Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.
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Supporting Material

Visible Light Initiated Release of Calcium Ions through Photochemical Electron Transfer Reactions.

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1. Method for Photolysis of Ca-EDTA Solutions

Photolysis samples were all prepared by dilution of concentrated stock solutions to achieve the desired molar concentrations of each species and at a 1 mL photolysis volume. The EDTA and Ca^{2+} stocks were both 100 mM, purchased from Fisher Scientific and used without further adjustment. Sensitizer stock solutions were prepared by dissolving the desired reagent in deionized water and the pH of the samples was adjusted to between 6.5-7.3 with NaOH before the final concentration was verified using UV-Vis.

Samples were photolyzed in a 1 mL quartz cuvette having a 1 cm path length while being stirred. Photolysis at 350 nm was achieved using a 12 bulb, 35 W Rayonet photoreactor from the Southern New England Ultraviolet company. Photolysis at the other wavelengths were done on a 150 W Hg-Xe medium pressure lamp, using cut off filters as indicated in Table 2.

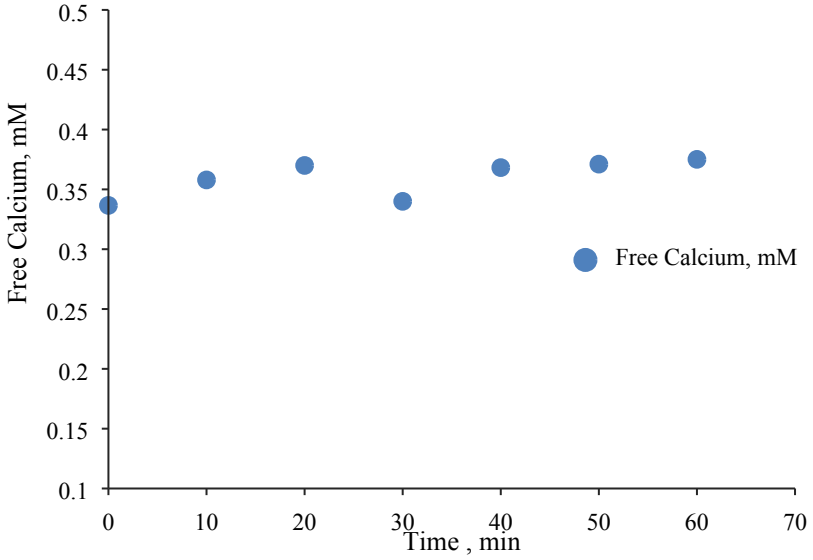


Figure S1: Control experiment illustrating the background level of free Ca^{2+} detected in our assay after photolysis (350 nm) for the given time in the absence of sensitizer.

2. Photo-degradation of EDTA with AQ2S and RBTA in Water

NMR spectra were taken on a Bruker 600MHz and 400MHz, with a BBI probe. Samples were in H_2O/D_2O mixtures of up to 80% water. Proton spectra were 32 scans with water suppression. The coaxial method was used for an internal standard of t-butanol because of its stability under photolysis conditions.

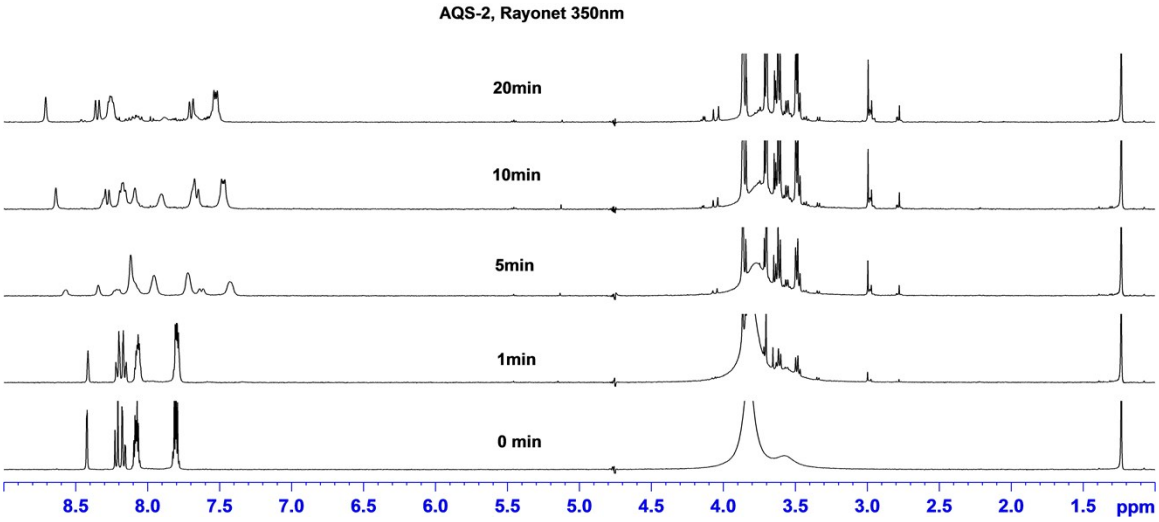


Figure S2: Photolysis of AQ2S and EDTA in H_2O/D_2O. Photolysis at 350 nm in a 35 W, 12-bulb photoreactor for the given times.

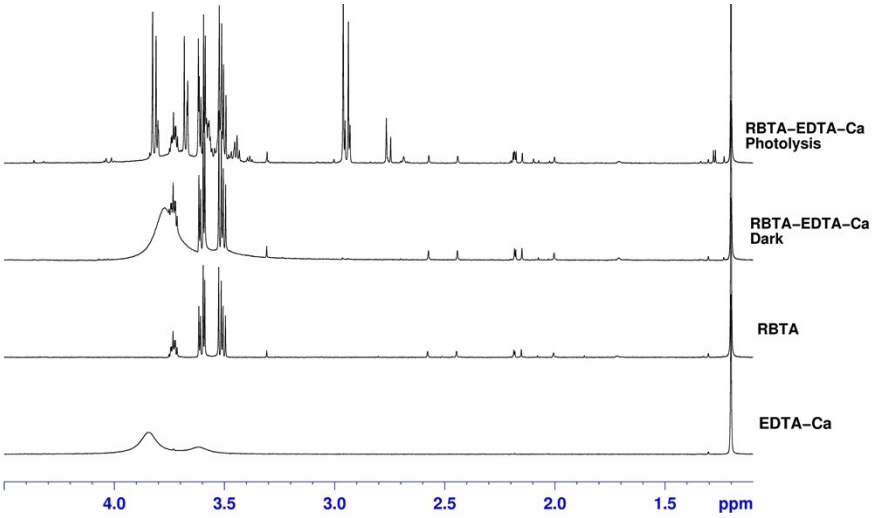


Figure S3: Photolysis of RBTA (2.1 μM) and Ca-EDTA (10mM) in H_2O/D_2O with a Hg lamp with a 360 nm cutoff filter. Photolysis for 40 minutes.

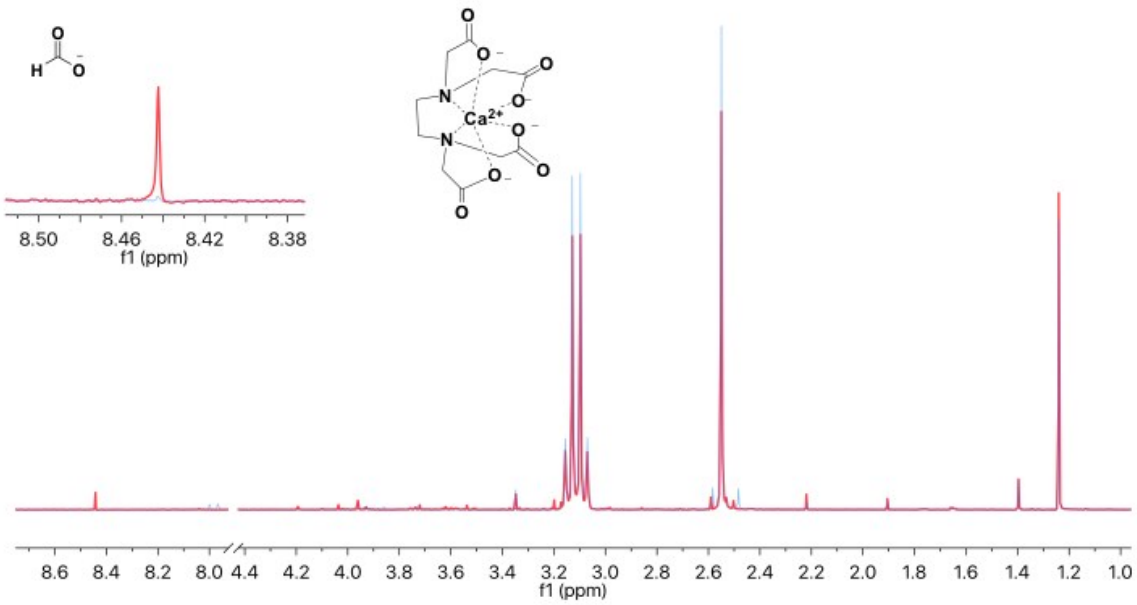


Figure S4: Stacked ^{1}H NMR of pre (blue) and post (red) photolysis of a solution containing 75uM Riboflavin, 1 mM Ca-EDTA, at pH 7.3. Photolysis wavelength was 447 nm for 30min using a 1 W, CW diode laser. The following peaks were identified: 3.1 ppm quartet and 2.5ppm singlet are the Ca-EDTA complex and 8.4 pmm signal is formate. The magnified window shows the appearance of formate after photolysis.

3. Preparation of Alginate Hydrogels

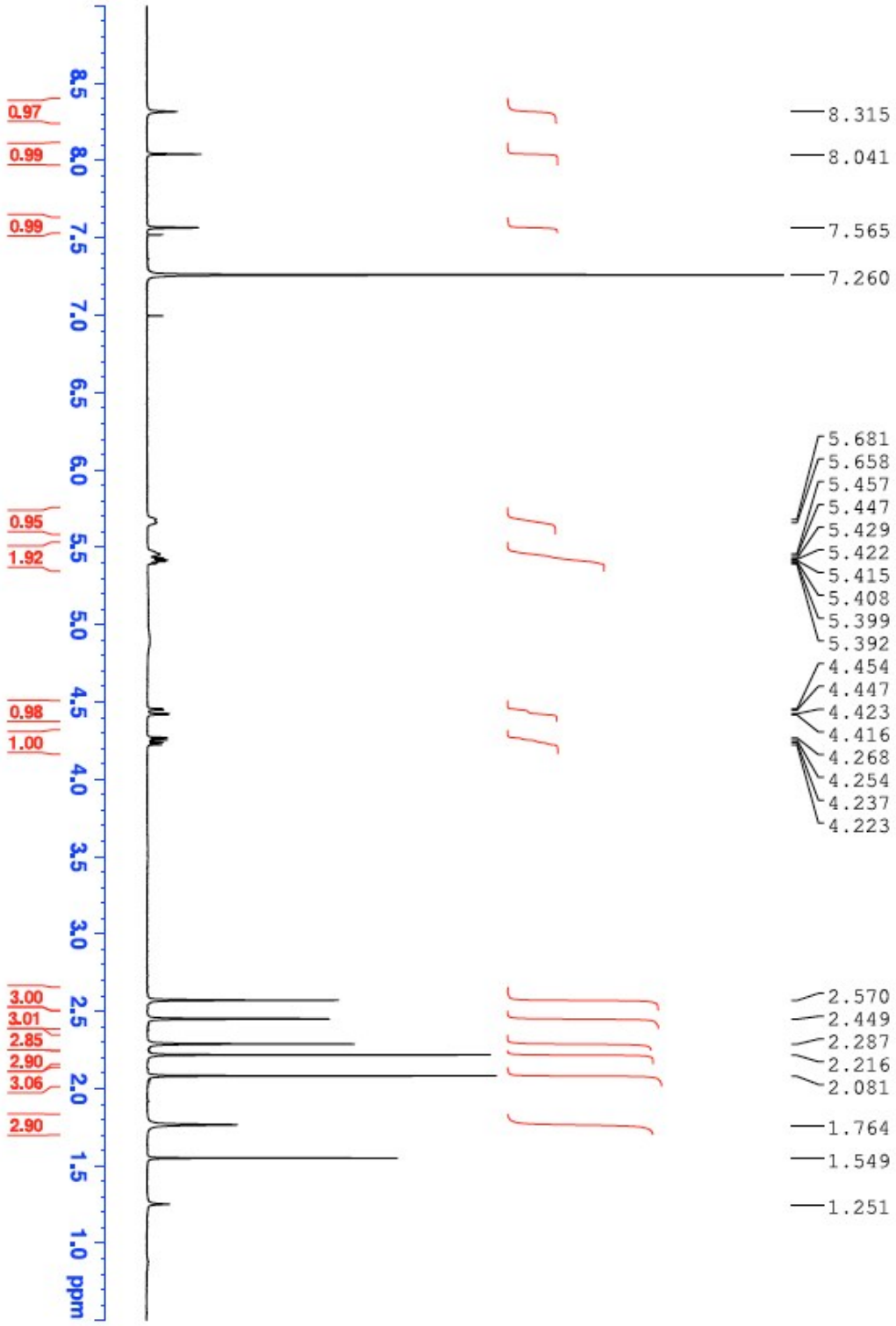
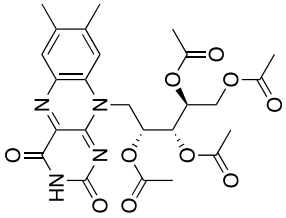
Stock solutions of RB (0.26 mM), Ca-EDTA (50 mM) and sodium alginate (3.75 wt%) were prepared in pH = 9.3 buffered carbonate/bicarbonate buffered water. Additionally, $CaCl_2$ standard 0.1 M (Sigma Aldrich) was used. Final solution concentration before photolysis was 0.084 mM RB, 16 mM EDTA, 19 mM Ca^{2+}, 1.21 wt% sodium alginate.

(a) 350 nm photolysis

Photolysis solutions were prepared by mixing 1 mL each of RB and Ca-EDTA stock solutions with 1 mL of sodium alginate in a 5 mL vial with a stirbar. To this was added 100 μL of 0.1 M $CaCl_2$ standard. The solution was carefully mixed prior to photolysis. The sample was then irradiated for 2 hours using a 350 nm, 12-bulb, Rayonet photoreactor. The sample was continuously stirred during photolysis. After photolysis the presence of a free-standing gel was observed while the dark control showed no significant gelation.

(b) 447 nm photolysis

The solution was carefully mixed prior to photolysis. The sample was then irradiated for 2 hours using a 447 nm CW diode laser. The sample was continuously stirred during photolysis. After photolysis the presence of a free-standing gel was observed while the dark control showed no significant gelation.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