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Synthesis and optical and electrochemical properties of polycyclic aromatic compounds based on bis(benzothiophene)-fused fluorene

Guiting Chen [a,*], Xin Li [a,**], Ziyun Chen [a], Chunbao Tang [a], Wei Yang [b], Yong Cao [b]

[a] *School of Chemistry and Environment, Jiaying University, Meizhou 514015, China*

[b] *Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China*

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ABSTRACT

Novel polycyclic aromatic compounds (FBTPhO3 and FBTPhO4), which are based on bis(benzothiophene)-fused fluorene functionalized with oligo(ethylene glycol)-substituted phenyl, were synthesized through an intramolecular electrophilic cyclizing reaction. Thermal measurements revealed their excellent thermal stability and amorphous state. Photoluminescence spectra suggested that they both show deep blue light emission. Cyclic voltammetry tests exhibited that the ionization potentials of FBTPhO3 and FBTPhO4 are 5.67 and 5.68 eV, respectively, implying their good inoxidizability. These compounds may be promising building blocks for high-performance optoelectronic functional materials.

1. Introduction

Conjugated organic small molecules and polymers are a class of functional materials that have been widely used in optoelectronic devices including organic light-emitting diodes (OLEDs) [1,2], organic photovoltaics (OPVs) [3–5], organic field effect transistors (OFETs) [6,7], electrochromic devices [8,9], chemo-/bio-sensors [10,11], and so on. Their properties such as thermotics, light absorption and emission, electronic energy level structures, charge transport, and so on can be tailored by modifying their chemical structures, which is beneficial for realizing high-performance organic electronic devices.

Among the building blocks for conjugated organic semiconductors, fluorene has drawn great attention because of its advantages such as low cost and high reactivity, and a mass of fluorene-based small molecules and polymers has been developed and applied to organic optoelectronic devices. For instance, in OLED field, polyfluorenes (PFs) have emerged as the most attractive blue emitters resulting from their high luminescent efficiencies [12–14]. However, one of the most serious drawbacks for 9,9-dialkylated PFs is that they often formed fluorenone defects after thermal annealing or during the long-term device operation, as a result of thermal, photo-oxidative, or electro-oxidative degradation [15,16]. The fluorenone defects red-shifted the electroluminescence spectra and subsequently reduced the spectral stability of OLEDs. Importantly, it has been confirmed that bis-alkoxyphenyl substitution at the 9-position of fluorene could effectively improve the structural stability of molecules incorporating

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[*] Corresponding author.

[**] Corresponding author.

E-mail addresses: 576146400@qq.com (G. Chen), mzlixin@mail.nankai.edu.cn (X. Li).

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fluorene, leading to higher device performance [17–19]. For instance, our group got highly efficient and spectrally stable blue-light-emitting PFs via introducing two 4-(2-ethylhexyloxy)phenyl groups into the 9-position of fluorene to suppress the generation of fluorenone defects [15].

Sulfur (S)-containing heterocyclic aromatic units such as thiophene [20], benzothiophene [21], dibenzothiophene [22], and benzodithiophene [23] have been a series of efficient bricks for organic semiconductors that have greatly promoted the development of organic electronic devices (e.g., OPVs [5,24–31] and OFETs [6,24,32–35]). For instance, Zhao et al. [25] synthesized a polymer donor and a small molecule acceptor, which were both based on various S-containing aromatic scaffolds, and applied them as the active layer components to fullerene-free OPV, during which a record power conversion efficiency as high as 13.1% was achieved. Our group developed a p-type small molecule based on benzothiophene-fused indolocarbazole, and the OFET devices incorporating this molecule displayed high hole mobility of 0.17 $cm^2\ V^{-1}\ s^{-1}$ and excellent stability with little roll-off of hole mobility in air [6].

Herein, we present the design and synthesis of two novel S-containing polycyclic aromatic small molecules: 9,9-bis(4-(2-(2-methoxyethoxy)ethoxy)phenyl)fluorene bis[2,3-*b*;6,7-*b*]benzo[*d*]thiophene (FBTPhO3) and 9,9-bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)fluorene bis[2,3-*b*;6,7-*b*]benzo[*d*]thiophene (FBTPhO4). As compared with the compound (FBT) reported by our group previously [36], the introduction of phenyl at the 9-position of fluorene cores is expected to increase the thermal stability and inoxidizability toward light and electricity, which may be beneficial for improving the performance of optoelectronic devices. Their thermal, optical, electrochemical properties, and morphology as well as theoretical computation were investigated in detail. This class of compounds may be promising building blocks for high-performance optoelectronic functional materials.

2. Experimental section

2.1. Measurement and characterization

^{1}H NMR and ^{13}C NMR measurements were carried out using a Bruker AV-500 spectrometer (Bruker, Rheinstetten, Germany) operating at 500 MHz (for ^{1}H NMR) and 75 MHz (for ^{13}C NMR) with tetramethylsilane as the internal reference. Atmospheric pressure chemical ionization-mass spectrometry (APCI-MS) analyses were obtained from an Acquity Waters UPLC equipped with a Waters Acquity TQ detector (Thermo Finnigan LCQ Fleet system; Waters, Milford, MA). Elemental analyses were performed using a Vario EL elemental analysis instrument (Elementar Co., Langenselbold, Germany). Melting points (mp) were tested on a micro melting point apparatus (Beijing Tech Instrument Co. Ltd., Beijing, China). Thermogravimetric analysis (TGA) tests were conducted using a NETZSCH TG 209 at a heating rate of 10 °C min^{-1} under nitrogen flow. Differential scanning calorimetry (DSC) tests were measured using a Netzsch DSC 204 under nitrogen flow at a heating rate of 10 °C min^{-1} and a cooling rate of 20 °C min^{-1}. UV–vis absorption spectra were recorded using an HP 8453 spectrophotometer. Photoluminescence (PL) spectra were recorded using an Instaspec IV CCD spectrophotometer (Oriel Co., Stratford, CT). Cyclic voltammetry (CV) measurements were characterized on a CHI600D electrochemical workstation with a standard three electrode cell based on a Pt wire counter electrode and a Pt working electrode, against a saturated calomel electrode (SCE) as the reference electrode at a scan rate of 50 mV s^{-1} within a nitrogen-saturated anhydrous solution of 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphates in acetonitrile versus ferrocene/ferrocenium (Fc/Fc^+) as the internal reference. The theoretical computation was carried out using Gaussian 09 at the B3LYP/6-31G(d) level. Atomic force microscope (AFM) studies were carried out using a Digita Instrumental DI Multimode Nanoscope IIIa in taping mode.

2.2. Materials

All reagents, unless otherwise specified, were purchased from Aladdin Chemical Co., Sigma-Aldrich Chemical Co., Alfa Aesar Chemical Co., and J&K Chemical Co. and were used as received. The solvents were further purified by normal procedures and distilled before use. All air and water sensitive synthetic manipulations were performed under dry argon or nitrogen atmosphere. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-9,9-bis(4-(2-ethylhexyloxy)phenyl)fluorene (**1**) [15], 1-bromo-2-(methylsulfinyl)benzene (**2**) [36], 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (**7**) [37], and 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (**8**) [37] were synthesized according to the previously published methods.

2.2.1. 2,7-Bis(2-(methylsulfinyl)phenyl)-9,9-bis(4-(2-ethylhexyloxy)phenyl)fluorene (3)

Compound **1** (2.48 g, 3.0 mmol), **2** (1.64 g, 7.5 mmol), $Bu_4N^+Br^-$ (50 mg), K_2CO_3 aqueous solution (2 M, 6.0 mL), $Pd(PPh_3)_4$ (0.347 g, 0.30 mmol), and 30 mL of toluene were mixed together under argon. The reaction was heated to 85 °C and stirred overnight with argon protection. Then the mixture was cooled to room temperature (r.t.) and water was added. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layer was washed with brine and then dried over anhydrous $MgSO_4$. The organic solvent was evaporated and the crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/4, v/v) as eluent to afford **3** as a colorless oil (1.35 g, 53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.11–8.09 (d, *J* = 10 Hz, 2H), 7.87–7.85 (d, *J* = 10 Hz, 2H), 7.62–7.59 (m, 2H), 7.54–7.51 (m, 2H), 7.40–7.37 (m, 4H), 7.34–7.33 (d, *J* = 10 Hz, 2H), 7.16–7.06 (m, 4H), 6.84–6.69 (m, 4H), 3.83–3.71 (m, 4H), 2.32 (s, 6H), 1.72–1.65 (m, 2H), 1.43–1.24 (m, 16H), 0.93–0.84 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 158.41, 153.09, 143.83, 139.44, 139.27, 137.56, 130.72, 130.30, 128.94, 128.90, 128.83, 128.58, 126.97, 123.53, 120.86, 114.27, 70.43, 64.39, 41.40, 39.35, 30.47, 29.05, 23.80, 23.01, 14.07, 11.09. MS (APCI) calculated for $C_{55}H_{62}O_4S_2$: 851.2, found: 852.3.

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