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Synthesis and Characterization of a New Family of Solvate Ionic Liquids
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Project Overview

The principle goal of this research project is to synthesize a new family of solvate ionic liquids (SILs) that are based on molecular solvents containing ether oxygen atoms and tertiary amines. Specific objectives include,

- Synthesizing the new molecular solvents and verifying products.
- Screening the molecular solvents in terms of their ability to produce SILs.
- Characterizing the spectroscopic, thermal, and transport properties of the new SILs.

Our first year of the project saw the synthesis of four molecular solvents as well as initial characterization. The second year of this grant has proven to be exceptionally productive as the PIs have continued to make progress towards our original research goals.

Accomplishments Achieved

A total of eight molecular solvents from our original proposal were examined during the first year of the project. Of these, three were commercially available and the remaining five were synthesized in-house. All of the compounds in our proposed plan of study are oligomers of ethylene oxide and/or tertiary amines. The IUPAC names for many of these compounds are rather long and cumbersome. For the sake of brevity, we refer to the compounds according to the sequence of oxygen and nitrogen present in the molecule. Therefore, OOOO represents triethylene glycol dimethyl ether, while OOOON is 1-[2-(*N*,*N*-dimethylamino-2-ethoxy)ethyl]-2-[2-(2-methoxyethoxy)ethyl]ether. Our overall progress to create lithium-based SILs is summarized in the following table.

				Spectroscopic Characterization		Thermal Analysis	Transport Properties
Compound	**Source**	**SIL Screening[a]**		**FT-IR**	**FT-Raman**		
OOOO	Commercial	LiOTf	Forms SIL	Complete	Complete	Complete	Complete
		LiTFSI	Forms SIL	Complete	Complete	Complete	Complete
		$LiPF_6$	Stability Issues	N/A	N/A	N/A	N/A
OOON	Synthesized[b]	LiOTf	Forms SIL	In Progress	In Progress	In Progress	In Progress
		LiTFSI	Forms SIL	In Progress	In Progress	In Progress	In Progress
NOON	Synthesized	LiOTf	Forms crystal	Complete	Complete	Complete	Complete
		LiTFSI	Forms SIL	Complete	Complete	Complete	Complete
NNNN	Commercial	LiOTf	Forms crystal	In Progress	In Progress	In Progress	In Progress
		LiTFSI	No SILto date	N/A	N/A	N/A	N/A
OOOOO	Commercial	LiOTf	Forms SIL	Complete	Complete	Complete	Complete
		LiTFSI	Forms SIL	Complete	Complete	Complete	Complete
OOOON	Synthesized[b]	LiOTf	In Progress	In Progress	In Progress	In Progress	In Progress
		LiTFSI	In Progress	In Progress	In Progress	In Progress	In Progress
NOOON	Synthesized	LiOTf	Forms crystal	Complete	Complete	Complete	Complete
		LiTFSI	Form SIL	Complete	Complete	Complete	Complete
NNNNN	Synthesized	LiOTf	No SIL to date	N/A	N/A	N/A	N/A
		LiTFSI	Forms SIL	Complete	Complete	Complete	Complete

[a]LiOTf and LiTFSI are abbreviations for lithium trifluoromethanesulfonate and lithium bis(trifluoromethylsulfonyl) imide, respectively.
[b]Additional analysis is warranted to conclusively demonstrate the target product is realized.

As indicated in the table, we have completed the synthesis and characterization for most of the compounds studied. In general, solvents with greater amounts of nitrogen (e.g., NNNN or NNNNN) produce higher viscosities and lower ionic conductivities than OOOO and OOOOO. However, this portion of the experiment is on-going, and it should be

remembered that the remaining solvent systems need to be studied before drawing conclusions on the relationship between solvent molecular structure and SIL properties.

Single crystals of LiOTf complexed with NNNN, NOON, and NOOON were isolated and submitted to the Chemical Crystallography Laboratory at the University of Oklahoma for structural analysis. The Li^+ ions occupy four-fold coordination sites in all of the crystals. The OTf^- anions form $Li^+\cdots OTf^-$ ion pairs in (NNNN)LiOTf and $[Li_2OTf]^+$ aggregates in (NOON)$(LiOTf)_2$ and (NOOON)$(LiOTf)_2$. The crystallographic results will prove invaluable in interpreting our spectroscopic data on these systems.

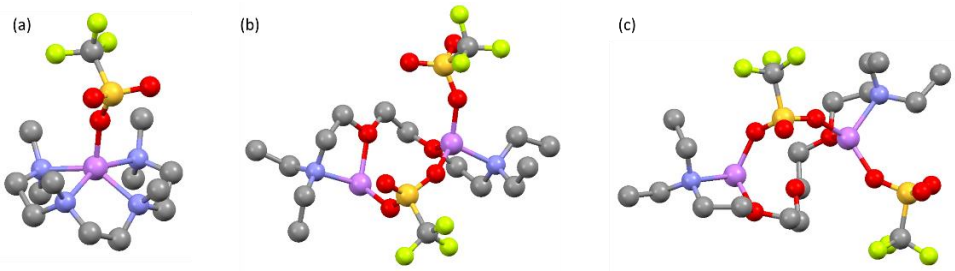

Figure 1. Asymmetric units for (a) (NNNN)LiOTf, (b) (NOON)$(LiOTf)_2$, and (c) (NOOON)$(LiOTf)_2$ unit cells. Hydrogen atoms excluded for clarity.

Non-methylate analogues to OOOO, OOOOO, NNNN, and NNNNN were added to the project in our first year. Since these solvents contain O-H and N-H moieties, any resulting SILs will be able to interact via hydrogen bonding interactions. We have completed the synthesis and characterization of LiTf- and LiTFSI-based SILs from these materials, and a manuscript describing our findings is currently being drafted.

We attempted to create Ag-based SILs by mixing AgTFSI with the NOON and NOOON. Rather than forming SILs, the AgTFSI produced a suspension of Ag. The resulting fluid is immiscible with hexane and 1-hexene. We are currently measuring the efficiency of the Ag particle suspension in extracting hexene from a hexene/hexane mixture.

Challenges and Potential Solutions

The ^{1}H NMR spectra of OOON an OOOON solvents contain incorrect intensity ratios. Thus, we not confident the isolated compounds are the desired products. For this reason, we have changed the characterization status for these materials to “in progress” in the Table. We are currently exploring other characterization and purification techniques that may yield additional insight into the origin of the spurious NMR signals.

Research Outlook for the Second Year

The 2019-20 academic year will be used to further validate the synthesis of the OOON and OOOON compounds. We will also direct efforts toward the synthesis of additional compounds from our original solvent list, starting with ONNO and OONOO. Once synthesized, these molecular solvents will be screened for SIL formation and characterized. The hexene/hexane separation project will be completed and the results analyzed.

Professional Impact on Faculty and Students

This research project has enhanced the professional careers of the faculty and students in several tangible ways. First, we have explored synthetic procedures, established protocols for characterizing the materials, and leveraged the research program to extend our professional network. Students have learned organic synthesis, spectroscopic and thermal characterization, and how to properly handle materials that are air/water sensitive. In addition, they have learned how to trouble shoot difficulties in the laboratory, how to properly analyze experimental results, and how to maintain adequate records when working in a large group. We are especially pleased that one of our 2018-19 undergraduate students joined is now pursuing a M.S. degree at NSU working on this project. Part of our goals with this research project was to create opportunities for our students to pursue graduate studies. It is especially gratifying to see how the support of the ACS PRF grant is helping our students meet this goal.