Supporting Information for

Spectral Probe for Electron Transfer and Addition Reactions of Azide Radicals with Substituted Quinoxalin-2-ones in Aqueous Solutions

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Contents:

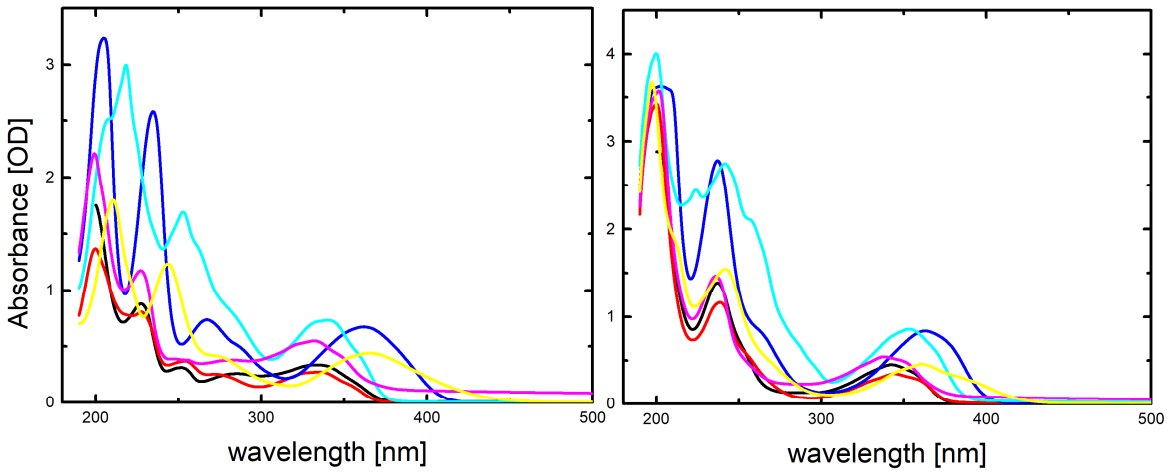


Figure S1. Ground-state absorption spectra of 7-R-3-MeQ derivatives: −H (—), −CF_3 (—), −OCH_3 (—), −CN (—), −F (—), −NH_2 (—) in aqueous solutions containing 0.1 mM 7-R-3-MeQ at pH 7 (A) and pH 11.3 (B)

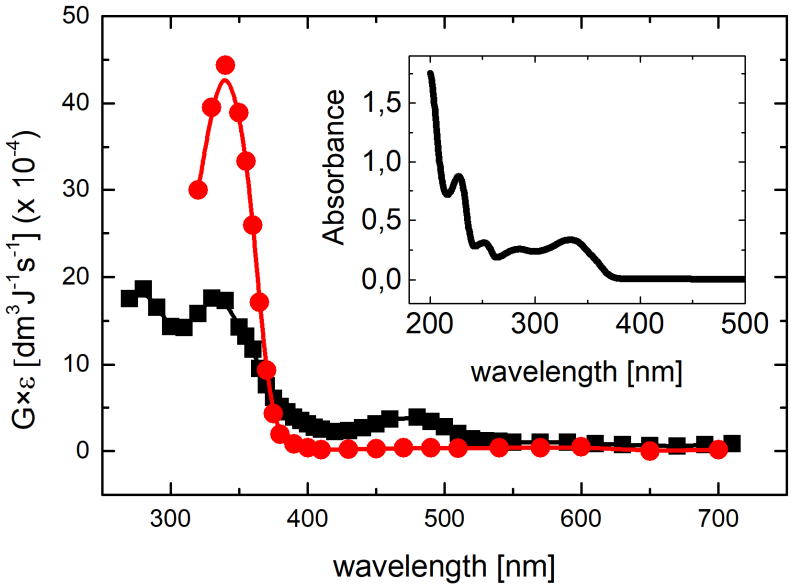


Figure S2. Corrected for the ground-state absorption of 3-MeQ transient absorption spectra recorded in aqueous solutions containing 0.1 mM 3-MeQ at pH 7: (■) 10 μs after the electron pulse in Ar-saturated containing 0.1 M $K_2S_2O_8$ and 0.5 M *tert*-BuOH and (■) 3 μs after the electron pulse in N_2O-saturated and containing 0.1M NaN_3. Inset: Ground-state absorption spectrum of 3-MeQ in aqueous solutions containing 0.1 mM 3-MeQ, at pH 7.

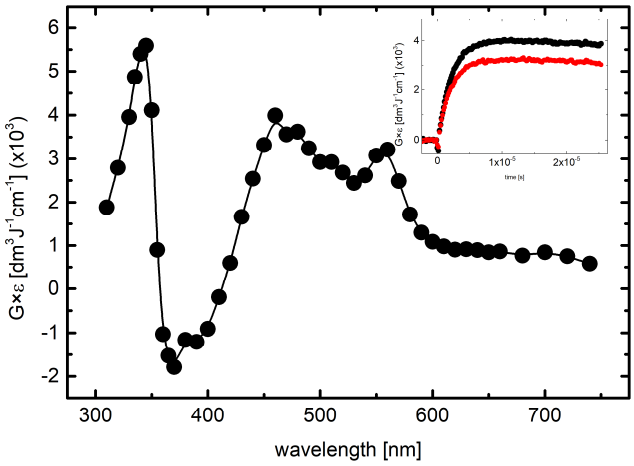


Figure S3. Transient absorption spectra recorded 10 μs after the electron pulse in N_2O-saturated aqueous solutions containing 0.1 mM 7-NH_2-3-MeQ and 0.1M NaN_3 at pH 7. Inset: Time profiles representing growth of transient absorptions at λ = 460 nm (●) and 530 nm (●).

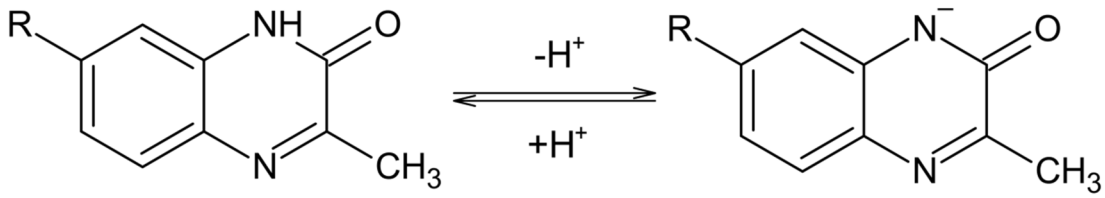


Figure S4. Acid-base equilibria of 7-R-3-MeQ derivatives in the investigated pH range.

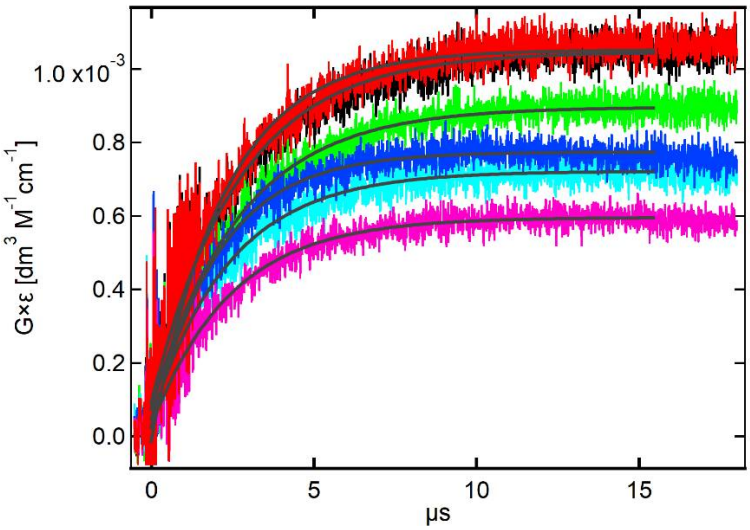


Figure S5. Time profiles representing growth of transient absorptions at λ = 530 nm recorded after the electron pulse in N_2O-saturated aqueous solutions at pH = 7 containing 0.1 M NaN_3 and various concentrations of 7-OCH_3-3-MeQ: (—) 0.05 mM, (—) 0.1 mM, (—) 0.2 mM, (—) 0.3 mM, (—) 0.4 mM and (—) 0.5 mM.

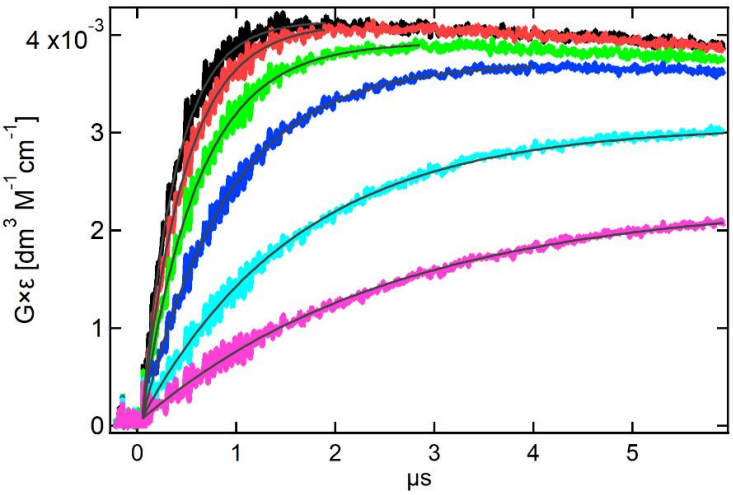


Figure S6. Time profiles representing growth of transient absorptions at λ = 530 nm recorded after the electron pulse in N_2O-saturated aqueous solutions at pH = 11.3 containing 0.1 M NaN_3 and various concentrations of 7-OCH_3-3-MeQ: (—) 0.05 mM, (—) 0.1 mM, (—) 0.2 mM, (—) 0.3 mM, (—) 0.4 mM and (—) 0.5 mM

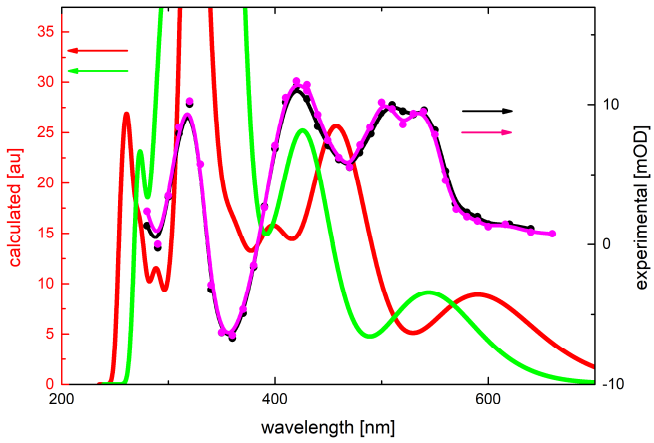
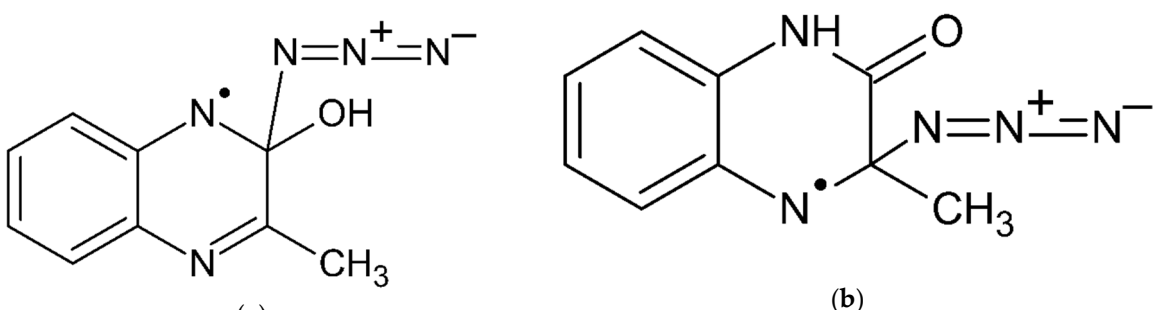


Figure S7. Comparison of the transient absorption spectrum recorded in Ar-saturated aqueous solutions containing 0.1 mM 7-OCH_3-3-MeQ, 0.1 M $K_2S_2O_8$ and 0.5 M tert-BuOH at pH = 4 (●, —) and 7 (●, —) and the ωB97XD/ aug-cc-pVTZ calculated UV-Vis spectra of the 7-OCH_3-3-MeQ$^{\bullet+}$ (—) and 7-OCH_3-3-MeQ$^{\bullet}$ (—) species. Calculated spectra are shifted by 130 nm towards longer wavelengths.



(**a**) (**b**)

Figure S8. Structures of the $N_3^{\bullet}$ adducts at the C2 carbon atoms (**a**) and the C3 carbon atoms (**b**) in 3-MeQ

Table S1. Reduction potentials of inorganic redox couples used in the study

Redox couple	E^0 (V) [1]
$SO_4^{\bullet-}$/ SO_4^{2-}	+2.437 ± 0.019
Tl^{2+}/ Tl^{+}	+2.225 ± 0.007
$CO_3^{\bullet-}$/ CO_3^{2-}	+1.57 ± 0.03
$N_3^{\bullet}$/ N_3^{-}	+1.33 ± 0.01
$(SCN)_2^{\bullet-}$/ 2 SCN^{-}	+1.30 ± 0.02

[1]measured vs. Normal Hydrogen Electrode

Table S2. pK_a values of the acid-base equilibria of 7-R-3-MeQ derivatives

Substituent	pK_a [1]
–CN	8.3
$–CF_3$	9.1
–F	9.1
–H	9.4
$–OCH_3$	9.6
$–NH_2$	10.0

[1] measured in this work