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Cuprous Iodide Pseudo-polymorphs Based on Imidazole Ligand and Their Luminescence Thermochromism

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ABSTRACT: Two cuprous iodide pseudo-polymorphs, formulated as $[(Cu_4I_4)(MBI)_2]_{\infty}$ (MBI=1,1'-methylene-bis(imidazole)) with irregular cubane-like Cu₄I₄ cluster as tetrahedrally coordinated secondary building unit and imidazole derivative as bridging ligand, have been synthesized and characterized by single-crystal X-ray diffraction analysis. Both of two compounds only exhibited single broad low-energy cluster-centered (³CC) triplet emission band between room temperature and 77 K. Of particular interest, these two Cu₄I₄-imidazole pseudo-polymorphs still displayed thermochromic luminescence originating from red shift of such tunable single cluster-centered triplet emission, being different from that observed in the previously reported Cu₄I₄-pyridine system by balancing temperature-dependent multiple emissions (high-energy and low-energy) derived from their energetically distinct triplet states.

INTRODUCTION

Complexes based on cuprous iodide are currently at the forefront of coordination chemistry and crystal engineering research because of the quest for active materials in optoelectronics.¹⁻⁶ Such research interests mainly stem from the increasing demand for more affordable complexes in preference to other luminescent metal complexes based on precious (i.e. the platinum group) and rare-earth metals, which are often quite expensive and environmentally problematic.⁷⁻⁹ In fact, CuI-based complexes or coordination polymers possess several following advantages, which further stress their research interests and potential or practical applications as luminescent materials: 1) they have a large variety of coordination geometries, arising from many possible combinations of coordination numbers available for Cu(I) (two, three and four) and geometries adopted by the iodides (from terminal to μ_2 - and up to μ_8 -bridging);¹⁰⁻¹⁵ 2) they present different luminescent levels, which can be of a ligand centred, charge transfer in the case of polynuclear compounds, or even metal-centred nature:^{5,16,17} 3) most of cuprous iodide complexes are characterized by a remarkably high photoluminescent quantum yield in solid state;¹⁸ 4) the reagents are cheap and it is relatively easy to obtain the final products.^{7,11}

Photoluminescence (PL) tunability is always the focus of most concern for CuI-based complexes. They are generally highly luminescent at the room temperature, and the emissions are strikingly sensitive to the temperature.^{6,11,19} External stimulus (such as temperature, pH, solvent vapor, and mechanical grinding) can tune photophysical properties by balancing stimuli-responsive multiple emissions derived from their energetically distinct triplet states in CuI-based complexes.²⁰⁻²³ For example, the typical Cu₄I₄-pyridine system shows two unique triplet emissions at room temperature and at 77 K, respectively.¹⁷ The low-energy (LE) emission band at around 550-650 nm is dominant at room temperature, attributed to cluster-centered (³CC) triplet emission consisting of a mixture of iodide-to-copper charge transfer (³XMCT) and metal d \rightarrow s, p transitions. The high-energy (HE) emission band in the blue region (400-450 nm) is dominant at 77 K, assigned to iodide-to-ligand charge

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transfer (³XLCT) and metal-to-ligand charge transfer (³MLCT) transitions. The PL intensity ratio of LE and HE band at different temperature could effectively control the emission color of CuI-based complexes. In addition, it is generally accepted that terminal or bridging ligands with variable substituted groups play vital roles in controlling the size and geometry of CuI-based clusters and their assembled structures, which further tune their luminescent properties by altering cuprophilic interaction owing to its sensitivity with respect to distortions within the Cu₄I₄ cluster.^{7,16,18,22}

In most of previous studies on cuprous iodide coordination compounds, ligands were focused on pyridine, ^{17,24,25} alkylphosphine^{2,20,22} or triethylenediamine²⁶⁻³¹. Few investigations have been performed on imidazole and its derivatives as terminal or bridging ligand.^{22,23} Whether could the CuI-imidazole complexes show similar thermochromism luminescence with CuI-pyridine system? In fact, although the thermal stimuli-responsive behavior of CuI clusters is fairly studied through various examples, their emission shifts, colors, and shift directions are still unpredictable. In this paper, we aimfully synthesized Cu₄I₄ cluster-based structures with imidazole derivative as terminal and bridging ligands to probe their thermochromic luminescence. The current work for the first time reveals that Cu₄I₄-imidazole system only displays a single broad ³CC excited state emission band, which still generates remarkable thermochromic luminescence realized through dramatic red shift of the single broad cluster-centered (³CC) triplet emission.

EXPERIMENTAL SECTION

General Procedures. Copper (I) iodide (CuI, AR, 99.5%), potassium iodide (KI, AR, 99%), 1-methylimidazole (C₄N₂H₆, AR 99.5%), N, N-dimethylformamide (DMF, AR, 95%), N, N- dimethylacetamide (DMA, AR, 99%), acetonitrile (CH₃CN, AR, 99%) were purchased from Aladdin Industrial, Inc. All chemicals were used as received without further purification. Powder X-ray diffraction (XRD) measurements on the purity of samples were carried out with a Bruker D2 phaser diffractometer using Cu-K α (λ =1.54056 Å) radiation operated at 30 kV and 10 mA (Figure S1). The

PL spectra were collected on a HORIBA scientific Fluorolog-3 steady state and time-resolved fluorescence spectrophotometer equipped with a 450 W xenon lamp. Single crystal X-ray diffraction (SCXRD) data were performed on Agilent diffractometers at room temperature (295 K) with graphite monochromated Mo K α (λ =0.71073 Å) radiation. The structures were solved by direct methods using SHELXS-97 and the refinements against all reflections of the compounds were performed using SHELXL-97.

Synthesis of ligand 1, 1'-methylene bis(imidazole) (MBI). NaOH (17.98 g, 0.4495 mol), imidazole (4.750 g, 0.0698 mol), tetraethylammonium bromide (440 mg, 2.095 mmol), H₂O (25 g, 1.389 mol), dichloromethane (100 mL) were mixed in a 250 mL round-bottomed flask. The mixture was refluxed for 24 hours under 45 °C, then white needle-like crystals were obtained with the yield of 3.254 g.

Synthesis of $[(Cu_4I_4)(MBI)_2]_{\infty}$ (Guest) (1). CuI (0.5929 mmol, 0.1152 g), MBI (0.1973 mmol, 0.0292 g) were mixed in the presence of acetonitrile (3.0 mL) and DMA (4.0 mL). The mixture was stirred at room temperature for 10 min to give precipitate, and then this heterogeneous mixture was placed in a 15 mL Teflon-lined steel autoclave and heated to 150 °C for three days. The resulting colorless block crystals were obtained by filtration, washed by acetonitrile, and air-dried for the subsequent measurements.

Synthesis of $[(Cu_4I_4)(MBI)_2]_{\infty} \cdot (C_2H_3N) \cdot 8(H_2O)$ (2). A solution of CuI (0.016 g, 0.084 mmol) in saturated potassium iodide (KI) solution (2 mL) was mixed with a solution of MBI (0.028 g, 0.188 mmol) in acetonitrile (2 mL) and H₂O (1 mL). Then this mixture was placed in a 15 mL Teflon-lined steel autoclave and heated to 150 °C for five days. The resulting colorless needlelike crystals were obtained by filtration, washed by ethanol, and air-dried.

Synthesis of $[(Cu_4I_4)(MIM)_4]$ (3). CuI (0.209 mmol, 0.040 g), 1-methylimidazole (MIM, 0.026 mmol, 2.13 mg) were combined together in the presence of acetonitrile (0.6 g) and ethanol (1.6 g). Then the mixture was placed in a 3 mL glass tube and

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heated to 120 °C for three days. The resulting colorless rod-like crystals were obtained by filtration, washed by ethanol, and air-dried.

RESULTS AND DISCUSSIONS



Figure 1. (a) Four-coordinated Cu_4I_4 cubane unit simplified into a tetrahedron in compounds 1 and 2. (b) Tetrahedrally coordination mode of Cu_4I_4 cluster by linear bridging ligand. (c) Two-dimensional layered structure in compound 1. (d) Three-dimensional single net in compound 2. I, purple ball; Cu, light blue ball; C, gray ball; N, blue ball; and Cu_4I_4 cluster was represented by green tetrahedron.

Single-crystal X-ray diffraction analysis revealed that compound 1 crystallizes in monoclinic system with $P2_1/c$ space group, and the crystallographically asymmetric unit consists of four independent Cu(I) ions, four iodide ions, and two MBI ligand moieties (Figure S2 and Table S1). Each Cu(I) adopts tetrahedral coordination geometry bonded to three iodide ions and one nitrogen atom from MBI ligand. The Cu–I bond lengths locate in the range of 2.677(4) and 2.758(3) Å and I–Cu–I bond

angles are in the range of 109.477(3) and 117.296(3) °. The Cu···Cu distances range from 2.634(6) to 2.750(1) Å, being shorter than the sum of Vander Waals radii of Cu(I) (2.8 Å) and implying strong metal-metal cuprophilic interaction in the cluster.^{20,22} Compound **1** possesses two-dimensional layered (4, 4)-connected coordination network constructed by imidazole derivative (MBI) as linear bridging ligand and Cu₄I₄ cubane cluster as secondary building unit. Each Cu₄I₄ unit is bridged by four organic ligands MBI to form a two dimensional structure (Figure1a-1c).

Compound 2 crystallizes in hexagonal system with R3c space group, and the crystallographically asymmetric unit also consists of four independent copper (I) ions, four iodide ions, and two MBI ligands (Figure S3). Similar to copper (I) coordination environment occurring in compound 1, each Cu in compound 2 also tetrahedrally bonds to three iodide ions and one nitrogen donor from MBI ligand. Cu-I bond lengths locate in the range of 2.641(6) and 2.801(4) Å and I-Cu-I bond angles are in the range of 109.316(2) and 117.337(2) °. The Cu…Cu distances range from 2.646(8) to 2.721(4) Å, being less than the sum of the Vander Waals radii of Cu(I) (2.8 Å) and implying strong metal-metal cuprophilic interactions. Like compound 1, each Cu_4I_4 cubic unit in compound **2** is connected to four ligands to form four-connected network. However, due to different distortion configuration of flexible MBI ligand, compound 2 adopts two-fold interpenetrated 3D network (Figure 1d and Figure S4). Topological analysis shows that single network in compound 2 possesses an unprecedented four-connected self-penetrating topological net with short and long Schläfli symbol of 86 and 87.87.87.87.86.86, respectively, when treating Cu₄I₄ as 4-connected node and MBI ligand as linear linker (Figure S5). To better understand the structure of compound 2, its network can be parsed in different way, as shown in Figure 2. The Cu₄I₄ cubane unit with four MBI ligands (Figure 2a) could form single helix (Figure 2b and 2d) and double helix (Figure 2c and 2e) along *c*-axis. The adjacent single helix and double helix fuse together to form 3D network with trigonal symmetry (Figure 2f).

Although compounds 1 and 2 are pseudo-polymorph with the same Cu_4I_4 cubane unit and bridging ligand, the different distortion configuration of flexible MBI ligand still results in subtle variation in the Cu–I bond length and I–Cu–I bond angle (Table S2 and S3). To further probe the effect of imidazole ligand on the configuration of Cu_4I_4 cluster, we purposely synthesized compound **3**, formulated as $[(Cu_4I_4)(MIM)_4]_{\infty}$, consisting of discrete Cu_4I_4 cluster with 1-methyl imidazole (MIM) as terminal ligand (Figure S6). The Cu–I bond lengths, I–Cu–I bond angles as well as Cu…Cu distances are all in the rational range (Table S4), being similar with that observed in compounds **1** and **2**.



Figure 2. Structure analysis of compound **2**. (a) Cu_4I_4 cluster bonded to four MBI ligands. (b, d) one-dimensional helical structure viewed from *b*-axis and *c*-axis, respectively. (c, e) double helical structure viewed from *b*-axis and *c*-axis, respectively. (f) single network in two-fold interpenetrated three-dimensional framework. (g) two-fold interpenetrated three-dimensional framework. I, purple ball; Cu, light blue ball; C, gray ball; N, blue ball; and Cu_4I_4 cluster was represented by green tetrahedron.

Emission spectra of compounds 1-3 at room temperature, as shown in the Figure 3, all display a single broad low-energy emission band centered at 600 nm for 1 (λ_{ex} = 315 nm), 645 nm for 2 (λ_{ex} = 350 nm), and 636 nm for 3 (λ_{ex} = 350 nm) in agreement with the observed orange-red light. Obviously, the origin of the emission signatures in 1-3 at 298 K can be attributed to ³CC-transitions, as the Cu···Cu distances in them do not exceed 2.80 Å. Cu···Cu distance is the decisive factor in control of fluorescence properties of CuI-based compounds. In addition, the internal quantum yields of the compounds were determined to be 1.72%, 1.71%, and 5.85% for 1, 2, and 3, respectively (Table S5).



Figure 3. Photoluminescent excitation and emission spectra of compounds 1, 2 and 3 at room temperature.



Figure 4. Top: Temperature-dependent excitation and emission spectra of compound 1 from 10-298 K in the solid state (λ_{ex} =315 nm). Down: Photos of sample 1 and 1* (ground) under ambient light and UV light.

То investigate the thermochromic properties of compounds 1-3, temperature-dependent solid-state excitation and emission spectra from room temperature down to 10 K were recorded, as shown in Figure 4-6. For compound 1, with the temperature decreasing to 150 K, the LE emission intensity increases with emission peak slightly red-shifted. However, when below 98 K, the LE emission continues red shifting and begins to weaken. At the range of 68 K to 10 K, LE band at around 648 nm is still dominated, being accompanied by a new weak emission band at approximate 510 nm. The new emission band is not in blue light region, so it cannot be attributed to the imidazole-involved high-energy excited state, such as

iodine-to-ligand charge-transfer (XLCT) and metal-to-imidazole charge-transfer (MLCT). This weak green emission is possibly assigned as originating from a ligand-to-copper transition(LMCT).¹⁷ For compound **2**, with the temperature decreasing from room temperature to 10 K, the LE emission band is progressively red-shifted from 645 to 685 nm and accompanied with a shoulder at 550 nm. All the same, no obvious HE emission band at around 400-500 nm is observed during the temperature decreasing. This dramatic red shift of about 40 nm makes it easy to detect the color change by naked eye (Figure 5). Similar to compound **2**, upon lowering the temperature to 10 K, luminescence in compound **3** is also dominated by cluster-centered (³CC) emission. The single broad LE emission band is marginally red-shifted to 668 nm, which is accompanied by widening of the bandwidth.



Figure 5. Top: Temperature-dependent excitation and emission spectra of compound 2 from 10-298 K in the solid state (λ_{ex} =370 nm). Down: photos of compounds 2 and 2* (ground) under ambient light and UV light.



Figure6. Top: Temperature-dependent excitation and emission spectra of compound **3** from 10-298 K in the solid state (λ_{ex} =370 nm). Down: photos of compound **3** under ambient light and UV light.

Above data show that the origin of thermochromic luminescence in **1-3** is originated only from a single broad tunable LE emission, being quite different from typical Cu₄I₄(pyridine)₄ cluster-based compounds where relative intensities of LE (³CC) and HE (XLCT) emissions at different temperature are responsible for thermochromic luminescence. The absolute predomination of LE emission at room

temperature and the absence of HE emission at low temperature in compounds 1-3 possibly are the synergistic effects coming from Cu_4I_4 cluster with strong cuprophilic interaction in it and imidazole ligand with unmatchable π^* molecular orbital for ligand-involved triplet transition. As displayed in structural data, the relatively flexible bridging ligand MBI and terminal ligand MIM cannot cause the serious distortion of Cu_4I_4 cluster. The Cu···Cu distances in compounds 1-3 is in the narrow range and always less than the sum of the Vander Waals radii of Cu(I) (2.8 Å). Only strong stimulus, such as pretty low temperature, can cause a subtle change in the Cu···Cu distances, which further results in the large positive Stoke's shift in its PL spectrum. Weak stimulus, such as mechanical attrition treatment, can not lead to further alteration in the Cu···Cu distances. Thus, compared with the unground sample, the similar emission color for ground sample is observed, as shown in Figure 4-6.

■ CONCLUSION

pseudo-polymorphs In summary, two cuprous iodide with 1,1'-methylene-bis(imidazole) as bridging ligand were successfully synthesized and structurally characterized by single-crystal X-ray diffraction analysis. Although compounds 1 and 2 have the same Cu_4I_4 cubane unit and bridging ligand, they exhibited totally different topological network due to different distortion configuration of ligand. Different from compound 1 with a typical 2D (4.4) net, compound 2 displayed unprecedented 3D two-fold interpenetrated net with self-penetrating 4-connected topological framework. The average Cu...Cu distances in those compounds are shorter than the sum of the Vander Waals radii of copper, so compounds 1 and 2 only exhibited a single broad low-energy cluster-centered $({}^{3}CC)$ triplet emission band at room temperature and 77 K. Even so, these two pseudo-polymorphs still displayed consistent thermochromic luminescence originating from the single cluster-centered triplet emission, which is red-shifted upon lowering temperature. Current study indicates that organic ligand bonded to Cu_4I_4 cluster can effectively control thermochromic behavior. This work promotes us to

carry out further investigation on other type of organic ligands for enriching luminescent thermochromism behavior from CuI-ligand systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:10.1021/??????

Crystallographic parameters, experimental and calculated powder XPD diffraction diagrams (PDF)

Single crystal X-ray diffraction crystallographic file (CCDC 1445345-1445347) (CIF)

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Notes

The authors declare no competing financial interest.

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