

Supporting Information

for

**GENERATION OF FREE OXYGEN ATOMS O(³P) IN SOLUTION BY
PHOTOLYSIS OF 4-BENZOYLPYRIDINE N-OXIDE**

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References

Experimental Detail

Materials. The following items were of the best available quality, and were used as received: iron(III) perchlorate hydrate, iron(II) perchlorate hydrate, palladium(II) acetate, nickel(II) perchlorate hydrate, manganese(II) perchlorate hydrate, 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), deuterium oxide (99.9 % D), 4-benzoylpyridine, 1,10-phenanthroline, methanol, 2-propanol, chromotropic acid (all Sigma Aldrich), perchloric acid (70 %), phosphoric acid (85 %), benzophenone, trifluoroacetic acid, dimethylsulfoxide, sodium iodide, sodium bromide, sodium chloride (all Fisher Scientific), silver(I) nitrate, potassium chromate (both Baker), acetonitrile (Honeywell), and acetonitrile-d₃ (99.8 % D) (Cambridge Isotopes). 4-Benzoylpyridine N-oxide,¹ *trans*-[Cr(cyclam)(CN)₂](CF₃SO₃) (cyclam = 1,4,8,11-tetraazacyclotetradecane),^{2,3} *trans*-[Cr(cyclam)(H₂O)₂](CF₃SO₃)₃,^{2,3} and perchlorate salts of Ni(cyclam)²⁺,⁴ Ni(Me₆-cyclam)²⁺,⁵ Ni(Me₄-cyclam)²⁺,⁶ Ni(Me₁₀-cyclam)²⁺,⁷ and UO₂²⁺⁸ were available in our laboratory supplies.

UV-Visible spectra of BPyO: The key spectral features in water are λ_{\max} 292 nm ($\epsilon = 1.97 \times 10^4$ M⁻¹ cm⁻¹), and in acetonitrile λ_{\max} 322 nm ($\epsilon = 2.12 \times 10^4$ M⁻¹ cm⁻¹). The data in aqueous solution are in good agreement with the previously reported spectrum.¹

Acid dissociation constant of BPyOH⁺ in water was determined from the effect of H⁺ on UV-Vis spectra. The data were collected for solutions containing 38 μ M BPyO and 0 - 6 M HClO₄ (6 M ionic strength adjusted with HClO₄ + NaClO₄). The absorbance at 292 nm decreases only slightly above 3 M HClO₄, showing that nearly all of BPyO is present as BPyOH⁺ at 6 M HClO₄. Full protonation of BPyO is not observed at 1 M ionic strength; therefore, more data were collected at 6 M ionic strength. The absorbance of BPyO at 292 nm was the same in 1 M and 6 M NaClO₄, but the value in 1 M HClO₄ was slightly larger than in 6 M HClO₄ (Abs_{292 nm} = 0.5

and 0.6 for $\mu = 6 \text{ M}$ and 1 M HClO_4 , respectively). Data are shown in Figure S2. The absorbance at 292 nm was plotted as a function of $-\log[\text{HClO}_4]$ (Figure S3), and the data were fitted to eq S1 (see derivation below) to yield $K_a = 1.2 \pm 0.5 \text{ M}^{-1}$.

Derivation of equation S1

$$[\text{BPyO}]_{\text{tot}} = [\text{BPyO}] + [\text{BPyOH}^+]$$

$$[\text{BPyO}] [\text{H}^+] / [\text{BPyOH}^+] = K_a$$

$$\text{Abs}_{292 \text{ nm}} = \text{Abs}_{292 \text{ nm}}^{\text{BPyO}} + \text{Abs}_{292 \text{ nm}}^{\text{BPyOH}^+} = [\text{BPyO}] \varepsilon_{292 \text{ nm}}^{\text{BPyO}} + [\text{BPyOH}^+] \varepsilon_{292 \text{ nm}}^{\text{BPyOH}^+}$$

$$\text{Abs}_{292 \text{ nm}} = [\text{BPyO}] \varepsilon_{292 \text{ nm}}^{\text{BPyO}} + ([\text{BPyO}]_{\text{tot}} - [\text{BPyO}]) \varepsilon_{292 \text{ nm}}^{\text{BPyOH}^+}$$

$$[\text{BPyO}]_{\text{tot}} = [\text{BPyO}] + ([\text{BPyO}] [\text{H}^+] / K_a) \Rightarrow [\text{BPyO}] = [\text{BPyO}]_{\text{tot}} (K_a / ([\text{H}^+] + K_a))$$

$$\text{Abs}_{292 \text{ nm}} = [\text{BPyO}]_{\text{tot}} (K_a \varepsilon_{292 \text{ nm}}^{\text{BPyO}} + [\text{H}^+] \varepsilon_{292 \text{ nm}}^{\text{BPyOH}^+}) / (K_a + [\text{H}^+])$$

$$\text{Abs}_{292 \text{ nm}} = [\text{BPyO}]_{\text{tot}} (K_a \varepsilon_{292 \text{ nm}}^{\text{BPyO}} + 10^{-\log[\text{HClO}_4]} \varepsilon_{292 \text{ nm}}^{\text{BPyOH}^+}) / (K_a + 10^{-\log[\text{HClO}_4]}) \quad (\text{eq S1})$$

Acid dissociation constant of BPyOH⁺ in acetonitrile ($K_a^{\text{BPyOH}^+}$) was determined by a method similar to that described for aqueous solutions. Because the acidity of pyridine oxides in acetonitrile varies widely with water content,⁹ $\text{CF}_3\text{CO}_2\text{H}$ ($\text{p}K_a$ in MeCN = 12.65 ± 1.38)¹⁰ was used as the source of H^+ . Solutions containing 1.09 mM BPyO and 0 - 94 mM $\text{CF}_3\text{CO}_2\text{H}$ were prepared in 0.1 cm cells, and spectra were collected, see Figure S4. No further decrease in absorbance at 322 nm was observed at $\text{CF}_3\text{CO}_2\text{H}$ concentrations above 94 mM. The spectrum of BPyO was obtained in the absence of added acid, and that of BPyOH^+ was measured at ≥ 94 mM $\text{CF}_3\text{CO}_2\text{H}$. The difference in molar absorptivities between these two forms at 322 nm, $\Delta\varepsilon_{322}$, is $19,700 \text{ M}^{-1} \text{ cm}^{-1}$. Absorbance changes at 322 nm caused by successive additions of $\text{CF}_3\text{CO}_2\text{H}$ to

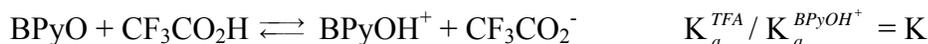
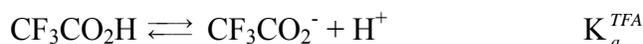
BPyO, were fitted to eq S2 to give $K_a = (4 \pm 2) \times 10^{-13} \text{ M}^{-1}$. The change in absorbance at 322 nm was used to calculate $[\text{BPyOH}^+]$. The concentrations of the remaining species were calculated as follows:

$$[\text{BPyOH}^+] = [\text{CF}_3\text{CO}_2^-] = [\text{BPyO}]_{\text{total}} - \Delta\text{Abs}_{322\text{nm}}^{\text{BPyO}} / \Delta\epsilon_{322\text{nm}};$$

$$[\text{BPyO}] = [\text{BPyO}]_{\text{total}} - [\text{BPyOH}^+];$$

$$[\text{CF}_3\text{CO}_2\text{H}] = [\text{CF}_3\text{CO}_2\text{H}]_{\text{total}} - [\text{CF}_3\text{CO}_2^-].$$

Derivation of equation S2



$$K = [\text{BPyOH}^+][\text{CF}_3\text{CO}_2^-] / ([\text{BPyO}][\text{CF}_3\text{CO}_2\text{H}])$$

$$K_a^{\text{BPyOH}^+} = K_a^{\text{TFA}} [\text{BPyO}][\text{CF}_3\text{CO}_2\text{H}] / ([\text{BPyOH}^+][\text{CF}_3\text{CO}_2^-]) \quad (\text{Eq S2})$$

GCMS of the products of BPyO photolysis shows the presence of five new isomers of BPyO (parent mass: 199.20 g/mol) which eluted at 15.78, 15.85, 16.73, 17.04, and 17.46 minutes. Unreacted BPyO at 18.32 minutes and trace amounts of BPy (183.20 g/mol) at 15.32 minutes were also observed.

¹H NMR of an aqueous solution of BPyO (initial concentration 1.3 mM) that had been photolyzed to 85 % completion exhibited the following chemical shifts (δ /ppm) in D₂O: δ 8.77 d, 8.49 d, 8.46 s, 7.97 d, 7.87 t, 7.79 t, 7.74 d, 7.62 q, 7.48 t, Figures 9 and S11-S13. Several of these chemical shifts overlap those of BPyO and/or BPy. The signals at 8.49, 7.97, 7.87, and

7.62 ppm are from unreacted BPyO. The downfield portion of the 7.62 ppm quartet is consistent with both BPyO and BPy. Two new signals at 8.46 and 7.74 ppm are assigned as aromatic C-H's of a hydroxylated ring. The signals at 8.77 and 7.48 ppm are close, but slightly shifted (by +0.1 and -0.07 ppm, respectively) from those expected for BPy. The 8.77 resonance is tentatively assigned as α -CH of one or more hydroxylated BPy's. The signal at 7.48 ppm is very small, and even if it is assigned as BPy, the yield of BPy is no more than 4% of consumed BPyO.

^1H NMR collected after irradiation (65 % consumption) of degassed 2 mM BPyO in $\text{CH}_3\text{CN}-d_3$ provides additional information because in this solvent the O-H chemical shifts can be seen, Figure S13. As in D_2O , several chemical shifts overlap BPyO (doublets at 8.19 and 7.79 ppm) and BPy (doublets at 8.79 and 7.83 ppm), Figures S12-S13, and both with a triplet at 7.68 ppm and quartet at 7.56 ppm. The remaining signals are assigned as C-H signals on OH-substituted aromatic rings: 7.76 d, 7.62 d, and 7.51 t; or as O-H singlets: 9.67, 6.48, 6.46, 6.41, 6.10, and 3.97 ppm which disappear upon addition of D_2O . The signal at 9.67 ppm is assigned as an O-H on the carbon *ortho* to BPy nitrogen.

A yellow product, $\lambda_{\text{max}} \sim 400$ nm, was observed several minutes after completion of photolysis in CH_3CN . The yellow color formed faster in the presence of O_2 and under ambient light. ^1H NMR spectra of such solutions were no different than those obtained for samples that were kept air-free and in the dark. From these results we surmise that the yellow species is a minor product with a large molar absorptivity ($\epsilon_{400 \text{ nm}} \geq 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) such as one might expect for quinones and related compounds.

Generation of BPyO $^{\bullet-}$ for spectral measurements

BPyO $^{\bullet-}$ was obtained in 0.1 M aqueous HClO_4 by LFP of 40 μM BPyO in the presence of 10 mM Fe^{2+} . The detailed chemistry is described in Results. The concentration of $^3\text{BPyO}^*$ was

calculated from the absorbance immediately following laser flash ($\epsilon_{490 \text{ nm}} = 1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). All of ${}^3\text{BPyO}^*$ was reduced within the first 3 μs following the flash. The absorbance 3 μs after the flash yielded $\epsilon_{490 \text{ nm}} = 1950 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{BPyO}^{\bullet-}$.

Quantum yield of ${}^3\text{BPyO}^*$ in water was determined relative to ${}^*\text{Ru}(\text{bpy})_3^{2+}$. An air-free solution of 6.6 μM BPyO in a 1 cm square fluorescence cell ($\text{Abs} = 0.092$ at 308 nm) was subjected to a laser flash. The absorbance increase caused by ${}^3\text{BPyO}^*$ ($\lambda_{\text{mon}} = 380 \text{ nm}$, $\Delta\epsilon_{380 \text{ nm}} = 3.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) was 0.032 (0.7 cm pathlength) corresponding to 1.3 μM ${}^3\text{BPyO}^*$. A solution of $\text{Ru}(\text{bpy})_3^{2+}$ (6.3 μM , $\text{Abs}_{308} = 0.091$) was flashed in the same fashion. The absorbance increase at 380 nm was 0.034, i. e. $[{}^*\text{Ru}(\text{bpy})_3^{2+}] = 5.6 \mu\text{M}$ on the basis of $\Delta\epsilon_{380} = 8700 \text{ M}^{-1} \text{ cm}^{-1}$.¹¹ The quantum yield for ${}^*\text{Ru}(\text{bpy})_3^{2+}$ is unity, which leads to $\Phi = 0.2$ for ${}^3\text{BPyO}^*$ in H_2O .

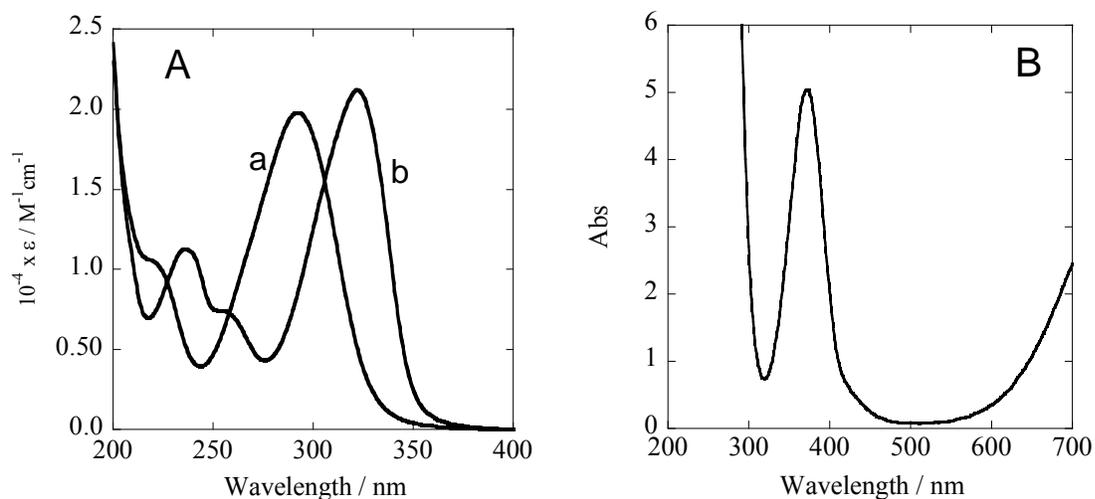


Figure S1. A: UV-vis spectra of BPyO in water (a) and acetonitrile (b). **B:** Composite UV-Vis spectrum of 1 mM K_2CrO_4 + 0.33 M CuSO_4 in water, 1 cm pathlength.

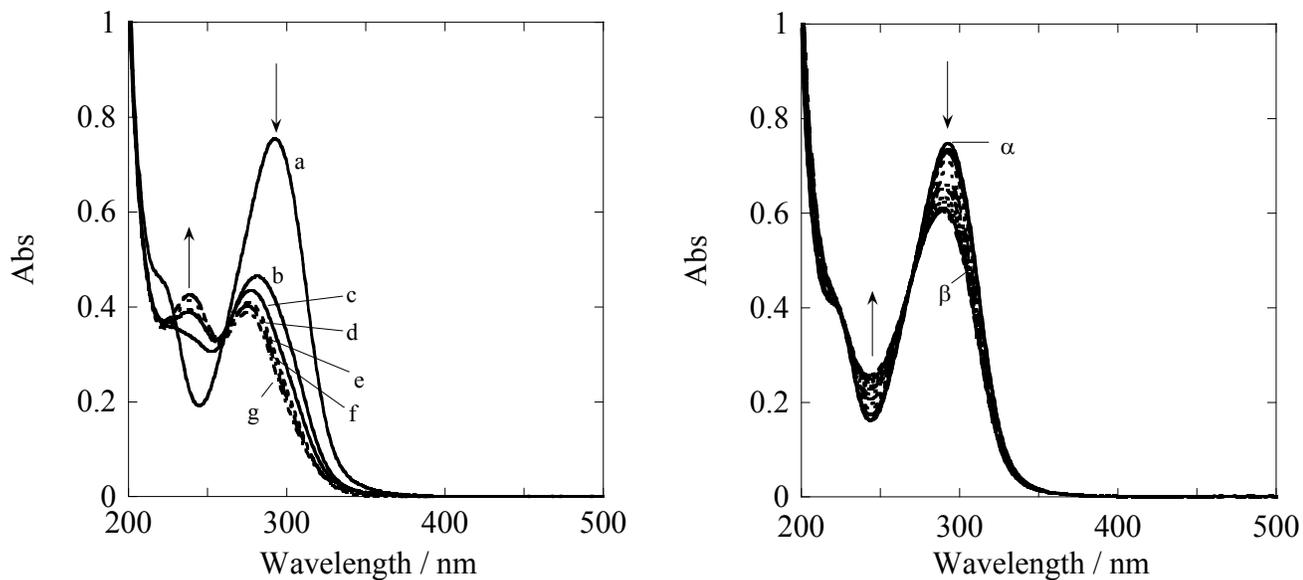


Figure S2. Effect of H^+ on UV-Vis spectra of 38 μM BPyO in aqueous HClO_4 . **LEFT:** Ionic strengths = 6 M, added $[\text{HClO}_4]$ = 0 (a), 0.98 M (b), 1.95 M (c), 2.93 M (d), 3.90 M (e), 4.88 M (f), and 5.85 M (g). **RIGHT:** Ionic strength = 1M, added $[\text{HClO}_4]$ = 0 (α), 9.7 mM, 0.098 M, 0.20 M, 0.29 M, 0.39 M, 0.49 M, 0.59 M, 0.69 M, 0.78 M, 0.88 M, 0.98 M (β).

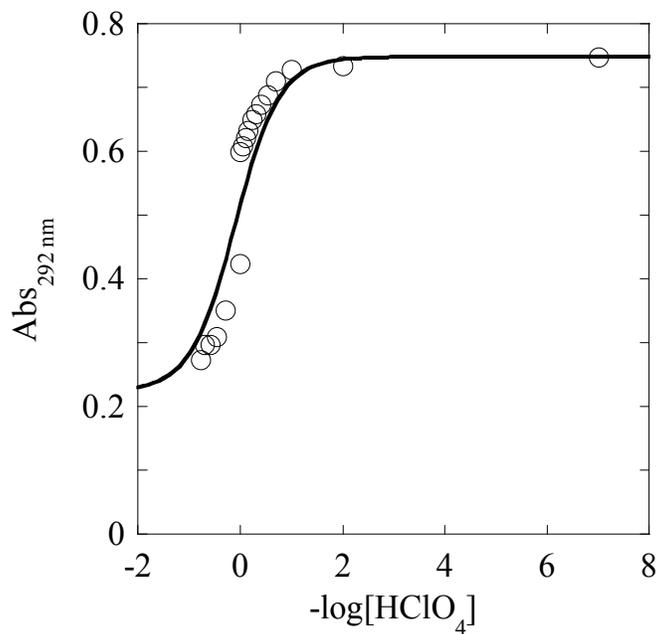


Figure S3. Plot of $Abs_{292\text{ nm}}$ vs $-\log([HClO_4])$ (circles) and a fit to equation S1. $[BPyO]_{\text{tot}} = 38\ \mu\text{M}$, $\epsilon_{292\text{ nm}}^{BPyO} = 19,700\ \text{M}^{-1}\ \text{cm}^{-1}$, $\epsilon_{292\text{ nm}}^{BPyOH^+} = 5,900\ \text{M}^{-1}\ \text{cm}^{-1}$ (from UV-Vis spectrum at 5.85 M $HClO_4$, Figure S2). The fit yields $K_a = 1.2 \pm 0.2$

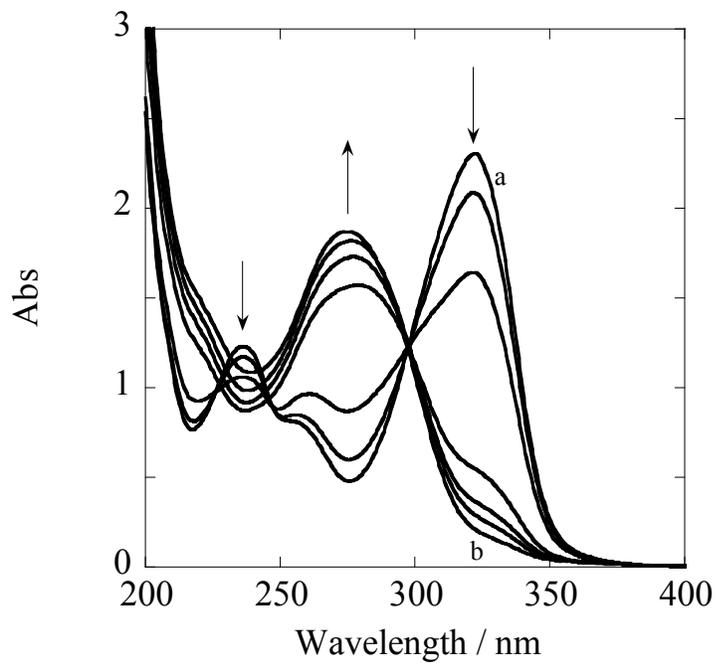


Figure S4. UV-Vis spectra (1 mm path length) of 1.09 mM BPyO in AN in the presence of 0 mM (a), 0.94 mM, 3.75 mM, 30.1 mM, 53.7 mM, 74.8 mM, and 94.0 mM (b) CF₃CO₂H. The difference in spectrum (a) and (b) yielded $\Delta\epsilon_{322\text{ nm}} = 19,700\text{ M}^{-1}\text{ cm}^{-1}$.

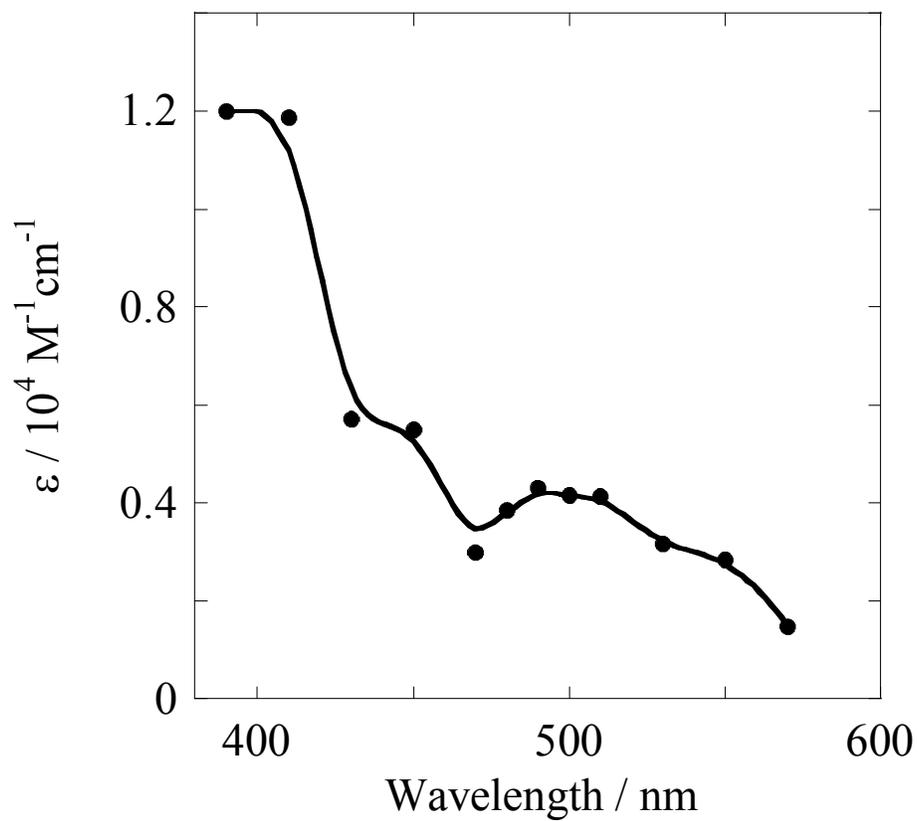


Figure S5. Transient absorption spectrum of ${}^3\text{BPyO}^*$ in AN obtained from 308 nm LFP of degassed solutions. Molar absorptivities represent the lower limit obtained under the assumption that $\Phi = 1.0$.

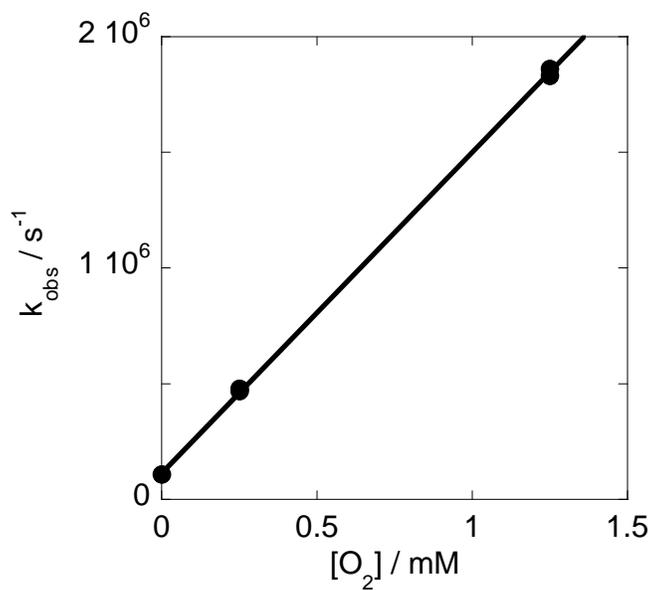


Figure S6. Plot of k_{obs} vs. $[\text{O}_2]$ for the quenching of ${}^3\text{BPyO}^*$ with O_2 in water. $[\text{BPyO}] = 50 \mu\text{M}$

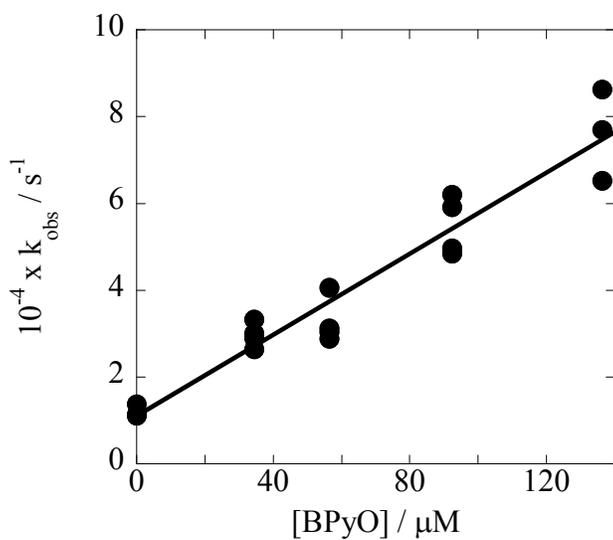


Figure S7. Plot of k_{obs} vs $[\text{BPyO}]$ for the reaction with UO_2^{2+*} . $\lambda_{\text{exc}} 490 \text{ nm}$, $\lambda_{\text{mon}} 495 \text{ nm}$ (emission). $[\text{UO}_2^{2+}] = 3.0 \text{ mM}$.

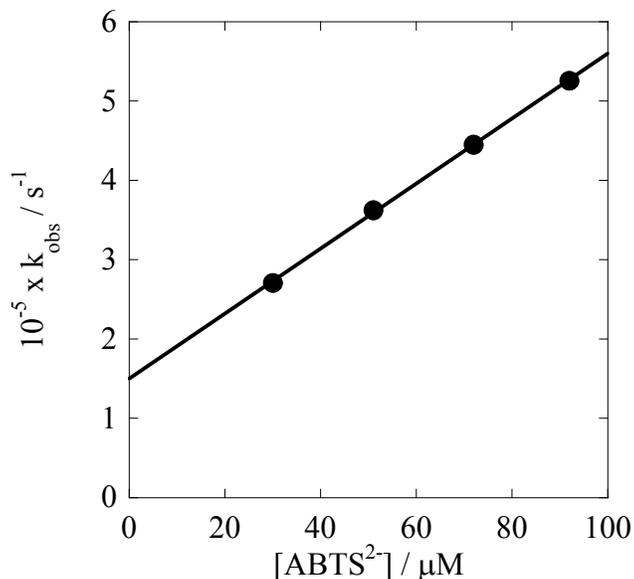


Figure S8. Plot of k_{obs} vs $[\text{ABTS}^{2-}]$ for the reaction with ${}^3\text{BPyO}^*$ in air-free aqueous solutions containing 40 μM BPyO and 30 - 93 μM ABTS^{2-} . λ_{mon} 417 nm ($\epsilon = 34,700 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{ABTS}^{\bullet-}$).

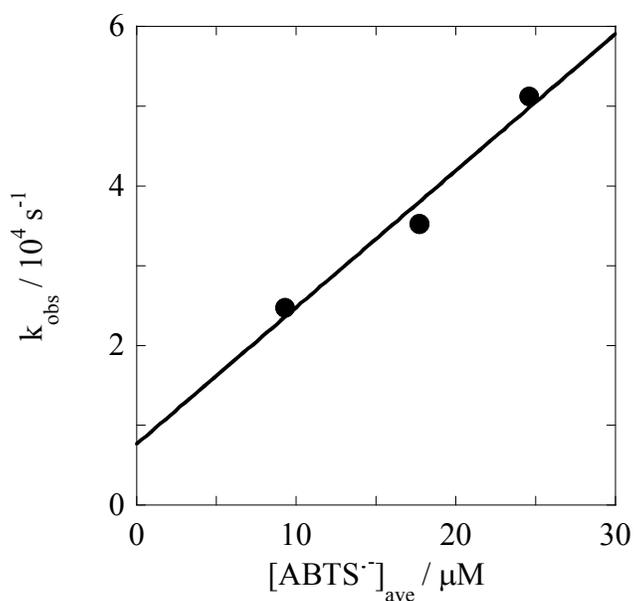


Figure S9. Plot k_{obs} vs $[\text{ABTS}^{\bullet-}]$ for the back reaction with $\text{BPyO}^{\bullet-}$. Conditions: 40 μM BPyO, 50 μM ABTS^{2-} , 7 - 21 μM $\text{ABTS}^{\bullet-}$. λ_{mon} 417 nm. $[\text{ABTS}^{\bullet-}]_{\text{ave}} = [\text{ABTS}^{\bullet-}]_0 + 0.5 \Delta[{}^3\text{BPyO}^*]$; $\Delta[{}^3\text{BPyO}^*] \sim 5 \mu\text{M}$ per laser shot.

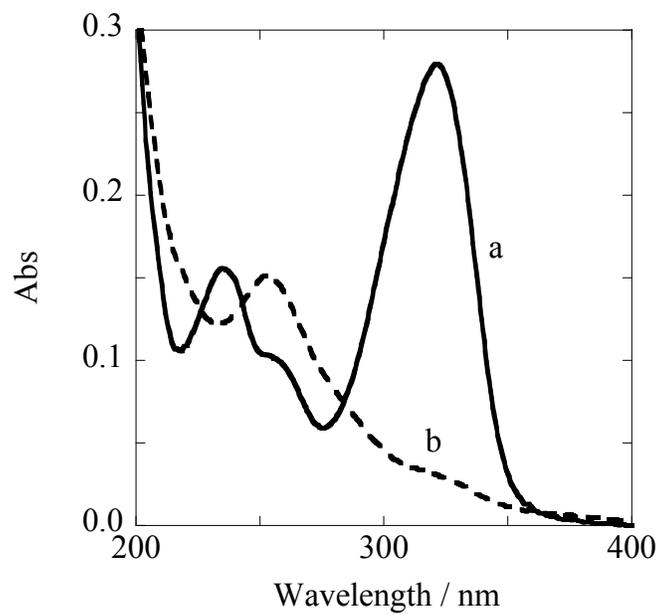


Figure S10. UV-vis spectra (1 mm cell) before (a) and after (b) irradiation at 313 nm of 0.13 mM BPyO in an air-free acetonitrile solution.

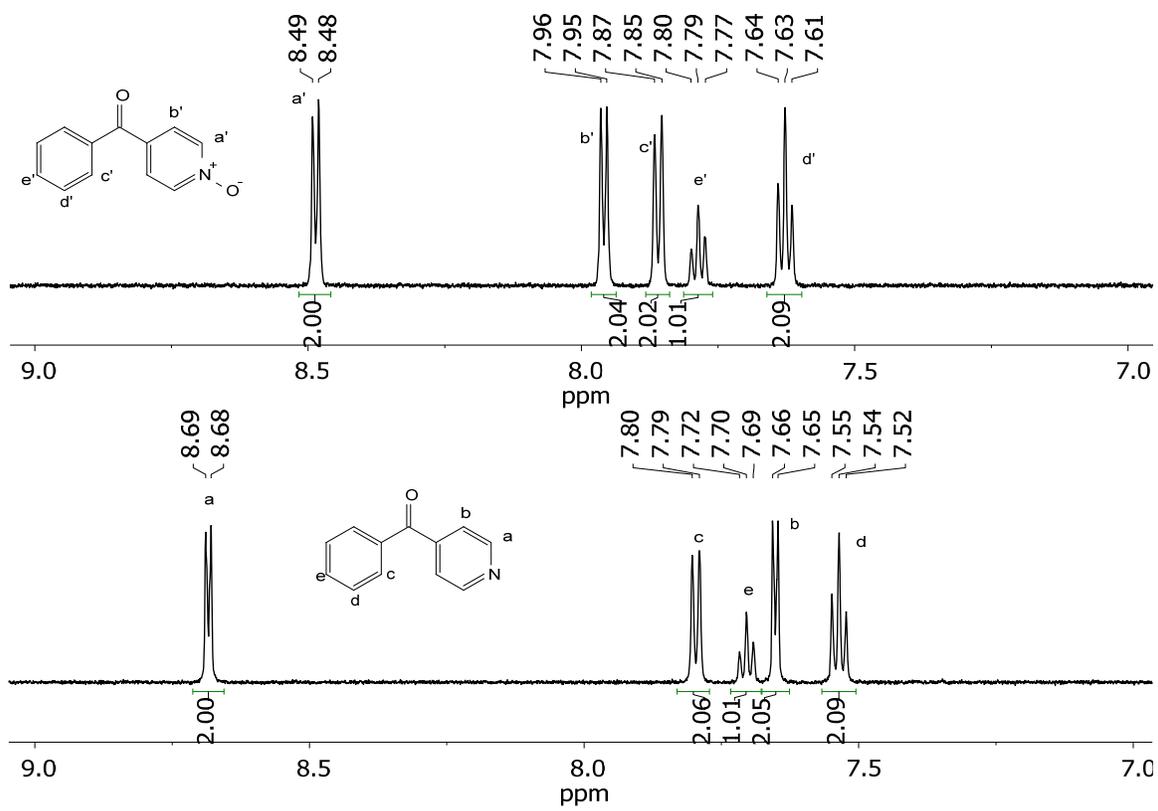


Figure S11. ^1H NMR (600 MHz) of BPyO (top) and BPy (bottom) in D_2O

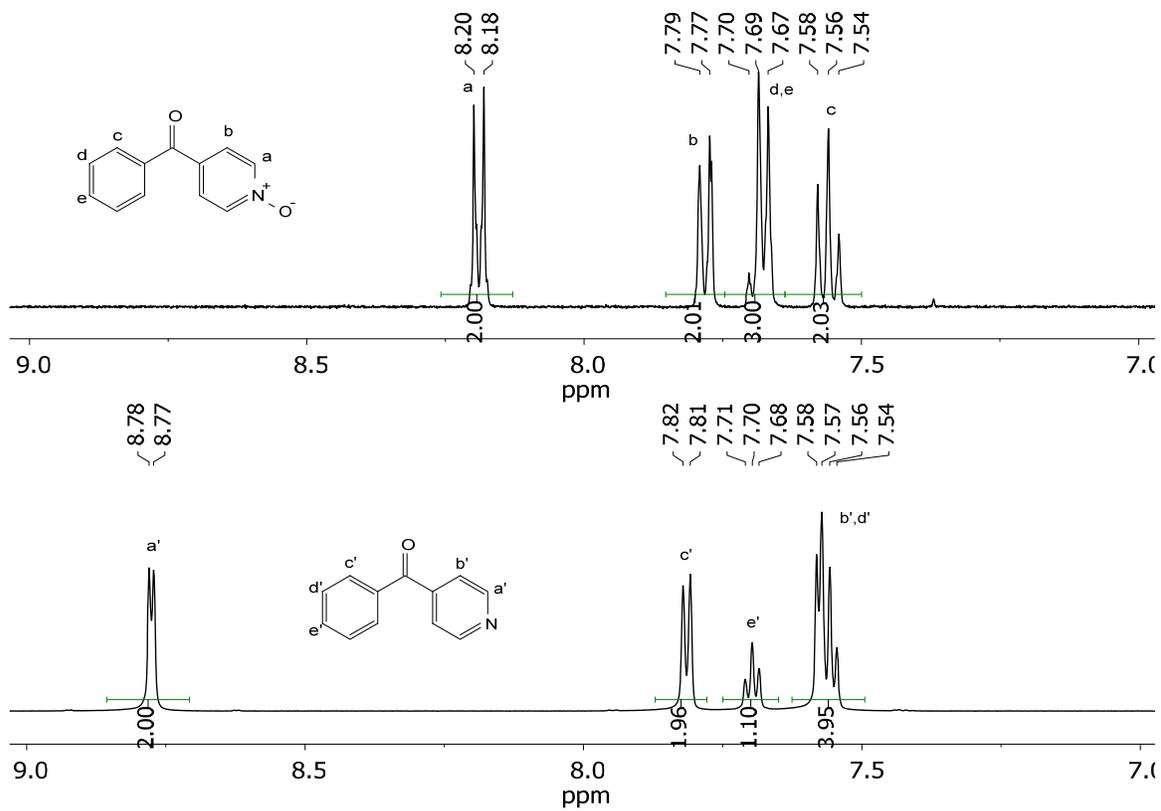


Figure S12. ^1H NMR of BPyO (top) and BPy (bottom) in CD_3CN

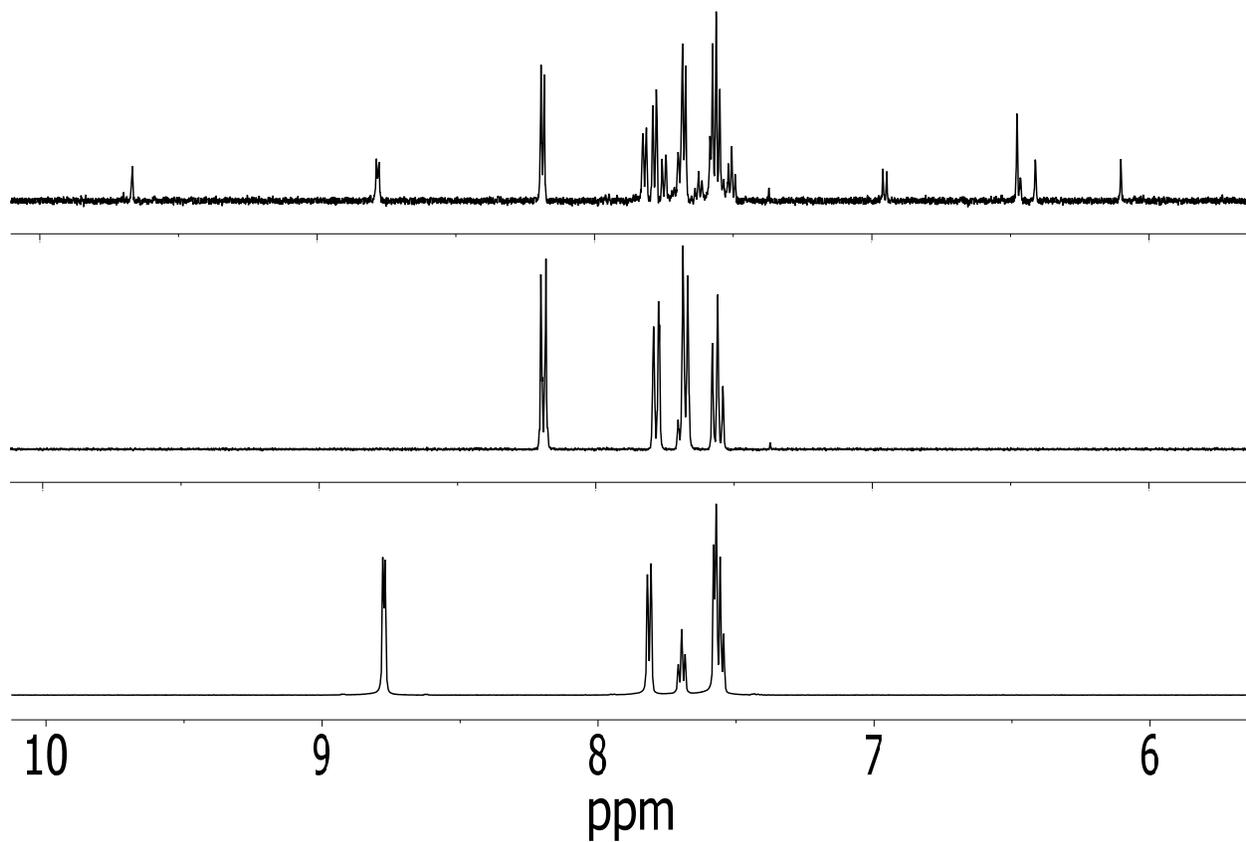


Figure S13. Top: ¹H NMR spectrum of products obtained by photolysis of 2 mM BPyO (65% completion) in CD₃CN. Middle: genuine BPyO. Bottom: genuine BPy.

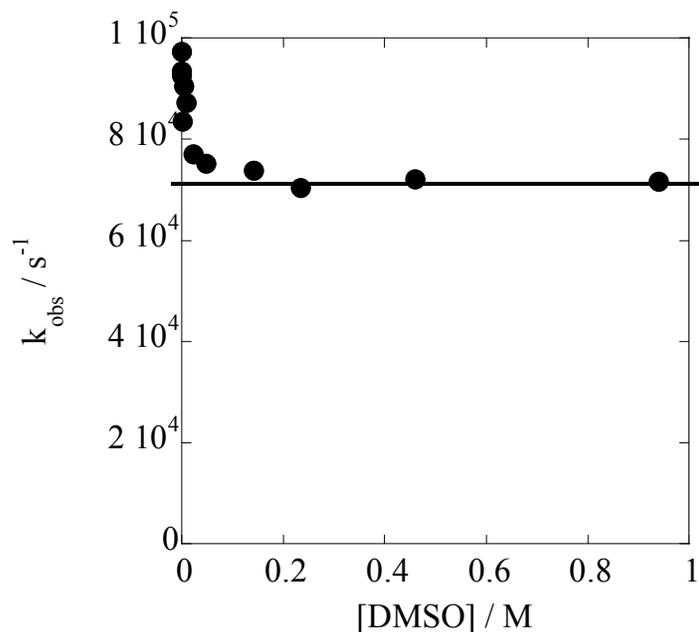


Figure S14. Plot of k_{obs} vs [DMSO] for the reaction with ${}^3\text{BPyO}^*$ in air-free aqueous solutions.

[BPyO] = 45 μM .

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