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Competition between charge transfer via superexchange and thermally activated energy transfer in porphyrinheterodimer– quinone systems $\stackrel{\Rightarrow}{}$

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Abstract

Electron transfer is observed in semi-rigid heterodimers of free base and zinc porphyrin covalently linked to the electron acceptor p-benzoquinone (Q). The rate of transfer critically depends on the relative spatial arrangement of the zinc and free-base porphyrin unit with respect to Q and varies up to two orders of magnitude in time. Complexation of the zinc porphyrin subunit with pyridine influences the energetics and transfer dynamics of the system. Excitation energy transport among the porphyrin subunits controls the efficiency of electron transfer to a large extent. Temperature-dependent measurements reveal the superposition of two processes, one of which is interpreted as superexchange mediated electron transfer. Electronic coupling elements for such a process are estimated from the analysis of the temperature dependence of electron transfer rates.

1. Introduction

Although electron transfer processes have been studied intensively [1], there are still several unsolved problems. One of these is the question of what the relevant mechanism for the very fast first step in charge separation in the photosynthetic reaction centre (RC) is. There is an ongoing debate, as to whether electron transport is sequential for all steps, i.e. following the shortest pathway along the donor/acceptor array or whether so-called spectator states mediate the process via superexchange without participating in the transfer directly [2–5]. Despite the fact that recent publications provide evidence for a sequential transfer in modified RCs of *Rhodobacter sphaeroides* at room temperature [6] it cannot be excluded that the superexchange mechanism may play a role at lower temperatures or in different kinds of RCs. Theoretical investigations still allow for this possibility [7,8]. Such effects are important for a large variety of other systems such as quantum well structures and interfaces [9], in which long-range electron transfer on the basis of superexchange or tunnelling occurs.

Besides investigating the electron transfer steps in photoreaction centres directly, model systems are valuable tools for elucidating details of sequential electron transfer, because they allow for systematic variations of distances, optical excitation energies and redox potentials [10]. One demand in designing

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such model systems is that geometric constraints are as rigid as possible. This has been realised recently for several model systems [11-15]. Another demand is that for mimicking photosynthetic reaction centres, model chromophores should be closely related to chlorophylls with respect to their electronic properties. For this reason a large variety of covalently linked porphyrin systems have been synthesised [10]. In most cases the porphyrins are electron donors while covalently linked quinones act as electron acceptors in analogy to the chlorophyll donor and quinone acceptors in photosynthetic RCs.

In order to investigate the role of superexchange in electron transfer, model systems containing at least three components are necessary: a donor, an acceptor and a mediator molecule. In this kind of porphyrin-quinone compound Rodrigues et al. [11] and Osuka et al. [12,13] have reported long range electron transfer which they explain by a superexchange mechanism. This explanation is based on the fact that the excited state of a free base porphyrin (distal) exhibits a significant reduction in lifetime, when it is linked to the electron acceptor quinone by a second porphyrin subunit (proximal), compared to the linkage with a non-porphyrin spacer with the same distance. This reduction was found to be roughly the same at room temperature and at 77 K. However, the authors do not present a complete temperature dependence of the electron transfer rates, which would allow for the determination of activation energies and electronic coupling elements.

Previously we reported the competition between excitation energy and electron transfer in tetraphenyl porphyrin (homo)dimers semi-rigidly linked to a benzoguinone molecule [16–18]. In this Letter we will extend the investigation to electron transfer in triads, in which porphyrin heterodimers are covalently linked to Q. The two donor chromophores, namely free base porphyrin (H₂P) and Zn- porphyrin (ZnP), can be placed at two different positions with respect to the electron acceptor benzoquinone (Q) (Fig. 1). These triad systems are similar to those of Rodriguez and Osaka. Therefore, they may be expected to show superexchange-mediated electron transfer as well. We will show that the temperature dependent fluorescence lifetimes can be used to discriminate between different pathways for electron or energy transfer.

2. Experimental

The picosecond excitation and fluorescence detection system has been described in detail elsewhere [16,17]. The overall time response of the spectrometer is 50 ps. This time response is taken into account by deconvolution techniques.

 $ZnP-H_{2}P^{Q}$ and $H_{2}P-ZnP^{Q}$ were synthesized by a modification of the procedure of Adler et al. [19]. Pyrrole (13.4 g), benzaldehyde (12.85 g), terephthalaldehyde (2.68 g) and 4-hydroxybenzaldehyde (4.88 g) were refluxed in 500 ml toluene and 100 ml propionic acid. A roughly cleaned mixture of the monohydroxyphenyl substituted substances H₂P-H₂P^POH and H₂P-H₂P-POH was obtained after several processes of washing and flash chromatography, during which most of the monomeric compounds and polyhydroxyphenyl substituted compounds were removed. After repeating this reaction several times, 227 mg of this mixture were obtained (vield 0.7%). Separation by MPLC (with chloroform on slightly deactivated silica gel) yielded two fractions A and B of 80 and 40 mg, respectively. The ratio of products is in accordance



Fig. 1. Structure of homo- and heterodimeric porphyrin-quinone compounds and the equivalent precursors.

with statistical considerations that the amount of $H_2P-H_2P^{POH}$ should be twice that of $H_2P H_2P$ -POH. The assignment of fraction A to H_2P -H₂P^{POH} was confirmed by NMR and mass spectroscopy. The benzoquinone adduct of this fraction was prepared following the method described by Maruyama et al. [20], i.e. a solution of 20 mg $H_2P-H_2P^POH$ and 106 mg of *p*-benzoquinone in 70 ml benzene and 7 ml acetonitrile over 600 mg of Na₂CO₃ was illuminated by a Hg-lamp for 24 h. By column chromatography the remaining adducts could be removed to yield $H_2P-H_2P^Q$ (41%). Metallation of this compound was carried out dissolving it in CH₂Cl₂ and careful addition of zinc acetate dissolved in THF. Immediately following this thin layer chromatography (on silica gel with chloroform) led to four different fractions, the first and last of which could be easily assigned to $H_2P-H_2P^{Q}$ ($R_f = 0.72$) and $ZnP-ZnP^{Q}$ ($R_f = 0.30$) while the two fractions in between, which were close, were assigned to the heterodimer systems. The assignment of these two fractions a $(R_f = 0.55)$ and b $(R_f = 0.51)$ to ZnP- H_2P^Q and H_2P-ZnP^Q , respectively, was made on the basis of their different fluorescent behaviour, as will be discussed in the following.

Samples were diluted to concentrations of less than 10^{-5} M in spectroscopic grade solvents and were used immediately after thin layer chromatography in a 10 mm rectangular quartz cell.

3. Results

The absorption spectrum of the porphyrin heterodimer H_2P -ZnP is shown in Fig. 2 in comparison with the spectrum of an equimolar mixture of ZnP and H_2P monomers. The heterodimer spectrum shows the well known splitting of Soret bands (550 cm⁻¹) caused by excitonic coupling between the monomeric subunits. The Q-bands are nearly a superposition of the spectra of the ZnP and H_2P monomers. They do not show a splitting, which is well explained by the fact, that the absorption and thus the square of the transition dipole moment of the Q-bands is approximately 20 times smaller than those of the Soret bands. This causes a reduction of the excitonic coupling by the same factor which is beyond the spectral resolution. For both compounds



Fig. 2. Absorption spectra of an equimolar mixture of H_2P and ZnP monomers (_____) and the heterodimer H_2P -ZnP-Q (- - -).

a and b the spectrum is almost unchanged when Q is covalently linked to the porphyrin-dimer (apart from an additional absorption at 250 nm [16]). Spectral shifts are at most in the range of 2 nm.

It is well known, that a red-shift in the absorption of ZnP is observed when it is complexed at the central Zn atom with suitable ligands such as pyridine or dioxane. In this way the energy gap between excited states such as H_2P^* -ZnP^Q and H_2P -ZnP * ^Q can be varied to investigate its influence on the energy or electron transfer properties of the triad.

Contrary to the absorption spectra the fluorescence emission spectra of the heteroporphyrin systems are not simply the sum of the emission spectra of the subunits. In both compounds a and b the ZnP component is strongly quenched. We have already shown [17] that in the case of the quinone free system $(ZnP-H_2P)$ this is due to fast energy transfer from ZnP to H₂P. The timescale of this transfer is beyond the time resolution of our spectrometer (< 10ps) and much faster, than any electron transfer step so far observed in this kind of system [16,18,21]. In compound a, the H₂P fluorescence is also substantially quenched as compared to compound b under the same conditions of excitation. This unambiguously shows that compound a is $ZnP-H_2P^Q$, as in this case the H₂P fluorescence will be quenched by efficient electron transfer to Q as in monomeric $H_{2}P-Q$ [16]. On the contrary, for $H_{2}P-ZnP^{2}Q$ (compound b), H_2P is not in close contact with Q and expected to show the intrinsic quantum yield of $H_{2}P.$



Fig. 3. H_2P fluorescence decay curves in CH_2CI_2 for H_2P-H_2P (a); $H_2P-ZnP-Q$ (b); $H_2P-ZnP-Q$ complexed with pyridine (c) and $ZnP-H_2P-Q$ (d).

Time resolved experiments have been performed with an excitation wavelength of 550 nm. Both subunits (H₂P and ZnP) absorb at this wavelength. The fluorescence was detected on the H_2P band at 720 nm (where the ZnP fluorescence is almost zero). Fig. 3 shows a comparison of the fluorescence decay for various heterodimers in the solvent CH₂Cl₂, along with that of the free base homodimer. The decay times vary by about a factor of 50 among each other. The slowest decay time is observed for H₂P- H_2P and the fastest one for ZnP-H₂P^Q. H_2P -ZnP^Q shows an intermediate decay time which is strongly shortened upon complexation of the ZnP subunit with pyridine. No effect is observed when complexing ZnP-H₂P^Q. In all cases a small contribution (< 10%) of a long-lived component with a



Fig. 4. Temperature dependence of $k = \tau^{-1} - \tau_0^{-1}$ for H₂P-H₂P-Q (\Box) and H₂P-ZnP^Q (\bullet), where τ corresponds to the measured fluorescence lifetime and τ_0 to the fluorescence lifetime of hydroquinone substituted compounds. In the case of (\Box) only guidelines are shown, for (\bullet) (----) corresponds to a fit with two activation energies.

lifetime close to 8.5 ns is observed which corresponds to the lifetime of the intrinsic fluorescence decay of H_2P , which is known from independent experiments. Because the relative contribution of this long-lived component depends on the sample preparation procedure we assign it to spurious amounts of heterodimers, which lack the quinone substituent or are reduced to the non-electron accepting hydroquinone.

The main component of the fluorescence decay, however, could be fitted with a single decay time.

Table 1

Decay times τ (short component) of H₂P fluorescence in different molecules measured at 720 nm

Molecule	Solvent	τ (ns)	$k_{\rm ET} (10^8 {\rm s}^{-1})$	$\Delta E (eV)$	
H ₂ P–Q	MTHF	0.38 ± 0.04	25.0 ± 3.0		
	CH_2Cl_2	0.06 ± 0.01	170.0 ± 30		
	cyclo	2.3 ± 0.2	3.2 ± 0.5		
ZnP-H ₂ P^Q	MTHF	0.37 ± 0.04	26.0 ± 3.0	0.186	
	CH ₂ Cl ₂	0.06 ± 0.01	170.0 ± 30	0.200	
	cyclo	2.2 ± 0.2	3.4 ± 0.5	0.231	
ZnP-H ₂ P^Q + Pyr	CH ₂ Cl ₂	0.05 ± 0.01	200.0 ± 30	0.155	
$H_2P-ZnP^Q + Pyr$	CH ₂ Cl ₂	0.40 ± 0.04	24.0 ± 3	0.155	
	cyclo	1.0 ± 0.1	8.9 ± 1	0.171	
H ₂ P–ZnP^Q	MTHF	2.1 ± 0.2	3.6 ± 0.5	0.186	
	CH_2Cl_2	2.8 ± 0.3	2.3 ± 0.5	0.200	
	cyclo	8.3 ± 0.8	0.0 + 0.3	0.231	

The transfer rates k_{ET} are calculated according to $k_{\text{ET}} = \tau^{-1} - \tau_0^{-1}$ with τ_0 9.3 ± 1.0, 8.1 ± 0.8 and 8.7 ± 0.9 ns for H₂P-Q and with $\tau_0 = 8.9 \pm 0.9$, 7.8 ± 0.8 and 8.7 ± 0.9 ns for the porphyrin-dimer compounds in MTHF, CH₂Cl₂ and cyclohexane, respectively. (The τ_0 values were obtained for H₂P and H₂P-H₂P, respectively.) ΔE is the energy difference between the H₂P fluorescence maximum and the ZnP absorption maximum

The H_2P fluorescence decay times for H_2P-Q and the different heterodimers are collected in Table 1.

Electron or energy transfer rates for the various porphyrin heterodimer-quinone systems were obtained by correcting the monitored H_2P fluorescence decay rates by the independently measured H_2P fluorescence decay of H_2P-H_2P homodimers. This method is assumed to be correct within only 10% of the intrinsic fluorescence decay because quinone substitution may slightly change the intrinsic fluorescence lifetime as has been shown in the case of hydroquinone substitution [16,18].

Temperature dependent experiments have been carried out in MTHF for H_2P-ZnP^Q . In this case, a heterodimer substituted by hydroquinone (H_2P-ZnP^HQ) was available as a reference compound. The temperature dependent electron transfer rates are plotted in Fig. 4 together with data for $H_2P-H_2P^Q$ in a Marcus plot [22] versus 1/T.

4. Discussion

4.1. Routes of electron transfer

Porphyrin-quinone compounds are subject to electron transfer from the porphyrin to the quinone entity [1,10,16]. Recently, we have shown that for covalently linked free base porphyrin-quinone monomers and homodimers, electron transfer (ET) takes place on timescales between 50 to 300 ps depending on the solvent [16,18]. Identification of this process has been made on the basis of the strong dependence of the fluorescence lifetime on solvent polarity and temperature. Additional evidence is provided by the fact that when hydroquinone is used instead of quinone, no reduction of the fluorescence lifetime occurs because hydroquinone does not act as an electron acceptor due to the change in redoxpotential upon hydration [16,18].

In the case of the heterodimers where H_2P is proximal with respect to Q (ZnP-H₂P^Q), the observed transfer rates k_{ET} are almost identical to those in H₂P-Q. This is in accord with a model, in which the energy levels of ZnP^{*}-H₂P^Q, ZnP-H₂P^{*} ^Q and ZnP-H₂P⁺ ^Q⁻ are arranged in the form of a cascade. Either the first or the second of these states is excited by the laser pulse. In the case



The situation is completely different for H₂P-ZnP^Q. In this case, H_2P is separated from Q by ZnP. This leads to a considerably weaker electronic coupling between H_2P^* and Q and thus no electron transfer from H_2P^* to Q is expected. The energetic situation is depicted in Fig. 5. Following selective ZnP excitation $(H_2P-ZnP^* Q)$, the system may undergo either charge separation with a rate $k_{\text{FT}}^{\text{Zn}}$ to $H_2P-ZnP^+ \wedge Q^-$ (as in ZnP-Q) or energy transfer (k_{-}) to H_2P^* -ZnP^Q. As shown in Fig. 5, the population of H_2P^* which is monitored in the experiment, can decay via four different channels. These four possibilities are: (i) intrinsic fluorescence decay within about 8.5 ns, (ii) thermally activated back-energy transport to ZnP (with a rate constant k_{+}) followed by fast electron transfer to Q [16], (iii) and (iv) direct or sequential electron transfer from H₂P to Q.

Additionally, the influence of an excitonic coupling between the porphyrin subunits must be taken into account. With respect to electron transfer behaviour, such a coupling implies that the wavefunction of H_2P^* -ZnP^Q includes a certain admixture of H_2P -ZnP*^Q, which facilitates direct charge transfer from H_2P^* to Q. This admixture can be estimated using the well known formulae for excitonic coupling [23] and the static absorption spectra.





H₂P-ZnP^Q

The Soret band of the H₂P-ZnP heterodimer shows a splitting of 0.07 eV. As the Soret bands of the individual monomers are almost isoenergetic, this splitting is twice the coupling energy W_{12} . For the question under consideration, the lowest lying Qbands and the coupling between the corresponding states $|H_2P^*-ZnP^Q\rangle$ and $|H_2P-ZnP^*^Q\rangle$ are of interest. The absorption coefficient of these Q-bands is approximately 80 times lower than that of the Soret band and the coupling is reduced by the same amount because both the absorption coefficient and the excitonic coupling are proportional to the square of the transition moment. Additionally, the energy difference of 0.2 eV between states $|H_2P^*-ZnP^Q\rangle$ and $|H_2P-ZnP^* \land Q\rangle$ must be taken into account. This leads to a mixing angle $tan(\Theta) \approx 4 \times 10^{-3}$. $|H_2P-ZnP^* \land Q\rangle$ is admixed to $|H_2P^*-ZnP^{\land}Q\rangle$ with a factor of $\sin(\Theta/2)$. Since the coupling matrix element $\langle H_2 P - ZnP^* \land Q | H | H_2 P - ZnP^+ \land Q^- \rangle$ enters quadratically into k_{ET} , this admixture may result in a transfer rate, which is 4×10^{-6} times that of ZnP-Q. The latter is estimated to be at most 10^{12} s⁻¹ which leads to a transfer rate due to the coupling between $|H_2P^*-ZnP^Q\rangle$ and $|H_2P-ZnP^*^Q\rangle$ of 4×10^6 s^{-1} . Excitonic coupling can therefore be excluded as an explanation for the observed fluorescence decay of the H_2P^* subunit.

The influence of route (i) has already been taken into account when calculating $k_{\rm ET}$ from the observed decay time τ (see Table 1). Route (ii) will strongly depend on the difference of singlet excitation energies of ZnP* and H₂P*. This energy difference ΔE_1 was deduced from the maxima of the 0-0 bands of H₂P fluorescence and ZnP absorption, respectively. Values for ΔE_1 are also included in Table 1. The effect of ΔE_1 on $k_{\rm ET}$ will be discussed in the following section.

It is clearly evident from Table 1 that $k_{\rm ET}$ decreases with the increase in ΔE_1 which would be in accordance with route (ii). The temperature dependence of the decay rates should provide a good test of whether route (ii) is indeed the dominant path for the H₂P^{*} decay. In this case, an activation energy corresponding to the energy gap ΔE_1 (between H₂P^{*} and ZnP^{*}) would be expected. Inspecting Fig. 4, it becomes clear that the temperature dependence cannot be explained by one single activation energy. Therefore, we have analysed the experimental data

collected for the fluorescence decay of H_2P^* -ZnP^Q in MTHF as being due to a sum of two different processes with different activation energies. For temperatures above 250 K, the data follow an activation energy of 0.19 ± 0.03 eV which is close to $\Delta E_1 = 0.186$ eV and thus in excellent agreement with route (ii). However, at temperatures below 250 K k_{ET} has a much weaker *T*-dependence. In this range, the activation energy is only 0.02 ± 0.01 eV. This is a striking difference to data obtained with homodimers [18]. The depopulation of H_2P^* -ZnP^Q at low temperatures is even faster than in the homodimer H_2P - H_2P^Q !

The change in activation energy from a small value at low temperatures to a larger one at higher temperatures cannot be attributed to a crossover from the adiabatic to the non-adiabatic regime as was done for the homodimers [18]. In this case the opposite sequence of activation energies should be observed.

As route (ii) cannot describe the results over the whole temperature range, we must also consider routes (iii) and (iv). We will make use of the Marcus description for electron transfer. For the sequential transfer process (iv) the change in free energy ΔG_1 and the reorientation energy λ_1 for the first step $H_2P^*-ZnP^-Q \rightarrow H_2P^+-ZnP^--Q$ may be estimated to be +0.49 and 0.8 eV, respectively ¹. With these values for ΔG_1 and λ_1 , the exponential term $(\exp[-(\Delta G + \lambda)^2/(4\lambda kT)])$, which governs charge transfer according to classical Marcus theory, is (depending on temperature) between 6 and 15 orders of magnitude smaller than the one which governs energy transfer via route (ii). Therefore (iv) can be neglected and we are finally left with possibility (iii).

 $\Delta G(\epsilon) = \frac{e^2}{4\pi\epsilon_0} \left[\left(\frac{1}{2r_{\rm D}} + \frac{1}{2r_{\rm A}} - \frac{1}{r_{\rm DA}} \right) \frac{1}{\epsilon} - \left(\frac{1}{2r_{\rm D}} + \frac{1}{2r_{\rm A}} \right) \frac{1}{\epsilon'} \right] \\ [25,26]; E_{\rm D}^{\rm ox} - E_{\rm A}^{\rm red} = 2.44 \text{ eV} [11]; r_{\rm D} = r_{\rm A} = 5.5 \text{ Å and } r_{\rm DA} = 12.5 \text{ Å from space filling models; } \epsilon = \epsilon (\text{MTHF}) = 6.24 [27]; \\ \epsilon' = \epsilon (\text{CH}_2 \text{Cl}_2) = 9.08 [28]; \end{cases}$

$$\lambda = \lambda_i + \lambda_S; \ \lambda_S = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}} \right) \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_S} \right)$$
[25];

 $\epsilon_{\infty}(\text{MTHF}) = 2.0 \ [29]; \ \lambda_i = 0.3 \ \text{eV} \ [30].$

¹ The following formula and data have been used: $\Delta G = E_{\rm D}^{\rm ox} - E_{\rm A}^{\rm red} + \Delta G(\epsilon) - E_{\rm S}$, where D and A stand for the donor (H₂P) and the acceptor (ZnP), respectively;

4.2. Estimation of the superexchange contribution

Route (iii) corresponds to an ET over a quite long distance with no covalent link between the donor and acceptor molecules. It is therefore tempting to explain the present results in terms of superexchange models which have recently been applied [5,24]. These models assume that a 'spectator' state $|2\rangle$ mediates the electron transfer from a donor $|1\rangle$ to an acceptor $|3\rangle$ resulting in an effective transfer rate

$$k_{13} = \frac{2\pi}{\hbar (4\pi\lambda k_{\rm B}T)^{1/2}} \left(\frac{V_{12}V_{23}}{\delta E}\right)^2 \exp\left(\frac{-E_{\rm a}}{k_{\rm B}T}\right).$$
 (1)

In the present situation $|1\rangle$, $|2\rangle$ and $|3\rangle$ correspond to $H_2P^*-ZnP^{-}Q$, $H_2P^+-ZnP^- Q$ and $H_2P^+-ZnP^{-}Q^{-}$, respectively. V_{12} and V_{23} are the matrix elements for the processes $H_2P^*-ZnP^{-}Q \rightarrow H_2P^+-ZnP^{-}Q$ and $H_2P^+-ZnP^{-}Q \rightarrow H_2P^+-ZnP^{-}Q^{-}$, respectively, which are both unknown. The term

$$\delta E \approx \Delta G_1 + \lambda_1, \tag{2}$$

combines the free energy ΔG_1 and the reorientation energy λ_1 for the process $H_2P^* - ZnP^*Q \rightarrow H_2P^+ - ZnP^- Q$ [5]. E_a corresponds to

$$E_{a} = \frac{\left(\Delta G + \lambda\right)^{2}}{4\lambda} \tag{3}$$

for the overall process $H_2P^* - ZnP^{Q} \rightarrow H_2P^+ - ZnP^{Q}^-$. The most interesting term with respect to the superexchange mechanism, is $(V_{12}V_{23}/\delta E)^2$ which replaces V^2 in the ordinary Marcus equation.

Within this framework, we will now discuss the low temperature behaviour which cannot be attributed to route (ii) and is characterised by an activation energy of 0.02 ± 0.01 eV. In the case of superexchange the temperature dependence of process (iii) should yield an activation energy E_a according to Eq. (3). In order to get an impression of whether the experimentally determined activation energy is indeed in accordance with a superexchange model, we will first calculate λ according to Eq. (3), from the experimentally determined value of E_a and an estimation for $\Delta G = -0.64$ eV ². Following this procedure we obtain $\lambda = 0.9 \pm 0.2$ eV. This experimentally determined value for λ may be compared to the value which is calculated from the geometry of the molecule and from ϵ_{∞} and $\epsilon_{\rm S}$ of the solvent. With $r_{\rm A} = 3.2$ Å (as radius for Q) and the values for ϵ_{∞} , $\epsilon_{\rm S}$, $r_{\rm D}$, $d_{\rm PQ}$ and λ_i already used the reorganisation energy is 1.17 eV. Taking the crude assumptions underlying the formula for calculating λ into account, the agreement between the experimentally determined value of 0.9 ± 0.2 eV and the calculated one of 1.17 eV must be regarded as satisfying.

Extrapolating the low temperature behaviour of the transfer rate to $T^{-1} \rightarrow 0$, we can calculate $(V_{12}V_{23}/\delta E)$ from the intercept with the $\ln(k\sqrt{T})$ axis according to Eq. (1) to be 0.11 ± 0.05 meV (using $\lambda = 0.9 \pm 0.02$ eV). Taking this value, we would also like to make separate estimates for V_{12} and V_{23} . In the simplest molecular orbital approximation, the matrix element V_{23} (H₂P⁺ZnP⁻^Q \rightarrow $H_2P^+ZnP^-Q^-$ is the same as V (ZnP^{*}-Q \rightarrow ZnP^+-Q^-), which has been deduced from temperature dependent measurements of k_{ET} in ZnP-Q to be 2.2 meV [15]. Again using $\Delta G_1 = 0.49$ eV and $\lambda_1 \approx 0.8 \text{ eV}, \delta E$ becomes 1.29 eV. With these values for V_{23} and δE , we estimate V_{12} to be 65 meV. However, assuming realistic errors for δE and V_{23} to be of the order of ± 0.5 eV and ± 1 meV respectively, V_{12} may yield values between 15 and 240 meV.

As compared to theoretical calculations [32], the value for $V(ZnP^*-Q \rightarrow ZnP^+-Q^-)$ is quite reasonable, whereas 65 meV for V_{12} seems to be quite high at first sight. For the photosynthetic reaction centre (PRC) the equivalent matrix elements (between the primary donor bacteriochlorophyll-dimer and the bacteriochlorophyll-monomer) were calculated to be in the range of 2.4 to 12 meV [5]. However, as opposed to the PRC, the phenyl ring connecting the two constituents will be conjugated with the porphyrins in the case of the heterodimer which will result in a considerable increase in the V_{12} matrix element. Moreover, one must take into account the crude assumption $V_{23} = V$, which had to be made due to the lack of theoretical or experimental information. Indeed, this latter assumption is critical,

² ΔG was obtained using $E_{D}^{\text{ox}} - E_{A}^{\text{red}} = 1.42 \text{ eV}$ [31], $E_{S} = 1.90$ eV, $d_{PQ} = 14.4$ Å (the distance between H₂P and Q), and the value for ϵ_{S} already used.

because porphyrins with D_{4h} -symmetry have orbitally degenerate LUMOs which makes an a priori prediction difficult. The correct symmetry of the LUMOs of H₂P and ZnP, respectively, will be crucial for the calculation of V_{12} . However, a comparison with MO calculations [33] suggests that $V_{23} > V$, which will reduce V_{12} . Taking all these arguments into account, a value of 65 meV for V_{12} is within reasonable limits.

Now that we have finally determined the order of magnitude for V_{12} we can again examine whether it was justified to discard the first step in the sequential process of route (iv). As the adiabaticity parameter $\kappa = (4\pi V_{12}^2 \tau/\hbar \lambda)$ [34] is greater than 8 even for the lowest possible V_{12} values of about ≈ 15 meV, the transfer rate can be calculated in the adiabatic limit [34] according to

$$k = \sqrt{\frac{\lambda_1}{16\pi T k_{\rm B}}} \frac{1}{\tau} \exp\left(-\frac{\left(\Delta G_1 + \lambda_1\right)^2}{4\lambda_1 k T}\right), \qquad (4)$$

where τ is the longitudinal relaxation time of 1.5 ps (which was estimated from the rotational correlation time of THF of 5 ps [35] and $\tau_{\rm L} = \tau_{\rm D} \epsilon_{\infty} / \epsilon_{\rm S}$). According to Eq. (4) the electron transfer rate $k_{\rm ET}({\rm H}_2{\rm P}^*-{\rm Zn}{\rm P}^-{\rm Q} \rightarrow {\rm H}_2{\rm P}^+-{\rm Zn}{\rm P}^-{\rm Q})$ becomes 953 s⁻¹ at 300 K and even less at lower temperatures (i.e. five orders of magnitude smaller than the experimental value). Again this supports our initial conclusion, that route (iv) can be neglected.

5. Conclusions

In summary we have found that the quenching of the H_2P^* -ZnP^Q fluorescence is characterised by two different temperature regimes which may be attributed to two completely different processes. (i) At high temperatures thermally activated energy transfer from H_2P^* -ZnP^Q to H_2P -ZnP*^Q is followed by charge transfer resulting finally in H_2P -ZnP*^Q⁻. (ii) At low temperatures, a long-range (approximately 15 Å with no covalent link) electron transfer H_2P^* -ZnP^Q $\rightarrow H_2P^+$ -ZnP^Q⁻ occurs which can be reasonably modelled by a superexchange mechanism.

The dominance of a thermally activated energy transfer at high temperatures is in contrast to results obtained by Rodriguez et al. [11] and Osuka et al. [12,13] who found evidence for temperature independent superexchange mediated charge separation in similar systems. These differences may be caused by slightly different porphyrin-subunits. In the systems of Rodriguez and Osuka the phenyl group spacer is approximately perpendicular to the respective porphyrin planes due to steric hindrance while in our system the spacer is at an angle of about 55° with respect to the porphyrin planes [16]. This will result in an increased coupling between the porphyrin subunits due to better overlap of the π -systems of the porphyrins and the phenyl ring. Therefore energy transfer will be more efficient. Indeed, we observe an energy transfer rate $(ZnP^*-H_2P \rightarrow ZnP-H_2P^*)$ $\geq 2 \times 10^{11}$ s⁻¹ which is three times faster than the corresponding one reported by Osuka and Rodriguez $(5.9 \times 10^{10} \text{ s}^{-1}).$

Apart from discriminating between two deactivation processes via the analysis of temperature dependent electron transfer rates, temperature variation has proven to be useful in estimating some of the relevant parameters (V_{12} , λ) of a superexchange mechanism for electron transfer in supramolecular assemblies. One unexpected observation is that this mechanism makes electron transfer from H_2P^* to Q even more effective (at low temperatures) than the direct process in case of a H_2P-Q molecule, even though the transfer distance has been increased from 10.5 to 14.4 Å. This process may also be responsible for the fast depopulation of the excited H_2P in self-organised porphyrin-quinone systems, which was reported recently [21].

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