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Solution-processed n-type organic field-effect transistors based on electronegative oligothiophenes having fully oxo-substituted terthiophenes

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An electronegative π-conjugated system comprising difluorodioxocyclopentene-annelated thiophene and dialkyl-substituted naphtho[2,3-*c*]thiophene-4,9-dione has been synthesized as a candidate material for fabricating solution-processable n-type organic field-effect transistors (OFETs). The photophysical and electrochemical properties of the above-mentioned compounds were investigated, and their frontier-orbital energy levels were estimated from the experimental and calculated data. OFETs fabricated by spin coating revealed good n-type characteristics with electron mobilities up to 0.016 $cm^2 V^{-1} s^{-1}$. Further, the performance of the fabricated OFETs were investigated under biased or air-exposure conditions.

1. Introduction

π-Conjugated systems have emerged as indispensable advanced materials for application to organic field-effect transistors (OFETs) since they can be potentially fabricated on large-area and/or flexible substrates [1–5]. Remarkable progresses have been achieved in the development of p-type OFET materials [3,6]. In contrast, progress in the development of n-type OFET materials has been relatively limited, regardless of the existing guidelines for rational molecular design aimed toward lowering the lowest unoccupied molecular orbital (LUMO) energy level and realizing molecular ordering in the solid state [7–11]. Another difficult challenge faced in the study of n-type materials is the realization of both electron-transporting characteristics and solution-processability, which enable us to use solution deposition techniques for the fabrication of OFET devices. In fact, only a few π-conjugated systems such as naphthalene or rylene carboxylic diimide [12–18] and dicyanomethylene-substituted quinonoid derivatives [19–21] are known to fulfill these criteria, and further developments are essential for stimulating further research in this field.

In our previous paper, we have reported a new class of electronegative π-conjugated systems comprising the difluorodioxocyclopentene-annelated thiophene (**B**) [22] (Fig. 1). The **B** unit in these systems effectively contributes towards enhancing the electronegative character of oligothiophenes, and the LUMO energy level of fully difluorodioxocyclopentene-annelated terthiophene **1**, estimated by cyclic voltammetry (CV), is −4.17 eV; this level is located at the propensity of an n-type semiconductor. However, its low solubility and non-stacking characteristic in the solid state precluded its application to solution-processable OFET materials. In order to improve the solubility in organic solvents, we have synthesized oligothiophene **2** consisting of difluorodioxocyclopentene-annelated thiophene and

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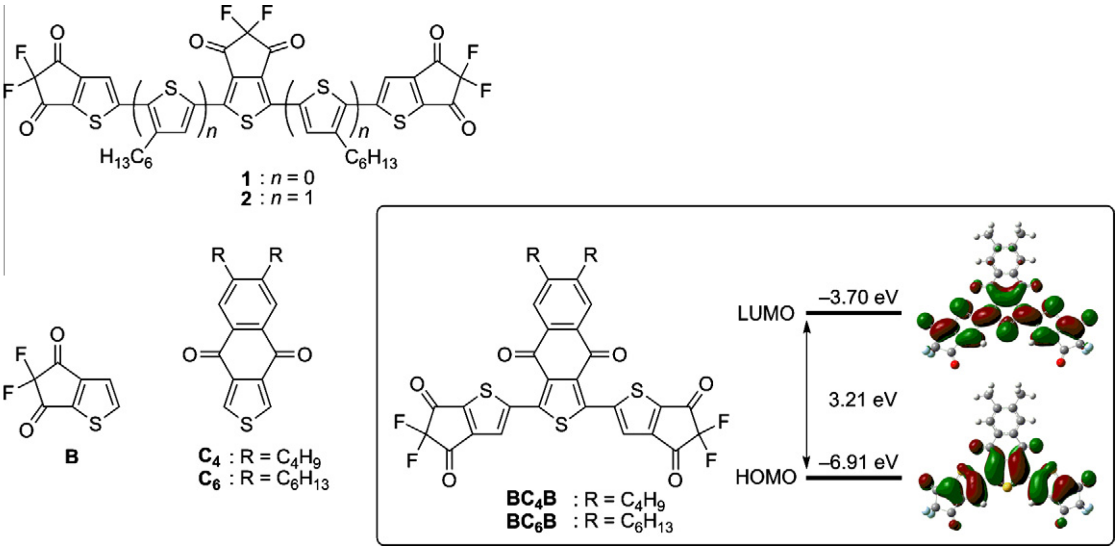

Fig. 1. Chemical structures of **1**, **2**, **B**, **C_4**, **C_6**, **BC_4B**, and **BC_6B**, and HOHO and LUMO energies of model compound (R=CH_3).

3-hexylthiophene [23]. It should be noted that the presence of electron-donating 3-hexylthiophene causes **2** to exhibit a relatively high LUMO energy level (−3.54 eV). In spite of this fact, OFETs fabricated using **2** by spin coating exhibited a field-effect electron mobility of $1.9 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$. Furthermore, X-ray diffraction (XRD) measurements indicated that the films fabricated using **2** were amorphous or less ordered. For further improving the electron mobility, it is important to both decrease the LUMO energy level and increase the efficiency of self-assembly in the solid state. Therefore, keeping this in mind, we have designed a dialkyl-substituted naphtho[2,3-*c*]thiophene-4,9-dione (**C_4** and **C_6**) unit to be introduced into electronegative oligothiophenes. Herein, we describe the synthesis and properties of newly developed **BC_4B** and **BC_6B**; we also report a substantial improvement in the performance of n-type OFETs, which is in the order of two orders of magnitude.

2. Material and methods

2.1. General Information

Preparative gel-permeation chromatography (GPC) was carried out with Japan Analytical Industry LC-908 equipped with JAI-GEL 1H/2H columns. ^1H NMR spectra were recorded on JEOL LA-400 in $CDCl_3$ with tetramethylsilane as an internal standard. Mass spectra were obtained on Shimadzu GCMS-QP-5050. UV–vis spectra were recorded on Shimadzu UV-3100PC. CVs were carried out on a BAS CV-620C voltammetric analyzer. Elemental analyses were performed on PerkinElmer LS-50B. The surface morphology of organic films was observed using an atomic force microscopy (Shimadzu, SPM-9600), and the film crystallinity was evaluated using an X-ray diffractometer (Rigaku, UltimaIV). X-ray diffraction patterns were obtained using Bragg–Brentano geometry with Cu Kα radiation as an X-ray source with an acceleration voltage of 40 kV and a beam current of 40 mA. $\theta - 2\theta$ scans were obtained between 2.5° and −30° a scanning step of 0.01°. The thickness of active-layer organic films was determined using a spectroscopic ellipsometer (HORIBA.UVISEL LT NIR-NNG).

2.2. Synthesis

4a: Compound **3** [24] (366 mg, 1.00 mmol) was placed in a two-necked round-bottomed flask, dissolved in CH_2Cl_2 (10 mL), and degassed with nitrogen. Next, anhydrous aluminum trichloride ($AlCl_3$) (533 mg, 4.00 mmol) was added to it at 0 °C. A solution of 1,2-dibutylbenzene (228 mg, 1.20 mmol) in CH_2Cl_2 (2 mL) was then added dropwise to the stirred mixture at 0 °C. After stirring the reaction mixture at 0 °C for 3 h, it was poured over ice and extracted with $CHCl_3$. The resulting organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to yield **4a** (240 mg, 50%).

Yellow solid; Mp 133.5–134.5 °C; ^1H NMR ($CDCl_3$) δ 8.07 (s, 2H), 2.76 (t, 4H, *J* = 7.9 Hz), 1.62 (m, 4H), 1.45 (m, 4H), 0.97 (t, 6H, *J* = 7.3 Hz); MS (EI) *m/z* 484 (M^+); Anal. Calcd. for $C_{20}H_{20}Br_2O_2S_1$: C, 49.61; H, 4.16. Found: C, 49.89; H, 4.21.

4b: Compound **4b** was synthesized by following the procedure used for the preparation of **4a**, as a yellow solid with a yield of 74%. Mp 89–90 °C; ^1H NMR ($CDCl_3$) δ 8.06 (s, 2H), 2.74 (t, 4H, *J* = 7.9 Hz), 1.66 (m, 4H), 1.33 (m, 12H), 0.90 (t, 6H, *J* = 7.3 Hz); MS (EI) *m/z* 540 (M^+); Anal. Calcd. for $C_{24}H_{28}Br_2O_2S_1$: C, 53.35; H, 5.22. Found: C, 53.14; H, 5.08.

BC_4B: Compounds **4a** (58 mg, 0.12 mmol), **5** [22] (150 mg, 0.27 mmol), and tetrakis(triphenylphosphine)palladium(0) (25 mg, 0.02 mmol) were placed in a test tube; they were then dissolved in toluene (1 mL) and degassed with nitrogen. The resulting mixture was refluxed