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Supporting Information for:

Colloidal Synthesis of Monolayer-Thick Formamidinium Lead Bromide Perovskite Nanosheets with Lateral Size of Micrometer[†]

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Experimental Section

Chemicals. Formamidine Acetate (FAAc, 99%, Aladdin), Lead(II) Acetate Trihydrate (PbAc₂· 3H₂O, 99.5%, Aladdin), Hydrobromide Acid (HBr, 48 wt. % in H₂O, 99.99%, Aladdin), 1-Octadecene (1-ODE, 90%, Aladdin), Oleic Acid (OA, AR, Aladdin), Hexanoic Acid (HexAc, 99%, Aladdin), Hexylamine (HexAm, 99%, Aladdin), Diethyl Ether (AR, Sinopharm Chemical Reagent Co. Ltd), Hexane (AR, Sinopharm Chemical Reagent Co. Ltd), Ethyl Acetate (AR, Sinopharm Chemical Reagent Co. Ltd), Isopropyl Alcohol (IPA, AR, Sinopharm Chemical Reagent Co. Ltd), Toluene (AR, Sinopharm Chemical Reagent Co. Ltd). All chemicals were used as received without any further purification.

Preparation of HexAmBr and DHABr Precursors. 315 μL HexAm, 95 μL DHA and 340 μL HBr were dispersed into 1 mL diethyl ether. The mixture was loaded on a 220 °C hot plate for 75 sec, and then dispersed into 800 μL hexane and 3.2 mL ethyl acetate for further use.

Synthesis of FAPbBr₃ Nanosheets. 18.7 mL 1-ODE, 950 μL OA and 375 μL HexAc were loaded into a threeneck flask and dried under vacuum at 160°C for 1h. Then, 197 mg FAAc and 228 mg PbAc₂· 3H₂O were added into the mixture and dried under vacuum at 60 °C for 30 min. The mixture was then heated to 130 °C, followed by the injection of as-prepared HexAmBr and DHABr precursors. After 10 sec, the reaction mixture was cooled by an ice water bath.

Isolation and Purification of FAPbBr₃ Nanosheets. The as-synthesized nanosheets were separated by centrifugation at 3000 rpm for 5 min at room temperature, washed twice with non-polar solvent (hexane or toluene), and dispersed into hexane or toluene for further use.

Characterization. Ultraviolet and visible (UV-vis) absorption spectra were recorded with a Shimadzu UV-3600 plus spectrophotometer at room temperature. PL spectra were measured with a Horiba PTI QuantaMaster 400 steady state fluorescence system at room temperature. The topography of the nanosheet was investigated using a Bruker Multimode 8 Atomic Force Microscope (AFM) working in auto mode. Scanning electron microscopy (SEM) was performed on a ZEISS ULTRA55 electron microscope operating at 3 kV. Transmission electron microscope (TEM) and high-resolution TEM were performed on a FEI Tecnai G2 F20 electron microscope

operating at 200 kV. X-ray diffraction (XRD) measurements were employed a Rikagu Ultima III X-ray diffractometer equipped with Cu K α radiation (λ =1.541841Å). X-ray photoelectron spectroscopy (XPS) measurements were performed using an achromatic Al K α source (1486.6 eV) and a double pass cylindrical mirror analyzer (ULVAC-PHI 5000 Versa Probe). The Raman spectra were recorded on a system provided by a SOL confotec MR200 micro-PL-Lifetime and Raman system equipped with a 785 nm laser at room temperature. The fluorescence decay processes were recorded with time-correlated single-photon counting (TCSPC) technique on a system provided by a SOL confotec MR200 micro-PL-Lifetime and Raman system at room temperature. Time-resolved PL decay curves were fitted to a bi-exponential decay curves of.

$$A(t) = A_1 \times \exp(-\frac{t}{\tau_1}) + A_2 \times \exp(-\frac{t}{\tau_2})$$
 (1)

Table S1. Reaction conditions for the synthesis of FAPbBr3 nanocrystals and their PL peaks (line with bold font

Sample	Acid :	Long-Chain	Ratio	Short-Chain	Ratio	Long-Chain	Ratio	Short-Chain	Ratio	2-class	Ratio	PL
(Fig. S1)	Amine	Acid	[1]	Acid	[2]	Amine	[3]	Amine	[4]	Amine	[5]	/nm
a	4:1	OA	70%	OctAc[6]	30%	OAm[7]	20%	OctAm[8]	80%	×	×	536
b	4:1	OA	50%	OctAc	50%	OAm	×	OctAm	100%	×	×	538
c	4:1	OA	50%	OctAc	50%	×	×	OctAm	100%	BEHA[9]	×	532
d	4:1	OA	50%	OctAc	50%	×	×	OctAm	80%	BEHA	20%	533
e	4:1	OA	50%	OctAc	50%	×	×	OctAm	50%	BEHA	50%	538
f	4:1	OA	50%	HexAc	50%	×	×	HexAm	100%	DHA	×	530
g	4:1	OA	50%	HexAc	50%	×	×	HexAm	80%	DHA	20%	523
h	2:1	OA	50%	HexAc	50%	×	×	HexAm	100%	DHA	×	434/528
i	2:1	OA	50%	HexAc	50%	×	×	HexAm	80%	DHA	20%	437

represents the most proper synthetic condition).

[1] Ratio of long-chain acid (mol) to sum of both long-chain acid and short-chain acid (mol)

[2] Ratio of short-chain acid (mol) to sum of both long-chain acid and short-chain acid (mol)

[3] Ratio of long-chain amine (mol) to sum among long-chain amine, short-chain amine and 2-class amine (mol)

[4] Ratio of short-chain amine (mol) to sum among long-chain amine, short-chain amine and 2-class amine (mol)

[5] Ratio of 2-class amine (mol) to sum among long-chain amine, short-chain amine and 2-class amine (mol)

[6] OctAc=Octanoic Acid

[7] OAm=Oleylamine

[8] OctAm=Octylamine

[9] BEHA=Bis(2-ethylhexyl)amine



 $\label{eq:Figure S1.} Figure \ S1. Role \ of \ Ligands. \ TEM \ images \ and \ PL \ spectra \ of \ FAPbBr_3 \ nanocrystals, \ the \ ligand \ composition \ is$

shown in Table S1.

Table S2. Reaction conditions (Ratio of HexAm to DHA) and stability of FAPbBr3 nanosheets (Line with bold

Acid : Amine	Long-Chain Acid	Ratio	Short-Chain Acid	Ratio	1-class Amine	Ratio	2-class Amine	Ratio	Stability
2:1	OA	50%	HexAc	50%	HexAm	100%	DHA	×	\times (Less than 1 min)
2:1	OA	50%	HexAc	50%	HexAm	95%	DHA	5%	\times (Less than 1 min)
2:1	OA	50%	HexAc	50%	HexAm	90%	DHA	10%	\times (Less than 1 min)
2:1	OA	50%	HexAc	50%	HexAm	80%	DHA	20%	Stable

font represents the most proper synthetic condition).

Table S3. Reaction conditions (Ratio of OA to HexAc) and stability of FAPbBr₃ nanosheets (Line with bold font represents the most proper synthetic condition).

Acid : Amine	Long-Chain Acid	Ratio	Short-Chain Acid	Ratio	1-class Amine	Ratio	2-class Amine	Ratio	Stability
2:1	OA	80%	HexAc	20%	HexAm	80%	DHA	20%	\times (Less than 1 min)
2:1	OA	70%	HexAc	30%	HexAm	80%	DHA	20%	\times (Less than 1 min)
2:1	OA	50%	HexAc	50%	HexAm	80%	DHA	20%	Stable
2:1	OA	30%	HexAc	70%	HexAm	80%	DHA	20%	\times (Less than 1 min)
2:1	OA	20%	HexAc	80%	HexAm	80%	DHA	20%	\times (Less than 1 min)



Figure S2. SEM images of as-synthesized FAPbBr₃ nanosheets with different magnification.



Figure S3. Raman spectra of the micron-size FAPbBr₃ nanosheets of a single-unit-cell thickness. The Raman spectra of the precursors, such as FAAc, and the ligands, such as hexanoic acid-HBr, di-n-hexylamine-HBr, the oleic acid, and silicon substrate were also listed for comparison.



Figure S4. XPS spectra of (a) FAPbBr₃ nanosheets and (b~e) selected elements.

Element	Content/a. u.
Br	24.97
Pb	8.14
N (FA, HexAm and DHA)	25.83
O (OA and HexAc)	1.71

Table S4. Element content of FAPbBr3 nanosheets, measured by XPS.



Figure S5. (a) PL Spectra and (b) Normalized PL intensity variation of FAPbBr₃ nanosheets which is dispersed in toluene and tested at room temperature.



Figure S6. Time-resolved PL decay spectra of 437 nm PL peak in $FAPbBr_3$ nanosheets.

Table S5. Time-resolved PL decay of FAPbBr₃ nanosheets.

Sample	τ_1/ns	τ_2/ns	A_1	A_2	$%A_1$	$%A_2$	Ave. τ/ns
FAPbBr ₃ , 437 nm	0.46279	4.28643	1013.6900	95.1177	53.50%	46.50%	2.24071



Figure S7. (a) PL Spectrum and (b) Time-resolved PL decay spectra of a FAPbBr₃ nanosheet sample with 3 PL peaks, which is isolated and purified by both hexane and IPA, at 437 nm (responding monolayer-thick nanosheets), 511 nm (responding thicker nanosheets) and 539 nm (responding 3D bulk crystal), respectively.