Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information for

Fabrication of Two-Dimensional Hybrid Organic-Inorganic Lead Halide Perovskites by Liquid-Phase Pulsed Laser Ablation

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1. Preparation of $MAPbBr_3$ single crystal target

Reagents. All chemical reagents were used as received without further purification. Lead bromide ($PbBr_2$, 99.999 %) and methylammonium bromide (MABr, 98 %) were purchased from Sigma Aldrich. N,N-dimethylformamide (DMF, 98 %) was purchased from Fujifilm Wako.

Synthesis of $MAPbBr_3$ crystals. Single crystals of $MAPbBr_3$ were prepared by inverse temperature crystallization (ITC) method.[1] In the ITC method, abnormal solubility of materials that decreases as the temperature increases is utilized. 2 mmol of MABr and 2 mmol of $PbBr_2$ were dissolved in 2 ml of DMF. The solution was filtered using a hydrophilic PTFE membrane filter with pore size of 0.45 μm for removing large-sized solids. Then, the solution was put into a glass vial. The vial was sealed and heated in a water bath up to 80 ℃. After 3 hours of heating at 80 ℃, many small crystallites of $MAPbBr_3$ appeared on the bottom of the vial. One crystallite with good crystal shapes was selected among them and picked out from the solution for use as a seed crystal. The remaining crystallites in the solution were dissolved again after the solution was cooled down to room temperature. The seed crystal was put into the solution and heated up again. After heating at 80 ℃ for 5 hours, the seed crystal grew up to a 5 mm × 5 mm × 2 mm-sized single crystal with a rectangular plate shape.

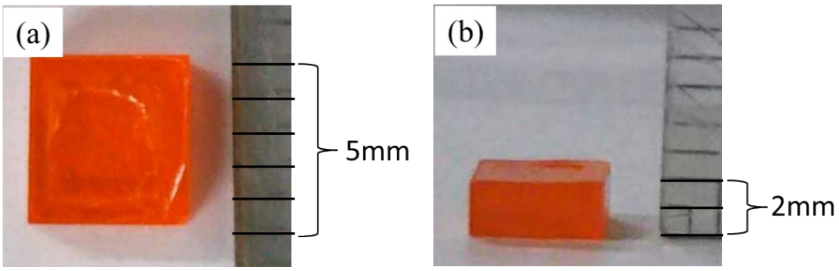


Fig. S1 $MAPbBr_3$ single crystal.

2. LPLA method

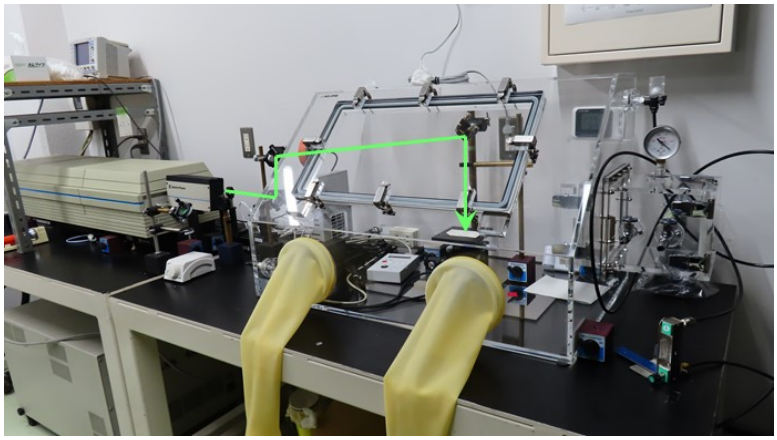
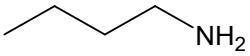


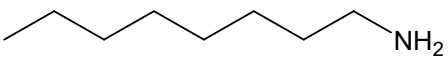
Fig. S2 LPLA apparatus

3. Alkylamines

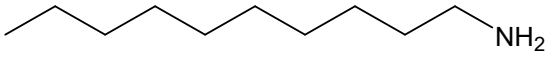
buthylamine (BA, $C_4H_9NH_2$)



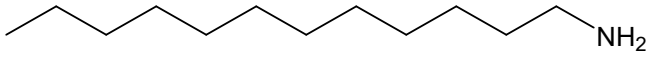
octhylamine (OA, $C_8H_{17}NH_2$)



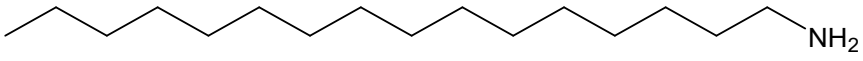
decylamine (DA, $C_{10}H_{21}NH_2$)



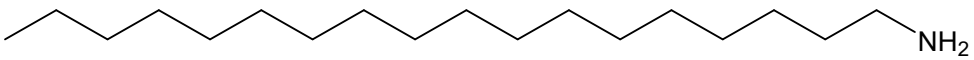
dodecylamine (DDA, $C_{12}H_{25}NH_2$)



hexadecylamine (HDA, $C_{16}H_{33}NH_2$)



octadecylamine (ODA, $C_{18}H_{37}NH_2$)



4. $MAPbBr_3$ particles produced by LPLA

Figure S3 shows photographs of the LPLA product obtained without addition of amines, that was $MAPbBr_3$ particles.

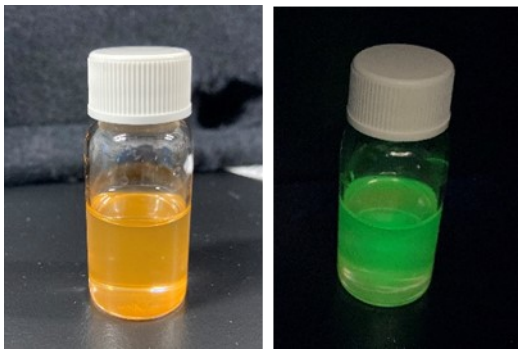
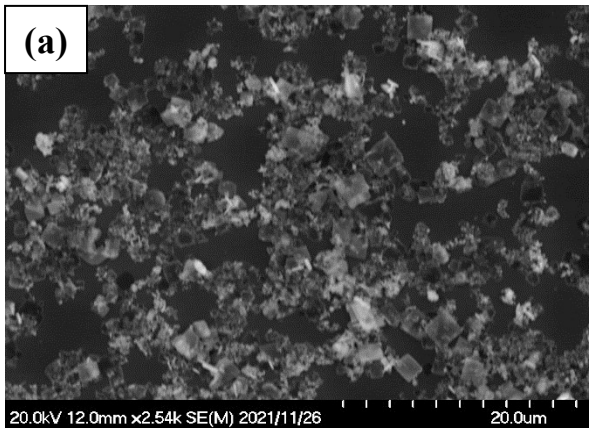
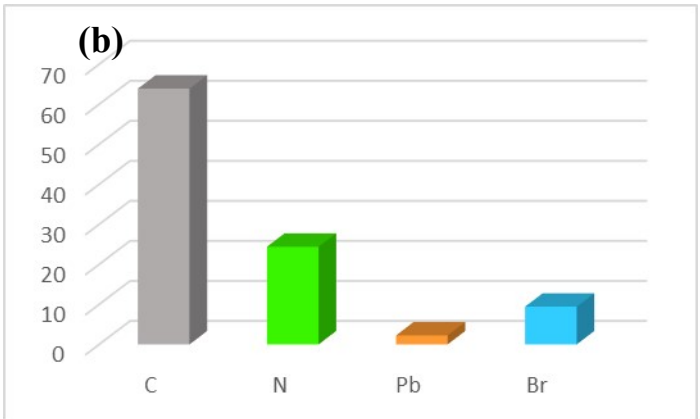


Fig. S3 Photographs under room light (left) and UV light (right) of the LPLA products obtained without addition of amines dispersed in toluene.

5. SEM/EDX measurements

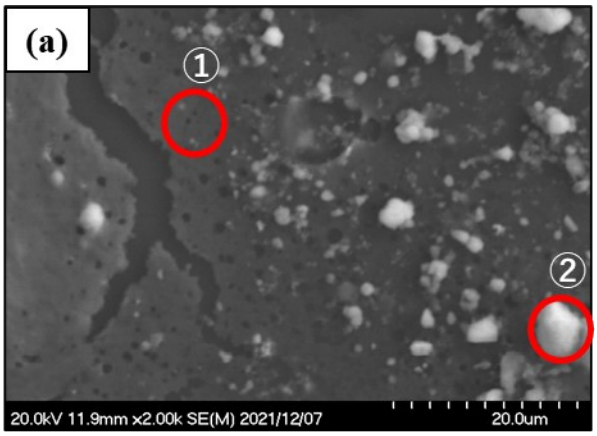
Figures S4—S9 show the SEM images of the ablation products deposited on the silicon substrates and results of their elemental compositions measured by EDX. Except for the image of the 2D perovskite composed of BA (Fig. S4), we can see numerous numbers of white particles with their size ranging from several to ten μm scattered on a dark background (Figs. S5—S9). The EDX analyses exhibited that Pb, Br, C, and N were detected from all of these samples. The composition ratios between Pb and Br in atomic ratios were estimated to be Pb:Br = 1:2.84—1:3.16 from the particles and 1:3.77—1:4.43 for the background regions, respectively. These results strongly suggest that the granular materials are the 3D perovskites of $MAPbBr_3$ (Pb:Br = 1:3) and the 2D perovskites of $XAPbBr_4$ (Pb:Br = 1:4, XA indicates amines) uniformly exist as finer particles on the substrates. The composition ratio estimated for the 2D perovskite with BA (Fig. S4) was Pb:Br ≈ 1:4 from any areas on the substrate, which is also consistent with the composition of the 2D perovskites.

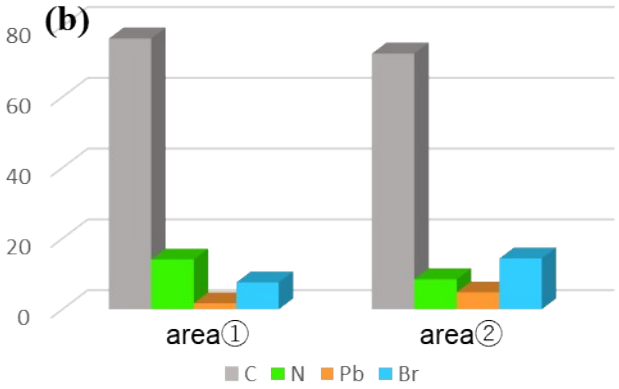




C	N	Pb	Br	Pb:Br
63.91 %	24.39 %	2.26 %	9.44 %	1 : 4.19

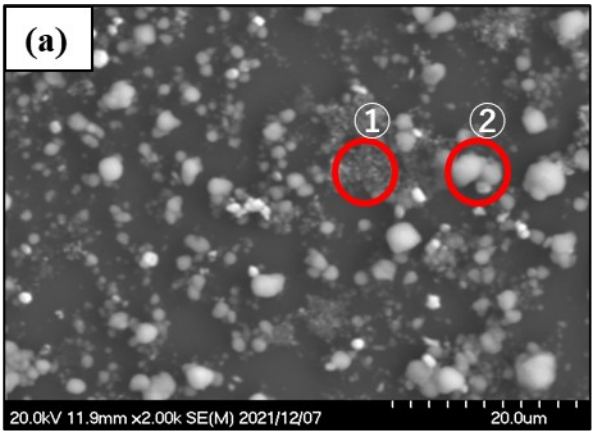
Fig. S4 (a) SEM image and (b) elemental compositions of the LPLA products synthesized by addition of BA.

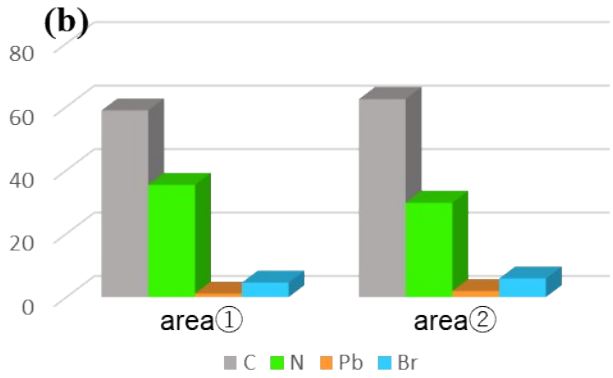




	C	N	Pb	Br	Pb:Br
area①	76.55 %	14.08 %	1.73 %	7.65 %	1 : 4.43
area②	72.31 %	8.49 %	4.81 %	14.40 %	1 : 2.99

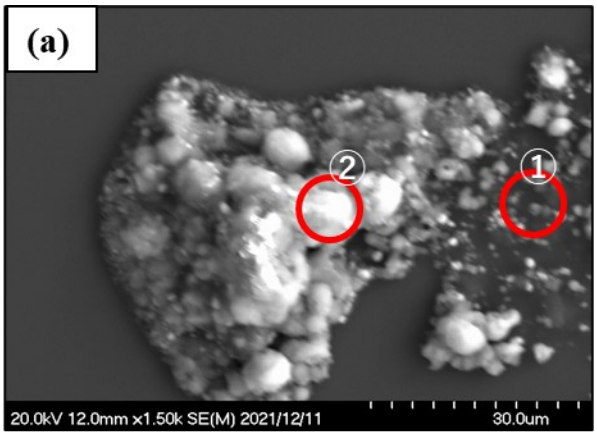
Fig. S5 (a) SEM image and (b) elemental compositions of the LPLA products synthesized by addition of OA.

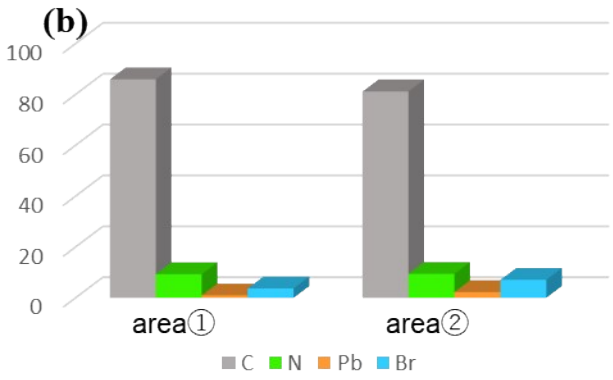




	C	N	Pb	Br	Pb:Br
area①	58.87 %	35.39 %	1.142 %	4.60 %	1 : 4.03
area②	62.43 %	29.76 %	1.92 %	5.90 %	1 : 3.07

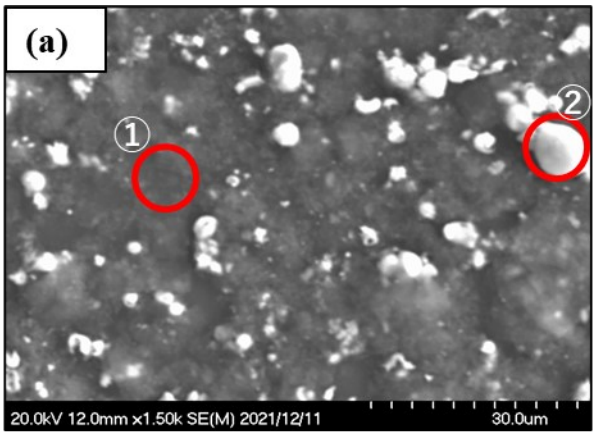
Fig. S6 (a) SEM image and (b) elemental compositions of the LPLA products synthesized by addition of DA.

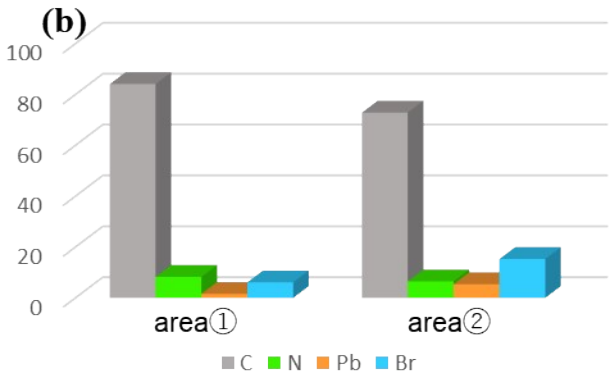




	C	N	Pb	Br	Pb:Br
area①	85.97 %	9.31 %	0.99 %	3.74 %	1 : 3.77
area②	81.20 %	9.44 %	2.26 %	7.10 %	1 : 3.16

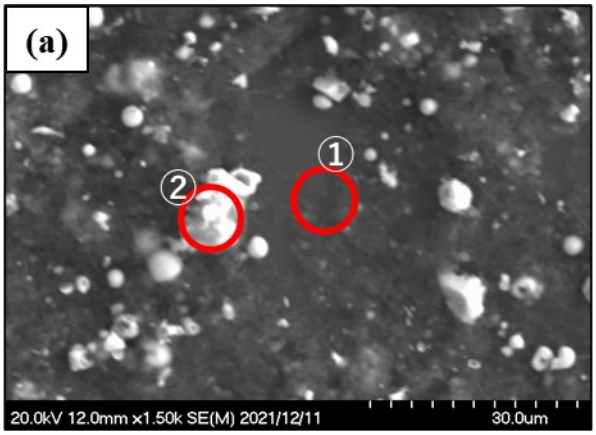
Fig. S7 (a) SEM image and (b) elemental compositions of the LPLA products synthesized by addition of DDA.

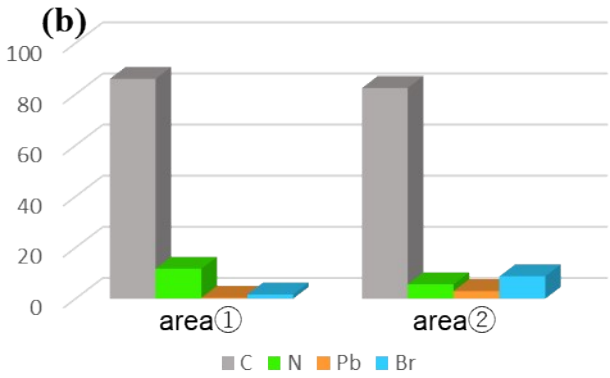




	C	N	Pb	Br	Pb:Br
area①	84.11 %	8.23 %	1.57 %	6.10 %	1 : 3.88
area②	72.86 %	6.48 %	5.38 %	15.28 %	1 : 2.84

Fig. S8 (a) SEM image and (b) elemental compositions of the LPLA products synthesized by addition of HDA.





	C	N	Pb	Br	Pb:Br
area①	86.09 %	11.78 %	0.44 %	1.69 %	1 : 3.89
area②	82.49 %	5.68 %	3.00 %	8.83 %	1 : 2.94

Fig. S9 (a) SEM image and (b) elemental compositions of the LPLA products synthesized by addition of ODA.

6. The control experiments without laser irradiation and effect of excess alkylamine additives

Figure S10 shows the photographs of the $MAPbBr_3$ target crystal placed in toluene containing 1.18 mmol of octhylamine (OA). The amount of OA is equal to that was used for synthesis of the 2D perovskite by LPLA experiment. As shown in these photographs, there have been no changes on the target crystal even after 2 hours soaked in mixed solvent. This result indicated that laser ablation is essentially required for synthesis of the 2D perovskites and only presence of amines cannot produce 2D perovskites. However, when quantity of OA additive was increased, a drastic change was observed. Figure S11 show results of the similar experiment carried out with addition of 11.8 mmol of octhylamine (OA) and no laser irradiation. The target crystal was immediately attacked, and perfectly decomposed after 2 hours. The solvent became opaque and there was no solid target. The absorption spectrum of this opaque solution and XRD pattern of the products are shown in Fig. S12. A sharp absorption peak at 312 nm was observed and the periodic diffraction peaks were observed in the XRD pattern. Liu et al. reported absorption spectra and diffraction patterns closely resembled to these data for intermediate products as they synthesized colloidal perovskite nanocrystals. They attributed them to the $PbBr^{3-}$ complex.[2] Consequently, we concluded that the $MAPbBr_3$ crystal can be easily decomposed and $PbBr^{3-}$ complex is produced in case that excess amount of amine exists.

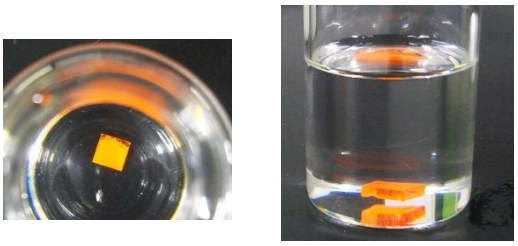


Fig. S10 Photographs of the $MAPbBr_3$ target in toluene. Left: Just after addition of 1.18 mmol of OA. Right: After 2 hours.

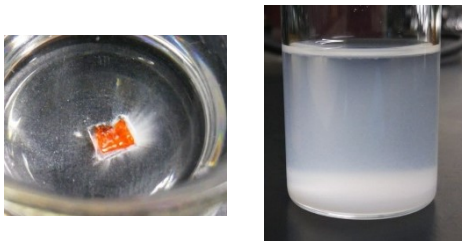


Fig. S11 Photographs of the $MAPbBr_3$ target in toluene. Left: Just after addition of 11.8 mmol of OA. Right: After 2 hours.

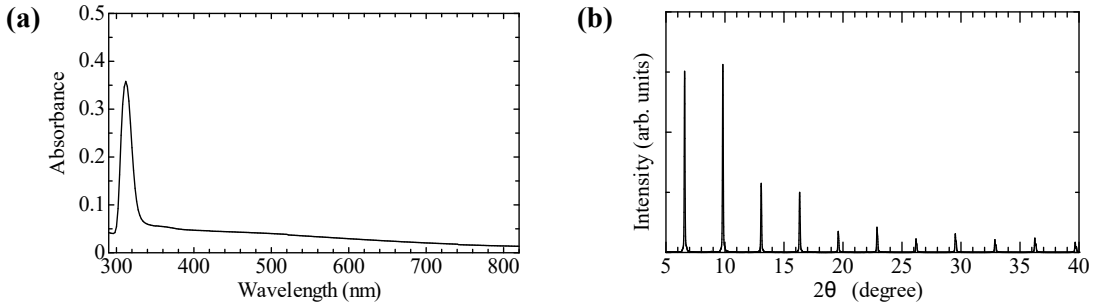


Fig. S12 (a) Absorption spectrum and (b) XRD pattern of the products obtained from $MAPbBr_3$ crystal placed in toluene containing 11.8 mmol of OA for 2 hours.

7. XRD of crystalline phase of octhylamine

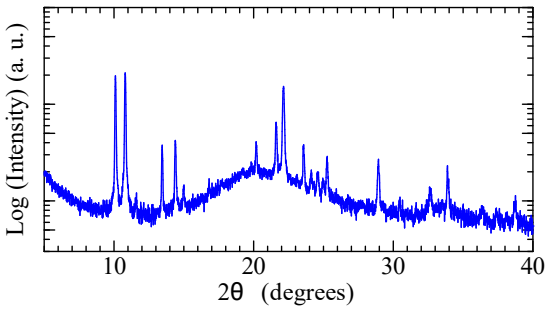


Fig. S13 XRD pattern of OA deposited on a silicon substrate.

References

1. M. I. Saidaminov, A. L. Abdelhady, B. Murali, E. Alarousu, V. M. Burlakov, W. Peng, I. Dursun, L. Wang, Y. He, G. Maculan, A. Goriely, T. Wu, O. F. Mohammed and O. M. Bakr, *Nat. Commun.*, 2015, **6**, 7586.
2. A. Liu, C. Bi, X. Qu and J. Tian, *J. Phys. Chem. C*, 2021, **125**, 14204.