Synthetic Metals 209 (2015) 119–127

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Use thiophene as a comonomer alternative to triphenylamine combine with 4, 8-dithienylbenzo [1,2-b: 4, 5-b'] dithiophene as a polymer dye in sensitized solar cells

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ARTICLE INFO

Article history:
Received 14 April 2015
Received in revised form 30 June 2015
Accepted 3 July 2015
Available online 23 July 2015

Keywords:
Polymer dyes
Donor
Triphenylamine
Dye-sensitized solar cells

ABSTRACT

Triphenylamine (TPA) and its derivatives are well-known pigments with excellent electron donating abilities and chemical, thermal and photochemical stabilities, and have been used in various optical and electronic fields. In this context, the polymer **PPAB7** containing a TPA and a 4, 8-dithienylbenzo [1,2-b: 4, 5-b'] dithiophene (BDT) as the donor group in the main chain and a cyanoacetic acid accepter in the side chain, linked by a thiophene unit is synthesized. To study the influence of donor in the backbone, we crop out the TPA and use the linker thiophene unit as a comonomer directly then a new polymer **PPTB8** is synthesized. Combining a mesoporous titania film grafted by these two simple polymer dye with I^-/I_3^- redox couple, the none TPA sensitizer **PPTB8** based DSSC obtained higher power conversion efficiency (PCE) of 3.78% than **PPAB7** of 2.21% with a degree of polymerization (DP) of ~5 and ~6, respectively, at an irradiance of the AM 1.5 G sunlight. To understand the improvement performance of **PPTB8**, theoretical calculations, absorption-emission spectra, electrochemistry, infrared spectroscopy and photovoltaic measurements are used to compare the photophysics, interfacial and photovoltaic property of the two polymers. The results suggest that the increased photovoltaic property of the simplified structure (**PPTB8**) is due to its broader spectra and higher efficient electron injection property resulting in higher short current.

1. Introduction

In the worldwide theme of searching for eco-friendly and low-cost technologies for the conversion of abundant solar energy to clean electricity, a large amount of research interest has been devoted to Dye-sensitized solar cells (DSSCs) in the past two decades [1,2]. Among the DSSCs components, sensitizers play a crucial role in improving the conversion effiency [3]. In the past decennium, sensitizers based on metal complex have shown excellent solar-to-electric power conversion efficiencies when used in DSSCs, for its high molar extinction coefficients and relatively broad absorbtion [4,5]. However, great efforts have been dedicated to the development of metal-free organic dyes to avoid some defect of metal complex dyes such as cost and environmental issues [6–9]. Conducting polymers are remarkable in that combining the electrical and optical properties of metal complex and inorganic semiconductors with the mechanical properties and processing advantages of organic polymers [10–13]. The advantages of tunable energy levels, large absorption coefficients and excellent structural stability owing to thermal and solvent resistance make conjugated polymers possible candidates as sensitizers in DSSCs [14–16].

The application of conjugated polymers as dye sensitizers in DSSCs has been reported in recent years [16–20]. Studies have shown that triphenylamine-based conjugated polymer with donor-π-acceptor architecture was successfully used as the sensitizer for DSSCs. In 2009, Bin Liu et al. introduced triphenylamine as the donor in the backbone and achieved a power conversion efficiency of 3.39% [17]. In 2013, our research group, H. J. Tan et al. synthesized a series of conjugated polymer dye employing triphenylamine as electron donating, carbazole as the other comonomer and cyanoacetic acid as electron accepting with conjugated thiophene units as the linkers, resulting in a power conversing efficiency of 4.4%, which is the record efficiency achieved in polymer DSSCs so far [16]. Some other structures were also used as sensitizer in recent years, such as poly (fluorenylene-vinylene) with cyanoacetic acid were used for DSSCs, achieving a conversion efficiency vary from 0.68% to 0.88% [18]. In 2010, S. T. Tan group reported a hyperbranched conjugated polymer as

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http://dx.doi.org/10.1016/j.synthmet.2015.07.002
0379-6779/

organic sensitizer for DSSCs with a power conversion efficiency of over 3.9% [19]. In 2011, J. B. Baek group synthesized RCP-1, which comprises an electron donating backbone (carbazole) and an electron-accepting side chain (cyanoacetic acid) connected through conjugated vinylene and terthiophene, and tested as a photosensitizer, to reach a power conversion efficiency of over 4% [20]. All these conjugated polymers have normal V_{oc}, but a comparatively low J_{sc}, which may be the major defect of low PCE.

Mention to the design of polymer dyes, the former works are mainly use a "donor–donor" backbone as electron donor and a branched π-bridge and accepter [16–20], afterwards studied the photophysics, photochemistry and photovoltaic characteristics of polymers but few refer to the effect of acquiescent "D–D" backbone on light absorption, intramolecular electron transfer and short-circuit current. In this work, we designed and synthesized two "D–D" backbone polymer dyes (**PPAB7** and **PPTB8**) based on 4, 8-dithienylbenzo [1,2-b: 4, 5-b'] dithiophene (BDT) with/or without electron donor triphenylamine (TPA) in main-chain as photosensitizers. Finally, we fabricated devices and examined the effects of with or without triphenylamine on the photovoltaic performance of DSSCs.

The result exhibited that the **PPAB7** dye with triphenylamine achieved a best power conversion efficiency of 2.21%. When crop out triphenylamine and replace with thiophene as polymerized monomer, the **PPTB8** dye achieved a higher power conversion efficiency of 3.78%. The study of theoretical calculations, electronic absorption spectra, voltammetric measurements and electrochemical impedance spectroscopy show that the simplified structure (**PPTB8**) has broader spectra and higher efficient electron injection property, as a result contributed to a higher short-current and finally a better photovoltaic performance.

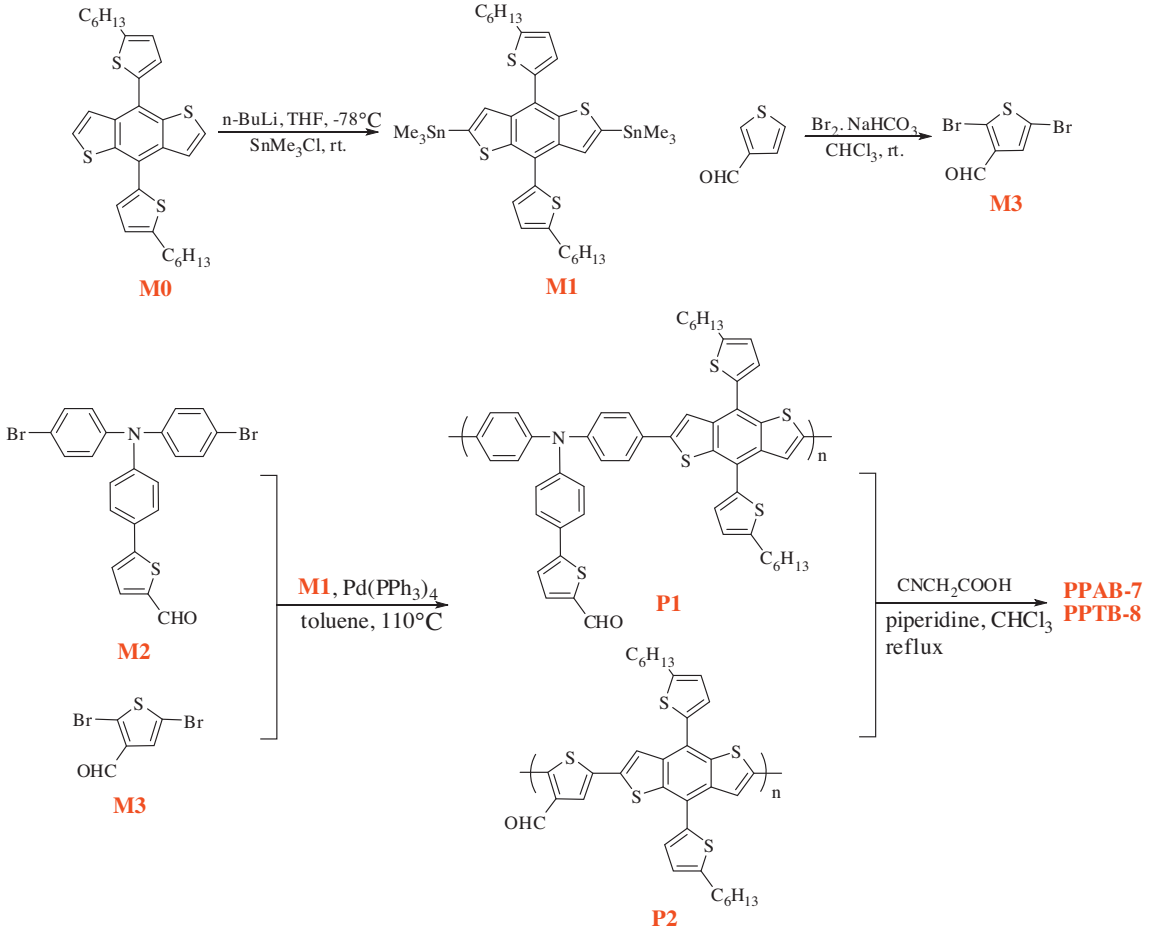
2. Experimental

2.1. Materials

Acetonitrile (AN), tetrahydrofuran (THF), toluene, 1, 2-dichloroethane (DCM), $CHCl_3$ were redistilled before use. $SnMe_3Cl$, $CNCH_2COOH$, piperidine and n-butyllithium were purchased from Energy Chemical. 4, 8-Dithienylbenzo[1,2-b:4,5-b']dithiophene (BDT) and 5-(4-(bis(4-bromophenyl) amino) phenyl) thiophene-2-carbaldehyde (**M2**) were synthesized according to the relevant literature methods [21,22]. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMITFSI), 1, 3-dimethylimidazolium iodide (DMII), guanidinium thiocyanate (GNCS) and 4-tert-butylpyridine (TBP) were purchased from Sigma–Aldrich.

2.2. Synthesis

As shown in Scheme 1, all the dyes were synthesized according to the traditional methods including bromination, Suzuki-coupling, Stille-coupling, and knoevenagel condensation. Detailed synthesis and characterization data are shown below. The precursor polymer **P1** and **P2** with aldehyde groups were synthesized via Stille-coupling reactions. The coupling of trimethyl tin with BDT, and dibromide triphenylamine with thiophene carbaldehyde or thiophene with caibaldehyde was catalezed by Pd



Scheme 1. Synthetic routes of **PPAB7** and **PPAB8**.