

A Highly Emissive Heteroleptic Copper(I) Bis(phenanthroline) Complex: [Cu(dbp)(dmp)]⁺ (dbp = 2,9-Di-*tert*-butyl-1,10-phenanthroline; dmp = 2,9-Dimethyl-1,10-phenanthroline)

Mark T. Miller, Peter K. Gantzel, and Timothy B. Karpishin*

Department of Chemistry and Biochemistry
University of California, San Diego
La Jolla, California 92093-0358

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Photoluminescent diimine complexes of Ru^{II} have been extensively investigated for a wide variety of applications including solar-energy conversion and molecular sensing.^{1–4} Although much less studied, certain Cu^I bis(diimine) complexes display useful properties including strong visible absorption, long (>100 ns) excited-state lifetimes, and excited-state redox potentials that render them viable as photocatalysts.^{5–9} Because of the substantial price differential between copper and ruthenium, copper-based devices and sensors are economically attractive. A central problem associated with the use of Cu^I systems has been the low quantum yields ($\phi \approx 0.1$ – 0.4%)^{8,10} of the complexes. Here we report a Cu^I complex that exhibits impressive photophysical properties in solution and in the solid state. In the solid state, the quantum yield is equivalent to the most widely studied Ru^{II} complex ([Ru(bpy)₃]²⁺; bpy = 2,2'-bipyridine), and the excited-state lifetime is longer.

The ligand dmp has been known for more than fifty years,¹¹ but it was not until 1980 that Blaskie and McMillin demonstrated that [Cu(dmp)₂]⁺ is emissive upon excitation into the visible MLCT band.¹² It is now known that 2 and 9 phenanthroline substituents are necessary for [Cu(NN)₂]⁺ complexes (NN = a 1,10 phenanthroline) to be emissive.¹³ The 2 and 9 substituents sterically inhibit molecular distortion that occurs in the vibrationally relaxed excited state.⁵ This distortion results from the tendency of the Cu^{II} ion to adopt a square-planar (flattened) geometry, the MLCT state having considerable Cu^{II} character. Recent work has shown that increasing the steric requirements of the 2 and 9 substituents leads to improvements in the excited-state lifetimes (τ) and quantum yields (ϕ) of [Cu(NN)₂]⁺ complexes by further inhibiting excited-state distortion.¹⁰ There is a limit however. Increasing the substituent size by too much leads to the inability to form the [Cu(NN)₂]⁺ complex. Utilizing molecular models, we predicted that only one ligand in a [Cu(NN)₂]⁺ complex needs to have bulky 2 and 9 substituents to prevent the flattening distortion. Thus, a heteroleptic complex in which one phenanthroline contains *tert*-butyl groups at the 2 and 9 positions (dbp) should lead to a complex with an extremely rigid coordination sphere. Because of the lability of Cu^I com-

plexes, heteroleptic complexes are expected to scramble. The beauty of the dbp ligand is that it allows the preparation of a heteroleptic complex since the formation of [Cu(dbp)₂]⁺ is sterically impossible.¹⁴ Here it is demonstrated that [Cu(dbp)(dmp)]⁺ shows much larger improvements in τ and ϕ than previously examined homoleptic complexes; these effects are attributed to the size of the *tert*-butyl groups of dbp (vide infra). Importantly, this report represents the first demonstration of how significant photophysical effects can be achieved with heteroleptic Cu^I complexes and opens the door to a family of molecules for further investigation.

The complex [Cu(dbp)(dmp)](PF₆) (**1**) is prepared by first stirring 1 equiv of dbp¹⁵ with 1 equiv of [Cu(CH₃CN)₄](PF₆)¹⁶ in CH₂Cl₂ under N₂. One equivalent of dmp is then added, and the solution immediately turns from yellow to deep orange. Recrystallization (MeOH) is sufficient for purification from a small amount of the side product [Cu(dmp)₂](PF₆) and yields the air-stable, orange **1**.¹⁷ The crystal structure of **1** demonstrates the heteroleptic coordination about the copper (Figure 1).¹⁸ The coordination geometry is distorted from a D_{2d} pseudotetrahedral geometry that might be expected for a d¹⁰ ion. The geometry is best described as trigonal pyramidal with molecular C_s symmetry, in which the dmp ligand is canted from D_{2d} symmetry along a mirror plane. Several structures of [Cu(dmp)₂]⁺ have been shown to adopt geometries distorted from D_{2d} symmetry.¹⁹ In most cases, the largest distortion is a flattening of the phenanthroline (phen) ligands with respect to each other, attributed to crystal-packing forces.^{20,21} In the structure of **1**, however, the *tert*-butyl groups of the dbp ligand prevent the flattening distortion and result in a nearly orthogonal orientation of the two phen planes.²² In addition, in the structure of **1**, there are two independent molecules of [Cu(dbp)(dmp)]⁺ in the asymmetric unit. However, each of the complex cations adopts identical geometries (rms error = 0.022 Å for the CuN₄ cores, see Supporting Information).

Complex **1** emits brightly at room temperature upon illumination with a hand-held UV lamp. Since many of the applications of luminescent inorganic complexes require the complexes attached to solid supports or embedded in solid matrices,^{23–25} the properties of **1** in the solid state are of interest. The excited-state lifetime and emission spectrum (Figure 2) of the complex were recorded upon excitation into the MLCT band ($\lambda_{\text{max}}^{\text{abs}} = 454$ nm, mineral oil mull).²⁶ Complex **1** emits with a maximum at 595 nm, and the decay is best fit by multiple exponentials (Figure 2).²⁸ The solid-state lifetime and emission spectrum of [Ru(bpy)₃]-

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(17) The ¹H NMR spectrum of **1** is found in the Supporting Information.

(18) Complex **1** crystallizes in space group P2₁ with $a = 15.489(7)$ Å, $b = 11.983(7)$ Å, $c = 18.102(13)$ Å, $\beta = 91.23(5)^\circ$, $V = 3359(4)$ Å³, and $Z = 4$. For 6359 unique data with $F > 4.0\sigma(F)$, $R = 6.48\%$.

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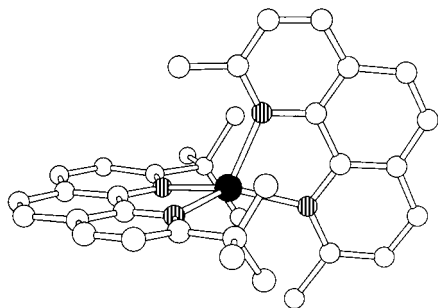


Figure 1. One of the independent $[\text{Cu}(\text{dbp})(\text{dmp})]^+$ complex cations. Hydrogens have been removed for clarity. Selected bond lengths (\AA) and angles (deg) for both independent cations: $\text{Cu}(1)-\text{N}(1)$, 2.051(6); $\text{Cu}(1)-\text{N}(2)$, 2.087(6); $\text{Cu}(1)-\text{N}(2\text{A})$, 2.088(6); $\text{Cu}(1)-\text{N}(1\text{A})$, 2.094(6); $\text{Cu}(2)-\text{N}(2\text{B})$, 2.064(6); $\text{Cu}(2)-\text{N}(1\text{B})$, 2.080(7); $\text{Cu}(2)-\text{N}(1\text{C})$, 2.085(6); $\text{Cu}(2)-\text{N}(2\text{C})$, 2.096(6); $\text{N}(1)-\text{Cu}(1)-\text{N}(2)$, 81.4(3); $\text{N}(1)-\text{Cu}(1)-\text{N}(2\text{A})$, 131.5(2); $\text{N}(2)-\text{Cu}(1)-\text{N}(2\text{A})$, 113.3(2); $\text{N}(1)-\text{Cu}(1)-\text{N}(1\text{A})$, 133.6(2); $\text{N}(2)-\text{Cu}(1)-\text{N}(1\text{A})$, 114.6(2); $\text{N}(2\text{A})-\text{Cu}(1)-\text{N}(1\text{A})$, 83.9(2); $\text{N}(2\text{B})-\text{Cu}(2)-\text{N}(1\text{B})$, 81.2(3); $\text{N}(2\text{B})-\text{Cu}(2)-\text{N}(1\text{C})$, 132.1(3); $\text{N}(1\text{B})-\text{Cu}(2)-\text{N}(1\text{C})$, 115.7(2); $\text{N}(2\text{B})-\text{Cu}(2)-\text{N}(2\text{C})$, 131.0(2); $\text{N}(1\text{B})-\text{Cu}(2)-\text{N}(2\text{C})$, 115.0(3); $\text{N}(1\text{C})-\text{Cu}(2)-\text{N}(2\text{C})$, 84.4(2).

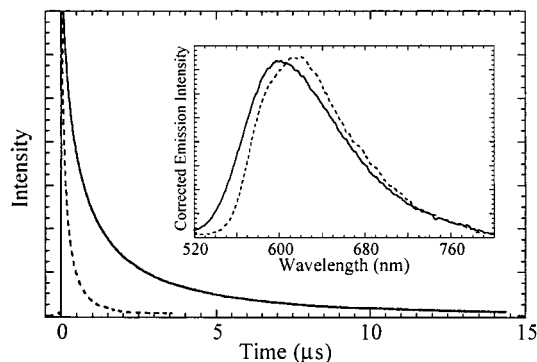


Figure 2. Time-resolved, room-temperature photoluminescent spectra of $[\text{Cu}(\text{dbp})(\text{dmp})](\text{PF}_6)$ (—) and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (- - -) at 675 nm; $\lambda^{\text{ex}} = 455$ nm. Since each decay is best-fit by multiple exponentials, an effective half-life (τ^{eff}) was calculated from the time the total area under the curves decreased by 50%: τ^{eff} , $[\text{Cu}(\text{dbp})(\text{dmp})](\text{PF}_6) = 1.5 \mu\text{s}$; τ^{eff} , $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2 = 0.21 \mu\text{s}$. Inset: corrected solid-state emission spectra of $[\text{Cu}(\text{dbp})(\text{dmp})](\text{PF}_6)$ (—) and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (- - -); $\lambda^{\text{ex}} = 450$ nm.

$(\text{PF}_6)_2$ were also measured using identical methods (Figure 2). The quantum yield of **1** was determined to be 1.19 ± 0.25 times higher than $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ under ambient conditions.^{31,32} We estimate the solid-state ϕ of **1** is at least 50 times higher than that of one of the most emissive, previously examined $[\text{Cu}(\text{NN})_2]^+$ complexes, $[\text{Cu}(\text{bfp})_2](\text{PF}_6)$.^{33,34} Further, the solid-state lifetime of **1** is considerably longer than that found for $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (Figure 2).

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(34) Although the solution-state quantum yield of $[\text{Cu}(\text{bfp})_2](\text{PF}_6)$ has been measured ($\phi = 0.33\%$),³³ the solid-state emission spectrum of $[\text{Cu}(\text{bfp})_2](\text{PF}_6)$ was very weak, only allowing an estimate of the value of ϕ relative to **1**.

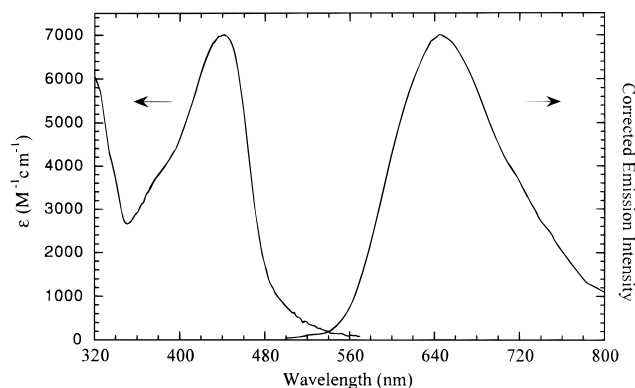


Figure 3. Absorption spectrum and corrected emission spectrum ($\lambda^{\text{ex}} = 450$ nm) of **1** in CH_2Cl_2 at room temperature.

The absorption and emission spectra of **1** were recorded in CH_2Cl_2 (Figure 3). The absorption bands centered at 440 nm ($\epsilon = 7000 \text{ M}^{-1} \text{ cm}^{-1}$) are assigned to MLCT transitions, analogous to those of $[\text{Cu}(\text{dmp})_2]^+$.³⁵ Complex **1** emits in CH_2Cl_2 with a maximum at 646 nm (Figure 3); the absolute quantum yield is 1.0%.³⁶ The excited-state lifetime of **1** in degassed CH_2Cl_2 is 0.73 μs .³⁸ Previous to this report, the longest τ and ϕ for a $[\text{Cu}(\text{NN})_2]^+$ complex in solution were found for $[\text{Cu}(\text{dsbp})_2]^+$ (dsbp = 2,9-di-*sec*-butyl-1,10-phenanthroline) $\tau = 0.40 \mu\text{s}$ and $\phi = 0.45\%$.¹⁰ Relative to $[\text{Cu}(\text{dsbp})_2]^+$, **1** exhibits an 82% increase in τ and a 120% increase in ϕ . The higher ϕ and longer τ of **1** versus $[\text{Cu}(\text{dsbp})_2]^+$ are primarily attributed to a substantial reduction (–45%) in the nonradiative rate constant, k_{nr} .³⁹ This likely results from the maximal interligand steric interactions in **1** (Figure S6) that prevent adoption of a flattened geometry in the vibrationally relaxed excited state, leading to a higher energy emissive state, which in turn reduces the vibrational overlap between the emitting⁴⁰ and ground states.

Complex **1** represents a landmark improvement in the photo-physic of $[\text{Cu}(\text{NN})_2]^+$ complexes.⁴¹ This study also illustrates that inexpensive copper-based complexes can exhibit photophysical properties that are equivalent to, or better than, ruthenium-based analogues.

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Supporting Information Available: Stereoviews, ORTEP diagrams, positional parameters, bond lengths, bond angles, anisotropic thermal parameters, H-atom coordinates, an NMR spectrum, and a space-filling view of **1** (PDF). An X-ray crystallographic file, in CIF format for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(36) The absolute quantum yield ($\pm 20\%$) of **1** was determined in degassed CH_2Cl_2 using $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ as the standard: $\phi(\text{H}_2\text{O}) = 0.042$.^{27,37}

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(38) Lifetime data were determined with excitation at 445 or 455 nm with observation at 675 or 690 nm; the error in τ is estimated to be $\pm 5\%$.

(39) The k_r and k_{nr} values are: **1**, $k_r = 1.37 \times 10^4 \text{ s}^{-1}$, $k_{\text{nr}} = 1.36 \times 10^6 \text{ s}^{-1}$; $[\text{Cu}(\text{dsbp})_2]^+$, $k_r = 1.13 \times 10^4 \text{ s}^{-1}$, $k_{\text{nr}} = 2.49 \times 10^6 \text{ s}^{-1}$.

(40) The emitting state is likely composed of at least two MLCT excited states.³⁵

(41) Although complex **1** is stable in CH_2Cl_2 and MeOH, upon dissolution in CH_3CN or DMSO, it readily dissociates to $[\text{Cu}(\text{dmp})_2]^+$, $[\text{Cu}(\text{dbp})\text{S}_2]^+$ (S = solvent) and dbp. We believe that dissociation occurs in CH_3CN and DMSO because the stability of the complex is not high enough to offset the formation of $[\text{Cu}(\text{dbp})\text{S}_2]^+$.