

Electron Tunneling through Oligo-*p*-xylene Bridges

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A series of rigid rodlike molecules having a phenothiazine donor, oligo-*p*-xylene bridges, and a rhenium(I) tricarbonyl phenanthroline acceptor were synthesized and studied in the context of long-range electron transfer. By optical absorption spectroscopy, the *p*-xylene bridges are found to have essentially length-independent HOMO–LUMO energy gaps, which is in clear contrast to oligo-*p*-phenylene spacers. Nanosecond time-resolved luminescence spectroscopy reveals an exponential decrease of electron transfer rates with increasing donor–acceptor distance; the attenuation factor β is 0.52 \AA^{-1} for the xylene bridges, which is strikingly close to β values reported previously for unsubstituted phenylene spacers.

Introduction

Long-range electron transfer has been found to play a key role in many biologically important processes, for instance, in photosynthesis and respiration.^{1,2} It has also become evident that efficient charge transport over long distances is pivotal for the development of artificial molecular materials that might be suitable for electronic applications.² Much recent work has therefore focused on so-called molecular wires.^{3,4} These are typically strongly π -conjugated molecules such as oligo-*p*-phenylenevinyls which mediate charge transfer through a hopping mechanism. Energy matching of

the donor/acceptor levels relative to those of the bridge appears to be the key to achieving wirelike behavior.³ However, it has been rather difficult to investigate this important issue systematically, because the electronic structure of most π -conjugated bridging molecules is strongly dependent on their length. Oligo-*p*-phenylenes are a case in point: There, the equilibrium dihedral angle between individual phenyl units is $\sim 30^\circ$; that is, increasing π conjugation with increasing bridge length seriously alters the overall electronic structure.⁵ In 2,7-oligofluorenes, bridge lengthening also induces a red-shift of the π – π^* absorptions,^{6,7} but in these systems, the oxidation potentials, relevant for hole transfer, remain relatively constant. We became interested in oligo-*p*-xylene bridges because we expect them to exhibit a more length-independent electronic structure than that observed for the unsubstituted oligo-*p*-phenylenes: For steric reasons, one would expect the dihedral angle between two xylene units to be significantly greater than between two unsubstituted phenyls. In other words, increasing π conjugation with increasing bridge length should be less important for the xylenes than for the phenyls.

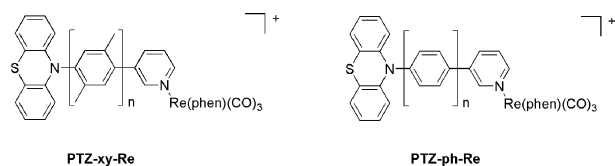
The specific systems studied in this work are shown in Scheme 1; they have the general formulas PTZ–xy_{*n*}–Re and

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Scheme 1

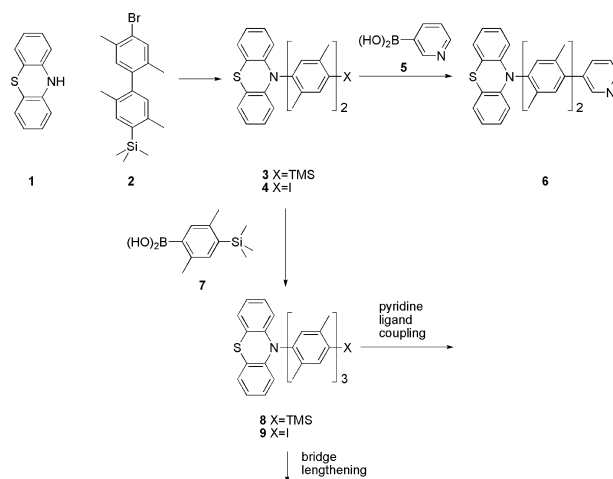


PTZ-ph_n-Re where PTZ stands for the phenothiazine donor, xy_n for the *p*-xylylene bridge, ph_n for a *p*-phenylene bridge, and Re for the rhenium(I) tricarbonyl 1,10-phenanthroline (phen) acceptor. The molecules with $n = 1-5$ were studied, whereby the donor-acceptor distance was varied from 10.6 Å ($n = 1$) to 27.9 Å ($n = 5$).⁸ The choice of electron donor and acceptor was based on both synthetic and photophysical arguments. Rhenium(I) tricarbonyl diimines become potent oxidants when excited to their metal-to-ligand charge-transfer (MLCT) states,^{9,10} which allows phototriggering of the electron transfer. Indeed, there exists a relatively large body of literature on photoredox processes between phenothiazine donors and rhenium(I) tricarbonyl acceptors,¹⁰ including a study on long-range electron transfer between these two reactants.¹¹

Results and Discussion

As far as the synthesis of our molecules is concerned, we found that the palladium(0)-catalyzed coupling between phenothiazine and bromoarenes proceeds with remarkable efficiency (Scheme 2).¹² Indeed, this reaction is a key step: It not only results in very high yields (>90%), but it also allows for direct donor-bridge coupling without the need of additional functional groups that may alter electronic coupling between the individual parts of the final donor-bridge-acceptor molecules. Trimethylsilyl/halogen exchange as well as the synthesis of the asymmetric *p*-xylylene molecule **7** (required for bridge lengthening) followed a previously published protocol.¹³ Suzuki coupling to 3-pyridineboronic acid **5** afforded the donor-bridge ligands, which were subsequently reacted with a [Re(phen)(CO)₃(triflate)] precursor.¹⁴ The oligo-*p*-phenylene-bridged reference molecules

Scheme 2



(PTZ-ph_n-Re; Scheme 1) were synthesized following an analogous strategy.

Figure 1 shows the optical absorption spectra of the PTZ-xy₁₋₄-Re (left) and PTZ-ph₁₋₄-Re (right) donor-bridge-acceptor molecules in dichloromethane solution. The spectra of the four xylene-bridged dyads on the left are practically superimposable onto one another, but there exist marked differences between the individual phenylene-bridged molecules on the right: With an increasing number of phenyl units, there is a pronounced red-shift of some of the UV absorption bands. This comparison confirms our initial hypothesis: Increasing π conjugation with increasing length is much less important for the oligo-*p*-xylenes than for the oligo-*p*-phenylenes. Indeed, π conjugation appears to play a very minor role in the former: Upon an increase in the number of bridging units from one to four, the $\pi-\pi^*$ absorption band edge at $\epsilon = 20\,000\text{ M}^{-1}\text{ cm}^{-1}$ red-shifts by 7 nm for the xylenes and by 50 nm for the unsubstituted phenyls. This indicates that the dihedral angle between individual *p*-xylylene units must be substantially greater than between two phenyls. Prior crystallographic studies found that the two phenyl rings of an unsubstituted biphenyl molecule can be almost coplanar,¹⁵ whereas the two xylylene rings in a bi-*p*-xylylene molecule were orthogonal to one another.¹⁶ It is obvious that from these solid-state data one cannot conclude that in solution the *p*-xylylene units will be strictly perpendicular to one another as well.

Another important observation made from the data in Figure 1 is that, in the oligo-*p*-xylylene molecules, the weak Re \rightarrow phen MLCT bands around 400 nm do not overlap with other absorptions, not even for long bridges. In other words, this MLCT state remains unperturbed by the bridge. This will be of key importance for the study of the photoinduced charge transfers which initiate from that particular MLCT state. In the PTZ-ph_n-Re molecules, on the other hand, the MLCT state is perturbed by the bridge. We refrain from discussing the resulting more-complex

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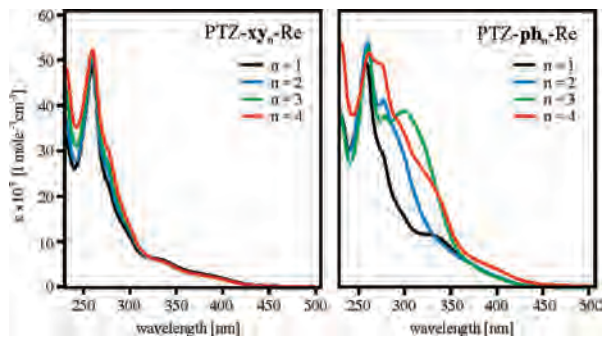


Figure 1. Optical absorption spectra of the PTZ- xy_n -Re (left) and PTZ- ph_n -Re (right) donor-bridge-acceptor molecules in dichloromethane solution.

photophysics of these systems here and restrict the rest of this paper to the PTZ- xy_n -Re dyads.

Cyclic voltammetry experiments demonstrate that the oligo-*p*-xylene bridge mediated electronic donor-acceptor coupling is small: In all PTZ- xy_n -Re dyads, the phenothiazine oxidation occurs at +0.72 V versus a saturated calomel electrode (SCE) in acetonitrile, and a rhenium complex based reduction is observed at -1.22 V versus SCE. For reference, the corresponding potentials for free 10-methyl-phenothiazine and [Re(phen)(CO)₃(pyridine)]⁺ molecules are +0.79 and -1.21 V versus SCE, respectively.^{17,18}

Steady-state luminescence experiments performed on the PTZ- xy_n -Re molecules show that there is a very strong dependence of the MLCT emission intensity upon bridge length. However, the emission band shape remains unaffected; in all PTZ- xy_n -Re molecules investigated, the first MLCT excited state is around 2.6 eV, which makes the rhenium complex a powerful excited-state oxidant with $E^0(\text{Re}^{+*/0}) \approx 1.4$ V versus SCE.^{9,10} Electron transfer from phenothiazine to the photoexcited metal complex is thus moderately exergonic in all xylene dyads considered.

When the [Re(phen)(CO)₃(pyridine)]⁺ reference complex is excited at 410 nm with short (<10 ns) laser pulses, its MLCT luminescence intensity at 560 nm decays with a lifetime of 2900 ns in deoxygenated dichloromethane solution.¹⁸ In the PTZ- xy_n -Re molecules, this lifetime is reduced to 2350 ns ($n = 5$), 1150 ns ($n = 4$), 95 ns ($n = 3$), and 20 ns ($n = 2$) under identical experimental conditions (left part of Figure 2).¹⁹ This quenching is attributed to PTZ → *Re electron transfer: The closer the two redox partners are, the more efficient this process is, and the shorter the MLCT lifetime becomes. The interpretation of the luminescence quenching in terms of electron transfer is corroborated by transient absorption experiments. The red trace in Figure 3 is the transient absorption spectrum of the PTZ- xy_3 -Re dyad; the data are representative of the entire PTZ- xy_n -Re series. Superimposed on this spectrum is the (ground-state) absorption spectrum of the 10-(*p*-xylene)-phenothiazine

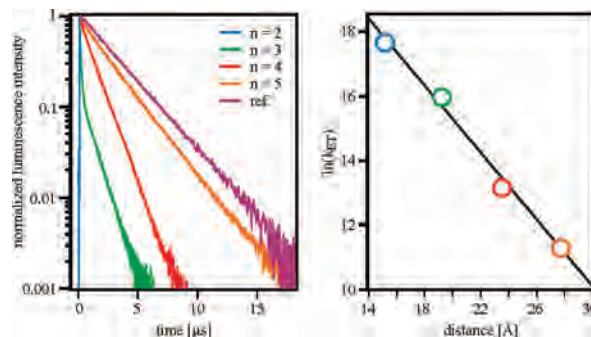


Figure 2. (Left) Luminescence decays observed (at 560 nm) from the PTZ- xy_n -Re dyads ($n = 2, 3, 4, 5$) and the [Re(phen)(CO)₃(pyridine)]⁺ reference complex following 10 ns laser pulses at 410 nm.¹⁹ (Right) Plot of $\ln(k_{\text{ET}}/S^{-1})$ versus the donor-acceptor distance for the PTZ- xy_n -Re molecules ($n = 2, 3, 4, 5$).⁸ The straight line is a fit to the four data points. Its slope is 0.52 \AA^{-1} .

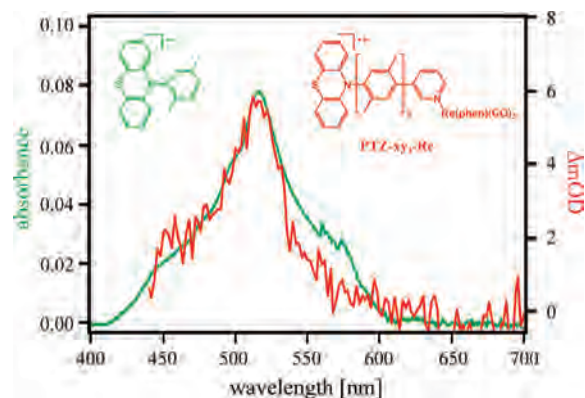


Figure 3. (Green trace, left y axis) Absorption spectrum of the 10-(*p*-xylene)-phenothiazine radical cation shown in the inset as observed after oxidation of the charge-neutral species with Br₂ in CH₂Cl₂. The spectrum is baseline-corrected for the Br₂ absorption. (Red trace, right y axis) Transient absorption spectrum as observed after pulsed 410 nm excitation of PTZ- xy_3 -Re in CH₂Cl₂. Time delay, 1 μs; time gate, 10 μs.

radical cation (green trace) as generated by oxidation of the neutral species with bromine. The similarity of the two spectra is striking. Moreover, we note that they are nearly identical to those previously reported for the phenothiazine and 10-methylphenothiazine radical cations,^{10c,20,21} and they are clearly distinct from the spectrum of the long-lived phenothiazine triplet excited state.²⁰ In short, the evidence for the luminescence quenching being due to electron transfer is compelling.

Rate constants for this intramolecular electron transfer were calculated using the relation

$$k_{\text{ET}} = \tau^{-1} - \tau_{\text{ref}}^{-1} \quad (1)$$

where τ is the luminescence lifetime of the PTZ- xy_n -Re dyads and τ_{ref} is the emission lifetime of the abovementioned reference complex.^{11,22,23} The natural logarithms of the

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resulting k_{ET} values are plotted versus the donor–acceptor distance in the right part of Figure 2. The four data points fall onto a single line, revealing an exponential dependence of electron transfer rates on distance.⁸ This is typical behavior for superexchange tunneling. A distance decay parameter β of 0.52 \AA^{-1} is obtained from a linear regression fit to the data in Figure 2. Prior studies have reported β values for oligo-*p*-phenylenes that range from 0.4 \AA^{-1} to 0.65 \AA^{-1} .^{22,24} Thus, the oligo-*p*-xylene bridges investigated in this work mediate long-distance electron tunneling almost equally as well as oligo-*p*-phenylenes, despite the higher degree of π conjugation in the latter. A previous investigation of oligo-*p*-xylenes revealed that long-range electron tunneling from a tertiary amine electron donor to photochemically generated ruthenium(III) proceeds with $\beta = 0.76 \text{ \AA}^{-1}$.^{16,25} It is possible that our relatively low β value is a manifestation of a small tunneling barrier that is associated with charge transfer in the PTZ- xy_n -Re molecules; the barrier to hole tunneling is expected to be relatively low in these specific systems. Recent work by various researchers provides experimental evidence for the importance of such tunneling barrier effects for long-range electron transfer.^{26–28}

Conclusions

Our study provides direct experimental support for the prior notion that β distance decay parameters are to be considered donor–bridge–acceptor system-dependent parameters and *not* solely bridge-specific parameters. Contrary to oligo-*p*-phenylenes, the oligo-*p*-xylene bridges have

essentially length-independent HOMO–LUMO energy gaps. For mechanistic investigations of tunneling barrier effects on long-range charge transfer, bridges with length-independent electronic structures are clearly advantageous. An important issue in this context is whether or not the absolute energies of the bridge HOMOs and LUMOs are length-dependent. In theory, it is imaginable that both levels accidentally shift by the same amount each time an additional xylene unit is added, whereby their difference in energy would remain constant. Future investigations must address the question whether this is the case or not.

Experimental Section

Detailed synthetic procedures and physical characterization data for the nine investigated dyads and all necessary reaction intermediates are given in the Supporting Information. ¹H NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer, and high-resolution mass spectra were measured on a QSTAR XL (AB/MDS Sciex) instrument. Cyclic voltammetry was performed using a Versastat3-100 potentiostat equipped with the K0264 microcell kit from Princeton Applied Research. A silver wire was employed as a quasi-reference electrode. Optical absorption spectra were measured on a Cary 5000 UV–vis–NIR spectrophotometer from Varian, and steady-state luminescence experiments were made on a Horiba Fluorolog-3. The luminescence lifetime and the transient absorption spectra were measured on the experimental setup of the group of Professor Andreas Hauser, Department of Physical Chemistry, University of Geneva. Details regarding this setup have been published recently.²⁹

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Supporting Information Available: Synthetic protocols, product characterization data, and the luminescence decay of the PTZ- xy_2 -Re dyad on an expanded time scale. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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