

SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

SCHOLAR NAME:	Lauren Martin
FACULTY ADVISOR:	Prashant Kamat
PROJECT PERIOD:	May 30th through August 5th, 2023
PROJECT TITLE:	
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 checked="" 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
Establish An Energy Transfer in My Assembly, Thereby Completing the Project	Full experiments were run, and analysis of the data proved the presence of a singlet energy transfer within my light harvesting assembly.	100%
Practice and Present Scientific Information	In addition to creating and presenting a poster at the Summer Undergraduate Research Symposium, I created and presented a presentation to give to my research group, facilitating discussion surrounding the topic and brainstorming ideas for further research.	100%
Express Scientific Information in the Written Form	An initial draft of a journal article has been crafted, but it needs to undergo further edits and revisions by myself and other collaborators.	50%

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	Journal Article in Writing Stage
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	Summer Undergraduate Research Symposium, Energy Transfer in Lead Halide Perovskite-Molecular Hybrid Assemblies, 07-26-2023, University of Notre Dame, Notre Dame IN 46556
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)	

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?

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.)

In order to facilitate efficient energy capture and transfer in semiconductor nanocrystals, sensitizing dyes are employed to create assemblies that can capture photons over a wide range of visible and near-infrared regions. With proper tailoring, these assemblies can trigger nonlinear optoelectronic processes like triplet-triplet annihilation (TTA) and singlet fission (SF); processes that theoretically overcome power conversion efficiency barriers in traditional photovoltaic cells. In this work, we focus on CsPbI₃ nanocrystals (NCs) as the sensitizer and the near-infrared tricyanocyanine dye (IR-125) as the acceptor molecule. The presence of functional groups on the IR-125 dye helps to bind strongly on the surface of the CsPbI₃ NCs with an apparent association constant of $K_{app} = 2 \times 10^5 \text{ M}^{-1}$, facilitating energy transfer between the two species. Fluorescence quenching of CsPbI₃ NCs and evolution IR-125 emission was observed upon increasing the concentration of IR-125 dye (Figure 1). The origin of IR-125 emission was investigated using photoluminescence excitation (PLE) spectroscopy (Figure 2). The contribution of CsPbI₃ excitation in the IR-125 emission was observed from PLE spectra. The kinetic analysis of the energy transfer was achieved using photoluminescence (PL) lifetime and transient absorption spectroscopy. The PL lifetime of CsPbI₃ decreased from 42.8 ns to 2.4 ns for 0 and 4.6 μM IR-125, respectively and had a calculated energy transfer efficiency of $\eta_{ET} = 94.4\%$ (Figure 3). Transient absorption spectroscopy further supported evidence of energy transfer through faster decay kinetics of CsPbI₃ bleaching at 670 nm in the presence of IR-125 dye. Taken together, the evidence provided in this paper confidently supports the presence of a singlet energy transfer between CsPbI₃ and IR-125 hybrid assemblies and the importance of tailoring sensitizing dye - semiconductor assemblies to optimize power conversion efficiency.

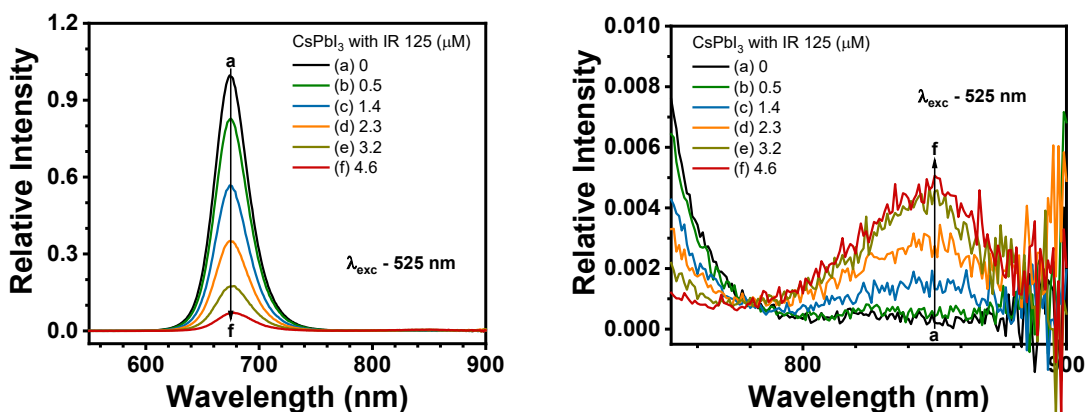


Figure 1. Progressive Addition of IR-125 to CsPbI₃. Panel A shows the entirety of data set and Panel B zooms in to show emission between wavelengths 800-900 nm.

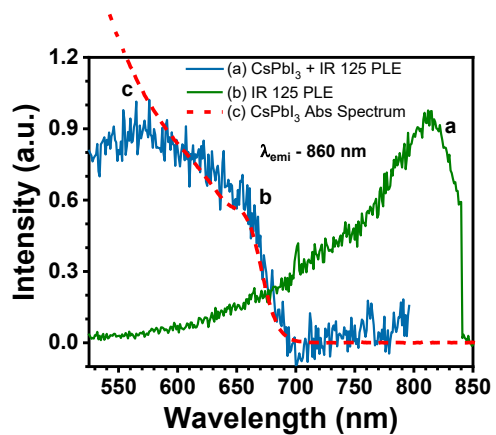


Figure 2. Overlay of CsPbI₃ IR-125 assembly PLE (trace a), IR-125 PLE (trace b), and CsPbI₃ absorbance (trace c).

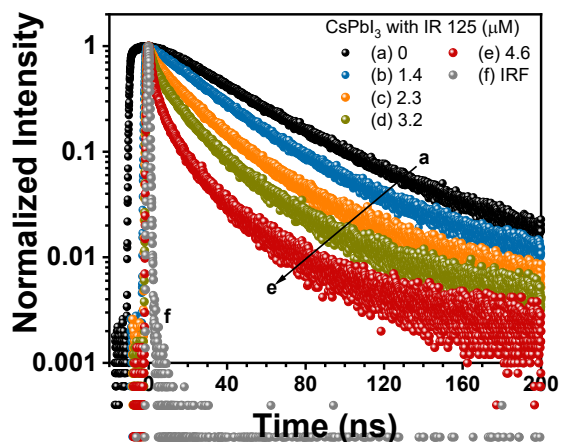


Figure 3. PL Decay of CsPbI₃ IR-125 assembly with emission wavelength of 673 nm.

Energy Transfer in Lead Halide Perovskite-Molecular Hybrid Assemblies



Lauren Martin, Jishnudas Chakkamalayath, and Prashant Kamat
Radiation Laboratory, University of Notre Dame, Notre Dame IN 46556, USA

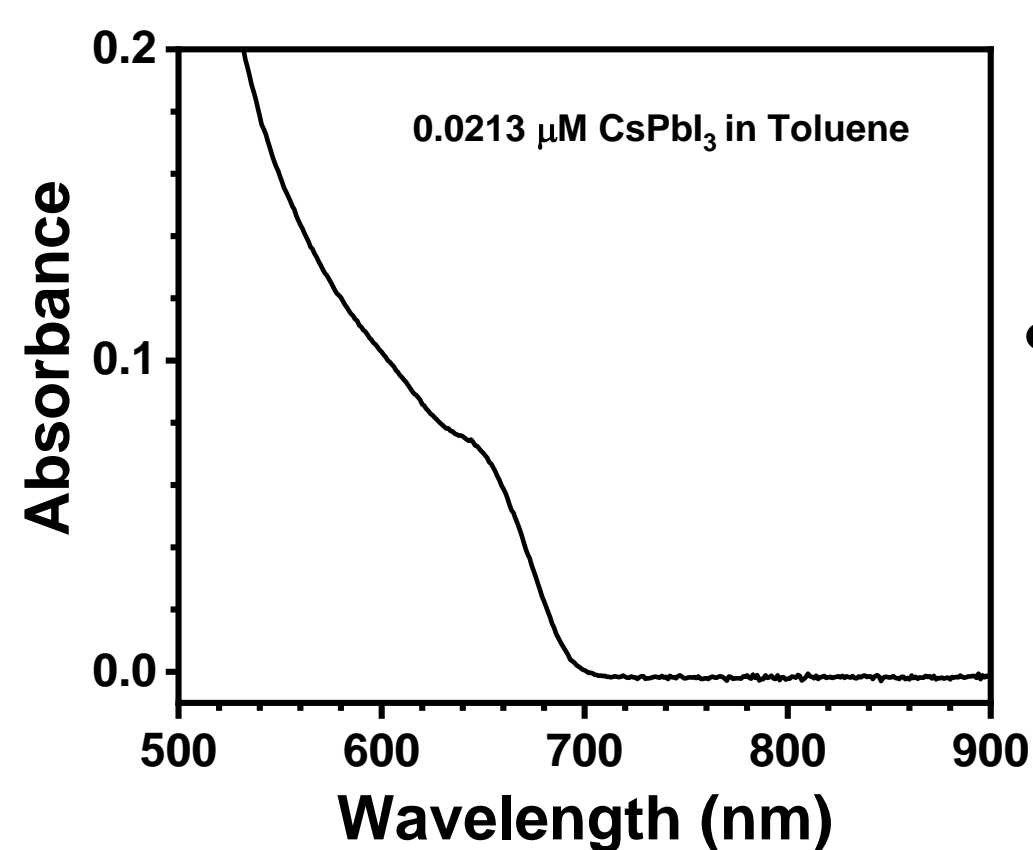


Introduction

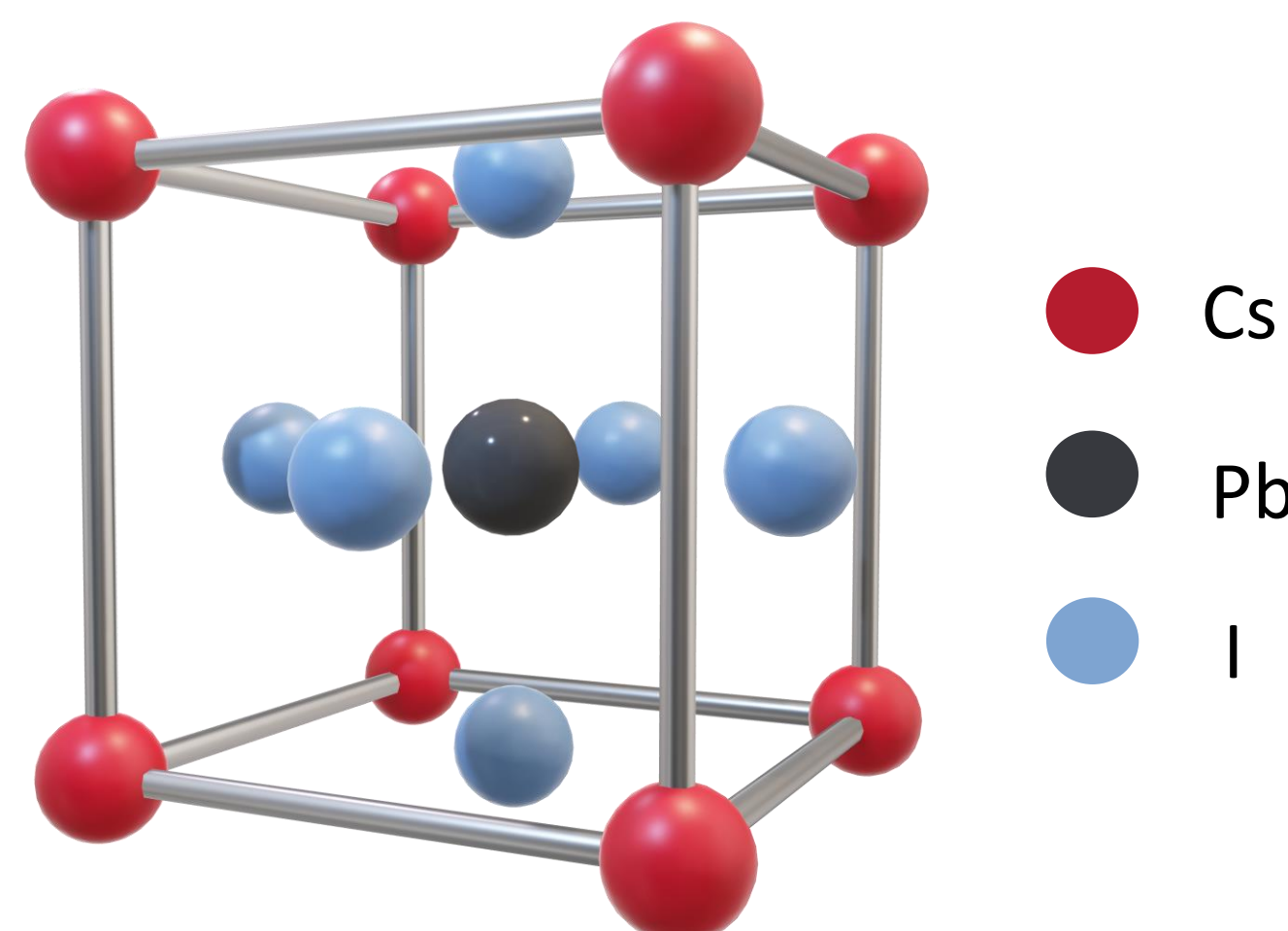
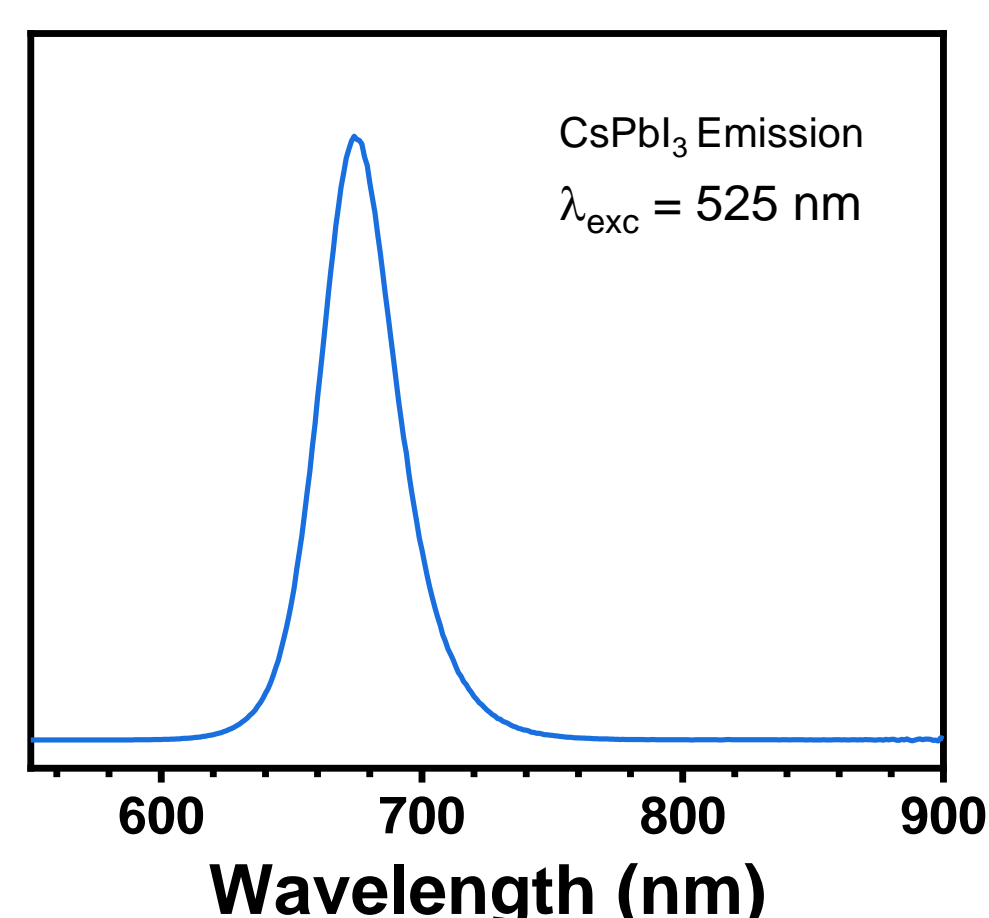
- Solar energy is an underutilized and abundant resource with a promising future. However, current solar energy devices lack the energy capture and conversion efficiency necessary for widespread implementation.
- Nature has optimized solar energy conversion in plants, so we want to create a synthetic photochemical architecture following that blueprint.
- Semiconductors, combined with different surface bound dyes, can capture and transfer energy like photosynthesis

The Goal of this Project is to establish a light harvesting assembly using CsPbI₃ and IR-125 dye that can capture both visible and near infrared wavelengths of light, as well as an energy transfer between the two species

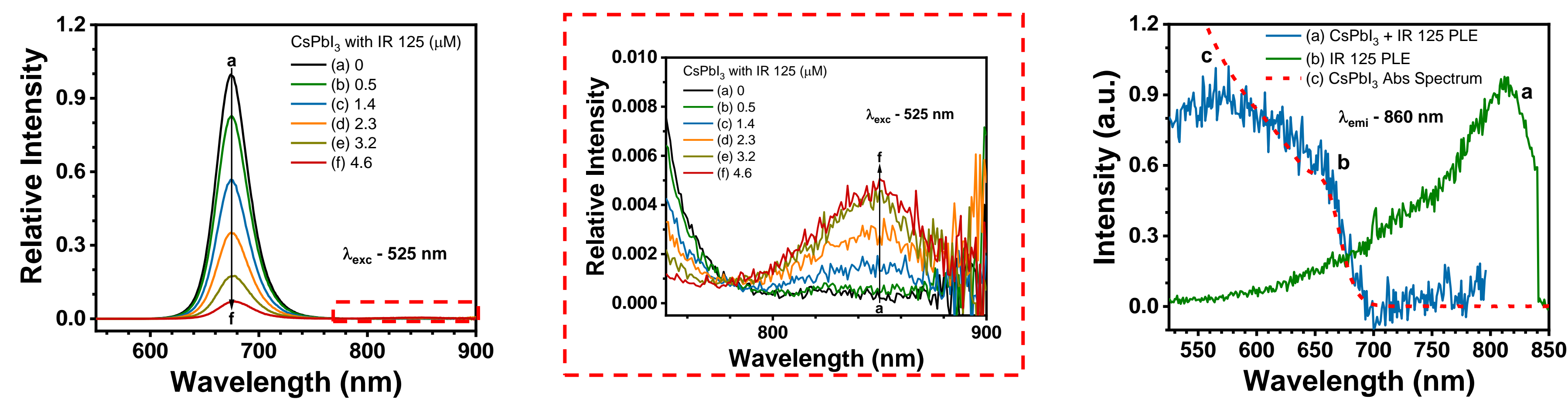
CsPbI₃ Semiconductor Nanocrystals



- CsPbI₃ is a Lead Halide Perovskite with the structure ABX₃
- Perovskites offer tunable surface and optical characteristics, strong absorption, and potential for low-cost production

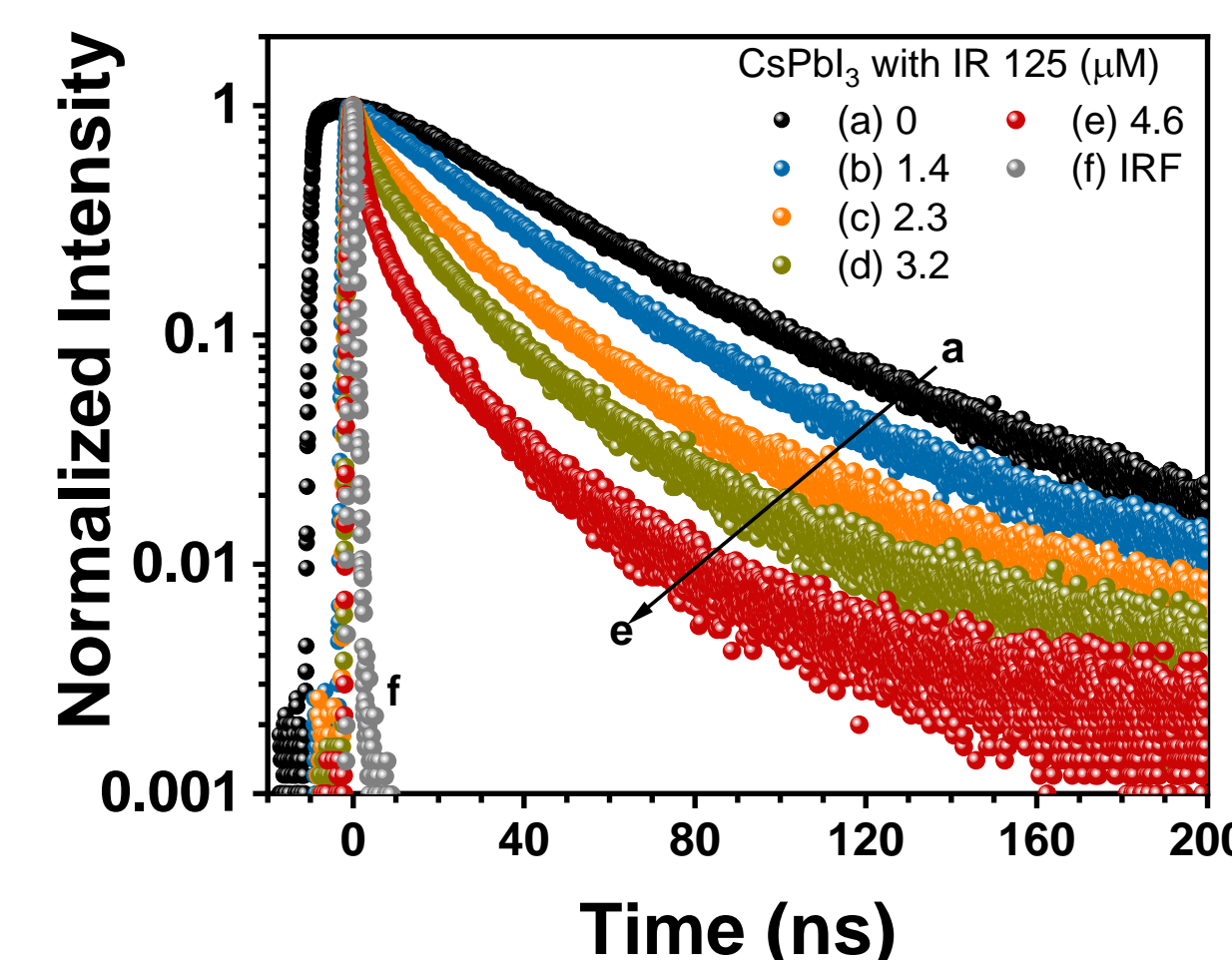


Fluorescence Quenching and IR-125 Emission



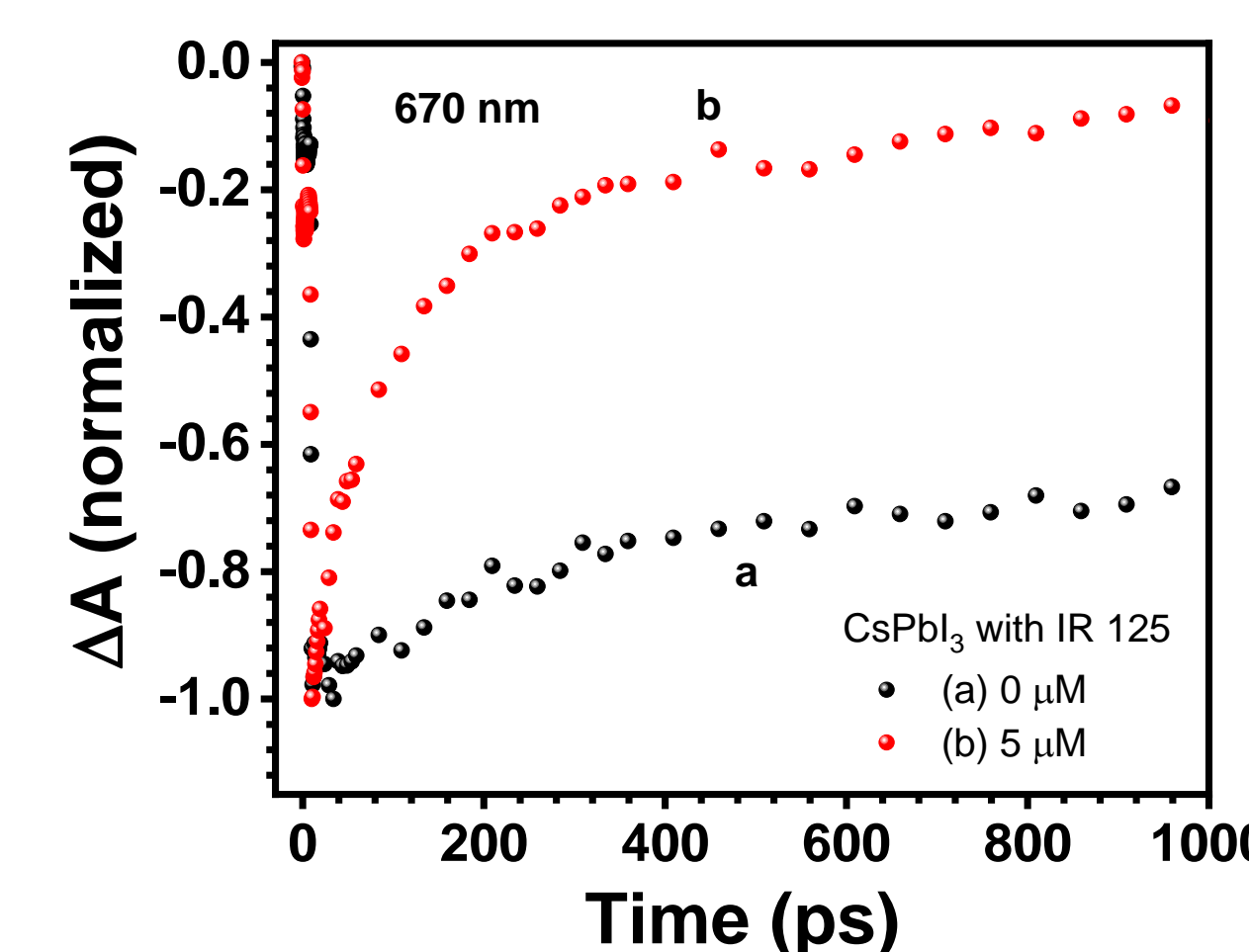
- Upon progressive addition of IR-125 to CsPbI₃, not only was fluorescence quenching observed, but also the evolution of IR125 emission at 860 nm
- the origin of emission investigated using Photoluminescence (PL) Excitation spectroscopy, confirming the contribution of CsPbI₃ in the IR125 emission.

Singlet Energy Transfer



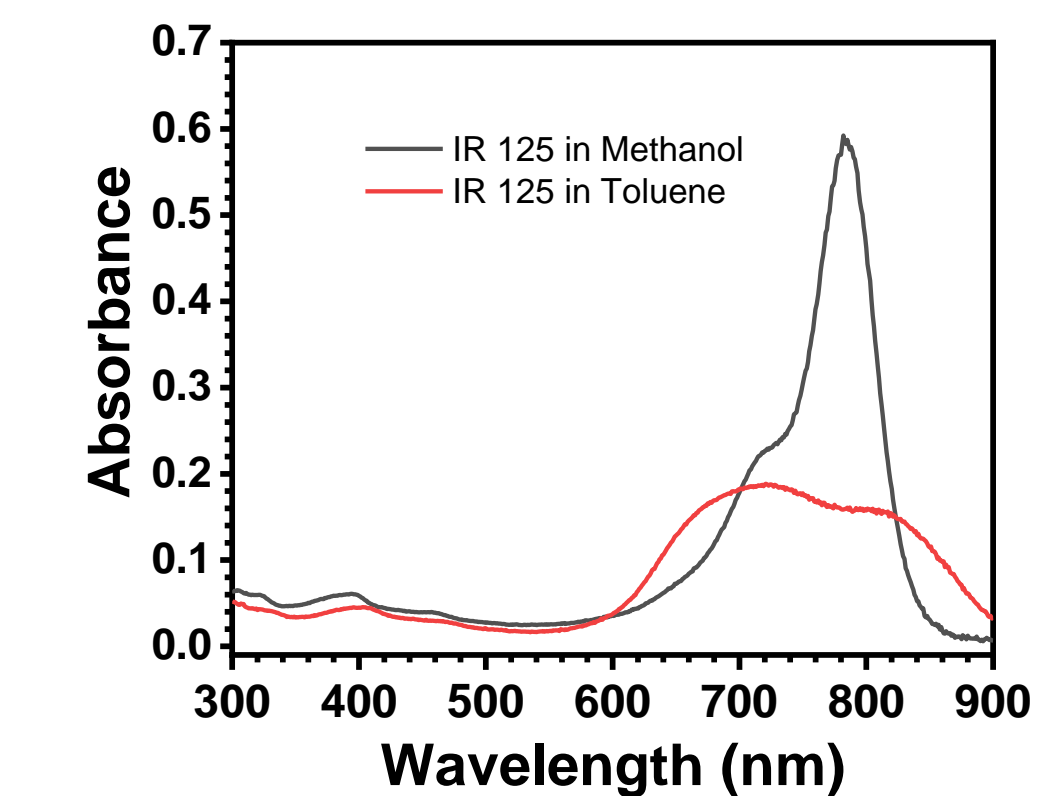
- Singlet Energy Transfer expects a decrease in the lifetime of the perovskite
- PL Decay shows lifetime of CsPbI₃ decreased from 42.8 ns to 2.4 ns for 0 and 4.6 μM IR-125
- Calculated Energy transfer of 94.4% at 4.6 μM IR-125 via biexponential fits of decay traces

Transient absorption spectroscopy further supported evidence of energy transfer through faster decay kinetics of CsPbI₃ bleaching at 670 nm in the presence of IR-125 dye.

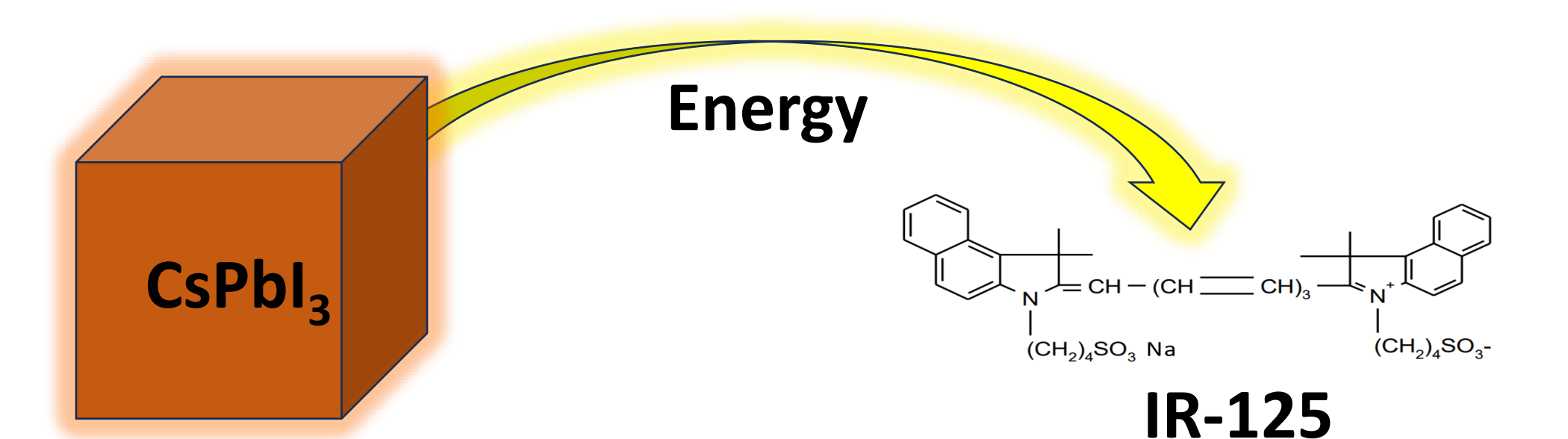
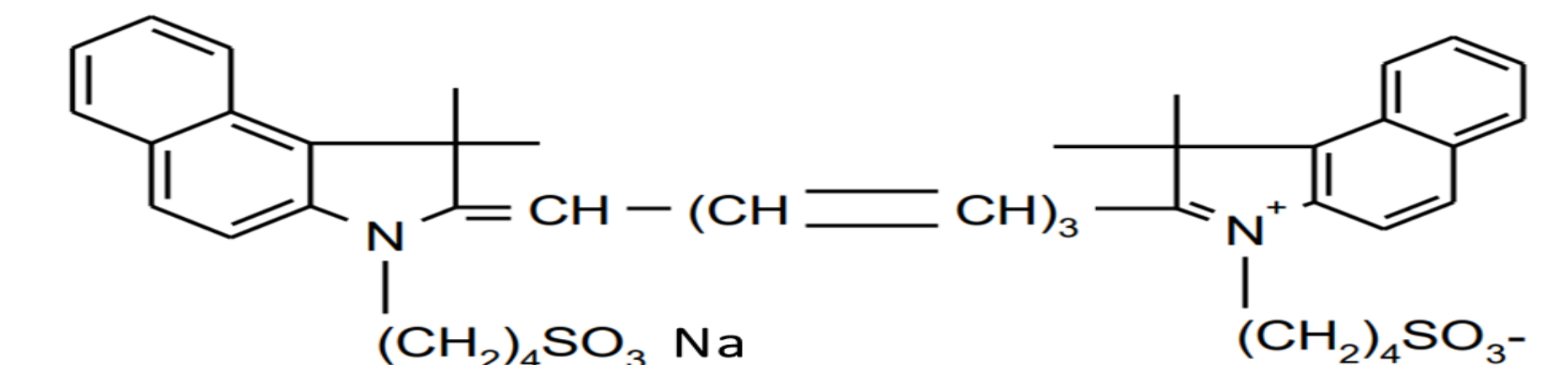


A Singlet Energy Transfer was Established Between CsPbI₃ and IR-125

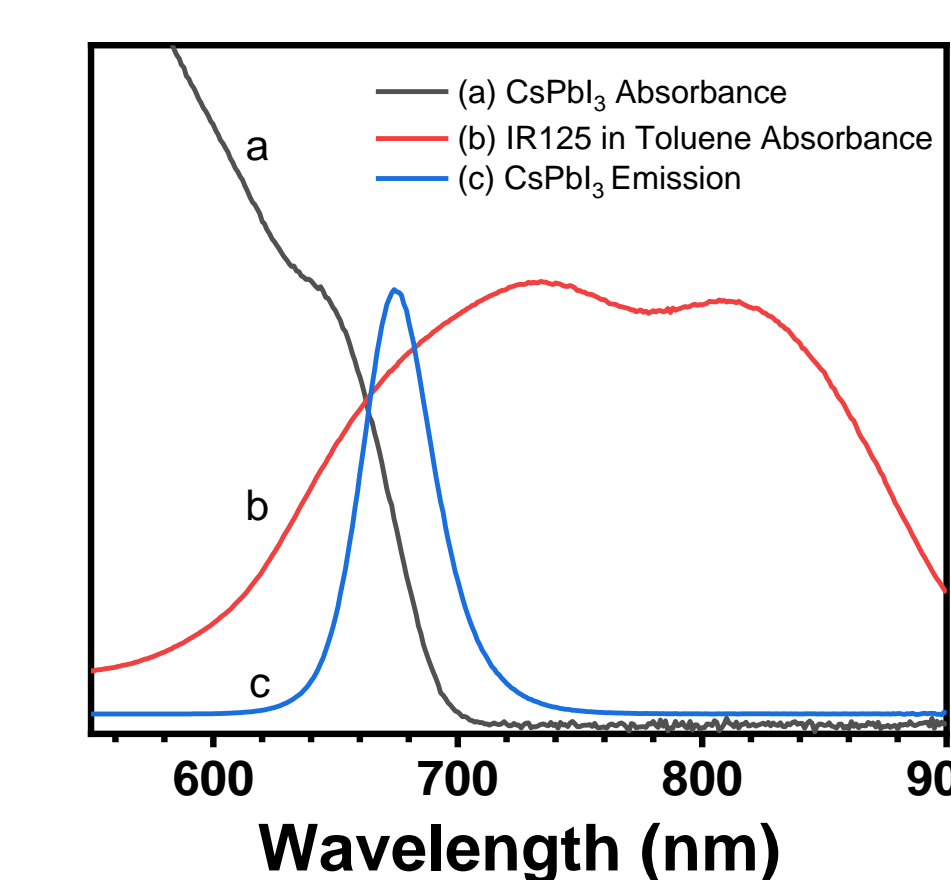
IR-125 Dye



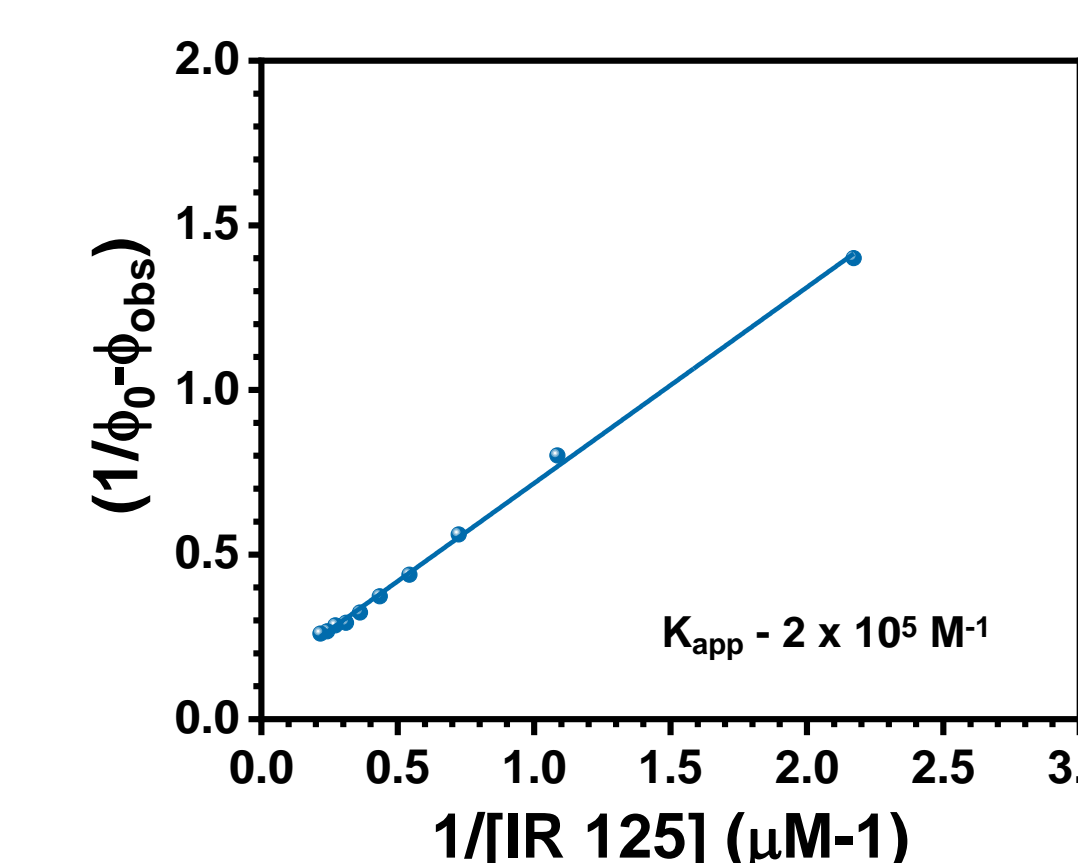
- near infrared tricyanocyanine dye
- commonly used in laser diodes



Assembly Characterization



- the overlap between the CsPbI₃ emission at nm and the absorbance of IR-125, indicates that the energy absorbed and subsequently emitted by CsPbI₃ will most likely be absorbed by IR-125 and re-emitted.



- $K_{app} = 2 \times 10^5 \text{ M}^{-1}$
- large apparent association indicates strong binding characteristics, which should facilitate energy transfer.

Acknowledgements:

Work for this Project was partially funded by the Vincent P. Slatt Fellowship for Undergraduate Research in Energy Systems and Processes.



References:

- DuBose, J. T.; Kamat, P. V. Energy Versus Electron Transfer: Managing Excited-State Interactions in Perovskite Nanocrystal-Molecular Hybrids. *Chem. Rev.* **2022**, 122, 12475-12494.
- DuBose, J. T.; Kamat, P. V. How Pendant Groups Dictate Energy and Electron Transfer in Perovskite-Rhodamine Light Harvesting Assemblies. *J. Am. Chem. Soc.* **2023**, 145, 4601-4612.