Supplementary Information (SI) for Materials Chemistry Frontiers.

Perovskite-inspired low-dimensional hybrid azetidinium bismuth halides: $[(CH_2)_3NH_2]_3Bi_2X_9$ (X=I, Br, Cl)

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Preparation of Azetidinium Bromide (AzBr) and Azetidinium Iodide (AzI)

Azetidinium bromide (AzBr): AzBr powder was synthesized by hydrobromic acid (HBr, 48%) and Azetidine (98%, purchased from Thermo Fisher Scientific). 11g of HBr was added to 5g of azetidine onto the ice bath. The acquired powders and liquid solution were dried in a vacuum oven until left with bright yellow powder. It was washed with diethyl ether to remove excess bromine and then recrystallized using isopropanol. It was completely dried in a vacuum oven, and then kept in a N_2 filled glove box, since we confirmed that AzBr is moisture sensitive. ^{1}H NMR spectra of the obtained product is shown in Fig. S1.

Azetidinium Iodide (AzI): AzI powder was synthesized by hydroiodic acid (HI, 55 - 58%) and Azetidine (98%, purchased from Thermo Fisher Scientific). 13g of HI was added to 5g of azetidine onto the ice bath. The acquired powders and liquid solution were dried in a vacuum oven until left with a bright orange powder. It was washed with diethyl ether several times to remove excess iodine, recrystallized using isopropanol, and then cleaned with acetonitrile. After drying, the small white needle-like powder was obtained. ^{1}H NMR spectra of the obtained product is shown in Fig. S1.

Thin film deposition

We used sol-gel method to deposit the thin film of $(Az)_3Bi_2X_9$ via spin coating process. 0.3 M of the precursor solution was used for all $(Az)_3Bi_2X_9$. All substrate was prepared with 20 x 20 mm scales and was cleaned by acetone for 15 minutes, distilled water for 15 minutes, and then ethanol for 15 minutes in an ultra-sonicator. The cleaned substrates were exposed to UV-ozone treatment equipment for 30 minutes.

$(Az)_3Bi_2I_9$: To prepare the precursor, 0.9 mmol of AzI, and 0.6 mmol of BiI_3 were dissolved in N,N-dimethylformamide for 1 day, and filtered by a PTFE membrane filter of 0.7 μm pore size. The spin-coating process was carried on at 2000 rpm for 30 s, and then the coated film was annealed at 150°C for 30 minutes on a hot plate in a N_2 filled glove box.

$(Az)_3Bi_2Br_9$: To prepare the precursor, 0.9mmol of AzBr, and 0.6 mmol of $BiBr_3$ were dissolved in dimethylsulfoxide for 1 day, and filtered by a PTFE membrane filter of 0.45 μm pore size. The spin-coating process was carried on at 2000 rpm for 30 s, and then the coated film was annealed at 150°C for 30 minutes on a hot plate in a N_2 filled glove box.

$(Az)_3Bi_2Cl_9$: To prepare the precursor, 0.9 mmol of AzCl, and 0.6 mmol of $BiCl_3$ were dissolved in N,N-dimethyformamide for 1 day, and filtered by a PTFE membrane filter of 0.45 μm pore size. The spin-coating process was carried on at 2000 rpm for 30 s, and then the coated film was annealed at 150°C for 30 minutes on a hot plate in a N_2 filled glove box.

X-ray Diffraction measurement (XRD) and structure analysis

Powder diffraction data for the structure analysis were collected on a STOE StadiMP powder diffractometer equipped with a DECTRIS MYTHEN2 microstrip detector and a Ge(111) monochromator supplying Cu $K\alpha_1$ radiation ($\lambda = 1.54059$ Å), or on a PANalytical X'pert PRO diffractometer (Cu $K\alpha_{1/2}$ radiation, 1.5406 Å + 1.5444 Å) equipped with a PIXcel3D-Medipix3 detector. Since grinding the material reduced their crystallinity narrow glass capillaries could not be used as sample holders. Flat samples were used instead which, however, showed some preferred orientation of the crystals. A correction of the preferred orientation (modified March's function) was included in the refinements. The structural models (obtained by Direct Methods) were refined using the FullProf 2K program [xx] with scattering factors as implemented there. Hydrogen atoms of the azetidinium cations could not be located. Therefore, the occupancy factors of the carbon atoms used to describe the azetidinium cations were adequately increased to cover the scattering power of the hydrogen atoms. For the Rietveld refinement, soft distance restraints were used on the BiX_6 octahedra with d(Bi-Cl) = 2.80(2) Å, d(Bi-Br) = 2.90(2) Å, d(Bi-I) = 3.00(2) Å and also appropriate soft distance restraints on carbon-carbon distances - depending on the symmetry of the particular structure - to refine the azetidinium cation as a pseudo rigid body. Six additional parameters were necessary to describe the anisotropic peak widths. The displacement parameters of the heaviest atom, bismuth, were refined anisotropically. X-ray diffraction measurement of the thin film was performed using the PANalytical X'pert PRO diffractometer (Cu $K\alpha_{1/2}$ radiation, 1.5406 Å + 1.5444 Å) equipped with a PIXcel3D-Medipix3 detector using a scanning line detecting mode (0.04 rad soller slit, 1/8° fixed divergence slit, 10.8 mm mask, 9.1 mm anti-scatter slit were used on the incident beam path, and 0.04 rad soller slit was used on the diffracted beam path).

Scanning Electron Microscopy (SEM)

Scanning electron microscopic images were captured by the equipment from Jeol (JSM-7500F). All the samples were gold-coated by sputter coater.

FT-IR spectroscopy

Fourier transform infrared spectroscopy (FT-IR) for polycrystalline powders was performed by ALPHA Platinum FT-IR spectrometer with ATR mode from Bruker.

Raman spectroscopy

Raman spectroscopy for polycrystalline powders and thin films was performed with the wavelength of 532 nm by the inVia confocal Raman microscope from Renishaw.

UV-Vis Spectroscopy

Absorbance spectra of the thin film and reflectance spectra of the polycrystalline powder were acquired by a Shimadzu UV2600 UV-vis spectrophotometer (Japan). $BaSO_4$ powder was used for the reference of reflection data. Tauc plots for bandgap estimation were extracted, and converted by % diffuse reflectance spectra of the polycrystalline powder samples.

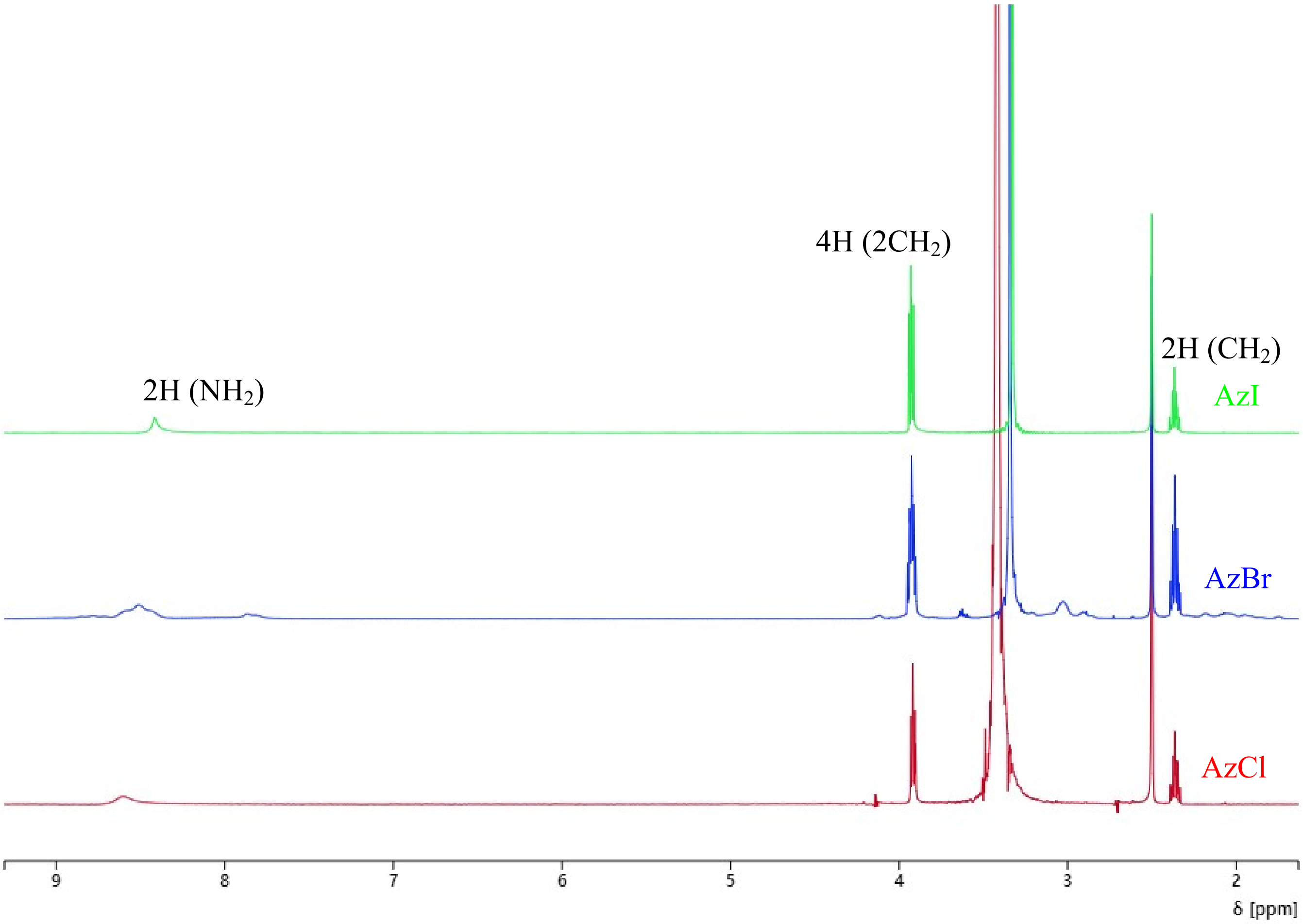

Fig. S1. ^{1}H NMR spectra of Azetidinium halides (in dimethyl sulfoxide-d_6). The peaks at δ: 2.3-2.4 (2H, CH_2), δ: 3.8-3.9 (4H, 2(CH_2)), δ: 8.4-8.6 (2H, NH_2) shows the signal from protons in Azetidinium. The peak at around 2.5 ppm originates from the solvent, dimethyl sulfoxide-d_6, and the peak at around 3.3 ppm - 3.4 ppm originates from water in the solvent.

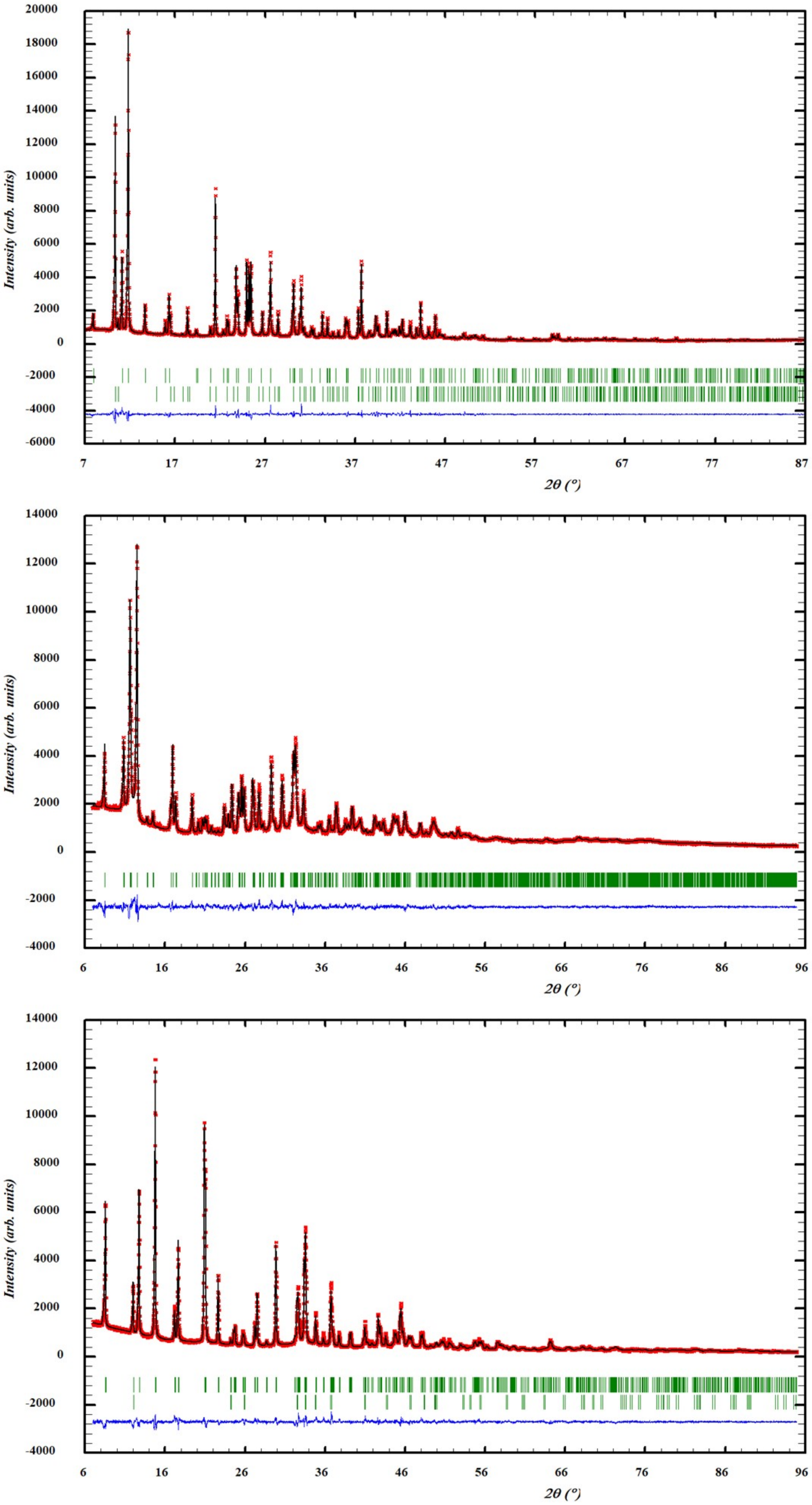

Fig. S2. Final Rietveld plots of $(Az)_3Bi_2X_9$ structures, refined against diffraction data from polycrystalline powders. $(Az)_3Bi_2I_9$ (top), $(Az)_3Bi_2Br_9$ (middle), $(Az)_3Bi_2Cl_9$ (bottom).

Atom	x	y	z	occ.	U11	U22	U33	U12	U13	U23	U(iso)
Bi1	0.66667	0.33333	0.50000	1.0000	0.102(8)	0.102(8)	0.115(10	0.051(8)	0	0	
Bi2	0.66667	0.33333	0.3151(3	1.0000	0.246(14)	0.246(14)	0.039(8)	0.123(14)	0	0	
I1	0.5117(2)	0.4883(2)	0.3979(5)	1.0000							0.1751(14)
I2	0.3482(16)	0.1741(16)	0.5664(5)	1.0000							0.1751(14)
I3	0.3756(15)	0.1878(15)	0.2317(5)	1.0000							0.1751(14)
C1	0.529(4)	0.265(4)	0.7024(15)	0.9200							0.266(17)
C2	0.7791(20)	0.3895(20)	0.266(17)	0.9200							0.266(17)
C3	0.530(4)	0.265(4)	1.0462(12)	0.9200							0.266(17)
C4	0.7782(20)	0.3891(20)	1.0462(12)	0.9200							0.266(17)
C5	0.143(4)	0.071(4)	0.3681(16)	0.9200							0.266(17)
C6	0.0562(10)	0.1124(10)	0.3681(16)	0.9200							0.266(17)

Table. S1a. Atomic coordinates of (Az)$_3$Bi$_2$I$_9$. The azetidinium cation was simulated by six carbon atoms. The occupancy factors of the carbon sites were fixed and chosen such to represent the complete scattering power of the disordered cation (3 C,1 N, 8 H).

Atom	x	y	z	occ.	U11	U22	U33	U12	U13	U23	U(iso)
Bi1	0.00000	0.1705(6)	0.1786(5)	1.0000	0.193(8)	0.076(11)	0.045(3)	0	0	0	
Bi2	0.00000	0.1711(6)	0.3732(5)	1.0000	0.013(3)	0.087(11)	0.173(6)	0	0	0	
Br1	0.2343(6)	0.2379(3)	0.2751(8)	1.0000							0.1088(11)
Br2	0.00000	0.3149(12)	0.1070(9)	1.0000							0.1088(11)
Br21	0.00000	0.3153(12)	0.4447(9)	1.0000							0.1088(11)
Br3	-0.2495(14)	0.1012(10)	0.4364(5)	1.0000							0.1088(11)
Br31	-0.2219(12)	0.1047(10)	0.0996(5)	1.0000							0.1088(11)
Br4	0.00000	0.0330(5)	0.2761(8)	1.0000							0.1088(11)
C1	0.00000	0.1441(12)	0.6409(7)	1.3750							0.172(7)
C2	0.00000	0.1742(12)	0.5440(7)	1.3750							0.172(7)
C3	0.00000	0.0965(10)	0.5814(9)	1.3750							0.172(7)
C4	0.00000	0.2200(10)	0.6044(9)	1.3750							0.172(7)
C5	0.00000	0.5360(11)	0.2073(8)	1.3750							0.172(7)
C6	0.00000	0.4469(11)	0.1965(8)	1.3750							0.172(7)
C11	0.00000	0.1070(10)	0.9076(9)	1.3750							0.172(7)
C21	0.00000	0.1324(11)	0.9752(8)	1.3750							0.172(7)
C31	0.00000	0.2189(10)	0.9549(9)	1.3750							0.172(7)
C41	0.00000	0.1900(11)	0.8892(8)	1.3750							0.172(7)
C51	0.00000	0.4409(10)	0.2669(9)	1.3750							0.172(7)
C61	0.00000	0.5293(11)	0.2760(9)	1.3750							0.172(7)

Table. S1b. Atomic coordinates of (Az)$_3$Bi$_2$Br$_9$. The azetidinium cation was simulated by four carbon atoms. The occupancy factors of the carbon sites were fixed and chosen such to represent the complete scattering power of the disordered cation (3 C,1 N, 8 H).

Atom	x	y	z	occ.	U11	U22	U33	U12	U13	U23	U(iso)
Bi1	1.00000	1.00000	0.63993(19)	1.0000	0.0817(20)	0.0817(20)	0.069(2)	0.0408(20)	0	0	
Bi2	0.33333	0.66667	0.80158	1.0000	0.080(2)	0.080(2)	0.0424(19)	0.040(2)	0	0	
Cl1	0.5527(15)	0.9881(12)	0.8702(5)	1.0000							0.109(3)
Cl2	0.3289(11)	0.134(2)	0.5721(5)	1.0000							0.109(3)
Cl3	0.3315(14)	0.200(2)	0.2247(5)	1.0000							0.109(3)
C41	-0.026(3)	-0.1282(18)	0.9306(7)	0.9200							0.136(11)
C42	0.107(2)	-0.016(3)	0.8654(7	0.9200							0.136(11)
C51	0.307(3)	0.757(2)	0.2764(6)	0.9200							0.136(11)
C52	0.2267(18)	0.639(3)	0.2010(7)	0.9200							0.136(11)
C61	0.2183(19)	0.663(2)	0.5717(6)	0.9200							0.038(13)
C62	0.338(2)	0.7779(18)	0.5053(7)	0.9200							0.038(13)

Table. S1c. Atomic coordinates of $(Az)_3Bi_2Cl_9$. The azetidinium cation was simulated by six carbon atoms. The occupancy factors of the carbon sites were fixed and chosen such to represent the complete scattering power of the disordered cation (3 C,1 N, 8 H).

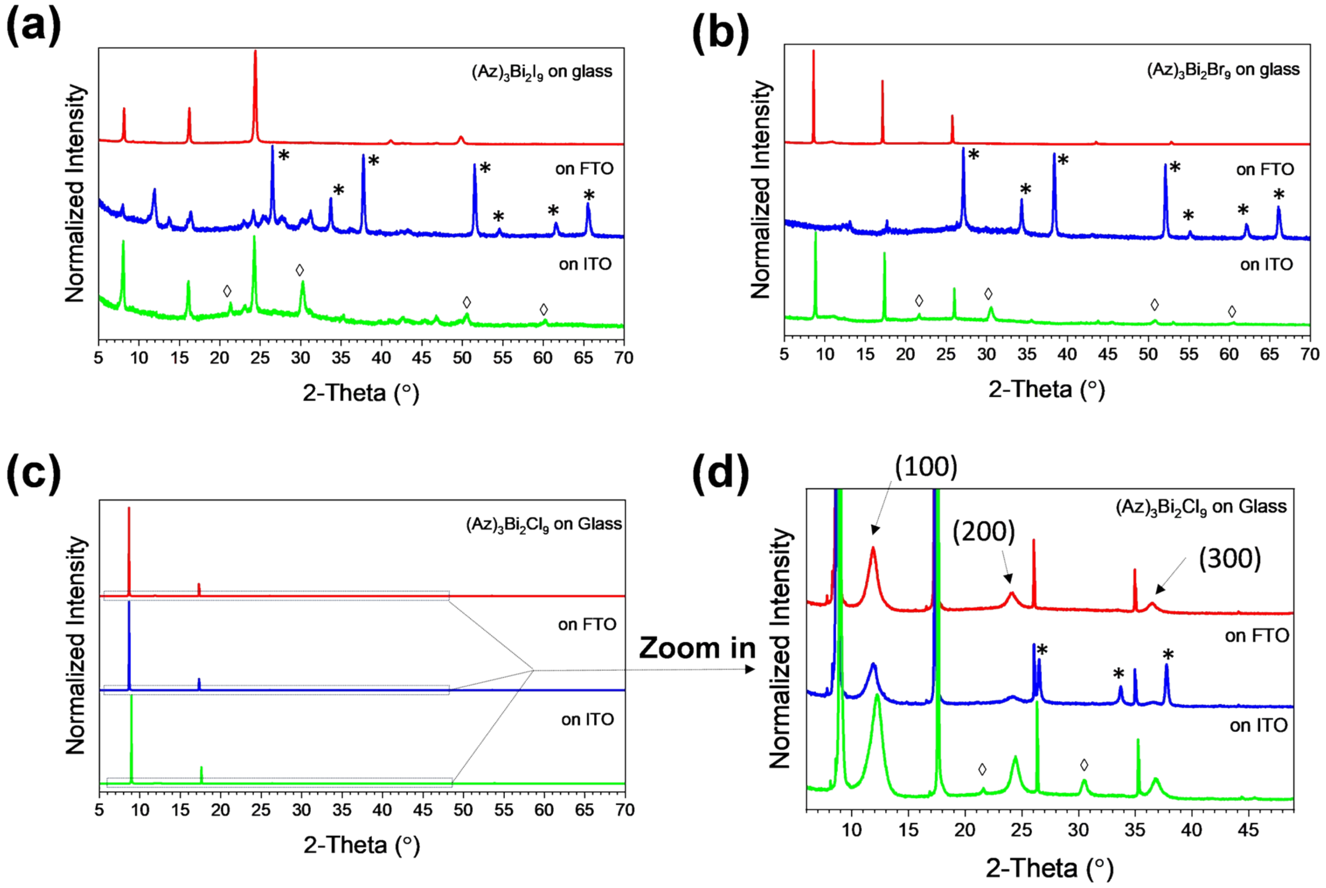

Fig. S3. X-ray diffraction data of (a) $(Az)_3Bi_2I_9$, (b) $(Az)_3Bi_2Br_9$, and (c) $(Az)_3Bi_2Cl_9$ thin film deposited on different substrates (Glass, FTO, and ITO; * indicates the X-ray diffraction peaks of the FTO substrate, and ◊ indicates those of the ITO substrate), (d) a zoomed-in view of the low-intensity region for the $(Az)_3Bi_2Cl_9$ thin film.

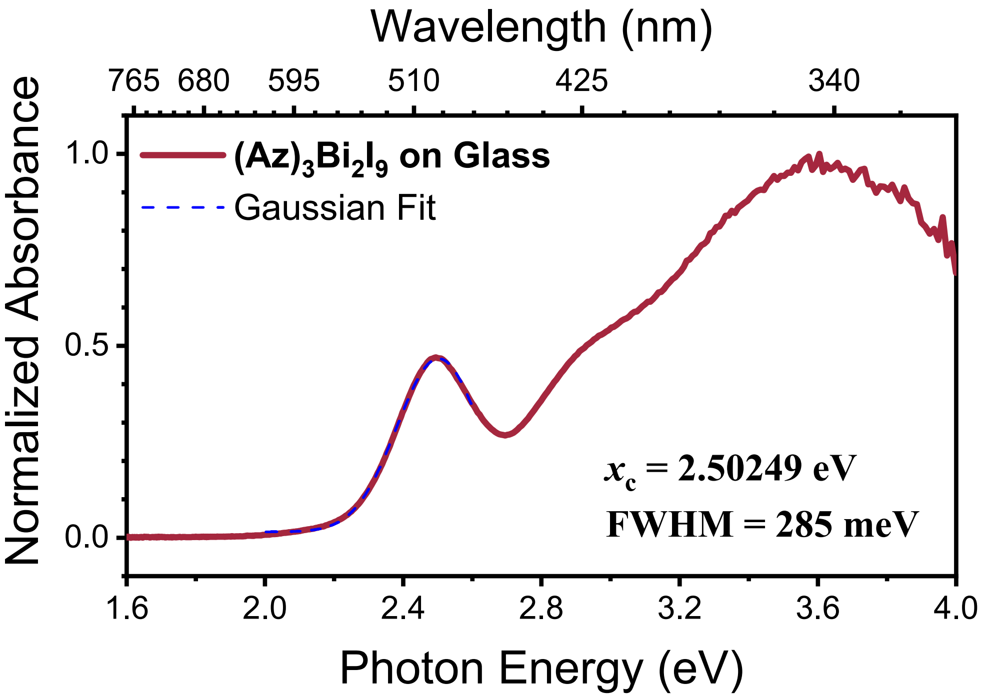

Fig. S4. Gaussian function fitting with 2.50249 eV of the excitonic peak, and 285 meV of FWHM at absorption spectrum of $(Az)_3Bi_2I_9$ thin film on glass