Accumulative Charge Separation Inspired by Photosynthesis

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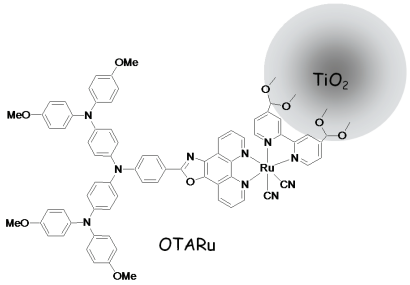
ABSTRACT. Molecular systems that follow the functional principles of photosynthesis attract increasing attention as a method for direct production of solar fuels. This could give a major carbon-neutral energy contribution to our future society. An outstanding challenge in this research is to couple the light-induced charge separation – that generates a single electron-hole pair – to the multi-electron processes of water oxidation and fuel generation. New design considerations are needed to allow for several cycles of photon absorption and charge separation of a single artificial photosystem. Here we demonstrate a molecular system with a regenerative photosensitizer that shows two successive events of light-induced charge separation, leading to high yield accumulation of redox equivalents on single components without sacrificial agents.

Photosynthetic reaction centers provide a blue-print for the conversion of light to chemical energy by a chain of photoinduced electron transfer events.[1-2] Each photon absorption induces rapid transfer of an electron from the central chlorophylls and, by subsequent migration of the hole onto the donor side cofactors, the chlorophylls are regenerated and ready to undergo another cycle of charge separation. The resulting redox equivalents are accumulated on separate sites, storing parts of the combined energy of the absorbed photons for use in subsequent multi-electron catalytic reactions. There are currently several strong efforts to develop similar chemistry in man-made molecular systems by functional mimics of this process.[3-9] The target is direct production of solar fuels, such as molecular hydrogen or reduction products of carbon dioxide. An outstanding challenge in this research is to couple the single-electron photoinduced charge separation in a donor-acceptor pair to multi-electron catalytic reactions, without other sacrificial agents than the catalysis substrates. This calls for the development of molecular systems that are capable of several cycles of light absorption and charge separation before recombination occurs, leading to accumulation of chemical redox equivalents in analogy with the photosynthetic reaction centers. Only a handful of molecular donor-acceptor systems with such functionalities can be found in the literature.[5,10-13] The majority of these systems accumulate only either electrons or holes and rely on external sacrificial electron donors or acceptors for the other half-reaction. This terminates the electron transfer chain instead of providing both electrons and holes for the catalytic reactions. Herein we report a donor-acceptor system (Scheme 1) that gives a fully reversible two-electron charge separated state in high yield upon multiple photoexcitation. The system is based on the regenerative use of a single photosensitizer, mimicking natural photosystems, and no sacrificial reactions are required.



Scheme 1. The **OTARu** dye anchored onto nanocrystalline TiO_2.

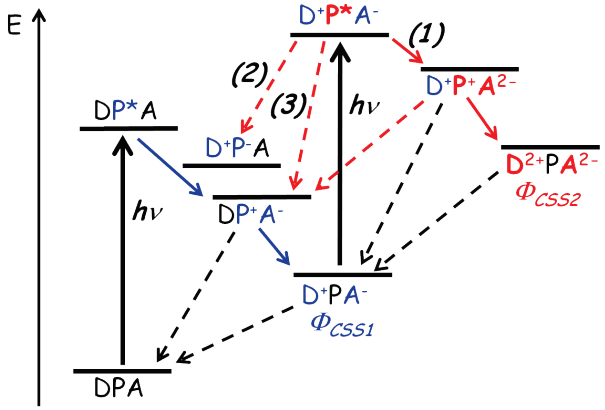


Figure 1. General reaction scheme for photoinduced electron transfer in a Donor(D)-Photosensitizer(P)-Acceptor(A) system upon single (blue) and double (red) photoexcitation.

A general scheme for the electronic states involved in step-wise excitation of a Donor-Photosensitizer-Acceptor (DPA) system is given in Figure 1. The yield of the single-electron charge separated state D^+PA^- (CSS1) is a result of kinetic competition between the productive and unproductive reaction pathways, where the charge separated state recombines and the system returns to the ground state as indicated by dashed arrows. Further excitation of the first charge separated state (D^+PA^-) gives the $D^+P^*A^-$ state. In addition to the productive pathway *(1)* leading to the second charge separated state (CSS2 = $D^{2+}PA^{2-}$), a number of additional decay pathways are available of which some have no direct parallel in the decay pathways from the DP*A state. For example, in the $D^+P^*A^-$ state the excited photosensitizer P* is

surrounded by both a reductant (A^-) and an oxidant (D^+) which might result in reverse electron transfer from A^- *(2)* or to D^+ *(3)*. Additional unproductive reactions may occur due to low-lying excited states or the paramagnetic nature of the A^- and D^+ intermediates. The challenge these additional decay pathways present are beautifully met in photosystem II, where intermediate acceptors and donors between the central chlorophylls and the final donor (the oxygen-evolving $CaMn_4$ cluster) and acceptor (plastoquinone) ensure that the electrons and holes are quickly removed from the proximity of the photosensitizer. From this we learn that a viable strategy to promote the productive formation of the charge accumulated state $D^{2+}PA^{2-}$ in high yield in a DPA system is to make sure that process *(1)* in Figure 1 is very fast, and kinetically outcompetes the unproductive reactions.

To investigate this possibility to promote charge accumulation upon multiple photoexcitation and electron transfer we have designed a DPA system consisting of an oligo(triarylamine)-ruthenium(II)-polypyridine dye, **OTARu**, anchored onto titanium dioxide nanoparticles via the carboxylate groups (see Scheme 1). The titanium dioxide nanoparticle acceptor was chosen because of the documented rapid ultra-fast electron injection from ruthenium(II)polypyridine dyes and subsequent slow recombination in similar systems, and its ability to accept several electrons per particle.[14-16] In cyclic voltammetry of **OTARu** in solution (CH_2Cl_2, Bu_4PF_6 0.15 M), the first two oxidation peaks at +0.33 V and +0.58 V *vs.* SCE were assigned to the first and second oxidation of the OTA donor unit[17], well below the $Ru^{III/II}$ oxidation of the sensitizer at +0.93 V (Table S1). Thus, if Ru^{III} is produced by photoinduced injection into the TiO_2, it is thermodynamically able to oxidize the OTA donor unit in two steps upon multiple excitations.

The OTA^+ and OTA^{2+} species are spectroscopically distinct, as shown by chemical oxidation in solution and spectro-electrochemical investigations on **OTARu** sensitized TiO_2 films (Fig. S3, S5). The electronic absorption of the singly oxidized species OTA^+ is characterized by positive absorption above 435 nm with band maxima at 495 nm and 590 nm *vs* the uncharged species. Below 435 nm the OTA^+ absorbs less than the uncharged OTA species, resulting in net bleach in the difference absorption spectrum in this region. When oxidizing the oligotriarylamine moiety further, from the OTA^+ to OTA^{2+}, the most significant changes are a shift of the bleach to 400 - 500 nm with positive absorption from 500 nm, and increased intensity in the broad absorption band at 600 nm. From studies of similar dicationic poly-triarylamine structures, we can assume that the holes are delocalized over the OTA^{2+} unit.[16]

To investigate the formation of CSS1, the **OTARu**-sensitized TiO_2 film was excited by ~120 fs laser pulses at 510 nm in a 1 M $LiClO_4$ (propylene carbonate) electrolyte. Multi-exponential electron injection from the excited Ru moiety to the TiO_2 was observed,, forming **OTARu**$^{III}TiO_2^{(-)}$ within 5 ps (Fig. S6)[18]. The Ru-sensitizer was then regenerated by hole transfer to the OTA donor on a slower timescale; a biexponetial fit yielded rate constants of k_{HT} = (29 ps)$^{-1}$ and k_{HT} = (1.2 ns)$^{-1}$, see SI. This was shown by the growth of OTA^+ features concomitant with Ru^{II} ground state recovery at 490 nm. The total yield of charge separation was found to be very high ($\Phi_{CSS1} \approx$ 100%), as estimated from the amplitude of the maximum OTA^+ absorption (ε_{495} = 5×10^3 M^{-1} cm^{-1}; Fig. S5) relative to the initial ground state bleach a few ps after excitation ($\Delta\varepsilon_{495}(Ru^{III} - Ru^{II}) \approx$ -1×10^4 M^{-1} cm^{-1})[19]. The high yield is in agreement with the rapid kinetics of injection and hole migration that compete efficiently with intrinsic $*Ru^{II}$ excited state decay and $Ru^{III}TiO_2^{(-)}$ recombination, respectively.

Upon nanosecond single-pulse excitation (480 nm, 10 ns pulse duration) the obtained spectrum, shown in black in Figure 2, agreed well with the expected signature from the OTA^+ monocation (blue solid line Figure 2) combined with the weak, structureless absorption from electrons injected into the TiO_2 conduction band ($\Delta\varepsilon_{800} \approx$ 800 M^{-1} cm^{-1} for a 4 μm thick film).[20] Approximately 30% of the dye molecules were excited and produced the $OTA^+Ru^{II}TiO_2^{(-)}$ after a single pulse, as estimated from the magnitude of the OTA^+ absorption generated relative to the initial dye absorption (OD_{480} = 0.1; Fig. S4). Recombination of the charge separated state was found to be multi-exponential (Figure 2, inset, black trace), typical for Ru-dyes on TiO_2,[16] with complete recombination on the millisecond timescale.

When a second laser pulse at 480 nm was applied 1 μs after the first one the regenerated Ru sensitizer was again excited and initiated further charge separation. Compared to single excitation experiments the transient spectrum immediately after the second excitation pulse (green circles in Figure 2) showed increased absorption at 600 nm, along with a bleach at 400-500 nm causing a red shift of the isosbestic point to 460 nm. The unique features after the second excitation pulse are highlighted by the double difference spectrum (orange circles, Figure 2). The latter was obtained by subtracting 1.4 times the first pulse spectrum from the double-pulse spectrum, to remove contributions from $OTA^+Ru^{II}TiO_2^{(-)}$ species.[21] These features agree well with the optical signature of OTA^{2+} observed upon electrolysis of the dye on TiO_2, also included in Figure 2. We conclude that in the second excitation pulse, a fraction of the second charge separated state $OTA^{2+}Ru^{II}TiO_2^{(2-)}$ has been formed from the excited state $OTA^+(Ru^{II})^*TiO_2^{(-)}$. Hole transfer in the $OTA^+Ru^{III}TiO_2^{(2-)}$ state after the second excitation was faster than the time resolution (~15 ns) of the nanosecond experiments.[22] The $OTA^{2+}Ru^{II}TiO_2^{(2-)}$ product was also observed in high photon-flux single-pulse experiments, where multiple excitations can occur within the same pulse (Fig. S10).

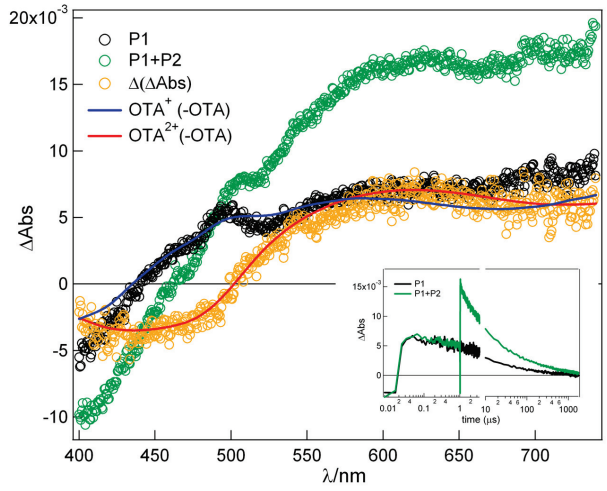


Figure 2. Transient absorption spectra (circles) for **OTARu**TiO_2 directly after single (P1) and double-pulse (P1+P2) excitation (480 nm, 10 ns pulses separated by 1 μs). The double difference spectrum (orange symbols) highlights the features of OTA^{2+} formed after the second pulse; see text. Difference spectra of OTA^+ and OTA^{2+} (solid lines) obtained from spectroelectrochemistry, linearly scaled for a best fit, are shown for comparison. Inset: Transient absorption at 620 nm after single (black) and double-pulse (green) excitation.

The nanosecond transient absorption spectra shown in Figure 2 were used to evaluate the yield of formation of the $OTA^{2+}Ru^{II}TiO_2^{(2-)}$ state. As shown above, 30% of the dye molecules were excited and produced the $OTA^{+}Ru^{II}TiO_2^{(-)}$ by a single pulse. The two excitation pulses were equivalent in pulse intensity and duration, so that the fraction of dye molecules that were excited by two photons was in total ca. 10% ($0.30^2 = 0.09$) of the sample in the probe volume. The fraction of OTA^{2+} formed after the second pulse was approximately 10%, calculated from the transient spectral amplitudes at 495 nm and 600 nm immediately after the second excitation and the extinction coefficients of OTA^{+} and OTA^{2+} (Fig. S5). This corresponds to 100% quantum yield of formation (Φ_{CSS2}) of the second charge separated state $OTA^{2+}Ru^{II}TiO_2^{(2-)}$ from $OTA^{+}(Ru^{II})^{*}TiO_2^{(-)}$. This remarkably high yield is primarily ascribed to the very fast electron injection into TiO_2 (process *(1)* in Figure 1) that successfully competes with unproductive pathways. It can also be noted that while the electronic coupling favors the injection process, the electrons and holes are sufficiently decoupled in $OTA^{+}Ru^{III}TiO_2^{(2-)}$ to prevent unproductive recombination from this intermediate state.

The OTA^{2+} signature was shown to contribute to the spectral features with an approximately constant fraction at least up to 100 μs (Fig. S11). Following the multi-exponential decay at separate wavelengths, there are no indications that the $OTA^{2+}Ru^{II}TiO_2^{(2-)}$ state lifetime differs significantly from that of the first charge separated state. This may be expected if electron trapping and transport kinetics within TiO_2 are limiting the recombination.[15-16] Thus, the **OTARu**TiO_2 system shows accumulative charge separation lifetimes compatible with the catalytic turnover rates in Photosystem II.[1]

Regarding the intramolecular nature of OTA^{2+} generation we note that the dye surface coverage ($OD_{480} = 0.1$) is an order of magnitude lower than for the typical monolayers used in dye-sensitized TiO_2 films. Thus intermolecular electron transfer between Ru^{III} and OTA units on different molecules is unlikely to compete efficiently with the intramolecular, through-bond reactions. This is supported by the fact that the $OTA^{2+}Ru^{II}TiO_2^{(2-)}$ state shows the same slow decay kinetics as the $OTA^{+}Ru^{II}TiO_2^{(-)}$ state, suggesting that electron transfer between neighboring OTA and OTA^{2+} units is very slow in spite of a moderate driving force ($\Delta G^0 = -0.25$ eV). It is therefore reasonable to assign the hole accumulation observed to intramolecular reactions between the Ru and OTA units.

In conclusion, we demonstrate here a system where the absorption of two photons leads to accumulation of two holes at the donor site and of electrons at the acceptor site, in near unity yield, by the regenerative use of a single photosensitizer.[23] The doubly charge separated state conserves much of the energy of the absorbed photons, in contrast to systems that rely on sacrificial donors or acceptors. The rapid electron injection is the key to obtaining the doubly charge separated state in high yield in **OTARu**TiO_2, avoiding the competing unproductive pathways *(2)* and *(3)* as illustrated in Figure 1. This strategy could most likely be incorporated in the design of other molecular systems for photoinduced electron transfer to obtain charge accumulation with minimum losses. The fundamental study of photoinduced accumulative electron transfer in model systems such as the one described here aid our understanding of the specific challenges that accompany accumulative charge separation, which is important for the efficient use of photo-driven multi-electron processes, e.g. solar fuels production.

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Supporting information available: Synthesis of OTARu, experimental details and additional data. This material is available free of charge via the Internet at http://pub.acs.org

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(22) In ultrafast double-pulse experiments, the fraction of doubly excited dyes was too small to give a clearly distinguishable signal.
(23) Note that this result is very different from dye-sensitized TiO_2 cells where the holes are transferred to an external electrolyte instead of being accumulating on a molecular unit by the regenerative action of a sensitizer.