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Evidence for $\pi-\pi$ Interactions in the S_1 State of Zinc Porphyrin Dimers Revealed by Picosecond Time-Resolved Resonance Raman Spectroscopy

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The S_1 states of Zn(II)−porphyrin dimers have been investigated with picosecond time-resolved resonance Raman spectroscopy. The transient absorption and Raman spectra of porphyrin dimers, in which two Zn(II)−porphyrins are covalently linked at the ortho or meta positions of phenylene spacers, are compared with those of their component monomer unit. Although the Q-band of the ortho dimer was definitely different from those of the meta dimer and reference monomer, the ground-state Raman spectra of the ortho and meta dimers are nearly the same as that of the monomer, suggesting that the porphyrin $\pi-\pi$ interactions strongly appear in the excited state but little in the ground state in the ortho dimer. Several characteristic Raman bands were observed for the S_1 excited state at 2 ps after photoexcitation. The monomer S_1 state gave the marker bands at slightly lower frequencies (by 3−4 cm^{-1}) than the corresponding ground state, and they showed no frequency shifts with time between 2 and 300 ps. On the contrary, in the case of the ortho dimer S_1 state, two characteristic bands (ν_2, ν_4) appeared at frequencies significantly lower (by 10−13 cm^{-1}) than the corresponding ground-state bands, and in addition, the frequency of the ν_4 band exhibited an upshift around 10−20 ps following photoexcitation. This frequency shift of the ortho dimer was appreciably perturbed by steric hindrance between the two porphyrins groups when bulky *tert*-butyl groups at the para position were incorporated. The behaviors of transient Raman bands of the meta dimer appeared intermediate between the monomer and the ortho dimer. These observations give the first clear evidence for the presence of $\pi-\pi$ interactions in the S_1 excited state of porphyrin dimers with phenylene spacer and the occurrence of geometric relaxation toward the monomer-type structure in several tens of picoseconds.

Introduction

Relations between a structure and electronic properties of porphyrin dimers are of current spectroscopic concern, since the photosynthetic reaction centers of plants and bacteria always contain a dimer structure. The initial charge separation takes place only from the excited state of the closely interacting bacteriochlorophyll dimer (special pair; SP),[1,2] although mixing of excited states of the SP with those of other chromophores in the reaction center protein complex was also recently noted.[3,4] Therefore, detailed characterization of the initial excited state of a porphyrin dimer is indispensable to understand a mechanism of the initial charge separation process in the photosynthetic reaction center protein complexes. To elucidate the essential factors that control the charge separation processes, many porphyrin-containing model compounds have been synthesized and examined from the viewpoint of ultrafast phenomena.[5−7] Of these, we have developed diporphrin−porphyrin−pyromellitimide triad models in which long-lived charge-separated states are formed upon photoexcitation via a series of efficient electron-transfer reactions in a manner similar to those of natural systems.[7−9] Although the S_1 state of 1,2-phenylene-bridged Zn(II)−porphyrin dimer plays an essential role in these charge separation processes, the details of its structure and properties still remain unclarified. The next point to be clarified is a role of the excited state of the dimer, which is distinct from that of the monomer based on the transient absorption spectra observed.

Resonance Raman spectroscopy has a unique advantage that can give insights into the conformational and electronic structures of the porphyrin macrocycle in the excited as well as in the ground electronic states.[10−16] The molecular orbitals of simple metalloporphyrin monomers have been studied at a sufficiently high level,[17] and on the basis of the bonding and antibonding characters of specific chemical bond for a given molecular orbital, we can deduce some plausible changes of individual chemical bonds accompanied by electron promotion. Several studies of metalloporphyrin π-cation radicals have pointed out that the highest occupied molecular orbitals (HOMO) of metallo-octaethylporphyrin (MOEP) and metallo-tetraphenylporphyrin (MTPP) have the a_{1u} and a_{2u} symmetry in the D_{4h} approximation, respectively, while the lowest empty molecular orbital (LUMO) has the e_g symmetry for both.[18] Moreover, it is now technically possible to pursue the excited-state structual dynamics of more complicated molecules by using time-resolved Raman technique.[16]

In this study 1,2-phenylene-bridged (ortho) Zn(II)−porphyrin dimer and 1,3-phenylene-bridged (meta) Zn(II)−porphyrin dimer were chosen to explore the implicated relations between

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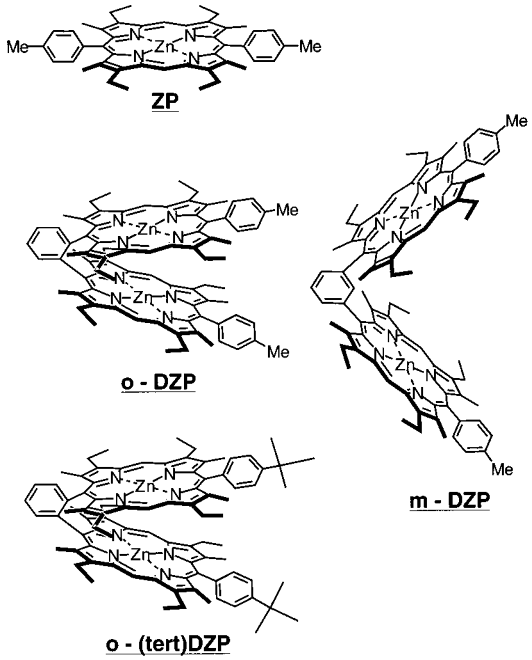

Figure 1. Compounds used in the experiments.

geometric and electronic structures in the excited state. The properties of the S_1 state of Zn(II)−porphyrin dimers, which may serve as a model of the SP of the photosynthetic reaction center, are of particular interest, since they determine the efficiency to proceed to the electron-transfer reaction. We applied the picosecond time-resolved resonance Raman spectroscopy and succeeded in detecting the Raman spectra of the S_1 state of Zn(II)−porphyrin dimers for the first time and finding frequency shifts with time in the excited state, which is unique for the ortho dimer. The observed results strongly suggest the presence of a $\pi-\pi$ interaction between the two porphyrins of a molecule only in the excited state and some structural relaxation occurring in the excited state.

Experimental Section

The compounds used are depicted in Figure 1. Samples were synthesized and purified by the method described before.[9] Monomer Zn(II)−porphyrin (ZP), which is a component unit of dimers, has a structure similar to octaalkylporphyrin except that two aryl groups attached at 5- and 15-*meso* positions. Zn(II)−porphyrin dimers, o-DZP and m-DZP, have 1,2-phenylene and 1,3-phenylene spacers, respectively. o-DZP is expected to have larger $\pi-\pi$ interactions between the porphyrins than m-DZP. In another dimer (o-(tert)DZP), 4-tolyl substituents are replaced by 4-*tert*-butylphenyl substituents in order to increase the steric repulsion between the two porphyrins. All these porphyrins were dissolved in tetrahydrofuran (THF) (∞ pure, Wako Pure Chemical), which was used without further purification. The concentration of porphyrin was adjusted to 500 μM. About 3 mL of the sample solution was put into a 10 mm square quartz cuvette, and before the Raman measurements, N_2 gas was bubbled into the solution to remove dissolved oxygen.

Steady-state absorption spectra were measured with a Shimadzu UV-260 spectrophotometer. Picosecond transient absorption spectra were measured using the dye laser photolysis system pumped by a second harmonic of a mode-locked Nd^{3+}:YAG laser (Quantel, Picochrome YG-503C/PTL-10), while details of the system were described elsewhere.[8] The excitation wavelength was selected to be 600 nm for o-DZP and 580 nm for other compounds. The transient absorption spectra were obtained for several delay times, although the spectra for one selected delay time will be presented.

The system for picosecond time-resolved resonance Raman measurements was previously explained in detail.[16] Briefly, spectra were measured with a picosecond Ti:sapphire laser that is pumped by an Ar^+ laser and amplified by a Nd^{3+}:YLF laser (Spectra Physics, Tsunami/Spitfire). The amplifier was operated at 1 kHz of repetition rate. Excitation of a porphyrin to the S_1 state was performed by the light pulse (570 nm, 15 mW, 1 kHz, fwhm = 2 ps) obtained with the OPG and OPA system from the second harmonic. The Raman spectra of the S_1-state porphyrin was probed by the first Stokes shifted line of CH_4 (for o-DZP:442 nm; for m-DZP,ZP:460 nm, 2 mW, 1 kHz) excited by the second harmonic of the Ti:sapphire laser. The probe wavelengths were selected to match the peak position of the S_n-S_1 absorption determined by the transient absorption spectra observed. The probe beam was guided to the optical delay line, which was controlled by a stepping motor, to yield an appropriate delay time (Δt) from the pump pulse. The pump and probe beams were spatially overlapped using a dichroic mirror and were focused onto the cuvette, in which the sample solution was always stirred by a rotating magnetic stirrer during data accumulation, in a 135° backscattering geometry using a cylindrical focusing lens. Scattered light was collected, dispersed in a single spectrograph (Chromex, 500IM-CM) and detected by a liquid nitrogen-cooled CCD detector (Prinston Instruments, CCD-1100PB). The zero point of the delay line was determined by the excited-state absorption spectrum of Rhodamine 6G dissolved in methanol and/or the sample itself, detected by a Si photodiode.

Both the mirror position in the optical delay line and data acquisition from the CCD detector were controlled by a computer programmed so as to achieve the quasi-simultaneous measurements.[15,19] By using this method, the spectra for various delay times and also the probe-only spectra could be measured under the same conditions and at nearly the same time. This procedure ensures that the spectral changes observed have in fact arisen from temporal changes of the excited molecule. When there was evidence for photodamage or formation of irreversible product in the observed Raman spectra, the subsequent spectra were discarded. Absorption spectra were also examined before and after each Raman measurement to confirm the sample integrity during the experiment. Typically, the accumulation time for individual spectrum was 20 s, and about 50 cycles were repeated for one selected value of delay times to accumulate the data in a computer. Accordingly, the total accumulation time for the pump−probe and probe-only spectra with a specified value of Δt was ~15 min. The sample was replaced with a fresh one every 2−3 h to avoid the effect of generated photoproducts. The Raman spectra of the excited state were obtained by subtracting the probe-only spectra from pump−probe spectra with an appropriate factor. The value of the factor was determined so as to minimize the intensity of the solvent peaks, and it was confirmed that any negative peak and/or positive peaks of the ground state also disappeared. Since the probe-only and pump−probe spectra were obtained under the same conditions and at almost the same time, and careful subtractions were performed, the resulting difference spectra can be attributed to a transient excited state.

Results

Ground-State Absorption and Raman Spectra. Absorption spectra of ZP, m-DZP, and o-DZP in THF are shown in

TABLE 1: Ground- and Excited-State Vibrational Frequecies of ZnOEP, ZP, m-DZP, and o-DZP in THF and Their Assignments

	ZP[a]		m-DZP[a]		o-DZP[a]		ZnOEP[b]	
vibrational mode	S_0/cm^{-1}	S_1/cm^{-1}	S_0/cm^{-1}	S_1/cm^{-1}	S_0/cm^{-1}	S_1/cm^{-1}	S_0/cm^{-1}	S_1/cm^{-1}
$\nu_{10}(C_\alpha{-}C_m)$					1611		1614	
$\nu_2(C_\beta\text{-}C_\beta)$	1581	1578	1581	1575	1581	1571	1583	1562
$\nu_3(C_\alpha{-}C_m)$	1486		1486		1486		1483	1447
$\nu_{29}(C_\alpha{-}C_\beta)$	1406	1401	1406	1400	1406		1400	
$\nu_4(C_\alpha{-}N)$	1345	1342	1347	1339 → 1342	1346	1333 → 1342	1373	1355
$\nu_1(C_m{-}Ph)$			1258		1254			
$\nu_5(C_\beta{-}C_1)$	1131	1128	1131	1126	1133		1136	1132

[a] This work. [b] Reference 10a.

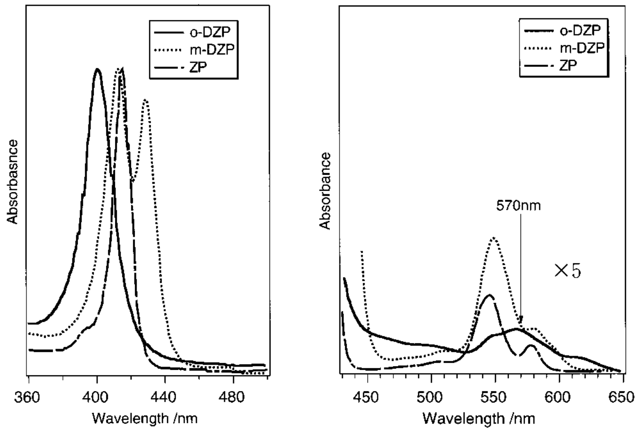

Figure 2. Absorption spectra of ZP, m-DZP, and o-DZP in THF: (left) Soret band region; (right) Q-band region.

Figure 2. The spectrum of o-(tert)DZP was nearly the same as that of o-DZP. In the Q-band region, the spectra of ZP and m-DZP had a similar shape and the intensity of m-DZP was roughly twice as large as that of ZP, suggesting simple addition of the two monomer bands. This means that the electronic structures of the component porphyrins in m-DZP in the S_1 state are close to that of ZP, and the interaction between two porphyrins is relatively weak. In its Soret band region, however, the exciton splitting was observed for m-DZP, indicating that the two porphyrins are interacting in the S_2 state to split into new doublet states. On the other hand, the Q-band in the o-DZP, changed drastically from that in ZP and there was a large blue shift of Soret band of o-DZP from that of ZP, indicating the parallel geometry of the interacting transition dipoles.[9c] The configuration interaction in the dimer must be changed from that of the monomer, and it would alter the mixing ratio of the S_1 and S_2 states in these dimers. This should arise from the strong $\pi{-}\pi$ interactions between two porphyrin moieties.

Figure 3 shows the resonance Raman spectra of ZP, m-DZP, and o-DZP in the electronic ground state. Although the ground-state absorption spectra were completely different among ZP, m-DZP, and o-DZP, their ground-state resonance Raman spectra were alike. Except for the ν_4 band, the positions and pattern of bands are similar to those of Zn(II)−octaethylporphyrin (ZnOEP) excited at 413 nm,[10b] and accordingly, the observed bands are assigned to each vibrational mode from the correspondence to those of ZnOEP in Table 1. The ν_4 frequencies of ZP, m-DZP, and o-DZP are appreciably lower than that of ZnOEP and are rather close to that of ZnTPP, indicating the appearance of the effect of two phenyl substituents only in the ν_4 mode.

Among the three spectra shown in Figure 3, only the spectrum of o-DZP gave slightly different features. One is that the ν_{10} band (1611 cm^{-1}), which is mainly associated with $\nu(C_\alpha C_m)$, was observed only for o-DZP but unrecognizable in the other two spectra, and the other is that the ν_1 band (1254 cm^{-1}), which arises from $\nu(C_m{-}\text{phenyl})$ was more enhanced in o-DZP. This may suggest that the angle between aryl groups and porphyrin planes is more deviated from a right angle in o-DZP. Except for these minor differences, the three spectra are alike. Accordingly, despite the distinct difference in absorption spectra, the molecular vibrations are almost the same among ZP, m-DZP, and o-DZP in the ground electronic state.

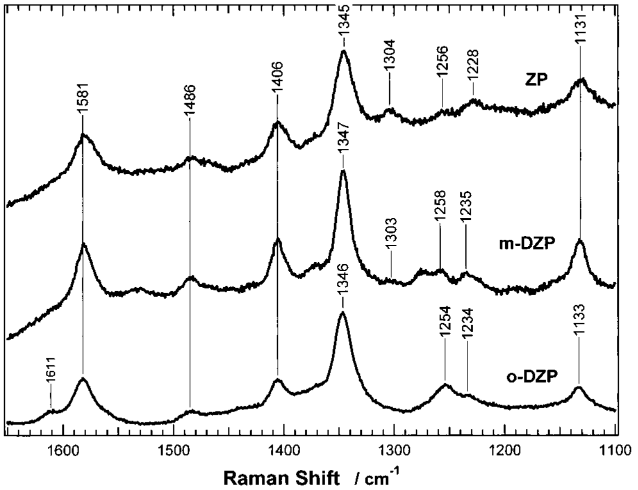

Figure 3. Steady-state Raman spectra of ZP and m-DZP excited at 460 nm and o-DZP at 442 nm, respectively, in THF.

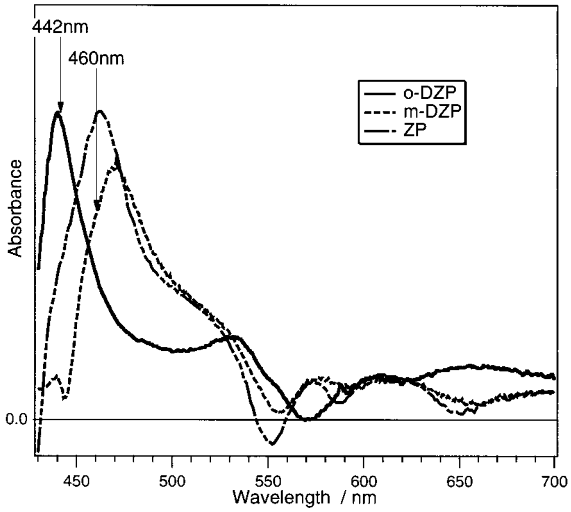

Figure 4. Transient absorption spectra of ZP, m-DZP, and o-DZP in THF pumped at 610 nm. The delay time (Δt) is 100 ps.

Picosecond Transient Absorption and Resonance Raman Spectra. Transient absorption spectra of ZP, m-DZP, and o-DZP at 100 ps after excitation are shown in Figure 4. The S_1 spectra of ZP and m-DZP are alike except for the blue side shoulder

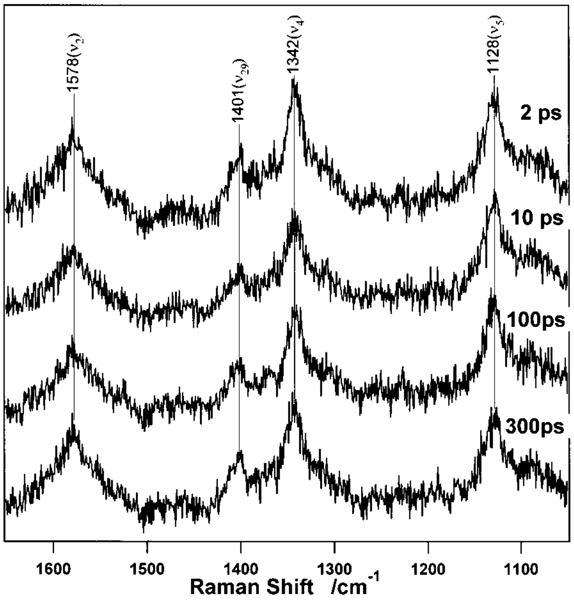

Figure 5. Time-resolved resonance Raman spectra of ZP in THF. The delay time for each spectrum is shown in the figure.

around 460 nm. Since there is a ground-state strong absorption band at 438 nm, the bleaching of the ground state might slightly scrape the shoulder of the S_1 absorption peak of m-DZP. On the contrary, the S_1 spectrum of o-DZP is distinct from others. The shape of these transient absorption spectra did not change in the time range from 10 ps to 1 ns (not shown). On the basis of these transient spectra, the probe wavelengths for the S_1-state Raman spectra were chosen to be 442 nm for o-DZP and 460 nm for ZP and m-DZP.

The results of picosecond time-resolved resonance Raman spectra of ZP are shown in Figure 5. The delay time, Δt, was changed from -2 to $+300$ ps. While no bands were observed at $\Delta t = -2$ ps (not shown), four characteristic bands were observed after 2 ps of the delay time and their frequencies and assignments are denoted in the figure. The peak positions of bands, which did not change with time until 300 ps, and the spectral pattern resemble those of the S_1 excited state of ZnOEP (Table 1) except for ν_4. Both ν_2 ($1581 \rightarrow 1578$ cm^{-1}) and ν_4 ($1545 \rightarrow 1542$ cm^{-1}) bands exhibited small downshifts upon excitation to S_1 compared with the ground state, but the relative intensities of the bands are almost unaltered by electronic excitation similar to the case of H_2OEP[14a] and ZnOEP.[10b] These features can be explained by assuming that the S_1 state is an admixture of the ($a_{1u} \rightarrow e_g$) and ($a_{2u} \rightarrow e_g$) excited states as proposed for H_2OEP and ZnOEP.[10b,14a] The core size of the porphyrin remains unaltered by promotion of an electron from the HOMO to the LUMO.

Figure 6 displays the time-resolved Raman spectra of o-DZP for Δt values from 0 to 300 ps together with the spectrum of the ground state for comparison. In the transient spectra, two characteristic bands (ν_2 and ν_4) are prominent and their frequencies are significantly lower (by 10−13 cm^{-1}) than those of the ground state. The most interesting feature is the upshift of ν_4 with time ($1333 \rightarrow 1341$ cm^{-1}); in early delay time ($\Delta t <$ 10 ps), it appeared at 1333 cm^{-1}, but later it shifted to higher frequencies (1341 cm^{-1} at 300 ps). On the other hand, the ν_2 band stayed at the same position (1571 cm^{-1}). Both bands are shifted downward compared with those of the S_1 state of ZP. To further confirm that this feature appears from the $\pi-\pi$ interaction, we tried to reduce the $\pi-\pi$ interaction within the ortho form by introducing the steric hindrance between bulky groups.

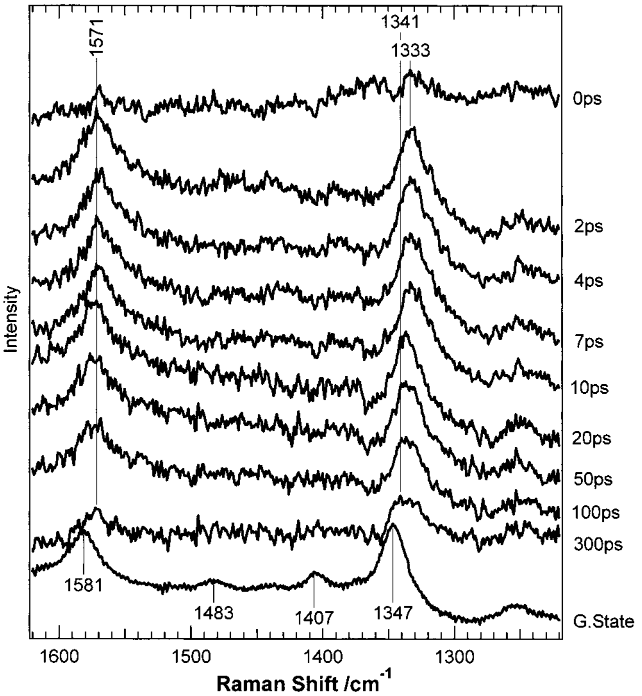

Figure 6. Time-resolved resonance Raman spectra of m-DZP in THF. The delay time for each spectrum is shown in the figure.

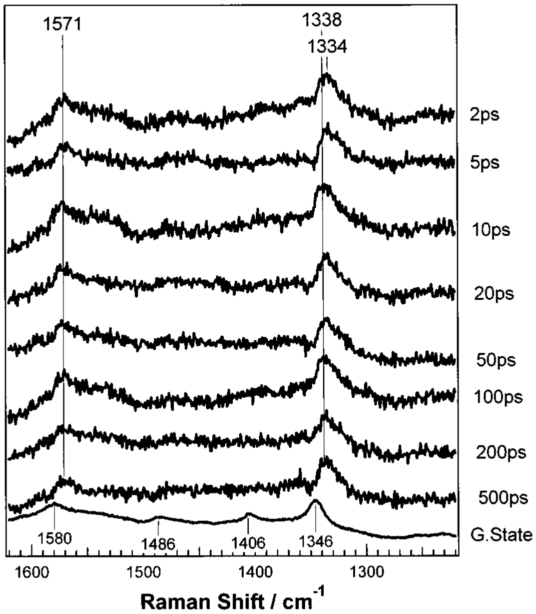

Figure 7. Time-resolved resonance Raman spectra of o-DZP in THF. The delay time for each spectrum is shown in the figure.

Figure 7 shows the time-resolved Raman spectra of o-(tert)-DZP, to which tertiary butyl groups were incorporated into phenyl rings at opposite sites of porphyrin of the ortho dimer, together with its ground-state spectrum (bottom). The frequencies of Raman bands of o-(tert)DZP in the ground state are similar to those of o-DZP, indicating that effects of the tertiary butyl group on vibrations of porphyrin are negligible in the ground electronic state. In the transient spectra, the ν_2 and ν_4 bands are observed at the same frequencies as those of o-DZP for $\Delta t = 2$ ps, and the ν_4 band exhibited an upshift with time. However, the final ν_4 frequency for $\Delta t = 500$ ps is slightly lower than that of o-DZP at $\Delta t = 300$ ps, and accordingly, the size of the frequency shift ($1334 \rightarrow 1338$ cm^{-1}) was smaller for o-(tert)DZP than for o-DZP.

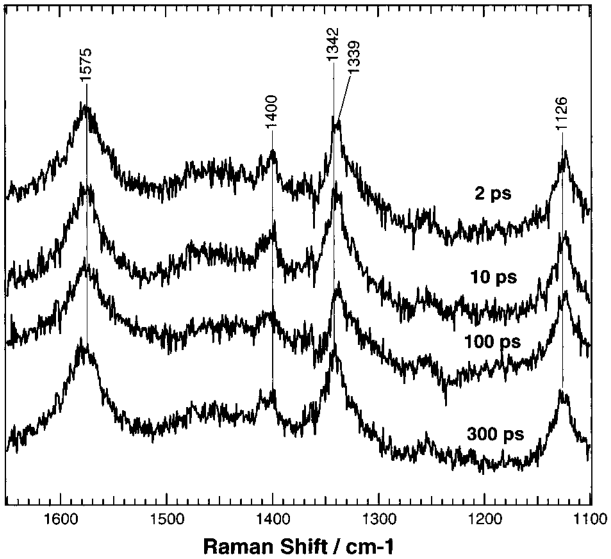

Figure 8. Time-resolved resonance Raman spectra of o-(tert)DZP in THF. The delay time for each spectrum is shown in the figure.

Figure 8 shows the transient Raman spectra of m-DZP for Δt values of 2, 10, 100, and 300 ps. The band center frequencies in the spectrum for $\Delta t = 2$ ps are lower than the corresponding ground-state frequencies by 5−6 cm^{-1}, but the spectral patterns are unaltered with time and similar to those of the ground state. There seems to be a small upshift with time for the ν_4 band (1339 → 1342 cm^{-1}). The magnitudes of the frequency difference between the S_1 and ground states and of the temporal change of the ν_4 frequency both are of intermediate size between those of ZP and o-DZP. This suggests that the frequency lowering in the S_1 state is due to the $\pi-\pi$ interactions between the two porphyrin groups, which is strongest in o-DZP, of medium size in o-(tert)DZP and m-DZP, and absent in ZP. Thus, it became confident that there exist the $\pi-\pi$ interactions between two porphyrins in the S_1 excited state.

Discussion

Since the vibrational frequencies are strongly correlated with the properties of the electronic states of the molecule, examining the origin of the Raman shifts will give us the insights about the interactions in the S_1 excited states. On the basis of Goutermann's four-orbital theory,[20] Sato et al.[14] explained the upshift and downshift of ν_2 bands observed for the S_1 state of H_2OEP and H_2TPP, respectively, in terms of the difference in the orbital symmetry of the HOMO between OEP and TPP. On the other hand, Kumble et al. applied the same four-orbital model to interpret the Raman shift of the S_1 state of ZnOEP.[10a] They qualitatively explained the downshifs of ν_2 and ν_4 bands in the S_1 state compared with those of the ground state, incorporating an idea of the admixture of a singly occupied HOMO with a singly occupied LUMO, which is caused by the configuration interaction. Since the ν_2 and ν_4 associate mainly with the C_β-C_β and C_α−N stretching modes, respectively, the changes of bond strength upon electron promotion are essential for discussing the present results.

The highest occupied a_{2u} orbital has bonding and antibonding characters on the $C_\beta-C_\beta$ and C_α−N bonds, respectively, and the highest occupied a_{1u} orbital has the antibonding and nonbonding characters for the $C_\beta-C_\beta$ and C_α−N bonds, respectively, while the lowest empty e_g orbital has antibonding character on the C_α−N bond and practically no net trend on the $C_\beta-C_\beta$ bond.[17] Accordingly, promotion of an electron from the a_{2u} to e_g orbital is expected to weaken the C_β-C_β bond but may slightly strengthen the C_α−N bond. In contrast, promotion of an electron from the a_{1u} to e_g orbital is expected to weaken the C_α−N bond but may strengthen the $C_\beta-C_\beta$ bond. Actually, the two excited states are strongly mixed through configuration interactions to yield the S_1 and S_2 states,[20] and therefore to discuss the size of frequency shifts upon electronic excitation from the ground state, precise numerical calculations for the configuration interactions are required. As shown in Table 1, the ν_2 and ν_4 frequencies of the monomer in the S_1 state were lower than those of the ground state by 3 cm^{-1}. This reflects the resultant effects of the configuration interactions within a monomer porphyrin, and the electronic transition from the ground state to the S_1 excited state slightly increases the antibonding character in both $C_{\beta-\beta}$ and C_α−N bonds in this monomer case.

Since the e_g LUMO is more extended than the a_{1u} and a_{2u} HOMO, it is quite reasonable that the $\pi-\pi$ interactions between the two porphyrin groups appear only in the excited state. In fact, since no net differences were observed between the monomer and the dimers in ground-state Raman spectra, it is obvious that the $\pi-\pi$ interactions in the ground state were rather small and could not change the electron density on the HOMO of each monomer. Therefore, the $\pi-\pi$ interaction that is also observed in absorption spectrum must come from the interaction between e_g LUMOs. Next we will discuss this interaction in the excited state.

In the case of dimer, we first assume an exciplex-like weak interaction in the excited state. Suppose that the frontier molecular orbital of the interacting dimer, $e_g(D)$, is represented by the admixture of two e_g orbitals of the monomer, $e_g(M)$, by eq 1, where a and b stand for individual monomer porphyrins

$$e_g(D) = c_a e_g{}^a(M) + c_b e_g{}^b(M) \tag{1}$$

and c_a and c_b denote their contributions. When the two porphyrins are weakly interacting without a change of their e_g(M) orbitals and the overlap integral between $e_g{}^a(M)$ and $e_g{}^b$(M) is S, the wave function would be represented by eq 2, where

$$e_g(D) = (\sqrt{1 + \lambda^2 + 2\lambda S})^{-1}(e_g{}^a(M) + \lambda e_g{}^b(M)) \tag{2}$$

$c_a/c_b = \lambda \ll 1$. Under this approximation the electron density on the e_g orbital of each monomer in the exited state of the dimer becomes smaller due to delocalization of the $e_g(D)$ orbital, and accordingly, the changes in bond order accompanied by electronic transition from the ground state to the S_1 state would be smaller than the case localized within a monomer. This trend that reduces antibonding character, should increase in principle, as S becomes larger. Then the frequency shift between S_0 and S_1 states becomes smaller than that of the monomer. However, the frequency shifts of the ν_2 and ν_4 modes observed for o-DZP at $\Delta t = 2$ ps are much larger than those for the monomer. Therefore, the formulation of an exciplex based on the weak intermolecular interactions cannot explain the present results.

It means that as the overlap between the LUMO of two porphyrins becomes larger by electronic excitation, the configuration interaction within a monomer is significantly influenced and $e_g(M)$ itself must be altered. The $e_g(M)$ in the interacting dimer would change toward increasing antibonding characters in both the $C_\beta-C_\beta$ and C_α−N bonds as just occurring in the S_1 state of ZnOEP. When a new geometry of the two porphyrins is settled immediately after the electronic excitation, the magnitude of overlap integral of the new $e_g(M)$ orbitals, which is completely different from the original monomer e_g orbital, would be determined. Accordingly, the larger frequency reduction of the ν_2 and ν_4 modes upon electronic excitation to the S_1 state compared with the case of the monomer, could be explained by this strong $\pi-\pi$ interaction in the excited state. Comparing with the frequency shifts of ν_2 and ν_4 between o-DZP and m-DZP, the magnitudes of frequency shifts of m-DZP are smaller than those of o-DZP but larger than those of the monomer. This means that when the $\pi-\pi$ interaction in the excited state decreases in m-DZP compared to that of o-DZP, antibonding characters are reduced and frequency shifts become close to those of the monomer.

Two features were observed in the temporal frequency shifts of ν_4 in the S_1 state. In the o-(tert)DZP case, where the bulk tertiary butyl groups were incorporated for increasing steric repulsion between the two porphyrins, the initial frequency of ν_4 was the same (1333 cm^{-1}) as that of o-DZP, but the final frequency (1338 cm^{-1}) was slightly lower than that of o-DZP-(1342 cm^{-1}). This shows that steric repulsion of two porphyrins by bulk tertiary butyl groups prevents further relaxation. The other point is that the temporal change appears in ν_4 but not in ν_2. Since the phenyl substituents at the meso positions raise the energy of the a_{2u} orbital and accordingly they change the electron density on C_α and N atoms, the ν_4 is sensitive to the C_m situations.[17] Actually, since the ground-state frequencies of ZP are close to those of ZnOEP except for ν_4, the ν_4 mode would also be most sensitive to the phenyl substitution at C_m in this case. From these results, it can be said that a small change in a torsional angle around the C_m−phenyl bond at the spacer phenyl group causes a frequency change of ν_4 but not ν_2 in the S_1 state. In fact, a structural relaxation of such a bulky group is reported to take place on the order of several tens of picoseconds.[21] It is very likely that the size of this geometric change is influenced by the $\pi-\pi$ interaction in the S_1 state; the temporal shift is largest for o-DZP, for which the frequency differences between the S_1 and S_0 states are also much larger than those for m-DZP (Table 1). Since the torsional relaxation around the C_m−phenyl bond changes the angle between the π orbital on each porphyrin from almost parallel toward a slightly tilted direction, this relaxation presumably reduces the $\pi-\pi$ interactions and causes a shift of the ν_4 frequency toward that of the monomer (1341 cm^{-1}). When there are bulk tertiary groups at opposite sites of the phenyl, this relaxation is blocked and cannot reach its final position.

In conclusion, we have observed the resonance Raman spectra of Zn−porphyrin dimers in the S_1 state using picosecond time-resolved technique and succeeded in demonstrating the presence of $\pi-\pi$ interactions in the S_1 state of the dimer but not in the S_0 state and in observing of some features of structural relaxation for the first time. We are now proceeding to a dimer−acceptor system and a triad system of dimer−spacer−acceptor by extending the present technique.

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