Electronic Supplementary Information for

Extending Lead-free Hybrid Photovoltaic Materials to New Structures: Thiazolium, Aminothiazolium and Imidazolium Iodobismuthates

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Table S1: Bond Lengths in Å for **$[TH]_3[Bi_2I_9]$**.

Atom	Atom	Length/Å
Bi1	I1	3.2758(12)
Bi1	I2	3.2405(12)
Bi1	I3	3.2354(12)
Bi1	I4	2.9619(12)
Bi1	I5	2.9585(12)
Bi1	I6	2.9624(12)
S1	C1	1.668(15)
S1	C2	1.610(15)
N1	H1	0.87
N1	C1	1.314(19)
N1	C2	1.388(19)
C1	H1A	0.94
C1	H1B	0.94
C2	C2	1.334(17)
C2	H2A	0.94
C2	H2B	0.94
S2	C3	1.628(12)
S2	C5	1.627(17)
S2A	C3A	1.667(10)
S2A	C5A	1.667(10)
N2	H2	0.87
N2	C3	1.329(15)
N2	C4	1.366(17)
C3	H3	0.94
C3A	H3A	0.94
C3A	N2A	1.3169
C4	H4	0.94
C4	C5	1.352(18)
C5	H5	0.94
C5A	H5A	0.94
C5A	C4A	1.3519
C4A	H4A	0.94
C4A	N2A	1.3392
N2A	H2AA	0.87

Table S2: Bond Angles in ° for **$[TH]_3[Bi_2I_9]$**

Atom1	Atom2	Atom3	Angle/°
I2	Bi1	I1	80.30(3)
I3	Bi1	I1	79.97(3)
I3	Bi1	I2	83.20(3)
I4	Bi1	I1	94.96(4)
I4	Bi1	I2	92.78(4)
I4	Bi1	I3	173.97(4)
I4	Bi1	I6	93.38(4)
I5	Bi1	I1	94.20(4)
I5	Bi1	I2	172.99(3)
I5	Bi1	I3	91.60(4)
I5	Bi1	I4	92.02(4)
I5	Bi1	I6	92.94(4)
I6	Bi1	I1	168.82(3)
I6	Bi1	I2	91.88(4)
I6	Bi1	I3	91.25(4)
Bi1	I1	Bi1	81.80(4)
Bi1	I2	Bi1	82.89(4)
Bi1	I3	Bi1	83.05(4)
C2	S1	C1	92.5(11)
C1	N1	H1	118.8
C1	N1	C2	122(3)
C2	N1	H1	118.8
S1	C1	S1	117.9(14)
S1	C1	H1A	121
N1	C1	S1	15(3)
N1	C1	S1	104.9(19)
N1	C1	N1	91(3)
N1	C1	H1B	134.5
N1	C1	H1B	134.5
S1	C2	H2A	120.9
N1	C2	H2B	129.4
C2	C2	S1	118.2(6)
C2	C2	N1	101.2(13)
C2	C2	H2A	120.9
C2	C2	H2B	129.4
C5	S2	C3	100.3(10)
C3A	S2A	C5A	91.5(5)
C3	N2	H2	123.1
C3	N2	C4	113.8(16)
C4	N2	H2	123.1
S2	C3	H3	127
N2	C3	S2	106.0(11)
N2	C3	H3	127
S2A	C3A	H3A	125.4
N2A	C3A	S2A	109.2(3)

N2A	C3A	H3A	125.4
N2	C4	H4	121.9

Atom1	**Atom2**	**Atom3**	**Angle/°**
C5	C4	N2	116.2(19)
C5	C4	H4	121.9
S2	C5	H5	128.1
C4	C5	S2	103.8(16)
C4	C5	H5	128.1
S2A	C5A	H5A	123.6
C4A	C5A	S2A	112.8(3)
C4A	C5A	H5A	123.6
C5A	C4A	H4A	125.7
N2A	C4A	C5A	108.6
N2A	C4A	H4A	125.7
C3A	N2A	C4A	117.8
C3A	N2A	H2AA	121.1
C4A	N2A	H2AA	121.1

Table S3: Bond Lengths in Å for **[AT][BiI_4]**.

Atom	Atom	Length/Å
Bi1	I1	3.2134(5)
Bi1	I1	3.1275(5)
Bi1	I2	2.9219(5)
Bi1	I3	3.0246(5)
Bi1	I3	3.2648(5)
Bi1	I5	2.9511(6)
N5	H5A	0.91
N5	H5B	0.91
N5	H5C	0.91
N5	C1	1.327(12)
S1	C1	1.705(9)
S1	C3	1.711(10)
N2	C1	1.368(12)
N2	C2	1.395(12)
C2	H2	0.95
C2	C3	1.327(12)
C3	H3	0.95

Table S4: Bond Angles in ° for **[AT][BiI_4]**

Atom	Atom	Atom	Angle/
I1	Bi1	I1	86.955(14)
I1	Bi1	I3	87.630(14)
I1	Bi1	I3	81.844(14)
I2	Bi1	I1	94.573(16)
I2	Bi1	I1	89.349(15)
I2	Bi1	I3	89.644(15)
I2	Bi1	I3	170.804(17)
I2	Bi1	I5	99.254(17)
I3	Bi1	I1	89.749(15)
I3	Bi1	I1	174.613(16)
I3	Bi1	I3	87.686(14)
I5	Bi1	I1	85.297(15)
I5	Bi1	I1	168.842(16)
I5	Bi1	I3	97.347(17)
I5	Bi1	I3	89.817(16)
Bi1	I1	Bi1	93.046(14)
Bi1	I3	Bi1	92.314(14)
H5A	N5	H5B	109.5
H5A	N5	H5C	109.5
H5B	N5	H5C	109.5
C1	N5	H5A	109.5
C1	N5	H5B	109.5
C1	N5	H5C	109.5
C1	S1	C3	91.0(5)
C1	N2	C2	110.7(7)
N5	C1	S1	123.6(7)
N5	C1	N2	124.2(8)
N2	C1	S1	112.1(7)
N2	C2	H2	122.6
C3	C2	N2	114.8(9)
C3	C2	H2	122.6
S1	C3	H3	124.3
C2	C3	S1	111.3(8)
C2	C3	H3	124.

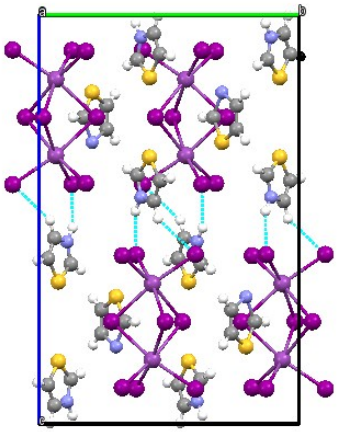

Figure S1. Short contacts in the unit cell of **$[TH]_3[Bi_2I_9]$**

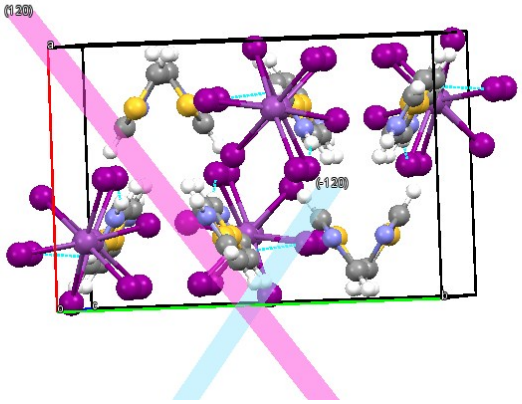

Figure S2. (1, 2, 0) and (-1, 2, 0) Miller Indices planes in the unit cell of **$[TH]_3[Bi_2I_9]$**

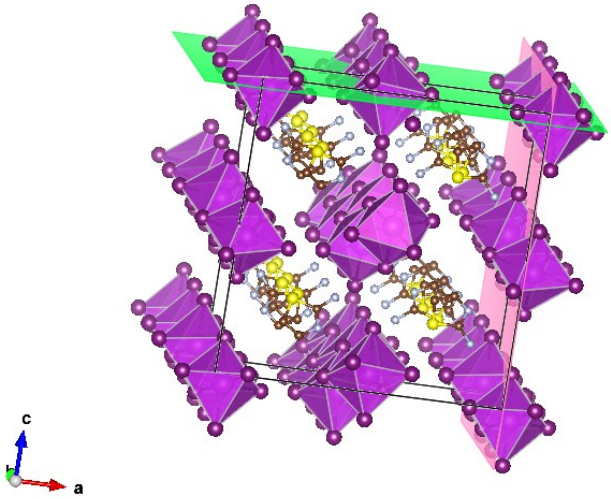

Figure S3. (0 0 2) and (2 2 0) planes 4in in the unit cell of **[AT][BiI$_4$]**

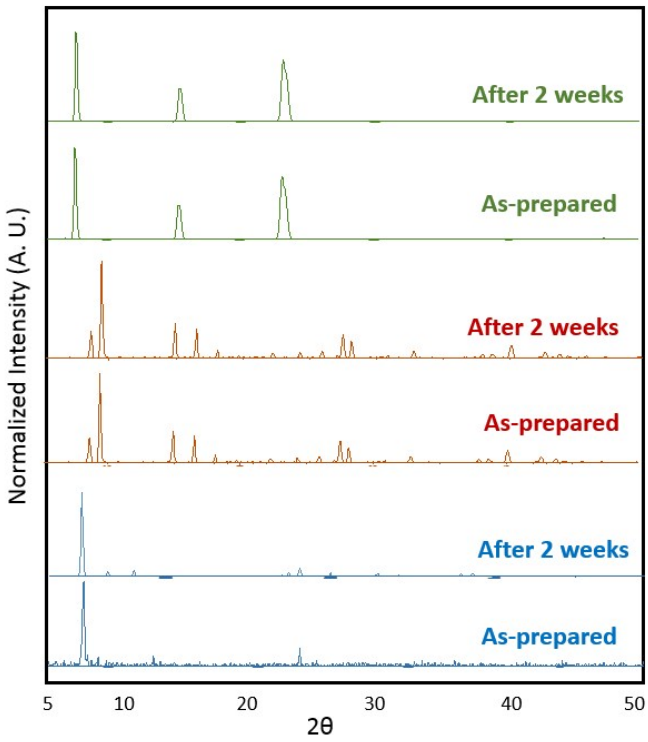

Figure S4. Powder XRD of three materials as thin films after two weeks exposure to air in dark.

Blue: **[TH]$_3$[Bi$_2$I$_9$]**; red: **[AT][BiI$_4$];** green: **[IM]$_3$[Bi$_2$I$_9$]**

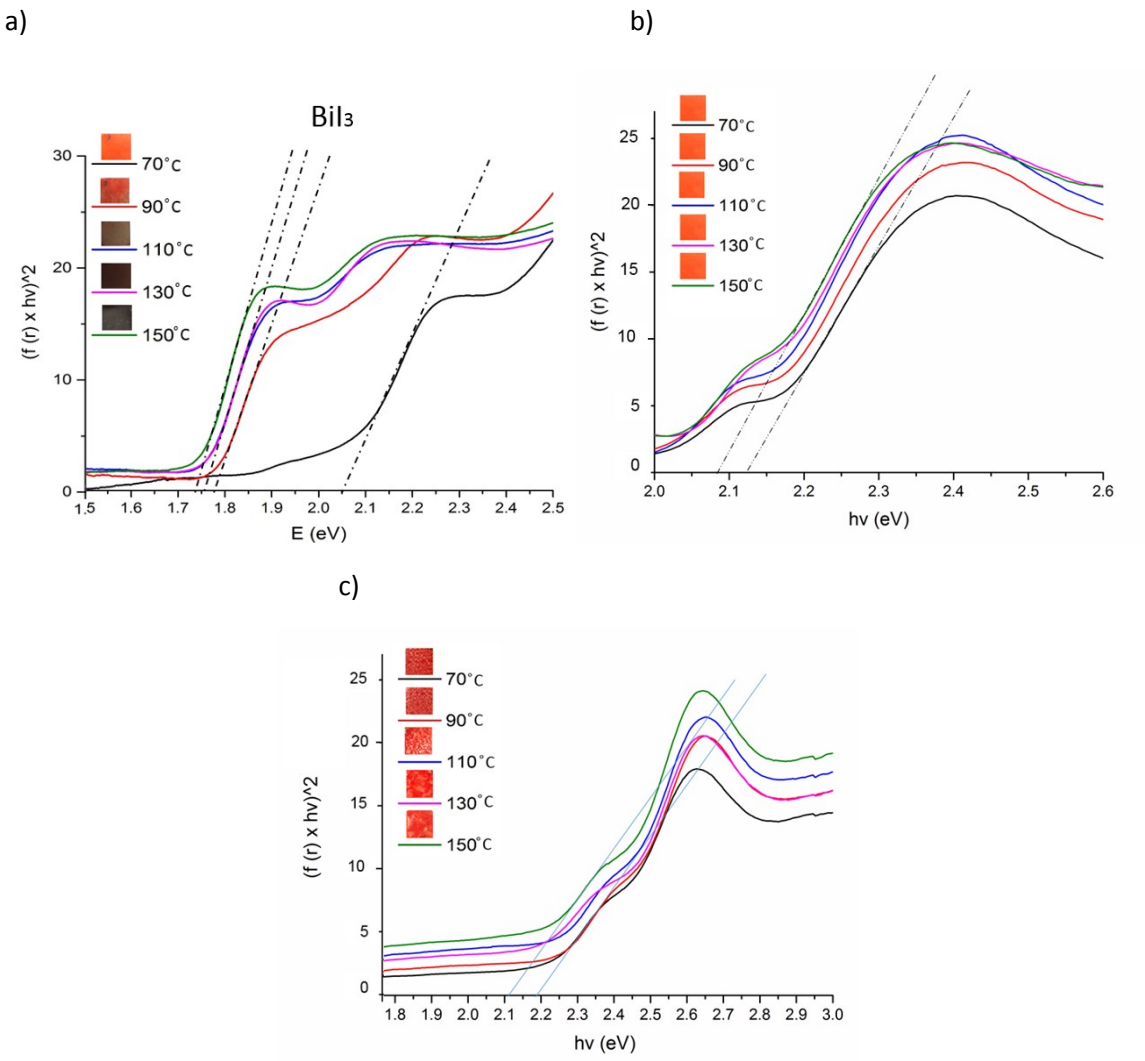

Figure S5. Tauc plots and band gap estimations of **$[TH]_3[Bi_2I_9]$** (a), **$[IM]_3[Bi_2I_9]$** (b), and **[AT] $[BiI_4]$** (c) thin films annealed at different temperatures. Coloured squares are pictures of the actual thin-films surface.

a) b)

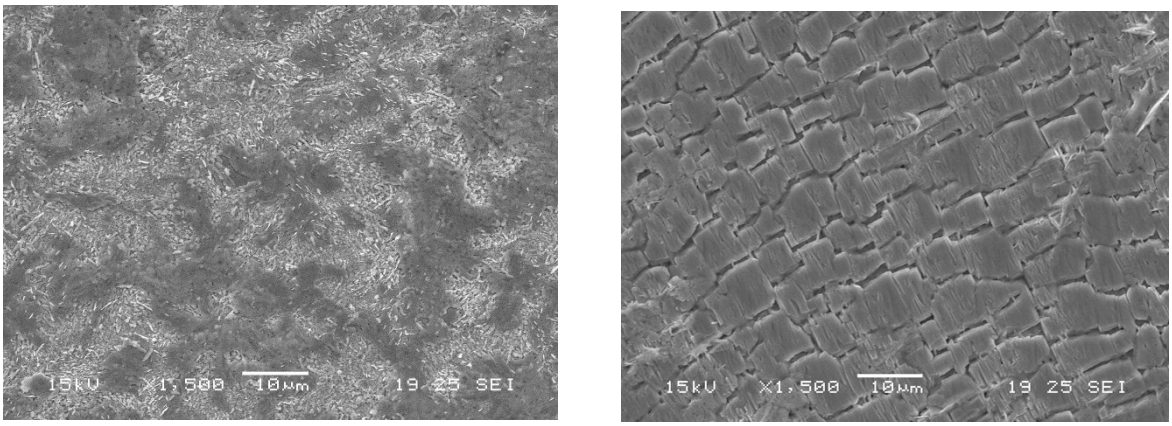

Figure S6. SEM image of THB (a) and ATB (b) as spin-coated on glass slide.

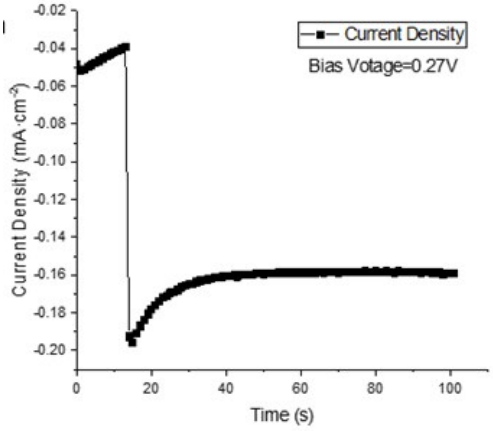

Figure S7. Stabilised current measurement of **[AT][BiI$_4$]** solar cell with forward scan bias voltage

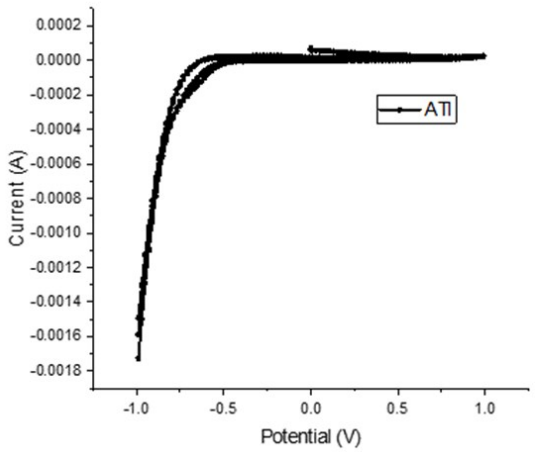

Figure S8. Cyclic voltammetry of a **[AT][BiI$_4$]** solar cell under dark.

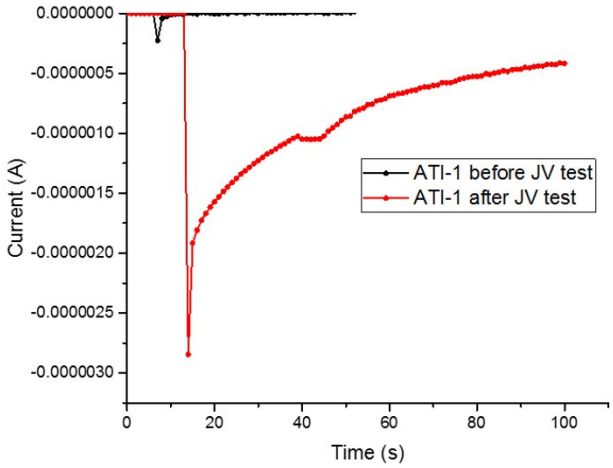

Figure S9. Short-circuit current test for **[AT][BiI$_4$]** devices without light