Supplementary Information (SI) for Sustainable Energy & Fuels.

Selection of appropriate solvent additives for the preparation of high-performance $Cs_2AgBiBr_6$ solar cells

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1. Experimental section

1.1 Materials

Titanium tetrachloride ($TiCl_4$, 98%), ethylenediamine (EDA, 99%), isopropyl alcohol (IPA, 99.5%), Dimethyl sulfoxide (DMSO, 99.7%), poly (3,4-ethylenedioxythiophene)-poly (styrene sulfonic acid ester) (PEDOT:PSS, 1.3-1.7 wt% solution in water), [6,6]-phenyl-C61-butyricacid methyl ester (PCBM, 99%), TiO_2 paste (30 NR-D), and cesium bromide (CsBr, 99.9%) were purchased from Sinopharm Chemical Reagent Co., Ltd.., J&K Chemical Ltd., and Xi'an Polymer Light Technology Corp.., respectively. Bismuth bromide ($BiBr_3$, 98%), silver bromide (AgBr, 99.9%), N,N'-dimethylpropyleneurea (DMPU, 99%), methylimidazole (MeIm, 99%), and 2,2′,7,7′-tetra (N,N-bis-p-methoxyaniline)-9,9′-spirodifluorene (Spiro-OMeTAD, 99.8%) were purchased from Aladdin, and Ningbo Borun New Material Co., Ltd.., respectively. All materials and reagents were used directly in the experiments without undergoing purification.

1.2 Preparation of $Cs_2AgBiBr_6$ precursor solution

1.2.1 $Cs_2AgBiBr_6$ (DMSO as solvent) precursor solution: a precursor solution of $Cs_2AgBiBr_6$ was prepared by dissolving 1 mmol of CsBr, 0.5 mmol of AgBr, and 0.5 mmol of $BiBr_3$ in 1 mL of DMSO. The mixture was stirred at 60 °C until all the salts were fully dissolved.

1.2.2 $Cs_2AgBiBr_6$ (DMPU as additive) precursor solution: a precursor solution of $Cs_2AgBiBr_6$ was synthesized by dissolving 1 mmol of CsBr, 0.5 mmol of AgBr, and 0.5 mmol of $BiBr_3$ in a mixture of 30 μL (0.25 mmol) of DMPU and 970 μL of DMSO. The solution was stirred at 60 °C until all the salts were fully dissolved.

1.2.3 $Cs_2AgBiBr_6$ (MeIm as additive) precursor solution: a precursor solution of $Cs_2AgBiBr_6$ was created by dissolving 1 mmol of CsBr, 0.5 mmol of AgBr, and 0.5 mmol of $BiBr_3$ in a mixture of 20 μL (0.25 mmol) of MeIm and 980 μL of DMSO. The solution was stirred at 60 °C until the salts were completely dissolved.

1.2.4. $Cs_2AgBiBr_6$ (EDA as additive) precursor solution: a precursor solution of $Cs_2AgBiBr_6$ was synthesized by dissolving 1 mmol of CsBr, 0.5 mmol of AgBr, and 0.5 mmol of $BiBr_3$ in a mixture of 17 μL (0.25 mmol) of EDA and 983 μL of DMSO. The mixture was stirred at 60 °C until all the salts were fully dissolved.

1.3 Device fabrication

The cleaning process of FTO glass and the preparation process of the compact TiO_2 (c-TiO_2) layer can be found in our recent work.[S1] The m-TiO_2 layer was deposited by spin-coating the TiO_2 paste (30NR-D)/ethanol mixture (1:8 w/w) at 5000 rpm for 30 s on the surface of FTO/c-TiO_2, which was then calcined at 500 °C for 30 min. The as-prepared FTO/c-TiO_2/ m-TiO_2 substrates were treated with UV-ozone for 30 min before further deposition. $Cs_2AgBiBr_6$ precursor solution was spin-coated on the as-prepared FTO/c-TiO_2/ m-TiO_2 substrates at 1000 rpm for 10 s and 4000 rpm for 40 s, adding drops of 180~200 μL IPA before the end of the second step. Follow by, the film was annealed at 260 °C for 5 min. Spiro-OMeTAD (43.38 mg) dissolved in 1 mL of chlorobenzene, 10.5 μL of Li-TFSI (520 mg/mL, acetonitrile) and 17.2 μL of TBP were added, and spin-coated on the absorber layer, rotating at 4000 rpm for 30 s. Finally, an Ag electrode was deposited by thermal evaporation at a pressure of 1×10^{-4} mbar with an effective area of 0.04 cm^2 by using a metal mask.

1.4 $Cs_2AgBiBr_6$ single-hole devices fabrication

The PEDOT:PSS layer was deposited by spin-coating the PEDOT:PSS (1.3-1.7 wt% solution in water) at 4000 rpm for 30 s, which was then annealed at 140 °C for 15 min. $Cs_2AgBiBr_6$ precursor solution was spin-coated on the as-prepared FTO/PEDOT:PSS substrates at 1000 rpm for 10 s and 4000 rpm for 40 s, dropping 180~200 μL IPA before the end of the second step. The film was annealed at 260 °C for 5 min. Spiro-OMeTAD (43.38 mg) was dissolved in 1 mL of chlorobenzene, 10.5 μL of Li-TFSI (520 mg/mL, acetonitrile) and 17.2 μL of TBP were added, and the solution was spin-coated on the absorber layer, rotating at 4000 rpm for 30 s. Finally, an Ag electrode was deposited by thermal evaporation at a pressure of 1×10^{-4} mbar with an effective area of 0.04 cm^2 by using a metal mask.

1.5 $Cs_2AgBiBr_6$ single-electron devices fabrication

$Cs_2AgBiBr_6$ precursor solution was spin-coated on the as-prepared FTO/c-TiO_2/m-TiO_2 substrates at 1000 rpm for 10 s and 4000 rpm for 40 s, dropping 180~200 μL IPA before the end of the second step. The film was annealed at 260 °C for 5 min. PCBM (18 mg) dissolved in 1 mL of chlorobenzene, and spin-coated on the absorber layer, rotating at 4000 rpm for 30 s. Finally, an Ag electrode was deposited by thermal evaporation at a pressure of 1×10^{-4} mbar with an effective area of 0.04 cm^2 by using a metal mask.

1.6 Characterization

The FTIR spectrum of the $Cs_2AgBiBr_6$ films were recorded using Fourier transform infrared spectroscopy (Thermo Nicolet 6700). SEM images and cross-section images were measured by a high-resolution field emission scanning electron microscope (Regulus 8230). The surface smoothness of $Cs_2AgBiBr_6$ films was characterized by an atomic force microscope (Bruker Dimension Icon). The crystallinity of $Cs_2AgBiBr_6$ film was studied by X-ray diffractometer (Malvern PANalytical X-Pert PRO MPD, Cu Kα radiation). The optical properties of $Cs_2AgBiBr_6$ films were analyzed using UV-vis spectrophotometer (Shimadzu UV2550) and photoluminescence spectrometer (Horiba PTI QM400). The TRPL spectra measurements of $Cs_2AgBiBr_6$ films were carried out using the time-resolved fluorescence spectrometer (FLS1000, Edinburgh). The *J-V* curve for the $Cs_2AgBiBr_6$ solar cell was measured using a solar simulator (Newport Oriel Sol3A) under AM 1.5G irradiation at 100 mW/cm^2. The light intensity of 100 mW cm^{-2} was calibrated by using a standard silicon solar cell. The active area of the device was 0.04 cm^2. The IPCE spectra were obtained with an IPCE measurement kit (Newport) under AC mode. The electrochemical impedance spectroscopy (EIS) and the Mott-Schottky curves of the devices were collected on an electrochemical workstation (CHI660D, Shanghai Chenhua Instruments Co., Ltd.).

Supplementary Note 1:

According to the abrupt junction *J*-*V* equation as expressed in Equation (S1), and its formula manipulation as given in Equations (S1), the reverse saturation current density (J_0) of $Cs_2AgBiBr_6$ solar cells can be obtained:[S2]

$$J = J_0 \exp\left[\frac{q(V - JR_s}{AV_{th}}\right] + GV - J_L \qquad (S1)$$

where q is the electron charge, A is ideality factor, R_s is series resistance, V_{th} is the thermal energy ($k_B T/q$) and is generally regarded to be 0.026 eV at room temperature, G is shunt conductance, J_L is the photocurrent density, and k_B is the Boltzmann's constant.

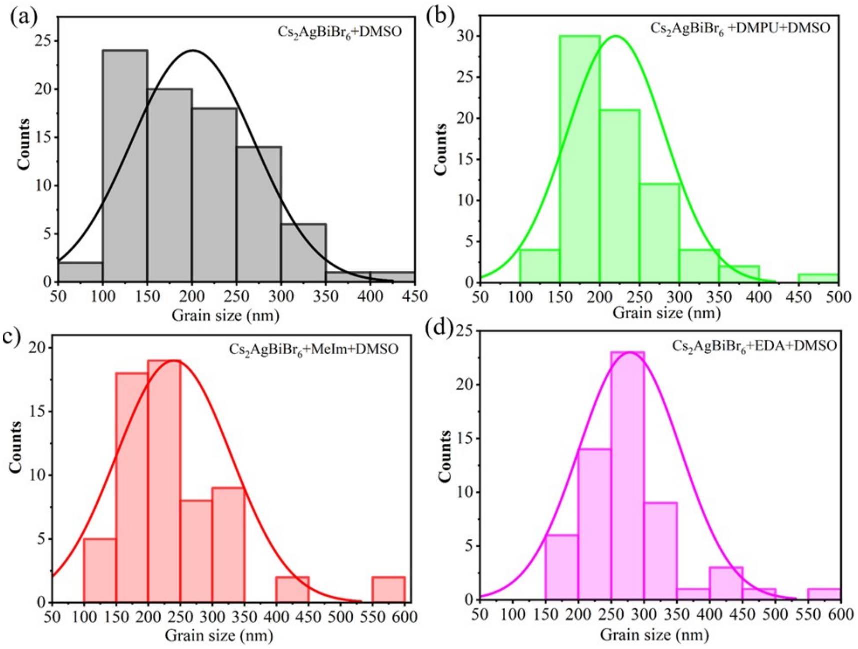

Fig. S1 Grain size distribution of (a) $Cs_2AgBiBr_6$+DMSO film, (b) $Cs_2AgBiBr_6$+DMPU+DMSO film, (c) $Cs_2AgBiBr_6$+MeIm+DMSO film, (d) $Cs_2AgBiBr_6$+EDA+DMSO film.

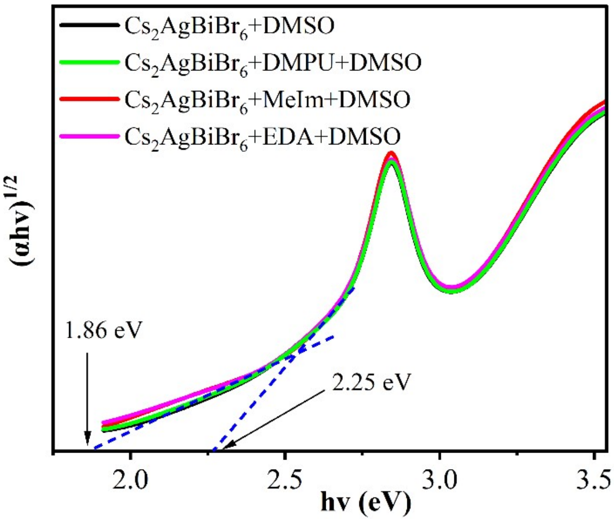

Fig. S2 Tauc plots extract from the UV-vis absorption spectra of Cs$_2$AgBiBr$_6$ films.

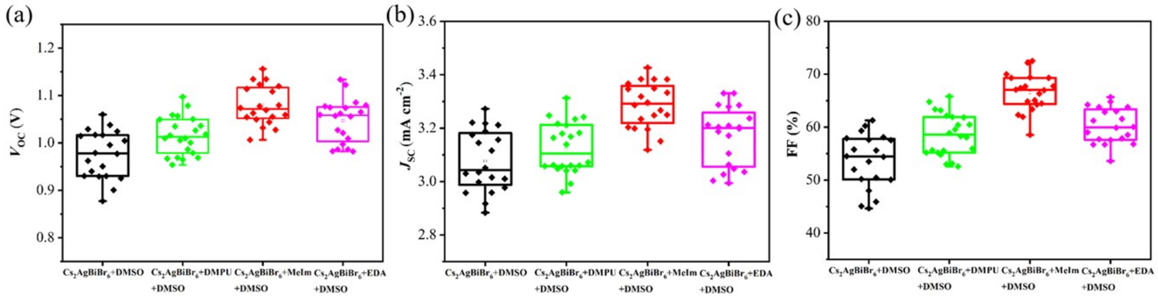

Fig. S3 Statistical distribution of (a) V_{OC}, (b) J_{SC}, and (c) FF of Cs$_2$AgBiBr$_6$ solar cells.

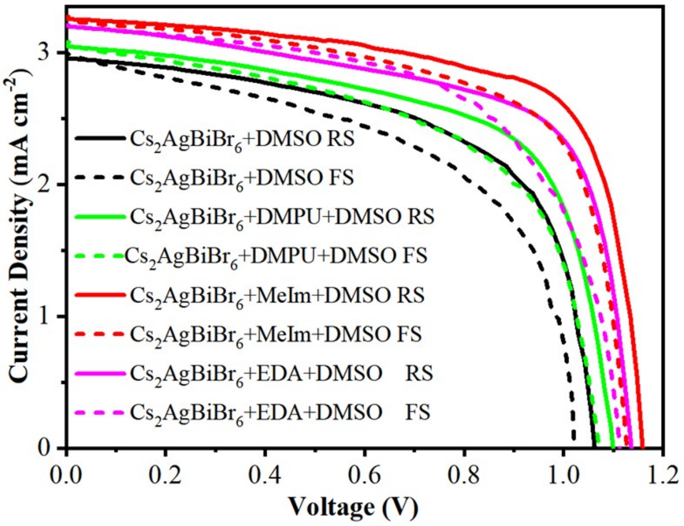

Fig. S4 *J*-*V* curves base on forward scan (FS) and reverse scan (RS) of Cs$_2$AgBiBr$_6$ solar cells.

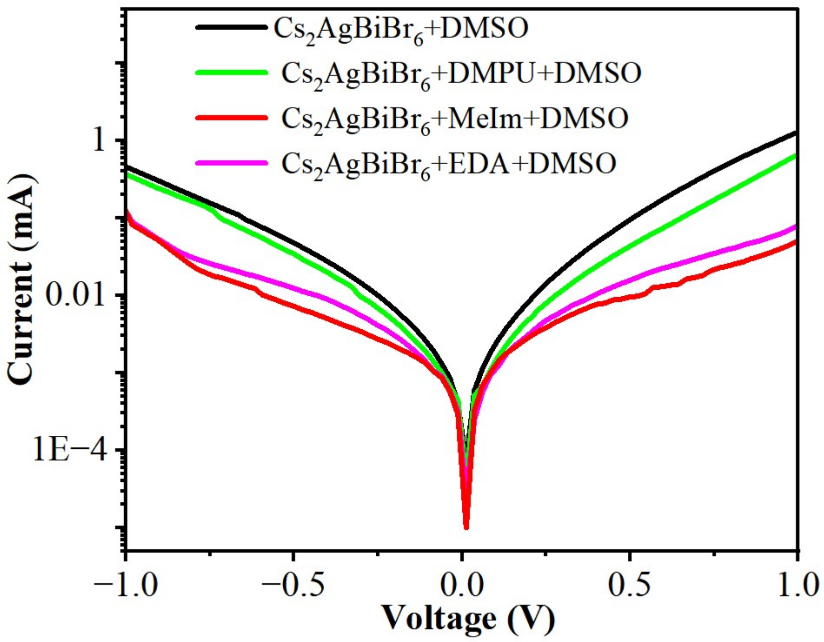

Fig. S5 Dark *J-V* of $Cs_2AgBiBr_6$ solar cells.

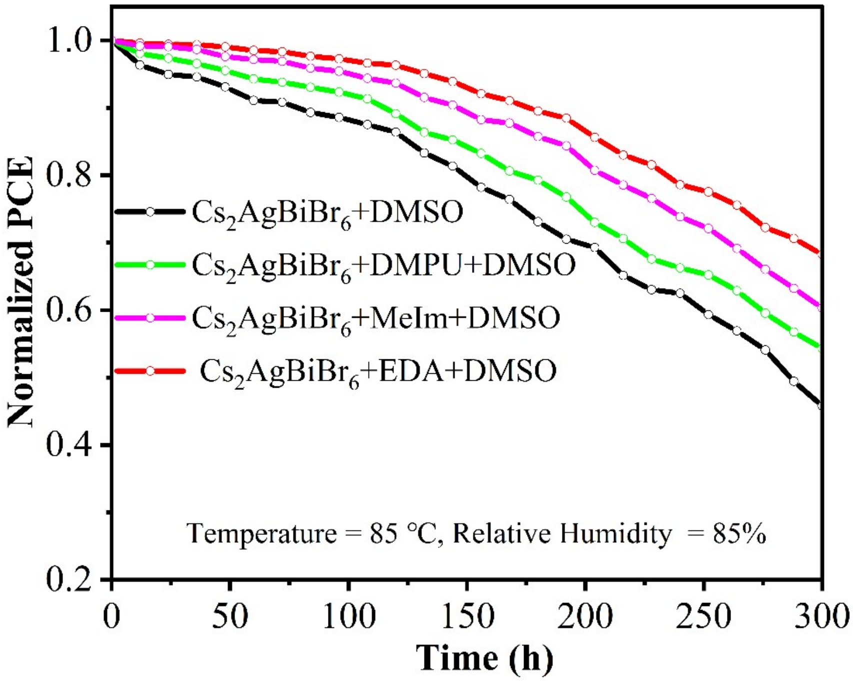

Fig. S6 Normalized PCE decay curves of the $Cs_2AgBiBr_6$ solar cells.

Table S1 Lifetime parameters derived from the TRPL spectroscopy of Glass/$Cs_2AgBiBr_6$ films. ($\tau_{ave}=\frac{\sum A_i\tau_i^2}{\sum A_i\tau_i}$)

Sample	τ_1 *(ns)*	A_1 *(%)*	τ_2 *(ns)*	A_2 *(%)*	τ_{ave} *(ns)*

$Cs_2AgBiBr_6$+DMSO	0.44	92.27	22.49	7.73	18.34
$Cs_2AgBiBr_6$+DMPU+DMSO	0.43	91.63	40.70	8.37	35.98
$Cs_2AgBiBr_6$+Me-Im+DMSO	037	89.89	62.04	10.11	58.93
$Cs_2AgBiBr_6$+EDA+DMSO	0.40	90.54	57.01	9.46	56.63

Table S2 The photovoltaic parameters and hysteresis index (HI) of $Cs_2AgBiBr_6$ solar cells.

Devices	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{max} (%)	HI (%)
$Cs_2AgBiBr_6$+DMSO (FS)	1.02	3.02	53.6	1.65	12.4
$Cs_2AgBiBr_6$+DMSO (RS)	1.06	2.96	60.2	1.89	
$Cs_2AgBiBr_6$ +DMPU+DMSO (FS)	1.07	3.08	56.5	1.87	11.8
$Cs_2AgBiBr_6$ +DMPU+DMSO (RS)	1.10	3.05	63.2	2.11	
$Cs_2AgBiBr_6$+MeIm+DMSO (FS)	1.13	3.27	64.4	2.38	8.9
$Cs_2AgBiBr_6$+MeIm+DMSO (RS)	1.16	3.26	69.3	2.61	
$Cs_2AgBiBr_6$+EDA+DMSO (FS)	1.11	3.22	59.8	2.14	10.0
$Cs_2AgBiBr_6$+EDA+DMSO (RS)	1.13	3.20	65.7	2.38	

The formula of hysteresis index is $HI = (PCE_{RS} - PCE_{FS})/PCE_{RS}$.

Table S3 Fitting parameters of EIS for $Cs_2AgBiBr_6$ solar cells.

Devices	R_s (Ω)	R_{rec} (Ω)
$Cs_2AgBiBr_6$+DMSO	13.3	584.9
$Cs_2AgBiBr_6$ +DMPU+DMSO	10.5	1084.0
$Cs_2AgBiBr_6$+MeIm+DMSO	11.0	1379.0
$Cs_2AgBiBr_6$+EDA+DMSO	11.2	1339.0

References

[S1] L. Zhang, Y. Xu, P. Niu, M. Lyu, H. Lu, J. Zhu, *J. Phys. D: Appl. Phys.* 2023 **56**, 075501.

[S2] Y. Qi, Y. Li, Q. Lin, *Appl. Phys. Lett.* 2022, **120**, 221102.