

Development of a Visible Light Photoluminescence Microspectrometer

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An undergraduate thesis advised by Matt W. Graham
submitted to the Department of Physics, Oregon State University
in partial fulfillment of the requirements for the degree of BSc in Physics

Draft submitted on June 2, 2020

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), 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 when it comes to 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. Using the instrument's sample chamber or while coupled to 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 accelerates 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 have studied several organic photovoltaics (OPVs) including functionalized derivatives of pentacene, benzothiophene, and anthradithiophene (ADT) [3–5]. 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.

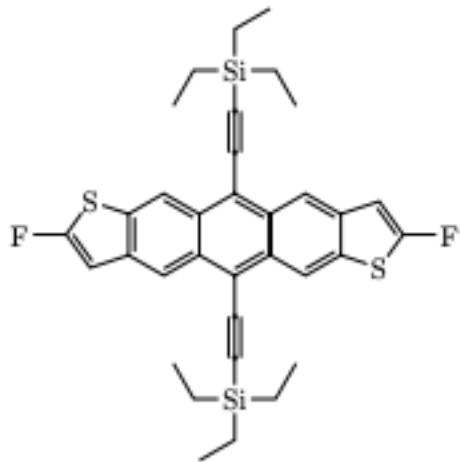


Figure 1: Molecular diagram of fluorinated anthradithiophene (ADT) with triethylsilyethynyl (TES) side group. A drop-cast sample of this molecule was provided by the Ostroverkhova group at Oregon State University, and used for demonstration of our microspectrometer instrument following a study by Lam [6]. Diagram from Shepherd *et al.* [3].

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 [7, 8].

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. ~~Because of the loss of energy to vibrational transitions, we expect the energy of this photon to be lower than that of the absorbed photon,~~ and the wavelength longer.

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.

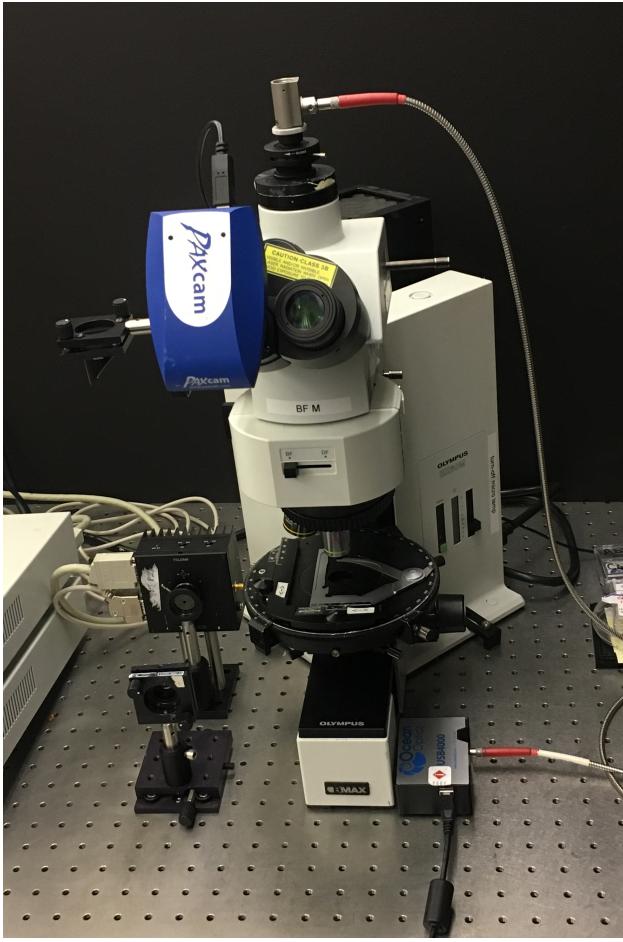


Figure 2: Front view of microspectrometer instrument (laser controllers not pictured) built around Olympus BX60M fluorescence microscope. The laser diode mount and mirrors are shown on the left. Digital camera for sample imaging is mounted to the microscope eyepiece. We have mounted a collimating mirror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

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.

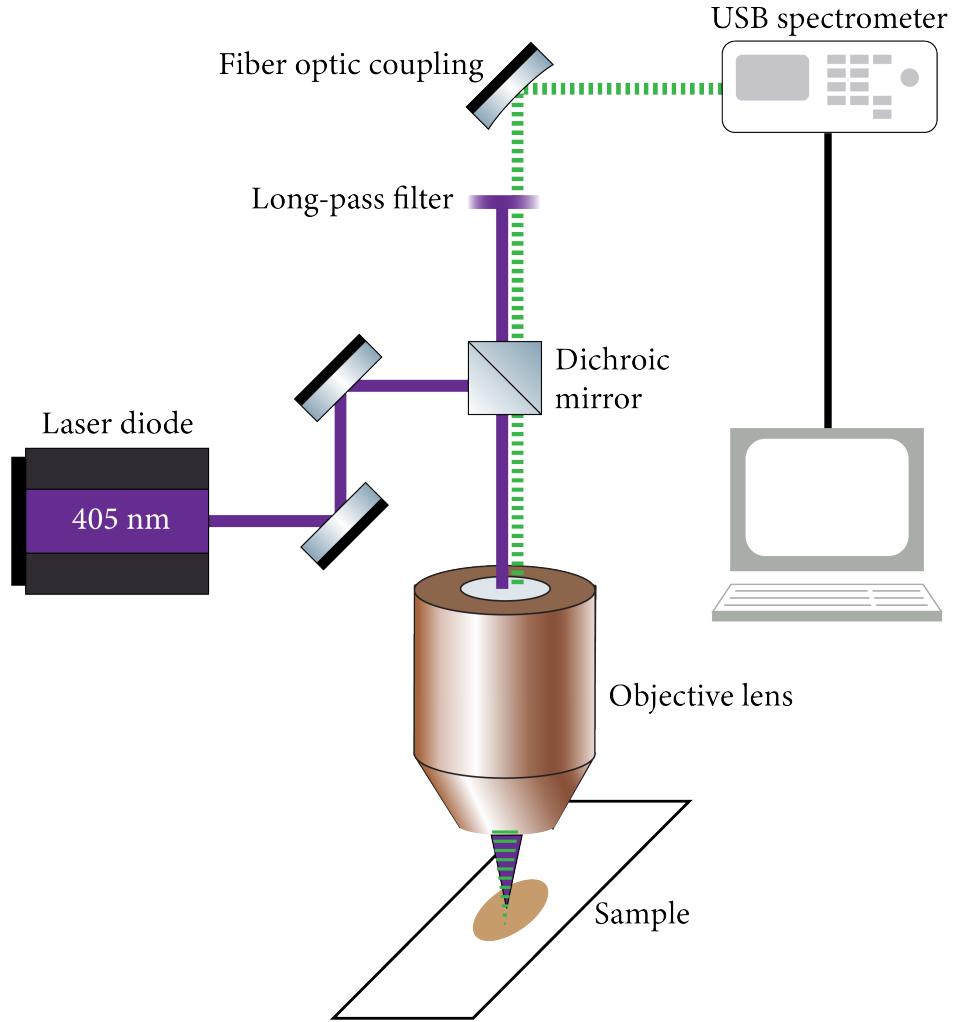


Figure 3: Schematic diagram of the microspectrometer instrument.

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 allowed for precise alignment of the laser to the optical axis of the microscope, which allows for maximal transmission of excitation light through the objective lens and onto the sample stage.

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.

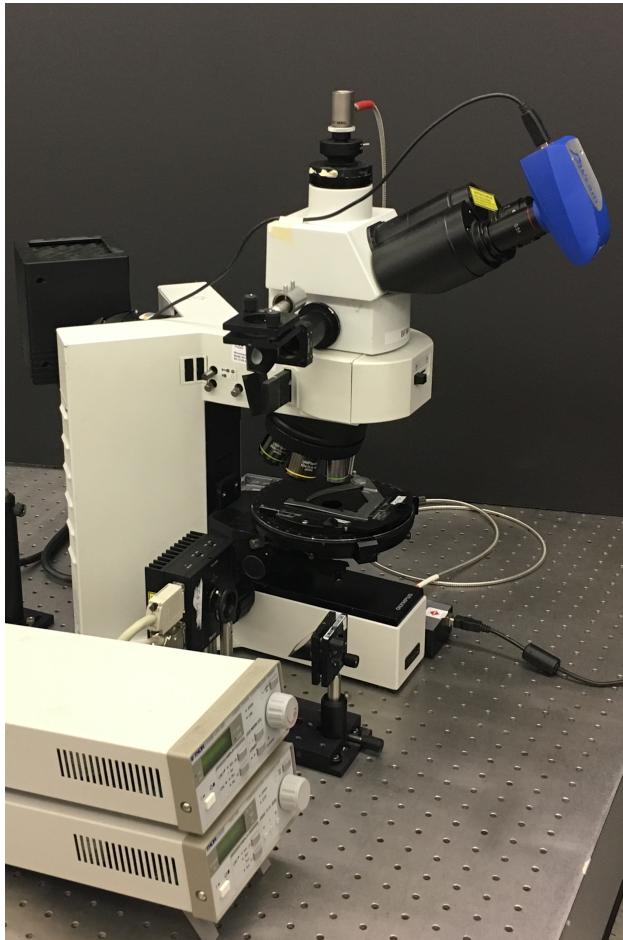


Figure 4: Side view of microspectrometer instrument. Laser controllers are shown in the foreground. Between the controllers and the microscope, two flat mirrors and a dichroic mirror (not visible here) couple the laser light into the microscope's optical path.

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. This causes nearly all of the excitation light to be reflected in the direction of the sample. Because fluorescence will nearly always have a longer wavelength than the exciting photons, we expect the mirror to pass most of the light emitted by the sample and block any reflected excitation light.

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.

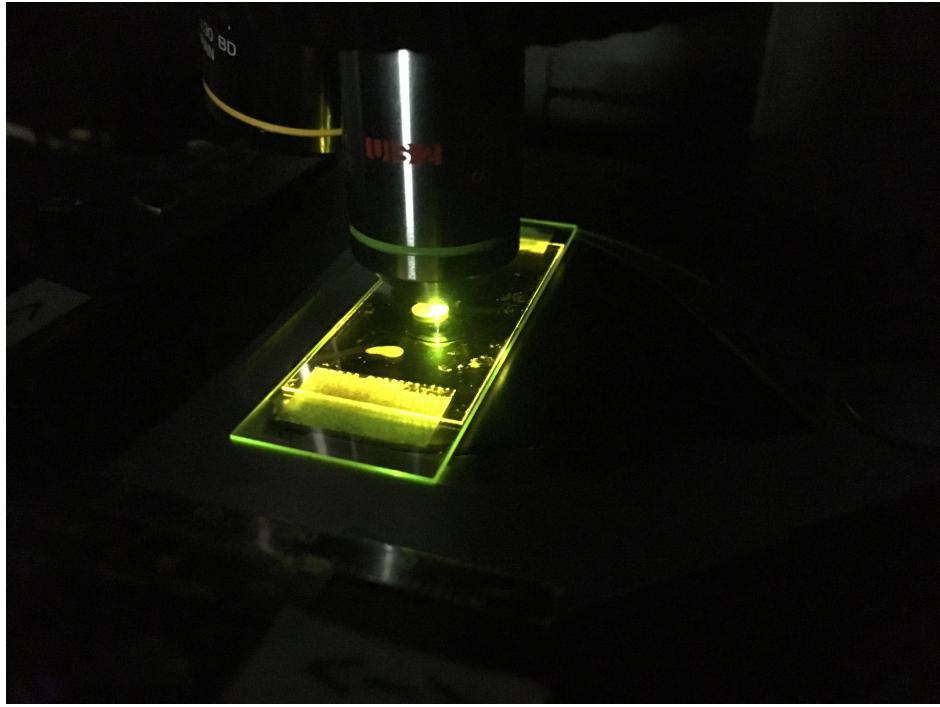


Figure 5: A sample of CdSe quantum dots under laser illumination at 405 nm. Some of the violet laser light is reflected by the sample, but is difficult to distinguish from the sample's intense green emission.

With adapters on hand, we were able to fix a digital camera to the binocular optic for simple imaging of samples. 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

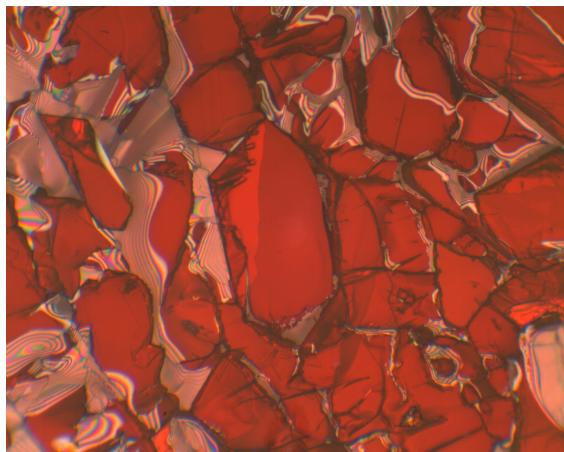
microscope nosepiece, where our target is the optical axis of the objective lens. In place of a lens, we fix an iris diaphragm to the nosepiece. We adjust the second mirror to position the laser in the center of the mostly-closed iris, which marks the location of the optical axis of a lens. This process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

3 Results and Discussion

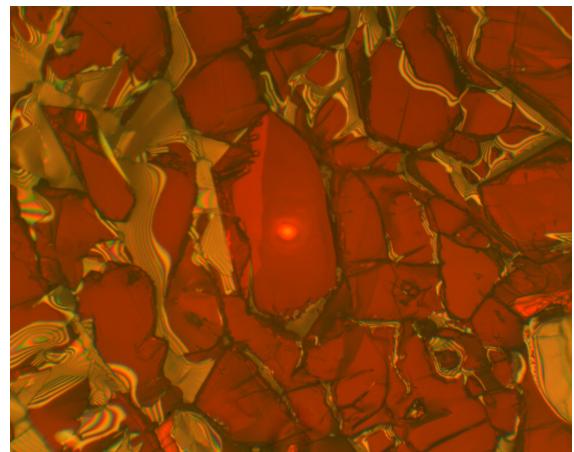
[NOTE: Make this section more about the device and how well it works, less about the actual measurements we got. To talk about the measurements, examine why they match up with literature or not. How is that related to the instrument? Hint: we didn't calibrate shit.]

In order to test the new microspectrometer instrument, we measure the fluorescence spectra of two

3.1 ADT TES-F



(a)



(b)

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.

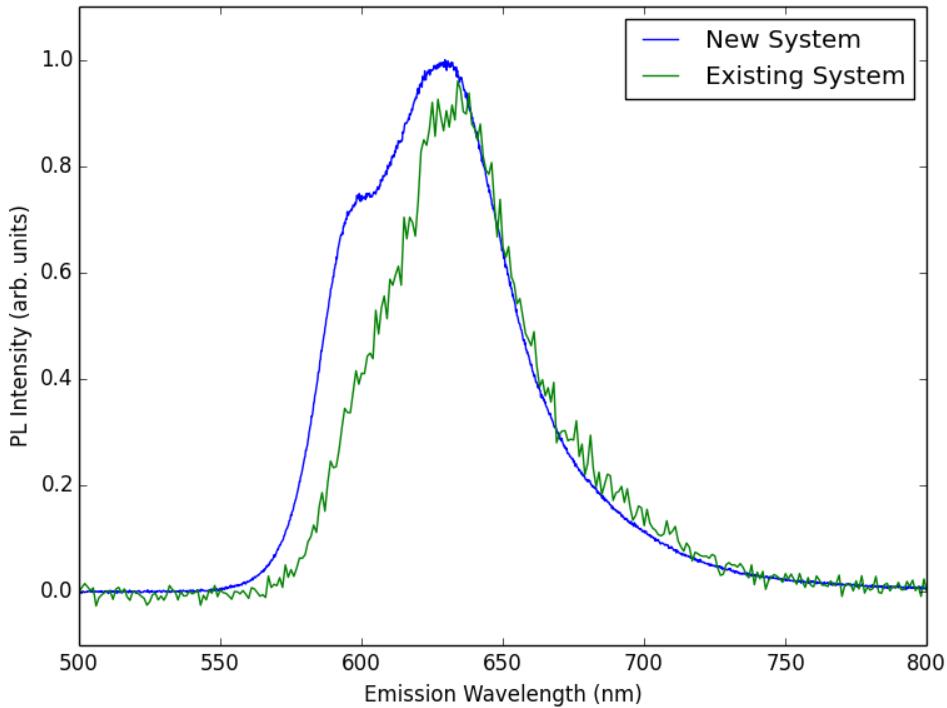


Figure 7: PL emission spectrum of ADT TES-F, excited at 405 nm. Wide-field illumination used by the existing system to excite the sample yields a noisy spectrum, and does not excite the secondary peak that is shown clearly in the results from the new system. A single crystal, larger than the laser spot, was selected among smaller neighboring crystals for this measurement.

For a drop-cast sample of ADT TES-F on glass, we selected a region of interest which appeared to be a single crystal, with few visually distinguishable defects (Figure 6). The crystal was also selected such that its surface area was larger than the area illuminated by the microspectrometer’s laser spot. The emission spectra of the region of interest are shown in Figure 7.

Using the fluorimeter instrument, we were able to illuminate and measure the PL spectrum of the same region of interest, plus an indeterminate area of the sample around this region.

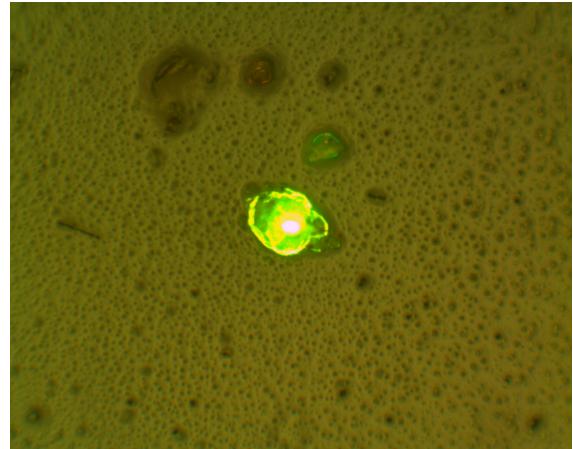
Both spectra in Figure 7 show a clear peak around 630nm. The spectra measured by the microspectrometer also shows a secondary peak just below 600 nm, which is not evident

in the spectrum taken by the fluorimeter. [6][2][5]**[NOTE: All 3 citations in this paragraph have spectra with peaks similar to mine, but different intensity. This must be because they excited at a different wavelength, but how do I use that?]**

3.2 CdSe Quantum Dots



(a)



(b)

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.

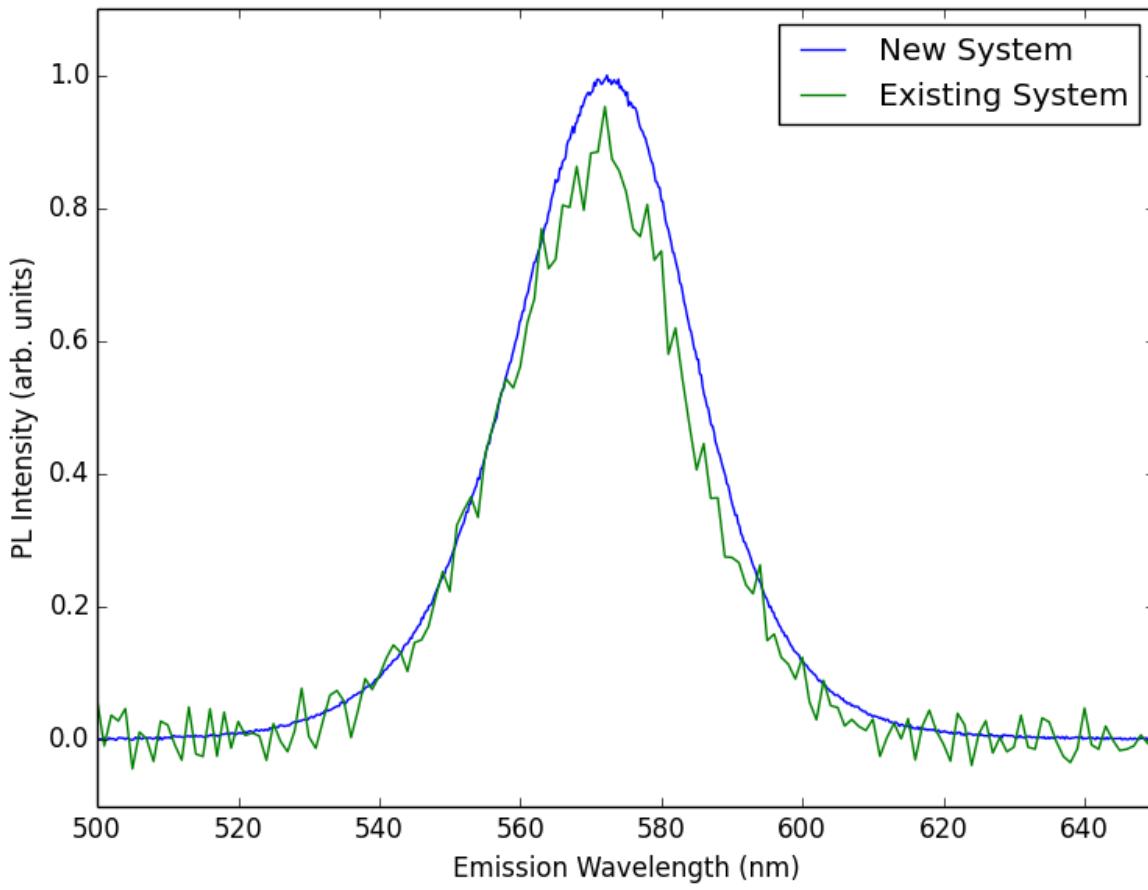


Figure 9: PL emission spectrum of a cluster of CdSe quantum dots, excited at 405 nm.

Figure 9 shows the PL emission of CdSe quantum dots [TODO: on what substrate?]. There is one broad, clear peak that aligns well with the same measurement taken on the fluorimeter, between 520 and 620 nm. This peak seems to agree with other studies of CdSe quantum structures.[7]

Unlike the same measurement taken on ADT, this measurement was taken in a region of interest which is sparsely populated with quantum dots, with one target grouping illuminated by the laser.

[TODO: What else do I write about here? Need to find more resources on analysis of PL, i.e. what information we get about the material. This will also be

useful for Background section.]

4 Conclusion

[TODO: Conclusion]

References

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