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Microsecond charge recombination in a linear triarylamine–Ru(bpy)₃²⁺–anthraquinone triad†‡

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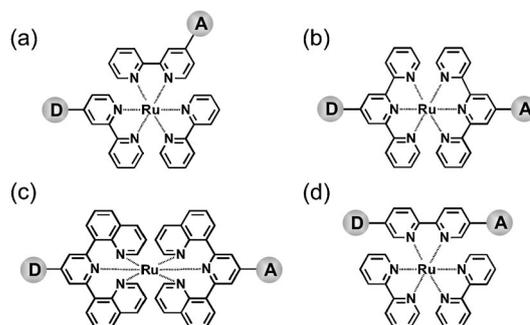
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Linear triads with ruthenium photosensitizers are frequently based on the Ru(terpyridine)₂²⁺ unit. We report on vectorial photoinduced electron transfer in a linear triad based on the Ru(bipyridine)₃²⁺ photosensitizer. Electron–hole separation over a 22 Å-distance is established with a quantum yield greater than 64% and persists for 1.3 μs in acetonitrile.

Photogeneration of long-lived charge-separated states is one of the key goals of research on artificial photosynthesis. Aside from porphyrins,¹ d⁶ metal diimine complexes are popular photosensitizers in artificial dyads and triads.² There are many examples of linear donor–photosensitizer–acceptor triads with porphyrins,^{1,3} but so far this has not been achieved with the Ru(bpy)₃²⁺ (bpy = 2,2′-bipyridine) photosensitizer. When electron donor (D) and acceptor (A) units are attached to different bipyridine ligands, a mixture of isomers results (Scheme 1a),⁴ and the kinetics of the photoinduced reactions become difficult to elucidate in detail.⁵

In order to avoid this problem, much research has focused on triads incorporating the Ru(tpy)₂²⁺ (tpy = 2,2′;6′,2′′-terpyridine) motif with electron donor and acceptor units attached to the central pyridine ring of the two tridentate ligands (Scheme 1b).^{6–9}

However, Ru(tpy)₂²⁺ has an excited state lifetime that is about three orders of magnitude shorter than that of Ru(bpy)₃²⁺,¹⁰ and consequently the excited-state population decays too rapidly in order for electron transfer to be efficient.^{11,12} One possibility to circumvent this problem is to replace the Ru(tpy)₂²⁺ sensitizer by the isostructural Ir(tpy)₃³⁺ motif.¹³ Triads with this sensitizer have yielded spectacularly long-lived charge-separated states which are formed with high quantum yields.^{13,14} However, photoexcitation has to occur at relatively short wavelengths, and the reaction conditions to effect iridium(III) coordination by two tpy ligands are very harsh. A recently explored possibility involves the use of a bis(diquinolonyl)pyridine (dqp) ligand which



Scheme 1 Possibilities for incorporation of ruthenium(II) photosensitizers in donor–photosensitizer–acceptor triads. (a)–(c) are scenarios which have been previously explored, (d) represents the newly explored case of the present study.

is structurally similar to tpy (Scheme 1c).¹⁵ Due to an increased bite angle, the Ru(dqp)₂²⁺ motif exhibits an excited-state lifetime in the microsecond regime,¹⁶ thereby allowing efficient photoinduced electron transfer chemistry. Here, we report on a Ru(bpy)₃²⁺-based system that is comprised of a rigid rod-like donor–bipyridine–acceptor moiety and two ancillary bpy ligands (Scheme 1d), which exhibits very favorable light-induced photochemistry.

Scheme 2 illustrates the synthetic pathway to the rigid rod-like donor–bipyridine–acceptor molecule used for the triad in this work. The starting point is 5,5′-dibromo-2,2′-bipyridine (**1**) to which *p*-xylene units (**2**) are attached by Suzuki coupling.¹⁷ Following trimethylsilyl (TMS)–halogen exchange, the resulting dibromo compound (**4**) is reacted with a boronic acid pinacol ester of 9,10-anthraquinone (**5**). The final step is a palladium catalyzed N–C coupling between molecule **6** and dianisylamine (**7**). The overall yield for the four reaction steps from bipyridine **1** to the final molecular rod **8** is 33%. Reaction with Ru(bpy)₂Cl₂ affords the triad of central interest to this study, hereafter referred to as TAA–Ru²⁺–AQ (TAA = triarylamine; AQ = 9,10-anthraquinone). Detailed synthetic protocols and product characterization data are given in the ESI.†

In acetonitrile solution, the optical absorption spectrum of the triad essentially corresponds to a superposition of its individual molecular components (see Fig. S1 in ESI†), confirming our expectation that the electronic coupling between donor, photosensitizer, and acceptor is weak. Following pulsed laser

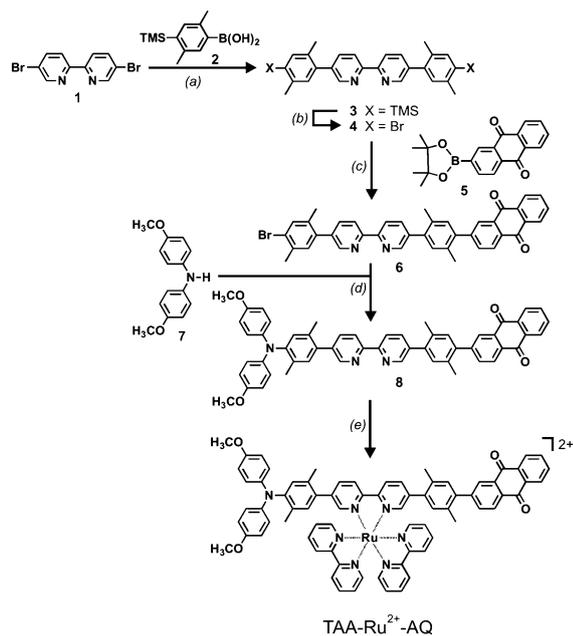
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Scheme 2 Synthesis of the molecular triad: (a) Pd(PPh₃)₄, Na₂CO₃, THF/water 1 : 1 at reflux; (b) Br₂, NaOAc, THF, 0 °C; (c) PdCl₂(dppf), KOAc, DMSO, 80 °C; (d) ¹BuOK, Pd(dba)₂, P(^tBu)₃, toluene, 60 °C; (e) Ru(bpy)₃Cl₂, CHCl₃/C₂H₅OH, reflux. For further details see the ESI.†

excitation, the ³MLCT population of the Ru(bpy)₃²⁺ unit in the triad decays with a time constant of 8 ns in deoxygenated acetonitrile solution, which is an instrumentally limited value in the setup used for the time-resolved experiments reported here (see ESI†). Given a ³MLCT excited state lifetime of 855 ns of unbound Ru(bpy)₃²⁺ under identical conditions,¹⁸ this indicates that more than 99% of the ³MLCT population of the TAA-Ru²⁺-AQ triad is fed into a nonradiative process.

The transient absorption data in Fig. 1 provide direct evidence that this nonradiative process involves two consecutive electron transfer steps. The spectrum shown in Fig. 1a was obtained in a 200 ns time gate starting immediately after ruthenium excitation at 450 nm. It shows three prominent absorption bands centered at 770 nm, 565 nm, and 378 nm, which can be explained by the simultaneous presence of TAA^{•+} radical cations and AQ^{•-} radical anions. This interpretation is corroborated by the spectroelectrochemistry data shown in Fig. 1b and c: upon electrochemical oxidation of a TAA reference molecule (see ESI† for the exact molecular structure) in acetonitrile solution, an absorption band centered around 762 nm becomes observable (Fig. 1b). Following electrochemical reduction of 9,10-anthraquinone, absorption bands centered at 540 nm and 392 nm become detectable (Fig. 1c). On this basis (and in agreement with literature spectra)^{5,14} we assign the three absorption bands in the transient absorption spectrum shown in Fig. 1a to TAA^{•+} (770 nm) and AQ^{•-} (565 nm, 378 nm), and we conclude that 450 nm excitation of TAA-Ru²⁺-AQ leads to a fully charge-separated state of the type TAA^{•+}-Ru²⁺-AQ^{•-}.

The TAA^{•+} and AQ^{•-} absorption bands at 770 nm and 565 nm in Fig. 1a build up within the 8-ns laser pulse used for these experiments, in line with the observation of an

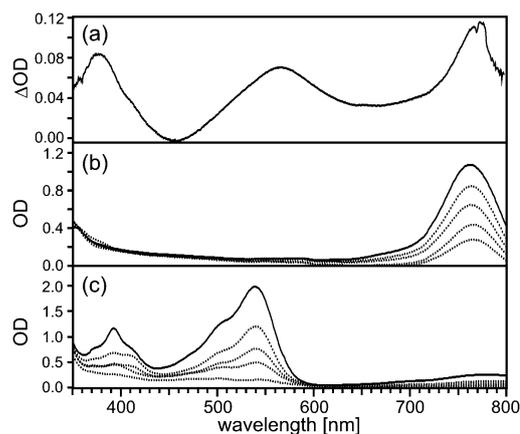


Fig. 1 (a) Transient absorption spectrum measured in a 200 ns time window after excitation of TAA-Ru²⁺-AQ in deoxygenated acetonitrile solution at 450 nm with 8 ns laser pulses; (b) optical absorption spectra measured after different time periods of electrochemical oxidation of a TAA reference molecule in acetonitrile solution; (c) optical absorption spectra measured after different time periods of electrochemical reduction of AQ in dichloromethane solution.

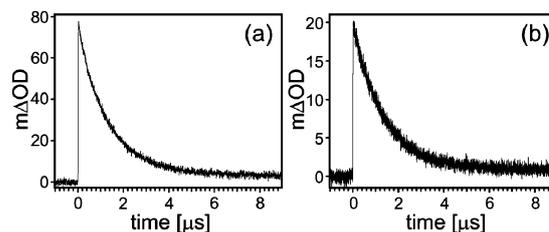


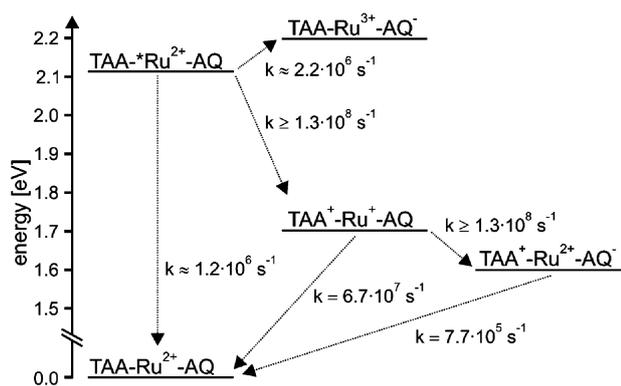
Fig. 2 Decays of the transient absorption signals from Fig. 1a at 565 nm (a) and 770 nm (b).

instrumentally limited ³MLCT luminescence lifetime (see above). The decays of the transient absorption intensities at 770 nm and 565 nm are shown in Fig. 2.

Single exponential fits yield essentially identical decay constants of 1.3 μs in both cases, as would be expected for an intramolecular thermal charge-recombination process between the TAA^{•+} and AQ^{•-} radical ion species. Importantly, the rate constants for photoinduced charge-separation (*k*_{CS}) and thermal charge-recombination (*k*_{CR}) differ by more than a factor of 160. Such high *k*_{CS}/*k*_{CR} ratios are not without precedent in triads, and they are usually explained by the fact that forward electron transfer can happen in two consecutive steps occurring over relatively short distances, while the reverse reaction can only take place in a single step over a substantially longer distance.^{13,19}

In the present case, the two forward electron transfers likely involve first TAA to Ru(bpy)₃²⁺ electron transfer, followed by electron transfer from reduced Ru(bpy)₃²⁺ to AQ (Scheme 3). The opposite sequence is unlikely on energetic grounds: based on cyclic voltammetry data (Table 1 and Fig. S2 in ESI†), oxidative quenching of the Ru(bpy)₃²⁺ ³MLCT state by anthraquinone is endergonic by 0.1 eV, while reductive quenching by TAA is exergonic by 0.4 eV.

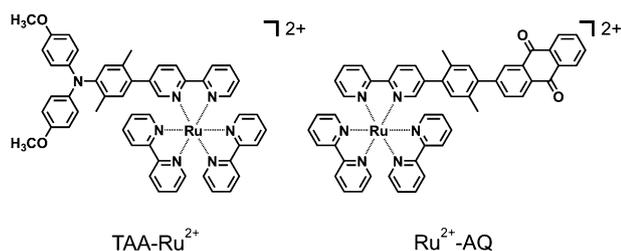
Indeed, experiments on reference dyad TAA-Ru²⁺, comprised of a triarylamine unit connected to a Ru(bpy)₃²⁺ complex (Scheme 4, left), confirms that electron transfer from TAA to



Scheme 3 Energy level scheme showing the relevant charge separated states which can be formed after photoexcitation of the $\text{Ru}(\text{bpy})_3^{2+}$ photosensitizer. Rate constants (k) for the individual electron transfer steps were estimated as described in the text.

Table 1 Reduction potentials of the individual redox-active components of the $\text{TAA-Ru}^{2+}\text{-AQ}$ triad. Cyclic voltammetry was performed in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. Excited-state potentials were calculated from ground-state potentials using the common approximations¹⁰

Redox couple	V vs. Fc^+/Fc
$\text{Ru}(\text{III})/\text{Ru}(\text{II})$	1.03
$\text{TAA}^{\bullet+}/\text{TAA}$	0.42
$\text{AQ}/\text{AQ}^{\bullet-}$	-1.2
$^*\text{Ru}(\text{II})/\text{Ru}(\text{I})$	0.8
$\text{Ru}(\text{III})/^*\text{Ru}(\text{II})$	-1.09



Scheme 4 Molecular structures of two reference dyads investigated in the course of this work.

photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ takes place within less than 8 ns, hence $k_{\text{ET}} \geq 1.3 \times 10^8 \text{ s}^{-1}$. In reference dyad $\text{Ru}^{2+}\text{-AQ}$, comprised of a $\text{Ru}(\text{bpy})_3^{2+}$ moiety connected to an anthraquinone unit (Scheme 4, right), the ³MLCT population decays with a lifetime of 300 ns (Fig. S3 in ESI†), indicating that photoinduced ruthenium-to-AQ electron transfer occurs with a rate constant of roughly $2.2 \times 10^6 \text{ s}^{-1}$. Given a decay rate constant of $1.2 \times 10^6 \text{ s}^{-1}$ for the ³MLCT population of the $\text{Ru}(\text{bpy})_3^{2+}$ unit,¹⁸ we may conclude that in the triad the singly charge-separated state $\text{TAA}^{\bullet+}\text{-Ru}^+\text{-AQ}$ forms with a quantum yield of at least 97% from the initially excited $\text{Ru}(\text{bpy})_3^{2+}$ MLCT state. In the triad, the singly charge separated state is undetectable with nanosecond time resolution, because the doubly charge separated state ($\text{TAA}^{\bullet+}\text{-Ru}^{2+}\text{-AQ}^{\bullet-}$) forms with a rate constant of $\geq 1.3 \times 10^8 \text{ s}^{-1}$ (see above). In the TAA-Ru^{2+} reference dyad, the $\text{TAA}^{\bullet+}\text{-Ru}^+$ charge-separated state is observable and exhibits a lifetime of 15 ns (Fig. S4 in ESI†), hence the rate

constant for thermal charge recombination between $\text{TAA}^{\bullet+}$ and Ru^+ in the triad can be estimated to $6.7 \times 10^7 \text{ s}^{-1}$. This in turn permits the conclusion that in the triad the doubly charge separated state is formed with a yield greater than 64% from the initially excited $\text{Ru}(\text{bpy})_3^{2+}$ MLCT state.

Subsequent thermal charge recombination between $\text{TAA}^{\bullet+}$ and $\text{AQ}^{\bullet-}$ ($k_{\text{ET}} = 7.7 \times 10^5 \text{ s}^{-1}$) may be slow not only because of the long distance between the reaction partners ($\sim 22 \text{ \AA}$ center-to-center), but inverted driving force effect and spin selection rule may play a non-negligible role as well.²⁰

In summary, we have demonstrated vectorial electron transfer in a linear triad incorporating the $\text{Ru}(\text{bpy})_3^{2+}$ complex. Due in large part to the use of this particular photosensitizer, a long-lived charge separated state is formed with high quantum yield. An interesting aspect will be to elucidate how the rate constants and quantum yields for the individual charge separation and charge recombination processes depend on distance.^{21,22,23}

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