A Time-Resolved Electron Paramagnetic Resonance Study of Excited Triplet Porphyrins in Fluid Solution

Jun-ichi Fujisawa, Yasunori Ohba, and Seigo Yamauchi*

Institute for Chemical Reaction Science
*Tohoku University*
Katahira 2-1-1, Aoba-ku, Sendai 980-77, Japan

Time-resolved electron paramagnetic resonance (TREPR) signals of excited triplet (T_1) porphyrins were observed in fluid solution for the first time. The TREPR spectra exhibit remarkable effects of the molecular tumbling depending on temperature and viscosities of solvents and involve electron spin polarizations even at room temperature. Spin-lattice relaxation (SLR) times and lifetimes of the T_1 state were directly measured from decays of TREPR signals in solution. The SLR time is dependent both on the temperature and the viscosity of solvents, also showing dependence on the structure of the porphyrin.

Time-resolved electron paramagnetic resonance (TREPR) is a powerful technique for studies of excited triplet (T_1) states in solid[1] and even in liquid crystals.[2] There are, however, very few studies on T_1 in fluid solution; the T_1 states of fullerenes in liquid phase were observed, and the spin dynamics has been studied in detail by TREPR and pulsed-EPR.[3] In this case, the TREPR spectra provide little information about intrinsic properties of the T_1 state due to both the fast molecular tumbling and the rapid electron-hopping over the Jahn−Teller states. In this paper, we report on the observation of the TREPR spectra and direct determination of the spin−lattice relaxation (SLR) times of the T_1 states of porphyrins in fluid solution.

We examined three kinds of *meso*-tetraphenylporphyrins (MTPP; M = H_2, Mg, Zn). The T_1 polarizations of MTPPs are well-known to vary by changing the central atom(s), low-field emission/high-field absorption for H_2TPP[2] and MgTPP,[4] and the opposite for ZnTPP.[2] The details of the TREPR apparatus have been described previously.[5,6] The porphyrins were synthesized according to the methods described in the literature.[7] Spectral-grade toluene and 2-butanol and special-grade liquid paraffin were used as solvents having different viscosities (η^{283K}) of 0.6,[3d] 5,[8a] and ~160 cP,[8b] respectively. The solutions ($0.4-5 \times 10^{-4}$ M) were deaerated by repeated freeze−pump−thaw cycles.

TREPR spectra were observed for MgTPP in toluene at 0.0−0.1 μs after the laser excitation as shown in Figure 1. The
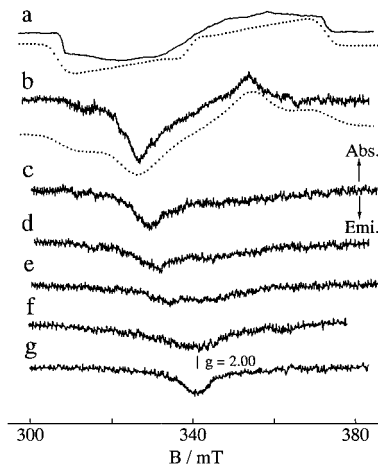
Figure 1. TREPR spectra of MgTPP in toluene observed at 0.0−0.1 μs and (a) 173 K (solid phase), (b) 183 K ($\tau = 12$ cP), (c) 213 K (2.9 cP), (d) 233 K (1.6 cP), (e) 253 K (1.0 cP), (f) 273 K (0.7 cP), and (g) 293 K (0.6 cP). The dotted lines denote the simulation of the spectra, using the parameters described in the text. The viscosities were calculated by using the equation reported in ref 3d.
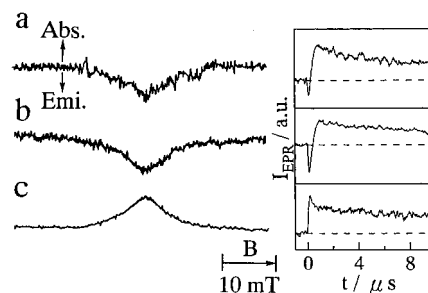
Figure 2. TREPR spectra observed at 0.0−0.1 μs and 283 K in toluene and the time profiles obtained for (a) H_2TPP, (b) MgTPP, and (c) ZnTPP.

spectrum obtained at 173 K, a little below the melting point (178 K) of toluene, was simulated by polarized T_1 MgTPP with the zero-field splitting (zfs) parameters of $D = 0.93$ and $E = 0.29$ GHz and the intersystem crossing (isc) ratio of $P_x:P_y:P_z = 1:1:0$.[4] Here, the z axis is perpendicular to the porphyrin plane. A drastic change of the spectrum was observed at 183 K, a little above the melting point, and the spectrum of EEE/AAA type was simulated with $D = 0.93$ GHz, $E = 0$ GHz, and $P_x:P_y:P_z = 1:1:0$. The result suggests that an in-plane anisotropy (E) of the zfs is averaged out by rapid hopping between the Jahn−Teller states and/or molecular rotation around the z axis. As the temperature rises above 183 K, the spectrum exhibits further averaging of the zfs (D) and turns into a broad and nearly symmetric line at room temperature. The emissive polarization observed above 213 K is consistent with the polarization below 183 K. Similar spectral changes were observed at room temperature in various solvents with different viscosities. These spectral changes can be explained by molecular tumblings around the in-plane axes, as reported by Freed et al.[9] and Levanon et al.[3b,10]

We now focus our attention on the T_1 signals at 283 K. TREPR spectra at 0.0−0.1 μs and time profiles are shown in Figure 2. Each spectrum exhibits a broad peak with a full width at a half maximum of 9.4 ± 0.6 mT, showing little dependence on the central atom(s). Decay curves were analyzed by two

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(6) An OPO laser (MOPO-730 Spectra Physics) pumped by a Nd:YAG laser (GCR 170 Spectra Physics) was employed to excite the porphyrins to the S_1 states. Temperature was controlled with a N_2 gas-flow system (ES-DVT3 JEOL).

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Table 1. Spin−Lattice Relaxation Time of T_1 Porphyrin at 283 K

	$\tau_1/\mu s^a$		
	toluene	2-butanol	liquid paraffin
H_2TPP	0.21	c	0.52
MgTPP	0.20	0.20	0.32
ZnTPP	ca. 0.02^b	0.18	0.30

^{a} Experimental errors are ± 0.03 μs. ^{b} See the text. ^{c} Not observed owing to low solubility.

components with the equation[11] reported by Steren et al.[3d] The obtained decay constants are 0.21 ± 0.03 and 458 ± 15 μs for H_2TPP, 0.20 ± 0.03 and 77 ± 5 μs for MgTPP, and ≤ 0.1 and 536 ± 15 μs for ZnTPP. The fast components are emissive signals for H_2TPP and ZnTPP and absorptive for ZnTPP. In contrast the slow components are absorptive and showed no microwave-power dependence in all systems. These signals were effectively quenched by molecular oxygen in aerated toluene with a time constant of 0.47 ± 0.1 μs, which is consistent with the reported value (ca. 0.4 μs) for T_1 porphyrin.[12] Triplet decay times were determined by triple−triplet optical absorption at 470 nm as 447 ± 15 μs for H_2TPP, 76 ± 5 μs for MgTPP, and 526 ± 15 μs for ZnTPP, which are in good agreement with those obtained from the absorptive EPR signals. On the basis of these results, it is concluded that the slowly decaying absorptive signals are due to triplets at thermal equilibrium. The fast components, whose polarities are the same as those obtained at 77 K, are then assigned to spin-polarized triplets. These assignments are consistent with the spectral changes observed by varying the temperature and solvent. The decay time of the fast component, which remains constant at the microwave-power of <3 mW, is attributed to the SLR time of the T_1 state in fluid solution: 0.21 and 0.20 μs for H_2TPP and MgTPP, respectively. The obtained decay time (≤ 0.1 μs) for T_1 ZnTPP is mostly governed by time resolution (ca. 0.08 μs) of our system. The SLR time of T_1 ZnTPP is reported as 28 ns in ethanol from a pulsed EPR study.[13] On the basis of the viscosities of toluene ($\eta^{283K} = 0.6$ cP) and ethanol ($\eta^{283K} = 1.2$ cP), the SLR time of T_1 ZnTPP in toluene is estimated as ca. 0.02 μs.[14]

The SLR times of the T_1 porphyrins were also determined in 2-butanol and liquid paraffin solutions from analogous decay analyses of T_1 polarizations. The obtained values at 283 K are summarized in Table 1. The SLR times in liquid paraffin show a field dependence[15] and are given for the lower resonance field with $B_0 \perp z$. The table shows that the SLR times of T_1 H_2TPP

and T_1 MgTPP are significantly longer than that of T_1 ZnTPP in toluene, indicating the dependence on the central atom(s). It is also found that the difference in the SLR time among the T_1 states decreases with increasing the viscosity of solution.

Fluctuations in two kinds of interactions, spin−spin and spin−rotation interactions, are considered to cause the SLR of the T_1 state in solution. In examined porphyrins, zfs is known to be dominated by the spin−spin interaction. The D value (1.1 GHz) for H_2TPP is a little larger than those (0.93 GHz) for MgTPP and ZnTPP.[16] If the spin−spin interaction dominantly contributes to the SLR process,[2d] the faster relaxation is expected for H_2TPP, which is not the case. Next, we consider the spin−rotation mechanism, where the magnitude of the contribution to the SLR time (τ_1) is expressed as follows:[17]

$$(\tau_1)^{-1} = (\Delta g_{\parallel}^2 + 2\Delta g_{\perp}^2)/(9\tau_R) \tag{1}$$

Here, $\Delta g = g_e - g$ ($g_e = 2.0023$) and τ_R is a rotational correlation time.[17] The isotropic g values of T_1 MgTPP and T_1 ZnTPP are estimated to be 2.003 and 2.001.[5,18] Although a larger contribution of the spin-rotation mechanism is expected for T_1 ZnTPP than for T_1 MgTPP as observed, the calculated value of τ_1 (4 μs) of ZnTPP[20] is 2 orders of magnitude larger than the observed one (0.02 μs). Therefore, a large contribution is not expected from the spin−rotation interaction if eq 1 applies. At the moment we do not know the exact reason for the difference in τ_1 in toluene. The slightly shorter τ_1 observed in liquid paraffin for T_1 MgTPP and T_1 ZnTPP as compared with that observed for T_1 H_2TPP is interpreted in terms of the hopping between Jahn−Teller states. An averaging in zfs over the Jahn−Teller states is also indicated by different types of spectral changes observed for these porphyrins.[21] It is also noted that τ_1 is not remarkably dependent on the solvent viscosity (Table 1 vs eq 1), which is characteristic to T_1 porphyrins and might be due to strong anisotropy in molecular rotation.

We will present detailed analyses of the spin−lattice relaxation and the average in zfs parameters in the forthcoming full paper.

(11) The decay curves were analyzed by the equation[2d] $I(t) = A[(exp(-k_d t) + (P - 1)exp(-(k_1 + k_d)t)][1 - B'exp(-k_d t)]^{-1}$, where $B = k_t N_0/(k_d + k_t N_0)$, and k_1, k_d, and k_t are the spin−lattice relaxation rate, the first-order decay rate, and the triplet−triplet annihilation rate of the T_1 porphyrins, respectively. P is an initial spin polarization relative to the thermal equilibrium populations. N_0 is the concentration of the T_1 porphyrin at $t = 0$. A is a proportionality factor.

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(20) The SLR time in toluene was calculated as 4 μs by using the g value[19] of the anion radical of ZnTPP and $\tau_R = 80$ ps with the molecular radius of 5 Å.

(21) The TREPR spectrum of T_1 H_2TPP was observed in toluene at 183K with $D = 1.1$ and $E = 0.24$ GHz, showing the same zfs parameters as those obtained in solid,[2] in contrast to the cases of MgTPP and ZnTPP. Therefore, the results of $E = 0$ GHz observed for MgTPP and ZnTPP are not considered to be due to molecular rotations around the z axis.