

Resonance Raman spectroscopic study of fused multiporphyrin linear arrays

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For prospective applications as molecular electric wires, triply linked fused porphyrin arrays have been prepared. As expected from their completely flat molecular structures, π -electron delocalization can be extended to the whole array manifested by a continuous redshift of the HOMO-LUMO transition band to infrared region up to a few μm as the number of porphyrin units in the array increases. To gain an insight into the relationship between the molecular structures and electronic properties, we have investigated resonance Raman spectra of fused porphyrin arrays depending on the number of porphyrin pigments in the array. We have carried out the normal mode analysis of fused porphyrin dimer based on the experimental results including Raman frequency shifts of two types of ^{13}C -isotope substituted dimers, Raman enhancement pattern by changing excitation wavelength, and depolarization ratio measurements as well as normal-mode calculations at the B3LYP/6-31G level. In order to find the origins for the resonance Raman mode enhancement mechanism, we have predicted both the excited state geometry changes (A-term) and the vibronic coupling efficiencies (B-term) for the relevant electronic transitions based on the INDO/S-SCI method. A detailed normal mode analysis of the fused dimer allows us to extend successfully our exploration to longer fused porphyrin arrays. Overall, our investigations have provided a firm basis in understanding the molecular vibrations of fused porphyrin arrays in relation to their unique flat molecular structures and rich electronic transitions. © 2003 American Institute of Physics.

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I. INTRODUCTION

In the fabrication of molecular photonic and electric wires the long and rigid rodlike molecular structure is indispensable because any deformations such as kinked, bent, and folded geometries can act as an energy or charge sink in light energy or electron flow along the array. In this respect, the directly *meso-meso* linked Zn(II)porphyrin arrays up to 128 porphyrin units connected together linearly¹ have proven to be ideal in that they maintain the orthogonality between the adjacent porphyrin units, and consequently the conformational heterogeneity should be minimized.^{2,3} Overall, the directly linked porphyrin arrays have provided a promise as potential candidates for molecular photonic wires since they

transmit singlet excitation energy rapidly over the array mediated by ample electronic interactions between the neighboring porphyrin moieties.⁴⁻⁶

On the other hand, these orthogonal porphyrin arrays are expected to exhibit poor electrical conductivity due to their maintenance of relatively high HOMO-LUMO band gap energy as the number of porphyrin pigments increases in the array.⁷ The overall orthogonal conformation between the adjacent porphyrin units in the porphyrin array disrupts π -electron conjugation over the array.⁷ To realize molecular wires as good conducting organic material, the connection of as many π -conjugated molecular systems as possible with a completely flat structure like graphite is highly desired, which results in maximization of π -electron conjugation. But long π -conjugated organic molecules inevitably experience the effective conjugation length (ECL) effect due to the bond alternation in these molecules.^{8,9} The adaptation of partially charged conjugated systems such as cyanine and oxanil dyes¹⁰ or a series of covalently linked flat $[n]$ acenes^{8,9} ($n = 1-7$) has proven to overcome the ECL limit by escaping

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from bond alternation within a confined pigment number.

Thus, for the possible future application as molecular electric wires, triply linked fused porphyrin arrays (**Tn**, $n = 1, 2, \dots, 12$) up to twelve porphyrin units by connecting two additional β positions from the adjacent porphyrin moieties in the directly linked Zn(II)porphyrins arrays were successfully synthesized (scheme 1).^{11–14} These fused porphyrin arrays exhibit even much stronger exciton coupling between the Soret bands along with a systematic redshift of the Q bands to the IR region (up to a few μm) due to much enhanced π -electron delocalization throughout the entire fused porphyrin arrays.¹⁵ These unique electronic properties are in contrast with other types of electronically conjugated porphyrin arrays such as ethylene-^{16–18} and butadiyne-^{19–22} bridged porphyrin arrays which show a saturation behavior in the shift of the lowest energy transition bands. In this regard, not only as molecular electric wires but as IR sensors and nonlinear optical materials the fused porphyrin arrays could open up new opportunities in molecular electronics.

As the absorption bands of **Tn** are intrinsically different from each other in their electronic properties, the resonance Raman (RR) spectroscopy can be utilized in discerning the nature of the electronic transition by monitoring the RR enhancement pattern depending on the excitation wavelength. In the present work, we have performed the RR spectroscopic experiments to explore the electronic transitions of **Tn** as a function of the number of porphyrin units. In order to describe the electronic nature of each transition in a detailed manner, we have also carried out the INDO/S-SCI MO calculations. Based on the MO calculations and the normal mode analysis, the electronic properties of the fused porphyrin arrays have been addressed.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Synthesis of fused porphyrin arrays

The details of the synthetic and purification procedures of the fused porphyrin arrays were given elsewhere.^{11–14} Basically, the oxidative double-ring closure (ODRC) reaction of *meso-meso* linked Zn(II)porphyrin arrays yields the corresponding fused porphyrin arrays. The ODRC reaction was conducted by refluxing orthogonal porphyrin oligomers in toluene in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and scandium trifluoromethanesulfonate [$\text{Sc}(\text{OTf})_3$]. This type of ODRC reaction was nicely applied to longer fused porphyrin arrays [scheme 1(a)].

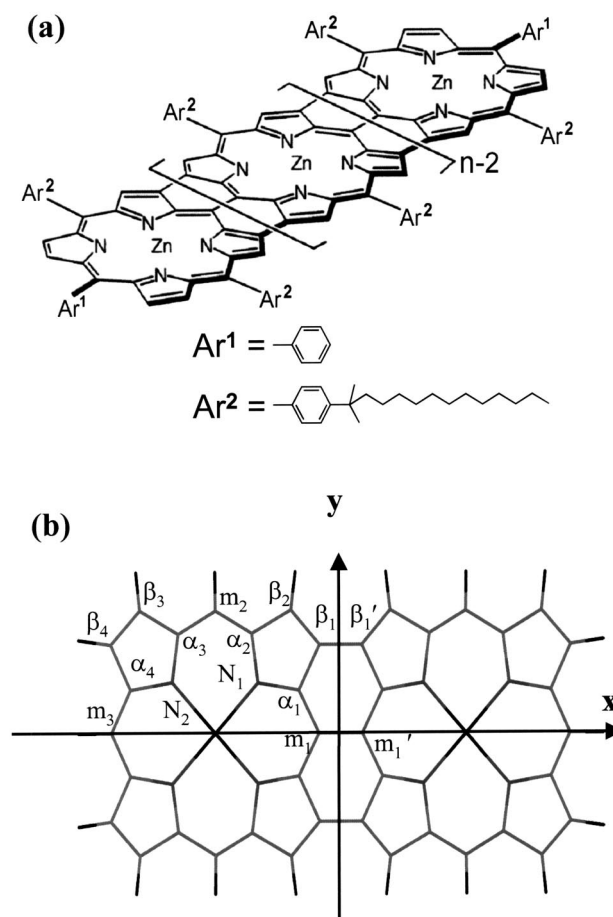
B. Resonance Raman spectra measurements

The ground-state resonance Raman spectra of the fused porphyrin arrays were obtained by photoexcitation using two lines (457.9 and 514.5 nm) of a cw Ar ion laser (Coherent INNOVA 90), 406.7 nm line of a cw Kr ion laser (Coherent INNOVA 70K), and 441.6 nm line of a cw He–Cd laser (Omnichrome series 74). A 416 nm line was generated by hydrogen Raman shifting of the third harmonics (355 nm) from a nanosecond Q-switched Nd:YAG laser. Raman scattering signals were collected in a 90° scattering geometry. Two Raman detection systems were used: a 1-m double

monochromator (ISA Jobin-Yvon U-1000) equipped with a thermoelectrically cooled photomultiplier tube (Hamamatsu R943-02) and a single pass spectrograph (Acton Research 500i) equipped with a charge-coupled device (PI LN/CCD-1152E). For depolarization ratio measurement, a polarizer was placed between the collection lens and the monochromator entrance slit and a scrambler was placed after the polarizer to compensate the grating efficiency for light polarized horizontal and vertical to the incident polarization. The depolarization ratios for the Raman bands of CCl_4 were measured as a reference. A modified Pasteur pipette whose end has a tiny capillary tube attached was used as a Raman cell to make sample solution flow to minimize its consumption and photodecomposition by the laser excitation.

C. Normal mode analysis

The vibrational normal modes of porphyrin monomers have been extensively studied experimentally and theoretically. Spiro *et al.* have provided normal mode analyses of nickel tetraphenylporphyrin (Ni^{II} TPP) (Refs. 23 and 24) and nickel octaethylporphyrin (Ni^{II} OEP) (Ref. 25) based on the isotope frequency shifts and normal mode calculations with the GF matrix method and a valence force field using semi-empirical parameters. In the present work, we adopted the B3LYP hybrid density-functional theory as implemented in



Scheme 1. (a) Molecular structures of the fused porphyrin linear arrays. (b) The axis notation and the atomic labeling scheme ($C_{m1,\alpha2,\beta3,\dots}$).

the GAUSSIAN 98 suite of programs²⁶ to calculate the optimized geometry and normal modes of the fused porphyrin arrays. The basis set used is the 6-31G set for carbon, nitrogen, and hydrogen atoms (Ref. 27), and Huzinaga's (14s8p5d) set contracted to [5s3p2d] for Zn.²⁸

The fused porphyrin dimer (**T2**), the simplest structure among the fused porphyrin arrays (**Tn**), is treated as a starting point in the normal mode analysis of **Tn**. **T2** is still a huge molecule with 304 atoms including bulky peripheral aryl groups attached at *meso*-positions. Thus in order to simplify the calculation and treat pure porphyrin modes separately from peripheral aryl modes, we adopted a model compound of the fused porphyrin dimer (**T2'**) that has no peripheral substituents but hydrogen atoms at *meso*-positions. **T2'** is assumed to have a planar structure with D_{2h} symmetry based on the structure of **T2**. The longest molecular axis and the normal axis to the molecular plane are defined as *x*- and *z*-axes [scheme 1(b)], respectively, following the axis notation used for MO description.¹⁵ **T2'** has 68 atoms and accordingly has 198 vibrational modes,

$$\Gamma = 34 A_g + 33 B_{1g} + 18 B_{2g} + 14 B_{3g} + 15 A_u \\ + 18 B_{1u} + 33 B_{2u} + 33 B_{3u}.$$

The vibrational modes with *ungerade* symmetry are not activated in Raman scattering under D_{2h} symmetry due to the exclusion rule. Among the *gerade* modes the B_{2g} and B_{3g} modes are out-of-plane vibrations and the A_g and B_{1g} modes are in-plane ones. In the planar porphyrin complexes the transition dipoles of π - π transitions with visible photoexcitation lie in the molecular plane and thus the out-of-plane vibrational modes are not resonance-activated but the in-plane vibrational modes are activated. Consequently, we treat only the A_g and B_{1g} modes in this work.

In order to assign the RR bands of a new compound, we took the following steps: (1) The geometry optimization of **T2'** and then its normal mode calculations were performed sequentially at the B3LYP level. Normal mode calculations were performed also for phenyl substituted fused porphyrin dimer (**T2''**) at *meso*-positions instead of bulkier aryl groups as well as for a fused porphyrin trimer (**T3'**) with no peripheral groups at *meso*-positions. The molecular symmetry of **T2'** and **T3'** was assumed to be D_{2h} while that of **T2''** was reduced to D_2 due to a nonorthogonal orientation of peripheral phenyl groups with respect to the porphyrin plane (the optimized dihedral angle is $\sim 68^\circ$). We confirmed that no imaginary frequencies were obtained in the normal mode calculations of all the molecules using their optimized geometries. Note that all the normal-mode frequencies reported in this paper are multiplied by a factor of 0.96 to match well with the experimental ones. (2) The depolarization ratios for the RR bands were measured experimentally for various photoexcitation lines. The A_g modes in D_{2h} symmetry are totally symmetric and then have depolarization ratio values of $\rho = 1/3$ theoretically while the B_{1g} modes are depolarized or inversely polarized with $\rho \geq 3/4$. This simple relation enabled us to classify the observed RR bands into different symmetry blocks. (3) We have utilized ^{13}C -isotope substitutions at *meso*-carbons to correlate the calculated normal

modes with the observed RR modes. Two different types of phenyl substituted diporphyrins with ^{13}C -isotope labeling (**T2A** and **T2B**) and one without isotope labeling (**T2''**) were synthesized: **T2A** has ^{13}C -labels at its m_1 , m'_1 , m_3 , and m'_3 positions and **T2B** does at its m_2 and m'_2 positions [scheme 1(b)]. (4) We have monitored the RR enhancement pattern of **T2** varying the photoexcitation lines from 416 to 514.5 nm.

D. Excited geometry displacement and vibronic coupling

We have calculated the electronic excited states of **T2''** by the single excited configuration interaction (SCI) method within the framework of the intermediate neglect of differential overlap model for spectroscopy (INDO/S) Hamiltonian.²⁹ The two-center Coulomb interactions were evaluated by the Nishimoto–Mataga formula.³⁰ Note that all the one-electron levels were considered in the SCI expansion taking advantage of the molecular D_2 symmetry to reduce the size of the Hamiltonian matrix. To characterize each excited state in terms of charge-transfer (CT) nature on the basis of the SCI transition density matrix³¹ ρ^{ge} , we have calculated the charge-transfer probability $\mathbf{P}_{e-h}$ defined by

$$P_{e-h}(r,s) = (\rho_{rs}^{ge})^2/2 \quad (1)$$

which represents the probability of simultaneously finding an electron at r and a hole at s . On the basis of the SCI density matrix ρ^e , we have calculated the excited-state bond order between atoms α and β ,

$$B_{\alpha\beta}^e = \sum_r^\alpha \sum_s^\beta (\rho_{rs}^e)^2. \quad (2)$$

Comparing the $B_{\alpha\beta}^e$ with that of the ground state provides an insight into the geometrical relaxation in the excited state which is relevant to the RR enhancement via the A-term scattering.

In order to find the origins for the RR mode enhancement via the B-term scattering mechanism in relation to a particular type of electronic transition in which resonance excitation is involved, we have evaluated the vibronic coupling integral on the basis of the SCI transition density matrix. The vibronic coupling of the excited states e and f mediated by the normal mode a is given by

$$\langle f | \frac{\partial H}{\partial Q_a} | e \rangle = \sum_\alpha \mathbf{F}_\alpha(e,f) \frac{\partial \mathbf{R}_\alpha}{\partial Q_a}, \quad (3)$$

where the transition force $\mathbf{F}_\alpha(e,f)$ represents a force acting on nucleus α associated with the relevant electronic transition,

$$\mathbf{F}_\alpha(e,f) = \langle f | \frac{\partial H}{\partial \mathbf{R}_\alpha} | e \rangle = Z_\alpha e^2 \langle f | \frac{r - \mathbf{R}_\alpha}{|\mathbf{R}_\alpha|^3} | e \rangle. \quad (4)$$

According to Eq. (3), the magnitude of vibronic coupling depends on the scalar product of $\mathbf{F}(e,f)$ and the normal-mode eigenvector. Using the atomic-orbital (AO) representation and applying the zero-differential-overlap (ZDO) approximation, Eq. (4) leads to

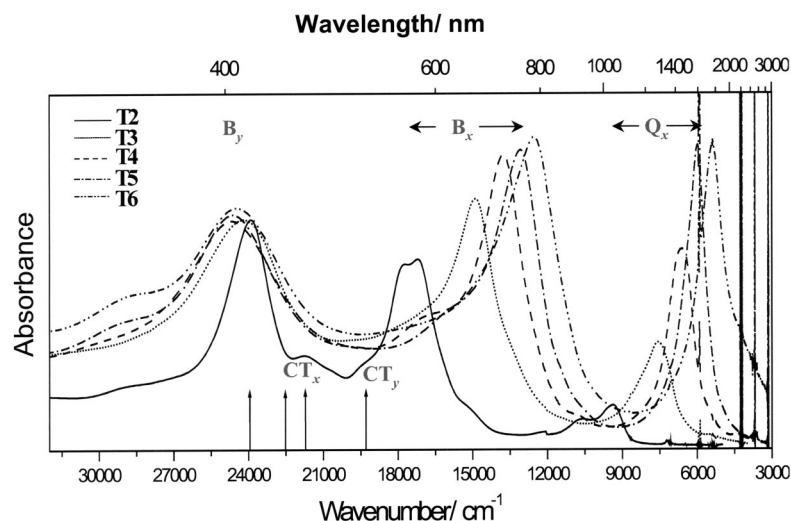


FIG. 1. The ultraviolet-visible-infrared absorption spectra of the triply linked fused porphyrin arrays from **T2** to **T6** taken in CHCl_3 at room temperature. The background absorptions at ~ 6000 , ~ 4000 , ~ 3500 cm^{-1} arise from the overtones of C-H vibration of the solvent. The arrows depict the laser lines used for resonance Raman excitation, corresponding to 416, 441.6, 457.9, and 514.5 nm, respectively.

$$\mathbf{F}_\alpha(e, f) = Z_\alpha e^2 \sum_s \langle s | \frac{\mathbf{r} - \mathbf{R}_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|^3} | s \rangle \rho_{ss}^{ef}, \quad (5)$$

where ρ_{ss}^{ef} is the diagonal elements of the transition density matrix. Since the contribution of those terms with s centered on α cancel out in Eq. (5) for a centrosymmetric molecule, it is essential to consider the terms with s on the other atoms. To evaluate these matrix elements in Eq. (5), we approximate the AO by a δ function, $|s(\mathbf{r})\rangle \cong \delta(\mathbf{r} - \mathbf{R}_\beta)$, then obtaining the final expression for $\mathbf{F}_\alpha(e, f)$,

$$\mathbf{F}_\alpha(e, f) = Z_\alpha e^2 \sum_{\beta (\neq \alpha)} \frac{\mathbf{R}_{\alpha\beta}}{R_{\alpha\beta}^3} \sum_s \rho_{ss} \quad (6)$$

which provides an insight into the resonance enhancement via the B-term scattering.

Transition density matrix has been successfully applied to reveal the characteristics of RR enhancement in relation to a particular electronic transition activated via the B-term scattering.^{32–34} More recently, the calculation of RR intensities of particular modes became possible, which enabled more quantitative analysis of RR activity. In this study, however, qualitative description of RR intensities using graphical description of transition density is appropriate for the understanding of the overall pictures of fused porphyrin dimer and arrays due to intrinsic difficulties involved in the calculation of large macromolecules.

III. RESULTS

A. Steady-state absorption spectra of fused porphyrin arrays

Figure 1 shows the UV/visible/IR absorption spectra of the fused Zn(II)porphyrin arrays in CHCl_3 . The fused porphyrin arrays display drastically redshifted—even to IR region—absorption spectra reflecting extensive π -electron delocalization over the array. The absorption bands of the fused arrays are roughly categorized into three distinct well-separated bands, which are marked as B_y , B_x , and Q bands in near UV, visible, and IR regions, respectively, on the basis of their transition properties revealed by the PPP-SCI calcu-

lations (Fig. 1).¹⁵ The bands at near UV region retain nearly the same positions as that of Zn(II)porphyrin monomer, but a significant broadening in their bandwidths occurs. In contrast, the absorption bands in visible and IR regions continuously shift to red as the number of porphyrin units increases. The efficient π -conjugation along the x -axis lifts the accidental cancellation of the transition dipole moments of the Q -bands, hence intensifying the Q_x band (HOMO $\rightarrow$ LUMO) and weakening the Q_y band (HOMO-1 $\rightarrow$ LUMO+1) that is, consequently, buried under the strong Q_x band. Along with a continuous redshift in the absorption bands of longer arrays, the relative intensities of the B_x and Q_x bands are increasingly stronger as compared with the B_y bands. It is also noteworthy that the absorption in the interval wavelength regions between three distinct absorption bands becomes enhanced upon elongation of the fused porphyrin arrays, which implies that more complicate and congested electronic states lie in energy regions between three main bands of longer fused Zn(II)porphyrin arrays.

B. Molecular orbital (MO) considerations

The frontier orbital energy levels of Zn(II)tetraphenylporphyrin (**ZnTPP**) and **T2''** are shown in Fig. 2 as obtained by the INDO/S self-consistent field (SCF) calculations. As indicated in Fig. 2, the highest four occupied and the lowest four unoccupied orbitals of **T2''** are formed by the combinations of monomer's "four orbitals"³⁵ with their significant energy splittings relative to the monomer levels. Since the orbital pattern of these eight orbitals is essentially the same as that obtained by the previous PPP calculation,¹⁵ only the HOMO and LUMO among them are depicted in Fig. 2. It is noteworthy that the LUMO of **T2''** exhibits significant bonding amplitudes at all of the three linkages (*meso-meso* and two $\beta_1-\beta'_1$), while the antibonding contribution is essentially restricted to the *meso-meso* linkage for the HOMO in consistent with the much larger energy-shift of the former than that of the latter. Therefore, the progressive redshift of the Q_x band of **Tn** would be largely attributed to such a nature of the LUMO.^{15,36}

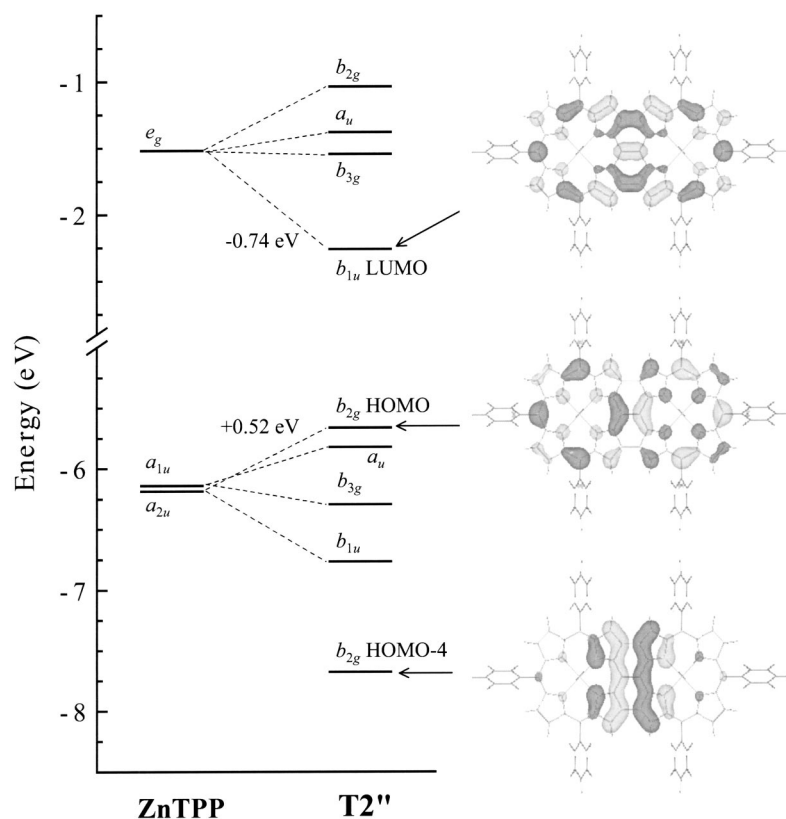


FIG. 2. Energy levels of frontier orbitals of **T2''** compared with those of the Zn(II)TPP monomer as obtained by the INDO/S calculations. Shown in the right panel are the orbital patterns of HOMO-4, HOMO, and LUMO of **T2''**.

For **T2''**, the INDO/S-SCI calculated absorption spectrum is shown in Fig. 3 and the transition properties of the lowest 18 singlet excited states are summarized in Table I. Based on the present calculation, the Q_x , B_x , and B_y absorption bands in the **T2** spectrum are assigned to the $1B_{3u}$, $2B_{3u}$, and $3B_{2u}$ states (in the D_{2h} notation), respectively, indicating that the transition dipole moment is parallel to the long molecular x axis for the Q_x and B_x bands, while it is aligned along the short molecular y axis for the B_y band. Although the splitting of the monomer's B band into the B_x

and B_y bands is consistent with the exciton-coupling scheme, the CT character of the $2B_{3u}$ and $3B_{2u}$ states is significantly enhanced as compared with the corresponding excited states of *meso-meso* linked Zn(II)-diporphyrin.³⁷ For the SCI expansion of the $1B_{3u}$ state (Q_x band), the contribution of the HOMO to LUMO transition amounts to 72% while that of the HOMO-1 to LUMO+1 transition is only 15%. Then, the overall transition dipole moment of this state is dominated by that of the former transition resulting in the markedly intensified Q_x band as compared with the $Q(0,0)$ band

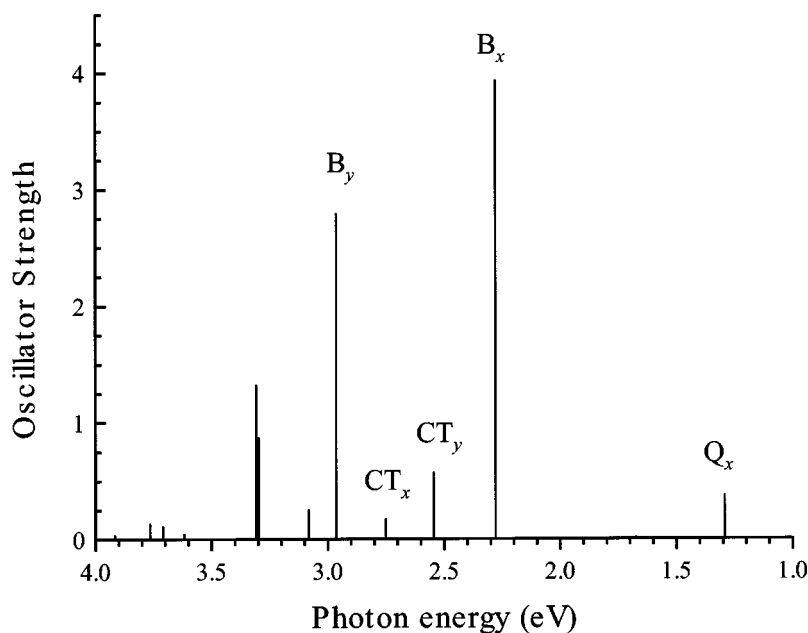


FIG. 3. The INDO/S-SCI simulated electronic absorption spectrum of **T2''**.

TABLE I. Transition properties and electronic structures of the lowest 18 singlet excited states of **T2**^a, as obtained from INDO/S-SCI calculations on the basis of B3LYP/6-31G optimized geometry.

Band	State ^a		$\Delta E(\text{eV})^b$	f^c	$P_{\text{CT}}(\%)^d$	$W_8(\%)^e$
	D_{2h}	D_2				
Q_x	$1B_{1g}$	$1B_1$	1.21	1×10^{-5} (z)	35	96
	$1B_{3u}$	$1B_3$	1.29 (1.16)	0.371 (x)	31	96
Q_y	$1B_{2u}$	$1B_2$	1.67	0.011 (y)	18	96
	$2A_g$	$2A_1$	1.8	0	10	95
B_x	$2B_{1g}$	$2B_1$	2.07	2×10^{-4} (z)	30	86
	$2B_{3u}$	$2B_3$	2.28 (2.13)	3.929 (x)	26	94
CT_y	$2B_{2u}$	$2B_2$	2.54 (~ 2.4)	0.568 (y)	63	90
	$3A_g$	$3A_1$	2.68	0	68	92
CT_x	$3B_{3u}$	$3B_3$	2.75 (~ 2.7)	0.170 (x)	41	22
	$4A_g$	$4A_1$	2.92	0	76	91
B_y	$3B_{2u}$	$3B_2$	2.96 (2.97)	2.786 (y)	35	87
	$3B_{1g}$	$3B_1$	2.99	1×10^{-4} (z)	42	40
	$4B_{3u}$	$4B_3$	3.08	0.250 (x)	71	69
	$4B_{1g}$	$4B_1$	3.14	4×10^{-4} (z)	24	34
	$5A_g$	$5A_1$	3.18	0	15	89
	$5B_{3u}$	$5B_3$	3.30	0.866 (x)	21	25
	$4B_{2u}$	$4B_2$	3.31	1.32 (y)	48	89
	$5B_{1g}$	$5B_1$	3.41	3×10^{-4} (z)	51	69

^aSince the two porphyrin rings are completely coplanar, excited states are referred by D_{2h} notation throughout this paper.

^bExcitation energy. The experimental values are listed in parentheses.

^cOscillator strength. The direction of transition dipole moment is indicated in parentheses.

^dInterunit charge-transfer probability defined by

$$P_{\text{CT}} = \sum_{I \neq J} \sum_{r \in I} \sum_{s \in J} P_{e-h}(r, s)$$

where $I(J)$ represents one porphyrin subunit in a dimer including peripheral phenyl groups.

^eThe weight of the transitions within eight-orbitals in the SCI wave function.

of the porphyrin monomer which is very weak due to a mutual cancellation of transition dipole moments of nearly degenerate $^1(a_{1u}, e_g)$ and $^1(a_{2u}, e_g)$ configurations. The intensification as well as the red-shift of the Q_x band of **T2** can be attributed to the above-mentioned orbital splitting which is caused by efficient π -conjugation through the triple linkage.

In the energy region between the B_x and B_y bands, at least two absorption bands are detected at ~ 458 and 515 nm. We assign these absorption bands to the $3B_{3u}$ (CT_x band) and the $2B_{2u}$ (CT_y band) states, respectively. The low-energy intersubunit CT states are described as one-electron transition from the a_{1u} or a_{2u} MO of one unit to one of the e_g MOs of the other unit. In the previous INDO/S-SCI study on *meso-meso* linked diporphyrin,³⁷ we found that such eight CT states are accidentally located in the energy region spanned by the split B bands. Since such situation should be caused by the close proximity of the constituent porphyrin subunits, it is also expected for **T2**. Although a complete assignment of all eight CT states is difficult for **T2**^a due to a significant mixing of localized exciton (LE) and CT nature in the excited states, the $2B_{2u}$ can be unambiguously assigned to one of such CT states based on its P_{CT} and W_8 values (Table I). On the other hand, the $3B_{3u}$ state (CT_x band) can be hardly described by transitions within eight orbitals and the contribution of the HOMO-4 to LUMO transition amounts to 60% in its SCI description; the orbital pattern of the HOMO-4 is also depicted in Fig. 2. The admixing of such low-lying orbital would be due to a significant configuration mixing which is caused by efficient π -conjugation in

T2. For longer arrays, the CT states of both origins described above establish a band of intermediate levels between the B_x and B_y bands with moderate oscillator strengths being responsible for the enhanced absorption in the corresponding energy region (Fig. 1).¹⁵

C. Resonance Raman spectra of fused porphyrin dimer

In **T2**, three major absorption bands (B_y , B_x , and Q_x) are observed at 418, 580, and 1070 nm, respectively, and several charge-transfer bands exist between these bands as revealed by the calculations. Due to the closely lying transitions in visible region we can expect a significant change in the RR enhancement pattern depending on the electronic nature of the relevant electronic transition. Figure 4 shows a series of the RR spectra of **T2** obtained by photoexcitations at 416, 441.6, 457.9, and 514.5 nm. In each RR spectrum, top and bottom ones correspond to parallel and perpendicular polarizations, respectively. The observed and calculated Raman frequencies of **T2** are listed in Table II. In the RR spectrum by 416 nm excitation only polarized RR bands having mostly $\rho \approx 1/3$ are observed. The RR enhancement of totally symmetric modes indicates that the $3B_{2u}$ state (B_y band) contributes to the RR enhancement via the Franck-Condon scattering. As the excitation wavelength is changed to longer wavelength, the relative intensities of the polarized RR bands at 1238, 1270, 1339, 1349, 1460, and 1531 cm^{-1} decrease but those at 1366 and 1411 cm^{-1} increase. In addition, the

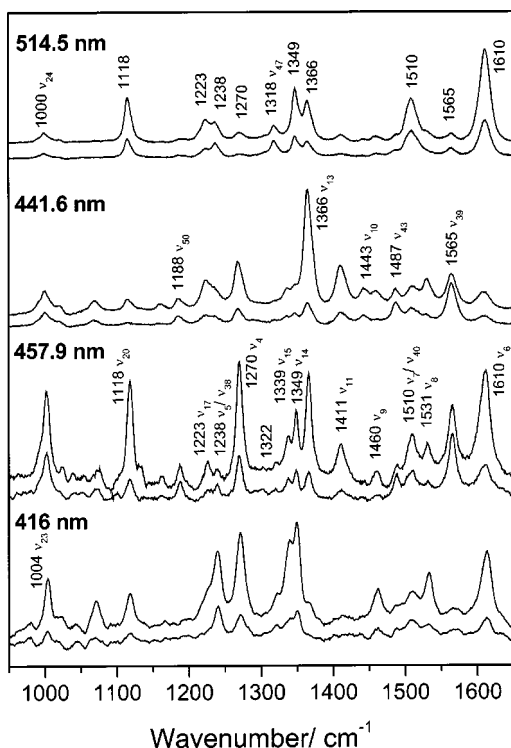


FIG. 4. The resonance Raman spectra of **T2** in THF by excitation at 416, 441.6, 457.9, and 514.5 nm (from bottom to top). For each excitation line the top and bottom spectra correspond to the parallel and perpendicular polarizations to the incident polarization, respectively.

RR bands at 1238, 1318, 1487, and 1565 cm^{-1} with ρ values larger than 0.75 are enhanced. The appearance of anomalously polarized Raman bands with B_{1g} symmetry reveals that a certain electronic transition with B_{3u} symmetry lying close to the $3B_{2u}$ state is involved by vibronic mixing, leading to RR enhancement via the Herzberg–Teller scattering. The RR enhancement pattern of the polarized RR bands by photoexcitation at 457.9 nm is different from that by photoexcitation at 416 nm. For instance, the RR bands at 1339, 1349, and 1610 cm^{-1} are largely diminished but those at 1366, 1411, and 1565 cm^{-1} become strong by photoexcitation at 457.9 nm. It is noteworthy that the RR enhancement pattern by 441.6 nm excitation is roughly a summation of the RR spectral features by 416 and 457.9 nm excitations. This feature is consistent with the fact that photoexcitation at 441.6 nm corresponds to a middle point between the B_y ($3B_{2u}$) and CT_x ($3B_{3u}$) transitions. As the excitation wavelength is shifted to 514.5 nm, the RR enhancement pattern becomes also different from that by photoexcitation at 457.9 nm. This feature also reflects that the CT_y ($2B_{2u}$) transition near 514.5 nm is different from the CT_x ($3B_{3u}$) transition at 457.9 nm in its electronic character.

D. Resonance Raman spectra of the ^{13}C -isotope substituted fused porphyrin dimer

We have recorded the RR spectra of the fused diporphyrins with different ^{13}C -isotope labelings by photoexcitation at

TABLE II. The observed and calculated RR frequencies of **T2** and its isotope-substituted analogs (**T2A** and **T2B**). Only modes localized on the fused porphyrin rings are listed here.

T2		T2A		T2B		ν_i	ρ^b	Symmetry
Obs.	Calc. ^a	Obs.	Calc.	Obs.	Calc.			
1610	1611	1610	1611	1610	1610	ν_6	1.45	A_g
1565	1577	1562	1573	1545	1553	ν_{39}	1.43	B_{1g}
1531	1532	1528	1528	1528	1530	ν_8	0.17	A_g
1510	1509	1503	1497	1505	1503	ν_{40}/ν_7	0.78	B_{1g}/A_g
1487	1491	1487	1491	1487	1491	ν_{43}	1.92	B_{1g}
1460	1460	1453	1452	1459	1460	ν_9	0.12	A_g
1443	1443	1443	1443	1435	1436	ν_{10}	0.51	A_g
1411	1409	1406	1405	1405	1402	ν_{11}	0.32	A_g
1366	1352	1365	1352	1364	1349	ν_{13}	0.18	A_g
1349	1336	1346	1334	1345	1333	ν_{14}	(0.28) 0.71	A_g
1339	1314	1337	1312	1336	1310	ν_{15}	(0.26) 0.53	A_g
1322	1257	1318	1254	1317	1256	ν_{16}	...	A_g
1318	1320	...	1319	...	1317	ν_{47}	[1.26]	B_{1g}
1270	1244	1265	1239	1266	1240	ν_4	0.34	A_g
1238	1210	1235	1206	1238	1209	ν_{38}	(0.47) 0.95	B_{1g}
	1212		1210	1220	1208	ν_5		A_g
1223	1202	1223	1201	1208	1188	ν_{17}	0.40	A_g
1188	1186	1188	1186	1186	1185	ν_{50}	0.92	A_g
1160	1169	1160	1169	1158	1166	ν_{18}	0.35	A_g
1118	1120	1118	1120	1112	1113	ν_{20}	0.25	A_g
1071	1089	1071	1089	1071	1089	ν_{21}	0.46	A_g
1018	1012	1016	1010	1017	1010	ν_{22}	0.59	A_g
1004	999	1003	998	1004	998	ν_{23}	...	A_g
1000	987	999	987	1000	986	ν_{24}	0.55	A_g

^aCalculation was performed on **T2'**. All of the calculated values are multiplied by a factor of 0.96.

^bDepolarization ratios measured by 457.9 nm excitation, defined by $I_{\perp}/I_{\parallel}$. The values in the parentheses are measured by 416 nm excitation, and the ones in brackets are obtained by 514.5 nm excitation.

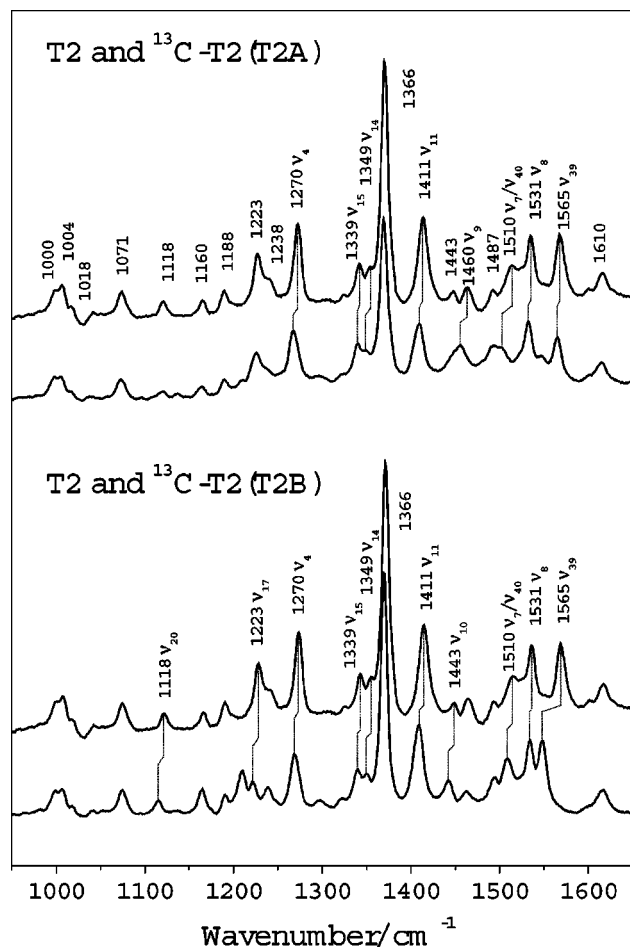


FIG. 5. The resonance Raman spectra of the fused diporphyrins with different ^{13}C -isotope labelings in THF by photoexcitation at 457.9 nm. **T2** is a phenyl substituted diporphyrin without isotope labeling, **T2A** has ^{13}C -labels at its m_1 , m'_1 , m_3 , and m'_3 positions, and **T2B** does at its m_2 and m'_2 positions. For each set of RR spectra the top one corresponds to **T2** and the bottom one corresponds to **T2A** or **T2B**.

457.9 nm to monitor frequency shifts by ^{13}C -isotope substitution (Fig. 5). The observed frequencies, depolarization ratios, and their assignments are summarized in Table II. The RR bands at 1270, 1339, 1349, 1411, and 1531 cm^{-1} exhibiting frequency shifts in both types of ^{13}C -isotope substituted diporphyrins (**T2A** and **T2B**) are assigned to the ν_4 , ν_{15} , ν_{14} , ν_{11} , and ν_8 modes, respectively (Supplemental Material).³⁸ The 1443 cm^{-1} band shows frequency shift only in **T2B** and the 1460 cm^{-1} band does only in **T2A**, which is exactly coincident with the ν_{10} and ν_9 modes, respectively. The ^{13}C -isotope substitution at four *meso*-carbons along the long molecular axis (**T2B**) also gives rise to large frequency shift of $\sim 20 \text{ cm}^{-1}$ for some RR bands such as those at 1223 and 1565 cm^{-1} . The 1223 cm^{-1} band corresponds to the ν_{17} mode that is characteristic of $\text{C}_{m1}-\text{C}_{m1'}$ stretching vibration, and the 1565 cm^{-1} band, which is inversely polarized, is assigned to the ν_{39} mode that has large contribution of $\nu(\text{C}_{m1}-\text{C}_{\alpha 1})_{\text{asym}}$ as well as small contribution of $\nu(\text{C}_{m2}-\text{C}_{\alpha})_{\text{asym}}$ and $\nu(\text{C}_{m3}-\text{C}_{\alpha 4})_{\text{asym}}$ (Supplemental Material).³⁸ The RR bands at 1610, 1487, and 1188 cm^{-1} show little frequency shifts by ^{13}C -isotope substitution, and thus are assigned to the normal modes having $\nu(\text{C}_{\beta}-\text{C}_{\beta})$,

$\nu(\text{N}-\text{C}_{\alpha})$ or $\nu(\text{C}_{\alpha}-\text{C}_{\beta})$ motions. The RR band at 1610 cm^{-1} is assigned to the ν_6 mode which has exclusively $\nu(\text{C}_{\beta 1}-\text{C}_{\beta 2}) + \nu(\text{C}_{\beta 1}-\text{C}_{\beta 1'})$ stretching motions. Similarly, the RR band at 1188 cm^{-1} is assigned to the ν_{50} mode based on its polarization property. The 1487 cm^{-1} band is anomalously polarized with $\rho = 1.6$, and assigned to the $\nu_{43}(\text{B}_{1g})$ mode that is associated with $\nu(\text{C}_{\beta}-\text{C}_{\beta})$ vibration analogous to the ν_{11} mode of $\text{Ni}^{\text{II}}\text{TTP}$. The RR band at 1510 cm^{-1} shows frequency downshifts of 7 and 5 cm^{-1} in **T2A** and **T2B**, respectively, and thus can be assigned to the mode that involves $\nu(\text{C}_{m1}-\text{C}_{\alpha 1})_{\text{asym}} + \nu(\text{C}_{m2}-\text{C}_{\alpha})_{\text{asym}}$. This RR band is observed in the RR spectrum by 416 nm excitation by which only polarized RR bands are resonance-activated. As the excitation line is changed from 416 to 514.5 nm, the ρ value changes considerably from 0.54 to 1.0, which is apparently beyond experimental error. These features seem to reflect that the ν_{40} and ν_7 modes with similar frequencies appear to be overlapped.

E. Normal mode analysis of fused porphyrin dimer

As mentioned above, we treated the following 67 Raman modes among 198 normal modes of **T2'**:

$$\Gamma' = 34 A_g + 33 B_{1g}.$$

Table III shows the frequencies of the calculated normal modes of **T2'** classified by the symmetry species. A standard frequency numbering is to number the individual mode within each symmetry block in order of descending frequency, which has been widely adopted for frequency notation of porphyrins.^{39,40}

The calculated vibrational frequencies of **T2'** were compared with those of the fused porphyrin dimer with phenyl substituents at *meso*-positions (**T2''**). The calculated normal modes of **T2''** reveal that some of porphyrin internal modes are considerably mixed with phenyl vibrational modes. For instance, the ν_4 and ν_5 modes with C_m-H stretching vibration at 3077 cm^{-1} is shifted to the low-frequency C_m-Ph stretching mode appearing at below 1250 cm^{-1} . Some Raman bands that have little involvement of $\text{C}_{\text{Ph}}-\text{C}_{m2}$ or m_3 stretching such as the ν_{11} , ν_{20} , and ν_{21} modes show relatively small frequency differences less than 17 cm^{-1} (Supplemental Material).³⁸ Most of other Raman bands having significant contribution from m_2 - or m_3 -carbon movement exhibit large frequency differences by more than 40 cm^{-1} such as the ν_7 , ν_{15} , and ν_{40} modes involving large $\text{C}_m-\text{C}_{\alpha}$ and/or C_m-X movements (Supplemental Material).³⁸ The frequency lowering in these modes is mostly due to the replacement of hydrogen atoms at *meso*-positions by heavy phenyl groups. Among the Raman modes with little RR enhancement, observed are some modes that have large frequency shift by phenyl substitution at *meso*-positions such as the ν_{25} and ν_{27} modes. These modes include symmetric/asymmetric pyrrole deformation ($\sim 800 \text{ cm}^{-1}$). The large frequency up-shift is caused by near-resonant interaction with phenyl deformation modes.^{25,41}

The calculated frequencies of two types of ^{13}C -isotope labeled analogs of **T2** at *meso*-positions are also included in Table II. Type A (**T2A**) has ^{13}C atoms at m_2 positions and

TABLE III. The calculated normal modes of fused porphyrin dimer with and without phenyl peripheral rings.

No phenyl		Phenyl			Comments
ν_i	T2'	T2''	$^{13}\text{C-T2A}$	$^{13}\text{C-T2B}$	
A_g modes					
ν_1	3152	3180	3180	3180	$\nu(\text{C}_{\beta 3,4}\text{H})_{\text{sym}}$
ν_2	3140	3169	3169	3169	$\nu(\text{C}_{\beta 2}\text{H})$
ν_3	3129	3159	3159	3159	$\nu(\text{C}_{\beta 3,4}\text{H})_{\text{asym}}$
ν_4	3077	1244	1239	1240	$\nu(\text{C}_{m2}\text{X})^a + \nu(\text{C}_{m3}\text{X}) + \nu(\text{NC}_\alpha)$
ν_5	3076	1212	1210	1208	$\nu(\text{C}_{m2}\text{X}) + \nu(\text{C}_{m3}\text{X}) + \nu(\text{NC}_\alpha)$
ν_6	1605	1611	1611	1610	$\nu(\text{C}_{\beta 1}\text{C}_{\beta 2}) + \nu(\text{C}_{\beta 1}\text{C}_{\beta 1'})$
ν_7	1567	1512	1500	1506	$\nu(\text{C}_{m1}\text{C}_{\alpha 1})_{\text{sym}} + \nu(\text{C}_{m2}\text{C}_\alpha)_{\text{asym}} + \nu(\text{C}_{m1}\text{C}_{m1'})$
ν_8	1528	1532	1528	1530	$\nu(\text{C}_{m3}\text{C}_{\alpha 4})_{\text{sym}} + \nu(\text{C}_{\beta 3}\text{C}_{\beta 4}) + \nu(\text{C}_{m2}\text{C}_\alpha)_{\text{sym}}$
ν_9	1472	1460	1452	1460	$\nu(\text{C}_{m2}\text{C}_\alpha)_{\text{sym}} + \nu(\text{C}_{m1}\text{C}_{\alpha 1})_{\text{sym}} + \nu(\text{C}_{m1}\text{C}_{m1'})$
ν_{10}	1449	1443	1443	1436	$\nu(\text{C}_{m3}\text{C}_{\alpha 4})_{\text{sym}} + \nu(\text{C}_{m1}\text{C}_{\alpha 1})_{\text{sym}} + \nu(\text{C}_{m1}\text{C}_{m1'})$
ν_{11}	1417	1409	1405	1402	$\nu(\text{C}_{m1}\text{C}_{\alpha 1})_{\text{sym}} + \nu(\text{C}_{m1}\text{C}_{m1'}) + \nu(\text{C}_{m2}\text{C}_{\alpha 2})$
ν_{12}	1377	...	...	...	$\delta(\text{C}_{m2}\text{X})$
ν_{13}	1341	1352	1352	1349	$\nu(\text{C}_{\alpha 1}\text{C}_{\beta 1}) + \nu(\text{C}_{\alpha 4}\text{C}_{\beta 4}) + \delta(\text{C}_{\alpha 4}\text{C}_{m3}\text{C}_{\alpha 4})_{\text{sym}}$
ν_{14}	1324	1336	1334	1333	$\delta(\text{C}_{\beta 3,4}\text{H})_{\text{asym}}$
ν_{15}	1272	1314	1312	1310	$\nu(\text{pyr. half-breath.})^b + \nu(\text{C}_{m1}\text{C}_{m1'}) + \nu(\text{C}_{m3}\text{X})$
ν_{16}	1253	1257	1254	1256	$\delta(\text{C}_{\beta 3,4}\text{H})_{\text{asym}} + \delta(\text{C}_{\beta 2}\text{H})$
ν_{17}	1219	1202	1201	1188	$\nu(\text{C}_{m1}\text{C}_{m1'}) + \nu(\text{N}_1\text{C}_{\alpha 1})$
ν_{18}	1183	1169	1169	1166	$\delta(\text{C}_{\beta 2}\text{H})$
ν_{19}	1161	225	225	225	$\delta(\text{C}_{\beta 3,4}\text{H})_{\text{asym}} + \delta(\text{C}_{m2}\text{X})$
ν_{20}	1105	1120	1120	1113	$\delta(\text{C}_{\beta 2}\text{H}) + \delta(\text{C}_{\alpha 1}\text{C}_{m1}\text{C}_{\alpha 1}) + \nu(\text{C}_{m1}\text{C}_{m1'})$
ν_{21}	1072	1089	1089	1089	$\delta(\text{C}_{\beta 3,4}\text{H})_{\text{sym}}$
ν_{22}	1020	1012	1010	1010	$\delta(\text{N}_2\text{C}_{\alpha 3}\text{C}_{m2}) + \delta(\text{C}_{\alpha 2}\text{C}_{m2}\text{C}_{\alpha 3})$
ν_{23}	992	999	998	998	$\nu(\text{pyr. breath.})^b + \nu_{12}(\text{Ph})$
ν_{24}	986	987	987	986	$\nu(\text{pyr. breath.})$
ν_{25}	829	893	884	893	$\nu(\text{pyr. deform.})_{\text{asym}}$
ν_{26}	807	875	873	866	$\delta(\text{C}_{\alpha 4}\text{C}_{m3}\text{C}_{\alpha 4}) + \delta(\text{C}_\alpha\text{C}_\beta\text{C}_\beta)$
ν_{27}	726	849	842	849	$\delta(\text{C}_{\alpha 4}\text{C}_{m3}\text{C}_{\alpha 4}) + \delta(\text{C}_{\alpha 2}\text{C}_{m2}\text{C}_{\alpha 3})$
ν_{28}	543	579	578	579	$\delta(\text{Pyr. transl.}) + \text{naphthalene deform.}$
ν_{29}	458	484	483	484	$\delta(\text{Pyr. rot.}) + \text{naphthalene deform.}$
ν_{30}	383	403	403	403	$\nu(\text{NM})$
ν_{31}	380	399	398	399	$\delta(\text{Pyr. rot.})$ or $\nu(\text{N}_2\text{M})$
ν_{32}	295	303	302	303	$\delta(\text{Pyr. transl.})$
ν_{33}	234	204	204	204	$\delta(\text{Pyr. transl.}) + \delta(\text{N}_1\text{MN}_2)$
ν_{34}	151	110	110	110	$\delta(\text{Pyr. transl.})$
B_{1g} modes					
ν_{35}	3151	3180	3180	3180	$\nu(\text{C}_{\beta 3,4}\text{H})_{\text{sym}}$
ν_{36}	3137	3167	3167	3167	$\nu(\text{C}_{\beta 2}\text{H})$
ν_{37}	3129	3159	3159	3159	$\nu(\text{C}_{\beta 3,4}\text{H})_{\text{sym}}$
ν_{38}	3076	1210	1206	1209	$\nu(\text{C}_{m2}\text{X})$
ν_{39}	1611	1577	1573	1553	$\nu(\text{C}_{m1}\text{C}_{\alpha 1})_{\text{asym}} + \nu(\text{C}_{m2}\text{C}_\alpha)_{\text{asym}} + \nu(\text{C}_{m3}\text{C}_{\alpha 4})_{\text{asym}}$
ν_{40}	1560	1509	1497	1503	$\nu(\text{C}_{m1}\text{C}_{\alpha 1})_{\text{asym}} + \nu(\text{C}_{m2}\text{C}_\alpha)_{\text{asym}}$
ν_{41}	1537	1524	...	...	$\nu(\text{C}_{m2}\text{C}_\alpha)_{\text{asym}}$
ν_{42}	1512	1494	...	...	$\nu(\text{C}_{m2}\text{C}_\alpha)_{\text{sym}}$
ν_{43}	1485	1491	1491	1491	$\nu(\text{C}_\beta\text{C}_\beta)$
ν_{44}	1424	1422	1420	1421	$\nu(\text{C}_{m2}\text{C}_\alpha)_{\text{sym}}$
ν_{45}	1377	236	...	...	$\delta(\text{C}_{m2}\text{X}) + \delta(\text{C}_{m3}\text{X})$
ν_{46}	1359	278	278	278	$\delta(\text{C}_{m2}\text{X}) + \delta(\text{C}_{\beta 3,4}\text{H})_{\text{asym}}$
ν_{47}	1317	1320	1319	1317	$\delta(\text{C}_{\beta 2,3,4}\text{H})_{\text{asym}}$
ν_{48}	1302	1301	1300	1299	$\nu(\text{N}_1\text{C}_\alpha) + \nu(\text{C}_{\alpha 1,2}\text{C}_{\beta 1,2})$
ν_{49}	1284	535	534	535	$\delta(\text{C}_m\text{X}) + \delta(\text{C}_{\beta 3,4}\text{H})_{\text{asym}}$
ν_{50}	1207	1186	1186	1185	$\delta(\text{C}_{m3}\text{X}) + \delta(\text{C}_{\beta 2}\text{H}) + \delta(\text{C}_{\beta 3,4}\text{H})_{\text{asym}}$
ν_{51}	1149	236	236	236	$\delta(\text{C}_{m3}\text{X}) + \delta(\text{C}_{m2}\text{X}) + \delta(\text{C}_{\beta 2}\text{H})$
ν_{52}	1140	156	156	156	$\delta(\text{C}_{m3}\text{X}) + \delta(\text{C}_{m2}\text{X}) + \delta(\text{C}_{\beta 3,4}\text{H})_{\text{asym}}$
ν_{53}	1069	1089	1088	1088	$\delta(\text{C}_{\beta 3,4}\text{H})_{\text{sym}}$
ν_{54}	1041	1051	1051	1045	$\delta(\text{C}_{\beta 2}\text{H})$
ν_{55}	996	1001	999	1000	$\delta(\text{C}_\alpha\text{N}_2\text{M}) + \delta(\text{C}_\beta\text{H})$
ν_{56}	988	996	996	996	$\nu(\text{C}_{\alpha 3,4}\text{C}_{\beta 3,4}) + \nu(\text{NC}_\alpha)$
ν_{57}	976	981	979	981	$\delta(\text{NC}_\alpha\text{C}_\beta)$
ν_{58}	868	892	887	890	$\nu(\text{Pyr. def.})$
ν_{59}	798	862	857	859	$\delta(\text{C}_{\alpha 3,4}\text{C}_\beta\text{C}_\beta) + \delta(\text{N}_2\text{C}_\alpha\text{C}_\beta), \nu(\text{Pyr. def.})$

TABLE III. (Continued.)

ν_i	No phenyl		Phenyl		Comments
	T2'	T2''	^{13}C -T2A	^{13}C -T2B	
				B_{1g} modes	
ν_{61}	737	842	...	...	$\nu(\text{N}_2\text{C}_{\alpha 3}\text{C}_{m2})_{\text{asym}}$
ν_{62}	546	577	576	576	$\delta(\text{Pyr. rotation}) + \delta(\text{C}_{\alpha 1}\text{C}_{\beta 1}\text{C}_{\beta 1'}) + \text{benzene rot.}$
ν_{63}	418	427	426	427	$\delta(\text{Pyr. transl.})$
ν_{64}	377	443	443	443	$\delta(\text{Pyr. rot.})$
ν_{65}	296	356	355	355	$\delta(\text{Pyr. transl.})$
ν_{66}	204	206	206	206	$\delta(\text{Pyr. transl.}) + \nu(\text{NM})$
ν_{67}	167	199	199	198	$\nu(\text{NM})$

^aX represents H or phenyl group depending on the peripheral substitution.^bFrom Ref. 23. All the calculated values are multiplied by a factor of 0.96.

type B (**T2B**) does at m_1 and m_3 positions. The ν_4 mode that is predominantly contributed by C_{m2} -Ph and C_{m3} -Ph stretching exhibit a frequency downshift of $\sim 4\text{ cm}^{-1}$ in both **T2A** and **T2B** (Supplemental Material).³⁸ The ν_5 mode that is similar to the ν_4 mode but has larger vibrational contribution at C_{m3} -Ph stretching shows a little more downshift in **T2B**. The ν_7 mode at 1512 cm^{-1} which is a mixed vibration of $\nu(\text{C}_{m1}-\text{C}_{\alpha 1})_{\text{sym}}$ and $\nu(\text{C}_{m2}-\text{C}_{\alpha})_{\text{asym}}$ shows frequency downshifts of 12 and 6 cm^{-1} in **T2A** and **T2B**, respectively. The ν_{40} mode at 1509 cm^{-1} shows the same frequency shift as the ν_7 mode, since its eigenvector is similar to the ν_7 mode composed of $\nu(\text{C}_{m1}-\text{C}_{\alpha 1})_{\text{sym}}$ and $\nu(\text{C}_{m2}-\text{C}_{\alpha})_{\text{asym}}$ motions. Significant movement of the $\text{C}_{m1}-\text{C}_{m1'}$ bond is observed in the ν_7 and ν_{40} modes, which is caused by large movement of $\text{C}_{m1}-\text{C}_{\alpha 1}$ bonds. The ν_9 and ν_{11} modes are similar to the ν_7 mode but are mostly $\nu(\text{C}_m-\text{C}_{\alpha})_{\text{sym}}$ vibration while the latter is composed of $\nu(\text{C}_{m1}-\text{C}_{\alpha 1})_{\text{sym}}$ vibration. The $\text{C}_{m1}-\text{C}_{m1'}$ stretching motion is of special interest since the $\text{C}_{m1}-\text{C}_{m1'}$ bond connects two porphyrin units and interporphyrin interactions occur through this bond. The ν_7 , ν_{11} , ν_{17} , and ν_{20} modes are composed of $\text{C}_{m1}-\text{C}_{m1'}$ stretching motion and accordingly, they show large frequency shifts in **T2B**. More specifically, the ν_{17} and ν_{20} modes show frequency shifts only in **T2B** but not in **T2A**, since they involve significant movements of only C_{m1} carbons. Another linking site between two porphyrin units is the $\text{C}_{\beta 1}-\text{C}_{\beta 1'}$ bond. The ν_6 mode has an eigenvector mostly localized on $\text{C}_{\beta 1}-\text{C}_{\beta 2}$ and $\text{C}_{\beta 1}-\text{C}_{\beta 1'}$ bonds, exhibiting no frequency shift by ^{13}C -isotope labeling (Table III). This mode is quite different from the ν_2 mode of Ni^{II} TPP that involves $\nu(\text{C}_{\beta}-\text{C}_{\beta})$ stretching. The ν_8 and ν_{43} modes are represented by the eigenvectors with delocalized $\nu(\text{C}_{\beta}-\text{C}_{\beta})$ motions through the whole porphyrin plane bearing a resemblance to the ν_2 (A_g) and ν_{11} (B_{1g}) modes of Ni^{II} TPP, respectively.

F. Resonance Raman spectra of fused porphyrin arrays

The RR spectra of a series of fused porphyrin arrays with photoexcitation at 457.9 nm , which is in resonance with the $\text{CT}_x(3B_{3u})$ transitions, are displayed in Fig. 6. At first glance, the overall RR spectra of **Tn** are quite complicated

especially in high-frequency region ($1000\text{--}1700\text{ cm}^{-1}$) as compared with the porphyrin monomer and change quite differently from the RR spectrum of **T2** with an increase of the porphyrin units in the array. The RR spectra of **Tn** are dominated by the polarized Raman bands except some depolarized Raman bands at 1318 , 1487 , and 1565 cm^{-1} (Table IV). In addition, the relative RR enhancement changes as the porphyrin array length becomes longer such that the RR bands at 1223 , 1411 , 1531 , and 1565 cm^{-1} become relatively stronger (Table IV). The suppression of the low-frequency RR bands below 1000 cm^{-1} is still maintained in the fused porphyrin arrays longer than **T2**. The RR bands at 1118 , 1160 ,

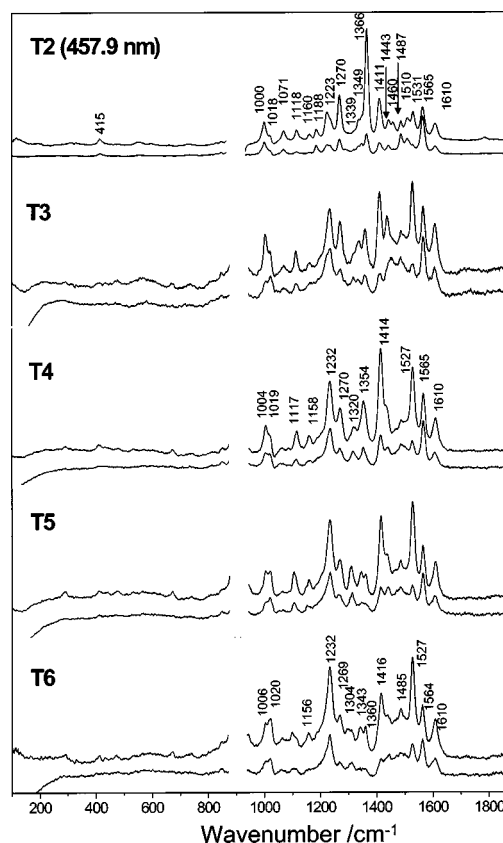


FIG. 6. The resonance Raman spectra of the fused porphyrin linear arrays in THF by photoexcitation at 457.9 nm . For each set of spectra the top and bottom spectra correspond to the parallel and perpendicular polarizations to the incident polarization.

TABLE IV. The observed RR frequencies of **Tn**.

Modes	Raman frequencies (cm^{-1})				
	T2	T3	T4	T5	T6
ν_6	1610 (1611) ^a	1610 (1609) ^b	1610	1610	1610
ν_{39}	1565 (1577)	1565 (1586)	1565	1564	1564
ν_8	1531 (1532)	1529 (1533)	1527	1527	1527
ν_{43}	1487 (1491)	1487 (1491)	1485	1485	1485
ν_{10}	1443 (1443)	1439 (1450)	1435	1435	1436
ν_{11}	1411 (1409)	1412 (1424)	1414	1415	1416
ν_{13}	1366 (1352)	1359 (1345)	1354	1345	1343
ν_{14}	1349 (1336)	... (1331)	~1344	~1344	~1344
ν_{15}	1339 (1314)	~1339 (1317)	...	...	...
ν_{47}	1318 (1320)	1316 (1324)	1316	~1310	~1310
ν_4	1270 (1244, 3077 ^c)	1270 (3095)	1270	1270	1269
ν_{17}	1223 (1202)	1232 (1234)	1232	1232	1232
ν_{18}	1160 (1169)	1158 (1175)	1157	1157	1156
ν_{20}	1118 (1120)	1115 (1115)	1117	1109	1102
ν_{22}	1018 (1012)	1018 (1021)	1019	1020	1020
ν_{23}	1004 (999)	1004 (996)	1005	1006	1006

^aThe values in the parentheses represent the calculated frequencies of **T2'**.^bThe values in the parentheses represent the calculated frequencies of **T3'**.^cThe calculated frequency from **T2'** for a comparison with **T2'**. All the calculated values are multiplied by a factor of 0.96.

1318, 1366, 1443, 1487, and 1531 cm^{-1} exhibit systematic shifts to lower frequencies with an increase of the porphyrin units in **Tn** (Table IV). On the contrary, the RR bands at 1004 , 1018 , 1223 , and 1411 cm^{-1} display slight shifts to higher frequencies as the fused porphyrin arrays become longer. Some other RR bands such as those at 1270 , 1565 , and 1610 cm^{-1} remain at the same frequencies as the number of porphyrin units increases. The overall spectral features become simplified in going from **T2** to **T6** showing mostly polarized RR bands. This reflects that the redshift of the absorption maximum becomes being closer to the resonance excitation line resulting in the RR enhancement of predominantly polarized Raman bands. At the same time, the enormously broadened spectral features explain the observation of a few depolarized RR bands, which are definitely caused by the Herzberg–Teller scattering involving relatively weak CT transitions. The diminishment of the strongest RR band at 1366 cm^{-1} in **T2** with an increase of the porphyrin array length is consistent with the very weak RR enhancement of this band in the RR spectrum of **T2** by the 416 nm excitation that is close to the absorption maximum of the B_y band (Fig. 4). The diminishment of the RR bands at 1004 , 1270 , and 1610 cm^{-1} , which are very strong in the RR spectrum of **T2** by the 416 nm excitation, is regarded as representing geometry changes with an increase of the porphyrin array length. The 1223 cm^{-1} band (ν_{17}) of **T2** with a shoulder at 1238 cm^{-1} (ν_{38} or ν_5) appears shifted to high frequency at $\sim 1232\text{ cm}^{-1}$ in going from **T2** to **T6**. The ν_{17} mode shows an increase in calculated frequency from **T2** to **T3** while the ν_{38} mode shows a decrease in calculated frequency. Thus the 1232 cm^{-1} band in the longer porphyrin arrays is considered to be a mixture of a polarized band (ν_{17}) and an anomalously polarized band (ν_{38}). The RR band at 1000 cm^{-1} in **T2** assigned to the ν_{24} mode is apparently shifted by $\sim 5\text{ cm}^{-1}$. However, the RR bands at $\sim 1005\text{ cm}^{-1}$ in the longer porphyrin arrays should be attributed to the ν_{23} mode appearing

at 1004 cm^{-1} in **T2** by the 416 nm excitation based on the increased relative enhancement of the ν_{23} mode as the excitation line becomes closer to the B_y band (Table IV).

IV. DISCUSSION

A. Resonance Raman enhancement via the A-term scattering

Subtle changes in molecular structures can affect significantly the RR bands.^{42,43} Geometry changes are directly reflected in the RR bands resonantly activated by the A-term scattering mechanism when the photoexcitation line lies close to a strong electronic transition, and also reflected in the RR enhancement activated by the B-term scattering mechanism in which Raman vibrations having large overlap with the transition density matrix between the transition in resonance with the photoexcitation line and another nearby transition with large oscillator strength are enhanced.⁴⁴ The A-term contribution represents the scattering amplitude deriving from the pure electronic transition moment at the equilibrium geometry and the extent to which the minimum of the resonant excited-state potential surface is displaced along the normal coordinate. The B-term contribution represents the scattering amplitude deriving from the pure electronic transition moment and the derivative of the electronic transition moment with respect to the normal coordinate. In the case that the B-term scattering is dominant in the RR enhancement, the oscillator strength of the resonant excited transition is weak and the RR enhancement is derived from the derivative term that explains so-called intensity borrowing from a strong electronic transition lying nearby.

To obtain further information on the RR enhancement for specific Raman modes in relation to the A-term scattering mechanism, we have predicted the excited state geometry changes of **T2** on the basis of the INDO/S-SCI calculated bond orders as defined by Eq. (4) (Fig. 7). The excited-state

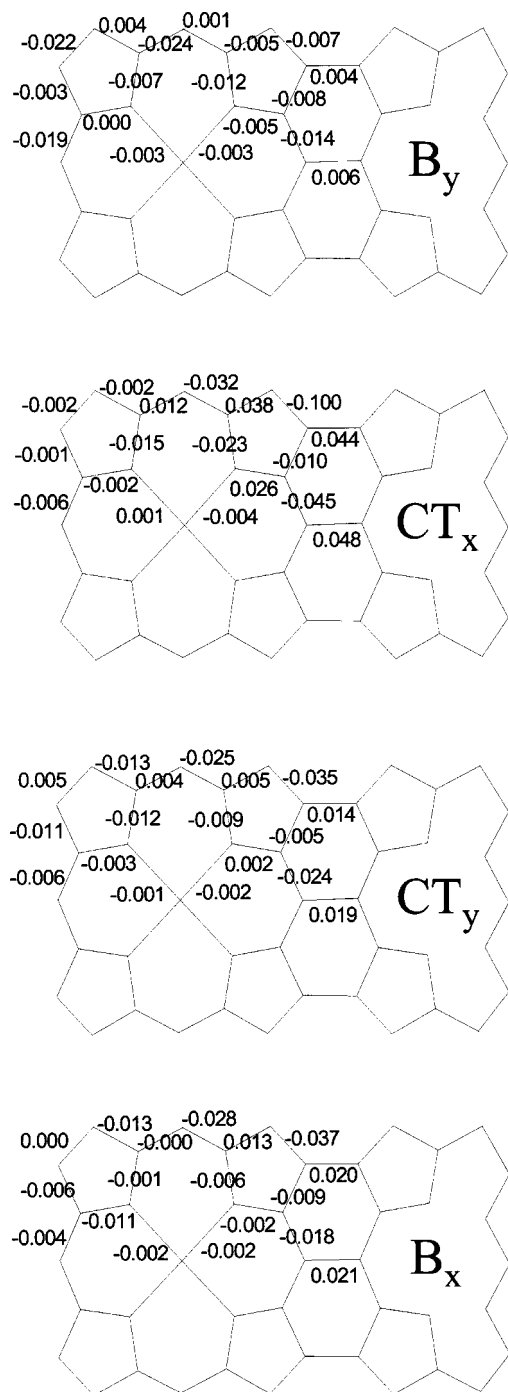


FIG. 7. Bond order changes in the B_y , CT_x , CT_y , and B_x states (from top to bottom) with respect to the ground state of $T2''$ as obtained by the INDO/S-SCI calculations.

geometry of the B_y band shows relatively large bond length changes in the $C_{m1}-C_{\alpha1}$, $N_1-C_{\alpha2}$, $C_{m2}-C_{\alpha3}$, $C_{\beta3}-C_{\beta4}$, and $C_{m3}-C_{\alpha4}$ bonds exhibiting an alternative pattern in the bond length change like a Kekulé-type structure of benzene. The ν_8 and ν_9 modes appearing at 1531 and 1460 cm^{-1} , respectively, exhibit eigenvectors mostly sensitive to these structural changes (Supplemental Material).³⁸ The other Raman bands could be also explained qualitatively based on the excited geometry change. However, the graphical information could not be always applied successfully to the specific RR enhancement for every Raman mode. For example, the

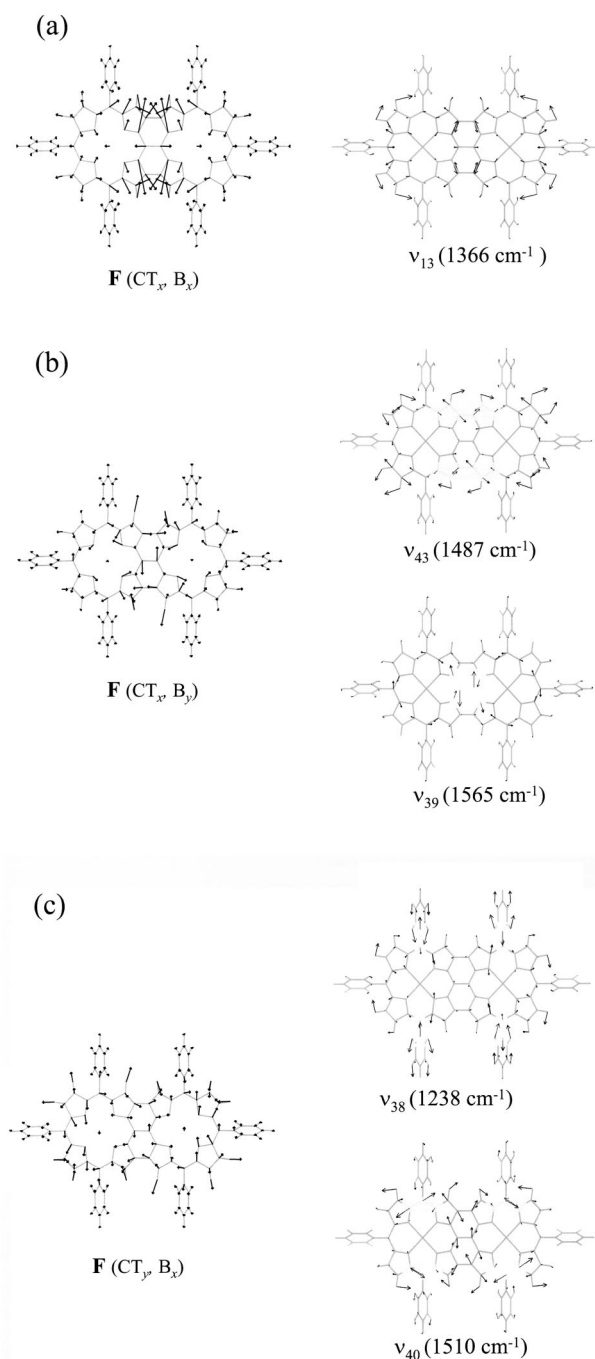


FIG. 8. Transition-force vector plots for $T2''$ associated with the electronic transitions between CT_x and B_x states (a), between CT_x and B_y states (b), and between CT_y and B_x states (c) as calculated by Eq. (9) at the INDO/S-SCI level. Shown in the right panel are the normal-mode eigenvectors obtained at the B3LYP/6-31G level which are similar in main portion to each transition-force vector.

ν_{11} and ν_{13} modes are hardly activated even though their eigenvectors involve large movements in the $C_{m1}-C_{\alpha1}$ and $C_{\alpha1}-C_{\beta1}$ bonds.

While the anomalously or depolarized Raman bands are observed via the Herzberg–Teller scattering with longer laser-line excitations, the polarized RR bands such as the strongest RR band at the 1366 cm^{-1} (ν_{13} mode) are also significantly enhanced by 457.9 nm excitation (CT_x band). The RR enhancement of the A_g modes should be understood

differently from that of the B_{1g} modes because the vibronic interaction between the CT_x and B_y transitions and between the CT_y and B_x transitions cannot activate the A_g modes due to symmetry property. For the A_g modes to be activated via the B-term scattering the CT_x transition should be coupled with the B_x transition, and the CT_y transition with the B_y transition. Considering that the energy differences are smaller than the band gap between the B- and Q-bands of the porphyrin monomer, these vibronic interactions are not improbable. As seen in Fig. 8(a), the $F(CT_x, B_x)$ acting on $C_{\alpha 1}$ is significant and directed nearly parallel to the corresponding component of the ν_{13} mode eigenvector indicating a pronounced vibronic coupling between the CT_x and B_x transitions mediated by this normal mode. Meanwhile, we cannot neglect the possibility of the A-term contribution in the RR activation of the A_g modes by photoexcitation at the charge-transfer bands since the CT_x and CT_y transitions, even if relatively weak transitions, have considerable oscillator strengths due to a proper mixing with the excitonic transitions, B_y and/or B_x .¹⁵ The large RR enhancements of the ν_{13} and ν_{11} modes at 1366 and 1411 cm^{-1} , respectively, support this argument. More specifically, the ν_{13} mode is associated with $\nu(C_{\alpha 1}-C_{\beta 1})$, and the ν_{11} mode has a large contribution of $\nu(C_{m1}-C_{\alpha 1}) + \nu(C_{m1}-C_{m1'})$ (Supplemental Material).³⁸ These modes are expected to be activated by the A-term scattering considering the large displacement of these bonds in the excited-state geometry of the CT_x transition (Fig. 7). It is noteworthy that such large displacement can be attributed to the localized nature of HOMO-4 (Fig. 2), since the CT_x state is dominated by the transition from the HOMO-4 to LUMO as described above. The diminishment of these modes in the RR spectrum by 514.5 nm excitation is consistent with this feature since the excited-state geometry changes of the CT_y transition in these bonds are relatively less significant than those of the CT_x transition (Fig. 7). However, the ν_7 and ν_{20} modes at 1510 and 1118 cm^{-1} do not quite follow the same strategy. This implies that the Herzberg-Teller scattering is more operative in these modes than the Franck-Condon scattering. The participation of the two scattering mechanisms is not abnormal phenomena in such a porphyrin system featuring complex electronic structures with closely lying transitions. Depending on the extent of scattering amplitudes and phases from the two scattering terms, destructive or constructive interaction can be incurred and also one term can prevail over the other.

In this regard it is worthwhile to note that the ν_{20} and ν_6 modes at 1118 and 1610 cm^{-1} lose their intensities in the RR spectrum by the 457.9 nm excitation. The former mode is mostly $C_{m1}-C_{m1'}$ stretching vibration and the latter one is totally $C_{\beta 1}-C_{\beta 1'}$ stretching vibration. Thus, they should be resonantly-enhanced via the A-term scattering based on the extremely large displacement of the $C_{m1}-C_{m1'}$ and $C_{\beta 1}-C_{\beta 1'}$ bonds in the CT_x excited-state geometry. However, this is not the case in the observed RR spectrum, and this mode becomes even more enhanced by photoexcitation at the CT_y transition in which the bond displacement is, even if not so small, smaller than that in the CT_x excited state geometry. This seems to be due to the resonance de-enhancement^{43,44} caused by the destructive interaction between

the A-term scattering by photoexcitation at the CT_x transition and the B-term scattering involving another nearby transition with large oscillator strength such as the B_x transitions.

B. Resonance Raman enhancement via the B-term scattering

The B_{1g} modes are nontotally symmetric vibrations spanning xy or R_z . Rotational symmetry species, R_z , correspond to $xy-yx$, resulting in an antisymmetric Raman tensor. Thus the corresponding vibrational modes are anomalously polarized with $\rho > 0.75$. The anomalously polarized Raman bands observed in the RR spectra with photoexcitation at 441.6, 457.9, and 514.5 nm are B_{1g} modes, which are resonantly activated via the Herzberg-Teller scattering.

When the excitation line is changed from 416 to 441.6 nm and even further to 457.9 nm, new RR bands with the depolarization ratios larger than 0.75 begin to appear at 1565, 1487, and 1188 cm^{-1} corresponding to the ν_{39} , ν_{43} , and ν_{50} modes with B_{1g} symmetry, respectively (Fig. 4). The photoexcitation at 457.9 nm corresponds to the CT_x transition. For the B_{1g} Raman modes to be resonantly enhanced via the B-term scattering by photoexcitation at the CT_x transition of B_{3u} symmetry, an appropriate transition should have B_{2u} symmetry due to symmetry consideration. The nearby transitions with B_{2u} symmetry are the B_y and CT_y transitions. Considering the oscillator strength difference between the two transitions, the B_y transition would be appropriate for vibronic mixing with the CT_x transition. Figure 8(b) represents the transition force vectors between the excitonic band (B_y) and the charge-transfer band (CT_x) of **T2**. The region of large transition forces occurs around the junction area between the two porphyrin units, especially on C_{m1} , $C_{\beta 1}$, and $C_{\alpha 2}$. Therefore, the vibrational modes selected by the transition density operator are those involving the movement of these carbons. The ν_{39} mode depicts vigorous movements of $C_{m1}-C_{\alpha 1}$ bonds [Fig. 8(b)] and the ν_{43} mode involves large movement of $C_{\beta 2}C_{\beta 1}C_{\beta 1'}$. The moving pattern of $C_{\alpha 1}-N_1-C_{\alpha 2}-C_{m2}$ of the ν_{50} mode also reveals a consistency with the pattern of the transition force vectors in this position (Supplemental Material).³⁸ These features explain the observed RR enhancement of the ν_{39} , ν_{43} , and ν_{50} modes.

There is one thing to be noted in the RR spectral changes as the excitation line is changed from 457.9 to 514.5 nm. The relatively intense ν_{39} , ν_{43} , and ν_{50} modes by the 457.9 nm excitation become diminished in the RR spectrum by the 514.5 nm excitation. The ν_{38} and ν_{40} modes, on the other hand, becomes stronger as the excitation line is changed to longer wavelength. The 514.5 nm excitation corresponds to the charge-resonance transition, CT_y with B_{2u} symmetry. For the B-term scattering to be considered to explain the RR enhancement of the B_{1g} Raman modes, the B_x transition (B_{3u}) instead of the B_y transition (B_{2u}) should be treated due to symmetry consideration. Figure 8(c) represents the transition force vectors between the excitonic band (B_x) and the charge-transfer band (CT_y) of **T2**. The map represents that the transition forces on the C_{m1} positions and also be-

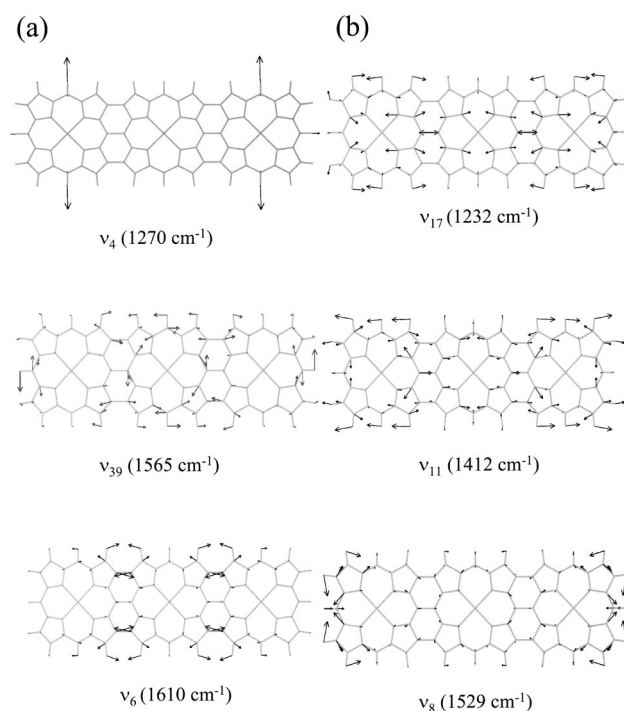
TABLE V. The observed depolarization ratios of the RR bands by various excitation lines.

Observed frequencies (cm^{-1})	ρ			
	416 nm	441.6 nm	457.9 nm	514.5 nm
1610	0.34	0.23	0.45	0.38
1565	0.89	0.93	1.43	1.1
1531	0.15	0.35	0.17	0.36
1510	1.0	0.59	0.78	0.54
1487	...	0.98	1.6	0.53
1460	0.32	0.44	0.12	0.04
1443	...	0.44	0.51	0.34
1411	...	0.31	0.32	0.51
1366	0.17	0.27	0.18	0.37
1349	0.28	0.47	0.71	0.36
1339	0.26	0.55	0.53	...
1322	0.62	...	...	1.1
1318	...	0.44	...	1.3
1270	0.27	0.34	0.34	0.55
1238	0.47	0.82	0.95	0.95
1223	...	0.39	0.4	0.34
1188	...	0.71	0.92	...
1160	...	0.55	0.35	...
1118	0.41	0.17	0.25	0.42
1071	0.37	0.71	0.46	...
1018	...	...	0.59	0.65
1004	0.26	0.47	0.55	0.53

tween the $C_{\beta 1}-C_{\beta 2}$ bonds are dramatically reduced and the moving pattern along the $C_{\alpha 1}-N_1-C_{\alpha 2}-C_{m 2}$ is also diminished. This is consistent with the reduced enhancement of the ν_{39} , ν_{43} , and ν_{50} modes by photoexcitation at the B_y transition. The enhancement of the ν_{38} and ν_{40} modes is related to the increased contribution from $C_{m 2}$ -phenyl and $C_{m 2}-C_{\alpha 3}$ stretching [Fig. 8(c)]. The enhancement of the ν_{47} mode is not so obvious from the transition force map, but the phase of the movement along $C_{\beta 1}-C_{\beta 2}-C_{\alpha 2}-C_{m 2}-C_{\alpha 3}$ matches well with the nuclear transition vector [Fig. 8(c)].

C. Depolarization dispersion of fused porphyrin arrays

Along with the RR enhancement the depolarization ratios of the RR bands are also regarded to exhibit interference effects between scatterings from different states. For some antisymmetric RR bands the dispersion in the depolarization ratios has been observed,^{43,45-47} which has been also explained theoretically by showing the maximum depolarization ratio at the center of the two interacting transitions.⁴⁷ Table V shows the depolarization ratios of the observed RR bands at various excitation lines from 416 to 514.5 nm. Some RR bands maintain the same depolarization ratios within experimental errors but some other RR bands such as those at 1349, 1366, 1487, 1510, and 1565 cm^{-1} show large deviations. Especially, the 1510 and 1565 cm^{-1} Raman bands with antisymmetric Raman tensors show the maximum depolarization ratios by photoexcitation at 457.9 nm. It may be possible to think that the observed RR bands are actually the superpositions of independent modes of different symmetries with different resonance behaviors. It is, however, difficult to believe that such accidental degeneracies

FIG. 9. Representative vibrational eigenvectors of the fused porphyrin trimer without phenyl substituents ($T3''$).

could occur for several RR bands. The dispersion in the depolarization ratios illustrates that the real Raman tensor should be described as a linear combination of Raman tensors with different symmetries.^{43,45-47} The mixing of different symmetries in the Raman tensors indicates that the molecular symmetry is somewhat perturbed from the perfect D_{2h} symmetry.⁴⁶ This leaves a potential existence of the Jahn-Teller activity in the fused porphyrin arrays along the oblique distortion, which is not improbable considering the enormous broadening of the absorption bands.

D. Normal mode analysis of fused porphyrin arrays

A series of RR spectra of **Tn** are obtained by photoexcitation at 457.9 nm (Fig. 6). Most of the RR bands of **Tn** except the ν_4 (1270 cm^{-1}), ν_{39} (1565 cm^{-1}), and ν_6 (1610 cm^{-1}) modes show frequency shifts as the number of porphyrin units increases (see also Table IV). Since the ν_4 mode is localized on *meso*-carbons parallel to the long molecular axis and the other two modes are localized on the bridge carbons of the dimeric porphyrin ring [Fig. 9(a)], the influence by addition of another porphyrin unit seems to be not so significant. On the other hand, the RR bands showing frequency shifts such as the ν_{17} , ν_{11} , and ν_8 modes include $C_{m 3}$ -phenyl, $C_{\beta 3}-C_{\beta 4}$ stretching, and $C_{\beta}-H$ bending vibrations [Fig. 9(b)]. The frequency shifts of these Raman modes can be explained by environmental changes at $C_{\beta 3}$, $C_{\beta 4}$, and $C_{m 3}$ positions (mostly outer carbons of the dimeric porphyrin ring) as the number of porphyrin units increases from **T2** to **T6**. The ν_{17} (1223 cm^{-1}), ν_{11} (1411 cm^{-1}), and ν_8 (1531 cm^{-1}) modes in the RR spectrum of **T2** are moderately enhanced. However, these RR bands become gradually stronger in going from **T2** to **T6**. It is noteworthy that

these modes involve the vibrations of *meso-meso* carbons connecting two porphyrin rings as well as adjacent $C_{\alpha 1}$ carbons. The $C_{\alpha 1}-C_{m1}-C_{\alpha 1}$ bending motion yields a normal mode that is delocalized over the fused porphyrin dimer. This feature leads to an enhancement of this mode due to an increase of polarizability.⁴⁸ On the contrary, the 1610 cm^{-1} band involving the $C_{\beta 1}-C_{\beta 1'}$ stretching vibration maintains its intensity as the number of porphyrin units increases. Accordingly, since the $C_{\beta 1}-C_{\beta 1'}$ stretching vibration is localized on the linking part of **T2**, this mode does not contribute to the delocalization of the molecular vibrations throughout the fused dimer [Fig. 9(a)].

It is interesting to note that the low-frequency RR bands below 800 cm^{-1} are largely diminished in the RR spectra of **Tn**. In the RR spectrum of the porphyrin monomer, most of the low-frequency RR bands involve out-of-plane modes of porphyrin macrocycle. The lack of out-of-plane vibrational modes in **Tn** is likely to arise from the completely flat molecular structures of **Tn**. The *meso-meso* linked diporphyrins strapped with a dioxymethylene group of various lengths (**Sn**, $n = 1, 2, 3, 4, 8$, and 10 ; n is the number of carbon atoms in the chain) revealed that the low-frequency RR bands gradually lose their intensities with a decrease of the dihedral angle in going from **S10** to **S1**.⁴⁹ Since **T2** can be regarded as a porphyrin dimer that has zero dihedral angle, the observation that the low-frequency RR bands significantly lose their intensities is similar to the cases observed in **Sn**. The vibrational modes that correspond to the $\nu(\text{NM})$ and $\delta(C_{\alpha}C_mC_{\alpha})$ modes are not activated in **T2** while these modes are significantly enhanced in the orthogonal porphyrin dimer appearing at 381 and $\sim 660\text{ cm}^{-1}$, respectively. The transition force vectors of **T2** between the CT_x and B_y states as well as the CT_y and B_x ones reveal little enhancement of these vibrational modes. On the other hand, the bond length changes induced by the B_y transition is not so significant along the nuclear coordinates of the modes as seen in Fig. 7. Thus, these modes are little enhanced by either the Franck-Condon scattering or the Herzberg-Teller scattering.

V. CONCLUSION

The lowest electronic transitions of **Tn** are continuously redshifted to the IR region (up to a few μm) due to much enhanced π -electron delocalization throughout the entire fused porphyrin array. This unique feature provides a promising possibility for the application of **Tn** as electric wires in molecular electronics. To investigate the electronic transition in relation to the molecular structures of **Tn**, the resonance Raman spectra of **Tn** were recorded by changing the photoexcitation wavelength. The RR spectra reveal that most of the RR bands of **T2** are polarized by photoexcitation at 416 nm , while some depolarized or anomalously polarized RR bands appear by photoexcitation at 457.9 and 514.5 nm . On the basis of the normal mode analysis using the B3LYP/6-31G Gaussian method, we could assign the Raman bands of **T2**. Since the RR spectra of **T2** became complicated, being distinctly different from the RR spectrum of the porphyrin monomer, new atom labeling was adopted to reveal the vibration modes of **T2**. The INDO/S-SCI calculations have successfully predicted the geometry changes as well as the

vibronic coupling strengths for the essential excited states, revealing the resonance enhancement mechanism of specific modes via the A-term and B-term scatterings. In the arrays, the Raman bands including $\nu(C_{m3}-\text{phenyl})$, $\nu(C_{\beta 3}-C_{\beta 4})$, $\delta(C_{\alpha 1}-C_{m1}-C_{\alpha 1})$, and $\delta(C_{\beta}-\text{H})$ modes exhibit systematic frequency shifts as well as enhancements in their intensities with an increase of the number of porphyrin units in **Tn**. These features were explained by substitution environmental changes at $C_{\beta 3,4}$ and C_{m3} positions and increasing polarizability in going from **T2** to **T6**. Collectively, our data from the RR spectroscopic measurements as well as the quantum chemical calculations provide a clear picture on the electronic transitions in relation to the molecular structures of **Tn**.

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