## Takematsu Lab, Summer 2023:

Development of a Schiff base Synthetic Platform for 8-phenyliminonaphthol Photoacids

Photoacids, compounds that undergo excited state proton transfer (ESPT), are used to spatially and temporally control pH for several chemical and biological processes, such as acid-catalyzed polymerization and acid-initiated protein folding (Figure

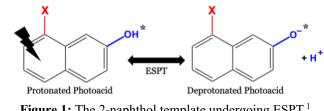


Figure 1: The 2-naphthol template undergoing ESPT.<sup>1</sup>

1).<sup>1,2</sup> The Takematsu group is interested in developing a synthetic platform that allows for the systematic investigation of structural impacts on the ESPT mechanism and energetics of photoacid candidates. Naphthols, such as 2-naphthol, are a well-studied class of photoacids (Figure 1). Perturbations, namely adding a functional group "X", to the naphthol structure can enhance or inhibit photoacidity, create new ESPT pathways, and/or introduce competing excited state pathways. In this work, Schiff base chemistry was utilized to develop a photoacid library using naphthols as templates (Figure 2A). The addition of a Schiff base, or carbon nitrogen double bond, may introduce photoisomerization, another excited state pathway, which may affect the ability of the photoacid to undergo ESPT.<sup>3</sup>

From my honors research, a library of Schiff base photoacid candidates was established

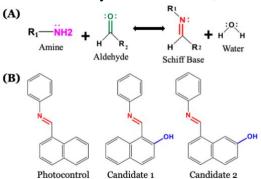


Figure 2: (A) A general Schiff base synthesis.<sup>2</sup> (B) A sub-set of the Takematsu Schiff base photoacid library.

(Figure 2B). Candidate 1 was previously synthesized by the Zeigler group. Nuclear magnetic resonance (NMR) spectroscopy was used to characterize the Photocontrol and Candidate 2 after synthesis. The purity of the products was determined using NMR and steady state fluorescence spectroscopy. Candidate 1 and the Photocontrol were found to be pure (>98%), but Candidate 2 was crude. A purification strategy was implemented but was unsuccessful in completely removing unreacted amine and aldehvde starting products. I then utilized ultraviolet-visible absorption to study the two photoacid candidates in the ground state, and their stability in various solvents (Figure 3).

The project successfully demonstrated that a library of candidates could be prepared

using Schiff base photochemistry. Moving forward, time-resolved absorption and emission spectroscopy will be implemented to study the excited state pathways of these candidates. The Schiff base synthetic platform will also be utilized to synthesize new photoacid and photobase candidates. Conducting postbaccalaureate research allowed me to advance my honors research and gain experience mentoring undergraduate students in lab. The skills I developed this summer will be beneficial as I begin my PhD program at the University of Pennsylvania next year.

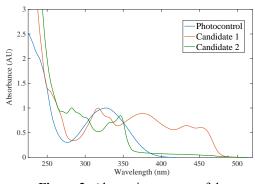


Figure 3: Absorption spectra of the photocontrol and both target candidates in

Citations: (1) Agmon, Noam. J PhyChem A 2005 109, no. 1: 13–35. (2) Sambath, Karthik, et al. Org Let 2020 22 3, 1208-1212 (3) G.Y. Nagesh. J of Molec Struc, 2015, Volume 1085.