ABSTRACT: Stabilization of perovskites without addition of foreign surface-passivating ligands in aqueous media is essential for their applications in optoelectronics, biomedical science, and catalysis. However, these materials instantly degrade in water due to its intrinsic ionic nature. By controlling the peripheral layer of octahedral perovskite geometry, we reproducibly synthesized a series of rod-shaped fluorescent hybrid perovskites in both acidic and basic media at ambient conditions in large scale without capping ligands. The band gap is tunable from the red to sky-blue region with sharp emission. The lead bromide perovskites are stable more than 6 months in water without structural change. Our simple synthetic route has resolved the longstanding problems for its practical application in aqueous environment.

Fully inorganic perovskites and hybrid lead halides have been the essence of the materials research community, especially in solar cells, solid-state light-emitting diodes, and many more optoelectronic devices. However, intrinsic ionic properties of both perovskites make them extremely unstable in water. This holds back all of the possible applications where water is present. Several efforts have been made to passivate metal halide perovskites by zwitterions, organic−inorganic hybrid ion pairs, organic Lewis bases such as thiophene and pyridine, and several metal oxides such as SiO2, Al2O3, and Ta2O5. These methods are highly appreciable toward solving the stability issue in water. Furthermore, in some cases, water was introduced during the synthesis of perovskite. This indicates that perovskite can be synthesized in water media by choosing appropriate conditions such as controlling the pH, appropriate metal halide salts, different phases of organic components, etc.

In this Letter, we report an easy, facile, and cost-effective aqueous synthesis of a series of water-stable hybrid and fully inorganic perovskites (1–11) following the Lewis base vapor diffusion (LBVD) method, except for 1 and 10 (Scheme 1 and Figure 1). (See the Supporting Information for synthesis of all of the compounds and sample colors in Figure S1). Compounds 3, 5, 7, 9, and 11 were water-stable and exhibited rod-shaped morphology, which has great potential in device applications as well as exciting optoelectronic properties. In synthetic conditions, MAPbBr3 (3) (MA = CH3NH3+) and CsPbBr3 (11) exhibited bright green fluorescence, and MAPbBr3−xClx (5) showed cyan blue color under UV light (365 nm) in highly basic solutions (Figure 2). The photoluminescence (PL) maximum of the hybrid perovskite was tuned from 763 to 491 nm. The highest internal PL quantum yield (PLQY) of the solid sample was achieved for CsPbBr3 (53.9%). Dried MAPbBr3 (3) and MAPbBr3−xClx (5)
and CsPbBr₃ (11) were highly stable in water for more than 6 months, retaining their bright fluorescence.

During the synthesis, we observed that cubic-shaped perovskites were stable in an acidic medium, while rod-shape ones (especially micrometer-sized rods) were preferably formed in a basic medium. CsPbBr₃ was first discovered by Wells in 1893,²³ and hybrid perovskites were discovered in 1978²⁴ by Weber. Yet, there has been no report on long-time stabilization of these materials in neutral water.

In a typical synthesis, metal halides were dissolved individually in halide acids in a 20 mL vial. The vial without a cap was kept in the MAm bottle in capped conditions (Scheme 1). MAm was slowly diffused into the solution of the metal halide precursor. In the case of MAPbBr₃ synthesis, orange-colored precipitate was observed immediately. At that time, the pH was below 1. The precipitation was completed within 1 h. Then, the color of the precipitate changed to greenish white, and it showed bright green fluorescence under UV light (Figure 2). The precipitate was kept for 10 days in the MAm environment without removing it from the solution. Then, the pH of the solution was again checked after 1 week and found to be above 12. The precipitate was removed from the solution and washed with water several times to remove the basic MAm solution and dried at 60 °C to obtain 3. Compound 3 was much more stable than intermediate 2, which was degraded in neutral water within a fraction of a second. The greenish white precipitate (3) was stable in water more than 6 months. In a similar way, MAPbBr₃₋ₓClₓ (5), MAPbBr₃₋ₓIₓ (7), and MAPbI₃ (9) were also synthesized successfully. The dried sample 5 showed ultrastability in water, exhibiting bright cyan blue fluorescence.

Synthesis of fluorescent CsPbBr₃ (11) was carried out in a different way from that of hybrid perovskite. We synthesized CsPbBr₃ by dissolving PbBr₂ in HBr, and the subsequent addition of Cs₂CO₃ yielded yellow-colored bulk CsPbBr₃.

Figure 1. All of the perovskites including intermediates and their morphology analyses. SEM images of (1) MAPbBr₃ synthesized by direct addition of MAm solution, (2) MAPbBr₃-intermediate before forming 3, (3) MAPbBr₃ (dried end-product), (4) MAPbBr₃₋ₓClₓ-intermediate before forming 5, (5) MAPbBr₃₋ₓClₓ (dried product), (6) MAPbBr₃₋ₓIₓ-intermediate before forming 7, (7) MAPbBr₃₋ₓIₓ (dried product), (8) (MA)₂PbI₄·2H₂O, (9) MAPbI₃ (dried product), (10) CsPbBr₃, obtained after addition of Cs₂CO₃ into the PbBr₂ + HBr solution, and (11) dried CsPbBr₃ (scale bar 10 μm) isolated after 1 day.

Figure 2. Images under synthetic condition. Samples 3, 5, and 11 exhibited bright green, cyan blue, and cyan green color in basic media during synthesis under UV light.
precipitate (10), which showed no fluorescence under UV light. This was kept in a MAm vapor environment to synthesize water-stable fluorescent CsPbBr3. After a few minutes, the precipitate changed to light orange color. After 1 day, the color again changed to greenish white, which showed bright cyan green fluorescence under UV light (365 nm) illumination (Figure 2).

The crystal structures of perovskites powders were confirmed by powder X-ray diffraction (PXRD) measurement (Figures 3 and S2). All of the compounds except 11 exhibited a cubic phase along with some other peaks in final products. Sample 11 exhibited an orthorhombic phase.25 The diffraction peaks of 2 revealed its cubic phase.26,27 Some extra peaks, which were assigned for Pb(OH)2 [mp-690727, collected from the Materials Project data repository], were also present in 1, 2, and 3. The hydrated product (Pb(OH)2·2H2O) was isolated from hydrobromic acid. Sample 8 was separated from a highly basic solution. At the initial stage, 10 exhibited a Br/Pb ratio of 3.68, indicating a highly Br-rich surface as it was isolated from hydrobromic acid. Sample 11, isolated after 1 day from the starting point, exhibited two different colors in the solid state: green and orange, which are named P8 and Po, respectively. The hydrated product (P8) changed its color from greenish to orange (Po) upon drying the sample at 60 °C and regained its green color upon the addition of water. We observed this phenomenon reversibly and tested it for three cycles, after which P8 still exhibited bright cyan blue fluorescence (Figure S6). This is due to the fact that the surface was not properly passivated by Pb(OH)2 within a short time. Water was present in the crystal, as confirmed from IR (discussed later). Upon heating, these water molecules were removed, leaving some void spaces in crystals. Those void spaces took water molecules and regained its green color. To address this issue, we have done the PXRD, IR (discussed later), and SEM analyses for P8 and Po. Both CsPbBr3 and CsPbI3 were present in P8, as indicated by the characteristic PXRD peaks (Figure S7). However, the peaks of CsPbBr3 were more prominent upon heating the sample. This indicated that the crystallinity of CsPbBr3 increased to a great extent upon heating. From SEM analysis of P8, it was found that still cubic-shaped CsPbBr3 was present along with the rod-shaped structure, indicating that the reaction was not completed within this short time (Figure S8a). The cubic shape of P8 was broken in Po as indicated by SEM images (Figure S8b).

The Br/Pb and Cl/Pb ratios in 1 and 2 were 3.38 and 3.4, respectively, and that in 3 was 1.05. Because 1 and 2 were isolated from a hydrobromic acidic solution, these perovskite surfaces were bromide-rich. However, 3 was isolated from basic solution and the Br/Pb ratio deviated from its ideal value of 3 due to the presence of Pb(OH)2 on the surface of MAPbBr3 rods. A similar case was also observed for MAPbI3. Sample 8 and 9 have I/Pb ratios of 4.38 and 1.26, respectively. This is because 8 was isolated as (MA)4PbI6·2H2O from hydroiodic solution, but Pb(OH)2-coated 9 was separated from a highly basic solution. Compound 3 exhibited Br/Pb and Cl/Pb ratios of 3.56 and 0.039, respectively. The Cl content in 3 was very small due to the high concentration of bromide ion in solution, and these bromide ions replaced chloride ions. The Pb/Br and Cl/Pb ratios in 4 were 0.92 and 0.001, respectively, due to the presence of Pb(OH)2. At the initial stage, 10 exhibited a Br/Pb ratio of 3.68, indicating a highly Br-rich surface as it was isolated from hydrobromic acid. Sample 11, isolated after 1 day from the starting point, exhibited two different colors in the solid state: green and orange, which are named P8 and Po, respectively. The hydrated product (P8) changed its color from greenish to orange (Po) upon drying the sample at 60 °C and regained its green color upon the addition of water. We observed this phenomenon reversibly and tested it for three cycles, after which P8 still exhibited bright cyan blue fluorescence (Figure S6). This is due to the fact that the surface was not properly passivated by Pb(OH)2 within a short time. Water was present in the crystal, as confirmed from IR (discussed later). Upon heating, these water molecules were removed, leaving some void spaces in crystals. Those void spaces took water molecules and regained its green color. To address this issue, we have done the PXRD, IR (discussed later), and SEM analyses for P8 and Po. Both CsPbBr3 and CsPbI3 were present in P8, as indicated by the characteristic PXRD peaks (Figure S7). However, the peaks of CsPbBr3 were more prominent upon heating the sample. This indicated that the crystallinity of CsPbBr3 increased to a great extent upon heating. From SEM analysis of P8, it was found that still cubic-shaped CsPbBr3 was present along with the rod-shaped structure, indicating that the reaction was not completed within this short time (Figure S8a). The cubic shape of P8 was broken in Po as indicated by SEM images (Figure S8b). We hypothesize that there might also exist a dynamic equilibrium between CsPbBr3 and CsPbI3, which can be achieved through the reaction Cs4PbBr6·2H2O = CsPbBr3 + 3CsBr + 2H2O.17,18

Figure 3. Structural analysis. X-ray diffraction patterns for hybrid perovskites (a,b) and fully inorganic perovskites (c,d). Panels (b) and (d) are zoomed versions of (a) and (c), which exhibit the peak shifts in Pb(OH)2-coated perovskites. The Pb(OH)2 cif [mp- 690727] was collected from the Materials Project data repository.
The surface chemistry of 3, 5, 7, 9, and 11 was explored by the X-ray photoelectron spectroscopy (XPS) analysis (Figure S9). Compound 3 exhibited two peaks for oxygen at 529.73 and 533.05 eV corresponding to the PbO and Pb(OH)$_2$, respectively. Samples 5, 7, and 9 had only one peak for oxygen at 530, 530.46, and 530.32 eV, respectively, which represented the PbO peak. The peak at 531.19 eV of 11 indicated that PbCO$_3$ was present in the sample. In the presence of water, CsPbBr$_3$ or another perovskite degraded into PbCO$_3$ and Pb(OH)$_2$, and Pb(OH)$_2$ might further break into PbO and H$_2$O. The stoichiometric reaction for CsPbBr$_3$ can be formulated as follows: $2\text{CsPbBr}_3\cdot\text{H}_2\text{O} + \text{O}_2 + \text{CO}_2 = 2\text{CsBr} + \text{PbCO}_3 + \text{Pb(OH)}_2 + \text{Pb(OH)}_2 = \text{PbO} + \text{H}_2\text{O}$. We observed no diffraction peaks of PbO and PbCO$_3$ in the PXRD. This indicates that these were amorphous in nature or they were present in low quantity that was beyond the detection limit. The Pb 4f peaks of 11 at 137.15 and 141.96 eV corresponded to Pb 4f$_{7/2}$ and Pb 4f$_{5/2}$, respectively. PbCO$_3$ peaks appeared at 139.3 and 144.2 eV, while the Br 3d$_{5/2}$ and 3d$_{3/2}$ peaks appeared at 67.09 and 67.93 eV, respectively.

To confirm the presence of Pb(OH)$_2$ in all of the final products, we also performed Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) measurements (Figure S10). All of the intermediates (2, 4, 6, and 7) showed IR frequencies of MA$^+$ (Tables S1 and S2). As the final compounds (3, 5, 7, 9, and 11) were coated with Pb(OH)$_2$, we observed a strong O–H stretching frequency at around 3500 cm$^{-1}$ (Figure S10), but the intensity of other IR peaks corresponding to MA$^+$ were either very small or invisible (in some cases). This is due to the fact that in IR spectroscopy the impinging photons interact with the surface of a compound and reflect from the surface. In FTIR, we observed that IR peaks for MA$^+$ were present in both P$_g$ and P$_o$. Moreover, the IR peak of H$_2$O was also present in the full orange intermediate sample (P$_{int}$) obtained during the formation of 11, and the IR peak of water in P$_g$ appeared at 3418 cm$^{-1}$. However, 12, isolated after 10 days, showed no IR peak of H$_2$O or MA$^+$ due to proper surface passivation by Pb(OH)$_2$ (Figure S10). In 8, we observed an O–H stretching frequency that indicated the presence of water molecules as 8 required two water molecules for its crystallization.

We have carefully studied the mechanism for formation of water-stable hybrid and fully inorganic perovskites. To investigate the role of HBr in the synthesis, we performed two control experiments where bulk MAPbBr$_3$ (100 mg) was taken in 2 mL of toluene with 100 μL of aqueous HBr (i) and without aqueous HBr (ii) and then kept in a MAm environment. For (i), we observed fluorescence under UV light, while for (ii), the MAPbBr$_3$ structure was broken, yielding a white precipitate, which showed no fluorescence under UV light (Figure S11). For (i), we envisaged that MAm vapor diffused into the highly concentrated acidic HBr solution. In contact with acid, MAm formed MABr, which reacted with the acidic metal halide solution. If there was no acid in the precursor solution, only MAm diffused into the crystal, breaking the crystal structure, as observed in (ii). Thus, we conclude that HBr was required for the synthesis of perovskite. Water was also necessary in the reaction mixture to produce hydroxide in the presence of MAm in the solution. After completion of the stoichiometric reaction of acid and MAm, the solution became neutral and changed to a basic medium, producing hydroxide ions. The hydroxide anions reacted with the peripheral layer of the perovskite and formed Pb(OH)$_2$ at the surface of perovskite, breaking the labile surface layer of octahedral [PbX$_6$]$^{2-}$. The metal hydroxide layers acted as strong diffusion barriers for water. The reduction of the surface layer rendered the cubic structure...
into a rod structure, as evidenced from the SEM analysis (Figure S4). During the synthesis, we observed that bare perovskites were stable in acidic condition, but these isolated and dried products were not stable in neutral water. This is due to the fact that MAm and water remained protonated in the highly acidic solution where the concentration of halide ions was also high. However, in neutral water media, water diffused into the structure and both bromide and MA⁺ were hydrated; therefore, these sizes increased to a great extent, compelling them to go outside of the perovskite and break the moiety. The formation mechanism of water-stable CsPbBr₃ is a little bit different from that of the water-stable hybrid perovskite growth mechanism. The formation of water-stable CsPbBr₃ from its precursor salts occurred through several steps (Figure 4). Intermediate products were characterized by PXRD, SEM, and IR analyses. First, CsPbBr₃ was formed by the reaction of HBr solution of PbBr₂ and Cs₂CO₃, and then, MAm was incorporated inside of the CsPbBr₃ crystal structure by diffusion and the color changed gradually from yellow to orange. The orange product (isolated (Figure S12)). The presence of CH₃NH₃ was confirmed by IR analysis (Figure S10). Over the time, the solution became basic as more and more MAm vapor diffused into the solution, producing hydroxide ions in the solution.

Those hydroxide ions had strong nucleophilicity and reacted with the peripheral layer of the octahedral moiety, [PbX₆]⁴⁻, where both Cs⁺ and MA⁺ were present. Thus, there occurred a solid-solution interaction at the surface of the fully inorganic perovskite. This time, the color changed from orange to greenish white, which was stable in water. The dried product isolated after 10 days did not change its color and was highly stable in water. To address this issue, we performed PXRD, SEM, and FTIR-ATR analyses for 10, the full orange intermediate product (Pint) (Figure 4c), and 12 (isolated after 10 days). From PXRD, we observed that the peak at 15.16° gradually shifted to a lower angle and reached 14.83°. This may be due to the fact that the radius of MA⁺ (2.70 Å) is higher than that of Cs⁺ (1.81 Å). As more and more MA⁺ was incorporated in the crystal structure of CsPbBr₃, forming CsₓMA₁₋ₓPbBr₃ (Pint) and finally CsₓMA₁₋ₓPbBr₃ (12), the Bragg’s diffraction angle was shifted to a lower angle (Figure S13). From SEM-EDS analysis, we have confirmed the presence of Cs⁺ in the rod morphology of 12 (Figure S12).

As FTIR analysis gave the surface properties of a compound, we did not observe the characteristic IR peaks of MA in the final product, Pb(OH)₂-coated 12 (Figure S10e), but the O–H peak at 3514 cm⁻¹ was present. The IR peaks of MA⁺ were observed in Pint which confirmed the presence of MA⁺ in the CsPbBr₃ crystal. The procedure for conversion of CsPbBr₃ to MAPbBr₃ in a more controlled way is currently under investigation.

To check the ultrastability of all of the final products (3, 5, 11), we grinded them for a long time and added water, for which the bright fluorescence was still observed as before grinding (Figure S14). Even after a long time of sonication of 3, 5, and 11 in water, we observed bright fluorescence in water (Figure S15). This indicated that all of the final products were efficiently interfaced with Pb(OH)₂, which rendered them ultrastable in water.
indicated that Pb(OH)$_2$-coated perovskites were highly stable in water. In summary, we demonstrated the aqueous synthesis of various hybrid and fully inorganic halide perovskites in acidic and basic media. The rod perovskites were stable in water for more than 6 months, and these were highly fluorescent in both the solid state and solution. We found that there exists a very rich chemistry of perovskites under water, yet to be explored. Our new synthetic approach will open up a new research area for perovskite materials.

**Table 1. Optical Properties of 3, 5, 9, and 11**

<table>
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<tr>
<th>perovskite</th>
<th>$\lambda_{	ext{abs}}$ (nm)</th>
<th>$\lambda_{	ext{em}}$ (nm)</th>
<th>fwhm$^\text{a}$ (nm)</th>
<th>EQY$^\text{b}$ (%)</th>
<th>IQY$^\text{c}$ (%)</th>
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<tr>
<td>MAPbBr$_3$ (3)</td>
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<td>518</td>
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<td>MAPbCl$_{1-x}$Br$_x$</td>
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<td>763</td>
<td>50</td>
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<tr>
<td>CsPbBr$_3$ (11)</td>
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<td>508</td>
<td>45</td>
<td>12.1</td>
<td>53.9</td>
</tr>
</tbody>
</table>

$^\text{a}$Full width at half-maximum (fwhm). $^\text{b}$External quantum yield. $^\text{c}$Internal quantum yield.

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**REFERENCES**


**Notes**

The authors declare no competing financial interest.

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