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Unexpected Hydrated Electron Source for Preparative Visible-Light Driven Photoredox Catalysis

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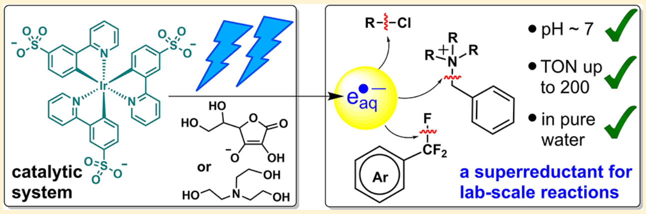
Supporting Information



ABSTRACT: The hydrated electron is experiencing a renaissance as a superreductant in lab-scale reductions driven by light, both for the degradation of recalcitrant pollutants and for challenging chemical reactions. However, examples for its sustainable generation under mild conditions are scarce. By combining a water-soluble Ir catalyst with unique photochemical properties and an inexpensive diode laser as light source, we produce hydrated electrons through a two-photon mechanism previously thought to be unimportant for laboratory applications. Adding cheap sacrificial donors turns our new hydrated electron source into a catalytic cycle operating in pure water over a wide pH range. Not only is that catalytic system capable of detoxifying a chlorinated model compound with turnover numbers of up to 200, but it can also be employed for two novel hydrated electron reactions, namely, the decomposition of quaternary ammonium compounds and the conversion of trifluoromethyl to difluoromethyl groups.

■ INTRODUCTION

Many important chemical reactions require very strong reductants, but photocatalytic mechanisms driven by a single visible photon can only provide limited reducing power. For instance, the widely used Ir(ppy)$_3$ complex is capable of reducing aryl iodides and bromides,[1] but aryl chlorides are out of range and require multiphoton excitation processes when using visible photons.[2] In 2014, the interest in two-photon approaches received a boost by the discovery of novel mechanisms[2,3] with far-reaching laboratory applications for reductive transformations, in organic solvents[4−9] and water.[10−13] Given that intense irradiation is required for two-photon mechanisms to be efficient, the availability of cheap light sources with high photon fluxes such as high-power LEDs and cw lasers laid the grounds for the ongoing rapid development[14−25] in that research field.

Concerning challenging reductions in aqueous solution, the hydrated electron ($e_{aq}^{\bullet-}$) is the most promising initiating species, because with a standard potential as high as that of alkali metals (−2.9 V vs. NHE)[26] and a lifetime much longer than excited singlet or doublet states can possess (~1 μs under conditions suitable for applications), that species provides the perfect balance between thermodynamic and kinetic reactivity. Two basic pathways for the catalytic generation of $e_{aq}^{\bullet-}$ are conceivable, which both consume two visible photons and a sacrificial donor.[3,27] Following the first light absorption event by the catalyst, either the excited state is directly photoionized, producing the one-electron oxidized form of the catalyst as byproduct (Figure 1b),[27] or a photoinduced electron transfer converts the catalyst into its one-electron reduced form, serving as $e_{aq}^{\bullet-}$ precursor (Figure 1a).[3] Whereas the applicability of both mechanisms was demonstrated using pulsed lasers for illumination,[10,27,28] so far only the latter pathway has been viable with nonpulsed light sources such as those nowadays available in most chemistry laboratories.[11−13] However, these recent studies rely on the exploitation of anionic micelles[11,12] or sophisticated Coulombic interactions[13] to stabilize relevant reaction intermediates, rendering these methods somewhat cumbersome.

During the past decade, $e_{aq}^{\bullet-}$ has been employed for the decomposition of persistent halogenated pollutants,[29] for nitrogen[30] or carbon dioxide fixation,[31] and for versatile chemical syntheses.[11−13] However, the lack of easy-to-handle visible-light driven $e_{aq}^{\bullet-}$ sources still hampers its broad usage. This initiated our quest for a novel catalytic system operating in pure water without relying on supramolecular interactions. As we will show by addressing both detailed mechanistic investigations and preparative photoredox catalysis (see Supporting Information for details), a water-soluble analogue of *fac*-Ir(ppy)$_3$ (**Irsppy**, Figure 1c)[32] has ideal properties to act as a photocatalyst for $e_{aq}^{\bullet-}$ production via the mechanism of Figure 1b. In contrast to the long-standing opinion that pulsed lasers (~$20 000) with power densities of ~100 MW cm^{-2} are required for that mechanism to work,[3,6,27] we will demonstrate preparative-scale applications with an inexpensive (~$1 000) blue cw laser and optics for beam collimation (Figure 1d), whose combination ensures a photon flux per area on the order of 1 kW cm^{-2} (Supporting Information, section 1.2).

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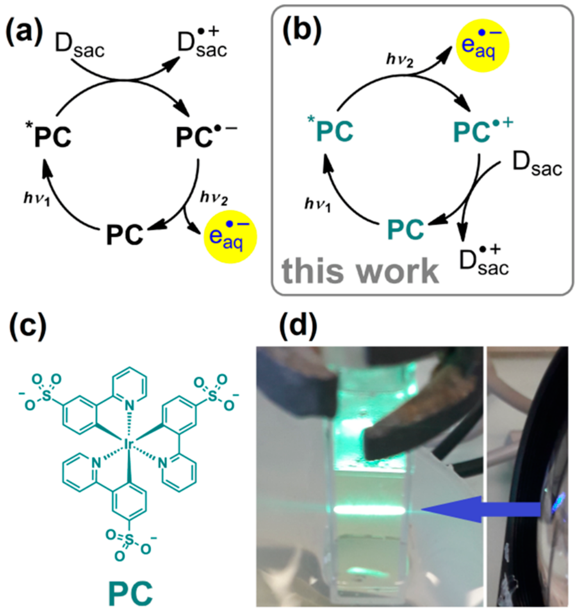

Figure 1. (a) Catalytic cycle of aqueous radical anion photoionization.[3] (b) Catalytic generation of e$_{aq}^{\bullet-}$ through the visible-light driven ionization of the photocatalyst (PC) **Irsppy** (structure given in (c)) with subsequent catalyst regeneration using a sacrificial donor D$_{sac}$. (d) Photograph showing the experimental conditions required for the novel e$_{aq}^{\bullet-}$ production system; the key point is the beam collimation of a blue continuous wave (cw) laser (447 nm, 1 W) to a spot smaller than 1 mm^2 (as visualized by the catalyst emission). For further explanations, see text and Supporting Information (section 1.2).

RESULTS AND DISCUSSION

Mechanistic Investigations. Our trisulfonated **Irsppy** is a perfect water-soluble stand-in for its famous parent compound *fac*-Ir(ppy)$_3$,[33] as the photophysical properties presented in Figure 2a demonstrate: its ground state absorbs below 500 nm (cyan trace), the ^{3}MLCT shows characteristic green luminescence (light green trace) with a very high quantum yield, and the emissive excited state decays with a lifetime of ~1.6 μs, which is shown in the inset of Figure 2a by time-resolved luminescence (510 nm), excited-state absorption (367 nm), and ground-state bleaching measurements (278 nm). Beyond these steady-state and lifetime experiments, we carefully corrected and calibrated the excited-state absorption spectrum of **Irsppy** (orange trace in Figure 2a; see Supporting Information for details), which forms the basis for quantitative measurements.

Thermodynamic considerations (Supporting Information, section 3) predict the photoionization (i.e., the light-driven release of e$_{aq}^{\bullet-}$) of excited **Irsppy** (^{3}**Irsppy**) to be more favorable than that of excited ruthenium(tris)bipyridine[34] [Ru(bpy)$_3$]$^{2+}$ by ~0.6 eV. The ionization of ^{3}[Ru(bpy)$_3$]$^{2+}$ requires highly energetic photons (λ < 400 nm),[3,35,36] and therefore we anticipated that the absorption of a second low-energy photon by ^{3}**Irsppy** might result in efficient e$_{aq}^{\bullet-}$ formation via an "all-visible" biphotonic ionization mechanism (mechanism of Figure 1b). To test this, we performed two-pulse laser flash photolysis[23,28,37,38] using a pulse sequence as illustrated at the top of Figure 2b. An initial 430 nm pulse was followed by a 532 nm pulse (delayed by 450 ns). This allowed the generation of ^{3}**Irsppy** with the first pulse, while the second pulse (532 nm) selectively excites that ^{3}**Irsppy** photoproduct

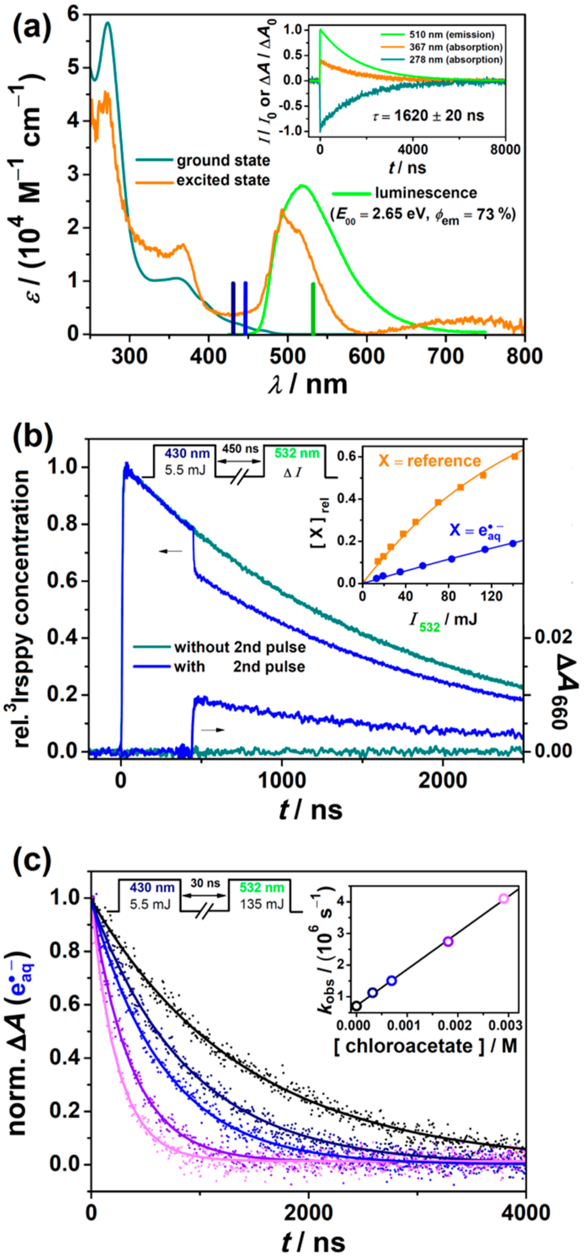

Figure 2. Photochemical properties of **Irsppy** in its ground and excited state (panel a); two-pulse experiments on the photoionization mechanism (Figure 1b) of **Irsppy** (panel b); and unambiguous identification of e$_{aq}^{\bullet-}$ as product by monitoring its reaction with chloroacetate ClAc$^-$ (panel c). All experiments carried out in Ar-saturated aqueous solutions containing 50 μM **Irsppy**. (a) Calibrated absorption and corrected luminescence spectra; wavelengths used for excitation (laser flash photolysis, 430 and 532 nm; prep. photolysis, 447 nm) indicated as vertical lines. Inset: Kinetic traces upon excitation with 430 nm laser pulses (5 mJ). (b) Kinetic data for excited **Irsppy** (upper traces, left *y*-axis) and e$_{aq}^{\bullet-}$ (lower traces, right *y*-axis) in a representative two-pulse experiment (pulse scheme above traces) with the second laser (135 mJ) blocked (cyan) or unblocked (blue). (Inset) Excited **Irsppy** bleaching/e$_{aq}^{\bullet-}$ formation (blue) at different intensities of the second laser and reference reaction (excitation of [Ru(bpy)$_3$]$^{2+}$, orange) used for relative actinometry, both relative to the prepulse concentration of the respective signal precursor. (c) Experimental e$_{aq}^{\bullet-}$ decay (dots) in the presence of variable amounts of ClAc$^-$ after excitation with the pulse scheme shown above the traces. (Inset) Corresponding Stern−Volmer plot. For further details, see text and Supporting Information.

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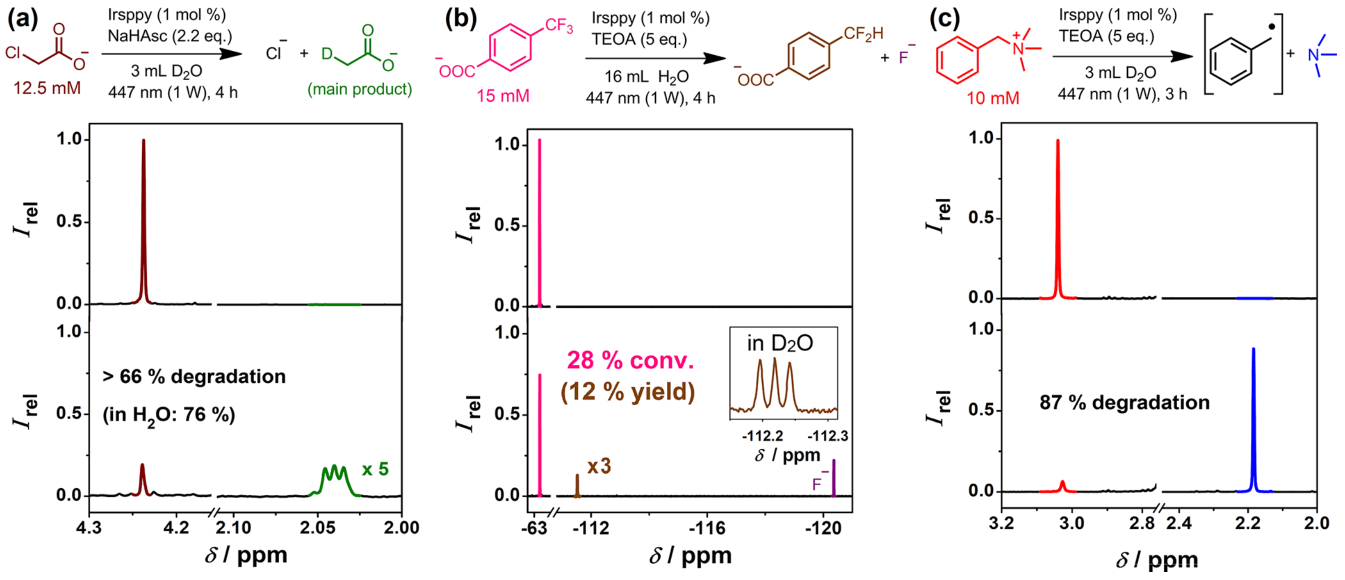

Figure 3. Lab-scale reactions carried out with the new blue-light driven $e_{aq}^{\bullet-}$ source in Ar-saturated solution with the pertinent conditions given at the respective equations. (a) Detoxification of $ClAc^-$. (b) Monodefluorination of 4-(trifluoromethyl)benzoate. (c) Degradation of the benzyltrimethylammonium cation. Quantitative NMR measurements ($ClAc^-$ and benzyltrimethylammonium cation, ^1H NMR; 4-(trifluoromethyl)benzoate, ^{19}F NMR) are displayed before (upper trace) and after (lower trace) irradiation; the same color codes as in the reaction equations have been used. For further details, see the text and Supporting Information, sections 1 and 7.

(vertical lines in Figure 2a; Supporting Information, pp S12–S15). The second pulse brings about ^{3}**Irsppy** bleaching on a large scale (Figure 2b, blue trace), as is evidenced by two-pulse experiments with luminescence detection (λ = 510 nm), because these measurements are able to monitor ^{3}**Irsppy** (the proposed intermediate in our consecutive two-photon mechanism) without interferences from other species (see section 6 of the Supporting Information for details). Monitoring additional transient absorptions under the same experimental conditions revealed the appearance of a new second-pulse induced species absorbing in the red and possessing a 1.4 μs lifetime. Quenching experiments of the absorptions of this species with chloroacetate ($ClAc^-$, Figure 2c) yielded a rate constant (1.15×10^9 M^{-1} s^{-1}) practically identical with that previously observed for the reaction between $e_{aq}^{\bullet-}$ and $ClAc^-$,[26] which is a reliable reference reaction.[11,28,29] Control experiments established that ^{3}**Irsppy** itself does not react with chloroacetate (Supporting Information, last paragraph of section 5). All these results, together with additional two-pulse experiments with spectral detection (Supporting Information, section 6), unambiguously identify the new species as $e_{aq}^{\bullet-}$. By changing the energy of the second pulse with all other parameters unmodified, the intensity dependence of $e_{aq}^{\bullet-}$ formation was obtained. That dependence (Figure 2b, inset) exhibits a linear low-intensity regime indicating the ^{3}**Irsppy** ionization to be monophotonic. Relative actinometry with the excitation of $[Ru(bpy)_3]^{2+}$ as reference[28,35] (Supporting Information, section 6) gave a quantum yield of 1.3% for the green-light ionization of ^{3}**Irsppy**.

Compared to a two-photon mechanism with quasi-persistent radical anions as intermediates (Figure 1a), the mechanism of Figure 1b with rather short-lived excited states unavoidably militates for many unproductive catalyst excitations. This prompted us to study the stability of our catalyst. In comparative stability assays using blue light (Supporting Information, section 2), **Irsppy** turned out to be much more photostable than the widely employed catalyst $[Ru(bpy)_3]^{2+}$.

With the insights gained in both the ionization mechanism and the catalyst stability, the lab-scale application of our novel $e_{aq}^{\bullet-}$ source to challenging reductions became a realistic objective. With an excited-state oxidation potential of −1.64 V vs NHE, ^{3}**Irsppy** is itself capable of reducing numerous compounds. In addition to imine reduction,[32] we observed the direct reductive acetophenone activation with a rate constant close to the diffusion limit and the preparative dehalogenation of 4-chlorobenzoic acid (Supporting Information, p S9), i.e., two reactions that hitherto required $e_{aq}^{\bullet-}$ to be initiated in aqueous solution.[10,12] On these grounds, we carefully performed control experiments (see Supporting Information) with all substrates of Figure 3 and confirmed that catalyst-derived species do not contribute to the observed lab-scale transformations.

Applications of the Novel Hydrated Electron Source. We first investigated the preparative dehalogenation of $ClAc^-$ using a collimated 447 nm diode laser (Supporting Information, section 7), which can excite both **Irsppy** and ^{3}**Irsppy** (blue vertical line in Figure 2a), and employed ascorbate ($HAsc^-$) because that sacrificial donor is known to reduce the one-electron oxidized catalyst,[32] thereby completing the catalytic photoionization mechanism of Figure 1b.

^{1}H NMR studies revealed the successful catalytic decomposition of 66% (Figure 3a, lower limit due to interferences with other NMR signals) of that model compound for recalcitrant and toxic chloro-organics,[10,27,29] together with the formation of acetic acid as main product (Supporting Information, section 7.1). Because no species in our system other than $e_{aq}^{\bullet-}$ is able to reduce nonactivated chloro-organics, the reaction must occur via the $e_{aq}^{\bullet-}$ induced dissociative electron transfer.[29] That reasoning is further substantiated by the electrochemical detection of chloride ions corresponding to 76% conversion. Furthermore, we carried out chloroacetate degradation experiments at different excitation power densities. The photon flux per area was modified by either changing the beam size (Supporting Information, section 1.2) or the total output of our light source (Supporting Information, section 7.1 and Figure S11). Both sets of experiments confirmed the biphotonic character (mechanism of Figure 1b) of the catalytic photoreaction.

We next tested triethanolamine (TEOA) as sacrificial donor, because that donor is not prone to fast oxidation in solution facilitating the experimental procedure. Under standardized conditions, we indeed observed efficient $ClAc^-$ dechlorination with a TON as high as 203, whereas in experiments with $[Ru(bpy)_3]^{2+}$ there is no $ClAc^-$ conversion at all, only rapid catalyst decomposition (Supporting Information, section 7.1). These experiments clearly demonstrate that the combination of a highly stable photocatalyst with favorable thermodynamic properties and a collimated cw laser allows production of the superreductant $e_{aq}^{\bullet -}$ for laboratory applications. Compared to other photoredox studies relying on two-photon excitation, our TON of 203 is encouraging. For reference, dehalogenation reactions with Rhodamine 6G[5] or perylene diimide (PDI)[2] seemed to require catalyst loadings of at least 5%, limiting the maximum achievable TON to 20.

Subsequently, we turned to the activation of trifluoromethyl arenes, which is currently of significant interest in pharmaceutical research.[39] In contrast to the only photoredox strategy available for that task,[40] an $e_{aq}^{\bullet -}$ based approach for the direct reduction would likely not be limited to activated trifluoromethyl arenes with strongly electron-withdrawing groups. Our first try with the model compound 4-(trifluoromethyl)-benzoate afforded a conversion of 66% but yielded only traces of the desired monodefluorinated product. However, by simply switching off the light once the maximum concentration of 4-(difluoromethyl)benzoate is reached, quite promising results (Figure 3b) were obtained given the well-known selectivity problems of such reactions.[36] Simultaneously, we upscaled the reaction and extracted a crude product (30 mg) containing 4-(trifluoromethyl)benzoate and 4-(difluoromethyl)benzoate in a 6/1 ratio (Supporting Information, section 7.2), showing the usefulness of our method for larger-scale applications. The reaction yield is still low, but the proof-of-concept is now made. Separation of that mixture (compare main plot of Figure S12) was not carried out. However, the isolation of 4-(difluoromethyl)benzoic acid might be feasible via column chromatography[41] or preparative high-performance liquid chromatography (HPLC).[42] Given that difluoromethyl arenes—if commercially available at all—are usually much more expensive than the corresponding trifluoromethyl derivatives, both the further optimization of our catalytic system and its application to other defluorination reactions seem worthy of further investigation in future studies.

Prior spectroscopic investigations using pulse radiolysis gave a rate constant for the direct reduction of trifluoromethylbenzene by $e_{aq}^{\bullet -}$ as high as $1.8 \times 10^9\ M^{-1}\ s^{-1}$.[43] Hence, the $e_{aq}^{\bullet -}$ induced activation (with subsequent defluorination) should in principle be applicable to a very broad range of trifluoromethyl arenes. Another attractive feature of our method is that deuteration[12,44] of intermediate radicals is feasible when the reactions are carried out in heavy water, which is illustrated by the 1:1:1 triplets of both the CH_2 NMR signal in Figure 3a and the CF_2 NMR signal in Figure 3b (inset of the figure).

Finally, we addressed the reduction of quaternary ammonium compounds (QACs). QACs are large-scale industrial products with many applications; however, their stability (hampering the degradation during wastewater treatment) causes accumulation of QACs in the environment.[45] Although QACs have long been known to be environmentally risky, the quest for efficient QAC elimination procedures is still ongoing. Using the benzyltrimethylammonium cation, which is the basic structure of many QACs, we observed very efficient degradation with our photocatalytic system (Figure 3c and Supporting Information). We regard our novel lab-scale approach relying on $e_{aq}^{\bullet -}$ generated with visible photons as a potentially very interesting alternative to gamma-ray[45−47] or UVC-photon[48,49] induced degradation methods for benzyltrialkylammonium compounds. Traditional monophotonic ionizations of inorganic anions with wavelengths around 250 nm[29,50] would not be applicable to the conversion of both phenyl-containing substrates presented herein, because they are efficient light blockers below 300 nm.

Compared to the only other system that is able to produce $e_{aq}^{\bullet -}$ with visible photons from a nonpulsed light source in homogeneous aqueous solution,[13] our new $e_{aq}^{\bullet -}$ source has—despite operating through a different mechanism—both similar performance for applications and setup costs (with our setup being cheaper by ~50%). Furthermore, both systems rely on a tailor-made metal complex catalyst. The more attractive reaction conditions of our system (pH range from 7 to 10 vs strongly alkaline solutions[13] even able to attack glass), however, offer a decisive advantage. Under acidic conditions, the hydrated electrons would be quenched by protons, yielding less-reactive hydrogen atoms.

Diode lasers currently have practically the same acquisition costs as comparable high-power LEDs suitable for immediate laboratory use (equipped with housing, cooling unit, and power supply). Moreover, the usage of diode lasers operating in continuous wave (cw) mode is comparable to that of an LED, because cw lasers do not suffer from the health and safety hazards connected with pulsed lasers.

■ CONCLUSIONS

In summary, we have developed a new system for the catalytic generation of the superreductant $e_{aq}^{\bullet -}$ under very attractive conditions and demonstrated its lab-scale application to challenging reductions of relevance for pharmaceutical research and for the degradation of environmentally problematic detergent components. Operating in pure water while only consuming blue photons from an inexpensive light source and an extremely cheap sacrificial donor, our novel $e_{aq}^{\bullet -}$ source could further contribute to the ongoing rethinking of using green solvents such as water.[51,52] Given the current interest in two-photon phenomena, we anticipate that our first photoredox applications with a nonpulsed light source through the mechanism presented herein—the consecutive absorption of two photons with an excited state as intermediate—have important implications for future directions in harnessing light for challenging chemical reactions. Following the recent surge of interest in replacing precious one-photon catalysts,[53−55] we think that our first example for the mechanism of Figure 1b, which uses a precious Ir-based complex, could initiate the search for alternative (cheaper) photocatalysts with properties suitable for the consecutive two-photon absorption.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b12223.

General experimental details, additional results and control experiments, further laser flash photolysis data, and application-related details (PDF)

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Notes

The authors declare no competing financial interest.

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J. Am. Chem. Soc. XXXX, XXX, XXX−XXX