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Picosecond Dynamics and Mechanisms of Photoexcited Cu(II)-5,10,15,20-*meso*-tetrakis(4-*N*-methylpyridyl)porphyrin Quenching by Oxygen-Containing Lewis-Base Solvents

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Deactivation of the lowest excited triplet (π,π^*) state, $^3(\pi,\pi^*)$, of the cationic water-soluble Cu(II)-5,10,15,-20-*meso*-tetrakis(4-*N*-methylpyridyl)porphyrin (CuTMpyP4) was studied by femtosecond transient absorption spectroscopy in three oxygen-containing solvents (Lewis bases) of various polarity, water, methanol, and dimethyl sulfoxide (DMSO). In all of these solvents, the $^3(\pi,\pi^*)$ state depopulation follows biexponential kinetics. A majority of the $^3(\pi,\pi^*)$ state population (∼80%) deactivates very quickly with a time constant of about 1−2 ps to give rise to formation of an exciplex (CuTMpyP4)*-L between the porphyrin in its excited (d,d) state and a solvent molecule, L, the latter playing the role of porphyrin axial ligand. The exciplex lifetime is found to depend on the solvent dielectric constant ϵ and increases from 7 ps in water ($\epsilon = 78.3$) to 27 ps in methanol ($\epsilon = 32.7$), through 23 ps in DMSO ($\epsilon = 46.5$). A minor part of the initial $^3(\pi,\pi^*)$ state population (∼20%) deactivates to the ground state, without any detectable intermediate, with time constants of 25, 8, and 11 ps in water, DMSO, and methanol, respectively. These rather fast pathways (picosecond time scale) of excitation deactivation to the ground state are interpreted in terms of quenching influence of some low-lying intramolecular charge-transfer states that belong to four- and five-coordinate CuTMpyP4. A partitioning mechanism of $^3(\pi,\pi^*)$ state CuTMpyP4 molecules into two populations decaying by different paths, that is, through exciplex formation and "directly" to the ground state, is proposed.

1. Introduction

Quenching of the "tripdoublet-tripquartet" $^{2,4}T_1(\pi,\pi^*)$ manifold (thereafter "triplet (π,π^*) state", or "$^3(\pi,\pi^*)$ state")[1] of Cu(II) porphyrins (CuPs) in solution by axial ligation of oxygen-containing solvent molecules was revealed in the middle of the 80s[2] and later studied in detail.[3] It has been shown[3] for Cu(II) tetraphenylporphyrin (CuTPP) and Cu(II) octaethylporphyrin (CuOEP) in such solvents as 1,4-dioxane and tetrahydrofuran that this quenching goes through the formation of relatively long-lived exciplexes (lifetimes of tens to a few hundreds of picoseconds) between the excited[4] CuP and the oxygen-containing solvent molecule, which plays the role of an axial ligand. Formation of such an exciplex was independently found for the cationic water-soluble Cu(II)-5,10,15,20-*meso*-tetrakis-(4-*N*-methylpyridyl)porphyrin (CuTMpyP4) bound to natural or model DNA in the vicinity of thymine or uracil residues[5a−g] (see also ref 5h as a review), the C═O groups of which play the role of an axial ligand.[5d,e] For free CuTMpyP4 in water a very fast (picosecond time scale) quenching of the $^3(\pi,\pi^*)$ state was also found, resulting in exciplex formation with water molecules.[5e,6]

Despite a large number of publications devoted to the study of exciplexes between excited CuP and oxygen-containing organic molecules (oxygen Lewis bases), many questions concerning the electronic structure of the exciplex and its dynamics of formation and decay still remain open:

(i) It is not clear why the exciplex formed by the same Cu(II) porphyrin but with different axial ligands (or even with the same axial ligand but in a different environment) may vary its lifetime up to 1000-fold. For example, the exciplex formed between CuTMpyP4 and H_2O as an axial ligand has a lifetime of about 5−10 ps.[6a,c] In contrast, when the porphyrin is bound to short oligothymidylates, d(pT)$_n$ ($n = 1-18$), or to [poly(dA−dT)]$_2$, the exciplex formed between CuTMpyP4 and thymine C═O groups has a lifetime of about 900 ps[5g] and 2−3 ns,[5e,f] respectively.

(ii) The question is also open why the CuP $^3(\pi,\pi^*)$ state quenching by oxygen-containing Lewis bases is often accompanied by an exciplex formation, whereas the quenching by nitrogen-containing organic Lewis bases does not result in the formation of any intermediate.[7]

In an attempt to answer these questions, in the present work, we used femtosecond transient absorption spectroscopy to

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investigate the dynamics of excited-state formation and decay of CuTMpyP4 in various oxygen-containing Lewis bases, namely, water, methanol, and dimethyl sulfoxide (DMSO).

2. Experimental Section

CuTMpyP4 (tosylate) was prepared from H_2TMPyP4 (tetra-*p*-tosylate salt, Aldrich) and purified according to Pasternack et al.[8] Time-resolved transient absorption measurements were performed with the pump−probe laser system previously described.[9] Photoexcitation in the Q-band of CuTMPyP4 was achieved in the 550−560 nm wavelength interval with a pulse width of 40 fs. Transient absorption was probed after adjustable delay with a wide spectrum pulse from a continuum, the group velocity dispersion of which was minimized at 425 nm by means of prisms. Difference absorption spectra, ΔA, were measured, where ΔA = [transient spectrum] − [equilibrium (i.e., ground state) spectrum]. The same sample quartz cell (1-mm optical path length) was used to record equilibrium spectra and kinetic measurements. Sample absorbance was typically in the 0.5−0.8 OD range at the Soret band maximum for 1 mm path length. A total of 20−60 scans were recorded and averaged for each time delay.

3. Results

Background. Before analyzing the difference absorption spectra and kinetics obtained for CuTMpyP4 in three different solvents, let us first consider the features of those excited electronic states of CuPs that may, in principle, be detected in transient absorption (TA) experiments. It is known that the lowest excited singlet (π,π*) state, $^1(\pi,\pi^*)_1$, of all Cu(II) porphyrin compounds deactivates to the lowest triplet $^3(\pi,\pi^*)$ state in an ultrashort time (about 30 fs).[1g,h] Such a short-lived $^1(\pi,\pi^*)_1$ state has not been observed earlier in TA experiments. The time resolution of our experimental setup is also not sufficient to detect reliably the $^1(\pi,\pi^*)_1$ state, especially if one takes into account that absorption spectra of the $^1(\pi,\pi^*)_1$ and $^3(\pi,\pi^*)$ states of CuTMpyP4 are likely very close to each other, as are the $S_1 \rightarrow S_n$ (π,π*) and $T_1 \rightarrow T_n$ (π,π*) absorption spectra of all porphyrin compounds over the visible spectral region.[10] Therefore, the $^3(\pi,\pi^*)$ state should be the first (in time) transient state observed in our TA experiments on CuTMpyP4.

In noncoordinating solvents (e.g., benzene and toluene), the $^3(\pi,\pi^*)$ state of CuPs deactivates to the ground state within 20 to ~200 ns.[11] In coordinating nitrogen-containing Lewis-base solvents (e.g., pyridine and piperidine), the $^3(\pi,\pi^*)$ state deactivation occurs much faster, in tens of picoseconds; in so doing, no additional intermediate state was ever detected.[7] The concept prevails that this $^3(\pi,\pi^*) \rightarrow S_0$ radiationless transition, stimulated by nitrogen-containing bases, goes through some "spectroscopically dark" charge-transfer (CT) state, the energy of which is located below that of the $^3(\pi,\pi^*)$ state, owing to the base nitrogen attachement to CuP as an axial ligand.[7c] A quenching process of the CuP $^3(\pi,\pi^*)$ state has also been found in oxygen-containing Lewis-base solvents, but in contrast to nitrogen bases, a population of an intermediate state has been detected.[2,3] On the basis of resonance Raman and absorption spectra of the transient state, we interpreted it in terms of an excited [d(z^2), d($x^2 - y^2$)] state of the five-coordinate Cu(II) porphyrin,[3a,b] that is, a so-called "exciplex". There also are data that demonstrate that the quantum efficiency of exciplex formation between CuPs (CuOEP and CuTPP) and oxygen-containing Lewis bases (tetrahydrofurane and 1,4-dioxane) is lower than unity; this was interpreted as evidence that some appreciable portion of the CuP $^3(\pi,\pi^*)$ state molecules is quenched to the ground state without formation of any detectable transient, likely through the same "spectroscopically dark" CT state as through quenching by N-containing bases.[3a,b] Finally, the $^3(\pi,\pi^*)$ state deactivation of the cationic porphyrin CuTMpyP4 in mere water has also been found to proceed through the formation of an exciplex between excited porphyrin and water molecule.[5e,6]

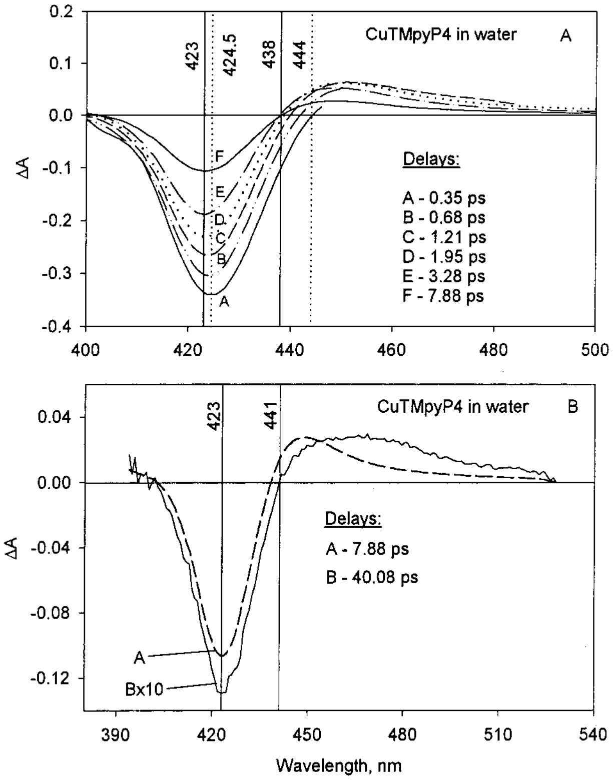

Figure 1. Transient absorption difference spectra obtained for CuTMpyP4 in water at the pump−probe time delays indicated. The intensity of the 40.08-ps delayed spectrum is multiplied by 10 in panel B.

CuTMpyP4 in Water. Spectral changes induced by photoexcitation of CuTMpyP4 in water are shown in Figure 1A. Note that the difference absorption spectra presented here are not corrected from the wavelength dependence of the "zero delay time" due to the refractive index dispersion of the setup optical elements. The latter were arranged in such a way that the optical path of the probe pulse was the shortest at the Soret band maximum, 425 nm. At other wavelengths (longer or shorter), the further from 425 nm was the probe beam wavelength, the longer was the optical path. As a result, in all of the difference spectra, the region close to 425 nm corresponds to a maximum time delay as compared to other regions. For example, if there is an ~1-ps delay between probe and pump pulses in the difference spectrum near 425 nm, a "zero delay" is reached right at 460 nm. This may result in fairly strong distortions of the difference spectra profiles, but only if very fast spectral changes are to be observed (time constant ~1 ps and less) or if broad spectral regions are considered or both.

Figure 1A shows difference absorption spectra of CuTMpyP4 in water at different delays (0.35−7.88 ps) between pump and probe pulses (indicated delays correspond to the 425 nm wavelength). Analysis of the TA difference spectra obtained at very short time delays (≤0.5 ps, see spectrum A in Figure 1A as an example) shows that these spectra are characterized by a bleaching maximum at 424.5 nm and an isosbestic point (i.e., the wavelength at which $\Delta A = 0$) at 444 nm. Because for Cu(II) porphyrins the first (in time) excited state, which may be detected after excitation, should be the $^3(\pi,\pi^*)$ state (see Background), we assume that the above characteristics have to belong to the $^3(\pi,\pi^*)$ state. Analysis of spectral data obtained for Cu(II) porphyrins that have a more long-lived $^3(\pi,\pi^*)$ state[10] confirms this interpretation.

Let us remember that the position of an isosbestic point, along with positions of the positive and negative maxima of difference spectra, is an important and constant characteristic for a given transient spectrum of any excited state at any time after excitation. Because the isosbestic point positions and other characteristics of the difference spectra of Figure 1A change as time elapses, this implies that the $^3(\pi,\pi^*)$ state depopulation is accompanied by the formation of new other transient species: at longer delays (curves C−F, Figure 1A), there is a general intensity decrease of the difference spectra, isosbestic point and maximum of bleaching in the Soret region shift to shorter wavelengths, and the ratio R of the Soret bleaching to the positive ΔA maximum near 450 nm decreases. This tendency holds until a ∼3.5-ps delay after excitation (curve E in Figure 1A); then only the amplitude of the difference spectrum decays without any change in its shape during the next 10−15 ps (curve F in Figure 1A): isosbestic point and bleaching maximum stay at 438 and 423 nm, respectively.

All of these findings reveal that, after initial population of the $^3(\pi,\pi^*)$ state, a new transient state is populated, which also participates in the excitation energy degradation. All experimental data reported so far in the literature on Cu(II) porphyrin photophysics in the presence of oxygen-containing Lewis bases indicate that this new transient state very likely is an excited (d,d) state of the five-coordinate porphyrin, that is, in our case this is the exciplex formed between CuTMpyP4 in its excited (d,d) state and a water molecule as an axial ligand. On the other hand, TA difference spectra E and F (and those observed during the following 10−15 ps) do not bear the specific spectral features characteristic for the metalloporphyrin (d,d) states well-studied for Ni(II) porphyrins:[12] first, spectra E and F show a marked transient absorption over the whole spectral region located between the Soret and Q-bands, whereas ΔA should have a negligible value in this region in case of a "real" (d,d) state,[12] and second, the R ratio is rather high ($R \approx 4$), that is, intermediate between its typical values for the porphyrin triplet ($R \approx 7$) and for the (d,d) spectra ($R \approx 1.0-1.5$).[10,12]

We assume that this apparent contradiction may be (at least partially) alleviated if we assume that the actual exciplex formation between CuTMpyP4 and water that occurs during the first few picoseconds is not accompanied by a complete vanishing of the $^3(\pi,\pi^*)$ state population, that is, some part of the porphyrin molecules at all times remain in the $^3(\pi,\pi^*)$ state of the four-coordinate species.

Consideration of later spectral changes, in the 20−50 ps time interval after excitation, gives additional support to this assumption. At a 40 ps delay (i.e., when, from the Soret bleaching decay, ∼95% of excited molecules are back to the ground state), it turns out from Figure 1B, curve B that the TA difference spectrum again more resembles the typical $^3(\pi,\pi^*)$ state spectrum than that observed during the 4−15 ps delay interval: the isosbestic point shifts back to longer wavelengths and reaches 441 nm, transient absorption between Soret and Q-bands is considerably increased, and the R value increases and becomes close to 5. It implies that during the 20−50 ps time interval after excitation, the relative contribution of the $^3(\pi,\pi^*)$ state absorption to the total spectrum increases.

Let us now proceed to the analysis of the kinetics, $\Delta A(t)$, of the difference absorption at various selected wavelengths. As shown above, the difference spectra change their shape as time elapses. This is due to (i) transitions between $^3(\pi,\pi^*)$ and (d,d) excited states and (ii) decay of both excited states to the ground state; thus, the $\Delta A(t)$ kinetics at arbitrary wavelengths may be rather difficult to interpret. It is more reasonable to analyze separately the kinetics of formation and decay of the $^3(\pi,\pi^*)$ state (of the four-coordinate CuTMPyP4), on one hand, and of the exciplex state (of the excited five-coordinate CuTMPyP4), on the other. Fortunately, despite strongly overlapping absorption spectra of the $^3(\pi,\pi^*)$ and exciplex states, one can make use of the specific properties of the isosbestic points for each of these two states. The problem appears only in an accurate determination of such isosbestic points.

As mentioned above, the isosbestic point of the $^3(\pi,\pi^*)$ state lies near 444 nm. The determination of the exciplex isosbestic point is more difficult because, at any time after excitation, the five-coordinate exciplex coexists with the four-coordinate CuP in the $^3(\pi,\pi^*)$ state and furthermore the relative concentration of $^3(\pi,\pi^*)$ state molecules even increases after an ∼20-ps delay. The highest relative exciplex concentration is observed in the 7−20 ps interval; under these conditions, the $\Delta A = 0$ point lies at 438 nm. We estimate that the isosbestic point of the "pure" exciplex spectrum should be somewhat shifted from this value to shorter wavelengths, that is, approximately at 435−436 nm. Kinetic measurements support this evaluation.

Figure 2A shows the kinetics of OD changes measured at 444 nm (i.e., at the isosbestic point of the $^3(\pi,\pi^*)$ state). The $^3(\pi,\pi^*)$ state is not visible at this wavelength, and therefore, this kinetics monitors the formation and decay of the exciplex only. One can see that it is delayed as compared to the very short excitation pulse duration (∼40 fs) and can be well-fitted with a monoexponential build-up law $[1 - \exp(-t/\tau_r)]$, with a rise-time constant $\tau_r = 1.0 \pm 0.2$ ps, followed by a decay well-fitted by a monoexponential law with a lifetime $\tau_d = 7.0 \pm 0.5$ ps.

The kinetics of $^3(\pi,\pi^*)$ state formation and decay shown in Figure 2B is quite different (recorded at 436 nm). The $^3(\pi,\pi^*)$ state population rises without delay from the excitation pulse, and ∼85% of the $^3(\pi,\pi^*)$ state molecules deactivate with a time constant $\tau_{d1} = 1.0 \pm 0.2$ ps. For a minor part of excited molecules (about 15%), a much slower monoexponential decay is observed with a time constant $\tau_{d2} = 25 \pm 3$ ps. Besides, a weak additional component is observed, which corresponds to a relatively slow increase of the triplet state population (rise time $\tau_{r1} = 7 \pm 3$ ps). We suggest that this rise component is due to a partial back dissociation of the exciplex toward the initial $^3(\pi,\pi^*)$ state of four-coordinate CuP (see Discussion).

The kinetics measured at 424 nm, that is, close to the Soret band maximum (Figure 2C), is more complex and includes a rise time constant of about 0.5 ps and a biexponential decay with time constants of about 5 ps ($A_1 = 0.80$) and 25 ps ($A_2 = 0.20$). Because the decay time of a majority (∼85%) of the $^3(\pi,\pi^*)$ state population is equal to the time constant of exciplex formation, thus the major part of the $^3(\pi,\pi^*)$ state population decays (with a time constant of about 1.0 ps) at the benefit of the exciplex, that is, five-coordinate CuP in its excited (d,d) state with water, the latter then decaying with an ∼7 ps lifetime. The lack of a long-lived decay component (∼25 ps) in the exciplex decay proves that this observed long-lived kinetics actually belongs to the part of the $^3(\pi,\pi^*)$ state population that is not a precursor of the exciplex. This minor part of the $^3(\pi,\pi^*)$ state population decays to the ground state without formation

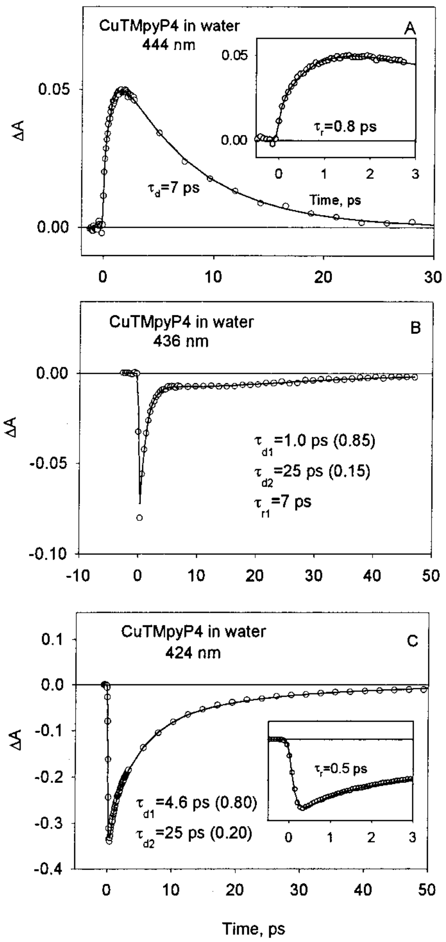

Figure 2. Time evolution of the absorption difference of CuTMpyP4 in water at wavelengths of (A) 444 nm (the triplet-state isosbestic point), (B) 436 nm (the exciplex-state isosbestic point), and (C) 424 nm (Soret band maximum).

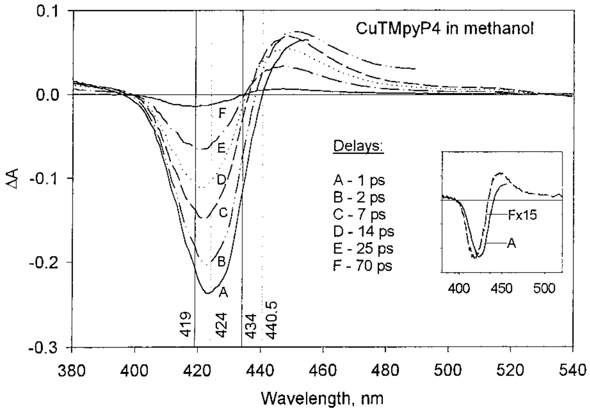

Figure 3. Transient absorption difference spectra obtained for CuTMpyP4 in methanol at the pump−probe time delays indicated. The intensity of the 70-ps spectrum is multiplied by 15 in the inset.

of any detectable transient species. (This 25 ps lifetime, nevertheless, is about 3 orders of magnitude shorter than that of CuP in a noncoordinating environment.[11])

CuTMpyP4 in Methanol. Difference absorption spectra and kinetics of CuTMpyP4 in methanol (Figure 3) qualitatively resemble those measured in water. The 1-ps delay spectrum after excitation (curve A in Figure 3) corresponds (mostly) to initially populated excited $^3(\pi,\pi^*)$ state. The isosbestic point and Soret band bleaching maximum of the $^3(\pi,\pi^*)$ state difference spectrum are located at 440.5 and 424 nm, respectively. Then, for the first few picoseconds after excitation, a considerable shift of the isosbestic point to shorter wavelengths occurs, the *R* value decreases, and the spectrum acquires a more symmetrical derivative-like profile. We assume that, by analogy with water solution, this is because the relative contribution of the exciplex to the measured difference spectrum increases. This tendency keeps going (but more slowly) for ~70 ps after excitation. Then the difference profile stabilizes within the accuracy of our measurements and does not show any shift back to longer wavelengths as it does in water solution.

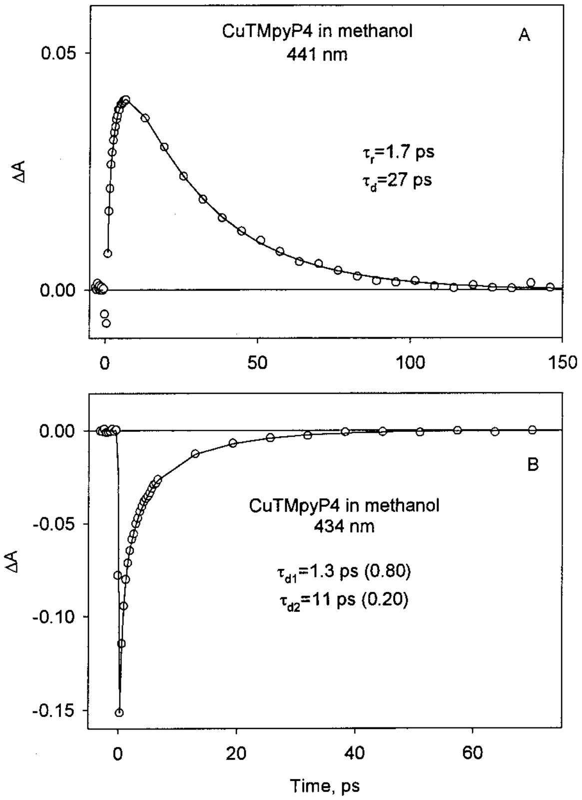

Figure 4. Time evolution of the absorption difference of CuTMpyP4 in methanol at wavelengths of (A) 441 nm (the triplet-state isosbestic point) and (B) 434 nm (the exciplex-state isosbestic point).

Figure 4A shows the exciplex formation and decay kinetics measured at the $^3(\pi,\pi^*)$ state isosbestic point near 441 nm. It shows a monoexponential increase of exciplex population ($\tau_r = 1.7 \pm 0.3$ ps) followed by a monoexponential decay. The $^3(\pi,\pi^*)$ state decay measured at 434 nm (Figure 4B) is well fit by a biexponential curve with $\tau_{d1} = 1.5 \pm 0.3$ ps (80%) and $\tau_{d2} = 11 \pm 2$ ps (20%) time constants. The first component corresponds well to the rise time of the exciplex. This implies that, during the first 1.5 ps after excitation, ~80% of CuP molecules in $^3(\pi,\pi^*)$ state deactivate with a formation of exciplex. The second decay component of the $^3(\pi,\pi^*)$ state, that is, $\tau_{d2} = 11 \pm 2$ ps, has no counterpart in the exciplex kinetics. This may only imply that ~20% of the CuP molecules in $^3(\pi,\pi^*)$ state deactivate to the ground state without exciplex formation with methanol molecules. It is worth noting that the shorter lifetime of the part of the $^3(\pi,\pi^*)$ state population that deactivates directly to the ground state ($\tau_{d2} = 11$ ps) as compared to the exciplex lifetime ($\tau_d = 27$ ps) well explains why, in contrast to what happens in water, the relative contribution of the $^3(\pi,\pi^*)$ state population does not increase with time at long delays.

CuTMpyP4 in DMSO. Although difference absorption spectra of CuTMpyP4 in DMSO (Figure 5) qualitatively

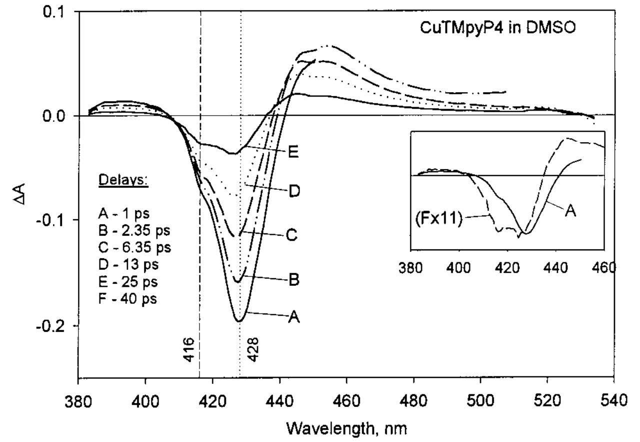

Figure 5. Transient absorption difference spectra obtained for CuTMpyP4 in DMSO at the pump−probe time delays indicated. The intensity of the 40-ps spectrum is multiplied by 11 in the inset.

resemble those measured in water and methanol solutions, they possess some peculiarities. The most important is that the shifts of the isosbestic point to shorter wavelengths (from 444 to 435 nm) and of the Soret band bleaching maximum (from 428 to 426 nm) are accompanied by some change of the spectral shape in the Soret band region: a new bleaching shoulder component appears nearby 416 nm, that is, on the blue limb of the "normal" bleaching maximum at 426 nm (see also inset of Figure 5). As a result, the bleaching decay kinetics measured in the Soret band region at 416 and 426 nm are somewhat different from each other. This may result from exciplex formation by DMSO axial ligation not only through oxygen but also through the sulfur atom. Indeed, DMSO complexes are reported in the literature in which sulfur behaves as a donor atom.[13]

The exciplex formation and decay kinetics measured at 444 nm (Figure 6A) are well-fit by monoexponential rise ($\tau_{r1} = 1.4 \pm 0.4$ ps) and decay laws ($\tau_d = 23 \pm 2$ ps). The $^3(\pi,\pi^*)$ state decay measured at 435 nm (Figure 6B) is well-fit by a biexponential curve with $\tau_{d1} = 1.0 \pm 0.3$ ps (80%) and $\tau_{d2} = 8 \pm 1$ ps (20%) time constants. The first component corresponds well to the rise time of exciplex. This implies that, during the first picosecond after excitation, about 80% of the CuP molecules in the $^3(\pi,\pi^*)$ state deactivate with a formation of exciplex between CuP (in the (d,d) excited state) and DMSO. The second decay component, that is, $\tau_{d2} = 8 \pm 1$ ps, has no counterpart in the exciplex decay kinetics. This may only imply that about 20% of the CuP molecules in the $^3(\pi,\pi^*)$ state deactivate to the ground state without exciplex formation with DMSO.

4. Discussion

Experimental data show that in all three solvents *two different types* of CuTMpyP4 molecules in the excited $^3(\pi,\pi^*)$ state are observed, which decay by different ways and kinetics: (i) about 80% of the four-coordinate CuTMpyP4 molecules in their $^3(\pi,\pi^*)$ state are quenched (with a time constant of ca. 1−1.5 ps) by solvent; this quenching gives rise to the formation of an exciplex in which a solvent molecule acts as an axial ligand of excited CuTMpyP4, and (ii) about 20% of the CuP molecules in $^3(\pi,\pi^*)$ state are quenched to the ground state without exciplex formation. How may this occur in a homogeneous medium? Indeed, deactivation of *only one kind* of excited molecules by two different but simultaneous ways, with rate constants k_1 and k_2, induces a total rate constant of deactivation ($k_1 + k_2$). This results in a monoexponential excited-state decay kinetics with a unique lifetime of $1/(k_1 + k_2)$. In contrast, observation of two different decay kinetics requires that all of the CuTMpyP4 molecules in the excited $^3(\pi,\pi^*)$ state are divided into two different populations, independent from each other at least during the excited $^3(\pi,\pi^*)$ state lifetime. It is difficult to find a sound reason for such CuTMpyP4 partitioning in the ground state. For the excited triplet (π,π^*) state, several possible mechanisms may be suggested.

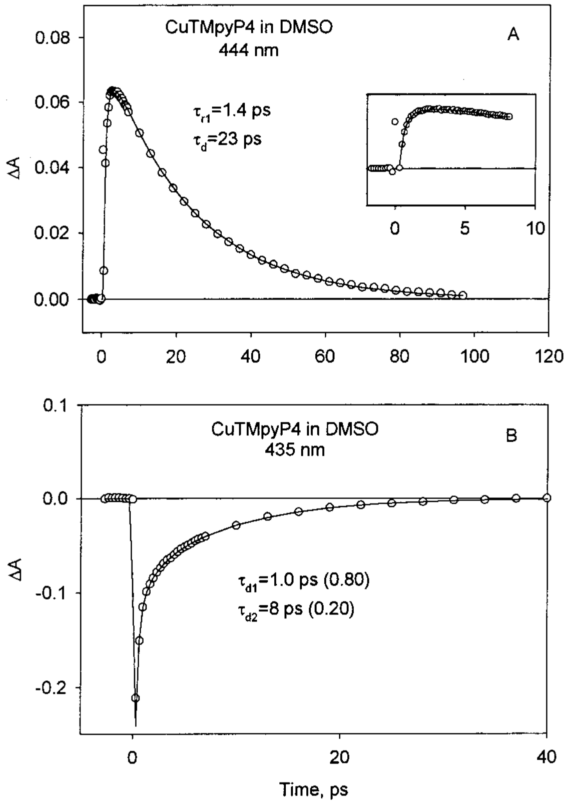

Figure 6. Time evolution of the absorption difference of CuTMpyP4 in DMSO at wavelengths of (A) 444 nm (the triplet-state isosbestic point) and (B) 435 nm (the exciplex-state isosbestic point).

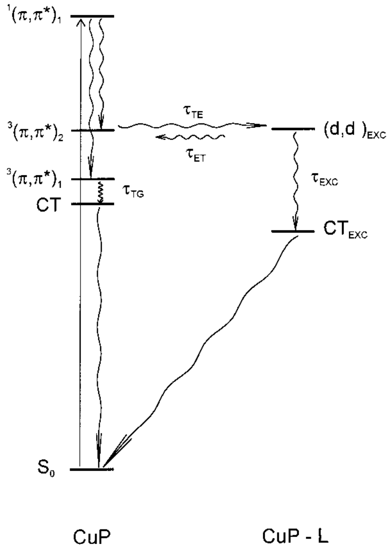

Figure 7. Schematic energy-level diagram showing proposed pathways of the excitation energy degradation (mechanism 1).

Mechanism 1. In the scheme proposed in Figure 7, the idea is that there may be two different low-lying $^3(\pi,\pi^*)$ states the energies of which are located below that of the $^1(\pi,\pi^*)_1$ (or Q) state. Indeed, there are numerous quantum-chemical calculations, both semiempirical[14] and ab initio,[15] that predict, for both free base and metal porphyrins, the presence of two low-lying $^3(\pi,\pi^*)$ states, that is, $^3(\pi,\pi^*)_1$ and $^3(\pi,\pi^*)_2$, below the $^1(\pi,\pi^*)_1$ state. In the framework of a simplified "four orbital" model, these two triplet (π,π^*) states are characterized by "pure" electronic configurations $^3(1a_{1u}4e_g)$ and $^3(1a_{2u}4e_g)$, while in more complex approaches, there exists a considerable predominance of one of the above configurations. Only recently, the presence of the second low-lying triplet (π,π^*) state, that is, $^3(\pi,\pi^*)_2$, has been shown experimentally.[16] Two evident bands were found in $^3(\pi,\pi^*) \rightarrow S_0$ luminescence excitation spectra of Pd porphyrins under excitation in low-intensity $S_0 \rightarrow {}^3(\pi,\pi^*)$ transitions.[16] The $^3(\pi,\pi^*)_2$ state was found to lie 1870 and 630 cm^{-1} above the $^3(\pi,\pi^*)_1$ state in case of PdOEP and PdTPP, respectively.

In Figure 7, the $^3(\pi,\pi^*)_2$ state of the four-coordinate CuP (left part of the scheme) lies between the $^3(\pi,\pi^*)_1$ and $^1(\pi,\pi^*)_1$ states, as found experimentally for Pd porphyrins.[16] As discussed above, the binding state of five-coordinate CuPs is most likely the (d,d) excited state (level (d,d)$_{\text{exc}}$ in the right part of the scheme). Numerous calculations show[7c,17] that the energy of this state strongly depends on the distance between the Cu(II) ion and the ligand heteroatom. For four-coordinate species, that is, in the absence of any ligand molecule in the nearest surrounding, the (d,d) state lies sufficiently high, that is, between $^1(\pi,\pi^*)_1$ (or Q) and $^1(\pi,\pi^*)_2$ (or B) states; it is not shown in the left part of the scheme (Figure 7). When a ligand heteroatom approaches the Cu(II) ion, the energy of the (d,d) state considerably drops so it may fall nearby that of the $^3(\pi,\pi^*)_1$ and $^3(\pi,\pi^*)_2$ states. In the proposed Figure 7 scheme, it is assumed that the energy of the stable exciplex ((d,d)$_{\text{exc}}$ level in the right part of Figure 7) is comparable with that of the higher triplet, that is, $^3(\pi,\pi^*)_2$, whereas the $^3(\pi,\pi^*)_1$ state lies below. As a result, only the $^3(\pi,\pi^*)_2 \rightarrow$ (d,d)$_{\text{exc}}$ transition turns out to be energetically favorable in the presence of liganding solvent molecules. We correlate this transition to the ultrafast exciplex formation kinetics (time constant τ_{TE} in Figure 7).

In contrast, the $^3(\pi,\pi^*)_1$ state population cannot contribute to stable exciplex formation for energetic reasons, and therefore, the $^3(\pi,\pi^*)_1$ state may only deactivate to the ground state. We correlate this $^3(\pi,\pi^*)_1$ state deactivation (time constant τ_{TG}) to the experimentally observed component of triplet (π,π^*) state deactivation (lifetime τ_{d2} in Figures 2, 4, 6).

We assume that this type of quenching is analogous to that found earlier for the CuP $^3(\pi,\pi^*)_1$ state quenching in the presence of nitrogen-containing bases.[7] We speculate that this type of quenching may not be accompanied by the formation of any real five-coordinate excited CuP and likely results from the electric field influence of polar solvent molecules on the electronic energy of an intramolecular CT state of four-coordinate CuP. Solvents with high polarity can stabilize the CT state energy enough to drop it below the $^3(\pi,\pi^*)_1$ state energy and thus can quench the latter. This second type of quenching, which may be called "contact quenching", is likely active for both $^3(\pi,\pi^*)_1$ and $^3(\pi,\pi^*)_2$ states all the time after excitation, but for the $^3(\pi,\pi^*)_2$ state, during the very first picoseconds after excitation, it cannot compete with the much faster quenching through exciplex formation.

The ultrashort exciplex lifetime, τ_{exc} (7−27 ps, depending on the solvent), requires a special consideration. Such a short lifetime might result from a very low energy of the (d,d) state of five-coordinate CuTMpyP4, that is, from a small energy gap between ground and excited (d,d) states. We believe, however, that this is not the case and the energy of this (d,d) state is likely close to that of the $^3(\pi,\pi^*)_2$ state of four-coordinate CuTMpyP4. This is supported by (i) theoretical calculations,[7c,17] which predict an energy of the [d(z^2), d($x^2 - y^2$)] state of the five-coordinate CuP close to that of the $^3(\pi,\pi^*)$ state, and by (ii) the observation of the $\tau_{\text{r1}} = 7$ ps rise component in the $^3(\pi,\pi^*)$ state kinetics in water (see Figure 2B). This rise component likely corresponds to a (minor) back dissociation of the exciplex (the lifetime of which is 7 ps) to initial four-coordinate CuP in its $^3(\pi,\pi^*)_2$ state (time constant τ_{ET} in Figure 7). Obviously, this process could not take place if the electronic energy of the exciplex were considerably lower than that of the $^3(\pi,\pi^*)$ state.

TABLE 1: Kinetic Parameters of the CuTMpyP4 Triplet-State Quenching by Water, Methanol, and DMSO (See Notations in Figure 7)

solvent	ϵ^a	τ_{TE}, ps	τ_{TG}, ps	τ_{exc}, ps
water	78.3	1.0 ± 0.2	25 ± 3	7 ± 1
DMSO	46.5	1.2 ± 0.4	8 ± 1	23 ± 2
methanol	32.7	1.5 ± 0.3	11 ± 2	27 ± 2

[a] Dielectric constant at 25 °C.

Therefore, ultrafast deactivation of the (d,d) state cannot be explained by a very small energy gap between (d,d) and ground electronic states. Most likely, the exciplex (d,d) state deactivates via some intermediate located below the (d,d) state in energy. An intramolecular CT state of the five-coordinate CuP (level (CT)$_{\text{exc}}$ in Figure 7) may play such a role of a low-lying state. All calculations available so far predict such a low energy of this state for five-coordinate CuP complexes.[7c,15,17]

Therefore, quenching of the excited $^3(\pi,\pi^*)$ state of CuTMPyP4 in three different oxygen-containing Lewis-base solvents (water, methanol and DMSO) may be described by the common scheme shown in Figure 7 (corresponding time constants are summarized in Table 1). The main peculiarity of this scheme is that there are two $^3(\pi,\pi^*)$ states, and only the $^3(\pi,\pi^*)_2$ state is able to form the exciplex. As experimental data show, in all three solvents, about 80−85% of the $^3(\pi,\pi^*)$ state CuP molecules deactivate via the exciplex formation with characteristic time constants τ_{TE} of ca. 1−1.5 ps. The remaining excited CuP molecules, being in the lower-lying $^3(\pi,\pi^*)_1$ state, cannot form a stable exciplex and decay to the ground state with the time constant τ_{TG}. They are likely quenched by polar solvent molecules that influence the energy of an intramolecular CT state: in polar solvents, the energy of the four-coordinate CuP CT state lies below that of the $^3(\pi,\pi^*)_1$ state and quenches it.

As seen in Table 1, the exciplex lifetime τ_{exc} explicitly increases when the solvent dielectric constant ϵ decreases. A parallel tendency was earlier obtained for the CuTMPyP4 exciplex formed in the presence of short oligothymidylates of various lengths in aqueous solutions: the porphyrin exciplex lifetime increased from 30 ps for CuTMPyP4 complexed with d(pT)$_1$ to 160 ps for CuTMPyP4 complexed with d(pT)$_5$.[5g] It was assumed in ref 5g that this effect is governed by the effective polarity of the porphyrin microenvironment, which (polarity) decreases as the screening effect of thymine residues increases as their number in the vicinity of the porphyrin increases. In a framework of the scheme (Figure 7), this solvent polarity dependence of exciplex lifetime may be formally accounted for in terms of increase of some energy barrier (not shown) between (d,d)$_{\text{exc}}$ and CT$_{\text{exc}}$ states as solvent polarity decreases.

It is worth noting that the time constant τ_{TG} of "contact" quenching of the $^3(\pi,\pi^*)_1$ state likely has an opposite dependence on solvent polarity (see Table 1): it decreases, in general, with a decrease of solvent polarity, from 25 ps in water to 8 ps in DMSO and 11 ps in methanol. This is connected with the fact that the triplet quenching is by nature a bimolecular process and depends to a larger extent on peculiarities of the quencher structure and diffusion in solution than on microenvironment polarity. In contrast, exciplex deactivation (and subsequent dissociation) is a monomolecular process, which is more adequately described in terms of influence of surrounding medium macroscopic parameters such as the dielectric constant.

Mechanism 2. A picosecond dynamics study of photoexcited Cu(II)TMPyP4 in water has recently been reported in ref 6c. The time dependence of TA spectra shown by the authors corresponds well to what we obtained in the present work. They found that the initially populated $^3(\pi,\pi^*)$ state (which is a $^2T_1$ tripdoublet in their interpretation) is quenched with a 1.2-ps time constant and results in (i) formation of an exciplex with water as an axial ligand and (ii) population of the tripquartet $^4T_1$ state (see their Figure 5[6c]). Exciplex and $^4T_1$ tripquartet state deactivations to the ground state were found to occur with ∼4 and ∼25 ps time constants, respectively, without suggestions about participation of any additional intermediate state.

It is worth noting that the lifetime of the “long-lived” fraction of $^3(\pi,\pi^*)$ state population determined here (25 ps) is exactly the same as that found in ref 6c, while their exciplex lifetime is estimated as slightly shorter: this may result from some short-lived $^3(\pi,\pi^*)$ state contribution because their exciplex deactivation kinetics was measured at an arbitrary wavelength, that is, not at the $^3(\pi,\pi^*)$ state isosbestic point. Indeed, similar ∼4−5-ps components were found in our experiments when TA kinetics were similarly measured not at the $^3(\pi,\pi^*)$ state isosbestic point but at arbitrary wavelength (see Figure 2C as an example).

In our opinion, the deactivation scheme presented in ref 6c is sufficiently plausible although there are questions that require additional explanations: (i) why only tripdoublet $^2T_1$ state but not tripquartet $^4T_1$ state decays through the exciplex formation with water, (ii) why $^4T_1$ state population occurs in 1.2 ps although equilibration time between $^2T_1$ and $^4T_1$ states is known to be ∼450 ps,[18] and (iii) why both $^4T_1$ and exciplex states could deactivate so quickly to the ground state (in picoseconds) without participation of any additional low-lying quenching state.

Mechanism 3. This mechanism, which considers only one $^3(\pi,\pi^*)$ state, consists of different ligation ability of vibrationally “hot” and “cool” excited CuP molecules. Indeed, because of the extremely fast $^1(\pi,\pi^*)_1 \rightarrow {}^3(\pi,\pi^*)$ radiationless transition, the $^3(\pi,\pi^*)$ state population occurs in a few tens of femtoseconds with a release of a large (at least ∼3000 cm^{-1}) excess of vibrational energy. This vibrational energy excess, which may remain unequilibrated in electronically excited porphyrins during about 10 ps after electronic excitation,[19] is suggested to be responsible for different deactivation pathways of “vibrationally hot” CuP $^3(\pi,\pi^*)$ molecules, which decay through (very fast) axial ligation of Cu(II) atom by water, as compared to “vibrationally cool” CuP $^3(\pi,\pi^*)$ molecules, which (much more slowly) decay to the ground state. This suggestion is based on an idea that low-frequency out-of-plane porphyrin vibrations may be important for the reaction of axial coordination of water to the Cu(II) ion.

Therefore, fast depletion of hot vibronic levels of the $^3(\pi,\pi^*)$ state by axial ligand association may play the role of a “switch” that redirects the $^3(\pi,\pi^*)$ state deactivation from one channel (through the exciplex formation) to the other (directly to the ground state). Thus, in this framework, only those $^3(\pi,\pi^*)$ state molecules that are able to overcome some energy barrier can form an exciplex with water. Only “vibrationally hot” (in terms of out-of plane vibrations) $^3(\pi,\pi^*)$ state molecules can likely do it. A major part of the $^3(\pi,\pi^*)$ state molecules can cross this barrier (i.e., to form the exciplex) in 1.0 ps because (i) a large excess of vibrational energy they have obtained, a part of it being likely localized in nonplanar vibrational modes of the macrocycle, which facilitate the exciplex formation, and (ii) fast rotational diffusion of small-size solvent molecules providing convenient orientation of oxygen atom to bind the Cu(II). At least in water, solvent rotational diffusion is a rate-limiting factor in the exciplex formation kinetics; indeed, the time constant of exciplex formation (1.0 ps) is very close to that of rotational reorientation of water (0.7 ps).[20]

Mechanism 4. It has been recently found that Cu(II)-5,10,15,20-*meso*-tetrakis(aryl)porphyrins exist in solutions at 77 K as a mixture of two spectral forms, I and II, that yield different luminescence spectra and lifetimes and different luminescence excitation spectra as well.[21] Spectral form I has a luminescence lifetime of about 500 μs and is ascribed to a planar CuP conformer, whereas spectral form II shows a luminescence lifetime of 0.5−0.7 μs and is tentatively identified with a nonplanar CuP conformer. One may suggest that the two deactivation pathways found in this work for CuTMpyP4 $^3(\pi,\pi^*)$ state may be just related to the existence of two CuTMpyP4 conformers that are quenched by different mechanisms. It is difficult, however, to check this hypothesis directly in the manner performed in ref 21 because polar cationic porphyrins are dissolved only in polar O- and N-containing solvents, which quench CuTMpyP4 luminescence.

At present, we consider mechanisms 1 and 4 as the more plausible ones, although the other two mechanisms cannot be completely ruled out.

5. Conclusion

The results obtained here enable the questions of the Introduction to be answered in the following way:

(i) The lifetime of the exciplex formed between excited CuTMpyP4 and an oxygen-containing solvent molecule indeed increases when the solvent dielectric constant decreases. This may be accounted for in two ways. First, this may result from an increase of some energy barrier between the $(d,d)_{exc}$ and CT_{exc} states as the solvent polarity decreases. Second, this may be a consequence of the plausible fact that the exciplex not only is a “pure” (d,d) excited state of the five-coordinate CuP but also possesses some properties of a CT state, of which the contribution increases as the solvent polarity increases, this in turn enhancing the radiationless deactivation of the “mixed” exciplex state. A similar conclusion about a complex character of the exciplex state (mainly (d,d) with a contribution of CT) was made in ref 17a on the basis of calculations.

(ii) CuP triplet state quenching directly to the ground state is not characteristic for nitrogen-containing solvents only, but also in some extent for oxygen-containing solvents in which it competes with quenching through exciplex formation. It is not clear, however, what mechanism is responsible for partitioning between these two types of quenching. One may suggest two types of relaxation schemes based on (i) the presence of two low-lying triplet states (or two conformers) of different abilities to bind an axial ligand and (ii) different abilities to bind an axial ligand by “vibrationally hot” and “vibrationally cool” CuTMpyP4 molecules. Experiments are now in progress in our groups that will enable us to find out what mechanism is more suitable to explain the data obtained in this work.

References and Notes

(1) (a) As a result of the coupling of the unpaired d electron of copper with π electrons of the conjugated porphyrin macrocycle, the ground $^1S_0$ and excited $^1S_1$ (π,π^*) singlet states become doublet or, using terminology of Gouterman,[1b] "singdoublet" $^2S_0$ and $^2S_1$ (π,π^*), respectively, whereas the excited triplet $^3T_1$ (π,π^*) state splits into the "tripdoublet" $^2T_1$ (π,π^*) and "tripquartet" $^4T_1$ (π,π^*).[1c−f] Because the state of multiplicity is not essential in our transient absorption experiments, for the sake of simplicity we shall call further the "tripdoublet−tripquartet" manifold $^{2,4}T_1$ as "triplet (π,π^*) state" or $^3(\pi,\pi^*)$. (b) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter 1. (c) Smith, B. E.; Gouterman, M. *Chem. Phys. Lett.* **1968**, *2*, 517. (d) Ake, R. L.; Gouterman, M. *Theor. Chim. Acta* **1969**, *15*, 20. (e) Eastwood, D.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *30*, 437. (f) Gouterman, M.; Mathies, R. A.; Smith, B. E.; Caughey, W. S. *J. Chem. Phys.* **1970**, *52*, 3795. (g) Aronowitz, Y. J.; Gouterman, M. *J. Mol. Spectrosc.* **1977**, *64*, 267. (h) Arabei, S. M.; Solovyev, K. N.; Egorova, G. D. *J. Porphyrins Phthalocyanines* **2000**, *4*, 604−609.

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(4) One group[2,3a,b] suggests that the exciplex is an excited electronic (d,d) state of the five-coordinate CuP, a second one believes[3d] that this is an excited CT state of (π,d) nature, and a third group[3c] does not make any definite choice between these two possibilities.

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