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Time-Resolved Resonance Raman Spectroscopic Study on Copper(II) Porphyrins in Various Solvents: Solvent Effects on the Charge Transfer States

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Time-resolved resonance Raman (TR³) spectroscopic investigations were done on copper(II) tetraphenylporphyrin (Cu^{II}TPP) and copper(II) octaethylporphyrin (Cu^{II}OEP) in various solvents to elucidate the electronic nature of the excited states involved in the deactivation processes. In noncoordinating solvents, the frequency shift and enhancement pattern in the Raman spectrum of excited state Cu^{II}TPP were identified as the simultaneous contribution from the ²T/⁴T (π, π^*) manifold and the (π, d) charge transfer state (CT₁). These observations were also consistent with the small energy gap between the ²T/⁴T (π, π^*) manifold and the (π, d) charge transfer state of Cu^{II}TPP, as suggested by the previous picosecond transient absorption results. On the contrary, our TR³ spectrum of Cu^{II}OEP represented the characteristic features mainly induced by the ²T/⁴T (π, π^*) manifold with no indication of the contribution from the (π, d) charge transfer state, which was suggested to be located in an energy well above the ²T/⁴T (π, π^*) manifold. In coordinating solvents, however, the TR³ spectra of Cu^{II}TPP and Cu^{II}OEP, as indicated by the significant shifts of the ν_2 and ν_4 bands relative to those in noncoordinating solvents, exhibited the involvement of a new (π, d) charge transfer state (CT₂) associated with the formation of the five-coordinated species with solvent as an axial ligand in the excited state. The identification of the electronic nature and the axial ligand dynamics in the excited states of Cu^{II}TPP and Cu^{II}OEP was demonstrated by examining the relationship between the core size expansion upon axial ligation and the shift and enhancement pattern of characteristic Raman bands.

Introduction

Copper(II) porphyrins have been the most extensively investigated among the paramagnetic metalloporphyrins.^{1–4} Cu^{II} has a d⁹ electronic configuration with an unpaired electron in the d_{x²–y²} orbital. The interaction of the half-filled d_{x²–y²} orbital with a π -electronic system of the porphyrin ring is responsible for the formation of singdoublet, ²S(π, π^*), tripdouplet, ²T(π, π^*), and triquartet, ⁴T(π, π^*), states, exhibiting peculiar photophysical properties. Copper(II) porphyrins do not show any fluorescence, but the unusual phosphorescence from the ²T and ⁴T (π, π^*) states in thermal equilibrium is observed.^{5–8} The tripdouplet lies above the triquartet by 200–700 cm^{–1}, depending on the peripheral substituents of the porphyrin macrocycles, and the two states are apparently different in both radiative and nonradiative decay rates.^{7,8}

In copper(II) porphyrins, several electronic transitions in addition to the (π, π^*) transition are possible:^{1,3–4} first, the (π, d) transition from ring a_{1u}(π) or a_{2u}(π) to metal d_{x²–y²}, second, the (d, π^*) transition from the metal d_{x²–y²} electron to a ring e_g(π^*), and finally, the (d, d) transition between d orbitals are predicted to have a comparable energy to the (π, π^*) transition. The lack of emission in paramagnetic metalloporphyrins is attributed to one of the (π, d) or (d, π^*) charge transfer (CT) states lying below the normally emissive ²T and ⁴T (π, π^*) states.⁴

In copper(II) octaethylporphyrin (Cu^{II}OEP), a number of observations suggest that the CT state lies in energy above the ²T and ⁴T (π, π^*) manifold in noncoordinating solvents (four-coordinated Cu).^{9,10} On the other hand, the CT state of

copper(II) tetraphenylporphyrin (Cu^{II}TPP) has dropped its energy comparable to the ²T and ⁴T (π, π^*) states.¹⁰ The (π, d) CT states of Cu^{II}TPP and Cu^{II}OEP in noncoordinating solvents have been implicated as the states responsible for the solvent and temperature dependent excited state dynamics. The drastic lifetime reduction of Copper(II) porphyrins in coordinating solvents like pyridine is also ascribed to the fast deactivation through the CT state. The lowering of the CT state in the energy below the ²T/⁴T (π, π^*) manifold upon the acquisition of an axial ligand in the excited states would be required to enhance the effective deactivation of photoexcited copper(II) porphyrin complexes.¹⁰

While the excited state dynamics of copper(II) porphyrins have been investigated with transient absorption and fluorescence spectroscopies, the structural change of the CT state has not been described in detail. In addition, three different types of theoretical calculations, IEH,¹¹ X α ,¹² and PPP,¹³ did not lead to a decisive conclusion as to the nature of the CT states. The vibrational spectra are generally capable of providing the detailed structural information, especially when the band assignments are complete. In fact, the previous Raman spectroscopic investigations indicate that the porphyrin ring core expands with an addition of axial ligand, which is also accompanied by a metal out-of-plane geometry.¹⁴ And another Raman study indicates that the lowering of the vibrational frequencies of the copper(II) tetrakis(4-*N*-methylpyridyl)porphyrin–DNA (Cu^{II}TMPyP(4)–DNA) complex is due to the cationic nature of the porphyrin induced by the intermolecular charge transfer exciplex.¹⁵ This complex is suggested to be formed by an intermolecular charge transfer from the highest occupied molecular orbital of copper(II) porphyrin into the lowest vacant orbital of a thymine residue. Therefore, to explore

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the nature of the low-lying CT state, this report presents nanosecond time-resolved resonance Raman (TR³) spectra of the excited states of Cu^{II}TPP and Cu^{II}OEP in various solvents. In addition, picosecond TR³ spectra were also recorded for copper(II) porphyrin in strongly coordinating solvents like pyridine to keep track of the states involved in the fast electronic relaxation.

Experimental Section

Cu^{II}TPP and Cu^{II}OEP were purchased from Porphyrin Products (Logan, UT) and used without further purification. The ground state absorption and Raman spectra of these compounds agree with the previously reported spectra. All the solvents used were spectroscopic grade and further purified by fractional distillation.

TR³ spectra on Cu^{II}TPP and Cu^{II}OEP were obtained using a nanosecond Q-switched Nd:YAG laser generating pump pulses at 532 nm (5-ns fwhm at 10 Hz and 0.03 mJ/pulse). The probe pulses at 435 nm (3.5-ns fwhm at 10 Hz and 0.01 mJ/pulse) were prepared from the first anti-Stokes shifted Raman line of H₂, excited by 532-nm pulses. The time delay between pump and probe pulses was controlled by an optical delay line. TR³ spectra were collected with an HR 640 spectrograph (Jobin-Yvon), a gated intensified photodiode array detector (Princeton Instruments IRY700), a delay generator (Stanford Research DG535), and a pulse generator (Princeton Instruments FG135). As for picosecond transient Raman spectra, picosecond pulses at 435 nm were generated by an H₂ Raman shifter from 532-nm (70 ps and 25 mJ/pulse) outputs of the combination of a mode-locked Nd:YAG (Coherent Antares 76S) and a Nd:YAG regenerative amplifier (Continuum RGA-20) system. In all the measurements, the sample solutions (*ca.* 1 mM) were flowed through a glass capillary (0.8-mm id) at a rate sufficient enough to ensure that each pulse encountered a fresh volume of the sample. We carefully checked the sample decomposition by comparison with the ground state Raman spectra of the fresh sample. Ground state absorption spectra were measured on a Varian UV-vis spectrophotometer (Cary 5), and the ground state Raman spectra were recorded by a continuous wave (cw) Ar ion laser, a Raman U1000 double monochromator (Jobin-Yvon), and a photon counting electronics (Hamamatsu).

Results and Discussion

Cu^{II}TPP. Figure 1 shows TR³ spectra of Cu^{II}TPP in benzene at a 7-ns time delay between the pump (532 nm) and probe (435 nm) pulses, which are in resonance with the Q(0,1) absorption band and the T₁–T_n absorption of Cu^{II}TPP, respectively. The Raman spectral features for the solvent and the ground state Cu^{II}TPP were subtracted to yield the excited state Raman spectra, using a subtraction factor to eliminate any contribution from ground state Cu^{II}TPP. In Cu(II) metal, there is no empty d-orbital that is available to receive π -donation from an axial ligand. For the solvent, benzene was selected because it does not contain atoms such as O and N which can afford σ -type donation to the unoccupied p_z-orbital of the central metal. The ground state Raman bands are readily assigned from the normal mode analysis of Cu^{II}TPP.¹⁶ The bottom spectrum of Figure 1 was obtained with one-color pump/probe (435 nm) pulses; the Ph₄ (phenyl) mode at 1600 cm⁻¹, the ν_2 mode at 1563 cm⁻¹, the ν_4 mode at 1363 cm⁻¹, and the ν_1 mode at 1237 cm⁻¹, respectively. A characteristic change was observed for the Raman spectrum of the excited state Cu^{II}TPP in benzene (top spectrum of Figure 1), being similar to that of Zn^{II}TPP.¹⁷ The strong phenyl mode enhancement at 1598 cm⁻¹ upon excitation can be ascribed to the increase in the Franck–Condon

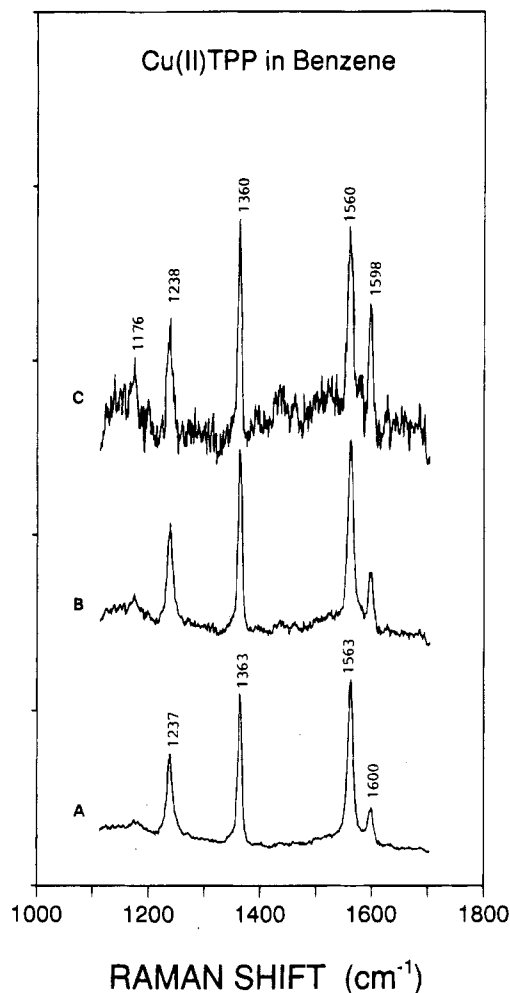


Figure 1. Nanosecond TR³ spectra of Cu^{II}TPP in benzene with 532-nm photoexcitation and a 435-nm probe at a delay time of 1 ns: (A) the probe only, (B) the pump and probe, and (C) the difference (B – A) with a proper subtraction factor.

overlap between the porphyrin e_g and phenyl π^* -orbital excitation in the T₁–T_n electronic transition at 435 nm.²⁰ Furthermore, Ph₆ (phenyl) and ν_1 modes of Cu^{II}TPP at 1176 and 1238 cm⁻¹, respectively, were moderately enhanced in the excited triplet state. In this point of view, we suggest that the transient RR bands of the ²T⁴T (π, π^*) manifold of Cu^{II}TPP should resemble those of the triplet state of Zn^{II}TPP, because both the ²T⁴T (π, π^*) and ³T (π, π^*) states are composed of the porphyrin ring (π, π^*) electronic transitions. On the other hand, the expected enhancement and downshift of the B_{1g} and B_{2g} modes, for example ν_{10} , were not observed. Actually, the B_{1g} and B_{2g} modes provide the distorted coordinates appropriate for the Jahn–Teller effect,^{18,19} which is usually observed in the system having two closely spaced HOMO's, especially in Cu^{II}TPP⁺ and Zn^{II}TPP⁺.¹⁶ Thus, our results indicated that the ²T⁴T (π, π^*) states of Cu^{II}TPP do not contain any significant pseudo-Jahn–Teller activity.

It is also noteworthy that upon excitation ν_2 and ν_4 bands at 1563 and 1363 cm⁻¹ of ground state Cu^{II}TPP were markedly enhanced and slightly shifted down to 1560 and 1360 cm⁻¹, respectively, in contrast to those of Zn^{II}TPP. This change in the TR³ spectrum for Cu^{II}TPP is probably caused by the population of the (π, d) charge transfer state (CT₁), whose energy is close to that of ²T⁴T (π, π^*) excited states. This (π, d) charge transfer state is believed to involve the a_{2u}(π) HOMO of the porphyrin ring instead of the a_{1u}(π) orbital, because the A_{2u}-type cation radical is predominantly formed in Cu^{II}TPP⁺.¹⁶

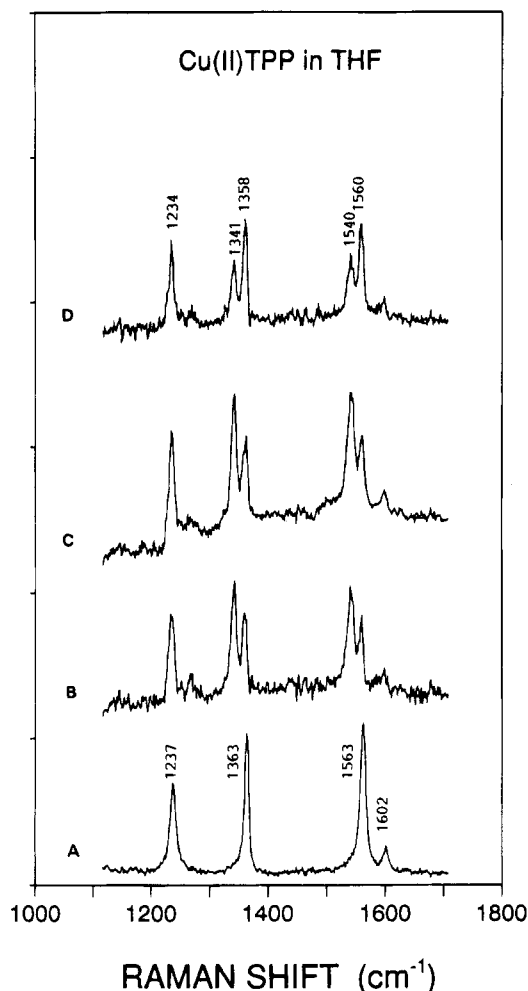


Figure 2. Nanosecond TR³ spectra of Cu^{II}TPP in THF with 532-nm pump and 435-nm probe pulses: (A) the probe-only spectrum and (B–D) the difference spectra. The delay times in the pump/probe spectra are 1 ns for B, 3 ns for C, and 7 ns for D, respectively.

According to the previous transient absorption studies, the lifetime of the $^2T/{}^4T$ (π, π^*) states of Cu^{II}TPP in noncoordinating solvents (~ 40 ns) is significantly shorter than those of the normal (π, π^*) triplet states of the closed-shell transition metal porphyrins.¹⁰ This is attributed to the thermal deactivation to the (π, d) state from the ring 2T and 4T (π, π^*) excited states.¹⁰ The simultaneous detection of the charge transfer (CT₁) state and the $^2T/{}^4T$ (π, π^*) manifold in the TR³ spectra of Cu^{II}TPP in benzene indicates that the energy of this charge transfer state is close to that of the $^2T/{}^4T$ (π, π^*) manifold, being populated rapidly together with this manifold. This observation is also in good accordance with the picosecond transient absorption investigation of Cu^{II}TPP.¹⁰

Figure 2 depicts a series of difference Raman spectra, the two-color pump/probe spectrum minus the probe-only spectrum, of Cu^{II}TPP in tetrahydrofuran (THF) at various time delays. These TR³ spectra reveal that both ν_2 and ν_4 modes show a large downshift of ~ 20 cm⁻¹ in the excited state (Table 1). With an increase of the time delay, the relative intensities at 1560 and 1358 cm⁻¹ for the ν_2 and ν_4 modes of the charge transfer (CT₁) state were changed compared with the intensities of the bands at 1540 and 1341 cm⁻¹. This observation indicated the existence of a new excited state, which is different from the (π, d) CT₁ state and the $^2T/{}^4T$ (π, π^*) manifold. It also indicates that this new state participates in the decay dynamics of Cu^{II}TPP in THF with a fast decay rate. Thus, this excited state is possibly a second charge transfer state (CT₂) associated

with the higher affinity of copper(II) porphyrins for ligands (solvents) in the transient states traversed in the course of the electronic deactivation. It has been proposed that the axial ligand binding of a σ -donor molecule to an excited state copper(II) porphyrin destabilizes the copper(II) porphyrin molecular orbitals, with a subsequent energy lowering in the intramolecular charge transfer (π, d) state below the $^2T/{}^4T$ (π, π^*) states and radiationless decay through this state.⁹ This process results in an instant ligand release and a fast relaxation to the ground state. It is noteworthy that the oxygen of THF interacts weakly as an axial ligand, as exemplified by the separation of the Fe^{II}TPP-(THF)₂ complex.²⁰

Figure 3 represents the TR³ spectra of Cu^{II}TPP in dioxane with an excitation of one-color pump/probe (435 nm) pulses having different laser powers. The relaxation process of the excited state Cu^{II}TPP in dioxane occurs faster than that in THF due to the stronger interaction of dioxane solvent with Cu^{II}TPP as an axial ligand. This phenomenon can be explained as follows; the formation of five-coordinated Cu^{II}TPP in dioxane in both ground and excited states is more feasible than in THF, and consequently it decreases significantly the average lifetime of the excited state Cu^{II}TPP in dioxane by providing more effective deactivation channels by lowering the energy of the (π, d) CT state in five-coordinated Cu^{II}TPP below the $^2T/{}^4T$ (π, π^*) manifold. Thus, only the one-color pump/probe experiment would be feasible for monitoring the TR³ spectra of Cu^{II}TPP in dioxane contributed by both CT₁ and CT₂ states. The top spectrum of Figure 3 depicts the difference spectrum between the high-power and the low-power spectra. The overall Raman spectral change of Cu^{II}TPP in dioxane was similar to that observed in THF at a short time delay between the pump and probe pulses. The intensities of the bands originated from the CT₁ state (1560 and 1358 cm⁻¹) were weaker than those of the CT₂ state (1540 and 1341 cm⁻¹). The TR³ experiment was also carried out on Cu^{II}TPP in pyridine, where pyridine interacts strongly with Cu^{II}TPP as an axial ligand. This experiment, however, could not detect any transient species due to the fast decay process of excited state Cu^{II}TPP in pyridine. These results are also in good accordance with the reported fast decay processes (< 100 ps) of photoexcited copper(II) porphyrins in strongly coordinating solvents like pyridine and piperidine.¹⁰ It was reported that about half of Cu^{II}TPP exists as a five-coordinated complex in pyridine⁹ and its ground state RR spectra are somewhat shifted from those of a four-coordinated one.^{2,10,14} To verify whether the same type of transient species is involved in the decay processes of photoexcited copper(II) porphyrins in pyridine, we also carried out picosecond TR³ studies on Cu^{II}TPP in pyridine (Figure 4). After the subtraction of the Raman features for the pyridine solvent and the ground state Cu^{II}TPP with a proper scaling factor, the apparent picosecond TR³ spectrum was obtained as shown in Figure 4. In order to find out the exact Raman frequency shifts of some smaller peaks at the shoulder of the intense Raman bands, the transient RR spectra were fitted by a Lorentzian line shape function; their frequencies are listed in Table 1. With the one-color picosecond pump/probe experiment, although it is difficult to know exactly whether or not the observed spectra resulted from the early stage of the decay process of the photoexcited Cu^{II}TPP in pyridine, we can draw the conclusion that the two intermediate states (CT₁ and CT₂) contribute to the very fast decay process of Cu^{II}TPP in pyridine, as observed in the case of THF solvent.

At this point, we consider the possibility of another intermediate, the (d,d) state, being involved in the deactivation process of Cu^{II}TPP. Since the Raman frequency shifts are small (~ 3 cm⁻¹) for the formation of the CT₁ state of Cu^{II}TPP in

TABLE 1: Assignment of the Vibrational Modes (cm^{-1}) of Excited State $\text{Cu}^{\text{II}}\text{TPP}$ in THF (Dioxane) and Pyridine

assignment	THF (dioxane)					pyridine				
	S_0	CT_1	shift	CT_2	shift	S_0	CT_1	shift	CT_2	shift
Ph_4 , $\nu(\text{phenyl})$	1602	1599	-3	a		1600	1595	-5	a	
ν_2 , $\nu(\text{C}_\beta-\text{C}_\beta)$	1563	1560	-3	1541	-22	1558	1551	-7	1529	-29
ν_4 , $\nu(\text{pyr half-ring})_{\text{sym}}$	1363	1358	-5	1341	-22	1360	1352	-8	1336	-24
ν_1 , $\nu(\text{C}_m-\text{Ph})$	1237	1235	-2	a		1235	1229	-6	a	
$\nu(\text{Ph}-\text{H})$	1180	1176	-2	a						
ν		1440		b						
ν		1267		b						
ν							1211		b	
ν							1452		b	
ν							1480		b	

^a These bands cannot be isolated from that of CT_2 due to positional overlap. ^b New bands recorded only in the transient spectrum.

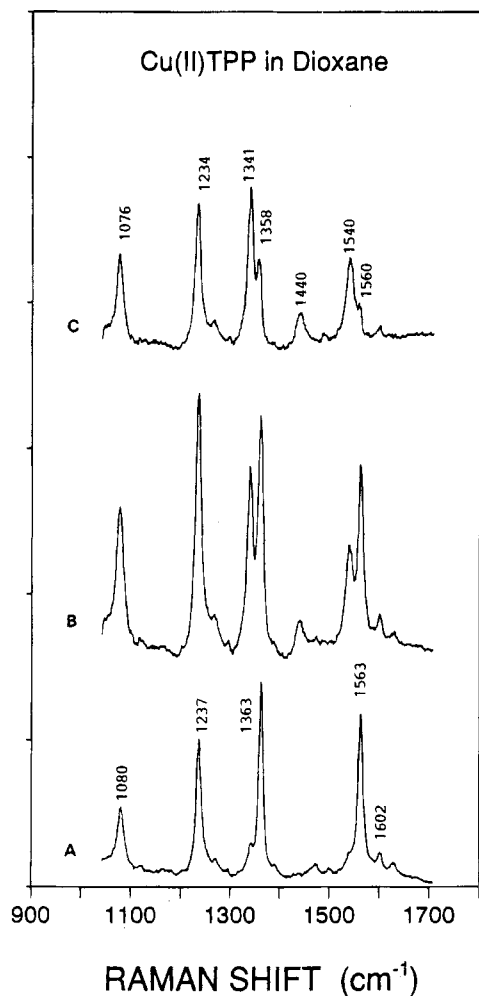


Figure 3. Nanosecond TR^3 spectra of $\text{Cu}^{\text{II}}\text{TPP}$ in dioxane with both pump and probe pulses at 416 nm: (A) the low-power, (B) the high-power, and (C) the difference spectra ($B - A$) with a proper subtraction factor.

benzene (Figure 1), the (d,d) state can be considered to represent the CT_1 state. The Raman frequency shifts, however, for the CT_1 states of $\text{Cu}^{\text{II}}\text{TPP}$ in THF, dioxane, and pyridine are larger than those in benzene, and moreover, the frequency shifts of $\text{Cu}^{\text{II}}\text{TPP}$ in pyridine are especially larger than those in the other solvents (Table 1). Since the (d,d) state is formed by the electronic transition between the Cu metal orbitals, the Raman frequency change for this intermediate is expected to be relatively insensitive to the solvent polarities. With the same analogy, the Raman frequency change for the formation of the CT_2 state of $\text{Cu}^{\text{II}}\text{TPP}$ is too large to be explained by the participation of the (d,d) state, because there is no spin state change in Cu metal between the ground state and the (d,d) state.

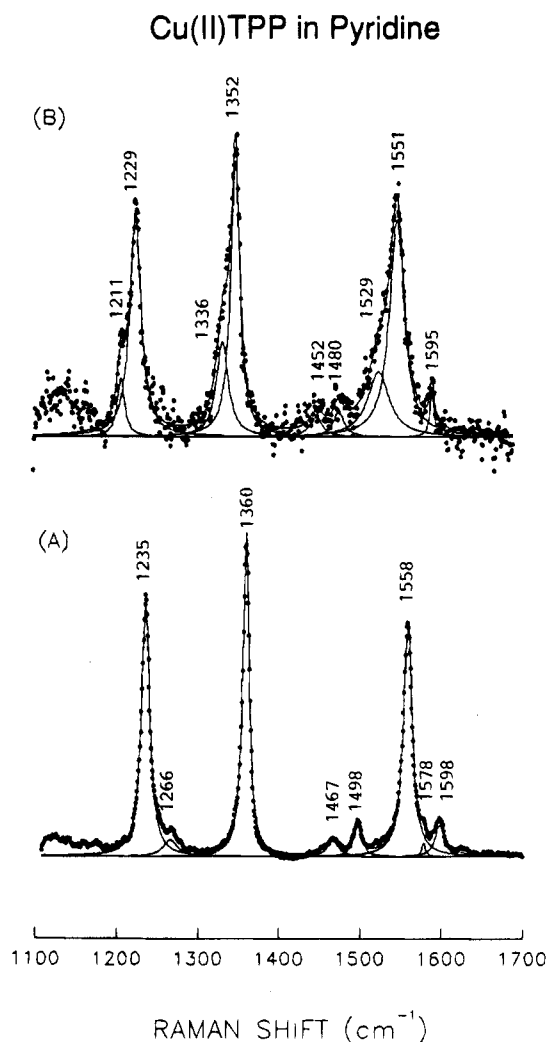


Figure 4. Picosecond TR^3 spectra of $\text{Cu}^{\text{II}}\text{TPP}$ in pyridine with both pump and probe pulses at 435 nm (pulse width: ~ 70 ps): (A) the low-power and (B) the high-power spectra.

$\text{Cu}^{\text{II}}\text{OEP}$. Figure 5 shows the TR^3 spectra of $\text{Cu}^{\text{II}}\text{OEP}$ in benzene obtained with the two-color pump/probe experiment (532-nm pump and 435-nm probe pulses) at the time delay of 7 ns. The top difference spectrum in the high-frequency region shows Raman bands at 1590, 1472, 1320, and 1252 cm^{-1} . It is noteworthy in the difference spectrum that the spectral features¹⁶ such as the broadening of the bands and the frequency shift pattern are similar to the triplet state RR spectra of $\text{Zn}^{\text{II}}\text{OEP}$.²¹ This can be ascribed to the fact that both the $^2\text{T}^4\text{T}$ (π, π^*) state of $\text{Cu}^{\text{II}}\text{OEP}$ and the $^3\text{T}(\pi, \pi^*)$ state of $\text{Zn}^{\text{II}}\text{OEP}$ are composed of porphyrin ring (π, π^*) electronic transitions. If the tentative assignment for the TR^3 bands of $\text{Cu}^{\text{II}}\text{OEP}$ follows

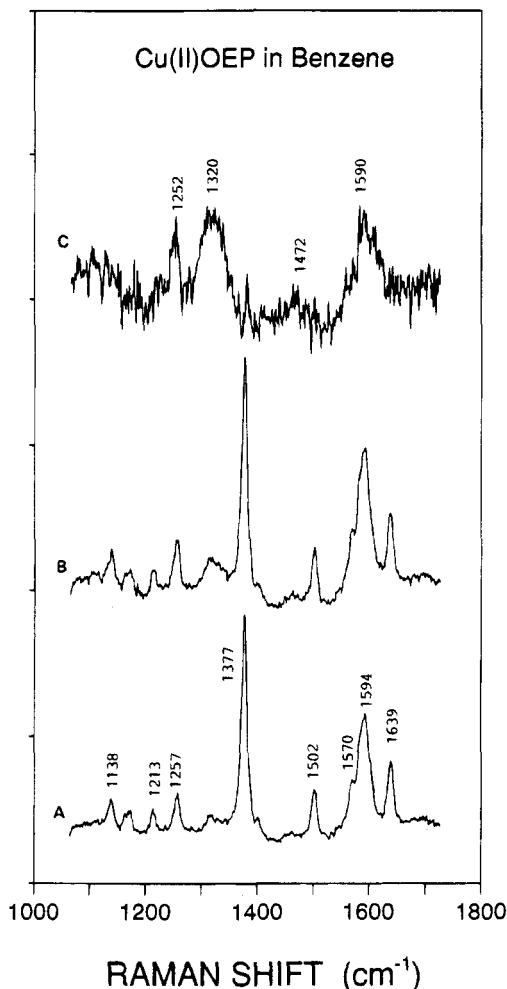


Figure 5. Nanosecond TR³ spectra of Cu^{II}OEP in benzene with 532-nm pump and 416-nm probe pulses: (A) the probe only, (B) the pump and probe (time delay: 7 ns), and (C) the difference (B - A) with a proper subtraction factor.

the previously reported one of Zn^{II}OEP, the broad bands centered around 1590 and 1320 cm⁻¹ could be attributed to ν_2/ν_{11} and CH₂ wagging modes, respectively. It is of interest to compare these two modes in the excited state with Raman frequency shift patterns for Cu^{II}OEP/Cu^{II}OEP⁺ and Cu^{II}OEP/Cu^{II}OEP⁻ pairs, because the electronic promotion for the HOMO a_{1u} orbital to the LUMO e_g^* orbital in Cu^{II}OEP resembles the cationic and the anionic electronic structures of the porphyrin macrocycle, respectively. But the formation of Cu^{II}OEP⁻ was known to be difficult due to its intrinsic instability. Thus, the Raman frequency change for the Zn^{II}-OEP/Zn^{II}OEP⁻ pair was considered here instead of that for Cu^{II}OEP⁻.

	Cu ^{II} OEP/Cu ^{II} OEP ⁺ 16	Zn ^{II} OEP/Zn ^{II} OEP ⁻ 22
$\Delta\nu_2, \nu(C\beta-C\beta), \text{cm}^{-1}$	21	0
$\Delta\nu_{11}, \nu(C\beta-C\beta)_{\text{asym}}, \text{cm}^{-1}$	33	0
$\Delta A_1 (\text{CH}_2 \text{ wag}), \text{cm}^{-1}$	0	0

If the $^2T/{}^4T (\pi, \pi^*)$ manifold of Cu^{II}OEP is treated as a combination of anionic and cationic electronic structures, the resulting slight downshift of the ν_2 and ν_{11} modes is not in accordance with the electronic nature of $^2T/{}^4T (\pi, \pi^*)$ states. A similar behavior was also observed in the $T(\pi, \pi^*)$ state Raman spectrum of Zn(II)OEP²¹. The Jahn-Teller effect was suggested to be responsible for the lack of expected upshift of ν_2 and/or ν_{11} modes. The TR³ spectrum for Cu^{II}OEP in benzene is only indicative of $^2T/{}^4T (\pi, \pi^*)$ states and is also in good

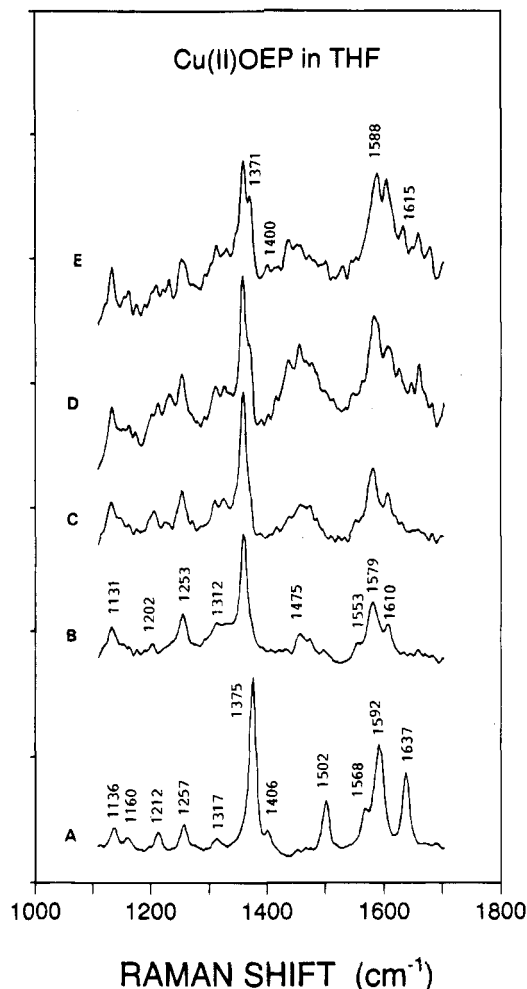


Figure 6. Nanosecond TR³ spectra of Cu^{II}OEP in THF with 532-nm pump and 435-nm probe pulses: (A) the probe-only and (B - E) the difference spectra with pump/probe time delays of (B) 1 ns, (C) 3 ns, (D) 5 ns, and (E) 7 ns, respectively.

agreement with the transient absorption results that the suggested (π, d) CT quenching state lies in energy above the $^2T/{}^4T (\pi, \pi^*)$ states in noncoordinating solvents like benzene, consequently giving rise to the longer lifetime of this manifold (~ 150 ns).⁹ In order to find out more information on the electronic structure of the $^2T/{}^4T (\pi, \pi^*)$ manifold, it is necessary to obtain the TR³ spectra for several isotopically labeled copper(II) porphyrins as well as the polarization dependence experiment. Since the main objective of this report is to find the solvent effect on the dynamics of the excited state copper(II) porphyrins and the nature of the CT (quenching) state having an energy comparable to the tripmultiplet states, further research on the electronic nature of tripmultiplet states will be the subject of future investigation.

Figure 6 shows the effect of THF solvent on the TR³ spectra of Cu^{II}OEP at delay times of 1, 3, 5, and 7 ns. The Raman frequency shifts contributed by the excited state Cu^{II}OEP are summarized in Table 2. The emergence of the new Raman bands at 1615, 1588, 1400, and 1371 cm⁻¹ was observed with an increase in the time delay between the pump and probe pulses. This observation indicated that the state other than the (π, d) CT state described above participates in the decay process of excited state Cu^{II}OEP in THF. Furthermore, this state was thought to be different from the $^2T/{}^4T (\pi, \pi^*)$ manifold in the electronic structure. This second excited state was possibly implicated with the ligand dissociation/association dynamics of Cu^{II}OEP in THF. The previous investigations^{9,10} reported that

TABLE 2: Assignment of the Vibrational Modes (cm⁻¹) of Excited State Cu^{II}OEP in THF

assignment	S ₀	CT ₂	shift
ν_{10} , $\nu(\text{C}_\alpha\text{--C}_m)_{\text{asym}}$	1637	1610	-27
ν_2 , $\nu(\text{C}_\beta\text{--C}_\beta)$	1592	1579	-13
ν_{11} , $\nu(\text{C}_\beta\text{--C}_\beta)_{\text{asym}}$	1568	1553	-15
ν_3 , $\nu(\text{C}_\alpha\text{--C}_m)_{\text{sym}}$	1502	1475	-27
ν_{29} , $\nu(\text{pyr quater ring})$	1406		
ν_4 , $\nu(\text{pyr half-ring})_{\text{sym}}$	1375	1360	-15
ν_5 , $\nu(\text{C}_\beta\text{--C}_1)_{\text{sym}}$	1136	1131	-5
ν_{13} , $\nu(\text{C}_m\text{--H})$	1212	1202	-10
A ₁ (CH ₂ wag)	1317	1312	-5
A ₁ (CH ₂ twist)	1257	1253	-2
ν_{30} , $\nu(\text{pyr half-ring})_{\text{asym}}$	1160		

the photoexcited copper(II) porphyrins pick up one axial ligand, which lowers the energy of the (π ,d) state below the ²T⁴T-(π , π *) state and deactivates radiationlessly through this state. In this process, an axial ligand attached to the copper(II) porphyrin dissociate while returning to the ground state. In addition, Cu^{II}OEP is less acidic than Cu^{II}TPP, being reluctant to make five-coordinated species in the ground state.⁹ Thus, upon photoexcitation of an uncoordinated Cu^{II}OEP, a five-coordinated Cu^{II}OEP(THF)* is formed in the excited state, as revealed in the distinct Raman spectral features corresponding to the excited (π ,d) CT₂ state. With an increase in the time delay, the axial ligand attached to Cu^{II}OEP dissociates, representing the spectral features attributable to the CT₁ state. The extent of Raman frequency shifts for the (π ,d) CT₁ state of uncoordinated Cu^{II}OEP was believed to be smaller relative to the five-coordinated species, as shown by the core size correlation in five-coordinated copper(II) porphyrin–water.⁹

The charge transfer states (CT₁ and CT₂) involved in the photodynamics of Cu^{II}OEP are suggested to be formed by the electronic transition from the a_{1u}(π) HOMO of the porphyrin ring to the metal d_{x²-y²} orbital, because the electrochemical oxidation of Cu^{II}OEP produces an A_{1u}-type cation radical.¹⁶ Thus, the electronic nature of the (π ,d) CT states of Cu^{II}TPP and Cu^{II}OEP is different in the origin of the electronic transition, as observed in the generation of two types of cation radicals.

In order to further investigate the axial ligand interaction of Cu^{II}OEP, dioxane was introduced as a solvent. Dioxane is believed to be more strongly interacting with Cu^{II}OEP relative to THF. As expected, the TR³ spectra contributed by excited state Cu^{II}OEP in dioxane could not be obtained by the nanosecond pump/probe experiment with a time delay. Only a one-color nanosecond pulse experiment was successful in acquiring TR³ spectra, implying the lifetime of excited Cu^{II}OEP in dioxane is much shorter than that in THF (less than a few nanoseconds). Figure 7 shows the TR³ spectra of Cu^{II}OEP in dioxane recorded with a 416-nm nanosecond single pulse (first Stokes H₂ shift of 355 nm). The overall spectral feature of the difference Raman spectrum for Cu^{II}OEP in dioxane resembles that in THF at a short time delay, indicating that the same intermediate state is involved in the deactivation dynamics of photoexcited Cu^{II}OEP in THF and dioxane in different time scales.

The efforts have also been made to obtain the TR³ spectra of Cu^{II}OEP in pyridine. Under any condition in our nanosecond experiment, neither the decrease of the Raman intensities for the ground state Cu^{II}OEP nor the increase of the TR³ bands contributed by the excited state Cu^{II}OEP could be observed. These are consistent with the results of the earlier transient absorption and luminescence experiments of Cu^{II}OEP in strongly interacting basic solvents. Lifetime of the transient intermediate

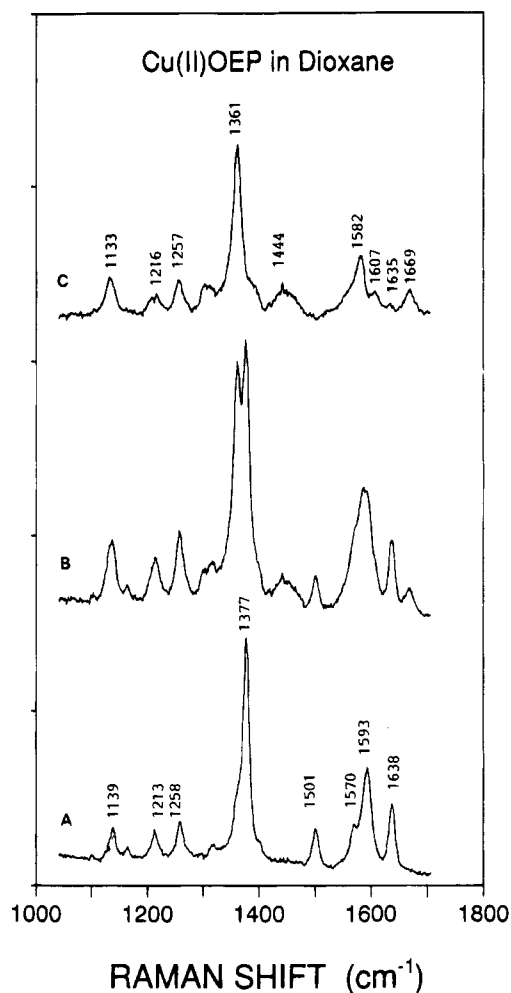


Figure 7. Nnanosecond TR³ spectra of Cu^{II}OEP in dioxane with both pump and probe pulses at 416 nm: (A) the low-power, (B) the high-power, and (C) the difference spectra (B - A) with a proper subtraction factor.

of Cu^{II}OEP in pyridine was reported to be in the range of 100 ps, which is too short to be detected with our nanosecond pulses.^{9,10}

In Cu^{II}OEP, the lifetime of the excited state is strongly dependent on the dielectric constants of the solvents. If the (d,d) state is predominantly responsible for the decay process of Cu^{II}OEP, this state would be less sensitive to the solvent polarities than the (π ,d) CT state, because the (d,d) state involves the electronic transition only in Cu metal. Thus, although we cannot totally eliminate the possibility of the participation of the (d,d) state in the decay process of Cu^{II}TPP and Cu^{II}OEP, the (π ,d) ring-to-metal charge transfer state associated with the solvent binding/release as an axial ligand is suggested to be the main decay channel in copper(II) porphyrins.

Core-Size Correlations of the Charge Transfer State. The frequencies of some in-plane vibrational modes of porphyrin macrocycles have been well-known to be correlated with the center to pyrrole nitrogen distance *d* or the core size of metalloporphyrins. This dependence has been described usually by the expression of $\nu = K(A - d)$, where *K* and *A* are parameters characteristic of the porphyrin macrocycles. It is often invoked that the parameter *K* should be indicative of the potential energy distribution (PED) and increases as the percentage of $\nu(\text{C}_\alpha\text{--C}_m)$ vibration contribution increases. Employing the reported values of parameter *K* for the ν_3 , ν_{10} , ν_2 , and ν_{11} modes (383, 415, 243, and 197 cm⁻¹/Å, respectively), the difference between the core sizes of the excited state and the

ground state $\text{Cu}^{\text{II}}\text{OEP}$, ($d_{\text{ex}} - d_{\text{gr}}$), can be derived as follows:

$$\nu_{\text{gr}} = K(A - d_{\text{gr}})$$

$$\nu_{\text{ex}} = K(A - d_{\text{ex}})$$

$$\Delta = K(d_{\text{gr}} - d_{\text{ex}})$$

for ν_3 , 0.07 Å; ν_{11} , 0.075 Å; ν_2 , 0.055 Å; and ν_{10} , 0.065 Å, respectively. It is noteworthy that these values are all comparable to those of the IEH calculation on copper(II) porphyrin with and without H_2O as an axial ligand, allowing for the expansion of the core size and the metal out-of-plane geometry. In that calculation, the lowest CT state in the ligating solvent is suggested to be the $^2[\text{a}_{2u}(\pi), \text{d}_{xz-y^2}]$ state, and the Cu atom moves 0.5 Å out of the porphyrin macrocycle plane. From this geometry, the center to ring distance can be derived to be 2.05 Å, which is larger than that of the ground state copper(II) porphyrin by 0.07 Å. Thus, the observed values were in good agreement with the theoretical values, suggesting that the lowest quenching state involved in $\text{Cu}^{\text{II}}\text{OEP}$ in ligating solvents is the (π, d) CT_2 state.

The ν_4 mode indicates the extent of the electron delocalization of the metal to porphyrin ring.²³ The observed large decrease ($\sim 15 \text{ cm}^{-1}$) in frequency in the excited state could be interpreted as the charge transfer among the ligand (in this case THF), metal (Cu), and porphyrin ring. As stated above, the theoretical results on the ligated copper(II) porphyrin–water suggested that $^2[\text{a}_{2u}(\pi), \text{d}_{xz-y^2}]$ should be a candidate for the low-lying charge transfer state. It was also proposed that the axial ligation raises the energy level of the filled d_{z^2} orbital to the level of the frontier orbital as a result of mixing with the ligand p_z orbital, and then increase the charge density on the porphyrin ring through $[\text{d}_{z^2}, \text{e}_g(\pi^*)]$ charge transfer. If the dynamics of the excited state copper(II) porphyrins proceed through the former state, the resulting state resembles a cation radical, and *via* the latter, in contrast, the anion radical. At present, it is known that ν_4 of the $\text{Cu}^{\text{II}}\text{OEP}^+$ cation radical is 15 cm^{-1} lower than that of a neutral form.¹⁶ Since it is difficult to generate the anionic copper(II) porphyrin, the frequency shift for the anion radical is only conjectured to be small because a 7 cm^{-1} lowering of ν_4 was observed for the $\text{Zn}^{\text{II}}\text{OEP}^-$ anion radical. This also suggests that the (π, d) charge transfer state is the lowest electronic state involved in the excited state decay dynamics of $\text{Cu}^{\text{II}}\text{OEP}$ in THF.

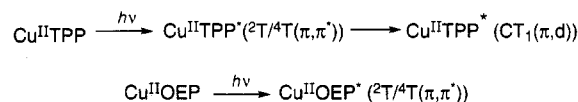
For CT_2 of $\text{Cu}^{\text{II}}\text{TPP}$, the core size difference ($d_{\text{ex}} - d_{\text{gr}}$) was calculated to be 0.065 Å *via* the same procedure as that for $\text{Cu}^{\text{II}}\text{OEP}$ using $K = 312.5$ and the downshift of ν_2 .^{20b} However, with the reported value of $K = 138.9$ for the shift for ν_4 ,^{20b} a much larger core size difference (0.15 Å) was derived. This discrepancy can be explained by the fact that the variation of ν_4 depends on the extent of the electron delocalization between the metal atom and the porphyrin ring as well as the core size difference. Until now, it has been known that ν_4 of $\text{Cu}^{\text{II}}\text{TPP}^+$ is 10 cm^{-1} lower than that of a neutral species,¹⁶ and for $\text{Zn}(\text{II})\text{TPP}^-$ 4 cm^{-1} lower¹⁹, or 1 cm^{-1} lower.¹⁷ For CT_1 , the core size difference as well as the delocalization of d_{π} electrons should be negligible compared with the CT_2 of $\text{Cu}^{\text{II}}\text{TPP}$. By the same analogy applied to $\text{Cu}^{\text{II}}\text{OEP}$ in THF, CT_2 corresponded to the five-coordinated excited $\text{Cu}^{\text{II}}\text{TPP}(\text{THF})^*$ (π, d) charge transfer state and CT_1 to the deligated excited $\text{Cu}^{\text{II}}\text{TPP}^*$ (π, d) charge transfer state, respectively. The difference in the decay dynamics between $\text{Cu}^{\text{II}}\text{OEP}$ and $\text{Cu}^{\text{II}}\text{TPP}$ in THF was that both CT_1 and CT_2 states were simultaneously observed at a short time delay only for $\text{Cu}^{\text{II}}\text{TPP}$, because $\text{Cu}^{\text{II}}\text{TPP}$ has the intrinsically faster decay process than $\text{Cu}^{\text{II}}\text{OEP}$.⁹ From the frequency

shift of the ν_2 mode of $\text{Cu}^{\text{II}}\text{TPP}$ in pyridine, the extents of the core size differences ($d_{\text{ex}} - d_{\text{gr}}$) were determined to be 0.02 and 0.09 Å for CT_1 and CT_2 , respectively. These values were slightly larger than those of $\text{Cu}^{\text{II}}\text{TPP}$ in THF. The strength of the solvent basicity was possibly responsible for the extent of the core size expansion.

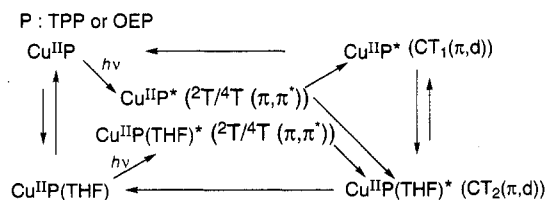
Conclusions

TR³ spectra on copper(II) porphyrins in several solvents gave us some profound structural and electronical information on their excited states. With the addition of a nucleophilic solvent to the central metal, the energy of the charge transfer state, the core size of the porphyrin ring, and the position of the central Cu were perturbed significantly. Furthermore, this investigation revealed that at least two types of charge transfer states participated in the decay process of photoexcited copper(II) porphyrin in ligating solvents; moreover, conclusive evidence on the electronic structure responsible for each charge transfer state is provided. From the extent of Raman frequency shifts and the time scale of the formation of these charge transfer states, the nature of these states was proposed, one being less affected by the ligating solvent (CT_1 ; (copper(II) porphyrin)*), and the other strongly influenced by the axial ligand σ -donor (CT_2 ; (copper(II) porphyrin–ligand)*). In the case of $\text{Cu}^{\text{II}}\text{OEP}$, the former could not be generated directly without any help from the σ -donor; however, in $\text{Cu}^{\text{II}}\text{TPP}$, CT_1 was readily populated because it has lower energy than the $^2\text{T}/^4\text{T}(\pi, \pi^*)$ manifold. These observations can be summarized in the following mechanisms:

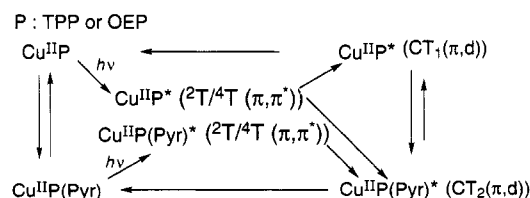
in noncoordinating solvents



in weakly coordinating solvents (THF, dioxane)



in strongly coordinating solvents (pyridine)



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