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Luminescence Quenching of Copper(II) Porphyrins with Lewis Bases

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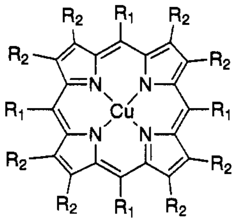
We report quenching studies of the emissions from Cu(TPP), Cu(TMP), and Cu(OEP) in toluene where TPP, TMP, and OEP denote the doubly deprotonated forms of tetraphenylporphyrin, tetramesitylporphyrin, and octaethylporphyrin, respectively. The quenchers are a series of Lewis bases including acetonitrile, DMF, DMSO, three different pyridines, and THF. Results with a sterically encumbered pyridine along with the correlation between quenching ability and donor strength prove that formation of a five-coordinate adduct induces the quenching. Small positive enthalpies of activation for quenching suggest that adduct formation is reversible, at least with the weaker donors. We conclude that the quenching is not intrinsic to the intraligand excited state of the adduct but is due to the influence of another excited state. The available evidence suggests that a d–d state involving $z^2 \rightarrow x^2 - y^2$ excitation is probably responsible for the quenching.

Introduction

The luminescence from copper(II) porphyrins, such as Cu(TPP) depicted below, stems from close-lying trip-doublet and trip-quartet states. The two multiplet states arise because of the interaction of the electron in the $x^2 - y^2$ orbital of the copper center with the unpaired electrons of the intraligand $^3\pi-\pi^*$ excited state.[1,2] On the basis of studies of the temperature dependence of the emission, various workers have proposed that there is a nearby charge-transfer state as well that quenches the emission.[3-6] Just such a low-energy charge-transfer state quenches the porphyrin emission entirely in corresponding Ag(II) systems.[6] In addition, Antipas et al. attributed a weak absorption band that falls below the Q(0,0) band of the copper(II) porphyrins to the charge-transfer state.[6] However, Asano et al. have since assigned this to absorption by a trip-doublet state.[7]



	Cu(TPP)	Cu(TMP)	Cu(OEP)
R_1	phenyl	mesityl	H
R_2	H	H	ethyl

In addition to being sensitive to temperature, the emission from copper(II) porphyrins is quite solvent sensitive. Most importantly, in basic solvents like pyridine or piperidine the excited-state lifetime is extremely short, and there is virtually no emission.[3,6] Kim et al. attributed this to formation of a nonemissive, five-coordinate adduct.[3] In line with these results, our group has shown that the cationic porphyrin Cu(TMPyP4) exhibits no emission in water.[8,9] (TMPyP4 denotes the doubly deprotonated form of 5,10,15,20-tetra(*N*-methylpyridinium-4-yl)porphyrin.) Since the TMPyP4 complex appear to be four-coordinate in solution,[10] we proposed that solvent quenches the emission via a dynamic process involving attack at an axial coordination position.[8] However, we have found that Cu(TMPyP4) is emissive when intercalated into DNA because axial attack is not as feasible.[8] The emission intensity varies with the composition of the DNA because guanine–cytosine base pairs support intercalation while adenine–thymine base pairs favor an external mode of binding.[8-12]

Originally, Gouterman and co-workers concluded that formation of a five-coordinate adduct promoted quenching via the stabilization of the charge-transfer state. More specifically, on the basis of iterated extended Hückel calculations, they assigned the quenching state as a metal-to-ligand charge-transfer state.[6] Subsequent Xα calculations indicated that the low-lying charge-transfer states actually have ligand-to-metal charge-transfer character.[13] More recently, Shelnutt et al. carried out additional calculations that indicated that the ligand-to-metal charge-transfer state does, in fact, drop to lower energy as the fifth ligand approaches and the copper center moves out of the plane of the porphyrin.[14] They also noted that the doublet state associated with the metal-centered $z^2 \rightarrow x^2 - y^2$ transition drops in energy upon addition of the fifth ligand.

With all of the experimental and theoretical work to date, we still do not understand the influence the fifth ligand very well. In most cases investigators have simply varied the solvent. This complicates the interpretation because the polarity of the

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Table 1. Absorption and Emission Data from Copper Porphyrins in Toluene at 25 °C

	absorption		emission	
compd	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	τ, ns
Cu(TPP)	417	420 000	807	30
	539	21 300		
	575 sh			
Cu(TMP)	416	363 000	766	100
	540	15 500		
Cu(OEP)	399	372 000	687	115
	525	21 000	732	
	562	48 200		

medium also influences relative energies of states. To focus on adduct formation alone, we began studies of a series of quenchers in the noncoordinating solvent toluene. The variation in the quenching constants with the stereoelectronic properties of the quenchers strongly supports the idea[3,6] that the addition of a fifth ligand induces radiationless decay.

Experimental Section

Materials. Midcentury Chemical Co. supplied 5,10,15,20-tetraphenylporphyrin (H_2TPP) and 5,10,15,20-tetramesitylporphyrin (H_2TMP). They also supplied the copper(II) derivative of 2,3,7,8,12,13,16,17-octaethylporphyrin, or Cu(OEP). We obtained DMF, DMSO, and toluene from Burdick and Jackson as high-purity, distilled-in-glass grade chemicals. Fisher supplied other solvents as reagent grade materials. We purchased the laser dye, Coumarin 540A, from Exciton.

Methods. We used a literature method to prepare the copper complexes Cu(TPP) and Cu(TMP).[15] Except for a few compounds, we deemed commercial reagents as pure materials. In the case of Cu(OEP) we purified the complex by means of a dry-column chromatography method.[16] We distilled the THF from sodium and benzophenone, and we used published methods to purify the pyridines.[17]

Before making luminescence measurements, we deoxygenated the samples with repeated freeze—pump—thaw cycles. For lifetime studies a 700 nm long-wave-pass filter served to isolate the luminescence signal. We analyzed the decays with the user-written BASIC program TAU.RES which fits an exponential to the decay data. In all cases, the residual plots justified the use of a single exponential. Stern—Volmer plots of the lifetime data yielded quenching rate constants.[18]

Equipment. We used a Perkin-Elmer Lambda 4C spectrophotometer for absorbance measurements and an SLM SPF 500C fluorimeter for luminescence measurements. For lifetime studies the excitation source was an EG&G Princeton Applied Research Model 2100 nitrogen-pumped dye laser. A Hamamatsu R928 phototube powered by a Pacific Instruments Model 227 high-voltage supply monitored the emission decay. We captured the decay with a Tektronix TDS 520 digitizing oscilloscope interfaced to a microcomputer and stored the traces on floppy disks with TEKDIG software. A Laude K-2/RD temperature controller regulated the sample temperature.

Results

Absorption and Emission. Table 1 contains a list of the absorption maxima and the molar extinction coefficients. The larger molar absorptivity for the Soret band of Cu(TPP) compared with Cu(TMP) may reflect the difference in the mesomeric interaction with the aryl substituent. (The peak widths are similar, so the ratio of areas under the absorption bands is similar to the ratio of peak heights.) By extending the conjugation, phenyl substituents should enhance the dipole lengths of the $\pi-\pi^*$ transitions of the porphyrin ligand.[19] The phenyl substituents would have the maximum effect if they were in the plane of the ligand; however, steric interactions involving ring hydrogens destabilize the planar conformation. Thus, in the solid state the average torsion angle in Cu(TPP) is about 72°.[20] The torsion angle is likely to be even greater in Cu(TMP) due to the methyl groups in the ortho positions. Comparisons with Cu(OEP) are less straightforward because the intensities also vary with the separation between the a_{1u} and a_{2u} orbitals of the porphyrin; vide infra.[7,21]

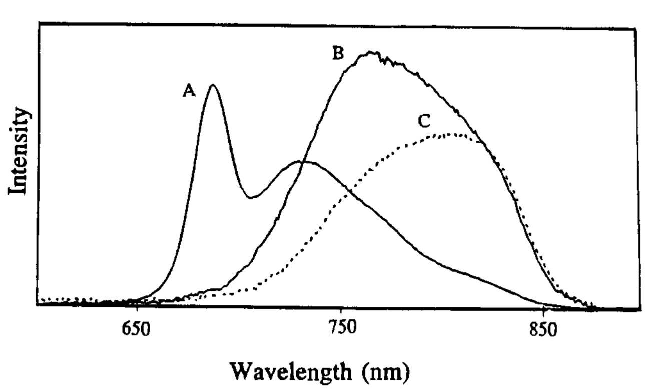

Figure 1. Uncorrected emission spectra measured in toluene at 25 °C: (A) Cu(OEP); (B) Cu(TMP); (C) Cu(TPP). The gain is 4-fold higher for spectra B and C. The absorbance in the Soret region was the same for each sample. The excitation and emission slits were at 10 nm.

Table 2. Rate Constants for Quenching by Pyridines in Toluene at 25 °C

	k_q, M^{-1} s^{-1}	
quencher	Cu(TPP)	Cu(TMP)
pyridine	2.3×10^9	1.1×10^9
2-methylpyridine	1.7×10^9	7.7×10^8
2,6-dimethylpyridine	2.3×10^6	6×10^5

Table 1 also gives the uncorrected emission maxima and lifetimes for the series. In agreement with Asano et al., we find that Cu(OEP) exhibits a structured emission spectrum while Cu(TPP) gives a broad-band emission.[7] See Figure 1. We could not measure quantum yields because the emission spectrum extends beyond the red response region of the spectrofluorimeter. Thus, we could not obtain reliable corrected spectra.

Quenching Studies. The quenching data in Table 2 for the series of substituted pyridines are consistent with quenching induced by coordination of an axial ligand. For both Cu(TPP) and Cu(TMP), 2-methylpyridine is a weaker quencher than pyridine itself, but the effect is small. However, the effect of adding a second methyl substituent is dramatic. Thus, the quenching constants are about 3 orders of magnitude smaller in the case of 2,6-dimethylpyridine. There is good evidence in the literature that the steric bulk of the ortho methyl substituents inhibits adduct formation with most metal centers.[22] A comparison of the data for Cu(TPP) and Cu(TMP) suggests that the steric requirements of the porphyrin are also important. Thus, the quenching constants for the pyridine systems are consistently smaller with Cu(TMP) than with Cu(TPP). It is possible that the mesityl groups inhibit formation of the five-coordinate

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Table 3. Quenching Constants for Lewis Bases in Toluene at 25 °C

		k_q, M^{-1} s^{-1}		
quencher	DN[a]	Cu(TPP)	Cu(TMP)	Cu(OEP)
CH_3CN	14.1	0.39×10^9	1.39×10^8	2.2×10^8
THF	20.0	1.0×10^9	4.7×10^8	
DMF	24.0	1.1×10^9	4.5×10^8	4.8×10^8
DMSO	29.8	1.1×10^9	7.8×10^8	
pyridine	33.1	2.3×10^9	1.1×10^9	9.1×10^8

[a] Gutmann, V. *Chimia* **1977**, *31*, 1–7.

Table 4. Quenching Data for Cu(TMP) in Toluene with Different Lewis Bases

		$10^{-8}k_q$, M^{-1} s^{-1}		
T, K	τ_0, ns	THF	DMSO	CH_3CN
281	120	7.7	5.8	1.4
290	110	7.9	6.2	1.5
298	100	8.9	7.8	1.6
306	85	8.9	8.9	1.7

Table 5. Activation Parameters for the Quenching of Cu(TMP) in Toluene

quencher	$\Delta H_q^\ddagger$, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}
CH_3CN	1.8	−82
THF	2.3	−67
DMSO	11	−40

adducts by directly interacting with the axial ligands. On the other hand, the influence of the mesityl groups could be to inhibit the bowing of the porphyrin ligand that usually occurs in five-coordinate forms.[23]

For a series of Lewis bases that present minimum steric complications, the quenching constant increases with the donor ability (Table 3). Here we use the Gutmann donor number DN as a crude measure of the donor strength. From the weakest donor acetonitrile to the strongest donor pyridine there is almost an order of magnitude change in the quenching constant for the aryl-substituted porphyrins. With Cu(OEP) the change is about a factor of 4.

For three different bases with the Cu(TMP) system, we measured quenching constants as a function of temperature. Table 4 contains the various quenching constants as well as the lifetime (τ_0) measured at each temperature in the absence of quencher. Eyring plots yielded the enthalpies and entropies of activation found in Table 5. As expected for a second-order process, the entropies of activation are strictly negative. However, both activation parameters tend to increase with the donor strength.

Discussion

Emitting States. As discussed by Gouterman, the $^3\pi-\pi^*$ excited state that gives rise to the emissive trip-doublet and trip-quartet states of a copper(II) porphyrin has a well-defined electronic configuration.[1] This is in contrast to the related singlet excited states which involve a mixture of two dominant configurations. Spectral data indicate that the lowest energy triplet state in Cu(OEP) corresponds to an $a_{1u} \rightarrow e_g$ excitation, whereas for Cu(TPP) the excitation is $a_{2u} \rightarrow e_g$.[7,21] Here a_{1u} and a_{2u} represent the two highest filled π levels of the porphyrin ligand, and e_g represents the lowest unoccupied level under the assumption of D_{4h} symmetry. The time-resolved resonance Raman data of Spiro and co-workers are consistent with these assignments and indicate that the triplet involving excitation from a_{2u} is also lowest in Zn(TPP).[24] In comparing Cu(OEP) and Cu(TPP), Asano et al. have proposed that the difference in the orbital parentage accounts for the broader band shape and shorter lifetime of the Cu(TPP) system in that excitation from the a_{2u} orbital leads to a greater shift in equilibrium geometry of the excited state.[7] However, we find that, while the emission from Cu(TMP) is broad band, in toluene it has an emission lifetime comparable to that of Cu(OEP). At this juncture we can only speculate about the vibronic effects that give rise to the broad Franck–Condon envelopes of the emission signals from the aryl-substituted porphyrins. It may be significant in this regard that the a_{2u} molecular orbital, in contrast to the a_{1u}, contains admixtures of the $p\pi$ atomic orbitals of the meso carbons (C5, C10, C15, and C20) as well as the pyrrole nitrogens.[1] This could allow torsional motions of the aryl groups and/or low-frequency deformations of the metal–ligand bonds to influence the band shape. The explanation may not be that simple, however. Asano et al. have found that the Cu(TPP) derivative with fluorines in the para positions of the phenyl substituents exhibits a structured emission much like that of Cu(OEP).[7]

Mechanism of Quenching. The correlations with steric effects and donor strength prove that coordination at an axial position promotes quenching. This type of quenching is rare, but a related reaction has been observed with the charge-transfer excited states of copper(I) phenanthrolines.[25–27] Similar quenching also occurs in supramolecular copper(I) complexes[28] and in certain polynuclear copper(I) complexes.[29] With the copper(I) phenanthrolines, some of the adducts appear to live long enough to be regarded as authentic excited state complexes, i.e., exciplexes.[30]

There are at least two possible explanations for the fact that adduct formation induces quenching. One possibility is that the trip-doublet and trip-quartet states of the five-coordinate complex are intrinsically prone to efficient radiationless decay. However, there is no indication of a significant change in the energy of the $\pi-\pi^*$ excited state of the copper(II) porphyrins because the visible spectrum changes very little upon formation of the ground state adduct.[31] As suggested in the literature,[3,4] a more likely possibility is that addition of a fifth ligand stabilizes another short-lived excited state that efficiently quenches the trip-doublet and trip-quartet excited states. We will consider the identity of the quenching state below; for now, we will simply call it the ^2X state. Figure 2 presents a minimal quenching scheme. States associated with the four-coordinate porphyrin appear on the left; five-coordinate states are on the right. For simplicity, we show the emitting trip-doublet state, ^2T, but omit the corresponding trip-quartet. In the figure we show the quenching state at lower energy than the $\pi-\pi^*$ state when the copper is in the five-coordinate form. This is not necessary; the only requirement is facile conversion to the short-lived $^2X'$ state. If we treat $^2X'$ as a steady-state species, there

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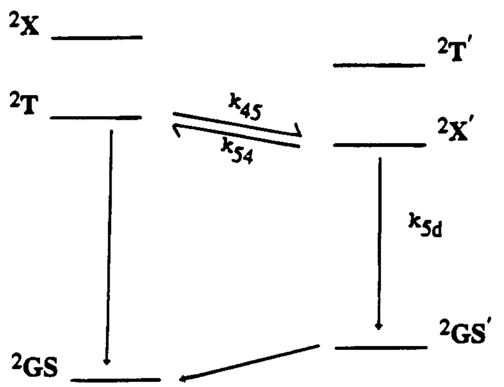

Figure 2. Minimal quenching scheme. The states on the left represent a four-coordinate copper(II) porphyrin; the primed states on the right pertain to a five-coordinate form. The relevant doublet states include the ground state (GS), the trip-doublet (T) excited state, and the quenching state (X). To simplify the diagram, we omitted the trip-quartet state.

are two important limiting cases of the kinetic scheme for decay.[32] If $k_{5d} \gg k_{54}$, then $k_q \approx k_{45}$. Call this case I behavior. In this limit, the rate of attack of the fifth ligand controls the quenching, and the five-coordinate adduct is either a transition state or a successor complex. As a successor complex, the ^{2}X′ state could live long enough to undergo vibrational relaxation, in which case it would be a type of exciplex. Case II occurs when $k_{54} \gg k_{5d}$, whereupon $k_q \approx k_{45}k_{5d}/k_{54}$. In this limit, the ^{2}X′ state is an exciplex in quasi-equilibrium with the ^{2}T state. This type of five-coordinate species is, however, quite distinct from the exciplexes formed when quinones quench an excited-state porphyrin.[33,34]

To date, the evidence that the five-coordinate adducts of interest here live long enough to be called exciplexes is very circumscribed. Kim et al. carried out flash photolysis studies of Cu(TPP) in pyridine but could not detect the five-coordinate excited state.[3] Apanasevich et al. had more success with their transient absorbance and transient Raman studies of Cu(OEP) in the presence of various Lewis bases.[35] For some weak oxygen donors like THF, they detected evidence of an adduct with a picosecond lifetime. On the basis of the transient absorption data, they assigned this species as an exciplex in a d−d excited state.[35] An alternative possibility for the transient would be the five-coordinate ground state that is also on the decay pathway (Figure 2). However, if this were the case, one would expect to detect the adduct for stronger donors like pyridine as well.

Our temperature-dependent quenching studies support the possibility of exciplex formation. To see this, note that, in the case II limit, formation of the five-coordinate adduct is reversible. This can lead to a small positive, or even a negative, enthalpy of activation, which is, in fact, good evidence for the existence of an exciplex.[30] Although the enthalpies of activation in Table 5 are all positive, they are quite small, especially with a weak donor. Thus, the kinetics for acetonitrile certainly approach case II behavior. The trend in the enthalpy data in Table 5 is also sensible because reversible binding should be more likely, the weaker the donor.

Finally, Mojzes et al. have carried out time-resolved resonance Raman studies of Cu(TMPyP4) bound to various oligonucleotides and double-stranded polynucleotides such as poly(dA-dT)·poly(dA-dT).[36] They detected a short-lived exciplex with core size-sensitive marker bands shifted 15−17 cm^{-1} to lower frequency. They pictured the exciplex as five-coordinate with a C4 carbonyl oxygen of a thymine residue axially coordinated to copper. This type of adduct formation would also be consistent with the lack of emission from Cu(TMPyP4) bound near adenine−thymine rich regions of DNA.[8]

Charge-Transfer or d−d State? There have been three distinct proposals for the type of excitation involved in the formation of the ^{2}X quenching state:[3,6,8]

$$(a)\ x^2 - y^2 \rightarrow \pi^*; \quad (b)\ \pi \rightarrow x^2 - y^2; \quad (c)\ z^2 \rightarrow x^2 - y^2$$

The most recent theoretical calculations seem to rule out possibility a.[13,14] Another problem with explanation a is that experimental data suggest that Cu(III) systems prefer a low-spin, square planar configuration over a five-coordinate form.[37] As regards possibility b, it is not intuitively obvious that the addition of a fifth ligand would stabilize a state in which there is a *decrease* in the formal oxidation state of the central metal. However, the calculations by Shelnutt et al. suggest that this is the case when the metal comes out of the plane of the porphyrin.[14] Evidently, the resulting decrease in charge donation from the porphyrin ligand facilitates the addition of the axial ligand.

Although the issue remains in doubt, we think explanation c will ultimately turn out to be the correct one. Thus, there is a good deal of experimental evidence that the addition of the fifth ligand stabilizes the d−d state associated with $z^2 \rightarrow x^2 - y^2$ excitation.[38,39] The available calculations agree but suggest that the energy of the d−d state remains too high to permit facile quenching.[13,14] However, it is very difficult to calculate excited-state energies with the necessary precision for systems as complicated as metalloporphyrins. Perhaps the most relevant evidence to date comes from Apanasevich et al., who have argued that population of a d−d excited state offers the best interpretation of the absorption spectrum of the transient they have detected.[35]

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