

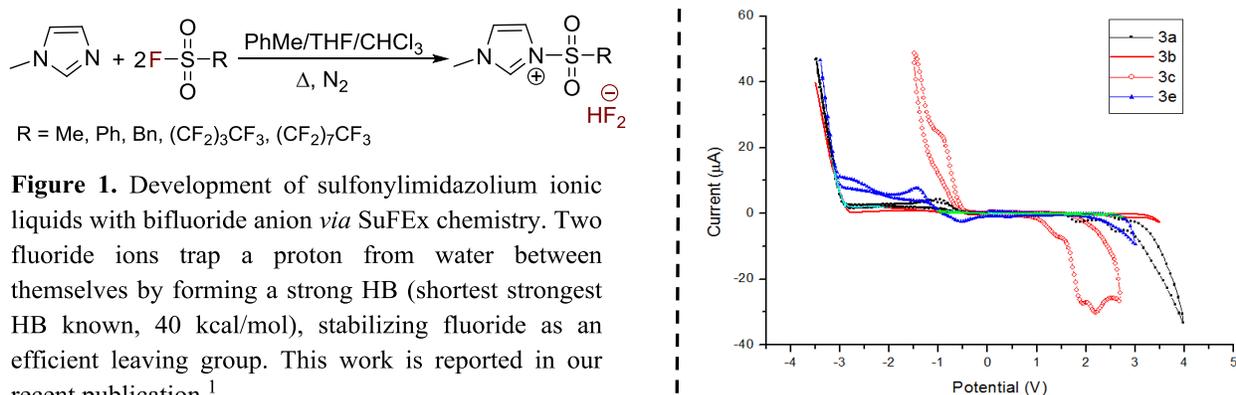
# Click synthesis and physicochemical characterization of amphiphile ionic liquids with enhanced fluidity and diverse functionalities

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Ionic liquids are a class of cutting-edge organic materials, which have become a rapidly growing area in for both fundamental and applied research fields. The synthesis/functionalization of ionic liquids is complicated process because the majority of ionic liquids are amorphous and have close to zero vapor pressure, making crystallization and distillation the ineffective processes for their purification.

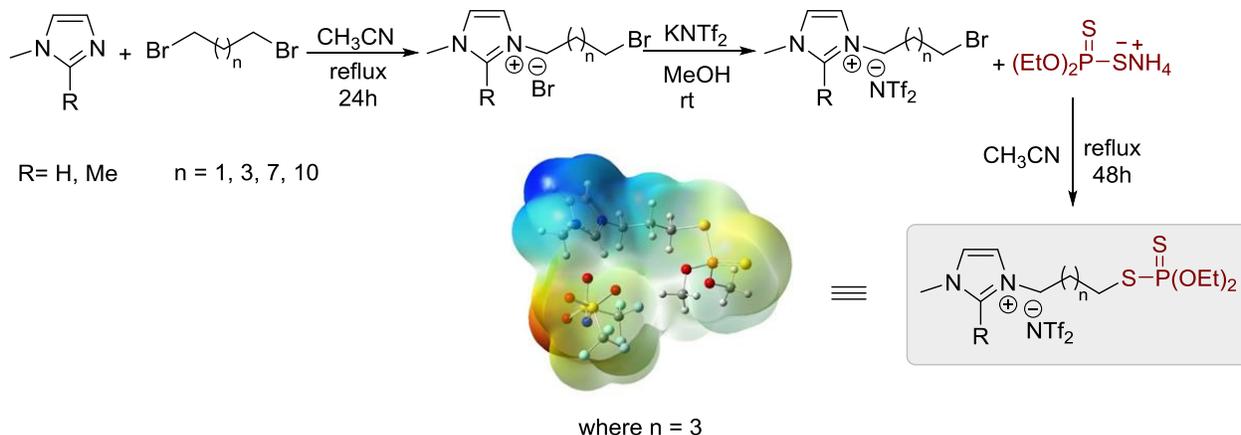
During the first year of this grant, our group sought to create these salts *via* high-yielding, simple covalent chemistry and accurate planning to minimize the formation of undesired by-products. In particular, we exploited the sulfur(VI) fluoride exchange (SuFEx) click reaction for the autocatalytic and HF-free development of a structurally varied sulfonylimidazolium bifluoride ionic liquids.<sup>1</sup> We studied their empirical structure-property relationships by measuring their phase transition behaviors sand decomposition temperatures, and electrochemical stability via DSC, TGA and CV, respectively. The ionic liquid products with alkyl, aryl and perfluoroalkyl side chains exhibited high electrochemical stability – i.e., between 5.5 V – 6.0 V. The synthetic strategy along with their electrochemical windows are outlined Figure 1.



**Figure 1.** Development of sulfonylimidazolium ionic liquids with bifluoride anion *via* SuFEx chemistry. Two fluoride ions trap a proton from water between themselves by forming a strong HB (shortest strongest HB known, 40 kcal/mol), stabilizing fluoride as an efficient leaving group. This work is reported in our recent publication.<sup>1</sup>

Additionally, a simple and efficient synthetic strategy was exploited to synthesize twelve novel *O,O'*-diethyl phosphorodithioate-functionalized ionic liquids (Scheme 1)<sup>2</sup>. The (EtO)<sub>2</sub>P(=S)S functionality was incorporated to the structures of the cations, providing the flexibility to incorporate long linkers and task-specific anion to enhance hydrophobicity. Each ionic liquid contains alkyl linkers (C<sub>3</sub>-C<sub>12</sub>) between the various cations (i.e. imidazolium, ammonium, and phosphonium) and the functional moiety *O,O'*-diethyl phosphorodithioate, paired with bis[(trifluoromethylsulfonyl) imide] ([NTf<sub>2</sub>)<sup>-</sup>] anion. These functionalized ILs, of varying cationic nature, were synthesized, for extracting precious metals from aqueous solution. An objective in this study is testing the complexation process of those ionic liquids towards the Pd(II)

element from  $0.10 \text{ mol dm}^{-3}$  HCl. Tested by  $^{31}\text{P}$  NMR spectroscopy, it was noted that elongation of the carbon chain lengths between the imidazolium cation and the phosphorodithioate functional group dramatically increases the binding ability of the ionic liquids with Pd(II).



**Scheme 1.** Synthesis of *O,O'*-diethyl phosphorodithioate-bearing hydrophobic imidazolium-based ionic liquids as media for Pd extraction and the electrostatic potential energy map of the ionic liquid where n = 3, reported in our publication.<sup>2</sup>

We also carried out computational studies in the electronic structure and vibrations of a methimazolium-based ionic liquids with the  $[\text{NTf}_2]^-$  anion *via* the DFT and IR spectroscopy to gain insight into conformation equilibria in the bulk phase [3]. Infrared spectroscopy coupled with computational simulations is a powerful tool to characterize the interactions and conformational equilibria in these ionic liquids.

In summary, during the first year of this project, we synthesized several structurally-diverse *S*-centered cations, paired with  $[\text{NTf}_2]^-$  as a known highly hydrophobic anion, which have reduced melting points. Furthermore, their physicochemical properties were studied to develop new soft materials for specific tasks. Finally, we note that thanks to the results generated as a consequence of ACS-PRF funding, we have published three papers (*vide infra*) and applied for a NSF-RUI grant.

## References (undergraduate co-authors are underlined)

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- [3] N. R. Dhumal, A. Mirjafari, H. J. Kim, Deconvolution of conformational equilibria in methimazolium-based ionic liquid ion pair: Infrared spectroscopic and computational study. *J. Mol. Liq.* **2018**, 266, 194-202.