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Excitonic Coupling between B and Q Transitions in Porphyrin Aggregates *

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The properties of meso-tetraphenylporphine (TPP) aggregates formed in acidic aqueous-organic solutions are investigated by UV-vis spectroscopy. According to the absorption spectra, the Q band absorption of the aggregated TPP shows red shift and intensity enhancement, and a model that includes the participation of water molecules in a porphyrin aggregation complex is proposed, then a qualitative explanation based on Gouterman's excition coupling theory is presented. Calculations including eigenenergies, eigenstates and the transition dipole strength of the coupled states are carried out.

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Porphyrin aggregates and the resulting changes in visible light absorption have important consequences in connection with the functions of chlorophyll aggregates in photosynthetic organisms in plants and bacteria,[1−3] and water as an indispensable material in organisms, in most reactions, not only is an initial component involved in the reduction-oxidation processes but also serves as an environment where all these processes are carried out. Thus the investigation of interaction between porphyrin pigments and water is playing an important role in connection with mimicking of events of the photosynthetic conversion of the solar energy.

Porphyrins in particular are well known for their tendency to aggregate in aqueous solution,[3−8] changes in the environmental characteristic, such as ionic strength or pH, have received many scientists' attention,[5,6,9] as they can affect the electrostatic between the porphyrin molecules in aggregation resulting in perturbations to their electronic absorption spectra. In this study, the protonated TPP in acidic aqueous-organic solution can form the aggregates which not only include the interaction of π bond of macro-porphyrin, but also the interaction of the donor-accepter and the hydrogen bands between the porphyrin and water molecule. We provide a suitable model which represents not only the interactions between porphyrins but also the interaction between the porphyrins and the water molecule. From the UV-visible absorption spectra, a large split of the B band and an intensity enhancement of all the Q bands are observed, and the closer the Q band to the B band, the greater the enhancement of the Q absorption bands. This phenomenon is due to the role of water in the aggregation, which can stimulate the coupling of the B and Q bands between the two porphyrin molecules. Finally we present a qualitative calculation of the excitonic coupling based on Gouterman's four-orbital model in order to explain the absorption spectral phenomena.

Synthesis of the TPP was carried out according to the procedures described elsewhere;[10] tetrahydrofuran is an analytical grade reagent, Sigma-Aldrich. For the preparation of aqueous-organic solutions, deionized water and double distilled water were used. The absorption spectra of TPP solution were recorded using a Uv-Vsible spectrometer of the Beijing Purkinje General Instrument Co, Ltd, TU-1901.

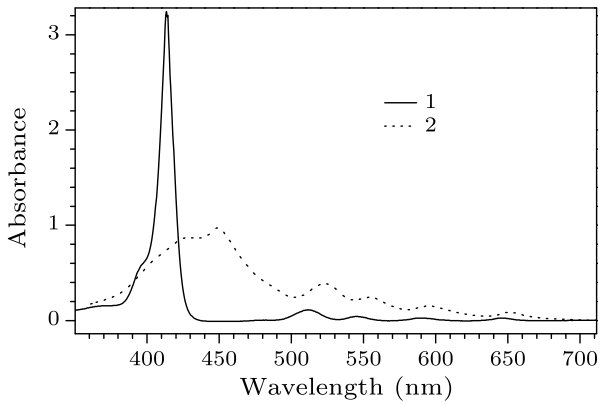


Fig. 1. Absorption spectra of TPP in tetrahydrofuran (dotted) and TPP in water-tetrahydrofuran solution (9:1) in the presence of 0.01 M hydrochloric acid (solid).

Figure 1 shows the absorption spectra of the monomer and protonated aggregated forms of TPP. Compared to the monomer case, the Q bands of the aggregated TPP show red shift, and an intensity enhancement, the closer the Q bands to the B band, the greater the enhancement. Normally, the intensity gained by Q bands can be transferred of the dipole strength from other spectral regions, since the intraband excitonic interactions only cause a redistribution of the absorption intensity, conserving the total strength of the absorption band. This phenomenon

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can be explained using a model proposed in Fig. 2,[11] there is a possibility for stabilization of the π-electron structure of the porphyrin macrocycle. According to this model, stabilization of the π-electron structure of macrocycle in dimeric monocation can occur via its interaction with one water molecule, which leads the electron to the protonated nitrogen atom and the proton to the neighboring porphyrin molecule. Another water molecule forms hydrogen bonds with ternary nitrogen atoms of these porphyrin molecules because stabilization of the π-electron structure of dimeric monocation requires addition of the proton or electron. Hence, neighboring porphyrin molecules in dimer are coordinated via two water molecules with the formation of hydrogen bands between them. It appears that the water molecule, which forms hydrogen bands, may be considered as a neutral one, whereas another water molecule is involved in the donor-accepter interaction with porphyrin. The water molecules as the intermediate of the interaction of two porphyrin molecules make the coupling of the B and Q transition of the different monomers come true, then lead to the redistribution of absorption bands.

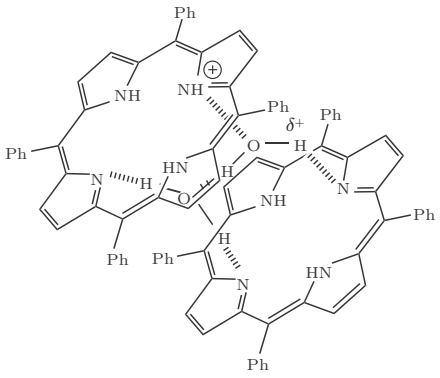


Fig. 2. Model of the protonated TPP in aqueous-organic solution, ph represents the benzene ring.

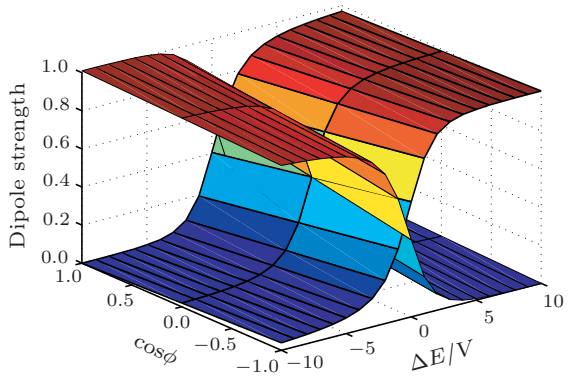


Fig. 3. Transition dipole strength of the two coupled transitions versus the angles ϕ between $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, the ratio of their distance and the coupling potential.

On the basis of the four-orbital model,[12,13] we use Gouterman's exciton coupling method in porphyrin dimer to explain the phenomena occurred in the absorption spetctra.[14] In Fig. 2, assuming the two identical monomers (TPP) M and N, each carrying two monomer transition dipoles B and Q (Q represents an arbitrary transition of the four Q bands), we then obtain the following exciton Hamiltonian matrix:

	M_Q	N_Q	M_B	N_B
M_Q	E_Q	V_{QQ}	O	V_{QB}
N_Q	V_{QQ}	E_Q	V_{QB}	O
M_B	O	V_{QB}	E_B	V_{BB}
N_B	V_{QB}	O	V_{BB}	E_B

In this matrix, E_Q and E_B are the energy of monomer transitions, V_{QB}, V_{QQ} and V_{BB} are the excitonic interactions between the monomer transition dipoles of the two molecules. Thus the eigenstate of the TPP dimer can be obtained from solving the eigenproblem of the above Hamilton matrix. We then transform the matrix by the equations

$$Q^+ = 2^{-1/2}(M_Q + N_Q), \quad Q^- = 2^{-1/2}(M_Q - N_Q),$$
$$B^+ = 2^{-1/2}(M_B + N_B), \quad B^- = 2^{-1/2}(M_B - N_B).$$

Then the Hamilton matrix can be transformed into

$$\begin{pmatrix} E_Q - V_{QQ} & 0 & -V_{QB} & 0 \\ 0 & E_Q + V_{QQ} & 0 & V_{QB} \\ -V_{QB} & 0 & E_B - V_{BB} & 0 \\ 0 & V_{QB} & 0 & E_B + V_{BB} \end{pmatrix}.$$

Regrouping the above matrix, we can obtain the two-dimensional matrix

$$\begin{pmatrix} E_Q - V_{QQ} & -V_{QB} & 0 & 0 \\ -V_{QB} & E_B - V_{BB} & 0 & 0 \\ 0 & 0 & E_Q + V_{QQ} & V_{QB} \\ 0 & 0 & V_{QB} & E_B + V_{BB} \end{pmatrix}.$$

Thus the eigenstates of the dimer can be obtained by solving the eigenproblem of the following 2×2matrix, E represents $E_Q - V_{QQ}$ and $E_Q + V_{QQ}$, separately, ΔE represents $E_B - V_{BB} - E_Q + V_{QQ}$ and $E_B + V_{BB} - E_Q - V_{QQ}$ separately, and V represents $\pm V_{QB}$, then we have

$$\begin{pmatrix} E & V \\ V & E + \Delta E \end{pmatrix}.$$

The energies are given by

$$E^{\pm} = E + \frac{\Delta E}{2} \pm \sqrt{\frac{\Delta E^2 + 4V^2}{4}}.$$

The eigenstates are given by

$$\psi^{\pm} = N\left\{\left[\frac{\Delta E}{2V} \pm \frac{\sqrt{\Delta E^2 + 4V^2}}{2V}\right]^2 \varphi_1 + \varphi_2\right\}.$$

where N is a normalization factor, φ_1 and φ_2 are the wave function of the original states of energy E and $E+\Delta E$. The transition dipole strength of the coupled states is then given by

$$D^{\pm} = N^2\left\{\left[\frac{\Delta E}{2V} \pm \frac{\sqrt{\Delta E^2 + 4V^2}}{2V}\right]^2 \mu_1^2 + \mu_2^2 + 2\left[\frac{\Delta E}{2V} \pm \frac{\sqrt{\Delta E^2 + 4V^2}}{2V}\right]\boldsymbol{\mu}_1\boldsymbol{\mu}_2\cos(\phi)\right\},$$

where $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ are the transition dipole moments to the original states, and ϕ is the angle between $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$. The outcome of the above equation is shown in a 3D map for the different values of $\Delta E/V$ and angles $\phi(-\pi/2, \pi/2)$.

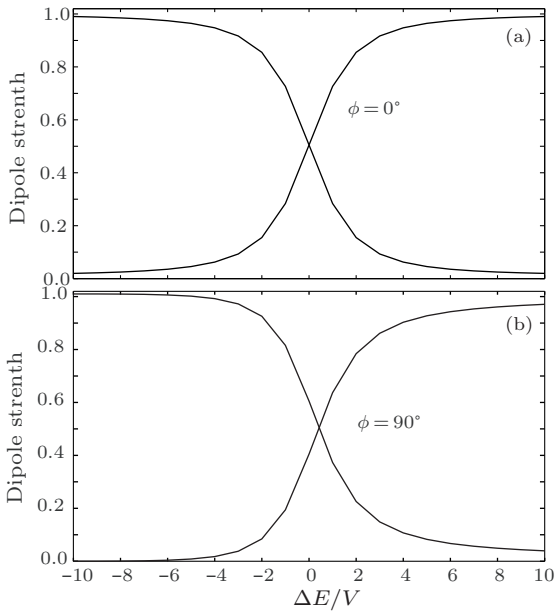


Fig. 4. Transition dipole strength of the coupled transitions on the angles $\phi = 0°$ and $\phi = 90°$.

In Fig. 3, the magnitude of the ratio of $\boldsymbol{\mu}_1$ to $\boldsymbol{\mu}_2$ is set as 0.1, which is determined by the ratio of the absorption intensity of the Q and B bands, and we can see from Fig. 3 that a redistribution of the transition dipole strength between the two coupled states occurs. The extent of the intensity transfer depends on the ratio $\Delta E/V$ of the energetic distance and coupling of the two states, and the mutual orientation of the uncoupled transition dipoles $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, the coupling causes an intensity gain of one of the two transitions at the expense of the other for arbitrary ϕ. Under the parallel and mutual perpendicular orientation of the uncoupled transitions condition (Fig. 4), we can obtain a glancing conclusion that the value of $\Delta E/V$ must be between -10 and -1, so from this point of view the scope of eigenvalue of excitonic interactions between the monomer transition dipoles of the two molecules can be calculated in detail.

According to the proposed model, the direct involvement of water molecules in the structure of dimeric complex of TPP in acidic aqueous-organic solution makes the coupling of the B and Q bands between the two TPP molecules more easy. This coupling makes a redistribution of the whole transition strength. Moreover, in the other experiments, the intensity transfer takes place between the Q bands, and a more detailed analysis is underway.

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