Supplementary Information

One plus one greater than two: high-performance inverted planar perovskite solar cells based on a composite CuI/CuSCN hole-transporting layer

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Supplementary Figures and Tables:

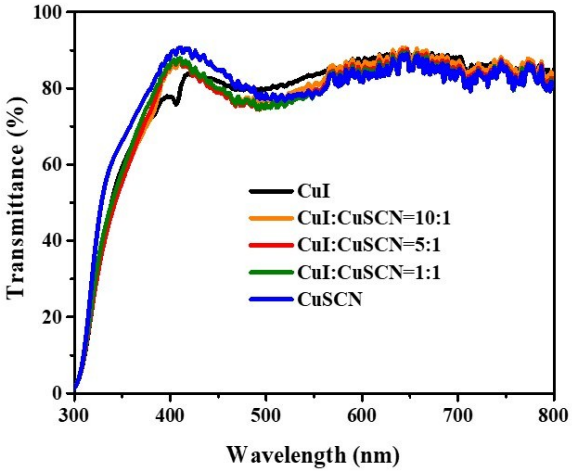
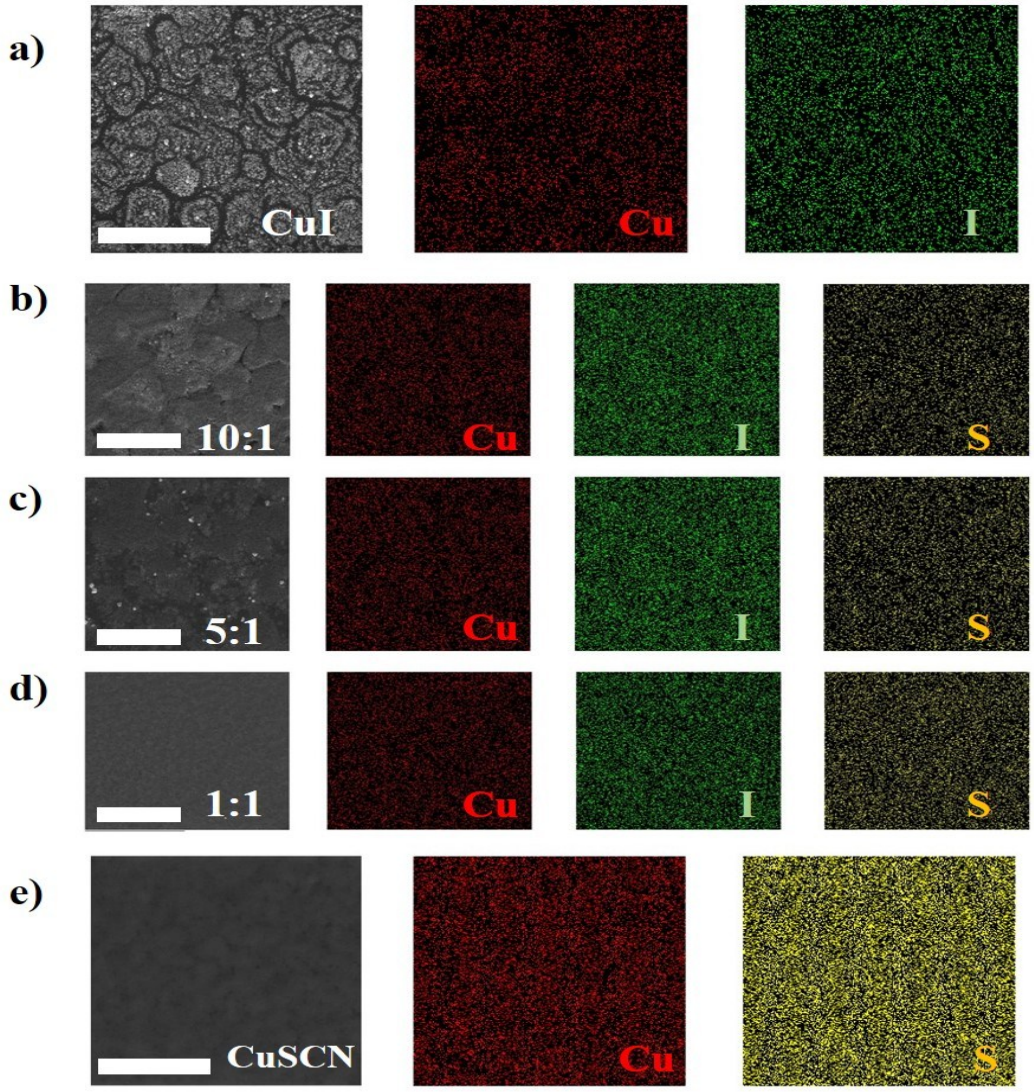


Fig. S1 Optical transmission spectra of the different HTL films with thicknesses of ~30 nm on ITO substrates.



Samples	Cu	I	S	I/S atomic ratio
CuI	2.62 %	4.86 %	----	----
10:1	10.65 %	10.60 %	1.86 %	5.73
5:1	4.78 %	4.62 %	1.36 %	3.40
1:1	4.12 %	2.36 %	2.07 %	1.14
CuSCN	5.29 %	----	4.89 %	----

Fig. S2 EDS elemental mapping of Cu, I, and S in different HTLs on ITO substrates obtained from top-view SEM images: a) CuI, b) CuI:CuSCN = 10:1, c) CuI:CuSCN = 5:1, d) CuI:CuSCN = 1:1, and e) CuSCN. The scale bar is 7 µm.

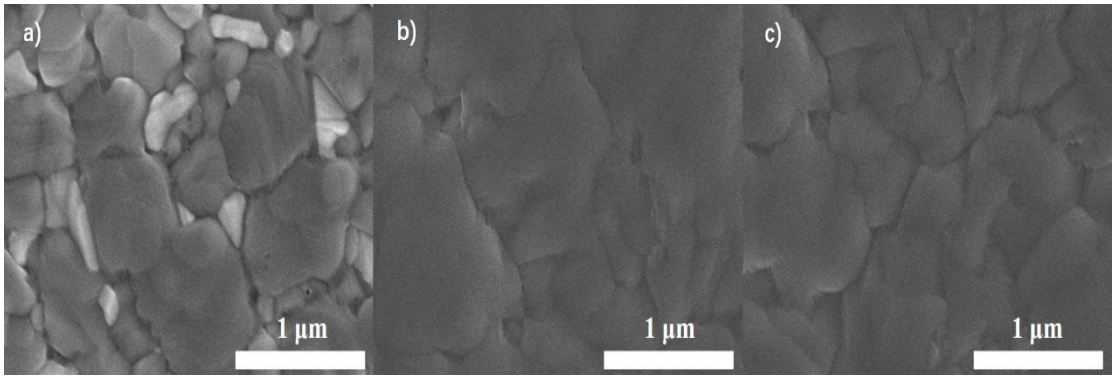


Fig. S3 Top-view SEM images of $MAPbI_{3-x}Cl_x$ perovskite deposited on a) CuI, b) CuI/CuSCN = 5:1, and c) CuSCN substrates, respectively.

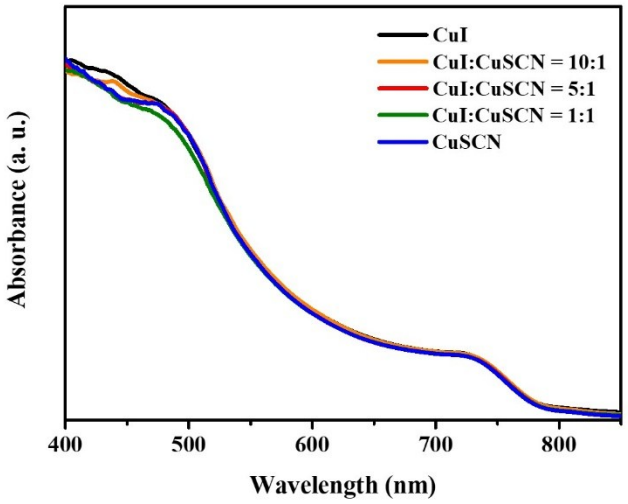


Fig. S4 UV-visible absorption spectra of the perovskite films deposited on different HTL substrates.

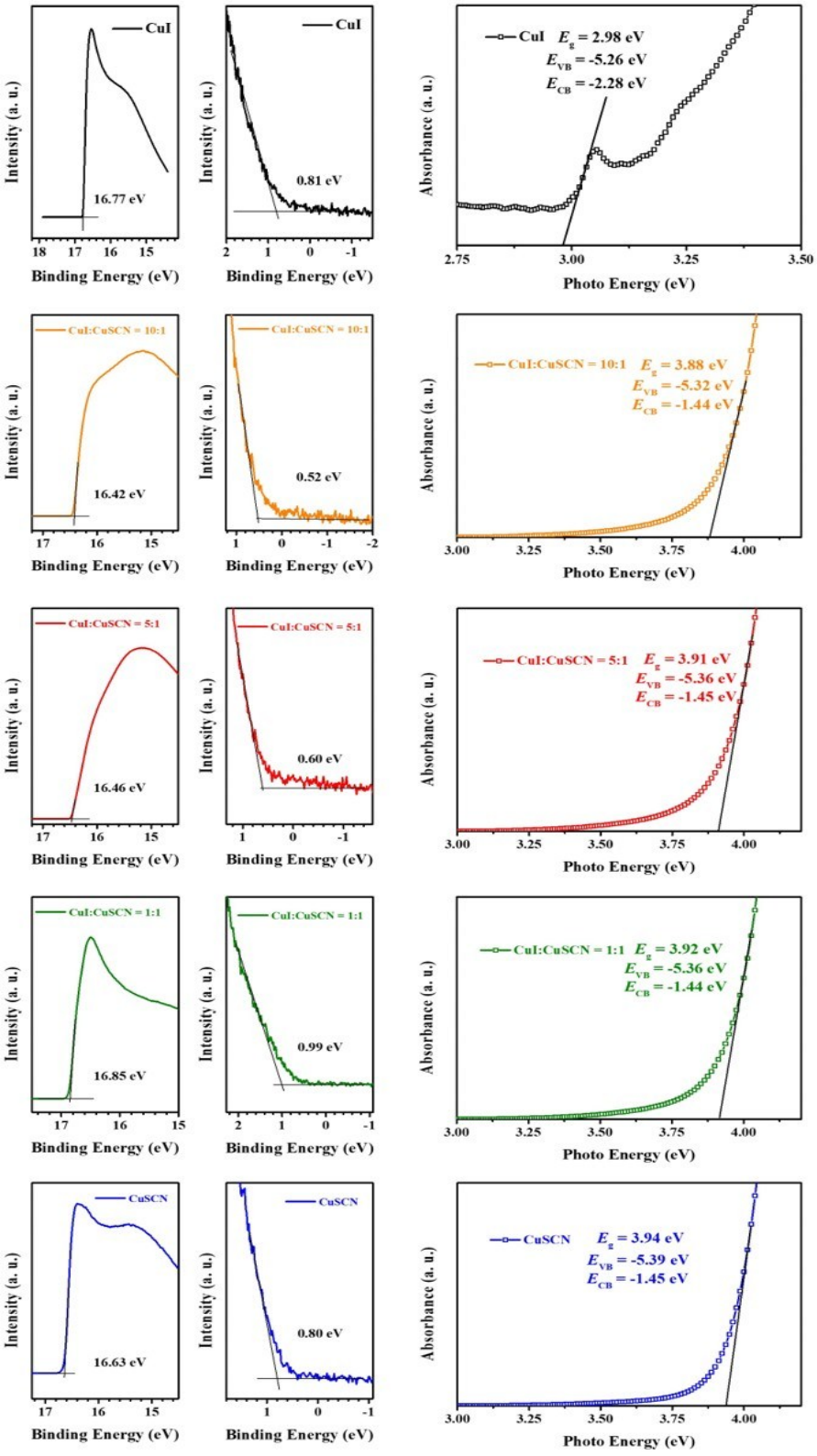


Fig. S5 UPS spectra of different HTLs on ITO substrates and the Tauc plot of the absorbance spectra for different HTLs on ITO substrates.

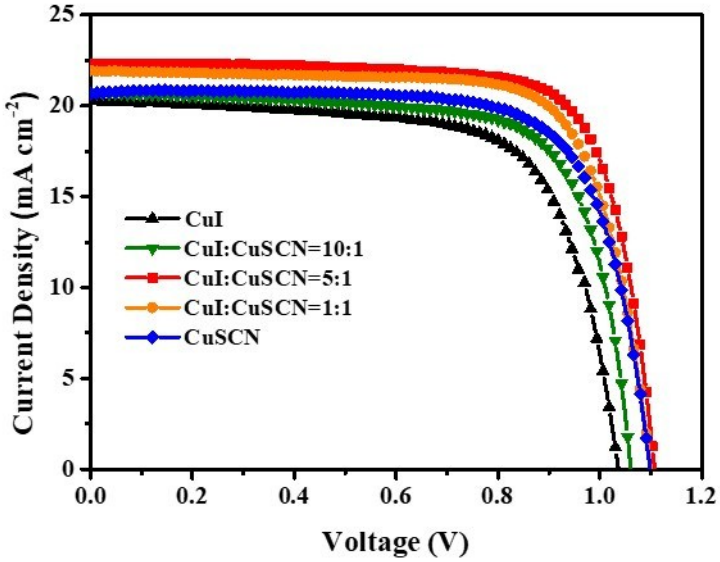


Fig. S6 *J*–*V* curves of the best PSCs based on different HTLs under 100 mW cm^{-2} irradiation (AM 1.5G).

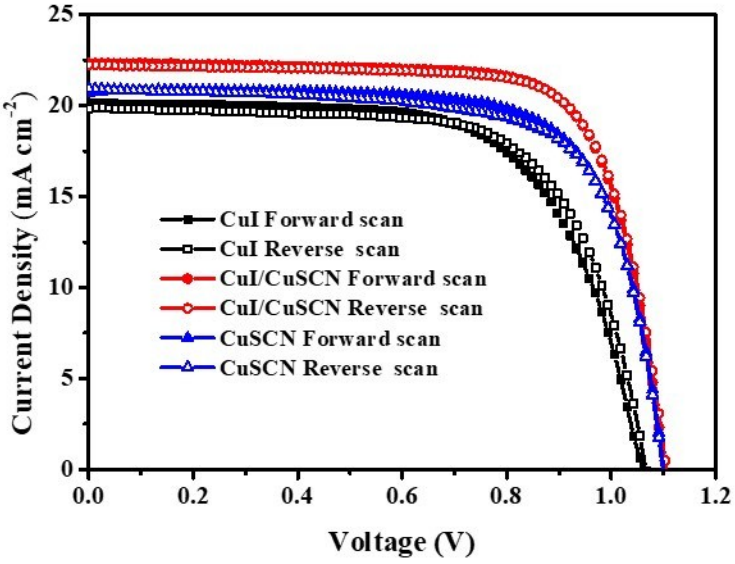


Fig. S7 *J*–*V* curves of PSCs containing CuI, CuI/CuSCN, and CuSCN as HTLs measured at different scan directions under 100 mW cm^{-2} illumination (AM 1.5G).

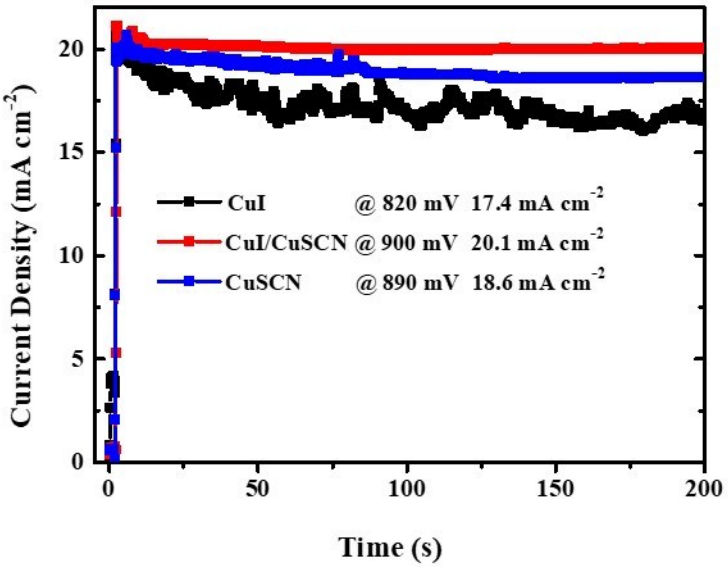


Fig. S8 The steady-state photocurrent density at the maximum power point of the corresponding PSCs under continuous simulated one sun illumination for 200 s.

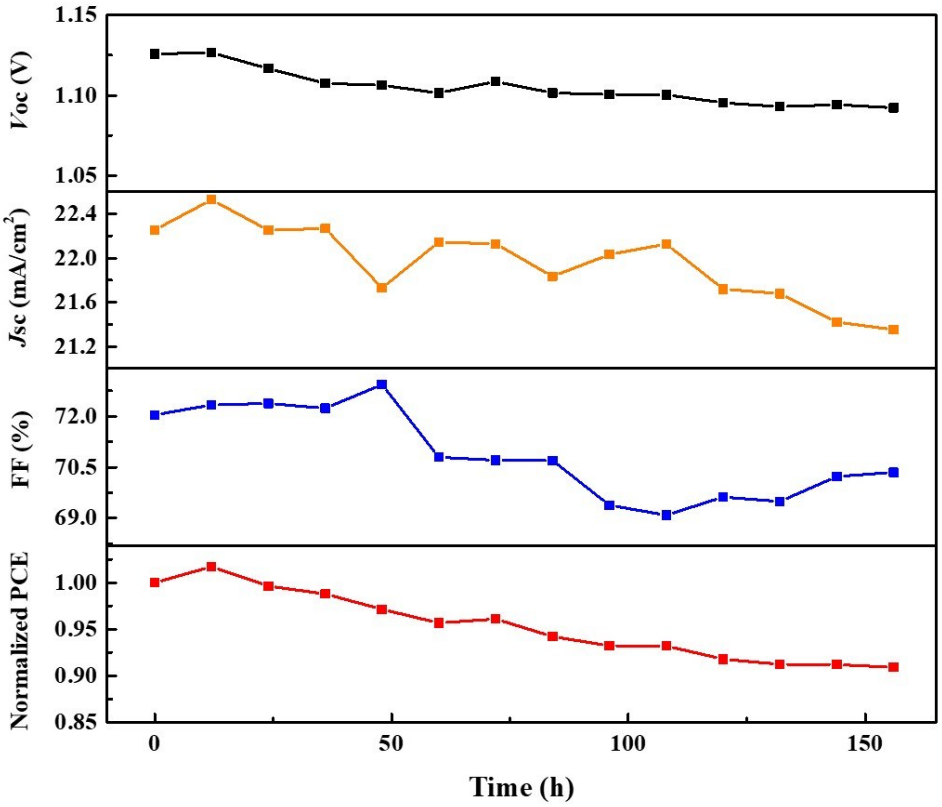


Fig. S9 Evolution of photovoltaic parameters of a representative PSC device based on CuI/CuSCN as HTLs measured at reverse scan under continuous one sun illumination (100 mW cm^{-2}, AM 1.5G) with encapsulation.

Table S1. The conductivity of different HTLs obtained from four-point probe measurements.

Samples	Conductivity	Reference Value
CuI	–	10–100 S/m[S1]
10:1	0.23 S/m	–
5:1	0.20 S/m	–
1:1	0.14 S/m	–
CuSCN	0.093 S/m	0.1–1 S/m[S2]

Table S2. Photovoltaic parameters of the optimized PSCs with different HTLs under 100 mW cm^{-2} illumination (AM 1.5G).

HTL	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	R_s (Ω cm^2)	R_{sh} (Ω cm^2)
CuI	1.05	20.05	0.69	14.53	6.09	1467.45
10:1	1.08	20.42	0.69	15.40	5.58	1573.55
5:1	1.11	22.33	0.76	18.76	3.05	5642.99
1:1	1.10	21.39	0.74	17.52	4.04	4683.25
CuSCN	1.10	20.76	0.73	16.66	4.44	4434.95

Table S3. Photovoltaic parameters of the best-performing PSCs with different thicknesses of HTLs under 100 mW cm^{-2} illumination (AM 1.5G).

HTL	Conc. (M)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
CuI	0.04	1.00	12.50	0.65	8.08
	0.08	1.05	20.05	0.69	14.53
	0.12	1.01	18.06	0.65	11.73
CuI/CuSCN	0.04	1.08	18.65	0.72	14.47
	0.08	1.11	22.33	0.76	18.76
	0.12	1.10	20.76	0.73	16.66
CuSCN	0.04	1.07	19.32	0.67	13.77
	0.08	1.10	20.76	0.73	16.66
	0.12	1.07	19.90	0.70	15.03

Table S4. Photovoltaic parameters of of the PSCs with different HTL measured at different scan directions under100 mW cm^{-2} illumination (AM 1.5G).

HTL	*Scan directions*	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
CuI	Forward	1.05	20.18	0.63	13.31
	Reverse	1.06	19.89	0.68	14.36
CuI/CuSCN	Forward	1.11	22.35	0.74	18.36
	Reverse	1.11	22.26	0.75	18.34
CuSCN	Forward	1.10	20.82	0.72	16.56
	Reverse	1.10	20.90	0.71	16.33

Table S5. Summary of the PL lifetime parameters from fitting curves of the TRPL decay measurements.

Samples	A_1	τ_1 [ns]	A_2	τ_2 [ns]	*Weighted average* τ [ns]
w/o HTL	0.48	25.00	0.52	95.26	81.56
CuI	0.86	6.65	0.14	19.70	19.43
CuI/CuSCN	0.97	3.52	0.03	11.60	4.27
CuSCN	0.98	4.90	0.02	23.35	6.54

Table S6. Photovoltaic parameters of PSCs based on CuI/CuSCN as HTLs measured at reverse scan under continuous 1 sun illumination (100 mW cm^{-2}, AM 1.5G) with encapsulation at different stages during stability test.

Time	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
0 h	1.13	22.25	0.72	18.05
48 h	1.11	21.72	0.73	17.53
96 h	1.10	22.03	0.69	16.82
156 h	1.09	21.35	0.70	16.41

References

S1. W. Yan, S. Ye, Y. Li, W. Sun, H. Rao, Z. Liu, Z. Bian, C. Huang, *Adv*. *Energy Mate*r., 2016, **6**, 1600474.

S2. F.-L. Schein, H. von Wenckstern, M. Grundmann, *Appl*. *Phys*. *Lett*., 2013, **2**, 092109.