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Photoinduced Processes in Fluorene-Bridged Rhenium–Phenothiazine Dyads – Comparison of Electron Transfer Across Fluorene, Phenylene, and Xylene Bridges

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The photoinduced processes occurring after pulsed laser excitation of a series of donor–bridge–acceptor molecules comprising a phenothiazine electron donor, variable-length fluorene bridges, and a rhenium(I) electron acceptor were investigated. A dyad with a single fluorene bridge unit exhibits electron transfer from phenothiazine to the rhenium(I) complex upon photoexcitation, whereas in dyads with fluorene oligomers bridge-localized triplet excited states are formed rather than electron transfer products. In the monofluorene-bridged system with a donor–acceptor distance of ca. 15 Å, electron transfer occurs with a time constant of 1.9 ns. The equidistant electron transfer between the same donor and acceptor is considerably slower across a biphenyl bridge (3.9 ns) or a bi-*p*-xylene spacer (20 ns). This finding is interpreted in terms of different tunneling barrier heights associated with the charge transfer across the three different types of molecular bridges.

Introduction

Fluorene materials are of interest as organic light-emitting devices and plastic solar cells.[1] For both of these applications, charge and energy transfer processes play key roles in determining the overall efficiencies of practical devices. In addition to fundamental studies of charge transport in polyfluorene,[2] there has been much recent work on fluorene oligomers that serve as simple and well-defined model systems for polyfluorene. This includes the investigation of the chain-length dependence of the singlet- and triplet-excited state energies of oligofluorenes,[3] their redox potentials,[4] fluorescence and phosphorescence properties,[3,5] and charge and energy transfer across oligofluorene bridges with covalently attached donors and acceptors.[3b,4,6] An important finding is that the distance dependence of charge transfer through oligofluorenes can be very shallow; attenuation factors (β) of 0.093 and 0.09 $Å^{-1}$ have been determined,[4,6c] which compare favorably to oligophenylene vinylene and oligophenylene ethynylene wires that can have β-values between 0.01 and 0.4 $Å^{-1}$.[7] For reference, protein backbone mediates charge transfer with $\beta \approx 1.1$ $Å^{-1}$,[8] whereas charge tunneling across noncovalent gaps in (frozen) organic solvents proceeds with $\beta \geq 1.26$ $Å^{-1}$.[9] Thus, oligofluorenes are excellent bridges for long-range charge transfer, despite difficulties in elucidating the exact mechanism.[6a]

These previous studies on the distance dependence of charge transport through fluorene oligomers were performed on entirely organic systems in which the charge transfer originates from a singlet excited state, either from a photoexcited perylenebis(dicarboximide) or a fullerene.[4,6a,6c] In this work, we investigate mono-, bi-, and tri-fluorene-bridged donor–acceptor dyads Re-fl$_n$-PTZ (Scheme 1, top, left), which include a transition metal complex as a photosensitizer. In order to fully understand the photoinduced processes that occur upon photoexcitation of these dyads, the simultaneous investigation of reference molecules Re-fl$_n$ comprising the rhenium complex and the fluorene bridges, but lacking the phenothiazine (PTZ) donor (Scheme 1, top, right) has proven necessary. Phenylene- and xylene-bridged dyads (Re-ph$_{1,2}$-PTZ, Re-xy$_{1,2}$-PTZ) with the same donor and acceptor (Scheme 1, lower half) were also investigated for direct comparison of the charge-transfer properties of fluorene, *p*-phenylene, and *p*-xylene bridges.

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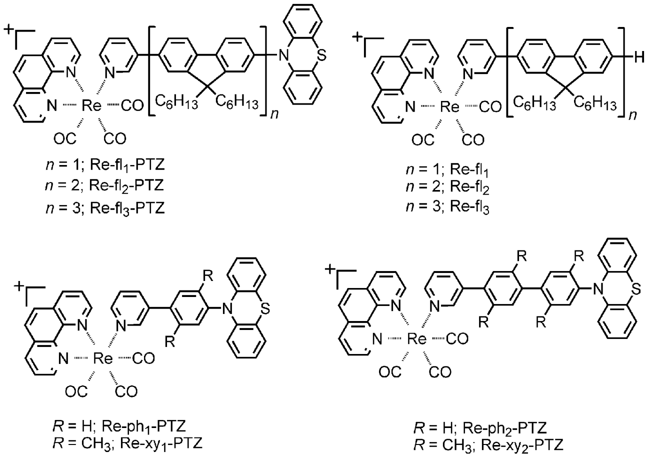


Scheme 1. Formulae of the donor–bridge–acceptor molecules investigated in this work.

Results and Discussion

Bridge-Length Dependent Electronic Structure of Fluorene-Bridged Dyads

Figure 1a shows optical absorption spectra of the Re-fl$_n$-PTZ dyads (solid traces) and the Re-fl$_n$ reference compounds (dashed traces) in dichloromethane solution at room temperature.

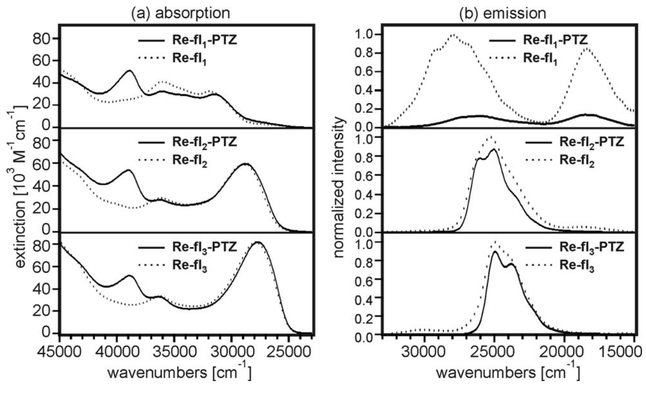


Figure 1. (a) Optical absorption spectra of the Re-fl$_n$-PTZ dyads and Re-fl$_n$ reference molecules from Scheme 1 in CH$_2$Cl$_2$ solution at room temperature. (b) Emission of these molecules in deoxygenated CH$_2$Cl$_2$ solution after excitation at 300 nm.

Inspection of the Re-fl$_1$-PTZ absorption spectrum (top panel, solid trace) reveals four discernible absorption features. There is a PTZ-localized π-π* transition at ca. 39000 cm^{-1},[10] a phenanthroline-localized π-π* transition at ca. 36000 cm^{-1},[11] a fluorene absorption at ca. 32000 cm^{-1},[3–4] and a much weaker band below 30000 cm^{-1} that can be attributed to a rhenium(I)-to-phenanthroline metal-to-ligand charge transfer (MLCT).[11] The Re-fl$_1$ absorption spectrum (top panel, dashed trace) differs from the Re-fl$_1$-PTZ absorption only in that it lacks the PTZ band at ca. 39000 cm^{-1}. This is also true for the bifluorene and trifluorene systems in the middle and lower panels. The energetic positions of the PTZ and phenanthroline absorptions are not affected by fluorene bridge elongation, but the fluorene band itself shifts to longer wavelengths, which is a well known phenomenon for these molecules.[3,4] This redshift has important implications regarding the emission properties of the molecules investigated (Figure 1b). Upon excitation of a Re-fl$_1$ solution at wavelengths below 300 nm, this molecule exhibits two intense emissions (top panel, dashed trace), one centered around 28000 cm^{-1} with vibrational fine structure and a structureless band at 18500 cm^{-1}. In deoxygenated acetonitrile solution, the former decays in less than 10 ns, whereas the latter has a lifetime of 3.9 µs (see Supporting Information). Based on their energies, bandshapes, and lifetimes, the two emissions can be attributed to fluorescence from the fluorene moiety (28000 cm^{-1}) and ^{3}MLCT emission (18500 cm^{-1}) from the [Re(phen)(CO)$_3$(pyridine)]$^+$ complex. Excitation spectroscopy (data not shown) suggests that the fluorene emission is due to an impurity, i.e. this is not a case of a true dual emission as observed frequently for lanthanides or for some transition metals.[12] The Re-fl$_1$-PTZ dyad exhibits the same two emissions, but their intensities are reduced significantly with respect to the Re-fl$_1$ reference compound. Moreover, the ^{3}MLCT emission in the dyad decays with a lifetime shorter than 10 ns. This indicates that an additional nonradiative excited-state relaxation process is active in this molecule.

Under identical experimental conditions, each of the longer congeners of the fluorene dyads and reference molecules from Scheme 1 exhibits only one single emission band which is structured and short lived ($\tau < 10$ ns). Figure 1b shows that the emission band maximum redshifts upon elongation of these molecules, and this redshift parallels that observed in Figure 1a for the lowest-energy fluorene absorption bands. These observations suggest that emission occurs from fluorene-localized (singlet) excited-states, and this interpretation is in line with prior studies of the emission properties of fluorene oligomers.[3] The lack of emission quenching in the Re-fl$_2$-PTZ and Re-fl$_3$-PTZ dyads with respect to the Re-fl$_2$ and Re-fl$_3$ reference molecules is another important difference to the monofluorene systems Re-fl$_1$-PTZ and Re-fl$_1$. This indicates that the additional nonradiative relaxation process occurring in Re-fl$_1$-PTZ is inactive in Re-fl$_2$-PTZ and Re-fl$_3$-PTZ.

Figure 2a shows transient absorption spectra measured on deoxygenated 10^{-4} M solutions of the fluorene-based molecules depicted in Scheme 1 in a time window ranging from 0.5–10.5 µs after laser excitation at 355 nm or 410 nm with laser pulses of ca. 10 ns duration. No long lived photoproduct is formed in the case of Re-fl$_1$, but for the Re-fl$_1$-PTZ dyad an absorption signal peaking at around 520 nm is observed (top panel, solid trace). Prior work and our own spectroelectrochemical studies indicate that this absorption signal can be attributed to the phenothiazine radical cation:[10,13] The top panel in Figure 3 shows optical absorption spectra of the Re-fl$_1$-PTZ and Re-fl$_1$ molecules measured under application of oxidative potentials to acetonitrile solutions of these molecules in an optically transparent thin-layer electrochemical cell.[14]

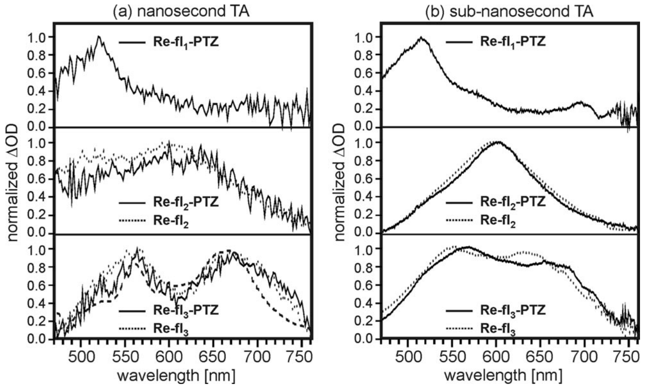


Figure 2. (a) Transient absorption spectra measured on deoxygenated CH_3CN solutions of the fluorene molecules depicted in Scheme 1 after excitation with 10 ns laser pulses at 410 nm. The spectra were detected in a 10 μs time gate starting 500 ns after the excitation pulse. The dashed trace is the triplet-triplet absorption spectrum of trifluorene at 77 K as taken from the literature.[3a] (b) Transient absorption of the same molecules in CH_3CN detected with a time delay of 1 ns after excitation at 400 nm with pulses of 150 fs width.

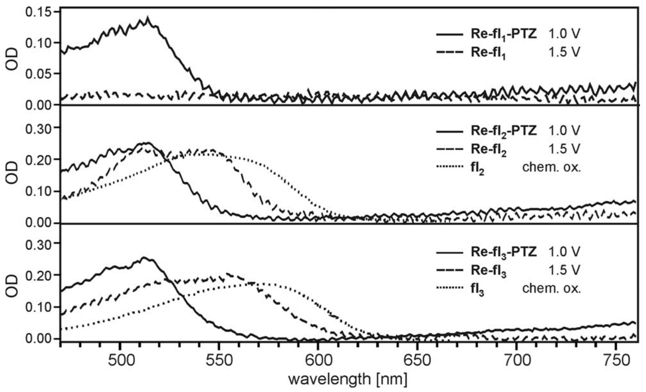
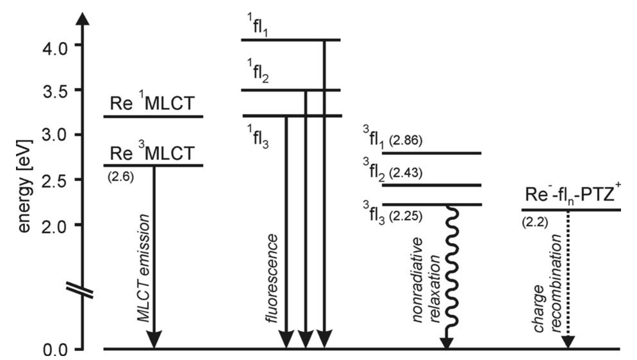


Figure 3. Spectroelectrochemistry of the Re-fl$_n$-PTZ dyads in CH_3CN solution. Potentials are reported vs. SCE. The dotted traces are the radical cation spectra of bifluorene (fl$_2$) and trifluorene (fl$_3$) taken from the literature.[16a]

The wavelength range of Figure 3 corresponds exactly to that used in Figure 2, notably a spectral region in which the parent (unoxidized) compounds are transparent. The absorption band observed for Re-fl$_1$-PTZ in the spectroelectrochemical experiment (Figure 3) corresponds to that observed in transient absorption (Figure 2). Cyclic voltammetry (see Supporting Information) shows that the PTZ radical cation forms at a potential of 0.8 V vs. SCE, which is in line with prior investigations.[13a,13d] Thus, it is clear that an electron transfer photoproduct is observed for the monofluorene-bridged dyad.

The transient absorption spectra of Re-fl$_2$-PTZ and Re-fl$_3$-PTZ in Figure 2a (middle and bottom panels) are markedly different from that observed for Re-fl$_1$-PTZ (top panel). The absorption peak at 520 nm is absent in the spectra of the longer congeners, indicating that a $PTZ^{\cdot +}$ radical cation is not formed in these instances. Furthermore, the transient absorption spectra of the two longer dyads strongly resemble those observed for the respective reference molecules that lack the PTZ moiety. For both Re-fl$_2$-PTZ and Re-fl$_2$ there is a single broad band centered around 600 nm, whereas for both Re-fl$_3$-PTZ and Re-fl$_3$ there is a double band with peaks at around 560 and 670 nm. The question arises of what species these absorption bands are due to. Since photoexcited tricarbonylrhenium(I) diimines are strong electron acceptors,[15] one possibility to be considered is the formation of oxidized fluorene oligomers. Up to oxidizing potentials of 1.0 V vs. SCE, spectroelectrochemical investigations of the Re-fl$_2$-PTZ and Re-fl$_3$-PTZ dyads (Figure 3) only produce evidence for the $PTZ^{\cdot +}$ radical cation, whereas the Re-fl$_2$ and Re-fl$_3$ reference molecules stay transparent in the spectral region of interest. At a potential of 1.5 V vs. SCE, also the reference molecules exhibit spectroelectrochemical signals (dashed traces). The resulting spectra are similar to those previously reported for chemically oxidized bi- and trifluorene (dotted traces in Figure 3),[16] and are attributed to the fluorene-localized radical cations.[17] The spectral signatures of these radical cations are clearly different from the transient absorption signals in Figure 2, and the inescapable conclusion is that the photoproducts in Re-fl$_2$, Re-fl$_2$-PTZ, Re-fl$_3$, and Re-fl$_3$-PTZ are not bi- or trifluorene radical cations.

The dashed trace in the bottom panel of Figure 2a is the triplet-triplet absorption spectrum of trifluorene in a 2-methyltetrahydrofuran glass at 77 K as taken from literature.[3a] The similarity of this spectrum to the transient absorption spectra of Re-fl$_3$ and Re-fl$_3$-PTZ is striking, and it appears plausible to conclude that a trifluorene-localized triplet excited state is populated upon photoexcitation of these molecules. By analogy, the photoproduct observed for the shorter Re-fl$_2$ and Re-fl$_2$-PTZ molecules is assigned to a bifluorene-localized triplet state, although the triplet-triplet absorption spectrum of bifluorene does not appear to have been reported in the literature so far. A prior study of the phosphorescence properties of fluorene oligomers at 77 K showed that the energy of their lowest lying triplet excited states is strongly dependent on the length of the oligomers (Scheme 2).[3]



Scheme 2. Energy-level diagrams for the Re-fl$_n$-PTZ molecules. The energies of the fluorene-localized excited states are taken from the literature.[3]

For monofluorene this state (^{3}fl$_1$) is at 2.86 eV, for bifluorene (^{3}fl$_2$) at 2.43 eV, and for trifluorene (^{3}fl$_3$) at 2.25 eV. The energy of the rhenium/phenanthroline ^{3}MLCT excited state is ca. 2.6 eV,[11] i.e., this state is energetically below the ^{3}fl$_1$ state, but above the ^{3}fl$_2$ and ^{3}fl$_3$ levels. This sequence of energy levels is consistent with all of the above experimental observations: (i) in Re-fl$_1$-PTZ and Re-fl$_1$ the lowest-lying excited state is the ^{3}MLCT level, hence the observation of ^{3}MLCT emission in addition to fluorene fluorescence in these two molecules (Figure 1b, top panel), (ii) in Re-fl$_2$-PTZ, Re-fl$_2$, Re-fl$_3$-PTZ, and Re-fl$_3$ the lowest-lying excited states are fluorene-localized triplets, hence the observation of their spectral signatures in transient absorption (Figure 2a, middle and bottom panels), and hence the absence of ^{3}MLCT emission in these compounds. Phosphorescence from the fluorene triplets is not observed at room temperature.

Femtosecond time-resolved transient absorption spectroscopy (Figure 2b) shows that the abovementioned photoproducts form almost immediately after excitation. After 1 ns, the PTZ$^{\cdot+}$ radical cation signature is already observed for Re-fl$_1$-PTZ (top panel). Likewise, the spectral signatures of the bi- and trifluorene triplets (^{3}fl$_2$ and ^{3}fl$_3$) are observed after this time delay for Re-fl$_2$-PTZ, Re-fl$_2$, Re-fl$_3$-PTZ, and Re-fl$_3$ (middle and bottom panels). The temporal evolution of these signals after pulsed excitation at 400 nm is shown in Figure 4a. The PTZ$^{\cdot+}$ population (detected at 520 nm) in Re-fl$_1$-PTZ (top panel) builds up with a time constant of 1.9 ns. In Re-fl$_2$-PTZ and Re-fl$_2$ the ^{3}fl$_2$ state (as detected at 600 nm) is populated with time constants of 1.3 and 1.8 ns, respectively, whereas in Re-fl$_3$-PTZ and Re-fl$_3$ the ^{3}fl$_3$ population (detected at 660 nm) builds up with time constants of 0.9 and 1.3 ns, respectively. As illustrated by Figure 4b, all of these photoproducts decay on a microsecond time scale. The lifetime of the PTZ$^{\cdot+}$ radical cation of Re-fl$_1$-PTZ in deoxygenated acetonitrile solution is 1.3 µs, i.e., thermal back-electron transfer from the reduced rhenium complex to the oxidized amine is slow. Long-lived charge-separated states are not uncommon for rhenium–phenothiazine donor–acceptor systems due to the occurrence of an inverted driving force effect.[18] The charge separated state with oxidized phenothiazine and reduced rhenium complex is roughly 2.2 eV above the ground state (Scheme 2),[18] thereby making charge recombination highly exergonic and comparatively slow.[13a,19] Furthermore, the charge recombination process here is spin forbidden. Under identical experimental conditions, the ^{3}fl$_2$ lifetimes of Re-fl$_2$-PTZ and Re-fl$_2$ are 8.1 and 7.0 µs, respectively, whereas the ^{3}fl$_3$ lifetimes of Re-fl$_3$-PTZ and Re-fl$_3$ are 3.6 and 5.5 µs, respectively.

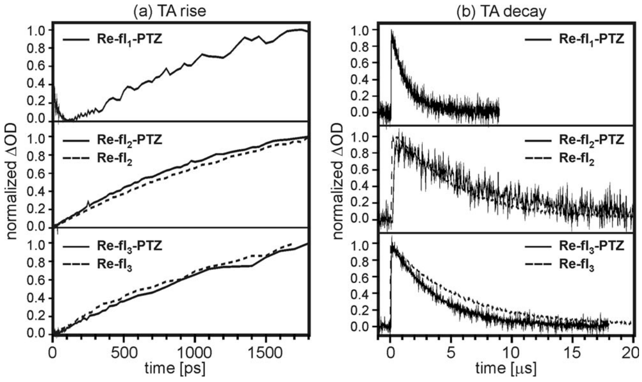


Figure 4. (a) Temporal evolution of the transient absorption intensities at 520 nm (Re-fl$_1$-PTZ), 600 nm (Re-fl$_2$-PTZ, Re-fl$_2$) and 660 nm (Re-fl$_3$-PTZ, Re-fl$_3$) after excitation of CH$_3$CN solutions at 400 nm with laser pulses of 150 fs duration. (b) Decays of the transient absorption intensities from (a) in deoxygenated CH$_3$CN.

A noteworthy observation is the direct decay of the ^{3}fl$_2$ and ^{3}fl$_3$ excited states in Re-fl$_2$-PTZ and Re-fl$_3$-PTZ to the ground states. In these dyads, the respective fluorene triplet excited states are at higher energies than the charge separated state (Scheme 2). In principle, electron transfer from PTZ to rhenium is therefore energetically possible from the ^{3}fl$_2$ and ^{3}fl$_3$ states. However, transient absorption spectroscopy provides no evidence for the formation of photoproducts other than these fluorene-localized triplets even after long time delays (Figure 2a). In this regard, these fluorene dyads behave like rhenium–anthracene or rhenium–phenanthrene dyads, in which triplet excited states on the anthracene and phenanthrene moieties are formed upon photoexcitation.[18,20]

Comparison of Electron Transfer in Fluorene-, Phenylene-, and Xylene-Bridged Rhenium–Phenothiazine Dyads

Figure 5a shows transient absorption spectra measured on acetonitrile solutions of the xylene- and phenylene-bridged rhenium–phenothiazine dyads from the lower half of Scheme 1. In all three cases shown in Figure 5a, the spectral signature of the PTZ$^{\cdot+}$ radical cation is observed after a time delay of 1 ns, and this signal remains detectable even after 2 µs.

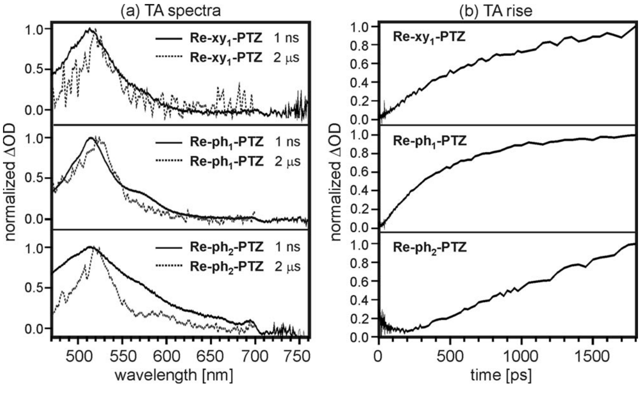


Figure 5. (a) Transient absorption spectra measured on CH$_3$CN solutions of the dyads from the lower half of Scheme 1 after time delays of 1 ns and 2 µs. (b) Rise of the transient absorption intensities at 520 nm (PTZ$^{\cdot+}$ radical cation).

In the case of the Re-ph$_2$-PTZ molecule (bottom panel), the initial spectrum is somewhat broadened, but nevertheless exhibits the typical features of the PTZ$^{\cdot+}$ spectrum. The rise of the transient absorption intensities at 520 nm after excitation at 400 nm are shown in Figure 5b. The $PTZ^{\cdot +}$ electron-transfer product forms with time constants of 770 ps in Re-xy_1-PTZ, 450 ps in Re-ph_1-PTZ, and 3900 ps in Re-ph_2-PTZ. In prior studies, we reported the kinetics of phenothiazine-to-rhenium electron transfer in a series of Re-xy_n-PTZ molecules with the bridge length n varying from 2 to 5.[21] The distance dependence of the electron transfer in this series is exponential (open circles in Figure 6), and a distance decay parameter (β) of 0.52 $Å^{-1}$ was determined. The newly measured data point for Re-xy_1-PTZ using laser equipment with higher time resolution (circle at a donor–acceptor distance of 10.6 Å in Figure 6) is in line with our prior investigations.[21,22] The electron transfer rate constant (k_{ET}) for the bi-*p*-xylene-bridged system Re-xy_2-PTZ as determined previously is $5 \times 10^7\ s^{-1}$, i.e., PTZ-to-rhenium electron transfer occurs with a time constant of 20 ns.[21]

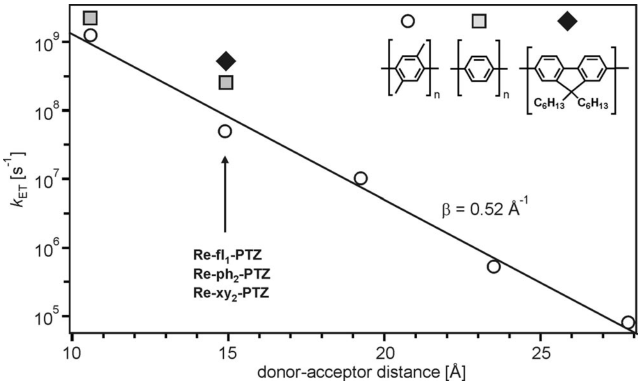


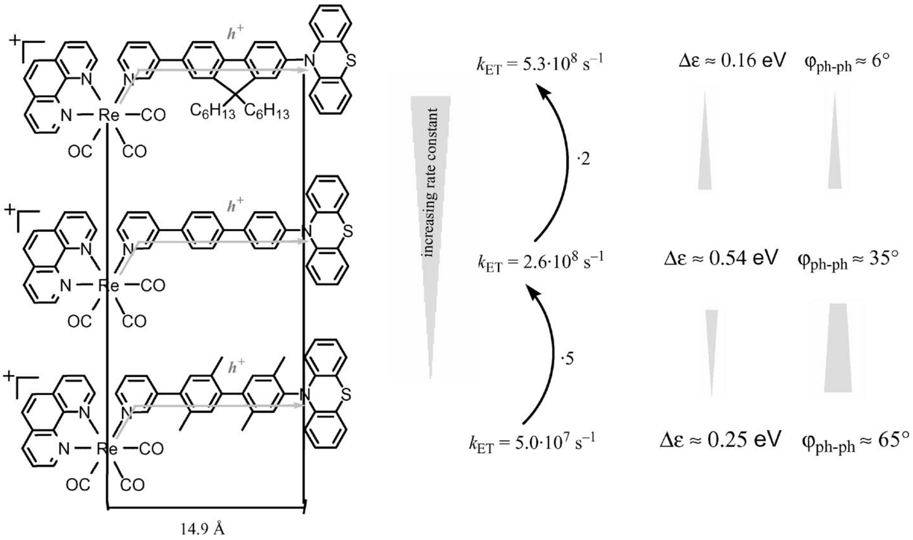
Figure 6. Rate constants (k_{ET}) for photoinduced hole transfer from rhenium to phenothiazine for various bridges and different donor–acceptor distances.

It is interesting to compare the kinetics of electron transfer in the Re-xy_2-PTZ, Re-ph_2-PTZ, and Re-fl_1-PTZ dyads because the donor–acceptor distance in these three molecules is virtually the same (14.9 Å). With the electron donors and acceptors also being identical, the only difference is the molecular bridge connecting the two redox partners. Yet, the experimentally determined electron transfer rate constants (Figure 6) differ significantly between the three molecules. For Re-xy_2-PTZ $k_{ET} = 5 \times 10^7\ s^{-1}$, for Re-$ph_2$-PTZ $k_{ET} = 2.6 \times 10^8\ s^{-1}$, and for Re-$fl_1$-PTZ $k_{ET} = 5.3 \times 10^8\ s^{-1}$ (Scheme 3).

Thus, electron transfer across the fluorene bridge is a factor of two faster than for the biphenyl spacer and an order of magnitude more rapid than electron transfer across the bi-*p*-xylene bridge. The exponential distance dependence of k_{ET} in the xylene systems is clear evidence for a tunneling process,[21a,23] and it is plausible to assume that electron transfer in the phenylene- and fluorene-bridged dyads occurs with the same type of mechanism. According to superexchange theory, the electronic coupling between distant donors and acceptors (H_{DA}) bridged by n identical spacer units is a function of donor–bridge (h_{Db}), bridge–bridge (h_{bb}), and bridge–acceptor (h_{bA}) couplings, as well as the so-called tunneling energy gap Δε [Equation (1)]: [24]

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

In Re-xy_2-PTZ, the methyl substituents at the two bridging units enforce a significantly greater dihedral angle between the two xylyl spacers than is the case for the two unsubstituted phenyl units in Re-ph_2-PTZ.[21a] Electronic coupling between individual phenyl units depends crucially on the torsion angles between them,[25] and therefore h_{bb}



Scheme 3. Comparison of rate constants (k_{ET}) for hole tunneling across fluorene-, biphenyl- and bi-*p*-xylene-bridged rhenium–phenothiazine donor–acceptor couples. Estimates for the tunneling energy gap (Δε) and equilibrium torsion angles between the two phenyl units (ϕ_{ph-ph}) of each molecular bridge are also compared. Equation (1) predicts an increase of charge transfer rate constants for decreasing Δε and increasing h_{bb}. The latter increases with decreasing ϕ_{ph-ph}. A *hole* tunneling rather than *electron* tunneling mechanism is active in these systems.[21]

can be expected to be significantly greater for Re-ph$_2$-PTZ than for Re-xy$_2$-PTZ. This provides a plausible qualitative explanation for the higher electron transfer rate in the biphenyl system with respect to the bi-*p*-xylene dyad, and it is in line with the previously observed stronger distance dependence of electron transfer rates in oligo-*p*-xylene bridges relative to oligo-*p*-phenylenes.[26]

As far as the fluorene spacer in Re-fl$_1$-PTZ is concerned, its two phenyl rings may be considered as individual bridge units that are oriented relative to each other at an even lower dihedral angle than in the biphenyl system. Crystallographic studies show that the torsion angle between the two phenyl units of a given fluorene moiety may be as low as 6°,[27] whereas the typical (equilibrium) torsion angle in biphenyl is around 35° (Scheme 3).[28] Thus, one may argue that the additional lowering of the phenyl–phenyl torsion angle is responsible for the higher rate of electron transfer in Re-fl$_1$-PTZ with respect to Re-ph$_2$-PTZ. However, due to large differences between the redox potentials of biphenyl and fluorene, it appears more reasonable to consider the entire fluorene as one single bridge unit. In this case, the electron transfer rate acceleration in Re-fl$_1$-PTZ can be explained by a comparatively low tunneling energy gap $\Delta\varepsilon$. This physical quantity is not directly accessible from experiment,[23] but may be approximated by the difference in the redox potentials of the donor and the bridge.[29] The relevant donor potential for rhenium–phenothiazine dyads is the excited state oxidation potential of the rhenium complex because charge transfer in these system occurs through a hole tunneling (rather than electron tunneling) mechanism.[21] The relevant bridge potential for hole transfer is the oxidation potential of fluorene, which has been reported as 1.58 V vs. SCE.[4,16b] For reference, biphenyl is oxidized at 1.96 V vs. SCE.[30] With an excited state oxidation potential of 1.42 V vs. SCE for the rhenium hole donor,[21a] one thus arrives at estimates for $\Delta\varepsilon$ of 0.16 eV for the fluorene bridge and 0.54 eV for the biphenyl spacer (Scheme 3).[21b] Such a large difference in tunneling energy gaps is expected to lead to significant differences in the overall donor–acceptor coupling (H_{DA}) according to Equation (1). Since $k_{ET} \propto H_{DA}^2$,[31] this can explain the increased electron transfer rate constant of Re-fl$_1$-PTZ relative to Re-ph$_2$-PTZ qualitatively.

Conclusions

Electron transfer across fluorene *oligomers* cannot be investigated with rhenium(I) tricarbonyl diimine photosensitizers because of the formation of fluorene-localized triplet-excited states that do not exhibit any charge transfer chemistry. If coordination complexes are to be used in this context, they must have ^{3}MLCT states that are energetically below 2.2 eV. Thus, $Ru(bpy)_3^{2+}$ may be an appropriate choice, although this may require the use of a stronger electron donor than phenothiazine.[26a,32]

The intramolecular 15 Å hole transfer from phenothiazine to a photoexcited rhenium complex is found to be dependent on subtle variations in the covalent linker between the two redox partners. For a bi-*p*-xylene bridge, the process is slower than for a biphenyl spacer due to weaker electronic coupling caused by a greater equilibrium torsion angle between the methyl-substituted bridge units. For a single fluorene spacer, the process is faster than for biphenyl due to a smaller tunneling energy gap caused by the lower oxidation potential of fluorene with respect to biphenyl. Taken together, these results highlight the importance of both conformational effects and bridge redox potentials for long-range charge transfer.

Experimental Section

General: All ^{1}H NMR measurements were performed using a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported relative to the tetramethylsilane signal. Finnigan MAT SSQ 7000 and QSTAR XL (AB/MDS Sciex) instruments were used for electrospray mass spectrometry. Elemental analyses were conducted by Dr. Hansjörg Eder from the School of Pharmaceutical Sciences at the University of Geneva.

For optical absorption spectroscopy, a Cary 5000 UV/Vis/NIR spectrophotometer from Varian was used, and steady-state luminescence spectra were measured with a Horiba Fluorolog-3 (Jobin–Yvon) or a Cary Eclipse (Varian) instrument.

Nanosecond transient absorption was conducted with an experimental set-up with an excitation source comprising a Quantel Briliant Nd:YAG laser with integrated Magic Prism OPO, and a probe source consisting of a 900-W tungsten lamp. The detection system comprised a Spex 270M monochromator, a Hamamatsu photomultiplier, and Tektronix TDS 540B oscilloscope. Time-resolved luminescence experiments with a temporal resolution of $\geq$15 ns were performed with the same set up. For all nanosecond time-resolved experiments, 10^{-4} M solutions of the samples were deoxygenated in home-built quartz cuvettes via three subsequent freeze–pump–thaw cycles.

Subnanosecond transient absorption spectroscopy was performed with the experimental set up described previously.[33] Sample excitation in this case occurred at 400 nm, and the probe beam was a white light continuum obtained by focusing an 800-nm laser beam onto a CaF_2 window of 3 mm thickness. Samples with optical densities around 0.1 in a 1-mm cuvette were used for these experiments, and nitrogen gas was bubbled through the solutions during the experiments.

For luminescence decay measurements with subnanosecond time resolution, samples were excited at 395 nm by a picoquant laser diode and detected with a Hamamatsu photomultiplier tube. Veril and interference filters were used to select the wavelength range for detection. Acetonitrile or dichloromethane of spectrophotometric grade from the Fluka chemical company was used for all optical spectroscopic experiments.

Cyclic voltammetry and spectroelectrochemical experiments were performed using a Versastat3–100 potentiostat from Princeton Applied Research equipped with the K0264 microcell kit. A silver wire served as a quasireference electrode. The supporting electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate in dry acetonitrile. Prior to voltage scans at rates of 200 mV/s, nitrogen gas was bubbled through the solutions. For spectroelectrochemical experiments an OTTLE cell (Omni-cell from Specac) was employed.[34]

Supporting Information (see also the footnote on the first page of this article): Protocols for syntheses and product characterization data, cyclic voltammetry data, luminescence decay data.

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