Luminescence thermochromism of two entangled copper-iodide networks with a large temperature-dependent emission shift†

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The luminescence thermochromism properties of two entangled copper(I)-iodide coordination polymers formulated \([\text{Cu}_4\text{I}_4(\text{dmimpr})_2]_n\) (1) and \([\text{Cu}_4\text{I}_4(\text{dimb})_2]_n\) (2) \((\text{dmimpr} = 1,3\text{-di(2-methyl-imidazol-1-yl)propane, dimb} = 1,4\text{-di(imidazol-1-yl)butane})\) are reported. Upon cooling by liquid nitrogen, their solid-state luminoses at room temperature are drastically changed with the large red-shifts of 41 and 78 nm for 1 and 2, respectively. The correlation between luminescence thermochromism and temperature-dependent variation of the Cu···Cu distance is also elucidated.

Anyway, despite some sporadic reports on thermochromic complexes,\(^8\) these kind of smart molecules are still in their infancy and the correlation between luminescence thermochromism and structural parameters is still unclear. The continuing interest in the luminescence thermochromic materials\(^8\) and the scant research on this field prompt us to explore the luminescence thermochromic copper(I)-iodide complexes with novel structural motifs. Herein we report on the syntheses, crystal structures, and luminescence thermochromism properties of two copper-iodide coordination polymers, namely, \([\text{Cu}_4\text{I}_4(\text{dmimpr})_2]_n\) (1) and \([\text{Cu}_4\text{I}_4(\text{dimb})_2]_n\) (2) \((\text{dmimpr} = 1,3\text{-di(2-methyl-imidazol-1-yl)propane, dimb} = 1,4\text{-di(imidazol-1-yl)butane})\).

Reaction of dmimpr or dimb with CuI (ratio of ligand/CuI = 1:5) via a solvothermal method in mixed solvents of dimethylformamide (DMF) and acetonitrile yielded yellow block crystals of 1 and 2 (see ESI†). Single-crystal X-ray diffraction at 298 K reveals that 1 and 2 crystallize in the orthorhombic \(Pm\text{t}2\) and the monoclinic \(C2/c\) space group, respectively. In 1, cubic \(\text{Cu}_4\text{I}_4\) clusters are extended by the dmimpr ligand with \(\text{anti-gauche}\) conformation to form the resulting 2D layer, in which \(\text{Cu}_4\text{I}_4\) clusters define the corners and the dmimpr ligands the edges. The \(\text{Cu}···\text{Cu}\) distances are 2.7486(16), 2.7817(12) \(\text{Å}\) in the \(\text{Cu}_4\text{I}_4\) cluster, which are shorter than or comparable to the sum of the van der Waals radii of copper(I) (2.80 Å)\(^{11}\) and thus imply strong metal···metal bonding interactions. The two imidazole rings on each dmimpr ligand were orientated so that methyl groups pointed in the nearly same direction and the rings were tilted by 65.5(3)° with respect to each other. Topologically, considering \(\text{Cu}_4\text{I}_4\) clusters as 4-connected nodes, the 2D layer could be simplified to a \(4^4\)-squl network with a square window size of 13.8 \(\times\) 13.8 \(\text{Å}\) (Fig. 1a). As shown in Fig. 1b, a pair of identical 2D single nets interpenetrate in a \(2\text{D} + 2\text{D} \rightarrow 2\text{D}\) parallel fashion. Two of the windows are interpenetrated in such a manner that the square centres of a net-plane are approximately located in the middle of the edges of the second one, as a consequence, the large windows of the network are occupied, preventing the formation of the large channels. The interpenetrating nets have parallel mean planes and are coincident, and thus an overall 2D entanglement is produced.\(^{12}\)

X-ray analysis revealed that complex 2 incorporates both cubane-type \(\text{Cu}_4\text{I}_4\) and rhomboid-type \(\text{Cu}_4\text{I}_2\) clusters. Each \(\text{Cu}_4\text{I}_4\) cubic

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cluster is connected by four dimb ligands, which further link four Cu₄I₄ rhombic clusters to form the resultant 2D highly undulated sheet (Fig. 2a). The Cu···Cu distances span from 2.480(3) to 2.882(3) Å. Notably, the shortest Cu···Cu contact of 2.480(3) Å in the rhomboid-type Cu₄I₄ cluster appears to be comparable to those found in [Cu₃(napy)₂][ClO₄]₂ (napy = 1,8-naphthyridine) [2.506(2) Å],¹³ and [Cu₃(L)₂]⁺ ([H₂L = N,N’-bis(2,6-diy)-bis-(4-methylbenzenesulfonamide)] [2.466(1) and 2.468(1) Å].¹⁴ This distance is 0.12 Å longer than the shortest Cu···Cu contacts known, 2.348(2) and 2.358(2) Å observed in [Cu₃(tolN₅tol)₃] (HN₅ = 1,4-pentazadiene, tol = p-toly).¹⁵ We also searched the examples with Cu···Cu contacts shorter than 2.48 Å in CSD,¹⁶ and only five hits were obtained.¹⁷ In these, such a short Cu···Cu contact is hardly observed in copper(i)-iodide coordination complexes.

In the 2D sheet, dimb ligands show anti–gauche–anti and anti–anti–anti conformations, which are defined as A- and B-type, and they play different roles in the construction of the 2D sheet. Similar to 1, the basic structure of 2 is also a 4₄-sq₁ net with a rhomboid window size of 16.2 × 30.9 Å which is constructed by the Cu₄I₄ cubic cluster, and two kinds of 2-connected linkers, which are the [Cu₄I₄(A-type-dimb)₃] subunit and B-type-dimb. A more fascinating structural feature is the presence of identical 2D single nets which catenate with each other in a 2D + 2D → 3D parallel fashion, as shown in Fig. 2b. The 2D → 3D dimensional increase can be regarded as being caused by polycatenaion of the nets. In other words, as shown in Fig. 2c, each window (blue window) is simultaneously catenated by the other two (red and green windows). Different from 1, although the interpenetrating nets in 2 also have parallel mean planes, these mean planes are not coincident but are offset, and thus an overall 3D entanglement is formed. The high degree of entanglement is due to (i) the enough large windows of the net and (ii) the highly undulated nature of the single 4₄-sq₁ net. The structural differences between 1 and 2 are caused by different bidentate N-donors with different lengths, flexibility and substituents.

At room temperature, under UV irradiation, 1 and 2 emit an intense yellow light (Fig. 3, inset). The fascinating and visually impressive phenomenon of thermochromic luminescence of 1 and 2 is revealed by immersing the samples into liquid nitrogen. When exposed to UV light, the crystalline solids undergo a chromic process from a bright yellow luminescence at room temperature and an orange-red or red luminescence when cooled in liquid nitrogen. Once the samples are taken out and progressively warmed up to room temperature, the yellow emission is recovered, indicating a completely reversible thermochromic luminescence for 1 and 2. The variable temperature luminescence spectra and excitation spectra at room temperature are shown in Fig. 3 and Fig. S3 (ESI†), respectively. The emission maximum in the solid-state luminescence spectrum for 1 (λ(em) = 365 nm) of 1 appears considerably red shifted (555 → 565 → 572 → 596 nm) when the temperature is decreased from 298 to 77 K. The red shift of 41 nm for 1 is large enough to make the color change visible by the naked eye. The maxima of the emission bands of 2 were observed at 549, 615, 620 and 627 nm (λ(em) = 365 nm) in the solid state at 298, 220, 183 and 77 K, respectively. The red shift of the emission peak (78 nm) is larger than that of 1. The absolute luminescent quantum yields were determined by means of an integrating sphere, and the values obtained at an excitation of 365 nm are 0.20 and 0.36 for 1 and 2, respectively, at room temperature. The solid state lifetime at room temperature is on the scale of microseconds (2.36 and 2.19 µs for 1 and 2), suggestive of their phosphorescent character (Fig. S4, ESI†). Their emission bands
could be attributed to triplet cluster-centered (\(^3\)CC) excited states, a combination of iodide-to-copper charge transfer (XMCT) and d–s transitions.

To reveal the relationship between the luminescence thermochromism and the molecular structures in the crystalline states, we have performed multi-temperature X-ray crystal structure analyses on the same single crystals of 1 and 2 at 298 K, 220 K, 160 K, and 100 K (Table S1, ESI†), respectively, which reveal a correlation of the structural parameters of 1 and 2 versus their luminescence thermochromism as a function of temperature. Table S3 (ESI†) lists the X-ray Cu...Cu distances of 1 and 2 at four different temperatures. The analysis of the structural data reveals the shrinkage of the unit cell from 1757.6(2) Å\(^3\) (298 K) to 1675.22(18) Å\(^3\) (110 K) (4.7%) and 4665(2) Å\(^3\) (298 K) to 4460.9(10) Å\(^3\) (110 K) (4.4%) for 1 and 2, respectively. It is also noted that as the temperature decreases, the mean Cu...-Cu distances decrease from 2.8048 Å (298 K) to 2.7140 Å (100 K) (\(\Delta = 0.09\) Å) and 2.704 Å (298 K) to 2.669 Å (100 K) (\(\Delta = 0.04\) Å) for 1 and 2, respectively. Therefore, the emission red shifts caused by cooling are intensively related to compression of the Cu...Cu distances instead of a chemical process involving phase transition (Table S1, ESI†). The overall variation tendency of emission maximum and Cu...Cu distance against the temperature is plotted in Fig. S7 (ESI†), which gives a good linear relationship between the maximum emission wavelength and temperature for 1 (Fig. S8, ESI†). This linear relationship can be fitted as a function of \(T = 608.58 - 0.19\nu_{\text{max}}\) with a correlation coefficient of 0.968. But this is not the same for 

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\frac{1}{2} \nu_{\text{max}} = 608.58 - 0.19T
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To reveal the relationship between the luminescence thermochromism of copper(I)-iodide coordination polymers is caused by temperature-dependent Cu...Cu distances on the luminescence thermochromism properties of 1 and 2. Finally, the dramatic luminescence color changes in the materials reported herein upon temperature variation are promising for sensor applications.

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References