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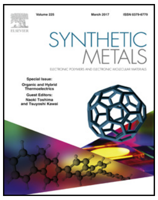

Well-designed poly(3-hexylthiophene) as hole transporting material: A new opportunity for solid-state dye-sensitized solar cells

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ABSTRACT

All solid-state dye-sensitized solar cells (ss-DSSCs) based on the reference **D102** organic dye and using poly(3-hexylthiophene) (**P3HT**) as hole transporting material were fabricated and compared to the most used 2,2′,7,7′-tetrakis-(N,N-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (**spiro-OMeTAD**). Power conversion efficiency of 4.78% was reached with **P3HT** *vs.* 3.99% with **spiro-OMeTAD**, which emphasizes that polythiophene derivatives remain serious alternatives to **spiro-OMeTAD** for efficient and low-cost photovoltaic energy conversion. Here, **P3HT** combining high regioregularity, medium-range molecular weight and narrow dispersity was targeted. The ability of those **P3HT** chains to form semicrystalline domains upon annealing leads to improved hole mobility, photocurrent collection and thus, device performance.

1. Introduction

The challenges stemming from dwindling fossil resources, global population increase and environmental issues require more than ever finding cheap, sustainable and efficient alternative sources of energy. Photovoltaic cells are considered as one of the greenest ways to produce electrical energy. In this context, considerable attention is being paid on photovoltaic materials and manufacturing processes with the aim of increasing power conversion efficiency (PCE) and reducing costs. Even if silicon based solar cells have reached PCEs of 25% [1], they require expensive production processes [2]. In order to simplify the device fabrication, increase the production rate and reduce the cost, new concepts based on solution-processed photovoltaics were developed. Among these technologies, dye-sensitized solar cells (DSSCs), pioneered by Grätzel and colleagues, have attracted considerable interest due to their low-cost production over silicon photovoltaic devices [3,4].

A DSSC consists of a mesoporous nanocrystalline *n*-type semiconductor (typically TiO_2) sensitized with a dye, deposited onto an anode and infiltrated by a redox active electrolyte (generally triiodide/iodide ions), completed by a counter-electrode (cathode). Even if PCEs over 13% have been reached for liquid-electrolyte DSSCs [5], this technology hardly meets commercial applications due to several drawbacks, especially regarding the presence of a liquid electrolyte. Besides potential leakage issues, the commonly used I_3^-/I^- system is corrosive and dissolves many of sealants and metal interconnects in the cell. Although several alternative redox couples less corrosive than iodide such as the Co^{3+}/Co^{2+} [6,7] or the Cu^{2+}/Cu^+ systems have been reported [8], their long-term stability remains unproved [9]. If the devices containing these liquid electrolytes are not perfectly sealed, the liquid evaporates away and facilitates the entry of impurities such as water and oxygen [4,9]. As such, these DSSCs are not appropriate to a widespread commercialization by industry as the liquid electrolyte requires a careful packaging [9].

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Several approaches have been proposed to replace liquid electrolytes using either quasi-solid electrolyte [10–12] or solid-state hole-transporting materials (HTM) in solid-state DSSCs (ss-DSSCs) [13]. Among solid-state HTMs, 2,2′,7,7′-tetrakis(N,N-di-*p*-methoxyphenylamine)-9-9′-spirobifluorene (**spiro-OMeTAD**) remains the most successful one, owing to a number of advantages such as its glass transition temperature, its good solubility, its ionization potential, its absorption spectrum and its solid-state morphology [14]. Although **spiro-OMeTAD** HTM allows achieving PCEs up to 7.2% in classical ss-DSSCs [15], it has some drawbacks such as a quite modest hole mobility in its pristine form ($\approx 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$)[16] and a relatively complex multistep and expensive synthesis [17].

Consequently, conjugated polymers such as polyaniline [18,19], polypyrrole [20,21], poly(3,4-ethylenedioxythiophene) [22–24], and poly(3-hexylthiophene) (**P3HT**) [25,26] have been intensively investigated as alternative HTMs with the aim of overcoming these problems. **P3HT** exhibits a higher hole mobility as well as superior film-formation properties compared to **spiro-OMeTAD** [27,28]. Besides, the ability of **P3HT** to absorb visible light (450–600 nm) can in principle improve the light-harvesting capacity of the devices and thus, contribute to the photocurrent through charge and/or energy transfer pathways [29].

Unfortunately, the device performances obtained with **P3HT** as HTM still require improvements compared to **spiro-OMeTAD**, especially due to a reduced pore filling capacity in the mesoporous TiO_2 layer [30]. The size of polymer chains may limit pore filling by **P3HT** and thus, the effective thickness of the mesoporous TiO_2 layer [31]. This parameter is important since increasing the TiO_2 layer thickness would enable increasing light absorption and efficiency [31].

In this communication, we demonstrate that a specifically-designed **P3HT**, combining (i) high regioregularity, (ii) medium-range molecular weight and (iii) narrow dispersity, can be a more suitable HTM for efficient ss-DSSCs than **spiro-OMeTAD**, using a classical glass/FTO/TiO_2/**D102**/HTM/Au device structure. The commercially available metal free dye D102 was chosen since it exhibits high extinction coefficients (55 800 $L\,mol^{-1}\,cm^{-1}$) and necessitates no additional co-adsorbent during the dye impregnation [32–34]. To provide further insight into the device operation, UV–vis absorption spectroscopy, incident photon-to-current efficiency (IPCE), atomic force and scanning electron microscopies (AFM and SEM, respectively) have been employed. To the best of our knowledge, this is the first report where **P3HT** appears as the best HTM in organic ss-DSSCs, giving a new impetus to the use of polythiophene derivatives for efficient and potentially low-cost third-generation photovoltaic cells.

2. Experimental

2.1. Materials

Titanium(IV) isopropoxide (97%, Aldrich), titanium(IV) chloride (98%, Aldrich), D102 dye (95%, Aldrich), TiO_2 paste (Dyesol 18NR-T, Aldrich) bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) (99%, Aldrich), 4-*tert*-butylpyridine (96%, Aldrich), **spiro-OMeTAD** (99%, Solaronix), absolute ethanol were used as received without further purification. **P3HT** (M_n = 23 000 $g\,mol^{-1}$, M_w = 28 500 $g\,mol^{-1}$, Đ = 1.24) was prepared according to methods reported in literature [35,36]. Number-averaged (M_n) and weight-averaged (M_w) molecular weights, and molecular weight distribution (Đ) of **P3HT** were estimated using size exclusion chromatography (SEC) on a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate of 1 $mL\,min^{-1}$), a Marathon autosampler (loop volume of 200 mL, solution conc. of 1 $mg\,mL^{-1}$), a PL-DRI refractive index detector and three columns: a PL gel 10 mm guard column and two PL gel Mixed-B 10 mm columns (linear columns for separation of molecular weight polystyrene standards ranging from 500 to 10^6 Daltons). The eluent used was THF at a flow rate of 1 $mL\,min^{-1}$ at 40 °C. Polystyrene standards were used to calibrate the SEC. UV–vis spectra were recorded at room temperature on a Safas D.E.S UV–vis spectrometer.

2.2. Fabrication of the solar cells

Solar cells were prepared according to the following procedure [34]: FTO-coated conducting glass substrates (Solaronix) were cleaned in ultrasonic baths in water, acetone and isopropanol for 10 min each before being treated for 5 min by UV-ozone. A compact layer of TiO_2 was deposited by spray-pyrolysis at 450 °C from a solution of titanium isopropoxide and acetylacetone in ethanol followed by annealing at 450 °C for 20 min in air. A nanoporous TiO_2 layer was applied by spin-coating a solution of a commercial TiO_2 nanoparticle paste diluted in ethanol at a 1:1 weight ratio. The layers were then gradually annealed from 250 °C up to 500 °C over 45 min. The substrates were then treated in a 0.02 M $TiCl_4$ aqueous solution for 2 h, rinsed with water and annealed at 450 °C for 45 min. The electrodes were finally immersed in a D102 dye solution (0.3 mM) in a acetonitrile:*tert*-butanol mixture (1:1) for 15 h in the dark. After rinsing the electrodes and drying in air, HTMs were deposited by spin-coating a **spiro-OMeTAD** (200 $mg\,mL^{-1}$) or **P3HT** solution (25 $mg\,mL^{-1}$) in chlorobenzene containing tert-butylpyridine and LiTFSI as additives (LiTFSI was predissolved in acetonitrile at a concentration of 189 $mg\,mL^{-1}$). Gold top electrodes were finally evaporated in vacuum (10^{-6} mbar) using shadow masks that define two active areas per substrate (around 0.15 cm^2 each).

2.3. Characterization of the solar cells

The current density-voltage (J-V) measurements, in the dark and under illumination, were performed in air using a Keithley model 2400 digital source meter by applying independent external voltage to the cell and by measuring the photogenerated current. The spectral mismatch between the emission of the solar simulator (NEWPORT class A, 1 600 W) and the global AM1.5G solar spectrum (IEC 60904-3 Ed.2) was corrected using a mismatch factor and the solar simulator irradiance was adjusted accordingly using a certified silicon reference cell in order to achieve an equivalent AM1.5G irradiance of one sun (100 $mW\,cm^{-2}$) on the test cells. The incident photon-to-current efficiency (IPCE) was estimated using a monochromated 75 W xenon lamp (Newport) in static regime, with a calibrated picoamperater (Keithley 485) and a calibrated photodiode. All data shown in this work were the average values of four independent parallel tests.

2.4. Fabrication of the organic field-effect transistors

Bottom gate/bottom contact prefabricated OFET substrates (Ossila) were cleaned by an ultrasonic treatment with chlorobenzene, acetone, ethanol and isopropanol for 10 min each, before being dried under nitrogen flow. The structures are based on a p-type silicon substrate as gate electrode and silicon oxide as gate dielectric. Gold drain and source electrodes, deposited on top of SiO_2, define a 1 mm wide and 30 μm long OFET channel. The hole transporting materials (HTMs), *i.e.* **P3HT** or **spiro-OMeTAD**, were deposited by drop-casting from a chlorobenzene solution at a concentration of 1 $mg\,mL^{-1}$ and the substrate was then dried in air in the dark. Additional annealing up to 150 °C for 5 min was carried out for some samples before the electrical measurements. All film deposition, annealing and current-voltage characterization were