Dyes and Pigments 98 (2013) 11–16

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

A new isoindigo-based molecule with ideal energy levels for solution-processable organic solar cells

Ting Wang [a], Yanhua Chen [a,b], Xichang Bao [a], Zhengkun Du [a], Jing Guo [a], Ning Wang [a], Mingliang Sun [b,*], Renqiang Yang [a,*]

[a] *Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China*
[b] *Institute of Material Science and Engineering, Ocean University of China, Qingdao 266100, China*

ARTICLE INFO

Article history:
Received 17 December 2012
Received in revised form
31 January 2013
Accepted 1 February 2013
Available online 21 February 2013

Keywords:
Isoindigo
Thieno[3,2-*b*]thiophene
Organic photovoltaic effect
Low bandgap
Small molecule
Energy level

ABSTRACT

A new easily-accessible solution-processed oligomer, with an isoindigo group as an electron acceptor and a thieno[3,2-*b*]thiophene flanked by thiophenes as electron donors, has been synthesized by a Stille coupling reaction. Through introducing the extended π-conjugated groups into isoindigo, the electro-optical properties of the material can be fine-tuned. The isoindigo oligomer has a broad absorption in the region from 300 to 800 nm with a narrow bandgap (1.54 eV), which is believed to be an ideal bandgap as donor materials. The oligomer possesses low HOMO energy level (−5.39 eV). The potential of optical and electronic properties encouraged us to explore the photovoltaic performance using the oligomer as the donor material in bulk heterojunction organic solar cell along with 6,6-phenyl-C61-butyric acid methyl ester as the acceptor. The solar cell based on the oligomer with an inverted device configuration provided a power conversion efficiency of 1.41% under the AM 1.5G illumination with an intensity of 100 mW cm^{-2} from a solar simulator.

1. Introduction

In the past decade organic photovoltaics (OPVs) have achieved remarkable progress due to unique advantages such as low cost, light weight and applications in flexible large-area devices [1–4]. At present intensive efforts have been dedicated to improving the power conversion efficiencies (PCEs) of polymer bulk heterojunction (BHJ) architectures, and their PCEs have gradually exceeded 7% [5–8]. Despite these advancements, the efficiency of a polymer-fullerene solar cell device is limited by factors such as complex synthesis and unknown long-term stability [9], so there remains a significant challenge for OPVs toward commercialization. An emerging alternative to polymer BHJ solar cells involves the use of solution-processed small molecule BHJ which combine the advantages of well-defined chemical structure, reproducible synthesis, high purification, and more straightforward analysis of structure property relationships [10–12]. A combination of structural design, morphology control, and device engineering has led to PCEs reaching the 6–7% for soluble small molecule solar cells [13,14].

The PCEs of the OPVs are proportional to open circuit voltage (V_{OC}), short circuit current density (J_{SC}), and fill factor (FF). The three parameters interplay each other, for example, V_{OC} is mainly related to the energy level difference between the LUMO of the acceptor and the HOMO of the donor [15]. However, sometimes, a lower HOMO level of the donor would lead to an increased bandgap and less efficient light absorption. High V_{OC} and high J_{SC} are difficult to obtain concurrently [16]. In order to achieve higher PCEs, a delicate balance between the bandgap and energy level is needed via judicious control over the physical properties of a donor [17]. 6,6-phenyl-C61-butyric acid methyl ester (PCBM) has a LUMO energy level of −4.2 eV. It is estimated that a minimum LUMO energy difference of 0.3 eV between the donor and the acceptor is required to facilitate exciton splitting and charge dissociation [18]. Accordingly, it is believed that the ideal lowest possible LUMO level of the donor would be near −3.9 eV [19]. Furthermore, low bandgap materials can absorb more light, increasing the J_{SC}. However, lowering the bandgap requires an increase of the HOMO which would reduce V_{OC} normally. Thus an optimal bandgap of 1.5 eV is proposed to be a compromise between the two competing factors. Consequently, the HOMO of the "ideal" donor would be around −5.4 eV [3,19] (Fig. 1). Following the basic requirements and scientific issues in the molecular design mentioned above, it is important to synthesize materials with an ideal bandgap and energy level for further increasing photovoltaic performance.

Isoindigo (ID) which has been used in the dye industry for a long time [20] has some advantages similar to diketopyrrolopyrroles

---

* Corresponding authors.
E-mail addresses: mlsun@ouc.edu.cn (M. Sun), yangrq@qibebt.ac.cn (R. Yang).

0143-7208/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.dyepig.2013.02.003

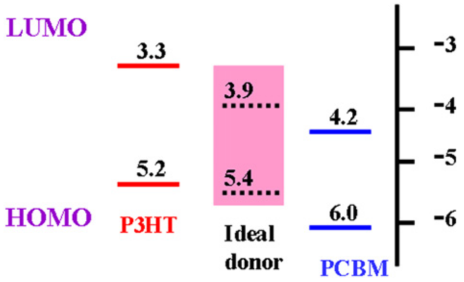
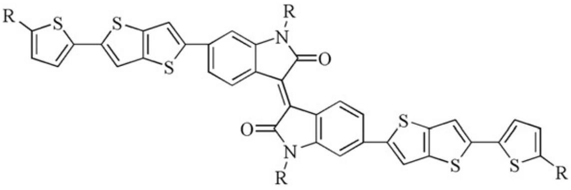


Fig. 1. Electronic energy levels of P3HT, ideal donor and PCBM.

(DPP) [21–24], such as strong electron-withdrawing ability (derived from its two lactam rings), low HOMO levels, relatively small bandgaps and planar architectures. Meanwhile, compared to DPP, isoindigo can be obtained easily from various natural sources, and also has much better solubility than DPP. It seems that isoindigo is suitable for OPVs, yet the application of isoindigo in organic solar cells was first introduced in 2011 [25], with state-of-the-art isoindigo-based BHJ solar cells reaching a PCE of 6.3% [26]. This result shows particular potential of isoindigo as an electron-deficient unit toward high efficient OPVs. Until now most of the research about isoindigo has focused on polymer solar cells, while there are few reports on isoindigo-based small molecules except for one example reported by Reynolds et al. recently [27]. However, the optical bandgap of isoindigo-based materials is too large and the HOMO level is not low enough to afford a high V_{OC}, so it will make sense to fine-tune the optical and electronic properties of isoindigo derivatives through molecular design.

In this work we focus on the design and synthesis of a new isoindigo-based molecule with ideal optical and electrical properties in order to significantly increase the photovoltaic performance of the material. The incorporation of fused thiophenes and other aromatic structures into conjugated architectures would increase planarity and rigidity which will lead to a lower optical bandgap [28–30]. The rigid and coplanar thieno[3,2-*b*]thiophene (TT) consists two fused thiophenes and the material based on a TT unit shows high hole mobility and good light absorption because of closely π stacking in the solid state [31–33]. On the basis of the above consideration, in this contribution, TT unit was incorporated with isoindigo to achieve a new easily-accessible and fully solution-processed small molecule donor IDTTT (see Scheme 1 for its molecular structure). The conjugated component, TT unit, will increase the conjugation length of the donor, thus make the new molecule close to an ideal model. 2-ethylhexyl was selected as a substitute to improve the solubility. As we know, inverted solar cells have some advantages superior to regular device structure, such as interface stability, a stable metal electrode, design flexibility for tandem or stacked cells [34–36]. Therefore, we will explore the inverted solar cells using the new molecule IDTTT and PCBM blending as the active layer. This is the first example for isoindigo-based materials applied in inverted structure.



IDTTT

R=2-ethylhexyl

Scheme 1. Chemical structure of isoindigo-based molecule IDTTT.

2. Experimental

2.1. Materials and characterization methods

All reagents and starting materials were purchased from J&K, Alfa Aesar and used without further purification, unless otherwise noted. Solvents were distilled before use. Thieno[3,2-*b*]thiophene (**1**) [37], (E)-6,6′-dibromoisoindigo (**4**) [38] and 2-trimethylstannane-5-(2-ethylhexyl)thiophene (**8**) [39] were prepared according to the literature methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-600 (600 MHz) spectrometer. FT-IR spectra were taken on a Nicolet 6700 spectrophotometer by using KBr pellets. High resolution mass spectra were recorded under APCI mode on a Bruker Maxis UHR TOF spectrometer. UV–vis spectra were measured on a Varian Cary 50 UV/vis spectrometer. Surface roughness and morphology of thin films were characterized by atomic force microscopy (AFM) on an Agilent 5400. Cyclic voltametry (CV) was performed by a CHI 660D System with a three-electrode cell in a solution of 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane (DCM) solution at a scan rate of 100 mV/s. The film thickness was measured by a Veeco Dektak 150 surface profiler. The current density–voltage (*J*–*V*) characteristics were recorded with a Keithley 2420 source measurement unit under simulated 100 mW/cm^2 (AM 1.5G) irradiation from a Newport solar simulator.

2.2. Device fabrication and characterization

The inverted photovoltaic devices were prepared and characterized. All cells were fabricated on ITO-coated glass substrates with a nominal sheet resistance of 15 Ω/sq. The substrates were cleaned in an ultrasonic bath with detergent, ultra-pure water, acetone, and isopropyl alcohol for 20 min, respectively, and dried in a laboratory oven at 80 °C for one night. The ZnO solution was prepared using zinc acetate and the equally molar monoethanolamine dissolved in 2-methoxyethanol, and then the mixture was stirred vigorously at 60 °C to yield a homogeneous transparent solution. The ITO surfaces were coated by the above ZnO solutions with spin speeds at 2000 rmp for 40 s, and then, baked in an oven at 100 °C for 16 h. A blend solution of IDTTT and 6,6-phenyl-C61-butyric acid methyl ester (PCBM) (American Dye Sources Inc.) with different weight ratios (at a total solids concentration of 20 mg/mL) were prepared in deoxygenated anhydrous chlorobenzene (Sigma–Aldrich) and stirred in a nitrogen filled glove box for 4 h, and then spin-coated on ZnO-coated ITO substrate to form the active layer (~90 nm) in glove box. Subsequently, MoO_3 (3 nm) and Ag (80 nm) were thermal evaporated followed by post-annealing at 120 °C for 10 min. The cathode area defines active area of the devices, which is 0.1 cm^2.

2.3. Synthesis of isoindigo-based oligomer IDTTT

2.3.1. Synthesis of triisopropyl(thieno[3,2-b]thien-2-yl)silane (2)

In a dry flask *n*-butyllithium (2.4 M in *n*-hexane, 1.25 mL, 3.0 mmol) was added dropwise to a solution of the thieno[3,2-*b*] thiophene (**1**, 420 mg, 3.0 mmol) in tetrahydrofuran (THF, 20 mL) at 0 °C under nitrogen atmosphere (Scheme 2). After 1 h of stirring at this temperature, neat triisopropyl chlorosilane (0.74 mL, 3.45 mmol) was added dropwise. The solution was stirred for another 3 h and allowed to warm to room temperature, followed by dilution with hexane and washing with water and brine. The organic layer was collected and dried over anhydrous Na_2SO_4. After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel, eluting with hexane to yield silyl compound **2** (774 mg, 87%) as a white solid. ^{1}H NMR (600 MHz,