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Copper(I)–Pyrazolate Complexes as Solid-State Phosphors: Deep-Blue Emission through a Remote Steric Effect

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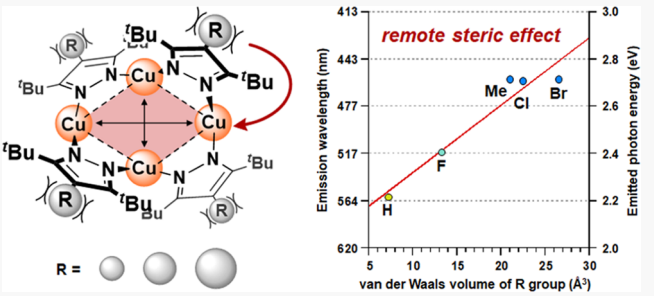
ABSTRACT: We describe a novel manifestation of rigidochromic behavior in a series of tetranuclear Cu(I)–pyrazolate (Cu_4pz_4) macrocycles, with implications for solid-state luminescence at deep-blue wavelengths (<460 nm). The Cu_4pz_4 emissions are remarkably sensitive to structural effects far from the luminescent core: when 3,5-di-*tert*-butylpyrazoles are used as bridging ligands, adding a C4 substituent can induce a blue shift of more than 100 nm. X-ray crystal and computational analyses reveal that C4 units 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 the 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 phosphors with rigid excited-state geometries.



INTRODUCTION

Advances in organic light-emitting devices (OLEDs) are being driven by the discovery and development of luminescent materials for a high external quantum efficiency (EQE), which scales in proportion to singlet and triplet exciton production efficiencies (η_r) as well as photoluminescence (PL) quantum yield (Φ_{PL}).[1,2] These factors can be optimized by tuning molecular features of light-emitting compounds or metal complexes, given an appropriate set of design principles. In this regard, several classes of organometallic compounds and coordination complexes hold great potential as emitters with tunable triplet states. Early successes were based on organometallic compounds containing Pt or Ir,[3,4] but more recent attention has been focused on earth-abundant elements such as Cu.[5,6] Both mononuclear and polynuclear Cu(I) complexes have shown promise as molecular emitters, with demonstrations of their potential for OLED applications.[7,8]

Common approaches toward Cu(I) triplet emitters employ either conventional phosphorescence or thermally activated delayed fluorescence (TADF) mechanisms.[9] Both are capable of producing excitons with quantitative efficiencies (η_r), and recent efforts have succeeded in designing efficient triplet emitters.[10] Irrespective of the photoemission mechanism, control over triplet energy and excited-state structure is vital for efficient luminescence, and requires mechanisms for suppressing nonradiative decay processes. In particular, structural or conformational rigidity is very important, as changes in excited-state structures can give rise to unproductive relaxation pathways that compromise radiative decay. For example, rigid and bulky ligands based on phenanthrolines,[11] phosphines,[10] and carbenes[7,12] have been employed to reduce nonradiative decay rates, thereby achieving Φ_{PL} close to unity.

Despite the apparent success of Cu(I) triplet emitters, mononuclear complexes are susceptible to aggregation-caused quenching.[13] Polynuclear Cu(I)–halide clusters have garnered recent attention because of their robust solid-state emissions;[14,15] for example, conformationally rigid Cu(I) iodide clusters with bulky phosphine ligands can produce sky-blue emissions in the solid state with a Φ_{PL} of 0.65.[8] A potential drawback associated with polynuclear clusters is the complex entanglement of triplet states that are accessed through different pathways. Phosphorescent metal clusters are well known to produce emissions from a variety of charge-transfer states (e.g., ligand-to-metal charge transfer (^{3}LMCT) and ligand/halogen-to-ligand charge transfer (^{3}L/XLCT) and also the cluster-centered triplet state (^{3}CC), which is generally thought to be a low-lying orbital that is sensitive to temperature and chemical stimuli).[16] Energy migration to the

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^{3}CC state can produce multiple radiative pathways, making it difficult to generate single-mode emissions with higher energy. Indeed, the ^{3}CC state is often viewed as a hindrance in the design of polynuclear phosphors for blue emissions.[8]

Here, we introduce a new approach toward the design of Cu(I)-based clusters using a tetranuclear Cu(I)−pyrazolate (Cu_4pz_4) macrocycle scaffold with emissions that can be channeled through the ^{3}CC state at much higher energies than previously reported.[17,18] By adjusting substituents at the periphery of the luminescent Cu_4pz_4 cluster, its photoemission energies can be tuned to produce solid-state emissions across the visible spectrum including the coveted deep-blue region (λ_{em} = 458 nm; Figure 1a, vide infra), from which all other colors can be produced by down-conversion.[1] This latter attribute is vital for achieving white OLED technologies with low material cost and energy consumption.[19,20] Remarkably, experimental and computational studies indicate that 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 increase the conformational rigidity of the Cu_4pz_4 macrocycle and suppress reorganization of the Cu_4 core in the solid state.

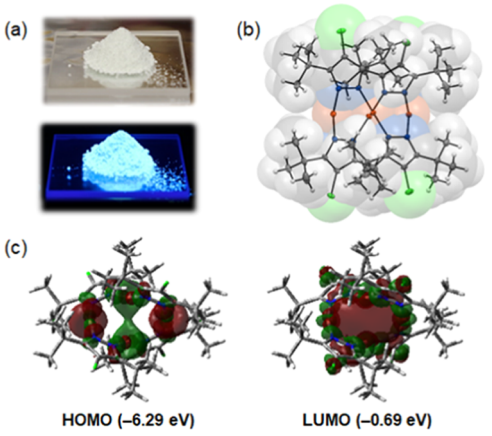


Figure 1. Molecular and electronic structures of Cu_4pz_4 complexes. (a) Photographs of **3** (R = Cl) in powder form taken under ambient light (top) and with 254 nm excitation (bottom), producing a blue emission. (b) Oak ridge thermal ellipsoid plot (ORTEP) representation of X-ray crystal structure of **3**; thermal ellipsoids drawn at the 50% probability level. (c) Frontier molecular orbital structures and energies of complex **3**.

RESULTS AND DISCUSSION

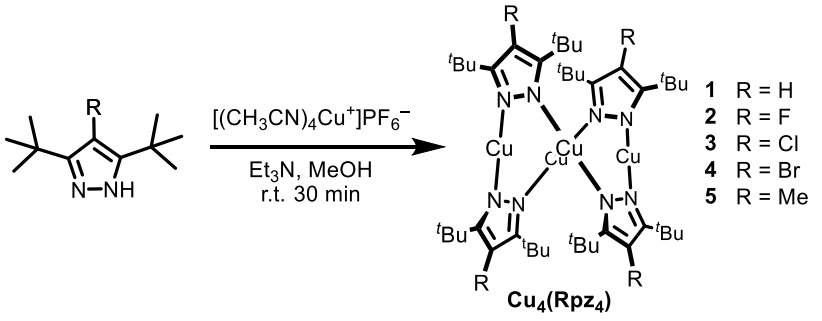
Molecular Design. Tetranuclear Cu(I)−pyrazolate clusters (Cu_4pz_4) bearing phenyl, isopropyl (^{i}Pr), trifluoromethyl (CF_3), and *tert*-butyl (^{t}Bu) substituents in the C3- or C5-positions have been previously reported, several of which are strongly luminescent.[17,18,21,22] In our study, we focus on a series of Cu_4pz_4 complexes made from 3,5-di-^{t}Bu-pyrazole having variable substituents at C4, including known complex **1** (R = H)[17,21,22] plus four new complexes **2**−**5** (R = F, Cl, Br, and CH_3; Scheme 1). Cu_4pz_4 complexes can be prepared on a gram scale by treating a 1:1 mixture of corresponding pyrazole and $(CH_3CN)_4CuPF_6$ with 1 equivalent of Et_3N (further details in the Supporting Information). The products precipitate as colorless but luminescent powders in good to high yield (Figure 1a).

X-ray crystallography of the Cu_4pz_4 complexes confirmed their existence as discrete, saddle-shaped macrocycles with each pyrazole ring separated by linear N−Cu−N bonds, so that the four Cu nuclei form a nearly planar rhombus (Figure 1b). Density functional theory (DFT) calculations indicate that the Cu atoms do not share valence electrons in the ground state but are close enough to support a well-defined CC nature of the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO), enabling direct emission with minimum contributions from other types of charge transfer (Figure 1c).

Photophysical Characterizations. PL studies on thin-film samples of the Cu_4pz_4 complexes **1**−**5** reveal a remarkable shift in solid-state emission wavelengths from yellow (**1**; R = H) to green (**2**; R = F) to deep blue (**3**−**5**; R = Cl, Br, Me; Figure 2a). Most complexes also exhibit high Φ_{PL} in the solid state, with that of **3** and **5** being close to unity, and PL decay lifetimes (τ) in the μs range (Figure 2b and Table 1). By presenting emission wavelengths according to their Commission Internationale de L'Eclairage (CIE) coordinates, it is apparent that complexes **3**−**5** fall squarely within the deep-blue region (Figure 2c).

Quantum chemical calculations of **1**−**5** indicate radiative decay through the ^{3}CC state (Figure S1 and Tables S2 and S3) to be the primary mechanism for solid-state luminescence. However, complex **4** may involve considerable metal-to-ligand charge transfer (^{3}MLCT) due to spin−orbit coupling with a heavy Br atom on the ligand (Figure S2).[23] The radiative decay rate (k_r of 3.08×10^4 s^{-1}) for **4** was found to be 10 times lower than that of the nonradiative decay rate (k_{nr} of 3.54×10^5 s^{-1}). This likely indicates that competing ^{3}MLCT processes increase the k_{nr} for **4**, resulting in a low Φ_{PL} of 0.08 (Table 1).

Scheme 1. Synthesis of Cu_4pz_4 Derivatives 1−5 from 3,5-di-^{t}Bu-pyrazoles (R = H, F, Cl, Br, and CH_3 (Me), Respectively)



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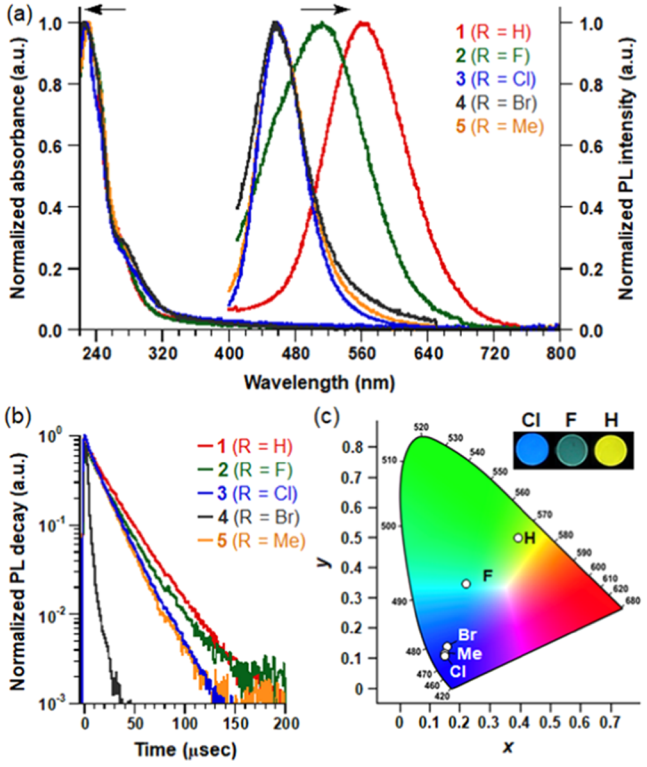

Figure 2. (a) Absorption and solid-state PL spectra of Cu_4pz_4 complexes **1**–**5**. (b) PL lifetime analyses of **1**–**5** cast as thin films; exponential fits to the data are reported as τ in Table 1. (c) CIE 1931 [x, y] coordinates for **1**–**5**. Inset: photoemissions from spin-cast thin films of **1**–**3** (λ_{ex} = 254 nm).

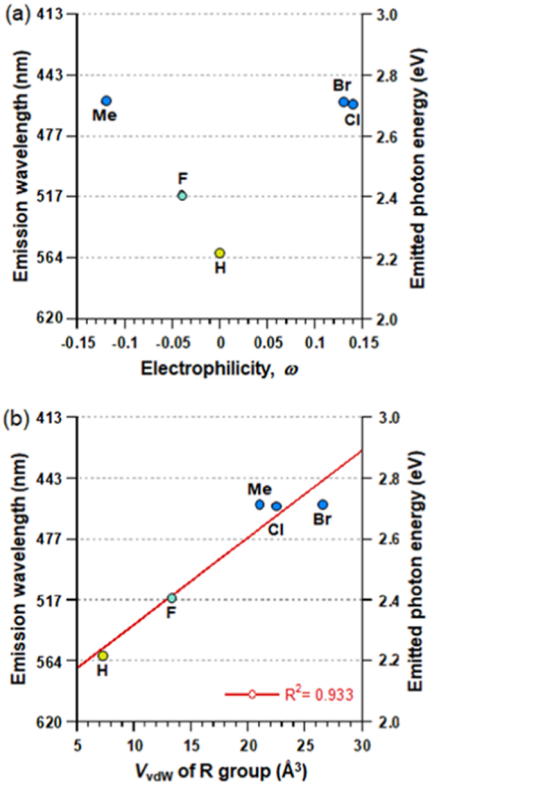

Figure 3. Parameterization of substituent effects on Cu_4pz_4 luminescence. (a) Electrophilicity (ω) has no discernible correlation with photoemission energy. (b) Increases in the van der Waals volume (V_{vdW}) of the C4 substituent correlate strongly with a blue shift in photoemission.

It is worth noting that the PL properties of microcrystalline powders of Cu_4pz_4 are essentially identical to those measured with amorphous thin films (Figures S13–S19 and Tables 1 and S13), indicating phosphorescence to be insensitive to the lattice structure. The solid-state photoemission energies of Cu_4pz_4 are also independent of concentration; for example, thin films of complex **3** blended with 1,3-bis(*N*-carbazolyl)-benzene (mCP), a conventional host matrix for OLEDs, produce the same emission wavelength regardless of ratio (Figure S17). These results confirm that the solid-state PL properties of Cu_4pz_4 complexes are entirely molecular in nature (further details in the Supporting Information).

Structure–Property Relationships. To better understand the influence of C4 substituents on the PL properties of Cu_4pz_4 complexes, we examined several parameters commonly used to determine linear free-energy relationships. Electronic parameters do not produce any meaningful trends (Figure 3a);[24] instead, a strong correlation (R^2 = 0.93) is obtained by plotting photoemission energies against the V_{vdW} of the C4 units, indicating the substituent effect to be steric in nature (Figures 3b and S19e).[25−27] In particular, we note that the Cl and Me groups in **3** and **5** have similar V_{vdW} values (22.45 Å^3 for R = Cl; 21.00 Å^3 for R = Me) but very different electrophilicities (ω(Cl) = +0.14; ω(Me) = −0.12), while their photoemission energies are nearly identical.

Further insights can be gleaned by a careful analysis of structural data from X-ray crystallography. Inspection of the ^{t}Bu groups on the pyrazole ligands reveals their solid-state conformations to be influenced by the size of the neighboring C4 substituents (Figure 4a). For Cu_4pz_4 complexes **1** (R = H) and **2** (R = F), at least one ^{t}Bu unit adopts an eclipsed geometry with respect to the R groups. In contrast, all ^{t}Bu groups in complexes **3**–**5** (R = Cl, Br, and Me) adopt bisected geometries to accommodate the larger V_{vdW} of the C4 substituents.

The influence of local steric interactions was further examined using DFT calculations to determine the conformational preferences for ^{t}Bu groups on each pyrazole ligand as a function of the dihedral angle. Except for **1**, three equivalent

Table 1. Solid-State Photophysical Properties for Cu_4pz_4 Complexes Cast as Thin Films

Cu_4pz_4 complex	Φ_{PL} [a]	λ_{em} [b] (nm)	FWHM (nm)	CIE [x, y]	τ [c] (μs)	k_r [d] (s^{-1})	k_{nr} [e] (s^{-1})
1 (R = H)	0.94	559	115	0.39, 0.50	20.9	4.50×10^4	2.87×10^3
2 (R = F)	0.61	513	139	0.22, 0.35	17.7	3.45×10^4	2.20×10^4
3 (R = Cl)	0.99	458	65	0.15, 0.11	16.2	6.11×10^4	6.17×10^2
4 (R = Br)	0.08	457	80	0.16, 0.14	2.6	3.08×10^4	3.54×10^5
5 (R = Me)	0.82	457	68	0.15, 0.13	15.6	5.26×10^4	1.15×10^4

[a]Determined using an integrating sphere. [b]λ_{ex} = 280 nm. [c]λ_{ex} = 300 nm. [d]$k_r = \Phi_{PL}/\tau$. [e]$k_{nr} = (1-\Phi_{PL})/\tau$.

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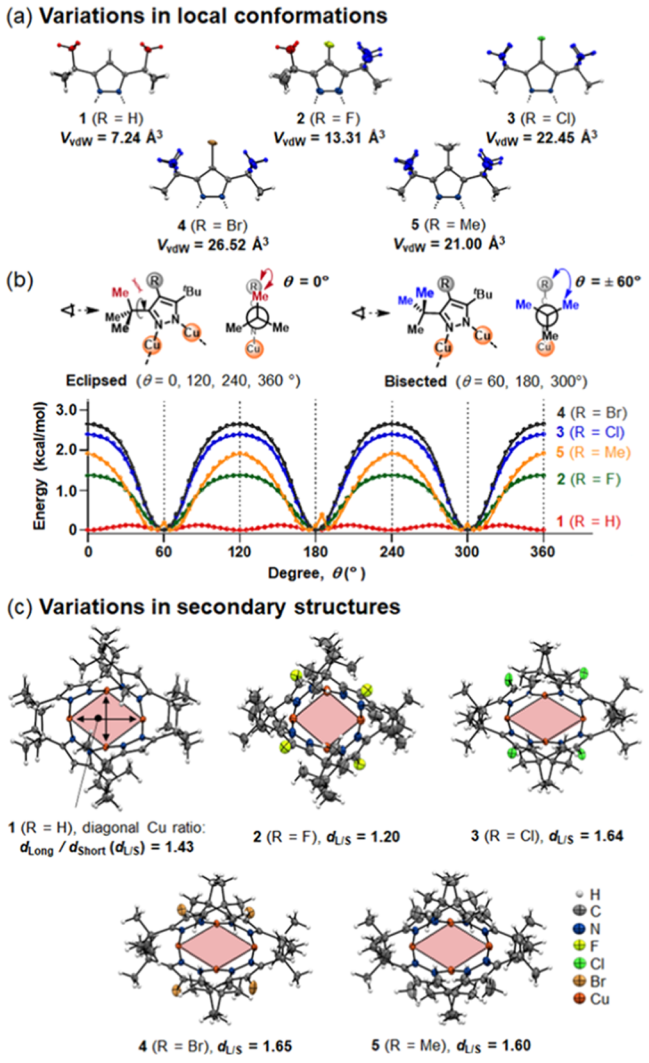

Figure 4. Secondary structural analysis of Cu_4pz_4 complexes based on X-ray crystallographic data. (a) ORTEP representations of pyrazolyl groups with thermal ellipsoids drawn at the 50% probability level. The Me group(s) of ^{t}Bu units having eclipsed or bisected geometries relative to the R group are highlighted in red and blue, respectively. (b) Conformational energy profiles of ^{t}Bu groups on the pyrazole ligands with Newman projections of conformers in eclipsed and bisected geometries. (c) ORTEP representations with a plan view of the Cu_4 core. The rhombus aspect ratio is defined as d_L/d_S, the Cu···Cu distances along the long and short axes, respectively. Solvents and disordered ligands have been omitted for clarity.

minima corresponding with bisected conformations (θ = 60, 180, 300°) were obtained, separated by rotational barriers (Figure 4b). Quantitative estimates for these barriers correspond with gas-phase conformations; however, their relative differences can be applied meaningfully to the solid state as well: pyrazole ligands with C4 substituents of $V_{vdW} \geq$ 21 Å^3 adopt stable conformations with rotational barriers of 2.0 kcal/mol or more, well above the threshold for thermal motion at room temperature (k_T ~0.6 kcal/mol). It is thus reasonable to expect that Cu_4pz_4 complexes **3**−**5** are conformationally more rigid than complexes **1** and **2** and that their rigidochromic behavior is likely an important factor for their emissions in the deep-blue region.

We also evaluated the macrocyclic cores of each complex for differences in the secondary structure (Figure 4c). The distances between adjacent Cu atoms in complexes **1**−**5** are essentially constant (Table S5). However, the distances between Cu atoms across the Cu_4pz_4 macrocycle vary according to the size of the C4 substituent: the short Cu···Cu distance (d_S) is 3.4 Å for **1** (R = H) and 3.7 Å for **2** (R = F) but approximately 3.0 Å for **3**−**5** (R = Cl, Br, and Me). These structural differences are even more apparent in the rhombus defined by the Cu_4 cluster: the long and short Cu···Cu distance ratios (d_L/d_S) are 1.60 or higher for blue-emitting complexes **3**−**5** but less than 1.43 for yellow- and green-emitting complexes **1** and **2** (Figure 4c). Despite these variations, all Cu_4 clusters have very similar metal cluster-centered molecular orbitals, an indication that they share a common PL mechanism involving a radiative decay through ^{3}CC states (Figure S1). Given the distance of the C4 substituents from the Cu_4 core and the insignificant differences in the electronic structure, we dub their influence on macrocycle conformation as a remote steric effect.

It should be noted that Dias, Omary, and co-workers recently reported a greenish-yellow Cu_4pz_4 emitter prepared from 3,5-di-^{i}Pr,4-Br-pyrazole (λ_{em} ~550 nm) with emission through the ^{3}CC state.[18] However, we believe that the Br unit at C4 does not influence the conformational behavior of the smaller ^{i}Pr substituents at C3 and C5. X-ray crystal analysis of this cluster indicates the Cu_4 rhombus to have a d_L/d_S ratio of 1.52, which is lower than that of the Cu_4 rhombus in complex **4** (d_L/d_S = 1.65; Figure 4). This comparison indicates that the flanking ^{t}Bu groups in Cu_4pz_4 complexes **3**−**5** are important for enforcing rigidochromic behavior.

Further insights into the remote steric effect were obtained using DFT and time-dependent DFT (TD-DFT) calculations. The energies and optimized structures of the ground state (S_0) and first excited triplet (T_1) state for Cu_4pz_4 complexes **1**−**3** were calculated at the PBE0/TZVP level, with the LANL2DZ basis set for the effective core potential (ECP) addition to Cu atoms in the gas phase. Ground-state calculations yield geometries in close agreement with X-ray crystal structures, but the analysis of the excited-state structure of **1** (R = H) reveals that its T_1 state is accompanied by a contraction of the Cu_4 core, with modest yet significant reductions in d_S and d_L (Figure 5a and Tables S2−S4). The Cu_4 core contraction is less pronounced for F-substituted Cu_4pz_4 complex **2** and least of all for Cl-substituted Cu_4pz_4 complex **3** (Figure 5b). TD-DFT calculations of **1**−**3** produced adiabatic T_1 energies (E_{T_1}) that were in good agreement with experimental emissions and correlated strongly with the V_{vdW} values of the C4 substituents (Figure 5c). We also established an inverse correlation between V_{vdW} and Cu_4 core contractions, which is parameterized as the sum of changes in d_S and d_L (Figure 5b).

These correlations effectively couple the remote steric effect to both photoemission energy and the rigidity of the Cu_4pz_4 macrocycle, namely, its ability to resist excited-state contraction. Importantly, this effect is intramolecular and distinct from solid-state packing effects or inter-ion interactions.[28−31] We thus conclude that the remote steric effect in Cu_4pz_4 complexes is a valuable parameter for establishing rational control over their solid-state emissions, regardless of their crystallinity.

While the steric influence of the C4 substituents on photoemission energies is clearly established by free-energy relationships, its causal connection with the Cu_4pz_4 secondary structure is not immediately obvious. One possibility is that the

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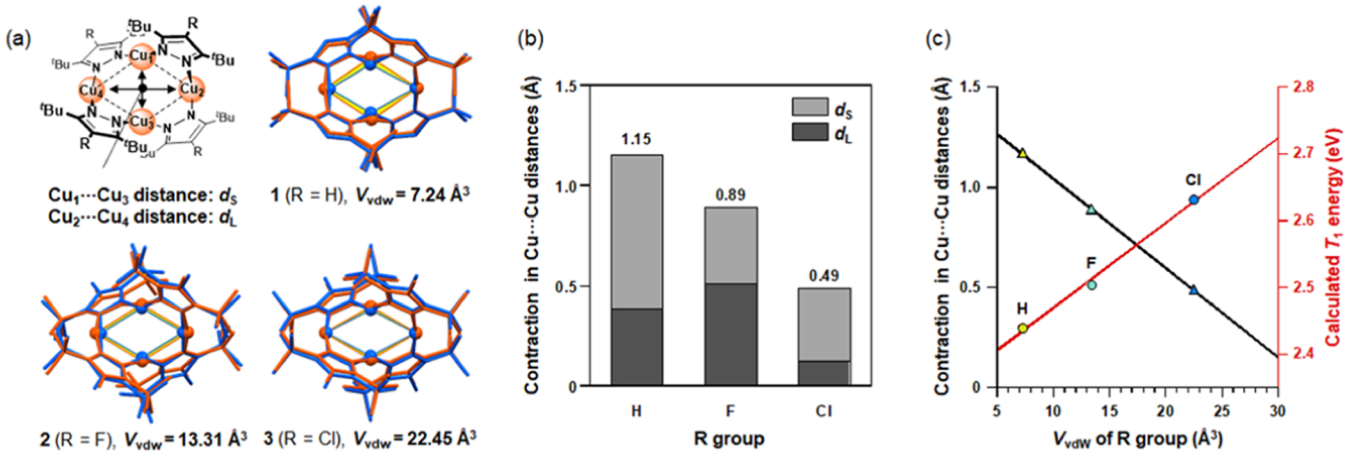

Figure 5. Computational (TD-DFT) analyses of ground- and excited-state Cu_4pz_4 complexes. (a) Optimized geometries of complexes **1**−**3** (R = H, F, and Cl) in the S_0 (orange) and T_1 (blue) states. All hydrogen atoms are omitted for clarity. (b) Contraction of the Cu_4 core between the S_0 and T_1 states; light and dark gray bars represent decreases in the Cu···Cu distances along d_S (Cu_1···Cu_3) and d_L (Cu_2···Cu_4) axes, respectively. (c) Correlations between the size (V_{vdW}) of the C4 substituent versus Cu_4 core contraction parameter in Figure 5b (black) or adiabatic T_1 energy, E_{T_1} (red).

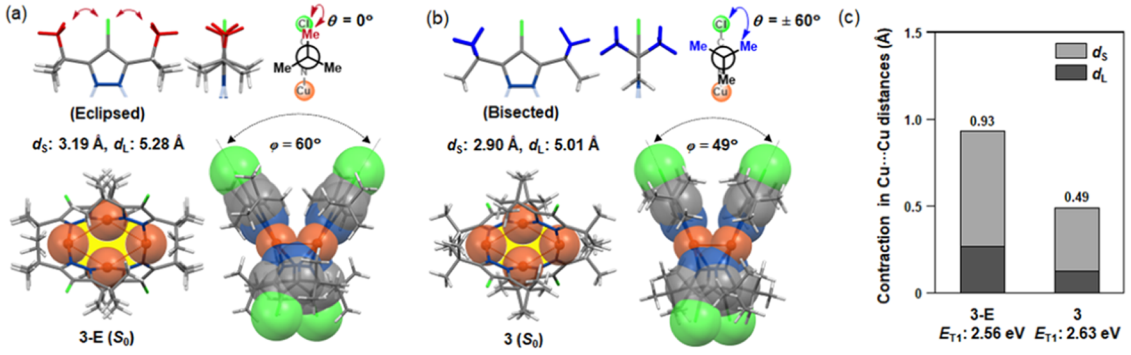

Figure 6. Computational (TD-DFT) models reveal the effects of ^{t}Bu conformations in Cu_4pz_4 complex **3** (R = Cl). (a) Cu_4 core diagonal distances (d_S, d_L), cross-sectional gap (in yellow), and dihedral angles (φ) of the opposing pyrazole ligands with ^{t}Bu groups in eclipsed conformations (**3-E** (S_0)). (b) The same parameters for **3** with ^{t}Bu groups in bisected conformations (**3** (S_0)). (c) Cu_4 core contraction and calculated E_{T1} energies; the 0.07 eV difference between **3** and **3-E** corresponds with a 13 nm shift in emission wavelength.

orientations of the ^{t}Bu groups directly impact the preferred geometry of the Cu_4pz_4 macrocycle in the solid state, thereby correlating local conformational effects (Figure 4b) with global structure. To address this, we conducted TD-DFT calculations of complex **3** (R = Cl) with ^{t}Bu groups in eclipsed conformations relative to adjacent C4 substituents (θ = 0°). In the optimized S_0 geometry (**3-E**; Figure 6a), the ^{t}Bu groups remain in their eclipsed conformations but the Cu···Cu distances across the macrocyclic core (d_L and d_S) are increased, relative to those in the optimized S_0 geometry of **3** with ^{t}Bu groups in bisected conformations (Figure 6b). In addition, the global conformation of **3-E** is less compact relative to **3**, as judged by the larger dihedral angle formed between the opposing pyrazole ligands (φ = 60° for **3-E** versus φ = 49° for **3**). Finally, in the geometry for **3-E**, d_L and d_S experience greater contraction than that observed in the corresponding geometry for **3**, as well as a lower E_{T1} value for the ^{3}CC state (Figures 6c and S3 and Tables S3 and S4).

The ^{3}CC state is often found in luminescent d^{10} metal complexes having short distances between the metal atoms but is usually associated with the emission of low-energy PL.[8,32−36] In our study, Cu_4pz_4 complex **3** produces deep-blue phosphorescence at room temperature in either microcrystalline or amorphous forms, suggesting that their solid-state conformations are predisposed to support high-energy ^{3}CC states. It is noteworthy that the compact conformation of **3** permits vdW contact between ^{t}Bu groups on opposing pyrazole ligands and also enforces the close packing of the four Cu atoms, which interact weakly in their ground state (Figures 6 and S3).[37] In the excited state, the Cu atoms are already pinned and thus less prone to further contraction. Our computational study further supports our hypothesis that photoemission energies depend on the conformational rigidity of the Cu_4pz_4 core in its ground and especially excited states.

CONCLUSIONS

This work highlights a previously unrecognized approach for designing tetranuclear Cu(I)−pyrazolate clusters as deep-blue phosphors by virtue of a remote steric effect. Peripheral substituents at the C4 position of the pyrazolate ligands can suppress the motional freedom of adjacent ^{t}Bu groups, with subsequent compression of the Cu_4pz_4 macrocycle and rigidification of both ground- and excited-state conformations. Reducing conformational mobility results in room-temperature phosphorescence at deep-blue wavelengths channeled through the ^{3}CC state, independent of the solid-state lattice structure.

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TD-DFT calculations reveal the relationship between local conformations at the ligand periphery and global conformations that enable the Cu_4 core to resist the excited-state contraction. Understanding how the remote steric effect can influence excited-state dynamics will clarify how the evolving concept of rigidochromism can be applied toward phosphor design, with implications for PL lifetime engineering and solid-state lighting.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c13462.

Experimental section and data as well as the characterization data; Figures S1−S53, Tables S1−S13, and additional crystallographic information (PDF)

Accession Codes

CCDC 2115892−2115897 and 2154769 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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