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Supporting Information
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Stable Sn²⁺ Doped FAPbI₃ Nanocrystals for Near-infrared LED

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Experimental Procedures

Chemicals: Propionic acid (ACS grade reagent, >99.5%), formamidine acetate (99%), toluene (anhydrous, 99.8%), 1-octadecene (tech. grade, 90%), lead iodide (99.999%, perovskite grade), oleic acid (reagent grade, 99%) oleylamine (tech. grade, 70%). All chemicals are purchased from Sigma-Aldrich. Octadecene, oleic acid and oleylamine were dried at 150 °C, with continuous stirring, under vacuum condition for about 3 h. Purged N₂ gas, before we store it as such for further uses.

Synthesis of FAPbI₃ Nanocrystals: The nanocrystals were synthesized following a method reported by Protesescu et al.^[1] However, we used formamidine propionate (FA-PA) instead of FA-oleate. The first step involves synthesis of FA-PA. About 5 ml of propionic acid is added to 0.26 g of formamidine acetate and continuously stirred at 80 °C for about 30 minutes.

Synthesis of undoped FAPbI₃ NCs: About 5 ml of dried octadecene is added to PbI₂ (0.086 g) taken in a 2-neck round bottom flask. About 1 mL of dried oleic acid and 650 µL of dried oleylamine are injected to the reaction flask in vacuum condition. Heating at 120 °C for about 1 h follows this. When PbI₂ dissolves completely, the temperature is reduced to 75 °C. At that temperature, 1 ml of FA-propionate (pre-heat to 80 °C) is injected. The reaction flask is immediately transferred to an ice-water bath.

Synthesis of Sn²⁺-doped FAPbI₃ NCs: For Sn doping, we used three different concentrations of tin iodide. Both Sn and Pb iodide are added together, along with 5 ml of octadecene, 1 ml of oleic acid and 650 µL of oleylamine. The rest is like the synthesis and purification of undoped NCs.

Isolation and Purification: The NCs in octadecene were centrifuged at 8000 RPM. The precipitate is collected and re-dispersed in 10 mL of anhydrous toluene. The NCs are then washed with anti-solvent, acetonitrile (toluene: acetonitrile= 2:1), centrifuged again at 8000 RPM. The pellet obtained is re-dispersed in 10 mL of anhydrous toluene. Centrifuged once again at 3000 RPM to discard the bigger particles. The top part is used for further characterizations.

For LED device fabrication, the pellet obtained after acetonitrile washed, is re-dispersed in 1 mL of anhydrous toluene and centrifuged at 3000 RPM. The pellet formed is discarded and used the top part as ink.

Characterizations: The UV-visible and PL spectra of the NCs were collected using Shimadzu UV1800 Spectrophotometer and FluoroMax-4 spectrofluorophotometer, respectively. Powder XRD patterns were recorded in a XRD Bruker D8 Advance in thin film mode. The average sizes of the NCs were determined by using a Tecnai transmission electron microscope (TEM, model FEI Tecnai F20). For powder XRD measurements, the NCs in toluene are deposited on a glass substrate and for TEM on a carbon-coated copper grid. ICP-OES measurement was done using Perkin Elmer Optima 7300DV instrument, samples were digested with acid before measurement. XPS measurements were done using a pass energy of 26 eV and 0.1 eV per step. The XPS instrument model used is Quantera II from Ulvac-Phi. The absolute PLQY was measured with the sample in an integrating sphere using 400 nm laser excitation

SUPPORTING INFORMATION

and the emission was collected with charge-coupled device array (Princeton Instruments, Pixis) coupled to a monochromator (Acton, Spectra Pro). Time-resolved PL was performed using a streak camera system (Optronis Optoscope). The 400 nm pump pulse laser was generated by frequency doubling the 800 nm laser from the regenerative amplifier (Coherent Libra, pulse width 50 fs, repetition rate 1kHz) using a BBO crystal.

Device fabrication: As-purchased indium-tin oxide (ITO; Pre-etched, sheet resistance $\sim 8 \Omega \text{ cm}^{-1}$; Wuhan Jinge Solar Energy Technology Co., Ltd) glass substrates were used for device fabrication. The ITO glass substrates were washed in detergent solution, acetone, ethanol, and 2-propanol in an ultrasonication bath, followed by drying and treatment under UV-ozone for 20 min. The hole transporting layer, PEDOT:PSS (Clevios 4083; filtered with $0.45 \mu\text{m}$ PVDF filter) was then spin-coated at 4000 rpm for 1 min and thermally annealed at 130°C for 10 min to remove any residual solvent. The substrates were then transferred to an argon-filled glovebox for the spin coating of emitter layer. The Sn-doped FAPbI₃ NCs inks were spin-coated at 500 rpm for 1 min on top of the PEDOT:PSS [poly(3,4-ethylenedioxythiophene) polystyrene sulfonate] layer. Followed by thermal evaporation of electron transporting layer (POT2T, 2,4,6-Tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine) of thickness 45 nm under high vacuum (10^{-6} torr). Finally, thermal evaporation of electrode materials Calcium (7 nm) and Aluminium (80 nm) using a metal shadow mask, to define the device active area of 3 mm^2 .

Device characterization: Prior to electroluminescence characterization, all LED devices were encapsulated with epoxy resin and the encapsulation is done inside the argon-filled glovebox. A Keithley 2612B was used to obtain the current-voltage characteristics of the LED devices using a scan rate of 1 V s^{-1} (step size 0.1 V , step interval 0.1 s). The light emission was collected by an integrating sphere (OceanOptics FOIS-1) coupled to a calibrated spectrophotometer (OceanOptics QEPro). OceanOptics HL-3 Plus vis-NIR light source, calibrated using a procedure and documentation patterned after the ISO 17025, IEC Guide 115 and JCGM100:2008 (GUM) protocols, is used to calibrate the absolute irradiance measurement of the spectrometer. As LED devices are placed on outside of the integrating sphere, only forward emission is captured while the edge emission contribution is lost outside the integrating sphere.

Figure S1. Survey X-ray photoelectron spectra (XPS) of (A) undoped (B) 1.8% Sn- doped (C) 11.4% Sn-doped FAPbI₃ NCs. High- resolution XPS analysis corresponding to (D) Pb 4f, (E) C 1s, (F) N 1s, (G) O 1s and (H) I 3d5/2. The high-resolution spectra were also recorded corresponding to the core levels of C 1s, N 1s, O 1s, Pb 4f and I 3d5/2 for the undoped NCs and the other Sn-doped NCs and the peak positions are found to be same as of doped NCs.

Figure S2. TEM image of 1.8% Sn-doped FAPbI₃ NCs

Figure S3. Tauc Plot of undoped FAPbI₃ NCs and those doped with different percentage of Sn²⁺.

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Figure S4. (A) Absorption spectrum (B) Tauc plot of 11.4% Sn-doped FAPbI₃ NCs.

Figure S5. Energy difference, ΔE (meV) versus % Sn-doping in FAPbI₃ NCs.

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Sample	t1	a1	t2	a2
Undoped NCs	48 ns	0.69	278 ns	0.31
1.8% Sn-doped	40 ns	0.78	132 ns	0.22
2.44% Sn-doped	16 ns	0.85	154 ns	0.15

Figure S6. Time-resolved PL decays of undoped and Sn-doped FAPbI₃ NCs with bi-exponential fittings (green solid lines). The table shows the fitted decay lifetimes (t_i) and the related amplitudes (a_i).

Figure S7. Powder XRD patterns of undoped FAPbI₃ NCs, 1.8% Sn-doped and 2.44% Sn-doped FAPbI₃ NCs.

SUPPORTING INFORMATION

Figure S8. Photographs of undoped FAPbI₃ NCs washed with acetonitrile and then dispersed in toluene and stored under ambient condition (a) Day 1 (b) Day 2, samples got precipitated, no phase degradation was observed (c) Day 3, phase degradation starts from the precipitate (d) Day 3, few hours later degraded completely.

Figure S9. Photographs of 2.44% Sn-doped FAPbI₃ NCs washed with acetonitrile and then dispersed in toluene and stored under ambient condition (a) Day 1 (b) Day 7 (c) One month later, slight precipitation occurs (d) more than two months, sample get precipitated, the image is of the top part, after discarding precipitate, no phase degradation was observed.

Figure S10. XRD patterns of (A) 1.8% Sn-doped FAPbI₃ NCs deposited on glass substrate after 2 months of synthesis (dispersed in toluene and stored under ambient condition), showed no extra peaks; (B) the same NCs deposited after more than 3 months, showed few extra peaks (marked by blue asterisk*) that corresponds to δ -FAPbI₃ phase and (C) 2.44% Sn-doped FAPbI₃ NCs, deposited more than 3 months after synthesis (dispersed in toluene and stored under ambient condition), showed two extra peaks (marked by red asterisk*).

- [1] L. Protesescu, S. Yakunin, S. Kumar, J. Bär, F. Bertolotti, N. Masciocchi, A. Guagliardi, M. Grotevent, I. Shorubalko, M. I. Bodnarchuk, C.-J. Shih, M. V. Kovalenko, *ACS Nano* **2017**, *11*, 3119-3134.