

Aggregative Luminescence from Perovskite Precursors

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Abstract:

In this work, we conducted a detailed investigation into the optical properties of all-inorganic perovskite (CsPbBr₃) precursors. The absorption, photoluminescence (PL), and photoluminescence excitation spectra of the precursors were analyzed in a broad concentration and various solvents. In specific solvents (such as DMSO, DMF, and NMP), the CsPbBr₃ precursor gradually transformed from solution into a colloid and exhibited aggregation-induced emission (AIE) as the concentration increased, and the luminescence intensity and color of the colloid could be controlled by changing the solvent and precursor ratio. Understanding the optoelectronic properties of the precursor may provide deeper insight into the mechanisms that govern the formation and crystallization processes of perovskites, which is vital for the solution-process device performance. Besides, we discussed the difference between the aggregates in the organic system (such as TPE) and the inorganic system (such as CsPbBr₃).

Keywords: Perovskite precursor, Aggregation-induced emission, CsPbBr₃, Colloid, Solvent effect.

Over the past decade, perovskite materials have sparked a revolution in the field of optoelectronic semiconductors, achieving remarkable advancements in areas such as solar cells, light-emitting diodes (LEDs), and photodetectors.^{1,2} Notably, devices prepared through the solution process have emerged as the dominant approach in both academic investigations and industrial applications. In essence, the basic operation of the solution process involves dissolving the precursor of perovskite in a solvent, followed by spin-coating to form a film, and ultimately obtaining a perovskite film with a specific crystal structure/morphology through annealing and crystallization. For various applications such as LEDs and solar cells, typical perovskite precursors are dissolved in solvents such as dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) or their binary mixtures.³⁻⁵ By adjusting parameters such as precursor concentration, spin-coating process, and annealing processes, perovskite films with entirely different properties can be obtained to meet the specific requirements of corresponding devices. Further understanding of the correlation between the nucleation process in the precursor solution and how it influences the crystal growth of the perovskite film is also crucial as the majority of the perovskite films are fabricated using a solution-based process.

In this work, we conducted a detailed investigation into the optical properties of all-inorganic perovskite (CsPbBr_3) precursors. The all-inorganic CsPbBr_3 system was selected to reduce the interaction between A-site ions (such as MA and FA) and solvent molecules, thereby highlighting the interaction between Pb^{2+} and solvent molecules. Precursor of $\text{CsBr}:\text{PbBr}_2=1:1$ (molar ratio) with concentrations ranging from 10^{-3} to 10^2 mM in DMSO were obtained. As shown in Figure 1a, all the precursors were colorless and transparent. At a concentration of 10 mM, the Tyndall effect is observed, suggesting the precursors are colloidal state, which became more pronounced at a concentration of 100 mM. Meanwhile, it was also found that when the colloid formed, especially at a concentration of 100 mM, the precursor exhibited a green emission under UV light. Furthermore, the relationship between the colloidal and precursors photophysics properties was investigated. In dilute solution (concentration = 10^{-3} and 10^{-2}

² mM), the UV curves were almost identical (Figure 1b). With the increase in concentration, the slope of the UV curve also redshifts. Interestingly, as the concentration gradually increased, the PL intensity gradually increased, but the PL peak did not change significantly, stable at 656 nm (Figure 1c). The photoluminescence excitation spectra show a peak at 338 nm at 10 mM and gradually redshift to 378 nm at 100 mM and 392 nm at 500 mM. The Time-resolved photoluminescence lifetime of 100 mM is about 10 ns.

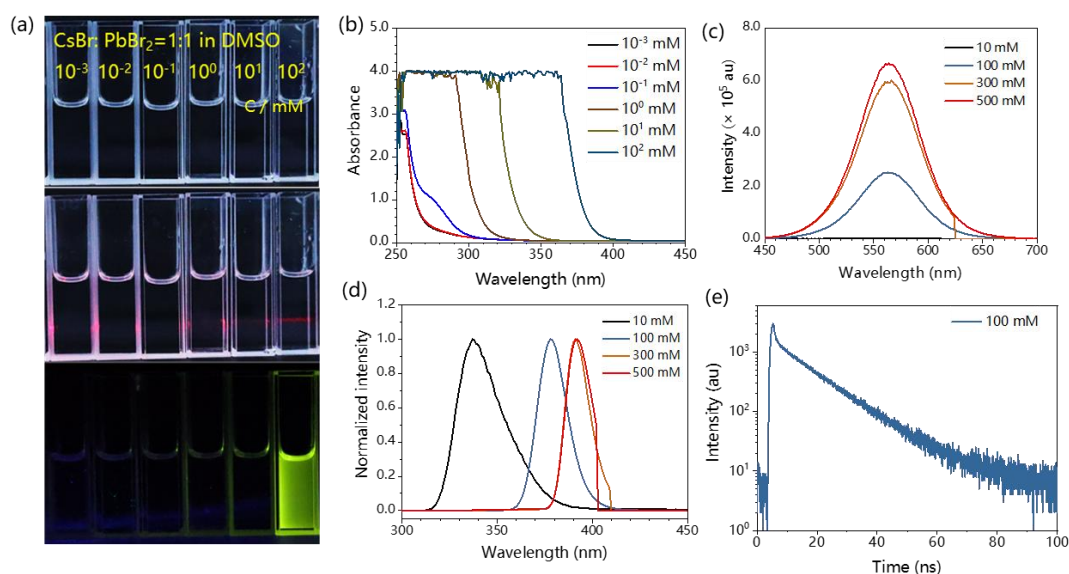


Figure 1. Concentration-induced perovskite precursor transformation from solution to colloid in DMSO (molar ratio of CsBr: PbBr₂=1:1): (a) photographs taken under room light (up), the Tyndall Effect (middle), and the 365 nm UV lamp (down). (b) absorption spectra, (c) photoluminescence spectra, (d) photoluminescence excitation spectra, and (e) Time-resolved photoluminescence of 100 mM.

For comparison, we also prepared solutions of CsBr and PbBr₂ at different concentrations in DMSO (Figure 2) and found that the properties of PbBr₂ in DMSO were basically consistent with those of CsBr: PbBr₂, indicating that Pb²⁺ dominated this series of changes. As the PbBr₂ concentration increases in DMSO, the precursor transforms from solution to colloid and shows AIE property with an emission at 656 nm as well. For the CsBr, whose solubility is low in DMSO, no Tyndall Effect and emission are observed, and the UV spectra are almost identical for all concentrations.

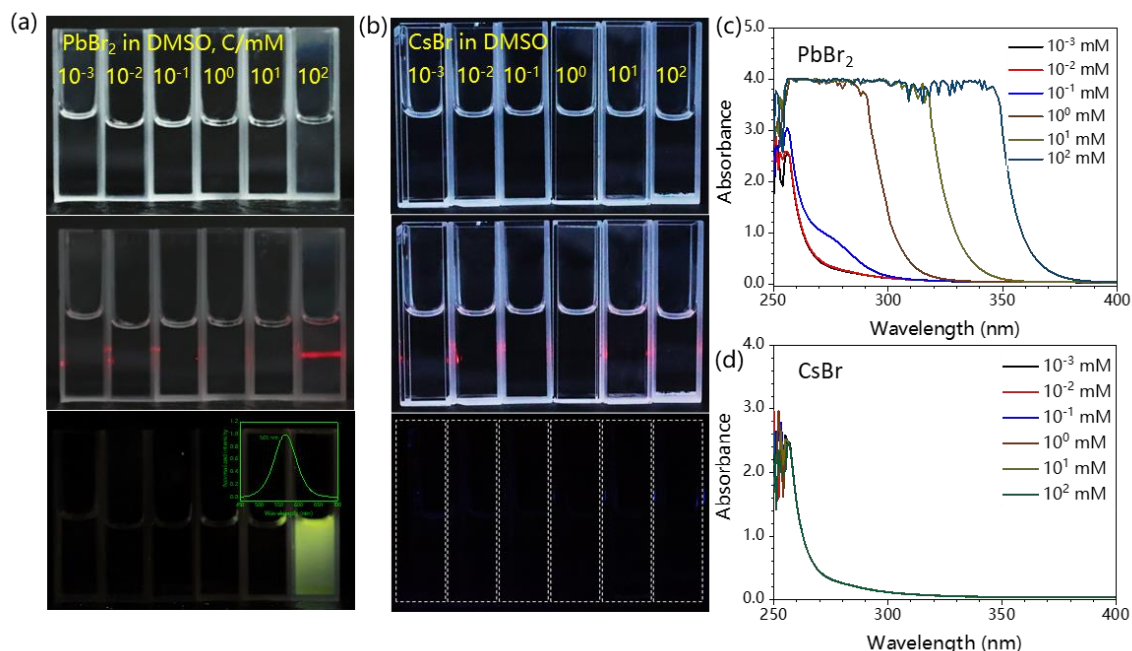


Figure 2. Photographs taken under room light (up), the Tyndall Effect (middle), and the 365 nm UV lamp (down) of (a) PbBr₂ and (b) CsBr. Absorption spectra of (c) PbBr₂ and (d) CsBr.

Due to the interesting luminescent properties of CsPbBr₃ precursors in DMSO, we explored further with several common polar solvents. We obtained colloidal solutions of the PbBr₂ in water, DMSO, ethylene glycol (EG), DMF, acetonitrile (ACN), acetone, and THF. As shown in Figure 3, the colloids exhibited distinct Tyndall effects, but varied greatly in size. The maximum particle size was 1890 nm in water and the minimum was 200 nm in DMSO. Remarkably, only the precursors in DMSO and DMF emitted visible fluorescence under UV light, with different emission colors. The DMSO precursor emitted green light with a peak at 565 nm, while the DMF precursor emitted deep red light with a peak at 612 nm. The fluorescence intensity in DMF was significantly higher than that in DMSO. We further investigated the luminescent behavior of the precursors in a binary solvent mixture of DMSO and DMF. The luminescence gradually shifted from green to red as the solvent changed from DMSO-rich to DMF-rich. At a 1:1 ratio, the green color dominated, suggesting a stronger interaction between DMSO and Pb²⁺. These findings indicate that the luminescence of the colloids is not solely determined by the colloid formed but also by the "quality" of the colloids.

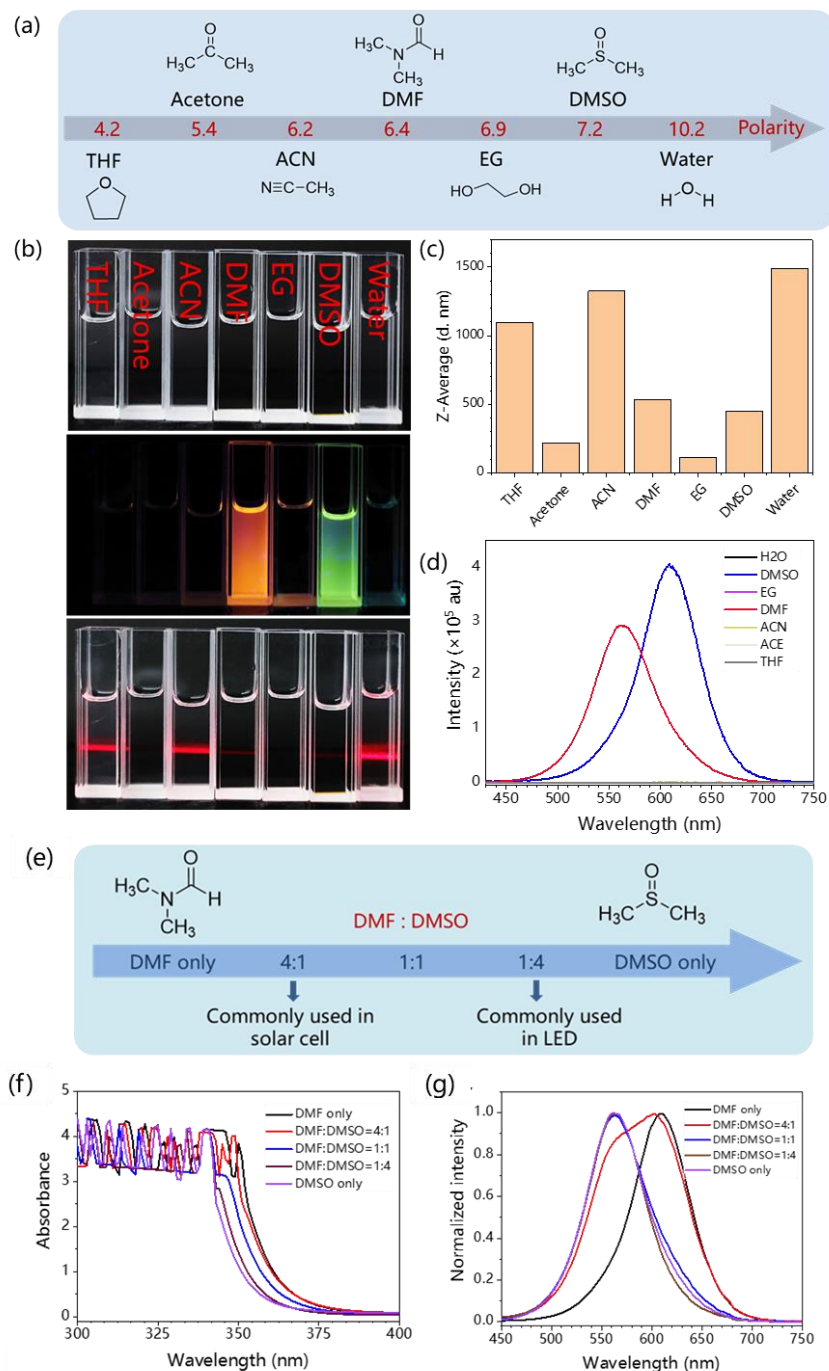


Figure 3. PbBr₂ colloid prosperity in different solvents. (a) Polarity and chemical structure of several common solvents. THF: Tetrahydrofuran. ACN: acetonitrile. DMF: Dimethyl formamide. EG: Ethylene glycol. DMSO: Dimethyl sulfoxide. (b) Photographs of PbBr₂ in different solvents taken under room light (up), a 365 nm UV lamp (middle), and Tyndall Effect (down). (c) The DLS profile, and (d) photoluminescence spectra. (e) chemical structure of DMSO and DMF. (f) absorption spectra and (g) PL spectra of PbBr₂ in DMF and DMSO binary solution.

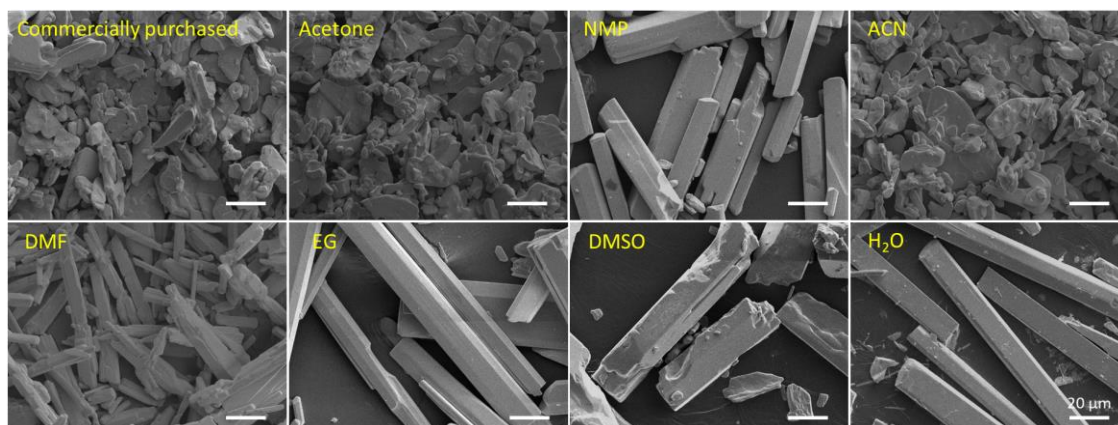


Figure 4. SEM images of supersaturated precipitated PbBr_2 in different solvents.

PbBr_2 was supersaturated precipitated from different solvents and observed its morphology, as shown in Figure 4. Commercially purchased PbBr_2 exhibited thin flakes with sizes of 20-100 μm , and PbBr_2 precipitated from acetone and acetonitrile exhibited a similar morphology. However, PbBr_2 precipitated from NMP, DMF, EG, H_2O , and DMSO transformed from flakes to rods.

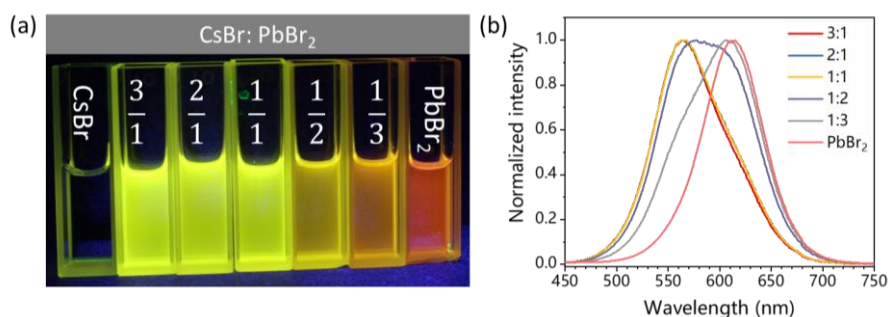


Figure 5. Photographs of precursor in different ratios of $\text{CsBr}:\text{PbBr}_2$ under a 365 nm UV lamp and (b) photoluminescence spectra in DMF solution ($c = 50 \text{ mM}$).

The luminescence color of the precursors can also be tuned by adjusting the CsBr to PbBr_2 ratio. The composition and charge balance of the colloids change with ion concentration. In DMF solvent, pure PbBr_2 exhibits red luminescence with a PL peak at 612 nm. As the CsBr ratio increases, the precursor solution shows green luminescence when $\text{CsBr}:\text{PbBr}_2 = 1:1$.

In summary, this work presents a systematic study of the intrinsic properties of CsPbBr_2 precursors. The study found that the perovskite precursors can form colloids in various solvents at mM-level concentrations, but only in DMSO and DMF can produce visible fluorescence, with different emission colors: green in DMSO and red in DMF. The

difference in luminescence color is due to the preferential growth of PbBr_2 on different crystal faces in different solvents. Our findings suggest the significance of the precursors, which could be an effective means of screening favorable precursor solvents, optimizing precursor ratios, studying the effects of additives on perovskite properties, and screening perovskite additives.

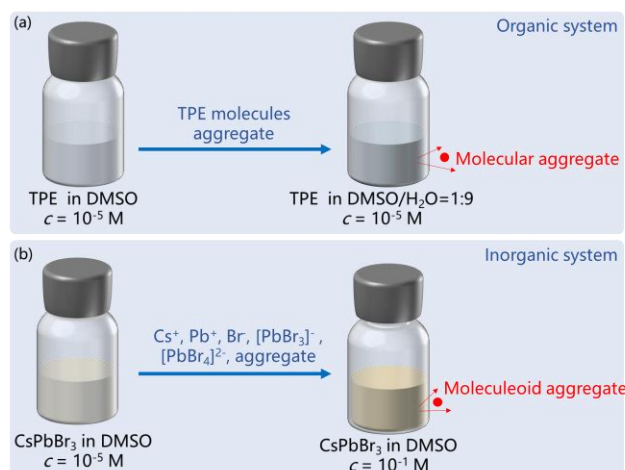


Figure 6. Comparison of TPE aggregates and CsPbBr_3 precursor aggregates. The red spheres represent nanoparticles. Moleculeoid means species that look or behave like molecules.

In addition, the perovskite system studied in this paper is an inorganic system with AIE properties. The concept of AIE originated from the organic small molecule hexaphenylsilole (HPS) and was further developed by tetraphenylethene (TPE) and its derivatives, referring to the phenomenon where the chromophores show weak fluorescence or nonfluorescence in the solution state but enhanced emission in the aggregate form.⁶ As shown in Figure 6a, the organic systems, especially small molecule systems (such as TPE), have well-defined molecular structures and can be studied in a single-molecule state (dilute solution). Beyond molecules, controlling the molecular aggregation behavior can further regulate the properties of their aggregates (nanoparticles, powders, film, etc.). In inorganic systems, especially well-studied inorganic crystals, the empirical formulas (such as CsPbBr_3) are typically used to represent the basic structure of the material, and it is usually impossible to obtain a stable unit cell. As shown in Figure 6b, in the CsPbBr_3 precursor, there are solvated Cs^+ , Pb^+ , Br^+ , $[\text{PbBr}_3]^-$, $[\text{PbBr}_4]^{2-}$ etc., These "moleculeoid" species, like molecules in organic

systems, determine some basic properties of substances. And the moleculeoid aggregation behavior can also regulate the properties of their aggregates. In other words, when studying an inorganic aggregate, we are investing in a moleculeoid aggregate rather than a true molecular aggregate.

Conflict of interest

The authors declare no competing financial interest.

Acknowledgments

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Reference

- 1 Zhang, H. *et al.* A universal co-solvent dilution strategy enables facile and cost-effective fabrication of perovskite photovoltaics. *Nat Commun* **13**, 89, doi:10.1038/s41467-021-27740-4 (2022).
- 2 Kim, J. *et al.* Unveiling the Relationship between the Perovskite Precursor Solution and the Resulting Device Performance. *J Am Chem Soc* **142**, 6251-6260, doi:10.1021/jacs.0c00411 (2020).
- 3 Yan, K. *et al.* Hybrid halide perovskite solar cell precursors: colloidal chemistry and coordination engineering behind device processing for high efficiency. *J Am Chem Soc* **137**, 4460-4468, doi:10.1021/jacs.5b00321 (2015).
- 4 Li, W., Fan, J., Li, J., Mai, Y. & Wang, L. Controllable Grain Morphology of Perovskite Absorber Film by Molecular Self-Assembly toward Efficient Solar Cell Exceeding 17%. *J Am Chem Soc* **137**, 10399-10405, doi:10.1021/jacs.5b06444 (2015).
- 5 Wu, Y. *et al.* Retarding the crystallization of PbI₂ for highly reproducible planar-structured perovskite solar cells via sequential deposition. *Energy Environ. Sci.* **7**, 2934-2938, doi:10.1039/c4ee01624f (2014).
- 6 Mei, J., Leung, N. L., Kwok, R. T., Lam, J. W. & Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem Rev* **115**, 11718-11940, doi:10.1021/acs.chemrev.5b00263 (2015).