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Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) based on an active layer composed of a conjugated polymer as the donor and fullerene derivative as the acceptor have received increasing attention for their ease of fabrication, mechanical flexibility, light weight, and low-cost fabrication of large-area devices. During the past decades, extensive efforts have been focused on the improvement of the power conversion efficiency (PCE) and device stability for economically viable applications by molecular structure engineering,^{1,2} morphology control,³⁻⁵ and device optimization.6-10 To date, the highest reported PCE of PSCs has approached 10%.¹¹⁻¹⁷ The most common conjugated polymer for donor and acceptor materials are poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM).¹⁸⁻²¹ However, their performance is limited for the low short circuit current (I_{sc}) and open-circuit voltage (V_{oc}) originating from the relative wide band gap of P3HT donor and low energy of the lowest unoccupied molecular orbital (LUMO) of PC₆₁BM.

Self-assembled buffer layer from conjugated diblock copolymers with ethyleneoxide side chains for high efficiency polymer solar cells[†]

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In this article, we present a novel and promising approach to enhance the device performance and stability by the simple incorporation of all conjugated polythiophene diblock copolymers, poly(3-hexylthiophene)*b*-poly(3-triethylene glycol thiophene) (P3HT-*b*-P3TEGT), into the active layer based on inverted device structures. During the spin-coating process, the triethylene glycol side chains of P3HT-*b*-P3TEGT would spontaneously migrate vertically towards the active layer surface and form a nanoscale self-assembled anode buffer layer, which simultaneously drives the orderly packing of donor polymer chains and vertical phase separation morphology, allowing electrons and holes to move more efficiently to the respective electrode. Moreover, the nanoscale self-assembled buffer layer can form interfacial modification and ohmic contact between the active layer and Ag (or MoO₃/Ag) electrode, reduce the contact resistance of the device, and increase the electrical conduction of the device, especially upon chelating lithium ions (Li⁺) to the triethylene glycol side chains of P3HT-*b*-P3TEGT. Combining the above advantages, the efficiency and stability of the polymer solar cells are enhanced. A remarkable improvement in the PCE with 7.3% (measured in air) is obtained for PBDTTT-C-T:PC₇₁BM devices.

> To enhance the PCE, the lower band gap copolymers instead of P3HT and a higher LUMO energy acceptor material were considered. In addition, the morphology control of the active layer is also processed to increase the efficiency such as thermal annealing,²² solvent annealing,²³ additives,²⁴⁻²⁸ and solvent mixture.^{29,30} These techniques have been proven to be very effective to obtain lateral nanoscale phase-separated structures (the phase separation size is equal to the exciton diffusion length). In particular, it should be noted that the nanoscale vertical phase segregation morphology of the active layer is equally critical for the enhancement of PCE. The vertical components' distribution, *i.e.* the p-type copolymers donor are rich near the high work function (WF) anode and n-type acceptor materials are rich near the low WF metal cathode, can form an efficient pathway for carrier transfer and allows electrons and holes moving towards the cathode and anode more efficiently.31,32

> On the other hand, in order to achieve high-performance BHJ PSCs, the interfacial engineering of OPVs is another important approach. In BHJ PSCs, to decrease the energy barriers for electron- and hole-extraction, the WFs of cathode and anode should effectively match the acceptor's LUMO and donor's highest occupied molecular orbital (HOMO), respectively. The energy barriers between the electrodes and the active layer could often be reduced effectively by inserting buffer layers at the cathode/anode. Over the past years, considerable efforts have been expended in exploring a material that could act as an efficient hole extraction layer for BHJ PSCs. The anode buffer



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layer should form an ohmic contact at the interface between the active layer and anode electrode and possess higher WF and higher hole mobility for hole transportation and collection.³³ From these points of view, it is wise to select thiophene derivatives as a hole transport layer (HTL) to provide an ohmic contact with the donor material.^{34,35} Traditionally, the buffer layer is fabricated into the device by an additional step. However, such an additional process will complicate the device fabrication processes, and consequently, increase the cost.

To achieve the nanoscale vertical phase segregation morphology of the active layer, as well as obtain the buffer layer without an additional spin-coating process, the self-assembled buffer layer is utilized in the BHJ PSCs. It had been reported that a fullerene derivative (F-PCBM) as a buffer layer between the cathode and active layer could improve the performance of BHJ PSC resulting from the spontaneous surface segregation of fluorocarbon chains onto the surface of the active layer.³⁶ Moreover, the vertical phase separation and self-assembled buffer layer *via* the spontaneous migration of PEG to the top could also be obtained for efficient and air-stable PSCs by blending the poly(ethylene glycol) (PEG) molecules or fullereneend-capped PEG (PEG-C₆₀) into the photoactive layer.^{33,36-39}

In addition, compared with conventional BHJ PSCs, invertedtype devices exhibited better long-term ambient stability by avoiding the need for corrosive and hygroscopic hole-transporting poly(3,4-ethylenedioxylenethiophene):poly(styrenesulphonic acid) (PEDOT:PSS) and low WF metal cathode, both of which were harmful towards the device lifetime.

Here, we demonstrated an interesting and promising way to improve the performance and air stability of PSCs based on inverted device structures ITO/ZnO/active layer/Ag (or MoO₃/Ag) by introducing poly(3-hexylthiophene)-b-poly(3-triethylene glycol thiophene) (P3HT-b-P3TEGT), an all diblock copolymer containing polythiophene derivative segments whose side chain was triethylene glycol, into the P3HT:PC₆₁BM or PBDTTT-C-T:PC71BM active layers. During the spin-coating and solvent evaporation processes, P3HT-b-P3TEGT would spontaneously self-segregate onto the film and form nanoscale self-assembled buffer layers due to the vertical migration of triethylene glycol side chains to the active layers' surface. The chain orientation of P3HT-b-P3TEGT at the surface would also force the donor copolymer chains in the active layer to adopt the same orientation due to the high crystallinity of copolymer donors and simultaneously induce the vertical phase segregation morphology of the active layer. Furthermore, the presence of triethylene glycol side chains between the active layer and anode electrode (Ag or MoO₃/Ag) would form an amphiphilic interface, decreasing the energy barriers for hole collection and forming an ohmic contact, especially upon chelating the lithium ion (Li⁺) to the triethylene glycol side chains of P3HT-b-P3TEGT (P3HT-b-P3TEGT:Li⁺), leading to further enhancement of the device performance and stability.

Results and discussion

The P3HT-*b*-P3TEGT diblock copolymers were synthesized following the procedure of McCullough and co-workers⁴⁰

successfully (ESI[†]). Furthermore, the resulting copolymers were purified by sequential Soxhlet extraction using methanol, acetone, hexane and chloroform solvents. The weight ratios of the two blocks were determined to be 8:1, 4:1 and 2:1 (P3HT:P3TEGT) using ¹H NMR spectroscopy; thus, we also abbreviated these diblock copolymers (P3HT-b-P3TEGT) as H8T1, H4T1 and H2T1, respectively, in the data, which were reported in our previous work.41 The gel permeation chromatography (GPC) using tetrahydrofuran (THF) as the eluent were processed to estimate the number-average molecular weight $(M_{\rm p})$ of the diblock copolymers. When the P3HT-*b*-P3TEGT or P3HT-b-P3TEGT:Li⁺ diblock copolymer was added to the P3HT:PC₆₁BM or PBDTTT-C-T:PC₇₁BM active layers, it would spontaneously migrate to the surface and form the nanoscale self-assembled buffer layer between the active layer and Ag or MoO₃/Ag anode electrode, simultaneously inducing the orientation of the donor copolymer chains and vertical distribution of the active layer components (Scheme 1).

To investigate the vertical surface segregation of P3HT-b-P3TEGT during the spin-coating process, the X-ray photoelectron spectroscopy (XPS) profiles are shown in Fig. 1. All the films were prepared on ZnO coated-ITO glass substrates by spincoating the P3HT:PC61BM solutions blended with various concentrations of H4T1, pure Li⁺ and 0.6 mg mL⁻¹ H4T1 chelated with Li⁺ ion (H4T1:Li⁺) with a fixed concentration of P3HT at 20 mg mL $^{-1}$. It was observed that the peak of O 1s at 531.8 eV became stronger with the gradual increase of the H4T1 amount and even showed a slight red-shift of H4T1:Li⁺, which could belong to the chelation of the triethylene glycol side chains with Li⁺.⁴²⁻⁴⁵ Moreover, the Li 1s spectra showed that the intensity of the peaks at 49.3 eV and 63.3 eV, resulting from the Li⁺ salt, became stronger with the addition of Li⁺ salt into the P3HT:PC₆₁BM solution, especially for the P3HT:PC₆₁-BM:H4T1:Li⁺ film. The O/C atomic ratios calculated from the copolymer blend compositions in solution and measured from the XPS results of the films surface were plotted as a function of the H4T1 concentration. From the results, the O/C ratios of the films' surface measured from the XPS results were much higher than the calculated ratio from the copolymer blend compositions for all the concentrations, revealing the vertical migration of H4T1 or H4T1:Li⁺ to the film surface during the spin-coating process. When the concentration of H4T1 increased to \sim 0.6 mg mL^{-1} , the O/C atomic ratio (measured by the XPS) attained the saturation point, which was consistent with the results of the water contact angles in Fig. S1 (ESI[†]).46 On the other hand, the H8T1 and H2T1 diblock copolymers also demonstrated the saturation point at concentrations of \sim 1.2 mg mL⁻¹ and $\sim 0.3 \text{ mg mL}^{-1}$, respectively. The saturation behavior was also observed in our previous work on self-organized HTLs based on fluorinated side chains diblock copolymers.10 The active layer surface was almost covered by the triethylene glycol side chains of P3HT-b-P3TEGT diblock copolymers completely above the saturation point. In addition, the approximate thicknesses of P3HT:PC₆₁BM, P3HT:PC₆₁BM:P3HT-*b*-P3TEGT the and P3HT:PC61BM:P3HT-b-P3TEGT:Li⁺ films calculated from the AFM analysis were 100 nm, as shown in Fig. S2,† revealing that the buffer layer segregated on the surface of the active layer was



Scheme 1 Schematic illustration of (a) inverted bulk heterojunction polymer solar cells device based on the vertical segregation of P3HT-b-P3TEGT chelated with Li^+ on the active layer surface, (b) the morphology of active layer: Li^+ and active layer: $P3HT-b-P3TEGT: Li^+$, (c) the chemical structures of donor and acceptor materials in the active layer used in this study.

very thin, possibly a monolayer or having a thickness of several layers.

We optimized the electrical and optical characterizations of the P3HT:PC₆₁BM:H4T1 active layer by changing the concentration of H4T1 in 1,2-dichlorobenzene (DCB) solution using the UV-vis absorption and X-ray diffraction (XRD) measurements. The normalized absorption spectra of the polymer films spin-coated from the DCB solution (Fig. S3†) were similar and revealed that the absorption band of thiophene chains appeared at about 510, 560 and 610 nm and that of PC₆₁BM at 330 nm. Compared with the pristine P3HT:PC₆₁BM film, the absorption peaks of thiophene chains in P3HT:PC₆₁BM:H4T1 films was somewhat red-shifted by approximately 6 nm, and simultaneously, a stronger absorption was observed at 610 nm, while the absorption peak of PC₆₁BM displayed no shift. This demonstrated that the active layer was organized into supermolecular assemblies and exhibited increasing planarity, even

more orderly and highly crystalline than the packed P3HT chains induced by the orientation of the surface segregation of H4T1. To further validate the ordering and crystalline of thiophene chains, the X-ray diffraction (XRD) was monitored (Fig. 2). The XRD results revealed that the introduction of H4T1 or H4T1:Li⁺ into the P3HT:PC₆₁BM system could improve the crystalline and ordered structures of P3HT in the active layer. The pristine P3HT:PC₆₁BM film showed a diffraction peak at 2θ \approx 5.4°, corresponding to a *d*-spacing value of 16.3 Å of P3HT. After the introduction of H4T1 or H4T1:Li⁺ into the P3HT:PC₆₁BM solution, all the d-spacing peaks were shifted slightly, which was expanded by \sim 1.0 Å. It was more interesting that a new diffraction peak appeared at $2\theta \approx 6.5^{\circ}$ (d-spacing of \sim 13.58 Å) in the ternary blends, which was probably a result of the self-assembly of thiophene chains of copolymers in the active layer. Moreover, the results also indicated that the P3HT polymer chains might have a slight preference in the face-on or



Fig. 1 (a) O 1s and (b) Li 1s regions of the X-ray photoelectron spectroscopy (XPS) profiles of the surface of P3HT:PC₆₁BM (PP) films with different H4T1 concentrations, pure Li⁺ ion, H4T1 and H4T1 (0.6 mg mL⁻¹):Li⁺, (c) O/C atomic ratio of the P3HT:PC₆₁BM:H4T1 (PP:H4T1) films and the PP:H4T1 (0.6 mg mL⁻¹):Li⁺ film surfaces measured by XPS and the O/C atomic ratio of PP:H4T1 solutions calculated from the polymer chemical compositions as a function of the H4T1 concentration.



Fig. 2 XRD patterns of P3HT:PC_{61}BM (PP) blended with different concentrations of H4T1 and 0.6 mg mL^{-1} H4T1 chelated with Li⁺ films.

the co-existence of the face-on and other tiled chain orientations⁴ facilitated by the driving force from the vertical surface separation of P3HT-*b*-P3TEGT or P3HT-*b*-P3TEGT:Li⁺.

The morphology of the active layer was critical to determine the performance of BHJ PSCs. With a large interfacial area and bicontinuous vertical distribution of the active layer components, the charge separation from the donor copolymer to acceptor fullerene derivative could be enhanced and charge carriers collection from the active layer to the respective electrode also could be maximized. We used atomic force microscopy (AFM) in the tapping mode to measure the surface morphology of P3HT:PC₆₁BM (1:1, w/w) with various H4T1 concentrations (height images in Fig. S4†) and H4T1:Li⁺

(three-dimensional images in Fig. 3). In addition, AFM images were also examined to elucidate the effect of H4T1 or H4T1:Li⁺ on the phase separation of P3HT:PC₆₁BM thin films. The surface morphology of pristine P3HT:PC₆₁BM demonstrated a fine phase separation and bicontinuous network image with 2.3 nm root-mean-square (RMS) roughness. Considering the pristine H4T1 films showed a 2.84 nm RMS, it could be inferred that increasing the H4T1 concentration would lead to aggregation of the triethylene glycol side chains on the surface of the active layer and the films exhibited a rougher surface. However, adding H4T1 flattened the film surface and made it uniform with the RMS values of 0.62, 0.68 and 1.62 nm for H4T1 concentrations of 0.2, 0.6 and 1.0 mg mL^{-1} , respectively. On the other hand, we also utilized AFM measurements to investigate the effect of H4T1:Li⁺ on the orientation and distribution of P3HT:PC₆₁BM active layer components and surface morphology⁴⁷ shown in Fig. 4. The added Li⁺ ions could chelate with the triethylene glycol side chains of P3HT-b-P3TEGT and drive the polymer chains to self-assemble into the nanowire morphology, according to our previous work in ref. 41. A wellordered lamellar structure of H4T1:Li⁺ covering P3HT:PC61BM active layer surface was found at concentrations of 0.06 mg mL^{-1} and 0.18 mg mL^{-1} of Li^+ salt, resulting from the Li^+ ions driving the diblock copolymer chains into nanowires on the surface of the active layer.48 Furthermore, uniform film morphology with 1.88 and 1.59 nm RMS induced by the vertical surface segregation of triethylene glycol side chains of polythiophenes was observed during spin-coating. However, upon further increasing the concentration of H4T1:Li⁺, large aggregations gradually appeared on the surface with the RMS values of 2.78 and 2.92 nm, and even the well-ordered lamellar structures disappeared.

We fabricated the inverted devices based on P3HT:PC₆₁-BM:Li⁺ and P3HT:PC₆₁BM:H4T1:Li⁺ active layers to investigate the effect of Li⁺ doping on the device performance. The effects of different Li⁺ concentrations in P3HT:PC₆₁BM and P3HT:PC₆₁BM:H4T1 solutions on the device performance were studied and the device parameters are plotted in Fig. 5 as functions of the Li⁺ concentration. The J-V curves of these devices are shown in Fig. S5[†] and the correlated parameters are summarized in Table S1.† All the parameters of the devices based on P3HT:PC₆₁BM:Li⁺ dropped sharply with an increase in the Li⁺ concentration. However, the parameters of the devices based on P3HT:PC₆₁BM:H4T1:Li⁺ first rose and then decreased gradually with the increase of the Li⁺ concentration. Compared with the P3HT:PC₆₁BM:Li⁺ device, the better performance and stability of the device based on P3HT:PC61BM:H4T1:Li⁺ was mainly due to the chelation of the triethylene glycol side chains of H4T1 with Li⁺ ions, which could drive the H4T1 diblock copolymer chains into nanowires and to migrate onto the surface of the active layer. On the contrary, the addition of Li⁺ into P3HT:PC61BM might not form an efficient anode buffer layer and resulted in a dramatic decrease of the PCE. The results indicated that the photovoltaic properties of BHJ PSCs could be easily improved by introducing P3HT-b-P3TEGT:Li⁺ into the active layer system.10 On the other hand, the dark J-V characteristics of devices based on active layer P3HT:PC61BM,



Fig. 3 Three-dimensional atomic force microscopy (AFM) images of P3HT:PC₆₁BM (PP) with various H4T1 concentrations ranging from 0 mg mL⁻¹ to 1.0 mg mL⁻¹, 0.6 mg mL⁻¹ H4T1 chelated with Li⁺ and pristine H4T1 films. All the image sizes are 5 μ m × 5 μ m.

 $P3HT:PC_{61}BM:Li^+$, $P3HT:PC_{61}BM:H4T1$ or P3HT:PC₆₁-BM:H4T1:Li⁺ in the range of -2 to 2 V were obtained (Fig. S6[†]). Obviously, adding a small amount of Li⁺ ions into the P3HT:PC₆₁BM solution, the dark J-V curve presented a relatively large leakage current density. However, the device with P3HT:PC₆₁BM:H4T1 containing Li⁺ ions showed significantly suppressed leakages, resulting in the best photovoltaic performance. More importantly, the low dark current densities of the device based on P3HT:PC₆₁BM:H4T1:Li⁺ indicated that a larger open-circuit voltage (V_{oc}) could be obtained in the inverted device with a vertical phase separated buffer layer when compared with those without the nanoscale buffer layer. Towards the end, the J-V curves of the devices were modeled with an equivalent circuit and a single diode comprising a shunt resistance (R_{SH}) and series resistance (R_S) . The addition of a parallel photocurrent source, J_{ph} , resulted in the following well-known equation:

$$J = J_0 \left[\exp \left(\frac{q(V - R_{\rm S}AJ)}{nkT} \right) - 1 \right] + \frac{V - R_{\rm S}AJ}{R_{\rm SH}A} - J_{\rm ph}(V)$$

where *k* represents the Boltzmann's constant, *T* represents the temperature, *q* represents the electron charge, and $J_{\rm ph}$ represents the voltage-dependent photocurrent. When the condition

is open circuit (J = 0) and $J_{ph} = J_{sc}$, V_{oc} could be written as follows:

$$V_{\rm oc} \approx \frac{nkT}{q} \ln\left(\frac{J_{\rm sc}}{J_0}\right)$$

The J_0 value represents the reverse dark current density. A higher V_{oc} value could be obtained for lower J_0 according to this equation. Therefore, V_{oc} of the inverted devices with a buffer layer was higher than those devices without a buffer layer.

To further analyze the reason for the improvement of the device performance, we performed the UV photoelectron spectroscopy (UPS) measurement to study the interfacial dipole effect induced by the P3HT-*b*-P3TEGT and P3HT-*b*-P3TEGT:Li⁺ self-assembled interfacial layer between the active layer and Ag anode electrode. The UPS profiles of P3HT:PC₆₁BM:H4T1/Ag as a function of H4T1 concentration and P3HT:PC₆₁BM:H4T1:Li⁺ (0.6 mg mL⁻¹ H4T1 blending with 0.18 mg mL⁻¹ Li⁺ ions)/Ag are displayed in Fig. 6. As measured from UPS, the WFs of Ag were shifted by 0.67, 0.81, 0.82 and 0.98 eV for 0.2, 0.6, and 1.0 mg mL⁻¹ H4T1 and H4T1:Li⁺, respectively, indicating that increasing the amounts of P3HT-*b*-P3TEGT could enhance the interfacial contact and raise the WF of the Ag electrode,



Fig. 4 The height (above) and phase (below) the atomic force microscopy (AFM) images of P3HT:PC₆₁BM (PP) blended with H4T1:Li⁺ at various Li⁺ concentrations ranging from 0.06 mg mL⁻¹ to 1.8 mg mL⁻¹ at a fixed H4T1 concentration of 0.6 mg mL⁻¹. All the image sizes are 5 μ m \times 5 μ m.



Fig. 5 The photovoltaic parameters of the PSCs based on P3HT:PC₆₁BM (PP) and P3HT:PC₆₁BM:H4T1 (PP:H4T1, 0.6 mg mL⁻¹ H4T1) with various Li⁺ concentrations under illumination of AM 1.5G (100 mW cm⁻²).

especially upon adding P3HT-*b*-P3TEGT:Li⁺. The "metal-onorganic" interfaces were more complicated:^{49,50} the rise in the effective WF of Ag might attribute to the interfacial modification effect, originating from the vertical surface segregation of triethylene glycol side chains of P3HT-*b*-P3TEGT or P3HT-*b*-P3TEGT:Li⁺ during the spin-coating process. The modification

effect provided by P3HT-b-P3TEGT or P3HT-b-P3TEGT:Li⁺ might result in the rise of WF of the anode electrode and further allowed holes to be collected by the anode electrode more easily; hence, it might lead to the improvement of J_{sc} and V_{oc} of the device.¹⁰ On the other hand, the WF of P3HT:PC₆₁BM:H8T1/Ag and P3HT:PC61BM:H2T1/Ag were also shifted by 0.77 and 0.72 eV for the saturation points of \sim 1.2 mg mL⁻¹ and \sim 0.3 mg mL^{-1} , respectively, when compared with the film with 5 nm Ag deposited on the active layer without the addition of P3HT-b-P3TEGT. Fig. 6 shows the band energy diagram in relation to the relative energy levels of the devices. More importantly, when comparing with other devices, the experimental value observed for the P3HT:PC₆₁BM:H4T1:Li⁺/Ag thin film (5.18 eV) was very close to the HOMO energy level of P3HT or PBDTTT-C-T donor, which might be more favorable and responsible for the hole collection when compared with P3HT:PC₆₁BM:H8T1/Ag (4.97 eV), P3HT:PC₆₁BM:H4T1/Ag (5.01 eV) and P3HT:PC₆₁BM:H2T1/ Ag (4.92 eV). On the other hand, P3HT-b-P3TEGT could increase the energy level and passivate the surface defects of MoO_3 by interfacial modification originating from the triethylene glycol side chains of diblock copolymer in Fig. 6, which might be beneficial for the energy level matching with Ag electrode and the improvement of $J_{\rm sc}$.⁵¹

The formation of interfacial modification and the enhancement of WF of the anode electrode induced by the triethylene glycol side chains of P3HT-*b*-P3TEGT and P3HT-*b*-P3TEGT:Li⁺ were expected to promote the exciton dissociation and increase the hole-carrier collection.⁵² The $J^{0.5}$ –V characteristics of hole-only



Fig. 6 (a) The ultraviolet photoelectron spectroscopy (UPS) of 5 nm thick layer Ag films deposited on the active layer (P3HT:PC₆₁BM) (PP) with various concentrations of P3HT-*b*-P3TEGT (H4T1) on the ITO substrate: 0.0 mg mL⁻¹, 0.2 mg mL⁻¹, 0.6 mg mL⁻¹, 1.0 mg mL⁻¹ and 0.6 mg mL⁻¹ chelated with Li⁺ salt, (b) ultraviolet photoelectron spectroscopy (UPS) of 5 nm thick layer Ag films deposited on various diblock copolymers films surface, (c) The ultraviolet photoelectron spectroscopy (UPS) of pure MoO₃ and MoO₃ deposited on H4T1 diblock copolymers surface, (d) schematic representation of the band energy diagram for inverted BHJ PSCs devices based on different hole buffer layers vertically segregating on the active layer surface.

devices were fabricated to assess the hole mobility with a structure of ITO/PEDOT:PSS/active layer/MoO₃/Au, by using the space charge-limited-current (SCLC) model according to the Mott–Gurney equation (detailed description of the mobility

measurement is provided in the ESI[†]).^{53–55} As plotted in Fig. S7,[†] the hole mobility of the devices increased from 1.68×10^{-4} cm² V⁻¹ s⁻¹ to 2.78×10^{-4} cm² V⁻¹ s⁻¹, 5.77×10^{-4} cm² V⁻¹ s⁻¹ and 1.15×10^{-3} cm² V⁻¹ s⁻¹ (Table S3[†]) after the insertion of

Table 1 Device performance parameters of inverted solar cells with different active layers by incorporating H4T1 at various concentrations or incorporating H4T1:Li⁺

Device ^{<i>a,b</i>}	$J_{\rm sc}~({ m mA~cm^{-2}})$	$V_{\rm oc}$ (V)	FF (%)	PCE (%)	$R_{\rm s} \left(\Omega \ {\rm cm}^2\right)$	$R_{\rm sh} \left(\Omega \ {\rm cm}^2\right)$
ITO/ZnO/PP ^c /PEDOT:PSS/Ag	7.5	0.57	54	2.3 ± 0.3	10.3	630
ITO/ZnO/PP ^c /Ag	6.07	0.53	50	1.6 ± 0.2	12.9	268
ITO/ZnO/PP ^c :H4T1 $(0.2)^d$ /Ag	7.5	0.57	53	2.3 ± 0.2	9.3	396
$ITO/ZnO/PP^{c}:H4T1(0.6)^{d}/Ag$	9.74	0.59	59	3.4 ± 0.2	5.1	310
ITO/ZnO/PP ^c :H4T1 $(1.0)^d$ /Ag	9.52	0.57	58	3.1 ± 0.2	6.7	598
$ITO/ZnO/PP^{c}:H4T1 (0.6)^{d}:Li^{+} (0.18)^{e}/Ag$	9.91	0.59	62	3.6 ± 0.2	1.3	367
ITO/ZnO/PP ^c :H4T1 (0.2) ^d /MoO ₃ /Ag	9.52	0.58	58	3.2 ± 0.2	1.2	728
ITO/ZnO/PP ^c :H4T1 (0.6) ^d /MoO ₃ /Ag	10.9	0.60	59	3.9 ± 0.2	13.2	467
ITO/ZnO/PP ^c :H4T1 (1.0) ^d /MoO ₃ /Ag	10.8	0.61	54	3.6 ± 0.2	3.5	455
$ITO/ZnO/PP^{c}:H4T1(0.6)^{d}:Li^{+}(0.18)^{e}/$	11.2	0.60	62	4.2 ± 0.2	1.4	372
MoO ₃ /Ag						
ITO/ZnO/PBP ^c /Ag	11.39	0.73	57	4.7 ± 0.3	4.5	170
$ITO/ZnO/PBP^{c}:H4T1 (0.6)^{d}/MoO_{3}/Ag$	17.01	0.77	56	7.3 ± 0.1	1.3	545
$ITO/ZnO/PBP^{c}:H4T1(0.6)^{d}:Li^{+}(0.18)^{e}/$	16.88	0.75	53	6.7 ± 0.1	2.8	170
MoO ₃ /Ag						

^{*a*} All the values represent averages from fifteen 0.04 cm² devices on a single chip. ^{*b*} Device structure: ITO/ZnO (20 nm)/active layer (150 nm)/MoO₃/Ag. ^{*c*} PP represented P3HT:PC₆₁BM (PP) (1 : 1 w/w) with thermal annealing at 150 °C for 10 min and PBP represented PBDTTT-C-T:PC₇₁BM (PBP) (1 : 1.5 w/w) with 3% DIO additive. ^{*d*} The values in the parentheses presented the concentrations (mg mL⁻¹) of H4T1 with different block ratios in the active layer solutions. ^{*e*} The values in the parentheses presented the concentrations (mg mL⁻¹) of Li⁺ in the active layer solutions. All the MoO₃ layers were 6 nm.

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PEDOT:PSS as HTL or the introduction of P3HT-*b*-P3TEGT or P3HT-*b*-P3TEGT:Li⁺ in the P3HT:PC₆₁BM active layer at an applied voltage of 1 V, respectively, when compared with the device without HTL. The results indicated that the incorporation of P3HT-*b*-P3TEGT or P3HT-*b*-P3TEGT:Li⁺ into the active layer would form a self-assembled HTL interlayer, resulting in the increase of the hole mobility and a more balanced charge transport in the devices. On the other hand, the self-assembled interlayer could also reduce the thickness of the device, reduce contact resistance and increase the electrical conductivity of the inverted devices, which are beneficial in improving the device efficiency (the relevant results of R_s and R_{sh} are shown in Tables 1 and S2,† respectively).

The photovoltaic performance of the devices based on ITO/ ZnO/active layer/Ag (or MoO₃/Ag) inverted device structures by introducing P3HT-b-P3TEGT or P3HT-b-P3TEGT:Li⁺ into the P3HT:PC₆₁BM or PBDTTT-C-T:PC₇₁BM active layers was studied. Devices were fabricated by spin-casting the active layer blends from the DCB solution atop the ZnO interface layer on glass substrates patterned with indium tin oxide (ITO), followed by the deposition of 90 nm Ag or MoO₃ (6 nm)/Ag (90 nm) anode electrode. The overall ratio of polymer donors and fullerenes remained at 1 : 1 (wt%) with a fixed concentration of P3HT at 20 mg m L^{-1} . The detailed information of the device fabrication and characterization is provided in the ESI.† Current densityvoltage (I-V) characteristics of the devices measured under AM 1.5G irradiation are shown in Fig. 7. Furthermore, the resulting J_{sc}, V_{oc}, FF and PCE values, determined from the J-V curves, are summarized in Tables 1 and S2.† We could observe a better device performance when employing the MoO₃/Ag anode electrode mainly due to the high conductivity of MoO₃ and decrease of the energy level (Fig. 6) and surface defects of MoO₃ by interfacial modification between the triethylene glycol side chains of diblock copolymer and MoO₃. Firstly, the P3HT and PC61BM systems blended with P3HT-b-P3TEGT or P3HT-b-P3TEGT:Li⁺ were selected as the active layer components. We optimized the device properties by changing the concentration of P3HT-b-P3TEGT and found that the optimized concentration is 1.2 mg mL⁻¹, 0.6 mg mL⁻¹ and 0.3 mg mL⁻¹ for H8T1, H4T1 and H2T1, respectively, in this sequence (Tables 1 and S2[†] and Fig. 7). When the amount of P3HT-b-P3TEGT exceeded the optimized concentration, FF and Jsc largely decreased due to the excessive segregation of P3HT-b-P3TEGT polymer chains at the top of the active layer, thus interrupting the holes transport. Then, Li⁺ was added into the P3HT:PC₆₁BM:P3HT-*b*-P3TEGT system at the optimized concentration of P3HT-b-P3TEGT. Surprisingly, relative to the ITO/ZnO/P3HT:PC61BM/ PEDOT:PSS/Ag device, the incorporation of P3HT-b-P3TEGT or P3HT-*b*-P3TEGT:Li⁺ in the active layer increased J_{sc} , V_{oc} and FF, and consequently, the PCE enhanced from 2.3% to 3.4% for the ITO/ZnO/P3HT:PC₆₁BM:H4T1/Ag device and 3.6% for ITO/ZnO/ P3HT:PC₆₁BM:H4T1:Li⁺/Ag. Encouragingly, the PCE of the device could further be boosted to 3.4%, 3.9% and 2.6% for H8T1, H4T1 and H2T1 addition in ITO/ZnO/P3HT:PC61-BM:P3HT-b-P3TEGT/MoO₃/Ag device structures, and even 3.9%, 4.2% and 3.9% for H8T1:Li⁺, H4T1:Li⁺ and H2T1:Li⁺ addition in ITO/ZnO/P3HT:PC₆₁BM:P3HT-*b*-P3TEGT:Li⁺/MoO₃/Ag device structures, respectively.

The EQE values for the devices based on ITO/ZnO/ P3HT:PC₆₁BM:P3HT-*b*-P3TEGT (or P3HT-*b*-P3TEGT:Li⁺)/Ag (or MoO₃/Ag) were over 70% in the range of 450 nm to 625 nm, which were much higher than the ITO/ZnO/P3HT:PC₆₁BM/



Fig. 7 J-V curves of the PSCs based on P3HT:PC₆₁BM (PP) with PEDOT:PSS as the anode buffer layer or different H4T1 concentrations (from 0 to 1.0 mg mL⁻¹) and H4T1 (0.6 mg mL⁻¹):Li⁺ (0.18 mg mL⁻¹) self-assembled buffer layer following (a) without and (b) with 6 nm MoO₃ layer under illumination of AM 1.5G, 100 mW cm⁻² (c) PSCs based on PBDTTT-C-T:PC₇₁BM (PBP) (1 : 1.5 w/w, 3% DIO additive) with H8T1 : Li⁺, H4T1 : Li⁺ and H2T1 : Li⁺ anode buffer layers with MoO₃ layer under illumination of AM 1.5G, 100 mW cm⁻².



Fig. 8 External quantum efficiency spectra of the PSCs based on (a) $P3HT:PC_{61}BM$ (PP) and (b) $PBDTTT-C-T:PC_{71}BM$ (PBP) with different selfassembly anode buffer layers, (c) the total absorption spectra in similar devices with different interfacial layers, followed by a 6 nm MoO₃ layer on the interfacial layer surface measured in the reflection geometry (inset shows the device structure), (d) the normalized PCEs for inverted BHJ PSCs with PEDOT:PSS, P3HT-*b*-P3TEGT and P3HT-*b*-P3TEGT:Li⁺ anode interfacial layer, followed by MoO₃ layer as a function of storage time in air under ambient conditions.

PEDOT:PSS/Ag device (Fig. 8). Moreover, the lower response at short wavelengths may originate from the vertical dispersion of the active layer components and the reflection mode from the cathode electrode, resulting in more light absorption of the donor material. The EQE results agreed well with the J_{sc} results. On the other hand, the enhancement in J_{sc} of BHJ PSCs could be attributed to the greater light reflection and the UV-filter effect imposed by the P3HT-b-P3TEGT:Li⁺ interfacial layer on the active layer surface of the device, indicating that there was a strong optical interference effect induced by P3HT-b-P3TEGT:Li⁺ (Fig. 8). Moreover, the increase of V_{oc} was attributed to the better interfacial contact between the active layer and Ag (or MoO₃/Ag) anode electrode because P3HT-b-P3TEGT or P3HT-b-P3TEGT:Li⁺ could exhibit vertical phase separation into the top of the active layer acting as the buffer layer. The ideal vertical component distribution morphology of the active layer originating from the driving force of P3HT-b-P3TEGT or P3HTb-P3TEGT:Li⁺, which spontaneously segregated on the surface of the active layer during the spin-coating process, could increase the charge transport and collection efficiency, and consequently, enhance J_{sc} and V_{oc} of the devices. In addition, it should be noted that we could observe hysteresis effect in the J-V curves of devices with the addition of Li ions. While testing the J-V curves of devices with the addition of Li ions, it exhibited normal behavior at first, but degenerated immediately in succeeding tests; however, it exhibited normal performance again after a period of time.

Overall, the improvement of the photovoltaic performance of the PSCs by introducing P3HT-b-P3TEGT or P3HT-b-P3TEGT:Li⁺ into the active layer should benefit from better ohmic contact, higher electrical conductivity, the formation of interfacial modification and the vertical phase separation morphology induced by the spontaneous migration of P3HT-b-P3TEGT to the active layer surface. The research paved a way for the further development of PSC BHJ solar cells with high efficiency by introducing diblock copolymer with triethylene glycol side chains into the active layer system. Therefore, we further investigated the effect of P3HT-b-P3TEGT or P3HT-b-P3TEGT:Li⁺ on other active layer systems. The second type of device was based on a low-band gap 2D-conjugated polymer poly(4,8-bis(5-(2-ethyl-hexyl)-thiophene-2-yl)-benzo[1,2-b:4,5-b']dithiophene-alt-alkylcarbonylthieno[3,4-b]thiophene) (PBDTTT-C-T)56-58 and the [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM), i.e. a PBDTTT-C-T/ PC71BM active layer system, applying the same inverted device structure. Interestingly, the devices also showed enhanced photovoltaic performance and the PCE could reach 6.9%, 7.3% and 7.1% after adding H8T1, H4T1 and H2T1, and 6.4%, 6.7% and 6.6% after adding H8T1:Li⁺, H4T1:Li⁺ and H2T1:Li⁺, respectively, from 4.7% of the pristine device without any buffer layers (Tables 1 and S2[†] and Fig. 7). It should be mentioned that the PCE decreased for the PBDTTT-C-T/PC71BM system upon adding P3HT-b-P3TEGT:Li⁺ when compared with the same system blended with P3HT-b-P3TEGT. The detailed mechanism is not very clear at the present stage. The EQE data are presented in Fig. 8. Observing from the AFM images of PBDTTT-C-T:PC₇₁BM, PBDTTT-C-T:PC71BM:P3HT-b-P3TEGT and PBDTTT-C-T:PC71BM:P3HT-b-P3TEGT:Li⁺, an effective phase separation of the donor/acceptor appeared on the active layer surface after introducing P3HT-b-P3TEGT into the active layer, while larger and more orderly nanofibers appeared after introducing P3HT-b-P3TEGT:Li⁺ (Fig. S8[†]). Furthermore, the incorporation of P3HT-b-P3TEGT or P3HT-b-P3TEGT:Li⁺ into the active layer and the formation of a self-assembled buffer layer between the active layers and anode electrodes during the spin-coating process could promote the stability of the inverted devices (Fig. 8). All the devices (no encapsulation) were located in air continuously at room temperature and the PCEs remained above 85% of the original value for P3HT-b-P3TEGT, 75% for P3HT-b-P3TEGT:Li⁺ and 10% for PEDOT:PSS even after exposing to air for more than 4 weeks, no matter whether the devices were with or without the MoO₃ layer.

Conclusions

The device performance and stability could be enhanced by the application of polythiophene conjugated diblock copolymers containing polythiophene derivative segments whose side chain was triethylene glycol (P3HT-b-P3TEGT) or P3HT-b-P3TEGT chelated with Li⁺ (P3HT-b-P3TEGT:Li⁺) in the active layer system. Due to the spontaneous vertical migration of P3HT-b-P3TEGT or P3HT-*b*-P3TEGT:Li⁺ to the surface of the active layer during the spin-coating process and the formation of a selfassembled anode buffer layer, a vertical distribution of the components in the active layer and the orderly arrangement of donor polymer chains were obtained at the same time, which was the ideal BHJ morphology allowing holes and electrons moving to the anode and cathode electrode more efficiently, respectively. In addition, the self-assembled anode buffer layer could provide the interfacial modification between the active layer and Ag (or MoO₃/Ag) anode electrodes, enhance the WF of the anode electrode, increase the electrical conduction of the device, and consequently, remarkably improve the device performance and stability. The PCE increased to 7.3% for devices based on PBDTTT-C-T:PC71BM. Such research paved a way for the further development of highly efficient and stable PSC BHJ solar cells by simply introducing conjugated diblock copolymer with a triethylene glycol side chain into the active layer system.

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