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LETTERS

First Observation of the Excited Doublet State of a Radical−Triplet Pair in Solution: W-Band High-Field Time-Resolved Electron Paramagnetic Resonance Spectroscopy

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Using W-band time-resolved EPR (TREPR) (95 GHz), the lowest excited doublet (D_1) state was observed in solution for the first time together with the excited quartet (Q_1) and doublet ground (D_0) states in a complex of MgTPP (TPP; tetraphenylporphyrin) and an axial-ligating *p*-pyridylnitronylnitroxide radical (nit-*p*-py). The *g* value obtained for D_1 was in good agreement with the calculated value. The spin polarization of D_1 varied with time from an emission to an absorption as well as that of Q_1 and D_0. The result shows that the spin polarizations are produced by a radical−triplet pair mechanism with a ferromagnetic coupling ($J > 0$). The sign of the exchange coupling is consistent with that obtained in the X-band TREPR experiment (Fujisawa, J.; Ishii, K.; Ohba, Y.; Yamauchi, S.; Fuhs, M.; Möbius K. *J. Phys. Chem. A* **1997**, *101*, 5869).

1. Introduction

Time-resolved electron paramagnetic resonance (TREPR) spectroscopy exhibits a high ability in detection of short-lived paramagnetic species, such as reaction intermediate radicals and excited triplet (T_1) states, in which nonthermal electron spin polarization (ESP) is used as a probe.[1] So far, very little attention has been paid to studies of excited high-spin states, although novel physical properties are expected to appear.[2] Recently, Corvaja and collaborators and our groups reported investigations of excited quartet (Q_1) and doublet (D_1) states of a radical−excited triplet pair (RTP) by TREPR, where RTP is generated by photoexcitation of a diamagnetic molecule linked to a stable radical using fullerenes and metalloporphyrins.[3,4] These studies have opened a field of molecule-based excited high-spin states and enabled us to elucidate the electronic and magnetic interactions, kinetics, and spin relaxations. In solid phase, Q_1 and D_1 in RTP were detected and the zero-field splitting and spin polarizations due to spin−orbit couplings for Q_1 were evaluated by spectral simulations.[4a,c] On the other hand, in solution, observation of the D_1 state has not been achieved yet.

Two ESP mechanisms, an electron spin polarization transfer (ESPT)[5,6a] and a radical−triplet pair mechanism (RTPM)[5−9] are established in a system of a radical and a triplet. It is reported that the spin polarization of RTP in solution is produced by RTPM with doublet and quartet precursors, where the polarization is inverted with time from an emission of microwaves to an absorption under a ferromagnetic coupling ($J > 0$) and an absorption to an emission under an antiferromagnetic coupling ($J < 0$).[3,4]

In this letter, we have concentrated on observation of the D_1 state in solution by means of W-band (95 GHz) TREPR, where the D_1 signal could be separated from the Q_1 and D_0 signals

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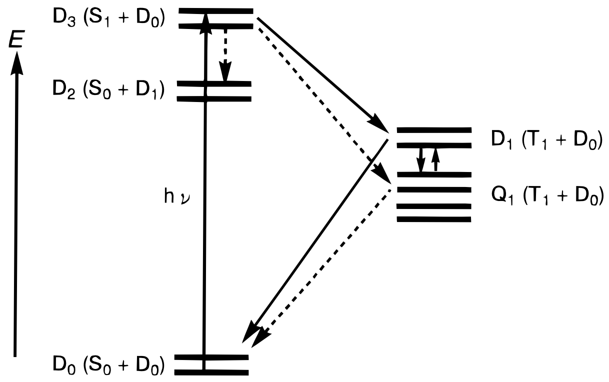
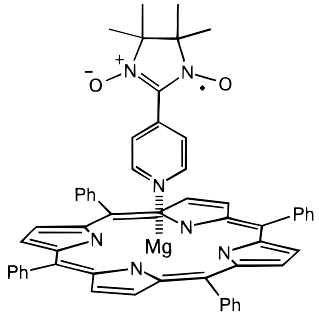


Figure 1. Energy level diagram of the electronic states of the radical complex with $J > 0$ in a finite static magnetic field. The electronic states in parentheses denote the corresponding states of MgTPP and nit-*p*-py.

reported in our previous paper.[4b] An exchange coupling between the radical and triplet was examined from analysis of spin polarizations and compared with that reported in the X-band TREPR experiment.[4b] The examined molecule is MgTPP (TPP; tetraphenylporphyrin) axially coordinated with a *p*-pyridylnitronylnitroxide radical (nit-*p*-py), 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-l*H*-imidazol-1-oxy-3-oxide, as shown below.



The electronic states of the radical complex are shown in Figure 1.[10]

2. Experimental Section

MgTPP[11,12] and nit-*p*-py[13] were synthesized according to methods described in the literature. Spectral-grade toluene (Wako Pure Chemicals) was used as the solvent without further purification. The concentrations of MgTPP and nit-*p*-py were ca. 2×10^{-3} M, where the concentration of the complex is calculated as ca. 1.3×10^{-3} M from the reported equilibrium constant (K_{eq} = ca. 2500 M^{-1})[4b] of the axial ligation. The solution was deaerated by repeated freeze−pump−thaw cycles on a vacuum line.

Time-resolved W-band TREPR measurements were carried out at room temperature using a home-built spectrometer without field modulation. The details of the apparatus have been described previously.[14,15] Photoexcitation was made to the D_3 state of the complex (Figure 1) by the second harmonic (λ = 532 nm) of a Nd:YAG laser (Spectra Physics). *g* values were calculated by use of the standard Mn^{2+}/MgO sample.[15]

3. Results

W-band TREPR spectra were measured at 20−60 ns after the laser pulse in the MgTPP−nit-*p*-py system, as shown in Figure 2. Three kinds of emissive EPR signals are observed in the spectrum (Figure 2a). The first signal consists of five peaks centered at $g = 2.0068 \pm 0.0002$ and has hyperfine splittings of 0.74 ± 0.02 mT. The EPR parameters are in good agreement with those ($g = 2.0067 \pm 0.0002$ and 0.74 ± 0.01 mT) of the nit-*p*-py radical. Therefore, this signal is readily assigned to that of the D_0 state of the complex and/or free nit-*p*-py. The second signal is observed at $g = 2.0042 \pm 0.0002$ with a full-width at half maximum ($\Delta B_{1/2}$) of 1.5 ± 0.2 mT. These parameters agree well with the reported values[4b] of the Q_1 signal, and the second signal is attributed to the Q_1 state. The quartet signal has been found to be due to the transition of $|Q + {}^1/_2\rangle \rightleftarrows |Q - {}^1/_2\rangle$ from a spectral simulation based on the hyperfine splittings.[4b] The transitions of $|Q \pm {}^3/_2\rangle \rightleftarrows |Q \pm {}^1/_2\rangle$ are expected to exhibit a much broader spectrum owing to insufficient averaging of the zero-field splitting by molecular motion. The third signal is observed at a higher field than the Q_1 signal and is very weak compared to the Q_1 and D_0 signals, as obviously displayed in Figure 2b. In order to obtain the *g* value and line width of the third signal, a simulation of the overall spectrum was carried out using a Gaussian line shape and the obtained EPR parameters of the D_0 and Q_1 signals, where the intensity ratio of the hyperfine sublevels in the D_0 signal is 1:2:3:2:1, as shown in Figure 2. The *g* value and line width ($\Delta B_{1/2}$) of the third signal were obtained to be 2.0016 ± 0.0002 and 2.8 ± 0.2 mT, respectively. Although the line widths obtained at earlier gate times are affected by microwave effects,[1] the line width of the third signal is certainly larger than that of the Q_1 signal.

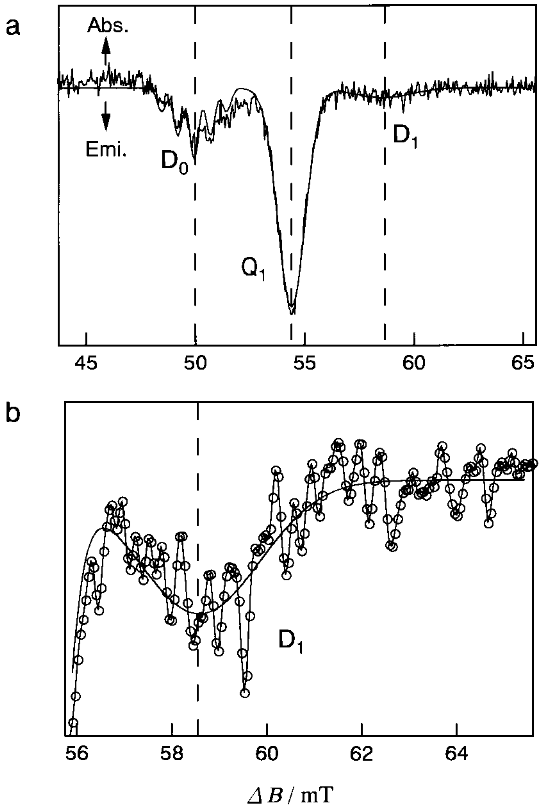


Figure 2. (a) W-band TREPR spectrum observed at 20−60 ns after the laser pulse in the MgTPP and nit-*p*-py complex and the simulation curve (—). The vertical dotted lines describe the fields at $g = 2.0068$, 2.0042, and 2.0016. (b) TREPR spectrum (○) obtained under the same condition with more averaging, and the simulation curve (—). The details of the simulation are described in the text. ΔB measures the deviation from the center field B_0 = 3.336T.

Time profiles of the three signals were measured, as shown in Figure 3. It is found that the spin polarizations of all the signals are emissions at earlier times and inverted to absorptions at later times.

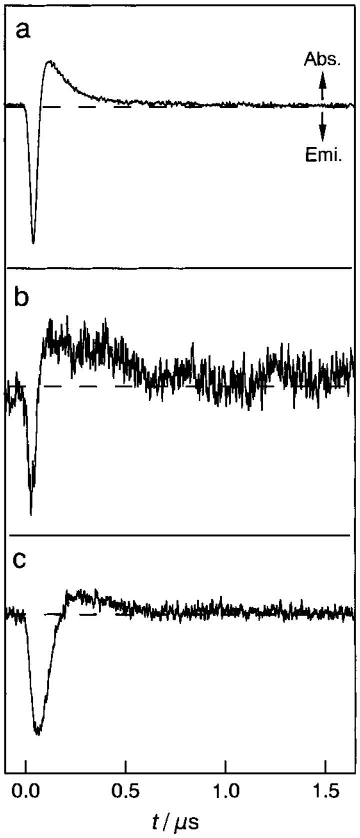


Figure 3. Time profiles of the W-band EPR signals of the (a) Q_1, (b) D_1, and (c) D_0 states in the MgTPP and nit-*p*-py complex.

4. Discussion

We first assign the third signal observed at $g = 2.0016 \pm 0.0002$. In the radical-ligated porphyrin, four excited states, Q_1, D_1, D_2, and D_3 should be considered as candidates for giving the signals (Figure 1). D_2 and D_3 are expected to decay much faster than the time resolution of the spectrometer (20 ns), because of their spin-allowed characters of transitions to D_0. Thus, involvement of the D_2 and D_3 states can be reasonably ruled out. The *g* values of the Q_1 and D_1 states in RTP are calculated by the following equations, using the *g* values of nit-*p*-py (g_R) and triplet MgTPP (g_T)[4]

$$g(Q_1) = (g_R + 2g_T)/3 \tag{1}$$

$$g(D_1) = -(g_R - 4g_T)/3 \tag{2}$$

Equation 2 is adequate under the condition that the D_1 spin function is approximately expressed by a coupled product of the triplet and doublet spin functions, as described later. The g_T value was calculated from g_R, $g(Q_1)$, and eq 1 as 2.0029 ± 0.0002, in accordance with the reported value (2.003).[4b] By using g_T and g_R, the *g* value of D_1 is estimated to be 2.0016, which is in very good agreement with the experimental value (2.0016 ± 0.0002) of the third signal. On the basis of this result, it is concluded that the third signal is ascribed to the D_1 state.[16] It is found from the above equations that the difference between $g(D_1)$ and g_R is 2 times larger than that between $g(Q_1)$ and g_R, which is consistent with the experimental values.

The spin polarizations of the three states, Q_1, D_1, and D_0, are found to be inverted with time from emissions to absorptions. A schematic diagram of the radical−triplet pair mechanism (RTPM) with a ferromagnetic coupling ($J > 0$) is shown in Figure 4. The RTPM mixing between $|D_1 - {}^1/_2\rangle$ and $|Q_1 + {}^3/_2\rangle$ by the triplet dipolar coupling gives rise to spin-sublevel dependence in all nonradiative transitions, by which the Q_1, D_1, and D_0 states are spin-polarized emissively at earlier times and absorptively at later times.[18] Similarly, the RTPM polarization with $J < 0$ varies with time from an absorption to an emission. Thus, the observed spin polarizations of the Q_1, D_1, and D_0 states are interpreted by RTPM with $J > 0$. This conclusion is consistent with that from the X-band experiments.[4b] It is the first time that RTPM is demonstrated in a RTP system by observing the spin polarizations of Q_1, D_1, and D_0. The nonradiative transition from D_3 to Q_1 is also considered to produce an emissive spin polarization by anisotropic spin−orbital couplings (SOC) of MgTPP.[4a,c] Such polarizations are, however, negligibly small in the W-band EPR region because the zero-field splitting ($D \approx 3 \times 10^8$ Hz)[4a,c] for the Q_1 state of the complex is much smaller than the Zeeman energy ($\sim 10^{11}$ Hz).[19] On the other hand, the RTPM polarization does not decrease in the same way, because RTPM mixings between Q_1 and D_1 occur close to the level-crossing region. It is interesting that a ferromagnetic coupling is present for RTP of MgTPP−nit-*p*-py in both magnetic fields of ~340 mT for the X-band and ~3400 mT for the W-band experiment. This result definitively shows that the Q_1 state is more stable in energy than the D_1 state in this system, as shown in Figure 1, and also supports the exchange coupling mechanism proposed in our previous paper.[4b]

Next we discuss the nonradiative transitions between D_1 and other doublet states of D_0, D_2, and D_3. The spin Hamiltonian for exchange couplings among three unpaired electrons is expressed by

$$H_{ex} = -J_1 S_{T1} S_{T2} - J_2 S_{T1} S_R - J_3 S_{T2} S_R \tag{3}$$

In this system, J_1 is estimated from absorption and phosphorescence spectra of the complex as ca. 4000 cm^{-1}.[10] Under the condition of $|J_1| \gg |J_2 - J_3|$, the transition from D_1 to D_0 is no longer totally spin-allowed, because the D_1 spin function is approximated by a coupled product of the triplet and doublet

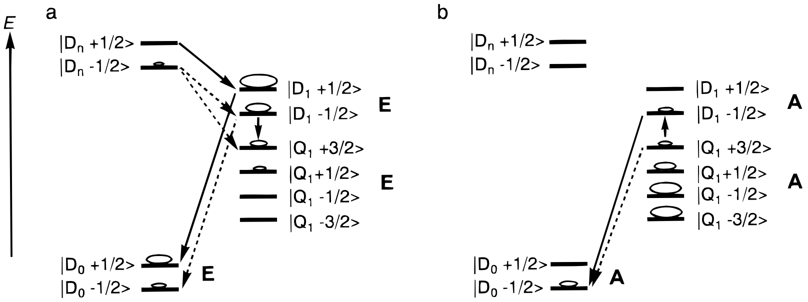


Figure 4. Schematic diagram of RTPM processes with $J > 0$ at (a) earlier times and (b) later times after the laser excitation. E and A (bold) stand for an emission and an absorption of microwave, respectively.

spin functions, as reported by Hoytink.[20] In contrast, the internal conversions from D_2 and D_3 to D_0 are spin allowed. This fact explains why the lifetime of D_1 is longer than those of D_2 and D_3. The intrinsic decay of D_1 is, however, reasonably expected to be faster than the spin-forbidden intersystem crossing from Q_1 to D_0 due to the partially spin-allowed nature of the D_0-D_1 transition. In Figure 3, it is shown that the decay rate of the absorptive polarization of D_1 is almost the same as that of Q_1. The result indicates that the decay kinetics of D_1 is not only determined by the internal conversion to D_0, but also by thermal population from the metastable Q_1 state. The thermal population mainly occurs via a mixing between $|Q + {}^3/_2\rangle$ and $|D - {}^1/_2\rangle$ by the triplet dipolar coupling of MgTPP, generating an absorptive RTPM polarization, as described before. This result supports our assignment of the spin polarizations to RTPM.

The larger line width (2.8 mT) of the D_1 signal observed and compared with that (1.5 mT) of Q_1 can be explained by lifetime broadening of the D_1 state with a faster decay. The weak signal observed for D_1 is partially attributed to the fact that the transition probability of D_1 is 4 times smaller than that of Q_1 ($\langle S^+{}_{|Q+1/2\rangle \rightleftarrows |Q-1/2\rangle}\rangle^2 = 4$ and $\langle S^+{}_D\rangle^2 = 1$). Detailed analysis of the EPR time profiles including time-dependence and/or distribution of J is necessary for quantitative discussion about kinetics and spin relaxations, which will be given elsewhere.

5. Conclusion

We succeeded in observing the EPR signal of D_1 separate from those of Q_1 and D_0 for the radical-ligated porphyrin in solution by W-band TREPR spectroscopy. The assignment of the D_1 signal was made on the basis of good agreement between the calculated and observed g values. The line width of the D_1 signal was shown to be larger than those of Q_1 and D_0. The observation of the EPR signals of the three states allowed us to confirm the RTPM more confidently. The exchange coupling between the triplet and radical was found to be ferromagnetic in the W-band field region, analogous to that in X-band EPR.

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(16) In this system, free MgTPP is also excited and T_1 MgTPP is generated. However, the T_1 MgTPP signal has a g value of 2.0029 and a line width of ~10 mT, which denies assignment of the third signal to T_1 MgTPP.[17]

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(18) The nonradiative transition of $|D_1 - {}^1/_2\rangle$ with D_0 or D_n becomes slower than that of $|D_1 + {}^1/_2\rangle$ owing to the mixing with $|Q_1 + {}^3/_2\rangle$. On the other hand, the nonradiative transition of $|Q_1 + {}^3/_2\rangle$ with D_0 or D_n is faster than those of other quartet sublevels owing to the mixing with $|D_1 - {}^1/_2\rangle$.

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