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The synthesis and properties of novel π-conjugated 2,1,3-benzothiadiazole oligomers

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A series of novel, 2,1,3-benzothiadiazole-based oligomers were synthesized by the self/cross-coupling reaction of monobromo-substituted benzothiadiazole compounds in a catalyst system comprising $Pd(OAc)_2$/PEG (polyethylene glycol)/DMF. The oligomers displayed good linear correlation between E_g^{opt} (or $\lambda_{max,\ abs}$ or $\lambda_{max,\ em}$) and the reciprocal of the numbers of the benzothiadiazole units. The LUMO values of the compounds decreased with increasing number of benzothiadiazole units on the backbone of the molecules.

1. Introduction

π-Conjugated polymers and small molecules containing the 2,1,3-benzothiadiazole unit have received much attention in the past few decades because of their potential applications in many areas such as biology [1], iatrology [2] and optoelectronics [3–7]. These compounds are usually electrochemically active and show light-emitting properties depending on their chemical structures, and sometimes have a low π–π^* transition energy Therefore, they have been well investigated and widely used in detection of bacteria and virus [2], recognition of the disfigurement in DNA and RNA [1], and used as the basic materials for organic solar cells [3], organic light-emitting diodes (OLEDs) [4], organic field-effect transistors (OFETs) [5], chemosensors [6] and two-photo absorption (TPA) system [7].

However, there has been much less interest in the investigation of the compounds that are composed of more than two benzothiadiazole units [8]. Structurally, the 2,1,3-benzothiadiazole unit is a typical electron-withdrawing unit, and introducing such a unit to the backbone of the other molecules may improve the electron-injection/or transportation properties and tune band gap of such hybrid molecules [3–5]. Additionally, for the molecules containing multi-benzothiadiazole units, their interesting chemical structures may endow new properties to the compounds, such as stronger electron-accepting and electron-transporting abilities. Thus, the study of well-defined molecules containing multi-benzothiadiazole units would be very useful not only for understanding the relationship between the structure and the properties of the compounds but also for the development of novel organic materials. Hence, we have designed and synthesized a series of benzothiadiazole-based oligomers, and those oligomers which show interesting optical properties and stronger electron-accepting behavior. Here, we report the details.

2. Results and discussions

2.1. Synthesis

The synthetic procedure for the new benzothiadiazole oligomers was shown in Scheme 1. The starting reactants, 4,7-dibromobenzothiadiazole (**1**) and 4-bromobenzothiadiazole (**3**), were prepared by a previously reported procedure [9]. It was found that the compounds containing multi-benzothiadiazole units showed poor solubility [8], which restricted the full characterization of the obtained compounds. To improve the solubility, an alkyl side chain ($-C_6H_{13}$) was introduced to the backbone of 2,1,3-benzothiadiazole units by Negishi reaction [10], and compounds **2** and **6** were thus obtained. To avoid bromination of the side chain [9], the intermediate **7** was prepared under a gentle condition in 85% yield. The target products, **DH2BT** and **DH4BT** were synthesized in the yields of more than 75% by the self-coupling of **2** or **7** using a catalyst system of $Pd(OAc)_2$/PEG [11]. Analogously, **DH3BT** was obtained in a yield of 40% by the cross-coupling reaction between **2** and **7**. Here, **DH3BT** showed a lower yield that was probably due to the

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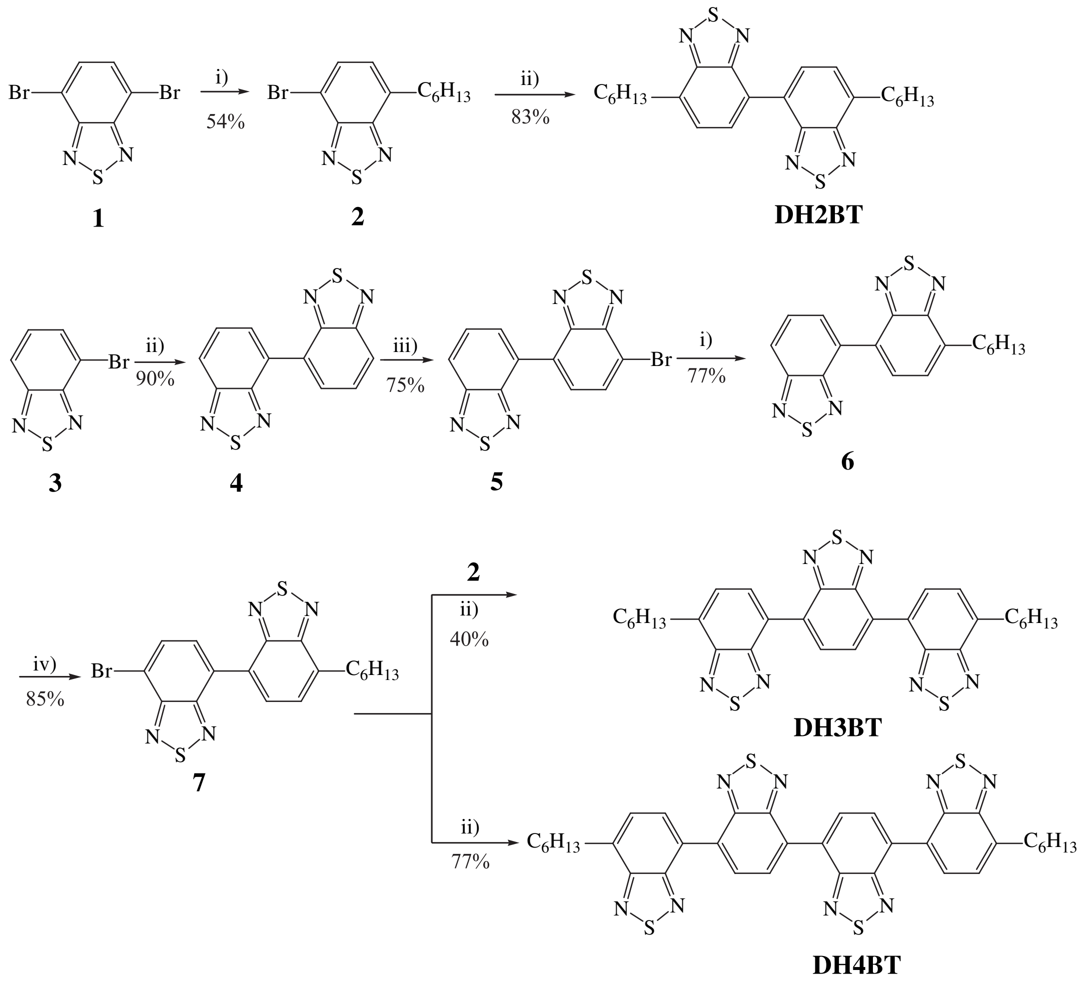

Scheme 1. Synthesis of the new benzothiadiazole oligomers. Regents and conditions: (i) Zn, $C_6H_{13}Br$, DMAC, I_2, $Pd(PPh_3)_4$; (ii) $Pd(OAc)_2$, PEG 4000, K_2CO_3, DMF; (iii) HBr (40 wt% aq.), Br_2, reflux; (iv) HBr (40 wt % aq.), Br_2, 70 °C.

formation of by-products, e.g., the self-coupling products of **2** and **7**. To the best of our knowledge, this is the first example of the self/cross-coupling reaction of monobromo-substituted benzothiadiazole units using Palladium as the catalyst. Although the self-coupling of some bromosubstituted benzothiadiazoles can be achieved by using ether Yamamoto coupling or nickel-catalyzed Ullman reaction, those procedures were practically limited due to either the using of very expensive catalyst ($Ni(COD)_2$) with high sensitivity to air and moisture [8] or the employing of a large amount of catalyst ($Ni(PPh_3)_2Br_2$) and reduction agent (zinc

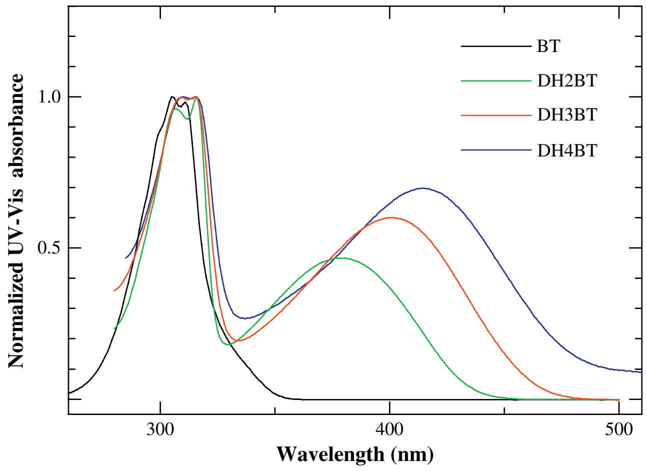

Fig. 1. Normalized UV–vis absorption spectra of BT and **DHnBT** in $CHCl_3$ (5×10^{-5} mol/L).

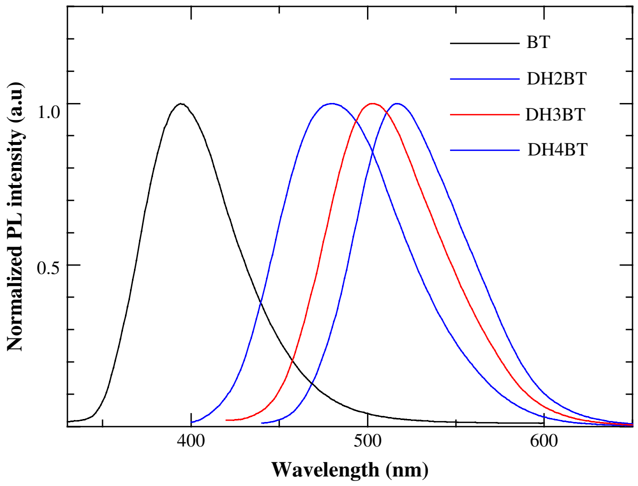

Fig. 2. Normalized PL spectra of **BT** and **DHnBT** in $CHCl_3$ (5×10^{-5} mol/L).

Table 1
Optical and electrochemical properties of oligomers

Compounds	$\lambda_{max,abs}$ (nm) (log ε)[a]	$\lambda_{max,em}$ (nm)[b]	E_g^{opt} (eV)[c]	E_{Red} (eV)[d]	E_{onset} (eV)[e]	LUMO (eV)[f]	HOMO (eV)[g]
BT	305 (4.33)	394	3.49	–	–	–	–
DH2BT	316 (4.42), 379 (4.08)	480	2.74	−1.73	−1.25	−3.15	−5.89
DH3BT	315 (4.47), 401 (4.25)	502	2.55	−1.70	−1.08	−3.32	−5.87
DH4BT	310 (3.97), 415 (3.82)	517	2.43	−1.64	−1.05	−3.35	−5.78

[a] Maximum UV–vis absorption, $\lambda_{max,\ abs}$, measured in $CHCl_3$ (5×10^{-5} mol/L). The values in parentheses are molar absorption coefficient (dm^3/mol/cm).

[b] Maximum photoluminescent emission, $\lambda_{max,\ em}$. In all cases, UV–vis absorption wavelengths of the compounds were used as excited wavelengths.

[c] Estimated from the onset positions of the UV–vis absorption band of the compounds.

[d] Measured in a $CHCl_3$ solution of 0.10 M $[Bu_4N]ClO_4$ with a scan rate of 50 mV/s. The concentration of the oligomers was 1.2×10^{-5} mol/L.

[e] Estimated from the UV–vis absorption onset wavelength of the **DHnBT**.

[f] Calculated according to LUMO = $-(4.40 + E_{onset})$ [15].

[g] Calculated from HOMO = LUMO − E_g^{opt}.

powder) [12,13]. Obviously, the $Pd(OAc)_2$/PEG/DMF catalyst system is efficient and practical for the preparation of the derivatives composed of multi-benzothiadiazole units.

The chemical structures of the obtained compounds were confirmed by ^1H NMR, ^{13}C NMR, elemental analysis (EA), mass spectra and FTIR spectra. All data were consistent with the proposed structures. The melting points of the dyes (**DHnBT**) increased with the length of the molecule cores, e.g., 76–78, 218–220 and 316 °C for **DH2BT**, **DH3BT** and **DH4BT**, respectively.

2.2. *Optical properties*

The UV–vis spectra of **DHnBT** ($n = 2, 3, 4$) were shown in Fig. 1 that indicated the solutions of oligomers gave two peaks: the first located at about 310 nm and was assigned a benzothiadiazole unit (Fig. 1); the second band was observed between 340 and 480 nm, shifting to longer wavelengths (λ) as the conjugation level increased due to the π–π^* transition. The maximum absorptions ($\lambda_{max,\ abs}$) were at 379, 401 and 415 nm, for **DH2BT**, **DH3BT** and **DH4BT**, respectively. Photoluminescent (PL) spectra of the oligomers were given in Fig. 2. The oligomers showed only one emission peak ($\lambda_{max,\ em}$), e.g., 480, 502 and 517 nm for **DH2BT**, **DH3BT** and **DH4BT**, respectively. Compared with the $\lambda_{max,\ em}$ of benzothiadiazole (**BT**, Fig. 2), those of the oligomers exhibited a stepwise red-shift, further conforming that the π-conjugation length for the oligomers became longer as the increasing n of **BHnBT**. The optical band gaps (E_g^{opt}) of the oligomers were estimated from the onset positions of the UV–vis absorption band of the compounds (cf. Fig. 1), and the results were listed in Table 1. As shown in Table 1, there was an order of the conjugation level of **BT** < **DH2BT** < **DH3BT** < **DH4BT**, e.g., the E_g^{opt} values decreased with the increasing of the n in **BHnBT**. Moreover, a good linear correlation between E_g^{opt} (or $\lambda_{max,\ abs}$, or $\lambda_{max,\ em}$) with the reciprocal number of the benzothiadiazole units ($1/n$) was observed (Fig. 3), and the linear correlation can be described mathematically by the following equations: e.g., $\lambda_{max,\ abs} = 1.45001/n + 2.59918$ ($r^2 = 0.99734$, where, r was linear regression coefficient), $E_g^{opt} = 1.41685/n + 2.06684$ ($r^2 = 1$), and $\lambda_{max,\ em} = 1.00796/n + 2.12503$ ($r^2 = 1$), respectively. According to the equations, the maximum absorption wavelength ($\lambda_{max,\ abs}$) of the ideal polymer with infinite number of benzothoadiazole units would be at 477 nm (in solution). Analogously, the maximum emission wavelength and optical band gap of the polymer would be at 583 nm and 2.07 eV. Such extrapolation has been reported for estimation of the optical properties of the polythiophene from thiophene oligomers [14].

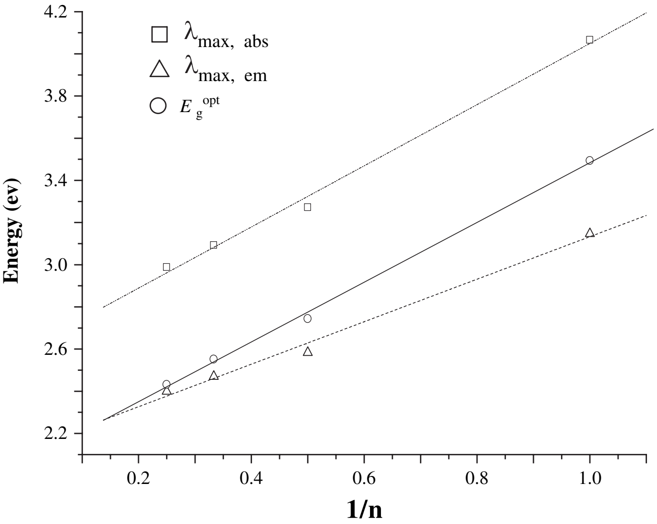

Fig. 3. Correlation and linear fit of E_g^{opt}, $\lambda_{max,\ abs}$, $\lambda_{max,\ em}$ with the reciprocal number of the benzothiadiazole units ($1/n$).

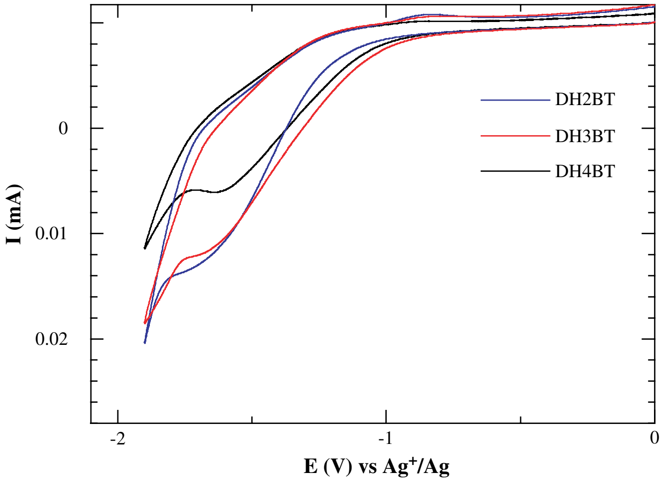

Fig. 4. CV curves of **DHnBT** ($n = 2$–4) in $CHCl_3$ at a scan rate of 50 mV/s.

2.3. *Electrochemical properties*

The electrochemical behavior of the new oligomers was characterized by cyclic voltammetry (CV) in $CHCl_3$ solution, and the detailed data were summarized in Table 1. As can be seen from Fig. 4, the electrochemical reduction of **DHnBT** ($n = 2, 3, 4$) started at −1.25, −1.08, and −1.05 V vs Ag/Ag^+, respectively, and gave the reduction peaks at −1.73, −1.70 and −1.64 V, respectively. These data suggested that the electron-withdrawn abilities for the oligomers had an increasing tendency with the increasing of the n in **DHnBT**. According to the relationship between the reduction onset potential and LUMO energy [15], LUMO values of the three compounds can be estimated, and the results were also listed in Table 1. In comparison with a prevalent electron-transporting material 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, with a electron affinity (EA) of −2.4 eV, **DH3BT** and **DH4BT** showed the EA of −3.32 and −3.35 eV, resulting in a reduced energy barrier to electron injection from the cathode, e.g., Mg (−3.7 eV) [16].

3. Conclusions

To summarize, we have synthesized a series of electron-deficient benzothiadiazole-based oligomers by employing the

Pd-catalyzed coupling reaction. The oligomers showed a good linear correlation between the 1/*n* and their maximum UV–vis absorption (or PL emission peaks or the optical band gaps). Electrochemically, the electron-withdrawn ability of the oligomers had an increasing tendency as the length of **DHnBT** grew. Compared with a commercial electron-transporting material 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, **DH3BT** and **DH4BT** showed much lower LUMO values, suggesting that the energy barriers between the oligomers and the cathode were greatly reduced when they were used in OLED. These optoelectronic properties showed that the oligomers were promising electron-transporting materials.

4. Experimental section

*4.1. Synthesis of 4-bromo-7-hexyl-2,1,3-benzothiadaizole (**2**)*

Under argon atmosphere, a solution of *N*,*N*-dimethylacetamide (DMAC, 20 mL), I_2 (0.25 g, 1 mmol) and zinc dust (2.0 g, 31 mmol) was stirred at room temperature until the red color disappeared. Then 1-bromohexane (2.8 mL, 20 mmol) was added and the mixture was reacted at 80 °C for 4 h. After being cooled to room temperature, the obtained alkylzinc reagent was added to a mixture of 4,7-dibromo-2,1,3-benzothiadiazole (7.8 g, 27 mmol), $Pd(PPh_3)_4$ (0.57 g, 0.49 mmol) and DMAC (30 mL) at room temperature. The reactants were allowed to heat at 80 °C for overnight, and then cooled to room temperature. The mixture was poured into water, filtered and washed with water and ethanol, respectively. After evaporation of the solvent, the residue was purified by chromatography on silica gel using a mixture of petroleum ether and CH_2Cl_2 (6:1, v/v) as the eluent to give **2** as a colorless liquid, 3.16 g, yield of 54%. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.75 (d, $J = 7.2$, 1H), 7.24 (d, $J = 7.2$, 1H), 3.08 (t, $J = 8.4$, 2H), 1.72–1.84 (m, 2H), 1.25–1.45 (m, 6H), 0.88 (t, $J = 6.9$, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.7, 153.4, 136.0, 132.0, 127.7, 111.2, 32.0, 31.6, 29.6, 29.1, 22.6, 14.0. IR (KBr, cm^{-1}): 2956, 2928, 2858, 1596, 1532, 1483, 1466, 1326, 1227, 938, 883, 842. MS (EI) *m*/*z*: 300. Elemental analysis, calculated for $C_{12}H_{15}BrN_2S$: C, 48.17%; H, 5.05%; N, 9.36%; S, 10.72%; Br, 26.70%. Found: C, 48.35%; H, 5.06%; N, 9.57%; S, 10.84%; Br, 26.75%.

*4.2. Synthesis of 7,7′-bihexyl-4,4′-bibenzothiadiazole (**DH2BT**)*

A mixture of compound **2** (1.4 g, 4.7 mmol), K_2CO_3 (0.64 g, 4.7 mmol), PEG 4000 (4.7 g, 1.2 mmol), $Pd(OAc)_2$ (0.052 g, 0.23 mmol), and DMF (20 mL) was stirred at 120 °C for 24 h under argon, and the resulting solution was cooled to room temperature and then poured into 200 mL of water. The aqueous was extracted by $CHCl_3$. The organic phase washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel with a mixture of petroleum ether and CH_2Cl_2 (5:1, v/v) as the eluent to afford **DH2BT** as a yellow solid, 0.84 g, yield of 83%. Mp, 76–78 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.17 (d, $J = 6.9$, 2H), 7.55 (d, $J = 6.9$, 2H), 3.20 (t, $J = 7.5$, 4H), 1.82–1.93 (m, 4H), 1.45–1.52 (m, 4H), 1.33–1.40 (m, 8H), 0.91 (t, $J = 6.9$, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 153.4, 136.0, 132.1, 127.8, 111.2, 32.1, 31.6, 29.6, 29.2, 22.6, 14.1. MS (EI) *m*/*z*: 438. IR (KBr, cm^{-1}): 2952, 2917, 2854, 1579, 1552, 1471, 1114, 913, 868, 844, 838. Elemental analysis, calculated for $C_{24}H_{30}N_4S_2$: C, 65.71%; H, 6.89%; N, 12.77%; S, 14.62%. Found: C, 65.76%; H, 6.88%; N, 12.79%; S, 14.44%.

*4.3. Synthesis of 4,4′-benzothiadiazole (**4**)*

A mixture of compound **3** (15 g, 72 mmol), K_2CO_3 (10 g, 72 mmol), PEG 4000 (72 g, 18 mmol), $Pd(OAc)_2$ (0.81 g, 3.6 mmol), and DMF (150 mL) was stirred at 120 °C for 24 h under argon, and the resulting solution was cooled to room temperature and then poured into water. The solid was filtered, washed with water, and dissolved in $CHCl_3$ to obtain a solution. The organic phase was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel with a mixture of petroleum and CH_2Cl_2 (2:1, v/v) as the eluent to give **4** as a yellow solid, 8.73 g, yield of 90% .^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.27 (d, $J = 6.9$, 2H), 8.12 (d, $J = 8.4$, 2H), 7.81 (t, 2H).

*4.4. Synthesis of 7-bromo-4,4′-bibenzothiadiazole (**5**)*

Bromine (0.80 mL, 15 mmol) was added slowly to a mixture of HBr (40 wt% aq, 50 mL) and **4** (2.1 g, 7.78 mmol) at 100 °C. Then the reactants were maintained the temperature for 1.5 h. After being cooled to room temperature, the mixture was poured into saturated aqueous $NaHSO_3$ and extracted with chloroform. After removal of the solvent, the residue was recrystallized from a mixture of chloroform and ethanol to give **5** as a yellow solid, 2.05 g, yield of 75%. Mp 258–260 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.27 (d, $J = 7.2$, 1H), 8.20 (d, $J = 7.5$, 1H), 8.13 (d, $J = 8.7$, 1H), 8.06 (d, $J = 7.5$, 1H), 7.81 (dd, $J = 7.2$, $J = 8.7$). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 132.2, 131.4, 130.9, 129.5, 122.0. MS (EI) *m*/*z*: 348. IR (KBr, cm^{-1}): 1595, 1542, 1478, 1309, 1309, 1150, 872, 849, 824, 808, 751. Elemental analysis, calculated for $C_{12}H_5BrN_4S_2$: C, 41.27%; H, 1.44%; N, 16.04%; 18.36%; Br, 22.88%. Found: C, 41.11%; N, 16.00%; H, 1.60%; S, 18.28%; Br, 22.60%.

*4.5. Synthesis of 7-hexyl-4,4′-bibenzothiadiazole (**6**)*

Under argon atmosphere, a solution of DMAC (30 mL), I_2 (0.42 g, 1.6 mmol) and zinc dust (3.0 g, 46 mmol) was stirred at room temperature until the red color disappeared. Then 1-bromohexane (4.2 mL, 30 mmol) was added and the mixture was allowed to keep at 80 °C for 4 h. After being cooled to room temperature, the obtained alkylzinc reagent was added dropwise to a mixture of **5** (4.8 g, 13.7 mmol), $Pd(PPh_3)_4$ (0.50 g, 0.43 mmol), and DMAC (30 mL) at room temperature. The reactants were heated at 80 °C for overnight and then cooled to room temperature. The mixture was poured into water, filtered and washed with water, dried in an oven, and washed with $CHCl_3$. The residue was purified by flash chromatography on silica gel using a mixture of hexane and CH_2Cl_2 (5:1, v/v) as the eluent to give **6** as a yellow solid, 3.72 g, yield of 77%. Mp, 100–103 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.24 (d, $J = 6.9$, 1H), 8.2.0 (d, $J = 6.9$, 1H), 8.09 (d, $J = 8.7$, 1H), 7.80 (dd, $J = 7.5$, $J = 8.7$, 1H), 7.56 (d, $J = 7.5$, 1H), 3.214 (t, $J = 7.8$, 2H), 1.84–1.92 (m, 2H), 1.45–1.52 (m, 2H), 1.3–1.4 (m, 4H), 0.91 (t, $J = 7.2$, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.5, 153.8, 153.7, 136.7, 131.2, 130.5, 130.3, 129.5, 127.3, 127.3, 121.2, 32.4, 31.7, 29.7, 29.4, 22.7, 14.1. IR (KBr, cm^{-1}): 2958, 2926, 1583, 1538, 1475, 1313, 869, 849, 825, 810, 755. MS (EI) *m*/*z*: 354. Elemental analysis, calculated for $C_{18}H_{18}N_4S_2$: C, 60.99%; H, 5.12%; N, 15.80%; S, 18.09%. Found: C, 61.14%; H, 5.28%; N, 15.77%; S, 18.31%.

*4.6. Synthesis of compound 7-bromo-7′-hexyl-4,4′-bibenzothiadiazole (**7**)*

Bromine (0.06 mL, 1.17 mmol) was added to a mixture of HBr (40 wt% aq, 6 mL) and **6** (0.22 g, 0.62 mmol) at 70 °C, then the reactants were maintained the temperature for 1.5 h. After being cooled to room temperature, the mixture was poured into saturated aqueous $NaHSO_3$ and extracted with chloroform. After removal of the solvent, the residue was purified by column chromatography on silica gel using a mixture of hexane and CH_2Cl_2 (5:1, v/v) as the eluent to give **7** as a yellow solid, 0.23 g, yield of 85%. Mp, 120–121 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.19 (m, 2H), 8.04 (d, $J = 7.8$, 1H), 7.56 (d, $J = 7.2$), 3.21 (t, $J = 7.8$, 2H), 1.82–1.92 (m, 2H), 1.45–1.52 (m, 2H), 1.33–1.4 (m, 4H), 0.91 (t, $J = 6.9$, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.5, 153.9, 153.5, 153.4, 137.1, 132.2, 131.2, 131.1, 129.7, 127.3, 126.5, 113.9, 32.4, 31.7, 29.7, 29.3, 22.6, 14.1; IR (KBr, cm^{-1}): 2962, 2918, 1596, 1532, 1483, 1326, 938, 883, 842, 768; MS (MALDI) m/z: 433.1; Elemental analysis, calculated for $C_{18}H_{17}BrN_4S_2$: C, 49.88%; N, 12.93%; H, 3.95%; Br, 18.44%; S, 14.80%. Found: C, 49.88%; N, 12.65%; H, 4.29%; Br, 18.50%; S, 14.65%.

4.7. Synthesis of **DH3BT**

A mixture of **7** (1.8 g, 41 mmol), **2** (3.9 g, 13 mmol), K_2CO_3 (2.43 g, 17.6 mmol), PEG 4000 (18 g, 4.5 mmol), $Pd(OAc)_2$ (0.19 g, 0.85 mmol), and DMF (40 mL) was stirred at 120 °C for 24 h under argon. After being cooled to room temperature, the resulting solution was poured into water, and the solid was filtered and washed with water to give crude product, which was further purified by Soxhlet extraction using ethanol and recrystallized from a mixture of chloroform and ethanol to give **DH3BT** as a yellow solid, 0.98 g, yield of 41%. Mp, 218–220 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.44 (s, 2H), 8.25 (d, $J = 7.2$, 2H), 7.59 (d, $J = 7.2$, 2H), 3.23 (t, $J = 7.8$, 4H), 1.85–1.95 (m, 4H), 1.47–1.53 (m, 4H), 1.32–1.42 (m, 8H), 0.92 (t, $J = 6.9$, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 155.6, 154.3, 153.9, 136.8, 131.2, 130.8, 129.9, 127.5, 32.5, 31.7, 29.7, 29.4, 22.7, 14.1. MS (MALDI) m/z: 573.0. IR (KBr, cm^{-1}): 2955, 2925, 2857, 1699, 1550, 1508, 871, 831. Elemental analysis, calculated for $C_{30}H_{32}N_6S_3$: C, 62.90%; H, 5.63%; N, 14.67%; S, 16.79%. Found: C, 62.92%; H, 5.74%; N 14.78%; S, 17.05.

4.8. Synthesis of **DH4BT**

A mixture of **6** (1.1 g, 2.54 mmol), K_2CO_3 (0.35 g, 2.54 mmol), PEG 4000 (2.54 g, 0.63 mmol), $Pd(OAc)_2$ (0.028 g, 0.124 mmol), and DMF (10 mL) was stirred at 120 °C for 24 h under argon, and the resulting solution was cooled to room temperature and then poured into 200 mL of water. The solid was filtered and washed with water to give crude product, which was further purified by Soxhlet extraction using acetone. The residue was recrystallized twice from a mixture of chloroform, alcohol and CF_3COOH to give **DH4BT** as a yellow solid, 0.69 g, yield of 77%. Mp 361 °C (DSC). ^{1}H NMR ($CDCl_3/CF_3COOH$, 300 MHz, ppm) δ 8.36 (d, $J = 7.5$ Hz, 2H), 8.26 (d, $J = 6.9$ Hz, 2H), 8.09 (d, $J = 6.9$ Hz, 2H), 7.29 (d, $J = 7.5$, 2H), 3.26 (d, $J = 7.8$ Hz, 4H), 1.91 (m, 4H), 1.563 (m, 4H), 1.36–1.48 (m, 8H), 0.93 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR ($CDCl_3/CF_3COOH$, 100 MHz, ppm): δ 154.9, 153.9, 153.8, 153.5, 137.8, 132.6, 132.6, 132.0, 131.8, 130.8, 130.0, 129.0, 116.3, 115.3, 116.3, 115.3, 113.5, 113.0, 32.5, 31.8, 29.8, 29.4, 22.7, 13.8; IR (KBr, cm^{-1}): 2955, 2925, 2857, 1548, 1507, 1462, 1268, 870, 827. Elemental analysis, calculated for $C_{36}H_{34}N_8S_4$: C, 61.16%; H, 4.85%; N, 15.85%; S, 18.14%. Found: C, 60.84%; H, 4.70%; N, 15.54%; S, 18.03%. MS (MALDI) m/z: 707.

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References

[1] (a) Chi CY, Mikhailovsky A, Bazan GC. J Am Chem Soc 2007;129:11134–45;
(b) Neto BAD, Lapis AAM, Mancilha FS, Vasconcelos IB, Thum C, Basso LA, et al. Org Lett 2007;9:4001–4;
(c) Hong JW, Hemme WL, Keller GE, Rinke MT, Bazan GC. Adv Mater 2006;18:878–82;
(d) An L, Tang Y, Feng F, He F, Wang S. J Mater Chem 2007;17:4147–52;
(e) Liu B, Bazan GC. J Am Chem Soc 2004;126:1942–3.

[2] (a) Belen'kaya IA, Yasinskaya OG, Ivanova VV, Sirik SA. Khimiko-Farm-atsevticheskii Zhurnal 1995;29:54–5;
Chem Abstr 1995;V123:306048. Also see:;
(b) Tomoji A, Kentarou K, Nagatoshi W, Kouki I. JP Patent. 100,859; 2002. (c) Ramesh U, Look G, Huang J, Singh R, Mattis RB. US Patent. 158,957; 2005.

[3] (a) Kim Y, Cook S, Choulis SA, Nelson J, Durrant JR, Bradley DDC. Chem Mater 2004;16:4812–8;
(b) Sevensson M, Zhang F, Veenstra SC, Verhees WJH, Hummelen JC, Kroon JM, et al. Adv Mater 2003;15:988–91;
(c) Dhanabalan A, Dongen JL, Duren JJKJ, Janssen M, Hal PA, Janssen RAJ. Macromolecules 2001;34:2495–501;
(d) Dhanabalan A, Duren JKJ, Hal PA, Dongen JLJ, Jassen RAJ. Adv Funct Mater 2002;12:709–12;
(e) Dhanabalan A, Duren JKJ, Hal PA, Dongen JLJ, Jassen RAJ. Adv Funct Mater 2001;11:255–62;
(f) Shin WU, Kim SC, Lee SJ, Jeon HS, Kim MK, Naidu BVK, et al. J Polym Sci Polym Chem 2007;45:1394–402;
(g) Mühlbacher D, Scharber M, Morana M, Zhu Z, Waller D, Gaudiana R, et al. Adv Mater 2006;18:2884–9;
(h) Soci C, Hwang I, Moses D, Zhu Z, Waller D, Gaudiana R, et al. Adv Funct Mater 2007;17:632–6;
(i) Blouin N, Michaud A, Leclerc A. Adv Mater 2007;19:2295–300;
(j) Velusamy M, Thoms KRJ, Lin JT, Hsu YH, Ho KC. Org Lett 2005;7:1889–920.

[4] (a) Thomas KRJ, Lin J, Velusamy M, Tao Y, Chuen C. Adv Funct Mater 2004;14:83–90;
(b) Thomas KRJ, Lin J, Sun S, Tao Y, Chuen C. Chem Commun 2004;24:2328–9;
(c) Huang J, Li C, Xia Y, Zhu X, Peng J, Cao Y. J Org Chem 2007;72:8580–3;
(d) Fang Q, Xu B, Jiang B, Fu H, Chen X, Cao A. Chem Commun 2005;25:1468–70;
(e) Chen C, Lin J, Yeh M. Org Lett 2006;8:2233–6;
(f) Campbell AJ, Bradley DDC, Antoniadis H. Appl. Phys. Lett. 2001;79:2133–5;
(g) Herguth P, Jiang X, Liu M, Alex KYJ. Macromolecules 2002;35:6094–100;
(h) He Y, Gong S, Hattori R, Kanicki J. Appl Phys Lett 1999;74:2265–7;
(i) Morteani AC, Dhoot AS, Kim JS, Silva C, Greenham NC, Murphy C, et al. Adv Mater 2002;14:1834–7;
(j) Kim JS, Ho PKH, Murphy CE, Friend RH. Macromolecules 2004;37:2861–71;
(k) Hou Q, Zhou Q, Zhang Y, Yang W, Yang R, Cao Y. Macromolecules 2004;37:6299–305;
(l) Huang J, Xu Y, Hou Q, Yang W, Yuan M, Cao Y. Macromol Rapid Commun 2002;23:709–12;
(m) Shi C, Wu Y, Zeng W, Xie Y, Yang K, Cao Y. Macromol Chem Phys 2005;206:1114–25;
(n) Xia Y, Deng X, Wang L, Li X, Zhu X, Cao Y. Macromol Rapid Commun 2006;27:1260–4;
(o) Li X, Zeng W, Zhang Y, Hou Q, Yang W, Cao Y. Eur Polym J 2005;41:2923–33.

[5] (a) Akhtaruzzaman M, Kamata N, Nishida JI, Ando S, Tada H, Tamura M, et al. Chem Commun 2005:3183–5;
(b) Kono T, Kumaki D, Nishida JI, Sakanoue T, Kakita M, Tada H, et al. Chem Mater 2007;19:1218–20.

[6] Aldakov D, Palacios MA, Anzenbacher P. Chem Mater 2005;17:5238–41.

[7] (a) Kato SI, Matsumoto T, Ishi-i T, Thiemann T, Shigeiwa M, Gorohmaru H, et al. Chem Commun 2004;24:2342–3;
(b) Kato SI, Matsumoto T, Shigeiwa M, Gorohmaru H, Maeda S, Ishi-i T, et al. Chem Eur J 2006;12:2303–17.

[8] Kanbara T, Yamamoto T. Chem Lett 1993;22:419–22.

[9] Pilgram K, Zupan M, Skiles R. J. Heterocycl Chem 1970;7:629–33.

[10] Huo S. Org Lett 2003;5:423–5.

[11] (a) Wang L, Zhang Y, Liu L, Wang Y. J Org Chem 2006;71:1284–7;
(b) Liu L, Zhang Y, Wang Y. J Org Chem 2005;70:6122–5.

[12] (a) Fukushima T, Okazeri N, Miyashi T, Suzuki K, Yamashita Y, Suzuki T. Tetrahedron Lett 1999;40:1175–8;
(b) Akhtaruzzaman M, Tomura M, Nishida J, Yamashita Y. Synth Met 2003;137:873–4;
(c) Akhtaruzzaman M, Tomura M, Nishida J, Yamashita Y. J Org Chem 2004;69:2953–8.

[13] Suzuki T, Okubo T, Okada A, Yamashita Y, Miyashi T. Heterocycles 1993;35:395–406.

[14] Promarak V, Punkvuang A, Meunmat D, Sudyoadsuk T, Saengsuwan S, Keawin T. Tetrahedron Lett. 2007;48:919–23.

[15] Wu TY, Chen Y. J Polym Sci Polym Chem 2003;41:1444–8.

[16] Pommerehne J, Vestweber H, Guss W, Mahrt RF, Bässler H, Porsch M, et al. Adv Mater 1995;7:551–4.