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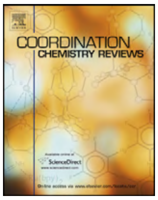

Review

Importance of covalence, conformational effects and tunneling-barrier heights for long-range electron transfer: Insights from dyads with oligo-*p*-phenylene, oligo-*p*-xylene and oligo-*p*-dimethoxybenzene bridges

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ABSTRACT

This review reports on our recent studies of phototriggered charge transfer in rigid rod-like donor-bridge-acceptor molecules in liquid solution as well as between randomly dispersed electron donors and acceptors in frozen organic glasses. Investigation of the distance dependence of the rates of these reactions provides detailed insight into the various factors that govern long-range charge transfer efficiencies. The importance of covalence can be probed by a comparison of charge tunneling through a frozen toluene matrix to tunneling across an oligo-*p*-xylene bridge. The distance decay constants for these two processes are $\beta = 1.26\,\text{Å}^{-1}$ and $\beta = 0.52\,\text{Å}^{-1}$, respectively, indicating that charge tunneling across a covalent xylene–xylene contact is ~2 orders of magnitude more efficient than that across a noncovalent toluene–toluene contact. Conformational effects were investigated by comparing hole tunneling across oligo-*p*-xylene and oligo-*p*-phenylene bridges. The latter are significantly more π-conjugated and mediate long-range hole tunneling with $\beta = 0.21\,\text{Å}^{-1}$ between a ruthenium–phenothiazine donor–acceptor couple. Quantitative analysis indicates that in this particular instance, tunneling across a phenylene–phenylene contact is roughly 50 times more efficient than tunneling across a xylene–xylene contact. The use of oligo-*p*-dimethoxybenzene wires instead of the structurally very similar oligo-*p*-xylene bridges was found to lead to a strong acceleration of long-range hole transfer rates: The 23.5-Å charge transfer step across four xylene units occurs within 20 μs, but the charge transfer over the same distance across four dimethoxybenzene units takes only 17 ns. This is attributed to a tunneling-barrier effect that is caused by a large difference in oxidation potentials between the two types of bridges.

1. Introduction

Long-range electron transfer reactions play important roles in chemistry, biology, and physics. Controlled electron flow over long distances is necessary for photosynthesis and respiration [1]. Controlling (long-range) electron transfer rates is also a prerequisite for artificial light-to-chemical energy conversion [2], and efficient charge transport across molecular bridges is needed for a molecular electronics technology [3]. This has stimulated much experimental and theoretical work on biological and artificial donor-bridge-acceptor systems. *Biological* examples include ruthenium(II)-modified azurins [4,5] and other proteins and pep-

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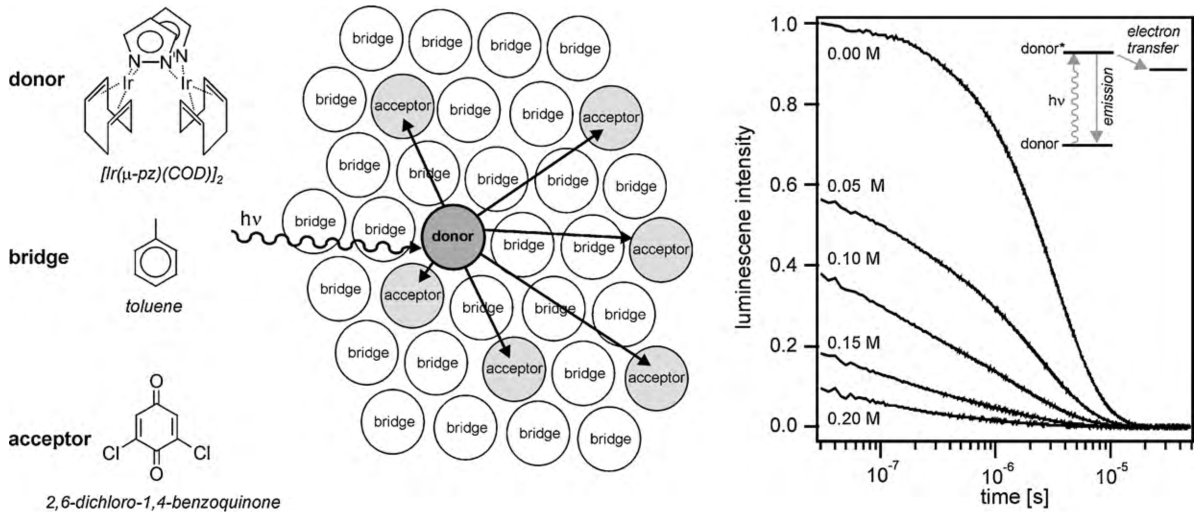


Fig. 1. Left: Donor, bridge, and acceptor molecules used for photoinduced electron tunneling across a frozen toluene matrix [80,81]. Middle: Random dispersion of the charge-neutral donors and acceptors in the toluene glass and illustration of the long-range electron tunneling steps involving a random distribution of donor–acceptor distances. The frozen solution is very dilute in donor (~50 mM) but concentrated in acceptor (0.05–0.20 M). Right: Decays of the luminescence emitted by the iridium donor complex in the presence of variable acceptor concentrations; inset: energy level scheme illustrating the physical origin of the luminescence quenching.

tides equipped with inorganic photosensitizers [6–15], work that yielded detailed insight into how protein/peptide backbone mediates long-range charge transfer. Similar research on DNA has led to a relatively clear picture of charge transport in this biomolecule [16–20]. Among the numerous *artificial* donor-bridge-acceptor systems investigated, the early work on rigid saturated hydrocarbon [21,22] and aromatic bridges [23,24] is particularly noteworthy since much of the later research has built on these landmark studies. This later work includes for example the investigation of long-range charge and energy transfer across oligo-*p*-phenylene [25–38], oligo-*p*-phenylene vinylene (OPV) [39–43], oligo-*p*-phenylene ethynylene (OPE) [44–49], and oligo-fluorene bridges [50–52]. Some of these molecular entities act as true molecular wires in that they mediate long-range charge transfer with very shallow distance dependences, and this makes them interesting for molecular electronics applications. Other research is more concerned with establishing long-lived charge-separated states which store solar energy that could potentially be used to drive other chemical reactions that are thermodynamically uphill [2,53–56]. In this context, porphyrin–fullerene molecules have led to particularly spectacular results [57–59], but systems based on ruthenium(II) [60–63], iridium(III) [64–66], and platinum(II) [67–70] have also attracted significant attention. Despite all these efforts, the conversion of light energy into useful chemical energy remains a challenge as illustrated for example by photochemical hydrogen production: Many of the newly explored systems still rely on the use of sacrificial electron donors [71–74].

Our own research in the area of long-range electron transfer has been concerned with more fundamental problems. Over the past three years we have sought to explore the importance of factors such as covalence, molecular conformation, and so-called tunneling-energy effects on the rates of long-range charge transfers [75]. Here, we give a review of this work in which we have focused mostly on rigid rod-like donor-bridge-acceptor molecules with ruthenium(II) and rhenium(I) sensitizers to phototrigger the charge transfers. As molecular bridges, oligo-*p*-xylenes have become our benchmark as they represent an intermediate case between strongly π-conjugated wires and relatively poor conductors such as alkanes. This allows investigation of charge tunneling processes by the superexchange mechanism over reasonably long distances without interference from incoherent charge hopping mechanisms. Starting from the oligo-*p*-xylene systems, it is possible to obtain quantitative insight into the importance of covalent linkages between the individual bridging units by comparison to long-range charge tunneling through a frozen toluene matrix (Section 2). A direct comparison of the distance dependence of long-range charge transfer rates across oligo-*p*-xylene and oligo-*p*-phenylene bridges addresses the importance of conformational effects (Section 3), and tunneling-energy effects were explored by comparing oligo-*p*-xylene bridges to structurally similar oligo-*p*-dimethoxybenzene molecules (Section 4).

2. Importance of covalence: comparison of long-range charge transfer across covalent xylene and noncovalent toluene bridges

Mechanistic investigations of long-range electron transfer reactions frequently aim at exploring their distance dependences. In order to extract meaningful information from such studies, it is usually necessary to keep electron donors and acceptors at a fixed distance. This is often done by connecting them via rigid spacers [2], but it is also possible to randomly disperse non-connected donors and acceptors in solid or viscous matrices in which diffusion is much slower than the electron transfer events [76–79]. In principle, such investigations are possible with all solvents and solvent mixtures that form glasses upon cooling. The simplest aromatic solvent that fulfils this requirement is toluene. Recent work shows that with suitable electron donors and acceptors it is possible to investigate phototriggered long-range electron tunneling across a toluene glass at 77 K [80,81]. The choice of donor/acceptor couple is crucial in this type of experiment. At 77 K, there are only ~50 cm^{-1} of thermal energy available, and consequently, the electron transfer has to be very nearly driving-force optimized to ensure that it occurs at appreciable rates at long (>10 Å) distances. Moreover, a significant decrease in driving-force is usually associated with the rigidification of a solvent matrix upon glass formation [82–85]. This is because in liquid solution, solvent dipoles reorient around an ion pair formed by photoinduced electron transfer, whereas in a frozen glass such a stabilization of the ion pair state is not possible any more. As a result, the energy level of the ion pair is much higher in the rigid glass, and often this shuts down the photoinduced electron transfer completely. The consequence of this is that only donor/acceptor couples providing very high solution driving-

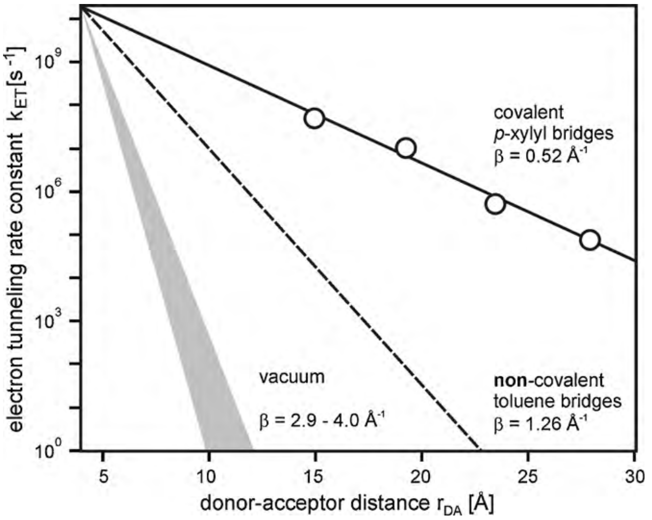
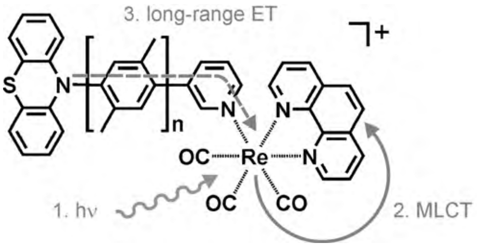


Fig. 2. Distance dependence of long-range charge tunneling through vacuum [93], a frozen toluene glass [80,81], and a covalent oligo-*p*-xylene bridge [97].



n	k_{ET} [s^{-1}]
1	$\geq 1{\cdot}10^8$
2	$5.0{\cdot}10^7$
3	$1.0{\cdot}10^7$
4	$8.7{\cdot}10^5$
5	$4.2{\cdot}10^5$

Fig. 3. Donor-bridge-acceptor molecules for investigation of long-range charge tunneling across oligo-*p*-xylene bridges [97]. Excitation of these molecules with blue or UV light (1) produces a long-lived (2.9 μs) metal-to-ligand charge transfer (MLCT) state (2), which is sufficiently oxidizing to induce phenothiazine-to-rhenium long-range electron transfer (3). The table on the right lists the rate constants for this process as a function of bridge length (n = number of bridge units).

forces stand a chance to remain functional in a frozen glass. At the moment when the glass is formed, the donors and acceptors should be charge-neutral species, otherwise electrostatic interactions may impede the formation of a random dispersion of donors and acceptors. What is more, for photoinduced electron transfer initiating from a donor with a long-lived emissive excited state, there must be no spectral overlap between the donor emission and the acceptor absorption – otherwise there will be competing energy transfer processes. Lastly, the electron acceptor must be soluble at fairly high concentrations (~1 M) in the frozen glass and the glass quality should still be such to allow comparative luminescence quantum yield measurements. A donor/acceptor couple that fulfills all these requirements is shown in the left part of Fig. 1 [80,81]. This couple is comprised of a dinuclear iridium complex $[Ir(\mu\text{-}pz)(COD)]_2$ (μ-pz = μ-pyrazolyl, COD = 1,5-cyclooctadiene), and a 1,4-benzoquinone acceptor.

The $[Ir(\mu\text{-}pz)(COD)]_2$ complex is a very potent photoreductant with $E(^{+}Ir_2/^{*}Ir_2) = -1.81$ V vs. SCE in fluid acetonitrile [86,87], whereas 2,6-dichloro-1,4-benzoquinone has a redox potential of $E(Q/Q^{-}) = -0.18$ V vs. SCE [88]. This yields approximately 1.6 eV of driving-force for photoinduced electron transfer between these two species in fluid solution. In the frozen toluene glass, the benzoquinone acceptor induces pronounced quenching of the luminescence emitted by the iridium complex which is a manifestation of electron transfer. Energy transfer quenching can be ruled out due to the absence of a spectral overlap between the iridium emission and the benzoquinone absorption [80,81]. The luminescence decays in the right part of Fig. 1 are strongly non-exponential due to the fact that an ensemble of different donor–acceptor distances is probed (Fig. 1, middle). Under the assumption that the donor–acceptor distribution is completely random, it is possible to analyze these luminescence decays quantitatively using a model originally developed for energy transfer [89–91]. Provided the time-integrated relative luminescence intensities in absence and presence of variable amounts of quencher are known, it is possible to extract a distance decay constant (β-value) for the electron tunneling process [89–92]. For the $[Ir(\mu\text{-}pz)(COD)]_2$/2,6-dichloro-1,4-benzoquinone couple in frozen toluene this analysis yields $\beta = 1.26$ Å^{-1} [80,81].The dashed straight line in Fig. 2 illustrates the distance dependence of electron tunneling through the frozen toluene matrix. As seen from this plot, tunneling can occur at appreciable rates even at a donor–acceptor distance of 20 Å. For comparison, electron tunneling through vacuum proceeds with $\beta = 2.9$–4.0 Å^{-1} (grey wedge) [93], and consequently a 20-Å tunneling step is an extremely unlikely event in this medium. One important conclusion that may be drawn from the β-value for toluene is that, as in other instances [94–96], through-solvent charge tunneling is relatively efficient.

An interesting question is how much more efficient this bridge-mediated tunneling process would become if covalent linkages were introduced between the individual toluene molecules. Since toluene and *p*-xylene are chemically similar, it appears reasonable to address this question by comparing electron tunneling through a toluene glass to electron tunneling across covalent oligo-*p*-xylene spacers. The series of donor-bridge-acceptor molecules from Fig. 3 may be used for this purpose [97]. In these dyads, photo-excitation of the rhenium(I) tricarbonyl complex triggers an intramolecular electron transfer from the phenothiazine donor to the excited metal complex, as observed previously for shorter related dyads with other linkers [98–102]. Using time-resolved luminescence and transient absorption spectroscopy, it is possible to determine the rate constants for the intramolecular electron transfer events [97,103], yielding the numerical values given on the right in Fig. 3. The four measurable data points fall onto a single line in the semilogarithmic plot of Fig. 2 (solid line), i.e., the rate for phenothiazine-to-rhenium charge transfer decreases exponentially with the length of the oligo-*p*-xylene bridge. This is a clear indication of a tunneling process [104]. A fit to the experimental data yields $\beta = 0.52$ Å^{-1} for the covalent oligo-*p*-xylene bridges in this particular instance [97].

Thus, there is a substantial difference between the β-values obtained for noncovalent toluene bridges on the one hand (1.26 Å^{-1}) and the covalent xylene bridges on the other hand (0.52 Å^{-1}). If the toluene glass is approximated as a face-centered cubic lattice of spherical particles, then the nearest-neighbor center-to-center distance is approximately 6.3 Å [80,81]. Using $\beta = 1.26$ Å^{-1} one can infer from Eq. (1) that charge transfer rates decrease by a factor of 2800 per toluene–toluene contact.

$$k_{ET}(d) = k_0 \exp(-\beta d) \tag{1}$$

In the oligo-*p*-xylene bridges the xylene–xylene center-to-center distance (d) is 4.3 Å, and from $\beta = 0.52$ Å^{-1} and Eq. (1) it is found that charge transfer rates decrease only by a factor of 9 per xylene–xylene contact. Over a 6.3-Å distance, the calculated decrease amounts to a factor of 26.

The conclusion from this simple analysis is that when going from a noncovalent toluene–toluene contact to a covalent xylene–xylene contact, this accelerates the charge transfer event by roughly two orders of magnitude per bridge–bridge contact [80,97]. This finding underscores the importance of covalent bonds for artificial long-range electron transfer, and it speaks to the relevance of tunneling pathway models for the interpretation of biological electron transfer. The best tunneling pathways in proteins must involve many covalent bonds and few van der Waals gaps. The role of the protein

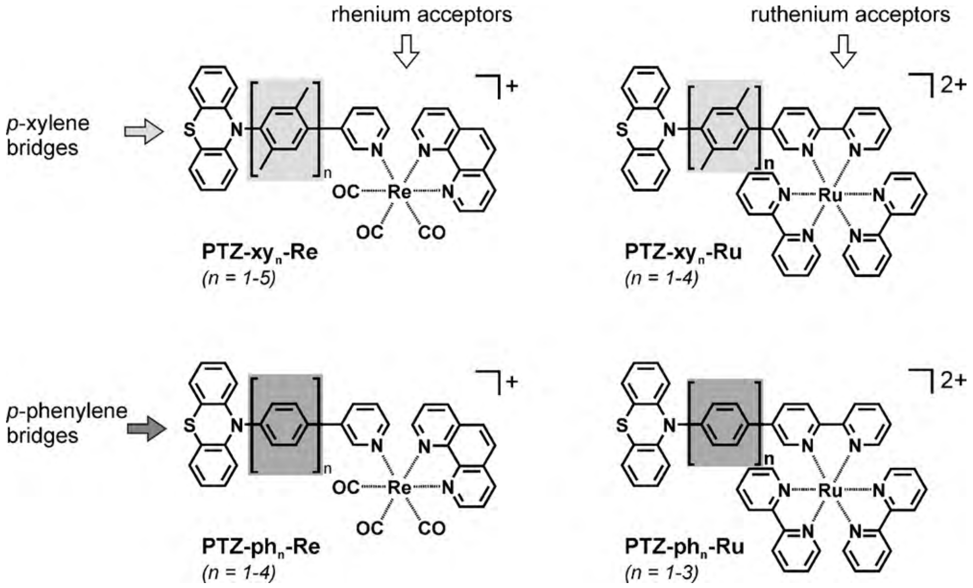


Fig. 4. Molecular structures of oligo-*p*-xylene and oligo-*p*-phenylene bridged rhenium(I)–phenothiazine and ruthenium(II)–phenothiazine dyads [97,105,106].

backbone is to ensure that there is a reasonable balance between covalent and noncovalent contacts [80,81].

3. Conformational effects: comparison of oligo-*p*-xylene and oligo-*p*-phenylene bridges

Using nearly identical methodologies as those employed for the synthesis of the donor-bridge-acceptor molecules from Fig. 3, analogous oligo-*p*-phenylene bridged rhenium(I)–phenothiazine as well as xylene- and phenylene-bridged ruthenium(II)–phenothiazine dyads are synthetically accessible (Fig. 4) [97,105,106].

Fig. 5 shows the optical absorption spectra obtained from dichloromethane and acetonitrile solutions of these dyads. Inspection of these UV–vis data reveals the presence of the typical MLCT and intraligand absorptions commonly observed for ruthenium(II) diimine and rhenium(I) tricarbonyl diimine complexes [107–110]. However, the most important observation concerns the spectral variations that are associated with lengthening of the molecular bridges. Significant spectral changes occur upon lengthening of the oligo-*p*-phenylene bridges (Fig. 5, lower half). In particular, there is a pronounced red-shift of the absorption features around 300–350 nm, an effect that is much less important in the oligo-*p*-xylene bridged systems (Fig. 5, upper half). This contrasting behavior is attributed to differences in π-conjugation between the phenylene and xylene bridges [97,106,111]. In oligo-*p*-phenylenes, the equilibrium dihedral angle (ϕ_{ph}) between neighboring phenyl units is 35–40° according to DFT calculations [26,112–114]. Analogous calculations performed on oligo-*p*-xylenes have produced equilibrium dihedral angles (ϕ_{xy}) of 65–70° between two adjacent xylene units [106]. Evidently, the additional methyl groups present on the xylene spacers represent sufficient steric bulk to force the individual xylene units into a pronounced out-of-plane equilibrium conformation, and π-conjugation is much more important for the oligo-*p*-phenylenes than for the oligo-*p*-xylenes [115]. In the former, each additional phenyl unit increases π-conjugation further,

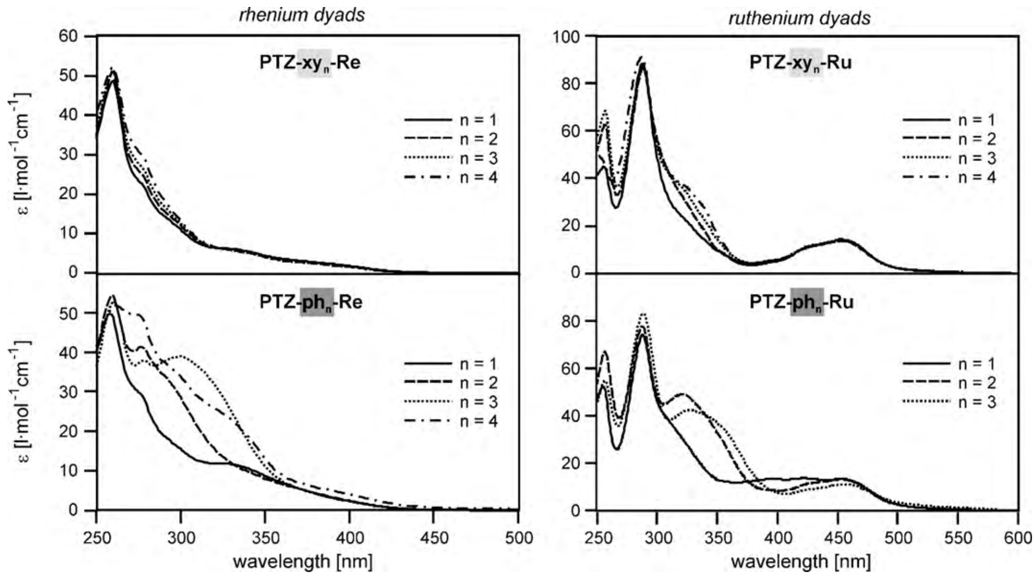


Fig. 5. Optical absorption spectra measured on room-temperature solutions of the donor-bridge-acceptor molecules from Fig. 4. Left: rhenium(I)–phenothiazine dyads in CH_2Cl_2 [97], right: ruthenium(II)–phenothiazine dyads in CH_3CN [105,106].

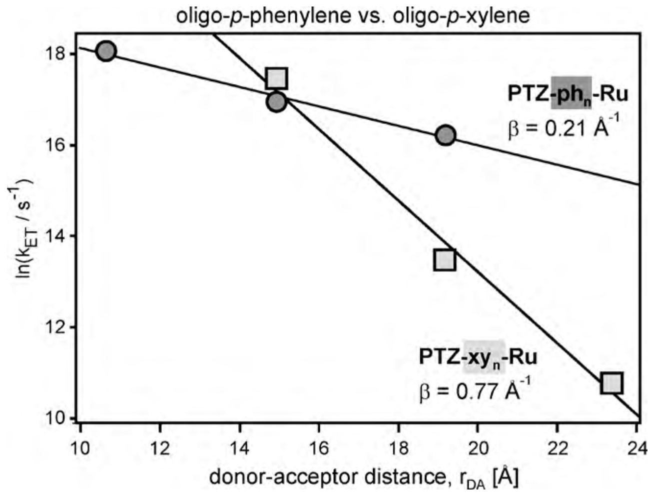


Fig. 6. Distance dependence of charge transfer in the ruthenium(II)–phenothiazine dyads from Fig. 4 [105]. Circles: Electron transfer from $\text{Ru(bpy)}_3{}^+$ to $\text{PTZ}^{\bullet+}$ across oligo-*p*-phenylenes [106], measured after photo-excitation of $\text{Ru(bpy)}_3{}^{2+}$ and subsequent (fast) $^*\text{Ru(bpy)}_3{}^{2+}$-to-PTZ (forward) electron transfer. Squares: Electron transfer from PTZ to $\text{Ru(bpy)}_3{}^{3+}$ across oligo-*p*-xylenes [105]. In this case, the oxidized $\text{Ru(bpy)}_3{}^{3+}$ species was photo-generated by a so-called flash-quench technique using excess methylviologen [116–120].

hence the abovementioned absorption band shifts between 300 and 350 nm. In the xylenes this effect is relatively weak.

This difference in π-conjugation has important consequences for the long-range electron transfer behavior of the two types of bridges. Through combination of time-resolved luminescence and transient absorption spectroscopies it has been possible to investigate the distance dependence of phototriggered charge transfer across the oligo-*p*-phenylene and oligo-*p*-xylene spacers in the ruthenium(II)–phenothiazine dyads from the right part of Fig. 4 [105,106]. As seen from Fig. 6, the difference in distance dependences of charge transfer rates is remarkable. Charge tunneling across the phenylene bridges proceeds with $\beta = 0.21\,\text{Å}^{-1}$, whereas for the xylene spacers $\beta = 0.77\,\text{Å}^{-1}$. It should be noted that for technical reasons [106], two quite different electron transfer processes were monitored for obtaining the data in Fig. 6, namely (back-)electron transfer from reduced $\text{Ru(bpy)}_3{}^+$ to oxidized phenothiazine ($\text{PTZ}^{\bullet+}$) in the phenylene systems, and phenothiazine (PTZ) to $\text{Ru(bpy)}_3{}^{3+}$ electron transfer in the xylene systems (see caption of Fig. 6). The driving-forces for these two processes differ quite significantly [106], which explains why the two lines in Fig. 6 intersect in the middle of the plot.

When analyzing these β-values, it is reasonable to depart from the usual assumption that the distance dependence of electron transfer rates is essentially due to a decrease in electronic donor–acceptor coupling (H_{DA}) upon bridge lengthening. According to superexchange theory [121], the electronic coupling mediated by a bridge comprised of *n* identical repeat units is a function of four parameters (Eq. (2)).

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

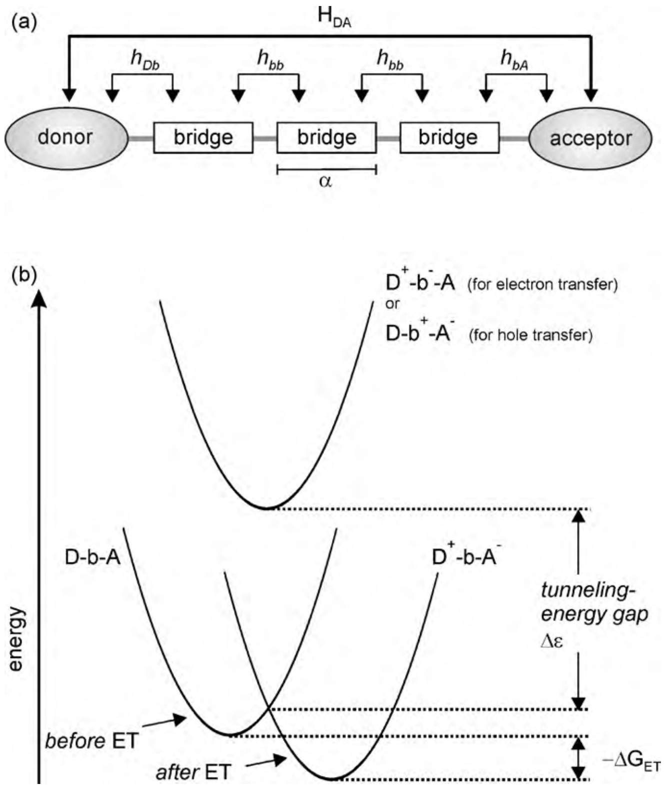


Fig. 7. Graphical illustration of the parameters involved in the superexchange model [105,122]. $-\Delta G_{\text{ET}}$ is the driving-force for electron transfer from the donor (D) to acceptor (A). Δε is the so-called tunneling-energy gap.

The four parameters are: donor–bridge coupling (H_{Db}), bridge–bridge coupling (h_{bb}), bridge–acceptor coupling (h_{bA}) and the so-called tunneling-energy gap Δε. As illustrated by Fig. 7, the latter is defined as the energy difference between the donor/acceptor system at the transition-state configuration and the one-electron reduced or oxidized states of the bridge, depending on whether electron or hole transfer is considered. It can be shown that in this model the distance decay constant is only a function of h_{bb}, Δε, and the length (α) of an individual bridge unit [106,122]:

$$\beta = \frac{2}{\alpha}\ln\left(\frac{\Delta\varepsilon}{h_{\text{bb}}}\right) \tag{3}$$

For the phenylene and xylene units $\alpha = 4.3\,\text{Å}$. The tunneling energy gaps Δε for the dyads can be estimated from redox potentials in reasonable approximation (Section 4) [106]. Consequently, using the experimental β-values from Fig. 6, the relative magnitudes of phenyl–phenyl ($h_{\text{bb,ph}}$) and xylyl–xylyl coupling ($h_{\text{bb,xy}}$) can be estimated. The result is that $h_{\text{bb,ph}} \approx 7\cdot h_{\text{bb,xy}}$ [106], and this is consistent with prior investigations of the influence of torsion angles on electron and energy transfer rates [123–126].

According to semiclassical theory, electron transfer rates k_{ET} are proportional to the square of the electronic coupling matrix elements. [104,127]. Consequently, when going from a poorly π-conjugated xylyl–xylyl contact ($h_{\text{bb,xy}}$) to a more strongly π-conjugated phenyl–phenyl contact ($h_{\text{bb,ph}}$), this accelerates long-range electron transfer by a factor of ∼50 ($\approx 7^2$) per bridge–bridge contact.

4. Importance of tunneling-barrier heights

4.1. Tunneling-barrier variation through change of the donor redox potential: ruthenium versus rhenium

Depending on whether rhenium(I) or ruthenium(II) photosensitizers are used, different distance dependences for charge transfer across oligo-*p*-xylene bridges are observed. For the rhenium–phenothiazine dyads (Fig. 4, upper left), charge tunneling across the xylene spacers proceeds with $\beta = 0.52\,\text{Å}^{-1}$ (Fig. 2) [97], whereas for the ruthenium–phenothiazine dyads (Fig. 4, upper right) $\beta = 0.77\,\text{Å}^{-1}$ for exactly the same bridge (Fig. 6) [105]. A similar observation has been reported previously for long-

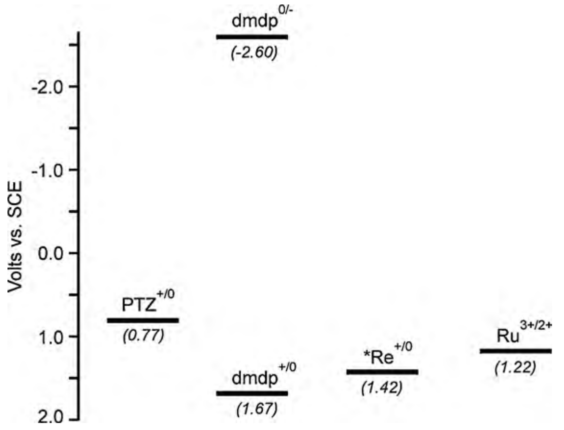


Fig. 8. Redox potentials of donor, bridge, and acceptor moieties in the rhenium and ruthenium oligo-*p*-xylene dyads from Fig. 4 [105].

range electron transfer across DNA hairpins [122,128,129]. Indeed, research in the past few years has provided much evidence for the fact that distance decay constants (β-values) are not bridge-specific parameters, but rather a property of the entire donor-bridge-acceptor system [128–137]. Thus, in order to rationalize where the above difference in xylene β-values comes from, it is necessary to consider the energetics for charge transfer in the two respective dyad series.

In the rhenium(I) dyads, electron transfer occurs from phenothiazine to the photoexcited metal center. The electrochemical potential for PTZ oxidation in these molecules is 0.77 V vs. SCE, the potential for reduction of the excited rhenium complex is ~1.4 V vs. SCE (Fig. 8) [97,105]. The redox potentials of the oligo-*p*-xylene bridges cannot be measured directly. The best guess for their potentials comes from an electrochemical investigation of the 4,4′-dimethyldiphenyl (dmdp) molecule [138]. This reference molecule is oxidized at 1.67 V vs. SCE and reduced at −2.60 V vs. SCE. Given the much closer energetic proximity of the one-electron *oxidized* dmdp states to the relevant PTZ and rhenium states compared to the one-electron *reduced* dmdp states, a *hole* tunneling mechanism must prevail over *electron* tunneling in the oligo-*p*-xylene bridges [105]. Therefore it is reasonable to consider the photoexcited rhenium complex as a hole donor and the neutral phenothiazine molecule as a hole acceptor. This terminology is used in Fig. 9 in which the PTZ hole acceptor level is set arbitrarily to an energy of 0 eV. On the basis of the redox potentials from Fig. 8, the *Re(I) hole donor level is 0.65 eV higher in energy, whereas the one-electron oxidized bridge level is 0.9 eV above the PTZ level (Fig. 9, left) [105].

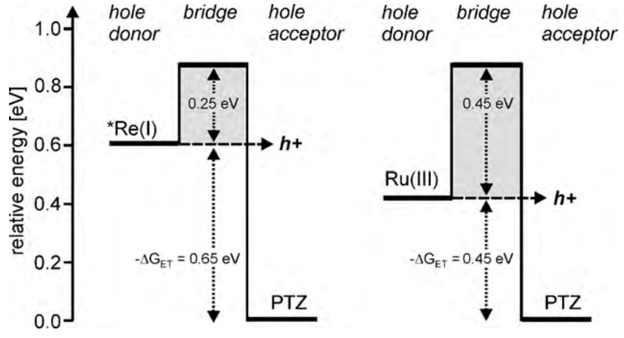


Fig. 9. Energy level diagrams for hole tunneling in dyads with two different hole donors (photoexcited $[\mathrm{Re(phen)(CO)_3(pyridine)}]^+$ and photo-generated $\mathrm{Ru(bpy)_3}^{3+}$, respectively) but the same bridge (oligo-*p*-xylene) and the same hole acceptor (PTZ) [105].

An analogous energy level diagram can be established for the ruthenium–phenothiazine dyads (Fig. 9, right). In these molecules, there is hole transfer from a photochemically generated $\mathrm{Ru(bpy)_3}^{3+}$ complex to PTZ [105], and consequently the Ru(III/II) ground-state redox potential is relevant (Fig. 8). As seen from Fig. 9, this results in an energetic situation that is significantly different from that encountered for the rhenium dyads [105]. First, the driving-force ($-\Delta G_{\mathrm{ET}}$) for charge transfer decreases when going from rhenium to ruthenium. Second, the barrier for hole tunneling is smaller in the rhenium systems than in the ruthenium dyads. This second point is in qualitative agreement with the shallower distance dependence observed for charge tunneling with the rhenium photosensitizer: The probability κ for a particle to tunnel through a square potential energy barrier is dependent on the mass (m) of the particle, the width (d) of the barrier, and its height (ΔE_{eff}) [139]:

$$\kappa \propto \exp\left(-\frac{2}{\hbar}\sqrt{2m\Delta E_{\mathrm{eff}}}\,d\right) \propto \exp(-\beta d) \qquad (4)$$

The mathematical relationship between *effective* tunneling barriers (ΔE_{eff}) and distance decay constants for electron transfer (β-values) is the following [104,105,137]:

$$\Delta E_{\mathrm{eff}} = \left(\frac{\hbar^2}{8m_{\mathrm{e}}}\right)\beta^2 \qquad (5)$$

In Eq. (5), m_{e} is the mass of the electron, which leads to a numerical value of 0.952 eV Å^2 for the prefactor in brackets [104,105]. For β = 0.52 Å^{-1} (rhenium dyads) this expression yields ΔE_{eff} = 0.26 eV, and for β = 0.77 Å^{-1} (ruthenium dyads) one obtains ΔE_{eff} = 0.55 eV [105]. Both of these *effective* tunneling barriers compare very favorably to the barriers in Fig. 9 (0.25 and 0.45 eV, respectively) estimated from redox potentials. While this close agreement may be a mere coincidence, this analysis nevertheless supports the interpretation of the different distance dependences in the rhenium and ruthenium oligo-*p*-xylene dyads in terms of different tunneling-barrier heights, and it narrows the role played by the simultaneous driving-force variation [105]. Furthermore, it suggests that the use of redox potentials to estimate the experimentally inaccessible tunneling-energy gap $\Delta\varepsilon$ (Fig. 7b) is reasonable. In short, in lieu of the potential well picture of Fig. 7b, one may use the oversimplified picture of Fig. 9. This implies that the tunneling-energy gap $\Delta\varepsilon$ may be approximated as the donor-bridge energy gap.

4.2. Tunneling-barrier variation through change of the bridge redox potential: oligo-p-xylenes versus oligo-p-dimethoxybenzenes

The distance dependence of hole tunneling through oligo-*p*-xylene bridges is significantly steeper than that commonly observed for charge transfer across unsubstituted oligo-*p*-phenylenes [25–38,105,106]. As discussed in Section 3, this is essentially due to smaller bridge–bridge coupling matrix elements (h_{bb}) for the xylenes relative to the unsubstituted phenylenes caused by larger equilibrium torsion angles. According to Eq. (3), this leads to larger β-values for the substituted bridges. However, the same equation also suggests that the decrease in h_{bb} may be compensated by a simultaneous decrease in the tunneling-energy gap $\Delta\varepsilon$. In order to address this issue, the two donor-bridge-acceptor molecules shown in Fig. 10 were investigated in a comparative study [140].

Both dyads contain exactly the same hole donor (a ruthenium complex) and hole acceptor (a phenothiazine). The bridges are *para*-disubstituted phenylenes in both cases: Either tetra-*p*-xylene (left) or tetra-*p*-dimethoxybenzene (right), yielding an identical donor–acceptor distance of ~23.5 Å in both dyads. The bridge length dependence of the optical absorption spectra for a series of

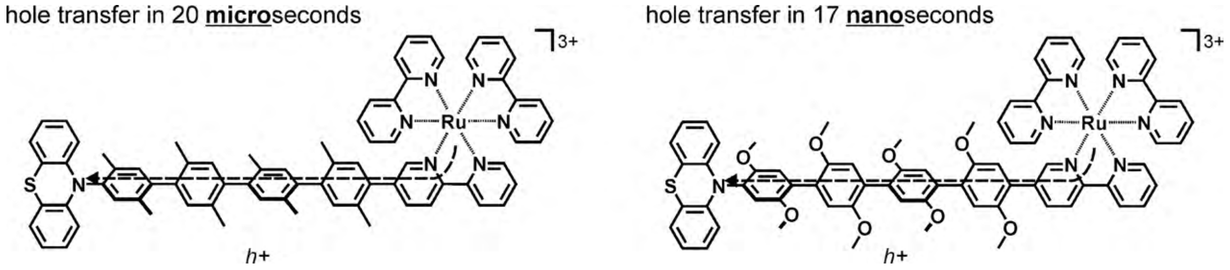


Fig. 10. Donor-bridge-acceptor molecules for phototriggered hole (*h+*) transfer over a 23.5-Å distance. Replacement of the *p*-xylene bridging units by *p*-dimethoxybenzene units leads to a 1000-fold acceleration of hole transfer due to a decrease in the tunneling-energy gap $\Delta\varepsilon$ [140]. In both dyads, charge transfer was triggered by rapid photogeneration of a highly oxidizing $\mathrm{Ru(bpy)_3}^{3+}$ species from the initial $\mathrm{Ru(bpy)_3}^{2+}$ complex via a so-called flash-quench technique. Methylviologen was used as a quencher for this purpose [105].

phenothiazine–dimethoxybenzene–ruthenium dyads is similarly weak as for the corresponding xylene-bridged species [140]. This is a strong indication for similarly large torsion angles between two adjacent *p*-dimethoxybenzene units as between two neighboring *p*-xylenes, suggesting that h_{bb} is indeed similar for both types of bridges.

A so-called flash-quench technique is used to trigger charge transfer in the dyads from Fig. 10 [116–120]. Specifically, this triggers hole transfer from photo-generated $\mathrm{Ru(bpy)_3}^{3+}$ to PTZ, which is a ground-state charge transfer process [105]. The important finding is that hole transfer across the tetra-*p*-xylene bridge takes 20.4 μs [105], whereas that across the tetra-*p*-dimethoxybenzene bridge only takes 17 ns [140]. The evidence for this comes from transient absorption spectroscopy, monitoring both the kinetics of phenothiazine oxidation at 520 nm and ruthenium(III) reduction at 450 nm [105,140].

This 1000-fold rate acceleration can be understood on the basis of a tunneling-energy effect. An analysis identical to that from Section 4.1, using redox potentials to approximate $\Delta\varepsilon$, leads to the energy level diagrams of Fig. 11 [140]. The key point here is that the barrier for hole transfer is much lower for the dimethoxybenzene bridge than for the xylene spacer, due to the fact that *p*-dimethoxybenzene is oxidized much more readily than *p*-xylene [138]. On the basis of redox potentials, $\Delta\varepsilon \approx 0.5$ eV for the xylene-bridged dyad and $\Delta\varepsilon \approx 0.1$ eV for the dimethoxybenzene-bridged molecule [140]. The latter barrier is sufficiently small for a hopping mechanism to become potentially relevant, although the nanosecond time-resolved experiments performed so far have been unable to provide direct spectroscopic evidence for dimethoxybenzene radical cation intermediates. Recent work on peptide electron transfer has shown that *tri*methoxybenzenes can act as stepping stones for charge hopping [141].

The bottom line is that the change from methyl- to methoxy-substitutents on a tetra-*p*-phenylene backbone leads to a 1000-fold acceleration of hole transfer over a 23.5-Å distance. The physical origin of this effect is a decrease in the donor-bridge energy gap [140].

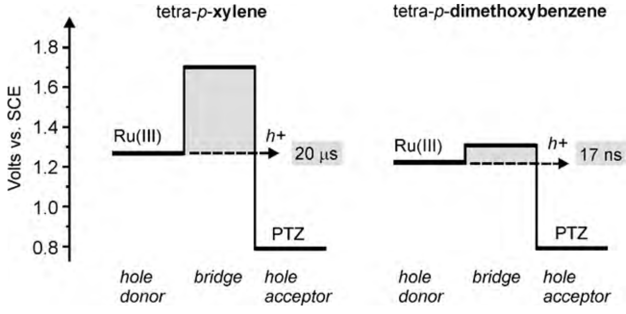


Fig. 11. Energy level diagrams for hole (*h+*) transfer from flash/quench-generated Ru(III) to phenothiazine (PTZ) through tetra-*p*-xylene and tetra-*p*-dimethoxybenzene bridges in the molecules from Fig. 10 [140].

5. Summary and conclusions

The use of oligo-*p*-xylene bridges as benchmark systems provides a means for quantitative investigation of the importance of covalence, conformational effects, and tunneling-barrier effects for long-range charge transfer. Distance dependence studies of electron transfer rates play a central role in this research. The comparison of charge transfer through a frozen toluene matrix to that across covalent oligo-*p*-xylene spacers (Section 2) shows that charge tunneling rates increase by two orders of magnitude per bridge-bridge contact when going from a noncovalent toluene–toluene contact to a covalent xylene–xylene contact [80,81,97,105]. Conformational effects are also very important: Unsubstituted oligo-*p*-phenylene bridges are significantly more π-conjugated than the oligo-*p*-xylene spacers, and this is found to lead to a factor of 50 difference in charge tunneling rates per bridge-bridge contact (Section 3) [106]. Important tunneling-barrier effects for hole transfer are observed upon exchange of a ruthenium hole donor by a rhenium hole donor (Section 4.1) [105], and upon replacement of an oligo-*p*-xylene bridge by an oligo-*p*-dimethoxybenzene wire (Section 4.2) [140].

In combination, the work presented in this article confirms that covalence has the biggest effect on long-range charge transfer efficiencies [2,80,81], but it also indicates that conformational effects (influencing primarily h_{bb} in Eq. (3)/Fig. 7) [106] and tunneling-energy effects ($\Delta\varepsilon$ in Eq. (3)/Fig. 7) can be of similar importance relative to each other [105,140].

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References

[1] I. Bertini, H.B. Gray, E.I. Stiefel, J.S. Valentine, Biological Inorganic Chemistry, University Science Books, Sausalito, California, 2007.
[2] V. Balzani, Electron Transfer in Chemistry, VCH Wiley, Weinheim, 2001, p. 3.
[3] J. Jortner, M.A. Ratner, Molecular Electronics, Blackwell, London, 1997.
[4] H.B. Gray, J.R. Winkler, Ann. Rev. Biochem. 65 (1996) 537.
[5] J.R. Winkler, H.B. Gray, Chem. Rev. 92 (1992) 369.
[6] D.S. Wuttke, M.J. Bjerrum, J.R. Winkler, H.B. Gray, Science 256 (1992) 1007.
[7] C. Shih, A.K. Museth, M. Abrahamsson, A.M. Blanco-Rodriguez, A.J. Di Bilio, J. Sudhamsu, B.R. Crane, K.L. Ronayne, M. Towrie, A. Vlček, J.H. Richards, J.R. Winkler, H.B. Gray, Science 320 (2008) 1760.
[8] S.A. Serron, W.S. Aldridge, C.N. Fleming, R.M. Danell, M.H. Baik, M. Sykora, D.M. Dattelbaum, T.J. Meyer, J. Am. Chem. Soc. 126 (2004) 14506.
[9] R.A. Malak, Z.N. Gao, J.F. Wishart, S.S. Isied, J. Am. Chem. Soc. 126 (2004) 13888.
[10] K.S. Schanze, K. Sauer, J. Am. Chem. Soc. 110 (1988) 1180.
[11] H.K. Rau, N. DeJonge, W. Haehnel, Proc. Natl. Acad. Sci. U.S.A. 95 (1998) 11526.

[12] T.R. Prytkova, I.V. Kurnikov, D.N. Beratan, Science 315 (2007) 622.
[13] J.N. Gehlen, I. Daizadeh, A.A. Stuchebrukhov, R.A. Marcus, Inorg. Chim. Acta 243 (1996) 271.
[14] F. Millett, B. Durham, Biochemistry 41 (2002) 11315.
[15] G. McLendon, J.R. Miller, J. Am. Chem. Soc. 107 (1985) 7811.
[16] C.J. Murphy, M.R. Arkin, Y. Jenkins, N.D. Ghatlia, S.H. Bossmann, N.J. Turro, J.K. Barton, Science 262 (1993) 1025.
[17] C.J. Murphy, M.R. Arkin, N.D. Ghatlia, S. Bossmann, N.J. Turro, J.K. Barton, Proc. Natl. Acad. Sci. U.S.A. 91 (1994) 5315.
[18] F.D. Lewis, R.L. Letsinger, M.R. Wasielewski, Acc. Chem. Res. 34 (2001) 159.
[19] S. Priyadarshy, S.M. Risser, D.N. Beratan, J. Phys. Chem. 100 (1996) 17678.
[20] B. Elias, J.C. Genereux, J.K. Barton, Angew. Chem. Int. Ed. 47 (2008) 9067.
[21] H. Oevering, M.N. Paddon-Row, M. Heppener, A.M. Oliver, E. Cotsaris, J.W. Verhoeven, N.S. Hush, J. Am. Chem. Soc. 109 (1987) 3258.
[22] M.N. Paddon-Row, Acc. Chem. Res. 27 (1994) 18.
[23] A. Helms, D. Heiler, G. McLendon, J. Am. Chem. Soc. 113 (1991) 4325.
[24] A. Helms, D. Heiler, G. McLendon, J. Am. Chem. Soc. 114 (1992) 6227.
[25] B. Schlicke, P. Belser, L. De Cola, E. Sabbioni, V. Balzani, J. Am. Chem. Soc. 121 (1999) 4207.
[26] E.A. Weiss, M.J. Ahrens, L.E. Sinks, A.V. Gusev, M.A. Ratner, M.R. Wasielewski, J. Am. Chem. Soc. 126 (2004) 5577.
[27] M.T. Indelli, C. Chiorboli, L. Flamigni, L. De Cola, F. Scandola, Inorg. Chem. 46 (2007) 5630.
[28] T. Lazarides, D. Sykes, S. Faulkner, A. Barbieri, M.D. Ward, Chem. Eur. J. 14 (2008) 9389.
[29] M.T. Indelli, F. Scandola, L. Flamigni, J.-P. Collin, J.-P. Sauvage, A. Sour, Inorg. Chem. 36 (1997) 4247.
[30] F. Barigelletti, L. Flamigni, M. Guardigli, A. Juris, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin, J.-P. Sauvage, Inorg. Chem. 35 (1996) 136.
[31] F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E.C. Constable, A.M.W.C. Thompson, J. Am. Chem. Soc. 116 (1994) 7692.
[32] E.A. Weiss, M.J. Tauber, R.F. Kelley, M.J. Ahrens, M.A. Ratner, M.R. Wasielewski, J. Am. Chem. Soc. 127 (2005) 11842.
[33] P.P. Lainé, S. Campagna, F. Loiseau, Coord. Chem. Rev. 252 (2008) 2552.
[34] P.P. Lainé, F. Bedioui, F. Loiseau, C. Chiorboli, S. Campagna, J. Am. Chem. Soc. 128 (2006) 7510.
[35] H.A. Meylemans, C.F. Lei, N.H. Damrauer, Inorg. Chem. 47 (2008) 4060.
[36] S. Welter, F. Lafolet, E. Cecchetto, F. Vergeer, L. De Cola, ChemPhysChem 6 (2005) 2417.
[37] A.J. Berresheim, M. Müller, K. Müllen, Chem. Rev. 99 (1999) 1747.
[38] E. Lörtscher, M. Elbing, M. Tschudy, C. von Hänisch, H.B. Weber, M. Mayor, H. Riel, ChemPhysChem 9 (2008) 2252.
[39] W.B. Davis, W.A. Svec, M.A. Ratner, M.R. Wasielewski, Nature 396 (1998) 60.
[40] J.F. Eckert, J.F. Nicoud, J.F. Nierengarten, S.G. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, L. Ouali, V. Krasnikov, G. Hadziioannou, J. Am. Chem. Soc. 122 (2000) 7467.
[41] H.D. Sikes, J.F. Smalley, S.P. Dudek, A.R. Cook, M.D. Newton, C.E.D. Chidsey, S.W. Feldberg, Science 291 (2001) 1519.
[42] E.E. Neuteboom, S.C.J. Meskers, P.A. van Hal, J.K.J. van Duren, E.W. Meijer, R.A.J. Janssen, H. Dupin, G. Pourtois, J. Cornil, R. Lazzaroni, J.L. Brédas, D. Beljonne, J. Am. Chem. Soc. 125 (2003) 8625.
[43] F. Giacalone, J.L. Segura, N. Martín, D.M. Guldi, J. Am. Chem. Soc. 126 (2004) 5340.
[44] S. Creager, C.J. Yu, C. Bamdad, S. O'Connor, T. MacLean, E. Lam, Y. Chong, G.T. Olsen, J.Y. Luo, M. Gozin, J.F. Kayyem, J. Am. Chem. Soc. 121 (1999) 1059.
[45] J. Fortage, E. Goransson, E. Blart, H.C. Becker, L. Hammarström, F. Odobel, Chem. Commun. (2007) 4629.
[46] B. Albinsson, M.P. Eng, K. Pettersson, M.U. Winters, Phys. Chem. Chem. Phys. 9 (2007) 5847.
[47] M. Wielopolski, C. Atienza, T. Clark, D.M. Guldi, N. Martín, Chem. Eur. J. 14 (2008) 6379.
[48] M.P. Eng, J. Mårtensson, B. Albinsson, Chem. Eur. J. 14 (2008) 2819.
[49] M. Hissler, A. El-ghayoury, A. Harriman, R. Ziessel, Angew. Chem. Int. Ed. 37 (1998) 1717.
[50] R.H. Goldsmith, L.E. Sinks, R.F. Kelley, L.J. Betzen, W.H. Liu, E.A. Weiss, M.A. Ratner, M.R. Wasielewski, Proc. Natl. Acad. Sci. U.S.A. 102 (2005) 3540.
[51] C. Atienza-Castellanos, M. Wielopolski, D.M. Guldi, C. van der Pol, M.R. Bryce, S. Filippone, N. Martín, Chem. Commun. (2007) 5164.
[52] S. Asaoka, N. Takeda, T. Lyoda, A.R. Cook, J.R. Miller, J. Am. Chem. Soc. 130 (2008) 11912.
[53] G.L. Closs, J.R. Miller, Science 240 (1988) 440.
[54] D. Gust, T.A. Moore, A.L. Moore, Acc. Chem. Res. 34 (2001) 40.
[55] L.S. Fox, M. Kozik, J.R. Winkler, H.B. Gray, Science 247 (1990) 1069.
[56] J.H. Alstrum-Acevedo, M.K. Brennaman, T.J. Meyer, Inorg. Chem. 44 (2005) 6802.
[57] H. Imahori, D.M. Guldi, K. Tamaki, Y. Yoshida, C.P. Luo, Y. Sakata, S. Fukuzumi, J. Am. Chem. Soc. 123 (2001) 6617.
[58] H. Imahori, Y. Sekiguchi, Y. Kashiwagi, T. Sato, Y. Araki, O. Ito, H. Yamada, S. Fukuzumi, Chem. Eur. J. 10 (2004) 3184.
[59] Y. Kobori, S. Yamauchi, K. Akiyama, S. Tero-Kubota, H. Imahori, S. Fukuzumi, J.R. Norris, Proc. Natl. Acad. Sci. U.S.A. 102 (2005) 10017.
[60] M. Borgström, N. Shaikh, O. Johansson, M.F. Anderlund, S. Styring, B. Åkermark, A. Magnuson, L. Hammarström, J. Am. Chem. Soc. 127 (2005) 17504.
[61] M. Borgström, O. Johansson, R. Lomoth, H.B. Baudin, S. Wallin, L.C. Sun, B. Åkermark, L. Hammarström, Inorg. Chem. 42 (2003) 5173.
[62] C. Goze, C. Leiggener, S.X. Liu, L. Sanguinet, E. Levillain, A. Hauser, S. Decurtins, ChemPhysChem 8 (2007) 1504.
[63] C. Chiorboli, S. Fracasso, F. Scandola, S. Campagna, S. Serroni, R. Konduri, F.M. MacDonnell, Chem. Commun. (2003) 1658.
[64] L. Flamigni, J.-P. Collin, J.-P. Sauvage, Acc. Chem. Res. 41 (2008) 857.
[65] B. Geiss, C. Lambert, Chem. Commun. (2009) 1670.
[66] J.C. Freys, G. Bernardinelli, O.S. Wenger, Chem. Commun. (2008) 4267.
[67] J.E. McGarrah, R. Eisenberg, Inorg. Chem. 42 (2003) 4355.
[68] J.E. McGarrah, Y.J. Kim, M. Hissler, R. Eisenberg, Inorg. Chem. 40 (2001) 4510.
[69] S. Chakraborty, T.J. Wadas, H. Hester, R. Schmehl, R. Eisenberg, Inorg. Chem. 44 (2005) 6865.
[70] C. Monnereau, J. Gomez, E. Blart, F. Odobel, S. Wallin, A. Fallberg, L. Hammarström, Inorg. Chem. 44 (2005) 4806.
[71] S. Rau, B. Schafer, D. Gleich, E. Anders, M. Rudolph, M. Friedrich, H. Gorls, W. Henry, J.G. Vos, Angew. Chem. Int. Ed. 45 (2006) 6215.
[72] H. Ozawa, Y. Yokoyama, M. Haga, K. Sakai, Dalton Trans. (2007) 1197.
[73] H. Ozawa, M.A. Haga, K. Sakai, J. Am. Chem. Soc. 128 (2006) 4926.
[74] E.D. Cline, S.E. Adamson, S. Bernhard, Inorg. Chem. 47 (2008) 10378.
[75] J.C. Freys, D. Hanss, M.E. Walther, O.S. Wenger, Chimia 63 (2009) 49.
[76] T. Guarr, M. McGuire, S. Strauch, G. McLendon, J. Am. Chem. Soc. 105 (1983) 616.
[77] S. Strauch, G. McLendon, M. McGuire, T. Guarr, J. Phys. Chem. 87 (1983) 3579.
[78] J.R. Miller, J.A. Peeples, M.J. Schmitt, G.L. Closs, J. Am. Chem. Soc. 104 (1982) 6488.
[79] R.K. Huddleston, J.R. Miller, J. Phys. Chem. 86 (1982) 200.
[80] O.S. Wenger, B.S. Leigh, R.M. Villahermosa, H.B. Gray, J.R. Winkler, Science 307 (2005) 99.
[81] O.S. Wenger, H.B. Gray, J.R. Winkler, Chimia 59 (2005) 94.
[82] G.L. Gaines, M.P. Oneil, W.A. Svec, M.P. Niemczyk, M.R. Wasielewski, J. Am. Chem. Soc. 113 (1991) 719.
[83] M.R. Wasielewski, D.G. Johnson, W.A. Svec, K.M. Kersey, D.W. Minsek, J. Am. Chem. Soc. 110 (1988) 7219.
[84] P.Y. Chen, T.J. Meyer, Inorg. Chem. 35 (1996) 5520.
[85] K.V. Mikkelsen, M.A. Ratner, Chem. Rev. 87 (1987) 113.
[86] J.L. Marshall, S.R. Stobart, H.B. Gray, J. Am. Chem. Soc. 106 (1984) 3027.
[87] D.C. Smith, H.B. Gray, Coord. Chem. Rev. 100 (1990) 169.
[88] S. Fukuzumi, S. Koumitsu, K. Hironaka, T. Tanaka, J. Am. Chem. Soc. 109 (1987) 305.
[89] M. Inokuti, F. Hirayama, J. Chem. Phys. 43 (1965) 1978.
[90] A. Blumen, J. Manz, J. Chem. Phys. 71 (1979) 4694.
[91] A. Blumen, J. Chem. Phys. 72 (1980) 2632.
[92] A. Ponce, H.B. Gray, J.R. Winkler, J. Am. Chem. Soc. 122 (2000) 8187.
[93] J.N. Onuchic, D.N. Beratan, J.R. Winkler, H.B. Gray, Annu. Rev. Biophys. Biomol. Struct. 21 (1992) 349.
[94] K. Kumar, I.V. Kurnikov, D.N. Beratan, D.H. Waldeck, M.B. Zimmt, J. Phys. Chem. A 102 (1998) 5529.
[95] J.M. Nadeau, M. Liu, D.H. Waldeck, M.B. Zimmt, J. Am. Chem. Soc. 125 (2003) 15964.
[96] A.M. Napper, I. Read, R. Kaplan, M.B. Zimmt, D.H. Waldeck, J. Phys. Chem. A 106 (2002) 5288.
[97] D. Hanss, O.S. Wenger, Inorg. Chem. 47 (2008) 9081.
[98] K.S. Schanze, L.A. Cabana, J. Phys. Chem. 94 (1990) 2740.
[99] P.Y. Chen, T.D. Westmoreland, E. Danielson, K.S. Schanze, D. Anthon, P.E. Neveux, T.J. Meyer, Inorg. Chem. 26 (1987) 1116.
[100] A. Vlček, M. Busby, Coord. Chem. Rev. 250 (2006) 1755.
[101] K.S. Schanze, D.B. MacQueen, T.A. Perkins, L.A. Cabana, Coord. Chem. Rev. 122 (1993) 63.
[102] D.J. Liard, M. Busby, I.R. Farrell, P. Matousek, M. Towrie, A. Vlček, J. Phys. Chem. A 108 (2004) 556.
[103] D. Hanss, O.S. Wenger, Inorg. Chim. Acta 362 (2009) 3415.
[104] H.B. Gray, J.R. Winkler, Proc. Natl. Acad. Sci. U.S.A. 102 (2005) 3534.
[105] D. Hanss, O.S. Wenger, Inorg. Chem. 48 (2009) 671.
[106] D. Hanss, O.S. Wenger, Eur. J. Inorg. Chem. (2009) 3778.
[107] D.M. Roundhill, Photochemistry and Photophysics of Metal Complexes, Plenum Press, New York, 1994.
[108] J.M. Weber, M.T. Rawls, V.J. MacKenzie, B.R. Limoges, C.M. Elliott, J. Am. Chem. Soc. 129 (2007) 313.
[109] L. Sacksteder, A.P. Zipp, E.A. Brown, J. Streich, J.N. Demas, B.A. DeGraff, Inorg. Chem. 29 (1990) 4335.
[110] L. Wallace, D.P. Rillema, Inorg. Chem. 32 (1993) 3836.
[111] M.E. Walther, O.S. Wenger, Dalton Trans. (2008) 6311.
[112] S. Bouzakraoui, S.M. Bouzzine, M. Bouachrine, M. Hamidi, J. Mol. Struct. 725 (2005) 39.
[113] V. Lukeš, A.J.A. Aquino, H. Lischka, H.F. Kauffmann, J. Phys. Chem. B 111 (2007) 7954.
[114] C. Grave, C. Risko, A. Shaporenko, Y.L. Wang, C. Nuckolls, M.A. Ratner, M.A. Rampi, M. Zharnikov, Adv. Funct. Mater. 17 (2007) 3816.
[115] O.S. Wenger, Coord. Chem. Rev. 253 (2009) 1439.
[116] M.J. Bjerrum, D.R. Casimiro, I.-J. Chang, A.J. Di Bilio, H.B. Gray, M.G. Hill, R. Langen, G.A. Mines, L.K. Skov, J.R. Winkler, D.S. Wuttke, J. Bioenerg. Biomembr. 27 (1995) 295.
[117] G.A. Mines, M.J. Bjerrum, M.G. Hill, D.R. Casimiro, I.J. Chang, J.R. Winkler, H.B. Gray, J. Am. Chem. Soc. 118 (1996) 1961.
[118] M.L.A. Abrahamsson, H.B. Baudin, A. Tran, C. Philouze, K.E. Berg, M.K. Raymond-Johansson, L.C. Sun, B. Åkermark, S. Styring, L. Hammarström, Inorg. Chem. 41 (2002) 1534.

[119] M. Cordes, B. Giese, Chem. Soc. Rev. 38 (2009) 892.
[120] D. Hanss, J.C. Freys, G. Bernardinelli, O.S. Wenger, Eur. J. Inorg. Chem. (2009) 4850.
[121] H.M. McConnell, J. Chem. Phys. 35 (1961) 508.
[122] O.S. Wenger, Chimia 61 (2007) 823.
[123] A.C. Benniston, A. Harriman, P.Y. Li, P.V. Patel, C.A. Sams, Phys. Chem. Chem. Phys. 7 (2005) 3677.
[124] A.C. Benniston, A. Harriman, Chem. Soc. Rev. 35 (2006) 169.
[125] A.C. Benniston, A. Harriman, P.Y. Li, C.A. Sams, M.D. Ward, J. Am. Chem. Soc. 126 (2004) 13630.
[126] A.C. Benniston, A. Harriman, Coord. Chem. Rev. 252 (2008) 2528.
[127] R.A. Marcus, N. Sutin, Biochim. Biophys. Acta 811 (1985) 265.
[128] F.D. Lewis, J.Q. Liu, W. Weigel, W. Rettig, I.V. Kurnikov, D.N. Beratan, Proc. Natl. Acad. Sci. U.S.A. 99 (2002) 12536.
[129] G.S.M. Tong, I.V. Kurnikov, D.N. Beratan, J. Phys. Chem. B 106 (2002) 2381.
[130] M.P. Eng, B. Albinsson, Angew. Chem. Int. Ed. 45 (2006) 5626.
[131] M.P. Eng, B. Albinsson, Chem. Phys. 357 (2009) 132.
[132] J. Wiberg, L.J. Guo, K. Pettersson, D. Nilsson, T. Ljungdahl, J. Mårtensson, B. Albinsson, J. Am. Chem. Soc. 129 (2007) 155.
[133] M.P. Eng, T. Ljungdahl, J. Mårtensson, B. Albinsson, J. Phys. Chem. B 110 (2006) 6483.
[134] K. Pettersson, J. Wiberg, T. Ljungdahl, J. Mårtensson, B. Albinsson, J. Phys. Chem. A 110 (2006) 319.
[135] K. Kilså, J. Kajanus, A.N. Macpherson, J. Mårtensson, B. Albinsson, J. Am. Chem. Soc. 123 (2001) 3069.
[136] B. Albinsson, J. Mårtensson, J. Photochem. Photobiol. C 9 (2008) 138.
[137] P.P. Edwards, H.B. Gray, M.T.J. Lodge, R.J.P. Williams, Angew. Chem. Int. Ed. 47 (2008) 6758.
[138] K. Ishiguro, T. Nakano, H. Shibata, Y. Sawaki, J. Am. Chem. Soc. 118 (1996) 7255.
[139] G. Gamov, Z. Phys. 51 (1928) 204.
[140] M.E. Walther, O.S. Wenger, ChemPhysChem 10 (2009) 1203.
[141] M. Cordes, A. Kottgen, C. Jasper, O. Jacques, H. Boudebous, B. Giese, Angew. Chem. Int. Ed. 47 (2008) 3461.