

Takematsu Lab, Summer 2023:

Exploring Photobasicity and Schiff Base Chemistry with Quinolines

Photobases are compounds that can undergo excited state proton transfer (ESPT). Once irradiated with light (Figure 1), the compounds become more basic, thus abstracting a proton from their surroundings more readily.¹ While, photobases have remained understudied compared to their photoacid counterparts, photobases are equally involved in effectively moving protons within systems such as in hydrogen fuel production.² In order to control and understand the meticulous processes involved in proton movement, the Takematsu Lab is interested in exploring the properties of photobases while also investigating how their structure can affect ESPT mechanisms and introduce photoinduced pathways.

This summer, I studied quinoline, a prototypical photobase, (Figure 1) because it served as a template for structural alterations. I utilized ultraviolet-visible light spectroscopy to characterize the protonation states of quinoline in the ground state. I then utilized steady-state emission spectroscopy to examine distinct protonation states in the excited state (Figure 2B). In the UV-Vis absorption spectra, I identified the presence of a protonated and deprotonated species when altering the pH levels of the solution containing the quinoline. However, only the protonated species was observed in the steady-state fluorescence emission spectra.

Building on these results, I examined the effect of chemical

functionalization on photobases by replacing the X group on the quinoline template (Fig. 1) with a Schiff base, or carbon-nitrogen double bond (Figure 3). My proposed synthesis used benzaldehyde and 8-aminoquinoline as the reagents to prepare 8BNQ (Figure 3). This chemical addition introduced a potential new photoinduced pathway (C=N isomerization) that may affect the existing ESPT pathway at the quinoline N site. In the future I plan to purify the product and work towards characterizing the compound using similar methods as quinoline.

Figure 3: Schiff base synthesis of the compound, 8BNQ, using benzaldehyde and 8-aminoquinoline. Reactants were refluxed in an equimolar amount in methanol and catalyzed with acetic acid.

Through this experience I have enhanced my practical laboratory skills, including spectroscopy, chemical synthesis, and most importantly, collaboration in the sciences. I plan to further study excited state pathways and apply this experience towards future laboratory work as well as my future honors project.

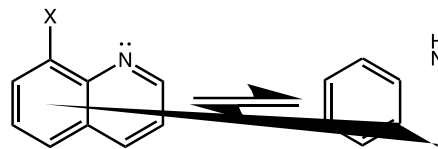


Figure 1: Quinoline with a substituent group, X, on the 8th carbon, irradiated with light. Afterwards, compound reaches excited state and becomes protonated. Experimentation with X group included, NH₂ and Schiff base N=C-R.

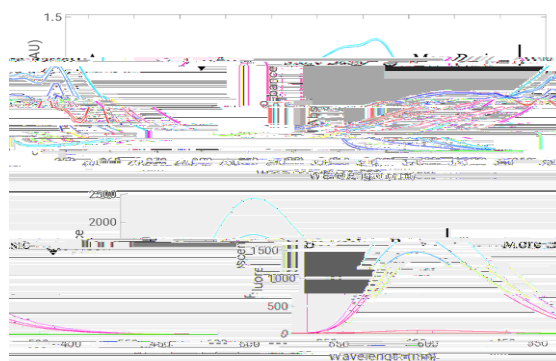


Figure 2: (A) UV-vis spectra of quinoline in water at pH levels ranging from 2 – 11 . (B) Steady state fluorescence of quinoline in aqueous solution ranging in 2-11 pH levels.

¹Almudun, Petit, et al. JPC A 2020, 2537-2546

² Fang, Stolarczyk, et al. Nat Commun. 2020, 11: 5179