Perovskite Nanostructures as LEDs: Towards Flexible Displays

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Summary

Light Emitting Diode (LED) displays recently become to replace conventional CRT and LCD displays and have witnessed enormous growth in the field with the costs of LED displays decreasing by the day. Numerous studies are on-going for the next generation of displays that are flexible. There is an immediate need to design and develop novel materials that can be made flexible and provide vivid color purity through out the entire visible region with greater luminescence efficiencies. In recent years, perovskite materials have gained enormous research attention as they have shown highest solar cell efficiencies (~22%) and also have the potential to made flexible.

Perovskites have the advantage in having low exciton binding energies, ease of fabrication and excellent photo-stability. At the nanoscale, these perovskites have shown increased exciton binding energies that make them suitable for LED applications and thus we propose to use the advantages of perovskites to develop LED displays that are flexible. Using a hot-injection method, we synthesized different $CsPbX_3$ (X=Cl, Br, I) nanomaterials that yielded photoluminescence through out the visible spectrum. Under TEM scans, it was determined that the sizes of the perovskites are approximately 10 nm. To fabricate LED displays, interaction of perovskites with different polymer structures were studied and two different geometries of LEDs were fabricated. Perovskite/PDMS nanocomposite was found to be the best material to make LED displays. The results have shown bulk-heterojunction approach can lead to enhanced luminescence intensities when compared to layer by layer approach.

Introduction

With the advent of the information revolution, the demand for displays and their application in numerous devices has significantly increased. With the increasing demand, consumers in addition to desiring energy efficient and high resolution displays, they desire vivid displays that output high color purity and flexibility.

Perovskites have recently gained attention as a promising materials for optoelectronic devices particularly in their usage as solar panels. Due to their narrow and easily tunable band gap, they exhibit excellent photovoltaic performance. However these properties are also beneficial for light-emitting diodes (LEDs) when nanoparticles are made from such systems. This forms the motivation of the research project to use novel perovskite materials for fabricating flexible LEDs.

These specific type of perovskite known as inorganic halide with a specific crystal structure ABX_3 (X = Cl, Br, I & mixed halides) (Figure 1). These perovskite materials have strong absorption in the visible region. The perovskites exhibit high photoluminescence quantum yield (PLQY) and high color purity or color saturation with narrow emission line-widths. Because of that, these inorganic halide perovskites are shown to be promising LEDs that can overcome the inherent problems of conventional display technology like organic light-emitting diodes. It was shown in recent years that $CH_3NH_3PbI_3$ perovskites can achieve solar conversion efficiency of 22%. They can be made into nanocrystalline with enhanced PLQYs and can be easily made into thin films. With these advantages, we propose the use of a combination of perovskites and polymers to understand their interactions and to fabricate LED displays and study their properties.

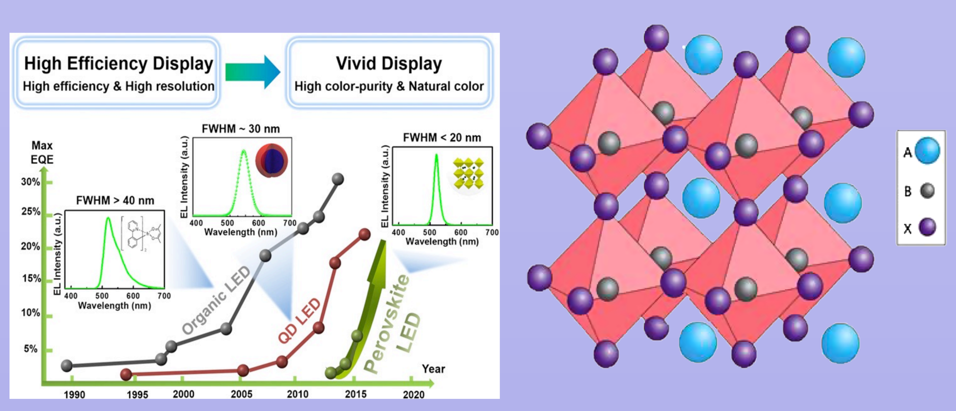

Figure 1: Major trend of various display technology and the generic structure of a perovskite, where A and B are cations (blue and grey) and X is the halide (purple).

Research Approach

Research Objectives

- Synthesize and characterize $CsPbX_3$ perovskite nanomaterials with organic capping agents and understand their optical properties. We propose to use hot injection method to synthesize perovskite nanomaterials (Figure 2) and use TEM to characterize the size of nanoparticles.
- Study the interactions of perovskite nanomaterials with polymers so that they can be used for fabricating thin films.
- Fabricate the LED Displays via two different approaches: (1) Layer by layer and (2) Bulk hetero-junction. The hypothesis is that the bulk heterojunction approach is easier to fabricate, possesses less interfaces for losses and potentially can provide getter LED efficiencies.

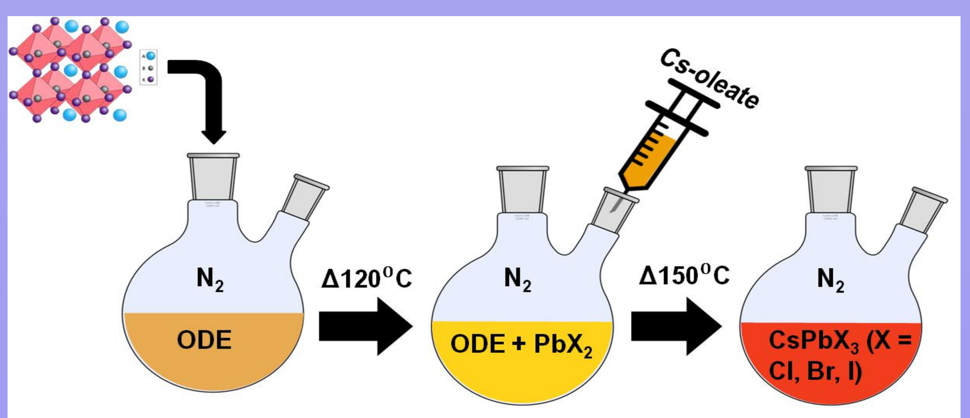

Figure 2: Schematic representation of the perovskite nanomaterial synthesis.

Techniques Used

- UV/vis absorption spectrophotometer
- Steady-state fluorescence measurements
- Photoluminescence lifetimes and film luminescence measurements

Investigated Systems

Characterization of $CsPbX_3$ Perovskite Nanomaterials

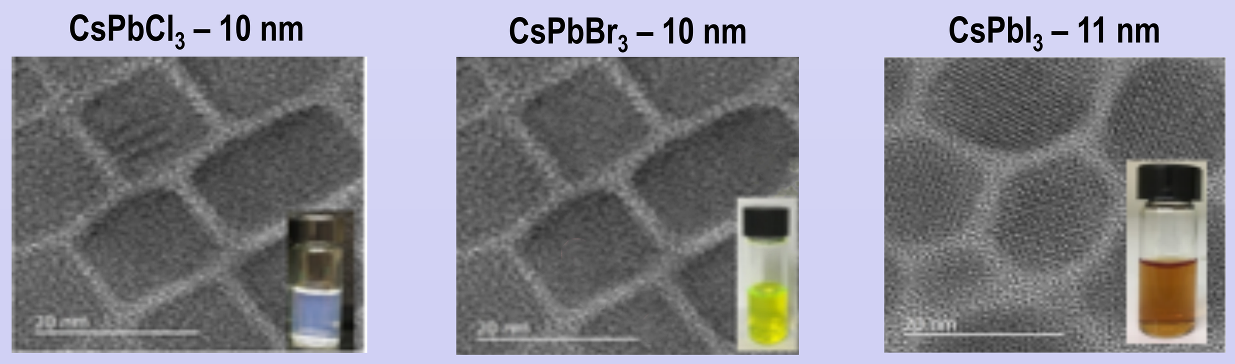

Figure 3: TEM scans of representative perovskite nanoparticles. Note the cuboidal structures $CsPbBr_3$ and $CsPbCl_3$ and the hexagonal structure of the $CsPbI_3$. All of the perovskites have an size close to 10 nm.

Perovskite Nanomaterials

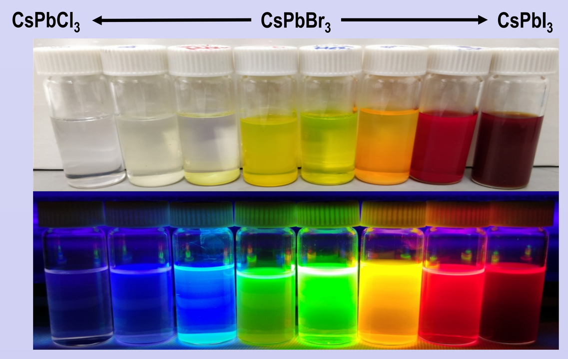

Figure 4: The images of synthesized perovskites with different halides and under UV illumination (bottom).

Results and Discussion

Optical Properties of the Synthesized $CsPbX_3$ Perovskite Nanomaterials

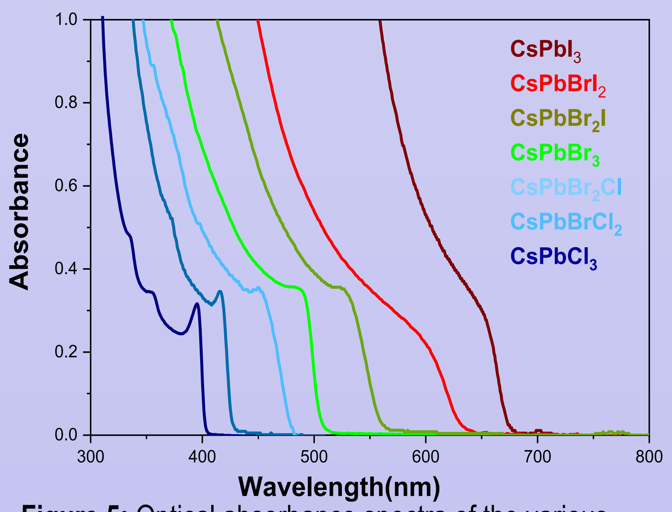

Figure 5: Optical absorbance spectra of the various inorganic halide perovskites synthesized. It is quite evident the shift to longer wavelengths with change from chloride to iodide. Also the perovskites absorb strongly in the visible region.

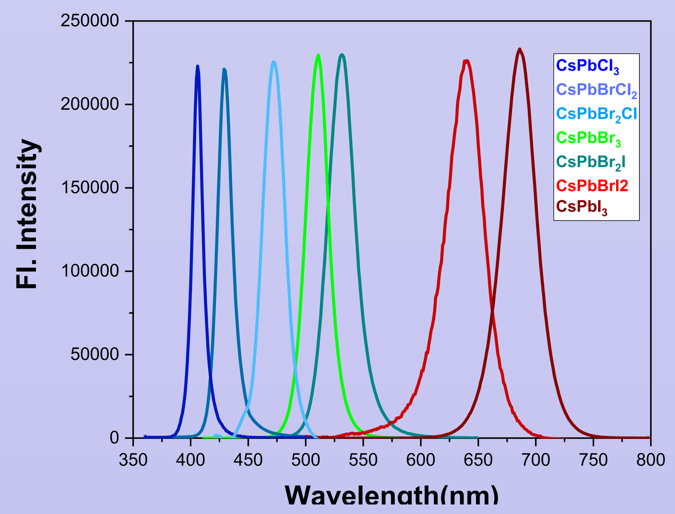

Figure 6: Photoluminescence spectra of the various inorganic halide perovskites synthesized. All perovskite nanomaterials give strong luminescence in the visible region with narrow emission band widths.

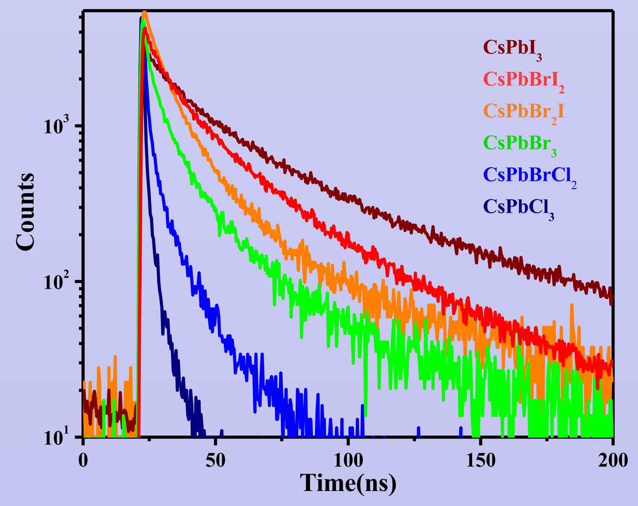

Figure 7: Lifetime decay traces of the synthesized perovskite nanomaterials. The lifetimes of Iodide perovskites are longer than chloride and match with what was reported earlier.

Interaction of Perovskite Nanomaterials with P3HT (Poly(3-hexylthiophene-2,5-diyl))

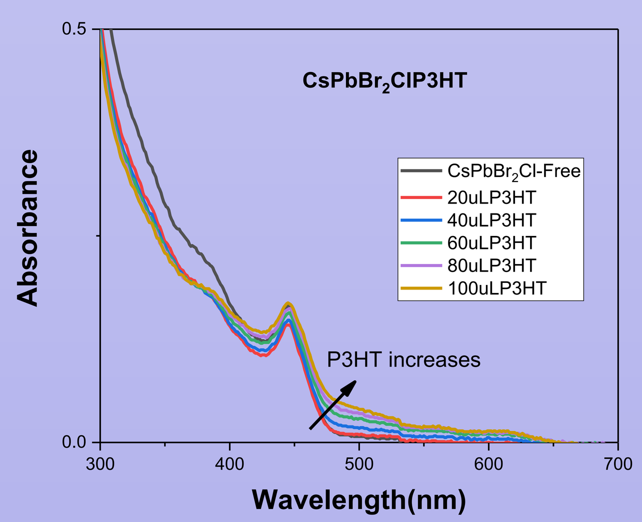

Figure 8: Optical absorbance spectra of $CsPbBr_2Cl$ perovskite at varying P3HT concentrations. No change in the absorption is observed suggesting minimal ground state interaction.

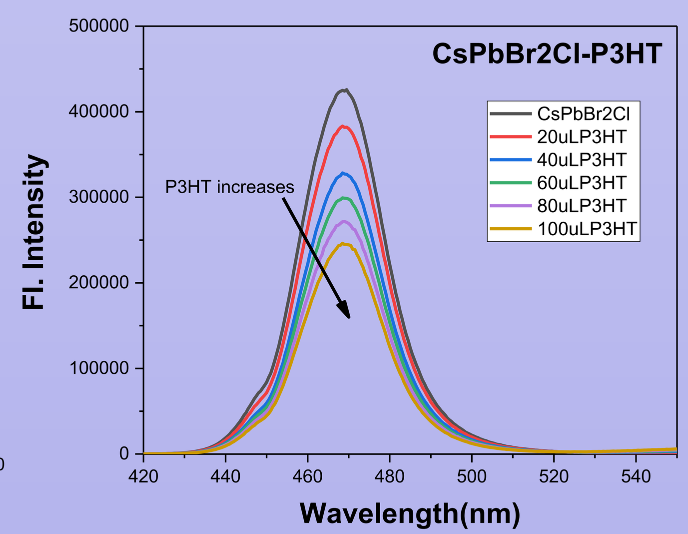

Figure 9: Photoluminescence spectra of $CsPbBr_2Cl$ at varying P3HT concentrations. P3HT seems to quench the PL of perovskite and probably has donor-acceptor interaction.

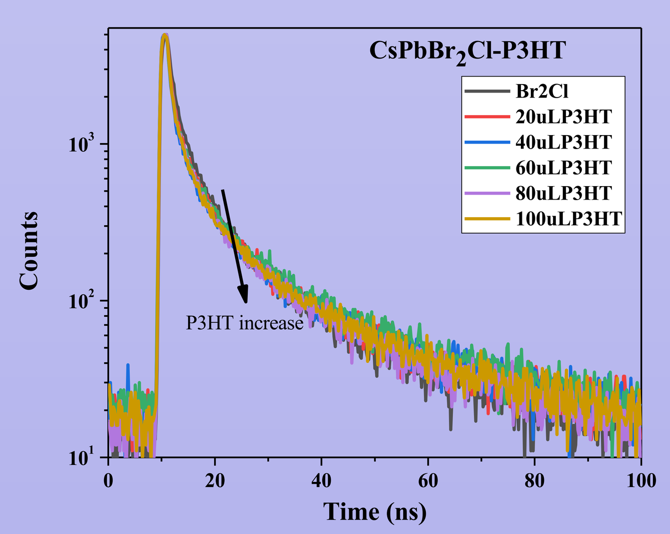

Figure 10: Lifetime scan of $CsPbBr_2Cl$ at varying P3HT concentrations. Lifetime decreased with P3HT suggesting an excited state interaction via charge transfer.

Interaction of Perovskite with PDMS (Polydimethylsiloxane)

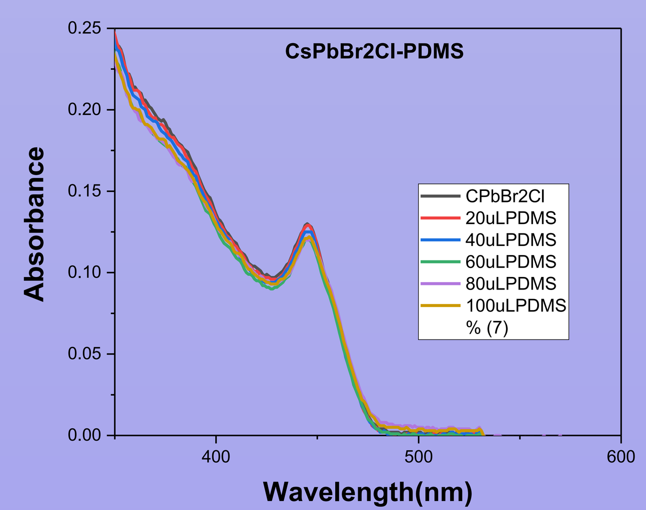

Figure 11: Optical absorbance spectra of $CsPbBr_2Cl$ perovskite at varying PDMS concentrations. No change in the absorption is observed suggesting minimal ground state interaction.

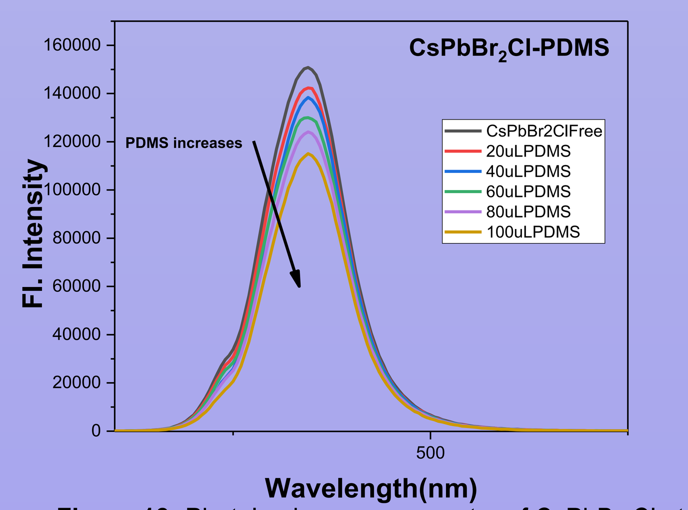

Figure 12: Photoluminescence spectra of $CsPbBr_2Cl$ at varying PDMS concentrations. Very little change in PL is observed indicating no excited state interaction but made the sample more flexible.

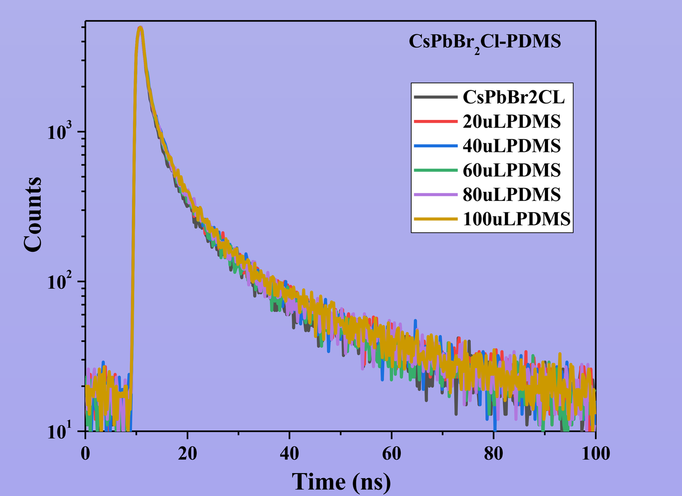

Figure 13: Lifetime scan of $CsPbBr_2Cl$ at varying PDMS concentrations. No change in PL lifetimes were observed indicating no excited state interaction.

Interaction of Perovskite with PDMS (Polydimethylsiloxane)

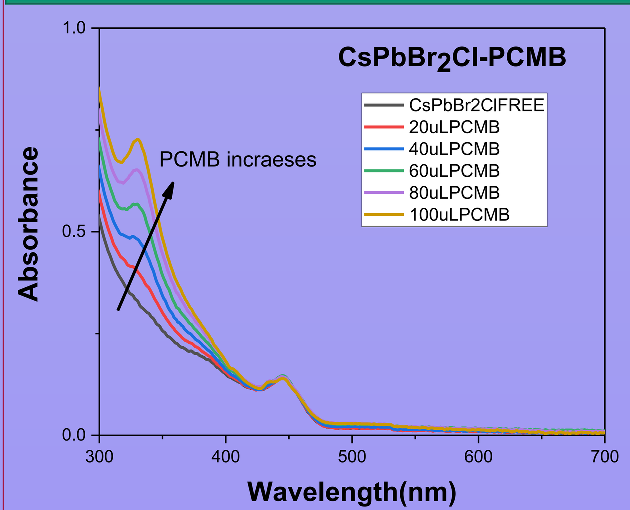

Figure 14: Optical absorbance spectra of $CsPbBr_2Cl$ perovskite at varying PCBM concentrations. No change in the absorption is observed suggesting minimal ground state interaction.

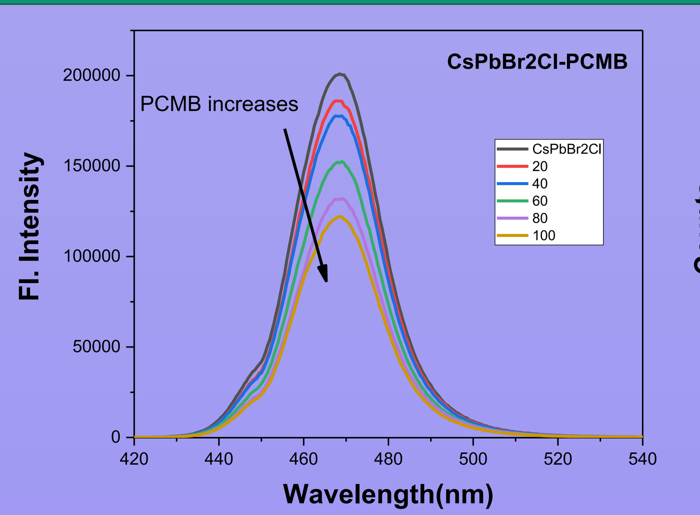

Figure 15: Photoluminescence spectra of $CsPbBr_2Cl$ at varying PCBM concentrations. PCBM seems to quench the PL of perovskite and probably has donor-acceptor interaction.

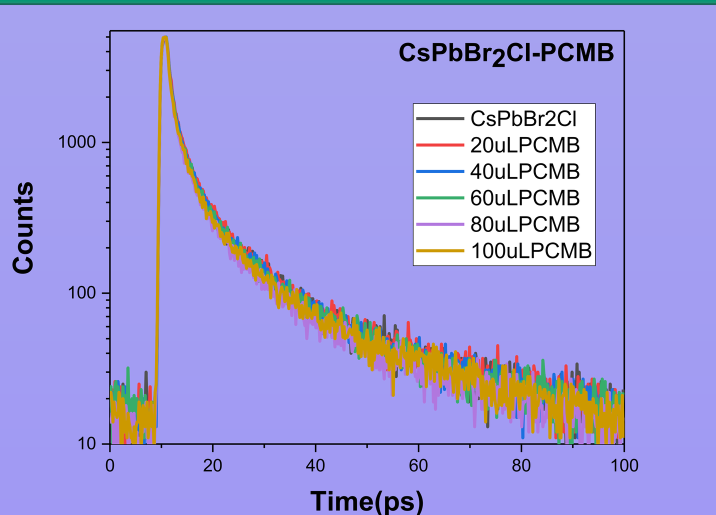

Figure 16: Lifetime scan of $CsPbBr_2Cl$ at varying PCBM concentrations. Lifetime decreased with PCBM suggesting an excited state interaction via charge transfer.

LED Displays (Layer by Layer (LbL))

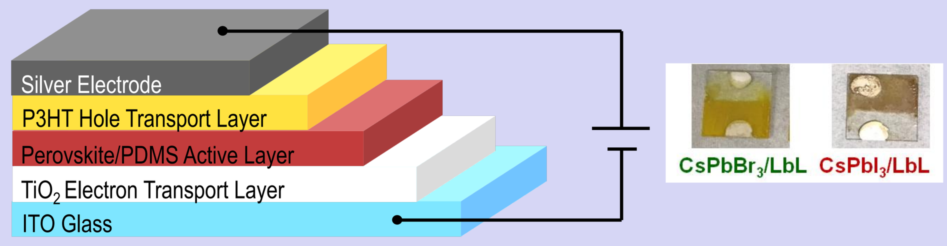

Figure 17: Schematic representation of the layer by layer perovskite display structure that was fabricated in the laboratory. The layers were spin-coated and drop-casted. Right side shows the picture of the displays that were fabricated.

LED Displays (Bulk-Heterojunction (BHj))

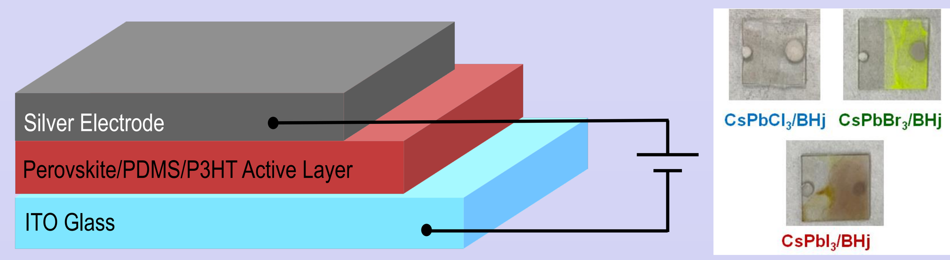

Figure 18: Schematic representation of the bulk-heterojunction perovskite display structure that was fabricated in the laboratory. The layers were drop-casted. Right side shows the picture of the displays that were fabricated.

Displays and their Luminescence

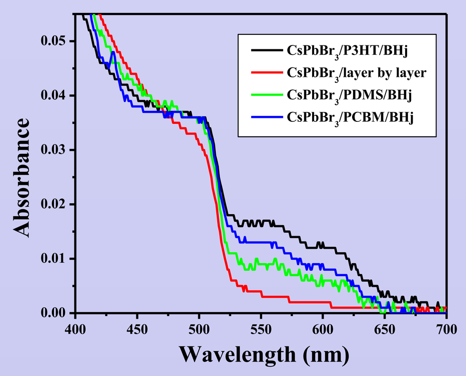

Figure 19: Optical absorption spectra of fabricated displays from $CsPbBr_3$. All of them show good absorption in the visible region.

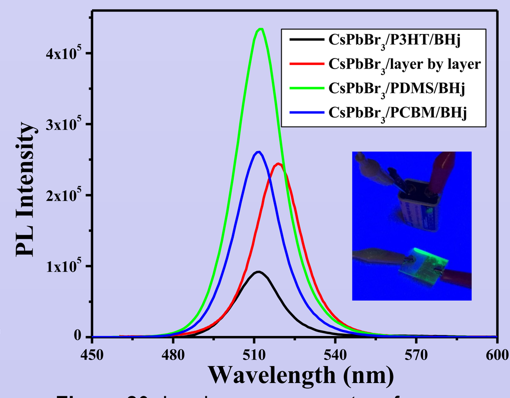

Figure 20: Luminescence spectra of fabricated displays from $CsPbBr_3$. P3HT quenched the PL but BHj is better over LbL.

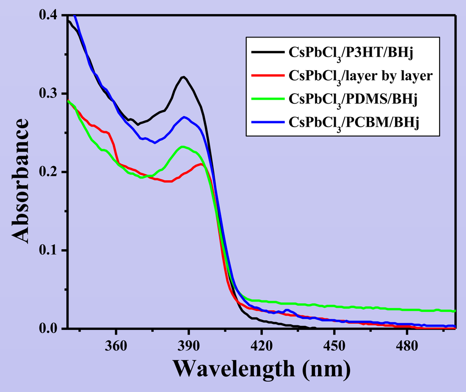

Figure 21: Optical absorption spectra of fabricated displays from $CsPbCl_3$. All of them show good absorption in UV region.

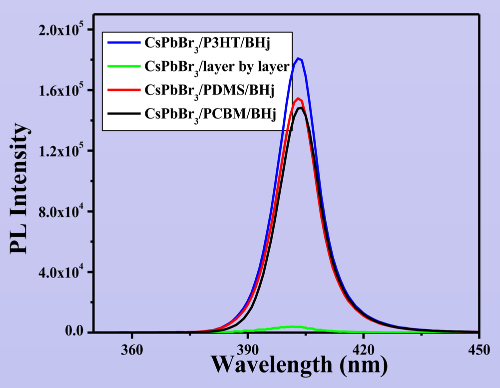

Figure 22: Luminescence spectra of fabricated displays from $CsPbCl_3$. LbL fabrication quenched the PL and was not good and BHj was better.

Conclusions

- $CsPbX_3$ (X=Cl, Br, I and mixed halide) perovskite nanostructures were synthesized using hot injection method with oleic acid as capping agent. The TEM images show that all perovskite nanocomposites have cuboidal symmetry except that of $CsPbI_3$ that has a hexagonal structure.
- All synthesized perovskites have shown absorption and photoluminescence spectra similar to what was reported earlier and narrow PL bands were observed. The lifetimes increased from chloride to iodide indicating longer exciton lifetimes and binding energies suitable for LED applications.
- Perovskite-polymer interactions were studied so that perovskites can be mixed with polymers to make them flexible. Steady-state and time-resolved PL measurements have shown PDMS is be the ideal polymer to make perovskite-polymer nanocomposites.
- Two types of displays were fabricated – One via the layer by layer assemblies with TiO_2/perovskite/P3HT and another via bulk-heterojunction with ITO/polymer-perovskite composites. Absorption and luminescence was tested for both display to determine efficacy.
- Bulk-heterojunction approach of making LEDs gave strong luminescence for all perovskite nanocomposites when compared to layer by layer approach and shows these materials can be screen printed to make flexible LED displays on ITO-coated plastic.

References

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Images:

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