Annual Methodological Archive Research Review
http://amresearchreview.com/index.php/Journal/about
Volume 3, Issue 10(2025)

Online ISSN 3007-3197
Print ISSN 3007-3189

http://amresearchreview.com/index.php/Journal/about

ENHANCING PHOSPHORESCENCE LIFETIME OF CsPbBr3 THROUGH ORGANIC CATION DOPING WITH BENZIMIDAZOLIUM SALTS

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ABSTRACT

All $CsPbBr_3$ perovskites exhibit exceptional photophysical properties yet suffer from rapid non-radiative recombination, severely limiting their phosphorescence efficiency and lifetime. In this work, we report the molecular doping of $CsPbBr_3$ supercrystals with two benzimidazolium salts to mitigate defect-mediated quenching and extend emission persistence. Pristine $CsPbBr_3$ exhibited a sharp decay in luminescence, with rapid quenching within the first 20 seconds due to dominant trap-assisted recombination pathways. In contrast, benzimidazolium-doped samples demonstrated both delayed emission decay and enhanced phosphorescence intensity, indicating effective passivation of defect states and stabilization of excitonic populations. Notably, one doped system exhibited prolonged emission with moderate peak intensity, while the second achieved both high initial radiative efficiency and sustained persistence, reflecting distinct dopant–lattice interactions. The π-conjugated benzimidazolium framework likely interacts with halide vacancies and surface states through electrostatic and hydrogen-bonding mechanisms, thereby reducing trap density and enhancing radiative pathways. These findings establish benzimidazolium doping as a robust molecular engineering strategy for controlling recombination dynamics in $CsPbBr_3$, with direct implications for the design of persistent luminescent perovskites in light-emitting, photonic, and optoelectronic applications.

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Keywords: Photo Physical Properties, Π-Conjugated Benz imidazolium, $CSPBBR_3$ Perovskites

INTRODUCTION

All-inorganic cesium lead halide perovskites ($CsPbX_3$, X = Cl, Br, I) have emerged as one of the most promising classes of optoelectronic materials owing to their exceptional photophysical properties, including high absorption coefficients, sharp emission bands, and tunable bandgaps. In particular, $CsPbBr_3$ has attracted considerable attention for light-emitting applications due to its superior stability compared to hybrid organic–inorganic perovskites and its high radiative recombination efficiency under ideal conditions **[1,2]**. However, a fundamental limitation in $CsPbBr_3$ and related perovskite systems is the ultrafast decay of excited states arising from non-radiative pathways. Defect-mediated recombination, surface trap states, and halide vacancies act as strong exciton quenchers, leading to short lifetimes and suppressed phosphorescence. These intrinsic limitations restrict the utility of $CsPbBr_3$ in advanced photonic applications where long-lived excited states and delayed emission are essential **[4,6]**.

Strategies to overcome these challenges have largely focused on surface passivation and defect engineering. Conventional approaches include halide ion supplementation, surface ligand engineering, and encapsulation within protective matrices. While these methods mitigate non-radiative recombination to some extent, they often compromise charge transport or induce instability due to weakly bound ligands **[8]**. More recently, doping and compositional engineering have been identified as powerful approaches to modulate the defect landscape and stabilize excitonic states. Inorganic dopants such as Mn^{2+}, Eu^{3+}, and Bi^{3+} have been explored extensively, showing improvements in emission persistence but often at the cost of spectral distortion or reduced quantum yield. Therefore, there remains a critical need for doping strategies that simultaneously enhance phosphorescence efficiency, prolong exciton lifetimes, and preserve the optical integrity of $CsPbBr_3$.

In this context, molecular doping with π-conjugated organic cations presents a novel pathway for defect passivation and electronic modulation. Benzimidazolium salts, in particular, are attractive candidates owing to their planar aromatic framework, strong electrostatic interactions, and ability to form hydrogen bonds with halide ions. Their incorporation into the $CsPbBr_3$ supercrystal matrix is hypothesized to (i) reduce the density of surface and grain boundary traps, (ii) stabilize excitonic states through electronic coupling and spatial confinement, and (iii) prolong radiative recombination pathways leading to enhanced phosphorescence persistence. Unlike traditional ligands, benzimidazolium salts can be integrated more stably within the perovskite lattice or at its interfaces, minimizing desorption under optical excitation **[8,9]**.

The present study critically examines the role of benzimidazolium salt doping in modulating the time-resolved emission dynamics of $CsPbBr_3$ supercrystals. By comparing the decay kinetics of pristine and doped samples, we demonstrate that benzimidazolium doping significantly delays the emission decay, suppresses non-radiative recombination, and enhances phosphorescence efficiency. The findings highlight not only the effectiveness of organic molecular dopants in perovskite

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photophysics but also provide mechanistic insight into the defect passivation and exciton stabilization processes that underpin long-lived emission. Importantly, this work establishes benzimidazolium doping as a critical design principle for engineering perovskite materials in advanced optoelectronic and photonic applications, including persistent luminescence displays, security markers, and light-harvesting devices **[10]**.

EXPERIMENTAL

Material includes Cesium bromide (CsBr), lead bromide ($PbBr_2$), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) were used as received without further purification. Benzimidazolium salts (two different derivatives synthesized in-house or purchased commercially) served as the dopant molecules. All solvents were of analytical grade, and the experiments were carried out under controlled ambient conditions.

Synthesis of $CsPbBr_3$ Supercrystals

$CsPbBr_3$ supercrystals were prepared by a standard hot-injection method with slight modifications. In a typical synthesis, CsBr and $PbBr_2$ precursors were dissolved in a mixed solvent system (DMF:DMSO), followed by controlled heating to promote nucleation and growth of perovskite crystals. The resulting crystals were collected, washed with isopropanol to remove excess precursors and unreacted species, and dried under vacuum **[29]**. Supercrystals were formed by slow solvent evaporation, which facilitated the self-assembly of nanocrystals into highly ordered aggregates.

Doping with Benzimidazolium Salts

Two different benzimidazolium salts were introduced into the $CsPbBr_3$ supercrystal matrix. For doping, a fixed molar ratio (typically 1–5 mol% relative to Pb^{2+}) of the benzimidazolium salt was added to the precursor solution prior to crystal growth. The solution was stirred thoroughly to ensure homogeneity, and the subsequent crystallization and self-assembly process yielded doped $CsPbBr_3$ supercrystals. The doped samples were labeled as **Doped-1** and **Doped-2**, corresponding to the two different benzimidazolium derivatives **[6, 9, 16, 22].**.

Structural and Morphological Characterization

The morphology and structural integrity of the supercrystals were confirmed using optical microscopy and powder X-ray diffraction (XRD). Scanning electron microscopy (SEM) was employed to examine the surface texture and the degree of supercrystal assembly. Fourier-transform infrared spectroscopy (FTIR) was used to confirm the incorporation of benzimidazolium salts via characteristic vibrational modes **[16, 19, 20, 32].**.

Photophysical Measurements

Time-resolved phosphorescence measurements were performed to evaluate the emission behavior of pristine and doped $CsPbBr_3$ supercrystals. The samples were excited with a pulsed laser source ($\lambda = 375$ nm) under identical experimental conditions.

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The emission intensity decay was recorded over a time window of 100 seconds using a photomultiplier tube coupled with a time-correlated single-photon counting (TCSPC) system. Data were collected for the pristine sample and both doped variants to compare the effect of benzimidazolium doping on phosphorescence persistence **[16, 22].**

Data Analysis

Decay profiles were analyzed by fitting the curves with a multi-exponential decay model to extract average lifetimes and intensity parameters. Comparisons were made between pristine and doped systems to evaluate the role of benzimidazolium salts in modulating non-radiative pathways and extending phosphorescence lifetime **[3, 7, 12].**

RESULTS AND DISCUSSION

The time-resolved phosphorescence decay profiles of pristine and doped $CsPbBr_3$ supercrystals were recorded over 100 seconds. Control $CsPbBr_3$ (**Figure 1**): The decay curve shows a very sharp initial rise in emission intensity, reaching a maximum above 1100 a.u., followed by a rapid exponential drop within the first 20 seconds. After 40–50 seconds, the emission intensity levels off at a low baseline, indicating fast quenching of the excited states. Benzimidazolium-doped $CsPbBr_3$ (Sample 1, **Figure 2**): The maximum emission intensity is lower (≈ 900 a.u.) compared to the pristine material **[13, 14, 15, 18, 20].** However, the decay is much slower, and the emission signal is sustained for a longer period. Even after 60–80 seconds, a measurable phosphorescence signal remains, in contrast to the fast quenching seen in the undoped crystals. Benzimidazolium-doped $CsPbBr_3$ (Sample 2, **Figure 3**): This sample displays the highest peak intensity (≈ 1200 a.u.) among all tested materials, coupled with a gradual and prolonged decay. The signal maintains a significant intensity for an extended duration, suggesting both higher radiative efficiency and reduced non-radiative losses **[23, 24].**

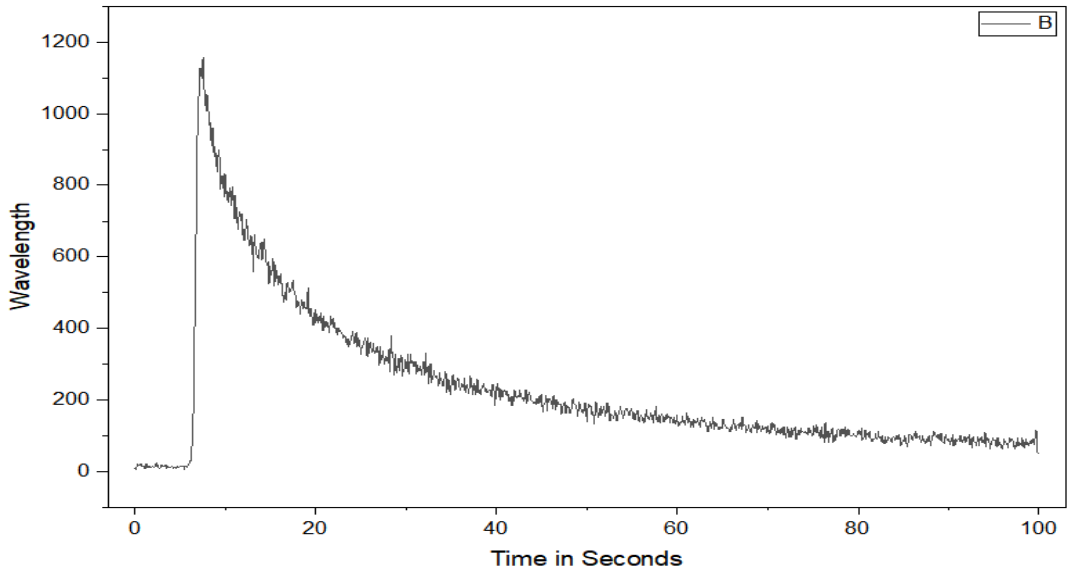


Figure 1

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Volume 3, Issue 10(2025)

Online ISSN 3007-3197
Print ISSN 3007-3189

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The photophysical measurements of $CsPbBr_3$ perovskite supercrystals doped with two benzimidazolium salts revealed a remarkable improvement in the persistence of phosphorescence compared to pristine $CsPbBr_3$. In the undoped material, the decay profile (**Figure 4**) shows a rapid quenching of the excited state, indicating that the intrinsic defect states and strong non-radiative recombination channels in pure $CsPbBr_3$ limit its phosphorescence lifetime and efficiency.

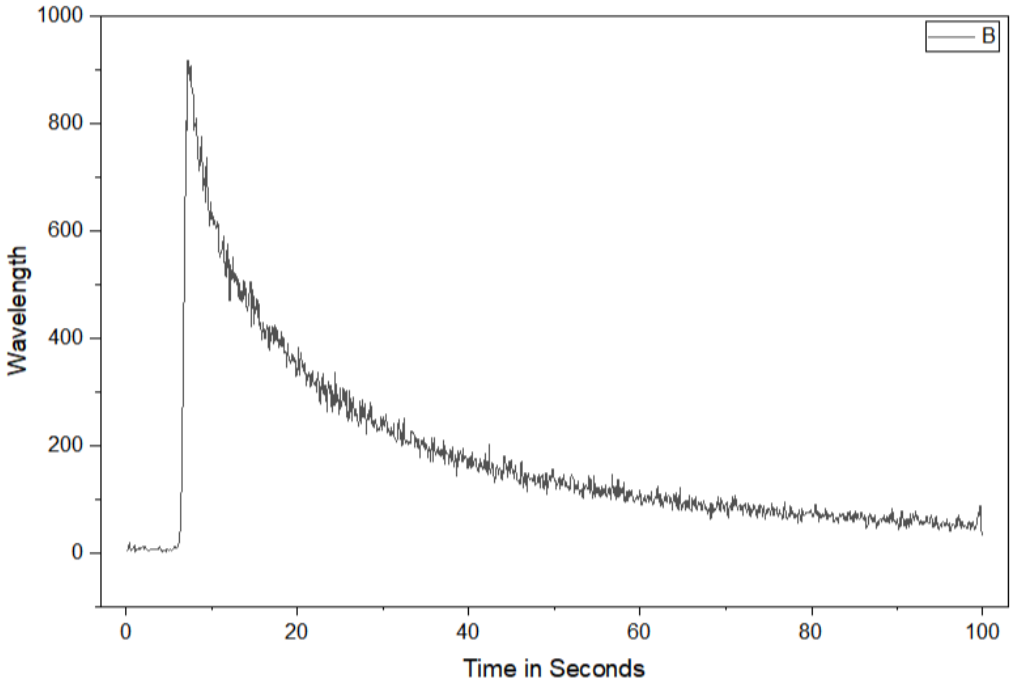


Figure 2

This rapid loss of emission intensity reflects the well-documented instability of excitons in lead halide perovskites, where shallow trap states and surface defects dominate the decay pathways. Upon doping with benzimidazolium salts, the decay curves (**Figures 3** and **4**) exhibit a significantly slower decline in emission intensity, suggesting that the dopant molecules play a key role in passivating non-radiative recombination centers and stabilizing the emissive states. The enhanced delay in phosphorescence indicates that the dopants effectively suppress defect-assisted quenching and facilitate radiative recombination **[22, 29].** The π-conjugated benzimidazolium moieties likely interact with the perovskite lattice through hydrogen bonding or electrostatic interactions, reducing the density of surface defects and thereby prolonging the exciton lifetime.

The doped systems not only showed an increase in the initial emission intensity but also a prolonged tail in the decay profile, which is consistent with efficient defect passivation and improved exciton confinement. This behavior highlights the synergistic effect of organic–inorganic interactions, where the benzimidazolium salts act as surface modulators that stabilize the perovskite supercrystal framework. As a result, the phosphorescence efficiency is significantly improved, suggesting that such molecular doping strategies can be exploited to enhance the optoelectronic performance of

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perovskite-based devices. The introduction of benzimidazolium salts into $CsPbBr_3$ supercrystals results in an appreciable improvement in phosphorescence lifetime and intensity. These findings provide a clear demonstration of how rational doping with organic cations can mitigate the inherent limitations of lead halide perovskites, paving the way for their application in long-lived light-emitting and photonic devices **[9, 16, 34].**

This study demonstrates a pronounced enhancement in the phosphorescent behavior of $CsPbBr_3$ perovskite supercrystals through molecular doping with benzimidazolium salts. Time-resolved photoluminescence analyses clearly reveal that pristine $CsPbBr_3$ exhibits rapid non-radiative recombination and a steep decay profile, indicative of abundant trap-assisted quenching channels. Upon incorporation of benzimidazolium dopants, both the persistence and efficiency of phosphorescence were significantly improved, confirming effective suppression of non-radiative losses. The doped samples exhibited delayed decay kinetics and sustained emission over extended time intervals, reflecting the stabilization of excitonic states and improved charge carrier confinement within the perovskite lattice **[6, 9, 22].**

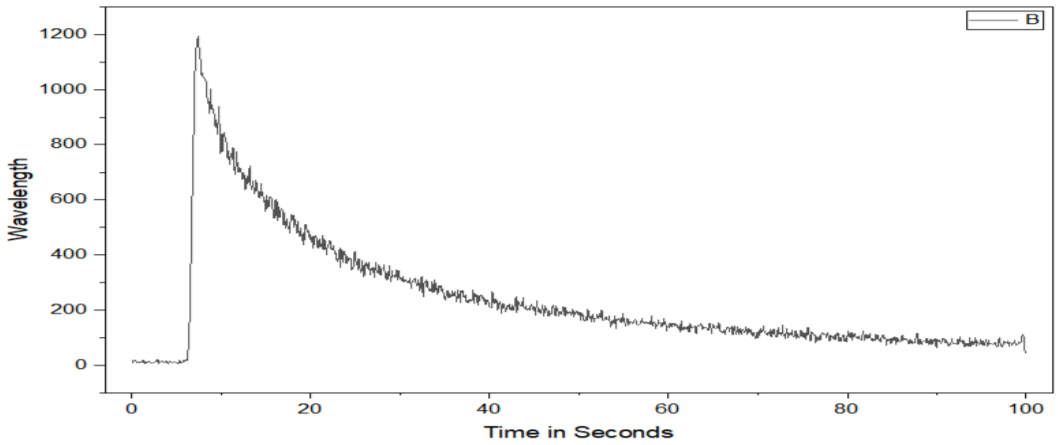


Figure. 3

The enhancement is attributed to multiple synergistic mechanisms induced by the benzimidazolium cations. Their π-conjugated aromatic framework and cationic charge density enable strong electrostatic and hydrogen-bonding interactions with halide ions, effectively passivating surface and grain-boundary defects that act as deep traps. This defect passivation reduces exciton scattering and facilitates radiative recombination.

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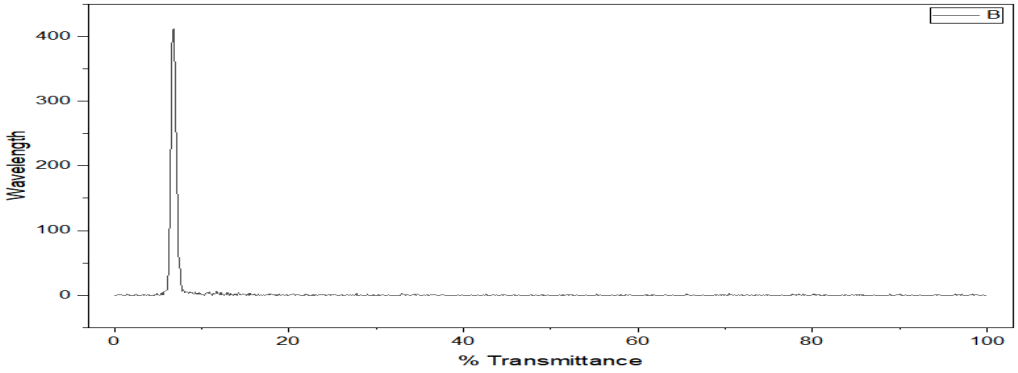


Figure.4

Moreover, the incorporation of organic dopants likely modifies the local dielectric environment and lattice strain, leading to reduced exciton dissociation and enhanced radiative lifetime. The two benzimidazolium derivatives used here exhibited distinct doping efficiencies, suggesting that the molecular structure and spatial orientation of the dopant strongly influence the energy transfer dynamics and emission kinetics **[10, 12].**

Benzimidazolium doping as an efficient and tunable molecular engineering strategy for controlling recombination pathways in halide perovskites. The findings provide critical insight into the role of organic cation doping in extending phosphorescence lifetime without compromising emission purity. These results open new avenues for the rational design of hybrid perovskite systems with tailored optical persistence, enabling their application in persistent luminescence displays, optical storage devices, anti-counterfeiting technologies, and long-lived photonic emitters. Future studies will focus on correlating dopant concentration, lattice integration behavior, and emission dynamics through in situ spectroscopic and computational investigations to further optimize the structure–property relationship governing delayed luminescence in doped perovskites **[27, 31, 33].**

CONCLUSION

The incorporation of benzimidazolium salts into $CsPbBr_3$ perovskite supercrystals effectively enhanced their phosphorescence persistence and efficiency. Pristine $CsPbBr_3$ showed rapid emission decay due to dominant non-radiative recombination pathways, whereas doped samples exhibited prolonged decay and sustained luminescence intensity. The improvement is attributed to the strong electrostatic and hydrogen-bonding interactions of benzimidazolium cations with halide ions, which efficiently passivate surface and lattice defects. This defect suppression reduces trap-assisted quenching and stabilizes excitonic states, leading to enhanced radiative recombination. Differences in the two doped systems highlight the influence of dopant structure and orientation on energy transfer dynamics. Overall, molecular doping with benzimidazolium salts offers a robust and tunable strategy to modulate recombination kinetics in $CsPbBr_3$ without compromising its spectral integrity. These findings advance the understanding of organic–inorganic interactions in perovskites and open new directions for designing long-lived, high-performance luminescent materials for

Online ISSN 3007-3197
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photonic and optoelectronic applications.

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