ELECTRONIC SUPPLEMENTARY INFORMATION

Exploring the Role of Halide Mixing in Lead-Free BZA_2SnX_4 Two Dimensional Hybrid Perovskites

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Table 1 - Lattice parameters (Å) and space groups of different compounds studied by single-crystal X-ray diffraction.

	BZA_2SnI_4	BZA_2SnBr_4	BZA_2SnCl_4	$BZA_3Sn(Br_xI_{1-x})_5$
space group	*Pbca* (# 61)	$Cmc2_1$ (# 36)	$Cmc2_1$ (# 36)	$P2_1/c$ (# 14)
a	9.1105(14)	33.2806(15)	33.505(3)	14.5383(4)
b	8.6776(13)	8.1046(4)	7.7784(6)	8.46698(19)
c	28.754(6)	8.1036(4)	7.7678(5)	26.2932(6)
β	90	90	90	105.410(3)

Table 2: Atomic coordinates in the structure of BZA_2SnI_4 resolved from single crystal X-ray diffraction.

		x	*y*	*z*	*msd* (Å^2)	*s.f.*
Sn	Sn1	0.5	0	0.5	0.03688(13)	1
I	I1	0.28824(4)	0.29076(4)	0.49275(2)	0.04951(13)	1
I	I2	0.54468(5)	0.02018(5)	0.39134(2)	0.05508(14)	1
N	N1	.5804(6)	00.4342(7)	0.4134(2)	0.0616(13)	1
C	C1	0.4755(11)	0.5499(9)	0.3934(3)	0.076(2)	1
C	C2	0.4428(7)	0.5136(7)	0.3438(3)	0.0547(14)	1
C	C3	0.3334(7)	0.4091(10)	0.3330(3)	0.076(2)	1
C	C4	0.2993(9)	0.3781(14)	0.2872(4)	0.099(3)	1
C	C5	0.3741(12)	0.4491(11)	0.2522(3)	0.089(3)	1
C	C6	0.4825(11)	0.5524(11)	0.2625(3)	0.084(2)	1
C	C7	0.5162(9)	0.5835(9)	0.3081(3)	0.0721(19)	1
H	H1NA	0.5471	0.3395	0.4080	0.092	1
H	H1NB	0.5884	0.4490	0.4439	0.092	1
H	H1NC	0.6680	0.4455	0.4001	0.092	1
H	H1A	0.3851	0.5492	0.4112	0.091	1
H	H1B	0.5179	0.6522	0.3955	0.091	1
H	H3	0.2826	0.3595	0.3568	0.092	1
H	H4	0.2250	0.3084	0.2802	0.119	1
H	H5	0.3515	0.4273	0.2214	0.107	1
H	H6	0.5333	0.6016	0.2387	0.101	1
H	H7	0.5905	0.6535	0.3148	0.087	1

Table 3: Atomic coordinates in the structure of BZA_2SnBr_4 resolved from single crystal X-ray diffraction.

		x	*y*	*z*	*msd* (Å^2)	*o.f.*
Sn	Sn1	0.5	0.2503(2)	0.5221(5)	0.0411(2)	1
Br	Br1	0.5	0.4385(3)	0.2085(3)	0.0594(7)	1
Br	Br2	0.5	-0.0623(3)	0.3325(2)	0.0524(6)	1
Br	Br3	0.41079(3)	0.2505(4)	0.5218(8)	0.0738(3)	1
N	N1	0.4224(3)	0.1703(19)	0.0996(14)	0.067(3)	1
C	C1	0.4012(3)	0.291(3)	-0.003(3)	0.080(5)	1
C	C2	0.3569(2)	0.258(3)	0.011(3)	0.081(3)	1
C	C3	0.3352(7)	0.136(3)	-0.068(4)	0.122(10)	1
C	C4	0.2938(7)	0.129(4)	-0.047(6)	0.185(16)	1
C	C5	0.2748(4)	0.238(4)	0.060(6)	0.190(15)	1
C	C6	0.2968(6)	0.357(3)	0.143(5)	0.159(13)	1
C	C7	0.3380(6)	0.364(3)	0.119(4)	0.111(10)	1
H	H1NA	0.4488	0.1880	0.0930	0.101	1
H	H2NB	0.4145	0.1805	0.2040	0.101	1
H	H3NC	0.41689	0.0689	0.0640	0.101	1
H	H1A	0.4097	0.2814	-0.1169	0.096	1
H	H1B	0.4071	0.4022	0.0347	0.096	1
H	H3	0.3482	0.0584	-0.1338	0.146	1
H	H4	0.2788	0.0521	-0.1051	0.222	1
H	H5	0.2472	0.2302	0.0757	0.228	1
H	H6	0.2841	0.4312	0.2131	0.191	1
H	H7	0.3531	0.4414	0.1773	0.134	1

Table 4: Atomic coordinates in the structure of BZA_2SnCl_4 resolved from single crystal X-ray diffraction.

		x	*y*	*z*	*msd* (Å^2)	*o.f.*
Sn	Sn1	0.5	0.25148(18)	0.5294(6)	0.0454(2)	1
Cl	Cl1A	0.5	0.4088(18)	0.234(3)	0.070(4)	0.5
Cl	Cl1B	0.5	0.4675(18)	0.181(3)	0.070(4)	0.5
Cl	Cl2A	0.5	-0.0346(13)	0.3622(12)	0.0384(15)	0.5
Cl	Cl2B	0.5	-0.1143(12)	0.3355(14)	0.0384(15)	0.5
Cl	Cl3	0.41561(7)	0.2558(7)	0.5318(18)	0.0800(7)	1
N	N1	0.4254(3)	0.1832(17)	0.1179(13)	0.057(2)	1
C	C1	0.4033(3)	0.269(2)	-0.0205(16)	0.065(4)	1
C	C2	0.35900(19)	0.2689(16)	0.0268(16)	0.064(2)	1
C	C3	0.3378(5)	0.143(2)	-0.060(2)	0.096(6)	1
C	C4	0.2971(4)	0.131(2)	-0.034(3)	0.117(7)	1
C	C5	0.2783(3)	0.240(3)	0.079(3)	0.142(11)	1
C	C6	0.2993(4)	0.362(3)	0.171(3)	0.126(8)	1
C	C7	0.3400(4)	0.374(2)	0.143(2)	0.085(5)	1
H	H1NA	0.4200	0.2343	0.2178	0.085	1
H	H1NB	0.4514	0.1898	0.0967	0.085	1
H	H1NC	0.4181	0.0733	0.1232	0.085	1
H	H1A	0.4073	0.2090	-0.1284	0.079	1
H	H1B	0.412689	0.38639	-0.0338	0.079	1
H	H3	0.3507	0.0683	-0.1342	0.115	1
H	H4	0.048658	0.282381	-0.093367	0.140	1
H	H5	0.2509	0.2318	0.0945	0.171	1
H	H6	0.2866	0.4344	0.2485	0.151	1
H	H7	0.3548	0.4545	0.2036	0.102	1

Table 5 - Octahedral interatomic distances in the structure of BZA_2SnX_4.

	BZA_2SnI_4	BZA_2SnBr_4	BZA_2SnCl_4
apical	3.1557(9) Å (x 2)	2.977(1) Å (x 2)	2.823(3) Å (x 2)
equatorial	3.200(3) Å (x 2)	2.965(4) Å (x 1)	3.015(11) Å (x 1)
		2.964(4) Å (x 1)	2.966(11) Å (x 1)
	3.183(2) Å (x 2)	2.940(4) Å (x 1)	2.743(10) Å (x 1)
		2.942(4) Å (x 1)	2.690(11) Å (x 1)

Table 6 - Sn-X-Sn bond angles within the inorganic layer in the structure of BZA_2SnX_4.

	BZA_2SnI_4	BZA_2SnBr_4	BZA_2SnCl_4
Sn-X1-Sn	160.57(2)°	151.9(1)°	151.1(4)°
Sn-X2-Sn	-	152.4(1)°	144.3(4)°

Table 7: Atomic coordinates in the structure of $BZA_3Sn(Br_xI_{1-x})_5$ resolved from single crystal X-ray diffraction.

		x	*y*	*z*	*msd* (Å^2)	*s.f.*
Sn	Sn1	0.47938(3)	0.51806(4)	0.33246(2)	0.03654(12)	1
I	I1	0.27258(3)	0.50385(6)	0.27551(2)	0.05074(18)	0.705(8)
Br	Br1					0.295(8)
I	I2	0.45932(3)	0.72741(5)	0.42358(2)	0.05239(16)	0.927(8)
Br	Br2					0.073(8)
I	I3	0.49802(4)	0.81420(6)	0.26269(2)	0.04739(19)	0.314(7)
Br	Br3					0.686(7)
I	I4	0.46490(4)	0.23012(5)	0.39661(2)	0.05487(17)	0.853(8)
Br	Br4					0.147(8)
I	I5	0.27135(3)	0.99076(6)	0.12891(2)	0.05781(18)	0.986(8)
Br	Br5					0.014(8)
N	N1	0.3457(5)	0.5863(8)	0.1577(2)	0.0731(19)	1
C	C1A	0.2937(7)	0.5070(11)	0.0342(3)	0.085(2)	1
C	C1B	0.2582(10)	0.5466(15)	-0.0181(4)	0.120(3)	1
C	C1C	0.1679(10)	0.6071(16)	-0.0294(6)	0.127(4)	1
C	C1D	0.1097(10)	0.6179(18)	0.0032(5)	0.139(4)	1
C	C1E	0.1508(9)	0.5715(16)	0.0542(5)	0.114(3)	1
C	C1F	0.2423(5)	0.5138(8)	0.0708(3)	0.0633(17)	1

C	C1G	0.2817(10)	0.4691(13)	0.1250(4)	0.108(3)	1
N	N2	0.3153(5)	1.0857(8)	0.2671(3)	0.0641(15)	1
C	C2A	0.1629(6)	1.0987(11)	0.3357(3)	0.071(2)	1
C	C2B	0.0728(7)	1.1210(13)	0.3411(4)	0.085(3)	1
C	C2C	-0.0020(6)	1.0438(12)	0.3091(4)	0.080(2)	1
C	C2D	0.0126(6)	0.9447(12)	0.2716(4)	0.084(3)	1
C	C2E	0.1025(6)	0.9206(10)	0.2664(3)	0.072(2)	1
C	C2F	0.1796(5)	0.9947(8)	0.2999(3)	0.0540(15)	1
C	C2G	0.2796(6)	0.9619(9)	0.2963(4)	0.067(2)	1
N	N3	0.6571(5)	0.4662(9)	0.4902(3)	0.0707(18)	1
C	C3A	0.8157(6)	0.4753(11)	0.5982(3)	0.068(2)	1
C	C3B	0.9041(7)	0.4287(14)	0.6289(3)	0.086(3)	1
C	C3C	0.9836(6)	0.4588(13)	0.6127(4)	0.083(3)	1
C	C3D	0.9773(6)	0.5376(13)	0.5660(4)	0.082(3)	1
C	C3E	0.8895(6)	0.5831(11)	0.5351(3)	0.068(2)	1
C	C3F	0.8080(5)	0.5525(9)	0.5513(3)	0.0555(16)	1
C	C3G	0.7133(6)	0.6009(11)	0.5176(3)	0.071(2)	1
H	H1NA	0.3300	0.6824	0.1445	0.11	1
H	H1NB	0.4057	0.5652	0.1578	0.11	1
H	H1NC	0.3400	0.5822	0.1906	0.11	1
H	H1A	0.3568	0.4735	0.0454	0.102	1
H	H1B	0.2922	0.5325	-0.0432	0.144	1
H	H1C	0.1433	0.6454	-0.0635	0.153	1
H	H1D	0.0472	0.6538	-0.0080	0.167	1
H	H1E	0.1151	0.5795	0.0786	0.137	1
H	H1G1	0.3167	0.3711	0.1259	0.13	1
H	H1G2	0.2295	0.4487	0.1407	0.13	1
H	H2NA	0.2825	1.0789	0.2329	0.096	1
H	H2NB	0.3777	1.0728	0.2714	0.096	1
H	H2NC	0.3046	1.1802	0.2792	0.096	1
H	H2A	0.2135	1.1556	0.3569	0.085	1
H	H2B	0.0629	1.1892	0.3669	0.102	1
H	H2C	-0.0633	1.0588	0.3128	0.096	1

H	H2D	-0.0389	0.8927	0.2493	0.1	1
H	H2E	0.1118	0.8540	0.2401	0.086	1
H	H2G1	0.3218	0.9541	0.3317	0.08	1
H	H2G2	0.2807	0.8611	0.2789	0.08	1
H	H3NA	0.6868	0.4234	0.4680	0.106	1
H	H3NB	0.5996	0.4997	0.4723	0.106	1
H	H3NC	0.6511	0.3943	0.5138	0.106	1
H	H3A	0.7613	0.4543	0.6092	0.081	1
H	H3B	0.9092	0.3768	0.6607	0.103	1
H	H3C	1.0429	0.4258	0.6332	0.1	1
H	H3D	1.0321	0.5598	0.5555	0.098	1
H	H3E	0.8848	0.6345	0.5032	0.082	1
H	H3G1	0.6779	0.6529	0.5393	0.085	1
H	H3G2	0.7223	0.6765	0.4916	0.085	1

Table 8 - Lattice parameters of the $BZA_2Sn(Br_xI_{1-x})_4$ solid solution from powder X-ray diffraction in the same setting (see main text for details).

x	*a*	*b*	*c*
1.0	8.1007(6)	8.0993(8)	33.287(3)
0.75	8.2367(9)	8.2318(9)	32.207(5)
0.625	8.297(2)	8.290(1)	32.056(5)
0.50	8.285(8)	8.268(8)	32.184(7)
0.30	8.584(4)	8.496(3)	31.524(8)
0.25	8.660(3)	8.532(3)	31.166(9)
0.0	9.101(1)	8.680(1)	28.802(3)

Table 9 – Elemental composition of some selected samples probed by EDX, where *x* refers to $BZA_2Sn(Br_xI_{1-x})_4$ composition and X/Sn indicates the halide to Sn ratio, which is 4 for a full 2D composition. E.s.d. for the measurements is around 5%.

nominal x	exp x	exp X/Sn
1.000	-	3.90
0.750	0.753	4.10
0.625	0.636	4.14
0.250	0.275	4.09
0.000	-	3.96

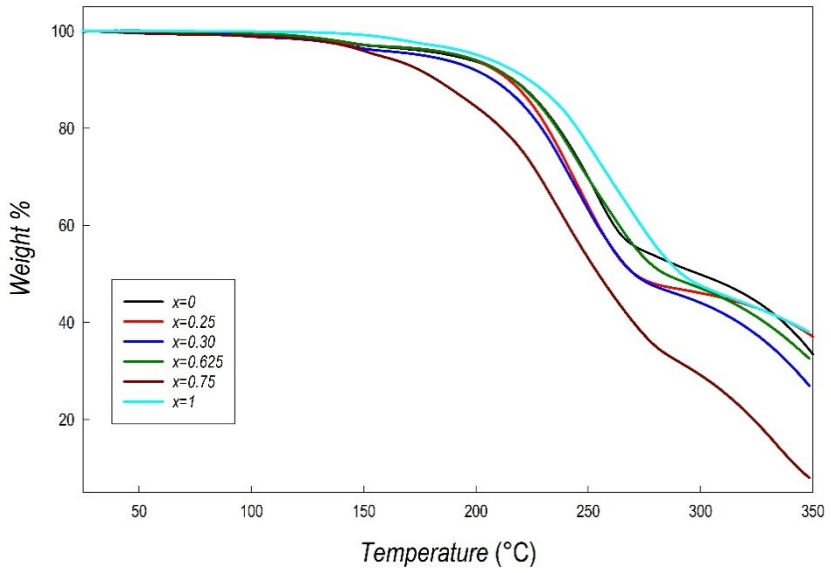

Figure S1. TGA traces for the $BZA_2Sn(Br_xI_{1-x})_4$ solid solution as a function of *x* in the range from RT to 350°C.

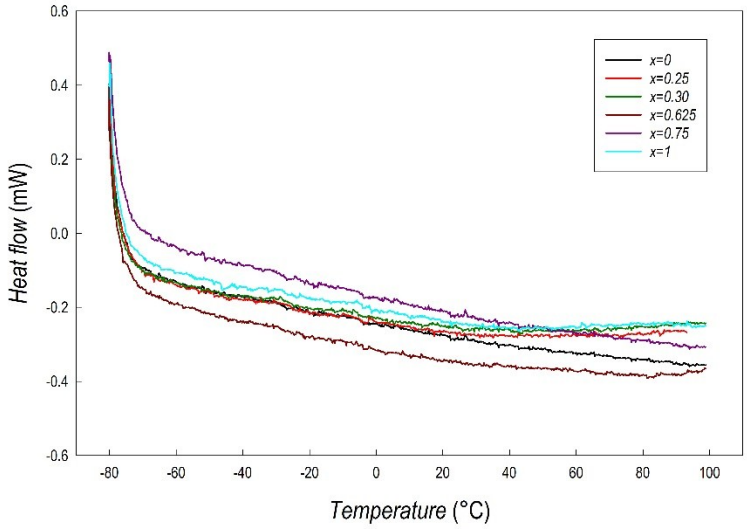

Figure S2. DSC traces for the $BZA_2Sn(Br_xI_{1-x})_4$ solid solution as a function of *x* in the range from -80°C to 100°C.

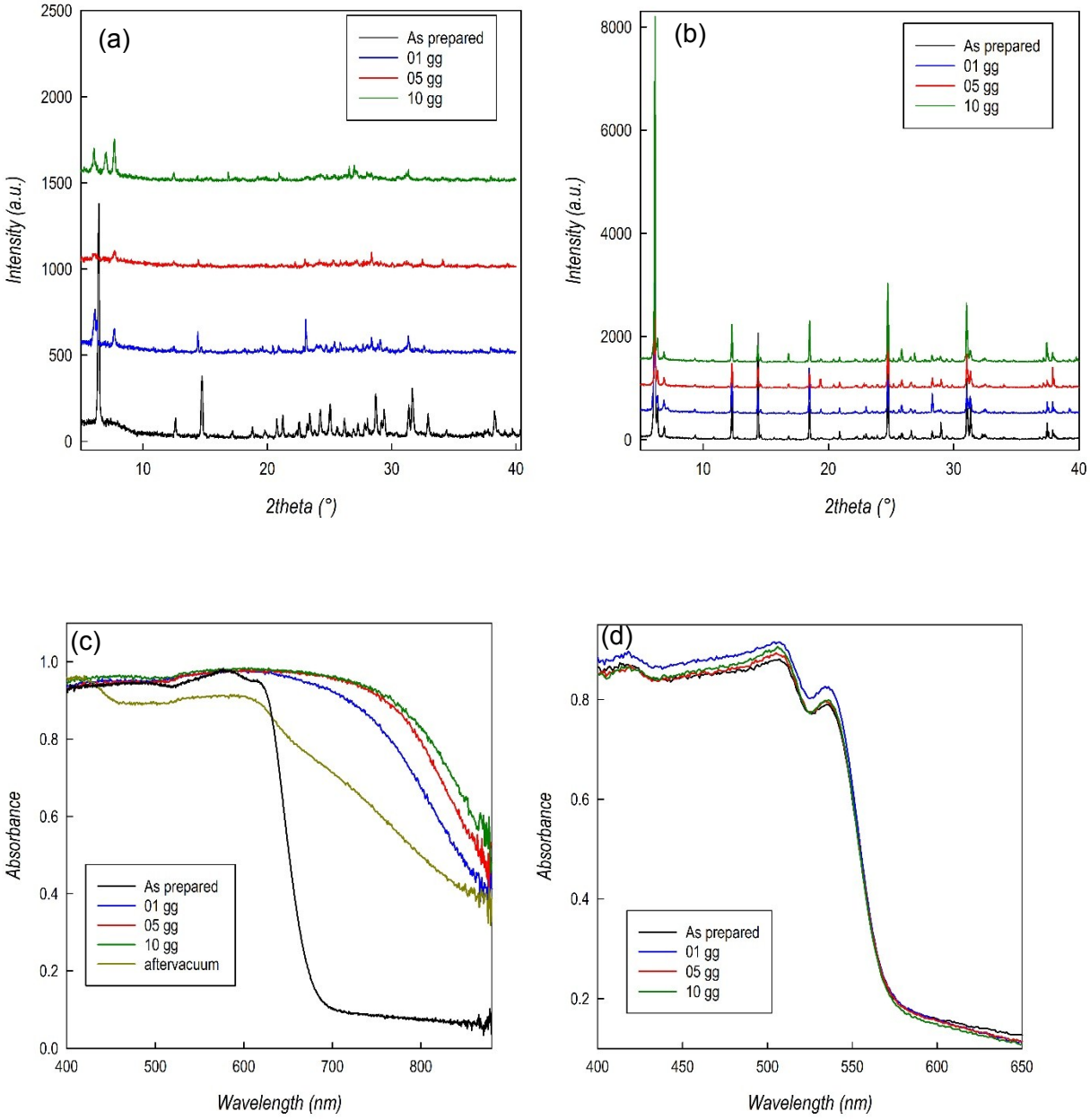

Figure S3. XRD patterns of BZA_2SnI_4 (a) and BZA_2PbI_4 (b) as a function of time under laboratory-air exposure and UV-Vis spectra of BZA_2SnI_4 (c) and BZA_2PbI_4 (d) as a function of time under laboratory-air exposure.

Table 10 - Optimized lattice parameters for BZA_2SnX_4 (X=Cl, Br, and I) with experimental values

Composition	***a* (Å)**	***b* (Å)**	***c* (Å)**
BZA_2SnI_4 Theory	9.317	8.867	30.3618
Exp.	9.1105(14)	8.6776(13)	28.754
Error %	2.26	2.18	5.59
BZA_2SnBr_4 Theory	33.979	8.111	8.0226
Exp.	33.2806(15)	8.1046(4)	8.1036(4)
Error %	2.09	0.08	0.99
BZA_2SnCl_4 Theory	34.68	8.1139	7.873
Exp.	33.505(3)	7.7784(6)	7.7678(5)
Error %	3.4	4.1	1.33

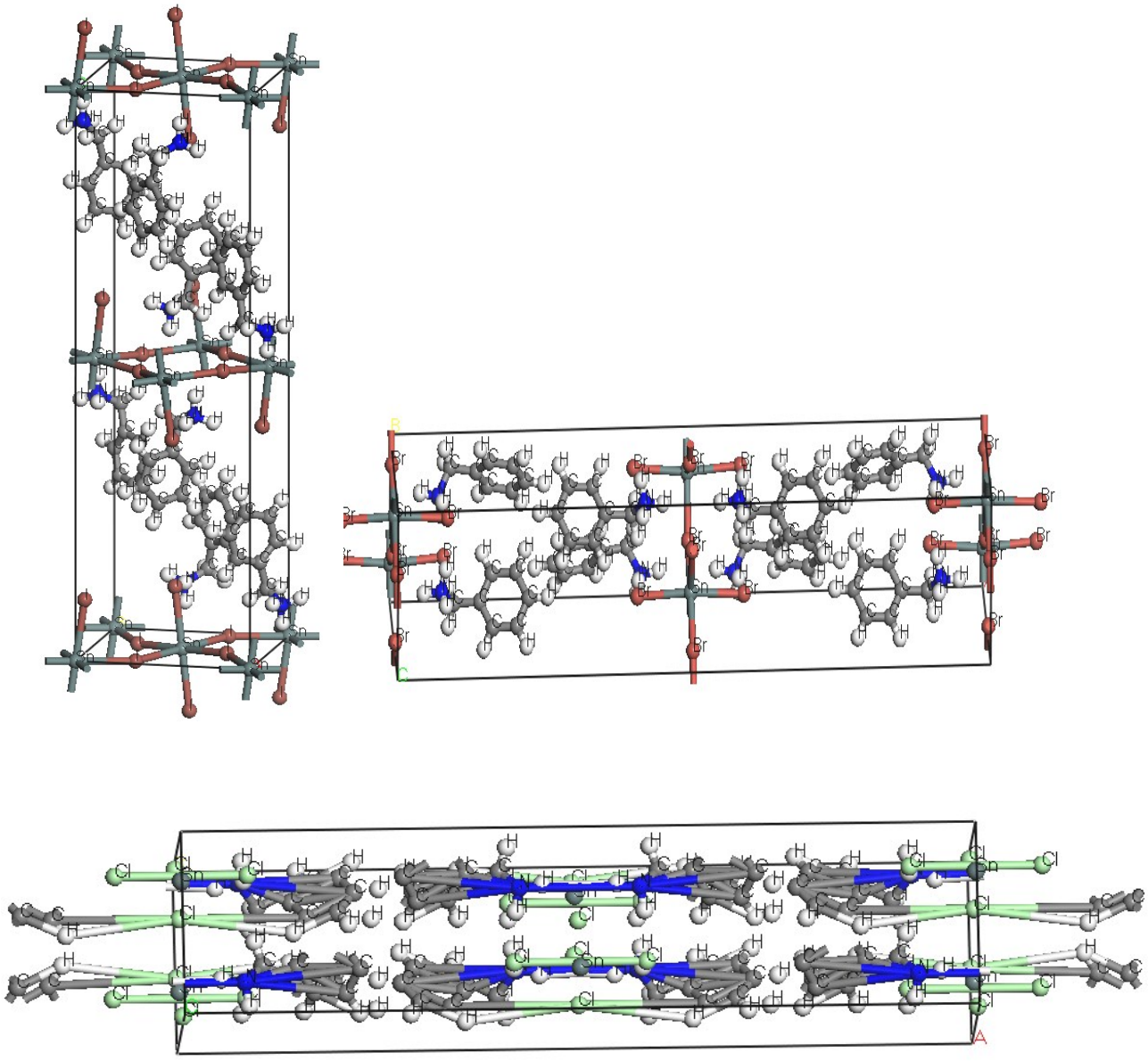

Figure S4. Optimized unit cell for BZA_2SnX_4 (X=I, Br, and Cl)

Table 11. Optimized unit cell for BZA_2SnX_4 (X=I, Br, and Cl)

x	**a1**	**t1 (ns)**	**a2**	**t2 (ns)**
0	2,30E-02	1,50E+02	7,5	0,011
0,25	2,90E-02	240	13	0,011
0,3	3,40E-02	250	22	0,02
0,625	4,90E-02	240	16	0,012
0,75	2,40E-02	240	16	0,011
1	1,00E-02	230	27	0,01
BZA_2SnCl_4	1.61-2	120	44	0,0099