

# SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

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<b>FACULTY ADVISOR: HIROTAKA SAKAUE</b>	
<b>PROJECT PERIOD: FALL 2020</b>	
<b>PROJECT TITLE: INVESTIGATION OF LUMINESCENT PROBE FOR PHASE-CHANGE AND TEMPERATURE IMAGING</b>	
<b>CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):</b>	<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 checked="" 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
<b>Characterize luminophores as conducive or non-conductive to the development of a novel ice sensor capable of resolving temporal and spatial temperature information.</b>	Nearly all candidate luminophores housed in Sakaue laboratory were characterized, including Pyranine, Acid Red 52, tris-(Bathophenanthroline) Ruthenium (II) Chloride, and Tris(2, 2'-bipyridyl ruthenium (II) chloride hexahydrate. A spectrometer was used to measure the ideal excitation wavelengths and corresponding emission peaks of these luminophores individually and in experimental combination mixtures. The primary characteristics that were sought in identifying whether or not a luminophore would be conducive to ice-sensor production was the known "temperature-dependence" of a luminophore and the presence of two distinct emission peaks when exposed to single wavelength. Of the luminophores characterized, Pyranine, Pyrene, and their derivative luminophores are currently being pursued as favorable novel ice sensor candidates. In the pursuit of perfecting sensor characteristics, new luminophores and potential luminophore additives are continually being ordered to the lab for testing. Thus, although this goal as it was originally conceived has been achieved, the process of characterizing luminophores is a continual aspect of developing luminescent ice sensors and will thus never truly be complete.	95%
<b>Using characterized luminophores, develop, and improve current samples of, a novel ice sensor capable of resolving temporal and spatial temperature information.</b>	Key breakthroughs were made in the late Fall 2020, early Spring 2021 research periods. For much of Fall 2020, the idea of a temperature-dependent luminophore mixture with two distinct emission peaks in the liquid phase was key to finding favorable candidates for novel ice sensor development. It was within this conceptual framework that Pyranine was used extensively as the luminophore of choice in early luminescent ice sensor samples (Pyranine's characterization data indicated it as highly conducive to novel ice sensor development). Experiments conducted during the interim Winter 2020-2021 period led to a shift in this conceptual framework. It was discovered that the combination of luminophores with other non-luminescent additives provided promising spectral performance	45%

in the ice phase. In Spring 2021, the focus has thus shifted to characterization and analysis of luminophore-additive mixtures. Pyrene and several of its derivatives have been characterized with various additives as part of this effort. An intensive study of Pyrenesulfonic Acid (PSA) is currently ongoing: spectrometer ice and liquid phase characterization has been completed with salt, sucrose, copper oxide, aluminum oxide, and sulfuric acid additives. The apparent local concentration affecting properties of aluminum oxide when combined with PSA have led to a yet more focused effort in identifying the particular properties of *this* mixture and how these properties can be leveraged for the creation of an effective novel ice sensor.

### 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	
EXTERNAL AWARDS RECEIVED	
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	
INTERNAL COLLABORATIONS FOSTERED	
EXTERNAL COLLABORATIONS FOSTERED	
WEBSITE(S) FEATURING RESEARCH PROJECT	
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	

### 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?

**I have thoroughly enjoyed my research experience thus far. My time at Sakaue Lab has been fulfilling, informative, and engaging. The members here have been incredibly helpful, and have ensured that I have access to all the instrumentation and advice necessary to conduct my research. My expectations have certainly been met. Due to my general satisfaction, then, I have little in the way of suggestions for improvement. It should be noted that the COVID-19 pandemic has, without doubt, slowed the rate of my research and changed the lab environment in certain ways, but such adjustments are to be expected in such a crisis.**

### 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.)

Research in Fall 2020 began with the characterizing various luminophores already present in Sakaue Lab. The goal was to determine which, if any, of these luminophores were conducive to the production of a novel ice sensor. The luminophores were tested in both individual and combined mixtures, and were kept at standard room temperature during the tests. A spectrometer was used to excite the luminophore mixtures at various wavelengths, and to record the intensity of light emission from the excited mixture in a range of wavelengths. The overarching idea was to find a dual-luminophore mixture that would emit two distinct emission peaks of relatively similar intensity when excited at a single wavelength. It was reasoned that, should such a mixture be created, the temperature dependence of *one* of the luminophores in the mixture could allow for comparative imaging techniques. The ratio of emission intensities between the temperature dependent and non-

temperature dependent luminophore would change as the novel ice sensor warmed or cooled, thus allowing for temporal and spatial resolution of temperature information.

Individual luminophore mixtures were tested first at 0.1 mmol in 50 mL of H<sub>2</sub>O; they were Pyranine, Acid Red 52, tris-(Bathophenanthroline) Ruthenium (II) Chloride, and Tris(2, 2'-bipyridyl ruthenium (II) chloride hexahydrate. It was found that Tris(2, 2'-bipyridyl ruthenium (II) chloride hexahydrate experienced a single emission peak at wavelengths approximately between 605 and 609 nm, Pyranine experienced two emission peaks, one between 365 and 407 nm and another between 511 and 513 nm, Acid Red 52 experienced one emission peak between 599 and 600 nm, and tris-(Bathophenanthroline) Ruthenium (II) Chloride experienced one emission peak between 614 and 615 nm. The presence of two emission peaks in the individual Pyranine mixture made it an immediate candidate for further study. Unfortunately, shortly after the testing of these four individual luminophore mixtures, the spectrometer in Sakaue Lab experienced a mechanical failure. It required maintenance that could only be completed by a technician brought in after the end of the Fall 2020 semester. Subsequent luminophore analysis was, then, completed using visual and concentration-manipulation techniques. Mixtures analyzed using these techniques included a combination of 0.05 mmol of tris(2,2) and 0.05 mmol of Pyranine, an individual mixture of 0.05 mmol EUTTA, an individual mixture of 0.05 mmol of Pyrene, a combination of 0.05 mmol EUTTA and 0.05 mmol tris(2,2), a combination of 0.05 mmol EUTTA and 0.05 mmol tris-(Bath.), an individual mixture of 0.1 mmol Fluorescein, an individual mixture of 0.1 mmol Coumarin, a combination of 0.1 mmol Pyranine and 0.1 mmol tris-(Bath.), a combination of 0.05 mmol of Acid Red 52 and 0.05 mmol of tris-(Bath.), a combination 0.05 mmol EUTTA and 0.05 mmol Pyranine, a combination of 0.05 mmol Coumarin and 0.05 mmol tris-(Bath.), a combination of 0.1 mmol tris-(Bath.) and 0.1 mmol Fluorescein, a combination of 0.05 mmol Acid Red 52 and 0.0975 mmol Pyrene, and a combination of 0.1827 mmol Coumarin and 0.05 mmol Acid Red 52.

Such luminophore combinations were tested on a concentration-part basis – i.e. individual mixtures with the various concentrations listed above were created before combination, then combined by adding 5 mL samples of each and analyzing results. For example, in the mixture of Acid Red 52 and Pyrene, one 5 mL sample of Acid Red 52 and one 5 mL sample of Pyrene were added together. This yielded a “1pt Acid Red 52, 1pt Pyrene mixture.” 5 mL “pts” (or “parts”) were of the non-dominant emitting luminophore were slowly added, and the change in emission color was observed. Favorable mixtures exhibited a color that was some combination of the color of the two mixed luminophores. Particularly favorable mixtures were identified in the Acid Red 52 – Pyrene mixture and the tris-(Bath.) and Fluorescein mixture. Figures 1, 2, and 3 below feature photos of the Acid Red 52 and Pyrene mixture.



**Figure 1.** A photo of 0.05 mmol of Acid Red 52 in 50 mL of H<sub>2</sub>O.



**Figure 2.** A photo of 1pt 0.05 mmol Acid Red 52 and 3pts 0.0975 mmol Pyrene. Each pt (or “part”) is comprised of a 5 mL liquid mixture



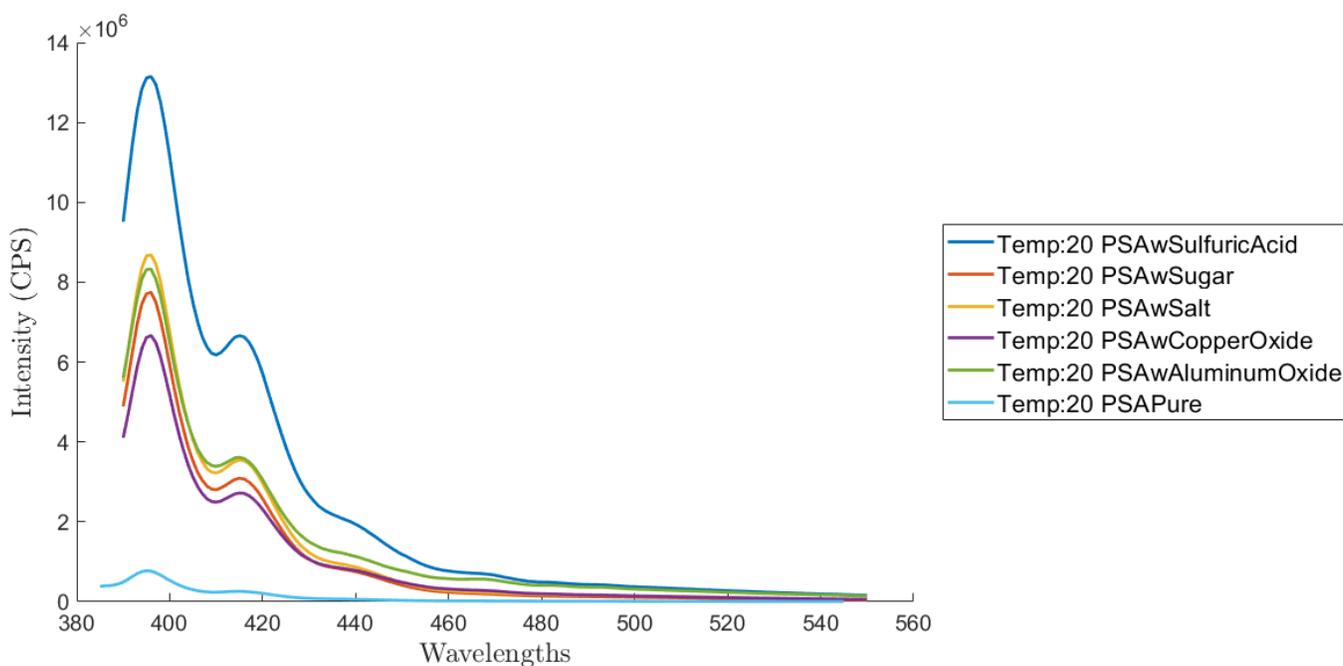
**Figure 3.** A photo of 0.0975 mmol of Pyrene in 50 mL of H<sub>2</sub>O.

Concerning more recent research findings, the discovery that certain non-luminescent additives combined with specific luminophores led to the appearance of unique emission peaks in the ice phase has somewhat changed the direction of my research. Emphasis is now on the characterization of *singular* luminophores when combined with additives. Particular attention is being paid to the temperature-dependent qualities of these luminophore-additive mixtures. A cooling plate is used to set the temperature of a mixture to a desired value before spectrometer analysis is applied. In this way, the properties of the ice and liquid phases of the mixtures can be observed – i.e. the exact degree of temperature-dependence of a mixture can be assessed in real time

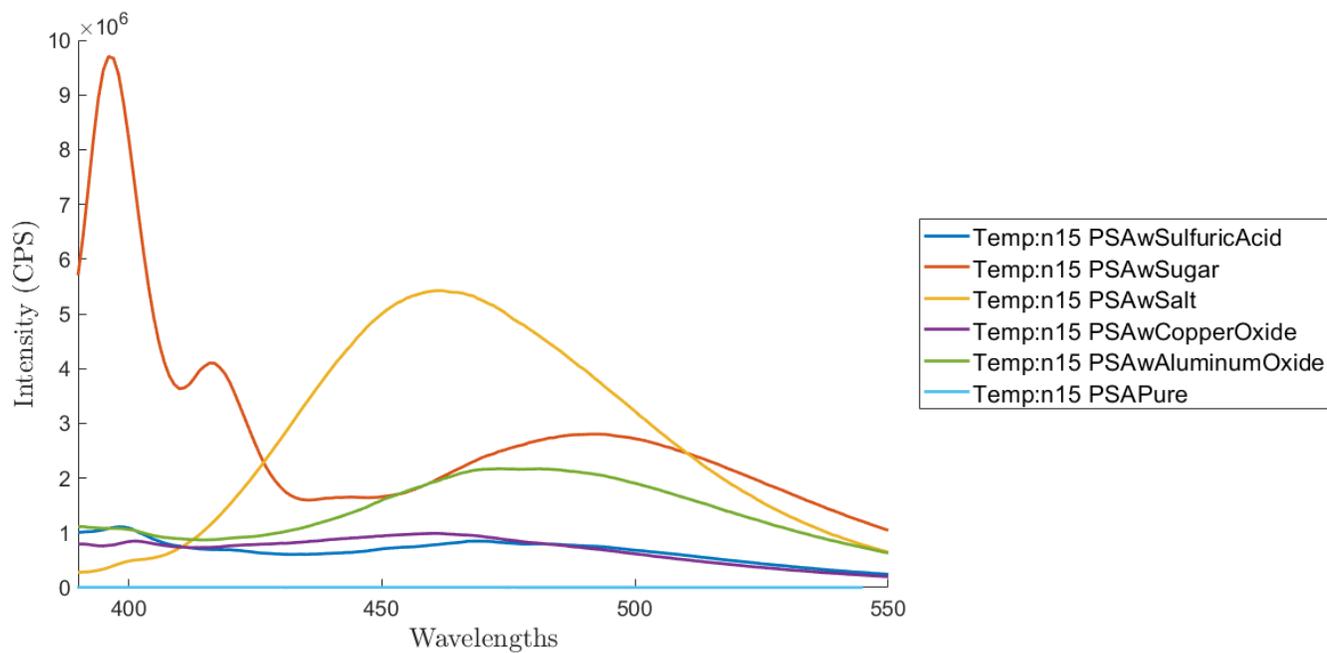
Work this semester began on a characterization of the properties of Pyrene, a luminophore that exhibits unique emission peak behavior when combined with certain additives. It was determined that a series of “quick” tests of multiple additives should be conducted to efficiently assess the characteristics of each mixture. Those deemed most conducive to the production of luminescent ice would then be selected for further study. The experimental process was as follows. Mixtures of 0.1 mmol Pyrenesulfonic Acid (a derivative of Pyrene), 10 mL of H<sub>2</sub>O, and 20 mmol additive were placed in the spectrometer tested chamber. Using a Peltier cooler, they were brought to a temperature of approximately 20°C. They were then excited at a wavelength of approximately 365 nm and the spectrometer recorded the relative intensity of emissions from the sample in a wavelength range of 390 nm to 550 nm. The temperature of the mixtures were then lowered to -15°C – they were transitioned to the ice phase – and an identical spectrometer analysis was done. The resulting data was a set of distinct intensity vs. wavelength plots, one set corresponding with the liquid phase mixture 20°C and another with the ice phase mixture -15°C. Favorable PSA-additive mixtures exhibited a new, relatively high-intensity emission peak in the ice phase at a wavelength distinct from the emission peak observed in the liquid phase. This indicated a degree of temperature-dependence, and the distinctiveness of the peak indicated viability as a sensor (changing emission color with temperature is a key component of the

desired novel ice sensor). Because, however, tests of each of the PSA-additive mixtures were conducted on different days and under minutely variable conditions, it was reasoned that the relative intensity of the emission peaks could not be the only determiner of mixture viability. Thus, the ratio of blue to green emission wavelength intensity was used as the primary indicator of the viability of a particular PSA-additive mixture. Below, Figures 4 and 5 feature plots of the “Counts-Per-Second” (a measure of the relative intensity) of the emission peaks of various mixtures in the liquid and ice phase versus emission wavelength, Figure 6 features a plot of the blue-green ratios of various mixtures in the liquid phase, and Figure 7 features a plot of the blue-green ratios of various mixtures in the ice phase.

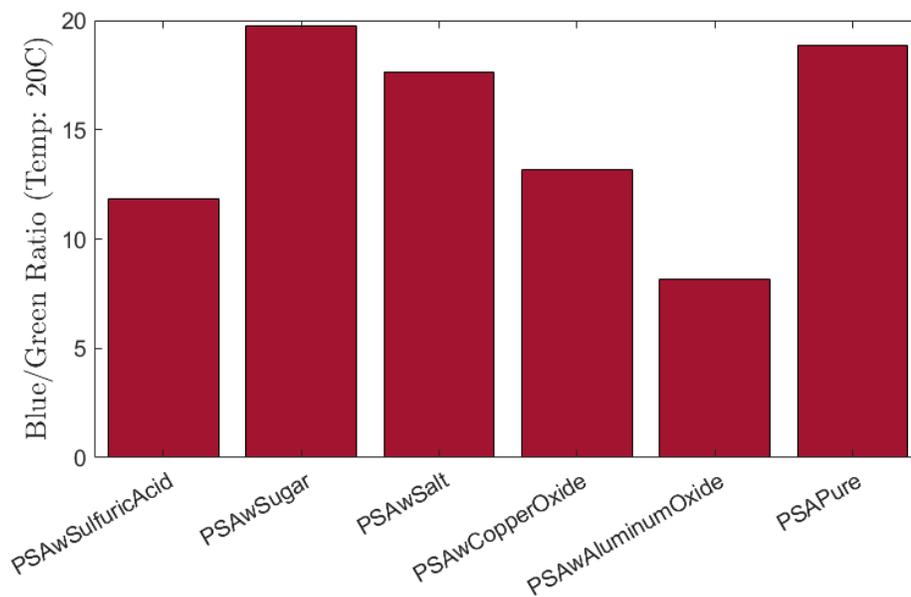
The blue/green ratios in Figures 2 and 3 were derived by numerically integrating the CPS-wavelength data from Figure 1 and dividing the total “blue” signal by the total “green” signal. It was noted from the above data analysis that the PSA with Aluminum Oxide mixture had, in both liquid and ice phase, the lowest blue/green ratio of the mixtures tested. This property of the mixture was promising, as it indicated noticeable change in dominant emission color with temperature – i.e. while most mixtures emitted as blue in liquid phase and continued to emit as blue in the ice phase, the PSA with Aluminum Oxide additive mixture emitted blue in the liquid phase and emitted a different shade – green-blue – in the ice phase. For this reason, the PSA-Aluminum Oxide mixture in the subject of current study. A parametric study of the effect of Aluminum Oxide concentration in the mixture was recently conducted, and it was found that relatively high concentrations of Aluminum Oxide (15 mmol and above) cause unpredictable change in the emission color of liquid phase PSA. It is predicted that this is due to a localized change in concentration of PSA in the mixture as it reacts with the porous structure of Aluminum Oxide. Studies of the mixture behavior over time are being conducted to further ascertain the nature of this strange phenomenon and its potential uses in the production of the novel ice sensor.



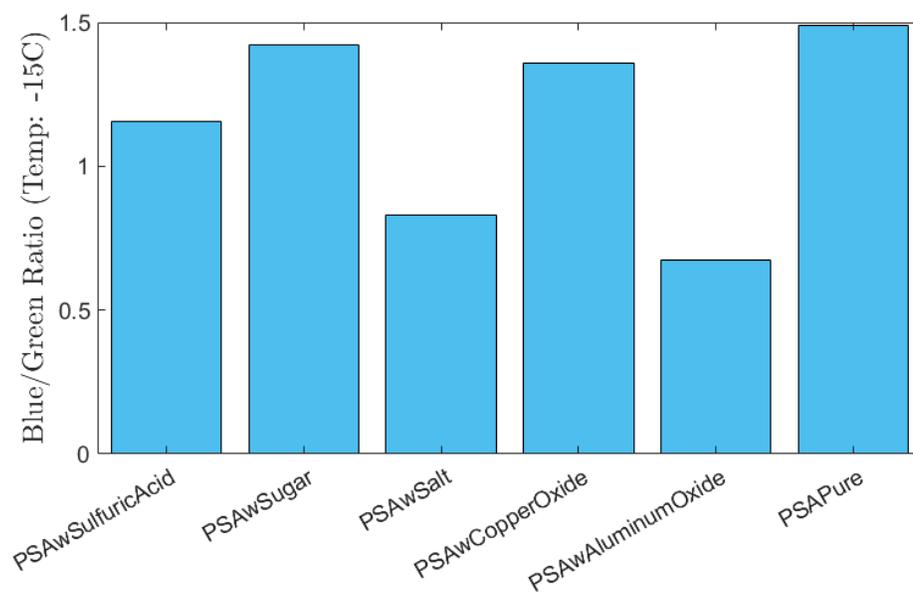
**Figure 4.** Intensity (CPS) vs. emission wavelengths for various Pyrenesulfonic Acid additive mixtures at 20°C (liquid phase). CPS is a relative measure of light intensity recorded by the spectrometer.



**Figure 5.** Intensity (CPS) vs. emission wavelengths for various Pyrenesulfonic Acid additive mixtures at -15°C (ice phase). CPS is a relative measure of light intensity recorded by the spectrometer.



**Figure 6.** Blue/Green Ratios for various Pyrenesulfonic Acid additive mixtures at 20°C (liquid phase). Blue signals are here defined as those emissions at wavelengths less than 465 nm, and green signals are those emissions at wavelengths greater than 465 nm.



**Figure 7.** Blue/Green Ratios for various Pyrenesulfonic Acid additive mixtures at -15°C (ice phase). Blue signals are here defined as those emissions at wavelengths less than 465  $\mu\text{m}$ , and green signals are those emissions at wavelengths greater than 465  $\mu\text{m}$ .