

EPR Spectra, Luminescence Data, and Radiationless Decay Processes of Copper(II) Porphyrins

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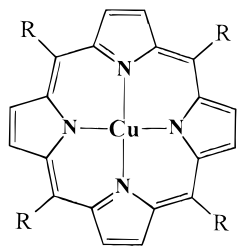
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For a series of copper(II) porphyrins, we report EPR data from solid solutions as well as E_0 values for the first ring oxidation, emission spectra, and luminescence lifetimes in methylene chloride. Although the EPR parameters are fairly constant, the potentials vary by almost 700 mV, and the room-temperature lifetimes range from 300 ns for Cu(TCl2PP) to 15 ns for Cu(TMeOPP), where TCl2PP denotes 5,10,15,20-tetra(2',6'-dichlorophenyl)porphyrin and TMeOPP denotes 5,10,15,20-tetra(4'-methoxyphenyl)porphyrin. The data show that the variation in the lifetime of the emitting $\pi-\pi^*$ state is not due to the thermal population of another excited state of either d–d or charge-transfer parentage. However, the results are consistent with a model originally introduced by Asano et al. who proposed that an important vibronic distortion occurs in the emitting trip-doublet and trip-quartet states when the excitation involves the a_{2u} orbital of the porphyrin (Asano, M.; Kaizu, Y.; Kobayashi, H. *J. Chem. Phys.* **1988**, *89*, 6567–6576). In view of the fact that the distortion is unique to the copper systems, we suggest that it involves movement toward a sitting-atop structure, consistent with the role the d^{10} configuration is likely to have in the excited-state wave function.

Introduction

The photophysics of copper(II) porphyrins have been of great interest for a number of reasons including the multiplet structure^{1–3} and the sensitivity of the lifetime toward the solvent environment.⁴ In addition, the luminescence from a water-soluble copper(II) porphyrin has also proven useful in characterizing DNA-binding interactions.⁵ Gouterman and co-workers have shown that, at least in non-coordinating solvents, the photoluminescence from copper(II) porphyrins such as the 5-, 10-, 15-, 20-substituted derivative shown as follows originates from a triplet $\pi-\pi^*$ ($^3\pi-\pi^*$) state of the ligand.^{1,2}



However, due to interactions with the unpaired electron in the metal $d(x^2-y^2)$ orbital, there is a multiplet structure that entails two emissive states, the so-called trip-doublet (2T) and trip-quartet (4T) states.^{1,2} Here, the prefix “trip” denotes the intrinsic $^3\pi-\pi^*$ state character, and the suffix designates the overall spin multiplicity. After pulsed excitation into a higher energy absorbing state, time-resolved studies indicate that the system first relaxes to the 2T state. Under most conditions, this state then equilibrates with the 4T state such that both states decay with the same lifetime.^{3,6}

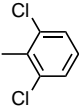
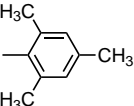
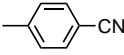
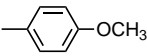
As shown by Yan and Holten,⁷ however, the temperature dependence of the lifetime suggests a more complicated energy level scheme that includes some type of deactivating state. For example, in the case of Cu(OEP), where OEP denotes doubly deprotonated 2,3,7,8,12,13,17,18-octaethylporphyrin, the lifetime increases from 270 ns to 10 μ s in methylcyclohexane as the temperature decreases from 298 to 150 K. On the basis of the Arrhenius plot, Yan and Holten invoked a radiationless decay process that occurred via a short-lived, thermally accessible excited state, designated for now as 2X .⁷ At the same time, they showed that the lifetime of Cu(TPP), where TPP denotes doubly deprotonated 5,10,15,20-tetraphenylporphyrin, remained roughly constant at ca. 35 ns over the same temperature range. On the other hand, in rigid matrices at 77 K the TPP complex can exhibit a lifetime of hundreds of microseconds.^{1,8} In view of these observations, Yan and Holten proposed that the 2X quenching state lies very near the 4T emitting state of Cu(TPP). In neither case did the energy of the 2X state correspond to the known energy of the trip-doublet state. They assigned the quenching state as a ligand-to-metal charge transfer (CT) state, in light of published excited-state energy calculations.^{9,10} Moreover, Gouterman and co-workers had previously proposed that the broad band shape of the emission from Cu(TPP) was due to the influence of a nearby CT state.¹¹ The other virtues of a low-lying CT state were that it could account for the solvent dependence of the lifetime of Cu(OEP) and explain the lack of emission in coordinating solvents. The assumption was that the CT state drops below the emitting 4T state when a fifth ligand binds to the metal.^{4,11} More recently, we have proposed that the five-coordinate form deactivates through a d–d excited state instead.^{5,12}

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Table 1. Ligand Information and Analytical Data

complex	R substituent ^a	analytical data					
		calculated			observed		
		%C	%H	%N	%C	%H	%N
1. Cu(TCl2PP)		55.52	2.12	5.89	56.05	1.98	5.82
2. Cu(TMP)		79.66	6.16	6.64	79.29	6.18	6.77
3. Cu(TF5PP)	—C ₆ F ₅	51.01	0.78	5.41	50.91	0.70	5.21
4. Cu(OEP)	—CH ₂ CH ₃ ^b	72.50	7.45		72.44	7.42	
5. Cu(TPP)	—H	78.14	4.17	8.29	77.81	3.95	7.94
6. Cu(TCNPP)		74.20	3.12	14.43	73.83	2.82	14.72
7. Cu(TOMePP) ^c		67.98	4.29	6.65(6.21) ^d	68.33	4.26	6.51(6.59) ^d

^a See structure in text. ^b The eight ethyl groups reside at the β -carbon of the pyrrole rings. ^c Analyzed as the hemisolvate containing chloroform. ^d Chlorine analysis.

Several groups have attempted to detect the ²X quenching state by time-resolved resonance Raman techniques,^{13–15} but there is as yet no real consensus about the interpretation of the results, even for the five-coordinate systems. All workers seem to agree that the oxygen-donor tetrahydrofuran forms an adduct with an excited state of Cu(TPP). In the Raman spectrum of this transient, the core marker vibrations ν_2 and ν_4 of the porphyrin both appear about 20 cm⁻¹ lower in energy than they do in the ground state spectrum of Cu(TPP). Jeong et al.¹⁵ and de Paula et al.¹³ assign the transient as a CT excited state of Cu(TPP), but Kruglik et al. regard it as a d–d excited state.¹⁴ Complications involved in these experiments include spectral overlap with solvent bands as well as bands of the normal ground-state porphyrin and the possible participation of a transient, five-coordinate ground-state photoproduct.

In a series of papers, Kaizu and co-workers have offered an alternative explanation for the different types of photophysics observed for the four-coordinate Cu(OEP) and Cu(TPP) systems.^{6,16} They argue that the emitting ²T and ⁴T states of the two systems do not have the same orbital parentage and that the shapes of the respective potential energy surfaces differ as well. According to this model, thermal population of excited vibrational levels within the emitting electronic state of Cu(TPP) promotes deactivation. More specifically, they propose that a low-frequency ring-doming mode may explain the broad line shape and the strong quenching observed with Cu(TPP) at relatively low temperatures.¹⁶ However, this model does not carry over to systems like Pd(TPP) and Pt(TPP) that exhibit relatively long emission lifetimes.¹⁷

In order to shed more light on the possible participation of a CT state or a d–d state in the excited-state deactivation of four-

coordinate Cu(TPP)-like systems, we have measured electrode potentials and EPR spectra for a series of copper porphyrins in conjunction with their luminescence lifetimes. The results show that neither type of excited state plays a direct role in the radiationless decay process.

Experimental Section

Materials. Mid-Century Chemical Co. supplied the 5,10,15,20-substituted porphyrins with the substituents indicated in Table 1 as well as the Cu(OEP). The copper(II) acetate monohydrate came from Aldrich Chemical Co., while Fisher Chemical Co. supplied neutral alumina and various reagent grade solvents. The methylene chloride used for the luminescence measurements was Burdick and Jackson distilled-in-glass grade solvent from Scientific Products. The tetrabutylammonium hexafluorophosphate (TBAH) electrolyte came from Aldrich, as did the 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ). Laser Science supplied the dye Coumarin 540A.

Methods. The method of Adler et al.¹⁸ or that of Barnett et al.¹⁹ proved adequate for the preparation of most of the copper(II) porphyrins. A dry-column chromatography procedure removed a green-brown impurity,²⁰ where chloroform was the mobile phase. In the case of Cu(TCl2PP) the initial product was impure and appeared to contain a chlorin derivative that gave an absorbance band at 624 nm. Elution from neutral alumina after treatment with a couple of equivalents of DDQ in a mixture of methylene chloride and benzene yielded the pure compound. For Cu(TF5PP) we developed a different synthetic method that incorporated mercuric acetate as a catalyst.²¹ With this method, we heated the free ligand (H₂TF5PP) with 5 equiv of copper(II) acetate monohydrate in a 30:20 by volume mixture of chloroform and methanol for 15 min in the presence of 0.2 equiv mercury acetate. After a series of extractions with water, we evaporated the organic layer to dryness and isolated pure Cu(TF5PP) from a neutral alumina column by elution with methylene chloride. Analytical data for the various complexes appear in Table 1.

The solvent for the cyclic voltammetry studies was methylene chloride containing 0.1 M TBAH as the supporting electrolyte. The scan rate at the working electrode, which was a gold disk, was typically

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Table 2. Physical Data Measured in Methylene Chloride at Room Temperature

compound	λ_{max} , ^a nm (ϵ , $\text{mM}^{-1} \text{cm}^{-1}$)	E_0 , V vs Cu(TPP) ⁺⁰	τ , ^b ns
Cu(TCl2PP)	415 (560), 541 (24.5), 576	0.03	300
Cu(TMP)	415 (436), 540 (23.6), 575	-0.02	220
Cu(TF5PP)	407 (490), 534 (19.2), 570 (9.7)	0.44	155
Cu(OEP)	397 (225), 524 (8.7), 560 (16.9)	-0.24 -0.20 ^c	110
Cu(TPP)	414 (463), 538 (19.2), 574 (sh)	0.00	40
Cu(TCNPP)	416 (386), 539 (18.4), 573 (sh)	0.11	25
Cu(TOMePP)	418 (367), 540 (16.9), 578	-0.17	15

^a Absorption maxima. ^b Lifetime in deoxygenated solution, error $\pm 10\%$. ^c Reference 11.

50 mV s⁻¹, and the auxiliary electrode was a platinum wire. In the actual experiments, the reference electrode was a AgCl/Ag electrode in contact with 3 M KCl, but for reporting purposes we relate the potentials to the Cu(TPP)⁺⁰ system which serves, in effect, as an internal reference. For the sake of comparison, it had a potential of 0.66 V versus ferrocene and 1.19 V versus the AgCl/Ag electrode. During the electrochemical measurements, the solution was under an atmosphere of dinitrogen.

To minimize complications from magnetic interactions, we measured the EPR spectra of powders that contained about 10% copper(II) porphyrin by mass. The addition of ethanol to a chloroform solution of excess ligand and copper(II) porphyrin yielded the desired powder. For the spectral measurements the microwave frequency fell in the range of 9.443 to 9.453 GHz, the modulation amplitude was 1 mT, the microwave power was 20 mW, and the cavity temperature was 110 K. A literature algorithm yielded spectral simulations.²² The calculations assumed axial symmetry, a common axis system for the **g** tensor and the hyperfine tensor, and an isotopic coupling interaction with the ligand nitrogens. The simulations also took no account of the isotopic composition of copper.

For the luminescence lifetime studies, we deoxygenated the sample via a sequence of freeze-pump-thaw cycles. During the luminescence decay measurements, a 650 or a 700 nm long wave-pass filter protected the phototube from spurious light. A standard analysis¹² yielded the lifetimes from the decay data, and in each case the residual plots justified the assumption of a single-exponential decay.

Instruments. Perkin-Elmer Lambda 4C and SLM-Aminco SPF 500C spectrophotometers provided absorbance and steady-state luminescence spectra, respectively. A description of the system used to monitor the luminescence decay appears in the literature.¹² The excitation source was either the nitrogen-pumped dye laser described previously¹² or a Laser Science 337ND-S nitrogen laser with a DLMS-220 dye laser attachment. The cyclic voltammograph was a Model CV-27 from Bioanalytical Systems Inc. The EPR spectrometer was a Bruker ESP300E spectrometer equipped with an ER 4121VT temperature controller.

Results

Absorption and Emission Data. The data in Table 2 reveal that the wavelength maxima of the Soret bands of most of the copper porphyrins studied fall in the narrow range of 416 ± 2 nm. The exceptions are Cu(TF5PP) and Cu(OEP) which each exhibit a Soret maximum at shorter wavelength. At longer wavelengths each derivative also exhibits a visible absorbance that typically involves two components, the Q(O,O) and Q(1,O) transitions. Both relate to the lowest-energy, spin allowed $\pi-\pi^*$ excitation of the porphyrin. The vibrationally allowed Q(1,O) transition involves one quantum of vibrational excitation and is often the more intense of the two absorptions. The reason is the excited-state wave function is an admixture of two electronic configurations with oppositely directed transition moments,^{1,2} such that Q(O,O), the pure electronic transition, often carries little dipole strength. In reality, the Q(1,O) band is the envelope

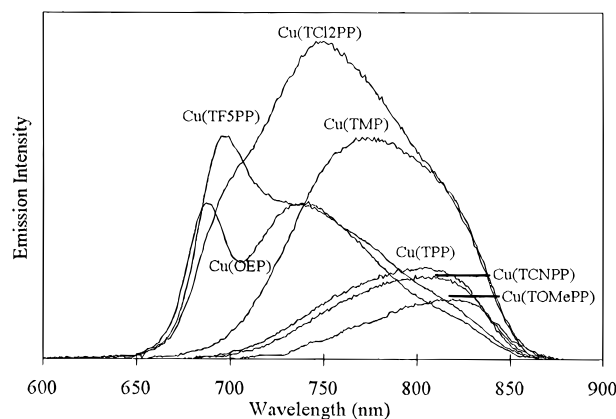


Figure 1. Uncorrected emission spectra from absorbance-matched solutions excited at 540 nm in methylene chloride at room temperature. The bandpass settings were 10 nm for the excitation and emission beams.

of several simultaneous electronic and vibrational excitations involving different enabling modes.² Uncorrected emission spectra from room-temperature methylene chloride solutions appear in Figure 1. It was not possible to obtain corrected spectra because of the limitations of the phototube response at such long wavelengths. Once again, the Cu(OEP) and Cu(TF5PP) systems are distinctive, in this case because of the well-resolved vibrational structure in their emission spectra. Vestiges of vibrational structure are also evident in the emission from Cu(TCl2PP). For the other copper porphyrins in the series, the emission spectra were broad and essentially devoid of structure. The emission lifetimes listed in Table 2 are the values obtained from room-temperature, deoxygenated methylene chloride solutions. A reviewer suggested that methylene chloride is a weakly coordinating solvent that could partially quench the emissions. Actually, the emission lifetimes are generally longer in methylene chloride than they are in toluene. Reported emission lifetimes in deoxygenated toluene include the following: Cu(TMP), 100 ns;¹² Cu(TF5PP), 69 ns;⁶ Cu(TPP), 30 ns;¹² Cu(OEP), 105 ns.⁶ A reviewer questioned whether the hexafluorophosphate ion of the electrolyte might coordinate to the copper center of the porphyrin in solution. As a test, we added electrolyte to a solution of Cu(TF5PP) in methylene chloride. However, the emission spectra with and without electrolyte were superimposable.

Electrode Potentials. Table 2 also contains the potentials for the first oxidation of the copper complexes. As expected in light of previous work involving unmetalated porphyrins,^{23,24} we find that the introduction of substituents on the meso phenyl groups has a strong influence on the potential. In particular, the potential shifts in the negative (cathodic) direction with the introduction of electron-donating groups such as the methoxy or the methyl group. Contrariwise, the electron-withdrawing cyano group induces a shift in the positive direction. Like the lifetimes, the potentials range widely, but there is no correlation between the two variables (Figure 2).

EPR Spectra. For many of the copper(II) porphyrins investigated, the character of the EPR spectrum varied markedly with the method of sampling. Figure 3 shows the spectrum obtained from Cu(OEP) under different conditions. As is often the case with simple copper complexes, the pure solid exhibited g_{\parallel} and g_{\perp} values, but no hyperfine structure due to exchange interactions Figure 3B.^{25,26} The fact that a frozen solution of

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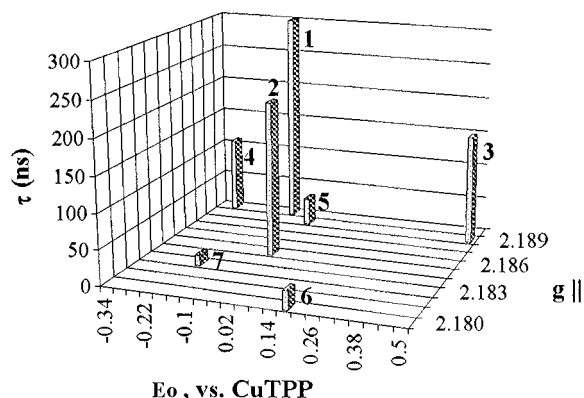


Figure 2. A 3D bar plot of the emission lifetimes versus $g_{||}$ and the reduction potential for the first oxidation of the copper(II) porphyrin. See Table 1 for the key to the numbering system.

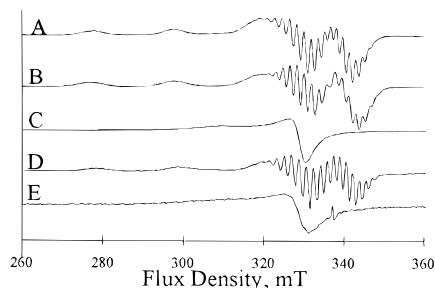


Figure 3. EPR spectra of Cu(OEP) samples at 100 K: (A) coprecipitated with the free porphyrin $H_2(OEP)$; (B) simulated spectrum; (C) pure solid; (D) in frozen 2-methyltetrahydrofuran; (E) in frozen $CHCl_3$ solution. The sharp line signal at 338 mT, most evident in E, is a cavity artifact.

Cu(OEP) in chloroform gave a similar result (Figure 3E) indicates that aggregation and microcrystallite formation occur during the freezing process. Previous authors have also reported problems with aggregation in frozen solution.^{27–29} Following Assour,²⁹ we prepared a magnetically dilute sample by doping the copper derivative in a matrix of the free porphyrin and obtained the well-resolved spectrum in Figure 3A. In this case we also obtained high-quality data with 2-methyltetrahydrofuran as solvent, but some of the other porphyrins did not dissolve in this medium.

If the energies of low-lying d–d excited states varied in a systematic way with the lifetimes, the EPR parameters in Table 3, would reflect the trend because the g and the A values depend on the energy differences between d orbitals.^{29,30} Thus, in the simplest approximation, which ignores the influence of covalent mixing, the following equations describe the g values:

$$g_{||} = 2.0023 - \frac{8\lambda}{\Delta_{||}} \quad (1)$$

$$g_{\perp} = 2.0023 - \frac{2\lambda}{\Delta_{\perp}} \quad (2)$$

where λ (inherently negative) is the spin–orbit coupling constant of the free Cu^{2+} ion, $\Delta_{||} = E(x^2 - y^2) - E(xy)$, and $\Delta_{\perp} = E(x^2 - y^2) - E(xz, yz)$.³⁰ To the extent that there is any correlation

Table 3. EPR Parameters from Powder Containing Free Porphyrin

porphyrin	$g_{ }$	g_{\perp}	$A_{ }(Cu)^a$	$A_{\perp}(Cu)^a$	$A(N)^a$
Cu(TCl2PP)	2.190	2.036	206	24	16
Cu(TMP)	2.185	2.031	208	26	16
Cu(TF5PP)	2.189	2.034	207	26	16
Cu(OEP)	2.190	2.035	210	24	16
Cu(TPP)	2.189	2.035	204	31	16
	2.187	2.035	203		14.4–15.2 ^b
	2.193	2.071	202	29	14.5–16.1 ^c
Cu(TCNPP)	2.180	2.034	206	29	16
Cu(TMeOPP)	2.183	2.031	208	24	16

^a Hyperfine coupling constants in units of 10^{-4} cm^{-1} . ^b In $CHCl_3$. Alston, K.; Storm, C. B. *Biochemistry* **1979**, *20*, 4292–4298. ^c In $CHCl_3$ containing H_2TPP .²⁹

between $g_{||}$ and the lifetime, Figure 2 shows that a complex with a larger $g_{||}$ value tends to exhibit a longer lifetime.

Discussion

Emitting States. As Gouterman has shown,² an intraligand ${}^3\pi - \pi^*$ excited state is ultimately responsible for the emission from copper(II) porphyrins. Most treatments classify the orbitals involved in terms of D_{4h} point symmetry, i.e., without regard for any symmetry reduction introduced by the peripheral substituents. In the usual coordinate system the x and y axes fall along the metal–nitrogen bonds. In this view the lowest unoccupied energy level is doubly degenerate with e_g symmetry, and the highest occupied level has either a_{1u} or a_{2u} symmetry, depending on the substituents.^{31,32} In the makeup of the a_{2u} molecular orbital, the $p\pi$ atomic orbitals of the pyrrole nitrogens play a significant role as do the $p\pi$ atomic orbitals of the meso carbon atoms (C5, C10, C15, and C20).² This orbital is important in the luminescence processes of Cu(TPP) and most of its derivatives as they have a lowest energy ${}^3\pi - \pi^*$ state that derives from $a_{2u} \rightarrow e_g$ excitation.^{6,16} However, when there are sufficiently electron-withdrawing substituents on the phenyl groups, as in Cu(T5FPP)⁶ and Zn(T5FPP),^{31,32} the a_{2u} orbital falls below the a_{1u} orbital. The a_{1u} orbital, which has zero amplitude at the meso carbon positions, then becomes the highest occupied orbital. This is also true of protoporphyrin derivatives such as Cu(OEP). As the $p\pi$ atomic orbitals of the C α and C β carbons of the pyrrole rings contribute most of the amplitude for the a_{1u} orbital,² this is easily the highest occupied ligand orbital in Cu(OEP) due to the influence of the electron-donating ethyl substituents.^{31,33} With either a_{1u} or a_{2u} excitation, further energy states arise as a result of repulsive interactions with the unpaired electron in the $d(x^2 - y^2)$ orbital of the metal. Because of the participation of the nitrogen $p\pi$ orbitals in the a_{2u} molecular orbital, the splitting is larger in systems like Cu(TPP).¹ More specifically, the ${}^2T/{}^4T$ splitting is around 200 cm^{-1} for Cu(OEP) and around 700 cm^{-1} for Cu(TPP).^{6,7,34} For completeness, we note that a Jahn–Teller effect and/or spin–orbit coupling may induce further splittings.³⁵

Quenching States. Yan and Holten have argued that there is another low-energy state and that it is responsible for the strong temperature dependence of the emission lifetimes of four-coordinate copper(II) porphyrins.⁷ Figure 4A illustrates an expanded state diagram. This diagram is highly schematic and only shows the relative state energies for a single molecular geometry. To be effective at quenching, the 2X state would probably have to have a different equilibrium geometry than

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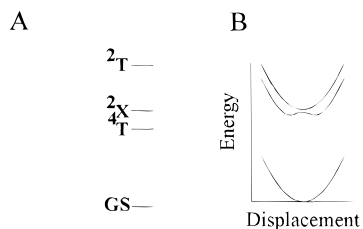


Figure 4. Excited states of a copper(II) porphyrin: (A) state energies for a fixed nuclear configuration, where GS denotes the ground state (see the text for an explanation of the other labels; energies not to scale); (B) slices through the potential energy surfaces of the ground state and two $\pi-\pi^*$ excited states. The double minimum represents the ${}^4T(a_{2u})$ state.

either the 4T state or the ground state in order to have Franck–Condon factors that are favorable for radiationless decay. In the model of Yan and Holten, the 2X state is analogous to the CT state that they invoked to explain emission quenching in the five-coordinate forms of copper(II) porphyrins.^{4,11} Recently, however, Kruglik et al. have argued that the vibrational energies and the Raman excitation profile of the five-coordinate excited state are more consistent with a d–d assignment.^{14,36} In contrast, for the four-coordinate porphyrin even the assignment of the vibrational modes of the $\pi-\pi^*$ state^{36,37} has proven to be difficult, although Jeong et al. claim to have identified a CT excited state of four-coordinate Cu(TPP).¹⁵ Nevertheless, our data are quite inconsistent with the existence of a thermally accessible excited state of either CT or d–d character. Consider first the possibility of a CT state. There is a wealth of evidence that the electrochemical potentials of the centers involved govern the energy of a CT excited state.^{38,39} Accordingly, for ring-to-metal excitation, the more easily oxidized porphyrins should exhibit the lower energy CT states. But the data in Figure 2 reveal that systems with relatively low reduction potentials, e.g., Cu(OEP) and Cu(TMP), exhibit some of the longer lifetimes in this series. There is no way to reconcile these data with the notion that a thermally accessible CT state promotes deactivation.

It is just as evident that deactivation via a d–d excited state is not feasible. Thus, Yan and Holten have suggested that the energy difference between 2X , the quenching state, and the emitting ${}^2,{}^4T$ states is about 1000 cm^{-1} greater in four-coordinate Cu(OEP) than it is in Cu(TPP).⁷ According to the EPR data, the energies of the d–d states are practically constant throughout the series and are too high to mediate excited-state relaxation. Indeed, indications are that the d–d states of copper(II) porphyrins have energies on the order of $20\,000\text{ cm}^{-1}$.^{29,40} If, in fact, the d–d energies varied by 1000 cm^{-1} , we would expect on the order of a 5% variation in the g values listed in Table 3. The actual variations are much smaller. Moreover, some of the systems with relatively long-lived emissions exhibit large g values. These results are incompatible with the idea that low-energy d–d states are responsible for the differences in the lifetimes. The same conclusion follows from the fact that Cu(TPP) and Cu(TMP) exhibit lifetimes near the opposite extremes found in Table 2 despite the fact that their d–d states must occur at similar energies.

Vibronic Mixing. The other possibility is that the nature of the 4T potential energy surface itself determines the emission lifetime and the emission band shape. In fact, Kaizu and co-workers have pointed out that the emission from systems with a relatively temperature-independent lifetime and a broad emission band shape generally stems from a 4T state that involves excitation from the a_{2u} molecular orbital, i.e., a ${}^4T(a_{2u})$ state. They have gone on to propose that in these systems a vibronic interaction broadens the potential energy surface and facilitates radiationless conversion to the ground state.^{6,16} Figure 4B depicts representative forms for the potential energy surfaces envisioned for the ${}^4T(a_{1u})$ and ${}^4T(a_{2u})$ states. Other workers studying free porphyrins with broad fluorescence spectra have invoked a similar structural distortion.^{41,42} According to the band shape criterion, the broad, red-shifted emission spectra from the Cu(TMP), Cu(TCNPP), and Cu(TMeOPP) systems (Figure 1) are all consistent with emission from a ${}^4T(a_{2u})$ excited state as is that of Cu(TPP). By the same token, the emissions from Cu(TF5PP) and Cu(OEP) are of the ${}^4T(a_{1u})$ type.⁶ The emission from the Cu(TCl2PP) system is unique in that the spectrum is rather broad, but the onset of the emission occurs at a wavelength comparable to that of Cu(TF5PP). Moreover, the emission shows vestiges of vibronic structure. It is possible that the ${}^4T(a_{1u})$ and ${}^4T(a_{2u})$ states have similar energies in this derivative and that the system exhibits multiple emissions. However, in view of the long lifetime it seems more likely that the emission originates from a state with a mixed orbital parentage. The possibility of populating a higher energy ${}^4T(a_{2u})$ state could, on the other hand, account for the temperature dependence of the lifetime of Cu(OEP).

One possible explanation for the double-minimum profile of the ${}^4T(a_{2u})$ state in Figure 4B is a Jahn–Teller effect. In the case of Zn(TPP) Walters et al. have used a pump–probe method to show that b_{1g} and b_{2g} stretching modes of the porphyrin become active in the resonance Raman spectrum of the 3E_u excited state.⁴³ The modes are active because they represent totally symmetric vibrations when the 3E_u state is unstable with respect to distortion to a lower symmetry like D_{2h} . However, Jeong et al. have measured the time-resolved resonance Raman spectrum of Cu(TPP) and have argued that its 4T excited state does not undergo the same type of Jahn–Teller distortion.¹⁵ In any event, a distortion based on a low-amplitude, high-frequency vibration involving mainly C=C stretching motions is unlikely to account for the way in which the medium influences the photophysics of Cu(TPP). Thus, Yan and Holten showed that the emission lifetime remained practically constant between 30 and 40 ns in solution in the temperature range from 150 to 300 K.⁷ But, Ake and Gouterman reported that emission from Cu(TPP) had a relatively long lifetime and showed multiexponential decay in a low-temperature poly(methyl methacrylate) matrix.¹ More specifically, at 77 K one component had a lifetime of $610\ \mu\text{s}$, and there was a 1.14 ms component at 25 K. The obvious way to reconcile these results is to assume that a rigid matrix inhibits the vibronic distortion that facilitates the decay in fluid solution. A low-frequency, out-of-plane deformation would be more compatible with this type of rigid matrix effect.

Indeed, Asano-Someda and Kaizu have proposed that the particular form of distortion that the ${}^4T(a_{2u})$ states of Cu(TPP) and related systems undergo may involve a doming or a ruffling

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of the porphyrin core.¹⁶ They reasoned that the ${}^4T(a_{2u})$ state might be especially prone to the distortion because excitation to the ${}^4T(a_{2u})$ state shifts electron density from the donor nitrogens to $C\alpha$ and $C\beta$ carbons. However, if elongation of the Cu—N bonds occurs, a ruffling distortion seems improbable because this motion normally provides for the formation of shorter metal—nitrogen bonds.^{44,45} Doming would be more consistent with Cu—N bond lengthening,^{46,47} but there is also a problem with this model. If a shift in electron density within the π system promotes doming, why does the distortion not occur in the more strained palladium(II) derivative which has a longer metal-to-nitrogen distance than Cu(TPP)?^{48,49} Unlike what we find with Cu(TPP), the phosphorescence spectrum of the palladium derivative exhibits well-resolved vibrational structure, even at room temperature.^{50,51}

Whatever the nature of the distortion, it seems to be particular to the copper derivative, and the hallmark of copper is the stability of the copper(I) state. We suggest that the distortion may involve the formation of a sitting-atop structure that is more typical of copper(I) with its larger ionic radius. In the sitting-atop configuration,⁵² the metal moves out of the mean plane of the porphyrin as do two of the ring nitrogens such that there are two relatively short Cu—N bonds. This distortion is consistent with $a_{2u} \rightarrow e_g$ excitation because contour plots show that excitation to a particular component of the e_g level shifts electron density off of only one pair of nitrogen atoms on opposite sides of the porphyrin ring. Excitation to the the other e_g component would give rise to a similar structure in which the other pair of nitrogens follow copper out of the plane of the porphyrin. It is worth noting that the sitting-atop structure is achievable via a Jahn—Teller distortion of a porphyrin like Cu(TPP). Consider the conformation with the phenyl substituents rotated as in Figure 5A. The point group is then D_{2d} , and it is convenient to redefine the x and y axes such that they lie along the C_2' axes, bisecting the N—Cu—N angles. The lowest energy $\pi-\pi^*$ excited state has E symmetry in the D_{2d} point group, and the vibrational modes that support a first-order Jahn—Teller distortion have the following symmetry:

$$E \otimes E = A_1 + A_2 + B_1 + B_2$$

Although the ordinary Jahn—Teller effect cannot give rise to an out-of-plane distortion of a D_{4h} system, this is possible in D_{2d} symmetry. In fact, the modes indicated in Figure 5A,B are both compatible with a Jahn—Teller distortion from D_{2d} symmetry, and a combination of these deformations gives the sitting-atop structure.

The attractive feature of this model is a recognition of the legitimate role that the d^{10} configuration can play in the photophysics even if the CT states themselves are thermally inaccessible. Thus, the emitting state can take on an admixture of a CT excited-state configuration in conjunction with a vibronic distortion. In this way, the CT state indirectly

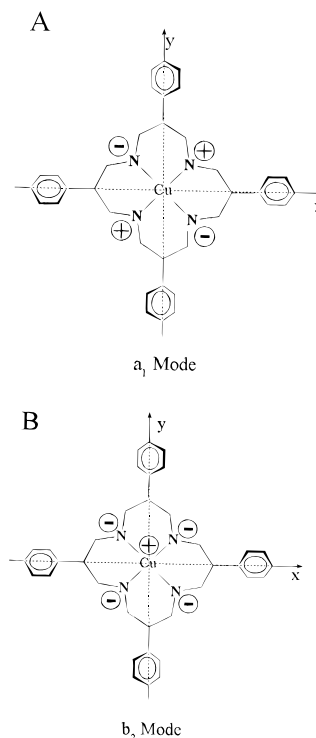


Figure 5. Out-of-plane displacements of the copper and/or nitrogen atoms in D_{2d} symmetry: (A) a totally symmetric (a_1) motion; (B) a doming distortion with b_2 symmetry.

influences the decay process by helping shape the active potential energy surface. Indeed, an interaction with a CT state that has the same symmetry as the excited state in the final point group (B_1 or B_2 in C_{2v} symmetry) could enhance the distortion via a second-order Jahn—Teller effect.⁵³ However, neither of the two highest-energy occupied porphyrin π orbitals gives rise to a $\pi \rightarrow d$ state with appropriate symmetry.

Conclusions

The lifetimes of copper(II) porphyrins are quite variable in fluid solution at ambient temperature. Indeed, in the series of Cu(TPP) derivatives investigated herein, the lifetimes vary by more than a factor of 10 in methylene chloride. From the E_0 data it is clear that the effect is not due to a variable energy CT state that mediates decay, and EPR data exclude the possibility of a thermally accessible d—d state. The results are most consistent with the model of Asano et al. which posits that a vibronic distortion within one of the $\pi-\pi^*$ excited states is responsible for the short lifetimes.⁶ There are, however, several qualifications to keep in mind: (1) The vibronic distortion is only important when the emitting state involves excitation from the a_{2u} orbital of the porphyrin. (2) Even in these systems, bulky groups like the mesityl substituents in Cu(TMP) or the 2,6-dichlorophenyl groups in Cu(TC12PP) apparently inhibit the quenching pathway.¹⁶ (3) The distortion probably involves out-of-plane motion and perhaps the formation of a sitting-atop structure. (4) Finally, CT states may influence the lifetime, albeit indirectly, via vibronic interactions that help shape the potential energy surface of the emissive state.

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