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Excimer and exciplex formation in a pair of bright phosphorescent isomers constructed from $\text{Cu}_3(\text{pyrazolate})_3$ and Cu_3I_3 coordination luminophores†

Shun-Ze Zhan,^a Mian Li,^a Xiao-Ping Zhou,^a Dan Li^{*a} and Seik Weng Ng^b

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Reported herein are a pair of supramolecular *pseudo*-isomers, namely, $(\text{Cu}_3\text{I}_3)(\text{Cu}_3\text{L}_3)_2 \cdot \text{H}_2\text{O}$ (**1**) and $(\text{Cu}_3\text{I}_3)(\text{Cu}_3\text{L}_3)_2$ (**2**) ($\text{L} = 3$ -(4-pyridyl)-5-isobutyl-pyrazolate), both of which incorporate Cu_3Pz_3 ($\text{Pz} = \text{pyrazolate}$) and Cu_3I_3 clusters as luminophores. The two complexes show distinct yellow (570 nm) and orange (638 nm) emissions, which are ascribed to the formation of the excimer and exciplex involving the same or different copper(I)-cluster-based luminophores.

In the increasingly important field of the photofunctional d^{10} metal complexes,¹ the cyclic, trinuclear coinage-metal (Cu, Ag and Au) complexes have garnered considerable interest owing to their fundamental and applied potentials in the areas of metalloaromaticity, metallophilic and excimeric bonding, host/guest chemistry, and metal–organic optoelectronics.^{2–6} These applications have to link to the π -acid/base property of the metal cyclotrimers that leads to the formation of extended binary stacking, and more specifically, to the formation of an excimer and exciplex when photoluminescence is present.^{3,5,6}

Omary and coworkers once computationally assessed the π -acidity/basicity of M_3Pz_3 ($\text{M} = \text{Cu, Ag or Au}$),^{3a} and indeed experimentally implemented the manipulation of their π -acidity/basicity *via* multiple cooperative supramolecular interactions, warranting their luminescence tuning and sensing functions.^{3b,c,d} Our group has been investigating the structural and luminescent features of copper(I) cluster-based oligomers and polymers—particular attention has been paid to copper(I)-pyrazolates^{4,5,7} and copper(I)-halide⁸ complexes. In an attempt to combine these two entities for generating multi-emissive materials, in a recently embarked project we have realized that Cu_3Pz_3 and Cu_nI_n may be complementary in the consideration of their π -acidity/basicity. On one hand, both Cu_3Pz_3 and Cu_nI_n are neutral and can be readily formed; this means that an extra electrostatic effect and additional

charge balance can be excluded when inter-cluster (between the same or different clusters) interplay occurs. On the other hand, the planar Cu_3Pz_3 motif exhibits weak π -acidity^{2b,3a,6b} and is usually subject to perpendicular supramolecular interactions such as $\text{Cu} \cdots \text{Cu}$ and $[\text{Cu}_3\text{Pz}_3] \cdots \text{halide}$ forces, *etc.*,^{2–6} whereas in Cu_nI_n aggregates there exist both electron-donor (*i.e.* iodide ions with lone pair electrons) and electron-acceptor (*i.e.* copper(I) ions with vacant coordination sites) regions that, respectively, cope with Lewis acids and bases.⁸ Furthermore, both Cu_3Pz_3 and Cu_nI_n clusters are renowned coordination luminophores whose intense, low-energy and long-lived phosphorescence originates from cuprophilic interaction based triplet excited states.^{1,8} Therefore, coupling these two luminophores may facilitate the formation of an excimer and exciplex, and generate interesting multi-emissions.

In this work, by introducing a new pyridyl-pyrazole ligand,^{4b,5b,7} namely, 3-(4-pyridyl)-5-isobutyl-1*H*-pyrazole (HL), to react with CuI under solvothermal conditions (see ESI† for experimental details), a pair of supramolecular *pseudo*-isomers,⁹ namely, $(\text{Cu}_3\text{I}_3)(\text{Cu}_3\text{L}_3)_2 \cdot \text{H}_2\text{O}$ (**1**) and $(\text{Cu}_3\text{I}_3)(\text{Cu}_3\text{L}_3)_2$ (**2**), are yielded simultaneously. They can be mechanically separated as bright yellow block crystals for **1** and light yellow column crystals for **2** through naked eyes under natural light. Interestingly, under UV-lamp irradiation, **1** and **2** are visually distinguishable, showing bright yellow and orange colours, respectively (Fig. S4 in ESI†).

X-Ray crystallographic analysis (see ESI†) reveals the structures of **1** and **2** are closely related: they both crystallize in $P\bar{1}$ space group with a similar chemical composition, and both contain Cu_3Pz_3 and Cu_3I_3 units that are connected *via* $\text{Cu}-\text{N}_{\text{pyridyl}}$ bonds (Fig. 1), surrounded by different supramolecular interactions (Fig. 2). The Cu_3Pz_3 triangles in both **1** and **2** are slightly deviated from its observed planar arrangement,^{2,5a,6c} due to the cooperative multiple interactions surrounded. The Cu_3I_3 aggregates exhibit an unusual six-membered cyclic array with alternating copper and iodide sites, leaving both the Cu and I sites unoccupied and exposed for further interactions. According to our review on copper(I) halide aggregates^{8a} and the survey in the latest version of the Cambridge Structural Database (CSD),^{10a} among a few reports of neutral Cu_3I_3 aggregates, only one such cyclic Cu_3I_3 array was documented.^{10b}

As shown in Fig. 1, the linkages of Cu_3Pz_3 and Cu_3I_3 units in **1** and **2** are subtly different. The pyridyl groups are arranged asymmetrically around the Cu_3Pz_3 periphery, and two of the three

^aDepartment of Chemistry, Shantou University, Guangdong, 515063, P. R. China. E-mail: dli@stu.edu.cn

^bDepartment of Chemistry, University of Malaya, Kuala Lumpur, 50603, Malaysia

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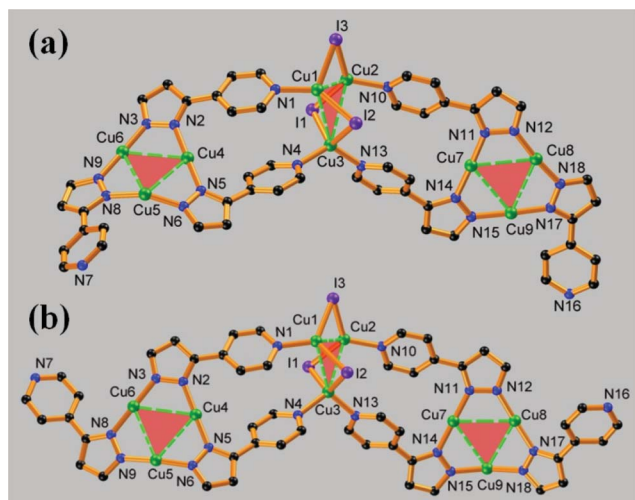


Fig. 1 Asymmetric units of **1** (a) and **2** (b), showing different connecting orientation between Cu_3Pz_3 and Cu_3I_3 units. All H atoms, isobutyl groups and crystallized water molecules are omitted for clarity. Color codes: C in black, N in blue, Cu in green and I in purple.

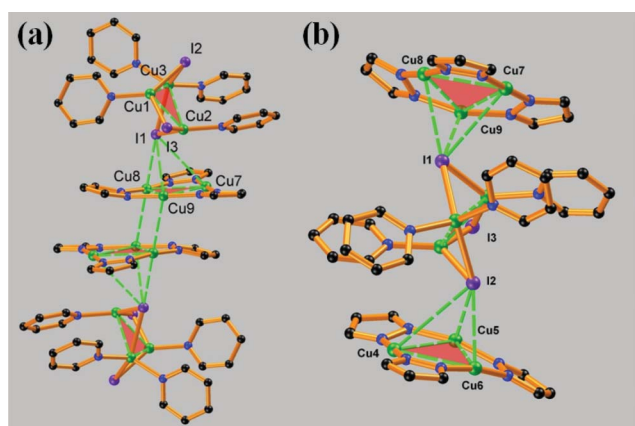


Fig. 2 Partial views of the structures of **1** (a) and **2** (b), showing the formation of $[\text{Cu}_3\text{Pz}_3]_2$ excimer in **1** and $[\text{Cu}_3\text{Pz}_3-\text{Cu}_3\text{I}_3]$ exciplex in both **1** and **2**. The $\text{Cu}\cdots\text{Cu}$ and $\text{Cu}\cdots\text{I}$ interactions are depicted as green dashed bonds. Color codes: C in black, N in blue, Cu in green and I in purple.

pyridyl groups attached the same Cu_3Pz_3 unit point to the same direction and link with a Cu_3I_3 unit, which is supported by two symmetry-independent Cu_3Pz_3 through a total of four binding pyridyl groups. In both **1** and **2**, Cu1 and Cu2 ions show planar triangular geometry and Cu3 ion adopts tetrahedral geometry, all completed by μ_2 -bridging iodide ions in addition to pyridyl coordination. Notably, the orientations of the third pyridyl groups in the coordination environments of **1** and **2** are different: in **1** it orients toward the vector of $\text{I}3\rightarrow\text{Cu}3$ whereas in **2** the case is reversed, exhibiting “M” (Fig. 1a) and “W” (Fig. 1b) shapes for the fragments, respectively. Such arrangements result into the remarkably different extended structures of **1** and **2**.

In complex **1**, the asymmetric units are connected *via* N16–Cu5 bonds to form a 1-D coordination polymer¹¹ with a head-to-tail fashion (Fig. S5a in ESI†). The third vacant pyridyl group (N16, Fig. 1a) attached to one Cu_3Pz_3 unit coordinates to one copper(I) ion (Cu5) from another Cu_3Pz_3 unit in neighbouring asymmetric unit,

while its counterpart in the same asymmetric unit, another pyridyl group (N7), forms a hydrogen bond with one of the hydrogen atoms from crystallized water molecule (Table S4, Fig. S7a and S7b, and *Hydrogen bonds discussion* in ESI†). The distance of this linking N16–Cu5 bond is 2.120(5) Å, slightly larger than the normal value, and the bond angle of N6–Cu5–N8 is 152.1(2)°, causing the distortion of the locating Cu_3Pz_3 triangle (Cu4–Cu5–Cu6). Two adjacent 1-D chains are attracted to each other through an intertrimeric $\text{Cu}\cdots\text{Cu}$ interaction between another type of Cu_3Pz_3 triangle (Cu7–Cu8–Cu9, Fig. 2a and Fig. S5b in ESI†), ones that show relatively planar features to warrant an eximeric dimerization with a chair stacking conformation.^{2c,5} The $\text{Cu}\cdots\text{Cu}$ distance is 2.9867(10) Å, comparable with those in similar dimer of trimers of $\{[3,5\text{-}(\text{Me})_2\text{Pz}]\text{Cu}\}_3$ and $\{[3,5\text{-}(i\text{-Pr})_2\text{Pz}]\text{Cu}\}_3$,^{2,4} indicating a strong cuprophilic interaction and the formation of a $[\text{Cu}_3\text{Pz}_3]_2$ excimer. Additionally, careful examination reveals these dimers are further capped from both top and bottom by I1 ions from Cu_3I_3 units, forming typical π -acidic $[\text{Cu}_3\text{Pz}_3]\cdots\text{I}$ supramolecular interaction (Fig. 2a and Fig. S5c in ESI†). The distances between the Cu and I ions in this $[\text{Cu}_3\text{Pz}_3]\cdots\text{I}$ force range from 3.35 to 3.85 Å, slightly longer than those reported.^{6b} These centrosymmetric Cu_3I_3 – Cu_3Pz_3 – Cu_3Pz_3 – Cu_3I_3 arrangements extend the 1-D chains to 2-D layers paralleling the *ab* crystallographic plane (Fig. S5c in ESI†).

In contrast, in complex **2** the N16–Cu5 coordination bond sustaining 1-D polymeric structure of **1** is not formed, and hence **2** is a 0-D oligomer with one asymmetric unit as a whole molecule. There are two dangling pyridyl group (N7 and N16, Fig. 1b) left, meaning both Cu_3Pz_3 triangles in a molecule are relatively planar (N–Cu–N bond angles range from 161.4 to 178.8°) without further coordination. Only N17 atom weakly binds to H49(C49) atom from another coordination molecule to form a hydrogen bond (Table S4, Fig. S7c, and *Hydrogen bonds discussion* in ESI†). However, no $[\text{Cu}_3\text{Pz}_3]_2$ dimer of trimers is found in **2**; instead, the supramolecular π -acidic $[\text{Cu}_3\text{Pz}_3]\cdots\text{I}$ interaction dominates the stacking of these oligomers, forming 1-D supramolecular chains along the *c* axis (Fig. 2b and Fig. S6 in ESI†). All Cu_3Pz_3 triangles (both Cu4–Cu5–Cu6 and Cu7–Cu8–Cu9) are subject to a $[\text{Cu}_3\text{Pz}_3]\cdots\text{I}$ interaction, with corresponding $\text{Cu}\cdots\text{I}$ distances ranging from 3.16 to 3.90 Å, shorter than those found in **1**, suggesting a stronger π -acidic $[\text{Cu}_3\text{Pz}_3]\cdots\text{I}$ attraction (see Table S3 in ESI†). Given that in **2** the existence of the $[\text{Cu}_3\text{Pz}_3]\cdots\text{I}$ force overwhelms the formation of the $\text{Cu}\cdots\text{Cu}$ interaction, and **2** emits at even lower energy than **1** (discussed below), the formation of the $[\text{Cu}_3\text{Pz}_3-\text{Cu}_3\text{I}_3]$ exciplex, existing in both **1** and **2**, is speculated.^{3,6}

This pair of concomitant supramolecular *pseudo*-isomers exhibit diverse luminescence properties. Their emissive colours are distinguishable by naked eyes under UV lamp at room temperature, being bright yellow (**1**) and orange (**2**), respectively (Fig. 3 inset photographs and Fig. S4 in ESI†). Upon excitation at 380 nm (Fig. S12a in ESI†), complex **1** shows a yellow emission with a maximum at 570 nm (Fig. 3a). The emission spectrum presents broad tailing, implying the possible coupling of a weaker, lower-energy band, which exists at all measured temperatures (Fig. S9 in ESI†). The Gaussian fitting is applied to these spectral bands (Fig. S8 in ESI†), giving, *e.g.* at 298 K, two Gaussian peaks (562 and 625 nm, $R^2 = 0.9908$; $\chi^2 = 1.04 \times 10^{-3}$, Fig. 3a). When cooling down to 30 K, the emission intensity drastically increases (Fig. S9a in ESI†),

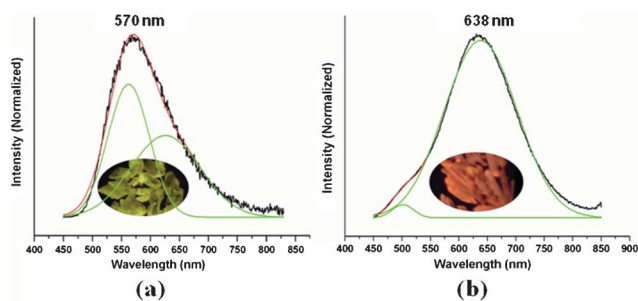


Fig. 3 Solid-state photoluminescence spectra of **1** (a) and **2** (b) at room temperature (black) and their Gaussian fitting profiles (red and green). The inset photograph shows the visual colours of the crystals under a UV lamp with a wavelength maximum of 365 nm.

especially in the range from 250 K to 200 K, and the emission peak shows a slight red shift of about 20 nm (Fig. S9b in ESI†). The decay profile fits well with a monoexponential curve at room temperature, with the lifetime being 10.34 μ s (Fig. S13a in ESI†).

Complex **2** presents an orange emission with a maximum at 638 nm (Fig. 3b) upon excitation at 380 nm (Fig. S12b in ESI†). Compared with that of **1**, the emission spectra of **2** show more regular single Gaussian bands at all measured temperatures (Fig. S11 in ESI†), but with a small shoulder at the higher-energy region. The Gaussian fitting curves (Fig. S10 in ESI†) indicate, e.g. at 298 K, the emission band can be fitted into two Gaussian peaks (501 and 638 nm, $R^2 = 0.9943$; $\chi^2 = 6.1 \times 10^{-4}$, Fig. 3b). When lowering the temperature down to 30 K, the emission intensity increases gradually (Fig. S11a in ESI†), and the peak is also red shifted by about 12 nm at 50 K (Fig. S11b in ESI†). Also the decay profile is similar, being monoexponential at 298 K and with a lifetime of 10.75 μ s (Fig. S13b in ESI†).

The photoluminescence behaviors and origins can be rationalized in light of the above spectral data. The μ s scale lifetimes indicate phosphorescence, consistent with the assignment of the copper(I) based triplet excited states. Several rational statements can be made: i) the emission band of **1** is separated into 562 and 625 nm; the former can be clearly assigned to the $[\text{Cu}_3\text{Pz}_3]_2$ excimer,^{2,4,5} whereas the latter coincides with the major peak of 638 nm for **2**, and hence is assigned to the $[\text{Cu}_3\text{Pz}_3\text{-Cu}_3\text{I}_3]$ exciplex, which can be structurally identified in both **1** and **2**. ii) The slight red shift (ca. 13 nm) of the exciplex band for **2** (638 nm, compared with 625 nm for **1**) corresponds to shorter (ca. 0.2 Å for the shortest distance) and stronger $[\text{Cu}_3\text{Pz}_3]\cdots\text{I}$ contacts than those of **1**. iii) Under cryogenic conditions, the increment of emission intensity is due to the reduction of non-irradiation decay processes, and the slight red shifts are reasonable because of lattice contraction, and thus the enhancement of $\text{Cu}\cdots\text{Cu}$ and $[\text{Cu}_3\text{Pz}_3]\cdots\text{I}$ interactions. The origin of the minor shoulder of 501 nm for **2** is unclear at this stage.

In conclusion, we have obtained two concomitant supramolecular pseudo-isomers based on copper(I) and a new pyridyl-pyrazole

ligand. In both complexes, the renowned Cu_3Pz_3 and the unusual Cu_3I_3 coordination luminophores are involved, which are found to be interactive with each other, forming a $[\text{Cu}_3\text{Pz}_3]_2$ excimer and $[\text{Cu}_3\text{Pz}_3\text{-Cu}_3\text{I}_3]$ exciplex, by taking advantage of the π -acidity of the Cu_3Pz_3 triangle. These structural features give rise to their distinct phosphorescence properties, showing readily distinguishable bright yellow and orange emissions, respectively.

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