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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.

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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-C₆₁-butyric acid methyl ester (PC₆₁BM). 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(5trimethylstannyl-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 9H-2,7dibromofluorene, affording dendritic carbazole-appended 2,7dibromofluorene 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 CHCl₃, 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 $M_{\rm p}$ 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 $^\circ C$ 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 CHCl₃ 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-C21** showed these two absorption bands at 539 and 386 nm, a slightly blue-shifted from that of **PFDTBT-C12**. However, in case of **PFDTBT-C23**, 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-C23** is larger than those of **PFDTBT-C12** and **PFDTBT-C21**, the actual polymerization degree (the average number of repeating units in one polymer chain) of **PFDTBT-C23** was small. This would be one of the possible reasons for the above blue-shifted observation with **PFDTBT-C23**. Another possible reason may be attributed by the large carbazole dendritic substituents, which



Scheme 1. Syntheses of PFDTBT-Cz1 and PFDTBT-Cz3.

would exert a large steric hindrance on the PFDTBT backbone and induced a most twisted configuration, and thus disfavor to π conjugation. Anyway, as compared with those of **PFDTBT-C12** and **PFDTBT-C21**, the narrower absorption spectrum of **PFDTBT-C23**, would be one of important factors that suggest it is not a good material for photovoltaic applications. In addition to the above two bands, **PFDTBT-C21** exhibited two other peaks around 348 and 334 nm (Fig. 2a, Table 2), consistent with those of compound **C21-Br**. Therefore, these two peaks can be assigned to the absorption of the periphery carbazole units. In case of **PFDTBT-C23**, three peaks observed around 343, 327, and 317 nm originate from the periphery dendritic carbazole units. Since the number of carbazole units is large in **PFDTBT-C23**, the absorption bands of dendritic carbazole units becomes more intense than those of conjugated backbone.

In film state, polymer **PFDTBT-C12** showed an absorption band centered at 567 nm for its conjugated backbone, 25 nm red-shifted from that in solution (Fig. 2b, Table 2). This peak appeared at 560 and 544 nm for **PFDTBT-C21** and **PFDTBT-C23**, respectively, about 21 nm red-shifted from their solution ones. These observations indicate the introduction of carbazole units does not have great impact on the interchain interactions among the conjugated backbone in solid state, and further imply that the original hole transportation channel among polymer backbone would be reserved even after attaching a large dendritic side chains. On the other hand, the absorption band of carbazole units in both **PFDTBT-C23** and **PFDTBT-C23** films showed up at 349 and 346 nm,

respectively (Fig. 3b, Table 2). Only 1 and 3 nm red shifts were observed as compared with those in solution, suggesting that carbazole units almost stay in isolated state even in films. Calculated from the absorption onsets of the film spectra (**PFDTBT-C12**: 680 nm, **PFDTBT-C21**: 673 nm, and **PFDTBT-C23**: 665 nm), the optical band gap of these three polymers is 1.82, 1.84, and 1.86 eV, respectively (Table 2).

In CHCl₃ solution, all three polymers fluoresced when excited at their absorption peak-tops of the conjugated backbones (Fig. 3a, Table 2). PFDTBT-Cz1 showed an emission band around 630 nm, similar to **PFDTBT-C12** (628 nm). Whereas. **PFDTBT-Cz3** displayed a fluorescent band around 620 nm, 8-10 nm-blue shifted from those of PFDTBT-C12 and PFDTBT-Cz1. When normalized the absorbance of the excitation wavelength to be 0.1, the area intensity of the emission band increased following the order of 13,800 (PFDTBT-Cz1), 24,440 (PFDTBT-C12), and 42,128 (PFDTBT-Cz3). This result means the fluorescence from PFDTBT conjugated backbone enhances when the introduction of dendritic carbazole units (Cz3), but quenches when attaching single carbazole units (Cz1) into its side chains. Since carbazole derivatives can generally behave as electron donating quencher, the fluorescence titration experiments were carried out. As shown in Fig. 3b, upon addition of Cz1-Br into the solution of PFDTBT-C12, its fluorescence was gradually quenched with a Stern–Volmer constant (K_{SV}) of 1.26×10^3 M⁻¹, indicating **Cz1-Br** is really a quencher for the fluorescence of PFDTBT. The fact suggests the occurrence of photo-

| Table 1 Molecular weig Cz3. | ht and thermal stabilities | of PFDTBT-C12, PFDTBT-Cz | 1, and PFDTBT |
|-----------------------------------|----------------------------|---------------------------------|------------------------|
| Polymer | So-prepared | SEC fraction ^a | $T_{d}^{b}(^{\circ}C)$ |

| Polymer | So-prepared | | SEC fraction | | $I_{d}^{-}(^{\circ}C)$ | |
|------------|----------------------|-------------------|----------------------|------|------------------------|--|
| | M _n (KDa) | PDI | M _n (kDa) | PDI | | |
| PFDTBT-C12 | 10.1 | 2.10 | 7.50 | 1.99 | 407 | |
| PFDTBT-Cz1 | 21.9 | 17.9 | 7.95 | 1.24 | 399 | |
| PFDTBT-Cz3 | 7.84 ^c | 1.28 ^c | _ | _ | 346 | |

 $^{\rm a}$ After treated by preparative size-exclusion chromatography (SEC) and used in the study.

^b Decomposition temperature at 5% weight loss.

^c **PFDTBT-Cz3** was not subjected to preparative size-exclusion chromatography and used directly in the study.

induced electron transfer between the PFDTBT backbone and the side carbazole units in **PFDTBT-Cz1**. The much larger quenching extent for **PFDTBT-Cz1** than the titration experiment implies a more efficient photo-induced electron transfer when carbazole units are covalently attached. Although the fluorescence titration experiments (Fig. 3c) also showed that compound Cz3-Br can quench the fluorescence of **PFDTBT-C12** with a K_{SV} of 1.76×10^3 M⁻¹, the fluorescence of **PFDTBT-Cz3** still enhanced as compared with that of **PFDTBT-C12**. This fluorescence enhancement phenomenon has been often observed in dendrimer chemistry when optoelectronic functionalities are encapsulated in a large dendritic wedge [16]. In such cases, the dendrimer encapsulation allows optoelectronic functionalities isolated from each other and then avoids collision fluorescence quench. In the case of PFDTBT-Cz3, a lot number of dendritic carbazole units may impose two conflictive effects on the PFDTBT backbone: fluorescence quench by means of photo-induced electron transfer, and fluorescence enhancement by means of dendritic encapsulation effect. Since fluorescence quench effect is weak, PFDTBT-Cz3 finally exhibits fluorescence enhancement.

Carbazole derivatives are good emitters in general. In this study, we also found that **Cz1-Br** and **Cz3-Br** showed very intense fluorescence with bands around 368 nm and 390 nm, respectively, upon excitation at 348 nm (Fig. 4a). However, these bands were almost quenched when they were attached to PFDTBT side chains. Since no spectral position change was observed for the absorption bands of carbazole units of **PFDTBT-Cz1** and **PFDTBT-Cz3** in solution as compared with those of **Cz1-Br** and **Cz3-Br** respectively (Fig. 2a), the fluorescence quench would not cause by the chromophoric packing effect among carbazole units. This implies that energy transfer between carbazole units and PFDTBT backbone

Fig. 1. TGA of PFDTBT-C12, PFDTBT-C21, and PFDTBT-C23 under N_2 atmosphere with a heat rate of 10 $^\circ C$ min $^{-1}$.

would be a main reason. Indeed, upon excitation at carbazole units at 348 nm, all polymers showed a fluorescence peak in the range of 550-750 nm (Fig. 4b), which is corresponding to the emission band of PFDTBT backbone. The area intensity of this band was 12.007. 12.002. and 30.535 for PFDTBT-C12. PFDTBT-Cz1. and PFDTBT-Cz3. respectively, under the same polymer concentration $(1.0 \times 10^{-6} \text{ M})$. Although the area intensity of **PFDTBT-Cz1** was almost the same as that of **PFDTBT-C12**. the occurrence of energy transfer from carbazole units to the PFDTBT backbone can be deduced from the above mentioned fluorescence quench fact of PFDTBT-Cz1 as referred to PFDTBT-C12. In the case of PFDTBT-Cz3, the fluorescence enhancement ratio is 2.54 (30,535/12,007), larger than that when excited at PFDTBT backbone with 542 nm light (42,128/ 24,440 = 1.72). This analysis clearly confirms that energy transfer took place from dendritic carbazole units to the PFDTBT backbone. The existing of energy transfer indicates that carbazole units could behave as light-absorption antenna to enhance light acquisition in the UV region, which may be favorable for their photovoltaic properties.

2.3. Electrochemical properties

The electrochemical properties of the prepared polymers were investigated by means of cyclic voltammetry (Fig. 5). The polymer film samples were prepared by casting their CHCl₃ solutions onto a glassy-carbon working electrode and measured in deoxygenated MeCN containing 0.1 M Bu₄NPF₆ supporting electrolyte at room temperature with a Pt plate counter electrode and a Ag/AgNO₃ reference electrode at a scan rate of 100 mV s⁻¹. The onset oxidation potential (E_{ox}) was determined to be 0.65 V for **PFDTBT-C12**, and 0.63 V for both **PFDTBT-C21** and **PFDTBT-C23** (Table 2). Under the same conditions, the redox potential of ferrocenium (Fc⁺)/ferrocene (Fc) was 0.13 V. Since the absolute energy level of Fc⁺/Fc redox

Fig. 2. . The UV–vis absorption spectra of PFDTBT-C12, PFDTBT-C21, and PFDTBT-C23 (a) in CHCl₃ solution and (b) in film state at room temperature. The UV–vis absorption spectra of compounds C21-Br and C23-Br in CHCl₃ solution are also displayed for comparison.

| Table 2 | | | |
|-------------------------------|---------------------------|---------------|-----------------|
| Optical and electrochemical p | properties of PFDTBT-C12, | , PFDTBT-Cz1, | and PFDTBT-Cz3. |

| Polymer | $\lambda_{abs, \ soln}^{a}(nm)$ | $\lambda_{FL, soln}^{b}(nm)$ | $\lambda_{abs, film}^{c}(nm)$ | $\lambda_{abs, onset}^{d}(nm)$ | $E_{g, opt}^{e}(eV)$ | $E_{\text{ox, onset}}^{f}(V)$ | $E_{\rm HOMO}^{\rm g}({\rm eV})$ | E_{LUMO}^{h} (eV) |
|------------|---------------------------------|------------------------------|-------------------------------|--------------------------------|----------------------|-------------------------------|----------------------------------|---------------------|
| PFDTBT-C12 | 542 (3.28), | 628 | 567, | 680 | 1.82 | 0.65 | -5.32 | -3.50 |
| | 388 (2.90) | | 394 | | | | | |
| PFDTBT-Cz1 | 539 (3.07), | 630 | 560, | 673 | 1.84 | 0.63 | -5.30 | -3.46 |
| | 386 (2.76), | | 394, | | | | | |
| | 348 (2.00), | | 349, | | | | | |
| | 334 (1.63) | | 336 | | | | | |
| PFDTBT-Cz3 | 523 (2.24), | 620 | 544, | 665 | 1.86 | 0.63 | -5.30 | -3.44 |
| | 372 (2.62), | | 386, | | | | | |
| | 343 (3.20), | | 346 | | | | | |
| | 327 (3.25), | | | | | | | |
| | 317 (3.37) | | | | | | | |

^a Absorption bands in CHCl₃ solution at room temperature, their molar absorption coefficients are shown in parentheses with a unit of 10⁴ M⁻¹ cm⁻¹.

^b Fluorescence bands in CHCl₃ solution at room temperature when excited at their absorption peak-top.

^c Absorption bands in film state at room temperature.

^d Absorption onset in film state.

^e Optical band gap, calculated by $E_{g, opt} = 1240/\lambda_{abs, onset}$.

^f Oxidation onset measured by CV.

 $E_{\rm HOMO} = -e \, (E_{\rm ox, onset} + 4.8 - 0.13).$

^h $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g, opt}}$.

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coupling is 4.8 eV below vacuum [17], the HOMO energy level of the polymers can be derived by the following equation:

 $E_{\rm HOMO} = -e(E_{\rm ox} + 4.8 - 0.13) \rm eV$

The results were -5.32 eV for **PFDTBT-C12** and -5.30 eV for both **PFDTBT-Cz1** and **PFDTBT-Cz3**. Following the same method, the onset oxidation potential for the both reference compounds, **Cz1-Br** and **Cz3-Br**, was determined to be 0.63 V, giving their HOMO level of -5.30 eV. This value is the same as that of **PFDTBT-Cz1** and **PFDTBT-Cz3**, and no substantially different from that of **PFDTBT-C12**, implying that hole can freely transfer between carbazole units and the PFDTBT backbone. From the HOMO energy level and optical band gap, the lowest unoccupied molecular orbital (LUMO) of **PFDTBT-C12**, **PFDTBT-Cz1** and **PFDTBT-Cz3** are calculated to be -3.50, -3.46, and -3.44 eV, respectively (Table 2).

2.4. Hole mobility

In order to check the effect of the introduced single and dendritic carbazole side chains on the polymer charge transportation properties, the hole mobility of the polymer films were measured by space-charge-limited current (SCLC) method with a device configuration of glass/ITO/PEDOT:PSS/polymer film/Au. According to Mott–Gurney law, SCLC theory can be described as

$$I = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{\left(V_{\rm a} - V_{\rm bi}\right)^2}{d^3},$$

where I is current density, ε_0 is permittivity of vacuum $(8.85 \times 10^{-12} \text{ F m}^{-1})$, ε_r is relative permittivity of the material and generally taken as 3 for organic polymers, μ is mobility, V_a is applied voltage, V_{bi} is built-in voltage (0.1 V in this work by taking 5.1 eV for the work function of Au and 5.0 eV for work function of PEDOT:PSS), and *d* is the thickness of the active film [18]. For each material, at least five devices with film thickness in the range of 50-120 nm were checked and averaged for the final results. Fig. 6 displays the current density-voltage data of the check devices at SCLC region and their fitting curves. By this method, the hole mobility of PFDTBT-C12 film was determined to be (4.5 \pm 0.4) \times 10^{-7} cm^2 V^{-1} s^{-1}, while those of **PFDTBT-Cz1** and **PFDTBT-Cz3** films to be $(1.5 \pm 0.2) \times 10^{-6}$ and $(2.8 \pm 0.3) \times 10^{-6}$ cm² V⁻¹ s⁻¹ respectively. The data obviously show that **PFDTBT-Cz1** film possessed a higher hole mobility than PFDTBT-C12, while PFDTBT-Cz3 film further improved the value slightly. This result confirms that the introduction of carbazole units indeed improves charge transportation

Fig. 3. (a) Fluorescence spectra of **PFDTBT-C12** (excited at 542 nm), **PFDTBT-C21** (excited at 542 nm), and **PFDTBT-C23** (excited at 522 nm) in CHCl₃ solution at room temperature normalized by the absorbance at the excitation wavelength to be 0.1, and fluorescence spectral change of **PFDTBT-C12** (1 × 10⁻⁵ M) in CHCl₃ at room temperature excited at 542 nm upon titration with (b) **C21-Br**, and (c) **C23-Br**. Insets show their Stern–Volmer plots.

Fig. 4. (a) Fluorescence spectra of **PFDTBT-C12**, **PFDTBT-C21**, **PFDTBT-C23**, and compound **C21-Br** and **C23-Br** in CHCl₃ solution at room temperature upon excitation at 348 nm. The spectra were normalized by the concentration of **PFDTBT-C12**, **PFDTBT-C23**, **PFDTBT-C23** to be 1.0×10^{-6} M, while that of **C21-Br** and **C23-Br** to be 2.0×10^{-6} M. (b) The enlarged region from 550 to 750 nm of the spectra shown in Fig. 4a. The peaks around 700 nm are the frequency-doubled harmonic peaks of the excitation light.

properties of the polymer, which would be favor for their photovoltaic applications.

2.5. Photovoltaic properties

The photovoltaic properties of the polymers were studied with bulk heterojunction OPV cells having a structure of glass/ITO/PEDOT:PSS/active layer/Ca/Al. The active layer was casted from a 1,2-dichlorobenzene solution and composed of the blend of the checked polymer and PC₆₁BM with an optimized weight ratio of 1:3. Upon irradiation by an AM 1.5 G solar simulator with a light density of 100 mW cm⁻², the cell based on the blend of **PFDTBT-C21**/PC₆₁BM showed the best performance, having a V_{OC} of 0.84 V, a short-circuit current (J_{SC}) of 3.03 mA cm⁻², a fill factor (FF) of 39.3%, giving a PCE of 1.00% (Fig. 7a, Table 3). Under the same conditions, the **PFDTBT-C12**-based device exhibited a V_{OC} of 0.77 V, a J_{SC} of 2.48 mA cm⁻², a FF value of 32.5%, then affording a PCE of 0.62%. While, the device based on **PFDTBT-C23** displayed the smallest values of V_{OC} (0.54 V) and J_{SC} (0.63 mA cm⁻²). Combined with its FF value (38.4%), the efficiency of the **PFDTBT-C23**-based cell was only 0.13%.

The observed device performance difference can be explained by their external quantum efficiency (EQE) spectra (Fig. 7b). The device based on **PFDTBT-C12** showed photovoltaic response in the range of 300–700 nm, consistent with its absorption spectrum.

Fig. 5. CV curves of **PFDTBT-C12**, **PFDTBT-C21**, and **PFDTBT-C23** films on glass carbon working electrode in CH₃CN containing 0.1 M Bu₄NPF₆ at a scan rate of 0.1 V min⁻¹ at room temperature, Pt disk and Ag/AgNO₃ electrode as counter and reference electrodes, respectively.

However, the EQE values in this range were all around 15%, resulting in small J_{SC} and FF values. As compared with that of **PFDTBT-C12**-based device, the spectrum of **PFDTBT-C21**—based cell clearly had larger EQE values in the range of 300–450 nm, which is corresponding to the absorption band of carbazole units. This suggests that the introduction of a large number of carbazole units enhances the light absorption in the UV region and then contributes more photocurrent. As a contrast, the introduction of dendritic carbazole unit (**C23**) did not enhance but decreased EQE values in the whole spectral range (less than 7%), resulting in the worst device performance for the **PFDTBT-C23**-based cell. From their EQE data and the AM 1.5 G solar spectrum, the J_{SC} value were calculated to be 2.4, 2.97, and 0.6 mA cm⁻² for the devices based on **PFDTBT-C12**, **PFDTBT-C21** and **PFDTBT-C23**, respectively. The error between the measured and the calculated J_{SC} values is less than 5%.

As mentioned in the above, the property comparison among the three polymers indicate that the integration of dendritic carbazole units does increase the hole mobility and also enable a much intense light-absorption band in the UV region. However, PFDTBT-Cz3 exhibited so inferior photovoltaic performance to PFDTBT-C12 and PFDTBT-Cz1. In order to know the reason, we firstly measured the SCLC hole and electron mobilities for three polymer/PC61BM blend films, which compositions were the same as the active layers of their PV devices. The device configuration for hole mobility measurement was the same as that for pure polymer films, while that for electron mobility changed to Al/blend film/Al. As shown in Table 3, we found that there was no big difference in hole and electron mobilities among three polymer/PC₆₁BM blend films. All these blend samples had a hole mobility in the range of $6.3-8.1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an electron mobility in the range of $4.0-6.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Obviously, charge transportation should not be a cause for their photovoltaic performance differences. Secondly, the charge separation efficiency between donor polymer and PC₆₁BM was checked by fluorescence quenching experiment. As illustrated in Fig. 8, all three blend films displayed an extinguished fluorescence spectrum as compared with their pure films. However, their quenching extents were quite different. For PFDTBT-C12 and PFDTBT-Cz1, both quenching extents were over 90%. But for **PFDTBT-Cz3**, the quenching extent was only 80%, suggesting a much less efficient charge separation process between PFDTBT-Cz3 and PC₆₁BM. Again, this may be related to site encapsulation effect that dendritic carbazole side units impose on the central PFDTBT core. Such effect may not only prevent the collision fluorescence quenching but also hamper electron transfer process between PFDTBT backbone and outside units. The latter would reduce the charge separation efficiency between PFDTBT

Fig. 6. Current density-voltage characteristics and their fitting curves at SCLC region of hole-only devices based on PFDTBT-C12, PFDTBT-C21, and PFDTBT-C23 films.

backbone and $PC_{61}BM$, and thus finally lead to poor photovoltaic performance. Thirdly, the morphology of the active layers for the photovoltaic devices were checked by atomic force microscopy (AFM, Fig. 9). Of interest, a number of short fiber-like objects appeared in the blend film of **PFDTBT-C12**/PC₆₁BM (Fig. 9a). In the case of **PFDTBT-C21**/PC₆₁BM, a large number of small dot-like aggregates appeared (Fig. 9b). However, the morphology of **PFDTBT-C23**/PC₆₁BM turned to bad with the appearance of many big aggregated lump-like structure (Fig. 9c). Obviously, such morphology is not good for efficient charge separation between the donor polymer and PC₆₁BM and would contribute the partial reason for its poor photovoltaic performance.

3. Conclusions

Efficient light harvesting, charge separation and transportation are three main basic requirements for high performance OPV materials. In this study, we have demonstrated that the integration of carbazole and dendritic carbazole units into the side chains of PFDTBT polymers have great impact on their basic optical properties, hole mobility and photovoltaic performance. The results showed that such structural modifications endow the polymers certain complicated photophysical and photochemical communications, including energy transfer, electron transfer and dendrimer site isolation effect, between carbazole side units and the PFDTBT backbone. It was found that the integration of carbazole or dendritic carbazole units does not only enhance light absorption in the UV region, but also improve the hole mobility for the pure polymer films. However, the site isolation effect that dendritic carbazole units impose on the central PFDTBT backbone may hamper the efficient charge separation process between PFDTBT backbone and $PC_{61}BM$, and thus deteriorate its photovoltaic performance. Furthermore, the large dendritic substitutes also brought **PFDTBT**-**Cz3** a narrow absorption spectrum and a poor film morphology when blending with $PC_{61}BM$, which would be important factors for its poor photovoltaic performance. Although the present work did not give a very positive example, the side chain modification with optoelectronic moieties would be one of important strategies to develop novel new organic optoelectronic materials, and would gain more and more attention in the future.

4. Experimental

4.1. Measurements and characterization

¹H NMR spectra were recorded on a Varain Mercury 300 MHz spectrometer. The chemical shifts were determined using tetramethyl silane (TMS) as an internal standard. MALDI-TOF mass spectroscopy was carried out on a Shimadzu Biotech Axima Performance Mass Spectrometer using dithranol or CHCA as a matrix. Molecular weights and polydispersity of the polymers were determined by a Waters 1515 HPLC with a Waters 2489 UV detector using monodispersed polystyrenes as the standard. The optical absorption and emission spectra were recorded on a Hitachi U-3310 UV-vis spectrometer and a Hitachi F-4600 fluorescence spectrometer, respectively. Cyclic voltammetry (CV) was performed on a CHI 660C instrument with a standard three-electrode cell using a glassy carbon as working electrode, a platinum wire as counter electrode, and Ag/AgNO₃ as reference electrode. The samples were first casted on glassy carbon to form a film, then measured in CH₃CN in the presence of 0.1 M Bu₄NPF₆ with a scan rate of 0.1 V min⁻¹. Thermogravimetric analysis (TGA) was performed by a TGA Q500 instrument under N₂ atmosphere with a heat rate of 10 °C min⁻¹. Atomic force microscopy (AFM) was performed on a Veeco Nanoscope IIIa multimode apparatus by a tapping mode with a silicon tip.

4.2. Solar cell device fabrication and characterization

The solar cell prototype devices were fabricated with a structural configuration of ITO glass/PEDOT:PSS/active layer/Ca/Al. First, ITO-coated glass substrates with sheet resistance $\leq 10 \Omega$ sq⁻¹ were cleaned by ultrasonic treatment in deionized water, acetone, and isopropyl alcohol, successively, and then subjected to UV/Ozone cleaning for 20 min. Second, poly(3,4-ethylenedioxythiophene)-

Fig. 7. (a) Current density-voltage curves of polymer PV cells based on the blend of **PFDTBT-C12**, **PFDTBT-C23** with PC₆₁BM (1:3, w/w) under AM 1.5 G illumination with a density 100 mW cm⁻². (b) EQE spectra of polymer PV cells based on the blend of **PFDTBT-C12**, **PFDTBT-C21**, and **PFDTBT-C23** with PC₆₁BM (1:3, w/w).

Table 3 Device parameters of polymer PV cells based on the blend of **PFDTBT-C12**, **PFDTBT-C21**, and **PFDTBT-C23** with PC₆₁BM (1:3, w/w).

| Polymer | V _{OC} (V) | J _{sc} (mA cm ⁻²) | FF (%) | PCE (%) | $\begin{array}{c} \mu_{\rm h}(10^{-5}{\rm cm}^2 \\ {\rm V}^{-1}{\rm s}^{-1}) \end{array}$ | $\begin{array}{c} \mu_{\rm e}(10^{-4}{\rm cm}^2 \\ {\rm V}^{-1}{\rm s}^{-1}) \end{array}$ |
|--------------------------|------------------------|---|--------------|------------|---|---|
| PFDTBT-C12 PFDTBT-Cz1 | 0.77 0.84 | 2.48 3.03 | 32.5 39.3 | 0.62 | 6.3 ± 0.2 6.6 ± 0.3 | 6.5 ± 0.1 4.0 ± 0.2 |
| PFDTBT-Cz3 | 0.54 | 0.63 | 38.4 | 0.13 | 8.1 ± 0.4 | 6.6 ± 0.1 |

poly(styrenesulfonate) (PEDOT:PSS, Heraeus Clevios P VP. Al 4083) was spin-coated from an aqueous solution and heated at 150 °C for 10 min, giving a thickness of about 30 nm. The active layer was composed of the checked polymer and PC₆₁BM (Lumitec LT-8905) in a weight ratio of 1:3, and prepared by spin-coating from a 1,2dichlorobenzene solution (40 mg/mL) at a speed of 3000 rpm for 30 s in a nitrogen-filled glovebox. Afterward, the substrates were transferred into an evaporator and pumped down to $2\times 10^{-6}\,\text{mbar}.$ Subsequently, the cathode of the device, consisting of 10 nm Ca and 100 nm Al, was thermally deposited onto the active layer. Finally, the devices were annealed at 110 °C for 10 min. The active area of the device was 7 mm^2 for each cell. Current density-voltage (*J*-*V*) characteristics were measured in the dark and under AM 1.5 G illumination by a solar simulator (Oriel 94043A, 450 W). The intensity was adjusted to be 100 mW $\rm cm^{-2}$ under the calibration with a NREL-certified standard silicon cell (Orial reference cell 91150). External quantum efficiency (EQE) was detected with a 75 W Xe lamp, Oriel monochromator 74125, optical chopper, lock-in amplifier and a NREL-calibrated crystalline silicon cell. All measurements were performed in a N2-filled glovebox at room temperature.

4.3. Materials

Unless indicated, all commercial reagents were used as received. Reaction solvents were dehydrated following common methods, tetrahydrofuran (THF), ether, and toluene refluxed over a mixture of Na and benzophenone, while chlorobenzene dried over CaH₂ under argon, and freshly distilled prior to use.

4.3.1. 4,7-Di(2-trimethylstannylthiophen-5-yl)-2,1,3-benzothiadiazole

To a solution of 2,2,6,6-tetramethylpiperidine (4.22 g, 29.9 mmol) in THF (85 mL), n-butyllithium hexane solution (1.6 M, 18.69 mL, 29.9 mmol) was added at a temperature of -78 °C. After stirring for 1 h at -78 °C, the reaction mixture was warmed up to room temperature, and then cooled again to -78 °C, followed with the dropwise addition of a solution of 4,7-di(2-thiophene)-2,1,3benzothiadiazol (3.45 g, 11.5 mmol) in THF (35 mL). After stirring at -78 °C for 2 h, Me₃SnCl hexane solution (1.0 M, 29.9 mL, 29.9 mmol) was added and the reaction mixture was warmed up to room temperature. After stirred for 12 h, the reaction was quenched with deionized water and extracted with diethyl ether. The organic phase was washed with deionized water several times, dried over MgSO₄, and evaporated to dryness. The residue was subjected to recrystallization affording from acetone, 4,7-Di(2trimethylstannylthiophen-5-yl)-2,1,3-benzothiadiazole (6.38 g) as orange crystals with a yield of 89%. ¹H NMR (300 MHz, CDCl₃, δ): 8.18 (d, *J* = 4 Hz, 2H), 7.87 (s, 2H), 7.30 (d, *J* = 4 Hz, 2H), 0.43 (s, 18H).

4.3.2. Cz1-Br

To a mixture of carbazole (5.02 g, 30 mmol), tetrabutyl ammonium bromide (0.39 g, 1.2 mmol) was added with 15 mL toluene, 1,12-dibromododecane (19.69 g, 60 mmol) and NaOH aqueous solution (50%, 15 mL). After stirred at 70 °C overnight, the reaction mixture was poured into water and extracted with ethyl ether. The organic phase was washed with water, dried over MgSO₄, and evaporated to dryness. The residue was subjected to silica column chromatography using chloroform/hexane (6:1, v/v) as an eluant, allowing to separate compound **Cz1-Br** (5.00 g) as white solid in a yield of 40%. ¹H NMR (300 MHz, CDCl₃, δ): 8.10 (d, *J* = 8 Hz, 2H), 7.44 (m, 4H), 7.22 (m, 2H), 4.30 (t, *J* = 8 Hz, J = 2H), 3.40 (t, *J* = 7 Hz, 2H), 1.84 (m, 4H), 1.24 (m, 16H).

4.3.3. F-Cz1

The mixture of **Cz1-Br** (3.03 g, 7.28 mmol), 2,7-Dibromo-9H-fluorene (0.78 g, 2.40 mmol), tetrabutyl ammonium iodide (0.09 g, 0.24 mmol), toluene (12 mL), and NaOH aqueous solution (50%, 12 mL) were stirred vigorously at 70 °C for 12 h. After the reaction mixture was cooled down to room temperature, the organic phase was separated, washed with water, dried over MgSO₄ and evaporated to dryness. The residue was subjected to silica column chromatography using chloroform/hexane (1:5, v/v) as an elunent, allowing to separate compound **F-Cz1** (2.38 g) as white solid in a yield of 100%. ¹H NMR (300 MHz, CDCl₃, δ): 8.10 (d, *J* = 8 Hz, 4H), 7.47–7.36 (m, 18H), 7.21 (t, *J* = 8 Hz, 4H) 4.25 (t, *J* = 8 Hz, 4H), 1.84 (m, 8H), 1.23–0.55 (m, 36H).

4.3.4. I-Cz

To a mixture of carbazole (16.72 g, 0.1 mol) and KI (21.58 g, 0.13 mol) was added with 280 mL glacial acetic acid. After heating to reflux to dissolve all the solids in glacial acetic acid, the mixture was cooled down and added with ground potassium iodate (32.1 g, 0.15 mol). Then, the reaction mixture was heated again to reflux for 1 h and afterward cooled down to room temperature. A large amount of compound **I-Cz** was precipitated during the reaction. The crude product was separated by filtration and washed with water, affording pure **I-Cz** (35.24 g) as gray solid in yield of 84%. ¹H NMR (300 MHz, CDCl₃, δ): 8.31 (s, 2H), 8.10 (s, 1H), 7.68 (d, *J* = 8 Hz, 2H), 7.21 (d, *J* = 8 Hz, 2H).

4.3.5. I-Cz-Amide

To a mixture of Compound **I-Cz** (48.60 g, 116 mmol) and acetic anhydride (188.5 mL), was added with boron trifluoride diethyl etherate (2.23 mL). Then, the reaction mixture was refluxed for 1 h and cooled to room temperature. During this procedure, a large amount of product **I-Cz-Amide** was precipitated. After separated by filtration, the crude product was sequently washed with water and alcohol, affording pure **I-Cz-Amide** (43.61 g) as brown solid in a yield of 82%. ¹H NMR (300 MHz, CDCl₃, δ): 8.22 (s, 2H), 7.94 (d, J = 9 Hz, 2H), 7.76 (d, J = 9 Hz, 2H), 2.84 (s, 3H).

4.3.6. Cz3-Amide

To a mixture of **I-Cz-Amide** (0.46 g, 1 mmol), carbazole (0.37 g, 2.2 mmol), and copper powder (0.43 g, 3 mmol) was added with *N*,*N*-dimethylacetamide (DMAc, 7 mL). The mixture was stirred at 170 °C for 36 h. After cooling to room temperature, the mixture was filtered through Celite and then added with water to precipitate the product. After filtration, the filtrate cake was subjected to silica column chromatography using chloroform/hexane (2:1, v/v) as an eluant, allowing to separate compound Cz3-Amide (0.21 g) as gray solid in a yield of 38%. ¹H NMR (300 MHz, CDCl₃, δ): 8.51 (d, *J* = 8 Hz, 2H), 8.15 (m, 6H), 7.74 (m, 2H), 7.40 (m, 8H), 7.29 (m, 4H), 3.04 (s, 3H, CH₃).

4.3.7. Cz3

To compound **I-Cz-Amide** (1.21 g, 2.24 mmol), was added with THF (78.5 mL), DMSO (33.5 mL), H_2O (2.24 mL), and then KOH (1.25 g, 22.28 mmol). The mixture was refluxed for 2 h, then cooled to room temperature, and added with water to precipitate the

Fig. 8. (a) Fluorescence spectra of PFDTBT-C12, PFDTBT-C21, and PFDTBT-C23 films in pure form and blended with PC₆₁BM (1:3, w/w) upon excitation at 560 nm. The spectra were normalized to the A_{560 nm} to be 0.1. (b) Fluorescence quenching extents of the above three blend films as referred to their pure films, respectively.

product. After filtration, the crude product was washed with water, affording pure C23 (1.01 g) as white solid in a yield of 91%. ¹H NMR (300 MHz, CDCl₃, δ): 8.50 (s, 1H), 8.21 (s, 2H), 8.17 (d, *J* = 8 Hz, 4H), 7.72 (d, *J* = 8 Hz, 2H), 7.63 (dd, *J* = 8 Hz, 2H), 7.39 (m, 8H), 7.29 (m, 4H).

4.3.8. Cz3-Br

To a mixture of tetrabutyl ammonium bromide (0.003 g, 0.01 mmol), and aqueous 50% sodium hydroxide (0.3 mL) was added a solution of 3,6-di(9H-carbazol-9-yl)-9H-carbazole (0.10 g, 0.2 mmol) and 1,12-dibromododecane (0.13 g, 0.4 mmol) in toluene (0.3 mL). The mixture was stirred at 70 °C overnight and then poured into water. The organic components were extracted with ethyl ether. The organic phase was washed with water and dried over MgSO₄. After removal of solvent, the residue was purified by column chromatography. The eluant was trichloromethane/hexane (2:1, v/v) giving the product (0.065 g, yield: 44%). 1H NMR (300 MHz, CDCl₃, δ): 8.22 (s, 2H), 8.17 (d, *J* = 8 Hz, 4H), 7.67 (s, 4H), 7.39 (m, 8H), 7.29 (m, 4H), 4.50 (t, *J* = 8 Hz, 2H), 3.40 (t, *J* = 7 Hz, 2H), 2.05 (m, 2H), 1.84 (m, 2H), 1.30 (m, 16H).

4.3.9. F-Cz3

The mixture of **Cz3-Br** (0.29 g, 0.39 mmol), 2,7-Dibromo-9Hfluorene (0.58 g, 0.18 mmol), tetrabutyl ammonium iodide (0.02 g, 0.05 mmol), toluene (20 mL), and NaOH aqueous solution (50%, 20 mL) were stirred vigorously at 70 °C for 12 h. After the reaction mixture was cooled down to room temperature, the organic phase was separated, washed with water, dried over MgSO₄ and evaporated to dryness. The residue was subjected to silica column chromatography using chloroform/hexane (2:3, v/v) as an elunent, allowing to separate compound **F-Cz3** (0.090 g) as white solid in a yield of 30%. ¹H NMR (300 MHz, CDCl₃, δ): 8.20 (s, 4H), 8.15 (d, J = 8 Hz, 8H), 7.63 (s, 8H), 7.46–7.37 (m, 22H), 7.27 (m, 8H), 4.45 (t, J = 8 Hz, 4H), 2.01 (m, 4H), 1.85 (m, 4H), 1.30–0.53 (m, 36H). MALDI-TOF MS (m/z (%)): 1651.6 (100) [M⁺].

4.3.10. PFDTBT-C12

To a mixture of 2,7-dibromo-9,9-didodecyl-fluorene (2.64 g, 4.0 mmol) and 4,7-di(2-trimethylstannylthiophen-5-yl)-2,1,3benzothiadiazol (2.50 g, 4.0 mmol) was added with freshly distilled toluene (60 mL). After degassed by freeze–pump–thaw cycle three times, the mixture was added with Pd(PPh₃)₄ (120 mg, 0.104 mmol) under Ar protection, and then subjected to freeze–pump–thaw cycle again to completely get rid of oxygen. After refluxing for 4 d, the reaction mixture was poured into methanol to precipitate the polymer product. After filtration, the crude product was subjected to Soxhlet extraction with methanol, acetone, and chloroform in sequence. The chloroform fraction was collected, evaporated off the solvent, and dried in vacuum, giving polymer **PFDTBT-C12** (620.2 mg) as purplish red solid in a yield of 19%. *M*_n: 10057, PDI: 2.10. ¹H NMR (400 MHz, 1,2-dichlorobenzene-*d*₄, 80 °C, δ): 7.97–6.53 (m, 12H) 2.03 (m, 4H), 1.07–0.59 (m, 46H).

4.3.11. PFDTBT-Cz1

To a mixture of **F-C21** (1.02 g, 1.03 mmol) and 4,7-di(2-trimethylstannylthiophen-5-yl)-2,1,3-benzothiadiazol (0.64 g, 1.03 mmol) was added with freshly distilled toluene (30 mL). After degassed by freeze–pump–thaw cycle three times, the mixture was added with $Pd(PPh_3)_4$ (31 mg, 0.027 mmol) under Ar protection, and then subjected to freeze–pump–thaw cycle again to completely get rid of oxygen. After refluxing for 4 d, the reaction mixture was poured into methanol to precipitate the polymer

Fig. 9. Topographical height AFM images (5 \times 5 μ m²) of blend films of (a) PFDTBT-C12, (b) PFDTBT-C21, and (c) PFDTBT-C23 with PC₆₁BM (1:3, w/w).

product. After filtration, the crude product was subjected to Soxhlet extraction with methanol, acetone, and chloroform in sequence. The chloroform fraction was collected, evaporated off the solvent, and dried in vacuum, giving polymer **PFDTBT-Cz1** (559.6 mg) as purplish red solid in a yield of 48%. M_n : 21,882, PDI: 17.9. ¹H NMR (400 MHz, 1,2-dichlorobenzene- d_4 , 80 °C, δ): 7.92–6.53 (m, 28H) 3.87 (t, J = 7 Hz, 4H), 2.03 (m, 8H), 1.47–0.66 (m, 36H).

4.3.12. PFDTBT-Cz3

To a mixture of F-Cz3 (0.089 g, 0.05 mmol) and 4,7-di(2trimethylstannylthiophen-5-yl)-2,1,3-benzothiadiazol (0.034 g, 0.05 mmol) was added with freshly distilled toluene (5 mL). After degassed by freeze-pump-thaw cycle three times, the mixture was added with Pd(PPh₃)₄ (31 mg, 0.027 mmol) under Ar protection, and then subjected to freeze-pump-thaw cycle again to completely get rid of oxygen. After refluxing for 4 d, the reaction mixture was poured into methanol to precipitate the polymer product. After filtration, the crude product was subjected to Soxhlet extraction with methanol, acetone, and chloroform in sequence. The chloroform fraction was collected, evaporated off the solvent, and dried in vacuum, giving polymer PFDTBT-Cz3 (50.7 mg) as purplish red solid in a yield of 53%. M_n : 7842, PDI: 1.28. ¹H NMR (400 MHz, 1,2-dichlorobenzene- d_4 , 80 °C, δ): 7.87-6.53 (m, 56H) 4.06 (s, 4H), 1.98-1.64 (m, 8H), 1.33-0.69 (m, 36H).

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