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**Electron Accumulation on Naphthalene Diimide
Photosensitized by [Ru(2,2'-Bipyridine)₃]²⁺**

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Electron Accumulation on Naphthalene Diimide Photosensitized by $[\text{Ru}(2,2'\text{-Bipyridine})_3]^{2+}$

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ABSTRACT

In a molecular triad comprised of a central naphthalene diimide (NDI) unit flanked by two $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) sensitizers, NDI^{2-} is formed after irradiation with visible light in de-aerated CH_3CN in presence of excess triethylamine. The mechanism for this electron accumulation involves a combination of photoinduced and thermal elementary steps. In a structurally related molecular pentad with two peripheral triarylamine (TAA) electron donors attached covalently to a central $[\text{Ru}(\text{bpy})_3]^{2+}$ -NDI- $[\text{Ru}(\text{bpy})_3]^{2+}$ core but no sacrificial reagents present, photoexcitation only leads to NDI^- (and TAA^+), whereas NDI^{2-} is unattainable due to rapid electron transfer events counteracting charge accumulation. For solar energy conversion, this finding means that fully integrated systems with covalently linked photosensitizers and catalysts are not necessarily superior to multi-component systems, because the fully integrated

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3 systems can suffer from rapid undesired electron transfer events that impede multi-electron
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5 reactions on the catalyst.
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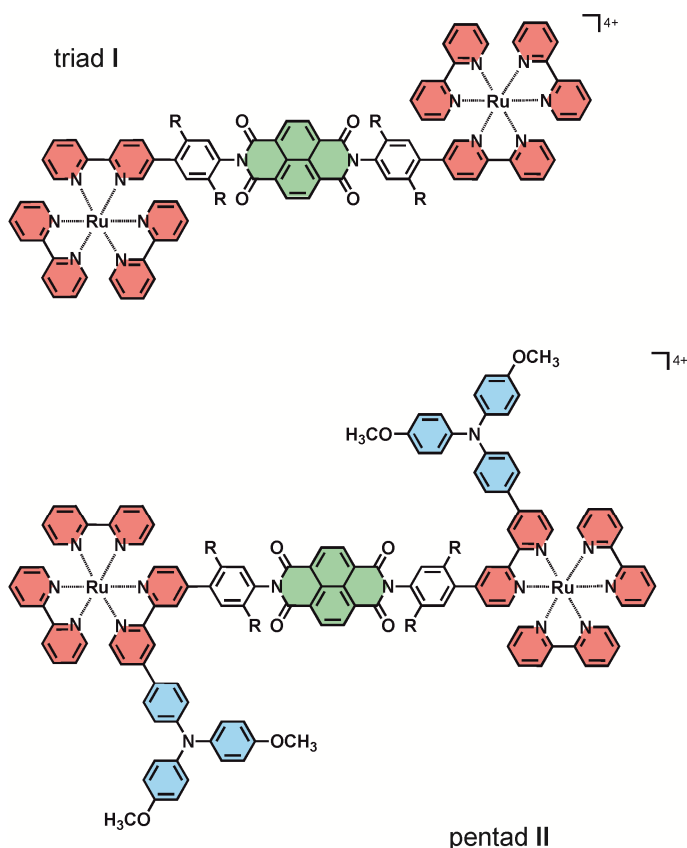
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16 In order to perform multi-electron redox chemistry using visible light as an energy input, it is
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18 desirable to understand the basic principles of the photo-driven accumulation of redox
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20 equivalents.^{1,2} Many prior studies employed sacrificial reagents to generate solar fuels using
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22 various molecular catalysts, but often the focus was mainly on product formation rather than on
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24 understanding the key elementary step of charge accumulation.³⁻¹⁵ Photosensitizers and catalysts
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26 are often attached covalently to each other, but in some cases the resulting fully integrated
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28 assemblies do not exhibit strongly improved properties compared to multi-component systems in
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30 which there are no covalent linkages between individual components or reactants. Against this
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32 background, we became interested in performing a direct comparison of light-induced charge
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34 accumulation in multi-component and unimolecular systems with particular focus on mechanistic
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36 aspects.
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42 Several prior studies concentrated specifically on the phenomenon of light-driven charge
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44 accumulation in artificial molecular systems, as highlighted in three recent reviews.¹⁶⁻¹⁸ Many of
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46 the studied systems relied on sacrificial reagents,¹⁹⁻²⁹ but newer systems (as well as a few older
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48 ones) exhibit intramolecular charge accumulation in absence of sacrificial substances.³⁰⁻³⁵
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50 Nevertheless, compared to the ordinary photoinduced transfer of single electrons, light-induced
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52 charge accumulation is still poorly explored, for example because multiple photons are usually
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3 required to drive multiple electron transfers, and because there can be many processes that
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5 counteract charge accumulation after primary charge separation.
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10 **Scheme 1.** Molecular structures of triad **I** and pentad **II**.



44 In this work, we explored triad **I** and pentad **II** (Scheme 1) with a view to obtaining doubly
45 reduced naphthalene diimide (NDI^{2-}) after excitation of the covalently attached $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy
46 = 2,2'-bipyridine) photosensitizers with visible light. NDI is well suited for studies with UV-Vis
47 spectroscopy because its neutral, singly, and doubly reduced forms exhibit diagnostic, easily
48 distinguishable signatures.³⁶ We aimed to explore how charge accumulation on NDI can be
49 achieved with a standard photosensitizer such as $[\text{Ru}(\text{bpy})_3]^{2+}$, to understand its mechanisms in
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3 detail, and to obtain insight into the factors limiting its overall efficiency. Through direct
4 comparison of triad **I** (which requires sacrificial electron donors) and pentad **II** (which has
5 covalently attached donors), we aimed to identify advantages and disadvantages of multi-
6 component versus fully integrated (covalently linked) systems for photo-induced charge
7 accumulation, and more generally, for artificial photosynthesis relying on multi-electron
8 chemistry.
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20 RESULTS AND DISCUSSION

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24 Syntheses and characterization data of triad **I** and pentad **II** are reported in the Supporting
25 Information (SI). Both compounds have the $[\text{Ru}(\text{bpy})_3]^{2+}$ -NDI- $[\text{Ru}(\text{bpy})_3]^{2+}$ core motif in
26 common, but with different connectivity between sub-units. This is owed to synthetic challenges
27 faced in the course of attempts to make a pentad which is structurally strictly analogous to triad **I**
28 (i. e., with 5,5'- instead of 4,4'-substituted bpy units). This structural difference is expected to
29 entail significantly stronger electronic communication between sub-units in the pentad because
30 electronic coupling across the 4- and 4'-positions of bpy is usually stronger than across its 5- and
31 5'-positions.^{37,38}
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43 The cyclic voltammograms of **I** and **II** are essentially a superposition of the individual
44 voltammograms of their sub-components (SI, Figure S1 and S2). The first two reductions are
45 NDI-based, whereas $[\text{Ru}(\text{bpy})_3]^{2+}$ -localized reductions appear at more negative potentials (Table
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Table 1. Redox potentials ($E_{1/2}$ in Volts vs. Fc^+/Fc) of the individual components of triad **I** and pentad **II** in CH_3CN at 25 °C. $E_{p,a}-E_{p,c}$ (in mV) is the difference in anodic and cathodic peak potentials.

| redox couple | triad I | | pentad II | |
|------------------------------|----------------|------------------------|------------------|------------------------|
| | $E_{1/2}$ [V] | $E_{p,a}-E_{p,c}$ [mV] | $E_{1/2}$ [V] | $E_{p,a}-E_{p,c}$ [mV] |
| TAA^+/TAA | N/A | N/A | 0.38 | 103 |
| NDI/NDI^- | -0.83 | 82 | -0.89 | 70 |
| $\text{NDI}/\text{NDI}^{2-}$ | -1.33 | 60 | -1.34 | 65 |
| bpy/bpy^- | -1.53 | 99 | -1.72 | 112 |

UV-Vis spectra of **I** and **II** in CH_3CN exhibit the typical MLCT absorptions of the $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophores and $\pi-\pi^*$ transitions on bpy, NDI, and TAA at shorter wavelengths (SI, Figure S3). Selective excitation of the $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophore in the visible spectral range is readily possible, but given the direct attachment of *p*-phenylene substituents to one of its bpy ligands, consideration of the ruthenium chromophore as an isolated $[\text{Ru}(\text{bpy})_3]^{2+}$ complex is a somewhat crude (but for our purposes nevertheless sufficient) approximation.³⁹

Charge accumulation studies were performed on $1.7 \cdot 10^{-5}$ M solutions of **I** in de-aerated CH_3CN containing various concentrations of triethylamine (Et_3N) or tetra-*n*-butylammonium 5,6-isopropylidene ascorbate ($\text{TBA}^+ \text{iAsc}^-$). Continuous irradiation at 410 nm with a flux of $(3.22 \pm 0.14) \cdot 10^{16}$ photons / s occurred in a commercial spectrofluorimeter over several minutes (see SI for details). In presence of 0.5 M Et_3N , the spectral changes shown in Figure 1a appear in the course of the first 30 s of photo-irradiation.

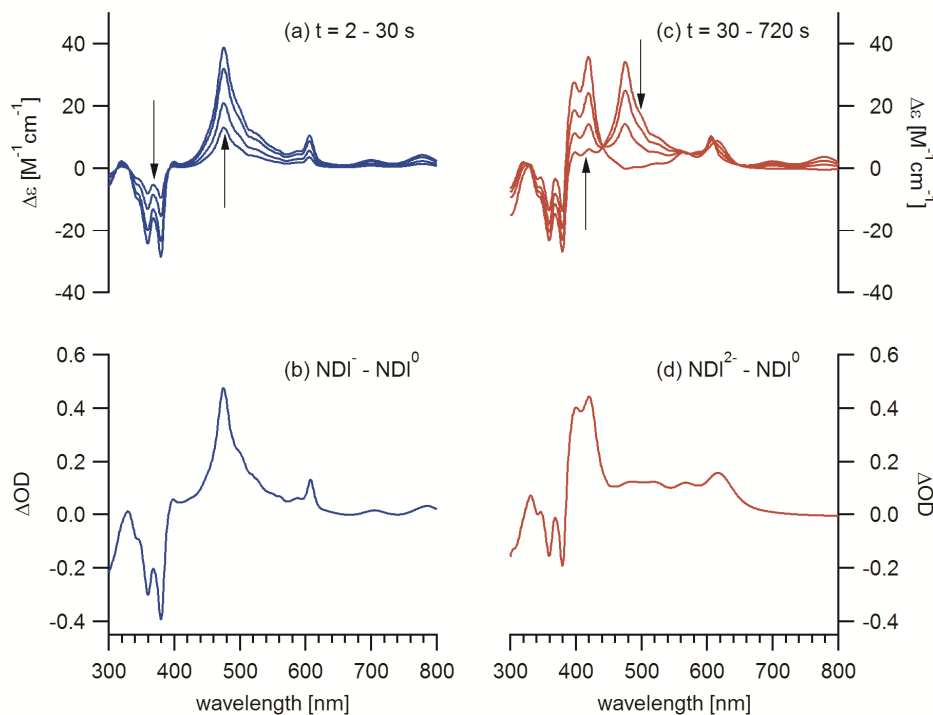
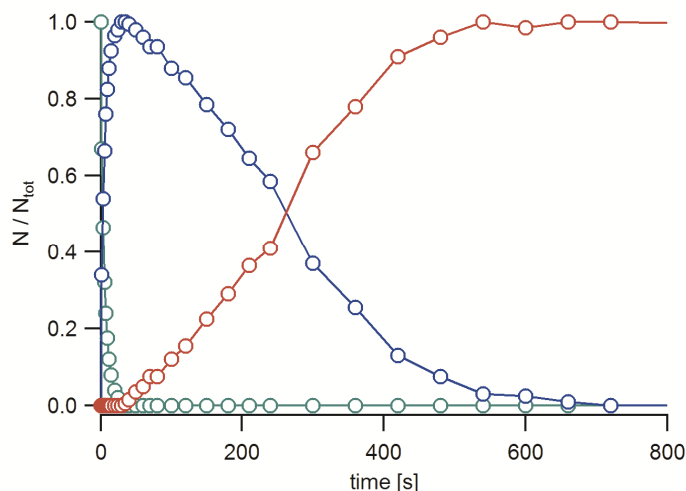


Figure 1. (a) UV-Vis difference spectra measured on a $1.7 \cdot 10^{-5}$ M solution of triad **I** in deaerated CH_3CN containing 0.5 M Et_3N . Irradiation occurred with a flux of $(3.22 \pm 0.14) \cdot 10^{16}$ photons /s at 410 nm over time intervals ranging from 2 s to 30 s. The spectrum measured at $t = 0$ s served as a baseline. (b) UV-Vis difference spectrum obtained after chemical reduction of the NDI unit in triad **I** to NDI^- , using benzophenone radical anion in THF as a chemical reductant. The spectrum of the triad prior to reduction served as a baseline. (c) UV-Vis difference spectra of the same solution as in (a) measured after irradiation times between 30 s and 720 s. (d) UV-Vis difference spectrum obtained after reduction of NDI in triad **I** to NDI^{2-} using benzophenone radical anion in THF; the spectrum measured prior to adding the chemical reductant served as a baseline.

Comparison with the UV-Vis difference spectrum obtained from an experiment in which the NDI unit of **I** in dry THF was reduced to NDI^- with benzophenone radical anion (Figure 1b)

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3 shows that the main photochemical reduction product after 30 s is NDI^- while $[\text{Ru}(\text{bpy})_3]^{2+}$ must
4 be in its initial (ground) state. Continued irradiation for another 690 s under the same conditions
5 then induces the spectral changes shown in Figure 1c. The final spectrum is compatible with the
6 formation of NDI^{2-} , as the comparison with the difference spectrum obtained after chemical
7 reduction of the NDI unit of **I** to NDI^{2-} in THF (Figure 1d) shows. From the difference spectra, it
8 becomes evident why 410 nm was chosen for excitation: At this wavelength the changes in
9 optical density in the course of the conversion of NDI to NDI^- and finally NDI^{2-} are
10 comparatively small, and it remains possible to excite relatively selectively into the $[\text{Ru}(\text{bpy})_3]^{2+}$
11 chromophore. Direct excitation into NDI^- or NDI^{2-} could potentially induce energy-wasting
12 electron transfer events (see below).^{17,31,40,41}



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46 **Figure 2.** Relative proportions (molar fractions) of NDI (green), NDI^- (blue), and NDI^{2-} (red)
47 present in triad **I** after different irradiation times. The flux used for excitation at 410 nm was
48 $(3.22 \pm 0.14) \cdot 10^{16}$ photons /s, and the sample contained $3.4 \cdot 10^{-8}$ mol of triad **I**. This corresponds to
49 roughly 2 photons per molecule per second. Some of the quantum yields reported in Table 2
50 were extracted from this data.
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Table 2. Quantum yields for formation of NDI^- and NDI^{2-} when irradiating triad **I** at 410 nm in de-aerated CH_3CN at 25 °C in presence of different concentrations of Et_3N . The experimental uncertainties are ~20%.

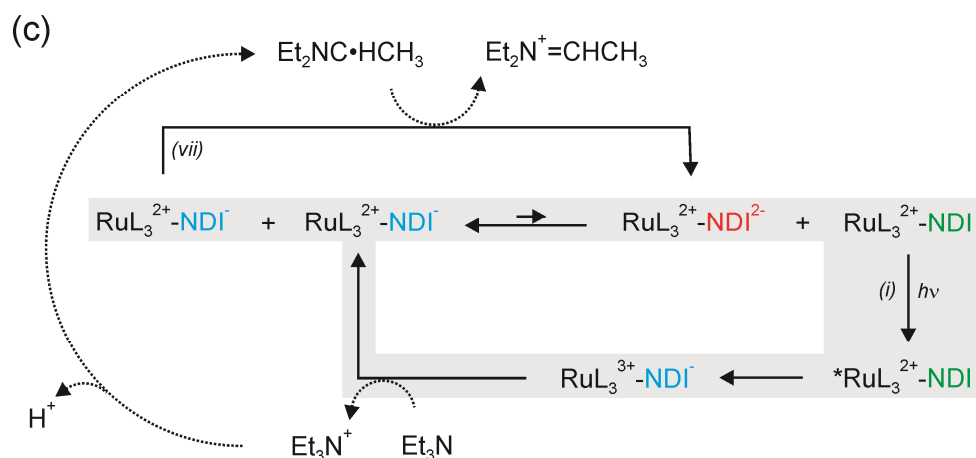
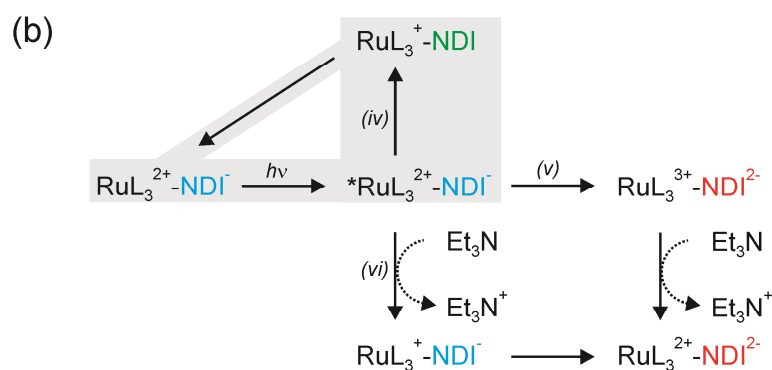
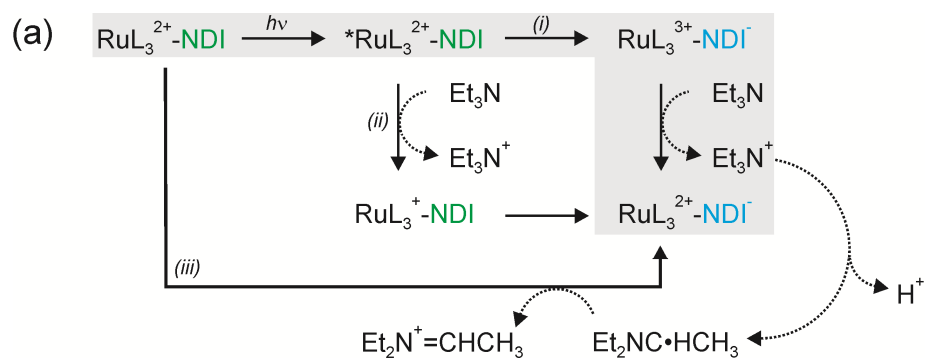
| $[\text{Et}_3\text{N}] / \text{M}$ | $\phi (\text{NDI} \rightarrow \text{NDI}^-)$ | $\phi (\text{NDI}^- \rightarrow \text{NDI}^{2-})$ |
|------------------------------------|--|---|
| 0.10 | 0.061 | 0.00026 |
| 0.25 | 0.079 | 0.00141 |
| 0.50 | 0.107 | 0.00150 |

From the difference spectra in Figure 1a and 1c the proportions of NDI^0 , NDI^- , and NDI^{2-} at different irradiation times can be determined. The resulting speciation curves (Figure 2) indicate that in presence of 0.5 M Et_3N the population of NDI^- maximizes at ca. 30 s, and after 720 s the formation of NDI^{2-} is essentially complete. When using 0.25 M Et_3N the kinetics are similar, but with 0.1 M Et_3N they are markedly slower (SI, Figures S4 and S5). These irradiation times are obviously dependent on triad concentration and irradiation flux, and consequently it is more meaningful to report quantum yields. In the first few seconds of the conversion of NDI^0 to NDI^- , as well as in the conversion of NDI^- to NDI^{2-} , the growth of the new absorption signals is approximately linear, and we used these (short) time regimes to estimate the quantum yields (ϕ) in Table 2. The key observation is that the conversion of NDI^- to NDI^{2-} has a markedly lower quantum yield than the formation of NDI^- from NDI^0 . Not surprisingly, the electron-accumulating step is therefore the more difficult one to accomplish.

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Mechanistic insight comes from transient absorption spectroscopy and luminescence quenching experiments. Excitation of triad **I** at 532 nm in de-aerated CH₃CN in absence of Et₃N induces intramolecular electron transfer from photoexcited [Ru(bpy)₃]²⁺ to NDI (SI, Figure S6) with a time constant of 300 ps (SI, Figure S7a). Subsequently, thermal charge recombination, i. e., electron transfer from NDI to [Ru(bpy)₃]³⁺, takes place with a time constant of ~20 ns (SI, Figure S7b). For ³MLCT excited-state quenching of [Ru(bpy)₃]²⁺ by Et₃N an upper rate limit of 10⁶ M⁻¹ s⁻¹ has been estimated in prior studies,⁴² hence at a concentration of 0.5 M Et₃N, the pseudo first-order rate constant for electron transfer from Et₃N to photoexcited [Ru(bpy)₃]²⁺ is < 5·10⁵ s⁻¹. This is more than 6600 times slower than intramolecular photoinduced electron transfer to NDI in triad **I**, and consequently it seems clear that the dominant reaction pathway for the formation of NDI⁻ in presence of Et₃N involves the sequence of intra- and inter-molecular electron transfer steps shown in Scheme 2a (process (i) rather than process (ii)).

Scheme 2. Reaction pathways leading to electron accumulation in triad **I** in presence of excess Et₃N. (Only one of the two photosensitizers (RuL₃²⁺) of the triad is indicated for brevity). Gray shaded areas mark the most important pathways. (a) Sequence of reaction steps leading to the formation of NDI⁻. (b) Unproductive electron transfer events leading to light absorption but no net photochemistry. (c) Displacement of the (unfavorable) disproportionation equilibrium through continuous removal of NDI⁰ and further formation of NDI²⁻ through a thermal reaction with a carbon-centered radical resulting from the decomposition of oxidized Et₃N.



Following the intramolecular step leading to $[\text{Ru}(\text{bpy})_3]^{3+}$ and NDI^- , regeneration of $[\text{Ru}(\text{bpy})_3]^{2+}$ by Et_3N is in competition with intramolecular thermal charge recombination. For the reaction between $[\text{Ru}(\text{bpy})_3]^{3+}$ and triethanolamine a rate constant of $1.67 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ has

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3 been reported.⁴³ Assuming that the reaction with Et₃N is similarly rapid, one expects a pseudo
4 first-order rate constant of $\sim 8 \cdot 10^6 \text{ s}^{-1}$ at an Et₃N concentration of 0.5 M. Since the rate constant
5 for intramolecular charge recombination between [Ru(bpy)₃]³⁺ and NDI⁻ is $\sim 5 \cdot 10^7 \text{ s}^{-1}$ (time
6 constant of $\sim 20 \text{ ns}$, see above), the bimolecular reaction between [Ru(bpy)₃]³⁺ and Et₃N is
7 comparatively slow. This explains why the quantum yields for the formation of NDI⁻ under the
8 steady-state irradiation conditions are limited to values in the range of 0.061 – 0.107 (Table 2).
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18 The mechanism leading from NDI⁻ to NDI²⁻ is more difficult to identify. Spontaneous thermal
19 disproportionation of NDI⁻ to NDI²⁻ and NDI⁰ is not possible, because it is exergonic by 0.4 eV
20 based on the redox potentials for triad **I** (Table 1). When a de-aerated solution of triad **I** in which
21 NDI⁻ has been formed photochemically with Et₃N is left standing in the dark, NDI²⁻ is not
22 formed (SI, Figure S8a), indicating that further light input is required for the electron-
23 accumulating step. Reductive quenching of ³MLCT-excited [Ru(bpy)₃]²⁺ by Et₃N (process (vi) in
24 Scheme 2b) is slow ($< 5 \cdot 10^5 \text{ s}^{-1}$ at 0.5 M, see above), and intramolecular electron transfer to NDI⁻
25 (process (v) in Scheme 2b) is energetically uphill by 0.14 eV based on the potentials in Table 1.
26 Moreover, intramolecular reductive ³MLCT quenching by NDI⁻ (process (iv) in Scheme 2b) is
27 exergonic by 1.4 eV. Given its high driving-force, this undesired charge shift event is likely to
28 represent the dominant reaction channel after absorption of a photon by triads in which NDI⁻ is
29 present. This process is expected to be followed by intramolecular thermal charge shift from
30 [Ru(bpy)₃]⁺ to NDI⁰, and the net result is the initial [Ru(bpy)₃]²⁺ / NDI⁻ couple, but a photon has
31 been consumed (grey shaded area in Scheme 2b). In view of all these pitfalls, the very low
32 quantum yields for the electron-accumulating step (Table 2) become understandable.
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54 After oxidation, Et₃N is known to deprotonate to form the highly reactive Et₂NC=CH₃ radical
55 which is able to reduce [Ru(bpy)₃]²⁺ to [Ru(bpy)₃]⁺ in the ground state, i. e., in a dark reaction.⁴⁴⁻
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⁴⁷ However, as noted above, the formation of NDI^{2-} from NDI^- does not proceed in absence of light (SI, Figure S8a), and it seems likely that the $\text{Et}_2\text{NC}\cdot=\text{CH}_3$ radicals react rapidly after they are formed. Presumably, they contribute to the formation of NDI^- already in the course of initial photo-irradiation (Figure 1a), as illustrated in Scheme 2a (process (iii)).

As noted above, spontaneous disproportionation of NDI^- can be excluded on thermodynamic grounds, but this disproportionation equilibrium can be shifted to the product side by constant removal of NDI^0 (Scheme 2c). When the solution contains largely NDI^- (i. e., after 30 s in Figure 1a), a residual concentration of $\sim 10^{-8} \text{ M}^{-1}$ of NDI^0 is expected in a solution containing an initial triad concentration of $1.7 \cdot 10^{-5} \text{ M}$ (based on a disproportionation constant of $1.7 \cdot 10^{-7}$ obtained from the redox potentials in Table 1). Prolonged irradiation will eventually bring even this small residual amount of NDI^0 to reaction with Et_3N to afford NDI^- , and with NDI^0 being continuously consumed, more and more NDI^{2-} is formed (grey shaded area in Scheme 2c), also by the reaction of newly produced $\text{Et}_2\text{NC}\cdot=\text{CH}_3$ radicals (process (vii) in Scheme 2c).⁴⁴⁻⁴⁷ It seems plausible that this thermal overall process (which, however, clearly relies on further light input) is in fact the main electron-accumulating step, particularly in view of the fact that excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ in triads containing NDI^- predominantly induces an unproductive sequence of photoinduced and thermal (intramolecular) charge shift reactions (grey shaded area in Scheme 2b).

With ascorbate as an electron source instead of Et_3N , electron accumulation on NDI is not possible. For solubility reasons, we used tetra-*n*-butylammonium 5,6-isopropylidene ascorbate as a donor and de-aerated methanol for steady-state photoirradiation of triad **I** at 410 nm,⁴⁸ but in this experiment not even NDI^- is formed in substantial amounts (SI, Figure S8b). Transient absorption studies demonstrate why: Once NDI^- is formed (SI, Figures S9 and S10), it recombines with ascorbate oxidation products on a timescale of $\sim 10 \text{ ms}$ (SI, Figure S11). In view

of the fact that ascorbate acts as a nonsacrificial quencher for $^3\text{MLCT}$ -excited $[\text{Ru}(2,2'$ -bipyrazine) $_3]^{2+}$,⁴⁹ this finding is not too surprising.

In a separate experiment, we photo-irradiated a three-component mixture containing $1.7 \cdot 10^{-5}$ M of an NDI reference molecule, 2 equivalents of $[\text{Ru}(\text{bpy})_3]^{2+}$, and 0.5 M Et_3N in de-aerated CH_3CN but were unable to observe charge accumulation on NDI in this case, possibly due to low cage escape yields (see Supporting Information for details). The quantum yield for formation of NDI in this case was 0.070.

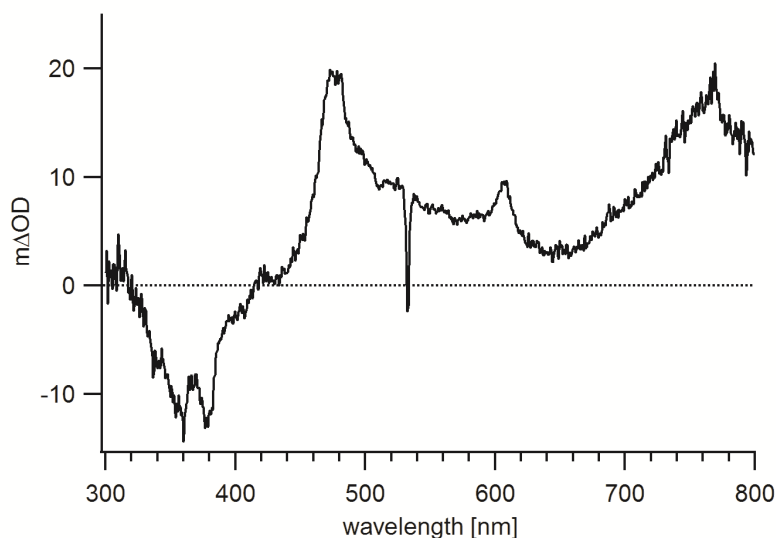
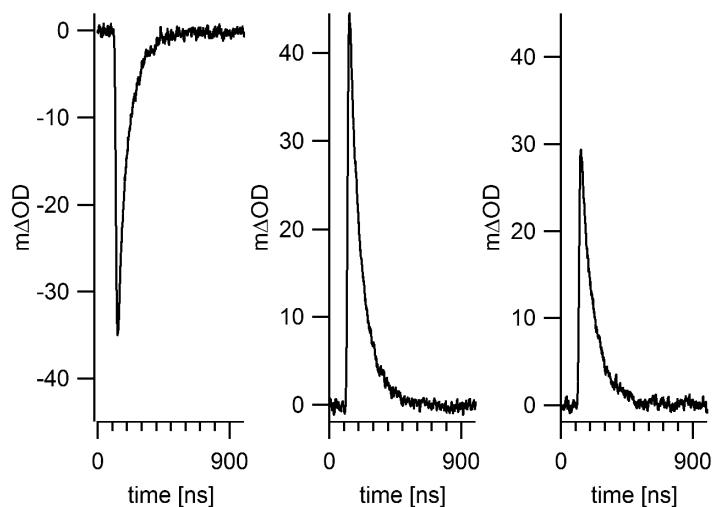


Figure 3. Transient absorption spectrum recorded from a $1.5 \cdot 10^{-5}$ M solution of pentad **II** in de-aerated CH_3CN . The sample was excited at 532 nm with laser pulses of ~ 10 ns duration, and detection occurred by time-integration over 200 ns immediately after excitation. The spike at 532 nm is due to laser stray light.

Pentad **II** has covalently attached TAA donors, and we hoped to achieve entirely intramolecular photoinduced electron accumulation in this case, similar to what we recently

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3 observed in a structurally related system with anthraquinone as a two-electron acceptor.³⁵
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5 Excitation of a $1.5 \cdot 10^{-5}$ M solution of pentad **II** at 532 nm with laser pulses of ~ 10 ns duration
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7 leads to the transient absorption spectrum in Figure 3. The transient absorption bands at 477 and
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9 606 nm signal the formation of NDI⁻ (SI, Figure S12, Figure 1b) while the bleaches at 355 and
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11 380 nm mark the disappearance of NDI⁰ (SI, Figure S3).³⁶ The band at 765 nm is diagnostic for
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13 TAA⁺ (SI, Figure S13).⁵⁰⁻⁵²
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38 **Figure 4.** Temporal evolution of the transient absorption signals at (a) 360 nm, (b) 480 nm, and
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40 (c) 770 nm in the spectrum from Figure 3.
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46 The transient absorption signals at 480 and 770 nm form with an instrumentally limited time
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48 constant of 30 ps (SI, Figure S14). They decay in single exponential manner with the same time
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50 constant as the bleach at 360 nm recovers (Figure 4), indicating that (intramolecular) thermal
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52 charge recombination between NDI⁻ and TAA⁺ occurs with a time constant of 120 ns in de-
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54 aerated CH₃CN at 25 °C. Based on the chemical reduction data in Figure 1d and based on prior
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3 studies,³⁶ one would expect NDI^{2-} to exhibit characteristic absorption bands at 400, 420, and 615
4 nm, and we searched carefully for such bands up to very high excitation pulse energies (~ 30 mJ).
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6 Due to the two-photon nature of the electron accumulation process,³⁵ the quantity of NDI^{2-}
7 potentially produced is expected to be very low. For example, in a scenario in which 10% of all
8 pentads are promoted to the $\text{NDI}^- / \text{TAA}^+$ charge-separated state, only $\sim 1\%$ can be expected to be
9 further promoted to a state in which NDI^{2-} is flanked by 2 TAA^+ units.³¹ We were unable to
10 detect any signals attributable to NDI^{2-} , even when using a sequence of two excitation pulses
11 (first pulse at 532 nm, 30 mJ; second pulse at 430 nm with a time delay of 50 ns, 21 mJ) in a so-
12 called two-color pump-pump probe experiment (SI, Figure S15). The second excitation pulse at
13 430 nm seemed advantageous over excitation with two photons at 532 nm within a single pulse,
14 because at 430 nm secondary excitation occurs predominantly into the MLCT absorption band of
15 $[\text{Ru}(\text{bpy})_3]^{2+}$, whereas at 532 nm $[\text{Ru}(\text{bpy})_3]^{2+}$ only absorbs weakly and there is also some NDI^-
16 absorption. (Excitation of NDI^- could potentially trigger energy-wasting charge recombination
17 reactions, but we estimate that under the conditions used in our experiment the absorbance of
18 photogenerated NDI^- at 532 nm is about 36 times weaker than that of $[\text{Ru}(\text{bpy})_3]^{2+}$, hence direct
19 excitation of NDI^- is expected to be a minor deactivation pathway).

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Even successful secondary excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ can trigger unwanted electron transfer reactions, in particular either reductive excited-state quenching by NDI^- or oxidative quenching by TAA^+ . Both of these processes have significantly higher driving-force than the desired charge accumulation step leading to NDI^{2-} and 2 TAA^+ units. These types of energy-wasting photoinduced charge recombination processes seem to be generally the most difficult ones to avoid when aiming at photoinduced charge accumulation,^{31,40,41} and in this regard, multi-component systems are advantageous compared to fully integrated, covalently linked systems.

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3 This is not only because of the large excess of sacrificial reagents in multi-component systems,
4 but also because the primary oxidation and reduction products can diffuse away from each other,
5 and when absorption of a second photon then takes place, the photoinduced charge
6 recombination events discussed above are far less probable. Furthermore, in multi-component
7 systems the primary charge-separated state (here comprised of NDI⁻ and oxidized Et₃N in the
8 case of **I**) is usually much longer-lived than in covalently connected systems (120 ns for NDI⁻
9 and TAA⁺ in pentad **II**), giving access to the disproportionation chemistry discussed above
10 (Scheme 2c).
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22 Attempts to favor the formation of NDI²⁻ by metal-ion coupled electron transfer (MCET)
23 through addition of the strong Lewis acid Sc³⁺ (50 mM Sc(OTf)₃) were unsuccessful.^{26,53,54}
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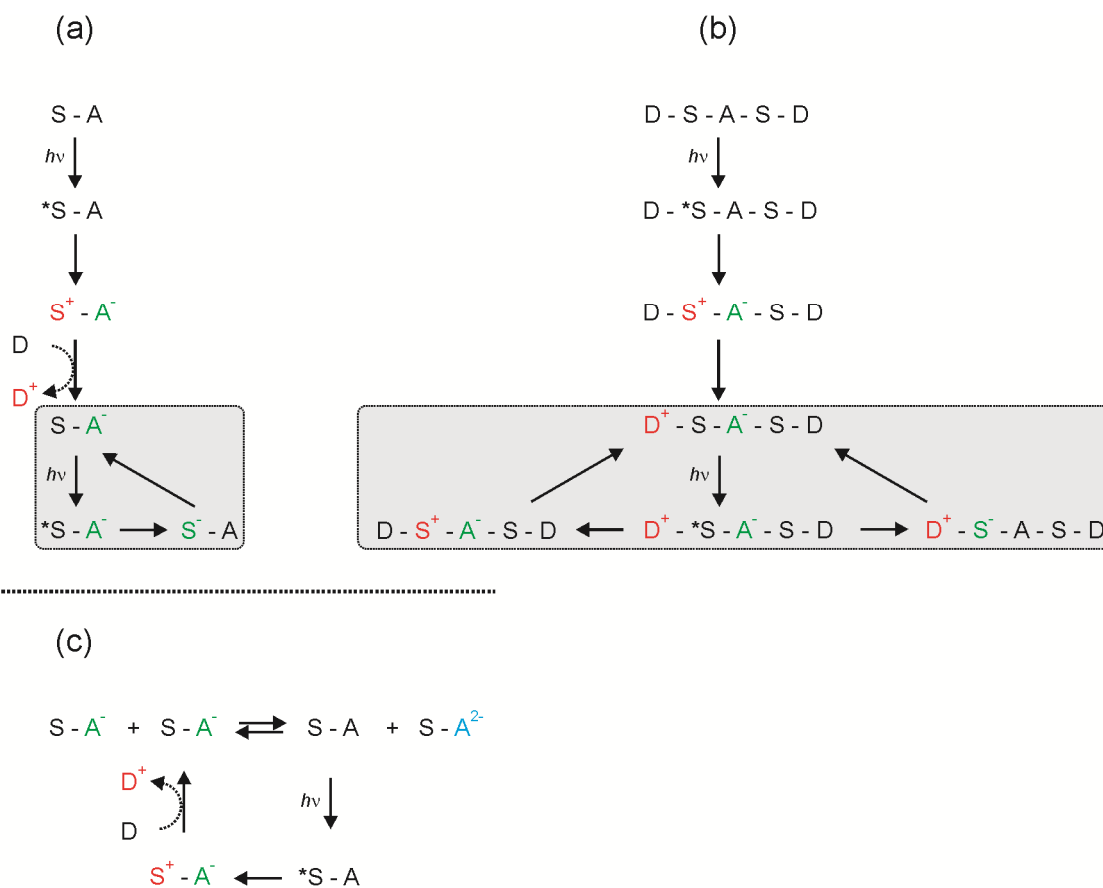
27 Finally, we note that the ³MLCT excited-state of pentad **II** can in principle be quenched by
28 energy transfer to TAA⁺ or NDI⁻. Both radical species have absorptions at wavelengths below
29 600 nm (Figure 1b, SI, Figures S12 and S13), indicating that they both have excited states which
30 are energetically below the lowest ³MLCT state of [Ru(bpy)₃]²⁺. The NDI⁻ and TAA⁺ are doublet
31 species, and it remains to be explored how spin selection rules affect the efficiency of energy
32 transfer in such a case.⁵⁵
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43 SUMMARY AND CONCLUSIONS

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48 Triad **I** is symmetrical with two photosensitizer units for ease of synthesis, but in principle it is
49 functionally analogous to simple sensitizer-acceptor (S-A) dyads. Photoreduction of the NDI unit
50 by one electron in triad **I** is readily possible by the sequence of intra- and intermolecular electron
51 transfer events outlined in Scheme 3a, leading ultimately to the S-A⁻ form. Further excitation of
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3 the latter principally induces reductive excited-state quenching of the sensitizer by A^- because
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5 the latter is a strong donor, and the excited sensitizer is a potent acceptor. The resulting S^-A
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7 form subsequently reverts spontaneously to the $S-A^-$ form via intramolecular thermal reverse
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9 electron transfer (grey shaded area in Scheme 3a). This unproductive (but energy-consuming)
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11 sequence of reactions is generally problematic in charge accumulation processes,^{17,31,40,41,56}
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13 unless A^- is rendered less reducing, for example through protonation in an overall proton-coupled
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15 electron transfer (PCET) reaction.⁵⁷⁻⁵⁹
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22 **Scheme 3.** Reaction pathways relevant for electron accumulation in (a) sensitizer-acceptor
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24 dyads, and (b) in donor-sensitizer-acceptor-sensitizer-donor pentads. The grey shaded areas mark
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26 unproductive yet important electron transfer sequences competing with the electron-
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28 accumulating step. (c) Shift of a disproportionation equilibrium through constant removal of the
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30 starting material via continuous photoexcitation as a key pathway to charge accumulation.
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In triad **I**, formation of the S-A^{2-} form is only possible thanks to the displacement of the (unfavorable) disproportionation equilibrium in Scheme 3c. Importantly, this thermal reaction requires further light input for continuous removal of the S-A starting material and the concomitant formation of the charge-accumulated S-A^{2-} species. This reaction pathway is only viable with sacrificial donors such as Et_3N , but not with reversible donors such as ascorbate. In cases in which the disproportionation of A^- to A and A^{2-} is thermodynamically favored, no further light input is evidently necessary. This should be the case for example in various benzoquinone derivatives.^{60,61}

In donor-sensitizer-acceptor-sensitizer-donor pentad **II**, the primary charge-separated state ($\text{D}^+ - \text{S-A}^- - \text{S-A}$) has a comparatively short lifetime (120 ns), and this makes bimolecular

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3 disproportionation ineffective. Further excitation of the primary charge-separated species
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5 predominantly induces the unproductive electron transfer events shown in the grey shaded area
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7 of Scheme 3b: The excited state of the sensitizer (*S) is quenched either reductively by A⁻ or
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9 oxidatively by D⁺. Again, PCET would be helpful to make A⁻ less reducing through protonation
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11 (see above), and to make D⁺ less oxidizing through deprotonation. Phenols would be an
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13 interesting choice as one-electron donors, because they usually undergo deprotonation in the
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15 course of oxidation.⁶²⁻⁶⁹

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20 Our direct comparison of a multi-component system (triad **I** with sacrificial donors) and a fully
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22 integrated compound (pentad **II** with covalently attached reversible donors) illustrates possible
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24 reaction pathways leading to electron accumulation and counteracting processes in both types of
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26 approaches. Our study demonstrates that for applications aiming at multi-electron (photo-)redox
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28 reactions, the covalent linkage of photosensitizers and catalytic reaction centers introduces
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30 significant challenges with regard to avoiding unproductive (but energy-consuming) electron
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32 transfer reactions upon sequential absorption of two (or more) photons. These unproductive
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34 electron transfers could presumably be decelerated significantly with suitable PCET
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36 photochemistry,⁷⁰⁻⁷⁴ leading ultimately to the accumulation of redox equivalents rather than the
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38 accumulation of charge, similar to what is observed in the oxygen-evolving complex of
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40 photosystem II.^{75,76}

41 42 43 44 45 46 47 48 ASSOCIATED CONTENT

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51 **Supporting Information.** Synthesis protocols, product characterization data, electrochemical,
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53 and optical spectroscopic data. This material is available free of charge via the Internet at
54
55 <http://pubs.acs.org>.

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Author Contributions

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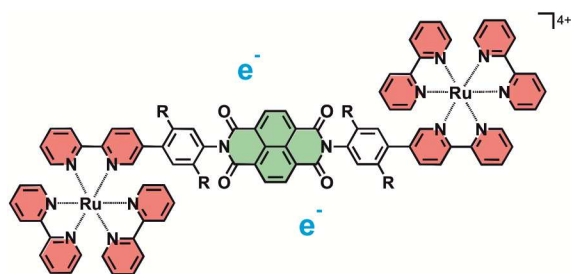
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Table of Contents Graphic and Synopsis



A series of intra- and intermolecular photoinduced electron transfer processes leads to accumulation of two electrons on a naphthalene diimide unit in a molecular triad, using sacrificial reagents as electron donors. In a molecular pentad with covalently attached reversible donors, electron accumulation remained unobserved.