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A Time-Resolved Electron Paramagnetic Resonance Study on the Excited States of Tetraphenylporphinatozinc(II) Coordinated by *p*-Pyridyl Nitronyl Nitroxide

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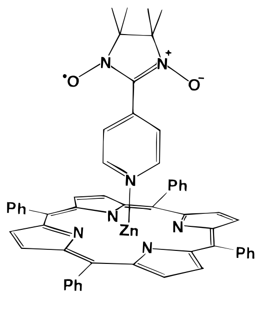
We report the first time-resolved electron paramagnetic resonance (TREPR) spectrum of a molecule having two paramagnetic centers composed of an excited triplet and a radical in toluene glass. The spectrum is analyzed as those of the excited doublet (D_1) and quartet (Q_1) states.

A TREPR technique is very useful for detection of paramagnetic intermediate species of photoreactions, such as radicals, radical pairs, and precursor excited triplet states, which are usually produced from diamagnetic molecules and show CIDEP (chemically induced dynamic electron polarization) effects. There are, however, very few CIDEP studies on spin-multiplet intermediates produced from paramagnetic molecules.[1,2] If such species are investigated by means of EPR, we will obtain novel information which is very important to evaluate the properties. Recently several works on interactions between excited triplets and stable radicals have been reported in relation to new types of CIDEPs, a radical-triplet pair mechanism[3] and an electron spin polarization transfer mechanism.[4] A direct observation of a transient radical-triplet pair (RTP) has, however, not yet been reported in these studies. The only candidate for a RTP reported so far is an excited quartet state of a covalently linked molecule of C_{60} with a nitroxide radical.[2] The transient EPR spectrum was observed in liquid phase and characterized by decreases in a hyperfine coupling constant and a *g* value as compared with those of the ground state. In this system only a transition between $|^1/_2\rangle$ and $|-^1/_2\rangle$ was observed and no information is obtained for zero-field splitting (zfs) values.

We here report a first TREPR study on excited states of a RTP in the solid phase. The examined molecule is tetraphenylporphinatozinc(II) (ZnTPP) coordinated by *p*-pyridyl nitronyl nitroxide (nitpy) (ZnTPP−nitpy). The TREPR spectra are analyzed by zfs and *g* values of the RTP.



Coordination of nitpy to ZnTPP was checked by observing absorption spectra, from which an equilibrium constant was estimated as 4.9(±1.5) × 10^3 M^{-1} at room temperature. Samples were deaerated by the freeze−pump−thaw method. Concentrations of ZnTPP and nitpy were (1−5) × 10^{-3} and 1 × 10^{-2} M, respectively, where coordination was almost completed even at room temperature (>96%). TREPR measurements were carried out at 20−40 K on a JEOL-FE2XG EPR spectrometer using an Oxford ESR 900 helium gas flow system. Samples were excited at 585 nm by a Lambda Physik LPD3000 dye laser pumped with a Lambda Physik LPX100i excimer laser. The details of the TREPR measurements have been reported elsewhere.[5]

A TREPR spectrum was observed for ZnTPP−nitpy in toluene glass at 0.5 μs and 20 K, as shown in Figure 1a. Three kinds of signals were observed; one is an outer pair of signals (I) giving an *A*/*E* pattern, which shows an absorption (*A*) and an emission (*E*) of microwave at low-field (291 mT) and high-field sides (356 mT), respectively. The second is an inner pair of signals (II) which appear at 307 and 342 mT, also showing the *A*/*E* pattern. The third emissive peak (III) was observed at $g(E) = 1.999 \pm 0.002$ similar to a radical peak. At lower concentrations (<5 × 10^{-3} M) of nitpy, relative intensities of the outer pair peaks increased, which indicates that uncoordinated ZnTPP gives the outer pair of peaks and that the inner pair of peaks and the central peak come from ZnTPP−nitpy. This interpretation is consistent with the obtained equilibrium constant (4.9 × 10^3 M^{-1}). The remaining very weak outer peaks (I) at the higher concentration of nitpy are considered to be due to a photoproduct and/or a diamagnetic impurity from nitpy. As a reference, the TREPR spectrum of ZnTPP coordinated by pyridine (ZnTPP−py)[5,6] was observed as shown in Figure 1d, where the characteristic features closely resemble the outer pair signals in Figure 1a.

We next observed a TREPR spectrum at 25 μs (Figure 1b), which provides totally absorptive broad and sharp peaks near the fields of signals II and III in the early time spectrum (Figure 1a). It was, however, found for the central peak that the polarity (*A*) and resonance field ($g(A) = 2.004 \pm 0.001$) vary with time. These absorptive signals are observed for a long period (>1 ms) and are considered to be due to the Boltzmann distribution. The observed *g* values of the central peaks are different from *g* of ZnTPP−nitpy in the ground state (D_0; $S_0 + D_R$), $g(D_0) = 2.007 \pm 0.001$. D_R denotes the ground state of nitpy.

As a result, three kinds of signal were observed for ZnTPP−nitpy; the first is the pair peaks of *A*/*E* type, the second is the radical type ($g = 1.999$) with *E* polarization, and the third is the radical type ($g = 2.004$) with *A* polarization. We discuss these signals in terms of those of the excited doublet and quartet states of ZnTPP−nitpy.

When the magnitude of an exchange interaction (>1 cm^{-1})[7] is much larger than that of the Zeeman interaction (∼10^{-1} cm^{-1}) and the magnetic dipolar−dipolar interaction (∼10^{-2} cm^{-1}), the *g* values of the quartet (Q) and doublet (D) states for RTP are given by[8]

$$g(\mathrm{Q}) = {}^1/_3 g(\mathrm{R}) + {}^2/_3 g(\mathrm{T}) \qquad (1)$$

and

$$g(\mathrm{D}) = -{}^1/_3 g(\mathrm{R}) + {}^4/_3 g(\mathrm{T}) \qquad (2)$$

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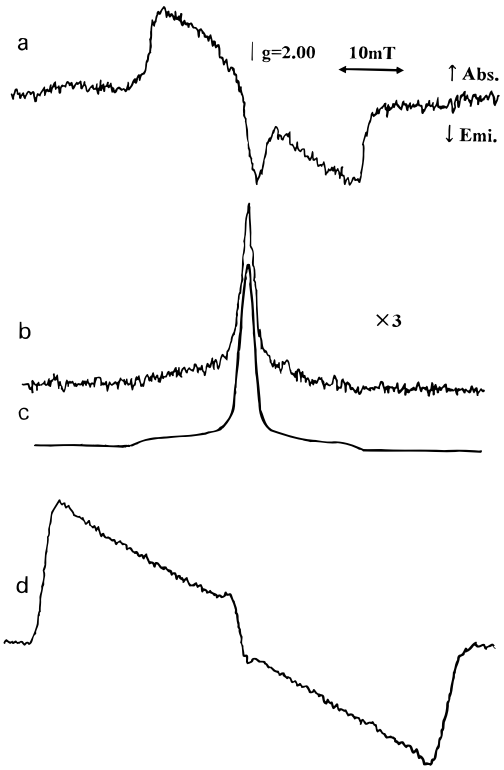

Figure 1. TREPR spectra of ZnTPP−nitpy at 0.5 (a) and 25 μs (b) and ZnTPP−py at 0.5 μs (d). All the spectra were observed at 20 K. (c) The simulated spectrum of the quartet state with EPR parameters, $D = 0.25$ and $E = 0.08$ GHz under the Boltzmann distribution.

A D value of the Q state is obtained from the equations[9] for low (l) and high (h) resonance fields at $B//z$ as,

$$B_z(\mathrm{l}) = (h\nu - 2D)/g_{zz}(\mathrm{Q}_1)\beta \tag{3}$$

and

$$B_z(\mathrm{h}) = (h\nu + 2D)/g_{zz}(\mathrm{Q}_1)\beta \tag{4}$$

Among the lower excited states, the $D_2(S_1 + D_R)$ state, which is expected to have a very short lifetime (<3 ns = the lifetime of S_1 ZnTPP),[10] would easily be missed in our TREPR experiment (time resolution of 100 ns). Two other radical-type transitions between the $|^1/_2\rangle$ and $|-^1/_2\rangle$ levels in both the D_1 and $Q_1(T_1 + D_R)$ states are possibly observed. Here, we tentatively assign our two radical-type signals to these transitions. From eqs 1 and 2, $g(Q_1)$ and $g(D_1)$ are calculated as 2.001 ± 0.003 and 1.995 ± 0.003, respectively, from the g values of the triplet and the radical. Here the middle components of the anisotropic g values are used for g(R) (2.007 ± 0.001)[11] and g(T) (1.998 ± 0.003), because the observed peaks are unresolved. By comparing these values with observed $g(E) = 1.999 \pm 0.002$ and $g(A) = 2.004 \pm 0.001$, the fast- and slow-decaying components are attributed to the $|^1/_2\rangle - |-^1/_2\rangle$ transitions in the D_1 and the Q_1 states, respectively. The longer decay time (>500 μs) is consistent with the phosphorescence decay of this system (4.3 ms). The faster decay in the D_1 state is justified in that the D_1-D_0 transition is a spin-allowed process.

The remaining broad pair signals of the *A*/*E* type are certainly assigned to those of the $|^1/_2\rangle - |^3/_2\rangle$ and $|-^1/_2\rangle - |-^3/_2\rangle$ transitions in the Q_1 state. From the observed stationary fields at $H//z$ (307 and 342 mT) and eqs 3 and 4, the $|D|$ value is obtained as 0.25 GHz, which is much smaller than that (0.912 GHz) of triplet ZnTPP−py. The validity of this value is checked by a simple calculation of D in the Q_1 state using the following equation:[8]

$$D(\mathrm{Q}_1) = {}^1/_3D(\mathrm{T}_1) + {}^1/_3D(\mathrm{RT}_1) \tag{5}$$

The value of $D(\mathrm{RT}_1)$ is calculated as −0.214 GHz using a point charge approximation,[12] where we used the HOMO and LUMO of ZnTPP,[5] the SOMO of nitpy,[13] and the structure of ZnTPP−nitpy.[14] The calculation indicates that the fine structure z axes are almost parallel to the out of plane z axis of ZnTPP. The D value in the Q_1 state is estimated as 0.233 GHz from eq 5 with $D(\mathrm{T}_1) = 0.912$ GHz and $D(\mathrm{RT}_1) = -0.214$ GHz. This value is in good agreement with the obtained $|D|$ value (0.25 GHz). We, therefore, conclude that the observed spectrum comes from the quartet state with $D = 0.25$ GHz. The E value is estimated as $|E| \approx {}^1/_3D$ (= 0.08 GHz) from the observed spectral pattern.[9] In Figure 1c we show the simulated EPR spectrum for the randomly oriented quartet state under the Boltzmann distribution.[15] This spectrum is consistent with the observed spectra at 0.5 and 25 μs.

Preliminary experiments were also made on ZnTPP coordinated by *m*-pyridyl nitronyl nitroxide, in which $|D|$ was obtained as 0.22 GHz being consistent with the calculated value, $D = 0.224$ GHz.[12] To obtain and produce more detailed discussion, the simulation of whole the spectrum including polarizations is now in progress.

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(12) $D(\mathrm{RT}_1)$ is calculated by the following equation, $D(\mathrm{RT}_1) = \langle\phi_{\mathrm{a2u}}(i)\phi_{\mathrm{R}}(j)|H_{\mathrm{D}}|\phi_{\mathrm{a2u}}(i)\phi_{\mathrm{R}}(j)\rangle + \langle\phi_{\mathrm{eg}}(i)\phi_{\mathrm{R}}(j)|H_{\mathrm{D}}|\phi_{\mathrm{eg}}(i)\phi_{\mathrm{R}}(j)\rangle$, where ϕ_{a2u}, ϕ_{eg}, and ϕ_{R} denote HOMO and LUMO of ZnTPP and SOMO of nipty, respectively. H_{D} is the zfs Hamiltonian.[5]

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