

EXTENDED ABSTRACT

**Energy Harvesting Dynamics of Ambient Stable Lead Halide  
Perovskites Nanocrystals**



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## SCOPE OF THESIS:

Inorganic perovskite nanocrystal (PNC) is an emerging class of photoluminescent nanomaterials having profound applications in solar cells, light-emitting diodes, and photodetectors. Notably, perovskite tandem solar cell (PSC) is a promising technology that can make silicon-based solar cell obsolete in this decade owing to its increased power conversion efficiency (PCE), more than >30%. High abundance, excellent defect tolerance and long carrier diffusion length of perovskites make them an outstanding nanomaterial for energy conversion, energy harvesting and in photocatalysis. Moreover, its unique structural feature ( $ABX_3$ ) allows easy access of sites A and B through metal doping for suppressing radiative recombination. Labile nature of ligand (X) for fast exchange contributes to tuning their band gaps across visible spectrum. The scope of the thesis is to address the ambient stability issue through methodology development and thereafter deepen our understanding on energy harvesting properties of perovskite nanocrystals. The following questions have been selected to answer in this thesis are-

- (i) How does hydrophilic-hydrophobic balance impact dimensional engineering of halide perovskite crystals ?
- (ii) Is it possible to synergize the defect tolerance with ambient stability of perovskite nanocrystals ?
- (iii) Why does a facet of perovskite nanocrystal dictate the energy transfer dynamics of light-harvesting complex ?
- (iv) How to resolve energy-transfer couple electron-transfer in PNC-based photocatalytic system ?

**Chapter 1- Introduction:** This chapter contains a detailed literature survey on different types of perovskites, their history and physical properties. All the different emerging synthetic methods are thoroughly illustrated here. Optoelectronic properties, ion exchange ability for tunable band gaps, different encapsulation techniques and metal ion doping to address the ambient stability and toxicity issues are also explained here. The applications like in solar cells LEDs, photodetector, CO<sub>2</sub> reduction and H<sub>2</sub> production have been elaborated as well.

**Chapter 2- Materials and Methodology:** It includes different chemicals used throughout the research, various equipment employed, synthetic method, purification techniques, and different spectroscopic and microscopic characterization. Experimental set up for time-correlated single photon counting and transient absorption spectroscopy have also been shown here. Methods of spectroscopic and microscopic data analysis have been presented as well.

**Chapter 3- PVDF-Directed synthesis, Stability and Anion exchange of CsPbBr<sub>3</sub>:** In this chapter, a polymer directed antisolvent method have been for the synthesis of halide perovskite at room temperature and observed that the thermodynamic stabilities of the crystals drive the formation of orthorhombic Cs<sub>4</sub>PbBr<sub>6</sub> and monoclinic CsPbBr<sub>3</sub>. Surprisingly hydrophobic PVDF can reduce the size of the perovskite crystals to nano dimension even at room temperature. On the other hand, CsPbBr<sub>3</sub> synthesized using the hot-injection method undergoes rapid encapsulation in PVDF matrices. There are three types of radiative recombination predominantly operative in nanocrystals-doped polymer- (i) surface defect caused radiative recombination (0.6-3 ns), (ii) exciton recombination (3-15 ns), and (iii) shallow trap assisted recombination (10-50 ns). The interface created at nanocrystal and polymer plays a decisive role in populating the shallow trap states in perovskite-polymer nanocomposite. These nanocomposites undergo fast halide exchange in aqueous hydroiodic acid solution and possess remarkable enhancement of water-/photo-stability up to one year. These polymer encapsulated perovskite nanocrystals show enhanced optoelectronic properties for being treated with water rather than the destruction of the nanocrystals.

**Chapter 4-Facet engineering and energy harvesting through metal ion doping:** In this chapter, facets of the amine-capped CsPbBr<sub>3</sub> perovskite nanocrystals have been engineered by doping with a trace amount of Ni and Co ions to use it as a light harvester. Ni-doped CsPbBr<sub>3</sub> (Ni:PNC) showcases structural heterogeneity with regular cubic shape, whereas bimetallic-doped CsPbBr<sub>3</sub> (Ni:Co:PNC) evolves to an elongated dodecahedron structure. Structural analysis using Rietveld refinement strongly corroborates the construction of a dodecahedron structure for Ni:Co:PNC through systematic displacement of Cs ions. Energy transfer from doped nanocrystals to rhodamine B (RhB) occurs through a dipole–dipole interaction, known as Förster resonance energy transfer (FRET). The emergence of the isoemissive point and rise time of RhB conclusively establishes the resonance energy transfer mechanism. A comparison

of energy transfer efficiency has also been made between thin films and in solution, in thin films it occurs at a much faster rate than in the toluene medium. {100} facet-dominated Ni:PNC registers a FRET efficiency of 94%, whereas {111} and {002} facet-dominated Ni:Co:PNC is restricted at 21% FRET efficiency. The distance between the donor and acceptor,  $R_{D-A}$ , dictates the dynamics of energy transfer, rather than spectral overlap and the photoluminescence quantum yield of these doped nanocrystals. The surface composition of facets, typically Cs ions, perhaps plays a decisive role in regulating the binding constant of the donor and acceptor.

***Chapter 5-Electron Transfer Coupled Energy Transfer in Metal doped CsPbBr<sub>3</sub>:*** In this chapter, Ni-doped CsPbBr<sub>3</sub>, Ni:PNC based light-harvesting system has been illustrated. An energy transfer-coupled electron transfer system has been developed where Ni:PNC acts as a donor, Rhodamine B (RhB) as an acceptor, whereas Methyl Viologen (MV<sup>+2</sup>) acts an electron acceptor respectively. Steady-state and time-resolved photoluminescence methods have been employed to resolve the competitive dynamics of energy transfer and electron transfer. Upon excitation at 400 nm energy gets transferred from Ni:PNC to RhB via FRET mechanism with an efficiency of 94%. Addition of electron acceptor, MV<sup>+2</sup> to Ni:PNC-RhB complex has resulted in gradual quenching of photoluminescence of both- Ni:PNC and RhB. The Stern-Volmer constant for Ni:PNC-RhB complex is much lower, 5.7 nM<sup>-1</sup> in comparison to that of for Ni:PNC alone, suggesting limited accessibility quencher to nanocrystal's surface. Femtosecond transient absorption study reveals the formation of methyl viologen radical signaling a broad peak ranging from 520 nm to 650 nm. The rate of electron transfer is estimated to be  $2.5 \times 10^{10} \text{ s}^{-1}$  for Ni:PNC-RhB-MV<sup>+2</sup> system. A careful analysis data highlights that RhB contributes to slow down the rate of electron transfer. The role of methyl viologen as an electron shuttle is further exploited by using benzoquinone (BQ) as a secondary electron acceptor.

#### ***Chapter -6 Impact of Transition metal ions on Energy and Electron Transfer Efficiency:***

In this chapter, the CsPbBr<sub>3</sub> nanocrystal is doped with trace amount of metal ions- Ni<sup>+2</sup>, Zn<sup>+2</sup>, Sn<sup>+2</sup> and Ge<sup>+2</sup>. Modified hot-injection methods have been used to synthesize these metal doped CsPbBr<sub>3</sub>. Spectroscopic analysis corroborates its superior ambient stability and high quantum yield over the undoped CsPbBr<sub>3</sub>. All these materials have been used for the energy transfer study to the acceptor Rhodamine B. Our study finds that the energy transfer efficiency is the

highest for the Ge-doped CsPbBr<sub>3</sub> and least for Sn-doped CsPbBr<sub>3</sub>. Larger size of Sn creates lattice strain in nanocrystal that becomes the retarding factor of the energy transfer dynamics. Steady-state and time-resolved photoluminescence methods have also been used to decipher electron transfer versus energy transfer kinetics in doped PNC-fluorophore complex.

**Chapter -7 Conclusion and Future Scope:** In this chapter experimental results have been summarized, and the future scope of this research work has been outlined.

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### References:

1. **S. Panda**, G. Roy, T. Basu, D. Panda\*, Facet {100} Fosters Resonance Energy Transfer in Ni/Co-Doped CsPbBr<sub>3</sub> Nanocrystals, *ACS Applied Energy Materials* 2024, 7, 10179–10188
2. **S. Panda**, A. Soni, V. Gupta, R. Niranjana, D. Panda\*, PVDF-directed synthesis, stability and anion exchange of cesium lead bromide nanocrystals, *Methods and Applications in Fluorescence* 2022 10, 044005.  
(Institute of Physics) IOP Publishing, Special Issue: Fluorescence Research in India
3. S. K. Pal, M. Parashar, B.B. Kanrar, **S. Panda**, N. Roy, P. Paira, D. Panda\*, N-doped yellow-emissive carbon nanodots from Gallic acid: reaction engineering, stimuli-responsive red emission, and intracellular localization, *Journal of Physical Chemistry C* 125 (2021) 5748–5759
4. **S. Panda**, D. Panda\*, How does Energy Transfer Relay Electron Transfer in a Ni-doped CsPbBr<sub>3</sub> Nanocrystal-based Light Harvesting system? 2025 (Manuscript under preparation)
5. **S. Panda**, D. Panda\*, Impact of Metal ions on Energy and Electron Transfer efficiency in a Metal doped CsPbBr<sub>3</sub> system 2025 (Manuscript under preparation).

### Conferences:

1. Recent Trends in Chemical Sciences (RTCS-2022) organized by IIT (ISM) Dhanbad, 16-18<sup>th</sup> December 2022.  
**Title – PVDF directed Synthesis, Stability, Anion Exchange of Cesium Lead Bromide Nanocrystals**
2. Inaugural conference of Society of Physical Chemistry (SoPhyc-2023) organized by IIT Kanpur, 29-31<sup>st</sup> October 2023.  
**Title – Fluorescence Resonance Energy Transfer from Ni/Co-doped Perovskite Nanocrystals to Rhodamine B: Unearthing the Role of Crystal Facets.**