



ELSEVIER

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Triple bulk heterojunctions as means for recovering the microstructure of photoactive layers in organic solar cell devices



Zhipeng Kan^a, Letizia Colella^{a,b}, Eleonora V. Canesi^{a,*}, Giovanni Lerario^a, R. Sai Santosh Kumar^a, Valentina Bonometti^c, Patrizia. R. Mussini^c, Gabriella Cavallo^b, Giancarlo Terraneo^{a,b}, Pichaya Pattanasattayavong^d, Thomas D. Anthopoulos^d, Chiara Bertarelli^{a,b}, Panagiotis E. Keivanidis^{a,**}

^a Center for Nano Science and Technology@Polimi, Istituto Italiano di Tecnologia, via Pascoli 70/3, 20133 Milano, Italy

^b Dipartimento di Chimica, Materiali e Ing. Chimica "G. Natta", Politecnico di Milano, piazza Leonardo da Vinci 32, 20133 Milano, Italy

^c Dipartimento di Fisica Chimica ed Elettrochimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy

^d The Blakett Laboratory, Department of Physics, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, United Kingdom

ARTICLE INFO

Article history:

Received 6 June 2013

Received in revised form

2 August 2013

Accepted 6 August 2013

Available online 23 September 2013

Keywords:

Organic photovoltaics

Ternary blend

Quinoid

Photon harvesting

n-Type acceptors

Additives

ABSTRACT

Herein we present a methodology for improving the power conversion efficiency of organic solar cells made by photoactive layers of poly(3-hexylthiophene) (P3HT) and phenyl-C₆₁ butyric acid methyl ester (PCBM) of non-optimized microstructure. In our study we achieve a 47% improvement in the power conversion efficiency (PCE) of the device by utilizing a thiophene-based quinoid (QBT) moiety as the third component in the P3HT:PCBM:QBT photoactive layers. Based on a set of independent characterization experiments we address the QBT composition dependent photophysical, electrical, thermal, structural and morphology-related properties of the ternary photovoltaic P3HT:PCBM:QBT system for elucidating the origin of the PCE improvement. In small amounts (0.3–0.6 wt%), QBT serves as a nucleation agent, it enlarges the size of the P3HT crystallites by 15% and it increases the fraction of well-ordered P3HT chains in the P3HT:PCBM:QBT layer. The improved microstructure of the photoactive layer in combination with the QBT-assisted photo-induced hole transfer step from PCBM to P3HT, lead to an increase of the charge photogeneration yield in the P3HT:PCBM:QBT triple bulk heterojunction. The relatively small optical gap of QBT facilitates a resonant energy transfer step from the photoexcited PCBM to the QBT followed by a charge transfer process between QBT and the P3HT matrix. Based on these findings we propose general guidelines for the design of next generation functional additives to be used in organic photovoltaics.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

During recent years significant improvements have been achieved in the power conversion efficiency (PCE) of organic photovoltaic (OPV) systems. Breakthrough PCE values, for active layers consisting of a conjugated polymer and a fullerene derivative, have risen from the early record of 2.5% [1] to the order of 10% [2–4], increasing the probability for OPV technology to gain access in commercial applications. One of the well-studied OPV composites consists of the electron-donor poly(3-hexylthiophene) (P3HT) polymer blended with the electron-acceptor phenyl-C₆₁-butyric acid methyl ester (PCBM) fullerene derivative [5]. In addition, new formulations of next-generation materials have been disclosed in the literature [6,7].

Apart from the search of new *n*-type materials that can replace the widely used fullerene based derivatives, smart processing protocols have been also sought for the alternative development of organic photovoltaic films based on the use of ternary photoactive composites [8,9] and solvent additives [10–13]. The positive effect of using a third photoactive additive in the binary OPV composite layer on the photovoltaic efficiency of devices has been demonstrated in several recent reports. The use of ternary solid state mixtures has been suggested as a practical method for imposing control over the layer morphology of the OPV layer [14]. Another report has suggested that the use of organic binary mixtures dispersed in insulating polymeric matrices can lead to the fabrication of mechanically robust flexible OPV devices [15]. More recently, a report on the photophysical properties of hybrid ternary photoactive composites based on near-infrared absorbing PbS quantum dots has addressed the mechanism of charge photogeneration in P3HT:PCBM:QD layers [16]. Furthermore, ternary OPV films exhibited improved P3HT crystallinity. [17,18].

* Corresponding author. Tel.: +39 0223994712.

** Corresponding author. Tel.: +39 0223999806.

E-mail addresses: eleonora.canesi@iit.it (E.V. Canesi), pekeivan@iit.it (P.E. Keivanidis).

The use of ternary mixtures for the optimization of device properties is therefore ongoing and further analysis on the properties of devices based on these systems is required. One of the main prerequisites for a successful realization of OPV ternary systems seems to be the favourable energetic alignment for achieving a cascade-like arrangement in the frontier orbitals of the photoactive components in the composite [19–21].

In this paper we demonstrate a simultaneous improvement in the microstructure and in the photon harvesting properties of an organic photovoltaic layer by using a minimal amount, i.e. 0.3 wt%–0.6 wt%, of a third component. In particular we use a thiophene-based phenanthrene derivative, 5,5'-bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-5,5'-dihydro-2,2'-bithiophene (QBT) for the realization of bulk triple-heterojunction photovoltaic devices based on P3HT:PCBM:QBT ternary blend films. We investigate the effects of varying the QBT content on the performance of the P3HT:PCBM:QBT composites by using a P3HT of high regio-regularity. In order to prevent losses in the open-circuit voltage of devices of these systems, caution was taken for utilizing a third QBT species with a LUMO level that is comparable to that of PCBM. With the use of QBT as the third component, our aim is two-fold, pointing both at the enhancement of the charge generation processes via the optimization of the layer microstructure and at the improvement of light harvesting strength of the modified P3HT:PCBM:QBT composite.

Based on composition dependent differential scanning calorimetry (DSC) and X-ray diffraction (XRD) experiments we show that the addition of the QBT component at low quantities improves the overall crystallinity of the P3HT matrix in the ternary layer and it results in the enlargement of the P3HT crystallites. Moreover, the use of QBT increases the fraction of the absorbed light that is used effectively for the production of photocurrent.

In a P3HT:PCBM binary blend photoexcited PCBM molecules can potentially undergo photoinduced hole-transfer to P3HT, however the efficiency of this step is expected to be limited by the large energetic gap (≈ 1 eV) between the HOMO levels of P3HT and PCBM. Previous studies on the QBT derivative have presented the occurrence of photo-induced hole transfer from QBT to a conjugated polymer with an ionization potential (IP) similar to that of P3HT, namely poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) [22]. We now extend the utilization of QBT by enabling an energy transfer step from PCBM to QBT that is followed by photo-induced hole transfer from QBT to P3HT. We thus suggest that the use of low content additives such as quinoid derivatives helps in the improvement of the device performance by utilizing the high energy photons of the absorbed light that are normally lost due to unfavourable energetic alignment in the HOMO levels of the donor and acceptor components that comprise the OPV photoactive layer. In addition, the light absorbing power of the QBT component at low photon energies in the spectral region of 700 nm enhances further the light harvesting capabilities of the P3HT:PCBM:QBT ternary system and it results in an improved photocurrent generation in devices made of the ternary layers.

Our strategy is verified by the observed 47% increase in the power conversion efficiency of ternary-based devices, in respect to the reference binary P3HT:PCBM device, and supported by spectroscopic evidences.

2. Materials and methods

2.1. Synthesis of QBT

All reactions were carried out under a dry, oxygen-free, argon atmosphere. Unless otherwise specified, all chemicals were

commercial (Sigma Aldrich). Dry solvents were freshly used or maintained over molecular sieves.

2.1.1. 1-Trimethylsilyloxy-2,6-di-*tert*-butyl-4-bromo benzene (1)

28 ml of butyllithium 2.5 M in hexane (70.1 mmol) were dropped in a solution of 4-bromo-2,6 di-*tert*-butyl-phenol (20 g, 70.1 mmol) in dry THF (100 ml) at -78°C . After 10 min, $(\text{CH}_3)_3\text{SiCl}$ (9.75 ml, 77.1 mmol) was added and after 15 min the mixture was slowly warmed to room temperature. After overnight stirring, H_2O was added and the reaction mixture was extracted with CH_2Cl_2 and dried over Na_2SO_4 . Purification by flash chromatography on silica gel (petroleum ether: $\text{CH}_2\text{Cl}_2=9:1$) afforded the desired product **1** as a yellowish solid in 99% yield. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.32 (s, 2H, Ph-H), 1.39 (s, 18H, t-Bu), 0.41 (s, 9H, $-\text{OSiMe}_3$).

2.1.2. Tris(3,5-bis-di-*tert*-butyl-4-trimethylsilyloxy phenyl)boroxin (2)

3.4 ml of butyllithium 2.5 M in hexane (8.4 mmol) were dropped in a solution of **1** (2 g, 5.6 mmol) in dry THF (20 ml) and TMEDA (4 ml) at -78°C . After 1 hour, $\text{B}(\text{OC}_3\text{H}_7)_3$ (5.2 ml, 22.4 mmol) was added and after 45 minutes the mixture was slowly warmed to room temperature. After overnight stirring, a saturated aqueous solution of NH_4Cl was added. The reaction mixture was extracted with diethyl ether/ H_2O and dried over Na_2SO_4 . Purification by flash chromatography on silica gel (petroleum ether:ethyl acetate=2:1) afforded the desired product **2** as a yellowish solid in 66% yield. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.18 (s, 6H, Ph-H), 1.49 (s, 54H, t-Bu), 0.46 (s, 27H, $-\text{OSiMe}_3$).

2.1.3. 5,5'-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,2'-bithiophene (3)

$\text{Pd}(\text{PPh}_3)_4$ (130 mg, 0.112 mmol), tris(3,5-bis-di-*tert*-butyl-4-trimethylsilyloxy phenyl)boroxin (**2**) (1 g, 1.10 mmol) and K_2CO_3 aq 1 M (907 mg, 6.58 mmol in 6.5 ml H_2O) were added to a solution of 5,5'-dibromo-2,2'-bithiophene (239 mg, 0.736 mmol) in 13 ml of degassed DME. After refluxing overnight, the reaction mixture was extracted with diethyl ether/ H_2O and dried over Na_2SO_4 . Purification by flash chromatography on silica gel (petroleum ether:ethyl acetate=2:1) afforded 360 mg of a yellow solid (**3**), in 86% yield. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.41 (s, 4H, Ph-H), 7.11 (d, 2H, Th-H, $J=3.8$ Hz), 7.08 (d, 2H, Th-H, $J=3.8$ Hz), 5.27 (s, 2H, $-\text{OH}$), 1.49 (s, 36H, t-Bu).

2.1.4. 5,5'-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-5,5'-dihydro-2,2'-bithiophene (QBT)

$\text{K}_3\text{Fe}(\text{CN})_6$ (1.42 g, 4.32 mmol) and KOH 0.2 M (2.42 g, 43.2 mmol) in 220 ml H_2O were added to a solution of **3** (0.250 g, 0.432 mmol) in CH_2Cl_2 (150 ml). After 3 h of vigorous stirring, the mixture was extracted with $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ and dried over Na_2SO_4 . After solvent removal, the desired product (QBT) was obtained in 98% yield. ^1H -NMR (400 MHz, CDCl_3), δ (ppm): 7.51 (m, 4H, Ph-H), 7.42 (d, 4H, Th-H, $J=5.14$ Hz), 1.37 (s, 36H, t-Bu).

2.2. Materials processing and solution preparation

Regio-regular P3HT ($M_w=65,200$ g mol^{-1} , $D=2.2$, $\text{RR}=95.7\%$) was purchased from Merck, amorphous polystyrene ($M_w=350,000$ g mol^{-1} , $D=2.05$) was purchased from Sigma Aldrich, PCBM was purchased from Solenne BV. All materials were used as received without any additional purification. Binary films of PS:QBT, P3HT:QBT and ternary blend films of P3HT:PCBM:QBT with increasing QBT content were fabricated by dissolving the materials in chlorobenzene, followed by stirring for 30 min before spin coating. Complete solubility of QBT in chlorobenzene is achieved for all the solution

Download English Version:

<https://daneshyari.com/en/article/10248674>

Download Persian Version:

<https://daneshyari.com/article/10248674>

[Daneshyari.com](https://daneshyari.com)