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Research on the stability of luminescence of CsPbBr₃ and Mn:CsPbBr₃ PQDs in polar solution

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Mn:CsPbBr₃ PQDs are achieved by hot injection method. As the amount of Mn doping is gradually increased, the photoluminescence (PL) spectra shows a slight blue shift. Mn-doped PQDs exhibit higher quantum efficiency of 83.9% and longer lifetimes of 267 ns. The stability test was performed to assess the susceptibility of the PQDs to polar solutions. It was figured out that although the stabilities of CsPbBr₃ PQDs and Mn-doped PQDs decreased as the polarity of solution increased, Mn-doped PQDs still maintained higher PL intensity than undoped PQD. Notably, 73% PL intensity of Mn:PQDs was maintained which is nearly three times as much as undoped PQDs in water. We found polarity would induce drastic degradation of CsPbBr₃ QDs. The steady-state spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD) verified that CsPbBr₃ QDs tend to aggregate to form larger particles under continuous light soaking. Our work reveals the main origin of instability in CsPbBr₃ QDs and provides reference to engineering such QDs towards optimal device application.

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1. Introduction

The low cost, high photoluminescence quantum yields (PLQYs), and narrow and adjustable emission spectra of perovskite quantum dots (PQDs) make them attractive emitting materials for illumination and display applications.^{1–4} In recent years, CsPbX₃ PQDs (X = Cl, Br, I) have attracted a great deal of attention from materials scientists as promising optoelectronic materials.^{5–10} Compared to organic–inorganic hybrid perovskite materials, all-inorganic perovskites have the advantages of simple preparation and good stability.^{11–16}

Despite plenty of advantages, the toxic nature of Pb and limited tolerance of all inorganic perovskites to moisture, ultraviolet (UV) light and the adjacent environment, cannot be ignored.^{17–22} It is very urgent to figure out some approaches to solve these the worrying issues. CsPbX₃ can be doped with heterogeneous metal ions to replace Pb²⁺, thus reducing the amount of Pb.^{23–26} Researchers also figured out that the doped ions can bring about new electric, optical, and magnetic properties.^{27–30} Kim *et al.* reported Ni²⁺-doped CsPbBr₃ PQDs in 2021. The stability of the Ni:CsPbBr₃ PQDs with distinct Ni/Pb ratios against moisture and UV light was tested. Doping with Ni²⁺ improved the stability of PQDs. Further, the Ni:CsPbBr₃ PQDs exhibited compatibility with real-world applications under harsh conditions.³¹ Zhou *et al.* successfully doped Zn²⁺ ions into CsPbBr₃ PQDs by ligand-assisted reprecipitation method, exhibiting an 85% enhancement of the PLQYs. In addition, the

optimized energy level alignment *via* Zn doping facilitates the carrier balance in the devices, improving the efficiencies. The obtained CsPbBr₃:Zn-based PeLED reaches a high luminance of 3124 cd m^{−2} and a maximum external quantum efficiency of 0.85%, which are excellent among those of CsPbBr₃-based PeLED. The results demonstrate that Zn doping significantly enhances the performance of PeLED, which increases the potential of these inverted PeLEDs connected with n-type TFTs towards practical applications.³² Among them, Mn²⁺ is an important choice, which can not only reduce Pb content to a certain extent but also reduce photon recycling, improve PLQYs, and expand luminous color gamut. An orange luminescence band due to the d–d transition of Mn²⁺ is introduced in addition to the intrinsic band-edge excitonic fluorescence. As well established previously, the efficient energy transfer from PQDs to Mn²⁺ only occurs when the Mn²⁺ content is high enough.^{33,34} Mn²⁺ doping brings many benefits to PQDs, however, it's regrettable that the stability of Mn-doped CsPbBr₃ in polar solutions hasn't been studied in preceding researches, which is critical to its application in various conditions.

In this work, we successfully synthesized partially Mn-doped CsPbBr₃ by hot injection technique.^{35–42} Then we demonstrate the Mn:CsPbMnBr₃ PQDs with a Mn substitution ratio up to 38%. The introduction of Mn²⁺ significantly increased the formation energy of Pb, Br, and Cs vacancies.^{43,44} The PL life-span was longer with Mn²⁺ doping, indicating the inhibition of non-radioactive recombination upon doping.⁴⁵ Besides the reduction of lead content, the as-prepared PQDs maintain the orthorhombic crystalline structure of the CsPbBr₃ host and exhibit strong PL emission of Pb-based PQDs.^{46–49} Mn²⁺ doping enhances the PLQYs of CsPbBr₃ from 52.6% to 83.9%. Finally,

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three polar solvents of acetone, *N,N*-dimethylformamide (DMF), water, were selected to analyze the stabilities of CsPbBr₃ and Mn:CsPbBr₃. According to our experimental results, the Mn-doped CsPbBr₃ is superior to its undoped counterpart in terms of stability in polar solutions.

2. Results and discussion

2.1. Structure and composition of Mn-doped PQDs

Mn:CsPbBr₃ PQDs with different Mn²⁺ doping concentrations were prepared by the hot injection method reported previously. Five samples with Mn : Pb ratios are 0 : 1, 1 : 1, 2.5 : 1, 3.5 : 1 and 5 : 1, TEM images of the resulting Mn:CsPbBr₃ PQDs are shown in Fig. 1a–e, respectively. Five samples with Mn/Pb ratios of 0, 1.25, 2.5, 3.75, and 5 exhibited lattice constants of 5.78 Å, 5.73 Å, 5.65 Å, 5.59 Å, and 5.56 Å, respectively. All the prepared samples exhibited excellent crystallinity, as observed in the high-resolution (HR-TEM) image, and the inter-planar distance of the (100) plane decreased from 5.77 Å to 5.56 Å depending on the feed of MnBr₂. The lattice shrinkage of the Mn²⁺ ion-doped CsPbBr₃ PNCs is mainly due to the synergistic effect of replacing the larger Pb²⁺ ions (1.19 Å) with smaller Mn²⁺ ions (0.67 Å). The corresponding HRTEM images of the Mn:CsPbBr₃ PQDs are shown in Fig. 1a–e. Elemental mapping and energy dispersive X-ray spectroscopy (EDS) (Fig. 1f) were performed for a typical Mn : Pb ratio of 2.5 for Mn-doped CsPbBr₃ PQDs. To confirm the integration of guest Mn²⁺ cations, the chemical composition of Mn:CsPbBr₃ PQDs (Mn : Pb = 2.5) was analyzed by EDS. The elements Cs, Pb, Mn, and Br were identified in Mn:CsPbBr₃ PQDs. The four target elements were evenly distributed throughout the selection region, indicating successful synthesis of Mn:CsPbBr₃ PQDs and effective doping of Mn²⁺.

Fig. 2a shows the XPS results, which depict the change in binding energy according to the doping element. The XPS spectrum reveals signals of the Cs, Pb, Br, and Mn elements in the Mn-doped CsPbBr₃ PQDs, and the corresponding high-resolution XPS spectrum shows a typical Mn 2P signal (Fig. 2b).

Selected area electron diffraction (SAED) patterns of the Mn:CsPbBr₃ also shows the presence of tetragonal (100) and (200) surfaces (Fig. 3a), confirming that the perovskite structure has not been destroyed. XRD patterns of the CsPbBr₃ doped with different concentrations of Mn²⁺ are shown in Fig. 3b. With increased Mn doping, there was no overall structural change.

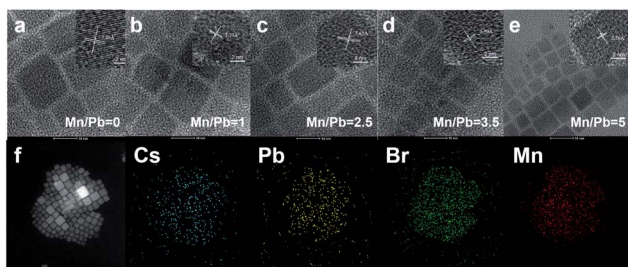


Fig. 1 (a) TEM images of CsPbBr₃ and (b)–(e) Mn:CsPbBr₃ PQDs (Mn : Pb = 1 to 5). (f) Elemental mapping images of the Mn:CsPbBr₃ PQDs (Mn : Pb = 2.5).

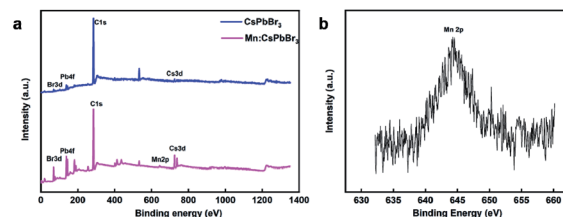


Fig. 2 (a) XPS spectra of Mn:CsPbBr₃ PQDs (Mn : Pb = 2.5). (b) High-resolution XPS spectra for Mn 2p of Mn:CsPbBr₃ PQDs.

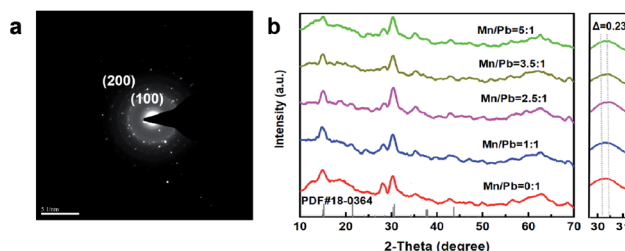


Fig. 3 (a) SAED pattern of Mn-doped CsPbBr₃ (Mn : Pb = 2.5). (b) XRD patterns of Mn:CsPbBr₃ PQDs (Mn : Pb from 0 to 5).

The orthorhombic CsPbBr₃ phase (PDF#18-0364, Fig. 3b) remained. The peak of (200) of the synthesized CsPbBr₃ PNCs shifted by 0.23° to the right when the Mn²⁺ concentration increased, indicating that the amount of Mn²⁺ dopant in the CsPbBr₃ PNCs increased. In addition, as the concentration of Mn increased, the intensity of the main peaks gradually increased. These results provide solid evidence for the efficient replacement of Mn²⁺ ions in the CsPbBr₃ PNC lattice. EDS were conducted to analyze the actual compositions of the Mn:CsPbBr₃ PQDs. When the feeding ratios are Mn : Pb = 1 : 1, Mn : Pb = 2.5 : 1, Mn : Pb = 3.5 : 1, and Mn : Pb = 5 : 1, the resulting products are CsPb_{0.961}Mn_{0.039}Br₃, CsPb_{0.798}Mn_{0.202}Br₃, CsPb_{0.729}Mn_{0.271}Br₃, and CsPb_{0.616}Mn_{0.384}Br₃, respectively (Table 1).

2.2 Optical properties

Fig. 4 shows the absorbance graph according to the Mn doping concentration. The absorption measurement results demonstrated that light of wavelength 500–513 nm was absorbed by the PQDs. Due to the decreased size of Mn:CsPbBr₃ PQDs, their UV-vis absorption spectra show a gradual blue shift with the increase Mn-to-Pb molar feed ratio. Since no new absorption band was observed after Mn doping, it is presumed that Mn doping has a negligible effect on the electronic structure of CsPbBr₃ PQDs.

Table 1 EDS of Mn:CsPbBr₃ PQDs (Mn : Pb from 1 to 5)

Mn : Pb	1 : 1	2.5 : 1	3.5 : 1	5 : 1
Mn	0.039	0.202	0.271	0.384
Pb	0.961	0.798	0.729	0.616

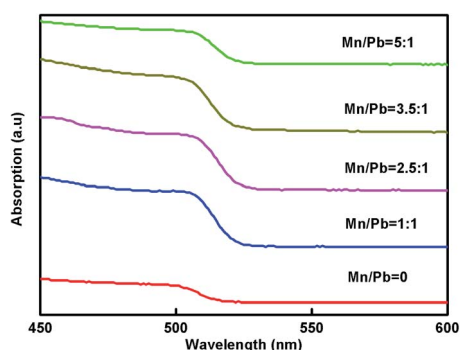


Fig. 4 Absorption of CsPbBr₃ and Mn:CsPbBr₃ PQDs.

Fig. 5a manifests the PL measurements. 508–518 nm marked the wavelength band of emitted light. The average half width proved to be 20.4 nm, which revealed high color purity. With the increasing doping concentration, because of the quantum confinement effect, the emission wavelength was going through a blue shift from 518 to 508 nm. A change in the energy level resulting from doping concentration resulted in a reduction in emission wavelength at the rate of 3–10 nm compared with the undoped sample. The PL intensity was on a gradual increase when substituted concentration of Mn²⁺ ions was growing larger. Nonetheless, the others PL peaks (Mn : Pb = 3.5, 5) was decreasing. Particularly speaking, the PL peak intensity of the sample (Mn : Pb = 2.5), when compared with the intensity of the undoped sample, was increasing at the rate of 3.8 times. According to Fig. 5b, the gradual conversion color converted from green to blue; the most striking luminous intensity was shown with the Mn : Pb = 2.5. The highest quantum efficiency could be seen at an Mn : Pb of 2.5 (Mn : Pb = 2.5, ≈83.9%), which differed by ≈27% with no doping (Mn : Pb = 0, ≈56.7%). For Mn : Pb = 3.5, however, the quantum efficiency decreased dramatically, indicating that the Mn²⁺ ion has a very strong effect upon the optical properties of PQDs. From the differences in defect levels offered by the doping material, a proper doping concentration able to gain high quantum efficiency can be attained. These results show that Mn²⁺ doping forms a Mn–Br ion pair to fill the Pb–Br ion vacancy, which effectively eliminates the non radiative recombination of excitons and improves the luminescence intensity of

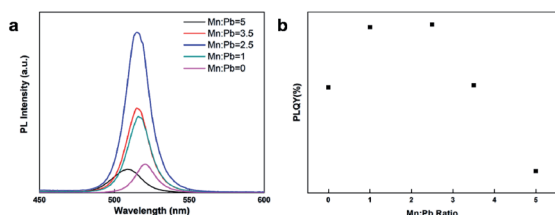


Fig. 5 (a) PL peaks of pristine and Mn:CsPbBr₃ PQDs with different Mn : Pb ratios; the insets show the corresponding normalized PL spectra. (b) PLQY with various Mn : Pb feed molar ratios of 0, 1, 2.5, 3.5, 5; the insets show the photograph of the Mn:CsPbBr₃ PQDs in hexane solution under an irradiation of a 360 nm UV lamp.

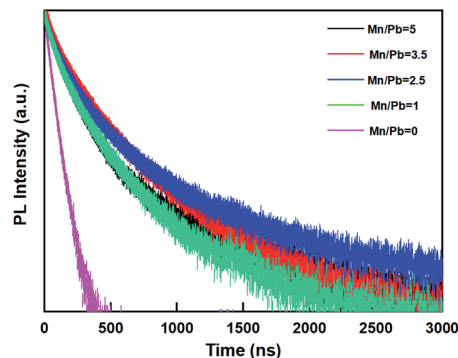


Fig. 6 Time-resolved PL decays of fresh CsPbBr₃ and Mn:CsPbBr₃ PQDs.

CsPbBr₃ quantum dots. As the Mn doping increasing, Mn–Mn ion pair appears. This phenomenon is observed in Pan's work of Ni²⁺ ion-doped CsPbCl_xBr_{3-x} PQDs.⁵¹

The average lifetime for excitonic luminescence of CsPbBr₃ PQDs added Mn²⁺ ions is observed to increase from 43.2 ns to 267.6 ns compared to undoped CsPbBr₃ PQDs. The radiative and non-radiative decay rates can also be calculated using PLQY and the average life. The radiative rate decreased slightly from 0.0662 ns⁻¹ to 0.0372 ns⁻¹, and the non radiative recombination, which must be controlled for optical properties, significantly decreased from 0.0506 to 0.0077 ns⁻¹. Therefore, the improvement in fluorescence performance can be attributed to the greatly reduced non-radiative attenuation of the incorporation of Mn:CsPbBr₃ PQDs.

For acetone, the PL intensity of the initial reference sample after 2 h was 20% lower than the initial value (Fig. 7a). In contrast, the steady-state PL intensity at 2 h was 11.0%, lower than the initial value of Mn:CsPbBr₃ PQDs (Fig. 6b). The decrease in the steady-state PL intensity of CsPbBr₃ is more noticeably than that of Mn:CsPbBr₃ PQDs in acetone, which indicates that Mn doping enhanced the stability of CsPbBr₃ PQDs.

Fig. 8 shows stability of pristine CsPbBr₃ and Mn:CsPbBr₃ PQDs (Mn : Pb = 2.5) in DMF. The PL intensity of CsPbBr₃ PQDs lower than 50% in DMF after 2 h. While PL intensity of Mn:CsPbBr₃ PQDs maintain 76%. As the polarity improved, the enhancement of stability of Mn²⁺ doping is more pronounced.

To investigate the water stability of the pre-synthesized Mn:CsPbBr₃ PQDs, the PQD solution was injected with a 5% volume ratio of deionized water (DIW). For comparison, the

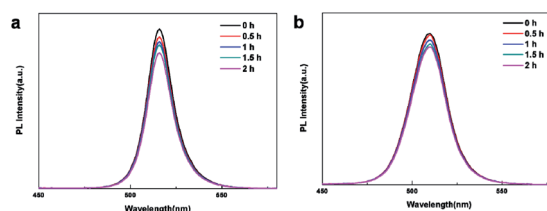


Fig. 7 (a) PL spectra of the pristine CsPbBr₃ and (b) Mn:CsPbBr₃ PQDs (Mn : Pb = 2.5) recorded at different time intervals in acetone.



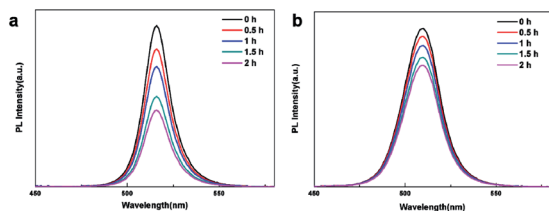


Fig. 8 (a) PL spectra of the pristine CsPbBr₃ and (b) Mn:CsPbBr₃ PQDs (Mn : Pb = 2.5) recorded at different time intervals in DMF.

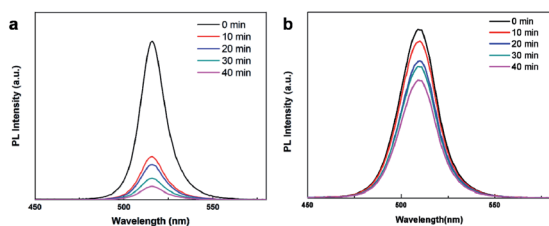


Fig. 9 (a) PL spectra of the pristine CsPbBr₃ and (b) Mn²⁺-substituted CsPbBr₃ PQDs (Mn : Pb = 2.5) recorded at different time intervals in water.

measurements were performed for pristine CsPbBr₃ PQDs at the same concentration as the Mn:CsPbBr₃ PQD solution over time. A quantitative study was conducted by recording the PL evolution; the results are summarized in Fig. 9. The corresponding PL spectra of undoped CsPbBr₃ PQDs and Mn:CsPbBr₃ PQDs were documented at separate time intervals after the addition of DIW. For Mn:CsPbBr₃ PQDs (Mn : Pb = 2.5), fluorescence quenching was comparatively slow and retained more than 73% of its initial performance, even over longer test periods. The PL spectra of the CsPbBr₃ PQDs (Fig. 9a) and Mn:CsPbBr₃ PQDs (Fig. 9b) based on the moisture test are shown. As shown in Fig. 9a, a small weakening of the emission intensity for Mn:CsPbBr₃ PQDs was confirmed, but strong fluorescence was still observed. However, the CsPbBr₃ PQDs lost majority of their brightness in just 1 min of testing, gradually changing fluorescent from green to colorless. The efficiency of CsPbBr₃ PQDs decreased owing to the aggregation and decomposition of CsPbBr₃ PQDs, and the optical properties of CsPbBr₃ PQDs weakened as the half-width broadened. Based on the above results, we speculate that Mn²⁺ ions occupy the lead site, which makes the structure of PQDs more stable in polar solutions.

3. Experimental section

3.1 Materials

All chemicals were used as received without further purification. Cesium carbonate (Cs₂CO₃, 99.9%, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Sigma-Aldrich), PbBr₂ (99.9%, Maclin), MnBr₂ (99.9%, Maclin), and oleylamine (OAm, 70%, Sigma-Aldrich).

3.2 Synthesis of Cs-oleate

Cs₂CO₃ (0.05 g), OA (0.5 mL), and ODE (10 mL) were placed in a 100 mL three-necked round-bottom flask. Next, the mixture

was heated at 110 °C for 1 h under vacuum to completely remove moisture and oxygen. After that, the reaction temperature was maintained at 120 °C under N₂ atmosphere and stirred until all Cs₂CO₃ reacted with OA to form Cs-oleate. A clear solution was obtained. Notably, Cs-oleate precipitated in the ODE at ambient temperature and had to be preheated to 100 °C before it could be used for the subsequent synthesis of PQDs.

3.3 Synthesis of CsPbX₃PQDs

The synthesis method of CsPbX₃ PQDs is similar to the approach of Protesescu *et al.*,⁵⁰ with a few insignificant modifications. In brief, 10 mL ODE and 0.2 mmol PbBr₂ were added to a 250 mL three-neck round-bottom flask and dried under vacuum at 110 °C for 1 h. The flask was purged with N₂, and OA (0.5 mL) and OAm (0.5 mL) preheated to 70 °C was injected into the flask. The flask was heated at 120 °C until PbX₂ completely reacted with OA and OAm. The temperature was then increased to 150 °C. The Cs-oleate precursor (0.8 mL) was quickly injected into the Pb-oleate. The solution was maintained at 150 °C for several seconds to allow the growth of the PQDs. The solution was cooled by soaking the flask in a cold-water bath.

3.4 Synthesis of Mn:CsPbX₃PQDs

The synthesis of the Mn-doped CsPbX₃ PQDs was performed in a manner similar to that of the CsPbX₃ PQDs, as described above. ODE (5 mL) and PbBr₂ were added to a 250 mL three-necked round-bottom flask and dried under vacuum at 110 °C for 1 h. All other steps remained the same.

3.5 Purification

The as-prepared CsPbX₃PQD and Mn-doped CsPbX₃PQD crude solutions were precipitated by centrifuging at 6000 rpm for 5 min. The colored supernatant was carefully discarded, and the precipitate was mixed with hexane (1.5 mL) using a vortex. The solution was centrifuged at 6000 rpm for 5 min. Finally, the PQDs were dispersed in hexane (1 mL) and centrifuged at 10 000 rpm for 2 min to remove any excess Cs-oleate, larger PQDs, and agglomerates. The precipitate was then collected and redispersed in hexane, resulting in a colloidal dispersion of the CsPbX₃ PQDs.

3.6 Characterization

The size, morphology, and crystallinity of the nanoparticles were characterized by field-emission transmission electron microscopy (FE-TEM, JEOL, JEM-F200) in EDS. TEM images were obtained using high-resolution transmission electron microscopy (HR-TEM, FEI, Tecnai 20). The lattice constant was determined from the HR-TEM images using GATAN software. The absorption spectra were obtained using a UV-vis spectrophotometer (Varian, Cary 50). PL excitation and emission spectra were measured using a steady-state spectrofluorometer (PTI, QuantaMaster) with an excitation wavelength of 360 nm. XRD patterns were collected on a powder diffractometer (Bruker New D8-Advance) with monochromatized Cu K α radiation (λ = 1.5418 Å). XPS was performed using a ULVAC-PHI X-TOOL

instrument. PLQY was measured using a spectrofluorometer (JASCO, FP-8500) with an integrating sphere. Time-resolved PL experiments were performed using the TCSPC method. The samples in the solutions were excited using a 360 nm pulse (LDH-P-C-520, Picoquant). The time-resolved PL signals emitted from the samples were resolved using a monochromator and detected by a photomultiplier tube (PMT).

4. Conclusions

In this work, a hot-injection method help achieving CsPbBr₃ perovskite QDs which possessing a high Mn-doping ratio. Consequently the properties of Pb-based perovskite QDs were improved. In order to gain their enhanced stability, different Mn : Pb ratio of CsPbBr₃ PQDs structure was achieved. The Mn substitution ratio reaches 38%, which leads to an increase of 3.8 times of the steady-state PL intensity, the lifetime increase to 267 ns. In comparison to the undoped sample, the quantum efficiency achieved the improved as large of 30.6%. The stability of the Mn:CsPbBr₃ PQDs with distinct Mn : Pb ratios against polar solutions was tested. Doping with Mn²⁺ improved the stability of PQDs according to our research.

Conflicts of interest

The authors state that they have no conflicts of interest to declare.

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