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How Donor−Bridge−Acceptor Energetics Influence Electron Tunneling Dynamics and Their Distance Dependences

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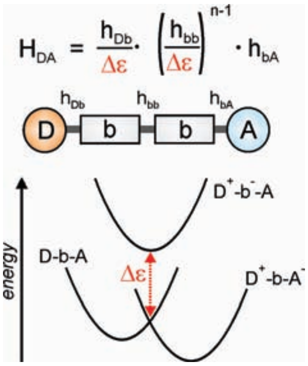

Long-range electron transfer may occur via two fundamentally different mechanisms depending on the combination of electron donor, acceptor, and the bridging medium between the two redox partners. Activating the so-called hopping mechanism requires matching the energy levels of the donor and the bridge. If electrons from the donor can thermodynamically access bridge-localized redox states, the bridge may be temporarily reduced before the electron is forwarded to the acceptor. As a result, electron transfer rates may demonstrate an extremely shallow dependence on distance. When transient reduction of the bridging medium is thermodynamically impossible, a tunneling mechanism that exponentially depends on distance becomes important for electron transport. Fifty years ago, superexchange theory had already predicted that electron transfer rates should be affected by donor−bridge−acceptor energetics even in the tunneling regime, in which the energy gap ($\Delta\varepsilon$) is too large for electrons to hop from the donor onto the bridge. However, because electron tunneling rates depend on many parameters and the influence of donor−bridge energy gaps is difficult to distinguish from other influences, direct experimental support for the theoretical prediction has been difficult to find. Because of remarkable progress, particularly in the past couple of years, researchers have finally found direct evidence for the long-sought but elusive tunneling-energy gap effect.

After a brief introduction to the theory of the tunneling mechanism, this Account discusses recent experimental results describing the importance of the tunneling-energy gap. Experimental studies in this area usually combine synthetic chemistry with electrochemical investigations and time-resolved (optical) spectroscopy. For example, we present a case study of hole tunneling through synthetic DNA hairpins, in which different donor−acceptor couples attached to the same hairpins resulted in tunneling rates with significantly different dependences on distance. Recent systematic studies of conjugated molecular bridges have demonstrated the same result: The distance decay constant (β), which describes the steepness of the exponential decrease of charge tunneling rates with increasing donor-acceptor distance, is not a property of the bridge alone; rather it is a sensitive function of the entire donor−bridge−acceptor (D-b-A) combination. In selected cases, researchers have found a quantitative relationship between the experimentally determined distance decay constant (β) and the magnitude of the tunneling-energy gap ($\Delta\varepsilon$).

The rates and efficiencies of charge transfer reactions occurring over long distances are of pivotal importance in light-to-chemical energy conversion and molecular electronics. Tunneling-energy gap effects play an intriguing role in the formation of long-lived charge-separated states after photoexcitation: The kinetic stabilization of these charge-separated states frequently exploits the inverted driving-force effect. Recent studies indicate that tunneling-energy gap effects can differentiate the distance dependences of energy-storing charge-separation reactions from those of energy-wasting charge-recombination processes. Thus, the exploitation of tunneling-energy gap effects may provide an additional way to obtain long-lived charge-separated states.

Introduction

Charge transfer between distant redox partners is an important fundamental step involved in many biochemical processes including photosynthesis and respiration. In proteins, tunneling of electrons over distances as great as 15 Å is not uncommon, albeit the hopping process also plays an important role in biological electron transfer.[1] In recent

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years, much of the research on long-range electron transfer has focused on the hopping process, often driven by the fact that charge transfer over spectacularly long distances may be observed when this mechanism is operative.[2−4] This Account focuses on the tunneling mechanism and the role played by the so-called tunneling-energy gap, a quantity that may be interpreted as a barrier height associated with the tunneling of charge carriers in a given donor−bridge−acceptor combination. The influence of the tunneling-energy gap on long-range charge transfer rates has long been difficult to capture experimentally; however, recent investigations have provided clear evidence for the long-sought tunneling-energy gap effect. The most relevant findings of some of these studies will be discussed here.

In semiclassical theory, electron transfer rates (k_{ET}) are described as a product of a frequency prefactor, an electronic factor, and a nuclear factor, with the latter defining the well-known Gaussian free-energy (ΔG_{ET}) dependence of electron transfer rates (eq 1).[5]

$$k_{ET} = \sqrt{\frac{4\pi^3}{\hbar^2 \lambda k_B T}} {H_{DA}}^2 \exp\left\{-\frac{(\Delta G_{ET} + \lambda)^2}{4\lambda k_B T}\right\} \qquad (1)$$

Long-range electron tunneling crucially depends on the electronic factor (H_{DA}^2) which can be nonzero even when electron donors and acceptors are separated by many angstroms. This may be understood in the framework of superexchange theory which describes bridge-mediated electronic coupling between distant donors and acceptors. Almost 50 years ago, McConnell developed a mathematical model (eq 2) describing the overall electronic coupling (H_{DA}) in a system in which the donor (D) and acceptor (A) are separated by *n* identical bridging units.[6] In this model, H_{DA} depends on three distinct electronic couplings (Figure 1), namely, on that between the donor and the first bridging unit (h_{Db}), coupling between adjacent bridging units (h_{bb}), and coupling between the last bridging unit and the acceptor (h_{bA}).

$$H_{DA} = \frac{h_{Db}}{\Delta\varepsilon}\left(\frac{h_{bb}}{\Delta\varepsilon}\right)^{n-1} h_{bA} \qquad (2)$$

The fourth parameter in this equation, $\Delta\varepsilon$, is called tunneling-energy gap. This quantity is the difference between the energy of the donor−acceptor system at the transition state configuration and the energy of the bridge-localized states (Figure 1). For *electron* tunneling, the one-electron reduced bridge states are relevant, and for *hole* tunneling the one-electron oxidized states of the bridge. From Figure 1, it becomes clear why the influence of $\Delta\varepsilon$ on tunneling rates is difficult to investigate: The tunneling-energy gap is related to the redox potentials of the donor, bridge, and acceptor components of the overall system, but it is defined as the vertical energy gap at the transition state configuration and as such is not readily accessible from experiment. Variations in the reaction free energy (ΔG_{ET}) may lead to alterations in the magnitude of $\Delta\varepsilon$ (and vice versa).

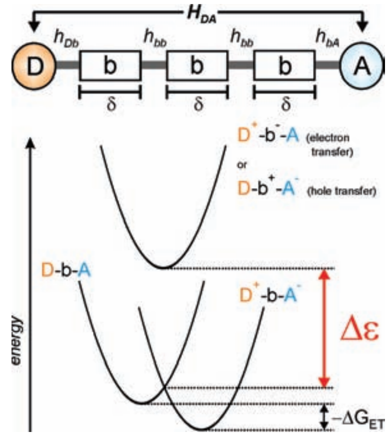

FIGURE 1. Illustration of the individual parameters involved in the superexchange model (eq 2). D = donor, b = bridging unit, and A = acceptor.[6]

The electronic coupling H_{DA} is expected to decrease exponentially with distance (*d*), and the steepness of the drop-off is captured by the distance decay constant β (eq 3).[7]

$${H_{DA}}^2 = {H_{DA}^0}^2 \exp(-\beta d) \qquad (3)$$

The distance dependence of electron tunneling rates (k_{ET}) originates in large parts from the distance dependence of the electronic coupling (H_{DA}), albeit the reaction free energy (ΔG_{ET}) and the reorganization energy (λ) may also vary as a function of donor−acceptor separation. In practice, it is difficult to separate the individual influences, and it is frequently assumed that H_{DA} plays the dominant role. In the superexchange model, the distance decay parameter (β) is a function of only three parameters (eq 4), namely, the tunneling-energy gap ($\Delta\varepsilon$), the electronic coupling between adjacent bridge units (h_{bb}), and the length of the individual bridging units (δ).[8]

$$\beta = \frac{2}{\delta} \ln\left(\frac{\Delta\varepsilon}{h_{bb}}\right) \qquad (4)$$

With the distance decay constant being a direct function of $\Delta\varepsilon$, the experimentally accessible β-parameter becomes of central interest for investigations of tunneling-energy gap effects. Indeed, the majority of studies in this context were aimed at evaluating distance decay constants for varying donor−bridge−acceptor combinations.

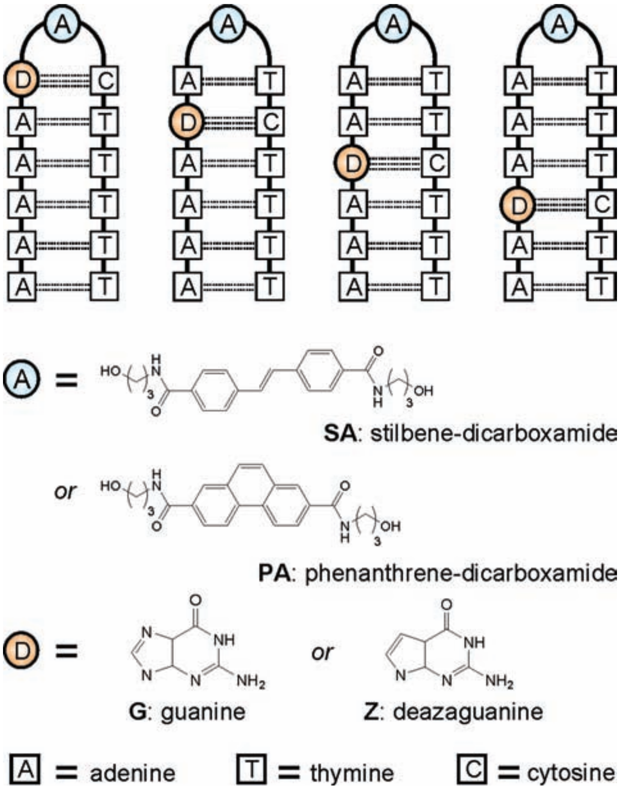

FIGURE 2. Structures of DNA hairpins with dicarboxamide electron acceptors and guanine/deazaguanine electron donors.[9,11,12]

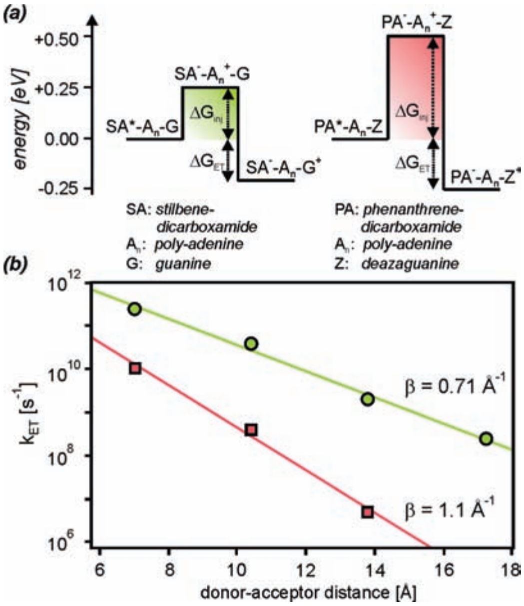

FIGURE 3. (a) Energetics of phototriggered hole transfer in the donor–bridge–acceptor hairpins from Figure 2. (b) Distance dependence of the rate constants for photoinduced hole tunneling from stilbene-dicarboxamide to guanine (green circles) and for hole tunneling from phenanthrene-dicarboxamide to deazaguanine (red squares).[9]

Hole Tunneling through DNA Hairpins

In order to determine the distance dependence of electron tunneling rates, it is necessary to keep the donor–acceptor distances constant on the time scale of the charge transfer event. This is possible, for example, in the artificial DNA hairpins of Figure 2 which contain rigid dicarboxamide linkers between a polyadenine and a polythymine strand.[9] These linkers do not only allow the formation of stable double strands, but they can also act as sensitizers for photoinduced charge transfer reactions: In their excited states, they are capable of oxidizing selectively the nucleobase guanine but none of the other three common DNA nucleobases. Thus, by introducing a guanine–cytosine pair at various positions in the polyadenine/polythymine double strand, it becomes possible to construct donor–bridge–acceptor systems with different well-defined distances between the guanine and dicarboxamide redox partners (Figure 2, top). The intermediate adenine base pairs play the role of the bridging units in these systems.

Electron transfer from the guanine donor to the photoexcited stilbene-4,4′-dicarboxamide (SA) acceptor is exergonic by 0.20 eV based on measurements of the relevant (ground- and excited-state) redox potentials. The one-electron oxidized states of the adenine bridging units are energetically much closer to the donor and acceptor levels than the one-electron reduced states; hence, the charge transfer process here is *hole* transfer rather than *electron* transfer. Nevertheless, hole injection from stilbene-dicarboxamide (SA) to adenine is endergonic by 0.25 eV (Figure 3a, left), and therefore, a hole *tunneling* rather than hole *hopping* mechanism is operative. The tunneling-energy gap $\Delta\varepsilon$ is closely related to the injection free energy (ΔG_{inj}).[10,11] The latter is defined as the energy difference between relaxed donor and bridge states and as such is a measurable quantity, whereas $\Delta\varepsilon$ is a transition-state quantity as described above. As the bridge states are moved further in energy from the donor and acceptor states, both ΔG_{inj} and $\Delta\varepsilon$ increase.

The rates for hole tunneling from excited stilbene-dicarboxamide (SA*) to guanine (G) across a variable number of adenine bridging units (A_n) were determined by transient absorption spectroscopy.[12] In the semilogarithmic plot of Figure 3b, the four experimental data points fall onto a single line (green filled circles), and a fit to these data yields $\beta = 0.71 \pm 0.07$ Å^{-1}. In a second series of DNA hairpins, the stilbene-4,4′-dicarboxamide (SA) hole donor was replaced by a phenanthrene-2,7-dicarboxamide (PA) sensitizer which allows the formation of equally stable donor–bridge–acceptor molecules with analogous structures (Figure 2). However, this phenanthrene-based photosensitizer is 0.25 V less oxidizing in its excited state than the stilbene-based sensitizer. In order to keep the free energy of the overall charge transfer process (ΔG_{ET}) as close as possible to that in the prior hairpin series, the guanine (G) redox partner was therefore replaced by deazaguanine (Z), which is easier to oxidize by 0.29 V. The donor–bridge–acceptor energetics for the resulting series of DNA hairpins are illustrated on the right of Figure 3a. The main difference between the SA–adenine$_n$–guanine (SA-A$_n$-G) and PA–adenine$_n$–deazaguanine (PA-A$_n$-Z) donor–bridge–acceptor molecules is a doubled injection free energy (ΔG_{inj} increases from 0.25 to 0.50 eV), whereas the overall reaction free energy is nearly identical in the two types of systems (ΔG_{ET} changes from −0.20 to −0.24 eV). The distance dependence of the rate constants for hole tunneling from photoexcited PA to deazaguanine (Z) was investigated by time-resolved fluorescence spectroscopy. The rate constants determined for hairpins with one to three bridging (adenine) units are represented by the red filled squares in Figure 3b. Again, the distance dependence is exponential as expected for a tunneling mechanism, but the drop-off is significantly steeper than that for the SA–adenine$_n$–guanine systems: The distance decay constant (β) for the PA–adenine$_n$–deazaguanine hairpins is 1.1 ± 0.1 Å^{-1}.[9]

The large discrepancy of β-values obtained for the same bridge equipped with different donor–acceptor couples was interpreted in terms of energy-gap modulated electronic donor–acceptor couplings: In the PA–deazaguanine systems, not only ΔG_{inj}, but also $\Delta\varepsilon$ must be substantially greater than in the SA–guanine molecules. Therefore, for a given donor–acceptor distance, the overall electronic coupling (H_{DA}) must be significantly stronger in the SA–guanine systems (eq 2), leading to higher charge transfer rate constants (eq 1). Moreover, the distance dependence of these rates is weaker, as predicted by eq 4. This DNA hairpin study represents one of the clearest examples for the importance of the tunneling-energy gap effect known to date.

Hole Tunneling across Oligo-*p*-xylene and Oligo-*p*-dimethoxybenzene Bridges

Fixed-distance electron tunneling can be investigated with a variety of artificial rigid rodlike bridges. However, too strongly π-conjugated systems such as oligo-*p*-phenylene vinylenes have energetically low lying redox states that permit charge transfer via the hopping mechanism.[4] Significantly less π-conjugated are oligo-*p*-phenylenes, yet, depending on their lengths, either tunneling or hopping mechanisms become prevalent.[13,14] The reason for this is the relatively strongly length-dependent electronic structure of oligo-*p*-phenylenes as a result of increasing π-conjugation with increasing length, favoring the hopping mechanism for longer congeners. The oligo-*p*-xylene bridges shown in Figure 4a do not suffer from this problem: Upon lengthening of this particular bridge, a comparatively minor increase of the overall π-conjugation is observed by optical absorption spectroscopy, thereby indicating that the length-dependence of the electronic structure is substantially less pronounced for oligo-*p*-xylenes than for oligo-*p*-phenylenes.[15−18] Therefore, the former are better suited for fundamental investigations of tunneling-energy gap effects because the superexchange model (eq 2) assumes length-independent electronic structures. Toward this end, d^6 metal diimine complexes and tertiary amine redox partners were attached covalently to oligo-*p*-xylene bridges, and the result was two series of variable-length donor–bridge–acceptor molecules as shown in Figure 4a.[15,19] Photoexcitation of the rhenium(I) tricarbonyl diimine generates a long-lived MLCT state in which the metal complex can abstract an electron from the phenothiazine (PTZ) donor. In the case of the ruthenium complex, the initially present Ru(II) center first has to be converted photochemically to a Ru(III) species before

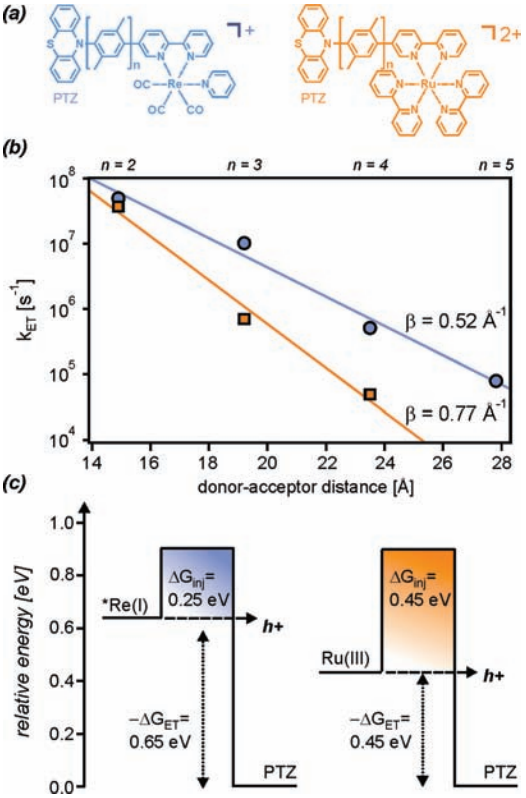

FIGURE 4. (a) Formulas of donor–bridge–acceptor molecules for investigations of phototriggered hole tunneling across variable-length oligo-*p*-xylene spacers. (b) Distance dependence of the rate constant for hole tunneling in these two types of molecules. (c) Energetics for hole tunneling from rhenium and ruthenium hole donors to phenothiazine (PTZ) hole acceptors through oligo-*p*-xylene bridges as estimated from redox potentials.[15,19]

electron transfer from phenothiazine to the metal complex can occur. The rate constants for the phototriggered charge transfer processes in the two series of molecules, as determined by time-resolved emission and transient absorption spectroscopy, are represented graphically in Figure 4b.

In this semilogarithmic representation, data points for a given donor−bridge−acceptor series fall onto a single line, an observation that is in accord with a tunneling mechanism in both cases. Interestingly, the steepness of the exponential distance dependence of k_{ET} is unequal for the rhenium ($\beta = 0.52$ Å^{-1}) and ruthenium ($\beta = 0.77$ Å^{-1}) systems, despite the fact that the molecular bridge is identical in both cases.[19]

This observation can be understood on the basis of differing donor−bridge−acceptor energetics. As for the DNA hairpins from above, the one-electron oxidized bridge states are energetically much closer to the relevant donor and acceptor states than the one-electron reduced bridge states, hence charge transfer is expected to occur via hole tunneling rather than electron tunneling. Due to different redox potentials for the photoexcited rhenium(I) complex and the photogenerated ruthenium(III) species, the free energies for hole injection into the bridge (ΔG_{inj}) differ by 0.2 eV between the two series of donor−bridge−acceptor molecules (Figure 4c). Likewise, due to the fact that the same hole acceptor (phenothiazine, PTZ) is used in both cases, the free energies for the overall donor-to-acceptor charge transfer (ΔG_{ET}) differ by the same amount. With ΔG_{inj} being substantially lower for the rhenium systems than for the ruthenium molecules, the shallower distance dependence of k_{ET} in the former is in qualitative agreement with a lower tunneling-energy gap. Additional support for this interpretation comes from the following analysis: The probability (κ) for an electron with mass m_e to tunnel through a square potential barrier of width d and height ΔE can be described by eq 5.[20]

$$\kappa \propto \exp\left(-\frac{2\sqrt{2m_e\Delta E}}{\hbar}d\right) \tag{5}$$

This equation takes the same form as eq 3 with an exponent comprising a prefactor that is multiplied by the barrier width (d). The prefactor in eq 5 may be regarded as a distance decay constant (β), and thus, one obtains a simple relation between experimentally accessible β-values and tunneling barrier heights (eq 6).

$$\Delta E = \left(\frac{\hbar^2}{8m_e}\right)\beta^2 = (0.952\ \text{eV} \times \mathring{A}^2)\beta^2 \tag{6}$$

The barrier height ΔE thus becomes an *effective* barrier height as estimated from the distance dependence of charge transfer rate constants.[8,21,22] For the rhenium−xylene−phenothiazine molecules, $\Delta E = 0.26$ eV, and for the analogous ruthenium systems $\Delta E = 0.55$ eV, based on the β-values from Figure 4b.[19] These effective barriers are strikingly close the injection free energies (ΔG_{inj}) estimated based on redox potentials (0.25 and 0.45 eV, Figure 4c). While such a close agreement between ΔE and ΔG_{inj} values may be a mere coincidence, this analysis nevertheless supports the interpretation of the different β-values for the rhenium and ruthenium based donor−bridge−acceptor molecules in terms of a tunneling-energy gap effect, and it narrows the role played by the simultaneous change in the overall free energy ΔG_{ET}. In conclusion, oligo-*p*-xylene based systems equipped with different hole donating photosensitizers provide evidence for the influence of donor−bridge−acceptor energetics on the distance dependence of charge tunneling rates.

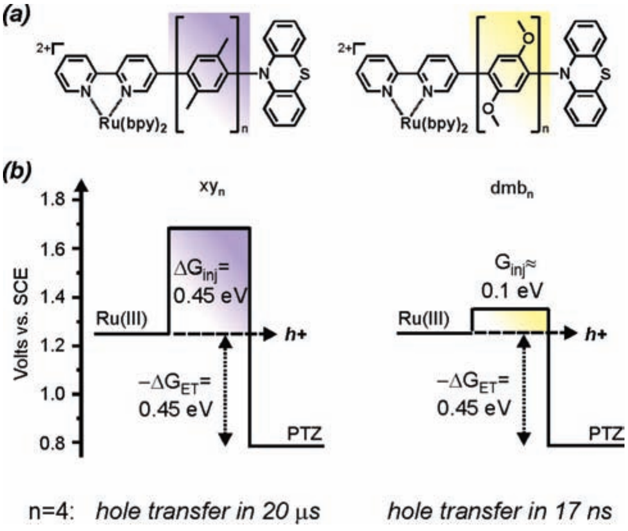

FIGURE 5. (a) Structures of ruthenium−phenothiazine dyads with oligo-*p*-xylene and oligo-*p*-dimethoxybenzene bridges. (b) Energetics and kinetics for hole tunneling from photogenerated ruthenium(III) to phenothiazine (PTZ) across a tetra-*p*-xylene bridge (left) and a tetra-*p*-dimethoxybenzene spacer (right).[23]

In the ruthenium−xylene−phenothiazine molecules from Figure 4 the barrier to hole transfer is relatively large ($\Delta G_{inj} = 0.45$ eV) because the bridge is rather difficult to oxidize. When the two methyl substituents on each of the bridging units are replaced by more electron-donating methoxyl groups (Figure 5a), the hole tunneling barrier is lowered substantially, while the overall π-conjugation of the oligo-*p*-dimethoxybenzene bridge remains comparable to oligo-*p*-xylenes.[23]

Indeed, donor−bridge−acceptor molecules containing between one and four adjacent *p*-dimethoxybenzene units all exhibit nearly identical optical absorption spectra, indicating that the electronic structure of the oligo-*p*-dimethoxybenzene (dmb_n) bridge is similarly length-independent as that of oligo-

p-xylene (xy$_n$) spacers. The oxidation potential of free *p*-dimethoxybenzene is 1.34 V vs SCE, whereas that of *p*-xylene is 2.06 V vs SCE. The difference between the oxidation potentials of the tetra-*p*-xylene and tetra-*p*-dimethoxybenzene spacers in the donor−bridge−acceptor molecules from Figure 5 is smaller;[23] hence, ΔG_{inj} decreases only from ~0.45 to ~0.1 eV. Yet this decrease has a strong influence on the rate for hole transfer from photogenerated ruthenium(III) to phenothiazine (Figure 5b): Tunneling across four *p*-xylene spacers occurs with a time constant of 20.4 μs, whereas tunneling the same distance through four *p*-dimethoxybenzene units (between the same donor and acceptor) takes place within 17 ns.[23] For $\Delta G_{\mathrm{inj}} \approx 0.1$ eV, a hopping mechanism may potentially become relevant, but in this particular instance transient absorption spectroscopy has failed to provide any evidence for bridge oxidation in the course of the overall charge transfer process. Technical limitations associated with the relatively slow photogeneration of the Ru(III) species impeded measurement of the hole transfer rates for ruthenium−phenothiazine systems with shorter oligo-*p*-dimethoxybenzene spacers, and the distance dependence for charge transfer across this type of bridge could not yet be determined. Nevertheless, the data for the molecules from Figure 5 are consistent with the interpretation of a lowered tunneling-energy gap when going from oligo-*p*-xylene to oligo-*p*-dimethoxybenzene bridges.

Electron Tunneling through Oligo-*p*-phenylene Ethynylene Bridges

Oligo-*p*-phenylene ethynylene (OPE) bridges represent an intermediate case between the very highly conjugated oligo-*p*-phenylene vinylene (OPV) molecular wires and the less conjugated oligo-*p*-phenylene bridges. As such they are amenable to studies of charge transfer via the tunneling mechanism and investigations regarding the importance of the tunneling-energy gap. This was accomplished in dyads containing a zinc(II) porphyrin electron donor and a gold(III) porphyrin acceptor connected by an OPE-based spacer at a center-to-center distance of 25 Å (Figure 6a).[24] Variation of the electronic structure of the bridge was effected by replacing the central benzene unit by either a naphthalene or an anthracene moiety. Upon photoexcitation of the zinc(II) porphyrin, both electron and energy transfer to the gold(III) porphyrin occur, although the latter process is significantly less important than the former, and transient absorption spectroscopy provides conclusive evidence for the predominant formation electron transfer photoproducts.

Rate constants for the 25 Å electron transfer step between the two porphyrins were determined in six different solvents with dielectric constants ranging from 2.4 (toluene) to 38.3 (dimethylformamide). The generally observed trend in all solvents is that electron transfer rates increase when going from benzene to naphthalene and anthracene central bridge units; that is, the more conjugated the central bridging unit, the faster the electron transfer. In dichloromethane, $k_{\mathrm{ET}} = 2.2 \times 10^9$ s^{-1} for a benzene central unit, $k_{\mathrm{ET}} = 4.3 \times 10^9$ s^{-1} for a naphthalene central unit, and $k_{\mathrm{ET}} = 9.1 \times 10^9$ s^{-1} when the central spacer is an anthracene moiety. From the solvent dependence of electron transfer rates as evaluated from time-resolved and steady-state experiments, the following estimates for the overall donor−acceptor electronic couplings (H_{DA}) were obtained (Figure 6b):[24] 5.5−7.5 cm^{-1} for benzene as a central unit, 7−10 cm^{-1} for naphthalene, and 11−17 cm^{-1} for anthracene. For these systems, estimation of tunneling-energy gaps from redox potentials turned out to be difficult, among other reasons because negative $\Delta\varepsilon$-values resulted for the anthracene system. These difficulties may have their origin in the simple fact that $\Delta\varepsilon$ is a vertical energy gap at the transition state of the electron transfer system (Figure 1), whereas redox potentials are values for relaxed species. At any rate, for the molecules from Figure 6a, the tunneling-energy gap was associated with the energy difference between the electronic origins of the lowest bridge absorption and the lowest donor absorption band as observed in UV−vis spec-

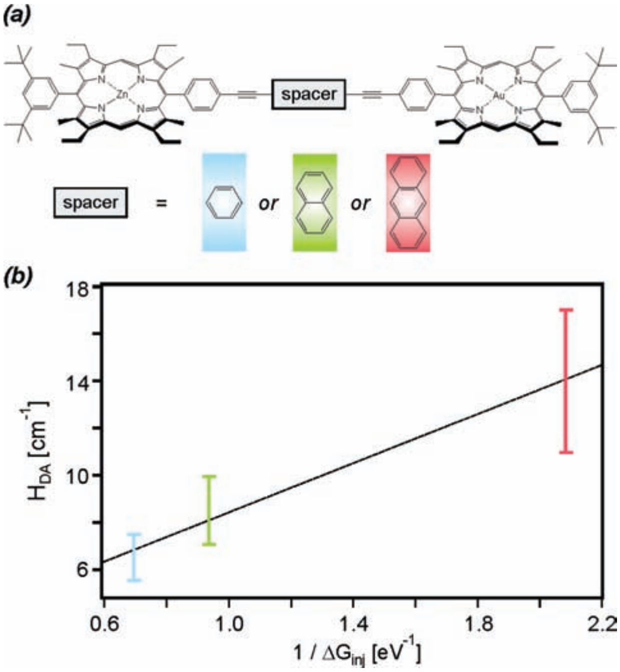

FIGURE 6. (a) Structures of three donor−bridge−acceptor molecules with variable central spacer units. (b) Bridge-mediated electronic coupling between the donor and the acceptor vs the inverse of the injection free energy.[22,24] The dashed line is a linear regression fit to the experimentally determined data.

troscopy. Justification for this procedure comes from the fact that the energy of the virtual bridge state involved in the superexchange mechanism for electron tunneling is proportional to the LUMO energy of the bridge. For the relevant bridging chromophores, the lowest-energetic absorption is a pure HOMO−LUMO transition, and the energy of the LUMO is proportional to the energy of the first excited state of the bridge.[24] This analysis yields ΔG_{inj}-values of 1.44 eV (benzene), 1.07 eV (naphthalene), and 0.48 eV (anthrancene). Figure 6b shows that there exists a correlation between the magnitude of the electronic donor−acceptor coupling (H_{DA}) and the inverse of the injection free energy (ΔG_{inj}) along the three systems. The linear correlation between H_{DA} and $\Delta G_{inj}{}^{-1}$ (or $\Delta\varepsilon^{-1}$, respectively) is in accord with the superexchange model (eq 2) when considering the entire molecular bridge comprising two phenylethynyl moieties attached to a central spacer as one single bridge entity. Thus, the bridge-dependent electron tunneling rate constants can be explained satisfactorily by invoking a tunneling-energy gap effect.

Closely related work focused on the distance dependence of electron transfer rates between the same zinc(II) and gold(III) porphyrins bridged by variable-length OPE spacers (Figure 7a). Molecules with bridges comprising one to four phenylethynyl units were investigated, thereby covering a donor−acceptor (edge-to-edge) distance range of 12.7−33.4 Å.[25] The OPE bridges are substantially more π-conjugated than the sterically more demanding oligo-*p*-xylenes; hence, strong red-shifts of the bridge absorption band edges are observed upon bridge lengthening. As in the prior OPE study, injection free energies (ΔG_{inj}) were estimated based on optical absorption data, yielding values ranging from 1.96 eV for the shortest bridge to 1.09 eV for the longest spacer (Figure 7b).

Thus, in contrast to the oligo-*p*-xylene study, in the series of molecules from Figure 7a, the donor−acceptor distance and the injection free energy (ΔG_{inj}) vary simultaneously. As the bridge length increases, ΔG_{inj} (and therefore $\Delta\varepsilon$) decreases, and a deviation from the exponential distance dependence of electron tunneling rates can be expected. Nevertheless, the four experimentally determined data points exhibit no significant deviation from an exponentially distance dependent behavior (Figure 7c), and the data can be fitted satisfactorily with a distance decay constant of 0.29 ± 0.04 Å^{-1} (for propionitrile solvent). Evidently, in this particular case, the influence of barrier *width* on electron tunneling rates is significantly greater than that of barrier *height*.[25] A plausible explanation for this behavior is found when considering the relative changes of donor−acceptor distances (d) and estimated tunneling-energy gaps. For the specific donor−bridge−acceptor series considered here, the total increase of d amounts to 163%, while the decrease in ΔG_{inj} along the series is only about 44%. Thereby, the absolute magnitude of ΔG_{inj} is of key importance: For the molecules from Figure 7a, even the smallest tunneling-energy gap is comparatively large (1.09 eV). When combined with donor−acceptor couples that lead to significantly smaller tunneling-energy gaps, OPE bridges should lead to distance dependences of electron transfer rates that deviate from the simple exponential behavior, even before these energy gaps become small enough for electron hopping. Recent theoretical work offers quantitative predictions regarding the nonexponential distance dependence of bridge-mediated electronic coupling.[26]

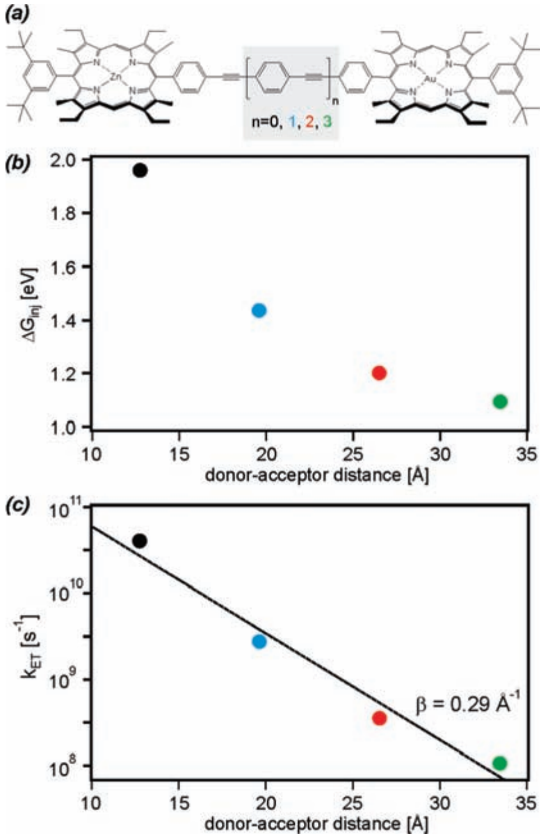

FIGURE 7. (a) Formulas of donor−bridge−acceptor molecules with variable-length oligo-*p*-phenylene ethynylene (OPE) spacers. (b) Injection free energy as a function of bridge length. (c) Distance dependence of the rate constant for electron tunneling from the zinc porphyrin donor the gold porphyrin acceptor.[25,27]

Once photoinduced charge transfer has occurred in the molecules from Figure 7a, a charge-separated state with oxidized zinc porphyrin and reduced gold porphyrin has formed. This energy-rich state is depopulated by thermal charge recombination, that is, a charge transfer event occurring in the reverse direction. For a given donor−bridge−acceptor molecule in Figure 7a, the rate for charge recombination (k_{CR}) is more than 1 order of magnitude slower than the rate for charge separation (k_{CS}), mainly because of differing driving forces (ΔG_{ET}) for the two processes.[27] An inverted driving-force effect seems to be at work here, since the slower recombination process is 0.22 eV more exothermic than the faster separation event. More interesting, because it is significantly less well documented in the literature, is the observation of substantially different distance dependences for photoinduced charge separation (CS) and thermal charge recombination (CR). In dimethylformamide solution, the former process yields $\beta_{CS} = 0.31$ Å^{-1}, whereas the latter gives $\beta_{CR} = 0.39$ Å^{-1}.[27] This discrepancy may be explained in terms of a larger tunneling-energy gap associated with charge recombination ($\Delta\varepsilon_{CR}$) than with charge separation ($\Delta\varepsilon_{CS}$). Energetic considerations lead to the conclusion that the energy difference between the initially excited zinc(II) porpyrin donor and the lowest-lying bridge states is smaller than the energy difference between the charge-separated state and the bridge levels and hence $\Delta\varepsilon$ is likely to be smaller for charge separation. This could be a rather general phenomenon, but its importance will largely depend on the relative magnitudes of $\Delta\varepsilon_{CS}$ and $\Delta\varepsilon_{CR}$. The biggest effect can be expected for donor−bridge−acceptor systems exhibiting photoinduced charge-separation reactions that are associated at the same time with small tunneling-energy gaps and large driving forces. Thus, tunneling-energy gap effects may in principle be exploited to discriminate between the rates of energy-storing and energy-wasting electron transfers.

Charge Tunneling through Frozen Solvent Matrices

An interesting alternative to covalently linked donor−bridge−acceptor molecules for investigation of fixed-distance electron transfer is to randomly disperse donors and acceptors in frozen solvent matrices.[28] The advantage of this approach is that significantly less synthetic work is necessary, and the disadvantage is that it is difficult to identify suitable donor−acceptor couples for which electron tunneling, at cryogenic temperatures in a medium in which solvent reorganization is essentially impossible, does not become prohibitively slow. For the quantitative analysis of the electron tunneling events in these matrices, the random dispersion of donors and acceptors and the resulting statistical distribution of donor−acceptor distances are of key importance (Figure 8a). When using the luminescence signal of an electron donor as an observable, strongly nonexponential luminescence decays result in the presence of electron acceptors (Figure 8b), and through variation of the acceptor concentration it becomes possible to extract distance decay constants for electron tunneling.[29,30] This experimental approach requires the formation of glassy matrices of good optical quality, a fact that severely limits the spectrum of suitable materials.

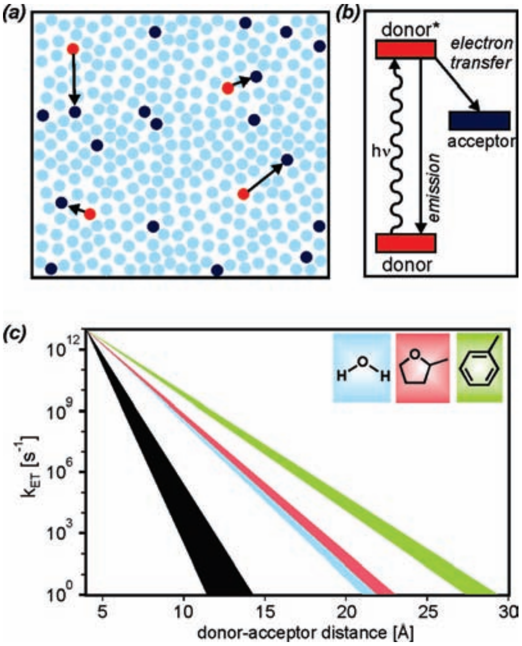

FIGURE 8. (a) Schematic representation of electron tunneling from photoexcited donors (red) to randomly dispersed acceptors (black) in a rigid solvent glass (blue). (b) Electron transfer leads to (partial) quenching of the donor luminescence. Due to the wide distribution of donor−acceptor distances present in the sample, nonexponential emission decays are the result.[32] (c) Distance dependence of electron tunneling in three solvent glasses: Water/sulfuric acid ($\beta = 1.68 \pm 0.07$ Å^{-1}, blue wedge),[30] 2-methyltetrahydrofuran ($\beta = 1.62 \pm 0.05$ Å^{-1}, red wedge),[31] toluene ($\beta = 1.23 \pm 0.05$ Å^{-1}, green wedge).[31] Also included is the distance dependence of electron tunneling through vacuum ($\beta = 2.9 - 4.0$ Å^{-1}, black wedge).[33]

Three examples of solvents that form glasses at 77 K and that have very distinct electronic structures are 2-methyltetrahydrofuran, toluene, and water. The latter requires addition of 25 wt % sulfuric acid in order to form glasses, but on a molar basis the resulting acidic matrix is still composed of more than 90% H_2O/H_3O^+.[30] Evidently, water is a particularly important medium for electron transfer, since aqueous-solution redox reactions are ubiquitous in chemistry and biology.[1] Electron tunneling from a luminescent $Ru(tpy)_2^{2+}$ (tpy = 2,2′;6′,2′′-terpyridine) donor to an $Fe(H_2O)_6^{3+}$ acceptor through the acidic water matrix was investigated using a combination of time-resolved and steady-state luminescence spectroscopies.[30] Quantitative analysis of these data afforded $\beta = 1.68$ Å^{-1} (blue wedge in Figure 8c), a value that is expectedly much greater than those obtained for covalent bridges. More intriguing is the relative inefficiency of water-mediated long-range electron tunneling compared to 2-methyltetrahydrofuran and toluene for which distance decay constants of 1.62 Å^{-1} (red wedge) and 1.23 Å^{-1} (green wedge) were determined using an analogous method with an iridium donor and a benzoquinone acceptor.[31,32] The superexchange model suggests that the distance decay constant is a function of three parameters (eq 4), namely, the size of the bridging units (δ), the electronic coupling between adjacent bridge molecules (h_{bb}), and the tunneling-energy gap ($\Delta\varepsilon$). The observed trend of increasing β-values along the series toluene, 2-methyltetrahydrofuran, water is broadly consistent with the decreasing size of the bridge units. Yet, it is interesting to note that for 2-methyltetrahydrofuran and water rather similar distance decay constants were obtained, despite the clearly different nature of bridge–bridge interactions in the two solvents: In 2-methyltetrahydrofuran, coupling between adjacent bridge units is mediated by van der Waals contacts, whereas in the aqueous glass individual water molecules are connected to one another by strong hydrogen bonds. One would thus expect h_{bb} to be significantly greater for water than for 2-methyltetrahydrofuran, even more so because several experimental investigations have shown that hydrogen bond mediated electronic couplings can be quite strong.[1,33] It is possible that the benefit of a smaller tunneling-energy gap associated with electron tunneling through 2-methyltetrahydrofuran compensates for the weaker electronic coupling relative to water, thereby leading to similar β-values for both solvents.

Comparison of the distance decay constants of toluene and 2-methyltetrahydrofuran also points to the occurrence of a tunneling-energy gap effect in solvent-mediated long-range electron tunneling: Toluene and 2-methyltetrahydrofuran molecules differ in size only marginally, and both of them only interact with neighboring solvent molecules of the same type via van der Waals interactions, suggesting that δ and h_{bb} are similar for these two solvents. The large difference in their β-values (1.23 vs 1.62 Å^{-1}) is therefore likely a manifestation of differing tunneling-energy gaps. However, reliable quantitative estimates of $\Delta\varepsilon$ or ΔG_{inj} remain elusive in these cases of photoinduced electron tunneling through glassy matrices.

Distance Dependence of λ in Mixed-Valence Ruthenium Complexes

The prior paragraphs of this Account deal almost exclusively with the influence of the tunneling-energy gap ($\Delta\varepsilon$) on the electronic donor–acceptor coupling (H_{DA}) and its impact on the distance dependence of electron tunneling rates. As stated already in the Introduction, the distance dependence of H_{DA} is frequently assumed to have the strongest influence on the distance dependence of k_{ET}, but this assumption does not always prove to be correct. The exponential term in eq 1, the so-called nuclear factor, may itself exhibit a significant distance dependence due to variations in the reorganization energy (λ) or reaction free energy (ΔG_{ET}) with increasing donor–acceptor distance.[34] Direct experimental evidence for a strong distance dependence of λ comes from a systematic study of the metal-to-metal charge transfer absorption bands in the mixed-valence ruthenium complexes from Figure 9a.[35] Upon increase of the Ru–Ru distance from 6 to 14 Å through variation of the bridging ligand between two pentaammineruthenium moieties, λ is found to increase from 0.64 to 1.12 eV (Figure 9b). On the basis of these data, the nuclear factor of eq 1 alone has been estimated to exhibit an exponential distance dependence with a decay constant of ~0.9 Å^{-1} for the specific case of the molecules from Figure 9a.[35] The important message from this is that the analysis of tunneling-energy gap effects through evaluation of the distance dependence of k_{ET} may be complicated by the fact that the reorganization energy (λ) may itself exhibit a non-negligible distance dependence. In certain instances, the same may be the case for the reaction free energy (ΔG_{ET}).[36]

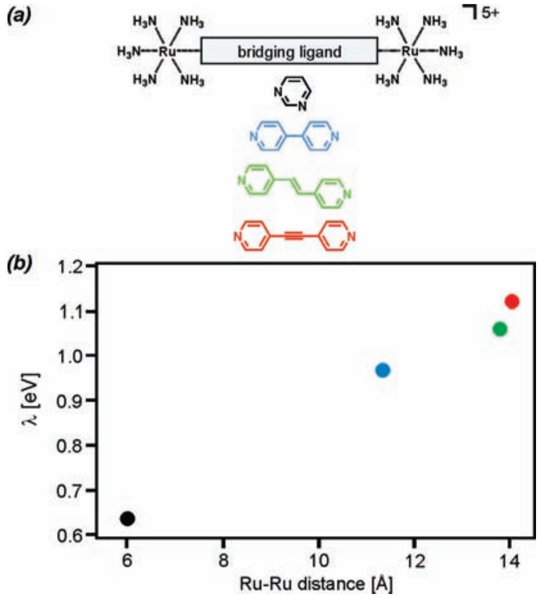

FIGURE 9. (a) Mixed-valence diruthenium complexes with four different bridging ligands. (b) Distance dependence of the reorganization energy (λ) associated with metal-to-metal electron transfer in the four mixed-valence complexes.[35]

Summary and Outlook

Theoretical predictions and calculations regarding the importance of the tunneling-energy gap for long-range electron tunneling have long been available,[6,37] but direct experimental evidence has emerged only over the past the couple of years. Estimates of the absolute magnitudes of tunneling-energy gaps ($\Delta\varepsilon$) are inherently difficult to obtain, and different approaches using either electrochemical or optical-spectroscopic data have been found useful. Distance dependence studies of electron tunneling dynamics prove to be particularly valuable for these investigations, since the distance decay constant (β) is the experimentally accessible parameter that is most uniquely sensitive to variations in $\Delta\varepsilon$. It has become clear that the distance decay constant is not a bridge-specific property, but rather it is a characteristic of a given donor−bridge−acceptor combination. In other words, donor−bridge energy matching is important not only for achieving molecular wire behavior through activation of the hopping mechanism, but it is important already in the tunneling regime.

Significant synthetic efforts are commonly associated with the construction of series of covalently linked model systems for distance dependence studies. Hence, investigations of charge transfer between free donors and acceptors that are randomly dispersed in glassy matrices hold great promise for further systematic evaluation of the influence of donor−bridge−acceptor energetics on long-range electron tunneling.

The fact that the tunneling-energy gaps associated with photoinduced charge-separation processes and thermal charge-recombination events may differ substantially is of interest for solar energy conversion, because it provides a means to discriminate between the rates of desired and undesired electron transfers. This is a promising approach to obtaining long-lived charge-separated states, particularly when combined with the exploitation of inverted driving-force effects.

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BIOGRAPHICAL INFORMATION

Oliver S. Wenger did his Ph.D. thesis between 1999 and 2002 under the supervision of Hans U. Güdel at the University of Bern in Switzerland. After postdoctoral work at the California Institute of Technology with Harry B. Gray from 2002 to 2004 and at Université Louis Pasteur in Strasbourg with Jean-Pierre Sauvage from 2004 to 2006, he started independent research as an assistant professor at the University of Geneva. In 2009, he moved to the University of Göttingen, where he now has a tenured position as an associate professor.

FOOTNOTES

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