Water/Alcohol Soluble Thickness-Insensitive Hyperbranched Perylene Diimide Electron Transport Layer Improving the Efficiency of Organic Solar Cells

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Abstract: The electron transport layer (ETL) is very crucial for enhancing the device performance of polymer solar cells (PSCs). Meanwhile, thickness-insensitive and environment-friendly water/alcohol soluble processing are two essential requirements for large-scale roll-to-roll commercial application. Based on this, we designed and synthesized two new n-type ETLs with tetraethylene pentamine or butyl sulfonate sodium substituted tetraethylene pentamine as the branched side chains and high electron affinities perylene diimide (PDI) as the central core, named as PDIPN and PDIPNSO$_3$Na. Encouragingly, both PDIPN and PDIPNSO$_3$Na can effectively reduce the interfacial barrier and improve the interfacial contact. In addition, both of them can exhibit strong n-type self-doping effects, especially the PDIPN with higher density of negative charge. Consequently, compared to bare ITO, the PCE of the devices with ITO/PDIPN and ITO/PDIPNSO$_3$Na ETLs has increased to 3–4 times. Our research results indicate that n-type self-doping PDI-based ETL PDIPN and PDIPNSO$_3$Na could be promising candidates for ETL in environment-friendly water/alcohol soluble processing large-scale PSCs.

Keywords: thickness-insensitive; electron transport layer; perylene diimides

1. Introduction

Polymer solar cells (PSCs) have attracted increasing attention due to their lightweight, flexibility, and easy large-area solution processability [1–11]. With the rapid progress in novel donor and acceptor material design and interfacial engineering, the power conversion efficiency (PCE) of the PSCs have been boosted over 14% [12,13]. Currently, most research focuses on the design of novel active layer materials for improving the power conversion efficiency (PCE) of the PSCs [14–19]. Interfacial modulating is also very crucial for enhancing the PCE of the device [20–24].

The mismatched energy lever between the active layer and electrode can cause the Schottky barrier, thus inhibiting the charge transfer and injection [25]. Suitable interfacial modification can decrease the interfacial barrier and increase the selectivity of charge, thus inhibiting the charge recombination and increasing the efficiency of charge injection [26,27]. Hence, inserting an interlayer between active layer and cathode electrode should be an effective strategy to increase the performance of the device.
To date, metal oxide semiconductor (TiO$_x$, ZnO, MoO$_x$), electrolytes and fullerenes derivates etc have been used as ETLs to modulate interfacial contact and reduce interfacial barriers [28–34]. However, inorganic metal oxide ETL usually shows incompatible with the organic light harvest. Moreover, most of inorganic metal oxide ETLs need to be treated with a high temperature, which cannot be satisfied with the demand of the solution-process large-scale commercial application.

In consequence, to explore environment-friendly water/alcohol soluble processing organic ETL with strong interfacial control capability is extremely urgent. It would be better if the ETL is thickness-insensitive and can be efficient in different interlayer thickness. Perylene diimide (PDI) is a famous n-type material, which has many strong points, such as good electron affinities, high conductivities and facile modification by simple substitution reaction [35–38]. Moreover, the high conductivity of the PDI originated from self-organized p-stacks in solid film can endow the PDT-based ETL with thickness-insensitive superiority, which can conquer the thickness restriction (<10 nm) of the reported organic ETL. Thus, PDT-based ETL may have the potential to realize large-area manufacturing techniques owing to its tolerance of certain thickness variation.

N-type self-doping phenomena of the ETLs can enhance the electron mobility and form additional big interfacial dipoles on the interface of ITO and active layer [39]. Combining the PDI and n-type self-doping at molecular level can endow the material with the advantages of both materials. Tetrathiafulvalene diimide (PDIPN) contains enough polar groups and unpaired electrons of the N atoms. Inspired by this, we designed and synthesized two new n-type ETLs PDIPN and PDIPNSO$_3$Na (Scheme 1) with perylene diimide (PDI) as central core and tetraethylene pentamine or butyl sulfonate sodium substituted tetrathiafulvalene pentamine as the branched side chains. Intriguingly, both n-type ETLs PDIPN and PDIPNSO$_3$Na can form favorable interfacial dipole due to the polar groups and n-type self-doping effect. In sharp comparison to the device without ETL, the PCEs of the inverted device based on ITO/PDIPN and ITO/PDIPNSO$_3$Na have been increased over two times. Furthermore, both PDIPN and PDIPNSO$_3$Na can obtain an acceptable efficiency among a wide range of ETL thickness. As a result, environment-friendly water/alcohol soluble thickness-insensitive PDIPN and PDIPNSO$_3$Na should be a promising ETL for large-scale commercial application.

Scheme 1. Synthetic routes of PDIPN and PDIPNSO$_3$Na.
2. Synthesis and Characterization

The detailed synthetic procedures of the hyperbranched perylene diimides ETLs PDIPN and PDIPNSO$_3$Na are provided in Scheme 1, and the synthetic route is depicted in the Supporting Information. The PDIPN is synthesized by one-step substitution reaction between 3,4,9,10-perylenetetracarboxylic diimides and tetraethylene pentamine with a catalytic amount of zinc acetate (127 mg). The PDIPNSO$_3$Na is prepared by PDIPN with NaH and 1,4-butanesultone via simple substitution reaction. Due to the existence of the polar group, the PDIPN and PDIPNSO$_3$Na ETL can realize non-polluted water/alcohol processing. The structures of PDIPN and PDIPNSO$_3$Na are verified by $^1$H nuclear magnetic resonance spectra ($^1$H NMR) (Figure S1–S2) and UV–Vis absorption (Figure 1).

![Figure 1](image_url)

**Figure 1.** (a) UV–Vis absorption and (b) cyclic voltammograms (CV) spectra of PDIPN and PDIPNSO$_3$Na films.

To calculate the optical bandgap ($E_{\text{gopt}}$) and electrochemical bandgap ($E_{\text{gec}}$) of the ETLs PDIPN and PDIPNSO$_3$Na, the UV–Vis and cyclic voltammetry (CV) are investigated, as shown in Figure 1. From Figure 1a, we can obviously see that the absorption band onset ($\lambda_{\text{onset}}$) of PDIPN and PDIPNSO$_3$Na are at 614 nm and 620 nm, an optical bandgap ($E_{\text{gopt}}$) can be calculated to be 2.02 eV for PDIPN and 2.00 eV for PDIPNSO$_3$Na. Meanwhile, a broad absorption peak can be easily observed at 800 nm and extended to 1100 nm both in PDIPN and PDIPNSO$_3$Na film, which should be ascribed to the absorption of polarons [40–42]. These results suggest that maybe there are n-type self-doping effects exist in PDIPN and PDIPNSO$_3$Na owing to the existence of unpaired electron in N atoms [43]. The unpaired electron of the N atoms can transfer to the perylene diimides nucleus, thus giving rise to the formation of n-type self-doping behavior. Furthermore, compared to PDIPNSO$_3$Na, PDIPN film shows stronger absorption band of polarons, indicating that the number of free electron of PDIPN is much more than that of PDIPNSO$_3$Na. Because one mole PDIPNSO$_3$Na has ten moles electron-withdrawing sodium sulfonate, the density of free electrons of PDIPNSO$_3$Na is lower than that of PDIPN. The n-type self-doping can form additional interfacial dipole, which is beneficial to reduce the interface barrier and enhance the electron injection efficiency, thus increasing the PCE of the device. The electrochemical energy levels are measured by cyclic voltammetry in an anhydrous nitrogen-saturated acetonitrile solution of n-Bu$_4$NPF$_6$, as depicted in Figure 1b. The PDIPN and PDIPNSO$_3$Na exhibit onset oxidation potentials at $-0.73$ eV and $-0.79$ eV, the HOMO of PDIPN and PDIPNSO$_3$Na are estimated to be $-5.59$ eV and $-5.67$ eV, respectively [44,45]. Meanwhile, we can calculate the LUMO of PDIPN and PDIPNSO$_3$Na to be $-3.67$ eV and $-3.61$ eV according to their onset reduction potentials; the detailed CV data are provided in Table S1.

To obtain further insight into the n-type self-doping behavior of PDIPN and PDIPNSO$_3$Na, the electron paramagnetic resonance (EPR) spectra are characterized. In Figure 2, obvious narrow
line shape signals at about 330G can be detected both in PDIPN and PDIPNSO$_3$Na films, these signals are consistent with the presence of unpaired electrons [43]. Moreover, in comparison to the PDIPNSO$_3$Na, the EPR signal of PDIPN is immensely stronger. These phenomena should because the density of negative charge of PDIPNSO$_3$Na has been significantly reduced owing to the electron-withdrawing sulfonate of the branched chain, hence inhibiting the electron from transferring to the perylene diimidess nucleus [42]. The result of the EPR is quite in agreement with that of the UV–Vis measurement. Furthermore, we can easily draw a conclusion that both PDIPN and PDIPNSO$_3$Na films possess n-type self-doping effect, and the PDIPN film show stronger n-type self-doping compared to that of PDIPNSO$_3$Na. The schematic diagram of self-doping process is shown in Scheme 1.

![Figure 2. Electron paramagnetic resonance (EPR) spectra of the PDIPN and PDIPNSO$_3$Na film.](image)

The X-ray photoelectron spectra (XPS) of pristine ITO and ITO/ETLs are conducted to investigate the interfacial interaction, as displayed in Figure 3a. Figure 3b is the N 1s XPS graph of the ITO, ITO/PDIPN and ITO/PDIPNSO$_3$Na. Obviously, there is no signal peak detected for bare ITO. Simultaneously, a broad peak at 400.04 eV is detected for ITO/PDIPN, which is associated to the N atoms of the imide and amine in PDIPN. Besides, for ITO/PDIPNSO$_3$Na, a broad strong peak at a value of 399.9 eV and a broad weak peak at 403.05 eV are found. Similarly, the peak at 399.9 eV belongs to the imide and amine. However, the new weak peak of 403.05 eV is assigned to N(CH$_2$)$_3$H$^+$. N(CH$_2$)$_3$ of PDIPNSO$_3$Na can be partially protonated and form N(CH$_2$)$_3$H$^+$ by reacting with the protons (H$^+$) from the water/methanol due to its basicity. From Figure 3c, a strong peak at 1070.80 eV is observed for ITO/PDIPNSO$_3$Na, which belongs to the sodium sulfonate branched chain. Nevertheless, Na 1s signal cannot be traced in the spectra of ITO and ITO/PDIPN due to no Na element. The spectra of S 2p with different ETLs are shown in Figure 3d, there are no peaks in bare ITO and ITO/PDIPN, while an obvious peak at 168.04 eV has been found for ITO/PDIPNSO$_3$Na film, which should be ascribed to the absorption of S atom in -SO$_3$Na terminal groups. It indicates that PDIPN and PDIPNSO$_3$Na have been triumphantly synthesized and spin-coated on ITO according to the high-resolution N 1s, Na 1s and S 2p spectra.

The XPS spectra of the In 3d and Sn 3d are carried out to further characterize the interfacial interactions and interfacial dipole between PDIPN and PDIPNSO$_3$Na and ITO (Figure 4). In comparison to the In 3d of bare ITO (Figure 4a), the resolution peaks of both ITO/PDIPN and ITO/PDIPNSO$_3$Na have moved to lower binding energy. The shift of the In 3d signal indicates that strong interfacial interaction occurs at the interface of the ITO/PDIPN and ITO/PDIPNSO$_3$Na. Similarly, the Sn 3d XPS spectra of ITO, ITO/PDIPN and ITO/PDIPNSO$_3$Na are also studied (Figure 4b). Bare ITO exhibits the Sn 3d peaks at 494.50 eV and 486.15 eV, and the corresponding peaks of ITO/PDIPN shift toward lower binding energies to 494.55 eV and 486.10 eV, respectively, and the corresponding peaks of ITO/PDIPNSO$_3$Na are observed at 494.25 eV and 485.94 eV. Both the
In 3d and Sn 3d signals shift to lower binding energy could once again demonstrate that the interfacial dipoles are indeed created and strong interfacial interactions are in the presence of ITO/PDIPN and ITO/PDIPNSO$_3$Na interfaces. Interestingly, a strong broad peak at 497.00 eV has been detected for ITO/PDIPNSO$_3$Na, which owing to the Na (KLL) Auger peak. The existence of Na (KLL) Auger peak originates from the KLL energy level transition of Na atoms proves that the PDIPNSO$_3$Na film has been spin-coated on the ITO surface.

**Figure 3.** (a) Survey X-ray photoelectron spectra of bare ITO, ITO/PDIPN and ITO/PDIPNSO$_3$Na (b) N 1s, (c) Na 1s, (d) S 2p.

**Figure 4.** Survey X-ray photoelectron spectra of bare ITO, ITO/PDIPN and ITO/PDIPNSO$_3$Na (a) In 3d and (b) Sn 3d.
The polar branched chains of the PDIPN and PDIPNSO$_3$Na are inclined to create preferable dipoles at the interface of the metal cathode electrode and active layer, which give rise to the shift of the vacuum-level, thus modifying the work function (WF) of the electrode [46]. The ultraviolet photoelectron spectroscopy (UPS) is carried out to confirm the positive influence of the ETLs PDIPN and PDIPNSO$_3$Na on the WF of ITO (Figure 5a). The high binding energy cutoffs ($E_{cutoff}$) for reference ITO is 16.7 eV. However, the $E_{cutoff}$ of ITO has been shifted toward higher energy to 17.1 eV and 17.4 eV after modified by PDIPN and PDIPNSO$_3$Na, respectively. Simultaneously, there was a slight shift of $E_{onset}$. The $E_{onset}$ values of ITO, ITO/PDIPN and ITO/PDIPNSO$_3$Na are 0.10 eV, 0.05 eV and 0.19 eV. Based on the equation [47]: $\Delta\Phi = h\nu - (E_{cutoff} - E_{onset})$, $h\nu = 21.22$ eV, the HOMO values of ITO, ITO/PDIPN and ITO/PDIPNSO$_3$Na are $-4.62$ eV, $-4.17$ eV and $-4.01$ eV, respectively. Therefore, the WF differences ($\Delta\Phi$) among ITO, ITO/PDIPN and ITO/PDIPNSO$_3$Na are $-0.45$ eV and $-0.61$ eV. The shifts of the energy levels demonstrate that both the PDIPN and the PDIPNSO$_3$Na can indeed significantly lower the WF of ITO. The decreased WF of ITO originates from the interfacial dipole, manifesting that the interfacial dipole is 0.45 eV for ITO/PDIPN and 0.61 eV for ITO/PDIPNSO$_3$Na. The detailed energy levels data are provided in Table 1. Kelvin probe microscopy (KPM) is used to obtain more information about the impact of the interface dipoles on the WF of ITO, as shown in Figure 5b. Based on the KPM matrix spectra, we can distinctly discover that the WF of ITO has been reduced after modified by PDIPN and PDIPNSO$_3$Na. The bare ITO shows a WF of 4.70 eV. Intriguingly, compared to bare ITO, the WF values of ITO/PDIPN and ITO/PDIPNSO$_3$Na have been decreased by 0.50 eV and 0.54 eV. The KPM results are quite coincide to those of UPS. Moreover, on the basis of the results of UPS and KPM, we can once again verify the interfacial dipole in the interface between ITO/PDIPN and ITO/PDIPNSO$_3$Na. The interfacial dipole is beneficial to reduce the work function of ITO, thus reducing the electron injection barrier and enhancing the efficiencies of charge separation and transfer.

![Figure 5](image_url)  
(a) Ultraviolet photoelectron spectroscopy (UPS) spectra of the inelastic cutoff region (left) and the HOMO region (right) of bare ITO, ITO/PDIPN and ITO/PDIPNSO$_3$Na ETLs and (b) Work function images from Kelvin probe microscopy matrix.

| ETL                  | $E_{cutoff}$ (eV) | $E_{onset}$ (eV) | HOMO (eV) | $\Delta\Phi$ (eV) | KPM (eV) |
|----------------------|------------------|-----------------|-----------|------------------|---------|
| ITO                  | 16.7             | 0.10            | $-4.62$   | -                | 4.70    |
| ITO/PDIPN            | 17.1             | 0.05            | $-4.17$   | $-0.45$          | 4.20    |
| ITO/PDIPNSO$_3$Na    | 17.4             | 0.19            | $-4.01$   | $-0.61$          | 4.16    |

$\Delta\Phi$ means the difference in the work function of ITO, ITO/PDIPN and ITO/PDIPNSO$_3$Na according to the UPS, $\Delta\Phi = h\nu - (E_{cutoff} - E_{onset})$, $h\nu = 21.22$ eV.
Surface morphology of the electron transport layer is very important for the charge separation and transfer. The atomic force microscopy (AFM) is measured to characterize the surface morphology of ITO/PDIPN and ITO/PDIPNSO₃Na. Figure S3a,b are the height images of ITO/PDIPN and ITO/PDIPNSO₃Na, and Figure S3c,d are the corresponding phase images. Delightfully, both PDIPN and PDIPNSO₃Na can form homogeneous morphology on the surface of ITO. The root-mean-square (RMS) roughness of ITO/PDIPN is 3.36 nm, and the RMS ITO/PDIPNSO₃Na is 3.22 nm. Besides, the three-dimensional AFM image of ITO, ITO/PDIPN and ITO/PDIPNSO₃Na are presented in Figure S4. The homogeneous and smooth morphology of ETL can facilitate charge transfer and transportation. In addition, the AFM images of the active layer are measured to confirm that whether the surface can become smoother by inserting PDIPN and PDIPNSO₃Na than that of without the presence of any ETL (Figure 6). In comparison to ITO/P3HT:PC₆₁BM with a RMS roughness of 11.3 nm, the RMS roughness of ITO/PDIPN/P3HT:PC₆₁BM and ITO/PDIPNSO₃Na/P3HT:PC₆₁BM is decreased to 6.55 nm and 9.45 nm, manifesting that both PDIPN and PDIPNSO₃Na ETL can exert a positive influence on the morphology of the corresponding active layer. The smoother morphology of the active layer is in favor of charge separation and transfer.

![Figure 6](image_url)

Figure 6. Atomic force microscopy (AFM) tapping mode height images the surface of (a) ITO/P3HT:PC₆₁BM, (b) ITO/PDIPN/P3HT:PC₆₁BM and (c) ITO/PDIPNSO₃Na/P3HT:PC₆₁BM.

To verify the positive roles of PDIPN and PDIPNSO₃Na ETLs in the PSCs, the PDIPN and PDIPNSO₃Na ETLs corresponding to inverted devices are fabricated. The schematic representation of the inverted device structure and an energy levels diagram of the PSCs are shown in Figure 7. From the energy levels diagram, we can clearly observe that both the LUMO levels of ITO/PDIPN and ITO/PDIPNSO₃Na are higher than that of PC₆₁BM, indicating that ohmic contact can be formed after inserting PDIPN and PDIPNSO₃Na ETLs. Meanwhile, compared to the HOMO level of P3HT, the ITO/PDIPN and ITO/PDIPNSO₃Na have lower HOMO levels, revealing that both PDIPN and PDIPNSO₃Na ETLs can block the hole transport.

![Figure 7](image_url)

Figure 7. (a) The inverted device structure of the PSC. (b) Energy-level diagram of the PSCs.

The J-V spectra of the device based on ITO, ITO/PDIPN and ITO/PDIPNSO₃Na are described in Figure 8a, and the relevant device performance data with different ETLs and different thicknesses
are filled in Table S2. The $J-V$ characteristics of the devices of ITO/PDIPN and ITO/PDIPNSO$_3$Na with different thicknesses are supplemented in Figure S5. The device with ITO obtains a PCE of 0.9%. Delightfully, after modified by PDIPN (11 nm), the PCE has been dramatically increased to 3.5% with a $V_{oc}$ of 0.61 V, a $J_{sc}$ of 8.95 mA/cm$^2$ and a fill factor (FF) of 64.8%. Meanwhile, the device with ITO/PDIPNSO$_3$Na (11 nm) shows a PCE of 3.1%, which is significantly improved compared to that of ITO. It is noteworthy that all the device parameters based on ITO/PDIPN and ITO/PDIPNSO$_3$Na, including $V_{oc}$, $J_{sc}$, PCE, and FF parameters have been significantly enhanced compared to that of bare ITO. The enhanced device properties should due to the improved interfacial contact and n-type self-doping effect. Manifestly, the photovoltaic performance of ITO/PDIPN is slightly higher than that of ITO/PDIPNSO$_3$Na under the same condition, the higher PCE originates from the higher $J_{sc}$ and FF. Compared to ITO/PDIPNSO$_3$Na, the better performance of ITO/PDIPN could owing to its stronger n-type self-doping effect. As we known, the higher n-type self-doping effect is favorable for charge transfer, thus enhancing the $J_{sc}$ and FF of the corresponding device. Moreover, when the thicknesses of the ITO/PDIPN and ITO/PDIPNSO$_3$Na are increased to 28 nm, the devices can still achieve an acceptable PCE of 3.1% and 2.8%, respectively. The n-type essence of PDIPN and PDIPNSO$_3$Na can endow them with thickness-insensitive superiority. The thickness-insensitive advantages can make them more suitable for large-scale commercial printing production. To further discuss the effects of the PDIPN and PDIPNSO$_3$Na on the photovoltaic properties, the dark $J-V$ curves are studied in the inset of Figure 8a. Encouragingly, the dark current densities of ITO/PDIPN and ITO/PDIPNSO$_3$Na are dramatically smaller than that of bare ITO under the reverse bias, suggesting that the charge recombination has been significantly inhibited by the contribution of PDIPN and PDIPNSO$_3$Na ETLs. The dark $J-V$ curves can further manifest that the preferable interfacial dipoles originate from the polar branched chain and n-type self-doping effect of PDIPN and PDIPNSO$_3$Na can efficiently suppress the leakage current, therefore increasing the charge injection efficiency of the devices. The research results of the dark $J-V$ curves are in accordance with that of illuminated $J-V$.

![Figure 8](image_url)

**Figure 8.** (a) $J-V$ curves of devices based on P3HT:PC$_{61}$BM with various ETLs under the illumination of AM1.5G, 100 mW cm$^{-2}$ (inset: under dark conditions), (b) EQE characteristics, (c) The standard deviations error bars of $V_{oc}$ and PCE and (d) the standard deviations error bars of and FF and $J_{sc}$. 
The external quantum efficiency (EQE) has been measured to make further consideration of the interfacial dipoles on the $J_{sc}$, as presented in Figure 8b. From the skeleton diagram of the EQE, we can clearly see that both ITO/PDIPN and ITO/PDIPNSO$_3$Na show more outstanding external quantum efficiency between 350 and 700 nm than bare ITO. Notably, ITO/PDIPN ETL exhibits the highest value among the three devices. The results from EQE are quite in consistent with those acquired from illuminated and dark $J$–$V$ characteristic. In brief, due to their interfacial modulating and thickness-insensitive properties, both PDIPN and PDIPNSO$_3$Na may become potential candidates as ETLs in polymer solar cells, especially for large-scale solution-processed PSCs. The integrated current values from EQE for ITO/ETLs in polymer solar cells, especially for large-scale solution-processed PSCs. The integrated current values from EQE for ITO/ETLs in polymer solar cells, especially for large-scale solution-processed PSCs. The standard deviations error bars of $V_{oc}$, PCE, FF and $J_{sc}$ are shown in Figure 8c,d, and the detailed information are shown in Table 2.

Table 2. Device Performance of the Inverted P3HT:PC$_{61}$BM Polymer Solar Cells with Various ETLs.

| Cathode Buffer Layer | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) |
|----------------------|-------------|----------------------|--------|---------|
| ITO                  | 0.45 ± 0.005| 6.69 ± 0.138         | 30.6 ± 0.54 | 0.9 ± 0.064 |
| ITO/PDIPN (11 nm)    | 0.61 ± 0.003| 8.95 ± 0.078         | 64.8 ± 0.79 | 3.5 ± 0.067 |
| ITO/PDIPNSO$_3$Na (11 nm) | 0.61 ± 0.007| 8.33 ± 0.341         | 60.5 ± 1.03 | 3.1 ± 0.052 |

The device parameters of each device are obtained from 10 devices, and the ± refer to the standard deviation.

The $J$–$V$ characteristics of electron-only devices based on P3HT:PC$_{61}$BM blends are measured to get more information regarding electronic mobility, as displayed in Figure 9. The bare-ITO device shows a low electronic mobility of $9.45 \times 10^{-7}$ cm$^2$ V$^{-1}$ s$^{-1}$. However, when inserting PDIPNSO$_3$Na as ETL, the electronic mobility has been dramatically increased to $1.61 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. Moreover, in contrast to ITO/PDIPNSO$_3$Na, the device with ITO/PDIPN ETL exhibits better electronic mobility of $4.18 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, which should be ascribed to the latter possesses higher n-type self-doping effect, thus supporting higher electronic mobility and higher $J_{sc}$. These results agree well with the electron paramagnetic resonance and $J$–$V$ spectra.

![Figure 9. $J^{0.5}$–$V$ characteristics of electron-only devices ITO/ETLs/P3HT:PC$_{61}$BM/Al with bare ITO, ITO/PDIPN and ITO/PDIPNSO$_3$Na ETLs.](image)

3. Conclusions

In conclusion, two new n-type water/alcohol-soluble thickness-insensitive ETLs PDIPN and PDIPNSO$_3$Na have been first designed and synthesized as ETL in PSCs. The appropriate energy levels and WF tuning properties of PDIPN and PDIPNSO$_3$Na cause the corresponding PSCs to
have acceptable PCE on a relatively broad range of interlayer thickness, especially in the device based on PDIPN ETL. Compared to the counterpart PDIPNSO$_3$Na, PDIPN with higher density of an unpaired electron exhibits higher n-type self-doping effect, thus, contributing to higher $J_{sc}$, FF and PCE. In comparison to ITO-only devices, the PCE of the device based on ITO/PDIPN and ITO/PDIPNSO$_3$Na ETLs has been increased from 0.9% to 3.1% and 3.5%, respectively. The outstanding properties of PDIPN and PDIPNSO$_3$Na should make them potential candidates as ETL in solution-processed high-efficiency organic photovoltaic devices.

**Supplementary Materials:** Supplementary materials can be found at http://www.mdpi.com/2073-4360/11/4/655/s1.

**Author Contributions:** Data curation, F.Y. and Q.Z.; Methodology, Y.Q.; Project administration, D.Z.; Resources, H.X., Y.T. and Y.Z.; Supervision, M.L. and Y.X.; Validation, R.Z.

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**Conflicts of Interest:** The authors declare they have no conflict of interest.

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