Steric Effects in the Ground and Excited States of $Cu(NN)_2^+$ Systems

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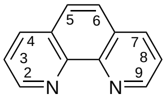
This investigation focuses on a series of pseudotetrahedral complexes of the form $Cu(NN)_2^+$, where NN denotes a 1,10-phenanthroline ligand with alkyl substituents in the 2 and 9 positions and the counterion is PF_6^-. In these copper(I) systems, steric effects are of considerable interest because the electronic configuration predisposes the reactive charge-transfer excited state to undergo a flattening distortion or to add a fifth ligand. Both effects lead to emission quenching and a shorter excited-state lifetime. Bulky substituents inhibit these processes, but the spatial distribution of the atoms involved is more important than the total molecular volume in determining the influence of a substituent. According to the results of this study, the effective size decreases in the following order: *sec*-butyl > neopentyl > *n*-octyl ≈ *n*-butyl > methyl. In conjunction with the electrochemical data, the absorption and the emission spectra reveal three kinds of steric effects: (1) Clashes between substituents on opposite phenanthroline ligands hinder D_2 flattening distortions in the oxidized form of the complex and in the charge-transfer excited state of the $Cu(NN)_2^+$ system itself. (2) Steric interactions connected with a highly branched substituent, like the neopentyl group, destabilize the $Cu(NN)_2^+$ ground state. (3) Finally, the presence of bulky groups disfavors expansion of the coordination number. The complex with *sec*-butyl substituents is noteworthy because it exhibits the longest excited-state lifetime (∼400 ns in CH_2Cl_2) ever measured for a $Cu(NN)_2^+$ system in fluid solution. In addition, it exhibits a luminescence lifetime of 130 ns in acetonitrile which is ordinarily a potent quencher of photoexcited $Cu(NN)_2^+$ systems.

Introduction

The complexes of low-valent metal centers such as Fe(II), Ru(II), or Cu(I) with chelating, heteroaromatic ligands like 1,10-phenanthroline (phen) form an important class of compounds. Due to the presence of the low-energy π* orbitals of the ligand, the adducts exhibit strong metal−ligand charge-transfer (CT) absorption bands in the visible spectrum. For labile metal centers such as Fe(II) and Cu(I), the adducts are useful in colorimetric analysis schemes.[1] In this regard, phenanthroline derivatives with moderately bulky substituents, e.g., methyl groups, in the 2 and 9 positions are highly selective for Cu(I) over Fe(II). The selectivity arises because interligand steric interactions hinder the formation of a low-spin, trischelate complex with iron(II), whereas pseudotetrahedral complexes with copper(I) form with relative ease.[2]



phen

Substituent groups in the 2 and 9 positions also have an important impact on the stability of the copper systems in the ground and the excited states. For example, the presence of alkyl substituents renders the copper(I) state air stable and facilitates colorimetric procedures. Even though alkyl groups tend to be electron donating, the presence of these groups elevates the $Cu^{2+/+}$ reduction potential.[3−6] Thus, the potential of the $Cu(dmp)_2^{2+/+}$ system, where dmp denotes 2,9-dimethyl-1,10-phenanthroline, is 0.68 V vs SCE in acetonitrile while the $Cu(phen)_2^{2+/+}$ couple has a potential of 0.04 V.[7] In dimethylformamide, the corresponding dmp and phen complexes have potentials of 0.58 and 0.08 V, respectively.[8] One reason for the shift in potential is that bulky substituents in the 2 and 9 positions limit the extent of the D_2 flattening distortion that occurs in the oxidized form of the complex.[3,6,9] In addition, the presence of the substituents inhibits the addition of a fifth ligand. In the case of the excited state, which formally involves a copper(II) center, Everly et al. showed that complexes with bulky substituents in the 2 and 9 positions exhibit an enhanced emission lifetime and higher energy emission relative to $Cu(dmp)_2^+$ in a low-temperature alcohol glass.[10] This is a consequence of a reduction in the extent of the D_2 flattening. Shinozaki and Kaizu reached a similar conclusion in their studies of $Cu(dmp)_2^+$ and $Cu(phen)_2^+$ in the solid state.[11]

Sterically active substituents also influence excited-state reactivity. Bulky substituents may enhance energy-transfer and electron-transfer processes by reducing Franck−Condon barri-

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Table 1. Ligand Information

ligand abbrev	2,9 substituents	ref
dsbp	$\mathrm{CH(CH_3)(C_2H_5)}$	21
dnpp	$\mathrm{CH_2C(CH_3)_3}$	21
dop	$\mathrm{CH_2(CH_2)_6CH_3}$	21
dbp	$\mathrm{CH_2(CH_2)_2CH_3}$	10
dmp	$\mathrm{CH_3}$	10

ers.[12,13] On the other hand, they should inhibit ligand addition reactions which induce a novel type of quenching known as exciplex quenching.[14−16] The solvent may act as the attacking ligand, but counterions such as $\mathrm{NO_3}^-$ and $\mathrm{ClO_4}^-$ are also effective quenchers.[17] Literature data show that the introduction of bulky phenyl substituents impedes exciplex quenching.[15,18,19] However, with aryl substituents the CT absorption intensity spreads over a broad region of the visible spectrum, apparently because of a low-symmetry structure in the ground state.[20] Systems with *N*-toluidinomethyl substituents in the 2 and 9 positions exhibit quite long lifetimes in a low-temperature glass but show essentially no useful emission in solution due to an intramolecular exciplex quenching mechanism that involves the coordination of one of the toluidine nitrogens.[10] To isolate the steric effects more effectively, there is clearly a need to develop 1,10-phenanthroline derivatives containing sterically active, but electronically innocent substituents in the 2 and 9 positions. The following report deals with a series of ligands with simple alkyl substituents. Some of the systems have remarkably long emission lifetimes in fluid solution, even in donor media.

Experimental Section

Materials. We obtained acetonitrile, tetrahydrofuran, and methylene chloride as Burdick and Jackson high-purity distilled in glass-grade chemicals from Scientific Products. The laser dyes, Coumarin 440 and Coumarin 540A, came from Laser Science, while J. T. Baker Chemical Co. supplied $\mathrm{[Ru(bpy)_3]Cl_2{\cdot}6H_2O}$, where bpy denotes the 2,2′-bipyridine ligand. Ferrocene came from Strem Chemical Co., and the tetrabutylammonium hexafluorophosphate (TBAH) came from Aldrich Chemical Co. The ligand abbreviations and references for the preparations of the $\mathrm{Cu(NN)_2}^+$ complexes, where NN denotes a phenanthroline ligand, appear in Table 1.

Methods. Where necessary, we used metathetical procedures to convert the copper complexes to the hexafluorophosphate salt. For example, we dissolved $\mathrm{[Cu(dnpp)_2]Cl}$ in a methanol/water mixture and precipitated $\mathrm{[Cu(dnpp)_2]PF_6}$ by addition of an excess of $\mathrm{KPF_6(aq)}$. As a further means of purification, we recrystallized the product from a mixture of methanol and water. A variation of the method of Sauvage and co-workers permitted the separation of the free NN ligand from the copper complex.[7]

For the cyclic voltammetry scans, the solvent was acetonitrile containing 0.1 M TBAH, and the scan rate was typically 50 mV/s. The working electrode was a gold disk, and the reference was a AgCl/Ag electode containing 3 M NaCl. However, we report potentials vs ferrocene in acetonitrile.

Prior to the luminescence studies, we deoxygenated the $\mathrm{Cu(NN)_2}^+$ solutions by a series of freeze−pump−thaw cycles. The copper concentration was ~50 μM. For the reference solution of $\mathrm{Ru(bpy)_3}^{2+}$ in water, we deoxygenated the cuvette with a stream of argon. A combination of 585 and 700 nm long-wave-pass filters served to isolate the luminescence signal for lifetime determination. We analyzed the decays with the user-written program TAU.RES. In all cases, the residual plots justified the use of a single exponential. The method of Parker and Rees[22] yielded emission quantum yields at 25 °C with $\mathrm{Ru(bpy)_3}^{2+}$ as the standard ($\Phi = 0.042$).[23] For the excitation we used a wavelength of 440 nm, and we calculated emission correction factors on the basis of a corrected spectrum of $\mathrm{Ru(bpy)_3}^{2+}$ that we obtained from R. J. Watts of the University of California at Santa Barbara.

Instrumentation. For absorption and emission spectra we used a Perkin-Elmer Lambda 4C spectrophotometer and an SLM SPF 500 C fluorometer. The description of the lifetime setup is in the literature.[13] The cyclic voltammetry apparatus was a Model CV-27 from Bioanalytical Systems, Inc.

Results

Electrochemistry and Absorption Data. The investigation centered on the first oxidation process in acetonitrile as well as in methylene chloride and the first reduction process for each copper complex in acetonitrile (Table 2). The cyclic voltammograms were unremarkable except for the $\mathrm{Cu(dnpp)_2}^+$ system in acetonitrile. Figure 1A shows that, after oxidation, this complex gave a return wave that was broad with two poorly resolved maxima in the range of 0.2−0.4 V (Figure 1A). Although the free ligand did not dissolve very well in acetonitrile, it was possible to run in the presence of excess dnpp. Under these conditions, there was additional anodic current due to free ligand near the switching potential, but the cathodic wave contained a single, albeit somewhat broad peak (Figure 1B). However, during subsequent scans the cathodic wave broadened further and evolved into two poorly resolved peaks once again. The most likely explanation of the results is that ligand dissociation occurs, especially after oxidation to copper(II):

$$\mathrm{Cu(dnpp)_2}^{n+} \rightleftarrows \mathrm{Cu(dnpp)}^{n+} + \mathrm{dnpp} \qquad (1)$$

where the assumption is that solvent molecules fill the available coordination sites. Karlsson et al. observed a similar effect in their studies involving the 2,3,8,9-tetraphenyl-1,4,5,8-tetraazaphenanthrene ligand.[24] According to this view, then, the second small wave at 0.3 V corresponds to the reduction of $\mathrm{Cu(dnpp)}^{2+}$. Once reduction occurs, reassociation of the ligand may explain the absence of an oxidation wave for $\mathrm{Cu(dnpp)}^+$. Copper(II)-induced oxidation of ligand may account for the loss of ligand that becomes apparent in subsequent scans of the sample in Figure 1B. Consistent with the operation of eq 1 in a coordinating solvent, the cyclic voltammogram of the $\mathrm{Cu(dnpp)_2}^{2+/+}$ couple showed no evidence of ligand dissociation in methylene chloride. The results in Table 2 reveal that the copper(II)/copper(I) potentials all shifted to more positive values in methylene chloride. This may be a reflection of the weak basicity of the chlorinated solvent and the fact that the oxidized form of the complex is prone to add a ligand. However, there is no correlation between the shift in potential and the steric requirements of the ligands in the series. The response for the

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Table 2. Physical Data

				E_o,[a] V vs ferrocene		
	λ_{max}^{abs}, nm (ϵ, M^{-1} cm^{-1})			CH_2Cl_2	CH_3CN	
complex	CH_2Cl_2	THF	CH_3CN	$Cu(NN)_2{}^{2+/+}$	$Cu(NN)_2{}^{2+/+}$	$Cu(NN)_2{}^{+/0}$
$Cu(dsbp)_2{}^+$	455 (6600)	452	452	0.68	0.50	−2.19
$Cu(dnpp)_2{}^+$	449 (5700)	445	445	0.61	0.43	
$Cu(dop)_2{}^+$	458 (7200)	456	454	0.61	0.43	−2.18
$Cu(dbp)_2{}^+$	457 (7000)	456	455	0.61	0.43	−2.18
$Cu(dmp)_2{}^+$	457 (7800)	455	455	0.50	0.27	

[a] Formal potential in a medium containing 0.1 M TBAH. The estimated error is ±0.02 V.

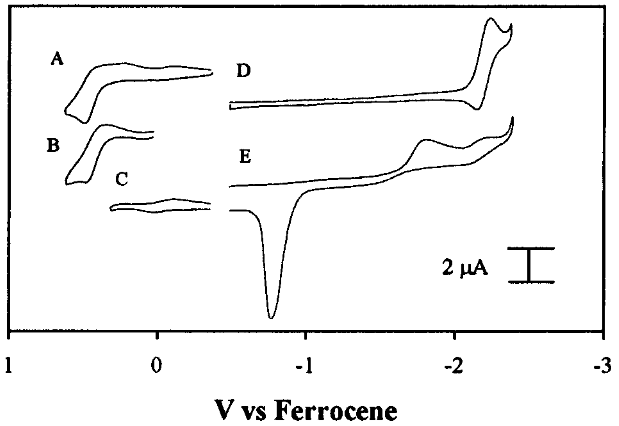

Figure 1. Cyclic voltammograms: (A) oxidation of $Cu(dnpp)_2{}^+$; (B) same as (A) with excess dnpp present; (C) truncated scan of the solution in (A); (D) reduction of $Cu(dsbp)_2{}^+$; (E) reduction of $Cu(dnpp)_2{}^+$ in the presence of excess dnpp. The solvent is acetonitrile containing 0.1 M TBAH. On the abscissa, 0.0 V corresponds to the E_o of ferrocene in the same medium.

$Cu(dsbp)_2{}^{+/0}$ couple in Figure 1D is consistent with a reversible ligand reduction process. The dop and dbp systems behaved similarly at essentially the same potential. However, for the dnpp complex as well as the dmp complex, the process was highly irreversible and yielded widely separated cathodic and anodic maxima (e.g., Figure 1E).

The position of the CT absorption maximum varied with the substituent as well as the solvent (Table 2). The solvent effect was generally small, and for any given complex, the wavelength maximum was nearly the same in THF and acetonitrile. Without exception, though, the absorption maximum shifted to a longer wavelength in methylene chloride. Inspection of Table 2 reveals that substituent variation induced larger changes. For a given solvent, the wavelength of the absorption maximum varied as follows with a change of ligand:

$$\text{dnpp} < \text{dsbp} < \text{dop} \approx \text{dbp} \approx \text{dmp} \qquad (2)$$

At dilute copper concentrations in acetonitrile, the absorption spectrum of the dnpp system was quite sensitive to the presence of excess ligand. In particular, the system exhibited increased absorbance at 360 nm relative to that at 445 nm in the absence of excess dnpp. This is consistent with ligand dissociation and the formation of $Cu(dnpp)^+$ in view of previous work regarding the absorption spectrum of the monophenanthroline complex $Cu(dmp)^+$.[25] Indeed, a spectrophotometric titration shows that $Cu(dnpp)_2{}^+$ is the major species in acetonitrile at a 2:1 dnpp-to-copper(I) ratio but that $Cu(dnpp)^+$ is clearly present until there is an excess of dnpp ligand. (See Supporting Information, Figure S1.)

Table 3. Emission Data from Deoxygenated Solutions[a]

		λ_{max}^{em}, nm (τ,[c] ns)		
complex	$10^4 \times \phi$[b]	CH_2Cl_2	THF	CH_3CN
$Cu(dsbp)_2{}^+$	45	690[d] 650 (400)	660 (200)	670 (130)
$Cu(dnpp)_2{}^+$	16	715[d] 665 (260)	675 (140)	685 (100)
$Cu(dop)_2{}^+$	10	725[d] 673 (155)	683 (55)	690 (50)
$Cu(dbp)_2{}^+$	9	725[d] 670 (150)	680 (50)	690 (35)
$Cu(dmp)_2{}^+$	4	730[d] 690 (90)	~700	~700

[a] From uncorrected spectra except as noted. [b] In deoxygenated methylene chloride. In view of the severe corrections involved, the precision is no better than ~20%. [c] The error in a lifetime measurement is ±5%. [d] From the corrected spectrum.

Luminescence. Both the solvent and substituent groups had a profound effect on the CT luminescence. In general, the emission maximum shifted to longer wavelength in a solvent with a higher dielectric constant. On the other hand, irrespective of the solvent, the data in Table 3 show that the wavelength of the emission maximum decreased as follows with a change of substituent:

$$\text{dsbp} > \text{dnpp} > \text{dop} \approx \text{dbp} > \text{dmp} \qquad (3)$$

The excited-state lifetimes varied in the same way. The lifetime obtained for the dsbp system in methylene chloride is noteworthy in that it is the longest ever reported for a $Cu(NN)_2{}^+$ system in room-temperature, fluid solution. As expected on the basis of exciplex quenching, the emission lifetime of a given complex was shorter in a donor solvent, but the lifetime was always greater in THF than it was in acetonitrile. The dsbp complex was most remarkable in that it exhibited an emission lifetime of 130 ns in acetonitrile, a solvent which virtually completely quenches the emission of the corresponding dmp system. The emission yield was also variable, and complexes that exhibited the most intense photoluminescence also had the longest excited-state lifetimes. For example, with methylene chloride as the solvent, the lifetime of $Cu(dsbp)_2{}^+$ is ~4.5 times greater than that of $Cu(dmp)_2{}^+$, and there is an 11-fold difference in the quantum yields of emission (Table 3). This may indicate that the radiative rate constant is larger in a complex with bulkier substituents, but this is not clear because of the uncertainties in the measured quantum yields. The spectrometer correction factors are the main source of error. Indeed, the falloff in the plot at the top of Figure 2 suggests that the reliability of the correction factors is doubtful at wavelengths beyond ~760 nm. An earlier report quoted an emission quantum yield of 2×10^{-4} for $Cu(dmp)_2{}^+$ in methylene chloride.[26] The value reported in

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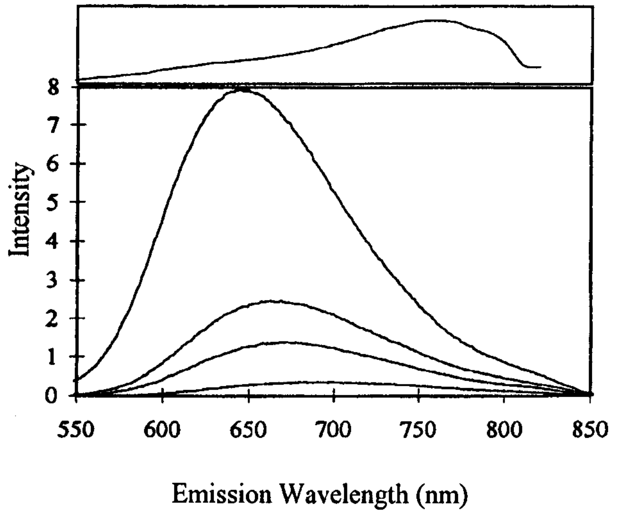

Figure 2. Uncorrected, room-temperature emission spectra of $Cu(NN)_2^+$ systems in methylene chloride. In order of increasing intensity the NN ligands are dmp, dbp ≈ dop, dnpp, and dsbp. Top: spectrometer correction factors.

Table 3 is higher almost certainly because of the quenching effect of the nitrate counterion in the previous study.[17] Figure 2 contains emission spectra of samples dissolved in methylene chloride.

Discussion

Character of the CT State. By comparison with the well-known $Ru(bpy)_3^{2+}$ system, the CT excited states of copper(I) complexes have some distinctive properties. Thus, in the CT excited state, a copper system tends to undergo a flattening distortion due to the "hole" created in a metal−ligand, σ-antibonding orbital.[10,11,27] Previous authors have argued that this type of distortion also accounts for the low-energy shoulder in the absorption spectrum.[28,29] Be that as it may, the geometry change has an important influence on the energetics. In the case of $Ru(bpy)_3^{2+}$, $E_{00} \approx 2.1$ V,[30] where E_{00} denotes the energy separation between the lowest energy vibrational levels of the ground and the emissive electronic excited states. For $Cu(dpp)_2^+$, where dpp denotes 2,9-diphenyl-1,10-phenanthroline, $E_{00} \approx 1.8$ V,[12,31] due in large part to the geometric relaxation that occurs in the copper system. On account of the increase in the formal oxidation state, either metal center will be a stronger Lewis acid in the CT excited state. For the four-coordinate copper systems, however, ligand addition reactions are much more sterically feasible, and this is the basis of the exciplex quenching mechanism noted above.[16,32] The fact is, though, that the excited-state adducts relax so rapidly that they do not accumulate in solution, and to date, they have even escaped direct spectroscopic detection.

Steric Influences within the Copper Systems. A priori, it is difficult to rank the substituents we have used in terms of their steric requirements. On the basis of the total atomic volume, the *n*-octyl group is obviously the largest since it has the most atoms. However, like the *n*-butyl group, the octyl group has a flexible chain structure that can adopt a host of conformations, so it is not the most effective substituent in terms of restricting structural reorganization within the coordination sphere of the metal center. Despite the fact that the *sec*-butyl group contains fewer atoms, it consumes a more significant region of space in the vicinity of the metal center due to the presence of the branched carbon atom. An even greater degree of branching occurs in the neopentyl group, but the branching originates at the β-carbon, somewhat farther from the site of metal binding. In the discussion that follows we will interpret the steric effects on three levels: (1) clashes between substituents on opposite phenanthrolines, (2) unfavorable interactions between the substituents on one ligand and the core of the opposite ligand, and (3) the barrier to the addition of a fifth ligand.

As emphasized by Everly et al.,[10] steric clashes between opposing substituents of the two phenanthroline ligands in a $Cu(NN)_2^+$ system inhibit the flattening distortion that occurs in the CT excited state. As a result, a complex with larger substituents undergoes less structural relaxation and exhibits higher energy emission. According to this criterion, the emission maxima in Table 3 indicate that the effective size of the substituents varies in accordance with eq 3. This trend is also consistent with the lifetime data because a complex with a higher energy excited state typically undergoes radiationless decay less efficiently. With the elevation in lifetime, the emission yield increases because the radiative pathway is more competitive. All else the same, the closer to tetrahedral, the more stable the copper(I) state, so the $Cu(NN)_2^{2+/+}$ potentials are also consistent with the steric ranking in eq 3. There is, however, one curious result. Everly et al. have pointed out that the degree of flattening also has a small impact on the position of the absorption maximum in that bulkier substituents generally induce a shift to a shorter wavelength.[10] Contrary to a prediction based on eq 3, Table 2 shows that the absorption maximum of the dnpp complex, not the dsbp complex, occurs at the shortest wavelength.

Most of the unusual properties of the dnpp system are probably explicable in terms of the steric constraints that its unique tertiary carbon centers impose. In particular, steric interactions with the phenanthroline core of the opposite ligand undoubtedly restrict the conformational freedom of the neopentyl substituents. It is therefore quite plausible that a sterically induced increase in the average metal−ligand separation results in a hypsochromic shift in the CT absorption maximum. Two other observations are consistent with this argument. For one, the evidence for ligand dissociation in acetonitrile points to unique steric interactions that destabilize the $Cu(dnpp)_2^+$ complex. The other indication of steric problems is the irreversible character of the reduction of the $Cu(dnpp)_2^+$ system at a platinum electrode. Thus, the reduced form of the complex decomposes on the time scale of the cyclic voltammetry experiment (Figure 1), and copper metal deposits on the working electrode. As regards the position of the emission maximum, however, the wavelength observed for the dnpp complex is in accordance with the steric ordering in eq 3. Due to the D_2 flattening distortion that occurs, the other complexes may also experience an increase in the average metal−ligand separation in the CT excited state.

The third manifestation of the steric consequences of the 2 and 9 substituents is apparent from the way in which they influence exciplex quenching. With the copper systems this involves the attack of a fifth ligand and, most likely, the formation of a trigonal-bipyramidal coordination geometry where one phenanthroline nitrogen from each ligand and the

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quencher bind at the equatorial positions.[14] Exciplex quenching is extremely efficient in the case of the dmp complex which is practically nonemissive in most donor solvents.[14,33] Indeed, this complex only shows emission in rigid matrices or in weakly donating solvents like methylene chloride or chloroform. The data in Table 3 confirm that the introduction of bulkier groups in the 2 and 9 positions inhibits exciplex quenching.[15] Thus, with a change of ligand, the lifetimes increase in THF or acetonitrile in accordance with eq 3. In this regard the dsbp group is particularly effective at inhibiting exciplex formation as the CT state of $Cu(dsbp)_2^+$ has a lifetime of 130 ns in a solvent as polar as acetonitrile. Since oxidation involves formation of copper(II), the destabilizing effect that bulky substituents have on the five-coordinate form may also help explain the substituent influence on the $Cu(NN)_2^{2+/+}$ potentials.

Finally, the data reveal that the steric properties of the quencher are important as well. Normally, the rate of exciplex quenching follows the Gutmann donor number, and stronger donors make better quenchers.[16] However, the results in Table 3 clearly show that acetonitrile is consistently a better quencher than THF, despite the fact that THF has a higher donor number.[34] This is probably a reflection of a steric interaction that involves the carbon−hydrogen framework of the THF ligand.

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Supporting Information Available: Plot of absorbance data that documents the equilibria of the copper(I)/dnpp system in acetonitrile (1 page). Ordering information is given on any current masthead page.

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