Supporting Information for:

Growth and Anion Exchange Conversion of $CH_3NH_3PbX_3$ Nanorod Arrays for Light-Emitting Diodes

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Methods:

Synthesis of $CH_3NH_3PbBr_3$ Nanorod Arrays: All chemicals were used as received without further purification. A commercial ITO on glass was washed and ultrasonically cleaned. After oxygen plasma treatment, the ITO substrates were coated with high conductivity grade PEDOT:PSS (Clevios) at 3000 rpm for 40 seconds. Afterwards, the coated ITO substrates were baked at 150 °C for 15 minutes. These substrates were coated with 10 µL of a saturated methanolic solution of lead acetate trihydrate (Aldrich), which spreads along the PEDOT:PSS layer. Dropcasting or spin coating are both suitable. The chips were annealed at 65°C for 30 minutes in air. After cooling, the chips were transported into a glove box filled with N_2 where they were suspended face down in a centrifuge tube. A freshly dissolved solution of CH_3NH_3Br (1-materials) with a concentration of 5 mg/mL to 9 mg/mL was prepared in 4 mL of anhydrous isopropanol (Aldrich). This solution was quickly added to the vial containing the ITO/PEDOT:PSS/lead acetate substrate to allow the lead acetate film to react with the CH_3NH_3Br solution uniformly. Within several minutes, an orange film began to grow on the substrate. The reaction was allowed to proceed for 20 to 30 hours. The $CH_3NH_3PbBr_3$ arrays were gently washed in isopropanol and dried under nitrogen. It is important to note that changing the concentration of CH_3NH_3Br can result in the formation of cubes, sheets, and disordered wires as shown in Figure S6.

Anion Exchange Reaction: Within a glovebox, a 20 mL glass vial was charged with 0.1 g of CH_3NH_3I. Afterwards, a chip containing a $CH_3NH_3PbBr_3$ nanorod array was placed in the vial face up. The vial was carefully sealed with a rubber septum and held in place using a cable tie, and the vial was placed half submerged in an oil bath at 140 to 150 °C. Alternatively, a capped vial heated in a glovebox with a hot plate set to 160°C could also be used. Crystals of CH_3NH_3I in direct contact with the array cause inhomogeneous conversion of the film. Conversion appears to occur most rapidly at the edges of the chip. After several hours, CH_3NH_3I deposition was apparent on the sidewalls of the vial. The reaction was allowed to proceed until the film was uniformly black, which required up to 100 hours for full conversion. Partial anion exchange could be achieved by limiting reaction time. In cases with insufficient exposure to CH_3NH_3I vapor to allow anion exchange or exposure to the air during heating, decomposition of the film was observed because of the separation of CH_3NH_3X and PbX_2.

Structural and Optical Characterization: SEM images were acquired using a JEOL JSM-6340F field emission scanning electron microscope. Characterization of the electron diffraction was conducted using a FEI Tecnai TEM at an accelerating voltage of 200 kV with decreased electron dose at high spot size values. The XRD pattern was acquired using a Bruker AXS D8 Advance diffractometer equipped with a lynxeye detector, which used Cu Kα radiation. PL was measured using a 325 nm excitation from a HeCd laser with emission collected on a Nikon A1 microscope coupled to a multimode fiber coupled to a liquid-nitrogen-cooled Si CCD (PI Acton). Optical images were acquired via an Olympus IX71 inverted microscope coupled to a Zeiss AxioCam MRc5 camera. The measurement of the absorption of the $CH_3NH_3PbBr_3$ was carried out using a Shimadzu UV-3101 UV-Vis spectrometer equipped with an integrating sphere. Time resolved photoluminescence was measured using a Picoquant Fluotime 300 instrument with a PMA 175 detector. The sample was excited by a LDH-P-C-405 diode laser with an excitation wavelength of 407.1 nm, and the sample was measured at 534 nm with a power of 11.84 pJ/pulse over an area of $3.8e^{-4}$ cm^2.

Device Fabrication: Device fabrication was an adaptation of previously reported methods.[1] Within a glove box, a solution of 10 mg/mL F8 (Aldrich) was dissolved in chlorobenzene by heating after stirring overnight. This solution was spin coated onto the $CH_3NH_3PbBr_3$ array at 3000 rpm and annealed at 100 °C for 10 minutes. A TEM image of a $CH_3NH_3PbBr_3$ nanorod coated with an F8 polymer shell is shown in Figure S7 with an average shell thickness of approximately 8 nm. Afterwards, 100 nm of Ca and 300 nm of Ag were thermally evaporated through a shadow mask to define the microscale contacts. The evaporation rate of the contacts was limited to 0.1 Å s^{-1} to prevent thermal decomposition.

Device Testing: A Keithley 2636 source-measure unit was used to provide bias to the device and measure the *I-V* characteristic. The devices were measured on a home-built probe station that could be coupled to a 60X objective in an inverted microscope. For pulsed DC measurements, the duration of the pulse was 100 ms while the time between pulses was 200 ms. The device was electrically contacted from the top of the metal electrode with a soft probe (Picoprobe T 4-10) coated with indium gallium eutectic (Aldrich).

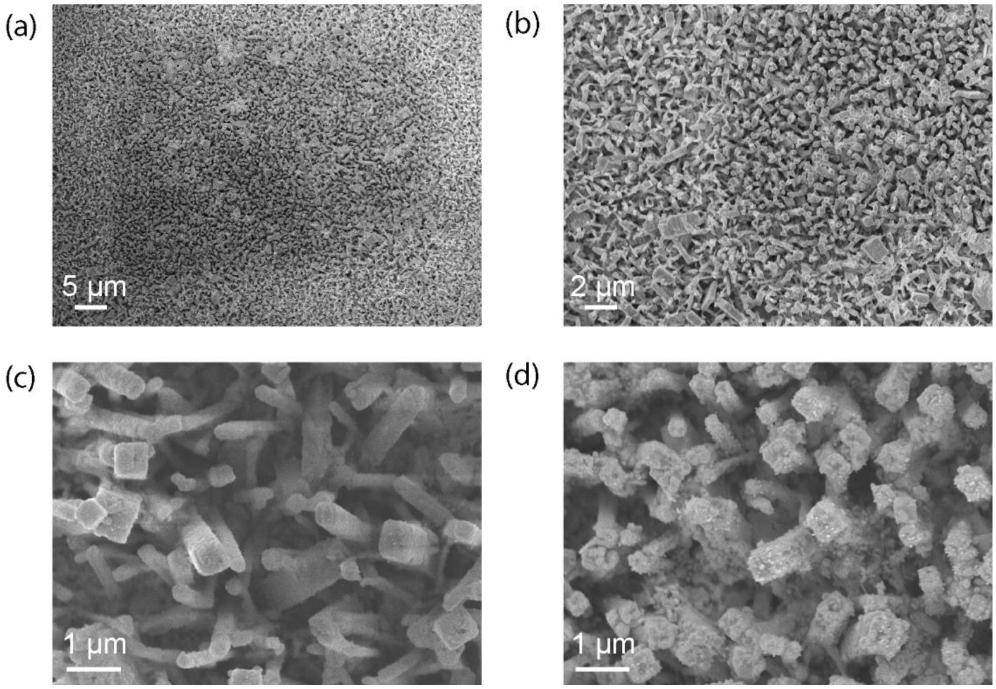

Figure S1. (a-b) SEM Image of Nanorod Array LED Device. The contrast of the evaporated metal contact pad can be seen. (c) Higher magnification SEM image showing the F8-coated nanorod array between contact pads. The nanorod morphology remains intact after the nanorods are coated with F8 and the after contacts are evaporated. (d) Higher magnification SEM image of nanorods under the contact pad after thermal evaporation.

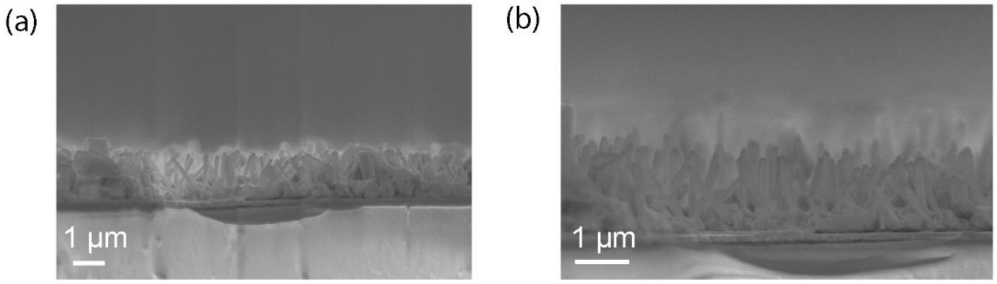

Figure S2. (a) Cross-sectional SEM image of nanorod array after coating with F8. (b) Higher magnification SEM image.

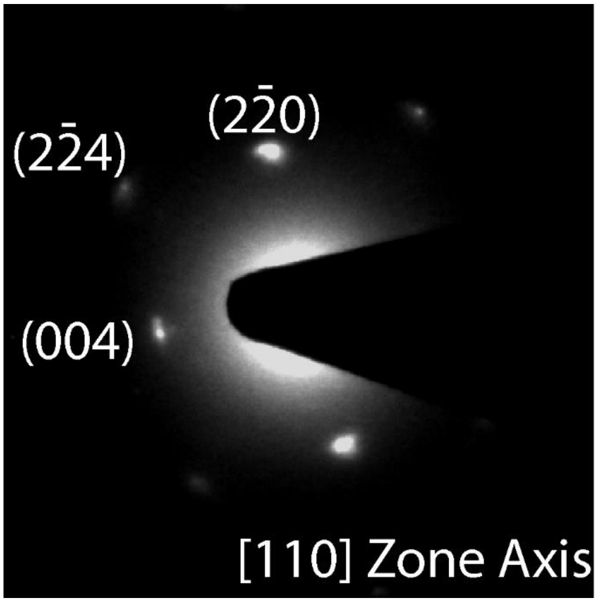

Figure S3. Selected area electron diffraction of a single $CH_3NH_3PbI_3$ nanorod after anion exchange from $CH_3NH_3PbBr_3$, indicating that the single crystalline nanorods remain single crystalline after the anion exchange reaction. The $CH_3NH_3PbI_3$ nanorods are rapidly damaged by the electron beam within several seconds, which causes the electron diffraction to quickly decrease in intensity.

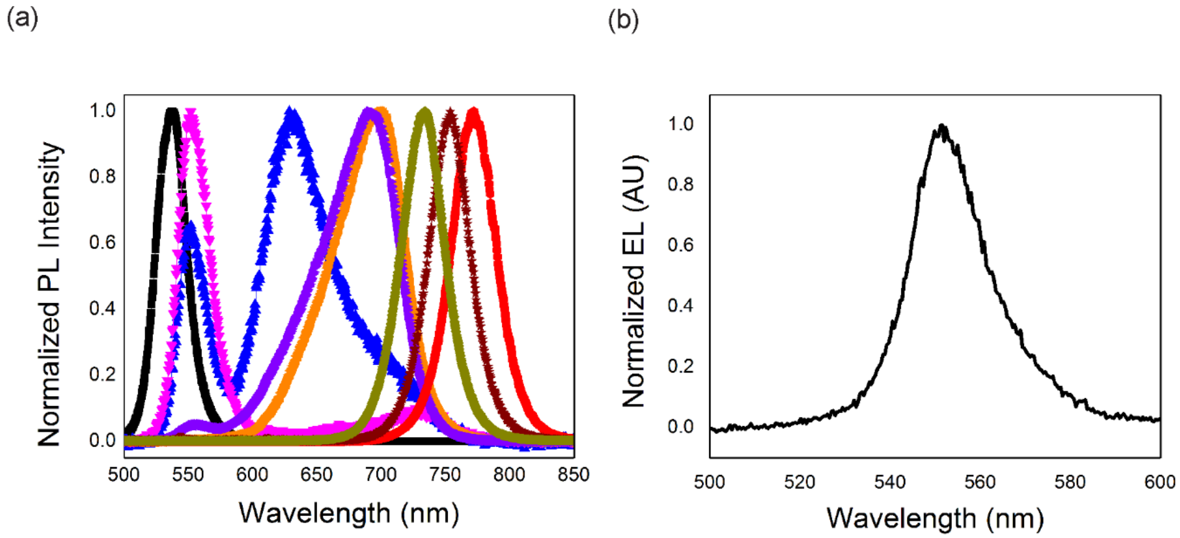

Figure S4. Characterization of $CH_3NH_3PbI_xBr_{3-x}$ nanorod arrays formed by partial anion exchange. (a) Photoluminescence of $CH_3NH_3PbI_xBr_{3-x}$ nanorod arrays with various compositions. Phase segregation under excitation is evident for compositions with peak emission from 550 to 700 nm. (b) Electroluminescence of $CH_3NH_3PbI_xBr_{3-x}$ nanorod array with a maximum electroluminescence of 551.5 nm, which is a red shift of 18 nm from 534 nm from electroluminescence by $CH_3NH_3PbBr_3$.

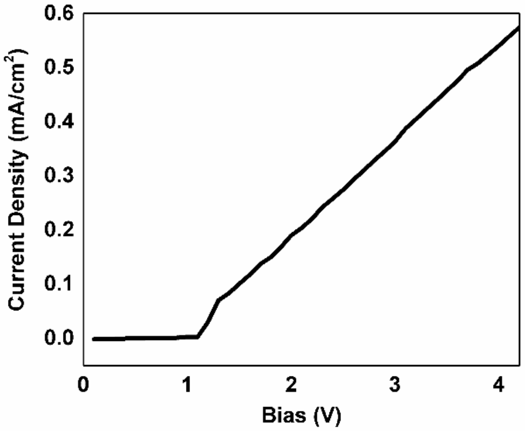

Figure S5. *IV* characteristic of $CH_3NH_3PbI_3$ nanorod array device. The short circuit current density is estimated from the electrode area, and the slope of the *IV* characteristic after threshold is attributed to a large series resistance in the device.

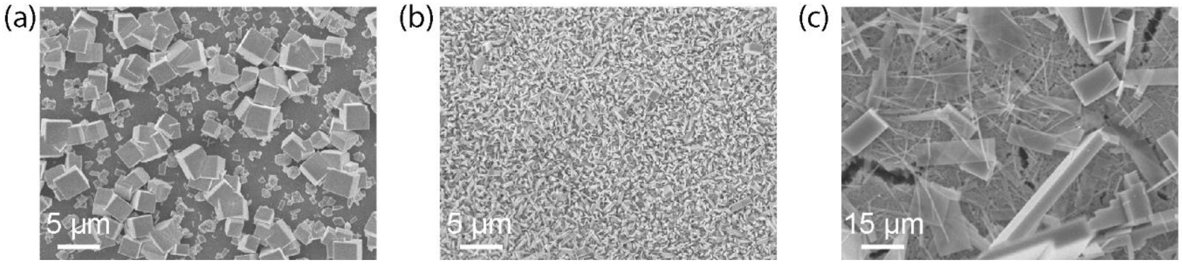

Figure S6. SEM Images from $CH_3NH_3PbBr_3$ nanorod arrays grown at differing concentrations of $CH_3NH_3PbBr_3$ prepared in parallel. (a) 3 mg/mL, cubes and short rods. (b) 9 mg/mL, array. (c) 12 mg/mL, disordered nanowires and plates.

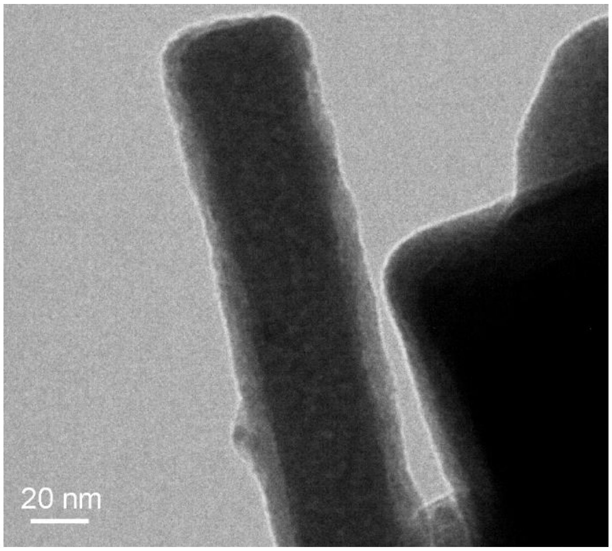

Figure S7. Low dose TEM image of $CH_3NH_3PbBr_3$ nanorod after coating with F8 polymer.

From the image, the F8 shell is estimated to have an average thickness on the order of 8 nm.

References:

1. Tan, Z.-K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H. *Nat. Nanotechnol.* **2014**, 9, 687–692.