

Charge Accumulation and Multi-Electron Photoredox Chemistry with a Sensitizer-Catalyst-Sensitizer Triad

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Abstract: Photoinduced electron transfer in donor-sensitizer-acceptor compounds usually leads to simple electron-hole pairs and photoredox catalysis typically relies on single electron transfer (SET) events. We report on a molecular triad able to accumulate two electrons on a central dibenzo[1,2]dithiin moiety flanked by two peripheral Ru(II) photosensitizers. Under continuous illumination, the doubly reduced form of the dibenzo[1,2]dithiin undergoes thiolate-disulfide exchange with an aliphatic disulfide substrate, thereby acting as a two-electron catalyst after two initial SET events with triethylamine at the Ru(II) sensitizers. The use of a relatively simple triad for coupling two separate SET processes to a subsequent two-electron reduction is an important conceptual advance from photoinduced SET and light-driven charge accumulation towards multi-electron photoredox catalysis. This is relevant for artificial photosynthesis and light-driven multi-electron chemistry in general.

Investigations of long-range electron transfer often rely on multi-component systems comprised of a donor (D), a photosensitizer (PS), and an acceptor (A) to result in molecular dyads or triads (Figure 1a).^[1] Excitation of the sensitizer then commonly leads to the formation of an electron-hole pair, and many studies focused on obtaining such photoproducts with optimal efficiency and on making them as long-lived as possible. Much of this research was inspired by the primary electron transfer events occurring in photosystem II, but it is yet a long way to artificial photosynthesis. One fundamental problem is that simple electron-hole pairs are not directly useable for fuel-forming reactions requiring multiple redox equivalents.^[2] Consequently, there is considerable interest in photoinduced multi-electron transfer and the light-driven accumulation of electrons and holes. In recent years, an increasing number of molecular systems following the concept illustrated by Figure 1b have been reported, in which excitation of two photosensitizers leads to electron accumulation on a central acceptor unit.^[3] Most of these studies relied on sacrificial donors, but there are now a handful of fully integrated (all-covalent) systems capable of completely reversible photoinduced multi-electron transfer.^[4]

Using the accumulated redox equivalents to catalyze chemical multi-electron conversions represents the next conceptually important advance that needs to be taken on the way to artificial photosynthesis (Figure 1c),^[5] and for some nanoparticle or quantum dot-based systems this has already been achieved.^[6] Building on the prior charge accumulation studies with molecular

systems, it seemed logical to incorporate a catalyst flanked by two peripheral photosensitizers in a molecular triad.

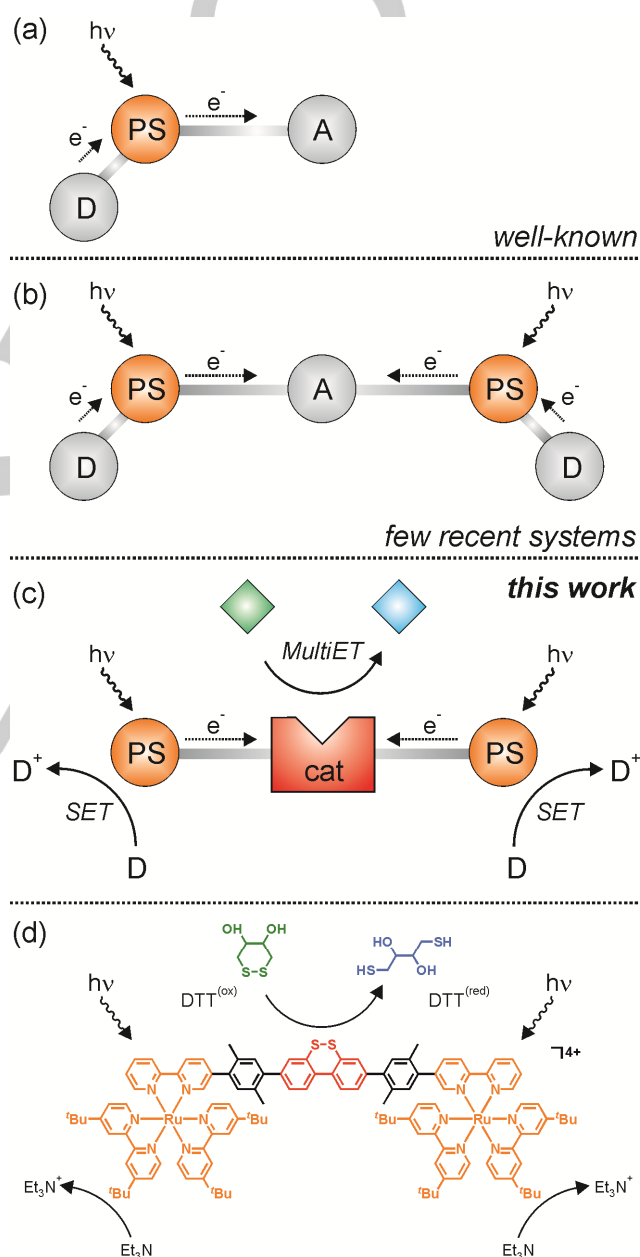


Figure 1. (a) Donor-photosensitizer-acceptor triad for SET; (b) donor-photosensitizer-acceptor ensemble for light-induced multi-electron transfer and charge accumulation; (c) sensitizer-catalyst-sensitizer triad for multi-electron photocatalysis; (d) specific system investigated in this work.

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We chose a dibenzo[1,2]dithiin unit as a central acceptor and catalyst (Figure 1d, red part), because this moiety is known to facilitate the uptake of multiple electrons through redox potential inversion (SI page S7),^[7] and because its reduced (dithiolate) form is able to undergo thiolate-disulfide exchange with aliphatic disulfides. This combined electron-accumulating and catalyst entity is connected on both sides to bpy (2,2'-bipyridine) ligands that chelate $[\text{Ru}(\text{Bubpy})_2]^{2+}$ fragments ('Bubpy' = 4,4'-di(*tert*-butyl)-2,2'-bipyridine). The aim was to irradiate the resulting triad in presence of excess electron donor (Et_3N in Figure 1d), and to investigate whether this would permit the light-driven two-electron reduction of an aliphatic disulfide to its dithiolate form. As a model substrate we chose *trans*-4,5-dihydroxy-1,2-dithiane (green in Figure 1d, $\text{DTT}^{(\text{ox})}$) which can be reduced to 1,4-dimercaptobutane-2,3-diol (blue in Figure 1d, $\text{DTT}^{(\text{red})}$). Whilst this particular conversion is not of specific interest for solar energy conversion its successful completion would represent an important proof-of-concept, particularly given the relative simplicity of the triad compared to previously reported donor-sensitizer-acceptor compounds investigated in the context of reversible multi-electron transfer and charge accumulation.^[4, 8] The triad in Figure 1d is comprised of only three components for the coupling of two separate photoinduced SET events to an overall two-electron reduction of an organic substrate, complementing prior work on sensitizer-catalyst systems geared at the photochemical H_2 production or the light-driven reduction of CO_2 .^[9]

The synthesis and characterization of the triad is described in the Supporting Information (SI, pages S2-S5). Its UV-Vis absorption spectrum in CH_3CN shows the expected MLCT and $\pi-\pi^*$ absorptions of the Ru(II) sensitizers at 450 / 290 nm (Figure 2a) and a band at 330 nm caused by the dibenzo[1,2]dithiin. Upon irradiation of the triad in de-aerated CH_3CN (87 μM) at 455 nm (LED, 3.5 W) in presence of 0.5 M Et_3N , the spectral changes in Figure 2b become observable. These changes signal the light-induced reduction of the sensitizer and dibenzo[1,2]dithiin units as discussed in the following. The increased optical densities at 385 and 510 nm as well as the bleaches at 290 / 450 nm are diagnostic for the reduced photosensitizer, as confirmed by the spectro-electrochemical data obtained for a $[\text{Ru}(\text{Bubpy})_2(\text{bpy})]^{2+}$ reference complex (Figure 2c, see SI page S3 for molecular structure). However, the difference spectra in Figure 2b exhibit an additional bleach at 330 nm that can be attributed unambiguously to the dibenzo[1,2]dithiin reduction product based on the spectro-electrochemical data of the isolated dibenzo[1,2]dithiin compound in Figure 2d. Importantly, the spectral change at 330 nm reflects the two-electron reduction, which is more facile than single reduction in this particular acceptor (SI page S7).^[4g, 7]

One-electron reduction is known to lead to a disulfide radical anion which dissociates only upon secondary reduction, thereby releasing considerable ring tension and causing the potential inversion in dibenzo[1,2]dithiin. Thus, based on the data in Figure 2 we conclude that the two-electron reduced form of the dibenzo[1,2]dithiin unit is obtained along with one-electron reduced photosensitizer upon continuous irradiation with blue light over several minutes (see SI page S8 for a mechanistic discussion).

This electron accumulation sets the stage for multi-electron catalysis. Aliphatic disulfides have one-electron reduction potentials varying from -2.72 V vs. SCE for di-*tert*-butyl disulfide to -1.77 V vs. SCE for 1,2-dithiolane,^[10] but the one-electron reduction potential of the $[\text{Ru}(\text{Bubpy})_2(\text{bpy})]^{2+}$ unit is only -1.36 V vs. SCE (SI page S7). Consequently, SET from the one-electron reduced photosensitizers to the $\text{DDT}^{(\text{ox})}$ substrate should be a disfavored reaction pathway. Moreover, $\text{DDT}^{(\text{ox})}$ has a cyclic structure that is expected to render disulfide bond cleavage upon SET reduction entropically less favored compared to acyclic disulfides. The combination of all these factors is expected to favor thiolate-disulfide exchange as a reaction pathway leading to the formation of $\text{DDT}^{(\text{red})}$, and this is only possible after initial accumulation of two electrons on the dibenzo[1,2]dithiin. Under the photochemical conditions with sacrificial Et_3N this two-electron reduction is expected to lead to a chemical equilibrium between dithiolate and dithiol forms of the reduced dibenzo[1,2]dithiin, and only the former (present as a minority species) can engage in thiolate-disulfide exchange with the $\text{DTT}^{(\text{ox})}$ substrate (see below and SI page S8). Nevertheless, our system should be useable to test the concept illustrated in Figure 1c.

However, it should be kept in mind that the oxidation of Et_3N liberates iminium ions ($\text{Et}_2\text{N}^+=\text{CHCH}_3$) which can be reduced to α -alkyl amine radicals under the conditions used here, and subsequent hydrogen atom transfer (HAT) with thiols (in particular $\text{DTT}^{(\text{red})}$) leads back to Et_3N (see SI page S9 for more detailed discussion (eqs. S3, S4)).^[11] This light-induced reverse

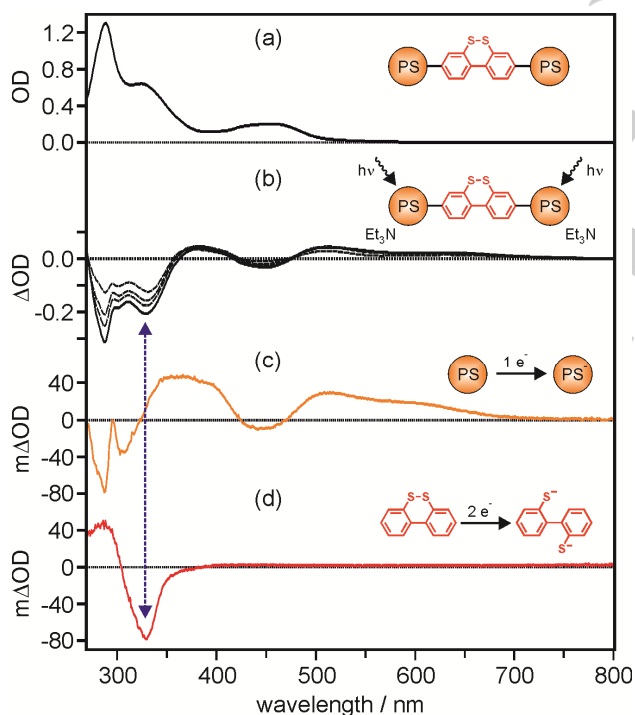


Figure 2. (a) UV-Vis absorption spectrum of the triad from Figure 1d (87 μM) in CH_3CN ; (b) UV-Vis spectral changes observed in the course of irradiation of the triad at 455 nm in presence of 0.5 M Et_3N ; (c) spectral changes associated with the electrochemical one-electron reduction of $[\text{Ru}(\text{Bubpy})_2(\text{bpy})]^{2+}$ at -1.8 V vs. SCE in CH_3CN ; (d) spectral changes associated with two-electron reduction of the disulfide acceptor to its dithiolate form at -2.0 V vs. SCE in CH_2Cl_2 , performed with the free (uncoordinated) key ligand of the triad.

reaction is expected to limit the overall attainable yield for conversion of $\text{DTT}^{(\text{ox})}$ to $\text{DTT}^{(\text{red})}$ considerably. Moreover, the chemical equilibrium between an aromatic (more electron-deficient) dithiol (the reduced triad) and an aliphatic (more electron-rich) dithiol ($\text{DTT}^{(\text{red})}$) is not in favor of $\text{DTT}^{(\text{red})}$ formation (SI page S9 (eq. S1)).

Table 1. Turnover numbers (TONs) for the light-driven reduction of (22 mM) $\text{DTT}^{(\text{ox})}$ to $\text{DTT}^{(\text{red})}$ performed in de-aerated CH_3CN at 22 °C under various conditions.

entry	catalyst	Et_3N	hv	TON
1	triad	0.1 M	455 nm	42
2	triad	0.1 M	none	0
3	triad	none	455 nm	0
4	$[\text{Ru}(\text{Bubpy})_2(\text{bpy})]^{2+}$	0.1 M	455 nm	4

Nevertheless, photoirradiation experiments performed with 20 μM triad, 22 mM $\text{DTT}^{(\text{ox})}$ and 0.1 M Et_3N in de-aerated CH_3CN at 22 °C demonstrate that a proof-of-principle is possible (Table 1, entry 1). Following illumination with a 455-nm LED (3.5 W) over 20 hours, roughly 4% of $\text{DTT}^{(\text{ox})}$ are converted to $\text{DTT}^{(\text{red})}$ according to $^1\text{H-NMR}$ experiments (SI pages S10-S12), and this corresponds to a turnover number (TON) of 42 (last column of Table 1) for the triad catalyst. Control experiments performed in absence of light or without Et_3N lead to no product at all (Table 1, entries 2 & 3). On the other hand, when using the $[\text{Ru}(\text{Bubpy})_2(\text{bpy})]^{2+}$ reference complex (40 μM) instead of the triad, some very modest conversion of $\text{DTT}^{(\text{ox})}$ to $\text{DTT}^{(\text{red})}$ is observed (entry 4). The yield in this case is 0.7% and the TON is 4. The reaction under these conditions must be due to SET and subsequent cleavage of the disulfide bond. After initial electron uptake, the disulfide bond elongates and a loose radical anion is formed with the SOMO localized at the disulfide bond, lowering its bond dissociation energy.³⁸⁻⁴¹ Cleavage of the S-S bond leads to a thiyl radical that can then be reduced in a second step. The use of Et_3N favors that pathway to a certain extent, because the Et_3N^+ oxidation product is known to react onwards as a proton/electron donor.^[12]

The key finding is that the TON for the triad is 10 times higher than for the $[\text{Ru}(\text{Bubpy})_2(\text{bpy})]^{2+}$ reference complex, and this is attributed to the mechanism illustrated by Figure 3. Light-driven charge accumulation on the dibenzo[1,2]dithiin unit leads to an aromatic dithiolate that subsequently undergoes dithiolate-disulfide exchange with the $\text{DTT}^{(\text{ox})}$ substrate. Electron accumulation is favored by redox potential inversion and the use of excess Et_3N , but overall conversion is modest due to reverse reactions involving the $\text{DTT}^{(\text{red})}$ reduction product (see above and SI page S9 (eqs. S3, S4); grey dotted arrows in Figure 3). Nevertheless, the large observable difference in TONs between the triad and the reference complex strongly suggests that the mechanism in Figure 3 operates more efficiently than SET pathways with our model substrate.

The triad in Figure 1d has a relatively simple molecular structure,^[4] and it provides the proof-of-concept that multi-electron photoredox chemistry on organic substrates after initial

charge accumulation is feasible using the integrated sensitizer-catalyst approach. This new strategy could provide access to photochemical conversions that have so far been unattainable with the classical SET approach.

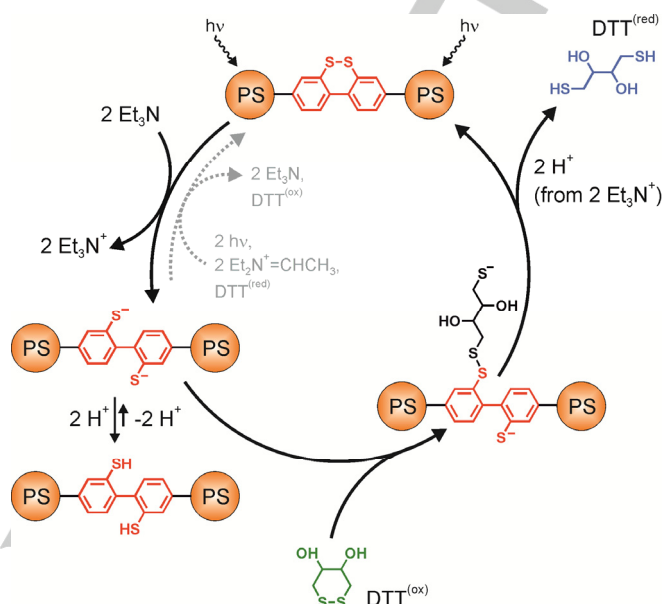


Figure 3. Proposed mechanism for the photochemical conversion of $\text{DTT}^{(\text{ox})}$ to $\text{DTT}^{(\text{red})}$: Electron accumulation on dibenzo[1,2]dithiin followed by dithiolate-disulfide exchange. The dotted grey arrows mark a counter-productive reaction. See SI pages S8-S9 (eqs. S1-S4) for further information.

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Keywords: electron transfer • donor-acceptor systems • photochemistry • photocatalysis • UV/Vis spectroscopy

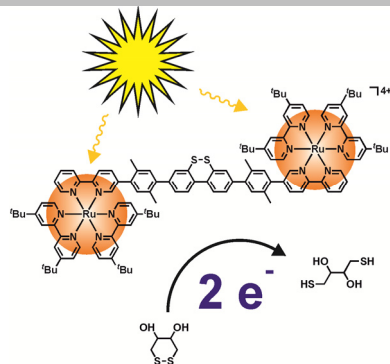
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Entry for the Table of Contents

COMMUNICATION

Photoinduced multi-electron transfer is made applicable to catalysis of an organic transformation, illustrating the usefulness of covalent sensitizer-catalyst constructs for initial charge accumulation followed by organic multi-electron photoredox chemistry.



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