2910 *Inorg. Chem.* **1996,** *35,* 2910−2914

State Mixings in the Excited Triplet and Singlet States of Fluorine-Substituted Magnesium Tetraphenylporphines Studied by Optical and Time-Resolved EPR Spectroscopy

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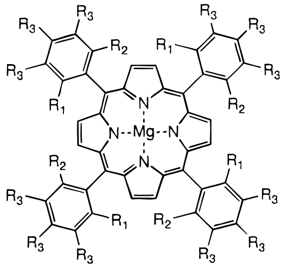
Received August 24, 1995⊗

Optical and time-resolved EPR(TREPR) studies were made on the excited states of fluorine-substituted magnesium tetraphenylporphines (MgF−TPPs) including related Mg porphyrins. From the analyses of TREPR spectra it was found that the zero-field splitting parameter, *D*, increased with an increasing number of substituents, e.g. fluorine atoms. This result is interpreted by the fact that $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ configurations are heavily mixed via vibronic couplings in the lowest excited triplet (T_1) states of MgF−TPPs. Other T_1 properties such as a T_1 energy, a triplet lifetime, and an appearance of the b_{1g} band in the phosphorescence supported the mixings. The mixings due to configuration interactions were studied in the lowest excited singlet (S_1) states of MgF−TPPs by measuring absorption coefficients and intensities of vibronic bands both in the absorption and fluorescence. The magnitudes of the mixings were also evaluated in the S_1 states of MgF−TPPs.

1. Introduction

HOMO and next HOMO orbitals of metalloporphyrins are assigned to be a_{2u} and a_{1u}, which are nearly degenerate, and their order depends on the substituents. In the excited singlet states two configurations, ($a_{2u}e_g$) and ($a_{1u}e_g$), are heavily mixed via a configuration interaction (CI) and provide the S_1 state with small ϵ and the S_2 state with very large ϵ ((4−6) × 10^5 M^{-1} cm^{-1}).[1] In contrast such CI is not expected to occur for the excited triplet states from a point of symmetry.[2] However, the interactions between these two states have been suggested to occur via a vibronic coupling in a few systems.[3] There have been no clear-cut results obtained on these mixings in the triplet states. In this report we discuss our systematic studies on this problem. We selected magnesium tetraphenylporphine (MgTPP) and magnesium 2-fluoro- (MgMTFPP), 2,6-difluoro- (MgDFTPP), and 2,3,4,5,6-pentafluorotetraphenylporphines (MgPFTPP) (Figure 1) as our model complexes to illustrate the state mixing based on the following reason.

Pentafluorotetraphenylporphyrins (PF−TPPs) were first synthesized and UV/visible spectral studies made by Longo, Finarelli, and Kim.[4] Recently, Gouterman and co-workers examined more quantitative studies on the absorption and emission spectra and the emission quantum yield for a free base and metallo (M)−PFTPPs (M = Zn, Cu, and Pd).[5] They concluded that the energies of the singlet and triplet excited states of the PFTPPs were located between those of octaethylporphyrins (OEP) and tetraphenylporphyrins (TPP). As we know that TPP and OEP have nearly the pure $T_1(a_{2u}e_g)$ and $T_1(a_{1u}e_g)$ states,[1,6] respectively, it is expected that $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ are close in energy for PFTPP and other fluorine-substituted TPPs.[5] For magnesium porphyrin complexes we have studied photochemical reactions in relation to the reaction center of the photosynthetic system.[7]



a) MgTPP; R_1=R_2=R_3=H : b) MgMFTPP; R_1=F, R_2=R_3=H : c) MgDFTPP; R_1=R_2=F, R_3=H : d) MgPFTPP; R_1=R_2=R_3=F

Figure 1. Molecular structures of fluorine-substituted magnesium tetraphenylporphines.

State mixings in the triplet states have been analyzed by using zero-field splittings (zfs) for many cases such as those between nπ^* and $\pi\pi^*$ states,[8] $\pi\pi^*$ and CT* states,[9] and exciton and charge resonance states.[10,11] We now use this technique to analyze the mixing between the ($a_{2u}e_g$) and ($a_{1u}e_g$) states in triplet porphyrins. The zfs were obtained by a time-resolved electron paramagnetic resonance (TREPR) technique. Triplet lifetimes and triplet energies were obtained from the phosphorescence measurements and were used to support the analyses by zfs. We also tried to obtain the mixing coefficients in the excited singlet states from the relative intensities of the 0−0 bands of the S_1(Q) and S_2(B) absorption. The S_1 and S_2 positions and their relative intensities of the 0−0 and 0−1 bands in the fluorescence and absorption spectra supported the magnitudes of the mixing in the S_1 states of fluorine-substituted TPPs.

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⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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S0020-1669(95)01108-6 CCC: $12.00

2. Experimental Section

Free base TPP, MFTPP, and DFTPP were synthesized following the method already reported.[12] Free base OEP and PFTPP were purchased from Wako Pure Chemicals and used without further purification. Mg complexes were synthesized in the dark according to the conventional method and were purified by column chromatography on alumina using a mixed solvent of hexane, dichloromethane, and chloroform as described previously.[7b] Ethanol and toluene were purified by distillation and dehydration with CaH_2 under an Ar atmosphere. The samples of 1×10^{-6} to 5×10^{-4} M in a mixed solvent of ethanol and toluene (1:1) were deaerated by the freeze−pump−thaw method and were sealed on the vacuum line.

Phosphorescence and fluorescence were observed with a Hitachi 850 fluorometer at 77 K and room temperature, respectively. Triplet lifetimes were measured by using an electrical shutter. Absorption spectra were observed on a Shimadzu UV-240 spectrometer at room temperature. Time-resolved EPR spectra were obtained by the method already reported.[13] In short, the samples in the cavity were excited by a Lambda Physik LPD3000 dye laser at 570−585 nm. EPR signals from the EPR unit of a JEOL FE2X EPR spectrometer were integrated by a NF BX-531 boxcar integrator at around 1 μs after the laser pulse without field modulation. Temperature was controlled by an Oxford ITC4 cryo-system at 10−80 K. Most of the spectra were obtained in 10−12 min.

3. Results

3.1. Fluorescence and Phosphorescence. Fluorescence and phosphorescence spectra of the compounds and their excitation spectra were observed in a mixed solvent of ethanol and toluene at room temperature and 77 K. Emission and absorption spectra of MgTPP, MgMFTPP, MgDFTPP, MgPFTPP, and MgOEP are shown in Figure 2. The concentrations of the samples were 5×10^{-4} M except MgDFTPP, where two kinds of phosphorescences were observed. We assigned the red-shifted one (λ_{max} = 788.5 nm) as that of the MgDFTPP dimer from the concentration dependence of the spectra[14] and set the concentration to be 5×10^{-5} M for the measurement of MgDFTPP. Absorption spectra were observed at room temperature with concentrations of 1×10^{-6}M. The data of the absorption and fluorescence for the singlet states (S_1 and S_2) are summarized in Tables 1 and 2, respectively. The data of the phosphorescence in the T_1 states were obtained at 77 K and were summarized in Table 3 together with the triplet lifetime.

From the figures and tables we obtained the following results.

(1) Both the fluorescence and phosphorescence were blue-shifted with respect to those of the parent molecule, MgTPP, in order of increasing number of the fluorine (F) atoms. The magnitudes of the shifts were about twice as large for the phosphorescence.

(2) The absorptions of the S_2(B) bands were also blue-shifted, though the magnitudes were smaller.

(3) The relative integrated intensities of the 0−0 to the 0−1 bands in both the S_0−S_1 absorption and the fluorescence increased with increasing the number of F atoms.

(4) The integrated intensities of the vibronic (0−1) bands in the S_0−S_1 absorptions were stronger than those of the fluorescence by a factor of ca. 3.

(5) The vibronic band ($\nu_p = 1340$ cm^{-1}) in the phosphorescence was only observed for MgPFTPP.

(6) The triplet lifetime became longer (120−250 ms) with the F substitutions except that (80 ms) of MgPFTPP.

3.2. Time-Resolved EPR. Time-resolved EPR spectra were observed for MgTPP, MgFTPPs, and MgOEP in ethanol + toluene (1:1) at 10−80 K. The typical spectra obtained at 1 μs after the laser pulse (λ = 585 nm) are shown in Figure 3. All the spectra except that of MgPFTPP showed EEE/AAA polarization patterns from low to high stationary fields, which

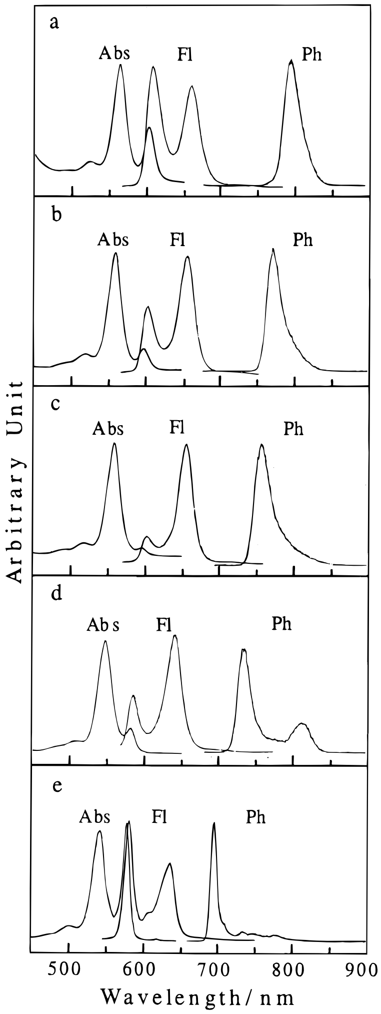

Figure 2. Fluorescence (Fl), phosphorescence (Ph), and absorption (Abs) spectra for (a) MgTPP, (b) MgMFTPP, (c) MgDFTPP, (d) MgPFTPP, and (e) MgOEP observed in ethanol + toluene (1:1) at room temperature (Fl and Abs) and 77 K (Ph).

Table 1. Optical Absorption Data for the S_1 and S_2 States[a,b]

	${}^1\nu_2(0,0)$/ cm^{-1}	${}^1\nu_1(1,0)$/ cm^{-1}	${}^1\nu_1(0,0)$/ cm^{-1}	$10^2 I[\nu_1(0,0)]$/ $I[\nu_2(0,0)]$	$I[\nu_1(0,0)]$/ $I[\nu_1(0,1)]$	A^2 [c]
MgTPP	23 460	17 740	16 650	1.9	0.42	0.64
MgMFTPP	23 570	17 830	16 690	0.79	0.18	0.59
MgFDTPP	23 580	17 890	16 770	0.53	0.09	0.57
MgFPTPP	23 760	18 300	17 240	0.98	0.16	0.40
MgOEP	24 380	18 370	17 220	2.6	0.54	0.34

[a] Peak positions at the origin (0−0) and the first vibronic (0−1) bands for the $S_1({}^1\nu_1)$ and $S_2({}^1\nu_2)$ states (±10 cm^{-1}). [b] Relative integrated intensities of the two bands (±10%). [c] Coefficients of ${}^1(a_{2u}e_g)$ character. See eq 9.

Table 2. Fluorescence Properties[a−c]

	${}^1\nu_f(0,0)$/cm^{-1}	${}^1\nu_f(0,1)$/cm^{-1}	$\Delta^1\nu_f$/cm^{-1}	$I_f(0,0)/I_f(0,1)$
MgTPP	16 330	15 060	1270	1.03
MgMFTPP	16 490	15 100	1390	0.59
MgDFTPP	16 610	15 230	1380	0.32
MgFPTPP	17 080	15 600	1480	0.49
MgOEP	17 080	15 640	1440	1.47

[a] Peak positions at the origin(0−0) and the first vibronic (0−1) bands (±10 cm^{-1}). [b] $\Delta^1\nu_f = {}^1\nu_1(0-0) - {}^1\nu_1(0-1)$. [c] Relative integrated intensities of the two bands (±10%).

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Table 3. Phosphorescence Properties[a,b]

	$^3\nu_p(0,0)$/cm^{-1}	$^3\nu_p(0,1)$/cm^{-1}	$\Delta^3\nu_p$/cm^{-1}	τ_p/ms[c]
MgTPP	12 560			120
MgMFTPP	12 910			180
MgDFTPP	13 150			250
MgPFTPP	13 650	12 310	1340	80
MgOEP	14 370			200

[a] Peak positions at the origin (0−0) and the first vibronic (0−1) bands (±10 cm^{-1}). [b] $\Delta^3\nu_p = {}^3\nu_p(0-0) - {}^3\nu_p(0-1)$. [c] Triplet lifetime (±5%).

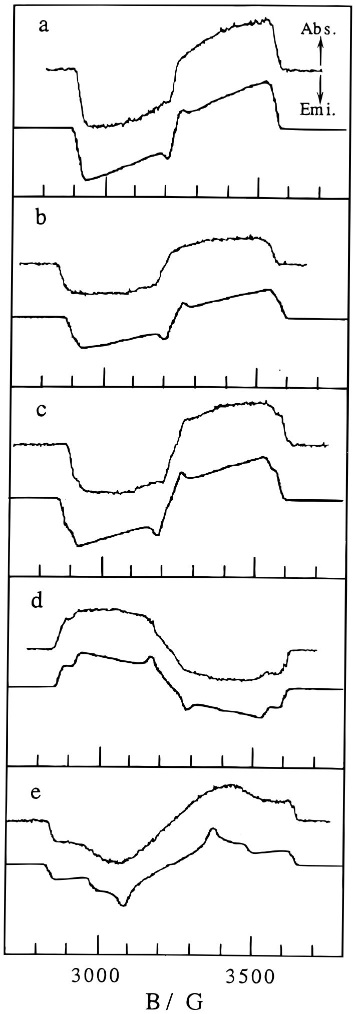

Figure 3. Time-resolved EPR spectra observed at 20 K and 0.4 μs and their simulations using the parameters summarized in Table 4 for (a) MgTPP, (b) MgMFTPP, (c) MgDFTPP, (d) MgPFTPP, and (e) MgOEP.

are the same as those already reported for the magnesium porphyrins.[7a,15,16] MgPFTPP showed an AAA/EEE pattern, where E and A denote an emission and an absorption of microwave. The spectra were simulated using the EPR parameters summarized in Table 4. From the figure and table we obtained the results as follows.

(1) The zfs parameter, $D(\equiv-(3/2)Z)$, increased monotonically with the F substitutions to the phenyl rings on TPPs; MgFTPPs have D values intermediate between those of MgTPP and MgOEP.

Table 4. Zero-Field Splittings and Relative isc rates in the T_1 States[a,b]

	X/GHz	Y/GHz	Z/GHz	P_x:P_y:P_z	D/GHz	E/GHz	a^2 [c]
MgTPP	0.585	0.035	−0.620	0.50:0.50:0	0.930	0.275	(1)
MgMFTPP	0.600	0.050	−0.650	0.49:0.51:0	0.975	0.275	0.78
MgDFTPP	0.585	0.067	−0.667	0.49:0.51:0	1.00	0.267	0.65
MgPFTPP	0.585	0.107	−0.692	0:0.01:0.99	1.04	0.236	0.45
MgOEP	0.480	0.270	−0.750	0.45:0.55:0	1.13	0.105	(0)

[a] Energies of the triplet sublevels, X, Y, and Z (±0.008 GHz). [b] Zero-field splitting parameters, $D \equiv -(^3/_2)Z$ and $E \equiv |X - Y|/2$. [c] Coefficients of $^3(a_{2u}e_g)$ character. The values in the parentheses are assumed ones. See also eq 1.

(2) The E values did not vary so much with the F substitutions. E (0.105 GHz) of MgOEP was smaller than those (0.236−0.275 GHz) of MgTPP and MgFTPPs.

(3) The relative S_1−T_1 intersystem crossing (isc) rates, P_i ($i = x, y, z$), were dominant in T_x and T_y for all Mg complexes examined except MgPFTPP, where T_z was dominant.

4. Discussion

4.1. Mixings in the T_1 States. The result (1) in section 3.1 is consistent with the results of Gouterman and co-workers that the fluorine substitutions make the energy difference between the a_{1u} and a_{2u} orbitals smaller.[6] This might provide a larger mixing between the $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ states. We have evaluated the mixing coefficients between the two excited states from the zfs on the basis of the following consideration. When states are mixed via some coupling, a wave function of the mixed triplet state ($^3\psi_M$) is described by a linear combination of the zeroth-order wave functions of the triplet a and b states, $^3\psi_a$ and $^3\psi_b$, as[17]

$$^3\psi_M = a{}^3\psi_a + b{}^3\psi_b \; (a^2 + b^2 = 1) \tag{1}$$

The zfs parameters, D and E, of the mixed state are given by

$$D_M = \langle{}^3\psi_M|H_D|{}^3\psi_M\rangle = a^2\langle{}^3\psi_a|H_D|{}^3\psi_a\rangle + 2ab\langle{}^3\psi_a|H_D|{}^3\psi_b\rangle + b^2\langle{}^3\psi_b|H_D|{}^3\psi_b\rangle \tag{2a}$$

$$E_M = \langle{}^3\psi_M|H_E|{}^3\psi_M\rangle = a^2\langle{}^3\psi_a|H_E|{}^3\psi_a\rangle + 2ab\langle{}^3\psi_a|H_E|{}^3\psi_b\rangle + b^2\langle{}^3\psi_b|H_E|{}^3\psi_b\rangle \tag{2b}$$

Here H_D and H_E are the Hamiltonians that reflect anisotropies toward an out-of-plane axis and within a plane in spin dipole−dipole couplings, respectively.[6] If the mixing occurs via a vibronic coupling, the cross term, $\langle{}^3\psi_a|H_D,H_E|{}^3\psi_b\rangle$, vanishes under the assumption that the wave functions of the a and b states are described by the crude BO wave functions as[18]

$$^3\psi_M = {}^3\phi_a(q,Q_0)\chi_a{}^0(Q) + {}^3\phi_b(q,Q_0)\chi_b{}^1(Q) \tag{3}$$

where ϕ and χ are electronic and vibrational wavefunctions, q and Q electronic and nuclear coordinates, and superscripts 0 and 1 the zeroth and the first vibrational levels, respectively. The cross term is represented by

$$\langle{}^3\psi_a|H_D,H_E|{}^3\psi_b\rangle = \langle{}^3\phi_a|H_D,H_E|{}^3\phi_b\rangle\,\langle\chi_a{}^0|\chi_b{}^1\rangle \tag{4}$$

As $\chi_a{}^0$ and $\chi_b{}^1$ are orthogonal to each other, $\langle\chi_a{}^0|\chi_b{}^1\rangle = 0$, the

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cross term should vanish. Then *D* and *E* of the mixed state are represented by

$$D_{\mathrm{M}} = a^2 D_{\mathrm{a}} + b^2 D_{\mathrm{b}} \tag{5a}$$

$$E_{\mathrm{M}} = a^2 E_{\mathrm{a}} + b^2 E_{\mathrm{b}} \tag{5b}$$

When the *D* and *E* values of the pure a and b states are known, we can easily calculate the mixing coefficients from eq 5 and observed *D* (=D_M) and *E* (=E_M).

From the theoretical and experimental studies on triplet metalloporphyrins,[1,6] MTPP and MOEP (M = Zn and Mg) are considered to have nearly the pure $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ configurations, respectively. Hyperfine coupling constants obtained for the MTPP and MOEP (M = Zn, Co) cations also indicate that these D_0 states belong to nearly the pure A_{2u} and A_{1u} representations, respectively.[6,19] On the basis of these results we evaluated the a^2 and b^2 values (eq 1) from the observed *D* values (Table 4) as summarized in Table 4. We found that the two states start mixing in MgMFTPP and are heavily mixed with an almost 1:1 ratio in MgPFTPP.

For the *E* values we expect that $E = 0$ for the molecules with D_{4h} symmetry. However, we observed $E \neq 0$ for all metalloporphyrins examined, which is considered to be due to the Jahn−Teller distortion within $^3(a_{2u}e_g)$ or $^3(a_{1u}e_g)$.[20] The larger *E* values observed for the TPP complexes are interpreted by the larger Jahn−Teller coupling operating in these triplet states.[20,21] Therefore, we do not use the *E* value for the evaluation of the magnitude of the mixing. Another possible mixing origin in the triplet is a configuration interaction (CI) occurring in the singlet states. As the symmetries of the molecules are now reduced ($E \neq 0$) from the D_{4h} symmetry due to the Jahn−Teller distortion and the addition of the substituted phenyl rings, $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ can mix through CI. However, as the larger zfs than those of the pure states were expected for the mixed states, this is not the case. This interpretation was applied to an explanation of the larger zfs observed for free-base (H_2) porphyrins.[8] The isc rates (P_i) were large for the T_x and T_y sublevels except for MgPFTPP, which is interpreted by large spin−orbit couplings between the $\sigma\pi^*$ ($n\pi^*$) and $\pi\pi^*$ states such as $\langle\sigma(n)|l_x|\pi\rangle$ and $\langle\sigma(n)|l_y|\pi\rangle$. The dominant isc to T_z observed for MgPFTPP is discussed in section 4.4.

4.2. Other Supporting Results. The mixings of the $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ states were quantitatively evaluated from the zfs for the fluorine-substituted MgTPPs. The proximity and the mixing were also supported from the phosphorescence properties. The observed blue shift in the phosphorescence (Table 3) can be interpreted in terms of changes in the orbital energies. The a_{2u} orbital is more stabilized by fluorine-substitution to the phenyl rings via an inductive effect,[6] which makes the $T_1(a_{2u}e_g)$ energy of MgTPP higher as observed. These blue-shifts were also observed for the S_1 and S_2 states (Tables 1 and 2). As the a_{1u} orbital is not expected to be affected by substitutions to the phenyl rings because of its nodes through the meso positions,[1] the $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ states become closer in FTPPs. Another evidence of the mixing was obtained from the triplet lifetime (τ_p). The τ_p of MgTPP (120 ms) is shorter than that (200 ms) of MgOEP (Table 3), which is interpreted by the larger spin density, namely the larger spin−orbit coupling, on the nitrogen atoms in the HOMO a_{2u} orbital of the TPP complexes. The longer lifetimes observed for MgMFTPP and MgDFTPP are consistent with the mixing of the $^3(a_{1u}e_g)$ character into the $T_1(a_{2u}e_g)$ state of the parent molecule, MgTPP. The shorter lifetime observed for MgPFTPP is discussed in the following section.

In the phosphorescence spectrum we only observed the vibronic band for MgPFTPP (Figure 2). Even if we consider less sensitivity in the longer wavelength region (≥850 nm), this result is consistent with the conclusion that $(a_{2u}e_g)$ and $(a_{1u}e_g)$ are heavily mixed in triplet MgPFTPP via the strong vibronic coupling. The observed vibration (ca. 1340 cm^{-1}) must be the b_{1g} (=$b_{2u} \times b_{3u}$) ν_{12} mode,[22] because the $E_u{}^3(a_{1u}e_g)$ and $E_u{}^3(a_{2u}e_g)$ states in D_{4h} symmetry become the B_{2u} and B_{3u} states in D_{2h} symmetry due to the Jahn−Teller distortion. We may assign the vibronic band ($\Delta\nu$ = 1316 cm^{-1}) observed in the phosphorescence spectrum of Zn porphine[21] as being due to the ν_{12} mode, where the two states are also considered to be close together.

4.3. Mixings in the S_1 and S_2 States. It is well-known that $^1(a_{2u}e_g)$ and $^1(a_{1u}e_g)$ are mixed thoroughly via CI giving the very strong S_2(B) and weak S_1(Q) absorptions. We examined semiquantitative estimates of the mixing coefficients. The wave functions are simply written as

$$\psi(S_1) = A\,{}^1\psi_A - B\,{}^1\psi_B \; (A^2 + B^2 = 1) \tag{6a}$$

$$\psi(S_2) = B\,{}^1\psi_A + A\,{}^1\psi_B \tag{6b}$$

The absorption strengths (*I*) of the S_1 and S_2 states are described by

$$I(S_1) = c|\langle\psi(S_1)|er|\psi(S_1)\rangle|^2 = c\{A^2\langle{}^1\psi_A|er|{}^1\psi_A\rangle - 2AB\,\langle{}^1\psi_A|er|{}^1\psi_B\rangle + B^2\,\langle{}^1\psi_B|er|{}^1\psi_B\rangle\} \tag{7a}$$

$$I(S_2) = c|\langle\psi(S_2)|er|\psi(S_2)\rangle|^2 = c\{A^2\langle{}^1\psi_A|er|{}^1\psi_A\rangle + 2AB\,\langle{}^1\psi_A|er|{}^1\psi_B\rangle + B^2\,\langle{}^1\psi_B|er|{}^1\psi_B\rangle\} \tag{7b}$$

If we use the approximation[23]

$$\langle{}^1(a_{1u}e_g)|er|{}^1(a_{1u}e_g)\rangle = \langle{}^1(a_{2u}e_g)|er|{}^1(a_{2u}e_g)\rangle = M_{ae} \tag{8}$$

and consider that $\psi_A = (a_{2u}e_g)$ and $\psi_B = (a_{1u}e_g)$, the mixing coefficients can be obtained from

$$I(S_1)/I(S_2) = (A^2 - 2AB + \mathrm{B}^2)/(A^2 + 2AB + B^2) = (1 - 2AB)/(1 + 2AB) \tag{9}$$

We used the integrated intensity for the 0−0 band of each transition as *I*(S) and obtained A^2 and B^2 from eq 9 as all together summarized in Table 1. From the table, we found the fact that A^2 and B^2 are passably different for MgTPP and MgOEP. The values for MgDFTPP were not determined just from the relative intensities of the S_1 and S_2 bands, where the values of 0.57 and 0.43 were obtained as A^2. We selected 0.57 by considering the magnitudes of changes in A^2 and energy shifts in the S_1 states (80 cm^{-1} for MgMFTPP and MgDFTPP and 470 cm^{-1} for MgDFTPP and MgPFTPP). The larger change is expected for the latter.

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The relative intensities of the 0-0 and 0-1 vibronic bands in both the adsorption and the fluorescence are also indexes of magnitudes of the mixings (A^2 and B^2) between the $^1(a_{2u}e_g)$ and $^1(a_{1u}e_g)$ states.[24] From Tables 1 and 2 we found that the intensity ratios of the 0-0 to 0-1 bands become smaller and we expected that the mixings would increase with increasing F substitutions. This expectation was realized by the above analyses of the absorption coefficients. The intensities of the vibronic bands in the fluorescence and S_1 absorption were different such that the (0-1) absorption is about three times as intense as the (0-1) emission (Tables 1 and 2). This is apparently consistent with the expectation by Perrin et al.[25] that a destructive interference ocurrs between the allowed (Franck−Condon) and forbidden (vibronic) transitions.

4.4. Internal Heavy Atom Effects. We observed rather anomalous behaviors in triplet MgPFTPP, a short lifetime and dominant isc to T_z, which are not expected from the vibronic mixing of the states. We propose that these are due to an internal heavy atom effect by the F atoms. Here we consider two possible mechanisms, the heavy atom effect[26] and the proximity effect,[27] as possible candidates giving the above properties. The latter is stimulating because the $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ states turned out to be close together in MgPFTPP from this work (section 4.1). However, this possibility can be denied for two reasons. First, owing to the proximity effect, a nonradiative transition is expected to be remarkably enhanced and the phosphorescence becomes weaker. Second, an in-plane distortion is expected to occur for the interactions between $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ resulting in the increases in P_x and P_y. Neither of these two expectations was realized in the experiments. The short lifetime is easily understood by the heavy atom effect. It may be considered that 80 ms is too short to be explained by the heavy atom effect of the F atoms. But we can refer to the triplet lifetime ($\tau_p = 270$ ms) of perfluoronaphthalene,[28] which is about one-tenth of that (2.3 s) of the parent naphthalene. In our case, τ_p (80 ms) is two-thirds of that (120 ms) of the parent MgTPP. The dominant P_z is also explained by considering that the fluorine atoms are located in out-of-plane positions with respect to the porphyrin $\pi\pi^*$ plane. Delocalizations of the π and π^* electrons over the n and σ orbitals on the fluorine atoms produce a new matrix element for a spin−orbit coupling such as $\langle n|l_z|\sigma\rangle$, which contributes to the increase in P_z.[29] Therefore, we conclude that the anomalous properties obtained for triplet MgPFTPP are due to the internal heavy atom effect on the fluorine atoms.[30]

5. Conclusion

We showed evidences for state mixings between $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ configurations in the excited triplet states of fluorine-substituted Mg tetraphenylporphines (MgFTPP) by measurements of a zero-field splitting parameter, *D*, a triplet lifetime, and a triplet energy. These properties of MgFTPPs were situated between those of nearly pure $^3(a_{2u}e_g)$ magnesium tetraphenylporphine and $^3(a_{1u}e_g)$ magnesium octaethylporphine. In magnesium pentafluoro-TPP the magnitude of the mixing was at a maximum (45:55) and the vibronic band involving a b_{1g} mode appeared in the phosphorescence spectrum. On the basis of these results we concluded that the mixing between the $^3(a_{2u}e_g)$ and $^3(a_{1u}e_g)$ states occurs via a vibronic coupling.

In the excited singlet states we evaluated the magnitudes of the well-known CI mixings from the absorption coefficients of the S_1 and S_2 states. The value was at a maximum for magnesium difluoro-TPP, indicating that the extents of the mixings are different for the T_1 and S_1 states.[5] The relative intensities of the 0-0 to 0-1 bands of the S_0-S_1 absorption increase with increased fluorine substitutions, which also supported the mixings occurring in the S_1 states. We obtained evidence for an interference effect occurring in the allowed (Franck−Condon) and the forbidden (vibronic) transitions of MgFTPPs.

Acknowledgment. The authors thank Dr. Muneteru Kozuka of our group for the discussion about the vibrational assignments. This work was supported by a Grant-in Aid for Scientific Research on Priority Area “Photoreaction Dynamics” from the Ministry of Education, Science, and Culture, Japan (No. 249/06239208).

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(30) The result that the polarization (AAA/EEE) of MgPFTPP is just reversed to that (EEE/AAA) of H_2PFTPP[15] is interesting. This fact is interpreted by the importance of (nπ^*) states in H_2PFTPP.