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Brightly Phosphorescent Tetranuclear Copper(I) Pyrazolates

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Described herein is the synthesis and photophysics of two tetranuclear copper complexes, $\{[3,5-(\text{Pr}^i)_2,4-(\text{Br})\text{Pz}]\text{Cu}\}_4$ and $\{[3-(\text{CF}_3),5-(\text{Bu}^t)\text{Pz}]\text{Cu}\}_4$ tailor-designed by manipulating the pyrazolyl ring substituents. Unlike their trinuclear analogues, the luminescence of the tetranuclear species is molecular (not supramolecular) in nature with extremely high solid-state quantum yields of ~80% at room temperature.

The homoleptic copper(I) pyrazolates form polynuclear complexes with interesting structures and properties.¹ For example, depending on the nature of pyrazolyl ring substituents, they adopt structures ranging from trimers, tetramers, to polymers. Among these, trinuclear systems have received the most attention due to their fascinating photophysical properties that are sensitive to temperature, solvent, and concentration.^{2–20} Aida et al. reported the use of trinuclear copper pyrazolates to fabricate “thermally rewritable phosphorescent paper”.⁶ The inter-trimer cuprophilic interactions are important for the bright phosphorescence of such trinuclear adducts.^{8, 21, 22}

In contrast to trimers such as $\{[3,5-(\text{Pr}^i)_2\text{Pz}]\text{Cu}\}_3$ (Figure 1, 1) and $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{Cu}\}_3$,² only a few well-authenticated copper(I) pyrazolate tetramers are known. They include $\{[3,5-(\text{Ph})_2\text{Pz}]\text{Cu}\}_4$,²³ $\{[3,5-(\text{Bu}^t)_2\text{Pz}]\text{Cu}\}_4$,^{3, 24} $\{[3,5-(\text{Et})(\text{Me})\text{HCO}(\text{O})_2\text{Pz}]\text{Cu}\}_4$,²⁴ $\{[3-(\text{Bu}^t),5-(\text{Pr}^i)\text{Pz}]\text{Cu}\}_4$,^{3, 25} and $\{[3-(\text{ferrocenyl}),5-(\text{CF}_3)\text{Pz}]\text{Cu}\}_4$.²⁶ These basket-shaped molecules do not show close inter-molecular $\text{Cu}\cdots\text{Cu}$ contacts (as in the trinuclear systems) but allow for intra-molecular $\text{Cu}\cdots\text{Cu}$ bonding. Therefore, they are ideal systems to probe

the photoluminescence of copper(I) pyrazolates in the absence of inter-molecular contacts. This paper describes the synthesis of two new tetranuclear copper pyrazolates complexes $\{[3,5-(\text{Pr}^i)_2,4-(\text{Br})\text{Pz}]\text{Cu}\}_4$, (2) and $\{[3-(\text{CF}_3),5-(\text{Bu}^t)\text{Pz}]\text{Cu}\}_4$, (3) and a detailed study of their photophysical properties.

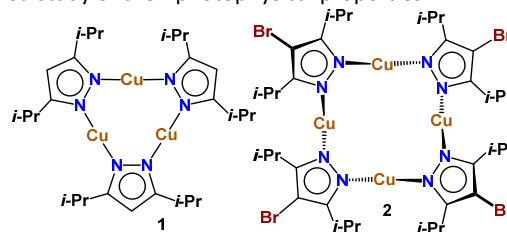


Figure 1. Trinuclear $\{[3,5-(\text{Pr}^i)_2\text{Pz}]\text{Cu}\}_3$ (1) and tetranuclear $\{[3,5-(\text{Pr}^i)_2,4-(\text{Br})\text{Pz}]\text{Cu}\}_4$ (2)

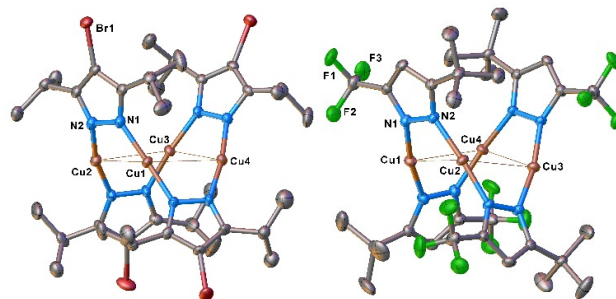


Figure 2. Molecular structures of complexes $\{[3,5-(\text{Pr}^i)_2,4-(\text{Br})\text{Pz}]\text{Cu}\}_4$, 2 (Left) and $\{[3-(\text{CF}_3),5-(\text{Bu}^t)\text{Pz}]\text{Cu}\}_4$, 3 (Right)

These copper pyrazolate adducts were obtained in high yield as colourless solids (see ESI for synthetic details). They have been characterized using NMR spectroscopy and by X-ray crystallography. As shown in the X-ray crystallographic data of Figures 2, S1, S2 and Tables S2–S10, complexes $\{[3,5-(\text{Pr}^i)_2,4-(\text{Br})\text{Pz}]\text{Cu}\}_4$ and $\{[3-(\text{CF}_3),5-(\text{Bu}^t)\text{Pz}]\text{Cu}\}_4$ have tetranuclear structures with essentially linear, two-coordinate copper centers. The pyrazolyl rings alternatively lie above and below the plane created by the Cu_4 core forming non-planar (saddle-

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shaped) basket structures that feature a 12-MC-4 azametalacrown arrangement in both complexes, following the terminology of Pecoraro and co-workers.²⁷ The intra-molecular Cu•••Cu distances of the Cu₄ core range from 2.9146(9) to 3.0204(9) Å for {[3-(CF₃),5-(Bu^t)Pz]Cu}₄ and from 2.9042(7) to 3.0217(7) Å in {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ similar to previously reported compounds (see Table S1). These separations are slightly longer than the widely-used but somewhat underestimated van der Waals contact of two copper atoms (2.80 Å).²⁸ The Cu•••Cu diagonal distances are much longer and range from 3.2426(6)–4.9733(9) Å. The Cu₄ core of {[3-(CF₃),5-(Bu^t)Pz]Cu}₄ is relatively more square in shape while that of {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ has a more diamond shape. The N–Cu–N angles are not notably different in the two copper complexes that range from 166.21(14)° to 175.73(14)°. The packing diagrams show that {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ and {[3-(CF₃),5-(Bu^t)Pz]Cu}₄ exist as discrete molecules in the solid state (see Figures S1 and S2). For example, the closest inter-molecular Cu•••Cu distance of 6.864(1) Å for {[3-(CF₃),5-(Bu^t)Pz]Cu}₄ and 7.085(1) Å for {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ are too long for any significant bonding interactions. These inter- or intra-molecular Cu•••Cu separations of {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ do not change significantly upon warming a crystal from 100 K to 276 K (see Tables S3 and S6).

A comparison of {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ and {[3-(CF₃),5-(Bu^t)Pz]Cu}₄ to other structurally characterized copper pyrazolate adducts provide useful information about the substituents effect on the nuclearity. The size of a CF₃ group has often been compared to the isopropyl moiety.^{29, 30} The steric effects of these groups on the copper nuclearity are similar in two-coordinate copper(I) complexes, since {[3-(CF₃),5-(Bu^t)Pz]Cu}₄ and {[3-(Bu^t),5-(Prⁱ)Pz]Cu}₄ adopt tetranuclear structures,^{3, 25} whereas {[3,5-(CF₃)₂Pz]Cu}₃ and {[3,5-(Prⁱ)₂Pz]Cu}₃ (1) are trinuclear species.² A comparison of {[3,5-(Prⁱ)₂Pz]Cu}₃ to {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ (Figure 1) shows that the replacement of a hydrogen atom on the pyrazolyl ring 4-position by a Br-atom is sufficient to cause a nuclearity change in the crystallized product. The Br-atoms force the CH₃ groups of the isopropyl substituents of {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ to orient away, effectively enhancing the steric profile, and creating a greater conflict between *i*-Pr groups of adjacent pyrazolates facing each other. This lead to a tetramer, analogous to {[3,5-(Bu^t)₂Pz]Cu}₄.^{3, 24} Overall for homoleptic Cu(I) pyrazolates with linear N–Cu–N geometry, the trinuclear to tetranuclear transition appears to occur when the steric demand of adjacent pyrazolyl ring substituents are somewhere between that of a CF₃/Prⁱ and a Bu^t group.

In solution at room temperature, {[3-(CF₃),5-(Bu^t)Pz]Cu}₄ shows complicated NMR spectra, indicating the presence of asymmetric structures or even different aggregates on the NMR time scale. Fujisawa *et al.* have reported similar observations with copper(I) tetramers involving asymmetrically-substituted pyrazolates.³ The ¹H NMR data of {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ show a concentration dependence, and indicate the formation of an increasing amounts of a different isomer, perhaps the trinuclear species, at lower concentrations.

Both complexes **2** and **3** studied herein show very intense luminescence at 298 K in the solid state; see Figure 3 while other detailed spectral data are in the ESI (Figures S3 – S10 and Table S11). There is a slight gain in intensity from RT to 4 K for both {[3-(CF₃),5-(Bu^t)Pz]Cu}₄ and {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ with very little shift in energy with temperature. This is much different from the other examples of tetramers in the literature (predominantly for Cu₄L₄X₄ clusters with L = a pyridine-like imine and X = iodo or other halo ligands) in which drastic luminescence thermochromism is seen whereby the emission colour changes from red to blue upon cooling.³¹ The assignment in the literature attributes this phenomenon to two separate emissive excited states, the lower-energy emission from a triplet cluster centred (³CC) state and the higher-energy band from a triplet halo-to-imine charge transfer (³XLCT) state.³¹

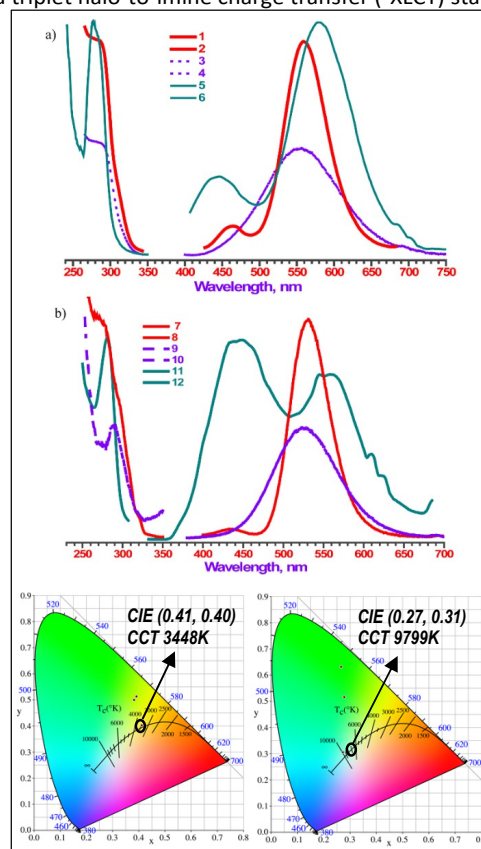


Figure 3. Steady-state photoluminescence excitation (left) and emission (right) spectra for a) {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄ solid at 4K (1-2), 298K (3-4) and its frozen toluene solution at 77K (5-6), and b) {[3-(CF₃),5-(Bu^t)Pz]Cu}₄ solid at 4K (7-8), 298K (9-10) and its frozen toluene solution at 77K (11-12). CIE colour coordinates for the emission spectra in a) and b) are shown in the bottom-left and bottom-right, respectively.

Our samples do show the growth of a new band in the blue region upon extreme cooling to 4K, but the intensity of this new band is too low to cause luminescence thermochromism. The radiative rate constant (*k_r*) was calculated based on a least-squares analysis (see Figures S9-S10, ESI) of the lifetime vs temperature data, attaining *k_r* = 2072 and 1,525 s⁻¹ for {[3-(CF₃),5-(Bu^t)Pz]Cu}₄ and {[3,5-(Prⁱ)₂,4-(Br)Pz]Cu}₄, respectively. The photoluminescence quantum yield (Φ_{4K}) approaches unity

at 4K, whereas the corresponding room temperature value (Φ_{298K}) was estimated by correcting the Φ_{4K} value for the peak area reduction at ambient temperature. Both complexes appear to be very intense at ambient temperature, consistent with the estimated very high quantum yield (Φ_{298K}) values of 0.81 and 0.77 for the neat solid-state form of $\{[3-(CF_3)_5-(Bu^t)Pz]Cu\}_4$ and $\{[3,5-(Pr^i)_2,4-(Br)Pz]Cu\}_4$, respectively. This points to an unusually diminished self-quenching in molecular solids. We and others described a few examples of d^{10} and d^8 complexes with such high Φ_{298K} values.^{32–35}

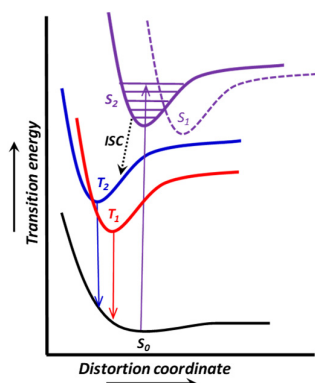


Figure 4. A postulated model for the photophysical transitions for the tetramers herein.

The excitation spectra shown in Figure 3a for $\{[3,5-(Pr^i)_2,4-(Br)Pz]Cu\}_4$ and Figure 3b for $\{[3-(CF_3)_5-(Bu^t)Pz]Cu\}_4$ are red-shifted versus those in dilute THF solution (Figures S5 and S8, ESI) by more than 5,500 cm^{-1} and 4,000 cm^{-1} , respectively. This indicates that the excitation may be a direct $S_0 \rightarrow T_1$ transition to 3CC ($3d \rightarrow 4s/4p$), consistent with absence of vibronic structure and the very large Stokes shift, factors that favours an excimeric type emission with shortened Cu-Cu distances within the Cu_4 cluster. On the other hand, the absorption as shown in Figures S5 and S8 is likely due to 1LC or 1MLCT singlet ligand-centred or metal-to-ligand charge transfer state, respectively -- due to the presence of vibronic fine structure. The major absorption peaks of Figures S3 and S6 are red-shifted relative to the free ligand, which is more consistent with a 1MLCT transition assignment as opposed to 1LC .

The frozen solution luminescence spectra in toluene (see Figures 3a, 3b, S4 and S7) are drastically different from those for the solids. Note that based on the NMR data analysis we believe the major signals in frozen solution are from tetramers though one cannot definitively rule out trimer presence. For trimers to play a role in the luminescence their concentration needs to be the major species or their quantum yield needs to be much higher than tetramers while at lower concentration whereas the data in this work suggest that the quantum yield of tetramers is at least as high as trimers so the concentration has the primary effect. In any event, high-energy band has now become a major feature in these frozen solutions and the low-energy band has red-shifted and is still intense. The emission to the naked eye appears white in colour, and gives rise to good warm-white and cool-white CCT and CIE colour metrics for **2** and **3**, respectively; see Figure 3/bottom. This emission disappears

after the solvent melts just above the freezing temperature, hence manifesting "luminescence rigidochromic".^{2, 36} The higher-energy emission potentially arises from a 3LMMCT (ligand-centred modified by excited-state Cu-Cu interactions) or a higher-lying 3CC state, as the latter is common for d^{10} complexes including the trimer analogues such as **1**.^{37, 38} We favour the higher-lying 3CC assignment due to the absence of vibronic structure that appeared in the 3LMMCT bands for the trinuclear and dinuclear analogues^{2, 39} but not for the tetramers herein. Figure 4 summarizes our postulated illustration of photophysical transitions for the tetramers herein. The absorption is depicted for an $S_0 \rightarrow S_2$ transition whereby the geometry distortion upon excitation is so minimal it allows for observation of vibronic fine structure, as observed experimentally (Figures S5 and S8, ESI). Intersystem crossing (ISC) then proceeds to T_2 to cause the higher-lying 3CC phosphorescence at cryogenic temperatures whereas internal conversion to T_1 occurs at higher temperatures to become the sole emission at room temperature from the lowest 3CC state. The T_1 and T_2 states are depicted such that both are so significantly distorted in geometry their transitions terminate in the continuum region of the S_0 ground state, hence lead to unstructured phosphorescence bands, as observed experimentally in Figure 3.

The blue band is discernible in solution for the complexes herein possibly due to the random distribution of structures in rigid media in which multiple combinations of $Cu \bullet \bullet Cu$ bonding arrangements exist. The number of close contacts between Cu atoms is five in the crystal structure of **2**, where the four Cu atoms form a rhombus and interact with one another while there is one diagonal pair (but not the other) of atoms that are close enough to interact at 3.2426(6) Å. This is contrasted with an analogous distance of 3.8202(9) Å in **3**, limiting its number of interactions to four. This difference in number of Cu-Cu interactions likely explains the red-shifted lower-energy phosphorescence in **2** vs **3**. The freedom of movement in solution for either complex allows for a change in population of the excited states, allowing the higher lying 3CC state with lesser Cu-Cu interactions to have increased population. However, computational analysis²¹ and time-resolved X-ray diffraction (i.e., "photocrystallography")⁴⁰ studies are both warranted to investigate the structure of the excited state that would examine these spectral assignment hypotheses. Applications of such materials include their potential use in solid-state lighting, especially if the white colour metrics above could be attained in doped thin films used OLEDs or silicone matrices used in LEDs, and temperature sensing given the fine-tuning attained within 77–298 K (Figure S11).

Overall, we describe the synthesis and photophysical properties of two rare tetranuclear copper complexes. We show that although $\{[3,5-(Pr^i)_2Pz]Cu\}_3$ is a planar, trinuclear species, increasing the steric bulk by the introduction of a Br-group at the 4-position of the pyrazolyl rings or changing the 3,5-substitution to 3-(CF_3),5-(Bu^t) leads to non-planar, tetrameric solids with a Cu_4N_8 core. We also describe the first detailed photophysical studies of tetranuclear copper pyrazolates, including quantum yield and lifetime data vs temperature

demonstrating favourable properties toward (O)LED phosphors and/or temperature sensors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Notes and references

‡ **Experimental Section:** Complexes **2** and **3** were synthesized under an air- and moisture free atmosphere using the pyrazoles [3,5-(*i*-Pr)₂,4-(Br)Pz]H and [3-(CF₃),5-(Bu^t)Pz]H and a copper(I) source.^{41,42} X-ray data collection, processing, and refinement were done by using Bruker software package and SHELXL⁴³ within Olex2⁴⁴ GUI. The luminescence measurements were carried out for crystalline powders with a PTI QuantaMaster Model QM-4 scanning spectrofluorometer. The synthesis and experimental details are provided in the ESI.

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