# Supplementary Information for Highly efficient green-light ionization of an aryl radical anion: key step in a catalytic cycle of electron formation

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## 1 Laser flash photolysis

For the laser flash photolysis experiments, the beams of a XeCl excimer laser (Lambda Physik LPX-210i, 308 nm) and a frequency-multiplied Nd:YAG laser (Continuum Surelite-III, 355 nm or 532 nm) were individually collimated, exactly superimposed with dielectric mirrors and directed through a suprasil cell with a rectangular entrance window of 4.0 mm width and 2.9 mm height, and a path length of 2.0 mm in the direction of the laser beam. The excitation intensities of the Nd:YAG laser were varied by the Q-switch delay, those of the excimer laser by a step-motor driven attenuator (metrolux ML2100/ML8010). The transient absorption was observed along the 4 mm axis of the cell. The detection system consisted of a xenon arc lamp (XBO 150) with IR filter, a step-motor driven filter wheel to suppress stray light, a step-motor driven grating monochromator (Oriel 77220), a photomultiplier (Hamamatsu R928) with programmable HV supply (Stanford Research PS310), a homemade preamplifier with a risetime of 5 ns and a digital storage oscilloscope (Tektronik TDS 540A). The timing of the two lasers was synchronized by a programmable delay generator (Quantum Composers QC9528). To avoid a depletion of the reactants, the irradiated volume was replaced by fresh solution after each data acquisition using a syringe-pump (Hamilton PSD/2) driven flow-through system.

All absorption measurements were corrected for luminescence, stray light and other artifacts by recording traces with the observation light unblocked and blocked by a shutter, but with all other experimental parameters unmodified.

### 2 Spectra and pertinent properties of the species in the system under study

The UV-Vis absorption spectra, in the spectral ranges relevant for the experiments, of all chemical species in our system are displayed in Figure S1.



**Figure S1:** Calibrated absorption spectra of all relevant species in the system under study. Gray dotted vertical lines indicate our excitation wavelengths. For abbreviations and further details, see text.

# 2.1 Ground state $NDS^{2-}$ of 1,5-naphthalene disulfonate

 $NDS^{2-}$  only absorbs light below 330 nm. The long-wavelength absorption band is red-shifted by about 10 nm compared to naphthalene and exhibits the vibrational structure typical for that class of compounds. The absorption spectrum, which agrees well with literature data,<sup>[1,2]</sup> remains unchanged in the pH range from 1 to 13.

We excited NDS<sup>2-</sup> with 308 nm ( $\varepsilon_{308} = 2260 \text{ M}^{-1} \text{ cm}^{-1}$ ), where our electron donor HAsc<sup>-</sup> is almost transparent. Although shorter wavelengths might seem better matched to the spectrum of NDS<sup>2-</sup>, the rapidly rising absorption of HAsc<sup>-</sup>, which is present in ten-fold excess over NDS<sup>2-</sup>, would lead to unacceptably strong filter effects in that range.

## 2.2 Triplet state ${}^{3}NDS^{2-}$

Excited NDS<sup>2-</sup> efficiently forms a high-energy triplet state ( $\phi_T = 0.88$ ,  $E_T = 2.58 \text{ eV}$ )<sup>[3]</sup>. Because of these favorable photophysical properties, which are quite similar to those of unsubstituted naphthalene in polar solvents,<sup>[4]</sup> NDS<sup>2-</sup> is a popular water-soluble triplet donor and a reference compound for chemical actinometry.<sup>[5,6]</sup> We recorded the absorption spectrum of <sup>3</sup>NDS<sup>2-</sup>, which compares well to that of the naphthalene triplet,<sup>[7]</sup> with 308 nm laser pulses that were attenuated so strongly as to avoid any photoionization. For calibration, we took the extinction coefficient at maximum from the literature ( $\varepsilon_{445} = 9900 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>[6]</sup>

At the excitation intensities used in the experiments of the main paper,  ${}^{3}NDS^{2-}$  decays by first-order kinetics with a natural triplet lifetime of  $\tau_0 = 57.5 \,\mu s$ . However, the triplet decay becomes more complex (mixed first- and second order kinetics) at high laser powers, *i.e.*,  ${}^{3}NDS^{2-}$  concentrations. We attribute that effect to triplet-triplet annihilation because we observed a delayed fluorescence, which is characteristic for such processes.<sup>[8]</sup>

#### 2.3 Radical anion NDS<sup>•3–</sup>

The quenching reaction, Equation (S1), has been investigated in detail in the main paper.

$${}^{3}\mathbf{NDS}^{2-} + \mathbf{HAsc}^{-} \to \mathbf{NDS}^{\bullet 3-} + \mathbf{HAsc}^{\bullet}$$
(S1)

The radical anion is already protonated to some degree on the timescale of its formation; this effect cannot be avoided by increasing the quenching rate because the nonnegligible absorption of **HAsc**<sup>-</sup> at the excitation wavelength precludes using higher quencher concentrations. A much more severe complication arises if the efficiency of the electron transfer  $\eta$ , which is *a priori* unknown, deviates from unity. Because  $\eta$  cannot be larger than unity, the direct comparison of the triplet decay and the rise of the radical-anion absorption can only yield a lower limit for the extinction coefficient of **NDS**<sup>•3-</sup> in that case (Equation (S2), where *E* and  $\varepsilon$  are the extinctions and extinction coefficients of the species given as the respective subscripts and the times *t* refer to the end of the 308 nm pulse, *i.e.*, to t = 0).

$$\varepsilon_{\mathbf{NDS}^{\bullet 3-}} = \frac{\varepsilon_{^{3}\mathbf{NDS}^{2-}}}{\eta} \frac{E_{\mathbf{NDS}^{\bullet 3-}}(t)}{E_{^{3}\mathbf{NDS}^{2-}}(0) - E_{^{3}\mathbf{NDS}^{2-}}(t)}$$
(S2)

A complementary approach is photoionizing the radical anion and comparing its bleaching with the electron formation. As the efficiency of photoionization  $\eta'$  in an elementary step cannot surpass unity, such measurements provide an upper limit for the extinction coefficient (Equation (S3), with the bleaching  $-\Delta E_{NDS^{\bullet 3-}}$  and the increase of the electron extinction  $\Delta E_{exc}$ ),

$$\varepsilon_{\text{NDS}^{\bullet^{3-}}} = \eta' \varepsilon_{\mathbf{e}_{\mathbf{a}q}^{\bullet^{-}}} \frac{-\Delta E_{\text{NDS}^{\bullet^{3-}}}}{\Delta E_{\mathbf{e}_{\mathbf{a}q}^{\bullet^{-}}}}$$
(S3)

but, as described in the main text, extensive control experiments gave no evidence for the formation of other species in the green-light photoionization of the radical anion, *i.e.*, indicated that  $\eta'$  is unity. By taking the extinction differences directly at the end of the ionizing pulse, we eliminated spectral distortions by the protonation of **NDS**<sup>•3-</sup> because that reaction is slow compared to the pulse duration (5 ns). To increase the precision of the calibration, we performed these experiments at different laser intensities with and without N<sub>2</sub>O (see, Section 2.5) and determined the extinction coefficient  $\varepsilon_{\text{NDS}^{\bullet 3-}}$  of the radical anion at 824 nm (2280 M<sup>-1</sup> cm<sup>-1</sup>) relative to that of the electron at the same wavelength from the slope of the plot shown in Figure S2.



**Figure S2:** Radical anion bleaching  $-\Delta E_{\text{NDS}^{\bullet 3-}}$  as function of the rise of the electron absorption  $\Delta E_{e_{aq}^{\bullet-}}$ , both at 824 nm. Pulse sequence and experimental parameters as in Figure 1a of the main text. The slope of the regression line equals the ratio of extinction coefficients of the two species.

Below 420 nm, an additional correction of the radical anion spectrum is necessary because the added electron scavenger N<sub>2</sub>O converts  $e_{aq}^{\bullet-}$  into hydroxyl radicals, which in turn oxidize our quencher extremely rapidly ( $k = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>[9]</sup> followed by immediate deprotonation to give Asc<sup>•-</sup>; under our experimental conditions, that whole reaction sequence is completed within less than 100 ns, and the somewhat slower reaction of the hydroxyl radicals with our substrate NDS<sup>2-</sup> ( $k = 5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>[1]</sup> cannot compete owing to the 14-fold smaller concentration of the latter. With the known electron concentration (obtained from the absorption at 824 nm) and the known spectrum of the ascorbate radical anion (see next section), this correction is thus straightforward. The three absorption maxima of NDS<sup>•3-</sup> (355 nm, 445 nm, and 725 nm) are in good agreement with those of the 2-naphthalene sulfonate radial anion in water (380 nm, 435 nm, and 720 nm)<sup>[10]</sup> and those of the naphthalene radical anion in DMF (368 nm, 437 nm, and 775 nm)<sup>[11]</sup>.

#### 2.4 Ascorbate ion **HAsc**<sup>-</sup> and its derived radical species

Because  $HAsc^-$  also absorbs weakly at the wavelength of our first laser pulse  $(\varepsilon_{308} = 70 \,\mathrm{M^{-1} \, cm^{-1}})$ , we performed a control experiment on our system, but with the substrate  $NDS^{2-}$  left out. Under the usual excitation conditions, we could not detect any transients, so conclude that  $HAsc^-$  does not undergo any direct photoreaction, specifically no photoionization, in all experiments of the main paper. As our quencher concentrations never exceeded 2.65 mM, corresponding to an absorption of only 8% of the laser energy by  $HAsc^-$ , inner filter effects are also negligible.

At the pH of our measurements in the main paper (7.6), the neutral radical **HAsc**<sup>•</sup> produced by the photoreduction according to Equation (S1) is deprotonated practically instantaneously to yield the donor derived radical anion  $Asc^{\bullet-}$ ,<sup>[12]</sup> which is stable for several milliseconds in neutral aqueous solution.<sup>[13]</sup> To obtain its spectrum in an independent experiment, we photoionized the ascorbate dianion ( $Asc^{2-} \rightarrow Asc^{\bullet-} + e_{aq}^{\bullet-}$ ), which is the predominant species in strongly alkaline ascorbate solutions, using an intense (280 mJ cm<sup>-2</sup>) 308 nm laser flash. In N<sub>2</sub>O-saturated solution, we recorded a spectrum (maximum at 360 nm), which perfectly agreed with literature reports.<sup>[12]</sup> The much higher extinction coefficient of the ascorbate dianion at 308 nm (6300 M<sup>-1</sup> cm<sup>-1</sup>) allowed us to reduce its concentration to  $4 \times 10^{-5}$  M in these measurements, *i.e.*, 50 times lower that that of the monoanion in all other experiments, which slowed down the reaction of  $Asc^{2-}$  with hydroxyl radicals so much that a calibration of the spectrum by equating the amounts of  $Asc^{--}$  and  $e_{aq}^{\bullet-}$  became straightforward.

### 2.5 Hydrated electron $e_{aq}^{\bullet-}$

For exact concentration determinations of  $\mathbf{e}_{\mathbf{aq}}^{\bullet-}$ , we monitored that species not at its absorption maximum (717 nm) but at 824 nm. Although the extinction coefficient ( $\varepsilon_{824} = 16900 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$ ) is only about three quarters of the maximum value ( $\varepsilon_{717} = 22700 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$ ), the detection sensitivity is significantly higher because the emission spectrum of our xenon lamp exhibits a maximum at 824 nm. To obtain the spectrum of  $\mathbf{e}_{\mathbf{aq}}^{\bullet-}$ , we photoionized our reaction medium, water, via its well-known two-photon absorption with an intense 266 nm laser flash<sup>[14]</sup> and used the recently redetermined extinction coefficient at the absorption maximum (22700  $\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$ )<sup>[15]</sup> for calibration.

 $N_2O$  scavenges  $e_{aq}^{\bullet-}$  selectively and rapidly according to Equation (S4).<sup>[16]</sup> In a saturated aqueous solution,  $e_{aq}^{\bullet-}$  are removed practically instantaneously on the timescale of our experiments (see, Figure S3).

$$\mathbf{e}_{\mathbf{aq}}^{\bullet-} + \mathbf{N}_2\mathbf{O} + \mathbf{H}_2\mathbf{O} \rightarrow \mathbf{N}_2 + \mathbf{H}\mathbf{O}^{\bullet} + \mathbf{H}\mathbf{O}^{-}$$
(S4)



Figure S3: Separation of the absorptions of NDS<sup>•3-</sup> and  $e_{aq}^{\bullet-}$ : Bottom, absorption traces at 824 nm in Ar-saturated solution (violet, both species contributing) and in N<sub>2</sub>O-saturated solution (red, only NDS<sup>•3-</sup> contributing); top, difference of the two traces, giving the pure signal of  $e_{aq}^{\bullet-}$ . Experimental conditions as in Figure 1a of the main text. The very small absorption remaining in the top trace at long times after the second laser flash is caused by secondary formation of NDS<sup>•3-</sup> through scavenging of  $e_{aq}^{\bullet-}$  by the substrate (which does not occur in the N<sub>2</sub>O experiment), and does not influence the initial signal rise after the pulse.

Under our experimental conditions, the resulting hydroxyl radicals are scavenged predominantly (97%) by **HAsc**<sup>-</sup>. That reaction does not cause any absorbances above 420 nm, so does not interfere with the determinations of  $\mathbf{e_{aq}^{\bullet-}}$  formation and **NDS**<sup>•3-</sup> bleaching. Only a negligible fraction of  $\mathbf{e_{aq}^{\bullet-}}$  is scavenged by the substrate to give **NDS**<sup>•3-</sup> (compare the later part of the top trace of Figure S3).

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