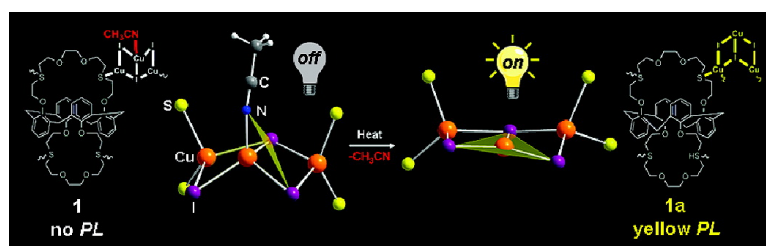


Communication

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Temperature-Dependent 3-D CuI Coordination Polymers of Calix[4]-*bis*-dithiacrown: Crystal-to-Crystal Transformation and Photoluminescence Change on Coordinated Solvent Removal

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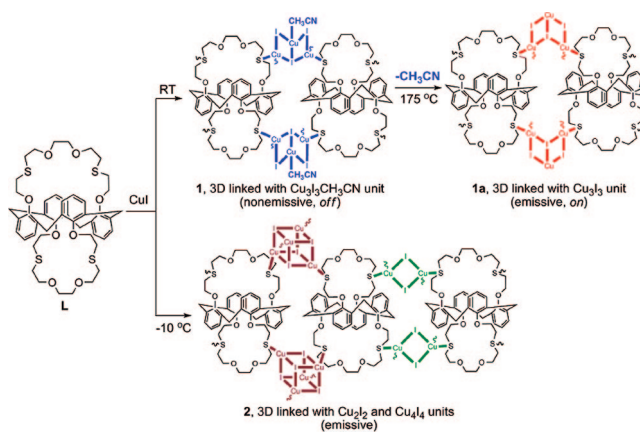
The recent upsurge in metal–organic frameworks (MOFs) based on d¹⁰ metal ions reflects their application in the areas of sensors and luminescent materials.¹ In particular, supramolecular systems showing single-crystal-to-single-crystal transformations associated with physical property changes have important implications for use as nanomaterials; however, the number of reported examples of these types is quite limited.²

Self-assembly processes involving copper(I) halides and multi-dentate ligands often lead to different types of MOFs containing structural motifs such as rhomboid dimers, cubane tetramers, and hexagonal prisms because of small energy differences between polymorphs. Thus, the formation of the different polymorphs depends on the synthetic conditions employed.³ Notably, such copper(I) halide clusters not only show structural variety but also often exhibit emission behavior that can vary markedly with the structure adopted.

Recently, we have reported calix[4]-*bis*-thiacrown based endo-coordinated disilver(I) complexes and exo-coordinated 3-D networks connected by the CuI-based clusters.⁴ The continuing interest in calix[4]-*bis*-thiacrowns and the relatively little research on their copper(I) coordination chemistry prompted us to investigate the possibility of fabricating new diverse structures of these types. Of particular interest was to probe the relationship between cuprophilic interactions in these systems and their photophysical properties. In this work, we were able to isolate two types of new 3-D CuI networks based on **L**, both syntheses being temperature-dependent (Scheme 1). An exciting feature of the results is the influence that the coordinated solvent has on the single-crystal-to-single-crystal transformation from tetrahedral (**1**) to trigonal (**1a**) coordination geometry, resulting in solvato-photoluminescence “off-on” behavior. Another intriguing result is the formation of alternating Cu₄L₄ and Cu₂I₂ units linked by **L** units in **2**.

L was synthesized as described previously by us.^{4a} At room temperature, the reaction of **L** in dichloromethane with 2 equiv of CuI in acetonitrile gave colorless single crystals exhibiting a 3-D polymeric array of formula $\{[(\text{Cu}_3\text{I}_3)\text{L}(\text{CH}_3\text{CN})](\text{CH}_2\text{Cl}_2)(2\text{H}_2\text{O})\}_n$ (**1**) [Figure 1a]. The overall geometry of **1** can be described as an interconnected layer where each **L** is linked by a three-runged ladder-type unit,⁵ Cu₃(μ₃-I)(μ-I)₂. Two Cu₃I₃ units bridge two **L** units via Cu–S bonds to yield a 2-D layer; then the adjacent 2-D layers are bridged via Cu–S bonds to form the 3-D framework (Supporting Information, Figure S2). Notably, the Cu2 atom is tetrahedrally coordinated by three I atoms and one acetonitrile; this is the first example of such a coordination sphere. No photoluminescence was observed for **1**.

Scheme 1



When crystal **1** was heated at 175 °C, the coordinated acetonitrile molecules were completely removed to yield a desolvated colorless solid of type $\{[(\text{Cu}_3\text{I}_3)\text{L}](0.5\text{H}_2\text{O})\}_n$ (**1a**). Thermogravimetric analysis (TGA) performed on **1** shows a sharp mass loss of 2.51% at around 175 °C, corresponding to the loss of coordinated acetonitrile (expected value 2.53%) (Figure S3). The IR spectrum of **1a** obtained after heating at 175 °C also confirms the removal of the acetonitrile by disappearance of absorption peaks at ca. 2300 cm⁻¹ (ν_{CN}) (Figure S4).

Since the single crystallinity was retained during the removal process of the coordinated solvent by heating, we were able to obtain the crystal structure of the solvent-free product **1a** successfully [Figure 1b]. The overall 3-D network structure of **1a** (Figure S6) is similar to that of **1** (Figure S2). The cell parameters, including the cell volume of **1a**, changed slightly compared with those of **1** (Table S1). Significant rearrangements of the molecular components in the crystal lattice were found to occur upon removal of the acetonitrile coordinated to the Cu2 atom in **1**. The three-runged ladder-type Cu₃I₃ units before (**1**) and after (**1a**) removal of the coordinated CH₃CN are compared [Figure 1c]. Importantly, the removal of CH₃CN from the Cu2 atom led to the coordination geometry around the Cu2 atom changing from tetrahedral (bond angles in **1**: 107.4–110.1°) to trigonal planar (bond angles in **1a**: 118.0–122.3°). Upon removal of the coordinated-acetonitrile, it is noteworthy that the folded conformation of the three-runged ladder-type Cu₃I₃ unit in **1** becomes flattened and is associated with a movement of Cu2 by ca. 0.9 Å [see Figure 1c]. As might be expected, reducing the coordination number of Cu2 from four to three causes the bond lengths around Cu2 to contract. The Cu⋯Cu distances are also shortened (Table S2); the Cu⋯Cu distances in **1** (Cu1⋯Cu2, 2.921; Cu2⋯Cu3, 2.851 Å) are longer than the van der Waals radii (2.80 Å), indicating no cuprophilic interaction.

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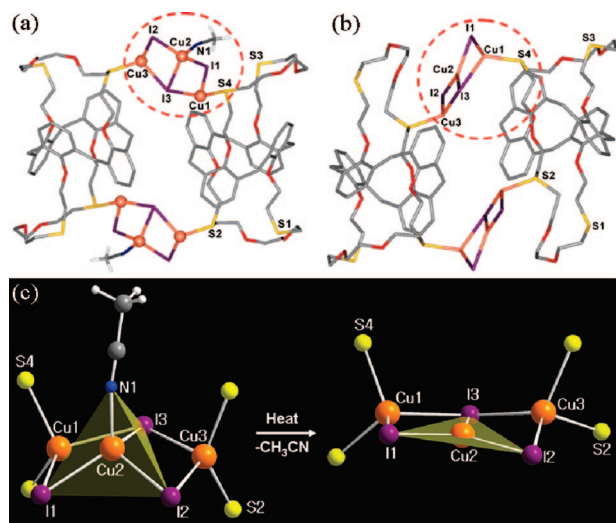


Figure 1. X-ray crystal structures of (a) **1**, $\{[(\text{Cu}_3\text{I}_3)\text{L}(\text{CH}_3\text{CN})](\text{CH}_2\text{Cl}_2)(2\text{H}_2\text{O})\}_n$ and (b) **1a**, $\{[(\text{Cu}_3\text{I}_3)\text{L}](0.5\text{H}_2\text{O})\}_n$; (c) single-crystal-to-single-crystal transformation of three-runged ladder-type Cu_3I_3 unit from **1** (left, tetrahedral) to **1a** (right, trigonal planar) by removal of coordinated acetonitrile.

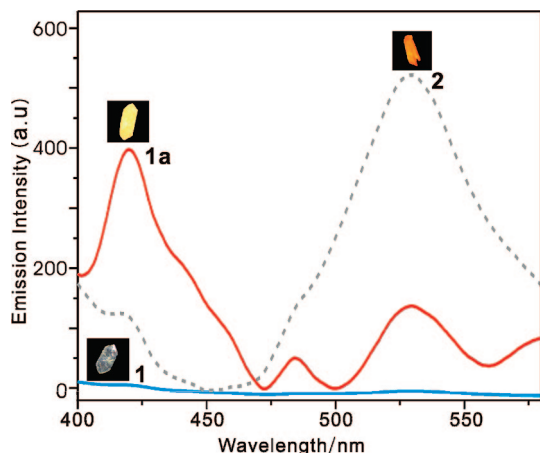


Figure 2. Photoluminescence spectra of **1**, **1a**, and **2** (λ_{exc} ; 320 nm).

Those in **1a** ($\text{Cu1}\cdots\text{Cu2}$, 2.729; $\text{Cu2}\cdots\text{Cu3}$, 2.685 Å), however, show evidence of cuprophilic interaction of the type that has been reported⁶ to induce photoluminescence behavior. Thus, while **1** is nonemissive, **1a** shows bright yellow photoluminescence dominated by emission at 420 nm (Figure 2), undoubtedly due to the generation of a cluster-centered excited-state with mixed halide-to-metal charge transfer character.⁷ The X-ray powder diffraction (XRPD) pattern of **1a** differs from that of **1**, indicating that the bulk crystallinity is maintained upon removing the acetonitrile, but the framework structure is changed (Figure S9).

On the basis of the single-crystal structures and TGA and XRPD data, solids **1** and **1a** are associated with a novel single-crystal-to-single-crystal transformation which gives rise to the observed cuprophilic interaction-based, solvato-photoluminescence “off-on” behavior due to the removal of the coordinated acetonitrile molecules. Immersing the desolvated sample **1a** in acetonitrile produced no change in the XRPD pattern, and the sample was

emissive both before and after. This result indicates that the removal-recoordination process of the coordinated solvent molecules is not reversible under these conditions. In addition, the coordinated acetonitrile molecules in **1** were not simply replaced by common solvents at room temperature.

Meanwhile, the reaction of **L** in dichloromethane with 2 equiv of CuI in acetonitrile at -10°C gave colorless single crystals of a 3-D polymeric product of formula $\{[(\text{Cu}_2\text{I}_2)\text{L}_2(\text{Cu}_4\text{I}_4)](\text{CH}_2\text{Cl}_2)(\text{CH}_3\text{CN})\}_n$ (**2**). X-ray analysis revealed that **2** has cubane-type Cu_4I_4 and rhomboid-type Cu_2I_2 units linked alternately by **L** units (Figures S10 and S11). This is the first example of such a CuI complex; all other CuI complexes reported thus far are linked by only a single type of CuI cluster. Complex **2** also exhibits an orange emission (531 nm) in the solid state arising from the C_4I_4 cubane unit.⁷

In summary, we have demonstrated the temperature-dependent assembly of 3-D CuI coordination polymers **1** and **2** containing the calix[4]-bis-thiacrown, with different networking motifs. Upon removal of the coordinated solvent molecules, the structural characteristics observed in the complexes **1** and **1a** reveal not only a single-crystal-to-single-crystal transformation but also a related solvato-photoluminescence “off-on” behavior. Further investigation of the structure-dependent emitting properties of this and related systems is in progress.

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Supporting Information Available: Crystallographic data and CIF files of **1**, **1a**, and **2**; synthesis; XRPD patterns and IR spectra of **1** and **1a**; TGA and DSC of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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