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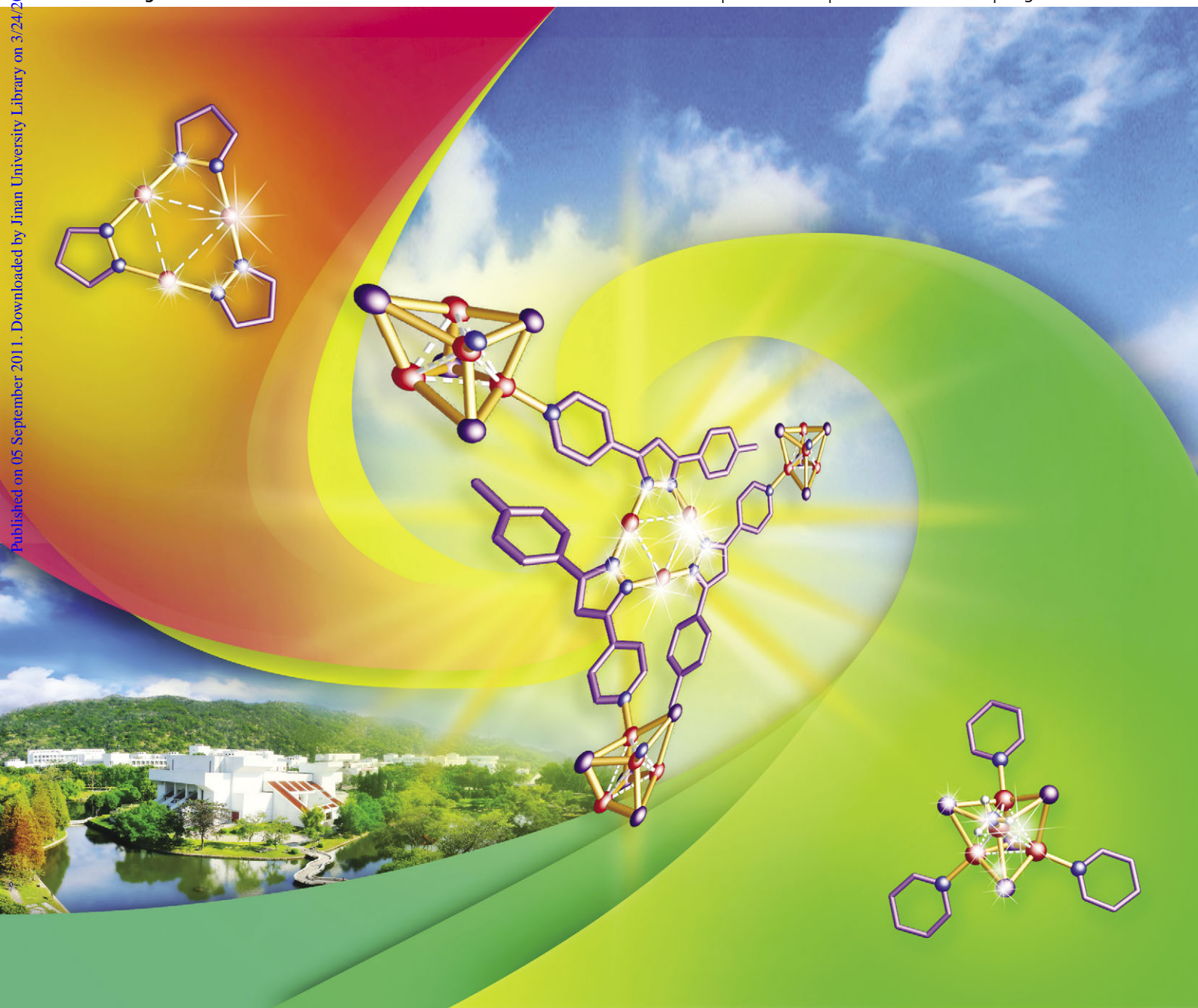
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When Cu_4I_4 cubane meets Cu_3(pyrazolate)$_3$ triangle: dynamic interplay between two classical luminophores functioning in a reversibly thermochromic coordination polymer†

Shun-Ze Zhan, Mian Li, Xiao-Ping Zhou, Jun-Hao Wang, Ju-Rong Yang and Dan Li*

A supramolecular dual emissive system incorporating two classical copper(I)-cluster-based luminophores, namely, Cu_4I_4 and Cu_3Pz_3 (Pz = pyrazolate), is reported. The targeted luminescent coordination polymer exhibits reversible thermochromism spanning from green to orange-red.

The role of coordination compounds in the territory of supramolecular photochemistry is assured by the presence of a number of classical, well investigated photofunctional metal complexes that promise applications ranging from optoelectronic devices to biomedical probes.[1–3] In the burgeoning field of luminescent coordination polymers,[4] one vital quest will be to develop well-defined microenvironments for immobilizing multi-cluster-based luminophores, and to realize the bimolecular processes[1] involving electron and/or energy transfer between different luminophores that lead to intriguing properties such as dual emission.[5,6] The scarcity of molecule-based dual emissive compounds[5] may be due to Kasha's rule which permits only the lowest excited state to emit, whereas in supramolecular systems it would be possible to simultaneously incorporate different luminophores. Nevertheless, it might be difficult to achieve the dynamic interplay between different luminophores in a supramolecular system in light of thermodynamic consideration—the thermal activation barriers are generally much higher than those in molecular dual emissive systems.

We have been interested in the construction of luminescent coordination polymers by utilizing some classical copper(I) clusters as essential and functional components.[7–9] Among others, tetranuclear Cu_4I_4[7,10,11] and trinuclear Cu_3Pz_3[9,12,13] have been extensively studied during past decades. These two classical copper(I) clusters might be a pair of luminophores suitable qfor demonstrating the above supramolecular dual emission protocol due to the following reasons. (i) The major contribution to the luminescent origin of Cu_4I_4 is believed to be the cluster-centered excited states (*Cu_4),[10a,11a] whereas the excimeric $[Cu_3Pz_3]_2$ dimer of trimers (*Cu_6) is usually responsible for the bright phosphorescence,[9c,12] and they both involve close Cu^I–Cu^I interactions (also known as cuprophilicity) as crucial stabilizing forces; this offers a thermodynamic possibility for the dynamic interplay between *Cu_4 and *Cu_6. (ii) Previous studies indicate that *Cu_4 usually emits at the wavelength of 540–580 nm upon excitation at 350–400 nm,[10a] whereas *Cu_6 usually exhibits higher-energy excitation of 270–320 nm and lower-energy emission of 630–720 nm;[9c] this avoids the coupling of the two excited states, and ensures that they can be excited by different wavelengths. (iii) *Cu_4 and *Cu_6 are both triplet, phosphorescent excited states with comparable microsecond lifetimes,[10a,13a] which make them distinguishable by normal instrumental probes.

Reported herein is a dual emissive supramolecular coordination polymer, namely, $[Cu_4I_4(NH_3)Cu_3L_3]_n$ (L = 3-(4-pyridyl)-5-p-tolyl-pyrazolate), in which two classical coordination luminophores, Cu_4I_4 and Cu_3Pz_3, are integrated via coordination bonds and stabilized via cuprophilic interactions. The crystalline sample of the complex was prepared from the solvothermal reaction of copper(I) iodide and the ligand in ethanol mixed with a small amount of aqua ammonia at 180 °C, and it crystallized in the $R\bar{3}$ space group (see ESI† for details). The overall structure exhibits a two-dimensional layer (Fig. 1) constructed from Cu_4I_4 and Cu_3Pz_3 clusters as secondary building units, which are linked via the pyridyl groups in L. The Cu_4I_4 cluster adopts a distorted cubane configuration
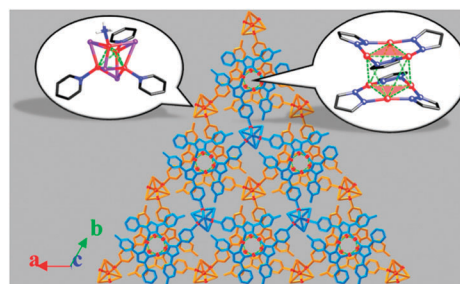
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Fig. 1 Representation of the double-layer (blue and orange) packing patterns of the reported coordination polymer immobilized with Cu_4I_4 and Cu_3Pz_3 as separated luminophores. $[Cu_4I_4(pyridyl)_3(NH_3)]$: left circle, $[Cu_3Pz_3]_2$: right circle. Cu^I–Cu^I interactions: green and dashed lines. Color codes: Cu in red, I in purple, N in blue, C in black; all H atoms are omitted except for the ones in coordinated NH_3 shown in the left circle.

(Fig. 1, left inserted circle) with Cu–Cu distances of 2.6490(5) to 2.8043(6) Å, similar to those reported.[7,11] Three of the four Cu sites in Cu_4I_4 are filled by the linking pyridyl groups in L, and the remaining site is completed by an NH_3 molecule (confirmed by the IR vibration of 3367 cm^{-1} and elemental analysis). The Cu_3Pz_3 triangle is constructed from three pyrazolate groups edge-bridging three linear-coordinated Cu^I ions (Fig. 1, right inserted circle). Compared with other Cu_3Pz_3 trimers, the present triangle is twisted, but the *intra*-trimeric and *inter*-trimeric Cu–Cu distances (3.2104(6) and 3.6459(7) Å, respectively) both lie in normal ranges.[9,12,13] Viewed from the *c* axis, these Cu_3Pz_3 triangles are connected by the C_3-symmetry Cu_4I_4 cubanes through the pyridyl groups, extending to a 2-D layer parallel to the *ab* plane.

Two adjacent 2-D layers are assembled into a double-layer arrangement *via* cooperative, *inter*-layer Cu^I–Cu^I interactions in the $[Cu_3Pz_3]_2$ units (Fig. 1, right inserted circle). The $[Cu_3Pz_3]_2$ dimers of trimers exhibit a centrosymmetric staggered stacking mode,[9c] which is believed to be the energetically favored conformation indicated by theoretical calculation,[12b] and is recently documented in a ligand-assisted $[Cu_3Pz_3]_2$ discrete compound.[13b] Within the double-layer, one Cu_3Pz_3 triangle faces another offset Cu_3Pz_3 triangle from the adjacent layer, while the Cu_4I_4 cubanes always face the voids of the adjacent layer, and the coordinated NH_3 groups attached to Cu_4I_4 clusters penetrate into these voids. Further, these double layers pack with each other along the *c* axis, but the stacking mode between two double layers is different from that within one double-layer. Between two double layers, the Cu_3Pz_3 triangles face the voids of the adjacent double layer, while one Cu_4I_4 cubane faces another Cu_4I_4 from the adjacent double layer (see Fig. S2 and S3 in ESI† for additional figures and structural description). The distances between two neighbouring Cu_3Pz_3 triangles from adjacent double layers are very long (~ 4.94 Å), suggesting no obvious Cu^I–Cu^I interaction between them. Cryogenic single crystal structure measurement (100 K) and temperature varied powder X-ray diffraction (293–523 K, Fig. S4 in ESI†) indicate no crystalline phase transition upon varying temperatures.

The photophysical behavior of this bi-cluster-based luminescent coordination polymer is interesting. The solid-state crystalline sample (purified, see ESI†) presents two major excitation bands at *ca.* 270 nm and 370 nm (Fig. S5 in ESI†). The excitation spectra are superposed by the solid-state diffuse reflectance UV-Vis spectrum (Fig. S6 in ESI†) that covers a broad range from 200 nm to 450 nm, suggesting that more than a single excited state may be populated. The excitation band at 270 nm is consistent with the excitation wavelengths of the $*Cu_6$ series,[9c] whereas the excitation band at 370 nm corresponds to the $*Cu_4$ excitations;[10a] this implies that both luminophores are excited simultaneously.

As expected, dual emission, with λ_{max} at 530 nm (higher-energy, HE) and 700 nm (lower-energy, LE), is detected upon excitation at both 370 nm (Fig. 2a) and 270 nm (Fig. 2b). Nevertheless, the yellow emission excited at 370 nm is much brighter than the orange emission excited at 270 nm (Fig. S7 in ESI†). Careful examination of the room-temperature (298 K) emission spectra reveals that the relative intensity of the HE band is stronger than that of the LE band ($I_{HE} : I_{LE} = 1.4$) when excited at 370 nm, whereas the situation is reversed ($I_{HE} : I_{LE} = 0.83$) when excited at 270 nm. This explains the
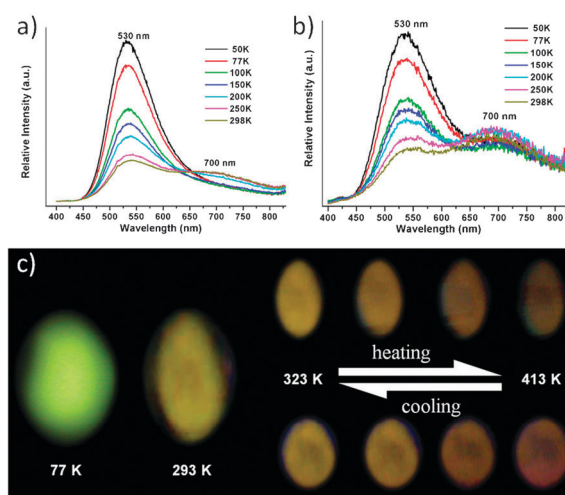

Fig. 2 Solid-state luminescent spectra upon excitation at 370 nm (a) and 270 nm (b) and varying the temperatures from 50 to 298 K. Photographs (c) showing luminescence thermochromism from green to orange-red of the solid sample upon heating and cooling when exposed to UV lamp (365 nm). Note the chromic processes are fast (within 1 minute) and reversible.

chromic luminescence at different excitation bands, and also suggests that $*Cu_4$ and $*Cu_6$ are separately responsible for the HE and LE emissions, consistent with previous studies.[8–13] Thus, the luminescence chromism (from bright yellow to dark orange) of this dual emissive system is dependent on excitation wavelength at room temperature.

Furthermore, this dual emissive system shows luminescence thermochromism that may originate from the dynamic interplay between $*Cu_4$ and $*Cu_6$. When excited at 370 nm and decreasing the temperature from 293 K to 77 K, the luminescence changes correspondingly from yellow to brighter green (Fig. 2c). This can be explained by examining the temperature-varied emission spectra (Fig. 2a), wherein the intensity of the HE band dramatically increases ($I_{HE} : I_{LE} = 10$ at 50 K) and gradually becomes the dominant contribution of the overall luminescence. The LE band also decreases in intensity, especially in the temperature range below 200 K where the LE peaks can hardly be observed in the spectra. In comparison, when increasing the temperature from 293 K to 413 K, the sample undergoes a chromic process from bright yellow to dark orange-red (Fig. 2c), which is believed to originate from the prevailing LE band in the higher temperature range. The chromic process is very fast and reversible upon cooling to room temperature, indicating that such luminescence thermochromism may be due to a physical process involving energy transfer through thermal activation, other than a chemical process involving phase transition, as evidenced by powder X-ray diffraction (Fig. S4 in ESI†).

Upon the excitation at 270 nm, the intensity increment of the HE band upon lowering the temperature is much smaller ($I_{HE} : I_{LE} = 2.5$ at 50 K) than that at 370 nm, and the LE band intensity does not change significantly except for reasonable thermal fluctuation (Fig. 2b). This is probable because the population of the LE excited states mainly originates from the 270 nm excitation, which disfavours the accumulation of the HE excited states at the first place of this excitation.
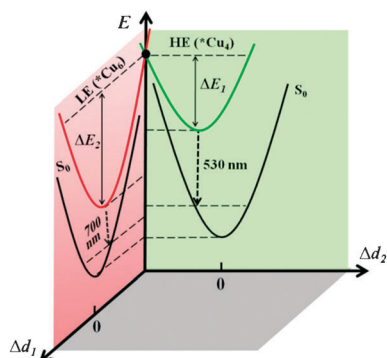
Fig. 3 Proposed potential energy diagram for the dual emission. Notes: Δd_1: the deviation of *inter*-trimeric Cu–Cu distances in the $[Cu_3Pz_3]_2$ unit (LE) between the excited state and ground state; Δd_2: the deviation of *intra*-tetrameric Cu–Cu distances in the Cu_4I_4 unit (HE) between the triplet excited state and ground state; E: energy.

The emission lifetime measurements (see Table S3 in ESI†) reveal a more complicated situation for the components and the interplay of the excited states. At all detection wavelengths (excited at 370 nm and 270 nm, monitored at 530 nm and 700 nm, respectively) and various temperatures (from 50 K to 293 K), the luminescence decays require fitting to triexponential equations other than biexponential ones. In light of our recent report[9c] showing that the *Cu$_6$ exhibits longer lifetime (at μs scale) and monoexponential decay, and literature[10a] showing that the *Cu$_4$ exhibits relatively shorter lifetime (also at μs scale) and its cluster-centered excited state is attributed to a combination of iodide to copper charge transfer and d–s transitions, we tentatively assign the shorter τ_1 and τ_2 to *Cu$_4$, and the longer τ_3 to *Cu$_6$. The fractional contributions of τ_3 at various temperatures are larger when excited at 260 nm and monitored at 700 nm than those when excited at 360 nm and monitored at 540 nm; this matches with the above excitation and emission data and testifies our assignment of τ_3 to *Cu$_6$ and τ_1 and τ_2 to *Cu$_4$.

We shall propose a photophysical model (Fig. 3) to illustrate the dynamic interplay between *Cu$_4$ and *Cu$_6$ functioning in this dual emissive and thermochromic complex. Upon excitation, the two excited clusters of HE (*Cu$_4$, with two coupled components) and LE (*Cu$_6$) emit their characteristic maximum emission bands at 530 nm and 700 nm, respectively. Ideally, the lower energy excitation (370 nm) can only populate the HE excited state, but at room and higher temperatures, a heating procedure favors the nonradiative relaxation of the HE excited state to the LE excited state by overcoming the energy barrier ΔE_1. When increasing the temperature, the population of the LE excited state becomes larger. However, in lower temperatures, the energy barrier ΔE_1 disfavors the conversion from HE to LE excited states. In contrast, the higher energy excitation (270 nm) can populate a major number of the LE excited state and a minor number of the HE excited state, and the conversion from LE to HE excited states is unlikely because the energy barrier ΔE_2 is much higher than ΔE_1. From the structural point of view, the difference of the photophysical behaviors between *Cu$_4$ and *Cu$_6$ derives from the different geometric flexibility of the excited states of Cu_4I_4 and $[Cu_3Pz_3]_2$. Previous theoretical studies indicate that the *inter*-trimeric Cu–Cu distances in $[Cu_3Pz_3]_2$ can contract up to 1.07 Å at the excited state,[9c,12]

whereas the *intra*-tetrameric Cu–Cu distances in Cu_4I_4 are reduced by less than 0.3 Å at the excited state.[11a] This speculation is verified by the much larger Stokes shift of LE ($22\,751$ cm^{-1}) than that of HE (8159 cm^{-1}) in this work.

Taken together, we have demonstrated and interpreted in this work a supramolecular dual emissive and thermochromic system incorporating two classical coordination luminophores, Cu_4I_4 and Cu_3Pz_3. The tunable dual emissive behavior of this luminescent coordination polymer is the consequence of a thermal equilibrium between two separated, competitive excited states. The strategy presented herein will be taken advantage by us to fabricate diverse photofunctional coordination polymers by finely tuning the structure and property of each separated luminophore.

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