SRF/ORF Sharing

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

Vivian YAM Lab

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Research

The major focus of our research is on the molecular design and synthesis of novel inorganic/organometallic metal complexes that may find potential applications as functional metal-based molecular materials. Of particular interest are luminescent polynuclear metal complexes that show weak metal-metal interactions and luminescent metal complex and supramolecular systems of charge-transfer excited states, with d⁶, d⁸ or d¹⁰ metal centres, in particular those containing alkynyl, chalcogenido, chalcogenolato, pnictogenido and polypyridyl ligands. Through the systematic study of the electronic spectroscopy of the newly synthesized metal complex systems, a fundamental understanding of the spectroscopic and luminescence origin as well as the structure-property relationship of these complexes could be established. Apart from their fundamental spectroscopic, mechanistic, electrochemical, photoluminescence (PL), and photochemical studies, attempts will be made to explore their potential applications as functional molecular materials in the following areas:

Optoelectronic Materials

The exploration of triplet emitters for electroluminescence (EL) applications has attracted immense interest. The project involves the design and synthesis of novel metal-based molecular triplet emitters as the emissive layer for the fabrication of high-efficiency organic light-emitting diodes (OLEDs). The emission colours could be readily tuned through a systematic variation of the nature of the metal centre and its ancillary ligands. Molecular materials for other optoelectronic applications will also be explored.









Application Details

Application

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

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

BACKGROUND INFORMATION

In the last three decades, copper(1) 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 nonemitting excited state can incorporate surrounding thermal energy to change states and

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, 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:

$$Cu_2O \xrightarrow{IIX} Cu(MeCN)_{\ell}X \xrightarrow{1. \text{depen}, D.CM. R.T. 2.h} [Cu_{\ell}u\text{-depen})_{\ell}(MeS, R.T. 1.h) \times [Cu_{\ell}u\text{-depen})_{\ell}(MeS)_{\ell}(X)_{2} \times FF_{\ell}^{-r}(1), BF_{\ell}^{-r}(2), ClO_{1}^{-r}(3) \times FF_{\ell}^{-r}(1), BF_{\ell}^{-r}(2), ClO_{1}^{-r}(2), ClO_{1}^{-r}(2)$$

R = OMe(L1), F(L2)



Attempt to synthesize chalcogenido clusters 4 and 5 with P^N^P type ligands (P^N^P = 1.1 and 1.2 respectively) was similar to the procedure for cluster 1, except lithium sulfide, carbon disulfide, and bis(trimethylsilyl)sulfide were used as the sulfide source. 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



(162 MHz, acetone-d₆, 298K) spectra in the attempt to synthesize 4.

Precursor of 4 (P1)



Figure 2. (a) ¹H NMR (400 MHz, acetone-d₆, 298K) and (b) ³¹P (¹H) NMR (162 MHz, acetone-d₆, 298K) spectra of P1.

From the ³¹P[⁴H] 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 $\delta = 70.3$ ppm was assigned to the unreacted L1 while the other two are from the precursors

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.

- 1	References		
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EMISSION SPECTROSCOPY

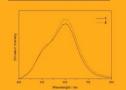


Figure 3. Solid-state emission spectra of clusters 1, 2 at 300 K. Excitation wavelength

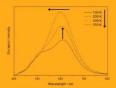


Figure 5. Solid-state emission spectra of cluster 2 between 100 K and 350 K upon excitation at

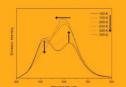


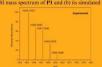
Figure 4. Solid-state emission spectra of cluster 1 between 100 K and 350 K upon excitation at

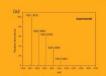
Cluster	Medium (TK)	λ _{em} / mm
1	Solid (300)	514, 601
	Solid (100)	513, 623
2	Solid (300)	514, 605
	Solid (100)	513, 613

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.







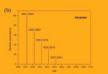


Figure 8. (a) ESI mass spectrum in the attempt to synthesize 5 and (b) its simulated isotopic pattern.

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(L1)₀]*. 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(L2)2]

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

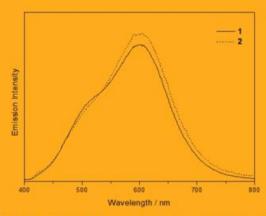


Figure 3. Solid-state emission spectra of clusters **1**, **2** at 300 K. Excitation wavelength at 350 nm.

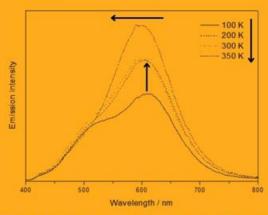


Figure 5. Solid-state emission spectra of cluster **2** between 100 K and 350 K upon excitation at 350 nm.

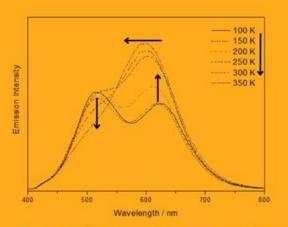


Figure 4. Solid-state emission spectra of cluster **1** between 100 K and 350 K upon excitation at 350 nm.

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!