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**Photoinduced Electron Transfer in an Anthraquinone-
[Ru(bpy)₃]²⁺-Oligotriarylamine-[Ru(bpy)₃]²⁺-Anthraquinone
Pentad**

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7 Photoinduced Electron Transfer in an
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11 Anthraquinone- $[\text{Ru}(\text{bpy})_3]^{2+}$ -Oligotriarylamine-
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15 $[\text{Ru}(\text{bpy})_3]^{2+}$ -Anthraquinone Pentad
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ABSTRACT

A molecular pentad comprised of a central multi-electron donor and two flanking photosensitizer-acceptor moieties was prepared in order to explore the possibility of accumulating two positive charges at the central donor, using visible light as an energy input. Photoinduced charge accumulation in purely molecular systems without sacrificial reagents is challenging due to the multitude of energy-wasting reaction pathways that are accessible after excitation with two photons. As expected, the main photoproduct in our pentad is a simple electron-hole pair, and it is tricky to identify the desired two-electron oxidation product on top of the stronger signal resulting from one-electron oxidation.

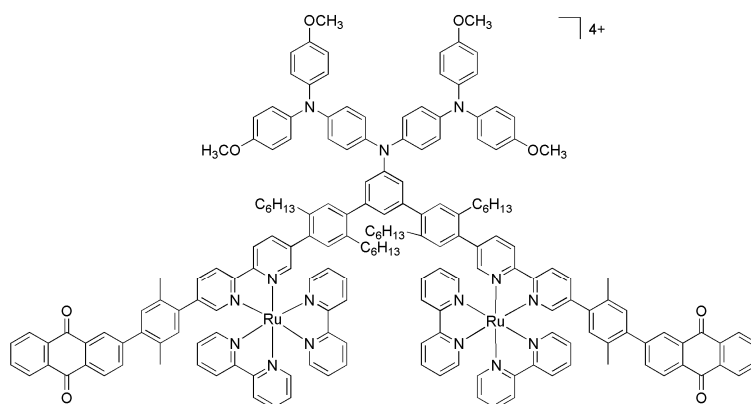
INTRODUCTION

Electron-hole pairs have been observed after photo-excitation of many different dyads,¹ triads,² tetrads,³ and pentads.⁴ However, light-driven accumulation of multiple electrons or holes on a given molecular unit is much less straightforward, at least when aiming at charge accumulation without using sacrificial reagents.⁵ At present, only a handful of prior studies have addressed this subject successfully.⁶

Charge accumulation is necessary for artificial photosynthesis, because fuel-forming reactions such as H₂ production or CO₂ reduction require multiple redox equivalents.^{5b, 7} Therefore, it is desirable to gain knowledge on how light-driven charge accumulation can be performed efficiently, ideally without sacrificial donors or acceptors. This was the purpose of the research presented in this paper.

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3 The molecular pentad in Scheme 1 is comprised of a central oligotriarylamine (OTA) donor
4 that is easily oxidized up to three times. The OTA multi-electron donor is connected to two
5 [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) photosensitizers each of which bears an anthraquinone (AQ)
6 acceptor. In principle, AQ can accept two electrons but here we aimed to explore whether
7 photoexcitation of both [Ru(bpy)₃]²⁺ units could lead to a charge-separated state in which OTA
8 has been oxidized to its dicationic state (OTA²⁺) while both AQ units have been reduced to their
9 mono-anionic form (AQ⁻). To the best of our knowledge, such photodriven hole accumulation in
10 a purely molecular system has never been achieved without sacrificial electron acceptors.
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24 **Scheme 1.** Chemical structure of the AQ-Ru^{II}-OTA-Ru^{II}-AQ pentad.
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RESULTS AND DISCUSSION

Synthesis. The key ligand for the AQ-Ru^{II}-OTA-Ru^{II}-AQ pentad from Scheme 1 was synthesized in 18 steps using standard C-C and N-C coupling reactions as described in detail in the Supporting Information. The final compound was characterized by NMR spectroscopy, high-resolution ESI mass spectrometry, and by elemental analysis.

Electrochemistry. Cyclic voltammetry was used to determine the reduction potentials of the individual components of the pentad. Measurements were performed in dry CH₃CN at 20 °C and provided the results in Table 1. Voltammograms and further experimental details are in the Supporting Information. OTA is oxidized reversibly to its mono- and dicationic forms at -0.01 V and 0.23 V vs. Fc⁺/Fc, in line with prior studies.^{6b, 8} Formation of OTA³⁺ at 0.65 V is quasi-reversible, as reported earlier.^{6b, 8} The redox potentials of the AQ and the [Ru(bpy)₃]²⁺ components of the pentad are similar to those found for neat anthraquinone or [Ru(bpy)₃]²⁺ under identical conditions.⁹

Based on these potentials, excitation of the pentad at one of its two photosensitizer units should lead to a charge-separated state comprised of OTA⁺ and AQ⁻, similar to what was observed in structurally related triads.^{2i, 10} The resulting AQ⁻-Ru^{II}-OTA⁺-Ru^{II}-AQ state is expected to be ca. 1.26 eV above the initial (ground) state. Excitation of the second photosensitizer unit can then potentially lead to reduction of the second AQ unit and oxidation of OTA⁺ to OTA²⁺. The resulting AQ⁻-Ru^{II}-OTA²⁺-Ru^{II}-AQ⁻ state is expected to be ca. 2.74 eV above the ground state, much lower in energy than a hypothetical AQ²⁻-Ru^{II}-OTA²⁺-Ru^{II}-AQ state in which two electrons are located on the same AQ unit. In the following optical spectroscopic studies, we searched for the AQ⁻-Ru^{II}-OTA²⁺-Ru^{II}-AQ⁻ photoproduct.

Table 1. Redox potentials (V vs. Fc⁺/Fc) in CH₃CN.^a

	pentad	[Ru(bpy) ₃] ²⁺	AQ ^b
Ru(III/II)	0.91	0.90	
OTA ⁺⁰	-0.01		
OTA ^{2+/+}	0.23		
OTA ^{3+/2+}	0.65		
bpy ^{0/-}	-1.67	-1.72	
bpy ^{0/-}	-1.92	-1.92	
bpy ^{0/-}	-2.20	-2.17	
AQ ^{0/-}	-1.25		-1.23
AQ ^{2-/-}	-2.0 ^c		-1.77

^a Measured in presence of 0.1 M TBAPF₆ as a supporting electrolyte using scan rates of 0.1 V/s. ^b From ref. ^{9a} for neat 9,10-anthraquinone in DMF; potential converted from SCE to Fc⁺/Fc following ref. ¹¹. ^c Irreversible.

UV-Vis spectroscopy and chemical oxidation. The black trace in Figure 1a is the absorption spectrum of the pentad in neat CH₃CN at 20 °C. Absorption bands with maxima at 455, 324, and 250 nm are attributable to [Ru(bpy)₃]²⁺, AQ, and OTA components, respectively; an additional band at 290 nm is due to bpy-localized π-π* transitions. The red trace was measured in presence of 2000 equivalents of *N,N'*-diphenylthiourea, which is able to form tight hydrogen-bonds to quinone radical anions.¹² We anticipated that this might facilitate AQ reduction, potentially leading to longer-lived charge-separated states and increased chances of observing the desired AQ⁻-Ru^{II}-OTA²⁺-Ru^{II}-AQ⁻ photoproduct.^{2l, 8b, 13} Brønsted acids or the strong H-bond donor

hexafluoroisopropanol lead to oxidation of OTA in the dark and were therefore not considered further.

The UV-Vis spectral changes occurring in the course of chemical oxidation of OTA to OTA^+ and OTA^{2+} by $\text{Cu}(\text{ClO}_4)_2$ ($E^0 = 0.57 \text{ V vs. Fc}^+/\text{Fc}$ in CH_3CN)^{11, 14} are shown in Figure 1b. The UV-Vis spectrum measured prior to adding any oxidant served as a baseline. The blue and green traces were measured after addition of 1.0 and 2.5 equivalents of $\text{Cu}(\text{ClO}_4)_2$ and are attributed to OTA^+ and OTA^{2+} , respectively, in line with prior studies.^{6a, b, 8b, c} These chemical oxidation experiments demonstrate that OTA^+ and OTA^{2+} are best distinguishable from each other in the near-infrared spectral range. The nanosecond transient absorption studies reported below therefore focused on the detection of a band at 1130 nm (attributable to OTA^{2+}) on top of a band at 1315 nm (caused by OTA^+).

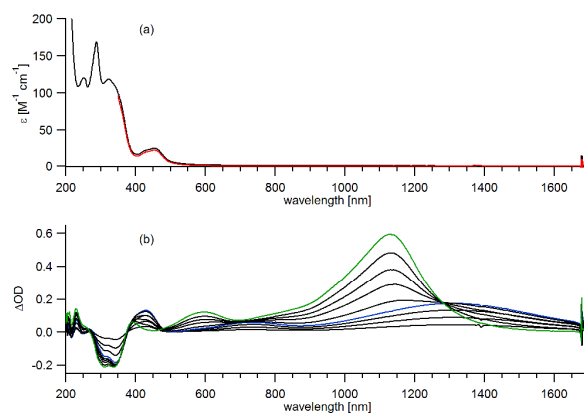
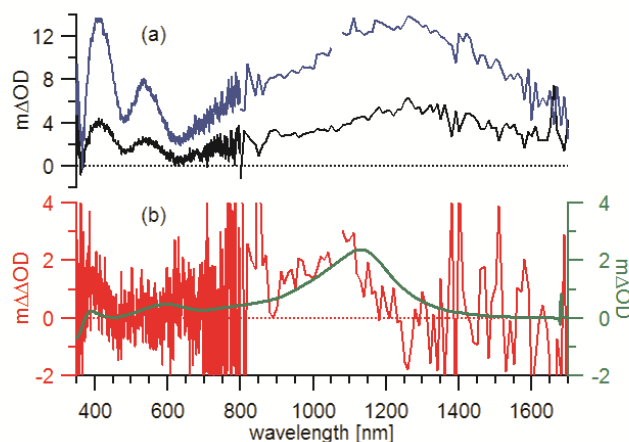


Figure 1. (a) UV-Vis absorption spectra obtained from 10^{-5} M solutions of the pentad in CH_3CN . Black trace: in neat solvent; red trace: in presence of 2000 equivalents of N,N' -diphenylthiourea. (b) UV-Vis difference spectra measured after addition of increasing amounts of $\text{Cu}(\text{ClO}_4)_2$ to a 10^{-5} M solution of the pentad in CH_3CN ; the spectrum prior to adding any $\text{Cu}(\text{II})$ oxidant served as a baseline. Blue trace: measured after addition of 1.0 equivalent of oxidant, spectrum

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3 attributed to OTA^+ ; green trace: measured after addition of 2.5 equivalents of oxidant, spectrum
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5 attributed to OTA^{2+} .
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11 *Nanosecond transient absorption.* A deaerated 10^{-5} M solution of the pentad containing 2000
12 equivalents of *N,N'*-diphenylthiourea was excited with laser pulses of ~ 10 ns duration at 532 nm,
13 resulting in the transient absorption spectra shown in Figure 2a. The black and blue traces were
14 obtained using pulse energies of 10 and 60 mJ, respectively. We estimate that this corresponds to
15 a flux of ca. ~ 4 and ~ 24 photons per molecule and pulse, respectively, and therefore multi-
16 photon processes should be possible.
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43 **Figure 2.** (a) Transient absorption spectra measured after excitation at 532 nm with laser pulses
44 of ~ 10 ns duration. Both spectra were time-integrated over a detection period of 200 ns
45 immediately after excitation. Black trace: excitation with 10 mJ/pulse; blue trace: excitation with
46 60 mJ/pulse. (b) Red trace: Difference spectrum obtained after subtraction of the black trace in
47 (a) from the blue trace in (a); prior to the subtraction the two spectra from (a) were scaled to
48 identical intensities at 1285 nm, see text for further details. Green trace: UV-Vis difference
49 spectrum associated with the formation of OTA^{2+} (green trace from Figure 1b).
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Both transient absorption spectra in Figure 2a exhibit prominent bands at 1280 and 410 nm which are compatible with the predominant formation of OTA^+ . An additional band at 540 nm in transient absorption can be attributed to AQ^- ,^{10a, b, 15} and hence it is clear that the majority photoproduct is the $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^+ \text{-Ru}^{\text{II}} \text{-AQ}$ state. This is not unexpected because only a fraction of all pentads that have absorbed a first photon will also absorb a second photon.^{6a-c} The transient absorption signals at 410, 540 and 740 nm (Supporting Information) decay with a lifetime of 160 ns irrespective of whether *N,N'*-diphenylthiourea is present (Table 2). Importantly, the $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^+ \text{-Ru}^{\text{II}} \text{-AQ}$ state is formed within 10 ns, hence the possibility for absorption of a (second) photon from this state within the same laser pulse is indeed given.

Table 2. Lifetimes of photoproducts in deaerated CH_3CN at 20 °C.

	τ_0 [ns]	τ_1 [ns]
neat, 10 mJ	160	
2000 eq thiourea, 10 mJ	160	
2000 eq thiourea, 60 mJ	100	290

In our search of evidence for the $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^{2+} \text{-Ru}^{\text{II}} \text{-AQ}^-$ state we subtracted the black trace from the blue trace in Figure 2a, in order to obtain a difference spectrum in which the dominant contribution from the simple $\text{AQ}^- / \text{OTA}^+$ electron-hole pair is eliminated. For this purpose the two spectra in Figure 2a were scaled to equal intensities at 1285 nm, which is an isosbestic point appearing in the course of the formation of OTA^+ and OTA^{2+} (Figure 1b). The result is shown as a red trace in Figure 2b together with the UV-Vis difference spectrum obtained for OTA^{2+} in the chemical oxidation experiment (green trace from Figure 1b). We note that there is indeed some

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3 agreement between the two difference spectra in Figure 2b, particularly in the near-infrared
4 spectral range around 1100 nm and near 400 nm where OTA^{2+} has characteristic absorption
5 bands. This observation suggests that a small fraction of the desired $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^{2+} \text{-Ru}^{\text{II}} \text{-AQ}^-$
6 state is indeed formed.
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12 Transient absorption decays measured after excitation with pulse energies of 60 mJ are bi-
13 exponential (Table 1, Supporting Information). In principle such behavior is compatible with two
14 independently decaying photoproducts such as the $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^+ \text{-Ru}^{\text{II}} \text{-AQ}^-$ majority state and
15 the desired $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^{2+} \text{-Ru}^{\text{II}} \text{-AQ}^-$ state. However, the relative contributions of the two decay
16 components are roughly 60% ($\tau = 290$ ns) to 40 % ($\tau = 100$ ns) at all detection wavelengths
17 (Supporting Information), which would imply a large contribution from the desired $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-}$
18 $\text{OTA}^{2+} \text{-Ru}^{\text{II}} \text{-AQ}^-$ state to the overall decay. Therefore, it seems more likely that the bi-
19 exponential decay behavior at high pulse energies is an effect which is not directly related to the
20 charge accumulated state. It is conceivable that this is a thermal effect.
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34 Pump-pump-probe experiments in which a first excitation pulse at 532 nm was followed by a
35 second excitation pulse at 480 nm (with a delay time of 10-20 ns) did not provide unambiguous
36 evidence for the formation of OTA^{2+} either (Supporting Information).
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41 As noted above, the desired $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^{2+} \text{-Ru}^{\text{II}} \text{-AQ}^-$ state is 2.74 eV above the ground state,
42 and consequently many decay channels to energetically lower states do potentially exist. One
43 might therefore expect this state to be rather short-lived, and for this reason transient absorption
44 studies with higher temporal resolution were performed.
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52 *Femtosecond transient absorption.* Excitation of the pentad in deaerated CH_3CN at 385 nm
53 using a setup with a ~ 150 fs instrument response function¹⁶ yielded the transient absorption
54 spectra in Figure 3a/b. Differences between the spectra obtained at low (0.4 mJ/cm^2 , Figure 3a)
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and high excitation densities (8.0 mJ/cm^2 , Figure 3b) are observed between 470 and 540 nm. The time evolution of the transient absorption at low excitation density could be well reproduced by global target analysis assuming three consecutive exponential steps $A \rightarrow B \rightarrow C \rightarrow D$ and yielded the species-associated decay spectra (SADS)¹⁷ shown in Figure 3c.

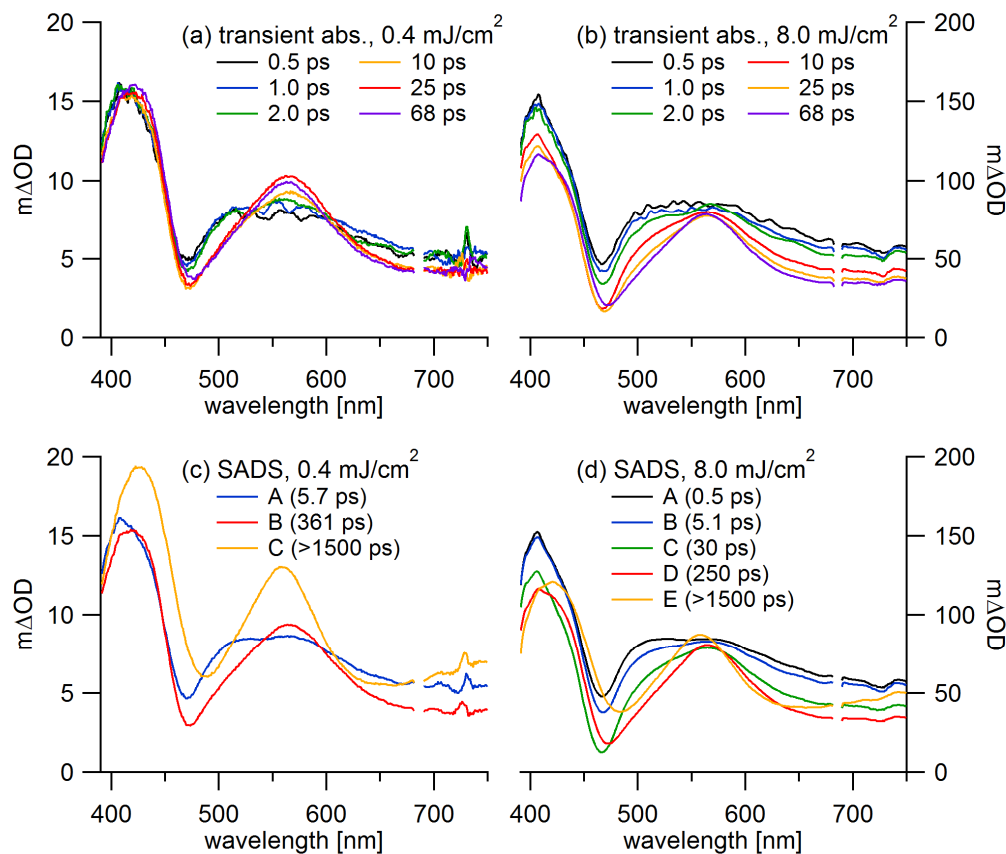


Figure 3. Transient absorption spectra recorded at different delay times after excitation at 385 nm with femtosecond laser pulses at low (a) and high (b) excitation densities.¹⁶ (c, d) Species-associated decay spectra (SADS) obtained from global target analyses of the data in (a) and (b) assuming a series of three (c) or five (d) consecutive exponential steps.

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3 Precise interpretation of these species/states is not straightforward, but A most probably
4 corresponds to the $^3\text{MLCT}$ state of the $[\text{Ru}(\text{bpy})_3]^{2+}$ sensitizer, although some contribution from
5 the triplet excited state of AQ cannot be excluded.¹⁸ On the other hand, C is more compatible
6 with $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^+ \text{-Ru}^{\text{II}} \text{-AQ}$ than with the desired $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^{2+} \text{-Ru}^{\text{II}} \text{-AQ}^-$ state.
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8 Unfortunately, measurements in the near-infrared spectral range, which would permit
9 distinguishing more clearly between OTA^+ and OTA^{2+} , cannot be performed on the
10 femtosecond setup. The spectrum of B resembles that of C but has smaller amplitude. This
11 suggests that B might be associated with an intermediate state, such as for example a charge-
12 separated state with the electron or the hole on the sensitizer. In any case, these data indicate that
13 the quenching of the excited sensitizer ($\text{A} \rightarrow \text{B}$) occurs within a few ps, whereas the $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-}$
14 $\text{OTA}^+ \text{-Ru}^{\text{II}} \text{-AQ}$ state (C) is populated in less than 400 ps.

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32 At high excitation density, two additional steps have to be added to properly account for the
33 observed transient absorption dynamics, with the SADS and time constants shown in Figure 3d.
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35 The last two species, E and F, have similar spectra and lifetimes as B and C in the low intensity
36 measurements, indicating that the $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^{2+} \text{-Ru}^{\text{II}} \text{-AQ}^-$ state is still not populated. The
37 SADS of A, B and C in the high intensity measurements are all very similar, except for their
38 amplitude, and resemble the SADS of A measured at low intensity. This indicates that these four
39 spectra are due to the same species / state, most probably $[\text{Ru}(\text{bpy})_3]^{2+}$ in the $^3\text{MLCT}$ state, and
40 that, at high excitation density, the decay of this state cannot be accounted for by a single
41 exponential function. Such dependence on the excitation intensity is typical of exciton
42 annihilation, and has been observed with many multichromophoric systems and aggregates.¹⁹ In
43 the present case, triplet-triplet annihilation between two $[\text{Ru}(\text{bpy})_3]^{2+}$ units in the $^3\text{MLCT}$ state is
44 the most probable origin of the non-exponential decay at higher excitation density. Such process
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3 is strongly detrimental to efficient accumulative electron transfer, but can be minimized by using
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5 sufficiently long excitation pulses, so that the first photoinduced charge separation process
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7 occurs before the second sensitizer is excited. This is clearly not possible with the 100 fs pulses
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9 used here for the femtosecond measurements, as quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the $^3\text{MLCT}$ state
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11 occurs within a few ps (A \rightarrow B step in Figure 3a). In the nanosecond measurements, pulses
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13 longer by a factor 10^5 are used, and therefore the probability for a pentad to have two excited
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15 $[\text{Ru}(\text{bpy})_3]^{2+}$ units none of which has yet participated in photoinduced electron transfer is very
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17 low, even with 60 mJ pulses. In the latter case, even though the energy per pulse is large, the
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19 irradiance is only $84 \text{ MW}/\text{cm}^2$ ($2.25 \cdot 10^{14}$ photons/ cm^2/ps), compared to $80 \text{ GW}/\text{cm}^2$ ($1.55 \cdot 10^{17}$
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21 photons/ cm^2/ps) with the high-intensity femtosecond measurements. This could explain why the
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23 double charge-separated state, $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^{2+} \text{-Ru}^{\text{II}} \text{-AQ}^-$, might be observed in the nanosecond
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25 measurements but not in the femtosecond studies.
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34 SUMMARY AND CONCLUSIONS

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38 Not surprisingly, photoexcitation of the pentad from Scheme 1 in CH_3CN leads primarily to
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40 the population of a charge-separated state in which one AQ is reduced and OTA is oxidized. This
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42 state is formed rapidly ($< 1 \text{ ns}$) and it lives for 160 ns in deaerated CH_3CN at $20 \text{ }^\circ\text{C}$. When using
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44 high excitation powers in nanosecond transient absorption spectroscopy, a weak signal that is
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46 compatible with the formation of OTA^{2+} becomes detectable, suggesting that small amounts of
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48 the desired $\text{AQ}^- \text{-Ru}^{\text{II}} \text{-OTA}^{2+} \text{-Ru}^{\text{II}} \text{-AQ}^-$ state are indeed formed. However, it has not been possible
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50 to corroborate this interpretation by exploring the excitation power dependence of this weak
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3 signal, or by measuring its temporal evolution. We conclude that there is some evidence for
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5 photodriven charge accumulation, but the case is not clear-cut.
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8 As noted in the introduction, we are unaware of prior studies that have reported on light-driven
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10 hole accumulation in purely molecular systems without using sacrificial electron acceptors. The
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12 reason why this is such a tricky task is the multitude of unproductive (energy-wasting) reaction
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14 pathways that are available after excitation with two photons. These pathways include thermal
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16 charge-recombination, energy transfer processes, and triplet-triplet annihilation events.
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18 Moreover, once the $AQ^- - Ru^{II} - OTA^+ - Ru^{II} - AQ$ state is formed, excitation of the second ruthenium
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20 photosensitizer could lead to reduction of OTA^+ to OTA , because OTA^+ is a good electron
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22 acceptor. Understanding the basic principles of photodriven charge accumulation remains an
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24 important challenge in view of artificial photosynthesis.
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32 ASSOCIATED CONTENT

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36 Syntheses and product characterization data, additional electrochemical and optical
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38 spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.
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55 REFERENCES

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1
2
3 (1) (a) Balzani, V., *Electron transfer in chemistry* **2001**, 3. (b) Wasielewski, M. R., *Chem.*
4 *Rev.* **1992**, 92, 435. (c) Fortage, J.; Goransson, E.; Blart, E.; Becker, H. C.; Hammarström, L.;
5 Odobel, F., *Chem. Commun.* **2007**, 4629. (d) Lainé, P. P.; Bedioui, F.; Loiseau, F.; Chiorboli, C.;
6 Campagna, S., *J. Am. Chem. Soc.* **2006**, 128, 7510. (e) Fanni, S.; Keyes, T. E.; Campagna, S.;
7 Vos, J. G., *Inorg. Chem.* **1998**, 37, 5933. (f) Weber, J. M.; Rawls, M. T.; MacKenzie, V. J.;
8 Limoges, B. R.; Elliott, C. M., *J. Am. Chem. Soc.* **2007**, 129, 313. (g) Gaines, G. L.; Oneil, M. P.;
9 Svec, W. A.; Niemczyk, M. P.; Wasielewski, M. R., *J. Am. Chem. Soc.* **1991**, 113, 719. (h) Fox,
10 L. S.; Kozik, M.; Winkler, J. R.; Gray, H. B., *Science* **1990**, 247, 1069. (i) Helms, A.; Heiler, D.;
11 McLendon, G., *J. Am. Chem. Soc.* **1991**, 113, 4325. (j) Oevering, H.; Paddon-Row, M. N.;
12 Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S., *J. Am. Chem. Soc.*
13 **1987**, 109, 3258. (k) Serron, S. A.; Aldridge, W. S.; Fleming, C. N.; Danell, R. M.; Baik, M. H.;
14 Sykora, M.; Dattelbaum, D. M.; Meyer, T. J., *J. Am. Chem. Soc.* **2004**, 126, 14506. (l) Dupont,
15 N.; Ran, Y. F.; Jia, H. P.; Grilj, J.; Ding, J.; Liu, S. X.; Decurtins, S.; Hauser, A., *Inorg. Chem.*
16 **2011**, 50, 3295. (m) Meylemans, H. A.; Lei, C. F.; Damrauer, N. H., *Inorg. Chem.* **2008**, 47,
17 4060. (n) Gabrielsson, A.; Hartl, F.; Zhang, H.; Smith, J. R. L.; Towrie, M.; Vlček, A.; Perutz, R.
18 N., *J. Am. Chem. Soc.* **2006**, 128, 4253. (o) Majewski, M. B.; de Tacconi, N. R.; MacDonnell, F.
19 M.; Wolf, M. O., *Inorg. Chem.* **2011**, 50, 9939. (p) Albinsson, B.; Eng, M. P.; Pettersson, K.;
20 Winters, M. U., *Phys. Chem. Chem. Phys.* **2007**, 9, 5847. (q) Wiberg, J.; Guo, L. J.; Pettersson,
21 K.; Nilsson, D.; Ljungdahl, T.; Mårtensson, J.; Albinsson, B., *J. Am. Chem. Soc.* **2007**, 129, 155.
22 (r) Atienza-Castellanos, C.; Wielopolski, M.; Guldi, D. M.; van der Pol, C.; Bryce, M. R.;
23 Filippone, S.; Martín, N., *Chem. Commun.* **2007**, 5164. (s) Vail, S. A.; Krawczuk, P. J.; Guldi, D.
24 M.; Palkar, A.; Echegoyen, L.; Tome, J. P. C.; Fazio, M. A.; Schuster, D. I., *Chem. Eur. J.* **2005**,
25 11, 3375. (t) Indelli, M. T.; Chiorboli, C.; Flamigni, L.; De Cola, L.; Scandola, F., *Inorg. Chem.*
26
27
28
29
30
31
32
33
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48
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4 **2007**, *46*, 5630. (u) Linton, K. E.; Fox, M. A.; Palsson, L. O.; Bryce, M. R., *Chem.-Eur. J.* **2015**,
5
6 *21*, 3997. (v) Moravec, D. B.; Hopkins, M. D., *Chem.-Eur. J.* **2013**, *19*, 17082. (w) Schanze, K.
7
8 S.; MacQueen, D. B.; Perkins, T. A.; Cabana, L. A., *Coord. Chem. Rev.* **1993**, *122*, 63. (x)
9
10 Banerji, N.; Bhosale, S. V.; Petkova, I.; Langford, S. J.; Vauthey, E., *Phys. Chem. Chem. Phys.*
11
12 **2011**, *13*, 1019.

13
14
15
16 (2) (a) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J. C.; Chachaty, C.; Bensasson, R. V.;
17
18 Land, E. J.; Doizi, D.; Liddell, P. A.; Lehman, W. R.; Nemeth, G. A.; Moore, A. L., *Nature*
19
20 **1984**, *307*, 630. (b) Baranoff, E.; Collin, J.-P.; Flamigni, L.; Sauvage, J.-P., *Chem. Soc. Rev.*
21
22 **2004**, *33*, 147. (c) Borgström, M.; Shaikh, N.; Johansson, O.; Anderlund, M. F.; Styring, S.;
23
24 Åkermark, B.; Magnuson, A.; Hammarström, L., *J. Am. Chem. Soc.* **2005**, *127*, 17504. (d)
25
26 Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Barigelletti, F.; Flamigni, L., *Angew. Chem. Int. Ed.*
27
28 **2000**, *39*, 1292. (e) Hung, S. C.; Macpherson, A. N.; Lin, S.; Liddell, P. A.; Seely, G. R.; Moore,
29
30 A. L.; Moore, T. A.; Gust, D., *J. Am. Chem. Soc.* **1995**, *117*, 1657. (f) Imahori, H.; Tamaki, K.;
31
32 Guldi, D. M.; Luo, C. P.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S., *J. Am. Chem. Soc.*
33
34 **2001**, *123*, 2607. (g) Lee, S.-H.; Chan, C. T.-L.; Wong, K. M.-C.; Lam, W. H.; Kwok, W.-M.;
35
36 Yam, V. W. W., *J. Am. Chem. Soc.* **2014**, *136*, 10041. (h) Liddell, P. A.; Kodis, G.; Moore, A.
37
38 L.; Moore, T. A.; Gust, D., *J. Am. Chem. Soc.* **2002**, *124*, 7668. (i) Lopez, R.; Leiva, A. M.;
39
40 Zuloaga, F.; Loeb, B.; Norambuena, E.; Omberg, K. M.; Schoonover, J. R.; Striplin, D.;
41
42 Devenney, M.; Meyer, T. J., *Inorg. Chem.* **1999**, *38*, 2924. (j) Geiss, B.; Lambert, C., *Chem.*
43
44 *Commun.* **2009**, 1670. (k) Klein, J. H.; Sunderland, T. L.; Kaufmann, C.; Holzapfel, M.;
45
46 Schmiedel, A.; Lambert, C., *Phys. Chem. Chem. Phys.* **2013**, *15*, 16024. (l) Hankache, J.; Niemi,
47
48 M.; Lemmetyinen, H.; Wenger, O. S., *J. Phys. Chem. A* **2012**, *116*, 8159. (m) Melomedov, J.;
49
50 Ochsmann, J. R.; Meister, M.; Laquai, F.; Heinze, K., *Eur. J. Inorg. Chem.* **2014**, *2014*, 1984. (n)
51
52
53
54
55
56
57
58
59
60

1
2
3 McGarrah, J. E.; Kim, Y. J.; Hissler, M.; Eisenberg, R., *Inorg. Chem.* **2001**, *40*, 4510. (o)
4
5 Yushchenko, O.; Villamaina, D.; Sakai, N.; Matile, S.; Vauthey, E., *J. Phys. Chem. C* **2015**, *119*,
6
7 14999. (p) Kuss-Petermann, M.; Wenger, O. S., *Angew. Chem. Int. Ed.* **2016**, *55*, 815.
8
9

10
11 (3) (a) Guldi, D. M.; Imahori, H.; Tamaki, K.; Kashiwagi, Y.; Yamada, H.; Sakata, Y.;
12
13 Fukuzumi, S., *J. Phys. Chem. A* **2004**, *108*, 541. (b) Benniston, A. C.; Harriman, A.; Li, P. Y., *J.*
14
15 *Am. Chem. Soc.* **2010**, *132*, 26.
16
17

18
19 (4) (a) Imahori, H.; Sekiguchi, Y.; Kashiwagi, Y.; Sato, T.; Araki, Y.; Ito, O.; Yamada, H.;
20
21 Fukuzumi, S., *Chem. Eur. J.* **2004**, *10*, 3184. (b) Harriman, A.; Stachelek, P.; Sutter, A.; Ziessel,
22
23 R., *Phys. Chem. Chem. Phys.* **2015**, *17*, 26175. (c) Villamaina, D.; Kelson, M. M. A.; Bhosale, S.
24
25 V.; Vauthey, E., *Phys. Chem. Chem. Phys.* **2014**, *16*, 5188.
26
27

28
29 (5) (a) Wouters, K. L.; de Tacconi, N. R.; Konduri, R.; Lezna, R. O.; MacDonnell, F. M.,
30
31 *Photosynth. Res.* **2006**, *87*, 41. (b) Manbeck, G. F.; Brewer, K. J., *Coord. Chem. Rev.* **2013**, *257*,
32
33 1660. (c) Pellegrin, Y.; Odobel, F., *Coord. Chem. Rev.* **2011**, *255*, 2578. (d) Zedler, L.; Kupfer,
34
35 S.; de Moraes, I. R.; Wachtler, M.; Beckert, R.; Schmitt, M.; Popp, J.; Rau, S.; Dietzek, B.,
36
37 *Chem.-Eur. J.* **2014**, *20*, 3793. (e) Elvington, M.; Brewer, K. J., *Inorg. Chem.* **2006**, *45*, 5242. (f)
38
39 Konduri, R.; de Tacconi, N. R.; Rajeshwar, K.; MacDonnell, F. M., *J. Am. Chem. Soc.* **2004**,
40
41 *126*, 11621. (g) Matt, B.; Fize, J.; Moussa, J.; Amouri, H.; Pereira, A.; Artero, V.; Izzet, G.;
42
43 Proust, A., *Energy Environ. Sci.* **2013**, *6*, 1504. (h) Polyansky, D.; Cabelli, D.; Muckerman, J. T.;
44
45 Fujita, E.; Koizumi, T.; Fukushima, T.; Wada, T.; Tanaka, K., *Angew. Chem. Int. Ed.* **2007**, *46*,
46
47 4169. (i) Knör, G.; Vogler, A.; Roffia, S.; Paolucci, F.; Balzani, V., *Chem. Commun.* **1996**, 1643.
48
49 (j) Oppelt, K. T.; Woss, E.; Stiftinger, M.; Schofberger, W.; Buchberger, W.; Knör, G., *Inorg.*
50
51
52
53
54
55
56
57
58
59
60

1
2
3 *Chem.* **2013**, *52*, 11910. (k) Asatani, T.; Nakagawa, Y.; Funada, Y.; Sawa, S.; Takeda, H.;
4
5 Morimoto, T.; Koike, K.; Ishitani, O., *Inorg. Chem.* **2014**, *53*, 7170.
6
7

8
9 (6) (a) Karlsson, S.; Boixel, J.; Pellegrin, Y.; Blart, E.; Becker, H. C.; Odobel, F.;
10 Hammarström, L., *Faraday Discuss.* **2012**, *155*, 233. (b) Karlsson, S.; Boixel, J.; Pellegrin, Y.;
11 Blart, E.; Becker, H. C.; Odobel, F.; Hammarström, L., *J. Am. Chem. Soc.* **2010**, *132*, 17977. (c)
12 O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L.; Wasielewski, M. R.,
13 *Science* **1992**, *257*, 63. (d) Ghaddar, T. H.; Wishart, J. F.; Thompson, D. W.; Whitesell, J. K.;
14 Fox, M. A., *J. Am. Chem. Soc.* **2002**, *124*, 8285.
15
16
17
18
19
20
21
22

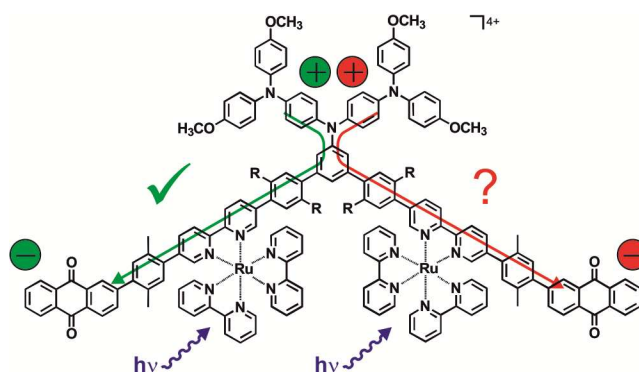
23
24 (7) (a) Du, P. W.; Eisenberg, R., *Energy Environ. Sci.* **2012**, *5*, 6012. (b) Sala, X.; Maji, S.;
25 Bofill, R.; Garcia-Anton, J.; Escriche, L.; Llobet, A., *Acc. Chem. Res.* **2014**, *47*, 504. (c) Fihri,
26 A.; Artero, V.; Razavet, M.; Baffert, C.; Leibl, W.; Fontecave, M., *Angew. Chem. Int. Ed.* **2008**,
27 *47*, 564. (d) Windle, C. D.; Perutz, R. N., *Coord. Chem. Rev.* **2012**, *256*, 2562. (e) Boston, D. J.;
28 Xu, C. D.; Armstrong, D. W.; MacDonnell, F. M., *J. Am. Chem. Soc.* **2013**, *135*, 16252. (f)
29 Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B., *Acc. Chem. Res.* **2009**, *42*, 1995.
30
31 (g) Hull, J. F.; Himeda, Y.; Wang, W. H.; Hashiguchi, B.; Periana, R.; Szalda, D. J.; Muckerman,
32 J. T.; Fujita, E., *Nature Chem.* **2012**, *4*, 383. (h) Sumliner, J. M.; Lv, H. J.; Fielden, J.; Geletii, Y.
33 V.; Hill, C. L., *Eur. J. Inorg. Chem.* **2014**, 635. (i) Chakraborty, S.; Wadas, T. J.; Hester, H.;
34 Schmehl, R.; Eisenberg, R., *Inorg. Chem.* **2005**, *44*, 6865. (j) Reisner, E.; Powell, D. J.; Cavazza,
35 C.; Fontecilla-Camps, J. C.; Armstrong, F. A., *J. Am. Chem. Soc.* **2009**, *131*, 18457. (k) Tong, L.
36 P.; Kopecky, A.; Zong, R. F.; Gagnon, K. J.; Ahlquist, M. S. G.; Thummel, R. P., *Inorg. Chem.*
37 **2015**, *54*, 7873. (l) Kato, S.; Jung, J. U.; Suenobu, T.; Fukuzumi, S., *Energy Environ. Sci.* **2013**,
38 *6*, 3756. (m) Sahara, G.; Ishitani, O., *Inorg. Chem.* **2015**, *54*, 5096.
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (8) (a) Hirao, Y.; Ino, H.; Ito, A.; Tanaka, K.; Kato, T., *J. Phys. Chem. A* **2006**, *110*, 4866.
4
5
6 (b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C., *Chem. Rev.* **2013**, *113*, 5322. (c) Bonn, A.
7
8 G.; Wenger, O. S., *Phys. Chem. Chem. Phys.* **2015**, *17*, 24001.
9
10
11 (9) (a) Babaei, A.; Connor, P. A.; McQuillan, A. J.; Umapathy, S., *J. Chem. Ed.* **1997**, *74*,
12
13 1200. (b) Lever, A. B. P., *Inorg. Chem.* **1990**, *29*, 1271.
14
15
16 (10) (a) Hankache, J.; Niemi, M.; Lemmetyinen, H.; Wenger, O. S., *Inorg. Chem.* **2012**, *51*,
17
18 6333. (b) Hankache, J.; Wenger, O. S., *Chem. Commun.* **2011**, *47*, 10145. (c) Hankache, J.;
19
20 Wenger, O. S., *Chem. Eur. J.* **2012**, *18*, 6443.
21
22
23
24 (11) Pavlishchuk, V. V.; Addison, A. W., *Inorg. Chim. Acta* **2000**, *298*, 97.
25
26
27
28 (12) (a) Greaves, M. D.; Niemz, A.; Rotello, V. M., *J. Am. Chem. Soc.* **1999**, *121*, 266. (b)
29
30 Huynh, M. H. V.; Meyer, T. J., *Chem. Rev.* **2007**, *107*, 5004.
31
32
33 (13) Okamoto, K.; Fukuzumi, S., *J. Phys. Chem. B* **2005**, *109*, 7713.
34
35
36 (14) Sreenath, K.; Thomas, T. G.; Gopidas, K. R., *Org. Lett.* **2011**, *13*, 1134.
37
38
39 (15) Opperman, K. A.; Mecklenburg, S. L.; Meyer, T. J., *Inorg. Chem.* **1994**, *33*, 5295.
40
41
42 (16) (a) Duvanel, G.; Banerji, N.; Vauthey, E., *J. Phys. Chem. A* **2007**, *111*, 5361. (b) Banerji,
43
44 N.; Duvanel, G.; Perez-Velasco, A.; Maity, S.; Sakai, N.; Matile, S.; Vauthey, E., *J. Phys. Chem.*
45
46 *A* **2009**, *113*, 8202.
47
48
49 (17) van Stokkum, I. H. M.; Larsen, D. S.; van Grondelle, R., *Biochim. Biophys. Acta*,
50
51 *Bioenerg.* **2004**, *1657*, 82.
52
53
54
55
56
57
58
59
60

1
2
3 (18) (a) Basu, S.; Chowdhury, A., *J. Lumin.* **2006**, *121*, 113. (b) Sun, Q. C.; Mosquera-
4 Vazquez, S.; Daku, L. M. L.; Guenee, L.; Goodwin, H. A.; Vauthey, E.; Hauser, A., *J. Am.*
5
6
7
8 *Chem. Soc.* **2013**, *135*, 13660.

9
10
11 (19) (a) Sundström, V.; Gillbro, T.; Gadonas, R. A.; Piskarskas, A., *J. Chem. Phys.* **1988**, *89*,
12 2754. (b) Moll, J.; Harrison, W. J.; Brumbaugh, D. V.; Muentner, A. A., *J. Phys. Chem. A* **2000**,
13 *104*, 8847. (c) De Belder, G.; Schweitzer, G.; Jordens, S.; Lor, M.; Mitra, S.; Hofkens, J.; De
14 Feyter, S.; Van der Auweraer, M.; Herrmann, A.; Weil, T.; Müllen, K.; De Schryver, F. C.,
15
16
17
18
19
20
21
22 *ChemPhysChem* **2001**, *2*, 49. (d) Morandeira, A.; Vauthey, E.; Schuwey, A.; Gossauer, A., *J.*
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Phys. Chem. A **2004**, *108*, 5741.

SYNOPSIS



A molecular acceptor-sensitizer-donor-sensitizer-acceptor pentad was explored with a view to achieving light-driven accumulation of two positive charges on the central donor unit. Photoinduced charge accumulation without sacrificial reagents is important for artificial photosynthesis.