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# Excitation energy transfer in donor–bridge–acceptor systems

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This perspective will focus on the mechanistic aspects of singlet and triplet excitation energy transfer. Well defined donor–bridge–acceptor systems specifically designed for investigating the distance and energy gap dependencies of the energy transfer reactions are discussed along with some recent developments in computational modeling of the electronic coupling.

## 1. Introduction

For intermolecular excitation energy transfer to be of practical use in technical applications it has to be, in addition to highly efficient, both predictable and reproducible. Such behavior is only expected to be realized in geometrically well-defined assemblies of donors and acceptors, such as the structurally highly complex antenna complexes found in the photosynthetic apparatus.<sup>1–4</sup> The donor–acceptor assemblies must therefore be held together by different highly directional bonding interactions, ranging from strong covalent interactions to weak intermolecular ones.<sup>5</sup> The influence imposed on the transfer process by a molecular bridge linking a donor and an acceptor opens up the possibility to tune the outcome of the transfer process. It is likely that the excitation energy transfer process has to be tunable or even switchable in many of its future applications. Knowledge about the relationship between the molecular structure of the intervening medium and its ability to mediate the interaction responsible for the transfer process will therefore be of utmost importance in the development of future optoelectronic devices.

The focus of this perspective is to highlight some of the experimental work that has appeared in the literature lately concerning excitation energy transfer mediated by various

bridges between excitation energy donors and acceptors. References will also be made to theoretical progress reported in the field. Bridge mediated transfer in well defined donor–acceptor systems has recently been reviewed and in ref. 6–9 the interested reader may find additional information.

## 2. Singlet energy transfer

### 2.1 The energy transfer phenomena

Transfer of excitation energy between the donor and the acceptor moieties of a donor–bridge–acceptor, D–B–A, system can occur by three distinctly different mechanisms: trivial transfer through emission and reabsorption of a photon, sequential transfer *via* a hopping mechanism and coherent transfer. At least one intermediate state is populated during the sequential transfer of excitation energy from the donor to the acceptor, whereas no intermediate states are populated in the coherent transfer.

Sequential transfer:  $D^*B-A \rightarrow D-B^*A \rightarrow D-B-A^*$

Coherent transfer:  $D^*B-A \rightarrow D-B-A^*$

The sequential energy transfer requires that the intermediate states are energetically attainable at the experimental conditions. The following discussion will concentrate on coherent transfer, *i.e.* it is assumed that the energy of the singlet and triplet excited states of the bridges in the discussed D–B–A systems are sufficiently larger than that of the donor so as not to be thermally accessible.

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Many factors influence the rate for electron and energy transfer reactions. In the semi-classical description of electron transfer reactions the rate is given by the Marcus equation, eqn (1).

$$k_{\text{ET}} = \sqrt{\frac{\pi}{\hbar^2 k_{\text{B}} T \lambda}} V^2 \exp\left(-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_{\text{B}} T}\right) \quad (1)$$

Here the driving force,  $\Delta G^0$ , the reorganization energy,  $\lambda$ , and the electronic coupling,  $V$ , are the molecular parameters (Fig. 1) that determine the rate. Both energy and photoinduced electron transfer reactions can be described as non-radiative decay processes and as long as the electronic coupling is sufficiently weak (diabatic coupling), the rates are governed by the Fermi Golden rule, eqn (2):

$$k_{\text{if}} = (2\pi/\hbar) V_{\text{if}}^2 \text{FCWD} \quad (2)$$

where the Franck–Condon weighted density of states (FCWD) accounts for the conservation of energy and describes the influence from the nuclear modes of the system. Unlike the singlet excitation energy transfer (SEET) reactions where this factor can be estimated from spectroscopic data, *vide infra*, the Franck–Condon weighted density of states for triplet energy or electron transfer reactions are approximated by the Gaussian dependence on the driving force (eqn (1)).

Compared to electron transfer and triplet excitation energy transfer, the mechanism for coherent singlet excitation energy transfer is complicated by the fact that it originates from two different donor–acceptor interactions working in concert. Transfer of singlet excitation energy is made possible by both a classical electrostatic Coulomb interaction and a quantum

mechanical electron exchange interaction. Triplet excitation energy transfer is, similarly to electron transfer, dominated by the electron exchange interaction.

The rate constant for excitation energy transfer due to the Coulomb interaction can in the dipole–dipole approximation be calculated according to eqn (3).<sup>10</sup> The original form of this equation was derived by Förster.<sup>11</sup>

$$k_{\text{EET}}^{\text{Förster}} = C \frac{\kappa^2 (|d_{\text{D}}||d_{\text{A}}|)^2}{n^4 R_{\text{DA}}^6} J_{\text{DA}} \quad (3)$$

In eqn (3)  $C$  refers to a constant. The orientation factor  $\kappa$  accounts for the relative alignment of the transition dipole moments  $d_i$  of the donor and acceptor components positioned at a centre-to-centre distance  $R_{\text{DA}}$  apart. The screening effect on the dipole–dipole interaction of the medium in which the donor and acceptor is embedded is accounted for by the refractive index  $n$ .<sup>12</sup> Finally, energy conservation is assured by the term  $J_{\text{DA}}$ , which is computed as the spectral overlap between the normalized donor emission and acceptor absorption. This term is related to the Franck–Condon weighted density of states. The electrostatic through-space interaction, can cause energy transfer over large distances. Transfer over distances in the range of 1 nm to 10 nm is routinely analyzed within the framework of the Förster model. At small donor–acceptor distances the point dipole approximation breaks down and it is to be expected that the distance dependence deviates from what is predicted by eqn (3). Due to the finite speed of the virtual photon establishing the Coulomb interaction, other distance dependencies are also found at very large donor–acceptor distances.<sup>13</sup>

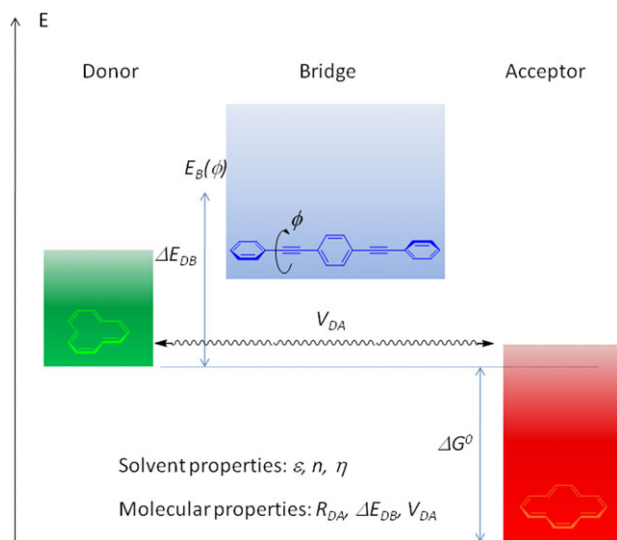
In contrast to the long-range electrostatic through-space interaction, the electron exchange interaction relies on orbital overlap, *i.e.* physical contact, between the donor and the acceptor. Assuming that the donor and acceptor molecules have orbitals with an average van der Waals radius  $L$  and that these at long distances decay exponentially, Dexter arrived at the following expression for the electron exchange energy transfer rate constant.<sup>14</sup>

$$k_{\text{EET}}^{\text{Dexter}} = C' J_{\text{DA}} e^{-\frac{2R_{\text{DA}}}{L}} \quad (4)$$

In eqn (4)  $C'$  refers to a constant and  $R_{\text{DA}}$  is now the edge-to-edge distance between the donor and the acceptor.

## 2.2 Influence of bridge structures on the SEET efficiency in D–B–A systems

The efficiency for excitation energy transfer by the exchange mechanism is expected to show stronger distance dependence than that for transfer by the dipole–dipole mechanism. The former decays exponentially whereas the latter falls-off with the sixth power of the donor–acceptor distance. Long-range excitation energy transfer between donors and acceptors, separated by distances substantially longer than their van der Waals radii, such that their mutual orbital overlap is vanishingly small, is therefore expected to occur *via* the Coulomb mechanism. Molecular arrays with large donor–acceptor distances that display SEET rates and efficiencies that are larger, or show a stronger distance dependence than those that can be accounted for by the Förster expression,



**Fig. 1** The excitation energy and electron transfer phenomena depend on a multitude of molecular and medium (solvent) parameters. This schematic energy diagram highlights the important relation between these molecular and solvent parameters. A donor and acceptor are held together at a distance  $R_{\text{DA}}$  by a molecular bridge that provide a tunneling barrier of height  $\Delta E_{\text{DB}}$ . The electronic coupling between the donor and acceptor,  $V_{\text{DA}}$ , is sensitive to both the width ( $R_{\text{DA}}$ ) and height ( $\Delta E_{\text{DB}}$ ) of the tunneling barrier and is therefore an important molecular control parameter when designing donor–acceptor systems with predictable rates for electron and energy transfer.

have therefore been given much attention. Deviations from what is expected on the basis of the two idealized models have most frequently been ascribed to superexchange, a long-range through-bond Dexter type of transfer.<sup>15–17</sup> More recently, mediated Coulomb type transfer affected by the linker connecting donor and acceptor has been put forward to explain observed anomalies.<sup>18,19</sup>

### 2.3 Superexchange

Superexchange refers to an influence of intervening structures on the electronic exchange coupling between donor and acceptor moieties. Superexchange interactions have regularly been inferred to explain unexpectedly efficient long-range electron transfer in donor–acceptor assemblies linked together by covalent bonds, as well as hydrogen bonds and other weak intermolecular bonding interactions. As a result of the mediating capability of the molecular structures linking donor and acceptor together, the fall-off in electronic exchange coupling with increasing donor–acceptor distance is much slower than expected from the fall-off in orbital overlap. The distance dependence for electron transfer rate constants has frequently been shown to follow the empirical exponential expression:

$$k = k_0 e^{-\beta R_{DA}} \quad (5)$$

The rate constant  $k$  decreases exponentially with increasing edge-to-edge distance from its maximum value  $k_0$  at van der Waals contact between the donor and the acceptor. The attenuation factor  $\beta$  has often been used as a characteristic measure of the mediating ability of a molecular framework.

The indirect exchange coupling between an electron donor and acceptor mediated by the connecting linker was originally developed by McConnell for electron transfer in the context of charge transfer in anionic radicals.<sup>20</sup> Based on the superexchange phenomena, first introduced by Kramers<sup>21</sup> in 1934 to explain interactions between paramagnetic ions, and the assumption that the donor and the acceptor was linked by a bridge of  $n$  identical repeating units, McConnell arrived at the following expression for the bridge-mediated donor–acceptor electron exchange interaction  $V_{DA}$ :

$$V_{DA} = \frac{v_{DB} v_{BA}}{\Delta E_{DB}} \left( \frac{v_{BB}}{\Delta E_{DB}} \right)^{n-1} \quad (6)$$

Accordingly, the donor–acceptor interaction is proportional to the exchange interactions between the donor and the bridge,  $v_{DB}$ , between the bridge and the acceptor,  $v_{BA}$ , and between the repeating units,  $v_{BB}$ , to the power of  $n - 1$ . Moreover, it depends inversely on the energy  $\Delta E_{DB}$  required to remove an electron from the donor and place it on a single repeating bridge unit.

If the edge-to-edge donor–acceptor distance  $R_{DA}$  is equal to  $n \times r_b$  where  $r_b$  is the length of one repeating bridge unit, then the electronic exchange interaction can be shown to decay exponentially with increasing donor–acceptor separation:

$$V_{DA} = V_0 e^{\frac{R_{DA}}{r_b} \ln\left(\frac{v_{BB}}{\Delta E_{DB}}\right)} = V_0 e^{-\frac{\beta}{2} R_{DA}} \quad (7)$$

This is in accordance with the observed decrease of the electron transfer rate constant with increasing donor–acceptor

distance according to eqn (5) above. The attenuation factor,  $\beta$ , can then be identified as:

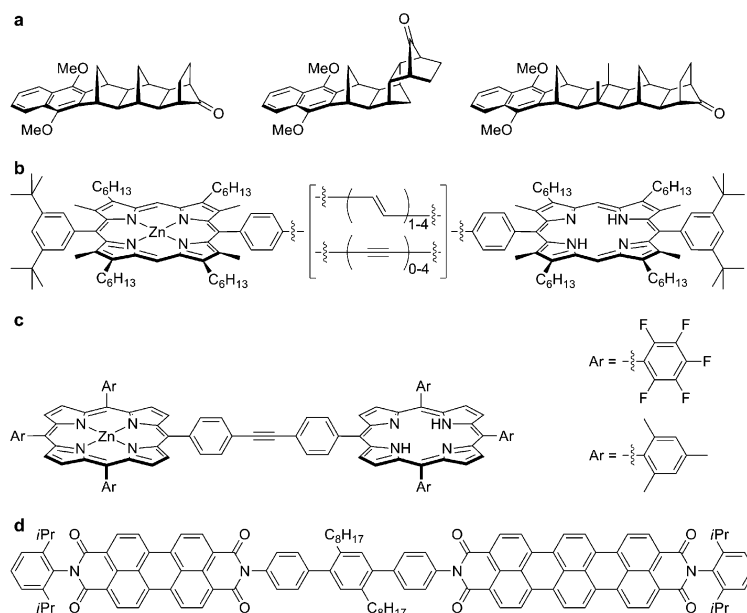
$$\beta = \frac{2}{r_b} \ln \left| \frac{\Delta E_{DB}}{v_{BB}} \right| \quad (8)$$

Short-range (Dexter type) excitation energy transfer is parallel to electron transfer in that it can be formalized as a two-electron exchange event. In analogy to electron transfer, the range for this type of transfer can be expanded by a bridge-mediated superexchange contribution.

Experimental evidence for through-bond mediated SEET started to accumulate in the beginning of the 1980s.<sup>22,23</sup> The decisive experimental results were presented in 1988 by Verhoeven and his group who reported on unexpectedly fast SEET between naphthalene and carbonyl chromophores covalently linked by  $\sigma$ -bonds in a series of rigid systems of varying length, see Fig. 2a.<sup>24</sup> The observed transfer rates decreased exponentially with the number of  $\sigma$ -bonds separating the donor and acceptor. The distance dependence was too shallow to be accounted for by the normal Dexter expression but too strong to conform to the Förster expression. The deviation from established models was advocated to be the result of a long-range through-bond coupling, a through-bond mediated exchange interaction. The best fit straight line obtained from a plot of the logarithm of the transfer rate *versus* the number of  $\sigma$ -bonds separating the donor and the acceptor gave a slope of  $-1.45$  per bond. Assuming a carbon–carbon bond length of  $1.54 \text{ \AA}$  this corresponds to a  $\beta$  value of  $0.94 \text{ \AA}^{-1}$ .

In analogy to what had already been shown for electron transfer,<sup>26,29</sup> Verhoeven and his group could also convincingly demonstrate that SEET was markedly dependent on the configuration/geometry around the  $\sigma$ -bonds connecting the donor and the acceptor.<sup>25</sup> Although the changes in arrangements had only a negligible effect on the through space distance between the donor and acceptor, the transfer was more efficiently mediated by saturated hydrocarbon chains with an all-*s-trans* configuration than those with one or more *gauche* or *s-cis* arrangements. These observations confirmed earlier predictions that through-bond interactions should be mediated more efficiently *via* saturated hydrocarbons in an all-*s-trans* configuration compared to alkyl chains in other conformations.<sup>30,31</sup> Comprehensive theoretical support for the idea of a through-bond mediated SEET was presented in 1996 by Scholes and Harcourt.<sup>32</sup> A four electron, four orbital model was employed to properly account for both the orbital overlap dependent interactions and long-range electromagnetic interactions. They deduced an expression for the electronic transfer matrix element for the excitation interaction that in its simplest form reduces to the expression for superexchange interactions derived by McConnell (eqn (6)). The similarity between excitation energy transfer and electron transfer was further emphasized by the observation that the leading orbital overlap dependent terms could be deduced to describe simultaneous electron and hole transfer from the donor to the acceptor. This verified the interpretation of Dexter-type triplet excitation energy transfer put forward by Closs *et al.* eight years earlier.<sup>33</sup>

In 1995, Osuka and coworkers reported efficient SEET transfer over  $27 \text{ \AA}$  in polyene- and polyene-linked



**Fig. 2** Donor–bridge–acceptor systems for which detailed studies of the SEET rates have been reported in the literature. (a) Examples of  $\sigma$ -bridged systems studied by Verhoeven and co-workers.<sup>24–26</sup> (b) The two series of polyene- and polyynyl-linked diporphyrins studied by Osuka and co-workers.<sup>27</sup> (c) Diphenylethynylene linked bisporphyrin in which the effect of orbital ordering was studied by Lindsey and co-workers.<sup>28</sup> (d) An oligophenylene linked perylene-diimide/terrylene-diimide system studied by Fückel *et al.*<sup>19</sup>

diporphyrins, see Fig. 2b.<sup>27</sup> The efficient long-range transfer was accounted for by a through-bond exchange mechanism. Applying the same empirical expression as for electron transfer for the distance dependence of the rate constant, the attenuation factor  $\beta$  for SEET in these systems was determined to be 0.08 and 0.1  $\text{\AA}^{-1}$  for the polyene and the polyynyl bridges, respectively. These attenuation factors are significantly smaller than that observed for Verhoeven's saturated systems, *i.e.* fully  $\pi$  conjugated bridges are much better conduits for electron exchange interactions than the  $\sigma$ -frameworks.

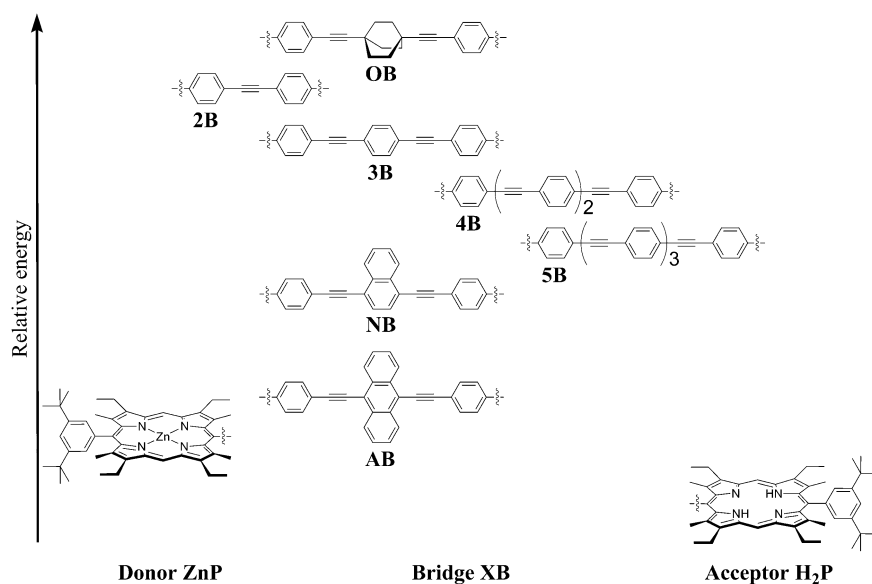
The contribution of an orbital dependent exchange interaction to long-range SEET through a  $\pi$ -conjugated bridge was nicely demonstrated by Strachan *et al.* in 1997.<sup>28</sup> This was achieved by a comparative study of two diphenylethynylene linked bisporphyrin systems, see Fig. 2c. Realized by the proper choice of substituents, the orbital order of the nearly degenerate HOMO – 1 and HOMO levels of the donor porphyrin was reversed in the two systems. In this way the orbital pattern of the HOMO orbital was drastically altered—from a sizable density to a node at the position of attachment of the bridge/linker. The alteration in pattern of the HOMO orbital, singly occupied in the excited donor, caused a change in communication between the donor and the acceptor, resulting in one order of magnitude difference in transfer rate constants for the two systems. This clearly demonstrates the importance of the “local” interaction between the donor and the bridge identified in the McConnell superexchange model. It also illustrates the two-electron nature of exchange dominated energy transfer depending both on the HOMO and the LUMO of the donor.

In 1997 we reported experimental evidence supporting the energy gap dependence that could be predicted by the superexchange model if applied to excitation energy transfer.<sup>34</sup> The

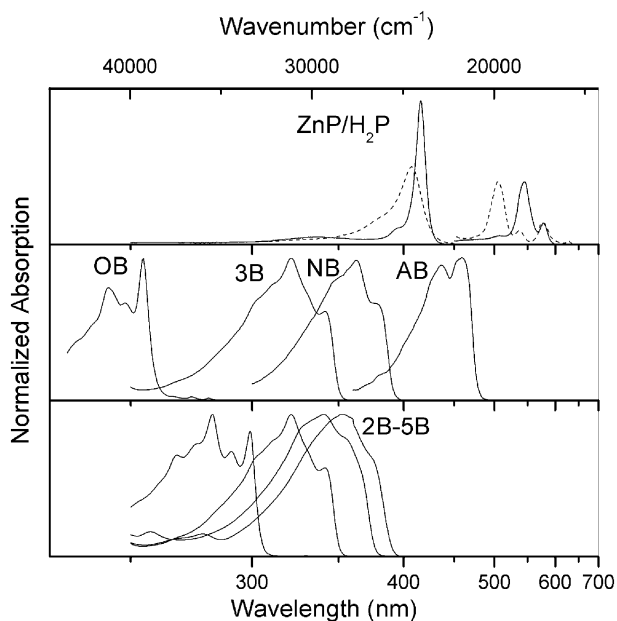
energy gap,  $\Delta E_{\text{DB}}$ , between the donor and bridge was defined as the differences in energy required to excite them to their first singlet excited states. The energy difference was varied throughout the series of zinc(II)/free-base diporphyrin systems studied by changing the electronic structure of the bridges while keeping their length constant, see Fig. 3 and 4.

Acknowledging that Coulomb and exchange interactions occur in concert, we explored the bridge-mediated energy transfer contribution,  $k_{\text{Med}}$ , to a first approximation as the difference between the observed rate,  $k_{\text{Exp}}$ , and the Coulomb contribution calculated according to the Förster equation,  $k_{\text{Förster}}$ :  $k_{\text{Med}} = k_{\text{Exp}} - k_{\text{Förster}}$ . In accordance with superexchange theory, the square root of the so-defined rate constants for mediated energy transfer was found to be proportional to the reciprocal energy gap between the bridge and the donor ( $(k_{\text{Med}})^{-1/2} \propto 1/\Delta E_{\text{DB}}$ ).<sup>34,35</sup> The relative Coulomb contribution to the overall energy transfer in these systems was found to be significantly decreased by coordination of pyridine to the zinc porphyrin. The coordination results in a significant decrease of the spectral overlap between the donor emission and acceptor absorption (Fig. 5), which leads to smaller Förster rate constants for the systems. Although not proven, the relative contribution from the two mechanisms seems to be sensitive to this spectroscopic alteration, and has been used to experimentally deconvolute their respective contributions.

The energy of the bridge located electronic states is usually covariant with the length of conjugated bridges (Fig. 4). In 2006 we reported on the influence of this covariation on singlet excitation energy transfer in a series of zinc(II)/free-base diporphyrin arrays linked by oligo(ethynylphenylene) bridges of varying length, see Fig. 3.<sup>36</sup> An expression for the rate constant  $k_{\text{med}}$  for bridge-mediated energy-transfer was derived by combining the reciprocal dependence on the square



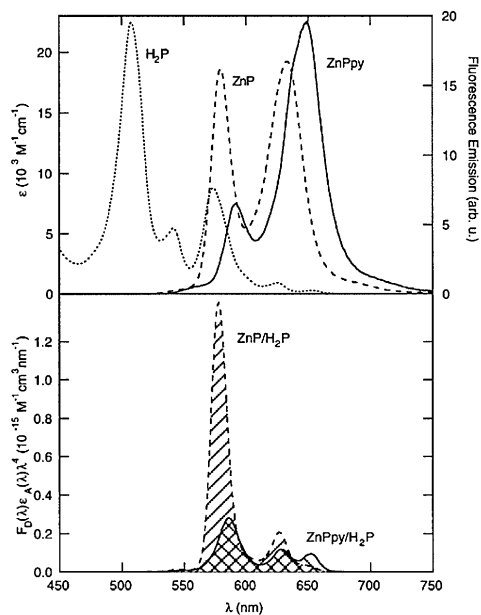
**Fig. 3** The series of zinc/free base porphyrin based D–B–A systems studied in the Albinsson–Mårtensson group. The series are abbreviated ZnP–XB–H<sub>2</sub>P, where X denotes the specific bridge structure. The series are divided into two subsets: the energy gap series ZnP–RB–H<sub>2</sub>P, with constant D–A distance, and the distance series ZnP–*n*B–H<sub>2</sub>P. The various central groups in the energy gap series are denoted by R = O, 3, N, or A. In the series with varying D–A distances, the length of the bridge is indicated by the number *n* that equals the number of phenylene units in the bridge. Pyridine coordinated zinc porphyrin is abbreviated, Zn(py)P.



**Fig. 4** Absorption spectra for the different components of the D–B–A systems shown in Fig. 3. The first (top) panel shows the absorption spectra of the absorption spectra of zinc porphyrin ZnP (—) and the free-base porphyrin H<sub>2</sub>P (---). The two lower panels show the two subsets of bridges; the energy gap series **RB** and the length series **nB**. The spectra were recorded in methylene chloride at room temperature.

of the energy gap,  $\Delta E_{DB}$ , and the approximate exponential distance dependence indicated by the superexchange model (combining eqn (5) and (6)).

$$k_{\text{Med}} = \frac{\alpha}{\Delta E^2} e^{-\beta R_{\text{DA}}} \quad (11)$$



**Fig. 5** The top panel shows the absorption spectrum of H<sub>2</sub>P (···) and the emission spectra of ZnP (---) and Zn(py)P (—) in CHCl<sub>3</sub> at room temperature. The bottom panel shows the spectral overlap between H<sub>2</sub>P and ZnP (///) and between H<sub>2</sub>P and Zn(py)P (\\\).

Here  $\alpha$  is a new pre-exponential factor,  $\beta$  the usual attenuation factor, and  $R_{\text{DA}}$  the donor–acceptor distance. Linearization of the equation and fitting to the data from the series of D–B–A systems with varying bridge lengths and minor variations in bridge energies gave a value of 43.5 for  $\ln \alpha$  and an attenuation factor  $\beta$  of 0.25 Å<sup>-1</sup>. The  $\beta$  value obtained in this way has, in contrast to most attenuation factors reported in the literature, been corrected for the changes in energy gaps between the

donor and the bridges. The uncorrected value obtained was  $0.20 \text{ \AA}^{-1}$ . Using this corrected value for the attenuation factor and the same expression in the analysis of the transfer rates obtained from the D–B–A systems with constant donor–acceptor distance but with large variations in bridge energies gave a value of 42.2 for  $\ln \alpha$ . The close conformity between the two values of  $\ln \alpha$  strengthens the validity of eqn (11) and emphasizes the caution by which the attenuation factor for SEET should be regarded as a bridge specific parameter. It should be considered a system specific parameter, that depends on the nature of the bridge as well as the energy levels of the donor and the acceptor with which the bridge is combined. This point will be further discussed in the context of triplet energy transfer below.

#### 2.4 Bridge mediated Coulomb energy transfer

It is well known from classical electrostatics that Coulomb interactions will decrease with increasing relative permittivity, *i.e.* increasing polarizability, of the medium. The reducing effect on energy transfer originating from a Coulomb interaction of the medium surrounding the donor and acceptor is accounted for by its refractive index in the Förster approximation, which equals the square root of the high frequency relative permittivity. These quantities are bulk properties of isotropic media related to the mean polarizability averaging over all directions. It is unlikely that such quantities can correctly account for the effect of the usually highly ordered media between donors and acceptors in covalently linked arrays or well-ordered supramolecular arrays held together by weak intermolecular forces. The bridges connecting donor and acceptor are highly directional with largely anisotropic polarizabilities.

A thorough theoretical discussion of bridge mediated Coulomb coupling and virtual photon mediated excitation energy transfer was published by Volhard May in 2008.<sup>13</sup> It was shown that the standard formula for mediated exchange interactions by intermediate levels (virtual states) could be derived for singlet excitation energy transfer in a three-site system mimicking a D–B–A system, provided that the levels were off-resonant to the initial and final levels. Consequently, bridge mediated coupling is not restricted to orbital overlap dependent exchange coupling but can involve electromagnetic coupling as well. Taking the full electromagnetic interaction into account, an expression for virtual photon mediation was derived. At short D–A distances, less than 20 nm, this expression agrees exactly with the one derived by Förster. At longer D–A distances the transfer rate is increased by several orders of magnitude compared to the Förster rate due to contributions from photon mediated singlet excitation energy transfer (approaching trivial transfer). Further, due to different dependencies on the orientation of the donor and the acceptor transition dipole moments, the energy transfer can be due exclusively to virtual photon mediation if the donor–acceptor geometry is such that the Förster orientation factor  $\kappa$  is equal to zero.

In the same year Fückel *et al.* published a study on donor–acceptor systems consisting of perylene-diimide and terrylene-diimide chromophores linked by oligophenylene

spacers, see Fig. 2d.<sup>19</sup> It was found experimentally that the SEET rate significantly exceeded the rate predicted from Förster theory. Theoretically the reason for the discrepancy was looked for in the approximative nature of the Förster theory and the bridge effect on the Coulomb coupling. At donor–acceptor distances longer than 5 nm and in the absence of any linking oligophenylene moiety, calculations of the coupling between isolated donors and acceptors showed that the dipole–dipole approximation is in good agreement with the full electromagnetic (Coulomb) coupling. Introduction of the bridge structure between the donor and acceptor in the model systems caused an increase in electronic coupling. A significantly larger increase was obtained when the full electromagnetic (Coulomb) coupling was calculated than when the dipole–dipole approximation was applied. This observation demonstrates the importance of higher-order multipole terms in bridge-mediated singlet excitation energy transfer. The exchange integrals were monitored and found to be small and, thus within this approximation it was concluded that the origin of the energy transfer was solely electrostatic. The multipole field emitted by the donor was altered by the polarizability of the linking oligophenylene structure resulting in a larger transfer rate than expected. Although the bridge in the topical systems augmented the overall donor–acceptor coupling, it was pointed out that the bridge-mediated coupling can either enhance or screen the donor–acceptor interaction depending on the relative phase compared to the direct donor–acceptor interaction. It was also emphasized that the bridge-mediated coupling does not open up a second channel for energy transfer; it just modifies the overall coupling.

In yet another theoretical study from the same year, Chen *et al.* showed that the dipole–dipole coupling is enhanced if the donor and acceptor transitions moments are aligned longitudinally to a polarizable bridge.<sup>18</sup> On the one hand, a twenty fold rate enhancements was predicted for favored model systems. On the other hand, a 30% reduction in energy transfer rate was predicted for arrays with donor and acceptor transitions oriented perpendicular to the long axis of the polarizable bridge. The authors also explored the effect of arrays of molecular coin piles intervening the donor and acceptor to explore the effect of large transversal polarizability relative to the transfer direction. The overall conclusion is that the Coulomb interaction can be modulated substantially by a polarizable bridge and the effect is strongly dependent on the relative orientation of the bridge. The authors also conclude that the Coulomb coupling can show atypical distance dependence. How rapidly the coupling decrease with distance depends on the orientation of the donor and acceptor transition dipole moments. Thus, an observed deviation from the  $R^{-6}$  distance dependence for SEET is not sufficient to conclude that exchange or higher-order multipole coupling contributes to the overall transfer rate.

Phenomenological studies of transfer phenomena are most successfully performed, as exemplified above, on geometrically well defined systems of components with their electronic integrity and intrinsic preserved. This approach may allow for the development of compact and predictive models based on simple structural and intrinsic parameters, such as absorption

and emission bands, oscillator strengths and radiative rate constants. The application side, however, is far more difficult to predict; superior transfer properties might be achieved by modulation of the intrinsic properties of some of the components in the array. Resulting from strong coupling between donor and bridge and/or between bridge and acceptor, changes in transition dipole moments and absorption spectra have been discussed to contribute to the efficient SEET observed in high-performing materials.<sup>10,19,37–39</sup>

All in all, a complicated picture for the singlet excitation energy transfer process emerges, revealing a complex dependence on geometrical parameters of the molecular array and on the intrinsic properties of its components. Several interrelated interactions work in concert. In general, this process can hardly be expected to be predicted with high accuracy except for simplified limiting cases.

### 3. Triplet excitation energy transfer

In this section we will describe how quite detailed information about triplet excitation energy transfer (TEET) in bridged donor–acceptor molecules can be extracted from combined experimental and theoretical studies. TEET has attracted much less attention than singlet excitation energy transfer and electron transfer. However, for systematic studies on how molecular properties control these transfer phenomena, and when comparing to quantum mechanical calculations, it is often beneficial to investigate TEET. Here we will describe how the transfer of triplet energy in D–B–A systems directly depends on several molecular design parameters such as: (1) the donor–bridge energy gap, (2) the donor–acceptor distance, (3) the influence of the distance dependence by the donor–bridge energy gap. TEET rates also depend indirectly on temperature through the thermally activated conformations with different electronic coupling. This chapter ends with presenting a model that have the possibility to predict the electronic coupling in D–B–A systems in general and the attenuation factor,  $\beta$ , in particular.<sup>40</sup>

#### 3.1 Relation between triplet energy and electron transfer reactions

As been discussed above (section 2.1) the electronic coupling for energy transfer can be split into additive Coulomb and exchange interactions leading to two different mechanisms for energy transfer. For the exchange interaction the transfer of excitation energy can be viewed as the simultaneous transfer of two electrons between the donor and the acceptor, *i.e.* electron transfer (ET) and hole transfer (HT). This is the dominating mechanism for most triplet energy transfer reactions since the Coulombic interaction is negligible for forbidden acceptor and donor electronic transitions. Due to this relation between the transfer of triplet excitation energy governed by the exchange mechanism and the transfer of electrons, it has been observed for saturated bridges that the electronic couplings for the two processes are related, eqn (12).<sup>33,41</sup>

$$|V_{\text{TEET}}| = C|V_{\text{ET}}||V_{\text{HT}}| \quad (12)$$

where  $C$  is a system specific constant. With this relation as a starting point we can envisage obtaining information on

molecular parameters dictating the rate for electron or triplet energy transfer from either measurement. As will be argued below it is often easier to study triplet energy transfer both experimentally and with theoretical methods.

From the semi-classical expression for the electron transfer rate (eqn (1)) it follows that the electronic coupling can be derived from the intercept of a plot of  $\ln(kT^{\frac{1}{2}})$  vs.  $T^{-1}$ . This procedure is often used but assumes that the parameters that enter the expression are temperature independent. As will be discussed thoroughly below, the electronic coupling can sometimes be strongly dependent on temperature. Further, many solvent properties that in one way or the other influence the transfer rates also depend on temperature. Thus, when studying the temperature dependence of intra-molecular charge and energy transfer processes it is important to account for these solvent effects.<sup>42</sup> Changes in solvent viscosity can have a significant impact on the effective electronic coupling, which has been shown to be crucially dependent on conformation.<sup>40,43–50</sup> In addition, both the dielectric constant and refractive index, two important solvent properties that influence both the reorganization energy and the driving force, are functions of temperature and to some extent also on viscosity. All these solvent induced effects obscure the effects of molecular parameters, such as energy gaps and conformation, on the studied transfer reactions.

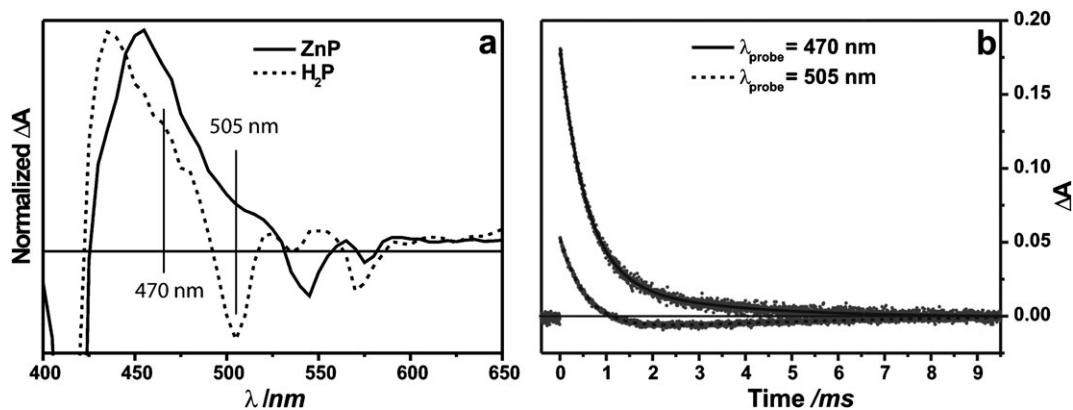
To facilitate comparison between experimental and theoretical results it is advantageous to reduce the influence of solvent induced effects on the parameter of interest. In this respect, studying TEET is very useful since the process does not involve the movement of charge. In marked contrast to ET, the effects of dielectric stabilization and variations in the outer reorganization energies are minimal. For this reason much of what will be presented below are results from theoretical and experimental studies of TEET.

#### 3.2 Mediated triplet energy transfer—energy gap dependence

The zinc/free-base porphyrin arrays (Fig. 3) that originally were designed for studies of SEET, also provide excellent systems for exploration of TEET.<sup>18,44,45,51</sup> In contrast to SEET, triplet excitation energy transfer is not expected to occur over large distances *via* the Coulomb mechanism because of the spin forbidden transitions involved. Instead, long-range TEET is expected to be mediated by through-bond or superexchange interactions (*vide supra*).

The triplet excited-states  $^3\text{ZnP}^*\text{-XB-H}_2\text{P}$  were efficiently formed from the singlet excited systems initially formed upon selective photoexcitation of the zinc porphyrin. The quantum yield for intersystem crossing for unconjugated zinc porphyrins is generally high, usually around 0.9.<sup>52</sup> The occurrence of triplet excitation energy transfer was then established by monitoring the triplet dynamics of the  $^3\text{ZnP}^*$ - and  $^3\text{H}_2\text{P}^*$ -states at 150 K (Fig. 6). Note that the lowest triplet state of both the zinc and the free-base 5,15-aryl- $\beta$ -octaalkylporphyrin consist of two conformers interrelated *via* a mother–daughter relationship.<sup>44</sup> This conformational transformation is thermally activated and virtually shut down at 150 K compared to the time scale of TEET, which greatly simplifies the analysis of the transfer kinetics.<sup>53</sup> At this temperature, the triplet





**Fig. 6** (a) The transient absorption spectra of ZnP (—) and H<sub>2</sub>P (---) monomers, after excitation at 544 and 505 nm, respectively, and (b) the transient absorption decay of the ZnP-5B-H<sub>2</sub>P molecule recorded at 470 (upper curve) and 505 nm (lower curve). Excitation at 544 nm. The fit of a double exponential decay model to the data is shown within the respective decay trace. The measurements were performed in 2-MTHF at 150 K.

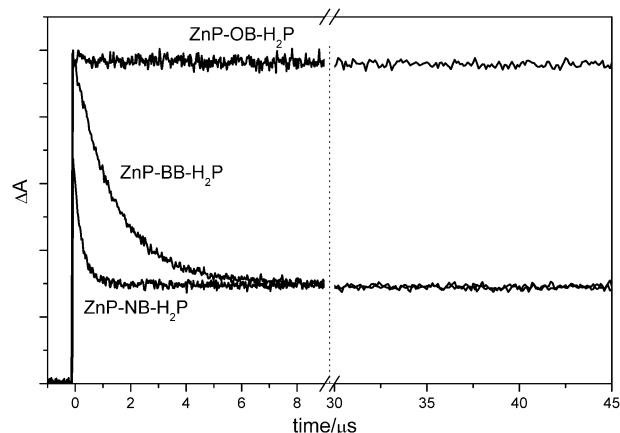
excited state lifetimes of the zinc and free-base porphyrin reference compounds are 2.9 and 3.1 ms, respectively.

Except for the OB system, substantially decreased lifetimes for the triplet-excited donors were observed at 470 nm where the <sup>3</sup>ZnP\* state absorption dominates (Fig. 6). Corroborating TEET, the corresponding rise-times were observed at a wavelength dominated (434 nm) by the acceptor triplet excited-state absorption.<sup>45</sup> The rate of <sup>3</sup>H<sub>2</sub>P\* formation due to TEET could also be resolved from kinetic traces recorded at 505 nm where the free-base porphyrin shows a negative absorption (bleaching) in the differential absorption spectrum (Fig. 6 shows a representative example). A very strong temperature dependence was also observed for the TEET process and this will be discussed below.<sup>50</sup>

We found a strong dependence of the observed TEET on the nature and the dynamics of the bridges in our systems. The OB bridge was observed to be insulating, whereas the fully conjugated bridges provided efficient electronic coupling. In accordance with the superexchange model, a substantial difference in rates between the 3B and the NB systems was observed, see Fig. 7.<sup>51</sup> In fact, the rates for these two systems were shown to be directly proportional to  $\Delta E_{DB}^{-2}$ , where  $\Delta E_{DB}$  is the donor-bridge energy gap. This energy gap was estimated from the spectroscopically observed triplet state energies for the zinc porphyrin and the various OPE-based bridging chromophores, and it should be close to the effective barrier through which the triplet energy exciton is tunneling (*cf.* the model of simultaneous hole and electron transfer). As described above, similar observations have been made for superexchange dominated singlet energy transfer<sup>34,35</sup> and electron transfer<sup>54</sup> in related D-B-A systems. Other examples of systems that have triplet energy or electron transfers showing strong dependence on the tunneling barrier height have been reported.<sup>55-59</sup>

### 3.3 Distance dependence of triplet energy transfer

The rate constant for TEET has been shown to fall off exponentially with distance in the vast majority of experimentally investigated systems.<sup>45,60,61</sup> This can be ascribed to an exponentially decaying electronic coupling (eqn (7)) since the other factors in eqn (1) are virtually independent of the

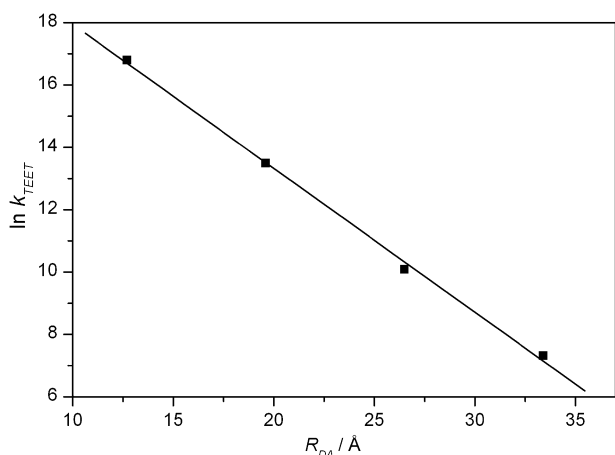


**Fig. 7** Triplet state decay ( $\lambda_{\text{pump}} = 532$  nm,  $\lambda_{\text{probe}} = 470$  nm) for the ZnP-OB-H<sub>2</sub>P, ZnP-3B-H<sub>2</sub>P, and ZnP-NB-H<sub>2</sub>P in 2-MTHF at 150 K. Please note that the two abbreviations 3B and BB symbolize the same bridge.

donor-acceptor separation (at least for TEET). Fig. 8 shows the TEET rates that were first measured at 150 K and found to decay exponentially with distance in the ZnP-nB-H<sub>2</sub>P series with an attenuation factor of  $0.45 \text{ \AA}^{-1}$ .<sup>45</sup> The largest rate ( $2.0 \times 10^7 \text{ s}^{-1}$ ) was observed for the system with the shortest 2B bridge and the slowest transfer ( $1.5 \times 10^3 \text{ s}^{-1}$ ) was observed in the longest 5B system. This attenuation factor was very different from the  $\beta$ -value determined for the quite similar system studied by Harriman and co-workers.<sup>60</sup> They found when attaching the Ru(terpy)<sub>2</sub>/Os(terpy)<sub>2</sub> donor/acceptor couple to OPE oligomers of varying length that  $\beta = 0.11 \text{ \AA}^{-1}$ . As will be shown in the next paragraph this, at the time quite unexpected, result is perfectly well explained within the generally accepted McConnell model for superexchange interactions.

### 3.3 The interplay between distance and energy gap dependencies in TEET reactions

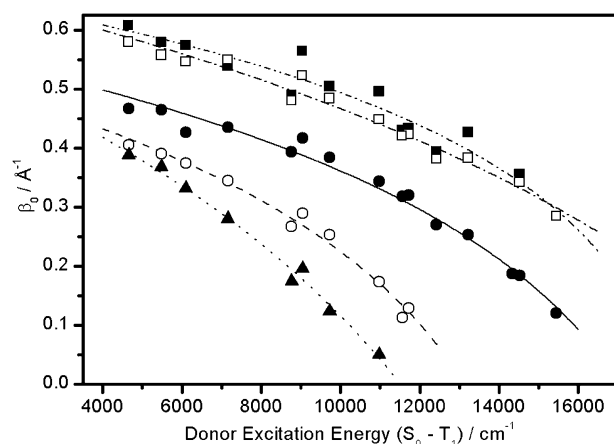
When studying both the distance and tunnelling energy gap dependencies of ET and TEET in a set of homologous molecules it falls naturally to ask what the relationship



**Fig. 8** The logarithm of the experimentally determined triplet energy transfer rate,  $k_{\text{TEET}}$ , in the ZnP-*n*B-H<sub>2</sub>P series of compounds and a linear fit to the data plotted against the donor-acceptor edge-to-edge distance,  $R_{\text{DA}}$ .

between the two is. In both the original formulation of the tunnelling phenomena<sup>62,63</sup> and the superexchange model<sup>20</sup> the tunnelling energy gap determines the decay parameter,  $\beta$ . The simple relation between  $\beta$  and the energy gap,  $\Delta E_{\text{DB}}$ , obtained from the McConnell model for superexchange is shown in eqn (8).<sup>64</sup> Naturally this relation holds only for bridges with repetitive subunits assuming a constant donor-bridge energy gap. Interestingly, eqn (8) quantitatively explains the different  $\beta$ -values found for the OPE-bridge appended with zinc/free-base porphyrins<sup>45</sup> and with Ru(terpy)<sub>2</sub>/Os(terpy)<sub>2</sub><sup>60</sup> as donor/acceptor simply as a consequence of the smaller donor-bridge energy gap for the latter system (*vide supra*). The mean energy gaps for the zinc/free base porphyrin systems and the Ru(terpy)<sub>2</sub>/Os(terpy)<sub>2</sub> are 4000 cm<sup>-1</sup> and 1500 cm<sup>-1</sup>, respectively.

In order to test the validity of eqn (8) and to explain some disturbing inconsistencies in the literature we decided to calculate the electronic coupling for TEET and ET as a function of D-A distances in bridged systems, *i.e.* to computationally estimate attenuation factors and their tunneling gap dependencies. These calculations were done for a series of donors/acceptors with different triplet energies (different LUMO energies for ET) and thereby for different donor-bridge energy gaps. The calculated  $\beta$ -values for quite an extensive selection of systems (Table 1 shows the 5 different bridges each appended with 10–15 donor/acceptor pairs) are summarized in Fig. 9 together with fits to eqn (8).<sup>40</sup> From this study it is obvious that the attenuation factor could not be regarded as a bridge specific parameter and that each system has a unique value depending on the specific combination of donor, bridge and acceptor. However, it also shows that the  $\beta$ -values varied in a systematic way with the donor-bridge energy gap and that unique bridge values of the electronic coupling between subunits,  $\nu_{\text{BB}}$ , could be obtained. Additional experimental evidence for the validity of eqn (8) was found in an elegant series of papers by Gray and co-workers.<sup>65,66</sup> In this study bimolecular electron transfer between randomly distributed donors and acceptors in frozen glasses was investigated and the tunneling energy gap was varied by simply changing solvent.



**Fig. 9** The calculated  $\beta$ -values (symbols) for TEET together with fits of eqn (8) to the data (lines) for planar OPE (solid circles and solid line), OPV (open circles and dashed line), OF (solid squares and dash-dotted line), OP (open squares and dash-dot-dotted line), and OTP (solid triangles and dotted line) bridge structures.

**Table 1** The repeating bridge structures used to investigate the energy gap and temperature dependencies of the attenuation factors for TEET

Name	Bridge structure <sup>a</sup>	
Oligophenylene		<b>OP</b>
Oligofluorene		<b>OF</b>
Oligo- <i>p</i> -phenyleneethynylene		<b>OPE</b>
Oligophenylenevinylene		<b>OPV</b>
Oligothiophene		<b>OTP</b>

<sup>a</sup>  $n = 2-5$  in this study.

The calculations presented in Fig. 9 were done for planar bridge structures. In most experimental situations at finite temperatures, however, the bridge can adopt multiple conformations with large variations in the ability to mediate the electronic coupling. We therefore also wanted to understand how bridge conformations influence the attenuation factor and ultimately how the electronic coupling and  $\beta$ -values at finite temperatures could be predicted. This is the topic of the rest of this section.

### 3.4 Conformational effects on electron exchange interactions

In this part we will explore the effect of molecular conformation on the bridge-mediated through-bond mechanism of TEET. The torsion angles between planes of rigid units within the D–B–A structure are shown to modulate the electronic coupling. This sometimes leads to quite strong temperature dependencies of the transfer process and this was explored, both experimentally and theoretically.<sup>40,67</sup> The magnitude of the impact of temperature on the electronic coupling is here modeled by taking into account both the Boltzmann distribution of conformations and the conformational dependence of the electronic coupling.

Many theoretical and experimental studies have found that the most important conformational variables that govern the electronic coupling in D–B–A systems built up by a series of individually planar  $\pi$ -conjugated systems are the dihedral angles between individual units as exemplified in Fig. 10.

To explore the conformational dependence of the electronic coupling through the OPE bridged D–B–A systems depicted in Fig. 3, we performed a series of calculations where the internal bridge angles (the  $\phi$ -angles in Fig. 10) were varied systematically. As expected the attenuation factor for TEET was strongly dependent on the bridge conformation. The values ranged from what is expected for a  $\pi$ -conjugated bridge ( $\beta \sim 0.2\text{--}0.3 \text{ \AA}^{-1}$ ) when all phenyls were co-planar, to values of the magnitude observed for  $\sigma$ -bridged systems ( $\beta \sim 1.0 \text{ \AA}^{-1}$ ) when all phenyls were mutually orthogonal (Fig. 11).

According to Arrhenius the temperature dependence of the rate constant,  $k$ , of an activated process is described by  $k = A \exp(-E_a/RT)$ , where  $E_a$  is the activation energy. In complex D–B–A systems, built up by several units, each rotation is associated with a unique rotational energy. It can thus be expected that the temperature dependencies of the transfer processes can be quite complex. If the minimum energy conformation is associated with the highest electronic coupling the transfer rate might even increase with decreasing temperature. This apparent negative activation has been observed for several D–B–A systems in limited temperature intervals.<sup>50,68</sup> The  $\text{ZnP-nB-H}_2\text{P}$  series shown in Fig. 3 may serve as an example. For some of the systems in this series the energy transfer rate increases with decreasing temperature (between 160 and 120 K), as shown in Fig. 12 where the logarithmic TEET rate is plotted *versus* the reciprocal temperature.

In an elegant series of experimental studies Harriman and co-workers probed the effect of the torsion angle between two phenyl units of a bridge separating a  $\text{Ru(II)(tpy)}_2$  donor and an  $\text{Os(II)(tpy)}_2$  acceptor. The average dihedral angle between the phenyl units was controlled by a covalent linker as shown in Fig. 13.<sup>46,48,69,70</sup>

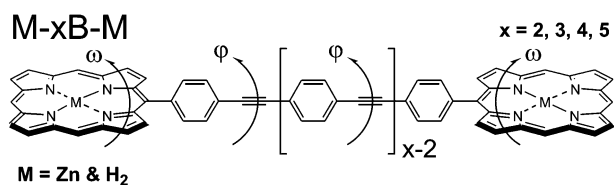


Fig. 10 The dihedral angles used to model the conformational dynamics.

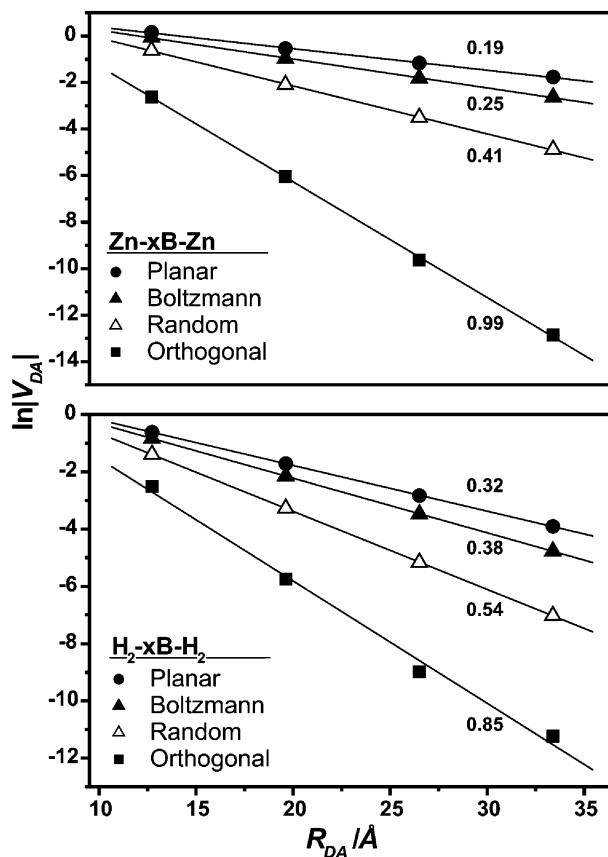


Fig. 11 The logarithm of the calculated electronic coupling,  $V_{DA}$ , plotted *versus* the corresponding donor–acceptor separation,  $R_{DA}$ , for the model systems  $\text{Zn-nB-Zn}$  (top) and  $\text{H}_2\text{-nB-H}_2$  (bottom). The electronic coupling was calculated for planar, Boltzmann averaged, randomized, and bridge units with all phenyl units orthogonal to each other. The resulting attenuation factors (in  $\text{\AA}^{-1}$ ) are indicated beside each linear fit.

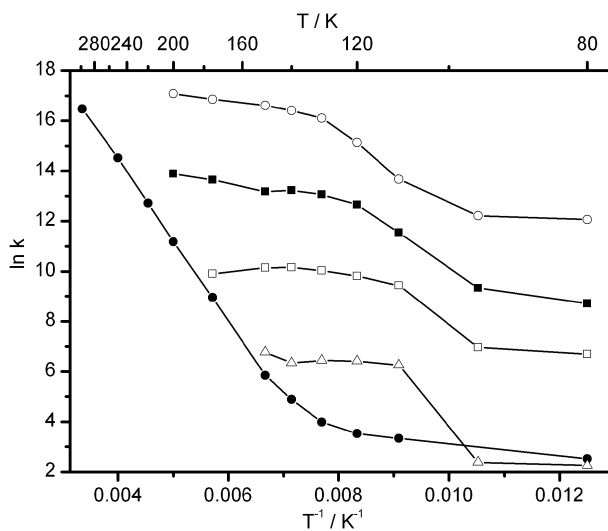
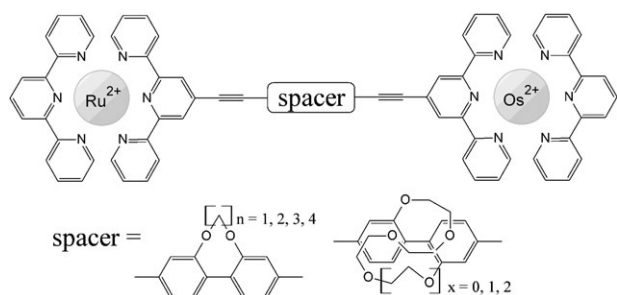


Fig. 12 The logarithmic rate constant for the relaxation to the ground state of the triplets state of the  $\text{ZnP-nB}$  reference compounds ( $\bullet$ ), and the logarithmic rate constants for TEET in  $\text{ZnP-nB-H}_2\text{P}$  with  $n = 2$  ( $\circ$ ),  $3$  ( $\blacksquare$ ),  $4$  ( $\square$ ), and  $5$  ( $\triangle$ ).



**Fig. 13** Molecular structures of the set of systems that Harriman and co-workers used to probe conformational effects on the rate for TEET.

The study revealed a pronounced conformational dependence where the electronic coupling is greatly reduced when the phenyl planes are close to orthogonal. In one of the systems a switch in transfer mechanism, from a combination of through-space and superexchange to a combination of hopping and superexchange, was noted when going from low temperatures and rigid media to high temperatures and fluid media.<sup>71</sup> Furthermore, in this series of studies it was experimentally confirmed that the dihedral angle-dependent electronic coupling for TEET follows the squared dependence of the overlap integral of two mutually rotating  $\pi$ -orbitals.<sup>43,68</sup> This is what would be expected for the dependence of the product of the electronic coupling for ET and HT.<sup>33,41</sup> Thus, for the normalized electronic coupling associated with the dihedral angle,  $\varphi$ , we have:

$$V_{\text{TEET}}(\varphi) = V_{\text{ET}}(\varphi)V_{\text{HT}}(\varphi) = \cos^2\varphi \quad (13)$$

Note that this only applies to the mediation by  $\pi$ -conjugated orbitals. There is also a small contribution from the  $\sigma$ -orbitals that is expected to show a different conformational dependence.<sup>72</sup>

### 3.5 Temperature dependence of TEET

Another, less synthetically demanding, way to control the conformation is to use temperature to vary the distribution of conformations. With this in mind, we have performed a series of parallel theoretical and experimental studies where the conformational impact on TEET in the  $\text{ZnP}-n\text{B}-\text{H}_2\text{P}$  series (see Fig. 3) was investigated.<sup>50,64</sup> Combined with the experimental studies a set of density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were used to derive a model for the Boltzmann averaged electronic coupling. How well the model reproduces the observed trends was evaluated by comparison with the experimental results obtained at different temperatures. The quite good conformity between experiments and model encouraged us to expand the theoretical study and to include a large set of donor and bridge structures with the aim of finding sets of parameters, for both ET and TEET, that would potentially enable *a priori* predictions of  $\beta$ -values.<sup>40</sup>

The quantum chemical calculations were performed using the Gaussian 03 program suite<sup>73</sup> at the B3LYP/6-31G(d) level and have been thoroughly described previously.<sup>40,50,64</sup> The modeling includes the calculation of the potential energy as a function of dihedral angles between the planes of individual

sub-units, identified as being the major parameters modulating the electronic coupling in this type of systems.<sup>40,43,44,46–50,64,68</sup>

There are two sets of dihedral angles relevant for the investigated systems: the dihedral angle between either the donor or the acceptor plane and the plane of the first phenyl unit of the bridge ( $\omega$ ), and a series of dihedral angles between planes defined by neighboring phenyl units of the bridge ( $\varphi$ ) (see Fig. 10). The potential energy as a function of dihedral angle was calculated by changing the angle followed by geometry optimization with respect to all other parameters at each point. For the calculations of the electronic coupling, symmetrical model systems— $\text{D}-n\text{B}-\text{D}$ ,  $n = 2, 3, 4$  and  $5$ —was used. The electronic couplings for ET and TEET were estimated as half the splitting between the LUMO and LUMO + 1 orbitals as well as half the triplet excitation energy difference between the two lowest triplet excited states, respectively. Avoided crossing geometries were achieved by ensuring that the system had a mirror plane or a  $C_2$ -rotation axis that forced the wave function to be equally distributed on the two donor moieties. The rotations described above were always done in such a way that the symmetry was preserved. The approximation of estimating the electronic coupling through state and orbital splitting is expected to be less valid for shorter donor–acceptor distances and when the donor/acceptor and bridge energies are not well separated. In this study we are concerned with systems that operate in the weak to very weak electronic coupling regime where the approximation should be valid.

In order to investigate the conformational dependence of the electronic coupling the angles between the various units were varied in analogy to the procedure described for the potential energy landscape, and for each of these configurations the electronic coupling was calculated. This procedure allowed complete mapping of the electronic coupling landscape for the smallest members of the series of  $\text{D}-\text{B}-\text{A}$  systems. For the larger systems we needed to find ways to reduce the number of independent variables. Through comparison between the complete mapping and models it was found that the total electronic coupling can be approximated by a product of one-parameter functions:  $V(\omega_1, \varphi_1, \dots, \varphi_{n-1}, \omega_2) = V(\omega_1)V(\varphi_1) \dots V(\varphi_{n-1})V(\omega_2)$ . This is the expected result from the McConnell model but was shown to be valid also with directly computed electronic couplings. Further it was found that, to a good approximation, the total energy for a given conformation could be described by the sum of one-parameter energy functions. As a consequence, the total Boltzmann averaged electronic coupling can be factorized into one-parameter functions according to:

$$\begin{aligned} \langle V_{\text{DA}}(\omega, \varphi_1, \varphi_2, \dots, \varphi_{n-1}) \rangle \\ = V_n \langle V(\omega) \rangle \prod_{m=1}^{n-1} \langle V(\varphi_m) \rangle = V_n \langle V(\omega) \rangle \langle V(\varphi) \rangle^{n-1} \end{aligned} \quad (14)$$

Here the bracketed properties are simple averages according to

$$\langle V(a) \rangle = \frac{\int V(a)e^{-E(a)/RT} da}{\int e^{-E(a)/RT} da} \quad (15)$$

where  $a$  represents any of the dihedral angles  $\omega$  or  $\varphi$ .

The derived model (eqn (14) and (15)) was found to give accurate predictions of the electronic coupling and distance dependence for TEET.<sup>50,64</sup> Further it was found that the attenuation factor,  $\beta$ , was independent on the value of  $\omega$ . This can more easily be visualised if one uses the exponential distance dependence (eqn (7)) of the electronic coupling. It then follows that  $\beta$  can be extracted from the derivative of the logarithmic electronic coupling:

$$\beta = -2 \frac{d \ln V_{\text{DA}}}{d R_{\text{DA}}} \quad (16)$$

Thus, the conformational dependence of  $\beta$  can be deduced from:

$$\ln \langle V_{\text{DA}} \rangle = \ln V_n + \ln \langle V(\omega) \rangle + (n-1) \ln \langle V(\varphi) \rangle \quad (17)$$

The first term in eqn (17) is a conformation independent constant that is unique for each bridge length and donor–bridge energy gap ( $\Delta E_{\text{DB}}$ ). These temperature independent constants are unique for each D–A distance and represent the donor–bridge energy gap dependent  $\beta$ -value for a planar bridge structure (*vide supra*). The second term is conformation dependent (donor–bridge angle,  $\omega$ ) but independent of bridge length, and will thus not affect the  $\beta$ -value. It will, on the other hand, provide a major contribution to the total electronic coupling and, thus, to a large extent govern the temperature dependence of the transfer rates. The last term of eqn (17) also depends on conformation and will, since  $n$  varies with  $R_{\text{DA}}$ , be the sole factor governing the conformational dependence of the  $\beta$ -value. Thus, the total  $\beta$ -value can be split into a temperature independent constant that will give the lowest attainable  $\beta$ -value for a given donor–bridge structure ( $\beta_0(\Delta E_{\text{DB}})$ ), and a temperature dependent variable that will reflect the average conformational disorder of the bridge  $\beta(T)$ :

$$\beta_{\text{tot}} = \beta_0(\Delta E_{\text{DB}}) + \beta(T) \quad (18)$$

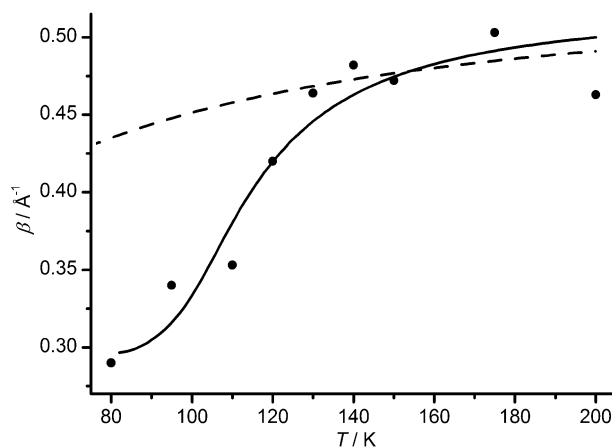
As was discussed above, the  $\beta$ -value depends on the donor–bridge energy gap. According to eqn (18) this only has an impact on the part of the  $\beta$ -value that is independent on conformation and therefore on temperature.

The factor  $\beta(T)$  that governs the temperature dependence of the  $\beta$ -value describes the influence on the electronic coupling due to conformational disorder of the bridge structure. In this factor the electronic coupling for a specific conformation is weighted with its corresponding potential energy. For the OPE bridge structure and some other bridges composed of linked planar  $\pi$ -systems the potential energy approximately follows  $E_\varphi \sin^2 \varphi$ , where  $E_\varphi$  is the rotational barrier height. If the electronic coupling follows a  $\cos^2 \varphi$  dependence the averaged bridge conformational dependence can be evaluated analytically. It turns out that the maximum variation in the temperature dependent part of the attenuation factor can be very simply expressed as  $0 \leq \beta(T) \leq 2 \ln 2/r_b$ , where  $r_b$  is the size of the repeating bridge unit.<sup>40</sup> The same maximum range is expected for all bridge structures with potential energy minima associated with planar conformations. Thus, using this relation, one can easily estimate the maximum effect of rotational disorder on the attenuation factor in any such D–B–A system. Different shapes and heights of the energy barrier for various bridge structures will give different

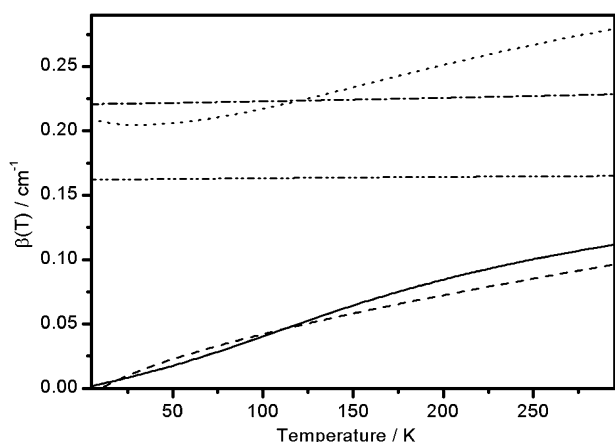
temperature dependencies but *not* affect the maximum range in  $\beta$ -values.

The observed temperature dependence of the TEET rate constants for the OPE bridged systems was shown in Fig. 12. As discussed above, this complex temperature dependence stems from many factors related to both changes in the thermodynamic parameters (driving force, reorganization energy) and the electronic coupling. In addition, the electronic coupling is also expected to contribute to this complexity because various conformational variables respond to temperature in different ways. This is one of the reasons for evaluating the temperature dependence of the attenuation factor instead of that for the transfer rate. As explained in the former paragraph, it is expected to have a less complex conformational dependence. Fig. 14 shows the observed temperature dependence of the attenuation factor for TEET through the ZnP–nB–H<sub>2</sub>P system.<sup>67</sup> The  $\beta$ -values changes significantly, from about 0.5 Å<sup>-1</sup> at “high” temperature to 0.3 Å<sup>-1</sup> at “low” temperature. In order to model the shape of the temperature dependence we had to include the influence of solvent viscosity. This is because at the lowest temperatures the matrix (2-MTHF) forms a solid glass where transfer rates are faster than molecular relaxation. Nevertheless, the experimental  $\beta$ -values ranges from 0.3 to 0.5 Å<sup>-1</sup>, which exactly span the range predicted ( $2 \ln 2/r_b = 0.20 \text{ Å}^{-1}$  with  $r_b = 6.8 \text{ Å}$ ). This result should be regarded as quite strong support for the simple model presented above.

The success of the developed model has encouraged us to extend the theoretical study to include a large set of donors and bridge structures.<sup>40,64</sup> This work is a tentative step towards building a library of parameters to enable *a priori* predictions of  $\beta$ -values when only a few parameters of the building blocks are known. The proposed method to achieve this is based on the donor–bridge energy gap-dependent minimum attenuation factor  $\beta_0(\Delta E_{\text{DB}})$  coupled with the temperature dependent bridge disorder factor,  $\beta(T)$  in accordance with eqn (18). Since the goal is to derive  $\beta$ -values, the main focus of this study is on the bridge structures and the appended donors are just a means to tune the donor–bridge energy gap. The studied



**Fig. 14** Experimentally determined  $\beta$  vs. temperature (solid circles) and fits of the theoretical model to the experimental data using a pure Boltzmann averaging (dashed line) and including viscous activation energy (solid line).



**Fig. 15** The temperature dependent part of the attenuation factor for TEET calculated for the OPE (solid line), OPV (dashed line), OF (dash-dotted line), OP (dash-dot-dotted line), and OTP (dotted line) repeating bridge structures.

bridge systems, oligo-*p*-pehnyleneethynylene (OPE), oligo-phenylenevinylene (OPV), oligothiophene (OTP), oligophenylene (OP), and oligofluorene (OF), are collected in Table 1.

Fig. 15 shows the computed  $\beta(T)$ -values for the 5 bridge structures at temperatures from 0 K to room temperature. The study showed that the bridges can be divided into two types based on their response to temperature changes. On the one hand, the OPE and OPV bridges have planar conformations that are the most energetically favorable and, thus, the  $\beta$ -value will increase as the temperature is raised in accordance with an, on average, less planar bridge structure. **The OP, OF, and OTP bridge structures, on the other hand, have lowest energy conformations that are not planar. For these systems increasing the temperature will simultaneously populate conformations associated with both higher and lower electronic coupling. Consequently, these bridges show a much weaker temperature dependence on their attenuation factors. This behavior has been observed experimentally for OP-bridged systems.**<sup>61</sup>

In summary, this section demonstrates how the attenuation factor for TEET can be understood in terms of donor-bridge energy gaps and the molecular disorder of the bridge. In principle, bridge specific parameters could be derived from experiments or quantum mechanical calculations allowing for *a priori* determination of the temperature independent part of the attenuation factor,  $\beta_0(\Delta E_{DB})$ . In addition, the bridge conformational dependence of the electronic coupling could be mapped for each bridge system. This allows for estimations of the factor,  $\beta(T)$ , which describes the influence of bridge disorder. For a couple of selected examples the total  $\beta$ -value, calculated as the sum of the two factors, have been shown to agree appreciably with literature values for TEET.<sup>40</sup>

#### 4. Concluding remarks

Excitation energy transfer has tremendous impact on modern science. It finds current applications in many fields from analytical assays in biosciences<sup>74</sup> to various optoelectronic devices. Even more importantly, a detailed understanding of these processes will be instrumental for the emerging fields of

molecularly designed harvesting of solar light (solar cells and fuels) and molecular nanoscience (*e.g.* molecular electronics). The design concepts that are discussed in this perspective have started to find their way into these emerging fields, *e.g.* through systematic studies of solar cell materials,<sup>75</sup> artificial photosynthesis<sup>76</sup> and functional nanostructures.<sup>77–79</sup> It is our hope that mechanistic studies of the kind presented here will have an impact on the development of future excitation energy transfer applications.

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