Dyes and Pigments 134 (2016) 251–257

Contents lists available at ScienceDirect

Dyes and Pigments

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

Synthesis, field-effect and photovoltaic properties of random difluorobenzothiadiazole-isoindigo electron donor-acceptor polymers

Ping Deng [a, 1], Yanlian Lei [b, 1], Bo Wu [b], Xuelin Zheng [c], Yong Lu [a], Furong Zhu [b], Beng S. Ong [a, *]

[a] Research Centre of Excellence, Institute of Creativity and Department of Chemistry, Hong Kong Baptist University, Hong Kong, China
[b] Department of Physics, Hong Kong Baptist University, Kowloon, Hong Kong, China
[c] College of Materials Science and Engineering, Fujian Normal University, Fuzhou 350007, China

ARTICLE INFO

Article history:
Received 13 May 2016
Received in revised form
14 July 2016
Accepted 16 July 2016
Available online 18 July 2016

Keywords:
Difluorobenzothiadiazole
Isoindigo
Conjugated polymer
Random polymer
Organic field-effect transistors
Organic solar cells

ABSTRACT

Two random electron donor-acceptor (D-A) polymers comprised of two acceptor moieties, difluorobenzothiadiazole and isoindigo, and one donor moiety (**P1** and **P2**) have been synthesized in good yields to study the effects of donor structures on organic thin-film transistor (OTFT) and bulk-heterojunction organic solar cell (BHJ-OSC) performance. Both polymers possess reasonably good solubility in common processing solvents for organic electronics. **P1**, which contains a benzodithiophene donor structure, shows poor charge transport ability in OTFTs and low solar power conversion efficiency (PCE) in BHJ-OSC devices with $PC_{71}BM$ acceptor. On the other hand, **P2**, with a dithienylthieno[3,2-*b*]thiophene donor moiety, exhibits distinctly higher hole field-effect mobility and significantly much better PCE under similar conditions. These results have demonstrated the decisive influence of donor moiety over the optoelectronic properties of D-A polymers.

1. Introduction

Organic conjugated polymers have received great interest for potential application in organic thin-film transistors (OTFTs) and bulk heterojunction organic solar cells (BHJ-OSCs) [1–4]. Utilization of appropriate electron donor and acceptor moieties as repeating units have led to conjugated electron donor-acceptor (D-A) polymers with enhanced ambient stability and superior semiconductor properties [5,6]. While the majority of donor moieties in the high-performing D-A polymers are derived from thiophene and its derivatives, the acceptor moieties are widely different; these include flourenone derivative, naphthalene diimide, perylene diimide, diketopyrrolopyrrole, isoindigo, benzothiazole, to name a few [7]. Among D-A polymers, those with 2,1,3-benzothiazole acceptor moiety [8], particularly the difluorinated derivatives, have attracted much attention recently as they have shown promising performance characteristics in OTFTs and OSCs [9–14]. Another interesting and widely employed acceptor moiety for D-A polymer semiconductors is isoindigo [15–19]. Notable interesting properties of isoindigo acceptor unit for D-A polymer design include extended π-conjugation, low-lying frontier orbital energy levels, and tunable solubility characteristics through *N*-alkylation as well as the ability to impart coplanarity to the backbone structure. In addition, appositely functionalized isoindigo monomer synthesis is generally high-yielding and scalable, which would facilitate rapid development of isoindigo-based D-A polymer materials for organic electronic applications.

Accordingly, it would appear interesting to study the optoelectronic and electrical properties of a D-A polymer comprised of both difluoro-2,1,3-benzothiazole and isoindigo acceptor moieties and a donor repeating unit on a single polymer backbone structure. From this perspective, we have synthesized two random D-A polymers, **P1** and **P2**, both with difluoro-2,1,3-benzothiazole and isoindigo as repeating acceptor moieties but each with a different donor repeating unit. We have selected to study random polymers instead of regioregular polymers because of the ease of synthesis and the fact that random polymers possess much higher solution processability leading to better film properties and easier device fabrication. The specific donor moieties for **P1** and **P2** are 4,8-bis(5-(2-ethylhexyl)-thiophen-2-yl)benzo[1,2-*b*:4,5-*b*′]dithiophene and

---

* Corresponding author. Tel.: +852 3411 2480, fax: +852 3411 7348.
E-mail address: bong@hkbu.edu.hk (B.S. Ong).

[1] These two authors contributed equally to this work.

http://dx.doi.org/10.1016/j.dyepig.2016.07.022
0143-7208/

2,5-bis(3-decyl- thiophen-2-yl)thieno[3,2-*b*]thiophene, respectively. The choice of 1:1 M ratio of combined acceptor moieties to donor moiety ($n = 0.5$) in our studies was to ensure a clear visualization on the effects of donor moieties on the optoelectronic and electrical properties of the resulting D-A polymers. The utilization of 1:1 M ratio of the two acceptor moieties was for structural simplicity and ease of synthesis. The incorporation of the branched alkyl-substituted isoindigo acceptor would not only extend the absorption spectra of the resulting polymers toward the infrared region but also greatly enhance the polymers' solubility characteristics. In addition, both **P1** and **P2** would be expected to assume a reasonably linear conformation in view of the relatively planar donor and acceptor structures, the rigidity of the polymer backbones, and absence of steric hindrance to polymer coplanarity.

P1 and **P2** were readily synthesized by random polymerization of appositely substituted donor and acceptor monomers via Stille cross-coupling reaction in good yields. **P2**, with a stronger dithienylthieno[3,2-*b*]thiophene donor moiety, exhibited field-effect transistor (FET) mobility of over one order in magnitude better than those of **P1**. Likewise in BHJ-OSCs as a donor polymer with PC$_{71}$BM acceptor, **P2** also showed much higher power conversion efficiency (PCE) of about 5% as compared to 2% for **P1**. These results have demonstrated the importance of both the donor and the acceptor moieties in constructing D-A polymers for OTFT and OSC applications.

2. Experimental section

2.1. Materials

All chemicals were purchased from Aldrich and used without further purification unless stated otherwise.

4,8-Bis[5-(2-ethylhexyl)thiophen-2-yl]-2,6-bis(trimethylstannyl)benzo[1,2-*b*:4,5-*b*′]- dithiophene [20] and (*E*)-6,6′-dibromo-1,1′-bis(2-decyltetradecyl)[3,3′-biindolinylidene]- 2,2′-dione [21] were prepared according reported procedures. The synthesis of 2,5-bis(3-decyl-5-(trimethylstannyl)thiophen-2-yl)-thieno[3,2-*b*]thio-phene is described in Supporting Information. All the reactions were carried out under nitrogen atmosphere.

2.2. Synthesis of polymers

2.2.1. Polymer *P1*

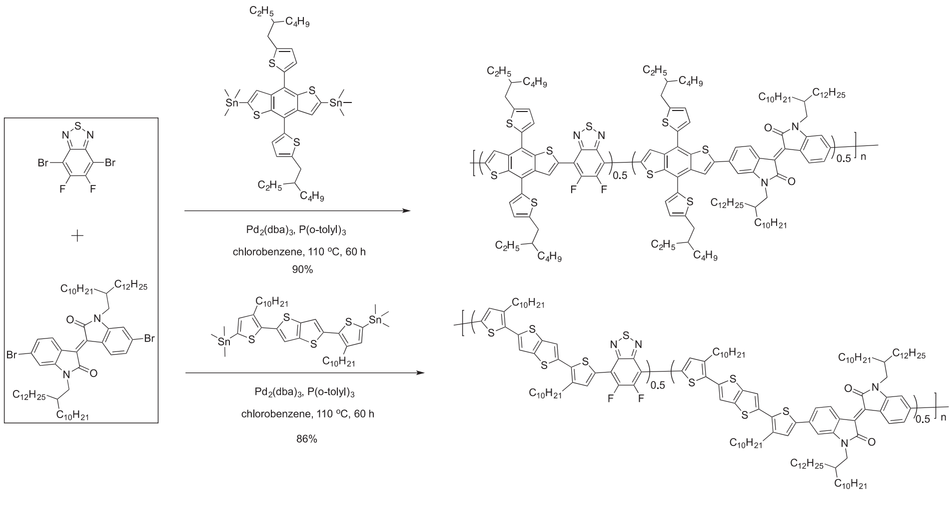
A mixture of 4,8-bis[5-(2-ethylhexyl)thiophen-2-yl]-2,6-bis(trimethyl- stannyl)benzo- [1,2-*b*:4,5-*b*′]dithiophene (0.2714 g, 0.3000 mmol), 4,7-dibromo-5,6- difluorobenzo[*c*] [1,2,5]- thiadiazole (0.0495 g, 0.1500 mmol), (*E*)-6,6′-dibromo-1,1′-bis(2-decyltetradecyl)- [3,3′-biindolinylidene]-2,2′-dione (0.100 g, 0.1510 mmol), Pd$_2$(dba)$_3$ (0.0028 mg, 0.0030 mmol), and P(*o*-tolyl)$_3$ (0.0037 mg, 0.0120 mmol) in anhydrous chlorobenzene (10 mL) was added to a Schlenk tube. The mixture was subjected to three cycles of evacuation and admission of nitrogen and then stirred at 110 °C for 60 h. The resulting reaction mixture was allowed to cool to room temperature and poured slowly into methanol with vigorous stirring. The precipitate was collected by filtration and further purified by sequential Soxhlet extractions with methanol, acetone, and hexane each for 24 h. The remaining residue after extraction was extracted with hot chloroform. The chloroform extract was concentrated and added dropwise to stirring methanol to give **P1** as a black solid (0.303 g, 90%).

^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 9.30–8.50 (br, 4H), 8.05–6.30 (br, 8H), 4.00–3.60 (br, 4H), 3.30–2.60 (br, 8H), 2.10–1.04 (br, 130H), 1.01–0.76 (br, 24H). GPC (THF): $M_n = 14.3$ kDa; $M_w = 46.6$ kDa; PDI = 3.27.

2.2.2. Polymer *P2*

A mixture of 2,5-bis(3-decyl-5-(trimethylstannyl)thiophen-2-yl)thieno[3,2-*b*]thiophene (0.273 g, 0.3000 mmol), 4,7-dibromo-5,6-difluorobenzo [*c*]- [1,2,5]thiadiazole (0.0495 g, 0.1500 mmol), (*E*)-6,6′-dibromo-1,1′-bis(2-decyl-tetradecyl)-[3,3′-biindolinylidene]-2,2′-dione (0.164 g, 0.1500 mmol), Pd$_2$ (dba)$_3$ (0.0056 mg, 0.0060 mmol), and P(*o*-tolyl)$_3$ (0.0074 mg, 0.0120 mmol) in anhydrous chlorobenzene (12 mL) was added to a Schlenk tube. The mixture was subjected to three cycles of evacuation and admission of nitrogen and then stirred at 110 °C for 60 h. The resulting reaction mixture was allowed to cool to room temperature and poured slowly into methanol with vigorous stirring. The precipitate was collected by filtration and further purified by sequential Soxhlet extractions with methanol, acetone and hexane each for 24 h. The remaining residue after extraction was extracted with hot chloroform. The chloroform extract was concentrated and added dropwise to stirring methanol to give **P2** as a black solid (0.292 g, 86%).

^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 9.30–8.70 (br, 2H), 7.24–6.30 (m, 12H), 3.95–3.55 (br, 4H), 2.90–2.70 (br, 8H), 2.05–1.05 (br, 146H), 1.00–0.76 (br, 24H). GPC (THF): $M_n = 20.7$ kDa; $M_w = 41.6$ kDa; PDI = 2.02.



Scheme 1. Synthesis of the polymers, **P1** and **P2**.