Organic Electronics 23 (2015) 17–27

Contents lists available at ScienceDirect

Organic Electronics

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

Effects of bridge units on the properties of indolo[3,2-*b*]carbazole-*co*-difluorobenzo[*d*][1,2,3]triazole based π-conjugated copolymers

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ARTICLE INFO

Article history:
Received 14 January 2015
Received in revised form 4 April 2015
Accepted 5 April 2015
Available online 7 April 2015

Keywords:
Donor-π-acceptor conjugated polymer
Selenophene π-bridge
Optoelectronic properties
Organic field effect transistors
Polymer solar cells

ABSTRACT

Two novel donor-π-acceptor type of conjugated polymers with thiophene or selenophene as the π-bridge between the electron-donating indolocarbazole and electron-accepting difluorobenzotriazole unit, were designed and synthesized through a palladium catalyzed Suzuki polymerization. The replacement of the thiophene bridge by selenophene shows negligible effects on the geometries of molecular chain, as indicated by theoretical calculation on the basis of density of functional theory. However, obvious bathochromic shift along with the increased intensity in the UV–vis absorption profile of selenophene based copolymers relative to their thiophene based counterparts are realized, as can be attributed to the more pronounced heavy atom effects of the selenium than the sulfur atom. Compared to the thiophene based copolymer, the selenophene based copolymer exhibited about one order of magnitude increase in hole mobility, from 0.0014 to 0.01 $cm^2\ V^{-1}\ s^{-1}$, and about two times of magnitude increase in power conversion efficiency, from 1.01% to 2.39%, as evaluated by field effect transistors and bulk heterojunction polymer solar cells, respectively. These results indicated that the selection of appropriate π-bridge by is crucial for the improvement of performance of π-conjugated polymers.

1. Introduction

In recent years, conjugated polymers have attracted tremendous interests owing to their great potential for the fabrication of low-cost, flexible, light-weight organic electronic devices including polymer solar cells (PSCs) [1], polymer light-emitting diodes (PLEDs) [2], organic field-effect transistors (OFETs) [3] and so forth [4]. As one of the most prevalent components, thiophene unit and its derivatives have been widely used for the construction of conjugated polymers due to their exceptional synthetic versatility and well-established π-conjugated characteristics [5]. It was found that replacing thiophene with other π-bridge units, such as furan, bithiophene [6,7], or thieno[3,2-*b*]thiophene [8], can significantly affect the properties of the polymers. An alternative π-bridge unit of selenophene has also drawn much attention as its thiophene counterpart, and a range of high-performance polymer for OFETs and PSCs have been developed on the basis of this moiety [9–16]. It has been demonstrated that the replacement of flanked thiophene units in 4,7-dithiophen-benzo[2,1,3]thiadiazole (DTBT) by the selenophene can lead to obvious bathochromic shift of the absorption spectra due to the less electron negativity along with the intermolecular Se···Se interactions of selenium atom, which can in turn result in the improved performance in polymer solar cells [9]. Compared to the thiophene unit, the lone pair electron on selenophene is more mobile and can thereby give rise to the more pronounced interchain interactions [10,11,14,17]. Recently, Kang et al. reported that copolymers based on selenophene-vinyl-selenophene type of species as electron-donating moiety can result in obviously improved hole mobilities with respect to the thiophene counterparts, as can be attributed to the stronger intermolecular interaction of the former [10,18].

Fluorinated benzo[d][1,2,3]triazole (BTz) [19–21] has been developed as an electron-deficient unit for the construction of donor–acceptor type of conjugated polymers, which possesses relatively deep highest occupied molecular orbital (HOMO) energy level and good charge carrier transport properties [22–26]. The specific advantage of the BTz unit over the benzo[2,1,3]thiadiazole (BT) counterpart is that the lone pair electrons on the nitrogen atom can be easily donated into triazole ring, resulting in the increased band gap of polymers. More to this point, the sp^3-hybrid nitrogen atom in the BTz unit can allow for the incorporation of solubilizing alkyl side chain without sacrificing the planarity of

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http://dx.doi.org/10.1016/j.orgel.2015.04.005
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the backbone. A range of efficient conjugated polymers comprising FBTz as the electron-acceptor and various electron-donating units have been developed for the application in PSCs.

Indolo[3,2-*b*]carbazole (ICz) has emerged as an electron-donating moiety for semiconducting polymers, which comprising two phenyl rings cyclic in the central phenyl through two nitrogen bridge. This enlarged coplanarity can impart improved charge carrier transport property for constructed conjugated copolymers [27–30]. Considering the relatively weak electron-donating property of ICz moiety, the relevant copolymers would exhibit relatively deep HOMO, which is beneficial for the attainment of high open circuit voltage (V_{OC}). In order to develop the medium bandgap polymers (>2.0 eV) for efficient solar cells, we herein demonstrated two donor-π-acceptor type of conjugated polymers by combining the relatively weak electron-donating ICz unit and the electron-accepting FBTz unit. It was recognized that the replacement of the thiophene π-spacer between the FBTz and ICz unit by the selenophene unit can distinctly affect the molecular conformation and electron structures of the resulted copolymers, leading to obviously improved hole mobility, well-extended absorbance, and hence improved photovoltaic performances. These results demonstrated that our current approach can be an effective strategy for the development and optimization of high-performance medium band-gap polymers for PSCs.

2. Results and discussion

2.1. Synthesis and thermal properties

Scheme 1 shows the synthetic routes of the monomers and the polymers. Based on 1,2-difluoro-4,5-dinitrobenzene (**1**) as the starting material, compound 2-dodecyl-5,6-difluoro-2*H*-benzo[d][1,2,3]triazole (**2**) was synthesized with a moderate yield of 36%. By treating **2** with lithium diisopropylamide (LDA) followed by quenching with iodine, the 4,7-diiodo-2-dodecyl-5,6-difluoro-2*H*-benzo[d][1,2,3]triazole (**3**) was obtained in a moderate yield of 57%. The intermediates of 2-dodecyl-5,6-difluoro-4,7-di(thiophen-2-yl)-2*H*-benzo[d][1,2,3]triazole (**TFBTz)** and 2-dodecyl-5,6-difluoro-4,7-di(selenophen-2-yl)-2*H*-benzo[d][1,2,3]triazole (**SFBTz**) were synthesized by a Stille coupling reaction of **3** with tributyl(thiophen-2-yl)stannane and tributyl(selenophen-2-yl)stannane, respectively. The bromination of TFBTz and SFBTz by *N*-bromosuccinimide (NBS) gives target 4,7-bis(5-bromothiophen-2-yl)-2-dodecyl-5,6-difluoro-2*H*-benzo[d][1,2,3]triazole (**M1**) and 4,7-bis(5-bromoselenophen-2-yl)-2-dodecyl-5,6-difluoro-2H-benzo[d][1,2,3]triazole (**M2**) in a good yield of ~70%.

Target copolymers PICz-TFBTz and PICz-SFBTz were synthesized on the basis of a palladium catalyzed Suzuki polymerization by **M1** and **M2** with 3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,11-di(9-heptadecanyl)indolo[3,2-*b*]carbazole (**M3**) [31], respectively. The copolymers were collected by filtration after precipitating the mixture in methanol, and were purified by Soxhlet extraction with methanol, acetone, hexane successively to remove small-molecular weight fractions. Then solids were dissolved in chloroform, reprecipitated with methanol, and collected by filtration. All the resulting copolymers can be readily dissolved in organic solvents including chloroform, tetrahydrofuran (THF), chlorobenzene, and so forth. The number-average molecular weights (M_n) and polydispersity index (PDI) of PICz-TFBTz and PICz-SFBTz were 27.0 kDa (PDI = 1.55) and 59.0 kDa (PDI = 2.0), respectively, as estimated by gel permeation chromatography (GPC) analysis using THF as the eluent and polystyrene standards.

Thermal properties of copolymers were evaluated by thermogravimetric analysis (TGA) and different scanning calorimetry (DSC) measurements. TGA characteristics (Fig. 1) showed that the 5% weight loss temperature were higher than 390 °C, implying good thermal stability of copolymers. The glass transition temperatures (T_g) of PICz-TFBTz and PICz-SFBTz as estimated by DSC were 98 and 104 °C, respectively, with corresponding characteristics shown in Fig. S1 in the Supporting information.

2.2. Characterization of model compounds

To get the disparity of the optical properties and electronic structures of thiophene or selenophene flanked benzo[*d*][1,2,3]-triazole (BTz) unit, we initially measured the UV–vis absorption of the two model compounds of TFBTz and SFBTz. Fig. 2a showed the UV–vis absorption spectra of TFBTz and SFBTz in chloroform solution with concentration of $1 \times 10^{-5}\ \mathrm{g\ mL^{-1}}$. As shown in Fig. 2a, the maximum absorption (λ_{max}) of SFBTz located at 384 nm along with the more pronounced shoulder located at 405 nm, which were distinctly bathochromic shifted relative to that of 374 nm (λ_{max}) and 394 nm (shoulder) for TFBTz, respectively. This observation can be attributed to the more pronounced heavy atom effects of the selenium in selenophene unit than that of the sulfur atom in thiophene unit [32].

In order to investigate the electron structures of the two model compounds, theoretical calculations were carried out on the basis of density functional theory (DFT) at the B3LYP/6-31G(d) level using Gaussian 09 package [33]. The alkyl side chains were replaced by methyl groups to simplify the calculations, and the calculated highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) levels were shown in Fig. 2b. It was noted that the selenophene-based compound SFBTz-Me exhibited reduced energy band gap with respect to thiophene-based TFBTz-Me, which was in good agreement with the bathochromic shift in the UV–vis absorbance of SFBTz-Me (Fig. 2a).

2.3. Photophysical properties

Fig. 3 illustrated the absorption spectra of copolymers PICz-TFBTz and PICz-SFBTz in dilute chloroform solution with concentration of $1 \times 10^{-5}\ \mathrm{g\ mL^{-1}}$ (a) and as thin films (b). From Fig. 3a one can realize that, in chloroform solution, the absorption profile of selenophene-based copolymer PICz-SFBTz exhibited an obvious bathochromic shift with respect to thiophene-based copolymer PICz-TFBTz, which is quite comparable with that realized in model compounds. In addition, both copolymers exhibited dual absorption characteristics as thin films (Fig. 3b), where the relatively weak absorbance in the range of 350–400 nm can be ascribed to π–π^* transitions of the π-conjugated backbone, while the low-energy absorbance with higher intensity can be attributed to the intramolecular charge transfer (ICT) effects [34,35] between the donor to acceptor units for copolymers PICz-TFBTz and PICz-SFBTz, respectively.

It is also worth noting that copolymer PICz-SFBTz exhibited a slightly higher absorption coefficiency of $9.8 \times 10^4\ \mathrm{cm^{-1}}$ than that of $7.1 \times 10^4\ \mathrm{cm^{-1}}$ for PICz-TFBTz, along with a more pronounced shoulder peaked at 529 nm corresponding the intermolecular aggregations. These observations implied that selenophene based PICz-SFBTz can potentially exhibited better absorptivity of sunlight as the photoactive layer of polymer solar cells, which is beneficial for the improved short circuit current of devices. The optical band gaps (E_g^{opt}) as estimated from the onsets of the absorbance were 2.28 and 2.18 eV for PICz-TFBTz and PICz-SFBTz, respectively. Further photoluminescence spectra of copolymers in chloroform solution and as thin films (Fig. S3 in the Supporting information) also exhibited the bathochromic shift of PICz-SFBTz, implying the narrower band gap of selenophene based copolymer which was in good accordance with the UV–vis measurements.