Photoinduced electron and energy transfer in phenylene oligomers

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Phenylene oligomers represent a borderline case between very strongly π-conjugated molecular wires such as oligo-p-phenylene vinylenes and saturated molecular bridges. Even subtle chemical modifications of phenylene oligomers can therefore have a strong impact on charge transfer rates and mechanisms. On the basis of recently published selected case studies, this tutorial review discusses the key factors that affect charge transfer kinetics in phenylene oligomers with particular focus on the role of donor–bridge energy matching. Selected examples of triplet–triplet energy transfer reactions across phenylene oligomers are also discussed.

1. Introduction

Charge transfer between distant redox partners plays a key role in chemistry, physics, and biology. Of particular interest are usually the kinetics of the electron transfer events and their dependence on reaction driving-force, distance, chemical environment or linkage between the donor and acceptor. The traditional approach to exploring long-range electron transfer involves the use of covalent donor–bridge–acceptor systems in which charge transfer is triggered by light, but investigations of electron transfer through molecules that are directly attached to two electrodes become increasingly en vogue.1 This review focuses on recent work performed on the subject of photoinduced charge transfer across rigid rod-like phenylene oligomers in covalent donor–bridge–acceptor molecules. The term “phenylene” is somewhat broadly defined for this purpose and encompasses unsubstituted oligo-p-phenylenes as well as substituted congeners such as oligo-p-xylenes, oligo-p-dimethoxybenzenes and even oligo-fluorene systems. Although structurally closely related, these four types of molecular bridges display a broad variety of charge transfer phenomena including tunneling as well as hopping processes.

Substitution of phenylene bridging units affects charge transfer in two ways: on the one hand it modulates the equilibrium conformation of the bridge and hence its extent of π-conjugation, and on the other hand it can have an important impact on the redox potential of the bridge through donation (or withdrawal) of electron density into the π-system. The importance of conformational effects has been reviewed in this journal five years ago and is fairly well understood.2 However, the influence of the bridge redox potential on long-range charge transfer is a research topic that has experienced much recent progress, and consequently this will be the central theme of this review.

Phenylene oligomers are particularly interesting because they are at the borderline between very strongly π-conjugated materials such as oligo-p-phenylene vinylenes (OPVs) or oligo-p-phenylene ethynlenes (OPEs) in which charge transfer essentially proceeds through hopping mechanisms (Fig. 1a),3,4 and unconjugated systems in which the transferring charge carriers have to tunnel in one single step through the barrier imposed by the bridging molecules (Fig. 1b).3 Minimizing the energy gap between the donor and the bridge is the key to activating the hopping mechanism, a fact that is conceptually rather simple.5,6 However, the importance of a related quantity that is relevant for the tunneling mechanism, the so-called tunneling-energy gap, is less evident and hence much less understood. The present review aims to shed more light on this facet of electron transfer.

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Oliver S. Wenger did his PhD thesis under the supervision of Hans U. Güdel at the University of Berne in Switzerland from 1999 to 2002. After a postdoctoral research stay at Caltech with Harry B. Gray from 2002 to 2004 and a second postdoc at Université Louis Pasteur in Strasbourg with Jean-Pierre Sauvage from 2004 to 2006, he started independent research at the University of Geneva, endowed with an assistant professorship of the Swiss National Science Foundation. In 2009 he moved to the University of Göttingen in Germany where he currently has a tenured position as an associate professor.
Distance dependence studies of transfer rates are particularly important in the field of long-range electron transfer. The key outcome of such investigations is usually a distance decay constant (or so-called \( \beta \)-value) that is of somewhat limited meaning to the non-expert. On the basis of a few selected case studies from the recent literature, this tutorial review shows that the experimentally accessible \( \beta \)-values can be translated into effective tunneling-barrier heights by using a simple physical model that was originally developed for description of the tunneling of radioactive \( \alpha \)-particles through a potential energy barrier. These effective tunneling-barrier heights are found to be directly comparable to the abovementioned tunneling-energy gap from the superexchange theory, i.e., the two different physical models appear to be complementary. The usefulness of theoretical models developed for the field of radioactivity to describe and understand charge tunneling phenomena will be another focal point of this review.

2. Torsion angles and tunneling-energy gaps

In many phenylene oligomers charge transfer proceeds through a tunneling mechanism, and therefore a brief recapitulation of some key points of the superexchange theory is adequate. The McConnell model rationalizes the long-range electronic communication between distant donors and acceptors through orbital overlaps that occur between neighboring components of a given donor–bridge–acceptor system.\(^7\) In the simplest case (Fig. 2a), the overall system is comprised of a donor–acceptor (D–A) couple separated by \( n \) identical bridging units (b).

The electronic donor–acceptor coupling (\( H_{DA} \)) is then given by a simple product of donor–bridge (\( h_{DB} \)), bridge–bridge (\( h_{bb} \)), and bridge–acceptor (\( h_{BA} \)) couplings (eqn (1)).

\[
H_{DA} = \frac{h_{DB}}{\Delta e} \left( \frac{h_{bb}}{\Delta e} \right)^{-1} h_{BA} \quad (1)
\]

As one might expect intuitively, the strength of the overall coupling (\( H_{DA} \)) is a direct function of the mutual electronic couplings between adjacent components of the overall system. However, there is an additional parameter, called tunneling-energy gap (\( \Delta e \)) that plays a key role. \( \Delta e \) is a non-equilibrium quantity that is best understood in a picture of potential energy wells (Fig. 2b): upon charge transfer, the donor–bridge–acceptor (D–b–A) system passes from the potential energy surface of the starting materials (denoted D–b–A) to the product surface (denoted D\(^+\)–b–A\(^-\) ) by way of a transition state that is reached at the intersection of these two potential wells. The tunneling energy gap is the energy difference between this transition state and the minimum of the bridge potential energy surface (denoted D\(^+\)–b–A for electron transfer and D–b\(^-\)–A\(^-\) for hole transfer). A major difficulty associated with \( \Delta e \) is that it represents a transition-state quantity that is not directly accessible from experiment.

According to the semiclassical theory, electron transfer rates (\( k_{ET} \)) are proportional to \( H_{DA}^2 \). The distance dependence of \( k_{ET} \) is often (but not always) dominated by the exponential dependence of \( H_{DA} \) on the donor–acceptor distance (\( r_{DA} \)), and therefore an exponential distance dependence of electron transfer rates (eqn (2)) is diagnostic for the tunneling mechanism.

\[
k_{ET}(r_{DA}) = k_{ET}(r_0) \exp[-\beta(r_{DA} - r_0)] \quad (2)
\]

The steepness of the exponential drop-off is captured by the distance decay constant (\( \beta \)), which is dependent on only three superexchange parameters: bridge–bridge coupling (\( h_{bb} \)), the tunneling-energy gap (\( \Delta e \)) and the length (\( \delta \)) of a given bridging unit (eqn (3)).\(^5\)

\[
\beta = \frac{2}{\delta} \ln \left( \frac{\Delta e}{h_{bb}} \right) \quad (3)
\]

Thus, the relative magnitudes of \( h_{bb} \) and \( \Delta e \) determine the distance dependence of charge tunneling. Ideally, strong bridge–bridge coupling is combined with a small tunneling energy-gap, but in practice the two parameters are difficult to optimize simultaneously. This is especially true for phenylene oligomers in which \( h_{bb} \) largely depends on the equilibrium torsion angle between adjacent phenyl units (\( \theta_{ph} \)). A cos\(^2\)(\( \phi_{ph} \))-dependence of \( h_{bb} \) is commonly found,\(^2,9,10\) and this leads to the expectation that bridge–bridge coupling is
maximal for unsubstituted oligo-p-phenylenes in which \( \phi_{ph-ph} \) adopts its minimal value of roughly 30° at equilibrium. On the other hand, introduction of electron-donating or withdrawing substituents can be used to minimize \( \Delta e \) for hole or electron tunneling, but this comes at the cost of de-optimizing \( h_{kb} \) due to increased torsion angles. \( \Delta e \) is also affected by \( \pi \)-conjugation which increases upon lengthening of unsubstituted oligo-p-phenylene bridges, and therefore the tunneling-energy gap may itself be a length-dependent quantity. In extreme cases, \( \Delta e \) becomes so small that a hopping mechanism can become active (see Section 3).

Fig. 3 shows three donor-bridge-acceptor molecules that were investigated recently with a view to exploring the interplay of torsion angles and tunneling-energy gaps in phenylene-bridged systems. Rhenium(i) tricarbonyl phenanthroline complexes are powerful photooxidants capable of abstracting an electron from phenothiazine (PTZ) donors upon excitation with blue light. Given the fact that the redox partners and donor-acceptor distances are identical in all three dyads from Fig. 3, the observed differences in electron transfer kinetics must be directly related to the molecular bridges. Time constants for electron transfer (\( \tau_{ET} = k_{ET}^{-1} \)) were determined by transient absorption spectroscopy and were found to vary from 20 ns for the bi-p-xylene bridged system (Re-xy2−PTZ) to 1.9 ns for the dyad with the fluorene spacer (Re-fl1−PTZ). The decrease of \( \tau_{ET} \) along the series bi-p-xylene > biphenyl > fluorene is broadly consistent with the decrease of \( \phi_{ph-ph} \) (and hence an increase of \( h_{kb} \)) along the same series. However, the tunneling-energy gap is expected to vary at the same time: Fig. 3 lists the \( \Delta e \) values expected for hole tunneling as estimated based on the difference between the oxidation potentials of the rhenium(i) complexes and those of the molecular bridges. The underlying assumption is that charge transfer in these dyads occurs through a hole tunneling mechanism because the D-b−A− intermediate states (Fig. 2b) are energetically much closer to the initial and final states than the D−b−A states. The \( \Delta e \)-values in Fig. 3 represent only very crude approximations since they are based on redox potentials that correspond to energy differences between relaxed states, but \( \Delta e \) is defined as the vertical energy gap at the transition-state configuration (Fig. 2b). Be that as it may, the strong electronic coupling provided by the fluorene spacer is likely to be due to the combined effects of large \( h_{kb} \) (thanks to small \( \phi_{ph-ph} \) and low \( \Delta e \). At any rate, it is clear from Fig. 3 that there are two parameters (\( \phi_{ph-ph} \) and \( \Delta e \)) that vary substantially along the three molecules, and it is impossible to disentangle their relative importance based on the available experimental data. This illustrates one of the key difficulties associated with exploring bridging medium effects on long-range charge transfer: even among a series of very similar molecules with essentially identical donor-acceptor distances and driving-forces for charge transfer, it is difficult to pinpoint differences in long-range electronic couplings to a single structural or electronic parameter.

3. The transition from tunneling to hopping

In the molecules from Fig. 4a a series of phenylene oligomers (ph\(_n\)) build the bridge between a phenothiazine (PTZ) electron donor and a perylene-3,4,9,10-bis(dicarboximide) (PDI)
electron acceptor.11,13 As in the abovementioned examples, it is physically more meaningful to interpret charge transfer in these molecules as hole rather than electron transfer, and consequently PDI is considered a hole donor and PTZ a hole acceptor. Justification for this approach comes again from the fact that oxidation of the phenylene oligomers occurs at significantly more decent potentials than their reduction. In selected other oligo-\(p\)-phenylene bridged systems it has even been possible to demonstrate experimentally that there is a preference for hole transfer over electron transfer.14 Here, the PDI unit can be photoexcited selectively to produce a singlet radical ion pair comprised of reduced PDI and oxidized PTZ (PDI–\(\text{ph}_{n}\)PTZ\(^+\)), which, depending on the solvent,15 subsequently undergoes efficient intersystem crossing to the corresponding spin triplet radical ion pair state. Transient absorption and time-resolved emission spectroscopies permit determination of the rate constants for charge separation (\(k_{\text{CS}}\), filled circles in Fig. 4b) and charge recombination (\(k_{\text{CR}}\), open squares). The distance dependence of \(k_{\text{CS}}\) for \(n = 1–4\) is exponential with a \(\beta\)-parameter of 0.46 Å\(^{-1}\), indicating that superexchange tunneling is the dominant reaction mechanism. The data point for the system with \(n = 5\) clearly does not fit into the picture of an exponentially distance dependent process and signals the changeover to a hopping mechanism. In the case of charge recombination, this changeover occurs already for \(n = 4\), moreover, in the tunneling regime (\(n = 1–3\)) the exponential distance dependence is significantly steeper (\(\beta = 0.67\) Å\(^{-1}\)). Noteworthy is also the increase of \(k_{\text{CR}}\) with increasing donor-acceptor distance (\(r_{\text{DA}}\)) observed between \(n = 4\) and \(n = 5\).

An important characteristic of unsubstituted oligo-\(p\)-phenylenes is their strongly length dependent electronic structure which manifests itself, \textit{inter alia}, in a strong red-shift of the phenylene-localized \(\pi-\pi^*\) absorptions and increasing ease of oxidation with increasing length. This latter point is illustrated in Fig. 4c which shows an energy level diagram for the initial, intermediate and final states involved in hole transfer in the PDI–\(\text{ph}_{n}\)PTZ molecules.11 For \(n = 1–3\) the intermediate (bridge-oxidized) states are energetically well above the initial and final states, but for \(n = 4\) and \(n = 5\) initial and intermediate states are nearly resonant. This is true for both charge-separation and charge-recombination, and it explains the changeover in the reaction mechanism from tunneling to hopping. The different \(\beta\)-values observed for charge-separation and charge-recombination in the tunneling regime may have their origin in the fact that different reactants and products are involved in the two processes: the former process involves photoexcited PDI and ground-state PTZ which are converted into a spin singlet radical ion pair, while the latter process departs from a spin triplet radical ion pair that reacts to PDI and PTZ in their electronic ground states. As will be discussed in Section 4, the observation of different \(\beta\)-values for a given bridge depending on the attached reactants is not uncommon—it is even predicted by theory.7 The drawing in Fig. 4c suggests that the charge-separated states in the five dyads are all at the same energy. In reality, they are expected to increase along the series \(n = 1–5\), and this leads to an additional lowering of the barrier for hole injection into the bridge with increasing length.

The magnitude of the singlet-triplet splitting (\(2J\)) in the radical ion pair state is a direct measure for the magnetic superexchange coupling provided by the phenylene bridges. For the molecules from Fig. 4a the distance dependence of \(2J\) was found to be exponential up to \(n = 5\) (\(\beta = 0.37\) Å\(^{-1}\)),11 and this supports the conclusion that the contribution of incoherent hopping to the overall charge transfer mechanism increases with increasing bridge length. A continuative study indicates that activation of the torsional motion, which allows adjacent phenylene units to assume temporarily a nearly coplanar conformation, plays a crucial role for enabling the hopping mechanism.13

In the molecules from Fig. 5a the same (PDI–PTZ) donor–acceptor couple is bridged by fluorene (fl\(_n\)) spacers. An important difference to the phenylene-bridged systems from Fig. 4a is the experimental observation of nearly length independent oxidation potentials for the bridging molecules.16 The distance dependence of hole transfer rates in this case is clearly not exponential, and a plot of \(k_{\text{ET}}\) versus \(1/r_{\text{DA}}\) (Fig. 5b) shows that the PDI–fl\(_n\)PTZ molecules with \(n = 2–4\) exhibit the type of ohmic behavior that is expected for charge transport \textit{via} the hopping mechanism.17 The energy barriers associated with charge injection from photoexcited PDI to fl\(_n\) are 0.35 eV for \(n = 1\) and \(\leq 0.15\) eV for \(n = 2–4\) (Fig. 5c). Thus it is plausible that charge separation in PDI–fl\(_n\)–PTZ...
occurs primarily via superexchange tunneling, whereas in the longer congeners hopping becomes dominant, even though analysis of the kinetic data using a model developed by Bixon and Jortner suggests that the distance dependence of \(k_{\text{ET}}\) alone cannot distinguish between tunneling and hopping.\(^{18}\)

As in the case of the phenylene-bridged molecules from above, determination of the singlet–triplet splitting (\(2J\)) in the radical ion pair formed upon photoexcitation provides insight into the magnitude of magnetic superexchange coupling that is mediated by the fluorene spacers.\(^{16}\) Fitting the experimental data to an exponential function yields a good fit for \(\beta = 0.27\ \text{Å}^{-1}\). The report of a \(\beta\)-value as low as 0.09 \(\text{Å}^{-1}\) for other oligo-fluorene bridged donor–acceptor systems is therefore clearly in line with charge transfer via the hopping mechanism.\(^{19}\)

At room temperature the distance dependence of \(k_{\text{CR}}\) in the PDI–fl–PTZ dyads is non-exponential, but at 90 K it can be described with eqn (2) and \(\beta = 0.08\ \text{Å}^{-1}\).\(^{20}\) The magnitude of this distance decay constant supports the idea that hopping dominates even at low temperatures.

Ladder-type pentaphenylene (Fig. 6) represent a variant of fluorene oligomers with particularly extended \(\pi\)-conjugation, because in these molecules torsion about formal single C–C bonds can only occur after every fifth phenylene unit.\(^{21,22}\) The result is exceptionally strong electronic coupling allowing detection of intramolecular electron transfer between tertiary amine and mesitylboron redox centers that are held at a distance of 22 Å. For instance, in the case of the radical monocation of the bis(triarylamine) molecule with \(n = 1\) (Fig. 6a), \(H_{\text{DA}} = 548\ \text{cm}^{-1}\) was obtained from Hush analysis of the intervalence absorption, and the system was categorized as a class II mixed valence ion. No significant electronic communication could be detected for the congeners with \(n = 2\) and \(n = 3\), presumably due to weak interaction between individual pentaphenylene units. However, within a given ladder-type pentaphenylene unit, significant charge delocalization appears to be achievable, and for photoinduced charge transfer occurring from electronically excited states this may potentially form the basis for hopping processes from one pentaphenylene stepping stone to the next.

4. Effective barrier heights from \(\beta\)-values

When tackling a fundamental scientific problem in a systematic manner, it is usually desirable to vary one single parameter at the time. In the course of distance dependence studies of electron transfer rates in unsubstituted oligo-\(p\)-phenylene, the heights and widths of the barriers associated with charge transfer vary simultaneously.\(^{11,23}\) As seen above, this problem can be overcome by resorting to oligo-fluorenes, but they mediate long-range charge transfer predominantly via hopping. If one aims to disentangle the barrier height and width dependence of electron tunneling processes, oligo-\(p\)-xylene and related substituted oligo-\(p\)-phenylene systems represent an attractive alternative. Fig. 7 compares the optical absorption spectra of two series of donor–bridge–acceptor molecules, one of them with unsubstituted oligo-\(p\)-phenylene bridges (a) and the other with oligo-\(p\)-xylene spacers (b). While the four phenylene systems exhibit strongly length-dependent behavior in the spectral region between 270 and 350 nm, the four xylene dyads give spectra that are virtually identical to each other.\(^{24}\) This shows that the HOMO–LUMO gap of the oligo-\(p\)-xylene bridges stays essentially constant, and even though the absolute energies of these orbitals cannot be determined easily by experimental means, it suggests that the bridge redox states are similarly length independent as in the case of the fluorene oligomers. The lack of increasing \(\pi\)-conjugation with increasing length is essentially due to steric constraints imposed by the methyl substituents and the comparatively large equilibrium torsion angles (\(\varphi_{\text{ph–ph}}\)) between individual xylene spacers with respect to the situation in unsubstituted phenylene units. In short, oligo-\(p\)-xylene bridges seem to be right at the borderline between strongly \(\pi\)-conjugated systems and unconjugated bridges such as alkane or bicyclo[2.2.2]octane spacers.
Fig. 8b shows how the rate for charge transfer ($k_{ET}$) across oligo-p-xylene spacers depends on the length of these bridges. The observation of exponential distance dependences for both donor–bridge–acceptor series shown in Fig. 8a is in line with the tunneling mechanism. The important finding here is that the distance dependences for the two series are different: with the rhenium photosensitizer one obtains $\beta = 0.52 \text{ Å}^{-1}$, whereas for the ruthenium sensitizer $\beta = 0.77 \text{ Å}^{-1}.25$ This difference can be rationalized when considering the energetics for hole transfer in the two different types of dyads (Fig. 8c): in the rhenium systems, hole transfer to the phenothiazine (PTZ) unit occurs from the excited state of the metal complex, and hence the excited-state oxidation potential of this complex ($E_{ox} \approx 1.42 \text{ V vs. SCE}$) is of interest in this case (Fig. 8c, left). In the ruthenium dyads, hole transfer occurs from photogenerated rhenium(III) in the ground state and hence the ground-state oxidation potential of Ru(2,2'-bipyridine)$_2^{2+}$ ($E_{ox} = 1.22 \text{ V vs. SCE}$) is of interest in this case (Fig. 8c, left). The oxidation potential of the oligo-p-xylene bridge in the dyads cannot be measured directly, but a value of 1.67 V vs. SCE measured for oxidation of a dimethyldiphenyl reference molecule represents a reasonable approximation. Keeping in mind that the tunneling-energy gap is a transition-state quantity (Fig. 2b), one may crudely approximate $\Delta E$ for hole transfer with the difference in metal and bridge oxidation potentials. This yields $\Delta E \approx 0.25 \text{ eV}$ for the rhenium systems (Fig. 8c, right) and $\Delta E \approx 0.45 \text{ eV}$ for the ruthenium dyads (Fig. 8c, left). Thus it appears that the shallower distance dependence for hole tunneling in the rhenium systems compared to the ruthenium dyads is caused by a smaller tunneling energy gap.25

Additional support for this interpretation comes from analysis of the experimentally determined $\beta$-values in terms of a model which was originally developed for description of the tunneling of radioactive $\alpha$-particles through potential energy barriers. The probability $\kappa$ for a particle to tunnel through a square potential energy barrier is dependent on the mass ($m$) of the particle, the width of the barrier ($d$), and the effective barrier height ($\Delta E_{eff}$) (eqn (4)).26

$$
\kappa \propto \exp \left( -2\sqrt{2m\Delta E_{eff}}d \right) 
$$

According to the superexchange model, the distance decay constant ($\beta$) for charge transfer in a donor–bridge–acceptor system as illustrated in Fig. 2a is merely a function of $h$ and $\delta$ with the latter parameter representing the length of the repeating bridge unit (eqn (3)). Combination of eqn (3) and (4) leads to an expression that relates experimentally accessible $\beta$-values to effective tunneling barrier heights ($\Delta E_{eff}$):5

$$
\Delta E_{eff} = \frac{h^2}{8m^*}\left(\frac{\beta^2}{\delta^2}\right) = 0.952 \text{ eV Å}^2
$$

Application of this expression (Fig. 8d) yields $\Delta E_{eff} = 0.26 \text{ eV}$ for the rhenium systems and $\Delta E_{eff} = 0.55 \text{ eV}$ for the ruthenium dyads. These effective tunneling barrier heights are strikingly close to the estimated tunneling-energy gaps of $\Delta E = 0.25 \text{ eV}$ and $0.45 \text{ eV}$, respectively. The close agreement of $\Delta E_{eff}$ and $\Delta E$ values strongly supports the interpretation of the different tunneling behavior in the rhenium and ruthenium dyads from Fig. 8b in terms of differences in tunneling barrier heights, and it narrows the role played by the simultaneous driving-force variation. The general applicability of this approach of combining the superexchange theory with the Gamov model for tunneling probabilities of radioactive particles (eqn (5)) is supported by a recent study that reports on a good correlation of distance decay constants ($\beta$-values) with tunneling barrier heights ($\Delta E_{eff}$) in a wide variety of different materials, ranging from semiconductors to proteins, water, and even vacuum.27,28

The experimental observation of different distance decay constants for the same bridge is analogous to the occurrence of different linear attenuation factors ($\mu$) associated with the penetration of $\gamma$-radiation into a given material as a function of the energy of the incoming radioactive radiation. For instance in lead, $\mu = 1.83 \text{ cm}^{-1}$ for 500 keV radiation, whereas $\mu = 1.42 \text{ cm}^{-1}$ for 600 keV radiation.29 Fig. 9 illustrates the different distance dependences of $\gamma$-ray penetration in lead for 500 keV and 600 keV photons. It underscores the important
point that for a given material, significantly different distance dependences of tunneling events may be observed. The rhenium complexes in Fig. 8a may be interpreted as donors of more energetic holes than the ruthenium photosensitizers, hence the occurrence of two different distance dependences for hole tunneling across the same oligo-p-xylene bridge is expected.

The bottom line is that the distance decay constant is dependent on the donor–bridge energy gap even in the tunneling regime, long before the hopping mechanism is activated. Under no circumstances it is a parameter specific to a given molecular bridge, neither theoretically nor in practice. The perhaps clearest experimental example for the importance of energy-gap effects in the tunneling regime is provided by a study of hole transfer in DNA hairpins. The same issue has also been addressed in great depth for more conjugated systems than phenylene oligomers.

5. Donor–bridge energy gaps in triplet–triplet energy transfer

Electron tunneling and Dexter-type triplet–triplet energy transfer are mechanistically similar because they are both based on electron-electron exchange. The theoretical concepts outlined in the prior sections are therefore to a wide extent also valid for triplet–triplet energy transfer. d5 metal dimine complexes are popular choices as donor–acceptor pairs for investigations of triplet–triplet energy transfer, particularly the Ru(bpy)32+–Os(bpy)32+ couple. In the uppermost donor–bridge–acceptor systems of Fig. 10a (Ru–ph5–Os) these two reactants are linked by variable-length oligo-p-phenylene bridges. Photoexcitation of the Ru(bpy)42+ complex ultimately populates the lowest triplet metal-to-ligand charge transfer (3MLCT) state at 2.12 eV from which energy transfer to the lowest 3MLCT state of Os(bpy)32+ is exergonic by roughly 0.4 eV (Fig. 10c, left). The lowest triplet states of the intermediary rigid rod-like spacers are at substantially higher energies, ranging from ~2.85 eV for biphenyl (ph2) to ~2.35 eV for the bridge comprised of 5 phenylene units (ph5). Thus, in the case of the Ru–ph5–Os dyads, the electronic excitation energy cannot be passed onto the oligo-p-phenylene bridge, and the global process of Ru(bpy)32+-to-Os(bpy)32+ energy transfer may be regarded as a tunneling phenomenon to which the molecular bridge imposes a barrier. Indeed, the energy transfer rate constant (kET) in the Ru–ph5–Os dyads is exponentially dependent on the donor–acceptor distance (filled circles in Fig. 10b) with an attenuation factor of β = 0.50 Å−1.33 As for the abovementioned unsubstituted oligo-p-phenylene bridged electron transfer systems, the β-value contains rather limited information regarding the dependence of the tunneling process on barrier width, because of the simultaneous strong variation of barrier height.

In the second dyad series shown in Fig. 10a (Ir–ph5–Ru), Ru(bpy)2+ acts as an energy acceptor while the donor is a cyclometalated iridium(III) complex with a lowest 3MLCT state at ~2.65 eV. The shift of the donor level to higher energies has important implications for the energy transfer process and its distance dependence: the lowest triplet states of the bridges with n > 2 are now energetically lower than the donor level (Fig. 10c, right). Thus, the iridium-to-ruthenium triplet–triplet energy transfer process may potentially occur via a hopping mechanism. As a matter of fact, the distance dependence of kET in the Ir–ph5–Ru series of dyads is substantially weaker than for the Ru–ph5–Os series (open squares in Fig. 10b), and the experimentally determined β-value of 0.07 Å−1 is in line with hopping.

In the dyads from Fig. 11a an aluminium trisquinolinate (Alq3) energy donor is connected to three platinum...
6. Accelerated hole transfer in electron-rich phenylene bridges

Oligo-\(p\)-dimethoxybenzene bridges exhibit similar length independent optical absorption spectra as oligo-\(p\)-xylenes (Fig. 7b), suggesting that the overall \(\pi\)-conjugation increases only to a minor extent upon bridge lengthening in both cases.\(^{37}\) This makes sense because \(p\)-dimethoxybenzene and \(p\)-xylene bridge units are sterically similarly demanding, and in both cases one may expect equilibrium torsion angles \((\phi_{ph-ph})\) between adjacent bridge units on the order of 60°. This compares to equilibrium \(\phi_{ph-ph}\) values around 30° for unsubstituted oligo-\(p\)-phenylenes, and it leads to weaker bridge–bridge coupling \((\text{h}_{bb})\) in \(p\)-dimethoxybenzene and \(p\)-xylene oligomers with respect to unsubstituted phenylenes. In consequence, the distance dependence for hole tunneling across oligo-\(p\)-xylenes was found to be significantly steeper than that for comparable oligo-\(p\)-phenylene systems,\(^{38}\) as predicted by eqn (3).

However, regarding \(p\)-dimethoxybenzene oligomers, what is lost in a lowered \(\text{h}_{bb}\)-value may be regained by a simultaneous lowering of \(\Delta_{e}\), because of a drastic lowering of the bridge oxidation potentials. In the two series of donor–bridge–acceptor molecules from Fig. 12a, photogenerated Ru(bpy)\(_3^+\) acts as a hole donor and phenothiazine (PTZ) as a hole acceptor. The oligo-\(p\)-xylene and oligo-\(p\)-dimethoxybenzene bridges are assumed to have similar \(\text{h}_{bb}\) (because of similar \(\phi_{ph-ph}\)), hence any significant difference in the distance dependence of the hole transfer rate \((k_{ET})\) is likely to reflect a difference in \(\Delta_{e}\) (eqn (3)). For the oligo-\(p\)-xylene bridges \(\beta = 0.77\) \(\text{Å}^{-1}\) (Fig. 12b), but for the oligo-\(p\)-dimethoxybenzene system \(k_{ET}\) is too large to be measurable for \(n \leq 3\), and one is forced to limit the comparison to the two dyads with \(n = 4\) (Fig. 12c): charge transfer across the tetra-\(p\)-xylene bridge is associated with a time constant (\(\tau_{CT}\)) of 20 \(\mu\)s, while for the tetra-\(p\)-dimethoxybenzene spacer the same process is 3 orders of magnitude more rapid with \(\tau_{CT} = 17\) ns.\(^{37}\) Fig. 12d illustrates the explanation for this large discrepancy: an energetic barrier to Ru(III)-to-PTZ hole transfer is imposed by the bridging molecules and their oxidation potentials. Free \(p\)-dimethoxybenzene is oxidized at substantially lower electrochemical potentials than \(p\)-xylene, hence the tunneling barrier is significantly smaller for oligo-\(p\)-dimethoxybenzenes than for oligo-\(p\)-xylenes. Based on the relevant redox potentials, in the specific case of the Ru-dmb\(_{1-4}\)-PTZ molecules this barrier is on the order of 0.1 eV, while for the Ru-xy\(_{1-4}\)-PTZ systems it is approximately 0.45 eV. As proposed already in Section 4, one may equate these values to the tunneling-energy gap \((\Delta_{e})\); but it must be kept in mind that this represents a crude approximation at best.

The time-resolution of the experiments from Fig. 12b is defined by the kinetics of Ru(III) formation through a bimolecular flash-quench technique and not by the temporal resolution of the laser used for photoexcitation.\(^{37}\) The photogeneration of oxidized ruthenium is a prerequisite for observation of charge transfer in these dyads, and therefore the distance dependence of \(k_{ET}\) using Ru-dmb\(_{n}\)-PTZ molecules with \(n < 4\) is not easily accessible. However, the donor–acceptor couple is identical in both series of dyads from

Fig. 11 (a) Molecules comprised of an aluminium trisquinolinate (Alq\(_3\)) energy donor, variable-length fluorene bridges (\(\text{fl}_n\), \(n = 1–4\)), and three platinum tetraphenylporphyrin (PtTPP) triplet energy acceptors.\(^{36}\) The residues R on the quinoline ligands denote the attachment of additional bridge–acceptor branches, i.e., there is one Alq\(_3\) donor and three equidistant PtTPP acceptors per molecule. (b) Semi-logarithmic plot of the rate constant for triplet–triplet energy transfer as a function of Alq\(_3\)-PtTPP distance. (c) Energies of the triplet excited states that are relevant for bridge-mediated long-range energy transfer. (Adapted with permission from ref. 36. Copyright 2006 American Chemical Society.)

tetraphenylporphyrin (PtTPP) acceptors by oligo-fluorene bridges.\(^{36}\) By contrast to the fluorene-mediated hole transfer from PDI to PTZ (Fig. 5), the distance dependence of the energy transfer rate constant here is exponential (Fig. 11b). Although in principle this points towards a tunneling process, the low \(\beta\)-value of 0.21 \(\text{Å}^{-1}\) suggests that there is an important contribution from the hopping mechanism. The fundamentally different distance dependences in Fig. 5b and 11b are likely due to the fact that the relevant bridge states are fundamentally different in the two cases: for hole transfer from PDI to PTZ, the one-electron oxidized states (\(\text{fl}_n^+\)) are important, while for the triplet–triplet energy transfer process from Alq\(_3\) to PtTPP the lowest triplet excited states of the fluorene oligomers (\(3\text{fl}_n^+\)) are relevant. Contrary to the \(\text{fl}_n^+\) states, the lowest \(3\text{fl}_n\) levels turn out to be strongly length dependent (Fig. 11c), and moreover they provide a large barrier to triplet–triplet energy transfer in the mono- and bi-fluorene systems. Only for the Alq\(_3\)-fl\(_n\)-PtTPP dyads with \(n = 3\) and \(n = 4\) does hopping seem energetically possible. Even longer oligomers would be needed in order to clearly identify an ohmic distance dependence for Alq\(_3\)-fl\(_n\)-PtTPP systems with \(n \geq 3\).
Fig. 12a, and one may therefore expect that $k_{ET}$-values for the Ru–xy$_n$–PTZ and Ru–dmb$_n$–PTZ systems adopt the same value when extrapolated to a donor–acceptor van der Waals contact distance (i.e., $r_{DA} = r_0$ in eqn (2)). This has been done in Fig. 12b, and the dotted straight line shows the exponential distance dependence that would be expected for the oligo-p-dimethoxybenzene systems based on this hypothesis. Its slope yields $b = 0.40$ Å/C0$^1$, which is a value practically on par with those reported for several unsubstituted oligo-p-phenylene systems. When converted to an effective barrier height by use of eqn (5), one obtains $\Delta E_{eff} = 0.15$ eV, which is reasonably close to the $\Delta \varepsilon$-value of 0.1 eV estimated above from redox potentials (Fig. 12d).

It is clear that several crude approximations are part of this distance dependence analysis, moreover, at barrier heights of only 0.1 eV, tunneling contributions may become important. Nevertheless, it does indeed appear that what is lost in $h_{sb}$ when going from unsubstituted oligo-p-phenylene to oligo-p-dimethoxybenzene, may be regained by a lowered tunneling-energy gap ($\Delta \varepsilon$). Additional support for this conclusion comes from an investigation of electronic coupling in the two mixed-valence bis(triarylamine) radical cations from Fig. 13: for the phenylene-bridged system $H_{DA} = 1000$ cm$^{-1}$ while for the p-dimethoxybenzene-bridged radical $H_{DA}$ is nearly twice as large, despite a simultaneous increase in the torsion angle between mutually connected aromatic units on the nitrogen–nitrogen axis.$^{39}$

Through combination of p-xylene and p-dimethoxybenzene units it is possible to construct oligomers comprised of building blocks that are structurally very similar yet impose strongly non-uniform overall barriers to hole transfer. This has been exploited in the system from Fig. 14b, in which a rhenium tricarbonyl hole donor is separated from a phenothiazine acceptor–bridge–acceptor systems for photoinduced hole transfer from a rhenium(I) tricarbonyl diimine donor to a phenothiazine (PTZ) acceptor.$^{40}$ The penta-p-xylene bridge (a) imposes an ordinary rectangular barrier to tunneling holes, while the bridge with the central p-dimethoxybenzene unit (b) imposes a double barrier. The time constants for hole transfer in the two cases differ by a factor of 55. (Reprinted from Inorg. Chim. Acta, Barrier heights in long-range electron tunneling, copyright (2011), with permission from Elsevier.)
(PTZ) hole acceptor by a sequence of two \( p \)-xylene, one \( p \)-dimethoxybenzene, and two more \( p \)-xylene units.\textsuperscript{40} Due to the strongly different oxidation potentials of the individual building blocks, this sequence of bridging units leads to an overall barrier that resembles a double barrier shape with a local dip at the central \( p \)-dimethoxybenzene spacer. This has important consequences for long-range charge transfer: photoinduced hole transfer in the system from Fig. 14b is associated with a time constant of 0.24 \( \mu s \), while in the reference system from Fig. 14a (with an ordinary rectangular barrier caused by a penta-\( p \)-xylene bridge), the same process occurs with a time constant of 13.2 \( \mu s \).\textsuperscript{40} This factor of 55 difference in charge transfer rates is in line with the factor of 32 acceleration reported in another study, in which photoinduced charge transfer from an aminonaphthalene imide donor to a naphthalene diimide acceptor occurs either across a single \( p \)-xylene unit or a single \( p \)-dimethoxybenzene spacer.\textsuperscript{41}

7. Through-bond versus through-space pathways for electron transfer

The vast majority of studies in the field of interest to this review deal with charge or energy transfer along covalent pathways, which rely on \( \sigma \)-bonds between individual phenylene units. In \( \pi \)-stacked phenylene systems, there is the possibility of charge or energy transfer across such stacks. This issue has received considerable attention in the context of DNA-mediated charge transfer due to the presence of short interplanar separations (\( \sim 3.5 \text{~Å} \)) between individual nucleobases,\textsuperscript{42} but for other classes of \( \pi \)-stacked structures, comparatively little is known about the importance of \( \pi \)-stack pathways for charge and energy transfer.

In the three molecules from Fig. 15a a zinc porphyrin electron donor is connected to a benzoquinone acceptor through 1,8-naphthyl pillaring motifs.\textsuperscript{43} In the simplest case (Fig. 15, left), the porphyrin and quinmine components are directly juxtaposed, leading to a donor–acceptor distance of only 3.3 \( \text{Å} \). Through inclusion of 1,8-phenyl-disubstituted naphthyl bridging units, donor–bridge–acceptor systems with more extended \( \pi \)-stacks can be obtained (Fig. 15a, middle and right). The distance between the C1- and C1’-phenyl carbons of 1,8-diphenylnaphthalene is 2.99 \( \text{Å} \), hence the resulting \( \pi \)-stack is strongly compressed with sub-van der Waals interplanar separations. Photoexcitation of these dyads leads to the formation of a charge-separated state with oxidized zinc porphyrin donor and reduced benzoquinone acceptor. The kinetics for formation and disappearance of this state are accessible by transient absorption spectroscopy, whereby the rate constants for charge-separation and charge-recombination are obtained. The distance dependences for the two processes are shown in Fig. 15b. In the case of the shortest member of this dyad series, the rate for charge-separation was so fast (\( \sim 10^{13} \text{~s}^{-1} \)) that it was considered an adiabatic process, and consequently its rate was not factored into the determination of the \( \beta \)-value.\textsuperscript{43} Both distance dependences in Fig. 15b are relatively soft when compared to those found for certain donor–acceptor substituted DNA hairpin structures (\( \beta = 0.7–1.1 \text{~Å}^{-1} \)).\textsuperscript{30,42} This is somewhat astonishing given the fact that large tunneling-energy gaps are to be expected for electron and hole transfer in the \( \pi \)-stacked phenylene: the one-electron reduction and oxidation potentials of benzene are \(-3.35 \text{~V} \) and 2.30 \( \text{~V} \) vs. SCE, while the photoexcited zinc porphyrin donor is oxidized at \(-1.21 \text{~V} \) vs. SCE, and the benzoquinone acceptor is reduced at \(-0.58 \text{~V} \) vs. SCE. Tunneling-energy gaps (\( \Delta E \)) of 2.14 \( \text{eV} \) for electron transfer and 2.88 \( \text{eV} \) for hole transfer might therefore be expected. The tunneling-energy gaps in some of the abovementioned DNA hairpins are considerably smaller, yet the dyads from Fig. 15a exhibit significantly weaker distance dependences for charge transfer. This may be due to shorter interplanar contacts (and hence larger \( h_{bb} \)) between individual phenyl units in the strongly compressed sub-van der Waals contact systems.

It is difficult to assess the relative contributions of \( \sigma \)- and \( \pi \)-pathways to the overall charge transfer in the molecules from Fig. 15a. Although the short arene–arene contacts of only \( \sim 3.0 \text{~Å} \) strongly speak to the importance of charge transfer across \( \pi \)-stacks, electron transport across the \( \sigma \)-backbone of these donor–bridge–acceptor molecules is not necessarily completely negligible. In this context, it would be interesting to compare these systems to an analogous series of dyads with 1,5-di(phenyl)naphthyl pillars, in which closely interacting phenyl–phenyl \( \pi \)-stacks cannot form, but a similar \( \sigma \)-pathway would still be present. Nevertheless, the efficiency of \( \pi \)-coupling pathways in stacked phenylene systems is beyond question, as the example of the two organic mixed valence systems from Fig. 16 underscores in convincing manner: the conformationally flexible ortho-xylene bridge in the molecule on the left allows a coplanar \textit{syn}-arrangement of the two 2,5-dimethoxytolyl moieties in the radical monocation of this system.\textsuperscript{44} In the hexafluoroantimonate salt, the interplanar...
Contrary to many other (simple) aromatic building blocks, the triplet excited states of fluorene units have spectroscopic signatures that are comparatively easy to detect and identify. Thus, using femtosecond transient absorption spectroscopy, it has been possible to observe (transitory) population of the $^3$hl$_2$ and $^3$hl$_3$ states in the course of benzophenone-to-naphthalene triplet–triplet energy transfer in the two longer dyads from Fig. 17a. Thus, there is unusually clear evidence for a hopping mechanism in the bi- and trifluorened bridged systems. For the dyad with a single fluorene spacer no such direct evidence for involvement of the bridge triplet state could be obtained. What is more, the overall reaction kinetics are consistent with direct Bp-to-Nap energy transfer via tunneling, despite the fact that the bridge is energetically accessible in this case as well. Tunneling is likely to be preferred for Np–fl$_1$–Nap because of the large free-energy change between the benzophenone and naphthalene triplet states ($^3$Bp, $^3$Nap) and the comparatively short distance between the donor and the acceptor. Due to the much stronger distance dependence of the tunneling process with respect to hopping (exponential versus $1/r_{DA}$), the percentage of population transferred by single-step tunneling was estimated to drop from 60% in Bp–fl$_1$–Nap to 28% in Bp–fl$_2$–Nap and 10% in Bp–fl$_3$–Nap. The basis for this estimation is a distance decay constant of 0.36 Å$^{-1}$ for tunneling. This rather low $\beta$-value may be due to the fact that the \( \pi \)-stacks are strongly compressed.

Aside from the unusual molecular structures of the Bp–fl$_n$–Nap molecules, the beauty of this particular study lies in the direct observation of the bridge-occupied states and the associated direct distinction between tunneling and hopping mechanisms. The crossover between the two mechanisms is usually only deduced indirectly from a “kink” in plots of the transfer rate against the donor–acceptor distance, as the case for example in Fig. 4b.

8. Summary

Phenylene oligomers offer the possibility to explore a plethora of charge and energy transfer phenomena ranging all the way from pure tunneling to downhill hopping. For fundamental mechanistic investigations of these processes, for example distance dependence studies of charge transfer rates, these oligomers are well suited because in many cases there exist synthetic (C–C coupling) methodologies for construction of variable-length donor–bridge–acceptor systems in modular (stepwise) fashion that are nowadays fairly straightforward. From the physical chemistry point of view, phenylene oligomers remain simple enough systems to allow systematic studies that can be used for testing of charge transfer theories. Through chemical modifications, fundamental quantities such as torsion angles and donor–bridge energy gaps can be fine-tuned, and their influence on charge and energy transfer can be studied in considerable depth. Some of the key insights that have emerged from such fundamental investigations are the following.

(i) Distance dependence studies of charge or energy transfer across unsubstituted oligo-\( p \)-phenylenes usually imply the simultaneous variation of two parameters that are decisive for transfer kinetics, namely barrier width and barrier height.

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**Fig. 16** Molecular structures of two isomeric organic mixed valence systems with vastly different electronic couplings \( (H_{DA}) \) between the two redox-active 2,5-dimethoxytolyl sites.\(^{44}\)

\[ H_{DA} = 400 \text{ cm}^{-1} \]

**Fig. 17** (a) Donor–bridge–acceptor systems for investigations of triplet–triplet energy transfer from a benzophenone (Bp) donor to a naphthalene (Nap) acceptor across \( \pi \)-stacked fluorene bridges.\(^{45}\) (b) Energies of the relevant donor, bridge, and acceptor triplet states in the overall energy transfer process. (Adapted with permission from ref. 45.)

The distance between 2,5-dimethoxytolyl units is only 3.2 Å, and an electronic coupling \( (H_{DA}) \) of 400 cm$^{-1}$ between the two redox active aryls has been estimated from intervalence absorption band analysis. For the analogous system with a \( \text{para-xylylene} \) bridge (Fig. 16b) such \( \pi \)-stacking is not possible, and there is no detectable electronic coupling between the two dimethoxytolyl units.\(^{44}\)

In the three molecules from Fig. 17a photoexcitation of a benzophenone (Bp) donor leads to triplet–triplet energy transfer to a naphthalene (Nap) acceptor across \( \pi \)-stacked fluorene units.\(^{45}\) Crystal structure analysis reveals that individual cofacially arranged fluorenes are separated by only \( \sim 3.0 \) Å at their closest contact, and NMR spectroscopy indicates that the \( \pi \)-stacks persist in solution. Interestingly, the energy of the lowest triplet excited states \( (^3\text{hl}_{\text{fl}_n}) \) of the bridging fluorenes is length independent, which is in clear contrast to the situation encountered in linearly conjugated oligo-fluorenes (Fig. 11c) or oligo-\( p \)-phenylenes (Fig. 10c). Triplet–triplet energy transfer therefore has virtually identical reaction energetics for all three donor–bridge–acceptor systems from Fig. 17a, regarding overall reaction free energy as well as donor–bridge energy gap. Indeed, triplet–triplet energy transfer is expected to be energetically downhill from the donor to the bridge and onwards to the acceptor in all three systems (Fig. 17b), and one might therefore expect that a hopping process will prevail for all them.
Barrier heights tend to decrease with lengthening, due to increasing overall π-conjugation of the oligomer. This leads to an acceleration of D-A process, which is superimposed on the (dominant) deceleration caused by increasing the barrier width. In extreme cases, there is a transition in mechanism from tunneling at short distances to hopping at long distances.\(^{11}\)

(ii) Disentanglement of the barrier height and width dependence is possible by reverting to oligo-fluorene, oligo-p-xylene or oligo-p-dimethoxybenzene bridges, which have energy levels that are considerably more length independent than those of unsubstituted oligo-p-phenylenes.\(^{16,25,37}\)

(iii) While the influence of conformational effects on barrier heights in phenylene oligomers is very important, the influence of tunneling-energy gaps cannot always be neglected. Through introduction of electron-donating methoxy-substituents, the overall π-conjugation of the oligomeric phenylene backbone is lowered, but at the same time the tunneling-energy gap for hole transfer is decreased considerably.\(^37,41\) and this may in fact outweigh the loss in π-conjugation.\(^39\) In OPVs and OPEs alkoxy-substitution is common to improve solubility of these strongly π-conjugated systems. However, the influence of electron-donating substituents on hole conduction in these molecular wire materials may be considerably more subtle, because they offer charge injection barriers that are inherently small.

(iv) An important point concerning the distance decay constant, which has been put forward in prior reviews,\(^{46,47}\) is further underscored by the studies presented herein: the \(\beta\)-value is not a bridge-specific parameter, but it is determined by the combination of a donor, bridge, and acceptor. This is due to the dependence of \(\beta\) on the donor–bridge energy gap (or more precisely: the tunneling-energy gap, \(\Delta\varepsilon\)), hence donor–bridge energetics are important even in the tunneling regime—long before hopping becomes activated.

(v) Tunneling-energy gaps (\(\Delta\varepsilon\)) cannot be measured directly because this is a transition-state quantity, but estimates for effective tunneling-barrier heights (\(\Delta\varepsilon_{\text{eff}}\)) are accessible from experimentally determined \(\beta\)-values.\(^5,23\) This approach relies on a physical model which was originally developed in the context of \(\pi\)-particle tunneling. The concept of \(\Delta\varepsilon_{\text{eff}}\) is also useful to rationalize the experimental observation of different \(\beta\)-values for a given molecular bridge depending on the donor–acceptor combination to which it is attached.\(^28\) Certain donor-acceptor combinations yield more energetic charge carriers than others, and consequently the tunneling probability (or \(\beta\)-value) is not exclusively a bridge-specific function. This is analogous to the penetration of \(\gamma\)-rays into a given material, which is also dependent on the energy of the incoming radioactive radiation.

(vi) Charge and energy transfer across π-stacked phenylene systems can be remarkably efficient. Direct observation of reaction intermediates in a hopping sequence represents one of the recent highlights from this field.\(^{45}\)

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Notes and references