SUPPORTING INFORMATION

Efficient Fully-Vacuum-Processed Perovskite Solar Cells Using Copper Phthalocyanine as Hole Selective Layers

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Fig. S1 XRD pattern of a 370 nm perovskite film deposited on an FTO substrate covered with a 5.5 nm C_{60} ESL.



Fig. S2 AFM images of (a) a 370 nm perovskite film deposited on an FTO substrate covered with a 5.5 nm C_{60} ESL and (b) a 60 nm CuPc film deposited on a 370 nm perovskite film.



Fig. S3 Top view SEM images of (a) a 20 nm, (b) a 40 nm (c) a 60 nm, (d) an 80 nm, and (e) a 100 nm CuPc films deposited on 370 nm perovskite films covered with 5.5 nm C_{60} ESLs.



Fig. S4 The linear curves of the relationship of -dV/dJ and $(J_{sc}-J)^{-1}$.



Fig. S5 *J-V* curves of the all-vacuum-processed perovskite solar cells using 60 nm CuPc HSLs and perovskite films with different thicknesses measured under reverse voltage scanning and AM1.5G illumination.



Fig. S6 Histograms of (a) V_{oc} 's, (b) J_{sc} 's, (c) FFs, and (d) PCEs for 40 cells using 5.5 nm C₆₀ ESLs, 370 nm CH₃NH₃PbI₃ films, and 60 nm CuPc HSLs measured under reverse voltage scanning.



Fig. S7 *J-V* curve of the best-performing perovskite solar cell using a 5.5 nm C_{60} ESL, a 370 nm CH₃NH₃PbI₃ film, and a 60 nm CuPc HSL on a PET/ITO flexible substrate measured under revers voltage scanning and AM1.5G illumination.



Fig. S8 (a) J-V curves of the best-performing perovskite solar cell using a 5.5 nm C₆₀ ESL, a 370 nm CH₃NH₃PbI₃ film, and a spiro-OMeTAD HSL measured under reverse and forward voltage scanning and AM1.5G illumination. (b) EQE spectrum of the best-performing cell using the spiro-OMeTAD HSL.



Fig. S9 Steady-state efficiency of the best-performing perovskite solar cell using a 5.5 nm C_{60} ESL, a 370 nm $CH_3NH_3PbI_3$ film, and a spiro-OMeTAD HSL at a constant bias voltage of 0.867 V and AM1.5G illumination.



Fig. S10 Nyquist plots of the perovskite solar cells using a spiro-OMeTAD HSL and a CuPc HSL in the dark.



Fig. S11 *J-V* curves of the perovskite solar cells without encapsulation using a spiro-OMeTAD HSL and a CuPc HSL measured under reverse voltage scanning and AM1.5G illumination after fabrication and 500 h later with exposure to ambient air. These devices were stored in ambient air without illumination. The humidity of the atmosphere was about 20%.

Table S1 Summary of photovoltaic parameters of the all-vacuum-processed perovskite solar cells using 60 nm CuPc HSLs and perovskite films with different thicknesses measured under reverse voltage scanning. The data are taken from Fig. S5.

CH ₃ NH ₃ PbI ₃ thickness	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
[nm]	[V]	$[mA_{2}cm^{-}]$	[%]	[%]
330	1.02	16.93	76.83	13.32
370	1.04	18.68	78.23	15.15
410	0.98	18.92	72.28	13.40

 $V_{\rm oc}$, open circuit voltage); $J_{\rm sc}$, short circuit current; FF, fill factor; PCE, power conversion efficiency.

Table S2 Summary of photovoltaic parameters of the best-performing perovskite solar cells using 5.5 nm C_{60} ESLs, 370 nm CH₃NH₃PbI₃ films, a spiro-OMeTAD HSL and a CuPc HSL measured under different voltage scanning with AM1.5G illumination. The data are taken from Fig. 5a and Fig. S8a.

	V _{oc}	$J_{ m sc}$	FF	PCE
	[V]	$[mA_{2}cm^{-2}]$	[%]	[%]
Spiro-OMeTAD Reverse	1.05	19.55	67.74	13.89
Spiro-OMeTAD Forward	1.03	19.48	66.78	13.36
Spiro-OMeTAD Average	1.04	19.52	67.26	13.63
CuPc Reverse	1.04	19.13	77.47	15.42
CuPc Forward	1.02	19.04	72.25	13.98
CuPc Average	1.03	19.09	74.86	14.7

Table S3 Summary of photovoltaic parameters of the perovskite solar cells without encapsulation using a spiro-OMeTAD HSL and a CuPc HSL measured under reverse voltage scanning and AM1.5G illumination after fabrication and 1000 h later with exposure to ambient air. The data are taken from Fig. S11.

	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
	[V]	$[mA_{2}cm^{2}]$	[%]	[%]
0 h Spiro-OMeTAD	1.04	19.19	68.59	13.66
1000 h Spiro- OMeTAD	0.97	17.57	49.18	8.38
0 h CuPc	1.03	18.54	74.63	14.21
1000 h CuPc	1.03	17.98	74.83	13.83