Reduced interface losses in inverted perovskite solar cells by using a simple dual-functional phenanthroline derivative

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A B S T R A C T

Interface losses at metal/organic interface is a critical issue in organic electronic devices. The interfacial layers play a significant role in enhancing the device performance and the interfacial material design criteria are ongoing challenges to be faced in optimizing the device performance. In this work, a simple Phenanthroline derivative Phen-I was synthesized through a quaternization reaction in a high yield without complicated purification process. Besides its good wettability and compatibility of the contact between metal electrode and organic layer, interestingly, Phen-I displays a dual functional property, i.e., it not only lowers the work function of the metallic cathode to increase electron extraction but also can be doped into electron transporting material to enhance the conductivity. The inverted perovskite solar cells (PSCs) with Phen-I as cathode interlayer (CIL) show superior performance both in power conversion efficiency, with a maximum PCE of 18.13%, and devices stability as compared with the control devices. Encouragingly, the best PCE of 19.27% was obtained when the perovskite layer based on FA\textsubscript{0.3}MA\textsubscript{0.7}PbI\textsubscript{2.7}Cl\textsubscript{0.3} perovskite system. Meanwhile, the devices with Phen-I as CIL show low J-V hysteresis during the forward and reverse bias sweeping. Subsequent studies demonstrate that the performance of the inverted PSCs also improves to 15.25% using 5% Phen-I:PC\textsubscript{61}BM as electron transporting layer (ETL). Herein, the interface between the metal electrode and ETL is carefully investigated using a series of electrical and surface potential techniques. These results demonstrate that Phen-I is a dual-functional interlayer material to reduce interface losses, which, highlights the broad promise of this new class of materials for applications in organic electronic devices. Meanwhile, owing to the simple molecular structure, low-cost and solution processible, these intriguing features render Phen-I more suitable for efficient organic electronics in large area printing process.

1. Introduction

Organic electronic devices, for example, organic light-emitting diodes (OLED)\textsuperscript{1}, organic thin film transistors (OTFT)\textsuperscript{2,3}, organic/inorganic hybrid photovoltaic\textsuperscript{4-6}, have recently attracted significant attention due to their high mechanical flexibility\textsuperscript{7} and low fabrication cost\textsuperscript{8,9} with a variety of choices available for material selection to improve the device performance. However, a critical issue for organic semiconductor devices, in general, is the interface losses at their electrode/organic interfaces\textsuperscript{10}. Excellent charge injection leads to a lower turn-on voltage and higher efficiency in OLEDs\textsuperscript{11,12}, smaller contact resistance in OTFT\textsuperscript{13} and a higher short-circuit current and open-circuit voltage in solar cells\textsuperscript{14-17}. Interface modification has been considered as an effective approach for fine-tuning the device performance due to its abilities to tune the energy level alignment, surface energy and recombination induced by surface states and/or imperfections\textsuperscript{18,19}. On the other hand, although the power conversion efficiency (PCE) of inverted PSCs has exceeded 20%\textsuperscript{20,21}, interface issue still need to be resolved\textsuperscript{22}, where a low work function metal is normally needed to match with the LUMO energy level of electron transporting layer (ETL), in which PCBM commonly used as ETL material due to its solution processability, high electron mobility and fine energy levels for efficient excitons dissociation. Therefore, interface engineering is of paramount importance for improving the performance of organic electronic devices.

Recently, an effective approach has been carried out to reduce interface losses by incorporating a cathode interlayer between organic layer and metal electrode\textsuperscript{23}. Thermally evaporated Ga, LiF\textsuperscript{24}, bathocuroine (BCP)\textsuperscript{25}, or functionalized fullerene derivatives\textsuperscript{26} have been reported as interfacial layer in inverted PSCs. Meanwhile, Some solution processed materials, for example, conjugated polyelectrolytes\textsuperscript{27,28}, thiol-functional cation surfactant\textsuperscript{29}, n-doped metal

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oxides [30], amino-functionalized polymer (PN4N) [31], amino-functionalized small molecules (C60-N [32], PDINO [10]), and carboxylic potassium salt [33] were also employed as an efficient interlayer to modify the interface between the PCBM and top metal contact. The Bis-C60 was already demonstrated to be a high efficient interfacial material [34,35] although its synthesis is complicated with relatively long synthetic routes [36]. In addition, Liao et al. reported costly Phen derivative 4,7-diphenyl-1,10-phenanthroline (Bphen) as CIL to modify the surface morphology of perovskite/PCBM and improve the performance of the devices [37]. Zou et al. introduced Bphen doped with bis(2-methyl dibenzofuran) (Bphen) as CIL [38]. However, either a high vacuum-based expensive deposition process or intricate expensive materials are required to fabricate the devices, which hinder the affordable use of the interfacial layer in printed and large-area devices. Here, we report a simple Phen derivative Phen-I, which was synthesized in one-step, using low-cost Phen as starting material and through a simple quaternization reaction with a high yield and without complicated purification process, for instance, costly chromatographic separations or tedious recrystallization process. The crude product was purified by simple washing with petroleum ether to afford a pure yellow solid. We demonstrated that high-performance inherited pSCs can be fabricated with Phen-I as an interlayer between PbS and silver electrode, achieving a maximum PCE of 18.13%. It has been demonstrated in a previous report that DMOAP can cause efficient n-doping of PCBM and achieve a high PCE of 18.1% [39]. However, DMOAP is highly unstable in air, which limits its further industrial application [40]. Interestingly, we found Phen-I could also n-dope PbS:PC61BM at the interface. The device performance with the Phen-I-doped PbS:PC61BM layer was then studied. In the case of 5 wt% Phen-I, the device demonstrated the best performance with a PCE of 15.25%, which is more than 42% increase compared with that of the control device. Kelvin probe force microscopy (KPFM), ESR spectroscopy, conductive atomic force microscopy (c-AFM) and steady-state photoluminescence (PL) were utilized to fully understand the influence of interface layer on the organic electronic device performance.

2. Material and methods

2.1. Synthesis of Phen-I

A nitrogen flushed round bottom flask was charged with Phen (1.8 g, 10 mmol), 1-iodohexane (2.3 g, 11 mmol). Acetonitrile (50 ml) was then added and the mixture was bubbled with nitrogen for 15 min. The mixture was then refluxed for 12 h. After removal of solvent, the crude product was purified by washing with petroleum ether for several times to afford a yellow solid (3.49 g, 89%). 1H NMR (CDCl3, 300 MHz): δ 10.20 (d, J = 5.9 Hz, 1H), 9.44 (d, J = 8.2 Hz, 1H), 9.22 (dd, J = 4.3, 1.8 Hz, 1H), 8.49 (dd, J = 8.2, 5.9 Hz, 1H), 8.36 (d, J = 8.8 Hz, 1H), 8.26 (d, J = 8.8 Hz, 1H), 7.92 (dd, J = 8.2, 4.2 Hz, 1H), 6.19-6.02 (m, 2H), 2.21-2.03 (m, 2H), 1.59 (p, J = 7.3 Hz, 2H), 1.44-1.21 (m, 3H), 0.86 (t, J = 7.0 Hz, 3H). 13C NMR (CDCl3, 300 MHz): δ 151.12, 149.76, 147.00, 139.88, 137.85, 136.58, 132.72, 132.06, 131.04, 127.34, 125.36, 125.09, 64.62, 31.82, 31.17, 25.89, 22.39, 13.92.

2.2. Materials characterization

Nuclear magnetic resonance (NMR) was taken on Bruker AVANCE III 300 MHz and 400 MHz Spectrometer. All chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm, unless otherwise stated. The absorption spectrum was recorded with UV-visible spectrophotometer (Shimadzu 2450). Cyclic voltammetry was determined by electrochemical workstation (Chenhua CHI660E).

2.3. Device fabrication

2.3.1. Solar cell fabrication and testing

NiOx thin films were prepared according to the literature. The perovskite precursor solution was prepared by mixing FAI, CsI, MAI, PbI2, and PbCl2 with molar ratio of 0.1:0.1:0.8:0.9:0.1 in γ-GBL:DMSO = 7:3 (v/v) at 1.4 mol/L and stirred at 60 °C for 6 h before use. Here, sequence three step spin coating process was applied to fabricate highly uniform perovskite thin films. In brief, the perovskite precursor solution was spin-coated on to the ITO/NiOx substrates at 1000 rpm and 5000 rpm for 10 s and 30 s, at the 5000 rpm for 20 s, toluene was used to treat the perovskite thin film. Then the perovskite thin films were thermal annealing on the hot plate at 100 °C for 10 min. The inverted PSCs were fabricated by spin coating of FTO/PEDOT/ITO thin film on ITO substrates and then coated with the perovskite thin films. The contact potential difference between the AFM probe and bare Ag electrode or Ag/Phen-I were measured by a MultiMode 8-HR AFM (Bruker Corporation, Germany). The conductivities of Phen-I can dope PC61BM thin film was measured by this AFM equipment too. The ESR spectroscopy of PC61BM/Phen-I blended sample was measured by an EMXplus−10/12 Electron Paramagnetic Resonance Spectrometer (Bruker Corporation, Germany). Steady state PL spectra of the Perovskite films with and without PC61BM were measured by FLS920 spectrofluorimeter (Edinburgh Instruments).

3. Results and discussions

The photophysical and electrochemical properties of Phen-I are summarized in Table S1 (in Supporting information), and the corresponding UV−vis absorption spectra are shown in Fig. 1a. Cyclic voltammetry (CV) measurements were used to measure the electronic energy levels of Phen-I. The LUMO energy levels were calculated from the onset reduction potential by assuming the energy level of ferrocene/ferrocenium (Fc/Fc+) to be −4.8 eV below the vacuum level. Fig. 1b displays the cyclic voltammograms of Phen-I in Bu4NPF6 (0.1 M in acetonitrile) solution at a scan rate of 100 mV s−1. The onset reduction potentials of Phen-I is −1.18 eV (vs. Fc/Fc+). Therefore, the LUMO energy level was calculated accordingly as −3.62 eV for Phen-I. The HOMO energy level of Phen-I was calculated from its LUMO level and optical band gap based on the equation of HOMO = LUMO − Eg. From 1a, the absorption edge of Phen-I is 473 nm, which correspond to the optical Eg of 2.62 eV. Hence, the calculated HOMO energy levels as shown in Fig. 4d, and the deep HOMO energy levels provide good hole.
blocking ability to prevent undesired charges reaching the cathode, which reduces hole-electron recombination at the cathode interface.

To examine the performance of inverted PSCs with Phen-I as CIL, we fabricated the inverted PSCs with the configuration of ITO/NiOx/Perovskite layer/PC61BM/CIL/Ag as shown in Fig. 2a. The CIL was prepared by spin-coating the methanol solution of Phen-I on the PC61BM layer. Control devices without CIL were also fabricated. The current density-voltage ($J-V$) characteristics of the optimized devices under illumination of AM 1.5G, 100 mW/cm$^2$ are shown in Fig. 2b and corresponding photovoltaic parameters of the devices are summarized in Table 1. It is obvious that devices with Phen-I as CIL show higher PCEs, which indicates that Phen-I is an effective choice to modify the cathode interface. With Phen-I as the CIL, the inverted PSCs exhibit the best PCE of 18.13%, a $V_{oc}$ of 1.13 V, a $J_{sc}$ of 20.51 mA/cm$^2$, and FF of 78.54%. The best Phen-I device shows a PCE value as high as 18.13%, while the control device showed only the best PCE of 10.7%, with $V_{oc}$ of 1.10 V, a $J_{sc}$ of 18.15 mA/cm$^2$, and FF of 53.56%, the improvement in

<table>
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<th>Cathode configuration</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC61BM/Ag</td>
<td>1.10</td>
<td>18.15</td>
<td>53.56</td>
<td>10.70</td>
</tr>
<tr>
<td>PC61BM/Phen-I/Ag</td>
<td>1.13</td>
<td>20.51</td>
<td>78.54</td>
<td>18.13</td>
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![Fig. 1.](image1.png) a) Uv–vis spectra of Phen-I in solution and thin film. b) Cyclic voltammograms of Phen-I.

![Fig. 2.](image2.png) a) Device configuration of the inverted PSCs with Phen-I as CIL. b) J-V curves of the devices with Phen-I and PC61BM as CIL, as measured under 100 mW/cm$^2$ Am 1.5G irradiation. c) EQE spectra of the corresponding solar cells. d) Hysteresis investigation of the device with Phen-I as CIL.
the performance of Phen-I device is attributed to higher J_{sc} and FF. Fig. 2c shows the external quantum efficiency (EQE) measurement which was applied to confirm the higher J_{sc} of device with Phen-I as CIL. Obviously, the EQE values in the entire photo response range between 300 nm and 750 nm are significantly enhanced after inserting the CIL, suggesting that electrons can be more efficiently extracted from perovskite layer to Ag. The calculated J_{sc} from EQE measurement is well consistent with the measured J_{sc} value within 5% mismatch. Meanwhile, the devices with Phen-I as CIL show low J-V hysteresis (Fig. 2d) upon forward and reverse bias sweeping illustrating a negligible number of defects in the perovskite active layer and interfaces.

To confirm power output reliability of the fabricated PSCs with Phen-I as CIL, a stabilized power output was measured under a constant voltage bias of 0.96 V near the maximum power output point and is shown in Fig. 3a. The Phen-I device shows high stable power output and a steady-state PCE of 18.10% is obtained. The scan rate dependence of the J-V characteristics in the Phen-I-based device is given in Fig. 3b, and no significant change in the J-V characteristics was observed up to delay time of 100 ms. A histogram of the performance of Phen-I-based devices obtained from 30 samples is summarized in Fig. 3c. Notably, more than 50% of the integrated devices showed PCE above 16.7%, indicating good reproducibility. These results demonstrate that Phen-I is a promising CIL for inverted PSCs.

In order to confirm a reduced injection barrier at PC_{61}BM/Ag by inserting Phen-I layer, we carried out Kelvin Probe Force Microscopy Measurement (KPFM) measurements to determine the contact potential differences (V_{CPD}) between the atomic force microscopy (AFM) probe and bare Ag electrode or Ag/Phen-I. The samples for KPFM were prepared by evaporating Ag onto a clean ITO glass, followed by spin-coating Phen-I from methanol. In a normal KPFM research work, firstly a pass scan is done in mechanically driven tapping mode to test topography, and then a second pass at AC voltage resonant frequency to determine V_{CPD}. Potential maps were showed in Fig. 4a and b. Potential histograms were made and fit with Gaussian curves to find the value of V_{CPD} for the sample. Representative V_{CPD} histograms for Ag electrode, Ag/Phen-I are shown in Fig. 4c. We found ΔV_{CPD} between bare Ag and Ag/Phen-I to be 0.18 ± 0.01. By the equation: V_{CPD}=(\phi_{probe}-\phi_{sample})/e we estimated a 0.18 eV \phi decrease when Phen-I is coated on Ag. This apparent decrease in Ag \phi arises from the presence of a negative interfacial dipole between Ag and Phen-I, and explains the improved Voc for devices containing Phen-I interlayer [41].

Increased conductivity of electron transporting layer is important to enhance electron transport and collection by cathode [42]. Previous study has demonstrated that the iodide functional small molecule can n-dope fullerene films and increase its conductivity [43]. To confirm whether Phen-I can dope PC_{61}BM thin film, electron spin resonance (ESR) spectroscopy was performed to further investigate the interface modification property. As shown in Fig. 5a, blended samples of PC_{61}BM/Phen-I with the 1:1 weight ratio were tested to study the charge transfer property between the two components. In the PC_{61}BM/Phen-I blend, an obvious resonance peak was detected. This result clearly suggests that electron transfer occurred from Phen-I to PC_{61}BM.
The results from the ESR study provide the evidence that Phen-I could n-dope PC61BM at the interface, leading to improve PSCs device performance. For investigation of the effect of Phen-I-doped PC61BM on the photovoltaic performance of PSCs, a configuration of glass substrate ITO/NiOx/Perovskite/Phen-I-doped PC61BM/Ag was fabricated (Device configuration in Fig. 5b). Fig. 5c shows the J-V characteristics of the best performing devices, and the detailed photovoltaic parameters are listed in Table 2. There is a large effect of Phen-I concentration on the device performance. In the case of 5 wt% Phen-I, the device...
demonstrated the best performance with a PCE of 15.25%, $J_{sc}$ of 20.16 mA/cm$^2$, $V_{oc}$ of 1.06V, and FF of 71.51%. It is found that the $J_{sc}$ and FF in Phen-I-based cells improve largely in contrast to reference device. The $J_{sc}$ increases from 18.15 to 20.16 mA/cm$^2$ and FF increases from 53.56% to 71.51%. Noticeably, the $V_{oc}$ reduces slightly from 1.10 to 1.06 eV.

To investigate the effects of Phen-I-doping and device performance, we initially examined and compared the conductivity of PC61BM film with different doping concentrations by performing conductive atomic force microscopy (c-AFM) measurements as described in Fig. 6a. The c-AFM images in Fig. 6c, d, e, f clearly illustrate different current levels and distributions between bare PC61BM and Phen-I:PC61BM films. Obviously increased vertical current is found in the Phen-I:PC61BM films, demonstrating enhanced electrical conductivity upon Phen-I doping, which could attribute to anion-induced electron transfer [43]. The I-V curves presented in Fig. 6b also indicate the enhancement in electrical conductivity upon Phen-I doping as compared to bare PC61BM. However, when the doping concentrations were increased beyond 5%, the conductivity decreased gradually which is consistent with the performance trend of PSCs. This deterioration could be ascribed to the tendency of excess Phen-I-caused aggregation [44]. Furthermore, the root-mean-square (RMS) roughness tests (Fig. S3) also indicate that higher doping concentration results in higher roughness.

To gain further insight into the charge transfer properties between Perovskite and PC61BM, we performed steady-state photoluminescence (PL). The PL properties of ITO/Perovskite, TiO/Perovskite/PC61BM, and TiO/Perovskite/Phen-I-doped PC61BM (doping concentration = 2, 5, 10 wt%) were measured under excitation at a wavelength of 450 nm. As shown in Fig. 7a, the significant PL quenching effect can be observed when the perovskite layer was deposited with either undoped PC61BM or doped PC61BM layers. The quenching of PL intensity is generally attributed to charge transfer at the perovskite/fullerene interface [45]. Compared with undoped PC61BM-coated sample, nearly all intensities are quenched for the doped PC61BM-coated sample (as shown in Fig. 7b), suggesting that charge carrier transfer at the perovskite/doped PC61BM interface is more efficient than that at the perovskite/undoped PC61BM interface, due to the higher electrical conductivity of doped PC61BM on the perovskite layer as discussed above.

In addition to the PCE, the stability is another important aspect that needs to be improved for the practical application of PSCs [46]. We investigated the stability of the devices with Phen-I as interlayer in the ambient conditions. We found that the insertion of the Phen-I layer is helpful to enhance the stability of the devices. As shown in Fig. 7c, the PCE of the devices without CBL drop rapidly. Merely 50% of the PCE remained after $\approx$ 200 h of storage in air. However, for the devices with CBL, the PCEs remained relatively stable even up to $\approx$ 300 h. After storing for 500 h in air, the PCEs still maintained 60% of the original PCE. These results illustrate that the Phen-I CIL may have a blocking effect on water and/or oxygen to some extent, which is greatly helpful to enhance the device stability.

It is worth mentioning that Phen-I was also successfully applied in other perovskite systems. We fabricated the inverted PSCs based on FA$_0.3$MA$_{0.7}$PbI$_2.7$Cl$_{0.3}$ perovskite system, which possesses a small bandgap. Encouragingly, the best PCE of 19.27% was obtained, with $J_{sc}$ of 23.14 mA/cm$^2$, $V_{oc}$ of 1.07 V, and FF of 77.98% (Fig. 8a) when Phen-I interlayer was incorporated. These results indicate that Phen-I can be used as a universal CIL for PSCs.

4. Conclusions

In conclusion, we synthesized a simple Phen derivative, Phen-I, and demonstrated a considerable enhancement in PCEs, from 10.70% to...
18.13% of inverted PSCs by inserting Phen-I as interlayer between metal electrode and ETL. The best PCE of 19.27% was obtained when the perovskite layer based on FA0.3MA0.7PbI2.7Cl0.3 perovskite system. Meanwhile, the performance of the inverted PSCs was also improved to 15.25% using 5% Phen-I:PC61BM as ETL. A variety of electrical and surface potential characterization measurements were used to study the interface between the metal electrode and ETL. KPFM measurements indicate a uniform and continuous work function decrease in the presence of the Phen-I layer. c-AFM measurements illustrate that the Phen-I-doping fully enhances the conductivity of PCBM film via anion-induced electron transfer. With the aid of these results we demonstrated Phen-I as a new dual-functional interlayer material to reduce interface losses for PSCs. Owing to the simple molecular structure and low-cost, Phen-I is also a good candidate for efficient organic electronics in large area printing process. The concept of such simple derivatives can be extended to explore new efficient interface materials.

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Notes

The authors declare no competing financial interest.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2017.11.014.

References

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