

Photoinduced Charge Transfer along a *meso,meso*-Linked Porphyrin Array

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Received: August 3, 1999; In Final Form: October 12, 1999

Electroabsorption spectra of *meso,meso*-linked zinc porphyrin arrays doped in a PMMA polymer film have been measured with a field modulation spectroscopy, and the change in electric dipole moment ($\Delta\mu$) and in molecular polarizability has been evaluated for the transition into each of the exciton splitting components of the Soret band. $\Delta\mu$ following photoexcitation is non-zero in the oligomers, and the magnitude becomes larger with the increasing number of linked molecules, suggesting that photoinduced charge transfer occurs along the linked porphyrin array.

1. Introduction

Linked porphyrin arrays developed as effective biomimetic models have attracted much attention because these are useful and promising to study the importance of interchromophore distance and orientation in intra- or intermolecular energy transfer and/or electron transfer reactions.^{1–5} Porphyrin arrays also have attracted much attention as an organic material with a large nonlinear optical susceptibility because not only of the large π -electron system with two-dimensional conjugated molecular structure but also of the presence of one-dimensionally delocalized electrons.^{6,7}

In covalently linked porphyrin arrays bridged by a variety of spacers, the optical absorption spectra are sometimes characterized by a splitting of the Soret band, reflecting the extent of the exciton coupling.² Recently, one of us reported the synthesis of directly *meso,meso*-linked porphyrin arrays, which also exhibit the splitting of the Soret band with the systematic increase of the energy separation with the increase of the number of the linked porphyrins.⁸ The splitting component located at a longer wavelength region shows a gradual red-shift with an increasing number of linked porphyrins, whereas the splitting component located in a shorter wavelength region is not shifted significantly even when the number of the linked porphyrins are increased. These phenomena as well as the electronic structure in the excited states of linked porphyrin arrays is not known well.

In the present study, the external electric field effects on absorption spectra have been examined to investigate both the electronic properties and the excitation dynamics following excitation into each of the splitting components of the Soret band for the porphyrin monomer and *meso,meso*-linked zinc porphyrin arrays doped in a PMMA polymer film.

2. Experimental

The molecular structure of zinc porphyrin oligomers employed in the present study are shown in Figure 1.⁸ The

porphyrins are connected directly at the *meso* position of the porphyrin ring. According to the number of the connected porphyrin ring, the oligomers are called as monomer (Z1), dimer (Z2), trimer (Z3), and tetramer (Z4), respectively, in the present paper. A certain amount of a benzene solution of PMMA containing porphyrin monomer or porphyrin oligomer was poured onto the ITO-coated substrate by a spin coating technique. The sample was dried slowly in the dark at room temperature. Then, a semitransparent aluminum (Al) film was deposited on the polymer film. The ITO and Al films were used as electrodes. A thickness of polymer films, which was typically 0.5 μm in the present experiments, was determined by using a film thickness measurement system (NanoSpec/AFT model 010-0180, Nanometrics Inc.).

Electric field modulation spectroscopy was used, and the field-induced change in absorption intensity, denoted by ΔA , was detected as a function of excitation wavelength with a lock-in amplifier (SR830, SRS) at the second harmonic of the modulation frequency. The details of the experimental procedures are described elsewhere.^{9,10} The strength of the externally applied field is represented in the rms value. By using a function generator (SG-4311, Iwatsu) combined with an amplifier (Trek, model 609A), ac voltage up to 100 V was applied.

All the optical spectra were measured as a function of wavelength, λ , with a fixed spectral width in wavelength under vacuum conditions. In the analysis, the observed spectra were translated to the ones plotted as a function of wavenumber, ν . Hereafter, plots of the field-induced change in absorption intensity as a function of wavelength (or wavenumber) are called as electroabsorption spectrum, which is abbreviated as EA spectrum.

3. Results

EA spectra in the region from 300 to 700 nm obtained with a field strength of 0.75 MV cm^{-1} are shown in Figure 1, together with the corresponding absorption spectra, where the concentrations of Z1, Z2, Z3, and Z4 relative to the monomer unit of PMMA were 0.33, 0.06, 0.06, and 0.04 mol %, respectively. The magnitude of ΔA is proportional to the square of the applied field strength in every case. The EA spectrum of the monomer in the region of the Soret band is very similar in shape to the

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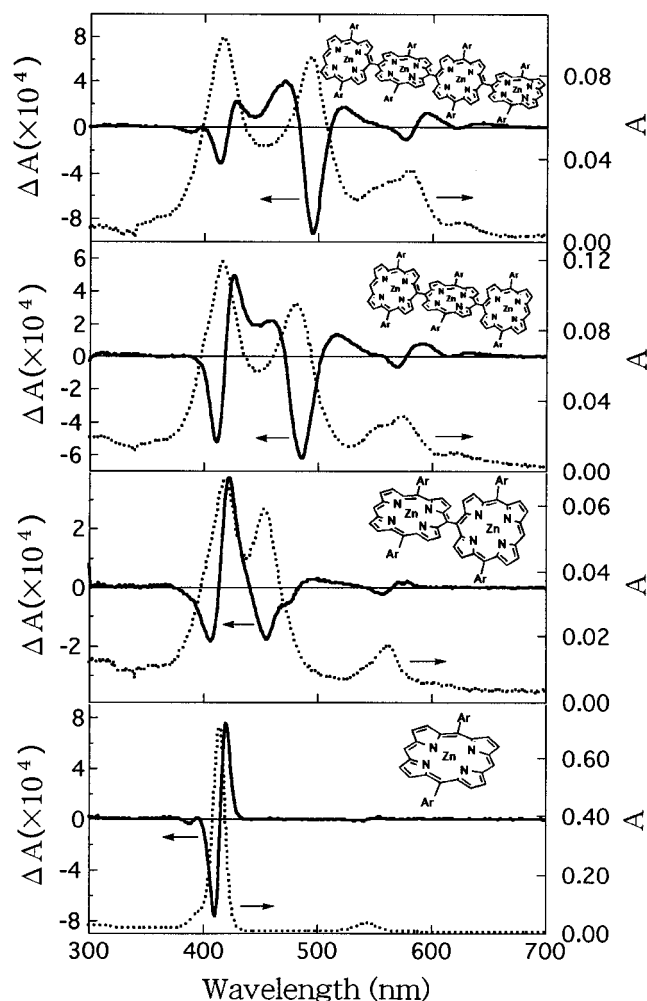


Figure 1. EA spectra of zinc porphyrin (Z1), its dimer (Z2), trimer (Z3), and tetramer (Z4) in a PMMA polymer film (from the bottom to the top) observed with a field strength of 0.75 MV cm^{-1} (solid line), together with the absorption spectra (dotted line). Molecular structure of each sample is shown in the figure. Ar = 3,5-di-*tert*-butylphenyl.

first derivative spectrum, as will be mentioned later, whereas the EA spectra of porphyrin oligomers are very different from the simple first derivatives of the absorption spectra. As will be mentioned later, the EA spectra are reproduced by a combination of the first derivative with the second derivative of the absorption spectrum for each exciton splitting component of the Soret band, suggesting that the splitting components of the Soret band show different behaviors of field dependence from each other.

We focus our attention on the EA spectra of only the Soret bands. The Soret band of Z1 shows a sharp peak at 413.7 nm in a PMMA film, while in oligomers Z2–Z4, this band splits and shows two strong peaks. The splitting component of the Soret band at the shorter wavelength side, referred to as band (A), is located at 417.7, 415.9, and 416.0 nm for Z2, Z3, and Z4, respectively, while another strong splitting component, referred to as band (B), is red-shifted with an increase in the number of the linked porphyrins. Note that the peak of band (B) is observed at 452.4, 480.1, and 492.6 nm for Z2, Z3, and Z4, respectively. The absorption bands located at wavelengths longer than 500 nm, which show a red-shift with an increase in the number of the porphyrin ring, are assigned as the Q bands, whose EA spectra are not discussed in the present manuscript.

4. Discussion

In polymer films where chromophores are randomly distributed, the absorption spectra are broadened by an applied electric field due to the change in electric dipole moment following optical transition ($\Delta\mu$) giving rise to a Stark effect's line shape which is approximately the second derivative of the absorption spectrum. If the change in molecular polarizability following photoexcitation ($\Delta\alpha$) is significant, the Stark effect's line shape is the first derivative of the absorption spectrum. If the magnitude of the transition moment is affected by an applied electric field, the Stark effect's line shape is the same as the absorption spectrum. Therefore, EA spectra of dye chromophores distributed in a polymer film can be expressed by a combination between the absorption spectrum, its first derivative, and the second derivative spectra.^{11–14} The integral of the EA spectrum across the Soret band gives a non-zero value, but the value is not significantly large in every case. As far as the field effect comes only from $\Delta\mu$ or $\Delta\alpha$, the total absorption intensity is not affected by an electric field. Therefore, a very small value of the integral of the EA spectra indicates that the change in transition moment is not significant. In fact, the present EA spectra could be simulated quite well by a combination between the first and the second derivatives of the absorption spectrum, as will be mentioned below.

The analysis of the EA spectra is described in detail by taking trimer (Z3) as an example (Figure 2). The integral of ΔA , i.e., $\int \Delta A \, d\nu$, and the integral of $f\Delta A \, d\nu$ are calculated as a function of ν . The integral is taken from the higher frequency side to the lower since the Q bands are located in the low energy region of the Soret band, to which the present attention is focused. The shape of $-\int \Delta A \, d\nu$ across band (A) is nearly the same as the absorption spectrum, implying that the EA spectrum of band (A) is close in shape to the first derivative of the absorption spectrum. Note that $\int \Delta A \, d\nu$ gives a shape which is the same as the absorption spectrum of A when ΔA is given by the first derivatives of A. Actually, the EA spectrum of band (A) also includes the shape of the second derivative of the absorption spectrum, as is known from the red-shift of the peak in $-\int \Delta A \, d\nu$ relative to the peak of absorption band (A). The shape of $f\Delta A \, d\nu$ across band (B) is similar to the first derivative of the absorption spectrum, in contrast with the shape across band (A). The further integral of $\int \Delta A \, d\nu$ gives a shape similar to the absorption spectrum, indicating that the EA spectrum across band (B) is close in shape to the second derivative of the absorption spectrum. These results imply that the permanent electric dipole moment is induced by photoexcitation into band (B). It is also known that the EA spectrum of band (B) includes the first derivative part of the absorption spectrum besides the second derivative since the peak position of the absorption band (B) is different from the corresponding peak in the integral of $\int \Delta A \, d\nu$.

For the simulation of the EA spectrum across the Soret band of Z3, two absorption bands which give a Gaussian profile were assumed to be concerned, i.e., band (a) and band (b), whose peak was taken to be the same as the one of bands (A) and (B), respectively. The spectral width of bands (a) and (b) was evaluated to be 890 and 1300 cm^{-1} , respectively, from the HWHM both of $\int \Delta A \, d\nu$ across band (A) and of the integral of $\int \Delta A \, d\nu$ across band (B). The EA spectra of Z3 could be reproduced quite well by a combination between the first derivative and the second derivative of bands (a) and (b), except for the intermediate region of bands (A) and (B), as is shown in Figure 2c. As a result, the magnitudes of $\Delta\alpha$ and $\Delta\mu$ following excitation into each of bands (a) and (b) are

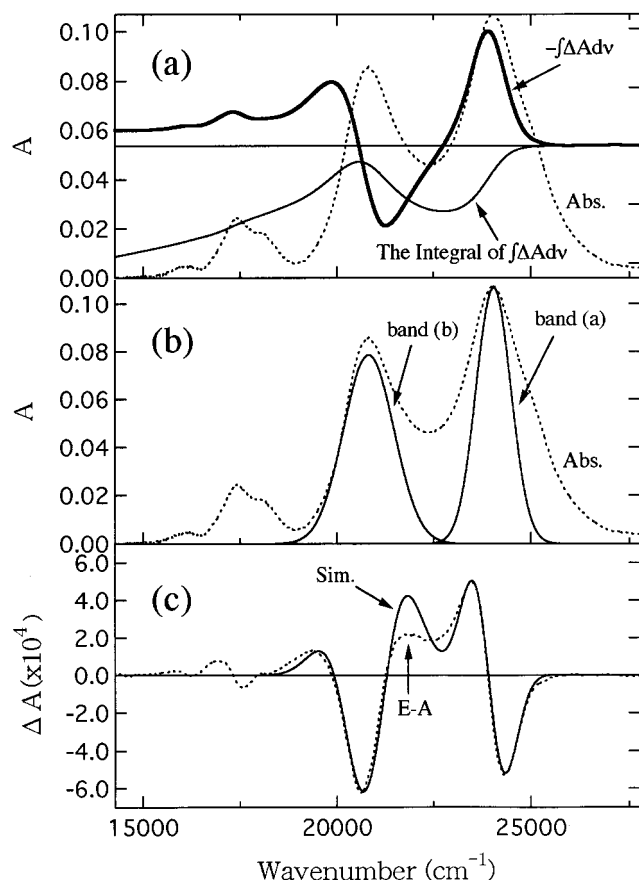


Figure 2. A series of optical spectra of Z3. (a) Absorption spectrum (dotted line), the integral of the EA spectrum, $-f\Delta A dv$ (thick solid line), and the integral of $f\Delta A dv$ (thin solid line); (b) absorption spectrum (dotted line) and two absorption bands, i.e., bands (a) and (b), each of which has a Gaussian shape, used for the simulation of the EA spectrum (solid line); (c) EA spectrum observed with a field strength of 0.75 MV cm^{-1} (dotted line) and the simulated spectrum (solid line). A continuum of the background is subtracted in the absorption spectra shown in (a) and (b).

TABLE 1: The Magnitude of $\Delta\mu$ and $\Delta\alpha$ for Excitation into Each of the Soret Bands of Porphyrin Monomer (Z1), Dimer (Z2), Trimer (Z3), and Tetramer (Z4)

band	peak (nm)	$\Delta\mu$ (D)	$\Delta\alpha$ ($4\pi\epsilon_0\text{\AA}^3$)
Z1	413.7	~ 0	56
Z2			
band (a)	413.6	~ 0	250
band (b)	452.4	12.0	-60
Z3			
band (a)	415.9	4.5	300
band (b)	480.1	16.6	-320
Z4			
band (a)	416.0	6.0	200
band (b)	492.6	21.5	-390

evaluated by employing the coefficients of the first and the second derivative parts of the simulated spectra, respectively.¹³ The results are shown in Table 1. The disagreement between the simulated spectrum and the EA spectrum in the intermediate region between bands (A) and (B) may result from the simple assumption of the Gaussian profile as the shape of bands (a) and (b). It is worth mentioning that the sum of the two bands (a) and (b) does not reproduce the absorption spectrum, implying that the absorption spectrum does not come from a single species. A superposition of the absorption bands belonging to different rotational isomers seems to make the absorption spectrum complicated. As far as the spectral shapes both of $f\Delta A$

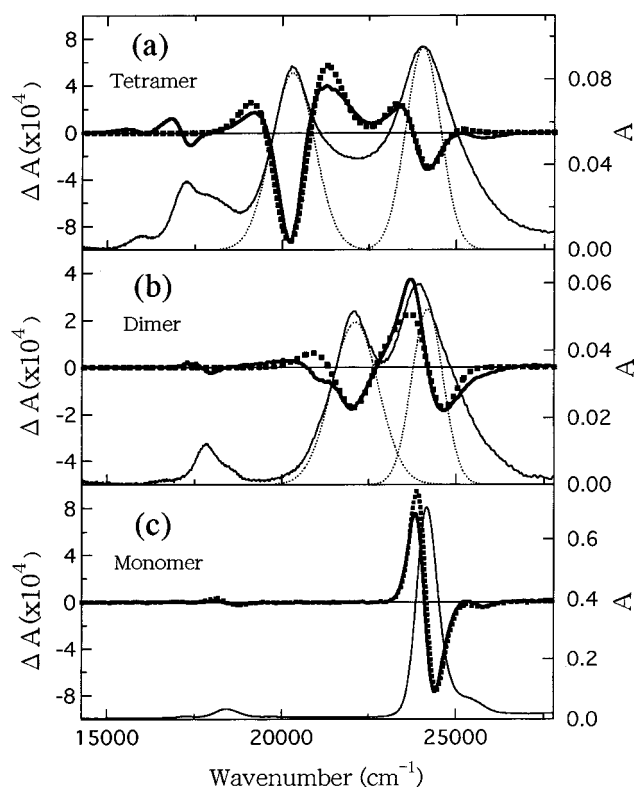


Figure 3. Thick dotted lines in (a) and (b) show the EA spectrum simulated by a linear combination between the first derivative and the second derivative of the absorption spectrum in Z4 and Z2, respectively. The thick dotted line in (c) shows the first derivative of the absorption spectrum of Z1. Thin solid lines in (a), (b), and (c) show the absorption spectrum of Z4, Z2, and Z1, respectively. Thin dotted lines in (a) and (b) show the absorption bands with a Gaussian shape used for the simulation. A continuum of the background is subtracted in the absorption spectra shown in (a) and (b).

dv and of the integral of $f\Delta A dv$ are carefully examined, it is very likely that only one species that gives the exciton splitting bands (a) and (b) gives a large Stark shift.

The EA spectra of Z2 and Z4 were similarly simulated with two absorption bands having a Gaussian profile, i.e., bands (a) and (b), whose bandwidths were determined from the HWHM both of the spectrum of $f\Delta A dv$ across band (A) and of the spectrum of the further integral of $f\Delta A dv$ across band (B), respectively, as in the case of Z3. The results are shown in Figure 3. Only the peak of band (a) of Z2 was assumed to be slightly red-shifted from the absorption peak of band (A), based on the spectrum of $f\Delta A dv$. The other peaks of bands (a) and (b) of Z2 and Z4 are assumed to be the same as the corresponding ones of bands (A) and (B). The absorption peak of band (A) of Z2 is exceptional in the sense that this peak is located at the wavelength longer than the peaks of band (A) of the other compounds not only in a polymer film but also in solution.⁸ It is noted that the present peak of band (a) of Z2 is nearly the same as the peak of the Soret band of Z1 (see Table 1). Therefore, it seems to be very likely in Z2 that the peak of absorption band (a) which gives a large electric field effect is different from absorption band (A). Based on the comparison between the EA spectra and the simulated spectra, the magnitudes of $\Delta\mu$ and $\Delta\alpha$ of Z2 and Z4 were evaluated, and the results are shown in Table 1. The negative sign of $\Delta\alpha$ shows that the magnitude of the molecular polarizability becomes smaller following excitation.

The magnitudes of $\Delta\mu$ and $\Delta\alpha$ shown in Table 1 were obtained by assuming that the internal field is the same as the

applied field and that the molecular polarizability is isotropic. Actual field strength on molecules (F_{eff}) is different from the applied electric field (F) because of the dielectric properties of the environment. Then, the evaluated values of $\Delta\mu$ and $\Delta\alpha$ shown in Table 1 may have to be multiplied by a correction factor given by $(F/F_{\text{eff}})^2$. Unfortunately, this factor is not known at the present, but the factor is considered to be common in all the samples under the present study since the concentrations of Z1–Z4 in PMMA are quite low. In the evaluation of $\Delta\mu$ in Table 1, the transition moment was assumed to be parallel with the direction of the linked porphyrin array for band (b), while it was assumed to be perpendicular to the direction of the linkage for band (a), in all the cases of Z2–Z4. The interaction between two transition dipoles whose directions are the same induces a large energy separation, whereas two dipoles whose directions are perpendicular with each other give no interaction.^{15,16} Band (B) shows a red-shift with an increase in the number of the linked porphyrins, implying the large dipole–dipole interaction whose strength increases with an increase of the number of the linked porphyrins. On the other hand, band (A), i.e., band (a), shows roughly the same peak position in Z1–Z4, implying that the dipole–dipole interaction is negligible. As mentioned above, therefore, the transition moments for bands (a) and (b) are considered to be directed perpendicular and parallel to the linked porphyrins array, respectively. In fact, the suggestion of an approximate perpendicular arrangement of the neighboring porphyrins implies no dipole–dipole interaction for band (a).⁸

The EA spectrum of Z1 across the Soret band at ~ 400 nm is essentially the same in shape as the first derivative of the absorption spectrum (see Figure 3), indicating that the field effect probably comes only from $\Delta\alpha$ (see Table 1). The result that $\Delta\mu$ is negligible in Z1 may be well understood since the porphyrin skeleton gives D_{4h} symmetry, where the permanent electric dipole moment is zero.

As is shown in Table 1, $\Delta\mu$ is non-zero in Z2–Z4, except for band (a) of Z2, and the magnitude of $\Delta\mu$ at band (b) is much larger than the one at band (a) in every oligomer. Further, the magnitude of $\Delta\mu$ monotonically increases with increasing the number of the linked porphyrins. This clear trend with increasing array size is impregnable, even when experimental error, which comes mainly from the uncertain evaluation of the absorption intensity of the Soret band superimposed by the Q-band, is assumed to be as large as 20%. As mentioned above, the direction of the transition moment of band (b) is considered to be directed along the linked porphyrin array. Therefore, the present result seems to show that photoinduced charge transfer occurs along the linked porphyrin arrays. In the simulation, the signs of the first derivatives of bands (a) and (b) are opposite

to each other, indicating that band (a) gives a red-shift, whereas band (b) gives a blue-shift in the presence of an external electric field. Interestingly, the magnitude of $\Delta\alpha$ at band (b) becomes smaller with increasing the number of the linked porphyrins, indicating that the magnitude of the decrease in molecular polarizability following excitation into band (b) becomes larger with an increase in the number of linked porphyrins. These results may be attributed to electron localization as a result of charge transfer along the linked porphyrin arrays.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan (No. 10440163).

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