DOI: 10.1002/adfm.201802055

Article type: Full Paper

***p*-Doping of Copper(I) Thiocyanate (CuSCN) Hole Transport Layers for High Performance Transistors and Organic Solar Cells**

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Keywords: Copper(I) thiocyanate; p-type doping; hole transport layers; organic solar cells; transparent transistors

Abstract

The ability to tune the electronic properties of soluble wide bandgap semiconductors is crucial for their successful implementation as carrier selective interlayers in large area opto-/electronics. Herein we report the simple, economical and effective *p*-doping of one of the most promising transparent semiconductors, copper(I) thiocyanate (CuSCN), using C₆₀F₄₈. Theoretical calculations combined with experimental measurements are used to elucidate the electronic band structure and density of states of the constituent materials and their blends. Obtained results reveal that although the bandgap (3.85 eV) and valence band maximum (-5.4 eV) of CuSCN remains unaffected, its Fermi energy shifts towards the valence band edge upon C₆₀F₄₈ addition - an observation consistent with *p*-type doping. Transistor measurements confirm the *p*-doping effect while revealing a tenfold increase in the channel's hole mobility (up to 0.18 cm²V⁻¹s⁻¹), accompanied by a dramatic improvement in the transistor's bias-stress stability. Application of CuSCN:C₆₀F₄₈ as the hole transport layer (HTL) in organic photovoltaics yield devices with higher power conversion efficiency, improved fill factor, higher shunt and lower series resistance and dark current, as compared to control devices based on pristine CuSCN or commercially available HTLs.

1. Introduction

Semiconducting interlayers that exhibit carrier selective transporting characteristics are of great importance for application in the emerging sector of large-area opto/electronics. Example devices that demonstrate enhanced performance upon the addition of carrier-selective interlayers include organic photovoltaic (OPV) cells,^[1–3] hybrid perovskite solar cells (PSCs)^[4–6], and organic light-emitting diodes (OLEDs)^[7–9]. Desirable properties of such interlayers include high optical transparency, chemical stability, processing versatility and solvent

orthogonality with adjacent layers. Transparent thin-film transistors (TFTs) for transparent microelectronic circuits also require materials with these valuable properties.^[10,11] Electron transporting metal oxides such as zinc oxide (ZnO) are widely available and extensively researched, and can exhibit field-effect electron mobility (μ_e) of $>10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in TFTs.^[12–14] In contrast, *p*-type semiconductors with similar characteristics are scarce^[15] with the best examples being those of nickel oxide (NiO_x),^[2,9] copper oxides (Cu_2O , CuO)^[16–18] and tin monoxide (SnO).^[19] While *p*-type metal oxides are occasionally reported to exhibit field-effect hole mobility (μ_h) of $>1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$,^[19,20] many are characterized by a narrow bandgap^[21–23] that renders them unsuitable for use as transparent interlayer materials. The requirement of high temperature annealing ($>200 \text{ }^\circ\text{C}$) to realize their full functionality^[24,25] can also limit their compatibility with temperature-sensitive plastic substrates.

Polymers such as the commercially available poly(3,4-ethylenedioxythiophene) polystyrene sulfonate [PEDOT:PSS] offer an alternative, as it exhibits good hole transport characteristics, relatively high transparency and solution-processability at low temperatures. However, limitations include the poor electron blocking properties of PEDOT:PSS^[26,27] that arise from its semi-metallic character, which creates an efficiency loss mechanism and necessitate the addition of an electron blocking layer to optimize device performance.^[28] Evidently, further progress in opto/electronics research demands the development of novel HTLs to overcome the challenges outlined above.

Copper(I) thiocyanate (CuSCN) is an inorganic, wide bandgap ($>3.4 \text{ eV}$), *p*-type semiconductor with promising physical characteristics (**Figure 1a**).^[29] It is inexpensive, solution-processable and has been employed in several device types including TFTs,^[30–32] OLEDs,^[33,34] OPVs^[35–37] and PSCs^[37,38]. We previously reported a novel deposition route for CuSCN using aqueous ammonia as the solvent.^[37] Thin-film transistors realized via the aqueous solvent route showed improved hole mobility (μ_h) of $0.05 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ as compared to $0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

1s^{-1} measured for CuSCN TFTs processed from diethyl sulfide (DES)-based solution. While the success of our aqueous processing route revealed the tremendous potential of CuSCN as an HTL for large-area applications, there remains an opportunity to further optimize its hole-transport properties to challenge *p*-type metal oxides. Increased carrier mobility (μ) means faster transistor switching, and consequently, rapid integrated circuit operation. Herein we report on efficient *p*-type doping of solution-processed layers of CuSCN using the fluorinated fullerene derivative $\text{C}_{60}\text{F}_{48}$ (**Figure 1b**) as the molecular dopant. Despite the simplicity of the physical blending approach adopted, we show that the resulting CuSCN layers can be tuned efficiently and reliably without compromising their microstructural integrity. Importantly, transistors and solar cells based on *p*-doped CuSCN: $\text{C}_{60}\text{F}_{48}$ layers are found to exhibit significantly enhanced performance characteristics.

2. Molecular Doping of Inorganic Semiconductors

Molecular doping of organic semiconductors has been shown to improve the electrical characteristics of organic TFTs,^[39–42] and enhance the power conversion efficiency in OPVs and PSCs.^[43–45] In contrast, substitutional or interstitial impurity doping is the conventional approach in inorganic semiconductor systems, and numerous studies on the successful doping of metal oxides with metals^[46,47] and halogens^[48,49] are found in the literature. While doping metal oxides can enhance μ_e and gate-bias stability in TFTs due to the generation of free electrons and passivation of traps,^[50–52] some researchers have measured lower μ in doped systems;^[53] this is primarily attributed to ionized impurity scattering often observed at higher doping concentrations.^[54] In solar cell applications, *p*-doping an inorganic HTL can improve the charge extraction efficiency due to increased conductivity.^[55] Provided that a *p*-dopant can efficiently generate free holes, its concentration can be modulated to optimize the HTL conductivity, although dopant induced morphology changes must also be considered.^[50,55]

The *p*-type character of β -CuSCN, the more energetically favorable polytype, is attributed to copper vacancies,^[56,57] but systematic studies on controlled extrinsic doping of CuSCN are seldom reported. To this end, doping experiments to date have focused on generating a stoichiometric excess of SCN in the CuSCN bulk.^[58–60] Premalal *et al.* achieved the most stable *p*-doped system by reacting CuSCN with triethylammonium thiocyanate in dipropyl sulfide,^[60] but the long reaction time (20 days) required to optimize the power conversion efficiency (3.39%) of dye-sensitized solar cells limits the practicality of this approach. The difficulty in *p*-doping CuSCN arises from its deep valence band (VB) edge energy of -5.4 eV.^[37] Consequently, identifying a substitutional *p*-dopant is not trivial and demands a complicated theoretical analysis, and hence, we propose an alternative doping strategy employing a prototypical molecular dopant.

The LUMO energy of C₆₀F₄₈ (**Figure 1a**) is typically reported as -5 eV or deeper,^[61–63] which makes it a candidate *p*-dopant for CuSCN. Its large molecular weight ($M_w = 1633 \text{ g mol}^{-1}$) is also advantageous because C₆₀F₄₈ exhibits lower diffusivity relative to common small molecule *p*-dopants such as tetrafluoro-tetracyanoquinodimethane (F₄TCNQ).^[64,65] Additionally, Li *et al.* observed that the fluorofullerene C₆₀F₃₆ exhibits lower volatility and superior thermal stability compared to F₄TCNQ, which is beneficial for device stability and lifetime.^[66] Despite the potential benefits in using C₆₀F₄₈ as an alternative to small molecule *p*-dopants, literature on its application in opto/electronic devices is scarce. Paterson *et al.* employed C₆₀F₄₈ as a bulk *p*-dopant in an organic semiconductor blend to maximize μ_h in *p*-channel TFTs,^[41,42] but literature on C₆₀F₄₈ as a *p*-dopant for inorganic systems is limited to surface charge transfer processes.^[67] Surface doping procedures are disadvantageous for opto/electronic applications due to the restrictions imposed on device architecture, and because the dopant deposition represents an additional fabrication step.

Here we report on the controlled, molecular *p*-doping of CuSCN with C₆₀F₄₈ using a simple, single-step, solution-based process. First, DFT calculations were used to visualize the electronic orbitals of C₆₀F₄₈ and determine its LUMO/HOMO energy levels. Next, material characterization techniques were employed to assess how the addition of C₆₀F₄₈ affected the electronic, structural and optical properties of CuSCN. After the chemical stability of the CuSCN:C₆₀F₄₈ system was verified, TFTs were fabricated and electrically characterized. The latter measurements confirmed that the optimum C₆₀F₄₈ doping level enhances the hole-transport properties in CuSCN with a 12× increase in the mean μ_h , and a change in the dominant charge transport process from trap-limited to percolation conduction. The effects of C₆₀F₄₈ on the contact resistance and bias stability in CuSCN-based TFTs were also investigated and found to be favorable. Finally, CuSCN:C₆₀F₄₈ HTLs were utilized in bulk-heterojunction OPV cells and shown to produce superior power conversion efficiency relative to similar cells employing pristine CuSCN and PEDOT:PSS HTLs. Despite its simplicity, the molecular doping strategy proposed here differs significantly from conventional surface doping and stoichiometric change techniques applied to inorganic materials. Hence, this work paves the way for further studies on the molecular doping of CuSCN and similar inorganic semiconductors.

3. Energy Level Structure of CuSCN and C₆₀F₄₈

Efforts were made to understand how the electronic properties of CuSCN and C₆₀F₄₈ would affect a CuSCN:C₆₀F₄₈ blend. An ambient atmosphere UV photoemission spectroscopy (APS) instrument equipped with an integrated Kelvin probe (KP) system was used to characterise three samples, namely, gold (Au), CuSCN and C₆₀F₄₈. The latter two samples were spin-cast on indium-tin-oxide (ITO) coated glass and annealed at 100 °C in nitrogen. The VB maximum ($VB_{\max}$) of solid CuSCN was measured at -5.40 (±0.05) eV using APS. The workfunction (*WF*)

of gold thermally evaporated on glass was measured using KP as $-5.0 (\pm 0.1)$ eV. After 30 min UV-ozone treatment of the gold surface, the *WF* had deepened to $-5.4 (\pm 0.1)$ eV – an effect attributed to the removal of surface contaminants and the possible formation of a native oxide layer.^[68] The deeper *WF* is a significantly better match to the VB_{max} of CuSCN and is expected to improve hole injection. The Fermi level (E_F) of solid C₆₀F₄₈ was measured as $-5.6 (\pm 0.1)$ eV using the KP system. Notably, the maximum photon energy of 7.0 eV provided by the UV source was insufficient to identify the highest occupied molecular orbital (HOMO) of C₆₀F₄₈; the lack of photoemission indicated that the HOMO energy was deeper than 7.0 eV.

The LUMO and HOMO energy levels of C₆₀F₄₈ were determined using density functional theory (DFT) calculations, which were performed with the quantum-chemistry code NWChem,^[69,70] the B3LYP exchange-correlation functional^[71] and the 6-311+g* basis. The LUMO energy of a C₆₀F₄₈ molecule was calculated at -5.31 eV. Hence, we propose that the doping mechanism is electron transfer from the VB of CuSCN to the LUMO of C₆₀F₄₈, which creates free holes in CuSCN. Our LUMO energy calculation compares favorably with several earlier publications on C₆₀F₄₈,^[61–63] and results from past doping studies. For instance, C₆₀F₄₈ has been utilized as a bulk *p*-dopant for organic semiconductors with HOMO energy deeper than -5.0 eV:^[41,42,72] the dopant should have a LUMO similar to or deeper than -5.0 eV to function as an electron acceptor. Promisingly, we found significant experimental evidence for our proposed integer charge transfer process, as discussed in **Sections 3-7**.

The HOMO energy of C₆₀F₄₈ was calculated at -10.72 eV using the NWChem code.^[69,70] This is in reasonable agreement with previously reported HOMO and ionization energy values of C₆₀F₄₈.^[61,62,73] As the HOMO does not participate in our proposed doping mechanism, verification of its energy is beyond the scope of the present work. **Figures 1c** and **1d** illustrates, respectively, the HOMO and LUMO of C₆₀F₄₈ based on DFT calculations with the code

Quantum Espresso (QE),^[74] while **Figure 1e** shows the derived energy levels for the various materials used.

4. Optical and Electronic Properties of CuSCN:C₆₀F₄₈ Solutions and Solid Layers

Ultraviolet-visible-near-infrared (UV-Vis-NIR) absorbance spectroscopy was used to study the effects of C₆₀F₄₈ on CuSCN solutions and solid layers (**Figure 2a**). Initially, three DES-based solutions (CuSCN, C₆₀F₄₈ and CuSCN:C₆₀F₄₈) were prepared at 1 mg mL⁻¹ total solid content. The CuSCN:C₆₀F₄₈ solution was prepared at 1:1 molar ratio to maximize any signal generated by the proposed electron transfer process. Remarkably, the CuSCN:C₆₀F₄₈ solution exhibited an additional absorption band at visible and NIR wavelengths (500-900 nm) that was not observed in the CuSCN or C₆₀F₄₈ solution spectra. This new absorption band is attributed to the formation of fullerene anions (C₆₀F₄₈⁻) due to electron transfer from the VB of CuSCN to the LUMO of C₆₀F₄₈. These observations are consistent with previous reports on the optical signatures detected when anions of C₆₀ and its derivatives are generated in solution.^[75–77] In **Figure 2a**, solution spectra are plotted using dashed lines and evidence of the *p*-doping process is indicated with an arrow.

Next, CuSCN and CuSCN:C₆₀F₄₈ (0.1 mol%) solid layers were spin-cast on quartz substrates from 5 mg mL⁻¹ DES solutions and annealed at 100 °C in nitrogen. UV-Vis-NIR absorbance spectra from solid layers are plotted using solid lines in **Figure 2a**; pristine and doped films exhibited an optical transparency of >93% in the 400-1400 nm wavelength range. The sample containing C₆₀F₄₈ exhibited a stronger absorption peak at UV wavelengths (200-400 nm), but the low signal strength resulting from the small layer thickness (20-30 nm) and limited spectral resolution did not offer conclusive evidence of a new absorption band. Tauc analysis was used to determine the optical bandgap (E_{OPT}) of the CuSCN:C₆₀F₄₈ (0.1 mol%)

layer from UV-Vis-NIR spectra (**Figure 2b**). Here, $(\alpha h\nu)^n$ was calculated as a function of photon energy ($h\nu$), where α is absorption coefficient, h is Planck's constant, ν is radiation frequency, and n is equal to 2 for an allowed direct bandgap transition and $\frac{1}{2}$ for an allowed indirect bandgap transition. The blue curve denoting the indirect transition offers a poor linear fit for a bandgap extraction. A linear fit applied to the red curve yielded a direct E_{OPT} of 3.85 (± 0.02) eV, which was an excellent match to our previous measurements of pristine CuSCN ($E_{OPT} = 3.85$ eV).^[37] This result revealed that CuSCN retains its wide bandgap semiconductor nature despite the addition of C₆₀F₄₈ molecules, and the bandgap is unaffected by the *p*-dopant at a concentration of 0.1 mol%.

APS and KP measurements were used to further investigate the electronic structure of CuSCN:C₆₀F₄₈ layers. Four samples were prepared: one pristine CuSCN reference sample and three CuSCN:C₆₀F₄₈ samples with different doping concentrations (0.01, 0.1 and 0.5 mol%). An energy of -5.4 (± 0.05) eV was obtained by APS for the VB_{max} of all four samples, and in conjunction with the bandgap measurement, confirmed that C₆₀F₄₈ had not significantly disrupted the CuSCN lattice and its energetics. E_F of each sample was determined via KP under inert atmosphere and is plotted in **Figure 2c**. Evidently, addition of C₆₀F₄₈ shifts the Fermi energy of CuSCN towards the VB_{max} , and a maximum change of -0.8 eV is observed for a doping concentration of 0.5 mol%. These results provide direct evidence of controlled *p*-doping in CuSCN:C₆₀F₄₈ layers, via the integer charge transfer mechanism discussed earlier.

5. Elemental Composition, Chemical Bonding and Density of States Analysis

To gain additional insight into the impact of C₆₀F₄₈ doping on the chemical bonding and electronic states in CuSCN, X-ray photoelectron spectroscopy (XPS) measurements were performed on CuSCN layers. Films were spin-cast on highly doped silicon (Si++) substrates

and annealed at 100 °C in nitrogen. The C 1s, N 1s, S 2p and Cu 2p core-level spectra of the pristine CuSCN layer (blue dashed lines) and of the CuSCN:C₆₀F₄₈ (0.1 mol%) layer (solid red lines) are presented in **Figure 3a-d**. All spectra are typical of CuSCN and core levels are detected at binding energies consistent with previous reports,^[37,78] the spectral positions of Cu 2p, N 1s, and S 2p indicate that there is no significant presence of oxygen.

Of special importance are the C 1s core level spectra (**Figure 3c**), which are characterized by two distinct peaks attributed to aliphatic and adventitious carbon (at 284.6 eV) and to –SCN bonds (at 286 eV). The peak corresponding to aliphatic C-C and adventitious C, which is associated with both C₆₀F₄₈ and CuSCN, increased in intensity relative to the –SCN peak when CuSCN was enriched with the carbonaceous species (C₆₀F₄₈). Notably, the spectral separation of the two peaks is smaller in CuSCN:C₆₀F₄₈ (0.1 mol%) than in pristine CuSCN: the binding energy difference between the two chemical environments is reduced by 0.4 eV upon C₆₀F₄₈ addition (**Figure 3c**). We propose that this could be evidence of electron transfer between C₆₀F₄₈ and CuSCN. Similar XPS results have previously been observed by Meyer *et al.* when graphene was *p*-doped with molybdenum trioxide (MoO₃) via surface charge transfer,^[79] where the C-C peak of C 1s core-level spectra decreased in binding energy by up to 0.25 eV upon the addition of MoO₃.

We previously reported the theoretical density of states (DOS) for CuSCN determined via DFT calculations.^[37,57] Based on the latter analysis, theoretically derived partial densities of states (pDOS) were corrected using one electron atomic cross sections from Yeh and Lindau^[80] to account for signal intensity differences, and a Gaussian broadening of 300 meV was applied for comparison with VB spectra acquired by XPS. In **Figure 3e**, the agreement between experimental data (lines) and the theoretical pDOS for CuSCN (shaded region) is remarkable. The feature closest to the E_F (1-4 eV) primarily consisted of Cu 3d states, while the adjacent feature (4-6 eV) also contained Cu 3d states but with greater hybridization of Cu 3p and S 3p

states. Importantly, there was a substantial decrease in the Cu 3*d* states when 0.1 mol% of C₆₀F₄₈ was incorporated into the CuSCN layer. We propose that the weaker contribution from Cu 3*d* states could be another indication of electron transfer from the VB of CuSCN to the LUMO of C₆₀F₄₈, and thus, is further evidence of *p*-doping. Interestingly, the VB spectrum of CuSCN:C₆₀F₄₈ did not show a distinguishable shift in E_F towards VB_{max} . We believe this to be due to limitations of the XPS technique. The adventitious carbon peak expected at 284.6 eV is the common binding energy reference, but changes to the C 1*s* envelope observed upon the addition of C₆₀F₄₈ (**Figure 3c**) introduces an uncertainty to the energy calibration. Furthermore, the dramatic enhancement in conductivity resulting from C₆₀F₄₈ doping (**see Section 7**) could change the charging properties of the CuSCN surface and introduce another error to the calculation of binding energies.

6. Surface Morphology of CuSCN:C₆₀F₄₈ Layers

The evolution of surface morphology with dopant concentration was investigated using atomic force microscopy (AFM). CuSCN:C₆₀F₄₈ layers with dopant concentrations in the range of 0.005-2 mol% were spin-cast on glass and glass/ITO substrates, which were similar to those utilized in TFT and OPV fabrication, respectively. CuSCN:C₆₀F₄₈ layers deposited on glass from 5 mg mL⁻¹ solutions were 20-30 nm-thick. Layers deposited on glass/ITO were substantially thicker (60-70 nm) due to the higher concentration employed (20 mg mL⁻¹) to optimize OPV performance.

Surface topography images acquired using a scan area of 1 μm² are presented in **Figure 4**. Images shown in **Figure 4a-d** are of layers deposited on glass, while images shown in **Figure 4 e-h** are of layers deposited on glass/ITO. CuSCN:C₆₀F₄₈ layers are continuous and nanocrystalline on both substrate types, with the surface morphology depending heavily on the

C₆₀F₄₈ concentration. Thus, it is evident that C₆₀F₄₈ not only functions as a *p*-dopant, but also as a nucleating agent resulting to smoother layers. The dramatic morphological changes in the CuSCN layers upon C₆₀F₄₈ admixing are expected to modify its hole-transport properties. In particular, one would expect carrier scattering mechanisms to be altered by the observed microstructural changes; this will be discussed in **Section 7**.

Figure S1 shows the topography and phase signals from a CuSCN:C₆₀F₄₈ (2 mol%) layer that exhibited some topographical non-uniformities. The unfavourable change in surface morphology is primarily attributed to reduced long-term stability of CuSCN:C₆₀F₄₈ solutions containing high concentrations (>1 mol%) of C₆₀F₄₈. Importantly, the topography image conclusively demonstrates that the larger crystallites nucleate upward from the smooth nanocrystalline base. Furthermore, as phase contrast signifies variation in chemical composition,^[81,82] the highly uniform phase signal confirmed there was no dopant agglomeration/segregation on the layer surface. Phase signals corresponding to the topography images in **Figure 4** were also recorded and yield similar results.

Figure 5a shows the line scan indicated in **Figure 4c**, which is a CuSCN:C₆₀F₄₈ (0.1 mol%) layer on glass. The typical diameter (Δx) of the smaller ellipsoidal grains (type I) was ≈ 20 nm and exhibited a relatively flat structure (platelet-like) with maximum surface height variation (Δz) of only ≈ 2.5 nm. In contrast, Δz measured from the larger irregular crystallites (type II) was 13-15 nm. **Figure 5b** shows the surface height distributions (scan area = 1 μm^2) extracted from three CuSCN-based layers on glass, namely, pristine CuSCN, CuSCN:C₆₀F₄₈ (0.5 mol%), and CuSCN:C₆₀F₄₈ (1 mol%). Peaks observed at a surface height (z) of ≈ 10 nm correspond to smaller ellipsoidal grains as determined by the standard deviations of Gaussian fits, while the broader peaks at higher z correspond to the larger irregular crystallites. **Figure 5c** summarizes the root-mean-square roughness (R_{rms}) statistics calculated from topography images of eight CuSCN-based layers on glass with C₆₀F₄₈ concentration in the range 0-1 mol%.

A larger scan area ($5\ \mu\text{m}^2$) was used to generate histograms that better represented the layers' surface characteristics. Mean R_{rms} and ΔR_{rms} range were plotted, where ΔR_{rms} was calculated from three AFM scans of each sample type. Remarkably, the average roughness of CuSCN layers decreased considerably with increasing $\text{C}_{60}\text{F}_{48}$ concentration until 0.5 mol%. Furthermore, $\text{C}_{60}\text{F}_{48}$ significantly improved the large-area surface uniformity in CuSCN layers as indicated by the smaller ΔR_{rms} range.

Figure 5d-e show, respectively, the surface height distributions (scan area = $5\ \mu\text{m}^2$) extracted from CuSCN-based films on glass/ITO and the R_{rms} of these distributions. The addition of $\text{C}_{60}\text{F}_{48}$ caused R_{rms} to decrease dramatically and monotonically with increasing $\text{C}_{60}\text{F}_{48}$ concentration up to 0.5 mol%. Secondary peaks are not observed due to the lower image resolution of $5\ \mu\text{m}^2$ scans. Interestingly, the skew changed in favor of lower surface heights with increasing $\text{C}_{60}\text{F}_{48}$ concentration, which is attributed to the aforementioned change in grain type. The planarization of the ITO anode achieved with the pinhole-free CuSCN: $\text{C}_{60}\text{F}_{48}$ (0.5%) layer is superior to that achieved with PEDOT:PSS, and is desirable for opto/electronic device applications because a smoother HTL surface is more likely to form a defect-free interface with adjacent layers and limit the formation of shunting pathways.^[83]

7. Application of *p*-doped CuSCN Layers in Thin-Film Transistors

Transistors based on CuSCN: $\text{C}_{60}\text{F}_{48}$ layers were fabricated to assess the impact of *p*-doping on the hole transport properties of CuSCN. Poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] was employed as the high-*k* polymer dielectric. The channel length (*L*) and width (*W*) of the TFTs were $30\ \mu\text{m}$ and $1000\ \mu\text{m}$, respectively. Transfer curves in **Figure 6a** were recorded at drain voltage (V_D) = -10 V and correspond to the saturation regime. Linear regime transfer curves (V_D = -2 V) are presented in **Figure S2**. The

output characteristics in **Figure 6b** were recorded by measuring the drain current (I_D) at gate voltage (V_G) in the range 0 V to -10 V. Overall, the operating parameters summarized in **Table S1** reveal that incorporation of C₆₀F₄₈ has a profound positive influence on the hole-transport properties of CuSCN transistors. These results confirm that the structural quality of the semiconductor is not compromised by the *p*-dopant.

Figure 6c shows plots of $\sqrt{I_D}$ vs. V_G calculated from the data in **Figure 6a**. The plots enable the extraction of the threshold voltage (V_T) as indicated. **Figure 6d** shows the evolution of V_T and turn-on voltage (V_{on}) with C₆₀F₄₈ concentration. The two variables monotonically shift towards positive voltages until the doping level reaches 0.5 mol%. Average voltage shifts of $\Delta V_T = +1.4$ V and $\Delta V_{on} = +3.6$ V were measured upon the addition of 0.5 mol% C₆₀F₄₈ to pristine CuSCN. V_T is partly associated with the V_G required to fill traps in the semiconductor.^[84,85] In non-ideal *p*-channel TFTs, hole traps must be filled before mobile holes can contribute to the channel current. A large trap density and a relatively low free hole concentration would be manifested as a strongly negative V_T , which is true for pristine CuSCN devices ($V_T = -3.1$ V). Hence, the systematic positive shift in V_T with increasing C₆₀F₄₈ concentration is evidence of hole trap passivation and enhanced hole current. Additionally, the shift in V_{ON} is accompanied by an increase in the channel off-current, and both observations indicate effective *p*-doping upon incorporation of C₆₀F₄₈ into the CuSCN channel. **Figure 6e** shows the evolution of channel on- and off-state currents (measured at $V_D = -10$ V) with C₆₀F₄₈ concentration. The off-current rises by an order of magnitude for 0.5 mol% C₆₀F₄₈ and indicates a significant enhancement in the channel conductivity, which is attributed to the increased free hole concentration. The on-current also rises with increasing C₆₀F₄₈ content up to 0.5 mol%, followed by a decrease for ≥ 1 mol% C₆₀F₄₈. This is unsurprising as high dopant concentrations are expected to increase the structural and energetic disorder of the host semiconductor, and act

as scattering centres due to Coulombic interactions between mobile holes and ionized C₆₀F₄₈ molecules.^[86,87]

Figure 6f shows the evolution of hole mobility in saturation (μ_{sat}) with C₆₀F₄₈ concentration. The maximum and mean μ_{sat} values measured from five pristine CuSCN transistors were 0.014 and 0.010 cm²V⁻¹s⁻¹, respectively, in good agreement with previous reports. A striking increase in μ_{sat} is achieved upon doping in the range 0.01-0.5 mol%. Maximum and mean μ_{sat} values of 0.18 cm²V⁻¹s⁻¹ and 0.12 cm²V⁻¹s⁻¹, respectively, were measured from five CuSCN transistors containing 0.5 mol% C₆₀F₄₈. Notably, 0.18 cm²V⁻¹s⁻¹ represents the highest mobility reported to date for CuSCN. Considering the significant reduction in R_{rms} observed in CuSCN:C₆₀F₄₈ (**Figure 4** and **Figure 5**), improved structural uniformity could certainly enhance the long-range hole-transport properties. Furthermore, in its secondary role as a nucleating agent, the fluorofullerene could induce a favorable change in crystalline phase, orientation and/or nature of grain boundaries. A further interesting point is the distribution of C₆₀F₄₈ in the CuSCN layer. Since the *WF* of gold cannot facilitate hole injection into the incredibly deep HOMO (-10.72 eV) of C₆₀F₄₈ (**Section 3**), localization of C₆₀F₄₈ at the CuSCN/dielectric interface is not expected to improve *p*-channel characteristics as observed. Hence, we propose that: (i) C₆₀F₄₈ is distributed within the bulk of the CuSCN layer as opposed to its surface, and (ii) C₆₀F₄₈ partly contributes to the mobility enhancement by deactivating hole traps through the formation of excess mobile holes (i.e., *p*-doping).^[42,88]

Surprisingly, and despite the overall device improvement observed, the subthreshold swing (*SS*) is found to increase upon *p*-doping from 0.9 V dec⁻¹ for pristine CuSCN TFTs, to 1.6 V dec⁻¹ for CuSCN:C₆₀F₄₈ (0.5 mol%) devices (**Table S1**). To explain this apparent increase in interface trap concentration, we propose that the addition of C₆₀F₄₈ forms traps at specific energies, but deactivates other trap types (already present in pristine CuSCN) as evident from the positive impact of C₆₀F₄₈ on hole transport.

Large S-D contact resistance (R_C) is a major limitation to efficient hole injection into the semiconductor VB, and hence, is detrimental to TFT performance. Doping is a proven strategy for minimizing R_C . The transmission line method (TLM) is commonly used to quantify R_C ^[89] and is based on the following relationship:

$$R_{tot} = \frac{\partial V_{D(lin)}}{\partial I_{D(lin)}} = LR_{chan} + R_C \quad (1)$$

In **Eq. 1**, R_{tot} is total device resistance, R_{chan} is the channel resistance and L is channel length. In order to determine R_C using **Eq. 1**, transistors with channel lengths in the range 30-100 μm were measured. **Figure 7a-b** show the R_C analysis for two types of transistors: (a) pristine CuSCN, and (b) 0.5 mol% C₆₀F₄₈ doped CuSCN. As evident from **Figure 7c**, p -doping CuSCN with an optimized C₆₀F₄₈ concentration reduces R_C by approximately an order of magnitude, and provides direct evidence of a pronounced p -doping effect.^[90] We propose that the reduction in R_C is caused by a change in the dominant hole injection mechanism at the metal-semiconductor junction from thermionic emission of holes over the Schottky barrier to field emission. For the latter, when the Fermi level of p -doped CuSCN shifts towards the VB_{max} (**Figure 2c**), the Schottky barrier becomes sufficiently narrow for hole tunnelling to occur at the top of the barrier. Consequently, the hole injection efficiency is enhanced, and the voltage drop across the contact reduces (i.e., R_C reduces).

Bias-stress measurements were performed to establish whether the aforementioned trap deactivation mechanism has improved the operating stability of CuSCN TFTs. **Figure 7d-e** show an analysis of bias-stress data from two devices: pristine CuSCN and CuSCN:C₆₀F₄₈ (0.5 mol%). Datasets were obtained under $V_G = V_D = -10$ V continuous bias stressing in nitrogen for a 2 h time (t) period; transfer curves in saturation ($V_D = -10$ V) were recorded at regular time intervals. **Figure S3** presents a comparison of transfer characteristics directly before ($t = 0$) and after ($t = 2$ h) bias-stress. **Table S2** quantifies key parameter changes calculated from the forward sweep datasets. V_T in the pristine CuSCN transistor exponentially decayed by -0.9 V

but exhibited no change in the C₆₀F₄₈-doped device. I_{D-on} deteriorated rapidly to 61% of its original value in the pristine CuSCN device but increased slightly (x1.09) in the doped system. Evidently, pristine CuSCN transistors contain a higher density of hole traps at the channel interface that appears to increase with increasing bias stress time. V_T and I_{D-on} plateau over time in the pristine CuSCN transistor (**Figure 7d-e**) and this corresponds to the highest density of traps for the chosen biasing conditions. These characteristic bias-stress results conclusively demonstrate that optimized C₆₀F₄₈ doping levels minimize the hole trap density at the channel interface and dramatically enhance the operating stability of CuSCN TFTs.

Finally, to elucidate the conduction mechanisms that underpin the enhancement in hole transport observed upon *p*-doping, V_G dependence of the linear regime field-effect hole mobility (μ_{lin}) was analyzed according to the power law equation:^[91]

$$\mu_{lin} = K(V_G - V_{T,P})^\gamma \quad (2)$$

Here, $V_{T,P}$ is the percolation threshold voltage, while the prefactor K and the exponent γ relate to the nature of the charge transport mechanism. Specifically, γ quantifies the hole-transport process that dominates channel conduction. Lee *et al.* previously demonstrated that a value for γ approaching 0.1 is the percolation conduction (PC) limit, while a γ value closer to 0.7 indicates trap-limited conduction (TLC).^[91] **Figure 7f** shows the evolution of μ_{lin} with V_G , and fitting **Eq. 2** to the high gate field region yields $\gamma = 0.53$ for pristine CuSCN, and $\gamma = 0.33$ for CuSCN:C₆₀F₄₈ (0.5 mol%) transistors. Hence, when the dopant concentration is optimized, the dominant conduction mechanism in the CuSCN channel appears to transition from TLC to PC, and is further evidence of C₆₀F₄₈ reducing the hole trap density at the CuSCN/dielectric interface.

8. Application of *p*-doped CuSCN Layers in Organic Photovoltaic Cells

CuSCN:C₆₀F₄₈ layers were incorporated into organic solar cells as the HTL, and their performance was compared with control cells based on conventional PEDOT:PSS HTLs. Standard architecture, bulk-heterojunction (BHJ) OPV cells were fabricated using poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) as the donor and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₀BM) as the acceptor. **Figures 8a-b** illustrate the chemical structures of the materials employed and their energetics, respectively, while **Figure 8c** displays the device architecture.

Figure 8d shows the current density-voltage (*J-V*) characteristics under AM1.5 illumination of three OPV cells that differ only by the HTL employed, namely, PEDOT:PSS, CuSCN (pristine) and CuSCN:C₆₀F₄₈ (0.005 mol%). The *J-V* curve of an inverted cell with an identical PCDTBT:PC₇₀BM active layer blend and ZnO electron transport layer (ETL) is also shown for comparison. Operating parameters are summarized in **Table 1**, which presents the mean and maximum values from 12-16 cells employing each HTL type. The values discussed correspond to averages unless explicitly stated otherwise. Notably, cells containing CuSCN-based HTLs achieved power conversion efficiency (PCE) of 6.3-6.6% and outperformed PEDOT:PSS-based devices (PCE = 5.6%), in accordance with published results.^[35]

Having confirmed the beneficial effects of using CuSCN as the HTL, we explored how *p*-doping of CuSCN interlayers with C₆₀F₄₈ affects the OPV performance. To this end, C₆₀F₄₈ concentration ≥ 0.1 mol% yielded low device performance. Based on the AFM analysis and transistor results, we propose a model where the optimum doping level is determined by a trade-off between competing mechanisms. Firstly, C₆₀F₄₈-induced morphological changes improve the uniformity of CuSCN HTLs; this increases the density of charge conduction pathways and decreases the density of shunting pathways. Secondly, incorporation of C₆₀F₄₈ into the HTL enhances the concentration of mobile holes and their field-effect mobility within CuSCN, while simultaneously reducing the trap density. As *p*-doped CuSCN HTLs are more conductive, they

are expected to exhibit lower series resistance and improved hole extraction characteristics in solar cells.

p-Doping of CuSCN HTLs with C₆₀F₄₈ at concentrations of 0.005-0.01 mol% yields enhanced cell performance (see **Table 1**). PCE of 6.3% was achieved with pristine CuSCN, while cells based on CuSCN doped with 0.005 and 0.01 mol% C₆₀F₄₈ yielded PCE of 6.4% and 6.6%, respectively. The latter is attributed to the improved fill factor (*FF*) from 59% (pristine) to 61% (doped), and to the increased *V*_{OC} from 0.91 (pristine) to 0.92 (doped). Importantly, the enhancement in the *FF* correlates with the fraction of operational solar cells: 25% of devices were short circuited when a pristine CuSCN HTL was employed, but only 12.5% of cells were defective when the HTL contained 0.005-0.01 mol% C₆₀F₄₈.

Upon *p*-doping of the CuSCN HTLs with C₆₀F₄₈, a substantial improvement in shunt resistance (*R*_{sh}) is observed. In cells utilizing pristine CuSCN HTLs the *R*_{sh} is inferior (460 Ω cm²) to PEDOT:PSS-based reference cells (710 Ω cm²), which is consistent with the presence of pinholes in the CuSCN layer (**Figure 4e**). In contrast, *R*_{sh} increases to 970 Ω cm² when 0.005 mol% of C₆₀F₄₈ is introduced to the CuSCN interlayer. Series resistance (*R*_s) of cells employing CuSCN interlayers doped with 0.005 and 0.01 mol% C₆₀F₄₈ were calculated at 13.0 Ω cm² and 11.7 Ω cm², respectively. Indeed, this remarkable improvement over cells based on pristine CuSCN (*R*_s = 19.8 Ω cm²) provides further evidence of the positive impact of *p*-doping.

Figure 8e shows the dark *J*-*V* characteristics of the same OPV cells. As expected, the shallow conduction band minimum (-1.5 eV) of CuSCN (**Figure 8b**) suppresses minority carrier injection from the anode to the active layer (and vice versa), which is manifested as a substantial reduction in the dark reverse current compared to PEDOT:PSS-based devices. The dark reverse current is further reduced when CuSCN is doped with C₆₀F₄₈, and is primarily attributed to improved HTL uniformity. Interestingly, the *J*_{SC} measured under

illumination for CuSCN:C₆₀F₄₈-based cells (**Figure 8d**) decreased slightly despite the increase in *FF*. This cannot be attributed to changes in parasitic interlayer absorption as evident from **Figure 2a**, and hence, additional studies should be undertaken on the recombination and charge extraction processes as a function of HTL composition.

Finally, transmission electron microscopy (TEM) was used to elucidate the impact of C₆₀F₄₈ doping on the cross-sectional structure of CuSCN HTLs. CuSCN and CuSCN:C₆₀F₄₈ (0.01 mol%) layers were spin-cast on ITO/glass and annealed at 100 °C. Results are presented in **Figure S3**; images displayed side-by-side were obtained at an identical imaging resolution. **Figure S3a-b** present high-angle annular dark/bright field (HAADF) cross-section images, and verify that both HTLs are identical in thickness, and differences in OPV performance cannot be attributed to HTL thickness. Notably, while the C₆₀F₄₈-doped HTL exhibited a closely packed nanostructure, greater variation in image intensity is observed across the pristine CuSCN cross-section. The latter is consistent with the voids observed at the pristine CuSCN surface via AFM, and indicates that the improved layer uniformity of CuSCN:C₆₀F₄₈ HTLs is partly responsible for the improved OPV performance. Lastly, electron energy loss spectroscopy (EELS) elemental mapping data are presented in **Figure S3c-d**. Although a clear distinction between the In-rich (ITO) and Cu-rich (CuSCN) layers can be made, identifying the presence of C₆₀F₄₈ via EELS proved impossible. This is attributed to the low concentration of the dopant and/or the good miscibility with CuSCN.

9. Conclusion

We reported on *p*-doping of CuSCN with C₆₀F₄₈ using a simple, single-step, solution-processing method. Through a combination of DFT calculations and experimental work, it was shown that C₆₀F₄₈ with a LUMO energy of -5.31 eV can facilitate the transfer of an electron

from the top of the CuSCN VB to its LUMO level. Absorption spectroscopy measurements provided direct evidence of the aforementioned charge transfer process in solution phase, while verifying that CuSCN:C₆₀F₄₈ layers retained the wide bandgap characteristics (3.85 eV) of pristine CuSCN. Additional evidence of *p*-doping were provided by Kelvin Probe measurements, which revealed a pronounced Fermi energy shift ($\approx|0.8|$ eV) towards the VB_{max} of CuSCN upon admixing 0.5 mol% of C₆₀F₄₈. X-ray photoelectron spectroscopy provided further evidence of a charge transfer process. In addition to the electronic effects, doping CuSCN with C₆₀F₄₈ was found to have a dramatic impact on the surface roughness of the resulting layers, indicating that the dopant also functions as a nucleating agent. Transistor measurements revealed that the *p*-doping process greatly increased the hole concentration in the channel, which was manifested as an increase in the channel on-current and a shift in V_{Th} . With an optimised doping level of 0.5 mol%, hole mobility in CuSCN TFTs increased by an order of magnitude to 0.18 cm²V⁻¹s⁻¹ as percolation conduction became the dominant transport mechanism. A remarkable enhancement in the bias stability of CuSCN TFTs accompanied by one order of magnitude reduction in the contact resistance, were also achieved with the optimum *p*-doping. When CuSCN:C₆₀F₄₈ layers were employed as the HTL in OPVs based on PCDTBT:PC₇₀BM, the resulting cells exhibited enhanced PCE (6.6%) compared with control devices based on pristine CuSCN (6.3%) and PEDOT:PSS (5.6%) HTLs. The enhanced cell performance was underpinned by an improvement in FF , accompanied by a substantial decrease in R_s due to the increased conductivity of the *p*-doped HTL, and a large increase in R_{sh} . Overall, the present study conclusively demonstrates a simple *p*-doping approach to control the hole-transport properties of CuSCN, and paves the way for numerous new experiments and device applications.

10. Experimental Section

Thin-Film Deposition: Substrates were solvent-cleaned using a sequential ultrasonication procedure: aqueous solution of Decon 90, deionized water, acetone, and isopropanol. Substrates were dried using a nitrogen flow and UV-ozone treated prior to solution deposition. CuSCN powder (Merck, 99%) was dissolved in DES (Merck, 98%) at concentrations of 5-20 mg mL⁻¹ by stirring for 1 h at room temperature. C₆₀F₄₈ was synthesized by Solomeshch and Tessler;^[92] the powder was dissolved in DES at concentrations of 5-20 mg mL⁻¹ by stirring overnight at room temperature. A solution-based, molecular doping strategy was developed by dissolving C₆₀F₄₈ powder in DES at room temperature, and then adding calculated quantities (molar ratios) of C₆₀F₄₈/DES solutions to CuSCN/DES solutions. All mixtures were left to stand at room temperature for 1 h prior to solution characterization or spin-casting in order to regulate the reaction time. C₆₀F₄₈ and CuSCN:C₆₀F₄₈ solutions were chemically stable for extended time periods (>7 days) at concentrations up to 10 mg mL⁻¹, but at higher concentrations (>10 mg mL⁻¹), traces of a precipitate were observed inside the vial after 2-3 days when the solution was left to stand. CuSCN:C₆₀F₄₈ solutions were prepared at dopant concentrations of 0.005-2 mol%. Precursor solutions were spin-cast at 800-2500 rpm for 60 s inside a glovebox, and films annealed at 100 °C for 20 min.

Kelvin Probe (KP) measurements and ambient-pressure ultraviolet photoemission spectroscopy (APS): CuSCN-based layers were spin-cast on solvent-cleaned ITO-coated glass substrates; full coverage of the conductive ITO was ensured. The instrument comprised of a KP Technology SKP5050 Scanning Kelvin Probe and an APS02 Air Photoemission System. Contact potential difference was measured relative to that of a polished silver reference sample, and E_F was calculated with respect to the WF of silver; the latter was verified as 4.70 ± 0.05 eV using APS. VB_{max} energy was determined by exposing CuSCN-based layers to UV radiation ($\lambda = 200$ -280 nm), and recording the photoemission signal as a function of photon energy. All data

were recorded and analyzed using the KP Technology system software, and processed further using Origin software.

Ultraviolet – visible – near-infrared (UV-Vis-NIR) spectroscopy: CuSCN-based layers were spin-cast on quartz substrates and their spectra were measured using a Shimadzu UV-2600 spectrophotometer equipped with an ISR-2600Plus integrating sphere. Transmittance spectra were recorded for $\lambda = 200\text{--}1400$ nm, and absorbance data were calculated. Reflectance spectra were also recorded to calculate E_{OPT} using Tauc analysis. All data were analyzed using Origin software.

X-ray photoelectron spectroscopy (XPS): Core level and valence band spectra were acquired by the XPS technique, with a Kratos Axis Ultra DLD UHV system operated at a base pressure (P_b) $< 5 \times 10^{-10}$ mbar. The XPS measurements were carried out at room temperature using a monochromatic Al $K\alpha$ radiation source, and a pass energy of 20 eV resulting to a broadening less than 500 meV for the Ag $3d^{3/2}$ line.

Tapping-mode atomic force microscopy (AFM): Surface morphology was studied using an Agilent 5500AFM system that employed a cantilever with a resonant frequency of ≈ 270 kHz and a force constant of 40 N m^{-1} . CuSCN-based films were spin-cast on glass from 5 mg mL^{-1} solutions at 800 rpm, and on ITO-coated glass from 20 mg mL^{-1} solutions at 2500 rpm; these are the processing parameters for TFTs and OPV HTLs cells, respectively. Images were recorded using PicoView scanning probe microscopy control software. Gwyddion and Origin software were used to analyze AFM data.

Transmission electron microscopy (TEM): Cross-sectional structures of CuSCN-based HTLs on ITO-coated glass were studied via TEM. Lamellae of the samples were prepared with the assistance of a scanning electron microscope (Helios 400s, FEI) equipped with a focused ion beam (FIB) and a nanomanipulator (OmniProbe, AutoProbe300). The following layers were

deposited on the sample surface to protect it from damage during the later procedures: carbon and platinum under the electron beam assistance; platinum under the ion beam assistance. The samples were then milled, and the lamellae were cut from the bulk with the gallium ion beam (30 kV, 9 nA). Each prepared lamella was attached to the copper grid according to a lift-out method. The attached lamella was then thinned down with the ion beam at a voltage of 30 kV and the current sequentially reduced from 3.0 nA to 0.1 nA. Finally, when the thickness of the lamella reached ≈ 90 -120 nm, the sample was cleaned with the ion beam (5 kV, 48 pA and then 2 kV, 28 pA) to remove possible areas of damage and other contamination. For high-angle annular dark/bright field (HAADF) imaging, a Titan ST transmission electron microscope (FEI) was used at an operating voltage of 300 kV. Elemental distribution maps were characterized by Electron Energy Loss Spectroscopy (EELS) via an energy filter model GIF Tridiem (Gatan). The core loss for carbon (edge location 284 eV) and copper edge (edge location 931 eV and 951 eV) were selected to generate the spectrum maps, via MULL fitting approach provided in the Digital Micrograph software (Gatan).

Transistor Fabrication and Characterization: 40 nm-thick gold S-D were thermally evaporated on glass substrates through shadow masks, and subsequently, were UV-ozone treated to deepen their *WF*. CuSCN-based layers were spin-cast and thermally annealed according to procedures detailed above. The high-k relaxor ferroelectric polymer dielectric, P(VDF-TrFE-CFE) was dissolved in 2-butanone (Merck, $\geq 99.0\%$). The dielectric solution was spin-cast on the semiconductor layer at 3000 rpm for 30 s, and annealed at 60 °C for 1 hour in nitrogen. TFTs were completed by thermally evaporating 40 nm-thick Al gate electrodes using shadow masks. Devices were electrically characterized at room temperature and atmospheric pressure in nitrogen using an Agilent B2902A parameter analyzer. The field-effect hole mobility in the saturation regime (μ_{sat}) was calculated using the second derivative method derived from the standard gradual channel approximation transistor model.

Organic photovoltaic cell fabrication and characterization: Standard structure OPV cells were fabricated using PEDOT:PSS and CuSCN-based HTLs. The as-received aqueous dispersion of PEDOT:PSS (CLEVIOS PH 1000, Heraeus) was spin-cast on ITO-coated glass at 7000 rpm and annealed at 140 °C for 20 min. CuSCN-based HTLs were spin-cast at 2500 rpm from 20 mg mL⁻¹ solutions and annealed at 100 °C in nitrogen. For the inverted structure solar cells, zinc acetate (99.99%, Merck) was dissolved at 110 mg mL⁻¹ in 2-methoxyethanol (anhydrous, 99.8%, Merck) containing 3% ethanolamine (99.5%, Merck). The ZnO precursor solution was spin-cast on ITO-coated glass at 4000 rpm and annealed at 150 °C for 20 min in the ambient air environment of a laboratory fume hood. For the BHJ active layer blend, PCDTBT (1-Material) and PC₇₀BM (Solenne BV) were dissolved in 1,2-dichlorobenzene (Merck, anhydrous, 99%) at a ratio of 1:2 and total concentration of 18 mg mL⁻¹ by stirring overnight at 80 °C. The active blend solution was spin-cast at 1250 rpm for 10 s in nitrogen. The cells were completed by thermally evaporating a 10 nm-thick layer of bathocuproine (BCP, 99.99%, Merck) followed by a 70 nm-thick Al electrode for standard structure solar cells, and a 10 nm-thick layer of molybdenum trioxide (MoO₃, 99.97%, Merck) followed by a 70 nm-thick silver electrode for the inverted structure solar cells, through shadow masks. *J-V* characteristics were measured in nitrogen using a Keithley 2400 source-meter. The AM1.5 illumination was provided by a Sciencetech Inc. Solar Simulator SF300-A. The active area of each cell was 5 mm² as defined by a metal stencil mask.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

N.W. and T.D.A. acknowledge financial support from the European Research Council (ERC) AMPRO grant number 280221, and the Engineering and Physical Sciences Research Council (EPSRC) grant number EP/L504786/1. The authors acknowledge the King Abdullah University of Science and Technology (KAUST) for the financial support. L.T. acknowledges support for the computational time granted from the Greek Research & Technology Network (GRNET) in the National HPC facility – ARIS – under project pr004034-STEM.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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Figures

Figure 1. Chemical structures of CuSCN (a), and C₆₀F₄₈ (b). (c) HOMO, and (d) LUMO of C₆₀F₄₈ derived via DFT calculations with the code Quantum Espresso. (e) Electronic energy level diagram of CuSCN, C₆₀F₄₈ and UV-ozone Au electrodes.

Figure 2. (a) UV-Vis-NIR absorbance spectra of DES and DES-based solutions (1 mg mL⁻¹). The solution containing a mixture of CuSCN:C₆₀F₄₈ (1:1 molar ratio) exhibit an absorption band at visible and NIR wavelengths (500-900 nm) that is not observed in CuSCN or C₆₀F₄₈ solution spectra. Spectra of pristine CuSCN and CuSCN:C₆₀F₄₈ (0.1 mol% $\approx$ 1000:1 molar ratio) solid layers spin-cast on quartz from 5 mg mL⁻¹ solutions and annealed at 100 °C are also shown. (b) Tauc analysis of UV-Vis-NIR spectra from a CuSCN:C₆₀F₄₈ (0.1 mol%) layer. (c) KP-APS measurements of E_F and VB_{max} in CuSCN:C₆₀F₄₈ blend films spin-cast on ITO-coated glass and annealed at 100 °C for different concentrations of C₆₀F₄₈.

Figure 3. X-ray photoelectron spectroscopy of pristine CuSCN (blue dashed lines) and CuSCN:C₆₀F₄₈ (0.1 mol%, red solid lines) layers spin-cast on Si++ from DES solutions and annealed at 100 °C. (a)-(d) Core level spectra including (a) Cu 2p, (b) S 2p, (c) C 1s, and (d) N 1s. Vertical lines indicate the binding energies of individual chemical bonds.^[78] The peak labelled C-C in the C 1s spectra corresponds to aliphatic C-C and adventitious C. (e) Valence band spectra and one electron cross section corrected density of states (DOS) for pristine CuSCN from DFT calculations. Addition of 0.1 mol% C₆₀F₄₈ reduces the spectral separation of peaks in the C 1s envelope (c), and decreases the contribution from Cu 3d states to the VB (e) – both are possible indications of a charge transfer process between CuSCN and C₆₀F₄₈.

Figure 4. AFM surface topography images (scan area = 1 μm^2) of CuSCN-based solid layers spin-cast from DES solutions on glass (a)-(d), and ITO-coated glass (e)-(h) substrates. The mol% concentration of C₆₀F₄₈ is specified where applicable. Lighter colours correspond to higher regions of the surface and the specified z-values denote the maximum height relative to the minimum ($z = 0$). The line scan marked on (c) is analyzed in **Figure 5a**.

Figure 5. (a) Line scan extracted from AFM topography data in **Fig. 4c** shows the two distinct grain types present in CuSCN: $C_{60}F_{48}$ solid layers. (b) Height histograms extracted from high resolution glass/CuSCN images (scan area = $1 \mu m^2$) in **Figure 4**; data from a plain glass substrate is shown as a reference. (c) RMS surface roughness statistics calculated from topography images (scan area = $5 \mu m^2$) of CuSCN: $C_{60}F_{48}$ (0-1 mol%) layers on glass. The top plot presents mean R_{rms} (± 0.1 nm), and the bottom plot presents ΔR_{rms} range calculated from three scans of each sample type. (d) Height histograms extracted from ITO/CuSCN images (scan area = $5 \mu m^2$); data from bare ITO is shown as a reference. (e) RMS surface roughness statistics calculated from topography images (scan area = $5 \mu m^2$) of CuSCN: $C_{60}F_{48}$ (0-0.5 mol%) layers on ITO-coated glass.

Figure 6. Transfer (a) and output (b) characteristics measured for CuSCN transistors with different $C_{60}F_{48}$ concentrations. (c) Square-root of I_D calculated from the transfer curves measured in saturation in (a). Example linear fits for V_T extraction are indicated with dotted lines. Inset shows a schematic of the staggered TG-BC transistor architecture employed with Au S-D contacts and Al gate electrode. (d) Turn-on voltage and threshold voltage dependence on $C_{60}F_{48}$ concentration. (e) Dependence of the channel on- and off-currents (at $V_G = -10$ V), and (f) hole mobility on $C_{60}F_{48}$ concentration. Parameters plotted in (d)-(f) were extracted from transfer characteristics in (a), with each data point representing the mean of at least five devices, and error bars indicating maxima and minima. All devices had the same channel dimensions of $L = 30 \mu\text{m}$ and $W = 1000 \mu\text{m}$.

Figure 7. Total channel resistance calculated for pristine (a), and C₆₀F₄₈-doped (b) CuSCN TFTs. (c) Contact resistance extracted from the y-axis intercepts of the linear fits in (a) and (b). (d) Variation of the channel on-current monitored at $V_G = V_D = -10$ V with respect to I_{D-on} at time (t) = 0. (e) Variation in threshold voltage (ΔV_T) relative to V_T at $t = 0$. (f) V_G dependence of linear hole mobility in pristine and p -doped CuSCN TFTs.

Figure 8. (a) Chemical structures of the active organic blend components namely PC₇₀BM and PCDTBT. (b) Energy levels of all materials employed. (c) Schematic cross-section of the standard cell architecture used. (d) *J-V* characteristics measured under AM1.5 illumination for OPV cells based on different HTLs, namely; PEDOT:PSS, CuSCN and *p*-doped CuSCN:C₆₀F₄₈ (0.005 mol%). The *J-V* curve of an inverted cell based on ZnO electron transport layer is also shown for comparison. Solar cell parameters are summarized in **Table 1**. (e) Dark *J-V* characteristics of five standard architecture OPV cells employing different HTLs, namely PEDOT:PSS, CuSCN and *p*-doped CuSCN:C₆₀F₄₈ (0.005–0.05 mol%).

Table 1. Summary of operating parameters for PCDTBT:PC₇₀BM blend OPV cells made with different HTLs, measured under AM1.5 illumination.

HTL ^{a)}	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE (%)	Short Circuits ^{b)}
PEDOT:PSS	11.1 (11.1)	0.86 (0.88)	0.59 (0.61)	5.6 (6.0)	0/16
CuSCN	11.8 (11.9)	0.91 (0.92)	0.59 (0.60)	6.3 (6.5)	4/16
CuSCN:C ₆₀ F ₄₈ 0.005 mol% ^{c)}	11.4 (11.4)	0.92 (0.92)	0.61 (0.67)	6.4 (7.0)	2/16
CuSCN:C ₆₀ F ₄₈ 0.01 mol% ^{c)}	11.5 (11.7)	0.92 (0.92)	0.61 (0.64)	6.6 (6.8)	2/16
CuSCN:C ₆₀ F ₄₈ 0.05 mol% ^{c)}	11.1 (12.0)	0.92 (0.92)	0.58 (0.59)	5.9 (6.5)	0/16
ZnO ETL (inverted)	10.9 (11.6)	0.89 (0.90)	0.61 (0.61)	5.9 (6.4)	1/16

^{a)}Mean values obtained from a set of 16 cells of each type excluding the minority that were short-circuited; data from the ‘champion’ cell given in brackets.

^{b)}Fraction of cells that exhibited incorrect OPV function, i.e., J - V curves indicated that the device was short-circuited.

^{c)}Specified value is the concentration of C₆₀F₄₈ dopant in the CuSCN layer.

Efficient *p*-doping of the wide bandgap semiconductor copper(I) thiocyanate (CuSCN) is demonstrated using the fluorofullerene derivative C₆₀F₄₈. Incorporation of the *p*-doped layers as the channel semiconductor in thin-film transistors and as the hole-transport interlayer in organic solar cells is shown to improve the operating characteristics of the devices.

Keywords: Copper(I) thiocyanate; *p*-type doping; hole transport layers; organic solar cells; transparent transistors

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***p*-Doping of Copper(I) Thiocyanate (CuSCN) Hole Transport Layers for High Performance Transistors and Organic Solar Cells**

ToC Figure

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Supporting Information

p-Doping of Copper(I) Thiocyanate (CuSCN) Hole Transport Layers for High Performance Transistors and Organic Solar Cells

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S1. Atomic Force Microscopy

Figure S1. (a) AFM topography, and (b) phase images (scan area = 1 μm^2) of a CuSCN:C₆₀F₄₈ solid layer spin-cast on glass from a DES solution and annealed at 100 °C; the concentration of C₆₀F₄₈ was 2 mol%. Lighter colours in the topography image correspond to higher regions of the surface and the specified *z*-value denotes the maximum height relative to the minimum at *z* = 0. This film exhibited significant surface non-uniformities compared to the images presented in **Figure 4**, which indicated that the addition of 2 mol% of C₆₀F₄₈ to CuSCN was detrimental to its function as an HTL. The non-uniformities are primarily attributed to the reduced long-term stability of CuSCN:C₆₀F₄₈ solutions that contain high concentrations (>1 mol%) of C₆₀F₄₈, where precipitates were observed when solutions were left to stand. In the phase image, lighter and darker regions correspond to local variations in energy dissipated by the AFM cantilever as it scanned the sample surface. Significant phase contrast – indicative of differences in chemical composition – was not observed in (b). The phase signal confirmed that both the smooth nanocrystalline region and the larger crystallites observed in CuSCN:C₆₀F₄₈ solid layers were composed of the same material, with no segregation of CuSCN and C₆₀F₄₈ at the HTL surface that forms a critical interface with the active layer. It is evident that the larger crystallites nucleate upward from the smooth nanocrystalline region, with no evidence of discontinuities arising from the presence of fluorofullerene molecules in the inorganic semiconductor layer.

S2. Thin-Film Transistor Characterization

Figure S2. Representative linear regime transfer characteristics of TFTs containing a P(VDF-TrFE-CFE) dielectric and a spin-cast CuSCN:C₆₀F₄₈ semiconductor layer annealed at 100 °C; all devices had channel dimensions of $L = 30\ \mu\text{m}$ and $W = 1000\ \mu\text{m}$. This data corresponds to the set of saturation regime transfer curves presented in **Figure 6a** and exhibits a similar trend with increasing concentration of C₆₀F₄₈.

Table S1. Summary of the device parameters for CuSCN transistors with P(VDF-TrFE-CFE) high- k polymer dielectric; channel dimensions are $L = 30\ \mu\text{m}$ and $W = 1000\ \mu\text{m}$.

C ₆₀ F ₄₈ ^{a)} (mol%)	I_{D-on} ^{b)} (μA)	I_{D-off} ^{b)} (nA)	On/off ratio ^{b)}	V_{on} ^{b)} (V)	V_T ^{b)} (V)	μ_{lin} ^{c)} ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	μ_{sat} ^{c)} ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	SS ^{d)} (V dec ⁻¹)
0	1	0.6	2×10^3	-0.2	-3.1	0.007 (0.009)	0.010 (0.014)	0.9
0.01	3	4	8×10^2	-0.1	-2.7	0.016 (0.019)	0.025 (0.026)	1.0
0.02	3	4	8×10^2	+0.7	-2.4	0.023 (0.027)	0.034 (0.038)	1.0
0.05	4	5	8×10^2	+1.3	-2.3	0.021 (0.026)	0.039 (0.042)	1.2
0.10	6	10	6×10^2	+1.9	-2.1	0.032 (0.035)	0.045 (0.049)	1.4
0.20	9	12	8×10^2	+2.2	-2.0	0.051 (0.057)	0.081 (0.085)	1.6
0.50	14	14	1×10^3	+3.4	-1.7	0.083 (0.10)	0.12 (0.18)	1.6
1.00	5	10	5×10^2	+3.3	-1.7	0.022 (0.028)	0.030 (0.036)	2.3

^{a)} Concentration of the C₆₀F₄₈ dopant in the CuSCN semiconductor layer.

^{b)} Mean values obtained from five TFTs; saturation regime data ($V_D = -10\ \text{V}$).

^{c)} Mean values obtained from five TFTs; data from the ‘champion’ device is given in brackets.

^{d)} Mean values obtained from five TFTs; linear regime data ($V_D = -2\ \text{V}$).

Figure S3. Analysis of bias-stress measurement data from CuSCN transistors ($L = 30 \mu\text{m}$ and $W = 1000 \mu\text{m}$) obtained under $V_G = V_D = -10 \text{ V}$ biasing conditions during a 2 h time period. Saturation regime transfer curves ($V_D = -10 \text{ V}$) were recorded at regular time intervals and key parameters were monitored. The plots show a comparison of transfer characteristics before and after the bias-stress period. The square-root of each curve and the linear fit from which the threshold voltage (V_T) was extracted are also shown. (a) Effect of bias-stress on a TFT containing a pristine CuSCN semiconductor layer. (b) Effect of bias-stress on a TFT containing a CuSCN:C₆₀F₄₈ (0.5 mol%) semiconductor layer – a dopant concentration that gives improved TFT performance. Quantitative results are summarized in **Table S2**. The addition of 0.5 mol% C₆₀F₄₈ to the CuSCN semiconductor layer significantly improves the transistor bias stability. Note: These results originate from a different batch of transistors to the batch analyzed in **Table S1**.

Table S2. Device parameter changes in CuSCN transistors following a 2 h bias-stress period under $V_G = V_D = -10 \text{ V}$ biasing conditions.

Semiconductor ^{a)}	ΔI_{D-on} ^{c)}	ΔV_{on} (V)	ΔV_T (V)
CuSCN (pristine)	0.61x	+1.1	-0.9
CuSCN:C ₆₀ F ₄₈ (0.5 mol%) ^{b)}	1.09x	+0.7	0

^{a)} TG-BC transistors with a P(VDF-TrFE-CFE) high-k polymer dielectric; channel dimensions are $L = 30 \mu\text{m}$ and $W = 1000 \mu\text{m}$.

^{b)} Concentration of the C₆₀F₄₈ dopant in the CuSCN semiconductor layer.

^{c)} On-current (I_{D-on}) is extracted at $V_G = -10 \text{ V}$ and x denotes I_{D-on} at time (t) = 0.

S3. Transmission Electron Microscopy

Figure S3. TEM cross section images of CuSCN-based solid layers spin-cast on ITO-coated glass from DES solutions and annealed at 100 °C. Images displayed side-by-side were obtained at an identical resolution. (a)-(b) High-angle annular dark/bright field (HAADF) cross-section images: (a) pristine CuSCN, (b) CuSCN doped with 0.01 mol% C₆₀F₄₈ – a dopant concentration that gives improved OPV performance. HAADF results verified that the two CuSCN films appear to be identical in thickness, and hence, the enhancement in solar cell performance observed when a pristine CuSCN HTL is replaced by a CuSCN:C₆₀F₄₈ (0.01 mol%) HTL cannot simply be attributed to a difference in HTL thickness. HAADF image intensity is proportional to Z^2 for samples of equal depth. Greater variation in image intensity across the pristine CuSCN layer reveals that the C₆₀F₄₈-doped HTL exhibits a more uniform nanostructure through its cross section. Hence, we propose that the superior performance of solar cells containing CuSCN:C₆₀F₄₈ HTLs with a dopant concentration of 0.005–0.01 mol% could also be correlated with an improvement in the bulk crystallinity, in addition to the change in surface morphology shown in **Figure 4** and **Figure 5**. Confirmation of such structural differences would require further study using X-ray reflectivity measurements to quantify any change in the HTL density. (c)-(d) Electron energy loss spectroscopy (EELS) elemental mapping: (c) pristine CuSCN, (d) CuSCN doped with 0.01 mol% C₆₀F₄₈. EELS results show that the copper, and thus the CuSCN, is uniformly distributed throughout the CuSCN:C₆₀F₄₈ layer. The images show no evidence of compositional non-uniformities arising from the presence of fluorofullerene molecules.