



The effect of the length of alkyl side-chains on the molecular aggregation and photovoltaic performance of the isoindigo-based polymers



Xiai Sun^a, Zhiquan Zhang^a, Rongyan Hou^a, Meihua Huang^{a,**}, Bin Zhao^{a,b,*},
Songting Tan^b

^a College of Chemistry and Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Xiangtan University, Xiangtan 411105, PR China

^b Key Laboratory of Advanced Functional Polymeric Materials of College of Hunan Province, Xiangtan University, Xiangtan 411105, PR China

ARTICLE INFO

Article history:

Received 8 October 2016

Accepted 17 December 2016

Available online 19 December 2016

Keywords:

Polymer solar cells

Side-chain engineering

Isoindigo

Alkyl substituents

Structure-property relationship

ABSTRACT

To investigate the length of the alkyl side-chains on the photovoltaic performance, three isoindigo-based polymers with different-length side chains on the thiophene-benzene-thiophene (TBT) (electron-donating) moiety and isoindigo (electron-withdrawing) moiety have been designed and synthesized, in which the total carbon atom numbers of the side chains in a constitutional repeating unit are completely identical. The results indicate that the polymer with longer branched side chains on the TBT units and shorter linear side chains on the isoindigo units shows stronger interchain interaction and light-harvesting capacity in 1,2-dichlorobenzene solution and thin film, lower band gaps, stronger π - π stacking interaction, more appropriate microphase separation with PC₇₁BM, higher hole mobility and better photovoltaic performance. As a result, the bulk heterojunction (BHJ) device based on PTBTOD-IDB with 2-octyldodecyl on the TBT moiety and *n*-butyl on the isoindigo moiety exhibits a power conversion efficiency (PCE) of 5.29%, which is almost eight times as high as that of PTBTEH-IDHD with 2-ethylhexyl side chain on TBT moiety and 2-hexyldecyl side chain on isoindigo moiety.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Polymer solar cells (PSCs) are a promising photovoltaic (PV) technology due to their potential application for low-cost flexible devices [1–4]. The power conversion efficiency (PCE), a key parameter to assess the performance of PSCs, has increased from 1% in the 1990s to over 11% just recently [5–10]. This impressive accomplishment is mainly achieved by the molecular engineering of the conjugated polymers [11–14], assisted by successes in interface modification and device optimization [15–18].

Recently, isoindigo (ID) has been considered as a remarkable electron-withdrawing moiety (A) because it is a symmetrical and perfect planar π -conjugated molecule, and its strong electron-deficient property leads to deep-lying energy levels of the lowest

unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) [19]. Several isoindigo-based copolymers with different electron-donating moieties (D) have shown high photovoltaic performance [19–24]. Wang et al. developed an isoindigo-based polymer (P3TI), which gave a PCE of 6.3% [22]. We also reported a polymer with isoindigo moieties in the side chains (PBDT-TID) and achieved a PCE value of 6.51% [20]. Subsequently, Geng and his coworkers reported the polymer P(IID-DTC), combined with dithieno[3,2-*b*;6,7-*b'*]carbazole as D moieties and isoindigo as A moieties, and achieved a PCE value of 8.2% [25].

The role of the alkyl chains on a conjugated polymer are to confer solubility of the rigid-rod-like structure in common organic solvents, appropriate side chains not only improve solubility but also influence the intermolecular packing (aggregation), absorption spectra, blend film morphology, charge-carrier mobility, and energy levels of the conjugated polymers [21,26–30]. Therefore, more and more researchers focus on side-chain engineering to obtain high-performance photovoltaic materials [31–40]. On the one hand, the chemical structure of the side chains shows an impact on

* Corresponding author. College of Chemistry, Xiangtan University, Xiangtan 411105, PR China.

** Corresponding author. Tel./fax: +86 0731 58292251.

E-mail addresses: xtuhmh@163.com (M. Huang), xtuzb@163.com (B. Zhao).

energy levels which decides the open circuit voltage (V_{oc}) and PCE values [32,41]. Typically, after substituting alkoxy groups by alkyl groups, the polymer PBnDTDTBT achieved a deep-lying HOMO energy level of -5.40 eV [42]. When alkoxy groups were replaced by alkylthio side chains, the HOMO energy levels of the polymers were reduced, and the corresponding PSC device achieved an enhanced V_{oc} [43–45]. On the other hand, the position of the alkyl side-chains and the position of alkyl chain branch position also play an important role in improving the photovoltaic performance of the polymers [27]. For examples, PDTSTTz-4 with a hexyl side chain on the 4-position of the thiophene units showed an order higher hole mobility ($7.8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [46] than PDTSTTz-3 with a hexyl side chain on the 3-position of thiophene units ($3.56 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [47]. The McCulloch group reported that a longer distance between alkyl-chain branching position and the backbone led to stronger intermolecular π - π stacking, red-shifted absorption, improved hole mobility and better photovoltaic performance [31]. Recently the McGehee group gave an opinion that a more sterically accessible acceptor moiety and a more sterically hindered donor moiety would lead to a better photovoltaic performance [41]. Subsequently, So et al. reported that the polymer PBDT(EtHex)-TPD(Oct) with linear *n*-octyl side chain on TPD unit showed smaller π - π stacking distance, higher hole mobility and better photovoltaic performance than BDT(EtHex)-TPD(EtHex) with a bulkier ethylhexyl side chain [36]. Though a few references reported that a more sterically accessible acceptor moiety would lead to a higher photovoltaic performance, the length effect of the side chains on D moiety and A moiety was hardly discussed when the total carbon atoms number of the side chains in a constitutional repeating unit was fixed.

Herein, three isoindigo-based polymers, with different alkyl chain length on the thiophene-benzene-thiophene (TBT) (electron-donating) moiety and isoindigo (electron-withdrawing) moiety have been designed and synthesized. Firstly, the polymer PTBTEH-IDHD with 2-ethylhexyl side chain on TBT moiety and 2-hexyldecyl side chain on ID moiety was reported in our early work [48]. Then, the polymer PTBTHD-IDEH (Fig. 1) with 2-hexyldecyl side chain on TBT moiety and 2-ethylhexyl side chain on ID moiety was designed and synthesized, and the position effects of these two kinds of side chains on the photovoltaic performance was investigated. Finally, the side chain on TBT moiety was extended to 2-octyldecyl and that on ID moiety was shortened to *n*-butyl to obtain the polymer PTBTOD-IDB. Among these polymers, the total carbon atom numbers of the side chains in a constitutional repeating unit remain unchanged in order to avoid the impact of the solubility

difference derived from the length difference of side chains. The length and position effects of the alkyl side chain on light-harvesting capacity, band gaps, aggregation, the morphology and hole mobility of the blend film with PC₇₁BM, and photovoltaic performance of the PSC devices have been studied in detail.

2. Experimental

2.1. Materials and chemicals

Tetrahydrofuran (THF) and toluene were refluxed over sodium and benzophenone, and distilled prior to use. DMF was dried and distilled under reduced pressure. All other materials, including the solvents and chemicals, were purchased from commercial suppliers (Aldrich, Energy Chemical, Alfa, etc.) and used without further purification unless stated otherwise.

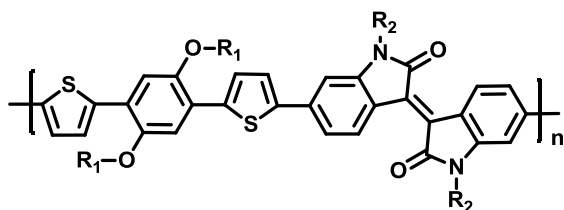
2.2. Characterization

The NMR spectra were measured using Bruker AVANCE 400 MHz spectrometer. Mass spectra were measured using a Solarix FF-ICR-MS Analyzer in the MALDI mode. The elemental analysis result was characterized by Elementar VarioEL CHNS. Solution and thin film (on a quartz substrate) UV-vis absorption spectra were recorded using a Perkin-Elmer Lambda 25 spectrophotometer. Electrochemical measurements were carried out under nitrogen in a deoxygenated solution of tetra-*n*-butylammoniumhexafluorophosphate (0.1 M) in CH₃CN using an electrochemical workstation with the polymer thin film on ITO (indium tin oxide) glass as the working electrode, Pt wire as the counter electrode, and Ag/AgNO₃ electrode as the reference electrode (100 mV s^{-1}). The potentials were referenced to ferrocene/ferrocenium couple by using ferrocene as an internal standard. Thermogravimetric analyses (TGA) were performed by using a Netzsch TG209 analyzer under nitrogen atmosphere at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$. The average molecular weight and polydispersity index (PDI) of the polymers were determined by Waters 1515 gel permeation chromatography (GPC) analysis with polystyrene as the standard. The nanoscale morphology of blended film was observed using a Digital Instruments Environ Scope atomic force microscope (AFM) in the tapping mode.

2.3. Fabrication and characterization of PSCs

The photovoltaic cells were constructed in a conventional sandwich structure of ITO/PEDOT:PSS(30 nm)/polymer:PCBM/LiF(0.4 nm)/Al(100 nm). The photosensitive blend layer of the polymers and PCBM was prepared by spin-coating the chlorobenzene solution (the polymer concentration is 15 mg mL^{-1}) onto the ITO/PEDOT:PSS(30 nm) electrode, and dried at room temperature for 30 min in a nitrogen-filled glove box. The cathode of the device, consisting of 0.4 nm of LiF and 100 nm of aluminum, was thermally deposited on the top of the blend film at $5 \times 10^{-4} \text{ Pa}$. The thickness of the active layer was measured by an Ambios Technology XP-2 surface profilometer. Current density-voltage (J - V) characteristics were measured by a computer controlled Keithley 2600 source measurement under AM 1.5G illumination conditions, 100 mW cm^{-2} . The measurement of monochromatic incident photon-to-current conversion efficiency (IPCE) was performed by using a Zolix DCS300PA Data acquisition system. All these measurements were performed under ambient atmosphere at room temperature.

Side chains in a constitutional repeating unit: C₄₈H₁₀₀



PTBTEH-IDHD : R₁= 2-ethylhexyl R₂= 2-hexyldecyl

PTBTHD-IDEH : R₁= 2-hexyldecyl R₂= 2-ethylhexyl

PTBTOD-IDB : R₁= 2-octyldecyl R₂= *n*-butyl

Fig. 1. The chemical structure of the polymers.

Download English Version:

<https://daneshyari.com/en/article/4766099>

Download Persian Version:

<https://daneshyari.com/article/4766099>

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