Experimental Evidence for a Selection Rule of Intersystem Crossing to the Excited Quartet States: Metallophthalocyanines Coordinated by 4-Amino-TEMPO

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Metallophthalocyanines (MPcs; M = Zn, Mg) coordinated by 4-amino-TEMPO (ATEMPO) in the excited quartet (Q_1) state, which are constituted by the excited triplet MPc and doublet ATEMPO, have been studied by a time-resolved electron paramagnetic resonance (TREPR) method. Two components were observed for both the Zn and Mg complexes, and are reasonably assigned to the Q_1 and doublet states by calculating the zero field splitting and *g* value, respectively. The polarization pattern of the Q_1 ZnPc-ATEMPO is *A*/*E*, and is opposite to that (*E*/*A*) of the Q_1 MgPc-ATEMPO, where the *A* and *E* denote absorption and emission of the microwaves, respectively. The Q_1 TREPR spectrum with the *E*/*A* polarization has been observed for the first time. The *A*/*E* and *E*/*A* polarization patterns are reproduced by selective intersystem crossing (ISC) to $|Q_1,\pm1/2'\rangle$ and to $|Q_1,\pm3/2'\rangle$, respectively. The selective ISC to $|Q_1,\pm1/2'\rangle$ is reasonably explained by the *z* component of SOC between the Q_1 and higher excited doublet states, while the ISC to $|Q_1,\pm3/2'\rangle$ originates from the *x* and *y* components of SOC. These experiments have proved that the selectivity of ISC to the Q_1 state is dependent on the components of SOC.

Introduction

Recently, chromophores covalently linked to or coordinated by stable nitroxide radicals have been studied with respect to two features.[1−3] The first is the observation of the excited multiplet states using time-resolved electron paramagnetic resonance (TREPR),[1,2] which is a useful method for investigating photoreaction intermediates, radicals and photoexcited triplet species. Although photoexcited triplet species, which are diamagnetic in the ground state, have been intensively examined,[4−6] there had been few TREPR studies on photoexcited multiplet species, which are paramagnetic in the ground state.[7] Recently, the excited quartet (Q_1) TREPR spectrum in solution has been observed for C_{60} covalently linked to a nitroxide radical for the first time.[1] Further, the Q_1 and excited doublet (D_1) states in the solid state have been observed for tetraphenylporphinatozinc coordinated by a nitronyl nitroxide radical (ZnTPP−nitpy).[2a,2c] These are not only important samples for establishing methods for evaluating the excited multiplet states, but also direct information of spin−sublevel dependence of quenching the excited singlet (S_1) and triplet (T_1) chromophores.[1,2,8] The second feature is photoinduced population transfer (PIPT) observed for phthalocyaninatosilicon covalently linked to two TEMPO radicals.[3] This PIPT is an interesting phenomenon as a new concept for controlling magnetic properties by photoexcitation.

In the former objectives, further examinations need to understand a selection rule of intersystem crossing (ISC) to the Q_1 state as follows. The Q_1 TREPR spectra of the ZnTPP−nitpy systems in the solid state have been observed with an *A*/*E* polarization pattern,[2a] where the *A* and *E* denote absorption and emission of the microwaves at the lower and higher magnetic fields, respectively. This *A*/*E* polarization is reproduced by selective ISC from the higher excited doublet (D_n) state to $|Q_1,\pm1/2'\rangle$ sublevels, which is reasonably interpreted by the *z* component (*z*: a fine structure axis) of spin−orbit coupling (SOC) between the D_n and $|Q_1,\pm1/2'\rangle$.[2c,9] Although an *E*/*A* polarization pattern should be observed by selective ISC to $|Q_1,\pm3/2'\rangle$ due to the *x* and *y* components of SOC, any Q_1 TREPR spectra with the *E*/*A* polarization has not been observed yet. Therefore, to establish the selection rule of ISC to the Q_1 state, it is necessary to examine a system having the *x* and *y* components of SOC and to confirm the *E*/*A* polarization.

In this report, we have studied tetra-*tert*-butylated metallophthalocyanines (MPcs; M = Zn and Mg) coordinated by a 4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy (ATEMPO) radical, as shown in Figure 1.[10] These complexes are appropriate to investigate effects of SOC for the following reasons. (1) While ISC from the S_1 state to the T_1 state occurs due to the *z* component of SOC for ZnPc, it is promoted by the *x* and *y* components of SOC for MgPc.[11] Since the fine structure *z* axis of the Q_1 state is almost parallel to that of the T_1 state, components of SOC can be selected easily. (2) The coordination structure of the Zn complex is similar to that of the Mg complex. (3) Since the energy of the excited doublet TEMPO is much higher than those of the S_1 and T_1 MPc,[8b,10] we can extract only effects of a TEMPO radical on the ISC from the S_1 to T_1 MPc. We have succeeded in observing an *E*/*A* polarization for the Q_1 MgPc−ATEMPO, while the Q_1 ZnPc−ATEMPO has an *A*/*E* polarization. Herein we prove experimentally that ISC from the D_n to Q_1 state is dependent on the components of SOC, and that ISC to $|Q_1,\pm1/2'\rangle$ is selective due to the *z* component of SOC, while selective ISC to $|Q_1,\pm3/2'\rangle$ is generated by the *x* and *y* components of SOC.

Experimental Section

ZnPc and MgPc were synthesized following the methods already reported.[12] ATEMPO and pyridine (py) were purchased from Tokyo Chemical Industry Co., Ltd. and Wako Pure Chemical Industries Ltd., respectively. Spectral grade toluene

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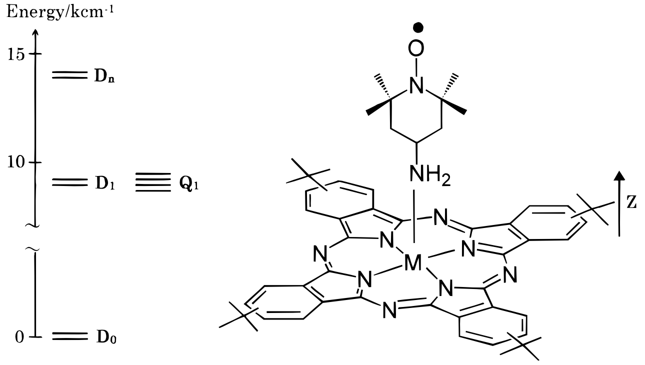

Figure 1. Molecular structure of MPc−ATEMPO (M = Zn, Mg) and the energy diagram. The D_1 and Q_1 states are constituted by the excited triplet MPc and doublet ATEMPO. The D_n state is constituted by the excited singlet MPc and doublet ATEMPO. The D_0 state is the doublet ground state of MPc−ATEMPO.

(Nacalai Tesque Inc.) was used as a solvent. The concentrations of MPcs were 1×10^{-4} and 1×10^{-3} M for ZnPc and MgPc, respectively. The concentration of ATEMPO was 3−10 times higher than that of the corresponding MPc. All samples were deaerated by freeze−pump−thaw cycles, and were examined under conditions where TREPR signals of MPc without an axial ligand, py or ATEMPO, were absent.

TREPR and steady-state EPR measurements were carried out at 20 K on a Bruker ESP 300E spectrometer.[2d,3] An Oxford ESR 900 cold gas flow system was used for controlling temperature. Samples were excited at 585 nm by a Lumonics HD 500 dye laser pumped with a Lumonics EX 500 excimer laser. The TREPR signals from the EPR unit were integrated using a LeCroy 9450A oscilloscope.

Results and Discussion

TREPR spectra of ZnPc−py and MgPc−py with their simulations are shown in Figures 2a and 2b, respectively. The *A*/*E* polarization pattern is observed for ZnPc−py, and is reproduced by selective ISC to T_{1z} sublevel (P_x: P_y: P_z = 0: 0: 1; P_i denotes population ratio of the T_{1i} sublevel). This selectivity originates from the *z* component of SOC, and the P_z is expressed as follows.[13,14]

$$P_z \propto |\langle \Psi_{Tz}|H_{SOz}|\Psi_S\rangle|^2 \qquad (1)$$

Here, Ψ_S and Ψ_{Tz} are the wave functions of the S_1 and T_{1z}, respectively. H_{SOz} denotes a Hamiltonian of the *z* component of SOC. Since this direct SOC is effective due to the d_π orbitals of zinc, $P_z > P_x, P_y$ for the Zn complex. On the other hand, the polarization pattern (*E*/*A*) of MgPc−py is reversed, and is reproduced by selective ISC to T_{1x} and T_{1y} sublevels (P_x: P_y: P_z = 0.46: 0.54: 0). This selective ISC originates from the *x* and *y* components of SOC between π and σ (π^* and σ^*) orbitals, since Ψ_S and Ψ_{Ti} ($i = x, y, z$) are admixed with ($\sigma\pi^*$) and ($\pi\sigma^*$) via vibronic coupling. In this case, the P_i ($i = x, y$) of MgPc−py is proportional to matrix elements of H_{SOi} with respect to the coordinate Q_p as follows:[13]

$$P_i \propto \sum_{p} |(\alpha/\alpha Q_p)\langle \Psi_{Ti}|H_{SOi}|\Psi_S\rangle|^2 \qquad (2)$$

since there are no direct SOC due to the lack of d_π orbitals, P_x, $P_y > P_z$ for the Mg complex. Zero field splitting (zfs) parameter *D* values are evaluated as 0.720 and 0.713 GHz for ZnPc−py and MgPc−py, respectively, and indicate the similarity of electronic structures between ZnPc−py and MgPc−py in the T_1 state. Therefore, the comparison between the Zn and Mg derivatives is evidently suitable for extracting effects of SOC, since only the components of SOC are varied without changing electronic structures.

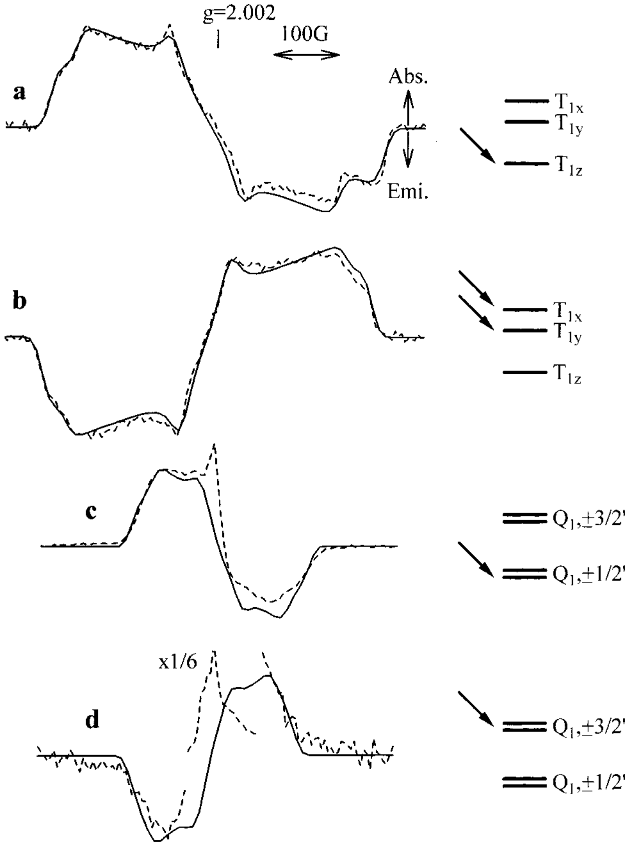

Figure 2. TREPR spectra (broken lines) of ZnPc−py (a), MgPc−py (b), ZnPc−ATEMPO (c), and MgPc−ATEMPO (d). These spectra were observed at 20 K and 0.7−1.3 μs after laser excitation. Spectral simulations (solid lines; a−d) were calculated using parameters described in the text.

TREPR spectra (broken lines) of ZnPc−ATEMPO and MgPc−ATEMPO are shown in Figures 2c and 2d, respectively. Three signals are observed for both ZnPc−ATEMPO and MgPc−ATEMPO. The polarization pattern of MgPc−ATEMPO is *EAA*, and is partially opposite to that (*AAE*) of ZnPc−ATEMPO. For ZnPc−ATEMPO the *g* value (= 2.005 ± 0.001) of the central *A* peak is almost the same as that (= 2.006 ± 0.001) of a peak position of a steady-state EPR spectrum at 20 K, and is accordingly assigned to the D_0 state. On the other hand, the *g* value of the central *A* peak is evaluated as 2.002 ± 0.002 for MgPc−ATEMPO. By comparison with the calculated *g* value (= 2.001 ± 0.003) of the D_1 state,[2,15,16] the central *A* peak is assigned to the D_1 state.[17] By reference to previous reports,[2] both the outer *A*/*E* signals of ZnPc−ATEMPO and *E*/*A* signals of MgPc−ATEMPO are considered as the Q_1 states. To discuss quantitatively, spectral simulations were carried out for the Q_1 states, using the methods previously reported.[2c] The simulation spectra are shown in Figures 2c and 2d (solid lines). The TREPR spectrum of ZnPc−ATEMPO is reproduced using D = 0.190 GHz, E = 0.035 GHz, and $P_{+3/2'}$: $P_{+1/2'}$: $P_{-1/2'}$: $P_{-3/2'}$ = 0: 1: 1: 0. On the other hand, the simulation spectrum of MgPc−ATEMPO is calculated using D = 0.175 GHz, E = 0.035 GHz, and $P_{+3/2'}$: $P_{+1/2'}$: $P_{-1/2'}$: $P_{-3/2'}$ =1: 0: 0: 1. To confirm the zfs, the *D* value was calculated under a point charge approximation.[2,15,18,19] The *D* value of MPc−ATEMPO was calculated as 0.16 GHz, and is similar to those evaluated by the spectral simulations. Therefore, the outer signals of ZnPc−

ATEMPO and MgPc−ATEMPO are evidently assigned to the Q_1 state constituted by the excited triplet MPc and doublet TEMPO.

The *E*/*A* polarization pattern is observed for the Q_1 MgPc−ATEMPO, and is the opposite polarization pattern (*A*/*E*) of the Q_1 ZnPc−ATEMPO. These *A*/*E* and *E*/*A* polarizations are reproduced by selective ISC to $|Q_1,\pm 1/2'\rangle$ and to $|Q_1,\pm 3/2'\rangle$, respectively. These results are consistent with the previous presumption, where selective ISC to $|Q_1,\pm 3/2'\rangle$ is promoted by the *x* and *y* components of SOC. That is, it is found experimentally that the Q_1 polarization is dependent on the components of SOC. To discuss more quantitatively, the relationship between the Q_1 MPc−ATEMPO and T_1 MPc−py complexes has to be clarified. Since it is confirmed from the point charge calculations that the fine structure *z* axis of the Q_1 MPc−ATEMPO is almost parallel to that of the T_1 MPc, the population ratio of the $|Q_1,K'\rangle$ sublevels, $P_{K'}$, is represented using P_x, P_y, and P_z as follows:[20,21]

$$P_{\pm 3/2'} \propto (P_x + P_y)/2 \tag{3a}$$

$$P_{\pm 1/2'} \propto 2P_z/3 + (P_x + P_y)/6 \tag{3b}$$

Equations 3a and 3b indicate that $P_{\pm 1/2'}$ is larger than $P_{\pm 3/2'}$, when $P_z > P_x$, P_y. In contrast, $P_{\pm 3/2'} > P_{\pm 1/2'}$, when P_x, $P_y > P_z$. That is, the experimental results of Zn and Mg complexes can be reasonably explained by eqs 3a and 3b.

In conclusion, it has been proved that the selectivity of ISC to the Q_1 state is dependent on the components of SOC, and that ISC to $|Q_1,\pm 1/2'\rangle$ is selective due to the *z* component of SOC, while selective ISC to $|Q_1,\pm 3/2'\rangle$ is promoted by the *x* and *y* components of SOC.

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(9) $|Q_1,K'\rangle$ ($K = \pm 1/2$, $\pm 3/2$) denotes eigenfunctions of the Q_1 state at zero-magnetic field.

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(14) In the S_1 and T_1 regions, $^{1,3}E_{ux}$ and $^{1,3}E_{uy}$ states, which are ($\pi\pi^*$), are degenerate. The *z* component of SOC between the $^1E_{ux}$ ($^1E_{uy}$) and $^3E_{uy}$ ($^3E_{ux}$) states is calculated for the Zn complex.

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(16) The *g* value of the D_1 state ($g(D_1)$) constituted by the excited triplet MgPc and doublet TEMPO is calculated using a following equation:[2,15]

$$g(D_1) = \{-g(R) + 4\, g(T_1)\}/3$$

Here, $g(R)$ and $g(T_1)$ are *g* values of the doublet TEMPO ($= 2.006 \pm 0.001$) and T_1 MgPc ($= 2.002 \pm 0.003$), respectively.

(17) The difference between the D_1 and D_0 polarizations is considered as follows. Since the D_0 polarization is generated in the Q_1 state,[2e] the D_0 states of the Zn and Mg complexes are expected to have *A* and *E* polarizations, respectively. However, since the Q_1 polarization of MgPc−ATEMPO is much weaker than that of ZnPc−ATEMPO, the D_0 polarization cannot be observed for MgPc−ATEMPO. On the other hand, the D_1 polarization is considered to originate from mixing between the D_1 and Q_1 states.[2c] For the weak Q_1 polarization, the D_1 polarization, which is more intense than the Q_1 polarization, is observed for MgPc−ATEMPO.

(18) Zfs tensor of the Q_1 state, $\boldsymbol{D}(Q_1)$, is represented as follows:[2,15]

$$\boldsymbol{D}(Q_1) = \{\boldsymbol{D}(T_1) + \boldsymbol{D}(RT_1)\}/3$$

Here, $\boldsymbol{D}(T_1)$ and $\boldsymbol{D}(RT_1)$ are zfs tensors of the excited triplet state and the magnetic dipole−dipole interaction between the excited triplet and radical, respectively. The $\boldsymbol{D}(RT_1)$ was calculated under a point charge approximation.[19] $\boldsymbol{D}(T_1)$ was obtained by TREPR measurements of the T_1 MPcs. The $D(Q_1)$ value is estimated by diagonalizing the $\boldsymbol{D}(Q_1)$.

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(21) In these calculations, wave functions of the D_n and Q_1 states are represented using wave functions of the excited singlet ($|\Psi_S\rangle$) and triplet ($|\Psi_{Ti}\rangle$; $i = x, y, z$) states as follows.[20]

$$|D_n,\pm 1/2'\rangle = |\Psi_S\Psi_{R\pm}\rangle,\ |Q_1,\pm 3/2'\rangle = |\Psi_{T\pm}\Psi_{R\pm}\rangle$$

$$|Q_1,\pm 1/2'\rangle = (|\Psi_{T\pm}\Psi_{R\mp}\rangle + \sqrt{2}|\Psi_{Tz}\Psi_{R\pm}\rangle)/\sqrt{3}$$

$$|\Psi_{T\pm}\rangle = \mp(|\Psi_{Tx}\rangle \pm i|\Psi_{Ty}\rangle)/\sqrt{2}$$

Here, $|\Psi_{R\pm}\rangle$ is the wave function of the TEMPO radical. Using these wave functions, matrix elements of SOC were calculated.