

Preparation and Luminescence Thermochromism of Tetranuclear Copper(I)–Pyridine–Iodide Clusters

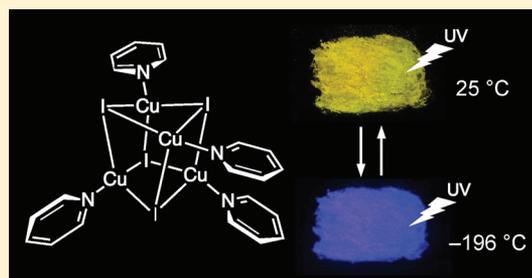
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Supporting Information

ABSTRACT: A simple and straightforward synthesis of a tetranuclear copper(I)–pyridine–iodide cluster is described as a laboratory experiment for advanced inorganic chemistry undergraduate students. The product is used to demonstrate the fascinating and visually impressive phenomenon of luminescence thermochromism: exposed to long-wave UV light, the crystalline solid shows a bright yellow fluorescence at room temperature and an equally intense blue-violet fluorescence when cooled in liquid nitrogen. The procedure was also extended to several other pyridine ligands to allow students to synthesize different clusters and compare their photophysical behavior.

KEYWORDS: Upper-Division Undergraduate, Inorganic Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Coordination Compounds, Fluorescence Spectroscopy, Physical Properties, Synthesis, Transition Elements, UV–Vis Spectroscopy



Luminescence thermochromism is the ability of a substance to vary the color of its fluorescence emission due to a change in temperature. The term was coined by H. D. Hardt¹ who discovered such phenomenon in a compound of Cu(I), iodide, and pyridine in a ratio of 1:1:1, which was later found to be a tetranuclear cubane-like cluster (Figure 1).² It is an off-white crystalline material that, upon exposure to long-wave UV light, exhibits a strong yellow fluorescence at room temperature and an equally intense violet fluorescence when cooled in liquid nitrogen.

In this experiment, Hardt's synthesis of the complex was adapted and extended to a few substituted pyridines. The

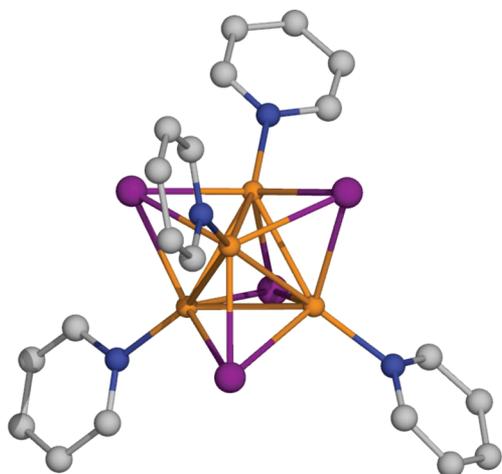


Figure 1. Structure of the $\text{Cu}_4\text{I}_4\text{py}_4$ cluster, redrawn from the crystal X-ray data: Cu orange, I purple, N blue, and C gray.

procedure has been successfully introduced in our undergraduate inorganic chemistry laboratory course, giving students an opportunity to synthesize a few of these unusual complexes, to become familiar with their unconventional structure and to observe the fascinating phenomenon of fluorescence thermochromism.

The literature provides several attractive examples of laboratory experiments devoted to the synthesis of transition-metal complexes that exhibit the “conventional” thermochromism in the solid state.³ However, the latter behavior is based on the temperature-dependent shift of the same band in the emission spectrum, often due to a change in geometry, which is a totally different physical phenomenon compared to that discussed in this experiment. Because the activity hereby presented is very short, it turned out to be particularly valuable as a complement to a lab session dedicated to the synthesis of one of these classical thermochromic complexes, based on Cu(II).^{3,4} Observing the two apparently similar effects and contrasting the very different physical backgrounds from which they are originated, students were stimulated to appreciate the difference, allowing for a more articulated discussion of the subject of thermochromism in the classroom.

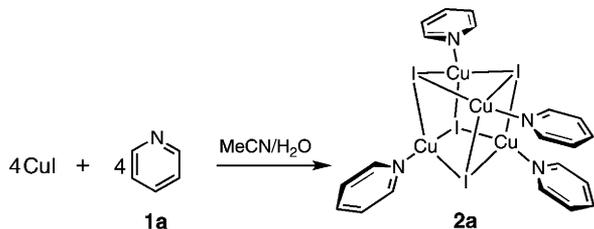
In our experience, both students and teachers are remarkably impressed the first time they witness the demonstration of this behavior, mainly because it is so neat and delightful. According to the criteria stated by R. W. Ramette, who wrote in this *Journal* on the amount of charm involved in chemical demonstrations and set down the “laws of charmdynamics”,⁵ this can be classified among the most “exocharmic” chemical demonstrations students are ever likely to see.

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EXPERIMENTAL OVERVIEW

The procedure was split into three sections: (i) preparation of CuI, (ii) synthesis of the clusters (Scheme 1), and (iii)

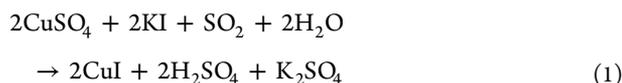
Scheme 1. Synthesis of the Tetranuclear $\text{Cu}_4\text{I}_4\text{py}_4$ Cluster **2a**



demonstration of luminescence thermochromism. Hardt's procedure¹ was readily scaled down and modified so that students could prepare their own CuI, starting with inexpensive copper(II) sulfate. Commercial CuI can be used for a shorter version of the experiment, starting with the synthesis of the clusters (see the Supporting Information).

Preparation of CuI

The preparation of CuI (eq 1) was adapted from a standard inorganic laboratory manual.⁶ CuSO_4 was dissolved in water, reduced with a slight excess of acidified sulfite solution, and copper(I) iodide was precipitated upon addition of a solution of potassium iodide.



CuI was then separated by vacuum filtration and washed twice with water. The yield is almost quantitative, if care is taken to transfer all of the solid. Drying of the product was unnecessary for the following step. The reaction could also be carried out in a disposable 50 mL polypropylene centrifuge tube, centrifuging the suspension to separate the solid, resuspending it in water, and separating it with another centrifugation step.

Synthesis of the Clusters

Damp CuI from the first step (or commercial CuI) and potassium iodide were dissolved in acetonitrile with a small amount of ascorbic acid added to prevent the oxidation of Cu(I) to Cu(II). A solution of pyridine (**1a**) in acetonitrile was added, turning the clear yellow solution milky, due to the incipient formation of the insoluble cluster (Scheme 1). Water was added to complete the precipitation of the compound, which was vacuum filtered and washed with water. If the alternative procedure using a disposable centrifuge tube was followed, an additional advantage was that the synthesis of the complex could be conveniently carried out in the same tube in which CuI was prepared: acetonitrile and reagents were added and the solid was again separated and washed in two centrifugation steps.

This very simple synthesis was successfully extended to four analogues of the title compound (**2b–2e**) employing substituted pyridines **1b–1e** (Figure 2). Several other substituted pyridines have been tested by the authors and judged unsuitable for the experiment (see the Supporting Information).

Demonstration of Luminescence Thermochromism

The last part of the experiment dealt with the demonstration of luminescence thermochromism. A spatula-tip sample of

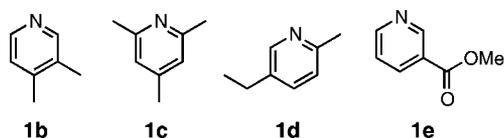


Figure 2. Substituted pyridines used for the synthesis of clusters **2b–2e**.

compound **2a** was spread on a piece of black cardboard (or nonbleached filter paper). Upon exposure to long-wave UV light, a bright yellow fluorescence was apparent. After dipping the strip in liquid nitrogen for 10–20 s, the fluorescence was bright violet. The spot gradually changed to red-orange and then back to yellow as the solid warmed to room temperature (Figure 3). Compounds **2b–2e** showed different color

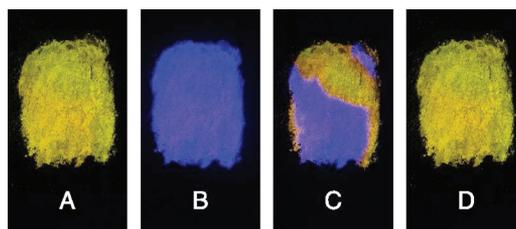


Figure 3. Luminescence thermochromism of compound **2a** exposed to UV light ($\lambda_{\text{max}} = 366 \text{ nm}$): (A) 25 °C; (B) –196 °C; (C) warming back to room temperature, and (D) 25 °C.

Table 1. Students' Qualitative Descriptions of the Color and Relative Brightness of the Clusters

Entry	Cluster	Pyridine Ring Substituents	Fluorescence Color ($\lambda_{\text{max}} = 366 \text{ nm}$)		Brightness ^a	Yield ^b (%)
			25 °C	–196 °C		
1	2a	H	yellow	violet	+++	93
2	2b	3,4-diMe	red	violet	+	92
3	2c	2,4,6-triMe	green	lime green	++	78
4	2d	2-Me-5-Et	aqua green	blue	++	89
5	2e	3-COOMe	none	green	+++	74

^aRelative brightness (+++ = most bright, ++ = bright, + = least bright).

^bAverage isolated yield obtained by students ($\pm 5\%$), calculated from CuSO_4 .

variations (Table 1), although somewhat less bright and less impressive than the parent compound (Figure 4). The color transition was very sharp, and, provided that the spot was large enough and the support was thick, a color-changing front could often be seen propagating through the surface of the material, starting from the outer edges where the solid warmed faster (Figure 3C, see the Supporting Information for a videoclip).

A standard TLC-viewing lamp worked perfectly as a source of long-wave UV light, as the sample spread on paper could be very small. Nevertheless, if desired, much larger samples could be prepared and displayed to the students in dimmed light, using a large Wood's lamp (as those used in discos, $\lambda_{\text{max}} \sim 366 \text{ nm}$) suspended with clamps above a black background (e.g., a cloth, see Figure S1 in the Supporting Information).

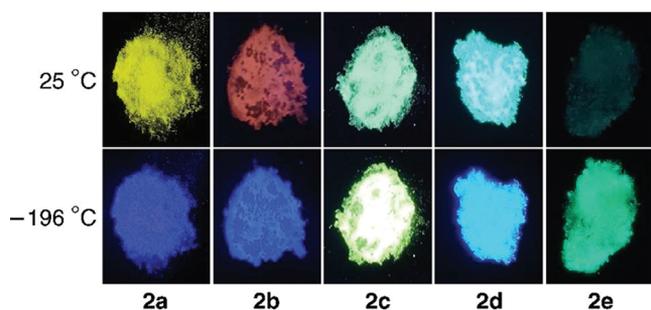


Figure 4. Comparison of the luminescence thermochromism of clusters **2a–2e**.

HAZARDS

Copper salts are harmful and dangerous for the environment. The waste aqueous and organic solutions should be collected in suitable waste containers and disposed of properly. Acetonitrile and pyridine are highly flammable. Concentrated sulfuric acid is corrosive and can cause burns. The preparation should be carried out under a fumehood since acetonitrile, pyridine, and 3,4-lutidine are toxic, and a small amount of SO_2 is evolved in the preparation of CuI . Gloves and goggles should be worn at all times and the MSDS of all chemicals used should be read beforehand. Liquid nitrogen can cause frostbite and must be handled in a well-ventilated room.

DISCUSSION

This experiment was performed during an advanced inorganic chemistry laboratory course by 16 pairs of students: each group was given instructions to synthesize both the simplest cluster (**2a**) and one of the analogues (**2b–2e**). In this way, each student performed one synthesis, and within each group of two students it was always possible to compare the properties of the analogue with the parent compound **2a**. The whole procedure described can be completed in less than 1 h, except the weighing of the dry material and calculation of the yield, which should be performed in the next lab session.

Clusters such as **2a** possess a distorted tetranuclear structure whose core is a tetrahedron of copper atoms, each face of which is capped by an iodide, forming a larger I_4 tetrahedron. The two intersected tetrahedra form an irregular cubane-like structure (Figure 1).² Pyridine ligands are linked to the apices of the Cu_4 tetrahedron so that each copper atom (d^{10} electronic configuration) is coordinated to three iodides and a pyridine nitrogen.

The solid-state emission spectra of clusters such as **2a** display two distinct bands: a very intense lower-energy (LE) band and an extremely weak higher-energy (HE) band (Figure 5). The marked temperature dependence of the apparent color of the luminescence of these clusters does not arise from a shift in the emission maximum, $\lambda_{\text{max}}^{\text{em}}$, but from a significant change in the relative intensities of the two bands. At room temperature, the HE band is barely detectable and the LE band is largely dominant, whereas below 80 K, the HE band overcomes the other.⁷ For the sake of strictness, it must be mentioned that a shift in $\lambda_{\text{max}}^{\text{em}}$ can actually be observed for the LE band (580 nm at 25 °C, 619 nm at -196 °C, Figure 5), but it is too small to justify any dramatic change in color.

The assignment of the bands and the explanation of the luminescence thermochromism behavior have been considerably challenging tasks, accomplished only after substantial

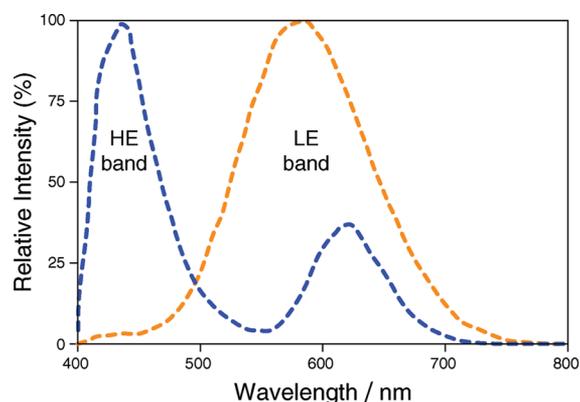


Figure 5. Normalized emission spectrum of compound **2a** at 25 °C (orange line) and at -196 °C (blue line). Data taken from ref 7.

experimental and computational work.^{8,9} The HE band is related to a triplet halide-to-ligand charge transfer ($^3\text{XLCT}$) excited state,¹⁰ whereas the LE band has been proven to originate from a triplet “cluster-centered” (^3CC) excited state, a combination of iodide-to-copper charge transfer and $d-s$ transitions.^{7,11} Both excited states have been characterized by time-dependent density functional theory studies.^{9c} A simplified energy-level diagram is given in Figure 6.¹² The predominance

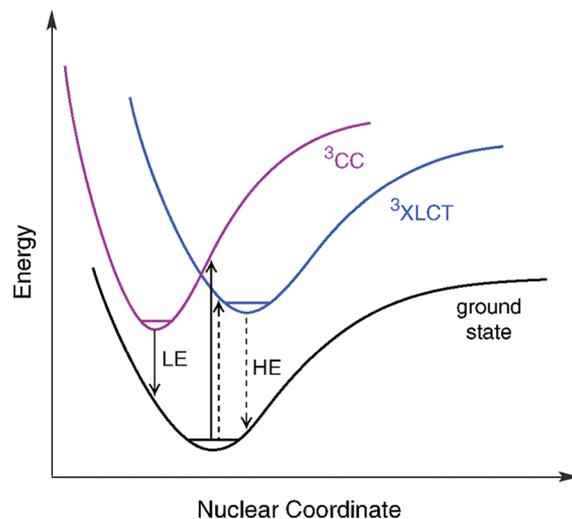


Figure 6. Simplified potential energy surface for cluster **2a**.

of one of the bands over the other at different temperatures (i.e., the luminescence thermochromism effect) is ultimately due to the variation in size of the inner Cu_4 core, originated by the closer crystal packing of the pyridine ligands: having partial ionic bonding character, the inner Cu_4I_4 framework can deform flexibly according to the “positive” or “negative” pressure exerted by the ligand packing at different temperatures, thereby favoring more one or the other excited states geometries, as it has recently been demonstrated.^{9c,13}

This lab experiment lends itself much more easily to an eye-catching display than to a strongly theory-oriented discussion, especially in an undergraduate course setting. Nonetheless, several interesting applications of the rich photophysical behavior of these complexes have been found, for example, the determination of volatile organic compounds (VOC) in air, exploiting the reversible change in the emission spectra

resulting from exposing these clusters to organic solvent vapors.^{8,14}

■ ASSOCIATED CONTENT

📄 Supporting Information

Videoclip of the demonstration of luminescence thermochromism of **2a**, detailed laboratory procedure for students, instructor's notes, additional pictures. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Hardt, H. D.; Pierre, A. *Z. Anorg. Allg. Chem.* **1973**, *402*, 107–112.
- (2) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 2153–2156.
- (3) (a) Willett, R. D. *J. Chem. Educ.* **1983**, *60*, 355. (b) Van Oort, M. J. M. *J. Chem. Educ.* **1988**, *65*, 84. (c) Choi, S.; Larrabee, J. A. *J. Chem. Educ.* **1989**, *66*, 774–776. (d) Hughes, J. G. *J. Chem. Educ.* **1998**, *75*, 57. (e) Changyun, C.; Zhihua, Z.; Yiming, Z.; Jiangyan, D. *J. Chem. Educ.* **2000**, *77*, 1206–1207. (f) Bukleski, M.; Petruševski, V. M. *J. Chem. Educ.* **2009**, *86*, 30. (g) Cui, A.-L.; Chen, X.; Sun, L.; Wei, J.-Z.; Yang, J.; Kou, H.-Z. *J. Chem. Educ.* **2011**, *88*, 311–312.
- (4) Fabbri, L.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1974**, *13*, 3019–3021.
- (5) Ramette, R. W. *J. Chem. Educ.* **1980**, *57*, 68–69.
- (6) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press, Inc.: London, 1963; Vol. 2, pp 1007–1008.
- (7) Kyle, K. R.; Ryu, C. K.; DiBenedetto, J. A.; Ford, P. C. *J. Am. Chem. Soc.* **1991**, *113*, 2954–2965.
- (8) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625–3647.
- (9) (a) Vitale, M.; Palke, W. E.; Ford, P. C. *J. Phys. Chem.* **1992**, *96*, 8329–8336. (b) Vitale, M.; Ryu, C. K.; Palke, W. E.; Ford, P. C. *Inorg. Chem.* **1994**, *33*, 561–566. (c) De Angelis, F.; Fantacci, S.; Sgamellotti, A.; Cariati, E.; Ugo, R.; Ford, P. C. *Inorg. Chem.* **2006**, *45*, 10576–10584.
- (10) Radjaipour, M.; Oelkrug, D. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 159–163.
- (11) (a) Hardt, H. D.; Pierre, A. *Inorg. Chim. Acta* **1977**, *25*, L59–L60. (b) Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1986**, *108*, 7211–7212. (c) Kyle, K. R.; Palke, W. E.; Ford, P. C. *Coord. Chem. Rev.* **1990**, *97*, 35–46.
- (12) Ford, P. C.; Vogler, A. *Acc. Chem. Res.* **1993**, *26*, 220–226.
- (13) Kitagawa, H.; Ozawa, Y.; Toriumi, K. *Chem. Commun.* **2010**, 46, 6302–6304.
- (14) Cariati, E.; Bourassa, J.; Ford, P. C. *Chem. Commun.* **1998**, 1623–1624.