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Effect of the incorporation of an Ag nanoparticle interlayer on the photovoltaic performance of green bulk heterojunction water-soluble polythiophene solar cells

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ABSTRACT

Two water-soluble regioregular poly(3-alkylthiophene)s, incorporating aminic groups at the end of the side chains, have been synthesized using a post-polymerization functionalization procedure on a ω-bromine substituted polyalkylthiophene. The high solubility of the obtained polymers in water allowed for the preparation of "green" bulk heterojunction solar cells which reached a power conversion efficiency of 4.85% when $PC_{61}BM$ was used as electron-acceptor material. Improved optical absorption and photocurrent have been obtained by interposing a layer of Ag nanoparticles between the buffer and the photoactive layer, leading to a final power conversion efficiency of 5.51%.

1. Introduction

Organic photovoltaic solar cells have been widely studied over the past few years since this technology offers many desirable advantages, such as easy preparation, lightweight, flexibility, semi-transparency and, contrary to conventional Si-based solar cells, the possibility to obtain photoactive thin films over large areas with fast and cheap techniques, like roll-to-roll printing [1]. A lot of research work has been made since the first device created by Tang in 1986 [2], reaching a power conversion efficiency of about 1% with a two-layer organic photovoltaic cell composed of copper phtalocyanine and a perylene tetracarboxylic derivative. Nowadays, the most employed architecture for the fabrication of polymer photovoltaic solar cells is constituted by a bicontinuous interpenetrating network prepared by blending a conjugated polymer as electron-donor and a fullerene derivative as electron-acceptor leading to a composite called bulk heterojunction. Since then, the bulk hetrojunction architecture has become the standard architecture for polymer photovoltaic solar cells [3]. Many synthetic efforts have been focused on improving the final efficiency mainly acting on the development of low band-gap conjugated polymers [4] and the employment of new electron-acceptor materials [5,6]. Moreover, it has also been reported that processing conditions are as critical as material design for solution-cast polymer solar cells, since materials solubility strongly impact both device optimization and characterization [7]. Among conjugated polymers, polythiophene and its derivatives are the most examined electron-donor materials, owing to their excellent optical, electrical and electronic properties [8]. They exhibit tunable chromic and optoelectronic responses and different sensitivity to external conditions (pH, pressure, temperature, oxidizing and reducing agents, presence of selected ions) [9–12] thanks to the co-operative response of the conjugated chains even in the presence of small perturbations [13].

Among polythiophenes, poly(3-hexylthiophene) (P3HT) has received a great attention in the last years as electron-donor polymer for the preparation of the photoactive blend for bulk hetrojunction solar cells. Thanks to its band-gap of about 1.9 eV, which can be further reduced by decreasing the aromatic character of the polymer [14], P3HT-based solar cells usually show high external quantum efficiency (EQE) [15] which indicates a high number of charge carriers generated per incident photon absorbed on the photoactive blend and a final power conversion efficiency of

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the solar cell around 4–5%. This value can be further increased acting on the morphology of the active layer by means of thermal or solvent annealing during device fabrication [16]. The use of solvent additives (e. g. 1,8-octanedithiol [17], 1,8-diiodooctane [18], 1-chloronaphtalene [19]) can also be a valuable strategy to achieve a better crystallinity of the donor polymer and a control of the phase separations in the photoactive blend [20], positively acting on charge mobility, photocurrent and power conversion efficiency of the solar cell [21,22]. The morphology of polyalkylthiophene/fullerene blends can also be effectively tuned by inserting suitable functional groups at the end of the oligomethylenic solubilizing side chains, the latter being generally linked to the 3-position of thiophene rings. Moreover, the insertion of surfactant-like side groups can endow polythiophenes with high solubility in polar solvents, offering a series of advantages for the assembling of optoelectronic devices. In particular, water-soluble polythiophenes allow for the fabrication of multilayer devices without interface mixing by depositing the single layers from orthogonal solvents [23] and the interface layers can be inserted between the electrodes and the photoactive blend to further enhance the charge mobility necessary to extract and transport electrons and positive holes to the different electrodes [24].

In this work, we focus on the synthesis of two new polythiophene derivatives: poly[3-(6-diethylaminohexyl)thiophene] (PT6NEt) and poly[3-(6-pyrrolidinylhexyl)thiophene] (PT6Pir). The selection of these polymers takes into account of their chemical structure: a high degree of structural order (98% head-to-tail dyads linkage), the presence of a hexamethylenic side-chain group able, at the same time, to give processability to the polymer and electronically-separate the polyconjugated backbone from the inserted functional groups, which are two different aminic substituents. The aminic groups strongly enhance the solubility in water of the prepared materials.

Herein we also present a detailed structural and chemical characterization of the synthesized polymers and of their blends with $PC_{61}BM$, the latter being used as photoactive layers for the assembling of solar cells with the bulk heterojunction architecture. An improved external quantum efficiency and photocurrent is observed by inserting a thin layer of Ag nanoparticles between the polymer blend and the buffer layer (PEDOT-PSS), which can be ascribed to presence of localized surface plasmons of metallic nanoparticles in the excited state.

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.

2.2. Measurements

^1H and ^{13}C NMR were recorded on a Varian Mercury Plus (400 MHz) spectrometer using TMS as a reference. IR spectra were taken on Ge disks using a Perkin Elmer Spectrum One and a Bruker Alpha Platinum spectrophotometers. 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 using an Edinburgh FLSP 920 spectrofluorimeter on samples prepared as described for UV–Vis analysis. Molecular weights were determined by gel permeation chromatography (GPC) by using tetrahydrofuran (THF) solutions on a Linear Instruments UVIS-200 apparatus operating at 254 nm, equipped with a Phenomenex Mixed bed column 5μ MXM type. The calibration curve was recorded using monodisperse polystyrene standards. Elemental analysis was performed by Redox Laboratories Srl, Monza, Italy. A DSC TA Instruments 2920 was used for the thermal analysis by varying the temperature from −50 °C to 250 °C at a rate of 5 °C min^{-1} in a nitrogen atmosphere. A TGA TA Instruments 2050, operating both in air and 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}. Cyclic voltammograms were recorded using an Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat at a potential scan rate of 100 mV/s on polymer films deposited on Pt electrodes from water solutions. The working electrode (polymer coated Pt disk), the counter electrode (Pt wire) and the reference electrode (aqueous saturated calomel electrode) were immersed in an acetonitrile solution with nBu_4NBF_4 0.1 M as supporting electrolyte using a single compartment three-electrode cell. AFM measurements were made on a Burleigh Vista 100 atomic force microscope in a non-contact tapping mode using high resolution silicon-nitride tips. X-ray diffraction data of polymer films were recorded at room temperature by using a CuKα ($\lambda = 1.5406$ Å) radiation source (Philips PW 1050) and a Bragg-Brentano diffractometer (Philips PW 1710) equipped with a graphite monochromator in the diffracted beam. The 2θ range between 2.0 and 90.0° was scanned by 881 steps of 0.1° with a counting time of 15 s for each step. SEM characterizations were carried out on a Zeiss Evo 50EP Electronic Microscope.

BHJ solar cells were prepared according to the following procedure: the Indium Tin Oxide (ITO) glass substrate (1 cm × 1 cm, surface resistance 21 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 0.75 × 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 (0.25 × 1 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 (PT6NEt+ or PT6Pir+), 10 mg of [6,6-phenyl-C_{61}-butyric acid methyl ester] ($PC_{61}BM$, SES Research, Texas, USA) in 1.5 ml of distilled water was sonicated for 15 min, filtered on a PTFE septum (0.25 μm pore size) and deposited by doctor blading on the slide in order to cover the PEDOT:PSS layer. The sample was then annealed in the glass oven under vacuum (10^{-3} mmHg) at 120 °C for 15 min. Finally, a 50 nm thick Al electrode was deposited over the polymeric layer through a shadow mask using an Edwards 6306A coating system operating at 10^{-6} mmHg. The active area of the cell was 0.25 × 0.25 cm^2. The current-voltage characteristics were measured in air using a Keithley 2401 source meter under the illumination of an Abet Technologies LS150 Xenon Arc Lamp Source AM 1.5 Solar Simulator (100 mW/cm^2) calibrated with an ILT 1400-BL photometer. The structure of the final devices were: ITO (80 nm)/PEDOT:PSS (100 nm)/active layer (150 nm)/Al (50 nm). Layer thicknesses were measured using a Burleigh Vista 100 AFM in a non-contact tapping mode. The spectral response of the solar cells