Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Optoelectronic and Photovoltaic Properties of the Air-Stable Organohalide Semiconductor $(CH_3NH_3)_3Bi_2I_9$

(Supporting Information)

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Crystallographic data

[Data collection: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.31; cell refinement: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.31; data reduction: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.31; software used to prepare material for publication: VESTA: {Momma, 2011 #544}

$(CH_3NH_3)_3Bi_2I_9$	a[Å]	c [Å]	d [nm]
Single crystal	8.582	21.767	≈ 2 x 10^5
Powder	8.575	21.747	205
Film 1	8.571	21.739	148
Film 2	8.571	21.741	154

Table S1: Hexagonal unit cell parameters and crystallite sizes of $(CH_3NH_3)_3Bi_2I_9$ crystals as single crystal, powder or thin film.

CCDC 1483450 contains the supplementary crystallographic data for the compound $(CH_3NH_3)_3Bi_2I_9$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; or email: deposit@ccdc.cam.ac.uk.

Space Charged Limited Current Measurements

Current-Voltage characteristics followed the symmetric nonlinear quadratic dependency complying the Lampert's theory of current injection in solids. The linear plot ($I \alpha V^{n=1}$) in the lower voltage regime followed ohmic behavior where the bulk carrier density exceeds the electrode injection. At a particular onset voltage in the higher bias regime, the conduction is governed by the traps ($I \alpha V^{n>3}$) known as trap filled limit (TFL). The density of traps (n_{traps}) in the perovskite crystals is estimated from the relation (1).

$$n_{Traps} = \frac{2\varepsilon\varepsilon_o V_{TFL}}{qL^2} \qquad (1)$$

Where L is the thickness of the crystal, ε is the dielectric constant of the material (~46 for MAIB) [1] and ε_o being the vacuum permittivity, and q is the electronic charge. At the higher bias, the TFL moves to the child's law ($I \alpha V^{n=2}$). Hence, we observe a clear transition from Ohm's to child's law through the TFL. The mobilities can be extracted from the child regime following the Mott-Gurney relation (2).

$$\mu = \frac{8JL^3}{9\varepsilon\varepsilon_o V^2} \qquad (2)$$

Where L is the thickness of the crystal. The carrier concentration in the doped crystals was estimated from the relation (3).

$$n_c = \frac{\sigma}{q\mu} \qquad (3)$$

Where n_c is the carrier concentration and σ is the conductivity.

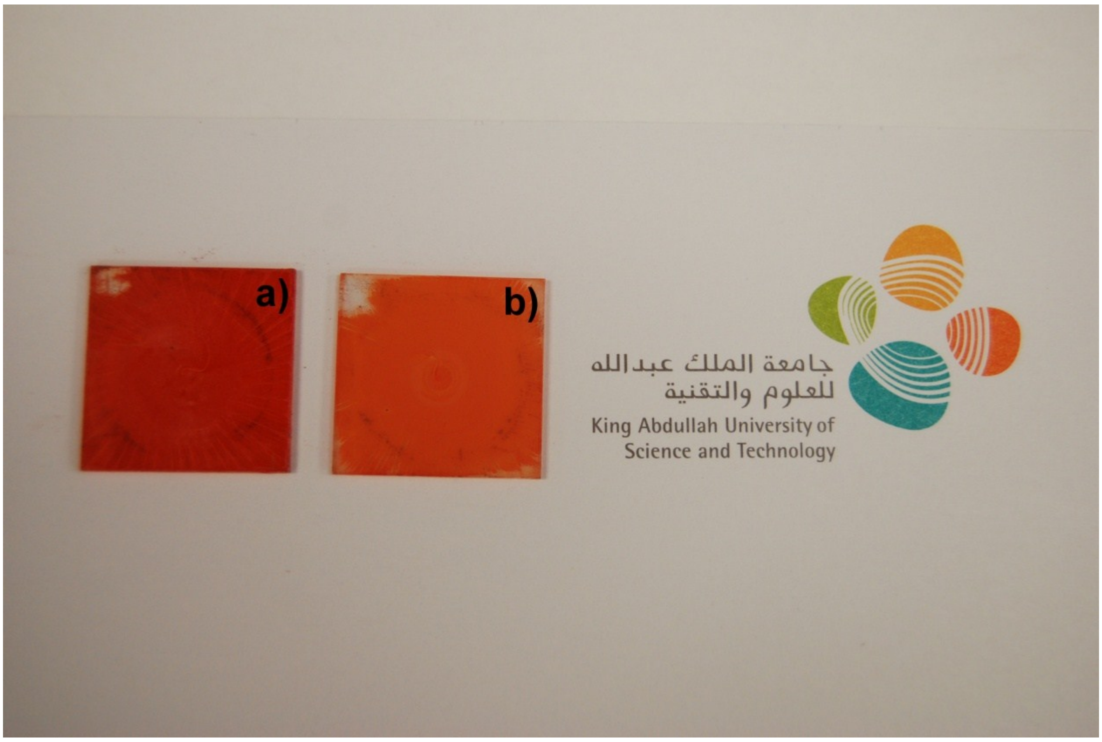

Figure S1: $(CH_3NH_3)_3Bi_2I_9$ thin films deposited on ITO by ASAC method a) from GBL/DMSO solvent mixture b) from GBL.

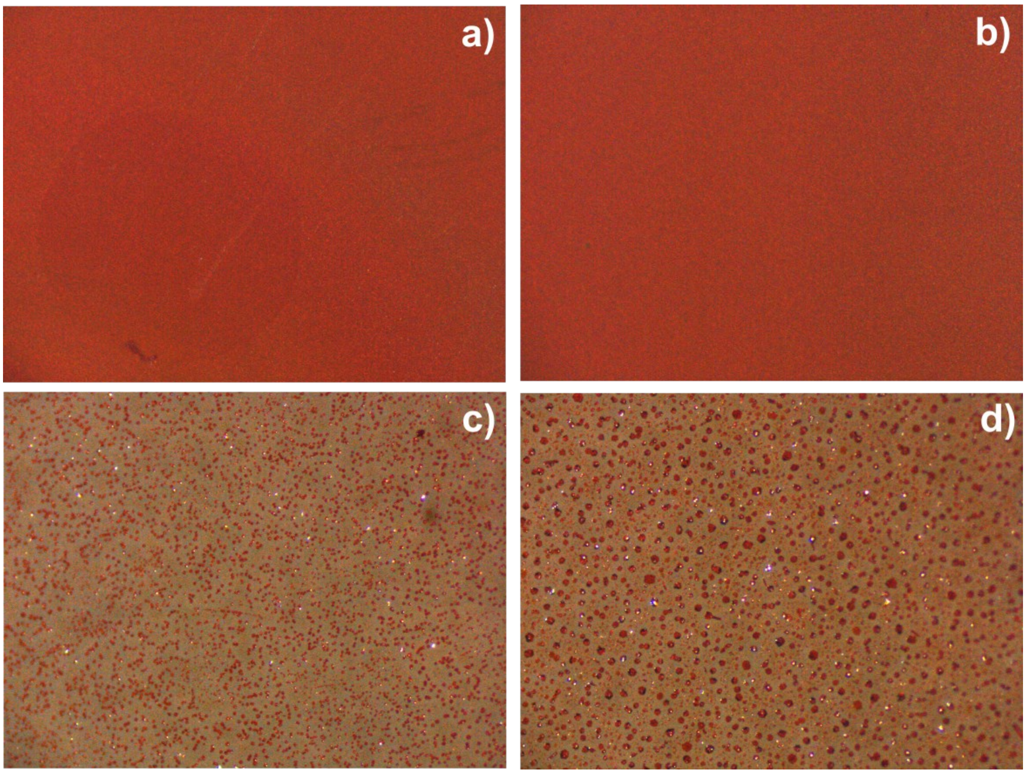

Figure S2: Microscope images of $(CH_3NH_3)_3Bi_2I_9$ incomplete devices cast by spin coating using different solvent and crystallization procedures. a) GBL, SASC b) GBL/DMSO 7:3 V/V, ASAC c) GBL, SVC d) GBL/DMSO 7:3 V/V SVC.

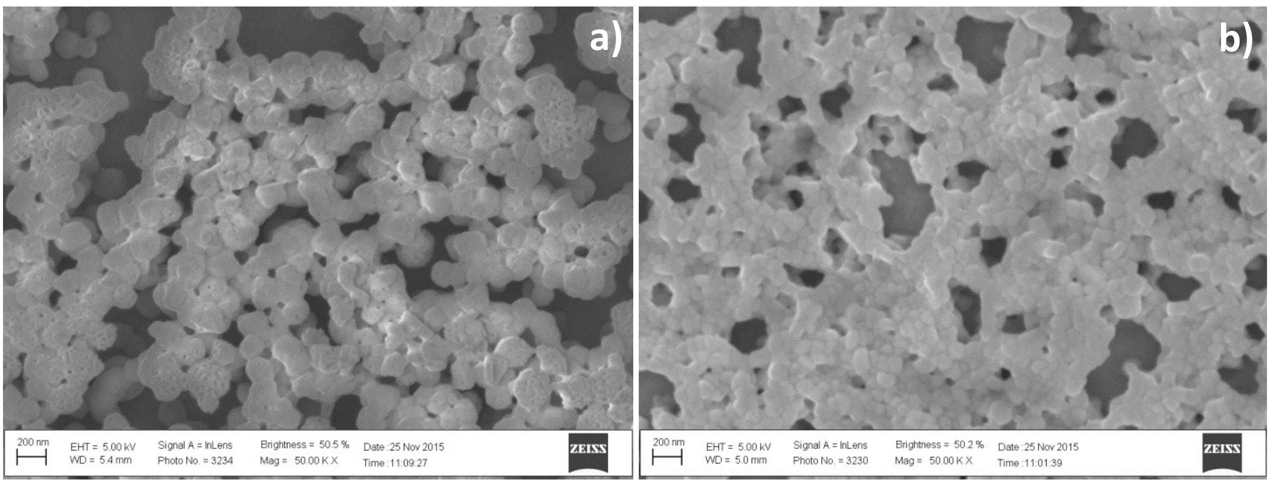

Figure S3: SEM images of $(CH_3NH_3)_3Bi_2I_9$ deposited by spin coating from a solution in GBL (a) and GBL/DMSO (b) mixture using the ASAC method.

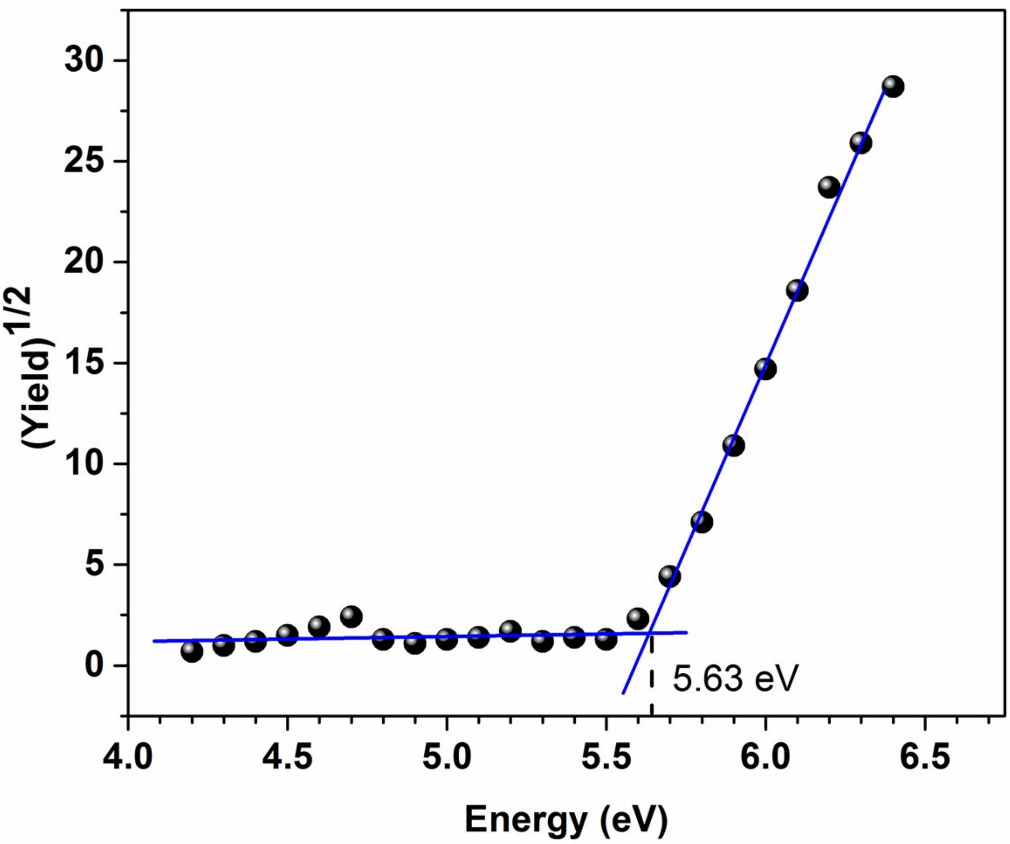

Figure S4: PESA spectrum of $(CH_3NH_3)_3Bi_2I_9$ deposited on ITO substrate (500 nm). The onset was determined from the intersection of linear regression of baseline and slope. The onset provides directly the valence band edge of the material.

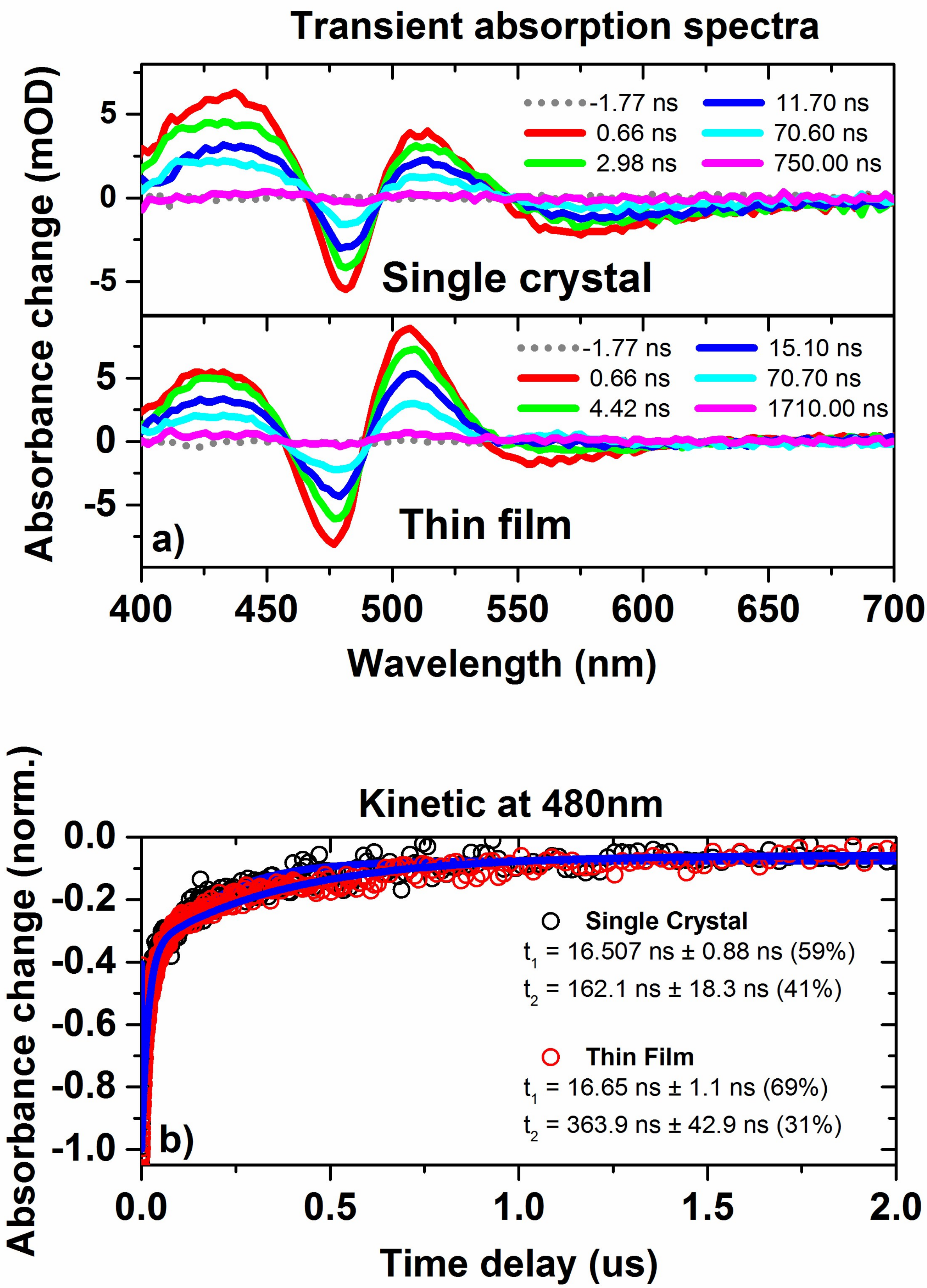

Figure S5: a) Transient absorption spectra of single crystal and thin film acquired at six time delays. **b)** Kinetic traces derived from transient absorption spectra at 480 nm for single crystal and thin film. The signal is reported as normalized absorbance change.

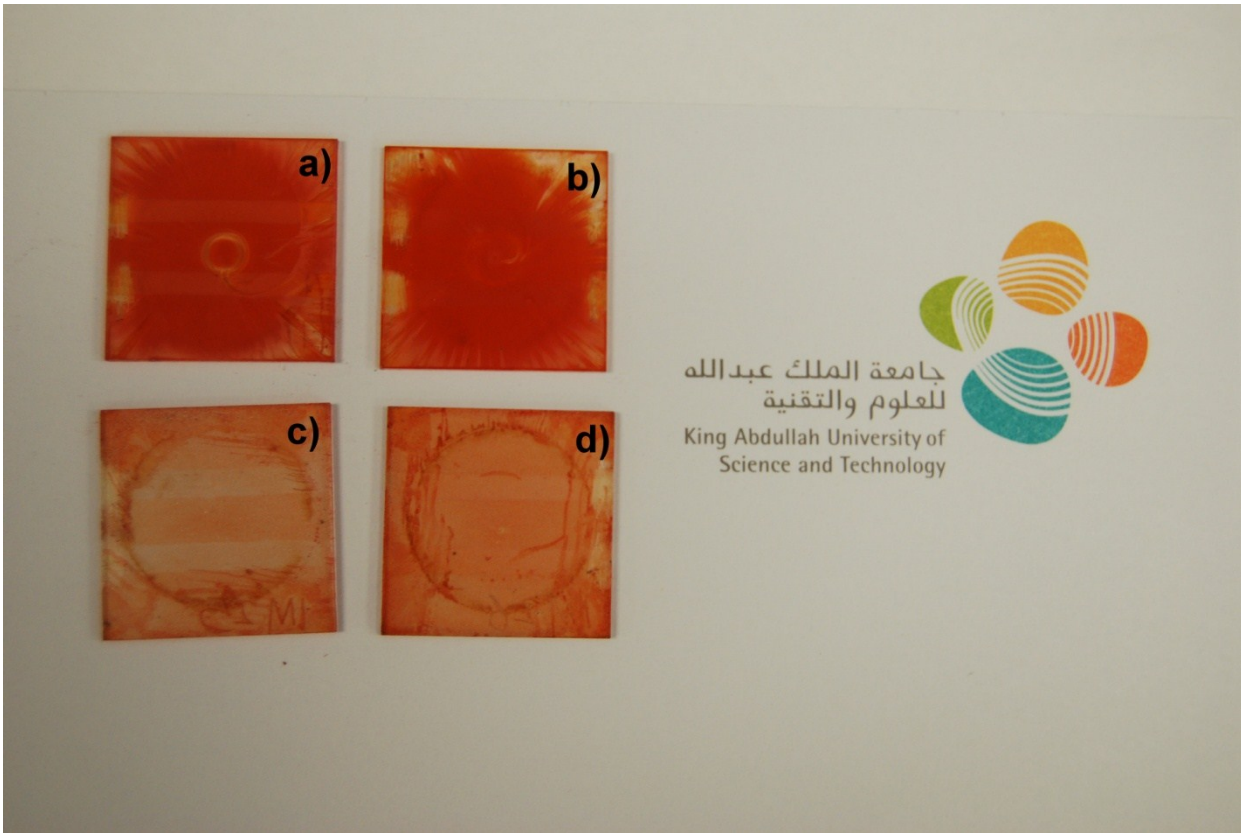

Figure S6: $(CH_3NH_3)_3Bi_2I_9$-based incomplete devices. The active layer was deposited by ASAC route (a and b) and by SVC route (c,d) yet using two different solvent systems; a,c GBL/DMSO and b,d GBL.

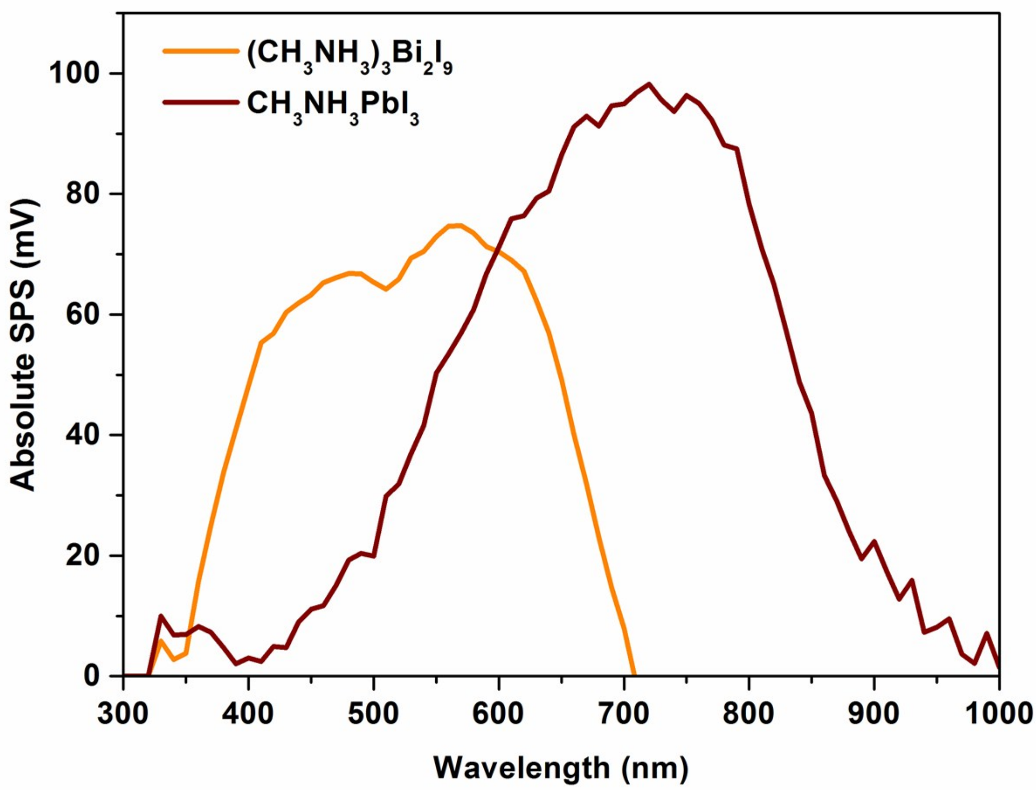

Figure S7: Absolute SPS spectra of $(CH_3NH_3)_3Bi_2I_9$ and of $CH_3NH_3PbI_3$ deposited on ITO substrates. With absolute one means that the value of work function in dark conditions has been subtracted to the raw SPS signal.

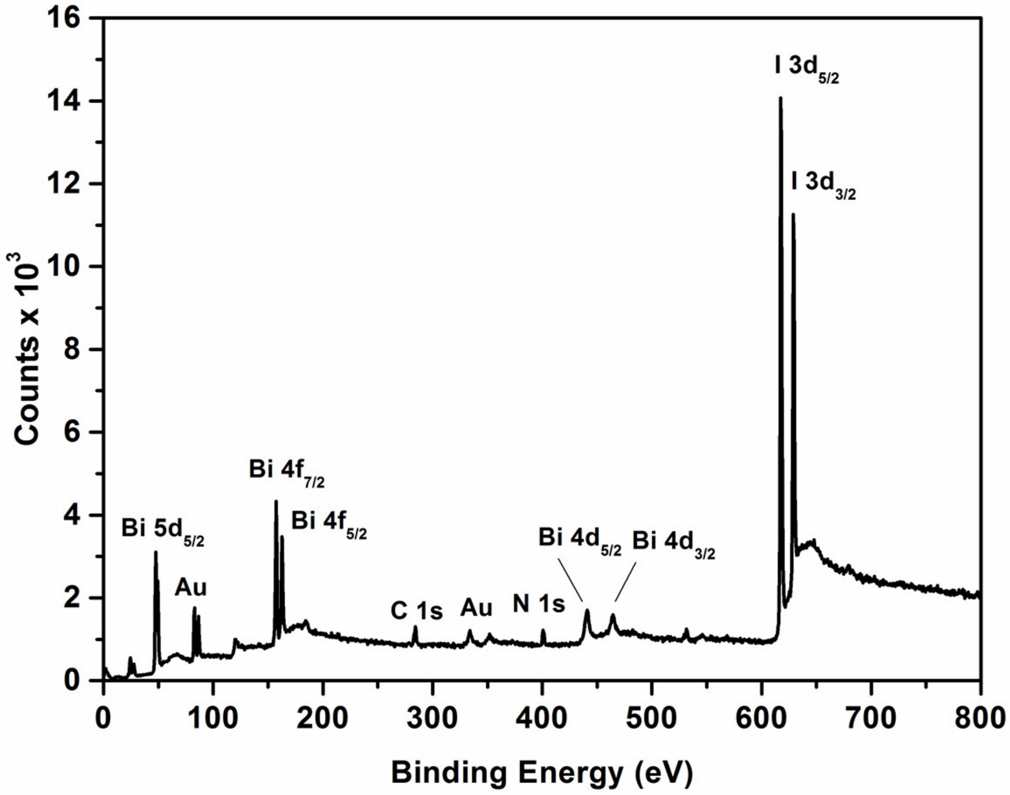

Figure S8: XPS spectrum of $(CH_3NH_3)_3Bi_2I_9$ deposited on Au substrate (30 nm).

References

1 Kawai, T. *et al.* Optical absorption in band-edge region of $(CH_3NH_3)_3Bi_2I_9$ single crystals. *Journal of the Physical Society of Japan* **65**, 1464-1468, doi:Doi 10.1143/Jpsj.65.1464 (1996).