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High Efficiency Organic Photovoltaic Cells Based on the Solution-Processable Hole Transporting Interlayer Copper Thiocyanate (CuSCN) as a Replacement for PEDOT:PSS

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Organic photovoltaic (OPV) devices are now recognized as a promising future source of affordable renewable energy due to their potential for high throughput manufacturing and low energy payback time.^[1] Recent advances in the design and synthesis of new active materials (polymers and small molecule organics) combined with microstructural engineering of the photoactive layers have led to the development of OPV devices with power conversion efficiencies (PCEs) approaching 10%.^[2, 3] In addition to the active materials, the effects of thin interfacial layers (or interlayers) inserted between the active layer and the device electrodes (i.e., anode and cathode) have also been studied extensively during the last decade

and their key role on the overall OPV performance has been demonstrated.^[3-11] To this end, an ideal interlayer system should combine the following much desired characteristics: (1) easy to process at room temperature over large area substrates; (2) having appropriate surface energy to allow deposition of subsequent active layers; (3) highly transparent from the ultraviolet to visible (UV-Vis) to the near infrared (NIR) part of the electromagnetic spectrum;^[4, 7, 12] (4) having appropriate energy levels in order to facilitate the formation of Ohmic contact with the active organic materials; and, (5) ability to block minority carrier flow towards the un-favored electrode. These interlayer materials characteristics have indeed been found to have a profound influence on overall OPV performance^[3-8] and further information can be found in relevant review articles.^[13-18] The ideal interlayer material system should additionally satisfy all or most of the above requirements independent from the choice of the active organic layer.

To date the vast majority of OPV devices are based on blends of poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) as the hole transporting interlayer system. Some of the reasons behind its widespread use include the straight-forward processing protocols which are able to deliver continuous and ultra-smooth films, the relatively good optical transparency (80-87%), and its deep work function (~5.1 eV) that results in the formation of Ohmic contact with a range of commonly used organic donor compounds. Despite these attractive properties, however, it is now well established that due to its acidic nature, PEDOT:PSS can react with organic active layers^[19, 20] as well as etch the underlying transparent indium tin oxide (ITO) electrode,^[21] both of which limit the cell's long-term operational stability. Moreover, recent studies suggest that the electron blocking properties of PEDOT:PSS are insufficient due to its semi-metallic nature.^[15, 22] Some of the negative effects can be moderated by removal of the PSS component, using vapor phase polymerized PEDOT (VPP-PEDOT)^[23] as well as various solvent treatments.^[24] In addition to PEDOT:PSS based materials, a number of alternative solution processable hole transporting

systems were recently demonstrated including conducting polymers,^[25, 26] solution processed metal oxides,^[27, 28] graphene-based materials,^[29] and carbon nanotubes.^[30] Despite the significant progress, however, there remains a clear need for the discovery and/or development of new hole transporting interlayer with improved physical characteristics for use in next generation inexpensive OPV devices and in plastic optoelectronics more generally.

We have recently reported the development of hole transporting (*p*-channel) transistors based on the inorganic molecular metal pseudo-halide semiconductor copper(I) thiocyanate (CuSCN).^[31, 32] It was shown that solution-processed layers of CuSCN exhibit intrinsic hole transporting characteristics and ultra-high transparency across the UV-Vis/NIR part of the electromagnetic spectrum due to its characteristic wide band gap (>3.5 eV).^[31, 32] These results imply that application of CuSCN could potentially be extended to other optoelectronic devices where high mobility hole transport and superior optical transparency are both highly desired. Despite the great promise, however, to date the use of CuSCN as hole transporting layer (HTL) in optoelectronic devices is limited to relatively thick top layers in solid state dye synthesized solar cells (DSSCs)^[33, 34], and more recently to hybrid perovskite solar cells.^[35]

Here we report on the use of CuSCN as a generic transparent anodic interlayer material in high efficiency solution-processed bulk-heterojunction OPV devices. The solubility and solvent orthogonality of CuSCN combined with its large optical gap and intrinsic *p*-type nature, enable the growth of highly transparent (average 89% between 400 and 1300 nm), high mobility hole transporting layers that are compatible with a variety of organic donor-acceptor (D-A) systems. The advantages of CuSCN as a HTL are demonstrated by fabricating several different OPV structures, each with an improved PCE in the range of 6-8%. Importantly, CuSCN-based devices are found to always outperform control OPV cells made with PEDOT:PSS as the HTL. The enhanced performance of the

prototype BHJ cells is attributed to the reduced parasitic absorption of CuSCN and possibly to its superior electron blocking properties - a key enabling characteristic that is absent from the PEDOT:PSS-based system.

The primary reason for the relatively limited use of CuSCN as a solution processible semiconductor to date is its low solubility.^[31-33] Dipropyl sulfide (DPS) is one among a handful of solvents known to dissolve CuSCN at appreciable concentrations and has been used extensively in the field of DSSCs.^[36, 37] However, the limited solubility of CuSCN in DPS dictates the use of saturated solutions which in turn leads to the formation of HTLs with insufficient uniformity/continuity especially when layer thicknesses over 20 nm are required. The solubility of CuSCN in the shorter n-alkyl sulfide, diethyl sulfide (DES), has been shown to be significantly higher than in DPS and used in DSSCs albeit with limited success (i.e., fabricated cells exhibited low PCE).^[33]

Motivated by this early work we have investigated the structural and electronic properties of CuSCN films processed from a 40 mg/ml diethyl sulfide solution using atomic force microscopy (AFM) and field-effect transistor measurements (FET). **Figure 1a** displays the surface topography and phase images of a 45 nm-thick CuSCN film deposited on a glass substrate. The film appears continuous and nanocrystalline in nature with an RMS surface roughness of ~5.2 nm. When the CuSCN films are integrated in top-gate, bottom-contact (TG-BC) transistor structures (inset, **Figure 1b**), clear hole accumulation can be observed (**Figure 1b**). The devices exhibit small operating hysteresis, low threshold voltage (-1.2 V), relatively high hole mobility (0.01-0.1 cm²/Vs) and relatively high on/off current ratio (~5×10³) indicative of the intrinsic semiconducting nature of DES-processed CuSCN films. It can therefore be concluded that the physical properties of CuSCN films processed from DES solution resemble very closely those processed from DPS^[32] but with the added advantage of

being able to grow thicker films due to the enhanced solubility of CuSCN in DES. Although this development appears to be relatively trivial, the implications for the field of OPVs are significant and will be discussed later.

Since PEDOT:PSS is the most widely used anodic HTL material, a detailed comparison was carried out of structural and optical properties for 45 nm-thick films of CuSCN and PEDOT:PSS. First, film formation was studied for the two HTL systems processed directly on top of pre-patterned transparent indium tin oxide (ITO) anodes on glass substrates. **Figure 2a** displays AFM surface topography images of the resulting PEDOT:PSS and CuSCN films. The PEDOT:PSS film surface appears ultra-smooth with an RMS surface roughness, $\Delta t_{\text{RMS}} = 1.54$ nm (**Figure 2b**), lower than that of the underlying ITO ($\Delta t_{\text{RMS}} = 3$ nm) (**Figure 2b**). CuSCN films on the other hand appear nanocrystalline (similar to those deposited on bare glass (**Figure 1a**)), with a surface roughness ($\Delta t_{\text{RMS}} = 3.44$ nm) that is significantly higher than for PEDOT:PSS. From these measurements we conclude that continuous films of CuSCN can indeed be solution processed onto glass/ITO electrodes, albeit with potential for further optimization.

One potential advantage of CuSCN interlayers relative to PEDOT:PSS is that there is substantially lower loss due to parasitic (unwanted) absorption/reflection across a broad range of the solar spectrum. In order to quantify this effect, we have measured the optical spectra of both HTL systems in the range 220-1400 nm. **Figure 2c** shows the transmission spectrum for a bare glass substrate together with the parasitic absorption spectra of ~45 nm-thickness films of CuSCN and PEDOT:PSS deposited on top. The latter were calculated directly from the transmission and reflection spectra shown in **Figure S1**. As can be seen, the CuSCN film exhibits very little absorption in the range 360-1400 nm, due to its wide optical gap (> 3.5 eV^[32, 38]). On the other hand, the PEDOT:PSS film shows significant absorption throughout the

visible and near infra-red (NIR) regions; the oxidative doping that introduces polaronic charges is accompanied by new intragap absorptions. In the case of OPV devices, parasitic absorption by the interlayer represents an important loss mechanism that reduces the overall PCE and for PEDOT:PSS this absorption peaks in the NIR – a critical region of the spectrum for solar cells.^[39] Integrating the standard reference solar spectrum (AM1.5G 1 sun) yields a power density of 100 mW/cm², the majority of which (~87.2 mW/cm²) comes from the 360-1400 nm region of the spectrum. The parasitic absorption of PEDOT:PSS in this spectral region leads to an estimated loss of 6% (~5.3 mW/cm²) of the available power, while the loss due to parasitic absorption in the CuSCN layer is only 0.6% (see **Figure S2**). As will be discussed later, this 10-fold decrease in parasitic absorption most likely dominates the large increase in PCE measured for the CuSCN-based devices although photonic effects due to the differences in the refractive indices of the two HTLs should also be considered.

In order to investigate the potential of CuSCN films as HTL in OPVs, bulk heterojunction (BHJ) cells were fabricated using the well-understood poly-3-hexyl thiophene (P3HT): indene-C₆₀ bisadduct (ICBA) (**Figure 3a**) blend system as active layer. The 45 nm-thick hole transporting layer (HTL) of either CuSCN or PEDOT:PSS was then spin-coated onto pre-patterned ITO electrodes on a glass substrate. The P3HT:ICBA (1:0.7 wt.%) blend was next deposited from a solvent mixture of chlorobenzene and 1.5% V/V chloronaphthalene^[40] and device fabrication was completed by *in vacuo* (10⁻⁶ mbar) thermal evaporation of a bi-layer Sm/Al cathode. We note that the HTL thickness of ~45 nm was chosen because it was found to yield the best performing P3HT:ICBA cells based on PEDOT:PSS. The latter HTL was then replaced with a CuSCN layer of equivalent thickness hence allowing direct assessment of the impact that this HTL system on the overall OPV performance. **Figure 3b** displays a schematic of the device architecture while **Figure 3c**

illustrates the key energy levels, namely the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs), of the materials employed.

Figure 3d displays the current density-voltage (J-V) characteristics for two best performing CuSCN and PEDOT:PSS-based OPV cells measured under simulated solar illumination (AM1.5G, 1 sun). Devices using CuSCN as HTL exhibits nearly identical open-circuit voltage (V_{OC}) and fill factor (FF) to PEDOT:PSS-based cells but with a significantly increased short-circuit current (J_{SC}). As a result the CuSCN-based cells exhibit consistently higher PCE (%) than PEDOT:PSS devices. The operating parameters calculated from a number of devices are summarized in **Table 1**. The equal V_{OC} (~ 0.83 V) measured for the two cell types suggests that the position of the valence band of CuSCN (~ 5.5 eV ^[31]) is not a limiting factor for device efficiency. Additionally, the similarity in FF values obtained for best performing CuSCN and PEDOT:PSS-based devices (0.69 and 0.73, respectively) indicates that CuSCN does not introduce excessive contact and/or bulk resistances; the latter being primarily influenced by carrier mobility since CuSCN is an intrinsic semiconductor.

Finally, to better understand the origin of the enhanced J_{SC} for CuSCN devices, external quantum efficiency (EQE) spectra were measured (**Figure 3e**). These show that CuSCN-based devices have approximately 5% higher EQE than corresponding PEDOT:PSS devices, across the whole 400 - 700 nm spectral range. It is evident from our data that CuSCN can indeed be used as a replacement for PEDOT:PSS and that doing so yields a surprisingly positive impact on overall device performance with significant room for further device optimization since the CuSCN layer thickness of ~ 45 nm used in these devices is not necessarily the optimum one. However, detailed assessment of the impact of the CuSCN layer thickness on the device performance is beyond the scope of this work and will be the subject of a future study.

In order to more generally demonstrate the potential of CuSCN as a ‘universal’ HTL, BHJ solar cells were fabricated with two further donor materials, namely, 7,7'-[4,4-Bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl]bis[6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5yl)benzo[c][1,2,5]thiadiazole] (DTS(FBTTh₂)₂)^[41] and poly(dithiophene-diketopyrrolopyrrole-2,5-di-2-thienylthieno[3,2-b]thiophene) (PDPP-2T-TT).^[42] PC₇₁BM was used as acceptor in both cases, adjusting the BHJ D-A weight ratio to maximize device efficiency (see *Experimental Section*). **Figures 4a** and **b** show, respectively, the molecular structures of DTS(FBTTh₂)₂, PDPP-2T-TT and PC₇₁BM and the associated HOMO/LUMO energy levels. The J-V characteristics measured for DTS(FBTTh₂)₂:PC₇₁BM and PDPP-2T-TT:PC₇₁BM BHJ cells are shown in **Figure 4c**, while **Table 2** summarizes their operating parameters. The J-V characteristic for CuSCN-based P3HT:ICBA cells from **Figure 3d**, is also re-plotted in **Figure 4c** for comparison. It is evident in all three cases that the CuSCN HTL performs well. Specifically, best performing OPV cells based on DTS(FBTTh₂)₂:PC₇₁BM yield Voc = 0.80 V, FF = 0.62, and Jsc = 14.2 mA/cm², with an overall PCE = 7.0%, - close to that reported for DTS(FBTTh₂)₂:PC₇₁BM cells with PEDOT:PSS as HTL.^[41] Best performing devices based on PDPP-2T-TT:PC₇₁BM show Voc = 0.70 V, FF = 0.69, and Jsc = 16.7 mA/cm² with PCE = 8.0%. These results provide strong evidence of the general utility of CuSCN as an OPV HTL system.

As already noted, one of the key benefits associated with the use of CuSCN as HTL is its reduced parasitic absorption relative to PEDOT:PSS (**Figure 2c**) in the UV-Vis-NIR part of the spectrum. In the absence of photonic effects (due to the associated changes in HTL refractive index) on the BHJ active layer absorption and given the increasing absorption of PEDOT:PSS into the NIR, the benefit of using CuSCN should be proportionately greater for BHJ blends employing narrower-gap donors.

To investigate this further, we prepared two sets of PDPP-2T-TT:PC₇₁BM OPV cells, one with CuSCN and the other with PEDOT:PSS as HTL and (for ease of comparison) with equal thickness BHJ blend and HTL films thicknesses. **Figure 4d** displays the *J-V* characteristics for representative cells prepared under the same conditions. As in the case of P3HT:ICBA cells, these devices deliver the same FF (0.69) and V_{OC} value (0.7 V), implying similar electrical properties. However, J_{SC} for the CuSCN-based cell is approximately 25 % higher. This increases the overall PCE to slightly over 8%, a notable enhancement relative to the 6.2% measured the PEDOT:PSS-based cells.

In order again confirm that the enhanced J_{SC} in the CuSCN-based devices arises primarily from the difference in HTL absorption, EQE measurements were carried out for both types of cell (**Figure 4d**). The observed differences in wavelength-dependent current generation agree well with the differences in parasitic absorption. Specifically, both devices exhibit broad EQE spectra that include contributions from the acceptor (PC₇₁BM absorption in the range 400-650 nm) and the donor (PDPP-2T-TT absorption in the range 600-900 nm) components, with a significantly increased EQE for the CuSCN-based device. The latter is most pronounced in the NIR region as expected from the PEDOT:PSS parasitic absorption spectrum (**Figure 2c**). Thus, without altering the device fabrication conditions, simple replacement of PEDOT:PSS with CuSCN as HTL results in a maximum PCE of slightly over 8%, the highest value reported to date for this specific D-A system.^[42] Although this level of performance may indeed appear to be high, we believe that further improvement may be possible through additional optimization of the cell's photonic architecture, making the application of CuSCN as a universal HTL even more attractive.

In summary, the application of CuSCN as a HTL material for high performance organic solar cells was reported. Substituting the commonly used PEDOT:PSS HTL in a P3HT:ICBA-based solar cell with CuSCN, is found to increase the J_{sc} while maintaining high V_{oc} and FF, hence increasing the cell's maximum PCE to $\sim 6.5\%$. The potential of CuSCN as a 'universal' HTL system was demonstrated through its use in OPVs based two further D-A BHJ systems. Both small-molecule (DTS(FBTTh₂)₂) and narrow bandgap polymer (PDPP-2T-TT) blends with PC₇₁BM gave higher efficiencies when CuSCN was used as HTL. The maximum performance achieved for the PDPP-2T-TT:PC₇₁BM blend was especially notable, increasing from 6.2% for PEDOT:PSS HTL-based cells to over 8% for best performing CuSCN HTL cells. EQE measurements indicate that this improvement is consistent with differences in interlayer parasitic absorption. Future work will explore the differences in photonic structure that arise when PEDOT:PSS is replaced as HTL by CuSCN as well as the possibility of doping CuSCN using suitable chemical species.

Experimental Section

Material Processing and Device Fabrication: 45 nm-thickness CuSCN (Aldrich) and PEDOT:PSS (Clevios PVP A14083 solution) HTLs were spin-coated at 2000 and 4000 rpm, respectively, on top of either cleaned glass (for AFM and UV-Vis-NIR spectra measurements) or glass/ITO substrates (for AFM measurements and OPV device fabrication). The HTLs thicknesses were measured using a Dektak 150 stylus profilometer. The BHJ active layer blends were next deposited in inert atmosphere (dry N₂ glove box) on top of the HTL layers (PEDOT:PSS or CuSCN) according to the following procedures:

1. P3HT:ICBA (1:0.7 weight ratio) was spin coated at 1000 rpm from a 20 mg/ml chlorobenzene solution containing 1.5 vol.% chloronaphthalene. As-deposited films were then annealed at 150 °C for 7 minutes resulting in a film thickness of ~ 90 nm.

2. Blends of DT-PDPP-2T-TT:PC₇₁BM (1:3 weight ratio) were prepared in a 8.3 mg/ml chloroform solution containing 7.5 vol.% o-DCB. The active layer was spin-coated at 1200 rpm.
3. Blends of DTS(FBTTh₂)₂:PC₇₁BM (3:2 weight ratio) were prepared in a 35 mg/ml chlorobenzene solution containing 0.4 vol.% DIO. Films were spin coated at 1500 rpm and annealed at 80 °C for 5 minutes resulting in a film thickness of ~ 100 nm.

These processing conditions and solvent mixtures/additives were chosen in order to control the active layer morphology according to procedures reported previously.^[43]

The OPV cells were then completed by thermal evaporation of a bilayer Sm/Al (10/90 nm) cathode in high vacuum (10⁻⁶ mbar).

Top-gate, bottom-contact transistors were fabricated on glass substrates with pre-patterned, thermally evaporated 30 nm-thickness Au source and drain (S-D) electrodes. The 5 mg/ml diethyl sulfide CuSCN solution was then spin coated on top at 800 rpm under inert atmosphere (dry N₂ glove box) at room temperature. The samples were then annealed at 100 °C for 5 minutes under nitrogen. Next, a 220 nm-thickness layer of the high-*k* gate dielectric P(VDF-TrFE-CFE) was spin-coated directly onto the CuSCN layer and annealed at 60 °C for 3 hours in nitrogen. The transistor structure was completed by thermal evaporation of a 50 nm-thickness Al gate electrode in high vacuum.

Morphological and Optical Characterization: Transmission and reflection UV–Vis–NIR spectra of PEDOT:PSS and CuSCN films were measured using a Shimadzu UV-2600 spectrophotometer equipped with an ISR-2600Plus integrating sphere. Atomic force microscopy (AFM) analysis was performed using an Agilent 5500 system in a tapping mode.

Device characterization: OPV device performance was characterized under inert atmosphere. J-V characteristics were measured using a Keithley 2400 source-meter with the devices placed under 1 sun AM1.5G simulated solar light (Sciencetech Inc. solar simulator SF300-A). EQE values were calculated from the device spectral response curves recorded under

mechanically chopped light from a 30 W quartz tungsten halogen lamp equipped with a monochromator and an optical filter wheel (Spectral Products). The resulting photocurrent was measured using a lock-in amplifier (Signal Recovery 7230) and the excitation light intensity monitored using an amplified and calibrated Si photodetector (Newport 918D-UV-OD3R).

Transistor measurements were carried out under nitrogen atmosphere using a Keithley 4200 semiconductor parameter analyzer. The hole field-effect mobility was extracted directly from the measured transfer characteristics in the saturation regime following the gradual channel approximation according to:

$$\mu_{\text{eff}} = \frac{W}{L C_i} \frac{\partial^2 I_{D(\text{SAT})}}{\partial V_g^2} \quad (2)$$

Here, W is the channel width, L the channel length, $I_{D(\text{SAT})}$ the channel current in saturation and C_i the geometric capacitance of the gate dielectric employed.

Supporting Information Supporting Information is available from the Wiley Online Library or from the corresponding authors.

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Figure 1. a) AFM topography (left) and phase (right) images of a CuSCN film deposited on a glass substrate. b) Transfer characteristics of a TG-BC CuSCN based thin-film transistor with channel length (L) and width (W) of $30\ \mu\text{m}$ and $1\ \text{mm}$, respectively. Inset: schematic of the TG-BC transistor architecture employed.

Figure 2. a) AFM topography images of CuSCN (right) and PEDOT:PSS (left) films deposited onto ITO electrodes on glass. b) Height histogram calculated from the AFM topography images in (a). A height histogram of bare ITO is also shown for comparison. c) Parasitic absorption spectra of 45 nm-thickness PEDOT:PSS (PEDOT:PSS line) and 45 nm-thickness CuSCN (red line) films. The transmission spectrum for the blank glass substrate (Glass substrate) is also shown for reference.

Figure 3. a) Chemical structures of the ICBA and P3HT materials used. b) Schematic of the BHJ cell structure c) HOMO/LUMO energy levels for the materials used. d) J-V characteristics measured under simulated solar light illumination for P3HT:ICBA cells, with PEDOT:PSS and CuSCN HTLs. e) External quantum efficiency (EQE) spectra measured for the PEDOT:PSS and CuSCN-based P3HT:ICBA cells.

Figure 4 a) Chemical structure of DT-PDPP-2T-TT, PC₇₁BM and DTS(FBTTh)₂. b) Schematic energy level diagram for the materials used. c) J-V characteristics measured under simulated solar light illumination for CuSCN HTL solar cells based on different D-A systems. d) J-V characteristics measured under simulated solar light illumination for PDPP-2T-TT:PC₇₁BM cells using PEDOT:PSS and CuSCN as HTL. e) EQE spectra for the PDPP-2T-TT:PC₇₁BM solar cells using on PEDOT:PSS and CuSCN as HTL.

Table 1. Summary of operating parameters for P3HT:ICBA cells based on CuSCN and PEDOT:PSS HTL materials. The data represent average values obtained from at least 8 individual cells fabricated in parallel under the same conditions.

Hole transport layer (HTL)	Voc (V)	Jsc (mA/cm ²)	FF	PCE (%)
CuSCN	0.83 ±0.005	10.8 ±0.53	0.69 ±0.01	6.20 ±0.29
PEDOT:PSS	0.83 ±0.005	9.8 ±0.59	0.72 ±0.02	5.87 ±0.31

Table 2. Summary of operating parameters for organic solar cells based on different D-A blends employing CuSCN as HTL. The data represent average values obtained from at least 8 individual cells fabricate in parallel under the same conditions.

D:A materials	Voc (V)	Jsc (mA/cm ²)	FF	PCE (%)
p-DTS(FBTTh ₂) ₂ : PC ₇₁ BM	0.80 ±0.005	13.9 ±0.60	0.62 ±0.01	6.89 ±0.17
PDPP-2T-TT : PC ₇₁ BM	0.70 ±0.005	16.3 ±0.42	0.68 ±0.012	7.72 ±0.29

The use of copper thiocyanate (CuSCN) as a universal solution-processable and highly transparent hole-transporting layer in organic bulk-heterojunction photovoltaic cells is demonstrated. When CuSCN is employed as a replacement for the commonly used PEDOT:PSS, organic solar cells with maximum power conversion efficiency PCE = 8%, are realized (see Figure) – a value approximately 1.27 times higher than for optimized control cells based on PEDOT:PSS.

Keyword: Solar cells, organic photovoltaics, copper thiocyanate, transparent interfacial layers, hole transporting layer

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High Efficiency Organic Photovoltaic Cells Based on the Solution-Processable Hole Transporting Interlayer Copper Thiocyanate (CuSCN) as a Replacement for PEDOT:PSS

ToC Figure

Supporting Information

High Efficiency Organic Photovoltaic Cells Based on the Solution-Processable Hole Transporting Interlayer Copper Thiocyanate (CuSCN) as a Replacement for PEDOT:PSS

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Figure S1. Transmission (top) and reflection (bottom) spectra of 45 nm-thickness PEDOT:PSS (dashed line) and CuSCN (dotted line) films on glass substrates. The transmission and reflectance spectra of the bare glass substrate are also shown for comparison (solid line). The measured spectra include both specular and diffuse components.

Figure S2. The upper panel displays the AM1.5G 1 sun Reference Solar spectral irradiance (ASTM G173-03) while the lower panel the power density loss spectra, due to absorption, for a 45 nm-thickness PEDOT:PSS and a CuSCN film calculated as the product of the absorption spectra presented in **Figure 2c** and the solar spectrum. The shaded area below the PEDOT:PSS and CuSCN lines represent the total losses due to the unwanted absorption by the corresponding HTL material system (both HTL have equal thickness of 45 nm).