DOI: 10.1002/adfm.201905810

Article type: Full paper

Use of the Phen-NaDPO:Sn(SCN)₂ blend as electron transport layer results to consistent efficiency improvements in organic and hybrid perovskite solar cells

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Keywords: tin (II) thiocyanate; Phen-NaDPO; electron transporting layer; non-fullerene acceptor; organic photovoltaics

Abstract: We report a simple approach that enables a consistent enhancement of the electron extracting properties of the widely used small-molecule Phen-NaDPO and its application in organic solar cells (OSCs). We show that addition of minute amounts of the inorganic molecule Sn(SCN)₂ into Phen-NaDPO improves both the electron transport and its film-forming properties. Use of Phen-NaDPO:Sn(SCN)₂ blend as the electron transport layer (ETL) in binary PM6:IT-4F OSCs leads to a remarkable increase in the cells' PCE from 12.6% (Phen-NaDPO) to 13.5% (Phen-NaDPO:Sn(SCN)₂). Combining the hybrid ETL with the best-in-class organic ternary PM6:Y6:PC₇₀BM systems results to a similarly remarkable PCE increase from 14.2% (Phen-NaDPO) to 15.6% (Phen-NaDPO:Sn(SCN)₂). The consistent PCE enhancement is attributed to reduced trap-assisted carrier recombination at the bulk-heterojunction/ETL interface due to the presence of new energy states formed upon chemical interaction of Phen-NaDPO with Sn(SCN)₂. The versatility of this hybrid ETL is further demonstrated with its application in perovskite solar cells for which an increase in the PCE from 16.6% to 18.2% is also demonstrated.

1. Introduction

Organic solar cells (OSCs) represent one of the most promising emerging photovoltaic technologies and have attracted extensive attention from both the scientific community and relevant industry due to a number of advantageous properties including lightweight, tuneable optical properties, low cost and a potential for high throughput manufacturing on large-area flexible substrates.^[1-7] The recent developments in small molecule acceptors allowed the power conversion efficiencies (PCE) to exceed 16% for single junction cells^[8-11] and over 17% for tandem devices,^[12] setting new benchmarks and attracting more interest to the field. As progress towards improving the absorption spectrum and carrier generation within the photoactive materials advances,^[13-15] other device components start becoming equally critical. One example is the carrier selective interlayers as they use often dictates the charge extraction process and hence the overall device performance. These layers are often sandwiched between the anode and cathode electrodes and the photoactive layer, and their main function is to facilitate efficient charge extraction while minimizing carrier recombination.^[16-20]

In the so-called ‘normal’ or ‘conventional’ cell architecture, the transparent anode, often a conductive indium tin oxide (ITO) electrode, collects the photogenerated holes. Commonly used hole-transporting layers (HTL) include PEDOT:PSS^[21-23] and CuSCN,^[24-26] which are deposited on top of the ITO electrode. From the cathode, a variety of materials have been used for the interfacial layer to transport electrons including alkali metal halides and oxides,^[27-29] organic small molecules,^[30] conjugated^[31] and non-conjugated^[32] polymers. Organic small molecules are particularly attractive for use as ETL as they possess well-defined chemical structures and they are easy to synthesize and process.^[33] One of the prototypical organic ETL materials for OSCs is the small molecule bathocuprione (BCP).^[34-37] Building on the BCP success, a number of other small molecules, such as bathophenanthroline (Bphen),^[38-39] zwitterions,^[40-42] pyridine derivatives^{[43-}

^{44]} and a variety of self-assembled ionic liquids,^[45] have been reported and shown to improve electron extraction in OSCs by providing suitable energy-level matching with the active layer. Among them, 3-[6-(diphenylphosphinyl)-2-naphthalenyl]-1,10-Phenanthroline (Phen-NaDPO) was shown to combine high electron mobility with good solubility in common solvents that are orthogonal to the organic active layer, enabling the development of OSCs with PCE of over 8.5 %.^[46-47]

Here, we report the development of an organic-inorganic hybrid electron extracting layer based on the Phen-NaDPO:Sn(SCN)₂ mixture, and its application in organic fullerene-free solar cells. Sn(SCN)₂ is a wide bandgap inorganic molecular semiconductor the properties of which have been studied recently by Wechwithayakhlung *et al.*^[48] However, initial attempts to use it as hole hole-extracting interlayer in PTB7:PC₇₁BM-based OSCs have resulted in reduced PCE (4%) as compared to reference cells made with PEDOT:PSS (8%).^[48] Herein we show that adding a small amount of Sn(SCN)₂ to Phen-NaDPO enhances its electron extracting characteristics and improves its layer morphology. Solar cells utilizing the Phen-NaDPO: Sn(SCN)₂ blend as the electron-transporting layer (ETL) exhibit substantially improved operating performance reaching a maximum PCE value of 15.6%, while constantly outperforms control cells made with pristine Phen-NaDPO and Sn(SCN)₂. Extensive analysis of Sn(SCN)₂, Phen-NaDPO, their blends and device characteristics, indicates the occurrence of chemical interaction between the two molecules and the formation of new complexes, which suppress trap-assisted carrier recombination at the bulk heterojunction (BHJ)/ETL interface through the formation of new energy states. The applicability of the hybrid ETL to perovskite solar cells is also demonstrated for which equally impressive performance enhancement is achieved.

2. Results and Discussion

2.1. Organic solar cell characterization and carrier recombination analysis

Figure 1a shows the molecular structures of the donor polymer PBDB-T-2F (also known as PM-6),^[49] Phen-NaDPO, and the non-fullerene acceptor (NFA) molecule IT-4F^[50] used for the binary BHJ. Cells were fabricated using the conventional architecture (**Figure 1b**) of ITO/PEDOT:PSS/PBDB-T-2F:IT-4F/ETL/Al, where the ETL composition was either pure Phen-NaDPO or a mixture of Phen-NaDPO and Sn(SCN)₂ with composition ranging between 1.25% to 10 mol% of Sn(SCN)₂ (**Table S1**). The relevant energy levels of the various materials used in this study are summarized in **Figure 1c**.

Figure 1. (a) Chemical structures of PBDB-T-2F, IT-4F and Phen-NaDPO. (b) Schematic of the conventional solar cells architecture employed. (c) Energy levels diagram of the materials used in the solar cells fabrication. The ionization potential (IP) and electron affinity (EA) values for Phen-NaDPO and Sn(SCN)₂ were measured using ultraviolet photoelectron spectroscopy (UPS), while for the rest of the materials via photoelectron spectroscopy in air (PESA). The work function of electrodes were measured using Kelvin probe under inert atmosphere. (d) *J-V* characteristics measured under standard solar illumination. (e) EQE and IQE spectra of the ‘pure’ (red) and ‘mixed’ (blue) ETL-based cells. Inset in (d) shows images that show the change in the physical

appearance of the Phen-NaDPO powder (pure) before and after the addition of Sn(SCN)₂ (5 mol%) (mixed).

In **Figure 1d** we show the current density versus voltage (*J-V*) characteristics measured under standard AM 1.5 solar irradiance for cells based on the pristine Phen-NaDPO (pure) and Phen-NaDPO:Sn(SCN)₂ (5 mol%) (mixed) ETLs. The inset in this figure are images of the Sn(SCN)₂, and Phen-NaDPO powder before (pure) and after addition of 5 mol% of Sn(SCN)₂ (mixed). The reference cell with PBDB-T-2F: IT-4F based on the ‘pure’ ETL exhibits a maximum PCE of 12.6% with an open circuit voltage (*V*_{OC}) of 0.85 V, a short circuit current density (*J*_{SC}) of 19.7 mA/cm² and a FF of 73%. Admixing of just 5 mol% of Sn(SCN)₂ with Phen-NaDPO yields device with increased *V*_{OC} and FF of 0.87 V and 76%, respectively, resulting in a maximum PCE value of 13.5%. **Table 1** summarizes the cells’ parameters for the two ETLs.

Table 1. Summary of operating parameters for the PBDB-T-2F: IT-4F cells with the ‘pure’ and optimized ‘mixed’ ETLs.

ETL	<i>V</i> _{OC} (V)	<i>J</i> _{SC} (mA/cm ²)	FF (%)	Avg. PCE (%)	Max. PCE (%)
pure	0.85	19.7	73	12.2	12.6
mixed	0.87	20.0	76	13.2	13.5

The external and internal quantum efficiency (EQE and IQE) spectra of the ‘pure’ and ‘mixed’ ETL-based BHJ solar cells are presented on **Figure 1e**. The integration of the measured EQE curves yields photocurrent values of 18.9 and 19.3 mA/cm² for the ‘pure’ and ‘mixed’ ETL devices in a good agreement with the *J*_{SC} values obtained from the *J-V* analysis (**Table 1**). The EQE spectra of both devices are quite similar, with the ‘mixed’ ETL device exhibiting 1-2% gain across the 350-750 nm wavelengths region compared to the ‘pure’ ETL cell. The IQE spectra are almost identical in the range 450-650 nm, followed by higher IQE values for the ‘mixed’ ETL cell up to 800 nm reaching a maximum value of 98% as compared to 87% for the reference ‘pure’ ETL

device. The all-around positive impact of the ‘mixed’ ETL on the cell’s performance is clearly illustrated in **Figure S1** where the J_{SC} , V_{OC} , PCE, and FF for >35 cells are plotted. Evidently, cells based on ‘mixed’ ETL not only outperform the ‘pure’ ETL devices, but also exhibit a characteristic narrowing in the spread of all critical parameters, further showcasing the effectiveness of the new hybrid ETL. Further increase of the $\text{Sn}(\text{SCN})_2$ content deteriorates all device parameters (**Table S1**). Additionally, device stability was studied for the first 80 h of storage in the controlled environment (O_2 and $\text{H}_2 \leq 10$ ppm) in darkness (**Figure S2**). Interestingly, the ‘mixed’ ETL cell retains its initial PCE value throughout the period of storage, while the efficiency of the reference pure ETL-based cell slightly drops to 96% of its initial value. This degradation mostly originates from the drop in FF for the ‘pure’ ETL cell. From this preliminary data we conclude that addition of $\text{Sn}(\text{SCN})_2$ to the Phen-NaDPO ETL does not adversely affects the cell’s stability.

To study the origin of the performance improvement of the ‘mixed’ ETL-based cells, we measured the J - V characteristics at various illumination intensities (P_{in}). The J_{SC} and V_{OC} dependence on P_{in} can provide useful information on the carrier recombination processes within the devices. To this end, prior studies have demonstrated that for OSCs, the J_{SC} usually follows the power-law

$$J_{SC} \propto P_{in}^{\alpha} \quad (1)$$

where α is the power factor.^[51-52] A linear dependence of J_{SC} on P_{in} ($\alpha \approx 1$) indicates that most carriers are successfully extracted before recombining i.e. small or no bimolecular recombination losses. On the other hand when $\alpha < 1$ it indicates that certain degree of bimolecular recombination exists.^[51-52] As shown on **Figure S3**, for both ‘mixed’ and ‘pure’ ETL-based solar cells, an α value of 0.989 is obtained, indicating that the process of charge extraction is almost free of bimolecular recombination.

The dependence of V_{OC} on P_{in} , on the other hand, provides insights on the degree of trap-assisted recombination in the cell. For example, a slope of V_{OC} vs. $\ln(P_{in})$ equal to kT/q is indicative of trap-free charge transport in the device, while a slope approaching $2kT/q$ reflects existence of traps across the active layer and/or at the BHJ/electrode interface(s).^[52-54] From **Figure 2a** we extract a slope of $1.18 kT/q$ for the ‘mixed’ ETL, and $1.37 kT/q$ for the ‘pure’ ETL-based OSCs. These results suggests that the lower V_{OC} and FF in the ‘pure’ ETL cell most likely originates from trap-induced recombination, while for ‘mixed’ ETL cell this particular loss mechanism is considerably suppressed. Since the composition and microstructure of the BHJ layer in both type of cells is identical, we conclude that the difference in the slopes exclusively originates from different trap concentration present within the ETL and/or at the BHJ/ETLs interface.

Figure 2. (a) Open-circuit voltage (V_{OC}) versus light intensity. (b) Electrochemical impedance spectroscopy (EIS) curves for the ‘pure’ (red) and ‘mixed’ (blue) ETL-based solar cells. The inset in (b) represents the equivalent circuit used for the curves fitting. Normalized transient short-circuit

current in response to a 200 μs white light (LED) pulse for ‘pure’ (c), and ‘mixed’ (d) ETL-based solar cells. The insets in (c) and (d) show the magnified parts of the turn-on dynamics of the respective traces.

The recombination mechanism(s) in these cells was investigated further using the transient photovoltage (TPV) and charge extraction (CE) techniques. Use of TPV and CE allows calculation of the charge carrier lifetime (τ) and the charge carrier density (n), respectively. The relation between these two parameters is given by

$$\tau = \tau_0 \left(\frac{n_0}{n} \right)^\lambda \quad (2)$$

where τ_0 and n_0 are constants.^[55] Using Eq. 2, the recombination exponent λ is calculated. **Figure S4** shows this relation for both ‘pure’ and ‘mixed’ ETL cells. We find that under standard AM 1.5 illumination the carrier lifetime τ is improved from 3.1 to 3.5 μs upon addition of 5 mol% of $\text{Sn}(\text{SCN})_2$ in Phen-NaDPO. Meanwhile the charge carrier density n remains similar for both ETL devices with the corresponding values of 5.81×10^{16} and $5.85 \times 10^{16} \text{ cm}^{-3}$, respectively, both in good agreement with the measured J_{SC} . The recombination order ($\lambda+1$) was estimated from **Figure S4** to be 2.46 and 2.51 for the ‘mixed’ and ‘pure’ ETL cells, respectively. It is known that when $\lambda+1=2$, the charges within the device recombine via a bimolecular process under open-circuit conditions.^[56] The values obtained in our case ($\lambda+1 > 2$) can be explained by the trapping and release processes in both energetic as well as morphology-related traps.^[56] However, the lower $\lambda+1$ for the ‘mixed’ ETL device, corroborates that the addition of $\text{Sn}(\text{SCN})_2$ reduces the trapping effect and increases the FF.

The effect of adding $\text{Sn}(\text{SCN})_2$ in Phen-NaDPO ETL, was further studied using electrochemical impedance spectroscopy (EIS) measurements (**Figure 2b**). Here the symbols represent the measured data whilst the solid lines are fittings calculated using the equivalent circuit on the inset, which has previously been shown to best represent OPV devices.^[57-58] It has been

reported that impedance response of the solar cell at low frequencies is related to R_{rec} , and at high frequencies – to R_t . Here R_t is the resistance in the device associated with the charge extraction at the electrodes, while R_{rec} – with the recombination processes in the bulk.^[58] As shown in **Table S2**, R_{rec} for both ‘mixed’ and ‘pure’ devices are similar (27 and 36 Ω , respectively), which is not surprising as the utilised photoactive layer is the same. However, as expected, there is a striking difference in R_t values: 364 Ω for the ‘pure’ ETL and 231 Ω for the ‘mixed’ ETL cells. This results provide further direct evidence that admixing 5 mol% $\text{Sn}(\text{SCN})_2$ to Phen-NaDPO improves charge transport/extraction within the ETL and at the BHJ/ETL interface while reducing contact resistance.

Additional information on trapping/de-trapping process and its effect on the charge transport was gathered using the transient photocurrent technique (TPC).^[59-62] Here the cell is excited by a square-shaped light pulse with varying intensity long enough for the current density to reach a steady state. The time taken for the device to reach steady state provides insights about the turn-on and turn-off dynamics, while the dependence of the photocurrent on the light intensity is indicative of the trapping/de-trapping of charge carriers.^[63] **Figure 2c-d** illustrate the current response of optimized ‘pure’ and ‘mixed’ ETL cells upon excitation with a white light pulse of varying intensity. For both ETLs, the turn-on and turn-off dynamics are fast and varying light intensity results in negligible changes in the current response. However, closer analysis of the curves, shown as insets in **Figure 2c-d**, reveals significant differences. Specifically, the rise/fall time (defined as the time taken to rise from 10 to 90% of the maximum current amplitude), is slightly reduced from 1.5 μs for the ‘pure’ reference to 1.1 μs for the ‘mixed’ cell. Interestingly, the shape of the response traces for the ‘mixed’ ETL-based cell remains independent of the light intensity (inset in **Figure 2d**), which indicates that the turn-on dynamics is mostly governed by the carrier (electrons) mobility with trapping/detrapping not playing any role.^[63] However, this is not

the case for the ‘pure’ ETL-based cell where a certain degree of turn-on overshoot is observed, particularly at higher light intensities (inset in **Figure 2c**). Moreover, the turn-off characteristics of the measured photocurrent for the ‘pure’ ETL devices shows a characteristic tail, which reduces in magnitude with increasing light intensity (**Figure S5**). Similar features in TPC traces have been previously attributed to charge trapping (particularly electrons), which leads to the redistribution of the internal electric field. Thus, on the basis of the EIS and TPC results, we conclude that addition of 5 mol% Sn(SCN)₂ in Phen-NaDPO enables trap-free electron transport across the hybrid ETL, with an overall positive impact on the performance of the OSC (**Figure S1**).

Lastly, we studied the difference of the electron transport properties on ‘pure’ Phen-NaDPO and ‘mixed’ Phen-NaDPO:Sn(SCN)₂(5 mol%) ETLs, by measuring the electron mobility in electron-only diodes comprised of ITO/ZnO/PBDB-T-2F:IT-4F/ETL/Al using the space charge limited current (SCLC) model.^[64] The diodes were fabricated using the optimized ‘pure’ and ‘mixed’ ETLs that were employed in best-performing OSCs and combined with BHJ layers of varying thickness. **Figure S6** shows the *J-V* curves for two sets of three diodes, each based on BHJ layers of different thickness. Details regarding the electron mobility calculations are provided in the *Experimental* section, whilst the extracted values are summarized in **Table S3**. Evidently, the apparent electron mobility in diodes based on the ‘mixed’ ETL is approximately 33% higher ($1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) as compared to the reference ‘pure’ ETL-based diodes ($7.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). These results are in line with the conclusions drawn from the aforementioned studies supporting our hypothesis that the ‘mixed’ ETL improves electron transport and extraction across the ETL and/or the BHJ/ETL interface.

2.2. Optical, Microstructural and Chemical Analysis of Phen-NaDPO:Sn(SCN)₂

To understand how $\text{Sn}(\text{SCN})_2$ affects the electron transport in Phen-NaDPO, we studied the physical properties of the different ETLs using a complementary range of characterization techniques. **Figure S7a** shows the absorption spectra of the neat Phen-NaDPO and $\text{Sn}(\text{SCN})_2$ films, and their mixtures. The pristine ‘pure’ Phen-NaDPO layer exhibits high transparency throughout the visible range from 440 to 800 nm with two distinct absorption peaks at 267 and 328 nm. The neat $\text{Sn}(\text{SCN})_2$ layer appears to absorb only slightly throughout the visible region from 400 to 800 nm, an effect most likely attributed to scattering, with strong absorption features in the deep-UV range (250-350 nm). **Figure S7b** shows the normalized absorption spectra for the pristine Phen-NaDPO (pure) and Phen-NaDPO doped with 2.5 and 5 mol% $\text{Sn}(\text{SCN})_2$ normalized to the absorption peak of Phen-NaDPO at 267 nm. As the $\text{Sn}(\text{SCN})_2$ concentration increases, a new broad absorption band in the range 450-750 nm, appears. The latter feature is also visible in **Figure S7a** for Phen-NaDPO: $\text{Sn}(\text{SCN})_2$ (10 mol%) layers and cannot be attributed to $\text{Sn}(\text{SCN})_2$. This feature is most likely responsible for the change in the physical appearance of the Phen-NaDPO powder from white to yellow shown in the inset of **Figure 1d**. The yellow precipitant was also observed and reported elsewhere.^[65] When the content of $\text{Sn}(\text{SCN})_2$ is increased to 10 mol%, all absorption peaks associated with Phen-NaDPO disappear, with the resulting spectrum resembling more that of $\text{Sn}(\text{SCN})_2$ but with the broad new band still present.

Powder X-ray diffractograms (XRD) of Phen-NaDPO, $\text{Sn}(\text{SCN})_2$ and the Phen-NaDPO: $\text{Sn}(\text{SCN})_2$ mixture (95:5 molar ratio) are presented in **Figure S8**. For pristine Phen-NaDPO, strong diffraction peaks at 21.8° , 22.5° , 24.5° , 26.3° and 38.4° , are observed. For pristine $\text{Sn}(\text{SCN})_2$, peaks at 21.2° , 23.7° , 28.4° and 30.3° , are recorded in agreement with previous reports.^[48] Interestingly, the mixed layer shows no major diffraction peaks, with some minor peaks at 22.5° and 26.4° reminiscent of the Phen-NaDPO. We thus conclude that ETL layers based on

the Phen-NaDPO:Sn(SCN)₂ mixture (95:5 mol ratio) exhibit significantly suppressed crystallinity, although some weak XRD peaks, associated primarily with NaDPO, remain visible.

The impact of Sn(SCN)₂ addition on the layer morphology of the blend ETL layer was studied using atomic force microscope (AFM). **Figure 3a** displays the surface topography data of the BHJ layer comprised of PBDB-T-2F:IT-4F deposited onto glass/ITO/PEDOT:PSS electrodes. The same stack but with the ‘pure’ Phen-NaDPO (**Figure 3b**) and ‘mixed’ Phen-NaDPO:Sn(SCN)₂ (**Figure 3c**) ETLs, deposited atop the BHJ. **Figure 3d** represent the surface height histograms extracted from the AFM images. Evidently, the surface of the BHJ prior to the ETL deposition is very smooth with the low surface root mean squared (rms) roughness of 1.5 nm.

Figure 3. AFM topography images of (a) ITO/PEDOT:PSS/PBDB-T-2F:IT-4F (BHJ), (b) ITO/PEDOT:PSS/PBDB-T-2F:IT-4F/Phen-NaDPO ETL (pure), and (c) ITO/PEDOT:PSS/PBDB-T-2F:IT-4F/Phen-NaDPO:Sn(SCN)₂ ETL (mixed). The scale bar in the AFM images is 500 nm, with the z-value denoting the maximum height. (d) Height histograms extracted from the AFM data on (a-c).

The surface of the ‘pure’ Phen-NaDPO layer exhibits a trimodal height distribution with a surface rms = 4.5 nm: the large spherical particles with the peak at ≈ 20.8 nm, the smaller particles with the peak at ≈ 9.2 nm and the flat regions. For the ‘mixed’ Phen-NaDPO:Sn(SCN)₂ ETL the second peak (≈ 20.8 nm) in the height histogram is eliminated, and the particles appear significantly smaller and distributed more homogeneously on the sample’s surface with a single dominant peak at ≈ 8.8 nm. As a result, the rms of the surface roughness for the ‘mixed’ ETL is reduced to 3 nm.

This significant change in the sample's topography reflects the large reduction in the intensity of the XRD peaks associated with Phen-NaDPO (**Figure S8**). It is thus clear that admixing $\text{Sn}(\text{SCN})_2$ with Phen-NaDPO changes the morphology of the resulting ETL by reducing the size of the formed particles, while making their distribution more homogeneous. These noticeable morphological changes may be, at least partly, responsible for the reduced impact of trap-induced recombination measured for BHJ cells based on the 'mixed' ETL, an effect shown to originate from the ETL and/or the BHJ/ETL interface.

We performed high-resolution solid-state nuclear magnetic resonance spectroscopy (SS-NMR) to analyse both the pure Phen-NaDPO and best-performing Phen-NaDPO: $\text{Sn}(\text{SCN})_2$ mixture (95:5 mol%), to determine whether the materials undergo any chemical interaction. As shown in **Figure 4a**, the ^{31}P NMR spectrum of the pristine Phen-NaDPO powder shows a sharp peak at 14.5 ppm assigned to the $\text{P}=\text{O}$ bond. In solid-state NMR contributions to the line shape are from anisotropic interactions, or chemical shift anisotropy (CSA). This means having an orientational dependence and in the presence of large rotational motions the molecule averages the CSA resulting in the motional narrowing of the magic-angle spinning (MAS) spectrum. In this case the ^{31}P sharp peak indicates that the Phen-NaDPO molecule is free and has rapid isotropic motion.^[66] In the case of the mixed powder the signal exhibits a downfield shift to 25 ppm and a characteristic line broadening. The deshielding effect can be explained by decreasing of the electron density around phosphorous atom coming from more electronegative atoms surrounding it upon mixing with $\text{Sn}(\text{SCN})_2$. The line shape characteristic of the CSA is broader after mixing, which suggests constrained motion of the Phen-NaDPO molecule. Both the line shift and broadening are most likely attributed to interaction between Phen-NaDPO and $\text{Sn}(\text{SCN})_2$ e.g. through formation of a new chemical bond in the vicinity of the phosphorous atom.

Figure 4. (a) Solid-state NMR spectra of ^{31}P , and (b) dynamic nuclear polarization (DNP) spectra of ^{15}N . c) XPS spectra of P 2p core level, and d) XPS spectra of N 1s of the pristine Phen-NaDPO (pure) and the Phen-NaDPO:Sn(SCN) $_2$ (95:5 molar ratio) mixture (mixed).

We also performed ^{15}N SS-NMR but the low sensitivity of conventional NMR necessitates the synthesis of a ^{15}N -labeling sample for efficient NMR signal detection. To this end, the recently introduced dynamic nuclear polarization (DNP) approach offers high sensitivity while substantially reducing the experimental time without the need for isotopically enhanced samples.

For the purpose of this study, DNP measurements were acquired at 100 K using TEKPol (stable radical) as the polarizing agent and 1,1,2,2-tetrachloroethane (TCE) as a solvent. **Figure S9** shows the ^1H MAS DNP spectrum of Phen-NaDPO and its mixture with $\text{Sn}(\text{SCN})_2$, both exhibiting excellent proton enhancement factor ϵ_{H} of 90 and 85, respectively. These measurements highlight the suitability of both samples for performing DNP measurements. The ^{15}N cross polarization (CP)-MAS DNP spectrum of the pristine Phen-NaDPO powder shows one peak at 303 ppm characteristic of $\text{N}=\text{C}$ as reported in **Figure 4b**. However, upon mixing with $\text{Sn}(\text{SCN})_2$ two additional peaks appear, one at 213 ppm and another at 193 ppm indicating that new chemical environment of nitrogen atoms exists after mixing. We assign these to a new chemical bond between Phen-NaDPO and $\text{Sn}(\text{SCN})_2$. The DNP measurements confirm the nitrogen interaction of Phen-NaDPO with $\text{Sn}(\text{SCN})_2$, which is in good alignment with the XPS data and DFT calculations that will be discussed later.

The ^{13}C spectra of the powders presented in **Figure S10a** show small differences without any considerable frequency shift. For the pristine Phen-NaDPO powder the well-resolved peaks are found between 120-132 ppm and 142-147 ppm and indicate the presence of the different aromatic carbon atoms connected to another carbon or nitrogen, respectively. Upon addition of $\text{Sn}(\text{SCN})_2$, the same peaks are present with the similar chemical shifts in the aromatic region accompanied by a small broadening effect. The latter suggests that the two compounds interact via either the P or the N sites in Phen-NaDPO, while the rest of the molecule does not undergo any detectable changes. The additional peak at 25 ppm can be assigned to carbon atoms, possibly residual CH_3 or grease contamination. The 2D ^1H - ^{13}C HETCOR NMR spectrum is given in **Figure S10b**.

Aiming to deepen our understanding of the chemical interaction(s) between Phen-NaDPO and $\text{Sn}(\text{SCN})_2$ upon physical mixing, we performed high resolution X-ray photoelectron

spectroscopy (XPS). The spectra of the P 2p core level for the pure Phen-NaDPO and the mixture Phen-NaDPO:Sn(SCN)₂ samples are shown in **Figure 4c**. The P 2p core level spectra show two peaks at 132.1 eV and 132.9 eV corresponding to a doublet P 2p_{3/2} and P 2p_{1/2}, respectively, along with a broad peak with low signal around $\approx$ 138 eV. The P 2p_{3/2} core level is attributed to phosphorous from Phen-NaDPO^[46], while the signal around $\approx$ 138 eV is assigned to oxidized P species. No significant changes were observed from both P 2p spectra upon admixing Sn(SCN)₂ indicating negligible interaction involving the P atom in Phen-NaDPO with Sn(SCN)₂.

We also performed high-resolution XPS measurements of the N 1s core level for the pristine powders and their mixture (**Figure 4d**). The spectrum for Phen-NaDPO was fitted with two components located at 398.8, and 401.0 eV, attributed to pyridinic nitrogen and to N-O species. The N 1s core level from Sn(SCN)₂ was fitted with a single component located at 398.6 eV attributed to nitrogen from the thiocyanate unit. As expected, N 1s core level from Phen-NaDPO:Sn(SCN)₂ exhibit two additional components located at 397.3, and 400.0 eV compared to Phen-NaDPO, attributed to newly formed Sn-N bond^[67] and to amine species originating from the formation of isothiocyanic acid (HNCS) upon retention of N-bridged thiocyanate in methanol solution^[65], respectively. The broad structure around $\approx$ 406 eV for all spectra is attributed to oxidized nitrogen species^[68]. Thus, both XPS and DNP measurements confirm the possible interaction between the Sn(SCN)₂ and Phen-NaDPO via the nitrogen atoms of the latter. However, while SS-NMR spectrum of the phosphorous atom of the pure Phen-NaDPO exhibits certain changes upon mixing with Sn(SCN)₂, this type of interaction has not been detected with XPS. To have better understanding of the possible interactions between two materials, we performed density functional theory (DFT) calculations and will be discussed next.

2.3 DFT calculations

In order to elucidate the atomic-scale details of the interactions between Phen-NaDPO and $\text{Sn}(\text{SCN})_2$ we performed Density Functional Theory (DFT) calculations with the code NWChem,^[69] the B3LYP exchange-correlation functional^[70-71] and the DZVP orbital basis.^[72]

Figure S11 depicts the Highest Occupied (HOMO) and Lowest Unoccupied (LUMO) Molecular Orbitals for a Phen-NaDPO molecule. The calculated energies are -6.26 eV for the HOMO and -2.10 eV for the LUMO. The corresponding DZVP HOMO (LUMO) energies for PBDB-T-2F and IT-4F are -5.43 eV and -5.90 eV (-2.73 eV and -3.84 eV), respectively. These HOMO values are in very good agreement with the experimental data on ionization potentials, while the calculated LUMO energies underestimate the electron affinities, as is typical in DFT studies.

Figure 5. Structure of complexes of a Phen-NaDPO molecule with (a)-(c) a $\text{Sn}(\text{SCN})_2$ group and (d) with two $\text{Sn}(\text{SCN})_2$ group with Sn-S linkage. (e)-(f) with a $\text{Sn}(\text{SCN})_2$ group with Sn-N linkage

(C: gray, H: white, P: orange, O: red, N: blue, S: yellow, Sn: dark green spheres). DZVP results for molecular energies E (referenced to the lowest E value) and E_{HOMO} , E_{LUMO} are also shown.

Since the beneficial effects of mixing $\text{Sn}(\text{SCN})_2$ with Phen-NaDPO are obtained only at low $\text{Sn}(\text{SCN})_2$ concentrations, we focused our DFT investigations on the interactions between the latter with individual $\text{Sn}(\text{SCN})_2$ chemical units. **Figure 5** shows a number of configurations that are obtained when one or two such units interact with a Phen-NaDPO molecule. A single $\text{Sn}(\text{SCN})_2$ molecule can be attached through its Sn atom either to the P through the O atom or to the N sites of Phen-NaDPO. Configurations with the Sn-S bonds in the adsorbed $\text{Sn}(\text{SCN})_2$ units (**Figure 5a-d**) tend to be less stable than the ones with Sn-N linkage (**Figure 5e-f**), but the relative small energy differences (in the range of 0.2-0.6 eV) suggest that all these structures are materialized in the experiments and most likely co-exist. Notably, attachment at the O atom as in **Figure 5e** leads to a calculated ^{31}P chemical shift of 37 ppm (**Table S4**), which is consistent with the pertinent ^{31}P chemical shift measured by SS-NMR for the mixed Phen-NaDPO: $\text{Sn}(\text{SCN})_2$ structure. Likewise, the DFT configurations with attachment of $\text{Sn}(\text{SCN})_2$ to the N sites of Phen-NaDPO are consistent with both the DNP and XPS N 1s experimental data, which clearly show that a reaction occurs in this area of the Phen-NaDPO molecule upon mixing with $\text{Sn}(\text{SCN})_2$.

Based on the above, the DFT calculations establish that $\text{Sn}(\text{SCN})_2$ interacts with Phen-NaDPO at the O and N sites. As reported in **Figure 5**, the result of these interactions is the drastic lowering of the Phen-NaDPO LUMO values by as much as 1.25 eV (for the configuration shown in **Figure 5c**), as compared to the LUMO energy of the pristine Phen-NaDPO molecule. This lowering brings the LUMO level in the hole blocking layer much closer to the LUMO level of IT-4F (and lower than that of PBDB-T-2F), but also to the work function of the Al electrode. In this way, electron extraction from IT-4F to the Al side is greatly enhanced compared to what can be

expected for the pristine Phen-NaDPO with its high-lying LUMO. In addition, these low LUMO levels for the Phen-NaDPO:Sn(SCN)₂ mixture make it easier for any electrons confined in the active layer or at its interface with the ETL to be transferred to the Al electrode. Finally, we should note that the stable DFT configurations comprising Phen-NaDPO and Sn(SCN)₂ are, in principle, consistent with the observed morphological modifications of the ETL upon mixing with Sn(SCN)₂, even though the quantitative details of these large-scale modifications are beyond the scope of a DFT study.

2.4 Application of Phen-NaDPO:Sn(SCN)₂ ETL to other solar cells

To demonstrate the wider applicability of the hybrid Phen-NaDPO:Sn(SCN)₂ ETL, we combined it with another promising BHJ system comprised of the donor polymer PBDB-T-SF^[50] (inset, **Figure S12b**) and the small molecule NFA IT-4F (**Figure 1a**). The solar cells were fabricated in the normal configuration consisting of ITO/PEDOT:PSS/PBDB-T-SF:IT-4F/ETL/Al (**Figure S12a**). We emphasize here that unlike the PBDB-T-2F:IT-4F system discussed previously (**Figure 2**), the PBDB-T-SF:IT-4F BHJ does not require any annealing following solution deposition. Without performing any extensive optimization of the ‘mixed’ ETL for this particular BHJ system, we still managed to increase the cell’s PCE from an average value of 11% for the ‘pure’ Phen-NaDPO-based cell, to an average/maximum values of 11.4/11.6% for the hybrid Phen-NaDPO:Sn(SCN)₂ ETL-based OSCs (**Figure S12b** and **Table S5**). More impressive improvement were achieved using a ternary BHJ system based on the mixture of PBDB-T-SF:Y6:PC₇₀BM (see *Experimental*). The structure of the Y6^[73] NFA is shown in the inset of **Figure 6a** while the schematic of the cell architecture in **Figure S12a**. As summarized in **Table 2**, ternary OSCs based on the Phen-NaDPO:Sn(SCN)₂ ETL results in both higher V_{OC} and FF, thus increasing the PCE from 14.2% to a champion value of 15.6%.

Table 2. Summary of the operating parameters of the ternary PBDB-T-SF:Y6:PC₇₀BM OSCs with the ‘pure’ and ‘mixed’ ETLs.

ETL	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Average PCE (%)	Maximum PCE (%)
pure	0.83	25.6	67	13.9	14.2
mixed	0.85	26.2	70	15.3	15.6

Finally, the hybrid Phen-NaDPO:Sn(SCN)₂ ETL was tested for organometal halide perovskite photovoltaic cells. The cell was fabricated in a p-i-n configuration ITO/NiO/CH₃NH₃PbI₃/PC₆₀BM/ETL/Ag as shown in the inset of **Figure 6b** and the J-V characteristics are given in **Figure 6b**. As summarized in **Table 3**, admixing Sn(SCN)₂ improves all device parameters, resulting in PCE of 18.2% in comparison to 16.6% for the pure Phen-NaDPO ETL cell. More information about device parameters and hysteresis is given in **Table S6**.

Figure 6. (a) *J*-*V* characteristics of PBDB-T-SF:Y6:PC₇₀BM ternary OSCs. (b) *J*-*V* characteristics of CH₃NH₃PbI₃ solar cells with the ‘pure’ and ‘mixed’ ETL measured under standard solar illumination in forward and reverse sweeps.

Table 3. Summary of the operating parameters of the CH₃NH₃PbI₃ perovskite solar cells based on Phen-NaDPO and the mixed Phen-NaDPO:Sn(SCN)₂ ETLs.

ETL	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Average PCE (%)	Maximum PCE (%)
pure	1.05	21.3	74	16.3	16.6
mixed	1.08	22.5	75	17.8	18.2

On the basis of these results it becomes clear that the hybrid Phen-NaDPO:Sn(SCN)₂ ETL can indeed be successfully applied in binary and ternary OPVs as well as hybrid perovskite solar cells and consistently deliver significant efficiency improvements.

3. Conclusion

To conclude, we developed a new hybrid electron transporting layer composed of the small molecule Phen-NaDPO and the inorganic molecule Sn(SCN)₂. Application of this hybrid ETL to binary BHJ OSCs was shown to significantly and consistently increase the FF and V_{OC} culminating to a maximum PCE of 13.5%. Importantly, the latter value is significantly higher than the maximum PCE of 12.6% measured for control cells based on pristine Phen-NaDPO as the ETL. Combining the hybrid ETL with best-in-class ternary organic BHJ systems and organometal halide perovskite active layers lead to similarly impressive PCE enhancements leading to maximum values of 15.6% and 18.2%, respectively. Importantly, and irrespective of the photo-active layer, the hybrid ETL offers an all-around performance improvement, which was manifested as a significant narrowing in the cells' parameters spread. This remarkable level of improvements was attributed to the reduction of trap-assisted recombination across the photo-active/ETL interface due to the formation of new energy levels in ETL upon chemical interaction between Sn(SCN)₂ and Phen-NaDPO. Experimental evidences of these interactions were provided by NMR and XPS measurements and corroborated by DFT-calculations.

4. Experimental Section

Synthesis of Sn(SCN)₂: Tin (II) thiocyanate was synthesized following a modified procedure reported earlier.^[74] Sodium thiocyanate 10 g (0.012 mol) was dissolved in 40 mL of water. Tin (II)

sulfate 6.62 g (0.031 mol) was also dissolved in water in a separate flask followed by slow addition of 1N sulfuric acid (7 mL) at room temperature and a resulting solution was transferred slowly to a previously prepared solution of sodium thiocyanate, flushed with argon for 5 min and placed in a fridge for 2 days. The resulting white crystals were filtered off and washed with a small amount (10 mL) of cold water and cold methanol (20 mL), dried at high vacuum overnight to yield tin (II) thiocyanate as white crystals (2.5 g, 34.5%).

Device fabrication and characterization: Solar cells were fabricated on ITO-patterned glass substrates from Kintec Company ($10\ \Omega\ \text{sq}^{-1}$, device area $0.1\ \text{cm}^2$). The substrates were cleaned by sonicating 15 min in each of sequential baths with acetone and isopropanol, dried with pressurized nitrogen and treated for 20 min by UV-ozone plasma. Then a thin 30 nm layer of PEDOT:PSS (Clevios Al4083, Heraeus) was spin-cast in air, followed by drying step on a heating plate at 140°C for 10 min. The donor polymers PBDB-T-2F, PBDB-T-SF and the acceptor small molecule IT-4F were purchased from 1-Materials Inc. The electron acceptors Y6 and PC₇₁BM were purchased from Solarmer Materials Inc.

The active layer solutions PBDB-T-2F:IT-4F and PBDB-T-SF:IT-4F were prepared in the dry nitrogen glovebox ($<3\ \text{ppm}\ \text{O}_2$) with a ratio 1:1 (wt/wt) in chlorobenzene with 0.5% (v/v) of the 1,8-diiodooctane (DIO) additive. The solutions were rigorously stirred for 1 h at 100°C before being spin casted. The active layers were spin-cast from the solutions at 100°C at an optimized speed for 40 seconds in the glovebox resulting in the films with ca. 100 nm thickness. For PBDB-T-2F:IT-4F cells the substrates then were thermally annealed at 100°C for 10 min in the glovebox. For PBDBT-2F:Y6:PC₇₁BM BHJs, the solution were prepared with ratio 1:1:0.2 with concentration of $15\ \text{mg}\ \text{mL}^{-1}$ in chloroform and added 0.5% (v/v) chloronaphthalene. The solutions were then spun to obtain active-layer thickness of 140 nm. Concerning perovskite solar cells, 1.1M of methylammonium iodide and lead iodide powders were mixed together in a

DMF:DMSO solvent mixture at 9:1 ratio. The precursor ink was deposited on pre-cleaned ITO glass substrates coated with NiO, at 4000rpm for 30 seconds. Films were then annealed at 100°C for 30 minutes. A thin layer of PC60BM (20mg/ml in chlorobenzene) was spin cast at 3500 rpm. Phen-NaDPO was purchased from 1-Materials Inc. For the pure ETL devices the solution of Phen-NaDPO in isopropanol (0.5 mg/ml) was spin-cast at 2000 rpm in the glovebox. Sn(SCN)₂ solution in methanol (0.25 mg/ml) was prepared in the glovebox. For the mixed ETL devices Sn(SCN)₂ was added to the Phen-NaDPO solution prior to spin-casting in the mentioned molar ratios. The solution mixture was cast at 2000 rpm. Then 100 nm-thick layer of Al was evaporated in a thermal evaporator under high vacuum (5×10^{-6} mbar). The solar cells then were finally tested in the glovebox with a Keithley 2400 source-meter and an Oriel Sol3A Class AAA solar simulator calibrated to 1 sun, AM1.5 G, with a KG-5 silicon reference cell certified by Newport. The same system was used for the stability measurements.

External/Internal Quantum Efficiency (EQE/IQE): EQE measurements were conducted at zero bias by illuminating the solar cell with monochromatic light supplied from a xenon arc lamp in a combination with a dual-grating monochromator. The number of incident photons was calculated for each wavelength by using a silicon photodiode calibrated by NIST. The IQE spectra were calculated from the Equation S1, where the reflectance (R%) were collected with the integrating sphere and the parasitic absorption was obtained from transfer matrix modelling.

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

Electrochemical Impedance Spectroscopy (EIS): EIS measurements were taken with Solartron 1260A Frequency Response Analyzer in dark under N₂ atmosphere. A 10 mA of ac sinusoidal signal with no dc bias is applied during the measurements for the frequency range between 10 Hz and 1 MHz. ZView is used for the modelling and fitting of the data. Zview was used for the data analysis.

Light-intensity dependent measurements, transient photovoltage (TPV), transient photocurrent (TPC) and charge extraction (CE): the measurements were conducted with the help of PAIOS 3.2 (Fluxim) equipped with a white LED with 200 mW/cm² maximum light intensity.

Space-charge-limited current (SCLC) mobility measurement: The electron mobilities for PBDB-T-2F:IT-4F solar cells were measured by fitting the dark currents for electron-only diodes to the SCLC model. The diodes device structure was as follows: Glass/ITO/a-ZnO/PBDB-T-2F:IT-4F/ETL/Al. The ITO-patterned glass substrates were cleaned and UV-ozone treated as described in the solar cells fabrication section. For amorphous ZnO layers, a precursor solution of zinc acetate dehydrate (200 mg) in 2-methoxyethanol (4 mL) and ethanolamine (55 µL) was prepared. The solution was left to stir at room temperature in air for a day. The solution was spun-cast at 4000 rpm onto the cleaned substrates and then they were baked at 150°C for 20 min. Then the substrates were transferred to the dry nitrogen glovebox (<3 ppm O₂), where the active layer solution was spin-cast to obtain the layers with the different thicknesses. The mixed and pure ETLs were deposited as described in the solar cells fabrication section. Finally, 100 nm of Al were thermally evaporated in a vacuum chamber at a base pressure less than 5×10⁻⁶ mbar. The active layer thicknesses were measured with a Tencor surface profilometer. The carrier mobilities were calculated by fitting the diodes' data to the Murgatroyd expression (Equation S2).^[62]

$$J(V) = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \exp\left(0.89\beta \sqrt{\frac{V-V_{bi}}{L}}\right) \frac{(V-V_{bi})^2}{L^3} \quad (\text{S2})$$

where, μ_0 is zero-field mobility, L is the film thickness, J is the dark current density, V - voltage, ε_0 is vacuum permittivity, ε_r is the dielectric constant (taken as 3.3 for the organic layer), and β is the field activation factor.

UV-Vis absorption: Steady-state absorption measurements were performed using an ultraviolet-visible-near infrared spectrometer Cary 5000 (Agilent Technologies). All measurements were performed using quartz substrates.

X-Ray diffraction (XRD): analysis was performed on a Bruker D8 Advance X-ray powder diffractometer using the Cu-K α radiation ($k = 1.54071 \text{ \AA}$).

Atomic Force Microscopy (AFM): A Dimension Icon atomic force microscope (Bruker) was used to perform all measurements in a tapping mode. The Gwyddion and Origin software were used to analyse the raw AFM data.

Solid-State Nuclear Magnetic Resonance Spectroscopy (S-S NMR): One-dimensional ^1H MAS and ^{13}C CP/MAS solid state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 600 MHz resonance frequencies for ^1H utilized a 2.5 mm double-resonance probe. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references TMS and adamantane for ^{13}C . One dimensional ^{31}P MAS solid-state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 400 MHz resonance frequency for ^1H with a conventional double resonance 4 mm CP/MAS probe at a spinning frequency of 10 kHz. ^{31}P NMR chemical shifts are reported with respect to the external references $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (6.6 ppm), the following sequence was used: 90° pulse (pulse length 2.5 μs). The delay between the scans was set to 4 s to allow the complete relaxation and the number of scans ranged between 3 000 - 10 000. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation. The 2D ^1H - ^{13}C heteronuclear correlation (HETCOR) solid state NMR spectroscopy experiments were conducted on a Bruker AVANCE III spectrometer using a 2.5 mm MAS probe. More information on the procedures is given in SI.

Dynamic Nuclear Polarization NMR spectroscopy (DNP): Data were acquired at Core Lab of King Abdullah University using 263 GHz/400 MHz Avance III Bruker DNP solid-state NMR spectrometer equipped with a 3.2 mm Bruker triple resonance low temperature magic angle spinning (LTMAS) probe and the experiments were performed at ca. 100 K with a 263 GHz gyrotron. The sweep coil of the main magnetic field was set for the microwave irradiation occurring at the ^1H positive enhancement maximum of the TEKPol biradical. For the ^{15}N CP-MAS DNP experiments, the acquisition parameters included a 3 s repetition delay and a ^1H $\pi/2$ pulse length of 2.3 μs to afford 100 kHz ^1H decoupling using the SPINAL 64 method. The contact time was typically 4 ms for the cross-polarization experiments. The MAS frequency varied between 8 and 12 kHz. More information on the sample preparation can be found in SI.

X-ray Photoelectron Spectroscopy (XPS): The high-resolution XPS measurements were carried out using a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of $\sim 10^{-9}$ mbar. All spectra were recorded within the limits of spatial resolution. The high-resolution spectra were collected at fixed analyzer pass energy of 20 eV. Samples were mounted in floating mode in order to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the C 1s peak of (C-C, C-H) bond which was set at 284.8 eV. The data were analyzed with commercially available software, CasaXPS.

Supporting Information

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

Acknowledgements

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 GRNET in the National HPC facility – ARIS – under project STEM-2.

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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The electron extracting properties of the widely used electron transporting layer (ETL) material Phen-NaDPO are remarkably enhanced via simple addition of the wide-bandgap inorganic molecule tin (II) thiocyanate ($\text{Sn}(\text{SCN})_2$). Use of this hybrid ETL system in organic and perovskite solar cells results to consistent efficiency improvements due to the reduced trap-assisted recombination and efficient electron extraction.

Keywords: tin (II) thiocyanate; Phen-NaDPO; electron transporting layer; non-fullerene acceptor; organic photovoltaics.

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Use of the Phen-NaDPO: $\text{Sn}(\text{SCN})_2$ blend as electron transport layer results to consistent efficiency improvements in organic and hybrid perovskite solar cells

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Supporting Information

Use of the Phen-NaDPO:Sn(SCN)₂ blend as electron transport layer results to consistent efficiency improvements in organic and hybrid perovskite solar cells

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Figure S1. Statistical distribution of key solar cell parameters based on Phen-NaDPO ‘pure’ and Phen-NaDPO:Sn(SCN)₂ (5 mol%) ‘mixed’ as the ETL. The data were obtained from at least 35 cells.

Figure S2. Stability data of the 'mixed' and 'pure' ETL cells. Time evolution of the device performance and figures of merit of the PBDB-T-2F:IT-4F solar cell devices.

Figure S3. J_{sc} as a function of light intensity of organic BHJ solar cells based on the 'pure' Phen-NaDPO and the 'mixed' Phen-NaDPO:Sn(SCN)₂ as the ETL.

Figure S4. Charge carrier lifetime (τ) obtained from TPV measurements, as a function of charge carrier density (n), calculated from CE measurements under V_{OC} bias conditions for cells based on the two (i.e. pure and mixed) ETLs.

Figure S5. Magnified turn-off dynamics of the normalized transient short-circuit current in response to a 200 μ s white light (LED) pulse for: (a) ‘pure’ and (b) ‘mixed’ ETL-based OSCs.

Figure S6. J - V characteristics measured in dark for electron-only diodes based on the same BHJ with different thicknesses utilizing: (a) Phen-NaDPO ‘pure’, and (b) Phen-NaDPO:Sn(SCN)₂ ‘mixed’ as the ETL.

Figure S7. (a) UV-Vis absorption spectra of the pure Phen-NaDPO and Sn(SCN)₂ films and their mixed layers. (b) Normalized absorption spectra of pristine Phen-NaDPO (pure), and its mixed (2.5 and 5 mol%) layers with Sn(SCN)₂.

Figure S8. XRD spectra of the pure Phen-NaDPO, $\text{Sn}(\text{SCN})_2$ and the 95:5 (Phen-NaDPO: $\text{Sn}(\text{SCN})_2$) mixed powders. The inset (bottom blue trace) shows the magnified peaks of the mixed powder spectrum highlighting diffraction peaks associated with Phen-NaDPO.

Figure S9. The ^1H MAS DNP spectrum of the a) pure Phen-NaDPO and b) mixed Phen-NaDPO: $\text{Sn}(\text{SCN})_2$ powders. TEKPol was dried under high vacuum (10^{-4} mbar) and the solvents were stirred over calcium hydride and then distilled in vacuo. A radical solution consisting of 16 mM TEKPol (TEKPol, MW= 905 g/mol) in 1,1,2,2-tetrachloroethane (TCE) was used. The compounds were finely ground in a mortar and pestle prior to preparation of DNP experiments. DNP samples were then prepared by incipient wetness impregnation. In a typical experiment, 15 mg of the samples were impregnated with the appropriate volume of 16 mM solution of TEKPol

(nTEKPol = 0.5 - 1.2 $\mu\text{mol/sample}$) and packed into a 3.2 mm o.d. sapphire rotor capped with a teflon plug. The packed samples were then immediately inserted into the pre-cooled DNP probe for experiments.

Figure S10. (a) NMR spectra for carbon atom for the ‘pure’ Phen-NaDPO, and Phen-NaDPO:Sn(SCN)₂ ‘mixed’ powders. The following sequence was used: 90° pulse on the proton (pulse length 2.4 s), then a cross-polarization step with contact time of typically 2 ms, and finally acquisition of the ¹³C signal under high-power proton decoupling. The delay between the scans was set to 5 s to allow the complete relaxation of the ¹H nuclei, and the number of scans ranged between 2000 and 10000 for ¹³C. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation. (b) The 2D ¹H-¹³C HETCOR NMR spectrum of the mixed Phen-NaDPO:Sn(SCN)₂ powder. The experiments were performed according to the following scheme: 90° proton pulse, *t*₁ evolution period, CP to ¹³C, and detection of the ¹³C magnetization under TPPM decoupling. For the cross-polarization step, a ramped radio frequency (RF) field centered at 75 kHz was applied to the protons, while the ¹³C channel RF field was matched to obtain an optimal signal. A total of 64 *t*₁ increments with 2000 scans each were collected. The sample spinning frequency was 15 kHz. Using a short contact time (0.2 ms) for the CP step, the polarization transfer in the dipolar correlation experiment was verified to be selective for the first coordination sphere to lead to correlations only between pairs of attached ¹H-¹³C spins (C-H directly bonded). There is a strong correlation of the aromatic protons at 8 ppm with the

aromatic carbons at 130 ppm indicating a direct bonding. The weak correlation for the carbon atoms relates to nitrogen at 143 ppm with its corresponding protons at 10 ppm.

Figure S11. Structure (top), Highest Occupied Molecular Orbital (HOMO), and Lowest Unoccupied Molecular Orbital (LUMO) of a Phen-NaDPO molecule (C: gray, H: white, N: blue, P: orange, O: red spheres). DZVP results are shown for the HOMO and LUMO energies. The corresponding $E_{\text{HOMO}}/E_{\text{LUMO}}$ values with the 6-31g* and 6-311g* basis are, respectively, -5.97 eV/-1.76 eV and -6.22 eV/-2.00 eV

Figure S12. (a) Schematic of the standard cell architecture employed. (b) J-V characteristics of PBDB-T-SF:IT-4F solar cells employing the Phen-NaDPO ‘pure’ and Phen-NaDPO:Sn(SCN)₂ ‘mixed’ ETLs.

Table S1. Summary of PBDB-T-2F:IT-4F cells optimization increasing content of Sn(SCN)₂ in the ETL mixture.

Sn(SCN) ₂ (mol%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Avg. (%)	PCE	Max. PCE (%)
0	0.85	19.7	73	12.2		12.6
1.25	0.86	19.5	76	12.8		13.0
2.5	0.86	19.5	76	12.9		13.0
5	0.87	20.0	76	13.2		13.5
7.5	0.86	19.7	74	13.0		13.1
10	0.86	19.4	70	11.7		11.9

Table S2. Summary of results obtained from fitting the EIS curves on **Figure 2b** to the equivalent circuit shown on the same figure.

ETL	Parameters (units)	Values of the parameters	Error (%)
pure	C_g (F)	2.27×10^{-9}	0.17
	R_s (Ω)	20.00	4.07
	R_t (Ω)	364.20	0.13
	R_{rec} (Ω)	27.18	6.87
	P_1 (F)	1.08×10^{-9}	1.30
	n_1 (-)	0.90	0.11
mixed	C_g (F)	2.40×10^{-9}	0.74
	R_s (Ω)	20.00	1.65
	R_t (Ω)	231.17	0.15
	R_{rec} (Ω)	36.67	5.88
	P_1 (F)	1.17×10^{-9}	5.37
	n_1 (-)	0.90	0.44

Table S3. Electron mobility values calculated from **Figure S5** via space charge limited conduction (SCLC) analysis.

ETL	Active layer thickness (nm)	$\mu_{0,e}$ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
pure	135	$(7.4 \pm 0.3) \times 10^{-4}$
	123	$(7.7 \pm 0.3) \times 10^{-4}$
	115	$(7.3 \pm 0.3) \times 10^{-4}$
mixed	135	$(1.1 \pm 0.1) \times 10^{-3}$
	129	$(9.8 \pm 0.6) \times 10^{-4}$
	120	$(9.3 \pm 0.5) \times 10^{-4}$

Table S4. Calculated (δ_{calc}) ^{31}P chemical shifts (referenced to H_3PO_4) based on DFT calculations with the B3LYP xc-functional and the DZVP basis.

Compound	δ_{calc} (ppm)
Phen-NaDPO	18.5
Phen-NaDPO:Sn(SCN) ₂ Figure 5a	47.8
Phen-NaDPO:Sn(SCN) ₂ Figure 5b	19.2
Phen-NaDPO:Sn(SCN) ₂ Figure 5c	20.7
Phen-NaDPO:Sn(SCN) ₂ Figure 5d	53.7
Phen-NaDPO:Sn(SCN) ₂ Figure 5e	37.4
Phen-NaDPO:Sn(SCN) ₂ Figure 5f	19.0

Table S5. Operating parameters of PBDB-T-SF:IT-4F organic solar cells based on Phen-NaDPO ‘pure’ and Phen-NaDPO:Sn(SCN)₂ ‘mixed’ as the ETLs.

ETL	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	Avg. PCE (%)	Max. PCE (%)
pure	0.89 ± 0.00	18.8 ± 0.2	66 ± 1	11.0 ± 0.2	11.2
mixed	0.90 ± 0.00	19.0 ± 0.2	67 ± 1	11.4 ± 0.2	11.6

Table S6. Operating parameters of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells based on Phen-NaDPO ‘pure’ and Phen-NaDPO:Sn(SCN)₂ ‘mixed’ as the ETLs.

ETL	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	Avg. PCE (%)	Max. PCE (%)
pure (reverse)	1.06 ± 0.00	21.4 ± 0.2	72 ± 1	16.2 ± 0.3	16.5
pure (forward)	1.05 ± 0.01	21.3 ± 0.1	74 ± 1	16.3 ± 0.3	16.6
mixed (reverse)	1.08 ± 0.00	22.6 ± 0.3	75 ± 1	18.0 ± 0.2	18.2
mixed (forward)	1.08 ± 0.00	22.5 ± 0.2	75 ± 1	17.9 ± 0.3	18.2