Pump-Pump-Probe Spectroscopy of a Molecular Triad Monitoring Detrimental Processes for Photoinduced Charge Accumulation

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Controlling light-induced accumulation of electrons or holes is desirable in view of multi-electron redox chemistry, for example for the formation of solar fuels or for photoredox catalysis in general. Excitation with multiple photons is usually required for electron or hole accumulation, and consequently pump-pump-probe spectroscopy becomes a valuable spectroscopic tool. In this work, we excited a triarylamine-Ru(bpy)$_3^{2+}$-anthraquinone triad (bpy = 2,2'-bipyridine) with two temporally delayed laser pulses of different color and monitored the resulting photoproducts. Absorption of the first photon by the Ru(bpy)$_3^{2+}$ photosensitizer generated a triarylamine radical cation and an anthraquinone radical anion by intramolecular electron transfer. Subsequent selective excitation of either one of these two radical ion species then induced rapid reverse electron transfer to yield the triad in its initial (ground) state. This shows in direct manner that after absorption of a first photon and formation of the primary photoproducts, the absorption of a second photon can lead to unproductive electron transfer events that counteract further charge accumulation. In principle, this problem is avoidable by careful excitation wavelength selection in combination with good molecular design.

Keywords: electron transfer • photochemistry • donor-acceptor systems • time-resolved spectroscopy • energy conversion

Introduction

In the vast majority of molecular electron transfer systems investigated to date, photoexcitation only leads to a simple electron-hole pair. For artificial photosynthesis, multi-electron redox chemistry and the accumulation of oxidative and reductive equivalents are highly relevant.[1] Light-driven charge accumulation in molecular compounds is readily possible with sacrificial electron donors or acceptors,[2] but ultimately the use of such energy-rich reagents is undesirable.[3] Consequently, it seems important to explore the fundamentals of light-driven charge accumulation. Molecular compounds with covalently linked donors, photosensitizers, and acceptors are well suited for this purpose, but in absence of sacrificial reagents, light-driven charge accumulation becomes very challenging.[4-6] To the best of our knowledge, there are currently only a handful of molecular systems in which charges were accumulated with light as an energy input without relying on sacrificial reagents. Two porphyrin-based triads were explored early and they both exhibited short-lived doubly reduced photoproducts ($\tau \leq 5$ ns).[7] In a third study, the twofold reduction of a methylviologen unit relied on short-wavelength ($\lambda = 266$ nm) photo-irradiation.[8] A more recent system exhibited hole accumulation after excitation with visible light, but relied on TiO$_2$ nanoparticles as electron acceptors.[9] In molecular pentad **I** (Figure 1a) long-lived electron accumulation ($\tau = 870$ ns) was achievable without sacrificial reagents with visible light as the sole energy input.[10] Remarkably, that charge-accumulated state stored an energy of ~3.5 eV, much more than commonly observed.[11]
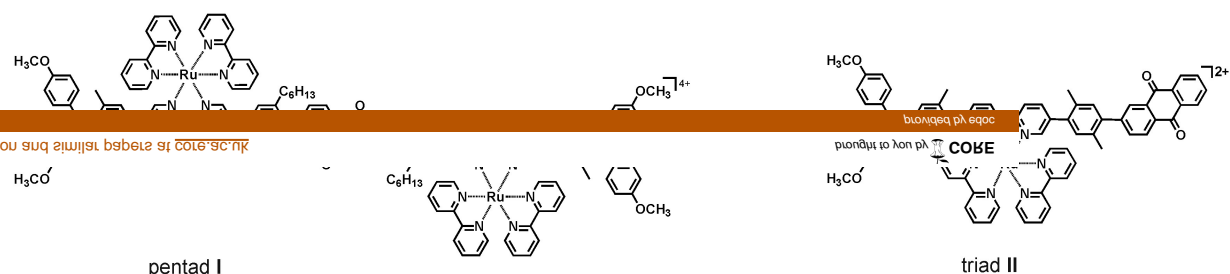
Figure 1. Molecular structures of pentad **I** (which is able to undergo photoinduced charge accumulation)[10] and molecular triad **II** which was investigated in this work

Prior to reporting pentad **I**, we attempted several times to achieve such light-driven charge accumulation in other molecular compounds, but failed to observe it unambiguously without sacrificial reagents.[12, 13] This is because many undesired reaction channels are open after absorption of a second photon by the same molecule,[4, 5] but we never probed any of these channels directly. In this work, we demonstrate the importance of one of these undesired processes by triggering it intentionally. Specifically, we use two temporally delayed laser pulses of different color for photoexcitation of molecular triad **II** (Figure 1b). This compound is unable to exhibit charge accumulation,[10] but it is a simpler

system than pentad **I**, and it is well suited to study the process of interest in this study. After absorption of a first photon by the $Ru(bpy)_3^{2+}$ photosensitizer, an electron-hole pair is generated rapidly in the form of a triarylamine radical cation (TAA^+) and an anthraquinone radical anion (AQ^-). The wavelength of the second photon is chosen such that either TAA^+ or AQ^- is excited selectively, and this induces rapid reverse electron transfer to result in the triad in its initial (ground) state. Thus, our pump-pump-probe experiment provides direct evidence for a process that can counteract light-induced charge accumulation. An earlier study investigated similar processes in the context of optical switching.[14]

Results and Discussion

Photoexcitation of triad **II** in CH_3CN at 532 nm occurs selectively into the low-energy tail of the ^1MLCT absorption band of the $Ru(bpy)_3^{2+}$ photosensitizer (Figure 2a). Previously we found that following intersystem crossing, the resulting ^3MLCT excited state is quenched reductively by TAA with a time constant of 9 ps, and subsequently electron transfer from the reduced sensitizer to AQ occurs with a time constant of 50 ps.[15] The resulting charge-separated state comprised of TAA^+ and AQ^- exhibits the transient absorption spectrum shown in Figure 2b.
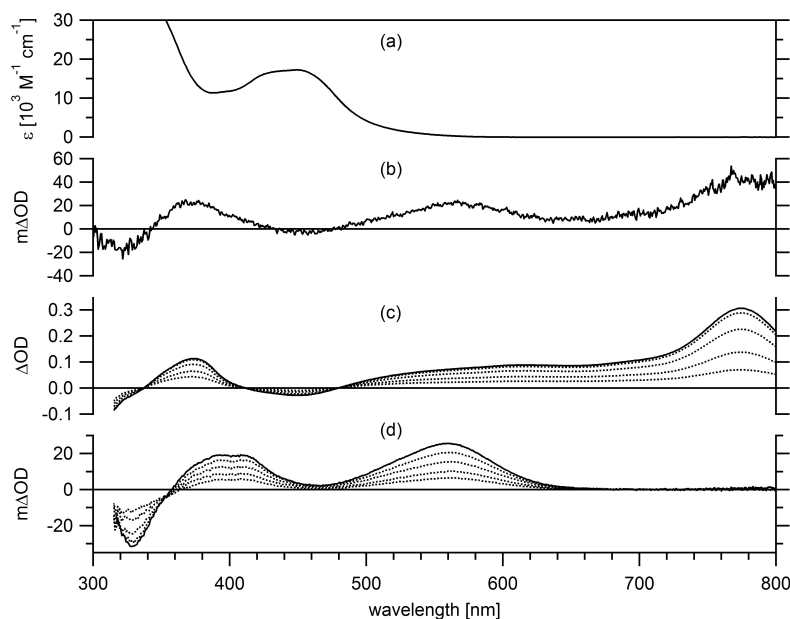

Figure 2. (a) Absorption spectrum of triad **II** in CH_3CN. (b) Transient absorption spectrum measured after excitation of $2 \cdot 10^{-5}$ M triad **II** in de-aerated CH_3CN at 532 nm (the signal was integrated over a time interval of 200 ns immediately after excitation with laser pulses of ~10 ns duration). (c) UV-Vis spectral changes observed when applying a potential of +0.9 V vs.SCE to a 0.1 mM solution of triad **II** in CH_3CN with 0.1 M $TBAPF_6$, monitoring the formation of TAA^+. (d) UV-Vis spectral changes observed when applying a potential of -1.0 V vs. SCE to the same solution, monitoring the formation of AQ^-.

Spectro-electrochemical data clearly confirm the formation of TAA^+ (bands at 370 and 775 nm, Figure 2c) and AQ^- (bands at 400 and 560 nm, Figure 2d). This charge-separated state stores ca. 1.6 eV, and we previously estimated that nearly 100% of the triads that are excited to the ^3MLCT state end up in this singly charge-separated state.[15] In de-aerated CH_3CN at room temperature, the TAA^+ and AQ^- spectral signatures both decay with a time constant of 1.6 μs (black traces in Figure 3), due to intramolecular thermal charge recombination.[15-18]

The black trace in Figure 3a is an exemplary transient absorption decay detected at 770 nm (TAA^+ band) following excitation at 532 nm with laser pulses of ~10 ns duration. The blue trace in Figure 3a results from a pump-pump-probe experiment in which a first series of laser pulses excited the triad at 532 nm, followed by a second series of laser pulses which excited the same sample at 450 nm with a time delay of 400 ns. At 450 nm, the photosensitizer in its ground state absorbs strongly (Figure 2a), while the TAA^+ and AQ^- radical species exhibit very little change in absorption with respect to the ground state (Figure 2b). The pulse energies used for the two lasers were 18 mJ at 532 nm and 12 mJ at 450 nm, yet the second series of pulses produces substantially increased transient absorption at 770 nm (blue trace in Figure 3a). The transient absorption spectrum recorded after the second series of pulses exhibits no spectral changes with regard to the transient absorption spectrum measured after the first series of pulses (Figure S1). This indicates that the second series of pulses does not lead to new photoproducts but simply produces more of the same. A substantial amount of additional TAA^+ / AQ^- pairs forms because the extinction coefficient of the MLCT excited state is significantly higher at 450 nm than at 532 nm (Figure 2a). Transients at detection wavelengths of 375 nm (monitoring TAA^+ and AQ^-, Figure S2a) and 560 nm (monitoring AQ^-, Figure S2d) are analogous to that in Figure 3a.
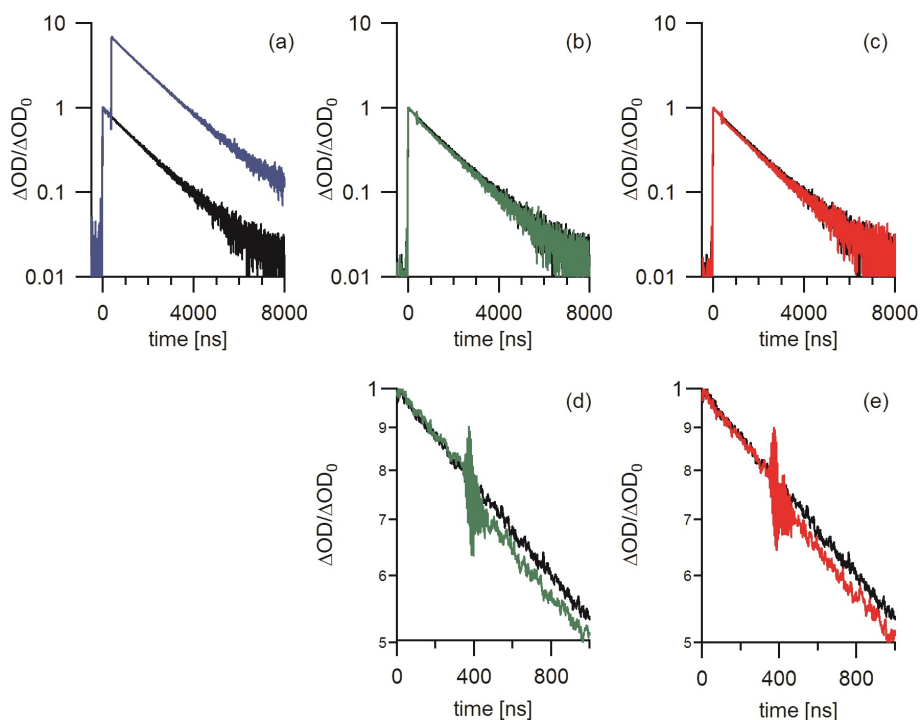
Figure 3. Temporal evolution of transient absorption signals recorded from a 2·10⁻⁵ M solution of triad **II** in de-aerated CH_3CN at room temperature. Primary excitation always occurred at 532 nm with laser pulses of ~10 ns duration, detection was always at 770 nm (for other detection wavelengths see the Supporting Information). Wavelengths used for secondary excitation were 450 nm (blue), 580 nm (green), and 810 nm (red). The time delay between the two series of excitation pulses was always 400 ns. The black traces result from ordinary pump-probe experiments using 532-nm excitation without subsequent secondary excitation. Panels (d) and (e) contain the data from panels (b) and (c) on enlarged scales.

The black trace in Figure 3b is again a transient decay measured at 770 nm after excitation with 532 nm pulses only, whereas the superimposed green decay results from a pump-pump-probe experiment in which the initial 532 nm series of pulses (18 mJ) was followed by a 580 nm pulse series (10 mJ). At 580 nm, there is essentially no absorption of the triad in its ground state (Figure 2a) but AQ^- exhibits an absorption maximum near this wavelength in neat CH_3CN (Figure 2b, d). Thus, only the fraction of triads which was promoted to the TAA^+ / AQ^- charge-separated state with the first series of pulses can be excited with the second pulse series, and only a subset of this fraction will indeed absorb a second photon. Consequently, the change in the green transient with respect to the black one is small and becomes only visible in Figure 3d, in which the data from Figure 3b are shown on enlarged scales. In Figure 3d the two decays are essentially identical in the first 400 ns, and then the green trace exhibits some noise (presumably of electronic origin) marking the pulsing of the second laser. Beyond 450 ns the black and the green transients decay in parallel, but the green transient now has about 5% diminished intensity relative to the black one. This indicates that a portion of the TAA^+ radical cations which were formed with the first pulse series have disappeared after the second series of pulses. Very similar transients are detectable when monitoring AQ^- at 560 nm or the combination of TAA^+ and AQ^- at 375 nm (Figure S3b, e). When recording the full transient absorption spectrum by time-integrating over 200 ns following the second series of laser pulses, no spectral changes with respect to the spectrum obtained after the first series of pulses are observable (Figure S1), again indicating that no new photoproducts are formed with the second pulse series. We conclude that excitation of AQ^- at 580 nm causes rapid (< 50 ns) charge recombination between AQ^- and TAA^+. We estimate that ca. 29% of all triads in the initially pumped sample volume are promoted to the TAA^+ / AQ^- charge-separated state (see Supporting Information for details) under the conditions used, and out of these ~29% only ~5% then undergo photoinduced charge recombination in consequence of direct AQ^- excitation.

Analogous observations are made in a pump-pump-probe experiment in which initial excitation at 532 nm (18 mJ) is followed by subsequent selective excitation of TAA^+ at 810 nm (Figure 3c, e). The pulses at 810 nm (8.5 mJ) occurring with a delay of 400 ns cause a rapid (< 50 ns) decrease of approximately 5% of the transient absorption signals at 770 nm (Figure 3e), 375 nm (Figure S3c) and at 560 nm (Figure S3f). In the time-integrated transient absorption spectrum, no significant spectral differences appear with respect to the ordinary pump-probe experiment (Figure S1). We conclude that excitation of TAA^+ causes charge recombination between AQ^- and TAA^+, in analogy to what is observed when exciting AQ^-.

The mechanism for photoinduced charge recombination cannot be inferred from the available data, and the excited states of TAA^+ and AQ^- are very short-lived.[19] However, photoexcited TAA^+ is expected to be a very strong acceptor while photoexcited AQ^- should be a very strong donor.[20] It is conceivable that these species are in fact sufficiently potent redox reagents for (temporary) oxidation or reduction of the central $Ru(bpy)_3^{2+}$ photosensitizer unit, and this would provide an efficient charge recombination pathway resembling a hopping mechanism.[21]

Conclusions

The absorption of a first photon and the formation of primary photoproducts in the course of a light-induced charge accumulation process leads to changes in the absorption spectrum, and when a second photon is then absorbed by the photoproducts, this may lead to undesired reactions. This is demonstrated here in direct manner by intentionally exciting into the primary photoproducts of triad **II** using two-color pump-pump-probe experiments. Triad **II** cannot undergo photodriven charge accumulation, but it is a well-suited model compound for the demonstration of the principle of photoinduced charge recombination.

The effect of the second pulse looks small at first glance (Figure 3), but two-photon experiments normally exhibit quadratic power dependences.[10, 22] We estimate that ~29% of the triads in the pumped sample volume are promoted to the TAA$^+$ / AQ$^-$ state with the first series of pulses under the conditions used here, but only ~5% of this subset of molecules is then undergoing photoinduced charge recombination while ~95% exhibit ordinary thermal charge recombination. In compounds that are set up for photoinduced charge accumulation, the percentage of molecules that can undergo absorption of a second photon is typically on the same order of magnitude hence the effect observed here is significant.[7, 9, 10]

In compounds designed specifically for charge accumulation it is normally more straightforward to use a single laser pulse of sufficient power rather than two temporally delayed excitation pulses of different color. For solar energy conversion, for example when charge accumulation is intended to occur on a catalytically active reaction center, then it is most likely desirable to perform continuous excitation in a specific wavelength range. For such applications, it becomes necessary to optimize donors, sensitizers, acceptors, and excitation wavelengths such that energy-wasting processes resulting from excitation of the primary photoproducts are minimized. Proper choice of the photosensitizer is particularly crucial in this regard, and it is desirable to know the spectroscopic signatures of the primary photoproducts.

In charge accumulation schemes, yet other unproductive and energy-wasting processes can be triggered upon absorption of a second photon.[5, 13] In triad **II**, specific key processes in this regard are reductive quenching of the photoexcited sensitizer unit by AQ$^-$ and oxidative quenching by TAA$^+$. There is no direct evidence for these two processes in our study (Figure 3a) because excitation with the second photon at 450 nm into the MLCT absorption of the sensitizer results in a large amount of additional TAA$^+$ / AQ$^-$ photoproducts, which overcompensates eventual losses by the abovementioned processes. In prior studies such processes seemed indeed detrimental,[13, 23] and we cannot exclude that they also play an important role in triad **II**. Thus, while our study is able to provide direct evidence for photoinduced charge recombination, other detrimental processes involved in charge accumulation schemes are still to be probed in further detail.

Experimental Section

The synthesis of triad **II** and its electrochemical properties were reported in a prior study.[16] Spectro-electrochemistry occurred as described previously.[18] Basic transient absorption studies of triad **II** (involving single excitation) were made in prior work.[15-17, 18, 24] The two-color pump-pump probe experiments reported herein were performed on an LP920-KS instrument from Edinburgh Instruments using the frequency-doubled output of a Quantel Brilliant b laser for the first excitation, and a Quantel Brilliant laser equipped with an OPO from Opotek for the second excitation. Synchronization of the two lasers occurred with a 9520 digital delay pulse generator from Quantum Composers.

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.

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Author Contribution Statement

M. K.-P. and O. S. W. conceived this work and designed experiments. M. K.-P. performed experiments. M. K.-P. and O. S. W. jointly analyzed and interpreted data and wrote the paper.

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Entry for the Table of Contents