Electronic Supplementary Information for

Pseudo-three-dimensional Organic-inorganic Iodobismuthates as Lead-free Solar Absorbers

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Compounds	[py][BiI_4]	[mepy][BiI_4]
Formula	$C_5H_6BiI_4N$	$C_6H_8BiI_4N$
$D_{calc.}$/ g cm^{-3}	3.83	3.749
μ/mm^{-1}	21.656	20.836
Formula Weight	796.69	810.71
Colour	red	red
Shape	plate	block
Max Size/mm	0.28	0.09
Mid Size/mm	0.21	0.06
Min Size/mm	0.09	0.06
***T*/K**	150	120
Crystal System	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$
***a*/Å**	12.6997(3)	7.7618(5)
***b*/Å**	28.3198(6)	14.0412(8)
***c*/Å**	7.7160(2)	13.1959(8)
β/°	95.2880(10)	92.959(6)
V/Å^3	2763.27(11)	1436.24(15)
Z	8	4
Z'	2	1
Θ_{min}/°	1.438	2.901
Θ_{max}/°	28.313	30.967
Measured Refl.	9303	7443
Independent Refl.	9303	7443
Reflections Used	7345	5413
Parameters	200	112
Restraints	72	0
Largest Peak /Å	3.098	2.285
Deepest Hole /Å	-2.356	-1.785
GooF	1.102	0.924
wR_2 **(all data)**	0.1785	0.0784
wR_2	0.165	0.075
R_1 **(all data)**	0.0859	0.0659
R_1	0.0634	0.0427

Table S1. Crystallographic information for **[py][BiI_4]** and **[mepy][BiI_4]**

Crystallographic information for [py][BiI$_4$]

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **[py][BiI$_4$].** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Bi1	19924.7(7)	5444.3(3)	17491.0(12)	19.4(2)
I1	18404.3(15)	6110.8(7)	15854(3)	40.2(5)
I2	21390.6(13)	5438.7(5)	14441(2)	24.5(4)
I3	21427.3(13)	4623.7(6)	19442(2)	26.5(4)
I4	21307.8(16)	6171.8(7)	19080(3)	39.8(5)
Bi2	14999.9(7)	7046.8(3)	11932.2(13)	20.5(2)
I5	16384.3(14)	7114.5(6)	15414(2)	29.0(4)
I6	13598.1(13)	7089.4(5)	8402(2)	25.2(4)
I7	16479.1(15)	6348.0(6)	10825(3)	35.1(4)
I8	13579.2(14)	6330.0(6)	13170(3)	31.3(4)
N1	20480(30)	6654(11)	13190(40)	61(7)
C1	21030(40)	7038(13)	13880(70)	72(11)
C2	20600(30)	7455(14)	13670(60)	67(10)
C3	19630(30)	7528(14)	12910(60)	61(9)
C4	19060(30)	7141(11)	12190(60)	61(9)
C5	19540(30)	6697(12)	12390(50)	53(7)
C10	24340(50)	5813(19)	17460(50)	95(11)
C9	23890(50)	5464(18)	17990(70)	103(12)
C8	24270(50)	5053(19)	17850(60)	98(12)
C7	25320(50)	5020(20)	17430(60)	97(12)
C6	25880(50)	5367(19)	16940(60)	103(12)
N2	25360(40)	5794(15)	16940(40)	96(10)

TableS3. Bond Lengths in Å for **[py][BiI$_4$]**

Atom	Atom	Length/Å	I5	Bi2[4]	3.2379(18)
Bi1	I1	2.9047(19)	I6	Bi2[3]	3.2878(18)
Bi1	I2	3.1326(19)	N1	C1	1.37(5)
Bi1	I2[1]	3.2872(17)	N1	C5	1.31(5)
Bi1	I3	3.2830(18)	C1	C2	1.30(5)
Bi1	I3[2]	3.0556(19)	C2	C3	1.33(6)
Bi1	I4	2.904(2)	C3	C4	1.40(5)
I2	Bi1[1]	3.2873(17)	C4	C5	1.40(5)
I3	Bi1[2]	3.0556(19)	C10	C9	1.23(7)
Bi2	I5[3]	3.2379(19)	C10	N2	1.39(7)
Bi2	I5	3.078(2)	C9	C8	1.27(7)
Bi2	I6	3.116(2)	C8	C7	1.40(8)
Bi2	I6[4]	3.2877(18)	C7	C6	1.30(7)
Bi2	I7	2.9105(19)	C6	N2	1.38(7)
Bi2	I8	2.9338(19)			

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[1]4-X,1-Y,3-Z; [2]4-X,1-Y,4-Z; [3]+X,3/2-Y,-1/2+Z

[4]+X,3/2-Y,1/2+Z

Table A3. Bond Angles in ° for **[py][BiI$_4$]**

Atom	Atom	Atom	Angle/°
I1	Bi1	I2^{1}	90.43(6)
I1	Bi1	I2	95.38(6)
I1	Bi1	I3	173.92(6)
I1	Bi1	I3^{2}	88.82(6)
I2	Bi1	I2^{1}	88.16(5)
I2	Bi1	I3	88.87(5)
I3^{2}	Bi1	I2	175.53(5)
I3	Bi1	I2^{1}	85.35(5)
I3^{2}	Bi1	I2^{1}	90.28(5)
I3^{2}	Bi1	I3	86.83(5)
I4	Bi1	I1	94.27(7)
I4	Bi1	I2^{1}	173.34(6)
I4	Bi1	I2	86.70(6)
I4	Bi1	I3^{2}	94.53(6)
I4	Bi1	I3	90.30(6)
Bi1	I2	Bi1^{1}	91.84(5)
Bi1^{2}	I3	Bi1	93.17(5)
I5	Bi2	I5^{3}	89.12(5)
I5	Bi2	I6	174.21(5)
I5	Bi2	I6^{4}	86.36(5)
I5^{3}	Bi2	I6^{4}	84.75(5)
I6	Bi2	I5^{3}	86.60(5)
I6	Bi2	I6^{4}	89.36(5)
I7	Bi2	I5	88.07(6)
I7	Bi2	I5^{3}	90.34(6)
I7	Bi2	I6^{4}	172.62(6)
I7	Bi2	I6	95.85(6)
I7	Bi2	I8	93.32(6)
I8	Bi2	I5^{3}	174.96(6)
I8	Bi2	I5	94.47(6)
I8	Bi2	I6	89.57(5)
I8	Bi2	I6^{4}	91.93(5)
Bi2	I5	Bi2^{4}	94.36(5)
Bi2	I6	Bi2^{3}	92.66(5)
C5	N1	C1	121(3)
C2	C1	N1	119(5)
C1	C2	C3	124(4)
C2	C3	C4	119(4)
C5	C4	C3	117(4)
N1	C5	C4	120(4)
C9	C10	N2	122(6)
C10	C9	C8	121(8)
C9	C8	C7	117(6)
C6	C7	C8	125(6)
C7	C6	N2	112(7)
C6	N2	C10	120(5)

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^{1}4-X,1-Y,3-Z; ^{2}4-X,1-Y,4-Z; ^{3}+X,3/2-Y,-1/2+Z; ^{4}+X,3/2-Y,1/2+Z

Crystallographic information for [mepy][BiI_4]

Table A4, Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for [mepy][BiI_4]. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

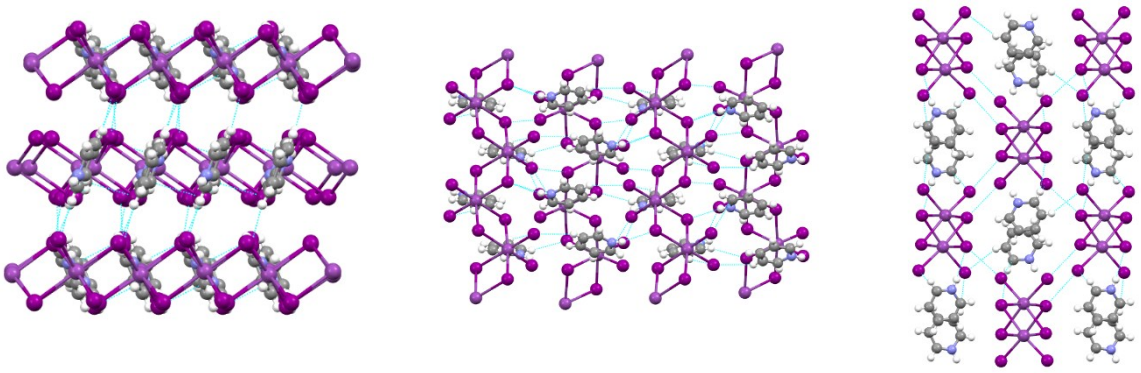
Atom	x	y	z	U_{eq}
Bi1	2494.0(6)	4100.8(3)	5094.0(3)	10.74(10)
I1	4115.6(9)	2786.6(5)	6557.2(5)	15.60(17)
I2	-597.8(9)	4340.5(4)	6471.4(5)	14.22(16)
I3	896.4(9)	2551.0(5)	3907.8(5)	16.30(16)
I4	5633.0(8)	4099.2(5)	3726.0(5)	13.81(16)
N1	7953(11)	1068(6)	5658(7)	17(2)
C1	7999(14)	126(7)	5554(8)	20(3)
C2	7264(15)	-287(8)	4714(9)	25(3)
C3	6529(16)	272(8)	3954(9)	29(3)
C4	6493(15)	1242(9)	4071(9)	27(3)
C5	7206(12)	1637(7)	4956(8)	14(2)
C6	8855(14)	1510(7)	6568(8)	19(2)

Table A5: Bond Lengths in Å for **[mepy][BiI_4]**

Atom	Atom	Length/Å
Bi1	I1	2.9098(8)
Bi1	I2	3.1027(9)
Bi1	$I2^1$	3.3029(7)
Bi1	I3	2.9195(8)
Bi1	I4	3.1063(8)
Bi1	$I4^2$	3.2699(7)
I2	$Bi1^1$	3.3029(7)
I4	$Bi1^2$	3.2699(7)
N1	C1	1.330(12)
N1	C5	1.332(13)
N1	C6	1.494(13)
C1	C2	1.352(15)
C2	C3	1.374(17)
C3	C4	1.372(17)
C4	C5	1.382(15)

Table A6: Bond Angles in ° for **[mepy][BiI_4].**

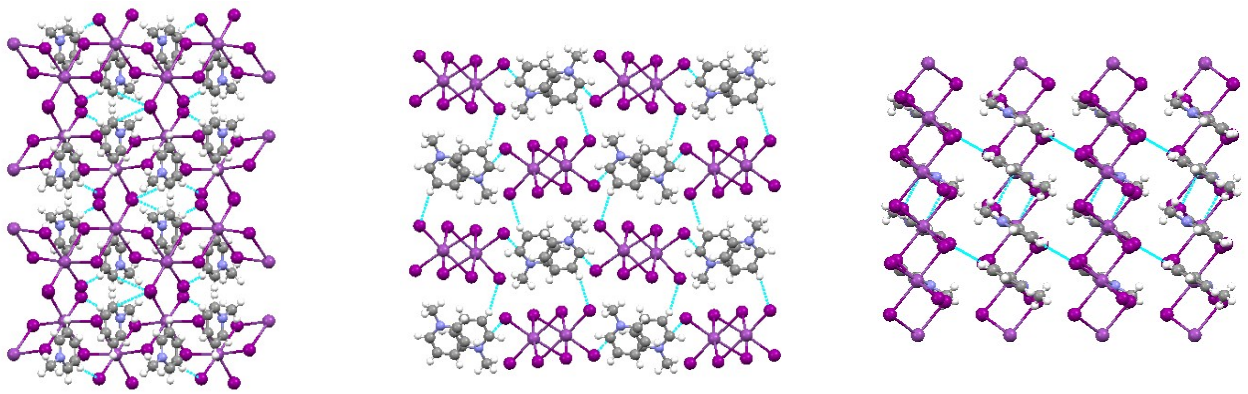
Atom	Atom	Atom	Angle/°
I1	Bi1	I2	90.07(2)
I1	Bi1	$I2^1$	177.14(2)
I1	Bi1	I3	92.31(2)
I1	Bi1	I4	93.43(2)
I1	Bi1	$I4^2$	90.44(2)
I2	Bi1	$I2^1$	87.79(2)
I2	Bi1	$I4^2$	88.60(2)
I2	Bi1	I4	173.79(2)
I3	Bi1	I2	94.30(2)
I3	Bi1	$I2^1$	89.74(2)
I3	Bi1	$I4^2$	176.00(2)
I3	Bi1	I4	90.69(2)
$I4^2$	Bi1	$I2^1$	87.620(19)
I4	Bi1	$I2^1$	88.54(2)
I4	Bi1	$I4^2$	86.25(2)
Bi1	I2	$Bi1^1$	92.21(2)
Bi1	I4	$Bi1^2$	93.75(2)
C1	N1	C5	122.5(9)
C1	N1	C6	118.8(9)
C5	N1	C6	118.6(8)
N1	C1	C2	120.0(10)
C1	C2	C3	119.6(10)
C4	C3	C2	119.7(11)
C3	C4	C5	118.9(11)
N1	C5	C4	119.2(10)



a. Short contacts looking into **b** axis

b. S **c**. Short contacts looking into **c** axis

Figure S1. Short contacts of **[py][BiI$_4$]** (shown in cyan dashed line) looking into different directions



a. Short contacts looking along **c** axis

b. Short contacts looking along **a** axis

c. Short contacts looking along **b** axis

Figure S2. Short contacts of **[mepy][BiI$_4$]** (shown in cyan dashed line) looking into different directions

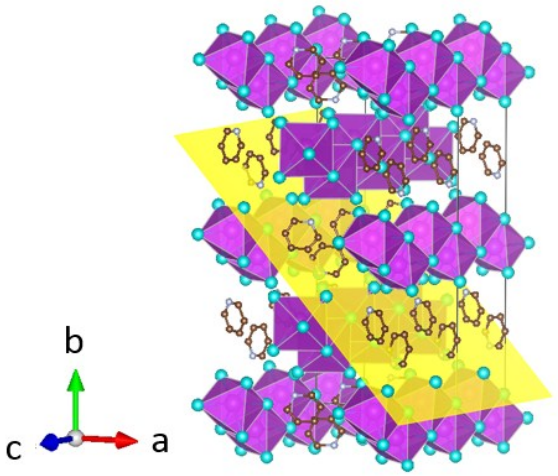


Figure S3. Strong preferred orientation on (1 2 0) plane for **[py][BiI$_4$]**

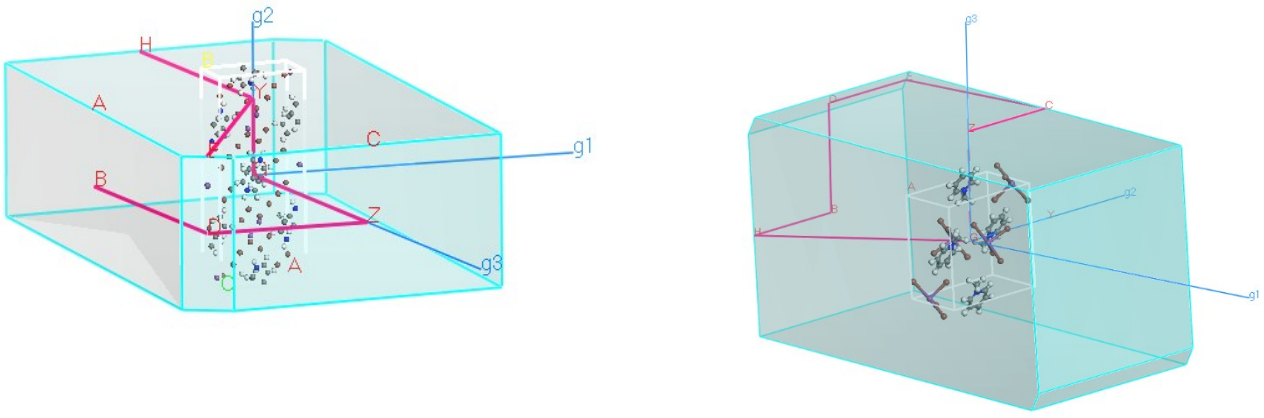


Figure S4. K-point path on the first Brillouin zone for **[py][BiI$_4$]** (left) and **[mepy][BiI$_4$]** (right)

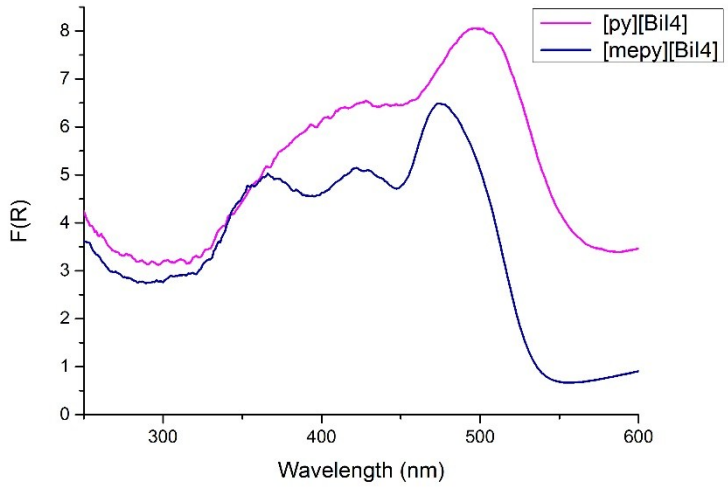


Figure S5. Kubelka-Munk function plots from diffuse reflectance measurements for compounds spin-coated on glass slides

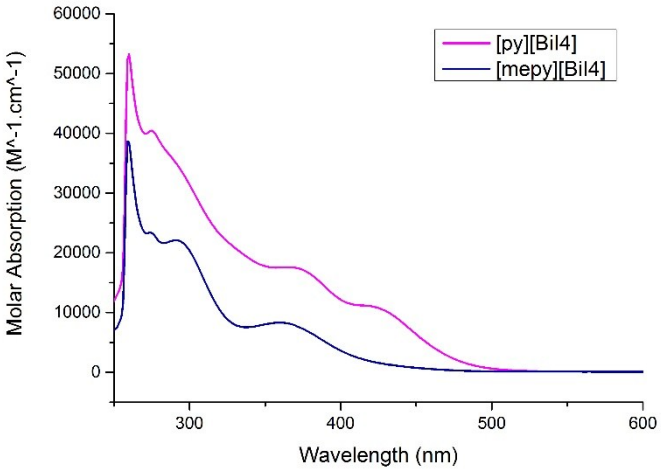


Figure S6. Solution-state UV-Vis absorption spectra for compounds dissolved in DMF

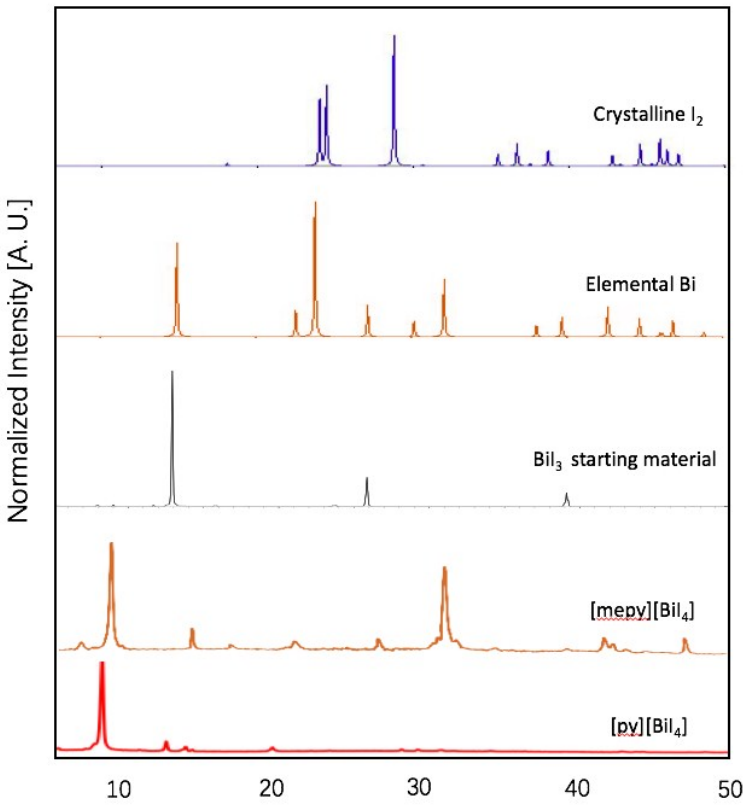


Figure S7. XRD patterns of **[py][BiI_4]**, **[mepy][BiI_4]**, BiI_3 starting materials, elemental Bi and crystalline I_2

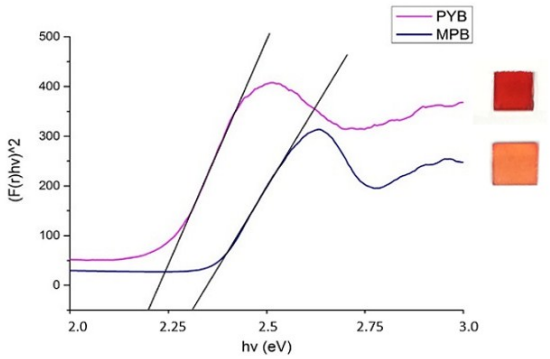
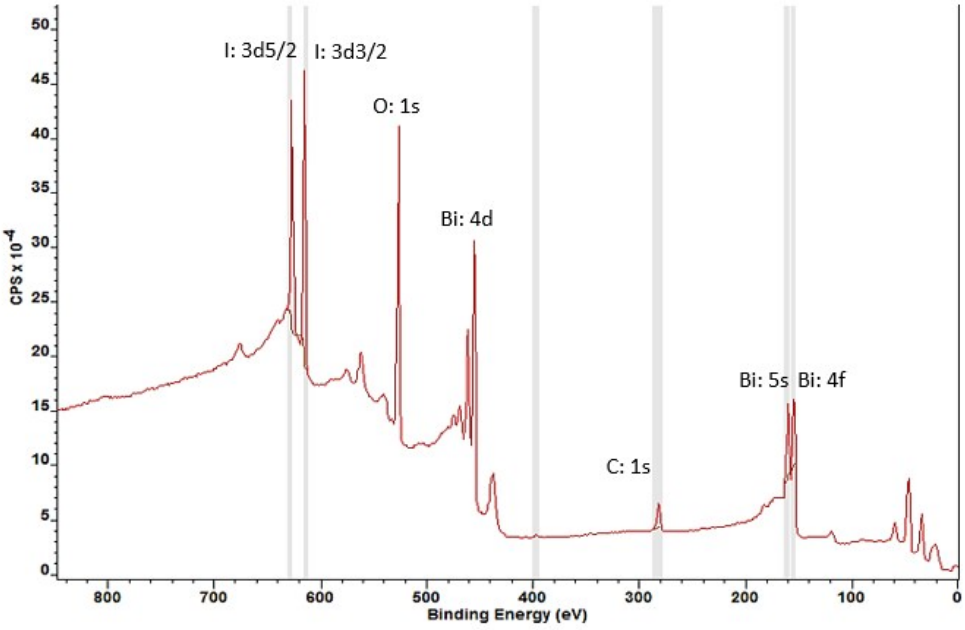


Figure S8. Tauc plots and bandgap value estimations of thin-film samples. Measured bandgap for **[py][BiI_4]** and **[mepy][BiI_4]** are 2.19 eV and 2.30 eV, respectively. Coloured squares on the right are cropped photos of the two compounds to illustrate their appearance.



Name	Position	Area/(RSF*T*MFP)	%At Conc
I 5p	615.00	64322	78.39
Bi 4f	160.00	14441.1	17.60
C 2p	282.00	3295.78	4.02
N 2p	1486.69	0	0.00

Figure S9. XPS survey spectrum and elemental composition for **[py][BiI$_4$]** thin film**.**

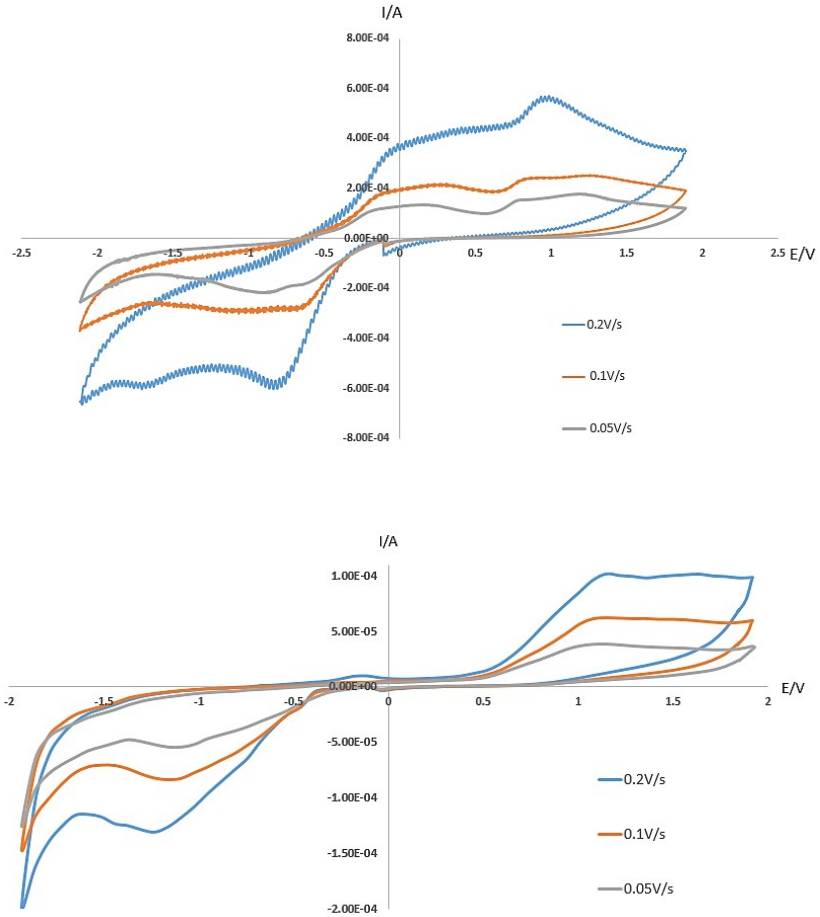


Figure S10. Cyclic voltammetry obtained from spin-coated thin films on conducting glasses of **[py][BiI$_4$]** (top) and **[mepy][BiI$_4$]** (bottom) at different scan rates.

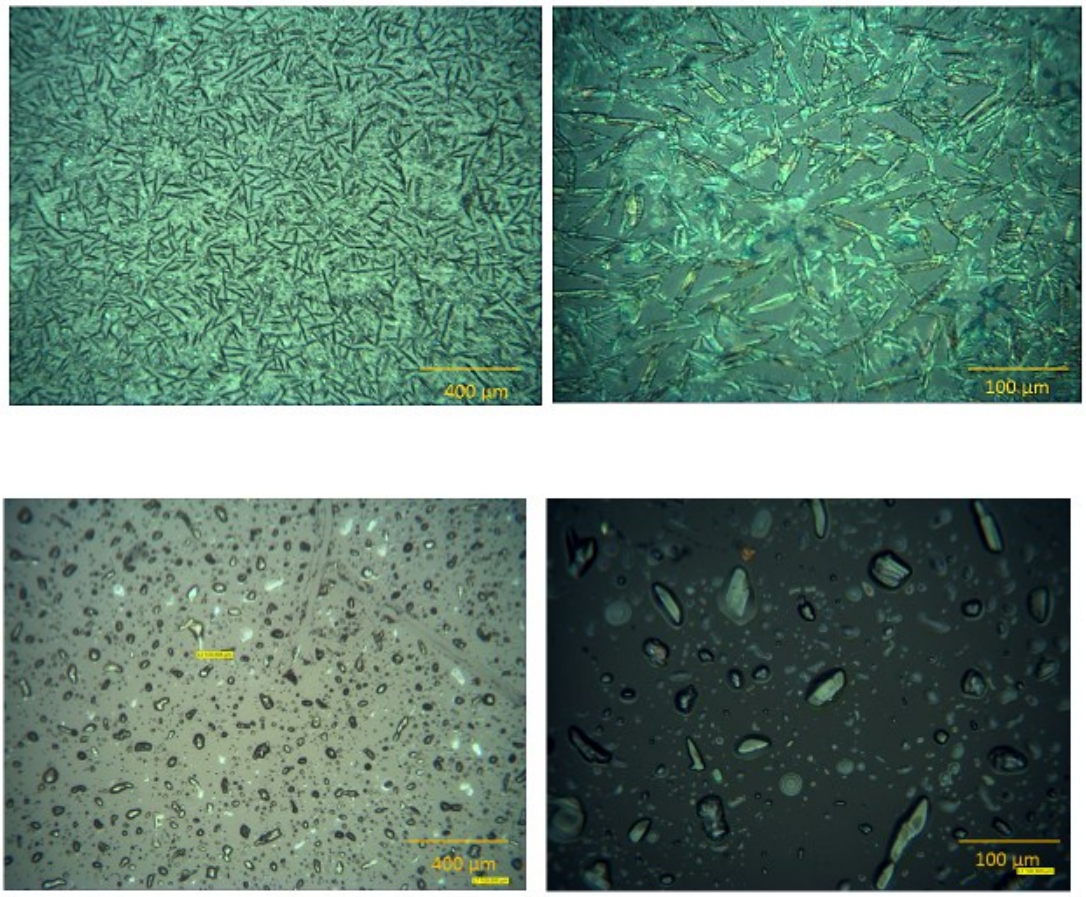


Figure S11. Microscopic images of **[py][BiI_4]** (top) and **[mepy][BiI_4]** (bottom) on blocking layer of TiO_2, with 100 times (left) and 400 times (right) magnifications.

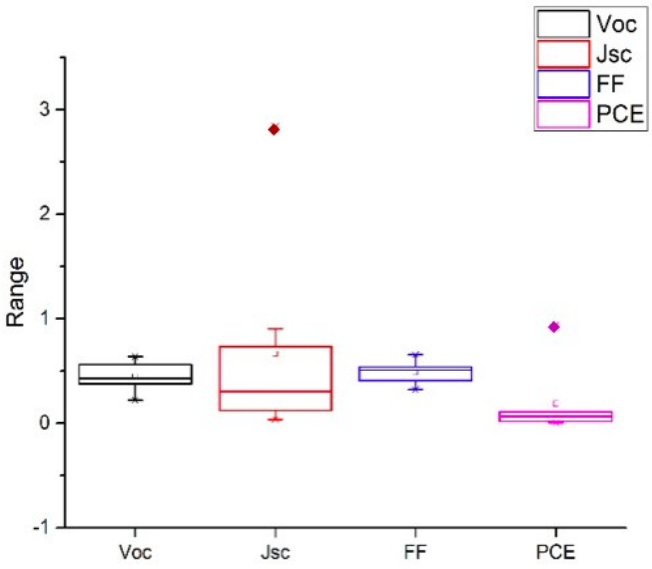


Figure S12. Box diagram of **[py][BiI$_4$]** solar cell parameters

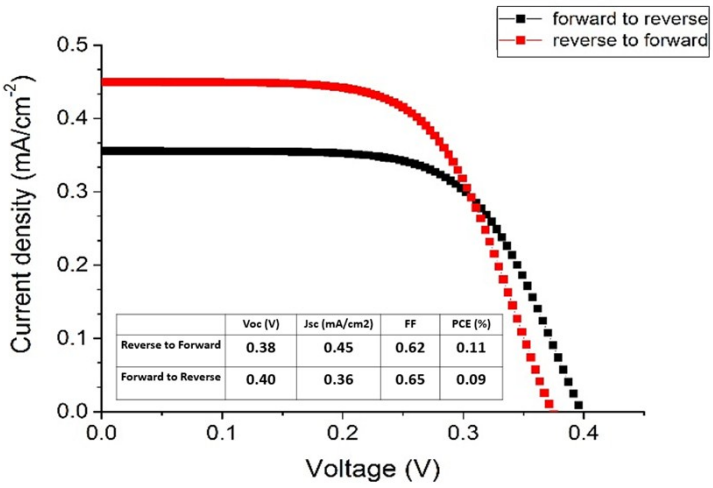


Figure S13. J-V curve of an **[py][BiI$_4$]** solar cell

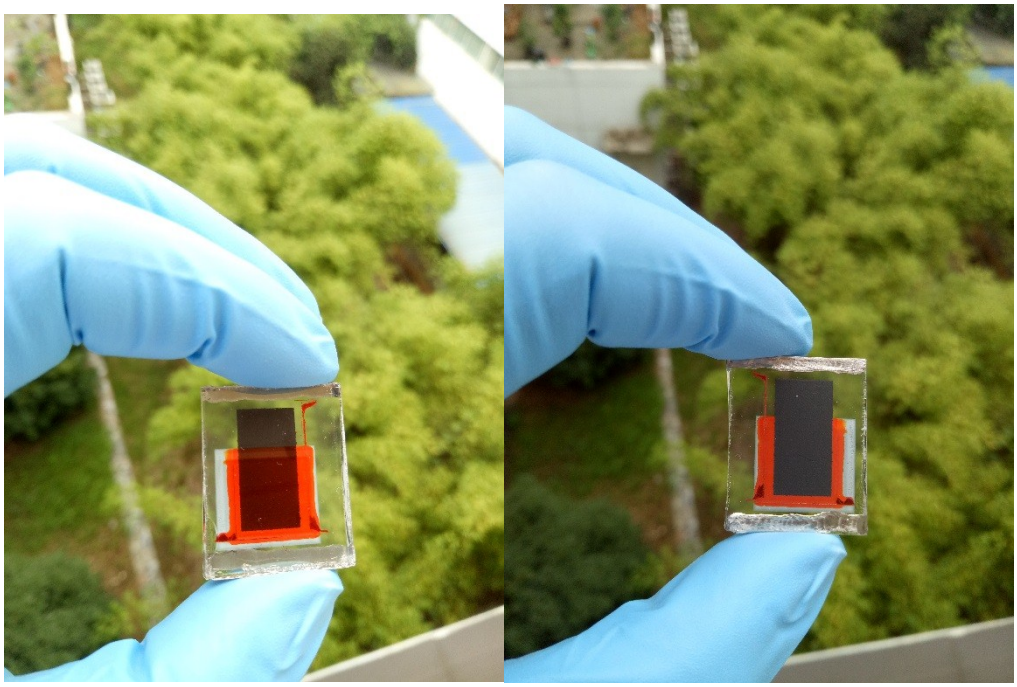


Figure S14. Solar cell devices made of **[py][BiI$_4$].** (Left: bottom; right: top)