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)

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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)

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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] complexes, 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)](PF$_6$) (**1**) is prepared by first stirring 1 equiv of dbp[15] with 1 equiv of [Cu(CH$_3$CN)$_4$](PF$_6$)[16] in CH$_2$Cl$_2$ under N$_2$. 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)$_2$](PF$_6$) 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 d[10] 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 CuN$_4$ 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 (λ_{max}^{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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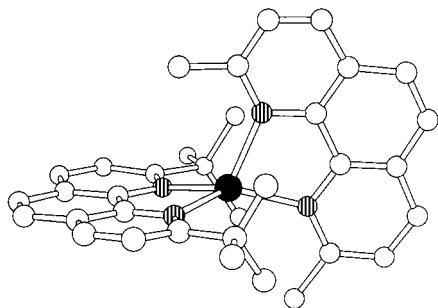
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(18) Complex **1** crystallizes in space group $P2_1$ with a = 15.489(7) Å, b = 11.983(7) Å, c = 18.102(13) Å, β = 91.23(5)°, V = 3359(4) Å³, and Z = 4. For 6359 unique data with $F > 4.0\sigma(F)$, R = 6.48%.
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Figure 1. One of the independent [Cu(dbp)(dmp)]$^+$ complex cations. Hydrogens have been removed for clarity. Selected bond lengths (Å) and angles (deg) for both independent cations: Cu(1)−N(1), 2.051(6); Cu-(1)−N(2), 2.087(6); Cu(1)−N(2A), 2.088(6); Cu(1)−N(1A), 2.094(6); Cu(2)−N(2B), 2.064(6); Cu(2)−N(1B), 2.080(7); Cu(2)−N(1C), 2.085-(6); Cu(2)−N(2C), 2.096(6); N(1)−Cu(1)−N(2), 81.4(3); N(1)−Cu(1)−N(2A), 131.5(2); N(2)−Cu(1)−N(2A), 113.3(2); N(1)−Cu(1)−N(1A), 133.6(2); N(2)−Cu(1)−N(1A), 114.6(2); N(2A)−Cu(1)−N(1A), 83.9-(2); N(2B)−Cu(2)−N(1B), 81.2(3); N(2B)−Cu(2)−N(1C), 132.1(3); N(1B)−Cu(2)−N(1C), 115.7(2); N(2B)−Cu(2)−N(2C), 131.0(2); N(1B)−Cu(2)−N(2C), 115.0(3); N(1C)−Cu(2)−N(2C), 84.4(2).
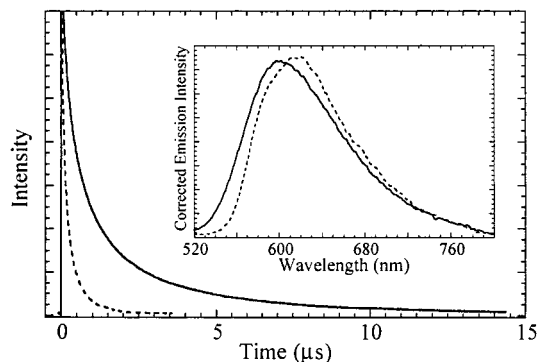
Figure 2. Time-resolved, room-temperature photoluminescent spectra of [Cu(dbp)(dmp)](PF$_6$) (——) and [Ru(bpy)$_3$](PF$_6$)$_2$ (- - -) at 675 nm; λ^{ex} = 455 nm. Since each decay is best-fit by multiple exponentials, an effective half-life (τ^{eff}) was calculated from the time the total area under the curves decreased by 50%: τ^{eff}, [Cu(dbp)(dmp)](PF$_6$) = 1.5 μs; τ^{eff}, [Ru(bpy)$_3$](PF$_6$)$_2$ = 0.21 μs. Inset: corrected solid-state emission spectra of [Cu(dbp)(dmp)](PF$_6$) (——) and [Ru(bpy)$_3$](PF$_6$)$_2$ (- - -); λ^{ex} = 450 nm.

(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 [Ru(bpy)$_3$](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 [Cu(NN)$_2$]$^+$ complexes, [Cu(bfp)$_2$](PF$_6$).[33,34] Further, the solid-state lifetime of **1** is considerably longer than that found for [Ru(bpy)$_3$](PF$_6$)$_2$ (Figure 2).

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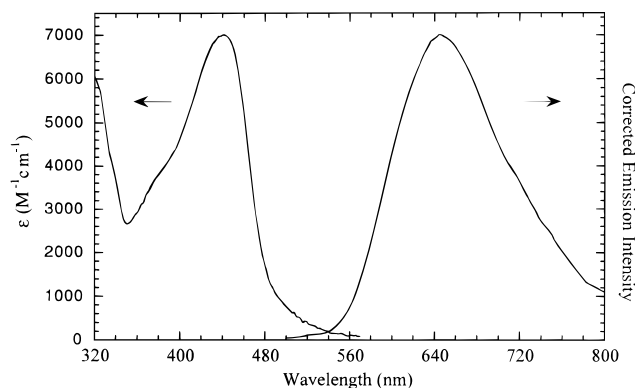

Figure 3. Absorption spectrum and corrected emission spectrum (λ^{ex} = 450 nm) of **1** in CH$_2$Cl$_2$ at room temperature.

The absorption and emission spectra of **1** were recorded in CH$_2$-Cl$_2$ (Figure 3). The absorption bands centered at 440 nm (ϵ = 7000 M^{-1} cm^{-1}) are assigned to MLCT transitions, analogous to those of [Cu(dmp)$_2$]$^+$.[35] Complex **1** emits in CH$_2$Cl$_2$ 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$_2$Cl$_2$ is 0.73 μs.[38] Previous to this report, the longest τ and ϕ for a [Cu(NN)$_2$]$^+$ complex in solution were found for [Cu(dsbp)$_2$]$^+$ (dsbp = 2,9-di-*sec*-butyl-1,10-phenanthroline) τ = 0.40 μs and ϕ = 0.45%.[10] Relative to [Cu(dsbp)$_2$]$^+$, **1** exhibits an 82% increase in τ and a 120% increase in ϕ. The higher ϕ and longer τ of **1** versus [Cu-(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 emitting[40] and ground states.

Complex **1** represents a landmark improvement in the photophysics of [Cu(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.

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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(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 ±5%.

(39) The k_r and k_{nr} values are: **1**, k_r = 1.37 × 10^4 s^{-1}, k_{nr} = 1.36 × 10^6 s^{-1}; [Cu(dsbp)$_2$]$^+$, k_r = 1.13 × 10^4 s^{-1}, k_{nr} = 2.49 × 10^6 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$_2$Cl$_2$ and MeOH, upon dissolution in CH$_3$CN or DMSO, it readily dissociates to [Cu(dmp)$_2$]$^+$, [Cu(dbp)S$_2$]$^+$ (S = solvent) and dbp. We believe that dissociation occurs in CH$_3$CN and DMSO because the stability of the complex is not high enough to offset the formation of [Cu(dbp)S$_2$]$^+$.