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Enhancement of the air-stability and optimization of V_{OC} by changing molecular conformation of polyelectrolytes

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ABSTRACT

Three conjugated polyelectrolytes(CPEs) based on thiophene, thieno[3,2-b]thiophene, and 2,2'-bithiophene were designed and synthesized. The CPEs were successfully incorporated into polymer solar cells as pH-neutral hole-transporting layer(HTL) via solution process. The interfacial dipole and work function(WF) of CPE-coated ITO were controlled by the dipole moment of the polymer, which was in turn determined by the stereochemical properties of the molecular structure. CPE-coated ITOs showed sequentially stronger dipole moments due to an increase in the electrostatic repulsion in the molecules. The PCE of device with PFT as the HTL was maintained accompanied by 16% decrease when PEDOT:PSS-based device decreased over 50%.

Introduction

In the past decades, polymer solar cells (PSCs) with the bulk heterojunction (BHJ) structure have drawn considerable interest as a promising clean energy source [1–3]. PSCs offer the potential advantages of being lightweight, flexible, and amenable to large-scale production by solution processing. To achieve high-performance PSCs, molecular design of the active materials to optimize the chemical and structural parameters has recently emerged as a major research area [4–6]. Using this approach, power conversion efficiencies (PCEs) of PSCs exceeding 10% have been achieved for single-junction inverted PSCs [7,8]. The rapid development of PCEs has been driven by the development of novel electron-donating and electron-accepting materials. However, the need for enhanced PCE and device stability remains a topical issue [9].

Morphology optimization and interface engineering of BHJ solar cells are also fundamentally important areas of interest. Significant effort has been devoted to the interface engineering of devices, suggesting that the performance and aging of the device are not only dependent on the active layer, but are also governed by the interface with the electrode [10–12]. Interfacial layer materials have played a critical role in enhancing the performance of PSCs. In PSCs, the interfacial layers help form the ohmic contact between the electrodes and active layers, which is of great importance for charge transport and charge collection. At present, developing new interfacial materials has become an effective way to improve the photovoltaic performance of PSCs [13].

In particular, the hole-transporting layer (HTL) between the active layer and conductive indium tin oxide (ITO) electrode of conventional PSCs critically influences the performance and stability of the PSCs [14–16]. Only a few materials have been successfully used as HTLs in PSCs, such as poly(3,4-ethylenedioxy thiophene):(styrenesulfonate) (PEDOT:PSS), MoO_3, WO_3, and V_2O_5 [17,18]. PEDOT:PSS is the most widely employed HTL material for PSCs because of its solution processability, suitable work function (WF), sufficient conductivity, and high optical transparency in the visible–near infrared region. However, PEDOT:PSS is highly acidic and hygroscopic. Furthermore, the strong electrical anisotropy of spin-coated PEDOT:PSS layers, originating from their lamellar structures, often limits charge collection in PSCs [15,16,19,20]. Specifically, this anisotropy determines the chemical instability between the active layer and electrodes in the long term.

It is well known that the stability and large-scale fabrication of PSCs are the two keys to eventual industrialization of PSCs. To meet the demands for industrializing PSCs, conjugated polyelectrolytes (CPEs) are recognized as ideal interfacial materials [21]. CPEs generally consist of three components: the π-conjugated backbone (hydrophobic), the side chains (hydrophobic), and the substituents such as polar/ionic functional groups (hydrophilic). The ionic functional groups are the major components that determine the properties such as the solubility in polar solvents, WF of electrode, and interfacial dipole interactions related to the

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series resistance, internal built-in voltage, and hole-extraction properties. It is conventionally accepted that the strength, charge selectivity, and direction of the interfacial dipole moment in CPEs are determined by the nature of ionic end-groups. A few researchers like Chen, Bazan, and Lee reported the synthesis of various cationic/anionic CPEs with various polar side chains using an identical backbone [22–24]. When two of these CPEs with identical backbones were applied as the cathode interlayer in PSCs, differences in the interfacial dipole formed by the CPEs arose from differences in the charge, counter-ions, and the pendant groups of them [25]. In the previous studies, the structure–activity relationship between the π-conjugated backbone and the interfacial dipole was not considered. In recent studies, it was reported that the atoms in the side chain or main backbone play a major role in changing the direction and strength of the electric dipole at the interface between the metal electrode and CPE [26,27]. Additionally, variation of the atoms in the side chain or backbone led to broad and stable WF tunability. However, no effective way to modulate the dipole strength was suggested in these studies. Thus, research has been devoted to the development of CPEs by variation of the polymeric structures, including the conjugated backbone [28]. The dipole moments of polymers have long been studied, and the results of experimental studies have demonstrated that the dipole moment of isotactic polymers may be different from that of syndiotactic polymers [29,30] because the conformation of the molecular units should depend on the stereochemical constitution of the chain and should affect the dipole moments of polymer.

In this study, we present the design and synthesis of three alcohol-soluble CPEs based on thiophene, thieno[3,2-b]thiophene, and 2,2'-bithiophene (designated as PFT, PFtT, and PFbT, see Scheme 1). Utilization of the CPEs (by dissolution in methanol) as HTLs instead of PEDOT:PSS is demonstrated. The strength and direction of the dipole moment of the polymer are determined and the effect of the structure of the backbone is analyzed stereochemically. The dipole moment and WF of the CPE-coated anode are controlled based on the number and dihedral angle of the heteroatoms in the polymer backbone. The surface structure of the CPE films is characterized by ultraviolet photoelectron spectroscopy (UPS), atomic force microscopy (AFM) and external electrostatic force microscopy (EFM) analysis. To determine the effects of the structural conformation of CPE, the surface energy, energy level, and hole mobility are investigated. The results demonstrate the importance of selecting a proper π-conjugated monomer with optimal electrical and structural properties for use as the HTL in PSCs. A photo-conversion efficiency (PCE) as high as 7.3% was obtained for the PSCs due to slight improvement of the short-circuit current (J_{sc}) by replacement of PEDOT:PSS with PFT. More importantly, the long-term stability was improved using CPEs as a HTL. Specially, the initial PCE of PFT-based device was maintained accompanied by 16% decrease when PEDOT:PSS-based device decreased over 50%.

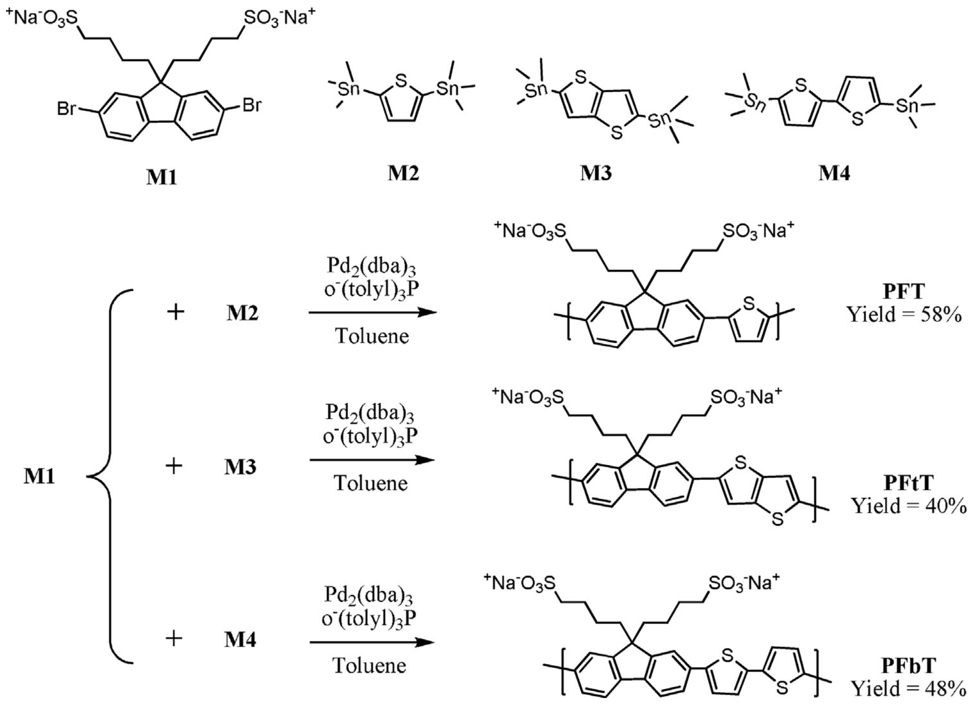
Experimental

Materials

All reagents and starting materials were purchased from chemical companies such as Alfa Aesar, Tokyo Chemical Industry (TCI) Co., Ltd., and Sigma Aldrich and used without additional purification. Sodium 4-(2,7-dibromo-9-(4-sulfonatobutyl)-9H-fluoren-9-yl)butyl sulfite (M1) was synthesized by following modified procedures from the literature [24]. Poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-C71 ($PC_{71}BM$) were acquired from 1-Material Products and were used as-received. Commercial poly[(9,9-bis(3'-(*N,N*-dimethylamino) propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) was also purchased from 1-Material Products and was utilized as the electron transport layer (ETL).

General polymerizations

The monomers, M1 (0.64 g, 1.0 mmol) and M2 (or M3 or M4) (1.0 mmol) (where M2–M4 are stannated thiophene, thieno[3,2-b]



Scheme 1. Synthetic routes of CPE copolymers.