

Supplementary Information

Type I and Type II photosensitization of DNA etheno adducts

Paloma Lizondo-Aranda, Gemma M. Rodríguez-Muñiz, Miguel A. Miranda, Belinda Heyne,
Virginie Lhiaubet-Vallet*

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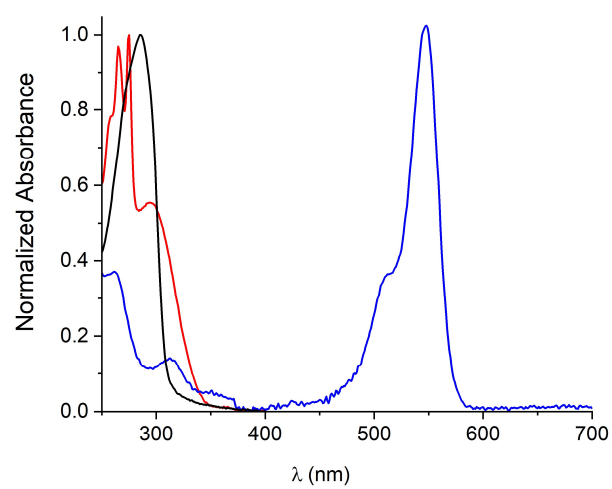


Figure S1. Normalized UV-Vis absorption spectra of RB²⁻ (blue), εdA (red), and εdG (black)

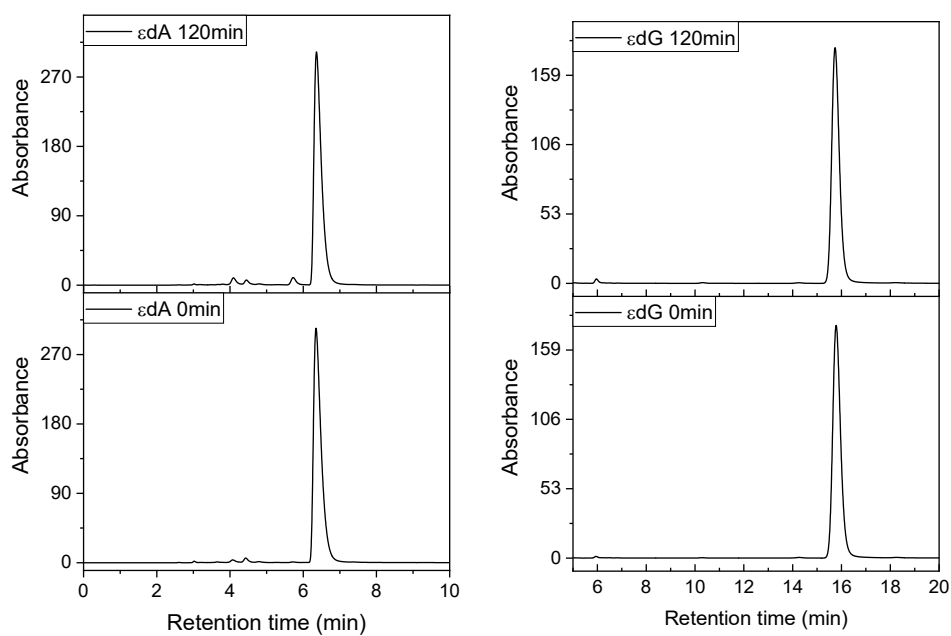


Figure S2. HPLC chromatograms registered at 260 nm obtained after 0 and 120 min of irradiation of a solution of 20:10 μM of ϵ -adduct and RB^{2-} in deuterated water using white light. HPLC conditions 5:95 (MeCN:H₂O), flow 0.4 mL min⁻¹

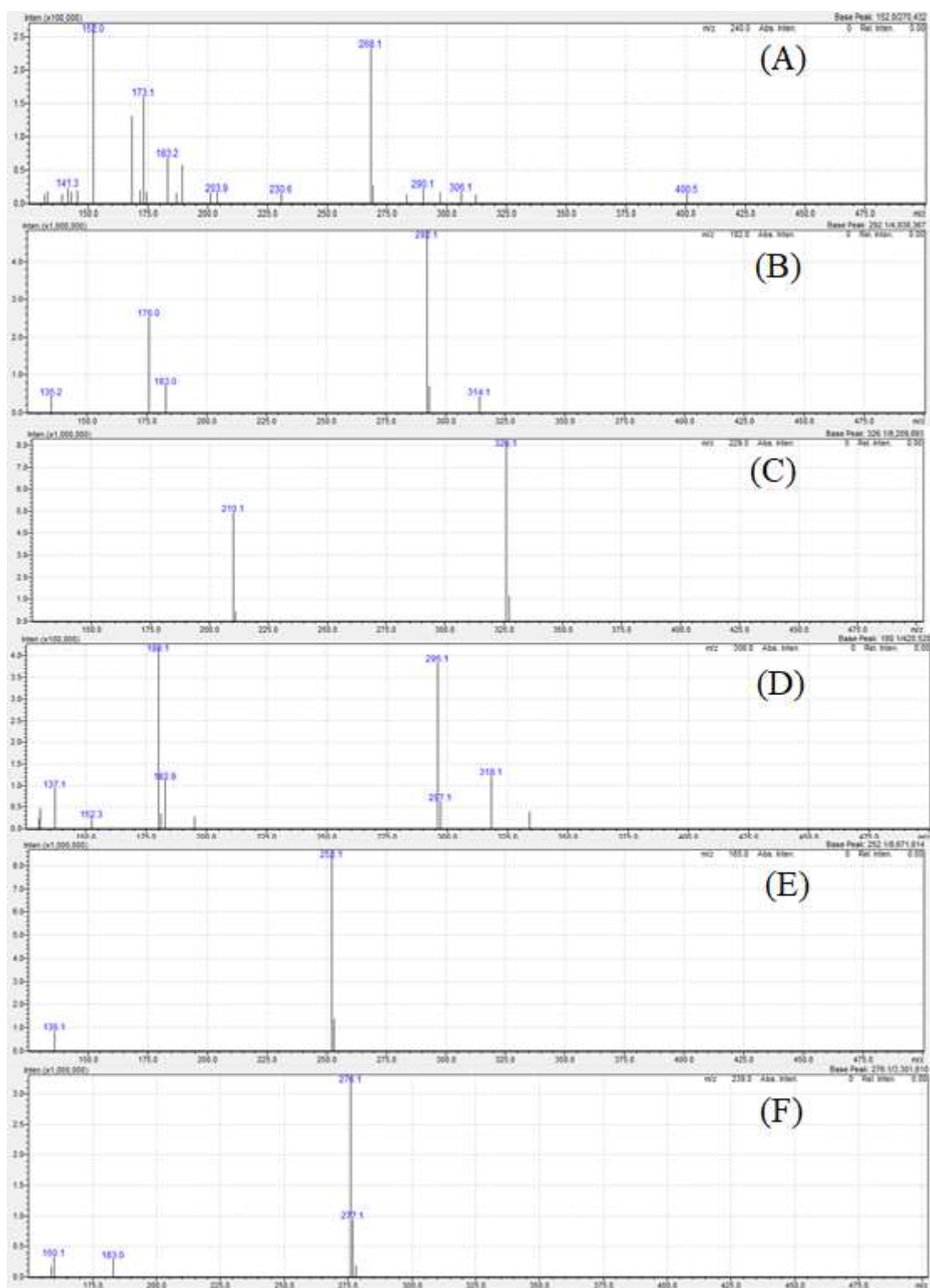


Figure S3. MS spectra of dG (A), εdG (B), intermediate III (C) and intermediate VIa/b (D) for an irradiated solution of RB²⁻ and εdG, and MS spectra of dA (E) and εdA for an irradiated solution of RB²⁻ and εdA

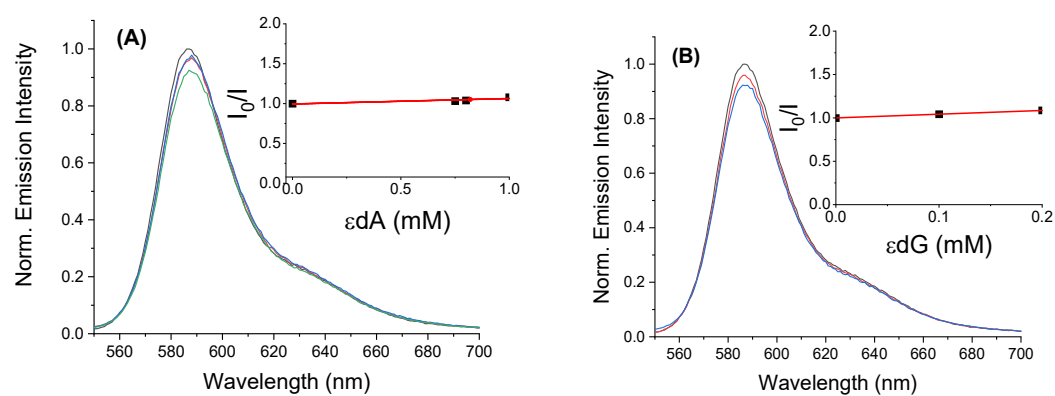


Figure S4. Fluorescence emission spectra obtained from $5 \mu\text{M RB}^{2-}$ ($\lambda_{\text{ex}} = 532 \text{ nm}$) in presence of increasing amounts of etheno adducts, from 0 to 1 mM and 0.2 mM for ϵdA (A) and ϵdG (B), respectively. Insets: corresponding Stern-Volmer plots.

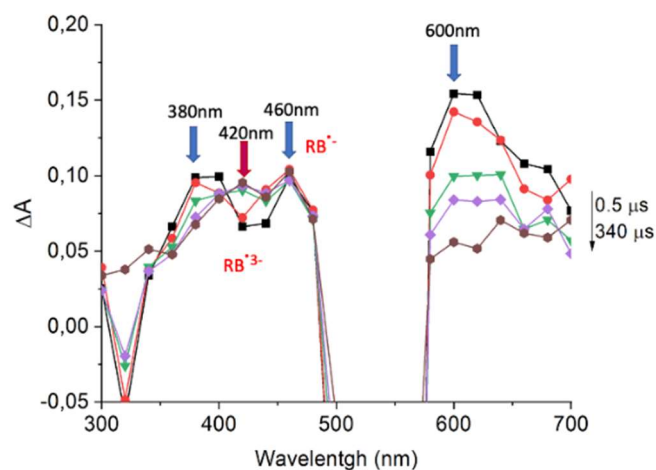
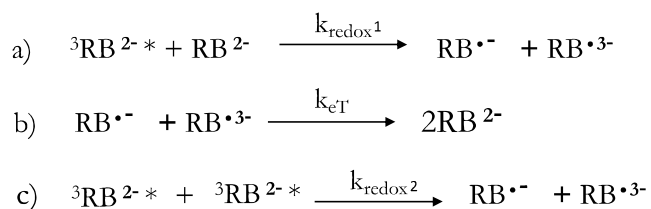


Figure S5. Transient absorption spectra of RB^{2-} in deuterated water under N_2 after 532 nm excitation.

Figure shows the formation of those radicals arising from an electron exchange between $^3\text{RB}^{2-*}$ and a molecule of RB^{2-} in its ground state to give both the reduced ($\text{RB}^{\bullet 3-}$) and oxidized ($\text{RB}^{\bullet -}$) species (see route a, Scheme below). The same species can also be obtained from a disproportionation (route c) taking place between two $^3\text{RB}^{2-*}$. Finally, the formed radical ions can undergo back electron transfer (k_{eT} , route b) and deactivate to regenerate RB^{2-} .



Scheme S1. Reactivity of $^3\text{RB}^{2-*}$: formation and reactivity of derived radicals.

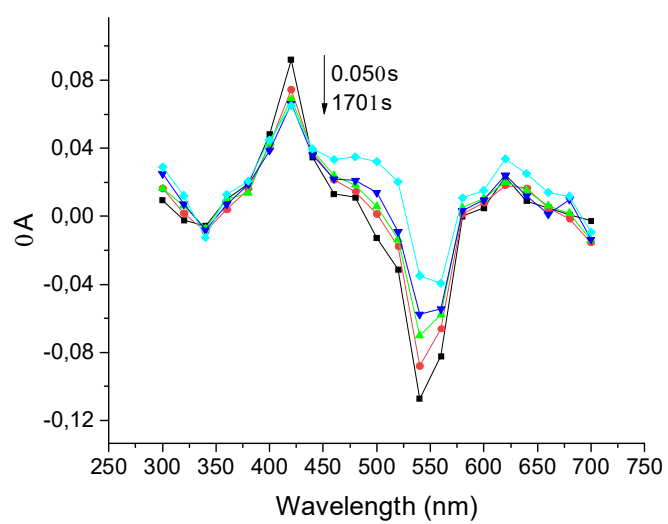


Figure S6. Transient absorption spectra of RB^{2-} in the presence of 5 mM of DABCO in water at different time after the 532 nm laser pulse.

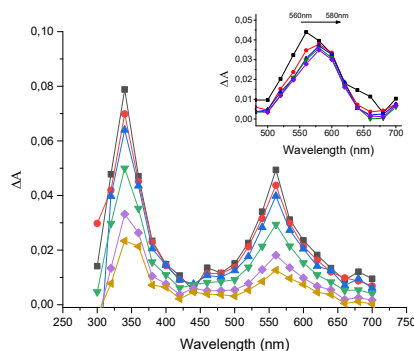
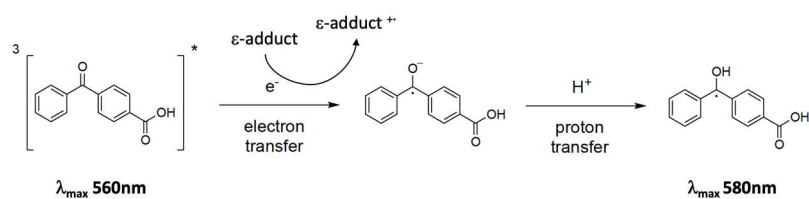


Figure S7. CBP transient absorption spectra in MeCN:H₂O (1:1, v:v) at different times, from 0.1 to 8 μ s, after the 355 nm laser pulse. Inset graph: CBP transient absorption spectra of the same solution adding 20% v:v of ethanol.



Scheme S2. Photooxidation mechanism triggered by 4-carboxybenzophenone (CBP) leading to the formation of its anion radical (CBP^{•-}) and subsequently to the ketyl radical (CBPH[•]).