Light-Driven Electron Accumulation in a Molecular Pentad

Margherita Orazietti,[†][a] Martin Kuss-Petermann,[†][b] Peter Hamm,[*][a] and Oliver S. Wenger[*][b]

Abstract: Accumulation and temporary storage of redox equivalents with visible light as an energy input is of pivotal importance for artificial photosynthesis because key reactions such as CO_2 reduction or water oxidation require the transfer of multiple redox equivalents. We report on the first purely molecular system, in which a long-lived charge-separated state ($\tau \approx 870$ ns) with two electrons accumulated on a suitable acceptor unit can be observed after excitation with visible light. Importantly, no sacrificial reagents were employed.

Molecular CO_2 reduction and water oxidation catalysts are commonly explored with sacrificial electron donors or acceptors to enable the underlying multi-electron redox chemistry,[1] however, in view of sustainable solar energy conversion, the light-driven accumulation and temporary storage of redox equivalents without the use of sacrificial reagents is highly desirable.[2] Photoinduced electron transfer in molecular systems has been investigated for several decades, but the vast majority of prior studies have reported exclusively on the transfer of single electrons.[3] Studies of photodriven charge accumulation commonly made use of sacrificial reagents,[4] with only a handful exceptions to that statement.[5] Nonetheless, until now it has not been possible to obtain long-lived charge-separated states ($\tau > 5$ ns), in which two electrons are accumulated on a single molecular acceptor.

With that goal in mind, we designed the pentad **I** shown in Scheme 1. We anticipated that two electrons can be accumulated on the central anthraquinone (AQ) unit after excitation of the two $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) photosensitizers; the two terminal triarylamine (TAA) moieties were expected to act as reversible (and not sacrificial) one-electron donors. The molecular triad **II** served as a reference compound, in which AQ can only be reduced by one electron after photoexcitation. Synthesis procedures and product characterization data are in the Supporting Information (SI). Both the UV-Vis spectra (SI page S8) and the cyclic voltammograms (SI page S9) are indicative of weak electronic coupling between the individual molecular components of **I** and **II**. The UV-Vis transient absorption spectra recorded in dry CH_3CN after pulsed

distinguish between AQ^- and AQ^{2-} on the basis of these data. Infrared spectroscopy is significantly better suited for this purpose.
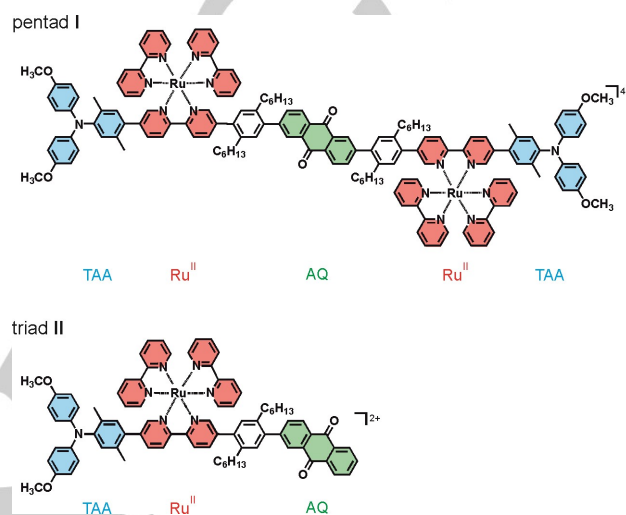
Scheme 1. Molecular structures of pentad **I** and triad **II**.

The transient IR difference spectra in Fig. 1a were measured after 0.5 ns following excitation of 1 mM solutions of **I** and **II** in dry, de-aerated CD_3CN. Excitation occurred at 415 nm selectively into the ^{1}MLCT manifold of the Ru(II) photosensitizers (SI page S8) with pulses of ~100 fs duration. Most of the spectral changes observed in the 1300-1700 cm^{-1} range are similar for **I** and **II**, for example a prominent new absorption at 1575 cm^{-1} and a bleach at 1510 cm^{-1}, both caused by oxidation of TAA to TAA^+.[7] Bleaches related to the depletion of AQ are detected at 1322, 1600, and 1680 cm^{-1} along with new bands at ~1450 and ~1485 cm^{-1}. The band at ~1485 cm^{-1} can clearly be assigned to AQ^-, as evidenced by the comparison to the IR spectro-electrochemical data shown in Fig. 1b, while the band at ~1450 cm^{-1} also might have contributions from TAA^+.[7] The most important absorption in Fig. 1a is a band at 1366 cm^{-1}, which ... for triad **II**. The IR spectro-electrochemical data in Fig. 1b, obtained from 5 mM 9,10-anthraquinone in dry CD_3CN, demonstrate that this band is caused by AQ^{2-}. At potentials up to -1.45 V vs. Fc^+/Fc, bands caused by AQ^- form at 1404 and 1492 cm^{-1}. However, at more negative potentials these absorptions disappear at the expense of a new band at 1366 cm^{-1}, which thus can be attributed to AQ^{2-}.[8] We conclude that after photoexcitation of pentad **I**, a charge-separated state with two TAA^+ and one AQ^{2-} unit is formed. By comparing the transient IR spectra with a weighted superposition of spectro-electrochemical difference spectra of AQ^- and AQ^{2-} we estimate that ca. 15% of the excited pentads end up in a doubly reduced state (CSS2), while 85% end up in a singly reduced state (CSS1) (SI page S12). In contrast in the

[a] Ms. M. Orazietti, Prof. Dr. P. Hamm
Department of Chemistry
University of Zurich
Winterthurerstrasse 190, 8057 Zurich (Switzerland)
E-mail: peter.hamm@chem.uzh.ch
[b] Dr. M. Kuss-Petermann, Prof. Dr. O. S. Wenger
Department of Chemistry
University of Basel
St. Johanns-Ring 19, 4056 Basel (Switzerland)
E-mail: oliver.wenger@unibas.ch
[†] These two authors contributed equally.

Supporting information for this article is given via a link at the end of the document.

triad **II,** an ordinary TAA$^+$ / AQ$^-$ couple forms, because there is only a single TAA donor (it is however not clear why the second AQ$^-$ band observed in the spectro-electrochemical difference spectrum at 1404 cm^{-1} shows up in the transient IR spectra only for the triad **II**, and not for the pentad **I**).
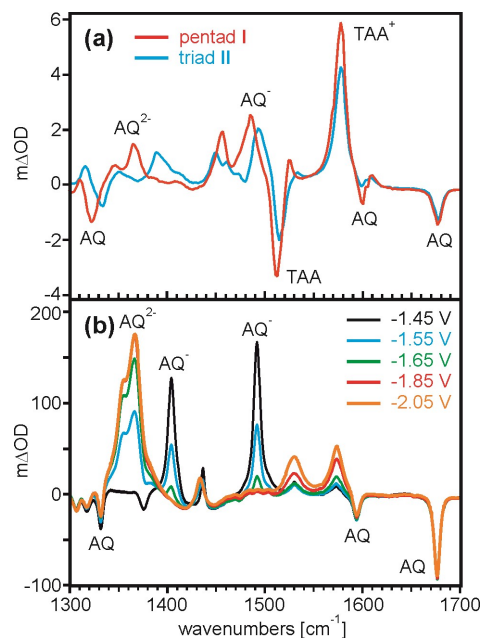

Figure 1. (a) Transient IR difference spectra measured after excitation of 1 mM solutions of pentad **I** and triad **II** in dry, de-aerated CD$_3$CN at 415 nm with laser pulses of ~100 fs duration. The excitation pulse energy was 2 μJ, the spectra were recorded 0.5 ns after excitation. (b) IR difference spectra measured after application of different potentials to a 5 mM solution of 9,10-anthraquinone in CD$_3$CN. The IR spectrum measured prior to application of any potential served as a baseline. Potentials are reported in Volts vs. Fc$^+$/Fc.
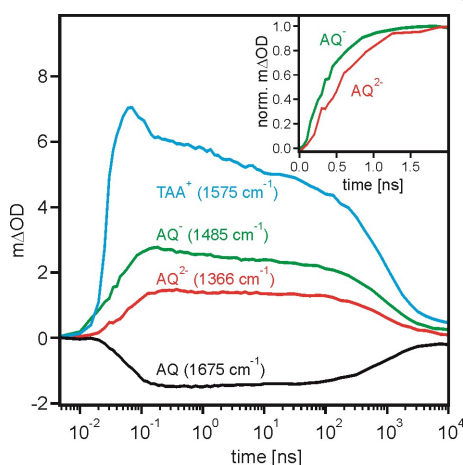

Figure 2. Temporal evolution of some of the key signals observed for pentad **I** in Fig. 1. The inset compares the normalized early rise of the bands originating from AQ$^-$ and AQ^{2-}.

The TAA$^+$ signal at 1575 cm^{-1} observed after excitation of pentad **I** rises with an instrumentally limited time constant of ~10 ps (blue trace in Fig. 2), indicating the formation of the charge-separated states TAA$^+$-Ru^I-AQ-Ru^{II}-TAA and TAA$^+$-Ru^I-AQ-Ru^I-TAA$^+$. The reduced photosensitizer (Ru^I) contributes a little bit to the absorption at 1575 cm^{-1}, hence the observation of a partial (~15%) decay of the initial signal with a time constant of 40 ps when the electron transfer from Ru^I to AQ occurs.[6a] Reduction of AQ manifests in a bleach of the signal at 1675 cm^{-1} with τ = 40 ps and a rise of the signal at 1485 cm^{-1} (AQ$^-$) with the same time constant (Fig. 2). The AQ^{2-}-related signal at 1366 cm^{-1} rises somewhat slower with τ = 65 ps (inset of Fig. 2).
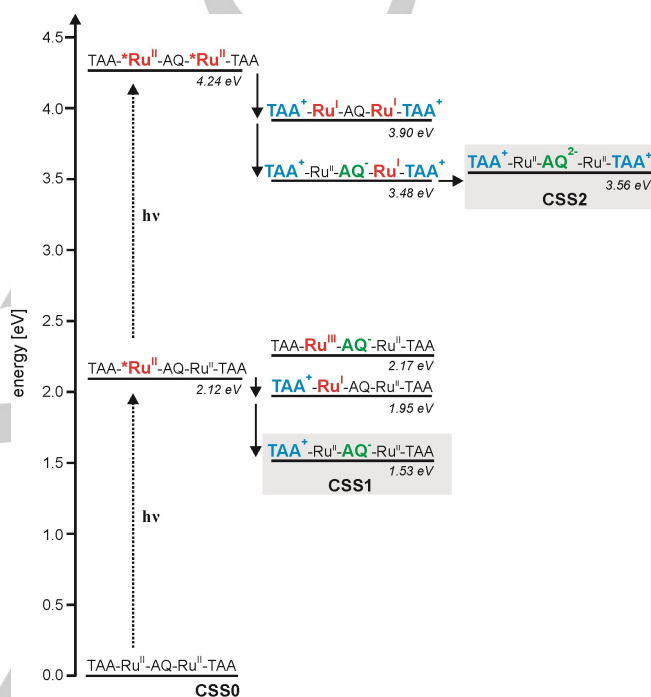
Scheme 2. Energy level diagram established on the basis of electrochemical and UV-Vis data (SI page S11). Energy estimates are accurate to ca. ±0.1 eV.

The electron transfer sequence observed above is in line with the energy level diagram in Scheme 2, which was established on the basis of redox potentials determined from cyclic voltammetry (SI page S11) and UV-Vis data. Absorption of a single photon leads to the TAA$^+$-Ru^{II}-AQ$^-$-Ru^{II}-TAA (CSS1) state at ~1.53 eV (τ = 40 ps), the majority photo-product seen also in triad **II** (TAA$^+$-Ru^{II}-AQ$^-$). Absorption of two photons within the same 100 fs pulse populates the TAA-*Ru^{II}-AQ-*Ru^{II}-TAA state at 4.24 eV. Reductive ^{3}MLCT excited-state quenching of both photosensitizers leading to the TAA$^+$-Ru^I-AQ-Ru^I-TAA$^+$ state at 3.90 eV cannot be temporally resolved on our setup. Subsequently, two electron transfer steps from the two Ru^I centers to AQ occur, going via the TAA$^+$-Ru^{II}-AQ$^-$-Ru^I-TAA$^+$ state that is estimated to be at 3.48 eV to finally the TAA$^+$-Ru^{II}-AQ^{2-}-Ru^{II}-TAA$^+$ state (CSS2) at 3.56 eV. Due to the multitude of overlapping processes, we cannot disentangle them all, nevertheless it is reasonable to assume that the last electron-accumulating step occurring with a 65 ps time constant is rate-

determining, because it has significantly smaller driving-force than the preceding electron transfer events. Based on the redox potentials (SI page S11) that electron-accumulating step would even be slightly endergonic (ΔG_{ET}^0 = 0.08 eV), but it should be kept in mind that the energy estimates in Scheme 2 are associated with uncertainties of ±0.1 eV.

The TAA^+-Ru^{II}-AQ^--Ru^{II}-TAA (CSS1) and TAA^+-Ru^{II}-AQ^{2-}-Ru^{II}-TAA^+ (CSS2) states then decay with time constants of 980 and 870 ns, respectively. While the lifetime of CSS1 is not surprising,[6, 9] the relatively long lifetime of CSS2 is remarkable in view of the multitude of decay channels which in principle are open to a state which is energetically ~3.56 eV above the ground state. However, we note that relaxation of CSS2 to CSS1 is associated with $\Delta G_{ET}^0 \approx$ -2.0 eV, hence it is possible that this reaction is decelerated by an inverted driving-force effect,[10] similar to what we observed for the charge-recombination from CSS1 in donor-bridge-acceptor molecules which are structurally closely related to triad **II**.[6b, 9]
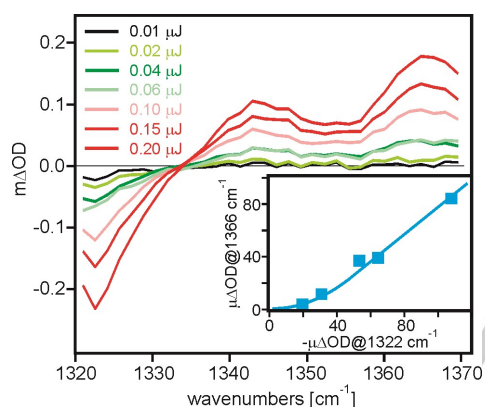

Figure 3. Dependence of the AQ bleach at 1322 cm^{-1} and the AQ^{2-} absorption band at 1366 cm^{-1} on the excitation pulse energy. The data have been averaged over various time points ranging from 1 to 100 ns to enhance the signal to noise ratio. The inset shows the change in optical density at 1366 cm^{-1} compared to that at 1322 cm^{-1}, which reports on the bleach of AQ and as such is used as an internal standard (which is free of the uncertainty originating from e.g. the alignment of the spatial overlap between pump- and probe pulse). The data are fit to a quadratic function up to a certain point, and to a linear function beyond.

Since population of CSS2 requires absorption of two photons, a quadratic dependence of the intensity of the signal at 1366 cm^{-1} on excitation power is expected. This is indeed the case, as the data in Fig. 3 show. At an excitation energy of 0.01 µJ, a bleach of the AQ band at 1322 cm^{-1} is already detectable whereas at 1366 cm^{-1} no trace of AQ^{2-} is recognizable yet, indicating the exclusive formation of AQ^- (CSS1) at the lowest pulse energy (E_p). At E_p > 0.01 µJ, the AQ^{2-} signal at 1366 cm^{-1} (CSS2) becomes observable, and for E_p > 0.04 µJ the bleach at 1322 cm^{-1} and the signal at 1366 cm^{-1} increase in parallel in essentially a linear fashion. The inset of Fig. 3 highlights that behavior by showing the expected quadratic power dependence seen at the very lowest E_p's. By comparing the amplitude of the transient IR response with the spectro-electrochemical difference spectrum (see SI Fig. S4), we estimate that the fractions of excited pentads, averaged over the excited volume,

amounts to 0.7% at E_p = 0.01 µJ. As an independent estimate of the excitation probability, we can also consider the extinction coefficient of the photosensitizer and the peak irradiance of the pump pulse, revealing an excitation probability of 1.1% at E_p = 0.01 µJ (SI page S12). The second estimate is somewhat higher, as it refers to the peak, in contrast to the averaged, excitation probability. In any case, the changeover to a linear power dependence (see Fig. 3, inset) at such low excitation probabilities is highly surprising. Likely, the early changeover from a quadratic into a linear regime has the same origin as the low maximal excitation probability of CSS2 (15% relative to CSS1) observed even for the largest pump pulse energies tested (E_p=2 µJ). At this stage, we do not know what the photo-physical processes are that give rise to both observations. Double-pulse excitation experiments with high time-resolution, along the lines of ref. [2a], might elucidate these processes.

In summary, we have achieved long-lived (τ = 870 ns) electron accumulation in a purely molecular system without sacrificial reagents, using visible light as the sole energy input. This observation is of key importance in the context of solar energy conversion, because the generation of so-called solar fuels (e. g., H_2, HCOOH or CH_3OH) from small inert molecules such as H_2O and CO_2 invariably relies on multi-electron redox reactions. Consequently, it is important to elucidate the basic principles of photodriven accumulation and temporary storage of redox equivalents without relying on sacrificial reagents. Our study reports on an important proof-of-concept in this regard.

Acknowledgements

[1]   a) X. Sala, I. Romero, M. Rodriguez, L. Escriche, A. Llobet, *Angew. Chem. Int. Ed.* **2009**, *48*, 2842-2852; b) J. J. Concepcion, J. W. Jurss, M. K. Brennaman, P. G. Hoertz, A. O. T. Patrocinio, N. Y. M. Iha, J. L. Templeton, T. J. Meyer, *Acc. Chem. Res.* **2009**, *42*, 1954-1965; c) A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer, G. L. Waldrop, *Chem. Rev.* **2013**, *113*, 6621-6658.

[2]   a) L. Hammarström, *Acc. Chem. Res.* **2015**, *48*, 840-850; b) Y. Pellegrin, F. Odobel, *Coord. Chem. Rev.* **2011**, *255*, 2578-2593; c) G. F. Manbeck, K. J. Brewer, *Coord. Chem. Rev.* **2013**, *257*, 1660-1675; d) S. Fukuzumi, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2283-2297; e) L. Favereau, A. Makhal, Y. Pellegrin, E. Blart, J. Petersson, E. Goransson, L. Hammarström, F. Odobel, *J. Am. Chem. Soc.* **2016**, *138*, 3752-3760; f) L. Zedler, S. Kupfer, I. R. de Moraes, M. Wachtler, R. Beckert, M. Schmitt, J. Popp, S. Rau, B. Dietzek, *Chem. Eur. J.* **2014**, *20*, 3793-3799.

[3]   a) V. Balzani, *Electron transfer in chemistry, Vol. 3*, VCH Wiley, Weinheim, **2001**; b) M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435-461; c) D. M. Guldi, *Chem. Soc. Rev.* **2002**, *31*, 22-36; d) M. Delor, T. Keane,

P. A. Scattergood, I. V. Sazanovich, G. M. Greetham, M. Towrie, A. Meijer, J. A. Weinstein, *Nature Chem.* **2015**, *7*, 689-695; e) C. Shih, A. K. Museth, M. Abrahamsson, A. M. Blanco-Rodriguez, A. J. Di Bilio, J. Sudhamsu, B. R. Crane, K. L. Ronayne, M. Towrie, A. Vlček, J. H. Richards, J. R. Winkler, H. B. Gray, *Science* **2008**, *320*, 1760-1762; f) M. B. Majewski, N. R. de Tacconi, F. M. MacDonnell, M. O. Wolf, *Chem. Eur. J.* **2013**, *19*, 8331-8341; g) J. H. Klein, D. Schmidt, U. E. Steiner, C. Lambert, *J. Am. Chem. Soc.* **2015**, *137*, 11011-11021.

[4]   a) R. Konduri, H. W. Ye, F. M. MacDonnell, S. Serroni, S. Campagna, K. Rajeshwar, *Angew. Chem. Int. Ed.* **2002**, *41*, 3185-3187; b) C. Chiorboli, S. Fracasso, F. Scandola, S. Campagna, S. Serroni, R. Konduri, F. M. MacDonnell, *Chem. Commun.* **2003**, 1658-1659; c) R. Konduri, N. R. de Tacconi, K. Rajeshwar, F. M. MacDonnell, *J. Am. Chem. Soc.* **2004**, *126*, 11621-11629; d) K. L. Wouters, N. R. de Tacconi, R. Konduri, R. O. Lezna, F. M. MacDonnell, *Photosynth. Res.* **2006**, *87*, 41-55; e) D. Polyansky, D. Cabelli, J. T. Muckerman, E. Fujita, T. Koizumi, T. Fukushima, T. Wada, K. Tanaka, *Angew. Chem. Int. Ed.* **2007**, *46*, 4169-4172; f) D. E. Polyansky, D. Cabelli, J. T. Muckerman, T. Fukushima, K. Tanaka, E. Fujita, *Inorg. Chem.* **2008**, *47*, 3958-3968; g) B. Matt, J. Fize, J. Moussa, H. Amouri, A. Pereira, V. Artero, G. Izzet, A. Proust, *Energy Environ. Sci.* **2013**, *6*, 1504-1508; h) A. G. Bonn, O. S. Wenger, *Phys. Chem. Chem. Phys.* **2015**, *17*, 24001-24010.

[5]   a) S. Karlsson, J. Boixel, Y. Pellegrin, E. Blart, H. C. Becker, F. Odobel, L. Hammarström, *Faraday Discuss.* **2012**, *155*, 233-252; b) S. Karlsson, J. Boixel, Y. Pellegrin, E. Blart, H. C. Becker, F. Odobel, L. Hammarström, *J. Am. Chem. Soc.* **2010**, *132*, 17977-17979; c) M. P. O'Neil, M. P. Niemczyk, W. A. Svec, D. Gosztola, G. L. Gaines, M. R. Wasielewski, *Science* **1992**, *257*, 63-65; d) H. Imahori, M. Hasegawa, S. Taniguchi, M. Aoki, T. Okada, Y. Sakata, *Chem. Lett.* **1998**, 721-722; e) A. G. Bonn, O. S. Wenger, *Chimia* **2015**, *69*, 17-21.

[6]   a) J. Hankache, M. Niemi, H. Lemmetyinen, O. S. Wenger, *Inorg. Chem.* **2012**, *51*, 6333-6344; b) M. Kuss-Petermann, O. S. Wenger, *J. Am. Chem. Soc.* **2016**, *138*, 1349-1358.

[7]   F. Ritschl, *Spectrochim. Acta A* **1967**, *A 23*, 655-675.

[8]   W. X. Cheng, B. K. Jin, P. Huang, L. J. Cheng, S. Y. Zhang, Y. P. Tian, *J. Phys. Chem. C* **2013**, *117*, 3940-3948.

[9]   M. Kuss-Petermann, O. S. Wenger, *Angew. Chem. Int. Ed.* **2016**, *55*, 815-819.

[10]   a) R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265-322; b) L. S. Fox, M. Kozik, J. R. Winkler, H. B. Gray, *Science* **1990**, *247*, 1069-1071.

Entry for the Table of Contents

Layout 1:

COMMUNICATION

Long-lived (τ = 870 ns) electron accumulation has been achieved in a molecular pentad without the use of sacrificial reagents. This is an important proof-of-concept for solar energy conversion and multi-electron photoredox chemistry.
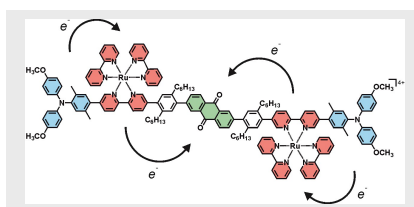
Margherita Orazietti[†], Martin Kuss-Petermann[†], Peter Hamm*, Oliver S. Wenger*

Page No. – Page No.

Light-Driven Electron Accumulation in a Molecular Pentad