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ORIGINAL PAPER

Synthesis and optical properties of π-conjugated polymers composed of diester-substituted bithiophene and dibenzothiophene or carbazole

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Abstract Novel π-conjugated polymers composed of diester-subsituted bithiophene and dibenzothiophene (PDBT-DEBT) or *N*-alkyl carbazole (PCz-DEBT) were prepared via the Stille cross-coupling polymerization using Pd(0) catalyst. The structures of obtained polymers were confirmed by ^{1}H NMR and IR spectroscopies. Optical properties of the polymers were investigated by UV–vis and photoluminescence spectroscopies. The photoluminescence spectra of the polymers showed strong emission peaks in the green region.

Keywords π-Conjugated polymer · Dibenzothiophene · Carbazole · Stille coupling reaction

Introduction

π-Conjugated polymers have been attracting much attention due to their wide applicable fields such as organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs), chemical sensors, and organic photovoltaics (OPVs). A large number of π-conjugated polymers for these applications have been reported so far. Poly(3-hexylthiophene) (P3HT) is a well-known π-conjugated polymer and has been intensively studied as a promising material for OTFTs and OPVs. The properties of polythiophenes can be adjusted by employing functional groups in the side chains. Polythiophenes with electron withdrawing ester groups in the side chain have been reported as materials for optoelectronic applications. For example, Pomerantz et al. synthesized alkyl ester-substituted polythiophene by the Ullmann

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reaction of alkyl 2,5-dibromothiophene-3-carboxylate or dialkyl 5,5′-dibromo-2,2′-bithiophene-4,4′-dicarboxylate as a monomer [1]. The resulting polymers were applied to OLED as emitting materials. Fréchet et al. reported that the polythiophene composed of diester-substituted bithiophene, and bithiophene in the main chain were applicable to OTFT to show high charge mobility of 0.06 cm^2/V s with on/off ratio $>10^5$ [2]. Polythiophenes bearing tertiary alkyl ester groups in the side chain have been prepared to utilize them as precursors of polythiophene with carboxylic acid and unsubstituted polythiophene by the thermal treatment [3–5]. Tricyclic fused aromatic compounds such as fluorene, carbazole, dibenzothiophene, etc., have been well employed as functional units for π-conjugated polymers. Many polymers involving fluorene and carbazole moieties in the main chain have been reported to exhibit promising properties as materials for OLEDs [6–9] and OPVs [9–12]. Polymers involving dibenzothiophene unit have been reported as thermally stable photo emissive materials [13, 14].

Herein, we report the preparation of novel π-conjugated polymers composed of bithiophene bearing alkyl ester groups at 4,4′- or 3,3′-positions as electron acceptor unit and planar heterocyclic units such as dibenzothiophene and carbazole as electron donor units. Their optical properties were also investigated by UV–vis and photoluminescence spectroscopies.

Experimental

General

^1H NMR spectra were recorded on a Varian INOVA 400 NMR spectroscopy using tetramethylsilane as an internal standard in chloroform-*d* ($CDCl_3$). IR spectrum was recorded from Thermo fishier Scientific NICOLET iS10. UV–vis spectroscopy was measured in dilute chloroform solution on JASCO V570 spectrometer. Photoluminescence spectra were obtained on Hitachi F-2500 fluorescence spectrophotometer. Polymer films for UV–vis measurement were prepared on a glass substrate by a spin coater (700 rpm for 10 s and then 3000 rpm for 60 s) using 10 mg/mL chloroform solution. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography with TOSOH HLC-8120GPC using a calibration curve of polystyrene standards and tetrahydrofuran (THF) as an eluent.

Material

THF and toluene were dried over sodium/benzophenone ketyl and distilled before use. N,N-Dimethylformamide (DMF) was distilled over CaH_2. 4,4′-dibromobiphenyl, dibenzothiophene, PPh_3, $LiAlH_4$, $Pd(PPh_3)_4$, NBS, 1-bromohexane, and trimethylstannyl chloride were obtained commercially and used without further purification. Monomers **11** [2] and **12**[1] were prepared as described in the literature.

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[1] The detailed synthetic conditions will be reported elsewhere.

Synthesis

Dibenzothiophene dioxide **2**

To a solution of dibenzothiophene **1** (5.0 g, 27.1 mmol) in acetic acid (70 mL) was added hydrogen peroxide (12.2 mL) (33% aqueous solution) at room temperature. After refluxed for 4 h, the mixture was poured into water, filtrated, and washed with water and methanol to afford 4.8 g (82%) of **2** as colorless solids. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dt, $J = 0.8$ and 7.6 Hz, 2H), 7.65 (dt, $J = 1.2$ and 7.6 Hz, 2H), 7.80 (dd, $J = 1.2$ and 7.6 Hz, 2H), 7.83 (dd, $J = 0.8$ and 7.6 Hz, 2H).

3,7-Diboromodibenzothiophene dioxide **3**

To a solution of **2** (1.00 g, 4.62 mmol) in conc. H_2SO_4 (30 ml) was added NBS (1.64 g, 9.24 mmol) at room temperature. After 24 h, the solution was poured into ice water carefully. Colorless solids were filtrated and washed with water and methanol. The obtained solids were recrystallized from chlorobenzene to afford 0.81 g (47%) of **3** as colorless needles. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (dd, $J = 2.0$ and 8.4 Hz, 2H), 8.19 (d, $J = 8.4$ Hz, 2H), 8.39 (d, $J = 2.0$ Hz, 2H).

3,7-Dibromodibenzothiophene **4** *[15]*

To a solution of **3** (0.50 g, 1.34 mmol) in diethyl ether (20 mL) was carefully added $LiAlH_4$ (0.20 g, 5.27 mmol). After the solution was refluxed for 30 min, water was added very carefully and then 3 mL of conc. HCl was added. Diethyl ether was removed under reduced pressure to give colorless solids, which were filtrated and washed with methanol to afford 0.26 g (57%) of **4** as colorless solids. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, $J = 2.0$ and 8.4 Hz, 2H), 7.96 (d, $J = 8.4$ Hz, 2H), 7.98 (d, $J = 2.0$ Hz, 2H).

3,7-Bis(trimethylstannyl)dibenzothiophene **5**

To a solution of **4** (1.00 g, 2.92 mmol) in THF (20 mL) was added *n*-BuLi (3.72 mL, 6.13 mmol) (1.65 M in *n*-hexane) at −80 °C. The mixture was stirred for 20 min at −80 °C and then for 10 min at 0 °C. After the mixture was cooled to −80 °C, trimethylstannyl chloride (1.34 g, 6.72 mmol) was added. After stirred for 4 h at room temperature, the mixture was hydrolyzed with water and extracted with diethyl ether. After organic layer was dried over $MgSO_4$, solvent was removed under reduced pressure to give a residue, which was purified with column chromatography (silica gel) using hexane as an eluent to afford 0.72 g (52%) of **5** as colorless solids. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.36 (s, –$SnMe_3$, 18H),7.54 (d, $J = 7.6$ Hz, Ph-H, 2H), 7.98 (s, Ph-H, 2H), 8.13 (d, $J = 7.6$ Hz, Ph-H, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ −9.30 (–$SnMe_3$), 121.01, 129.99, 131.09, 135.61, 139.36. UV–vis λ_{max} 302 nm. PL λ_{max} 375 nm.

4,4′-Dibromo-2-nitro-biphenyl **7**

To a solution of **6** (10.0 g, 32.1 mmol) in acetic acid (150 mL) was added nitric acid (46 mL) at room temperature. After stirred for 6 h at 100 °C, the solution was cooled to room temperature to afford a yellow precipitate. The precipitate was filtrated and washed with water and ethanol to give 7.2 g (63%) of **7** as yellow solids. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, $J = 8.6$, Ph-H, 2H), 7.29 (d, $J = 8.4$ Hz, Ph-H, 1H), 7.56 (d, $J = 8.6$ Hz, Ph-H, 2H), 7.76 (dd, $J = 2.0$ and 8.2 Hz, Ph-H, 1H), 8.04 (d, $J = 2.0$ Hz, Ph-H, 1H).

2,7-Dibromocarbazole **8** *[16]*

A solution of **7** (3.50 g, 9.80 mmol) and PPh_3 (6.43 g, 24.5 mmol) in *o*-dichlorobenzene (20 mL) was refluxed for 7 h. After cooled to room temperature, the resulting solution was purified with column chromatography (silica gel) using hexane/chloroform (1:1 to 1:2) as an eluent to give 1.95 g (61%) of **8** as white-off solids. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, $J =$ 1.6 and 8.4 Hz, Ph-H, 18H), 7.57 (d, $J =$ 1.6 Hz, Ph-H, 2H), 7.87 (d, $J =$ 8.4 Hz, Ph-H, 2H), 8.03 (s, N–H, 1H).

N-Hexyl-2,7-dibromocarbazole **9**

To a solution of **8** (2.00 g, 6.15 mmol) in DMF (60 mL) was added NaH (0.19 g, 8.00 mmol) at room temperature. After the solution was stirred for 30 min at room temperature, 1-bromohexane (1.22 g, 7.38 mmol) was added. After stirred for 20 h, the solution was poured into water and extracted with diethyl ether. Combined organic layer was dried over $MgSO_4$, and solvent was removed under reduced pressure to give a crude oil, which was purified with column chromatography (silica gel) using hexane/ethyl acetate (10:1) as an eluent to give 2.1 g (83%) of **9** as pale yellow solids. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, $J = 7.0$ Hz, $-CH_3$, 3H), 1.27–1.37 (m, $-CH_2-$, 6H), 1.79–1.86 (m, $-CH_2-$, 2H), 4.17 (t, $J = 7.4$, NCH_2-, 2H), 7.33 (dd, $J =$ 1.6 and 8.4 Hz, Ph-H, 2H), 7.52 (d, $J =$ 1.6 Hz, Ph-H, 2H), 7.88 (d, $J =$ 8.4 Hz, Ph-H, 2H).

N-Hexyl-2,7-bis(trimethylstannyl)carbazole **10**

To a solution of **9** (1.00 g, 2.44 mmol) in THF (30 mL) was added *n*-BuLi (3.11 mL, 5.13 mmol) (1.65 M in hexane) at −80 °C. The solution was stirred for 20 min at −80 °C and then for 10 min at 0 °C. After the solution was cooled to −80 °C, trimethylstannyl chloride (1.12 g, 5.61 mmol) was added. After stirred for 3 h at room temperature, the solution was poured into water and extracted with diethyl ether. Combined organic layer was dried over $MgSO_4$, and organic solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel) using hexane as an eluent to give a colorless oil, which was treated with methanol to give 0.75 g (53%) of **10** as colorless solids. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (s, $-SnMe_3$, 18H), 0.88 (t, $J = 7.2$ Hz, $-CH_3$, 3H),1.27–1.42 (m, $-CH_2-$, 6H), 1.86–1.93 (m, $-CH_2-$, 2H), 4.33 (t, $J = 7.2$ Hz,

NCH_2–, 2H), 7.32 (d, $J = 7.6$ Hz, Ph-H, 2H), 7.51 (s, Ph-H, 2H), 8.07 (d, $J = 7.6$ Hz, Ph-H, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ −9.22 (–$SnMe_3$), 14.02, 22.56, 26.93, 28.94, 31.52, 42.65, 115.66, 119.8, 122.97, 125.49, 139.22, 140.07. UV–vis λ_{max} 296 nm. PL λ_{max} 345 nm.

Polymerization

A typical procedure is as follows. To a solution of **5** (0.25 g, 0.50 mmol) and **11** (0.37 g, 0.50 mmol) in toluene (40 mL) and DMF (10 mL) was added $Pd(PPh_3)_4$ (46 mg, 0.040 mmol) at room temperature. After stirred for 48 h at 115 °C, the solution was cooled to room temperature and then poured into methanol (300 mL). The resulting precipitate was collected by filtration to give 0.34 g (88%) of PDBT-DE(4,4′)BT as yellow solids.

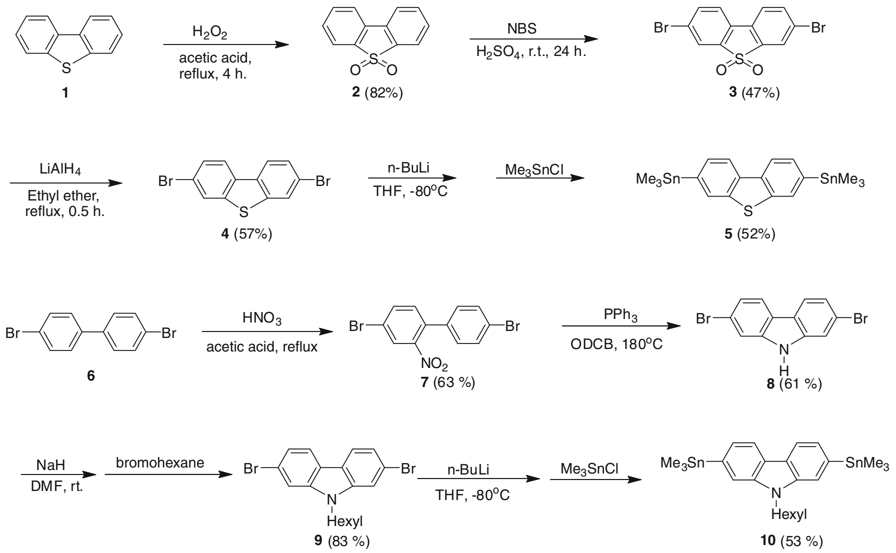
PDBT-DE(4,4′)BT. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, –CH_3, $J = 6.6$ Hz, 6H), 1.11–1.26 (m, –CH_2–, 40H), 4.18 (t, –OCH_2–, $J = 6.6$ Hz, 4H), 7.65–768 (m, Th–H and Ph-H, 4H), 8.00–8.05 (m, Ph-H, 2H), 8.18–8.22 (m, Ph-H, 2H). IR (ATR) 3055, 2920, 2850, 1705 (C=O), 1195 cm^{-1}.

PCz-DE(4,4′)BT. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, –CH_3, 9H),1.11–1.95 (m, –CH_2–, 48H), 4.34 (s, –NCH_2–, 2H), 7.44 (s, Ph-H, 2H), 7.61 (s, Th–H, 2H), 7.61 (s, Th–H, 2H), 7.68 (s, Ph-H, 2H), 8.81 (s, Ph-H, 2H). IR (ATR) 3064, 2921, 2851, 1713(C=O), 1191 cm^{-1}.

PDBT-DE(3,3′)BT. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, –CH_3, $J = 7.2$ Hz, 6H), 1.12–1.24 (m, –CH_2–, 36 H), 1.54 (br, –CH_2–, 4H), 4.14 (s, –OCH_2–, 4H), 7.66–7.77 (m, Ar–H, 4H), 7.86–7.89 (m, Ar–H, 4H), 8.04–8.16 (m, Ar–H, 4H). IR (ATR) 3050, 2919, 2850, 1705 (C=O), 1241, 1212 cm^{-1}.

Results and discussion

Monomers **5** and **10** were synthesized as shown in Scheme 1. The synthetic procedures for 3,7-dibromobenzeothiophene (**4**) [15] and 2,7-dibromocarbzaole (**8**) [16] were referred to the literatures. 3,7-Bis(trimethylstannyl)dibenzothiophene **5** was prepared from dibenzothiophene **1** as a starting material. **1** was oxidized by hydrogen peroxide to give dibenzothiophene dioxide **2** in 82% yield. Bromination of **2** was performed with *N*-bromosuccinimde in H_2SO_4 to give 3,7-diboromo-dibenzothiophene dioxide **3** in 47% yield. 3,7-Dibromodibenzothiophene **4** was prepared by the reduction of **3** with $LiAlH_4$ in 57% yield. 3,7-Dilithiodibenzothiophene prepared from **4**, and *n*-BuLi was reacted with trimethylstannyl chloride to afford monomer **5** in 52% yield. The synthesis of *N*-hexyl-2,7-bis(trimethylstannyl)carbazole **10** was conducted using 4,4′-bibromobiphenyl **6** as a starting material. The nitration of **6** with HNO_3 in acetic acid gave 4,4′-dibromo-2-nitro-biphenyl **7** in 63%. Cyclization of **7** in the presence of PPh_3 afforded 2,7-dibromocarbazole **8** in 61% yield. The addition of 1-bromohexane into the mixture **8** and NaH gave *N*-hexyl-2,7-dibromocarbazole **9** in 83% yield. *N*-Hexyl-2,7-bis(trimethylstannyl)carbazole **10** was prepared by a similar synthetic method for **5** with *N*-hexyl-2,7-dilithiocarbzaole prepared from **9** and *n*-BuLi, and trimethylstannly chloride in

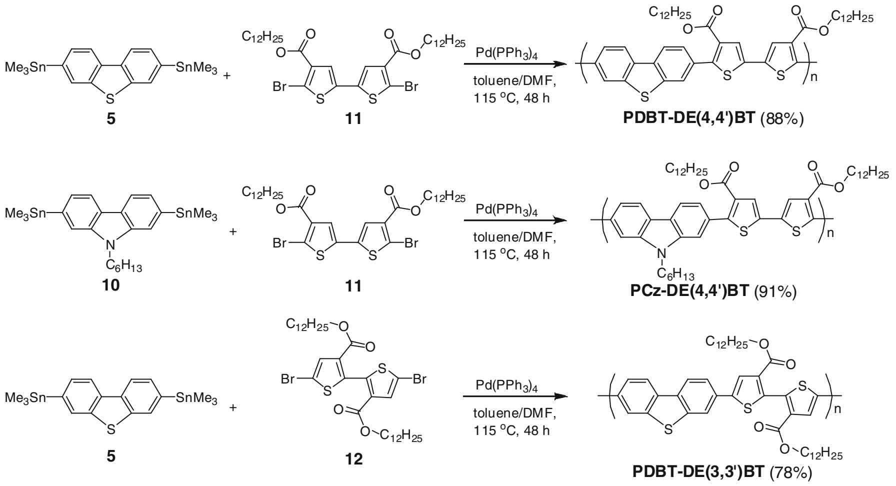


Scheme 1 Synthesis of monomers

53% yield. To the best of our knowledge, trimethylstannyl substituted compounds **5** and **10** have not been reported yet. **5** and **10** were obtained as colorless solids without decomposition during the purification step by silica gel column chromatography. The structures of **5** and **10** were confirmed by ^{1}H and ^{13}C NMR spectroscopies. Didodecyl 5,5′-dibromo-2,2′-bithiophene-4,4′-dicarboxylate **11** was prepared as described in the literature [2]. Didodecyl 5,5′-dibromo-2,2′-bithiophene-3,3′-dicarboxylate **12** was synthesized by the similar synthetic method for **11**.

Polymerization was conducted by the Stille cross-coupling polymerization using a catalytic amount of $Pd(PPh_3)_4$ in toluene/DMF (Scheme 2). The resulting polymers were purified by reprecipitation into methanol and collected by filtration. Polymerization of **11** with **5** or **10** afforded PDBT-DE(4,4′)BT and PCz-DE(4,4′)BT in 88 and 91% yields, respectively. The weight-average molecular weight (M_w) and distribution (M_w/M_n) were 1.24×10^4 and 3.9 for PDBT-DE(4,4′)BT and 8.80×10^3 and 1.9 for PCz-DE(4,4′)BT, respectively (Table 1). In order to compare the optical properties, the polymer bearing diester groups at the 3,3′-positions of bithiophene unit was designed as well. Polymerization of **12** with **5** gave PBDT-DE(3,3′)BT in 78% yield, together with $M_w = 7.50 \times 10^3$ and $M_w/M_n = 1.4$ (Table 1). All of the polymers were obtained as yellowish solids and soluble in organic solvents such as chloroform, toluene, and chlorobenzene. The structures of obtained polymers were confirmed by ^{1}H NMR and IR spectroscopies. The representative ^{1}H NMR spectrum of PCz-DE(4,4′)BT is shown in Fig. 1. The spectrum shows the signals of N-CH$_d$ and O-CH$_f$ with an integration ratio of 1:2, indicating that the polymer had an alternating structure.

Optical properties of prepared polymers were investigated by UV–vis and photoluminescence spectroscopies. First, absorption spectra of the polymers were



Scheme 2 Synthesis of polymers

Table 1 Results of polymerization

	Yield (%)[a]	M_w[b]	M_n[b]	M_w/M_n[b]
PDBT-DE(4,4′)BT	88	12400	3200	3.9
PCz-DE(4,4′)BT	91	8800	4600	1.9
PBDT-DE(3,3′)BT	78	7500	5500	1.4

[a] Insoluble part in methanol

[b] GPC (THF), polystyrene standards

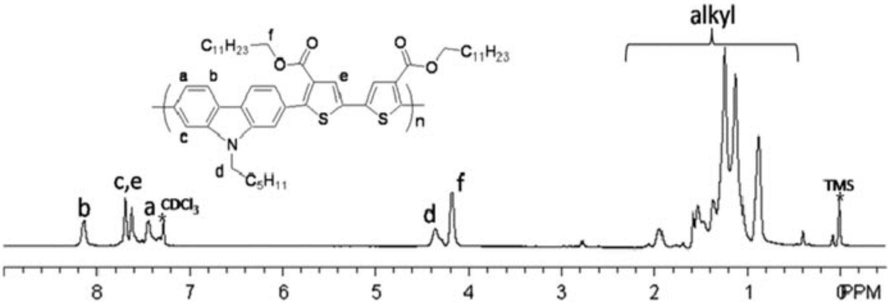


Fig. 1 ^1H NMR spectrum of PCz-DE(3,3′)BT in $CDCl_3$

measured in chloroform and in film states (Table 2; Fig. 2). Absorption maxima of PDBT-DE(4,4′)BT in chloroform and in film state appeared at 381 and 405 nm, respectively. Absorption maxima of PCz-DE(4,4′)BT were observed at 379 and 404 nm in chloroform and in film state, respectively. These results indicate that the change in the structure of main unit from dibenzothiophene to carbazole has no effect on the absorption maxima. A slight difference was observed in the long wavelength region; an absorption spectrum of PDBT-DE(4,4′)BT in chloroform reached up to around 500 nm, whereas the absorption edge of PCz-DE(4,4′)BT was around 470 nm. This result can be explained with the structural difference; PDBT-DE(4,4′)BT involving relatively rigid moiety of dibenzothiophene may have more planar conformation compared to PCz-DE(4,4′)BT having *N*-hexyl carbazole unit. Photoluminescence spectra of the polymers in chloroform were also investigated (Table 2; Fig. 2). Emission spectra of the polymer solutions exhibited absorption maxima at 479 and 480 nm for PDBT-DE(4,4′)BT and PCz-DE(4,4′)BT, respectively, with similar emission patterns as shown in Fig. 2. Optical properties of the polymers PDBT-DE(4,4′)BT and PBDT-DE(3,3′)BT bearing alkyl ester groups in the different positions were compared as well. Although absorption maxima of the polymers in chloroform did not show significant difference, their films revealed clear difference. An absorption maximum of PBDT-DE(3,3′)BT was blue-shifted by 15 nm than that of PDBT-DE(4,4′)BT, implying that the conjugation length can be controlled by changing the position of alkyl ester groups in the side chain. We conducted an annealing of polymer films at 150 °C in order to investigate absorption maximum shift by the polymer conformation change. However, no significant change was observed in absorption maxima, indicating that the conformations are retained even at increased temperature. On the other hand, interesting result was observed in the emission spectrum of PBDT-DE(3,3′)BT. The emission spectrum of PBDT-DE(3,3′)BT solution showed a drastic red shift compared to those of PDBT-DE(4,4′)BT and PCz-DE(4,4′)BT (Fig. 2). The emission behaviors in the film state were also investigated by irradiating the films under UV lamp (365 nm). The films of PDBT-DE(4,4′)BT and PCz-DE(4,4′)BT exhibited strong greenish emission, whereas that of PDBT-DE(3,3′)BT showed greenish yellow emission. The reason on the drastic red shift of an emission maximum of PDBT-DE(3,3′)BT compared to those of PDBT-DE(4,4′)BT and PCz-DE(4,4′)BT needs to be investigated further. Although the unusual phenomenon in the emission is not clear at present, it was found that an emission maximum and emission color of π-conjugated polymer can be adjusted by changing the substituent position in the side chain.

Table 2 Optical properties of polymers

Polymer	UV–vis λ_{max}/nm			Emission λ_{max}/nm
	Solution[a]	As-prepared film[b]	Annealed film[b,c]	Solution[a]
PDBT-DE(4,4′)BT	381	405	405	479
PCz-DE(4,4′)BT	379	404	404	480
PBDT-DE(3,3′)BT	382	390	389	517

[a] In chloroform

[b] Spin coated from chloroform solution

[c] At 150 °C for 10 min

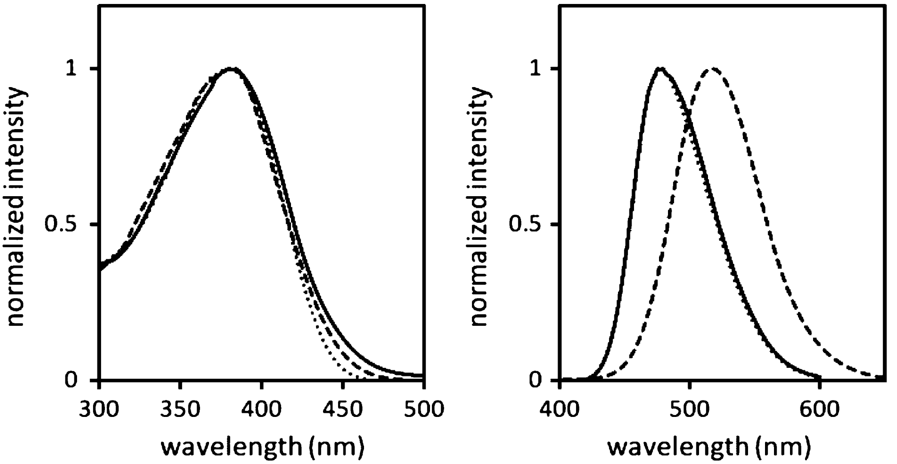


Fig. 2 UV–vis (left) and photoluminescence spectra (right) of PDBT-DE(4,4′)BT (*solid line*), PDBT-DE(3,3′)BT (*dashed line*), and PCz-DE(4,4′)BT (*dotted line*) in chloroform

Conclusion

Novel π-conjugated polymers, PDBT-DE(4,4′)BT, PDBT-DE(3,3′)BT, and PCz-DE(4,4′)BT were successfully prepared via the Stille cross-coupling polymerization. Optical properties of the resulting polymers were examined by UV–vis and photoluminescence spectroscopies. PDBT-DE(4,4′)BT and PCz-DE(4,4′)BT showed very similar absorption and emission behaviors in both solution and film states, implying that the replacement from dibenzothiophene to carbazole unit in the main chain did not affect the optical properties. However, the position of side chain in bithiophene unit significantly influenced on the absorption and emission; PDBT-DE(3,3′)BT film exhibited an absorption maximum at the shorter wavelength than PDBT-DE(4,4′)BT, whereas an emission maximum of PDBT-DE(3,3′)BT appeared at the longer wavelength than that of PDBT-DE(4,4′)BT. The spin-casted polymer films were irradiated by UV lamp (365 nm) to exhibit strong greenish emission for PDBT-DE(4,4′)BT and PCz-DE(4,4′)BT and greenish yellow emission for PDBT-DE(3,3′)BT, respectively.

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