Supporting Information for

Reduced-Dimensional Perovskites with Dithioketal-Containing Intercalating Cations for Near-Infrared Light-Emitting Diodes

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Experimental Section

Materials. Methylammonium iodide (MAI, 99.5%), lead (II) iodide (PbI$_2$, 99.99%), poly-[(9,9-dioctylfluorenyl-2,7-diyl)-alt-(4,4′-(N-(4-butylphenyl) (TFB, 99.8%), and molybdenum trioxide (MoO$_3$, 99.97%) were purchased from Xi'an p-OLED company. Polyethylenimine ethoxylated (PEIE, 80% ethoxylated solution), N, N'-dimethylformamide (DMF, 99.8%), isopropanol (IPA, 99.9%), and chlorobenzene (99.8%) were all purchased from Sigma-Aldrich Inc. Hydriodic acid (HI, 57% w/w), hypophosphorous acid (H$_3$PO$_2$, 50% w/w), zinc acetate dihydrate (99.99%), tetramethylammonium hydroxide pentahydrate (TMAH, 97%), dimethyl sulfoxide (DMSO, 99%), and formaldehyde solution (37% w/w% in water) were purchased from Aladdin Inc. Mercaptoethylammonium chloride (MEACl, 98%) was purchased from Innochem Inc. Acetone and toluene were purchased from Guangzhou Chemical Reagent Inc. Ethanol was purchased from Energy Chemical Reagent Inc. All chemicals were used directly without any additional purification steps.

Preparation of (PDSBA)PbI$_4$ single crystal. 113.6 mg of MEACl (1 mmol) and 230.5 mg of PbI$_2$ (0.5 mmol) were transferred to a 10-mL test tube and further dissolved in a mixed solution containing 1 mL of 57% w/w HI solution and 1 mL of 50% w/w H$_3$PO$_2$ solution by stirring at 100°C for about 5 min. 0.2 mL of acetone was subsequently added into the mixed solution under stirring, and some yellow crystals immediately formed. The solution was heated with stirring and maintained at 100°C until the yellow crystals were completely dissolved and the solution turned clear. Yellow plate-like crystals gradually formed and precipitated during the natural cooldown process to room temperature. The product crystals were separated using Buchner filtration and finally transferred to a nitrogen-filled glovebox for further use.

Preparation of (PDSBA)(MA)Pb$_2$I$_7$ single crystal. 230.5 mg of PbI$_2$ (0.5 mmol) was transferred to a 10-mL test tube and further dissolved in a mixed solution containing 1 mL of 57% w/w HI solution and 0.9 mL of 50% w/w H$_3$PO$_2$ solution by stirring at 100°C for about 5 min. ~227.8 mg of (PDSBA)PbI$_4$ (0.25 mmol) crystals synthesized above and 79.5 mg of MAI (0.5 mmol) were transferred from a nitrogen-filled glovebox and added to the mixed solution under stirring. 0.2 mL of acetone was subsequently added to the solution, and some red crystals immediately formed. The solution was heated with stirring and maintained at 100˚C until the red crystals were completely dissolved and the solution turned clear. Red plate-like crystals gradually formed and precipitated during the natural cooldown process to room temperature. The crystals were separated using Buchner filtration and finally transferred to a nitrogen-filled glovebox for further use.

Preparation of (PDSBA)(MA)$_2$Pb$_3$I$_{10}$ single crystal. 230.5 mg of PbI$_2$ (0.5 mmol) was transferred to a 10-mL test tube and further dissolved in a mixed solution containing 0.5 mL of 57% w/w HI solution and 0.5 mL of 50% w/w H$_3$PO$_2$ solution by stirring at 100°C for about 5 min. ~100.7 mg of (PDSBA)PbI$_4$ (0.11 mmol) crystals synthesized above and 79.5 mg of MAI (0.5 mmol) were transferred from a nitrogen-filled glovebox and added to the mixed solution under stirring. 0.2 mL of acetone was subsequently added to the solution, and some black crystals immediately formed. The solution was heated with stirring and maintained at 100˚C until the black crystals were completely dissolved and the solution turned clear. Black plate-like crystals gradually formed and precipitated during the natural cooldown process to room temperature. The crystals were separated using Buchner filtration and finally transferred to a nitrogen-filled glovebox for further use.

Preparation of (MSBA)PbI$_4$ single crystal. 113.6 mg of MEACl (1 mmol) and 230.5 mg of PbI$_2$ (0.5 mmol) were transferred to a 10-mL test tube and further dissolved in a mixed solution

containing 2 mL of 57% w/w HI solution and 1 mL of 50% w/w H_3PO_2 solution by stirring at 100°C for about 5 min. 0.2 mL of 37% w/w formaldehyde solution was subsequently added into the mixed solution under stirring, and some orange crystals immediately formed. The solution was heated with stirring and maintained at 100˚C until the orange crystals were completely dissolved and the solution turned clear. Orange plate-like crystals gradually formed and precipitated during the nature cooldown process to room temperature. The products were separated using Buchner filtration and finally transferred to a nitrogen-filled glovebox for further use.

Preparation of (MSBA)(MA)Pb$_2$I$_7$ single crystal. 230.5 mg of PbI$_2$ (0.5 mmol) was transferred to a 10-mL test tube and further dissolved in a mixed solution containing 1.2 mL of 57% w/w HI solution and 1 mL of 50% w/w H_3PO_2 solution by stirring at 100°C for about 5 min. 135.5 mg of (MSBA)PbI$_4$ (0.15 mmol) crystals synthesized above and 79.5 mg of MAI (0.5 mmol) were transferred from a nitrogen-filled glovebox and added to the mixed solution under stirring. 0.2 mL of 37% w/w formaldehyde solution was subsequently added, and some red crystals immediately formed. The solution was heated with stirring and maintained at 100˚C until the red crystals were completely dissolved and the solution turned clear. Red plate-like crystals gradually formed and precipitated during the nature cooldown process to room temperature. The crystals were separated using Buchner filtration and finally transferred to a nitrogen-filled glovebox for further use.

Preparation of (MSBA)(MA)$_2$Pb$_3$I$_{10}$ single crystal. 230.5 mg of PbI$_2$ (0.5 mmol) was transferred to a 10-mL test tube and further dissolved in a mixed solution containing 0.6 mL of 57% w/w HI solution and 0.6 mL of 50% w/w H_3PO_2 solution by stirring at 100°C for about 5 min. 53.4 mg of (MSBA)PbI$_4$ (0.06 mmol) crystals synthesized above and 79.5 mg of MAI (0.5 mmol) were transferred from a nitrogen-filled glovebox and added to the mixed solution under stirring. 0.2 mL of 37% w/w formaldehyde solution was subsequently added, and some black crystals immediately

formed. The solution was heated with stirring and maintained at 100˚C until the black crystals were completely dissolved and the solution turned clear. Black plate-like crystals gradually formed and precipitated during the nature cooldown process to room temperature. The crystals were separated using Buchner filtration and finally transferred to a nitrogen-filled glovebox for further use.

Powdery X-ray diffraction (PXRD) measurements. The PXRD patterns were measured using a Rigaku Miniflex 600 diffractometer (Cu-Kα, λ = 1.5406 Å) operating at a voltage of 45 kV and a current of 15 mA.

Single-crystal X-ray diffraction (SXRD). All single-crystalline samples were measured using an Agilent SuperNova X-ray single-crystal diffractometer at 150 K. The monochromatized Cu-Kα radiation source (λ = 1.5406 Å) was applied for the samples of $(MSBA)PbI_4$, $(PDSBA)(MA)Pb_2I_7$. The nomochromatized Mo-Kα (λ = 0.71073 Å) source was applied for the samples of $(MSBA)(MA)Pb_2I_7$, $(MSBA)(MA)_2Pb_3I_{10}$, and $(PDSBA)(MA)_2Pb_3I_{10}$; the Ga- Kα (λ=1.34138 Å) source was used for $(PDSBA)PbI_4$. All crystal structures were solved by the direct methods and refined by the full matrix least-square technique using the SHELXL package with OLEX2-1.5.

Stereo Fluorescence Microscope (SFM) measurements. The crystal samples were placed onto a clean silicon wafer (2 cm × 2 cm) for SFM imaging. The SFM photos were obtained using a Leica M205FA stereomicroscope with visible light or 365 nm ultraviolet illumination.

Preparation of MHP thin films. A series of $(MSBA)(MA)_{n-1}Pb_nI_{3n+1}$ and $(PDSBA)(MA)_{n-1}Pb_nI_{3n+1}$1 MHP precursor solutions were prepared by dissolving stoichiometric quantities of $(MSBA)PbI_4$ or $(PDSBA)PbI_4$, MAI and PbI_2 (with $[Pb^{2+}]$ kept in 0.6 mol L^{-1}) in DMF with mechanical stirring at 50°C until all solids were dissolved. All MHP precursor solutions were

filtrated through PTFE syringe filters (0.22 μm) before use. A 70 μL of MHP precursor solution was dropped onto the substrate, followed by a two-step spin-coating method: the first step was 1000 rpm for 10 s, and the second was 5000 rpm for 60 s. During the second step, 200 μL of toluene antisolvent was dropped on the rotating substrates at about 10~20 s. The films were subsequently annealed at 70°C for 10 min in a nitrogen-filled glovebox to complete the crystallization. After that, the films were cooled down to room temperature and stored in a nitrogen-filled glovebox for further use.

Photoluminescence (PL) and absorption measurements. The PL spectrums were recorded by a fluorescence spectrometer (FLS980, Edinburgh Instruments) equipped with a Xenon lamp with a monochromator. The excitation wavelength of the PL spectrum was set at 370 nm. As for the absorption measurements, the spectrums were recorded using a UV3600 fluorometer (Shimadzu Inc.).

Computational studies. All quantum chemistry computations were done using the Vienna ab initio simulation package (VASP-5.4.4)[1] with the projector augmented-wave (PAW) potentials[2] and PBE functional.[3] The cut-off energy for the plane wave basis set was set to 400 eV. And the k-points were set according to lattice parameters. They are summarized in Table S1. The LOBSTER-2.1.0 program was used to generate the DOS and pDOS.[4] All crystal structures were plotted using VESTA.[5]

Synthesis of ZnO nanoparticles. Colloidal ZnO nanoparticles were prepared by following a published solution-precipitation approach.[6] 1.308 g of zinc acetate dihydrate (6 mmol) was dissolved in 60 mL of DMSO, forming a colorless transparent solution. 1.68 g of TMAH (9 mmol) was dispersed in 20 mL of ethanol and then added dropwise into the zinc acetate solution with

magnetic stirring for 24 h under ambient conditions. After that, the products were precipitated by adding ~100 mL of ethyl acetate and redispersed in ~10 mL of ethanol. This purification procedure was repeated twice. 80 µl of ethanolamine was added during the second purification procedure as the surface capping ligands. The purified ZnO nanoparticles were finally dispersed in ethanol, forming a homogenous solution with a ZnO concentration of 10 mg mL^{-1}. The solution was filtrated through PTFE syringe filters (0.22 µm) before use.

Device fabrication. The ITO-coated glass substrates (1.48 cm × 1.48 cm) were cleaned consecutively with Triton X-100 solution, deionized water, ethanol, acetone, and isopropanol using sonication for 30 min each. The substrates were treated with plasma for 15 min before the device fabrication. The ZnO layer was spin-cast on the substrate at 2000 rpm for 1 min and subsequently annealed at 120°C for 15 min in air. The PEIE isopropanol solution (1.1 mg mL^{-1}) was spin-cast on top of the ZnO layer at 5000 rpm for 40 s and was annealed at 110°C for 15 min in air. After that, the MHP precursor solution was spin-cast on top of the PEIE layer, and the spin-cast process was similar to the preparation of the thin films mentioned above. The TFB chlorobenzene solution (6 mg mL^{-1}) was finally spin-cast on top of the MHP layer at 2000 rpm for 1 min to form a homogeneous TFB layer. For the top electrode, 7 nm of MoO$_3$ and 80 nm of Al were thermally deposited on the TFB film to complete the device (vacuum pressure $< 5 \times 10^{-4}$ Pa). Each ITO substrate was patterned to yield five devices, each with an active area of 8.0 mm^2.

Device characterization. Characterization of the LED was carried out at room temperature in a nitrogen-filled glovebox. Current density-voltage (J-V) characteristics were recorded by Keithley 2400 source meter with a step of 0.1 V (19 ms for each step). Forward-viewing radiant flux , EL spectra, and EQE values were measured by an integrating sphere of the C9920-12 EQE

measurement system (Hamamatsu Inc.). The active device area was 0.08 cm^2. The radiation flux is used for radiance calculation using the following method.

Radiance calculation. The radiance (L_e) can be expressed as[7]:

$$L_e = \frac{\partial^2 \phi_e}{\partial \Omega \partial S cos\theta}$$

where ϕ_e is the radiant flux, S is the emitting area of the light source, θ is the azimuthal angle of the detector position (colatitude), and Ω is the solid angle. In spherical coordinates there is a formula for the differential[7]:

$$d\Omega = \frac{dA}{R^2} = \frac{Rd\theta \cdot Rsin\theta d\varphi}{R^2} = sin\theta d\theta d\varphi$$

where A is the area size of the detector, R is the distance between the light source and the detector, and φ is another azimuthal angle of the detector position (longitude).The LEDs tested by integrating sphere could be considered as Lambertian scatterers, where the radiance at different azimuthal angles is a constant[7, 8]. Combining the following equations, we can get the radiance from the new formula:

$$\phi_e = \int_0^\pi \int_0^{\pi/2} \int_0^S L_e sin\theta cos\theta \, dSd\theta \, d\varphi = \pi S L_e$$

Table S1. Detailed calculation parameters of k-points with Γ-center meshes for sampling the Brillouin zones of MSBA- and PDSBA-based 2D MHP structures with various n values.

n value	k-point setup	
	$(MSBA)(MA)_{n-1}Pb_nI_{3n+1}$	$(PDSBA)(MA)_{n-1}Pb_nI_{3n+1}$
1	1 × 4 × 4	4 × 1 × 4
2	2 × 4 × 4	4 × 4 × 1
3	4 × 4 × 1	1 × 4 × 4

Table S2. Data summary of (MSBA)(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ (n = 1~3) MHP single crystals.

	compound		
	(MSBA)PbI$_4$	(MSBA)(MA)Pb$_2$I$_7$	(MSBA)(MA)$_2$Pb$_3$I$_{10}$
empirical formula	C$_5$H$_{16}$I$_4$N$_2$PbS$_2$	C$_6$H$_{22}$I$_7$N$_3$Pb$_2$S$_2$	C$_7$H$_{28}$I$_{10}$N$_4$Pb$_3$S$_2$
crystal system	monoclinic	monoclinic	monoclinic
space group	*C2/c*	*P2/c*	*I2/a*
color	orange	red	black
cell dimensions	a = 25.2413(6) Å	a = 18.6002(15) Å	a = 8.7507(2) Å
	b = 8.7370(2) Å	b = 8.7989(4) Å	b = 8.80529(19) Å
	c = 8.6774(2) Å	c = 8.7446(5) Å	c = 49.5412(13) Å
	α = 90.0°	α = 90.0°	α = 90.0°
	β = 102.882(2)°	β = 94.801(6)°	β = 93.213(2)°
	γ = 90.0°	γ = 90.0°	γ = 90.0°
volume (Å^3)	1865.49(8)	1426.13(16)	3811.26(17)
Z	4	2	4
density (g/cm^3)	3.1443	3.500	3.700
final *R* indices	R_1 = 0.0385	R_1 = 0.0685	R_1 = 0.0572
[$I > 2\sigma(I)$]	wR_2 = 0.0970	wR_2 = 0.1903	wR_2 = 0.1211
R indices	R_1 = 0.0397	R_1 = 0.0767	R_1 = 0.0664
[all data]	wR_2 = 0.0989	wR_2 = 0.1972	wR_2 = 0.1238

Table S3. Data summary of $(PDSBA)(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1~3) MHP single crystals.

|	compound		
	$(PDSBA)PbI_4$	$(PDSBA)(MA)Pb_2I_7$	$(PDSBA)(MA)_2Pb_3I_{10}$
empirical formula	$C_7H_{20}I_4N_2PbS_2$	$C_8H_{26}I_7N_3Pb_2S_2$	$C_9H_{32}I_{10}N_4Pb_3S_2$
crystal system	orthorhombic	monoclinic	monoclinic
space group	*Pnma*	*P2₁/c*	*Pc*
color	yellow	red	black
cell dimensions	a = 8.5801(17) Å	a = 8.6911(2) Å	a = 26.1723(6) Å
	b = 54.936(11) Å	b = 8.7395(2) Å	b = 8.7520(2) Å
	c = 8.6960(17) Å	c = 39.8628(14) Å	c = 8.7431(2) Å
	$\alpha = 90.0°$	$\alpha = 90.0°$	$\alpha = 90.0°$
	$\beta = 90°$	$\beta = 91.903(3)°$	$\beta = 91.710(2)°$
	$\gamma = 90.0°$	$\gamma = 90.0°$	$\gamma = 90.0°$
volume (Å³)	4098.9(14)	3026.14(14)	2001.80(8)
Z	8	4	2
density (g/cm³)	2.953	3.361	3.569
Final *R* indices [*I* > 2σ(*I*)]	$R_1 = 0.0341$ $wR_2 = 0.0866$	$R_1 = 0.1423$ $wR_2 = 0.3179$	$R_1 = 0.0697$ $wR_2 = 0.1776$
R indices [all data]	$R_1 = 0.0395$ $wR_2 = 0.0901$	$R_1 = 0.1825$ $wR_2 = 0.3320$	$R_1 = 0.0714$ $wR_2 = 0.1785$
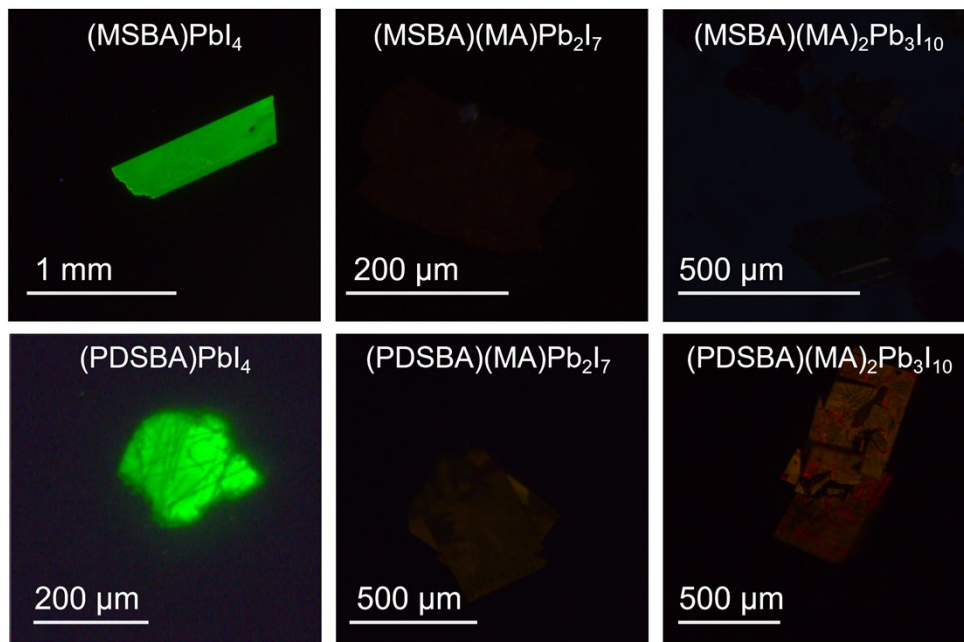
Figure S1. SFM images of the MSBA-based and PDSBA-based MHP single crystals under the illumination of 365-nm UV light.
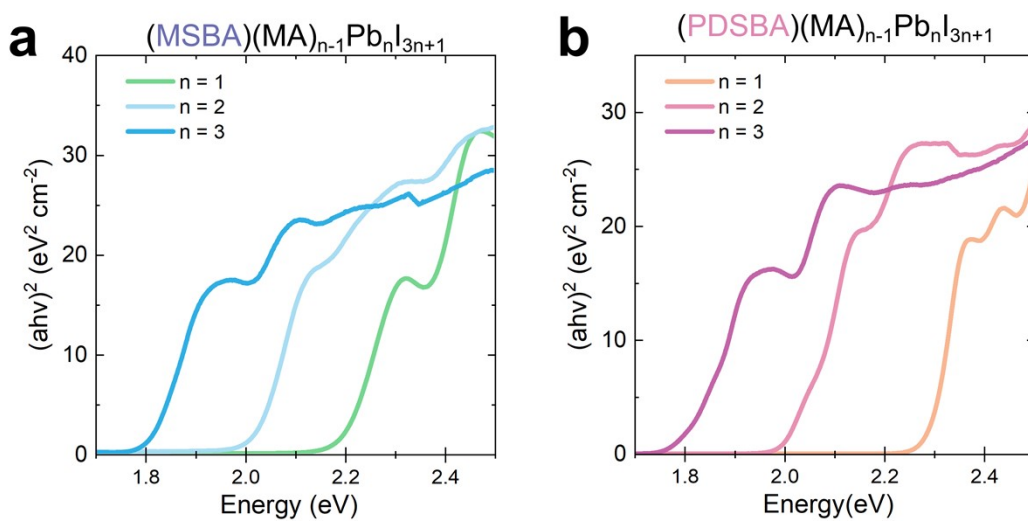

Figure S2. Tauc-plots of the optical absorption spectra of (a) MSBA-based and (b) PDSBA-based MHPs shown in Figures 3b and 3e.
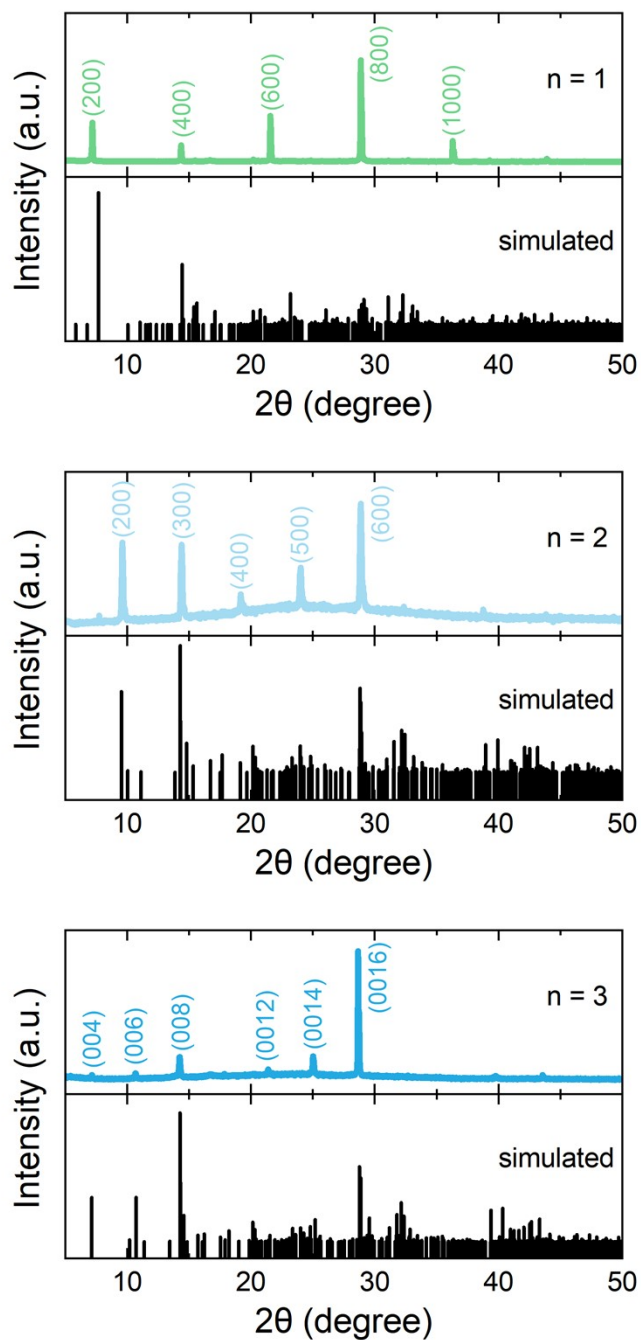
Figure S3. Simulated and experimental XRD results of the $(MSBA)(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1~3) MHPs. The relaxed single-crystal structures of those MHPs were used for the simulation of XRD patterns.
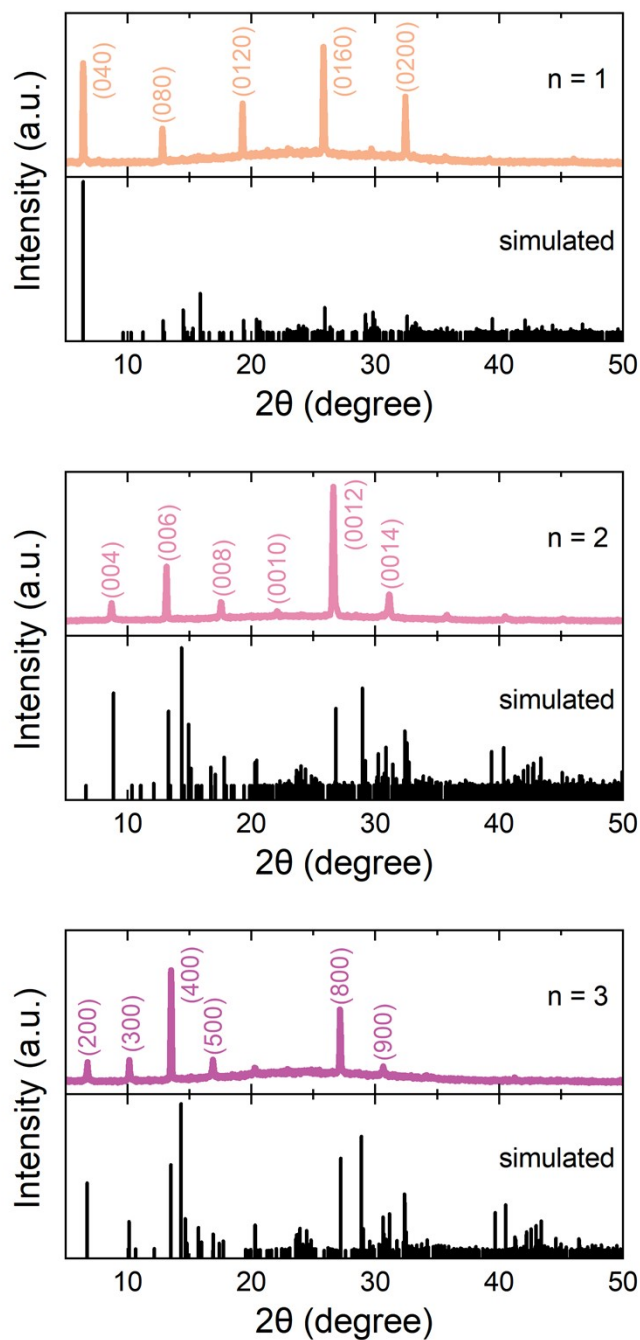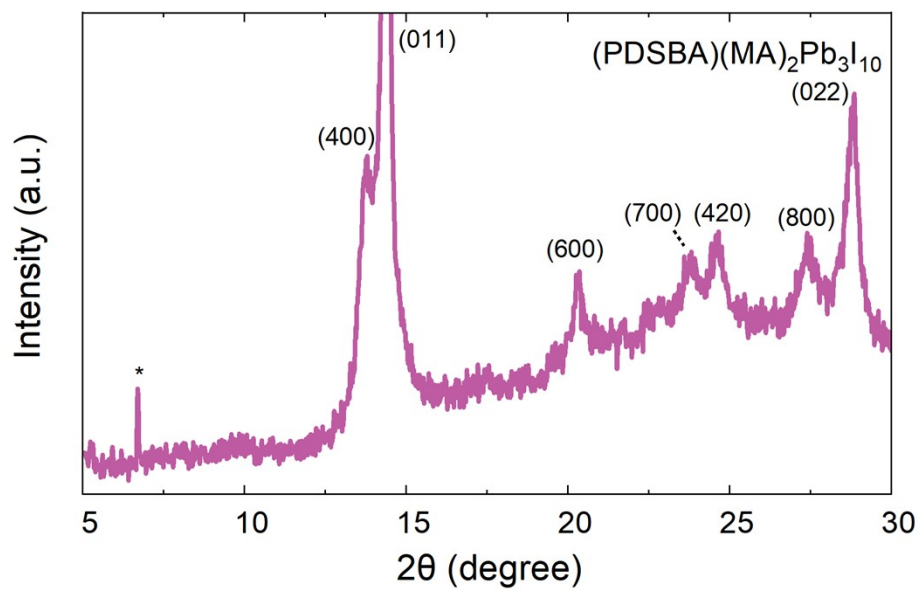
Figure S4. Simulated and experimental XRD results of the $(PDSBA)(MA)_{n-1}Pb_nI_{3n+1}$ (n=1~3) MHPs. The relaxed single-crystal structures of those MHPs were used for the simulation of XRD patterns.
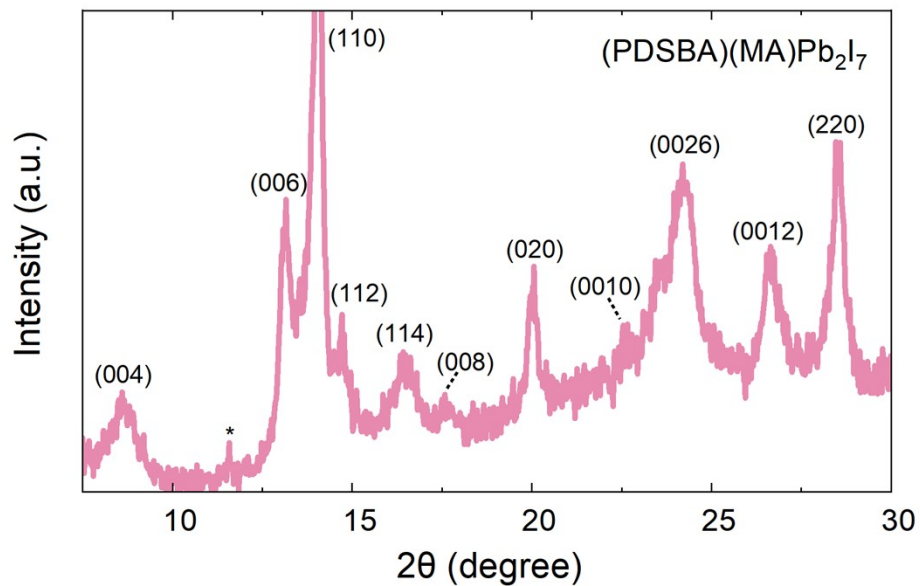
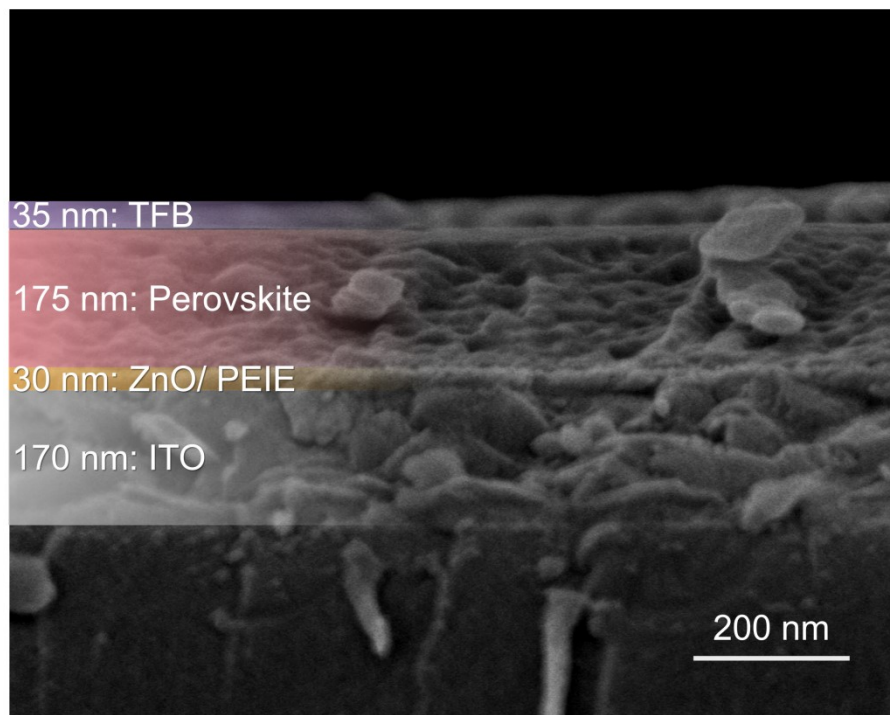**Figure S5.** Zoom-in XRD pattern of the PDSBA-based MHPs thin film with <n> values of 2 and 3, respectively.

Figure S6. Cross-sectional SEM image of the device with PDSBA-based <n> = 5 MHPs as the active layer.

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