

## Supporting Information For

# Generating hydrated electrons through photoredoxcatalysis with 9-anthrolate

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### S1. Calculations of the **AOL**<sup>-</sup> Ground State

Quantum mechanical calculations were carried out with the Gaussian 09 package.<sup>[1]</sup> At the DFT(B3LYP)/6-311++G(2d,2p) level, with solvation model IEFPCM for water, **AOL**<sup>-</sup> possesses not only the expected C<sub>2v</sub> symmetry but also a strikingly short C–O bond. Table S1 compares the C–O bond lengths so obtained for the three forms of our substrate as well as for phenol and phenolate; in the one case where a crystallographically determined structure is available (phenol)<sup>[2]</sup>, our calculated value agrees exactly with the experimental one. These data reveal a marked double-bond character for the C–O bond in **AOL**<sup>-</sup>, which is tantamount to a predominance of the carbanionic resonance structure displayed in Scheme 2 of the main paper. The latter is also borne out by a population analysis of the atomic orbitals at C<sub>10</sub> in **AOL**<sup>-</sup>. Evidently, the effect is more pronounced in the larger  $\pi$  system (anthrolate) than in the smaller one (phenolate).

**Table S1:** Computed C–O bond lengths of selected compounds; method, DFT(B3LYP)/6-311++G(2d,2p) with solvation model IEFPCM for water. For the structural formulas of **AOL**<sup>-</sup> and **AON**, see Scheme 2 of the main paper.

compound	C–O bond length
9-anthrol	1.39 Å
anthrolate <b>AOL</b> <sup>-</sup>	1.27 Å
anthrone <b>AON</b>	1.23 Å
phenol	1.37 Å
phenolate	1.30 Å

## S2. Intensity Dependence of AOL<sup>-</sup> Photoionization

The intensity dependences displayed in Figure 3 of the main paper were fitted on the basis of the following kinetic model. Let the first excited singlet state S<sub>1</sub> be formed with the intensity-dependent rate constant  $k_{\text{exc}}$  and decay with the sum of two rate constants, one of them intensity-independent ( $1/\tau_S$ , comprising radiationless decay, luminescence with quantum yield  $\varphi_{\text{lum}}$ , and possibly monophotonic ionization with quantum yield  $\varphi_{\text{mono}}$ ), the other intensity-dependent ( $k_{\text{bi}}$ , which describes ionization by the second photon). The intermediacy of the upper excited state that actually liberates the electron can be neglected because of its much shorter life.

Assuming a rectangular laser pulse extending from time  $t = 0$  to time  $t = \tau_L$ ,<sup>[3]</sup> this scheme leads to a time dependence of the S<sub>1</sub> concentration during the pulse according to Equation S1,

$$[S_1](t) = c_0 \frac{k_{\text{exc}}}{k_+ - k_-} \{ \exp[-k_- t] - \exp[-k_+ t] \}, \quad 0 \leq t \leq \tau_L \quad (\text{S1})$$

with the substrate concentration  $c_0$  and

$$k_{\pm} = \frac{1}{2} \left\{ k_{\text{exc}} + 1/\tau_S + k_{\text{bi}} \pm \sqrt{(k_{\text{exc}} + 1/\tau_S + k_{\text{bi}})^2 - 4k_{\text{exc}} (\varphi_{\text{mono}}/\tau_S + k_{\text{bi}})} \right\} \quad (\text{S2})$$

After the pulse end, an exponential decay follows,

$$[S_1](t) = [S_1](\tau_L) \exp\left[-\frac{t - \tau_L}{\tau_S}\right], \quad \tau_L \leq t \quad (\text{S3})$$

The total luminescence  $L$  is

$$L = \varphi_{\text{lum}} \left\{ (1/\tau_S) \int_0^{\tau_L} [S_1](t) dt + [S_1](\tau_L) \right\} \quad (\text{S4})$$

where the two terms of the sum give the amount of light generated during the pulse and after its end, respectively.

The electron concentrations obtained through the monophotonic and biphotonic pathways are given by the terms containing  $\varphi_{\text{mono}}$  and  $k_{\text{bi}}$  in Equation S5

$$[e_{\text{aq}}^{\bullet-}] = \varphi_{\text{mono}} \left\{ (1/\tau_S) \int_0^{\tau_L} [S_1](t) dt + [S_1](\tau_L) \right\} + k_{\text{bi}} \int_0^{\tau_L} [S_1](t) dt \quad (\text{S5})$$

Inserting Equations S1 and S2 into Equations S4 and S5 and rearranging leads to

$$L/c_0 = \frac{\varphi_{\text{lum}}}{\varphi_{\text{mono}} + k_{\text{bi}}\tau_S} \left\{ 1 - \frac{k_+ - k_{\text{exc}} (\varphi_{\text{mono}} + k_{\text{bi}}\tau_S)}{k_+ - k_-} \exp[-k_- \tau_L] + \frac{k_- - k_{\text{exc}} (\varphi_{\text{mono}} + k_{\text{bi}}\tau_S)}{k_+ - k_-} \exp[-k_+ \tau_L] \right\} \quad (\text{S6})$$

The prefactor of Equation S6 suggests a pole for vanishing ionization. In that case, however, the equation turns into

$$L/c_0 = \varphi_{\text{lum}} \left( \frac{k_{\text{exc}}}{k_{\text{exc}} + 1/\tau_S} \right)^2 \left\{ 1 - \exp \left[ -(k_{\text{exc}} + 1/\tau_S)\tau_L \right] + \frac{(k_{\text{exc}} + 1/\tau_S)\tau_L}{k_{\text{exc}}\tau_S} \right\} \quad (\text{S7})$$

as a series expansion shows.

The normalized electron concentration is given by

$$\left[ \text{e}_{\text{aq}}^{\bullet-} \right] / c_0 = 1 - \frac{k_+ - k_{\text{exc}}\varphi_{\text{mono}}}{k_+ - k_-} \exp[-k_- \tau_L] + \frac{k_- - k_{\text{exc}}\varphi_{\text{mono}}}{k_+ - k_-} \exp[-k_+ \tau_L] \quad (\text{S8})$$

Equations S6 and S8, together with Equation S2, were used as fit functions of the experimental dependences on the laser intensity  $I_{355}$ , after replacing all products  $k_i \tau_L$  by  $\kappa_i I_{355}$  (in the preexponential factors after multiplying numerator and denominator with  $\tau_L$ ),<sup>[3]</sup> and exploiting the fact that for our system  $\tau_S$  and  $\tau_L$  can be taken as identical. The simultaneous fits to both data sets thus require adjusting only three kinetic parameters ( $\kappa_{\text{exc}}$ ,  $\kappa_{\text{bi}}$  and  $\varphi_{\text{mono}}$ ). In contrast,  $\varphi_{\text{lum}}$  merely functions as a luminescence scaling factor, which would be needed anyway because our setup cannot measure absolute luminescence.

Because the fits and the stationary luminescence measurements indicate that mono-photon ionization plays no role in our system (see, the pertaining discussion in the main paper), we arbitrarily replaced the scaling factor  $\varphi_{\text{lum}}$  by 1, so that Equation S6 describes the total concentration of ground-state **AOL**<sup>-</sup> that is regenerated during and after the laser pulse. At maximum, that quantity is found to overshoot  $c_0$  by about 20 %, which shows that the similarity of  $\tau_L$  and  $\tau_S$  results in a noticeable amount of multiple excitations of a ground-state molecule. To compensate for the loss of the scaling factor, we multiplied the luminescence data with a constant such as to bring them into the range of the curve given by Equation S6 in this modified form.

With  $\varphi_{\text{mono}}$  set to zero, the best-fit parameters for the data of Figure 3 of the main paper are,  $\kappa_{\text{exc}} = 0.0634 \text{ cm}^2/\text{mJ}$ ,  $\kappa_{\text{bi}} = 0.0056 \text{ cm}^2/\text{mJ}$ . The expression  $\varepsilon(S_0)\kappa_{\text{bi}}/\kappa_{\text{exc}}$  equals the product  $\varepsilon(S_1)\varphi_{\text{bi}}$ ,<sup>[4]</sup> despite its rather low value ( $370 \text{ M}^{-1}\text{cm}^{-1}$ ), which explains why the quadratic feature of the electron yield at low laser intensities is nearly absent,<sup>[5]</sup> almost complete ionization of **AOL**<sup>-</sup> is attainable at our highest laser intensity. Should  $\varepsilon(S_1)$  eventually be determined, the quantum yield for the photoionization proper (of the  $S_1$  state) would immediately follow, the advantage of that approach being that the excitation of the ground state serves as inner standard.

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