

## Supplementary information

### Precisely Tailoring Precursor Solution for Efficient AgBiS<sub>2</sub> Solar

#### Cells

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## Experimental

### Materials

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (99.99%), Thiourea (99%) and  $\text{AgNO}_3$  (99.8%) was purchased from Aladdin. 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene (Spiro-OMeTAD) and fluorine-doped tin oxide (FTO)-coated glass were purchased from Youxuan Tech, China. lithium bis(trifluoromethylsulfonyl)imide salt (LiTFSI) and 4-*tert*butyl-pyridine (tBP, 96%) were purchased from Sigma-Aldrich. Chlorobenzene (CB, anhydrous), *N,N*-dimethylformamide (DMF, anhydrous) and acetonitrile (ACN) were purchased from Sigma-Aldrich.  $\text{SnO}_2$  colloid precursor was purchased from Alfa Aesar. All the materials were used without further purification.

### The Solution Preparation

Thiourea (Tu) and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were mixed in DMF and stirred for 30 min to obtain  $\text{Bi}^{3+}$ -Tu complexes solution. Tu and  $\text{AgNO}_3$  were mixed in DMF and stirred for 30 min to obtain  $\text{Ag}^+$ -Tu complexes solution. For the recipe Bi-Tu-Ag, Tu and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were mixed in DMF and stirred for 30 min, then  $\text{AgNO}_3$  was added to continue stirring for 2h. For the recipe Mixed, the  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , Tu and  $\text{AgNO}_3$  were mixed in DMF by stirring for 2 h. For the recipe Ag-Tu-Bi, Tu and  $\text{AgNO}_3$  were mixed in DMF and stirred for 30 min, then  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was added to continue stirring for 2 h. All precursor solutions were at a concentration of 0.5 M and stirred at 25 °C. The molar ratio for  $\text{AgNO}_3$ ,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and Tu is 1:1:3. The solution of hole transporting layer (HTL) was prepared by dissolving 18.8 mg Spiro-OMeTAD, 7.2  $\mu\text{L}$  tBP and 4.4  $\mu\text{L}$  Li-TFSI/ACN (520 mg  $\text{mL}^{-1}$ ) into 1 mL CB.

### Devices Fabrication

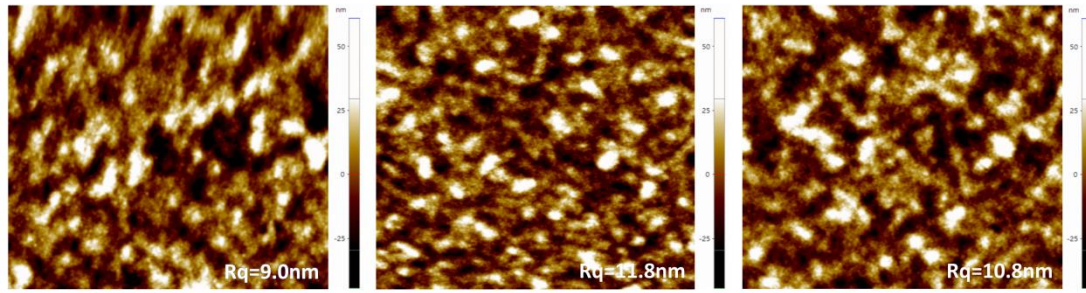
FTO glass substrates were cleaned with detergent, de-ionized water, acetone, and iso-propanol, in sequence, then dried in an oven at 120 °C for 30 min and treated with ultraviolet ozone for 15 min. A diluted  $\text{SnO}_2$  nanoparticle solution

(2.67 wt %) was deposited on FTO substrate at 4,000 rpm for 30 s, and then annealed at 150°C for 30 min. After cooling to room temperature, the substrates of FTO glass/SnO<sub>2</sub> were transferred into a N<sub>2</sub>-filled glovebox after ultraviolet ozone for 15 min. The prepared AgBiS<sub>2</sub> precursor solution was deposited on the SnO<sub>2</sub> substrate at 5,000 rpm for 30 s. Then, a multi-step annealing procedure was carried out for AgBiS<sub>2</sub> film at temperatures of 100 °C and 200 °C for 10 min, respectively. After cooling to room temperature, the second layer of AgBiS<sub>2</sub> film is deposited again in the same way. After cooling down to room temperature, the HTL was made by drop-casting HTL solution onto the AgBiS<sub>2</sub> absorbers at 4000 rpm for 30 s. Finally, Au electrode of 80 nm with an active area of ~0.05 cm<sup>2</sup> and an antireflection layer were deposited by a thermal evaporation at a rate of 0.1-1.0 Å s<sup>-1</sup> under the vacuum (< 4×10<sup>-4</sup> Pa) to complete device fabrication process.

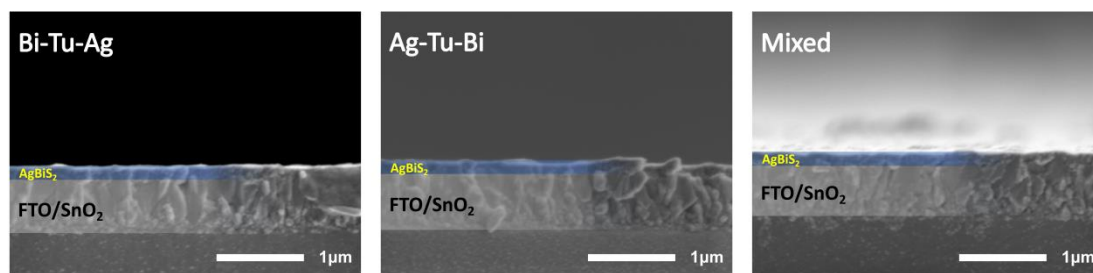
### **Measurements and Characterizations**

Photocurrent density-voltage (*J-V*) curves were measured in an N<sub>2</sub>-filled glovebox using a Keithley 2400 source meter at a step size of 20 mV and delay time of 10 ms under a simulated AM1.5G spectrum and a xenon arc lamp based solar simulator (EnliTech, Taiwan). The light intensity was calibrated to be 100 mW cm<sup>-2</sup> using a NIST-certified monocrystalline Si solar cell (Newport 532 ISO1599). The device performance parameters were calculated from the current-voltage curves of the photovoltaic device under a illumination. No protocol for preconditioning the device before its characterization was followed. The active area of the device is 0.05 cm<sup>2</sup>. Above tests are carried out in glove box filled with nitrogen at room temperature. The dark current measurements, light intensity and I-T measurements, stability measurements were all carried out with the same system. The external quantum efficiency was measured by an EQE instrument (Enlitech). NMR spectra was measured with a JOEL NMR spectrometer (JNM-ECZ400S, 400 MHz Japan). Fourier transform infrared spectrometer (FTIR) were measured by Bruker, INVENIO-S. DLS experiments were performed using a ZetaPALS instrument. TGA spectra were obtained using a

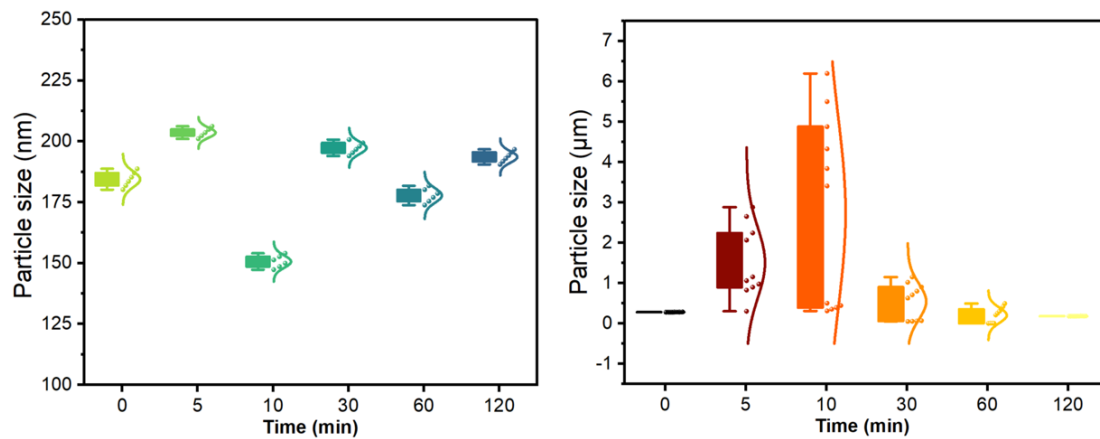
thermogravimetric analyzer TA Q500 with a flow rate of 20 mL min<sup>-1</sup>. The temperature is set from 25 to 500 °C at a rate of 15 °C min<sup>-1</sup>. The XAFS spectra of the Bi L3 edge (13419 eV) for precursor solution were characterized at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF). It is provided with a double Si (111) monochromator which was used to monochromatize the X-ray white beam. Spectral data were processed and analyzed using Athena. The X-ray diffraction patterns were performed using Cu K $\alpha$  radiation as the X-ray source by a Smart Lab diffractometer from Japan. Absorption spectra were acquired using a Shimadzu UV-3600 ultraviolet visible near-infrared spectrophotometer. The SEM images of the AgBiS<sub>2</sub> films were taken with a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi). Surface topographies AFM were imaged using an atomic force microscope (Keysight 5500).



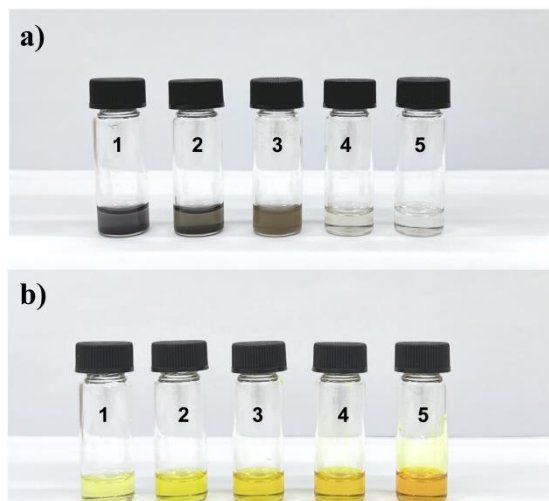
**Figure S1.** AFM surface topography profiles of the AgBiS<sub>2</sub> thin films prepared based on recipe Bi-Tu-Ag, Ag-Tu-Bi and Mixed. (scan range: 5 $\mu$ m  $\times$  5 $\mu$ m). Corresponding root-mean-square (Rq) roughness value was respectively labeled.



**Figure S2.** Cross-sectional SEM images of the films prepared based on different recipes.

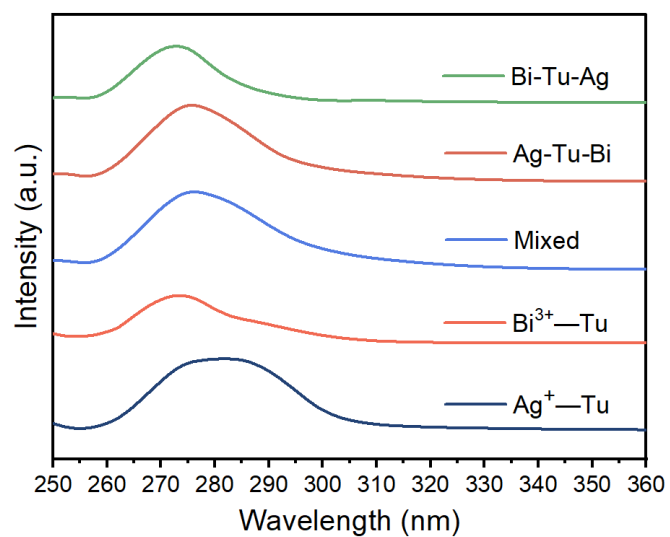


**Figure S3.** The size distributions of the different stirring times after addition of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  to  $\text{Ag}^+$ -Tu complexes solutions (left) and the different stirring times after the addition of  $\text{AgNO}_3$  to  $\text{Bi}^{3+}$ -Tu complexes solutions (right)

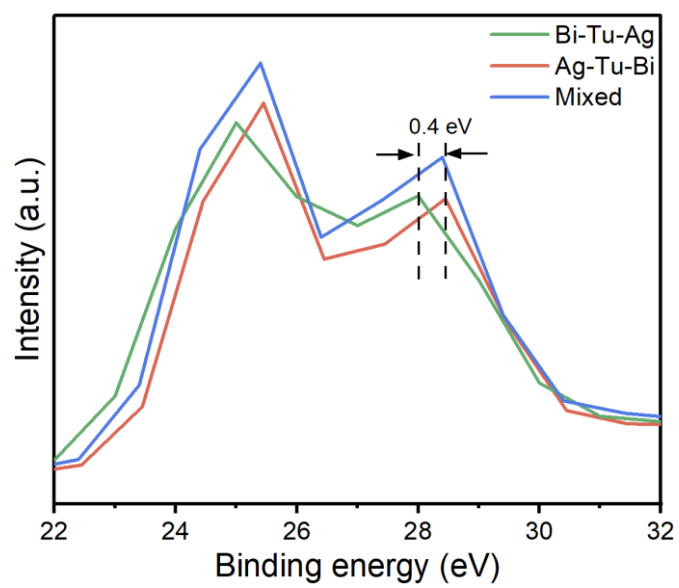


**Figure S4.** Photographs of Ag<sup>+</sup>-Tu complexes solutions (a) and Bi<sup>3+</sup>-Tu complexes solutions (b) with different Tu contents. For all precursors, the molar concentration of Ag equals to that of Bi, is 0.5 M, only the concentration of Tu varies. Here 1 Tu means that the concentration of Tu is 0.25 M. From a-1 (b-1) to a-5 (b-5), the Tu/M ratio is 0.5, 1, 1.5, 2 and 3.

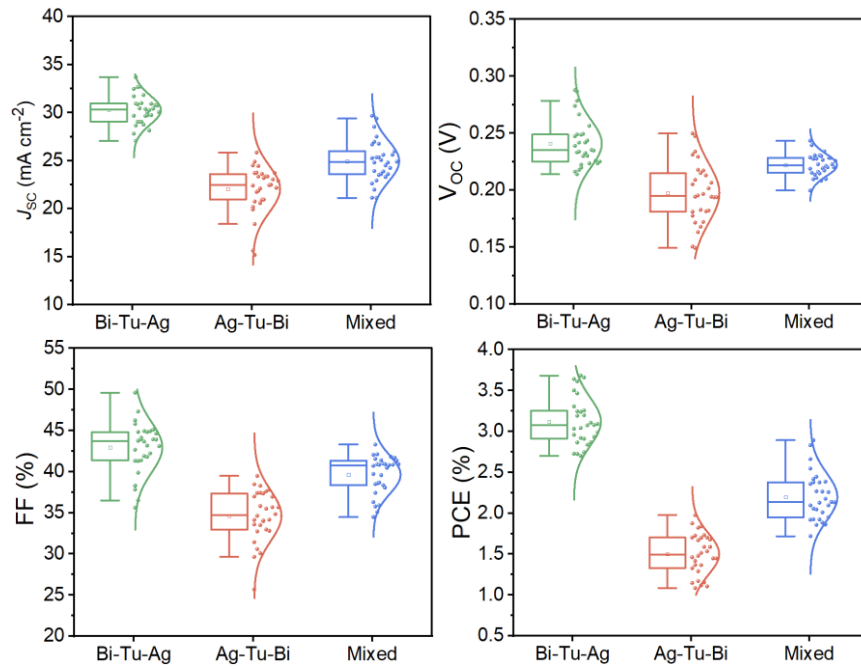




**Figure S5.** UV-vis spectroscopy of solutions prepared based on Ag<sup>+</sup>-Tu complexes, Bi<sup>3+</sup>-Tu complexes and different recipes.



**Figure S6.** XPS of of the AgBiS<sub>2</sub> films prepared based on different recipes.



**Figure S7.** Statistics photovoltaic parameters for the  $\text{AgBiS}_2$  thin films solar cells based on different recipes.

**Table S1.** FWHM (°) of the three main peaks of AgBiS<sub>2</sub> thin films prepared based on different recipes.

	(111)	(200)	(220)
Bi-Tu-Ag	0.223	0.225	0.315
Ag-Tu-Bi	0.266	0.300	0.339
Mixed	0.268	0.272	0.312

**Table S2.** X-ray diffraction angles of (111), (200) and (220) crystal planes of AgBiS<sub>2</sub> thin films prepared with different recipes compared to standard card of Schapbachite.

	(111)	(200)	(220)
Schapbachite	27.327	31.657	45.380
Bi-Tu-Ag	27.321	31.659	45.499
Ag-Tu-Bi	27.408	31.775	45.530
Mixed	27.429	31.756	45.550

**Table S3.** The photovoltaic parameters of the cells based on different recipes.

<b>Recipe</b>	<b><math>V_{oc}</math> (V)</b>	<b><math>FF</math> (%)</b>	<b><math>J_{sc}</math> (mA cm<sup>-2</sup>)</b>	<b><math>PCE</math> (%)</b>
Bi-Tu-Ag	0.28	41.9	30.9	3.68
Ag-Tu-Bi	0.19	38.6	24.3	1.86
Mixed	0.24	43.1	25.5	2.64