NATIONAL UNIVERSITY OF SINGAPORE

UNDERGRADUATE RESEARCH OPPORTUNITY PROGRAMME IN SCIENCE

Supervisor: Professor Ji Wei

Two-Photon Photoluminescence (2PPL) from Zinc-MOF Single Crystal

Yan Haoyuan

A0248484R

Abstract

In this research, we take the reference and sample spectrum to calculate the absorption coefficient. We are using laser at different intensity to confirm the nonlinear optical properties of a set of Zinc An2Py MOF single crystals. By blocking the linear and directly transmitted light from mode-locking laser, we manage to measure a spectrum reflecting the intensity of nonlinear outgoing light. After applying a log-log linear fitting, the two-photon photoluminescence is verified. Using method of angle-resolved, an angle-dependent intensity diagram is collected. With the linear data from 2PPL experiment, we calculate the two-photon absorption coefficient. Combining with the spectrum of white light on the Zinc An2Py MOF and glass substrate, we obtain the absorbance. In addition, we observed that 2PPL decays over time.

Acknowledgement

I would like to express my heartfelt gratitude towards my professor, Professor Ji Wei for being so patient in guiding me to the completion of this project. I am extremely grateful to and Dr Kottilil Dileep for actively assisting me in the collection of data and clarification of concepts despite their busy schedule.

Contents

Chapter 1

Introduction

Two-photon photoluminescence (2PPL) forms under high intensity mode-locking laser and generates a photon which has a shorter wavelength and higher energy than incident photon. As a kind of third order nonlinear optical mechanism, it has taken a great place on material characterization. Using different kinds of nonlinear optical phenomenon (Second Harmonic Generation (SHG), Four Wave Mixing (FWM), Coherent Raman Spectroscopy (CRS), Multi-Photon Photoluminescence (2PPL), etc.), it is much easier to observe structure or phase determination, defects and chemical dynamics of a variety of materials, such as metal–organic frameworks[1].

In recent years, Materials based on metal–organic frameworks (MOFs) have been extensively investigated as they hold the key for promising hybrid materials with unique properties. With the advantage of combined properties of the connected metal ions, a number of excellent materials which are functional in gas absorption, conductivity catalysis and other properties can be achieved.[2]

1.1Theory

This chapter will give a general understanding of what absorption coefficient, two-photon photoluminescence and Zinc-An2Py MOF are.

1.1.1 Absorbance, Reflectance and Transmittance

Material can reflect, transmits and absorb light and the ratios of three parts of light vary with the wavelength or the photon energy. The intensity absorbed, reflected and transmitted intensity by material is described by $A(\omega)$(absorbance), $R(\omega)$(reflectance) and $T(\omega)$(transmittance) which are described by Equations, where the influence of glass substrate is considered, below,

$$A(\omega) = log_{10}\left(\frac{1}{T_a(\omega)}\right) \tag{1.1}$$

$$R(\omega) = \frac{I_s^r}{I_g^r + I_g^t} \tag{1.2}$$

$$R(\omega) = \frac{I_D^t}{I_g^t} \tag{1.3}$$

where $T_a(\omega)$ is the ratio between light intensity incident into material and that transmit material, $I_g^r \; and \; I_g^t$ are reflected and transmitted intensity detected with only the glass substrate, respectively, I_s^r is the reflected intensity of sample on the glass substrate and I_D^t are intensity that transmit sample and glass and detected by spectrometer finally. Eq. can be considered as the ratio of intensity before

and after putting on a sample. The diagram is shown below

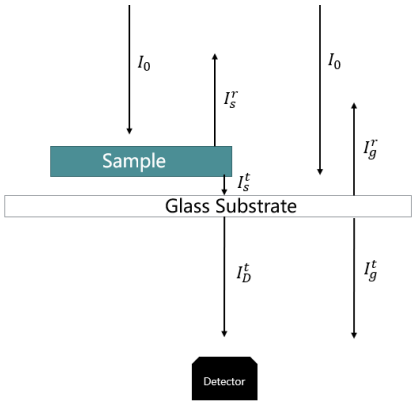


Figure 1.1 Diagram of light intensity.

1.1.2 Photoluminescence

Photoluminescence (PL) is when light energy, or photons, stimulate the emission of a photon from any matter. In essence, light is directed onto a sample, where it is absorbed and where photo-excitation can occur. The photo-excitation causes the material to jump to a higher electronic state, and will then release energy, (photons) as it relaxes and returns to back to a lower energy level.

1.1.3 Two-photon photoluminescence

In a process of Two-photon photoluminescence, an electron is excited to a high energy level by two-incident photons with same frequency. After dropping to a certain vibrational level, the electron will transit to the ground state while emitting one photon whose frequency is higher than the respective frequencies of the incident photons but lower than the sum. The transition diagram is shown in the Figure 1.1 below.

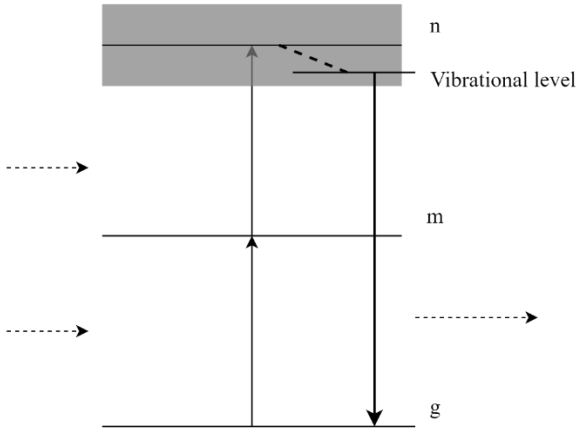


Figure 1.2 Diagram and definition of energy levels in the two-photon photoluminescence

The electron will transition to the ground state and emit a photon whose frequency is higher than the respective frequencies of the incident photons, but lower than the sum

Optical theorem can be used to understand the relationship between the number of photons involved in the 2PPL process and the corresponding nonlinear susceptibility order. This theory indicates that

an all-optical perturbation level m relate to a electronic transition with half the perturbation level (i.e., $m/2$). The Order in perturbation to calculate the probability magnitude of $\chi^{(n)}$ is $m = n + 1$. Since, in the case of 2PPL, a second-order electronic transition (m/2=2) is involved, the order of the nonlinear magnetic susceptibility is $n = m - 1 = 3$ from the optical theorem. As a result, it is a $\chi^{(3)}$ process.

The 2PPL can be described by following transition rate[3],

$$R_{ng}^{(2)} = \bar{\sigma}_{ng}^{(2)}(\omega)\bar{I}^2 \tag{1.4}$$

where I is the intensity of the incident light beam and $\bar{\sigma}_{ng}^{(2)}(\omega)$ is the two-photon action cross section.

The following equation can be used to calculate $\bar{\sigma}_{ng}^{(2)}(\omega)$,

$$\bar{\sigma}_{ng}^{(2)}(\omega) = \frac{1}{4n^2{\epsilon_0}^2c^2}\left|\sum_m \frac{\mu_{nm}\mu_{mg}}{\hbar^2(\omega_{mg}-\omega)}\right|^2 2\pi\rho_f(\omega_{ng}=2\omega) \tag{1.5}$$

where ρ_f is a density of states and $\mu_{nm} = \int u_n^*\hat{\mu}u_m d^3r$ is known as the electric dipole transition moment. State g, m and n are shown in Figure 1.1.

Multiphoton absorption and multiphoton ionization can lead to laser damage of optical materials, whi ch can lead to a possible decay of 2PPL over time[3].

In the process of 2PPL, two-photons are absorbed and one photon are emitted. The relation between photon numbers can work as an indicator to determine the 2PPL. This relationship leads to

$$Intensity_{out} \propto Power_{in}^2 \tag{1.6}$$

Therefore, 2PPL will show a line with scope of 2 in a log-log diagram of Intensity-Power relation.

1.1.3 Zinc An2Py MOF

Zinc-An2Py[bis-pyridinyl vinyl Anthracene]-MOF have 4-fold interpenetrating pcu topology structure[2], which are shown in Figure 1.2 below.

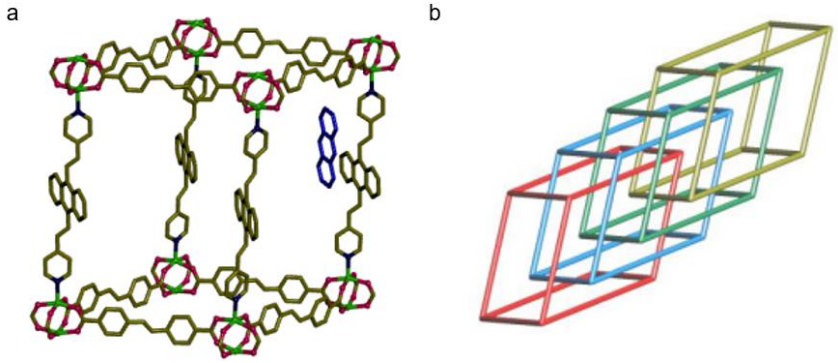


Figure 1.3 Structure of An2Py[2]. a) pcu packing of An2Py. b) Simplified topological net of 1-3 showing 4-fold interpenetrating pcu nets

1.2 Objectives of the experiment

- To experimentally obtain the absorption coefficient of Zinc An2Py MOF.
- To experimentally determine the 2PPL on Zinc An2py MOF and calculate two-photon absorption coefficient.
- To verify the angle-dependance of 2PPL on Zin An2Py MOF.

Chapter 2

Experiment Arrangement and Details

In chapter 1, we have gone through basic information of absorption, two-photon photoluminescence and Zinc An2Py MOF. We have described the transition process and the theoretical method to quantify 2PPL. We have also given the numerical relation and formula of absorption and the basic structure of Zinc An2py MOF. In addition, we have also briefly mentioned what are desired result that we hope to measured.

This chapter aims to give detailed presentation of experiment methods, equipment parameters and alignment.

2.1Equipment required

As below is the list of equipment that were used in the experiment:

1) Spectrometer & companion software	× 1
2) Halogen Lamp	× 1
3) Polarizer	× 1
4) Microscope with movable stage	× 1
5) Femtosecond laser system	× 1
6) Power meter	× 1
7) Flip mirror	× 1
8) CCD camera	× 1
9) Density Filter	× 1
10) Rotatable half wave plate	× 1
11) Beam splitter	× 1
12) Zinc An2Py sample	× 1

Table 2.1: Equipment required

2.2 Overall equipment arrangement and experiment methods

2.2.1 Experiment for absorption coefficient

In the experiment for absorption coefficient, a focused white light beam is emitted from a halogen lamp and transmit through a semi-transparent mirror. The transmitted white light shines onto the glass substrate directly at a constant intensity which should not exceed saturation limit of spectrometer. Upon being incident onto the sample, the light is partially reflected, transmitted, and absorbed. The reflected spectrum and transmitted spectrum will be collected by an optical fiber which connected a spectrometer. The data from glass substrate will be saved as reference. The same procedure will be applied for the sample on the glass substrate.

2.2.2 Experiment to determine the 2PPL

Figure 2.1 shows the general arrangement of the important equipment and the path of laser before and after 2PPL occurs.

A femtosecond laser beam at a wavelength of 800 nm transmits a series of optical lenses and a density filter, which allow us to change the incident laser intensity, before microscope. A linear polarizer is placed in the scanning box of microscope to generate linearly polarized incident laser. Objectives above and below the sample lens respectively ensure that the incoming laser will be focused on the sample and the outgoing beam will be fully collected. Finally, the outgoing beam transmits through a 720 nm short pass filter, which ensure that the directly transmitted laser will not pass, are detected by a spectrometer.

In order to change incident laser intensity numerically, a flip mirror before scanning box can reflect all intensity in to the power meter.

Mirror cube under sample can partially reflect the white light from halogen lamp (when laser is turned off), so that we can observe the size and shape of sample.

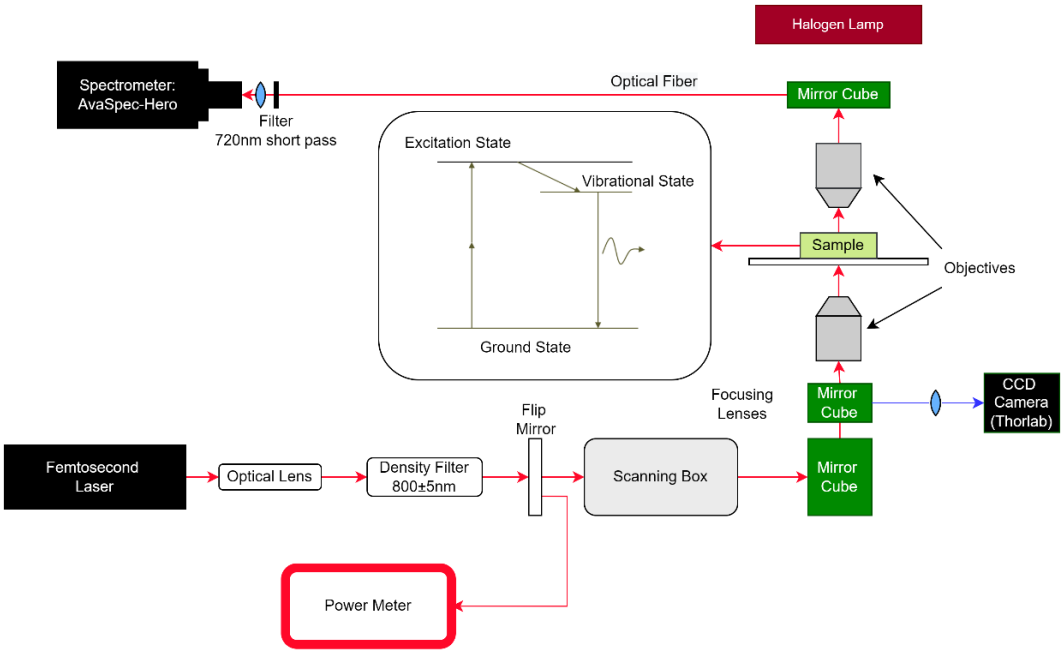


Figure 2.1: Schematic for overall equipment arrangement

2.2.3 Experiment for angle-dependent 2PPL

Angles between laser polarization direction and lattice orientation also have a effect on the 2PPL signal. In order to observe the dependence of on the angles, a rotatable half wave plate is placed between polarizer in the scanning box and sample.

2.3 Details in Equipment Arrangement

2.3.1 Alignment to Microscope

A series of optical lenses are used to operate laser before laser transmitted into microscope. These lenses construct the optical filtering system of Gaussian 00 mode

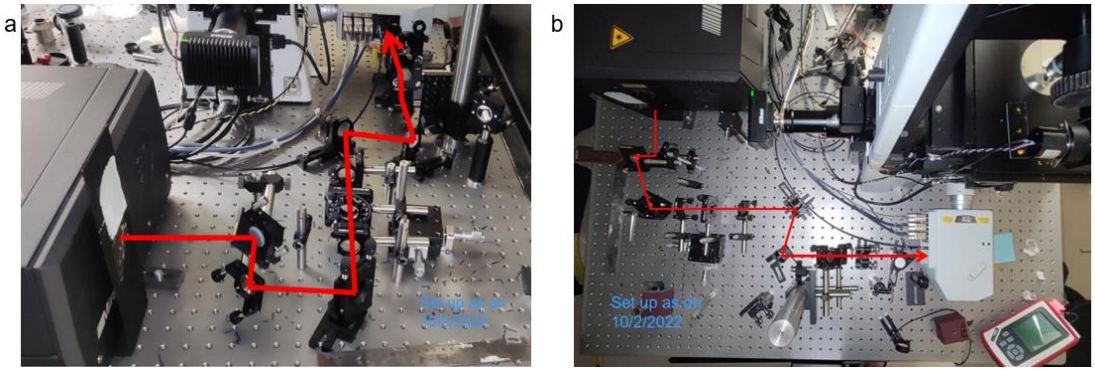


Figure 2.2: Alignment of optical lens. a) Side view. b) Top view.

2.3.2 Structure and Parameters of Multiphoton microscopy

We used a set of Nikon Eclipse microscopy in experiment.

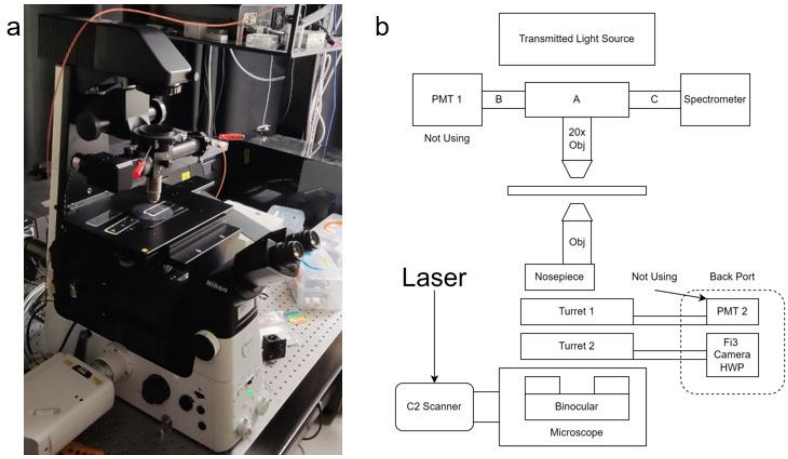


Figure 2.3: Structure of the Nikon Eclipse Ti2 microscopy. a) Actual picture of the microscopy. b) Block diagram of the microscopy

As below is the list of some of the components of the microscopy in the diagram (components which are irrelevant or unused in our experiment are not listed here)

A	2pcs of fully reflective mirror for reflected mode
	-1EA reflect to tube B (PMT 2)
	-1EA reflect to tube C (Spectrometer)
B	ET575/40m-25mmR
C	ET720sp-2p8
Turret 2	695dcxur (DM)
	ET720lp-2p8
	Rotatable half wave plate
Binocular	-Hot Mirror
Extra	ZT720sp
	ET390/40-25mmR

Table 2.2: Component of the Nikon Eclipse Ti2

2.3.3 Laser Specification

We used a laser at 532 nm to pump the mode-locking femtosecond laser which generate a high intensity pulse which is necessary for two-photon photoluminescence.

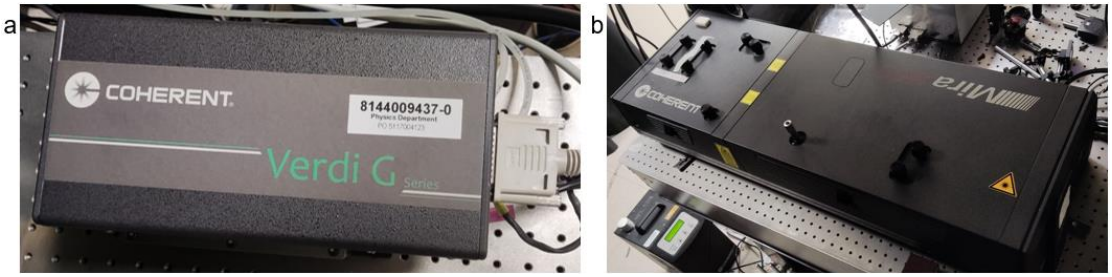


Figure 2.4: Lasers used in experiment. a) Pump laser at 523 nm. b) Femtosecond laser (modulated to 800 nm in experiment)

The parameters of two laser systems are listed in Table 2.3 below,

Parameter	Pump	Oscillator
Model	Verdi V5	Mira 900F
Wavelength	532 nm	750 nm – 900 nm
Type of laser	CW	Fs (Mode-locked)
Gain medium	Nd: YAG (SHG using KTP)	Ti: Sapphire
Max. Output power	5 W	~400 mW (Average power)@ 800 nm
Rep. rate	--	76.2 MHz
Pulse width	--	~ 160 fs
Spatial mode	TEM_{00}	TEM_{00}
Polarization	Horizontal	Horizontal

Table 2.3 Parameters of two laser systems

We measured the peak parameters and repetition of femtosecond after modulation to confirm the properties of output laser.

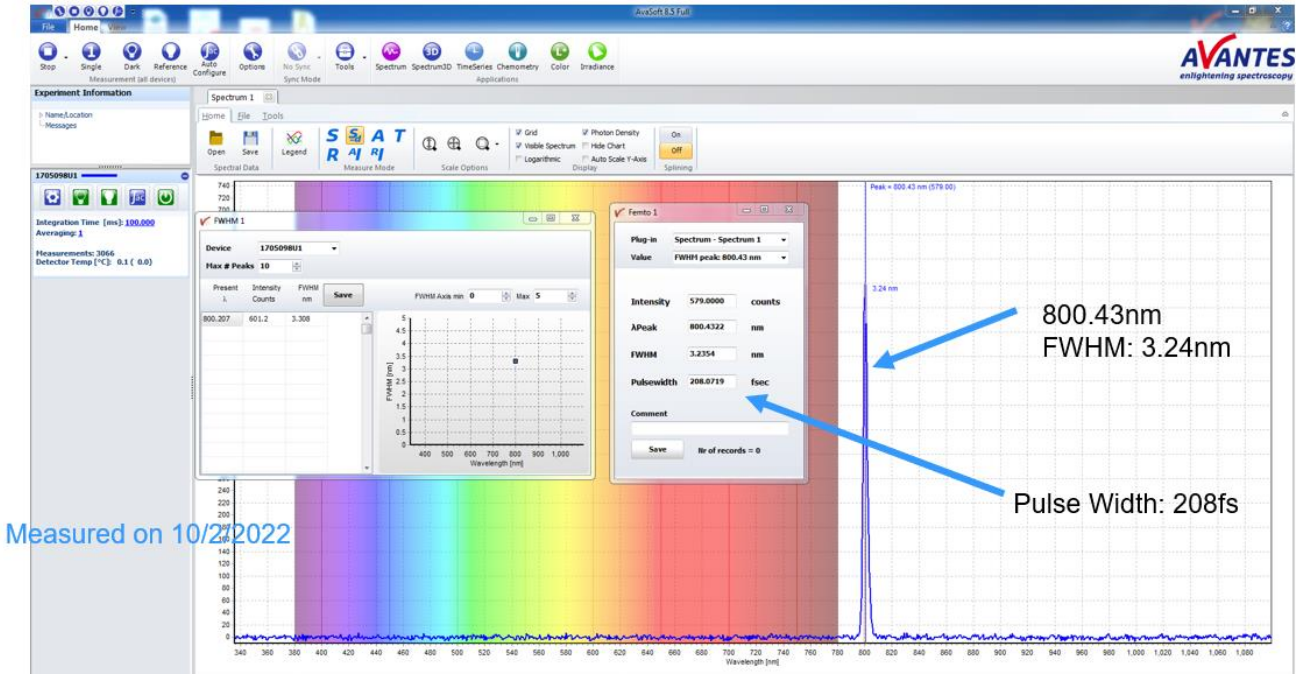


Figure 2.5 Measurement results from AvaSpec-Hero spectrometer on companion software. The pulse peak is at 800.43 nm; full width half maximum is 3.24 nm and the pulse width is 208 fs

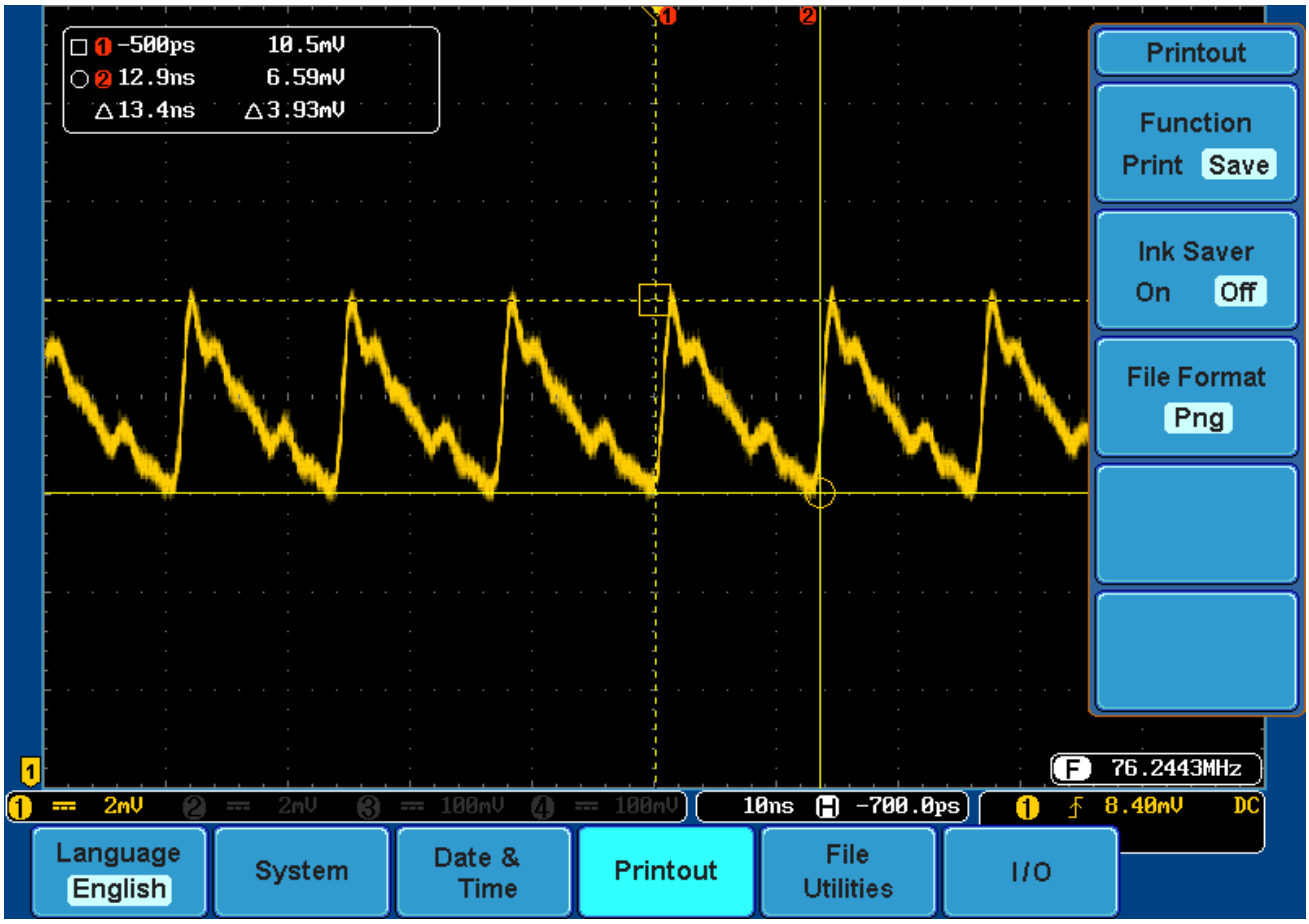


Figure 2.6 Repetition rate are 76.3 MHz from an InGaAs PIN photodiode detector. Measurement done by deflecting the laser beam using a glass slide.

Chapter 3

Results and Discussions

In chapter 2, we have explained the equipment arrangement and present the precise parameter of experiment instruments and output laser. In this chapter, we will firstly elaborate the experiment of absorption coefficient. Subsequently, by using 3 crystals (Figure 3.1) of different thickness, we will present the details that enable us to obtain a spectrum and other diagram suggesting the appearance of 2PPL. Furthermore, the two-photon absorption coefficient and angle-dependence will be described.

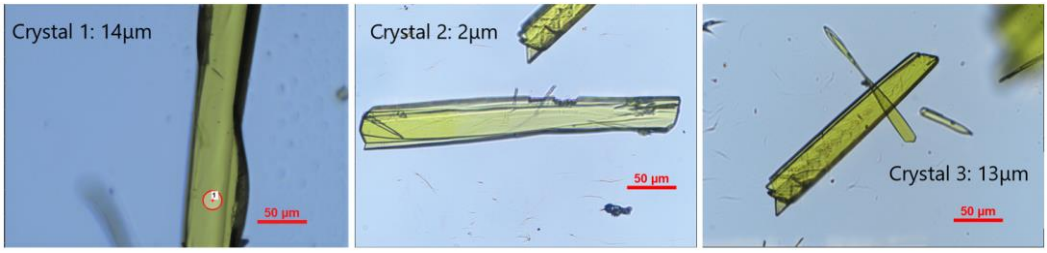


Figure 3.1 Images of Zinc An2Py MOF Crystal 1 to3 by the CCD camera and their respective thickness. Ligand of all three crystal is phorphyrin

3.1 Experiment of absorbance

Spectrum results are shown as Figure 3.2 below,

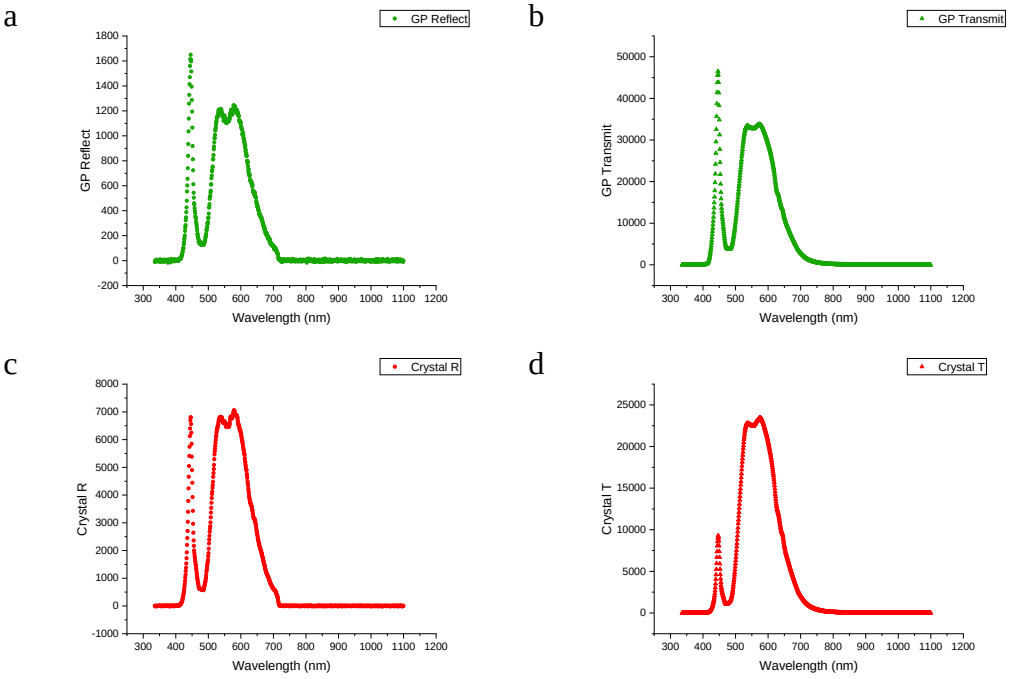


Figure 3.2 Spectrum result of crystal 1 and glass substrate. Image a and b are reflected and transmitted spectrum of glass substrate, respectively. Image c and d are reflected and transmitted spectrum of crystal 1, respectively.

Using spectrum form glass spectrum as a reference, the reflectance and transmittance are plotted in Figure 3.3 below,

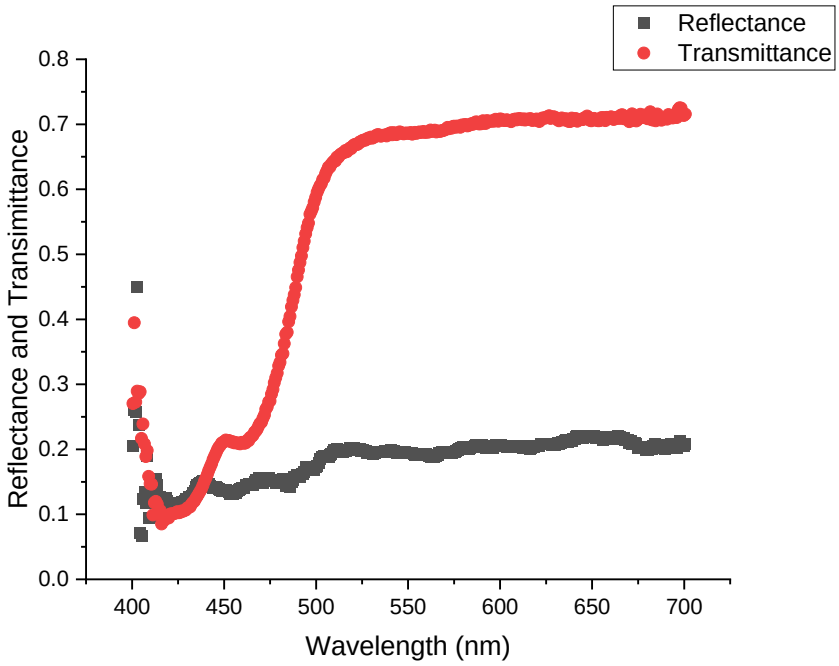


Figure 3.3 Reflectance and transmittance of Crystal 1

Using Eq.1.1, the absorbance can be calculated and plotted.

$$A = log_{10}\left(\frac{I_0 - I_s^r}{I_s^t}\right) \tag{3.1}$$

where I_0 is the intensity shine on sample, I_s^r is the intensity reflected by sample and I_s^t is intensity that transmits sample. Absorbance is plotted in Figure 3.4 below,

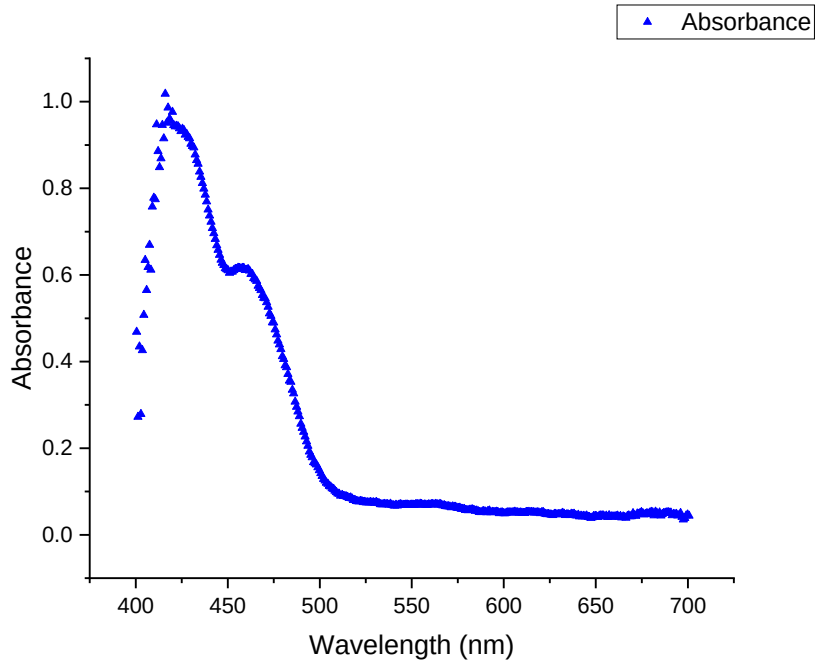


Figure 3.4 Absorbance of Crystal 1.

3.2 Experiment of two-photon photoluminescence

Great change of nonlinear optical signal may occur on the grain boundaries or multi-layer crystal and the reason and intensity of this kind of signal is yet to be qualified. In order to avoid the disturbance from that condition, all crystal we used during experiment is single crystal and the spot where we shine laser on is single-layer crystal.

We chose 6 spots which satisfy the requirement above on each crystal. The pulse laser of 800 nm will be shot on the laser with 5 different powers (average power are indicated by a power meter) in order observe the relation between laser power and excited signal. The excitation signal needs to be as high as possible within a safe range since the signal generated with lowest laser power are relevantly weak and we need to ensure a modest signal to noise ratio. In order to eliminate the interference of direct transmitted laser, the filter in the tube, which are connected with a spectrometer, block all the signal above 760 nm. The selected spot and the spectrum result are shown in Figure A1-3 and power are shown in Table A1.

Using Eq.1.6: $Intensity_{out} \propto Power_{in}^2$, a simpler and more intuitively relation between intensity and power can be derived,

$$log_{10}(Intensity_{out}) = 2log_{10}(Power_{in}) \tag{3.2}$$

We can check the slope of log-log curve to determine the 2PPL on sample.

Nevertheless, another kind of nonlinear optics, second harmonic generation (SHG), has the same expected slope of log-log curve as 2PPL. SHG has a similar transition process to 2PPL but electron will directly emit photon without dropping to a vibrational level. As a result, the excited signal of SHG will have a sharp peak at twice the incident photon energy while 2PPL will have a broader peak at less than twice the incident photon energy. The incident photon energy of 800 nm is 1.55 (using $E = hc/\lambda$) and there is no signal at $2 \times 1.55 = 3.1$ on any diagram. Therefore, we can conclude that SHG does not occur on the sample.

Before plotting the diagram, we need to determine x and y parameter. The number we recorded from the power meter is the average power, which we need to convert to fluence for the x parameter using Eq. 3.3 below,

$$Fluence = \frac{Avg.Power}{Rep.rate \times Area} \tag{3.3}$$

where repetition rate are 76.3 MHz and Area indicate area of laser spot on the sample which is $16\mu m^2$. All signals recorded by the spectrometer are 2PPL excitation. Therefore, we used integrated signal as y parameter (integrated range are shown in Table A2).

The results of linear fitting from log-log data of every spot are shown in Figure 3.5-3.7 below.

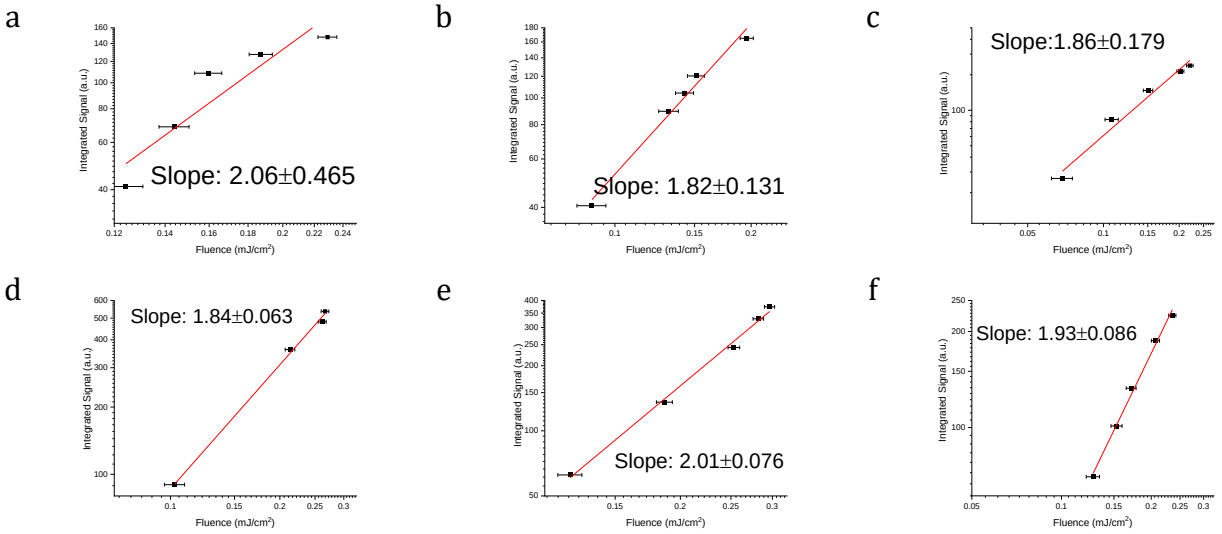


Figure 3.5 Results of log-log linear fitting of crystal 1. Image a-f are from spot 1-6 in order.

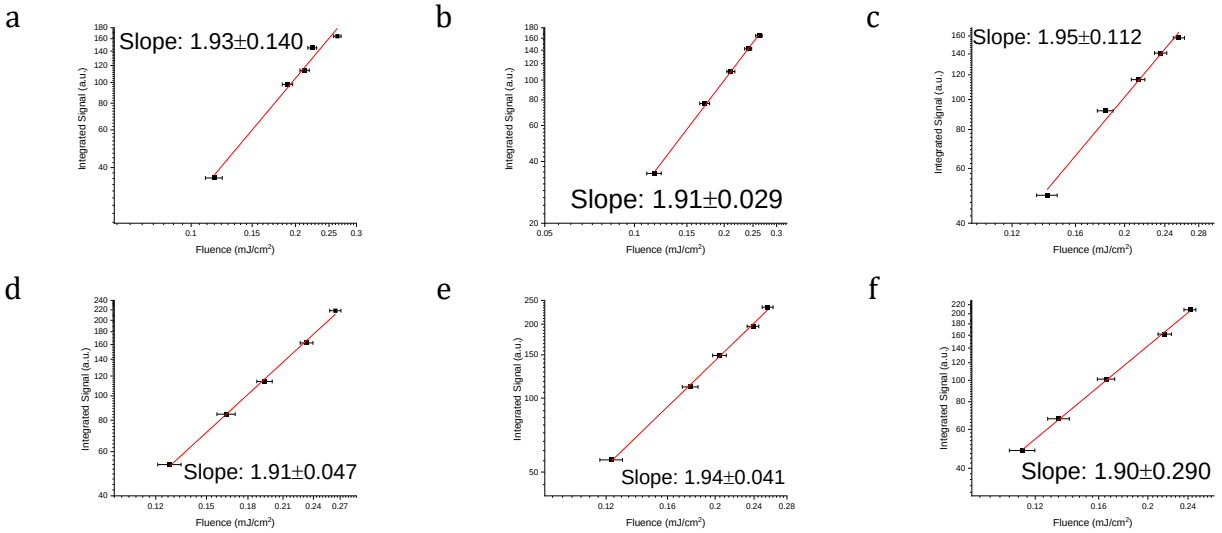


Figure 3.6 Results of log-log linear fitting of crystal 2. Image a-f are from spot 1-6 in order.

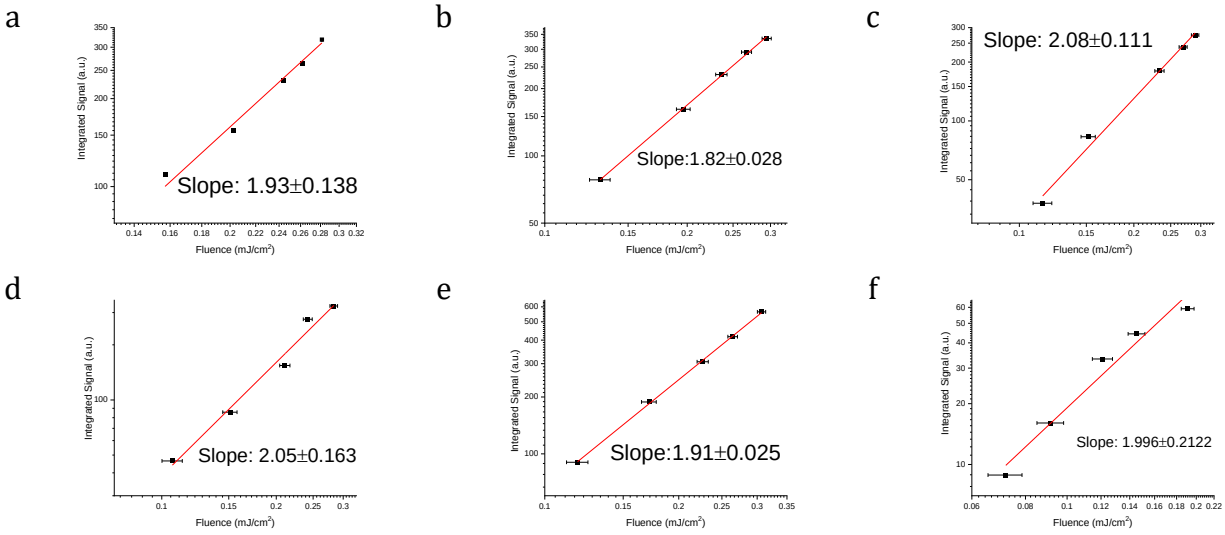


Figure 3.7 Results of log-log linear fitting of crystal 3. Image a-f are from spot 1-6 in order.

From the diagrams above, we observed that all slopes are around 2. Therefore, we can conclude that there is 2PPL on Zinc An2Py MOF.

The 2PPL efficiency of a sample material could be determined by comparison to a standard material[4]. The two-photon absorption action cross section, $\bar{\sigma}_{ng}^{(2)}(\omega)$, could be found using the Eq. below,

$$\frac{\#PL_{MOF}}{\#PL_{standard}} = \frac{\left(\bar{\sigma}_{ng}^{(2)}(\omega)\right)_{MOF} I_{MOF}^2 L_{2PPL}}{\left(\bar{\sigma}_{ng}^{(2)}(\omega)\right)_{standard} I_{standard}^2 \times 2z_0} \tag{3.4}$$

where $\#PL_{MOF}/\#PL_{standard}$ refers to the fluorescence signal strength of the MOF or standard material detected by the spectrometer, I is the incident beam intensity, z_0 is the Rayleigh length of the focused laser beam having a Gaussian profile and L_{2PPL} is the MOF thickness between Rayleigh length.

Using the reference data[4], we calculate the two-photon absorption action cross section which are shown in the Table 3.1 below,

	Reference (Rhb MOF)	Crystal 1 spot6	Crystal 2 spot1	Crystal 3 spot1
Integrated Signal	240.9759	225.0574	154.1214	324.0885
Signal ratio	1	0.933942	0.639572	1.3449
Power	43.5	36	40.4	43
Squared power ratio	1	0.684899	0.86255	0.977144
L	8	8	2	8
L ratio	1	1	0.25	1
Cross section/(cm/GW)	7.1	9.6817	21.05831	9.772147

Table 3.1 Calculation results of two-photon absorption action cross section

The average two-photon absorption action cross section is $13.504 \pm 5.342\ cm/GW$

The results also represent that the two-photon absorption action cross section of crystal 2 is higher than the other two. In order to confirm the reliability of data from crystal 2, the results from other spots on the crystal 2 is shown in Table 3.2 below,

	Reference	s1	s2	s3	s4	s5	s6
Integrated Signal	240.9759	154.1214	168.3318	162.1057	222.2813	238.2168	213.0636
Signal ratio	1	0.639572	0.698542	0.672705	0.922421	0.98855	0.88417
Power	43.5	40.4	40	39.1	40.4	39.1	37
Squared power ratio	1	0.86255	0.845554	0.807932	0.86255	0.807932	0.723477
L	8	2	2	2	2	2	2
L ratio	1	0.25	0.25	0.25	0.25	0.25	0.25
Cross section	7.1	21.05831	23.46225	23.64656	30.3713	34.74899	34.70796

Table 3.2 Calculation results of two-photon absorption action cross section from spots of crystal 2

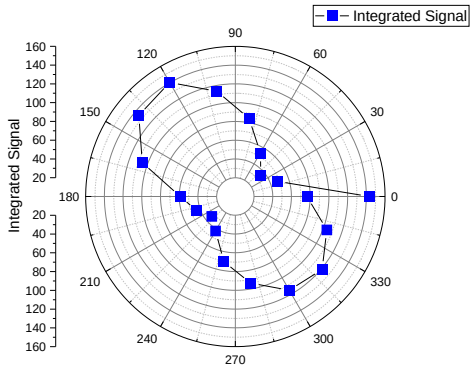
The results confirm that the two-photon absorption action cross section is higher on crystal 2.

3.3 Experiment of angle-dependence

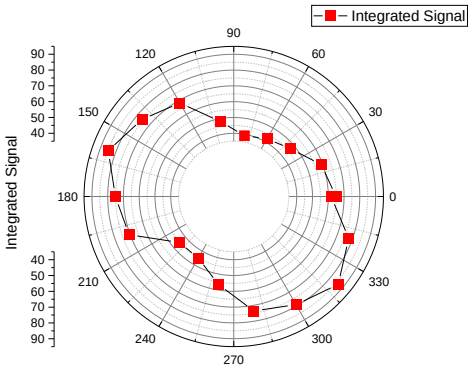
Using a rotatable half wave plate in the turret, we manage to shine linearly polarized lasers with different polarization directions. Therefore, an angle-dependent signal diagram can be obtained with fixed laser power.

We can observe angle-dependence from Image a and b of Figure 3.9 but Image c basically does not show angle-dependence.

a



b



c

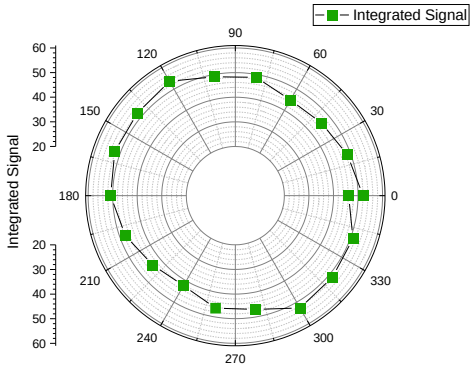


Figure 3.8 Angle-dependent signal diagram. Image a, b and c are diagram from spot 1 on crystal 1-3, respectively.

Signal at 0 and 360 degrees should be some theoretically but we observe that signal at 0 degree is higher than that at 360 degrees on each crystal. Combining with the fact that the experiment starts at 0 and ends at 360 degrees, we can say that 2PPL on Zinc An2Py MOF decays over time.

Conclusion

1. Absorbance curve are obtained in Figure 3.4 which shows high absorbance around 430 nm and low absorbance over 550 nm.
2. 2PPL on Zinc An2Py MOF is confirmed by two experiment results1: 1. All slopes of log-log diagram are around 2; 2. No signal at 3.1eV (two times of incident photon energy).
3. The two-photon absorption action cross section of three crystal is calculated and it is higher on crystal 2 than that on the other two.
4. Angle-dependance are observed in Crystal 1 and 2 while it does not appear on Crystal 3. During the experiment for angle-dependence, 2PPL signal on Zinc An2Py MOF are observed to decay over time.

Bibliography

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3. Boyd, R.W., *Nonlinear optics*. 2020: Academic press.
4. Gupta, M., et al., *Two-Photon Absorption and Fluorescence in Micrometer-Sized Single Crystals of a Rhodamine B Coordinated Metal–Organic Framework.* ACS Applied Nano Materials, 2018. **1**(10): p. 5408-5413.

Appendices

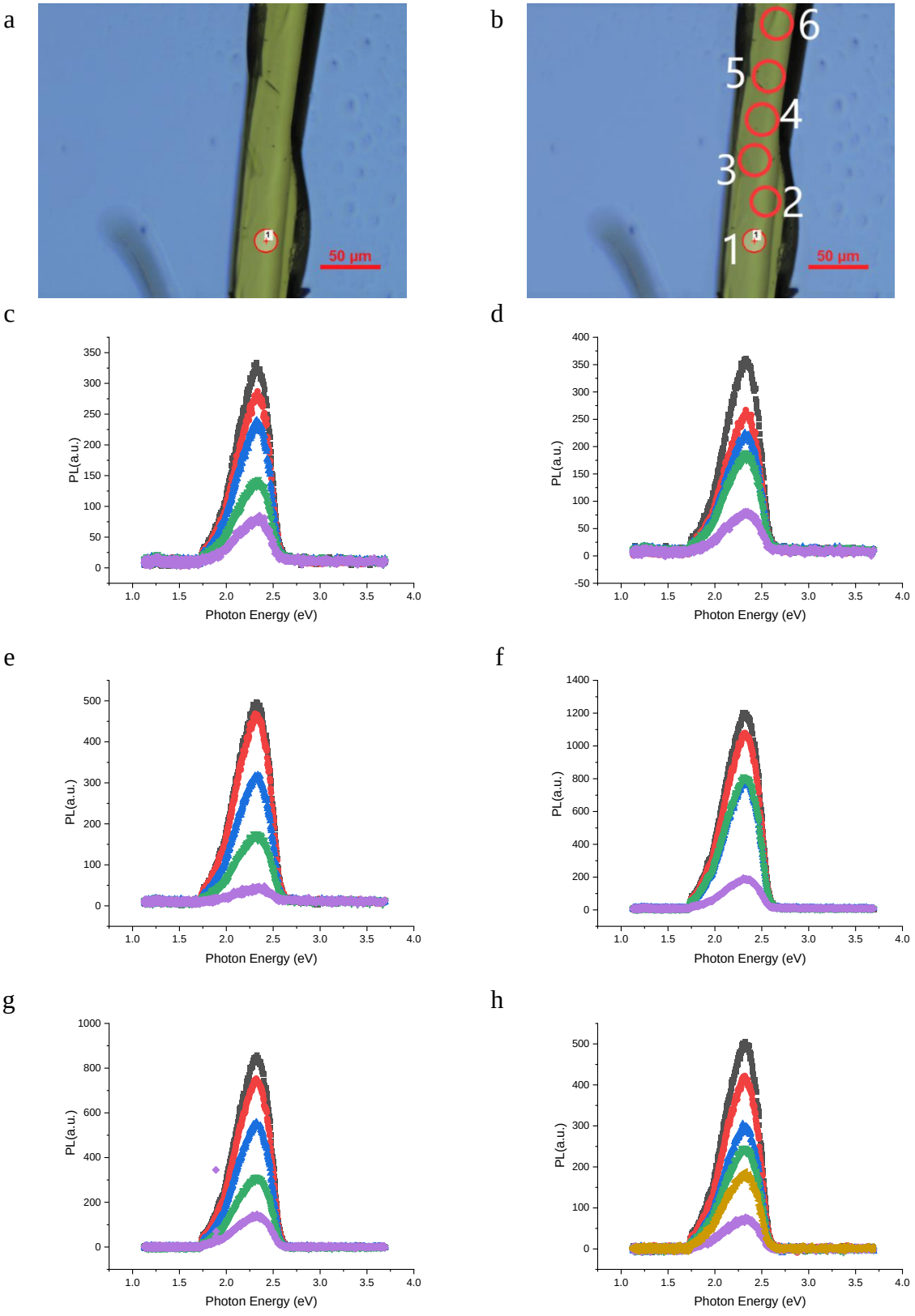

Figure A1 Six selected spot and the spectrum result of Crystal 1. Image b is processed to make the sequence number clearer. Image c-f are spectrum of spot 1-6 in order.

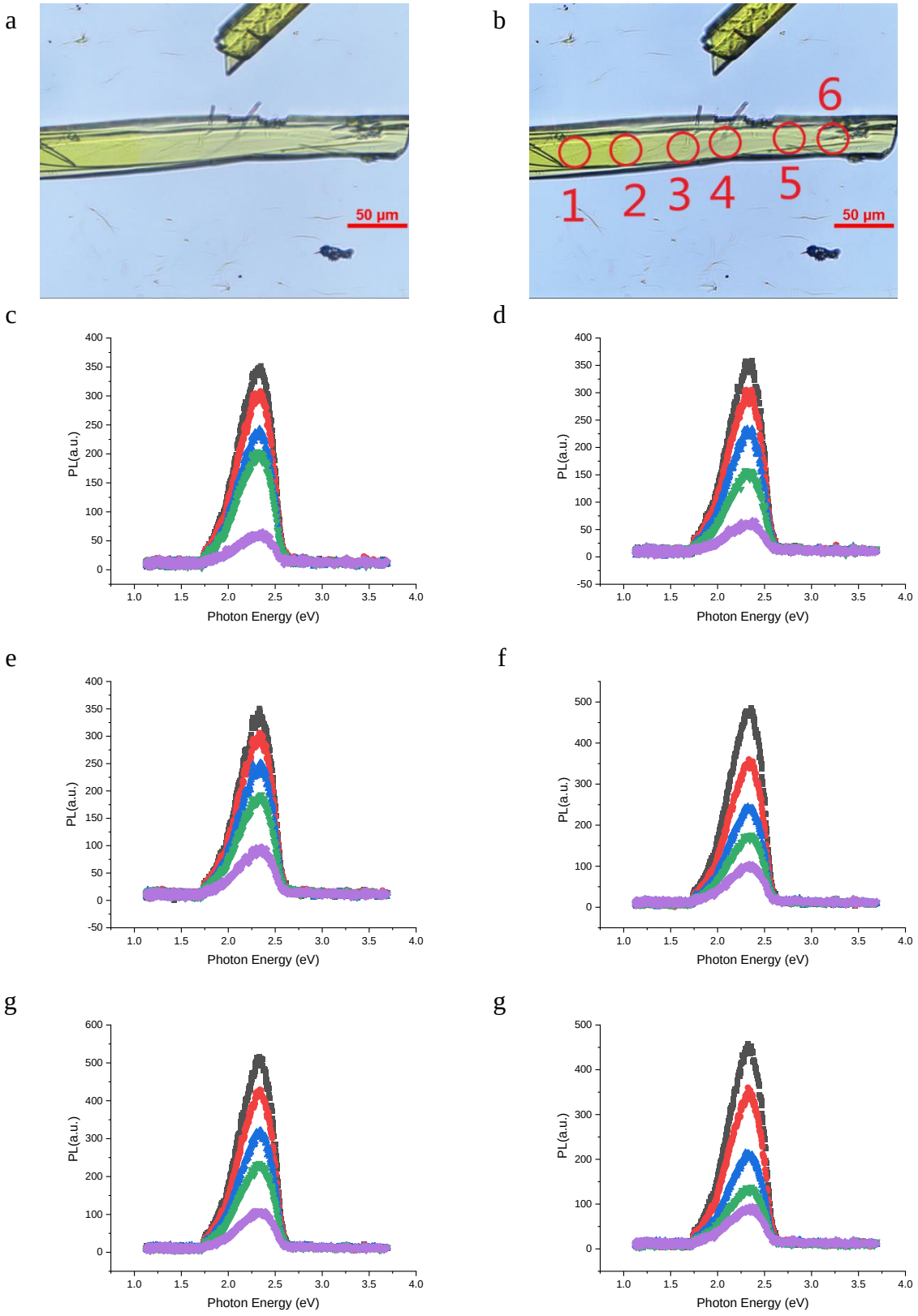

Figure A2 Six selected spot and the spectrum result of Crystal 2. Image b is processed to make the sequence number clearer. Image c-f are spectrum of spot 1-6 in order.

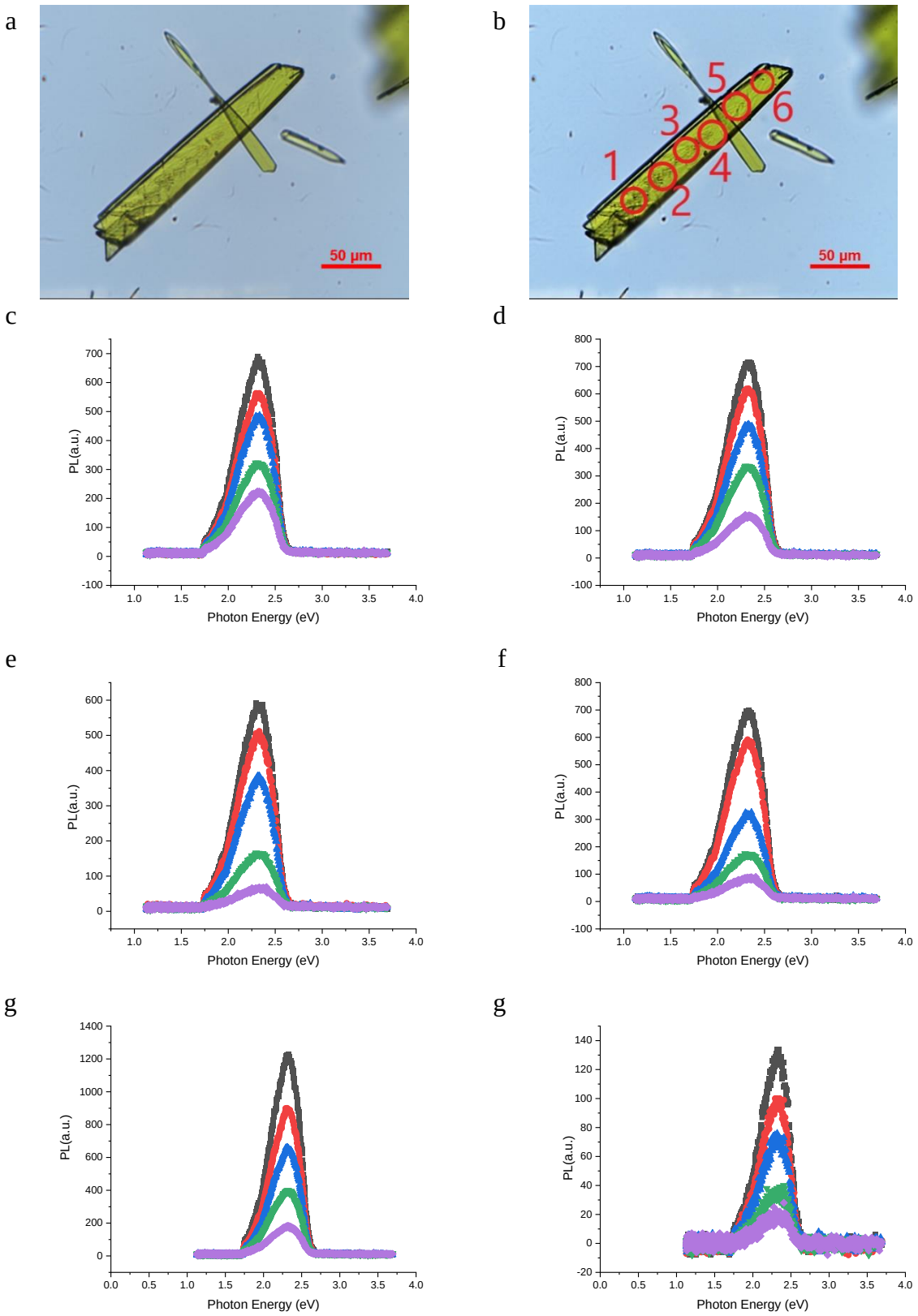

Figure A3 Six selected spot and the spectrum result of Crystal 1. Image b is processed to make the sequence number clearer. Image c-f are spectrum of spot 1-6 in order.

		Power 1/mW	Power 2/mW	Power 3/mW	Power 4/mW	Power 5/mW
Crystal 1	Spot 1	35.0	28.6	24.4	22.0	19.0
	Spot 2	29.9	23.1	21.8	20.1	13.6
	Spot 3	33.7	30.9	23.0	16.5	10.5
	Spot 4	40.7	40.0	32.6	15.7	
	Spot 5	45.3	43.1	38.7	28.5	18.8
	Spot 6	36.0	31.6	26.2	23.4	19.5
Crystal 2	Spot 1	40.4	34.2	32.5	29.0	17.8
	Spot 2	40.0	36.8	32.2	26.3	17.8
	Spot 3	39.1	36.0	32.5	28.0	21.5
	Spot 4	40.4	35.6	29.6	25.0	19.5
	Spot 5	39.1	36.5	31.2	27.2	18.8
	Spot 6	37.0	33.0	25.3	20.4	17.3
Crystal 3	Spot 1	43.0	40.0	37.3	31.0	24.0
	Spot 2	45.0	40.8	36.1	30.0	20.0
	Spot 3	44.3	41.2	35.7	23.2	17.6
	Spot 4	43.3	37.0	32.2	23.1	16.3
	Spot 5	46.9	40.4	34.6	26.2	18.1
	Spot 6	29.2	22.2	18.5	14.0	11.1

Table A1 Powers in experiment.

Crystal 1					
Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6
1.5-2.9	1.5-2.8	1.5-2.9	1.5-3.0	1.6-3.0	1.5-3.0
Crystal 2					
Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6
1.4-3.0	1.5-2.9	1.5-2.8	1.5-3.0	1.5-3.0	1.5-2.9
Crystal 3					
Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6
1.6-2.9	1.5-2.9	1.5-3.0	1.5-3.0	1.5-2.9	1.5-3.0

Table A2 Integration range.