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ABSTRACT

Various thieno[3,4-*b*]thiophene derivatives functionalized by *n*-octyl, 4-*tert*-butylphenyl, 4-*n*-butylphenyl, and 4-*n*-pentylphenyl were synthesized in a concise and efficient way. Previously reported synthetic processes were modified to produce target molecules in relatively high yields. Electrochemical and optical properties of polymers were examined by cyclic voltammetry and Vis–NIR spectrophotometry. The bandgap of electrochemically prepared polymers varied with substituents, ranging from 0.91 eV to 0.98 eV. While HOMO of conjugated polymers was raised by inductive effect of alkyl substituents, the bandgap was mainly determined by resonance stabilization of phenyl substituents.

Highly efficient synthesis of thieno[3,4-*b*]thiophene derivatives and (opto)electrochemical properties of new low bandgap conjugated polymers

1. Introduction

The conjugated polymers of low bandgap have received great attention recently because of potential applications in various emerging fields such as transparent electrodes [1], OLEDs [2], and OFET [3]. The employment of low bandgap conjugated polymers in polymer solar cells (PSCs) was also studied and has been proven successful due to absorption of a wide range of solar spectrum, greatly improving power conversion efficiencies [4–6]. For example, bulk heterojunction PSCs based on thieno[3,4-*b*]thiophene units showed much improved power conversion efficiencies (PCEs) up to over 6% [4–6]. The stable quinoidal structure from thieno[3,4-*b*]thiophene resulted in a low bandgap of the polymer, which can cover the terrestrial solar spectrum from red to near infrared to harvest the maximum photon flux [7]. Recently, great pieces of works were reported by Liang et al. and Chen et al., in which a series of polymers based on alternating thieno[3,4-*b*]thiophene and benzodithiophene units have been reported and PSCs fabricated from them exhibited greatly improved PCEs of around 6–7% [4,6].

Therefore, molecular engineering to finely tune a bandgap by choosing proper molecular units is of crucial importance. To easily reach this goal, development of concise and convenient synthetic routes for a variety of thieno[3,4-*b*]thiophene derivatives is an essential prerequisite. In this paper, we wish to report a new synthetic method for thieno[3,4-*b*]thiophene derivatives which can be easily reproduced in moderate yields unlike the previous reports [8–10]. Synthetic results of new thieno[3,4-*b*]thiophene monomers functionalized by octyl, 4-*tert*-butyl, 4-*n*-butylphenyl, and 4-*n*-pentylphenyl via the method presented in this paper are also reported. Optical and electrochemical properties of the polymers derived from them are described.

2. Experimental

Synthetic routes of thieno[3,4-*b*]thiophene derivatives were summarized in Scheme 1. Thieno[3,4-*b*]thiophenes of various substituents with different inductive and resonant effects were prepared.

2.1. Typical procedure for preparation of **2A**

The reaction mixture of 3,4-dibromothiophene (**1**, 3.0 g, 12.4 mmol), DBU (2.3 g, 14.9 mmol), *trans*-dichlorobis(triphenylphosphine)palladium (II) (0.4 g, 0.5 mmol), CuI (0.24 g, 1.24 mmol), and 1-decyne (2.1 g, 14.9 mmol) in acetonitrile was irradiated with microwave (85 W) for 15 min at 100 °C. After cooling to room temperature, the reaction mixture was poured into aq. NH_4Cl and extracted with ether. The combined organic layers were washed with water, brine, and then dried over $MgSO_4$. After concentrated under reduced pressure, the residue was purified by column chromatography on silica gel to give **2A** in a moderate yield (50%).

2.1.1. 3-Bromo-4-(dec-1-ynyl)thiophene (**2A**)

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, J = 3.6 Hz, 1H), 7.2 (d, J = 3.2 Hz, 1H), 2.42 (t, J = 6.8 Hz, 2H), 1.4–1.6 (m, 4H), 1.27–1.3 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 127.7, 125.2, 122.5, 113.9, 93.6, 73.9, 31.8, 29.2, 29.1, 28.8, 28.6, 22.6, 19.4, 14.1.

2.1.2. 3-Bromo-4-(2-(4-tert-butylphenyl)ethynyl)thiophene (**2B**)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.4–7.5 (m, 3H), 7.37 (d, J = 4.8 Hz, 2H), 7.26 (d, J = 3.2 Hz, 1H), 1.32 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.2, 131.4, 128.4, 125.4, 125.3, 122.8, 119.7, 113.9, 92.3, 82.1, 34.8, 31.1.

2.1.3. 3-Bromo-4-(2-(4-butylphenyl)ethynyl)thiophene (**2C**)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.48 (m, 3H), 7.26 (d, J = 3.2 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 2.62 (t, J = 8 Hz, 2H), 1.34–1.61 (m, 4H), 0.92 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.8, 131.6, 128.5, 128.4, 122.8, 119.9, 113.9, 92.4, 82.1, 35.6, 33.4, 22.3, 13.9.

2.1.4. 3-Bromo-4-(2-(4-pentylphenyl)ethynyl)thiophene (**2D**)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, J = 3.6 Hz, 1H), 7.46 (d, J = 8 Hz, 2H), 7.26 (d, J = 3.6 Hz, 1H), 7.16 (d, J = 4.4 Hz, 2H),

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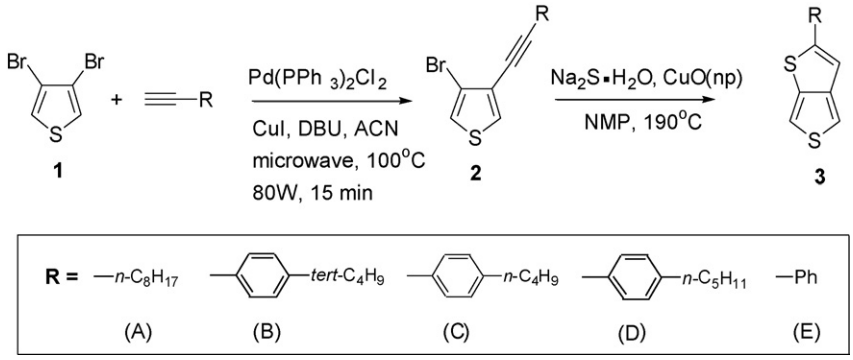

Scheme 1. Synthetic route of thieno[3,4-*b*]thiophene derivatives.

2.61 (t, *J* = 7.2 Hz, 2H), 1.61 (p, *J* = 8 Hz, 2H), 1.3 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.8, 131.6, 128.5, 128.4, 124.8, 122.8, 119.8, 113.8, 92.4, 82.1, 35.9, 31.4, 30.9, 22.5, 14.0.

*2.1.5. 3-Bromo-4-(2-phenylethynyl)thiophene (**2E**)*

^{1}H and ^{13}C NMR of isolated compounds were matched to those given in reference [4].

*2.2. Typical procedure for preparation of **3A***

The reaction mixture of 3-bromo-4(dec-1-ynyl)thiophene (0.3 g, 1.00 mmol), $Na_2S{\cdot}9H_2O$ (0.48 g, 2.00 mmol), CuO nanopowder (0.005 g, 0.05 mmol) in N-methylpyrrolidone (NMP, 20 mL) was stirred at 190 °C for 12 h. After cooled to room temperature, the reaction mixture was poured into water and extracted with ether. The combined organic layers were washed with water, brine, and then dried over $MgSO_4$. After concentrated under reduced pressure, the residue was purified by column chromatography on silica gel to give **3A** in 40% yield as pale yellow oil.

*2.2.1. 2-Octylthieno[3,4-b]thiophene (**3A**)*

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (s, 1H), 7.13 (s, 1H), 6.6 (s, 1H), 2.74 (t, *J* = 7.2 Hz, 2H), 1.69 (p, *J* = 7.2 Hz, 2H), 1.2–1.4 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 147.6, 138.7, 113.2, 110.2, 109.9, 31.9, 31.8, 30.3, 29.3, 29.2, 29.1, 22.6, 14.1; MS (EI) *m*/*z* 252 (M^+); Anal. Calcd. for $C_{14}H_{20}S_2$: C (66.61) H (7.99) S (25.40), Found: C (66.74) H (8.05) S (25.35).

*2.2.2. 2-(4-tert-Butylphenyl)thieno[3,4-b]thiophene (**3B**)*

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 2.8 Hz, 1H), 7.21 (d, *J* = 2.8 Hz, 1H), 7.15 (s, 1H), 1.31–1.35 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.1, 132.0, 125.9, 125.8, 111.8, 111.7, 110.6, 77.2, 75.8, 53.9, 34.7, 31.2; MS (EI) *m*/*z* 272 (M^+); Anal. Calcd. for $C_{16}H_{16}S_2$: C (70.54) H (5.92) S (23.54), Found: C (70.38) H (6.09) S (23.39).

*2.2.3. 2-(4-Butylphenyl)thieno[3,4-b]thiophene (**3C**)*

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 8.4 Hz, 2H), 7.17–7.26 (m, 2H), 7.2 (d, *J* = 8.4 Hz, 2H), 7.13 (s, 1H), 7.63 (t, *J* = 7.6 Hz, 2H), 1.61 (p, *J* = 7.2 Hz, 2H), 1.36 (h, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.1, 148.1, 143.6, 138.3, 132.2, 128.9, 128.7, 126.1, 125.5, 123.4, 111.7, 111.6, 110.6, 35.4, 33.5, 22.3, 13.91; MS (EI) *m*/*z* 272 (M^+); Anal. Calcd. for $C_{16}H_{16}S_2$: C (70.54) H (5.92) S (23.54), Found: C (70.47) H (5.94) S (23.29).

*2.2.4. 2-(4-Pentylphenyl)thieno[3,4-b]thiophene (**3D**)*

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.21 (m, 3H), 7.14 (s, 1H), 2.62 (t, *J* = 8 Hz, 2H), 1.63 (p, *J* = 8 Hz, 2H), 0.90 (t, *J* = 4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.1, 148.1, 143.6, 138.3, 135.6, 132.2, 128.9, 126.2, 126.1, 111.7, 111.6, 110.6, 35.7, 31.5, 31.1, 22.5, 14.0; MS (EI) *m*/*z* 286 (M^+); Anal. Calcd. for $C_{17}H_{18}S_2$: C (71.28) H (6.33) S (22.39), Found: C (71.30) H (6.39) S (22.24).

*2.2.5. 2-Phenyl[3,4-b]thiophene (**3E**)*

^{1}H and ^{13}C NMR of isolated compounds was matched to those given in reference [4].

2.3. Electrochemical characterization

The monomers (3A–3D) were electrochemically deposited on Pt or ITO (Delta Tech. CG-41IN-CUV) by scanning potentials in mixed solvents (acetonitrile/CH_2Cl_2 = 1/1) containing 50 mM tetrabutylammonium tetrafluoroborate ($TBABF_4$). Cyclic voltammograms of polymer films were obtained in the same electrolyte solutions free from monomers. Optical bandgaps of polymers prepared on ITO were recorded at various potentials using a UV–Vis–NIR spectrophotometer (JASCO V-670). The reference electrode was Ag wire and all the potentials were converted with respect to NHE using the ferrocene/ferrocenium couple. The potential was controlled via a potentiostat (BAS CV-50W).

3. Results and discussion

3.1. Synthesis of monomers

Commercially available 3,4-dibromothiophene (**1**) and various alkynes were employed as starting materials for **2**. The reaction of dibromothiophene and phenylacetylene using Sonogashira reaction was extensively studied in this system under various reaction conditions. Under usual conditions ($Pd(PPh_3)_2Cl_2$, CuI, Et_2NH) or slightly modified conditions, the reaction resulted in low yields along with complex coupling byproducts [8]. After examining a series of palladium catalysts, ligands, and bases, **2** was obtained in moderate yields at the reaction condition described in Scheme 1 ($Pd(PPh_3)_2Cl_2$, CuI, DBU, and acetonitrile as a solvent). However, the reaction was further optimized to improve the yield and to shorten the reaction time by employing microwave irradiation.

With **2** in hands, cyclization of **2** to form thieno[3,4-*b*]thiophene ring was attempted by the known procedure [9]. However, the procedure could not be successfully reproduced, resulting in extremely low yields and complicated byproducts. To solve this problem, we turned our attention to another route that was recently reported in the literature [10]. The cyclization was performed in the presence of $Na_2S{\cdot}H_2O$. For example, the reaction of **2E** with $Na_2S{\cdot}H_2O$ gave rise to the product **3E**, but still in low yields (~15%). The yield was further improved to give 35% by adding catalytic amount of