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Exploiting Potential Inversion for Photoinduced Multi-Electron Transfer and Accumulation of Redox Equivalents in a Molecular Heptad

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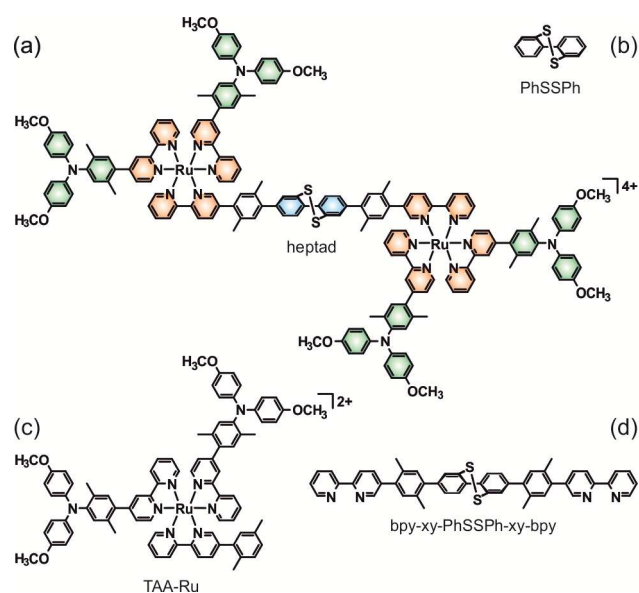
Supporting Information Placeholder

ABSTRACT: Photoinduced multi-electron transfer and reversible accumulation of redox equivalents is accomplished in a fully integrated molecular heptad comprised of four donors, two photosensitizers, and one acceptor. The second reduction of the dibenzo[1,2]dithiin acceptor occurs more easily than the first by 1.3 V, and this potential inversion facilitates the light-driven formation of a two-electron reduced state with a lifetime of 66 ns in de-aerated CH₃CN. The quantum yield for formation of this doubly charge-separated photoproduct is 0.5%. In acidic oxygen-free solution, the reduction product is a stable dithiol. Under steady-state photo-irradiation our heptad catalyzes the two-electron reduction of an aliphatic disulfide via thiolate-disulfide interchange. Exploitation of potential inversion for the light-driven accumulation of redox equivalents is unprecedented and the use of such a charge-accumulated state for multi-electron photoredox catalysis represents an important proof-of-concept.

Natural oxygenic photosynthesis relies on the temporary accumulation and storage of redox equivalents on plastoquinone and the oxygen-evolving complex before stable reduction and oxidation products are formed. Similar strategies could be interesting for artificial photosynthesis, and therefore significant attention is currently devoted to light-driven accumulation of redox equivalents in artificial systems.¹ With sacrificial electron donors or acceptors, the accumulation of multiple electrons or holes on a given molecular entity is readily achievable,² but use of such reagents does not permit sustainable solar energy conversion. Consequently, it is desirable to explore the basic concepts that allow for long-lived (> 10 ns) accumulation of redox equivalents without sacrificial reagents.

Photoinduced transfer of single electrons has been explored in many covalent donor-acceptor compounds,³ but the transfer of multiple electrons is yet a great challenge.⁴ Excitation with two or more photons can trigger a multitude of processes, many of which are either non-productive or even counter-productive.^{1, 5} Consequently, only a handful of prior studies achieved light-driven accumulation of redox equivalents in molecular systems without sacrificial reagents.^{1, 5a, 6, 7}

Scheme 1. Molecular structures of the heptad and three reference compounds.



In all these prior studies, the second redox process was thermodynamically more difficult to perform than the first, and this made the accumulation of redox equivalents all the more challenging. We hypothesized that an acceptor exhibiting redox potential inversion, i. e., a compound in which the second reduction occurs more easily than the first,⁸ could facilitate the light-driven accumulation of reduction equivalents. There are a number of possible acceptor units,⁸⁻⁹ and we were inspired by prior electrochemical and computational studies of bipyridinium disulfides and dibenzo[1,2]dithiin (PhSSPh) compounds.¹⁰ We decided to incorporate the latter as a central acceptor unit between two Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) photosensitizers equipped with peripheral tri-arylamine (TAA) donors (Scheme 1a). The plan was to excite both photosensitizers, and to search for a charge-separated state in which the central PhSSPh unit is reduced twice while two peripheral TAA donors are each singly oxidized.

The molecular heptad was synthesized in 18 individual reaction steps as described in the Supporting Information (SI pages S3-S14). The spatial separation of PhSSPh acceptor and TAA donors on separate bpy ligands simplified the synthesis but leads to a mixture of diastereomers (SI page S38). However, all elementary electron transfer steps are expected to follow predominantly through-bond pathways,¹¹ and thus the analysis of electron transfer kinetics should remain relatively straightforward.

Cyclic voltammetry of the PhSSPh reference compound (Scheme 1b) shows the typical features of potential inversion as reported previously for this and closely related compounds (SI page S16).^{10, 12} From cathodic scans, a peak potential of -1.6 V vs. SCE is measurable, while on return scans the corresponding re-oxidation wave is detected at -0.3 V vs. SCE. The shift of 1.3 V between corresponding (two-electron) half-waves is a manifestation of the redox potential inversion.¹⁰ Single reduction of PhSSPh generates a disulfide radical anion with considerable tension, which is only released after reduction with a second electron, leading to disulfide bond breaking and consequent rotation of the thiolate groups away from each other to minimize electrostatic repulsion. The peak potential at -1.6 V reflects the necessary potential for single reduction, while the potential for the second redox step is commonly associated with the peak potential of the return oxidation (-0.3 V). Thus, two-electron reduction of PhSSPh to its dithiolate form (PhS⁻PhS⁻) is thermodynamically easier by ca. 1.3 V than one-electron reduction to the dithiio monoanion (PhSSPh⁻). The potentials for TAA oxidation and all Ru(bpy)₃²⁺ related redox processes in the heptad are as expected (SI page S18).¹³

Transient absorption (TA) spectroscopy in conjunction with spectro-electrochemistry (Figure 1) provides direct evidence for the formation of the desired photoproduct comprised of two singly oxidized TAA units and the doubly reduced acceptor in de-aerated CH₃CN at 22 °C. The Ru(bpy)₃²⁺ units are excited selectively at 532 nm, and this is known to lead to reductive ³MLCT excited state quenching by TAA with a time constant of ca. 10-65 ps.^{7g, h, 13} Consequently, the characteristic absorption bands of TAA⁺ at 375 and 775 nm are readily detectable in the transient absorption spectrum recorded in neat CH₃CN (Figure 1a), in line with the difference spectrum obtained by chemical oxidation of the heptad with Cu(ClO₄)₂ (Figure 1b). The TA spectrum further exhibits a prominent absorption at 520 nm attributable to the reduced photosensitizer (Ru(bpy)₃⁺), as confirmed by comparison to the spectro-electrochemical data obtained from the TAA-Ru reference compound (Scheme 1c, Figure 1c). The most interesting spectral region is around 320 nm where the electrochemical reduction of the PhSSPh sub-unit to PhS⁻PhS⁻ leads to a diagnostic bleach (Figure 1d) due to a significant change in π -conjugation associated with this two-electron reduction. A negative signal is indeed observed in the transient absorption spectrum (Figure 1a) at 320 nm (blue dashed line). When subtracting the contribution of the oxidation product TAA⁺ (green trace in Figure 1b) from the TA spectrum (black trace in Figure 1a), the bleach at 320 nm is seen more clearly (Figure 1e). This derived spectrum indicates the formation of two different reduction products, namely PhS⁻PhS⁻ (bleach at 320 nm) and reduced photosensitizer (bands at 375 and 520 nm, bleach at 455 nm). We note that the latter exhibits significant absorption at 320 nm (Figure 1c), weakening the bleach caused by two-electron reduction of PhSSPh to PhS⁻PhS⁻ at that wavelength.

The observation of reduced photosensitizers is due to the formation of TAA⁺ / Ru(bpy)₃⁺ pairs, which can be considered as intermediates on the reaction pathway to the final desired photoproduct comprised of doubly reduced disulfide and two TAA⁺ moieties, as discussed below. The key photoproduct comprised of 2 TAA⁺ units and doubly reduced disulfide (PhS⁻PhS⁻) can only be reached as a result of the absorption of two visible photons (SI page S21), hence a quadratic power dependence of the 320-nm bleach would be expected.^{7g} Unfortunately, this signal is too weak for excitation power-dependent measurements (SI page S22), especially in the low-power regime for which such quadratic power dependence could be expected.^{7g, 14}

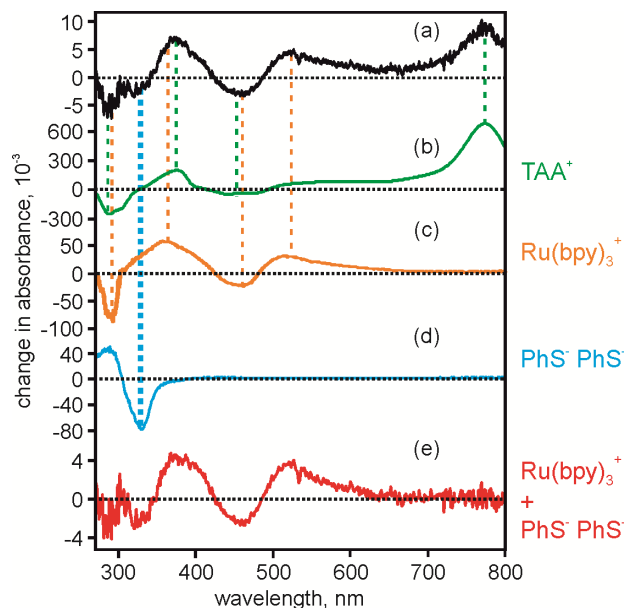


Figure 1. (a) TA spectrum of 5.0 μM heptad in CH_3CN , measured in a time window of 100 ns immediately following excitation at 532 nm. (b) Difference spectrum after oxidation of TAA to TAA⁺ using $\text{Cu}(\text{ClO}_4)_2$ and the heptad. (c) Difference spectrum after reduction of TAA-Ru in CH_3CN containing 0.1 M TBAPF₆ at -1.6 V vs. SCE. (d) Difference spectrum after (twofold) reduction of bpy-xy-PhSSPh-xy-bpy (99 μM) in CH_2Cl_2 at -2.0 V vs. SCE. (e) Spectrum obtained after subtracting the green trace in (b) from the black trace in (a). (Green trace scaled to match the intensity of the black trace at 775 nm prior to subtraction).

When monitoring the TA signal at 775 nm after excitation at 532 nm with laser pulses of ca. 10 ns duration in CH₃CN, one observes a tri-exponential decay with time components of ≤ 10 , 66, and 645 ns in relative importance of 80%:5%:15%, analogous decay behavior is detectable at other wavelengths (SI page S25). Thus, all photoproducts form within the duration of the laser pulses and start to decay immediately. The shortest, instrumentally limited decay component (≤ 10 ns) is attributed to a proximal TAA⁺ / Ru(bpy)₃⁺ pair. Charge recombination from this state is known to be rapid from closely related molecules.¹³ In time-gated measurements the 320-nm bleach is no longer detectable after a delay of 500 ns (SI page S26), and consequently the time constant of 66 ns is attributed to the key photoproduct (TAA⁺-Ru(bpy)₃²⁺-PhS⁻PhS⁻-Ru(bpy)₃²⁺-TAA⁺). However, the spectral signatures of TAA⁺ and Ru(bpy)₃⁺ remain observable even after 500 ns hence the lifetime of 645 ns must be caused by TAA⁺ / Ru(bpy)₃⁺ pairs undergoing slow reverse electron transfer. It seems possible that this occurs in a photoproduct of the type TAA⁺-Ru(bpy)₃²⁺-PhSSPh-Ru(bpy)₃²⁺-TAA, in which the oxidizing and reducing equivalents are on distant TAA and photosensitizer units (SI page S25). For an excitation pulse energy of ~ 34 mJ using a laser beam irradiating the entire cuvette, we determined an absolute quantum yield of 0.5% for formation of the desired two-electron reduction product (SI page S27). The formation of PhS⁻PhS⁻ via bimolecular disproportionation is not possible on a timescale of 10 ns at a sample concentration of 5 μM .¹⁵ On a given photosensitizer unit, the presence of both a TAA⁺ and a TAA unit leads to an organic mixed valence situation.¹⁶

Under acidic conditions, protonation of the dithiolate photoproduct is expected, and consequently we anticipated the formation of an even longer-lived dithiol product. Indeed, in de-aerated CH₃CN with 0.1 M monochloroacetic acid at 22 °C,

significantly slower transient absorption decays are observed (SI page S29). In the presence of 0.2 M of *p*-toluenesulfonic acid (TsOH) the dithiol photoproduct accumulates under steady-state irradiation with a 455-nm (3.5 W) LED (Figure 2). The UV-Vis difference spectra recorded as a function of irradiation time (Figure 2a) show both the characteristic changes expected for oxidation of TAA to TAA⁺ (Figure 2b) and those anticipated for the two-fold reduction of the PhSSPh sub-unit (Figure 2c). In this case, the possibility of bimolecular reactions between individual heptads can of course not be excluded.¹⁷

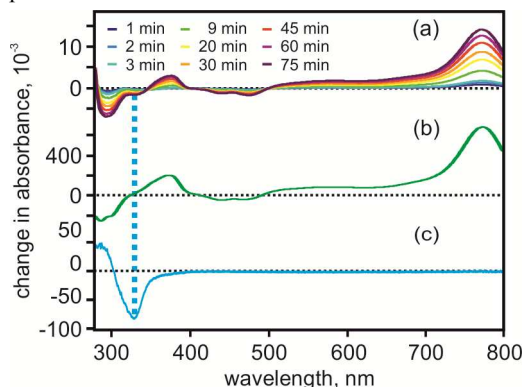
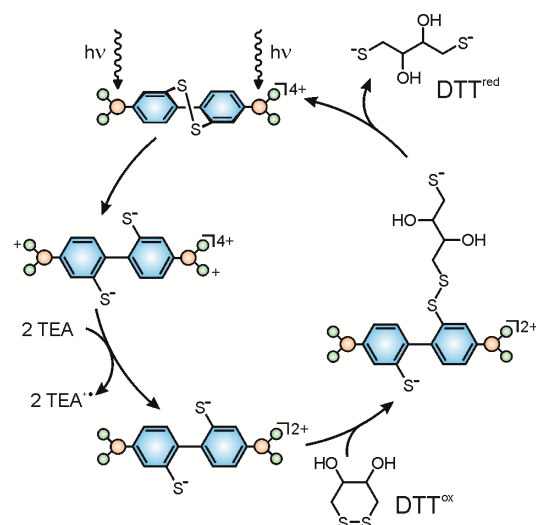


Figure 2. (a) UV-Vis difference spectra after different irradiation times ($\lambda_{\text{exc}} = 455$ nm) from a 5.3 μM solution of the heptad in CH_3CN with 0.2 M TsOH. (b) Difference spectrum obtained by chemical oxidation of the heptad with $\text{Cu}(\text{ClO}_4)_2$. (c) Difference spectrum obtained after reduction of bpy-xy-PhSSPh-xy-bpy (99 μM) in CH_2Cl_2 at -2.0 V vs. SCE.

Next, we explored whether the heptad can function as a multi-electron donating photocatalyst. With its photogenerated aromatic dithiolate or dithiol entity, the heptad was anticipated to undergo thiolate-disulfide interchange with aliphatic disulfides such as *trans*-4,5-dihydroxy-1,2-dithiane (DTT^{ox}) as illustrated in Scheme 2.¹⁸ We hypothesized that after formation of the PhS^-PhS^- photoproduct seen in Figure 1a/e, the TAA^+ moieties can be reduced back to neutral TAA with a sacrificial electron donor. Nucleophilic attack of the PhS^-PhS^- dithiolate at the DTT^{ox} disulfide can then form the aliphatic dithiolate DTT^{red} in two steps, coupled to oxidation of PhS^-PhS^- to the aromatic PhSSPh disulfide, thereby closing the catalytic cycle. Using 0.1 M triethylamine (TEA) as a sacrificial donor, 22 mM DTT^{ox} substrate, and 20 μM heptad in dry, de-aerated CH_3CN at 22 $^\circ\text{C}$, photoirradiation at 455 nm with an LED (3.5 W) for 20 hours led to the desired DTT^{red} product, and a turnover number (TON) of 41 was determined for the heptad catalyst (SI page S32). When using either 40 μM $\text{Ru}(\text{bpy})_3^{2+}$ or TAA-Ru reference compound, TONs of only 9 were determined. Absolute product yields are low (3.6% in the case of the heptad), because the equilibrium of the reaction $\text{PhS}^-\text{PhS}^- + \text{DTT}^{\text{ox}} \rightleftharpoons \text{PhSSPh} + \text{DTT}^{\text{red}}$ strongly disfavors product formation hence this is not a shortcoming of the heptad catalyst (SI page S33). The observation that the heptad catalyzes the reaction ca. 4.5 times better than the reference compounds is consistent with a significant contribution of the thiolate-disulfide interchange mechanism in Scheme 2 and represents an important proof-of-concept. The reference compounds instead are likely to lead to DTT^{red} via a single electron transfer route.¹⁹ The use of TEA favors this pathway, because its primary oxidation and deprotonation leads to a highly reducing α -aminoalkyl radical that can provide a second electron in a subsequent dark reaction after an initial light-induced reaction step.²⁰ Expectedly, control experiments performed in the dark or in absence of TEA led to no product (SI page S32).

Scheme 2. Proposed mechanism for the catalytic reduction of an aliphatic disulfide (DTT^{ox}).



In summary, potential inversion can be exploited for the light-driven accumulation of redox equivalents without sacrificial reagents. In neat CH_3CN , the aromatic disulfide acceptor is converted to its dithiolate form after excitation of two $\text{Ru}(\text{bpy})_3^{2+}$ sensitizers with visible light, and this photoproduct lives for ca. 66 ns before reverse electron transfer with the covalently attached TAA^+ occurs. The quantum yield for formation of this photoproduct was 0.5%. In the presence of strong acid, proton-coupled electron transfer (PCET) leads to a stable dithiol. When using excess external reductant, the heptad catalyzes thiolate-disulfide interchange with an aliphatic substrate, thereby providing the important proof-of-principle that charge-accumulated states of donor-sensitizer-acceptor compounds are useful for light-driven multi-electron catalysis.

ASSOCIATED CONTENT

Supporting Information

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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