

Probing proton transfer in imidazolium based ionic liquids with a cyano-naphthol super photoacid

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Proton transfer (PT) from acids to proton acceptors is a fundamental step in biological and chemical pathways. Proton transfer is influenced by its solvent environment,¹ and novel solvents have the potential to tune PT for desired applications. It is difficult to study PT from traditional acids because their PT equilibrium is quickly reached and maintained. Photoacids are a model to study PT dynamics since their PT can be temporally controlled. When a photoacid is excited by light, it becomes more acidic, enabling excited state proton transfer (ESPT) before relaxing back to its ground state (Fig. 1).¹ I probed the occurrence and kinetics of ESPT from two photoacids, 2-naphthol (2OH) and the “superphotoacid” 6-cyano-2-naphthol (6C2OH) (Fig. 1) in a range of solvents, using absorption spectroscopy, steady-state fluorescence spectroscopy, and time-correlated single-photon counting.

In an independent study, I had studied the ESPT of 2OH in water. To extend the study of PT to less polar solvents, we selected 6C2OH since cyano-substituted naphthols, termed “superphotoacids,” are known to be more photoacidic than 2OH and undergo ESPT in methanol.² I determined that 6C2OH not only undergoes ESPT in methanol but also in acetonitrile and dimethylsulfoxide. I also found that in water, the 6C2OH excited state species relaxes back to the ground state more quickly than 2OH.

This summer, I extended my solvent study to imidazolium-based ionic liquids (ILs). ILs have generated research interest for potential applications from chemical synthesis to battery electrolytes.^{3,4} PT in ILs is not yet well understood.⁵

In just three ILs (Fig. 2), all with the same cation, 1-ethyl-3-methylimidazolium ([emim⁺]), but different anions, 6C2OH showed divergent and unexpected behavior. In [emim⁺] trifluoromethanesulfonate, 6C2OH underwent ESPT fitting the same two-state model seen in methanol, water, and acetonitrile. In [emim⁺] trifluoroacetate, however, 6C2OH ESPT does not fit the two-state model because there is fluorescence from three excited state decay pathways. Published findings on another cyano-substituted naphthol in the same IL found similar evidence of three excited state species.⁵ Further control experiments will be needed to identify whether this third species is a complex with the solvent anion, an exciplex, or a new transient species. My most unexpected findings were in [emim⁺] tetrafluoroborate. Absorption spectra indicate that both 2OH and 6C2OH form a third species in the *ground* state (i.e. before excitation). Thus, to investigate this third species, future work could use control IL anions and additives to attempt replication of this species. This project and its presentation have honed my organization and communication skills, preparing me for future courses and lab work in biochemistry.

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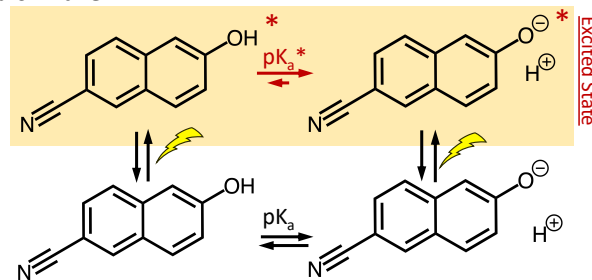


Figure 1. The two-state ESPT scheme of the photoacid 6C2OH is more acidic in its excited state ($pK_a^* = -0.4$) than in its ground state ($pK_a = 8.4$).¹ The excited state is denoted by “*”. Unsubstituted 2-naphthol has the same two-state ESPT scheme but is less acidic in its excited state ($pK_a^* = 2.8$).

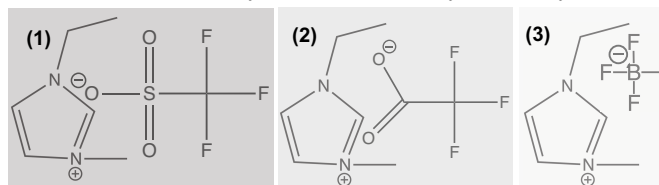


Figure 2. The three ionic liquids share the same cation, 1-ethyl-3-methylimidazolium, but have different anions: (1) trifluoromethanesulfonate, (2) trifluoroacetate, (3) tetrafluoroborate