# EXPERIMENT 5: Synthesis of Fluorescent Aluminum Complexes

**Purpose of the Experiment**

This experiment demonstrates how luminescent compounds can be synthesized by the addition of a metal ion to a relatively simple non-luminescent ligand.

**Background**

Luminescent organometallic complexes are of interest as the emitting layer materials in organic light-emitting diodes (OLEDs). These compounds exhibit excellent emission properties, good color purity, and relatively high stability. Often, the emission properties of these compounds can be tuned by changing both the substituents on the ligand responsible for the emission as well as the other “auxiliary ligands” on the bound metal.

**Outline of Procedure**

This experiment is divided into three parts. In Part I, SOAP will be synthesized by the reaction of o-aminophenol with salicylaldehyde. *(You have already done this)* In Part II, Al(III)-SOAP will be synthesized by the reaction of SOAP with diethyl aluminum chloride. In Part III, the aluminum complex will be used to detect the presence of various ions in aqueous solution.

**Safety Considerations**

Dimethyl formamide (DMF) is a common solvent that has some potentially hazardous properties. Exercise special care when using DMF, and be sure to promptly clean up any spills or splashes on your skin using plenty of soap and water.

Diethyl aluminum chloride is an air-sensitive, potentially **pyrophoric** reagent. Et2AlCl should only be used in the chemical fume hood and under strictly anhydrous conditions. All glassware should be dry and purged of air (*which contains water vapor*!) prior to introduction of Et2AlCl.

This experiment involves the use of inert atmosphere techniques in several places. The transition-metal complex to be synthesized, Al(III)-SOAP, is air stable, but the reagent Et2AlCl can react violently with water. To prevent reaction with water, the reagents/solvents used in this experiment will be anhydrous and all glassware should be dried in the oven and degassed to remove any residual water prior to addition of Et2AlCl. “Degassing the glassware” can be accomplished by evacuating the flask (or other closed apparatus) with vacuum and carefully refilling with dry nitrogen. This technique is often referred to as “vacuum-backfill” degassing and will be used several times during the course. This technique will be demonstrated by your instructor.A. Synthesis of Chloro-(*N*-salicylidene-*o*-aminophenol) aluminum(III) (Cl-Al(III)-SOAP)

**\*\*\*Be sure to dry the glassware in the oven for 30 minutes prior to assembling the apparatus\*\*\***

1. Set-up the apparatus to be used to synthesize Cl-Al(III)-SOAP, consisting of a 100 mL three-neck flask equipped with a magnetic stir bar, two septa, and a nitrogen inlet. You can assemble it while it is hot.
2. Weigh out 0.100-0.150 g of SOAP ligand into the cooled three-neck flask by quickly removing a septum and adding the reagent.
3. Degas the apparatus by evacuating the system and carefully refilling with nitrogen using the inlet adapter.
   1. Repeat this process three times.
4. Transfer 10 mL of anhydrous toluene to the flask using a pre-purged syringe.
5. Using a pre-purged, 1 mL disposable plastic syringe, add 0.5 mL of Et2AlCl dropwise with vigorous stirring.
   1. \*\*Be sure that the flask is open to nitrogen, as gaseous ethane is produce during this reaction.\*\*
6. Allow the reaction to proceed at room temperature for approximately 15 minutes.
7. Stop stirring and place the flask in an ice bath for approximately 20 minutes to promote crystallization/precipitation of the product.
8. Collect the solid by vacuum filtration. Wash with cold toluene (NOT ANHYDROUS!!).
9. Allow the solid to dry between filter papers in your drawer until next lab period. Determine your yield (in grams and %).
10. Characterize the product by FTIR and 1H-NMR spectroscopies.

### B. Fluorescence properties of (Cl-Al(III)-SOAP).

In this section the spectroscopic characteristics of the Al-SOAP complex will be determined.

1. Make 25.00 mL of 200 M Cl-Al-SOAP dissolved in Ethanol.
2. Make 100 M Cl-Al-SOAP solution by adding 1.00 mL of stock Cl-Al-SOAP (above) to 1.00 mL of DI H2O.
3. Determine the wavelength of maximum absorbance (max) for the Al-SOAP complex using the spectrophotometer in the Inorganic lab. *(You may need to dilute the sample if the Absorbance is too high).*
4. Use the max to determine the wavelength of maximum emission (em) for the 100 M solution of Al-SOAP using the fluorescence spectrometer in the instrument room.
5. Use the em to determine the wavelength of maximum excitation (ex). How does this compare to max?
6. Determine max, em, and ex for SOAP ligand dissolved in 50% Ethanol/H2O by following the Procedure outlined in Steps 1-5 above.

## Discussion Questions

1. Compare the absorbance and emission spectra for SOAP ligand and Cl-Al-SOAP. Discuss any differences you might observe.
2. Determine the Stokes shift for the aluminum complex using your data.
3. Sketch a Jablonski style diagram to explain how absorption and emission differ. (Use a picture to explain the origin of the Stokes Shift)