FORGASH STUDENT FELLOWSHIP
FINAL REPORT

FORGASH SCHOLAR:	Jeffrey DuBose
FACULTY ADVISOR:	Dr. Prashant Kamat
REPORT PERIOD:	CY 2021
PROJECT TITLE:	Revealing the Role of Ionic Liquids in Stabilizing Perovskite Solar Cells
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
Elucidate role of ionic liquid treatment on cation and anion migration in perovskites films	Using techniques available to us, we were unable to resolve cation migration in perovskite films. However, this research spawned a new direction, which was carried out in part by undergraduate Thomas Gonzales	25
Understand mechanism of perovskite phase segregation using electrochemistry	Using spectroelectrochemistry (applying voltage while probing w/ spectroscopy) we further identified the role of photo-generated electron vacancies ("holes") in inducing deleterious phase segregation. This led to a publication in *The Journal of Physical Chemistry Letters*	95
Controlling the flow of energy in perovskite-molecule complexes	We demonstrated that the primary mechanism of energy flow in perovskite-chromophore complexes occurs through a Förster-like singlet energy transfer event, which opens new doors for photon conversion in these systems. This research led to a publication in the *Journal of the American Chemical Society*	100
Stabilize the surface of perovskite nanoplatelets for photocatalysis	We determined the role of polar solvents in inducing a transformation from nanoplatelets to large nanocrystals and elucidated the thermodynamics of the ligand desorption / particle ripening process, opening the door to further study of these particles. Although we could not find a way to fully make the particles stable, our results can guide future research	85

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	• *ACS Energy Letters,* Advances in LIB Electrolyte, Stabilizing $CsPbBr_3$ in Mesoporous Silica, and Halide Segregation in Mixed Halide Perovskites. Choi, N.-S.; Vela, J.; DuBose, J. T.; Kamat, P. V. **2021**, *6,* 3, 1150–1152. • *Journal of Physical Chemistry Letters.,* Modulation of Photoinduced Iodine Expulsion in Mixed Halide Perovskites with Electrochemical Bias. DuBose, J. T.; Mathew, P. S.; Cho, J.; Kuno, M.; Kamat, P. V. **2021**, *12,* 10, 2615–2621. • *ACS Energy Letters,* Spacer Cations Dictate Photoinduced Phase Segregation in 2D Mixed Halide Perovskites. Mathew, P. S.; DuBose, J. T.; Cho, J.; Kamat, P. V. **2021**, *6,* 7, 2499–2501.

	• *Advanced Materials,* Photoinduced Halide Segregation in Ruddlesden–Popper 2D Mixed Halide Perovskite Films. Cho, J.; Mathew, P. S.; DuBose, J. T.; Kamat, P. V. **2021**, *33,* 2105585. • *Chemical Science,* $CsPbBr_3$–CdS heterostructure: stabilizing perovskite nanocrystals for photocatalysis. Kipkorir, A.; DuBose, J. T.; Cho, J.; Kamat, P. V. **2021**, *12,* 14815-14825. • *Journal of the American Chemical Society,* Directing Energy Transfer in Halide Perovskite–Chromophore Hybrid Assemblies. DuBose, J. T.; Kamat, P. V. **2021**, *143,* 45, 19214–19223. • *ACS Materials Letters,* Transformation of Perovskite Nanoplatelets to Large Nanostructures Driven by Solvent Polarity. DuBose, J. T.; Christy, A.; Chakkamalayath, J.; Kamat, P. V. **2022, *4*,** XXX, 93–101.
BOOKS AND CHAPTERS	N/A
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	Jeffrey DuBose, Preethi Mathew, Prashant V. Kamat Modulation of Photo Induced Iodide Expulsion in Mixed Halide Perovskites with Electrochemical Bias Virtual, April 17-23, 2021 Jeffrey DuBose, Prashant V. Kamat Surface Chemistry Matters: How Ligands Influence Excited State Interactions between CsPbBr3 and Methyl Viologen 239th Meeting of the Electrochemical Society, May 30- June 3, 2021 Jeffrey DuBose, Prashant V. Kamat Energy Transfer in Perovskite Nanocrystals: Is it a Singlet or a Triplet? 4th Annual ND Energy Research Symposium, Achieving Carbon Neutrality: An Emphasis on Global Partnerships and Climate Justice, June 3-4, 2021 Jeffrey DuBose, Prashant V. Kamat Light-Induced Halide Ion Migration in Perovskites ENFL Division Student Presentation Award Symposium, Virtual, August 21, 2021 Jeffrey DuBose, Prashant V. Kamat Interactions between Molecular Triplets and Perovskite Quantum Dots ACS Fall Meeting, Hybrid Virtual / Atlanta, Aug 22-26, 2021 Jeffrey DuBose, Prashant V. Kamat Directing Energy Transfer in Perovskite-Chromophore Complexes ACS Experimental and Theoretical Physical Chemistry Graduate Student Award Symposium, Virtual, September 17, 2021 Jeffrey DuBose, Prashant V. Kamat [e-Poster] Directing Energy Transfer in Perovskite-Chromophore Hybrid Assemblies QED-C Workforce Development Technical Advisory Committee Student/Postdoc Research e-Poster Sessions, Virtual, November 2, 2021 Jeffrey DuBose, Prashant V. Kamat Directing Energy Transfer in Perovskite-Chromophore Hybrid Assemblies PINDU, IU Bloomington, Indiana, November 6, 2021 Jeffrey DuBose, Prashant V. Kamat Directing Energy Transfer in Perovskite-Chromophore Hybrid Assemblies ND Energy Post-Doctoral & Graduate Student Luncheon, University of Notre Dame, Indiana, November 17, 2021 Jeffrey DuBose, Prashant V. Kamat Directing Energy Transfer in Perovskite-Chromophore Hybrid Assemblies News in Nanocrystals Seminar (NiNC), Virtual, December 1, 2021
AWARDS, PRIZES, RECOGNITIONS	Experimental Physical Chemistry Award for Excellence in Graduate Research, ACS PHYS Division, Sept. 27, 2021 Center for Environmental Science and Technology (CEST) Pre-Doctoral Fellowship, *Stabilizing the Surface of Perovskite Nanoplatelets for Photocatalysis*, May 2021
INTERNAL COLLABORATIONS FOSTERED	N/A

EXTERNAL COLLABORATIONS FOSTERED	N/A
WEBSITE(S) FEATURING RESEARCH PROJECT	https://jdubose0.wixsite.com/mysite
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	N/A

MAJOR GOALS AND ACCOMPLISHMENTS

Lead halide perovskites are a new class of synthetic material that have only been studied for solar applications within the last decade. Their inexpensive and low temperature processing, high efficiency, and ease of incorporation into existing technologies make them one of the most promising and exciting materials for solar energy conversion. Perovskites solar panels have already surpassed the efficiency of the gold-standard polycrystalline silicon panels. Utilizing low-cost processing techniques, companies like Tandem PV and Swift Solar are developing tandem silicon/perovskite solar cells with >30% efficiency.

One particularly useful property of perovskites lies in its chemical structure: by simply changing the ratio of certain atoms in the material (the 'halide' atoms: bromine, iodine) one can readily change what colors of light a perovskite absorbs or emits. With the support of the *The Forgash Fellowship for Solar Energy Research* we were able to leverage this property of perovskites to study the flow of energy between perovskite nanocrystals and chromophore molecules (Figure 1).

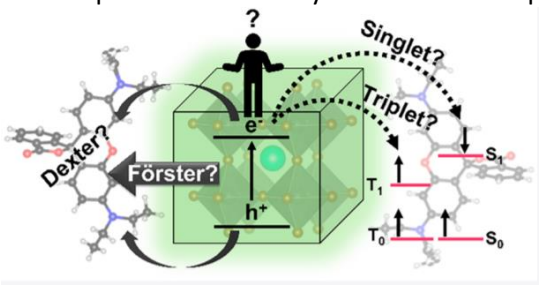

Figure 1. Scheme showing energy transfer from perovskite nanocrystals (green cube) to chromophore energy acceptor molecules (rhodamine B). Energy transfer can occur through several different pathways (Dexter vs. Forster mechanism) and with different electron spin

The results from our study revealed the mechanism of energy transfer and highlighted the importance of optimizing the properties of both the energy donor (perovskite) and energy acceptor (chromophore) for energy transfer processes relevant to solar applications. An intimate knowledge of the mechanism and nature of energy flow is crucial for a wide variety of applications, from photocatalysis to photon up-conversion. In up-conversion, otherwise unusable low energy infrared light is converted to higher-energy photons which can be harvested by a solar cell. The results from the study have been published in the prestigious Journal of the American Chemical Society (DuBose and Kamat, *J. Am. Chem. Soc.* **2021**, *143*, 19214–19223).

Broadly speaking, the mechanistic insights gleaned in this research will guide scientists and engineers in utilizing perovskites in a variety of renewable energy-related applications. This will undoubtedly lead to a new range of possibilities in photon up-conversion, photocatalysis, and potentially biomedical imaging