



Synthesis and photovoltaic properties of silafluorene copolymers substituted by carbazole and triphenylamine pendants



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ABSTRACT

In this paper carbazole and triphenylamine substituted 2,7-silafluorene-based copolymers with 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (DBT), namely **Cz-PSF-DBT** and **TPA-PSF-DBT**, respectively, were synthesized and their photovoltaic device performance was investigated with [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as the acceptor. These two polymers show nearly identical absorption spectra in the long wavelength range, which can be ascribed to the identical backbones consisting of silafluorene and DBT moieties. **Cz-PSF-DBT** shows a higher open circuit voltage of 1.0 V due to its higher oxidation onset coming from the σ conjugation between the silica atoms at 9-position and carbazole substituents compared to **TPA-PSF-DBT** of 0.93 V. However, the power conversion efficiency of **TPA-PSF-DBT** is much higher than that of **Cz-PSF-DBT**. The AFM images show the finer morphology of **TPA-PSF-DBT**:PC₇₁BM film than that of **Cz-PSF-DBT**:PC₇₁BM film with a rough surface and a large phase separation, which greatly influence the exciton separation at the donor/acceptor interface. The PL spectra indicate that the smoother morphology and smaller domain sizes can inhibit the radiative loss, which is in accordance with the corresponding device performance. It is demonstrated that different substituents in silafluorene-based polymers play a key role in determining the photovoltaic performance.

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1. Introduction

Silica containing conjugated polymer solar cells (PSCs) are of special interest to people due to their excellent optoelectronic properties. For example, 9,9'-dioctylsilafluorene-based copolymers with 4,7-dithienyl-2,1,3-benzothiadiazole (PSiFC8-DBT) is one of the earliest reported organic photovoltaic (OPV) materials with power conversion efficiency (PCE) exceeding 5% [1]. Dithienosilole is another famous silica-containing building block with a PCE of over 5% [2–6]. Recently, PCE of 7.56% was obtained by tuning the endcaps [7]. Silica atoms can lower the lowest unoccupied

molecular orbitals (LUMO) and the highest occupied molecular orbital (HOMO) of the final polymers, which effectively enhance the ambient stability against O₂ oxidation. It was reported by Helgesen et al. [8] that dithienosilole-based copolymer with DBT was proved to be about 5 times more stable than its carbon analog [9,10]. We firstly reported the synthesis of poly(3,6-silafluorene)s in 2005 [11,12], nearly at the same time as poly(2,7-silafluorene)s by Holmes group [13]. Subsequently, we reported the photovoltaic performance of 2,7-silafluorene-based copolymer with DBT [1]. This work received wide attention and was followed by many groups. For example, Bo's group synthesized a 2,7-silafluorene-based copolymer with dialkyloxy-substituted DBT (PSiFC8-DBTC8) and got high PCE of 6.05% [14] while with 5,6-Ddifluorobenzothiadiazole for organic photovoltaic cells and got a PCE of 4.03% was achieved [15]. Zhan's group synthesized 2,7-diketopyrrolopyrrole silafluorene molecule(SiFC6-2DPP) and got a PCE of 2.05% [16]. Huang's group [17] also reported poly(2,7-silafluorene)s with pendent acceptor groups and got a maximum

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PCE of 3.15%. Jin et al. [18] synthesized 3,6-silafluorene-based copolymer with DBT and got a PCE of 4.05%. More recently, Erlik et al. [19] reported 2,7-silafluorene-based copolymers with benzotriazole derivatives and got a maximum PCE of 2.57%. Marchiori et al. [20] investigated the annealing effect on the device performance and Garcia-Basabe et al. [21] studied the annealing effect on the charge transfer dynamics and molecular orientation of the typical PSiF-DBT. All of these silafluorene-based copolymers mentioned above have alkyl substituents at 9,9-positions.

We have been working on the synthesis of aryl substituted poly(2,7-silafluorene)s in these year for their potential application as blue emitters in polymer light-emitting diodes (PLED). Previously, PLEDs from alkyl substituted poly(2,7-silafluorene)s always showed quite low efficiencies [13,22–24]. The fundamental advance occurred in 2011 after we synthesized a 9,9-diphenyl substituted polysilafluorene [25] with a luminous efficiency (LE) of 2.3 cd/A, which is superior to its corresponding polyfluorene (ca. 1.9 cd/A) [26]. Recently, we synthesized polysilafluorenes with carbazole substituents and triphenylamine pendants [27]. These polysilafluorenes were found to have higher efficiencies than the corresponding polyfluorene analogs. Remarkably, PSF-Cz was found to be a new promising deep blue-light emitter with a LE of ca. 3.28 cd/A, which is among the best deep blue emitters for PLED applications until now. After inserting a triazine [28] layer between PEDOT:PSS and PVK, a higher LE of 4.50 cd/A can be obtained. So we can see the significant influence of the hole-transporting pendants on the PLEDs' performance. As 2,7-silafluorene-based copolymers are never reported to date, we are curious about the effect of the hole-transporting pendants on their OPV performance.

In this paper, we synthesized carbazole and triphenylamine substituted 2,7-silafluorene-based copolymers with 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (DBT), namely **Cz-PSF-DBT** and **TPA-PSF-DBT**, and investigated their OPV performance using [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as the acceptor. It is found **TPA-PSF-DBT** shows a PCE of 3.48%, much higher than **Cz-PSF-DBT** with a PCE of 1.71%, which is adverse to results in blue PLEDs that PSF-Cz has much higher electroluminescence performance than PSF-TPA. Based on the measurements of energy level, morphology and donor/acceptor (D/A) charge transfer PL spectra, etc. the effect of different substituents on silafluorene-based polymer OPV performance is demonstrated, shedding new light on developing silafluorene-based PSCs.

2. Experimental section

2.1. Materials

All chemicals and reagents were used as received from Aldrich, TCI and Acros Chemical Co. unless specified otherwise. All solvents were carefully dried and purified before use. All manipulations involving air-sensitive reagents were performed under a dry argon atmosphere. 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**DBT**) [29], 9,9-bis(N-(2'-ethylhexyl)-carbazole-3-yl)-2,7-dibromosilafluorene (**2**) and 9,9-bis(4-(10-(diphenylamine-4'-phenylmethoxy)-decyloxy)-phenyl)-2,7-dibromosilafluorene (**3**) were synthesized according to the reported procedure [27].

2.2. Characterization

NMR (600 MHz) spectra were obtained using a Bruker 600 MHz spectrometer with tetramethylsilane as an internal standard. C, H, N, S elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). Gel Permeation

Chromatography (GPC) analysis was conducted with a Waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. UV-visible absorption spectra were recorded on a HP 8453 UV-vis spectrophotometer. Cyclic voltammetry (CV) was carried out on a Potentiostat/Galvanostat Model 283 (Princeton Applied Research Co.) in a solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) in acetonitrile at a scanning rate of 100 mV/s at a room temperature under the protection of argon. Atomic force microscopy (AFM) experiments were carried out under ambient conditions by using a Veeco Multi Mode Nanoscope IIIa system operating in tapping mode. Silicon cantilevers with a resonance frequency of around 300 kHz were used.

2.3. 5,6-bis(octyloxy)-4,7-bis[5-(tributylstannyl)-2-thienyl]-2,1,3-Benzothiadiazole (**1**)

1 mL of Lithium diisopropylamide (2 M in pentane, 2 mmol) was added over 40 min to a solution 150 mg of 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (0.5 mmol) in 20 mL of dry THF at –78 °C under argon atmosphere. The mixture was stirred for a further 2 h at –78 °C. 0.55 mL of tributyltinchloride (2.0 mmol) was added dropwise, eventually allowed to rise to room temperature. After being stirred at room temperature for 16 h, the mixture was poured into water and extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate, and concentrated. The crude product was purified by gel chromatography (silica gel, toluene:hexane = 1:100–1:30 containing 0.5% triethylamine as gradient eluent) to afford 83 mg of **1** as a red solid (yield: 76%). Anal. Calcd for C₄₆H₉₂N₂O₉S₃Sn₂ (%): C, 48.01; H, 8.06; N, 2.43; O, 12.51; S, 8.36; Sn, 20.63. Found: C, 47.95; H, 8.08; N, 2.42; S, 8.34. ¹H NMR (600 MHz, CDCl₃) δ 8.57 (d, J = 3.4 Hz, 5H), 7.30 (d, J = 3.4 Hz, 5H), 4.12 (m, 4H), 2.00–1.88 (m, 4H), 1.69–1.55 (m, 12H), 1.50–1.41 (m, 4H), 1.41–1.24 (m, 32H), 1.21–1.13 (m, 12H), 0.99–0.83 (m, 24H). ¹³C NMR (150 MHz, CDCl₃) δ 151.8, 151.0, 139.8, 139.5, 135.1, 131.3, 117.6, 74.3, 31.9, 30.5, 29.7, 29.4, 29.0, 27.3, 26.1, 22.7, 14.1, 13.7, 10.9.

2.4. Poly[9,9-di(N-(2'-ethylhexyl)-carbazole-3-yl)silafluorene-2,7-diyl-alt-5,6-bis(octyloxy)-2,1,3-benzothiadiazole-4,7-diyl] (**2**, Cz-PSF-DBT)

1 (230 mg, 0.2 mmol), **2** (179 mg, 0.2 mmol) were dissolved in 4 mL of toluene. The solution was degassed with argon for 1 h, then Tris(dibenzylideneacetone)dipalladium(0) (6 mg, 0.006 mmol) and Tri(o-tolyl)phosphine (12 mg, 0.036 mmol) was added. The mixture was heated to reflux in argon atmosphere for two days. 60 mg of 2-tributylstannanethiophene in 1 mL of toluene was added and the mixture was stirred for another 12 h. At last, 120 mg of 4-bromothiophene in 1 mL of toluene was added and further reacted for 12 h to end up the reaction. After cooling down, the mixture was dilute with 20 mL of toluene, washed with H₂O for 3 times. The solvent was removed under reduced pressure, and the crude polymer was refluxed with 50 mg trithiocyanuric acid (TMT) and 5 g carbon black in 100 mL of THF for 24 h, filtered, concentrated and Soxhlet extracted with methanol, acetone, hexane and toluene. The solvent was stripped off and the residue was purified by column chromatography (silica gel, toluene as eluent). After concentration followed by reprecipitation twice from methanol, 162 mg of **Cz-PSF-DBT (2)** can be obtained as a red fiber (yield 62%). Anal. Calcd for **Cz-PSF-DBT** (%): C₈₂H₉₄N₄O₂S₃Si, C, 76.23; H, 7.33; N, 4.34; O, 2.48; S, 7.45; Si, 2.17. found: C, 76.18; H, 7.34; N, 4.32; S, 7.43. ¹H NMR (600 MHz, CDCl₃) δ: 8.58 (2H), 8.48 (2H), 8.27 (2H), 8.07 (2H), 7.99 (2H), 7.86 (m, 4H), 7.51 (2H), 7.47–7.40 (m, 4H), 7.38 (2H), 7.17 (2H), 4.16 (m, 8H), 2.1–1.9 (m, 6H), 1.6–1.1 (m, 36H), 0.85 (m, 18H).

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