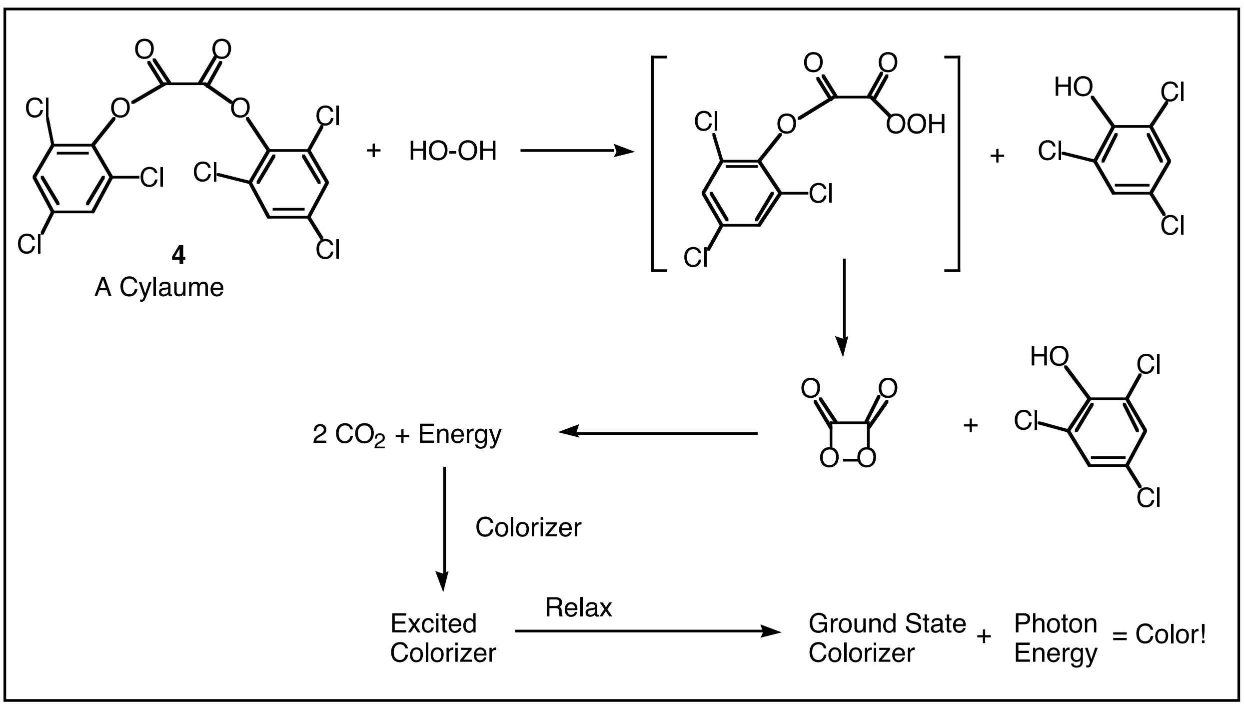
Chemiluminescence: Synthesis of Cyalume and Making it Glow

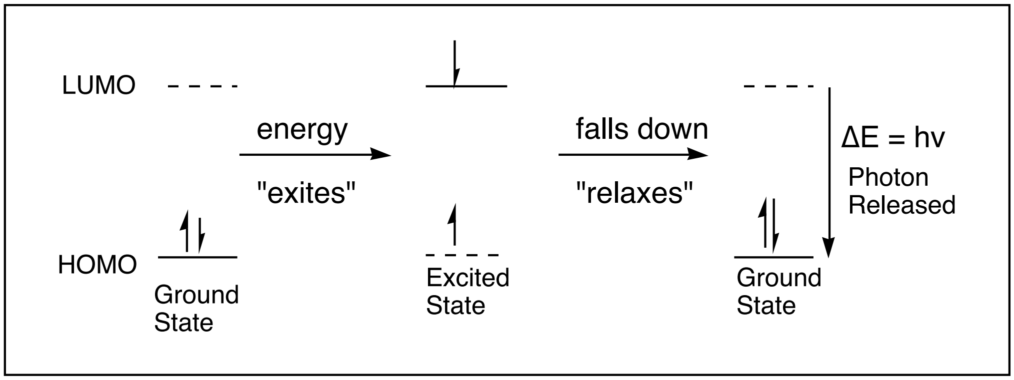
Intro *Chemiluminescence* is the process whereby light is produced by a chemical reaction. The flashes of the male firefly in quest of a mate is an example of natural chemiluminescence. In this experiment we will make Cyalume, the chemical used in "light sticks." A light stick contains a solution of cyalume containing a catalytic amount of a colorizing agent. Inside is a sealed vial of aqueous hydrogen peroxide. When you bend the light stick, the hydrogen peroxide vial breaks, the hydrogen peroxide reacts with the cyalume, and energy is released. This energy is absorbed/released by the colorizing agent, resulting in the bright glow of varying color. Cyalume is an invention of the American Cyanamide Company. In today's experiment, we will make some cyalume, then make up two glow solutions, one using a commercial colorizer and the other using a home-made colorizer that you will synthesize later this semester.

Nature of the Energy Release and Glow Formation

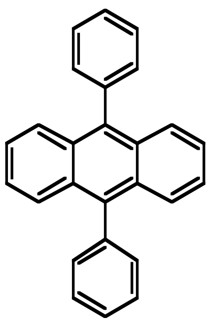
The chemistry that forms the color glow in a light stick is shown below. A cyalume is a symmetric diester, such as **4**. It reacts with hydrogen peroxide by oxygen exchange. Trichlorophenol is released as each of the two oxygens of hydrogen peroxide connect to the two carbonyl groups. The 4-memeberd ring "squarate" diester is unstable due to ring-strain, and fragments to give two molecules of carbon dioxide and energy.



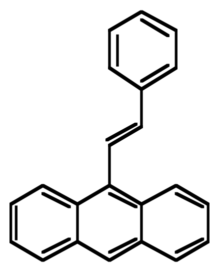
The energy released during the fragmentation "excites" a colorizing molecule that must be present. In other words, the energy of the colorizer gets "excited" from its ground state to an excited state. When it subsequently relaxes back to the ground state, a photon of energy is released. If the energy gap ΔE between the excited state and the ground state is in the visible region of the electromagnetic spectrum, then visible photons of distinctive color are released. This is what causes the bright color.



Several things to note about the exitation/relatation process: 1) The energy gap between the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) determines the photon frequency and the color of the photon released. 2) For most organics, the HOMO-LUMO gap is not in the visible frequency. 3) To have a HOMO-LUMO gap that's in the visible spectrum, extensive conjugation is required. The examples shown below are representative. 4) Only a catalytic amount of colorizer is required. Excitation and relaxation regenerates the original molecule in it's ground state, ready to repeat the process.



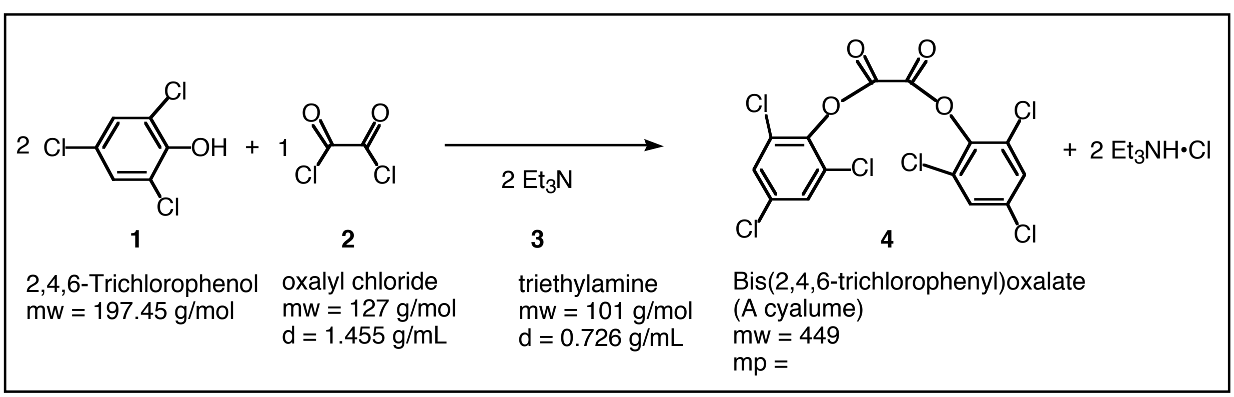
commercial colorizer (purple glow)



homemade colorizer (yellow/green flow)

Cyalume Synthesis Overview

The synthetic reaction is shown below. Oxalyl chloride is a symmetric acid chloride that is highly electrophilic and is very reactive because of the chloride leaving group. One oxalyl chloride reacts with two molecules of phenol **1** to give the diester **4**, which is a cyalume. (Not all cyalumes have the same 2,4,6-trichloro substitution pattern on the arene rings.) Triethylamine is an amine base which serves to absorb the two HCl's that get produced during formation of the diester.



Part I: Cyalume Synthesis Procedure

1. Work with partner
2. Add a stir bar (not the really small ones, the ones somewhat larger…)
3. Flame-dry a 25-mL round-bottomed flask containing a stir bar (not the really small ones, use the somewhat larger ones…)
4. Add 0.79 g of trichlorophenol
5. Add 6 mL of toluene (solvent, bp = 111ºC)
6. Add 0.56 mL of triethylamine by syringe, and swirl.
7. Cool the flask in an ice-water bath.
8. Bring to hood where instructor will inject 0.200 mL of oxalyl chloride. Swirl. The oxalyl chloride is a smelly lachrymator (makes you cry), and needs to be measured with a special syringe in the hood.
9. After swirling your mixture, attach a reflux condenser, and reflux the mixture gently while stirring for 20 minutes on a hot plate/stir plate to complete the reaction. Note: With no heat, the reaction is too slow. But with excess heat, decomposition can occur. You'd like to have it hot enough so that your toluene can barely boil, but you don't want to go to extremes and have it boiling super-crazy. Note: since the hot plate doesn't make very good contact with the flask, you will need to set your heat pretty high. Maybe start around 6 or so, and improvise as needed? (I'm just guessing here!)
10. Cool the mixture well, eventually in ice, and collect the solid (both cyalume and triethylamine hydrochloride salt) with a Hirsch funnel.
11. Use about 5 mL of hexane to rinse the flask and rinse the solids in the Hirsch funnel. Pour the liquid into the organic waste bottle.
12. Make sure the solid is pretty dry before the next step. Use some additional filter paper to press it dry if necessary.
13. Transfer the solid into a beaker, and add 10-12 mL of water. Stir the solution well with a spatula, trying to break up the solid chunks if necessary.
    - Purpose: The triethylamine hydrochloride, being ionic, should dissolve into the water. The cyalume, being organic, should remain insoluble.
14. Filter using a Hirsch funnel.
15. Rinse with an additional 5-10 mL of water.
16. Press to dry.
17. Transfer the cyalume solid into your smallest beaker. Add 2 mL of toluene.
18. Heat on a hot-plate until the toluene achieves a gentle boil. If your sample dissolves completely, you may achieve a normal recrystallization. If it doesn't dissolve completely, just maintain boil for 2-4 minutes, then remove from the heat and let the solution cool.
    - Heating a solid that doesn't dissolve completely is called "**digestion**". So long as the crystal has some solubility in the solvent, digestion still allows back-and-forth between solid phase and solution, and can frequently still allow impurities to be released to the solvent. In the current case, if you use more toluene in order to get a true recrystallization, sometimes it's hard to initiate crystal growth, and the loss of product to solvent is frequently very severe.
19. Filter on a Hirsch funnel.
20. Rinse with 2-4 mL of hexane (one or two pipets worth..).
21. Aspirate thoroughly.
22. Take mass. (Do this today, don't need to wait.)
23. Take out sample for melting point. (Can wait if you wish, but you can do this today if you want.)

Part II: The Chemiluminescent Reaction

1. Get two vials with covers.
2. Add 0.100 g of your synthesized cyalume into each of the vials.
3. Have instructor add about 3 mg of the commercial colorizer into Vial 1.
4. Have instructor add about 3 mg of the home-made colorizer into Vial 2.
5. Add 5 mL of diethyl phthalate (organic solvent, bp > 298ºC) into each of the two vials.
6. Warm the vials on a hot plate. (The heating is not essential. But the initial glow will be more dramatic if the temperature is hot, resulting in faster reaction.) Don't heat too much; you need to be able to carry the vials.
7. Arrange with instructor to bring your vials, with their caps, to the dark room.
8. The instructor will then inject 0.35 mL of 30% hydrogen peroxide/water.
9. Screw the covers back on, shake, and observe the pretty lights!
10. Each partner can take one of the vials home. Show them off to your roommates to show that chemistry is fun! (Woo hoo.) Watch to see how long you can still see them glow. Some students have glow for 2 days or even longer..
11. Eventually it's best to bring the vials back and pour the material out in the waste bottle in the hood. However, if you do drain the liquid in the sink or toilet, that's acceptable also.

Lab Report

- Write up a standard synthesis lab report for Part I. For data include mp, mass yield, and percent yield.
- You don't need to write anything up for Part II. That's just for fun!
- No assigned questions.