Supplementary Material for

Kinetic Analysis of Nitroxide Radical Formation Under Oxygenated Photolysis: Toward Quantitative Singlet Oxygen Topology

David F. Zigler, Eva Chuheng Ding, Lauren E. Jarocha, Renat R. Khatmullin, Vanessa M. DiPasquale, R. Brendan Sykes, Valery F. Tarasov, Malcolm D.E. Forbes*

Table of Contents

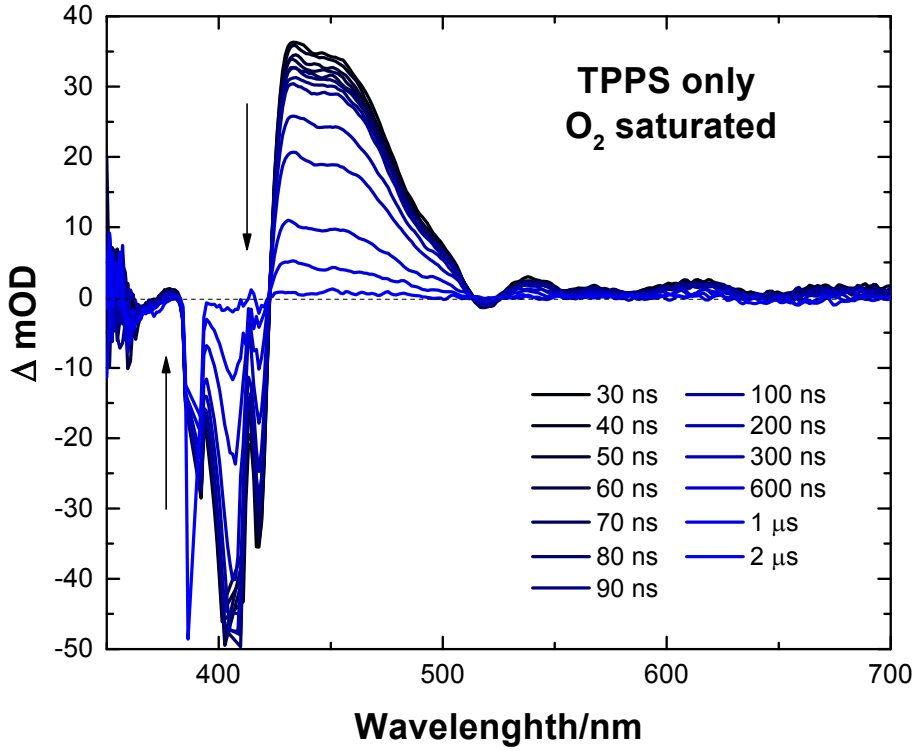


Figure S1. TA spectra at various time delays of 10 mM of TPPS solution in oxygen saturated, 50 mM aqueous sodium phosphate buffer at *p*H = 8.0 following a 388 nm excitation pulse.

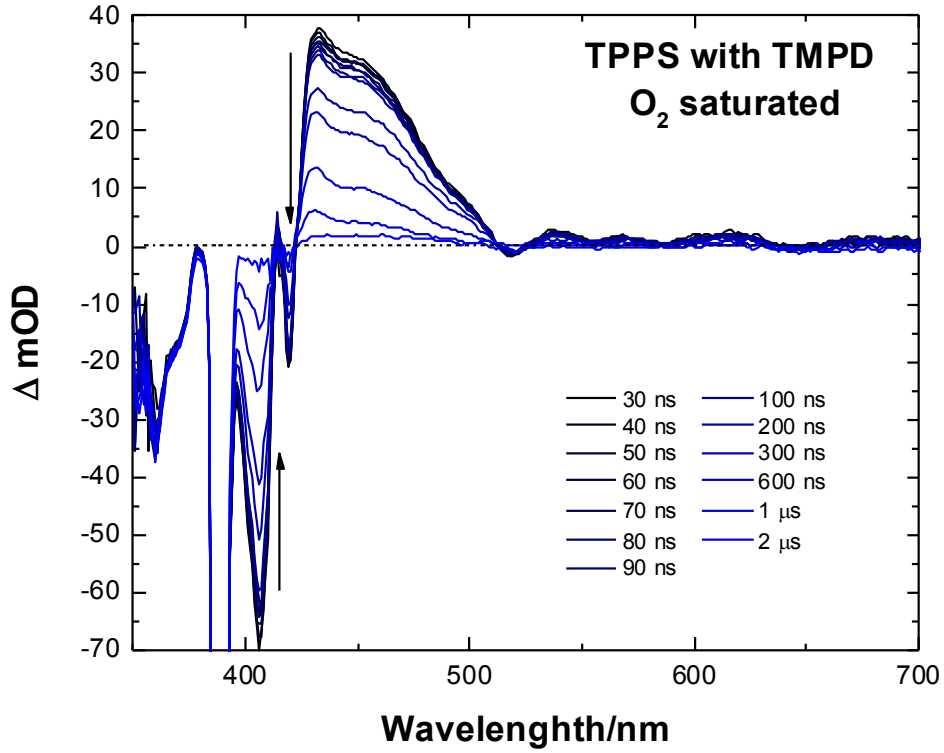


Figure S2. TA spectra at various time delays of 10 mM of TPPS solution with 50 mM TMPD in oxygen saturated, 50 mM aqueous sodium phosphate buffer at *p*H = 8.0 following a 388 nm excitation pulse.

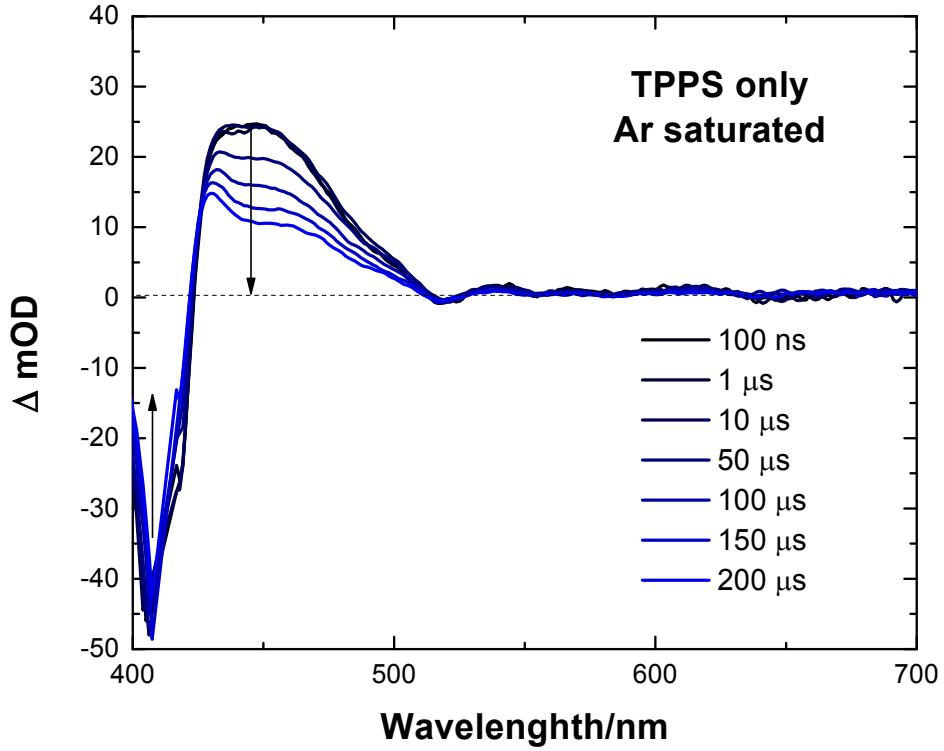


Figure S3. TA spectra at various time delays of 10 mM of TPPS solution in 50 mM aqueous sodium phosphate buffer at *p*H = 8.0 and under flowing Ar, following a 388 nm excitation pulse.

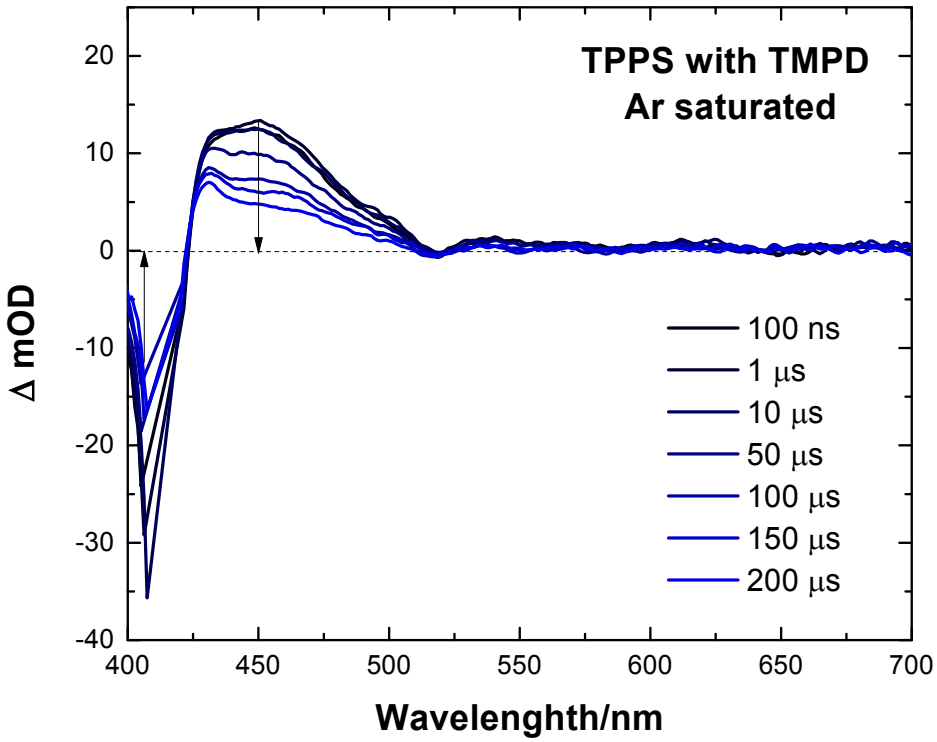


Figure S4. TA spectra at various time delays of 10 mM of TPPS solution with 50 mM TMPD in 50 mM aqueous sodium phosphate buffer at *p*H = 8.0 and under flowing Ar, following a 388 nm excitation pulse.

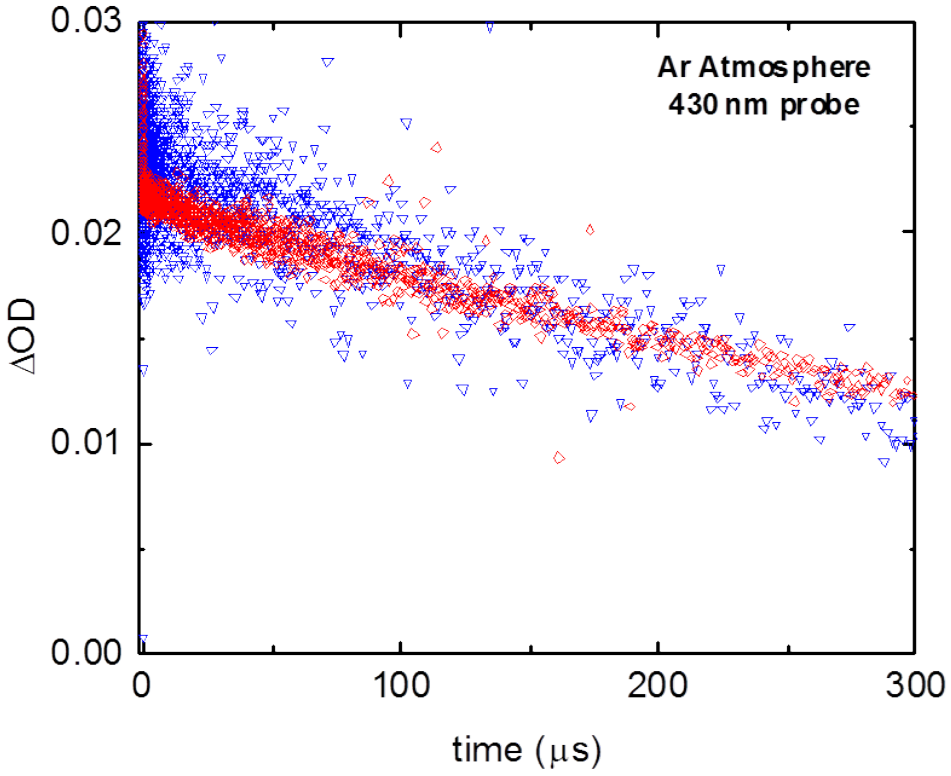


Figure S5. Decays of 10 mM of TPPS solution in argon saturated aqueous sodium phosphate buffer at *p*H = 8.0 probed at 430 nm in the absence (red) and presence (blue) of 50mM of TMPD. The following lifetimes were obtained by fitting the data in biexponential decay (red: τ_1 = 10.1(±0.4) ns and τ_3 = 409(±28) μs) ; (blue: τ_1 = 35(±13) ns and τ_3 = 442(±10) μs)).

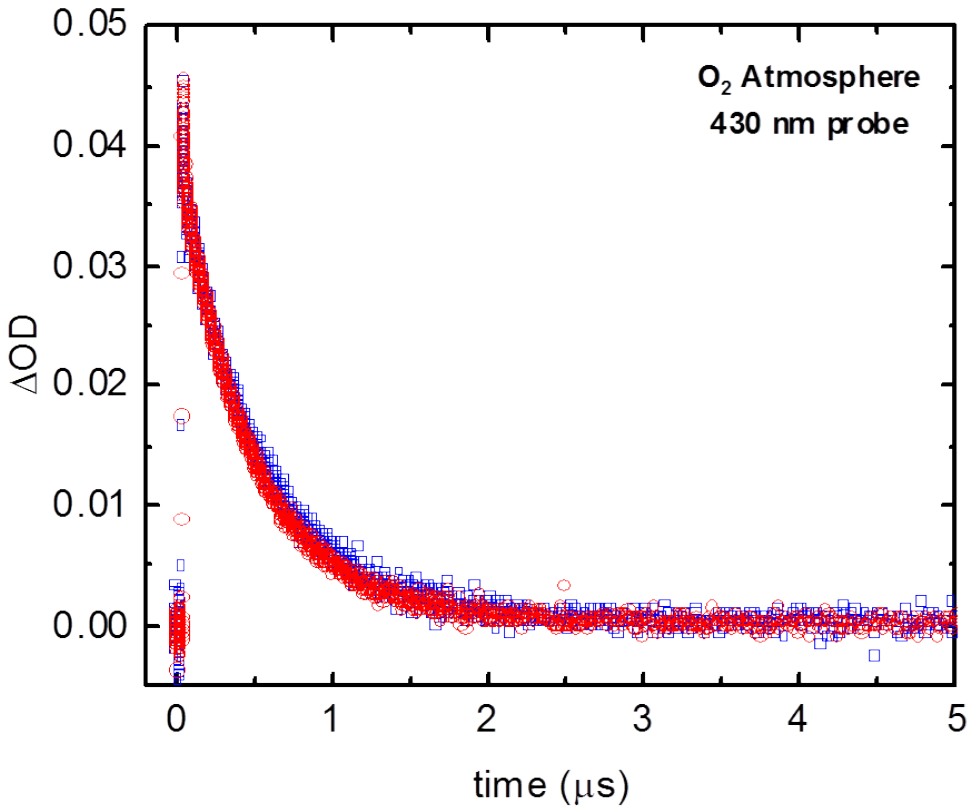


Figure S6. Decays of 10 mM of TPPS solution in oxygen saturated aqueous sodium phosphate buffer at *p*H = 8.0 probed at 430 nm in the absence (red) and presence (blue) of 50mM of TMPD. The following lifetimes were obtained by fitting the data in biexponential decay (red: τ_1 = 13.2(±0.5) ns and τ_3 = 0.482(±0.001) μs) ; (blue: τ_1 = 16.5(±0.1) ns and τ_3 = 0.537(±0.002) μs)). The deviation between the two is probably due to the poor signal to noise.

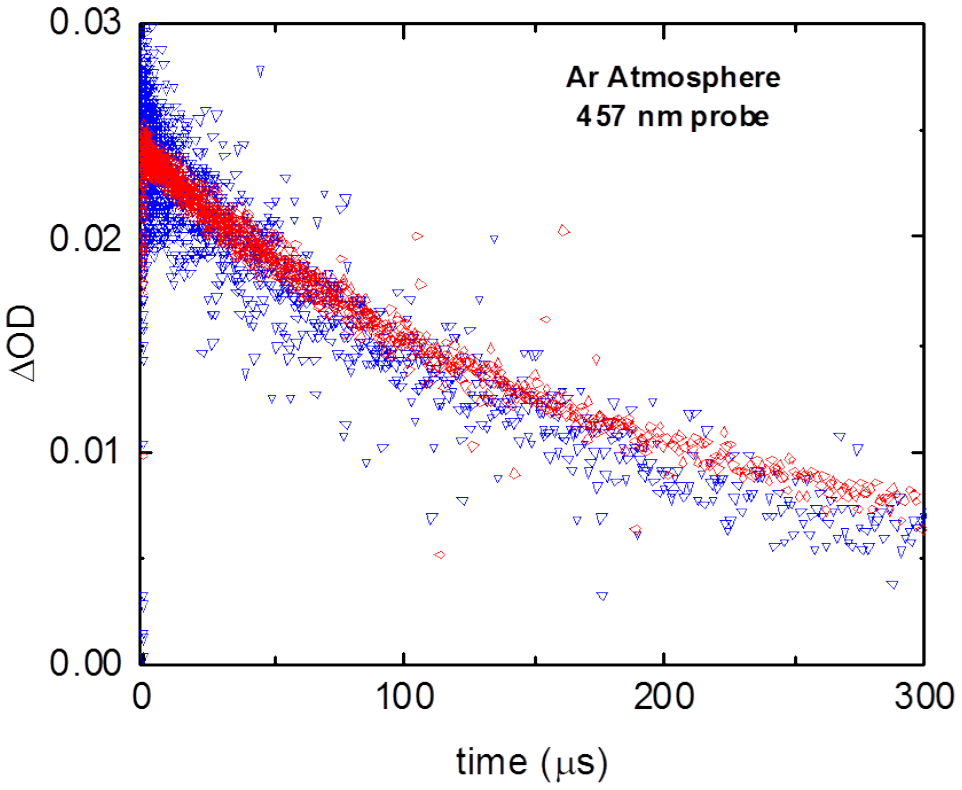


Figure S7. Decays of 10 mM of TPPS solution in argon saturated aqueous sodium phosphate buffer at *p*H = 8.0 probed at 457 nm in the absence (red) and presence (blue) of 50mM of TMPD. The following lifetimes were obtained by fitting the data in monoexponential decay (red: τ_3 = 197(±3) μs) ; (blue: τ_3 = 231(±1) μs).

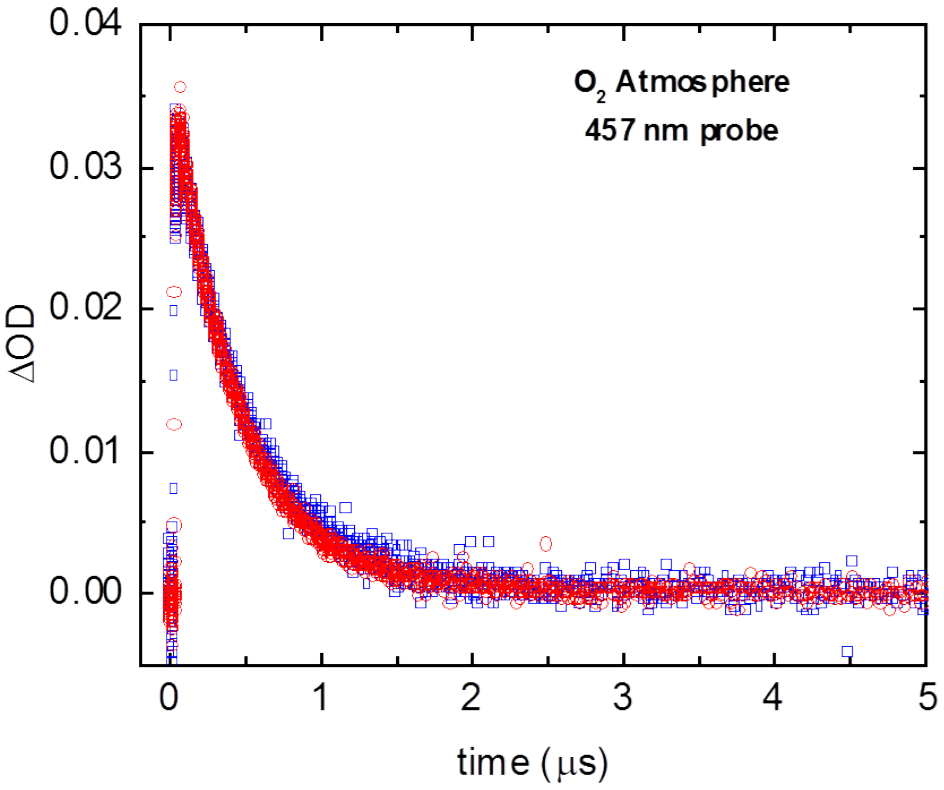


Figure S8. Decays of 10 mM of TPPS solution in O_2 saturated aqueous sodium phosphate buffer at *p*H = 8.0 probed at 457 nm in the absence (red) and presence (blue) of 50mM of TMPD. The following lifetimes were obtained by fitting the data in monoexponential decay (red: τ_3 = 0.436(±0.001) μs) ; (blue: τ_3 = 0.492(±0.002) μs).

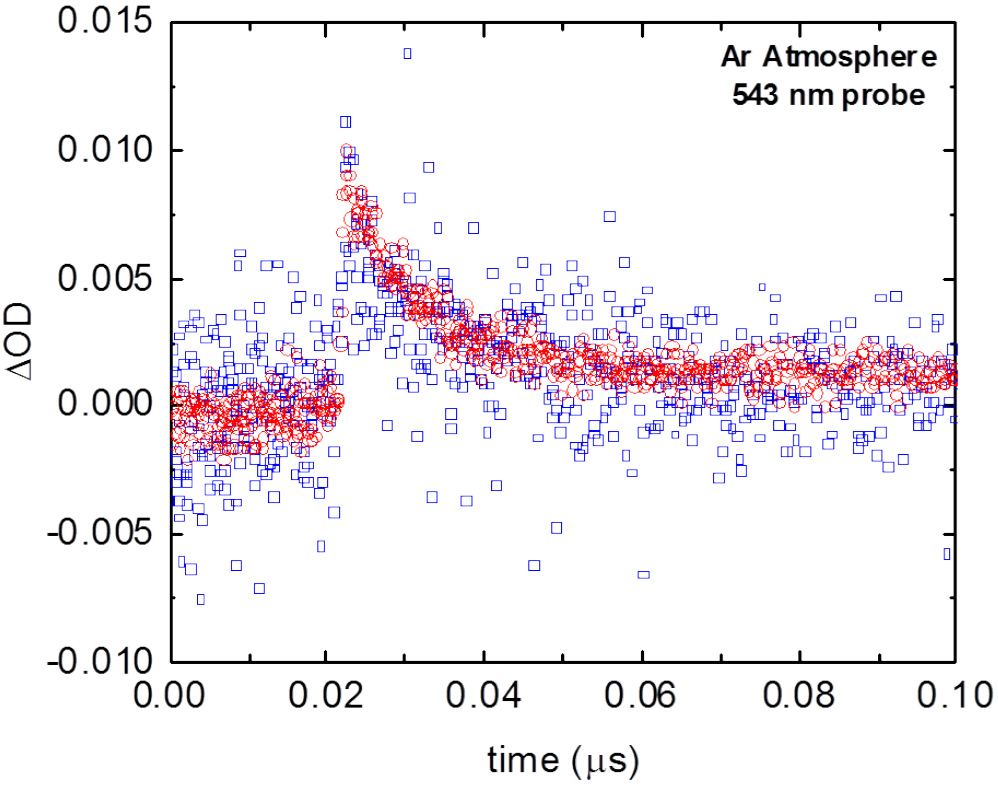


Figure S9. Decays of 10 mM of TPPS solution in argon saturated aqueous sodium phosphate buffer at *p*H = 8.0 probed at 543 nm in the absence (red) and presence (blue) of 50mM of TMPD. The following lifetimes were obtained by fitting the data in monoexponential decay (red: τ_1 = 10.1(±0.5) ns) ; (blue: τ_1 = 11(±1) ns).

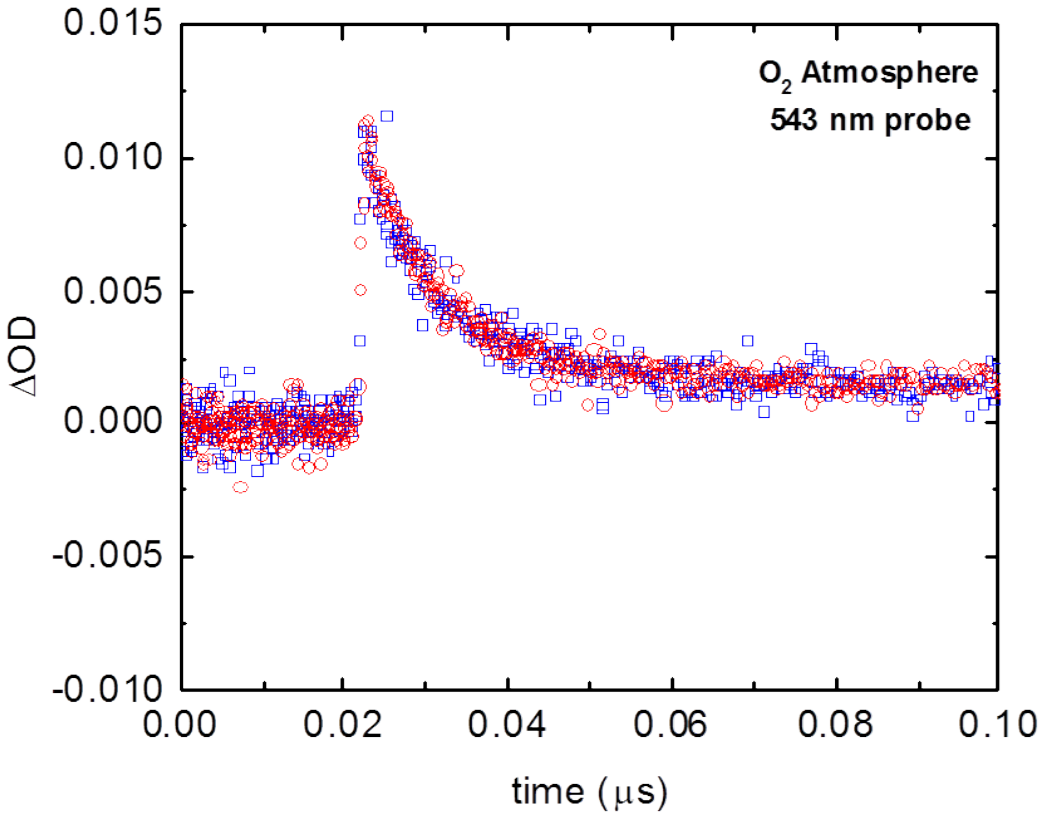


Figure S10. Decays of 10 mM of TPPS solution in argon saturated aqueous sodium phosphate buffer at *p*H = 8.0 probed at 543 nm in the absence (red) and presence (blue) of 50mM of TMPD. The following lifetimes were obtained by fitting the data in monoexponential decay (red: τ_1 = 10.7(±0.2) ns) ; (blue: τ_1 = 11.8(±0.3) ns).

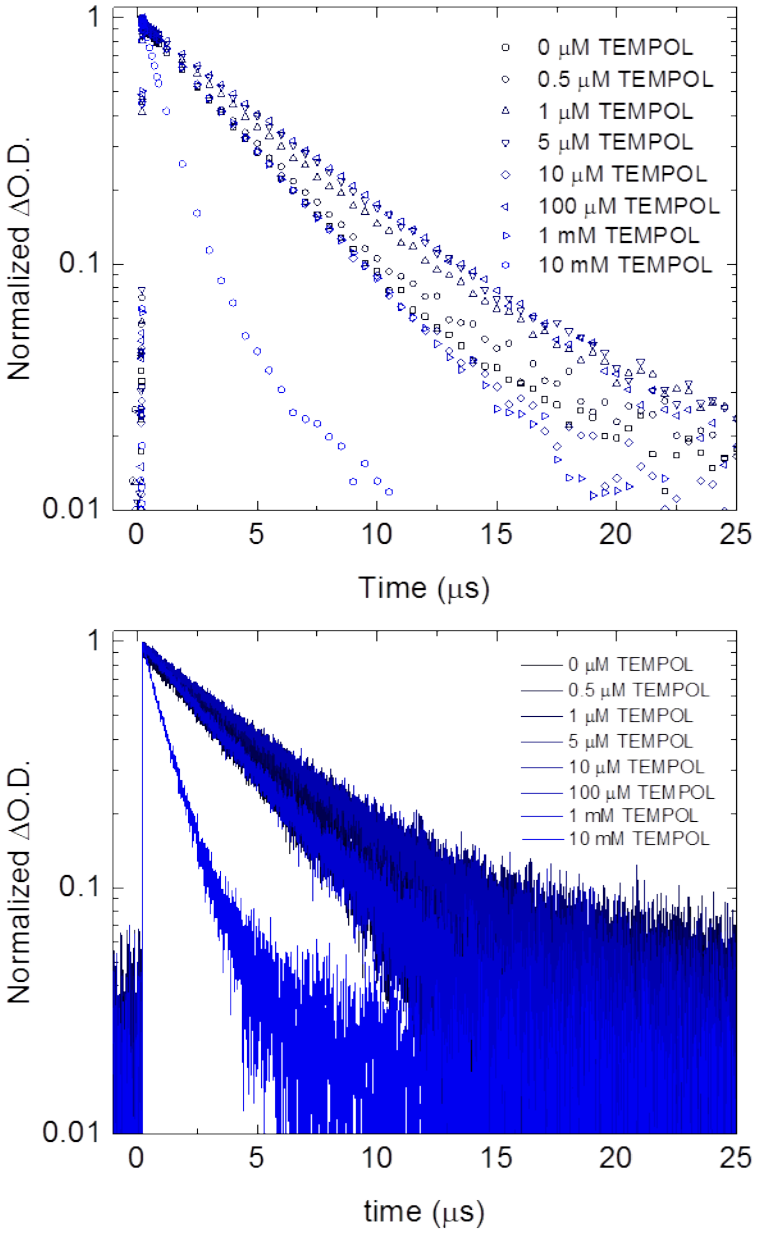
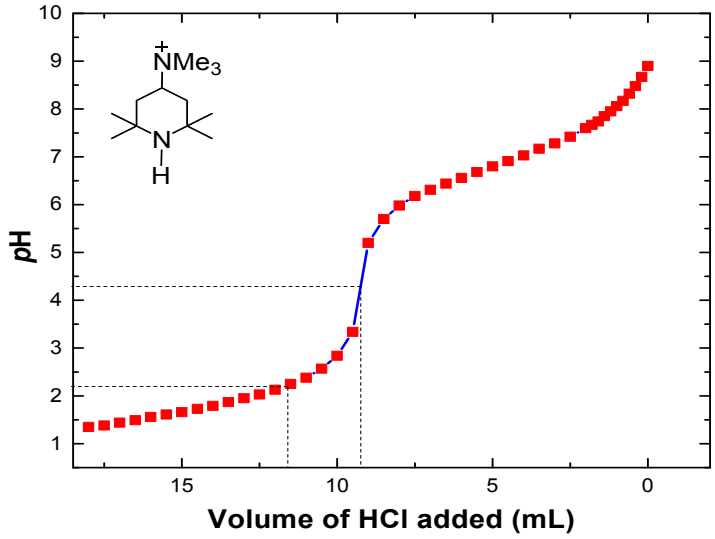


Figure S11. Decays dynamics of 10 mM of TPPS solution in aerated aqueous sodium phosphate buffer at *p*H = 8.0 collected at 490 nm following 490 nm excitation in the presence of varying concentrations of TEMPOL. The top and bottom decay traces are the same, except the bottom trace shows that all data points, illustrating the similarity of the decays except the one measured with 10 mM TEMPOL. Based on the increased observed rate, the quenching constant is estimated to be 6 x 10^7 $M^{-1}s^{-1}$.

A



B

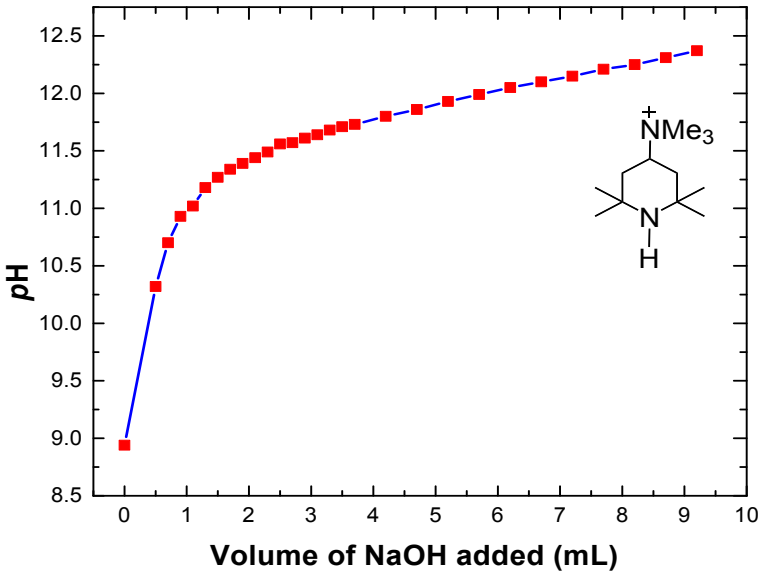


Figure S12. Titrations of 25 ml of 100 mM aqueous solutions of N-TMPCl with a): 200 mM NaOH; b) 200 mM HCl.

2,2,6,6-tetramethyl-4-piperidone hydrochloride (TMPD-HCl): TMPD-HCl was prepared by slow addition of 1.25 mL of concentrated hydrochloric acid to 5.00 g of 2,2,6,6-tetramethyl-4-piperidone (TMPD) in 450 mL anhydrous diethyl ether and 50 mL of absolute ethanol. The resulting white precipitate was removed by vacuum filtration and washed several times with diethyl ether. The filtrate was treated with an additional 1.25 mL of concentrated HCl and the second portion of off-white solid was collected and rinsed with ether. The combined solids were dried *in vacuo* to give 5.8 g of TMPD-HCl (94%). ESI: m/z 156 [M^+ calculated for $C_9H_{18}ON^+$]. ^1H NMR (400 MHz, CD_3CN-d_3) δ ppm 9.34 (s, 2H), 2.68 (s, 4H), 1.58 (s, 12H).

4-[N,N,N-trimethyl-ammonium]-2,2,6,6-tetramethylpiperidinyl chloride (N-TMPCl): The synthesis of N-TMPCl was adapted from the procedures published by Ramamurthy group.[66,67] 0.8 g of 90 % ice cold HCOOH was added to 0.5 g 4-amino-2,2,6,6-tetramethylpiperidine and 0.57 g of 37 % aqueous HCHO solution. The mixture was refluxed for 8 h, 0.35 g of conc. HCl was added, and the HCOOH and excess HCHO were removed under reduced pressure. The oily orange residue was dissolved in 2.5 mL of water and 1 g of solid NaOH was added. The orange layer was collected and lower aqueous layer was extracted twice with 5 mL of diethyl ether. The combined extract was added to the upper layer and dried over potassium hydroxide pellets. The ether layer was removed and distilled under reduced pressure to get a colorless liquid which was refluxed with 1.5 equivalent of methyl iodide at 75° C without any solvent for one day. The product was purified by triturating the reaction mixture with hexane to afford 4-[N,N,N-trimethyl-ammonium]-2,2,6,6-tetramethylpiperidinyl iodide as a white solid. The further exchange to chloride form was performed by addition of 2M NaOH solution followed by

neutralization with 12M of HCl. The precipitation of 4-[N,N,N-trimethyl-ammonium]-2,2,6,6-tetramethylpiperidinyl chloride was achieved by the excess addition of diethyl ether. ^{1}H NMR (300 MHz, D_2O) δ: 1.11 (s, 6 H), 1.12 (s, 6 H), 1.31 (dd, 2 H), 2.06 (d, 2 H), 2.14 (s, 1 H), 2.97 (s, 9 H), and 3.68 (dd, 1 H); ESI: m/z 199 [M^+ calculated for $C_{12}H_{27}N_2^+$].

Transient Absorption: Quenching of TPPS excited states by TMPD and TEMPOL was examined by transient absorption spectroscopy. For amine quenching the samples contained 10 μM TPPS, and 0 or 50 mM TMPD. Solutions were magnetically stirred while held under continuous flow of either high purity argon (for oxygen-free) or flowing oxygen. The solutions were pumped with frequency doubled Ti:Sapphire (388 nm, 250 fs pulse width, 1 kHz repetition rate, 150 nJ/pulse) and probed using a pulsed continuum with an Ultrafast Systems EOS Transient Absorption Spectrometer for detection (instrument response < 1 ns, full range 400 μs). TEMPOL quenching experiments were performed using 10 μM TPPS and 0, 0.5, 1, 5, 10, 100, 1000 μM, or 10 mM TEMPOL in aerated buffered solution. Following excitation at 420 nm (OPO pumped by frequency tripled Nd:YAG, 8 ns pulse, 1 mJ/pulse), the solution was probed using 490 nm light from a Xe-arc lamp selected by a monochromator and detected by photomultiplier tube (instrument response = 10 ns).