

Temperature Dependence of Electronic Coupling through Oligo-*p*-phenyleneethynylene Bridges

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Abstract: A series of donor-bridge-acceptor (D-B-A) systems with varying donor-acceptor distances has been studied with respect to the temperature dependence of the triplet excitation energy transfer (TEET) rates. The donor and acceptor, zinc(II) and free-base porphyrin, respectively, were separated by oligo-*p*-phenyleneethynylene (OPE) bridges, where the number of phenyleneethynylene groups was varied between two and five, giving rise to edge-to-edge separations ranging between 12.7 and 33.4 Å. The study was performed in 2-MTHF between room temperature and 80 K. It was found that the distance dependence was exponential, in line with the McConnell model, and the attenuation factor, β , was temperature dependent. The experimentally determined tem-

perature dependence of β was evaluated by using a previously derived model for the conformational dependence of the electronic coupling based on results from extensive quantum chemical, DFT and time-dependent DFT (TD-DFT), calculations. Two regimes in the temperature interval could be identified: one high-temperature, low-viscosity regime, and one low-temperature, high-viscosity regime. In the first regime, the temperature dependence of β was, according to the model, well described by a Boltzmann conformational distribution. In the latter, the molecu-

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lar motions that govern the electronic coupling are slowed down to the same order of magnitude as the TEET rates. This, in effect, leads to a distortion of the conformational distribution. In the high-temperature regime the model could reproduce the temperature dependence of β , and the extracted rotational barrier between two neighboring phenyl units of the bridge structure, $E_i = 1.1 \text{ kJ mol}^{-1}$, was in line with previous experimental and theoretical studies. After inclusion of parameters that take the viscosity of the medium into account, successful modeling of the experimentally observed temperature dependence of the distance dependence was achieved over the whole temperature interval.

Introduction

In recent years photoinduced energy and electron transfer (ET) have been extensively studied, with the potential development of molecular electronics,^[1–4] solar cells,^[5–9] and artificial photosynthesis^[10–16] as long-term goals. This has led to the design of many donor-bridge-acceptor (D-B-A) systems, which enable systematic investigations of how the transfer processes are mediated by the bridging chromophore. Triplet excitation energy transfer, TEET, and ET

processes are closely related, since they both involve electron exchange interactions, and much of what governs TEET also concerns ET processes.^[17–20] Thus, investigating TEET processes is expected to give valuable information about properties that also govern ET processes. ET is, in general, much more challenging to study experimentally, and the distance dependence of the electronic coupling is often obscured by the distance dependencies of the solvent reorganization energy and the driving force. TEET can be more convenient to study, since it often occurs on the nanosecond to millisecond timescale and the distance dependence of the reorganization energy is much weaker. It has previously been confirmed that various bridging units can mediate TEET and that varying the energy difference between the donor and bridge chromophores has a substantial effect on the mediation in accordance with the McConnell model ([Eq. (1)]).^[21–25] The donor-acceptor separation often has a large impact on the rates of electron exchange pro-

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cesses and this has motivated several studies of the distance dependence of TEET.^[26–28]

The distance dependence of the rate of bridge-mediated electron exchange processes are mainly governed by the electronic coupling, V_{DA} , between the states localized on the donor and acceptor, respectively. Many studies have therefore focused on developing theoretical methods for calculating the electronic coupling in D-B-A systems.^[17,29–37] The model most frequently used to evaluate the distance dependence of the electronic coupling found in experiments is the superexchange model developed by McConnell ([Eq. (1)].^[30]

$$V_{DA} = \frac{V_{DB}V_{BA}}{\Delta} \cdot \prod_i \left(\frac{v_i}{\Delta} \right) \quad (1)$$

Here V_{DB} and V_{BA} are the donor–bridge and bridge–acceptor electronic coupling, respectively, Δ is the energy difference between states localized on the donor and bridge units, and v_i is the electronic coupling between neighboring units within the bridge structure. If the bridge consists of a series of identical units this model predicts that the electronic coupling will decay exponentially with distance according to Equation (2).

$$V_{DA} \propto \exp\left(-\frac{\beta}{2}R_{DA}\right) \quad (2)$$

Here R_{DA} is the donor–acceptor edge-to-edge distance, and β is the attenuation factor. The magnitude of β depends on the electronic structure of the bridge (ν), the length of a repeating unit of the bridge (R_0), and on the energy difference between the donor and bridge unit localized states (Δ) according to Equation (3).

$$\beta = \frac{2}{R_0} \ln \left| \frac{\Delta}{\nu} \right| \quad (3)$$

The parameters in Equation (3) are, in general, not accessible, but Δ is closely related to the donor–bridge energy gap, ΔE_{DB} , that has been shown to influence β in analogy with Δ , both experimentally^[38] and theoretically.^[39]

The dividing of the bridge into weakly coupled subunits in the McConnell model, which gives the exponential distance dependence, is expected to be less valid for conjugated bridges. For systems with highly conjugated π bridges, the coupling element between the bridge units is very large and as the bridge is extended its energy can rapidly approach that of the donor. In such cases the distance dependence might become non-exponential and the electronic coupling may even increase with distance.^[39–41] However, in this study we utilize the McConnell model as it has been shown that the distance dependence for the studied series of OPE systems is exponential,^[38,39] and the β value is a convenient single-parameter description of the distance dependence.

In D-B-A systems where the donor, acceptor, and individual sub-units of the bridge can be divided into a series of

well-defined molecular planes it has been shown that the major conformational parameters that influence the electronic coupling are the dihedral angles between these neighboring planes.^[25,42–46] Since the average conformation of the system is expected to vary with temperature, the electronic coupling and, thus, the TEET rate is also expected to be temperature dependent. This work is a combined experimental and theoretical study of how the temperature influences the rate and distance dependence of TEET in a series of D-B-A systems where the donor–acceptor separation, R_{DA} , is varied, ZnP- x B- H_2P ($x=2, 3, 4, \text{ and } 5$). Here a zinc(II) 5,15-diaryl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (ZnP) acts as the donor, and the corresponding free-base porphyrin (H_2P) acts as the acceptor of the triplet excitation energy. The donor and acceptor chromophores are separated by oligo-*p*-phenyleneethynylene, OPE, bridge units (B) where the number (x) of phenylene groups varies between two and five, as shown in Figure 1.

To investigate the impact of temperature on the rates and

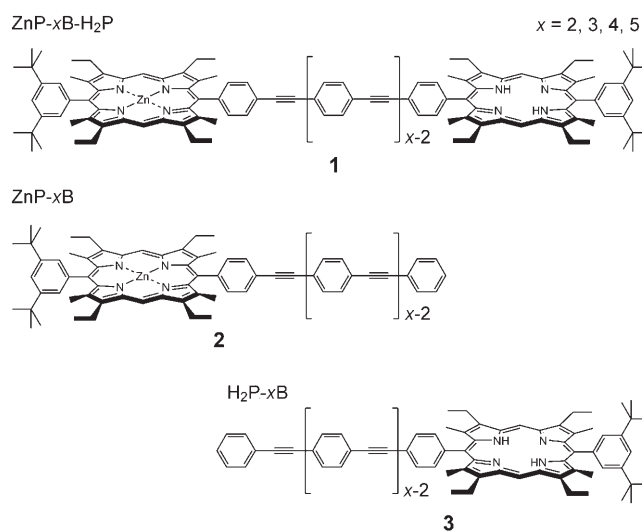


Figure 1. The donor(ZnP)-bridge(x B)-acceptor(H_2P) systems (1), reference compounds ZnP- x B (2), and H_2P - x B (3).

the distance dependence of TEET in the ZnP- x B- H_2P systems, transient absorption measurements were performed in 2-methyl tetrahydrofuran (2-MTHF) between 298 and 80 K. The experimentally determined dependence of β on the temperature was evaluated using a previously developed theoretical expression that models the electronic coupling in relation to the temperature dependent conformation of the bridge structure.^[38]

Calculations: All quantum-chemical calculations were performed with the Gaussian 03 program suite^[47] at the B3LYP/6–31G(d) level and have been thoroughly described previously.^[38] In short, the calculations include the evaluation of the potential energy as a function of rotation around several dihedral angles between the planes of individual sub-units, which have been identified as being the major param-

eters modulating the electronic coupling in this type of system.^[25,42–46] The relevant dihedral angles are the ones between the porphyrin plane and the plane of the first phenyl unit of the bridge (ω), and a series of dihedral angles between planes defined by neighboring phenyl units of the bridge (φ). The potential energy as a function of dihedral angle was calculated by changing the angle in 5° increments, followed by geometry optimization with respect to all other parameters at each point. To save calculation time the calculations were performed on the building blocks (compounds **5** and **6** in Figure 2) instead of the whole systems.

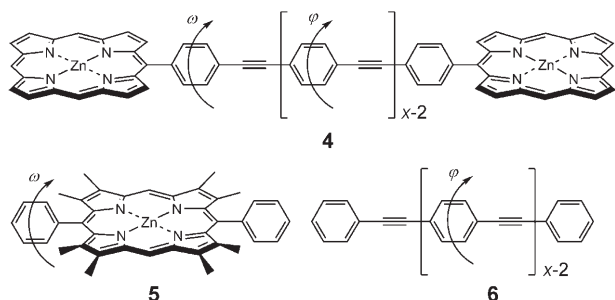


Figure 2. The symmetrical D-B-D compounds, Zn-xB-Zn, used for calculating the electronic coupling (**4**), the model compound used for calculating the donor-bridge rotation energy (**5**), and the structures used to calculate the rotation energy of the dihedral angle between phenyl planes within the bridge (**6**).

For the calculations of the electronic coupling, each symmetrical model system Zn-xB-Zn, $x=2, 3, 4$ and 5 (compound **4** in Figure 2) was stripped of saturated groups judged to have a minor impact on the electronic properties, and geometry optimized with D_{2h} symmetry constraints. This forced the porphyrin and bridge planes to be orthogonal ($\omega=90^\circ$) and the optimizations resulted in structures very similar to the ones obtained for optimizations of systems with the full substitution pattern used in the experimental study (see Figure 1). The resulting optimized geometries were used as starting points for the series of time-dependent density functional theory (TD-DFT) calculations of the vertical $T_1 \leftarrow S_0$ excitations. To investigate the conformational dependence of the electronic coupling, the angles between the various units were varied (cf. Figure 2) and the electronic couplings were calculated for each conformation. The electronic coupling was estimated as half the excitation energy difference between the two lowest excited triplet states of the porphyrin moieties. Importantly, for this procedure to be valid the system has to be at the avoided crossing geometry. Avoided crossing geometries were achieved by assuring that the system had a mirror plane or a C_2 -rotation axis, thus forcing the wave function to be equally distributed on the two porphyrins. The rotations described above were always done in such a way that the symmetries were preserved.

Results

The photophysics of the ZnP-xB-H₂P systems are well known through extensive studies.^[24,25,38,48,49] It has been established that the ground state absorption spectra of the D-B-A systems are described well by a sum of the spectra of the individual components. This shows that ground state or first excited singlet state interactions between the individual building blocks are small and that the electronic coupling is in the very weak region. This is ensured by the porphyrin substitution pattern, that is, the β -methyl groups, which keeps the bridge plane out of conjugation with the porphyrin planes.

The ZnP-xB and H₂P-3B reference compounds were excited at 544 and 505 nm, respectively, and decay traces were recorded at 470 nm. It was previously concluded that, at 150 K, there was no difference in lifetimes between the different ZnP-xB reference compounds,^[38] and this observation was confirmed in this study for all temperatures between 300 and 80 K. Transient absorption decays of the ZnP-xB-H₂P systems were recorded at 470 nm following excitation by a laser pulse with a wavelength of 544 nm. At this excitation wavelength, the ZnP moiety is excited with 90% selectivity. A representative decay trace is shown in Figure 3 and

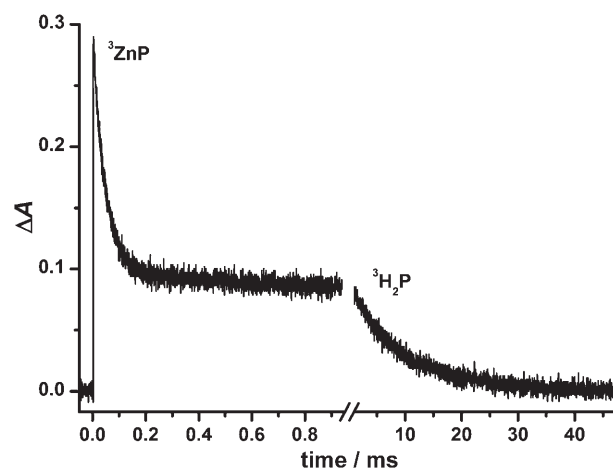


Figure 3. A representative decay trace showing the decay of the transient absorption signal recorded at 470 nm for the ZnP-4B-H₂P system at 130 K. The initial decay is due to the quenched ZnP moiety and the decay on a longer timescale matches the one for the H₂P-3B reference.

shows a fast initial decay, ascribed to the quenched ZnP triplet state, followed by a slower decay of lower amplitude, matching the lifetime of the H₂P-3B reference compound.

The decay traces of the ZnP-xB-H₂P systems were evaluated using Equation (4), in which the H₂P lifetime(s) (1 or 2) were fixed to the one(s) of the H₂P-3B reference at the same temperature.

$$\Delta A(T) = \sum_{i=1}^{1 \text{ or } 2} \alpha_i^{\text{ZnP}} \exp(-t/\tau_i^{\text{ZnP}}) + \sum_{j=1}^{1 \text{ or } 2} \alpha_j^{\text{H}_2\text{P}} \exp(-t/\tau_j^{\text{H}_2\text{P}}) \quad (4)$$

As previously reported, above 150 K the donor and acceptor reference compounds show biexponential decay kinetics, due to the transformation between two distinct conformations ($T_{1A} \rightarrow T_{1B}$) on the triplet surface.^[50–52] Below 150 K the transformation process is too slow to compete with the $T_{1A} \rightarrow S_0$ intersystem crossing process. In this study we are only interested in TEET from T_{1A} of the ZnP donor since this conformation is present at all temperatures. Above 200 K the $T_{1A} \rightarrow T_{1B}$ process of ZnP is fast, making TEET from the T_{1A} state very inefficient; instead TEET from T_{1B} could be seen.^[25] Between 200 and 130 K the main deactivation of the T_{1A} state in the ZnP-*x*B- H_2P systems is TEET, except for a few cases (for $x=4$ and 5 at temperatures above 175 and 150 K, respectively) where the transformations occur on the same (or faster) timescale impeding the determination of the TEET rate. In this temperature interval the decay traces (see Figure 3) could be well described by a single exponential contribution from the ZnP decay ($\alpha_2^{ZnP} = 0$ in [Eq. (4)]) and a subsequent biexponential decay on longer timescales, corresponding to the decay of the two H_2P triplet states. Below 130 K the decay of the quenched ZnP state in the D-B-A systems showed complex decay kinetics which required two exponentials to describe. However, in this temperature regime the intrinsic deactivation of the reference compounds is described well by single exponentials, indicating that complex TEET dynamics are responsible for the biphasic quenching (see the Discussion section). The subsequent H_2P decay is described well by a single exponential at these temperatures, so that no more than three exponentials in Equation (4) were required to fit the data at any temperature. The extracted, quenched, ZnP lifetimes from the fitting of Equation (4) to the experimental data are shown in Table 1.

For the temperature interval 200–130 K, the TEET rate was determined by comparing the reciprocal lifetime of ZnP in the D-B-A systems to that of the reference chromophore according to Equation (5).

$$k_{TEET} = \tau^{-1} - \tau_{ref}^{-1} \quad (5)$$

For temperatures below 130 K, where the decay of the quenched ZnP triplet was complex and the fit required a biexponential expression, the average ZnP lifetime in the

D-B-A systems, $\langle \tau \rangle$, was instead used to calculate the rate, as shown in Equation (6).

$$\langle \tau \rangle = (\alpha_1^{ZnP} \tau_1^{ZnP} + \alpha_2^{ZnP} \tau_2^{ZnP}) / (\alpha_1^{ZnP} + \alpha_2^{ZnP}) \quad (6)$$

The extracted TEET rates are compiled in Table 2 and shown in Figure 4. From Figure 4 it can be seen that the TEET process in these D-B-A systems has quite a complex temperature dependence, showing negative activation energies (increasing rate with decreasing temperature) in some

Table 2. The calculated TEET rates.

<i>T</i> [K]	ZnP-2B- H_2P	ZnP-3B- H_2P	ZnP-4B- H_2P	ZnP-5B- H_2P
	k_{TEET} [s^{-1}]			
200	2.62×10^7	1.08×10^6	–	–
175	2.08×10^7	8.40×10^5	2.01×10^4	–
150	1.64×10^7	5.27×10^5	2.55×10^4	875
140	1.33×10^7	5.53×10^5	2.57×10^4	566
130	9.86×10^6	4.71×10^5	2.28×10^4	629
120	3.74×10^6	3.11×10^5	1.84×10^4	616
110	8.71×10^5	1.03×10^5	1.26×10^4	520
95	2.18×10^5	1.13×10^4	1.06×10^4	10.8
80	1.74×10^5	6.02×10^3	8.13×10^2	9.50

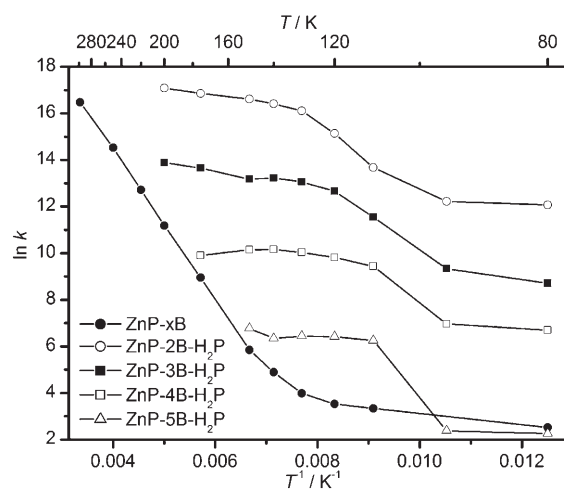


Figure 4. The logarithmic triplet state decay rate of the ZnP-*x*B (T_{1A} state) references (●) and the TEET rates of the ZnP-*x*B- H_2P systems with $x=2$ (○), 3 (■), 4 (□), and 5 (△). The lines between the data points are only guides to the eye.

Table 1. The experimentally determined lifetimes of the ZnP moiety (cf. [Eq. (4)]).

<i>T</i> [K]	ZnP-2B- H_2P			ZnP-3B- H_2P			ZnP-4B- H_2P			ZnP-5B- H_2P		
	τ_1 [ns]	τ_2 [μ s]	A_1/A_2 ^[a]	τ_1 [μ s]	τ_2 [μ s]	A_1/A_2 ^[a]	τ_1 [μ s]	τ_2 [ms]	A_1/A_2 ^[a]	τ_1 [ms]	τ_2 [ms]	A_1/A_2 ^[a]
200	38	–	–	0.87	–	–	–	–	–	–	–	–
175	48	–	–	1.2	–	–	36	–	–	–	–	–
150	61	–	–	1.5	–	–	41	–	–	0.82	–	–
140	75	–	–	1.8	–	–	43	–	–	1.3	–	–
130	110	–	–	2.1	–	–	47	–	–	1.4	–	–
120	150	0.52	68/32	2.5	6.7	83/17	35	6.7×10^{-2}	40/60	0.20	1.6	5/95
110	550	2.7	72/28	5.1	14	49/51	80	–	–	1.0	1.9	12/88
95	1.2×10^3	14	74/26	26	190	61/39	220	1.3	37/63	1.1	35	8/92
80	2.0×10^3	19	78/22	46	370	63/37	340	1.9	44/56	1.2	52	12/88

[a] In the bi-exponential fits the normalized pre-exponential factors are given.

cases. This can be explained by two opposing effects when the temperature is lowered causing low energy conformations to be more and more populated (see Discussion). Such complex temperature dependences have previously been observed for ET in similar D-B-A systems.^[44]

Figure 5 shows the logarithmic TEET rates plotted versus R_{DA} at four representative temperatures. At each temperature a different β value can be extracted. It can be seen that the β values (the slope of the fitted lines) decrease continuously with decreasing temperature.

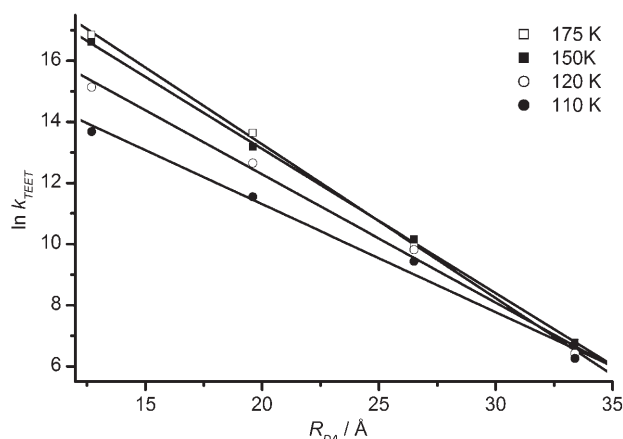


Figure 5. Representative “beta plots” and the respective linear fits (lines) at 175 K (□), 150 K (■), 120 K (○), and 110 K (●).

The experimentally determined β values are plotted versus temperature in Figure 6 (solid circles) together with the best fits of the theoretical model for a Boltzmann distribution (dashed line) and a distribution distorted by viscosity effects (solid line). The modeling of this temperature dependence will be discussed in the following section.

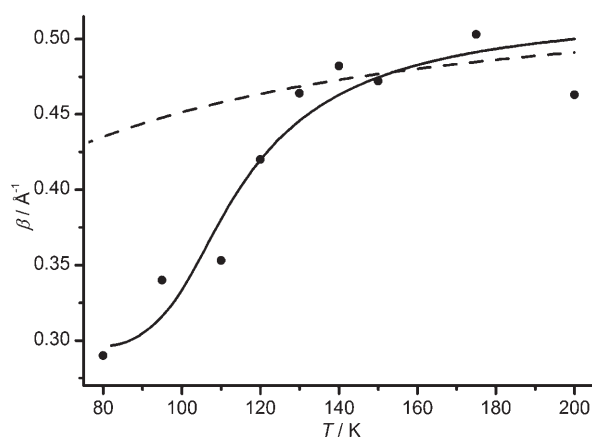


Figure 6. Experimentally determined β versus temperature (●) and fits of the theoretical model to the experimental data using a pure Boltzmann averaging (dashed line) and using viscous activation energy (solid line), see Discussion for details.

Discussion

The motivation of this study was to investigate how the temperature dependent average conformations of dihedral angles between sub-units of D-B-A systems influence the electronic coupling. This study is a continuation of previous work in which we determined the distance dependence at 150 K and derived a theoretical model that could describe the data.^[38] The model led to a factorized expression of the Boltzmann averaged total electronic coupling, given in Equation (7),

$$\langle V_{DA}(\omega, \varphi_1, \varphi_2, \dots, \varphi_{x-1}) \rangle_x = V_x \cdot \langle V(\omega) \rangle \cdot \prod_{m=1}^{x-1} \langle V(\varphi_m) \rangle \quad (7)$$

$$= V_x \cdot \langle V(\omega) \rangle \cdot \langle V(\varphi) \rangle^{x-1}$$

where $\langle \dots \rangle$ indicates an averaged property (please see ref. [38] for details). The magnitude of the total electronic coupling is given by the first term, V_x , whereas the other two terms, $\langle V(\omega) \rangle$ and $\langle V(\varphi) \rangle$, give the normalized dependence of the electronic coupling on the conformational parameters. From the McConnell model it follows that β can be extracted from the derivative of the logarithmic coupling (cf. [Eq. (2)]) as shown in Equation (8).

$$\beta = -2 \frac{d \ln V_{DA}}{d R_{DA}} \quad (8)$$

Thus, the temperature dependence of β derived from the model can more easily be visualized from the logarithmic averaged electronic coupling, given in Equation (9).

$$\ln \langle V_{DA} \rangle = \ln V_x + \ln \langle V(\omega) \rangle + (x-1) \ln \langle V(\varphi) \rangle \quad (9)$$

The first term is a temperature independent constant that is unique for each bridge length. This series of temperature independent constants will give β for a planar bridge structure, which was found from TD-DFT calculations^[38] to be $\beta_{\text{planar}} = 0.19 \text{ \AA}^{-1}$ for this particular OPE series.^[53] The second term is temperature dependent but independent of bridge length, and will thus not affect β . It will, on the other hand, be a major contribution to the total electronic coupling and, thus, to a large extent govern the temperature dependence of the TEET rates. The last term in Equation (9) is also temperature dependent and, since x varies, will, according to the model, be the sole factor governing the temperature dependence of β . The distance dependence inherent in this factor originates from the $(x-1)$ factor and the temperature dependence originates from $\langle V(\varphi) \rangle$. Thus, β can be split into a temperature independent constant that will give the lowest obtainable β value, and a temperature dependent variable that will reflect the average conformation of the bridge, as described in Equation (10).

$$\beta_{\text{tot}} = \beta_0 + \beta(T) \quad (10)$$

The factor that governs the temperature dependence of β is

the integrated Boltzmann weighted electronic coupling due to conformational disorder in the bridge structure. In this factor the conformational dependence of the electronic coupling is weighted according to the corresponding potential energy. Approximate analytical expressions for both the conformational dependence of the electronic coupling and the potential energy for OPE bridges have been derived from TD-DFT calculations.^[38]

The division of β into a constant and a temperature dependent part should be quite general for any series of D-B-A systems with repeating bridge units. We derived a very specific expression for the conformational dependence of the electronic coupling for OPE bridges.^[38] This expression is nearly the same as the one expected from consideration of overlap between two mutually rotating p-orbitals, which has previously been reported for TEET,^[43,45] and is given in Equation (11).

$$V(\varphi) = \cos^2\varphi \quad (11)$$

If the more general relation is used instead of the very specific one, analytical solutions of the Boltzmann integrals are possible. The normalized conformational dependence for any repeating bridge structure, with its minimal energy associated with a planar conformation, can with this assumption be approximated by Equation (12),

$$\langle V(\varphi) \rangle = \frac{\int e^{-\frac{E_\varphi \sin^2\varphi}{RT}} \cdot \cos^2\varphi \cdot d\varphi}{\int e^{-\frac{E_\varphi \sin^2\varphi}{RT}} \cdot d\varphi} = \frac{1}{2} \left(1 - \frac{I_1\left(\frac{-E_\varphi}{2RT}\right)}{I_0\left(\frac{-E_\varphi}{2RT}\right)} \right) \quad (12)$$

where $I_n(z)$ is the modified Bessel function of the first kind of order n and E_φ is the barrier to rotation of two bridge units in relation to each other. Evaluation of this expression reveals that $\langle V(\varphi) \rangle$ varies from 1 to 0.5 for a planar and randomized bridge structure, respectively, so that (cf. [Eq. (8)]) $0 \leq \beta(T) \leq 2 \ln 2 / R_0$. Thus, using this relation, one can easily estimate the maximum effect of rotational disorder, or lack thereof, on the attenuation in any D-B-A system based on repeating bridge units. Different shapes and heights of the energy barrier to rotation of neighboring units of the bridge will give different intermediate temperature behavior, but the limits will be the same. For the OPE bridges a planar conformation is the most energetically favorable. Thus, as the temperature is increased, β will also increase in accordance with, on average, a less planar bridge structure. Oligo(phenyl), OP, bridges, on the other hand, have an angle close to 45 degrees between neighboring units in the bridge associated with the lowest energy conformation. Increasing the temperature will, thus, simultaneously populate conformations associated with higher and lower electronic coupling. Attenuation in systems based on this type of bridge is thus expected to be less sensitive to temperature.

To model the experimentally determined temperature dependence of β (Figure 6) the energy barrier to rotation of the dihedral angle between the planes of two phenyl units in the bridge, E_i , and the constant part of the attenuation factor, β_0 , was varied so that the temperature dependence of β derived from the model was fitted to the experimental results. The extracted rotational barrier from this procedure was, $E_i = 1.1 \text{ kJ mol}^{-1}$, and the limiting β value, $\beta_0 = 0.29 \text{ \AA}^{-1}$. This rotational barrier height is in line with experimental and theoretical studies, which have shown that the rotational barriers in OPE structures are between 0–3.8 kJ mol^{-1} .^[54–59] Moreover, only the experimental data from the interval 200–130 K could be included, as the model did not describe the data at the lower temperatures. Figure 6 shows the result from the fitting procedure (dashed line). The model describes the experimental data down to 130 K, whereas at temperatures below 130 K the experimental β values decrease much faster than predicted by the Boltzmann distribution for this model.

This suggests that the temperature dependence of β can be divided into two regimes. At high temperatures (room temperature to 130 K) the Boltzmann distribution is maintained due to the fact that the internal rotational dynamics are much faster than the TEET rates. In contrast, at low temperatures (120–80 K) the interconversion between conformers is slow and occurs on the same timescale as TEET. Therefore, a distribution of TEET rates is expected in the low temperature regime, resulting in more complex decay kinetics of the ZnP quenching. This will cause a distortion of the Boltzmann distribution over time as the conformations associated with a high electronic coupling will transfer their energy quickly, depleting their population. Conformations with lower electronic coupling will be “left behind” and govern the decay kinetics at longer times. This will lead to a time-averaged distribution of conformations that is perturbed from the Boltzmann distribution so that conformations representing a higher electronic coupling will have a larger contribution.

A way to compensate for viscous friction is to correct the internal rotation energy with a temperature-dependent factor, resulting in a temperature dependent apparent activation energy, E_{app} ^[60], as shown in Equation (13), where E_i is the intrinsic energy barrier to rotation, $E_\eta = 1.3469 \text{ kJ mol}^{-1}$ and $T_0 = 81 \text{ K}$ for 2-MTHF, and typical α values are around 0.1 (depending on the sharpness of the barrier).

$$E_{app}(T) = E_i + \alpha E_\eta \frac{T^2}{(T - T_0)^2} \quad (13)$$

The result of using the fitted apparent activation energy is shown in Figure 6 (solid line) and the fitted parameters are: $E_i = 0.015 \text{ kJ mol}^{-1}$, $\alpha = 0.13$, and $\beta_0 = 0.30 \text{ \AA}^{-1}$. Although Equation (13) has not previously been used in the context of acquiring the effects of a perturbed Boltzmann distribution it has the necessary characteristics to do so for the distance

dependence of TEET mediated by OPE bridges. This is because the OPE bridge in a low energy conformation is associated with a *higher* electronic coupling. It will thus distort the Boltzmann population according to the discussion above. As an alternative, the Marcus equation^[61,62] in combination with the temperature dependence of the total electronic coupling could in principle be used to calculate directly the temperature dependence of the TEET rate. This procedure would, however, also require knowledge about the rotational barrier for the phenylporphyrin dihedral angles (ω) as well as the temperature dependence of the driving force and reorganization energy for the transfer reaction. Thus, the fitting procedure would involve a large number of unknown parameters. In contrast, fitting of an analytical expression for the temperature dependence of the distance dependence (i.e. β) to experimental data reduces the number of fitting parameters dramatically. Moreover, many of the unknown parameters are very nearly independent of distance and thus will not contribute to β . Studying the temperature dependence of β might, therefore, prove to be an alternative way of determining rotational barriers in bridge structures. However, this would benefit from as large a temperature interval as possible, and unfortunately the available temperature range is quite small for the systems studied here. This is due to the increased viscosity at low temperatures and the limited triplet lifetimes, caused by the transition between the two conformations ($T_{1A} \rightarrow T_{1B}$) of the ZnP donor at high temperatures. A donor chromophore with longer triplet lifetimes (e.g. a differently substituted zinc(II) porphyrin) might increase the available temperature range and improve the value of the determined rotational barrier.

In discussions of the temperature dependence of ET processes it has been suggested that a temperature dependent reorganization energy may serve as a simplification of fuller dynamic models.^[63] This is due to the fact that the slowing down of solvent relaxation will result in an apparently higher activation energy for reaching the avoided crossing geometry. The temperature dependent apparent activation energy used in this work will serve a similar purpose for TEET, where the limiting rate is not expected to be the acquiring of avoided crossing geometry, but rather the geometry of optimal electronic coupling. Further, we are studying the distance dependence, which removes the impact on activation energy for achieving the avoided crossing geometry, since it is the same for all systems, irrespective of donor-acceptor separation. In conclusion the derived theoretical model ([Eq. (7)]) was found to describe accurately the distance dependence of TEET mediated by OPE bridges at temperatures where the viscosity is not very high and the resulting rotational barrier is in line with previous studies. In regions where the viscosity is higher the model could describe β with the use of a temperature dependent apparent activation energy ([Eq. (13)]).

Experimental Section

The synthesis of the D-B-A systems used in the experimental study has been described elsewhere.^[64]

The solvent 2-methyl tetrahydrofuran (2-MTHF) (Merck) was distilled, to remove stabilizers and impurities, prior to use. The low temperature measurements were performed using a temperature-controlled liquid nitrogen cryostat (Oxford LN₂). Oxygen was removed in the samples by four to six freeze-pump-thaw cycles, effectively reducing the oxygen pressure to below 10⁻⁴ mbar.

Absorption spectra were recorded at room temperature using normal 1 cm quartz sample cells in a Cary 4B UV/Vis Spectrophotometer. A baseline of the pure solvent was also recorded for every spectrum.

The nanosecond to microsecond transient absorption measurements were performed on an experimental setup described previously^[65] where the excitation light is provided by a pulsed Nd:YAG laser (Continuum Surelite II-10, pulse width < 7 ns). The Nd:YAG laser pumps an OPO that gives a tunable excitation light source in the wavelength region between 400–700 nm. The probe light (a Xenon arc lamp), after passing the sample, is then passed through a monochromator (symmetrical Czerny-Turner arrangement) and detected by a five-stage Hamamatsu R928 photomultiplier tube. For each sample, 64 transient signals were collected and averaged on a 200 MHz digital Oscilloscope (Tektronix TDS2200 2Gs/s) and stored by a homemade LabView program controlling the whole system. To reduce the photochemical stress on the sample during measurements the probe light was filtered using a 460 nm interference filter and the power of the excitation pulses were kept below 10 mJ.

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- [1] V. Balzani, A. Credi, M. Venturi, *ChemPhysChem* **2003**, *4*, 49–59.
- [2] A. P. de Silva, N. D. McClenaghan, *Chem. Eur. J.* **2004**, *10*, 574–586.
- [3] A. P. de Silva, Y. Leydet, C. Lincheneau, N. D. McClenaghan, *J. Phys. Condens. Matter* **2006**, *18*, S1847–S1872.
- [4] U. Pischel, *Angew. Chem.* **2007**, *119*, 4100–4115; *Angew. Chem. Int. Ed.* **2007**, *46*, 4026–4040.
- [5] A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, *95*, 49–68.
- [6] A. Hagfeldt, M. Grätzel, *Acc. Chem. Res.* **2000**, *33*, 269–277.
- [7] J. R. Durrant, S. A. Haque, E. Palomares, *Coord. Chem. Rev.* **2004**, *248*, 1247–1257.
- [8] A. Hagfeldt, G. Boschloo, H. Lindström, E. Figgemeister, A. Holmberg, V. Aranyos, E. Magnusson, L. Malmqvist, *Coord. Chem. Rev.* **2004**, *248*, 1501–1509.
- [9] J. R. Durrant, S. A. Haque, E. Palomares, *Chem. Commun.* **2006**, 3279–3289.
- [10] G. M. Hasselman, D. F. Watson, J. R. Stromberg, D. F. Bocian, D. Holten, J. S. Lindsey, G. J. Meyer, *J. Phys. Chem. B* **2006**, *110*, 25430–25440.
- [11] M. Huber, *Eur. J. Org. Chem.* **2001**, 4379–4389.
- [12] R. Lomoth, A. Magnusson, M. Sjödin, P. Huang, S. Styring, L. Hammarström, *Photosynth. Res.* **2006**, *87*, 25–40.
- [13] D. Noy, C. C. Moser, P. L. Dutton, *Biochim. Biophys. Acta Bioenerg.* **2006**, *1757*, 90–105.
- [14] H. E. Song, C. Kirmaier, J. K. Schwartz, E. Hindin, L. H. Yu, D. F. Bocian, J. S. Lindsey, D. Holten, *J. Phys. Chem. B* **2006**, *110*, 19121–19130.
- [15] H. E. Song, C. Kirmaier, J. K. Schwartz, E. Hindin, L. H. Yu, D. F. Bocian, J. S. Lindsey, D. Holten, *J. Phys. Chem. B* **2006**, *110*, 19131–19139.
- [16] M. R. Wasielewski, *J. Org. Chem.* **2006**, *71*, 5051–5066.
- [17] M. D. Newton, *Chem. Rev.* **1991**, *91*, 767–792.

- [18] G. L. Closs, P. Piotrowiak, J. M. MacInnis, G. R. Fleming, *J. Am. Chem. Soc.* **1988**, *110*, 2652–2653.
- [19] G. L. Closs, M. D. Johnson, J. R. Miller, P. Piotrowiak, *J. Am. Chem. Soc.* **1989**, *111*, 3751–3753.
- [20] N. Koga, K. Sameshima, K. Morokuma, *J. Phys. Chem.* **1993**, *97*, 13117–13125.
- [21] A. El-ghayoury, A. Harriman, A. Khatyr, R. Ziessel, *J. Phys. Chem. A* **2000**, *104*, 1512–1523.
- [22] A. El-ghayoury, A. Harriman, A. Khatyr, R. Ziessel, *Angew. Chem.* **2000**, *112*, 191–195; *Angew. Chem. Int. Ed.* **2000**, *39*, 185–189.
- [23] A. El-ghayoury, A. Harriman, R. Ziessel, *J. Phys. Chem. A* **2000**, *104*, 7906–7915.
- [24] J. Andréasson, J. Kajanus, J. Mårtensson, B. Albinsson, *J. Am. Chem. Soc.* **2000**, *122*, 9844–9845.
- [25] J. Andréasson, A. Kyrchenko, J. Mårtensson, B. Albinsson, *Photochem. Photobiol. Sci.* **2002**, *1*, 111–119.
- [26] F. Barigelletti, L. Flamigni, V. Balzani, J. P. Collin, J. P. Sauvage, A. Sour, E. C. Constable, A. Thompson, *J. Am. Chem. Soc.* **1994**, *116*, 7692–7699.
- [27] A. Harriman, A. Khatyr, R. Ziessel, A. C. Benniston, *Angew. Chem.* **2000**, *112*, 4457–4460; *Angew. Chem. Int. Ed.* **2000**, *39*, 4287–4290.
- [28] B. Schlicke, P. Belsler, L. De Cola, E. Sabbioni, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 4207–4214.
- [29] J. Halpern, L. E. Orgel, *Discuss. Faraday Soc.* **1960**, *29*, 32–41.
- [30] H. M. McConnell, *J. Chem. Phys.* **1961**, *35*, 508–515.
- [31] R. J. Cave, M. D. Newton, *Chem. Phys. Lett.* **1996**, *249*, 15–19.
- [32] L. A. Curtiss, C. A. Naleway, J. R. Miller, *Chem. Phys.* **1993**, *176*, 387–405.
- [33] L. A. Curtiss, C. A. Naleway, J. R. Miller, *J. Phys. Chem.* **1993**, *97*, 4050–4058.
- [34] S. Larsson, *J. Am. Chem. Soc.* **1981**, *103*, 4034–4040.
- [35] J. N. Onuchic, D. N. Beratan, *J. Chem. Phys.* **1990**, *92*, 722–733.
- [36] M. A. Ratner, *J. Phys. Chem.* **1990**, *94*, 4877–4883.
- [37] M. J. Shephard, M. N. Paddon-Row, K. D. Jordan, *Chem. Phys.* **1993**, *176*, 289–304.
- [38] M. P. Eng, T. Ljungdahl, J. Mårtensson, B. Albinsson, *J. Phys. Chem. B* **2006**, *110*, 6483–6491.
- [39] M. P. Eng, B. Albinsson, *Angew. Chem.* **2006**, *118*, 5754–5757; *Angew. Chem. Int. Ed.* **2006**, *45*, 5626–5629.
- [40] J. W. Evenson, M. Karplus, *J. Chem. Phys.* **1992**, *96*, 5272–5278.
- [41] J. W. Evenson, M. Karplus, *Science* **1993**, *262*, 1247–1249.
- [42] A. Kyrchenko, B. Albinsson, *Chem. Phys. Lett.* **2002**, *366*, 291–299.
- [43] A. C. Benniston, A. Harriman, P. Y. Li, P. V. Patel, C. A. Sams, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3677–3679.
- [44] W. B. Davis, M. A. Ratner, M. R. Wasielewski, *J. Am. Chem. Soc.* **2001**, *123*, 7877–7886.
- [45] A. C. Benniston, A. Harriman, *Chem. Soc. Rev.* **2006**, *35*, 169–179.
- [46] I. Filatov, S. Larsson, *Chem. Phys.* **2002**, *284*, 575–591.
- [47] Gaussian 03, Revision B.05, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cio-slawski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
- [48] K. Pettersson, A. Kyrchenko, E. Rönnow, T. Ljungdahl, J. Mårtensson, B. Albinsson, *J. Phys. Chem. A* **2006**, *110*, 310–318.
- [49] K. Kilså, J. Kajanus, J. Mårtensson, B. Albinsson, *J. Phys. Chem. B* **1999**, *103*, 7329–7339.
- [50] V. Knyukshto, E. Zenkevich, E. Sagun, A. Shulga, S. Bachilo, *Chem. Phys. Lett.* **1998**, *297*, 97–108.
- [51] J. Andréasson, H. Zetterqvist, J. Kajanus, J. Mårtensson, B. Albinsson, *J. Phys. Chem. A* **2000**, *104*, 9307–9314.
- [52] A. Kyrchenko, J. Andréasson, J. Mårtensson, B. Albinsson, *J. Phys. Chem. B* **2002**, *106*, 12613–12622.
- [53] It is important to note that β can never reach the value expected for a planar bridge since there will always be zero point vibrations of considerable amplitude for distortions with as weak force constants as the dihedral twisting in the present system.
- [54] K. Okuyama, T. Hasegawa, M. Ito, N. Mikami, *J. Phys. Chem.* **1984**, *88*, 1711–1716.
- [55] P. V. James, P. K. Sudeep, C. H. Suresh, K. G. Thomas, *J. Phys. Chem. A* **2006**, *110*, 4329–4337.
- [56] M. Levitus, K. Schmieder, H. Ricks, K. D. Shimizu, U. H. F. Bunz, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2002**, *124*, 8181–8181.
- [57] K. Schmieder, M. Levitus, H. Dang, M. A. Garcia-Garibay, *J. Phys. Chem. A* **2002**, *106*, 1551–1556.
- [58] J. M. Seminario, A. G. Zacarias, J. M. Tour, *J. Am. Chem. Soc.* **1998**, *120*, 3970–3974.
- [59] P. K. Sudeep, P. V. James, K. G. Thomas, P. V. Kamat, *J. Phys. Chem. A* **2006**, *110*, 5642–5649.
- [60] B. Brocklehurst, R. N. Young, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 271–278.
- [61] R. A. Marcus, *J. Chem. Phys.* **1956**, *24*, 966–978.
- [62] B. S. Brunschwig, J. Logan, M. D. Newton, N. Sutin, *J. Am. Chem. Soc.* **1980**, *102*, 5798–5809.
- [63] B. M. Hoffman, M. A. Ratner, *Inorg. Chim. Acta* **1996**, *243*, 233–238.
- [64] T. Ljungdahl, K. Pettersson, B. Albinsson, J. Mårtensson, *Eur. J. Org. Chem.* **2006**, 3087–3096.
- [65] K. Pettersson, K. Kilså, J. Mårtensson, B. Albinsson, *J. Am. Chem. Soc.* **2004**, *126*, 6710–6719.

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