Construction of Effective Polymer Solar Cell Using 1,7-Disubstituted Perylene Diimide Derivatives as Electron Transport Layer

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ABSTRACT: The poor compatibility of an inorganic electron transport layer with the active layer and an ultrathin film organic material becomes a great obstacle in producing high-quality polymer solar cells with high-throughput roll-to-roll (R2R) method. Novel effective polymer solar cells had been fabricated by introducing 1,7-disubstituted perylene diimide derivatives PDIH, PDIC, and PDIN as an electron transporting layer. It was noteworthy that PDIN could obviously improve the power conversion efficiency of solar cells that incorporated a photoactive layer composed of poly[(3-hexylthiophene)-2, 5-diyl] (P3HT) and the fullerene acceptor [6, 6-phenyl-C 71-butyric acid methyl ester] (PC 71 BM). The power conversion efficiency varies from 1.5% for ZnO transparent cathode-based solar cells to 2.1% for PDIN-based electron transport layer-free solar cells. This improved performance could be attributed to the following reasons: the interaction between N atom in PDIN and O atom in indium tin oxide (ITO) reduced the work function of ITO, increased the built-in electric field, and thus lowered the electron transport barrier and improved the electron extraction ability of cathode, the appropriate roughness of the active layer increased the contact area with anode interfacial layer and enhanced the hole transport efficiency. These experimental results revealed that PDIN can be a promising novel effective material with a simplified synthesis process and lower cost as an electron transporting layer.

1. INTRODUCTION

Polymeric solar cells (PSCs) based on the photoactive layer have gained widespread attention due to their lightweight, flexibility, low cost, and easy large-area production in green energy.1−8 The highest power conversion efficiency (PCE) of PSCs has approached a milestone value of 12% with emerging materials and optimizing processes.9−14 PSCs are generally sandwich structures with cathode (collecting electrons), electron transport layers (ETLs), active layer (a mixture of conjugated polymers and fullerenes, and the most core structure), hole transport layer (transporting holes, directly contacting the active layer and the anode), and anode (collecting holes).15−19 The electron transport layer is one of the most important guarantees for constructing efficient PSCs. It plays a key role in active layer electron extraction, the dipole of interface adjustment, and electron transmission energy barrier reduction. A low work function metal (such as Ca) was inserted between the active metal (such Al as a cathode) and the active layer, which significantly improved PCE of PSCs.20−24 However, the PSCs lifetime is extremely short for the sensitivity of Ca on water vapor and oxygen, and such ETL is generally applied to the upright PSCs. In addition, the hole transport layer of upright PSCs is generally poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) with strong acidity and hygroscopicity in air, which will further corrode the indium tin oxide (ITO) electrode and reduce resistance to air. Inverted PSCs were developed to overcome the air sensitivity of the active metal cathode and the acidity of PEDOT:PSS.25,26 The air-stabilized high-work function metals (e.g., Au, Ag) collect holes as an anode and ITO as a cathode to collect electrons, and the stability and efficiency of the battery are simultaneously improved.27,28 What is more, n-type semiconductor metal oxides (such as ZnO, TiO 2) are inserted between the cathode and the active layer, which function as holes blocking an optical spacer and the self-assembled layer.29,30 However, due to its own intrinsic structure, the contact between the inorganic oxide and the active layer is poor, resulting in poor electron transport capability of the PSCs. Therefore, organic materials have been developed as a promising ETL.

In inverted PSCs, the conjugated polymers and small molecule compounds are used as ETL to replace the metal oxides due to their advantages, such as appropriate interfacial dipole formation suitable for matching the work function between the active layer and the cathode, excellent solubility in different solvents to allow fabricating of multilayer by solution
process, and easy modification of chemical and physical properties by altering the side chains.\textsuperscript{31–33} The latter ones are relatively attractive due to the properties of simple manufacturing processes, precise molecular weight, monodispersity, and unaffected by end groups to prepare PSCs with high batch repeatability. For example, fullerene modified by different side chains of pyrrole salt, pyrrolidine, tertiary amine, ammonium salt, and fluorinated alkyl have been successfully designed and synthesized.\textsuperscript{34–36} Another successful and advantageous interlayers are the derivatives of perylene imide used as ETL, which are stable to thermal stability and light due to its special molecular structure.\textsuperscript{37–39} Having the good planarity of the molecules and enhancement of π−π interaction between molecules, the electron migration ability is strengthened. Besides, the perylene imide derivatives facilitate PSCs PCE and assembly with the advantages of photochemical stability, strong electron affinity, easy modification, and simple synthesis. However, the poor film-forming property, low solubility, and weak solvent resistance restrict further development. When constructing an inverted PSCs multilayer structure, solvent resistance is particularly important. It is necessary to synthesize an alcohol/water-soluble ETL to resist corrosion from the active layer solvent. So far, most of the literature has introduced the alkyl and amino groups into the ends of perylene imide to gain alcohol or water solubility with great progress.\textsuperscript{40–42} Compared to the main chain, bay region modifications of perylene imide are rare, which is more direct to affect the solubility in alcohol or water.

In this paper, we synthesized three derivatives of phthalimide with different side-chain modifications by reacting dibromophthalimide derivatives with different phenol derivatives (PDIC, PDIC, and PDIN) Figure 1. Preliminary studies by UV−vis absorption spectroscopy and cyclic voltammetry (CV) showed that PDIP-N has good film-forming properties and alcohol or water solubility. The introduction of an o-methylphenoxy substituent at the bay position of PDI can alter the electron-attracting capability of the backbone, significantly increasing the reduction potential, thereby increasing or decreasing the lowest unoccupied molecular orbital (LUMO). Compared to PDIH and PDIC, we introduced the amine group into PDIN to improve the solubility in methanol and ensure that it is not corroded by the active layer solvent and facilitates solution processing. We further used PDIN as the electron transport layer of PSCs based on P3HT:PC\textsubscript{71}BM; it is found that the PCE with PDIN as ETL is significantly higher than that of ZnO, while PDIH and PDIC are much lower. The water contact angle, ultraviolet photoelectron spectroscopy, and atomic force microscopy (AFM) reveal that the interconnection between PDIN and cathode reduced the work function of ITO and reduced the barrier of electron transport to the cathode. The roughness of the active layer increases appropriately will significantly accelerate charge transport in active layer and achieve higher efficiency PSCs. These results reveal that water or alcohol-soluble PDI derivatives can be obtained by introducing various polar groups in the bay region, which can inspire the development of ETL for high-efficiency PSCs.

2. EXPERIMENTAL SECTION

2.1. Fabrication of PSCs. P3HT and PC\textsubscript{71}BM were obtained from Suna Tech Inc (www.SunaTechInc.com). The configuration of the ETL-free PSCs was ITO/P3HT:PC\textsubscript{71}BM:ETLs/MoO\textsubscript{3}/Ag, the normal inverted PSCs structure was ITO/ETLs/P3HT:PC\textsubscript{71}BM/MoO\textsubscript{3}/Ag. The ITO substrate was sequentially washed by an ultrasonic machine for 15 minutes with different solvents (detergent, deionized water, acetone, and isopropyl alcohol). The ZnO layer is spin-coated with a nano-ZnO precursor solution at 1500 rpm for 30 s on a spin coater, followed by annealing at 200 °C for 30 minutes. The concentration of PDIN in methanol was 0.5 mg mL\textsuperscript{−1} and it was annealed at 150 °C for 10 min. Thereafter, P3HT/PC\textsubscript{71}BM solution (D/A weight ratio is 1:1) or P3HT/PC\textsubscript{71}BM/ETL solution (P3HT/PC\textsubscript{71}BM/ETL = 40:40:1 wt) with the concentration in chlorobenzene is 20 mg mL\textsuperscript{−1} is used as the active layer. The active layer was spin-coated at 800 rpm for 30 s. Finally, the MoO\textsubscript{3} (10 nm) and Ag (100 nm) layers were evaporated in a vacuum chamber at a basic pressure of 1 × 10\textsuperscript{−5}.

2.2. Characterization. Nuclear magnetic resonance (NMR) spectra of all materials were obtained using a Bruker ARX MHz spectrometer (500 and 125MHz) with tetramethylsilane as the internal reference. Thermogravimetric analysis (TGA) was performed using a TA(Q600SDT) apparatus at a heating rate of 10 °C min\textsuperscript{−1}. Differential scanning calorimetry (DSC) was carried out on a Netzsch DSC200F3 at a heating rate of 10 °C min\textsuperscript{−1}. (a) Molecular structures of P3HT, PC\textsubscript{71}BM, PDIH, PDIC, and PDIN. Figure 1. (b) Device structures and ETL-free PSCs configuration without ZnO interlayer. (c) Energy levels of the different layers within PSCs. Energy level of Ag, MoO\textsubscript{3}, P3HT, PC\textsubscript{71}BM, PDIH, PDIC, and PDIN, and ITO.
rate of 10 °C min⁻¹ under a nitrogen atmosphere. UV-可见 absorption spectra were obtained using a Varian Cary 300 spectrophotometer. All films were uniformly coated on the ITO substrate. Work functions (WFs) of ITO substrates with different modifications were obtained using Thermo Scientific (EscaLab 250Xi). The water contact angle was measured on SDC-200 and the water was used as a test liquid. Surface morphology was determined by a Dimension Icon AFM instrument (Bruker). PSCs devices were characterized at room temperature under simulated AM 1.5 G conditions (Xe Lamp Oriel Sol3A Class AAA Solar Simulators 94023A) and calibrated to a certified Si reference cell with a KG-5 filter (PV Measurements, PVM624). J-V characteristics and charge carrier mobility were performed on a computer-controlled Keithley 2400 source meter. The external quantum efficiency (EQE) was measured on a QEPVSI-B measurement system (Newport).

2.3. Synthesis of PDIH, PDIC, and PDIN. The synthetic routes of target materials PDIH, PDIC, and PDIN are shown in Scheme 1. The substitution reaction of 1 and phenol derivative gave the target compound PDIH, PDIC, and PDIN in a good yield of 78.5, 81.0, and 65.0%, respectively.43,44 The molecular structures of PDIH, PDIC, and PDIN were determined by NMR.

All reagents were purchased from Sigma or TCI and used without further purification unless otherwise stated. The solvent was dried and purified using standard procedures.

2.3.1. PDIH. A mixture of phenol (23.5 mg, 0.25 mmol), K₂CO₃ (69.8 mg, 0.50 mmol), and 18-crown-6 (402 mg, 1.5 mmol) was added to 19.40 mL of anhydrous toluene and stirred for 20 min, under protection of argon, N,N-bis(2-ethylhexyl)-1,7-dibromo-3,4,9,10-perylene diimide (50 mg, 0.065 mmol) was added into solution. The reaction was then reacted for 4 h at 90 °C under an argon atmosphere. After cooling to room temperature, toluene was removed using a rotary evaporator. The crude product was washed with deionized water and filter through a Brinell funnel. The solid was dried at 60 °C for 16 h and purified by column chromatography. The eluent solvent was petroleum ether/dichloromethane = 1:1 to yield PDIH as a dark red solid (40.77 mg, 78.5%). 1H NMR (400 MHz, CDCl₃, δ/ppm): 9.60−9.58 (d, 2H), 8.60−8.59 (d, 2H), 8.33 (s, 2H), 7.48−7.44 (m, 6H), 7.19−7.16 (d, 4H), 4.14−4.03 (d, 4H), 1.95−1.86 (m, 2H), 1.38−1.25 (m, 16H), 0.90−0.85 (m, 12H). 13C NMR (400 MHz, CDCl₃, δ/ppm): 160.1, 157.0, 152.7, 130.8, 129.2, 128.4, 127.4, 122.9, 118.9, 117.2, 110.5, 47.0, 37.0, 31.7, 29.3, 25.7, 23.0, 14.1, 11.6.

2.3.2. PDIC. Compound PDIC was synthesized according to the same procedure as for preparing compound PDIH. The eluent solvent was petroleum ether/dichloromethane = 1:1 to yield PDIC as a dark red solid (46.5 mg, 81.0%). 1H NMR (400 MHz, CDCl₃, δ/ppm): 9.60−9.58 (d, 2H), 8.60−8.58 (d, 2H), 8.34 (s, 2H), 7.18−7.08 (d, 4H), 4.14−4.03 (d, 4H), 2.65−2.62 (m, 4H), 1.95−1.86 (m, 2H), 1.38−1.25 (m, 16H), 0.90−0.85 (m, 18H). 13C NMR (400 MHz, CDCl₃, δ/ppm): 160.1, 157.0, 152.7, 130.8, 129.2, 128.4, 127.4, 122.9, 118.9, 117.2, 110.5, 47.0, 37.9, 37.0, 31.7, 29.3, 25.7, 24.1, 23.0, 14.1, 13.7, 11.6.

2.3.3. PDIN. Compound PDIN was synthesized according to the same procedure as for preparing compound PDIH. The eluent solvent was petroleum ether/dichloromethane = 1:1 to yield PDIN as a dark red solid (39.8 mg, 65.0%). 1H NMR (400 MHz, CDCl₃, δ/ppm): 9.60−9.58 (d, 2H), 8.60−8.58 (d, 2H), 8.34 (s, 2H), 7.31−7.28 (d, 4H), 7.18−7.08 (d, 4H), 4.14−4.03 (d, 4H), 2.86−2.82 (m, 4H), 2.65−2.58 (m, 4H), 2.57−2.52 (m, 4H), 1.86−1.71 (m, 4H), 1.38−1.25 (m, 16H), 0.90−0.85 (m, 18H). 13C NMR (400 MHz, CDCl₃, δ/ppm): 160.1, 157.0, 152.7, 130.8, 129.2, 128.4, 127.4, 122.9, 118.9, 117.2, 110.5, 47.0, 37.9, 37.0, 31.7, 29.3, 25.7, 24.1, 23.0, 14.1, 13.7, 11.6.

Figure 2. (a) Thermal-gravimetric analysis curves of PDIH, PDIC, and PDIN. (b) Cyclic voltammetry of PDIH, PDIC, and PDIN coated on the glassy carbon electrode.
1.92–1.86 (m, 2H), 1.38–1.25 (m, 16H), 0.90–0.85 (m, 12H). 13C NMR (400 MHz, CDCl3, δ/ppm): 160.1, 157.0, 152.7, 130.8, 129.2, 128.4, 127.4, 122.9, 121.8, 118.9, 117.2, 110.5, 63.1, 47.0, 37.1, 32.9, 31.6, 29.5, 25.9, 23.1, 14.3, 11.4.

3. RESULTS AND DISCUSSION

3.1. Characterization of PDIH, PDIC, and PDIN. The thermal stability and electrochemical properties of PDIH, PDIC, and PDIN were acquired by TGA and CV, respectively. The corresponding characterization are depicted in Figure 2. We found that PDIH, PDIC, and PDIN had good thermal stability and the onset of the weight loss at 165, 172, and 208 °C, respectively. These materials meet the minimum temperature for device fabrication. Even if PDIH and PDIC are used to prepare ETL-free solar cells and anneal at 150 °C, which was much lower than the onset of the weight loss temperature of the two materials. The electron transport layer PDIN/methanol solution anneals at 150 °C and also satisfies the preparation temperature of the device, ensuring strong thermal stability.

We also tested the electrochemical performance of PDIH, PDIC, and PDIN by cyclic voltammetry. The glassy carbon electrode is working electrode, the platinum plate was used as the auxiliary electrode, Ag/Ag+ was the reference electrode, and ferrocene was used as a standard material. The electrolyte was a tetraethylammonium hexafluorophosphate/acetoniitrile solution at a concentration of 0.1 mmol mL−1. In addition, a film was prepared by PDIN/chloroform, PDIC/chloroform, and PDIN/methanol by deposition on a working electrode. The cyclic voltammetry curves of the three materials are shown in Figure 2b. It could be concluded that the initial oxidation potential (Eox) and the initial reduction potential (Ered) of PDIH were 0.87 and −0.69 V, while the Eox and Ered of PDIC were 0.90 and −0.73 V, and Eox and Ered of PDIN were 0.91 and −0.75 V, respectively. The electrochemical band gap of the three perylene diimide derivatives was calculated by the formula: $E_{HOMO} = -(E_{ox} + 4.4) \text{ eV}$, $E_{LUMO} = -(E_{red} + 4.4) \text{ eV}$. The calculated values are given in Table 1, and the resulting in changing in the maximum absorption wavelength. The propyl group of PDIC plays the role of a electron-donating group, which increases $\pi-\pi$ conjugation, while the nitrogen atom of the PDIN side chain reduces the conjugation effect of perylene diimide. However, in the film state, the maximum absorption peak of PDIH, PDIC, and PDIN were 562, 563, and 569 nm, respectively. It is known that the maximum absorption of PDIH and PDIC were not of much differences, but red shift occurred significantly compared to solution status, because in the state of film, the aggregation of material is much greater than that of the solution.47,48 In addition, the red shift of PDIN was stronger than that of PDIH and PDIC in film, this could contribute to stronger $\pi-\pi$ stacking by the induction of nitrogen atoms. According to the optical band gap formula $\Delta E = h\nu/\lambda$, the optical band gaps of PDIH, PDIC, and PDIN were 1.93, 1.97, and 1.90 eV, respectively.

3.2. Photovoltaic Properties of PSCs. To explore the photovoltaic performance of PDIH, PDIC, and PDIN, we observed to test the device structure containing only electrons ITO/ZnO/P3HT:PC71BM:PDIC/Ag. The PSCs device was optimized under sunlight (AM 1.5 G, 1000 W m−2) illumination. The photovoltaic characteristics, external quantum efficiency (EQE), and electron mobility curves of PSCs are shown in Figure 3. At the same time, Table 2 also listed the corresponding performance parameters of different PSCs. The traditional PSCs with ZnO as ETL obtained a $J_{SC}$ of 5.78 mA cm−2, $V_{OC}$ of 0.56 V, FF of 0.48, and PCE of 1.46%. The ETL-free PSCs with P3HT:PC71BM:PDIC as active showed a $J_{SC}$ of 2.80 mA cm−2, $V_{OC}$ of 0.56 V, FF of 0.42, and PCE of 0.65%. The ETL-free PSCs with P3HT:PC71BM:PDIN obtained a $J_{SC}$ of 2.48 mA cm−2, $V_{OC}$ of 0.56 V, FF of 0.36, and PCE of 0.46%. What is more, the PSCs with PDIN as ETL showed a $J_{SC}$ of 6.32 mA cm−2, $V_{OC}$ of 0.57 V, FF of 0.61, and PCE of 2.08%. The energy conversion efficiency of PDIN solar cells is significantly higher than that of PDIH and PDIC cells, mainly due to the higher short-circuit current and fill factor of PDIN.

When sunlight hits the surface of PSCs, the active layer material generates excitons and then the excitons diffuse to D/A interfaces, dissociating free electrons and hole pairs, EQE spectra is shown in Figure 3c, EQE of PDIN and ZnO was obviously higher than that of PDIC and PDIN, while the absorption efficiency of PDIN was slightly higher than that of ZnO, which also corresponded to the photoelectric characteristic curve. Due to the high photon conversion efficiency and electron transport efficiency, the short-circuit current of the PDIN PSCs was improved and energy conversion efficiency was higher.

To test the electron mobility of PSCs, we assembled the device structure containing only electrons ITO/ZnO/P3HT:PC71BM/Al, ITO/P3HT:PC71BM:PDIC/Al, ITO/P3HT:PC71BM:PDIC/Al, and ITO/P3HT:PC71BM/Al. The electron mobility test is displayed in Figure 3d. The electron mobility calculation was calculated according to the Mott–Gurney equation using the space charge limited current (SCLC) model:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon \mu \frac{V^2}{d^3}$$
Figure 3. (a) Normalized absorption spectra of PDIH, PDIC, and PDIN in solution and film status. (b) J–V characteristics of PSCs or ETL-free PSCs with PDIH, PDIC, and PDIN, respectively. (c) External quantum efficiency spectra of ZnO, PDIH, PDIC, and PDIN based inverted PSCs. (d) $J_{0.5}$–$V$ characteristics of the electron-only devices ITO/ETLs/P3HT:PC$_{71}$BM/Al with ZnO and PDIN as ETLs, while ITO/P3HT:PC$_{71}$BM:ETLs/Al with PDIH and PDIC as ETLs.

Table 2. Photovoltaic Characteristics of PDIH, PDIC, and PDIN Based on P3HT:PC$_{71}$BM Device, Under 100 mW cm$^{-2}$ Air Mass 1.5 Global (AM 1.5 G) Illumination

| electron transporting layer | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF | PCE (%) |
|-----------------------------|--------------------------|-------------|----|---------|
| ZnO                         | 5.66 ± 0.12              | 0.56 ± 0.01 | 0.46 ± 0.02 | 1.46 ± 0.13(1.59) |
| PDIH                        | 2.79 ± 0.11              | 0.56 ± 0.01 | 0.42 ± 0.01 | 0.65 ± 0.06(0.71) |
| PDIC                        | 2.36 ± 0.12              | 0.55 ± 0.02 | 0.36 ± 0.02 | 0.46 ± 0.07(0.53) |
| PDIN                        | 6.21 ± 0.11              | 0.56 ± 0.01 | 0.60 ± 0.01 | 2.08 ± 0.12(2.20) |
where $J$ is current density, $\mu$ is the charge carrier mobility, $d$ is film thickness of active layer (110 nm), $\varepsilon_r$ is the relative dielectric constant of the transport medium, $\varepsilon_0$ is the dielectric constant of the free space (8.854 \times 10^{-12} \text{ m}^{-1})$, and $V$ is the applied voltage. The electron mobility of PSCs modified with ZnO, PDIH, PDIC, and PDIN were $5.26 \times 10^{-5}$, $2.45 \times 10^{-6}$, $1.89 \times 10^{-6}$, and $8.28 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, respectively.

### 3.3. Interfacial Modification on ITO Electrode

The ETLs act as an interface material between the active layer and cathode and affect the work function of ITO straightly. To understand the role of ETLs in promoting the photovoltaic characteristics of PSCs, energy-level alignment of the active layer and ITO surface was studied by using ultraviolet photoelectron spectroscopy (UPS) (He I line, $h\nu = 21.2$ eV). Figure 4 presented the UPS spectra of the active layer surface and ITO. The work function (WF) is calculated as $h\nu = (E_{\text{cutoff}} - E_{\text{onset}})$, where $h\nu$ is the excitation source energy, $E_{\text{cutoff}}$ is the absissa of cutoff inflection point, and $E_{\text{onset}}$ is absissa of starting inflection point. The ITO work function was reported as 4.6 eV. It could be concluded that the work function of ITO/ZnO, ITO/PDIH, ITO/PDIC, and ITO/PDIN were 4.28, 4.49, 4.54, and 4.05 eV. The data of the work function are summarized in Table 3. The WF of ITO was reduced differently after modified by three perylene diimide derivatives. The reduction in work function insure a good ohmic contact between the ITO interfacial layer and the fullerene acceptor while increasing the built-in electric field of PSCs to achieve higher open circuit voltage. At the same time, the lower WF reduces the electron transfer energy barrier, enhancing the electron collection capability of the cathode and reducing the recombination rate of the active layer carriers.

![Figure 4](image)

**Figure 4.** (a) Ultraviolet photoelectron spectroscopy (UPS) spectra of ITO/ZnO, (b) ITO/PDIH, (c) ITO/PDIC, (d) ITO/PDIN films, and (e) ITO/different active layer.

| structure                  | work function (eV) |
|---------------------------|--------------------|
| ITO/ZnO                   | 4.28               |
| ITO/PDIH                  | 4.49               |
| ITO/PDIC                  | 4.54               |
| ITO/PDIN                  | 4.05               |
| ITO/P3HT:PC71BM           | 4.46               |
| ITO/P3HT:PC71BM:PDIH      | 4.20               |
| ITO/P3HT:PC71BM:PDIC      | 4.29               |

[Table 3. Surface Work Function of ITO and Different Active Layer]
P3HT:PC71BM:PDIC were 4.46, 4.2, and 4.29 eV, respectively. According to the characterization results, the secondary electron cutoff edge of PDIH mixing with an active layer is more positively moved forward than that of PDIC, which increased the binding energy and lowered the vacuum level. These results indicate that charge-mediated dipole is formed on the surface of the active layer, which enhances the charge transfer of the active layer, making PDIH a higher photoelectric conversion efficiency comparing to PDIC cells.12

Considering that the surface energy of the film plays an important role in the sequential deposition in the multilayer devices, we studied the wettability of the three materials by measuring the water contact angle. The measurement was carried out on the surface of the film by dropping deionized (DI) water, and the contact angle was determined by automatic image analysis. Figure 5 exhibited the images of

![Figure 5](image.png)

Figure 5. Contact angle measurements (DI water) of, (a) ITO, (b) ZnO, (c) PDIH, (d) PDIC, (e) PDIN, (f) P3HT:PC71BM, (g) P3HT:PC71BM:PDIH, and (h) P3HT:PC71BM:PDIC.

ZnO (77°), PDIH (81.5°), PDIC (92.3°), PDIN (92.5°), P3HT:PC71BM (98°), P3HT:PC71BM:PDIH (99°), P3HT:PC71BM:PDIC (103°), and bare ITO (75.5°). Figure Sb–h shows all UV-treated samples. Detailed results are summarized in Table 4.

### Table 4. Water Contact Angle and Surface Energy of PDIH, PDIC, PDIN, and Active Layer

| structure              | contact angle (deg) | surface energy (mN m⁻¹) |
|------------------------|---------------------|--------------------------|
| ITO                    | 75.5                | 40.40                    |
| ITO/ZnO                | 77                  | 34.33                    |
| ITO/PDIH               | 81.5                | 30.10                    |
| ITO/PDIC               | 92.3                | 29.96                    |
| ITO/PDIN               | 92.5                | 35.23                    |
| ITO/P3HT:PC71BM        | 98                  | 23.43                    |
| ITO/P3HT:PC71BM:PDIH   | 99                  | 22.05                    |
| ITO/P3HT:PC71BM:PDIC   | 103                 | 23.17                    |

Since PSCs are a “sandwich” structure, it possess different hydrophobicity. To a certain extent, the stronger hydrophobicity of interface between ITO and active layer is, the better ducility and phase separation of the active layer on top of ITO. It is worth noting that the contact angles of PDIH and PDIC increased and there is not much difference in the surface energies, respectively. The hydrophilicity of ITO increased after UV treatment, which enhanced the water contact angle and facilitated the spin coating of the ZnO solution. The water contact angle and hydrophobicity increased after annealing at 200 °C. In addition, the contact angle of ITO was increased with surface energy 35.23 mN m⁻¹ after the modification of PDIN, which was slightly larger than ZnO, indicating good ohmic contact between the ETLs and active layer. Among them, the contact angle and surface energy of active layer mixed with PDIH or PDIC were similar, instructing that the hydrophobicity of the active layer was not greatly affected.

Atomic force microscopy (AFM) was employed to research the surface morphology of the active layer coated on different ETLs and displayed in Figure 6. The root mean square (rms) roughness of different PSCs structure with P3HT:PC71BM, ZnO/ P3HT:PC71BM, P3HT:PDIC, and P3HT:PC71BM:PDIC, and PDIN/P3HT:PC71BM were 0.74, 0.71, 1.2, 0.93, and 0.79 nm, respectively. Compared to ZnO PSCs, the roughness of PDIH, PDIC, and PDIN PSCs increased by 0.49, 0.22, and 0.08 nm, respectively. Appropriate roughness enhances the internal interaction of active layer and hole transport rate, effectively decreasing the charge transport distance and increasing JSC, which increases the nanoscale texture, further enhances internal light scattering and light absorption. After laying on the box for 1 h, the fill factor tends to increase.53 Therefore, standing and longer annealing times may help remove residual solvent, reduce free volume, and improve interfacial contact with the electrode.

### 4. CONCLUSIONS

In summary, we designed and synthesized a novel material PDIN, which could be used to fabricate effective inverted PSCs. The PCE of PDIN was enhanced significantly compared to ZnO-modified PSCs. The improvements of PSCs performance was attributed to the following factors: the appropriate roughness of active layer increased the contact area with the hole transport layer and reduced the energy barrier of charge...
transport, the interaction between N atom in PDIN and O atom in ITO decreased the work function of ITO, which increased the built-in electric field and promoted the ability of electron extraction. These results show that by simply introducing polar chemical groups in the bay region can gain high conductive cathode interfacial material for effective PSCs.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The work was financially supported by the National Natural Science Foundation of China (S1663018), Outstanding Youth Funds of Jiangxi Province (20171BCB23056).

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