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Articles

Cooperative Substituent Effects on the Excited States of Copper Phenanthrolines

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Copper phenanthrolines are attractive as potential photosensitizers because of the ready availability of the metal, but efficient nonradiative decay including a solvent-induced quenching phenomenon ordinarily limits their utility. However, the present studies show that the addition of methyl substituents in the 3,8-positions of 1,10-phenanthroline can enhance the protective effect that bulky groups in the 2,9-positions have on the reactive charge-transfer excited state of a bis-ligand copper(I) derivative. Thus, the photoexcited $Cu(dbtmp)_2^+$ complex has a lifetime of 920 ns in dichloromethane, whereas the parent complex without the methyl substituents has a lifetime of only 150 ns under the same conditions (dbtmp = 2,9-di-*n*-butyl-3,4,7,8-tetramethyl-1,10-phenanthroline). In dichloromethane, the complex with the 2,9-diphenyl-3,4,7,8-tetramethyl-1,10-phenanthroline ligand also exhibits a long lifetime (480 ns). Even more importantly, the latter combination of substituents appears to eliminate the problem of solvent-induced exciplex quenching.

Introduction

Substituent effects have come to the fore in the development of the chemistry of copper(I) with 1,10-phenanthroline derivatives. (In the following, phen denotes the 1,10-phenanthroline ligand itself and NN designates a generic derivative.) A seminal finding was that the presence of moderately bulky substituents in the 2,9-positions enhances the ligand's selectivity for copper(I) binding and stabilizes the resulting copper(I) complexes against oxidation.[1,2] Subsequent work has shown that the same sterically active substituents enhance the energy, the intensity, and the lifetime of the emission from the lowest energy metal-to-ligand charge-transfer (CT) excited state.[3−5] Part of the explanation is that bulky substituents inhibit a flattening distortion that would otherwise promote nonradiative decay.[3,4,6] Bulky substituents also suppress ligand-addition reactions which are possible in the excited state due to the increase in the formal oxidation state of the metal ion. Such reactions represent a novel type of exciplex quenching.[7−9] Consistent with steric inhibition, Dietrich-Buchecker et al. showed that exciplex quenching is much less efficient for the CT excited state of $Cu(dpp)_2^+$ than for that of $Cu(dmp)_2^+$.[10] (dpp denotes 2,9-diphenyl-1,10-phenanthroline, and dmp denotes 2,9-dimethyl-1,10-phenanthroline.) Bulky alkyl substituents in the 2,9-positions have a similar effect.[4] Ultimately, however, interligand steric interactions destabilize the ground state if the substituents are too bulky. Thus, attempts to isolate the $Cu(NN)_2^+$ complex carrying *tert*-butyl or mesityl substituents in the 2- and 9-positions have proved unsuccessful,[11,12] though Karpishin and co-workers successfully prepared the complex of the 2,9-bis(trifluoromethyl)-1,10-phenanthroline ligand.[13]

The present report shows that buttressing methyl substituents in the 3,8-positions of the phenanthroline ligand enhance the influence of the substituents in the 2,9-positions. Thus, the CT states of the $Cu(NN)_2^+$ complexes of 2,9-di-*n*-butyl-3,4,7,8-tetramethyl-1,10-phenanthroline (dbtmp) and 2,9-diphenyl-3,4,7,8-tetramethyl-1,10-phenanthroline (dptmp) exhibit surprisingly long lifetimes even in donor media. Moreover, in dichloromethane, the dbtmp system has a lifetime of nearly 1 μs. The first hint that such cooperative substituent effects could be important came from a recent study of the $Cu(tptap)_2^+$ system[14] (tptap = 2,3,6,7-tetraphenyl-1,4,6,7-tetraazaphenanthroline). In that complex, the rigidity imposed by the juxtapositioned phenyl substituents resulted in a relatively low Franck−Condon barrier and unusually facile electron-transfer quenching.

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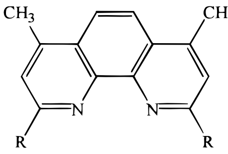
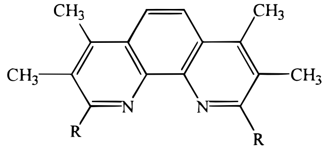


dbdmp, R = *n*-butyl
dpdmp, R = phenyl



dbtmp, R = *n*-butyl
dptmp, R = phenyl

Experimental Section

Materials. Scientific Products supplied Burdick and Jackson high-purity, distilled-in-glass-grade acetonitrile, *N*,*N*-dimethylformamide (DMF), dichloromethane (DCM), and tetrahydrofuran (THF). The laser dye Coumarin 440 came from Laser Science. The phen, dmp, 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp), $CuCl_2 \cdot 2H_2O$, KPF_6, *n*-butyllithium in hexanes, and phenyllithium in diethyl ether were from Aldrich Chemical Co. G. F. Smith provided the 4,7-dimethyl-1,10-phenanthroline (4,7-dmp). The complexes $[Cu(dbp)_2]PF_6$ and $[Cu(dpp)_2]PF_6$ were on hand from previous studies[4,15] (dbp = 2,9-di-*n*-butyl-1,10-phenanthroline).

Methods. The general method for the incorporation of the 2,9-substituents in the appropriate ligand precursor was that of Pallenburg and co-workers.[11] The desired product typically eluted as the first fraction off an alumina column with DCM as the mobile phase. The final purification step involved recrystallization from ethanol. The preparations of all $[Cu(NN)_2]PF_6$ compounds followed a published method.[16] H. Daniel Lee of Purdue University determined the microanalytical results.

2,9-Di-*n*-butyl-4,7-dimethyl-1,10-phenanthroline (dbdmp). Recrystallization of a pale yellow fraction off the alumina column yielded the solid as a white monohydrate. Anal. Calcd for $C_{22}H_{30}N_2O$: C, 78.06; H, 8.93; N, 8.28. Found: C, 78.10; H, 8.76; N, 8.14. In this and in all subsequent tabulations, the chemical shifts are relative to TMS. ^1H NMR ($CDCl_3$, δ in ppm): 7.92 (s, 2H), 7.34 (s, 2H), 3.19 (m, 4H), 2.74 (s, 6H), 1.88 (quintet, 4H), 1.51 (sextet, 4H), 1.00 (t, 6H). Melting point: 60−62 °C.

2,9-Di-*n*-butyl-3,4,7,8-tetramethyl-1,10-phenanthroline (dbtmp). The final product was a white solid. Anal. Calcd for $C_{24}H_{32}N_2$: C, 82.71; H, 9.25; N, 8.04. Found: C, 82.38; H, 8.98; N, 7.78. ^1H NMR ($CDCl_3$, δ in ppm): 7.92 (s, 2H), 3.18 (m, 4H), 2.67 (s, 6H), 2.50 (s, 6H), 1.90 (quintet, 4H), 1.55 (sextet, 4H), 1.07 (t, 6H). Melting point: 134−136 °C.

2,9-Diphenyl-4,7-dimethyl-1,10-phenanthroline (dpdmp). Recrystallization from a mixture of cyclohexane and acetone yielded a pale yellow hemihydrate. Anal. Calcd for $C_{26}H_{20}N \cdot 0.5H_2O$: C, 84.53; H, 5.73; N, 7.58. Found: C, 84.42; H, 5.39; N, 7.31. ^1H NMR ($CDCl_3$, δ in ppm): 8.49 (s, 4H), 8.00 (m, 4H), 7.55 (m, 6H), 2.85 (s, 6H). Melting point: 251−253 °C.

2,9-Diphenyl-3,4,7,8-tetramethyl-1,10-phenanthroline (dptmp). The final product was a cream-colored crystalline solid. Anal. Calcd for $C_{28}H_{24}N_2$: C, 86.56; H, 6.23; N, 7.21. Found: C, 86.18; H, 6.17; N, 7.04. ^1H NMR ($CDCl_3$, δ in ppm): 8.09 (s, 2H), 7.70 (d, 4H), 7.45 (t, 2H), 7.15 (t, 4H), 2.78 (s, 6H), 2.50 (s, 6H). Melting point: 282−284 °C.

$[Cu(dbdmp)_2]PF_6 \cdot {}^1/_2H_2O$. This compound crystallized out of aqueous ethanol as an orange solid. Anal. Calcd for $C_{44}H_{57}N_4O_{0.5}CuPF_6$: C, 61.56; H, 6.58; N, 6.53. Found: C, 61.52; H, 6.55; N, 6.46. ^1H NMR ($CDCl_3$, δ in ppm): 8.18 (s, 4H), 7.55 (s, 4H), 2.87 (s, 12H), 2.62 (m, 8H), 1.28 (quintet, 8H), 0.62 (sextet, 8H), 0.22 (t, 12H). The ^1H NMR spectrum confirmed the presence of the lattice water.

Table 1. Room-Temperature Absorption and Emission Data for $Cu(NN)_2^+$ Systems in CH_2Cl_2

ligand	λ_{max}(abs), nm	λ_{max}(em),[a] nm	τ, ns[b]	$10^3\phi$[c]
phen	440			
4,7-dmp	434			
tmb	430			
dbp	457	715	150	0.9[d]
dbdmp	456	710	145	
dbtmp	453	670	920	6.3
dpp	440	720	270	0.94
	560 sh	715[e]		0.97[e]
				1.0[f]
dpdmp	440	720	310	
	550 sh			
dptmp	467	715	480	3.7

[a] Corrected emission maxima (±5 nm). [b] Error ±5%. [c] Emission quantum yield (±10%); this work, except as noted. [d] Reference 4. [e] Ruthkosky, M.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1996**, *35*, 6406−6412. [f] Everly, R. M.; McMillin, D. R. *Photochem. Photobiol.* **1989**, *50*, 711−716.

$[Cu(dbtmp)_2]PF_6$. After recrystallization from water and ethanol, the solid was orange-brown. Anal. Calcd for $C_{48}H_{64}N_4CuPF_6$: C, 63.67; H, 7.12; N, 6.19. Found: C, 63.60; H, 6.81; N, 6.17. ^1H NMR ($CDCl_3$, δ in ppm): 8.17 (s, 4H), ∼2.82 (m, 8H), 2.78 (s, 12H), 2.50 (s, 12H), 1.15 (quintet, 8H), 0.40 (sextet, 8H), 0.10 (t, 12H).

$[Cu(dpdmp)_2]PF_6 \cdot (CH_3C(O)CH_3)$. Recrystallization of a wine-red material from water and acetone yielded dark red crystals. Anal. Calcd for $C_{55}H_{46}N_4OCuPF_6$: C, 63.25; H, 4.08; N, 5.67. Found: C, 63.01; H, 4.15; N, 5.48. ^1H NMR ($CDCl_3$, δ in ppm): 8.13 (s, 4H), 7.65 (s, 4H), 7.35 (d, 8H), 6.76 (t, 4H), 6.49 (t, 8H), 2.87 (s, 12H). The ^1H NMR spectrum confirmed the presence of acetone.

$[Cu(dptmp)_2]PF_6 \cdot 2H_2O$. Precipitation from water and ethanol yielded red needles. Anal. Calcd for $C_{56}H_{49}N_4O_{0.5}CuPF_6$: C, 67.63; H, 4.97; N, 5.66. Found: C, 67.37; H, 4.74; N, 5.63. ^1H NMR ($CDCl_3$, δ in ppm): 8.15 (s, 4H), 6.72 (d, 8H), 6.60 (t, 4H), 6.40 (t, 8H), 2.79 (s, 12H), 2.25 (s, 12H). The ^1H NMR spectrum confirmed the presence of the lattice water.

Prior to luminescence, lifetime, or quenching studies, a series of freeze−pump−thaw cycles removed dioxygen from the samples. A 525 nm long-pass filter protected the photomultiplier tube from stray light, while a 450 nm notch filter helped isolate the excitation wavelength. A user-written program provided fits to the luminescence decay curves, and in all cases, the residual plots justified the use of a single exponential. Reference 4 gives a detailed description of the methods for estimating emission quantum yields and obtaining corrected spectra. In the NMR experiments, the internal reference was the residual proton signal of the $CDCl_3$ solvent.

Instrumentation. The absorption and emission spectrophotometers were a Perkin-Elmer Lambda 4C and a SLM SPF 500C instrument, respectively. The description of the lifetime apparatus is already in the literature.[15] The ^1H NMR data were recorded on a 200 MHz Gemini spectrometer.

Results

Table 1 contains absorbance and emission data for the CT transitions of a number of $Cu(phen)_2^+$ derivatives. With or without other substituents present, the introduction of alkyl substituents in the 2,9-positions induces a distinct bathochromic shift in the CT absorption maximum. The length of the carbon chain is not especially critical because $Cu(dmp)_2^+$ absorbs at almost the same wavelength as $Cu(dbp)_2^+$.[4] Introduction of methyl substituents at the 3,8- and/or the 4,7-positions produces a smaller shift of the CT absorption toward shorter wavelengths. In order for there to be any appreciable emission signal in

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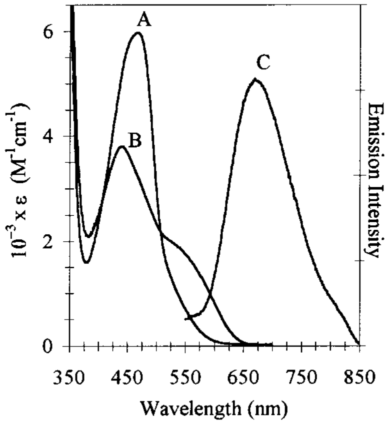

Figure 1. Absorption spectra of (A) $Cu(dptmp)_2^+$ and (B) $Cu(dpdmp)_2^+$ and uncorrected emission spectrum of (C) $Cu(dptmp)_2^+$ in DCM at room temperature.

Table 2. Solvent Dependence of Room-Temperature Emission from $Cu(NN)_2^+$ Systems[a]

	MeCN		THF		DMF	
NN	λ_{max}, nm	τ, ns	λ_{max}, nm	τ, ns	λ_{max}, nm	τ, ns
dbp	730	35	725	50		<10
dbtmp	690	440	670	630	685	170
dpp	740	120	730	190	735	70
dptmp	735	260	725	350	730	260

[a] All emission maxima (±5 nm) from corrected spectra.

solution, bulky groups must be present in the 2,9-positions, but the addition of methyl substituents in the 4,7-positions has little impact on the emission energy or the lifetime. In contrast, buttressing substituents at the 3,8-positions have a marked influence. Thus, the emission from the dbtmp system exhibits a much higher emission quantum yield and a longer lifetime than that from either the dbp or the dbdmp systems (Table 1). The same trend occurs when there are phenyl substituents in the 2,9-positions. The presence of the 3,8 methyl substituents also has an important effect on the absorption spectrum of the $Cu(dptmp)_2^+$ complex. The spectra of the dpp and the dpdmp analogues both display pronounced shoulders in the neighborhood of 560 nm (Figure 1); however, the spectrum of the dptmp complex shows only a very weak shoulder on the long-wavelength side of the CT absorption maximum, which falls at 467 nm.

Independent of the ligand, the CT absorption maximum remains constant, but the emission maximum shifts to lower energy in polar solvents such as DMF or acetonitrile (Table 2). The emission lifetime also decreases with the shift to lower energy. The donor strength of the solvent is also an important factor because of exciplex quenching. Thus, DMF, the most strongly coordinating solvent in the series, almost completely quenches the excited-state lifetime of the dbp complex and significantly reduces that of the dbtmp analogue. The dptmp complex is exceptional in that it shows essentially the same excited-state lifetime in acetonitrile and DMF.

Discussion

Absorption Spectra. The shape of the absorption spectrum of a $Cu(NN)_2^+$ complex can provide some insight into the solution structure in that systems with approximate D_{2d} symmetry exhibit an intense CT maximum in the neighborhood of 450 nm and a weak shoulder at longer wavelengths.[17,18] The spectra of those complexes with *n*-butyl substituents in the 2,9-positions and $Cu(dptmp)_2^+$ all conform to this classic pattern. Analyses suggest that a static or dynamic flattening distortion of the D_{2d} structure accounts for the weak but nonnegligible intensity and the polarization of the low-energy shoulder.[17,18] In the spectra of the dpp and the dpdmp complexes (Figure 1), the prominence of the shoulders suggests that each complex adopts a severely flattened structure in solution. Significant flattening is possible because in the solid state the dihedral angle between the two phenanthroline cores of the dpp system deviates 10−20° from the ideal value of 90° (D_{2d} symmetry), depending on the counterion.[19,20] The dihedral angle of the copper(II) analogue is even larger at 118.9°.[20] The competing forces include steric effects and π conjugation between each phenyl substituent and the phenanthroline core.[19] However, in the case of the dptmp complex, the mesomeric interactions should be relatively weak because the presence of the 3,8 methyl substituents biases the torsion angles of the adjacent phenyl substituents more toward 90° and a D_{2d} geometry.[21] Indeed, the intensity of the CT absorption of the dptmp complex is inconsistent with significant conjugation because the transfer of electron density into the π^* orbitals of the phenyl substituents would attenuate the transition dipole length.[22] The lack of a shoulder in Figure 1A is perhaps the best evidence of a D_{2d} structure for $Cu(dptmp)_2^+$.

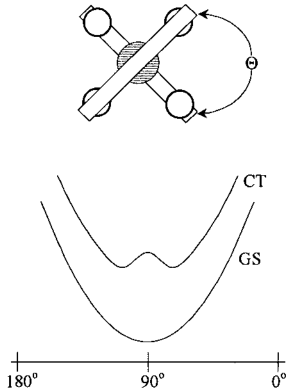

Figure 2. Distortion of a $Cu(NN)_2^+$ system as measured by the dihedral angle θ between the two phenanthroline ligands. The potential energy surface of the CT excited state exhibits a local maximum at $\theta = 90°$.

Photophysical Data. The extent of flattening that occurs in the CT excited state is a critical element in the emission spectrum of a $Cu(phen)_2^+$ system. In simple terms, the driving force for the distortion derives from the increase that occurs in the overlap of the σ-donating orbitals of the nitrogens with the (formally) half-occupied d(*xy*) orbital of the metal. The double-minimum potential energy surface in Figure 2 illustrates how the energy of the CT excited state depends on the dihedral angle between phenanthroline ligands. In the ground state, the complex has a pseudotetrahedral structure and so will the initially populated Franck−Condon excited state. However, subsequent geometric relaxation within the excited-state manifold can profoundly alter the emission energy and the lifetime.[3,5,7] The steric demands of the substituents in the 2,9-positions ultimately limit the extent of flattening. In accord with this model, the plot in Figure 3 shows that the emission energy increases with

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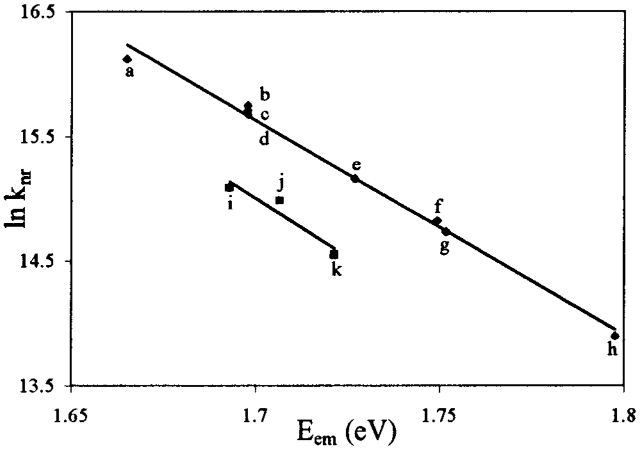

Figure 3. Correlation between the decay rate of the CT excited states of $Cu(NN)_2^+$ species and the emission energy. All data are from DCM solutions at 25 °C. E_m denotes the maximum in the corrected emission spectrum plotted versus energy. The NN ligands are dmp (a), dbdmp (b), dbp (c), 2,9-di-*n*-octyl-1,10-phenanthroline (d), 2,9-dineopentyl-1,10-phenanthroline (e), 2,9-diisopropyl-1,10-phenanthroline (f), 2,9-di-*sec*-butyl-1,10-phenanthroline (g), dptmp (h), dpp (i), dpdmp (j), and dptmp (k). The data for points d, e, and g were taken from ref 4, and the datum for point f was taken from ref 14.

the size of the substituents in the 2,9-positions and that the log of the decay rate varies linearly with the energy.

The logarithmic dependence is consistent with the familiar energy gap law,[23,24] but there are several caveats to bear in mind. One complication is that the emission maximum reflects, not one, but at least two excited states of the copper phenanthroline. More specifically, studies have shown that there are overlapping emissions from close-lying singlet and triplet CT excited states.[25] The equilibrium population of the singlet excited state is actually quite low, but the magnitudes of the radiative rate constants are such that an appreciable fraction of the room-temperature intensity derives from the higher lying state. Any variation in the relative participation of the two excited states could, of course, influence the trend in Figure 3. The theory behind the energy gap law also assumes that the emitting state nests within the ground-state surface,[24] but the flattening distortion complicates the picture for the copper phenanthrolines (Figure 2). Another qualification is that theory deals with the energy dependence of the nonradiative decay rate. However, for the systems at hand, the emission yields are so small that the nonradiative decay rate is virtually equal to the total decay rate. Finally, the energy range covered in Figure 3 is rather narrow, so one should be cautious about extrapolating the plots too far.

Despite the tensions noted above, the energy gap law provides a simple rationalization of the data. In this regard, it is noteworthy that the compounds with aryl substituents in the 2,9-positions give rise to a separate kind of correlation, almost parallel to that of the alkyl derivatives (Figure 3). Alford et al. have reported the same effect in their studies of ruthenium polypyridines.[26] The slopes in Figure 3 are, however, quite steep. For example, within the alkyl-substituted series, the decay rate increases by about 17.2 natural log units/eV, which is almost 3 times the rate as that observed by Meyer and co-workers for related osmium phenanthrolines.[23,27] When Cummings and Eisenberg varied substituents on the diimine (NN) of a mixed-ligand platinum(II) dithiolate, they also obtained a $\ln(k_{nr})$ versus E_{em} plot with a slope of -6.2 eV^{-1}.[28] On the other hand, in studies of the excited-state decay rates in the $Ru(NN)(CO)_2X_2$ and $Re(NN)(CO)_3X$ series, Stufkens and Vlček noted a very strong energy dependence when the halogen X ranged from Cl to Br to I.[29] They rationalized the results in terms of a changing orbital parentage. Specifically, when X = I, they concluded that the excited state had more $p\pi(X) \rightarrow NN$ than $d \rightarrow NN$ charge-transfer character and that there was less extensive geometric relaxation in the iodide. A geometric factor is also likely to be important in the case of the copper phenanthrolines because a change of substituent will shift the excited-state minimum along the distortion coordinate as well as the energy coordinate of Figure 2. From this perspective, it comes as no surprise that the Franck–Condon factors for crossing to the ground-state surface are extremely sensitive functions of the substituent.

The goal is to minimize the distortion that occurs in the excited state in order to maximize the lifetime. The most dramatic result is that the lifetime of the CT excited state of $Cu(dbtmp)_2^+$ is 6 times that of the dbp analogue and is the longest yet found for a $Cu(NN)_2^+$ system in fluid solution. The obvious explanation is that the 3,8 methyl groups restrict the conformational freedom of the groups in the 2,9-positions of the phenanthroline ligand and thereby increase the effective steric demand of the ligand. As a result, the complex emits at a shorter wavelength and exhibits a relatively long excited-state lifetime. The 3,8 methyl groups could exert an electronic effect as well, but it should be modest. In the case of the $Ru(NN)_3^{2+}$ analogues, for example, $Ru(tmp)_3^{2+}$ and the 4,7-dimethyl-1,10-phenanthroline-containing analogue exhibit almost the same lifetime.[30] Recently Karpishin and co-workers described a mixed-ligand $Cu(NN)_2^+$ system that also exhibits a relatively long excited-state lifetime in DCM.[31] Due to the steric constraints inherent in the combination of the dmp ligand with 2,9-di-*tert*-butyl-1,10-phenanthroline, the lifetime is 730 ns. However, the mixed-ligand complex undergoes ligand disproportionation reactions in donor solvents such as acetonitrile.[31]

Cooperative substituent effects also have a significant impact on the solvent dependence of the emission from copper phenanthrolines. As is the case with $Ru(NN)_3^{2+}$ systems, the emission energy normally varies inversely with the dielectric constant of the solvent. The reason is that polar solvents stabilize the CT excited state which develops $Cu^{2+}-(NN)^-$ character once the excitation localizes in the π^* orbital of one of the ligands.[32] For selected ruthenium systems, the lifetime varies in accordance with the energy gap law.[23] However, solvent-induced exciplex quenching obscures the trend in the case of most $Cu(NN)_2^+$ systems. Consider acetonitrile and DMF. Both solvents are relatively polar, although the emission generally occurs at a somewhat longer wavelength in acetonitrile (Table

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2). Due to the difference in basicity,[33] however, the lifetime is almost always shorter in DMF.[6] For example, DMF virtually extinguishes the emission from the dbp complex, though an emission signal persists for the more crowded Cu(dbtmp)$_2^+$ system. In the case of the dptmp system, however, the steric influence of the substituents is so great that exciplex quenching is virtually inconsequential. As a result, the emissive CT state has essentially the same lifetime in acetonitrile and DMF so that for this system the solvent dependence of the emission energy is principally responsible for the lifetime variation.

In conclusion, a conformational locking effect[34] induced by appropriately positioned, back-to-back substituents in a Cu(NN)$_2^+$ system restricts structural relaxation within the excited state, enhances the emission energy, and extends the excited-state lifetime. Energy-gap-law considerations have a major influence on the lifetime, but the suppression of exciplex quenching is an equally crucial factor in donor media.

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