Effect of Fluorine Substitution on Naphtho[2,1-*b*:3,4-*b'*]bis[1]-benzothiophene-Derived Semiconductors for Transistor Application

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Abstract

A novel series of air-stable, fluorinated naphtho[2,1-*b*:3,4-*b'*]bis[1]-benzothiophenes bearing various lateral alkoxy-substituents, NBBTF-*n* (*n* = 8, 10, and 12) and its unsubstituted analogue, NBBT-10 were synthesized and investigated with field-effect transistor properties. Fluorine substitution affords desirable properties including high melting transition, high thermal stability and low-lying highest occupied molecular orbital (HOMO) energy levels for air-stable semiconductors. The OFET devices based on annealed NBBTF-10 films exhibit superior hole transport with mobility up to $0.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to that of NBBT-10, attributed to the close molecular stacking induced by fluorine substitution.

Keywords: organic field-effect transistor, organic semiconductor, thienoacene, fluorine substitution, hole mobility,

1. Introduction

Over the past two decades, organic semiconductors have been widely explored as the key component for low-cost and flexible organic field-effect transistors (OFETs), which have demonstrated for various potential applications including radio frequency identification tags, flexible displays, electronic paper, sensors, and electronic skin [1-7]. Despite the tremendous progress in the development of organic semiconductors for OFETs in recent years [8-12], the overall requirements and performance are still behind the demand of the organic electronic industry. Thus, easy-accessible, air-stable and high-performance organic semiconductors are still needed for further advancement.

Among the currently developed organic semiconducting molecules for OFETs, thienoacene represents one of the most promising classes from which some of them have showed excellent device performance that is comparable to that of amorphous silicon despite the poor ambient stability and sophisticated device fabrication. Such a high carrier transport in thienoacene is attributed to the presence of intermolecular S...S and $\pi\cdots\pi$ interactions which would reinforce a close molecular stacking and thus facilitating the charge transport in the solid state [13-19]. In addition, there are different design strategies to promote strong intermolecular $\pi\cdots\pi$ stacking interactions between the neighbouring molecules and thus enhance the charge carrier mobilities in the solid state. One of the effective approaches is to expand the π -conjugation core by means of a fused aromatic ring which can not only extend π -electron delocalization and promote $\pi\cdots\pi$ molecular stacking but also render to improve air stability due to maintaining the low-lying HOMO energy level of the molecule [20-21]. Secondly, alkyl substituent(s) is/are often introduced into rigid and planar fused aromatic semiconducting molecules in order to enhance the solubility and processibility. Besides, appropriate alkyl chain can impose close molecular stacking in the solid state offering a useful means/tool to tune the molecular packing [22-24]. Furthermore, an incorporation of heteroatom into the fused aromatic system would be an alternatively attractive strategy to strengthen intermolecular interaction and hence promoting a close molecular packing. For instance, the strong electron-withdrawing fluorine atom, having a similar radius of hydrogen atom, can be incorporated into the π -conjugated core to induce the strong dipole-dipole interactions between neighbouring molecules which would give rise to closer stacking contacts for high charge carriers transport or improved power conversion

efficiency of bulk heterojunction (BHJ) solar cells [25-27]. However, this approach is seldom explored for *p*-type semiconducting materials.

Naphtho[2,1-*b*:3,4-*b'*]dithiophene has been used as an electron-rich building block to successfully develop high-performing organic semiconducting materials for organic electronics [28-33]. In this contribution, a novel series of air-stable, π -extended naphtho[2,1-*b*:3,4-*b'*]dithiophene derivatives namely, fluorinated naphtho[2,1-*b*:3,4-*b'*]bis[1]benzothiophene, NBBTF-*n* (*n* = 8, 10, and 12) incorporated with various solubilizing lateral alkoxy chains and its unsubstituted analogue, NBBT-10 for comparison was designed and synthesized (Fig. 1). The influence of fluorine substitution on the charge transport properties was investigated and the microstructure of thin films was also analyzed with Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD).

Fig. 1. The molecular structures of NBBTF-*n* (*n* = 8, 10, and 12) and NBBT-10.

2. Results and Discussion

2.1 Synthesis and characterization

Syntheses of naphtho[2,1-*b*:3,4-*b'*]bis[1]benzothiophene and its fluoro-substituted analogues are outlined in Scheme 1. 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzo[*b*]thiophene, 2 was synthesized from the commercially available benzo[*b*]thiophene by means of NBS bromination [34,35] and then followed by palladium catalyzed Miyaura borylation reaction [36]. 5-Fluorobenzo[*b*]thiophene-2-carboxylic acid, 4 was synthesized from 2,5-difluorobenzaldehyde through cyclization with ethyl thioglycolate and then hydrolysis of ester 3 with NaOH [37]. Copper catalyzed decarboxylation of 4 [38], followed by NBS bromination of 5 [39], and then Miyaura borylation of 6 afforded fluoro-substituted benzo[*b*]thiophene boronate ester 7 in good yield. The palladium-catalyzed Suzuki-coupling of 1,2-dibromo-4,5-dialkoxybenzene and the corresponding benzo[*b*]thiophene boronate ester, 2 or 7 gave the desired dibenzo[*b*]thiophene

intermediates, 8a-d with high yield of 92 - 98% [40]. The FeCl₃-catalyzed oxidative cyclization of 8a-d afforded the corresponding NBBT-10 or NBBTF-*n* (*n* = 8, 10, and 12) with good yield of 78 - 85% [41]. The molecular structures of NBBT-10 and NBBTF-*n* (*n* = 8, 10, and 12) were confirmed by ¹H NMR, ¹³C NMR, HRMS and element analysis. All the compounds exhibit a high thermal stability with decomposition temperature above 380 °C, particularly the fluorinated derivatives (*T_d* = 407 – 416 °C) as estimated by the thermal gravimetric analysis (TGA) with a heating rate of 10 °C/min (Fig. S1a). In addition, the fluorinated naphthobisbenzothiophenes, NBBTF-*n* exhibited much higher melting transitions than that of NBBT-10 as determined by differential scanning calorimetry (DSC) (Fig. S1b), suggesting much stronger intermolecular adhesions for fluorinated molecules, NBBTF-*n* in the solid state.

Scheme 1. Syntheses of naphtho[2,1-*b*:3,4-*b'*]bis[1]benzothiophene and its fluorinated analogs.

2.2 Calculations of the frontier molecular orbitals (FMOs)

Fig. 2 shows frontier molecular orbitals of naphtho[2,1-*b*:3,4-*b'*]dithiophene, NBBT-1, and NBBTF-1 calculated by Gaussian 09 using Density Functional theory (DFT) with B3LYP and 6-31+G(d,p) basis set, in which the methoxy-substituted analogs were employed for calculations

for simplicity [42]. Indeed, an extension of π -conjugated system by means of fused aromatic rings does not greatly destabilize the HOMO energy level despite the narrowing of the HOMO-LUMO energy gap. Instead, fluorine substitution leads to a significant stabilization of the frontier molecular orbitals, which would give rise to a more air-stable π -extended conjugated molecule.

Fig. 2. Frontier molecular orbital energy levels of naphthodithiophene, NBBT-1 and NBBTF-1 calculated by Gaussian 09 using Density Functional theory (DFT) with B3LYP and 6-31+G(d,p) basis set.

2.3 Optical and electrochemical properties

As shown in Fig. 3(a), NBBT-10 and NBBTF-*n* exhibit nearly identical absorption in CH_2Cl_2 with two major overlapped absorption bands in the range of 230 – 300 nm and 310 – 412 nm in which the lateral alkoxy groups and electron-withdrawing fluorine substituents do not perturb the absorption significantly. The optical energy gap was estimated to be ~ 3.06 eV for these NBBT molecules as determined by extrapolating the long-wavelength absorption edge [43].

Fig. 3. (a) UV-vis absorption spectra of NBBT series measured in CH_2Cl_2 . (b) Cyclic

voltammograms of NBBT series.

To determine the redox behavior of this NBBT series, cyclic voltammetric (CV) measurement was carried out using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and saturated calomel electrode (SCE) as a reference electrode using 0.1 M of Bu_4NPF_6 as a supporting electrolyte in CH_2Cl_2 with a scan rate of 100 mV/s. The onset oxidation ($E_{\text{oxd}}^{\text{onset}}$) and onset reduction potentials ($E_{\text{red}}^{\text{onset}}$) were calibrated with ferrocene as an external standard. The CV traces are shown in Fig. 3b and the HOMO energy level estimated from the CV data and the LUMO energy level calculated by the optical band gap and the HOMO are summarized in Table 1. Both fluoro-substituted, NBBTF-*n* and unsubstituted naphthodibenzothiophenes, NBBT-10 show very similar redox behavior with one quasi-reversible oxidation couple with $E_{\text{oxd}}^{\text{onset}}$ in the range of 1.17 – 1.27 V corresponding to the HOMO energy level of -5.51 – -5.61 eV and one irreversible reduction wave with $E_{\text{red}}^{\text{onset}}$ in the range of -0.57 – -0.74 V. The LUMO energy level estimated from the equation of HOMO + optical energy gap is in the range of -2.45 – -2.55 eV. Consistent to the theoretical prediction, the incorporation of fluorine atoms into the NBBT backbone slightly lowers the frontier molecular orbitals by ~ 0.1 eV with HOMO value of around -5.6 eV indicating that they are much more air-stable than pentacene (-4.6 eV) [44].

Table 1. Summary of physical measurements of NBBT-10 and NBBTF-*n*.

Compd	$E_{\text{oxd}}^{\text{onset}}$ (V) ^a	$E_{\text{red}}^{\text{onset}}$ (V) ^a	E_{HOMO} (eV) ^b	E_{LUMO} (eV) ^c	E_g (eV) ^d	<i>m. p.</i> (°C) ^e
NBBT-10	1.17	-0.74	-5.51	-2.45	3.06	103.3
NBBTF-8	1.24	-0.57	-5.58	-2.52	3.06	164.7
NBBTF-10	1.26	-0.60	-5.60	-2.54	3.06	160.3
NBBTF-12	1.27	-0.68	-5.61	-2.55	3.06	150.0

^a Determined in CH_2Cl_2 solution. ^b $E_{\text{HOMO}} = -(4.34 + E_{\text{oxd}}^{\text{onset}})$ eV. ^c $E_{\text{LUMO}} = (E_g + E_{\text{HOMO}})$ eV. ^d $E_g = 1240/\lambda$ eV. ^e Measured by differential scanning calorimeter with a heating rate of 10 °C/min.

2.4 OFET characteristics of NBBT series

To investigate the charge transport properties of NBBT-10 and NBBTF-*n* (*n* = 8, 10, and 12), the OTFT devices were fabricated in a bottom-gate bottom-contact (BGBC) configuration (gold

electrode on Si/SiO₂ substrates). The gold source-drain electrodes were prepared by photolithography, and then octadecyltrichlorosilane (OTS) treatment was performed on the gate dielectrics which were placed in a vacuum oven with OTS at a temperature of 120 °C for 3 hours to form an OTS self-assembled layer, followed by cleaning with *n*-hexane, alcohol and chloroform for 6 min in ultrasonic cleaner to remove the redundant OTS molecules or the hydrolysate physically absorbed on the electrode and OTS layer. Subsequently, the thin films were evaporated on the OTS modified SiO₂/Si substrates from the solutions. The OTFTs devices were annealed successively at 80, 120, and 160 °C for 6 min in air, and measured after each annealing step at room temperature in air by using a Keithley 4200 Semiconductor Characterization System. Both unsubstituted and fluoro-substituted naphthodibenzothiophenes show typical *p*-type transistor behavior. The typical output and transfer characteristics of the OFET devices based on NBBTF-10 and NBBTF-12 are shown in Fig. 4.

Fig. 4. Typical electrical characteristics of OFET devices, (a) transfer and (b) output characteristics of NBBTF-10 based transistor and (c) transfer and (d) output characteristics of NBBTF-12 based transistor.

The selected OFET device characteristics based on this NBBT series are summarized in Table 2. The OFET device performance is greatly dependent on the annealing temperature. The FET device based on NBBT-10 exhibited a hole mobility of $1.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after annealing

at 80 °C. In sharp contrast, the fluorinated naphthobisbenzothiophene counterparts, NBBTF-10 based device showed a hole mobility of $2.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for an as-fabricated film but a dramatically enhanced hole mobility up to $0.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a current on/off ratio of $10^6 - 10^7$ upon annealing at 160 °C and an average mobility of 5 devices was $\sim 0.24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These results suggest that the dipole-dipole interactions induced by the fluorine atoms on the NBBT π -conjugated system are favorable for molecular stacking. The influence of different chain lengths attached laterally on the NBBTF skeleton on the OFET device performance was also investigated. A relatively inferior OFET performance was obtained for a shorter alkoxy chain analogue, NBBTF-8 based device with the maximum mobility of $6.5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ even with the same annealing temperature. On the other hand, device based on a longer alkoxy chain analogue, NBBTF-12 exhibited better device performance with a hole mobility up to $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a current on/off ratio exceeding 10^6 under a relatively lower annealing temperature of 120 °C.

Table 2. Summaries of selected OFET device characteristics based on NBBT series fabricated by vacuum deposition.

Compd	$\mu \text{ (cm}^2 \text{ V}^{-1} \text{ s}^{-1}\text{)}$	$I_{\text{on}}/I_{\text{off}}^c$	$V_T \text{ (V)}^d$	$T_{\text{annealing}} \text{ (}^\circ\text{C)}^e$
NBBT-10	$1.87 \times 10^{-5}{}^a$	$10^3\text{--}10^4$	-2	RT
	$1.3 \times 10^{-2}{}^a$	$10^6\text{--}10^7$	-32	80
NBBTF-8	$1.7 \times 10^{-3} \text{ (}2.5 \times 10^{-3}\text{)}^b$	$10^4\text{--}10^5$	-45	RT
	$3.6 \times 10^{-2} \text{ (}6.5 \times 10^{-2}\text{)}^b$	$10^6\text{--}10^7$	-29	160
NBBTF-10	$1.8 \times 10^{-3} \text{ (}2.0 \times 10^{-3}\text{)}^b$	$10^5\text{--}10^6$	-54	RT
	$0.24 \text{ (}0.35\text{)}^b$	$10^6\text{--}10^7$	-20	160
NBBTF-12	$1.4 \times 10^{-2} \text{ (}2.4 \times 10^{-2}\text{)}^b$	$10^5\text{--}10^6$	-57	RT
	$6.1 \times 10^{-2} \text{ (}0.11\text{)}^b$	$10^6\text{--}10^7$	-54	120

^a the highest mobility with different annealing temperature.

^b average mobility calculated by 5 devices (maximum value listed in parentheses).

^c $I_{\text{on}}/I_{\text{off}}$ refers to the current on/off ratio.

^d V_T refers to the threshold voltage of the device with the highest mobility.

^e $T_{\text{annealing}}$ refers to the annealing temperature.

μ

2.5 The microstructure of thin films

To examine the morphological change upon high temperature annealing, Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD) measurements of these thin films were

performed. The AFM images of NBBTF- n ($n = 8, 10$ and 12) thin films annealed at different temperatures are shown in Fig. 5. In general, the grain style of as-evaporated films at room temperature changed from a thin feather-like to a flake-like shape with less grain boundaries after high temperature annealing at $120\text{ }^{\circ}\text{C}$ or $160\text{ }^{\circ}\text{C}$. Such a change in grain style was more apparent and dramatic for NBBTF-10 and NBBTF-12 thin films. The resulting morphological improvement was also consistent to the enhancement in charge transport of the annealed thin films.

Fig. 5. AFM images of thin film of NBBTF-8 with annealing temperature at (a) RT, (b) $160\text{ }^{\circ}\text{C}$; NBBTF-10 with annealing temperature at (c) RT, (d) $160\text{ }^{\circ}\text{C}$; and NBBTF-12 with annealing temperature at (e) RT, (f) $120\text{ }^{\circ}\text{C}$.

Fig. 6 shows the out-of-plane XRD patterns of NBBTF- n ($n = 8, 10$, and 12) thin films with various annealed temperature in which stronger diffraction peaks i.e. the higher intensity of the peaks and the narrower of the full-width-at-half-maximum are clearly shown for the annealed thin films relative to those as-evaporated ones, suggesting higher crystallinity of the thin films after high temperature annealing which are consistent to the improved device performance.²⁶ The primary diffraction peaks of the annealed films at 2.54 , 2.36 , and 2.12° correspond to the interlayer distance (d -spacing) of 3.47 , 3.74 , and 4.16 nm for NBBTF- n ($n = 8, 10$, and 12), respectively with an increase in the length of lateral alkoxy chains. Meanwhile, it was found that the d -spacing values calculated from the XRD data of NBBTF- n ($n = 8, 10$, and 12) are larger than those estimated by the full-extended molecular length, which are 2.53 , 3.03 , 3.53 nm , respectively. These findings suggested that the layers is comprised of multi-interdigitated molecules or inclined molecules but not vertical-standing molecules. Additionally, two-dimensional grazing incidence X-ray diffraction (2D-GIXRD) measurement was performed

to investigate the effect of fluorine substitution on NBBT-10. By comparing the 2D-GIXRD patterns of NBBT-10 and NBBTF-10 (Fig. 7), it is convinced that fluorine atom plays an influential role on the molecular stacking for high crystallinity, which is consistent to the better FET performance. **Fig. 6.** Out-of-plane X-ray diffraction patterns of thin films (a) NBBTF-8; (b) NBBTF-10; and (c) NBBTF-12 at various annealing temperatures.

Fig. 6. Out-of-plane X-ray diffraction patterns of thin films (a) NBBTF-8; (b) NBBTF-10; and (c) NBBTF-12 at various annealing temperatures.

Fig. 7. 2D-GIXRD patterns of thin films (a) NBBT-10 and (b) NBBTF-10 annealed at 80 °C and 160 °C, respectively.

3. Conclusion

In summary, novel air-stable, fluorinated naphtho[2,1-*b*:3,4-*b'*]bis[1]-benzothiophenes bearing various lateral alkoxy-substituents were developed. Fluorine substitution gives rise to desirable properties of organic semiconductors including high melting transition, high thermal stability and low-lying HOMO energy levels for FET applications. Thus, fluorine substitution provides an alternative tool to tune and optimize the functional and molecular properties of a material. In contrast to the inferior FET performance of NBBT-10, NBBTF-10 showed the best device performance as a *p*-type semiconductor with a mobility of $0.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a current on/off of $10^6 - 10^7$ after annealing at 160 °C among the series attributed to a close molecular

stacking induced by the fluorine substitution. On the other hand, the annealed devices based on NBBTF-8 and NBBTF-12 exhibited a hole mobility of 0.065 and 0.11 cm² V⁻¹ s⁻¹, respectively. As a result, fluorinated naphtho[2,1-*b*:3,4-*b'*]bis[1]benzothiophene framework shows potential as a useful building block to develop novel semiconducting materials for high performance organic electronics.

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Appendix A. Supplementary data

Supplementary data associated with this article included copies of ¹H and ¹³C NMR spectra for all compounds, MS spectra, results of the theoretical calculations and results of OFET device characteristics. This material can be found, in the online version.

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NBBT-10: $\text{R} = \text{H}$, $\mu_h = 0.013 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
(GIXRD left)

NBBTF-10: $\text{R} = \text{F}$, $\mu_h = 0.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
(GIXRD right)