

Room temperature synthesis of cesium lead bromide perovskite magic sized clusters with controlled ratio of carboxylic acid and benzylamine capping ligands

Ke Xu^{a,b}, Evan T. Vickers^b, Binbin Luo^c, Qihui Wang^a, A'Lester C. Allen^b, Hongmei Wang^d, Vivien Cherrette^b, Xueming Li^{a,*}, Jin Zhong Zhang^{b,**}

^a College of Chemistry and Chemical Engineering, Chongqing University, Chongqing, 401331, PR China

^b Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA, 95064, United States

^c Department of Chemistry, Shantou University, Guangdong, 515063, PR China

^d College of Biological, Chemical Sciences and Engineering, Jiaying University, Jiaying, 314001, PR China

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ABSTRACT

We demonstrate the synthesis of cesium lead bromide (CsPbBr₃) perovskite magic sized clusters (PMSCs) and how to control the transformation from CsPbBr₃ perovskite quantum dots (PQDs) to PMSCs by varying the amount of organic carboxylic acids (CAs), including mesitylacetic acid (MAA), oleic acid (OA), and phenylacetic acid (PAA), along with benzylamine (BZA) as capping ligands at room temperature. The PQDs and PMSCs are characterized by means of XRD, UV/vis, photoluminescence (PL), time-resolved PL (TRPL), and X-ray photoelectron spectroscopy (XPS). The concentration of CAs affects the excitonic absorption of both the CsPbBr₃ PMSCs ($\lambda = 389\text{--}428\text{ nm}$) and CsPbBr₃ PQDs ($\lambda = 460\text{--}516\text{ nm}$), with high concentration of CAs favoring CsPbBr₃ PMSCs over PQDs. With PAA at 45.45 mM, pure CsPbBr₃ PMSCs can be generated, which does not happen for MAA or OA, suggesting that PAA is a stronger ligand than MAA and OA. The results suggest that PMSCs require better passivation or stronger ligands than PQDs. This study establishes a simple and general method for synthesizing CsPbBr₃ PMSCs using a combination of BZA and CA capping ligands as a highly effective dual passivation system.

1. Introduction

Magic sized clusters (MSCs), small nanoparticles with either single size or very narrow size distribution, serve as good model system for studying the transitions from atoms/molecules to larger structures such as quantum dots (QDs) or bulk material [1–5]. They can also be used as well-defined building blocks for fabricating large nanostructures for applications in fields such as photovoltaics, biosensors, light emitting diodes (LEDs) [1,6,7]. Today, MSCs of various II–VI compounds have been studied in terms of both chemical synthesis and theoretical investigations, such as CdSe, CdS, ZnS, ZnTe, and CdTe [6,8–14]. However, study of lead halide perovskite MSCs (PMSCs, APbX₃; A = CH₃NH₃ and Cs; X = Cl, Br, and I) has been somewhat limited partly because their challenging synthesis [1,5,7,15]. Their structural characterization is also difficult since they tend to grow into larger structures when dried

into solid form from solution [7]. Therefore, there is strong interest in developing an improved synthesis for perovskite QDs (PQDs) to PMSCs.

Recently, Yang's group proposed a synthesis method based on a high concentration of oleylamine (OLA) as capping ligand to obtain ultra-small single-sized cesium lead bromide (CsPbBr₃) PMSCs at room temperature [16]. Xu and co-workers reported the synthesis of ~2 nm CsPbBr₃ PMSCs using oleic acid (OA) and OLA capping ligands, and the PMSCs can be further converted to single-crystalline CsPbBr₃ quantum nanoribbons with bright deep-blue emission at room temperature [15]. Likewise, we have synthesized the methylammonium lead bromide (CH₃NH₃PbBr₃) and CsPbBr₃ PMSCs and found a strong dependence on their capping ligand composition and concentration [1,7]. However, to our knowledge, there has been no study reported on the possible effect of using different capping ligands on synthesis of organo-metal halide PMSCs.

* Corresponding author.

** Corresponding author.

E-mail addresses: bbluo@stu.edu.cn (B. Luo), hongmei256@163.com (H. Wang), xuemingli@cqu.edu.cn (X. Li), zhang@ucsc.edu (J.Z. Zhang).

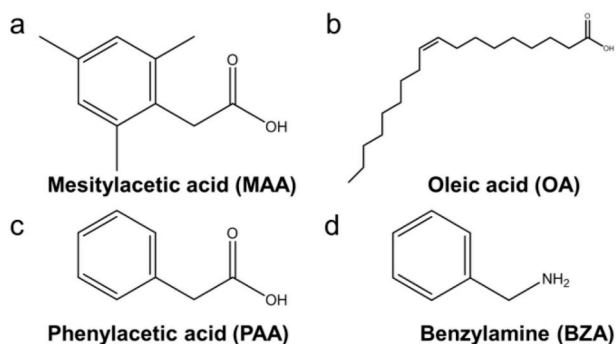


Fig. 1. Molecular structures of (a) mesitylacetic acid (MAA), (b) oleic acid (OA), (c) phenylacetic acid (PAA), and (d) benzylamine (BZA).

In this work, we demonstrate the synthesis of CsPbBr₃ PMSCs and their conversion to CsPbBr₃ PQDs by controlling the amount of organic carboxylic acids (CAs), including mesitylacetic acid (MAA), OA, and phenylacetic acid (PAA) together with benzylamine (BZA) as capping ligands at room temperature. The growth and optical properties of the PMSCs are found to be strongly dependent on the organic CAs used. High concentration of CAs favors CsPbBr₃ PMSCs over CsPbBr₃ PQDs. Pure

CsPbBr₃ PMSCs can be generated when the PAA concentration reaches 45.45 mM, which does not happen with OA or MAA, suggesting that PAA is a stronger ligand than MAA and OA. The results suggest that stronger binding ligands or higher concentration of ligands favors PMSCs over PQDs, indicating PMSCs requires better passivation.

2. Experimental methods

2.1. Materials

Cesium bromide (CsBr, 99.9%, Strem Chemicals), lead bromide (PbBr₂, 99.999%, Alfa Aesar), mesitylacetic acid (MAA, 98%, Alfa Aesar), oleic acid (OA, 98%, Fisher Chemical), phenylacetic acid (PAA, 99%, Aldrich), benzylamine (BZA, 99%, TCI), N,N-dimethylformamide (DMF, 99.5%, Fisher Scientific), toluene (100%, LabChem Inc). All the chemicals were used as received without further purification.

2.2. Synthesis and purification of CsPbBr₃ PMSCs and CsPbBr₃ PQDs

CsPbBr₃ PMSCs and CsPbBr₃ PQDs were synthesized using a solvent reprecipitation method at room temperature condition [7,17]. CsBr (8.51 mg, 40 μmol) and PbBr₂ (14.68 mg, 40 μmol) were dissolved into 1.0 mL DMF to prepare the precursor solution. Next, 0.025 mmol PAA

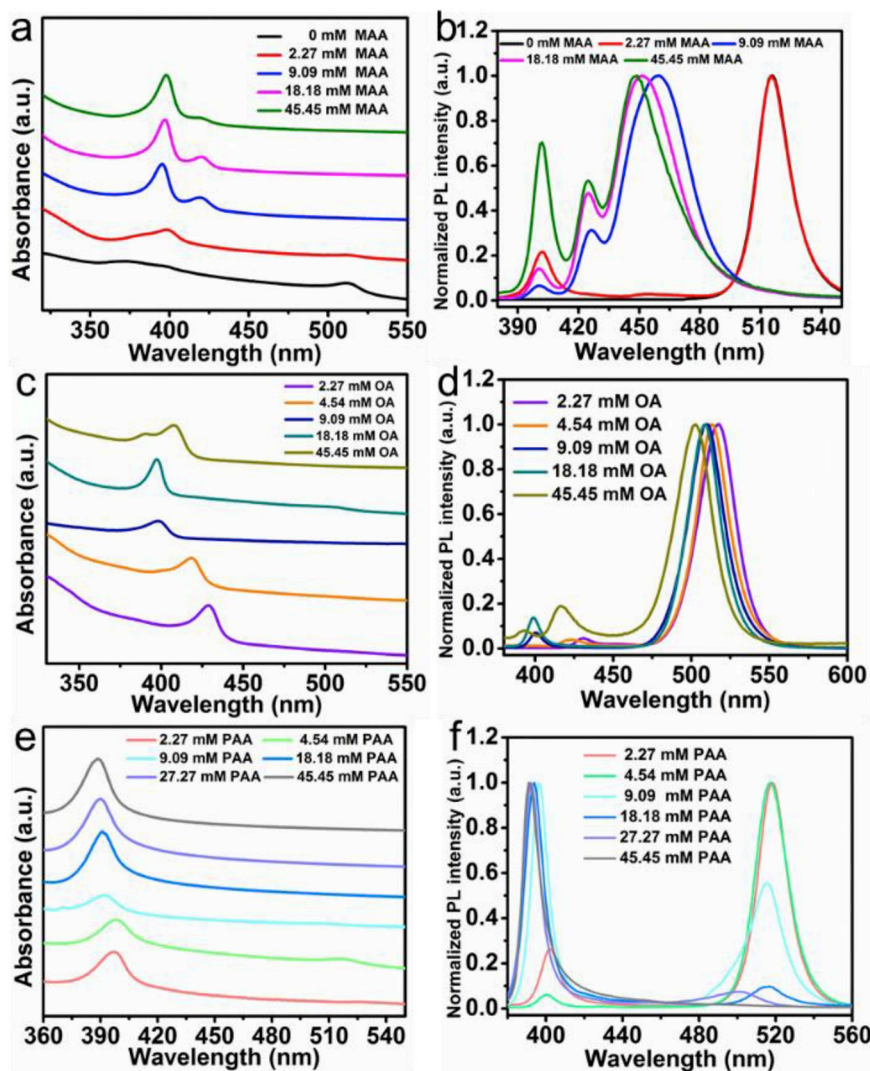


Fig. 2. (a) and (b), (c) and (d), and (e) and (f) are UV-vis absorption and PL spectra of BZA-MAA, BZA-OA, and BZA-PAA for CsPbBr₃ PQDs and CsPbBr₃ PMSCs samples.

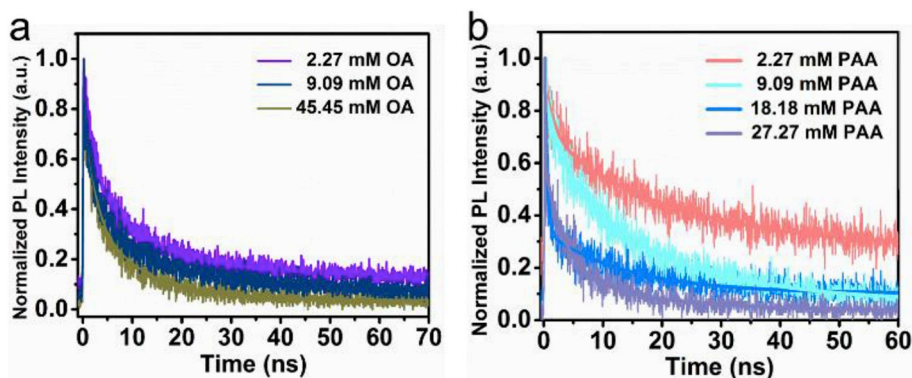


Fig. 3. Time-resolved photoluminescence decay curves of (a) BZA-OA and (b) BZA-PAA CsPbBr₃ samples.

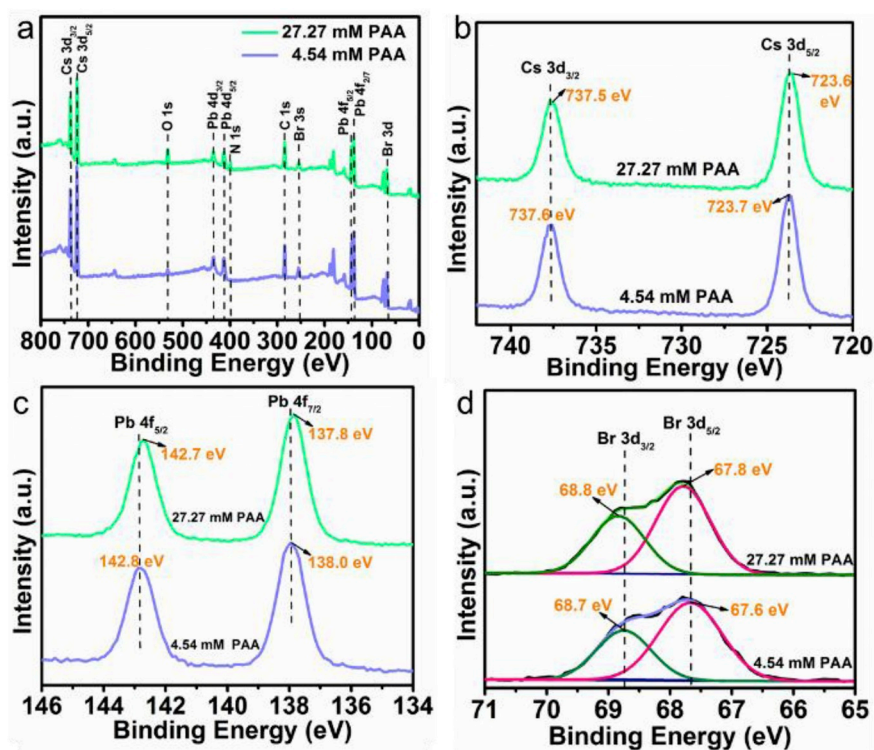


Fig. 4. (a) XPS survey spectra of BZA-PAA CsPbBr₃ PMSCs and PQDs. High resolution XPS analysis of BZA-PAA CsPbBr₃ PMSCs and PQDs corresponding to (b) Cs 3d, (c) Pb 4f, and (d) Br 3d.

and 0.001 mmol BZA were added to the precursor solution and dissolved. Then, the precursor solution was injected rapidly to 10.0 mL of toluene under vigorous stirring to obtain CsPbBr₃ PMSCs and PQDs. Similarly, using the same amount of BZA, the amount of PAA was varied to 0.050, 0.100, 0.200, 0.300 and 0.500 mmol to synthesize BZA-PAA CsPbBr₃ PMSCs and PQDs. For BZA-MAA and BZA-OA CsPbBr₃ PMSCs and PQDs. We also used the same amount 0.001 mmol BZA and changed the amount of MAA (0, 0.025, 0.100, 0.200, 0.500 mmol) and OA (0.025, 0.050, 0.100, 0.200, and 0.500 mmol) as capping ligands to add in CsBr (8.51 mg, 40 μ mol), PbBr₂ (14.68 mg, 40 μ mol) and 1.0 mL DMF to prepare the precursor solution, respectively. Then, the obtained BZA-MAA and BZA-OA precursor solution was injected rapidly to 10.0 mL of toluene under vigorous stirring to obtain CsPbBr₃ PMSCs and PQDs. After completion of the reaction, the as-synthesized CsPbBr₃ PQDs and CsPbBr₃ PMSCs were centrifuged at a speed of 2000 rpm for 5 min in toluene. Finally, the supernatant was collected for the first wash, and after that, the precipitate was collected after each wash at a speed of 10000 rpm for 10 min in toluene to get perovskite powders and vacuum

drying at 25 $^{\circ}$ C for 8 h for further characterization. For the pure BZA-PAA CsPbBr₃ PMSCs sample, the particles are too small to be centrifuged, thus it is stored in the form of the liquid.

2.3. Characterizations

Ultraviolet–visible (UV–vis) spectra were measured using UV–vis spectrometer (Agilent Technologies, Cary 60) and the fluorescence spectra were measured using a fluorometer (FluoroMax-3) using a quartz cuvette (1.0 cm $\times$ 1.0 cm) at room temperature. X-ray diffraction (XRD) data were acquired using a Rigaku American Miniflex Plus power diffractometer at a voltage of 40 kV and current of 30 mA, with scanning angle 10–60 (2θ) and rate of 3 $^{\circ}$ min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Thermo ESCALAB 250Xi spectrometer with an AlK α (1486.6 eV) excitation source to identify the chemical composition. Time correlated single photon counting (TCSPC) was measured by focusing on the sample using a 20 $\times$ objective with an effective power of 30 mW (λ_{ex} = 500 nm).

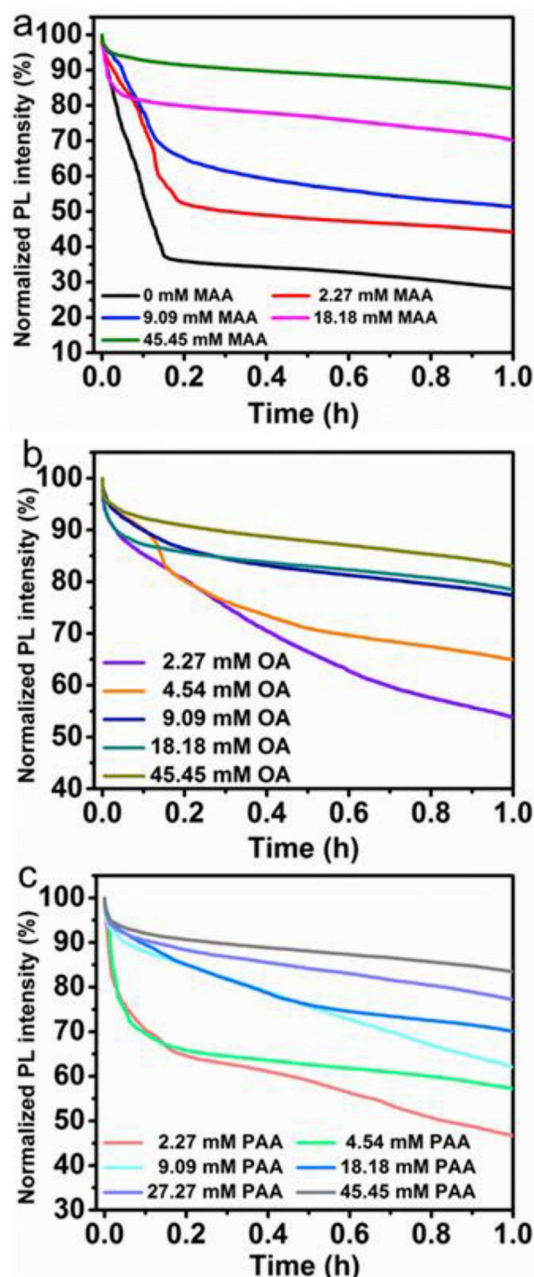


Fig. 5. Stability of BZA-MAA, BZA-OA, and BZA-PAA for CsPbBr₃ PQDs and CsPbBr₃ PMSCs solution in air and in the dark: the relative fluorescence intensity as a function of time.

3. Results and discussion

3.1. Optical properties of CsPbBr₃ PQDs and PMSCs capped with CAs and BZA

The chemical molecular structures of the MAA, OA, PAA, and BZA ligands used in these experiments are shown in Fig. 1. To obtain PMSCs, excess amount of MAA/OA/PAA capping ligands together with BZA was used.

Fig. 2a and b shows the UV-vis absorption and photoluminescence (PL) spectra of BZA CsPbBr₃ PQDs as well as BZA-MAA CsPbBr₃ PQDs and PMSCs, respectively. In the UV-vis spectra of CsPbBr₃ PQDs with 0.091 mM BZA, there is a strong excitonic absorption peak at 512 nm. With the same amount BZA, increasing the amount of MAA from 2.27 to 9.09, 18.18, and 45.45 mM resulted in BZA-MAA CsPbBr₃ samples with

two or three excitonic absorption peaks, and the PL spectrum of each sample shows three emission peaks. For BZA-MAA CsPbBr₃ sample with a small amount of 2.27 mM MAA, there are three excitonic absorption peaks at 399, 460, and 511 nm, and the three PL emission peaks at 401, 461, and 514 nm. However, for with 9.09 mM MAA sample, there are two excitonic absorption peaks at 395 and 521 nm, and three PL emission peaks at 400, 425, and 459 nm. The very strong PL emission peak at 459 nm is not expected based on the two UV-vis peaks observed and may be due to trap states of CsPbBr₃ PMSCs or CsPbBr₃ PQDs formed from CsPbBr₃ PMSCs during the PL measurement. Details of the UV-vis and PL peaks of BZA-MAA CsPbBr₃ samples with different MAA concentrations are summarized in Table S1.

Fig. 2c and d shows the UV-vis absorption and PL spectra of BZA-OA CsPbBr₃ PQDs and PMSCs samples with different OA concentrations, and magnified PL emission peaks for BZA-OA CsPbBr₃ PMSCs sample in Fig. S1a. The detailed excitonic absorption peaks and PL emission peaks are summarized in Table S1. For the 18.18 mM OA sample, there are two excitonic absorption peaks at 397 and 505 nm, and two PL emission peaks at 398 and 509 nm. However, for other OA concentrations studied, there is an extra PL peak at around 510 nm, which could be due to trap states or PQDs formed during PL measurement.

Fig. 3a and b shows the UV-vis absorption and PL spectra of BZA-PAA CsPbBr₃ PQDs and PMSCs with different concentrations of PAA, and magnified PL emission peaks for BZA-PAA CsPbBr₃ PMSCs in Fig. S1b and detailed spectral features are summarized in Table S1. For the four samples with high PAA concentration, there is one excitonic absorption peak at around 395 nm, but two PL emission peaks at around 400 and 515 nm. The around 400 nm PL peak is attributed to excitonic emission while the around 515 nm peak could also be due to trap states or formed PQDs during PL measurement, similar to the BZA-MAA and BZA-OA CsPbBr₃ samples.

Based on previous studies, a 430–520 nm broader excitonic absorption peak is attributed to CsPbBr₃ PQDs, while the strong and sharp excitonic absorption peak at around 410 nm or bluer is assigned to CsPbBr₃ PMSCs [5,7,15,18–20]. Interestingly, with increasing amount of CAs for all BZA-MAA, BZA-OA and BZA-PAA samples, the PL emission peak shows a blue shift in the range of 430–518 nm. Compared with BZA-OA and BZA-PAA samples, BZA-MAA samples show a larger blue shift, indicative of smaller particles. The results also show that more CA capping ligands favor CsPbBr₃ PMSCs over CsPbBr₃ PQDs, as we found previously [7]. In addition, with an excess amount of MAA and OA, the synthesized product is a mixture of CsPbBr₃ PQDs and PMSCs. However, for 45.45 mM PAA, the synthesized product is pure CsPbBr₃ PMSCs, which suggests that different CAs affect the ratio between PQDs and PMSCs.

3.2. Structural, dynamic, and electronic properties

Figures S2a, S2b and S2c compare the XRD patterns of BZA-MAA, BZA-OA and BZA-PAA CsPbBr₃ PQDs and PMSCs samples. The XRD pattern all show the main diffraction peaks at $2\theta = 15.2^\circ, 21.5^\circ, 26.3^\circ, 30.7^\circ, 37.6^\circ$ and 43.7° , corresponding to the interlayer spacing of the (100), (110), (111), (200), (211) and (202) crystal planes, respectively. These peaks confirm the cubic phase structure with space group of *Pm3m* (JCPDS No. 18-0364) [21,22]. However, all the samples also show some undetermined peaks, especially for the BZA-OA and BZA-PAA CsPbBr₃ samples. The undetermined peaks are most likely not from the original structures in solution but likely due to larger structures, such as aggregates, from CsPbBr₃ PMSCs upon drying to form the solid powders for XRD [7].

To better understand the dependence of the exciton lifetime on the amount of CAs, normalized time-resolved photoluminescence (TRPL) decay curves and related analysis data for BZA-OA and BZA-PAA CsPbBr₃ samples were carried out ($\lambda_{ex} = 500$ nm), as shown in Fig. 3 and Table S2. The PL decays were fitted using a double exponential function as given in Eq. (1) [2]:

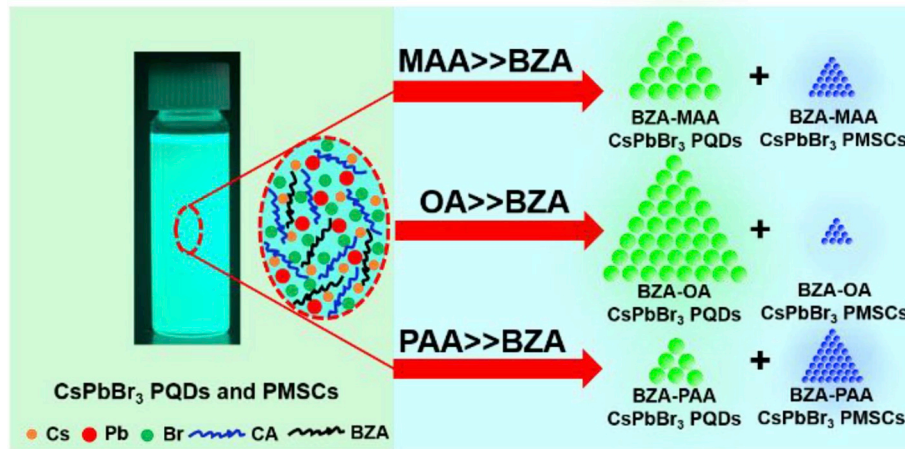


Fig. 6. Schematic illustration of the growth mechanism of CsPbBr₃ PQDs and CsPbBr₃ PMSCs at room temperature, and their dependence of transformation on the amount and type of CA.

$$I(t) = A_1 e^{(-t/\tau_1)} + A_2 e^{(-t/\tau_2)} \quad (1)$$

where A_1 and A_2 are the amplitudes of the fast and slow components (with $A_1 + A_2 = 1$); t is time; and τ_1 and τ_2 are the fast and slow decay lifetimes, respectively. All fitting parameters are reported in Table S2.

The average lifetime (τ_{ave}) is calculated using Eq. (2) [23]:

$$\tau_{ave} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (2)$$

The τ_{ave} for the BZA-OA and BZA-PAA CsPbBr₃ sample are calculated and shown in Table S2. With increasing CA concentration, the τ_{ave} becomes shorter. The τ_{ave} is determined by both radiative (τ_r) and non-radiative (τ_{nr}) lifetime. According to previous reports, τ_r is usually more dominated by the properties of the PQD core while τ_{nr} is more sensitive to the type of capping ligands or surface properties and thereby surface passivation [2,23,24]. Specifically, τ_r becomes longer with increasing PQD core size while τ_{nr} becomes longer when there are less defects and better surface passivation [2,24]. For the BZA-OA and BZA-PAA samples, the excitonic emission peaks blue shift, indicating decreasing PQD size with increasing CA concentration, which should lead to shorter τ_r . In the meantime, the BZA-OA and BZA-PAA samples have the same capping ligands, which should lead to similar τ_{nr} . Therefore, variation in τ_{ave} with CA concentration should be dominated by τ_r or the PQD core size. According to following Eq. (3) [2]:

$$\frac{1}{\tau_{ave}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}} \quad (3)$$

Therefore, it would expect τ_{ave} to become shorter with increasing CA concentration, which is consistent with we have observed.

To further study the effectiveness of passivation of CAs and BZA, XPS survey spectra were obtained. As shown in Fig. 4a, for the BZA-PAA CsPbBr₃ PMSCs and PQDs sample at 4.54 mM and 27.27 mM PAA, the main peaks of Cs 3d_{3/2}, Cs 3d_{5/2}, O 1s, Pb 4d_{3/2}, Pb 4d_{5/2}, N 1s, C 1s, Br 3s, Pb 4f_{5/2}, Pb 4f_{7/2} and Br 3d are observed, respectively [25–27]. For the low/high concentration of PAA samples, the binding energies of Cs 3d_{5/2} and 3d_{3/2} peaks in Fig. 4b appeared at 723.7/737.6 eV and 723.6/737.5 eV, respectively [27]. At the same time, for the low/high concentration of PAA samples, the Pb 4d_{7/2} and Pb 4d_{5/2} peaks are observed at 138.0/142.8 eV and 137.8/142.7 eV in Fig. 4c, respectively, and the peaks at 67.6/68.7 eV and 67.8/68.8 eV corresponded to Br 3d_{5/2} and Br 3d_{3/2} binding energies in Fig. 4d [27]. Therefore, there are about 0.1/0.1 eV and 0.2/0.1 eV negative shifts for Cs 3d and Pb 4d for the low/high concentration of PAA samples, while there are about 0.2/0.1 eV positive shifts for Br 3d. This indicates that the electron density around Cs 3d and Pb 4d increases while the electron density

around Br 3d decreases. This is consistent passivation of Cs⁺ and Pb²⁺ by –COO[–] and Br[–] by –NH₃⁺ [2].

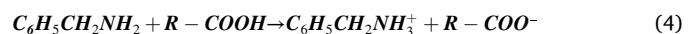
3.3. Stability study

The environmental stability of metal halide perovskites is a major character of interest [2,28–31]. To evaluate their stability, the relative PL intensities of BZA-MAA, BZA-OA, and BZA-PAA CsPbBr₃ solutions were studied for 1.0 h in air and dark conditions, with the results shown in Fig. 5. For the BZA-MAA CsPbBr₃ samples with different amount of MAA as shown in Fig. 5a, the relative PL intensity decreased to about 28, 44, 51, 71 and 85% after 1.0 h, respectively. As shown in Fig. 5b, for the BZA-OA CsPbBr₃ samples with different amount of OA, the relative PL intensity of the solution decreased to 54, 65, 77, 79, and 83% after 1.0 h, respectively. Fig. 5c, shows the PL decay with time for the BZA-PAA CsPbBr₃ samples. The CsPbBr₃ can degrade in air under dark conditions due to possible reaction with oxygen [29]. The good stability of the pure BZA-PAA CsPbBr₃ MSCs and the mixture of CsPbBr₃ PMSCs and PQDs suggests that the CsPbBr₃ PMSCs stability in air is much better than that of CsPbBr₃ PQDs.

3.4. Dependence of surface passivation on CAs and ratio between CAs and BZA

Fig. 6 illustrates the typical procedure for synthesizing CsPbBr₃ PQDs and CsPbBr₃ PMSCs using BZA-MAA, BZA-OA and BZA-PAA as capping ligands. A higher concentration of CAs favors CsPbBr₃ PMSCs over PQDs, attributed to the fact that PMSCs have a larger surface-to-volume (S/V) ratio than PQDs [1,7]. In addition, PAA, together with BZA, can more easily produce CsPbBr₃ PMSCs than MAA and OA due to its stronger acidity or binding ability of its conjugate base.

For effective passivation of PQDs or PMSCs, it is critical to use an acid and base pair [7]. In the current system, BZA is protonated with –NH₂ becoming –NH₃⁺, while CAs are deprotonated with –COOH becoming –COO[–] [2]. The reactions can be described by Eq. (4):



where R– means (CH₃)₃C₆H₅CH₂– for MAA, CH₃(CH₂)₇CH=CH(CH₂)₇– for OA, and C₆H₅CH₂– for PAA. RCOO[–] is expected to effectively passivate charged surface defects of Cs⁺ and Pb²⁺, while C₆H₅CH₂NH₃⁺ for Br[–].

The dissociation constants for the acid (pK_a) and base (pK_b) are pK_a = 4.31 for PAA, pK_a = 5.02 for OA, and pK_b = 4.66 for BZA [2,32,33]. Based on the molecular structure, we expect the acidity of MAA to be between PAA and OA, though the pK_a of MAA cannot be found in

literature [34]. Thus, the acidity of the three CAs is expected to be PAA > MAA > OA. Based on the calculation for the equilibrium constants (K_{eq}) and the comparison of the K_{eq} values in SI 5, PAA deprotonates more easily than OA or MAA when reacting with BZA, providing better passivation.

Furthermore, the ratio between CA and BZA is also found to be an important factor in the effectiveness of passivation. In most previous studies, the acid/base pair is based on OA/OLA with a ratio near 1 [17, 35, 36]. In this study, the acid/case ratio is much higher than 1 for optimal passivation. This is possibly due to more Cs^+ and Pb^{2+} surface defects and less Br^- surface defects in the structure of $CsPbBr_3$ PMSCs. To understand better the exact structure of $CsPbBr_3$ PMSCs, further work will be needed in the future.

4. Conclusion

In summary, we demonstrate the successful synthesis of $CsPbBr_3$ PMSCs and $CsPbBr_3$ PQDs using BZA-MAA, BZA-OA, and BZA-PAA as effective ligands at room temperature. The concentration of CAs affects the excitonic absorption of both $CsPbBr_3$ PMSCs and $CsPbBr_3$ PQDs, with high concentration of CAs favoring $CsPbBr_3$ PMSCs over PQDs, possibly due to PMSCs requiring better passivation than PQDs. Pure $CsPbBr_3$ PMSCs can be generated with 45.45 mM PAA, but not for MAA or OA at the same concentration, suggesting that PAA is a stronger ligand than MAA and OA, which likely passivates Cs^+ and Pb^{2+} related surface defects. The results suggest that $CsPbBr_3$ PMSCs require better passivation (stronger or higher concentration of ligands) than $CsPbBr_3$ PQDs. This work demonstrates a simple and general method for synthesizing $CsPbBr_3$ PMSCs using a combination of BZA and CA capping ligands as a highly effective dual passivation system.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.solmat.2019.110341>.

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