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Syntheses, structures and properties of asymmetric thiophene-containing pentacene-like heteroacenes organic semiconductors

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HIGHLIGHTS

- Pentacene-like semiconductors, BNT and BPT, were synthesized in high yield.
- New synthetic route was developed.
- BNT and BPT molecules form columnar π-stacking along crystallographic a-axis.
- Electrochmical and optical properties in solid state and thin films were studied.
- Multicolor emission property was observed for both BNT and BPT thin films.

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ABSTRACT

Two thiophene-containing pentacene-like semiconductors, benzo[d]naphtho[2,1-b]thiophene (BNT) and benzo[d]phenanthro[9,10-b]thiophene (BPT), were synthesized in a new route, and they were characterized by means of ultraviolet–visible absorption spectrum, thermo- and electro-chemistry analysis. Single crystals were obtained by vapor diffusion of solvent to analyze the correlation between charge transport and structure properties. The large band gaps and low-lying HOMO energy levels could result in much better stability. It was observed that the molecular packing in the herringbone motif is similar to that in pentacene, which is the benchmark of organic semiconductors. The BNT and BPT molecules form columnar π-stacking along the crystallographic a-axis direction with an interplanar separation of 3.535 and 3.442 Å, respectively, which suggests that the molecules adopt compact packing in solid state. The distances indicate the presence of $\pi-\pi$ interactions along the intermolecular stacking axis in the two materials. Face-to-face columnar π-stacking increases the effective dimensionality of the electronic structure and benefits charge transport. Multicolor emission property was observed for both BNT and BPT thin films.

1. Introduction

Organic field-effect transistors (OFETs) have various applications in electronics, such as smart cards, organic active matrix displays, and radio frequency identification tags [1,2], and have attracted much attention [3,4]. The applications are mostly based on many fine features including large-area processing, flexibility, and low-cost devices, which mainly rely on organic semiconductors with high performance, thermal stability, and easy accessibility in pure forms [5]. A class of fused oligoacenes meets the criteria of organic semiconductors for OFET applications, among which the most excellent one is pentacene [6]. The high OFET mobility, 1.5 $cm^2 V^{-1} S^{-1}$ has been reported [7], which is contributed by the intermolecular overlap of $\pi-\pi$ system in solid state originated from linearly condensed acene structures [8]. However, the oxidative instability and extreme insolubility of pentacene have been obstacles for practical applications [9]. This intrigues research interest to compounds with a structure similar to pentacene. Many pentacene derivatives and pentacene-like heteroacenes have therefore been investigated [10–12].

Recently, thiophene-containing heteroacenes with a minor change of the molecular structure of pentacene have been studied intensively [13,14]. The presence of sulfur heteroatom has positive effects on both properties and structures, including electronic and

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solid-state structures. In addition, to improve solubility of the molecule, the heteroatom-containing units can enhance π−stacking in crystal structures, and thus create a more densely packing in solid state and an increased charge transport [15]. However, most of the compounds are linear symmetric molecules, and there are only a few asymmetric molecules being used in OFETs [16], which induces researchers to conceive asymmetric compounds with similar structure of pentacene [17].

In this paper, we report a new synthetic route to thiophene-containing pentacene-like heteroacene, which avoids the appearance of byproducts and can achieve high yields. Two luminescent compounds, benzo[d]naphtho[2,1-b]thiophene (BNT) and benzo[d]phenanthro[9,10-b]thiophene (BPT), were synthesized and characterized. Although these two compounds have been synthesized as byproducts [18] in literature, their physical and chemical properties have not been investigated, and the semiconducting characteristics have not been developed yet. We investigate the properties of BNT and BPT, which are asymmetric molecules with bent structures, in order to fabricate OFETs with high performances.

2. Experimental

2.1. Chemicals and instruments

Starting materials, 2-bromo(methylsulfanyl)benzene **(1)**, naphthalen-1-ylboronic acid (**3**), and 9-bromophenanthrene (**6**) are commercially available and were purchased from local chemical company. Trifluoromethanesulfonic acid, isopropoxyboronic acid pinacol ester, and *n*-BuLi were purchased from Alfa Aesar, Aldrich, and ACROS, respectively. All other reagents were regular ones of analytical grade.

Structures of intermediates and final products were confirmed by spectrometric methods, including ^{1}H NMR (Bruker dmx 300NMR), ^{13}C NMR (Bruker dmx 400NMR), EI-MS (AEI-MS50), HRMS (Micromass GCT-MS), and elemental analysis (Carlo-Erba 1160 Elemental Analyzer). Cyclic voltammetry (CV) measurements were performed on an electrochemical analyzer, EG&G Potentiostat/Galvanostat model 283, in CH_2Cl_2 containing 0.1 M n-Bu_4NPF_6 as a supporting electrolyte. UV−visible (UV−vis) absorption and photoluminescent spectra were recorded on a Hitachi Model U-3010 and Hitachi F-4500 spectrometer, respectively. Thermogravimetry analysis (TGA) was carried out on a Perkin-Elmer Series 7 thermal system with a heating rate of 10 °C min^{-1} in nitrogen.

2.2. General synthetic procedures

Two compounds, BNT and BPT, were synthesized with high yields using a new method. The general synthetic routes are schematically outlined in Scheme 1. 2-Bromo(methylsulfinyl)benzene (**2**) was obtained quantitatively by oxidation in glacial acetic acid with hydrogen peroxide according to the literature [19]. 9-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenanthrene (**7**) was firstly synthesized by reacting 9-bromophenanthrene with an excess of *n*-BuLi at −78 °C, followed by quenching the lithiated complex with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Two precursors **4** and **8** were then obtained via the Suzuki coupling reactions of compound **3** and **7** with **2**, in the presence of a catalytic amount of $Pd(PPh_3)_4$ and 2 M K_2CO_3. Next, **4** was treated with trifluoromethanesulfonic acid to form an intermediate sulfonium salt **5**, and there was no need to isolate **5**. Subsequent demethylation with a water-pyridine mixture (5:1) afforded the final product benzo[d]naphtho[2,1-b]thiophene (BNT) in 50% yield. Similarly, **8** was treated with the same acid, and the intermediate sulfonium salt **9** was not isolated, and subsequent demethylation with the water-pyridine mixture afforded the other final product benzo[d]phenanthro[9,10-b]thiophene (BPT) in a higher yield of 88.7%. The target molecules BNT and BPT are soluble in most common organic solvents.

2.3. Synthesis and characterization of intermediates and target molecules

2-Bromo(methylsulfinyl)benzene (2) 2-Bromo(methylsulfanyl)benzene (**1**) (3.3 g, 16.25 mmol) was dissolved in glacial acetic acid (50 mL). The mixture was kept at 0 °C, and then hydrogen peroxide (30%, 2.11 g) was added dropwise to the solution. After a while, the mixture was stirred at room temperature for 24 h. The glacial acetic acid was removed by evaporation under vacuum and the crude product was then extracted by CH_2Cl_2, saturated with $NaHCO_3$ solution, and finally afforded 3.34 g (94.3%) of **2** as a rosiness liquid. EI-MS: m/z (%) = 218 (M^+, 100%).

1-(2-(Methylsulfinyl)phenyl)naphthalene (4) Suzuki coupling reaction was used for the synthesis of **4**. Naphthalen-1-ylboronic acid (**3**) (1.36 g, 8 mmol) and 2-bromo(methylsulfinyl)benzene (**2**) (1.743 g, 8 mmol) were mixed in THF (40 mL), and K_2CO_3 (2 M, 25 mL) was added. The mixture was then degassed and $Pd(PPh_3)_4$ (277 mg) was added in one portion under a nitrogen atmosphere. The mixture was stirred at 70 °C for 45 h. The organic phase was separated, washed with water and brine solution, and dried over anhydrous $MgSO_4$. Finally, the crude product was chromatographed on silica gel (10:1 petroleum-ethyl acetate) to give **4** (1.404 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.24−8.20 (t, J = 6.52 Hz, 1H), 7.95−7.91 (t, J = 8.2 Hz, 2H), 7.76−7.69 (m, J = 7.66 Hz, 1H), 7.64−7.57 (m, J = 6.83 Hz, 1H), 7.55−7.50 (m, J = 3.15 Hz, 3H), 7.48−7.42 (m, J = 8.32 Hz, 2H), 7.38−7.35 (m, J = 3.34 Hz, 1H), 2.15 (s, 3H). EI-MS: m/z (%) = 266 (M^+, 100%).

9-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenanthrene (7) 2.5 M *n*-BuLi (2.4 mL) was added dropwise to a solution of 9-bromophenanthrene (**6**) (1.28 g, 5 mmol) in anhydrous THF (30 mL) at −78 °C under nitrogen with stirring. The solution turned to be orange slowly. After stirred at −78 °C for 1 h, 4,4,5,5-tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane (1.225 mL, 6 mmol) was added. The reaction mixture was then warmed to room temperature and stirred overnight. The final solution was extracted by water and CH_2Cl_2, and then dried over anhydrous $MgSO_4$. A pure yellow solid **7** (1.2 g, 78.9%) was obtained by chromatographed on silica gel (2:1 petroleum-ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.84−8.81 (m, J = 2.54 Hz, 1H), 8.70−8.66 (m, J = 3.75 Hz, 2H), 8.39 (s, 1H), 7.94−7.92 (d, J = 7.83 Hz, 1H), 7.69−7.56 (m, J = 7.29 Hz, 4H), 1.49−1.45 (d, J = 15.8 Hz, 12H). EI-MS: m/z (%) = 304 (M^+, 100%).

9-(2-(Methylsulfinyl)phenyl)phenanthrene (8) 9-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenanthrene (**7**) (1.52 g, 5 mmol) and 2-bromo(methylsulfinyl)benzene (**2**) (1.09 g, 5 mmol) were dissolved in THF, and then K_2CO_3 (2 M, 15 mL) was poured into the solution. $Pd(PPh_3)_4$ (173 mg) was then added in one portion under a nitrogen atmosphere. The mixture was stirred at 70 °C for 48 h. The organic phase was separated, washed with water and brine solution, and dried over anhydrous $MgSO_4$. Then, the crude product was chromatographed on silica gel (10:1 petroleum-ethyl acetate) to give **8** (1.36 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.81−8.73 (m, J = 8.97 Hz, 2H), 8.27−8.23 (t, J = 7.95 Hz, 1H), 7.92−7.86 (m, J = 7.76 Hz, 1H), 7.76−7.63 (t, J = 7.72 Hz, 5H), 7.56−7.48 (m, J = 7.25 Hz, 3H), 7.43−7.40 (t, J = 6.41 Hz, 1H), 2.19 (s, 3H). EI-MS: m/z (%) = 316 (M^+, 100%).

Benzo[d]naphtho[2,1-b]thiophene (BNT) 1-(2-(Methylsulfinyl)phenyl)naphthalene (**4**) (872 mg, 3.27 mmol) was added to trifluoromethanesulfonic acid (10 mL). The solution was stirred at room temperature for 60 h and then poured slowly into a water-pyridine mixture (120 mL, 5:1). The mixture was heated at 100 °C