Supplementary Information

Electric field-induced hole transport in copper(I) thiocyanate (CuSCN) films processed from solution at room temperature

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Methods

XPS measurement:

An XPS survey spectrum, shown in Figure S1, was collected on a CuSCN thin film drop casted on an Au coated SiO₂ substrate. The 200 nm thick Au layer was prepared by sputtering Au onto 300 nm SiO₂ wafer pre-coated with a 10 nm adhesive layer of chromium. The film was immediately loaded in the UHV chamber after preparation. The measurements were performed with a commercial XPS system (Omicron NanoTechnology, Taunusstein, Germany) with a monochromatic Al source (1486.7 eV) and a hemispherical energy analyzer EIS-Sphera (Omicron NanoTechnology, Taunusstein, Germany). Core-level XPS scans of the carbon 1s, nitrogen 1s, copper 2p, and sulfur 2s regions were acquired at a pass energy of 20 eV and a step size of 0.05 eV. A base pressure of about 4.0x10⁻¹⁰ mbar was maintained throughout all experiments. The spectroscopic data were processed using CasaXPS software (Casa Software Ltd).

UPS measurement:

The UPS spectrum was collected on the same samples used for XPS. The UV source operating at 21.22eV was a HIS 13 capillary discharge lamp from Omicron NanoTechnology.

A pass energy of 5 eV and a resolution of 0.01 eV were applied during the measurement. A base pressure of about 4.0×10^{-10} mbar was maintained throughout all experiments.

Variable angle spectroscopic ellipsometry:

The optical properties and thickness of the spin-coated films were measured using variable angle spectroscopic ellipsometry (VASE) based on the M-2000XI rotating compensator configuration (J. A. Woollam Co., Inc). VASE spectra ranging from 210 nm to 1689 nm were recorded at a 18° angle of incidence with respect to the substrate normal from 45° to 79° with 6° increment. Optical analysis of VASE data was performed using the EASETM and WVASE32 software packages (J. A. Woollam Co. Inc). Optical modeling was performed assuming a homogeneous thin film exhibiting isotropic behavior. Refractive n and extinction coefficient *k* curves were recorded.

Transmission electron microscopy:

A Titan Cryo Twin (FEI Company) high-resolution transmission electron microscopy (HRTEM) operating at 300 kV was used to acquire micrographs and selected-area electron diffraction (SAED) patterns for a CuSCN film. The sample was floated on water and then transferred onto a carbon filmed TEM grid.

Grazing incidence wide angle X-ray scattering:

Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed on beamline 11-3 at the Stanford Synchrotron Radiation Laboratory (Stanford, CA, USA). Monochromatic light was used with a wavelength of 0.973571 Å (12.735 keV). A MAR345 Imaging Plate was used to record the scattering patterns and the exposure time was set to 30 seconds. The images were dark current corrected, distortion-corrected, and flat-field corrected by the acquisition software. Using a Lanthanum Hexaborade (LaB₆) standard, the sample to detector distance was determined to be 401.51 mm. The incidence angle of the X-ray beam was set to 0.12°.

Thin-film transistor fabrication and measurements

Thin-film transistors (TFTs) were fabricated by spin-casting the saturated solution of copper(I) thiocyanate (CuSCN) in dipropyl sulfide at 800 rpm for 60 secs on glass substrates with 30-nm bottom Au source/drain electrodes and annealed at 80°C for 15 mins. This was followed by the deposition of CYTOP dielectric also by spin-casting at 2000 rpm for 60 secs and annealed at 100 °C for 15 mins. The last step was the deposition of 50-nm top Al gate electrodes. All metal electrodes were deposited by thermal evaporation under high vacuum through a shadow mask. Electrical measurements were carried out under nitrogen atmosphere with a probe station and a semiconductor parameter analyzer (Keithley-4200).



Figure S1. XPS survey scan of a drop-cast film of CuSCN on a gold substrate, revealing peaks associated with Cu, N, S and C. No oxygen peak is observed in pristine films.

Element	Peak used for quantification	RSF	Peak position (eV)	Area	Concentration
Copper	Cu 2p3/2	10	932.45	66.0	25.3%
Sulfur	S 2s	1.25	227.60	8.3	25.4%
Nitrogen	N 1s component (Contribution from C≡N bond)	1.77	398.28	9.4	20.2%
	N1s component (Contribution from C=N bond).	1.77	399.45	0.9	3.6%
Carbon	C1s component (Contribution from C=N bond).	1	284.40	0.8	2.9%
	C1s component (Contribution from C≡N bond)	1	285.60	5.9	22.6%

Table S1. Surface chemical composition of the CuSCN films based on analysis of highresolution XPS scans (see Figure 1 in main text).



Figure S2. π excitation as the evidence of the presence of the C=N bond in the film.



Figure S3. High-resolution spectrum showing a secondary electron cut-off at 16.32 eV (i.e. work function = 4.9 eV).



Figure S4. High-resolution normal emission ultraviolet photoelectron spectrum of a dropcast film of CuSCN on gold. A bias of -5 V was applied to ensure that the electrons cleared the work function of the analyzer and to help separate the photoemitted electrons from the secondary electrons generated in the analyzer. The spectra are all shifted such that the Fermi energy is at 0 eV. The position of the photoelectron onset and secondary electron cut off are at 0.63 eV and 16.32 eV (see **Figure S3**), respectively with respect to the Fermi level.



Figure S5. Refractive index and extinction coefficient of spin-cast CuSCN films as obtained by variable angle spectroscopic ellipsometry (VASE). The inset shows the data as a function of photon energy.

Table S2. Parameters of the modified Gaussian model obtained by fitting the imaginary part of dielectric function $\varepsilon_2(E)$ of CuSCN film. Errors represent 90% confidence limit.

Thickness: 13.9 ± 0.1 nm					
$E_{\infty} = 1.24 \pm 0.05$					
UV Pole Amplitude. = 84.1 ± 5.7					
UV Pole Energy. = 8.74 ± 0.12 eV					
Gaussian peak parameters: A: amplitude, B: broadening, E: energy center.					
$A_1 = 0.382 \pm 0.004$	$B_1 = 0.223 \pm 0.003$	$E_1 = 4.088 \pm 0.001 \text{ eV}$			
$A_2 = 2.672 \pm 0.024$	$B_2 {=} 0.494 \pm 0.005$	$E_2 = 4.989 \pm 0.003 \text{ eV}$			
$A_3 = 0.754 \pm 0.036$	$B_3 = 0.384 \pm 0.009$	$E_3 = 5.355 \pm 0.007 \text{ eV}$			
$A_4 = 3.573 \pm 0.011$	$B_4 = 1.746 \pm 0.006$	$E_4 = 5.486 \pm 0.003 \text{ eV}$			



Figure S6. Plan view selected area electron diffraction (SAED) pattern of CuSCN film showing crystalline behavior. The d-spacings are calculated to be 3.3 Å, 2.7 Å, 1.9 Å, 1.6 Å, 1.3 Å, 1.1 Å and 0.9 Å, respectively.

Table S3. Proposed indexing of d-spacings as α or β phase reflections.

d-spacing (Å)	Alpha phase (hkl)	Beta phase (hkl)
3.3	002	100
2.9	131, 112	
2.7	400	004
1.9	331	110
1.6	204	202
1.3	271, 343, 234, 172, 413, 080	204, 107, 008
1.1	1000, 460, 840, 206	118, 300, 215, 302
0.9	080, 555, 446, 915, 280	312, 310



Figure S7. X-ray powder diffraction analysis of the CuSCN powder, showing predominantly α -phase in the bulk form prior to solution preparation.



Figure S8. The integrated line intensity along (a) the horizon and (b) the radially integrated intensity as labelled in **Fig. 3**. The corresponding different features (p1, p'1, p2 and s) are marked in the graphs.

Peak designation	Peak value (Å)	d-spacing (nm)
p 1	1.1437	0.549
p'1	2.2617	0.278
p ₂	1.9184	0.328

Table S4. Summary of the *d*-spacings derived for CuSCN films.



Figure S9. Output characteristics of top-gate CuSCN TFTs with channel length and width of $30 \mu m$ and 1.5 mm, respectively, measured in the dark at various gate voltages. (a) Results of as-fabricated CuSCN TFTs without exposure to air. (b) Results of CuSCN TFTs in which the CuSCN layer has been pre-exposed to air before deposition of the CYTOP/Al gate electrode layers.

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