EILERS GRADUATE STUDENT FELLOWSHIP
FINAL REPORT

EILERS FELLOW:	Preethi Susan Mathew
FACULTY ADVISOR:	Dr. Prashant V. Kamat
REPORT PERIOD:	Jan 2021- Dec 2021
PROJECT TITLE:	Spacer cations Dictate Photoinduced Phase Segregation in 2D Mixed Halide Perovskites
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	**( ) Energy Conversion and Efficiency** **( ) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution** **(✓) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels** **( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS:

List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Modulation of photoinduced iodine expulsion in Mixed halide perovskites using a bias	Designed and performed experiments. Co-authored a peer-reviewed publication	100
Understanding phase segregation in 2D mixed halide perovskites	Elucidated the role of spacer cations in the phase segregation of 2D mixed halide perovskites. Resulted in a peer-reviewed publication	100
Studying the lifetime of charge carriers in 2D perovskites	Designed experiments to compare how the lifetime of charge carriers in 2D perovskites change depending on the halide ion used	20

RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	N.A.
EXTERNAL AWARDS	N.A.
JOURNAL ARTICLES	1. ACS Energy Letters; Spacer cations dictate Photoinduced Phase Segregation in 2D Mixed Halide Perovskites; **Preethi S. Mathew**, Jeffrey DuBose, Junsang Cho, Prashant V. Kamat; May 19 2021; June 15 2021; 6; 2499-2501 2. The Journal of Physical Chemistry Letters; Modulation of Photoinduced Iodine Expulsion in Mixed Halide Perovskites with Electrochemical Bias; Jeffrey DuBose, **Preethi S. Mathew**, Junsang Cho, Masaru Kuno, Prashant V. Kamat; Feb 1 2021; March 9 2021; 12; 2615-2621 3. Advanced Materials; Photoinduced Halide Segregation in Ruddlesden-Popper 2D Mixed Halide Perovskites Junsang Cho, **Preethi S. Mathew,** Jeffrey DuBose, Prashant V. Kamat; 19 July 2021; 07 Oct 2021; 33; 2105585
BOOKS AND CHAPTERS	N.A.
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	PINDU Conference, Spacer cations Dictate Photoinduced Phase Segregation in 2D Mixed Halide Perovskites, Nov 6 2021, IU - Bloomington
AWARDS, PRIZES, RECOGNITIONS	Materials Research Society, Best Elevator Pitch, November 9 2021
INTERNAL COLLABORATIONS FOSTERED	Jeffrey DuBose, Notre Dame, Transient Absorbance measurements Junsang Cho, Notre Dame, experiment discussions

EXTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation)
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)	Recorded a LiveSlides presentation for a publication. The presentation is available on the following link https://doi.org/10.1021/acs.jpclett.1c00367 Spacer cation project featured on the cover of July 2021 edition of ACS Energy Letters

MAJOR GOALS AND ACCOMPLISHMENTS
(Additional Details, Technical Results, Charts and Graphics)

1. Modulation of Photoinduced Iodine expulsion in Mixed Halide Perovskites with Electrochemical Bias

Iodine migration in mixed halide perovskites (MHPs) has been shown to be a consequence of hole trapping. We found that the photoinduced iodine expulsion from mixed halide perovskites can be controlled using an externally applied electrochemical bias. At positive potentials relative to the reference electrode, electron extraction becomes efficient , and holes accumulate in the perovskite. This results in enhanced iodine expulsion at positive potentials.

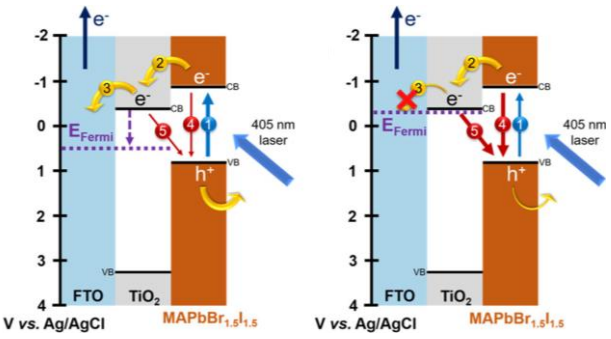

Figure 1: Band diagram schematic depicting pathways for charge carriers for MHP films held at positive bias (left) and negative bias (right)

2. Spacer cations dictate Photoinduced Phase Segregation in 2D Mixed Halide Perovskites

Under photoirradiation, MHPs separate into the respective halide-rich domains. This phenomenon is referred to as halide ion segregation. We found that in 2D MHPs, whether or not halide ion segregation occurs depends on the nature of spacer cation that is used. Phase segregation was observed in 2D MHPs with the aliphatic cation Butylammonium (BA) , under photoirradiation. On the other hand, 2D MHPs with aromatic cation, Phenethylammonium (PEA) did not undergo phase segregation.

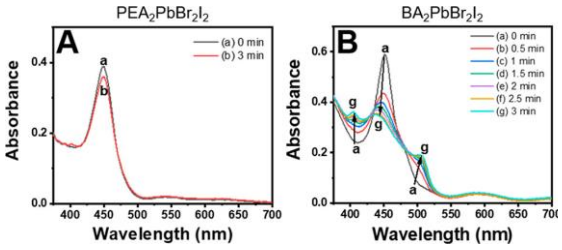

Figure 2: PEA mixed halide 2D perovskites do not phase segregate, while BA mixed halide 2D perovskites phase segregate as seen in the UV-Vis absorbance spectra of the perovskite films after irradiation

This project was featured on the cover of July 2021 issue of ACS Energy Letters.