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Synthesis and Characterization of Conjugated Low Band-Gap Terpolymers Incorporating Carbazole for Photovoltaic Application

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A series of photoactive conjugated low band-gap copolymer (CPSB) and terpolyemrs (TPSBCz-*n*, n = 1 to 4) based on *N*-alkyl carbazole, 4,4'-dialkyl dithienosilole, and bezothiadiazole were synthesized. The copolymer and terpolymers were built with the fraction of the carbazole unit varied for 0, 2.5, 5, 10 and 25 mol%. Among the mixtures, the composition of 25 wt% of terpolymer bearing 10 mol.% of the carbazole unit, TPSBCz-3, and 75 wt% of C₇₁-PCBM found a power conversion efficiency of 0.86% with a open-circuit voltage of 0.59 V, the short-circuit current of 4.85 mA and fill factor of 0.30 under AM 1.5 spectral illumination. Our findings suggest that terpolymer bearing low concentration of carbazole lead to a high power conversion efficiency with improved the short-circuit current due to hole mobility enhancement effect of carbazole unit.

Keywords: Organic Solar Cell, Terpolymer, Carbazole, Photovoltaic.

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1. INTRODUCTION

There has been a great deal of interests in organic photovoltaic system since the first report by $Tang^1$ and Sariciftci² in 1987 and 1992. Among many prerequisites required for a compound to be useful in solar cell application, high PCE (power conversion efficiency) with effective harvest of the solar spectrum is of utmost importance. For many years, several groups of chemists proposed new backbone structures for polymers for low band gap polymers as internal charge transfer from electron-rich to electron deficient unit.^{3–7}

The polycarbazole derivatives were widely investigated and applied in the OLED and OTFT due to photoconductive and high charge mobility of carbazole unit.^{8–11} Recently, Lelcerc group reported a new polycarbazole derivative, PCDTBT, bearing a secondary alkyl side chain on the nitrogen atom of the carbazole unit that showed high solubility and some organization, resulting in a relatively good PCE of 3.6%.¹² This result appears that it could be improved in the mobility of the charge carriers if carbazole group is introduced in the main chain to construct the conjugated backbones.

In general, the amorphous polymers showed low hole mobility to get low J_{sc} and PCE. In order to overcome

this, we introduced the small portion of carbazole moiety into the polymer backbone, by which the general polymer property is retained with the polymer without carbazole, but the hole transporting property have been expected to be improved. In this investigation, we would like to report the preparation and photovoltaic properties of terpolymers incorporating carbazole moiety.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

2.1.1. Representative Polymerization Procedure: Poly[2,6-(4,4'-dihexyldithienosilole)-Co-{4,7-(2,13-benzothiadiazole)}] (CPSB)

A mixture of compound 6 (0.40 g, 0.58 mmol) and 7 (0.17 g, 0.58 mmol), palladium(II) acetate (4.0 mg, 0.017 mmol) and tricyclohexylphosphine (15.0 mg, 0.052 mmol) were added to a degassed toluene (2 mL). The mixture was vigorously stirred at 120 °C for 48 h under a nitrogen atmosphere. After the mixture was cooled to room temperature, it was poured into a mixture of methanol and distilled water (10:1 (v/v)) while being stirred. Dark red precipitate was collected on a filter. The recovered polymer was washed with methanol followed by Soxhlet extraction with methanol to remove oligomers and

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catalyst residue. The recovered yield was 70% (0.20 g). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.23–7.31 (*m*, 4 H, Ar–H), 1.69–1.33 (*m*, 16 H, –CH₂–), 1.10–0.99 (*m*, 10 H, Si–CH₂– and CH₃).

2.1.2. TPSBCz-1

This polymer was prepared by the same manner as described above for the preparation of CPSB. A mixture of compound 6 (0.30 g, 0.44 mmol), 7 (0.12 g, 0.42 mmol) and 8 (0.011 g, 0.02 mmol), palladium(II) acetate (2.9 mg, 0.013 mmol) and tricyclohexylphosphine (10.8 mg, 0.039 mmol). The polymer obtained was a dark red solid. The yield was 60% (0.13 g). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.58–7.59 (*br*, 1.03 H, Ar–H), 7.48–6.81 (*br*, 1 H, Ar–H), 3.71 (*br*, 0.014 H, N–CH₂–), 1.66–1.31 (*br*, 8.02 H, –CH₂–), 1.10–0.99 (*m*, 4.95, Si–CH₂– and CH₃).

2.1.3. TPSBCz-2

The yield was 68% (0.14 g). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.58–7.55 (*br*, 1.08 H, Ar–H), 7.42–6.85 (*br*, 1 H, Ar–H), 3.71 (*br*, 0.042 H, N–CH₂–), 1.66–1.30 (*br*, 8.08 H, –CH₂–), 1.10–0.99 (*m*, 4.85, Si–CH₂– and CH₃).

2.1.4. TPSBCz-3

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The yield was 74% (0.18 g). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.58–7.59 (*br*, 1.17 H, Ar–H), 7.48–6.81 (*br*, 1 H, Ar–H), 3.71 (*br*, 0.088 H, N–CH₂–), 1.66–1.22 (*br*, 8.18 H, –CH₂–), 1.10–0.99 (*m*, 4.69 H, Si–CH₂– and CH₃).

2.1.5. TPSBCz-4

The yield was 55% (0.13 g). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.58–7.59 (*br*, 1.77 H, Ar–H), 7.48–6.81 (*br*, 1 H, Ar–H), 3.71 (*br*, 0.37 H, N–CH₂–), 1.66–1.22 (*br*, 8.91 H, –CH₂–), 1.10–0.99 (*m*, 5.02, Si–CH₂– and CH₃).

2.2. Measurements

Molecular weights of polymers were determined by gel permeation chromatography (GPC, Yong-Lin M930) equipped with TDA 302 detector and PL-gel (Varian) column using polystyrene as standard. THF was employed as an eluent.

Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821 instrument. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at the heating/cooling rate of 10 °C/min on a Mettler TGA 50 thermogravimetric analyzer. The redox properties of polymers were examined by cyclic voltammetry (EG&G 1025). Chlorobenzene as the solvent. The electrolyte the polymer thin films were dip-coated on a platinum rod (2 mm in diameter) using solution employed was 0.10 M tetrabuty-lammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile. The Ag/AgNO₃ and Pt wire (600 μ m in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was 50 mV/s.

2.3. Photovoltaic Device Fabrication

Composite solutions with polymers and C71-PCBM were prepared using a 1,2-dichlorobenzene (DCB). The concentration was controlled adequately in a range of 1.0-2.0 wt%. The polymer photovoltaic devices were fabricated with a typical sandwich structure of ITO/PEDOT: PSS/ active layer/LiF/Al. Current density-voltage (J-V) characteristics of all polymer photovoltaic cells were measured under the illumination of simulated solar light with 100 mW/cm² (AM 1.5 G) by Oriel 1000 W solar simulator. Electric data were recorded using a Keithley 236 sourcemeasure unit and all characterizations were carried out in an ambient environment. The illumination intensity used was calibrated by a standard Si photodiode detector from PV measurements Inc. which was calibrated at NREL. The incident photon-to-current conversion efficiency (IPCE) was measured as a function of wavelength from 360 to 800 nm (PV measurement Inc.) equipped with a halogen lamp as a light source, and calibration was performed using a silicon reference photodiode. Thickness of the thin film was measured using KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ± 1 nm.

3. RESULTS AND DISCUSSION

3.1. General Properties of Polymers

Synthetic routes to the preparation of monomer and polymers can be found in Scheme 1. All polymers were prepared by the Stille coupling reaction^{13,14} with 2,6-bis (tributylstannanyl)-4,4-dihexyldithienosilole (6), 4,7-dibromobenzo-thiadiazole (7) and 2.7-dibromo-N-dodecanyl carbazole (8). They are soluble at room temperature in common organic solvents such as chloroform, tetrahydrofuran (THF), toluene, xylene, and dichlorobenzene. Table I summarizes the polymerization results and general properties of the five polymers prepared in this investigation. The actual contents of the carbazole moiety (8) incorporated into the terpolymers are lower than the feed ratio, also molecular weights of terpolymers (TPSBCz-2 and 3) are significantly reduced when compared with the molecular weight of CPSB (Table I). Among the polymers, CPSB is unique in that it is of alternating sequence of dithienosilole and benzothiadiazole, whereas the other four terpolymers are random sequence.

Thermogravimetric analysis performed in a nitrogen atmosphere shows that thermal stability of the present

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Scheme 1. Synthetic route to the monomer and CPSB and TPSBCz-*n* polymers.

polymers is fairly good. The decomposition temperature is increased from 227 °C for CPSB to 243 °C for TPSBCz-4. The glass transition temperatures (T_g) of the polymers obtained by differential scanning calorimetry (DSC) are

74 °C for CPSB, 75, 77, 78, 83 °C for TPSBCz-1, 2, 3 and 4. The relatively lower T_g values than expected for these polyaromatic polymers can be ascribed to the relatively low M_w and the presence of long alkyl groups in the

Table I. General properties of copolymer (CPSB) and terpolymers (TPSBCz).

	Repeating unit ratio $(x/y/z)$		Average molecular weights		Transition and decomposition temperature (°C)	
Polymers	Feed ratio	Actual ratio (by NMR)	M_w	PDI	T_g	T_d
CPSB	50/50/0	50/50/0	8,500	3.1	74	227
TPSBCz-1	50/47.5/2.5	50/49.3/0.7	9,800	3.7	75	226
TPSBCz-2	50/45/5	50/47.9/2.1	6,700	2.8	77	234
TPSBCz-3	50/40/10	50/45.6/4.4	6,600	3.8	78	232
TPSBCz-4	50/25/25	50/31.3/18.7	11,200	2.1	83	243

Notes: All GPC measurements were performed by using THF as an eluent with polystyrene as the calibration standard. The actual fractions of TPSBCz-n were determined by ¹H NMR. DSC and TGA was performed under a nitrogen atmosphere at the heating/cooling rate of 10 °C/min.

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Fig. 1. UV-vis absorption spectra of the CPSB and TPSBCz-n in film.

dithienosilole and carbazole units. The presence of the carbazole units in the main chain of terpolymers appears to increase the glass transition temperature.

3.2. Optical and Electrochemical Properties

Figure 1 shows the absorption spectra of the five polymers in thin films. According to the UV-vis absorption spectra shown in Figure 1, co- and terpolymers display similar absorption spectral features in chloroform solution and in the film state. The first two peaks in short wavelength region are originated from carbazole and dithienosilole unit, the second from the $\pi - \pi^*$ transition of the whole conjugated systems.

The redox behaviors of the polymers were investigated by cyclic voltammetry (CV).¹⁵ The LUMO levels then were estimated from the HOMO levels and optical band gaps (E_g) of polymers determined from the absorption edges of their UV-vis absorption spectra. The work function of ITO was taken to be 4.8 eV. The results are summarized in Table II. The HOMO level of the main chain of the polymers steadily increased from -5.24 eV for CPSB to -5.17 eV for TPSBCz-4 with increasing the fraction of carbazole unit. The high value of HOMO can be attributed to the electron-donating effect of the nitrogen atom in carbazole moiety.^{16, 17}

 Table II.
 Optical and electrochemical properties of copolymer (CPSB) and terpolymers (TPSBCz).

Polymers	λ_{max} (in CHCl ₃)	λ_{\max} (in film)	$\lambda_{ m onset}$	$E_g^{ m opt}$ (eV)	E _{ox} (V)	HOMO (eV)	LUMO (eV)
CPSB	543	534	714	1.74	0.495	5.24	3.50
TPSBCz-1	531	547	704	1.76	0.453	5.20	3.44
TPSBCz-2	518	545	723	1.72	0.448	5.19	3.47
TPSBCz-3	542	560	728	1.70	0.429	5.17	3.47
TPSBCz-4	541	560	731	1.69	0.434	5.17	3.48

Notes: E_g stands for the band-gap energy estimated from the onset wavelength of optical absorption. E_{ox} is the onset potential of oxidation of polymers.

3.3. Photovoltaic Properties

The device configuration was glass/ITO/PEDOT:PSS (50 nm)/polymer: C_{71} -PCBM (~70 nm)/LiF (0.6 nm)/Al (120 nm). The active layer was spin-coated onto the PEDOT:PSS layer using the polymer/C₇₁-PCBM solution in dichlorobenzene. The optimal performances of polymers were obtained from the conformation of polymers/C₇₁-PCBM ratio of 25:75 (w/w%). The *I*–*V* characteristics and the power conversion efficiencies of representative cells prepared from CPSB or TPSBCz blend with C₇₁-PCBM are shown in Figure 2(b) and Table III. Among the mixtures, the TPSBCz-3 cell has highest power conversion efficiency (PCE) of 0.86%, with a short circuit current density (J_{sc}) of 4.85 mA/cm², an open circuit voltage (V_{oc}) of 0.59 V, and a fill factor (FF) of 0.30 under AM 1.5 spectral illumination.

The IPCE for solar cells with both active materials has been measured, as shown in Figure 2(a). The cell with a TPSBCz- $3/C_{71}$ -PCBM active layer exhibits a higher maximum IPCE (36% at 520 nm) and a wider coverage of the visible spectral range, as expected from the absorption spectrum of the polymers.



Fig. 2. (a) IPCE (incident photon-to-current conversion efficiency) and (b) current density–voltage characteristics of photovoltaic devices (CPSB or TPSBCz- n/C_{71} -PCBM) under AM 1.5 spectral illumination condition.

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Table III. Characteristic current–voltage parameters from device testing at standard AM 1.5 G condition.

Polymers	$J_{ m sc}$	$V_{ m oc}$	FF (fill factor)	PCE (%)
CPSB	1.74	0.43	0.28	0.21
TPSBCz-1	3.19	0.44	0.30	0.41
TPSBCz-2	2.02	0.54	0.28	0.31
TPSBCz-3	4.85	0.59	0.30	0.86
TPSBCz-4	2.49	0.64	0.29	0.47

The J_{sc} value of the polymers steadily increases from 1.74 for CPSB to 4.85 for TPSBCz-3 with increasing the fraction of carbazole unit, but the J_{sc} value of TPSBCz-4 is dropped than that of TPSBCz-3. Generally, J_{sc} is related to the hole mobility and absorption of polymers. Although by increasing the amount of carbazole moiety in terpolymer the J_{sc} was improved, but it dropped after passing critical point. It does appear that the alkyl carbazole in the terpolymer increases its solubility and mobility on one hand, but on other hand reduces the amount of light-absorbing chromophore in the active layer due to the low absorption coefficient of carbazole,¹⁸ so to find the optimal addition ratio may be a key issue in this terpolymer system.

4. CONCLUSION

This paper describes the successful synthesis and application of new terpolymers containing carbazole as donor materials in organic bulk heterojunction solar cells. The heterojunction solar cells based on the terpolymers as donor materials and C_{71} -PCBM as acceptor materials showed PCEs from 0.21 to 0.86%. Although the PCE value of synthesized polymers is not higher than previous best results, this result could serve as a guideline for improved organic bulk heterojunction solar cells.

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