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## 1. Introduction

Organic photovoltaics (OPVs) have attracted much attention in solar cell research due to their broad range of advantages, such as low cost, flexibility, light weight, and large area devices through roll-to-roll printing and environmental stability, over traditional solar cell technologies.<sup>1-3</sup> In OPVs, bulk heterojunction (BHJ) approaches,<sup>4</sup> formed by the binary blends of electron donor (low band gap conjugated polymers or small molecules) and electron acceptor (fullerene derivatives)

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# Carbazole linked phenylquinoline-based fullerene derivatives as acceptors for bulk heterojunction polymer solar cells: effect of interfacial contacts on device performance<sup>†</sup>

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To understand the effect of interfacial contact between the hole transporting layer (HTL) and fullerene derivatives in the active layer of bulk heterojunction polymer solar cells (BHJ PSCs), carbazole (Cz) linked phenylquinoline (PhQ)-based fullerene derivatives, PhQHCz-C<sub>61</sub>BM and PhQEOCz-C<sub>61</sub>BM, have been successfully synthesized. They are used as acceptors with a poly(3-hexylthiophene) (P3HT) donor in the active layer, and PEDOT:PSS and MoO<sub>3</sub> were used as the HTL. Both the derivatives are highly soluble in common organic solvents and possess high thermal stability. BHJ PSCs are fabricated with configurations of ITO/PEDOT:PSS/P3HT:PhQHCz-C<sub>61</sub>BM/LiF/Al, ITO/PEDOT:PSS/P3HT:PhQHCz-C<sub>61</sub>BM/LiF/Al, and ITO/MoO<sub>3</sub>/P3HT:PhQHCz-C<sub>61</sub>BM/LiF/Al, ITO/MoO<sub>3</sub>/P3HT:PhQEOCz-C<sub>61</sub>BM/LiF/Al, and the device characteristics were measured under AM1.5G (100 mW cm<sup>-2</sup>). Both derivatives exhibited much lower power conversion efficiencies (PCE) of ~0.1% when PEDOT:PSS was employed as the HTL. In contrast, the PCE increases to ~2.2% upon replacing PEDOT:PSS with MoO<sub>3</sub> as the HTL. This is due to the fact that protonation of the pyridyl nitrogen of the acceptor in the active layer by the  $-SO_3H$  group of PEDOT:PSS in the HTL, establishes a charge injection barrier at the interfacial contact and leads to restricted charge collection at the electrodes. This was indirectly confirmed by protonation of pyridyl nitrogen in PhQHCz-C<sub>61</sub>BM by the  $-SO_3H$  group in *p*-toluenesulphonic acid.

materials, have attracted great attention since last decade. In particular, the BHJ formed by the electron donor poly(3-hexylthiophene) (P3HT) and the electron acceptor [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM), has become a benchmark structure in OPVs with a maximum power conversion efficiency (PCE) of around 5%.<sup>5,6</sup>

To further improve the PCE of BHJ organic solar cells (OSCs), the following two factors are mainly considered by the scientific community: (1) design of new donor and acceptor materials for BHJ with suitable energy levels and nano scale morphology; (2) development of suitable hole and electron transport materials for interfacial layers to minimize the energy barrier at interfacial contacts for charge-extraction. Accordingly, huge numbers of conjugated polymers and small molecules have been synthesized and utilized as electron donors with PCBM as an electron acceptor in BHJ OSCs and a maximum PCE of  ${\sim}10\%$ has been achieved so far.7-9 When compared to the developments in low band gap conjugated polymers and small molecule based donor materials, the research on acceptor materials is very scarce. To date, two kinds of acceptor materials have generally been utilized in BHJ OSCs: (1) fullerene<sup>10</sup> and (2) non fullerene<sup>11,12</sup> based materials. In particular, fullerene based



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#### Paper

materials show very good acceptor properties compared with their non-fullerene counterparts due to their high electron affinity, electron mobility, tuneable solubility in organic solvents, tuneable energy levels and superior packing arrangement in the solid state by introducing various functional groups on the fullerene core.10,13 Thus, the development of new fullerene based acceptors toward increasing the PCE in combination with suitable polymer donors is still highly desirable. On the other hand, many types of hole14,15 and electron16,17 transporting materials are employed between the active layer and the indium tin oxide (ITO) substrate and also between the active layer and the metal electrode as hole and electron transporting layers, respectively, to improve the PCE. Even though research on interlayers in OPVs has not yet been fully completed, the number of papers has recently increased.<sup>18-21</sup> In particular, poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is a well-known conducting polymer that has been used as a benchmark hole transporting layer (HTL) in BHJ OSCs due to its energy level matching a wide range of low band gap donor polymers/small molecules.<sup>22-24</sup> However, the highly acidic and hygroscopic nature of PEDOT:PSS causes a reduction in device performance and longterm stability.<sup>25,26</sup> Very recently, Olson et al. demonstrated that the -SO<sub>3</sub>H group of PEDOT:PSS in the HTL protonates the basic pyridyl nitrogen in the donor material of the active layer, resulting in poor device performance.27 To overcome these challenges, wide band gap metal oxides such as MoO<sub>3</sub>,<sup>28</sup> V<sub>2</sub>O<sub>5</sub>,<sup>29</sup> and WO<sub>3</sub><sup>30</sup> were used as substitutes for PEDOT:PSS. In contrast, the highest reported PCE value (10.6%) of PSCs consists of PEDOT:PSS as the HTL.31 Thus, there is still room to mandate the structure-property relationship when using PEDOT:PSS as the HTL.

According to the Ikkala *et al.* report, each PCBM molecule can form non-covalent bonds with up to six 4-vinylpyridine monomer units.<sup>32</sup> As a continuation of this work, Mezzenga *et al.* reported that rod-coil poly(3-hexylthiophene)-*block*-poly(4-vinylpyridine) (P3HT-P4VP) block copolymers blend with PCBM *via* supramolecular weak interactions, in which the micro-phase segregated P3HT-rod domains act as electron-donating and the homogeneous P4VP-*block*-PCBM blends act as electron-accepting species, and they are applied to BHJ PSCs using PEDOT:PSS as the HTL. In this case, the PCE is decreased due to the hole collection barrier and/or interfacial dipoles nearer the device anode.<sup>33</sup>

Therefore, in order to develop new acceptor materials and explore further structure–property relationships within the active layer and with the adjacent layer, in this work, we have introduced basic pyridyl nitrogen on the carbazole (Cz) linked phenylquinoline (PhQ)-based fullerene derivatives, **PhQHCz-**C<sub>61</sub>**BM** and **PhQEOCz-C<sub>61</sub>BM**, and applied them as new acceptors for BHJ polymer solar cells (PSCs) with a P3HT donor. We expected the pyridyl and fullerene units to be located in the same molecule, which led it to self-assemble in a proper way that might prevent the protonation of the pyridyl nitrogen by the materials in the adjacent layer.

### 2. Experimental

#### 2.1 Materials and characterization

All chemicals and reagents were purchased from Aldrich Chemical Co., Ltd and TCI and used without further purification except for tetrahydrofuran and toluene, which were dried and purified by distillation over sodium and under  $N_2$ . Other solvents were used without additional purification. PC<sub>61</sub>BM was purchased from SES Research Co., Ltd. P3HT was obtained from Rieke Specialty Polymers Co., Ltd. Synthetic details and characterization data are described in the ESI.<sup>†</sup>

#### 2.2 Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury Plus 300 and 600 MHz spectrometer in CDCl<sub>3</sub> using tetramethylsilane as an internal standard. The UV-visible absorption spectra were recorded with a JASCO V-570 spectrophotometer at room temperature. The absorption spectra were measured using  $10^{-5}$  mol L<sup>-1</sup> chloroform solution. Thermal analyses were carried out on a Mettler Toledo thermogravimetric analyzer/ simultaneous differential thermal analyzer (TGA/SDTA) 851e instrument and a differential scanning calorimetry (DSC) 822e analyzer under N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup>. The cyclic voltammetry (CV) studies were carried out with a CHI 600C potentiostat (CH Instruments) at a scan rate of 100 mV s<sup>-1</sup> in a 0.1 M solution of tetrabutylammonium tetrafluoroborate in odechlorobenzene (o-DCB). A platinum wire and Ag/AgNO3 were used as the counter and reference electrodes, respectively. All of the electrochemical studies were carried out at room temperature. The lowest unoccupied molecular orbital (LUMO) energy levels of the new acceptors were calculated using the equation LUMO =  $(E_{red}^{onset} - E_{1/2}^{ferrocene} + 4.8)$  eV.<sup>34</sup> Where,  $E_{1/2} = 0.35$  V was calculated from the oxidation and reduction potential of ferrocene.

#### 2.3 Charge carrier mobility studies

The apparent charge carrier mobility was evaluated from the current density–voltage (*J–V*) characteristics of single charge carrier devices and the results were subsequently fit using the space-charge-limited-current (SCLC) method. In order to measure the SCLC of only one type of charge carrier in a blend, the other one must be suppressed by a large injection barrier, resulting in an electron or a hole-only device. The hole mobility was measured using the following device configuration: ITO/PEDOT:PSS/P3HT:acceptor/MoO<sub>3</sub>/Al and ITO/MoO<sub>3</sub>/P3HT:acceptor/MoO<sub>3</sub>/Al. The Mott–Gurney law, which includes the field-dependent mobility, is described by the following equation:<sup>35</sup>

$$J = \frac{9}{8} \varepsilon_{\rm r} \varepsilon_0 \,\mu_0 \,\frac{\left(V - V_{\rm bi}\right)^2}{L^3} \exp\left(0.89\beta \sqrt{\frac{V - V_{\rm bi}}{L}}\right)$$

where  $\varepsilon_0$  is the permittivity of free space (8.85 × 10<sup>-12</sup> F m<sup>-1</sup>),  $\varepsilon_r$  is the dielectric constant (assumed to be 3, which is a typical value for conjugated polymers), *L* is the thickness of the active layer,  $\mu_0$  is the zero-field mobility,  $\beta$  is the field activation factor and  $V_{\rm bi}$  is the built-in voltage due to the difference in work function of the two electrodes.

#### 2.4 Fabrication of BHJ PSCs

The BHJ PSCs were fabricated with configurations of ITO/ PEDOT:PSS, MoO<sub>3</sub>/P3HT:**PhQHCz-C<sub>61</sub>BM** or **PhQEOCz-C<sub>61</sub>BM**/ LiF/Al. The glass substrate was coated with a transparent ITO electrode (110 nm thick, 10–15  $\Omega$  square<sup>-1</sup>) and ultrasonically cleaned with detergent, distilled water, acetone, and isopropyl alcohol. It was then subjected to UV/ozone treatment for 20 min and used as an anode. A thin, 40 nm thick layer of PEDOT:PSS (Clevios PH1000) was spin-coated onto the ITO glass substrate. PEDOT:PSS spin-coated films were annealed at 150 °C for 30 min. The devices with  $MoO_3$  (9 nm) as the HTL were thermally evaporated onto the ITO glass substrate. P3HT:PhQHCz-C<sub>61</sub>BM and P3HT:PhQEOCz-C61BM were dissolved in chlorobenzene (CB) or o-DCB with appropriate weight ratios and stirred for 24 h. The blend solutions were then filtered with a 0.45  $\mu$ m PTFE syringe filter, spin-coated on top of the ITO and dried at room temperature for 30-40 min. LiF (0.5 nm) and the Al cathode (120 nm) were deposited on the top of the active layer under a vacuum of less than  $5.0 \times 10^{-6}$  Torr, to yield an active area of 9 mm<sup>2</sup> per pixel. The film thickness was measured with an  $\alpha$ -Step IO surface profiler (KLA Tencor, San Jose, CA). The performance of the BHJ PSC devices was measured using a calibrated AM1.5G solar simulator (Oriel® Sol3A<sup>™</sup> Class AAA solar simulator, models 94043A) with a light intensity of 100 mW cm<sup>-2</sup> adjusted using a standard PV reference cell (2 cm  $\times$  2 cm mono crystalline silicon solar cell, calibrated at NREL, Colorado, USA) and a computer-controlled Keithley 236 source measure unit. The incident photon to current conversion efficiency (IPCE) spectrum was measured using Oriel® IQE-200™. All fabrication steps and characterizations were carried out in an ambient environment without a protective atmosphere. While measuring the I-V curves for the OPV devices, a black mask was used and only the effective area of the cell was exposed to light irradiation. The device data reported here were confirmed over more than 5 iterations under the same conditions.

## Results and discussion

The synthesis of PhQHCz-C<sub>61</sub>BM and PhQEOCz-C<sub>61</sub>BM is outlined in Scheme 1. The alkyl and alkoxy groups were introduced into Cz in the presence of sodium hydride to obtain compounds 1 and 2, subsequent Friedel-Crafts acylation yields compounds 3 and 4, respectively. Friedlander condensation of 3 and 4 with 2-aminobenzophenone followed by Friedel-Crafts acylation with methyl 5-chloro-5-oxopentanoate yields 7 and 8, respectively. The keto-ester of 7 and 8 reacted with *p*-toluenesulfonyl hydrazide to give 9 and 10, respectively. Finally, the desired fullerene derivatives, PhQHCz-C<sub>61</sub>BM and PhQEOCz-C<sub>61</sub>BM, were synthesized via the standard 1,3-dipolar cycloaddition reaction of 9 and 10 with C<sub>60</sub>. The structure of the fullerene derivatives was confirmed by 1H, 13C NMR, FTIR and mass spectral studies (Fig. S1-S7, ESI<sup>†</sup>) Both PhQHCz-C<sub>61</sub>BM and PhQEOCz-C<sub>61</sub>BM are highly soluble in common organic solvents such as methylene chloride, tetrahydrofuran (THF), chloroform, CB, o-DCB, and toluene.

The thermal properties of **PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM** were measured by TGA and DSC analysis (Fig. S8 and S9, ESI†). The TGA data reveal that the 5% weight loss temperatures of **PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM** are at 478 and 423 °C, respectively, indicating their high thermal stability; the former has a higher thermal stability than the latter due to the presence



Scheme 1 Synthesis of PhQHCz-C<sub>61</sub>BM and PhQEOCz-C<sub>61</sub>BM.

of the 2-methoxyethoxyethyl group, which may reduce the crystallinity of the fullerene derivative. **PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM** have glass transition temperatures ( $T_g$ ) of 216 and 212 °C, respectively, without any crystallization between 25 and 350 °C in their DSC thermograms, indicating their amorphous nature.

The UV-visible absorption spectra of **PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM** in chloroform solution are shown in Fig. 1a. The absorption spectra of both derivatives are very similar to each other with a peak maximum around 320 nm. This indicates that there is no electronic effect on the nature of alkyl chains in the Cz unit. The optical band gaps were calculated from their absorption edges and found to be 1.71 and 1.73 eV for **PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM**, respectively. These photophysical properties indicate that these materials are potentially good candidates as electron acceptors for BHJ PSCs. The electrochemical properties of these derivatives were investigated by cyclic voltammetry (CV) to determine the highest occupied molecular orbital (HOMO) and LUMO energy levels. Fig. 1b shows the cyclic voltammograms of **PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM**, and the data are listed in Table 1.

As shown in Fig. 1b, both derivatives exhibit well defined quasi reversible reduction peaks indicating their n-type semiconductor nature. The LUMO energy levels of **PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM** were calculated from their onset reduction potentials and found to be -3.57 and -3.62 eV for



Fig. 1 (a) UV-visible absorption spectra in CF solution and (b) cyclic voltammograms in o-DCB at a scanning rate of 100 mV s<sup>-1</sup>, of PhQHCz-C<sub>61</sub>BM and PhQEOCz-C<sub>61</sub>BM.

Acceptor	$E_{\rm red}^1$ (V)	$E_{\rm red}^2$ (V)	$E_{\mathrm{red}}^{\mathrm{onset}}\left(\mathbf{V}\right)$	LUMO (eV)	HOMO (eV)
PC <sub>61</sub> BM PhQHCz-C <sub>61</sub> BM PhQEOCz-C <sub>61</sub> BM	$-0.98 \\ -1.01 \\ -1.00$	$-1.41 \\ -1.43 \\ -1.42$	$-0.82 \\ -0.88 \\ -0.84$	-3.63 -3.57 -3.61	-5.36 -5.28 -5.34

**PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM**, respectively, which are both higher than the LUMO value of PCBM (-3.63 eV). Generally, the fullerene derivative with higher lying LUMO values improve the  $V_{oc}$  of the resulting OPV devices.<sup>36</sup> The HOMO energy levels were calculated from their optical band gap and LUMO energy levels and the results are summarized in Table 1. These electrochemical results indicate that **PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM** are suitable acceptor materials for BHJ PSCs with a P3HT donor.

In order to analyze the effect of interfacial contact on the photovoltaic properties, PhQHCz-C<sub>61</sub>BM and PhQEOCz-C<sub>61</sub>BM were individually blended with P3HT and used as an active layer with a transparent ITO/PEDOT:PSS or ITO/MoO3 as the front contact and the reflective LiF/Al as the back contact of BHJ PSCs. The photovoltaic properties were measured under AM1.5G illumination at 100 mW cm<sup>-2</sup>. Several processing parameters such as the P3HT to acceptor weight ratio, active layer thickness (150 nm), and processing solvent were carefully optimized. The J-V plots of PhQHCz-C<sub>61</sub>BM and/or PhQEOCz-C<sub>61</sub>BM based devices with PEDOT:PSS as the HTL are shown in Fig. 2 and the data are listed in Table 2. As can be seen in Table 2, both **PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM** show much lower  $V_{oct}$   $J_{sct}$ and FF values yielding a very poor PCE of 0.12 and 0.13%, respectively. However, devices based on PC61BM acceptors and P3HT donors with similar processing conditions have a PCE of 2.53%.

This efficiency difference is quite usual and believed to be a result of restricted charge extraction at the interfacial contact between the HTL and active layer due to a charge injection/ extraction barrier; this may be caused by the protonation of the pyridyl nitrogen by a  $-SO_3H$  group in the PEDOT:PSS. This was further supported by using MoO<sub>3</sub> as the HTL instead of PEDOT:PSS, with similar device configuration and optimization conditions, because both had almost similar work functions (PEDOT:PSS: 5.2 eV and MoO<sub>3</sub>: 5.3 eV).<sup>14</sup> Fig. 2b shows the *J*-*V* plots of the optimized devices and the data are presented in Table 2. Surprisingly, both derivatives show drastically improved device performance compared to their PEDOT:PSS counterparts, as shown in Table 2. Particularly, the PCE of



Fig. 2 J-V plots of devices based on PhQHCz-C<sub>61</sub>BM and PhQEOCz-C<sub>61</sub>BM with (a) PEDOT:PSS and (b) MoO<sub>3</sub> as the HTLs.

**PhQHCz-C<sub>61</sub>BM** based devices increases from 0.12% to 2.27% when replacing the HTL PDOT:PSS by  $MoO_3$ . This confirms the existence of the charge injection/extraction barrier at interfacial contacts when PEDOT:PSS was used as the HTL.

The protonation reaction was further confirmed indirectly by UV-vis absorption spectra of PhQHCz-C<sub>61</sub>BM in o-DCB upon addition of p-toluenesulphonic acid (PTSA) as shown in Fig. 3; one new band appeared at 444 nm, accordingly, the pink coloured solution turned yellow, which turned back to its original colour by the addition of dilute base solution and confirms the protonation of pyridyl nitrogen by the -SO<sub>3</sub>H group. To gain insight about this effect, the hole mobility of PhQHCz-C<sub>61</sub>BM and PhQEOCz-C<sub>61</sub>BM based devices was measured using PEDOT:PSS and MoO<sub>3</sub> as HTLs by the SCLC method and the resulting data are summarized in Table 3. As can be seen in Table 3, both PhQHCz-C<sub>61</sub>BM and PhQEOCz-C<sub>61</sub>BM show higher hole mobility values with MoO<sub>3</sub> as the HTL compared with PEDOT:PSS. In addition, we measured the dark current of the devices based on PhQHC<sub>61</sub>BM using MoO<sub>3</sub> and PEDOT:PSS as the hole transporting layer (Fig. S9, ESI<sup>†</sup>). The J-V curves clearly show that the  $V_{\rm oc}$  of the devices based on PEDOT:PSS is significantly decreased compared to MoO<sub>3</sub>, due to the injection barriers generated at the contacts leading to induced charge recombination at the HTL/active layer interface.

Among the acceptors, **PhQHCz-C**<sub>61</sub>**BM** based devices show superior photovoltaic properties compared with **PhQEOCz-C**<sub>61</sub>**BM**. This can be explained on the basis of external quantum efficiency (EQE) and morphological studies. The EQE curves of **PhQHCz-C**<sub>61</sub>**BM** and **PhQEOCz-C**<sub>61</sub>**BM** based devices are shown in Fig. 3a. They clearly show that **PhQHCz-C**<sub>61</sub>**BM** based devices cover a broad wavelength from 400 to 650 nm with a maximum EQE of 43.6%, which is higher than that of the **PhQEOCz-C**<sub>61</sub>**BM** based device. This is consistent with the  $J_{sc}$  value obtained from the J-V measurements. The morphology of P3HT:**PhQHCz-C**<sub>61</sub>**BM** and P3HT:**PhQEOCz-C**<sub>61</sub>**BM** blend films was studied by

Table 2	Photovoltaic	properties c	of PhQHCz-C	C <sub>61</sub> BM and	PhQHCz-	C <sub>61</sub> BM
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P3HT/acceptor ratio	HTL	$V_{\rm oc}$ (V)	$J_{ m sc}~({ m mA~cm}^{-2})$	FF (%)	PCE (%)
<b>PhQHCz-C<sub>61</sub>BM</b> (1 : 0.8)	PEDOT:PSS	0.26	2.50	19	0.12
$PhQEOCz-C_{61}BM (1:0.8)$	PEDOT:PSS	0.28	2.27	20	0.13
PhQHCz-C <sub>61</sub> BM $(1:1)$	MoO <sub>3</sub>	0.62	6.40	58	2.27
PhQEOCz-C <sub>61</sub> BM $(1:1)$	$MoO_3$	0.57	6.17	60	2.09



Fig. 3 Visible colour change of PhQHCz-C<sub>61</sub>BM upon addition of PTSA in *o*-DCB.

Table 3 Hole mobility data for P3HT:acceptor blends

P3HT/acceptor device type	HTL	Hole mobility ( $\mu$ ) (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
PhQHCz-C <sub>61</sub> BM	PEDOT:PSS	$3.00 imes10^{-6}$
PhQEOCz-C <sub>61</sub> BM	PEDOT:PSS	$5.79 imes10^{-6}$
PhQHCz-C <sub>61</sub> BM	MoO <sub>3</sub>	$2.05\times10^{-4}$
PhQEOCz-C <sub>61</sub> BM	MoO <sub>3</sub>	$2.51\times10^{-4}$



Fig. 4 (a) EQE curves of  $PhQHCz-C_{61}BM$  and  $PhQEOCz-C_{61}BM$  based devices and the AFM images of (b)  $P3HT/PhQHCz-C_{61}BM$  and (c)  $P3HT/PhQEOCz-C_{61}BM$  films using  $MOO_3$  as the HTL.

atomic force microscopy (AFM) and the respective AFM images are shown in Fig. 4b and c, respectively. The root mean square roughness (rms) values of **PhQHCz-C<sub>61</sub>BM** and **PhQEOCz-C<sub>61</sub>BM** based blend films are 4.9 and 9.1 nm, respectively. In addition, **PhQHCz-C<sub>61</sub>BM** based devices show smoother surfaces than those of the **PhQEOCz-C<sub>61</sub>BM** based devices, as shown in Fig. 4, which leads to the superior device performance of **PhQHCz-C<sub>61</sub>BM** based devices.

### 4. Conclusions

In summary, we synthesized two kinds of fullerene derivatives, namely  $PhQHCz-C_{61}BM$  and  $PhQEOCz-C_{61}BM$ , as acceptors for BHJ PSCs and analysed their effects on the HTL as well as on the

active layer. We demonstrated that there is protonation of the pyridyl nitrogen of the acceptor in the active layer by the  $-SO_3H$  group of PEDOT:PSS in the HTL, which restricts charge collection at the interface and leads to a drastically lower PCE of  $\sim 0.12\%$ , compared to the PCE of  $\sim 2.2\%$  obtained when using  $MoO_3$  as the HTL. This is due to the fact that the protonation reaction creates a barrier at the interface between the active layer and the HTL interface, leading to enhanced charge recombination at the interface. In addition, among the two new acceptors, **PhQHCz-C<sub>61</sub>BM** shows quite high PCE values compared with **PhQEOCz-C<sub>61</sub>BM**, due to the good phase separation of the former with P3HT, compared to the latter. Finally, we conclude that pyridyl nitrogen in either the acceptor or donor derivatives is not suitable for BHJ OSCs when using PEDOT:PSS as the HTL.

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