

6.973 Lab 1: Excitonic Energy Structure of Organic Materials

1. Overview

In this lab we will perform measurements that allow us to observe the energy structure of excitons in some important optoelectronic organic materials. Essentially, we will measure the emission and absorption spectra of these materials in different environments. The environments will be chosen so as to best illustrate the important concepts in determining the exciton energies and energy transfer pathways (if any exist) in a given system. The organic materials we will study are TPD, Alq₃, and DCM2 (full chemical names and chemical structures given in Figure 1). Some additional materials will be used in this lab, and their chemical names and structures are given in Figure 2. *The idea is to develop a nice intuition about photoluminescence processes in organic materials.*

2. Sample Preparation

We will make two different kinds of samples: solutions and thin films. Since we will be spinning on our thin films (as opposed to evaporating them), we actually have to make solutions up for the thin films as well. In total we will look at four solution samples and four thin film samples. They are:

Solutions

- TPD in Benzene
- DCM2 in Benzene
- TPD in Dimethyl Sulfoxide (DMSO)
- DCM2 in DMSO

Thin Films

- TPD
- Alq₃
- Polystyrene(PS):DCM2
- TPD:DCM2

In the solution samples we are not particularly interested in the exact concentration of the solute, since the measurements we will perform are not overly sensitive to concentration. The following table summarizes the preparation details for the four solutions:

Solution	Solute Solubility	Preparation
1 (TPD in Benzene)	Moderate	~2.0 mg TPD into 20 mL Benzene
2(DCM2 in Benzene)	Moderate/Low	~2.0 mg DCM2 into 20 mL Benzene
3(TPD in DMSO)	Moderate/Low	~2.0 mg TPD into 20 mL DMSO
4(DCM2 in DMSO)	Moderate/Low	~2.0 mg TPD into 20 mL Benzene

Each solution might take a different amount of time to dissolve fully, but for simplicity all of the solutions are stirred for about 2 hours. Finally, all of the solutions are pushed

through a 0.2 μ m PTFE (Teflon) filter to make sure none of the undissolved material is transferred into the sample cuvettes.

For the thin film samples, it is more important to get the various concentrations of materials in solution correct. This table specifies the exact preparation of the thin films and precursor solutions.

Film	Solution Preparation		Spin Speed
	Solute	Solvent	
1	20 mg Alq ₃	2 mL CHCl ₃	2500 rpm
2	20 mg TPD	2 mL CHCl ₃	2500 rpm
3	40 mg PS 0.7 mg DCM2	2 mL CHCl ₃	2500 rpm
4	20 mg TPD 0.7 mg DCM2	2 mL CHCl ₃	2500 rpm

The last column, labeled “Spin Speed” gives the rotational speed (in rotations per minute, or rpm) that we will use when spinning the film onto our substrates.

One could use many different approaches to making the solutions. For the single component solutions, we will simply weight out the solute directly into a small vial and introduce the appropriate amount of solvent, and set it stirring until dissolved. Some of these solutions take a very long time to dissolve, and for simplicity we will stir all of our solutions overnight (or ~8 hours).

For the multi-component solution, it is very difficult to get the relative amounts of solute correct if one weighs all the solutes directly into one vial. So instead we will make an intermediate single component solution of 5.0 mg DCM2 in 15 mL CHCl₃ that we will use to get the final solution made. In this way we can make sure to only be weighing out a single material at a time directly into a vial. Using this, we can easily make the target solutions:

Film	Solution Prep		
	Intermediate Solution	Solid Solute	Pure CHCl ₃
1	None	20 mg Alq ₃	2 mL
2	None	20 mg TPD	2 mL
3	2mL of DCM2/CHCl ₃	40 mg PS	none
4	2mL of DCM2/CHCl ₃	20 mg TPD	none

With the all of the target solutions made, we can then make our thin film samples, which will be formed by spin casting. This is done by taking a cleaned glass square (1” x 1”) and placing it on the spinner chuck, squirting some solution over the surface of the substrate using a syringe, and then setting the spinner spinning. The spinner we will use is a Headway Research PMW-32, and we will use 6000 rpm/s for the spin acceleration and 60 s for the spin time. The spin speeds for each film were already listed above. The

physics of spin casting, and how fluid properties and material concentration relate to the film that you get are surprisingly complex. If you are not familiar with the basic premise, however, please ask questions during the lab session.

Once we have spun on the film, we would ideally package it in a moisture and oxygen free environment to minimize degradation of the optical properties of the material. Toward that end, we could have spun the film inside a nitrogen glove box, and then encapsulated the film by depositing a bead of epoxy around the edge of the substrate, sticking another piece of glass on the bead, and curing the epoxy. This would make a sealed sample. However, working in a glove box and encapsulating a sample, is time consuming, and it would be prohibitive to have everyone in the class make samples this way. So, when we perform our measurements, they will be on a set of encapsulated samples made by the TA in the manner just described. However, so that everyone understands the film deposition process, everyone will spin films, but do so in air, and the samples will not be encapsulated.

3. Measurements

There are two basic properties that we will measure in this lab: absorption spectra and photoluminescence spectra. In the first case we measure the distribution of incident photons absorbed by the material, and in the second case we measure the distribution of photons emitted by the material following excitation by a high energy light source.

The absorption measurement will be performed by shining a collimated beam of a broadband light source (an Oriel 150 W Xe Arc Lamp, P/N 6253) through the sample, and collecting the transmitted light into a fiber coupled to the inlet slit on an Acton 300i Spectrograph. This light passes through the slit and hits (at an angle) a grating inside the spectrograph housing. Depending on the wavelength of the light hitting the grating, the light will reflect at a different angle, and hence the beam of light that reflects from the grating is dispersed by wavelength. The grating is aligned to direct the wavelength dispersed signal onto a CCD, which we can think of as an array of photodetectors. A computer hooked up to the spectrograph and the CCD camera controls the exact grating alignment (which determines the range of wavelengths that hit the CCD), collects the intensity signal measured by the CCD pixels, and converts this into an intensity and wavelength calibrated spectrum. We first measure the signal for a “blank” which will consist of a cuvette full of pure Benzene or DMSO in the solvent experiments, or a packaged glass slide without any thin film in the thin film experiments. Then we measure the signal for the sample. By dividing the sample spectrum by the “blank” spectrum, we obtain the % transmission curve. We convert this into an absorbance spectrum by taking the natural log of the % transmission curve.

The emission measurement is performed by shining the beam from an LSI VSL-377ND-S 7 mW Nitrogen laser ($\lambda = 337.1$ nm) onto the sample, and collecting some of the emitted light into a fiber connected to the inlet slit of the spectrograph. By aligning the grating to avoid seeing any of the laser light, we can obtain the spectrum of the emitted light. (If we allow the detector to see the laser light, it will saturate the detector, which is

not good for the detector and can reduce the measurement accuracy.) We may also introduce a few other laser lines for excitation, and speculate on the differences observed.

We will obtain the absorption and emission spectra of all of our samples. However, we may find that a good absorption measurement is not possible for some of the thin film samples because they are not sufficiently absorbing to be detected with our setup. In this case, we will use data (for the similar samples) obtained using a Cary 500 UV-VIS-NIR Spectrophotometer. (This instrument is in the CMSE shared facilities labs on the fourth floor of building 13. Since you must be trained to use any of the instruments in this facility, it is not practical to have everyone in the class do the measurements with the Cary.)

4. Analysis/Discussion Questions

A. Calculate the shift between the absorption and emission peaks in the solvent samples. Are there any noticeable trends in the shape and spectral position of the emission and absorption spectra for the different solvents? Can you venture a guess why? (We will actually cover this later in the course, but you may already be familiar with the effect we're alluding to.)

B. Calculate the relative PL quantum efficiencies of the TPD, Alq₃, and PS:DCM2 films. (In the PS:DCM2 film, only consider photons absorbed and emitted by the DCM2.) If you assume that the TPD thin film is 35% quantum efficient, give the absolute quantum efficiencies of the Alq₃ and PS:DCM2 thin film. Please assume that all measurement conditions (slit width, integration time, detector position) are identical for each spectrum.

C. You were shown a film of pure DCM2 during the measurements. The quantum efficiency was far lower than for the PS:DCM2 film. Why?

D. And here is the tough question in which you determine the Forster energy transfer radius for exciton energy transfer from TPD to DCM2. Assume excitons do not diffuse, and assume your TPD:DCM2 thin film is a perfectly homogenous mixture of the components in the precursor solution, at the same mass ratio. Since the rate of energy transfer from TPD to DCM2 is proportional to $(R_F/R)^6$, you may assume that any TPD exciton this is less than R_F away from a TPD molecule will transfer to that DCM2 molecule. You can determine the Forster radius from the emission spectrum for the TPD:DCM2.

