Characterizing Proton Transfer in Aminonaphthol Models
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Introduction

Proton transfer (PT) is a fundamental chemical process that plays an important role in biological mechanisms as varied as the electron transport chain or firefly bioluminescence (Figure 1)[1]. Environment, including placement of transfer partners, degree of solvation, or local pH, impacts the mechanics of proton transfer. Because biological systems are typically complex, it is important to isolate conditions of interest, such as the presence of multiple functional groups, the spacing of those groups, and how pH affects the state of those groups. This can be done by creating models that simplify and isolate specific components of the environment, allowing us to determine their effects on the mechanisms of PT.

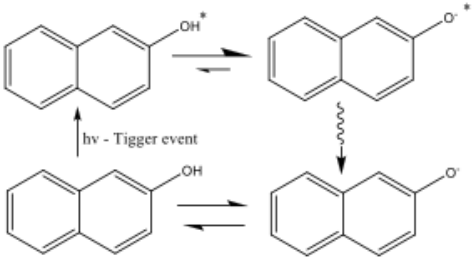

Figure 1. 2-Naphthol undergoing excitation and PT events. 2-Naphthol is a simple and well-studied model for PT.

The Takematsu lab focuses on 2-Naphthol (Figure 2), and aminonaphthols as model molecules for the study of proton transfer. Aminonapthols are similar in structure to naphthols, but with an added amine functional group that allows us to better model biological systems that have both nitrogen and oxygen proton binding sites. Specifically, we will be working with the structural isomers 5-amino-2-naphthol (3N2OH), 7-amino-2-naphthol (7N2OH), and 8-amino-2-naphthol (8N2OH) in order to probe the distal and electronic effects of functional group position around the ring.

Summer Goals and Accomplishments

The goals for this summer were to fully characterize the behavior 5-amino-2-naphthol and 8-amino-2-naphthol in bulk water. Work on 8-amino-2-naphthol had already been started by previous Takematsu lab member, Malcolm Groves and work on this molecule demonstrated reproducibility. Full characterization of 5-amino-2-naphthol was also completed, although more work may be done to prove reproducibility. My lab mate, Laura Cotter, began work on 7-amino-2-naphthol in bulk water conditions.

Characterization of the aminonaphthol species required proficiency in absorbance, steady-state emission, and time resolved emission spectroscopy techniques. Over the summer, I gained valuable skills with these machines, as well as proficiency in Matlab and DAS6 software, which allowed me to quantify, graph, and analyze the data. Using these techniques, we were able to demonstrate that the addition of the amine group did not have a major impact on ground state behavior of the molecule, but did impact its excited state behavior. Additionally, we were able to demonstrate that the 5-amino-2-naphthol and 8-amino-2-naphthol species demonstrate similar excited state behavior, suggesting that their electron distributions are similar when excited.

Future Directions

Because we wish to understand the use of aminonaphthols as environmental probes, next steps would include analyzing the PT mechanisms of all the species in different environments, such as water / methanol solutions or the non-bulk water conditions that would be created if the molecule were to form a complex with a protein model. Additionally, in order to better understand the molecule as a probe, we may begin to explore how changing the amine group to other functional groups impacts the electron density, and thus the proton affinity, of our naphthol derivative models.

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1. Pinto da Silva, L. and J.C.G. Esteves da Silva, *Chemiexcitation Induced Proton Transfer: Enolate Oxyluciferin as the Firefly Bioluminophore.* The Journal of Physical Chemistry B, 2015. **119**(6): p. 2140-2148.