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The lowest excited states of copper porphyrins[a)]

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Relaxation processes of excited copper porphyrins were studied with relevance to the structure of the substates of the lowest excited states. Lifetimes of luminescence at room temperature were determined as 17, 29, 69, and 105 ns for T(EtO)PPCu [T(EtO) PP: 5, 10, 15, 20-tetra (*p*-ethoxyphenyl)porphin], TPPCu(TPP: 5, 10, 15, 20-tetraphenylporphin), TFPPCu[TFPP: 5, 10, 15, 20-tetra(pentafluorophenyl)porphin], and OEPCu(OEP: 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphin) in toluene, respectively. Emission intensities and lifetimes of OEPCu and TFPPCu measured as a function of temperature show a variation ascribed to a Boltzmann distribution between the lowest trip–doublet and –quartet with an energy gap of 300–400 cm^{-1}. The anomalous temperature dependence for TPPCu and T(EtO)PPCu is explained by a larger energy gap and larger vibronic distortions in the excited state. The difference in behavior is attributed to the orbital nature of the triplet: $|^{2,4}[b^3{}_1(a_1e)]\rangle$ for OEPCu and TFPPCu but $|^{2,4}[b^3{}_1(a_2e)]\rangle$ for TPPCu and T(EtO)PPCu. The assumption of a low energy charge transfer state is not necessary for our analysis.

I. INTRODUCTION

Copper porphyrin exhibits a phosphorescence even at room temperature. Fluorescence is quenched for a prompt intersystem crossing to the lowest excited triplet stated by the interactions of an unpaired electron in the highest copper d_σ orbital and the $^{1,3}(\pi,\pi^*)$ excited configurations. Gouterman and his colleagues proposed that the interaction makes all singlets become doublets and triplets split into doublets (trip–doublet) and quartets (trip–quartet).[1–4]

An energy gap between the lowest trip–quartet and trip–doublet was estimated by the shift of emission maxima at around 80 and 23 K: 500 cm^{-1}, PCu (P: porphin); 150–300 cm^{-1}, OEPCu (OEP: 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphin).[2] Magnetically induced circular emission supported the trip–doublet and –quartet model and found a 100 cm^{-1} energy gap in OEPCu.[5] High-resolution emission spectra measured with PCu doped in a single crystal of *n*-octane at 77 and 4.2 K detected a gap of 320 cm^{-1} between the trip–quartet and trip–doublet.[6] The gap was also determined to be 267 cm^{-1} by the temperature dependence of phosphorescence of PCu in triphenylene and in anthracene.[7,8] Intensive studies including high-resolution analyses based on Zeeman experiments have been achieved on the lowest trip–quartet states of PCu.[9–13]

The relaxation processes of excited copper porphyrins and their d^9 and d^1 analogs have been studied at room temperature by use of picosecond flash photolysis technique.[14–18] Copper protoporphyrinIX dimethylester in the lowest excited sing–doublet ($^2S_1$) state relaxes into the lowest trip–doublet ($^2T_1$) state within 8 ps and then to a thermal equilibrium between the $^2T_1$ and the lowest trip–quartet ($^4T_1$) state with a time constant of 450–460 ps.[14] Phosphorescence of copper protoporphyrin observed at room temperature was ascribed to the emission from the $^2T_1$ component of the thermal equilibrium state, whose lifetime was estimated as longer than 1 ns.

Gadolinium porphyrin, which has seven unpaired electrons in the metal 4*f* orbitals, emits an intense phosphorescence whose lifetime is in the order of 10^1 μs at room temperature.[19] It should be noted the lifetimes of copper porphyrins which have only an unpaired electron in the metal $3d_\sigma$ orbital are around 10–100 ns at 300 K which were measured in the present work. In copper porphyrins, an admixing of the excited sing–doublets into the trip–doublets by exchange interactions between the metal unpaired electron and porphyrin π electrons grants transition intensities to the trip–doublet excited states.

Picosecond transient absorption and bleaching of copper porphyrins have been measured, however, the measurements can actually yield no information on the processes within the excited-state lifetime following the picosecond relaxation. In the present work, we directly observed emission and its decay to manifest the properties of the lowest trip–doublet states. The emission decay rate at ambient temperature depends on the energy gap between $^2T_1$ and $^4T_1$ states and also the relaxation rates from $^2T_1$ and $^4T_1$ to the ground state. Temperature dependence of the emission reveals not only the variation of the distribution between $^2T_1$ and $^4T_1$ states but also a variation of the relaxation processes of excited copper porphyrins to the ground state.

With decreasing temperature between 300–77 K, the emission spectrum of OEPCu increases prominence both in toluene and in poly(methylmethacrylate) film but shows only a small blue shift. In the case of TPPCu(TPP: 5, 10, 15, 20-tetraphenylporphin), however, the emission from polymer film is rather invariant with temperature, while a bell shaped emission is observed in toluene solution at room temperature and the maximum of the emission band is shifted to the red when temperature is decreased down to 200 K.

In this paper, we discuss photophysics of copper porphyrins in liquid media at ambient temperature and give a view of the structure of the trip–doublet and trip–quartet substates, on the basis of measurements of decay lifetimes

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[a)] A part of this paper was presented at the International Conference on Excited States and Dynamics of Porphyrins, Little Rock, AR, Nov. 17–19, 1985.

and emission intensities in a temperature region not so as to freeze the medium as well as analyses of absorption spectra of four kinds of copper porphyrin in liquid toluene solution.

II. EXPERIMENTAL

A. Materials

$TPPH_2$ was prepared and purified by the methods described elsewhere.[20] A chlorin contamination in $TPPH_2$ was oxidized by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.[21] $OEPH_2$ was prepared by the method in literature[22] and purified by chromatography on wet-packed silica gel (Wakogel C-200) with chloroform as eluent and recrystallization. $T(EtO)PPH_2$ [T(EtO)PP: 5, 10, 15, 20-tetra(*p*-ethoxyphenyl)porphin] was synthesized from pyrrole and *p*-ethoxybenzaldehyde[23] and purified by the similar method as $TPPH_2$. $TFPPH_2$[TFPP: 5, 10, 15, 20-tetra(pentafluorophenyl)porphin] was prepared according to Longo *et al.* from pyrrole and pentafluorobenzaldehyde.[24] Chlorin impurity was removed by the literature method.[25] Further purification of $TFPPH_2$ was carried out by recrystallization from CH_2Cl_2/hexane.

Copper(II) complexes were obtained by refluxing the corresponding free-base porphyrins in dimethylformamide (DMF) to which an excess of copper (II) acetate was added.[26] The products after dried were purified by chromatography on dry-packed columns of alumina [Merck alumina 90 (II-III)] and then of silica gel (Wakogel C-200) with CH_2Cl_2 or $CHCl_3$ as eluent and by recrystallization from CH_2Cl_2/ethanol or $CHCl_3$/ethanol mixtures.

Zinc(II) and nickel(II) porphyrins were prepared and purified by the similar methods as described with copper(II) porphyrins. Zinc and nickel complexes were recrystallized from CH_2Cl_2/hexane and toluene/ethanol, respectively.

Emission and excitation spectra of the copper(II) complexes prepared in this work indicated no contamination of zinc(II) and free-base porphyrins. Also no emission due to the emissive impurities was detected with nonemissive nickel porphyrins.

B. Measurements

Absorption spectra and their second-derivative spectra were recorded on a Hitachi 330 spectrophotometer. Emission and excitation spectra were taken on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu Photonics R928 photomultiplier.

Emission decay lifetimes shorter than 1200 ns, were measured by the single-photon-counting method on a PRA nanosecond fluorometer system with excitation by a nitrogen-gas discharge lamp. Time range was calibrated by an Ortec model 462 time calibrator. Emissions with lifetimes longer than 600 ns were measured through a Nikon P-250 monochromator by a R928 photomultiplier upon excitation by an NRG-0.5-5-150/B nitrogen laser. The emission signals were A/D converted on a Kawasaki Electronica transient memory model M-50E and accumulated on an NEC computer model PC9801F2. The lifetimes were determined by fitting the decay curves exponentially using an iterative least-squares method. Both methods were applied when the lifetime is between 600 and 1200 ns and confirmed to yield a coincident value of the lifetime.

Measurements at 200–300 K were carried out with the samples whose temperature was controlled by an Oxford cryostat model DN704.

Spectra and decay lifetimes of emission were measured with liquid toluene solutions. Toluene used for solvents was shaken with sulfuric acid, neutralized with dilute aqueous $NaHCO_3$ solution and then washed with water. After drying on $CaCl_2$, it was distilled on CaH_2. Toluene solutions of porphyrins were sealed in rectangular cuvettes or Pyrex tubes after degassing by freeze–pump–thaw cycles.

Measurements were also carried out with transparent poly(methylmethacrylate) (PMMA) films dispersing porphyrin in a variety of temperature. The PMMA (degree of polymerization: 7000–7500) was commercially available and purified three times by reprecipitation from CH_2Cl_2/methanol. The transparent films were obtained by spontaneous evaporation of a homogeneous viscous solution of PMMA and porphyrin in CH_2Cl_2 on a clean glass plate being covered with a Petri dish.

Transition intensities of an absorption band was determined by deconvolution of the spectral profile according to the following equation:

$$\epsilon(\tilde{\nu}) = \frac{4\pi^2 N_A}{3c\hbar 10^3 \ln 10} \sum_j g_{ja}\tilde{\nu}_{ja} f(\tilde{\nu},\tilde{\nu}_{ja})$$

$$= 7.0329\times 10^2 \sum_j g_{ja}\tilde{\nu}_{ja} D_{ja} f(\tilde{\nu},\tilde{\nu}_{ja}), \qquad (1)$$

where $\epsilon(\tilde{\nu})$ is observed molar extinction coefficient in $mol^{-1}\,dm^3\,cm^{-1}$, $\tilde{\nu}_{ja}$ is the wave number in absorption maximum of the transition $|j\rangle \leftarrow |a\rangle$, D_{ja} is dipole strength in $(a.u.)^2$, g_{ja} is the orbitary degeneracy of the transition, and $f(\tilde{\nu},\tilde{\nu}_{ja})$ is a normalized band-shape function with maximum at $\tilde{\nu}_{ja}$. In this work we defined $g_{ja} = 2$ for *B*, *Q* and *S–T* absorption bands. The band simulation was carried out by use of least-squares method.

III. RESULTS AND DISCUSSION

A. Spectra and lifetimes of the trip–doublet emission of copper(II) porphyrins

Figure 1 shows emission spectra of OEPCu, TFPPCu, TPPCu, and T(EtO)PPCu in toluene at ambient temperature. OEPCu and TFPPCu exhibit sharp band emission, while TPPCu and T(EtO) PPCu show rather diffuse band emission. The emission from toluene solution decays in a single exponential. The lifetimes were determined at 300 K with four copper porphyrins [OEPCu, 105 ns; TFPPCu, 69 ns; TPPCu, 29ns; T(EtO)PPCu, 17 ns]. The decays are much faster than those of phosphorescence of diamagnetic metalloporphyrins. It is noted that the lifetimes of the diffuse band emission of TPPCu and T(EtO)PPCu are rather short in contrast with those of the sharp band emission of OEPCu and TFPPCu.

Figure 2 shows absorption spectra of copper porphyrins in toluene. These copper porphyrins show absorption spectra which are very similar to those observed with the corresponding diamagnetic metalloporphyrins. All the metallo-

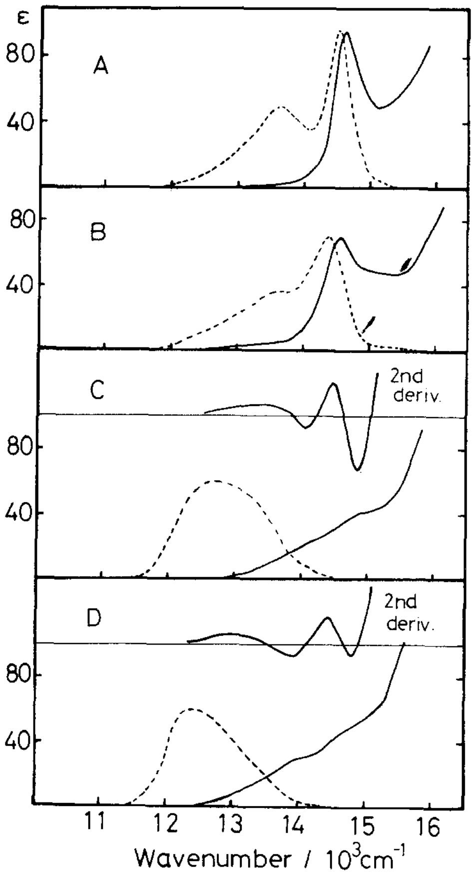

FIG. 1. Emission (---) and S–T absorption (—) spectra of OEPCu (A), TFPPCu (B), TPPCu (C), and T(EtO)PPCu (D) in toluene solution at room temperature. Lifetimes of emission at 300 K are determined as 105 ns (A), 69 ns (B), 29 ns (C), and 17 ns (D), respectively. The second derivative spectra of S–T bands are at the top of the corresponding absorption spectra in (C) and (D).

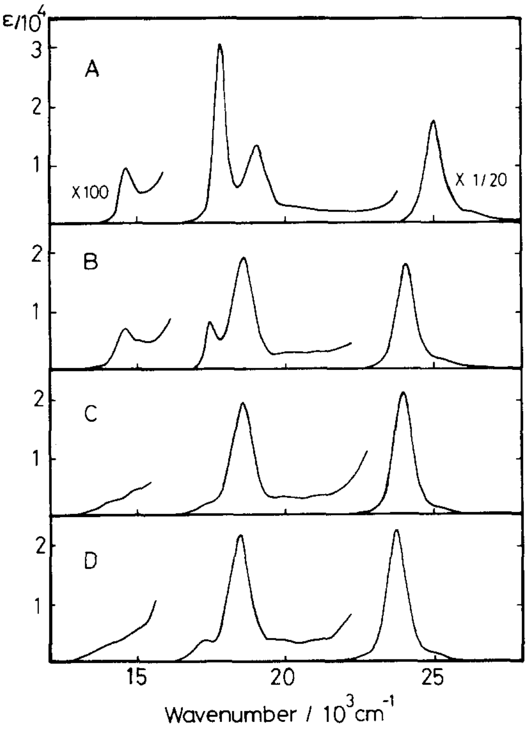

FIG. 2. Absorption spectra of OEPCu (A), TFPPCu (B), TPPCu (C), and T(EtO)PPCu (D) in toluene at room temperature.

porphyrins exhibit characteristic Q and B bands, which are ascribed to the (π, π^*) transitions of porphyrin macrocycles, in the visible and near-ultraviolet region, respectively. However copper porphyrins do exhibit a weak additional absorption band [OD(optical density) is about 0.1 for an almost saturated solution of 10^{-3} M] to the red of the characteristic Q band. The weak band is assigned to the S–T (*s*ing–doublet-to-*t*rip–doublet) transition enhanced its intensity by the interaction of an unpaired copper d_σ electron with porphyrin π electron system.[1] The sharp emission bands of OEPCu and TFPPCu are in the mirror image of corresponding S–T absorption bands as shown in Fig. 1. The absorption Q and B bands of TFPPCu are observed not so much different from those of TPPCu, while the emission and S–T absorption bands are similar to those of OEPCu. Figure 1 also shows the second-derivative absorption spectra of TPPCu and T(EtO)PPCu. The second-derivative spectra can detect the S–T (0,0) and (1,0) bands as minima in the less-resolved absorption shoulder. The S–T absorption bands correspond to the diffuse emission bands. The observed emission of copper porphyrins at room temperature can be assigned to trip–doublet emission. The emission band of TPPCu and T(EtO)PPCu shows a large Stokes shift from the S–T absorption band while the emission of OEPCu and TFPPCu exhibits only a small shift.

With decreasing temperature, the trip–doublet emission of OEPCu and TFPPCu in liquid media increases intensity almost maintaining its spectral profile. Figure 3 presents the temperature variation of emission spectra, relative intensities, and decay lifetimes of OEPCu and TFPPCu in toluene. The decay lifetime of the trip–doublet emission increases with decreasing temperature (OEPCu, 105 and 1200 ns; TFPPCu, 69 and 1250 ns at 300 and 200 K, respectively).

Copper(II) porphyrin in the lowest excited sing–doublet ($^2S_1$) state rapidly relaxes into the lowest trip–doublet ($^2T_1$) state[14,15] and then to the lowest trip–quartet ($^4T_1$)

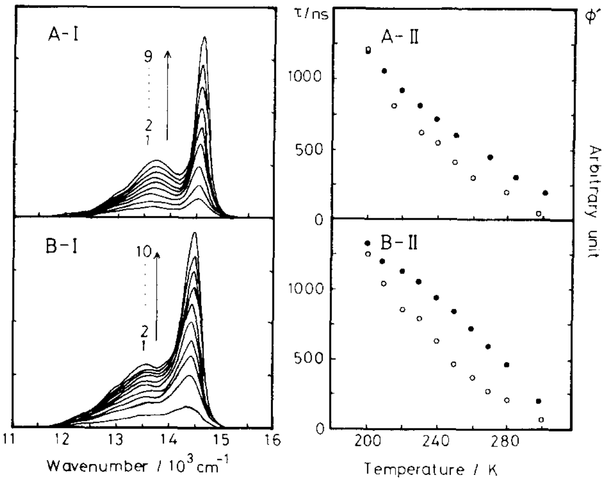

FIG. 3. Emission spectra of OPECu (A-I) and TFPPCu (B-I) as a function of temperature in toluene solution [OPECu: 300 K (1); 285 K (2); 270 K (3); 250 K (4); 240 K (5); 230 K (6); 220 K (7); 210 K (8); 200 K (9), TFPPCu: 300 K (1); 280 K (2); 270 K (3); 260 K (4); 250 K (5); 240 K (6); 230 K (7); 220 K (8); 210 K (9); 200 K (10)]. Plots of emission relative intensities (○) and decay lifetimes (●) of OEPCu (A-II) and TFPPCu (B-II) against temperature.

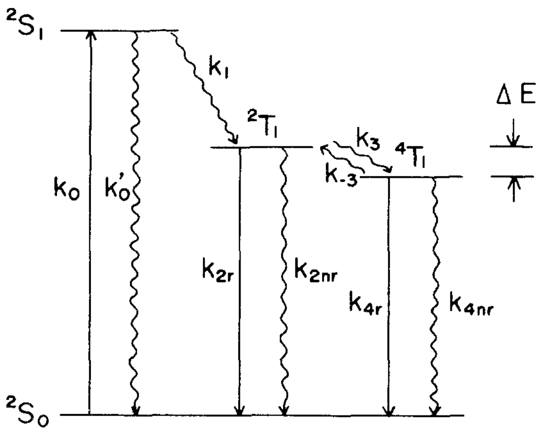

FIG. 4. A schematic diagram of relaxation processes of copper porphyrins.

state, from which copper porphyrin is thermally repopulated to the emitting $^2T_1$ state. Figure 4 is a schematic diagram of relaxation processes of copper porphyrins.

The yield of emission from the trip–doublet is given by

$$\phi_2 = k_{2r}\cdot\phi_{\rm ISC}\,\frac{K + k_4/k_3}{k_2K + k_4(k_2/k_3 + 1)} \tag{2}$$

in terms of the radiative rate constant of the $^2T_1$ state, k_{2r}; the equilibrium constant between $^2T_1$ and $^4T_1$ states, $K = (1/2)\exp(-\Delta E/kT) = k_{-3}/k_3$; the efficiency of intersystem crossing, $\phi_{\rm ISC} = k_1/(k_0' + k_1)$. Here k_0' is the deactivation rate from $^2S_1$ state directly to the ground state, k_1 is the rate of intersystem crossing ($^2S_1 \rightsquigarrow T_1$), k_2 and k_4 are the sums of the radiative (k_{2r}, k_{4r}) and nonradiative rates (k_{2nr}, k_{4nr}) of $^2T_1$ and $^4T_1$ states, respectively, and k_3 and k_{-3} are the deactivation and activation rates between $^2T_1$ and $^4T_1$ states with an energy gap of ΔE. The rate constants of the respective processes are given in Fig. 4. Provided that $k_3 \gg k_2$ and $k_{-3} \gg k_4$, it follows that $1 + k_2/k_3 \approx 1$ and $K + k_4/k_3 = K(1 + k_4/k_{-3}) \approx K$. Thus Eq. (2) is rewritten as

$$\phi_2 = k_{2r}\cdot\phi_{\rm ISC}K/(k_2K + k_4). \tag{3}$$

On the other hand, the emission decays with a rate being proportional to the concentration of emissive trip–doublet $[^2T_1]$:

$$[^2T_1] = C_1e^{-\alpha t} + C_2e^{-\beta t}$$
$$\binom{\alpha}{\beta} = \tfrac{1}{2}\{k_2 + k_3 + k_4 + k_{-3} \pm \sqrt{\{(k_2 + k_3) - (k_4 + k_{-3})\}^2 + 4k_3k_{-3}}\}, \tag{4}$$

where α and β are the fast and slow components of decay rate of the trip–doublet state, respectively. The fast component α corresponds to the prompt relaxation rate from $^2T_1$ to $^4T_1$ states just after pulse excitation. The slow component β is the decay rate observed in our experiments.

Provided that the thermal equilibrium between $^2T_1$ and $^4T_1$ states is accomplished very fast after the pulse excitation during the lifetime of excited state, $k_3, k_{-3} \gg k_2, k_4$ is obtained. Then the decay rate of emission is given by

$$\frac{1}{\tau} = \beta = \frac{k_2K + k_4}{1 + K}. \tag{5}$$

From Eqs. (3) and (5), it follows that

$$\tau/\phi_2 = \frac{1}{k_{2r}\cdot\phi_{\rm ISC}}\,\frac{1 + K}{K}. \tag{6}$$

Since k_{2r} and $\phi_{\rm ISC}$ are less dependent of temperature, the temperature variation of the ratio τ/ϕ_2 is ascribed only to the equilibrium constant K as a function of temperature. The observed ratios of lifetime and relative yield (ϕ') are correlated with K as follows:

$$\tau/\phi' = C(1 + K)/K. \tag{7}$$

The temperature dependence of k_2 and k_4 in Eqs. (2) and (4) can be eliminated by taking the ratio τ/ϕ'. Figure 5 shows the plots of τ/ϕ' [$= C(1 + K)/K$] against temperature. By use of a least-squares method, an energy gap between $^2T_1$ and $^4T_1$ states (ΔE) was evaluated (OEPCu, 310 cm^{-1}; TFPPCu, 390 cm^{-1}). The corresponding values 330 and 350 cm^{-1} can be also obtained from the spectroscopic parameters described later.

Figure 6 presents the temperature variation of emission spectra and decay lifetimes of TPPCu and T(EtO)PPCu in liquid toluene from 300 K down to 200 K. TPPCu shows a bell-shaped emission band at room temperature, however, the band maximum shifts to the red with reducing temperature. The lifetime, on the other hand, increases with decreasing temperature down to 250 K while it decreases upon further cooling (300 K, 29 ns; 250 K, 39 ns; 200 K, 27 ns). The emission of T(EtO)PPCu also shows a red shift at low temperature, while the lifetime simply decreases with decreasing temperature (300 K, 17 ns; 200 K, 13.5 ns). In these two copper porphyrins, however, lifetimes and emission intensities in toluene are rather invariant with temperature in contrast with those of OEPCu and TFPPCu.

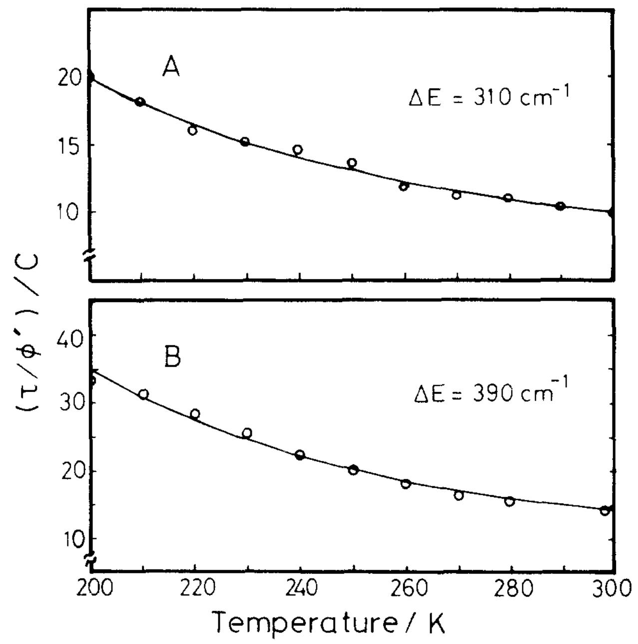

FIG. 5. Plots of $(\tau/\phi')/C$ [$= (1 + K)/K$] against temperature in OEPCu (A) and TFPPCu (B). Parameters C and ΔE were evaluated by use of a least squares method according to the relationship $K = (1/2)\exp(-\Delta E/kT)$. Solid lines are the best fit curves.

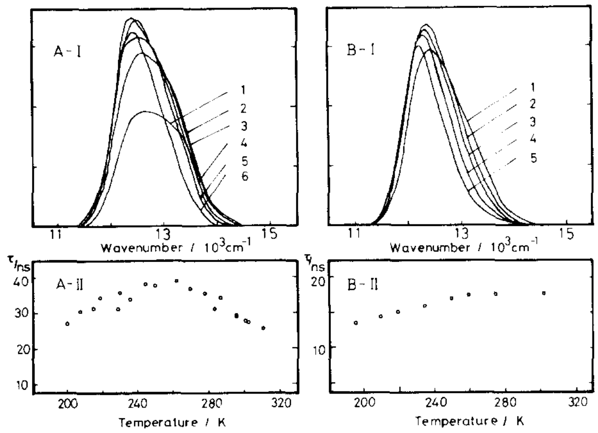

FIG. 6. Emission spectra of TPPCu (A-I) and T(EtO)PPCu (B-I) as a function of temperature in liquid toluene [TPPCu: 300 K (1); 280 K (2); 260 K (3); 240 K (4); 220 K (5); 200 K (6), T(EtO)PPCu: 300 K (1); 280 K (2); 260 K (3); 230 K (4); 200 K (5)]. Plots of emission decay lifetimes of TPPCu (A-II) and T(EtO)PPCu (B-II) against temperature.

Figure 7 shows emission spectra of copper porphyrins in poly(methylmethacrylate) (PMMA) films as well as in toluene at 300, 195, and 77 K. The emission spectra of OEPCu and TFPPCu in PMMA films well correspond to those in toluene. On the other hand, the emission profiles of TPPCu and T(EtO)PPCu in PMMA films are different from those of toluene liquid solution at 300 and 195 K. In rigid media such as PMMA films, the emission profiles are invariant with temperature. It should be noted that the emission spectra of TPPCu and T(EtO)PPCu in toluene at 77 K, where the medium forms rigid glass, are coincident with those in PMMA films.

All the emission from toluene solution decays single exponentially. However, the emission of TPPCu and T(EtO)PPCu in PMMA and toluene rigid glass decays multiexponentially in the temperature region used in the present work as has been pointed out in the literature.[2,3]

The *S–T* absorption as well as the phosphorescence emission shows an intense (0,0) component band in OEPCu and TFPPCu. As Fig. 1 shows, only a small Stokes shift is observed between the emission and the *S–T* absorption bands in OEPCu and TFPPCu and the sharp emission of these porphyrins is in the mirror image of the *S–T* absorption band.

A large Stokes shift observed between the diffuse emission and the *S–T* absorption bands of TPPCu and T(EtO)PPCu is primarily attributable to a greater gap between the corresponding vibronic component bands which are intense in TPPCu and T(EtO)PPCu in contrast with a small gap between the (0,0) component bands intensified in OEPCu and TFPPCu. This indicates a shift of potential energy surfaces between the excited and ground states in TPPCu and T(EtO)PPCu is greater than in OEPCu and TFPPCu.

Emission profiles of TPPCu and T(EtO)PPCu in toluene solution vary with temperature and the maximum of emission band shifts to the red with reducing temperature. The red shift of emission maximum is attributable to a shift of energy surface in the excited state.

The lowest excited trip–doublet and trip–quartet configurations of OEPCu and TFPPCu are mainly of $|^{2,4}[b_1{}^3(a_1e)]\rangle$, while those of TPPCu and T(EtO)PPCu are of $|^{2,4}[b_1{}^3(a_2e)]\rangle$. As revealed by a Stokes shift between the corresponding emission and absorption vibronic bands observed with TPPCu and T(EtO)PPCu, the configurations $|^{2,4}[b_1{}^3(a_2e)]\rangle$ must be susceptible of molecular distortions. The emission profiles of TPPCu as well as T(EtO)PPCu varied with temperature is attributable to a molecular distortion of the excited species released in liquid solution. An inspection of the calculated bond orders of the excited configurations of porphyrin macrocycle suggests that the configurations $^{1,3}(a_2e)$ are more tetragonally distorted than $^{1,3}(a_1e)$.[27]

In liquid media, the extent of the distortions of TPPCu and T(EtO)PPCu induced in the lowest excited state increases at lower temperature. However, since temperature-dependent thermal activation of the low-frequency large amplitude intramolecular vibrational and/or solvent librational modes plays a more important role in this particular case, the temperature variation of emission spectra and decay rates can not be attributed to the similar mechanism as described with OEPCu and TFPPCu. It should be noted that the emission decays of TPPCu and T(EtO)PPCu are rather invariant with temperature regardless of their variations of emission profile. With decreasing temperature of liquid media, however, the low-wave number(red) component band of the bell-shaped emission band increases the intensity relatively to the blue component band. In liquid

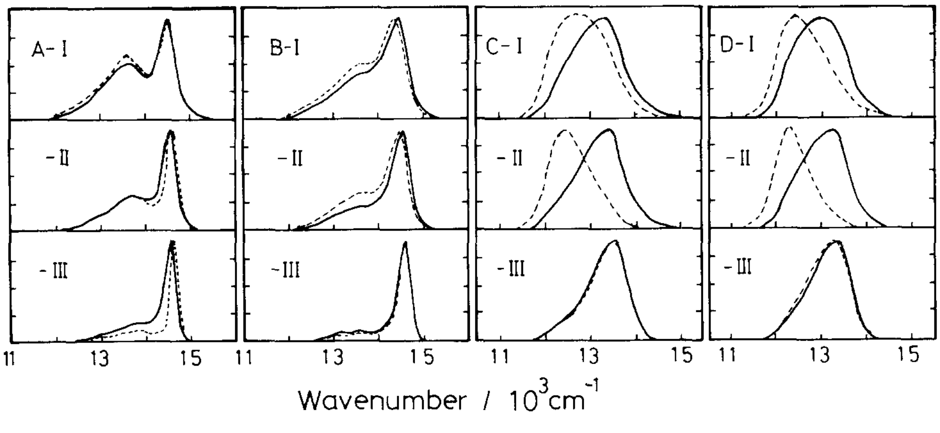

FIG. 7. Emission spectra of OEPCu (A), TFPPCu (B), TPPCu (C), and T(EtO)PP-Cu(D) in poly(methylmethacrylate) (PMMA) films (—) and in toluene (---) at 300 K (-I), 195 K (-II), 77 K (-III).

media, the decay is of a single exponential and a coincident value of the lifetime is obtained regardless whether it is measured in the red part or in the blue part of the bell-shaped emission band.

B. Structure of the trip–doublet and trip–quartet excited states in copper porphyrins

Absorption and emission spectra of the diamagnetic metalloporphyrins are determined essentially by the π electron system of porphyrin ring with only minor perturbation from the outer-shell electrons of the central metal ion. The Q band in the visible region is of forbidden character, however, it can be granted transition intensity mainly by vibronic coupling with the exclusively allowed B band in the near-ultraviolet region. The intensity of $Q(1,0)$ band is much less sensitive to the peripheral substituents, the axial ligands and the central metal ion, while that of $Q(0,0)$ band without excitation in the skeletal vibrational modes is sensitive to the substituents. The lowest (π,π^*) excited singlet configurations $^1(a_{1u}e_g)$ and $^1(a_{2u}e_g)$ are in accidental degeneracy. The forbidden character of the Q band is attributable to an equal but minus combination of these two excited configurations with almost equal transition moments.[28] When the substituents remove the accidental degeneracy, $Q(0,0)$ band is granted its intensity from B band. Thus the intensity ratio of $Q(0,0)$ band and B band, $D[Q(0,0)]/D(B)$, is given by [20,28]

$$D\,[Q(0,0)]/D(B) = \tan^2\theta, \tag{8}$$

$$2\theta = \tan^{-1}(\epsilon/K_1 - K_9), \tag{9}$$

where ϵ is a deviation from the accidental degeneracy given by

$$\epsilon = \{E\,[\,^1(a_{2u}e_g)] - E\,[\,^1(a_{1u}e_g)]\}/2 \tag{10}$$

and $K_1 - K_9$ is a half of the difference of diagonal energies of the B and Q states:

$$K_1 - K_9 = \{(\Delta + 2K_1) - (\Delta + 2K_9)\}/2. \tag{11}$$

Suppose a porphyrin with zero $Q(0,0)$ band, the Q and B states are at $\Delta + 2K_9$ and $\Delta + 2K_1$, respectively. The lowest excited triplet states of diamagnetic metalloporphyrins are ascribed to a single excited triplet configuration $^3(a_{1u}e_g)$ at $\Delta + \epsilon'$ or $^3(a_{2u}e_g)$ at $\Delta - \epsilon'$, where the configuration interaction vanishes for reason of symmetry. A screened-potential molecular orbital calculation predicts that ϵ' is slightly greater or almost equal to ϵ[27], since it depends mainly on a difference in the orbital energies but not on a difference in the two-electron terms,

$$\begin{aligned}\begin{pmatrix}\epsilon\\ \hline \epsilon'\end{pmatrix} &= \frac{1}{2}\{\epsilon(a_{1u}) - \epsilon(a_{2u})\}\\ &\quad + \frac{1}{2}\{(a_{1u}a_{1u}|e_ge_g) - (a_{2u}a_{2u}|e_ge_g)\}\\ &\quad \pm \binom{1}{0}\{(a_{2u}e_g|e_ga_{2u}) - (a_{1u}e_g|e_ga_{1u})\}.\end{aligned} \tag{12}$$

The values, ϵ and also ϵ', vary from positive to negative depending upon the molecular environment such as induced by peripheral substituents.

The ratios $D[Q(0,0)]/D[Q(1,0)]$ of TPPZn and T(EtO)PPZn in benzene increase in the presence of pyridine, while those of TFPPZn and OEPZn decrease. The a_{2u} orbital has a large population on the nitrogens, while the a_{1u} orbital lacks the population. A charge donation by the axial coordination of pyridine to the central metal ion stabilizes

TABLE I. Energy matrices of zinc(diamagnetic) and copper porphyrins.

Diamagnetic metalloporphyrins			
The excited singlet states[a]		The excited triplet states	
Q_x	B_x	$^3(a_1e_y)$	$^3(a_2e_x)$
$\Delta + 2K_q$	ϵ $\Delta + 2k_1$	$\Delta-\epsilon$	0 $\Delta + \epsilon$
Copper porphyrins			
The excited doublet states[b]			
$\vert^2[b_1{}^3(a_1e_y)]\rangle$	$\vert^2[b_1{}^3(a_2e_x)]\rangle$	$\vert^2Q_x\rangle$	$\vert^2B_x\rangle$
$\Delta - \epsilon + \gamma$	0 $\Delta + \epsilon + (6\delta + \gamma)$	$\sqrt{6}\gamma/2$ $\sqrt{6}(2\delta - \gamma)/2$ $\Delta + 2K_q + (\delta - \gamma)$	$-\sqrt{6}\gamma/2$ $\sqrt{6}(2\delta - \gamma)/2$ $\epsilon + \delta$ $\Delta + 2K_1 + (\delta - \gamma)$
The excited quartet states[b]			
$\vert^4[b_1{}^3(a_1e_y)]\rangle$	$\vert^4[b_1{}^3(a_2e_x)]\rangle$		
$\Delta - \epsilon - 2\gamma$	0 $\Delta + \epsilon - 2\gamma$		

[a] $\epsilon = \tan 2\theta$, $\tan^{2}\theta = D_Q/D_B$, where D_Q/D_B is the ratio of dipole strength $Q(0,0)$ and B bands.
[b] $\delta = (b_1a_2|a_2b_1)/4$, $\gamma = (b_1e|eb_1)/2$, and $(b_1a_1|a_1b_1) = 0$

the configuration $^1(a_{2u}e_g)$. The stabilization of $^1(a_{2u}e_g)$ yields an intensity variation attributable to an increase $|\epsilon|^2$ in TPPZn and T(EtO)PPZn but a decrease in TFPPZn and OEPZn: This indicates that ϵ in TPPZn and T(EtO)PPZn are negative while those of the others are positive.[29] A similar conclusion has been obtained on the sign switching of ϵ.[25,30,31]

In the case of paramagnetic copper porphyrins, however, an unpaired electron in copper b_1 $(d_{x^2-y^2})$ orbital migrates into the porphyrin nitrogens. Exchange interactions of the unpaired electron with electrons in porphyrin LUMOs and HOMOs give rise to a mixing between porphyrin lowest (π,π^*) excited singlets and triplets. Table I summarizes the configuration interactions in zinc (diamagnetic) and copper porphyrins.

The integrals $(b_1e|eb_1)(=2\gamma)$, $(b_1a_2|a_2b_1)(=4\delta)$, and $(b_1a_1|a_1b_1)$ stand for the exchange interactions between copper b_1 orbital and porphyrin LUMO e_g orbitals, HOMO a_{2u} and a_{1u} orbitals, respectively. Since the a_{1u} orbital has no population on the nitrogens, $(b_1a_1|a_1b_1)$ can be ignored as compared with $(b_1a_2|a_2b_1)$ and $(b_1e|eb_1)$.

In Table I, the off-diagonal interactions between trip–doublets and sing–doublets are much less than those of the diagonal terms and the configuration interaction between the two trip–doublet states vanishes. Since the contamination of other doublet states into the trip–doublets is small, a schematic energy diagram of trip–doublet and trip–quartet states can be given as Fig. 8 to the zero-order approximation.

In the case of $\epsilon > 0$, the lowest excited trip–doublet and trip–quartet states are described mainly by $|^{2,4}[b_1{}^3(a_1e)]\rangle$ configurations, while those in the case of $\epsilon < 0$ are by $|^{2,4}[b_1{}^3(a_2e)]\rangle$. It should be noted that an energy gap between $^2T_1$ and $^4T_1$ states is approximately given by 3γ in $\epsilon > 0$, while that in $\epsilon < 0$ by $6\delta + 3\gamma$. Since the exchange interaction $(b_1a_2|a_2b_1)(=4\delta)$ lifts the configuration $|^2[b_1{}^3(a_2e)]\rangle$, a greater energy gap is present between $^2T_1$ and $^4T_1$ when the lowest excited configurations are $|^{2,4}[b_1{}^3(a_2e)]\rangle$.

The molecular parameters Δ, K_1, K_9, and $\epsilon = \epsilon'$ of copper porphyrins were evaluated by interpolation of the empirical values of diamagnetic nickel and zinc porphyrins which reproduce the transition energies and the intensity ratios $D[Q(0,0)]/D(B)$.

The values of δ and γ of copper porphyrins were estimated so as to reproduce the transition energies $[Q(0,0), B, {}^2S_0 \to {}^2T_1]$ and the intensity ratios of $Q(0,0)$ and B bands $D[Q(0,0)]/D(B)$. The values around 100 cm^{-1} for δ and γ were obtained. Table II summarizes the empirical spectroscopic parameters of copper porphyrins obtained in the present work. Ake and Gouterman calculated $\delta = 150$ cm^{-1}, $\gamma = 200$ cm^{-1} for copper porphyrin by use of the wave functions obtained by extended Hückel molecular-orbital calculation.[1] Figure 9 presents the energy diagram of the lowest excited states including trip–quartets, trip–doublets, and sing–doublet (Q) calculated by means of the spectroscopic parameters summarized in Table II.

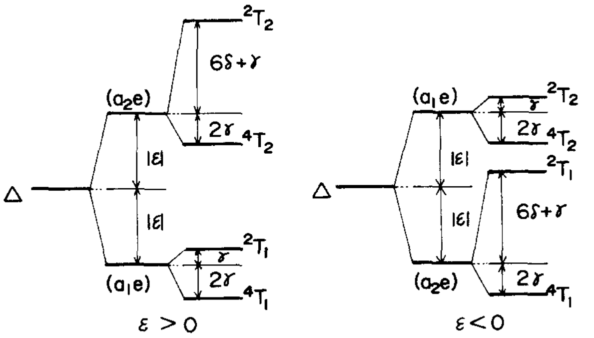

FIG. 8. A schematic energy diagram of trip–doublet and trip–quartet states to the zero-order approximation with a variation of the sign of ϵ.

TABLE II. Empirical spectroscopic parameters of copper porphyrins / 10^3cm^{-1}

	Δ	ϵ	K_1	K_9	δ	γ
OEPCu	16.33	1.86	4.08	1.02	0.08	0.12
TFPPCu	14.55	0.74	4.72	1.52	0.08	0.12
TPPCu	13.58	−0.49	5.19	1.90	0.08	0.10
T(EtO)PPCu	13.78	−0.64	4.97	1.74	0.08	0.10

The lowest trip–quartet and trip–doublet of OEPCu and TFPPCu are assigned to mainly of $|^{4,2}[b_1{}^3(a_1e)]\rangle$ origin, whereas $|^{4,2}(b_1{}^3(a_2e)\rangle$ turn out to be lower than $|^{4,2}[b_1{}^3(a_1e)]\rangle$ in TPPCu and T(EtO)PPCu. Energy gaps between $^2T_1$ and $^4T_1$ were obtained as 330 cm^{-1} for OEPCu and 350 cm^{-1} for TFPPCu, while ~700 cm^{-1} for TPPCu and ~800 cm^{-1} for T(EtO)PPCu. The values of the energy gap ΔE in OEPCu and TFPPCu obtained here well correspond to those from the kinetics described earlier. A small energy gap is present between $^2T_1$ and $^4T_1$ of OEPCu and TFPPCu while a larger gap in TPPCu and T(EtO)PPCu.

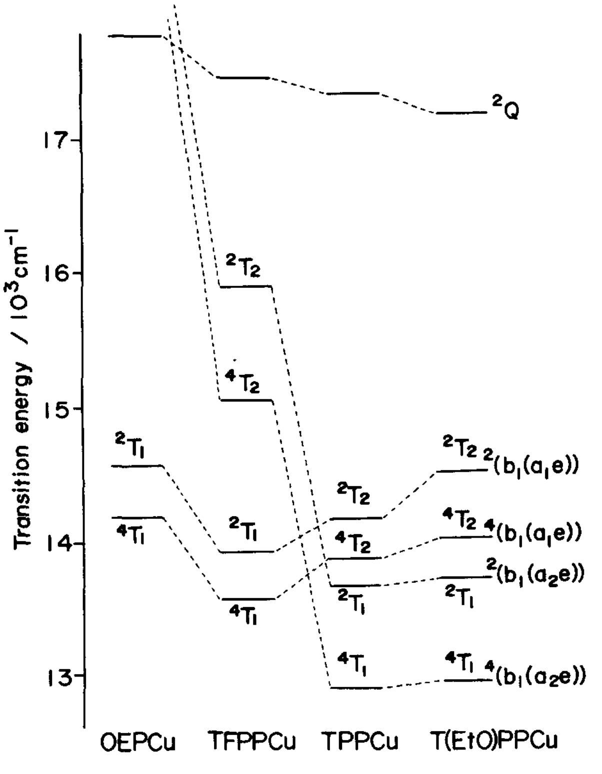

FIG. 9. The energy diagram of the lowest excited states including trip–quartets, trip–doublets, and sing–doublet (^2Q) calculated by use of the spectroscopic parameters in Table II.

The diagram given in Fig. 8 reveals that the energy gap of ${}^2T_1$ and ${}^4T_1$ in copper porphyrins depends on predominantly the sign of ϵ.

The exchange interactions give rise to admixings of the allowed sing–doublet excited states into the trip–doublet excited states. An exclusively large transition dipole strength of the second excited sing–doublet state ${}^2B$ is only partly granted to the lowest excited trip–doublet states. From the above parameters, the intensity of the lowest trip–doublet state (${}^2T_1$) with respect to that of ${}^2B$ state is estimated as $D(T_1)/D(B) = 5\text{–}8\times 10^{-4}$ and $2\text{–}5\times 10^{-4}$ for OEPCu and TFPPCu, respectively. Intensity ratios $D(T_1)/D(B) = 3\times 10^{-4}$ were observed both for OEPCu and TFPPCu.[32] The calculated values well reproduce the observed ones. On the other hand, the transition intensity ratio $D(T_1)/D(B)$ of TPPCu and T(EtO)PPCu are evaluated to be about $0.4\text{–}1.5\times 10^{-4}$.[33] The S–T absorption bands of these two copper porphyrins, however, are too diffuse to estimate their intensities accurately. Assuming an intensity of 1×10^{-3} (a.u.)^2 for the S–T band, the $D(T_1)/D(B)$ of these copper porphyrins is evaluated as to be about 0.8×10^{-4}.[34]

Kobayashi *et al.* reported kinetics of copper protoporphyrinIX dimethylester in benzene solution at room temperature.[14] They concluded that ${}^2T_1$, into which a Franck–Condon state ${}^2S_1$ decays within 8 ps after excitation, relaxes with a time constant 450–460 ps to the ${}^2T_1$ and ${}^4T_1$ thermal equilibrium state from which phosphorescence is emitted. Their observed time constant 450–460 ps is to be assigned to the fast component rate α in Eq. (4). The rate k_3 mainly limits the rate constant α. Assuming that $k_3 = 2\times 10^9\ \mathrm{s}^{-1}$, we can evaluate k_{-3} as a function of ΔE at 300 K according to the relationship $k_{-3}/k_3 = (1/2)\exp(-\Delta E/kT)$. Suppose $\Delta E = 300$ and $400\ \mathrm{cm}^{-1}$, it follows that $1/k_{-3} = 4.2$ and 6.8 ns. The observed emission decay lifetime of OEPCu in toluene solution at 300 K is 105 ns and that of TFPPCu is 69 ns. This implies that a thermal equilibrium is established between ${}^2T_1$ and ${}^4T_1$ states of OEPCu and TFPPCu. On the other hand, a variety of ΔE, 600, 700, 800, and $1000\ \mathrm{cm}^{-1}$, give the values of $1/k_{-3} = 17.7$, 28.7, 46.4, and 121 ns, respectively. These values of $1/k_{-3}$ as compared with the emission lifetime of TPPCu (29 ns) and T(EtO)PPCu (17 ns) suggest that the repopulation to ${}^2T_1$ is not so much faster than the relaxation rate to the ground state.

IV. CONCLUDING REMARKS

Decay lifetimes of emission were determined to be 17–105 ns with four copper porphyrins in toluene at 300 K. Emission observed in liquid solution at ambient temperature is ascribed to the phosphorescence from the trip–doublet state to which thermally repopulated from the trip–quartet state.

These copper porphyrins do exhibit a weak extra absorption band to the red of the characteristic porphyrin Q band. The weak band is in the mirror image of emission band and ascribed to an S–T absorption band.

Temperature dependence of the ratio emission intensity and lifetime yields an energy gap between ${}^2T_1$ and ${}^4T_1$ of OEPCu and TFPPCu as 310 and $390\ \mathrm{cm}^{-1}$, respectively. On the other hand, emission spectra and lifetimes of TPPCu and T(EtO)PPCu exhibit a temperature dependence much different from those of OEPCu and TFPPCu.

From the parameters obtained by analyses of spectroscopic data in the present work, an energy gap between ${}^2T_1$ and ${}^4T_1$ was evaluated to be $300\text{–}400\ \mathrm{cm}^{-1}$ for OEPCu and TFPPCu while those of TPPCu and T(EtO)PPCu are $600\text{–}1000\ \mathrm{cm}^{-1}$. The energy gaps obtained with OEPCu and TFPPCu well correspond to those from the kinetics study.

The lowest excited trip–doublet states of OEPCu and TFPPCu are ascribed mainly to $|{}^2[b_1{}^3(a_1e)]\rangle$, while those of TPPCu and T(EtO)PPCu to $|{}^2[b_1{}^3(a_2e)]\rangle$. The energy gap between ${}^2T_1$ and ${}^4T_1$ depends on the predominately contributing lowest excited configurations: a small energy gap is present between $|{}^2[b_1{}^3(a_1e)]\rangle$ and $|{}^4[b_1{}^3(a_1e)]\rangle$ whereas a large energy gap between $|{}^2[b_1{}^3(a_2e)]\rangle$ and $|{}^4[b_1{}^3(a_2e)]\rangle$. This difference is due to the nonzero exchange interaction $(b_1a_2|a_2b_1)$.

The exchange integrals between an unpaired electron in copper b_1 orbital and π electrons in porphyrin LUMO(e_g)s and HOMO(a_{2u}), which split porphyrin triplets into trip–doublets and trip–quartets, are estimated as $\delta[=1/4\,(b_1a_2|a_2b_1)] \approx 80\ \mathrm{cm}^{-1}$ and $\gamma[=1/2(b_1e|eb_1)] \approx 100\text{–}120\ \mathrm{cm}^{-1}$ so as to reproduce the absorption spectra. Those interactions give rise to an admixing of the allowed sing–doublet states into the trip–doublet states. Thus the trip–doublet states turn out to be granted an intensity from the ${}^2B$ state (Soret band).

The spectroscopic parameters also predicted an intensity of the lowest excited trip–doublet state to the order of 10^{-4} with reference to the intensity in ${}^2B$ state. The value reproduces the observed intensity ratio of S–T absorption and B bands.

A large energy gap between ${}^2T_1$ and ${}^4T_1$ exists in TPPCu and T(EtO)PPCu. Nonetheless, the observed emission lifetimes of these two copper porphyrins are shorter than those of OEPCu and TFPPCu. This indicates that the relaxation rate constants k_4 and/or k_2 are much enhanced in these complexes. The enhanced rates in TPPCu and T(EtO)PPCu may be understood, as usually explained by the energy-gap law,[35] for the observed red shifts of ${}^2T_1$ and ${}^4T_1$ states. However, a difference in the rate constants must be attributable to the difference in the nature of $|{}^{2,4}[b_1{}^3(a_2e)]\rangle$ and $|{}^{2,4}[b_1{}^3(a_1e)]\rangle$. In fact, emission profiles and their temperature dependence in TPPCu and T(EtO)PPCu are quite different from those of OEPCu and TFPPCu.

As temperature is decreased in solution, the emission band maxima of TPPCu and T(EtO)PPCu are shifted to the red. The decay lifetimes are inclined to be shorter and the nonradiative relaxation turns out to be faster in accordance with the red shift of emission as temperature is reduced. However, the red shift is to be attributed to a shift of the potential energy surface from that of the ground state induced by electronic excitation. An enhanced shift induced in TPPCu and T(EtO)PPCu is attributed to the electronic configuration mainly described by $|{}^{2,4}[b_1{}^3(a_2e)]\rangle$ but not by $|{}^{2,4}[b_1{}^3(a_1e)]\rangle$.

In fluid media such as toluene solution down to 200 K, low-frequency large amplitude vibrational modes largely depending upon temperature allow deformation of the excited molecules in solution, while in a rigid media most of those modes are inhibited. In fact, no red shift of emission band is observed with TPPCu and T(EtO)PPCu in rigid media: the profile of emission of all four porphyrins from PMMA films are rather invariant with temperature and those from toluene glass at 77 K well correspond to those of PMMA films. A greater Stokes shift between emission and *S–T* absorption bands observed with TPPCu and T(EtO)PPCu in fluid media in contrast with the small Stokes shift of OEPCu and TFPPCu indicate that the minimum in the energy surfaces of skeletal normal modes of the lowest excited trip–doublet states is much more shifted from that of the ground state in TPPCu and T(EtO)PPCu than in OEPCu and TFPPCu.

A charge transfer excited state lies close to the lowest trip–doublet,[15,36] although its nature has never been identified. Gouterman and co-workers assigned the weak absorption band to the charge transfer in TPPCu,[36] while we proposed in the present paper an assignment to *S–T* absorption band enhanced by paramagnetic perturbation of the central copper(II) ion. Kim *et al.* ascribed the quenching of emission of copper porphyrin by pyridine and piperidine at room temperature as due to a thermal activation to a nearby nonemissive charge transfer state.[15] So far, a variety of molecular orbital calculations were carried out on the properties of the excited states and the ground state of copper porphyrins.[37–40] As suggested by the molecular orbital calculations, the low-lying charge transfer excited state is likely to be in an energy region close to the lowest trip–doublet. However, the fact that copper porphyrin does emit phosphorescence indicates that the charge transfer excited state is higher than the lowest excited trip–doublet. Anomalous temperature dependence of emission in TPPCu and T(EtO)PPCu cannot be explained only by the contribution of the low-lying charge transfer state. The energy of the charge transfer excited state should not change much with temperature and thus it is difficult to consider that an interaction between the charge transfer state and the trip–doublet state makes the emission profile vary with temperature from 300 to 200 K in toluene solution but does not vary in PMMA film.

Emission bands of TPPCu and T(EtO)PPCu exhibit a red shift in fluid media with reducing temperature but do not shift in rigid media over the same temperature region. This strongly suggests that photodynamic character of excited copper porphyrins depends on the nature of the lowest trip–doublet whether it is mainly described $|^{2,4}[b_1{}^3(a_2e)]\rangle$ or $|^{2,4}[b_1{}^3(a_1e)]\rangle$ and anomalous temperature dependence of the emission of TPPCu and T(EtO)PPCu should be attributed to a distortion occurred in the lowest excited state. As revealed by the diffuse *S–T* band in TPPCu as compared with the sharp corresponding band in OEPCu and a larger Stokes shift between emission maximum and *S–T* absorption band in TPPCu than in OEPCu, a greater Franck–Condon overlap is obtained only at a highly excited state in the skeletal normal modes when the $|^{2,4}[b_1{}^3(a_2e)]\rangle$ configuration plays a more important role than the $|^{2,4}[b_1{}^3(a_1e)]\rangle$ configuration. The short lifetimes of TPPCu and T(EtO)PPCu are attributable to a greater shift of the energy surface in the excited state, whose configurations, mainly of $|^{2,4}[b_1{}^3(a_2e)]\rangle$, is easily influenced by environments around the excited porphyrins. It should be noted that the greater gap between parallel surfaces $|^2[b_1{}^3(a_2e)]\rangle$ and $|^4[b_1{}^3(a_2e)]\rangle$ found in the present work with TPPCu and T(EtO)PPCu does not necessarily yield an equilibrium of trip–doublet and trip–quartet within the excited state lifetime. The relaxation rate of the trip–quartet $|^4[b_1{}^3(a_2e)]\rangle$ to the ground state might be comparable with the observed decay rate.

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[33] In the case of TPPCu and T(EtO)PPCu, the calculated intensity values include subtraction errors because the interaction between $|^2[b_1{}^3(a_2e)]\rangle$ and $|^2B\rangle$ is described as $\sqrt{6}/2(2\delta - \gamma)$ while that of OEPCu and TFPPCu is $\sqrt{6}/2\gamma$.
[34] The value of the *S–T* absorption intensity 1×10^{-3} $(\mathrm{a.u.})^2$ is a third–a half of that of OEPCu. The observed transition dipole strengths of *B* band are

11.1 and 13.2 (a.u.)^2 in TPPCu and T(EtO)PPCu, respectively.

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