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COMMUNICATION

Cationic copper(I) iodide cluster MOF exhibiting unusual ligand assisted thermochromism

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Employing a tridentate thiophosphoramidate ligand, [(NHAQ)₃P=S] (AQ = 3-quinolinyl) a cationic MOF, **1** {[Cu₆I₅(L¹)₂](OH)·3DMF·2.5MeOH}_n was synthesized. Photo-physical studies on the 2D-MOF **1** showed an unusual thermochromic behaviour emitting a blue fluorescence at 298K due to the AQ chromophore and an orange-yellow phosphorescence at 77K due to the [Cu₆I₅]⁺ unit.

Coordination compounds that possess luminescent properties are well investigated because of their promising applications in the fields of chemical sensors, biomedical imaging and optoelectronic devices.¹ One of the prominent classes of luminescent coordination compounds are those of copper (I) iodide, [Cu_nI_m]^(n-m), clusters owing to their diverse structure dependant photo-physical properties.² Many of these clusters exhibit stimuli-responsive structural fluctuations and hence exhibit diverse photophysical signatures. Thus, they display properties such as thermochromism,³ mechanochromism⁴ and solvato/ vapochromism⁵ in response to the external stimuli effects of temperature, mechanical grinding and solvent/vapour contacts, respectively. In pursuit of developing smart photoactive materials for various technological applications, research on stimuli-responsive luminescent materials, especially those exhibiting thermochromism, have gained considerable attention.⁶ However, thermochromic materials are still unpredictable as the emission shifts *vis-à-vis* colours, magnitude and direction could not be precisely controlled.³ Studies on photo-functional metal-organic frameworks (MOFs) featuring copper(I) iodide (CuI) clusters and organic linkers are of major research interest as these clusters can not only provide rigidity to the framework but also can impart the desired photo-physical properties to it.⁷ Thus, it is possible to tune these MOFs for a range of emissions depending upon the nature of [Cu_nI_m]^(n-m) clusters, ligand environment and external stimuli. Although there are a handful number of CuI-MOFs known, only in few instances⁸ have they been shown to exhibit the thermochromic behaviour associated with discrete clusters such as Cu₂I₂ and Cu₄I₄.⁹

Herein, we report a CuI-MOF **1** of formula {[Cu₆I₅(L¹)₂](OH)·3DMF·2.5MeOH}_n starting from CuI and a thiophosphoramidate ligand L¹, [(NHAQ)₃P=S] (Scheme S1, ESI). Photo-physical studies reveal that **1** exhibits an unusual ligand assisted thermochromism

emitting a blue fluorescence at 298K due to the AQ chromophore and an orange-yellow phosphorescence at 77K from the triplet excited states of the cationic [Cu₆I₅]⁺ core. This is the first observation of its kind where the thermochromism in a CuI cluster MOF is shown to be controlled by ligand emissions.

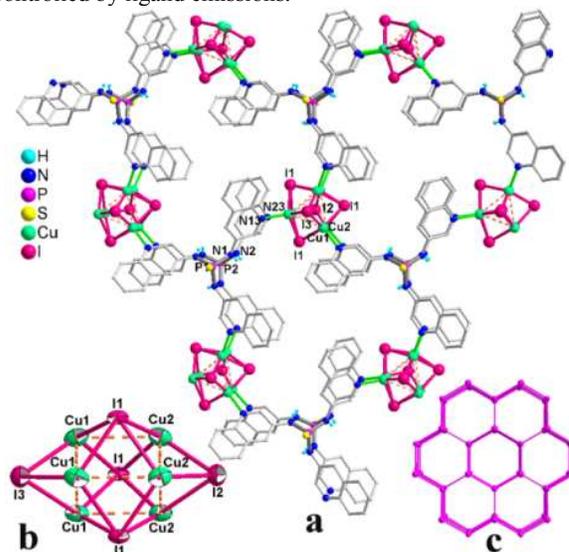


Figure 1. The double sheet structure (a) and the [Cu₆I₅]⁺ core (b) of **1**; (c) Packing diagram showing superimposed AAA type of arrangement in **1** along the c-axis. The ligand and the Cu₃-plane are depicted as small and big spheres, respectively, as 3-connected nodes.

The cluster MOF **1** was obtained by the respective reaction of L¹ (Figure S1, ESI) with CuI at room temperature as crystalline solid. The crystal structure of **1** was solved in the trigonal space group *P*-3 (Figure 1, and Figure S2, ESI). The molecular core consists of a rugby-ball shaped cationic [Cu₆I₅]⁺ cluster and two neutral ligand motifs (L¹), while the charge balance is restored by the presence of a hydroxide anion which presumably originates from the added water. The cluster core consists of the trigonal prismatic assembly of six Cu(I) ions that are tethered by three μ_4 -bridging Γ^- ions. The remaining two Γ^- ions are located at the two opposite triangular faces

of the prism as the μ_3 -capping units (Figure 1b). Each Cu(I) centre is tetrahedrally coordinated to three Γ ions and one ring N-donor from L^1 . Thus, the prismatic $[Cu_6I_5]^+$ cluster acts as a 6-connected node with each of its triangular Cu_3 -face is bound to three thiophosphate ligands. In return each ligand is connected to three Cu(I) centres resulting in a double-layer **hcb** network (Figure 1c). TOPOS^{10a} analysis for **1**, considering the $[Cu_6I_5]^+$ cluster as a single node, gave a binodal $(3c)_2,6c$ -net of MoS_2 type (3c for the ligand and 6c for the cluster) having the Schläfli symbol $(4^3)_2(4^3.6^{12})$.^{10b} As most cationic CuI-clusters were found to possess a triangular plane of Cu-atoms,¹¹ the C_3 -symmetric ligation of L^1 provides an ideal platform for stabilizing the cationic cluster in **1**. The solvent accessible void space, excluding the space occupied by the OH^- ions, was found to be 1393 \AA^3 (32.7% of the unit cell volume) (Figure S3, ESI). Attempts to prepare the guest free sample of **1** were unsuccessful due to the interaction of the OH^- ions with the solvated molecules. The absorption spectra of L^1 and **1** recorded in DMF show typical values expected of their chromophores ($L^1 = 330 \text{ nm}$; **1** = 345 nm). In addition, **1** shows weak absorptions at 385 nm, due to the iodide to ligand charge transfer (XLCT) transitions similar to that observed for $Cu_4I_4Py_4$ cluster.¹² The same observations were made when the spectra were recorded in the solid-state (Figure S4, ESI). The solid-state emission spectrum of L^1 at room temperature shows a sharp band at $\lambda_{em} = 411 \text{ nm}$ with a bright blue fluorescent emission (Figure 2 and Figure S5, ESI). Upon lowering the temperature to 77K, L^1 shows a new band (with shoulders) centred at $\lambda_{em} = 523 \text{ nm}$ in addition to the one at 411 nm and gives rise to a bluish-green emission corresponding to phosphorescence. Thus at 77K, the triplet state of the ligand is partially populated through inter-system crossing (ISC) from $S_1 \rightarrow T_1$ state and the emission occurs from both of these states. The decay time measured at 298K for L^1 fitted to a tri-exponential curve gave $\tau_1 = 0.09$, $\tau_2 = 0.05$ and $\tau_3 = 4.13 \text{ ns}$ characteristic of a fluorescence corresponding to the $S_1 \rightarrow S_0$ transition (Figure 3). Whereas the decay profile collected at 532 nm for the low energy (LE) bands for L^1 in DMF gave $\tau_{em} = 986 \text{ \mu s}$ confirming the presence of triplet excited state in it (Table S2, ESI).

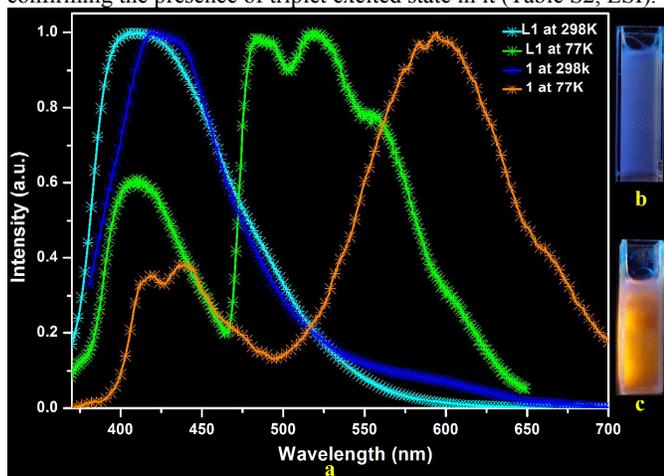


Figure 2. (a) Normalized emission spectra for L^1 and **1** ($\lambda_{ex} = 360 \text{ nm}$) in the solid-state. The emission colour of **1** in DMF suspension at (b) 298K and (c) 77K under the UV-lamp ($\lambda = 365 \text{ nm}$).

The emission spectrum of the crystalline solid-sample of **1** at 298K also shows a similar blue luminescence as that of L^1 in the high energy (HE) region with $\lambda_{em} = 419 \text{ nm}$ (Figure 2). Decay measurement at 298K fitted to a tri-exponential profile gave life time values of $\tau_1 = 0.07$, $\tau_2 = 0.08$ and $\tau_3 = 4.78 \text{ ns}$ (Figure 3a). This is attributed to the self-emission of the AQ moieties and rules out the possibility of the cluster based iodide to AQ charge transfer (3XLCT) transition which has a lifetime in the μs scale. Although **1** is a dual

chromophoric system comprising of the AQ segments and the cationic cluster, emission from both of them is forbidden according to Kasha's rule.¹³ Hence we thought that if the triplet states of **1** are populated at low temperature by an ISC process, it is possible to detect the phosphorescence due to the $[Cu_6I_5]^+$ motif. Accordingly, at 77K **1** gave a new orange-yellow emission centred at $\lambda_{em} = 594 \text{ nm}$ along with the weak HE band at 419 nm. The lifetime for the LE emission at 77K gave $\tau_{em} = 236.96 \text{ \mu s}$ (Figure 3b) characteristic of the emission from the triplet cluster-centred (3CC) excited state of $[Cu_6I_5]^+$ comprising of iodide to Cu charge transfer (3XMCT) and Cu centred $d \rightarrow s, p$ transitions.¹² Similarly, presence of the HE and LE emission bands at 298K and 77K, respectively, were observed in the DMF or DCM suspensions of **1** confirming its stability in these solvents (Figures S6, S7 and S8, ESI).

Temperature dependant measurements reveal that this 3CC -emission originates around 189K (Figure S7, ESI). It is to be noted that for most $Cu_4I_4L_4$ cubane clusters¹² the LE 3CC -band dominates at room temperature and the HE 3XLCT -bands are observed at low temperatures (sometimes below 10K). In contrast, **1** exhibits an unusual thermochromism that it shows the ligand-centred fluorescence at 298K (HE) and the 3CC phosphorescence at 77K (LE). Thus, the thermochromism in **1** is controlled by the emission characteristics of its ligand moieties. Comparison of the Cu...Cu and Cu...I distances in **1** obtained from the single-crystal X-ray data collected at 298K and 100K reveal that the Cu...Cu distances were notably shortened at 100K. In particular, Cu...Cu bonds between the two Cu_3 -units ($3.150(2)$ (298K) and $3.032(4) \text{ \AA}$ (100K)) are shortened by about 0.12 \AA at 100K (Figure S9, ESI). This infers that the cationic cluster might also contribute to the emission shifts in **1**.

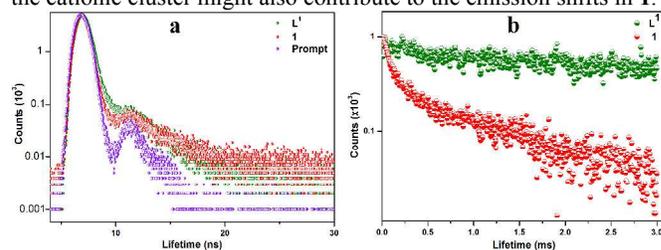


Figure 3. (a) TCSPC decay profiles of the 298K solid-state fluorescence in L^1 and **1** and (b) the 77K phosphorescence decay profile in L^1 (in DMF) and **1** (solid) measured using the W-lamp.

To get further insights into the photo-physical properties of **1**, preliminary DFT calculations (6-31g(d)/LANL2DZ) were performed on a discrete model compound $\{Cu_6I_5 [(AQNH)_2P=S]_6\}$ (**1a**) by using Gaussian 03 package.¹⁴ For the purpose of these calculations coordinates from the crystal structure were taken and then optimized for the gas phase structure. A closer look at the frontier orbitals in **1a** indicates that the electronic isodensity surfaces are located on both the AQ chromophores and the cluster core (Figure 4). It shows that majority of the highest occupied molecular orbitals (Hs) in **1a** comprise predominantly of the iodine 5p orbitals and the copper 3d orbitals to some extent (from H-4 to H). Similarly, the lowest unoccupied molecular orbitals (Ls) up to L+5 are exclusively on the AQ moieties whereas the L+6 is solely based on the cluster. Further, the optical properties of **1a** were determined by TDDFT calculations on the optimized structures and the first 40 transitions were computed. Thus, the weak band centred at 385 nm in the absorption spectrum of **1** corresponds mainly to the transitions H-2 \rightarrow L+3 and H-2 \rightarrow L+4 with each of them exhibiting significant positive oscillator strengths (0.0124) (Figure S11, Table S3, ESI). It is to be noted that L+6 did not feature in any of these transitions suggesting that this transition must be resulting from the mixture of 1XLCT and 1MLCT charge-transfer, as observed for the $Cu_4I_4Py_4 / Cu_4I_4(PR)_4$ cubane clusters.¹⁵ Whereas, the HE band centred at 345 nm in the

absorption spectrum of **1** is due to the ligand centred absorptions corresponding to the transitions **H-5**→**L**, **H-5**→**L+1**, **H-7**→**L+3** and **H-6**→**L+4** with each of them showing notably higher oscillator strengths (Figure S11 and Table S3, ESI).

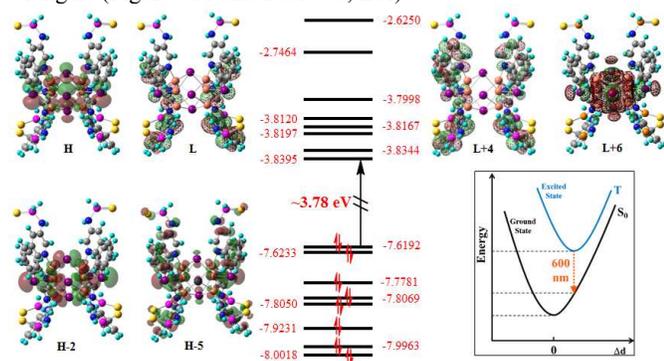


Figure 4. DFT derived surface diagrams and energies (in eV) of some relevant molecular orbitals at the S_0 optimized geometry for **1a**. Inset: proposed potential energy diagram for **1a** from single-point calculation on the optimized triplet geometry.

The energy separation between the ligand centred **L+5** and the cluster-centred **L+6** in **1a** is 1.05 eV (24.29 kcal/mol). Hence, it is highly likely that populating the low-energy ligand π^* orbitals in **1a** would preferably result in the fluorescent emission ($S_1 \rightarrow S_0$ fast radiative decay) than the cluster-centred phosphorescence (${}^3CC \rightarrow S_0$ slow radiative decay). However, by populating the cluster-centred triplet **L(s)**, phosphorescent emission from the 3CC -excited states could be achieved. Thus, the 3CC - transition can take place between cluster based **H-2** and **L+6** orbitals in the calculated structure of **1a** which exactly matches with the **H** and **L** computed for the bare cluster (Figure S13, ESI). The calculated emission wavelength of 600 nm from the adiabatic $S_0 \rightarrow T$ gap obtained from the single-point calculations¹⁶ on the triplet geometry of **1a** is in good agreement with the experimental value of 594 nm observed for **1** (Figure 4).

In summary, we have shown that tridentate ligand based on thiophosphoramidate backbone offers a C_3 -symmetric platform for obtaining a rugby-ball shaped cationic CuI cluster MOF. The MOF **1** showed an unusual thermochromism exhibiting ligand dependant fluorescence at 298K and the cluster dependant phosphorescence at 77K. DFT analysis on the model compound **1a** indicated that emission from the AQ chromophores is favoured at 298K as its π^* orbitals are lower in energy by 24.29 kcal/mol than the cluster based LUMOs in the S_0 optimized geometry. However, the ISC process at 77K can populate the cluster based triplet state (**L+6** orbitals) for the 3CC -phosphorescence emission. Currently, we are focussed on utilizing various P(V) based multi-site ligands for obtaining stimuli-responsive MOFs and studying their application as chemical sensors. This work was supported by the DST(SR/S1/IC-50/2012), India and IISER, Pune. A. Y. thanks the CSIR, India for fellowship. We thank Drs. M. Jayakannan, P. Hazra and A. Hazra for valuable discussions.

Notes and references

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Electronic Supplementary Information (ESI) available: experimental details, X-ray diffraction data and tables and additional figures. CCDC 968374, CCDC 968376-968377. For ESI and crystallographic data in CIF format see DOI: 10.1039/c000000x/.

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Graphical Abstract

Cationic copper(I) iodide cluster MOF exhibiting unusual ligand assisted thermochromism

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A cationic CuI cluster MOF **1**, $\{[\text{Cu}_6\text{I}_5(\text{NHAQ})_3\text{P}=\text{S}]_2(\text{OH})\cdot 3\text{DMF}\cdot 2.5\text{MeOH}\}_n$ (AQ = 3-quinolinyl), was shown to exhibit an unusual thermochromic luminescent behaviour emitting a blue fluorescence at 298K and pale-orange phosphorescence at 77K.

