Supporting Information

Stable α/δ Phase Junction of Formamidinium Lead Iodide Perovskites for Enhanced Near-Infrared Emission

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Experimental Section

Synthesis of Perovskite Precursors.

Unless otherwise stated, all materials were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Substrates were then cleaned sequentially in detergent, acetone, propan-2-ol and oxygen plasma. FAI was first prepared by directly mixing formamidine acetate and HI (45 wt % in water) at 0 °C for 2 h. The precipitate was collected by rotary drying at 65 °C for 30 min, which was followed by washing with a mixture of ethanol and diethyl ether by air pump filtration. The white solid was finally dried at 60°C under vacuum for 2 days. To form pure α-$FAPbI_3$ and δ-$FAPbI_3$ phase, FAI and PbI_2 were mixed in a 1:1 molar ratio dissolved in anhydrous N,N-dimethylformamide (DMF), at 1M of each reagent, to give a 1M perovskite precursor solution. Precursors with modified stoichiometry were prepared by fixed concentration of PbI_2 at 1 M and different molar ratios of FAI to PbI2(FAI:PbI_2 = 1.1:1, 1.2:1, 1.3:1, 1.4:1, 1.5:1, 2:1, 3:1), respectively.

Fabrication of Perovskite Films.

All the stoichiometrically modified perovskite precursor solutions were deposited on the pretreated FTO substrate at 4000 r.p.m. for 60 s, but annealed at different temperature to form different $FAPbI_3$ films: 170 °C for 10 min to form pure α-$FAPbI_3$ films, 60 °C for 15 min to form pure δ-$FAPbI_3$ and other films.

PeLED fabrication.

ITO-coated glass substrates were cleaned successively with acetone and isopropanol, followed by 10 min oxygen plasma treatment. PEDOT: PSS (Clevios P VP AI 4083) was spin-coated onto the substrate at 3000 r.p.m. for 60 s, and annealed at 200 °C for 10 min in air atmosphere. The perovskite precursor solution (FAI:PbI_2 = 1.2:1) was spin-coated onto PEDOT:PSS at 4000 r.p.m. for 60 s and annealed at 60 °C for 15 min. B3PYMPM(4,6-Bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine) as the electron-transport layer,(30 nm) , Cs_2CO_3 (2 .5 nm) and Al(150 nm) were successively deposited by vacuum thermal evaporation. Devices were tested in N_2 with encapsulation.

Characterizations.

X-ray diffraction (XRD) patterns were obtained with Smart LAB instruments with Cu Kα beam. Optical microscopy and spectroscopy were performed using a custom sample scanning confocal microscope by Olympus FV1200 fitted with an infinity corrected 100x oil objective. For measuring the fluorescent lifetime, a 485 nm or 405 nm pulsed diode laser was used for excitation with repetition rates at 40MHz. The Steady-state PL spectra of the $FAPbI_3$ films were measured by using a spectrofluorometer (FluoroMax-3) at room temperature. The photoluminescence quantum yield (PLQY) was measured using an absolute PL

measurement system (Hamamatsu Quantaurus-QY). A 50-nm-thick polymethylmethacrylate (PMMA) layer was deposited on each $FAPbI_3$film to prevent oxygen and moisture. Transmission electron microscopy (TEM) images were taken on a Hitachi HT7700 transmission electron microscope. TEM samples were prepared by first mounting a TEM grid on a cleaned FTO glass substrate. The same deposition and heat treatment procedure for the perovskites are then followed as above. The dielectric constants were measured by Agilent 4294A (Agilent Inc., Bayan, Malaysia) impedance analyzer. The morphology of the films was obtained on a Hitachi SU-8010(SEM). The size distributions were tested by zeta potential analyzer (Brookhaven ZetaPlus). UV-vis absorption spectra were performed on a Hitachi U-3010 spectroscope with an integrating sphere attachment operating in the region of 350–850 nm. The ultraviolet photoelectron spectroscopy measurements were performed using photoelectron spectrometer (Thermo Fisher ESCALAB 250Xi) equipped a He-discharge lamp providing He–I photons of 21.22 eV with a bias of -5.0 V and the position of Fermi edge was calibrated using a clean Ag film. The current–voltage characteristics were measured with a Keithley 4200 semiconductor characterization system and optical power was determined using a Newport 1936-C power meter coupled to a calibrated Newport 918D-UV-OD3 detector with a spectral response range from 200 to 1100 nm. The electroluminescence spectra of the OLEDs were obtained using a multichannel spectrometer (PR 705). The EQE of the NIR EL was determined according to the literature method, by measuring the light intensity in the forward direction and assuming the external emission profile to be Lambertian.

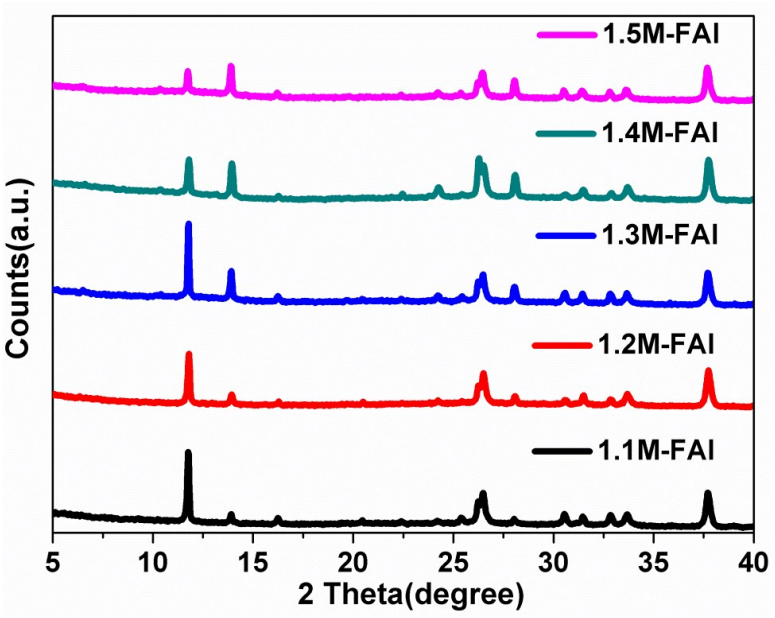

Fig. S1 Full XRD patterns of the $FAPbI_3$ films formed with different FAI/PbI_2 molar ratios from 1.1 to 1.5.

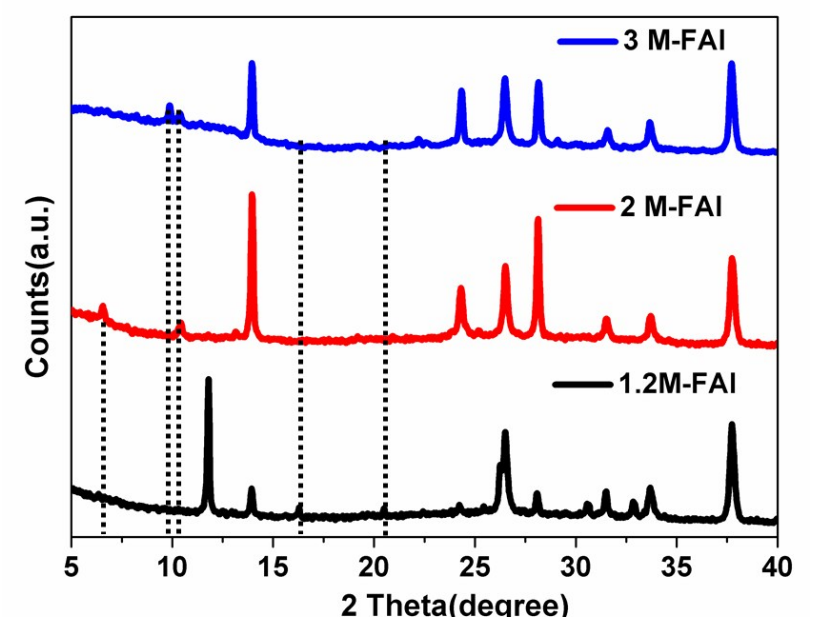

Fig. S2 Full XRD patterns of the $FAPbI_3$ films formed with different FAI/PbI_2 molar ratios of 1.2, 2, 3.

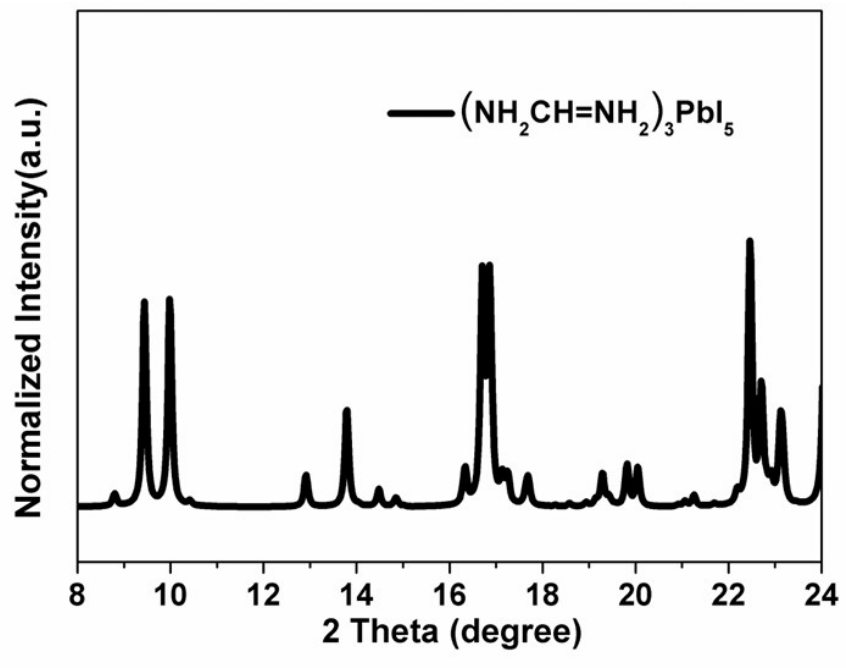

Fig. S3 Caculated X-Ray diffraction spectrum of FAI_3PbI_5 film.

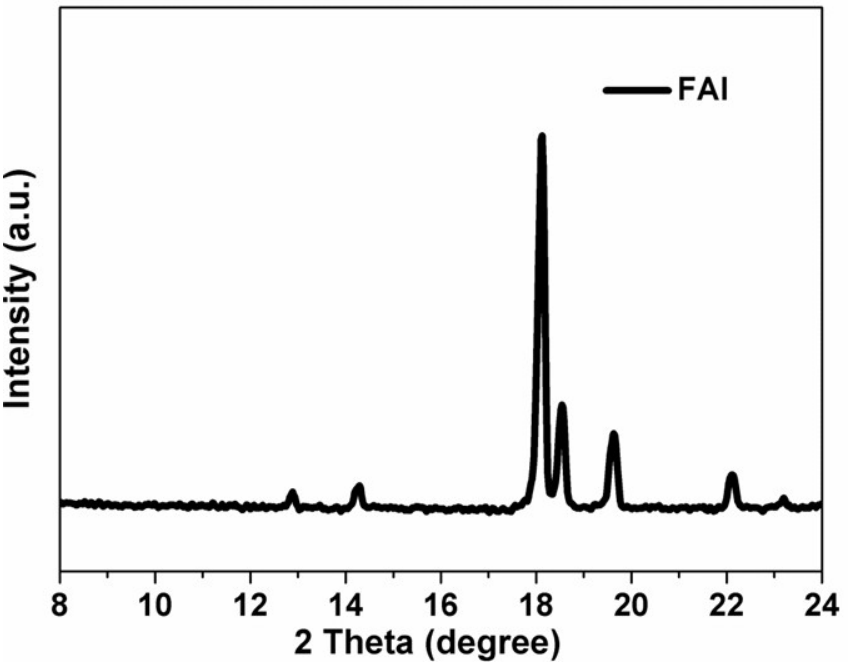

Fig. S4 X-Ray diffraction spectrum of FAI.

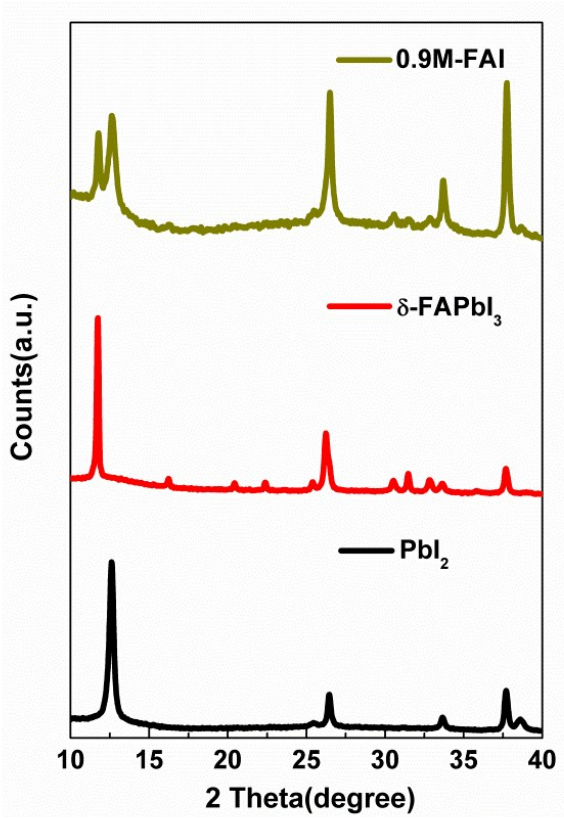

Fig. S5 Full XRD patterns of the δ-$FAPbI_3$, PbI_2 and 0.9 M-FAI film.

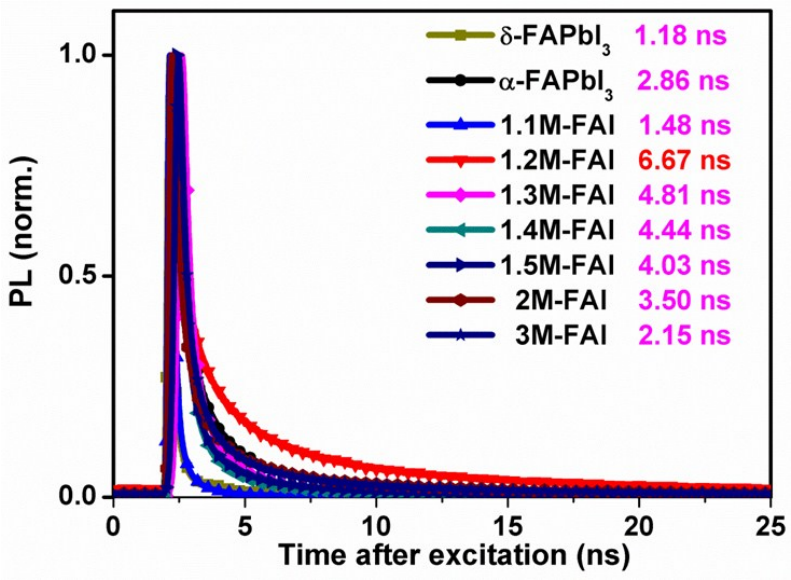

Fig. S6 Fluorescence Lifetime Imaging Microscopy (FLIM) decay curves of the $FAPbI_3$ films formed with different FAI/PbI_2 molar ratios in the precursor solutions.

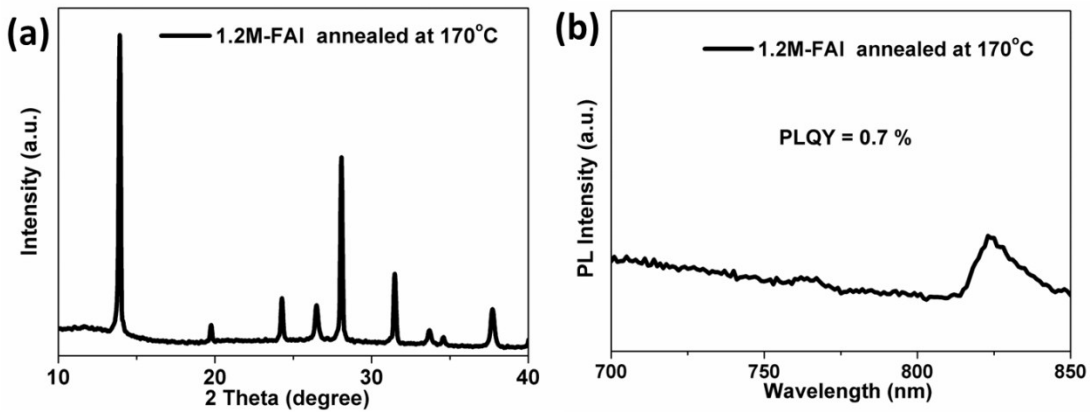

Fig. 7 (a) The XRD patterns of 1.2M-FAI annealed at 170°C without δ-$FAPbI_3$. (b) The PL spectra of 1.2M-FAI annealed at 170°C without δ-$FAPbI_3$.

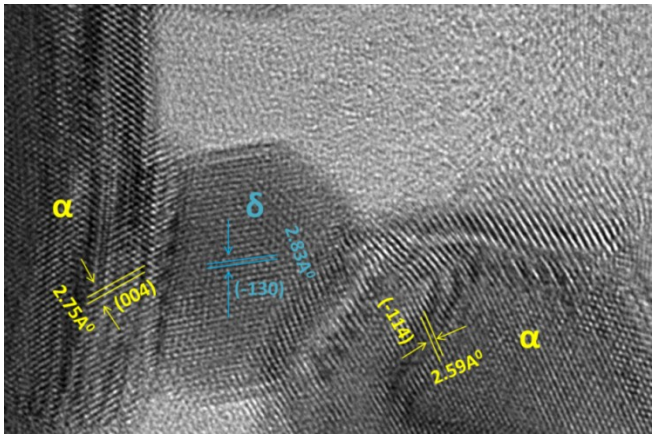

Fig. S8 HRTEM of the α/δ phase junction formed with 1.2M-FAI.

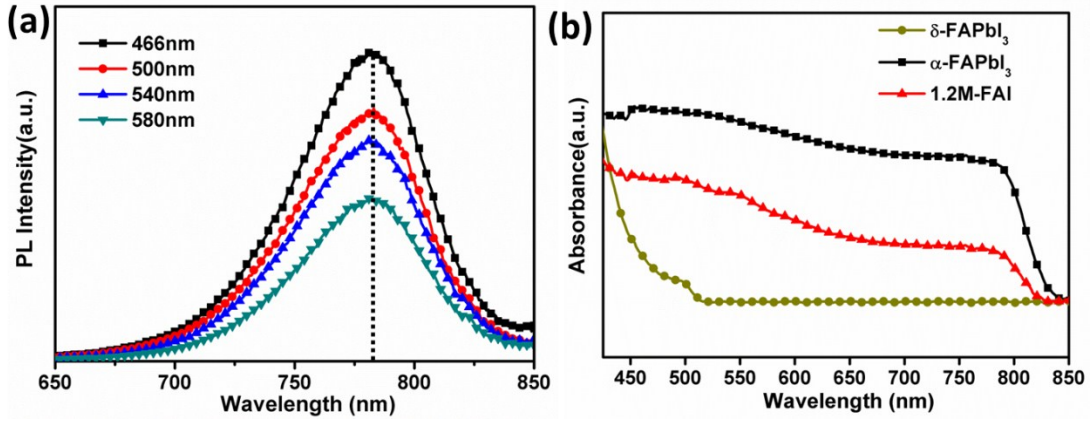

Fig. S9 (a) The PL emission spectra of the 1.2M-FAI film with α/δ phase junction excited at different wavelengths. (b) Ultraviolet-visible absorption spectra of films of α-$FAPbI_3$, δ-$FAPbI_3$, and α/δ phase junction at 1.2M-FAI.

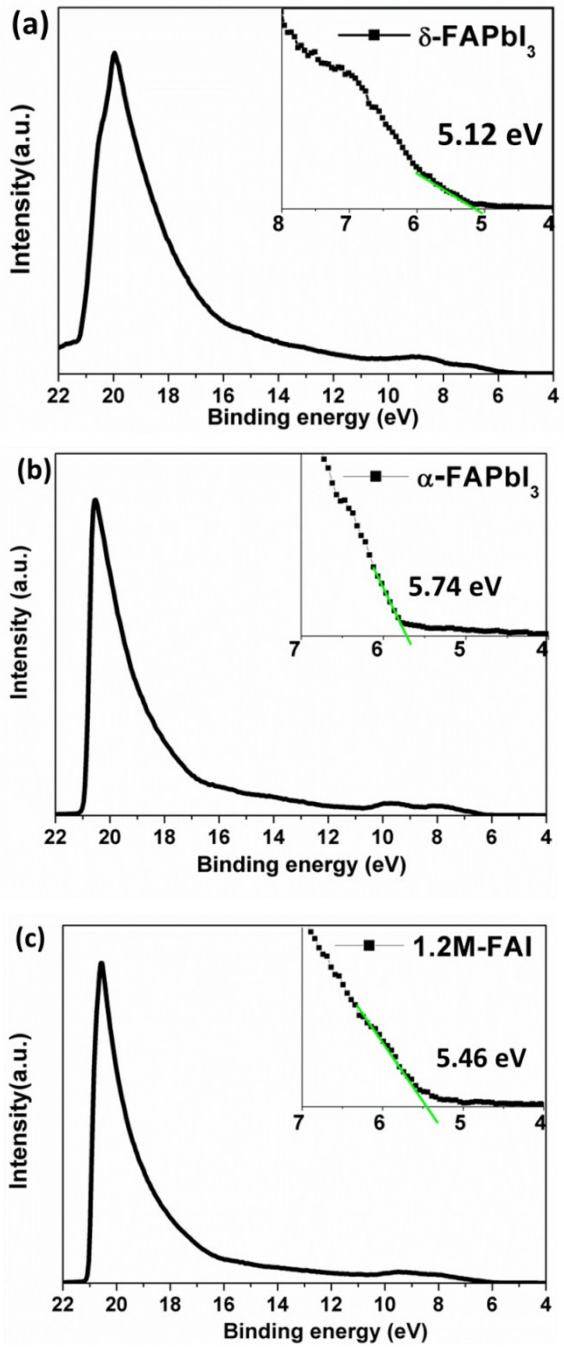

Fig. S10 UPS spectra of the films of pure α-$FAPbI_3$ (a), δ-$FAPbI_3$ (b), and the α/δ phase junction at 1.2M-FAI (c), where insets show linear fit of the data at the onset region to determine the valence band maximum (VBM) of the films.

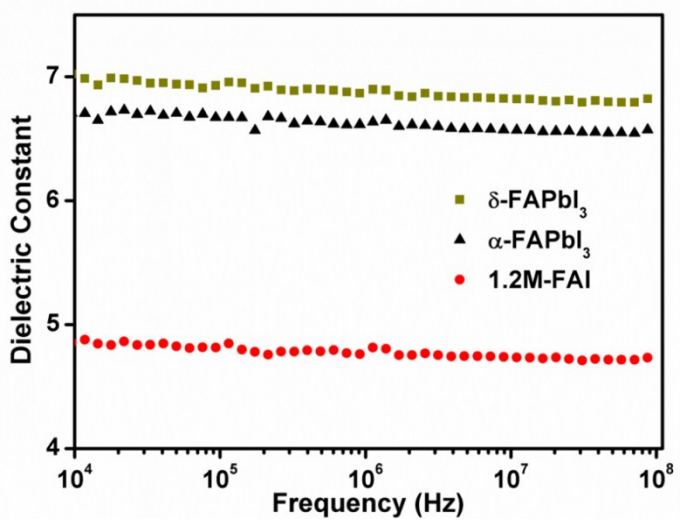

Fig. S11 Dielectric constants in different frequency regime of the films of pure α-$FAPbI_3$, δ-$FAPbI_3$ and α/δ phase junction at 1.2M-FAI.

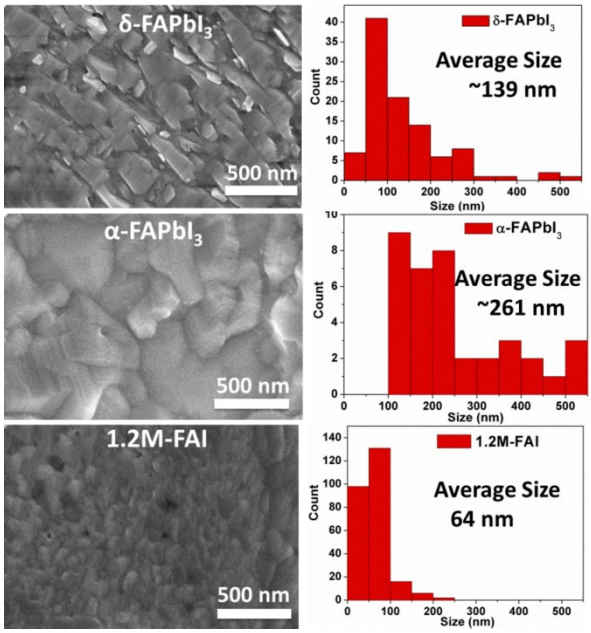

Fig. S12 Top–view SEM images and grain size distribution of the films of δ-$FAPbI_3$, α-$FAPbI_3$ and the α/δ phase junction at 1.2M-FAI.

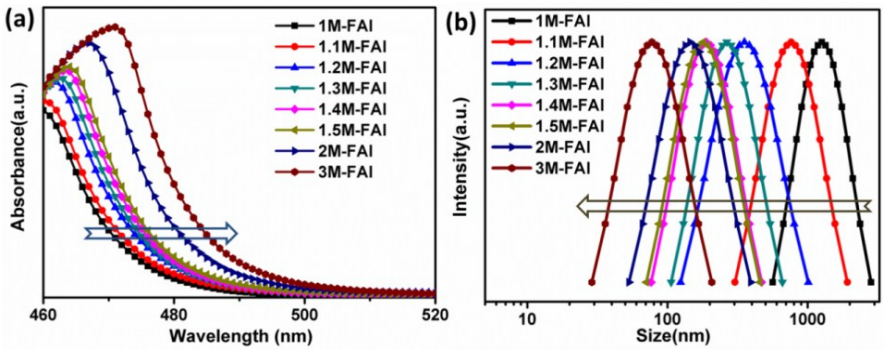

Fig. S13 Colloidal properties of perovskite precursors with different molar ratios of FAI/PbI_2 at room temperature. (a) UV spectra of colloids. (b) Size distribution by dynamic light scattering.

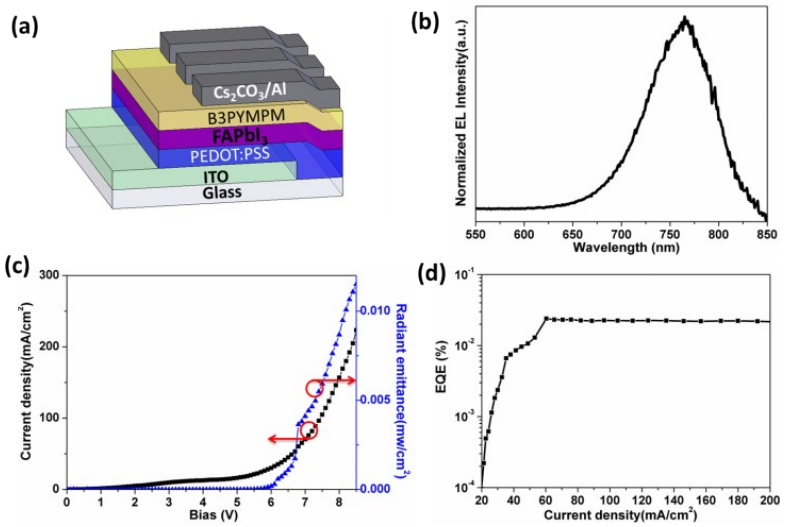

Fig. S14 Device architecture and performance of the FAPbI3 PeLED with α/δ phase junction: (a) device architecture, (b) Electroluminescent spectra, (c) Current density (J)–voltage (V)–radiant emittance (R) characteristics, (d) External quantum efficiency-current density characteristics.