Relationship between the Excited Multiplet EPR and Phosphorescence Lifetime in the Excited Triplet Octaethylporphinatozinc Coordinated by One TEMPO Radical

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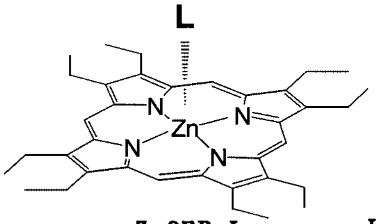
By the combined use of time-resolved electron paramagnetic resonance (TREPR) and phosphorescence emissions, two kinds of octaethylporphinatozinc coordinated by an axial ligand containing a nitroxide radical have been investigated.

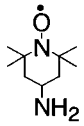
Interactions between chromophores in the excited state and other paramagnetic molecules result in some important photophysical and photochemical processes, such as quenching of chromophores in the excited state,[1] generation of excited singlet oxygen,[2] and photocontrol of magnetic properties.[3] A time-resolved electron paramagnetic resonance (TREPR) method, which is a powerful technique for observing paramagnetic intermediates after photoexcitation, has been shown to be useful for investigating the interactions between a molecule in the lowest excited triplet (T_1) state and stable radicals.[4–6] Recently, using TREPR, several systems consisting of a chromophore bonded to nitroxide radicals have been studied to directly examine the interactions.[3,7–9] Since the TREPR spectra are easily attributed to the T_1 state or excited multiplet states, the lowest excited doublet (D_1) and quartet (Q_1) states consisting of the T_1 chromophore and doublet nitroxide, they would be suitable for discriminating whether or not an electron exchange interaction between the T_1 chromophore and doublet nitroxide is much smaller than the zero field splitting (zfs). To confirm the TREPR assignments, it is necessary to check how the small electron exchange interaction which results in the T_1 TREPR spectrum affects the lifetime of the T_1 chromophore. However, the relationship between the TREPR spectra and phosphorescence lifetimes has not been clarified.

In this report, we have studied octaethylporphinatozinc (ZnOEP) coordinated by 4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy (ATEMPO) or 4-[((2,2,6,6-tetramethyl-1-oxy-piperidin-4-yl)oxy)carbonyl]pyridine (PTEMPO) by the combined use of TREPR and phosphorescence emission. In comparison with a pyridine complex (ZnOEP-Py), the relationship between the TREPR and phosphorescence lifetime is clarified.

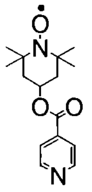
ZnOEP and PTEMPO were synthesized according to the methods previously reported.[9–11] ATEMPO and pyridine were purchased from Aldrich Chemical Co. and Wako Pure Chemical Industries, respectively. Spectral grade toluene (Nacalai Tesque Inc.) was used as the solvent for all measurements. All samples were deaerated by freeze-pump-thaw cycles.[12] Steady-state emission spectra were recorded with a Hitachi F-4500 fluorescence spectrometer. Phosphorescence lifetimes were measured by using a monochromator (JASCO CT-25CP) and a photomultiplier (Hamamatsu Photonics R446). TREPR measurements were carried out at 20 K on a Bruker ESP 300E spectrometer.[8] An Oxford ESR 900 cold gas flow system was used for controlling the temperature. For the phosphorescence lifetime and TREPR measurements, samples were excited at 532 and 575 nm by a Nd:YAG laser (Spectra Physics INDI 30) and a dye laser (Lumonics HD 500) pumped with an excimer laser (Lumonics EX 500), respectively, and the signals were integrated using a digital oscilloscope (Iwatsu-LeCroy LT342 or LeCroy 9450A).



ZnOEP-L



L: ATEMPO



PTEMPO

TREPR spectra of ZnOEP-ATEMPO, ZnOEP-PTEMPO, and ZnOEP-Py at 20 K are shown in Figure 1. The TREPR spectra of ZnOEP-PTEMPO and ZnOEP-Py are almost identical, and were reproduced using zfs parameters D = 1.10 GHz and E = 0.085 GHz. This similarity indicates that the electron exchange interaction between the T_1 ZnOEP and PTEMPO radical is much smaller than the D value.[9] The *A/E* polarization patterns (*A/E* denotes absorption (*A*) and emission (*E*) of the microwave at the lower and higher magnetic field sides, respectively) are interpreted by selective intersystem crossing (ISC) to the z sublevel of the T_1 state (z is an out of plane axis) due to spin-orbit coupling (SOC) of d_π orbitals on the zinc ion.[13]

On the other hand, the TREPR spectrum of ZnOEP-ATEMPO is clearly different from those of ZnOEP-Py and ZnOEP-PTEMPO, indicating a significant interaction between the T_1 ZnOEP and doublet nitroxide. This spectrum shows an *AAE* polarization pattern. In comparison with the calculated g and D values, the central A ($g = 2.000 \pm 0.0015$) and outer *A/E* signals are reasonably assigned to the D_1 and Q_1 states, respectively, which consist of the T_1 ZnOEP and doublet ATEMPO radical.[14–16] The Q_1 TREPR spectrum was well reproduced using D = 0.265 GHz, E = 0.085 GHz, and selective ISC to the ±1/2 sublevels of the Q_1 state, which is explained by the SOC of d_π orbitals on the zinc ion in analogy with the T_1 ZnOEP system.[8]

Steady-state emission spectra of ZnOEP-ATEMPO, ZnOEP-PTEMPO, and ZnOEP-Py at 77 K are shown in Figure 1. While both fluorescence (570–680 nm) and phosphorescence emissions (680–800 nm) are seen for all complexes, the phosphorescence intensity of ZnOEP-ATEMPO is much weaker than those of ZnOEP-Py and ZnOEP-PTEMPO. In order to discuss the results quantitatively, phosphorescence lifetimes were measured. Phosphorescence decays of the PTEMPO and Py complexes could be analyzed with single-exponential functions (Figure 1), and their lifetimes are similar within the exper-

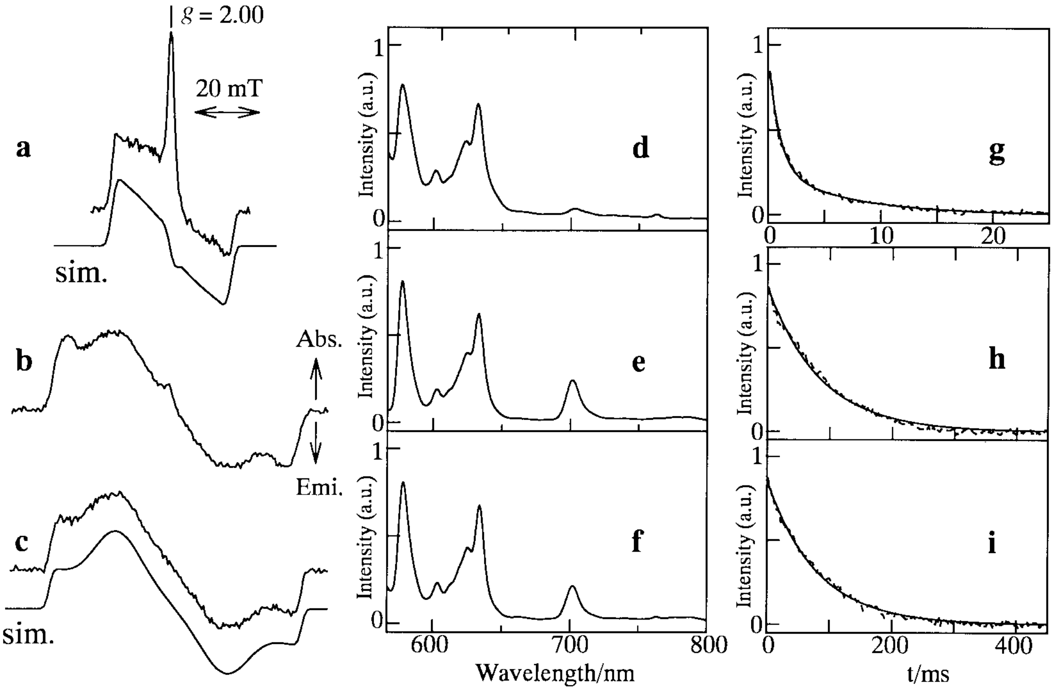


Figure 1. TREPR spectra (**a**, **b**, **c**), emission spectra (**d**, **e**, **f**), and phosphorescence decays (broken lines: **g**, **h**, **i**) of ZnOEP-ATEMPO (**a**, **d**, **g**), ZnOEP-PTEMPO (**b**, **e**, **h**), and ZnOEP-Py (**c**, **f**, **i**) with simulations (**a**, **c**) and fitted curves (solid lines: **g**, **h**, **i**).

imental error (ZnOEP-Py = 79 ms, ZnOEP-PTEMPO = 84 ms). That is, it is clearly demonstrated that the phosphorescence decay is not influenced by the small electron exchange interaction which results in the T_1 TREPR spectrum. On the other hand, the phosphorescence decay of ZnOEP-ATEMPO was analyzed with a double-exponential function (1.1 and 6.9 ms), which is much faster than that of ZnOEP-Py. The double-exponential decay and short lifetime are reasonably explained by generation of $Q_1 \rightarrow D_0$ and $D_1 \rightarrow D_0$ transitions (D_0: the doublet ground state) without the rapid averaging between the D_1 and Q_1 states,[17] which are consistent with the D_1 and Q_1 formations confirmed by the TREPR.

In conclusion, we have shown that the excited multiplet TREPR spectra correlated well with the phosphorescence lifetimes. This relationship is useful for understanding the photophysical properties of the radical-triplet pair.

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References and Notes

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12 It is found by changing concentration of pyridine (= 0–10^{-2} mol dm^{-3}) that fluorescence and phosphorescence peaks of ZnOEP (S_1 = 573.5 nm, T_1 = 694 nm) are obviously different from ZnOEP-Py (S_1 = 578 nm, T_1 = 701.5 nm). Therefore, it could be confirmed by emission spectra that coordination of axial ligands was completed in our experimental conditions ([ZnOEP] = 1×10^{-4} mol dm^{-3}, [L] = 1×10^{-3} mol dm^{-3}).
13 An weak *A* signal observed at g = 2.006 ± 0.0015 is assigned to the doublet ground state.
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15 g Values of the D_1 and Q_1 states were calculated as 2.001 and 2.005 by $\{-g(\mathrm{R}) + 4g(\mathrm{T_1})\}/3$ and $\{g(\mathrm{R}) + 2g(\mathrm{T_1})\}/3$, respectively, where the $g(\mathrm{R})$ and $g(\mathrm{T_1})$ denote the g values of the T_1 ZnOEP and doublet nitroxide radical (= 2.006), respectively.[8,14] The $g(\mathrm{T_1})$ value was evaluated as 2.002 by reference to the previous study.[8]
16 The D value of the Q_1 state was calculated as 0.28 GHz by $\{\boldsymbol{D}(\mathrm{T_1}) + \boldsymbol{D}(\mathrm{RT_1})\}/3$, where the $\boldsymbol{D}(\mathrm{T_1})$ and $\boldsymbol{D}(\mathrm{RT_1})$ denote the matrix of the excited triplet and magnetic dipole–dipole interactions between the T_1 ZnOEP and nitroxide radical, respectively.[8,14] The $\boldsymbol{D}(\mathrm{T_1})$ was evaluated from the TREPR spectrum of ZnOEP-Py, while the $\boldsymbol{D}(\mathrm{RT_1})$ was calculated under a point charge approximation.[8]
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