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Water-soluble polythiophenes as efficient charge-transport layers for the improvement of photovoltaic performance in bulk heterojunction polymeric solar cells

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ABSTRACT

Water-soluble regioregular poly{3-[(6-sodium sulfonate)hexyl]thiophene} (PT6S) and poly{3-[(6-trimethylammoniumbromide)hexyl]thiophene} (PT6N) have been synthesized and employed both as photoactive layers for the assembling of "green" bulk-heterojunction organic solar cells and as charge-collection layers in a cell with "classic" architecture. While the photovoltaic performances obtained with the two aforementioned polymers were lower than the reference cell, their latter use allowed to notably increase the inherent J-V properties, leading to a considerable enhancement in the overall photovoltaic output. The power conversion efficiency of the optimized multilayer BHJ solar cell reached 4.78%, revealing a higher efficiency than the reference cell (3.63%).

1. Introduction

Significant progress in the field of organic materials for electronic applications has been recently achieved by developing processable and conducting polymers. π-Conjugated polymers (CPs), characterized by a backbone with a delocalized electronic structure, are interesting materials which combine semiconducting properties with light-harvesting features, making them important components for optoelectronic devices, such as light-emitting diodes, field effect transistor and photovoltaic cells [1]. Moreover, although the photovoltaic electricity production is actually dominated by silicon technology, organic solar cells (OSCs) present some potential advantages over the most employed technology, such as light weight, flexibility and the possibility to fine-tune the optoelectronic properties by simply acting on the organic active material structure [2]. Currently, the most successful approach to build high-performance polymeric OSCs is the donor-acceptor bulk-heterojunction (BHJ) architecture. The photoactive layer of the cell is made of an intimate mixture of an electron-donor (ED) material (the semiconducting conjugated polymer, such as poly(3-hexylthiophene) (PT6H)) and a fullerene derivative (usually [6,6]-phenyl-C_{61}-butyric acid methyl ester, $PC_{61}BM$) acting as an electron-acceptor (EA). Both the components are deposited from a mixed solution using common organic solvents (generally chloroform or chlorobenzene) [3].

The photoactive layer is deposited over a wide range of substrates using solution-based methods, including printing techniques, spin-casting, roll-to-roll technology making the usage of these organic materials more and more cost-effective [4]. Recently, a 9.2% of photoconversion efficiency (PCE) has been obtained with a polymeric solar cell based on a fluorinated polythiophene derivative, making OSCs more competitive and performing for the rolling out of organic photovoltaic (OPV) technology in the wider mass market [5].

However, the production of OSCs by the current fabrication processes requires the consumption of large amounts of toxic chlorinated or aromatic organic solvents and some efforts have been made towards the study of large-scale environmentally friendly techniques involving the use of water-soluble conjugated polymers (WCPs) as photoactive components in the solar cells [6]. WCPs are generally composed of two main components: π-conjugated backbones and surfactant-like side chain substituents (i. e. amino, phosphate, carboxyl, sulfonic groups) that enhance the polymer solubility in polar solvents. WCPs have also been successfully employed to optimize both organic light-emitting diodes (OLEDs) and OPV devices by fabricating multilayer solar cells in which the water-soluble polymer can act as an electron-collection layer (ECL) or a hole-collection layer (HCL) which improves the electron

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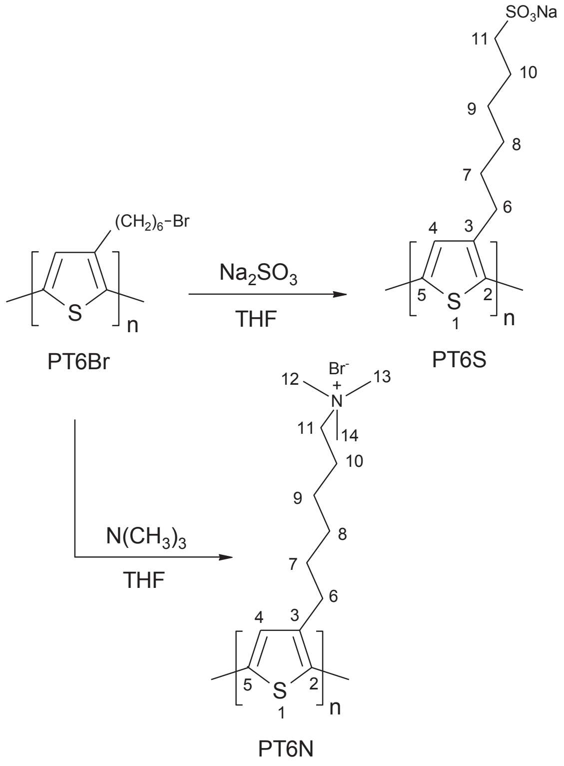
(hole) extraction and collection to the electrode [7,8]. It has been reported [9] that a thin film of an ECL polymer interposed between the photoactive blend and the Al electrode was able to double the efficiency of a PT6H:PC$_{61}$BM BHJ solar cell by restraining the penetration of Al atoms into the active layer. Moreover, the use of a thin layer of a cationic conjugated polymer between the active layer and the metal electrode can effectively increase the PCE of the solar cell, since the WCP is able, at the same time, to selectively transport electrons (while simultaneously blocking positive holes) and to suppress the diffusion and reaction between the metal electrode and the active layer components, acting as a chemical buffer layer [10,11]. On the other hand, interfacial optimization at the hole-collection electrode (HCE), usually ITO, has the same importance as that at the electron-collection electrode (ECE) in organic solar cell applications. Nowadays, PEDOT-PSS is the most employed HCL but it shows some drawbacks, since it is a composite material with a large ratio of non-conjugated polymer [6] and has a marked tendency to give inhomogeneous films especially when deposited from its concentrated solutions. Anionic conjugated polymers such as sulfonate-substituted polytriphenylamine [12] and poly(vinylcarbazole) sulfonate lithium salt [13] have been reported as efficient substitute of commonly used PEDOT-PSS. In addition, the high solubility of WCPs in highly polar solvents is particularly suitable for fabricating multilayer devices without interface mixing through the deposition of different layers from orthogonal solvents [14] in order to preserve the chemical and morphological integrity of any single layer.

In this study, we wish to report the synthesis and characterization of two water-soluble polythiophenic polymers: poly{3-[(6-sodium sulfonate)hexyl]thiophene} (PT6S, Scheme 1) and poly{3-[(6-trimethylammoniumbromide)hexyl]thiophene} (PT6N) prepared through an efficient and straightforward procedure based on the post-functionalization of a regioregular polymeric precursor. Both the synthesized polymers have been completely characterized using spectrochemical and morphological analysis and used either as active-layer or interface layer materials in polymeric solar cells with a BHJ architecture.



Scheme 1. Synthesis of PT6S and PT6N.

2. Experimental

2.1. Materials

All reagents were purchased from Sigma-Aldrich Chemical Co. and used without further purification where not expressly indicated otherwise. All solvents used (HPLC grade) were dried and purified by normal laboratory procedures, stored over molecular sieves and handled in a moisture-free atmosphere.

The reference polymer for OSCs, that is, poly(3-hexylthiophene) (PT6H, HT dyads: 97%, Mn: 25.800 g/mol; PDI: 1.18), was synthesized according to Ref. [15].

2.2. Instrumentation

^{1}H and ^{13}C NMR were recorded on a Varian Mercury 400 spectrometer (400 MHz) using TMS as a reference. IR spectra were taken on KBr disks using a Perkin Elmer Spectrum One spectrophotometer. UV–Vis spectra were recorded on a Perkin Elmer Lambda 19 spectrophotometer using 10^{-5} M polymer solutions in spectroquality solvents in Suprasil quartz cuvettes (1 cm × 1 cm) or films on quartz slides. Fluorescence spectra were recorded by means of an Edinburgh FLSP 920 spectrofluorimeter using samples prepared as described for UV–Vis characterization. Molecular weights were determined by gel permeation chromatography (GPC) by using THF solutions on a Linear Instruments UVIS-200 apparatus operating at 254 nm, equipped with a Phenomenex Mixed bed column 5μ MXL type. The calibration curve was recorded using monodisperse polystyrene standards. Cyclic voltammetry (CV) measurements were made using a Pt electrode coated with a thin film of polymer deposed by casting from a water solution ($CHCl_3$ for PT6H), by means of a single compartment three electrodes cell in acetonitrile solution with nBu_4NBF_4 0.1 M as supporting electrolyte. The working electrode was a Pt disk, the counter electrode a Pt wire and the reference an aqueous saturated calomel electrode (SCE). The data were collected by an Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat at a potential scan rate of 100 mV/s.

A DSC TA Instruments 2920 was used for the thermal analysis by varying the temperature from –50 °C to 250 °C (−50 °C to 300 °C for PT6S blend) at a rate of 5 °C min^{-1} in a nitrogen atmosphere. A TGA TA Instruments 2050, operating under inert atmosphere, was used to determine the decomposition temperatures of the samples by heating from 30 °C to 900 °C at a scan rate of 10 °C min^{-1}. Elemental analysis was performed by Redox Laboratories Srl, Monza, Italy. SEM characterizations were carried out on a Phenom World ProX electronic microscope.

BHJ solar cells were prepared according to the following procedure: the ITO glass substrate (1 cm × 1 cm, surface resistance 20 Ω/sq) was etched on one side by using a 10% wt aqueous solution of HCl and heated at 60 °C for 15 min in order to obtain an area of 1.5 × 1 cm covered by indium tin oxide. The glass was then cleaned in an ultrasonic bath (Elmasonic S30H) using acetone and then treated at 60 °C for 20 min with a solution of aqueous NH_3 (0.8 M) and H_2O_2 (0.5 M), rinsed with distilled water, 2-propanol and dried with a nitrogen flow. The final resistance of the ITO glass was 12 Ω/sq. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid (PEDOT:PSS, 2.8 wt% dispersion in water, viscosity 20 cps) was diluted 1:1 v/v with 2-propanol, sonicated, filtered on a Gooch G2 and the resulting solution (viscosity 12 cps) deposited over the previously treated ITO glass by the doctor blading technique using a Sheen Instrument Model S265674, leaving only a small (0.5 × 0.5 cm) area uncovered at the opposite side of the previously etched area. The PEDOT:PSS film was heated in a Büchi GKR-50 glass oven at 130 °C for 2 h under vacuum (10^{-3} mmHg). A solution made by mixing 10 mg of polymer (PT6S, PT6N or the reference polymer PT6H), 10 mg of [6,6-phenyl-C$_{61}$-butyric acid methyl ester] (PCBM, SES Research, Texas, USA) in 1.5 ml of water