Cationic and neutral copper(I) iodide cluster MOFs derived from tridentate N-donor functionalized P(V) ligands: synthesis, structure and photophysical properties[†]

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Abstract. Formation of cationic and neutral CuI cluster MOFs have been reported starting from tridentate phosphoramidate ligands, [(NHR)₃P = E] (L¹: R = 3-aminoquinoliny (AQ), E = S; L²: R = 3-pyridyl (PY), E = S; L³: R = 3-aminoquinoliny (AQ), E = O). By utilizing L¹, a cationic 2D-MOF {[L¹]₂(Cu₆I₅)}(OH) · 3DMF · 4MeOH)_n, **1** containing a rugby ball shaped discrete Cu₆I₅ cluster has been reported earlier. Formation of a new 3D-MOF {[L²]₂(Cu₆I₄)}(OH)₂ · 2DMF)_n containing a Zintl type [(Cu₆I₄)²⁺]_n cluster chains is reported in this paper. A neutral cluster MOFs **3** with formula unit of {[Cu₄I₄L³(CH₃CN)] · 2DMF · 3H₂O)_n has been prepared from the ligand L³. Formation of the smaller Cu₄I₄ clusters in the MOF **3** is due to the presence of a MeCN ligation at one of the Cu(I) atoms which not only precludes the extension of the assembly in three dimension but also reduces the size of the obtained cluster. Unlike **1** which showed a ligand-assisted thermochromism, photophysical studies on the 3D-MOF **2** exhibited green phosphorescence at both 298 K and 77 K. The occurrence of the phosphorescence at 77 K in **2** is due to triplet cluster centered (³CC) excited state of the cluster as there is no ligand-centered transition observed at 298 K. The 2D-MOF **3** does not show any characteristic luminescence behavior as the presence of the acetonitrile coordination at one of the Cu(I) ion is believed to quench the emission by non-radiative pathways. Further, luminescence quenching experiments on **1** and **2** with aromatic nitro-analytes showed a very high sensing selectivity for picric acid (TNP) over other aromatic nitro-analytes.

Keywords. Cationic CuI clusters; MOFs; photoluminescence; P-N ligands; nitro-aromatic sensing.

1. Introduction

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 photophysical properties to it.¹ Depending upon the nature of [Cu_nI_m]^(n-m) clusters, ligand environment and temperature, these CuI-MOFs can be tuned for a range of emissions from blue to green to red.² These cluster MOFs may typically be obtained in reactions involving CuI and suitable bi- and polydentate linker ligands.³ Among several [Cu_nI_m]^(n-m) type motifs, the

neutral clusters of Cu₂I₂ and Cu₄I₄ are the readily formed ones in most reactions and are widely studied for structural and photophysical characteristics,⁴ although there are handful number of reports for other neutral high nuclearity clusters.⁵ In contrast, cationic clusters such as [Cu₄I₂]²⁺, [Cu₄I₃]⁺, [Cu₆I₂]⁴⁺, [Cu₆I₄]²⁺, [Cu₆I₅]⁺, [Cu₇I₄]³⁺, [Cu₈I₆]²⁺, [Cu₁₀I₄]⁶⁺ and [Cu₂₄I₁₀]¹⁴⁺ are scarcely reported as they usually involve the unfavorable coordination of charge balancing, hard anionic ligands to the soft Cu(I) species.⁶ As most of these cationic clusters were found to possess a triangular plane of three Cu-atoms, we thought that use of a ligand which offers a C₃-symmetric ligation⁷ would generate a cationic CuI cluster MOF. Recently, utilizing a tridentate thiophosphoramidate ligand L¹, [(NHAQ)₃P=S] we have synthesized a cationic cluster MOF **1** of composition {[L¹]₂(Cu₆I₅)}(OH) · 3DMF · 2.5MeOH)_n

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[†]Dedicated to Prof. K C Kumara Swamy on the occasion of his 60th Birthday.

Chart 1. Some of the tripodal phosphoramidate ligands employed for synthesizing CuI cluster MOFs.

featuring a rugby-ball shaped $(\text{Cu}_6\text{I}_5)^+$ cluster core.⁸ This material exhibited an unusual ligand-assisted thermochromism showing two distinct high energy (HE) and low energy (LE) bands at 420 nm and 600 nm at 298 K and 77 K, respectively. Spurred by the unique structure and photophysical properties of **1**, we set out to explore the reactivity of phosphoramidate ligands $[(\text{NHR})_3\text{P}=\text{S}/\text{O}]$ (L^2 and L^4 : R = 3-pyridyl (PY); L^3 : R = 3-quinolinyl (AQ)) in reaction with CuI (Chart 1). These reactions yielded two new cluster-MOFs **2** and **3**. While the MOF **2** exhibits a cationic $[\text{Cu}_6\text{I}_4]^{2+}$ cluster chain that is structurally related to the $(\text{Cu}_6\text{I}_5)^+$ core of **1**, the MOF **3** contains a neutral Cu_4I_4 core. Photophysical studies indicate that the MOF **2** emits green phosphorescence at both 298 and 77 K, whereas the MOF **3** does not show any luminescent behaviour.

Despite the rich photophysical characteristics exhibited by several CuI clusters, use of these compounds for sensing application has been very limited.⁶ As these MOFs are having electron-rich cluster core and feature flat aromatic backbones in an ordered fashion, we explored their utility in selectively detecting electron-deficient aromatic nitro-compounds *viz.*, nitrobenzene, 4-nitrophenol, 1,3-dinitrobenzene (DNB), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT) and picric acid (2,4,6-trinitrophenol abbreviated as TNP). These studies revealed that both **1** and **2** exhibit significant selectivity in sensing picric acid (TNP) over other nitroaromatic compounds. Use of fluorescent MOFs for the selective detection of toxic and explosive analytes has emerged as an active area of research.⁹ Especially, selective and sensitive detection of picric acid is highly desired due to its routine usage in dyeing, leathering, fireworks and home-match industries in spite of its higher explosive power than trinitrotoluene (TNT).¹⁰

2. Experimental

2.1 General remarks

All manipulations involving phosphorus halides were performed under a dry atmosphere in standard Schlenk-glassware.

CuI, 3-aminopyridine, 3-aminoquinoline, PSCl_3 and PCl_5 were purchased from Aldrich and used as received. Thermal analysis data were obtained from a Perkin-Elmer STA-6000 thermogravimetric analyzer. Elemental analyses were performed on a Vario-EL cube elemental analyzer. FT-IR spectra were taken on a Perkin-Elmer spectrophotometer. The absorption spectra were recorded on a Perkin-Elmer Lambda 45 UV-Visible spectrophotometer. The emission studies were performed on a SPEX Fluorolog HORIBA JOBIN VYON fluorescence spectrophotometer with a double-grating 0.22 m Spex1680 monochromator and a 450 W Xe lamp as the excitation source. The excitation and emission spectra of the complexes were corrected at the instrumental function. The photoluminescence lifetime measurements were carried out using a SPEX Fluorolog HORIBA JOBIN VYON 1934 D phosphorimeter.

2.2 Synthesis

The ligands L^1 , L^2 , L^3 and L^4 were prepared by adopting our earlier reported procedure.^{8,11}

2.2.1: To a stirred solution of L^2 (34 mg, 0.1 mmol) in dichloromethane (5 mL) and MeOH (2 mL), CuI (57 mg, 0.3 mmol) in CH_3CN (15 mL) was added leading to an immediate formation of a white precipitate. To this mixture, 2 mL of DMF containing a few drops of water was added and the mixture was further stirred for 4 h at which point most of the precipitate were dissolved. The solution was then filtered through a thick pad of celite and left for crystallization. Colourless crystals of **2** suitable for X-ray diffraction were obtained after 15 days. Yield: 73 mg (80% based on Cu). FT-IR data in powdered sample (cm^{-1}): 3550, 3105, 2760, 1573, 1463, 1399, 1261, 1101, 1039, 924, 791, 701, 655. Anal. calc. for $\text{C}_{39}\text{H}_{53}\text{Cu}_6\text{I}_4\text{N}_{15}\text{O}_5\text{P}_2\text{S}_2$: C, 25.64; H, 2.92; N, 11.50; S, 3.51%. Found: C, 25.39; H, 2.85; N, 11.31; S, 3.67%.

2.2.2: To a stirred solution of Ligand (34 mg, 0.1 mmol) in MeOH (5 mL), CuI (57 mg, 0.3 mmol) in CH_3CN (15 mL) was added leading to an immediate formation of a yellow precipitate. To this mixture, 2 mL of DMF was added and the mixture was further stirred for 4 h at which point most of the precipitate were dissolved. The solution was then filtered through a thick pad of celite and left for crystallization. Yellow

Table 1. Crystal data

Compound	2	3
Chemical formula	C ₃₉ H ₅₂ Cu ₆ I ₄ N ₁₅ O ₅ P ₂ S ₂	C ₃₅ H ₃₈ Cu ₄ I ₄ N ₉ O ₃ P
Formula weight	1825.86	1425.47
Temperature	100(2) K	100(2) K
Crystal system	Hexagonal	Monoclinic
Space group	P6(3)/m	P21/n
a (Å); α (°)	14.707(3); 90	13.362(5); 90
b (Å); β (°)	14.707(3); 90	18.234(7); 94.322(8)°
c (Å); γ (°)	13.994(3); 120	21.917(8); 90°
V (Å ³); Z	2621.5(11); 2	5325(4); 4
ρ (calc.) mg m ⁻³	2.313	1.778
μ(Mo Kα) mm ⁻¹	4.945	3.963
2 θ _{max} (°)	56	50
R(int)	0.1812	0.1907
Completeness to θ	99.6%	96.2%
Data/param.	2250/122	9255/511
GOF	1.096	0.805
R1 [F > 4 σ (F)]	0.0725	0.0765
wR2 (all data)	0.2323	0.2066
max. peak/hole (e.Å ⁻³)	2.349/−3.926	1.652/−0.804

crystals of **3** suitable for X-ray diffraction were obtained after 15 days. Yield: 64 mg (60% based on Cu). FT-IR data in KBr pellet (cm⁻¹): 3453, 2921, 2852, 2257, 1656, 1457, 1344, 1209, 931, 744, 659. Anal. calc. for C₃₅H₃₈Cu₄I₄N₉O₃P: C, 28.70; H, 2.62; N, 8.61%. Found: C, 28.14; H, 2.25; N, 7.86%.

2.3 Crystallography

Reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using MoKα radiation (λ = 0.71073 Å) (Table 1). Structures were refined by full-matrix least-squares against F² using all data (SHELX97).¹² All non-hydrogen atoms were refined anisotropically if not stated otherwise. Hydrogen atoms were constrained in geometric positions to their parent atoms. The approximate positions of the two anionic oxygen atoms O1 and O2 in **2** were identified inside the packing cavity with great difficulty. Due to the smaller occupancy factors as well as the strongly absorbing nature of the iodine atoms, the thermal ellipsoids of O1 and O2 were big and hence were isotropically refined. The positions of these atoms were merely provided to satisfy the charge balance in **2**. Further evidence for these OH⁻ ions was derived from thermogravimetric and elemental analysis (Figure S1, see Supporting Information).

2.4 Emission lifetime measurements

The luminescence lifetimes of L² and **2** were measured at room temperature (289 K) as well as at low temperature (77 K). The room temperature fluorescence decay profiles were fitted to tri-exponential function. Similarly, the low temperature phosphorescence decay profiles were fitted to biexponential (77K) equation. In all the cases, the lifetimes

were fitted by using the DAS software and average lifetimes are reported for simplicity.

2.5 Computational details

The density functional theory (DFT) calculations have been performed by using Gaussian 03 program package.¹³ The B3LYP exchange-correlation functional was used throughout for all calculations.¹⁴ A combination of basis sets *i.e.*, 6-31g(d) for C, H, N, P and S, and LANL2DZ for Cu and I atoms,¹⁵ respectively, were used for the {Cu₆I₅[(PYNH)H₂P=S]₆} (**2a**) to obtain the geometry optimization and TDDFT calculations for the excitation energies. The theoretical emission wavelength of **2a** was derived by single point energy calculations on the optimized triplets as the energy difference between the lowest energy triplet state and its corresponding singlet state.

3. Results and Discussion

3.1 Synthesis and structure

The ligands L¹-L⁴ were synthesized by adopting the reported procedures in literature.^{8,11} The cluster MOFs **2** and **3** were obtained by the respective reaction of L² and L³ with CuI at room temperature as crystalline solids (Scheme 1). Treatment of L⁴ with CuI gave an insoluble impure residue. Synthesis and the molecular structure of **1** were described in a previous communication.⁸ It consists of a cationic rugby-ball shaped [Cu₆I₅]⁺ cluster core which is linked by six aminoquinolyl moieties to

Scheme 1. Synthetic scheme for the copper(I) iodide cluster MOFs **2** and **3**.

give an overall double-sheet hexagonal structure (Figure 1d). Remarkably, the P=S moieties of the ligands were found to be intact (and not hydrolysed to the P=O groups) in the structures of **1**, **2** and **3** despite the use of water as the reaction solvent. The thermal stability of the cluster-MOFs was determined from the thermogravimetric analysis (TGA) and it shows that ligands are stable up to 200°C while MOFs are stable above 300°C. The TGA of **1** and **2** showed weight losses up to 110°C corresponding to the loss of solvate molecules. Thus, a 17% weight loss due to the loss of three molecules of DMF and four molecules of MeOH in **1** and a 10% loss associated with three molecules of DMF in **2** have been assigned from the TGA data (Figure S1, in Supporting Information).

The crystal structure of **2** was solved in the hexagonal space group $P6(3)/m$ (Figure 1 and Figures S2, in Supporting Information). The molecular core consists of a similar rugby-ball shaped cationic cluster of composition $[\text{Cu}_6\text{I}_4]^{2+}$, two neutral ligand motifs (L^1) and two charge balancing hydroxide ions disordered over three positions. Each Cu(I) center is tetrahedrally coordinated to three I^- ions and one ring N-donor from L^1 . Similar to **1**, the $[\text{Cu}_6\text{I}_4]^{2+}$ cluster core consists of the trigonal prismatic assembly of six Cu(I) ions that are tethered by three μ_4 -bridging I^- ions. The remaining two I^- ions (labeled I_2) are located at the two opposite triangular faces of the prism and tether the neighbouring clusters in a μ_6 -bridging fashion to yield a $\{[\text{Cu}_6\text{I}_4]^{2+}\}_n$ type 1D-cluster chain assembly (Figure 1c). Thus, each $[\text{Cu}_6\text{I}_4]^{2+}$ segment in **2** acts as an 8-connected node and the two axial iodide ions in each of them connect the initially

formed double sheets to a 3D-network (Figure 1b). A further look at the 1D-chain structure of $\{[\text{Cu}_6\text{I}_4]^{2+}\}_n$ reveals that these μ_6 -bridged iodide ions are at the centers of inversion and bring about the non-superimposing arrangement of the adjoined cluster segments (Figure 1c). As a result, the adjacent individual double sheets in **2** are arranged in an ABAB fashion with a topology of a 'gra' net.¹⁶ Although there are two reports (including that of ours) for isolated cationic rugby-ball shaped clusters (Figure 1e),^{8,16} this could probably be the first instance where a CuI-MOF containing rugby-ball shaped $\{[\text{Cu}_6\text{I}_4]^{2+}\}_n$ 1D-polymer is constructed via the formation of a Zintl-type poly-cationic cluster chain. Further, the ligand amino protons are involved in H-bonding with the solvate DMF oxygen atoms.

The Crystal structure of **3** was solved in the monoclinic space group $P2_1/n$ (Figure 2). The asymmetric unit of this molecule consists of a Cu_4I_4 cluster core, one ligand motif, one coordinated MeCN, three solvate DMFs and three solvate molecules of water. Unusually, the Cu_4I_4 cluster in **3** acts as a three connected node in which three Cu(I) ions are attached to the donor N-sites of the ligand L^3 and the fourth one is coordinated to the MeCN solvent. Concomitantly, each ligand is attached with three cluster motifs and serves as three connected node that leads to a distorted hexagonal 2D-Network. Each of the four iodide ions is found in a μ_3 -bridged mode and each Cu(I) ion is tetrahedral with three I^- and one N-donor contacts. A closer look at the 2D-network reveals that the hexagonal rings are puckered which results in a zig-zag arrangement of the adjacent segment when viewed on to the c-axis. Further, the

Figure 1. (a) Ortep plots at 50% ellipsoid probabilities for the cationic segments of **2**; (b) View of the 3D-MOF assembly of **2** along the c-axis; (c) A small segment of the $\{[\text{Cu}_6\text{I}_4]^{2+}\}_n$ 1D-cluster chain; (d) Crystal packing showing the ABAB type of arrangement of the adjacent double sheets present in **2**. (e) View of the 2D-sheet structure of **1** and its discrete $[\text{Cu}_6\text{I}_5]^+$ cluster core (given for the sake of comparison with **2**).

phosphoryl groups ($\text{P}=\text{O}$) and the coordinated MeCN units are arranged in an anti-conformation above and below the 2D-layer. Of the three ligand amino protons, two of them are engaged in H-bonding with solvated DMFs and the third one with the phosphoryl oxygen atom of the adjacent layer. Topology analysis on **3** gave the ‘hcb’ network represented by the Vertex Symbol [6.6.6].

3.2 Photophysical studies

Photophysical properties of the 2D-MOF **1** were discussed in our previous report.⁸ It exhibits absorption maxima at 345 and 385 nm; the first one, due to the ligand chromophore and the second weak one, due to iodide to ligand charge transfer ($^1\text{XLCT}$) transitions. Interestingly, an unusual ligand assisted

Figure 2. (a) View of the 2D-MOF assembly of **3** along the b-axis; (b) the Cu₄I₄ cluster core; (c) Crystal packing showing the ABAB type of arrangement of the adjacent double sheets present in **3**. These individual sheets are connected *via* donor-acceptor type P-N-H...O=P H-bonding; (d) zig-zag side view of the 2D-sheet in **3**.

Figure 3. (a) Normalized emission spectra of L² and **2** in DMF (λ_{ex} = 320 nm and 350 nm, respectively); inset: (i) identical emission colour of **2** at 298 K and 77 K under the UV-lamp.

thermochromism has been observed for **1**. Thus, it exhibits fluorescence at 410 nm at 298 K due to the self-emission of the AQ moiety of the ligand and phosphorescent emission at 600 nm at 77 K due to triplet cluster centered (³CC) transition which comprises a mixture of halide to metal charge-transfer (³XMCT) and copper centered d → s, p transitions. Inspired by these observations, we examined the photophysical properties of the newly synthesized MOFs **2** and **3**.

The absorption and emission spectra of L² and **2** were recorded in DMF (Figure 3, Figures S3 and S4, in Supporting Information). The absorption spectrum of L² shows a maximum at 285 nm whereas **2** (in DMF suspension) shows an additional peak at 320 nm due to halide to ligand charge transfer transition (¹XLCT) apart from the ligand-centered parent peak at 285 nm. The emission spectrum of L² in DMF shows an intense peak at 360 nm due to the fluorescence band. Interestingly, the emission spectrum of **2** in DMF suspension at room temperature shows a strong LE band at 506 nm indicating a cluster centered (³CC) phosphorescence transition typically observed for Cu₄I₄Py₄ cubane clusters.¹⁷ No appreciable shift in its emission is observed upon lowering the temperature to 77 K except for a broadened emission signature (Figure 3). Similar signatures were also observed when the emission spectrum was recorded in the solid state. The time decay measurements at 298 K and 77 K indicate that the emission at 506 nm is due to phosphorescence with varied τ_{em} values of 0.30 and 67.0 μs , respectively (Figure 4). These values suggest that the origin of this phosphorescent emission is from the ³CC excited state of {[Cu₄I₄]²⁺}_n core. Although it can be presumed that both **1** and **2** can give rise to an HE halide to ligand charge transfer (³XLCT) band below 77 K,¹⁷ lack of very low temperature measurement setup (liquid helium cryostat) precludes such an observation.

Further insight into the photophysical properties of **2** were derived by performing DFT calculations on its

Figure 4. (a) TCSPC decay profiles of L² and 2 at 298 K; (b) at 77K for 2.

Figure 5. Stern-Volmer (SV) plot for complex 1 (4×10^{-5} M) in the presence of various nitro-aromatic analytes (1×10^{-3} M) that shows the selective detection of TNP. Inset: Emission spectra of 1 recorded after sequential addition of TNP and the visual change in the emission colours under UV light upon the addition of 100 μL of TNP (1×10^{-3} M).

Figure 6. Stern-Volmer (SV) plot for complex 2 (5×10^{-5} M) in the presence of various nitro-aromatic analytes (1×10^{-3} M) that shows a preferential detection of TNP. Inset: Emission spectra of 2 recorded after sequential addition of TNP and the visual change in the emission colours under UV light upon the addition of 150 μL of TNP (1×10^{-3} M).

discrete model compound $\{\text{Cu}_6\text{I}_5[(\text{PYNH})\text{H}_2\text{P}=\text{S}]_6\}$ (**2a**) and compared with that of the previously reported⁸ $\{\text{Cu}_6\text{I}_5[(\text{AQNH})\text{H}_2\text{P}=\text{S}]_6\}$ (**1a**). In both of them, the majority of the highest occupied molecular orbitals (HOMOs) are cluster-centered and the lowest unoccupied molecular orbitals (LUMOs) up to LUMO+5 are on the PY (or AQ) chromophore, whereas LUMO+6 are solely based on the cluster. While the energy separation between LUMO+5 and LUMO+6 in **1a** is 1.05 eV (24.29 kcal/mol),⁸ this is much lower in the case of **2a** (0.16 eV = 3.74 kcal/mol) at the S_0 optimized geometry (Figure S5, in Supporting Information). Thus, **1** exhibits a ligand-assisted fluorescent emission at 298 K due to the stabilization of LUMO+5. In contrast, the small energy

separation might populate the cluster based LUMO+6 in **2a** favouring a ³CC phosphorescent emission in **2**. Also, the weakly emitting nature of the PY chromophore does not favour any ligand based thermochromism as observed in the case of **1**. Further, the calculated emission wavelength of 553 nm from the adiabatic S_0 -T gap obtained from the single-point calculations¹⁸ on the optimized triplet geometry of **2a** is in fair agreement with the experimental value of 506 nm observed for **2** (Figure S6, in Supporting Information).

The absorption and emission characteristics of L³ have already been reported by us earlier. It shows an absorption and emission maxima at 330 and 367 nm, respectively, in DMF.¹¹ A similar absorption spectrum

Figure 7. Bar diagram showing the quenching efficiencies of **1** and **2** in the presence of various aromatic analytes.

has been observed for **3**. Although one can expect the emission signatures are similar to those of isolated Cu_4I_4 clusters, exhibiting HE and LE bands, no emission characteristics have been observed for these Cu_4I_4 based cluster MOFs. However, such an observation is not unprecedented as there are many examples for such non-emissive cluster MOFs based on these Cu_4I_4 cores.¹⁹ Nevertheless, it exhibits weak emission signatures due to the ligand AQ chromophore at 370 nm.

3.3 Sensing studies for nitro aromatic compounds

Spurred by the excellent concentration-dependent ratio-metric turn-on selective fluorescence detection of picric acid by L^3 ,^{11a} we intend to probe the sensing behaviour of the emissive cluster MOFs **1** and **2**. By looking at the flat and ordered aromatic surfaces of these MOFs, we were curious to explore their utility in sensing explosive nitro-aromatic compounds. Since the MOFs **1** and **2** possess electron-rich ligand and cluster centers and exhibit emission signatures from the different excited states, we thought that their interaction with electron-deficient nitro-aromatics would bring about selective turn-on detection for nitro analytes in general and picric acid (TNP) in particular. Especially we expected that for **1**, the ligand-centered emission might be quenched with the concomitant appearance of the cluster-centered (^3CC) emission due to the cluster core upon addition of TNP at room temperature. Thus, we performed titrations with various aromatic analytes such as nitrobenzene

(NB), 4-nitrotoluene (NT), 1,3-dinitrobenzene (DNB), 2,4-dinitrotoluene (DNT), 1,3,5-trinitrotoluene (TNT) and picric acid (TNP) with **1** and **2**, respectively, at room temperature (Figures 5 and 6). In a typical experiment, a 10^{-5} M solution of the substrate is titrated with a 10^{-3} M solution of the explosive analyte and the emission intensities were recorded for every 5 μL addition. For each of these experiments, a maximum of about 50 μL of the analyte was added and quenching of the emission intensities were monitored at 420 nm for **1** and at 506 nm for **2**, respectively (Figures S7 and S8, Supporting Information).

Figure 7 summarizes the data for various analytes. It is apparent that both **1** (75%) and **2** (55%) show maximum quenching for TNP. For the other six analytes, the MOF **2** shows a moderate quenching of about 35 and 25% for 4-NP and 1,3-DNB. Thus, it is apparent that the MOF **1** did not show the expected turn-on sensing for TNP, presumably due to the quenching of its absorbed energy (energy transfer to TNP) by a non-radiative pathway. However, the MOF **1** reveals a better selectivity for TNP and exhibits almost negligible quenching effect ($< 10\%$) for the rest of them. TNP being a stronger Brønsted and Lewis acid, compared to the other nitro-aromatics under study, has a strong tendency towards electrons. Since the cluster-MOFs **1** and **2** contain hydroxide counter anions, TNP strongly interacts with the hydroxide ions through its acidic protons while it can act as H-bond acceptor from the ligand N-H protons. Additionally, the free hydroxide ion can also interact with the nitro groups of the picric acid. Thus, the selective quenching by TNP over other nitroaromatics can presumably be due to its cumulative interactions with the various components of these MOFs (Figure 8) and thereby accepting the electronic charge from the excited states of these complexes (**1** and **2**) and quenching their luminescence. Though the ligand N-donor sites can also involve in strong interactions with the acidic protons of the TNP, their rigid coordination with Cu(I) ions may not facilitate such N_{donor} -TNP interactions. Whereas, for the analytes which do not possess the H-bonding acceptor sites, the extent of their stacking interactions ($\pi \dots \pi$) with the aromatic surfaces of MOFs (**1** or **2**) vary by only a small margin and results in negligible or moderate quenching of luminescence. Further, the DFT-computed energies of the LUMO orbitals in the model compound $\{\text{Cu}_6\text{I}_5[(\text{AQNH})\text{H}_2\text{P}=\text{S}]_6\}$, **1a** (-3.84 eV)⁸ are very close to that of TNP (-3.89 eV).⁹ Hence, there could be a better interaction between them in the excited states in comparison with other nitro-aromatic compounds favouring the electron transfer from the MOFs to the analyte.²⁰

Figure 8. Schematic representation showing the possible modes of interaction of picric acid with **1** leading to the quenching of its luminescence at room temperature.

4. Conclusions

In summary, we have shown that tridentate ligands based on thiophosphoramidate backbone offer C_3 -symmetric platforms for obtaining rugby-ball shaped cationic and cuboidal shaped neutral CuI cluster MOFs **1**, **2** and **3**. The MOFs **1** and **2** containing the cationic clusters were highly luminescent, whereas **3** do not show any luminescence. The MOF **1** shows thermochromism as it exhibits a ligand centered fluorescent emission at 298 K and cluster centered phosphorescence at 77 K. Interestingly, **2** exhibits a single phosphorescence emission peak at both 298 and 77 K due to the 3CC -excited state of the cluster. Sensing studies on **1** and **2** for the detection of nitroaromatic analytes showed a very high preference for picric

acid over other non-phenolic compounds. The selective detection of picric acid by the MOFs **1** and **2** pave the way for developing new low-cost sensors based on luminescent CuI materials.

Supplementary Information (SI)

Crystal data for the compounds are deposited at the Cambridge crystallographic data centre with the CCDC numbers 968378 and 1536151 and can be obtained via www.ccdc.cam.ac.uk/data_request/cif. Tables of bond lengths and angles, H-bonding table, TGA graphs, additional figures for absorption, excitation and emission data, emission titration plots for nitroaromatic analytes are available in Supplementary Information at www.ias.ac.in/chemsci.

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