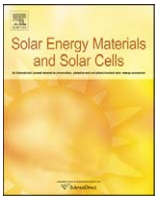
Solar Energy Materials & Solar Cells 93 (2009) 1792–1800

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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



Efficient hybrid bulk heterojunction solar cells based on phenylenevinylene copolymer, perylene bisimide and TiO_2

John A. Mikroyannidis [a,*], Minas M. Stylianakis [a], P. Suresh [b], G.D. Sharma [b,**]

[a] *Chemical Technology Laboratory, Department of Chemistry, University of Patras, GR-26500 Patras, Greece*
[b] *Physics Department, Molecular Electronic and Optoelectronic Device Laboratory JNV University, Jodhpur 342005, India*

ARTICLE INFO

Article history:
Received 19 May 2009
Received in revised form
10 June 2009
Accepted 13 June 2009
Available online 4 July 2009

Keywords:
Copolymerization
Phenylenevinylene
Anthracene
Organic solar cells
Hybrid bulk heterojunction
TiO_2

ABSTRACT

A soluble alternating phenylenevinylene copolymer **P** containing a side anthracene, which was attached to the thiophene ring via a vinylene bridge, was synthesized by Heck coupling. The copolymer had relatively low glass transition temperature (61 °C) and decomposed above 400 °C. The absorption maximum of **P** was located at 387–402 nm with an optical band gap of 2.32 eV. The emission spectra of **P** indicated that an intramolecular energy transfer from the side anthracene to the main chain took place via the vinylene bridge. In addition, a new symmetrical compound **A** based on perylene–anthracene was synthesized and used as electron acceptor in the device. Photovoltaic devices were fabricated using a blend of copolymer **P** as donor and compound **A** as acceptor, as photoactive layer film sandwiched between indium tin oxide-coated glass and Al electrodes. This device showed a power conversion efficiency of 0.72%. However, when TiO_2 nanoparticles were incorporated on the pristine **P**:**A** blend, the power conversion efficiency of the device was enhanced up to 1.32%, which is attributed to the enhanced photoinduced excitons due to the increase of the interfacial area and improved charge carrier mobility. The power conversion efficiency of the **P**:**A**:TiO_2 based photovoltaic device was further improved up to 2.64%, when the hybrid composite was treated with a mixture of Li salt and 4-tert-butylpyridine, which is attributed to the reduction in the recombination of charge carriers.

1. Introduction

Semiconducting conjugated polymers are promising materials for the development of low-cost optoelectronic applications [1]. In particular, a lot of efforts have been devoted in recent years to the design of polymer materials for solution-processed photovoltaic devices [2–10]. There have been reported many recent reviews relating to high performance photovoltaic devices, low band gap materials, morphology, stability and processing [11–18]. Relatively high-energy conversion efficiencies (above 5%) were achieved by using blends of poly(phenylenevinylene)s (PPVs) or poly(alkylthiophene)s with fullerene derivatives as photoactive layer. In these systems, the electron-donating polymers and electron-accepting fullerenes form an interpenetrated network, or donor–acceptor bulk heterojunction, with nanometer-sized domains. The resulting large donor–acceptor interfacial area in bulk heterojunction layer assists efficient exciton dissociation into free charge carriers while the nanoscale phase separation provides separate pathways for the photogenerated electrons and holes to reach the electrodes [19].

More recently, hybrid composites, which are blends of conjugated polymers and inorganic nanocrystals that offer high electron mobility or improved spectral coverage, have been investigated for photovoltaic applications [20]. The latter is perhaps the most versatile group: mixtures of polymers with nanoparticles of TiO_2 [21] and ZnO [22–24], ZnO nanorods [25], CdSe nanorods [26] and tetrapods [27,28], as well as polymers permeated in mesoporous networks of TiO_2 [29,30] have been successfully integrated in devices showing a photovoltaic effect. Recent developments concerning large area devices, polymer solar cell modules prepared using roll-to-roll methods and high efficiency bulk heterojunction solar cells have been reported [31–36].

Perylene bisimides are well-known as chemically, thermally, and photophysically stable and good light-harvesting dyes. Owing to their outstanding properties, they have been regarded as potential candidates for optical devices such as organic light-emitting diodes [37], photovoltaic devices [38], and optical switches [39]. Both PPV and perylene bisimide chromophores have been applied in bulk-heterojunction-like solar cell configurations as donor and as acceptor materials, respectively [40,41]. Finally, anthracene was one of the first organic materials

---

[*] Corresponding author. Tel.: +30 2610 997115; fax: +30 2610 997118.
[**] Corresponding author. Tel.: +91 0291 2720857; fax: +91 0291 2720856.
E-mail addresses: mikroyan@chemistry.upatras.gr, mikroyan@googlemail.com (J.A. Mikroyannidis), sharmagd_in@yahoo.com (G.D. Sharma).

0927-0248/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2009.06.013

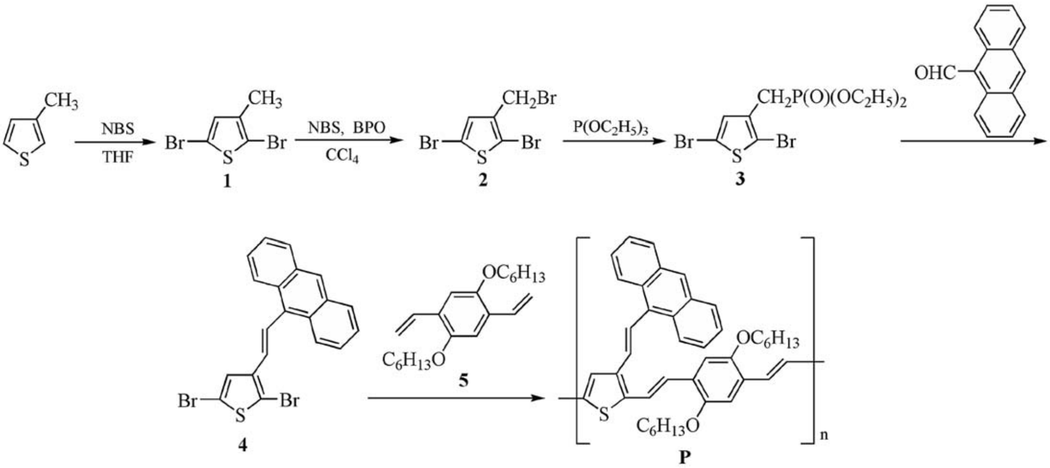
employed in organic light-emitting diodes. Recently, a diarylanthracene bearing two dihexyloxysubstituted benzene rings has been synthesized and used as donor for bulk heterojunction solar cells with [6,6]-phenyl C61-butyric acid methyl ester (PCBM) [42]. Devices fabricated with this material exhibited a power conversion efficiency (PCE) of up to 1.12%.

Herein, we report the synthesis and characterization of a novel conjugated alternating phenylenevinylene copolymer **P** (Scheme 1). It was successfully synthesized by Heck coupling of 1,4-divinyl-2,5-bis(hexyloxy)-benzene with a 2,5-dibromothiophene derivative. Copolymer **P** carried a side anthracene which was attached to the thiophene ring via a vinylene bridge. The incorporation of the anthracene to the thiophene ring is expected to lower the optical band gap and allow an intramolecular energy transfer from the anthracene to the main chain. Moreover, a new compound **A** (Scheme 2) based on perylene–anthracene was synthesized, characterized and used as an electron acceptor in the device. The photovoltaic properties of the copolymer **P** were systematically investigated. In particular, bulk heterojunction photovoltaic devices using pristine **P**:**A**, and hybrid **P**:**A**:inorganic metal oxide (TiO_2) as photoactive layers were fabricated and their performance was compared. We achieved a power conversion efficiency of 1.32% under the illumination intensity of 100 mW/cm^2 for hybrid **P**:**A** bulk heterojunction, which was further improved up to 2.64%, when the hybrid photoactive layer was treated with a mixture of Li salt and 4-tert-butylpyridine (TBP) for 10 min.

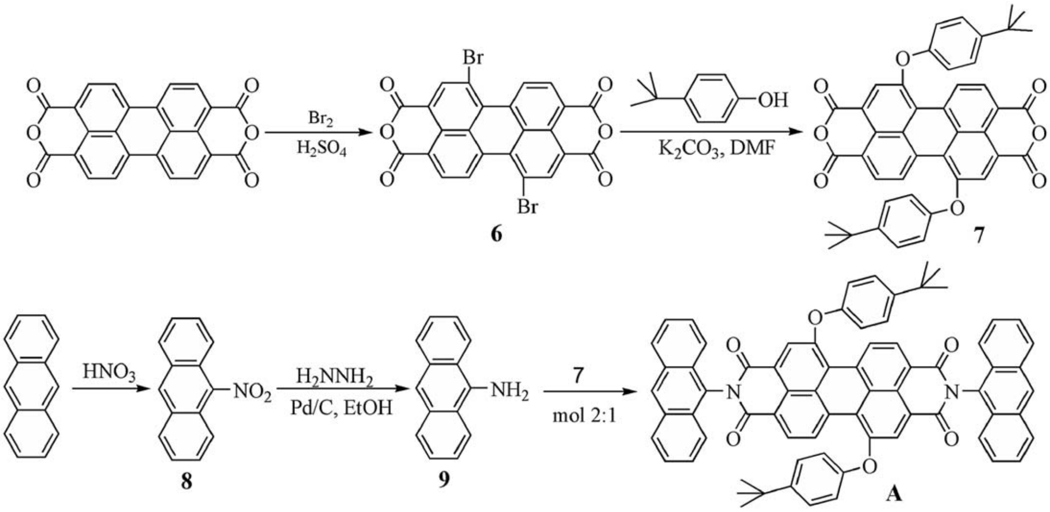
2. Experimental

2.1. Characterization methods

IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. ^{1}H NMR (400 MHz) spectra were obtained using a Brucker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV–vis spectra were recorded on a Beckman DU-640 spectrometer with spectrograde tetrahydrofuran (THF). The photoluminescence (PL) spectra were obtained with a Perkin Elmer LS45 luminescence spectrometer. The PL spectra were recorded with the corresponding excitation maximum as the excitation wavelength. TGA was performed on a DuPont 990 thermal analyzer system. Ground samples of about 10 mg each were examined by TGA and the weight loss comparisons were made between comparable specimens. Dynamic TGA measurements were made at a heating rate of 20 °C/min in atmospheres of N_2 at a flow rate of 60 cm^3/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a loaded



Scheme 1. Synthesis of copolymer **P**.



Scheme 2. Synthesis of compound **A**.