Exceptionally Long-Lived Photodriven Multi-Electron Storage without Sacrificial Reagents

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Abstract: Photo-excitation of a molecular pentad in presence of Sc^{3+} in de-aerated CH_3CN leads to a quinone dianion that is stable on the millisecond timescale. Light-driven electron accumulation on the quinone unit is sensitized by two $Ru(bpy)_3^{2+}$ complexes in an intramolecular process, which relies on covalently attached triarylamine donors rather than on sacrificial reagents. Lewis acid – Lewis base interactions between Sc^{3+} and quinone dianion are responsible for the exceptionally long lifetime of this photoproduct. Our study of photo-induced multi-electron transfer is relevant in the greater context of solar energy conversion.

Introduction

Because of the light-driven accumulation of redox equivalents, the Mn_4Ca cluster of photosystem II is able to oxidize water.[1] Similarly, the accumulation of reductive equivalents is important for the activation of small inert molecules such as CO_2 or N_2. Much effort has gone into the development of artificial water oxidation and CO_2 reduction catalysts in recent years, and impressive progress has been made.[2] However, in the vast majority of cases, sacrificial redox reagents were employed, and this is partly owed to the fact that the elementary principles of photoinduced multi-electron transfer are not nearly as well understood as those of single electron transfer. Sustainable solar energy conversion will not be possible with sacrificial reagents,[3] and therefore it is desirable to explore the basics of photoinduced charge accumulation.

The investigation of covalently linked donor-bridge-acceptor molecules has been very useful for understanding the basic principles of single electron transfer,[4] for example through driving-force variations,[5] distance dependence studies,[6] or bridge alterations.[7] Later, combined electron and proton transfer reactions were explored using the same donor-bridge-acceptor approach,[8] giving insight into proton-coupled electron transfer (PCET). For exploring photoinduced charge accumulation, donor-bridge-acceptor systems are promising as well, but at present, only a handful of suitable compounds is known.[9] Two early studies reported on intramolecular electron accumulation in molecular triads, but the lifetimes of the photoproducts were restricted to 5 ns.[10] In a related early study,

a very short excitation wavelength (266 nm) had to be used to generate a short-lived accumulated electron pair.[11] Later, a whole series of compounds in which redox equivalents can be accumulated with visible light was reported, but these systems all relied on sacrificial reagents.[12] Only relatively recently, accumulation of oxidative equivalents without the use of sacrificial reagents has been achieved, albeit in a system with TiO_2 nanoparticles.[13] We recently communicated molecular pentad **I** (Scheme 1),[14] which is the first purely molecular system in which long-lived (> 5 ns) electron accumulation is observed without sacrificial reagents. In pentad **I**, electron accumulation is an entirely intramolecular process in which the two covalently attached triarylamine (TAA) units act as (reversible) one-electron donors, whereas the central anthraquinone (AQ) acceptor stores two electrons for 870 ns in de-aerated CH_3CN at 20 °C.
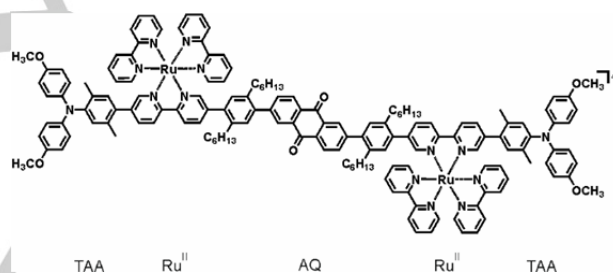
Scheme 1. Molecular structure of pentad **I** and labeling of its individual components.

It seems worthwhile to stress how important the conceptual difference between the covalently attached triarylamine donors in pentad **I** and the use of sacrificial, non-covalently attached electron donors in prior studies is. Sacrificial donors decompose after electron donation, making undesired re-oxidation of the substrate an essentially irreversible process. By contrast, as noted above, triarylamines are reversible donors that do not decompose, and hence undesired reverse electron transfers can readily occur after initial charge-separation. In fact the oxidized triarylamine is a strong electron acceptor that can easily impede electron accumulation at the central acceptor site due to large driving-force and due to covalent attachment.[9a, 15] With sacrificial quenchers this is far less problematic because they decompose to poor electron acceptors and moreover they diffuse away after initial electron transfer, leading to spatial separation between electrons and holes. Thus it is clear that obtaining electron accumulation in intramolecular fashion by using reversible electron donors is far more challenging than using non-covalently attached sacrificial donors.

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While our initial studies were conducted in neat CH_3CN leading to electron accumulation at anthraquinone, subsequent further investigations provided unprecedented mechanistic insight into multi-electron, multi-proton chemistry by studying the photophysics and the photochemistry of pentad **I** in presence of *p*-toluenesulfonic acid.[16] However, the lifetime of the charge-accumulated state was only extended from 870 ns to 4.7 μs in presence of Bronsted acid.[16]

In this work, we sought to stabilize the two electrons on AQ even further by exploiting metal ion-coupled electron transfer (MCET).[17] Prior studies have shown that Lewis acids such as Sc^{3+} or Y^{3+} can stabilize quinone radical anions,[18] and we hypothesized that Lewis acid - Lewis base interactions could also be useful for extending the lifetime of our photogenerated anthraquinone dianion species. This is indeed the case, and herein we demonstrate that MCET gives access to a charge-accumulated state with a lifetime in the millisecond regime, more than 3 orders of magnitude longer than in neat CH_3CN. Thus, our system is able to store redox equivalents on the same timescale as the oxygen-evolving complex of photosystem II.[19]

Results and Discussion

In order to detect photoinduced charge accumulation unambiguously, the various redox states of a system must be spectroscopically clearly distinguishable from one another. In prior work we demonstrated that this is the case for anthraquinone (AQ) in neat CH_3CN in the infrared spectral region, and we used transient IR studies to distinguish AQ^{2-} from AQ^{-} in pentad **I**.[14] In the present study, we explored charge accumulation in presence of the strong Lewis acid Sc^{3+} with UV-Vis transient absorption spectroscopy. As demonstrated in the following, the spectroscopic signatures of the various redox states of AQ in presence of Sc^{3+} resemble those of AQ in presence of Bronsted acids, and this forms the basis for unambiguous detection of doubly reduced AQ with Sc^{3+} bound to it.
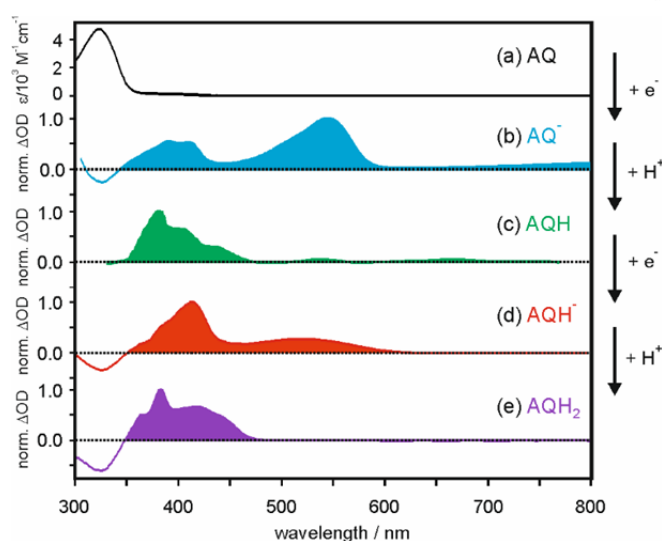

Figure 1. (a) UV-Vis absorption spectrum of 9,10-anthraquinone (AQ) in CH_3CN. The spectra in (b) – (e) are differential absorption spectra, i. e., they show the spectral changes associated with the conversion of a charge-neutral anthraquinone species into various reduced and protonated forms thereof. (b) Difference spectrum of 9,10-anthraquinone radical anion (AQ^{-}) in DMF.[20] (c) Difference spectrum of the semiquinone form (AQH) of 2-hydroxy-9,10-anthraquinone in water / isopropanol / acetone (30:5:1, v:v:v) mixture.[21] (d) Difference spectrum of the hydroquinone anion form (AQH^{-}) of 9,10-anthraquinone in DMF.[20] (e) Difference spectrum of the hydroquinone form (AQH_2) of 9,10-anthraquinone in DMF.[20]

AQ does not absorb significantly at wavelengths longer than 370 nm (Figure 1a), but upon reduction to AQ^{-} bands at 390, 410, and 545 nm emerge (Figure 1b).[20] Protonation of AQ^{-} to afford the semiquinone AQH leads to disappearance of the 545 nm band while absorption in the range from 370 to 420 nm persists (Figure 1c).[21-22] Further reduction to the hydroquinone anion AQH^{-} (doubly reduced and singly protonated AQ) causes absorptions centered at 412 and 520 nm (Figure 1d).[20] Finally, protonation of AQH^{-} to yield the neutral hydroquinone form AQH_2 leads to absorptions exclusively below 480 nm with a distinct narrow feature at ~380 nm (Figure 1e).[20]

For UV-Vis transient absorption spectroscopy, 20 μM solutions of pentad **I** in de-aerated CH_3CN in presence of 50 mM $Sc(OTf)_3$ were excited at 532 nm with pulses of ~10 ns duration. Since the focus of this study was on comparatively slow processes, experiments with shorter excitation pulses were not undertaken. Kinetic decays were recorded in 5 nm intervals between 320 and 800 nm, and subsequently the data were fitted globally to result in species-associated difference spectra (SADS).[23] The initial spectrum at t = 0 exhibits bands with maxima at 375, 585, and 770 nm (black trace in Figure 2a). The best global fits to this data set consisting of 97 decays in 20 μs time windows were obtained using a bi-exponential function with a residual, which reflects signals that persist for over 20 μs. The first SADS (blue trace in Figure 2a) has an associated lifetime of 170 ns and exhibits absorptions at 365 and 585 nm, as well as a negative signal at 410 nm. The bands at 365 and 585 nm are due to AQ^{-} (Figure 1b); in fact we and others have seen these two specific absorptions in many donor-bridge-acceptor compounds with AQ before.[6f, 24] Thus, the positive signals at 365 and 585 nm indicate that AQ^{-} disappears, whereas the negative signal at 410 nm indicates the formation of a new species with stronger extinction at this wavelength. It is plausible that this new species is the AQ^{-} / Sc^{3+} adduct, which should spectroscopically resemble AQH (Figure 1c).
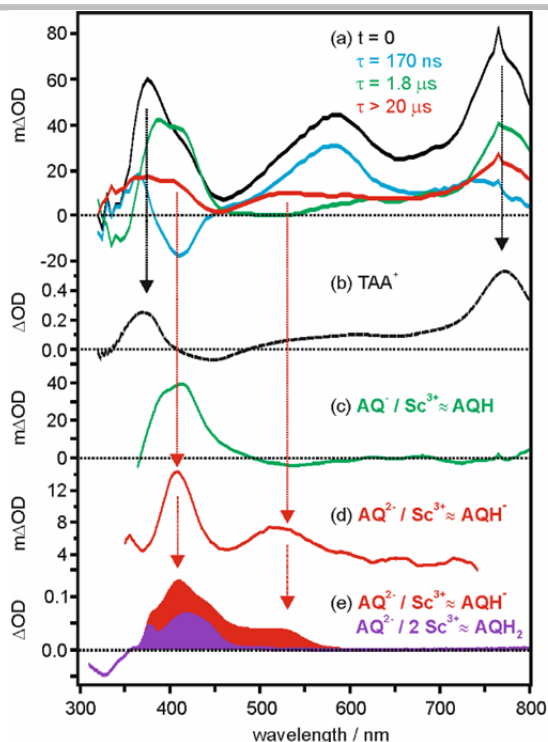
Figure 2. (a) Transient absorption spectra obtained from a de-aerated CH$_3$CN solution of 20 μM pentad **I** in presence of 50 mM Sc(OTf)$_3$ at 20 °C. Excitation was at 532 nm with laser pulses of ~10 ns duration. Black trace: Initial spectrum at t = 0. Blue, green, red traces: SADS with decay times as indicated in the inset. (b) Differential absorption spectrum showing the spectral changes associated with oxidation of TAA in pentad **I**, obtained by spectro-electrochemistry in CH$_3$CN (applied potential: 0.8 V vs. SCE). (c) Contribution of reduced AQ species to the overall 1.8 μs-SADS, obtained by subtracting the appropriately scaled spectrum from (b) from the green trace in (a); the resulting spectrum is similar to that of AQH in Figure 1c. (d) Contribution of reduced AQ species to the overall >20 μs-SADS, obtained by subtracting the appropriately scaled spectrum from (b) from the red trace in (a); the resulting spectrum is similar to that of AQH$^-$ in Figure 1d. (e) Differential absorption spectra obtained in the course of applying a potential of -1.6 V vs. SCE to a solution containing 0.5 mM AQ, 0.5 mM Sc(OTf)$_3$ and 0.1 M TBAPF$_6$ in CH$_3$CN; the spectrum obtained prior to applying the potential served as a baseline. The initially recorded purple signature resembles the spectrum of AQH$_2$ in Figure 1e, while the red signature measured later resembles the spectrum of AQH$^-$ in Figure 1d.

The second SADS (green trace in Figure 2a) has an associated lifetime of 1.8 μs, and it exhibits absorption maxima at 390, 410, and 770 nm. The band at 770 nm is caused by the triarylamine radical cation (TAA$^+$), [6f, 24e, 25] and the difference spectrum of TAA$^+$ in pentad **I** is shown in Figure 2b (dashed black trace). When scaling the TAA$^+$ difference spectrum such that it matches the ΔOD in the 1.8 μs-SADS at 770 nm (green trace in Figure 2a) and then subtracting it, the green trace in Figure 2c is obtained. This green spectrum represents the contribution of reduced anthraquinone species to the overall 1.8 μs-SADS. The respective spectrum resembles that of the semiquinone AQH (Figure 1c), suggesting that the observed photoproduct is indeed the AQ$^-$ / Sc^{3+} adduct anticipated above. The negative signal at 410 nm in the 170 ns-SADS (blue trace in Figure 2a) is compatible with the formation of this adduct.

The global fit to the transient absorption data yields a residual signal with a lifetime longer than 20 μs, exhibiting the spectral signature represented by the red trace in Figure 2a. When subtracting the contribution of TAA$^+$ from this spectrum, the red

trace in Figure 2d is obtained. This spectrum exhibits absorption maxima at 410 and 515 nm, and its overall appearance is very similar to the spectrum of AQH$^-$ (Figure 1d). Spectro-electrochemical studies performed with AQ in presence of Sc(OTf)$_3$ result in the spectra shown in Figure 2e. The red signature strongly resembles the spectrum in Figure 2d and the signature of AQH$^-$ (Figure 1d), and consequently is attributed to the AQ^{2-} / Sc^{3+} adduct. For these spectro-electrochemical experiments, a potential of -1.6 V vs. SCE was applied to a solution containing 5 mM 9,10-anthraquinone, 5 mM Sc(OTf)$_3$, and 0.1 M TBAPF$_6$ in CH$_3$CN. At that potential, AQ is reduced to AQ^{2-},[14] and initially one obtains the purple signature in Figure 2e. With its absorption band around 420 nm and a distinct narrow feature at ~380 nm this purple signature is very similar to the spectrum of AQH$_2$ (purple trace in Figure 1e), and consequently is attributed to the AQ^{2-} / 2 Sc^{3+} adduct, i. e., doubly reduced anthraquinone with two Sc^{3+} cations bound to it. In the course of reducing increasing amounts of AQ to AQ^{2-}, the purple spectrum converts to the red spectrum in Figure 2e, which we attributed above to the AQ^{2-} / Sc^{3+} (1:1) adduct. This shift in equilibrium from 1:2 to 1:1 adducts evidently occurs because at some point there is not enough Lewis acid present in solution to allow binding of 2 Sc^{3+} cations per electrochemically generated AQ^{2-} species. When using higher concentrations of Sc^{3+} (20 equivalents), only the 1:2 adduct is observed.

The AQ^{2-} / Sc^{3+} (1:1) adduct exhibits a diagnostic absorption at 515 nm (red traces in Figure 2a/d) that is absent in any of the other SADS (blue and green traces in Figure 2a), indicating that this signal is present from the very beginning. In other words, the AQ^{2-} / Sc^{3+} species is formed within the ~10 ns duration of the laser excitation pulses, and then exhibits a very slow (> 20 μs) decay. At a pentad concentration of 20 μM, such rapid charge accumulation is only viable in intramolecular fashion.

The extinction coefficient at 515 nm could not be determined reliably, but the relative amount of AQ^{2-} / Sc^{3+} adduct formed can be estimated on the basis of the ΔOD values at 770 nm. At that wavelength, TAA$^+$ is the only absorbing species (see above). When taking into account that the formation of AQ^{2-} / Sc^{3+} implies the presence of two TAA$^+$ units per pentad molecule, comparison of the optical densities at 770 nm in the red and the black traces in Figure 2a leads to the conclusion that ~19% of the observable photoproducts are charge accumulated species, whereas the remaining ~81% are due to the AQ$^-$ and AQ$^-$ / Sc^{3+} species discussed above. We note that this product ratio is expected to be excitation power-dependent,[14] and the values reported here were obtained using pulse energies of 18 mJ. In our prior communication,[14] we demonstrated that the concentration of charge accumulated species formed depends in quadratic fashion on the excitation power, at least at very low excitation powers. Such behavior is expected for a two-photon process.
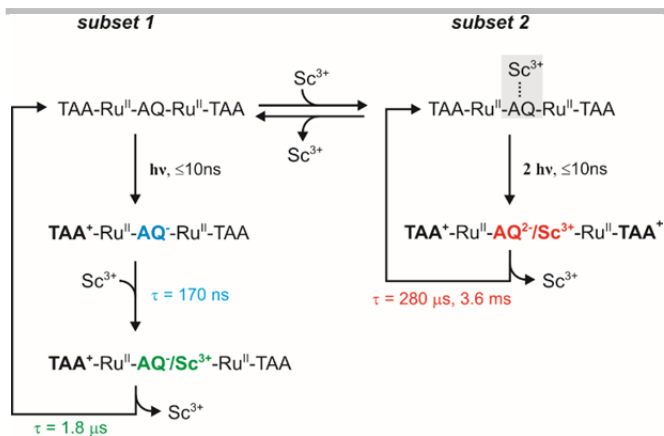
Scheme 2. Reaction sequences leading to the observable AQ$^-$, AQ$^-$ / Sc^{3+}, and AQ^{2-} / Sc^{3+} photoproducts after excitation of pentad **I** in presence of Sc^{3+}.
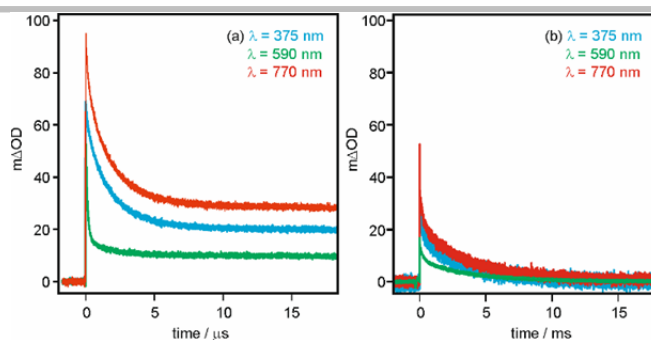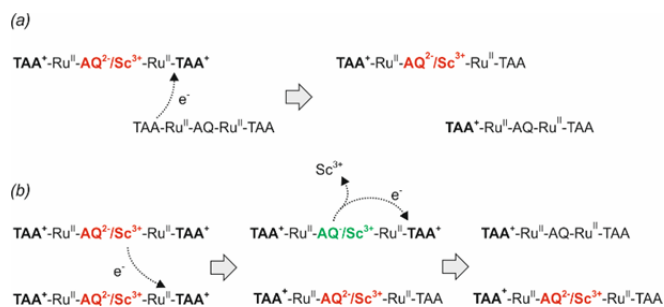

Figure 3. Decays of the transient absorption signals at different wavelengths on two different timescales. Measured after excitation of 20 μM pentad **I** in de-aerated CH$_3$CN at 532 nm. 50 mM Sc(OTf)$_3$ was present.

It seems plausible that the different photoproducts are formed in the fashion illustrated in Scheme 2. A first subset of pentad molecules has no associated Sc^{3+} cations when it is photo-excited and undergoes rapid (< 50 ps) charge separation to produce a TAA$^+$ / AQ$^-$ radical ion pair by pathways similar to those explored previously in simpler compounds.[24c, 26] Sc^{3+} cations then bind to this photoproduct with a time constant of 170 ns (blue trace in Figure 2a), and the resulting AQ$^-$ / Sc^{3+} adduct subsequently decays with a time constant of 1.8 μs (green trace in Figure 2a). A second subset of pentad molecules (Scheme 2, right) has weakly associated Sc^{3+} cations when it is excited, and then undergoes rapid (< 10 ns) intramolecular charge accumulation to form AQ^{2-} / Sc^{3+} and two TAA$^+$ units (red trace in Figure 2a). This photoproduct exhibits a lifetime > 20 μs, due to stabilization of quinone dianion by the strong Lewis acid Sc^{3+} (see below). Absorption of two photons by pentad molecules without associated Sc^{3+} cations does not lead to an observable long-lived charge accumulated state.

Two reference experiments were performed to corroborate this interpretation. First, we replaced Sc^{3+} by an equal concentration of the much weaker Lewis acid Ca^{2+}. No evidence for an AQ^{2-} / Ca^{2+} adduct is found (Supporting Information, Figure S1), indicating that the charge-accumulated species either does not form at all, or does not live long enough to be detectable on top of the more intense signal from the AQ$^-$···Ca^{2+} product. The transient absorption spectrum of the observed reduced species closely resembles the signature of hydrogen-bonded AQ$^-$ (Figure S2). Very likely, a long-lived charge accumulated state is inaccessible due to lack of significant pre-association between Ca^{2+} and AQ prior to photo-excitation. In the second reference experiment, the Sc^{3+} concentration was lowered from 50 to 5 mM (Figure S3). All photoproducts identified above remained detectable, but the decay of AQ$^-$ at the expense of the formation of AQ$^-$ / Sc^{3+} was now slower (470 instead of 170 ns), and the relative amount of AQ^{2-} / Sc^{3+} was now only 4% instead of 19%. These observations are all compatible with the view outlined in Scheme 2.

Experiments to quantify the pre-association between AQ and Sc^{3+} or Ca^{2+} by various experimental techniques (NMR, UV-Vis, IR) were unsuccessful. Prior studies demonstrated that this is possible for *o*-benzoquinones which can chelate small Lewis acids, but in the case of *p*-benzoquinones this pre-association generally seems to remain undetectable.[17-18] Upon reduction to AQ$^-$ and AQ^{2-}, the formation of Lewis acid – Lewis base adducts then becomes directly observable, for example by cyclic voltammetry (Figure S4, see below).

Under suitable conditions, two Sc^{3+} cations readily bind to the electrochemically generated dianionic form of 9,10-anthraquinone (purple trace in Figure 2e), but in pentad **I** only one Sc^{3+} cation binds to the photochemically generated AQ^{2-} species. In pentad **I**, the AQ unit is flanked by two phenylene bridging units bearing a total of 4 *n*-hexyl substituents, and hence steric effects could make cation binding more unfavorable in this case, leading to 1:1 rather than 1:2 association between AQ^{2-} and Sc^{3+}. Moreover, there is the possibility of electrostatic repulsion between Sc^{3+} and the adjacent Ru(bpy)$_3$$^{2+}$ units. The same effects can also explain the relatively slow adduct formation between AQ$^-$ and Sc^{3+} (170 ns, blue trace in Figure 2a).

The transient absorption experiment in Figure 2 was restricted to a time window of 20 μs. On longer timescales no further spectral changes occur (Figure S6), and the remaining transient absorption signal (red trace in Figure 2a) decays only very slowly. Figure 3 contains single-wavelength kinetics, monitoring the decay of the signals at 375, 590, and 770 nm on micro- and millisecond timescales. These transients contain the initial 170 ns and 1.8 μs decay components identified above (particularly evident in the green trace in Figure 3a), and bi-exponential fits to the remaining slower decays yield lifetimes of 280 μs and 3.6 ms. On such slow timescales bimolecular encounters can obviously occur,[24e] and therefore it is unlikely that these decay times reflect intramolecular events. One of the most plausible bimolecular reactions which can account for the longevity of the transient absorption signals is electron self-exchange between TAA$^+$ and TAA, which leads to a spatial separation of oxidation and reduction products on separate pentad molecules (Scheme 3a). By means of UV-Vis transient absorption spectroscopy the resulting products are indistinguishable from the initial photoproduct containing AQ^{2-} / Sc^{3+} and 2 TAA$^+$ units on a given pentad. Several other bimolecular reaction pathways are conceivable (e. g., that in Scheme 3b), but the key point is that the charge accumulated state comprised of the AQ^{2-} / Sc^{3+}

adduct (initially formed in an intramolecular reaction) persists on a millisecond timescale.

(a)

TAA⁺-Ru^{II}-**AQ^{2-}/Sc^{3+}**-Ru^{II}-**TAA⁺** → **TAA⁺**-Ru^{II}-**AQ^{2-}/Sc^{3+}**-Ru^{II}-TAA

TAA-Ru^{II}-AQ-Ru^{II}-TAA

TAA⁺-Ru^{II}-AQ-Ru^{II}-TAA

(b)

TAA⁺-Ru^{II}-**AQ^{2-}/Sc^{3+}**-Ru^{II}-**TAA⁺** → **TAA⁺**-Ru^{II}-**AQ^{-}/Sc^{3+}**-Ru^{II}-**TAA⁺** → **TAA⁺**-Ru^{II}-AQ-Ru^{II}-TAA

TAA⁺-Ru^{II}-**AQ^{2-}/Sc^{3+}**-Ru^{II}-**TAA⁺** **TAA⁺**-Ru^{II}-**AQ^{2-}/Sc^{3+}**-Ru^{II}-TAA **TAA⁺**-Ru^{II}-**AQ^{2-}/Sc^{3+}**-Ru^{II}-TAA

Scheme 3. Two possible bimolecular reaction sequences that can follow intramolecular photo-induced charge accumulation.

In order for bimolecular reactions to occur at appreciable rates between reactants present at μM concentrations, intramolecular charge separation between AQ^{2-} / Sc^{3+} and the 2 TAA⁺ units is required to persist for at least a few microseconds.[6f, 24e] In our prior transient IR study, the AQ^{2-} species exhibited a lifetime of 870 ns in neat de-aerated CH$_3$CN at 20 °C.[14] In the present study, the formation of an adduct with Sc^{3+} causes a substantial thermodynamic stabilization of the AQ^{2-} species (see below), and consequently the deceleration of intramolecular charge recombination to (at least) a few microseconds is not surprising. Cyclic voltammetry permits estimation of the thermodynamic stabilization of AQ^{-} and AQ^{2-} in presence of Sc^{3+}. In neat de-aerated CH$_3$CN, the AQ^{-}/AQ and AQ^{2-}/AQ^{-} redox couples appear at -0.91 and -1.34 V vs. SCE, respectively (black trace in Figure 4). In presence of 50 mM Ca(ClO$_4$)$_2$ (blue trace) or 50 mM Sc(OTf)$_3$ (red trace) the two redox couples are no longer resolvable from one another, similar to what was previously reported for other quinones in presence of Lewis acids,[17-18] or what is seen for *p*-benzoquinones in presence of Brønsted acids.[27] The reason for this is that both types of acids have a stronger influence on the AQ^{2-}/AQ^{-} potential than on the AQ^{-}/AQ couple, because binding to AQ^{2-} is stronger than to AQ^{-}, at least in isolated 9,10-anthraquinone. The stronger potential shift observed for Sc^{3+} with respect to Ca^{2+} reflects the difference in Lewis acidity between these two cations.[17-18] At the high cation concentrations used for the data in Figure 4 (50 mM), the observable redox waves are quasi-reversible (see Figure S3 for concentration-dependent studies), and a potential of 0.38 V vs. SCE is extracted for the two-electron reduction of AQ to AQ^{2-} in presence of 50 mM Sc^{3+}. The electrochemical potential for oxidation of TAA to TAA⁺ in pentad **I** is 0.69 V vs. SCE (Figure S5),[14] and consequently one can estimate that the intramolecular charge-accumulated state comprised of the AQ^{2-} / Sc^{3+} adduct and 2 TAA⁺ units is energetically ca. 2·*e*·(0.69 V – 0.38 V) = 0.62 eV above the ground state. For comparison, in absence of Sc^{3+} the respective charge-accumulated state stores 3.56 eV.[14] Given the very strong stabilization of the charge-accumulated state in presence of Sc^{3+}, it is not surprising that intramolecular charge-recombination is slowed down to an extent that bimolecular reactions leading to the very slow decays in Figure 3 become possible. No further redox waves are detectable in the -1.5 to 0.8 V vs. SCE potential range.
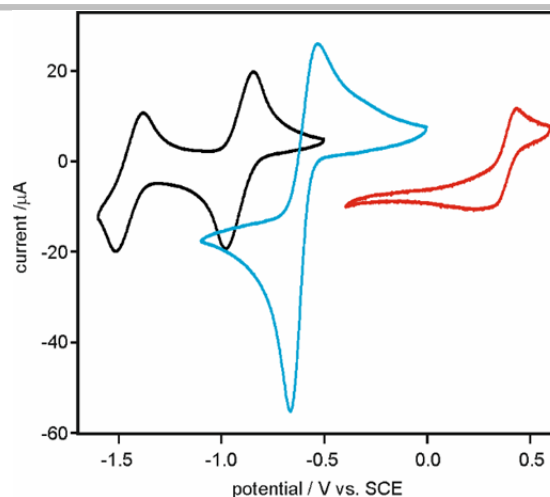

Figure 4. Cyclic voltammetry of 9,10-anthraquinone (AQ) in dry de-aerated CH$_3$CN containing 0.1 M TBAPF$_6$. Black trace: neat solvent. Blue trace: in presence of 50 mM Ca(ClO$_4$)$_2$. Red trace: in presence of 50 mM Sc(OTf)$_3$.

Conclusions

Exceptionally long-lived accumulation of electrons without sacrificial donors has been achieved through exploitation of Lewis acid – Lewis base interactions between Sc^{3+} and anthraquinone dianion, using visible light as the only energy input. Electron accumulation in pentad **I** is a reversible intramolecular process which relies on covalently attached donors, but the quinone dianion / Sc^{3+} adduct is so long-lived that ensuing bimolecular reactions lead to a spatial separation of oxidative and reductive equivalents on separate molecules even at concentrations as low as 20 μM. The net result is a charge-accumulated species with a lifetime in the millisecond regime, far exceeding the lifetime of 4.7 μs detected in presence of Brønsted acid.[16] The lifetime determined here in presence of the Lewis acid Sc^{3+} is in fact comparable to what is observed for some of the intermediates of the Kok cycle.[19] This finding is unprecedented for artificial molecular systems that do not rely on sacrificial reagents.

Experimental Section

The synthesis of pentad **I** has been reported previously.[14] UV-vis absorption, cyclic voltammetry, spectro-electrochemistry, and nanosecond transient absorption spectroscopy was performed using equipment described previously.[6f, 24e] For recording the transient absorption data that formed the basis for the determination of species-associated difference spectra (SADS), the so-called mapping option from Edinburgh Instruments was employed.

Acknowledgements

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Entry for the Table of Contents

FULL PAPER

Photoinduced charge accumulation is very difficult to achieve without sacrificial reagents. Metal ion-coupled electron transfer (MCET) is found to lead to an unusually long-lived charge-accumulated state in a molecular pentad.
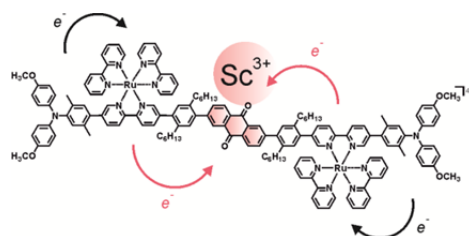
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Page No. – Page No.

Exceptionally Long-Lived
Photodriven Multi-Electron
Storage without Sacrificial
Reagents