

Role of Size and Shape in Photoluminescence and Ultra-Low-Frequency Raman of Methylammonium Lead Iodide Perovskite Quantum Dots

Nurwarrohman Andre Sasongko,[▽] Yeonsu Jeong,[▽] Safira Arta Paramita, Jaeseong Heo, Myoung Hwan Oh, Sebastian E. Reyes-Lillo,^{*} and Myeongkee Park^{*}



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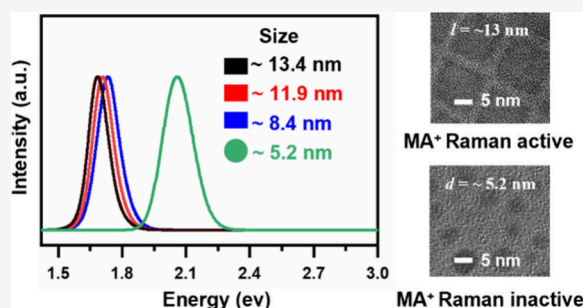


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ABSTRACT: The photophysical properties of methylammonium lead iodide (MAPbI₃) quantum dots (QDs) have not been systematically studied for size and shape dependence. Here, we synthesize MAPbI₃ QDs using ligand-assisted reprecipitation, controlling the injection speed and reaction times to produce QDs with different sizes and shapes. Dropwise injection yields ~5 nm spherical QDs, emitting photoluminescence (PL) at 2.06 eV. In contrast, swift injections yield larger (>10 nm) rectangular QDs with varying aspect ratios, supported by an infinite quantum well model. The PL lifetime of QDs increases with their size, and the size variation significantly influences the ultra-low-frequency Raman modes at 81, 107, and 127 cm⁻¹, in contrast to what is observed in polymorphic MAPbI₃ thin films. Our findings, supported by first-principles density functional theory, show that key PL and Raman properties are governed by the sizes and shapes of MAPbI₃ QDs. This study contributes to the understanding of the optical behavior of these QDs, which is crucial for their potential applications and environmental implications.



Hybrid organic–inorganic perovskite (HOIP) quantum dots (QDs) have attracted a considerable amount of attention because of their unique optical properties, such as their tunable light absorption range, adjustable photoluminescence (PL), and extended PL lifetime.^{1–4} These advantages make HOIP QDs a highly promising optoelectronic material for optoelectronic applications such as light-emitting diodes (LEDs), solar cells, and photodetectors.^{5–8} The unique physical properties of the HOIP QDs are mainly attributable to the quantum confinement effect and the interplay between organic cations and Pb–I frameworks.^{9–14} The hydrogen bond between organic cations and Pb–I octahedra affects the conduction band, triggering a dynamic change in the band gap that enhances the carrier diffusion length and suppresses electron–hole recombination.^{15,16}

Methylammonium lead iodide (MAPbI₃) is the most straightforward benchmark HOIP material.¹⁷ It was initially employed in the lead halide perovskite solar cell category, and subsequent studies have aimed to elucidate the interactions between organic dipoles and inorganic frameworks in HOIP.^{18,19} In particular, Raman studies have been reported for polymorphs, degradation pathways, and the phase transition of MAPbI₃ by measuring ultra-low-frequency Raman modes below 100 cm⁻¹.^{19–23} In addition, recent Raman experiments have presented the structural fingerprints associated with structural symmetries, crystal growth, and degradation under intense light illumination.^{23–27}

However, most studies have investigated the photophysical properties of the polycrystalline MAPbI₃ thin film rather than single crystals.^{19,23} This focus on the polycrystalline phase may originate from disagreements with theoretical calculations, which generally target single-crystal structures. The inconsistencies between experiments and theories can be resolved using single-crystal MAPbI₃ QDs. In contrast to the polycrystalline or multigrain film phase, MAPbI₃ QDs can exist as single-crystal colloids in an apolar solution, offering advantageous inherent passivation from ambient conditions such as atmospheric moisture.⁸

Recently, several bottom-up methods have been developed to synthesize MAPbI₃ QDs such as the hot injection method, ultrasonication method, solvothermal reaction, and ligand-assisted reprecipitation (LARP). The ultrasonication and solvothermal methods require extensive purification processes to eliminate bulky particles, resulting in a large amount of waste.^{28,29} The hot injection technique typically involves the use of high temperatures (>150 °C) to synthesize QDs, which

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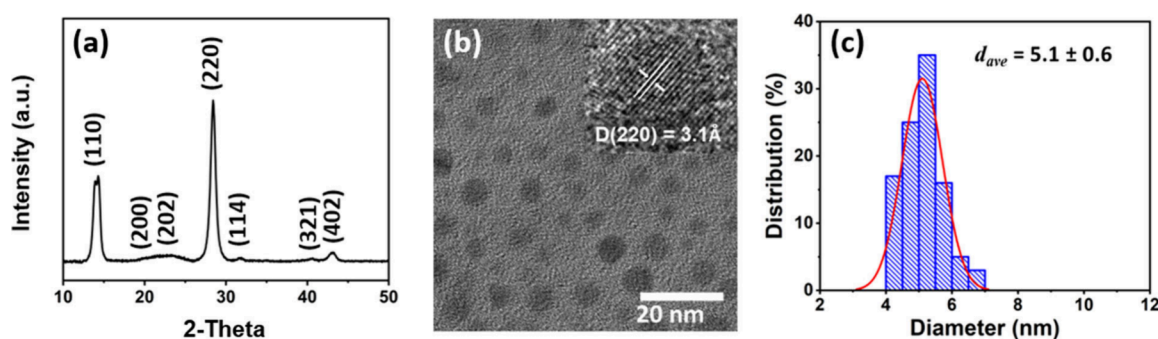


Figure 1. (a) XRD pattern, (b) TEM image, and (c) diameter distribution of QDs synthesized via dropwise injection. The inset of panel b shows a high-resolution TEM image with a lattice parameter of 3.1 Å, the (220) plane of MAPbI₃. The average QD diameter is 5.1 ± 0.6 nm.

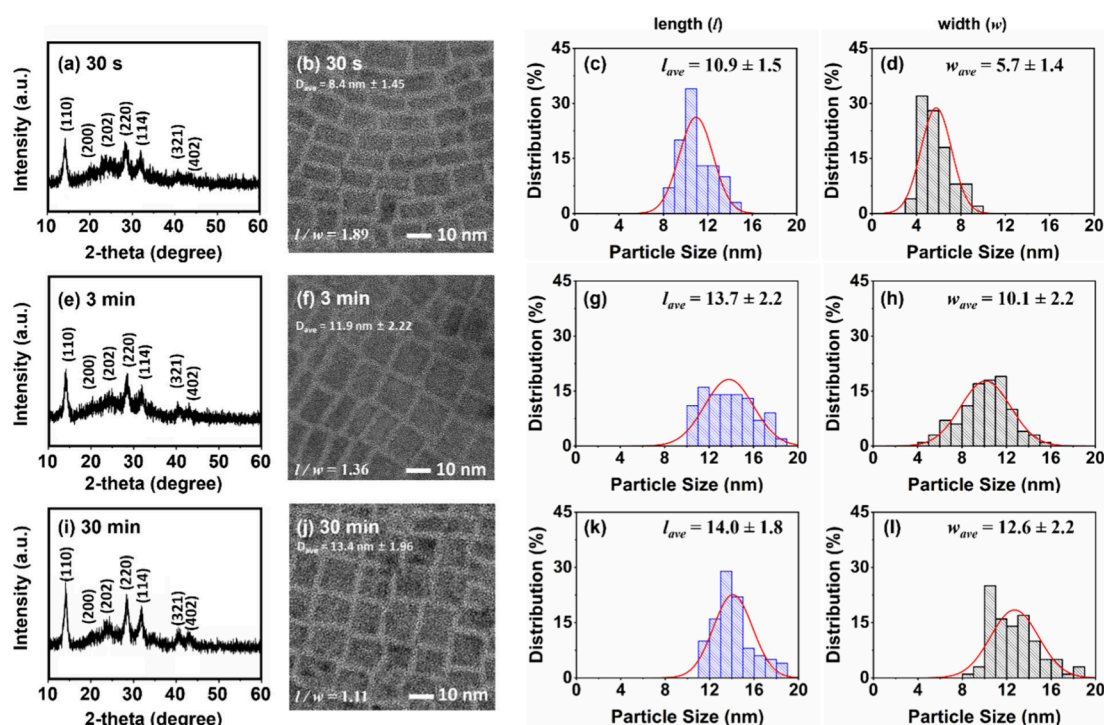


Figure 2. XRD patterns, TEM images, and size distributions of MAPbI₃ QDs synthesized by using swift injection with reaction times of (a–d) 30 s, (e–h) 3 min, and (i–l) 30 min. D_{ave} is the average of the lengths (l) and widths (w).

may lead to a thermal degradation of MAPbI₃ into PbI₂, ammonia, and methyl iodide.³⁰ In contrast, the LARP technique is a milder bottom-up approach for the synthesis of colloidal MAPbI₃ perovskite QDs, as it can operate at lower synthesis temperatures.^{31–34} By simply using a solubility difference, a polar solution containing precursors and stabilizing ligands is injected into an antisolvent (e.g., toluene) and the mixture vigorously stirred. Dot nucleation begins upon injection, followed by the growth of QDs. LARP offers precise control over the nucleation and growth of QDs by adjusting parameters such as injection speed, reaction time, and solvent composition.³⁵

In this study, we report PL and ultra-low-frequency Raman measurements of MAPbI₃ QDs with different shapes (spherical and rectangular) and sizes, synthesized via LARP by varying the injection speed and reaction time (Figure S1). In addition, we compare the Raman results to first-principles density functional theory calculations. Our spectroscopic analysis successfully reveals Raman fingerprints for the inorganic

framework and hydrogen bonding-connected MA cation pristine MAPbI₃.

Figure 1a shows the XRD patterns of the MAPbI₃ QDs synthesized by the dropwise injection method. The XRD patterns reveal that spherical MAPbI₃ QDs present diffraction peaks at 14.05° (110), 24.15° (200), 25.17° (202), 28.27° (220), 31.79° (114), 40.53° (321), and 42.95° (402) attributed to the tetragonal phase.³⁵ Panels b and c of Figure 1 show a TEM image of the QDs synthesized using the dropwise method and their diameter distribution. The QDs exhibit a spherical shape with a diameter of 5.1 ± 0.6 nm. In principle, dropwise injection leads to rapid nucleation, leading to the formation of a large number of spherical nuclei, followed by a limited growth process. This observation is consistent with a recent report showing that dropwise injections resulted in the formation of spherical MAPbI₃ QDs.³⁶ The interplanar distance was measured to be 3.1 Å, corresponding to the (220) plane of MAPbI₃.^{37,38}

Panels a, e, and i of Figure 2 show the XRD patterns of the MAPbI₃ QDs synthesized by the swift injection method with

reaction times of 30 s, 3 min, and 30 min, respectively. The XRD patterns reveal that all MAPbI₃ QDs are attributed to the tetragonal phase. TEM images of the MAPbI₃ QDs synthesized by the LARP method employing different reaction times are shown in Figure 2. The results show that swift injection produces rectangular MAPbI₃ QDs that are 10.9 ± 1.5 nm in length (*l*) and 5.7 ± 1.4 nm in width (*w*) with the shortest reaction time (30 s). With a reaction time of 3 min, the QDs measured 13.7 ± 2.2 nm in length (*l*) and 10.1 ± 2.2 nm in width (*w*). When the reaction time was extended to 30 min, the MAPbI₃ QDs measured 14.0 ± 1.8 nm in length (*l*) and 12.6 ± 2.2 nm in width (*w*). These results confirm that an increase in reaction time leads to the formation of larger QDs.³⁵ The reaction times also influence the length-to-width aspect ratio (AR) of the QDs. The ARs were calculated to be 1.89, 1.36, and 1.11 for reaction times of 30 s, 3 min, and 30 min, respectively. Shorter reaction times limit the isotropic growth of QDs, resulting in a higher AR. As the reaction time increases, QDs grow more isotropically, leading to a lower AR.³⁹

Figure 3a shows the UV–vis absorbance and PL spectra of the MAPbI₃ QDs synthesized via dropwise and swift injections.

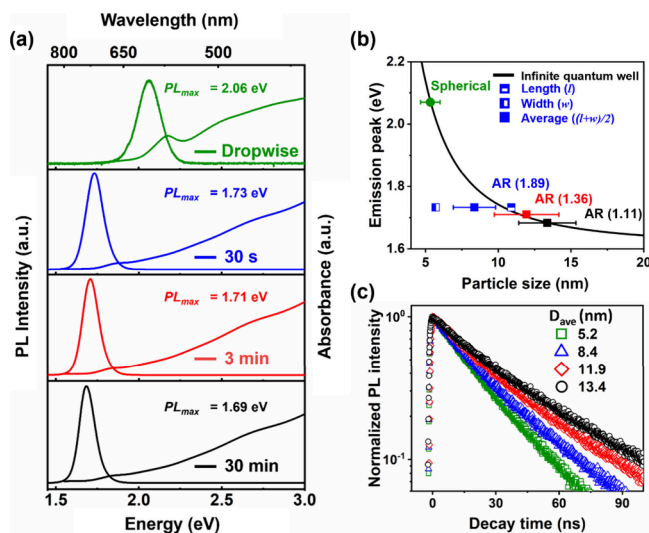


Figure 3. (a) UV–vis absorbance and PL spectra of size-controlled MAPbI₃ QDs. (b) PL peak centers plotted against the particle sizes determined experimentally and by the infinite quantum well model. The green filled circle shows the average diameter of the spherical MAPbI₃ QDs (~5.2 nm). The black, red, and blue filled squares represent the average length and width of the rectangular MAPbI₃ QDs, with values of ~13.4, ~11.9, and 8.4 nm, respectively. (c) Time-resolved PL of MAPbI₃ QDs.

By dropwise injection, the QDs show a PL peak at 2.06 eV, whereas the others show PL peaks at 1.73, 1.71, and 1.69 eV for reaction times of 30 s, 3 min, and 30 min, respectively, after the swift injections. The observed blue shifts of the PL peaks are the characteristics in terms of the quantum confinement effect.⁴⁰ We subsequently focused on this effect with the sizes calculated from the TEM images and infinite quantum well model in eq 1.³⁶

$$E_{\text{infinite}}(R) = E_{\text{bulk}}(\infty) + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_{\text{CB}}^{\text{QW}}} + \frac{1}{m_{\text{VB}}^{\text{QW}}} \right) \quad (1)$$

where $E_{\text{infinite}}(R)$ represents the band gap energy of a crystal at radius *R* and $E_{\text{bulk}}(\infty)$ is the band gap of bulk MAPbI₃ (~1.61 eV). $m_{\text{CB}}^{\text{QW}}$ and $m_{\text{VB}}^{\text{QW}}$ are the effective masses of the electrons and holes in a quantum well, respectively, with values of 0.31 m_0 and 0.18 m_0 , respectively, where m_0 is the mass of the electron.³⁶

Figure 3b shows the PL peak centers plotted against the particle sizes determined experimentally and by the infinite quantum well model. The PL peak centers (Figure 3a) and diameters (Figure 1) of the isotropic spherical QDs are in good agreement with those predicted by the infinite quantum well model. In addition, the average sizes $[(l + w)/2]$ and PL peak centers of anisotropic MAPbI₃ QDs with low ARs of 1.36 and 1.11 are also consistent with the infinite quantum well model.

However, the average size of the rectangular QD with the highest AR of 1.89 (blue filled square) does not match the center of the PL peak predicted by the infinite quantum well model. Interestingly, the prediction via the infinite quantum well model was in good agreement with the value for a longer dimension (10.9 nm). This suggests that the band gap energies in rectangular QDs with a high AR are more affected by the longer dimensions. A recent study supports the significance of AR, showing that the band gap of InAs/GaAs QDs with a higher AR is influenced by longer dimensions due to shifts in the valence band.⁴¹ Consequently, the shape of QDs plays an important role in regulating the quantum confinement effect, complementing the significance of the dimensions of the QDs controlled by reaction times.

Figure 3c shows the size-dependent time-resolved photoluminescence (TRPL) of MAPbI₃ QDs. The decay profiles exhibit a biexponential behavior with fast (A_1 and τ_1) and slow (A_2 and τ_2) components. The average lifetimes (τ_{avg}) are also calculated by eq 2 and presented in Table 1.

$$\tau_{\text{avg}} = \frac{\sum_{i=1}^n A_i \tau_i^2}{\sum_{i=1}^n A_i \tau_i} \quad (2)$$

Table 1. Fitting Parameters of Time-Resolved PL and Diffusion Lengths (L_D) of Size-Controlled MAPbI₃ QDs

D_{ave} (nm)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{avg} (ns)	L_D (μm)	PLQY (%)
5.2	0.93	21	0.08	61	25	1.9	41
8.4	0.76	22	0.25	55	29	2.1	55
11.9	0.75	25	0.27	68	36	2.3	69
13.4	0.60	25	0.39	65	41	2.5	78

The τ_{avg} values of the QDs with diameters of 5.2, 8.4, 11.9, and 13.4 nm are 25, 29, 36, and 41 ns, respectively, demonstrating that smaller QDs show faster exciton recombinations due to the larger contribution of A_1 . The increased PL lifetime of larger QDs is in agreement with recent studies that reported PL lifetimes of ~11, ~18, ~32, and ~43 ns for 6.6, 9.8, 10.6, and 11.7 nm QDs, respectively.³⁶ This implies that charge carriers in larger QDs have a longer distance to travel before recombining, contributing to the extended PL lifetimes. Interestingly, our smaller QDs show distinctive longer (~2-fold) lifetimes, indicating the lower density of structural defects despite their large surface energies. In addition, the photoluminescence quantum yields (PLQYs) of the QDs with diameters of 5.2, 8.4, 11.9, and 13.4 are 41%, 55%, 69%, and

78%, respectively, based on a comparison with average lifetimes reported in a recent study.³⁶

We calculated the diffusion length (L_D) of MAPbI₃ QDs using eq 3.

$$L_D = \sqrt{D\tau_{\text{avg}}} \quad (3)$$

where D is the diffusion coefficient of MAPbI₃ that can be calculated using the Einstein–Smoluchowski relation shown in eq 4.

$$D = \mu k_B T / e \quad (4)$$

where k_B is the Boltzmann constant (1.38×10^{-23} J/K), T is the temperature (300 K), e is the electron charge (1.6×10^{-19} C), and μ is the charge carrier mobility of MAPbI₃, $59 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, corresponding to low-defect and long-lifetime MAPbI₃ single crystals.⁴²

The smallest QD has a diffusion length (L_D) of $1.9 \mu\text{m}$ shown in Table 1. This L_D increases with QD size, reaching $2.5 \mu\text{m}$ for the largest QDs. These values are significantly higher than the L_D of $1 \mu\text{m}$ found in polycrystalline thin-film MAPbI₃, attributed to crystal defects in thin films, such as atomic vacancies and grain boundaries.⁴² Moreover, the longest L_D of $2.5 \mu\text{m}$ in QDs (13.4 nm) approaches the L_D of low-defect single crystals MAPbI₃ ($2.8 \mu\text{m}$).⁴² We summarized the correlation between QD size and PL lifetime (Figure S2).

Panels a–c of Figure 4 show the vibrational modes of the different-sized MAPbI₃ QDs and thin film in the low-frequency range of $<170 \text{ cm}^{-1}$. The Raman peaks measured in the QDs and thin film are free from degradation products such as PbI₂ and PbO₂, which are commonly formed by MAPbI₃ degradation due to humidity and intense irradiation (Figure S3).⁴³ Figure 4a shows the Raman spectrum of the spherical ($\sim 5.2 \text{ nm}$ diameter) MAPbI₃ QDs, which exhibit a weak but distinctive Raman peak at 107 cm^{-1} . Figure 4b shows that the rectangular MAPbI₃ QDs synthesized by the swift injection method with reaction times of 30 s, 3 min, and 30 min exhibit relatively clearer Raman peaks at 81 and 127 cm^{-1} in addition to the peak at 107 cm^{-1} . The rectangular MAPbI₃ QDs with different ARs show no significant differences in their lattice vibrations. In contrast, Figure 4c shows that the MAPbI₃ thin film has a Raman peak at 127 cm^{-1} and largely overlapped Raman features below 120 cm^{-1} , indicating a typical broad structural distribution in a bulk system. These complex Raman features are attributed to the presence of intricate crystal structures, including polymorphs, grain boundaries, and structural defects.^{44,45}

The overall Raman intensity of the smallest dot is relatively weak (low signal-to-noise ratio) due to the low density of the well-defined unit cells within a diameter of 5.2 nm , resulting from a distorted structure enduring higher constraints and surface energies (Figure S4). The weak vibrational mode of the MA cation in the spherical QDs is consistent with a recent study on the MAPbBr₃ QDs.⁴⁶ In contrast, Raman spectra of the larger QDs exhibit an even higher signal-to-noise ratio (Figure 4b). The Raman peaks at 81 , 107 , and 127 cm^{-1} closely match first-principles density functional theory (DFT) calculations with an error of $\sim 3 \text{ cm}^{-1}$. They are the axial Pb–I stretching along the c -axis (81 cm^{-1}), the equatorial Pb–I stretching in the a – b plane (107 cm^{-1}), and the combined motion of the axial Pb–I stretching and MA motion (127 cm^{-1}), respectively (Figure 4d–f). Thus, these three Raman

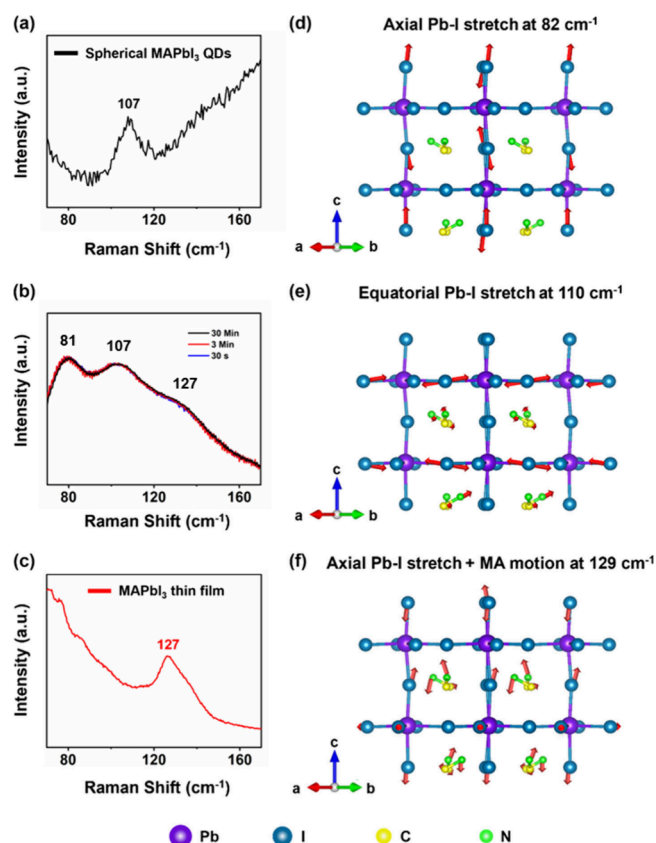


Figure 4. Raman spectra of (a) spherical and (b) rectangular MAPbI₃ QDs and (c) thin film MAPbI₃, (d) Axial Pb–I stretch at 82 cm^{-1} along the c -axis, (e) equatorial Pb–I stretch in the a – b plane at 110 cm^{-1} , and (f) mixed motion of the axial Pb–I stretch and MA motion at 129 cm^{-1} . The directions and amplitudes of the Raman modes are indicated by the red arrows derived from first-principles DFT.

features can serve as spectroscopic fingerprints for pristine single-crystal MAPbI₃ perovskites.

Interestingly, the c -axis Pb–I stretchings at 81 and 127 cm^{-1} are hardly detected in the spherical QDs ($\sim 5.2 \text{ nm}$ diameter) except for the mode at 107 cm^{-1} , the equatorial motion of I–Pb–I in the a – b plane. This Raman difference arises from the critical role of MA⁺ ions in holding a solid unit cell. DFT calculation shows that the effective hydrogen bonding interactions exist along the c -axis (Figure 5), where the N–H...I bond distance is shorter along the c -axis ($\sim 2.65 \text{ Å}$) than in the a – b plane ($\sim 3.05 \text{ Å}$). This indicates that the structural strains in the smaller QDs stimulate a lower density of well-defined MA cations (Figure S4). The more intense hydrogen bondings to the axial iodines restrict the vibrations, making the axially vibrating motions difficult to detect. In contrast, the equatorial motions at 107 cm^{-1} are less affected by those interactions, allowing them to vibrate more freely.

In summary, MAPbI₃ perovskite QDs of various sizes and shapes were successfully synthesized by using the LARP technique. TEM imaging and the infinite well quantum model revealed that the longer dimension significantly influences the PL emission of the QDs with the higher AR. The PL lifetime and diffusion length were found to increase with QD size. In addition, the three distinct Raman peaks at 81 , 107 , and 127 cm^{-1} were identified for pristine MAPbI₃ as Raman fingerprints of MAPbI₃, supported by first-principles DFT calculations. These results contrast with the complex Raman

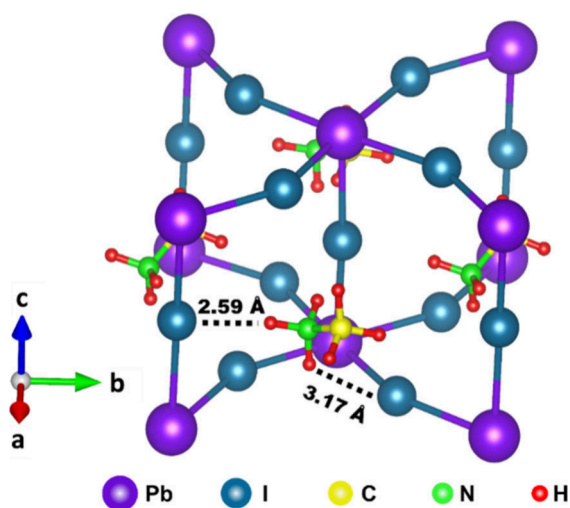


Figure 5. Optimized structure of MAPbI₃. The distances between NH₃ and I in the *c*-axis and *a*–*b* plane are 2.59 and 3.17 Å, respectively.

spectra observed in the bulk system. Thus, our findings highlight two aspects: (1) importance of the AR-related behavior of QDs with specific PL properties, enhancing their application in fields such as bioimaging, light-emitting devices, and solar cells, and (2) the use of Raman fingerprints of pure MAPbI₃ as an effective barometer for quality control, even in bulk MAPbI₃. This is particularly important for applications in optoelectronics where material quality directly impacts performance.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.4c03612>.

Experimental methods, computational details, size-dependent diffusion lengths and PL lifetimes of MAPbI₃ QDs, Raman peaks of PbI₂ and PbO₂, unit cells composed in spherical (~5.2 nm) and rectangular (~13 nm) MAPbI₃ QDs, and Raman peaks of rectangular MAPbI₃ QDs with different ARs (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Myeongkee Park – BB21 Plus Program, Department of Chemistry, Pukyong National University, Busan 48513, Republic of Korea; orcid.org/0000-0002-5307-2564; Email: bikeplay@pknu.ac.kr

Sebastian E. Reyes-Lillo – Departamento de Física y Astronomía, Universidad Andres Bello, Santiago 837-0136, Chile; Email: sebastian.reyes@unab.cl

Authors

Nurwarrohan Andre Sasongko – BB21 Plus Program, Department of Chemistry, Pukyong National University, Busan 48513, Republic of Korea; orcid.org/0000-0003-2228-3999

Yeonsu Jeong – BB21 Plus Program, Department of Chemistry, Pukyong National University, Busan 48513, Republic of Korea

Safira Arta Paramita – BB21 Plus Program, Department of Chemistry, Pukyong National University, Busan 48513, Republic of Korea

Jaeseong Heo – BB21 Plus Program, Department of Chemistry, Pukyong National University, Busan 48513, Republic of Korea

Myoung Hwan Oh – Department of Energy Engineering, KENTECH Institute for Environmental and Climate Technology, Korea Institute of Energy Technology, Naju 58330, Republic of Korea

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.jpclett.4c03612>

Author Contributions

[†]N.A.S. and Y.J. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AR, aspect ratio; HOIP, hybrid organic–inorganic perovskite; LARP, ligand-assisted reprecipitation; MAPbI₃, methylammonium lead iodide; PL, photoluminescence; QDs, quantum dots

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