Accelerated hole transfer across a molecular double barrier†

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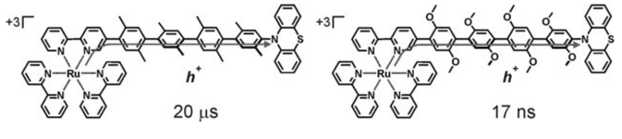
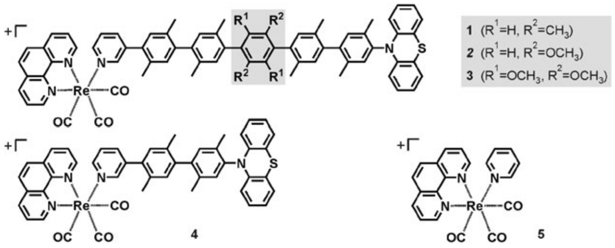
We report on a dyad in which photoinduced hole transfer through a non-uniform molecular double barrier is more than one order of magnitude more rapid than hole transfer across a comparable uniform (rectangular) tunneling barrier.

Long-range charge transfer may occur *via* hopping or tunneling mechanisms.[1] Hopping plays an important role in artificial molecular wires such as oligo-*p*-phenylene vinylenes and DNA.[2–8] Tunneling processes occur in less π-conjugated molecular bridges and in many different proteins.[1,9,10] Recent investigations indicate that biological electron transfer may regularly involve a sequence of tunneling and hopping processes,[1,11,12] in which amino acids with aromatic side chains serve as hopping stations. Such hopping stations can also be introduced deliberately into artificial oligo-peptide bridges in order to accelerate the long-range charge transfer rates.[13] Despite recent work on molecular diodes and molecular bridges with redox gradients,[14] chemists have been mostly concerned with the two extreme mechanistic cases of one-step tunneling across uniform (rectangular) barriers and multi-step hopping.[1] In semiconductor physics, tunneling through so-called double barriers plays a very important role.[15,16] In this work, we created a molecular bridge that imposes such a double barrier to hole transfer and investigated the charge transfer kinetics across this molecular bridge.

In a recent study, we found that phototriggered hole transfer between photogenerated $Ru(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) and phenothiazine (PTZ) occurs three orders of magnitude more rapidly across a tetra-*p*-dimethoxybenzene bridge than across a structurally very similar tetra-*p*-xylene spacer (Scheme 1).[17] This is due to the fact that *p*-dimethoxybenzene is oxidized at significantly lower potential (1.35 V *vs.* SCE) than *p*-xylene (2.06 V *vs.* SCE),[18] which leads to a decrease of the donor–bridge energy gap and a lowering of the tunneling barrier for holes.



Scheme 1 Hole tunneling across tetra-*p*-xylene and tetra-*p*-dimethoxybenzene bridges.[17]



Scheme 2 Formulae of the molecules investigated herein.

Here, we report on hole transfer between photoexcited rhenium(I) complexes and PTZ redox partners that are separated by a combination of *p*-xylene and methoxybenzene bridging units (Scheme 2). Dyad **1** contains five identical *p*-xylene spacers and serves as a reference molecule, whereas dyads **2** and **3** with central *p*-dimethoxybenzene and tetramethoxybenzene bridging units are the actual compounds of interest. Dyad **4** is a reference molecule with the PTZ redox partner at the same position where the methoxybenzene units are located in dyads **2** and **3**.

Optical absorption spectroscopy shows that the lowest excited state is the rhenium/phenanthroline MLCT state in all cases, and the differences between the spectra of the individual compounds are relatively minor (see ESI†). Fig. 1a shows the steady-state MLCT luminescence spectra measured on dichloromethane solutions of the five molecules from Scheme 2 after excitation at 410 nm, where all samples had an identical optical density of 0.1. Reference complex **5** shows the strongest emission, followed by dyads **1** and **3**. Only the emissions of dyads **2** and **4** are strongly quenched. The temporal evolution of the luminescence signals from Fig. 1a after excitation at 410 nm with 10 ns pulses is shown in Fig. 1b.

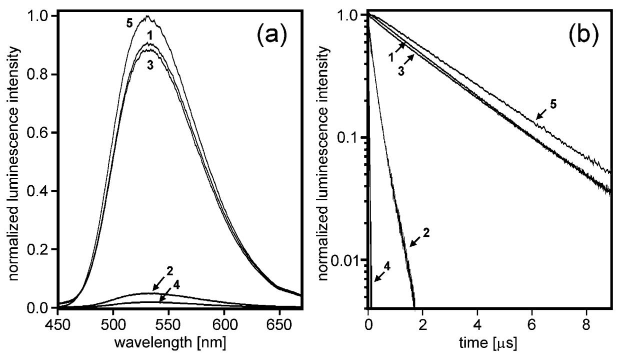


Fig. 1 (a) Steady-state emission of molecules **1–5** in deoxygenated CH_2Cl_2 after excitation at 410 nm. (b) Temporal evolution of these emissions under the same experimental conditions.

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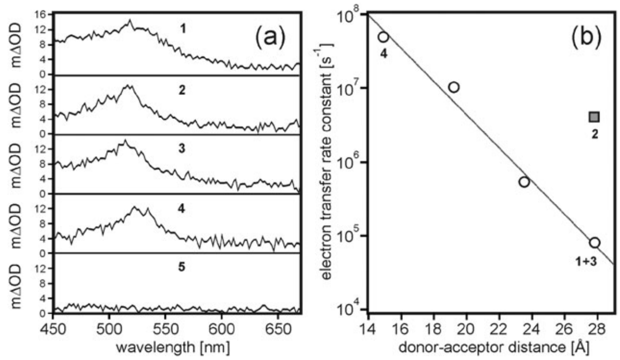


Fig. 2 (a) Transient absorption spectra of molecules **1–5** measured under the conditions described in the text. (b) Plot of the charge transfer rate constants in dyads **1–4**. The four open circles stand for a homologous series of Re–(*p*-xylene)$_n$–PTZ molecules, and the straight line is a linear regression fit to these data yielding a distance decay constant (β) of 0.52 Å^{-1}.[20,21]

The time-resolved data show exactly the same trend with respect to emission quenching as the steady-state spectra: weak MLCT excited-state quenching for dyads **1** and **3**, intermediate quenching for dyad **2**, and strong quenching for dyad **4**. Luminescence quenching of rhenium(I) tricarbonyl diimines by PTZ has long been known to occur by electron transfer, whereas energy transfer can be excluded on thermodynamic grounds.[19] Direct evidence for an electron transfer product is provided by Fig. 2a, which shows transient absorption spectra measured in a 5 μs time window starting 4 μs after pulsed excitation at 410 nm of the molecules from Scheme 2.

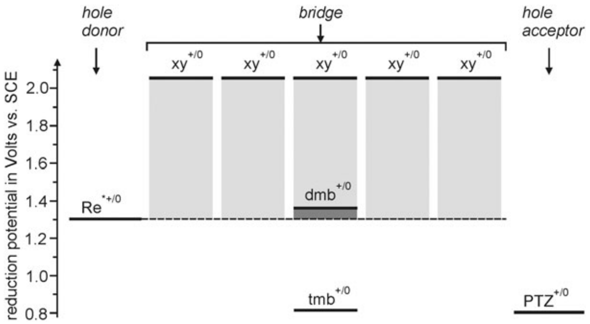
Dyads **1–4** all exhibit a nearly identical transient absorption spectrum, which can be attributed to the PTZ$^{\bullet+}$ radical cation.[22] Of key interest in this study are the rates with which the charge transfer processes occur. The preferred method for determining these rates is usually to monitor the build-up of the transient absorption signals associated with the charge transfer products.[17] Unfortunately, this method is technically not feasible in our case: in the accessible visible spectral range only the phenothiazine radical cation has a clear spectroscopic signature, but it coincides spectrally with the emission originating from the rhenium complex. Thus, we are limited to determining the sought-after rate constants indirectly from luminescence decay data, a method that has been applied successfully in many different previous instances.[23–25] In this method, the rate constant for charge transfer (k_{CT}) is approximated by:[23–25]

$$k_{\mathrm{CT}} = \tau_{\mathrm{dyad}}{}^{-1} - \tau_{\mathrm{dyad}}{}^{-1} \qquad (1)$$

In deoxygenated dichloromethane solution, the luminescence of complex **5** decays with a lifetime of $\tau_{\mathrm{reference}}$ = 2.90 μs. Under the same conditions (data in Fig. 1b), τ_{dyad} = 2.50 μs for dyad **1**, 0.24 μs for dyad **2**, 2.48 μs for dyad **3** and 0.02 μs for dyad **4**. The calculated k_{CT}-values for the individual compounds from Scheme 2 are displayed graphically in Fig. 2b along with two data points that originate from a prior investigation.[20] The four open circles mark k_{CT}-values for rhenium–(*p*-xylene)$_n$–phenothiazine molecules with bridge lengths (*n*) varying from two (dyad **4**) to five *p*-xylene units (dyad **1**), revealing an exponential drop-off with a distance decay constant (β) of 0.52 Å^{-1}.[20] However, the most important observation is the large k_{CT}-value of dyad **2** with respect to dyads **1** and **3** despite identical donor–acceptor distances in all three cases.

A hole transfer rather than electron transfer picture is useful to understanding charge transfer in our dyads.[21,26] While in its long-lived ^{3}MLCT excited state, rhenium complex **5** (Re) is a potent oxidant with $E_{\mathrm{red}} \geq 1.3$ *vs.* SCE,[27] whereas the relevant PTZ reduction potential is ~0.8 V *vs.* SCE (see ESI†).[16] The *p*-xylene bridge units (xy) are oxidized at 2.06 V *vs.* SCE.[18] Hence, in dyad **1** a large rectangular tunneling barrier of roughly 0.76 eV height is imposed to hole transfer across the five *p*-xylene spacers (Scheme 3).

In dyad **2**, the central *p*-dimethoxybenzene (dmb) unit is structurally similar to *p*-xylene, but it is significantly easier to oxidize. Free *p*-dimethoxybenzene is oxidized at a potential of 1.35 V *vs.* SCE,[18] which results in a local lowering of the barrier height to only ~0.05 eV. Hence, the overall shape of the barrier associated with hole transfer from Re to PTZ in dyad **2** is that of a double barrier (Scheme 3). With an estimated local barrier height of only ~0.05 eV at the central bridging unit, a two-step hopping mechanism may become potentially relevant for Re to PTZ hole transfer in dyad **2**, but transient absorption spectroscopy has failed to provide direct evidence for the dmb$^{\bullet+}$ radical cation. Moreover, we note that for two-step hopping, charge transfer in dyad **2** is relatively slow ($k_{\mathrm{CT}} = 4.1 \times 10^6$ s^{-1}). Both the hole transfer from Re to dmb and the hole transfer from dmb to PTZ would involve tunneling across a bi-*p*-xylene spacer, and in dyad **4** hole tunneling across such a bi-*p*-xylene bridge occurs with $k_{\mathrm{CT}} = 5 \times 10^7$ s^{-1}. Therefore, despite the fact that the two consecutive steps involved in the (hypothetic) hopping mechanism in dyad **2** would involve different driving-forces, it appears plausible that charge transfer in this molecule occurs *via* (accelerated) one-step tunneling across all five bridging units. Indeed, to explain the physical origin of the rate acceleration of the charge transfer process in dyad **2** with respect to dyad **1**, it is not necessary to invoke a hopping mechanism. According to superexchange theory, the electronic donor–acceptor coupling (H_{DA}) is a function of donor–bridge (h_{Db}), bridge–bridge (h_{bb}), and bridge–acceptor (h_{bA})



Scheme 3 Energy level diagrams for hole transfer from the photo-excited rhenium complex to PTZ through the molecular bridges of dyads **1–3** (xy = *p*-xylene; dmb = *p*-dimethoxybenzene; tmb = 1,2,4,5-tetramethoxybenzene).

couplings, as well as the so-called tunneling energy gap $\Delta\varepsilon$ that may be approximated as the donor–bridge energy gap:[28]

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

In dyad **2**, h_{bb} is likely to be similar for xy–xy and xy–dmb contacts since the expected equilibrium torsion angles between these *para*-disubstituted units are similar. However, at the central dmb unit, $\Delta\varepsilon$ is locally drastically lower, leading to significantly enhanced overall donor–acceptor coupling with respect to the situation in dyad **1**.

In dyad **3**, the overall Re to PTZ hole transfer is equally slow as in dyad **1** despite the presence of a central tetramethoxybenzene (tmb) unit. Free tmb is oxidized at an electrochemical potential of 0.81 V *vs.* SCE (Scheme 3 and ESI†),[18] and therefore our initial expectation was that this would permit Re to tmb hole transfer and enable an efficient two-step hopping process for the overall Re to PTZ charge transfer. However, the slow MLCT quenching rate observed for this dyad indicates that our expectation is not fulfilled. Moreover, nanosecond transient absorption spectroscopy fails to provide evidence for the $\text{tmb}^{\bullet +}$ radical cation. A likely reason for these observations is that the electronic coupling of tmb to its neighboring *p*-xylene bridge units is exceptionally weak. The four-fold methoxy-substituted tmb moiety is sterically much more demanding than the xylene or dmb units,[29] a fact that becomes manifest also in low yields obtained for the C–C coupling reactions that involve the tmb building block (see ESI†). A larger equilibrium torsion angle between tmb and *p*-xylene compared to the respective angles in dmb–xy and xy–xy contacts will lead to (locally) weaker electronic coupling (locally smaller h_{bb}),[30–33] a fact that does not reflect from the simple (reduction potential) diagram of Scheme 3. At any rate, the experimental evidence indicates that $\text{PTZ}^{\bullet +}$ is the final photoproduct (Fig. 2a), and rapid quenching of the Re MLCT state is not observed (Fig. 1). Thus, there is no benefit from replacing the central *p*-xylene unit by a tetramethoxybenzene spacer, and it appears that in dyad **3**, hole tunneling occurs from the metal complex directly to PTZ.

In conclusion, manipulation of tunneling barrier shapes in molecular wires is possible through variation of the reduction potentials of individual bridging units, but this approach to controlling long-range charge transfer rates appears to reach its limitations when sterically demanding building blocks are involved.

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