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A small molecule composed of anthracene and thienothiophene devised for high-performance optoelectronic applications

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ABSTRACT

An asymmetric small molecule composed of anthracene and alkylated thienothiophene (2-(anthracen-2-yl)-5-hexylthieno[3,2-b]thiophene) was synthesized via the Suzuki coupling reaction. The thermal stability, photochemical properties, and morphological characteristics were investigated using thermogravimetric analysis, differential scanning calorimetry, cyclic voltammetry, UV–visible spectroscopy, and X-ray diffraction techniques. The compound demonstrated a good thermal stability of 5% at a decomposition temperature of 336 °C. The solution-processed single-crystal transistor, devised with 2-(anthracen-2-yl)-5-hexylthieno[3,2-b]thiophene, exhibited high performance with a hole mobility of 0.1 cm^2/Vs. Furthermore, by utilizing the high mobility of 2-(anthracen-2-yl)-5-hexylthieno[3,2-b]thiophene, we demonstrated its unprecedented high photoresponsivity of 3370 A/W, a finding that can be attributed to the very efficient photoconductive behavior of a single crystal of 2-(anthracen-2-yl)-5-hexylthieno[3,2-b]thiophene.

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1. Introduction

During the last few decades, organic semiconductors have emerged as viable alternatives to inorganic semiconductors due to their advantages over their inorganic counterparts [1–5]. For instance, extensive industrial applications of organic thin-film transistors (OTFTs) are now relatively close to implementation because of the great success of OTFTs in the field of flexible displays [6] as well as their cost-effective promise in the fields of radio-frequency identification (RFID) tags [7,8] and sensors [9,10]. This great success of organic semiconductors can be attributed to smart molecular design, enabling not only solution processability in various organic solvents [11,12] but also unprecedented high charge-carrier mobility. There have been tremendous research efforts expended to enhance the charge-carrier mobilities of OTFTs using both small-molecule semiconductors and polymeric semiconductors, including using benzothiadiazole (BTD) [13], diketopyrrolopyrrole (DPP) [14], isoindigo (IDG) [15], benzobisthiadiazole (BBT) [16], and arylene diimides [17] as key building blocks of potential organic semiconductors.

Polymeric semiconductors for OTFTs have several advantages over small molecules in terms of physical robustness, chemical stability, and electrical reproducibility. These properties make them a better choice than small molecules for OTFT applications. Nonetheless, the simplicity of synthesis along with the ease of purification of small molecules make them attractive candidates for high-performance OTFTs, especially for low-cost organic electronics. Traditionally, linear acene derivatives have shown satisfactory results in OTFT applications. Representative examples include anthracene [18,19], naphthalene [20], and thienothiophene [21] derivatives.

After considering the aforementioned issues, an asymmetric small-molecule organic semiconductor containing an anthracene attached to a thienothiophene was designed and synthesized. The alkyl chain introduced on the thienothiophene facilitated the solubility of the compound in common organic solvents. 2-(Anthracen-2-yl)-5-hexylthieno[3,2-b]thiophene (ASCTT) was synthesized via the Suzuki coupling reaction between 2-bromoanthracene (compound 2) and 2-(5-hexylthieno[3,2-b]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 6).

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The photophysical, electrochemical, structural, and electrical characteristics of ASCTT were systematically investigated. Under the single-crystal field-effect transistor (SCFET) geometry, ASCTT revealed a high hole mobility of 0.1 cm^2V^{-1} s^{-1}. Moreover, we demonstrated the very efficient, trap-limited photoconductive behavior of ASCTT, resulting in a photoresponsivity up to 3370 A/W.

2. Experimental

2.1. Materials and syntheses

2.1.1. Materials

All reagents and chemicals were purchased from Sigma Aldrich Co., TCI, or Alfa Aesar Co. Solvents such as tetrahydrofuran (THF), diethyl ether, toluene, and methylene chloride were used after distillation in the presence of sodium/benzophenone or calcium hydride under nitrogen gas.

2.1.2. Synthesis of 2-bromoanthraquinone (compound 1)

2-Aminoanthraquinone (3 g, 13.44 mmol), tert-butyl nitrite (3.69 mL, 30.9 mmol), and copper (I) bromide (6.9 g, 30.9 mmol) were added to acetonitrile (50 mL). The mixture was stirred for 2 h at 65 °C. The reaction mixture was cooled to room temperature. The reaction was quenched with 6 N HCl. The precipitate was filtered, washed with chloroform, and dried in a vacuum desiccator to give compound 1 as a pure brown solid. Yield: 2.4 g (62%). ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): *δ* 8.42 (d, 1H, *J* = 2.1 Hz), 8.32–8.28 (m, 2H), 8.18–8.15 (d, 1H, *J* = 8.1 Hz), 7.94–7.90 (dd, 1H, *J* = 2.1, 1.8 Hz), 7.84–7.81 (q, 2H, *J* = 3.3 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): δ 182.36, 137.16, 134.48, 134.36, 133.13, 130.02, 129.02, 127.38, 127.34; EI, MS *m*/*z* (%): 286 (100, M^+).

2.1.3. Synthesis of 2-bromoanthracene (compound 2)

Compound 1 (2 g, 6.9 mmol), hydroiodic acid (10.6 mL), and hypophosphorous acid (6.4 mL) were dissolved in acetic acid (17 mL). The mixture was stirred for 96 h at 150 °C. The reaction mixture was cooled to room temperature. The precipitate was filtered and washed with ethanol. The solid was purified via soxhlet extraction with toluene, yielding compound 2 as a pure yellow solid. Yield: 1.1 g (61%). ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 8.44–8.41 (t, 1H, *J* = 6.9 Hz), 8.34–8.30 (d, 2H, *J* = 10.2 Hz), 8.19–7.99 (q, 2H, *J* = 3.3 Hz), 7.91–7.87 (d, 1H, *J* = 6.0 Hz), 7.91–7.73 (dd, 1H, *J* = 9.0, 9.3 Hz), 7.68–7.49 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): δ 133.65, 129.89, 129.83, 129.65, 128.87, 128.23, 128.19, 128.12, 126.58, 126.55, 126.05, 126.00, 125.78, 125.37; EI, MS m/z (%): 256 (100, M^+).

2.1.4. Synthesis of 2-hexanoylthieno[3,2-b]thiophene (compound 4)

Hexanoyl chloride (4.0 mL, 28.55 mmol) was added to a solution of compound 3 (2.6 g, 18.54 mmol) in CH_2Cl_2 (70 mL). Aluminum chloride (3.7 g, 27.81 mmol) was added in portions over 10 min. The mixture was stirred for 1 h at room temperature. Water was added to the reaction solution to quench the reaction and then the solution was extracted with dichloromethane. The organic phase was dried with anhydrous $MgSO_4$ and the solvent was removed under vacuum. The crude residue was purified via silica-gel chromatography using hexane as the eluent to give compound 4 as a pale yellow solid. Yield: 4.0 g (91%). Mp: 83 °C; IR (KBr, cm^{-1}): 3091 (sp^2 C–H), 2947–2860 (sp^3 C–H), 1655 (C]O), 1452 (C]C); ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 7.92 (s, 1H), 7.63 (d, 1H, *J* = 5.1 Hz), 7.31 (d, 1H, *J* = 5.1 Hz), 2.94 (t, 2H, *J* = 7.4 Hz), 1.85–1.75 (m, 2H), 1.42–1.38 (m, 4H), 0.93 (t, 3H, *J* = 7.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): δ 194.21, 146.00, 144.73, 139.09, 132.32, 124.17, 120.06, 39.03, 31.54, 24.68, 22.49, 13.93; EI, MS m/z (%): 238 (100, M^+).

2.1.5. Synthesis of 2-hexylthieno[3,2-b]thiophene (compound 5)

Compound 4 (4 g, 16.78 mmol) was added to a stirred mixture of hydrazine (2.3 mL, 73.83 mmol), potassium hydroxide (3.77 g, 67.12 mmol), and triethylene glycol (24 mL). The mixture was stirred for 2 h at 210 °C. The reaction mixture was then cooled to the ambient temperature. The reaction was quenched with cold water and extracted with dichloromethane; the crude residue was purified via silica-gel chromatography with hexane to yield compound 5 as a pale yellow oil. Yield: 3.2 g (85%). IR (KBr, cm^{-1}): 2953–2852 (sp^3 C–H), 1462 (C]C); ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 7.29 (d, 1H, *J* = 5.4 Hz), 7.20 (dd, 1H, *J* = 0.9 Hz, *J* = 0.9 Hz), 6.97 (d, 1H, *J* = 0.9 Hz), 2.92–2.87 (m, 2H), 1.35–1.28 (m, 8H), 0.88 (t, 3H, *J* = 8.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): δ 148.57, 138.74, 137.33, 125.22, 119.43, 116.13, 37.14, 31.97, 30.08, 29.75, 22.73, 14.14; EI, MS m/z (%): 224 (100, M^+).

2.1.6. Synthesis of 2-(5-hexylthieno[3,2-b]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 6)

In THF (24 mL) at −78 °C, n-butyllithium (5.35 g, 13.37 mmol) was added dropwise to a solution of compound 5 (2 g, 8.91 mmol). After the mixture had been stirred at −78 °C for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.73 g, 13.37 mmol) was added to the mixture, and the resulting mixture was stirred at −78 °C for 1 h and then warmed to room temperature and further stirred overnight. The mixture was poured into water, extracted with diethyl ether, and then dried over $MgSO_4$. The solvent was removed via rotary evaporation, and a yellow oil was obtained after flash-column chromatography using hexane/ethyl acetate (10:1) as the eluent. Yield: 2.7 g (86%). IR (KBr, cm^{-1}): 2950–2849 (sp^3 C–H), 1465 (C]C); ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 7.69 (s, 1H), 6.98 (s, 1H), 2.89 (t, 2H, *J* = 7.8 Hz), 1.75–1.68 (m, 2H), 1.35–1.25 (m, 18H), 0.88 (t, 3H, *J* = 8.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): δ 151.54, 145.24, 140.08, 138.82, 129.13, 116.35, 84.11, 82.81, 60.38, 34.66, 31.58, 31.33, 28.72, 26.21, 25.27, 24.78, 24.73, 22.64, 21.00, 14.08; EI, MS m/z (%): 350 (100, M^+).

2.1.7. Synthesis of 2-(anthracen-2-yl)-5-hexylthieno[3,2-b]thiophene (ASCTT)

To a solution of compound 2 (0.1 g, 0.33 mmol) and compound 6 (0.12 g, 0.39 mmol) in toluene (4 mL), a 2 M K_2CO_3 solution (0.5 mL, 1.65 mmol) was added, and the mixture was degassed for 10 min. Next, $Pd(PPh_3)_4$ (0.023 g, 0.02 mmol) was added and the resulting mixture was stirred while being refluxed for 12 h under a nitrogen atmosphere. The reaction mixture was quenched with water and extracted with methylene chloride. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified via column chromatography using hexane as an eluent, yielding ASCTT as a yellow solid. Yield: (46%). IR (KBr, cm^{-1}): 2850 (sp^3 C–H), 1517 (C]C); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.44 (d, 2H), 8.21 (s, 1H), 8.05–7.99 (t, 3H, *J* = 4.5 Hz), 7.79–7.75 (dd, 1H, *J* = 3.45 Hz), 7.60 (s, 1H), 7.49–7.46 (m, 2H), 7.00 (s, 1H), 2.95–2.90 (m, 2H), 1.75–1.65 (m, 2H), 1.35–1.20 (m, 6H), 0.88 (t, 3H, *J* = 8.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): δ 143.20, 138.24, 133.36, 132.28, 131.72, 130.23, 128.16, 126.92, 125.14, 124.19, 116.29, 115.74, 31.58, 30.97, 29.73, 29.69, 22.60, 14.11; EI, MS m/z (%): 400 (100, M^+).

2.2. Measurements

^{1}H and ^{13}C NMR spectra were recorded on 300-MHz and 75-MHz spectrometers, respectively. The chemical-shift values were reported in δ units (ppm). IR analysis was carried out using a Mattson genesis series FT-IR spectrophotometer. Mass-spectral analysis was carried on a JMS-700, JEOL. UV–visible absorption was obtained using a Shimadzu UV-1065PC UV–Vis

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