

## Accumulative Charge Separation Inspired by Photosynthesis

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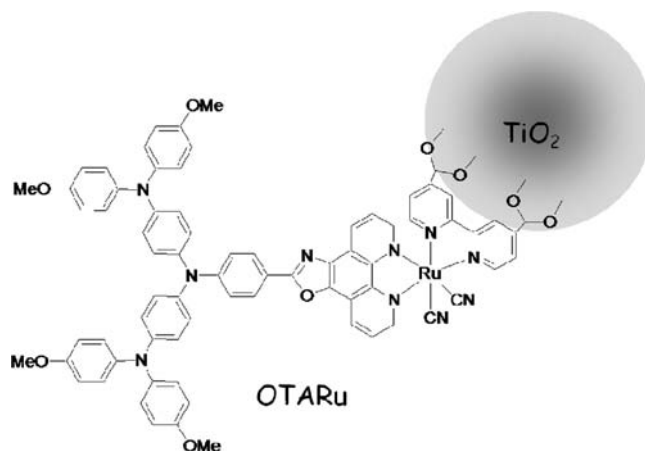
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**Abstract:** Molecular systems that follow the functional principles of photosynthesis have attracted increasing attention as a method for the direct production of solar fuels. This could give a major carbon-neutral energy contribution to our future society. An outstanding challenge in this research is to couple the light-induced charge separation (which generates a single electron–hole pair) to the multielectron 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.

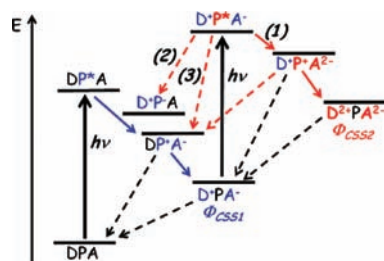
Photosynthetic reaction centers provide a blueprint for the conversion of light to chemical energy by a chain of photoinduced electron transfer events.<sup>1,2</sup> Each photon absorption induces rapid transfer of an electron from the central chlorophylls, and by subsequent migration of the hole onto 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 multielectron catalytic reactions. There are currently several strong efforts to develop similar chemistry in human-made molecular systems by functional mimics of this process.<sup>3–9</sup> The target is the direct production of solar fuels, such as molecular hydrogen or the 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 multielectron catalytic reactions without sacrificial agents other 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 the accumulation of chemical redox equivalents by analogy with the photosynthetic reaction centers. Only a handful of molecular donor–acceptor systems with such functionalities have been reported in the literature.<sup>5,10–13</sup> 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

**Scheme 1.** OTARu Dye-Anchored onto Nanocrystalline TiO<sub>2</sub>



the regenerative use of a single photosensitizer, mimicking natural photosystems, and no sacrificial reactions are required.

A general scheme for the electronic states involved in stepwise 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, in which 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,  $D^{2+}PA^{2-}$  (CSS2), a number of additional decay pathways are available, some of which have no direct parallel in the decay pathways from the singly excited  $DP^*A^-$  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 due to low-lying excited states



**Figure 1.** General reaction scheme for photoinduced electron transfer in a donor–photosensitizer–acceptor (DPA) system upon single (blue) and double (red) photoexcitation.

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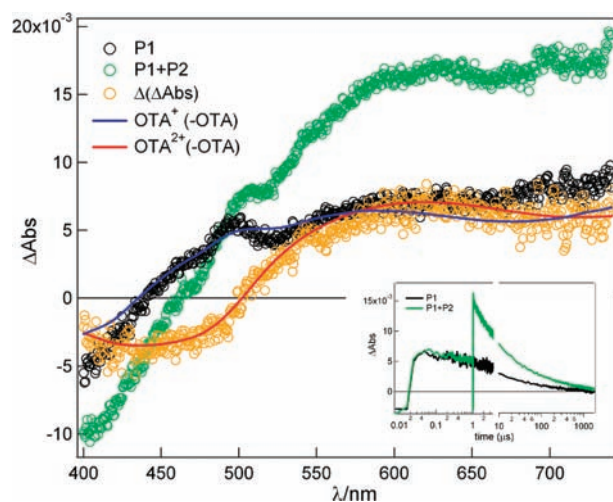
or the paramagnetic nature of the  $A^-$  and  $D^+$  intermediates may also occur. The challenge these additional decay pathways present are beautifully met in photosystem II, where intermediate acceptors and donors between the central chlorophylls and the final donor (the oxygen-evolving  $\text{CaMn}_4$  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 for promoting 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 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  $\text{TiO}_2$  nanoparticle acceptor was chosen because of the documented rapid ultrafast electron injection from ruthenium(II) polypyridine dyes and subsequent slow recombination in similar systems as well as its ability to accept several electrons per particle.<sup>14–16</sup> In cyclic voltammetry of **OTARu** in solution ( $\text{CH}_2\text{Cl}_2$ ,  $\text{Bu}_4\text{PF}_6$  0.15 M), the first two oxidation peaks at +0.33 and +0.58 V vs SCE were assigned to the first and second oxidations of the OTA donor unit, respectively;<sup>17</sup> these are well below the  $\text{Ru}^{\text{III/II}}$  oxidation of the sensitizer at +0.93 V (Table S1 in the Supporting Information). Thus, if  $\text{Ru}^{\text{III}}$  is produced by photoinduced injection into the  $\text{TiO}_2$ , it is thermodynamically able to oxidize the OTA donor unit in two steps upon multiple excitations.

The  $\text{OTA}^+$  and  $\text{OTA}^{2+}$  species are spectroscopically distinct, as shown by chemical oxidation in solution and spectroelectrochemical investigations on **OTARu**-sensitized  $\text{TiO}_2$  films (Figures S3 and S5 in the Supporting Information). The electronic absorption of the singly oxidized species  $\text{OTA}^+$  is characterized by positive absorption above 435 nm with band maxima at 495 and 590 nm vs the uncharged species. Below 435 nm, the  $\text{OTA}^+$  absorbs less than the uncharged OTA species, resulting in net bleaching in the difference absorption spectrum in this region. When the oligotriarylamine moiety is further oxidized from  $\text{OTA}^+$  to  $\text{OTA}^{2+}$ , the most significant changes are a shift of the bleached region to 400–500 nm with positive absorption above 500 nm and increased intensity in the broad absorption band at 600 nm. From studies of similar dicationic polytriarylamine structures, we can assume that the holes are delocalized over the  $\text{OTA}^{2+}$  unit.<sup>16</sup>

To investigate the formation of CSS1, the **OTARu**-sensitized  $\text{TiO}_2$  film was excited using  $\sim 120$  fs laser pulses at 510 nm in a 1 M  $\text{LiClO}_4$  (propylene carbonate) electrolyte. Multiexponential electron injection from the excited Ru moiety to the  $\text{TiO}_2$  was observed, forming  $\text{OTARu}^{\text{III}}\text{TiO}_2^-$  within 5 ps (Figure S6).<sup>18</sup> The Ru sensitizer was then regenerated by hole transfer (HT) to the OTA donor on a longer time scale; a biexponential fit yielded HT rate constants ( $k_{\text{HT}}$ ) of  $(29 \text{ ps})^{-1}$  and  $(1.2 \text{ ns})^{-1}$  (see the Supporting Information). This was shown by the growth of  $\text{OTA}^+$  features concomitant with  $\text{Ru}^{\text{II}}$  ground-state recovery at 490 nm. The total yield of charge separation was found to be very high ( $\Phi_{\text{CSS1}} \approx 100\%$ ), as estimated from the amplitude of the maximum  $\text{OTA}^+$  absorption ( $\epsilon_{495} = 5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ; Figure S5) relative to the initial ground-state bleach a few picoseconds after excitation [ $\Delta\epsilon_{495}(\text{Ru}^{\text{III}} - \text{Ru}^{\text{II}}) \approx -1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ].<sup>19</sup> The high yield is in agreement with the rapid kinetics of injection and hole migration, which compete efficiently with intrinsic  $\text{Ru}^{\text{II}}$  excited-state decay and  $\text{Ru}^{\text{III}}\text{TiO}_2^-$  recombination, respectively.

Upon nanosecond single-pulse excitation (480 nm, 10 ns pulse duration) the obtained spectrum (shown in black in Figure 2) agreed



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

well with the expected signature from the  $\text{OTA}^+$  monocation (blue solid line in Figure 2) combined with the weak, structureless absorption from electrons injected into the  $\text{TiO}_2$  conduction band ( $\Delta\epsilon_{800} \approx 800 \text{ M}^{-1} \text{ cm}^{-1}$  for a 4 μm thick film).<sup>20</sup> Approximately 30% of the dye molecules were excited and produced  $\text{OTA}^+\text{Ru}^{\text{II}}\text{TiO}_2^-$  after a single pulse, as estimated from the magnitude of the generated  $\text{OTA}^+$  absorption relative to the initial dye absorption ( $\text{OD}_{480} = 0.1$ ; Figure S4). Recombination of the charge-separated state was found to be multiexponential (Figure 2 inset, black trace), which is typical for Ru dyes on  $\text{TiO}_2$ ,<sup>16</sup> with complete recombination on the millisecond time scale.

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. In comparison with the 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 bleaching 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 in Figure 2), which was obtained by subtracting 1.4 times the first pulse spectrum from the double-pulse spectrum to remove contributions from  $\text{OTA}^+\text{Ru}^{\text{II}}\text{TiO}_2^-$  species.<sup>21</sup> These features agree well with the optical signature of  $\text{OTA}^{2+}$  observed upon electrolysis of the dye on  $\text{TiO}_2$ , which is also included in Figure 2. We conclude that in the second excitation pulse, a fraction of the second charge-separated state,  $\text{OTA}^{2+}\text{Ru}^{\text{II}}\text{TiO}_2^{2-}$ , was formed from the excited state  $\text{OTA}^+(\text{Ru}^{\text{II}})\text{TiO}_2^-$ . Hole transfer in the  $\text{OTA}^+\text{Ru}^{\text{II}}\text{TiO}_2^-$  state after the second excitation was faster than the time resolution ( $\sim 15$  ns) of the nanosecond experiments.<sup>22</sup> The  $\text{OTA}^{2+}\text{Ru}^{\text{II}}\text{TiO}_2^{2-}$  product was also observed in high-photon-flux single-pulse experiments, where multiple excitations can occur within the same pulse (Figure S10).

The nanosecond transient absorption spectra shown in Figure 2 were used to evaluate the yield of formation of the  $\text{OTA}^{2+}\text{Ru}^{\text{II}}\text{TiO}_2^{2-}$  state. As shown above, 30% of the dye molecules were excited and produced  $\text{OTA}^+\text{Ru}^{\text{II}}\text{TiO}_2^-$  by a single pulse. The two excitation pulses were equivalent in pulse intensity and duration,

so the fraction of dye molecules that were excited by two photons was in total  $\sim 10\%$  ( $0.30^2 = 0.09$ ) of the sample in the probe volume. The fraction of  $\text{OTA}^{2+}$  formed after the second pulse was  $\sim 10\%$ , as calculated from the transient spectral amplitudes at 495 and 600 nm immediately after the second excitation using the extinction coefficients of  $\text{OTA}^+$  and  $\text{OTA}^{2+}$  (Figure S5). This corresponds to a 100% quantum yield of formation ( $\Phi_{\text{CSS2}}$ ) of the second charge-separated state,  $\text{OTA}^{2+}\text{Ru}^{\text{II}}\text{TiO}_2^{2-}$ , from  $\text{OTA}^+(\text{Ru}^{\text{II}})\text{TiO}_2^-$ . This remarkably high yield is primarily ascribed to the very fast electron injection into  $\text{TiO}_2$  [process (1) in Figure 1] that successfully competes with unproductive pathways. It should also be noted that while the electronic coupling favors the injection process, the electrons and holes are sufficiently decoupled in  $\text{OTA}^+\text{Ru}^{\text{II}}\text{TiO}_2^{2-}$  to prevent unproductive recombination from this intermediate state.

The  $\text{OTA}^{2+}$  signature was shown to contribute to the spectral features with an approximately constant fraction, at least up to 100  $\mu\text{s}$  (Figure S11). Following the multiexponential decay at separate wavelengths, there were no indications that the  $\text{OTA}^{2+}\text{Ru}^{\text{II}}\text{TiO}_2^{2-}$  state lifetime differed significantly from that of the first charge-separated state. This may be expected if electron trapping and transport kinetics within  $\text{TiO}_2$  limit the recombination.<sup>15,16</sup> Thus, the  $\text{OTARuTiO}_2$  system shows accumulative charge separation lifetimes compatible with the catalytic turnover rates in photosystem II.<sup>1</sup>

In regard to the intramolecular nature of  $\text{OTA}^{2+}$  generation, we note that the dye surface coverage ( $\text{OD}_{480} = 0.1$ ) is an order of magnitude lower than for the typical monolayers used in dye-sensitized  $\text{TiO}_2$  films. Thus, intermolecular electron transfer between  $\text{Ru}^{\text{II}}$  and  $\text{OTA}$  units on different molecules is unlikely to compete efficiently with the intramolecular, through-bond reactions. This is supported by the fact that the  $\text{OTA}^{2+}\text{Ru}^{\text{II}}\text{TiO}_2^{2-}$  state shows the same slow decay kinetics as the  $\text{OTA}^+\text{Ru}^{\text{II}}\text{TiO}_2^-$  state, suggesting that electron transfer between neighboring  $\text{OTA}$  and  $\text{OTA}^{2+}$  units is very slow in spite of a moderate driving force ( $\Delta G^0 = -0.25$  eV). It is therefore reasonable to assign the observed hole accumulation to intramolecular reactions between the Ru and  $\text{OTA}$  units.

In conclusion, we have demonstrated here a system in which the absorption of two photons leads to accumulation of two holes at the donor site and two electrons at the acceptor site in nearly 100% yield by the regenerative use of a single photosensitizer.<sup>23</sup> 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  $\text{OTARuTiO}_2$ , 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 aids our understanding of the specific challenges that accompany accumulative charge separation, which is important for the efficient use of photodriven multielectron processes, such as production of solar fuels.

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**Supporting Information Available:** Synthesis of  $\text{OTARu}$ , experimental details, and additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (21) The difference spectrum was obtained by linear subtraction of the spectrum after single-pulse excitation from the spectrum after double-pulse excitation. A scaling factor was used to account for the singly charge-separated state  $\text{OTA}^+\text{Ru}^{\text{II}}\text{TiO}_2^-$  that was created from the remaining unreacted dyes in the second excitation.
- (22) In ultrafast double-pulse experiments, the fraction of doubly excited dyes was too small to give a clearly distinguishable signal.
- (23) It should be noted that this result is very different from that for dye-sensitized  $\text{TiO}_2$  cells, where the holes are transferred to an external electrolyte instead of being accumulated on a molecular unit by the regenerative action of a sensitizer.

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