Interplanar interactions in the triplet dimers of Zn and metal free complexes of crowned porphyrin and phthalocyanine studied by time-resolved electron paramagnetic resonance

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ABSTRACT

The intermolecular interactions were analyzed by the time-resolved EPR technique for crown ether substituted porphyrins and phthalocyanines. The contributions of charge resonance-type(CR) and exciton-type(EX) interactions were directly estimated on the basis of the zero field splitting parameters, D, of the excited triplet (T_1) states of the monomers and their crown ether bridged dimers. In the case of T_1 porphyrin, $^3(a_{2u}, e_g)$, it was found that the central metal(Zn) plays an important role on the interplanar interaction in contrast to a small effect observed in T_1 phthalocyanine ,$^3(a_{1u}, e_g)$. These results are interpreted in terms of the interaction between the $4p_z$ orbital of Zn and a_{2u} of porphyrin. The magnitude of CR contribution is correlated well with those of the red shifts in the lowest excited singlet and triplet states of the dimers.

A. INTRODUCTION

Porphyrins and phthalocyanines are well investigated with a variety of methods as model compounds of the reaction center in photosynthesis and electroconductor, respectively. Especially the studies on the excited states of the dimers and polymers are important in understanding their interesting properties. Many works have also been done for analyses of intermolecular interactions between composite molecules of these dimers[1–4]. The magnitude of the interaction is mostly evaluated from the energy shift of the excited state and the MO calculation, which is usually model-dependent. Here we propose a new method to analyze intermolecular interactions in more direct way using zero field splittings(zfs) in the lowest excited triplet(T_1) state.

As zfs' reflect spin distribution in the T_1 state, the value varies depending on an extent of excitation delocalization in the dimer. We show that the analysis is very simple, by applying this method to a face to face sandwich type dimer. We are able to obtain the magnitude of the charge resonance(CR) interaction,

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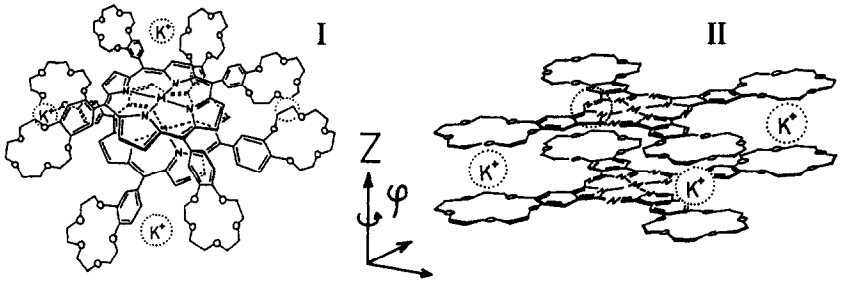
which is a measure of excitation delocalization. We here select the crown ether(K^+) bridged dimers of tetraphenylporphine(TPP;I) and phthlocyanine(PC;II) with Zn and metal free complexes. We used the abbreviations $(ZnCRTPP)_2$, $(H_2CRTPP)_2$, $(ZnCRPC)_2$, and $(H_2CRPC)_2$ for the dimers. The zfs' are measured by means of time-resolved EPR(TREPR). We also obtained the shifts in the transition energies (ΔE) of the S_1 and T_1 states from the observation of fluorescence, phosphorescence and absorption spectra, and compared the results with those from the EPR analyses.



Willigen et al., reported the zfs parameters of T_1 for the monomers and dimers of ZnCRTPP and H_2CRTPP by using a light modulated EPR technique with an Ar^+ laser or a high pressure Xe lamp as a light source[4]. In their case, however, as both monomer and dimer are excited simultaneously, EPR spectra are not well separated giving the incorrect zfs for the dimer. In this study we used a dye laser for selective excitation and obtain nearly pure EPR spectra for both the monomers and dimers. We discuss the effect of a difference in orbital configuration of the T_1 state, $^3(a_{2u}, e_g)$ for TPP and $^3(a_{1u},e_g)$ for PC, and the effect of the central metal ion (Zn^{2+}).

B. EXPERIMENTAL

H_2CRTPP, ZnCRTPP, H_2CRPC and ZnCRPC were synthesized following the methods described in the literature [5, 6]. The dimers of these compounds were obtained by adding an excess of K^+ as potassium acetate. The face to face cofacial configurations of the dimers are confirmed by NMR, EPR and absorption measurements. The distances(r) between the central metals were determined by EPR for the CuCRTPP and CuCRPC dimer complexes as 4.2A and 4.1A, respectively [6, 7].

TREPR signals were observed with a JEOL FE2XG EPR spectrometer equipped with a fast preamplifier and an NF BX-531 digital boxcar integrator[8], where the magnetic field modulation was not used. The magnetic field strength and the microwave frequency were measured with an Echo Electronic FEM 2000 field meter and a Takedariken TR 5501 frequency counter, respectively. Samples were selectively excited at the S_1 region by a Lambda

Physik LPX 100i excimer laser (XeCl, 308nm) pumped Lambda Physik LPD 3000 dye laser. All EPR signals were obtained for the samples(ca.10^{-4}M)in toluene–ethanol(1:1 v/v)solutions at liquid nitrogen temperature. Zfs parameters, D and |E|, and relative populating rates, P_i(i = x, y and z) were determined by spectral simulation. Absorption spectra were obtained at room temperature with a Shimadzu UV240 spectrophotometer. Fluorescence and phosphorescence spectra were observed at 77 K with a Hitachi 850 fluorometer and a laboratory–made photon counting system at Tokyo Institute of Technology(Prof. Kaizu's Lab.)[9], respectively.

C. THEORETICAL

The wavefunction of a dimer is expressed by a linear combination of two configurations, exciton (EX) and Charge resonance (CR) types, where an excitation is localized on one ring and is delocalized over two rings, respectively. The equation holds as

$$\Psi_{DM} = a\Psi_{EX} + b\,\Psi_{CR} \tag{1}$$

The EPR parameter D, which is a measure of anisotropic spin–spin interactions towards out of plane direction(z) is expressed similarly as

$$D_{DM} = \langle \Psi_{DM} | 3g^2\beta^2 (r^2 - 3z^2) / 4r^5 | \Psi_{DM} \rangle = a^2 D_{EX} + b^2 D_{CR} \tag{2}$$

where we use an approximation of a zero differentical overlap($D_{EXCR} = 0$). When we apply this method to face to face sandwich type dimers the equation is simplified as

$$b^2 = D_{DM} - D_M / D_{CR} - D_M \tag{3}$$

where $D_M = D_{EX}$ and M denotes the monomer unit. From eq.(3) we can easily calculate D_{CR} with a point–charge approximation [10] using appropriate MO's, and obtain D_M and D_{DM} by experiments. Therefore, the magnitude of charge resonance character, b^2, is evaluated from the obtained D values of the monomer and the corresponding dimer. As for the other EPR parameter E, which is a measure of anisotropy within the ring plane, is difficult to be analyzed because of an involvement of Jahn–Teller interactions[11].

D. RESULTS

Fluorescence and phosphorescence spectra were observed for the monomer and dimer of ZnCRTPP as shown in Fig. 1. For other compounds no phosphorescence was observed. The transition energies of S_1, summarized in Table 1, were determined from the fluorescence excitation spectra for CRTPP and the absorption spectra for CRPC.

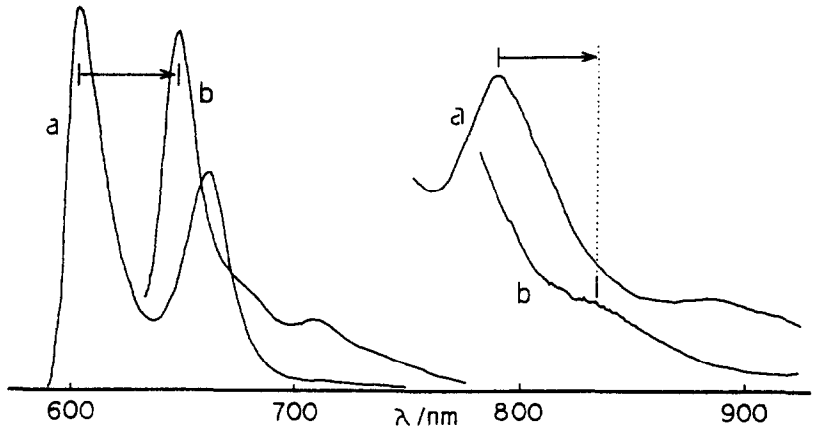


Fig. 1 Fluorescence and phosphorescence spectra of the monomer(a), and dimer(b), of ZnCRTPP observed at 77K in ethanol–toluene(1:1 v/v).

TABLE 1 Zero field splittings, relative populating rates and transition energies

	D/GHz	| E |/GHz	P_x:P_y:P_z	$E_{S1}(E_{T1})$/cm^{-1}
H_2 CRTPP	1.12	0.24	0.2:0.8:0	15430
$(H_2CRTPP)_2$	1.01	0.21	0.4:0.6:0	14810
ZnCRTPP	0.93	0.29	0:0.2:0.8	16750(12690)
$(ZnCRTPP)_2$	0.75	0.23	0:0.1:0.9	15550(12020)
H_2CRPC	0.77	0.06	0.5:0.5:0	14300
$(H_2CRPC)_2$	0.71	0.06	0.5:0.5:0	15600
ZnCRPC	0.77	0.08	0:0.1:0.9	14800
$(ZnCRPC)_2$	0.69	0.08	0:0.2:0.8	15750

We found that both S_1 and T_1 of CRTPP are red-shifted and S_1 of CRPC blue-shifted by dimerization. The magnitude of the shift for ZnCRTPP is twice as large as that for H_2CRTPP. By analyzing the absorption spectra the monomer and dimer complexes are selectively excited with the dye laser. Time-resolved EPR spectra were observed at 0.3–1 μs after the laser pulse. The typical spectra observed and their simulations are shown in Fig.'s 2a and 2b. The analyzed zfs', D and $|E|$, and relative populating rates (P_i) are summarized in Table 1. The values for the monomer and dimer of H_2CRTPP are the same as those reported by Chandrashekar et al.[5]. In all cases D decreases with dimerization, and the degree of reduction is most remarkable for ZnCRTPP. P_i's are consistent with those reported for other TPP and PC[3,12].

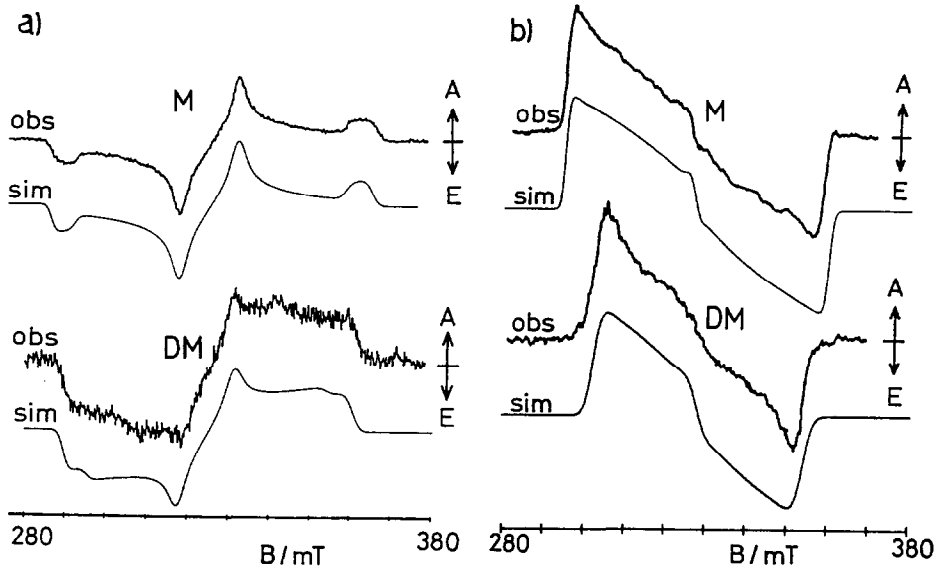


Fig. 2 Time-resolved EPR spectra of the monomers(M) and dimers(DM) for H_2CRTPP (a), and ZnCRTPP (b), at 0.3 μs and 77K in ethanol-toluene(1:1 v/v).

E. DISCUSSION

We first calculate the D value for CR configuration, D_{CR}, by using a point-charge approximation and PPP MO's[10]. The values obtained are −0.189 and −0.093 GHz for the TPP(r = 4.2A, φ =45°) and PC(r = 4.1A, φ = 0°)complexes, respectively. Combining these values with D_M and D_{DM}(Table 1) we can evaluate the contribution of CR character(b^2) from eq.(3) as summarized in Table 2, from which we found that the CR contribution is largest for $(ZnCRTPP)_2$ and does not vary so much among the other three dimer complexes. The shifts of S_1 and T_1 are also shown in Table 2.

TABLE 2 Magnitudes of CR contribution and shifts of S_1 and T_1

	b^2	$\Delta E_{S1}(\Delta E_{T1})$ / cm^{-1}
$(H_2CRTPP)_2$	0.084	− 620
$(ZnCRTPP)_2$	0.16	−1200(−670)
$(H_2CRPC)_2$	0.070	+1300
$(ZnCRPC)_2$	0.093	+ 950

$\Delta E_{S1} = E_{S1}(DM) - E_{S1}(M)$

These results are interpreted well by considering the interactions between the metals(Zn) and between the TPP moiety and the central metal. For the latter interactions there are two possible routes, $4p_z$(Zn)–a_{2u}(TPP) and $3d_{zy}$, $3d_{zx}$(Zn)–e_g(TPP and PC). The experimental results indicate that the interaction between $4p_z$ of Zn and a_{2u} of TPP is very important in the interplanar interactions. The smaller differences between the CRTPP and CRPC systems, and between the H_2CRPC and ZnCRPC systems may be explained by larger overlaps expected for TPP($\varphi = 45°$) than for PC($\varphi = 0°$)[13], and weaker interactions between $3d_{zy}$, $3d_{zx}$–e_g for ZnCRPC, respectively. The importance of the CR interaction for ZnCRTPP is also supported by the large red–shifts observed both in the S_1 and T_1 states(Table 2)[1,2]. The bule shifts observed for S_1 of CRPC having large extinction coefficients are explained by the EX interaction.

The metal–metal and metal–TPP and/or PC interactions play important roles on the intermolecular interactions in the crown ether bridged TPP and PC dimers.

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