

SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

SCHOLAR NAME:	Andrew L. Smith
FACULTY ADVISOR:	Brandon Ashfeld
PROJECT PERIOD:	2020-Ongoing
PROJECT TITLE:	Preparation and Analysis of Photoswitchable Ionic Liquids
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Design synthetic method to access target IL framework	Considered four different strategies, one emerged as clearly dominant because of its capacity for synthetic divergence.	100%
Demonstrate viability of designed synthetic method	The dominant synthetic strategy failed to synthesize sterically hindered substrates in practice. A clear work around could not be identified	80%
Synthesize range of target ILs	Preliminary target ILs without structural, chemical diversity were accessed to demonstrate the existence of such an IL.	50%
Characterize target ILs by UV/Vis, NMR, MP	Characterized the above ILs (s.t. MP < 100oC) by UV/Vis, NMR. Showed photoswitchable behavior between two states following 256 nm irradiation.	50%
Identify target ILs with desired LCST/UCST properties	Not yet successful in identifying any ILs with target LCST/UCST behavior.	0%
Demonstrate utility of ILs with desired LCST/UCST property	Not yet successful in identifying any ILs with target LCST/UCST behavior.	0%

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	(Sponsor, Project Title, Pls, Submission Date, Proposal Amount)
EXTERNAL AWARDS RECEIVED	(Sponsor, Project Title, Pls, Award Date, Award Amount)
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	(Event, Presentation Title, Presentation Date, Location)
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	(Purpose, Title, Date Received) Norbert L. Weich Award for Outstanding Junior Chemist, February 2020, The award recognizing the highest research and academic merit of the Junior Class of Chemistry majors at the University of Notre Dame
INTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions)
EXTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions)
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL)
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail)

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

COVID 😞! Had more opportunities been available, it is undeniable that more would have been accomplished.

FINAL WRITTEN REPORT

(Please use the space below to describe your research project and objectives, any findings and results you can share, and graphs, charts, and other visuals to help us understand what you achieved as a result of this research experience.)

Cooling systems are extensively employed in a variety of essential industrial procedures; however, these systems are generally reliant upon energy-inefficient materials, contributing to the process' environmental impact. To improve the design of coolants with an eye towards efficiency, new polymers have been considered, specifically for absorption-cooling systems because of these materials' unique stimuli-responsive absorption of water. One of the most common stimuli-responsive material studied is the set of thermoresponsive polymers, of which some possess upper- or lower-critical solution temperatures (UCST/LCST), whereby they separate into immiscible biphasic mixtures upon raising or lowering the temperature of solution. In addition to polymers, some ionic liquids (ILs) have also displayed similar thermoresponsive properties. Furthermore, the structure of ILs has been demonstrated to greatly influence their observed UCST or LCST. Recently, it has been demonstrated that two ILs generated from the *cis* and *trans* isomers of betenedioate and the tetrabutylphosphonium cation exhibited contrasting UCST and LCST properties, respectively. It follows that control of the structural isomer comprising the IL imparts significant control on its thermoresponsive properties.

The *azo* functionality, characterized by the R-N=N-R' chemical bond, is a well-established photoswitchable chemical functionality, whereby irradiation of certain wavelengths can engender the *azo*-containing species to flip between its *cis* and *trans* isomers. Thus, we suggest that the incorporation of the *azo* functionality into an IL species could render an IL photoswitchable. Upon identification of a UCST or LCST-demonstrating photoswitchable IL (PSIL), it follows that its opposite photostable state, either *cis* or *trans* isomer, could possess contrasting critical solution behavior, much akin to the aforementioned ILs generated from the *cis* and *trans* isomers of betenedioate. Such a PSIL, possessing controllable UCST/LCST derived from its controlled photostable state, could revolutionize coolant systems as the thermal dependence of absorption-cooling systems could be replaced, in part at the least, by photo driven processes.

In this project, we aim to generate the hypothesized PSILs, synthesizing their underlying photoswitchable framework, demonstrate controlled photoswitchable behavior, and demonstrate unique UCST/LCST behavior between the two photostable states of the PSIL. The synthesis of such an IL has yet to be published, so the design of a synthesis accessing the IL possessing a photoswitchable framework was required. Following trial and error, we were able to settle on one design, owing to its capacity for synthetic divergence at multiple steps, enabling the production of a wide variety of PSILs with a shared photoswitchable framework. Before the pandemic, the synthesis had been demonstrated for a few preliminary PSILs; however, significant steric complications resulted when attempting to deviate from these preliminary products. Nonetheless, these initial PSILs were confirmed ILs, and their photoswitchable behavior was demonstrated by UV/Vis analysis following irradiation of a sample at 256 nm. Despite this success, these first PSILs were not demonstrated to possess observable UCST or LCST behavior in aqueous mixtures. Following the pandemic, we intend to improve the quality of the synthesis to access these PSILs; additionally, we are hopeful to identify a PSIL generated from this synthesis that possesses the desired UCST/LCST properties between its two photostable states.

We would like to thank ND Energy and the Slatt Undergraduate Research Fellowship for their funding to promote our investigation and discovery of PSILs!