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A multimer model for P680, the primary electron donor of photosystem II

(excitons/disorder/reaction center)

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ABSTRACT **We consider a model of the photosystem II (PS II) reaction center in which its spectral properties result from weak (≈100 cm^{-1}) excitonic interactions between the majority of reaction center chlorins. Such a model is consistent with a structure similar to that of the reaction center of purple bacteria but with a reduced coupling of the chlorophyll special pair. We find that this model is consistent with many experimental studies of PS II. The similarity in magnitude of the exciton coupling and energetic disorder in PS II results in the exciton states being structurally highly heterogeneous. This model suggests that P680, the primary electron donor of PS II, should not be considered a dimer but a multimer of several weakly coupled pigments, including the pheophytin electron acceptor. We thus conclude that even if the reaction center of PS II is structurally similar to that of purple bacteria, its spectroscopy and primary photochemistry may be very different.**

The primary processes of photosynthesis involve the absorption of solar energy by an array of light-harvesting pigments, typically chlorophyll, embedded in pigment–protein complexes within a lipid membrane. The resulting chlorophyll excited state is rapidly transferred to a primary electron donor species within a photosynthetic reaction center, where the energy is trapped by a sequence of electron transfer reactions (1). The close proximity of the chlorophylls within the pigment–protein complexes gives rise to dipole–dipole coupling between the pigments. This coupling is responsible for Förster energy transfer between the chlorophylls and may also result in energetic shifts and delocalization of the excited states (exciton interactions) (1). Exciton interactions are important for photosynthetic function in, for example, defining the precursor state to the initial charge separation reaction (2) and are also important in many nonbiological supramolecular systems (3). Moreover, as exciton interactions can strongly influence the properties of optical transitions monitored in many studies of photosynthetic complexes, their consideration can be essential in the interpretation of experimental results.

In this paper we consider the importance of exciton interactions within the photosystem two (PS II) reaction center. The initial charge separation reaction in PS II results in oxidation of the primary electron donor, a chlorophyll species referred to as P680 (due to a characteristic bleaching observed at 680 nm upon oxidation of this species) and reduction of a pheophytin molecule. This electron transfer reaction is of particular interest as the resulting species $P680^+$ is thought to be the most oxidizing species found in living organisms, with a potential of +1.1 eV (compare with 0.4–0.5 eV for the primary electron donors of other photosynthetic reaction centers). This high oxidizing potential is essential to PS II's ability to extract electrons from water, thereby releasing molecular oxygen and generating our oxygenic atmosphere.

There appear to be extensive similarities between the PS II reaction center and the reaction center of the photosynthetic purple bacteria. Therefore the structure of the purple bacterial reaction center, determined by x-ray crystallography (4) (see Fig. 1), has been widely used as a model for PS II (5–7). Some aspects of this structural model of PS II have been experimentally confirmed, such as the residues that bind the pheophytin electron acceptor (ref. 8 and references therein). Other aspects of the structural model remain poorly defined, and indeed there must be some differences in order to generate the high oxidizing potential of $P680^+$ (9).

The PS II reaction center exhibits a much greater degree of spectral overlap than the bacterial reaction center, particularly for the functionally important S_0–S_1 (Q_y) transitions. In purple bacteria, about half of the splitting of these transitions is attributed to excitonic interactions between the special pair bacteriochlorophylls (P_L and P_M) (2), which constitute the bacterial primary electron donor (P870/P960). This coupling ($V \approx 550$ cm^{-1} for P870 and 950 cm^{-1} for P960) results in a red-shifted special pair excited state, which is an energetic trap for excited states within the isolated reaction center. In contrast, in PS II, P680 exhibits only a small red shift relative to the other reaction center pigments and is therefore only a weak trap for excitation energy. Indeed after optical excitation of P680 in isolated PS II reaction centers, excitation energy rapidly equilibrates between the majority of reaction center singlet excited states, and primary charge separation proceeds from this equilibrated state (1, 10).

Studies of the PS II reaction center have resolved some, albeit relatively weak, exciton coupling between pigments. Evidence for such interactions has been obtained from the circular dichroism spectrum (11–13) and from absorption changes caused by formation of the P680 triplet state (14–16) or the P680 excited singlet state (10). Exciton transitions have been resolved at ≈680 nm and ≈667 nm, with the 680-nm band carrying a much greater oscillator strength (10, 12, 15, 16). The splitting of these transitions indicates a maximum coupling strength of $V \approx 140$ cm^{-1}, which is 3–4 times less than the coupling of the bacterial special pair. These observations have been interpreted in terms of P680 being a weakly coupled special pair of chlorophylls (12–14). However, such special pair models of P680 are complicated by the observation that the triplet state of P680 appears to be localized upon a single chlorophyll with an orientation similar to one of the monomeric bacteriochlorophylls (B_L and B_M) in the bacterial reaction center (17, 18). This has led to suggestions that P680 should be considered structurally analogous to B_L, with weak exciton coupling to its structural neighbors (18) or that P680

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Abbreviations: PS II, photosystem II; P680, primary electron donor of PS II; Ch*n*, chlorophyll *n*; Ph*n*, pheophytin *n*.

is an asymmetric special pair with one chlorophyll of the dimer orientated at a similar angle to B_L (9, 19).

The models of P680 discussed above have principally considered exciton coupling within a chlorophyll special pair but have not considered the effect of exciton interactions between the other reaction center chlorins. The possibility that these interactions may be important has, however, previously been suggested by Tetenkin *et al.* (11). Moreover, it has recently been pointed out by one of us (20) that if the structural arrangement of the chlorins is maintained between PS II and purple bacteria, then the dipole–dipole coupling between "monomeric" accessory chlorophylls (e.g., B_L/Ch1) and the adjacent pheophytin (H_L/Ph1) and special pair pigments (P_M/Ch2) are of the order of 100 cm^{-1} (see Fig. 1, discussed in detail below; Ch1 and Ch2 are chlorophylls 1 and 2; Ph1 is pheophytin 1). These couplings are of similar magnitude to the coupling strengths experimentally observed for P680. Therefore it may be essential to include them in models of the exciton interactions within the PS II reaction center (20).

In this paper, we develop a model of the excited singlet states of the PS II reaction center in which we take into account all of the dipole couplings between the pigments and the effect of transition energy disorder (inhomogeneous disorder). The inclusion of disorder in our calculations is important since the coupling strength and disorder are of similar magnitude. We conclude that P680 should be considered a "multimer" of several weakly coupled pigments whose excited states may be rather heterogeneous. We present a theoretical description of this multimer model of P680 and consider the extent to which such a model is in agreement with experimental observations.

THEORETICAL METHODS

The theoretical analysis used in this paper is based upon a description of Frenkel excitons as applied by Fidder *et al.* (21) to calculate the properties of molecular (J-) aggregates. Each reaction center chlorin is treated as a point dipole, and only one excited state is considered. Charge transfer states, simultaneous excitation of more than one reaction center chlorin, and electron–phonon coupling are neglected. Within these assumptions, the electronic exciton states of the reaction center can be described by a Hamiltonian:

$$H = \sum_n (\langle \varepsilon_n \rangle + d_n)|n\rangle\langle n| + \sum_{n,m,\, n\neq m} \sum V_{nm}|m\rangle\langle n|. \quad [1]$$

Here $|n\rangle$ denotes the state in which chlorin n is excited, and the summations are over all reaction center chlorins. $\langle \varepsilon_n \rangle$ is the average monomer transition energy of the chlorin n, and d_n is the (static) inhomogeneous offset energy of this chlorin, reflecting the effect of disorder imposed by the surrounding protein environment (diagonal disorder). In practice, the d_n may be considered as random variables taken from a Gaussian probability distribution with full width at half-maximum Γ_{inh}. V_{nm} is the dipole–dipole coupling between chlorins determined using the point dipole approximation (1), following Knapp *et al.* (2), who found the point dipole and extended dipole models yielded similar interaction energies for the *Rhodopseudomonas viridis* reaction center.

For a particular realization of the disorder, the exciton eigenstates are found by diagonalizing the matrix H_{nm}. Then the ith eigenvalue E_i gives the energy of the ith exciton state $|\psi_i\rangle$, whereas the normalized ith eigenvector $\mathbf{a}_i = (a_{i1}, ..., a_{i6})$ specifies the amplitude of each pigment's contribution to each exciton state:

$$|\psi_i\rangle = \sum_n a_{in}|n\rangle. \quad [2]$$

The optical properties of a particular reaction center can be readily calculated from these eigenvalues and eigenvectors (2, 21). Comparison of this model with experiment requires ensemble averaging to calculate the optical properties that a sample might exhibit. Further details of this numerical approach, in which the disorder is randomly generated according to the Gaussian probability distribution, are given by Fidder *et al.* (21).

Following Fidder *et al.* (21), we define the spatial extent (delocalization) of these exciton states $N_{del} = 1/\Sigma_n (a_{in})^4$. Using this definition, $N_{del} = 1$ for monomer, 2 for a undisordered, symmetric dimer, 3 for a trimer, etc.

RESULTS AND DISCUSSION

Exciton Calculations. The exciton calculations presented in this paper are based upon the structure of the reaction center of the purple bacterium *R. viridis* (4) but using chlorophyll a/pheophytin a dipole strengths (see Fig. 1). The coupling strengths shown in Fig. 1 are of similar magnitude to those observed experimentally for P680 ($\leq$140 cm^{-1}) (11–13, 15), with the exception of the 418-cm^{-1} coupling between Ch2 and Ch3, corresponding to the bacterial special pair. Several structural modifications have been proposed previously to reduce the coupling between Ch2 and Ch3, including increasing their separation (12), rotation of either Ch2 or Ch3 (19), or deletion of Ch3 (9, 20). Because the main conclusions presented in this paper were found to be largely independent of which modification was used, results are presented here for only one modification, an increased separation of Ch2 and Ch3.

The reaction center model shown in Fig. 1 includes only four chlorophyll molecules, whereas the most widely studied isolated PS II reaction center preparations bind at least six chlorophyll molecules per two pheophytin molecules. However, it appears that these two additional chlorophyll molecules are only very weakly coupled ($V \approx$ 5–10 cm^{-1}) to the other reaction center pigments, as demonstrated by slow (10–50 ps) energy transfer from these pigments to P680 (ref. 22 and references therein), and they are most probably bound on the exterior of the PS II reaction center (6). These "peripheral" pigments, which have absorption maxima near 670 nm (ref. 22

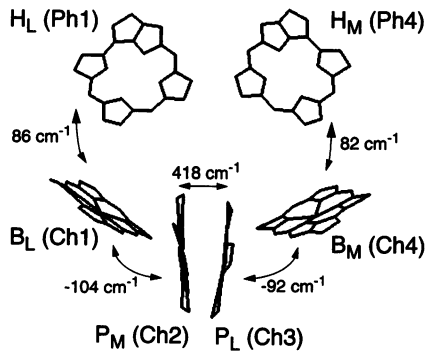

FIG. 1. Structural arrangement of the pigments in the reaction center of the *R. viridis*. This figure also shows the magnitudes of the strongest dipolar couplings between the pigments after substitution of chlorophyll a and pheophytin a for bacteriochlorophyll b and bacteriopheophytin b (the maximum coupling experimentally observed for P680 is $\approx$140 cm^{-1}). Dipole strengths of 23 and 14 debye^2 were used for chlorophyll a and pheophytin a, respectively (5) (compare with 51 debye^2 for bacteriochlorophyll b). This model is used in the exciton calculations for the PS II reaction center presented in the text, with the addition of a small structural modification to reduce the coupling between Ch2 and Ch3. However, the key conclusions of these calculations are found to be insensitive to the details of the structural model used.

Table 1. Exciton interaction energies (cm^{-1}) V_{nm} for a model of the PS II reaction center based on the *R. viridis* structure but with the separation of Ch2 and Ch3 increased by 2.8 Å along their connecting axis

	Ph1	Ch1	Ch2	Ch3	Ch4	Ph4
Ph1	$\langle\varepsilon_1\rangle + d_1$	86.3	17.3	−1.2	−5.7	2.7
Ch1		$\langle\varepsilon_2\rangle + d_2$	−101	−42.7	15.8	−5.5
Ch2			$\langle\varepsilon_3\rangle + d_3$	120	−37.9	−1.7
Ch3				$\langle\varepsilon_4\rangle + d_4$	−90.2	17.2
Ch4					$\langle\varepsilon_5\rangle + d_5$	82.3
Ph4						$\langle\varepsilon_6\rangle + d_6$

Diagonal elements are the monomer transition energies, where $\langle\varepsilon_n\rangle$ = 14,860 cm^{-1}.

and references therein), are therefore not included in the exciton calculations presented in this paper.

Table 1 gives the calculated dipole coupling strengths for the structural model of the PS II reaction center where the separation of Ch2 and Ch3 has been increased by 2.8 Å. Results of exciton calculations for this model are shown in Figs. 2 and 3. In these calculations, the transition energies $\langle\varepsilon_n\rangle$ of all six pigments were assumed to be at 14,860 cm^{-1} (673 nm), although we show below that this assumption is not critical. The calculations used Γ_{inh} = 210 cm^{-1}, based upon experimental observations of inhomogeneous broadening (full width at half-maximum ≈ 120 cm^{-1}) at low temperature and assuming an exciton exchange narrowing of $\sqrt{N_{del}}$ (see below) (23). However we show below that our results are also rather insensitive to the value of Γ_{inh} used.

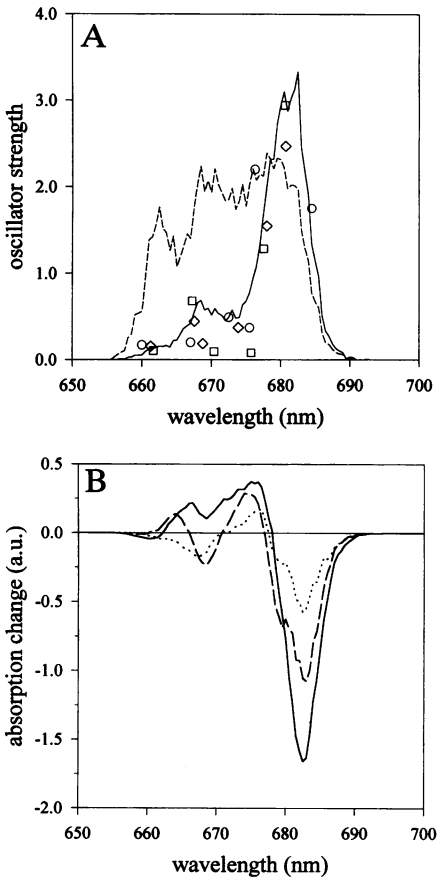

FIG. 2. (*A*) Plot of oscillator strength (in units of $|\mu_{Ch1}|^2$) against wavelength for the exciton states calculated for three individual PS II reaction centers (◇, □, ○) with different values of the energetic disorder (d_n) taken from a Gaussian distribution with standard deviation Γ_{inh} = 210 cm^{-1}. Other details are as in Table 1. Also shown are the absorption spectrum (—) and density of exciton states (– – – –) generated by an ensemble average over 2000 reaction centers, with a 0.5-nm spectral resolution. (*B*) The change in reaction center absorption resulting from deletion of one chlorin: Ch2 (—), Ch1 (– – – –), or Ph1 (·····). This simulates the presence of a localized excitation (cation, anion, or triplet state) upon these pigments, neglecting excited state absorption and electrochromic shifts. a.u., arbitrary units.

Fig. 2*A* shows the results of ensemble averaging over 2000 reaction centers. It is apparent that while the density of states is relatively broad and symmetrically distributed around 673 nm (the monomer transition wavelength), the reaction center absorption spectrum is dominated by the absorption from high oscillator strength states near 680 nm. Also shown are the results from the three individual reaction centers with different inhomogeneous shifts, d_n.

Fig. 2*B* shows the predicted change in reaction center absorption resulting from formation of a localized excited state (e.g., triplet, cation, or anion) upon either Ph1, Ch1, or Ch2 (this simulation neglects excited state absorption and electrochromic shifts). In all three cases, the absorption difference spectrum is dominated by a bleaching at 680 nm, consistent with experimental observations that formation of *any* PS II reaction center chlorin cation, triplet, or anion state (or singlet oxygen-induced photobleaching) results in an absorption bleach at 680 nm (except for bleaching of the peripheral 670 nm absorbing chlorophylls).

In Fig. 2*A* it can be seen that the lowest energy exciton state lies near 680 nm and carries the oscillator strength of two to three chlorophyll molecules. Fig. 3 shows how for the three individual particles of Fig. 2*A*, these three lowest energy states are distributed over the reaction center chlorins. Several chlorins contribute to each of these optical (exciton) transitions (N_{del} ≈ 3). However, the different realizations of the disorder for each reaction center results in the three states being delocalized over different chlorins: in other words, these three states, while exhibiting similar absorption maxima and oscillator strengths, are spatially heterogeneous.

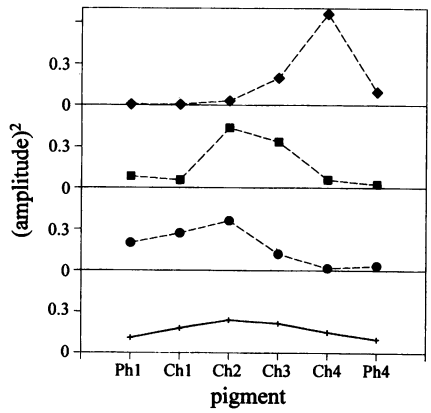

FIG. 3. Site populations $|a_{in}|^2$ of the wavefunctions $|\psi_i\rangle$ corresponding to the three lowest energy states selected from (Fig. 2*A*) (◆, ■, ●), illustrating the delocalization of these exciton states over several reaction center chlorins. Also shown (solid line) is the result of ensemble averaging over 2000 reaction centers. Other details are as in Fig. 2.

Exciton Delocalization and Energetic Disorder. The delocalization of the exciton states is driven by dipolar coupling. Our calculations indicate that this delocalization can be limited by heterogeneity in the monomer transition energies (diagonal disorder). This heterogeneity may result from site-specific shifts (due to specific pigment–protein interactions) or random disorder (inhomogeneous broadening). The width of the PS II reaction center Q_y absorption band indicates that site-specific shifts can be no more than ± 130 cm^{-1}. Our numerical simulations indicate that while such site-specific shifts will have some effect on the details of the exciton states, they are insufficient to alter the overall conclusions. Similarly, calculations for a range of values of the magnitude of the inhomogeneous disorder indicate that for all reasonable values of the disorder, significant delocalization is observed. This is illustrated in Fig. 4, which shows a plot of the mean delocalization (N_{del}) of the exciton states as a function of Γ_{inh}. It can be seen that some delocalization of the exciton states is predicted even for values of Γ_{inh} several times greater than the experimentally observed value for the inhomogeneous line width.

The exciton model used in this paper neglects electron–phonon coupling. It also assumes that the disorder is static and is therefore strictly only valid at low temperatures. However, the center of gravity of the PS II reaction center's absorption bands appears to be rather insensitive to temperature, suggesting that this model may also be applicable at room temperature. This would be consistent with recent studies of photosynthetic complexes, which have indicated that static inhomogeneous broadening is the dominant contribution to the observed spectral dynamics at room temperature (ref. 24 and references therein).

It is interesting to note that exciton theory predicts a greater delocalization of the exciton states in PS II reaction centers than in the bacterial reaction center, despite the reduced strength of the coupling in PS II. This results from the much greater spectral overlap in PS II. In the bacterial reaction center, spectral (and therefore energetic) degeneracy is broken both by the strong coupling within the special pair and by site-specific shifts of the bacteriochlorophyll and bacteriopheophytin monomer transition frequencies (2), which result in localization of the lowest energy exciton state upon the special pair.

The Multimer Model of P680: Comparison with Experiment. The calculations presented in this paper suggest that the excited singlet states of the PS II reaction center chlorins should be described by a multimer model. The term multimer is used to indicate that dipolar couplings produce exciton transitions that are delocalized over several, but not necessarily all, reaction center chlorins. In addition, the comparable magnitudes of the coupling strengths and the inhomogeneous disorder, with no two pigments being particularly strongly coupled, result in spatially heterogeneous exciton states.

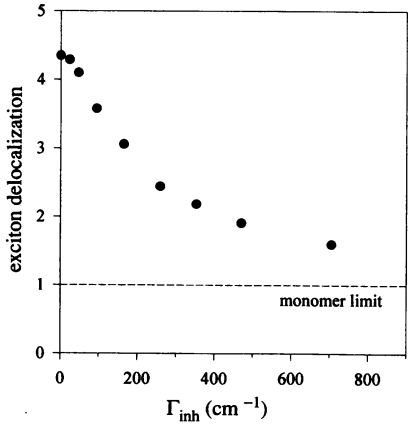

FIG. 4. Plot of the mean delocalization (N_{del}) of the reaction center exciton states as a function of the magnitude of the transition energy disorder Γ_{inh} (inhomogeneous disorder). The inhomogeneous linewidth of P680 has been determined at 4 K to be ≈ 120 cm^{-1} (17, 18) although this may be up to a 2-fold underestimate of underlying disorder due to exciton exchange narrowing (23). Other details are as in Fig. 2.

Our calculations demonstrate that this multimer model is in good agreement with experimental observations, including the presence of exciton transitions near 680 nm and 665 nm, with the lower energy transitions carrying the majority of the oscillator strength. Additional calculations (not shown) indicate that the transition dipoles for the 680/665-nm exciton transitions are approximately orthogonal, which is also in agreement with experimental observations (17). Moreover our model suggests that P680 is likely to be spectrally heterogeneous, again consistent with experimental observations (13, 15, 17, 25). The low amplitude of the 670-nm shoulder in the calculated spectrum is due, at least in part, to exclusion of the peripheral weakly coupled chlorophylls from our calculations.

The inclusion of pheophytin in the P680 multimer is supported by the observation that reduction of the photoactive pheophytin results in a significant decrease in the reaction center circular dichroism spectrum (11), indicating that this pigment is excitonically coupled to other reaction center chlorins. This conclusion is also supported by the observation of a large bleaching of the pheophytin Q_x absorption band observed directly (within 300 fs) after 694 nm excitation of isolated PS II reaction centers (26). In addition our model is readily reconciled with localization of the P680 triplet state upon a chlorophyll structurally equivalent to B_L (i.e., Chl), as has been experimentally observed (17, 18), as in this multimer model "P680" effectively includes this chlorophyll.

For "special pair" models of P680 to be meaningful, the dipole coupling between the special pair chlorins must be much greater than the dipole coupling to the other reaction center chlorins. The special pair coupling in PS II has been experimentally shown to be ≤ 140 cm^{-1} (12, 15, 16). Thus all the other dipole couplings would have to be $\ll 140$ cm^{-1} (e.g., ≤ 20 cm^{-1}). Such weak coupling strengths are clearly inconsistent with a structural model of PS II based upon the bacterial reaction center. In addition such weak coupling strengths would be inconsistent with the experimental observation that excitation energy equilibrates between the majority of reaction center pigments in ≈ 100 fs (10).

Our prediction of exciton states delocalized over several reaction center pigments is not strongly dependent upon the structure used. Indeed, any PS II reaction center structure in which several chlorins with overlapping Q_y optical transitions are placed in sufficient proximity to give rapid charge separation and 100-fs energy transfer would be likely to produce a similar conclusion. Therefore while our calculations indicate that experimental observations of PS II are consistent with a purple bacterial reaction center structure modified only in the region of the special pair, other arrangements of the pigments in PS II are possible, which would also be consistent with our model.

P680. The 870/960 nm transitions of the bacteriochlorophyll a/b primary electron donors are delocalized only over the special pair bacteriochlorophylls, as are the corresponding triplet and cation states. There is therefore no ambiguity in using the terms P870 and P960 to refer both to an optical transition and a structural component of the reaction center. The results presented in this paper suggest that term P680 should be used with considerably more caution.

The P680 triplet state, and most probably the P680 cation state, are localized upon single reaction center chlorophylls (14, 15) (it is, however, possible that these states are localized upon different chlorophylls). We suggest in this paper that the Q_y optical transitions of the reaction center are delocalized

over several pigments, and therefore the spectroscopy of P680 can only be understood by considering the optical properties of the reaction center as a whole. In particular, our model suggests that PS II's primary electron donor and acceptor share common ground-state transitions, and it is therefore not surprising that a bleach at 680 nm is caused by either donor oxidation or acceptor reduction. Finally it should be pointed out that as the precursor state to primary charge separation may be delocalized over both the primary electron donor and acceptor, it is possible that the charge separation process in PS II should be described not as a conventional intermolecular electron transfer reaction but as a charge transfer reaction within a supramolecular complex.

We conclude by considering possible biological functions of the reduced exciton coupling observed for P680 relative to P870/P960. Chlorophyll monomer cations are more oxidizing than dimer cations, and the reduced dipolar coupling may be a side effect of the requirement for a localized P680 cation. The reduced coupling results in P680 being only a shallow trap for excitation energy, thereby slowing down the trapping of excitation energy from the antenna chlorophylls, would facilitate the regulation of energy transfer to the reaction center achieved by the turning on of quenching pathways in the antenna (q_E quenching) under stress conditions. Finally the high redox potential of $P680^+$ requires the trapping of a greater proportion of the incident photon energy, which might preclude a larger free energy difference between the singlet excited states of P680 and antenna chlorophylls.

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