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Photoacidic properties of 8-amino-2-naphthol in imidazolium salts

Photoacids are molecules that become more acidic upon excitation and undergo excited-state proton transfer (ESPT).^{1,2} They have been used in various material and chemical applications due to their ability to spatially and temporally control pH.³⁻⁵ The enhanced acidity of photoacids has been attributed to intramolecular charge redistribution in the excited state. Subsequently, the photoacidity can be enhanced or reduced based on the solvent's ability to stabilize the charge redistribution.^{1,6} The ESPT mechanism is also solvent-dependent, as in intermolecular ESPT, the solvent acts as a proton acceptor (Figure 1). 8-amino-2-naphthol (8N2OH) is a diprotic photoacid that has been shown to undergo different ESPT pathways at either the NH₃⁺ or OH site, depending on the solvent environment. Considering that charge redistribution is integral in the ESPT mechanism, introducing a charged solvent, such as ionic liquids (IL), could further impact the ESPT mechanism. We employed a variety of spectroscopic techniques including steady-state and time-resolved absorption and emission spectroscopy, to examine the effect of a family of ILs, imidazolium salts (Figure 2), on the ESPT mechanism of 8N2OH.

Glycerol was used as a non-charged solvent to develop a protocol for preparing solutions in highly viscous solvents, such as ILs. Studies of 8N2OH in glycerol-water mixtures revealed site-specific ESPT as cationic 8N2OH only underwent ESPT at the OH site. The structural dependence of the IL on the photochemistry of 8N2OH was examined using the following cation,

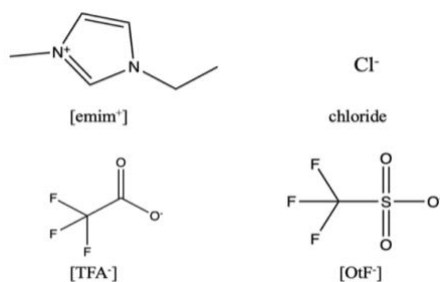


Figure 2. Proposed ions for ionic liquids; [emim⁺], [Cl⁻], [TFA⁻], and [OTf⁻].

complex between the photoacid and anion.

Further controls for water contamination were conducted. It was found that small amounts of water had no impact on excited-state pathways of any of the target photoacids in [emim⁺][TFA⁻]. It was only after adding significant amounts of water that changes in emission were observed (Figure 3). Future work needs to be conducted regarding water/IL mixtures, other IL anions and cations, and other target photoacids.

This summer allowed me the space and resources to explore my academic interests as well as prepare for graduate programs. Similarly, being a mentor taught me numerous lessons and has been an invaluable experience for me.

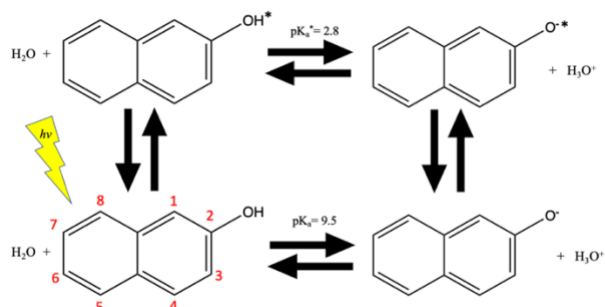


Figure 1. ESPT process of the photoacid 2-naphthol (2OH) in water. There is only one protic site on 2OH. Thus, upon excitation, 2OH can either relax back to the ground state or deprotonate. The carbons of 2OH in the ground state is numbered according to naming conventions.

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Studies of 8N2OH in glycerol-water mixtures revealed site-specific ESPT as cationic 8N2OH only underwent ESPT at the OH site. The structural dependence of the IL on the photochemistry of 8N2OH was examined using the following cation, 1-ethyl-3-methylimidazolium [emim⁺], and varying anions combinations: Cl⁻, trifluoroacetate ([TFA⁻]), and trifluoromethanesulfonate ([OTf⁻]). The anionic structure greatly impacted both the ground and excited-state chemistries of 8N2OH and control photoacids 2-naphthol (2OH) and 1-naphthylamine (1N). The effect of the anion on the ground state chemistry was surprising as previous research had only reported effects in the excited state. The spectral evidence also supported formation of an excited-state

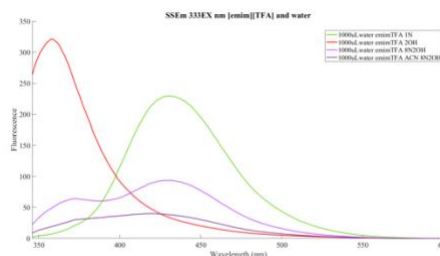


Figure 1. Steady-state emission spectra of target photoacids in IL/water mixtures after 25% water by volume was added. A second emission peak at 430 nm for 8N2OH was observed.

- (1) Agmon, N. *J. Phys. Chem. A* **2005**. (2) Tolbert, L. M.; Haubrich, J. E. *J. Am. Chem. Soc.* **1994**. (3) Zhou, P.; Han, K. *Acc. Chem. Res.* **2018**. (4) Amdursky, N. et al. *J. Phys. Chem. B* **2014**. (5) Li, J. et al. *J. Phys. Chem. O* **2018**. (6) Groves, M. S.; Nelson, K. J.; Nelson, R. C.; Takematsu, K. *Phys. Chem. Chem. Phys.* **2018**.