

Supporting Information

Photoredox Halogenation of Quinolones: Dual Role of Halo-fluorescein Dyes

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Experimental Details:

EPR Spectroscopy: Electron Paramagnetic Resonance (EPR) spectrum was recorded using Bruker EMX 1444 EPR spectrometer operating at 9.455 GHz. Diphenylpicrylhydrazyl, DPPH ($g = 2.0037$), was used for the calibration. A solution of 2-phenylquinolin-4(1H)-one **1a** (0.01 mmol) and Eosin Y (0.0035 mmol) in ACN (1 mL) was transferred to a capillary and EPR spectrum was recorded. On irradiating reaction mixture with green LED for 2.5 h, a sharp signal of a trapped radical was observed suggesting the formation short-lived quinolone radical species.

UV-Vis Spectroscopy: The UV-Vis absorption spectra were taken using a PerkinElmer Lambda 1050 spectrophotometer. The UV-Vis spectroscopic experiments were performed using reaction mixtures at different time with 5×10^{-5} M DMF solution in a quartz cuvette with 10.0 mm optical path length. UV-Grade DMF was used for the spectroscopic experiments. Wavelength reported in nanometres (nm).

Cyclic Voltammetry (CV): CV was carried out using a computer controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of both platinum working and auxiliary electrodes and SCE as reference electrode. All the electrochemical measurements were carried out in Ar-purged dichloromethane solvent with $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte. The scan rate for the measurements were typically 200-300 mV/s.

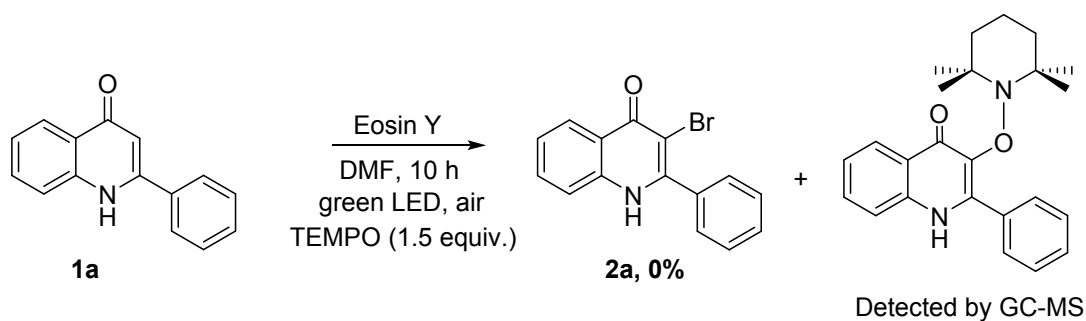
Experiments for mechanistic study

1. Radical trapping experiment with TEMPO:

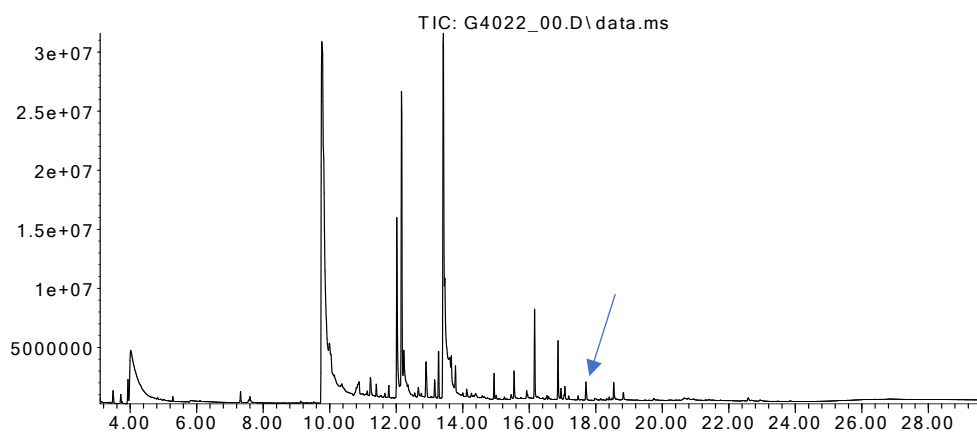
An oven dried test tube was charged with magnetic stirrer, 2-phenylquinolin-4(1H)-one **1a** (110 mg, 0.5 mmol), Eosin Y (0.175 mmol) in DMF (5 mL) as the solvent. In the reaction mixture, TEMPO (39 mg, 77 mg, 117 mg corresponding to 0.5, 1, and 1.5 equiv.) was added, and the contents were stirred at room temperature under green LED for 10 h in presence of air. The reaction was diluted with water (60 mL) and the aqueous layer was extracted with ethyl acetate (3×15 mL). The residue was purified over a flash chromatography using ethyl acetate-hexane as the eluent. The yield of desired product **2a** was found to decrease in a dose dependent manner as shown below.

S.No.	Concentration of TEMPO	Yield of 2a
1	0.5 equiv.	20%
2	1.0 equiv.	5%
3	1.5 equiv.	0%

Table S1



Abundance



Abundance

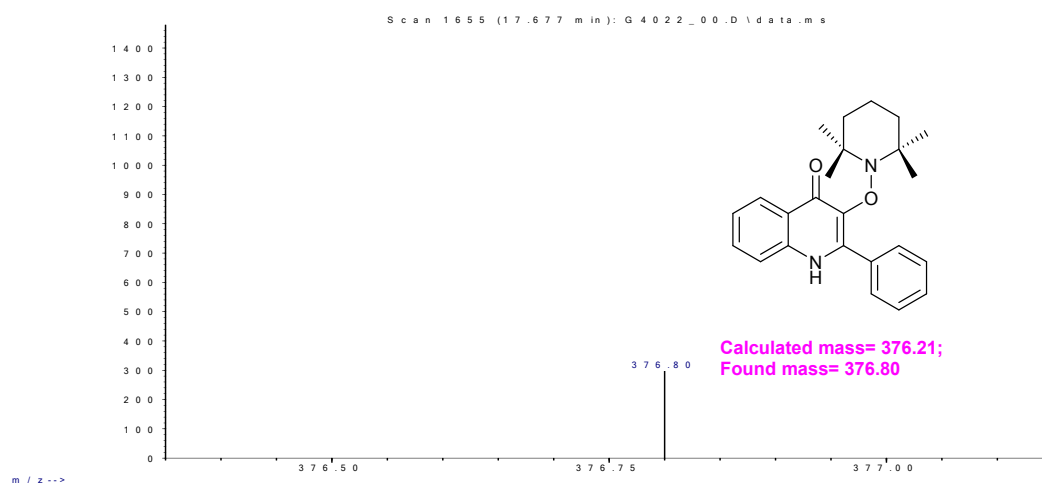


Fig. S1: GCMS of the reaction mixture.

2. Investigation of mechanism by EPR

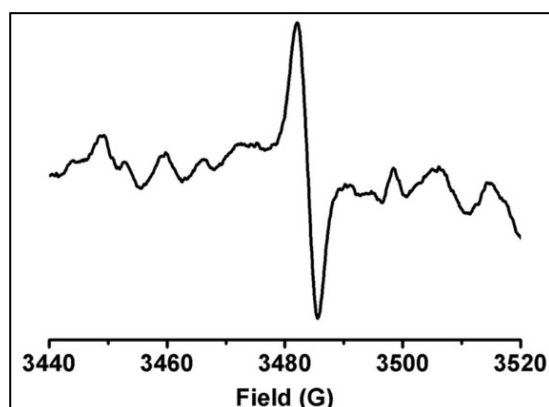


Fig. S2: EPR spectrum of the reaction mixture.

3. UV-Vis spectroscopic studies:

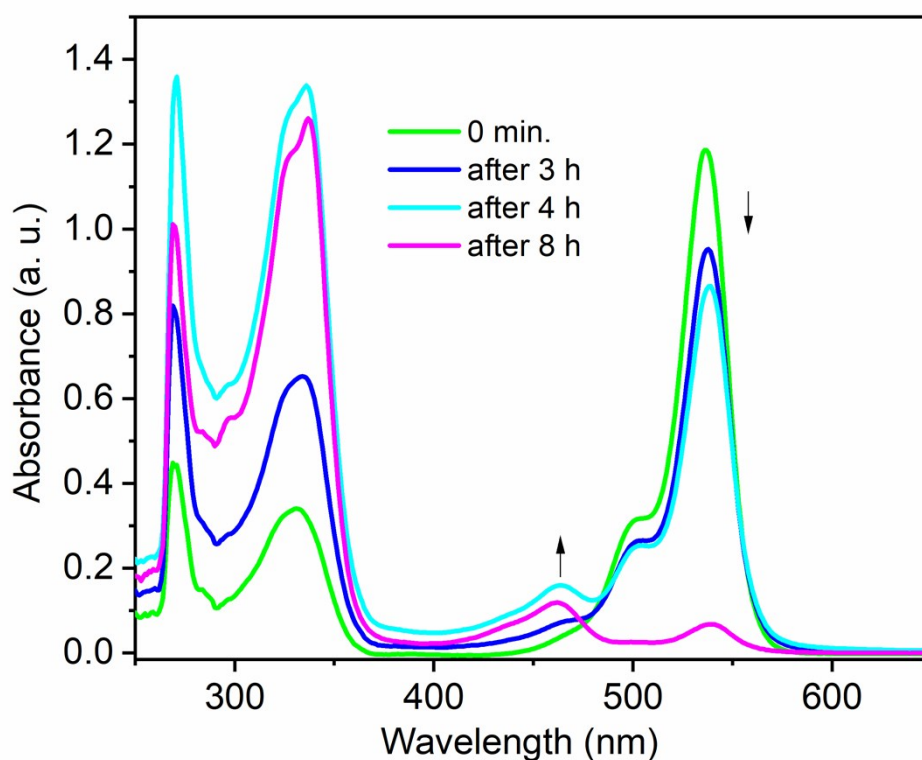


Fig. S3: Time dependent UV-Vis spectra of the reaction mixture in DMF at 5×10^{-5} M.

4. Singlet Oxygen ($^1\text{O}_2$) trapping Experiment:

An oven dried test tube was charged with magnetic stirrer, 2-phenylquinolin-4(1H)-one **1a** (110 mg, 0.5 mmol), Eosin Y (0.175 mmol) in DMF (5mL) as the solvent. In the reaction mixture, terpinene (68 mg, 0.5 mmol) was added, and the contents were stirred at room temperature under green LED for 10 h in presence of air. The reaction mixture was monitored

by thin layer chromatography. A small aliquot of the reaction mixture was injected into the mass spectrometer. The desired product **2a** was formed and a peak corresponding to terpene adduct (**4**) was seen in the mass spectrum given below (**Fig. S4**).

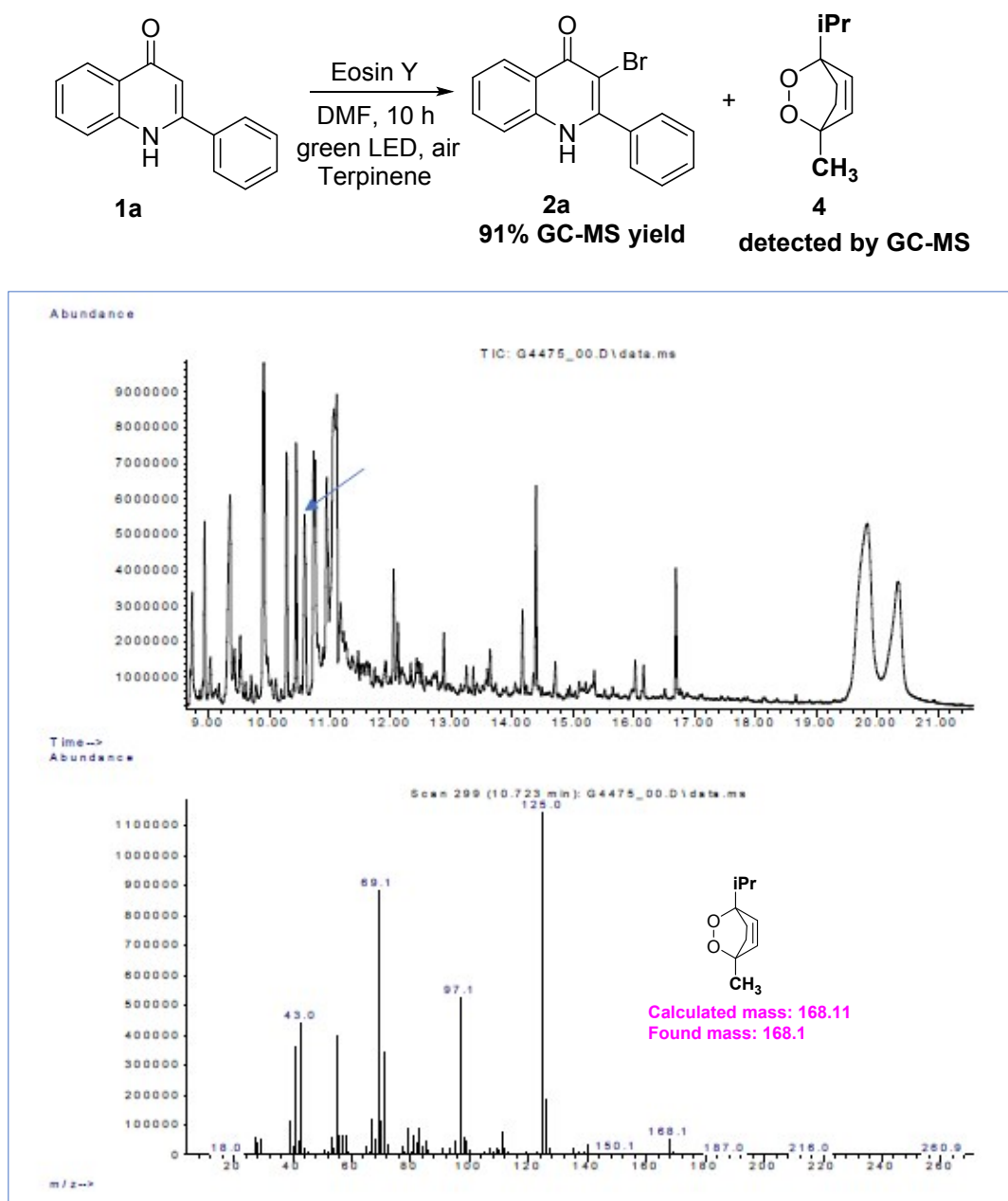


Fig. S4: GCMS spectrum of the reaction mixture.

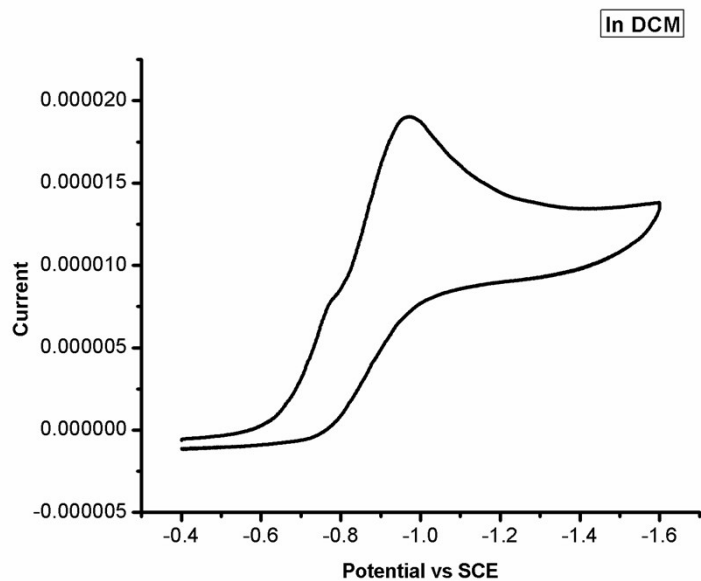
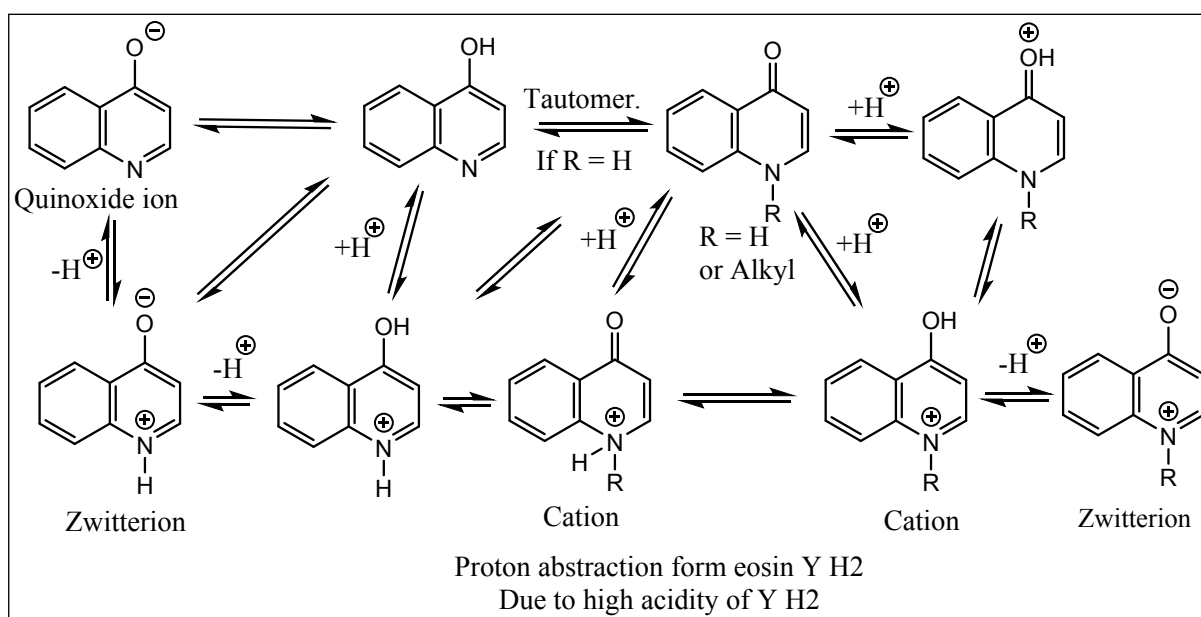
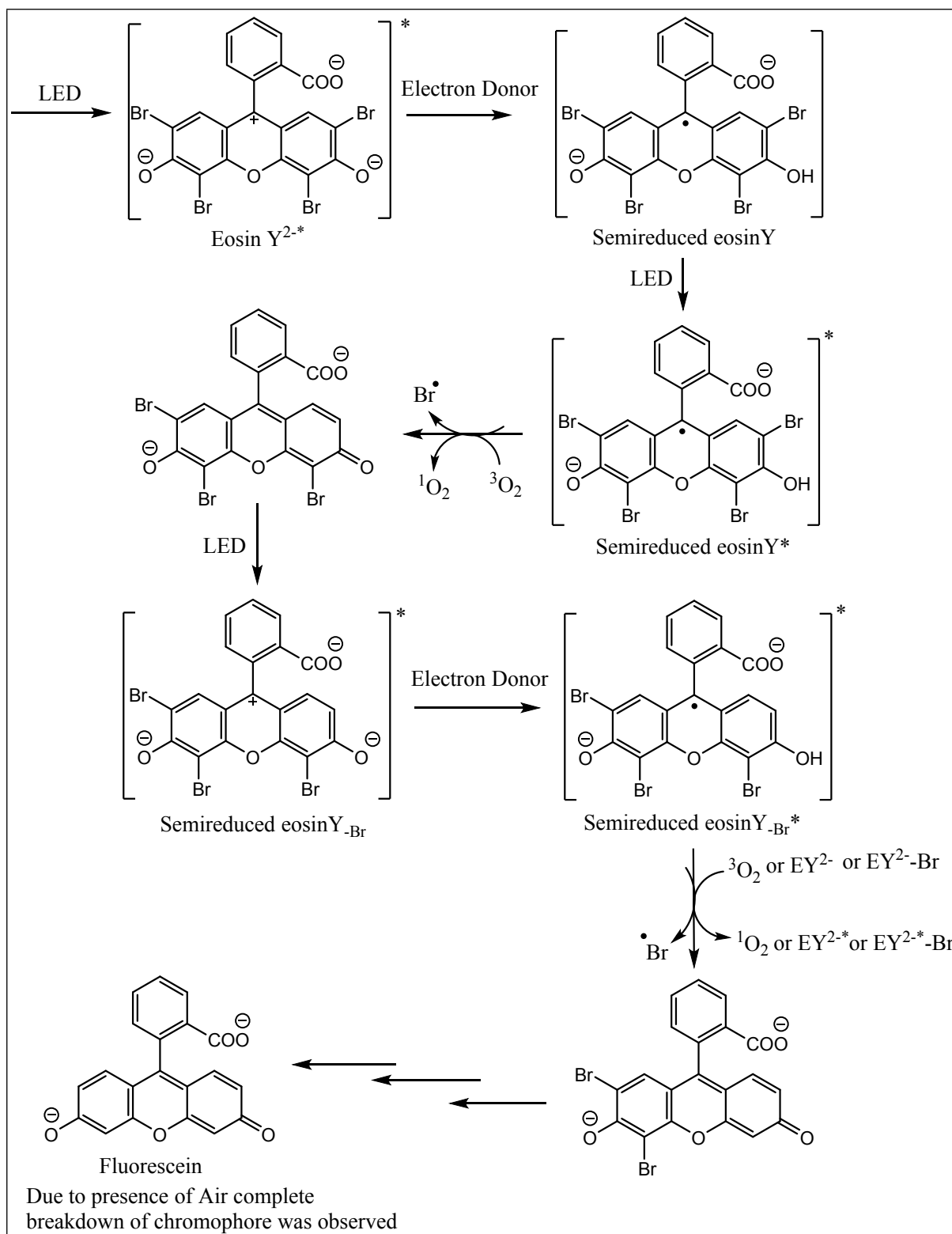


Fig. S5: Cyclic voltammetry (CV) shows oxidation of 2-phenylquinolin-4(1H)-one (**1a**) Conditions: 5×10^{-4} M in DCM; reference electrode, SCE; working and auxiliary electrodes, Pt with 0.1 M Bu_4NPF_6 ; 298 K; scan rate, 200 mV/s. [1^{st} oxidation 0.79 V and 2^{nd} at 1.18 V].



Scheme S1: **a)** Proton abstraction from Eosin YH_2 and stabilization, **b)** formation of $(\text{EY}^{2-} \cdot 2\text{HQ}^+)$ complex.



Scheme S2: Complete degradation of the Eosin Y under light. Starting from active eosin Y.

Copies of ^1H and ^{13}C NMR spectra

