Electronic Supplementary Information

$[NH_3(CH_2)_4NH_3]SnX_4$ (X = Br, I): Dion-Jacobson type 2-D Perovskites with Short Interlayer Spacing

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Experimental Section

Materials. 1,4-Butanediamine (Sigma Aldrich, 99%), Tin metal (Sigma Aldrich, <150 μm particle size, 99.5% trace metal basis), 48 wt.% HBr in H_2O (Merck, India), 57 wt.% HI in H_2O (Merck, India) and 50 wt.% H_3PO_2 in H_2O were purchased from commercial sources. All the compounds reported here were synthesised hydrothermally as single crystalline materials and structurally characterized from single crystal X-ray diffraction data.

Synthesis of (1,4BDA)$SnBr_6$.1,4-Butanediamine (87.70 mg, 101 μL, 1.0 mmol) was added to a 23 mL Teflon vial containing Sn (118 mg, 1.0 mmol), (3mL) of 48 wt.% aqueous HBr and (110 μL, 2.0 mmol) of H_3PO_2 50 wt.% in H_2O. The Teflon vial was kept in a stainless-steel autoclave and heated in an oven at 160 °C for 24 hours. The reaction was cooled to room temperature at a cooling rate of 0.5°C/min, yielding yellow crystals. The yellow crystals of **(1,4-BDA)$SnBr_6$** were rapidly filtered out of the mother liquor, pressed with Whatman filter paper, and dried in a vacuum oven.

Synthesis of (1,4-BDA)$SnBr_4$. 1,4-Butanediamine (87.70 mg, 101 μL, 1.0 mmol) was added to a 23 mL Teflon vial containing Sn (118.0 mg, 1.0 mmol), (452 μL, 4.0 mmol) of 48 wt.% aqueous HBr and 2 mL of H_3PO_2 50 wt.% in H_2O. The Teflon vial was kept in a stainless-steel autoclave and heated in an oven at 200 °C for 2 hours. The reaction was cooled to room temperature by switching off the oven, and the Teflon vial was opened after 12 hours, which yielded yellow crystals. The yellow crystals of **(1,4-BDA)$SnBr_4$** were rapidly filtered out of the mother liquor, pressed with Whatman filter paper, and dried in a vacuum oven.

Synthesis of (1,4-BDA)SnI_4. 1,4-Butanediamine (87.70 mg, 101 μL, 1.0 mmol) was added to a 23 mL Teflon vial containing Sn metal (118.0 mg, 1.0 mmol), (530 μL, 4.0 mmol) of 57 wt.% aqueous HI, and 2mL of H_3PO_2 50 wt.% in H_2O. The Teflon vial was kept in a stainless-steel autoclave and heated in an oven at 200 °C for 2 hours. The reaction was cooled to room temperature by switching off the oven, and the Teflon vial was opened after 12 hours, which yielded red crystals. The red crystals of **(1,4-BDA)SnI_4** were rapidly filtered out of the mother liquor, pressed with Whatman filter paper, and dried in a vacuum oven.

Single crystal X-ray diffraction. Single crystals of each sample were mounted on a quartz fibre with the help of silicon grease on a Bruker D8 Venture diffractometer equipped with photon detector and graphite-monochromatic Mo-Kα X-ray source (wavelength = 0.71073 Å). Data were integrated by using APEX-3 software. XPREP was used to check for the possibility

of higher symmetry. The data were solved and refined by using SHELX 14.0[S1] and Olex2.[S2] All non-hydrogen atoms were refined anisotropically. The crystal structure figures were drawn by using VESTA 3.5.7.[S3]

Powder X-ray diffraction. Crystals were powered in mortar and pestle before being placed in a PXRD sample holder. The PXRD data were collected on a Rigaku Smart Lab diffractometer equipped with a Cu-Kα X-ray source (wavelength = 1.54059 Å).

UV-visible spectroscopic studies. Agilent Cary 5000 UV-VIS-NIR spectrophotometer instrument was used in reflectance mode, and reflectance in the range of 250-800 nm was obtained to determine the band gap.

X-ray photoelectron spectroscopy (XPS). The XPS data of the samples was collected on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer equipped with a monochromatic, micro-focused, low-power Mg-Kα X-ray source. The samples were powdered and then mounted on the XPS sample holder using double-sided copper tape. Survey scan spectra were measured in the 10 eV-1000 eV range, and core-level spectra were recorded for each sample.

Field emission scanning electron microscopy (FESEM) and energy dispersive spectrometry (EDS) mapping. FESEM images were collected ZEISS Gemini SEM – Field Emission Scanning Electron Microscope and Energy Dispersive Spectrometry (EDS) images were collected on OXFORD ULTIM MAX-40.

Photoluminescence spectroscopy. Photoluminescence spectrum was measured on FLS1000 Spectrometer of Edinburgh Instruments, equipped with 450 W ozone free Xenon arc lamp as the excitation source and visible PMT 900 (250 nm – 900 nm) detector.

Thermogravimetric analysis (TGA). The TGA data of all the compounds were collected under an inert nitrogen atmosphere on a Mettler Toledo TGA 1 STAR^e instrument.

Differential scanning calorimetry (DSC). Mettler Toledo DSC 3 STAR^e calorimeter was used to collect DSC with a 10 K/min ramp rate in a nitrogen atmosphere.

Table S1. Comparison of reported Dion-Jacobson type 2D A'$SnBr_4$ and A'SnI_4 perovskites.[a]

Compound	**Δ*d***	**σ^2**	**Interlayer Spacing** (Å)	**Experimental Bandgap (eV)**	**Ref**
(1,8-ODA)$SnBr_4$	8.18 x 10^{-5}	3.69	13.426	Not available	[S4]

(1,4-BDA)$SnBr_4$	4.462 x 10^{-3}	18.6252	9.549	2.64	This work
$[C_5H_{11}N(CH_2)_2NH_3]SnI_4$	3.16 X 10^{-3}	26.29	10.364	Not available	S5
$[NH_3(CH_2)_5NH_3]SnI_4$	2.82 X 10^{-4}	2.416	10.216	Not available	S5
$[C_3H_4N_2(CH_2)_2NH_3]SnI_4$	1.15 X 10^{-3}	9.649	10.022	1.67	S6
$[(CH_3)_3N(CH_2)_2NH_3]SnI_4$	2.704 x 10^{-5}	2.12	10.129	1.97	S7
$[(C_3H_6N_2)_2]SnI_4$	6.32 X 10^{-3}	22.90	9.492	Not available	S8
$[C_8H_8N_4]SnI_4$	1.963 X 10^{-7}	8.625	10.597	1.79	S9
(1,4-BDA)SnI_4	7.448 X 10^{-6}, 3.0043 X 10^{-6}	3.3198, 3.1313	10.181	1.94	This work

[a]Only phases with crystallographic data are listed.

Table S2. Single crystal data and structure refinement details of (1,4-BDA)$SnBr_6$.

CCDC No.	2303742
Empirical formula	(1,4BDA)$SnBr_6$
Formula weight	688.28
Temperature	273(2) K
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	a = 10.1731(4) Å α = 90° b = 7.5558(3) Å β=99.2730(10)° c = 10.3974(4) Å γ= 90°
Volume	788.76(5) $Å^3$
Z	2
Density (calculated)	2.839 mg/m^3
Absorption coeff.	16.785 mm^{-1}
θ range	2.028 to 27.107 °
Reflections collected	13694
Independent reflections	1876 [R(int) = 0.0784]
Data completeness	99.9 %
Data/restraints /parameters	1876 / 0 / 76
GoF on F^2	1.023
Final *R* indices [I>2sigma(I)]	*R*1 = 0.0577, *wR*2 = 0.1727
R indices (all data)	*R*1 =0.0680, *wR*2 = 0.1844

Table S3. Single crystal data and structure refinement details of (1,4-BDA)$SnBr_4$.

CCDC No.	2303743
Empirical formula	(1,4BDA)$SnBr_4$

Formula weight	528.48
Temperature	300(2) K
Crystal system	Monoclinic
Space group	*C*2/c
Unit cell dimensions	a = 11.6179(5) Å α = 90° b = 11.8042(5) Å β =100.415(2) ° c = 19.4177(8) Å γ = 90°
Volume	2619.07(19)Å^3
Z	8
Density (calculated)	2.681 mg/m^3
Absorption coeff.	14.113 mm^{-1}
θ range	2.133 to 27.100 °
Reflections collected	21599
Independent reflections	2900 [R(int) = 0.1354]
Data completeness	100.0 %
Data/restraints /parameters	2900 / 0 / 104
GoF on F^2	0.970
Final *R* indices [I>2sigma(I)]	*R*1 = 0.0432, *wR*2 = 0.0654
R indices (all data)	*R*1 = 0.0956, *wR*2 = 0.0777

Table S4. Single crystal data and structure refinement details of (1,4-BDA)SnI_4.

CCDC No.	2303744
Empirical formula	(1,4BDA)SnI_4
Formula weight	179.12
Temperature	299(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.4665(8) Å α = 77.434(3)° b = 8.8203(7) Å β = 68.287(3) ° c = 11.2697(10) Å γ= 89.901(3)°.
Volume	760.26(12) $Å^3$
Z	8
Density (calculated)	3.130 mg/m^3
Absorption coeff.	9.766 mm^{-1}
θ range	2.000 to 27.273 °
Reflections collected	26535
Independent reflections	3404 [R(int) = 0.0931]
Data completeness	100.0 %
Data/restraints /parameters	3404 / 0 / 105
GoF on F^2	1.079
Final R indices [I>2sigma(I)]	$R1$ = 0.0459, $wR2$ = 0.1288
R indices (all data)	$R1$ =0.0611, $wR2$ = 0.1377

Table S5. Bond distances & bond angles as obtained from the SCXRD data of the compounds reported in this study. We have also included nonbonding N-H·····X distances.

(1,4-BDA)$SnBr_6$	
Bond lengths (Å)	*Bond angles* (°)
Sn(1)-Br(1) = 2.6076(9) x 2 Sn(1)-Br(2) = 2.6252(15) Sn(1)-Br(3) = 2.5797(8) x 2 Sn(1)-Br(4) = 2.5989(13)	Br(4)-Sn(1)-Br(3) = 90.61(4) Br(3)-Sn(1)-Br(3) = 92.41(4) Br(1)-Sn(1)-Br(3) = 88.69(3) x 2 Br(1)-Sn(1)-Br(1) = 90.20(4) x 2 Br(2)-Sn(1)-Br(1) = 88.66(4) Br(2)-Sn(1)-Br(3) = 90.59(4) Br(4)-Sn(1)-Br(1) = 90.11(4) x 2
(1,4-BDA)$SnBr_4$	
Bond lengths (Å)	*Bond angles* (°)
Sn(1)-Br(1) = 2.7902(10) Sn(1)-Br(2) = 2.9752(6) Sn(1)-Br(3) = 3.1970(12) Sn(1)-Br(4) = 2.9808(6) Sn(1)-Br(5) = 3.3009(9) Sn(1)-Br(5) = 2.7426(9) N-H·····Br *distances* (Å) N(1)-Br(1) = 3.418(8) N(1)-Br(3) = 3.366(8) N(1)-Br(5) = 3.605(9) N(2)-Br(1) = 3.446(6) N(2)-Br(2) = 3.497(6) N(2)-Br(3) = 3.373(6) N(2)-Br(5) = 3.591(7)	Br(5)-Sn(1)-Br(3) = 100.40(3) & 84.17(3) Br(5)-Sn(1)-Br(2) = 89.32(4) & 87.89(4) Br(5)-Sn(1)-Br(4) = 92.43(4) & 90.00(4) Br(5)-Sn(1)-Br(1) = 88.34(4) & 86.98(3) Br(4)-Sn(1)-Br(3) = 91.83(3) Br(3)-Sn(1)-Br(2) = 92.48(3) Br(1)-Sn(1)-Br(4) = 90.85(3) Br(1)-Sn(1)-Br(2) = 84.54(3)
(1,4-BDA)SnI_4	
Bond lengths (Å)	*Bond angles* (°)
Sn(1)-I(1) = 3.1439(7), 3.1440(7) Sn(1)-I(3) = 3.1641(6) Sn(1)-I(4) = 3.1596(6) Sn(2)-I(2) = 3.1485(7), 3.1486(7) Sn(2)-I(3) = 3.1610(6) Sn(2)-I(4) = 3.1592(6) N-H·····I *distances* (Å) N(1)-I(1) = 3.675(11) N(1)-I(2) = 3.586(13) N(1)-I(3) = 3.658(10) N(2)-I(2) = 3.621(10) N(2)-I(4) = 3.694(12) N(2)-I(3) = 3.988(11)	I(1)-Sn(1)-I(3) = 90.068(19) & 89.932(19) I(1)-Sn(1)-I(4) = 87.030(19) & 92.970(19) I(2)-Sn(2)-I(3) = 87.153(19) & 92.847(19) I(2)-Sn(2)-I(4) = 90.127(19) & 89.873(19)

Bond length deviation (Δd) : It was calculated using the below formula:[S10]

$$\Delta d = \frac{1}{6}\Sigma_i\left[\frac{d_i - d}{d}\right]^2$$

where d_i is the length of i^{th} M-X bond; d is the averaged M-X bond length.

Bond angle variance (σ^2) : It was calculated using the below formula:[S11]

$$\sigma^2 = \Sigma_i\frac{1}{11}(\theta_i - 90)^2$$

where θ_i is the i^{th} X-M-X bond angle.

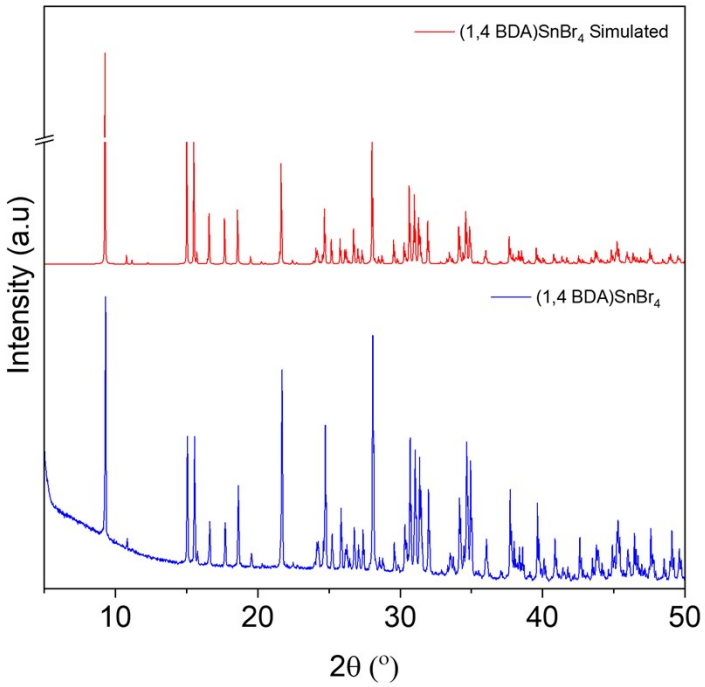

Fig. S1. Simulated and experimental powder X-ray diffraction patterns of (1,4-BDA)$SnBr_4$.

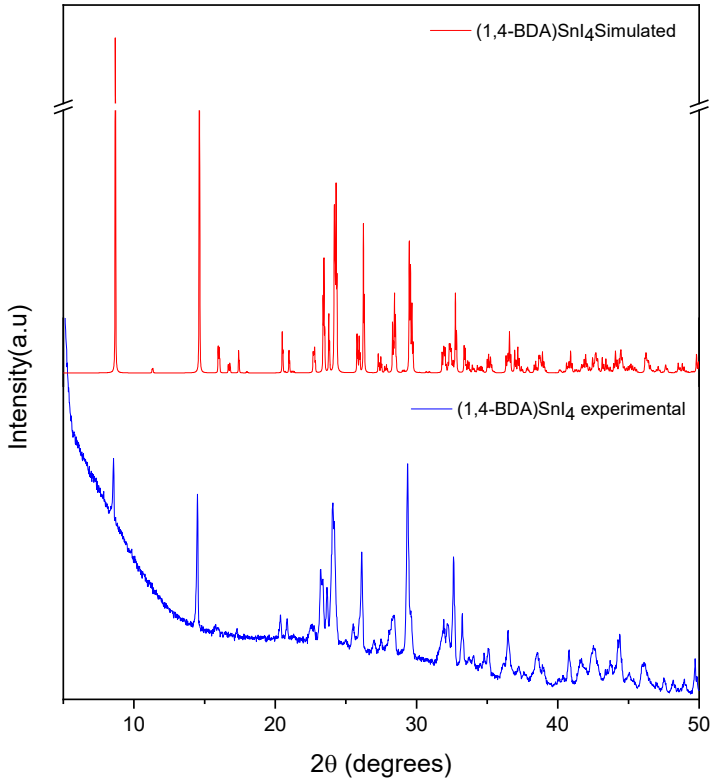

Fig. S2. Simulated and experimental powder X-ray diffraction patterns of (1,4-BDA)SnI_4.

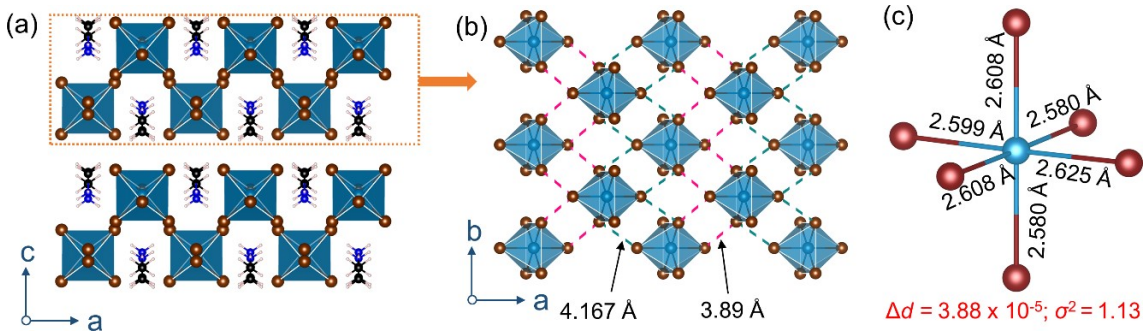

Fig. S3. Single-crystal structure of **(1,4-BDA)$SnBr_6$**: (a) Packing diagram viewed along the *b*-axis. (b) Arrangement of $[SnBr_6]^{2-}$ octahedra in the *ab*-plane, showing the nearest neighbour Br···Br distance by green and red dashed lines (1,4-BDA) molecules are shown for sake of clarity). (c) An $[SnBr_6]^{2-}$ octahedron showing the Sn-Br bond lengths (values for the bond length deviation & bond angle variance indices are also provided).

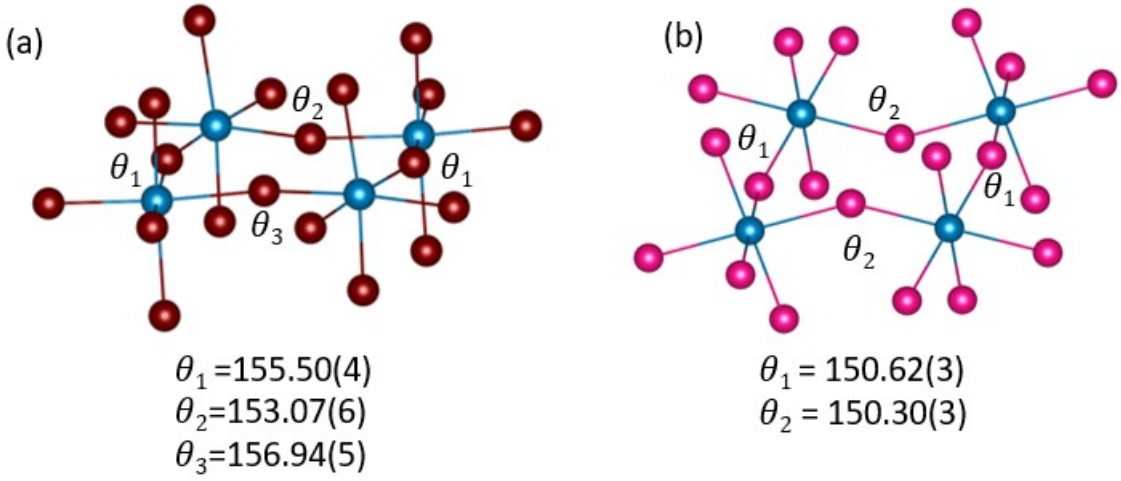

Fig. S4. (a) and (b) are Ball and Stick model of the perovskite layer illustrating the connection between the $(SnBr_6)^{4-}$ and $(SnI_6)^{4-}$ and corresponding M-X-M bond angles in (1,4-BDA)$SnBr_4$ and (1,4-BDA)SnI_4 respectively.

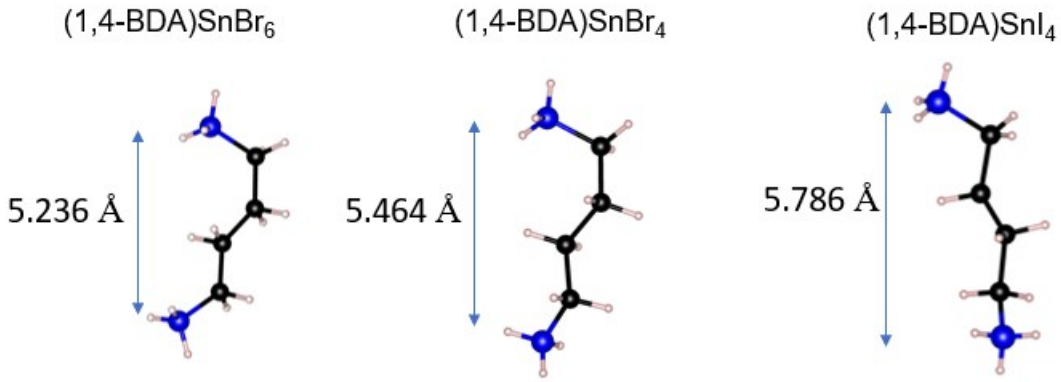

Fig. S5. Orientation of BDA in three different structures reported in this study, the distance between the NH_3^+ terminals are also given for comparison.

Table S6. Elemental ratio (atomic %) obtained from the EDS spectra.

Compound	C	N	Sn	Br	I
(1,4-BDA)$SnBr_4$	51.46	22.86	5.38	20.31	-
(1,4-BDA)SnI_4	67.70	7.43	5.33	-	19.54

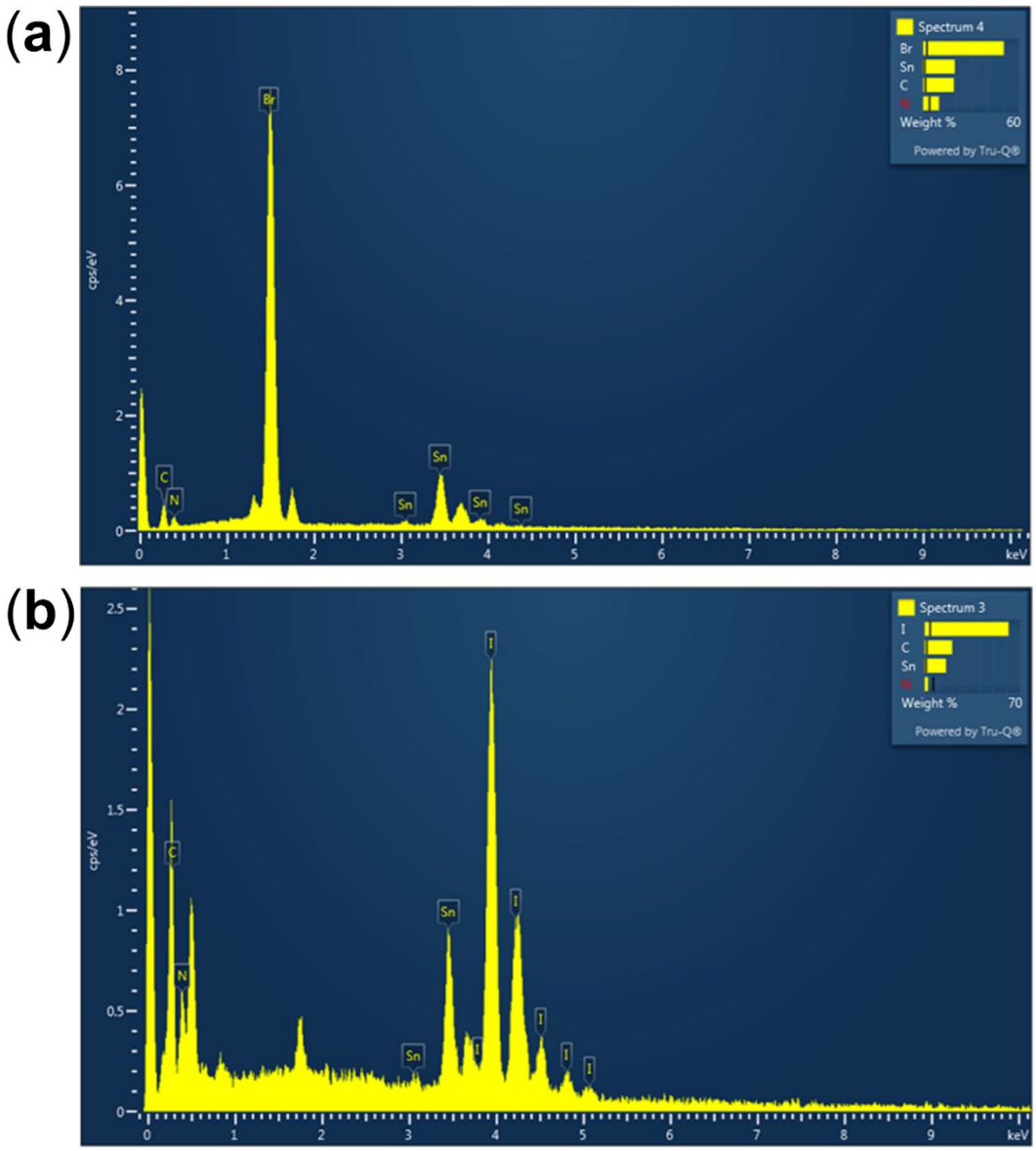

Fig. S6. Energy-dispersive X-ray spectra of (a) (1,4-BDA)$SnBr_4$ and (b) (1,4-BDA)SnI_4.

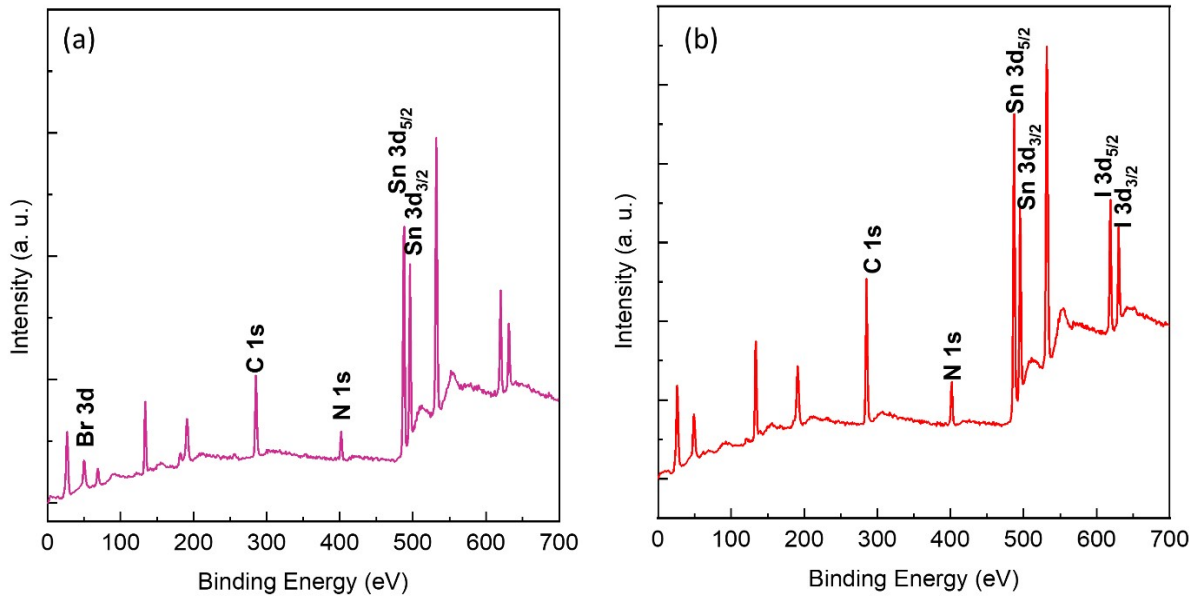

Fig. S7. XPS survey spectra of (a) (1,4-BDA)$SnBr_4$ and (b) (1,4-BDA)SnI_4.

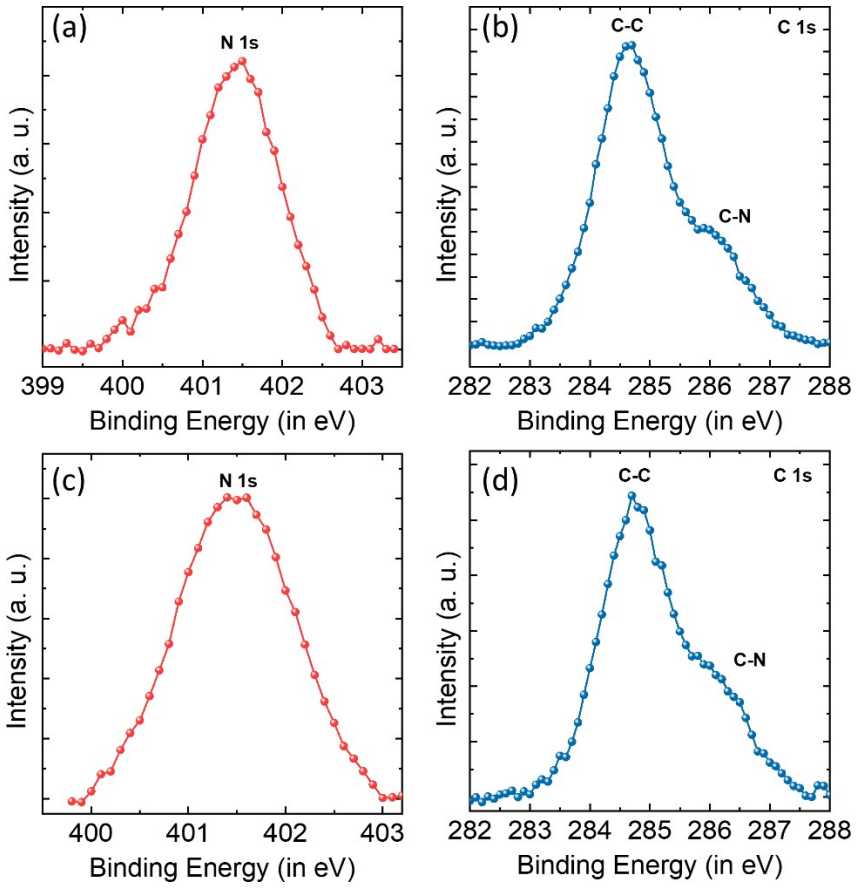

Fig. S8. (a) & (b) Core level N1s and C1s XPS spectra of (1,4-BDA)$SnBr_4$. (c) & (d) Core level N1s and C1s XPS spectra of (1,4-BDA)SnI_4.

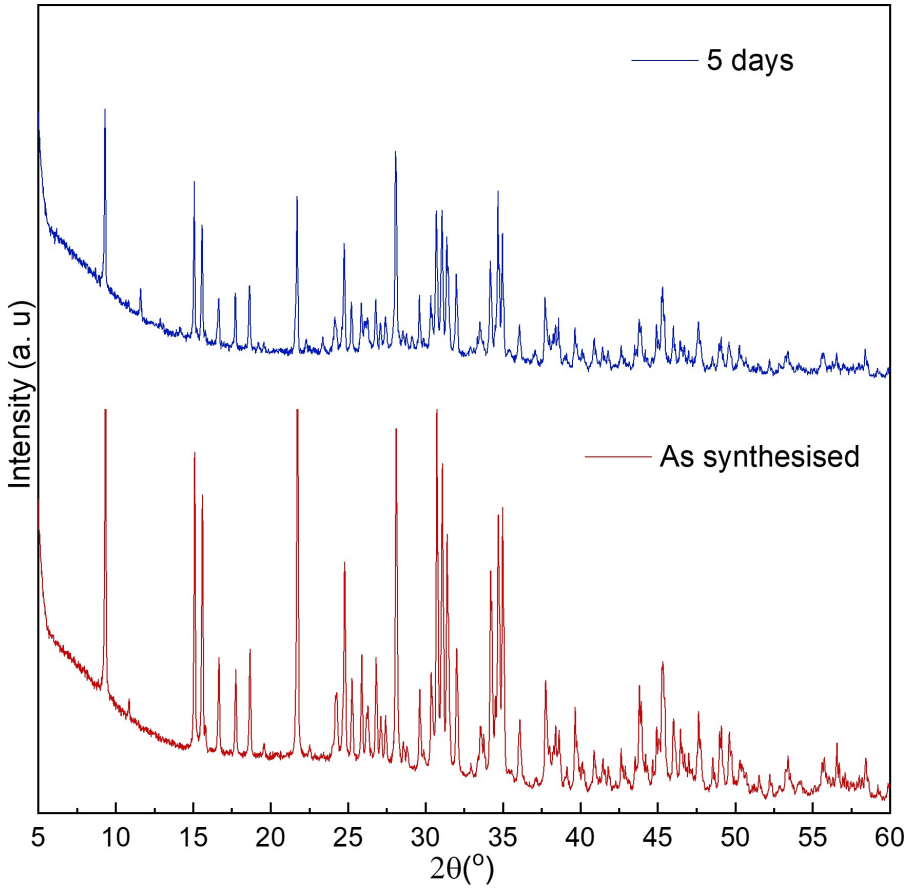

Fig. S9. PXRD pattern comparing the ambient stabilities of (1,4-BDA)$SnBr_4$.

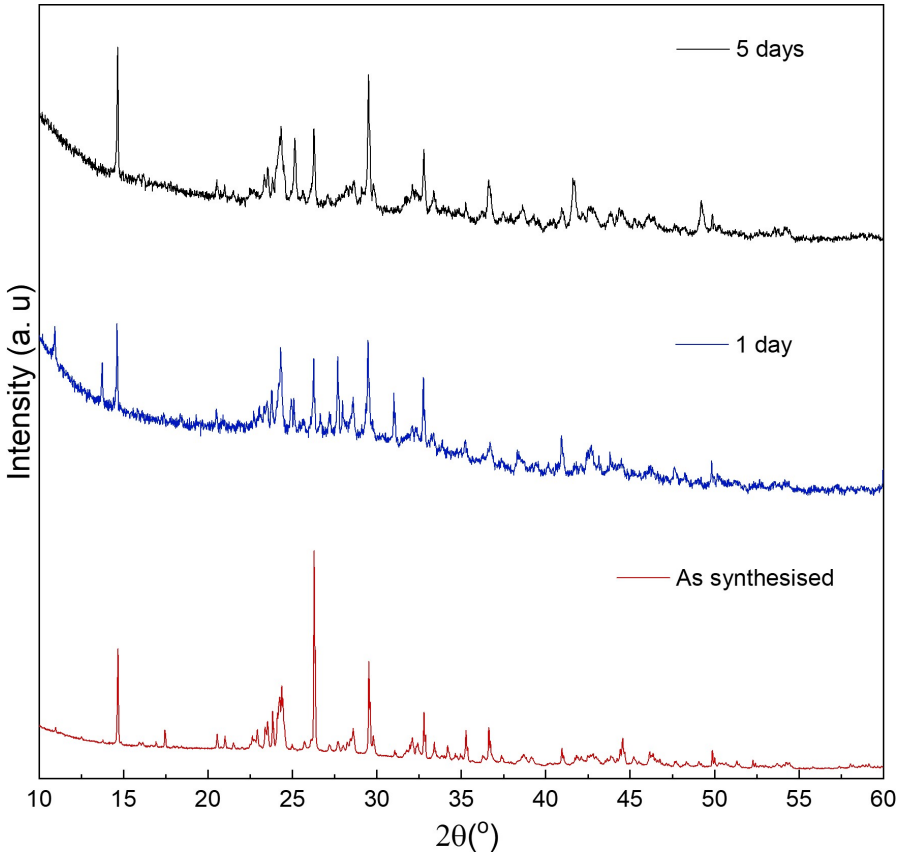

Fig. S10. PXRD pattern comparing the ambient stabilities of (1,4-BDA)SnI_4.

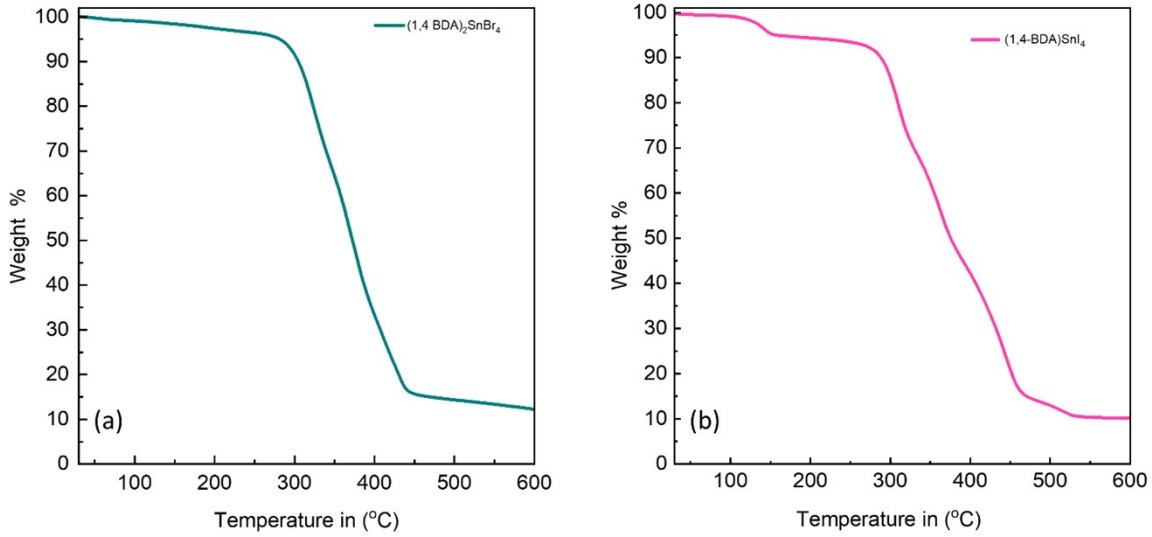

Fig. S11. TGA curves of (a) (1,4-BDA)$SnBr_4$ and (b) (1,4-BDA)SnI_4.

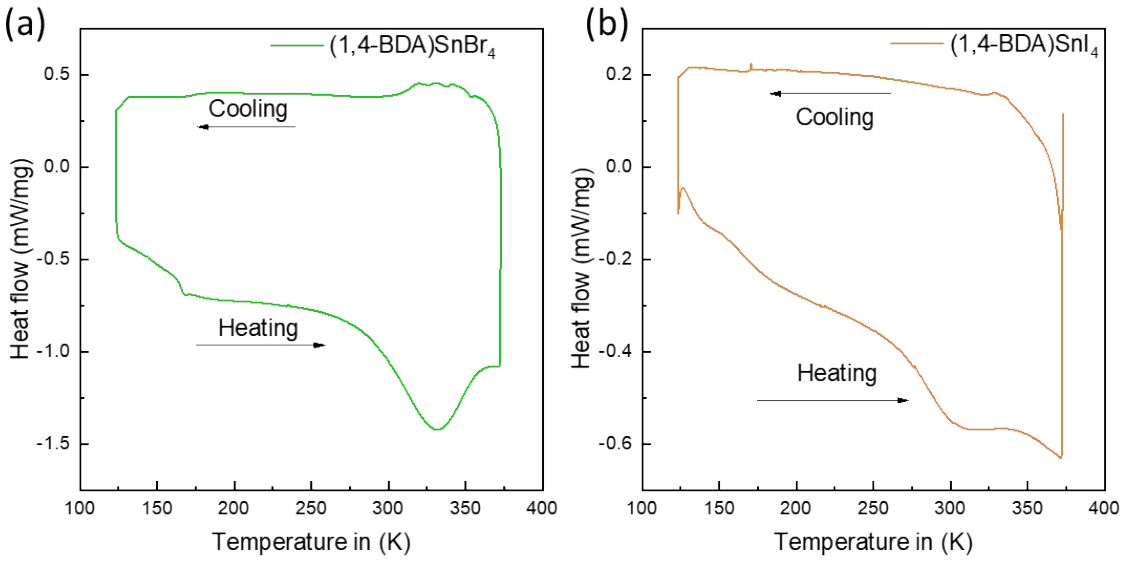

Figure S12. DSC plots of (a) (1,4-BDA)$SnBr_4$ and (b) (1,4-BDA)SnI_4.

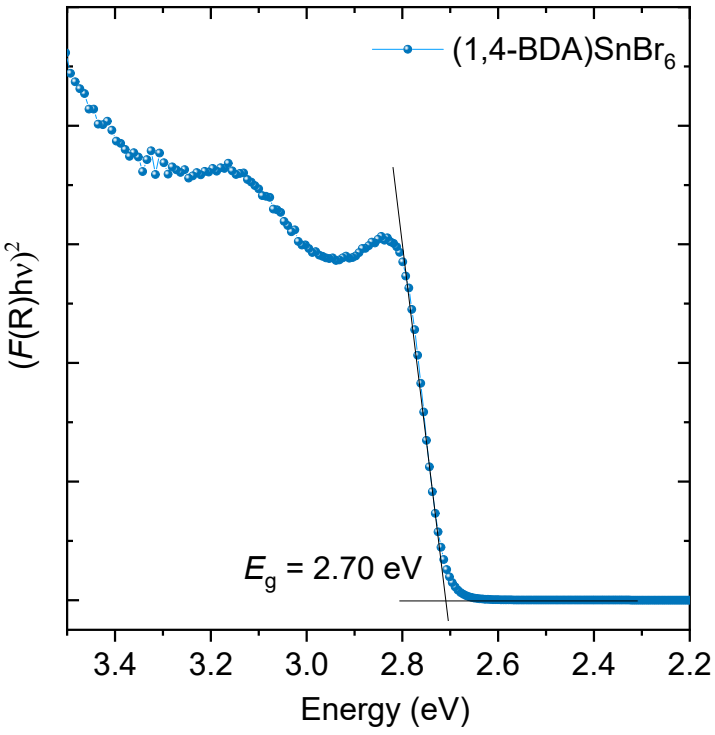

Fig. S13. Tauc plot for (1,4-BDA)$SnBr_6$.

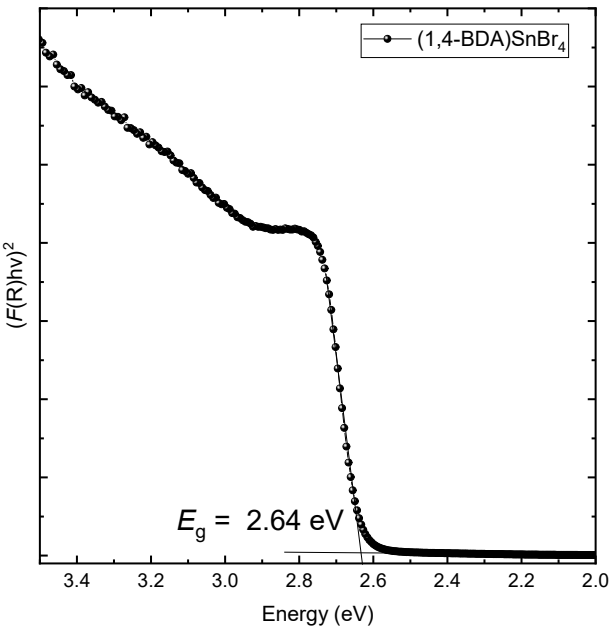

Fig. S14. Tauc plot for (1,4-BDA)$SnBr_4$.

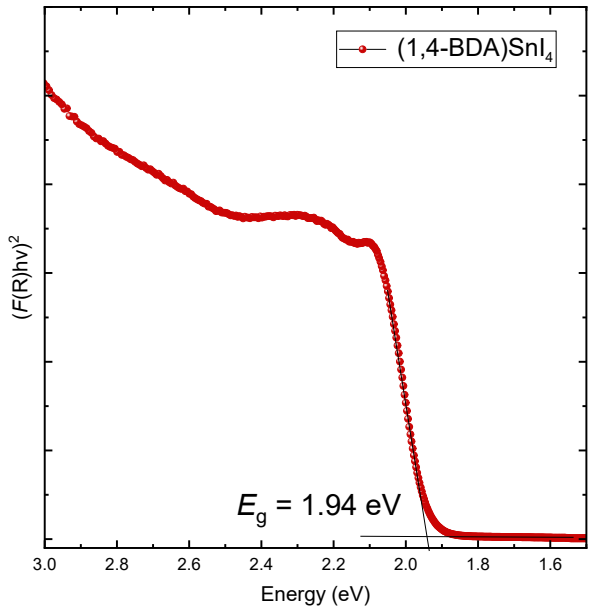

Fig. S15. Tauc plot of (1,4-BDA)SnI_4.

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