Copper(I)-pyrazolate clusters as solid-state phosphors: Tunable emissions via a remote steric effect

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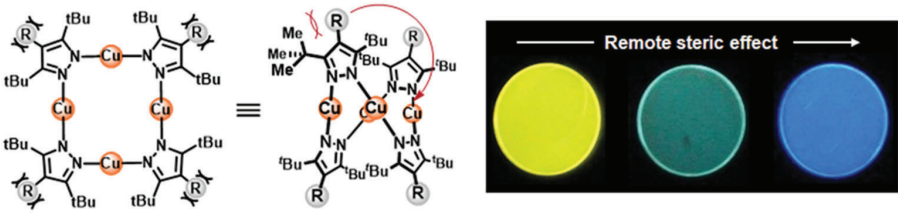
Optoelectronics depends on luminophores that emit brightly at red, green, and blue, but access to the latter is hindered by the limited availability of phosphors that can produce blue emissions in the solid state. Here, we describe a novel manifestation of rigidochromic behavior in a series of tetranuclear Cu(I)–pyrazolate (Cu_4pz_4) macrocycles, with implications for solid-state luminescence at deep-blue wavelengths (λ_{em} < 460 nm). The Cu_4pz_4 emissions are remarkably sensitive to structural effects far from the luminescent core: When 3,5-di-*tert*-butylpyrazoles are used as bridging ligands, adding a C4 substituent can induce a blueshift of more than 100 nm. We focus on a series of Cu_4pz_4 complexes having five different substituents at C4, including known complex **1** (R = H, λ_{em}: 559 nm)[1,2,3] plus four new complexes **2**–**5** (R = F, λ_{em}: 513 nm, Cl, Br, and CH_3, λ_{em}: 457–458 nm). Remarkably, X-ray crystal and computational analyses indicate the photoemission energies correlate with changes in their van der Waals volume (V_{vdW}) of the remote C4 substituents rather than electronic factors. This long-range steric effect can influence the conformational behavior of adjacent *tert*-butyl groups, with a subsequent impact on the global conformation of the Cu_4pz_4 complex. Emissions are mediated primarily through a cluster-centered triplet (^{3}CC) state; compression of the Cu_4 cluster into a nearly close-packed geometry prevents reorganization of its excited-state structure, and preserves the ^{3}CC energy at a high level. The remote steric effect may thus offer alternative strategies toward the design of blue phosphors with rigid excited-state geometries.



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