

Development of a Visible Light Photoluminescence Microspectrometer

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Abstract

Photoluminescence (PL) is the process by which light is absorbed and re-emitted by a material. In solid-state physics, PL is an important characteristic measurement for studying the electron band structure of molecules. Here we report the design and construction of a simple instrument which can measure PL in thin-film materials on a micron spatial scale. We accomplish this by coupling a diode laser system to a metallurgical microscope[†] using optical filters to block reflected light and pass fluorescent emissions. The instrument is equipped with a digital camera for imaging[‡], and a compact spectrometer for measuring fluorescence spectra. We demonstrate the use of the instrument on thin-film samples of crystalline anthradithiophene and cadmium selenide quantum dots.

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1 Introduction

Photoluminescence (PL) is the process by which a molecule re-emits a photon after having absorbed a photon of sufficient energy to excite an electron out of its ground state. Fluorescence occurs when the electron occupies its excited state for a short time — on the order of nanoseconds — before returning to the ground state, emitting a photon in the process. Fluorescence is commonly measured to characterize the band structure of molecules. Basic fluorescence measurements are emission and excitation; emission measurements excite the sample at a fixed wavelength (typically in the ultraviolet range)⁴ and measure the relative intensity of light emitted over many wavelengths. Excitation measurements vary the wavelength used to excite the sample and measure the intensity of light emitted at a fixed wavelength. By combining these two methods, one can build an emission map — a surface which describes the sample’s fluorescence as a function of both emission and excitation wavelengths. The scope of this project includes only emission measurements.

The Micro-Femto Energetics (μfE) group at Oregon State University uses advanced optoelectronic methods to characterize materials, especially thin-layer materials and micron-scale semiconducting devices. The group’s workhorse for PL measurements is a Horiba Fluorolog-3 spectrofluorometer (“the fluorimeter”), often coupled to a microscope via optical fibers. The fluorimeter’s excitation light source is a 450 W xenon arc lamp. A double-grating monochromator selects the chosen excitation wavelength, and this excitation light is directed into an optical fiber by a flat mirror. Delivering the excitation light to the sample via optical fiber provides flexibility when reconfiguring the system to meet the specific needs of a project. For example, the microscope can be used in a transmission or reflection mode by illuminating the sample from below or above, respectively. With the aid of computer software, the fluorimeter is able to measure both fluorescence emission and excitation.

1.1 Motivation

While the Fluorolog-3 is an incredibly flexible and useful instrument, it is particularly limited with regards to how it illuminates samples. When taking measurements via the instrument's sample chamber or via a microscope in transmission mode (such that light transmitted by optical fiber is incident directly on the sample), a region on the scale of centimeters is excited. Even in reflection mode, the excited region is made only proportionally smaller than the cross-sectional area of the optical fiber as the excitation light passes through the objective lens. For many applications, particularly biological fluorometry and fluorescence imaging, excitation on this scale is called for. For others, it may be desirable to excite highly localized, micron-scale regions of a sample.

~~With the goal of taking similar fluorescence measurements on a much smaller scale,~~ we designed and built a photoluminescence microspectrometer. In its current form, the instrument is capable of measuring fluorescence emissions in the visible spectrum, using a diode laser as its excitation source. This paper reports the process of designing the instrument, lessons learned during construction, and demonstrates the use of the instrument on two distinct samples of fluorescent molecules.

1.2 Optoelectronic Materials

Optoelectronic materials convert light to electric energy and/or electric energy to light. The study of these materials goes back as far as the early 1900s, but accelerated rapidly in the 1960s with the advent of the light emitting diode and semiconductor laser [1]. Optoelectronic devices are ubiquitous; they have enabled the rapid growth of information technologies around the world, and are fundamental in modern telecommunication and internet infrastructure. Modern optronics research explores new materials that can be used to create faster, more efficient, and smaller optoelectronic devices.

1.2.1 Organic Photovoltaic: ADT

Organic optoelectronic materials are not a new discovery, but have become increasingly popular in recent decades as methods for creating them have advanced [2]. The Ostroverkhova group at Oregon State University has studied several organic photovoltaics (OPVs) including functionalized derivatives of pentacene, benzothiophene, and anthradithiophene (ADT) [3, 4]. A drop-cast sample of fluorinated ADT with triethylsilyethynyl (TES) functional group, provided by the Ostroverkhova group, is used for demonstration of the new microspectrometer device in Chapter 3.

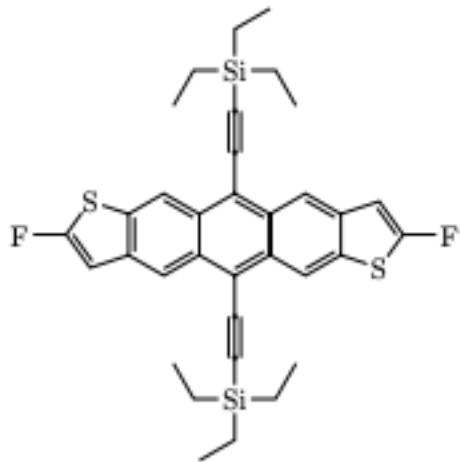


Figure 1: Molecular diagram of fluorinated anthradithiophene (ADT) with triethylsilyethynyl (TES) side group. A drop-cast sample of this molecule was provided by the Ostroverkhova group at Oregon State University, and used for demonstration of our microspectrometer instrument following a study by Lam [5].

1.2.2 Quantum Dots: CdSe

Quantum dots (QDs) are artificial semiconductor particles. They are typically only a few nanometers in size, and there has been a fair amount of research on the tunability of optoelectronic properties in QDs by varying their size and shape. Quantum dots have many of

the same potential applications as other optoelectronic materials, but are attractive for their size and reproducibility. Previous studies have shown how quantum dots can be produced en masse,~~—~~with a high degree of control over their shape and size [6, 7].

A sample of CdSe quantum dots, suspended in solution and drop-cast on a glass slide, is used to demonstrate the new microspectrometer device in Chapter 3.

1.3 Mechanics of Photoluminescence

Photoluminescence occurs in molecules where the valence and conduction bands are separated by a small band gap near the Fermi level. A molecule absorbs a photon with energy greater than or equal to its band gap, exciting an electron from its ground state in the valence band to an excited state in the conduction band. The electron lives in this excited state for a short time, and then relaxes back to the ground state.

The electron can relax non-radiatively~~—~~losing energy as it transitions through vibrational modes — or radiatively, losing a small amount of energy to vibrational transitions and then returning to the ground state. When it returns to the ground state, the energy is emitted as a photon. We expect the energy of this photon to be lower than that of the absorbed photon (and the wavelength longer) because of the loss of energy to vibrational transitions.

Measurement of fluorescent emissions yields information about the energy of these electron transitions, and allows us to map out the electron band structure of molecules.

2 Methods

2.1 Design

2.1.1 Microscope

The starting point of the project was an Olympus BX60M fluorescence microscope. The BX60M is built for reflection microscopy, and includes a housing for brightfield and dark-field mirrors. For the new instrument, we added a mirror cube housing between the bright-field/darkfield mirror housing and the observation tube. This additional component housed a dichroic mirror, which enabled us to couple an external light source into the instrument and filter that light out of the path through the observation tube.

2.1.2 Laser Excitation

The BX60M is equipped with a xenon arc lamp, which is used for general observations under white light illumination. In order to measure photoluminescence, we require the use of a (mostly) monochromatic light source which is energetic enough to excite electrons in the sample.

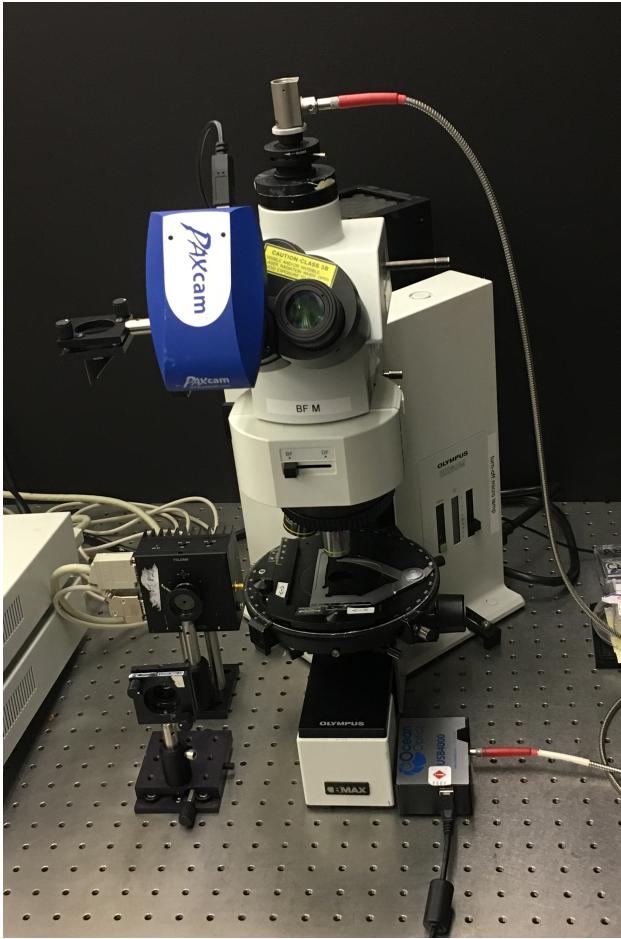


Figure 2: Front view of microspectrometer instrument (laser controllers not pictured) built around Olympus BX60M fluorescence microscope. The laser diode mount and mirrors are shown on the left. Digital camera for sample imaging is mounted to the microscope eyepiece. We have mounted a collimating mirror to the observation tube (at the top of the microscope), which collects emissions and transmits them into a USB spectrometer via optical fiber.

Our instrument uses a diode laser as its light source. Specifically, we used a ThorLabs L405P20 laser diode (405 nm), TCCLDM9 thermoelectrically-cooled mount, LDC 202 laser diode controller, and TED 200 temperature controller. To couple the laser and microscope, we used a set of two mirrors in a vertical beam fold configuration. This enabled precise

alignment of the laser to the optical axis of the microscope, which maximizes transmission of excitation light through the objective lens and onto the sample stage.

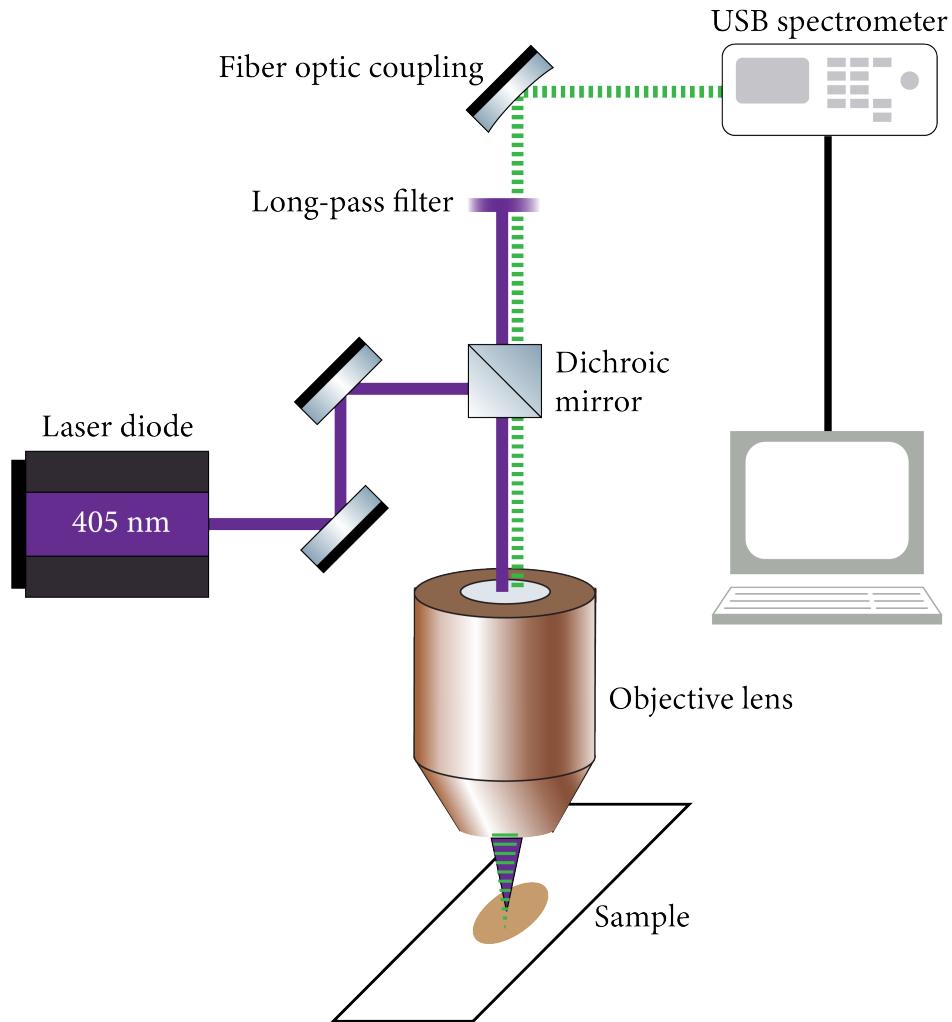


Figure 3: Schematic diagram of the microspectrometer instrument.

The laser diode housing and first mirror were mounted to an optical table. The laser starts parallel to the surface of the table, and the first mirror directs the beam upward. The second mirror in the beam fold was mounted to the end of a tube that extends out the side of the mirror cube housing. This mirror directs the vertical beam horizontally into the mirror. It seems preferable to mount both mirrors to the optical table for stability, but we were successful with this method by mounting the microscope to the table so that it and the second mirror did not move relative to the laser beam during normal operation.

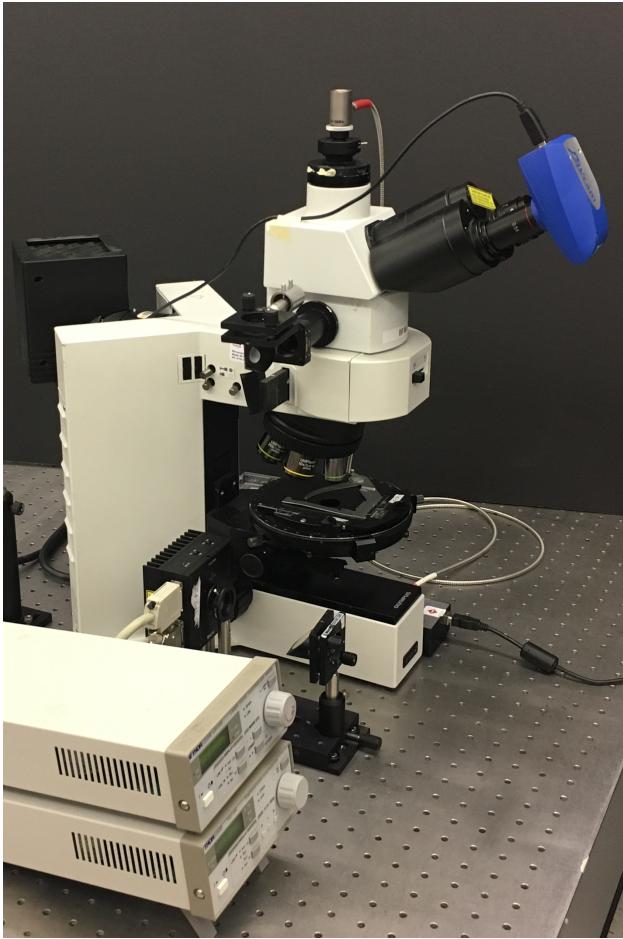


Figure 4: Side view of microspectrometer instrument. Laser controllers are shown in the foreground. Between the controllers and the microscope, two flat mirrors and a dichroic mirror (not visible here) couple the laser light into the microscope's optical path.

~~Due to limited space on the optical table~~, it was not feasible to align the laser diode housing and mirror cube housing in the plane of the table. To overcome this, our beam fold configuration also turns the beam 90 degrees in the plane of the table. The configuration we used has the laser beam initially pointed in the direction of the operator, then directed upward by the first mirror, then directed into the side of the mirror cube housing. While in operation, but particularly during laser alignment, precautions must be taken to protect the operator's eyes from direct exposure to the laser beam. The optical power of the laser is low

enough that laser safety glasses (with high optical density near 405 nm) are sufficient, but beam blocks on the table may also be desirable in some cases.

We used a longpass dichroic mirror with a cutoff wavelength slightly higher than the excitation wavelength at 405 nm, causing nearly all of the excitation light to be reflected in the direction of the sample. A longpass mirror with cutoff wavelength slightly higher than the excitation wavelength is ideal because it will pass most of the light emitted by the sample, as we expect fluorescence to nearly always have a longer wavelength than the exciting photons.

The observation tube on the Olympus BX60M is at the top of the microscope's optical path, and the operator can toggle between using the observation tube or binocular optic. To collect and measure the spectrum of fluorescent emissions, we fixed a collimating adapter to the observation tube. This allowed us to collect emissions and transmit them via optical fiber to our spectrometer.

We used an Ocean Optics (now Ocean Insight) USB2000 miniature spectrometer to measure the spectra shown in Chapter 3. The USB2000 is sensitive to light between about 350 nm and 1000 nm, so in this case we are only able to measure fluorescent emissions in the visible spectrum and a small part of the near-infrared spectrum. This detector can easily be exchanged for one with a different range as required for future projects.

The USB spectrometer is connected to a nearby desktop computer, with Ocean Optics software installed for measuring spectra.

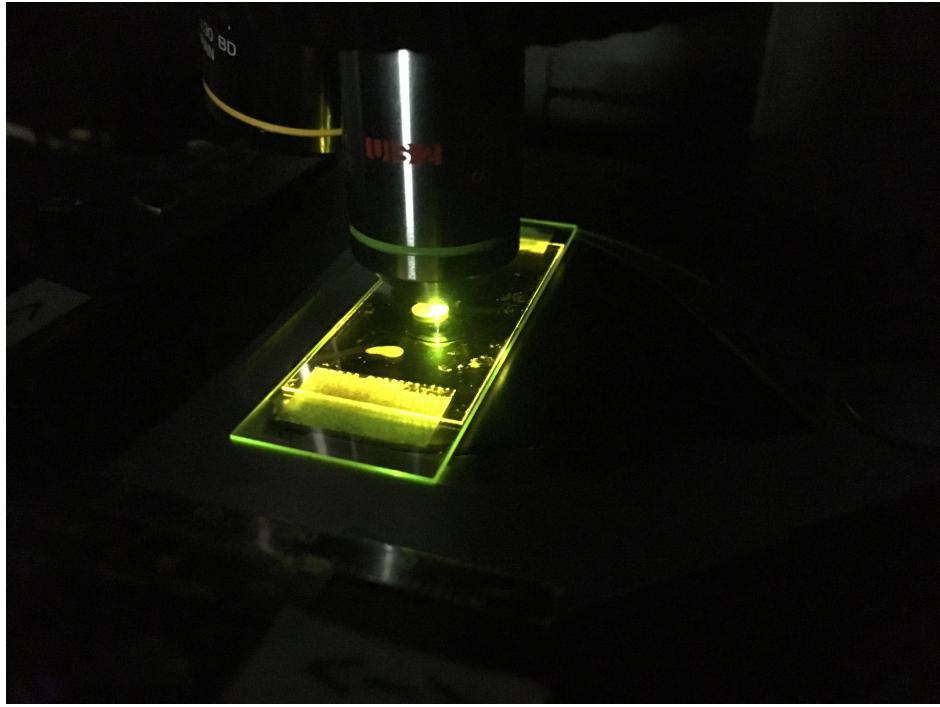


Figure 5: A sample of CdSe quantum dots under laser illumination at 405 nm. Some of the violet laser light is reflected by the sample, but is difficult to distinguish from the sample's intense green emission.

We were able to fix a digital camera to the binocular optic for simple imaging of samples with adapters on hand. The camera is connected via USB to a desktop computer with software for capturing images. Example images are shown in Figures 6 and 8.

2.2 Laser Alignment

We aligned the laser to the microscope's optical axis by iteratively adjusting the two flat mirrors that direct the beam into the side of the microscope. First, we adjust the position of the beam as it enters the mirror cube housing by moving the first mirror. A reticle made of photoluminescent laser viewing material was a particularly useful target when fixed to the opening on the side of the mirror cube housing.

We then adjust the second mirror in the beam fold to change the angle at which the beam is incident on the dichroic mirror. This translates the beam across the back of the

microscope nosepiece, where our target is the optical axis of the objective lens. In place of a lens, we fix an iris diaphragm to the nosepiece. We adjust the second mirror to position the laser in the center of the mostly-closed iris, which marks the location of the optical axis of a lens. This process is repeated until the laser spot is centered on both targets.

3 Results and Discussion

In this chapter we demonstrate the use of the new microspectrometer instrument by measuring photoluminescence in samples of two materials, introduced in Chapter 1.2. Samples of the anthradithiophene derivative ADT-TES-F and of cadmium selenide quantum dots were both drop-cast from solution on glass slides. Both samples were excited at 405 nm, with our detector measuring emissions between approximately 450 nm and 1000 nm.

For each sample we were able to measure PL in approximately the same regions of interest with both the Horiba Fluorolog-3 and our new instrument. Figures 7 and 9 compare the resulting spectra measured by each device.

We also demonstrate the use of our instrument for imaging. Figures 6 and 8 show images of the region of interest used for PL measurements of each sample.

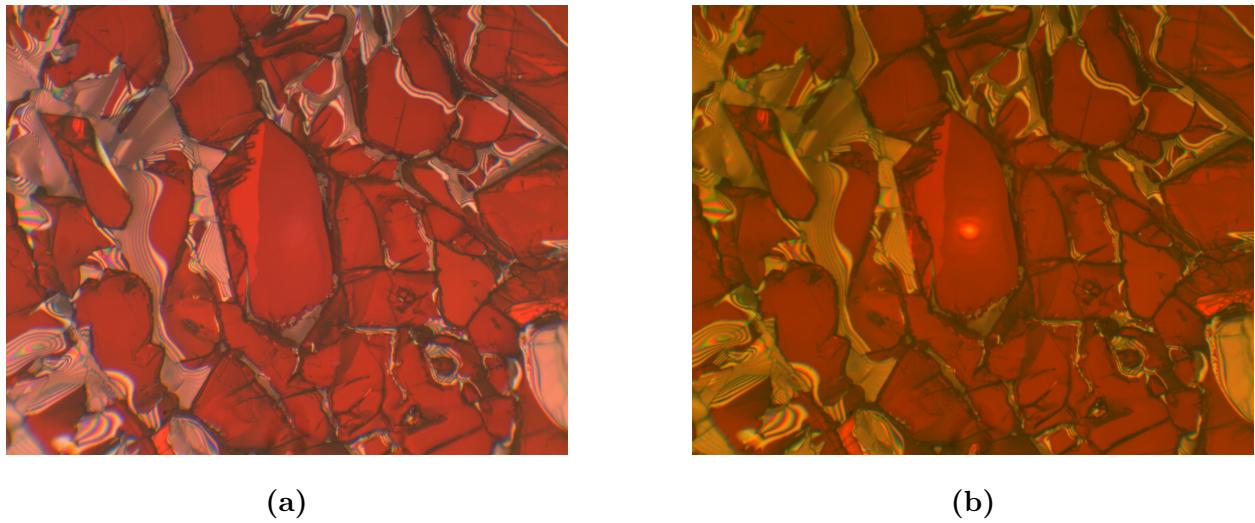


Figure 6: Images of ADT TES-F sample under white light (6a) and under laser excitation light (6b). Reflected excitation light was optically filtered out of Figure 6b using a dichroic mirror and colored glass longpass filter. Photoluminescence spectra of this region are shown in Figure 7.

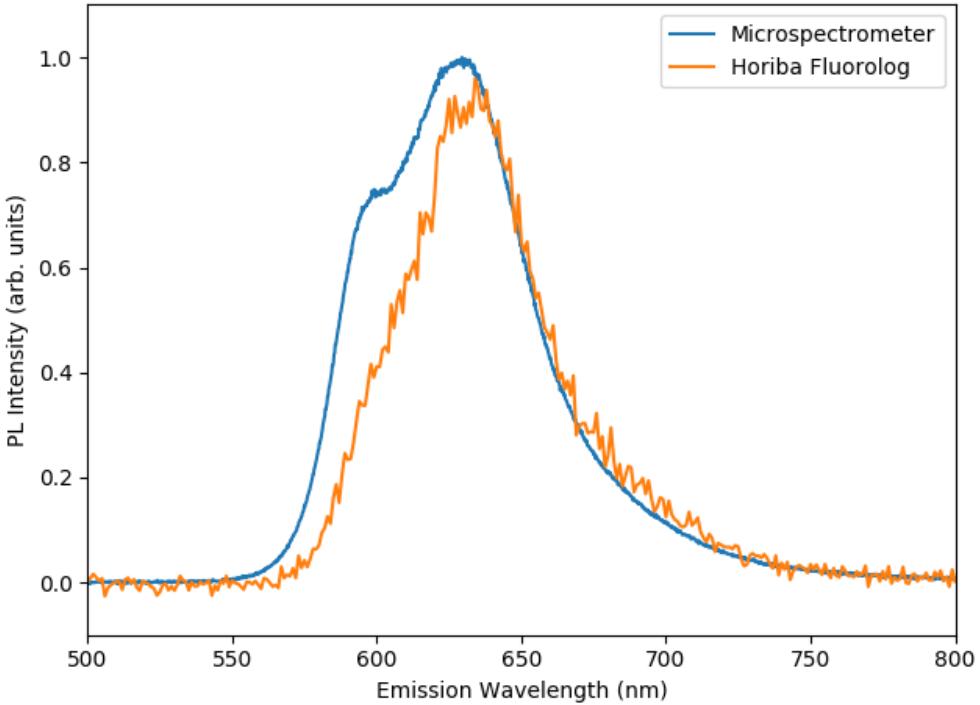


Figure 7: PL emission spectrum of ADT TES-F, excited at 405 nm.

The results from the microspectrometer show an emission maximum at 630 nm for the ADT TES-F sample; a less intense local maximum is also shown at about 600 nm. The spectrum measured with the Fluorolog has similar features to that of the microspectrometer, but is not precisely the same. The peak appears narrower overall in the Fluorolog data than in the microspectrometer data. The lower-wavelength side of the peak begins to rise at a higher wavelength in the Fluorolog data, and the emission maximum is red-shifted by about 4 nm. The local maximum at 600 nm is much less prominent in the Fluorolog data than in the microspectrometer data.

The microspectrometer data shows emission peaks similar to the ones reported by Shepherd *et al.*, who used a similar drop cast sample and the same model Ocean Optics spectrometer [3]. Unlike Shepherd, we were not able to calibrate our detector with a reliable instrument; this could be a cause for the slight shift between peaks in the Fluorolog data as compared to our microspectrometer data.

Crystal aggregates and orientation with respect to the polarization of the excitation light

have been shown to affect the emission spectra in ADT derivatives [5]. As shown in Figure 6, we were able to excite what appears to be a single crystal domain — assuming that this domain has few defects and a relatively uniform stacking structure, we expect it to fluoresce with a distinct spectrum. The Fluorolog excites a much wider area of the sample, which may include many crystal domains, defects, and slightly different stacking structures. Thus, it is conceivable that the resulting fluorescence spectrum is an aggregate of several slightly different spectra.

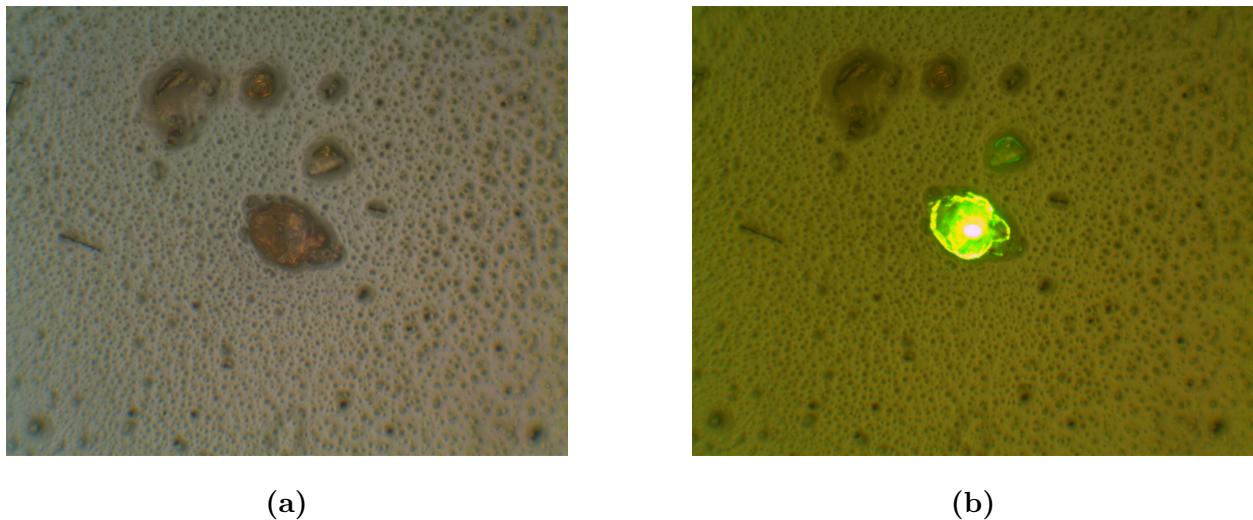


Figure 8: Images of CdSe quantum dot sample under white light (8a) and under laser excitation light (8b). Reflected excitation light was optically filtered out of Figure 8b with a dichroic mirror and colored glass longpass filter. Photoluminescence spectra of this sample are shown in Figure 9.

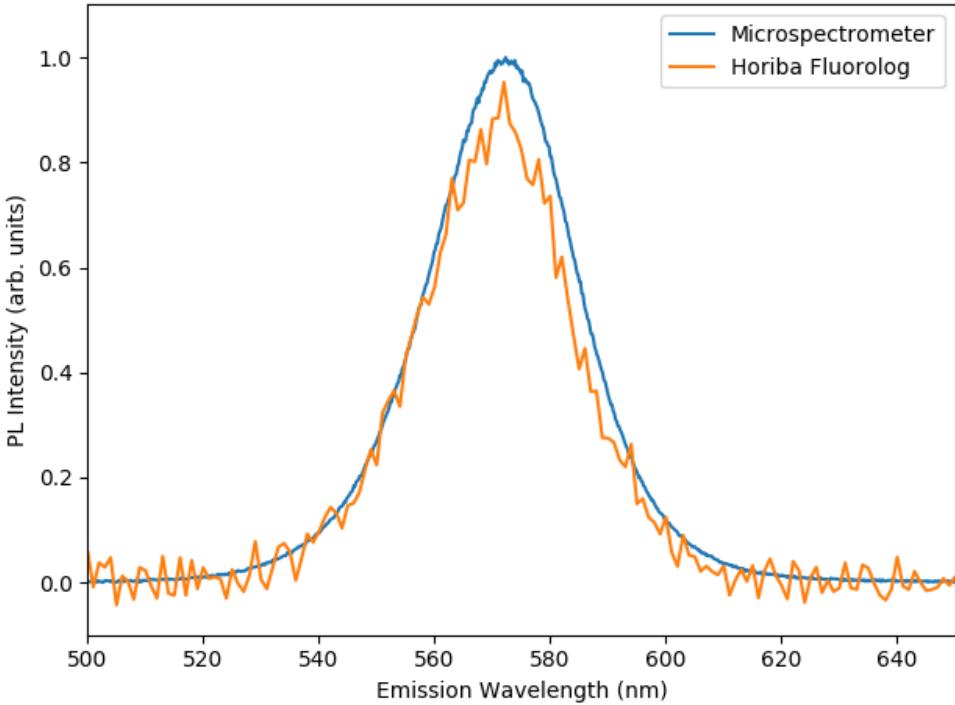


Figure 9: PL emission spectrum of a cluster of CdSe quantum dots, excited at 405 nm.

The microspectrometer data shows an emission maximum at 572 nm for our sample of CdSe quantum dots. Peaks in both the Fluorolog and microspectrometer data are well-aligned, though there is a very slight blue-shift in the higher-wavelength leg of the peak of the Fluorolog data.

The peak at 572 nm is also reported by Empedocles *et al.* in their paper, "Photoluminescence Spectroscopy of Single CdSe Nanocrystallite Quantum Dots" [6]. They report a much narrower peak than we found (13 meV FWHM to our 110 meV), but measure PL at a very high excitation intensity. We are unable to thoroughly compare our results to those published by Empedocles because we do not have excitation intensity data, ~~but~~ it is possible that excitation intensity affected the width of our emission peak. It is also possible that fundamental differences in our sample and methods resulted in a wider peak — it is well known that fluorescence in quantum dots varies with their shape and size, and Empedocles used techniques beyond the scope of this project to measure PL of single quantum dots.

Data from the Fluorolog is notably more noisy than data from our microspectrometer. It is possible that this is the result of smoothing by the Ocean Optics spectrometer and its software, though we have found no evidence to support this. It has been suggested that low excitation intensity when using the Fluorolog may result in noisy data, but we are unable to verify this because we do not have excitation intensity data for either of the instruments used in this work [8]. Future work with our microspectrometer instrument should make optical power measurements a high priority.

4 Conclusion

The goal of this project was to design and build a photoluminescence spectrometer with basic components, capable of exciting samples on the micron scale. We accomplished this using a simple diode laser system, metallurgical microscope, portable fiber-coupled spectrometer, and a few basic optical components. We demonstrated the functionality of the new instrument by measuring samples of photoluminescent materials ADT TES-F and cadmium selenide quantum dots, then compared our results to previous publications and our own measurements of the same samples taken with a Horiba Fluorolog-3 spectrophotometer.

This project handled the fundamental optical design and functionality of our new instrument; future students could expand on this work in a variety of ways. The microspectrometer can be fitted with different detectors for measuring PL at wavelengths outside the visible spectrum. New laser diodes can be used to excite samples at different wavelengths; a tunable laser system could be coupled into the instrument to enable PL excitation measurements. Optical power measurements — of excitation or emission light — would be a very useful feature to add to this instrument in the near future, and would enable more sophisticated characterization of optoelectronic materials.

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