Tetramethoxybenzene is a Good Building Block for Molecular Wires: Insights from Photoinduced Electron Transfer

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Supporting Information

ABSTRACT: Two donor bridge−acceptor molecules with terminal triarylamine and Ru(bpy)32+ (bpy = 2,2′-bipyridine) redox partners were synthesized and investigated by cyclic voltammetry, opticalabsorption, luminescence, and transient absorption spectroscopy. The two dyads differ only by the central bridging unit, which was tetramethoxybenzene (tmb) in one case and unsubstituted phenylene (ph) in the other case. Photoirradiation of the Ru(bpy)32+ complex of the two dyads triggers intramolecular electron transfer from the triarylamine to the 3MLCT-excited metal complex, and this process occurs with time constants of 1.5 and 6.8 ns for the tmb- and ph-bridged dyads, respectively. Thermal electron transfer in the reverse direction then leads to disappearance of the photoproduct with a time constant of 10 ns in both dyads. The faster rate of photoinduced charge transfer in the tmb-bridged dyad can be understood in the framework of a hole-tunneling model in which the electron-rich tmb bridge imposes a more shallow barrier than the less electron-rich ph spacer. Until now tmb-based molecular wires have received very little attention, and alkoxy substituents have been mostly used for improving the solubility of oligo-p-phenylene vinylene (OPV) and oligo-p-phenylene ethynylene (OPE) wires. Our study illustrates how four alkoxy-substituents on a phenylene backbone can have a significant influence on the charge-transfer properties of a molecular wire, and this is relevant in the greater context of a future molecular electronics technology.

INTRODUCTION

Long-range electron transfer can occur either via tunneling or hopping mechanisms.1−3 The latter requires redox-active units in the electron transfer pathway, which can temporarily be reduced or oxidized, and such units have sometimes been called "stepping stones".4−6 Even though in the tunneling regime the bridge is neither oxidized nor reduced, its electronic structure plays a key role in mediating electronic coupling between the donor and the acceptor.7−12 Many researchers have attempted to optimize molecular bridges to obtain fast electron or energy transfer over long distances (>10 Å).10,11,13−36 In some of our own recent work we found that electron transfer from a phenothiazine donor to a photogenerated Ru(bpy)33+ (bpy = 2,2′-bipyridine) species across a series of four p-xylene spacers proceeds with a time constant of ~20 μs, whereas equidistant charge transfer between the same donor and acceptor across four p-dimethoxybenzene units occurred ~1000 times faster (Scheme 1).37 Dimethoxybenzene is oxidized significantly more easily than xylene, and consequently hole tunneling is associated with a more shallow barrier in the case of p-dimethoxybenzene than when p-xylene bridging units are present.8,38,39 Related observations have been made on various systems by different researchers.38,40−44

1,2,4,5-Tetramethoxybenzene (tmb) is oxidized even more readily than p-dimethoxybenzene,45−47 and therefore we reasoned that a molecular bridge containing tmb might be able to mediate long-range charge transfer even more efficiently. The electrochemical potential for one-electron oxidation of tmb is in fact so low that the transition from a tunneling to a hopping regime appeared possible in
In combination with a triarylamine (TAA)/Ru(bpy)$_2$$^{2+}$ redox couple. In a prior study we connected tmbr directly to a Ru(bpy)$_3$$^{2+}$ complex and a neighboring p-dimethoxybenzene bridge unit. This molecular design turned out to be suboptimal because the steric demand of tmbr caused large equilibrium torsion angles between tmbr and its neighboring building blocks. This is detrimental for long-range electron transfer because π-conjugation is reduced substantially when increasing the torsion angle between adjacent phenyl or pyridine rings. For the present study we therefore flanked the tmbr bridging unit with ethynyl groups, resulting in the TAA-tmb-Ru$_2^{2+}$ dyad shown in Scheme 2. An analogous compound with an unsubstituted phenylene (ph) instead of the tmbr unit was explored as a reference system (TAA-ph-Ru$_2^{2+}$).

**RESULTS AND DISCUSSION**

**Synthesis and X-ray Crystallography.** The two dyads from Scheme 2 each contain a ligand in which a bpy motif is connected to a triarylamine (TAA) electron donor, either via a tmbr or a ph bridging unit. These two ligands (21 and 22) were synthesized as illustrated by Scheme 3.

For the TAA-tmb-Ru$_2^{2+}$ dyad, synthesis started from 2,5-dihydropyridoxy-1,4-benzquinone (1), which was converted to 1,4-diethynyl-2,3,5,6-tetramethoxybenzene (7) in six steps in 53% overall yield. For the TAA-ph-Ru$_2^{2+}$ dyad, the 1,4-diethynylbenzene (10) building block was available in only two steps from commercial chemicals (11, 12). The iodoxylene-equipped bpy fragment 16 was accessible in three steps from commercial chemicals (11, 12), in addition to the two-step synthesis of 4-(trimethylsilyl)phenylboronic acid (14) from 2,5-dibromo-p-xylene. The iodo-substituted TAA unit 20 was prepared in two steps from bis(p-anisyl)amine (17) following a previously published method. One-pot Sonogashira coupling reactions involving the iodo-substituted TAA donor unit 20, diethynyl-equipped bridging units 7 and 10, and the iodoxylene-equipped bpy fragment 16 then afforded the desired ligands 21 and 22.

The result of an X-ray diffraction study of single crystals of ligand 21, grown by slow evaporation from acetone solution, is shown in Figure 1. Ligand 21 crystallizes in space group P1 with two molecules per unit cell. The triarylamine donor unit adopts its common propeller-shaped structure, and the bipyridine ligand has its two pyridine units oriented in opposite fashion to each other, as commonly observed. The central tetramethoxybenzene unit is nearly coplanar with the adjacent phenyl rings with torsion angles of 10.1° and 34.1° relative to the p-xylene unit and the relevant phenyl from the triarylamine, respectively. The distance between the triarylamine N atom and the center of the bpy ligand is 22.9 Å; consequently, the N–Ru (donor–acceptor distance) in the dyad will be roughly 23 Å. Ligand 21 arranges in sheets that lie in the crystallographic $ab$ plane.

**UV–vis Spectroscopy and Electrochemistry.** In Figure 2 the optical absorption spectra of TAA-tmb-Ru$_2^{2+}$ and TAA-ph-Ru$_2^{2+}$ in CH$_3$CN are shown along with the UV–vis spectrum of the Ru(bpy)$_3$$^{2+}$ reference complex measured under identical conditions. In the two dyads, the MLCT absorption band of the photosensitizer is merely a shoulder to more intense, ligand-centered absorption bands, yet it seems likely that the lowest-energetic electronically excited state is the MLCT state of the Ru(bpy)$_3$$^{2+}$ fragment in both dyads.

Cyclic voltammograms obtained using solutions of the two dyads in CH$_3$CN in the presence of 0.1 M TBAPF$_6$ as a supporting electrolyte are shown in Figure 3. Oxidative and reductive potential sweeps with rates of 0.1 V/s were conducted separately because this gave higher quality results. In the reductive sweeps one easily recognizes three subsequent reversible waves corresponding to consecutive one-electron reduction of each of the three bpy ligands of the photosensitizer between −1.8 V and −2.2 V versus Fc$^-$/Fc$, as commonly detected. In the oxidative sweeps, there is a wave due to triarylamine oxidation around 0.2 V versus Fc$^-$/Fc$^+$ and a wave caused by the Ru(II)/Ru(III) couple around 0.8 V versus Fc$^-$/Fc, both in line with expectation. For the isolated 1,2,4,5-tetramethoxybenzene (tmbr) molecule an oxidation potential of 0.42 V versus Fc$^-$/Fc$^+$ has been reported, but in Figure 3 there is no sign of tmbr oxidation, perhaps because its oxidation overlaps with that of the triarylamine. All relevant reduction potentials are summarized in Table 1.

Identification of Photoproducts. In Figure 4a,d transient absorption spectra obtained after excitation of $2 \times 10^{-5}$ M solutions of the two dyads in aerated CH$_3$CN at 532 nm with laser pulses of ~10 ns duration are shown. The spectra were recorded by averaging over a time period of 200 ns starting immediately after the excitation pulses. Use of this wavelength leads to selective excitation of the Ru(bpy)$_3$$^{2+}$ photosensitizer of TAA-tmb-Ru$_2^{2+}$ and TAA-ph-Ru$_2^{2+}$. For both dyads a similar transient absorption spectrum is obtained: There are absorption bands centered at 740 and 470 nm in addition to a bleach at 390 nm. These three spectral features can be explained by the formation of TAA$^-$·tmbr$^+$ and TAA$^-$·ph-Ru$^+$ photoproducts as a result of electron transfer from TAA to the photoexcited Ru(bpy)$_3$$^{2+}$ complex as explained in the following.

The UV–vis difference spectra in Figure 4b,e were measured after addition of 1 equiv of Cu(ClO$_4$)$_2$ to solutions of TAA-tmb-Ru$_2^{2+}$ and TAA-ph-Ru$_2^{2+}$ in CH$_3$CN, which leads primarily to oxidation of the triarylamine, the spectra obtained before addition of any chemical oxidant served as baselines in both cases. One observes increased absorption at ≈750 and ≈475 nm as well as decreased absorption at ≈400 nm in both dyads. The bands at ≈750 and ≈475 nm are typical for triarylamine radical cations.
The UV−vis difference spectra in Figure 4c,f were obtained by applying a potential of −1.8 V versus Fc+/Fc to solutions of TAA-tmb-Ru2+ and TAA-ph-Ru2+ in CH3CN (using a Pt grid electrode); the spectra obtained before applying any potential served as baselines in both cases. At this potential the Ru(bpy)32+ unit in both dyads can be reduced selectively (Table 1). In both cases this leads to increased absorption above ∼400 nm and to a bleach at shorter wavelengths.

For both dyads the transient absorption spectra (Figure 4a,d) are essentially a 1:1 superposition of the spectro-electrochemical data illustrating the formation of TAA+ and Ru(bpy)3+. This is clear evidence for intramolecular electron transfer from TAA to photoexcited Ru(bpy)32+ in TAA-tmb- and TAA-ph-Ru2+.
Table 1. Reduction Potentials ($E^0$) for the Individual Redox-Active Components of the Two Dyads from Scheme 2

<table>
<thead>
<tr>
<th>Component</th>
<th>$E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(III)/(II)</td>
<td>0.80</td>
</tr>
<tr>
<td>TAA$^{10-}$</td>
<td>0.23</td>
</tr>
<tr>
<td>bpy$^{2+}$</td>
<td>0.42$^{bc}$</td>
</tr>
<tr>
<td>TAA-tmb-Ru$^{2+}$</td>
<td>2.10$^{de}$</td>
</tr>
</tbody>
</table>

*In CH$_3$CN with 0.1 M TBAPF$_6$, measured with potential sweep rates of 0.1 V/s. All potentials are given in Volts relative to the Fc$^-$/Fc couple.

**Reported in ref 45 and 46 for the 1,2,4,5-tetramethoxybenzene molecule in CH$_3$CN.

Converted from a potential reported in V vs SCE to V vs Fc$/Fc$ according to ref 68.

$^c$Reported in ref 67 for the benzene molecule in CH$_3$CN.

Ru$^{2+}$ and TAA-ph-Ru$^{2+}$. The reaction free energy ($\Delta G_{\text{ET}}^0$) for this process can be estimated with the Weller equation (eq 1),

$$\Delta G_{\text{ET}}^0 = e(E^0(\text{TAA}^{4+/3-}) - E^0(\text{bpy}^{2+/1-})) - E_0 - e^2/(4 \pi \varepsilon_0 \varepsilon_s R_{DA})$$

(eq 1)

$$\lambda_o = (e^2/4 \pi \varepsilon_0)[(2\tau_p)^{-1} + (2\tau_o)^{-1} - R_{DA}^{-1}].$$

(eq 2)

Assuming that the total reorganization energy ($\lambda$) is dominated by the outer-sphere contribution ($\lambda_o$), this analysis then leads to the conclusion that photoinduced electron transfer from TAA to photoexcited Ru(bpy)$_3^{2+}$ takes place in the so-called normal regime in both dyads ($-\Delta G_{\text{ET}}^0 > \lambda$), whereas the reverse (thermal) electron transfer occurs in the Marcus inverted region ($-\Delta G_{\text{ET}}^0 < \lambda$). The latter process is in fact closer to the barrierless point; hence, one might anticipate more rapid thermal reverse electron transfer than photoinduced (forward) electron transfer.

**Kinetics of Photoinduced Electron Transfer.** A combination of pico- and nanosecond transient absorption spectroscopy was necessary to explore the electron transfer kinetics in the two dyads from Scheme 2. Following excitation at 400 nm with a femtosecond laser pulse, the series of transient absorption spectra shown in Figure 5 was obtained for TAA-tmb-Ru$^{2+}$ and TAA-ph-Ru$^{2+}$, where the latter dyad is in the Supporting Information (Figure S1).

**Figure 4.** Transient difference spectra of (a) TAA-tmb-Ru$^{2+}$ and (d) TAA-ph-Ru$^{2+}$ in aerated CH$_3$CN (2 x 10$^{-5}$ M) measured after excitation at 532 nm with laser pulses of ~10 ns duration. The signal was averaged over a time interval of 200 ns immediately after excitation. The asterisks (*) mark signals due to laser stray light. UV–vis difference spectra of (b) TAA-tmb-Ru$^{2+}$ and (e) TAA-ph-Ru$^{2+}$ measured in CH$_3$CN after addition of one equivalent of Cu(ClO$_4$)$_2$ as a chemical oxidant. UV–vis difference spectra of (c) TAA-tmb-Ru$^{2+}$ and (f) TAA-ph-Ru$^{2+}$ measured in CH$_3$CN after applying a potential of ~1.8 V vs Fc$/Fc$ to induce reduction of Ru(bpy)$_3^{2+}$ to Ru(bpy)$_3^{+}$.

In (b, c, e, f) the UV–vis spectra recorded before applying any potential or before adding any chemical oxidant served as baselines.

**Figure 5.** Transient absorption spectra measured at different time delays after excitation of TAA-tmb-Ru$^{2+}$ in aerated CH$_3$CN at 400 nm using a fs/ps TA setup. Analogous data for the TAA-ph-Ru$^{2+}$ dyad are reported in the Supporting Information (Figure S1).
time constants in addition to the species-associated difference absorption spectra (SADS) shown in Figure 6. The SADS for

Figure 6. Species-associated difference spectra (SADS) extracted from the global target analysis of the fs/ps TA spectra measured for TAA-tmb-Ru²⁺ in Figure 5. Analogous SADS for TAA-ph-Ru²⁺ are given in the Supporting Information (Figure S2).

species D is compatible with the TAA⁺-B-Ru⁺ photoproduct, and the SADS for species C is attributed to the 3MLCT state of the Ru(bpy)₃²⁻ unit of TAA-B-Ru²⁺. Precise identification of species A and B is not possible, but the initial ultrafast processes are likely to involve internal conversion from the optically excited (ligand-centered) state to the 1MLCT, intersystem crossing to the 3MLCT state, and (vibrational and solvent) relaxation of the 3MLCT state.⁷⁷

For the TAA-ph-Ru²⁺ dyad very similar transient absorption spectra are obtained (Figure S1), but the kinetics analysis yields time constants that are different from those obtained for TAA-tmb-Ru²⁺. Specifically, 0.9 ps, 1.5 ps, ~4 ns, and >5 ns are found; the respective SADS of an A → B → C → D → E reaction sequence are shown in Figure S2. In analogy to TAA-tmb-Ru²⁺, species “C” is attributed to the 3MLCT state, and species “D” is assigned to the TAA⁺-ph-Ru⁺ photoproduct. Given the 0–1.5 ns time window of the experimental (fs/ps) setup, only an approximate value of ~4 ns can be estimated for the time constant for the photoinduced electron transfer process C → D.

Additional experiments, which permit detection of transient absorption spectra beyond 1.5 ns, were therefore performed on a different setup using excitation at 355 nm.⁷⁸ These experiments allow more reliable determination of the rate constants for photoinduced electron transfer (process C → D) and for thermal reverse electron transfer (process D → E). Transient absorption spectra recorded with this (sub-nano-second/microsecond) setup at different time delays for the TAA-tmb-Ru²⁺ dyad in deaerated CH₃CN are shown in Figure 7. Expectedly, the same spectral features as detected above (Figure S) are observed, but they can be followed over a significantly longer time range. On the nanosecond time scale one can identify three decay times, namely, 1.5, 10, and 560 ns. The respective SADS are shown in Figure 8. The time constant of 1.5 ns is attributed to intramolecular electron transfer from TAA to photoexcited Ru(bpy)₃²⁻, and this value is in line with that extracted from the fs/ps studies (1.6 ns) reported above (Figure S). The time constant of 10 ns is attributed to intramolecular reverse electron transfer from the reduced ruthenium photosensitizer to oxidized TAA⁺ (process D → E); to maintain consistency between Figures S and Figure 7, the respective species is labeled “D” in both cases. This value is more accurate than that extracted from the fs/ps studies in Figure S; in the studies with higher temporal resolution reported above it was merely possible to determine a lower limit of 5 ns for thermal reverse electron transfer in the TAA-tmb-Ru²⁺ dyad. Finally, the time constant of 560 ns is attributed to an impurity that escaped detection in the analytical methods used to characterize TAA-tmb-Ru²⁺ but which contributes (to a minor extent) to the transient absorption spectra in Figure 6. The respective SADS in Figure 8 is labeled with “X”.

Analogous experiments were performed with the TAA-ph-Ru²⁺ reference dyad in CH₃CN, and the respective transient absorption spectra are reported in Figure S3. From the SADS in Figure S4, three species-associated decay times can be extracted. In this case they are 6.8, 10, and 490 ns. In analogy to the TAA-tmb-Ru²⁺ dyad, they are attributed to the time constants for electron transfer from TAA to 3MLCT-excited Ru(bpy)₃²⁻ (process C → D), to thermal reverse electron transfer (process D → E), and to a (minor) impurity, respectively. All relevant rate constants for intramolecular electron transfer are summarized in Table 2.

Physical Origin of Different Rate Constants for Photoinduced Electron Transfer. In both dyads the time constants for photoinduced electron transfer (second column in Table 2) are significantly shorter than the time constant for
in TAA-tmb-Ru\(^{2+}\) and TAA-ph-Ru\(^{2+}\) and amount to \(-1.78\) V versus Fe\(^+/\text{Fe}^-\) in the electronic ground state (Table 1). In the 3MLCT excited state, they are 0.34 V versus Fe\(^+/\text{Fe}^-\) because the 3MLCT energy is 2.12 eV. Consequently, the estimated tunneling energy gaps are \(\Delta \epsilon = 0.08\) eV for TAA-tmb-Ru\(^{2+}\) and \(\Delta \epsilon = 1.76\) eV for TAA-ph-Ru\(^{2+}\). This difference is substantial, and it can explain the difference in time constants for photoinduced electron transfer in the respective two dyads (1.5 vs 6.8 ns, Table 2).

In the superexchange model for electron transfer, the one-electron reduced or oxidized states of the bridges are never actually populated, but they are merely virtual states that define the height of the tunneling barrier associated with long-range electron transfer.\(^{3,82}\) However, in the TAA-tmb-Ru\(^{2+}\) dyad the estimated \(\Delta \epsilon\) value is very low (0.08 eV). Given the uncertainty associated with its approximation, the possibility of a hole-hopping process in which oxidized tmb is formed as a reaction intermediate cannot be excluded a priori. However, the ultrafast time-resolved experiments reported above provide no evidence for the formation of tetramethoxybenzene cation with its characteristic absorption at 450 nm.\(^{83}\) In any case it seems plausible that the low oxidation potential of tmb compared to ph plays a key role for the kinetics of photoinduced electron transfer.

Curiously, the time constants for thermal reverse electron transfer from the reduced ruthenium complex to the oxidized triarylmethane are identical in both dyads (10 ns, Table 2). Assuming a hole-transfer mechanism is operative, one estimates \(\Delta \epsilon = 0.19\) eV and \(\Delta \epsilon = 1.87\) eV for the charge-shift from TAA\(^+\) to tmb and ph, respectively, and this leads to the expectation of more rapid hole transfer in the tmb-bridged dyad. However, it is possible that the accelerating effect brought about by the lower \(\Delta \epsilon\) value in the tmb dyad is outbalanced by weaker electronic coupling (\(h_{\text{ph}}\)) between tmb and TAA\(^+\) with respect to ph and TAA\(^+\); the formation of triarylmethane monocation is expected to be associated with geometrical changes that may include torsion along the C–C triple bond between tmb/ph and TAA\(^+\), and this effect could be more pronounced in the sterically more demanding tmb unit relative to the unsubstituted ph spacer.\(^{49,80,84}\)

**SUMMARY AND CONCLUSIONS**

Alkoxy-substituents are frequently used to improve the solubility of rigid rodlike oligo-p-phenylene vinylene (OPV) and oligo-p-phenylene ethynylene (OPE) wires.\(^{11,13,36,85–98}\)
Usually, the phenylene units of these oligomers or polymers are substituted with two alkoxy-groups in para-position to each other, because this leads to the desired solubility enhancement. We hypothesized that fourfold methoxy substitution would lower the oxidation potential of the resulting molecular wire to the extent that significant rate enhancement for hole transfer can be achieved. This hypothesis was verified by the comparative study of the two dyads from Scheme 2, which showed that the tetramethoxybenzene spacer of $\text{TAA-\text{tmdb-Ru}^{2+}}$ permits more rapid charge transfer by about a factor of 4.5 than the unsubstituted phenylene spacer of $\text{TAA-ph-Ru}^{2+}$. Consequently, fourfold alkoxy substitution might be generally less likely to have a detrimental effect on overall $\pi$-conjugation than in OPVs. In OPVs there might be some steric hindrance between alkoxy-groups and adjacent alkene H atoms, but at present we have no evidence that fourfold alkoxy-substitution on OPVs should not be possible.

**ASSOCIATED CONTENT**

Supporting Information

Synthetic protocols and product characterization data, description of equipment and methods, details from X-ray diffraction analysis of ligand 21, additional transient absorption data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b03649.

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**Notes**

The authors declare no competing financial interest.

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