

Supporting Information for:

Possibilities and limitations of $\text{CsBi}_3\text{I}_{10}$ as photovoltaic material

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EXPERIMENTAL DETAILS

Materials

Caesium iodide (CsI , >99%) was obtained from TCI. Bismuth (III) iodide (BiI_3 , $\geq 99.998\%$), fullerene (C_{60}) and chlorobenzene (99.8%, anhydrous) were purchased from Sigma Aldrich. Poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (poly-TPD) was purchased from ADS Dyesource. N4,N4',N4'-tetra([1,1'-biphenyl]-4-yl)-[1,1':4',1'-terphenyl]-4,4'-diamine (TaTm) was provided by Novald GmbH. Molybdenum (VI) oxide (MoO_3) and bathocuproine (BCP) were purchased from Lumtec. Tin (IV) oxide (SnO_2 , 15% in H_2O colloidal dispersion) was provided by Alfa Aesar. All chemicals were stored in a nitrogen-filled glovebox and used without further purification. Photolithographically patterned ITO coated glass substrates were purchased from Naranjo Substrates.

Mechanochemical Synthesis

Stoichiometric amounts of $\text{CsI}:\text{BiI}_3$ powders were weighted to the desired stoichiometry and mixed in a nitrogen-filled glovebox. Then, the precursors powders introduced under nitrogen in 10 mL zirconia jars with two zirconia beads of 10 mm in diameter, both from Retsch. Ball milling was performed with an MM-400 straight ball mill from Retsch at a frequency of 30 Hz for 90 minutes.

XRD characterization

X-ray diffraction scans were measured with a powder diffractometer model D8 Avance A25 Bruker brand equipped with $\text{CuK}\alpha$ anode. Single measurements were acquired with a range of $2\theta = 10^\circ$ to 50° and a step size of $2\theta = 0.025^\circ$, in Bragg-Brentano geometry in air.

Thermal characterization

Thermogravimetric analysis were performed with a TA Discovery TGA550 (TA Instruments) equipped with a continuous flow of nitrogen. Measurements were carried out with a ramp of $10^\circ\text{C}/\text{min}$ from room temperature to 600°C .

$\text{CsI}:\text{BiI}_3$ thermal co-deposition

Deposition and characterization of the thin films were carried out inside a clean-room ISO 7 10000. Glass substrates underwent an extensive cleaning procedure using subsequent sonication in water with soap,

deionized water and 2-propanol baths. Then, they were dried with an N₂ flow and placed in a UV Ozone cleaner for 15 minutes.

CsBi₃I₁₀ thin films were prepared by dual source vacuum deposition by co-deposition of the two precursors CsI and BiI₃ onto the aforementioned substrates. To obtain a 210 nm-thick film of CsBi₃I₁₀, the deposition parameters were as follows:

	Rate (Å/s)	Temperature (°C)	Set final thickness (nm)	Chamber pressure (mbar)
CsI	0.4	408	58	10 ⁻⁶
BiI ₃	1.3	191	180	

The thermal evaporator was placed in air, outside a glovebox. This fact made the calibration of the deposition rate for both reagents difficult, due to their high hygroscopicity. For this reason, we believe the temperatures and pressure are more reliable parameters in order to obtain reproducible results than the deposition rates and set thicknesses.

Optical characterization

UV-visible absorption spectra of the films and powders were collected using an integrating sphere coupled to an Avantes Avaspec-2048L optical detector (Avantes BV). Photoluminescence for powders was measured with a continuous wave 522 nm laser diode with a 550 nm coloured glass filter (Thorlabs Inc.) and an Avantes Avaspec-2048L optical detector (Avantes BV), inside a nitrogen-filled glovebox. For a typical measurement, three scans with an integration time of 100 ms were collected and averaged. The photoluminescence characteristics for the thin-films were studied using a Microscopy Hyperspectral Imager IMA VIS from Photon Etc, coupled to a continuous-wave laser of 532 nm. For the analysis, the exposure time was set to 9 seconds and the field of view was 65x65 µm.

Scanning Electron Microscopy

SEM images were obtained using a Hitachi S-4800 Scanning-Electron Microscope, operating over platinum-metallized samples at an accelerating voltage of 20 kV.

Atomic Force Microscopy

Surface morphology of the co-evaporated thin-films was analysed using a Veeco Multimode SPM Atomic Force Microscopy (AFM).

Air Photoelectron Spectroscopy

The ionization energy of the materials was determined with an Ambient Pressure Photoemission Spectroscopy Systems (APS02) from KP Technology (KP Technology Ltd, Highlands and Islands, United Kingdom).

Device fabrication

Patterned ITO-covered glass substrates were cleaned using the same procedure as before. On top of them, a 5% aqueous solution of SnO₂ was deposited by spincoating and annealed at 150 °C for 30 minutes to achieve a film thickness of 30 nm, approximately. After that, substrates were transferred into a vacuum chamber in a glovebox in order to deposit 10 nm of C₆₀ at a pressure of 10⁻⁶ mbar. Subsequently, CsBi₃I₁₀ was deposited by co-evaporation of CsI and BiI₃ inside an air-placed vacuum thermal evaporator, following the same procedure as before. Then, a 15 nm-layer of TaTm and a 5 nm-layer of MoO₃ were consecutively deposited in a vacuum chamber inside a nitrogen-filled glovebox. To complete the devices, gold electrodes were evaporated until a thickness of 100 nm.

Device characterization

The electrical characterization was performed using a solar simulator by Abet Technologies (model 10500 with an AM1.5G xenon lamp as the light source). For calibrating the lamp, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cut-off filter (KG-3, Schott). The layout used to test the solar cells has sixteen equal areas with an active area of 0.05 cm². J-V curves were recorded between -1 and 1.2 V with 0.01 V steps.

Pulsed-radiolysis time-resolved microwave conductivity (PR-TRMC)

PR-TRMC measurements determine the mobility and lifetime of charge carriers in crystalline semiconductor materials by irradiation with a high energy electron pulse (3 MeV) and probing with GHz microwaves. If after irradiation there are mobile charge carriers, they will absorb part of the microwave power. This decrease in microwave power is directly related to the changed of conductivity and ultimately to the mobility of charge carriers.¹ The crystalline powders (~45 mg) are placed in a Polyether ether ketone (PEEK) holder. The PEEK block with the sample is placed inside a rectangular waveguide cell (chemically inert gold-plated copper). The cell is contained in a cryostat in which the temperature can be varied between 123K and 473K. The irradiation intensity was varied between pulse lengths of 2 ns and 20 ns (charge carrier concentrations $\sim 2 \times 10^{16} \text{ cm}^{-3}$ to $1 \times 10^{17} \text{ cm}^{-3}$) at a frequency of 30.5 GHz. The frequency scan (28-38 GHz) fits were measured at a pulse length of 2 ns ($\sim 2 \times 10^{16} \text{ cm}^{-3}$).

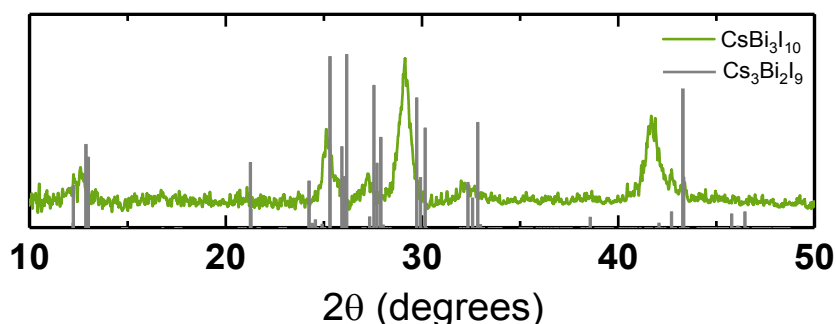


Figure S1. XRD diffractograms of the CsBi₃I₁₀ powders compared with the diffractograms for Cs₃Bi₂I₉, a specie that can be obtained with the same starting reagents as CsBi₃I₁₀.

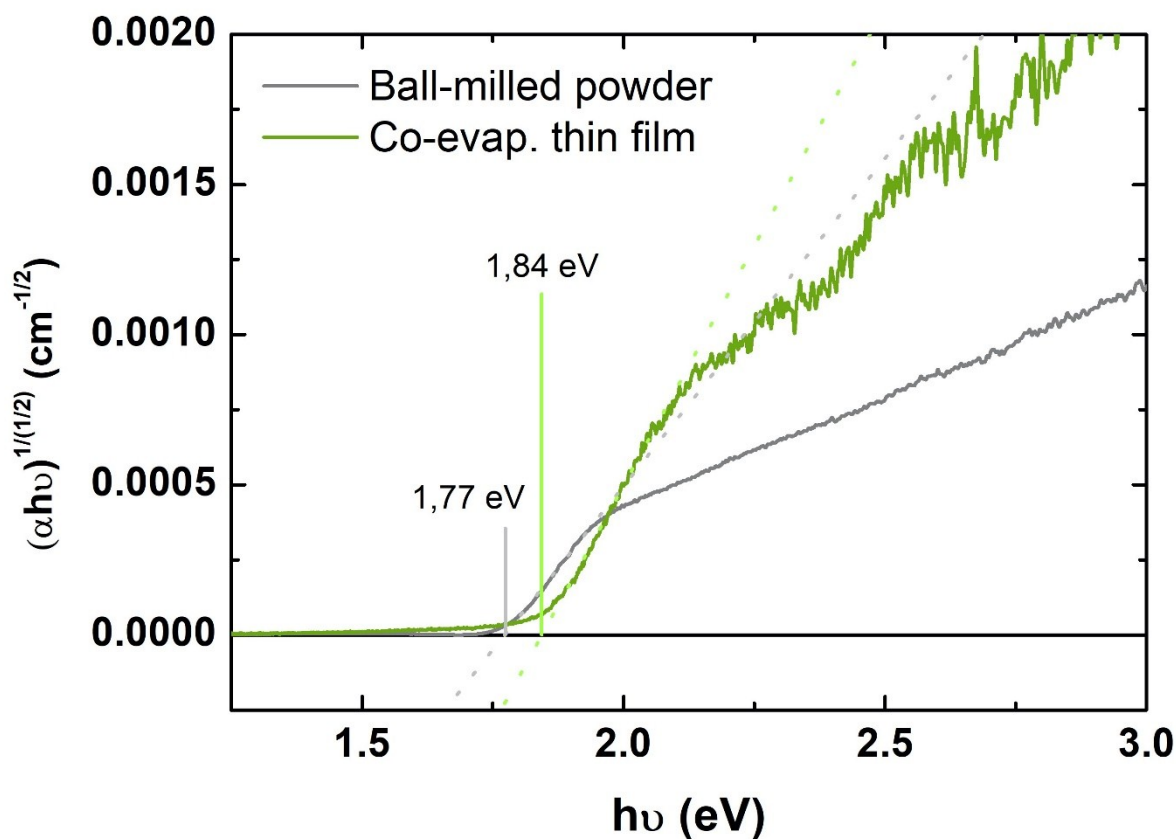


Figure S2. Tauc plots derived from optical absorbance of ball-milled and thin film samples. The slight mismatch in bandgap is discussed in the manuscript.

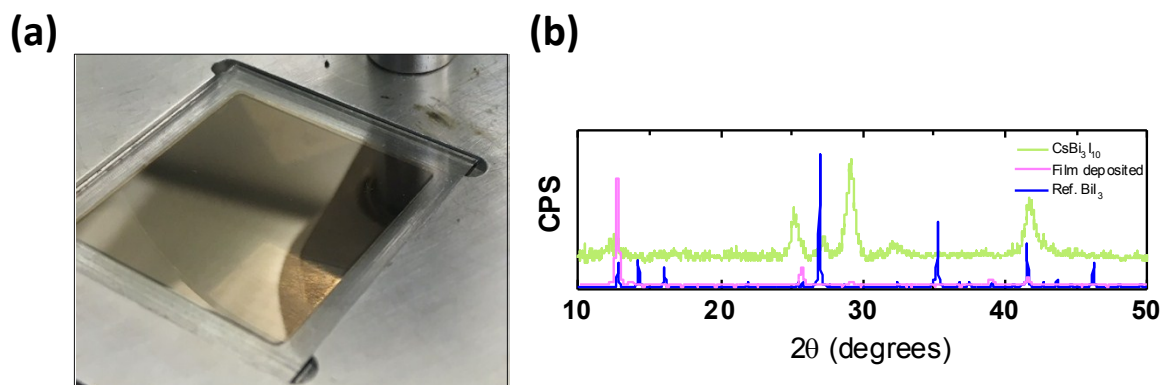


Figure S3. (a) Appearance of the thin film deposited by SSVD of $\text{CsBi}_3\text{I}_{10}$ and (b) XRD diffractograms of the $\text{CsBi}_3\text{I}_{10}$ in powder (starting material for the SSVD), the thin film obtained and BiI_3 (starting reagent of $\text{CsBi}_3\text{I}_{10}$). It is worth noting that the diffractogram of the thin film is different from the BiI_3 in powder state, but not in thin film by thermal evaporation, as reported by other authors.^{2,3}

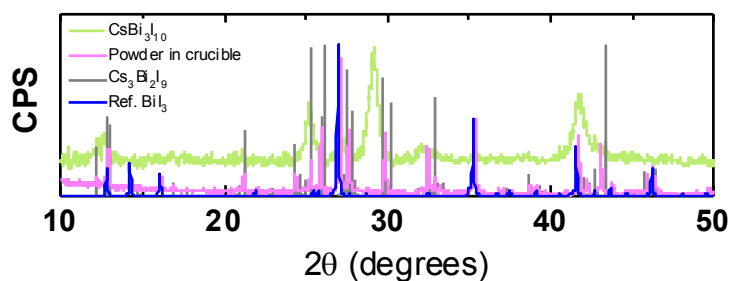
(a)**(b)**

Figure S4. (a) Appearance of the remaining material in the crucible after the SSVD of $\text{CsBi}_3\text{I}_{10}$ and (b) XRD diffractograms of the $\text{CsBi}_3\text{I}_{10}$ in powder (starting material for the SSVD, green), the remaining powder in the crucible (pink), $\text{Cs}_3\text{Bi}_2\text{I}_9$ (possible decomposition product, grey) and BiI_3 (starting reagent of $\text{CsBi}_3\text{I}_{10}$, ICSD 56573, blue).

Table S1. Ratios of Cs:Bi:I for each temperature of annealing, calculated from XPS measurements. Calculations have been done taking the ideal stoichiometry (10) of iodide as a reference.

Temperature	Cs 3d	Bi 4f	I 3d
Pristine	1.55	2.81	10
50 °C	0.92	3.38	10
80 °C	1.04	3.37	10

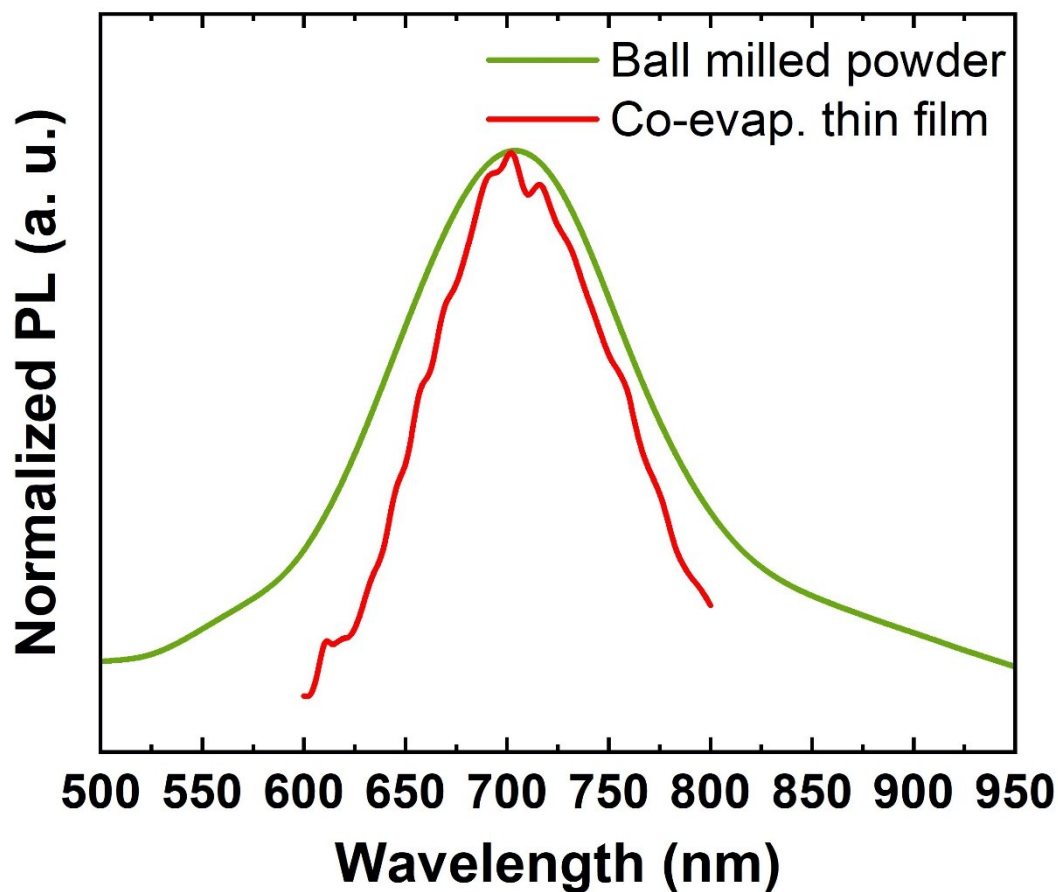


Figure S 5. Overlaid normalized PL spectra of thin film and powder sample. Differences in FWH are discussed in the main text.

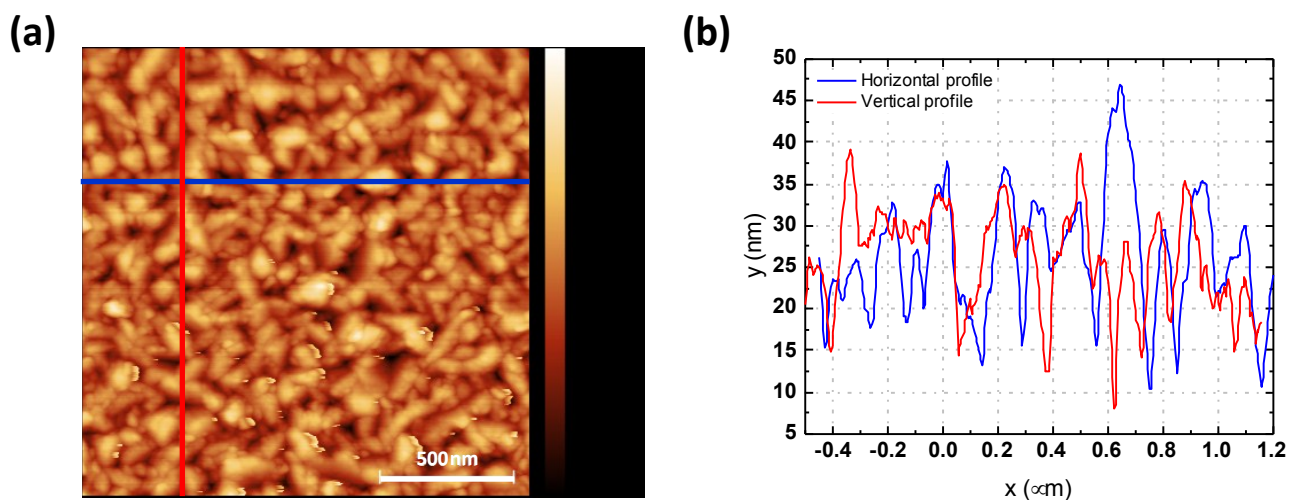


Figure S6. AFM topography (a) and horizontal and vertical profile indicating the roughness of the surface (b) of a $\text{CsBi}_3\text{I}_{10}$ thin-film deposited by co-evaporation.

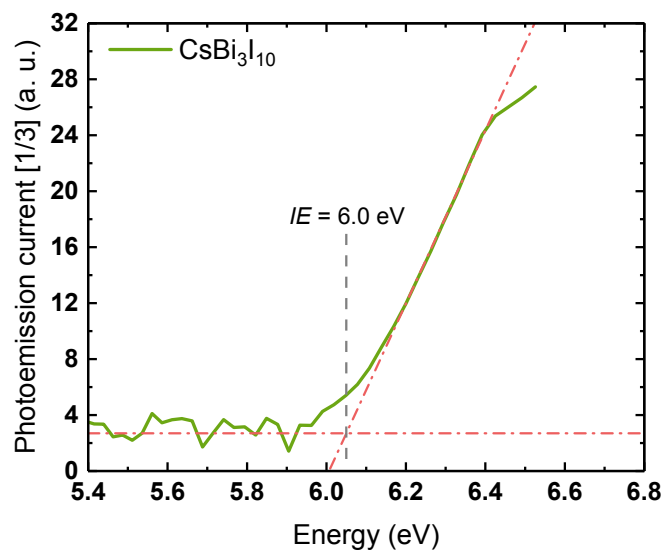


Figure S7. Photoemission spectra in air (APS) of $\text{CsBi}_3\text{I}_{10}$.

Table S2. Energy states for $\text{CsBi}_3\text{I}_{10}$. Values for energy levels are negative as they are referred to the VL.

<i>Compound</i>	<i>Bandgap (eV)</i>	<i>VBM (eV)</i>	<i>CBM (eV)</i>
$\text{CsBi}_3\text{I}_{10}$	1.8	-6.0	-4.2

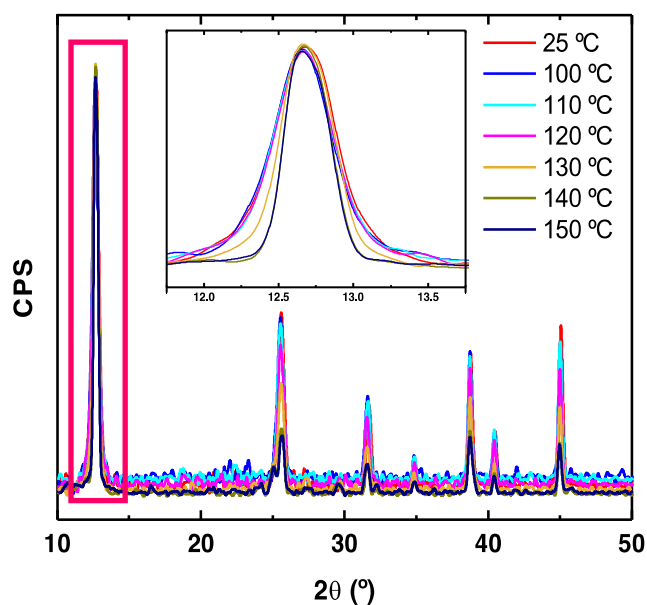


Figure S8. Overlay of X-Ray diffractograms at variable temperatures of a $\text{CsBi}_3\text{I}_{10}$ thin-film. A special inset is given for the specified region (in red) to show the sharpening of the peaks upon annealing. Applying Scherrer formula to the 25°C and 150°C samples, a grain growth from 24.3 nm to 27.9 nm is obtained. While the growth is undeniable, the absolute values are most likely underestimated as instrumental broadening is unknown and therefore not taken into account.

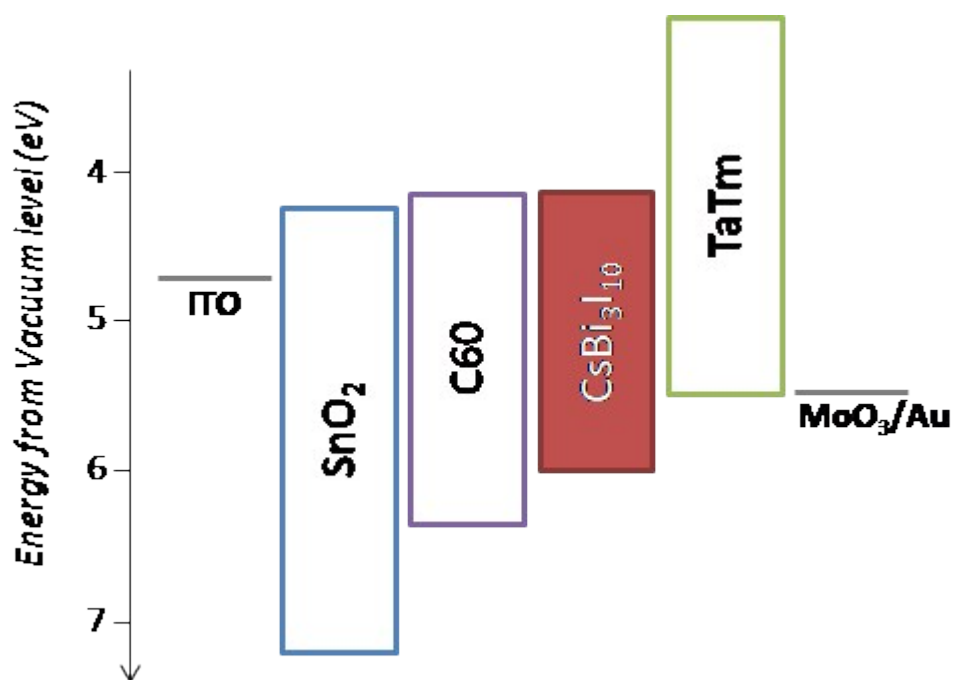


Figure S 9. Flat band energy diagram for the set of materials used in thin-film solar cells. Data for CsBi₃I₁₀ are estimated from APS measurements and the bandgap, the rest are from literature.

SUPPLEMENTARY REFERENCES:

- 1 J. Warman, M. De Haas, G. Dicker and F. Grozema, *Chem. Mater.*, 2004, 4600–4609.
- 2 N. F. Coutinho, S. Cucatti, R. B. Merlo, J. M. C. Silva Filho, N. F. B. Villegas, F. Alvarez, A. F. Nogueira and F. C. Marques, *Sci. Rep.*, 2019, **9**, 11785.
- 3 N. F. Coutinho, R. B. Merlo, N. F. V. Borrero and F. C. Marques, *MRS Adv.*, 2018, **3**, 3233–3236.