

## LETTERS

### Excitonic Coupling between B and Q Transitions in a Porphyrin Aggregate

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Aggregation distinctively changes the absorption and fluorescence anisotropy spectrum of  $\beta$ -tetraethyl-tetrapyrrolyl-porphyrin **1**. A large excitonic splitting of the B band occurs, and the Q band absorption is distinctively enhanced. The latter effect must be attributed to intensity transfer from the B- to the Q-band region that is mediated by an excitonic coupling between B and Q transition dipoles. In the fluorescence anisotropy spectrum of the aggregate of **1**, all Q bands and the red-shifted B band are polarized parallel, reflecting the strong interband excitonic coupling. A qualitative explanation of the observed excitonic effects is given.

Porphyrin systems are widely used to study excitonic effects in supramolecular structures. However, models so far are mainly restricted to interactions between identical monomer transitions. We emphasize that interband excitonic coupling between B and Q transitions, usually neglected, may distinctively influence the spectral and kinetic properties of such systems, as evident from the porphyrin aggregate presented in this communication.

$\beta$ -Tetraethyl-tetrapyrrolyl-porphyrin **1** aggregates in water at pH 2.5 in the form of soluble monolayer leaflets.<sup>1</sup> The absorption spectrum is changed distinctively by aggregation (Figure 1a). Most visibly, a large excitonic splitting of the B band and a distinctive enhancement of the Q-band region occur. The gain of intensity in the Q-band region must be attributed to a transfer of dipole strength from other spectral regions since intraband excitonic interactions cause only a redistribution of the absorption intensity, conserving the total dipole strength of the absorption band.<sup>2</sup> Obviously, the intensity gained by the Q

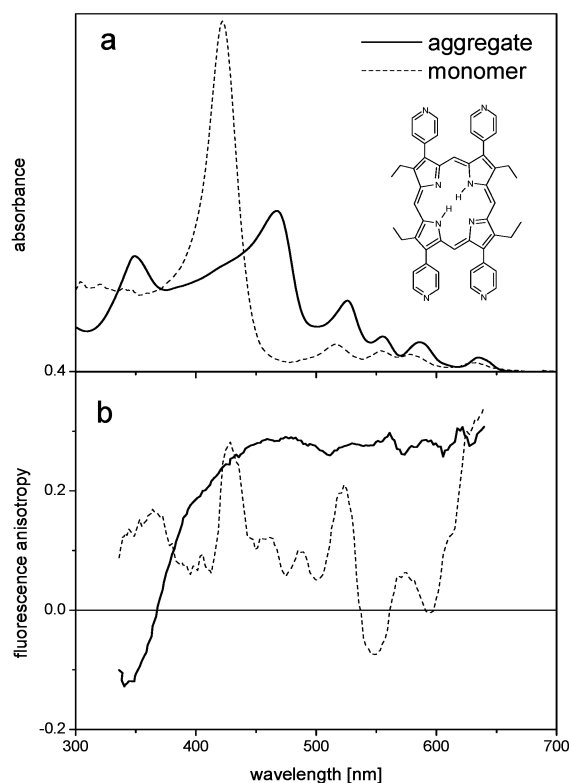
bands is transferred from the strong B band lying close in energy to the Q-band region. Aggregation also affects strongly the fluorescence anisotropy of **1** (Figure 1b). Whereas the monomer anisotropy spectrum shows several bands, the anisotropy of the aggregate stays almost constant at about 0.3 above 450 nm. At the blue side of the spectrum, the fluorescence anisotropy drops to a value of  $-0.1$ ; the monomer has an anisotropy of about 0.13 in this spectral range.

The striking changes in both the absorption and fluorescence anisotropy spectrum, in particular these in the Q-band region, have not been observed to this extent in other porphyrin systems. However, a distinctive enhancement of Q-band absorption exists in most porphyrin aggregates that possess a red-shifted aggregate B band.<sup>4</sup> A proper model of the excitonic interaction within such aggregates thus must include the coupling between the different monomer transitions, in particular the coupling between the strong B and the weak Q transition dipoles. However, excitonic coupling between monomer transition dipoles of different origin has not gained much attention in the literature. Although a large number of papers address excitonic interaction in a wide variety of supramolecular systems,<sup>2b,3</sup> usually only interactions between the same type of monomer transition

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**Figure 1.** Absorption and fluorescence anisotropy (emission at 670 nm) spectra of the monomer and aggregate of **1** in aqueous solution at pH 1.5 and 2.7, respectively. The monomer concentration was the same in both measurements.

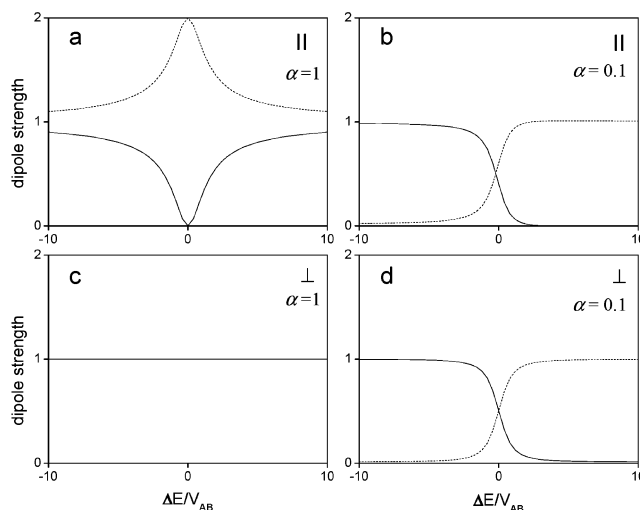
dipoles are considered. Gouterman et al.<sup>5</sup> first included excitonic coupling between Q and B transitions of porphyrins to model the spectra of scandium porphyrin dimers, though the effects caused by Q–B coupling were of minor importance in this particular system. However, Gouterman's dimer model is providing a qualitative explanation for the excitonic effects observed in the aggregate spectra of **1**. In brief, assuming a dimer of two identical monomers, each carrying two monomer transition dipoles A and B, the following exciton Hamiltonian matrix is obtained in first-order perturbation theory:

$$\begin{pmatrix} E_A & V_{AA} & 0 & V_{AB} \\ V_{AA} & E_A & V_{AB} & 0 \\ 0 & V_{AB} & E_B & V_{BB} \\ V_{AB} & 0 & V_{BB} & E_B \end{pmatrix} \quad (1)$$

where  $E_A$  and  $E_B$  are the monomer energies of the transitions, and  $V_{AA}$ ,  $V_{BB}$ , and  $V_{AB}$  are the excitonic interactions between the monomer transition dipoles of the two molecules. If the sub-matrices of the A–A and B–B interaction are diagonalized independently, matrix (1) is transformed into:

$$\begin{pmatrix} E_A - V_{AA} & 0 & V_{AB} & 0 \\ 0 & E_A + V_{AA} & 0 & V_{AB} \\ V_{AB} & 0 & E_B - V_{BB} & 0 \\ 0 & V_{AB} & 0 & E_B + V_{BB} \end{pmatrix} \quad (2)$$

Both monomer states are symmetrically split into two exciton states separated by twice the respective interaction potential, well-known for dimers. The transition into the “plus” states (corresponding to the eigenvalues  $E_x + V_{xx}$ ) would carry twice the dipole strength of the respective monomer transition; the transition into the “minus” states would be forbidden. If



**Figure 2.** Transition dipole strength of two coupled transitions in dependence on the ratio of their energetic distance and the coupling potential. (a,b) Parallel, and (c,d) mutual perpendicular orientation of the uncoupled transitions; (a,c) ratio of  $\alpha = 1$ , and (b,d) ratio  $\alpha = 0.1$  of dipole strength of the uncoupled transitions. See also Supporting Information.

$V_{AB} = 0$ , i.e., no cross coupling between the monomer transitions exists, this would be the final result since matrix (2) was diagonal.

Interestingly, the coupling  $V_{AB}$  is transformed into the diagonals of the off-diagonal quarter matrices. The interband excitonic interaction thus mediates a coupling between the excitonic “plus” and “minus” dimer states rather than the unperturbed monomer states. However, these states are not degenerate. A coupling of nondegenerate states also causes an energetic splitting and a redistribution of the transition dipole strength between the two coupled states. The latter effect is referred to as intensity transfer since dipole strength is exchanged between different monomer transitions. The extent of intensity transfer depends on the ratio  $\Delta E/V_{AB}$  of energetic distance and coupling of the two states, and the mutual orientation of the uncoupled transition dipoles (Figure 2). If both unperturbed transitions carry the same dipole strength (Figure 2a,c), the coupling causes an intensity gain of one of the two transitions at the expense of the other if both transition dipoles are oriented parallel, but no intensity transfer occurs for mutual perpendicular orientation. On the other hand, if one unperturbed transition is much weaker than the other (Figure 2b,c), the same result is obtained for both parallel and perpendicular orientation. Dipole strength is transferred from the stronger to the weaker transition dipole, and both transitions have the same transition dipole strength at the point of degeneracy. A coupling of a strong aggregate transition dipole with weaker transition dipoles of other exciton bands thus always causes an intensity transfer if the energetic distance between the two exciton bands is small enough. Even if a small amount of transition dipole strength is transferred, the effect on the weaker transition is still distinctive since it remarkably gains intensity compared to the uncoupled case.

In an aggregate of  $N$  identical molecules, each monomer transition forms an exciton band that contains  $N$  electronic states. Only one of the transitions into the exciton band is strongly dipole allowed and thus observable in absorption, all other transitions are weak or dipole forbidden. As shown above, excitonic coupling between different monomer transition dipoles has an effect if the corresponding exciton bands are overlapping or close in energy. Thus, even if two monomer transitions are

well separated, excitonic coupling between the corresponding excitonic transitions may exist. Applying the dimer results, the aggregate absorption spectrum of **1** can be interpreted qualitatively. In free-base porphyrins, the B band is a convolution of two almost degenerate, mutual perpendicular oriented transitions of similar dipole strength.<sup>6</sup> Thus, two B exciton bands appear in the aggregate spectrum, and no intensity is transferred between them (Figure 2c). However, due to the geometry of the aggregate, one B exciton band is red-shifted,<sup>1a</sup> lying close to the Q-band region and thus facilitating intensity transfer. Since all Q transitions are much weaker than the B transition, intensity is transferred independently of the actual orientation of the Q transition dipoles (Figure 2b,d). The amount of intensity transferred is clearly dependent on the energetic distance between the red-shifted B band at 470 nm and the respective Q band, dropping distinctively for the more distant Q bands. However, even the lowest energetic Q band at about 630 nm is still enhanced compared to the monomer spectrum.

The fluorescence anisotropy spectrum directly proves this interpretation of the aggregate absorption spectrum. Since the two aggregate B bands descend from mutual perpendicular oriented monomer transitions, they should be oriented perpendicular to each other. In fact, the two aggregate B bands at 350 and 470 nm are almost perpendicularly oriented, showing an anisotropy of  $-0.1$  and  $0.3$ , respectively. The anisotropy of the aggregate is almost uniform in the range above 450 nm. This indicates a parallel orientation of the aggregate B band at 470 nm and all the Q bands, whereas the monomer Q bands each show a different anisotropy. The equalization of the orientation of the aggregate Q bands can be explained by the intensity transfer from the red-shifted B band. A considerable amount of their dipole strength originates from the B band, thus turning their orientation into the direction of the B transition dipole.

However, the two lowest energetic Q bands are enhanced by only about 40% compared to their monomer dipole strength, and the angle between the two corresponding monomer transition dipoles is quite large. For this reason, intensity transfer from the red-shifted aggregate B band is obviously not sufficient to fully explain the parallelization of all aggregate Q bands. Most likely, an intensity transfer takes place also between the several aggregate Q bands, resulting in a stronger mixing of the monomer Q and B transition dipoles. A more detailed quantitative analysis of the aggregate absorption spectrum of **1** is under way.

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**Supporting Information Available:** Supporting information is available for how to obtain the graphs shown in Figure 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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