SRF/ORF Sharing

Or King Long, Ivan

2023 SRF Participant

Rundown

Things to prepare

Application details

Research Proposal

Research Experience

Things to prepare

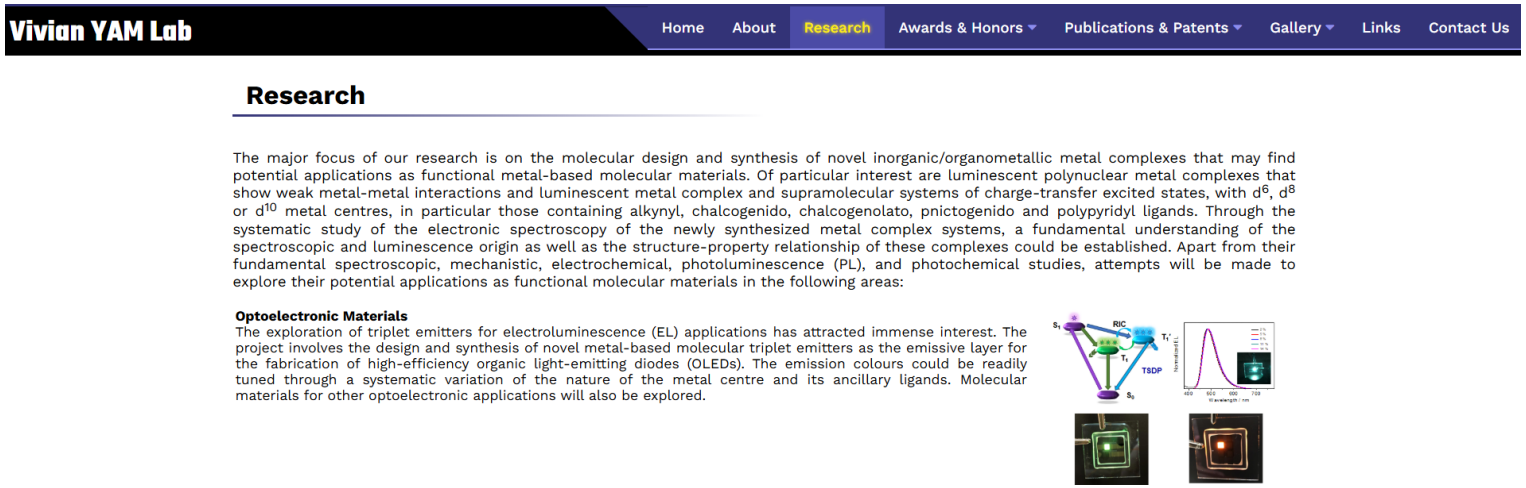
1. Research of the research

→ Choose an interested topic (Important!!!)

→ Check the lab website for details

2. Contact the potential supervisor via email

→ Include CV to show your ability



Application Details

Application

Completed application form has to be submitted via the Science Online Application Submission System (OASS) along with a recommendation letter and a research proposal (not more than 500 words on **ONE** A4 sized paper).

Deadline:
SRF Scheme: February 17, 2025 (Monday)
ORF Scheme: February 17, 2025 (Monday) / April 14, 2025 (Monday)

Late application will not be considered. Applicants will be invited to an interview.

Research Proposal

- Research proposal is the hardest part in the application
- Discuss with the potential supervisor on the interested topic
- Provide a suitable workflow in the proposal (Not doing 1000 experiments within two months)
- Frankly, it is not practicable to start a new topic for a summer student → ask for details about ongoing project may help to write

Research Proposal

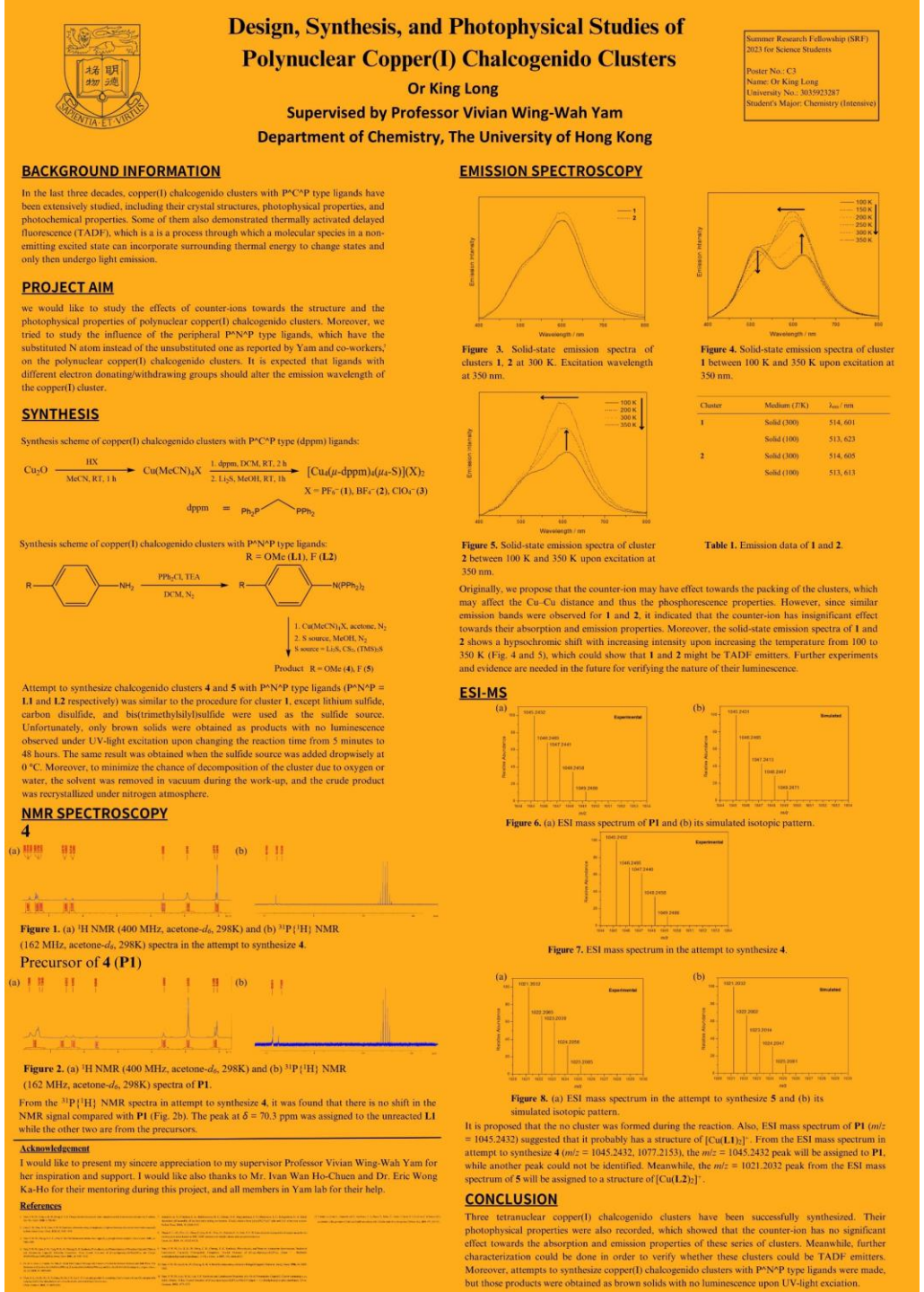
PROJECT AIM & BACKGROUND

METHODOLOGY (E.G. CHEMISTRY, WHAT KIND OF EXPERIMENTS? HOW TO ANALYZE?)

READ SOME JOURNALS ABOUT THE TOPIC MAY BENEFIT THE BACKGROUND

My research experience in SRF

- Design, Synthesis, and Photophysical Studies of Polynuclear Copper(I) Chalcogenido Clusters (Yam Group)



Design, Synthesis, and Photophysical Studies of Polynuclear Copper(I) Chalcogenido Clusters

Or King Long

Supervised by Professor Vivian Wing-Wah Yam

Department of Chemistry, The University of Hong Kong

Summer Research Fellowship (SRF) 2023 for Science Students

Poster No.: C3
Name: Or King Long
University No.: 3035923287
Student's Major: Chemistry (Intensive)

BACKGROUND INFORMATION

In the last three decades, copper(I) chalcogenido clusters with P^C^P type ligands have been extensively studied, including their crystal structures, photophysical properties, and photochemical properties. Some of them also demonstrated thermally activated delayed fluorescence (TADF), which is a is a process through which a molecular species in a non-emitting excited state can incorporate surrounding thermal energy to change states and only then undergo light emission.

PROJECT AIM

we would like to study the effects of counter-ions towards the structure and the photophysical properties of polynuclear copper(I) chalcogenido clusters. Moreover, we tried to study the influence of the peripheral P^N^P type ligands, which have the substituted N atom instead of the unsubstituted one as reported by Yam and co-workers,[1] on the polynuclear copper(I) chalcogenido clusters. It is expected that ligands with different electron donating/withdrawing groups should alter the emission wavelength of the copper(I) cluster.

SYNTHESIS

Synthesis scheme of copper(I) chalcogenido clusters with P^C^P type (dppm) ligands:

Synthesis scheme of copper(I) chalcogenido clusters with P^N^P type ligands:

Attempt to synthesize chalcogenido clusters **4** and **5** with P^N^P type ligands (P^N^P = **L1** and **L2** respectively) was similar to the procedure for cluster **1**, except lithium sulfide, carbon disulfide, and bis(trimethylsilyl)sulfide were used as the sulfide source. Unfortunately, only brown solids were obtained as products with no luminescence observed under UV-light excitation upon changing the reaction time from 5 minutes to 48 hours. The same result was obtained when the sulfide source was added dropwisely at 0 °C. Moreover, to minimize the chance of decomposition of the cluster due to oxygen or water, the solvent was removed in vacuum during the work-up, and the crude product was recrystallized under nitrogen atmosphere.

NMR SPECTROSCOPY

4

Figure 1. (a) ^{1}H NMR (400 MHz, acetone-d_6, 298K) and (b) ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6, 298K) spectra in the attempt to synthesize **4**.

Precursor of **4** (**P1**)

Figure 2. (a) ^{1}H NMR (400 MHz, acetone-d_6, 298K) and (b) ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6, 298K) spectra of **P1**.

From the ^{31}P{^{1}H} NMR spectra in attempt to synthesize **4**, it was found that there is no shift in the NMR signal compared with **P1** (Fig. 2b). The peak at δ = 70.3 ppm was assigned to the unreacted **L1** while the other two are from the precursors.

Acknowledgement

I would like to present my sincere appreciation to my supervisor Professor Vivian Wing-Wah Yam for her inspiration and support. I would like also thanks to Mr. Ivan Wan Ho-Chuen and Dr. Eric Wong Ka-Ho for their mentoring during this project, and all members in Yam lab for their help.

References

EMISSION SPECTROSCOPY

Figure 3. Solid-state emission spectra of clusters **1**, **2** at 300 K. Excitation wavelength at 350 nm.

Figure 4. Solid-state emission spectra of cluster **1** between 100 K and 350 K upon excitation at 350 nm.

Figure 5. Solid-state emission spectra of cluster **2** between 100 K and 350 K upon excitation at 350 nm.

Cluster	Medium (77K)	λ_{max} / nm
1	Solid (300)	514, 601
	Solid (100)	513, 623
2	Solid (300)	514, 605
	Solid (100)	513, 613

Table 1. Emission data of **1** and **2**.

Originally, we propose that the counter-ion may have effect towards the packing of the clusters, which may affect the Cu–Cu distance and thus the phosphorescence properties. However, since similar emission bands were observed for **1** and **2**, it indicated that the counter-ion has insignificant effect towards their absorption and emission properties. Moreover, the solid-state emission spectra of **1** and **2** shows a hypsochromic shift with increasing intensity upon increasing the temperature from 100 to 350 K (Fig. 4 and 5), which could show that **1** and **2** might be TADF emitters. Further experiments and evidence are needed in the future for verifying the nature of their luminescence.

ESI-MS

Figure 6. (a) ESI mass spectrum of **P1** and (b) its simulated isotopic pattern.

Figure 7. ESI mass spectrum in the attempt to synthesize **4**.

Figure 8. (a) ESI mass spectrum in the attempt to synthesize **5** and (b) its simulated isotopic pattern.

It is proposed that the no cluster was formed during the reaction. Also, ESI mass spectrum of **P1** (*m/z* = 1045.2432) suggested that it probably has a structure of $[Cu(\mathbf{L1})_2]^+$. From the ESI mass spectrum in attempt to synthesize **4** (*m/z* = 1045.2432, 1077.2153), the *m/z* = 1045.2432 peak will be assigned to **P1**, while another peak could not be identified. Meanwhile, the *m/z* = 1021.2032 peak from the ESI mass spectrum of **5** will be assigned to a structure of $[Cu(\mathbf{L2})_2]^+$.

CONCLUSION

Three tetranuclear copper(I) chalcogenido clusters have been successfully synthesized. Their photophysical properties were also recorded, which showed that the counter-ion has no significant effect towards the absorption and emission properties of these series of clusters. Meanwhile, further characterization could be done in order to verify whether these clusters could be TADF emitters. Moreover, attempts to synthesize copper(I) chalcogenido clusters with P^N^P type ligands were made, but those products were obtained as brown solids with no luminescence upon UV-light exciation.

My research experience in SRF

- Design, Synthesis, and Photophysical Studies of Polynuclear Copper(I) Chalcogenido Clusters (Yam Group)

EMISSION SPECTROSCOPY

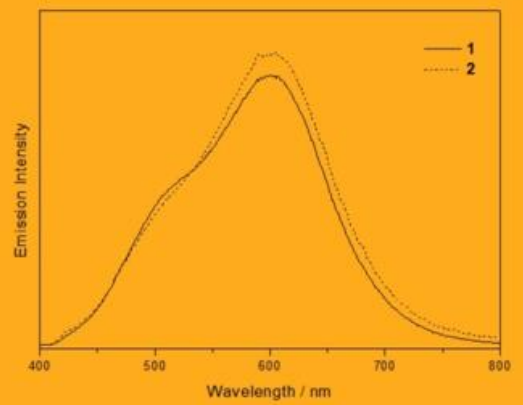


Figure 3. Solid-state emission spectra of clusters **1**, **2** at 300 K. Excitation wavelength at 350 nm.

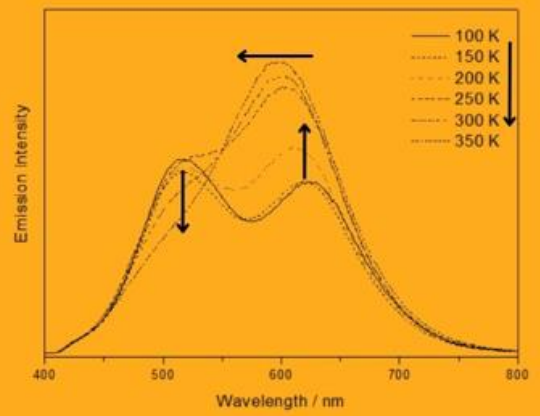


Figure 4. Solid-state emission spectra of cluster **1** between 100 K and 350 K upon excitation at 350 nm.

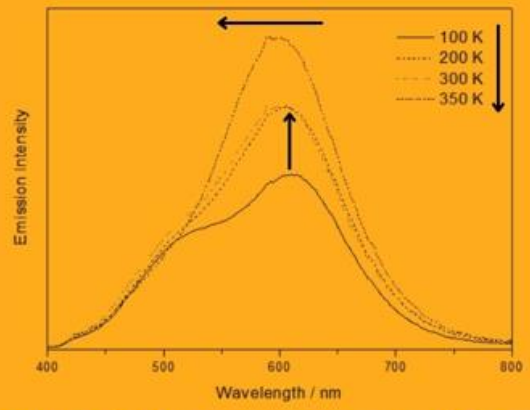


Figure 5. Solid-state emission spectra of cluster **2** between 100 K and 350 K upon excitation at 350 nm.

Cluster	Medium (T/K)	λ_{em} / nm
1	Solid (300)	514, 601
	Solid (100)	513, 623
2	Solid (300)	514, 605
	Solid (100)	513, 613

Table 1. Emission data of **1** and **2**.

Thank you and good luck!