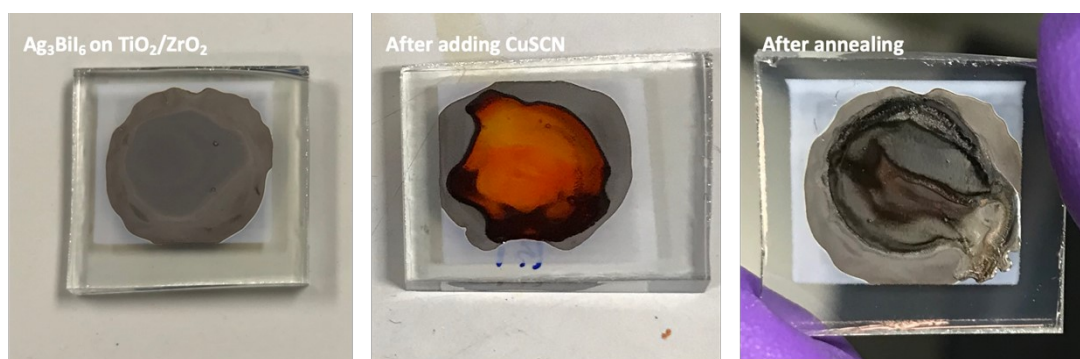Electronic Supplementary Material (ESI):

Bismuth Silver Pnictohalide Alternative to Perovskite in Fully-Printable Triple-Mesoscopic Solar Cells

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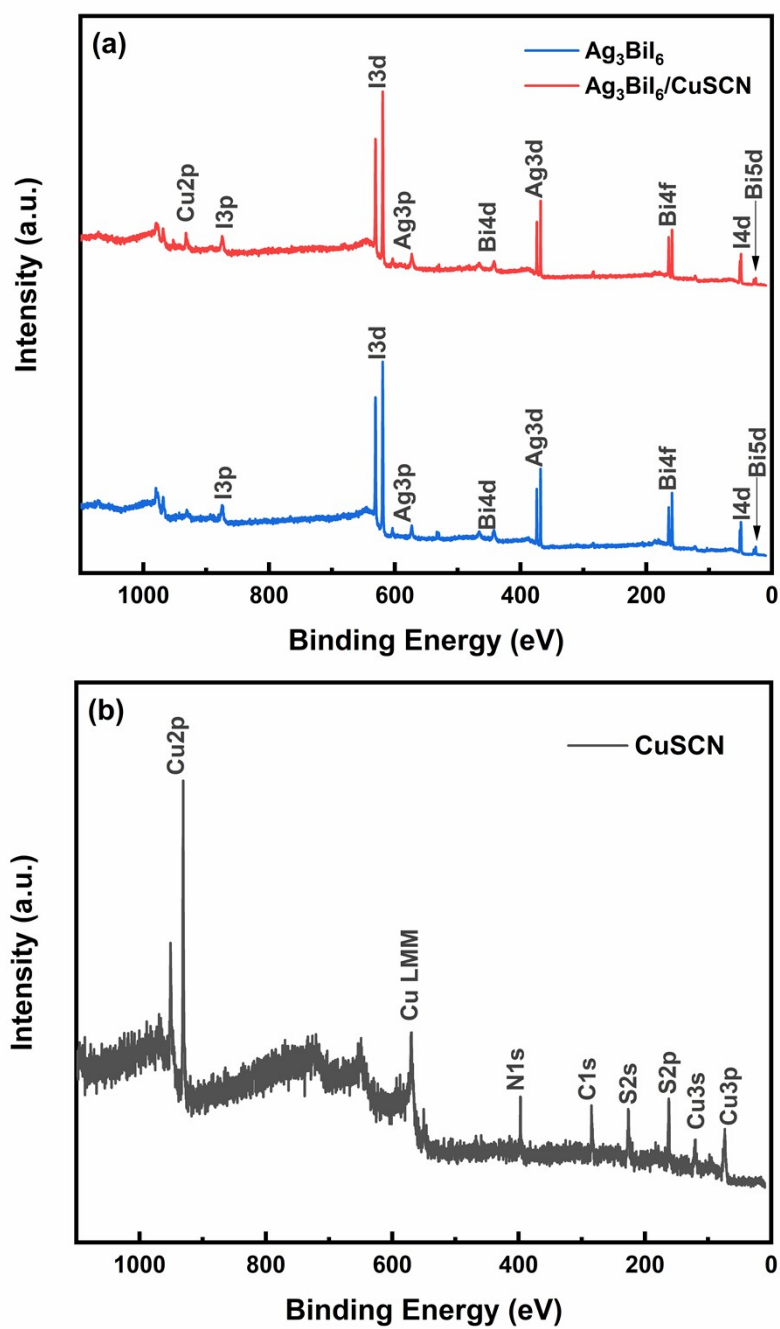
Figure S1 Digital pictures of Ag_3BiI_6 on TiO_2/ZrO_2 changes with adding CuSCN.
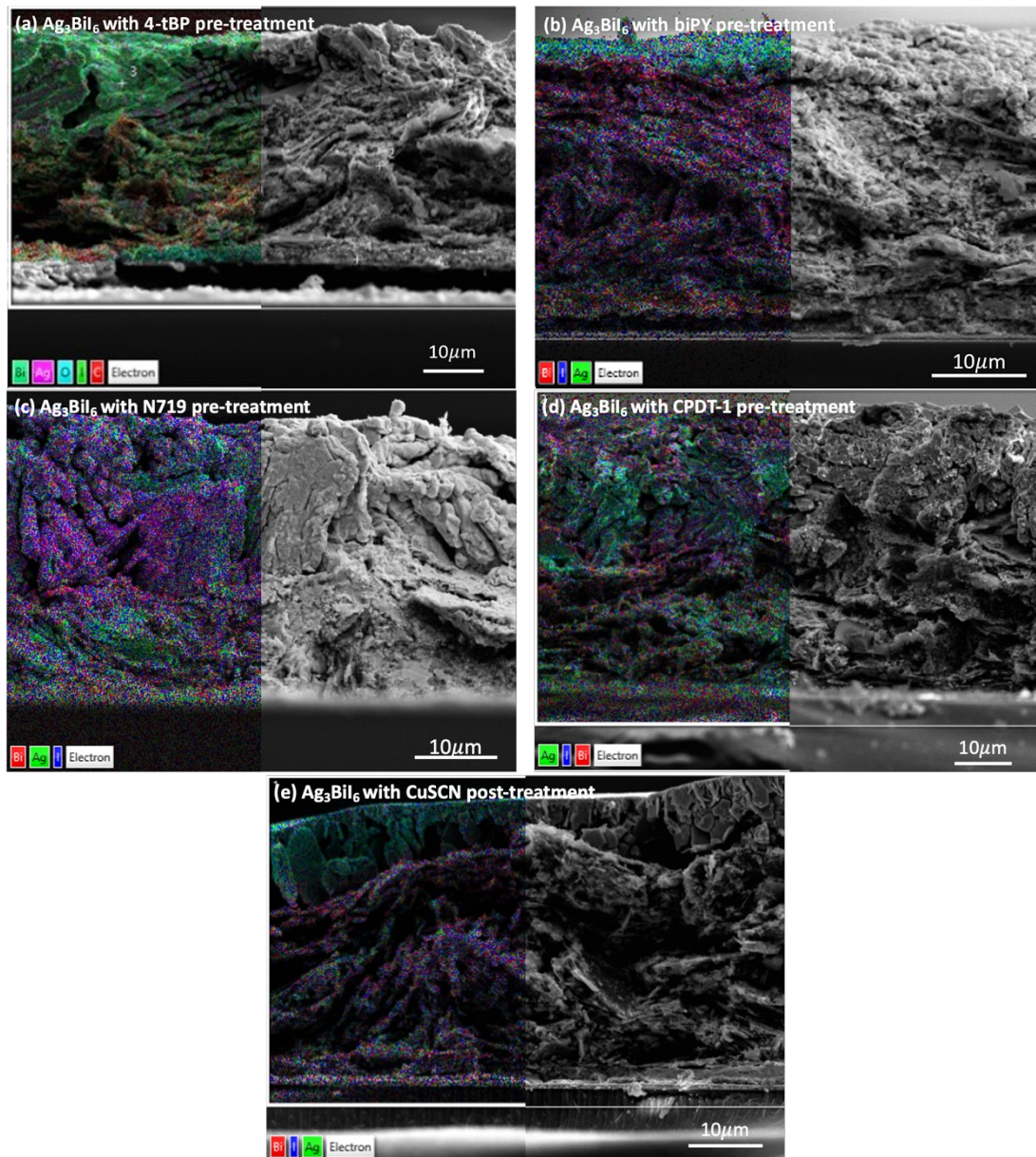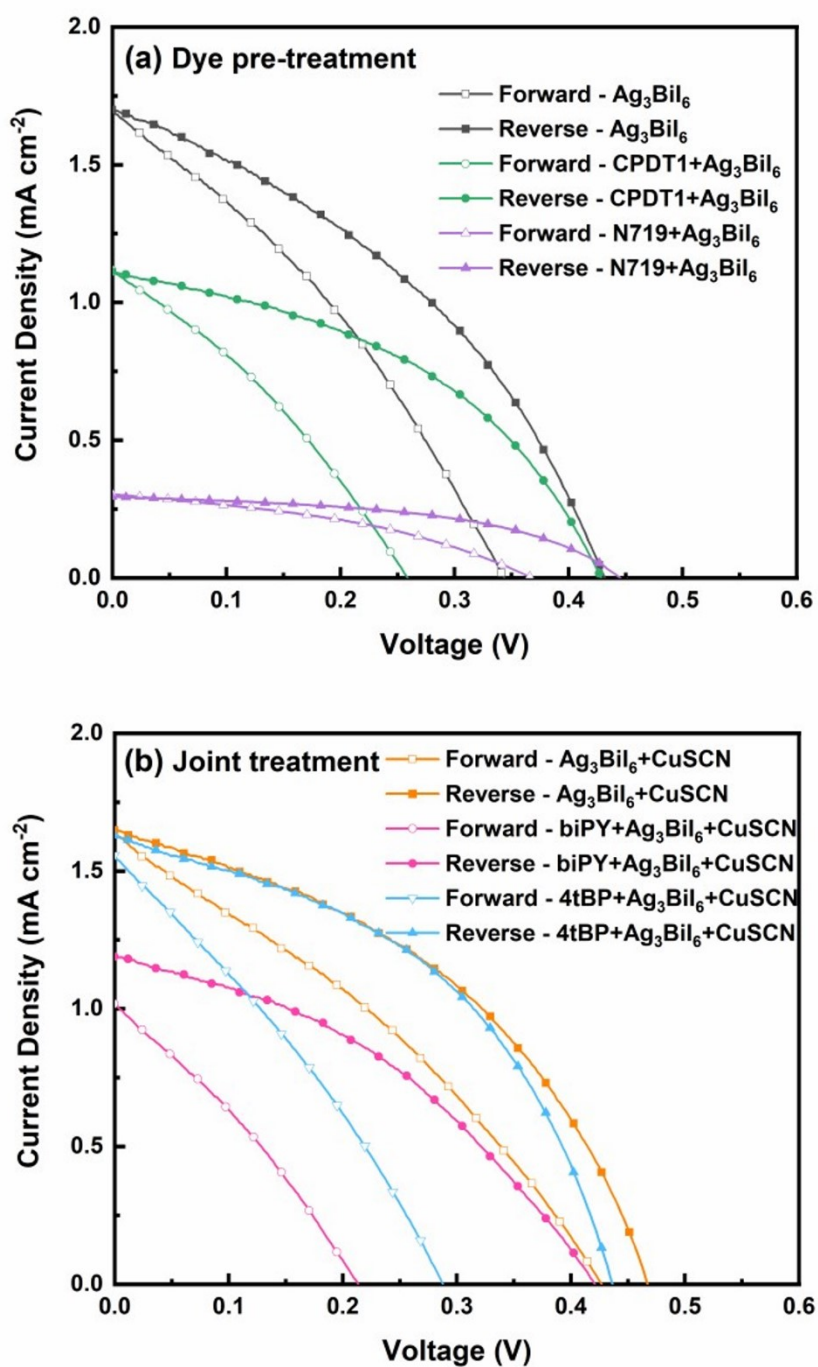
Figure S2 Cross-sectional EDS layered image of Ag_3BiI_6 with pre-treatment: (a) 4tBP, (b) biPY, (c) N719, (d) CPDT-1; and post-treatment: (e) CuSCN.
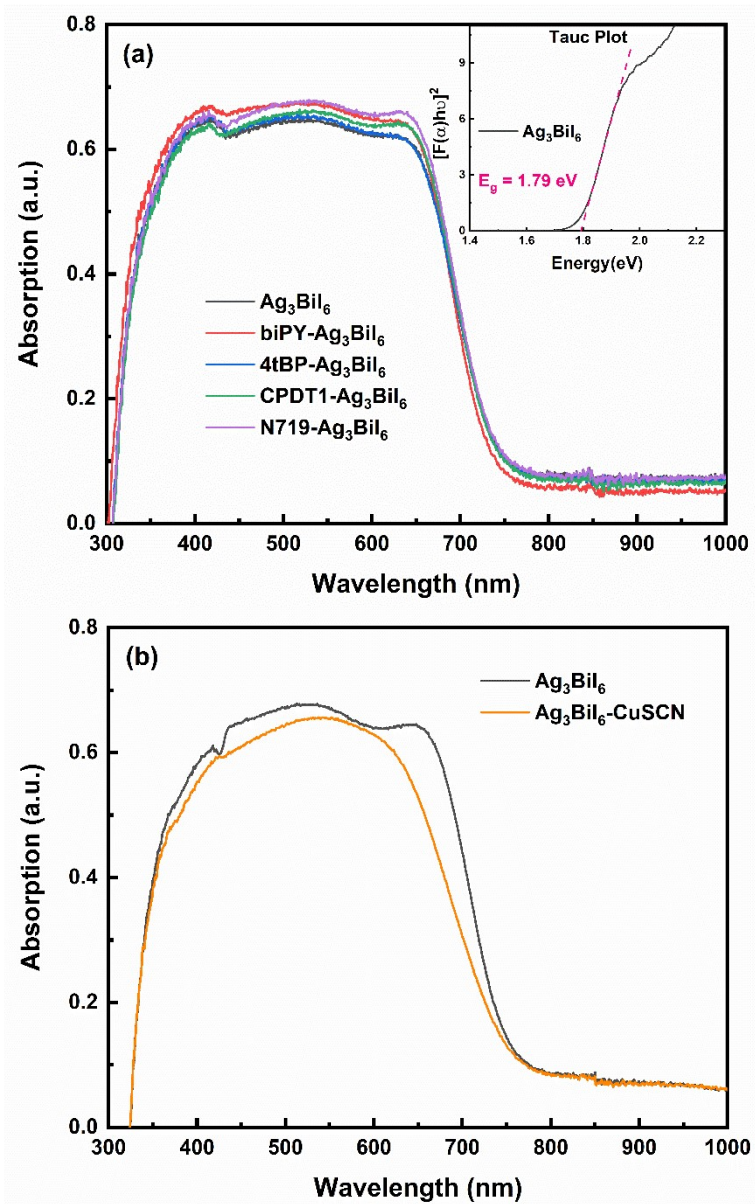
Figure S3 Absorption spectra of solid-state Ag_3BiI_6 with (a) pre-treatment and (b) post-treatment. Tauc-plot of the Ag_3BiI_6 is inserted in (a).

**Figure S4** XPS survey spectra of (a) Ag_3BiI_6 (red) and Ag_3BiI_6/CuSCN (blue) films; and (b) CuSCN.

**Figure S5** J-V curves of as-prepared Ag_3BiI_6 devices with (a) dye molecules and (b) joint-treatment.

Table S1 J-V characteristics of as-prepared Ag₃BiI₆ in TM-SCs based on different pre-treatments, CuSCN post-treatment and joint-treatments.

Device	Scan	J_{sc} [mA·cm-2]	V_{oc} [V]	*FF*	PCE [%]	HI*
Ag₃BiI₆ only	Forward	1.69 (1.48 ± 0.28)	0.34 (0.34 ± 0.02)	0.33 (0.31 ± 0.02)	0.19 (0.16 ± 0.04)	0.32
	Reverse	1.69 (1.50 ± 0.28)	0.43 (0.42 ± 0.02)	0.39 (0.36 ± 0.03)	0.28 (0.24 ± 0.06)	(0.32 ± 0.04)
Pre-biPY	Forward	1.12 (1.06 ± 0.16)	0.45 (0.44 ± 0.02)	0.32 (0.31 ± 0.04)	0.16 (0.14 ± 0.04)	0.39
	Reverse	1.05 (0.99 ± 0.12)	0.48 (0.48 ± 0.01)	0.53 (0.49 ± 0.04)	0.27 (0.23 ± 0.02)	(0.38 ± 0.13)
Pre-4tBP	Forward	1.22 (1.16 ± 0.20)	0.36 (0.36 ± 0.04)	0.33 (0.32 ± 0.04)	0.14 (0.13 ± 0.03)	0.55
	Reverse	1.34 (1.23 ± 0.28)	0.44 (0.44 ± 0.01)	0.53 (0.46 ± 0.07)	0.32 (0.24 ± 0.05)	(0.44 ± 0.14)
Pre-CPDT-1	Forward	1.11 (0.49 ± 0.39)	0.26 (0.31 ± 0.07)	0.32 (0.30 ± 0.06)	0.09 (0.04 ± 0.03)	0.56
	Reverse	1.11 (0.51 ± 0.40)	0.43 (0.44 ± 0.01)	0.44 (0.40 ± 0.05)	0.21 (0.09 ± 0.07)	(0.46 ± 0.20)
Pre-N719	Forward	0.30 (0.18 ± 0.07)	0.37 (0.37 ± 0.02)	0.52 (0.38 ± 0.04)	0.04 (0.03 ± 0.01)	0.33
	Reverse	0.29 (0.18 ± 0.07)	0.44 (0.44 ± 0.01)	0.50 (0.48 ± 0.04)	0.06 (0.04 ± 0.02)	(0.31 ± 0.02)
Post-CuSCN	Forward	1.63 (1.47 ± 0.21)	0.43 (0.40 ± 0.02)	0.32 (0.34 ± 0.05)	0.22 (0.20 ± 0.04)	0.31
	Reverse	1.65 (1.46 ± 0.21)	0.47 (0.46 ± 0.01)	0.42 (0.43 ± 0.04)	0.33 (0.29 ± 0.05)	(0.30 ± 0.06)
biPY/CuSCN	Forward	1.06 (0.91 ± 0.13)	0.23 (0.25 ± 0.03)	0.30 (0.29 ± 0.01)	0.07 (0.07 ± 0.01)	0.64
	Reverse	1.21 (1.05 ± 0.15)	0.42 (0.42 ± 0.01)	0.38 (0.39 ± 0.02)	0.20 (0.17 ± 0.03)	(0.61 ± 0.05)
4tBP/CuSCN	Forward	1.54 (1.10 ± 0.30)	0.29 (0.28 ± 0.01)	0.30 (0.28 ± 0.02)	0.13 (0.09 ± 0.03)	0.58
	Reverse	1.63 (1.23 ± 0.26)	0.43 (0.42 ± 0.02)	0.45 (0.40 ± 0.03)	0.32 (0.21 ± 0.07)	(0.59 ± 0.02)

*HI: Hysteresis index.
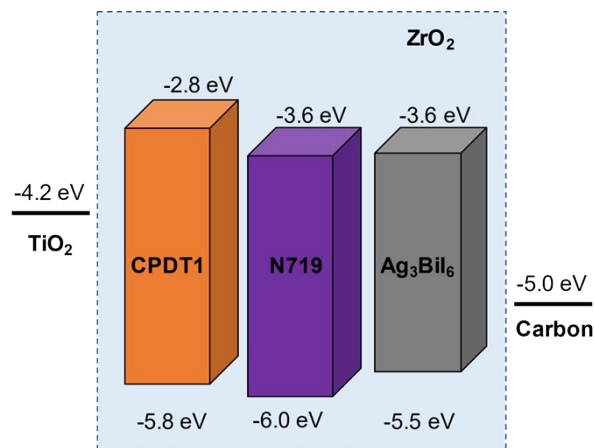
Figure S6 Energy level alignment diagram of CPDT-1, N719 and Ag₃BiI₆ in TM-SCs.
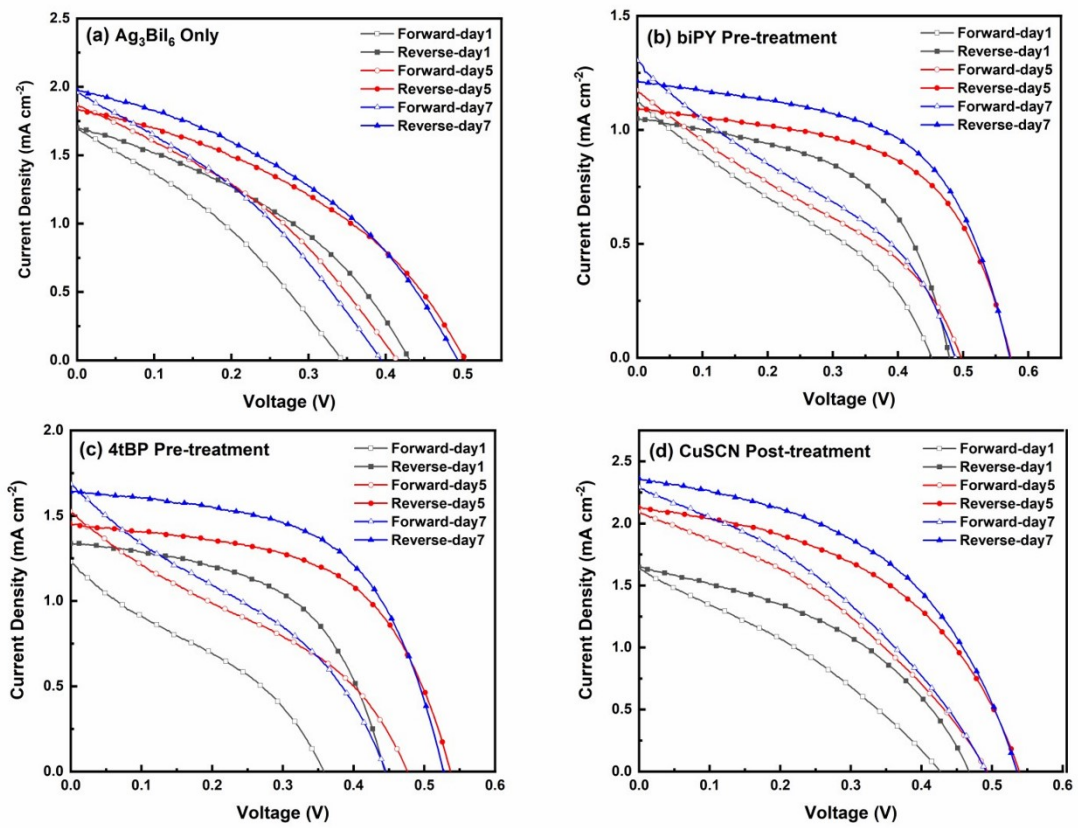
Figure S7 J-V curves of devices within one-week ageing: (a) Ag$_3$BiI$_6$ only, (b) biPY pre-treatment, (c) 4tBP pre-treatment and (d) CuSCN post-treatment.

Table S2 J-V characteristics of aged devices.

(a) J-V characteristics of Ag$_3$BiI$_6$ devices on day 1,5 and 7.

Days	Scan	J_{sc} [mA·cm^{-2}]	V_{oc} [V]	FF	PCE [%]	HI
Day 1	Forward	1.69 (1.48 ± 0.28)	0.34 (0.34 ± 0.02)	0.33 (0.31 ± 0.02)	0.19 (0.16 ± 0.04)	0.32
	Reverse	1.69 (1.50 ± 0.28)	0.43 (0.42 ± 0.02)	0.39 (0.36 ± 0.03)	0.28 (0.24 ± 0.06)	(0.32 ± 0.04)
Day 5	Forward	1.87 (1.61 ± 0.24)	0.41 (0.39 ± 0.03)	0.35 (0.33 ± 0.03)	0.27 (0.21 ± 0.06)	0.25
	Reverse	1.83 (1.62 ± 0.24)	0.50 (0.48 ± 0.05)	0.40 (0.37 ± 0.03)	0.36 (0.30 ± 0.08)	(0.28 ± 0.03)
Day 7	Forward	1.95 (1.75 ± 0.40)	0.39 (0.37 ± 0.05)	0.34 (0.32 ± 0.03)	0.26 (0.21 ± 0.08)	0.32
	Reverse	1.97 (1.79 ± 0.36)	0.49 (0.49 ± 0.02)	0.39 (0.35 ± 0.05)	0.38 (0.32 ± 0.10)	(0.34 ± 0.08)

(b) J-V characteristics of Ag$_3$BiI$_6$ devices with biPY pre-treatment on day 1,5 and 7.

| Days	Scan	J_{sc} [mA·cm^{-2}]	V_{oc} [V]	FF	PCE [%]	HI
Day 1	Forward	1.12 (1.06 ± 0.16)	0.45 (0.44 ± 0.02)	0.32 (0.31 ± 0.04)	0.16 (0.14 ± 0.04)	0.39
	Reverse	1.05 (0.99 ± 0.12)	0.48 (0.48 ± 0.01)	0.53 (0.49 ± 0.04)	0.27 (0.23 ± 0.02)	(0.38 ± 0.13)
Day 5	Forward	1.17 (1.01 ± 0.12)	0.50 (0.48 ± 0.01)	0.32 (0.31 ± 0.02)	0.19 (0.15 ± 0.03)	0.46
	Reverse	1.09 (0.96 ± 0.09)	0.57 (0.57 ± 0.01)	0.56 (0.50 ± 0.07)	0.35 (0.27 ± 0.05)	(0.43 ± 0.10)
Day 7	Forward	1.30 (1.12 ± 0.12)	0.49 (0.47 ± 0.02)	0.33 (0.33 ± 0.01)	0.21 (0.17 ± 0.03)	0.46
	Reverse	1.21 (1.07 ± 0.10)	0.57 (0.57 ± 0.01)	0.56 (0.50 ± 0.06)	0.39 (0.30 ± 0.05)	(0.42 ± 0.07)

(c) J-V characteristics of Ag$_3$BiI$_6$ devices with 4-tBP pre-treatment on day 1,5 and 7.

| Days	Scan	J_{sc} [mA·cm^{-2}]	V_{oc} [V]	FF	PCE [%]	HI
Day 1	Forward	1.22 (1.16 ± 0.20)	0.36 (0.36 ± 0.04)	0.33 (0.32 ± 0.04)	0.14 (0.13 ± 0.03)	0.55
	Reverse	1.34 (1.23 ± 0.28)	0.44 (0.44 ± 0.01)	0.53 (0.46 ± 0.07)	0.32 (0.24 ± 0.05)	(0.44 ± 0.14)
Day 5	Forward	1.52 (1.33 ± 0.28)	0.47 (0.45 ± 0.03)	0.33 (0.33 ± 0.02)	0.24 (0.19 ± 0.03)	0.45
	Reverse	1.45 (1.31 ± 0.28)	0.54 (0.51 ± 0.02)	0.56 (0.45 ± 0.09)	0.44 (0.30 ± 0.09)	(0.33 ± 0.15)
Day 7	Forward	1.68 (1.33 ± 0.26)	0.44 (0.42 ± 0.03)	0.34 (0.34 ± 0.03)	0.25 (0.19 ± 0.04)	0.48
	Reverse	1.64 (1.33 ± 0.27)	0.52 (0.51 ± 0.02)	0.57 (0.46 ± 0.09)	0.49 (0.31 ± 0.11)	(0.37 ± 0.10)

(d) J-V characteristics of Ag$_3$BiI$_6$ devices with CuSCN post-treatment within 28 days.

| Days	Scan	J_{sc} [mA·cm-2]	V_{oc} [V]	FF	PCE [%]	HI
Day 1	Forward	1.63 (1.47 ± 0.21)	0.43 (0.40 ± 0.02)	0.32 (0.34 ± 0.05)	0.22 (0.20 ± 0.04)	0.31
	Reverse	1.65 (1.46 ± 0.21)	0.47 (0.46 ± 0.01)	0.42 (0.43 ± 0.04)	0.33 (0.29 ± 0.05)	(0.30 ± 0.06)
Day 5	Forward	2.09 (1.90 ± 0.33)	0.49 (0.45 ± 0.04)	0.36 (0.37 ± 0.05)	0.38 (0.32 ± 0.06)	0.30
	Reverse	2.13 (1.90 ± 0.38)	0.54 (0.51 ± 0.03)	0.47 (0.47 ± 0.05)	0.53 (0.45 ± 0.05)	(0.30 ± 0.09)
Day 7	Forward	2.28 (2.16 ± 0.53)	0.49 (0.45 ± 0.03)	0.36 (0.37 ± 0.04)	0.40 (0.35 ± 0.07)	0.32
	Reverse	2.35 (2.17 ± 0.62)	0.53 (0.51 ± 0.02)	0.47 (0.48 ± 0.05)	0.60 (0.52 ± 0.09)	(0.32 ± 0.07)
Day 14	Forward	2.06 (2.04 ± 0.58)	0.50 (0.48 ± 0.04)	0.39 (0.39 ± 0.06)	0.40 (0.38 ± 0.13)	0.26
	Reverse	2.10 (2.02 ± 0.61)	0.54 (0.52 ± 0.03)	0.48 (0.49 ± 0.05)	0.55 (0.50 ± 0.13)	(0.25 ± 0.09)
Day 21	Forward	2.22 (2.14 ± 0.54)	0.51 (0.49 ± 0.05)	0.39 (0.39 ± 0.06)	0.44 (0.41 ± 0.12)	0.26
	Reverse	2.27 (2.12 ± 0.60)	0.54 (0.53 ± 0.03)	0.48 (0.48 ± 0.05)	0.59 (0.54 ± 0.11)	(0.24 ± 0.12)
Day 28	Forward	2.74 (2.31 ± 0.76)	0.53 (0.49 ± 0.05)	0.37 (0.38 ± 0.06)	0.54 (0.43 ± 0.14)	0.27
	Reverse	2.78 (2.30 ± 0.81)	0.56 (0.54 ± 0.03)	0.48 (0.49 ± 0.05)	0.74 (0.59 ± 0.15)	(0.28 ± 0.09)

The average results in bracket were calculated from 5 individual devices for each type.
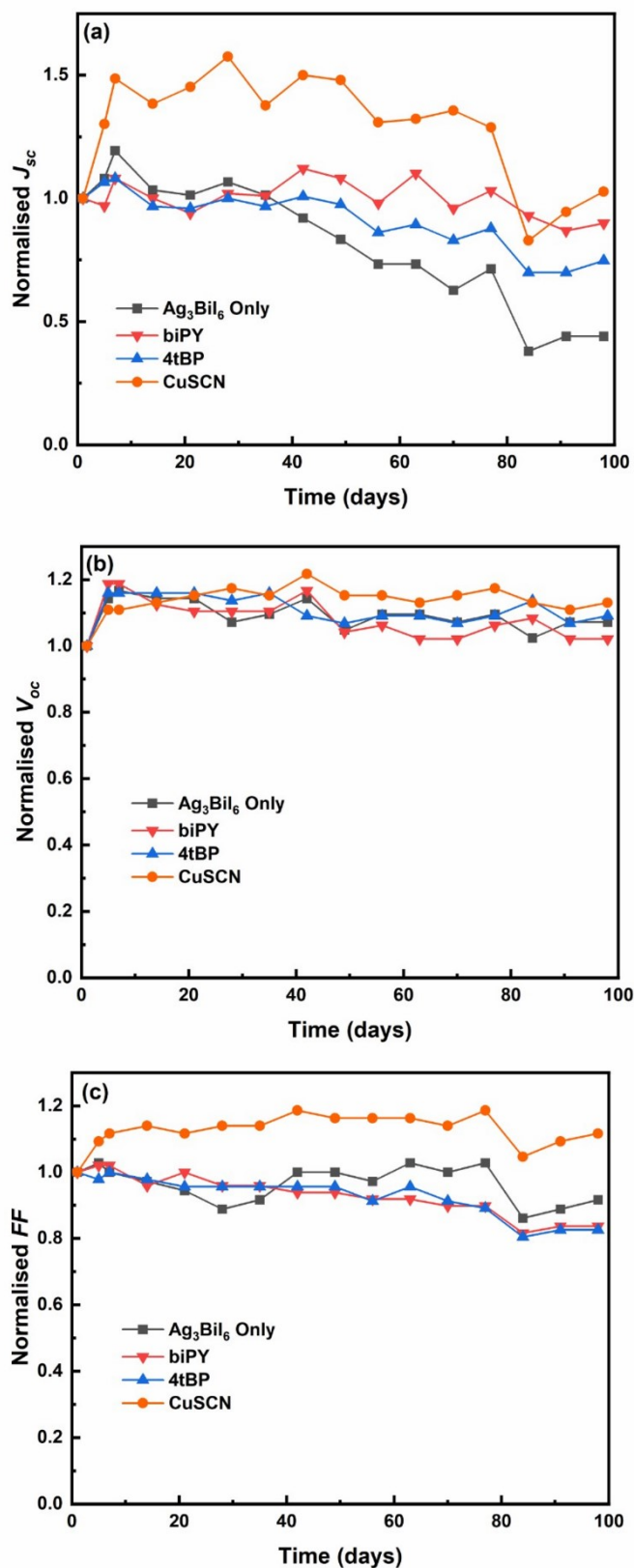
Figure S8 Dark storage stability (reverse scan) of Ag_3BiI_6 device regarding (a) J_{sc}, (b) V_{oc} and (c) FF in atmosphere.
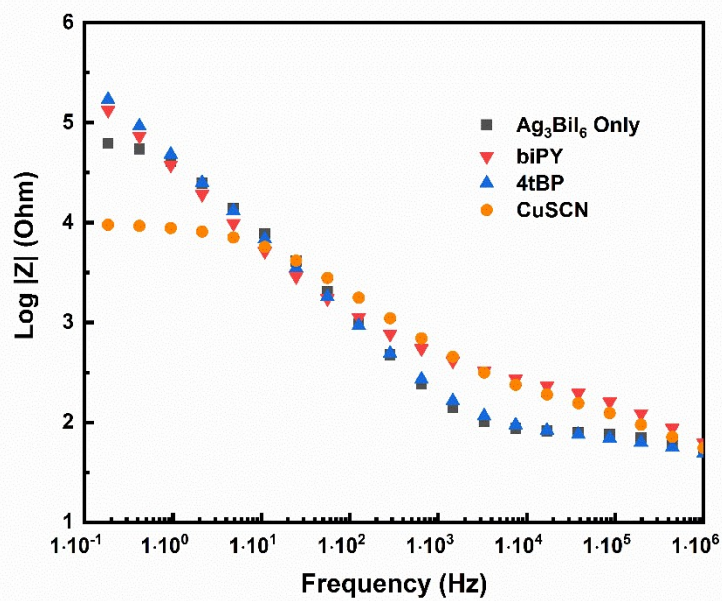
Figure S9 Bode plots of Ag_3BiI_6 TM-SCs with different treatment at 450 mV under dark.
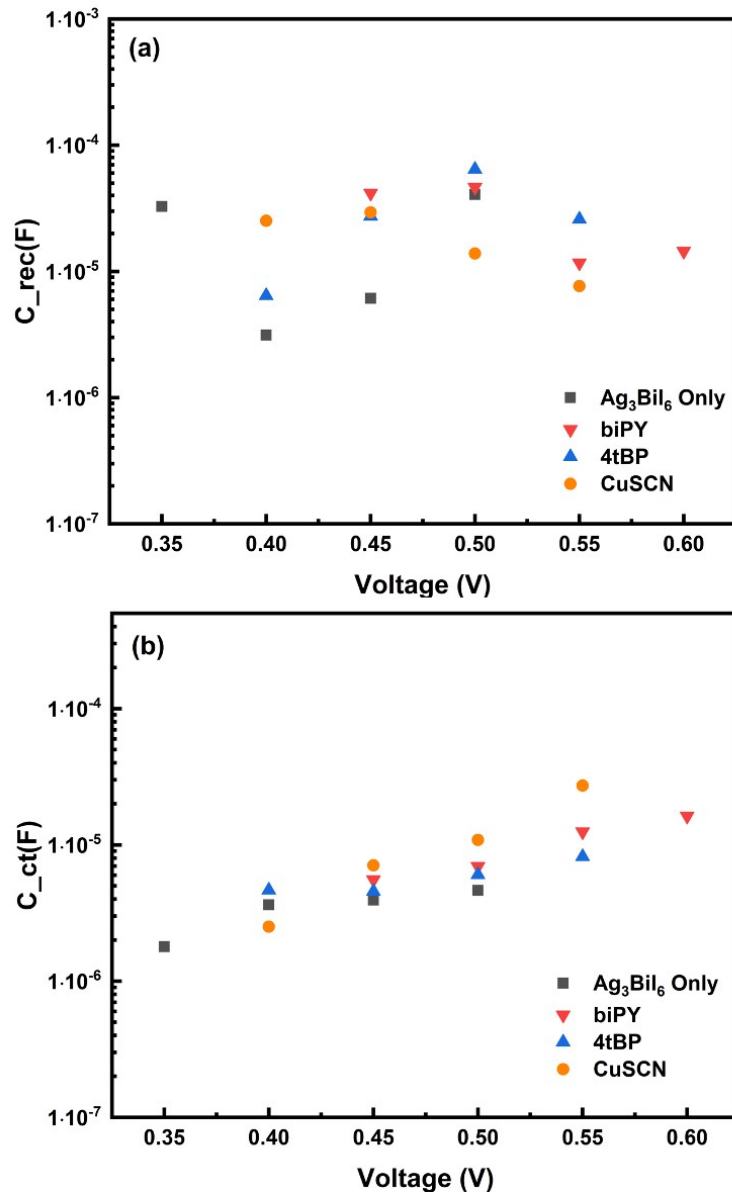
Figure S10 Values of extracted resistance of (a) C_{rec} and (b) C_{ct} obtained from EIS of Ag$_3$BiI$_6$ devices at given bias under dark.