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Photoinduced Electron Transfer Coupled to Donor Deprotonation and Acceptor Protonation in a Molecular Triad Mimicking Photosystem II

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Supporting Information

ABSTRACT: The first artificial donor−sensitizer−acceptor compound in which photoinduced long-range electron transfer is coupled to donor deprotonation and acceptor protonation is reported. The long-lived photoproduct stores energy in the form of a radical pair state in which the charges of the donor and the acceptor remain unchanged, much in contrast to previously investigated systems that exhibit charge-separated states comprised of electron−hole pairs. This finding is relevant for light-driven accumulation of redox equivalents, because it exemplifies how the buildup of charge can be avoided yet light energy can be stored. Proton-coupled electron transfer (PCET) reactions at a phenol donor and a monoquat acceptor triggered by excitation of a Ru(II) sensitizer enable this form of photochemical energy storage. Our triad emulates photosystem II more closely than previously investigated systems, because tyrosine Z is oxidized and deprotonated, whereas plastoquinone B is reduced and protonated.

In photosystem II, electrons are transferred over long distances upon photoexcitation, leading to temporary separation of redox equivalents. Many artificial donor−sensitizer−acceptor compounds emulated the primary charge separation events, and in numerous cases long-lived electron−hole pairs were formed.[1] However, in photosystem II, there is no simple electron−hole generation, but instead the resulting reduction and oxidation products both undergo proton-coupled electron transfer (PCET) for further stabilization.[2] Specifically, tyrosine Z oxidation (Y_Z in Figure 1a) is coupled to deprotonation yielding a neutral phenoxyl radical, and the plastoquinone B acceptor (Q_B in Figure 1a) is protonated upon reduction.[2,3] We present the first artificial donor−sensitizer−acceptor compound that is able to emulate this entire series of events seen in photosystem II, namely photoinduced long-range electron transfer coupled to proton release at the donor in combination with proton uptake at the electron acceptor. The net result is the formation of a long-lived radical pair state, instead of the simple electron−hole separation observed many times before (Figure 1b). While there have been prior studies in which photoinduced electron transfer was coupled to proton transfer at either the donor or the acceptor site,[4] to the best of our knowledge, our triad is the first purely molecular system in which PCET reactivity is possible at both reactants. Moreover, in many previously investigated systems phototriggered PCET actually occurred between species in their electronic ground states (e.g., between Ru(III) complexes and phenols), and there was no intramolecular energy storage.[4a,b,f,k] Some of the previously investigated systems exhibited charge-shift reactions without any charge build-up.

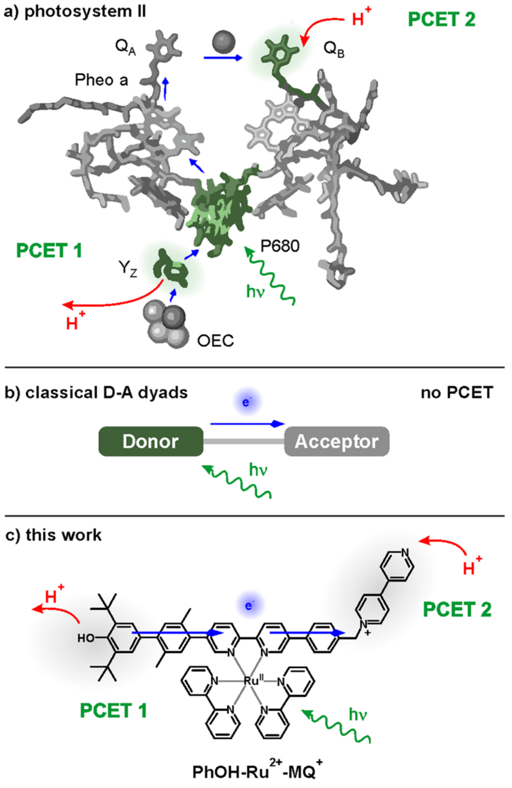

Figure 1. (a) Primary and secondary electron transfer events (blue arrows) in photosystem II after excitation of P680 (green central part). PCET occurs at tyrosine Z (green, lower left) and at plastoquinone B (green, upper right).[3] (b) Generic donor−acceptor compound exhibiting simple electron−hole separation. (c) Investigated triad comprised of a phenol donor (PhOH) resembling tyrosine Z (PCET 1), a Ru(II) sensitizer mimicking the function of P680, and a monoquat acceptor (MQ^+) playing the role of plastoquinone B with regard to uptake of one electron and one proton (PCET 2).

Our key compound is a molecular triad (Figure 1c) comprised of a $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) photosensitizer, a monoquat (MQ^+, *N*-methyl-4,4′-bipyridinium) acceptor, and a

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di-*tert*-butylphenol (PhOH) donor. Its synthesis including full characterization is reported in the Supporting Information (pp S2−S13). In CH_3CN, excitation of the Ru(II) sensitizer at 532 nm merely leads to ^{3}MLCT luminescence and no photochemistry occurs (SI pp S15−S16). Not surprisingly, in order for the anticipated reductive and oxidative PCET events to become viable photochemical reaction pathways, acids and bases must both be simultaneously present. Pyridine (py) turned out to be optimal as solvent, and through addition of some triflic acid, pyridinium (pyH^+) was formed (0.22 M). The resulting py/pyH^+ mixture was a suitable organic buffer for our spectroscopic studies. UV−vis and ^{1}H NMR data indicate that the phenolic unit of the triad remains largely protonated in this solvent while the MQ^+ unit remains unprotonated (SI p S17−S20).

Selective photoexcitation of the Ru(II) sensitizer of the triad at 532 nm in the py/pyH^+ mixture leads to the formation of a long-lived photoproduct exhibiting the transient absorption spectrum shown as a green trace in Figure 2a. This spectrum is dominated by the spectral signature of $MQH^{\bullet+}$, i. e., the reduced and protonated form of the monoquat acceptor resembling the well-known methylviologen radical monocation spectrum.[5a,6] Comparison to the spectro-electrochemical data in Figure 2b (green trace), for which a MQ^+ reference compound (see inset) was protonated and reduced (see SI p S21 for details), corroborates this assignment. In neat py without pyH^+, $MQ^\bullet$ is instead formed, as seen from comparison of the black traces in Figure 2a (transient absorption) and Figure 2b (spectro-electrochemistry). The same observation is made with other bases, for example with pyrrolidine (see SI pp S35−S36).

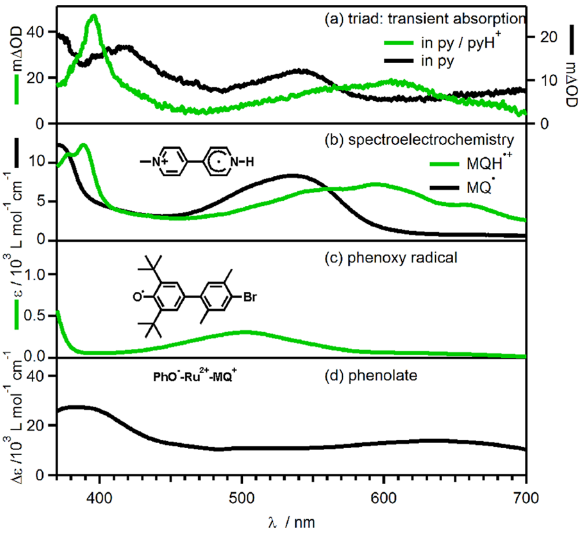


Figure 2. (a) Transient absorption spectra after excitation of the triad at 532 nm in pyridine with 0.22 M pyridinium (green, 34 μM triad), and in neat pyridine (black, 55 μM triad). Detection occurred in a 200 ns time window 2 μs after excitation with pulses of ~10 ns duration. (b) Electrochemically generated spectra of $MQH^{\bullet+}$ (green) and $MQ^\bullet$ (black) using a reference compound (inset) in CH_3CN with 0.1 M $TBAPF_6$. (c) Spectrum of chemically generated $PhO^\bullet$ using a reference compound (see inset) in 6:1 toluene/pyridine. Extinction coefficients were estimated based on previously published spectra (SI pp S21−S22).[5] (d) Difference spectrum obtained from a solution of the triad in CH_3CN before and after addition of 4 equiv of TBAOH, in order to determine the spectral contribution of PhO^-.

While the formation of $MQH^{\bullet+}$ from MQ^+ in the py/pyH^+ solution is immediately evident, identification of the oxidation product requires somewhat more effort. The spectral signature of the anticipated phenoxyl radical ($PhO^\bullet$) was determined by oxidizing a suitable reference compound under alkaline conditions (Figure 2c; see SI p S22 for details). The main absorption bands of $PhO^\bullet$ overlap spectrally with those from $MQH^{\bullet+}$, and the extinction coefficients of $PhO^\bullet$ at the relevant wavelengths are about an order of magnitude weaker than those of $MQH^{\bullet+}$ (Figure 2b/c);[5b,c] hence, direct observation of $PhO^\bullet$ is hampered.

Several lines of evidence nevertheless clearly indicate that $PhO^\bullet$ is formed after photoexcitation of the triad. First, the photoproduct observed in deaerated py/pyH^+ at 25 °C has a lifetime (τ) of 1.9 ± 0.2 μs (see below), compatible with the μs-lifetimes of long-range electron−hole separation in comparable triarylamine-Ru(II)-quinone compounds and other related triads.[7] By contrast, in a reference dyad comprised of only the Ru(II) sensitizer and the MQ^+ acceptor no long-lived photoproduct is formed ($\tau \leq 10$ ns, SI pp S37−S40), indicating that the phenolic reaction site plays a key role in stabilizing the 1.9 μs-photoproduct observed for the triad. Furthermore, according to electrochemical studies phenols undergo concerted PCET in the presence of pyridine, leading to a substantial lowering of the oxidation potential due to coupled proton release.[8] It is clear that PhOH cannot be oxidized to $PhOH^{\bullet+}$ by ^{3}MLCT-excited $Ru(bpy)_3^{2+}$ due to lack of sufficient driving force ($\Delta G^\circ_{ET} = +0.5$ eV; SI p S29), but oxidation to $PhO^\bullet$ is readily possible ($\Delta G^\circ_{PCET} = -0.4$ eV; see below).[4a−m,9] Lastly, in neat pyridine a transient absorption band appearing at 420 nm (black trace in Figure 2a) signals the formation of phenolate (PhO^-) as an additional photoproduct to the above-mentioned $MQ^\bullet$ species formed under these acid-free conditions (SI p S32 for further details). The PhO^- species appears as a result of initial formation of $PhO^\bullet$ and $Ru(bpy)_3^+$ by reductive ^{3}MLCT quenching and subsequent rapid thermal reverse electron transfer leading to PhO^- and $Ru(bpy)_3^{2+}$ in a subset of triads (SI p S31). The net result is simple proton release at the phenol upon Ru(II) excitation, and such apparent photoacid behavior has been reported previously for Ru(II)-phenol and Re(I)-phenol dyads.[10] Thus, the PhO^- signature at 420 nm indicates the intermediacy of $PhO^\bullet$ in neat pyridine.

Given these three lines of evidence (1.9 μs lifetime of the triad photoproduct compared to sub-10 ns lifetimes of several Ru(II)−MV^{2+} dyads (SI pp S37−40);[11] known PCET chemistry of PhOH in the presence of pyridine;[8,9] PhO^- signature in neat py signaling the intermediacy of $PhO^\bullet$), it is safe to conclude that the main photoproduct after excitation of the triad in py/pyH^+ is indeed comprised of $PhO^\bullet$ and $MQH^{\bullet+}$.

The mechanism for formation and decay of this radical pair state is elucidated in the following. After excitation of the triad at 532 nm with pulses of ~10 ns duration, the ^{3}MLCT luminescence emitted by the Ru(II) photosensitizer at 630 nm in deaerated py/pyH^+ decays in biexponential fashion (green trace in Figure 3a) with $\tau = 68 \pm 7$ ns (85%) and $\tau' = 780 \pm 80$ ns (15%). The $MQH^{\bullet+}$ related transient absorption signals at 395 and 610 nm rise with $\tau = 68 \pm 7$ ns and then decay with $\tau'' = 1.9 \pm 0.2$ μs (green traces in Figure 3b/c). Thus, 85% of all excited triads undergo photoreaction to the $PhO^\bullet$ and $MQH^{\bullet+}$ products, whereas 15% exhibit ordinary ^{3}MLCT decay like the isolated $Ru(bpy)_3^{2+}$ complex. In py/pyD^+ where the phenolic moiety of the triad is deuterated, the major ^{3}MLCT luminescence decay component and the rise of the transient absorption signals at 395/610 nm are decelerated to $\tau' = 150 \pm 15$ ns. Thus, photoproduct formation occurs with an H/D kinetic isotope effect (KIE) of 2.2 ± 0.2, indicating that proton motion is involved in the rate-determining reaction step. By

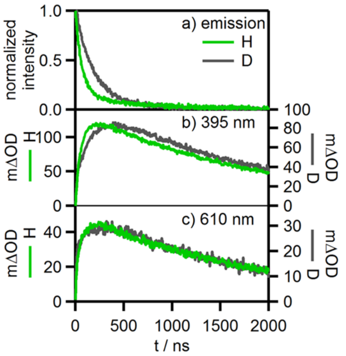


Figure 3. (a) Temporal evolution of luminescence recorded at 630 nm. (b, c) Temporal evolution of transient absorption signals at 395 and 610 nm. Excitation of 34 μM triad in deaerated py/pyH$^+$ (green) or py/pyD$^+$ (gray) occurred at 532 nm with laser pulses of ~10 ns duration.

contrast, the decay of the photoproduct exhibits no significant KIE (0.9 ± 0.2).

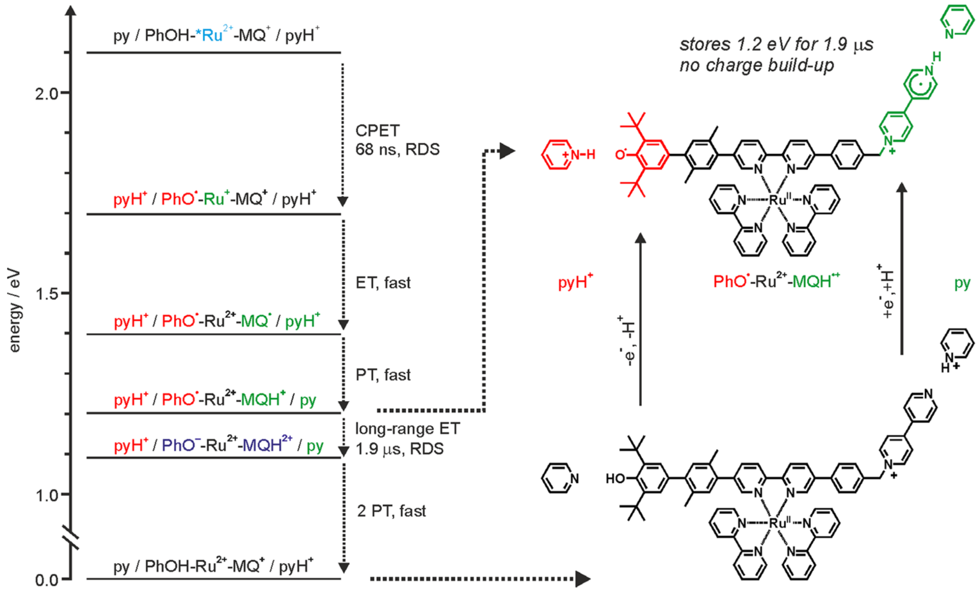
Oxidative quenching of ^{3}MLCT-excited photosensitizer by MQ$^+$ is endergonic by 0.2 eV (SI p S29), and even when occurring in concert with proton uptake at the acceptor there is no significant driving force for this reaction step. The observation of essentially unquenched ^{3}MLCT emission in the Ru(II)−MQ$^+$ reference dyad in py/pyH$^+$ compared to pyridine solution corroborates this interpretation. (SI pp S37−S40). Reductive ^{3}MLCT quenching by PhOH is endergonic by 0.5 eV, but concerted PCET yields a driving force of ca. −0.4 eV (SI p S29). Thus, it is plausible that reductive quenching by PhOH with concerted proton release to py is the rate-determining reaction step (uppermost dashed downward arrow in Scheme 1, labeled RDS), in line with the H/D KIE of 2.2 ± 0.2 and in agreement with complementary studies in neat pyridine (SI pp S33−S34). Subsequent electron transfer from reduced photosensitizer to MQ$^{\bullet+}$ is then exergonic by 0.3 eV (second dashed downward arrow in Scheme 1, 'Ru^{+}' denotes Ru(bpy)$_3^{+}$), and protonation of MQ$^\bullet$ liberates another 0.2 eV (third dashed downward arrow in Scheme 1) (SI p S29). The final photoproduct observed in Figure 2a stores ca. 1.2 eV (Scheme 1, top right).

Based on the observable ΔOD values and the extinction coefficients of the photoproducts, we estimate that 85−90% of all ^{3}MLCT-excited triad molecules reach the radical pair state (SI pp S41−S42), in good agreement with the ^{3}MLCT decay behavior discussed above (15% unquenched ^{3}MLCT states).

The relevant acidity constants are such that in the py/pyH$^+$ mixture less than 0.1% of all triad molecules are expected to be deprotonated at the phenolic donor site (SI pp S17−S18), yet in 85−90% of all excited triads PhO$^\bullet$ and MQH$^{\bullet+}$ are formed (see above); hence, it seems clear that the observable photochemistry originates largely from triad molecules with their phenol moieties initially protonated, not from phenolate species. Furthermore, a dynamic shift of the acid−base equilibrium between PhOH and py after photoexcitation of the triad can be excluded as a major contributor, because the shift in equilibrium has only a rate constant on the order of 10^{-3} to 10^{-1} s^{-1} (SI p S43) whereas the observable time constant for product formation is several orders of magnitude faster ($\tau = 68 \pm 7$ ns; $\tau^{-1} \approx 1.5 \pm 0.2 \times 10^7$ s^{-1}).

Thus, we conclude that photoproduct formation proceeds according to the sequence of elementary steps illustrated in Scheme 1. Initial oxidation of PhOH by ^{3}MLCT-excited Ru(II) sensitizer occurs in concert with proton release to py and is rate-determining. Subsequent electron transfer from Ru(bpy)$_3^{+}$ to MQ$^+$ is followed by protonation of MQ$^\bullet$ by pyH$^+$. The overall PCET chemistry at the monoquat acceptor does not take place in concerted fashion because the initial step of the electron transfer, proton transfer sequence is sufficiently exergonic. The long-lived photoproduct stores ca. 1.2 eV and decays via a rate-determining intramolecular reverse electron transfer from MQH$^{\bullet+}$ to PhO$^\bullet$, leading to the formation of MQH^{2+} and PhO$^-$, in line with the absence of a H/D KIE for photoproduct decay. In the py/pyH$^+$ mixture, deprotonation of MQH^{2+} and protonation of PhO$^-$ are

Scheme 1. Energy Level Scheme Illustrating the Key Elementary Steps Leading to the Formation of the Long-Lived PhO$^\bullet$/MQH$^{\bullet+}$ Radical Pair and Its Subsequent Decay[a]



[a] See SI pp S21−S32 for details. CPET = concerted proton-electron transfer, ET = electron transfer, PT = proton transfer, RDS = rate determining step.

both rapid, and consequently these intermediates remain unobserved in this solvent. Only in neat pyridine can PhO^- be detected, as discussed above.

In summary, a single photon is required to drive PCET at both the phenolic donor and the monoquat acceptor, and a sequence of concerted and stepwise PCET processes is involved. The resulting long-lived radical pair state is different from simple electron–hole separation in that the charges of the donor and the acceptor remain unchanged, yet 1.2 eV of light energy are stored.

The stabilization of primary photoproducts resulting from electron transfer by coupled protonation and deprotonation reactions is important for multielectron photochemistry and the accumulation of redox equivalents. A specific key challenge is that once the first electron transfer step has occurred, electrons and holes are prone to recombine rapidly upon secondary photoexcitation.[12] However, proton uptake at the reduction site and proton release at the donor moiety produces stabilized intermediates which are less prone to recombine upon excitation with a second photon,[12,13] because there is no charge build-up. PCET photoproducts are therefore more likely to undergo secondary photoinduced electron transfer reactions that lead to the accumulation of oxidative and reductive equivalents. Nature has already implemented this strategy in photosystem II,[2] and our study represents an important step for artificial systems in that direction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b08761.

> Detailed synthetic protocols and characterization data, description of equipment and methods, supplementary electrochemical and spectroscopic data, and detailed thermochemical discussion (PDF)

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Notes

The authors declare no competing financial interest.

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