.5 min, and leave the solution to cool in an ice bath.   Filter the bright yellow flaky crystals using house vacuum, wash with a small volume of ethanol, and air-dry.   Record the melting point and yield of this product. Record an IR spectrum (vibrational spectrum; KBr pellet).

Preparation of Co(salen).   Weigh 2.0 g of salenH$_2$ into a 100 mL 3-necked flask fitted with a magnetic stirring bar, an addition funnel, and a condensor capped with a nitrogen inlet.   Add 60 mL of 95% ethanol.   Stir using the magnetic stir bar, and flush the apparatus with nitrogen (the synthesis requires the exclusion of oxygen, but extreme rigor is not neccessary).   Adjust the nitrogen flow to a steady rate (ca. one bubble/sec) and provide a steady flow of cooling water through the condensor.   Immerse the flask in a water bath maintained at 70-80 °C.   Cover the hot part of the system with Al foil. Dissolve 1.86 g of $Co(O_2CMe)_2 \cdot 4H_2O$ in 9 mL of hot water and put it in the addition funnel.   When the salenH$_2$ has all dissolved, add the cobalt acetate solution from the funnel.   Continue heating and stirring for about an hour, during which time a red precipitate should form.   Cool the flask by immersing it in cold water.   Discontinue the nitrogen flow and filter off the solid in the air. Wash three times with 5 mL of water, then with 5 mL of 95% ethanol. Dry the solid on the funnel and wash it two times with 5 mL of diethyl ether.   If further drying is needed use the vacuum desiccator (over drierite). Record your yield. Record an IR spectrum (KBr pellet).

Oxygen Uptake by Co(salen).   Oxygen uptake will be measured with the apparatus diagrammed below.   Stopper the side-arm test tube with a #49 suba seal when necessary. The movable arm is used to keep the pressure constant in the system. As oxygen is absorbed, the height of the movable arm must be changed to keep the water

level the same on both sides, which maintains a constant pressure on both sides. The difference in initial and final volume readings gives the amount of O$_2$ absorbed.
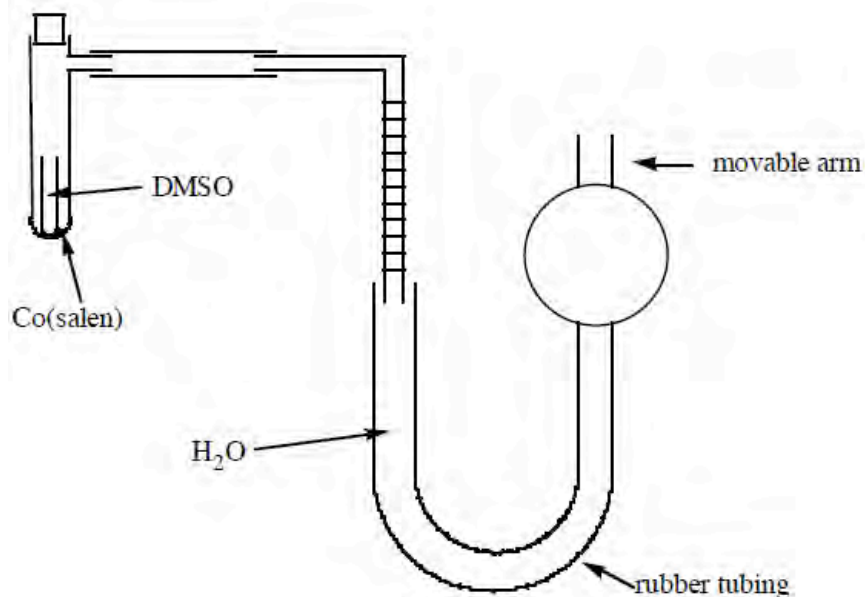
Weigh out 0.05-0.1 g of ground, dry Co(salen) into a side-arm test tube (1.5 x 15 cm). Place approximately 5 mL of DMSO in a beaker and bubble oxygen through it for a few seconds to saturate it with O$_2$. Transfer the DMSO into a small test tube (1 x 7.5 cm) until it is filled to about 2 cm from the rim. Tilt the side arm test tube and carefully lower the small test tube into the side-arm tube without spillage.

Flush the side-arm tube with a <u>gentle</u> stream of O$_2$. During flushing, the movable arm can be moved up and down to aid in the replacement of air with pure oxygen. Insert a tight-fitting rubber stopper in the mouth of the tube. Adjust the movable arm to make the water levels the same in both tubes (i.e., pressure within the apparatus is atmospheric). Note the water level in the graduated tube. Carefully invert the side-arm tube (holding near the stopper to minimize heating by the hand, but being careful not to push the stopper furhter into the tube causing a change in pressure) so that the DMSO is introduced onto the Co(salen) without spilling any on the tygon connecting tube. Gently shake the tube. As oxygen is absorbed the water level in the graduated tube should begin to rise. Note the changes that occur. The tube can be tipped to the side to increase the surface area of the solution and increase the rate of oxygen absorption. Continue shaking until no further change in water level occurs (5-10 min). Adjust the movable arm so that the water levels in the two tubes are again equal, and read off the new level in the graduated tube.

From the decrease in volume at room temperature and atmospheric pressure, the number of moles of O$_2$ absorbed per mole of Co(salen) can be calculated. You should do 2-3 O$_2$-uptake experiments to test reproducibility.

Behavior of the oxygen adduct in chloroform. Remove the stopper from the side-arm tube in the DMSO reaction, and remove as much as possible of the dark-brown suspension into a small test tube. Carefully remove the supernatant DMSO. To the residue in the tube (drying is not necessary) add 5-10 mL of chloroform without stirring. Observe the result and note your observations in your notebook.

Laboratory report

Table 1: Volumes or masses and moles of reactants used in synthesis.
Table 2: Melting point, color, and yield of salenH$_2$ and Co(salen) products.
Table 3: Oxygen binding data. Trial number; mass of Co(salen) used; mol of Co(salen) used; volume O$_2$ absorbed; mol of O$_2$ absorbed; mmol Co(salen)/mmol O$_2$
**Questions:**
   (1) Attach a copy of the IR spectra for salenH2 and Co(salen). Characterize and interpret the important aspects of each spectrum.
   (2) Why does the addition of DMSO activate the brown form of the Co(salen) complex?
   (3) Would addition of chloroform to the red form cause similar activation?
   (4) What are the oxidation state, spin state, and electronic configuration of cobalt in the O$_2$ adduct?
   (5) Give three possible dioxygen binding modes for the mononuclear or dinuclear metal-dioxygen complexes.
   (6) What does the ratio of Co(salen) to O$_2$ say about the binding mode(s) of the O$_2$ -
   (7) Co(salen) complex. Based on your average binding ratio, which is the dominant adduct?

Experiment 2: The Synthesis and Characterization of $YBa_2Cu_3O_x$ - the "1-2-3" Superconductor

Background:

The discovery of high temperature copper oxide superconductors (specifically the compound $YBa_2Cu_3O_7$, often referred to as 1-2-3 superconductors) created an extensive burst in the study of materials science and superconductivity theory which continues unabated even today. The resulting interest in chemical aspects of superconductivity and the ready availability of a refrigerant, liquid N_2 (bp = 77 K), necessary to demonstrate superconducting phenomena created a secondary increase in the incorporation of these topics in chemical education. The traditional method of ceramic synthesis involves the grinding of metal powder oxides in the proper stoichiometry, followed by heating in a furnace. These "shake and bake" methods have several disadvantages: the repeated mixing and grinding of the oxide powders needs to be conducted in a fume hood to minimize exposure to dust; the mixing itself might be incomplete due to the relatively large grain sizes of commercially available oxides, resulting in failure to achieve the intimate mixing necessary to create a homogeneous composition; and these methods do not reflect the various ways ceramic materials synthesis has been transformed through the application of chemical procedures. In fact, much research has been carried out in the past five years to improve the synthesis of these compounds in order to achieve a greater uniformity in their composition. The homogeneous co-precipitation synthetic method produces a reproducibly consistent ceramic precursor powder which can be processed into a reliable superconductor.

Synthesis of $YBa_2Cu_3O_x$. YBa_2Cu_3 oxide pre-ceramic powder is prepared by the method of homogeneous co-precipitation. An aqueous urea/oxalic acid solution of the metal salts in the proper 1-2-3 stoichiometry is prepared and heated. At a temperature between 80 and 100°C hydrolysis of urea takes place with the simultaneous evolution of CO_2 and NH_3 according to the following equation:

$$CO(NH_2)_2 \; + \; H_2O \; \longrightarrow \; 2\,NH_3 \; + \; CO_2$$
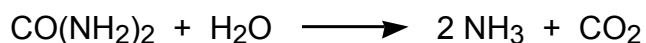
As the urea hydrolyzes, the pH of the solution gradually rises. Increasing the pH causes the metal ions to precipitate out as their hydroxide, oxalate or carbonate salts. The final stoichiometry of the powder is determined by the final pH of the solution which in turn is determined by the initial molarity of the urea solution. An initially high urea concentration favors the proper 1-2-3 stoichiometry in the pre-ceramic powder. The precipitate is separated, washed and dried. It is then heated at 900°C for a least 16 hours in air to burn out all the residual carbon. The powder obtained at this stage is pressed into a pellet and sintered at 900°C for 4 hours, followed by annealing in oxygen at 500°C for another 16 hours. This results in a material with a composition of

$YBa_2Cu_3O_x$ (6.5 < x < 7.0). The pre-ceramic powder synthesis part of the experiment can easily be carried out in one 3-4 hour laboratory period.   The calcining, pellet pressing, and final sintering and annealing necessitate additional work, but the total working time in the laboratory for these steps is short (~1 hour).

Literature References:

Several articles in *J. Chem. Ed*. **1987**, *64*, 836-853.
Liu, R.S.; Chang, C. T.; Wu, P. T. *Inorg. Chem*. **1989**, *28*, 154.
Holland, G. F; Stacy, A. M. *Acc. Chem. Res.* **1988**, *21*, 8.
Müller, K. A.; Bednorz, J. G. *Science* **1987**, *237*, 1133.
Pool, R. *Science* **1988**, *241*, 655.

Safety precautions:

In addition to the usual precautions, conduct all grinding and transfer operations in a hood wearing gloves. Barium is quite toxic and inhalation of it poses the most significant chemical hazard in this experiment.   The starch indicator solution is preserved with mercurous ion as a biocide.   This is also quite toxic.   It should be handled with care, with gloves, and if a spill occurs, it should be reported to your TA.

Equipment and Materials:

High Temperature Tube Furnace	Urea
Combustion Boats	Oxalic acid
Heat-proof gloves	$Y(NO_3)_3 \cdot 5H_2O$
Asbestos pad	$Cu(NO_3)_2 \cdot 5/2 H_2O$
$Ba(NO_3)_2$	Appropriate glassware

**Procedure (2 periods):**

1)   In a 250 ml flask, prepare 100 ml of solution that is 12 to 14 M in urea and 0.5 M in oxalic acid ($C_2O_4H_2 \cdot 2H_2O$). This typically involves 80 g of urea, 6.3 g of oxalic acid and 35 ml of deionized (DI) water.

2)   Warning - both the yttrium and copper nitrates are extremely hygroscopic (*i.e.*, they absorb moisture from the air and become nonstoichiometric). In a 50 ml beaker, weight 2.70 g of $Y(NO_3)_3 \cdot 5H_2O$, 5.10 g of $Cu(NO_3)_2 \cdot 2.5H_2O$, and 3.80 g of $Ba(NO_3)_2$ and stir the mixture with a spatula. Add this mixture to the urea solution and stir to dissolve.

3)   Place a 600 mL beaker (for water bath) onto a hot plate and clamp the flask inside the beaker. Add enough water to the beaker so as to cover the urea solution. Heat the solution until it is at 90-100°C and then continue heating for another hour. Evolution of CO_2 and NH_3 should be observed during heating.

4) After one hour of heating cool a small portion of the solution to room temperature and measure its pH with pH paper. If the pH is 7, allow the solution to cool to room temperature, otherwise, continue heating until the pH reaches a value of 7.

5) Add ~100 ml of DI water to the solution and stir it for 10 minutes before filtering. This will help dissolve any unreacted urea from the copper oxide precipitate. Filter the pale blue precipitate in a large (10 cm) Buchner funnel using a suction apparatus. If the mixture filters slowly, stir the precipitate with 100 ml more DI water and refilter.   Wash the precipitate with water followed with ethanol.   Leave the suction on for several minutes to dry the powder then place the mixture in a beaker and let it dry in an oven at 140°C for several hours.

6) Place the powder in a porcelain crucible and calcine it in air by heating at 900°C for 16 hours in a tube furnace.

7) Examine the powder after it has been removed from the oven and cooled. $YBa_2Cu_3O_x$ is black. A green coloration in the powder indicates the formation of Y_2BaCuO_5 and CuO caused by a non-1-2-3 stoichiometry in the starting preceramic powder.   The presence of the green phase usually does not interfere with the superconductivity. At this stage the powder can be molded into a 3 mm thick pellet through the use of a hydraulic press and an IR pellet maker similar to the kind used for making KBr pellets. The pellet should be pressed @ 15,000 psi for about 3 - 5 mins. The pellet must be removed with extreme care to avoid crumbling it. Consult your TA about use of the press. If you have enough material, press two pellets.

8) The pellets should be sintered under nitrogen to give them structural integrity. Place the pellets in a porcelain crucible and heat the material under nitrogen at 900°C for 4 hours followed by annealing at 500°C for 18-24 hours under oxygen. Turn off the furnace, and allow it to cool to room temperature while maintaining the oxygen flow. The material obtained after this procedure should be black.

Meissner Effect.
The determination as to whether or not the $YBa_2Cu_3O_x$ made is a high T_c superconductor is most easily done by observing the Meissner effect. Cooling a pellet of the material in liquid nitrogen (77 K) and levitating a ferromagnet over its surface is a positive test for superconductivity in these materials, whose superconducting transition temperature is ~90 K.   It is best to use samarium-cobalt or neodymium-iron-boron ferromagnets (which should be about one-third or less the size of the pellet) as they possess stronger magnetic fields which allow the magnet to levitate higher above the superconductor.   The cut off bottom of a styrofoam coffee cup makes a suitable reservoir for the liquid nitrogen and pellet.   A pair of plastic tweezers is useful for handling the magnets as they often drift off the superconductor and into the liquid nitrogen. Care must be observed when handling the liquid nitrogen as its extremely low temperature can cause frostbite.
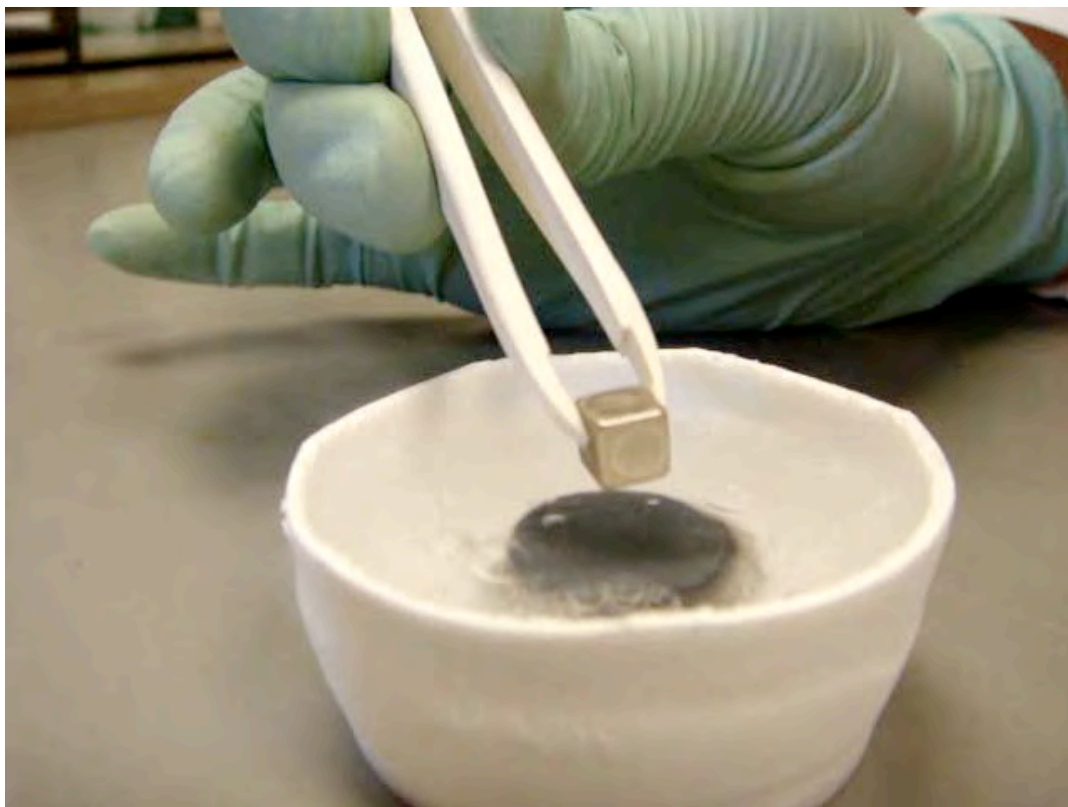
Samarium-cobalt ferromagnet cube being placed on cooled superconductor disk.

Laboratory report

Table 1:
Starting materials, amounts and moles for reaction synthesis.

Starting Material	MW (g/mol)	Amount (g)	Amount (mmol)	Stoichiometric coefficient
$Y(NO_3)_3 \cdot 5H_2O$	365.00			
$Ba(NO_3)_2$	261.34			
$Cu(NO_3)_2 \cdot 5/2\ H_2O$	232.60			
Urea $(H_2N)_2CO$	60.06			
Oxalic acid $C_2H_2O_4$	90.04			

Questions:

(1) Did your sample display the Meisner effect?
(2) Discuss why there are differences in the magnitude of the Meissner effect from sample to sample.
(3) How does the pH at which the reaction is terminated affect the nature of the final product?
(4) You placed your sample in the furnace three times. What was the purpose of each of these procedures?
(5) The superconducting phase of your material is sub-stoichiometric in O. What effect does this have on the conductivity properties of the material, and what type of charge carrier is introduced by this defect?

Experiment 3: Luminescent Ruthenium Complexes

Background:

Luminescence is the molecular property that describes the emission of a photon of light from an excited state. Excitation is usually brought about by absorption of photons. When the excited state has all of the electron spins paired, it is called a singlet, whereas when there are two spins unpaired, the state is a triplet. The properties of a molecule in the excited triplet state differ significantly from those of the excited singlet state. For example, the molecule is paramagnetic in the former and diamagnetic in the latter. More important is the fact that a singlet-triplet transition (or the reverse), which also involves a change in electronic state, is a much less probable event than the corresponding singlet-singlet transition. As a consequence, the average lifetime of an excited triplet state may range from 10^{-4} s to several seconds, as compared with an average lifetime of 10^{-6} s to 10^{-8} seconds for an excited singlet state.   When emission occurs from a singlet excited state, it is called fluorescence, whereas when the emitting state is a triplet, it is called phosphorescence.

In this lab, we will prepare and investigate a series of luminescent ruthenium(II) complexes that are emissive at room temperature in solution. The parent complex of the series, tris(bipyridyl)ruthenium(II) ($[Ru(bpy)_3]^{2+}$), is one of the most studied inorganic complexes of all time. The reasons that this complex has been so extensively studied result from its photochemical properties.

The complex $[Ru(bpy)_3]^{2+}$ was first prepared in 1959 by Paris and Brandt *(J. Am. Chem. Soc.* **1959**, *81,* 5001)*,* who showed that the complex emitted orange light in solution. The low-spin d^6 complex absorbs strongly in the visible region of the spectrum; these bands are metal-to-ligand charge transfer (MLCT) transitions. Since the lifetime of the complex in solution at room temperature is generally around 600 ns, it was originally labeled as fluorescence.   It has subsequently been shown that the lowest energy emitting state is best described as a triplet (^{3}MLCT) excited state. However, since the description of the excited spin state is not straightforward in these complexes, the general term "luminescent" is usually used to describe them, and not "phosphorescent".

The photostability, visible absorption, and excited-state properties of $[Ru(bpy)_3]^{2+}$ have led to huge interest in the molecule for solar energy conversion. The property which make the molecule unique is that the excited state has the capability of redox processes in fluid solution. Thus, light energy can be used to generate electrical energy.   In addition, the molecule has been investigated as a photocatalyst for the decomposition of water into hydrogen and oxygen. The use of light to generate H_2 and O_2 from water would clearly have enormous value.

Each group will prepare a ruthenium(II) tris(diimine) complex using one of the following ligands: bpy, dmb, dpb, phen, or dpp.
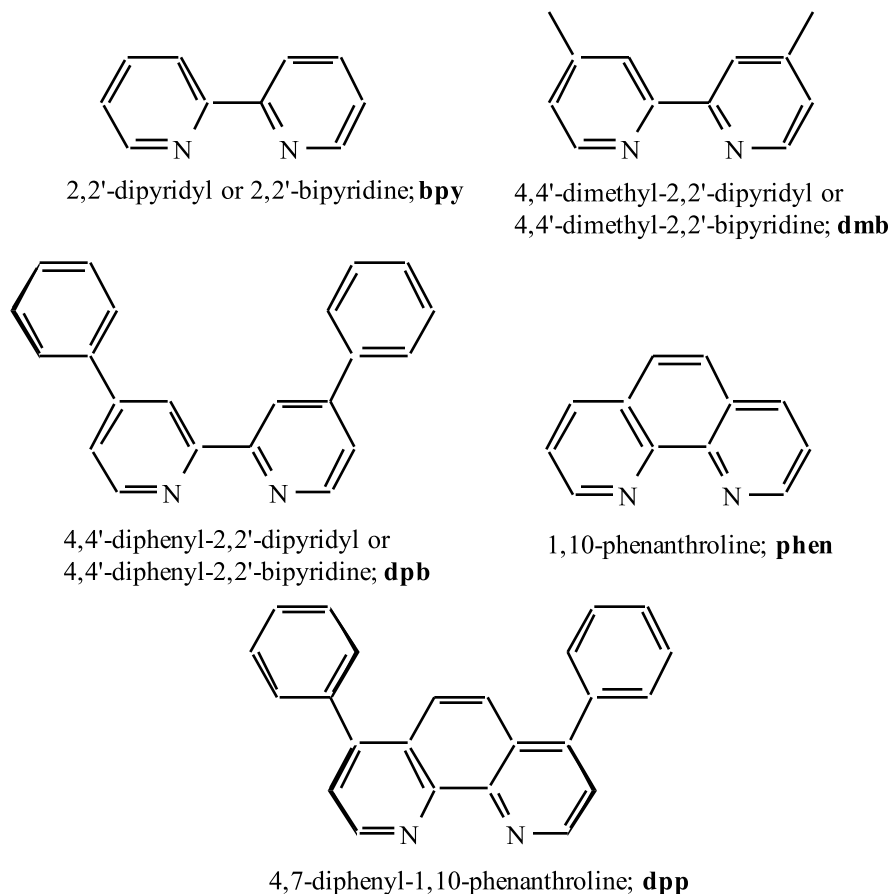
Figure 1. Ligands used in this experiment.

We will investigate the emission of the ruthenium complexes qualitatively. Absorption of visible or ultraviolet light in these complexes results in emission at about 600 nm. Two factors contribute to the brightness of emission: the quantum yield and the lifetime. The quantum yield (φ) is a measure of how much of the absorbed light is emitted. The lifetime (τ) is inversely related ($\tau = 1/k$) to the rate by which the excited state decays. The rate at which the complex decays, k, is actually composed of two rates, k_r and k_{nr} - the radiative rate constant and the non-radiative rate constant ($k = k_r + k_{nr}$). When a complex has a longer lifetime, it appears to be brighter. Also, when the quantum yield is higher, the complex appears brighter.

As you will see, ligand variations can change the brightness of emission in ruthenium tris(diimine) complexes. It has been observed that ligand variations primarily affect k_{nr}, and not k_r. Thus, the τ and φ values typically vary in a similar fashion between complexes - i.e., when τ increases, so does φ. This can be seen by looking at the two equations: $\varphi = k_r/(k_r + k_{nr})$ and $\tau = 1/(k_r + k_{nr})$.

Additional references:
1) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc. Dalton* **1973**, 204.

2) Watts, R. J. *J. Chem. Educ.* **1983**, *60,* 834.
3) Juris, A., et al. *Coord. Chem. Rev.* **1988,** *84*, 85 (the first 20 pages are useful).

Safety Precautions: Dimethylsulfoxide and acetonitrile are toxic.

Synthetic Procedures (3 periods):

Preparation of [Ru(dmso)$_4$Cl$_2$] - Dichlorotetrakis(dimethyl sulfoxide) ruthenium(II).
Transfer 1.00 g of ruthenium trichloride <u>hydrate</u> into a small beaker flask. Carefully add 15 mL of DMSO and a stir bar. Heat on a hot plate until the solution is deep red and there is no solid remaining (about 15 minutes; be ware that you need to replace the coordinated H_2O-ligand with DMSO ligands!). Do not boil but make sure that the crystal water is removed from that equilibrium via evaporation). Remove from hot plate and cool for 5 minutes at room temperature. With stirring, quickly add 20 mL of acetone. Collect the yellow precipitate and wash with small amounts of acetone and then diethyl ether. Suction dry and then air-dry the solid. If the solid is green in color, you must repeat the reaction. The product must be yellow. Calculate your yield assuming that the ruthenium starting material is the trihydrate.

Preparation of [Ru(diimine)$_3$](PF$_6$)$_2$.
Weigh out 300 mg of [Ru(DMSO)$_4$Cl$_2$] and 3.2 equivalents of your diimine ligand and place in a 100 mL round bottom flask equipped with a stir bar. Add 50 mL 95% ethanol and stir to dissolve the reagents. Start heating and gently bubble nitrogen through the solution for 5 minutes. Fit the flask with a condenser and blanket the system with nitrogen. After the solution has stirred at reflux for 1 hour, remove an aliquot and measure the absorption spectrum from 350-600 nm. Continue to stir the solution at reflux for a minimum of 24 hours. *Check all condenser lines carefully before leaving.* Remove solution from the heat and allow to cool to room temperature. Again, measure the absorption spectrum of an aliquot from 350-600 nm. Filter and transfer the solution to a 200 mL beaker. On a hot plate with stirring, reduce the volume to 20 mL. Be careful that the solution does not boil over or go dry. Slowly add (via a pipet) a solution of 500 mg NH$_4$PF$_6$ in 15 mL water to the gently boiling ethanol solution. Warm with stirring until the solution volume is about 30 mL (approximately 10 minutes). Allow to cool to room temperature. Filter the solid and wash with small amounts of diethyl ether. Dry in a 100 ˚C oven for at least 20 minutes before weighing and calculating your yield.

Characterization (1 period):

Absorption spectra.
Record absorption spectra of your [Ru(diimine)$_3$](PF$_6$)$_2$ complex from 300-800 nm in acetonitrile solution. Prepare solutions of known concentrations, approx. 1×10^{-4} to 10^{-5} M (or even more dilute) and **determine the extinction coefficient** (ε_{max} / M^{-1}cm^{-1}) of the absorption band maximum (at approx. 450 nm) in acetonitrile. Make sure that the absorption band maximum is somewhere between 0.5 and 1.5 A.U. Write the extinction coefficient and λ_{max} of your complex in acetonitrile on the blackboard. Record all of the data for the other complexes in your lab book.

Emission spectra.

Make a 5.0 x 10^{-4} M solution (50 mL will suffice) of your [Ru(diimine)$_3$](PF$_6$)$_2$ complex in acetonitrile.   Transfer about 5 mL of the solution to a large test tube.   Irradiate the solution with a long wavelength UV lamp (what is the wavelength?) at room temperature and 77 K in a darkened room. Note what happens to the solution upon cooling to 77 K. Compare the brightness and color of emission with the other four complexes prepared by your lab mates.   Specifically, compile a list of the brightest to weakest emitters at room temperature and 77 K.   Lastly, with two identical acetonitrile solutions in test tubes, bubble oxygen through one and nitrogen through the other for about 60 seconds and seal the test tubes. Compare the brightness of emission of these two solutions at room temperature.

Laboratory report

Table 1:
Starting materials, amounts, moles, and yield for [Ru(dmso)₄Cl₂] synthesis.

Starting Material	MW (g/mol)	Amount (g)	Amount (mmol)	% Yield
RuCl₃·H₂O				-
[Ru(dmso)₄Cl₂]				

Table 2:
Starting materials, amounts, moles, and yield for diimine synthesis.

Starting Material	MW (g/mol)	Amount (g)	Amount (mol)
[Ru(dmso)₄Cl₂]			
Diimine			
NH₄PF₆			
[Ru(dmso)₄Cl₂]			
Diimine			
NH₄PF₆			

Table 3:
Yield and properties of your two [Ru(diimine)₃](PF₆) complexes.

Product	MW (g/mol)	Yield (g)	% Yield	Color

Table 4:
Spectral properties of all five [Ru(diimine)₃](PF₆) complexes.

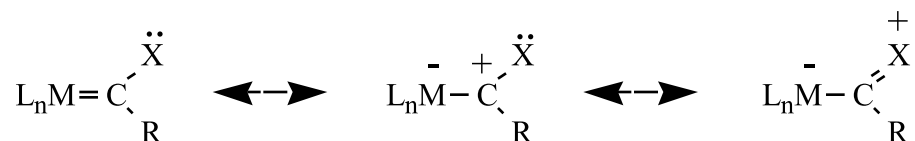| Complex	λ_{max} (absorption)	extinction coefficient	λ_{max} (emission)	emission intensity
Ru(bpy)₃²⁺				
Ru(dmb)₃²⁺				
Ru(dpb)₃²⁺				
Ru(phen)₃²⁺				
Ru(dpp)₃²⁺				

Questions:

(1) The preparation of [Ru(dmso)₄Cl₂] utilizes a ruthenium(III) starting material. What acts as the reducing agent in this reaction? What is the half-reaction?

(2) Do you expect the [Ru(dmso)$_4$Cl$_2$] complex to be a conductor in acetonitrile solution? Provide three possible structures for the [Ru(dmso)$_4$Cl$_2$] complex that you prepared.

(3) In your absorption spectra, what is the assignment of the band(s) at approximately 450 nm? What is the oxidation state of ruthenium in the photoexcited-state? Comparing the absorption maxima and extinction coefficients to the emission maximum of the solar spectrum, which dye would you use in a solar photovoltaic converter (such as the Graetzel cell)?

(4) Discuss the trends in emission intensity for the five complexes.

(5) Discuss the effects that temperature and O$_2$ have on the emission of these complexes. Dioxygen has been shown to quench the exicited state by an oxidative electron-transfer mechanism. Write out the equation for this type of quenching – what happens to O$_2$?

Experiment 4: Synthesis of a Carbene Complex, $(CO)_5W=CPh(OEt)$, and Homogeneous Catalysis. The Catalyzed Polymerization of Norbornene.
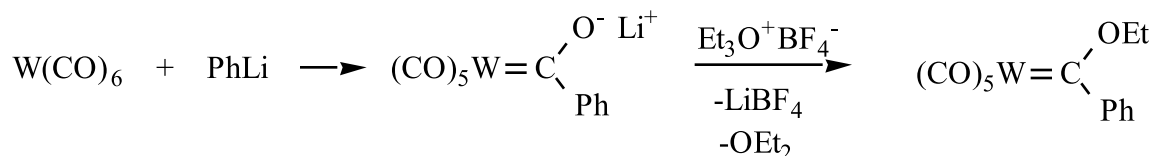
Objective: This experiment involves the synthesis of a tungsten carbene complex, $(CO)_5W=CPh(OEt)$, and its use in catalyzing a polymerization reaction. The ring-opening metathesis polymerization of norbornene will be used to obtain polynorbornene.

Background: A major advance in the history of organometallic chemistry occurred upon discovery of the first carbene complexes by E. O. Fischer. The first so-called "Fischer-type" carbene was $(CO)_5Cr=CPh(OMe)$, an analogue of the tungsten one prepared here, was reported in 1964. Fischer-type carbene complexes possess electrophilic, metal-bound carbon atoms and generally have a heteroatom substituent (e.g., alkoxide in the examples above) that stabilizes the carbene fragment via p_π-p_π donation:

$$L_nM=C\overset{\ddot{X}}{\underset{R}{}} \longleftrightarrow \quad L_n\overset{-}{M}-\overset{+}{C}\overset{\ddot{X}}{\underset{R}{}} \quad \longleftrightarrow \quad L_n\overset{-}{M}-C\overset{\overset{+}{X}}{\underset{R}{}}$$

The latter two resonance forms account for the electrophilic character of Fischer carbenes. A large number of carbene complexes are now known, with a wide range of electronic and chemical properties. Nucleophilic carbene complexes, often refered to as alkylidene complexes or "Schrock-type" carbene complexes, are largely based on Nb, Ta, Mo, W, and Re, and do not have heteroatom stabilization. Examples of Schrock-type carbenes include $(Me_3CCH_2)Ta=CH(CMe_3)$, $Cp_2Ta(=CH_2)Me$, and $(PMe_3)_2W(CH_2CMe_3)(=CHCMe_3)(\equiv CCMe_3)$, which contains an alkyl, an alkylidene, and an alkylidyne ligand in one molecule. For a more complete discussion of carbene complexes, refer to the chapter on organometallic chemistry in an inorganic textbook, or (more preferably) chapter 3 of Collman, Hegedus, Norton, and Finke, "Principles and Applications of Organotransition Metal Chemistry", 2nd Ed.

Syntheses of Fischer carbenes rely partially on activation of carbon monoxide toward nucleophilic attack by coordination to a transition metal. The two-step synthesis of $(CO)_5W=CPh(OEt)$ is outlined below:

$$W(CO)_6 \;+\; PhLi \;\longrightarrow\; (CO)_5W = C \overset{O^- \; Li^+}{\underset{Ph}{\diagup}} \xrightarrow[\substack{-LiBF_4 \\ -OEt_2}]{Et_3O^+BF_4^-} (CO)_5W = C \overset{OEt}{\underset{Ph}{\diagup}}$$
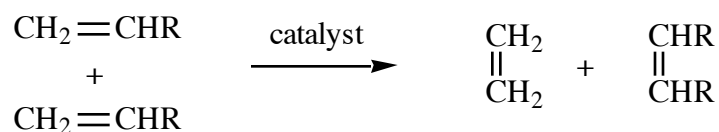
Alkylation of the intermediate acylate complex, which displays chemistry similar to that of an enolate, gives the final product.   Although alkyl halides can be used as the alkylating agent, oxonium salts such as triethyloxonium tetrafluoroborate give higher yields.

Carbene complexes have played an important role in the development of organometallic chemistry.   These complexes were among the first to draw attention to the ability of transition-metal fragments to stabilize, via coordination, a highly reactive species that would not exist under normal laboratory conditions.   In addition, it is now realized that carbene (or alkylidene) complexes serve as key intermediates in important metal-mediated reactions of organic comounds.   For example, they may transfer the carbene fragment to olefins to generate cyclopropane rings:
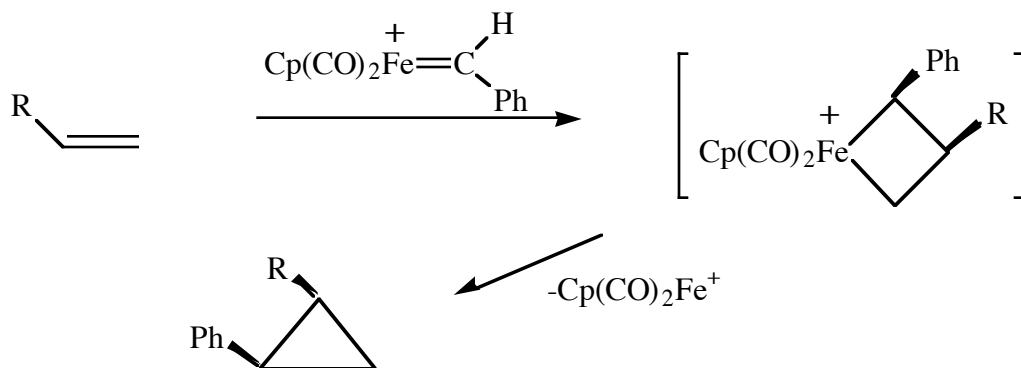
Metallacyclobutane intermediates such as the one shown above often participate in metal-catalyzed reactions of alkenes, such as the olefin metathesis reaction, a version of which is shown below:

$$\begin{array}{ccc} CH_2 = CHR & & CH_2 \qquad\qquad CHR \\ + & \xrightarrow{\;catalyst\;} & \overset{\|}{} \quad + \quad \overset{\|}{} \\ CH_2 = CHR & & CH_2 \qquad\qquad CHR \end{array}$$

The accepted mechanism for this reaction may be found in most modern textbooks on organometallic chemistry.   A modification involves use of a cyclic alkene, which is converted to a polymer via *ring-opening metathesis polymerization* (ROMP):
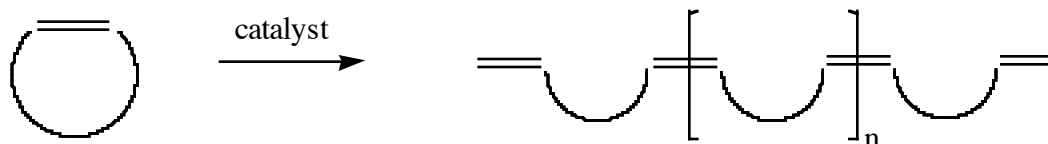
This reaction is catalyzed by a number of carbene complexes, the most efficient of which as based on Mo, W and Re. For background on this type of reaction, read the review article given below by Grubbs and Tumas.   We will carry out a ROMP polymerization of norbornene to polynorbornene, which is a synthetic elastomer developed in France for oil-spill recovery.   It swells very well and gives viscous solutions, so that the polymerization is readily visible.

Carbene complexes may also act as catalysts for the polymerization of alkynes. Polyacetylenes are currently attracting much research interest, because they conduct electricity when oxidatively or reductively doped. The mechanism for this polymerization is believed to involve addition reactions which maintain a metal-carbon double bond:

$$L_nM=CH\text{-(polymer)} + R\text{-}C\equiv CH \longrightarrow L_nM=CH\text{-}C(R)=CH\text{-(polymer)}$$
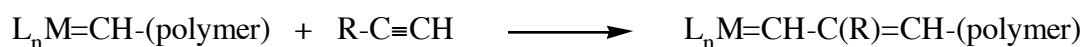
The above propagation step may also involve a metallacyclobutene intermediate.

Additional literature references:
> D. Villemin *J. Chem. Educ.* **1987**, *64,* 183, and references therein.
> R. H. Grubbs and W. H. Tumas *Science* **1989**, *243,* 907.
> R. R. Schrock *Acc. Chem. Res.* **1990**, *23,* 158.

Safety precautions: Since many of the compounds used in this experiment are toxic, conduct as much of the work as possible in a hood. Alkylating agents in general are extremely toxic.   Triethyloxonium tetrafluoroborate is less dangerous than many alkylating reagents, since it is nonvolatile. Gloves should be worn while handling this material. Note also that $Et_3O^+BF_4^-$ is highly hygroscopic.

Equipment and Materials:

2 250 mL round-bottom Schlenk flasks	norbornene
2 Schlenk tubes	$W(CO)_6$
drying oven	triethyloxonium tetrafluoroborate
magnetic stir-bars	dry diethyl ether
cannula	$MgSO_4$
sintered glass filter	DMSO
filter flask	cleaning solution
centrifuge	pentane
litmus paper	$CDCl_3$
5 mm NMR tubes	dry CH_2Cl_2

|	
reflux condensor with 2 24/40 joints	$AlCl_3$
KBr IR plates	basic alumina
graduated addition funnel with	acetone
2 24/40 joints and stop-cock on	methanol
side arm	phenyl lithium
	purified water

Procedure (3 periods): *Preparation of (CO)$_5$W=CPh(OEt).* A 250 mL round-bottom Schlenk flask, previously dried in a 100 °C oven, is loaded with tungsten hexacarbonyl (4.00 g, 0.0114 mol) and a stir bar. The flask, including the $W(CO)_6$, is pumped on with the Schlenk line for about 10 min (instructions for setting up and taking down the Schlenk line are given at the end of this experiment). Diethyl ether (ca. 50 mL, air and water-free, distilled from sodium benzophenone ketyl) is added to the flask via cannula. Using syringe Schlenk techniques, add an equivalent of phenyl lithium dissolved in diethyl ether (**calculate beforehand!**) slowly over 10-20 min. Purge your syringe with nitrogen from the reaction flask (3-5 times), before withdrawing the PhLi solution from the reagent bottle. At the end of the addition, all of the $W(CO)_6$ should be dissolved, and the solution should be orange. Evaporate the solution on the Schlenk line, and dissolve the resulting residue in ca. 50 mL of water, which has been degassed and saturated with nitrogen. Rapidly filter this solution with a sintered glass filter to remove excess $W(CO)_6$, and return the solution to a Schlenk tube that is being purged with N_2. Degas the solution, and add an excess of triethyloxonium tetrafluoroborate solution via syringe until the aqueous solution becomes acidic (an aliquot of the solution is tested with water-soaked litmus paper until it turns red) and the yellow mixture becomes red. The red carbene is extracted with N_2-saturated pentane (4 x 20 mL) and dried over magnesium sulfate. Filter the solution into a Schlenk tube, and concentrate the solution under vacuum until it is saturated (until crystals precipitate from solution). Gently warm the crystals back into solution (make sure your flask is vented to the bubbler), and cool to -70°C in the freezer. Isolate the crystals by cannula filtration. If necessary (usually not), recrystallization can be accomplished by redissolving the compound in ca. 100 mL of 1:1 OEt_2-pentane in a Schlenk tube, and cooling to -78 °C for ~1 h.

Characterize the complex by infrared spectroscopy, ^{1}H NMR spectroscopy, (in $CDCl_3$) and by its reaction with Me_2SO (DMSO) in an NMR tube.

Polymerization of norbornene. The tungsten carbene complex will polymerize norbornene thermally (50 °C over ca. 4 days), but it is more convenient to use a Lewis acid *cocatalyst,* which accelerates the polymerization apparently by enhancing the electrophilicity of the carbene. Norbornene (1.88 g, 20 mmol), the carbene (21 mg), and a magnetic stir bar are placed in a nitrogen atmosphere in a 100 mL round-bottomed flask, and the flask is capped with a suba-seal. N_2-purged dichloromethane (40 mL) is added to the flask. After complete dissolution, pulverized aluminum trichloride (50 mg) is quickly introduced (from transfer vials, prepared in the dry box). After 2 min the mixture is stirred under nitrogen in a water bath (30 °C). The viscosity increases rapidly,

and after 5 min the mixture is jelled. After 30 min, the gel is drawn out with a spatula and extracted with THF in a soxhlet extractor, giving a yellowish elastic gel. The gel is dried between two slides under vacuum for 24 h to give a dry elastomer (yield ca. 90%) suitable for physical analysis or a swelling demonstration (try various solvents). The round-bottomed flask is cleaned with a sulfochromic mixture. Characterize the polymer by infrared spectroscopy.

Schlenk Line Operation
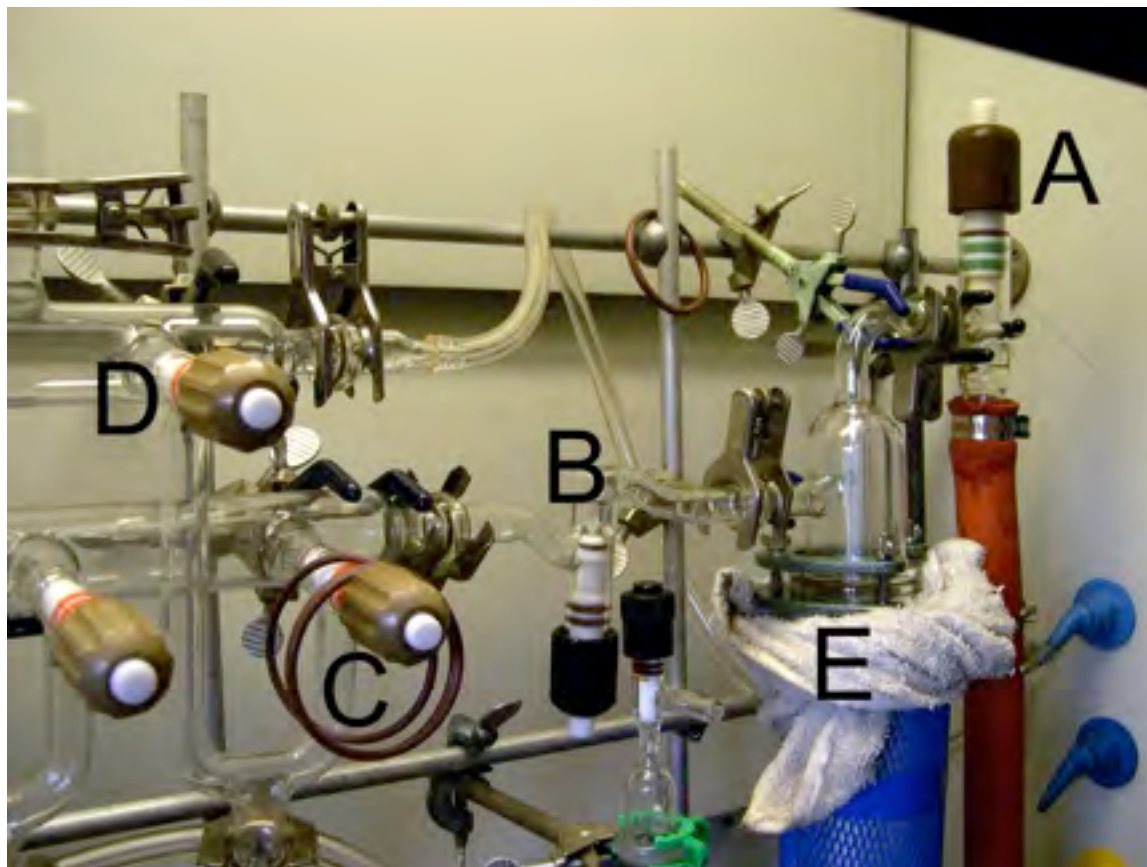
Starting up the line:
Close all valves (**A-D**)
1. Turn on power to the vacuum pump
2. Attach trap (**E**) to the line, make sure it is empty of any liquids and seated properly.
3. Open valve (**A and B**), pump out system
4. Fill liquid nitrogen dewar (**E**) to cool down trap

Shutting down the line:
1. Remove liquid nitrogen dewar from trap (**E**)
2. Open valve (**C**) to vent line and leave it open
3. Unplug pump (do this as soon as you can, after step (b))
4. Remove trap (**E**) and clean if necessary

Laboratory report

Table 1:
Starting materials, amounts, moles, and yield for catalyst synthesis.

Provide the infrared spectrum of your polymer

Questions:

   (1) Provide a mechanism for the synthesis of the tungsten carbene.
   (2) What is the structure of the reaction product of tungsten hexacarbonyl with phenyl
       lithium? Why is the addition of triethyloxonium tetrafluoroborate necessary?
   (3) Differentiate between Fischer and Schrock catalysts. Discuss the characteristics
       of the metals used in these complexes.
   (4) Provide a mechanism for the polymerization of norbornylene by the catalyst.
   (5) What is the role of aluminum trichloride in the mechanism of the polymerization
       reaction?

Experiment 5: Synthesis of Polyacetylene, a Conductive Polymer, Using the Ziegler-Natta Catalyst.

Developed by Michelle Grass, Andi Heard, and Deidre Johns
Chemistry 123 Advanced Inorganic Laboratory, University of California, San Diego,
1996

Objective:

This experiment involves the polymerization of acetylene gas using a Ziegler-Natta catalyst. The resulting polymer is referred to as "polyacetylene:"

$$H-C\equiv C-H \quad \xrightarrow[\text{Catalyst}]{\text{Z-N}} \quad \left[\text{\Large\char92/\char92/}\right]_n$$

Polyacetylene is an insulator, but it can be "doped" with an oxidizing agent to form a highly conductive "synthetic metal." The oxidant generates carbocations (called Solitons) on the polymer backbone. These charges are free to move along the polymer chains, imparting electronic conductivity to the material. In this experiment, you will use iodine vapor to dope polyacetylene:

$$\xrightarrow{3I_{2(g)}}$$
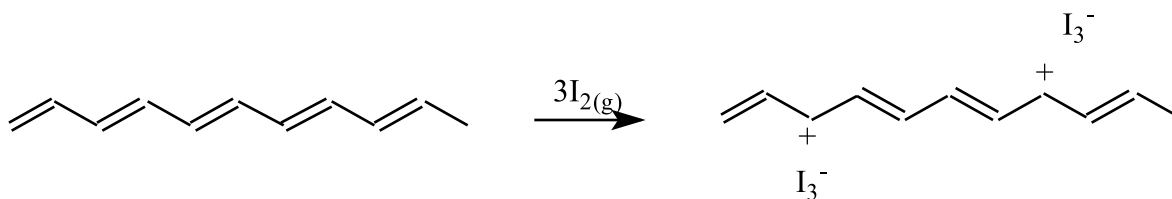
The conductivity of undoped and iodine-doped polyacetylene will be tested using the four-point-probe conductivity method.

Background:

Polyacetylene films are synthesized using a Ziegler-Natta catalyst, initially discovered by Shirakawa and colleagues[1]. This method polymerizes acetylene via a metathesis mechanism.

High-quality films result when polymerization is carried out at -78°C in toluene. In this experiment, polymerization will be carried out at room temperature. The higher temperature increases the *trans*-conformation content of the product. Low temperature polymerization results in high percentages of the *cis* form.[2] The more conductive and stable, trans-polyacetylene, can be obtained by heating or by doping.
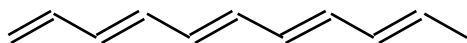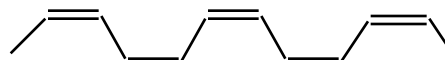
trans-polyacetylene   *cis*-polyacetylene

Iodine is used to oxidatively dope the polymer.   This p-type doping (p stands for "positive" because the charges on the polymer are cationic) dramatically increases the conductivity by removing electrons from the filled valence band.   This increases the mobility of the remaining electrons in the band, making it a metal-like conductor.

The conductivity can be calculated from the voltage drop (V) measured when a current (I) is passed through the polymer.   It is measured using the four-point probe method, which gives a more accurate value than a two-point probe[3].   The four-point probe device is pictured schematically below.
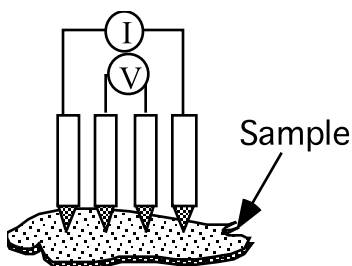
A constant current (I) is passed between the outer two probes, while the voltage drop (V) is measured between the inner two.   The conductivity (σ) is the reciprocal of the resistivity (ρ):

$$\sigma = 1/\rho \qquad\qquad\qquad (1)$$

The sheet resistance (R_s) is calculated from the measured   values of current and voltage, multiplied by a correction factor that is related to the sample geometry:

$$R_S = \frac{V}{I} \cdot CF$$

$$(2)$$

Where V is in volts and I is in amps.   The value of CF is 4.54 for an infinite sheet (this approximation is valid if the sample is over a factor of 10 larger in both the x and y directions than the probe tip spacing).   The units on sheet resistance are ohms/square.

Sheet resistance and resistivity are related by:

$$\rho = R_s W \qquad\qquad\qquad (3)$$

Where W is the thickness of the conductive material.   The usual units of resistivity are ohm-cm, so the thickness should be measured in cm.   Your samples will be sufficiently thin that you will need to measure them with a digital micrometer, not a ruler.

Electronically conductive polymers have potential commercial applications in solar cells, supercapacitors, and antistatic coatings.[4]

References:
1. Shirakawa, H. and Ikeda, S. *Synth. Met* **1**, 175 (1980).
2. Basescu, N. *Nature* **327**, 403 (1987).
3. Sze, S. M. *Physics of Semiconductor Devices* (2nd ed.), John Wiley and Sons, New York, 1981.
4. Naarman, H. and Theophilou, N. *Synth. Met*. **22**, 1 (1987).

Procedure:

Supplies:
3-Neck Round Bottom Flask
Syringes
Needles
Stir Bar
Suba Seal
Glass Stopper
Flow Adapter
Reaction Chamber
Rubber Balloon with 3-Way Valve
4-Probe Conductivity Measurement Apparatus
Toluene
Triethyl Aluminum
Tetrabutoxytitanium

Safety Precautions
Triethyl aluminum ignites when exposed to air and may be explosive. Tetrabutoxytitanium is air sensitive. Acetylene is highly flammable in air, and it may explode when heated or shocked by high pressure. It is also toxic.

Catalyst Synthesis
The catalyst will be prepared for you and stored in the dry box. It was made as follows: 20.0 mL (1.4×10^{-4} mol) triethyl aluminum was added to a three neck round bottom flask containing 25.0 mL dry toluene (this preparation produces enough catalyst for five polymerizations). While stirring, 15.0 mL (7.5×10^{-5} mol) of tetrabutoxy titanium was added over a period of 60 min. The catalyst solution has the appearance and consistency of strong Italian espresso. A syringe to add the catalyst solution to your reaction flask will be left in the drybox for your use.

Polymer Synthesis
In the dry box, add 5 to 10 mL of the catalyst solution to the reaction chamber. The catalyst solution should cover the bottom of the reaction vessel. Remove the reaction vessel from the drybox, and assemble the acetylene balloon apparatus using a three-way valve.
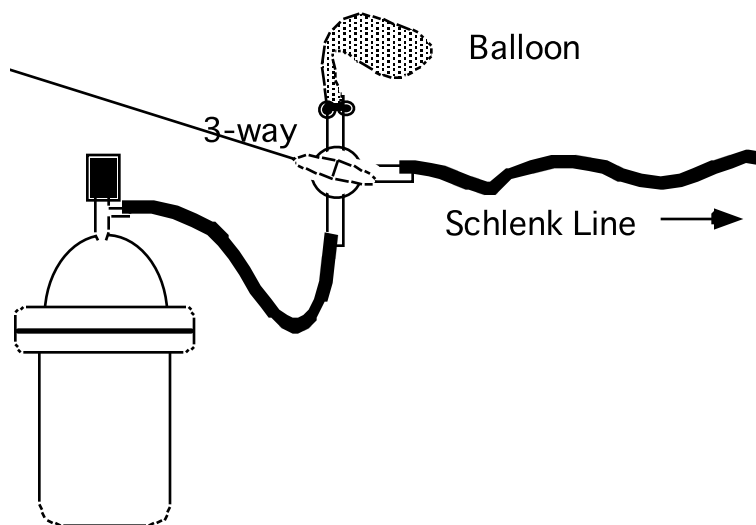
Apparatus for addition of acetylene to the reaction chamber

Purge the balloon with nitrogen and fill it with acetylene gas from the tank. *CAUTION: Acetylene gas is highly flammable. Be very careful to be sure no air gets mixed with the acetylene.* Attach the balloon apparatus to the reaction chamber as shown:

After briefly evacuating the reaction chamber, release acetylene into the chamber. The balloon will immediately deflate as the pressure in the chamber equalizes with the balloon. As the reaction proceeds, it will use up acetylene and the balloon will deflate further. Allow reaction to proceed until the acetylene balloon is flaccid (this should take approx. 30 minutes depending on the quality of your catalyst and how well you have been able to exclude air and water from the reaction). Evacuate the chamber to remove remaining acetylene. A polymer film should have formed at the catalyst solution/gas interface. Using a syringe, rinse the polymer with 5 mL aliquots of toluene until the washings are clear (may take 5-10 washings). In air, quickly and carefully remove the polymer from the chamber (the polymer is air-sensitive, but may be briefly exposed to air). Quickly clean out the remaining catalyst from the reaction vessel and return the polymer to the vessel. Store in an inert atmosphere under 10 mL toluene until the next lab period. Remove the toluene and vacuum dry the polymer for twenty minutes.

Conductivity Measurement
Using the four-point probe apparatus, quickly measure the conductivity across the dry, undoped polymer. This involves measuring the current and voltage simultaneously, as described above.   Note that your sample is decomposing every moment that it is exposed to air, so it is important to make these measurements quickly.   Dope the polymer by placing it in the reaction chamber with a few iodine chips. Evacuate the chamber and leave it under static vacuum (valves closed) to allow the iodine to sublime and permeate the polymer.   After twenty minutes, remove the iodine chips from the chamber and pump on the sample for 5-10 minutes to remove excess iodine. Measure the conductivity of the polymer once more. Repeat the doping process until you obtain a constant sheet resistance measurement. Record the thickness of the polymer.

Laboratory report

Table 1:
Starting materials, amounts, moles for synthesis.

Starting Material	MW (g/mol)	Amount (L)	Amount (g)	Amount (mol)
Acetylene gas				
Ziegler-Natta catalyst				

Table 2:
Product yield.

Product	MW (g/mol)	Yield (g)	% Yield
Polyacetylene			

Table 3:
Thickness and conductivity measurements (report averages with uncertainties using 95% confidence limits).

Thin film	Undoped	Doped
thickness (cm)		
ρ (Ω^{-1} cm^1)		
(σ Ω cm^{-1})		

Questions:

(1) Describe how the Ziegler-Natta catalyst catalyzes the polymerization of acetylene. Describe the polymerization mechanism including initiation, propagation, and termination steps.
(2) Describe how doping affects conductivity.
(3) Draw a mechanism showing how solitons move through polyacetylene.

Experiment 6: Synthesis of a Nanomaterial--Porous Silicon.

Tested and modified by Melin Lu, Andrew Samant, Shahin Saneinejad, Sara Thoi, Mathew Moranville, Xinyi Ng, Kathryn Kesselman, and Danh Do, March 2007

Objective:

This experiment involves the synthesis of nanostructured silicon by electrochemical etching.   You will prepare the material from single-crystal silicon wafers.   The nanomaterial displays quantum confinement effects, emitting visible light when excited with blue or ultraviolet light. You will characterize the luminescent "quantum dots" in this material by means of photoluminescence spectroscopy. You will also characterize the surface species by infrared spectroscopy.   Finally, you will quantify the capability of these materials to act as chemical sensors for gas-phase pollutants, using ethanol vapor as a test analyte.
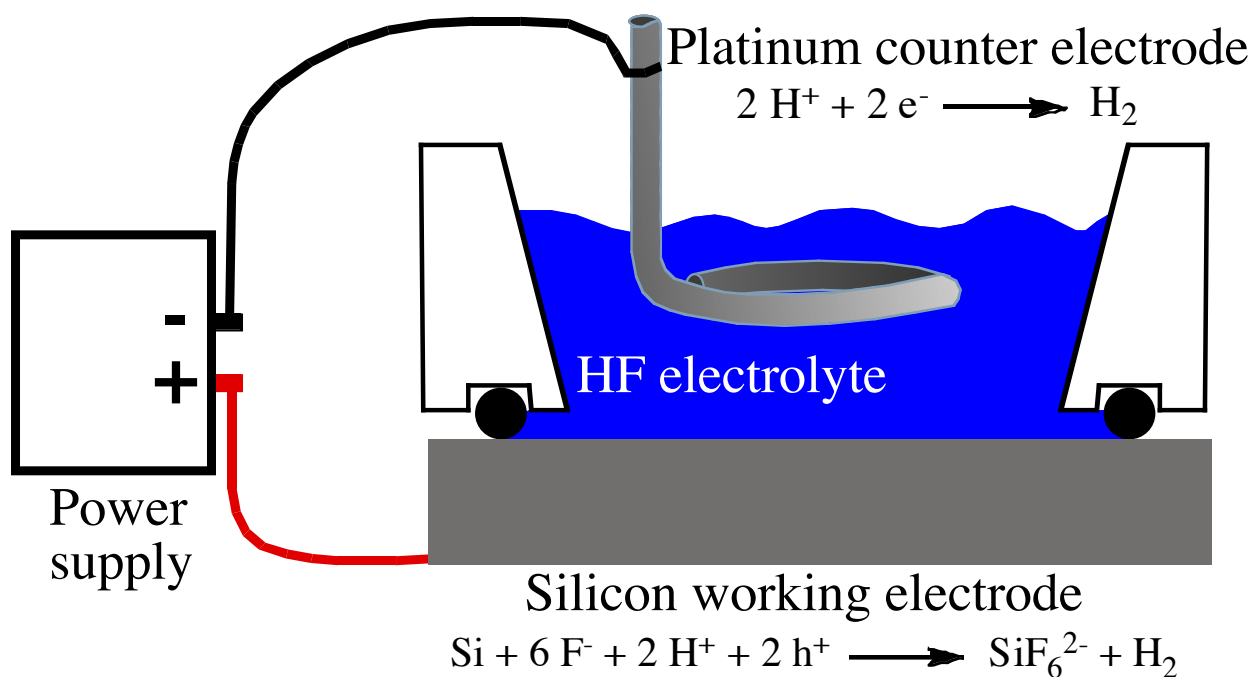

Platinum counter electrode

$$2 \text{ H}^+ + 2 \text{ e}^- \longrightarrow \text{H}_2$$

HF electrolyte

Power supply

Silicon working electrode

$$\text{Si} + 6 \text{ F}^- + 2 \text{ H}^+ + 2 \text{ h}^+ \longrightarrow \text{SiF}_6^{2-} + \text{H}_2$$

Figure 1. Schematic of the electrochemical etching cell you will use to prepare porous Si from a single crystal Si chip. The electrolyte used is typically a 3:1 mixture of 48% aqueous HF and ethanol.

Background:

Porous silicon was accidentally discovered by Uhlir and Uhlir at Bell Laboratories in the mid 1950s [1]. They were trying to develop a means to electrochemically machine silicon wafers for use in microelectronic circuits. They found that under the appropriate conditions of applied current and solution composition, the silicon did not dissolve uniformly but instead fine holes were produced, which propagated primarily in the <100> direction in the wafer. Since this did not provide the smooth polish desired, these

curious results were reported in a Bell labs technical note [1] and the material was pretty much ignored. In the 1970s and 1980s a moderate level of interest arose because the high surface area of porous Si was found to be useful as a model of the crystalline Si surface in spectroscopic studies [2-5], as a precursor to generate thick oxide layers on Si, and as a dielectric layer in capacitance-based chemical sensors [6]. Then, in the late 1980s, researchers in the United States and in England reasoned that the diaphanous Si filaments generated when the pores become large and numerous enough to overlap might display quantum confinement effects. This intuition turned out to be correct, and the electrochemically etched material was reported to fluoresce with a bright red-orange color [7, 8]. As expected from the quantum confinement relationship [9], this color occurs at an energy that is significantly larger than the bandgap energy for bulk Si, which appears in the infrared region of the spectrum.

With the discovery of efficient visible light emission from porous Si came an explosion of work focused on creating Si-based optoelectronic switches, displays, and lasers. Problems with the material's chemical and mechanical stability and its disappointingly low electroluminescence efficiency led to a waning of interest by the mid 1990s. In the same time period, the unique features of the material- its large surface area within a small volume, its controllable pore sizes, its convenient surface chemistry, and its compatibility with conventional silicon microfabrication technologies-inspired research into applications far outside of optoelectronics. Of particular relevance to this experiment are the sensor properties of the material.[19]

References:
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Procedure:

Supplies:
Teflon etching cell
n-type silicon chips, resistivity of 0.5 Ω-cm
3:1 aqueous HF (48%): ethanol solution
absolute ethanol in a wash bottle
plastic dropper
gloves, apron, and goggles
ultraviolet LED flashlight
1 M KOH solution

Safety Precautions
Hydrofluoric acid is toxic and can cause severe chemical burns that are very slow to heal. HF use is limited to a single fume hood #6), the hood windows should be used as additional splash protection between the work and your face and neck. Hands should be shielded by long gloves (see below) and apron sleeves.

Personal protection - You are already required to wear lab coats & closed shoes, along with lab eye protection. There are chemical splash goggles available, although you may wear safety glasses when appropriate to the task. Whenever you are handling HF

yourself or are in the vicinity of the etching station, you should wear a long lab apron and chemical splash goggles

Gloves –Nitrile inner gloves and neoprene outer gloves should be worn. The gloves should be removed as soon as the HF operation is finished and the inner gloves should be disposed in a waste box located in the HF work area.

Electrochemical Etch

Porous silicon is generated by etching crystalline silicon in an aqueous ethanolic hydrofluoric acid (HF) electrolyte.

(1) You will be supplied with a phosphorus-doped, n-type, polished (100) silicon wafer, with a resistivity of between 0.5 and 1 Ohm-cm, 2 x 2 cm and 400 microns thick. Rinse the sample with ethanol, dry it, and weigh it.

(2) Mount the chip in the a Teflon etch cell shown in Fig 2, using a piece of aluminum foil as a back contact and a Viton O-ring to seal the cell. Mount the aluminum on the Teflon base, and tape it in place with a small piece of tape. Make sure the tape does not cover the area where your Si wafer will make contact with the foil. Place the silicon chip in the Teflon cell. After gently tightening the screws by hand, tighten each screw one turn at a time so as to apply even pressure. If the wafer cracks, you will need to replace it. Once the screws are tightened test the cell for leaking by placing ethanol in the cell and allowing it to sit for a few minutes.

(3) Place your cell in the etching hood and add a 3:1 (v/v) mixture of 48% aqueous HF and absolute ethanol (approximately two droppers full) into the cell. The solution level should be a few mm below the top of the cell. Immerse a loop of platinum wire in the solution to use as the counter electrode. Make sure the platinum loop is fully submerged in the HF solution. Attach the platinum loop to the negative (black) lead of the power supply. Attach the positive (red) lead to the aluminum foil.

(4) Test the power supply to make sure that it is set to deliver a current density of 80 mA/cm^2. You will have to calculate the current needed based on the area of the silicon wafer exposed to the solution (1.36 cm^2) Turn on the illumination lamp and make sure it is centered. Activate the power supply and apply an anodic current density of 80 mA/cm^2 between the aluminum back contact (positive lead) and the platinum counter electrode (negative lead) for 15 minutes. Make sure to record the exact current and time used in your etch.

(5) After completion of the etch, turn off the power source and remove the HF solution from the cell using a plastic dropper. Rinse the cell three times with ethanol. Carefully, pick up the cell and rinse the face of the cell and the chip with ethanol into the waste container. Carefully take apart the cell and clean the chip with ethanol and blow it dry under a stream of nitrogen. Carefully rinse the pieces of the cell and the o-ring with ethanol. This procedure should be performed in the same hood in which you perform the etch. Weigh the sample after it is dry.
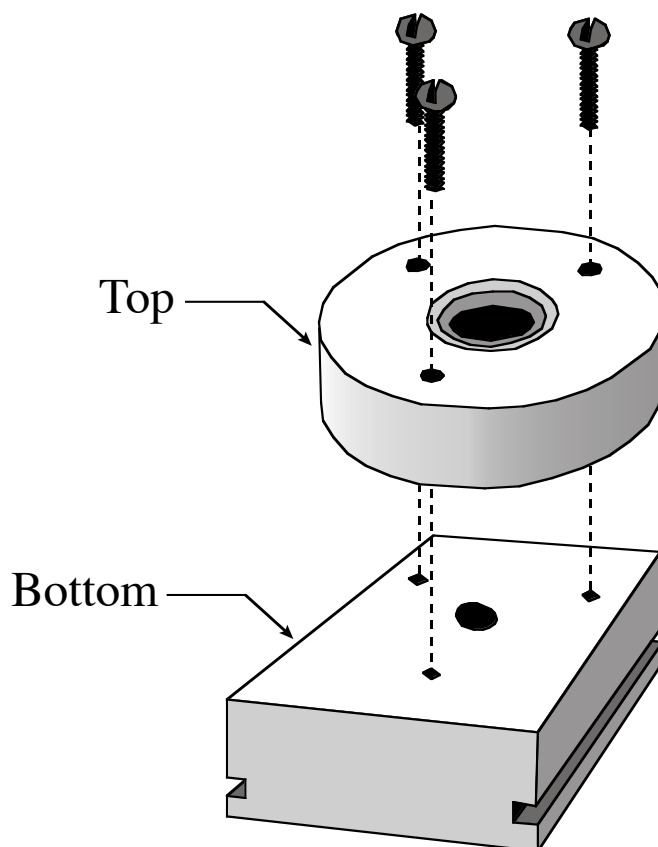
Figure 2. Schematic of the Teflon etching cell used in this experiment.

Infrared Measurement
Measure the infrared spectrum of the material, and assign the prominent bands observed.

Photoluminescence Measurement
Observe the photoluminescence from the sample by eye, using the UV lamp supplied. Measure the photoluminescence spectrum of the material using a UV LED excitation source and the Ocean Optics CCD spectrometer.

Luminescence Quenching Measurement
Observe the photoluminescence from the sample while exposing it to ethanol vapor. Record your observations.

Porosity and Thickness Measurement
You will measure porosity and thickness of your sample using gravimetric analysis. Since this is a destructive test, it must be done after you have obtained all your spectral data.   The gravimetric measurements are performed by weighing the sample before etch (m_1), after etch (m_2), and after chemical dissolution of the porous layer (m_3). For each weighing, you must be sure that your sample is completely dry (you can remove the ethanol by placing the sample in a dessicator for a few minutes)

To dissolve the porous layer, soak it in a beaker containing 10 mL of 1 M aqueous KOH solution for 30 min. You should be able to tell when the porous layer is completely dissolved by visual inspection--when you gently swirl the solution and no bubbles form on the wafer. Rinse it with ethanol and dry it thoroughly before obtaining the final mass (m_3). The porosity P is calculated using the following equation:[22]

$$P = \frac{m_1 - m_2}{m_1 - m_3}$$

The thickness W of the porous Si layer can be determined by applying the equation:

$$W = \frac{m_1 - m_3}{Sd}$$

where S is the wafer area exposed to HF during the electrochemical etching and d is the density of bulk Si. Report the porosity (in %) and thickness (in microns) of your porous layer.

Laboratory report

Table 1:
Porosity, thickness, and reaction stoichiometry by gravimetric measurement.

Quantity	Value
Wafer mass Initial (mg)	
Wafer mass after etch (mg)	
Wafer mass after dissolution of porous layer (mg)	
Dissolved silicon (mg)	
Moles electrons	
Etch stoichiometry (moles of electrons/moles Si removed)	
Porosity	
Thickness (cm)	
Thickness (μm)	

Table 2:
Product yield.

Product	MW (g/mol)	Yield (g)	% Yield
Polyacetylene			

Table 3:
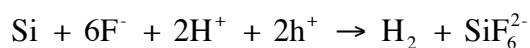Thickness and conductivity measurements (report averages with uncertainties using 95% confidence limits).

Thin film	Undoped	Doped
thickness (cm)		
ρ (Ω^{-1} cm^{1})		
(σ Ω cm^{-1})		

Questions:

(1) Silicon can be etched by either a 4-electron process:

$$Si \; + \; 6F^- \; + \; 4h^+ \; \rightarrow \; SiF_6^{2-}$$
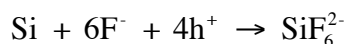
Or a 2-electron process:

$$Si \; + \; 6F^- \; + \; 2H^+ \; + \; 2h^+ \; \rightarrow \; H_2 \; + \; SiF_6^{2-}$$

Where h$^+$ are electronic holes in the valence band of the semiconductor. Which equation better fits your data?

(2) Attach a copy of the IR spectrum for the etched wafer. Characterize and interpret the important aspects of the spectrum.
(3) Why did you need to illuminate your sample during the etching process?
(4) Provide an explanation of the photoluminescence quenching effect (with ethanol vapor) that you observed.

Experiment 7: Fabrication of a dye-sensitized solar cell.

Tested and modified by Alex Carpenter, Stephen Lin, Craig Lee, Lawrence Tran, Jennifer Lee March, Christine Ko, Shaun Ooi, Patrick Saris, Michael Ventuleth, Amanda Rhea, Joanna Shen, 2011

Objective:

This experiment demonstrates a simple dye-sensitized solar cell—also known as a Grätzel cell after its inventor, Prof. Michael Grätzel. In this experiment you will prepare a dye sensitized solar cell using an anthocyanin dye extracted from blackberries. The experiment and the relevant materials used to make the solar cell are taken from a commercially available kit (the "Nanocrystalline Solar Cell Kit" from the institute for chemical education, http://ice.chem.wisc.edu/Catalog/SciKits.html).
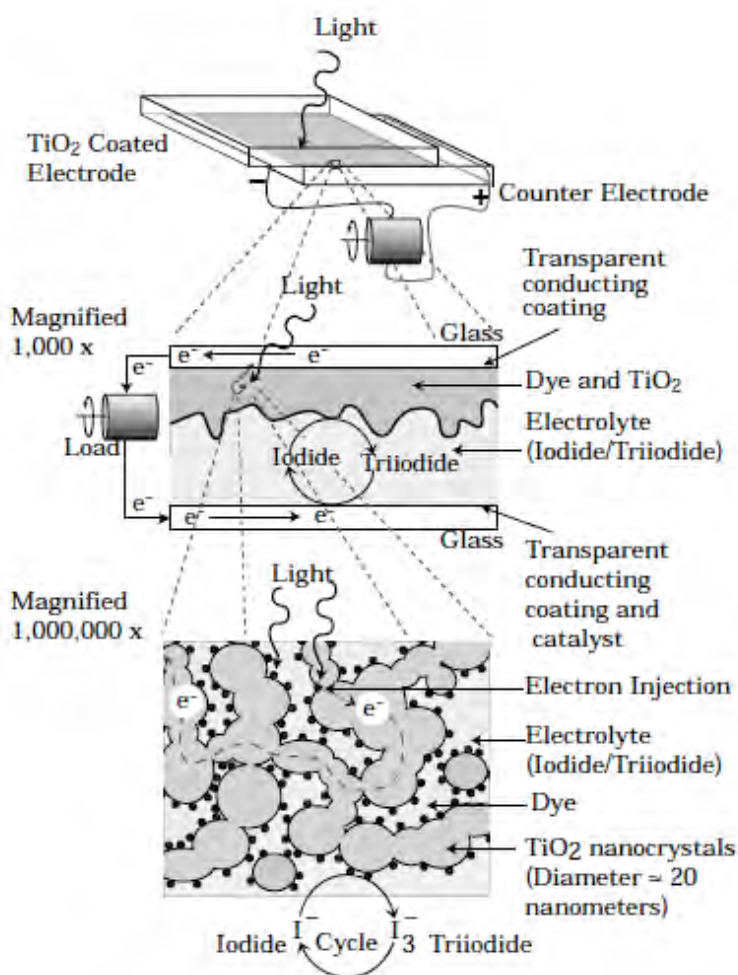

Figure 1. Schematic of a dye-sensitized solar cell. A photoexcited dye transfers an electron to the semiconducting TiO_2 nanoparticles. The injected electron is then transported through the porous TiO_2 layer and collected on a conductive (SnO_2) glass slide. Within the electrolyte, a mediator (I_2/I_3^-) undergoes oxidation at the dye and returns an electron to the dye. Taken from Smestad, G. P.; Grätzel, M., "Demonstrating Electron Transfer and Nanotechnology: A Natural Dye–Sensitized Nanocrystalline Energy Converter." *J. Chem. Ed.* **1998**, *75* (6), 752-756.

Background:

A solar cell converts sunlight into electricity by the photoexcitation of a semiconductor. In this experiment, particles of the semiconductor titanium dioxide (TiO_2) is used. The energy band gap of TiO_2 lies in the ultraviolet region of the spectrum. To provide sensitivity to visible light, a dye molecule is attached to the surface of the semiconductor. The dye absorbs visible light and injects an electron into the conduction band of the semiconductor, which is then collected by an electrical contact. In this experiment, an anthocyanin dye obtained from blackberries is bonded to TiO_2 nanocrystals. Absorption of light by this highly conjugated dye generates an energetic electron that is transferred to the TiO_2 nanocrystal. Electrons are then passed from the TiO_2 to a conductive glass microscope slide which is connected to a circuit that measures current and voltage. To complete the circuit an I_2/I_3^- electrolyte is used to return the electron to the dye and thus regenerate the system.

References:
1. Smestad, G. P.; Grätzel, M., Demonstrating Electron Transfer and Nanotechnology: A Natural Dye–Sensitized Nanocrystalline Energy Converter. J. Chem. Ed. 1998, 75 (6), 752-756.
2. "Nanocrystalline Solar Cell Kit," available from ICE (the Institute for Chemical Education), http://ice.chem.wisc.edu/Catalog/SciKits.html

Procedure:

Supplies:
500 ohm potentiometer
woodless HB graphite pencil
12 cm copper tape
binder clips
dropper bottle
ITO slides: glass slides coated on one side with a layer of indium-doped tin dioxide
Degussa P25 colloidal titanium dioxide powder
iodine electrolyte solution in a dropper bottle
10^{-3} M nitric acid
blackberries

Safety Precautions
The iodine electrolyte is corrosive and should be handled with care. Do not breathe the TiO_2 powder. Nitric acid is a strong oxidizer, and when in contact with other materials it may cause fire. Corrosive liquid and mist will cause severe burns to all body tissue, and may be fatal if swallowed or inhaled; may cause lung and tooth damage if inhaled.

Preparation of TiO₂-Coated ITO Slide

(1) Clean and dry a mortar and pestle. If they are not sufficiently clean, add a few drops of concentrated nitric acid to aid in dissolving any leftover contaminants. Caution: neutralize any acid spills before wiping up!

(2) Weigh 2g of the TiO_2 powder and place it into the mortar. To the powder, add 1mL of the 10^{-3} M HNO_3 solution via pipette. Carefully grind with the pestle until the powder is uniform in texture.   The powder should resemble a dry paste. Continue adding the HNO_3 solution until it attain the consistency of thick paint (about 2.5-3mL of HNO_3 solution per 2g TiO_2). Once the suspension is made, it can be saved in a tightly sealed container.

(3) The two ITO slides provided consist of a glass slide that has a thin layer of indium-doped tin dioxide (ITO) on one side , which makes this side Clean two ITO Slide conductive glass slides with ethanol and dry with Kimwipes. Use a multimeter (set to measure resistance in ohms) to determine which side of the slide is conductive; the reading should be between 10-50 ohms. Place one slide on your bench, conductive side up. This slide will be coated with the TiO_2 suspension. Place the other slide adjacent to the first glass slide, conductive side down.

(4) Apply two 6-7 cm pieces of Scotch (3M) adhesive tape to the top faces of the slides covering a strip approximately 1 mm wide on the two longer edges of the slides. Apply a third piece of tape along the top of the conductive slide to cover a 4-5 mm strip on the slide as shown in the Figure below:

slide with conductive side up

slide with conductive side down
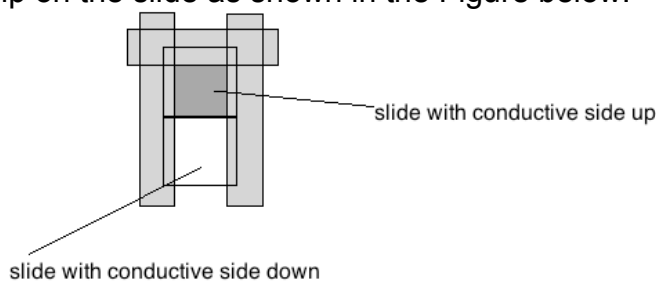
Placement of tape on ITO-coated glass slides

(5) Clean a glass stirring rod with ethanol and dry it with a Kimwipe. The TiO_2 suspension dries quickly, so the coating process should be done within twenty seconds. Apply a uniform line of the TiO_2 suspension sufficient to coat the surface of the top slide (the one with the conductive ITO layer facing up) to the edge of the slide near the tape using the dropper bottle. Slide the rod (held horizontally) over the slide to spread and distribute the TiO_2 coating evenly. Use a rapid sweeping motion (not rolling) of the rod toward the bottom of the slide and then back up two or three times without lifting the rod. If the coating is non-uniform, the material can be wiped off the slide with ethanol and the procedure repeated.

(6) Carefully remove the tape and place the TiO_2 coated slide in a petri dish. Allow the film to dry for one minute and then place a cover on the petri dish. Remove any TiO_2 from the slide that was conductive side down with ethanol and dry.

(7) Turn on the heat gun and allow it to warm up for a few seconds. Heat the ITO glass slide with the TiO_2 coating to anneal it for 10 minutes. You should perform the annealing process in your fume hood.

(8) After it has cooled, move the TiO_2 coated slide to the drying oven and anneal it for an additional hour at 150 °C.

Preparation of Graphite-Coated ITO Slide

(1) Using a graphite pencil, apply a uniform graphite coating onto the ITO-coated face of the second glass slide. Use tweezers to hold the slide, and make sure the coating is uniform and evenly spread across the entire face.

Dye Staining of TiO₂-Coated ITO Slide

(1) Mash 5-7 blackberries with a mortar and pestle, and dilute the fruit compote in a beaker with 10 mL of water. Transfer the suspension to a Buchner funnel (without filter paper) and collect the filtrate by gravity filtration to remove the seeds and larger chunks of pulp (do not use vacuum). Thoroughly clean the funnel and re-filter the filtrate, this time using filter paper and vacuum.

(2) Place the TiO_2 coated slide on a watch glass, TiO_2 side down, and carefully pipette the berry juice onto the watch glass until the TiO_2 face is submerged. Allow the submerged slide to stand for 3 min, then gently rinse off the excess juice in a water bath. Carefully rinse with ethanol and allow to air dry.

Note: If the TiO_2 film peels from the slide during staining, you can try to recover the experiment: add 1 mL ethanol to the watch glass and decant excess juice. Scrape the ethanol-wet TiO_2 back onto the slide, press it into a thin film, and allow to air dry.

Cell Assembly and Testing

(1) After ensuring that the dye-impregnated TiO_2 glass slide is clean and dry, place it on a flat surface with the TiO_2 film side up. The graphite-coated counter electrode should be placed graphite side down on top of it so that the two substances come into contact with one another. The two slides should be offset such that all of the dye-impregnated TiO_2 is covered with the counter electrode and the uncoated ITO on each glass slide is exposed. This step should be done quickly to limit exposure of the materials to air.

(2) Carefully pick up the two slides and place a binder clip on each of the longer edges to hold the assembly together. Place 1-2 drops of the 0.5 M iodide electrolyte solution at one edge of the slides. Open and close the binder clips to allow the solution to infiltrate the dye-impregnated TiO_2 film. Wipe off any excess iodine solution using a tissue dampened with ethanol. To facilitate electrical conductivity, wrap a small piece of copper foil around the edge of each of the exposed glass strips on either side of the cell. Attach the negative lead of the multimeter to the dye-impregnated TiO_2 coated glass and the positive lead

to the graphite counter electrode.
(3) Take the completed solar cell outside into the sun. Position the cell with the dye-impregnated TiO_2 side toward the sun to allow sunlight to enter the cell. Measure the open-circuit voltage with the multimeter set to measure volts, then set the multimeter to measure current and record the short-circuit current. Measure the open-circuit voltage and short-circuit current in the dark.

Laboratory report

Include one or two photographs of your completed cell with the measurement circuitry in place.

Table 1:

Quantity	Value
Open-circuit voltage (mV):	
Short-circuit current (mA):	
Exposed area of the solar cell (cm^2):	
Open-circuit voltage in the dark (mV):	
Short-circuit current in the dark (mV):	

Questions:

(1) Assuming a fill factor of 70%, what is the power output, in mW/cm^2, of your solar cell?
(2) A typical value for the power density of full sunlight in San Diego is 76 mW/cm^2. Assuming a fill factor of 70%, what is the power conversion efficiency of your solar cell?
(3) Did you measure a nonzero value of open circuit voltage or short circuit current from your cell in the dark? What would cause your cell to display a dark current or voltage?