ABSTRACT

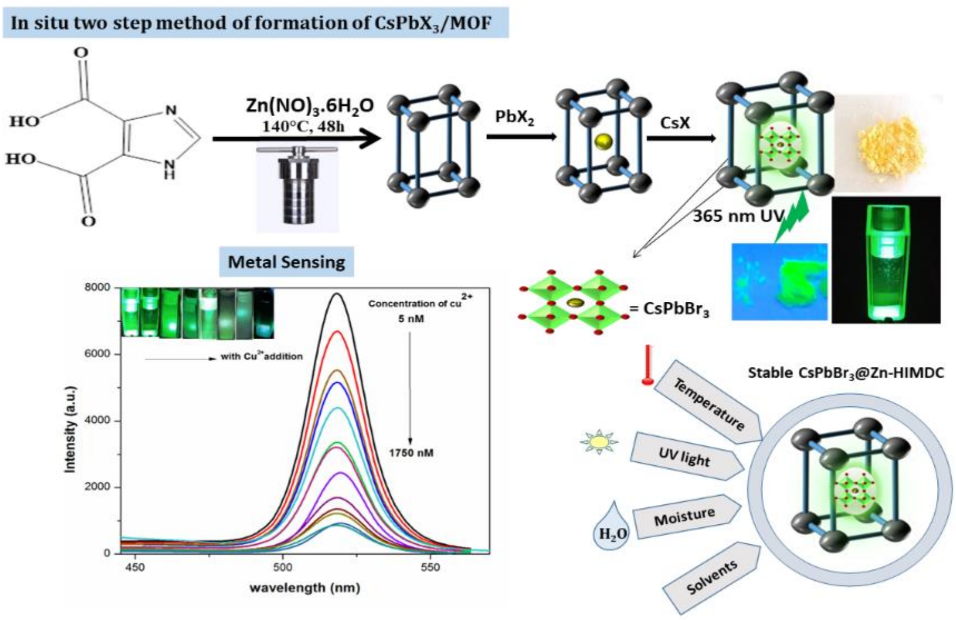
The rise of halide based perovskites is second to none in the field of optoelectronics, owing to their superior optical and electrical properties including direct band gap, longer carrier life time, high absorption coefficient, very high photo luminescence quantum yield, narrow and intense emission, tunable emission wavelength, etc. The physical and chemical nature of perovskite nano crystals (PeNCs) changes with environmental conditions like temperature, moisture, gases, solvents, ions etc. All these unique features of perovskites have allowed them to serve as ideal probes for variety of sensing applications. Inorganic $CsPbX_3$ (X=Br, Cl, I) PeNCs with the conventional perovskite architecture have recently demonstrated great potential as chemical sensor materials owing to their superior fluorescence characteristics. However, the degradation of perovskites in a humid environment leads to a decrease in photoluminescence intensity, making them non-functional as fluorescence probes. Metal organic frameworks (MOF) with high porosity, and large surface area, can offer an intriguing platform as a promising support matrix for the development of functional nanocomposites. Hence, the primary focus of this thesis is to synthesize and characterize stable and highly luminescent $CsPbBr_3$/MOF hybrid composites and explore their optically active sensing properties for the recognition of various target analytes of interest. In this research, different MOF matrix [e.g., Zinc (II) imidazole-4,5-dicarboxylate (Zn-HIMDC), zeolitic imidazole framework (ZIF-8), hierarchically porous zeolitic imidazole framework (HZIF-8), Eu (III) benzene-1,4-dicarboxylate (Eu-BDC)] are used to produce Perovskite-MOF composites. Various fluorescence sensing techniques e.g., fluorescence quenching (turn off), fluorescence enhancement (turn on), and fluorescence intensity ratio method (FIR) are employed to detect the target analytes. The thesis is subdivided into six chapters. The following comprises an overview of the chapters in the thesis-

Chapter 1. General Introduction

The first chapter includes a general introduction to the perovskite-based materials. This chapter provides a brief description of research background and the motivation behind the current investigation along with a brief historical background on perovskite materials. Perovskite materials are briefly described, along with their classifications and attributes. The crystal structure and general properties of metal halide perovskites are mentioned in detail in this chapter. Several synthetic routes of perovskites nanocomposites with their potential applications as sensor materials are emphasized. The applications of perovskite materials in solar cells and light emitting diodes are also highlighted in this chapter. The chapter

concludes with a discussion of the objectives and plan of the present study. The experimental parts were presented in next subsequent chapters (*viz.* Chapter 2, 3, 4 and 5).

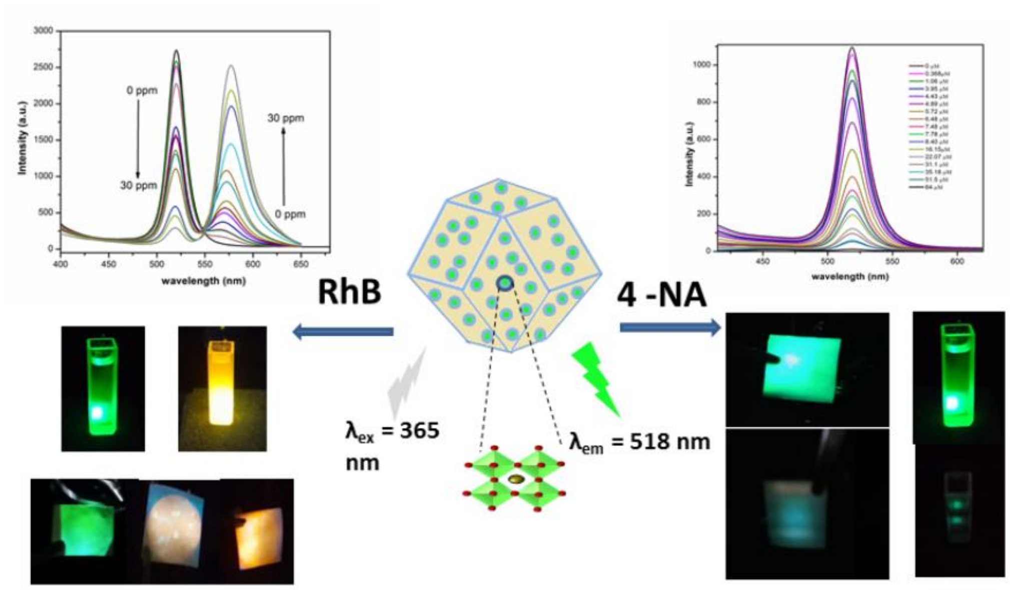
Chapter 2. $CsPbX_3$ (X= Br, Br/Cl) perovskite quantum dots stabilized in Zinc (II) imidazole-4,5-dicarboxylate metal organic framework for metal ion detection



This chapter presents the synthesis of a stable $CsPbX_3$ perovskite nanocomposite via a surfactant free two step in situ growth method by introducing them into porous Zn-HIMDC metal organic framework (MOF). The structural, morphological, and optical characterization of the synthesized composite are discussed herein. The stability tests reveal that $CsPbBr_3$/MOF composite display remarkable stability against moisture, ultraviolet light, and heat which reveals their excellent luminescent property over bare $CsPbBr_3$ quantum dots. Furthermore, this study utilizes its superior stability and processibility by using it as a fluorescent probe for metal sensing and was found to be very sensitive and selective towards the detection of Cu^{2+} metal ions with a LOD value of 63 nM. The $CsPbBr_3$/MOF composite displays excellent quenching efficiency up to 89.9% for Cu metal ion. The mechanism of current investigation also mentioned in this chapter. The quenching of $CsPbBr_3$/MOF signal was believed to occur via a dynamic quenching and electron transfer process.

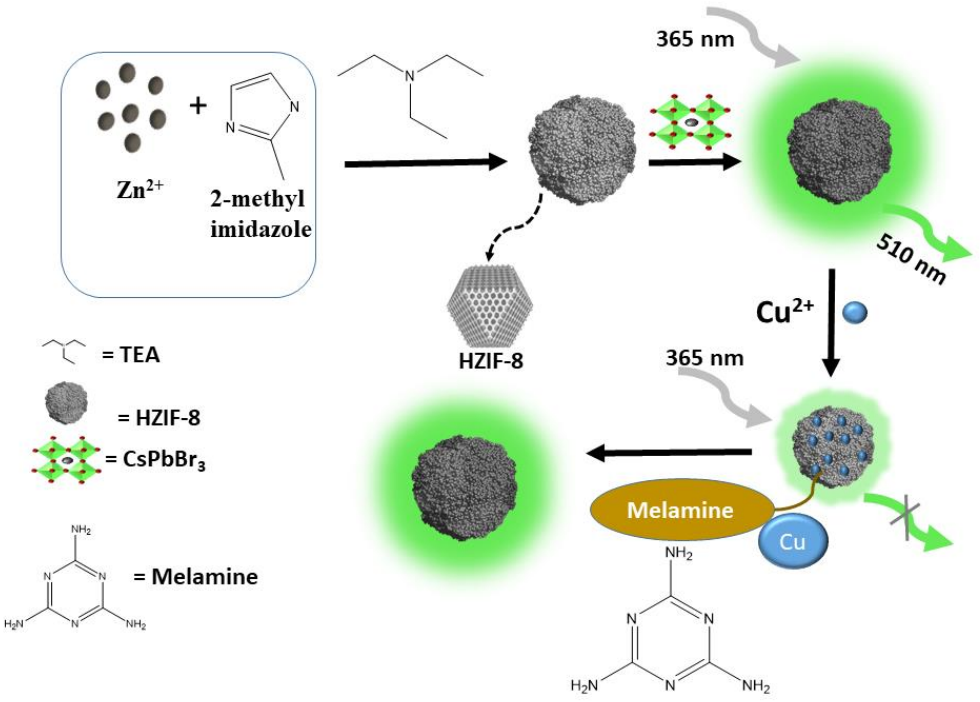
ABSTRACT

Chapter 3. Synthesis of $CsPbBr_3$ /ZIF-8 Pe-MOF composite: A fluorometric sensing probe for 4 – nitroaniline and rhodamine blue



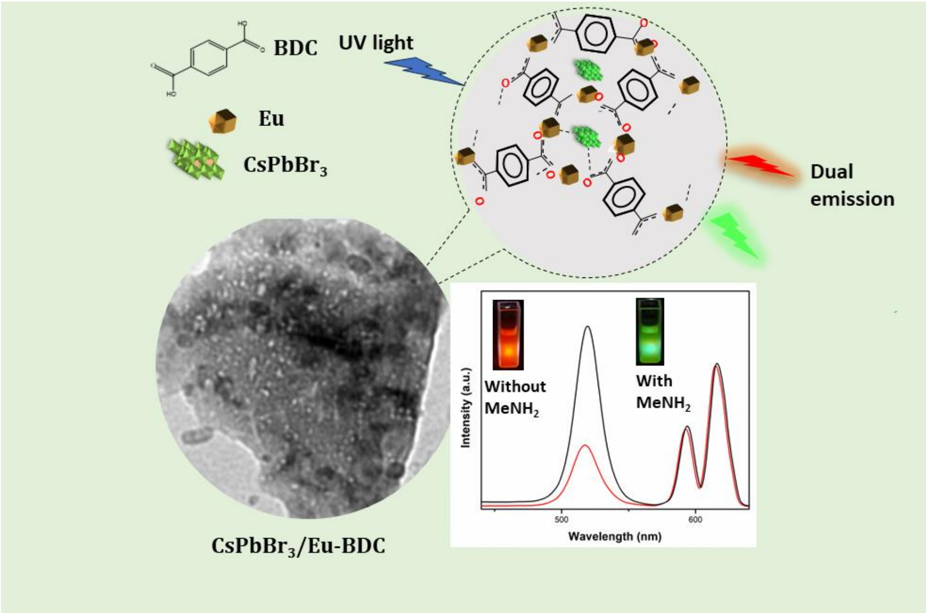
This chapter introduces design of a fluorescence sensor using $CsPbBr_3$ integrated chemically stable zeolitic imidazole framework (ZIF-8), via an in situ one step technique and established its stability in ambient atmosphere. Next, the luminescent $CsPbBr_3$@ZIF-8 composite's ability to recognize organic pollutants (nitroaromatics and dye molecules) was explored. Among various nitroaromatics, 4-nitroaniline quenches the luminescence signal of $CsPbBr_3$@ZIF-8 at 520 nm very effectively with a quenching efficiency value of 98%. It can selectively detect 4-nitroaniline having a detection limit of 8.367 ppb and a fast response time of 25 sec. The detection limit for rhodamine blue dye molecules was determined to be 0.088 ppm. The chapter additionally addresses the potential of this suggested sensor as a cheap portable visual test paper probe for analyte detection. A comprehensive investigation found that the quenching of the fluorescence signal occurred via Fluorescence resonance energy transfer (FRET) for rhodamine blue dye and a H-bonding interaction induced trap density mediated quenching mechanism was responsible for 4-NA detection.

Chapter 4. A hierarchically porous MOF confined $CsPbBr_3$ quantum dots: Fluorescence switching probe for detecting melamine in food samples



In this chapter, $CsPbBr_3$ is confined in a hierarchically porous ZIF-8 metal organic framework (HZIF-8) through a simple two step in situ growth method. $CsPbBr_3$ PeQDs are uniformly distributed within the HZIF-8 MOF matrix and exhibited intense green emission centered at 510 nm with a FWHM value of 25 nm in ambient conditions. The $CsPbBr_3$/HZIF-8 composite showed enhanced stability against moisture and UV light. The intense PL emission of the nanocomposite was well maintained in an aqueous solution also. $CsPbBr_3$/HZIF-8 composite was then utilized as an on-off-on luminescent probe for the detection of melamine. The Cu^{2+} metal ion can act as an effective quencher that quenches the emission of $CsPbBr_3$/HZIF-8 sensor. It was then recovered with the addition of the melamine to the fluorescence system, due to the strong interaction between the multifunctional melamine nitrogen and Cu^{2+} metal ion. The designed sensor is found to be very sensitive toward melamine detection, with a limit of detection value of around 2.64 nM for melamine. The practical applicability of the sensor is applied for the analysis of melamine in milk samples. Sensitivity and selectivity study of the designed sensor has been illustrated in this chapter.

Chapter 5. Dual emitting $CsPbBr_3$/Eu-BDC composite as a ratiometric photoluminescent turn on probe for aliphatic amine sensing



This chapter mainly highlighted the design of a ratiometric fluorescence sensor for toxic volatile organic amines. The ratiometric probes have advantages of high accuracy and sensitivity over single emission probe sensor. Thereby, in an attempt to create a self-calibrating amine sensor, a dual emitting fluorescent composite is made from combining $CsPbBr_3$ and Eu-BDC. The results presented here establishes the suggested sensor's quick and selective turn-on PL response to aliphatic organic amine derivatives. In presence of amines the selected $CsPbBr_3$/Eu-BDC sensor exhibits an enhancement of the PL signal of $CsPbBr_3$ at 518 nm and the Eu-BDC signal at about 615 nm served as a standard to construct the ratiometric sensing system. A visual color change from red to green is observed with the incremental addition of methyl amine to the probe. The present fluorescence sensor has been successfully applied for monitoring the meat freshness.

Chapter 6. Conclusion and future scope

This final chapter provides a summary of the previous chapters' major findings and discusses the potential future implications/scope of this study. In this research, as an approach towards the improvement of the stability, $CsPbX_3$ are incorporated in different porous MOF matrix (Zn-HIMDC, ZIF-8, HZIF-8, Eu-BDC) to produce perovskite/MOF hybrid composite. They exhibit superior optical properties when compared to their individual counterparts. All the

relevant properties of perovskites, such as structural, morphological, and optical properties were thoroughly studied in this thesis. Utilizing the as mentioned excellent properties of stabilized PeNCs, we have used the nanocomposites for the luminescent based detection of various target analytes such as Cu^{2+} metal ion, melamine in food samples, organic amines and dye molecules. The target analytes were detected by employing methods such as fluorescence quenching (turn off), fluorescence enhancement (turn on), and fluorescence intensity ratio method (FIR). Pe-MOF composite are in their infancy of research and there can be many unexplored opportunities. Therefore, further efforts will be performed to find useful applications for this material.