Synthesis and Structure–Property Relationship of Carbazole-*alt*-Benzothiadiazole Copolymers

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ABSTRACT: A series of four π-conjugated carbazole-*alt*-benzothiadiazole copolymers (PCBT) were prepared by Suzuki cross-coupling reaction between synthesized dibromocarbazoles as electron-rich subunits and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)−2,1,3-benzothiadiazole as electron-deficient subunits. The subunits were directly linked through 2,7- or 3,6-positions of the carbazole. In addition, the carbazole monomers have been *N*-substituted by a branched or a linear side-chain. The chemical structure of the copolymers and their precursors was confirmed by NMR and IR spectroscopies, and their molar masses were estimated by SEC. Thermal analysis under N_2 atmosphere showed no weight loss below 329°C, and no glass transition was observed in between 0 and 250°C. The band gaps of all PCBTs evaluated by optical spectroscopies and by cyclic voltammetry analysis were consistent with expectations and ranged between 2.2 and 2.3 eV. Finally, 2,7 and 3,6 linkages were shown to influence optical properties of PCBTs. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *00*, 000–000

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INTRODUCTION Over the last decades, organic semiconductors have been widely considered in the composition of numerous electrical and optical devices, as an alternative to their inorganic analogous.[1–3] These materials have been used as active layers in molecular electronics,[4] nonlinear optical devices,[5,6] sensors,[7,8] light-emitting diodes,[9–11] field-effect transistors,[12–14] memories,[15] and organic solar cells.[16–19] Their organic nature offers a great potential for low cost, lightweight, easy processability, and large-area flexible devices.

The synthetic progresses over decades have allowed a great versatility of methods and tailoring of π-conjugated polymers with specific properties. For instance, alternating electron-rich and electron-deficient moieties in polymeric systems (pull-push copolymer) have shown promising properties especially for photovoltaic applications, since they favour the formation of an intramolecular charge transfer (ICT), which, among other parameters, allows a narrowing of the band-gap.[20]

Among all π-conjugated polymers, such as poly(1,4-phenylene)s,[21] poly(phenylene vinylene)s,[22] and poly(thiophene)s[23–27] that have been widely studied over the years, polyfluorenes[28] and polycarbazoles[29] have attracted specific attention for application in Organic Light Emitting Diodes (OLEDs) or in Organic Photovoltaic (OPV). Nevertheless, carbazole derivatives are somehow preferred as they show better stability (both chemically and environmentally), the 9-position of carbazole being less sensitive than in the case of fluorene,[30,31] and still allowing the grafting of a solubilizing group.[32] Homopolymers of 2,7- and 3,6-carbazoles have been widely investigated as blue light emitters in OLED[33,34] and as semiconducting layer in organic field-effect transistors (OFET).[35] Due to the electron-donating character of the carbazole unit, its coupling with other aromatic electron-deficient moieties allowed an enhanced conjugation in push-pull type copolymers.[36] In this context, electron-deficient moieties such as benzothiadiazole,[37–40] benzoxadiazole,[41] quinoxaline,[42,43] were considered as comonomers and introduced at various ratios in combination with 2,7- and 3,6-linked carbazole subunits. For instance, carbazole-*alt*-benzothiadiazole copolymers have attracted particular attention since Witker and Reynolds demonstrated that this combination allows a significant decrease of the band gap.[37] In the

Additional Supporting Information may be found in the online version of this article.

literature, the band gaps of carbazole-*alt*-benzothiadiazole copolymers using thiophene units as spacers are weakly dependent of the molar masses[39,44] and the linkage position (2,7- or 3,6-) on the carbazole.[45] This can be explained by an equivalent effective intramolecular charge transfer. The influence of the linkage position had been studied by Park et al. on the latter materials.[46] The main difference was that (3,6-carbazole) derivatives exhibited higher hole mobility.

In this work, we investigated the alternation between carbazole and benzothiadiazole in the absence of any spacer in order to observe the direct influence of each subunit onto optoelectronic properties taking into account 2,7- and 3,6-linked carbazole moieties. We thus designed four copolymers which differ by their linkage position (2,7- and 3,6-) and the nature of their substituents. The properties of each polymer, such as thermal, optical, and electrochemical will be discussed.

EXPERIMENTAL

Materials

Ethyl formate and 4-4'-Dibromobiphenyl were purchased from Alfa Aesar and used without further purification. Tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), toluene and dimethylsulfoxide (DMSO) were purified from a solvent purification system (MBraun MB-SPS-800) prior to use. Dimethylformamide (DMF) was purchased from Scharlau and used as received. Poly(3,4-ethylenedioxy-thiophene):poly(styrene sulfonate) (PEDOT:PSS) was purchased from Baytron P and passed successively through a 0.8 μm and a 0.45 μm PVDF syringe filter before spin-coating. [6,6]-Phenyl-C61-butyric acid methyl ester (PCBM) was obtained from Solaris. All other reagents were purchased from Alfa Aesar, Sigma-Aldrich, Acros Organics or Strem Chemicals and used as received.

Synthesis of Precursors and Polymers

General Procedure for N-Dodecyldibromocarbazole Derivatives Synthesis

Dibromocarbazole derivative (1 eq), powdered K_2CO_3 (excess) and DMF were stirred at 80°C under argon, and then 1-bromododecane (1.5 eq) was added dropwise. The reaction medium was heated at 80°C for 16 h. The mixture was extracted with diethyl ether and water and dried over $MgSO_4$. After removing the solvent, the crude product was purified by flash chromatography (cyclohexane/ethyl acetate 9/1) to give:

N-Dodecyl-2,7-Dibromocarbazole (1).

White crystals (0.352 g, 47%). m.p. 70°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 1.5 Hz, 2H), 7.34 (dd, J = 8.3, 1.7 Hz, 2H), 4.18 (t, J = 7.4 Hz, 2H), 1.89 – 1.77 (m, 2H), 1.42 – 1.17 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 141.51, 122.66, 121.61, 121.42, 119.83, 112.16, 43.50, 32.05, 29.74, 29.70, 29.63, 29.47, 28.91, 27.31, 14.27. FTIR (ATR): $\nu = 2917$, 2847, 1586, 1447, 1423, 1314, 1239, 1223, 1129, 1052, 997, 911, 832, 818, 792, 721, 593 cm^{-1}. HRMS (EI+, m/z) [M]+ calculated for $C_{24}H_{31}Br_2N$: 491.0823, found 491.0815.

N-Dodecyl-3,6-Dibromocarbazole (3).

White crystals (5.503 g, 55%). m.p. 68°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 (d, J = 1.9 Hz, 2H), 7.57 (dd, J = 8.7 Hz, 2.0 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 4.25 (t, J = 7.2 Hz, 2H), 1.83 (m, 2H), 1.28 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 139.46, 129.14, 123.59, 123.40, 112.07, 110.53, 43.50, 32.05, 29.72, 29.66, 29.59, 29.47, 28.98, 22.83, 14.27. FTIR (ATR): $\nu = 2919$, 2847, 1469, 1434, 1288, 1224, 1148, 1057, 1017, 870, 831, 802, 785, 724, 648, 564 cm^{-1}. HRMS (EI+, m/z) [M]+ calculated for $C_{24}H_{31}Br_2N$: 491.0823, found 491.0810.

General Procedure for N-9'-Heptadecanyldibromocarbazole Derivatives Synthesis

Dibromocarbazole derivative (1 eq) and powdered KOH (excess) were stirred in DMSO under argon, and then solution of 9-heptadecanyl-*p*-toluenesulfonate (1.5 eq) dissolved in DMSO was added dropwise. The reaction medium was stirred at room temperature for 20 h. The mixture was extracted with cyclohexane and water and dried over $MgSO_4$. After removing the solvent, the crude product was purified by flash chromatography (cyclohexane) to give:

N-9-Heptadecanyl-2,7-Dibromocarbazole (2).

White crystals (0.519 g, 58%). m.p. 73°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.90 (t, J = 9.4 Hz, 2H), 7.69 (s, 1H), 7.54 (s, 1H), 7.33 (d, J = 3.7 Hz, 2H), 4.42 (tt, J = 10.2, 5.1 Hz, 1H), 2.26 – 2.13 (m, 2H), 1.96 – 1.84 (m, 2H), 1.31 – 1.07 (m, 22H), 1.04 – 0.91 (m, 2H), 0.83 (t, J = 7.0 Hz, 6H). Multiple and broad ^{1}H peaks are due to the phenomenon of atropisomerism.[45,47] ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 143.06, 139.59, 122.47, 121.62, 121.36, 120.98, 119.91, 114.68, 112.31, 57.10, 33.62, 31.88, 29.42, 29.40, 29.25, 26.87, 22.74, 14.20. Multiple ^{13}C peaks are due to the phenomenon of atropisomerism.[45,47] FTIR (ATR): $\nu = 2918$, 2850, 1585, 1450, 1421, 1331, 1235, 1218, 1131, 1058, 999, 922, 790, 721, 669, 607 cm^{-1}. HRMS (EI+, m/z) [M]+ calculated for $C_{29}H_{41}Br_2N$: 561.1606, found 561.1601.

N-9-Heptadecanyl-3,6-Dibromocarbazole (4).

White crystals (4.0 g, 77%). m.p. 55°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 (d, J = 8.6 Hz, 2H), 7.57 – 7.27 (m, 4H), 4.47 (tt, J = 10.1, 4.9 Hz, 1H), 2.27 – 2.15 (m, 2H), 1.94 – 1.82 (m, 2H), 1.38 – 1.03 (m, 22H), 0.99 – 0.86 (m, 2H), 0.83 (t, J = 7.1 Hz, 6H). Multiple and broad ^{1}H peaks are due to the phenomenon of atropisomerism.[45,47] ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.07, 137.53, 130.06, 129.14, 128.71, 124.65, 123.48, 123.14, 113.18, 112.05, 111.76, 110.66, 56.97, 33.77, 31.86, 29.41, 29.39, 29.23, 26.80, 22.72, 14.19. Multiple ^{13}C peaks are due to the phenomenon of atropisomerism.[45,47] FTIR (ATR): $\nu = 2921$, 2849, 1469, 1438, 1284, 1220, 1061, 1016, 863, 824, 801, 794, 723, 635, 552, 538 cm^{-1}. HRMS (EI+, m/z) [M]+ calculated for $C_{29}H_{41}Br_2N$: 561.1606, found 561.1599.

General Procedure for Suzuki Cross-Coupling Polymerization

Dibromocarbazole derivative (0.5 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (194 mg, 0.5 mmol) and tetrakis(triphenylphosphine)palladium(0) (15 mg, 0.013 mmol) were dissolved in 10 mL of a degassed THF/Toluene (1/1) mixture. Then, 10 mL of a degassed 2M K_2CO_3 aqueous solution was added. The reaction medium was heated at reflux under argon for 24 h. Afterwards, bromobenzene (6 μL, 0.05 mmol) in 1 mL of a degassed THF/toluene (1/1) mixture was added. The reaction was allowed to stir at reflux for 6 h, and benzeneboronic acid (12 mg, 0.1 mmol) in 1 mL of a degassed THF/toluene mixture (1:1 vol) was added, followed by stirring under reflux for 16 h. The reaction mixture was then poured into 200 mL of methanol. The orange precipitate was collected by filtration, washed with water and methanol, followed by purification on Soxhlet apparatus (methanol, pentane, and THF). No insoluble fraction remained. The THF fraction was precipitated in methanol. The resulting solid was recovered by filtration and dried under vacuum at 40°C overnight.

Poly(N-Dodecyl-2,7-Carbazole-alt-Benzothiadiazole) PCBT1.

Orange powder (75 mg, 32%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.48 – 7.35 (m, 8H), 4.49 (br, 2H), 2.13 – 1.78 (br, 2H), 1.73 – 0.95 (br, 18H), 0.92 – 0.62 (br, 3H). Due to a too small quantity of material available, a satisfying ^{13}C NMR spectrum could not be obtained. FTIR (ATR): $\nu = 2920$, 2851, 1454, 1434, 1335, 1258, 1094, 1020, 874, 843, 800, 754, 724, 695 cm^{-1}, Mn = 1800 g/mol (Đ = 1.3).

Poly(N-9-Heptadecanyl-2,7-Carbazole-alt-Benzothiadiazole) PCBT2.

Orange powder (145 mg, 50%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.48 – 7.38 (m, 8H), 4.81 (br s, 1H), 2.45 (br, 2H), 2.12 (br, 2H), 1.47 – 0.95 (m, 24H), 0.81 (t, J = 5.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 154.76, 143.19, 139.87, 135.52, 134.94, 134.38, 132.43, 132.33, 129.43, 128.81, 128.54, 120.85, 120.61, 120.46, 113.44, 110.63, 34.11, 31.95, 29.65, 29.55, 29.41, 27.09, 22.75, 14.20. FTIR (ATR): $\nu = 2922$, 2851, 1594, 1557, 1455, 1434, 1334, 1220, 1112, 1059, 999, 881, 842, 800, 754, 724, 657, 611, 557 cm^{-1}, Mn = 8100 g/mol (Đ = 2.2).

Poly(N-Dodecyl-3,6-Carbazole-alt-Benzothiadiazole) PCBT3.

Orange powder (173 mg, 74%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.92 – 7.29 (m, 8H), 4.50 – 3.72 (m, 2H), 2.07 – 1.57 (m, 2H), 1.55 – 0.99 (m, 2H), 0.87 (br, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 154.95, 141.31, 133.67, 128.38, 127.66, 127.46, 123.76, 123.36, 121.69, 121.39, 109.20, 32.05, 29.76, 29.65, 29.49, 29.24, 27.49, 22.82, 14.26. FTIR (ATR): $\nu = 2919$, 2849, 1627, 1600, 1473, 1384, 1343, 1278, 1231, 1143, 1025, 886, 846, 798, 720, 694, 646, 561 cm^{-1}, Mn = 4800 g/mol (Đ = 1.5).

Poly(N-9-Heptadecanyl-3,6-Carbazole-alt-Benzothiadiazole) PCBT4.

Orange powder (234 mg, 87%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.97 – 7.37 (m, 8H), 4.68 (br s, 1H), 2.39 (br s, 2H), 2.11 – 1.94 (m, 2H), 1.48 – 0.99 (m, 24H), 0.95 – 0.68 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 155.10, 142.77, 133.57, 130.04, 129.47, 128.80, 128.25, 127.61, 57.13, 34.06, 31.91, 29.62, 29.50, 29.35, 27.09, 25.74, 22.73, 14.20. FTIR (ATR): $\nu = 2921$, 2851, 1626, 1600, 1473, 1403, 1341, 1283, 1224, 1147, 1099, 1027, 885, 848, 799, 754, 721, 694, 670, 605 cm^{-1}, Mn = 2500 g/mol (Đ = 1.7).

Characterizations

The precursors and polymers were characterized by ^1H, ^{13}C, and ^1H-^{13}C HSQC NMR in order to determine the chemical structures of compounds. NMR spectra were recorded on a Bruker 400 MHz spectrometer from deuterated chloroform ($CDCl_3$) solutions. IR spectra were recorded with Bruker Tensor 27 spectrometer using a 0.6 mm-diameter beam and a 4 cm^{-1} resolution. Samples were analyzed with the attenuated total reflexion (ATR) method. A Kofler bench (Wagner and Munz Heizbank system Kofler type wme) was used to obtain melting points with a ±2°C precision. High resolution mass spectroscopy analyses were performed on an AutoSpec-Waters spectrometer (EI).

Molar masses were estimated by size exclusion chromatography with a refractive index detector (PL-GPC 50 plus Integrated GPC system from Polymer laboratories-Varian) from the soluble part of copolymer in THF which was eluted by THF at 40°C. Standard polystyrene samples were used for calibration.

Absorption and photoluminescence spectra were recorded for a polymer solution (2.5 g/L in *o*-dichlorobenzene) and a polymer film casted from an *o*-dichlorobenzene solution (10 g/L) using the spectrophotometers UV-3600, Shimadzu and Fluoromax-4, Horiba Scientific, respectively.

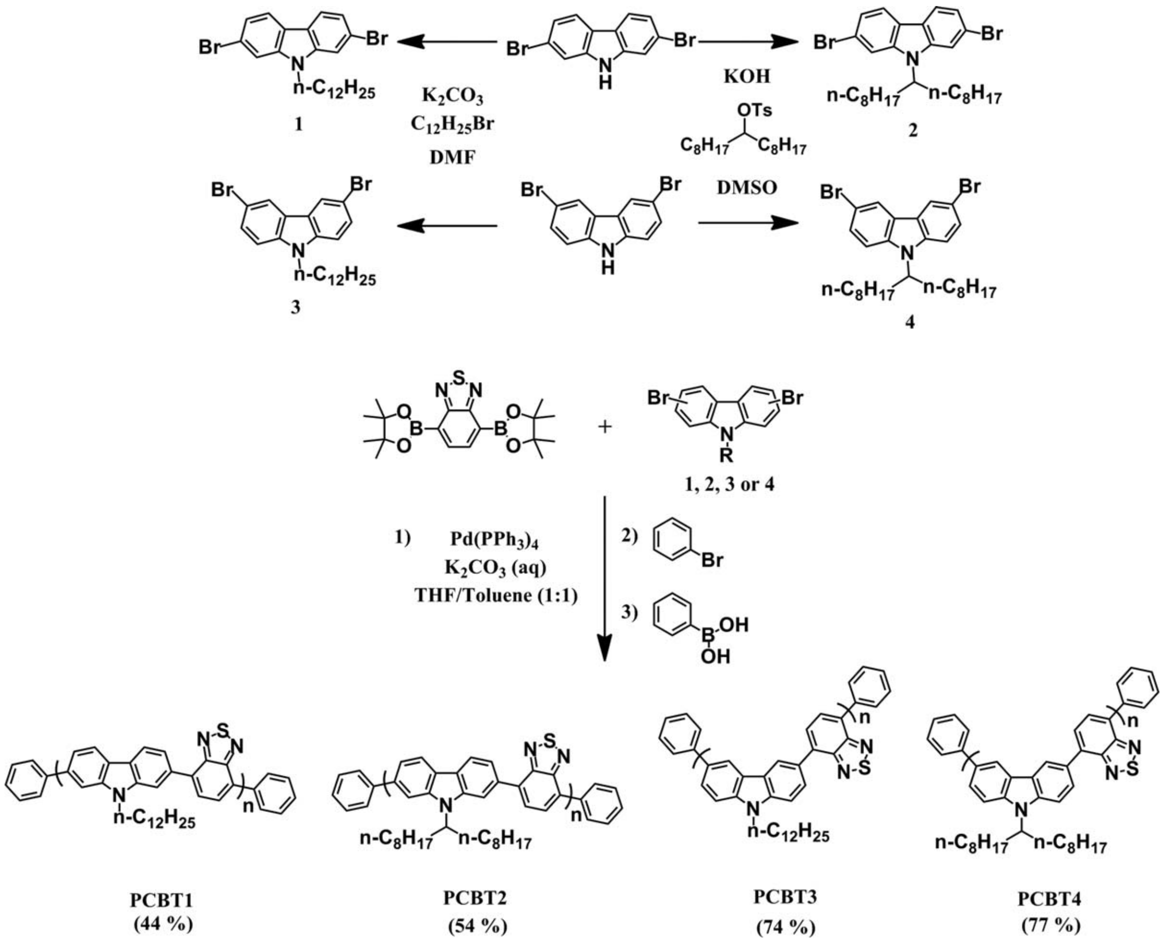
Energetic levels were evaluated by cyclic voltammetry in a glovebox using a potentiostat in the presence of electrolyte solutions of 0.1M TBAPF6 in dry CH_2Cl_2. Platinum was used for both working and counter electrodes and a silver wire was used as reference electrode. The obtained potentials were recalibrated outside the glovebox using ferrocene and saturated calomel electrode as reference.

RESULTS AND DISCUSSION

Synthesis of Monomers and Polymers

Four carbazole monomers have been synthesized bearing bromo functions at different positions for further chain catenation (i.e., at 2,7 and 3,6) and *N*-substituted by two different alkyl chains (i.e., *n*-dodecyl and 9-heptadecanyl). The general synthesis procedures are shown in Scheme 1.

To improve the solubility of the final polymers, side chains can be incorporated on the nitrogen atom of the carbazole unit. Linear (*n*-dodecyl) and branched (9-heptadecanyl) alkyl



SCHEME 1 Synthesis of carbazole monomers and subsequent PCBTs by Suzuki cross-coupling.

groups were chosen as substituents on the nitrogen atom to study their influence on the materials properties. Precursors were prepared from well-established synthetic procedure[45,48–50] (details available in Supporting Information).

The *N*-alkylation reaction was carried out under nucleophilic substitution conditions in the presence of strong base (K_2CO_3 or KOH) in polar solvent such as DMSO or DMF. The final dibromocarbazoles were obtained in good yields (47–77 %). Their chemical structures were confirmed by ^{1}H (Fig. 1), ^{13}C and ^{1}H-^{13}C HSQC NMR, as well as FTIR and HRMS (see Experimental Section and Supporting Information, Figs. S2–S9, for details).

The achievement of alkylated dibromocarbazoles was assessed with ^{1}H NMR through the disappearance of the signal at 8.04 ppm, assigned to the proton of the amine group of the carbazole and the appearance of signals at higher magnetic fields corresponding to the side chains. The ^{1}H NMR spectrum of **1** [Fig 1(a)] showed one triplet at 4.18 ppm, two multiplets in the 1.89–1.77 and 1.42–1.17 ppm regions and one triplet at 0.88 ppm, assigned to the linear dodecyl chain. For the branched derivative **2** one triplet of triplet at 4.42 ppm, four multiplets ranging between 2.26 and 0.91 ppm, and one triplet at 0.83 ppm could be distinguished, corresponding to the branched 9-heptadecanyl chain moiety [Fig. 1(b)]. We observed similar features when comparing the linear and branched 3,6-dibromocarbazoles derivatives **3** and **4** [Fig. 1(c,d)]. The multiple and broad peaks displayed in the case of carbazole derivative bearing the 9-heptadecanyl chain (**2** and **4**) were due to the phenomenon of atropisomerism, as already reported for similar compounds.[45,47]

All four dibromocarbazoles (**1–4**) were reacted separately with 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)−2,1,3-benzothiadiazole under Suzuki cross-coupling reaction conditions, leading to four different alternated π-conjugated polymers (Scheme 1). The polymerizations were carried out using tetrakis(triphenylphosphine)palladium(0) as catalyst and K_2CO_3 as base in a THF/Toluene (1/1) mixture for 48 h at reflux. An end-capping reaction was performed using benzeneboronic acid and bromobenzene, in order to ensure a better stability of the resulting materials by replacing reactive chain-ends with phenyl groups.[51] The polymers (**PCBT1–4**) were obtained as strong orange colored powders soluble in common organic solvents such as toluene, THF, dichloromethane, chloroform or *ortho*-dichlorobenzene (ODCB). The different polymers were subjected to Soxhlet extractions using selective solvents (i.e., methanol,

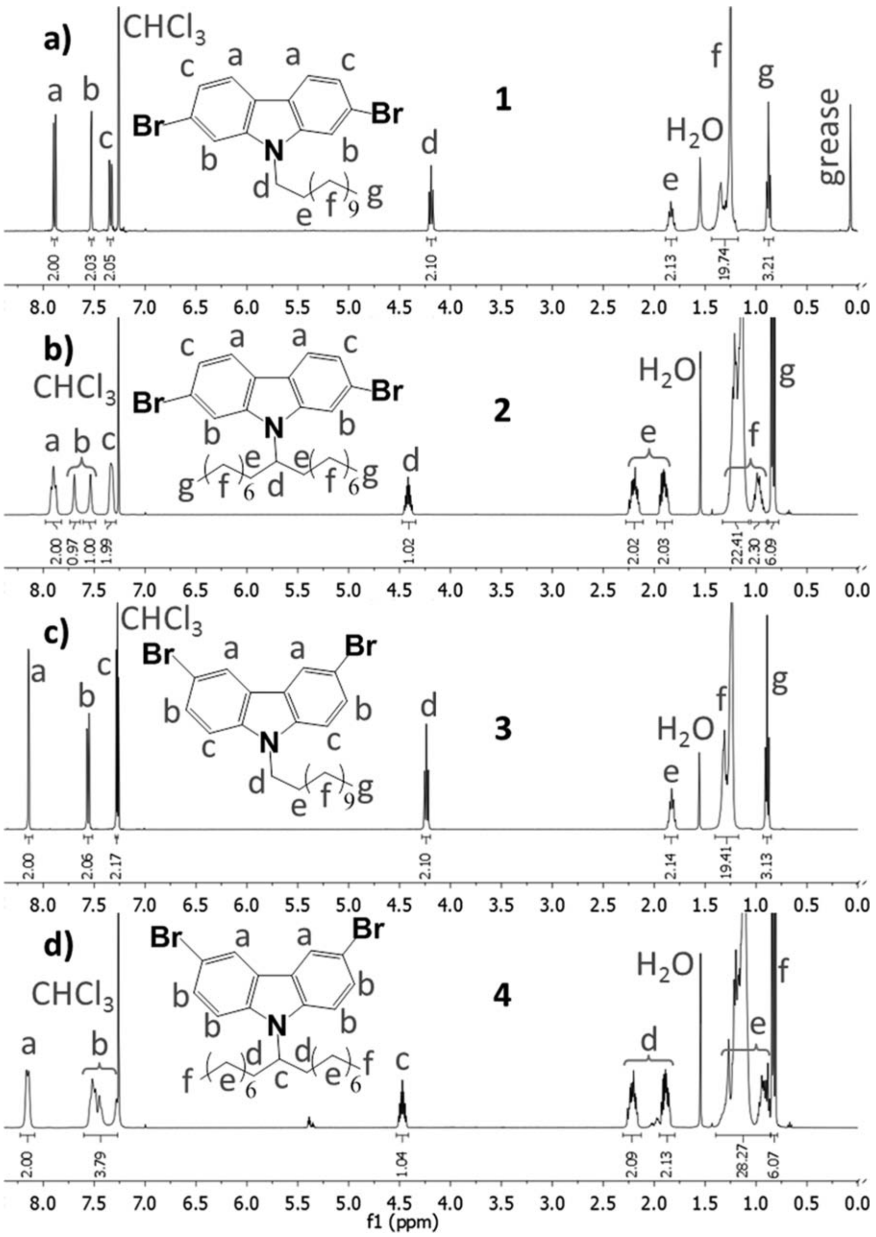


FIGURE 1 ^{1}H NMR (400 MHz) spectra of 2,7-dibromocarbazole (a) **1**, (b) **2** and 3,6-dibromocarbazole (c) **3**, (d) **4** in $CDCl_3$.

pentane and tetrahydrofuran) before characterizations. Their chemical structures were confirmed by FTIR and NMR analysis (see Supporting Information Figs. S10–S16) and their molar masses as well as dispersities were determined by SEC in THF (Table 1, traces in Supporting Information Figs. S17–S20).

The number-average molar masses of the polymers measured by SEC ranged from 1800 to 8100 g/mol. The difference between **PCBT1** and **2** could be attributed to a better solubility and thus reactivity of the formed chains bearing 9-heptadecanyl groups, explaining the higher molar masses in the case of **PCBT2**. However, this trend was not observed when comparing **PCBT3** and **4** for which purity of monomers along with more twisted reactants could be incriminated. While some of the materials (**PCBT1** and **4**) showed short chain lengths, such molar masses could be sufficient to show interesting opto-electronic features, since it was already reported that even oligomers with a suitable ICT could lead to small band-gaps.[44] Most of the measured dispersities were below 2, which is the theoretically expected for a step-growth polymerization mechanism. Herein, dispersities values lower than 2 can be assigned to the Soxhlet extraction procedures performed on the different copolymers. Several sharp peaks could be observed on the SEC traces of PCBT1 and 4. This is due to the relatively high molecular weights of the monomeric units, which makes the different chain lengths more noticeable in SEC for low

TABLE 1 Molar Masses and Thermal Properties of PCBT Copolymers

Copolymer	Mn (g.mol^{-1})[a]	Mw (g.mol^{-1})[a]	Đ (Mw/Mn)[a]	$T_{d,5\%}$ (°C)[b]	Total Weight Loss (%)[c]
PCBT1	1,800	2,300	1.3	400	99
PCBT2	8,100	17,600	2.2	329	50
PCBT3	4,800	7,000	1.5	400	33
PCBT4	2,500	4,200	1.7	423	41

[a] Determined by gel permeation chromatography (GPC) relative to polystyrene standards from the soluble part of PCBT in THF at 40 °C.

[b] Decomposition temperature at 5% weight loss, evaluated under N_2 at a heating rate of 10 °C/min.

[c] Total weight loss after TGA, evaluated under N_2 at a heating rate of 10 °C/min.

molecular weights sample (such as PCBT1 and 4). In order to prepare materials of higher molar masses we need to further investigate other type of catalytic systems.

The ^{1}H NMR spectra of the synthesized PCBTs showed a general broadening compared to those of the monomers, as depicted for instance in the spectrum of **PCBT1** (Fig. 2). The peaks corresponding to the alkyl protons in close vicinity to the nitrogen atom of the carbazole units (b) can be clearly identified in the 4–5 ppm region and were thus used as reference for signals integration. No residual peak corresponding to the boronic pinacol ester functions (sharp singlet at 1.44 ppm) could be observed, which could be assigned to a successful end-capping reaction or the occurrence of protodeborylation in the process of Suzuki coupling reaction. Furthermore, the ^{13}C and ^{1}H-^{13}C HSQC NMR spectra were consistent with the expected structures (see Supporting Information Figs. S11, S13, and S15).

Thermal Characterizations

Thermal properties of the polymers were first determined by thermogravimetric analysis under N_2 atmosphere at a heating rate of 10 C min^{-1} (see Supporting Information Fig. S21). All PCBTs showed a good thermal stability, with an onset temperature for decomposition ($T_{5\%}$) above 329°C (Table 1). It has been noticed that for **PCBT2 – 4**, the weight loss at $T_{5\%}$ is proportional within experimental errors to the weight of alkyl chain (calculated values of 36 and 45 %w for dodecyl and for 9-heptadecanyl chains, respectively). This indicated that the first degradation mechanism under inert atmosphere was related to the elimination of side-chains from the backbone and this is consistent with previous report from the literature.[46] The highest weight loss was observed for **PCBT1** (99 %w) and could be due to its lower molar mass. Second, differential scanning calorimetry analyses between 0 and 250°C did not show any clear glass transition nor crystallinity behavior, indicating the amorphous nature of these materials (see Supporting Information Fig. S22).

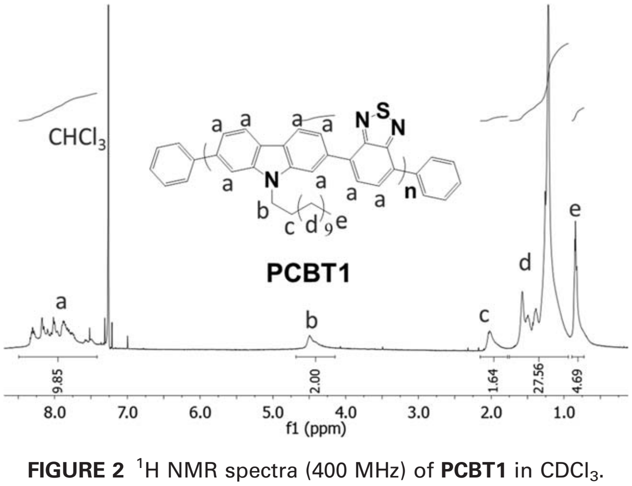


FIGURE 2 ^{1}H NMR spectra (400 MHz) of **PCBT1** in CDCl$_3$.

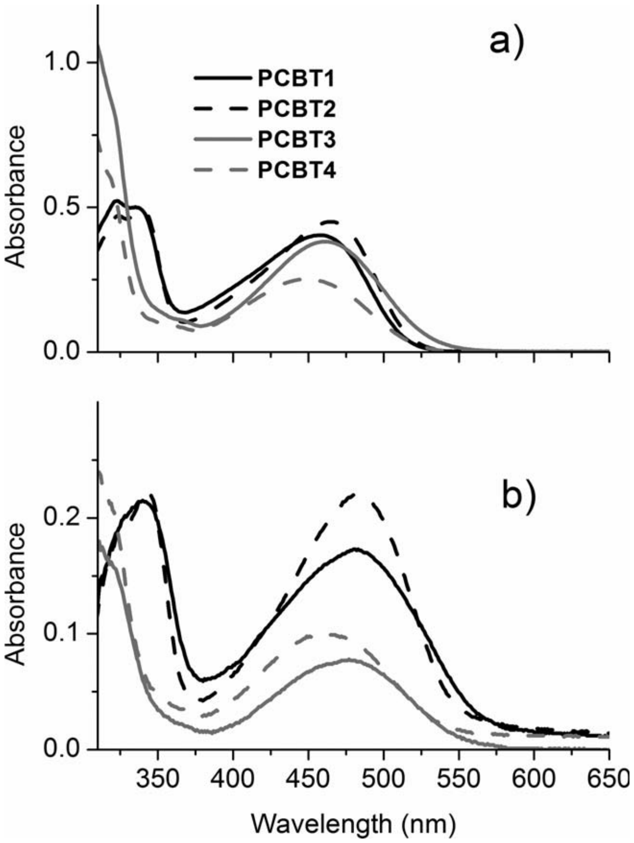


FIGURE 3 Absorption spectra of PCBT copolymers a) in ODCB solution (0.12 g/L) and b) in spin-coated film from ODCB solution.

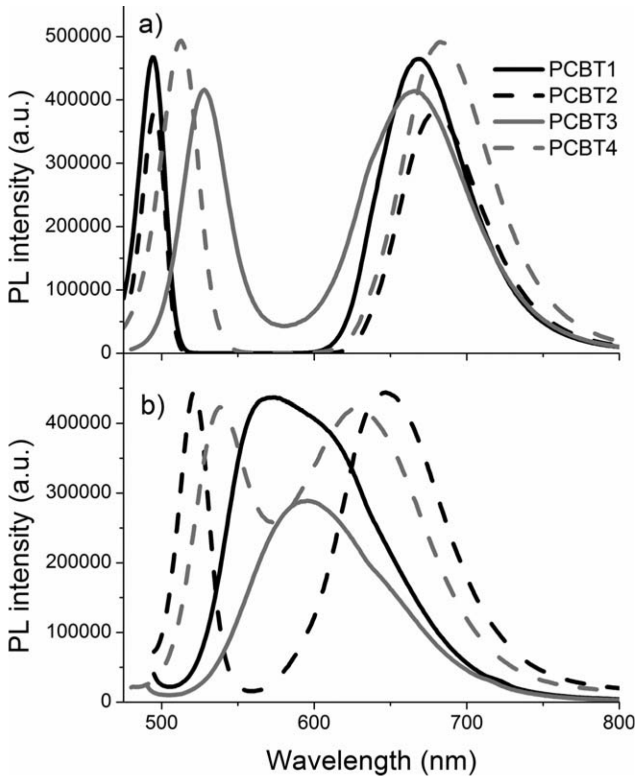


FIGURE 4 Photoluminescence spectra of PCBTs (a) in ODCB solution and (b) in spin-coated films, excited at respective λ_{max} measured in absorption spectra (461–481 nm).

Optical Characterizations

Absorption spectra of polymers **PCBT1 – 4** in ODCB solution and in films are shown in Figure 3. As frequently observed for alternated copolymers, all prepared PCBTs showed two broad absorption bands in the range of 300–350 nm and 440–500 nm in both solution and film states.[52] On the one hand, the high-wavelength band corresponds to the ICT from the electron-rich subunit (carbazole) to the electron-deficient one (benzothiadiazole) and its maximum intensity is similar for the four polymers.[32,53,54] On the other hand, the low-wavelength differs depending on the linkage, that is,. 2,7-**PCBT** versus 3,6-**PCBT**. Indeed, **PCBT3 – 4** showed a first absorbance around 305 nm, whereas it was observed around 330 nm for **PCBT1 – 2**. This indicates that the low-wavelength can be attributed to the absorption of the carbazole moiety.[46] The 3,6-dibromocarbazoles showed red-shifted bands compared to those of the 2,7-dibromocarbazoles, whereas in the case of polymers, the 2,7-PCBTs bands are red-shifted, especially in film state [Fig. 3(b)]. This might be explained by a better conjugation along the 2,7-PCBTs chain.[55] Indeed, the 3,6-PCBTs induce conjugation breaks on the nitrogen atom, which limits the conjugation length and thus lower the absorption wavelengths.[46]

The side chains have a weak influence in the PCBT absorbance in both solution and film states. All polymers showed good solubility in common solvents (in part due to quite low molar masses polymers) and no solvatochromic effect was observed. They showed red-shifted absorbance in solid state, which reveals an intermolecular arrangement between polymer main chains (π-stacking). However, the optical band gap determined by the onset of the high-wavelength absorption band achieved up to 2.2–2.3 eV and is similar for all polymers.

Photoluminescence spectra of neat polymers were recorded in ODCB solution and in films from the same samples as for the light absorption analyses (Fig. 4). The $\lambda_{excitation}$ of each sample was selected according to the previously observed λ_{max}. In solution, the four polymers showed two-peaks emission, which indicates that the light emission comes from two different sources. On the one hand, the lower-wavelength emission peak is probably due to the localization of the excited state on one unit (carbazole or benzodiathiazole). On the other hand, the higher-wavelength emission peak is probably due to an ICT excited state, resulting in a structure having a smaller band-gap (e.g., quinoid structure). It can be noticed that the lower-wavelength emission peak of 3,6-PCBTs is more red-shifted compared to the 2,7-PCBTs. This can be explained by the more stabilized excited state of the 3,6-configuration due to the participation of the nitrogen atom (positive charges are more stabilized when localized on nitrogen).

In the solid state, the two emission peaks shifted towards each other, and even merged in the case of polymers bearing linear alkyl chains (**PCBT1** and **PCBT3**), due to stronger intermolecular interactions of polymer chains.

Electrochemical Characterizations

Electrochemical properties were estimated by cyclic voltammetry under inert atmosphere (N_2) using dichloromethane solutions of **PCBT1 – 4**, tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte, silver for the reference electrode and the working electrode and counter-electrode were made of platinum (see Supporting Information Figs. S23–S26). The calculated values of the energy levels are summarized in Table 2. We noticed slight differences between the electrochemical and optical band-gaps, which can be explained by the fact that the redox peaks result from localized sites rather than from the conjugated backbone.[56] The LUMO energy level is similar for all **PCBTs** independently from the linkage and the side chain nature, and slightly higher than that of the P3HT.[57] Except for the **PCBT3**, the HOMO energy level is lower than that of the P3HT, which is below the air oxidation threshold[58] and made **PCBTs** good candidates for bulk heterojunction (BHJ) solar cells applications by having a positive impact on open-circuit voltage (V_{OC}).

Optical Characterizations of PCBT: PCBM Blends

Due to their low-lying HOMO levels, the prepared **PCBTs** might be considered as donor material in the active layer of BHJ solar cells. A suitable morphology of the active layer, which avoids loss of energy through charge transport and maximizes the efficiency of the device, is the key to achieve high performances of a BHJ solar cell.

TABLE 2 Optical and Electrochemical Properties of PCBT Copolymers

Copolymer	$\lambda_{\text{max}}^{\text{sol}}$ (nm)[a]	$\lambda_{\text{max}}^{\text{film}}$ (nm)[b]	E_g^{opt} (eV)[c]	HOMO (eV)[d]	LUMO (eV)[d]	E_g^{elec} (eV)[e]
PCBT1	456	481	2.2	−5.5	−3.0	2.2
PCBT2	465	481	2.3	−5.3	−3.0	2.3
PCBT3	462	477	2.2	−5.0	−2.8	2.2
PCBT4	447	461	2.3	−5.3	−3.0	2.3

[a] Determined at high wavelength in *o*-DCB solution

[b] Determined at high wavelength in film casted from a *o*-DCB solution.

[c] Estimated from the onset of the absorption edge in a film.

[d] Estimated from the oxidation and reduction potentials measured by cyclic voltammetry in $CHCl_3$ solution with the following equation: $E_{\text{HOMO}}(\text{eV})=-(E_{\text{ox vs (Fe/Fe}^+)}(V)+4.8)$; $E_{\text{LUMO}}(\text{eV})=-(E_{\text{red vs (Fe/Fe}^+)}(V)+4.8)$.

[e] Calculated by difference between oxidation and reduction potentials.

Thus, preliminary studies were carried out on the blend of **PCBT1 – 4** as donor and with phenyl-C_{61}-butyric acid methyl ester (PCBM) as acceptor in order to evidence interactions between these two components. Both materials were solubilised at different ratios in ODCB, and subsequently spin-casted onto a glass substrate coated with a PEDOT-PSS layer, simulating conditions to make BHJ devices.

The absorption spectra of **PCBT2** blended with different ratio of PCBM in solid state are shown in Figure 5(a). At constant amount of **PCBT2**, the increasing amount of PCBM led to a slight blue shift of absorption bands, which could be attributed to a decrease of the intermolecular interactions between polymer chains. Additionally, the light absorption of PCBM induces an intensity increase of the high energy absorption peak. Similar behavior was observed for the three other **PCBTs**. Photoluminescence spectra of the same samples were taken at 481 nm (λ_{max}) and are shown in Figure 5(b). The presence of PCBM induced a drastic decrease of the polymer fluorescence whatever the amount, which revealed a possible dissociation of photogenerated excitons in the semiconducting polymers by electron transfer to PCBM. The same behavior was observed in the case of all other **PCBTs**, whatever the linkage position and the substituent nature. Although this is an encouraging result for BHJ solar cells application, this effect could also originate from an energy transfer between the polymer and PCBM.

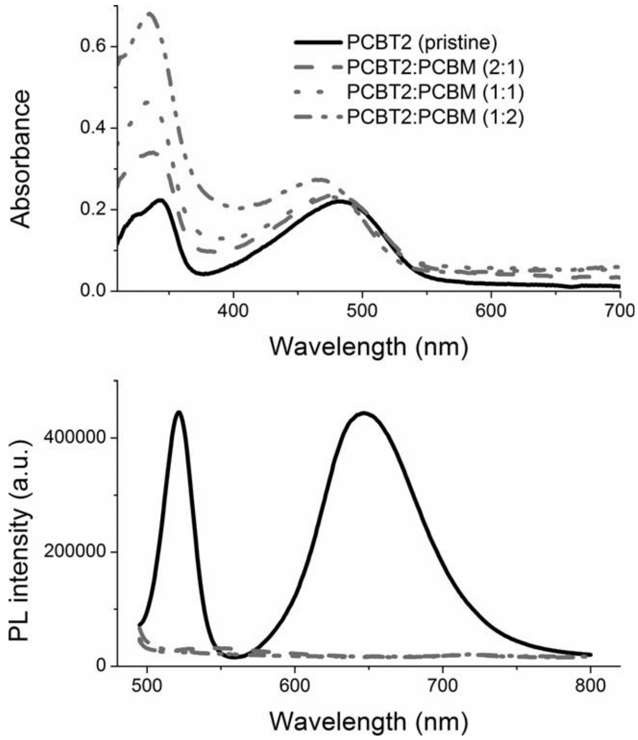


FIGURE 5 (above) Light absorption and (below) photoluminescence (excited at 481 nm) spectra of **PCBT2:PCBM** blends at different ratios in solid state.

In addition, the same blends were investigated in atomic force microscopy (AFM), which highlighted the presence of nanoscale domains (see Supporting Information Fig. S27). These preliminary studies on **PCBT/PCBM** interactions are promising as for the use of prepared PCBT polymers as donor material in the active layer of BHJ solar cells.

CONCLUSIONS

Four alternated π-conjugated copolymers (named PCBT) based on carbazole and benzothiadiazole subunits were successfully synthesized by Suzuki cross-coupling polycondensation. The carbazole and benzothiadiazole subunits were directly linked through 2,7- or 3,6- positions of a *N*-substituted carbazole bearing either linear or branched side-chain. Their structures were confirmed by NMR, FTIR and their molar masses were estimated by SEC. In the case of 2,7 configuration (**PCBT1** and **2**) a direct effect of the improved solubility with branched side-chain could be observed since higher molar masses were achieved. This effect was not confirmed for the 3,6 configuration (**PCBT3** and **4**), probably due to purification issues, catalytic system and/or twisted catenation. All prepared PCBTs were shown amorphous and found stable up to 329°C. Spectroscopic investigations highlighted the existence of a donor–acceptor ICT in the main chain, thus the band-gap of the PCBTs is lower than that of homopolymers based on carbazole. Although a red-shift effect was observed as a function of the position of the linkage (2,7-PCBT or 3,6-PCBT) for the low-wavelength absorption band, the optical band gap of the four PCBTs is similar and consistent to the measured electrochemical one. This indicates the predominant role of the ICT over the electrons delocalization along the backbone. The side chains proved to have a significant effect on the photoluminescence properties by enhancing intermolecular interactions in the case of linear alkyl groups. Preliminary studies showed that PCBT:PCBM blends formed small-scale domains and that PCBM quenched the polymers fluorescence, which indicates the exciton dissociation and is favourable for photovoltaic application. Further characterizations, such as measurements of the charge carrier mobility, are in progress.

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