

Photosensitization of Naphthols by $\text{Ru}(\text{bpy})_3^{2+}$

Photoacids are compounds that become more acidic when they enter an excited state after exposure to light. The applications of these compounds are limited by the short lifetimes of these excited states. In photochemical schemes, the triplet state, an energetic state in which an excited state electron flips its spin, has a longer excited lifetime as the spin flip prevents its immediate return to the ground state. Photosensitization has been a useful strategy to prepare excited molecules in the triplet state. For my Honors project, I explored using photosensitizers to initiate excited state chemistry. Specifically, I investigated the use of tris(bipyridine)ruthenium(III) ($\text{Ru}(\text{bpy})_3^{2+}$) to photosensitize the model photoacid 2-naphthol (2OH) and investigate whether naphthol undergoes photoinduced electron transfer. This photochemical strategy can then be extended to photosensitizers that induce triplet formation. I used the LP980 transient absorption spectrometer from Edinburgh Instruments to determine that $\text{Ru}(\text{bpy})_3^{2+}$ was likely oxidizing the naphthol anion, as evidenced by the formation of a transient absorption feature around 500 nm, shown in Figure 1. This spectral feature is consistent with a study by Sreekanth et al. in which pulse radiolysis was used to oxidize 2OH.¹ The ability of excited-state $\text{Ru}(\text{bpy})_3^{2+}$ to oxidize 2OH raised the possibility of using this reaction mechanism to induce proton coupled electron transfer (PCET), one of the key reaction mechanisms in artificial photosynthetic platforms.²

This summer, I investigated the photooxidation of diprotic photoacid, 8-amino-2-naphthol (8N2OH). The protonation state of the hydroxyl group on 2OH was crucial in the photooxidation mechanism by $\text{Ru}(\text{bpy})_3^{2+}$. With its two protonation sites, I hypothesized that 8N2OH might more effectively quench $\text{Ru}(\text{bpy})_3^{2+}$, and form reaction intermediates of interest. The transient absorption spectrum of anionic 8N2OH is shown in Figure 2. Quenching of the excited $\text{Ru}(\text{bpy})_3^{2+}$ is observed. While the 500 nm absorption feature seen with 2OH is not readily apparent, a new spectral feature appears at 515 nm, The wavelength decay was fit to a lifetime of 6.1 μs . This lifetime is far longer than that of $\text{Ru}(\text{bpy})_3^{2+}$ and is found at a wavelengths outside its transient absorption spectrum.³ This indicates that a transient reaction species is forming, though it isn't the same intermediate as the reaction between 2OH and $\text{Ru}(\text{bpy})_3^{2+}$. Due to the pH dependence of the quenching observed, it is likely that the hydroxyl group present on 8N2OH is still the site of the oxidation reaction, despite the addition of the amine group.

Future research may seek to identify the identity of this reaction intermediate, or the effect of alternate functional groups on the naphthol species. Through this research, I have developed the necessary skills to direct my own future research. Furthermore, I have gained expertise in lab techniques and skills that will make me a valuable addition to any commercial laboratory. I'm deeply grateful for the opportunity to continue my research this summer and am looking forward to making the best use of the skills I've developed.

- (1) Sreekanth, R.; Prasanthkumar, K. P.; Sunil Paul, M. M.; Aravind, U. K.; Aravindakumar, C. T. Oxidation Reactions of 1- and 2-Naphthols: An Experimental and Theoretical Study. *J. Phys. Chem. A* **2013**, *117* (44), 11261–11270. <https://doi.org/10.1021/jp4081355>.
- (2) Mora, S. J.; Odella, E.; Moore, G. F.; Gust, D.; Moore, T. A.; Moore, A. L. Proton-Coupled Electron Transfer in Artificial Photosynthetic Systems. *Acc. Chem. Res.* **2018**, *51* (2), 445–453. <https://doi.org/10.1021/acs.accounts.7b00491>.
- (3) Müller, P.; Brettel, K. $[\text{Ru}(\text{Bpy})(3)](2+)$ as a Reference in Transient Absorption Spectroscopy: Differential Absorption Coefficients for Formation of the Long-Lived (MLCT)-M-3 Excited State. *Photochem. Photobiol. Sci. Off. J. Eur. Photochem. Assoc. Eur. Soc. Photobiol.* **2012**, *11*, 632–636. <https://doi.org/10.1039/c2pp05333k>.

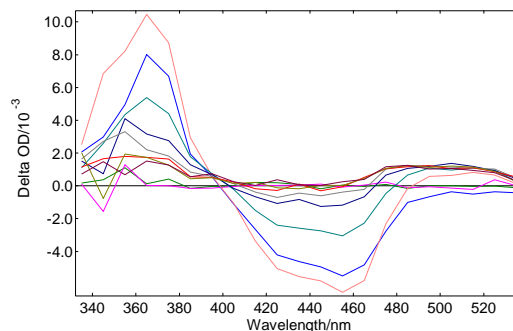


Figure 2: Transient absorption spectrum of 2OH and $\text{Ru}(\text{bpy})_3^{2+}$

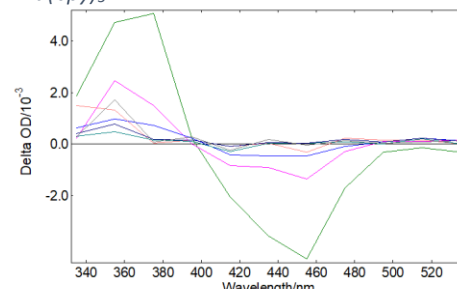


Figure 1: Transient absorption spectrum of 8N2OH and $\text{Ru}(\text{bpy})_3^{2+}$

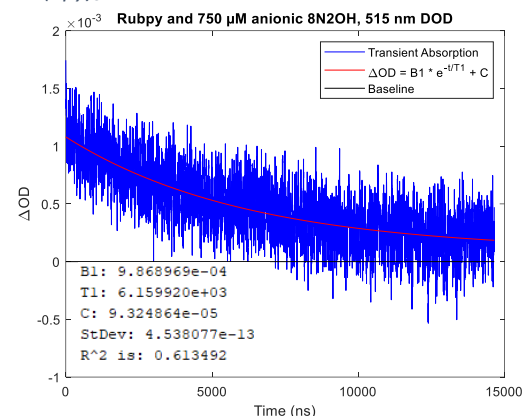


Figure 3: Single wavelength decay of absorption of 8N2OH and $\text{Ru}(\text{bpy})_3^{2+}$ at 515 nm