

Combining energy and electron transfer in a supramolecular environment for the highly efficient generation of hydrated electrons with green light

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Aqueous photoionizations produce the hydrated electron ($e_{\text{aq}}^{\bullet-}$), which is a super reductant with highly attractive chemical applications such as the reductive decomposition of recalcitrant pollutants^[1] and the direct reduction of carbon dioxide.^[2] However, all previous procedures to generate $e_{\text{aq}}^{\bullet-}$ had to rely on UV-C radiation,^[1,2] inherently making a solar application impossible. Our research focuses on the development of photoionizations that require only green light (532 nm, coinciding with the maximum of the terrestrial solar spectrum) and are based on catalytic cycles such that nothing but a bioavailable sacrificial donor is consumed, so might serve as a sustainable sources of $e_{\text{aq}}^{\bullet-}$.

Starting from our very first example of a completely green-light driven cyclic photoionization, in which the one-electron reduced ruthenium-tris(bipyridyl) complex functioned as ionizable intermediate,^[3] we have carried out further studies to improve the "green" $e_{\text{aq}}^{\bullet-}$ production. Since the mechanistic bottleneck of the first system was the photoionization step, whose quantum yield was as low as 1 %, we then investigated aryl radical anions^[4,5] as highly promising electron precursors. They are not only sufficiently energy-rich for their green-light photoionization to be feasible, but their rigid molecular skeletons also decelerate the radiationless deactivation of their excited states, which competes with ionization. In direct consequence of the latter, the quantum yields of aryl radical anion photoionizations are expected to be remarkably high, and indeed we found green-light ionization quantum yields of up to 27 %.^[4,5] For thermodynamic reasons, however, these radical anions cannot be generated with green light.

In this study, we succeeded in the construction of a novel catalytic cycle of $e_{\text{aq}}^{\bullet-}$ formation (Fig. 1) that is both sustainable, *i.e.* driven entirely by green light and consuming only a bioavailable donor, and efficient (owing to an pyrene radical anion, $\text{PyX}^{\bullet-}$, as ionizable intermediate).^[6] The mechanism couples an energy-transfer cycle, in which a light-harvesting ruthenium diimine complex ($[\text{Ru}(\text{NN})_3]^{2+}$) absorbs a first photon and passes the excitation energy on to a pyrene-based redox catalyst (reaction **EnT**), with an electron-transfer cycle, in which the resulting triplet is reductively quenched (reaction **ET**); the energy-rich aryl radical anion is finally ionized by a second photon. In this complex system, the supramolecular environment of an anionic micelle ensures the desired order of the reaction steps by selectively suppressing side reactions through noncovalent interactions. Our new approach comprises the pooling of two low-energy photons with energy and electron transfer processes in a (micro)heterogeneous system and might thus be regarded as an artificial realization of the highly optimized Z scheme of photosynthesis.

The separation of primary ($[\text{Ru}(\text{NN})_3]^{2+}$) and secondary absorber (aryl radical anion) permits choosing a redox catalyst with a nonabsorbing ground state and greatly facilitates the independent optimization of each component for its main function. Compared to our initial example of this mechanism,^[6] we were thus able to improve the overall efficiency of the $e_{\text{aq}}^{\bullet-}$ generation by a full order of magnitude. For that, we used a sensitizer with a longer excited state lifetime thereby increasing the energy transfer efficiency and the yield of intermediate formation accordingly, and a pyrene derivative (**PyX**) with a significantly higher green-light ionization quantum yield of its radical anion.

We will present not only detailed mechanistic investigations but will also demonstrate the applicability of the mechanism to the reductive detoxification of halogenated organic waste.

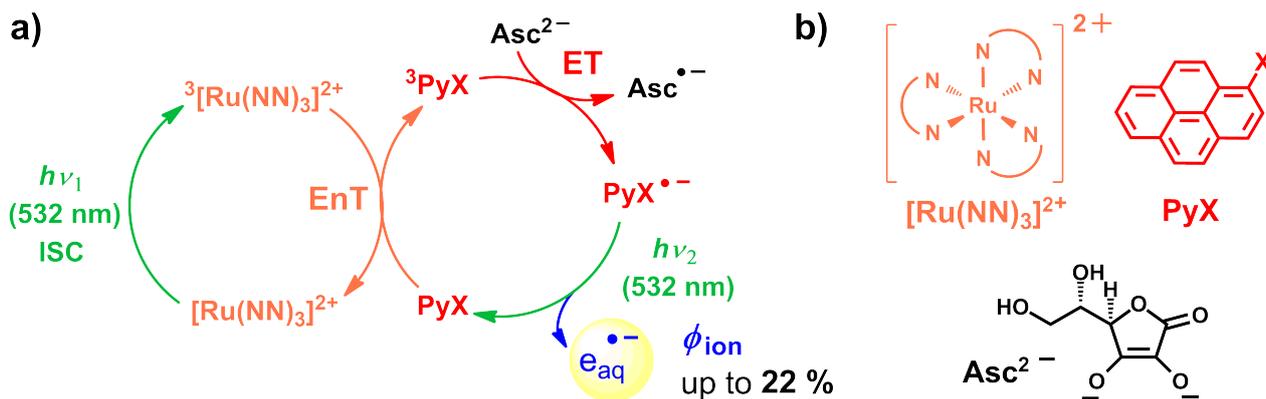


Figure 1: The current record holder in green-light photoionization. (a) Cyclic photoionization mechanism of a pyrene radical anion ($\text{PyX}^{\bullet-}$) in the presence of a sensitizer ($[\text{Ru}(\text{NN})_3]^{2+}$) and a sacrificial electron donor (Asc^{2-}). (b) Structural formulas of the key compounds.

Funding: Deutsche Forschungsgemeinschaft (grant Go615/15-1)

Acknowledgements: We thank R. Naumann as well as T. Kohlmann for carrying out some supporting experiments.

References:

- [1] X. Li, J. Ma, G. Liu, J. Fang, S. Yue, Y. Guan, L. Chen, X. Liu, *Environ. Sci. Technol.*, **2012**, 46, 7342.
- [2] L. Zhang, D. Zhu, G. M. Nathanson, R. J. Hamers, *Angew. Chem. Int. Ed.*, **2014**, 53, 9746.
- [3] M. Goetz, C. Kerzig, R. Naumann, *Angew. Chem. Int. Ed.*, **2014**, 53, 9914.
- [4] C. Kerzig, M. Goetz, *Phys. Chem. Chem. Phys.*, **2014**, 16, 25342.
- [5] M. Brautzsch, C. Kerzig, M. Goetz, *Green Chem.*, **2016**, 18, 4761.
- [6] C. Kerzig, M. Goetz, *Chem. Sci.*, **2016**, 7, 3862.