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Electronic Supporting Information

Antisolvent treatment of copper(I) thiocyanate (CuSCN) hole transport layer for efficiency improvements in organic solar cells and light-emitting diodes

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Experimental

CuSCN solution preparation. CuSCN solution was prepared by dissolving copper(I) thiocyanate powder (CuSCN, 99%, Sigma-Aldrich) in diethyl sulfide (DES, 98%, Sigma-Aldrich) at 20 mg ml^{-1}. The solution was stirred overnight and filtered using a nylon filter with 0.22-μm pore size under N_2 atmosphere inside a glove box.

CuSCN film deposition. Substrates were cleaned by sonicating sequentially in 1%v/v detergent solution (Liquinox, Alconox Inc.), deionization water, acetone, and isopropanol, each for 30 min then dried with N_2. Prior to usage, substrates were treated by UV ozone to improve the wettability. For the pristine (untreated) films, 100 μl of CuSCN solution was deposited onto the substrates by spin-coating at 3500 rpm for 60 s and annealed at 100 °C for 30 min in the glove box. For the treated films, 200 μl of an antisolvent was dispensed dynamically halfway during the spin-coating process (at 30 s mark). The antisolvents employed were tetrahydrofuran (THF, ≥95%, Honeywell), acetone (Ace, ≥95%, Carlo Erba), methanol (MeOH, >99.9%, Honeywell), or isopropanol (IPA, ≥95%, Carlo Erba). The resulting films were also annealed at 100 °C for 30 min in a glove box.

Film morphology characterization. The surface topography of pristine and antisolvent-treated CuSCN films was characterized by an atomic force microscope (Park Systems NX10) operated in a non-contact mode using Si cantilevers (Olympus OMCL-AC160TS, 7-nm tip radius, 26-N m^{-1} stiffness, 300-kHz resonance frequency). The histogram of AFM Z-height (Z_{AFM}) and the root-mean-square surface roughness (σ_{rms}) were obtained from 5 × 5 μm^2 images while the average grain size (D_{avg}) was obtained from 0.5 × 0.5 μm^2 images. All AFM images were processed using Gwyddion software (http://gwyddion.net/).[1] The thickness of the films was measured by a profilometer (Bruker Dektak XT).

Organic solar cell fabrication. CuSCN HTL (either untreated or antisolvent-treated) was deposited according to the procedure described above onto pre-patterned ITO-coated glass substrates (Instrument Glasses, ITO thickness ~90 nm, sheet resistance ≤ 20 Ω sq^{-1}). For reference devices, poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS, Clevios P VP AI4083, Heraeus) was employed as the HTL; it was spin-cast on ITO substrates at 5000 rpm for 30 s and annealed at 150 °C for 10 min, yielding 40-nm films. The photoactive bulk heterojunction (BHJ) layer was prepared by dissolving poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b'] dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl)] (PTB7-Th or PCE10, Ossila) in chlorobenzene (anhydrous, 99.8%, Sigma-Aldrich) at a concentration of 8.4 mg ml^{-1}. The solution was stirred at 75 °C for 2 h inside a glove box. After that, the PTB7-Th solution was filtered with a 0.45-μm PTFE filter and blended with 12.6 mg of [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$, > 99%, Ossila). The blend solution was continuously stirred at 75 °C for 8 h, after which 30 μl of 1,8 diiodooctane (DIO, 98%, TCI Chemicals) additive was added to the BHJ solution. The final solution was spin-coated onto the HTL at 1750 rpm for 30 s, and methanol was dispensed onto the BHJ film at 4000 rpm to remove the additive. The resulting BHJ films had a thickness of 90 nm and were kept overnight under vacuum (< 5.0×10^{-6} Torr or 6.7×10^{-4} Pa). The cells were completed by thermally evaporating 10 nm of bathocuproine (BCP, 95%, TCI) and 100 nm Al cathode through shadow masks under a base pressure of 5×10^{-6} bar using a physical vapor deposition system (ALS Technology E200 or Kurt J. Lesker Minispectros). The active area of each cell was 0.0707 cm^2. All fabrication steps were carried out under N_2 atmosphere in a glove box.

Organic solar cell characterization. Solar cell devices were packed into a sealed sample holder under N_2 atmosphere in a glove box prior to electrical measurements. The cells were illuminated with AM 1.5G spectrum from a solar simulator (SAN-EI ELECTRIC XES-301S), and the current density-voltage (J-V) curves were obtained with a source meter unit (ADCMT 6241A).

External and internal quantum efficiency (EQE and IQE) measurements. EQE spectra of the cells were obtained by a spectral response measurement system (Bunkoukeiki SM-250) equipped with a xenon light source and a monochromator under ambient environment. The irradiation intensity of each wavelength was measured with a calibrated silicon photodiode. The calculated J_{sc} of the cells were obtained from the EQE spectra using SR_PRO software. IQE spectra were calculated from

$$\text{IQE} = \frac{EQE}{(1-\%R)} \quad \text{(S1)},$$

where %R is the optical reflectance of devices measured using an ultraviolet-visible spectrophotometer equipped with an integrating sphere (PerkinElmer LAMBDA 1050).

Impedance spectroscopy (IS). Complex impedance spectra were recorded by an impedance gain-phase analyzer (Solartron 1260A) in the dark under N_2 atmosphere. A 50-mV AC sinusoidal signal with a 0.8-V DC bias (open-circuit condition) was applied during the measurements for the frequency range between 10 Hz and 1 MHz. The complex impedance data were fitted with an equivalent circuit as reported in main text using ZView software. The fitting parameters consist of: R_s = series resistance (contact), R_t = transport resistance across the cell, C_{geo} = geometric capacitance of the cell, R_{rec} = recombination resistance, and CPE = constant phase element or a non-ideal capacitor. R_{rec} in parallel with a CPE is related to internal charge transfer events.[2,3] The equivalent capacitance (C_{eq}) of the CPE is

$$C_{eq} = \frac{\tau_{avg}}{R_{rec}} = \frac{(R_{rec}Q)^{1/n}}{R_{rec}} \quad \text{(S2)},$$

in which τ_{avg} = average relaxation time, Q = magnitude of the CPE, and n = ideality factor. An ideal capacitor has n = 1.

Space charge limited current (SCLC) analysis. Hole mobility values of the CuSCN/BHJ stacks were obtained by SCLC analysis of hole-only devices. The device structure consisted of ITO/CuSCN/PTB7-th:$PC_{71}BM/MoO_3$/Au. 10 nm of MoO_3 and 60 nm of Au were also deposited by thermal evaporation, and the rest of the structure was fabricated using the same procedure as described for solar cell fabrication. The carrier mobilities were obtained by fitting the dark currents of hole-only devices to the Murgatroyd expression,[4,5]

$$J = \frac{9}{8}\mu\varepsilon\varepsilon_0 \exp\left(0.891\gamma\sqrt{\frac{V-V_{bi}}{L}}\right)\frac{(V-V_{bi})^2}{L^3} \quad \text{(S3)},$$

where μ_0 = zero-field mobility, L = thickness of the BHJ layer, V_{bi} = built-in voltage, ε_0 = vacuum permittivity, ε_r= relative dielectric constant, and β is field activation factor.

Organic light-emitting diode fabrication and characterization. CuSCN HTL was deposited onto ITO substrates by spin-coating at 2000 rpm for 60 s. The THF antisolvent treatment and the annealing step followed the same procedure described above. For reference devices, PEDOT:PSS was employed as the HTL and deposited according to the same procedure as described for the solar cell fabrication. The emissive layer (EML) was prepared by mixing 850 µl of 20 mg ml^{-1} solution of 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP, 99.5%, Ossila) in chlorobenzene with 150 µl of 20 mg ml^{-1} solution of bis(2-phenylpyridine)(acetylacetonate) iridium(III) [$Ir(ppy)_2$(acac), 99.5%, Ossila] also in chlorobenzene. The mixed solution was stirred for 2 h under N_2 atmosphere in a glove box before depositing on top of the HTL at 2000 rpm for 60 s and drying at room temperature, yielding EML films with a thickness of 50 nm. Subsequently, 40 nm of 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi, >98%, TCI), 0.5 nm of LiF, and 100 nm of Al were thermally evaporated through shadow masks to complete the device structure. The active area of each device was 0.04 cm^2. Current density-voltage-luminance (*J*-*V*-*L*) characteristics of the devices were measured using a source meter (Keithley 2400) and a spectral measurement system (Hamamatsu Photonics PMA-12). The absolute EQE was obtained by a quantum efficiency measurement system equipped with an integrating sphere (Hamamatsu Photonics C9920-12). All measurements were performed under ambient atmosphere at room temperature.

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Table S1 Average grain size (D_{avg}), root-mean-square roughness (σ_{rms}), and film thickness (h) data from AFM and profilometry measurements of CuSCN films treated with different antisolvents.

Film	**Treatment**	D_{avg} **(nm)**	σ_{rms} **(nm)**	h **(nm)**
CuSCN	Untreated	9.0	4.0	47
	THF	7.7	3.3	103
	Ace	8.4	3.4	83
	MeOH	8.8	3.7	83
	IPA	8.6	3.4	84

Table S2 Device parameters of OPV cells employing CuSCN treated by different antisolvents as a hole-transport layer (HTL). Results of devices based on PEDOT:PSS HTL are also included as a reference. The maximum (Max) or minimum (Min), average (Avg), and standard deviation (SD) values are reported for each parameter. J_{sc} = short-circuit current, V_{oc} = open-circuit voltage, FF = fill factor, PCE = power conversion efficiency, R_{sh} = shunt resistance, and R_s = series resistance. (Device area = 0.0707 cm^2).

HTL	**Treatment**	J_{sc} **(mA cm^{-2})**			V_{oc} **(V)**			**FF (%)**			**PCE (%)**			R_{sh} **(Ω cm^2)**			R_s **(Ω cm^2)**			**No. of devices**
		Max	*Avg*	*SD*	*Max*	*Avg*	*SD*	*Max*	*Avg*	*SD*	*Max*	*Avg*	*SD*	*Max*	*Avg*	*SD*	*Min*	*Avg*	*SD*	
CuSCN	Untreated	16.1	15.9	0.1	0.809	0.802	0.005	65.8	64.3	0.9	8.41	8.18	0.09	605	521	64	2.11	3.96	1.24	10
	THF	17.0	16.7	0.2	0.816	0.808	0.004	69.3	68.8	0.2	9.39	9.25	0.10	788	614	65	1.78	2.30	0.62	10
	Ace	16.5	16.4	0.1	0.813	0.810	0.002	69.1	68.5	0.6	9.22	9.16	0.08	861	727	68	3.25	3.74	0.40	10
	MeOH	16.1	15.7	0.2	0.812	0.806	0.003	68.7	68.1	0.4	8.76	8.60	0.12	711	605	61	1.64	2.76	0.89	10
	IPA	15.9	15.6	0.2	0.811	0.804	0.004	69.6	67.8	0.7	8.70	8.53	0.10	787	635	87	1.15	2.36	0.88	10
PEDOT:PSS	–	15.7	15.5	0.2	0.817	0.810	0.004	71.5	71.0	0.5	9.00	8.92	0.04	991	810	93	0.66	1.36	0.67	10

Table S3 Average external and internal quantum efficiencies (EQE and IQE) in the wavelength range of 400-700 nm along with the comparison between J_{sc} values calculated from the total EQE spectra and those obtained from the *J-V* measurements of OPV cells.

HTL	Treatment	Avg EQE (%)	Avg IQE (%)	Calculated J_{sc} from EQE (mA cm^{-2})	Measured J_{sc} (mA cm^{-2})
CuSCN	Untreated	65.2	72.7	15.7	15.9
	THF	67.5	76.0	16.0	16.7
	Ace	66.4	74.6	15.8	16.4
	MeOH	62.8	70.5	15.2	15.7
	IPA	63.4	71.2	15.4	15.6

Table S4 Fitting results from impedance spectroscopy of OPV cells employing CuSCN treated with different antisolvents as an HTL, measured under dark condition at a DC bias of 0.8 V (open-circuit condition). Symbols correspond to the equivalent circuit elements shown in Fig. 3a inset. Values in the parentheses represent the errors from fitting. (Device area = 0.0707 cm^2).

HTL	Treatment	R_s (Ω)	R_t (Ω)	C_{geo} (nF)	R_{rec} (Ω)	Q (nF)	n
CuSCN	Untreated	24.6 (0.6%)	358.7 (0.2%)	7.2 (0.3%)	185.2 (2.2%)	32.2 (0.1%)	0.96 (0.6%)
	THF	19.1 (1.2%)	83.9 (0.8%)	5.8 (1.6%)	183.7 (1.0%)	101.5(0.1%)	0.79 (0.1%)
	Ace	5.7 (1.5%)	125.8 (0.2%)	6.6 (0.2%)	184.4 (1.0%)	83.0 (0.2%)	0.83 (0.1%)
	MeOH	18.5 (0.1%)	290.6 (0.2%)	6.9 (0.1%)	181.7 (1.4%)	41.4 (3.3%)	0.92 (0.1%)
	IPA	26.0 (0.1%)	313.3 (0.2%)	7.7 (0.1%)	184.9 (2.0%)	40.8 (0.1%)	0.93 (0.1%)

Table S5 Hole mobility values (μ_h^{SCLC}) of hole-only devices calculated from the space charge limited current (SCLC) analysis.

HTL	**Treatment**	μ_h^{SCLC} **(×10^{-5} cm^2 V^{-1} s^{-1})**	**Fitting error (×10^{-5} cm^2 V^{-1} s^{-1})**
CuSCN	Untreated	9.5	0.3
	THF	14.1	1.0
	Ace	11.0	0.1
	MeOH	9.1	< 0.1
	IPA	8.8	< 0.1

Table S6 Device parameters of OLEDs employing CuSCN with or without THF treatment as an HTL. Results of OLEDs with PEDOT:PSS HTL are also included as reference. V_{on} = turn-on voltage, J = current density, L = luminance, CE = current efficiency, PE = power efficiency. (Device area = 0.04 cm^2)

HTL	**Treatment**	V_{on} **(V)**	J_{max} **(mA cm^{-2})**	L_{max} **(cd m^{-2})**	**Chromaticity**[a] **(*x*, *y*)**	**CE (cd A^{-1})**	**PE (lm W^{-1})**	**EQE (%)**
						Max / @L = 100 cd m^{-2} / @L = 1000 cd m^{-2}		
CuSCN	Untreated	2.9	387	17780	(0.341, 0.619)	19.4 / 9.4 / 17.6	11.0 / 7.1 / 9.8	5.2 / 2.5 / 4.7
	THF	3.1	281	16630	(0.338, 0.620)	29.9 / 29.6 / 25.3	22.8 / 20.9 / 13.0	8.2 / 8.0 / 6.9
PEDOT:PSS	–	5.1	547	45080	(0.324, 0.620)	25.0 / 23.7 / 23.4	12.5 / 12.2 / 10.2	6.7 / 6.4 / 6.2

[a] Based on the International Commission on Illumination (CIE) 1931 color space

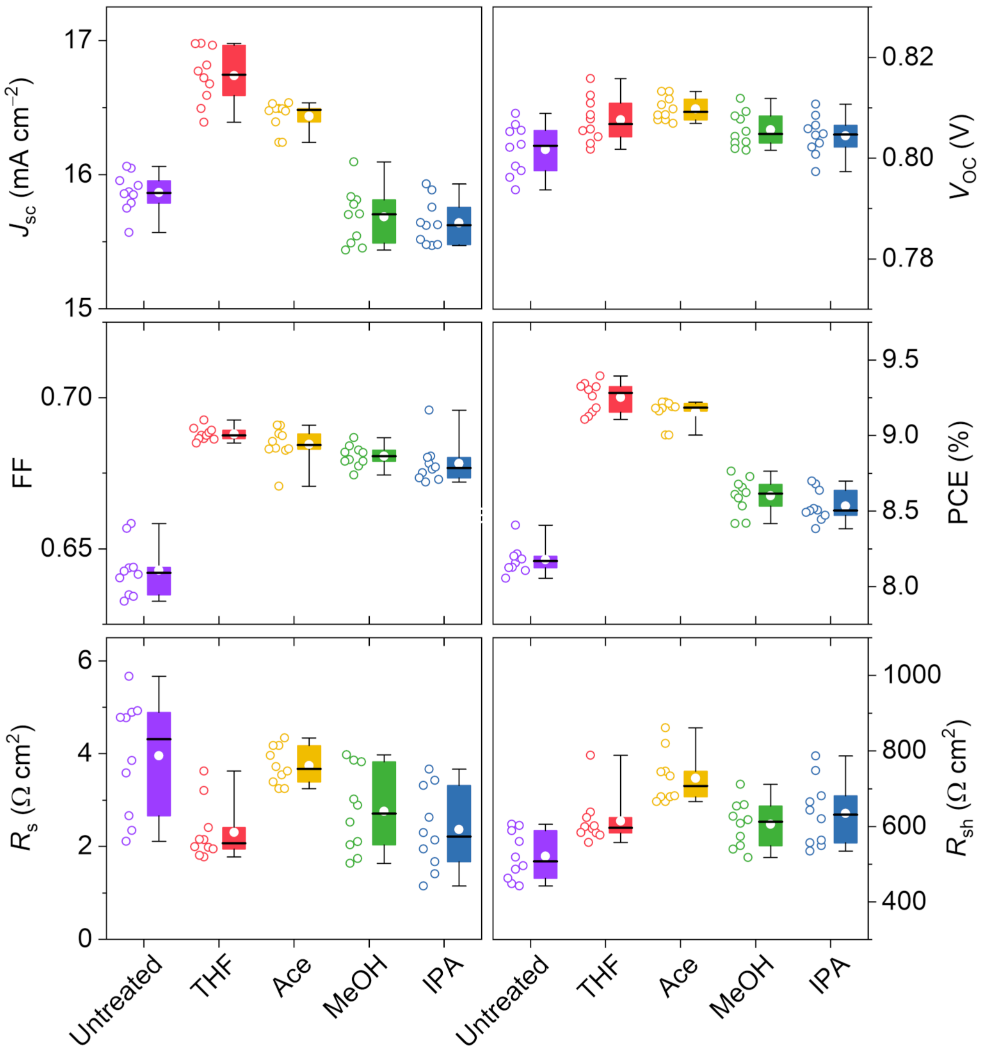

Fig. S1 Box and scattered data plots showing the cell parameters of PTB7-Th:PC$_{71}$BM OPVs with untreated and antisolvent-treated CuSCN as HTL. The boxes represent 25th – 75th percentiles with the horizontal lines indicating the 50th percentile. The white dots indicate the mean values, and the whiskers show the min-max ranges. The statistics are also reported in Table S2.

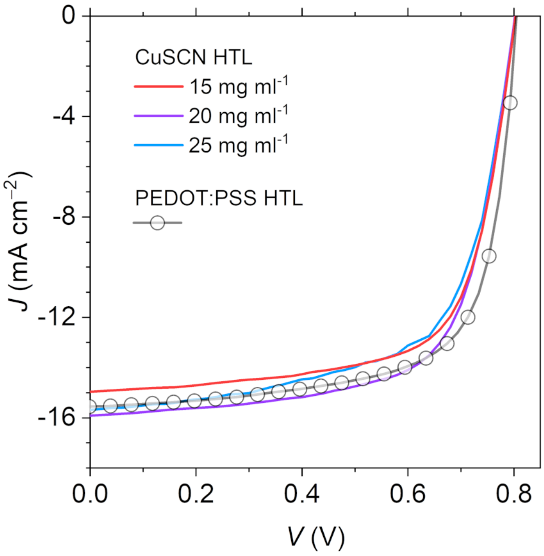

Fig. S2 *J*-*V* characteristics of OPV devices with untreated CuSCN HTLs of different thicknesses and PEDOT:PSS HTL.

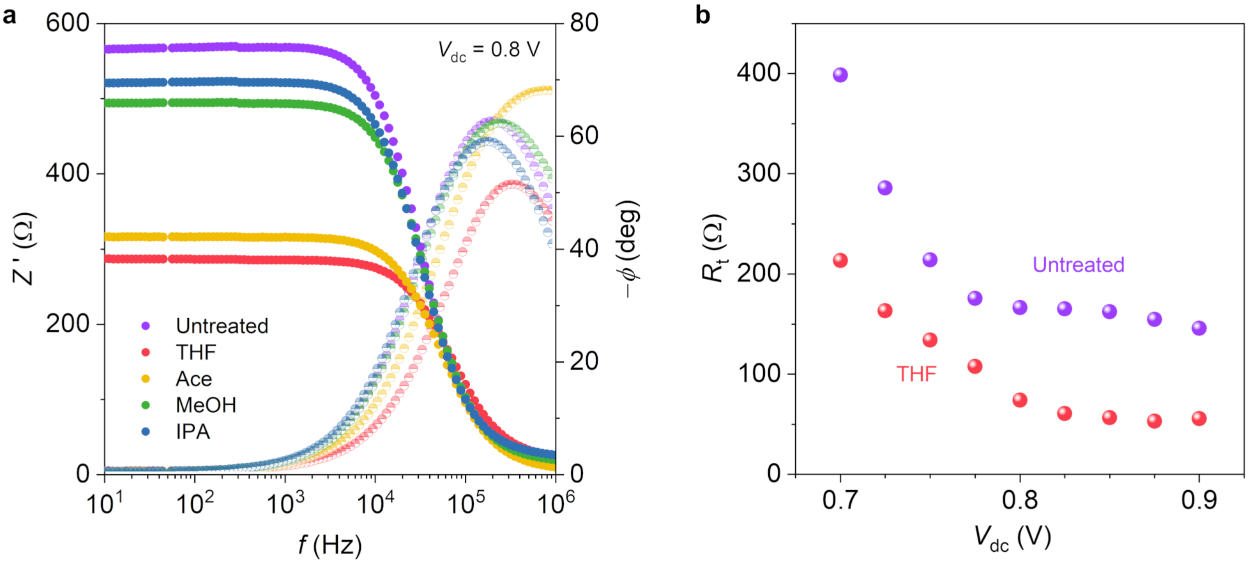

Fig. S3 (a) Bode plots of complex impedance data of OPV devices with different CuSCN HTLs. (b) R_t from impedance data fitting as a function of DC bias.

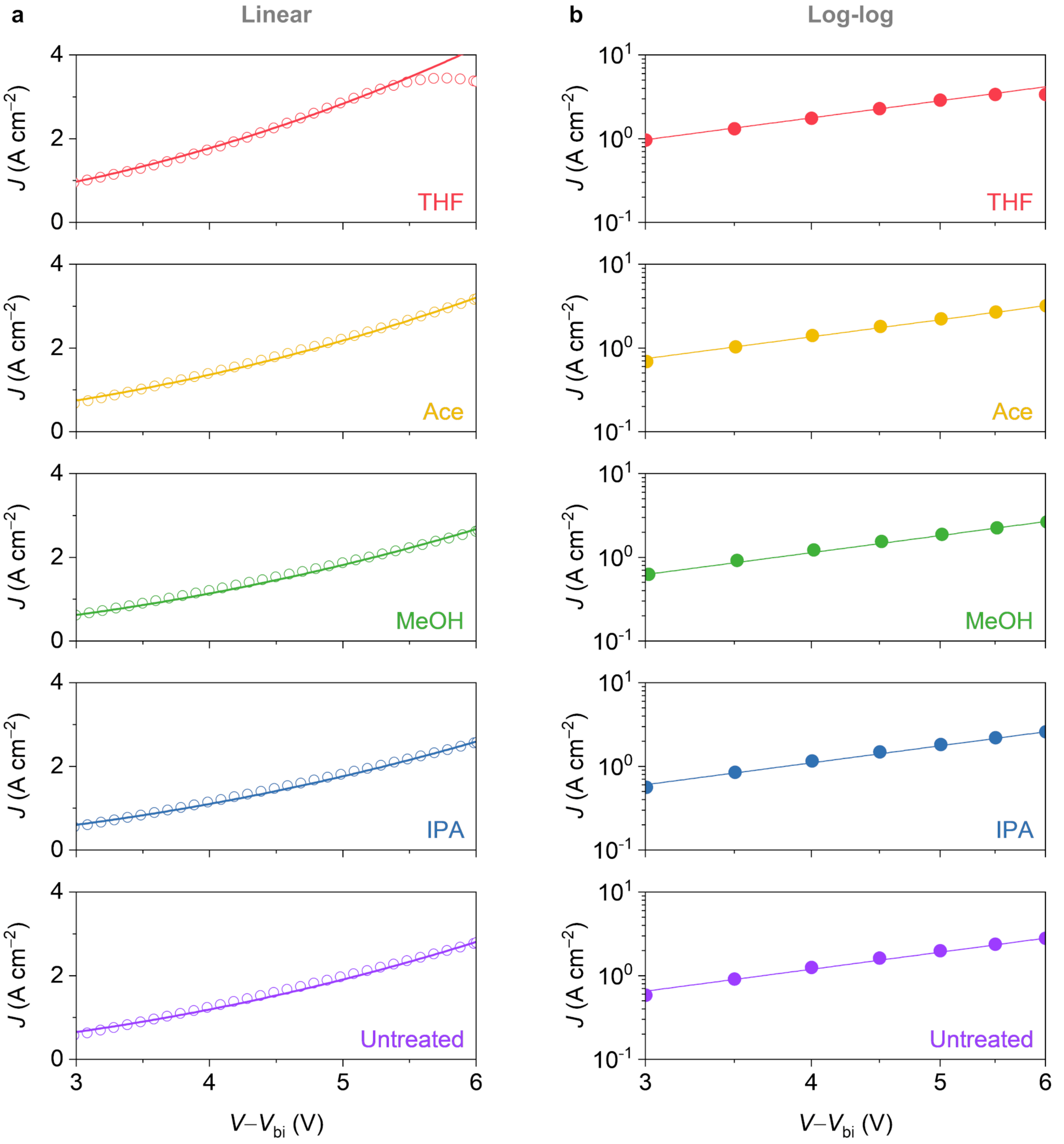

Fig. S4 Current-voltage characteristics of hole-only devices for SCLC analysis. Scattered plots are measured data points while solid lines are results from SCLC fitting. The plots are displayed in (a) linear and (b) log-log scales.