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Highly efficient polymer solar cells with PTB7-based narrow band-gap conjugated polyelectrolytes as cathode interlayers: Device performance dependence on the ionic pendants

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ABSTRACT

Narrow band-gap conjugated polyelectrolytes (NBGCPs) combine the advantages of narrow band-gap conjugated polymers and polyelectrolytes. However, they are limited reported and seldom used in polymer solar cells (PSCs). Herein, we design and synthesized two PTB7-based NBGCPs, cationic PTB7-NBr and zwitterionic PTB7-NSO_3, as cathode interlayers (CILs) in conventional PSCs. Compared to poly [4,8-bis(2-ethylhexyloxyl)benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl-*alt*-ethylhexyl-3-fuorothithieno[3,4-*b*]thiophene-2-carboxylate-4,6-diyl] (PTB7), both PTB7-NBr and PTB7-NSO_3 have similar absorption while PTB7-NBr has a higher HOMO level than PTB7 and PTB7-NSO_3. With PTB7-NBr and PTB7-NSO_3 as CIL and Al as cathode, the devices both exhibited high efficiencies. The optimal power conversion efficiencies (PCEs) of PTB7-NBr device and PTB7-NSO_3 device are about 9%. However, PTB7-NBr devices are less sensitive to the CIL film thicknesses and the PCEs of PTB7-NSO_3 device decrease sharply when the thickness of PTB7-NSO_3 over 3 nm. What's more, when the devices with an Ag cathode PTB7-NBr exhibits a much better interfacial modification than PTB7-NSO_3. Ultraviolet photoelectron spectroscopy (UPS) indicate that the work functions of PTB7-NBr and PTB7-NSO_3 film on Al are identical while on Ag they are different. We suggest the insensitivity to CIL thickness and good performance for Ag device of PTB7-NBr devices are attributed to the bromide anions in PTB7-NBr. The report on PTB7-based NBGCPs broads the types of organic cathode interfacial materials and is beneficial to the deep insight of ionic effect in electrolyte materials.

1. Introduction

Bulk heterojunction (BHJ) polymer solar cell (PSC) is a promising technology for conversion of solar energy directly into electrical energy [1–7]. In order to elevate the power conversion efficiency (PCE) of PSCs, a common and effective strategy is development of narrow band-gap conjugated polymers as donor materials in photoactive layer [8–14]. Another successful and versatile strategy is insertion of interlayers between photoactive layer and electrodes [15–18]. Among the reported interlayers, cathode interlayers (CILs) can not only tune energy level alignment of cathode and electrode but also reduce the work function (WF) of higher WF metal or indium tin oxides (ITO), which is benefit to both the performance and stability of PSCs [16,19–21].

Due to the solubility in polar solvents and possibility to fabricate multilayer devices by orthogonal solvent processing, conjugated polyelectrolytes (CPEs) have been extensively used in PSCs as interfacial materials [22,23]. CPEs are defined as conjugated backbone bearing ionic pendants. They combine the visible light-absorption and semiconducting properties of conjugated polymers and the properties related to electrostatic interactions of polyelectrolytes [24]. As cathode interlayers, the ionic pendants can form a strong interfacial dipole moments between photoactive

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layer and cathode electrode, and thus facilitate electron transport and extraction, improve the power conversion efficiency (PCE) of PSCs [25,26]. Besides, CPEs can also improve the device stability by adopting ITO or high WF metal as cathode electrode [27–29].

Narrow band-gap conjugated polymers are one class of the most successful absorption materials in PSCs [3,30,31]. Their absorption spectra can be fine-tuned to match the solar spectrum. Though both CPEs and narrow band-gap conjugated polymers have been widely used in PSCs, narrow band-gap conjugated polyelectrolytes (NBGCPs) were seldomly reported and researched [32–38]. Bazan and coworkers first reported cationic and anionic NBGCPs in 2013 year [32,33]. They presented that NBGCPs exhibited unique charge transporting and self-doping properties. By using NBGCP CPE-K as hole-transporting materials, they obtained highly efficient PSCs which was a general application in both polymer and small molecule BHJ solar cells [34]. Very recently, they even found CPE-K can be applied in perovskite solar cells to improve device stability in air [35]. Diketopyrrolopyrrole (DPP)-based polymers were another kind of NBGCPs which were successfully used in PSCs [36,37]. Because of the planar backbone and n-typed nature of DPP-based NBGCPs, it endowed good performances even PSCs with a thick film of CIL [38].

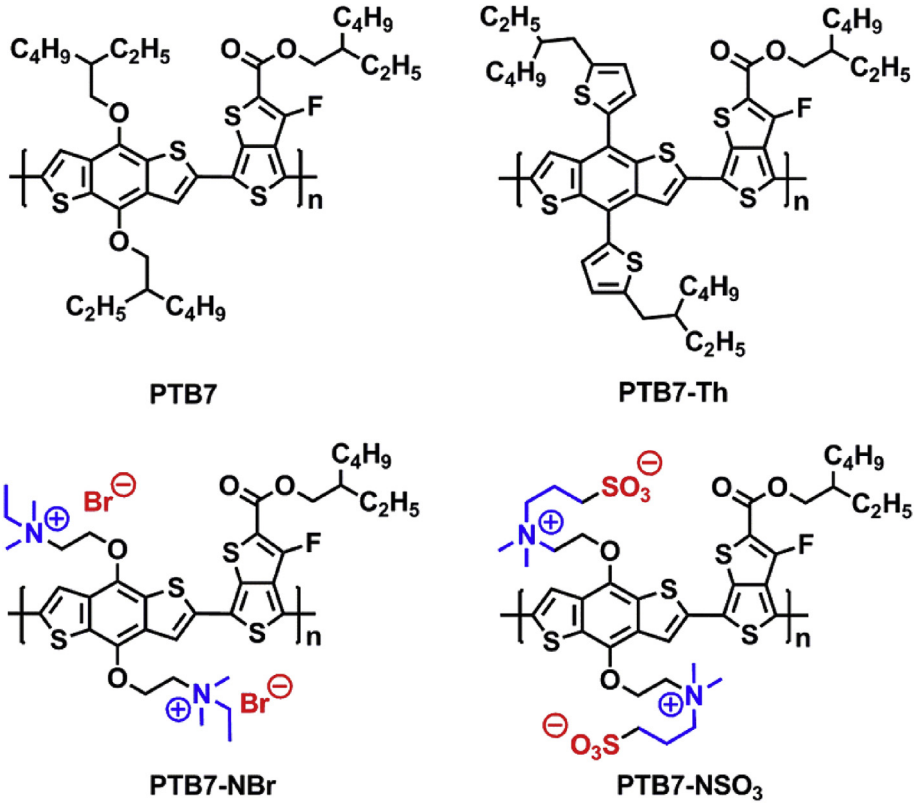
Poly[4,8-bis(2-ethylhexyloxyl)benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl-*alt*-ethylhexyl-3-fuorothithieno[3,4-*b*]thiophene-2-carboxylate-4,6-diyl] (PTB7) is a famous donor material for high efficiency PSCs [39]. In this article, we designed and synthesized two PTB7-based NBGCPs (Scheme 1), which possess a same backbone as PTB7 but bear quaternary ammonium cationic pendants (PTB7-NBr) [40] or zwitterionic pendants (PTB7-NSO_3). With PTB7 derivatives as donor polymers, the devices with PTB7-NBr and PTB7-NSO_3 as CILs both exhibited good performance and the conventional PSCs with PCE of 9.24% were obtained. To our surprise, though PTB7-NBr and PTB7-NSO_3 possess a same backbone, their photophysical properties were somewhat distinct. What's more, devices with PTB7-NBr or PTB7-NSO_3 as CIL had different replies to the CIL thickness and various cathode metals.

2. Experimental part

2.1. Materials and synthesis

The synthesis of PTB7-NBr and PTB7-NSO_3 is available in the Supporting Information. Donors PTB7 and poly[[4,8-bis[(5-ethylhexyl)thienyl]benzo[1,2-*b*;3,3-*b*′]dithiophene-2,6-diyl]-*alt*-ethylhexyl-3-fuorothithieno[3,4-*b*]thiophene-2-carboxylate-4,6-diyl] (PTB7-Th) were purchased from 1-Material Chemscitech Incorporated. (6,6)-Phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) and benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione were purchased from American Dye Source Incorporated and Derthon Optoelectronic Materials Science Technology Co LTD (Shenzhen, China) respectively. Other intermediate materials were purchased from Energy Chemical without further purification.

4,8-Bis(4-(2-(dimethylamino)ethoxy))benzo[1,2-*b*:4,5-*b*′]dithiophene (1): Benzo[1,2-*b*;3,3-*b*′]dithiophene-4,8-diol (1.00 g, 4.5 mmol) was dissolved in acetone (20 mL), followed by successive addition of K_2CO_3 (6.22 g, 45.0 mmol) and 2-chloro-*N*,*N*-dimethylethyl-1-amine hydrochloride (2.59 g, 18.0 mmol). The mixture was then refluxed for 2 day in a nitrogen atmosphere. After cooling down to room temperature, the mixture was filtered and washed with dichloromethane. The organic phase was combined and evaporated by rotatory evaporator. Column chromatography on silica gel using dichloromethane:methanol:triethylamine mixture as eluents yielded the compound 1 (1.50 g, 85%) as a light yellow solid. ^{1}H NMR (400 MHz, MeOH-d_4, δ, ppm): 7.55 (s, 4H), 4.37 (t, 4H,



Scheme 1. Chemical structures of the donor polymers and NBGCPs.