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Electron Transfer across *ortho*-Phenylene Wires

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Abstract:

Photoinduced electron transfer across rigid rod-like oligo-*para*-phenylenes has been thoroughly investigated in the past, but their *ortho*-connected counterparts are yet entirely unexplored in this regard. We report on three molecular dyads comprised of a triarylamine donor and a $Ru(bpy)_3^{2+}$ (bpy =2,2'-bipyridine) acceptor connected covalently by 2 to 6 *ortho*-phenylene units. Pulsed excitation of the Ru(II) sensitizer at 532 nm leads to the rapid formation of oxidized triarylamine and reduced ruthenium complex via intramolecular electron transfer. The subsequent thermal reverse charge-shift reaction to reinstate the electronic ground-state occurs on a timescale of 120 – 220 ns in de-aerated CH_3CN at 25 °C. The conformational flexibility of the *ortho*-phenylene bridges causes multi-exponential transient absorption kinetics for the photoinduced forward process, but the thermal reverse reaction produces single-exponential transient absorption decays. The key finding is that the flexible *ortho*-phenylene bridges permit rapid formation of photoproducts storing ca. 1.7 eV of energy with lifetimes on the order of hundreds of nanoseconds, similar to what is possible with rigid rod-like donor-acceptor compounds. Thus, the conformational flexibility of the *ortho*-phenylenes represents no disadvantage with regard to the photoproduct lifetimes, and this is relevant in the greater context of light-to-chemical energy conversion.

Introduction

Long-range electron transfers play key roles in many biological and artificial systems, and neither photosynthesis nor respiration would function without them.[1] With artificial photosynthesis as a long-term perspective, many prior investigations concentrated on obtaining long-lived electron-hole pairs in donor-bridge-acceptor compounds,[2-10] whereas other studies explored the distance or driving-force dependence of electron transfer rates (k_{ET}).[11-19] Rigid rod-like molecular bridges are usually preferred, because they yield systems with well-defined donor-acceptor distances and restricted conformational degrees of freedom, simplifying the analysis of kinetic data. Oligo-*para*-phenylenes are a prototype class of relatively rigid spacers and as such have received considerable attention,[20-36] but to our knowledge there have been no prior studies of photoinduced long-range electron transfer across oligo-*ortho*-phenylenes.

Recently, much progress has been made in the controlled synthesis of monodisperse *ortho*-phenylene oligomers,[37-45] and under favorable conditions helical folding was observed as a consequence of arene-arene interactions.[40,46-50] Furthermore, oligo-*ortho*-phenylenes were found to exhibit remarkably long effective conjugation lengths.[37,51] Against this background and given the role of the respective *para*-isomers as prototype molecular wires it seemed attractive to explore long-range electron transfer in oligo-*ortho*-phenylenes.

Results and Discussion

We synthesized a series of compounds comprised of a triarylamine (TAA) donor, variable-length *ortho*-phenylene bridges, and a $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) acceptor (Figure 1), relying on

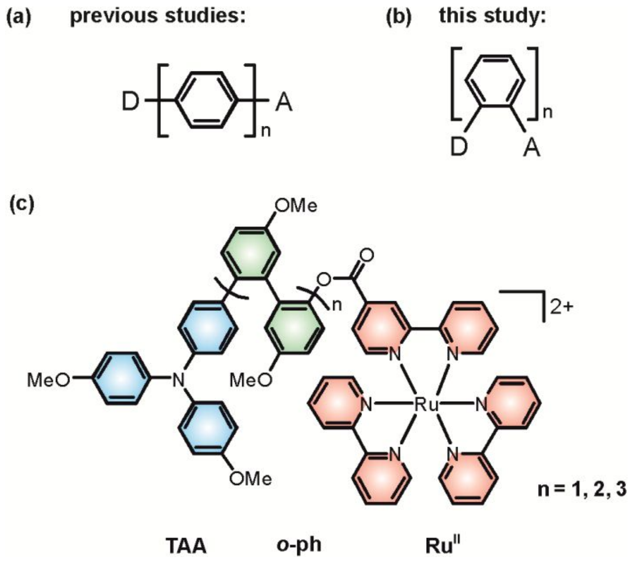

Figure 1. *Para*-phenylene (a) and *ortho*-phenylene (b) bridged donor-acceptor (D-A) dyads, along with the molecular structure of the specific donor-bridge-acceptor compounds synthesized and investigated in this work (c).

recently reported methodologies for modular bridge elongation (see Supporting Information (SI) pages S4-S24).[37] The TAA oxidation and $Ru(bpy)_3^{2+}$ reduction potentials are essentially invariant with increasing bridge length (SI pages S25-S27), and on the basis of the cyclic voltammograms of our dyads we estimate a reaction free energy of ca. -0.4 eV for electron transfer from TAA to ^{3}MLCT-excited $Ru(bpy)_3^{2+}$ in CH_3CN for all 3 compounds (SI page S28-S29). Expectedly, the common ^{3}MLCT luminescence detectable in the $Ru(bpy)_3^{2+}$ parent complex is quenched when this photosensitizer unit is integrated into our donor-bridge-acceptor compounds (SI page S30). The photoproducts forming as a result of non-radiative ^{3}MLCT deactivation can readily be identified as TAA^+ and $Ru(bpy)_3^+$ based on transient absorption spectroscopy (Figure 2a) combined with spectro-electrochemistry (Figure 2b). Following excitation of 20 μM solutions of the dyads from Figure 1c in deaerated CH_3CN at 532 nm using laser pulses of ca. 10 ns duration,

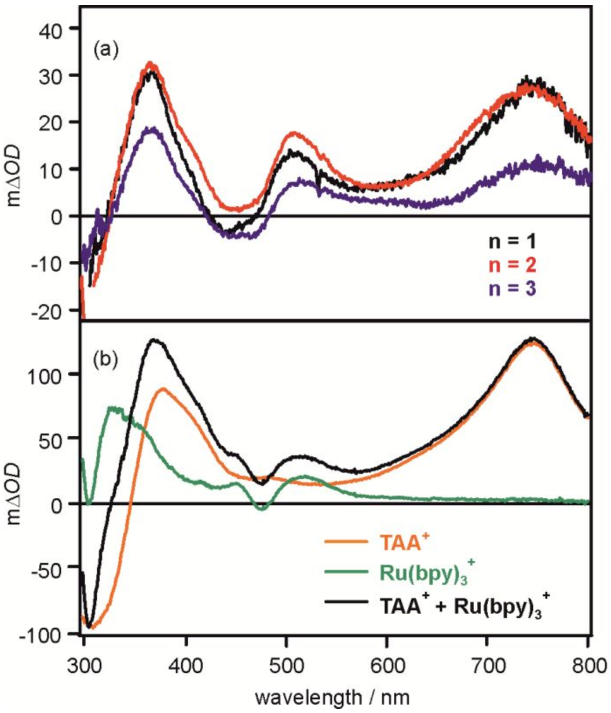

Figure 2. (a) Transient absorption spectra recorded immediately after excitation of the 3 compounds from Figure 1c at 532 nm with laser pulses of ca. 10 ns duration. The spectra were time-integrated over an interval of 200 ns. (b) Spectro-electrochemical UV-Vis difference spectra obtained after selective oxidation of the TAA unit (at a potential of 0.8 V vs. SCE, orange trace) or selective reduction of the $Ru(bpy)_3^{2+}$ acceptor (at a potential of -1.2 V vs. SCE, green trace) in the compound with n = 1. The solvent was de-aerated CH_3CN at 22 °C, the sample concentrations were 20 μM for transient absorption and 205 μM with 0.1 M $TBAPF_6$ for spectro-electrochemistry.

transient absorption bands with maxima at 370, 510, and 750 nm appear in all 3 compounds (Figure 2a). Selective oxidation of the TAA unit at a potential of 0.8 V vs. SCE shows that the formation of TAA^+ causes bands at 370 and 750 nm (orange trace in Figure 2b), whilst reduction of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^+$ at -1.2 V vs. SCE leads to absorptions with maxima at 330 and 510 nm (green trace in Figure 2b). The black trace in Figure 2b is a 1:1 superposition of the TAA^+ and $Ru(bpy)_3^+$ difference spectra, and this linear combination is in excellent agreement with the transient absorption data in Figure 2a. On this short timescale (< 200 ns) at such low sample concentration (20 μM), the TAA^+ and $Ru(bpy)_3^+$ photoproducts can only form via intramolecular electron transfer, as confirmed by the kinetic studies below.

Table 1. Time constants for intramolecular photoinduced electron transfer from TAA to ^{3}MLCT-excited $Ru(bpy)_3^{2+}$ (τ_{f1}, τ_{f2}) and thermal reverse electron transfer from $Ru(bpy)_3^+$ to TAA^+ (τ_b) in the compounds from Figure 1c.[a]

n	τ_{f1} / ps	τ_{f2} / ps	τ_b / ns
1	110 (51%)	870 (49%)	120
2	220 (43%)	1600 (57%)	170
3	320 (62%)	6200 (38%)	220

[a] In de-aerated CH_3CN at room temperature. Determined from the data in Figure 3 and Figure S10. Relative importance given in parentheses.

Picosecond transient absorption measurements reveal that the TAA^+ signal at 750 nm rises in bi-exponential fashion with time constants ranging from 110 to 6200 ps (Figure 3, τ_{f1} and τ_{f2} values in Table 1). In related donor-acceptor dyads with oligo-*p*-xylene bridges we previously observed strictly mono-exponential transient absorption kinetics.[33,52-55] Given the conformational flexibility of our oligo-*ortho*-phenylene bridges, it seems plausible that the bi-exponential nature of the transients in Figure 2 is due to the presence of slowly interconverting conformers. This interpretation is supported by variable-temperature NMR experiments, which demonstrate that

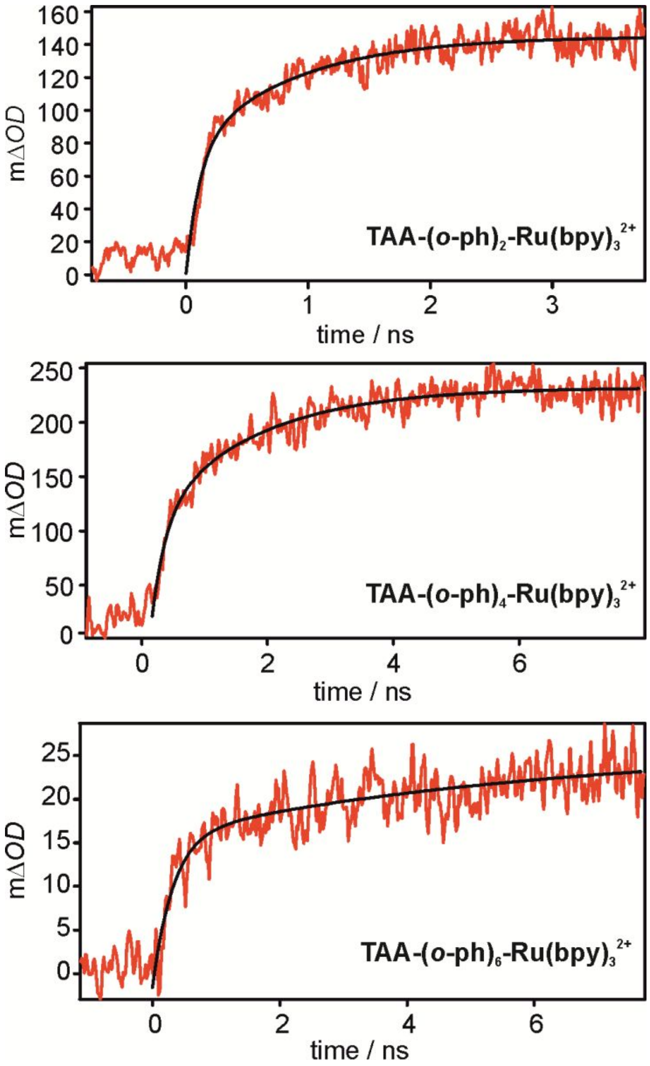

Figure 3. Temporal evolution of the transient absorption signal at 750 nm (red traces) of the three dyads following excitation at 532 nm with laser pulses of ca. 30 ps duration. Measurements were performed in de-aerated CH_3CN at 22 °C. Black curves are bi-exponential fits to the data, yielding the time constants reported in Table 1 (τ_{f1} and τ_{f2} values).

for the dyad with n = 2 there is a barrier of ca. 60 kJ/mol for interconversion between two different main sets of conformers (SI pages S35-S37). Assuming first-order reaction kinetics for interconversion over a barrier of 60 kJ/mol height, a half-life for conformational exchange of ~3 ms can be estimated with the Eyring equation (SI page S37). This is considerably longer than the timescale of the photoinduced electron transfer events in our dyads, and consequently the respective conformational exchange cannot occur during the intramolecular charge transfer processes studied herein. In the transient absorption studies, both sets of conformers are excited and both of them subsequently exhibit different electron transfer kinetics, leading to the observable bi-exponential transient absorption kinetics (Figure 3).

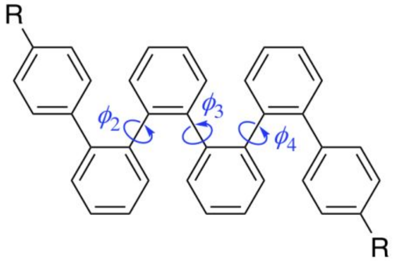

Figure 4. Key torsion angles in an *ortho*-phenylene hexamer.[47] A-type conformation: ϕ_i = -55° ("folded"); B-type conformation: ϕ_i = +133° ("unfolded"). The key conformers in Figure 5 and Table 2 are "A" or "B" for n = 1, "AA" or "BB" for n = 2, and "AAA" or "BBB" for n = 3.

In order to identify the key conformers of our dyads, we performed DFT calculations using Gaussian 09. The diffusion-corrected B97-D functional, which has previously been used to study the folding of *ortho*-phenylenes,[47] was used in combination with the 6-31G(d) basis set (LANL2DZ ECP for Ru atom) for structure optimization together with the IEFPCM/UFF model for CH_3CN solvent. There is considerable conformational flexibility in oligo-*ortho*-phenylene systems, and a complete conformational analysis is beyond our scope. As noted earlier, in a simple *ortho*-phenylene hexamer the backbone conformation is dictated by three key dihedral angles (ϕ_2, ϕ_3, ϕ_4) as illustrated in Figure 4.[47] Within a single *ortho*-phenylene strand each one of

Table 2. Relative energies (E_{rel}) of the individual conformers from Figure 5 and calculated distances ($d_{N\text{-}Ru}$) between the triarylamine N-atom and the Ru-center in the initial ground state (prior to electron transfer) and the photoproduct triplet state (formed as a result of intramolecular electron transfer; relevant structures shown in Figure S16).[a]

	ground state				photoproduct triplet state			
	unfolded		folded		unfolded		folded	
n	E_{rel} / kJ/mol	$d_{N\text{-}Ru}$ / Å	E_{rel} / kJ/mol	$d_{N\text{-}Ru}$ / Å	E_{rel} / kJ/mol	$d_{N\text{-}Ru}$ / Å	E_{rel} / kJ/mol	$d_{N\text{-}Ru}$ / Å
1	0 (B)	11.65	-36 (A)	7.29	0 (B)	13.30	-15 (A)	7.36
2	0 (BB)	9.25	-38 (AA)	8.18	0 (BB)	9.60	-42 (AA)	7.93
3	0 (BBB)	7.64	-17 (AAA)	15.91	0 (BBB)	7.36	-36 (AAA)	15.74

[a] Conformer types in notation used in main text indicated in parentheses. N-Ru distances measured through space.

these torsion angles (ϕ_2, ϕ_3, ϕ_4) can adopt one of two equilibrium values, referred to earlier as "A"-state (for ϕ_i = -55°) or "B"-state (for ϕ_i = +133°).[47] Our dyad with n = 3 contains this hexameric structure as a molecular bridge, and in our calculations we concentrated on its AAA and BBB conformers. In principle, there are four additional conformers (ABA, BAB, AAB, and ABB) for this particular backbone, but they were not considered because they lead to excessive steric strain in our dyads with covalently attached triarylamine and $Ru(bpy)_3^{2+}$ units. By analogy, for the two shorter dyads only the AA and BB conformers (for n = 2), as well as the A and B conformers (for n = 1) were considered. In the AAA and AA conformers (Figure 5f, d) there are

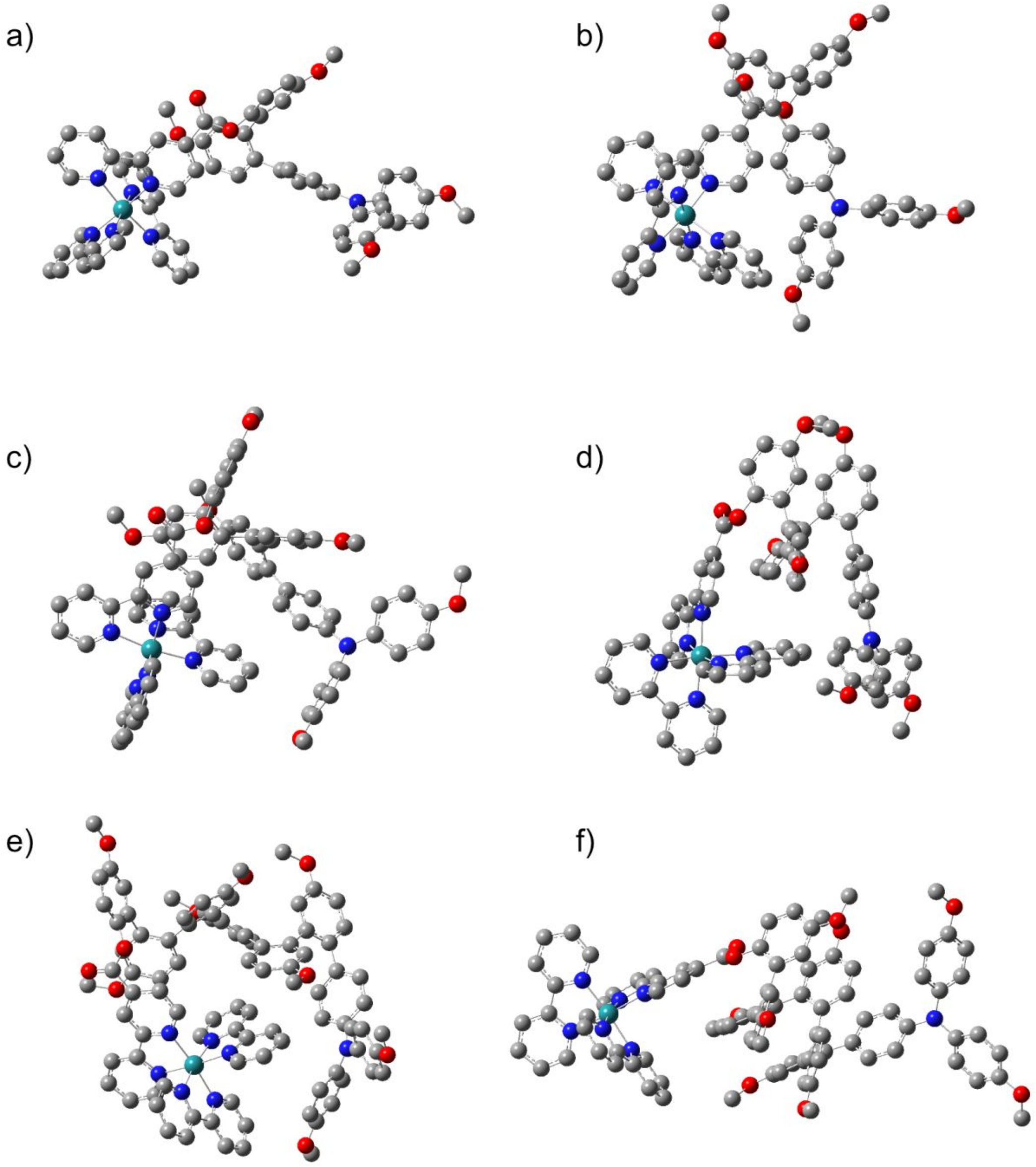

Figure 5. Key ground state conformer geometries of the *ortho*-phenylene bridged dyads: a) n = 1, unfolded B-form; b) n = 1, folded A-form; c) n = 2, unfolded BB-form; d) n = 2, folded AA-form; e) n = 3, unfolded BBB-form; f) n = 3, folded AAA-form. See SI page S38-S42 for details.

arene-arene interactions leading to the folded structures reported earlier for oligo-*ortho*-phenylenes, whereas the BBB and BB conformers (Figure 5e, c) can be considered unfolded structures without such arene-arene interactions. These calculations were performed for the dyads in their electronic ground state (Figure 5) as well as in their photoproduct states with oxidized triarylamine and reduced ruthenium photosensitizer (Figure S16). The AAA, AA, and A conformers are the most stable structures according to these calculations, lower in energy than the BBB, BB, and B conformers by 15 to 42 kJ/mol (Table 2). These two different types of conformers could in fact correspond to the two sets of conformers observed in the variable-temperature NMR experiments.

The distance between the triarylamine N-atom and the Ru atom is a useful proxy for the electron transfer distance in our dyads, and that distance (measured through space) is markedly different for different conformers of a given compound. For example, in the dyad with n = 3 the calculated N-Ru distance in the AAA conformer is 15.9 Å but in the BBB conformer it is only 7.6 Å (Table 2, Figure 5e, f). Such a marked difference in donor-acceptor distance can readily account for the bi-exponential transient absorption kinetics in Figure 3. However, it should be kept in mind that minor conformational changes are easily possible on the timescale of our electron transfer events, and it is not possible to attribute a certain measurable time constant to any specific computed conformer structure,[56] in particular because the observable rate constants could in fact correspond to a combination of rate constants for electron transfer and conformational changes.[57,58] Thus, our calculations primarily provide a qualitative rationale for the multi-exponential transient absorption kinetics, and they illustrate the difficulty of assessing a distance-dependence for electron transfer in the dyads from Figure 1c. Different conformers of the same compound can exhibit very different donor-acceptor distances, depending on whether the conformers are more U-shaped with donor and acceptor pointing into roughly the same direction (Figure 5e, $d_{N\text{-}Ru} \approx 8$ Å) or whether they are more Z-shaped with donor and acceptor pointing towards opposite directions (Figure 5f, $d_{N\text{-}Ru} \approx 16$ Å).

Interestingly, the thermal reverse charge-shift from $Ru(bpy)_3^+$ to TAA^+ gives rise to single-exponential transient absorption kinetics (SI page S32). The time constants for intramolecular backward electron transfer from $Ru(bpy)_3^+$ to TAA^+ (τ_b, Table 1) were determined from the decays of the transient absorption signals at 370, 510 and 750 nm (Figure S10). In all three dyads, the $Ru(bpy)_3^+$ / TAA^+ photoproduct state decays much more slowly than it forms, and the lifetimes τ_b vary only over the small range between 120 and 220 ns despite the very different lengths of the three dyads. As noted above, based on variable-temperature NMR studies it is to be expected that two sets of slowly interconverting (~ 3 ms) conformers are initially excited, manifesting in bi-exponential kinetics for the initial photoinduced electron transfer from TAA to ^{3}MLCT-excited $Ru(bpy)_3^{2+}$ (Figure 3). At first glance, the observation of mono-exponential kinetics for the ensuing thermal reverse charge-shift therefore looks peculiar. However, it seems plausible that in one of the two key conformer sets of each dyad the $Ru(bpy)_3^+$ / TAA^+ photoproduct disappears more rapidly than it is formed due to close donor-acceptor contacts, making its detection impossible for these specific conformers. Indeed, some of the calculated conformers for the $Ru(bpy)_3^+$ / TAA^+ photoproduct state exhibit N-Ru distances below 8 Å (Table 2), essentially corresponding to van-der-Waals contact distance for which very rapid reverse charge-shift is expected. However, there are other low-energy conformers for which the N-Ru distance is up to ca. 16 Å (Table 2), compatible with electron transfer kinetics on the 120 – 220 ns timescale.

In *para*-phenylene-bridged donor-acceptor systems, charges usually transfer along the σ-bonded backbone benefiting from extended π-conjugation, whereas through-space or through-solvent pathways play no significant role due to their linear rigid rod-like structure.[20,22,29,33,36,52-54,59,60] By contrast, in our conformationally flexible *ortho*-phenylene dyads through-bond, through-space or through-solvent pathways are in principle all viable,[61,62] and their relative contributions to the overall electron transfer kinetics cannot be disentangled from the available experimental and computational data. Consequently, the true distance dependence for electron transfer in our dyads cannot be determined, despite the variation of the number of phenylene units from 2 to 6 (Figure 1c).

As noted in the introduction, oligo-*ortho*-phenylenes can form folded structures with arene-arene interactions,[40,46-50] and the question whether photoinduced electron transfer could be observed in such folded structures seemed interesting, particularly because electron transfer across artificial foldamers is yet relatively little explored.[63-65] The DFT calculations performed for the compounds from Figure 1c indeed suggest that conformers with phenylene-phenylene interactions (AAA and AA conformers, Figure 5f, d) are significantly more stable than conformers lacking such interactions (BBB and BB conformers, Table 2). For instance, for the dyad with n = 3 the folded AAA-conformer is 36 kJ/mol more stable than the unfolded BBB-conformer in the photoproduct triplet state, and the calculated N-Ru distance of 15.7 Å is compatible with a time constant of 220 ns for thermal charge-shift between $Ru(bpy)_3^+$ and TAA^+ (Table 2). In passing we note that the additional electron on the reduced ruthenium complex should be largely localized on the electron-deficient ester-functionalized bpy ligand rather than the metal center, yet the N-Ru distance remains a useful proxy for the electron transfer distance. In case charge transfer across arene-arene interactions in foldamer structures would indeed play a significant role, then one might expect electron transfer rates to increase with decreasing temperature, due to increasing stabilization of the arene-arene contacts.[66,67] However, opposite behavior is observed (SI page S34), leading to ordinary Arrhenius-plots providing activation energies between 48 and 98 meV, in line with prior studies of *para*-phenylene based dyads that cannot fold.[33,54] Thus, it seems that if folded structures are indeed involved (as suggested by the computational results, see above), then the dominant charge transfer pathway is unlikely to involve the types of arene-arene interactions that cause the folding.

Regarding charge transfer along the σ-bonded backbone of our *ortho*-phenylene bridged dyads, the presence of methoxy-substituents deserves some attention. These electron-donating substituents lower the potential corresponding to bridge oxidation markedly, and consequently several prior studies on methoxy-decorated *para*-phenylene-bridged systems reported evidence for hole hopping.[68-71] We therefore synthesized a series of oligo-*ortho*-phenylene compounds without appended $Ru(bpy)_3^{2+}$ and TAA units and determined the potentials for their oxidation using cyclic voltammetry (SI page S26-S27). In a bridge model compound made from only two methoxy-substituted phenylene units, the first oxidation wave occurs at 1.70 V vs. SCE, whereas in longer congeners made from four and six methoxy-decorated *ortho*-phenylenes the first oxidation waves peak at 1.23 and 1.25 V vs. SCE, respectively. In the dyads from Figure 1c, TAA^+ reduction takes place at 0.60 V vs. SCE (SI pages S25-S27), and consequently hole transfer from TAA^+ to the bridge would be energetically uphill by 0.63 – 1.10 eV since the hole hopping mechanism implies temporary oxidation of the bridge.[72,73] Electron hopping is similarly unlikely, because the reduction potential of our bridges is more negative than -2.0 V vs. SCE, whereas $Ru(bpy)_3^+$ is oxidized at -1.2 V vs. SCE (SI pages S25-S26). Thus, we conclude that hopping mechanisms are unlikely to play an important role for the thermal charge-shift reaction in our dyads. The situation might be different in *para*-connected analogues,[59] but their investigation is beyond our scope here. In a direct comparison with *para*-connected isomers, the distance dependence of quantum yields for formation of charge-separated states would be an interesting aspect.[74]

Conclusions

Conformationally flexible *ortho*-phenylene bridges between a triarylamine donor and a $Ru(bpy)_3^{2+}$ acceptor permit rapid (<10 ns) photoinduced electron transfer even when up to six phenylene bridging units are present. The resulting photoproduct state comprised of oxidized triarylamine and reduced ruthenium complex stores ca. 1.7 eV of energy, and its lifetime is only weakly dependent on the number of phenylene bridging units, ranging from 120 ns for the compound with only two phenylene bridge units to 220 ns for the dyad with six phenylenes in de-aerated CH_3CN at room temperature. Given the conformational flexibility of these dyads enabling through-space and through-solvent pathways in addition to the through-bond pathways known from oligo-*para*-phenylenes, these photoproduct lifetimes are remarkably long. This shows that rigid rod-like molecular structures are not a key requirement for obtaining long-lived electron-hole separation.

Whilst folded conformers with arene-arene interactions seem to be formed in the donor-bridge-acceptor compounds studied herein, no direct evidence for charge transfer pathways involving the arene-arene interactions leading to foldamer structures could be found.

The distance dependence of charge (and energy) transfer across oligo-*para*-phenylenes has been investigated thoroughly in the past,[22,23,25,26,33,52-54,60,70,73,75-79] but similarly thorough insight into the distance dependence of electron transfer across oligo-*ortho*-phenylenes cannot be obtained from our study due to the many conformational degrees of freedom available in our compounds. Future studies might therefore focus on oligo-*ortho*-naphthalene connected systems with less conformational flexibility,[80-83] in which it might be more readily possible to enforce through-bond electron transfer. Photoinduced electron transfer across naphthalene-bridged systems has been explored relatively little until now.[84,85]

Supporting Information Description

Detailed synthetic protocols and characterization data, description of equipment and methods, supplementary electrochemical, spectroscopic, and computational data.

Acknowledgments

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