

Red-shifted emission spectra of several meso-substituted copper porphyrins in fluid solution

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Abstract

Medium dependence of the emission spectra of several meso-substituted copper porphyrins was studied at 300–77 K. Copper porphyrins emit from the lowest excited (porphyrin triplet) states in fluid solution as well as in rigid media. Emission spectra of several copper porphyrins in toluene liquid solution were red-shifted from those in rigid media such as PMMA (poly(methylmethacrylate)) film. The copper porphyrins, which give red-shifted emission in toluene solution, have ${}^2,4[b_1\ ^3(a_{2u}e_g)]$ configuration in the lowest excited states and the amount of the shift depends on meso-substituents ranging up to 1300 cm^{-1} . As the emission spectra in toluene rigid glass at 77 K coincide with those in PMMA film, the observed shift in ${}^2,4[b_1\ ^3(a_{2u}e_g)]$ -type porphyrins is attributable to distortion of the excited molecules in fluid solution. T(2,4,6-(MeO)₃)PPCu, in which bulky meso-substituents are likely to suppress torsion of the phenyl rings and distortion of the porphyrin plane, was found to show no shift of emission spectra, in spite of the ${}^2,4[b_1\ ^3(a_{2u}e_g)]$ configuration. In the case of TPrPCu, which has no phenyl group, red shift occurs as a result of the medium being changed to become non-rigid. An out-of-plane distorted structure is proposed. Lifetimes of the emission in toluene solution are remarkably shorter in the copper porphyrins that show a larger emission red-shift from the emission in PMMA film. This relation suggests that the distortion modes are connected with enhancement of the radiationless decay.

Keywords: Excited states of copper porphyrins; Distortion in fluid solution; Radiationless decay

1. Introduction

Planar and nonplanar structures of four-coordinated metalloporphyrins have been reported in crystals and recently their structures were studied by using resonance Raman spectroscopy [1–5]. Molecular mechanical calculations were applied to a series of porphyrins with various substituents which cause distortion in porphyrin planes [6]. This study is aimed at investigating the functions of nonplanar tetrapyrroles in heme proteins and other biological systems [7–11]. Dynamic properties of distorted porphyrins in various environments, especially in the excited states, are important in elucidating basic chemical reactions, ligand binding and electron transfer in those biological systems.

A number of studies has been made on the excited triplet states as well as the excited singlet states. The lowest excited triplet state (T_1) in the typical metalloporphyrins is approximately described as a single configuration of ${}^3(a_{1u}e_g)$ or ${}^3(a_{2u}e_g)$ depending on porphyrin macrocycle substituents, although the S_1 state

is described as a 50:50 admixture of the two configurations ${}^1(a_{1u}e_g)$ and ${}^1(a_{2u}e_g)$ [12]. Therefore, in the case of T_1 state, properties of the excited states can be discussed with relevance to their electronic structure by changing the peripheral substituents.

Most work dealing with the porphyrin triplets has been carried out in rigid media at low temperatures because of a longer lifetime and much more intense phosphorescence [12–15]. Emission from the porphyrin triplets is usually observed in diamagnetic and paramagnetic porphyrins which have neither metal-centered nor charge transfer excited states below T_1 state. For instance, nickel(II) porphyrins are non-emissive due to low-lying (d,d^*) states [16–21]. Diamagnetic zinc(II) and magnesium(II) porphyrins emit phosphorescence, although it is observed only in rigid media at low temperatures [22,23].

In the case of copper(II) porphyrins, emission from the lowest excited triplet manifolds is observed even at room temperature because of perturbation of an unpaired electron in the central metal ion. Exchange

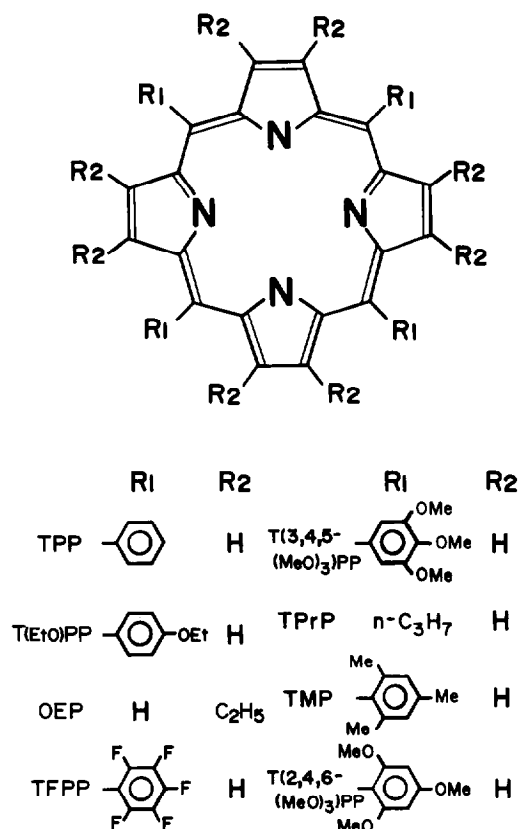


Fig. 1. Structural diagram of porphyrin macrocycles. Abbreviations: TPP, tetraphenylporphin; T(EtO)PP, tetra (*p*-ethoxyphenyl)porphin; OEP, octaethylporphin; TFPP, tetra(pentafluorophenyl)porphin; T(3,4,5-(MeO)₃)PP, tetra(3,4,5-trimethoxyphenyl) porphin; TPrP, tetrapropylporphin; TMP, tetramesitylporphin; T(2,4,6-(MeO)₃)PP, tetra(2,4,6-trimethoxyphenyl)porphin.

interaction between porphyrin π -electrons and a copper d_{σ} electron splits porphyrin triplets into trip-doublents (2T) and -quartets (4T) [24]. 2T and 4T states are porphyrin triplet by origin but spin multiplicities of the whole system in these states are doublet and quartet, respectively. The two lowest substates, 2T_1 and 4T_1 , are separated by several hundred cm^{-1} [25–30], while they remember much of porphyrin triplet nature. Relaxation processes from 2T_1 and 4T_1 states at ambient temperature in solution were studied by using of femto- and picosecond photolysis [31–35]. Luminescence of copper porphyrins at room temperature is ascribed to the emission from 2T_1 state which is activated thermally from the 4T_1 state.

In a previous paper [30], we reported that relaxation processes of copper porphyrins in the lowest excited manifolds ($^2,^4T_1$) depend on the electronic configuration of the π -electron system. Different temperature dependence of the emission intensities and lifetimes was observed in toluene solution among the two types of configuration. It should be noted that some of the $^2,^4[b_1^3(a_{2u}e_g)]$ -type copper porphyrins (b_1 denotes an unpaired electron in the copper d_{σ} orbital and $^3(a_{2u}e_g)$ denotes

a porphyrin triplet configuration) exhibit much red-shifted emission spectra in toluene solution from those in rigid media such as PMMA film, while $^2,^4[b_1^3(a_{1u}e_g)]$ -type does not.

In this work, we measured emission spectra and lifetimes of four more meso-substituted copper porphyrins in toluene and in PMMA film to investigate the origin of the red shift in liquid solution. A structural diagram of copper porphyrins described in this paper and their abbreviations are shown in Fig. 1. It was found that the degree of the shift of emission spectrum upon moving towards non-rigid medium depends on porphyrin macrocycle substituents and that it is in good correlation with the excited lifetime. On the basis of results on several meso-substituted copper porphyrins, we will propose that out-of-plane distortion associated with metal displacement play an important role in the excited structure and radiationless transitions.

2. Experimental details

2.1. Materials

TPrPH₂ (TPrP: 5, 10, 15, 20-tetra(*n*-propyl)porphin) was synthesized according to the condensed method of Gonsalves and Pereira [36] from *n*-butyraldehyde dimethylacetal and pyrrole. Normal butyraldehyde dimethylacetal was prepared from dimethoxypropane and *n*-butyraldehyde with a catalytic amount of *p*-toluene-sulfonic acid in dichloromethane and purified by distillation. Crude TPrPH₂ was obtained after dry alumina column chromatography and recrystallization from chloroform/methanol. The crude product contains byproducts, which exhibit very similar absorption spectra with TPrPCu. These byproducts can be removed by chromatography on wet packed silica gel column (Merck Kieselgel 60) eluting with benzene/dichloromethane (1:9 v/v). The first fraction was collected and the product was recrystallized from hot benzene/ethanol twice.

T(2,4,6-(MeO)₃)PPH₂ and T(3,4,5-(MeO)₃)PPH₂ were prepared by the method of Longo et al. [37,38]. Purification was carried out by silica gel column chromatography after removing chlorine contamination [39] and recrystallization. TMPH₂ was prepared according to the diluted method of Lindsey et al. [40,41] and purified by repeated silica gel chromatography and recrystallization. Free-base porphyrins used in this study were identified by UV-VIS and NMR spectroscopy.

Copper porphyrins were prepared by the method of the literature [42] and purified as described previously [30]. No contamination of corresponding free base porphyrins was confirmed by emission spectra.

2.2. Measurements

Emission spectra were measured by using a photon counting method. Samples were excited by an NEC GLG3300 Ar ion laser at 514.5 nm. After dispersion by a Nikon P-250 monochromator, emission was detected by a Hamamatsu photonics model C737 photon counter equipped with a Hamamatsu photonics R316 photo-multiplier (S1 sensitivity) and a preamplifier model C1556.

Emission lifetimes shorter than 1000 ns were measured by using a PRA nanosecond single-photon-counting system [43]. For the lifetimes longer than 600 ns, measurements were carried out as described previously [30] except that excitation was made at 532 nm by the second harmonics of a pulsed Nd:YAG laser Spectron model SL401.

Toluene used for solvents was purified by distillation on CaH_2 after removing impurities by shaking with sulfuric acid. Solutions of porphyrins were sealed in cuvettes degassed by freeze–pump–thaw cycles or purged with argon gas just before the measurements depending upon samples. Transparent PMMA films dispersing porphyrin were prepared as described previously [30]. Measurements at 195 K and 77 K were carried out in a quartz Dewar filled with dry ice–methanol and liquid N_2 , respectively.

3. Results

3.1. Emission spectra and the lowest excited triplet configuration

Fig. 2 shows absorption spectra of the four copper porphyrins in toluene solution in visible and near ultraviolet region. These spectra were very similar to those of TPPCu and T(EtO)PPCu. The π -electron systems of the four porphyrins are not much different from that of TPPCu. Particularly, TPrPCu in Fig. 2B have no phenyl group at meso-positions but it exhibits similar absorption spectra to the others. Interaction of π -electrons between the phenyl rings and the porphyrin macrocycle is negligible small in this energy region.

Fig. 3 shows the emission spectra of meso-substituted copper porphyrins obtained in the present study. All these spectra of the four copper porphyrins are broad and structureless as observed in TPPCu. It is generally observed that emission spectra of copper porphyrins in the lowest ${}^2,4[b_1^3(a_{2u}e_g)]$ configuration are broad and structureless while those of ${}^2,4[b_1^3(a_{1u}e_g)]$ exhibit a sharp (0,0) band and vibronic structure, as shown in Fig. 4 for comparison. TPPCu and T(EtO)PPCu, which have ${}^2,4[b_1^3(a_{2u}e_g)]$ configuration, show broad and structureless emission spectra. On the other hand, OEPCu and TFPCu with the lowest ${}^2,4[b_1^3(a_{1u}e_g)]$ configuration

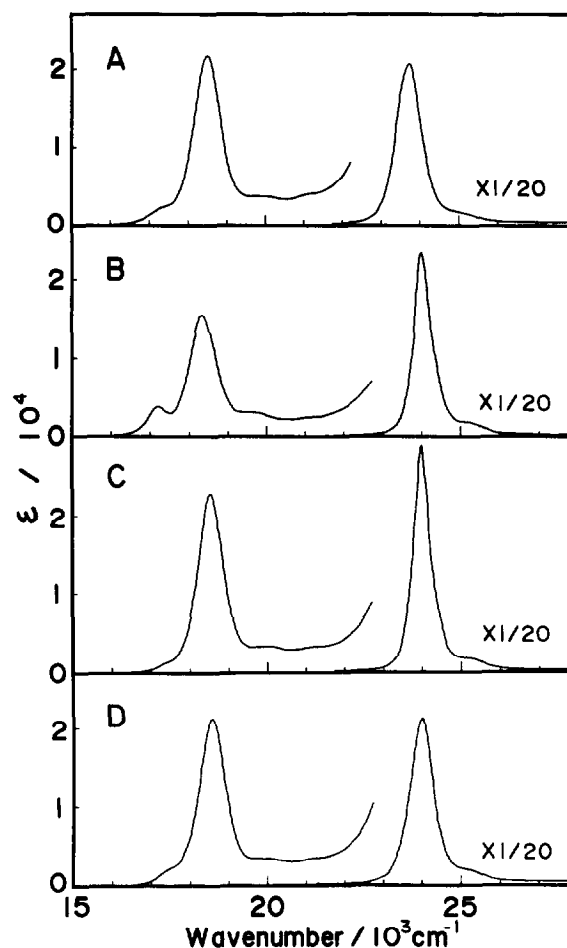


Fig. 2. Absorption spectra of T(3,4,5-(MeO)₃)PPCu (A), TPrPCu (B), TMPCu (C) and T(2,4,6-(MeO)₃)PPCu (D). (A) and (C) in toluene, (B) and (D) in CH_2Cl_2 . TPrPCu and T(2,4,6-(MeO)₃)PPCu were not enough soluble in toluene to determine the molar extinction coefficients in the absorption spectra and thus measurements were carried out in CH_2Cl_2 .

show a sharp (0,0) band of emission spectra [44]. The lowest excited configuration of the four copper porphyrins in Fig. 3 are verified by the following.

It is known that axial ligation of pyridine gives a judgment of which of ${}^1(a_{1u}e_g)$ and ${}^1(a_{2u}e_g)$ is the lower in metalloporphyrins of D_{4h} symmetry [23]. The lowest excited singlet and triplet states can be obtained by a promotion of an electron within the porphyrin π electron system. The LUMOs are e_g orbital pair while the two HOMOs, a_{1u} and a_{2u} orbitals, are almost equal in their energy. An electron donation by the axial coordination of pyridine to the central metal ion destabilizes a_{2u} orbital but does not a_{1u} orbital. This effect can be observed in the change of the intensity ratio of Q(0,0)/Q(1,0) absorption bands. The ratio is approximately proportional to the square of the energy gap between the orbital energy of a_{1u} and a_{2u} . For example, if a_{2u} is the higher, the intensity ratio increases by the ligation of pyridine and we can know the configuration ${}^{1,3}(a_{2u}e_g)$ is lower than ${}^{1,3}(a_{1u}e_g)$, respectively. Unfortunately,

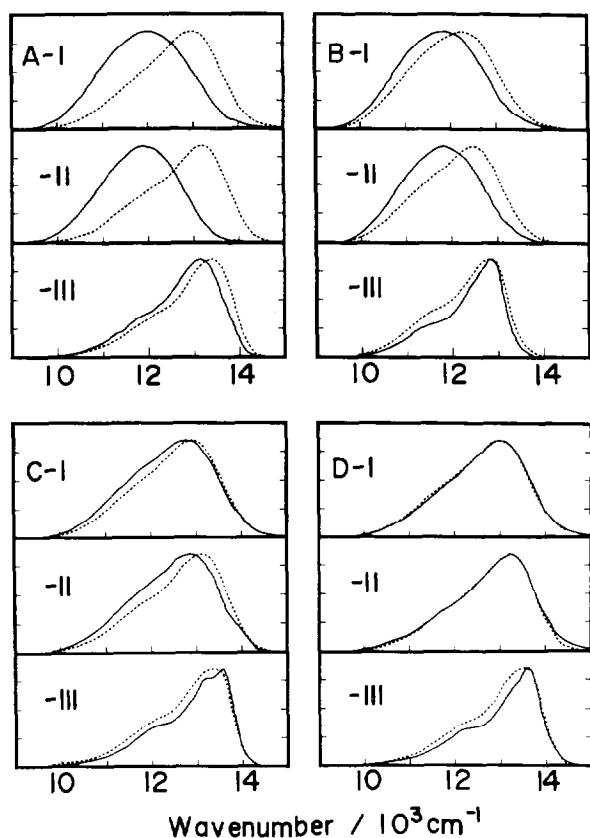


Fig. 3. Emission spectra of T(3,4,5-(MeO)₃)PPCu (A), TPrPCu (B), TMPCu (C) and T(2,4,6-(MeO)₃)PPCu (D) in toluene (—) and PMMA film (---) at 300 K (I), 195 K (II) and 77 K (III).

complex formation of copper porphyrins with pyridine is not completed even in neat pyridine solution [32], so that the measurement of the intensity ratio was made for the corresponding zinc(II) porphyrins, TPrPZn, TMPZn, T(2,4,6-(MeO)₃)PPZn and T(3,4,5-(MeO)₃)PPZn. The intensity ratios were found to increase by the ligation of pyridine: TPrPZn 0.36 (in toluene), 0.89 (in 1%pyridine/toluene); TMPZn 0.07, 0.34; T(2,4,6-(MeO)₃)PPZn 0.07, 0.21; T(3,4,5-(MeO)₃)PPZn 0.15, 0.49. This indicates that the energy of the a_{2u} orbital is higher than the a_{1u} orbital and thus the configuration $^3(a_{2u}e_g)$ is the lowest in these zinc(II) porphyrins. The relation between relative orbital energies of the a_{2u} and a_{1u} in copper porphyrins is considered to be the same with the corresponding zinc complexes. Thus the configuration $^{2,4}[b_1^3(a_{2u}e_g)]$ is the lowest in the four copper porphyrins.

3.2. Medium and temperature dependence of emission profile

In Fig. 3A, the emission spectra of T(3,4,5-(MeO)₃)PPCu in toluene solution at 300 K and 195 K are considerably red-shifted compared with those in PMMA films, while the emission spectrum at 77 K in toluene almost coincides with that in PMMA film. This

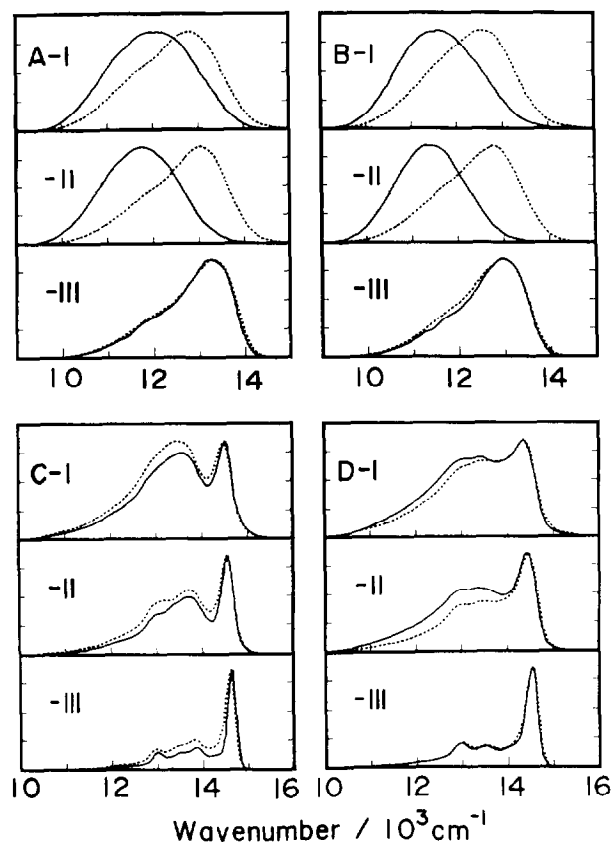


Fig. 4. Emission spectra of TPPCu (A), T(EtO)PPCu (B), OEPCu (C) and TFPPCu (D) in toluene (—) and PMMA film (---) at 300 K (I), 195 K (II) and 77 K (III). Sensitivity of the emission detection system in near infra-red region was improved in this work. Emission intensity in less than 12 000 cm⁻¹ region was defective in Ref. [30].

phenomenon is very similar to those of TPPCu in Fig. 4A. As indicated in the previous work, the emission maximum of TPPCu in toluene solution shifts to the red as decreasing temperature from 300 K down to 200 K. This temperature dependence was also observed in T(3,4,5-(MeO)₃)PPCu.

The emission spectra of TPrPCu in solution show also red shift from those in PMMA film although the amount of the shift was less than that of T(3,4,5-(MeO)₃)PPCu. In TMPCu in Fig. 3C, the emission spectra in solution show only a slight red-shift from those in PMMA film both at 300 K and at 195 K. These three copper porphyrins exhibit red-shifted emission spectra in fluid solution, but emission spectra at 77 K are almost superposition of those in PMMA film. In the case of the T(2,4,6-(MeO)₃)PPCu, emission profile in solution is exactly the same with that in PMMA film at 77–300 K as shown in Fig. 3D.

In short, the emission spectra of the $^{2,4}[b_1^3(a_{2u}e_g)]$ -type copper porphyrins in solution exhibit red shift from those in rigid media with the amount depending on substituents. However the emission profiles in rigid media are very similar among the $^{2,4}[b_1^3(a_{2u}e_g)]$ -type

Table 1
Emission lifetimes ^a and shifts of the emission maxima ^b

Compound	300 K		195 K	
	τ (ns)	shift (10 ³ cm ⁻¹)	τ (ns)	shift (10 ³ cm ⁻¹)
OEPCu	105 ^c	0	1200 ^c	0
TFPPCu	69 ^c	0	1250 ^c	0
T(2,4,6-(MeO) ₃)PPCu	55	0	1200	0
TMPCu	101	0.1	840	0.3
TPrPCu	53	0.5	235	0.7
TPPCu	29 ^c	0.8	29 ^c	1.3
T(3,4,5-(MeO) ₃)PPCu	28	1.0	32	1.3
T(EtO)PPCu	17 ^c	1.1	13.5 ^c	1.7

^a Lifetimes in toluene.

^b Shifts of the emission maxima in toluene from that in PMMA film.

^c From Ref. [30].

porphyrins. These properties are different from those of ^{2,4}[b₁³(a_{1u}e_g)]-type copper porphyrins, which show no shift of emission maxima as changing temperature and medium, as observed in OEPCu and TFPPCu.

3.3. Lifetimes

Emission signals of all the sample in toluene solution at 195 K and 300 K decay single-exponentially. The lifetimes in toluene and shifts of the emission maxima in toluene solution from those in PMMA film are listed in Table 1. Lifetimes of the copper porphyrins were found to be 17~101 ns at 300 K. As increasing the shift of the emission maximum, the lifetime decreases in ^{2,4}[b₁³(a_{2u}e_g)]-type copper porphyrins. At dry ice-methanol temperature lifetimes also decrease from 13.5 ns to 1200 ns as the shifts become larger.

4. Discussion

4.1. The red shift of emission spectra in fluid solution from those in rigid medium

In the meso-substituted copper porphyrins, the red shifts of emission spectra by changing medium were observed only in fluid solution. Complex formation of the excited copper porphyrins with solvent molecule is excluded because the emission spectra in toluene at 77 K is the same with that in polymer film. The red shift observed in fluid solution is attributable to certain distortion in the excited state. In rigid media deformation in the excited state is suppressed by the environmental constraint, while in fluid solution excited molecules are released from the constraint and are allowed to deform freely to have the most stable structure.

Since the emission spectra of the ^{2,4}[b₁³(a_{2u}e_g)]-type copper porphyrins are very similar to each other in

rigid media, the excited state structures of the copper porphyrins are supposed to be much the same in such media. It is considered that the amount of the red shift in fluid solution from that in rigid media represents the extent of distortion in fluid solution. T(2,4,6-(MeO)₃)PPCu and TMPCu do not show remarkable shift in their emission spectra. These two porphyrins are expected to have common properties which prevent the emission red-shift in fluid solution. The meso-substituents of the two porphyrins are ortho-substituted phenyl groups which suppress torsional motion of the phenyl rings. It should be noted that structural difference between T(2,4,6-(MeO)₃)PPCu and T(3,4,5-(MeO)₃)PPCu, which exhibits the red shift, is only substituted positions of the phenyl groups: in T(2,4,6-(MeO)₃)PPCu two ortho and para hydrogens are substituted by methoxy groups while in T(3,4,5-(MeO)₃)PPCu two meta and para hydrogens. These observations seem to imply that torsional distortion of the phenyl ring induce the red shift upon going to non-rigid medium. Torsional motion of the phenyl ring was observed in fluorescence excitation spectra of TPPMg and TPPZn in pulsed supersonic jets [45,46]. However, TPrPCu, which has no phenyl ring, exhibits the substantial red-shift of emission in fluid solution. This fact indicates that torsional distortion of the phenyl rings is not necessarily the origin of the red shift, even if the phenyl rings were distorted toward coplanar structure in the excited triplet state.

Bulky ortho-substituents of the phenyl rings in T(2,4,6-(MeO)₃)PPCu and TMPCu inhibit not only torsional distortion of the phenyl ring but also porphyrin out-of-plane distortion. Because the distortion which yields the red shift of the emission spectra in liquid solution does not take place in rigid media, it must be caused by low frequency large amplitude motion. There are considerable out-of-plane modes in the low frequency region [47]. Domed or ruffled structure is considered as suggested in porphyrin π cation radicals [48,49].

In a four-coordinated and out-of-plane distorted copper porphyrin, there are two equivalent structures to the original porphyrin plane. In such feature, the potential energy curve has two minima. Umbrella-like motion, that means the molecule in one of the minima changes to the other side through the plane structure, takes place. Such motion is a low frequency large amplitude motion and is likely to be allowed in only fluid solution but inhibited in rigid media.

4.2. Correlation between lifetimes in toluene and the red shift of the emission spectra by changing medium

Relaxation processes of the excited trip-doublet and -quartets states are dominated by radiationless transitions in the copper porphyrins, since the natural lifetimes of the trip-doublet states were estimated as

more than 10 ms from the S-T absorption bands [30]. Therefore, a shorter lifetime in Table 1 indicates a larger rate constant for the radiationless decay. Fig. 5 shows plots of $1/\tau$ (lifetimes) vs. the shifts of the emission maxima in toluene solution from those in PMMA film. The relation between lifetimes and the emission shifts leads to the conclusion that the radiationless transition was enhanced in the copper porphyrins which showed larger red-shift. As the amount of the shift is considered to represent an extent of the distortion of the excited molecule, the distortion modes take an important role in the relaxation processes, such as a promoting mode or accepting mode.

Presence of a charge transfer (CT) state at low energy has been suggested by molecular orbital calculations in copper porphyrins [50–54], although its nature was not clarified, metal-to-ligand or ligand-to-metal CT. In coordinating solvent such as pyridine, emission of copper porphyrins was quenched [32,35]. Holten et al. ascribed the quenching to fast relaxation to a low-lying electronic state and proposed a ligand-to-metal CT state [32]. On the other hand, McMillin et al. presented an explanation that (d,d*) excited state quenches the emission of five coordinate excited copper porphyrins because of a stabilized (d,d*) excited state [55]. A low-lying (d,d*) excited state was also suggested by resonance CARS study of OEPcCu in coordinating solvents [56]. An axial ligation to the central metal ion causes destabilization of metal d_{z^2} orbital and porphyrin a_{2u} orbital. That is why a low-lying electronic excited state can be present in coordinating solvents. In noncoordinating solvents, however, electronically excited states are absent in the low energy region. Observed short lifetimes in the copper porphyrins which exhibit larger red-shift are not due to fast relaxation to other excited states, but due to accelerated radiationless transition to the ground states.

Copper porphyrins with ${}^2,4[b_1^3(a_{2u}e_g)]$ configuration show medium dependence of emission spectra, while it is inhibited to some extent by steric factors. On the contrary, ${}^2,4[b_1^3(a_{1u}e_g)]$ -type copper porphyrins do not

show such dependence. The differences of medium dependence of emission spectra seem to reflect difference between nature of the two electronic configurations; ${}^2,4[b_1^3(a_{2u}e_g)]$ state is easily influenced by environments such as medium, while ${}^2,4[b_1^3(a_{1u}e_g)]$ is not.

One of the major differences between ${}^2,4[b_1^3(a_{2u}e_g)]$ and ${}^2,4[b_1^3(a_{1u}e_g)]$ configurations is a difference between nature of a_{2u} and a_{1u} orbitals. That is, a_{2u} orbital has large electron population at the four nitrogen atoms of the macrocycle while a_{1u} orbital has no population at the nitrogens [12,57]. Metal–nitrogen bonds of the excited states must be different between the two configurations. It is likely to cause a difference of distortion of the excited structure, emission properties, and radiationless transitions from the excited states.

5. Conclusion

Emission spectra and lifetimes of the lowest excited states of several meso-substituted copper porphyrins were measured in toluene and in PMMA film at 300–77 K. Copper porphyrins with ${}^2,4[b_1^3(a_{2u}e_g)]$ configurations in 2,4T_1 states showed the red shift of emission spectra in fluid solution from those in rigid media, while ${}^2,4[b_1^3(a_{2u}e_g)]$ -type copper porphyrins did not show any remarkable shift. The amount of the red shift observed in ${}^2,4[b_1^3(a_{2u}e_g)]$ -type copper porphyrins ranges up to 1300 cm^{-1} depending upon meso-substituents. This shift is attributed to distortion of the excited molecules in fluid solution. Out-of-plane distorted structure is proposed as an origin of the red shift of emission upon going to non-rigid medium. Correlation between lifetimes of the excited state and the red shift of the emission spectra in fluid solution suggests that radiationless transitions are increased by the distortion modes.

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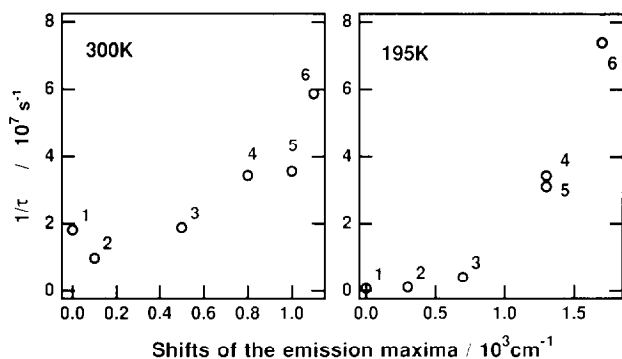


Fig. 5. Plots of emission lifetimes vs. the shifts of the emission maxima in toluene solution from those in PMMA film at 300 K and 195 K: T(2,4,6-(MeO)₃)PPcCu (1), TMPCu (2), TPrPCu (3), TPPcCu (4), T(3,4,5-(MeO)₃)PPcCu (5), T(EtO)PPcCu (6).

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