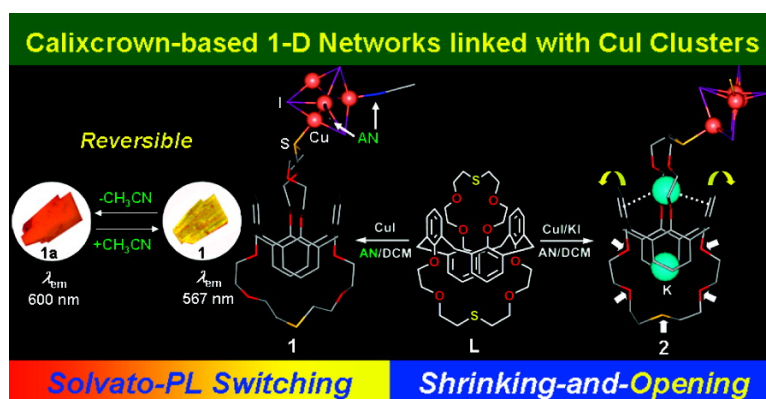


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Networking of Calixcrowns: From Heteronuclear Endo/Exocyclic Coordination Polymers to A Photoluminescence Switch

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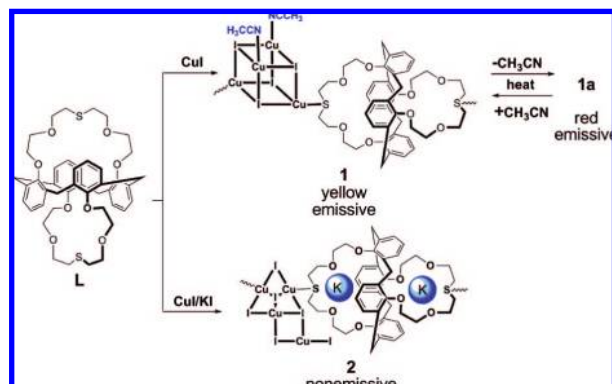
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Recently, there has been considerable interest in the photophysical properties of metal–organic frameworks (MOFs), particularly in view of their potential applications such as for sensors and electro- and photoluminescent materials.¹ Self-assembly processes involving copper(I) halides and multidentate ligands often lead to different discrete complexes and MOFs because the copper(I) halides are capable of adopting a variety of coordination modes ranging from discrete to three-dimensional networks that contain a variety of structural motifs such as rhomboid dimers, cubanes, hexagon prisms, 1-D chains, and double-stranded stairs.² Further, copper(I) halide derivatives exhibit not only a wide structural variety but also often bright emission behavior that varies markedly with both structure and environment.²

We have been interested in the assembly of supramolecular architectures based on the exocoordination of cyclic thioethers because the sulfur donor is expected to favor binding toward soft metal ions in an exocyclic mode.³ Recently, we have reported calix[4]-bis-dithiacrown-based, endocoordinated disilver(I) complexes as well as an exocoordinated 3-D network connected by CuI-based clusters.^{4a,b} Also, we have reported the temperature-dependent assembly of 3-D CuI coordination polymers containing the calix[4]-bis-dithiacrown.^{4c} Upon removal of the coordinated acetonitrile, in this case, the initial solvent-coordinated polymer undergoes a unique crystal-to-crystal transformation accompanying an irreversible photoluminescence change. In extending this work, we were interested in using a ligand-directed approach to construct new heterometallic networks as well as to achieve the construction of a reversible photoluminescence switch. Based on these considerations, the proposed calix[4]-bis-monothiacrown **L** employs one sulfur donor in the crown ring as a bridgehead for the required exocoordination which, in turn, will serve to minimize the softness of the crown rings (Scheme 1). In this work, we were successful in isolating two 1-D CuI networks (**1** and **2**) based on **L**. The intriguing feature of the study is the influence of coordinated solvent, which has been demonstrated to control observed reversible photoluminescence switching behavior. Another interesting aspect is the formation of endocyclic dipotassium and exocyclic copper(I) iodide clusters that link **L**, the first examples of such species yet reported.

L was synthesized by a bicyclization of 1,3-alternate tetratosylate **5**⁵ with the corresponding dialcohol (Supporting Information). Reactions of **L** with 2 equiv of CuI afforded the colorless crystalline product **1**. An X-ray analysis revealed that **1** is a 1-D polymeric array of formula [(Cu₄I₄)L(CH₃CN)₂]_n in which each **L** is linked to a cubane-type Cu₄I₄ unit (Figure 1a). The Cu₄I₄ moiety defines a slightly irregular cubane-type arrangement of alternating copper and iodine atoms.⁶ Two of the Cu centers (Cu1 and Cu2) have

Scheme 1



tetrahedral geometry but different coordination environments. For example, Cu1 is linked to three μ_3 -iodide atoms and one sulfur donor of **L** [Cu1–S1 2.297(11) Å]. Importantly, Cu2 is coordinated to three iodide atoms, and the fourth site is occupied by an acetonitrile molecule [Cu2–N1 2.002(4) Å].

When the metal salt was changed from 2 equiv of CuI to 2 equiv of CuI plus 2 equiv of KI, the 1-D polymeric array exhibiting interesting structural aspects, **2**, was obtained. Unlike **1**, complex **2** features a 1-D array of formula [K₂(Cu₄I₆)L]_n, with endocyclic dipotassium complexes linked by exocyclic Cu₄I₆²⁻ clusters via Cu–S bonds (Figure 1b). Such a scoop-type Cu₄I₆²⁻ cluster anion with four fused Cu₂I₂ rhomboids has not been reported previously. The coordination of each endocyclic K⁺ is completed by four K–O bonds (2.66–2.91 Å). In addition, there are additional cation $\cdots\pi$ interactions present. For example, K⁺ interacts with C atoms in the aromatic ring showing η^5 -type cation $\cdots\pi$ interactions (K \cdots C

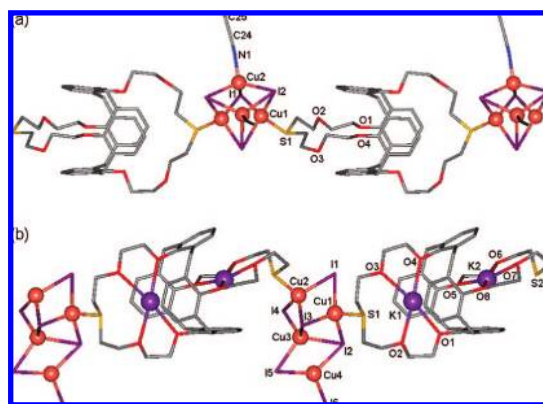


Figure 1. 1-D polymeric chains of **1** and **2**: (a) **1**, [(Cu₄I₄)L(CH₃CN)₂]_n linked with acetonitrile-coordinated Cu₄I₄ cubane units and (b) **2**, [K₂(Cu₄I₆)L]_n with heteronuclear endo/exocyclic coordination.

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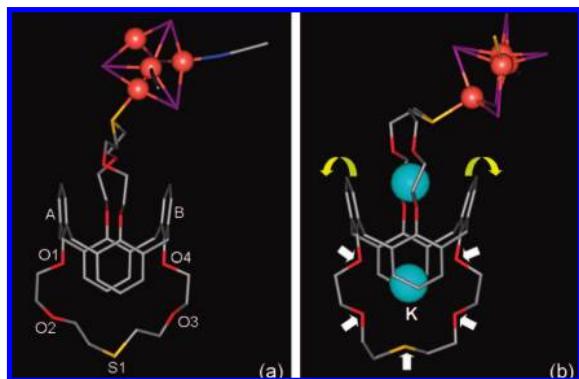


Figure 2. Closer view of calixcrown units in (a) **1** and (b) **2** (see also Figure 1). Conformational changes of the calixcrown unit upon endocomplexation with potassium ions (blue spheres), indicated by white and yellow arrows to emphasize the “shrinking-and-opening process”.

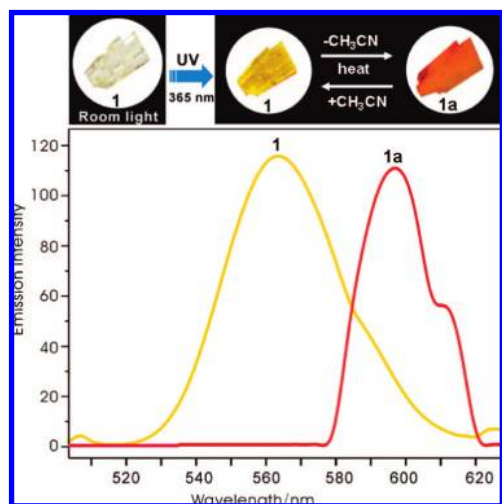


Figure 3. Solid-state photoluminescence spectra of **1** and **1a** at room temperature (excitation at 365 nm).

3.182–3.388 Å) (Figure S5). A limited number of the endo/exocyclic networks based on thiocrowns have reported previously by us^{6a} and others;^{6b,c} however, **2** is the first reported example of a calixarene derivative forming heterometallic endo/exocyclic networks.

Very interestingly, comparison of the dihedral angles between the two opposite aromatic rings in the 1,3-alternate calix[4]arene units belonging to **1** (8.6°) and **2** (26.2°) shows the effect of endocoordination of the crown ring to the K⁺ ion (Figure 2). Upon complexation, all the donors are associated with gauche conformation and the crown ring “shrinks” (Table S2) (see arrows in Figure 2b). This can be explained in terms of a “shrinking-and-opening process”.

Since the photoluminescence behavior of copper(I) halide clusters is often very dependent on their structures, the luminescent properties of the present systems were compared. In the case of **2**, no photoluminescence was observed. However, **1** exhibits a bright yellow emission ($\lambda_{\text{em}} = 567$ nm) due to a cluster-centered excited state with mixed halide-to-metal charge transfer character (Figure 3).⁷

To examine the effect of the coordinated acetonitrile in **1** on its photoluminescence properties and crystallinity, the crystalline sample **1** was investigated using TGA and DSC analysis. TGA performed on **1** showed first a sharp mass loss of 5.15% at ~150 °C which corresponds to the loss of one acetonitrile molecule

(expected mass loss 5.08%) (Figure S4). Then, the crystalline sample **1** was heated at 150 °C for 1 h to yield the acetonitrile-free sample **1a**. Interestingly, the acetonitrile-free **1a** shows bright-red photoluminescence dominated by the emission at 600 nm (Figure 3). The infrared spectrum of **1a** also confirms the removal of the coordinated acetonitrile (Figure S5).

The XRPD pattern of the acetonitrile-free sample **1a** differs from that of the original crystal of **1**; removal of the coordinated acetonitrile from **1** maintains the bulk crystallinity, but its framework structure is changed (Figure S6). Importantly, the powder XRD pattern of the acetonitrile-free microcrystalline sample **1a** after immersing in acetonitrile for 24 h is identical to that for the original crystal of **1**: both are emissive, indicating that the recoordination of the solvent molecule occurs reversibly. The TGA and XRPD data also support that the observed solvate-photoluminescence switching phenomenon is due to structural changes in **1** on removal of the coordinated acetonitrile.

In conclusion, we present two types of CuI coordination polymers incorporating the calix[4]-bis-monothiacrown in the absence (**1**) and presence (**2**) of KI. The structural motifs observed not only represent new arrangements for polymeric CuI-based networks but also display a unique reversible photoluminescence switching behavior reflecting the addition/removal of coordinated solvent molecules. Furthermore, upon inclusion of potassium ions the crown ring was observed to contract resulting in the “opening” of opposite aromatic rings in the host calixarene unit, rare behavior for this class of compound.

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Supporting Information Available: Crystallographic data and CIF files of **1** 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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