Lab rotation on optical spectroscopy of organic semiconductors

Objectives

- Gain experience in the use of optical and Raman spectroscopy to study the electronic and vibrational properties of organic semiconductors.
- To record absorption, photoluminescence and Raman spectra of a series of materials, and determine key parameters such as inhomogeneous linewidths, Stokes shifts and Huang Rhys factors.
- To explore the effect of temperature on the optical properties of a conjugated polymer.

Experiments

You have been supplied with solutions of the polymers PCDTBT, P3HT, PFO and F8BT (solutions in the solvent chloroform). You also have a sample of chloroform solvent.

Choose which materials you are most interested in and spin-coat thin films using the spin-coater in the fume-hood in the 2nd year lab.

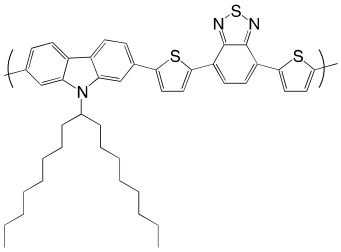
There are many possible experiments to do. You will not have time to do everything. Low temperature measurements will take a whole afternoon. We suggest you try the following (see how time goes…).

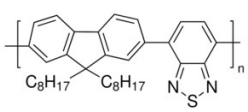
1. Absorption and PL at room temperature. Measure polymer absorption and fluorescence at air and at room temperature either in solution (using a cuvette) or from a thin-film. You will need to identify the most suitable laser to generate fluorescence after you have measured the absorption spectra.

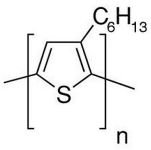
2. Raman spectroscopy. Using the Raman spectrometer, measure the Raman scattering spectrum of the various materials in solution. By comparing the emission, absorption and Raman spectra, you may be able to determine the energy of the vibrational mode that couples to the electronic transition. Perform a web-search to identify the origin of this mode. (Note that some materials have a high degree of inhomogeneous broadening, making the determination of vibronic modes in the PL spectrum difficult at room temperature).

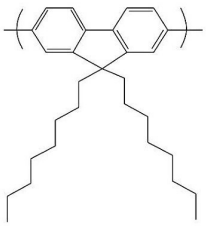
3. Temperature dependent spectroscopy. Measure the absorption and / or fluorescence emission of one polymer thin-film as a function of temperature. Here, you should use the cryostat to cool the sample down to 4K. You can analyse your spectra quantitatively by fitting a series of Gaussian functions, and plot changes in peak energies and widths. Note that the cryostat will

take at least 4 hours to approach 4K, and thus you need to load up your sample for low temperature measurements before lunchtime.









PCDTBT F8BT P3HT PFO

Raman spectroscopy: hints and tips

Open Ocean View with the spectrometer already connected to the computer and powered up. When the software opens there should be a window asking some questions – select Run a Wizard. Select Spectroscopy, then Raman. On the window that opens you can set various parameters. At the moment just set the integration time to about 1 second. With the Raman probe either with the shutter closed or not sampling any Raman active material click on the black bulb icon, click Apply then click Next. You should now have two windows/two tabs – one is a standard spectral view and the other in a Raman Shift View (with x-axis in cm^{-1}) – select the Raman View

Place the Raman probe on sample to be measured and record a Raman spectrum. You may need to click on the up and down arrow above the spectrum to maximize the y-axis. On top of the graph, there are two a floppy disk icons which allow you to save or retrieve a file. Save files in .txt or .csv format so you can then export them easily to analysis software. You can use the tools menu (spanner next to paper icon) to store data with an automatic file name increment label. Periodically review your data to check that it is OK and that you are taking good data.

You will need to play with the integration time and maybe scans to average until you get the settings you're happy with. Whenever you change the integration time you should make sure you take a new dark measurement (clicking on the black bulb icon). For sensitivity tests, you can adjust laser power (on laser driver box) and also increase integration time. You will need to subtract a water background. You can do this by measuring a pure water sample and then subtracting one data set from another using your data analysis software of choice.

Absorption and fluorescence: hints and tips

Turn on both deuterium and halogen lamps. For thin-film absorption measurements in air, position the light delivery fibre and light collection fibres each approximately 10 cm above and below the sample measurement stage.

For solution measurements, carefully unscrew SMA fibres and attach to the cuvette holder. There are a range of cuvettes available – make a choice depending on whether your samples have a high or low optical density (low optical density samples typically need a longer cuvette path-length). Once you have decided which cuvette to use, stick to your choice, as changing path length will introduce an un-needed variable.

To measure absorption, click on the appropriate absorption 'Wizard' on the Ocean View software. You will need to record a reference spectrum and a background spectrum (no light). The software will then calculate the relative absorption for you. For absorption measurements, you will need to play around with the integration time (between 10 and 100 ms work well) with an average of 2 – 5 scans.

To measure PL of thin film samples at room temperature, place the sample on the flat measurement stage. Turn on the laser, and check it strikes the middle of the film at around 45 degrees incidence. Adjust the position of the bottom fibre so it is as close as possible to the sample. Again, you should use OceanView software to make your measurements. Select the 'Fluorescence' Wizard. Note an integration time of 1000 ms or more may be needed. The laser source can be changed by un-mounting the laser from the aluminium tower using a M6 hex-driver, and then swapping laser. Be careful not to drop the lasers while you are doing this.

Save your data by clicking on the 'Disc' icon on the toolbar (centre of the screen). Use the save utilities (next to the disc icon) to set the location of the saved files, the root file-name and ASCII format. **Don't save by clicking on the disc icon on the left-hand of the screen** (near the top). This saves a project, and retrieving your data is then very difficult.

Make sure you periodically review your data to check that it is OK and that you are taking good data. You can import it into Excel to check things are OK.

Low temperature measurements: hints and tips.

Mount your sample on a piece of glass in the Oxford Instruments cryostat. To mount the sample, make sure the cryostat is not under vacuum (turn off the vacuum pump, and then vent the system to

atmosphere by unplugging the fine wires that are coupled into the turbo pump).

Open the cryostat by undoing the two finger-nuts that hold the cover plate with the optical access window. You should then remove the radiation shield, and the sample holder (ask for help here if you need!). Your sample can then be gently clamped to the cold finger using the small metal plate.

Re-assemble the cryostat, and turn on the pump. Watch the pressure gauge. It will start at around 2500, but after 5 mins or so will fall rapidly to ~ 10. After it has pumped down for 20 minutes or so, you can turn on the compressor. You can do this yourself by flicking the circuit breaker on the compressor unit to the ‘up’ position, and then turning on the green switch (ask for help of you need). The compressor system will make a loud, alarming noise, and the room will get quite hot. You can read off the temperature on the cryostat control electronics (this will slowly drop).

Make measurements of absorption and / or PL as the temperature drops. You will need to first re-position the fibre-optic cables used to deliver light to the sample. You can again mount a laser on the metal tower to generate PL. Make sure you block the white-light source when you measure PL, as this will otherwise pollute your measurement.

To turn-off the system to return to room temperature: turn the green-switch on the compressor to the off position and flick the circuit breaker to the down position. Leave the system to warm up (this will take many hours!).