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Modification of a donor-acceptor photovoltaic polymer by integration of optoelectronic moieties into its side chains

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ABSTRACT

In this study, a strategy to modify photovoltaic properties of a known material by integrating certain optoelectronic moieties in its side chains has been described. Thus, a plenty of single and dendritic carbazole units were introduced into the side chains of poly(2,7-(9,9-dialkyl-fluorene)-*alt*-5,5′-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)) (PFDTBT), a famous donor-acceptor alternative conjugated polymer, to see what and how they can change the latter optoelectronic properties. It was found that such modifications not only increase the polymer light-harvesting capabilities in the UV region, but also enhance hole mobility in the pure film state. Furthermore, complicated photophysical and photochemical processes, including energy transfer, electron transfer and site-isolation effect, were observed to take place between carbazole units and the PFDTBT conjugated backbone. These factors work comprehensively and finally improve the polymer photovoltaic properties when modified with single carbazole units, but deteriorate when modified with dendritic carbazole units.

1. Introduction

Polymer solar cells (PSCs) have attracted significant attention in terms of light-weight, solution-processable, low cost, and adaptable to flexible and large area devices. In the past decade, PSCs have achieved a substantial progress [1]. Power conversion efficiency (PCE) for single-junction devices has improved from 3 to 5% before 2005 [2] to nowadays over 9% [3], while that of tandem cells has surpassed 10% [4]. Such remarkable progress makes PSCs as a more attractive and realistic solar electric generation technology. In addition to the improvement in device fabrication technologies, the progressive innovation of active materials plays one of the most important roles to push the field forward [1,5]. Looking back the history of photovoltaic polymers, one may conclude three main streams in the new material design strategies: (1) invention of new conjugated building blocks [6], (2) newly choice and organization of known π-conjugated moieties for conjugated polymer backbone [7], and (3) aliphatic side-chain engineering in order to tune the solubility and interchain interactions among polymer chains [8]. However, little attention has been paid on the non-conjugated modification with optoelectronic moieties on the side chains of conjugated polymers. Up to date, only few examples have been reported [9,10]. For examples, certain mesogens were integrated into the side chain of conjugated polymers for tuning their packing structures in solid state [9]. Hole or electron-transporting units have been appended in the side chains of conjugated polymers for improving their light-emitting performances [10].

Recently, we endeavored to improve photovoltaic properties of conjugated polymers by integration of optoelectronic moieties into their side chains. Here, we report the work on poly(2,7-(9,9-dialkyl-fluorene)-*alt*-5,5′-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)) (PFDTBT) (Chart 1). PFDTBT is a famous donor-acceptor (D-A) conjugated polymer, firstly reported by Andersson et al., in 2003 [11] and laters by others [12]. The alternative electron-rich and -deficient structure in its backbone endows the polymer a broad and intense light absorption spectrum in the range of 450–700 nm. Moreover, PFDTBT possesses a deep highest occupied molecular orbital (HOMO) and has been demonstrated to give an impressing large open-circuit voltage (V_{OC}) (around 1 V) with its bulk heterojunction cells in conjunction with [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$). Although the above mentioned properties of PFDTBT are better than poly(3-hexylthiophene) (P3HT), its photovoltaic efficiency still lags behind P3HT [2]. One of possible reasons is coming from its low hole mobility [13]. Since carbazole

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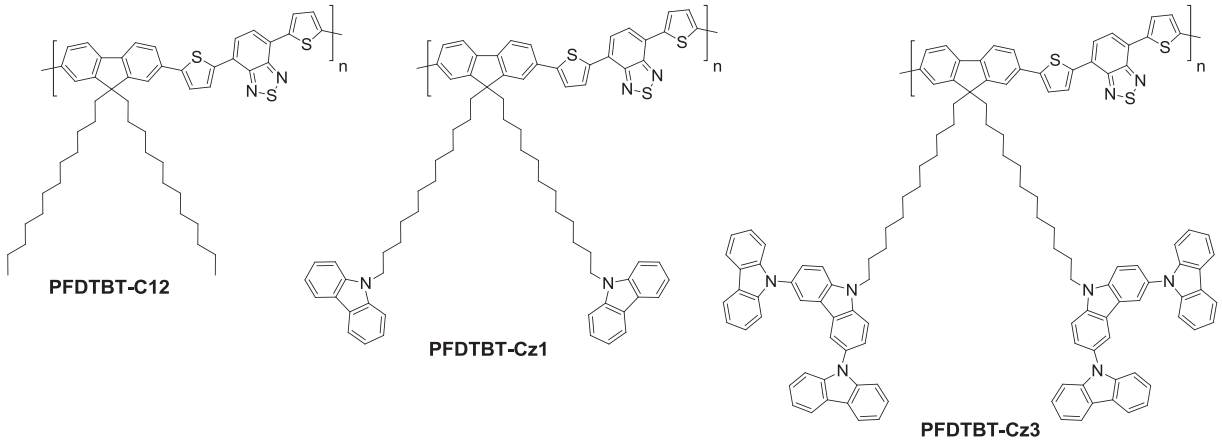

Chart 1. Chemical structures of **PFDTBT-C12**, **PFDTBT-Cz1** and **PFDTBT-Cz3**.

derivatives usually have good hole-transport properties and been widely used as hole transport materials in organic light-emitting diodes [14], we propose here to modify PFDTBT with carbazole units in its side chains. Thus, two polymers, **PFDTBT-Cz1** and **PFDTBT-Cz3**, having single or dendritic carbazole units respectively (Chart 1), were designed and synthesized. We anticipated that a large number of carbazole units surrounding the conjugated backbone would form their own network even in the amorphous state and serve as an additional hole-transport channel besides the conjugated backbone pathway, and thus improve charge transportation in polymer films. The amorphous materials with good charge-transport properties would be greatly welcomed for PSC real application, since they provide a solution to the poor stability and reproducibility of PSC devices owing to the variation and evolution of the microstructure of the active layer based on crystalline materials.

2. Results and discussion

2.1. Synthesis and characterization

The syntheses of single and dendritic carbazole-appended PFDTBT (**PFDTBT-Cz1** and **PFDTBT-Cz3**) are outlined in Scheme 1. The preparation of **PFDTBT-Cz1** started from the attachment of two carbazole units into the side chains of 2,7-dibromofluorene monomer (**F-Cz1**) via two steps from 9H-carbazole (**Cz**), and finished by Stille coupling polymerization of **F-Cz1** with 4,7-bis(5-trimethylstannyl-thienyl-2-yl-2,1,3-benzothiadiazole with a yield of 48%. On the other side, the synthesis of **PFDTBT-Cz3** is a little more complicated. Compound **Cz3**, an important dendritic carbazole precursor, was first prepared via Ullmann condensation reaction of acetyl-protected 3,6-diiodo carbazole (**I-Cz-Amide**) with 9H-carbazole and followed by deprotection. Afterward, **Cz3** was subsequently reacted with 1,12-dibromododecane and 9*H*-2,7-dibromofluorene, affording dendritic carbazole-appended 2,7-dibromofluorene monomer (**F-Cz3**). Stille coupling polymerization of this monomer with 4,7-bis(5-trimethylstannyl-thienyl-2-yl-2,1,3-benzothiadiazole finally produced **PFDTBT-Cz3** in a yield of 53%. In order to check the effect of the introduced single and dendritic carbazole units on their properties, PFDTBT without carbazole units in its side chains (**PFDTBT-C12**, Chart 1) was also prepared by similar Stille coupling polymerization and used as a reference.

All the synthesized polymers have good solubility in $CHCl_3$, chlorobenzene, and dichlorobenzene. Their molecular weight and polydispersity index (PDI) were determined by gel permeation chromatography using monodispersed polystyrenes as standard (Table 1). The data shows a large difference among three polymers. **PFDTBT-Cz1** has a number-average molecular weight (M_n) of 21,882 and a PDI of 17.91. The large PDI indicates the complexity for the Stille coupling polymerization. In contrast, **PFDTBT-Cz3** has a M_n of 7842 with a PDI of 1.28. The small molecular weight of **PFDTBT-Cz3** reflects that the large size of dendritic carbazole units may hamper the proceeding of the polymerization. The reference polymer **PFDTBT-C12** shows a moderate molecular weight and polydispersity (M_n = 10,057, PDI = 2.10). Since molecular weight and its polydispersity have been demonstrated to have great impact on the photovoltaic performance [15], the so prepared three polymers with such large molecular weight differences could not be directly used to investigate the effect of carbazole and dendritic carbazole units. Therefore, in order to exclude the influences of the molecular weight and its polydispersity, preparative size-exclusion chromatography (SEC) was applied on **PFDTBT-Cz1** and **PFDTBT-C12**. The fractions having molecular weight similar to that of **PFDTBT-Cz3** were collected (for **PFDTBT-Cz1**: M_n = 7950, PDI = 1.24; for **PFDTBT-C12**: M_n = 7504, PDI = 1.99) and used for the following property investigation. By means of thermogravimetric analysis (TGA), the thermal decomposition temperature at 5% weight loss was determined to be 407, 399, and 346 °C for **PFDTBT-C12**, **PFDTBT-Cz1**, and **PFDTBT-Cz3** respectively (Fig. 1 and Table 1), indicating the integration of carbazole units slightly decrease thermal stability of the polymers.

2.2. Optical properties

In $CHCl_3$ solution at room temperature, polymer **PFDTBT-C12** exhibited two main absorption bands centered at 542, and 388 nm, respectively (Fig. 2a, Table 2). These peaks originate from the conjugated backbone of PFDTBT. Similarly, polymer **PFDTBT-Cz1** showed these two absorption bands at 539 and 386 nm, a slightly blue-shifted from that of **PFDTBT-C12**. However, in case of **PFDTBT-Cz3**, the blue shifts became larger. The two bands appeared at 523 and 372 nm, 19 and 16 nm blue-shifted from those of **PFDTBT-C12**, respectively. Since the molar molecular weight of the repeating unit of **PFDTBT-Cz3** is larger than those of **PFDTBT-C12** and **PFDTBT-Cz1**, the actual polymerization degree (the average number of repeating units in one polymer chain) of **PFDTBT-Cz3** was small. This would be one of the possible reasons for the above blue-shifted observation with **PFDTBT-Cz3**. Another possible reason may be attributed by the large carbazole dendritic substituents, which