Electronic supplementary information for

Aqueous acid-based synthesis of lead-free tin halide perovskites with near-unity photoluminescence quantum efficiency

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EXPERIMENTAL SECTION

Chemicals: n-Octylamine (Aladdin, AR, 99%), Hypophosphorous acid (H_3PO_2, Aladdin, AR, 50 wt. % in H_2O), Hydrobromic acid (HBr, Aladdin, AR, 48 wt. % in H_2O), Hydroiodic acid (HI, Aladdin, AR, 55.0 - 58.0% with ≤1.5 % H_3PO_2), Stannous Oxide (SnO, Aladdin, AR, 99%), Polystyrene (PS, Aladdin) were purchased and used without further purification.

Synthesis of $(OCTAm)_2SnBr_4$: In a typical synthesis, stannous oxide (0.75 mmol) powder was dissolved in 2.5 mL hydrobromic acid by sonication until all SnO powder was dissolved. Then aqueous 15 mL H_3PO_2 was added to avoid the oxidation of the tin, in the meantime, 475 μL n-octylamine was added to the above tin-precursor solution under strong agitation. The solution was heated to 80 °C and maintained for 30 min. The colorless plate-like product with strong yellow fluorescence under UV light was slowly cooled at 4°C. For the synthesis of $(OCTAm)_2Sn(Br/I)_4$ or $(OCTAm)_2SnI_4$, the variable compositions were obtained by simply changing the ratios of the halide ions.

Synthesis of Other $(OCTAm)_2SnX_4$: The anion exchange reactions were conducted using $(OCTAm)_2SnBr_4$ as starting material, while hydroiodic acid was used as iodide source. Specifically, Hydroiodic acid was dropwise introduced into the starting solution under strong agitation for a few seconds and the complete anion exchange process was achieved within minutes.

PS-Perovskite Composite Film Fabrication: To obtain the film, firstly 25% Polystyrene (PS) dichloromethane solution was mixed with a certain amount of $(OCTAm)_2SnBr_4$ to get a turbid jelly-like solution. Then, the films were prepared by drop-casting the turbid jelly solution onto a glass slide and let it dried in ambient air.

White LEDs Lamp Fabrication: Various weight ratios of yellow $(OCTAm)_2SnBr_4$, blue ($BaMgAl_{10}O_{17}:Eu^{2+}$) and green (Eu doped silicates, G2762) phosphors were blended well with 25% Polystyrene (PS) dichloromethane solution. The blended phosphors of PS paste were dropped on 365 nm UV LED chip (1W) and dried in air to form white LEDs lamp.

Characterization Details. Powder X-ray diffraction (PXRD): PXRD was measured with a Bruker AXS D8 X-ray diffractometer equipped with monochromatized Cu Kα radiation (λ=1.5418 Å). The diffraction pattern was scanned over the angular range of 5-40 degree (2θ) with a step size of 0.03, at room temperature. Transmission electron microscopy (TEM): TEM was performed on an FEI Tecnai G2 F20 electron microscope operating at 200 kV. The available line resolution is about 0.1 nm. Scanning electron microscopy (SEM): SEM was performed on a ZEISS ULTRA55 electron microscope operating at 3.5 kV. Equipped with Energy-dispersive X-ray (EDX) detector. Steady State Photoluminescence Studies: The photoluminescence (PL) spectra were carried out with a Horiba PTI QuantaMaster 400 steady-state fluorescence system or with a homemade fiber fluorimeter system from Thorlabs operating under ambient conditions. Ultraviolet and Visible (UV–vis) Absorption Spectroscopy for Solid Samples: UV–vis spectra were recorded with a Shimadzu UV-3600 plus spectrophotometer equipped with an integrating sphere under ambient conditions. Absolute Photoluminescence Quantum Yields (PLQYs) Measurements for Solid Samples: The absolute fluorescence quantum yields were measured using a Horiba PTI QuantaMaster 400 steady-state fluorescence system with an integrated sphere and double-checked with a Hamamatsu Photonics Quantaurus-QY (model: C11347-11) under ambient conditions. Three independent experiments were done and the test errors of the absolute quantum yield values are below 1%. Time-Resolved Photoluminescence Lifetime Measurements for Solid Samples: Time-Resolved PL emission decay curves were collected at room temperature and detected by a Nikon Ni-U Microfluorescence Lifetime System (Confotec MR200, SOL, Belarus) with a 375 nm picosecond laser, and double-checked with a time-correlated single-photon counting system or a Hamamatsu Photonics Quantaurus-Tau (model: C11367-11) with 280 nm or 365 nm picosecond lasers under ambient conditions.

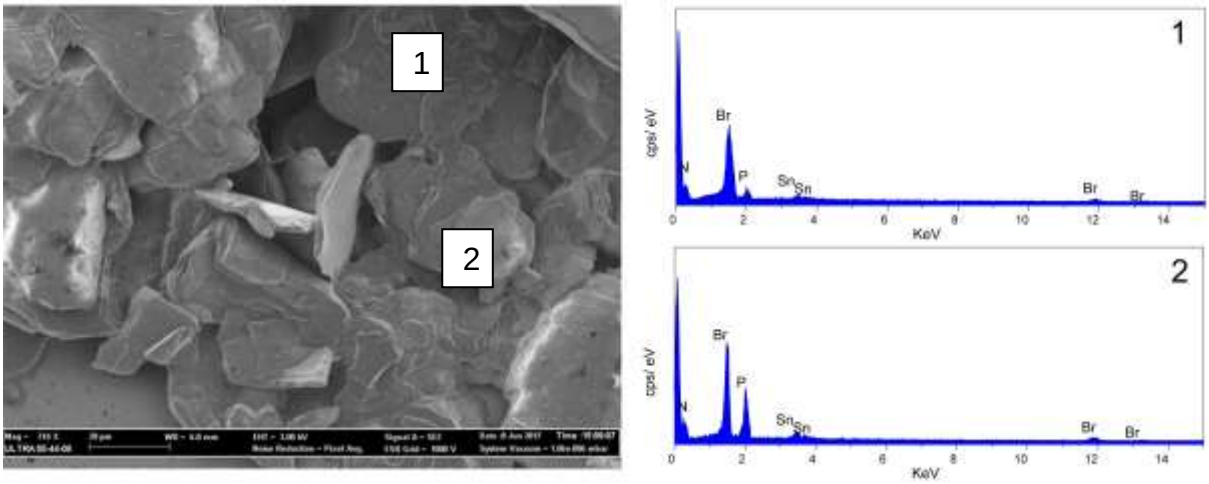

Figure S1. Additional scanning electron microscopy image of the as-prepared 2D $(OCTAm)_2SnBr_4$ perovskites without purification and corresponding EDS spectra of different area in the same sample.

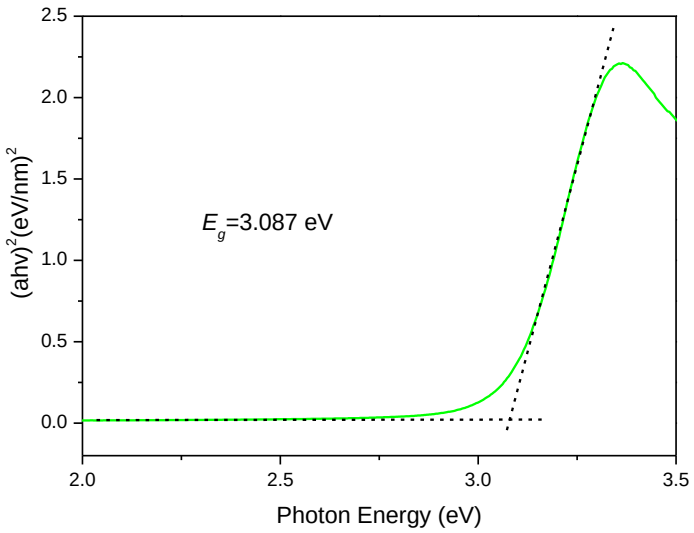

Figure S2. Plots of $(ahv)^2$ vs photon energy (hv) of 2D $(OCTAm)_2SnBr_4$ perovskite.

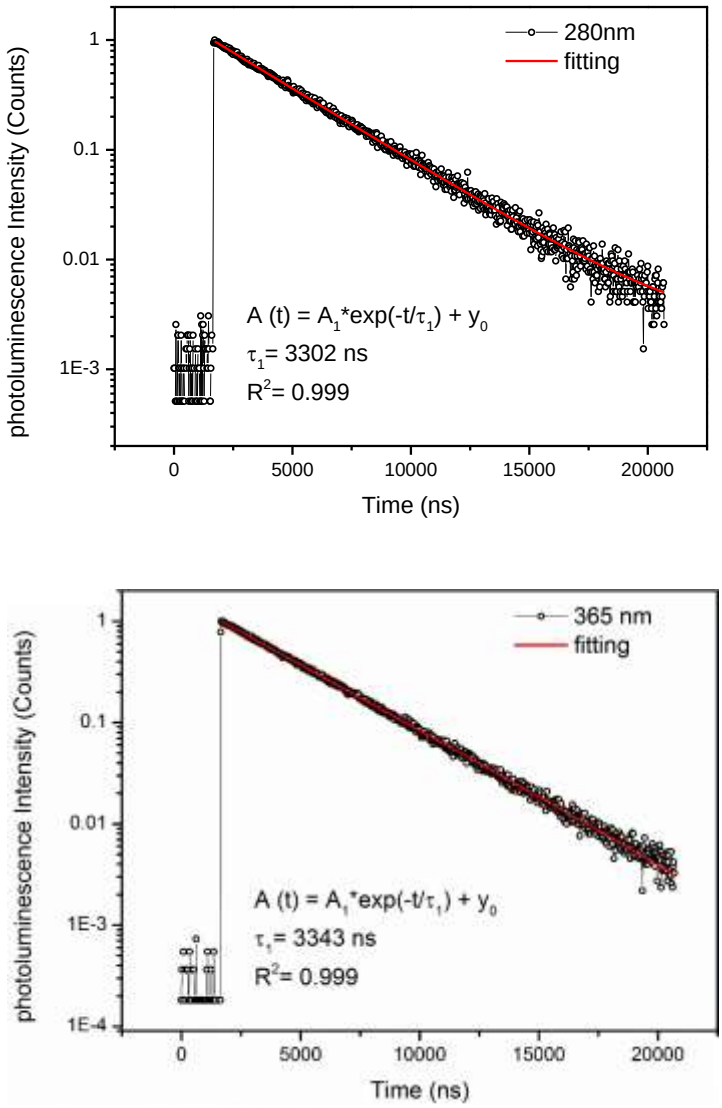

Figure S3. Time-resolved PL decay and the corresponding fitting curves of the 2D $(OCTAm)_2SnBr_4$ perovskites with PL emission at 600 nm and excitation wavelength of 280 nm or 365 nm.

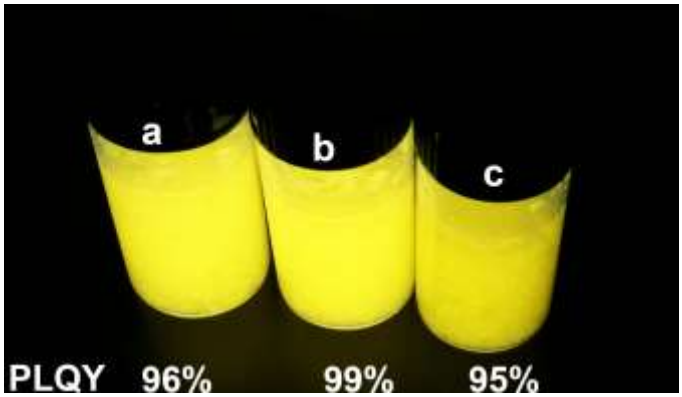

Figure S4. The photographs of products produced with different H_3PO_2 concentrations (a-c, 50, 25 and 12.5 wt. %) under UV light.

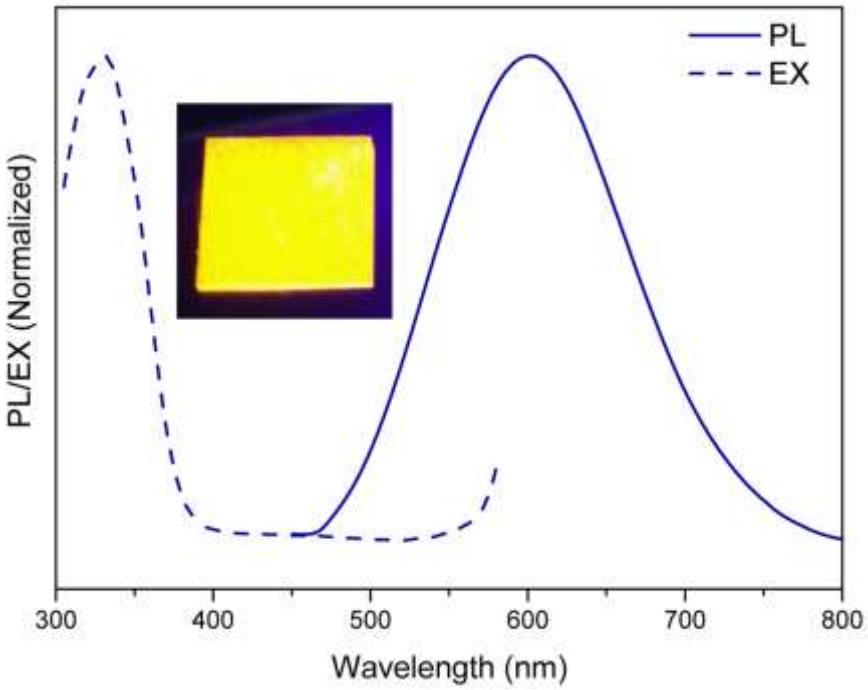

Figure S5. Normalized PL excitation (EX) and emission spectra (PL) of 2D $(OCTAm)_2SnBr_4$ PS-perovskite composite film. The inset shows photograph of 2D $(OCTAm)_2SnBr_4$ PS film under UV light.

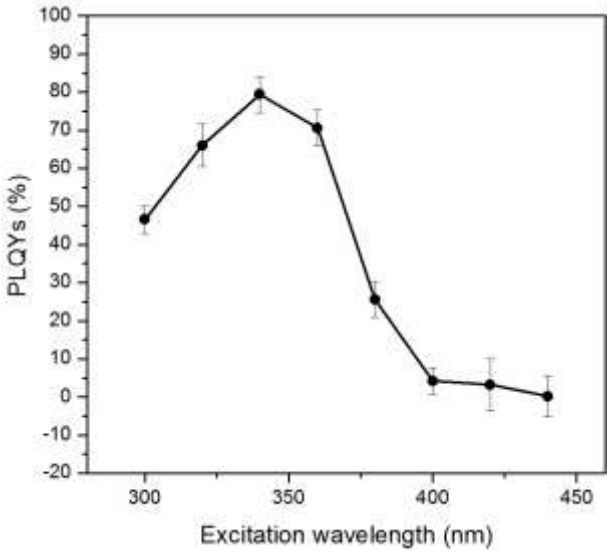

Figure S6. Absolute PL quantum yields spectrum of $(OCTAm)_2SnBr_4$ PS-perovskite composite film under different excitation wavelength.

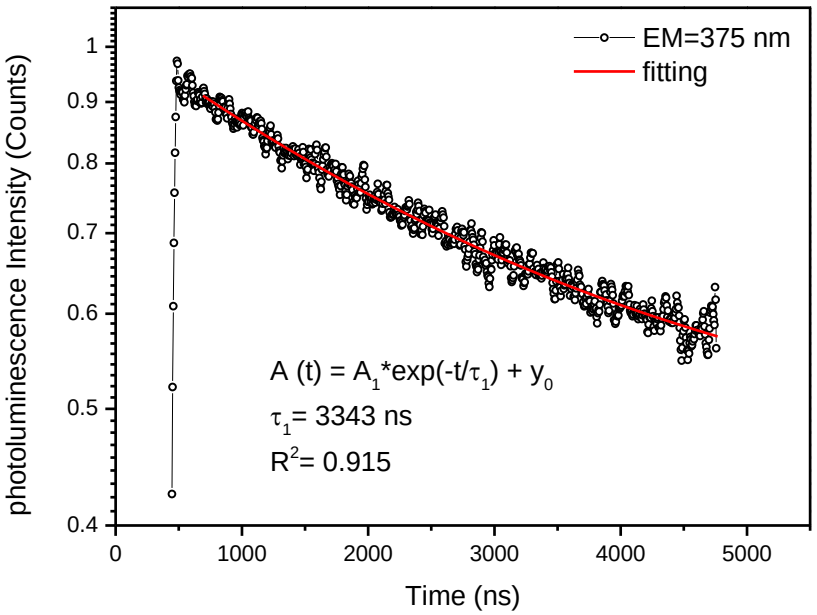

Figure S7. The time-resolved PL decay and fitting curves of $(OCTAm)_2SnBr_4$ PS-perovskite composite film with PL emission maximum at 600 nm and excitation wavelength of 375 nm.

Table S1. Comparison of PLQYs values of various halide perovskites synthesized under different conditions.

Materials	Structural dimensions	Size	PLQYs	Sythesis conditions	Ref.
α-(DMEN)$PbBr_4$	2D	bulk	--	aqueous	S1
(EDBE)$PbBr_4$	2D	bulk	9%	aqueous	S2
$CH_3NH_3PbX_3$	3D	Nano-crystal	40%	aqueous	S3
$CsPbBr_3$	3D	Micro-crystal	53.9%	aqueous	S4
$(PEA)_2SnI_4$	2D	Thin film	0.24%	DMF	S5
HMD_3SnBr_8	2D	bulk	86%	DMF/CH_2Cl_2	S6
$(C_4N_2H_{14}X)_4SnX_6$	0D	bulk	near unity	DMF/ CH_2Cl_2	S7
$(C_{18}H_{35}NH_3)_2SnBr_4$	2D	Micro-crystal	88%	octadecene	S8
$(OCTAm)_2SnBr_4$	2D	bulk	near unity	aqueous	This work

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