

Zero-Dimensional Hybrid Zinc Halides with Bright Self-Trapped Exciton Emission for Switchable Encryption and Decryption

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ABSTRACT Zero-dimensional (0D) hybrid metal halide materials exhibit great application potential in optoelectronic displays, bioimaging, and anti-counterfeiting owing to their strong exciton localization and prominent self-trapped exciton (STE) emission characteristics. However, low-toxicity, biocompatible hybrid zinc halides with blue emission remain scarce, primarily because the short Zn-halide tetrahedral separations facilitate nonradiative energy transfer, resulting in fluorescence quenching. Here, we report the synthesis of a zero-dimensional zinc bromide halide, MPAZnBr_4 , incorporating MPA (where MPA is N-(3-aminopropyl) morpholine) organic cations. The inorganic $[\text{ZnBr}_4]^{2-}$ frameworks are separated by 6.65–9.62 Å and interconnected with the organic cations via a robust hydrogen-bonding network. Upon photoexcitation, MPAZnBr_4 exhibits bright blue emission centered at 450 nm with a full width at half maximum of 135 nm. Wavelength-dependent emission mapping indicates a single radiative pathway, while temperature-dependent photoluminescence confirms triplet self-trapped exciton emission with an exciton binding energy of 55 meV, effectively suppressing exciton dissociation. As a proof-of-concept, we demonstrate switchable and rewritable information encryption and decryption, enabling the creation of complex luminescent patterns. Notably, the extensive hydrogen-bonding network endows MPAZnBr_4 with remarkable structural stability, showing negligible photoluminescence decay under prolonged excitation or storage conditions. These findings not only provide an effective strategy for constructing highly stable low-toxicity blue-emissive Zn-based 0D metal halides, but also highlight their promising prospects for advanced photonic and information-security applications.

Keywords: Zero-dimensional metal halides; Zinc bromide; Self-trapped excitons; Hydrogen-bonding network; Information encryption

INTRODUCTION

Zero-dimensional hybrid metal halide materials exhibit distinct advantages in solid-state lighting owing to their highly isolated emissive units and strong spatial confinement effects [1]. In 0D systems, inorganic emissive clusters are fully isolated by surrounding organic or inorganic matrices. This structural feature strongly suppresses charge carrier migration and promotes the rapid localization of photoexcited electron-hole pairs within individual emitting centers, unlike in conventional semiconductors. Under such structural conditions, strong exciton-phonon coupling readily induces pronounced local lattice distortion, leading to exciton self-trapping and the formation of self-trapped excitons (STEs) [2–8]. The radiative recombination of STEs is typically accompanied by large structural reorganization energy, resulting in broadband emission, large Stokes shift, and excellent defect tolerance [9,10]. These features render 0D metal halides highly promising for applications in solid-state lighting, displays, information encryption, and optical sensing.

In recent years, research on 0D luminescent materials has primarily focused on Sb-, and Bi-based emissive centers. Sb- and Bi-based materials, benefiting from their ns^2 lone-pair electron configurations, typically exhibit broadband orange-red or near-infrared self-trapped exciton emission. However, these heavy metal elements generally pose potential biological toxicity and environmental risks. Previous studies have reported that Sb^{3+} and Bi^{3+} possess low safety thresholds in biological systems, and their long-term exposure may lead to ecological and health concerns, thereby significantly limiting their applications in wearable electronics, bio-related optoelectronic devices, and sustainable green technologies. Consequently, the development of low-toxicity or nontoxic alternative emissive centers has become an important research direction in the field of 0D luminescent materials. Among low-toxicity metal candidates, Cu, Mn and Zn are considered promising alternatives. For instance, Cu-based 0D halide materials can achieve broadband orange-yellow

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