Photoinduced charge accumulation by metal ion-coupled electron transfer†

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An oligotriarylamine (OTA) unit, a Ru(bpy)3^2+ photosensitizer moiety (Ru), and an anthraquinone (AQ) entity were combined to a molecular dyad (Ru-OTA) and a molecular triad (AQ-Ru-OTA). Pulsed laser excitation at 532 nm led to the formation of charge-separated states of the type Ru^2+-OTA^2+ and AQ^-Ru-OTA^3+ with lifetimes of ≤10 ns and 2.4 μs, respectively, in de-aerated CH3CN at 25 °C. Upon addition of Sc(OTf)_3, very long-lived photoproducts were observed. Under steady-state irradiation conditions using a flux of (6.74 ± 0.21) × 10^15 photons per second at 450 nm, the formation of twofold oxidized oligotriarylamine (OTA^2+) was detected in aerated CH3CN containing 0.02 M Sc^3+, as demonstrated unambiguously by comparison with UV-Vis absorption spectra obtained in the course of chemical oxidation with Cu^2+. Photodriven charge accumulation on the OTA unit of Ru-OTA and AQ-Ru-OTA is possible due to the lowering of the O2 reduction potential caused by the interaction of superoxide with the strong Lewis acid Sc^3+. The presence of the anthraquinone unit in AQ-Ru-OTA accelerates the rate-determining reaction step for charge accumulation by a factor of 10 compared to the Ru-OTA dyad. This is attributed to the formation of Sc^3+-stabilized anthraquinone radical anion intermediates in the triad. Possible mechanistic pathways leading to charge accumulation are discussed. Photodriven charge accumulation is of key importance for solar fuels because their production will have to rely on multi-electron chemistry rather than single-electron reaction steps. Our study is the first to demonstrate that metal ion-coupled electron transfer (MCET) can be exploited to accumulate charges on a given molecular unit using visible light as an energy input. The approach of using a combination of intra- and intermolecular electron transfer reactions which are enabled by MCET is conceptually novel, and the fundamental insights gained from our study are relevant in the greater context of solar energy conversion.

1. Introduction

The primary events of natural photosynthesis are light absorption, energy transfer, and electron transfer. In the course of the Kok cycle, oxidative equivalents are accumulated on a calcium-containing manganese cluster, the so-called oxygen-evolving complex (OEC). In recent years, considerable efforts have been devoted to the development of artificial OECs, and in many cases it has been possible to catalyze the oxidation of water with sacrificial reagents such as Ce(IV) salts. The generation of solar fuels (e.g., H2 from H2O; methanol or methane from CO2) will inevitably require multi-electron chemistry, and in this greater context it is desirable to gain a more thorough understanding of how charges can be accumulated on a given molecular unit, ideally using visible light as an energy source.

Photoinduced charge accumulation has received significant attention in recent years. Recent studies demonstrated that 10 or more charges can readily be accumulated in nanoparticles, but in purely molecular systems already the accumulation of 2 electrons or holes represents a significant challenge. While systems based on nanoparticles are promising for applications, control over sample heterogeneity (e.g. regarding particle size and binding equilibria of redox-active surfactants) can be tricky to obtain, and one is often confronted with complications resulting from the involvement of surface states. For fundamental and mechanistic investigations, purely molecular systems therefore remain attractive. In the vast majority of cases explored to date, sacrificial redox reagents were used (e.g., triethylamine for reduction and peroxydisulfate for oxidation processes), and there are only very few exceptions. Using sacrificial reagents, photoinduced charge accumulation in purely molecular systems has been achieved for example in quinone-based triads, in various coordination compounds containing precious metals such as Rh, Ir, Pd or Pt, and in many cobaloximes in which the accumulation of two negative charges was employed for the formation of H2. Many other examples from the realms of...
biomimetic chemistry could be mentioned in this context.\textsuperscript{14} In several cases of hydrogen-evolving complexes it is not \textit{a priori} clear whether charge accumulation indeed occurs on a molecular catalyst, or whether a colloid formed in the course of photoirradiation is the catalytically active species.\textsuperscript{15} This important issue has been intensely debated in the recent past, and against this background it seems all the more relevant to explore chemically well-defined systems in which photoinduced charge accumulation can be detected unambiguously. The majority of prior studies of photo-production of H\textsubscript{2}, photo-oxidation of H\textsubscript{2}O, or photo-reduction of CO\textsubscript{2} have not focused on the elementary steps of charge accumulation.

We report here on the use of metal ion-coupled electron transfer (MCET) for photoinduced accumulation of two positive charges on the oligotriarylamine (OTA) units of the two compounds from Scheme 1. The first compound (Ru-OTA) is a molecular dyad comprised of an OTA donor unit which is connected to a Ru(bpy)\textsubscript{3}\textsuperscript{2+} (bpy = 2,2\textsuperscript{'}-bipyridine) photosensitizer. The second compound (AQ-Ru-OTA) is a molecular triad which contains an additional 9,10-anthraquinone (AQ) acceptor unit. Photoexcitation of the Ru\{bpy\}\textsubscript{2}\textsuperscript{2+} complex of Ru-OTA and AQ-Ru-OTA in the presence of oxygen and the strong Lewis acid Sc\textsuperscript{3+} leads to the formation of OTA\textsuperscript{2+} in both compounds, because MCET greatly stabilizes the superoxide reduction product. The stabilization of O\textsubscript{2}\textsuperscript{-} and quinone radical anions by various Lewis acids has been investigated in considerable detail, and the term MCET has been coined by Fukuzumi.\textsuperscript{16} Others have demonstrated how the Lewis acidity of a redox-inactive metal in artificial manganese clusters mimicking the naturally occurring OEC affects the redox properties, thereby illustrating the possible role of Ca\textsuperscript{2+} in the biological Mn\textsubscript{4} cluster.\textsuperscript{17} We are unaware of prior studies in which Lewis acids have been employed to achieve visible light-driven accumulation of positive charge carriers on a molecular unit.

2. Results and discussion

\textbf{Synthesis}

The key ligand of the Ru-OTA dyad was prepared as illustrated in the uppermost line of Scheme 2. 5-Bromo-2,2\textsuperscript{'}-bipyridine (1)\textsuperscript{18} was reacted with (2,5-dimethyl-4-(trimethylsilyl)phenyl)boronic acid (2)\textsuperscript{19} under standard Suzuki cross-coupling conditions, and the trimethylsilyl protection group of the coupling product (3) was substituted by an iodine atom using ICl.\textsuperscript{19} The resulting iodo-compound (4) was reacted with oligotriarylamine (5)\textsuperscript{8,20} in a Pd(0) catalyzed N–C coupling reaction to afford ligand 6,
which was subsequently refluxed together with Ru(bpy)3Cl2 to yield the Ru-OTA dyad. The overall yield for the synthesis of Ru-OTA was 61% with respect to 5-bromo-2,2'-bipyridine (1).

The key ligand of the AQ-Ru-OTA triad was synthesized as shown in the middle and lower part of Scheme 2. After cross-coupling of 2-bromo-9,10-anthraquinone (7) and (2,5-dimethyl-4-(trimethylsilyl)phenyl)boronic acid (2)19, the trimethylsilyl group of the reaction product (8) was substituted by an iodine atom using ICl to afford iodo-compound 9. In a Pd-catalyzed reaction with bis(pinacolato)diborane, the iodine atom of compound 9 was then replaced by a boronic ester group to afford compound 10. The latter was reacted with one equivalent of 5,5'-dibromo-2,2'-bipyridine (11) under standard Suzuki coupling conditions to yield compound 12. Subsequent reaction with (2,5-dimethyl-4-(trimethylsilyl)phenyl)boronic acid (2)19 gave compound 13, and the trimethylsilyl group of the latter was replaced by an iodine atom using ICl. The resulting iodo-compound 14 was reacted with oligotriarylamine 580,20 in a Pd-catalyzed N-C coupling reaction to afford ligand 15, which was subsequently coordinated to Ru(bpy)3Cl2 to give the AQ-Ru-OTA triad. The overall yield for the synthesis of AQ-Ru-OTA was 14% with respect to the 2-bromo-9,10-anthraquinone (7) starting material. Complete synthesis procedures and product characterization data are given in the ESI.†

Electrochemistry

Cyclic voltammetry was performed in dry, de-aerated CH3CN using 0.1 M TBAPF6 (tetra-n-butylammonium hexafluorophosphate) as a supporting electrolyte. The main purpose of these investigations was to establish the thermodynamics of photoinduced charge accumulation on the oligotriarylamine units of Ru-OTA and AQ-Ru-OTA. Voltammograms measured at a potential sweep rate of 0.1 V s⁻¹ are shown in Fig. 1 for (a) Ru-OTA, (b) AQ-Ru-OTA, and (c) Ru(bpy)3²⁺ as reference complexes. All electrochemical potentials extracted from these data are summarized in Table 1. Comparison of Fig. 1a and b with Fig. 1c readily permits the identification of redox waves which are either caused by the oxidation of Ru(II) to Ru(III), or by the consecutive one-electron reduction of the three bpy ligands. No significant differences in the respective redox potentials are observed between Ru-OTA/AQ-Ru-OTA and the reference complex, i.e., the electrochemical behavior of the ruthenium complex in the dyad and the triad is essentially unperturbed by the OTA-functionalized ligand.

Table 1  Electrochemical potentials (E in Volts vs. Fc⁺/Fc) of the individual redox-active units of Ru-OTA, AQ-Ru-OTA, and the Ru(bpy)3²⁺ reference complex in CH3CN.

<table>
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<tr>
<th>Compound</th>
<th>Ru(II/III)</th>
<th>AQ-0/−</th>
<th>Ru(bpy)3²⁺</th>
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<tr>
<td>Ru(bpy)3Cl2</td>
<td>0.94</td>
<td>0.91</td>
<td>0.90</td>
</tr>
<tr>
<td>bpy³⁻/²⁻</td>
<td>−1.68</td>
<td>−1.66</td>
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<tr>
<td>bpy²⁻/¹⁻</td>
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<td>bpy¹⁻/⁰</td>
<td>−2.11</td>
<td>−2.17</td>
<td></td>
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<tr>
<td>OTA²⁺/¹⁻</td>
<td>−0.02</td>
<td>−0.06</td>
<td></td>
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<tr>
<td>OTA¹⁻/⁰</td>
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<td>0.20</td>
<td></td>
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<tr>
<td>OTA⁰/−</td>
<td>0.68</td>
<td>0.64</td>
<td>−1.26</td>
</tr>
<tr>
<td>AQ⁰/−</td>
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</table>

Data extracted from the cyclic voltammograms shown in Fig. 1.

Three quasi-reversible one-electron oxidation waves are detected for the oligotriarylamine unit of Ru-OTA and AQ-Ru-OTA, as commonly observed.80,20,21 The first two oxidations occur at around 0.0 and 0.2 V vs. Fe⁺/Fe in line with expectation based on previously investigated related compounds.20,22 All electrochemical potentials in Table 1 are in good agreement with previously reported values for Ru(bpy)3²⁺, 2⁻ oligotriarylamines,80,21 and anthraquinones.22

Optical absorption and luminescence spectroscopy

The UV-Vis absorption spectra of Ru-OTA, AQ-Ru-OTA, and Ru(bpy)3²⁺ in CH3CN are shown in Fig. 2. In addition to the
The oligothiophene and anthraquinone units.

The absorption at around 290 nm, the dyad and the triad exhibit absorption at around 330 nm, which can be attributed to the oligothiophene and anthraquinone units.

The oligothiophene unit of Ru-OTA and AQ-Ru-OTA can readily be oxidized to its mono- and dicationic forms with Cu(ClO₄)₂ because the reduction potential of the latter is 0.57 V vs. Fe/C₇Fe in CH₃CN. For the series of UV-Vis difference spectra in Fig. 3a, the absorption spectrum of 10⁻⁵ M Ru-OTA in CH₃CN was used as a baseline, and the individual spectra were recorded after the addition of increasing amounts of Cu(ClO₄)₂. The green trace was obtained after adding 1 equivalent of chemical oxidant. In the respective spectrum, absorption bands at 430, 735, and 1310 nm are prominent, and they are attributed to OTA⁺, in line with prior studies. Upon addition of a second equivalent of Cu(ClO₄)₂, the abovementioned bands disappear, and new bands at 595 and 1130 nm gain intensity, compatible with the formation of OTA²⁺ (red trace). Analogous experiments with AQ-Ru-OTA (Fig. 3b) provide very similar results. The key finding from these chemical oxidation experiments is that one- and two-electron oxidation products (OTA⁺ vs. OTA²⁺) can easily be distinguished from each other on the basis of UV-Vis spectroscopy.

In passing we note that based on the abovementioned redox potentials, the oxidation of OTA to OTA²⁺ by Cu(II) is essentially complete. For instance, the equilibrium constant for the reaction Ru-OTA⁺ + Cu(II) ⇌ Ru-OTA²⁺ + Cu(I) is 3.8 × 10⁴. Only marginal amounts of Cu(I) therefore remain in solution, and these cannot account for the absorption features in Fig. 3.

Photoexcitation of de-aerated CH₃CN solutions at 450 nm shows that the emission of Ru-OTA and AQ-Ru-OTA is much weaker than that of Ru(bpy)₃²⁺ under identical conditions, indicating that the lowest 3MLCT excited state of the dyad and the triad is depopulated efficiently by a nonradiative process (data not shown). After pulsed excitation of de-aerated CH₃CN solutions at 532 nm, the luminescence lifetimes are 830 ns for Ru(bpy)₃²⁺, ≤10 ns for Ru-OTA, and ≤10 ns for AQ-Ru-OTA (data not shown). The luminescence lifetimes of the dyad and the triad are instrumentally limited, and this finding is compatible with their weak luminescence intensities relative to Ru(bpy)₃²⁺.

**Figure 3** UV-Vis difference spectra measured in the course of chemical oxidation of the dyad and the triad with Cu(ClO₄)₂ in aerated CH₃CN at 25 °C. The spectra of Ru-OTA (a) and AQ-Ru-OTA (b) measured prior to the addition of any oxidant served as baselines. The individual shown spectra were measured after increasing the amount of Cu(ClO₄)₂. The green traces are attributed to Ru-OTA⁺/AQ-Ru-OTA⁺, and the red traces are assigned to Ru-OTA²⁺/AQ-Ru-OTA²⁺.

**Figure 4** Transient absorption spectra measured after excitation of (a) Ru-OTA and (b) AQ-Ru-OTA in de-aerated CH₃CN at 25 °C with laser pulses of ~10 ns duration at 532 nm. The spectra were acquired by time-integration over the first 200 ns following excitation. The asterisk (*) marks a signal due to laser stray light. The spectra in (c) and (d) are the green traces from Fig. 3a and b, i.e., the UV-Vis difference spectra obtained for Ru-OTA⁺ and AQ-Ru-OTA⁺.
transfer from OTA to the $^3\text{MLCT}$-excited photosensitizer is approximately $-0.5$ eV (see ESI† for details).

As seen from Fig. 5a and b, the $\text{Ru}^{\text{3+}}-\text{OTA}^-$ and $\text{AQ}^-\text{Ru-OTA}^+$ photoproducts are formed within the $\sim 10$ ns duration of the excitation laser pulses. Our own recent work on closely related triarylamidine-$\text{Ru(bpy)}_3^{2+}$ and triarylamidine-$\text{Ru(bpy)}_3^{2+}$-antraquinone compounds (using equipment with higher temporal resolution) strongly suggests that the $\text{Ru}^{\text{3+}}-\text{OTA}^-$ and $\text{AQ}^-\text{Ru-OTA}^+$ charge-separated states are actually formed with rate constants on the order of $10^{10}$–$10^{11}$ s$^{-1}$.23,27

In de-aerated CH$_3$CN, the transient absorption signal of the dyad at 400 nm decays with an instrument limited lifetime of $\sim 10$ ns (black trace in Fig. 5a), explaining the low signal-to-noise ratio in the transient difference spectrum of Fig. 4a. In the triad, the transient absorption signals at 415, 565, and 685 nm all decay with a lifetime of $2.4 \mu$s (Fig. 5b), indicating that the OTA$^-$ and AQ$^-$ photoproducts disappear in a single reaction step involving thermal electron transfer from the reduced anthraquinone to the oxidized oligotriarylamine, as commonly observed in such triads.23,26,27

Importantly, no evidence could be obtained for photoinduced charge accumulation on either OTA or AQ in de-aerated CH$_3$CN using pulsed laser excitation. Since prior studies demonstrated that Lewis acids can stabilize quinone radical anions,16 we wondered whether the addition of Sc$^{3+}$ could enable photoinduced charge accumulation in $\text{AQ-Ru-OTA}^-$. However, when adding 2000 equivalents of Sc(OTf)$_3$ to $10^{-5}$ M solutions of Ru-OTA and AQ-Ru-OTA in CH$_3$CN, the samples did undergo rapid color changes upon exposure to light. Nanosecond transient absorption studies were essentially impossible to perform in the presence of Sc$^{3+}$, because a stable photoproduct accumulated between laser flashes. Even single-shot experiments were essentially impossible to perform because some OTA$^-$ photoproducts were formed already during sample preparation due to unavoidable light exposure. Moreover, in the transient absorption experiments the probe beam alone induced significant photoreaction. We therefore turned to experiments in which the compounds from Scheme 1 were irradiated continuously with visible light.

**Continuous photo-irradiation in the presence of Sc$^{3+}$**

For these experiments, $(1.0 \pm 0.1) \times 10^{-5}$ M solutions of the Ru-OTA dyad and the AQ-Ru-OTA triad in 3 ml of CH$_3$CN containing 0.02 M of Sc(OTf)$_3$ were irradiated in a thermostatted cell compartment of a fluorimeter. The latter provided a flux of $(6.74 \pm 0.21) \times 10^{15}$ photons per second at 450 nm, as determined by ferroxalate actinometry.26 The irradiated area was approximately 0.5 cm$^2$. The series of UV-Vis difference spectra in Fig. 6 were recorded after different irradiation times; in general the baseline is the UV-Vis spectrum of the dyad (left) or the triad (right) measured immediately after sample preparation. The red traces were all recorded after one hour of irradiation with the abovementioned photon flux, i.e. with a total number of $[2.43 \pm 0.08] \times 10^{19}$ photons (corresponding to $(4.0 \pm 0.1) \times 10^{-5}$ mol of photons).

In Fig. 6a the UV-Vis difference spectra measured for $10^{-5}$ M Ru-OTA in aerated CH$_3$CN with 0.02 M Sc(OTf)$_3$ are shown. Comparison with the UV-Vis difference spectra obtained after oxidation with Cu(ClO$_4$)$_2$ (Fig. 3a) shows that Ru-OTA$^+$ (with its characteristic band at 1320 nm) is formed over the first 4 minutes (green trace) of photo-irradiation, but after 1 hour (red trace) Ru-OTA$^{2+}$ (with its diagnostic band at 1130 nm) is clearly the dominant species. (The data are shown in more detail in Fig. S2 (ESI†), which clearly demonstrates that no reduced ruthenium is present.)

Fig. 6e shows analogous UV-Vis difference spectra of $10^{-5}$ M AQ-Ru-OTA in aerated CH$_3$CN with 0.02 M Sc(OTf)$_3$. In this case, already after 1 minute of irradiation time (green trace) a substantial amount of AQ-Ru-OTA$^-\text{Ru-OTA}^+$ is present. After 1 hour (red trace), AQ-Ru-OTA$^{2+}$ is clearly the dominant species. In fact, already the solution used for recording the baseline spectrum at $t = 0$ contains a significant amount of AQ-Ru-OTA$^+$, and this causes the bleach (negative signal) in the absorption spectra at around 1300 nm with increasing irradiation time (see ESI† for details). (The data are shown in more detail in Fig. S3 (ESI†), which clearly demonstrates that no reduced ruthenium or reduced anthraquinone is present.)

A series of reference experiments were performed to elucidate under what conditions OTA$^{2+}$ formation in Ru-OTA and AQ-Ru-OTA can occur. In the dark, OTA$^{2+}$ is not formed, neither in the dyad (Fig. 6b) nor in the triad (Fig. 6f). In the respective UV-Vis difference spectra one merely recognizes a weak band centered at around 1320 nm which is attributed to thermal oxidation of OTA by O$_2$. We recall that the red traces were recorded after 1 hour.

When freeze–pump–thaw de-oxygenated $10^{-5}$ M CH$_3$CN solutions of Ru-OTA and AQ-Ru-OTA with 0.02 M Sc$^{3+}$ are photo-irradiated, OTA$^{2+}$ is not formed (Fig. 6c and g). Instead, only weak absorption bands centered at 1320 nm are detected, indicating the formation of small amounts of OTA$^-$. This is attributed to oligotriarylamine oxidation caused by trace amounts of O$_2$ which remain in solution after the freeze–pump–thaw process. We estimate that the amount of residual O$_2$ in our cuvettes is on the order of $5 \times 10^{-9}$ mol, and the amounts of Ru-OTA$^+$ and AQ-Ru-OTA$^+$ formed as shown in Fig. 6c and g are similar.

Irradiation of $10^{-5}$ M Ru-OTA and AQ-Ru-OTA solutions in aerated CH$_3$CN in the absence of Sc$^{3+}$ does not lead to any observable photoproducts at all (Fig. 6d and h). After 1 hour of irradiation, one still obtains basically the baseline spectrum.
The combination of experiments summarized in Fig. 6 clearly demonstrates that charge-accumulation on the oligotriarylamine units of Ru-OTA and AQ-Ru-OTA is a photoinduced process which requires O₂ and Sc³⁺ to be simultaneously present. When either light, O₂, or Sc³⁺ is missing, OTA²⁺ is not formed. Prior studies demonstrated that strong Lewis acid/Lewis base interaction between Sc³⁺ and superoxide anions has important thermodynamic consequences for oxygen reduction.¹⁶ Hence, the AQ-Ru-OTA⁺ adducts (see above) clearly demonstrate that charge-accumulation on the oligotriarylamine units of Ru-OTA and AQ-Ru-OTA possible.

Mechanisms for charge accumulation

Intramolecular photoinduced electron transfer to establish the Ru-*OTA⁺* and AQ-*Ru-OTA⁺* charge separated states (Fig. 4) takes place with rate constants on the order of 10¹⁰–10¹¹ s⁻¹ (Scheme 3a and b, uppermost lines), as discussed above.²²,²⁷ Subsequent bimolecular electron transfer with O₂ in the presence of Sc³⁺ can then occur with essentially diffusion-limited kinetics, because of the high driving force for the formation of Sc³⁺/O₂⁻ adducts (see above). Given an O₂ solubility of 8 mM in CH₃CN at room temperature and a diffusion constant of 1.9 × 10⁻¹⁰ M⁻¹ s⁻¹ for O₂ in CH₃CN at 298 K,²⁸ we estimate that O₂ reduction occurs with a pseudo-first order rate constant of 1.5 × 10⁸ s⁻¹. This is competitive with decay of the Ru-*OTA⁺* photoproduc by intramolecular thermal electron transfer, which has been found above to occur with a rate constant of ≥ 10⁸ s⁻¹ (Fig. 5a). However, the AQ-*Ru-OTA⁺* state of the triad decays only with a rate constant of 3.8 × 10⁵ s⁻¹ (Fig. 5b), and consequently bimolecular electron transfer with O₂ should be far more efficient in this case. The time evolution and quantum yield studies discussed below provide indirect support for this assessment. Moreover, benzoquinone reductions in CH₃CN typically become easier by ca. 1.1 V due to strong Lewis acid/Lewis base interaction between Sc³⁺ and benzoquinone radical anions.¹⁶ Consequently, the AQ-*Ru-OTA⁺* photoproduc is further stabilized in the presence of Sc³⁺ (Sc³⁺/AQ-*Ru-OTA⁺* state on the first line of Scheme 3b), and this increases the probability for collisional encounters with O₂ that lead to the formation of Sc³⁺/O₂⁻ adducts via bimolecular electron transfer. Thus, after the absorption of a first photon, the photoproducts are Ru-*OTA⁺* or AQ-Ru-OTA⁺* and one equivalent of Sc³⁺/O₂⁻ adduct (Scheme 3a and b, uppermost lines). The beneficial effect of Sc³⁺ originates mostly in the fact that it stabilizes O₂⁻ against recombination with the oxidation products, thereby permitting charge accumulation. The mechanistic question whether MCET takes place in a concerted or stepwise fashion is beyond the scope of this study.

Subsequent absorption of a second photon can occur either by the Ru(bpy)³⁺ photosensitizer or the OTA⁺ units of Ru-OTA⁺ or AQ-Ru-OTA⁺. At the irradiation wavelength of 450 nm, the relevant extinction coefficients are 1.3 × 10⁴ M⁻¹ cm⁻¹.
(Ru(bpy)_3^{2+}) and 10^4 M^{-1} cm^{-1} (OTA^+, Fig. 3) hence only approximately half of all photons are absorbed by the photosensitizer, the other half directly excites OTA^+. There is a good spectral overlap between Ru(bpy)_3^{2+} emission and OTA^+ absorption (Fig. 3) hence one of the key conditions for intramolecular energy transfer is fulfilled. On the other hand, this process is formally spin-forbidden because Ru(bpy)_3^{2+} is excited to a 3MLCT state whereas OTA^+ has doublet spin multiplicity in its electronic ground state, 33 and consequently intramolecular energy transfer from photoexcited Ru(bpy)_3^{2+} to OTA^+ could in principle be relatively inefficient. 34 However, our investigations show that CH_3CN solutions of Ru-OTA^+ and AQ-Ru-OTA^+ (prepared by chemical oxidation using Cu(ClO_4)_2) are essentially non-luminescent. We conclude that energy transfer (EnT in Scheme 3) from photoexcited Ru(bpy)_3^{2+} to OTA^+ is a rather efficient process, at least when compared to radiative 3MLCT relaxation. (As noted above, the concentrations of unreacted Cu(ii) under the conditions used for these experiments are marginal hence oxidative bimolecular 3MLCT quenching by Cu(ii) is unlikely). Thus, ultimately the absorption of a second 450 nm photon leads to excitation of OTA^+, either directly or indirectly via energy transfer from Ru(bpy)_3^{2+} (see “either/or” labels in Scheme 3a and b). It is not possible to probe the relevant OTA^+ excited state directly, and its lifetime is unlikely to be much longer than 1 ns. This severely limits the probability for collisional encounters with O_2 and contributes to the relatively low efficiency of the overall charge accumulation process (see below).

Nevertheless, photoexcitation of triarylamine radical cations has previously been reported to trigger oxidation to their dicationic forms,33 and therefore it seems plausible that formation of the second equivalent of Sc^3+/O_2^- adducts involves directly the excited OTA^+ species. In some cases, phototriggered oxidation of triarylamine cations has been observed to result in carbazole formation,33 but in our compounds this seems unlikely because the addition of triethylamine to the final solutions rapidly leads to the recovery of the Ru-OTA and AQ-Ru-OTA starting materials.

Irrespective of whether the Ru(bpy)_3^{2+} or the OTA^+ unit of Ru-OTA^+ and AQ-Ru-OTA^+ is excited, reverse electron transfer (from the ruthenium photosensitizer to the oxidized amine) is a viable reaction pathway, which can severely limit the overall quantum yield of the charge accumulation process.

We did also consider the possibility of (thermal) disproportionation of 2 equivalents of OTA^+ to 1 equivalent of OTA^{2+} and 1 equivalent of neutral OTA. This reaction is thermodynamically unfavorable based on the redox potentials from Table 1, and when solutions containing Ru-OTA^+ and AQ-Ru-OTA^+ are left standing in the dark for 60 minutes, no significant formation of OTA^{2+} can be observed in both cases (see ESI,† Fig. S1).
Temporal evolution and quantum yield of photoinduced charge accumulation

UV-Vis difference spectra such as those in Fig. 6a and e have been recorded after photo-irradiation over 10–12 well-defined time intervals for the Ru-OTA dyad and the AQ-Ru-OTA triad. The respective spectra are included in the ESI† (Fig. S2 and S3). Each of these spectra can be adequately fitted by a linear combination of the UV-Vis difference spectra obtained for Ru-OTA+/AQ-Ru-OTA+ (green traces in Fig. 3a and b) and for Ru-OTA2+/AQ-Ru-OTA2+ (red traces in Fig. 3a and b). Thus, the relative proportions of OTA+ and OTA2+ can be quantified at any point in time, and one obtains the data in Fig. 7 (see ESI† for further details). The irradiation experiments were performed with 3 ml of CH2CN solutions containing (1.0 ± 0.1) × 10−5 M Ru-OTA or AQ-Ru-OTA and 0.02 M Sc3+, using a flux of (6.74 ± 0.21) × 1015 photons per second at a wavelength of 450 nm.

The circles in Fig. 7a indicate the concentration of Ru-OTA+ as a function of irradiation time (t). At t = 0, there are already (5.6 ± 0.6) μM of Ru-OTA+ present, and this turned out to be unavoidable in the course of sample preparation. Photo-irradiation leads to a relatively rapid increase of the Ru-OTA+ concentration up to (9.1 ± 0.9) μM, but then it decreases at the expense of an increase of the Ru-OTA2+ concentration (squares in Fig. 7a). After an irradiation time of 240 minutes, there is practically no Ru-OTA+ left, and the sample contains almost exclusively Ru-OTA2+.

Between t = 15 min and t = 30 min the increase in Ru-OTA2+ concentration is approximately linear, and during this period (1.5 ± 0.2) μM of charge-accumulated product have been formed. In the 3 ml volume used for these experiments, this corresponds to (4.5 ± 0.6) × 10−9 mol of Ru-OTA2+. In the time period of 15 minutes, (6.07 ± 0.19) × 1018 photons have reached the sample, corresponding to (1.01 ± 0.03) × 10−5 mol of photons. Consequently, the quantum yield (ϕ) for the formation of Ru-OTA2+ is (4.5 ± 0.7) × 10−4.

Analysis of the UV-Vis difference spectra obtained for the AQ-Ru-OTA triad as a function of irradiation time yields the data shown in Fig. 7b (see ESI† for details). In this case essentially no unreacted starting material is left at the beginning of the irradiation experiment, and (8.0 ± 0.8) μM of AQ-Ru-OTA+ and (1.6 ± 0.2) μM of AQ-Ru-OTA2+ are already present at t = 0 (due to unavoidable exposure to light during sample preparation).

In this case, the increase of the AQ-Ru-OTA2+ concentration is approximately linear between t = 1 min and t = 3 min. (1.6 ± 0.2) μM of charge-accumulated product are formed during this period, corresponding to (4.8 ± 0.6) × 10−9 mol in the 3 ml solution.

Given the photon flux reported above, (1.34 ± 0.04) × 10−6 mol of photons have reached the sample in the 120 s irradiation period. This leads to a quantum yield (ϕ) of (3.6 ± 0.6) × 10−3 for the formation of AQ-Ru-OTA2+.

Thus we find that the quantum yield for charge accumulation is a factor of 8 higher for the triad compared to the dyad. We attribute this to the fact that the radical anionic form of the anthraquinone (AQ−) can be stabilized by Sc3+, making both the AQ−/Ru-OTA− and the AQ−/Ru-OTA2− intermediates more long-lived (in the forms of Sc3+/AQ−/Ru-OTA− and Sc3+/AQ−/Ru-OTA2−, respectively; Scheme 3b). Consequently, the probability for collisional encounters with O2 is increased, and this has the observed positive effect on the charge accumulation quantum yield.

In a previously investigated antimony porphyrin compound, light-driven conversion of Sb(IV) into Sb(III) occurred with a quantum yield of 4 × 10−3.25

3. Summary and conclusions

Our study demonstrates for the first time that the photodriven accumulation of positive charges on a molecular unit is possible by exploiting metal ion-coupled electron transfer (MCET). Rapid (>1010 s−1) photoinduced charge-separation within the dyad and the triad produces the Ru−/OTA− and AQ−/Ru-OTA− states with lifetimes of ≤10 ns and 2.4 μs, respectively, and subsequent bimolecular electron transfer with O2 is facilitated by strong Lewis acid/Lewis base interaction between Sc3+ and superoxide anions.16,36 The longer lifetime of the charge-separated state in the triad and its stabilization by interaction of the anthraquinone radical anion with Sc3+ contribute to the 8 times higher quantum yield for charge accumulation in the triad with respect to the dyad. Absorption of a second 450 nm photon by the same compound leads to the excitation of OTA−, either directly or via intramolecular energy transfer from the Ru(bpy)32+ chromophore. The resulting excited species cannot be probed directly but is expected to be short-lived (~1 ns), and this significantly limits the efficiency of the overall charge accumulation process. Consequently, light-induced oxidation of OTA to its monocatic form is facile, but formation of the dicaticonic OTA2− is comparatively inefficient.

We note that Sc3+ and superoxide anions are in a binding equilibrium. A recent study has demonstrated that Sc3+ can be liberated from this equilibrium through the addition of protons, and this can lead to the formation of H2O2 in the presence of oxygen.37 Hydrogen peroxide may be regarded as a solar fuel.

Our study has provided direct insight into how a combination of intramolecular photoinduced electron transfer reactions and
MCET processes can be exploited to achieve the accumulation of two positive charges on a single molecular unit. The findings reported here are relevant in the greater context of artificial photosynthesis.

Acknowledgements

This work was supported by the Swiss National Science Foundation through grant no. 200021_146231/1. Support from COST action CM1202 is acknowledged.

Notes and references


