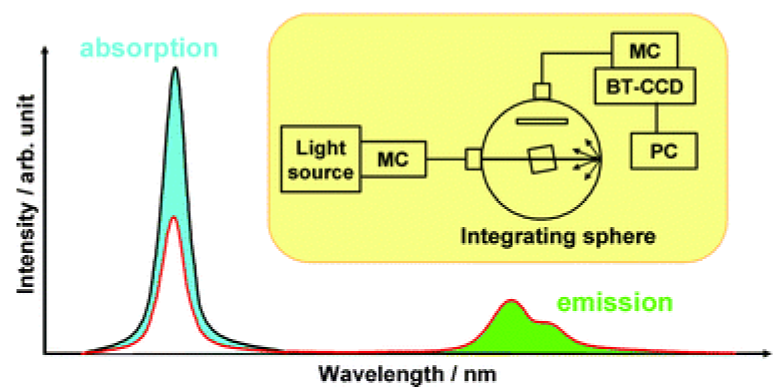
PLQY Measurement
Using Integrating Sphere
User Manual



Introduction

There has been a great deal of interest and much activity in studying the optical properties of thin films of molecular organic and polymeric materials. Such interest has been motivated by a wide variety of applications such as light emitting diodes (LEDs), photorefractive materials, photovoltaic technologies, and by the development of new materials.

In order to evaluate and enhance the performance of light emitting devices, measurement of their radiative quantum efficiency, also known as absolute photoluminescence quantum yield (Φ_{PL}) has been important. Accurate measurement of PLQY allows one to trace the dependence of the enhancement of (Φ_{PL}**)** in the optic materials on various factors, such as type of host/guest pair, their energy overlap, and the doping level.

Principles

PLQY

Photoluminescent quantum yield (PLQY) is defined by the ratio between the number of emitted photons and absorbed photons.

$$PLQY = \frac{\Phi emit}{\Phi absorb} = \frac{Photons\ Emitted}{Photons\ Absorbed} \quad \textbf{(1)}$$

Integrating Sphere

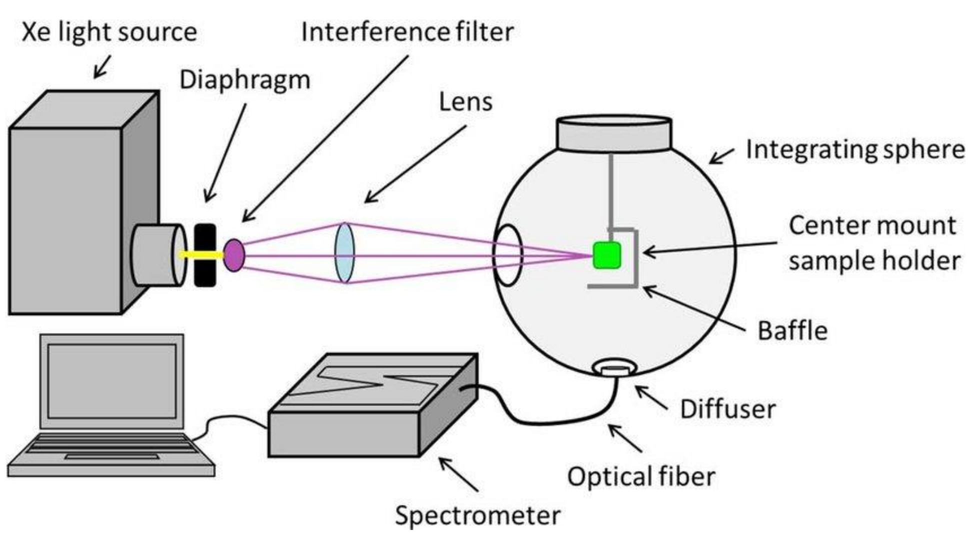


Figure 1. Schematic drawing of Integrating Sphere

One major advantage of using integrating spheres is that it enables reliable measurement of the PL quantum efficiencies irrespective of the reflective properties of the sample. The integrating sphere is a hollow sphere which has its inner surface coated with a diffusely reflecting material When a light source is placed in an ideal integrating sphere, the light is redistributed isotopically over the sphere interior-surface regardless of the angular dependence of the emission.

As *figure 1* shows, the incident beam is guided through the entrance aperture, with an optical fiber, onto the sample placed at the center of the sphere. The reflected signal (from the incident beam) is directed towards the exit aperture. A baffle placed between the sample and the exit port prevents the PL signal from directly reaching the detector. The PL signal, scattered within the sphere, is measured at the exit. As a result, over 95% of the incident light is reflected within the spheres. Hence, given enough integration time, the sphere can collect most of the photons reacted with/without the sample. (see *figure 2*)

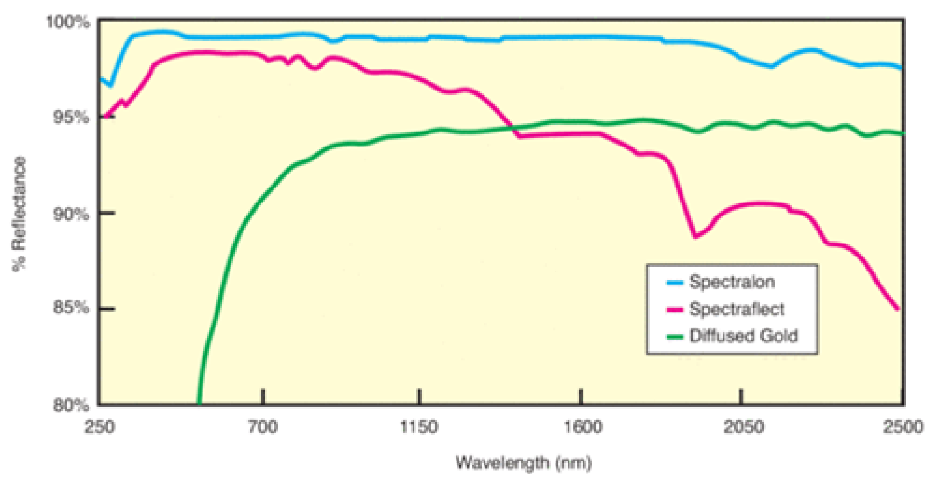


Figure 2. Reflectance % of integrating spheres according to coating material

Spectrometer

In the PLQY experiment, spectrometers are used in combination with integrating spheres to test the absorption and emission properties of thin film samples. However, the intensity signals directly obtained from the spectrometers must be calibrated and processed into a number of photons in order to get the accurate PLQY result. Types of spectrometers used in the experiment include QE Pro, USB2000, USB2000B. Each spectrometer has a different detection sensitivity and detection limits. LabVIEW and OceanView software were used to communicate with the spectrometer hardware.

QE Pro	USB2000	USB2000B

360 nm – 1100 nm	400 – 875nm	400 – 1000nm

Apparatus

- Neutral Density (ND) Filter
- Mirror
- Integrated sphere
- Spectrometer
    - Hardware: QEpro, USB2000, USB2000B
    - Software: LabVIEW, OceanView
- Thin film samples
- Stand
- Light intensity detector (Optional)

General PLQY Measurement Procedure

Obtaining PLQY using integrating sphere requires three major steps-- Calibration, Measurement, and Calculation. Calibration refers to the process in which photons per intensity is calculated. Measurement process measures the laser intensity with/without the light-sample interactions. Then manual/automatic calculation process can be followed for resulting PLQY.

Calibration

The data collected using spectrometer consists of light intensity spectrum of different wavelengths. The intensity spectrum is displayed as a form of x-y graph, in which x-axis represents wavelength, and y-axis represents intensity or counts. The y-axis value, the intensity or count, is proportional to the number of photons within a given wavelength interval. In other words, though they are related, the count can't be equated to the number of photons. Hence, calibration process is required to figure out spectrometers' response (Photons/ per count)

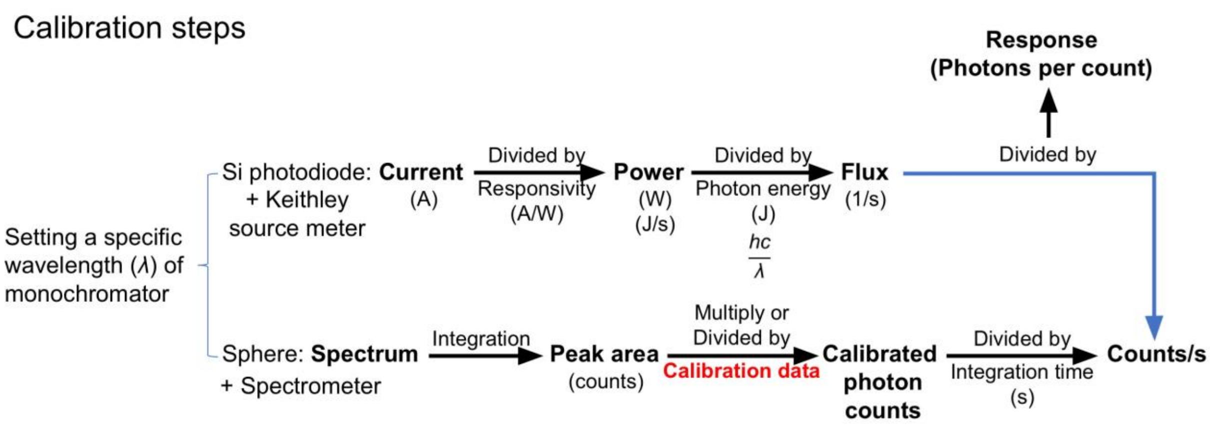


Figure 3. Calibration and calculation flow chart

Calibration Step

1. Set up the light source, integrating sphere, and spectrometer. Use mirror and ND filters to adjust the beam alignment and intensity.
2. Once the equipment is set, open OceanView application and check the light intensity peak. The peak must be of reasonable height (Not too small or saturated)
   - Increasing the integration time will enlarge the peak height.
   - Saturated peak can be adjusted either by decreasing the integration time or increasing the optical density of the ND filter.
3. To get rid of the background signal, set the application to dark by clicking the dark lightbulb.
4. Use LabVIEW program to adjust the wavelength.
5. Monitor the light intensity peak through OceanView and record the data each time.

How to get Photons/Count

1. Take the Current (A) at different wavelength using Keithley 2400. The range of wavelength must be selected according to the range of spectrometer. For QE Pro, the range is 400nm –880nm.

Keithley 2400

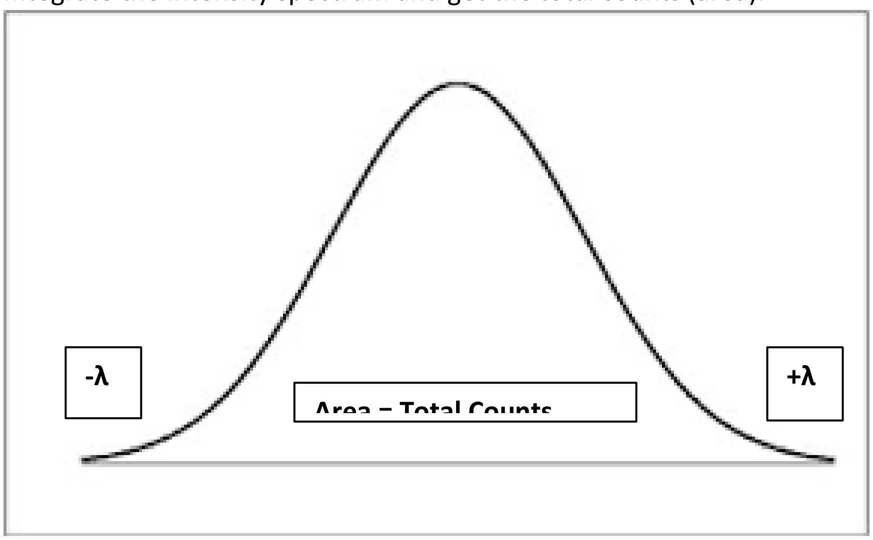
2. Divide the current data obtained from step 1. and divide with a known responsivity (A/W) to get the power.

$$\frac{current\ (A)}{responsivity\ \left(\frac{A}{W}\right)} = power\left(W\ or\ \frac{J}{s}\right)$$

3. Take the result of *step 1* and divide with energy of photons (hc/ **λ**) to get the flux.

$$\frac{power(W)}{energy\ of\ photon\ \left(\frac{hc}{\lambda}\right)} = flux\left(\frac{1}{s}\right)$$

4. Take the flux from *step 2* and divide it with integration time (in seconds).
5. Integrate the intensity spectrum and get the total counts (area).



6. Divide the flux (*step 3*) with integrated result (*step 5*) in order to get photons/count.

Measurement

Measurement Setup

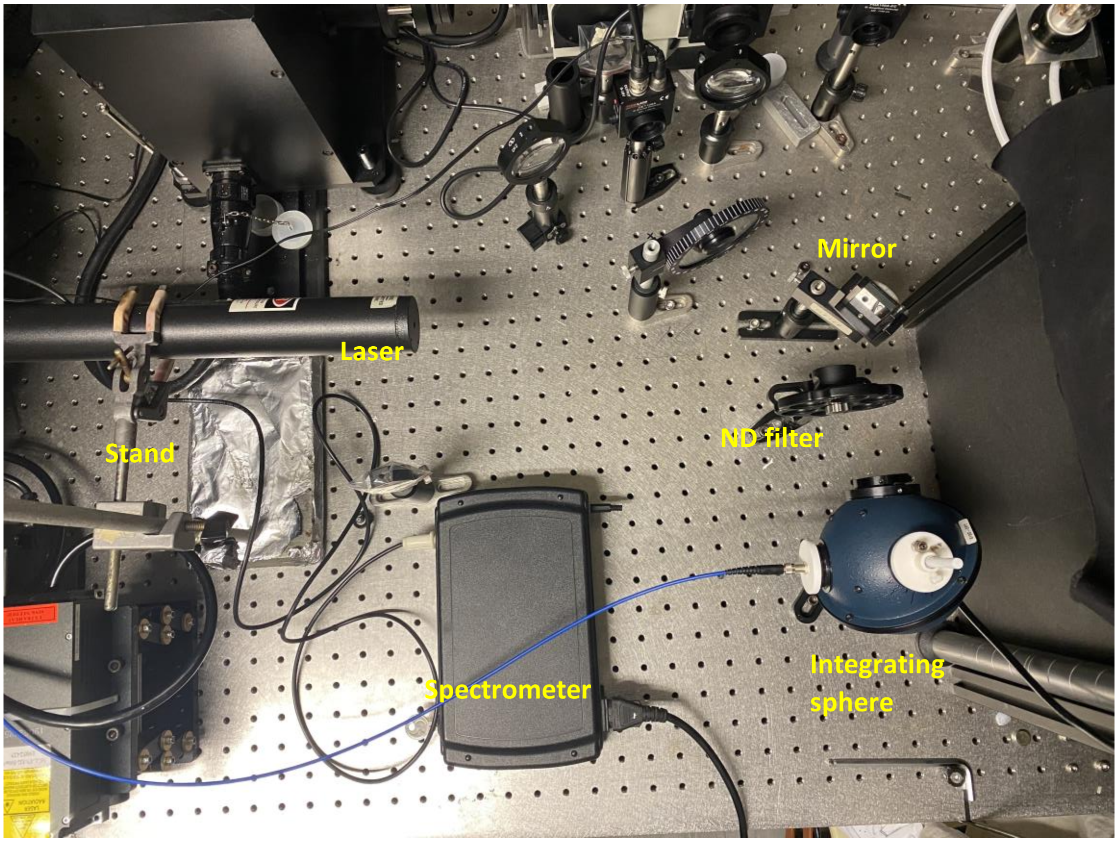
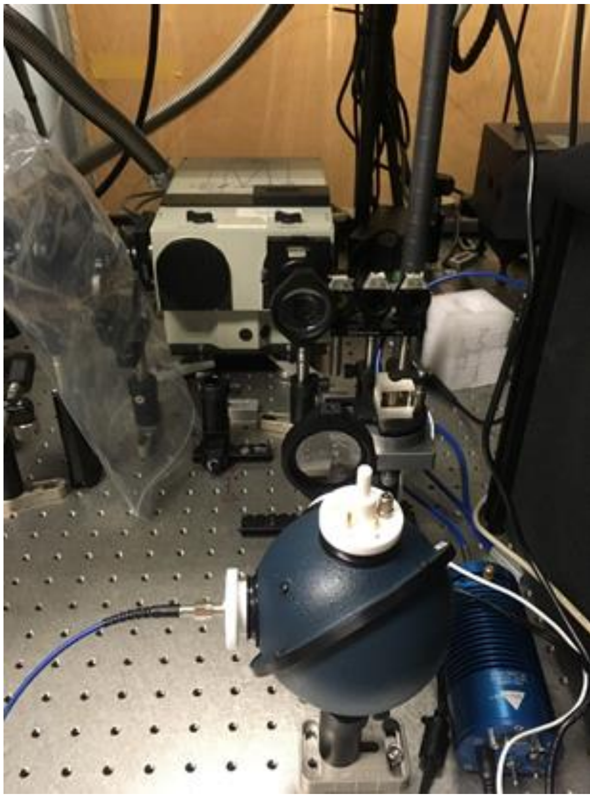
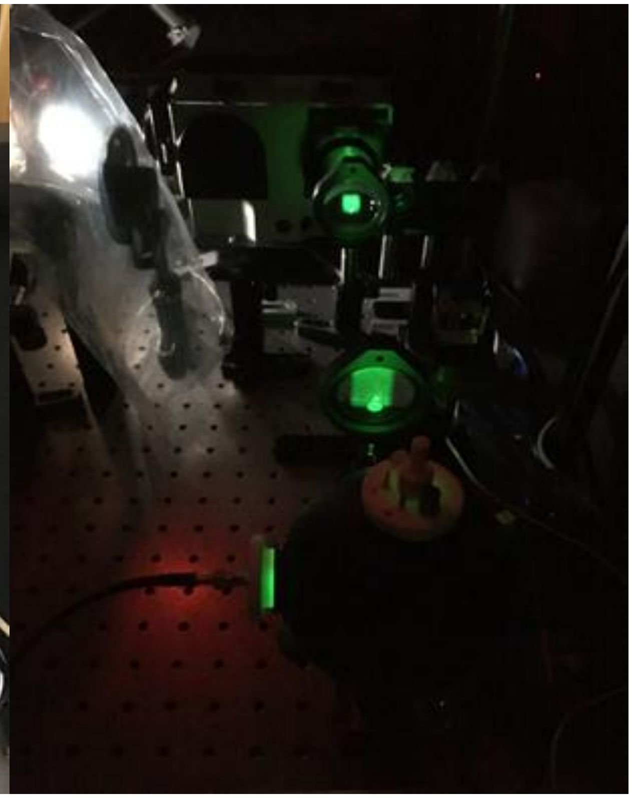
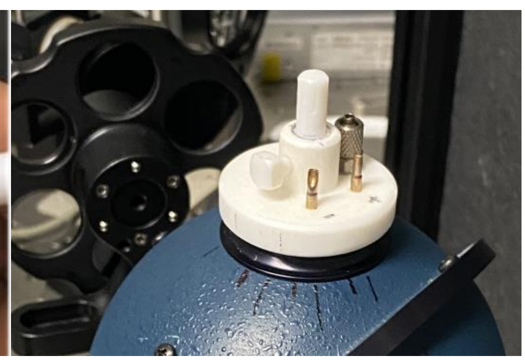


Figure 4. Experiment set-up in bird eye view

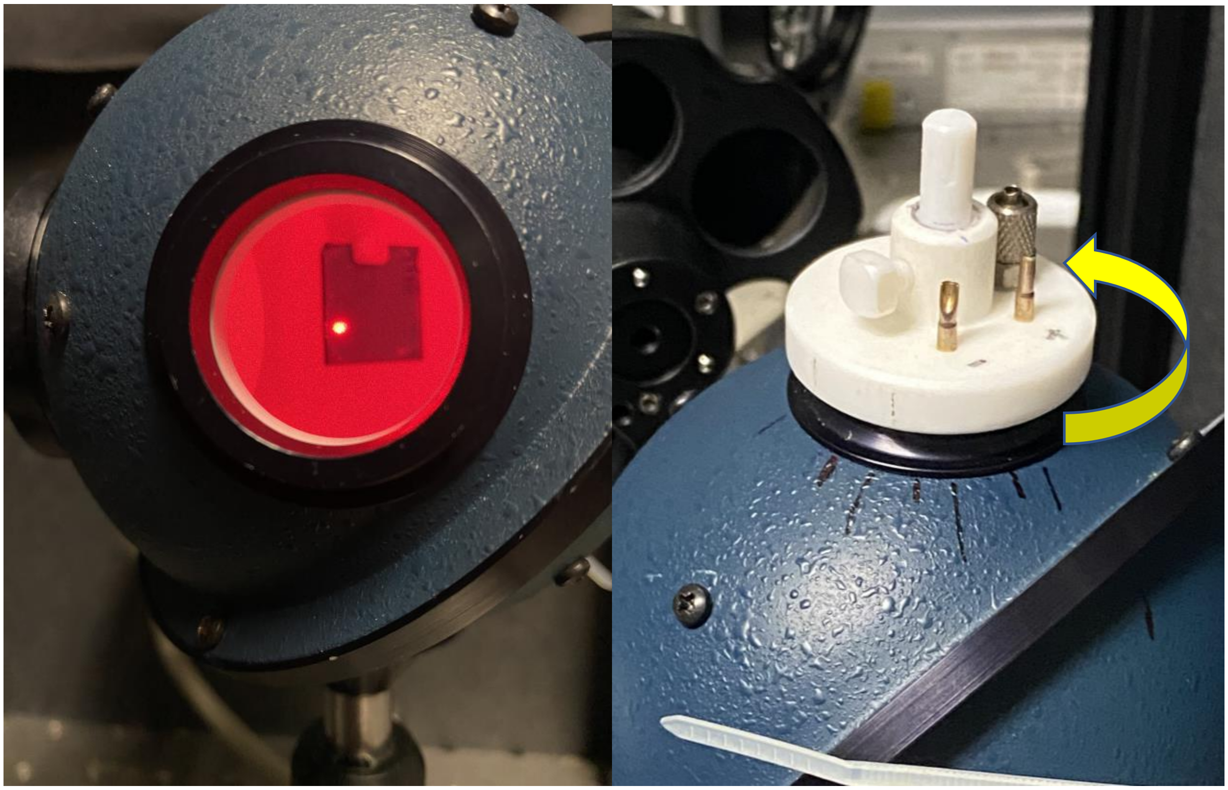
- Secure the laser light (or any light source) on a ring stand and redirect the right to integrating sphere using mirror.
- Place ND filter before integrating sphere to adjust the light intensity entering integrating sphere.
- As the filtered light goes into integrating sphere, record the intensity signals collected from spectrometer.

- Check the light within the sphere. Upon correct laser-mirror alignment, one should be able to see the laser light diffused evenly within the integrating sphere.

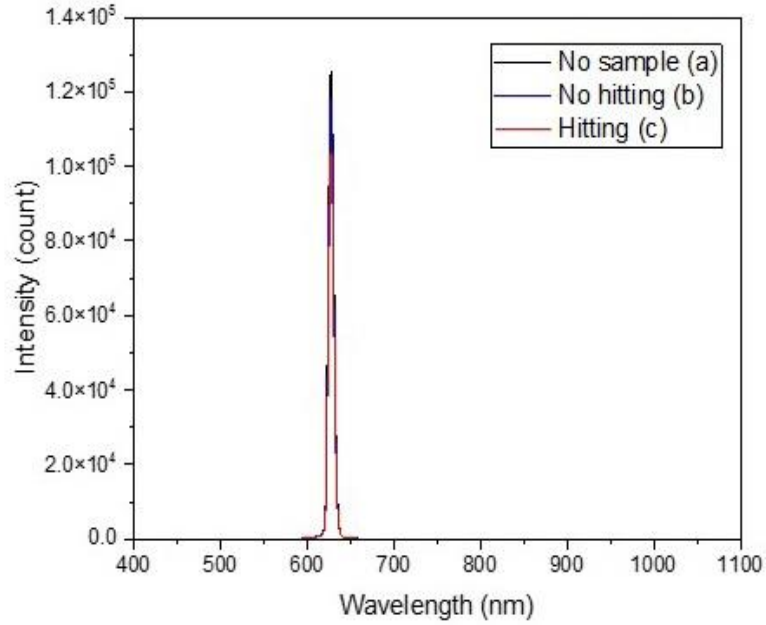
 

- Mount the sample on the holder which is placed on top of the integrating sphere. Use the tiny screw at the tip to amount/release the sample.
- Adjust the sample (or ray if necessary) direction so that the light hit the sample directly
- Adjust the angular orientation of the sample. The user can use the rough guideline drawn around sample holder circumference when measuring angular dependency of PLQY. Please check Appendix A for detailed explanation of angular orientation of film and PLQY.



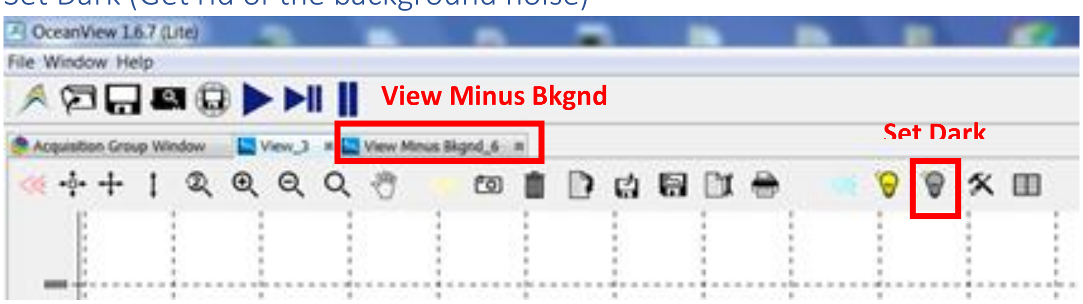
- Check for a bright clear spot on both sample and the sphere wall. A bright clear spot should be observed when both sample and light are in the right alignment.
- One way to check the alignment is to turn the sample around in different angles. If the alignment is correct, the user should be able to see the clear spot on the sample and sphere wall irrespective of the turning angle. For further details, please check *Appendix A*.

Laser Stability Check



After setting up the experiment equipment, the stability of the laser must be checked for accurate measurement. OceanView provides real-time light intensity curve which enables user to check the stability of the laser. The peak will stop fluctuating once the laser is stabilized. Note that it might take some time for laser to stabilize depending on the type of the laser. In addition, the peak height must be reasonable – large enough but not saturated. The user could adjust the measurement setting (integrating time, ND filter) to adjust the size of the peak. For alternative methods for checking stability, please check *Appendix B*.

Set Dark (Get rid of the background noise)



With initial setting, the graph may show some background noise depending on the environment. Hence, it is necessary to remove the background noise and set to dark (set zero) before proceeding to measurement.

- Block the light sources that may be contributing to the background noise signal. This includes laser light and room lighting.
- Once all the light that goes into the sphere is blocked, set to dark by clicking the dark lightbulb at the right upper hand corner.

- Now that the background noise is set to zero, proceed to measurement in the newly created "view minus bkgnd" tab.

Measurement

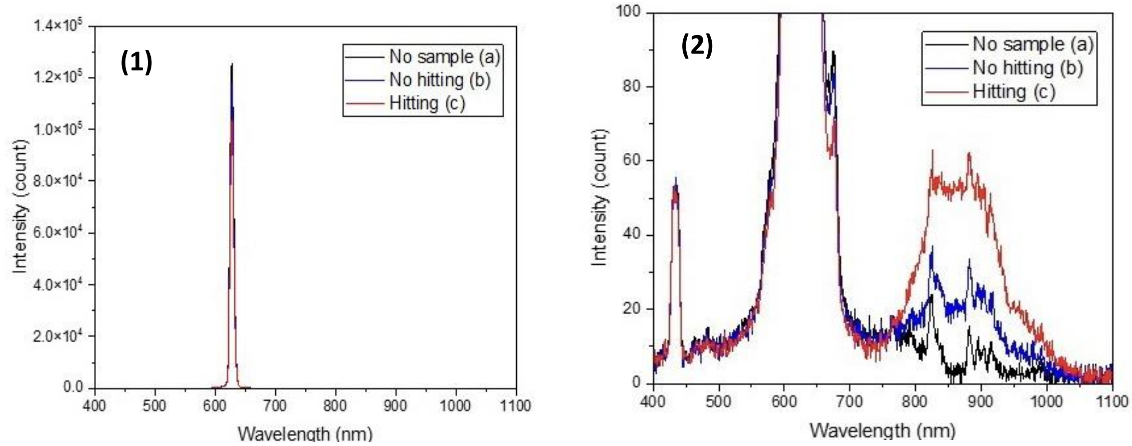
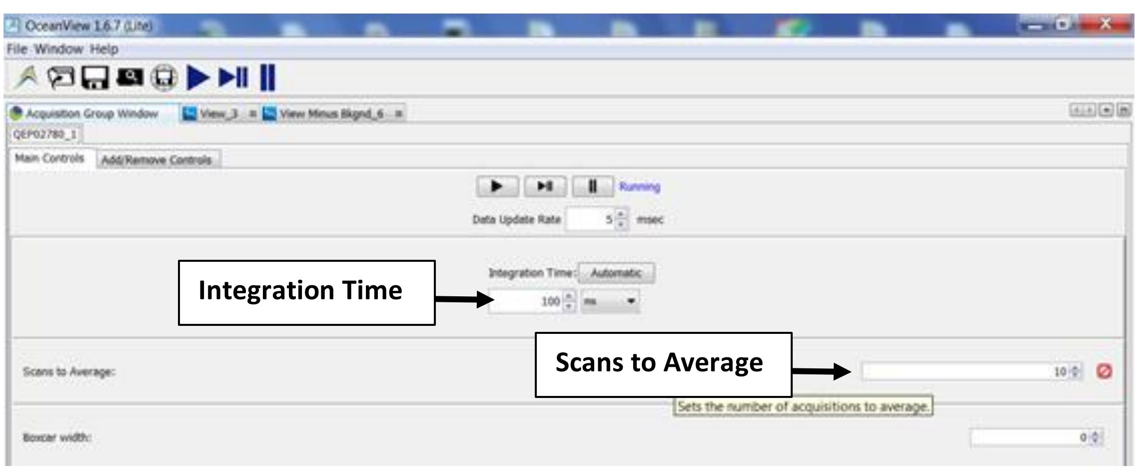


Figure 5. (1) Laser profile and (2) Photoluminescence (PL) profile of three sample configurations. Configuration (a) refers to empty sphere with no sample inserted (b) indirect illumination of sample (c) direct illumination on sample

After setting dark, remove the blockage between the light source and the integrating sphere. The intensity graph should resemble something like *figure 5*. The sharp peak at shorter wavelength corresponds to detection of the laser excitation. (*Figure 5.1*) The broader profile at longer wavelength corresponds to the emission(Figure 5.2). The user can check the broader profile by using the zoom-in function. For further information about OceanView functions, please check *Appendix C*.



Due to the considerably small profile size of PL emission curve (see figure *3.2)*, the PL signal must be examined simultaneously. While there are multiple factors to look out for during PL measurement, there are two major things to be extra cautious about. First is the overlap between laser profile and PL signal.

The strong overlap between two profiles must be avoided. Second is the reasonable clarity in signal. This includes a large enough profile size and sufficient contrast to the background noise.

If the signals are too small, the user can try increasing the "integration time" or check if the background is set to zero. It is strongly recommended to check the clarity of PL signals each time as PL signals are strongly affected by changes made in measurement setting. To reduce the odds of background noise, users are advised to set it to dark each time after changing the experiment parameters (sample types, integration time, average etc.)

In addition, the user can adjust the increase "Scans to Average" value for smoother graph.

Three configurations of the sphere are required for PLQY measurements (see *figure 4).*

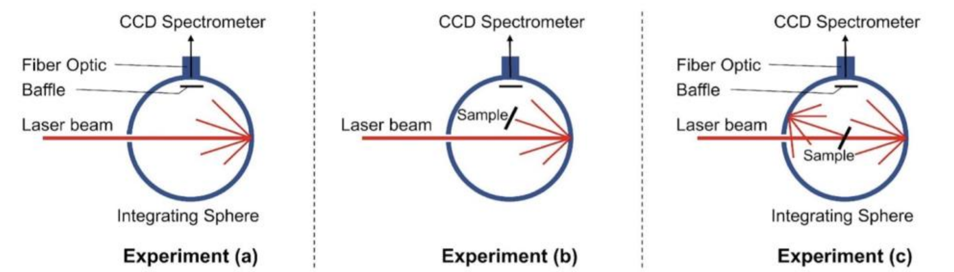


Figure 6. Three different configurations of integrated sphere.

a) Empty sphere
b) The sample is in place and the laser beam is directed onto the sphere wall
c) The sample is in place and the laser beam is directed onto the sample

PLQY Calculation

PLQY can be calculated with two different methods- one considering re-absorption and another without. The equations are shown below.

PLQY with reabsorption considered

$$A = 1 - \frac{Lc}{Lb} \quad \textbf{(2)}$$

$$PLQY = \frac{Pc-(1-A)Pb}{LaA} \quad \textbf{(3)}$$

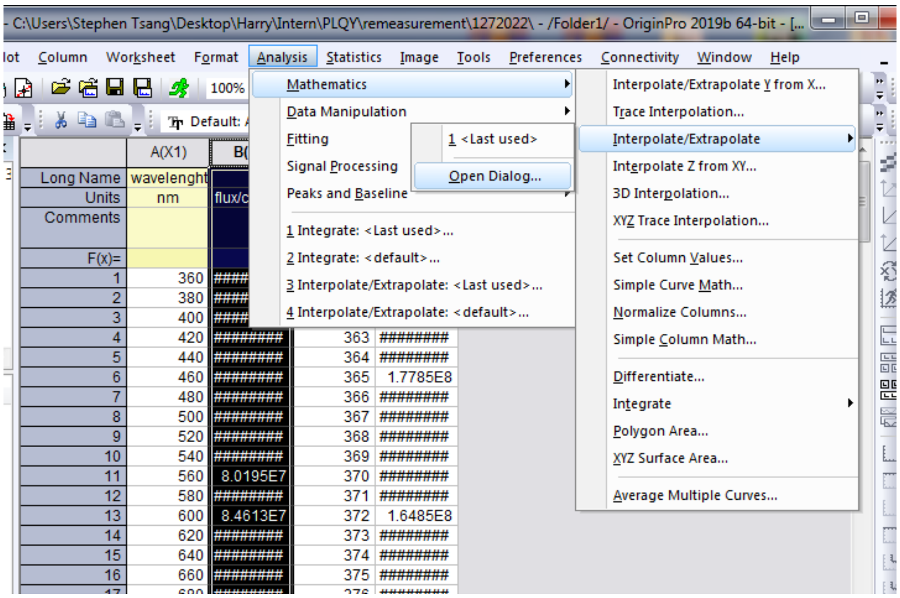
PLQY without reabsorption considered

$$PLQY = \frac{Pc}{La-Lc} \quad \textbf{(4)}$$

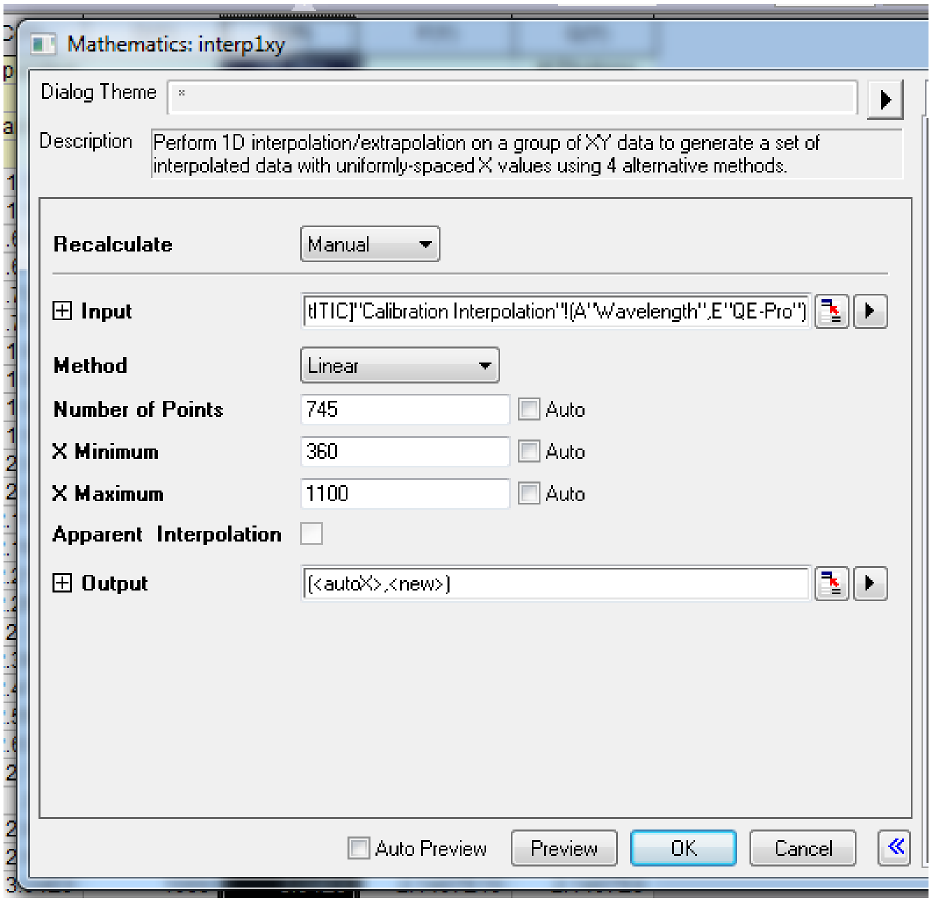
In both cases, L refers to laser profile and P refers to PL profile, and the subscript refers to experiment configuration (see *figure 6).* A is absorption of the thin film sample.

Manual Calculations using OriginPro

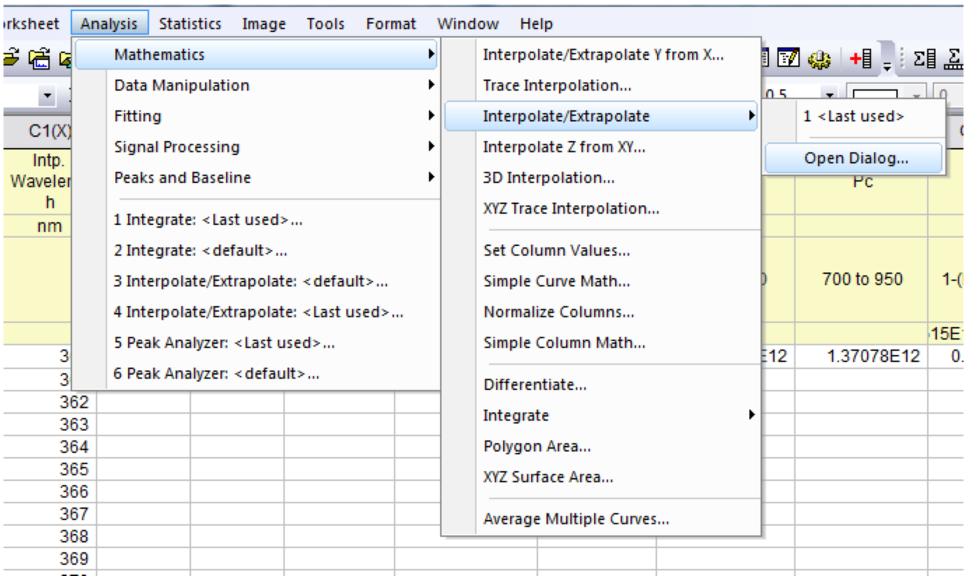
1. Click [Mathematics] [Linear Interpolation] function to manipulate the measurement and/or calibration. The data must be compatible in terms of count range and interval wavelength.
    - Select both X and Y values to interpolate.



    - [Method] --> “Linear”
    - Set [X minimum] and [X maximum]. The [Number of Points] should equal to (X Maximum - X Minimum +1)



2. By multiplying the measured counts (intensity) and calibration (Photons per count) result, flux can be obtained.
3. Divide the flux with integration time to get the actual number of photons. Note that the integration time must be converted to the unit of second.
4. Click [Mathematic] [Integration] function to get the laser/PL profile. Select the integration range that matches the profile range. The resulting area corresponds to the value of laser or PL profile.



5. Calculate PLQY according to the equation. *(See equation (2), (3), (4))* PLQY % can be calculated by multiplying the PLQY value with 100.

For further explanation of OriginPro, please refer to *Appendix D.*

Automatic Calculations using Python (NumPy)

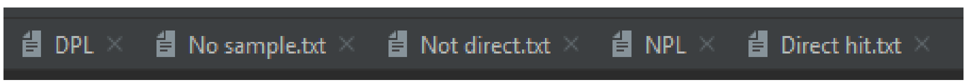
1. Select the profile range.

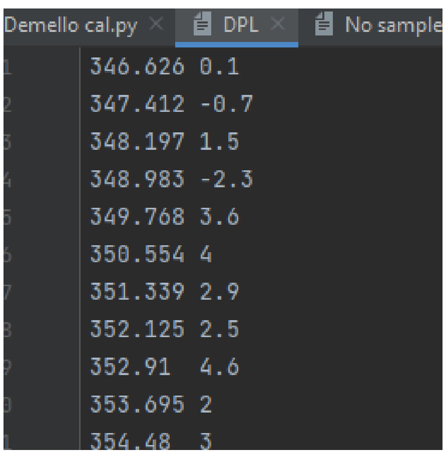
```
# Laser profile range
lsnm = list(np.arange(360, 660+1))
a1 = np.array(lsnm)
# PL profile range
plnm = list(np.arange(740, 1000+1))
a2 = np.array(plnm)
```

2. Input the integration time in seconds

```
# change time he
itime = 0.1
itime2 = 0.1
```

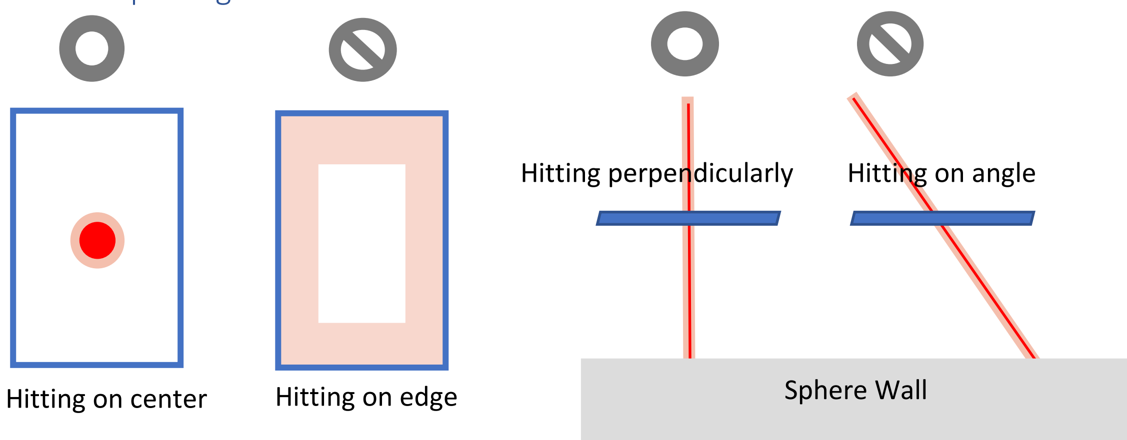
3. Copy your measurement data into these files (Numeric data only)





Appendix A: Laser-Sample Configuration

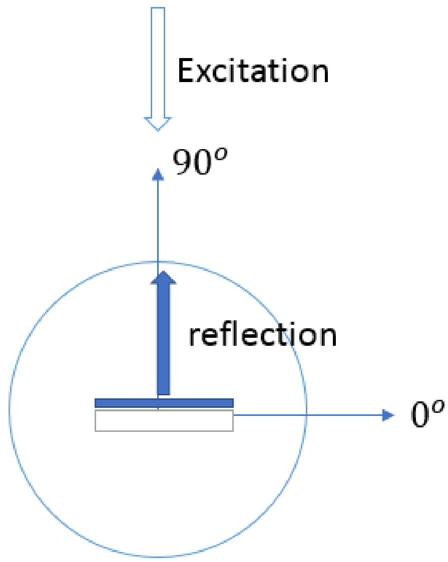
Laser-Sample Alignment



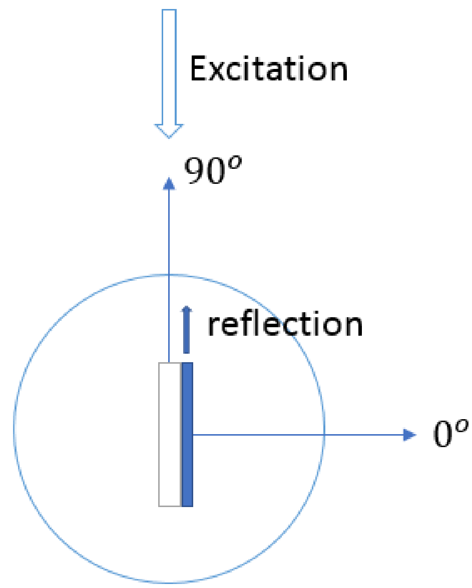
After the secured sample is inserted into the integrated sphere, the configuration of the sample and the laser must be adjusted carefully. The beam must be directed to hit the center of the sample rather than the edge. Also, the incident light must be adjusted to hit the sample and sphere wall perpendicularly for measurement accuracy. The user can turn around the sample within the sphere in order to check if the alignment is correct. If it is correct, the user should be able to see reflected laser spot on sphere wall regardless of the turning angle.

PLQY and Angular Configuration of Film Sample

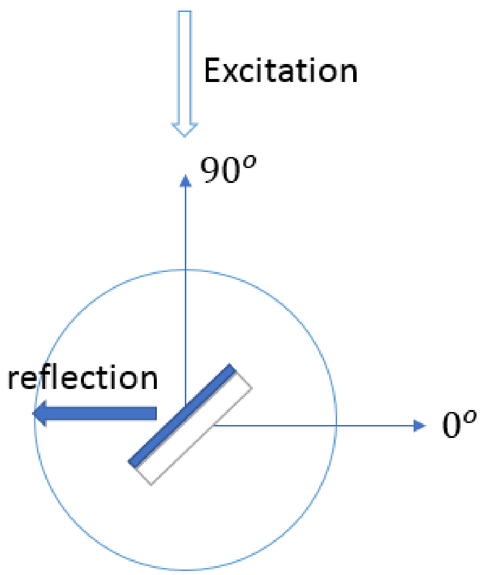
The experiment was conducted to measure the dependence of PLQY by varying film orientation. The result shows varying PLQY according to the varying angular orientation of the film. The sample is rotated 90, 0, +45, -45 degree and PLQY of each configuration is recorded. Note that the detector is at 180 degrees.



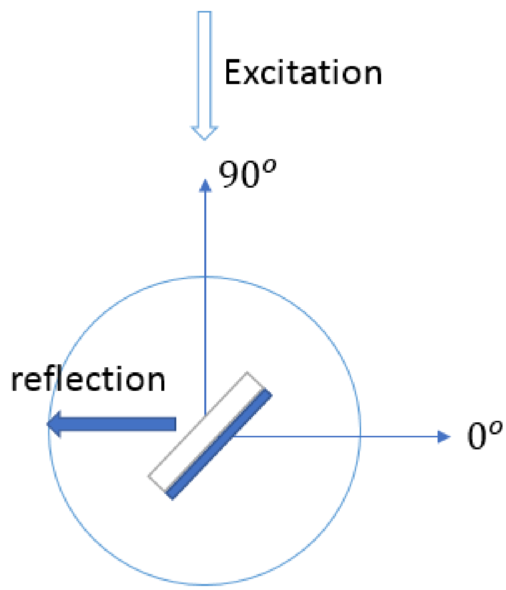
90 degree, QD film on the excitation side



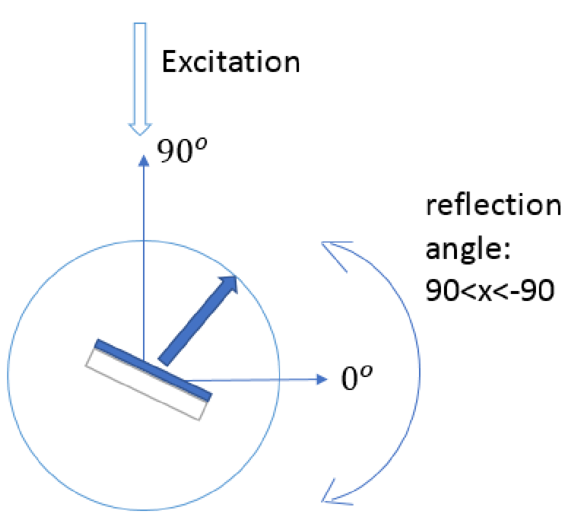
0 degree, small reflection



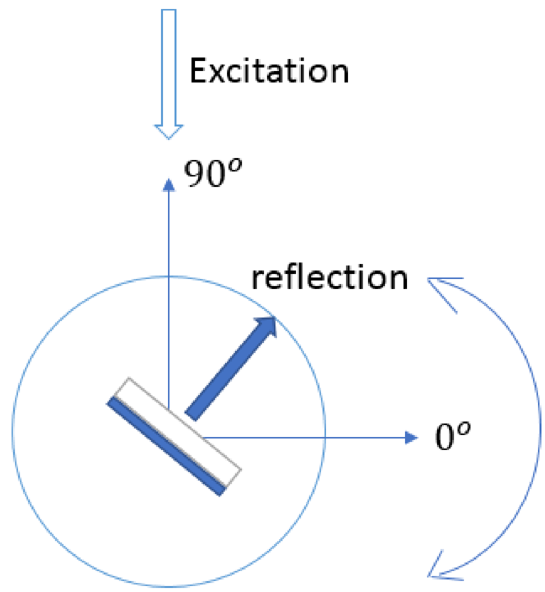
45 degree, film on the excitation side



45 degree, film on the opposite side



Switching a range angle with no change in PLQY;
Film on the excitation side



Film on the opposite side

The measured PLQY according to the angular orientations are shown below.

Excitation wavelength range: 405nm±10nm

The PL wavelength range: 470±10nm

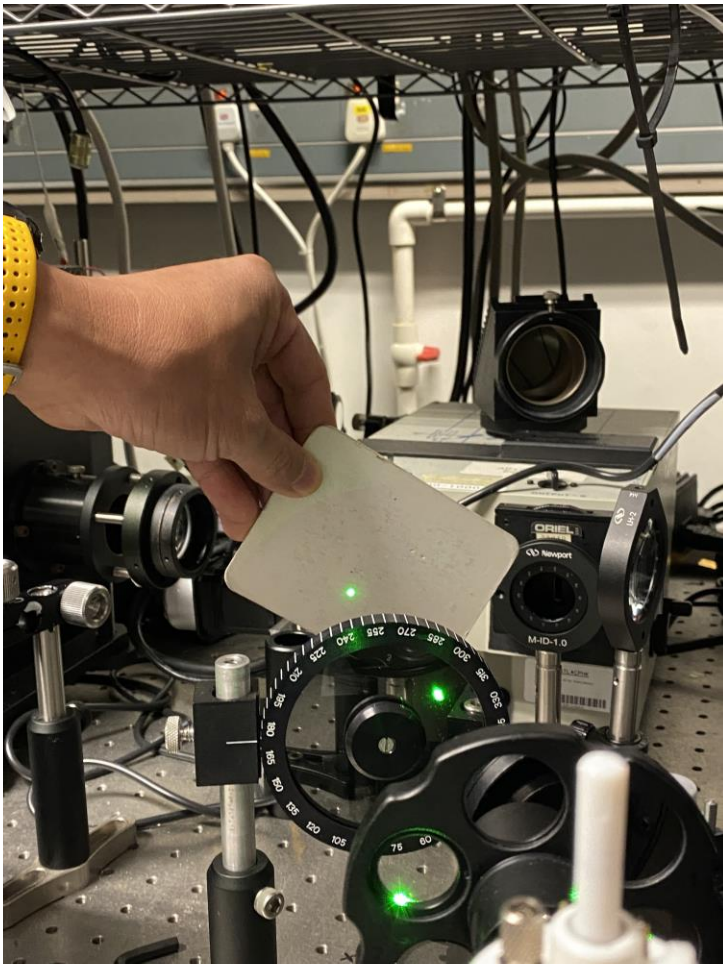
Substrate used: quartz

degree	90	0	45	45_2	pos	ne
PLQY(%)	51.39	94.67	50.3	69.66	22.85	30.93

Appendix B: Laser Stability Check and Tips for Measurement

Laser Stability Checking using Light Detector:

On some occasions, the stability of the laser may be hard to check through OceanView software. In this case, the stability of the laser can be checked with the help of external light detecting devices.



Set up an external light intensity detector across the mirror. Then adjust the reflected light intensity using adequate ND filter. To prevent damage to the equipment, it is recommended to check the filtered light intensity on the cardboard first before shining directly onto the detector. It is considered a adequate intensity when the reflected light is shown as a clear spot rather than a glare. Once the intensity of the laser is checked, the user can proceed to monitor the stability of the detector.

PLQY Measurement with Laser Instability:

If the laser is unstable, alternative approach must be taken in PLQY measurement. This alternative approach can also be used for low concentration diluted film as it often shows frequent fluctuation in absorption spectra depending on the measurement condition.

Alternative approach measures La, Lb, Lc multiple times each in a short time interval, and use average value to calculate final Lb and Lc.

1. Measure the maximum height of La multiple times. The fluctuations are expected as the laser is instable, but the fluctuation must be consistent within the reasonable range.
2. Repeat step 1 for Lb and Lc. Make the measurement interval short to keep the measurement setting as consistent as possible.

3. Calculate the value of Lb/La, Lc/La for each measurement trial. Take an average of each trial to get the total average Lb/La and Lc/La ratio.
4. Proceed to measure La (Laser Profile of empty sphere) again.
5. Upon getting a rather stable La value, multiply with the values obtained from step 3 in order to get the value of Lb and Lc.

Appendix C: OceanView User Manual

Please check [Chapter3: User Interface] for detailed explanation of OceanView Software

https://www.oceaninsight.com/globalassets/catalog-blocks-and-images/manuals--instruction-old-logo/software/oceanviewio.pdf

Appendix D: OriginPro User Manual

Please check out this manual for detailed features and functions of OriginPro Software.

https://www.originlab.com/pdfs/tutorials.pdf