

EILERS GRADUATE STUDENT FELLOWSHIP FINAL REPORT

EILERS FELLOW:	Triet S. Nguyen-Beck
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REPORT PERIOD:	02/01/2017-08/01/2017
PROJECT TITLE:	Origin of the Size-Dependent Stokes Shift in CsPbBr ₃ Perovskite Nanocrystals
CONNECTION TO ND ENERGY'S 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:

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
Model CsPbBr₃ nanocrystals with different sizes, morphologies, and defects	We constructed and calculated the electronic structure of CsPbBr ₃ nanocrystals with varying edge lengths (2.05, 2.64, 3.23, 3.82, and 4.40 nm), cubic and orthorhombic phases, Cs-Br and Pb-Br terminated, and degree of surface defect (5.3 to 58.6%). Subsequently computed Stokes shifts from various geometric models quantitatively agree with experimentally measured values.	100%
Investigate the impact of the nanocrystal fine structure on observed Stokes shifts	We constructed a Breit-Pauli spin-orbit coupling (SOC) Hamiltonian with electron-hole exchange interactions between the four spin-adapted excitation linking the CHS and the conduction band edge state. Triplet/ singlet fine structure splitting is therefore negligible for experimentally relevant sizes (i.e., ~4–13 nm). We conclude that fine structure SOC cannot explain observed size-dependent Stokes shifts.	100%
Explain the experimentally observed size-dependent Stokes shift	We identified an inherent, size-dependent confined hole state (CHS) level above the valence band edge state, with the CHS dark in absorption and bright in emission. The CHS is spatially confined by the NC size and hence possesses size-dependent energies. The study determines that absorbing and emitting states are distinct in CsPbBr ₃ NCs and simultaneously rationalizes observed Stokes shifts.	100%

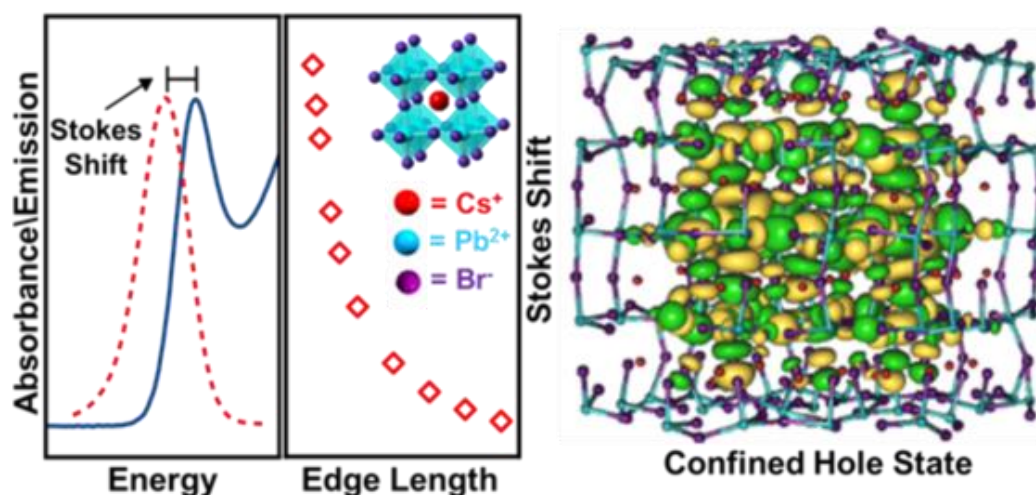
RESEARCH OUTPUT:

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

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount)
EXTERNAL AWARDS	(Sponsor, Project Title, PIs, Award Date, Award Amount)
JOURNAL ARTICLES	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) Journal of the American Chemical Society Title: Origin of the Size-Dependent Stokes Shift in CsPbBr ₃ Perovskite Nanocrystals Authors: Michael C. Brennan, John E. Herr, Triet S. Nguyen-Beck, Jessica Zinna, Sergiu Draguta, Sergei Rouvimov, John Parkhill, and Masaru Kuno Submission Date: June 1, 2017, Publication Date: August 3, 2017, Volume: 139, Pages: 12201-12208
BOOKS AND CHAPTERS	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)

PUBLIC PRESENTATIONS, SEMINARS, LECTURES	(Event, Presentation Title, Presentation Date, Location) ND Energy Postdocs and Graduate Students Luncheon Rationalizing the Size-Dependent Stokes Shift in CsPbBr ₃ Perovskite Nanocrystals September 20, 2017 – 202 Nieuwland Science Hall, University of Notre Dame
AWARDS, PRIZES, RECOGNITIONS	(Purpose, Title, Date Received)
INTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation) Masaru Kuno, ND Energy
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)	(Please describe each item in detail)

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



The origin of the size-dependent Stokes shift in CsPbBr₃ nanocrystals (NCs) is explained for the first time. Stokes shifts range from 82 to 20 meV for NCs with effective edge lengths varying from ~4 to 13 nm. We show that the Stokes shift is intrinsic to the NC electronic structure and does not arise from extrinsic effects such as residual ensemble size distributions, impurities or solvent-related effects. The origin of the Stokes shift is elucidated via first-principles calculations. Corresponding theoretical modeling of the CsPbBr₃ NC density of states and band structure reveal the existence of an intrinsic confined hole state 260 to 70 meV above the valence band edge state for NCs with edge lengths from ~2 to 5 nm. A size-dependent Stokes shift is therefore predicted and is in quantitative agreement with the experimental data. Comparison between bulk and NC calculations show that the confined hole state is exclusive to NCs. At a broader level, the distinction between absorbing and emitting states in CsPbBr₃ is likely a general feature of other halide perovskite NCs and can be tuned via NC size to enhance applications involving these materials.