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# Novel Thermochromism Relating to Supramolecular Cuprophilic Interaction: Design, Synthesis, and Luminescence of Copper(I) Pyrazolate Trimer and Polymer

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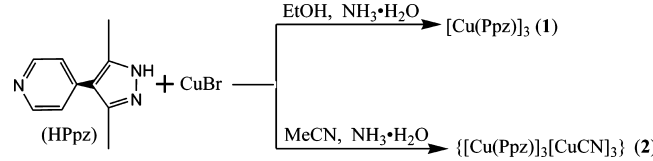
Solvothermal reactions of 4-(pyrid-4′-yl)-3,5-dimethylpyrazole (HPpz) with CuBr in two mixed solvents, $NH_3 \cdot H_2O$/EtOH and $NH_3 \cdot H_2O$/MeCN, afforded respectively a copper(I) trimer, $[Cu(Ppz)]_3$ (**1**), and a polymer, $\{[Cu(Ppz)]_3[CuCN]_3\}$ (**2**), both containing the $[Cu(Ppz)]_3$ entity as a building block. The products were found to be photoluminescent and, more interestingly, when cooled from room temperature to 10 K, they showed a blue shift followed by a red shift (hereafter shortened to a red-after-blue shift) of emission.

Recently, the triangular $M_3L_3$ (M = Cu, Ag, Au) complexes have received extensive attention because of their rich stacking modes in the crystal lattice and their fascinating optical properties.[1,2] Especially, those containing the trinuclear copper(I) pyrazolate as the coordination center, for their cheap cost and peculiar photoresponse, have received the most attention.[2] The systems are structurally identified, including a stable nine-membered $Cu_3N_6$ ring and, in crystal packing, showing supra- and intermolecular cuprophilic interactions. It has been proven that the tricopper center of complexes is responsible for the solid luminescence. For example, Dias et al.,[2] on the basis of a photophysical study on $[Cu(3\text{-R}, 5\text{-R}'\text{-pz})]_3$ (**Cu₃**; R, R′ = $CH_3$, $CF_3$, Ph, i-Pr; pz = pyrazole), discovered an intriguing luminescence chromism of these species with variation of the temperature, solvent, and solution concentration. Mechanistically, they attributed this to a complex effect of reaction conditions on the cuprophilic interactions.

**Scheme 1.** Synthetic Strategy of **1** and **2**




However, so far, the bulk of the studies have mainly focused on the 0D oligomers, leaving the 3D coordination polymer based on the **M₃** unit much less developed.[3] In a rare effort, we reported previously a **Cu₃**-based luminescent metal−organic framework (MOF),[3a] therein illustrating a synthetic strategy by introducing a **Cu₃** motif as a functional carrier to construct the photoluminescent MOF. To carry forward this strategy, the work used a pyridine-functionalized pyrazole, 4-(pyrid-4′-yl)-3,5-dimethylpyrazole (HPpz),[4] as the ligand to react with CuBr in two different solvent conditions (Scheme 1). Consequently, a **Cu₃**-centered trimer $[Cu(Ppz)]_3$ (**1**) and a trimer-based polymer $\{[Cu(Ppz)]_3[CuCN]_3\}$ (**2**) were obtained. The complexes, as expected, are luminescent. However, surprisingly, when the samples were cooled from room temperature to 10 K, they showed a red-after-blue shift of emission, which had never been documented before. Herein, we demonstrate the novelty of **1** and **2** by describing their syntheses, crystal structures, and variable-temperature solid luminescence.

**1** was obtained as yellow air-stable crystals from heating of a EtOH/$NH_3 \cdot H_2O$ solution of HPpz and CuBr (see the

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(1) (a) For examples, see: Balch, A. L.; Olmstead, M. M.; Vickery, J. C. *Inorg. Chem.* **1999**, *38*, 3494–3499. (b) Olmstead, M. M.; Jiang, F.; Attar, S.; Balch, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 3260–3267. (c) Hayashi, A.; Olmstead, M. M.; Attar, S.; Balch, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 5791–5795. (d) Singh, K.; Long, J. R.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997**, *119*, 2942–2943. (e) Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179. (f) Wang, X.-L.; Qin, C.; Wang, E.-B.; Su, Z.-M.; Li, Y.-G.; Xu, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 7411–7414.

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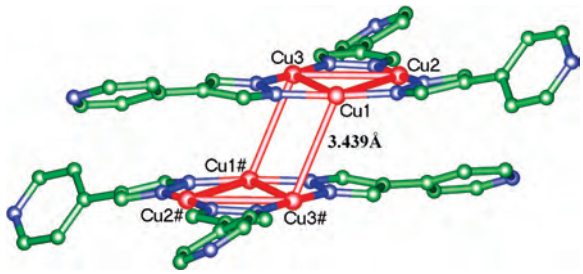


**Figure 1.** Perspective drawing of a dimeric $\{[Cu(Ppz)]_3\}_2$, showing its stagger assembly and the intra- and inter-**Cu$_3$** cuprophilic interactions (red stick). Color code: Cu, red; N, blue; C, green. The methyl groups on the pyrazole rings and all of H atoms are omitted for clarity. Symmetry code: $-x, -y, 2 - z$.

Supporting Information). X-ray diffraction[5] revealed a 0D trimer, featuring a **Cu$_3$** core embraced by three peripheral pyridyls (Figure S1 in the Supporting Information) that are potentially capable of binding more metal ions. The central $Cu_3N_6$ ring of **1** is nearly coplanar with a mean deviation of 0.0393Å, in which the $Cu^I$ ions are separated by 3.172−3.230 Å, very close to those of the known **Cu$_3$**-based complexes.[2] In the crystal lattice, the molecules of **1** are stacked in pairs (Figure 1), giving a short inter-**Cu$_3$** Cu···Cu distance (3.439 Å), smaller than those of Cu[3-$(CF_3)$,5-(Me)pz]$_3$ and Cu[3,5-$(CF_3)_2$pz]$_3$,[2] and so suggesting an intermolecular cuprophilic interaction. On the other hand, the Cu···Cu distance of **1**, compared with those of $\{Cu[3,5\text{-}(Me)_2pz]_3$ and Cu[3-$(CF_3)$pz]$_3$,[2] is remarkably longer, suggesting a repulsion among the pyridyls on the paired trimers. In view of crystal engineering, these facts imply that tuning the intertrimer Cu···Cu separation and further the emission property of a MOF by changing the substituent on the pyrazole ring is possible.

**2** resulted from a reaction of HPpz with CuBr in MeCN/$NH_3 \cdot H_2O$. Using acetonitrile as a solvent led to the involvement of $CN^-$, in situ generated from the C−C bond split of MeCN,[6] as a building block in the construction of **2**. Interestingly, the CN-enabled architecture also contained $[Cu(Ppz)]_3$ units, each as a tritopic metalloligand, binding three $Cu^I$ atoms (Cu3, Cu3A, and Cu4; Figure S1 in the Supporting Information). The trimer, like **1**, also includes a quasi-planar $Cu_3N_6$ ring with a mean deviation of 0.0555 Å and shows the intra-**Cu$_3$** cuprophilic interactions guaranteed by the Cu···Cu distances (3.249 and 3.128 Å). The resemblance of the $[Cu(Ppz)]_3$ unit in **2** to that in **1** suggests

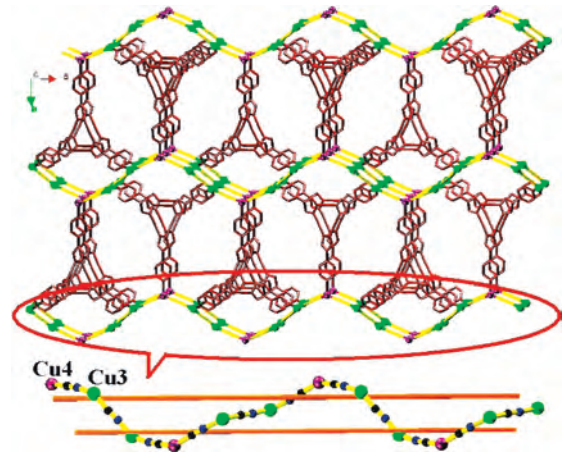


**Figure 2.** Presentation of a single porous network of **2** constructed from $[Cu(Ppz)]_3$ units and $[CuCN]_n$ chains. Methyl and H atoms are omitted for clarity. Color code: brown, $[Cu(Ppz)]_3$ unit; black: C; blue: N.

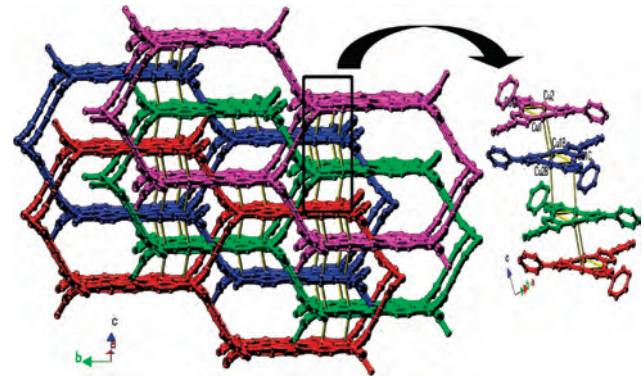

**Figure 3.** 4-fold interpenetration network of **2** with the $[\mathbf{Cu_3}]_n$ chains formed by internet cuprophilic interactions (Cu···Cu = 3.317 Å).

a stability of the Cu−pz configuration, which promises the feasibility of predesigning the **Cu$_3$** motif and introducing it as a functional carrier into a MOF.

Under the direction of $[Cu(Ppz)]_3$ units, the Cu−CN combination in **2** gives the twist-drill polymeric chains (Figure 2), in which the cyanides act as bitopic linkers, each connecting two $Cu^I$ atoms, and Cu3 and Cu4 are coordinated by a $N_{py}$ and two $X_{CN}$ (X = C/N) atoms. Incorporation of the $[Cu(Ppz)]_3$ units and the $[CuCN]_n$ chains generates a porous 3D framework, presenting hexameric loops, sized as 12 Å × 18 Å, and decameric loops, sized as 10 Å × 28 Å (Figure S2 in the Supporting Information). When the Cu3 and Cu4 atoms and $[Cu(Ppz)]_3$ entities are denoted as three-connected nodes and the CN−Cu and $N_{py}$−Cu bonds as linkers, the framework of **2** is reduced to a binodal $(6^2\cdot10)_2(6\cdot10^2)$ topologized network, similar to the one we reported previously.[3a,7] The large voids in the framework of **2** results in a 4-fold interpenetration, illustrated in Figure 3. In the [2 + 2] entanglement[8] of networks, the two equivalents in a set are related by a translation vector, [1, 0,

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(5) Crystal data for **1**: $C_{30}H_{30}Cu_3N_9$, $M_r = 707.28$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.483(6)$ Å, $b = 11.730(6)$ Å, $c = 11.891(6)$ Å, $\alpha = 88.584(9)°$, $\beta = 84.357(9)°$, $\gamma = 89.888(9)°$, $V = 1454.7(13)$ Å$^3$, $Z = 2$, $D_c = 1.615$ g cm$^{-3}$, $F(000) = 720$, $\mu = 2.211$ mm$^{-1}$, 12 526 reflections collected, 6500 unique ($R_{int} = 0.0195$), final R1 = 0.0547, wR2 = 0.1068, $S = 1.004$ for all data. Crystal data for **2**: $C_{33}H_{30}Cu_6N_{12}$, $M_r = 975.99$, monoclinic, space group $C2/c$ (No. 15), $a = 24.561(4)$ Å, $b = 20.118(3)$ Å, $c = 8.0845(12)$ Å, $\beta = 106.176(2)°$, $V = 3836.6(10)$ Å$^3$, $Z = 4$, $D_c = 1.690$ g cm$^{-3}$, $F(000) = 1944$, $\mu = 3.306$ mm$^{-1}$, 9980 reflections collected, 3377 unique ($R_{int} = 0.0327$), final R1 = 0.0686, wR2 = 0.1393, $S = 1.171$ for all data. Data collections ($2\theta \leq 56°$) were performed on a Bruker Smart Apex CCD diffractometer (Mo K$\alpha$, $\lambda = 0.710\,73$ Å) at $T = 298(2)$ K using SMART.

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(7) The first Schlafli symbol of $(6^2\cdot10)_2(6\cdot10^2)$ topology of **2** is for the $[Cu(Ppz)]_3$ unit and the Cu4 atom and the second for the Cu3 atom. Friedrichs, O. D.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr., Sect. A* **2003**, *59*, 22.

(8) (a) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *Chem.—Eur. J.* **2002**, *8*, 1519. (b) Wang, X.-L.; Qin, C.; Wang, E.-B.; Su, Z.-M. *Chem.—Eur. J.* **2006**, *12*, 2680–2691.

0] (24.561 Å), and those belonging to different sets are reachable by each other via a displacement of [$^1/_2$, $^1/_2$, 0] (15.874 Å) (Figure S3 in the Supporting Information). Noteworthy is the fact that the inter-**Cu$_3$** Cu···Cu distance of **2** (3.317 Å) is even shorter than that of **1**, which suggests a domination of cuprophilicity over the network organization.

For both containing the intrinsic luminophor **Cu$_3$**, **1** and **2** are photoemissive when irradiated by UV rays at room temperature, emitting a bright green light. Especially, upon excitation by 300 nm, **1** exhibits an asymmetric band with $\lambda_{max}$ = 564 nm (Figure S5 in the Supporting Information). The broad band symbolizes a contour of multiple emissions, arising from triplet metal-centered excited states. The assumption is confirmed by the conformity of the band with two Gaussian peaks (505 and 569 nm) ($R^2 = 0.9925$; $\chi^2 = 9.9 \times 10^{-4}$). The band of **1** is similar to that of [Cu(3,5-(Me)$_2$pz)]$_3$.[2a] However, in comparison, its $\lambda_{max}$ has a hypsochromic shift from the latter (656 nm), and likely for **1**, it has a longer intermolecular Cu···Cu contact (3.439 Å) than the reference (2.946 Å).[9]

When excited by 360 nm, **2** also demonstrates an asymmetric band with higher energy ($\lambda_{max}$ = 494 nm) than that of **1**. Accordingly, the band is attributed to metal-centered emissions. A Gaussian fitting gave a fine accord of this band with a mix of high-energy (HE; 492 nm) and low-energy (LE; 548 nm) bands ($R^2 = 0.9891$; $\chi^2 = 1.12 \times 10^{-3}$). With regards to the blue shift of **2** from **1**, a tentative explanation is that the rigidity of the framework of **2** restrains the distortion of excimers,[10] *[**Cu$_3$**]$_n$, and thus leads to a smaller Stokes' shift (7530 cm$^{-1}$) than that for **1** (15 600 cm$^{-1}$).

More surprisingly, upon cooling of the solids of **1** and **2**, both showed a novel chromism, described by the curves in Figure 4 (for more details, see Figures S6 and S7 in the Supporting Information). In particular, as **1** is cooled from room temperature to 150 K, its color changes from yellow-green ($\lambda_{max}$ = 564 nm) to green ($\lambda_{max}$ = 505 nm), and as it is further cooled to 10 K, it turns back to yellow-green ($\lambda_{max}$ = 555 nm). Also, in the same cooling scheme, the color of **2** changes first from green ($\lambda_{max}$ = 494 nm) to bluish-green ($\lambda_{max}$ = 486 nm) and then back to green ($\lambda_{max}$ = 498 nm).

Although the unilateral blue[2,11] and red[13] emission shifts of **M$_3$** species with cooling have been well established, the two-directional emission change demonstrated here, to the best of our knowledge, has never been reported. Concerning the red shift of similar **Au$_3$** species,[13] Burini and his coworkers ascribed it to a cooling-induced cell contraction, a process that enhances the M···M interaction. However, concerning the cooling-induced blue shifts of **Cu$_3$** species,[2] Dias et al. ruled out the possibility that they are caused exclusively by the lattice contraction; instead, he suggested,

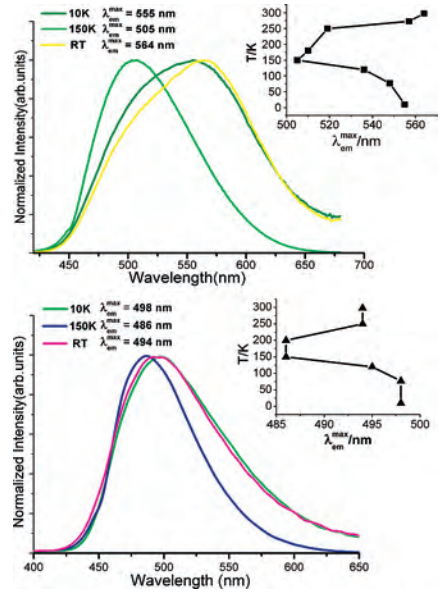


**Figure 4.** Solid emission spectra of **1** (top) and **2** (bottom) at three different temperatures (10 and 150 K and room temperature). Inset: $\lambda_{max}$ of **1** and **2** changing with temperature from room temperature to 10 K.

based on the theoretical calculations and the crystal facts of a time-resolved X-ray diffraction analysis,[12] that the chromism is subject to the structural changes of the multiplex excimer. In light of the elegant studies, we can assume the red-after-blue shift to be an effect of two competitive effects that are the contraction of the crystal and the thermal-dominated distortion of excited states. In the range of high temperature, the latter is possibly dominant and so the cooling led to a blue shift of emission, and in the low-temperature range, the former is more prominent, leading to a red shift.

However, it is seen in Figure 1 that the migration of the emission band of **1** with temperature is more dramatic than that of **2**. This is possibly because of the reason, mentioned above, that the more rigid framework of **2** restrains concurrently the volume reduction of the crystal and the distortion of the excimers.

Of course, a persuasive elucidation of the novel thermochromism needs more evidence. Currently, in-depth work is in progress. Anyways, isolation of two new complexes illustrates vividly a strategy using a designed tectonic motif as the functional carrier to fabricate the MOFs with the desired bulk performance. Moreover, the novel luminescence chromisms of **1** and **2** reveal first a profound effect of the temperature on the cuprophilic interactions and photoluminescence of the complexes.

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**Supporting Information Available:** Crystallographic data in CIF format, additional structural plots, X-ray powder diffraction, and solid luminescence spectra at low temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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