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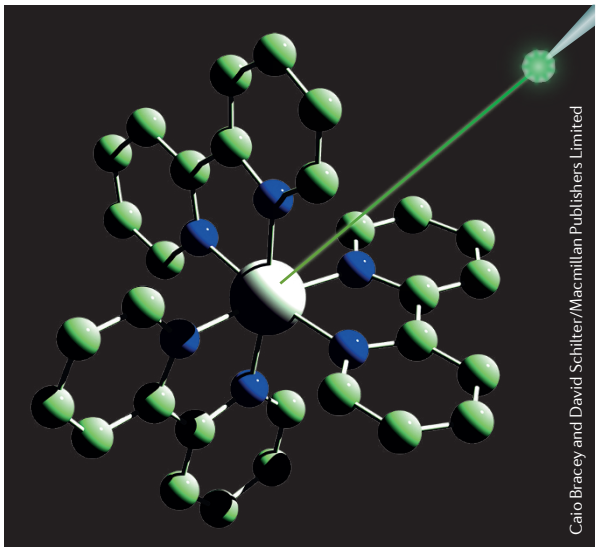
PHOTOCHEMISTRY

Electrons clean up by going green

> a different perspective will provide different answers, including observations and explanations of effects that have been overlooked

Inspired by photosynthesis, photochemists harness light as a stimulus for chemical reactions. However, using light efficiently to induce selective reactions over long periods of time has proved to be troublesome. Many chromophores absorb high-energy UV radiation, competing with organic substrates for photons. Once these chromophores do absorb light, they often react uncontrollably with any neighbouring molecules. Alternatively, molecules in a high-energy excited state can undergo unimolecular decomposition. Thus, our challenge lies in using low-energy light to give reactive intermediates that only participate in one reaction.

In a recent article in *Chemical Science*, Martin Goez and colleagues describe the conversion of green light and ascorbate (Asc^{2-}), catalysed by tris(2,2′-bipyridyl)ruthenium(II) (Rubpy), to produce hydrated electrons. A clear advantage of Rubpy over previous photocatalysts is its sensitivity to green light (532 nm, 2.33 eV). Of their simple methodology, "this combination affords one of the most powerful reductants — the hydrated electron — under extremely mild conditions," claims Goez. Rubpy is a well-known chromophore that undergoes rapid (<1 ps) photoinduced metal-to-ligand charge transfer to an excited state (^{3}MLCT) that is sufficiently long-lived to have a high likelihood of colliding favourably with nearby Asc^{2-}. The photoexcited triplet Rubpy oxidizes Asc^{2-} and, upon absorbing a second green photon, releases a hydrated electron. The concentration of hydrated electrons decays monoexponentially, with their mean lifetime of 165 ns equating to a decay rate of $6.1 \times 10^6\ s^{-1}$. Decay occurs primarily through reaction with monobasic ascorbate ($AscH^-$, $pK_a = 11.74$), the concentration of which was controlled by maintaining a high solution pH. Goez's team used a frequency-doubled Nd:YAG laser to generate a high enough photon flux to trigger the two-photon process, thereby obtaining a hydrated-electron concentration of ~15% relative to that of the catalyst. This photocatalytic system was quite stable, and no catalyst degradation occurred after 50 light pulses. Although Rubpy alone decomposes quickly after several minutes of illumination, the presence of Asc^{2-} protects the photocatalyst from rapid bleaching. Indeed, the ^{3}MLCT state reacts with Asc^{2-} so quickly that it does not get time to convert into a deleterious Ru $4d^6$ triplet.



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Goez and his team tested the utility of their system by performing several challenging reductions. The photogenerated, hydrated electrons effected the degradation of chloroacetic acid, a model compound for toxic chlorinated organic waste, into the benign products acetic acid and chloride. Degradation occurs when chloroacetic acid captures the hydrated electron and undergoes dissociative electron transfer, with the resulting carbon-centered radical then abstracting an H atom from $AscH^-$. Up to 91% of chloroacetic acid was converted within 1 hour of illumination, giving a turnover number (TON) of 186 with respect to Rubpy. On optimization, a TON of 1,400 was achieved at 47% conversion, with the selective production of acetate and only minimal amounts (<3%) of succinic acid, the radical dimerization product. The authors were also able to dechlorinate 4-chlorobenzoic acid and 4-chlorophenylacetic acid, molecules inert towards typical dechlorination reactions, achieving TONs of 135 and 30, respectively. This photochemical methodology was used to reduce the non-activated ketone 3,3-dimethyl-2-butanone, hinting that the method is generalizable.

Looking ahead, Goez notes that there are still more ways to improve the photocatalytic system, including the use of low-power light sources. Another direction earmarked for improvement is the replacement of Rubpy with a non-toxic, metal-free and more photostable chromophore — even Rubpy eventually degrades after enough illumination. Goez believes that this insight stems, in part, from his research attitude: "I think that looking at things from a different perspective will provide different answers, including observations and explanations of effects that have been overlooked so far."

Adam Weingarten, Associate Editor, Nature Communications

ORIGINAL ARTICLE Naumann, R., Kerzig, C. & Goez, M. Laboratory-scale photoredox catalysis using hydrated electrons sustainably generated with a single green laser. *Chem. Sci.* http://dx.doi.org/10.1039/C7SC03514D (2017)