

Novel cross-linked films from epoxy-functionalized conjugated polymer and amine based small molecule for the interface engineering of high-efficiency inverted polymer solar cells

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ABSTRACT

The modification of metal/metal oxide electrode is of great importance to the performance of inverted organic optoelectronic devices. Cross-linked films provide good chance to modify the metal/metal oxide electrode and enable the fabrication of high-performance multi-layer organic optoelectronic devices due to its superior ability to resist solvent erosion. However, most of the reported methods to prepare cross-linked films are suffering from harsh processing conditions such as high-temperature thermal treatment or long-time UV radiation. Here, we develop novel robust cross-linked thin films which are prepared from an epoxy-functionalized conjugated polymer (PFEX) and an amine-based small molecule (TAA). The cross-linking processing can be realized under mild heating due to the highly-efficient amine-epoxide reaction, and the resulting cross-linked films show good solvent resistibility. Moreover, the cross-linked films showed large tolerance with the composition of PFEX and TAA, which provides opportunity to modify the metal/metal oxide electrodes in a wide range using the cross-linked films. The modified indium tin oxide (ITO) using the cross-linked films show much lowered work function and hydrophobic property than pristine ITO, which indicates great potential application in inverted organic optoelectronic devices. Inverted polymer solar cells (IPSCs) using the modified ITO show remarkable enhanced power conversion efficiency (9.4%) than those with pristine ITO (6.8%). Our design and preparation of the novel cross-linked films and the finding on the correlation between cross-linked film and photovoltaic performance will be useful to design and prepare high-performance cross-linked films for inverted organic optoelectronic devices.

1. Introduction

Polymer solar cells (PSCs) have attracted considerable attention due to their advantages of light weight, flexibility and low-cost solution processing techniques [1–5]. The performance of PSCs can be optimized by rational design of conjugated polymers both for active layer and electron/hole transport layers (ETLs/HTLs) [6–19]. Another strategy to optimize the device performance is to design novel device architectures, such as inverted architectures and multi-layer architectures, which can optimize the morphology of the active layer and modulate the light absorption in the photovoltaic device [20–28]. For example, inverted polymer solar cells (IPSCs) with indium tin oxide (ITO) as the electron collection electrode showed higher device stability than the traditional

devices with low work function metals as cathode [29]. Moreover, the inverted structure can also enable favorable phase distribution of the donor and acceptors in the active layer [30–32]. However, the work function of ITO (around 4.8 eV) [33] is too high to collect electron from the active layer since the lowest unoccupied molecular orbital energy level (E_{LUMO}) of the electron acceptors are around -3.8 eV to -4.1 eV. Therefore, it is of great importance to decrease the work function of ITO to reach a good energy alignment with the electron acceptors [29]. Self-assembling monolayer/multilayer of small molecules or polymers onto the surface of ITO can effectively lower the work function of ITO and improve the electron collection in IPSCs [20,34–37]. Another highly-effective strategy to modify ITO for IPSCs is to insert a cathode interlayer between ITO and active layer to achieve good energy

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alignment, interface contact and electron collection. ZnO can serve as excellent cathode interlayer for IPSCs due to its low cost, good transparency and high mobility [38,39]. However, the process of ZnO requires high-temperature annealing and high-performance ZnO ETLs often need pre-/post-treatment such as doping and surface modification [39]. Conjugated polymers, which can be deposited via low-cost solution processing without annealing can also act as excellent cathode interlayer for IPSCs. Moreover, the varied structures of conjugated polymers can endow cathode interlayers extra functions (such as interface doping [24,40–42], tuning the phase separation of active layer [23]) and improve the photovoltaic performance. As most of the conjugated polymers for active layers are processed from non-polar solvents (such as chloroform, chlorobenzene, toluene etc.), it is quite reasonable to develop conjugated polymers that can withstand the erosion from the solvents for the fabrication of upper layer.

Cross-linking strategy provides one effective method to prepare insoluble thin films for the fabrication of multi-layer thin films [36,42–57] by precluding the interface miscibility between different layers [46,52–54]. Up to now, a large amount of cross-linking groups (such as oxetane [55], alkyl-bromide [56], azide [57] and vinyl groups [58] etc.) and their corresponding crosslinking methods have been developed. Generally, the crosslinking process is conducted in various conditions such as high-temperature thermal treatment, long-time UV radiation or addition of photo-acid generator. One drawback of the above crosslinking methods is that the harsh condition for cross-linking reaction may bring about some unfavorable effects on the materials and devices [57,58]. For example, the additive may be detrimental to the device performance, leading to significantly reduced generated current density output [59]. Besides, the long-time UV radiation may also cause the degradation of the conjugated polymers [60]. Therefore, it is quite necessary and important to develop highly efficient cross-linking strategy which can be conducted under mild condition and exempt the potential damage from high-temperature treatment, UV radiation and additives. Unfortunately, up to now, the highly efficient cross-linked strategy under mild conditions for the application of high-performance IPSCs is rare. We previously reported a fast UV-cross-linked polymer thin film, crosslinking alkylamine-functionalized polymer can be rapidly crosslinked by UV-curing based on the “click” chemistry of alkyne end-groups and the addition of 1,8-octanedithiol [23]. To further develop cross-linking strategy and explore the potential application of the cross-linked films in high-performance organic optoelectronic devices, herein, we developed novel cross-linked thin films from a tailored-made epoxy-functionalized conjugated polymer (PFEX, shown in Fig. 1) and amine based additive-TAA (shown in Fig. 1) for the interface engineering of IPSCs. PFEX, with epoxy side chain, can react with TAA via highly-efficient amine-epoxide reaction [61,62], resulting a highly crosslinking insoluble polymer network PFEX-TAA. Moreover, the composition of PFEX and TAA can be varied in a large range, leading to cross-linked thin films with different

modification capability to metal/metal oxide electrodes, which provide a tool to easily tune the properties of the cross-linked films. IPSCs with the cross-linked films delivered much higher efficiency than those without the cross-linked films. Of particular interest is that the device performance is positively correlated with amine density of the cross-linked film. Our design of the novel cross-linked films and their applications in the high-performance IPSCs will provide insights and inspiration to the design of novel and high-performance cross-linked films for high-performance opto-electronic devices.

2. Results and discussion

2.1. Synthesis and characterization of PFEX

The synthetic route of epoxy-functionalized conjugated polymer-PFEX is shown in Scheme 1 and the detail of the experimental procedure is shown in SI. Firstly, the dibromofluorene derivative, 2,7-dibromo-(9,9-diyl)bis(ethan-1-ol)-9H-fluorene (a2) was synthesized from 2,7-dibromofluorene using two-step reactions provided by the reported procedures [63]. And then a2 was converted to compound (2,7-dibromo-9,9-di(bis(ethane-2,1-diyl)bis(oxy)bis(methylene))bis(oxirane))-9H-fluorene (M1) by a nucleophilic substitution reaction with 1-bromo-2,3-epoxypropane. Finally, a standard palladium-catalyzed Suzuki polymerization between M2 (2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene) [64] and M1 gives the target polymer PFEX in a good yield of 80%. The resulted PFEX is readily soluble in non-polar solvent such as chloroform, toluene and tetrahydrofuran, which render the formation of high-quality film via solution casting.

The weight average molecular weight (M_w) and number average molecular weight (M_n) were recorded from a Gel permeation chromatography (GPC) where linear polystyrene as the standard and THF was used as the eluent. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of PFEX were estimated to be 57 kDa and 21 kDa, thus the polydispersity index (PDI) was calculated to be 2.72. PFEX was firstly characterized by ^1H and ^{13}C NMR using CDCl_3 as deuterated solvent. The ^1H and ^{13}C spectra of monomer M1 were also recorded for comparison. In the ^1H NMR spectra (shown in the Fig. 2), the ^1H chemical shifts of epoxy groups [65] in M1 are located in the range from 2.3 ppm to 3.3 ppm. It can be observed that two sharp peaks (H_1 , H_2) are located in 2.42 ppm and 2.68 ppm, which are attributed to the signals of hydrogen in the end carbon of epoxy group [66]. These two typical characteristic peaks of epoxy groups are the same with that in the reported reference, indicating the successful preparation of M1 [66]. The ^1H signals of H_2 , H_3 , H_4 and H_5 in the epoxy groups of PFEX slightly shifted to the lower field and delivered blunt and broaden peaks due to the effect from the π -conjugated backbone. Fortunately, the ^{13}C NMR spectrum of PFEX gives very nice peaks of the epoxy groups as well as the M1. The chemical shifts of ^{13}C (a, b, c, d) of epoxy groups in PFEX are located in 44.3 ppm, 50.6 ppm, 67.5 ppm and 71.4 ppm, respectively, which are almost the same with that in M1 (a, 44.2 ppm; b, 50.4 ppm; c, 67.0 ppm; d, 71.5 ppm), indicating the successful preparation of polymer PFEX.

PFEX was further characterized by FT-IR spectroscopy in powder state. A mixture powder of M1 and 2,7-dibromo-9,9-dioctyl-9H-fluorene (F8Br) was also recorded to achieve a directly comparison between the monomers and PFEX. As shown in Fig. 3, in the FT-IR spectrum of PFEX, the typical characteristics of C-H stretching vibrations in epoxy groups lies at about 3055 cm^{-1} and 2998 cm^{-1} , which are almost the same with that in M1 [67]. The C-O stretching vibrations in epoxy groups [67,68] of PFEX are located at 1252.67 cm^{-1} , 910.52 cm^{-1} and 850.04 cm^{-1} , while C-O stretching vibrations in epoxy groups of M1 showed almost the same wavenumbers at 1253.03 cm^{-1} , 910.15 cm^{-1} and 853.22 cm^{-1} , indicating the consistency of the epoxy groups in M1 and PFEX.

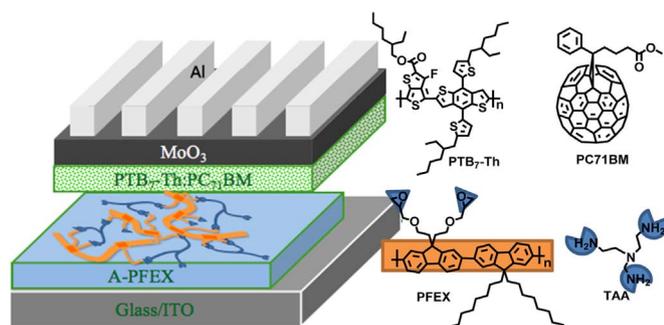


Fig. 1. The device architecture of the IPSC and the molecular structures of PTB₇-Th, PC₇₁BM, PFEX and TAA.

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