

Triplet Excitation Energy Transfer in Porphyrin-Based Donor–Bridge–Acceptor Systems with Conjugated Bridges of Varying Length: An Experimental and DFT Study

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A series of donor–bridge–acceptor (D–B–A) systems with varying donor–acceptor distances have been studied with respect to their triplet energy transfer properties. The donor and acceptor moieties, zinc(II), and free-base porphyrin, respectively, were separated by 2–5 oligo-*p*-phenyleneethynylene units (OPE) giving rise to edge-to-edge separations ranging between 12.7 and 33.4 Å. The study was performed in 2-MTHF at 150 K and it was established that triplet excitation energy transfer occurs with high efficiency in all of the studied D–B–A systems. The distance dependence was exponential with an attenuation factor, β , equal to $0.45 \pm 0.015 \text{ Å}^{-1}$. The experimental study was also supported by quantum mechanical DFT and TD–DFT calculations on a series of closely related model systems. A thorough analysis of the OPE-bridge conformational dynamics led to an equation that quantitatively models the distance dependence of the electronic coupling found in the experimental study.

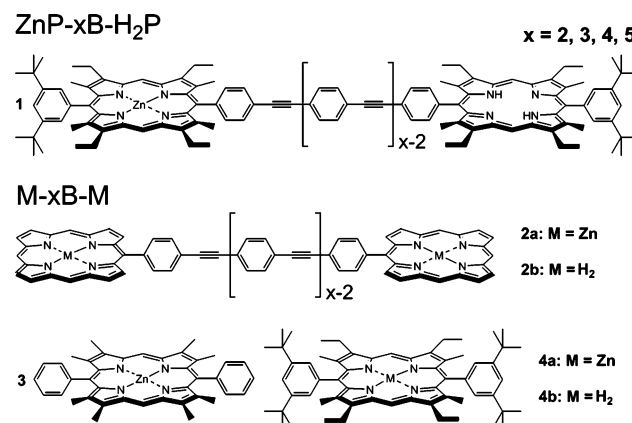
Introduction

In recent years photoinduced energy and electron transfer (ET) have been extensively studied, with the potential development of molecular electronics^{1–3} and artificial photosynthesis^{4,5} as long-term goals. This has led to the development of many donor–bridge–acceptor (D–B–A) systems facilitating systematic investigations of how the processes are mediated by the bridging chromophore.^{6–29} Studies have also been performed on molecular systems incorporated in self-assembled monolayers, SAMs.^{30,31}

This work is a combined experimental and theoretical study of how the donor–acceptor edge-to-edge distance, R_{DA} , affects the rate and efficiency of triplet excitation energy transfer (TEET) in a series of D–B–A systems, ZnP–xB–H₂P ($x = 2, 3, 4$, and 5). In these systems 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 (H₂P) acts as the acceptor of the triplet excitation energy. The donor and acceptor chromophores are separated by oligo-*p*-phenyleneethynylene (OPE) bridge units where the number of phenyleneethynylene groups (x) varies between 2 and 5 (Chart 1).

The study of TEET can, at a first glance, seem trivial, as nature cunningly avoids processes occurring on the triplet surface to save energy and to avoid unwanted reactions with oxygen but, since both ET and TEET involve electron exchange interactions, much of what governs TEET also concerns ET processes.^{16,17,32} Thus, investigating TEET processes is expected to give valuable information about properties that also govern ET processes which, in general, are much more challenging to study experimentally. It has previously been confirmed that various bridging units can mediate TEET^{23,24,33–36} and that varying the energy difference between the donor and bridge chromophores has a substantial effect on the mediation.^{6,8} There

CHART 1. The Donor (ZnP)–Bridge (xB)–Acceptor (H₂P) Systems (1), Model Systems Zn–xB–Zn (2a) and H₂–xB–H₂ (2b), Model Monomer (3), and Real Monomers ZnP (4a) and H₂P (4b).



are also previous studies investigating the distance dependence of TEET.^{30,36–38}

The distance dependence of the rates of mediated electron exchange processes is mainly governed by the distance dependence of the electronic coupling between the donor and acceptor states, V_{DA} . Many studies have, therefore, focused on developing theoretical methods for calculating the electronic coupling in D–B–A systems.^{12,32,36,39–44} In the superexchange model developed by McConnell, the electronic coupling decays exponentially with distance according to the following:⁴⁴

$$V_{DA} \propto \exp\left(-\frac{\beta}{2}R_{DA}\right) \quad (1)$$

Here R_{DA} is the donor–acceptor edge-to-edge distance, and β is the so-called attenuation factor. β is normally considered a constant specific for the series of homologous bridge systems studied.

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To investigate the distance dependence of the rate of TEET in the $\text{ZnP-xB-H}_2\text{P}$ systems transient absorption measurements have been performed in 2-MTHF at 150 K. A theoretical model for calculating the electronic coupling, based on the estimation of the electronic coupling element as half the energy splitting between the initial and final states at the avoided crossing geometry,^{12,27,28,40–43,45,46} has been applied to a series of model systems. The calculations have been done with considerable weight placed on the conformational dynamics of the bridging units, and the resulting distance dependence has been compared to the experimental results.

Materials and Methods

Synthesis. The synthesis of the D–B–A systems has been described elsewhere.⁴⁷

Solvents. 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 4–6 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 a setup described previously¹⁴ where the exciting light was provided by a pulsed Nd:YAG laser (Continuum Surelite II-10, pulse width <7 ns) pumping an OPO giving a tunable light source in the wavelength region between 400 and 700 nm. The probe light, penetrating the sample at an angle of 90 degrees relative to the excitation light, was provided by a Xenon arc lamp. After passing the sample, the probe light was 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 by a 200 MHz digital oscilloscope (Tektronix TDS2200 2 Gs/s) and stored by a homemade LabView program controlling the whole system. The transient absorption spectra of the monomer compounds were constructed from transient absorption decay curves recorded in 5 nm intervals between 400 and 650 nm. The intensity at each point in the spectra is an average of the monoexponential transient decay signal between 20 and 700 μs after the excitation pulse.

Quantum Chemical Calculations were performed with the Gaussian 03 program suite.⁴⁸ Calculation of the potential energy as a function of porphyrin-bridge angle rotation (ω) was done on a model monomer (compound 3 in Chart 1). The substitution pattern for the model monomer is the same as for the real ZnP monomer (compound 4a in Chart 1), except for the replacement of the β -ethyl groups for methyl groups and the removal of the *tert*-butyl groups on the phenyls. This small difference in substitution pattern should have minimal influence on the rotation energy and should greatly reduce the calculation time. The porphyrin-bridge angle was simulated by the porphyrin-phenyl angle in the model monomer, as the effect of a longer bridge-unit also should have minimal effect on the rotation energy. The porphyrin-phenyl angle was varied between 90 and 60 degrees in 5-degree increments, and the molecule was geometry optimized with respect to all other parameters at each point.

For the calculations of the electronic coupling, model systems consisting of the unsubstituted porphine derivatives were chosen

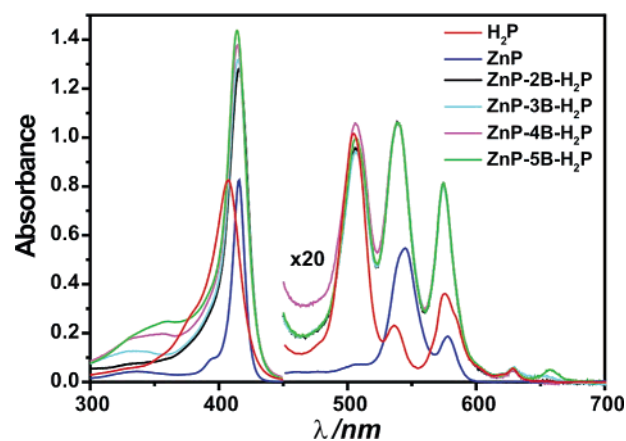


Figure 1. The absorption spectra of the studied compounds.

in order to decrease computation time and facilitate the assignment of symmetry. Each model system, M-xB-M , $\text{M} = \text{H}_2$ or Zn , and $x = 2, 3, 4$, and 5 , was first geometry optimized with D_{2h} and D_2 -symmetry constraints, respectively, using the B3LYP functional^{49–51} and the 6-31G(d) basis set.⁵² The symmetry constraints were considered to be justified as they forced the porphyrin and bridge planes to be orthogonal and the optimizations resulted in very similar structures as the ones obtained for optimizations of complexes with the full substitution pattern used in the experimental study. The resulting optimized geometries were used for time-dependent density functional (TD–DFT) calculations of the vertical triplet state excitations using the same functional and basis set as for the geometry optimizations. The electronic coupling was estimated as half the excitation energy difference between the two lowest excited triplet states of the porphyrin moieties. It is important to note that in order for this procedure to be valid, the system has to be at the avoided crossing geometry. Thus, calculations were performed on the symmetric M-xB-M systems (series 2a and 2b in Chart 1) instead of the experimentally studied $\text{ZnP-xB-H}_2\text{P}$ systems (series 1 in Chart 1). Avoided crossing geometries were achieved by ensuring 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. To investigate the conformational dependence of the electronic coupling, the angle between the various units was varied while keeping all other coordinates constant. Triplet state energies of the bridges were estimated by TD–DFT (B3LYP/6-31G(d)) calculations of the $T_1 \leftarrow S_0$ excitations of the optimized structures. It is well-known that TD–DFT underestimates the excitation energies for large extended π -systems with a high degree of conjugation,^{53,54} but the method is reported to capture trends in homologous series of moderate length.^{53,55} When the degree of conjugation is smaller, as in the OPE-bridges, TD–DFT have been shown to yield excellent results.⁵⁶

Experimental Results

In this section, the experimental study will be summarized. Figure 1 shows the ground-state absorption spectra of the $\text{ZnP-xB-H}_2\text{P}$ compounds along with the spectra of the donor (ZnP) and acceptor (H_2P) monomers (Chart 1). The spectra of the $\text{ZnP-xB-H}_2\text{P}$ compounds are well described by a sum of the spectra of the individual building blocks, except for small differences in the region below 400 nm. This shows that the electronic interaction between the building blocks is weak in the ground state.

Figure 2 shows the triplet energy diagram for the building blocks of the D–B–A systems. The diagram is a combination

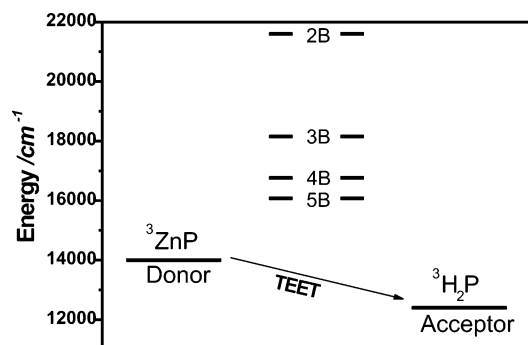


Figure 2. The triplet state energy diagram of the donor (ZnP), bridge (xB), and acceptor (H₂P) moieties. The energy of the ZnP triplet state was estimated from phosphorescence data,⁸ the triplet state excitation energies of the bridges were calculated with TD–DFT using the B3LYP functional and the 6-31G(d) basis set, and the H₂P triplet state energy was taken from ref 61.

TABLE 1: The Lifetimes of the ZnP Moiety (τ_{ZnP}), Rates of Triplet Energy Transfer (k_{TEET}), and Transfer Efficiencies (E_{TEET}) of the Studied Compounds in 2-MTHF at 150 K

compound	$\tau_{\text{ZnP}}/\text{s}$	$k_{\text{TEET}}/\text{s}^{-1a}$	$E_{\text{TEET}}(\%)^b$
ZnP (ref)	2.9×10^{-3}		
ZnP–5B	2.9×10^{-3}		
ZnP–2B–H ₂ P	54×10^{-9}	2.0×10^7	99.99
ZnP–3B–H ₂ P	1.4×10^{-6}	7.2×10^5	99.95
ZnP–4B–H ₂ P	41×10^{-6}	2.4×10^4	98.59
ZnP–5B–H ₂ P	0.55×10^{-3}	1.5×10^3	80.97

$$^a k_{\text{TEET}} = \tau^{-1} - \tau_{\text{ref}}^{-1}, \quad ^b E_{\text{TEET}} = 1 - \tau \cdot \tau_{\text{ref}}^{-1}.$$

of computational and experimental results in that the triplet state energies of the porphyrins are experimentally determined, and the bridge energies are calculated (TD–DFT) triplet excitation energies. The calculated triplet excitation energy for the 2B-bridge (tolane or diphenylacetylene) was found to be in excellent agreement with the experimentally determined triplet state energy.^{57,58} For the 3B-bridge (1,4-bis(phenylethynyl)benzene) the calculated excitation energy was found to be slightly lower than the emission maximum of the phosphorescence.⁵⁹ Thus, it can be suspected that the calculations also underestimate the triplet excitation energies of the 4B- and 5B-bridges. The main part of this underestimation is expected to originate from the conformational dynamics of the bridge units.^{59,60} Calculations of the triplet excitation energies were done for planar bridge units, the conformation expected to have the lowest triplet excitation energy. The underestimation is expected to be greater for the longer bridge units since they have more conformational degrees of freedom compared to the shorter bridge units. Figure

2 shows that triplet energy transfer is feasible on energetic grounds, $E(^3\text{ZnP}) > E(^3\text{H}_2\text{P})$. Stepwise transfer, via the bridge unit, can safely be ruled out for $x = 2, 3$, and 4 since the smallest energy difference between the donor and bridge units is around 3000 cm^{-1} , even with the underestimation of the bridge triplet state energies. Thermal activation to the excited triplet state of these bridge units is, thus, expected to be much slower than the lifetime of the ZnP reference compound (Table 1). However, thermal activation to the triplet state of the 5B-bridge cannot be completely ruled out since the estimated energy difference between donor and bridge is around 2000 cm^{-1} . Nevertheless, since no quenching was observed for the ZnP–5B reference chromophore and the energy difference most probably is underestimated, the contribution from thermally activated stepwise transfer process is expected to be very small. In addition, the TEET rate (k_{TEET}) for ZnP–5B–H₂P does not deviate from the observed trend (vide infra) indicating that no additional processes are active in ZnP–5B–H₂P compared to the other members of the series.

Figure 3a shows the transient absorption spectra of the donor and acceptor monomers, ZnP and H₂P, in 2-MTHF at 150 K following excitation by 544 and 505 nm, respectively. The signals were averaged between 20 and 700 μs ensuring that all singlets have decayed prior to signal collection. The spectra show the well-known features of the respective $T_1 \rightarrow T_n$ absorption spectra with a broad peak centered around 470 and 430 nm for ZnP and H₂P, respectively.^{62,63} Overlaid with the broad $T_1 \rightarrow T_n$ absorption features, that extends out to the far red, both spectra clearly show the negative peaks caused by ground-state bleaching, (cf., Figure 1). The transient decay signals at all wavelengths were, for both compounds, well described by monoexponential expressions with lifetimes of 2.9 and 3.1 ms for ZnP and H₂P, respectively.

Figure 3b shows two transient decay signals for the Zn–5B–H₂P compound recorded at different wavelengths following excitation at 544 nm. At this wavelength, the ZnP moiety is excited with 90% selectivity (Figure 1). The transient recorded at 470 nm (solid), where the ZnP triplet absorption dominates over the H₂P triplet absorption, was described by a biexponential expression

$$\Delta A(t) = \alpha_1 \exp\left(\frac{-t}{\tau_1}\right) + \alpha_2 \exp\left(\frac{-t}{\tau_2}\right) \quad (2)$$

where both preexponential factors (α_1 and α_2) were positive, τ_1 was 0.55 ms, and τ_2 was identified as the lifetime of the H₂P monomer (3.1 ms). The other transient signal (dashed) was

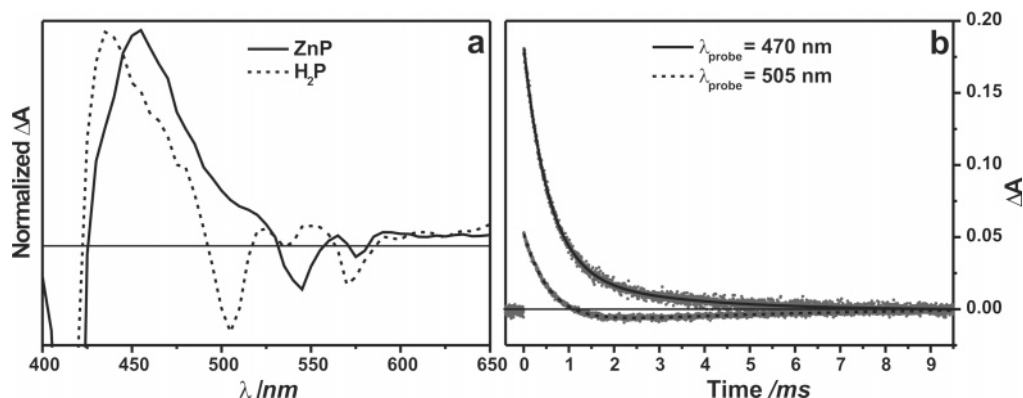


Figure 3. (a) The transient absorption spectra of ZnP (—) and H₂P (---) monomers, after excitation at 544 and 505 nm, respectively, and (b) the transient absorption decay of the Zn–5B–H₂P molecule recorded at 470 (top) and 505 nm (bottom). Excitation at 544 nm. The fit of eq 2 to the data is shown within the respective decay trace. The measurements were performed in 2-MTHF at 150 K.

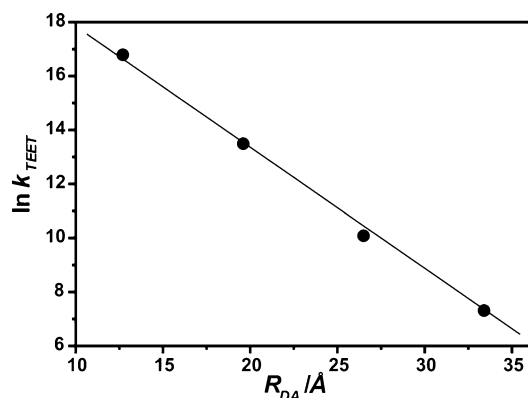


Figure 4. The logarithm of the experimentally determined triplet energy transfer rate, k_{TEET} , in the ZnP-xB-H₂P series of compounds and a linear fit to the data plotted against the donor-acceptor edge-to-edge distance, R_{DA} .

recorded at 505 nm, where the ZnP monomer spectrum has a positive signal and the signal of the H₂P monomer is characterized by a negative feature due to ground-state bleaching. This transient decay signal was also well described by the biexponential expression of eq 2 yielding the same two lifetimes as the transient recorded at 470 nm. However, the preexponential factor of the exponential containing the H₂P lifetime (α_2) was negative. This suggests that the shorter component in the transient decay recorded at 470 nm has the same rate constant as the appearance of a H₂P-bleaching band at 505 nm, a feature that indicates formation of the H₂P triplet. The shorter component can, thus, be ascribed to the ZnP triplet decay. Comparing the lifetimes of the ZnP moiety in the D-B-A compounds with that of the reference compound, $\tau_{ZnP} = 2.9$ ms, yield the TEET rates (Table 1). Another possible contribution to the quenching of the ZnP triplet in the ZnP-xB-H₂P compounds is a diffusion controlled bimolecular process, especially for the long-lived ZnP-5B-H₂P compound. However, even with an optimistic calculation of the diffusion coefficients and quenching efficiencies, a bimolecular process would only account for an apparent transfer efficiency of 7% for the ZnP-5B-H₂P compound. Thus, it can be concluded that bimolecular processes does not occur to any considerable extent.

Table 1 lists the determined lifetimes of the ZnP moieties in D-B-A systems along with the TEET rates (k_{TEET}) and efficiencies (E_{TEET}). Figure 4 shows the logarithm of the TEET rate versus the donor-acceptor edge-to-edge distance, R_{DA} . Since the rate is proportional to the square of the electronic coupling, the slope of a straight line fitted to the experimental data will yield the attenuation factor, β (eq 1). β for TEET in 2-MTHF at 150 K was determined to be $0.45 \pm 0.015 \text{ \AA}^{-1}$, for the ZnP-xB-H₂P series. The uncertainty in β was estimated by assuming an uncertainty of 10% for the determined lifetimes, τ and τ_{ref} .

Theoretical Modeling

This part will give a brief overview of the theoretical method we have derived for modeling the distance dependence of the electronic coupling in the compounds used in the experimental study. The derivation is more thoroughly described in the Appendix. In short, the method is based on previous findings that the torsion angles between the porphyrins and the bridge planes (ω) and the torsions between the phenyl units of the bridge (φ) are the main variables influencing the electronic coupling (Figure 5). Since the rotations are also associated with a change in potential energy, the calculated electronic coupling

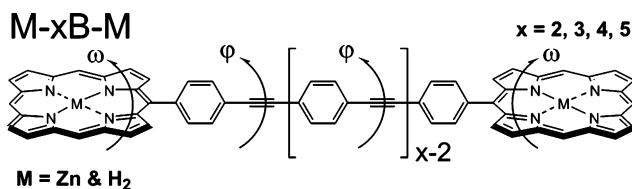


Figure 5. The dihedral angles used to model the conformational dynamics.

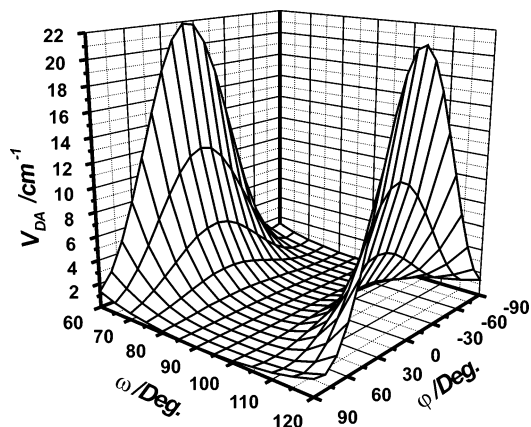


Figure 6. The calculated electronic coupling, V_{DA} , in the Zn-2B-Zn compound for combinations of various porphyrin-bridge (ω) and internal bridge (φ) dihedral angles.

for various conformations should be weighted with their respective Boltzmann factors.

The calculated electronic coupling landscape for the Zn-2B-Zn compound is shown in Figure 6. These results show that there is no connection between the ω and φ dependencies. Therefore, the electronic coupling was well described as a product of two one-dimensional functions, $V(\omega)$ and $V(\varphi)$. Calculations of the electronic coupling were then performed for many symmetric φ -rotations and combinations of φ -rotations for the Zn-xB-Zn systems with the porphyrin-bridge angle (ω) arbitrarily fixed to 60°. Extensive investigations of the resulting bridge conformational dependence of the calculated electronic coupling led to a compact factorized analytical expression describing the electronic coupling as a function of all of the conformational variables (eq A5, Appendix).

Further, the rotation angle dependence of the potential energy was shown to be a sum of the potential energies of the porphyrin-bridge angle rotation (ω) and the bridge unit rotations (φ). The bridge unit rotations were also found to be well approximated by a sum of one-angle rotations making it possible to describe the total potential energy as a sum (eq A8). Having an analytical expression for the electronic coupling as a product of one-variable factors and an expression for the potential energy as a sum of functions of the same variables makes evaluation of the Boltzmann integral (eq A2) very convenient. It allows for factorization of the multidimensional integral into one-dimensional integrals and leads to eq 3, which was used to calculate the average electronic coupling for the M-xB-M systems.

$$\langle V_{DA}(\omega, \varphi_1, \varphi_2, \dots, \varphi_{x-1}) \rangle_x = V_x \cdot \langle V(\omega) \rangle \cdot \prod_{m=1}^{x-1} \langle V(\varphi_m) \rangle = V_x \cdot \langle V(\omega) \rangle \cdot \langle V(\varphi) \rangle^{x-1} \quad (3)$$

From eq 3 it can be deduced that the factor containing the porphyrin-bridge angle, $V(\omega)$, will only shift the coupling by the same amount for all compounds in the series and will, thus,

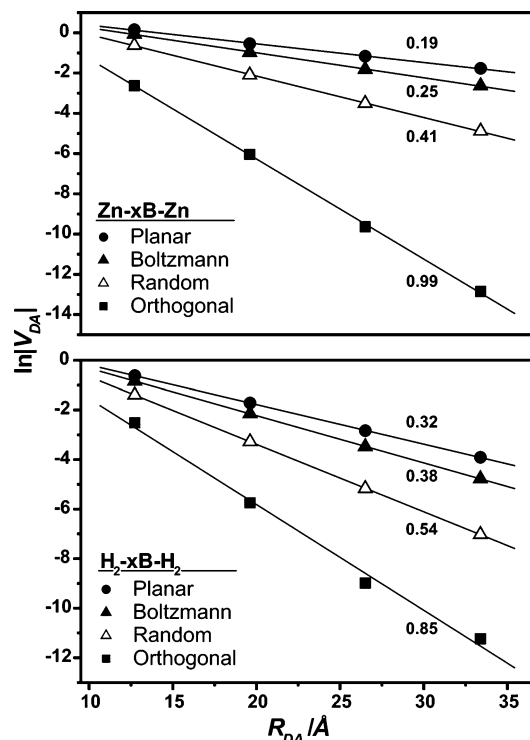


Figure 7. The logarithm of the calculated electronic coupling, V_{DA} , plotted versus the corresponding donor–acceptor separation, R_{DA} , for the model systems Zn–xB–Zn (top) and H₂–xB–H₂ (bottom). The electronic coupling was calculated for planar, Boltzmann averaged, randomized, and bridge units with all phenyl units orthogonal to each other. The resulting damping factors are indicated beside each linear fit.

not affect the distance dependence. The distance dependence will only be governed by the constant factor, V_x , and the factor describing the bridge angle dependence of the electronic coupling, $V(\varphi)$.

Figure 7 shows the logarithm of the calculated electronic coupling plotted versus the corresponding donor–acceptor separation, R_{DA} , for the M–xB–M systems. Apart from a constant factor, the distance dependence is only governed by the bridge conformations. Hence, the electronic coupling was calculated with the same Boltzmann averaged ω -contribution (using the first two terms of eq 3) for four different sets of bridge conformations: planar bridges, bridges with all phenyl units orthogonal to each other, Boltzmann averaged bridge conformations, and randomized bridge units. The randomization was done by setting the bridge conformation energies, $E(\varphi)$, to zero in eq 3 (A11) and, thereby, weighting all bridge conformations equally. A comparison is made between Zn–xB–Zn (top) and H₂–xB–H₂ (bottom). The resulting attenuation factor is indicated by each linear fit.

Discussion

Both the experimental and theoretical distance dependencies are exponential and well described by the McConnell superexchange theory (Figures 4 and 7). The experimentally determined attenuation factor, $\beta = 0.45 \pm 0.015$, is comparable in magnitude to previously reported values for ET in systems with OPE bridging units.^{25,31,36,43,46} This might seem surprising since β for TEET has been shown to be a sum of the β -values for ET and hole transfer (HT).¹⁶ However, as we will show below, β is sensitive to the donor–bridge energetics, which can differ markedly between ET and TEET. We have recently shown that the β -value for a similar set of systems showing ET were 0.29

± 0.04 which is, as expected, smaller than the present value for TEET.²⁹ A recent study of TEET in systems with Ru(terpy)₂/Os(terpy)₂ donor/acceptor couple and a similar set of OPE bridges yielded a much smaller value, $\beta = 0.11 \pm 0.01$.²⁴ This clearly contradicts a common notion that β is a bridge-specific parameter independent of the attached donor and acceptor. In fact β is not *bridge* specific but *system* specific since it is a function of the energy gap between the donor and the bridge chromophores according to^{43,44,46,64}

$$\beta = \frac{2}{R_0} \ln \left| \frac{\Delta}{\nu} \right| \quad (4)$$

Here R_0 is the “effective length” of a bridge-unit, Δ is the energy gap between the donor and an energy level representing the individual bridge-sites, and ν is the electronic coupling between adjacent subunits within the bridge. The higher triplet energy of the donor chromophore in ref 24 (~ 1500 cm^{−1}) along with lower triplet energies of the bridge units due to alkoxy-substitution (~ 1000 cm^{−1}, estimated from TD–DFT calculations on methoxy-substituted 2B) result in a smaller Δ for this series. If we assume that the “effective length” of a bridge-unit, $R_0 \approx 6.9$ Å (from DFT calculations), and the electronic coupling elements between the subunits of the bridges, ν , are unaffected by the difference in substitution pattern, we can easily estimate the effect of a changed Δ on the attenuation factor according to

$$\beta_2 = \beta_1 - \frac{2}{R_0} \ln \left| \frac{\Delta_1}{\Delta_2} \right| \quad (5)$$

The average donor–bridge energy gap in our study is approximately 4000 cm^{−1} (Δ_1) (Figure 2) and the corresponding estimated gap for the systems in ref 24 is 1500 cm^{−1} (Δ_2). Using eq 5, with these Δ -values yield an attenuation factor of 0.15 for the series in ref 24. This analysis is sensitive to the choice of both R_0 and Δ . But the values used above are reasonable and illustrate well the impact of variations in energetics on β . Thus, the big difference in attenuation factors (0.45 vs 0.11) between the two series of compounds is well accounted for by the difference in the donor–bridge energy gaps. The impact on the attenuation factor of varying the donor–bridge energy gap also becomes apparent when comparing the Zn and H₂-systems of the theoretical investigation (Figure 7). The main difference between these two series is the energy splitting between the donor and bridge excited states. The free-base porphyrin has a lower triplet energy and will, thus, give a larger energy difference between the donor and bridge sites. As can be deduced from Figure 7, this results in a smaller coupling and a larger attenuation factor for the H₂–xB–H₂ systems than for the Zn–xB–Zn systems. The effect of the donor and bridge energetics on the attenuation factor inspired us to perform a comprehensive theoretical investigation of this particular phenomenon.⁶⁵

The good fit of the simple expression of McConnell superexchange theory to the experimental and theoretical data could be considered to be coincidental since the electronic coupling element is also dependent on the energy difference between the donor and bridge chromophores

$$V_{DA} \propto \frac{V_{DB}V_{BA}}{\Delta E_{DB}} \quad (6)$$

This energy difference is clearly not constant, but changes as the distance is increased in the series (Figure 2).⁶⁶ The

dependence of the TEET rate on the energy difference, ΔE_{DB} , has been studied earlier^{21,34,35} and was found to be much weaker than the distance dependence. Going from the ZnP–2B–H₂P system to the ZnP–5B–H₂P system would, on energetic grounds alone, increase the coupling about three times, but the experimental results indicate that the coupling is around 115 times smaller in the ZnP–5B–H₂P system.

Since the TEET process occurs from the excited triplet state of the ZnP moiety to a resonant state on the H₂P moiety, the Zn–xB–Zn model systems should most accurately describe the energetics during the tunneling process in the ZnP–xB–H₂P systems. The following discussion will, thus, focus on the theoretical results for the Zn–xB–Zn series. The first term of eq 3 is an angle-independent constant specific for the bridge-length, and the second term, $V(\omega)$, is the same throughout the series. The derivation of an attenuation factor that can be compared to experimental results will, thus, mainly depend on the integral describing the contribution from the bridge conformation (eq A11). The "real" set of bridge conformations is expected to give rise to an attenuation factor between that of a planar bridge and a bridge with all phenyl groups orthogonal to each other. Thus, the attenuation factor should have a value between 0.19 and 0.99 (Figure 7, top). A Boltzmann averaged bridge conformation yields an attenuation factor of 0.25, a value that is not in agreement with the experimental value (0.45), while a randomized bridge conformation gives a damping factor of 0.41 in excellent agreement with the experimental results. This might seem counter intuitive, but even if the rotation barriers of the bridge units (Figure 10) is 3 times smaller the derived β -value would only reach 0.3. A randomized bridge structure is in line with previous studies of similar systems utilizing the OPE bridge units.^{31,36,43,46} They observed that the conformational dynamics of the bridge unit has a pronounced influence on the ET rate and the theoretical work achieved best agreement with experimental results for a randomized bridge conformation. Recent molecular dynamics simulations on a system based on the 2B chromophore also strongly supports that OPE bridges have randomized structure.⁶⁷

Conclusions

We have experimentally and theoretically investigated the distance dependence of TEET in a series of porphyrin based D–B–A systems. Comparison of the theoretical and experimental results suggests that the bridge conformation, described by the dihedral angles between the individual phenyl groups of the bridge, can be considered to be totally randomized on the time-scale of the transfer process. The method of calculating the distance dependence of the electronic coupling was found to successfully reproduce the experimental results and we predict this method to be useful for describing the electronic coupling in other systems.

Appendix

The goal of this part of the work is to give a thorough derivation of the theoretical method that has been used for modeling the distance dependence of the electronic coupling. The derivation will be given in a train-of-thought manner and will begin with some properties of the model systems. The most important is that the porphyrin-bridge (ω) and the bridge (φ) rotations have been found to be the main variables influencing the electronic coupling in these systems (Figure 5).⁸ Previous studies found that, for the Zn–3B–Zn system, the electronic coupling is increased as the porphyrin-bridge angle (ω) is rotated from an orthogonal configuration toward a more coplanar

configuration. Concerning the influence of the bridge structure, it was found that a more planar bridge promotes electronic coupling whereas a center unit orthogonal to the adjacent units efficiently decreases the coupling. This coupling dependence might appear logical if one studies the McConnell model for superexchange mediation by a bridge consisting of x homologous units:⁴³

$$V_{DA} = V_{DB} \cdot \prod_{i=1}^{x-1} \left(\frac{v_i}{\Delta} \right) \cdot \frac{V_{BA}}{\Delta} \quad (\text{A1})$$

Here, the total electronic coupling (V_{DA}) is factorized into a donor–bridge coupling (V_{DB}), a bridge–acceptor coupling (V_{BA}), and $x - 1$ internal coupling elements between adjacent bridge units (v_i). The bridge sites are separated from the donor–acceptor energy level by a common energy gap (Δ). All of the coupling elements in this model (V_{DB} , v_i , and V_{BA}) are favored by coplanarity of the π -systems of the individual units which is also clearly reflected in the conformational behavior of the electronic coupling in our model systems. It is also important to note that any rotation is associated with a change in ground-state potential energy. The lowest potential energy conformation, for the ground state of the experimentally studied systems (series 1 in Chart 1), is when both porphyrin planes are orthogonal to the bridge plane, $\omega = 90^\circ$, (because of steric hindrance from the β -methyl groups of the porphyrin) and when the bridge is planar, all $\varphi = 0^\circ$.

Since the conformation of the system is associated with a ground-state potential energy, the electronic coupling for a certain conformation must be weighted accordingly, and the experimental transfer rate should be compared to the Boltzmann averaged calculated electronic coupling:

$$\langle V(\omega, x, \varphi_1, \varphi_2, \dots, \varphi_{x-1}) \rangle = \frac{\int e^{-E_s(\omega, \varphi_1, \varphi_2, \dots, \varphi_{x-1})/RT} \cdot V(\omega, x, \varphi_1, \varphi_2, \dots, \varphi_{x-1}) \cdot d\omega \cdot d\varphi_1 \cdot d\varphi_2 \cdot \dots \cdot d\varphi_{x-1}}{\int e^{-E_s(\omega, \varphi_1, \varphi_2, \dots, \varphi_{x-1})/RT} \cdot d\omega \cdot d\varphi_1 \cdot d\varphi_2 \cdot \dots \cdot d\varphi_{x-1}} \quad (\text{A2})$$

It can easily be imagined that evaluating the integral in eq A2 will be increasingly difficult as the bridge gets longer and more variables are added. Efforts will, therefore, be put into finding ways to simplify the evaluation of eq A2. To this end, we will need analytical expressions for the angle dependencies of the electronic coupling and the ground-state potential energy.

As a starting point, the electronic coupling was calculated for the series of symmetric Zn–xB–Zn systems with planar bridges. The results are shown in Figure 8, and it was found that the data could be fitted to a common mathematical expression weighted by a bridge-length dependent factor, V_x :

$$V_{DA}(\omega, x) = V_x \cdot (\cos^2 \omega + V_\omega \cos^4 \omega) \quad (\text{A3})$$

where V_ω is a constant common to all systems ($V_\omega = 36$).

Figure 6 shows the calculated electronic coupling landscape for Zn–2B–Zn for various porphyrin-bridge (ω) and bridge (φ) rotations. After careful scrutiny of these data it can be shown that the total electronic coupling can be described as a product of one porphyrin-bridge angle (ω) dependent factor and one bridge rotation angle (φ) dependent factor. A factorized dependence of the total electronic coupling is also derived in the McConnell model (eq A1) which further motivates the factorized angle dependence. Fittings to mathematical expressions confirmed the factorization to be valid which also was

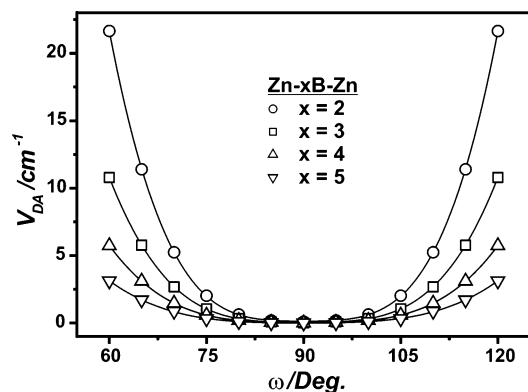


Figure 8. The calculated electronic coupling, V_{DA} , for the Zn- x B-Zn systems with planar bridge units. Also shown are fits of eq A3 to the data (lines).

found to be the case for the Zn-3B-Zn system. However, for the Zn-3B-Zn system, the dependence of the internal bridge rotation angle (φ) is much more pronounced. The reason for this was found to originate in that, for this system, the rotation was done around two ethynyl bonds simultaneously in order to maintain an avoided crossing geometry. After careful investigation and fittings to mathematical expressions, it was found that the φ -dependence for the Zn-3B-Zn system could be well described by the φ -dependence of the Zn-2B-Zn system raised to the power of two. After investigations of the other systems, the overall dependence for the bridge conformational dynamics of all systems was found to be well described by products of functions describing one-angle rotations. The one-angle rotation functions were all found to be very similar and the overall conformational dependence was found to be well described by products of one average function ($\cos^{2.5}\varphi_m$) where the product was made over the number of ethynyl bonds rotated around simultaneously, $x - 1$:

$$V_{DA}(\varphi_1, \varphi_2, \dots, \varphi_{x-1}) = \prod_{m=1}^{x-1} \cos^{2.5}\varphi_m; -90 \leq \varphi_m \leq 90 \quad (\text{A4})$$

In summary, the evaluation of the electronic coupling calculations concluded that, within a good approximation, the overall conformational dependence of the electronic coupling of a system with a bridge consisting of x units can be described by the following:

$$V_{DA}(\omega, x, \varphi_1, \varphi_2, \dots, \varphi_{x-1}) = V_x \cdot (\cos^2\omega + V_\omega \cos^4\omega) \cdot \prod_{m=1}^{x-1} \cos^{2.5}\varphi_m \quad (\text{A5})$$

where $x - 1$ is the total number of ethynyl bonds in the bridge unit, V_x is a bridge-length dependent constant, and the constant V_ω is common to all systems.

Having derived a compact expression for the electronic coupling as a function of the specified conformational parameters we now turn to investigating the potential energy landscape. Calculating the energy dependence for rotation of the porphyrin-bridge angle, the model system is not expected to give correct values since the systems used in the experimental study have methyl groups in the α -positions providing steric hindrance. Thus, for calculations of this dependence compound 3 in Chart 1 was used. This model differs only slightly, in ways that has minimal impact on the rotation barrier, from the monomer used in the experimental study. Further we also

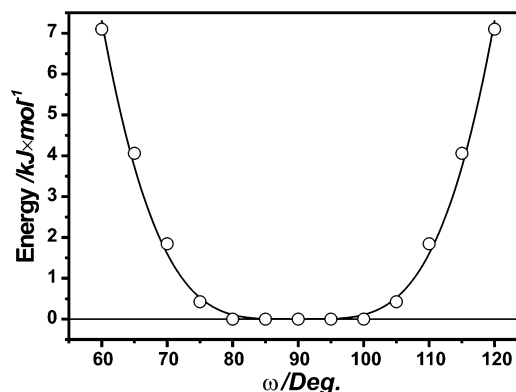


Figure 9. The calculated energy dependence of rotation of a phenyl unit of a zinc-diphenyl-octamethyl porphyrin (compound 3 in Chart 1), and the fit of eq A6 to the data.

assume that replacing the bridge unit with a single phenyl unit will have minimal effect on this rotation barrier. The calculations were performed so that the angle between the phenyl unit and the plane made by the two meso- α -bonds (ω) was held constant and all other variables were optimized. The variation of the angle was done incrementally in steps of five degrees, between 90 and 60 degrees. Due to symmetry the angle dependency between 90 and 120 degrees was assumed to be the same as that between 90 and 60 degrees. The result from this procedure is shown in Figure 9, together with the best fit of eq A6 to the data giving $E_\omega = 117 \text{ kJ} \times \text{mol}^{-1}$.

$$E(\omega) = E_\omega \cos^4\omega \quad (\text{A6})$$

The impact of porphyrin-bridge angle (ω) rotation on calculations of the potential energies of the ethynyl bond (φ) rotations was assumed to be negligible. This allows for the total potential energy to be described as a sum of the two variables and, thus, the ethynyl bond rotation energy calculations were done on bridge systems without porphyrins. As was the case for the porphyrin-bridge rotation energy calculations, the studied angle was incrementally varied and all other parameters were optimized. A full incremental analysis was performed for the 2B and 3B bridge units. For the longer bridges the same angular dependence as for 2B and 3B was assumed, and the energies for the orthogonal and planar conformations were calculated to determine the amplitude of the function. The calculations were done for all bridge lengths with different number of ethynyl bonds rotated simultaneously. The results from this procedure are displayed in Figure 10 and show that the energy barriers bunch together for the same number of simultaneous bond rotations, more or less independent of bridge length. This allows for an approximate description of the bridge potential energy as a sum of one angle rotations, with $E_\varphi \approx 4.5 \text{ kJ} \times \text{mol}^{-1}$:

$$E(\varphi_1, \varphi_2, \dots, \varphi_{x-1}) = E_\varphi \sum_{m=1}^{x-1} \sin^2\varphi_m \quad (\text{A7})$$

Thus, the total potential energy can be described by the following:

$$E_x(\omega, \varphi_1, \varphi_2, \dots, \varphi_{x-1}) = E_\omega \cos^4\omega + E_\varphi \sum_{m=1}^{x-1} \sin^2\varphi_m \quad (\text{A8})$$

where E_ω and E_φ are constants common to all systems. The expressions for the conformational dependence of the electronic coupling (eq A5), and the potential energy (eq A8) allow for

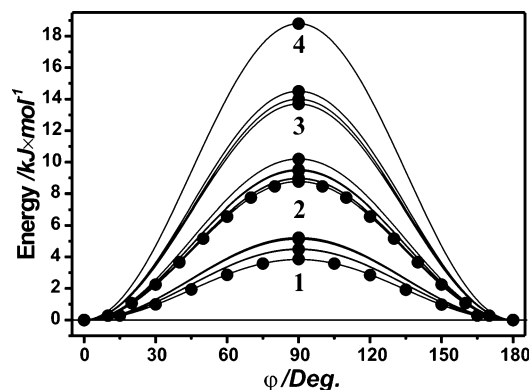


Figure 10. The calculated potential energy for rotation around a varying number of ethynyl bonds simultaneously in the bridge units (filled circles) together with fits of eq A7 to the data (lines). The number of bonds rotated simultaneously is indicated below each group of curves.

convenient evaluation of the Boltzmann integral (eq A2). As expected, when the coupling dependence is a product of dependencies of the different variables and the energy is a sum of dependencies over the same variables, we can factorize the integral according to the following:

$$\langle V_{DA}(\omega, \varphi_1, \varphi_2, \dots, \varphi_{x-1}) \rangle_x = V_x \cdot \langle V(\omega) \rangle \cdot \prod_{m=1}^{x-1} \langle V(\varphi_m) \rangle = V_x \cdot \langle V(\omega) \rangle \cdot \langle V(\varphi) \rangle^{x-1} \quad (\text{A9})$$

where V_x is a bridge-length dependent constant and the average couplings are given by

$$\langle V(\omega) \rangle = \frac{\int e^{-E_\omega \cos^4 \omega / RT} \cdot (\cos^2 \omega + V_\omega \cos^4 \omega) \cdot d\omega}{\int e^{-E_\omega \cos^4 \omega / RT} \cdot d\omega} \quad (\text{A10})$$

and

$$\langle V(\varphi) \rangle = \frac{\int e^{-E_\varphi \sin^2 \varphi / RT} \cdot \cos^{2.5} \varphi \cdot d\varphi}{\int e^{-E_\varphi \sin^2 \varphi / RT} \cdot d\varphi} \quad (\text{A11})$$

The problem of calculating $\langle V_{DA}(\omega, \varphi_1, \varphi_2, \dots, \varphi_{x-1}) \rangle$ for a given bridge consisting of x units, thus, reduces to evaluate the integrals of eqs A10 and A11 once, and to calculate the electronic coupling for each system with the planar bridge to obtain the bridge-length dependent constant, V_x .

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