
Yoshihito Kunugi1*, Ayami Maeda1, Teppei Arakawa1 and Kazuo Okamoto2

1Department of Applied Chemistry, Faculty of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka 259-1292, Japan
* kunugi@tokai-u.jp
2Research Laboratory, Ushio ChemiX Corporation, 2252-1 Goudo, Omaezaki 437-1613, Japan

Keywords: Organic Single Crystal Transistor, 21DNFU Derivative, U-shaped Organic Semiconductor

1. Introduction
Organic field-effect transistors (OFETs) promise to be useful in flexible, printable and lightweight electronic applications, such as displays, sensors and complementary integrated circuits [1-5]. Great effort has been put into developing new organic semiconductors for use in high-performance organic transistors. Fused, highly π-extended and plain π-conjugated materials, such as pentacene and dinaphtho[2,3-b:2’,3’-f]thieno[3,2-b]thiophene (DNTT), have been widely used as high-performance transistor materials [6-8]. These materials have very good molecular packing, which favors intermolecular charge transport, but in general, causes them to be relatively poorly soluble in organic solvents.

Takeya et al. recently reported the production of organic transistors based on the twisted π-extended U-shaped compounds, dinaphtho[2,1-b:1’,2’-d]furan (21DNFU) and dinaphtho[2,1-b:1’,2’-d]thiophene, which had high carrier mobilities of up to 1 cm²V⁻¹s⁻¹ [9,10]. In this paper, we synthesized the alkylphenyl substituted 21DNFU derivatives, 5,9-bis(4-propylphenyl)dinaphtho[2,1-b:1’,2’-d]furan (3P-21DNFU), 5,9-bis(4-pentylphenyl)-dinaphtho[2,1-b:1’,2’-d]furan (5P-21DNFU) and 5,9-bis(4-heptylphenyl)dinaphtho[2,1-b:1’,2’-d]furan (7P-21DNFU), and determined the characters of solution-processed single crystal OFETs based on these newly developed materials. Evaluating these organic single crystal transistors allowed us to investigate the fundamental aspects of organic semiconductors because of the nearly perfect periodicity in the molecular order in these crystals.

2. Experimental
All chemicals and solvents were of reagent grade or better unless otherwise indicated. 21DNFU derivatives were synthesized as shown in Scheme 1. The starting compound 21DNFU [11, 12] was brominated using N-bromosuccinimide (NBS) and the resulting compound A was reacted with the corresponding 2-(4-alkylphenyl)-1,3,6,2-dioxazaborocane. The crude products were purified by column chromatography, and the purified products were obtained in more than 80% yields. The compounds produced were characterized by ¹H and ¹³C NMR spectroscopy.

Figure 1. Molecular structures of alkylphenyl substituted 21DNFU derivatives.

Received April 4, 2014
Accepted May 15, 2014
reprecipitation from toluene and ethanol. X-ray crystal structural analysis was performed using a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-Kα (λ = 1.5418 Å) radiation at -100 °C.

Top-contact type single crystal OFET devices were prepared using a crystal lamination process [13, 14]. We used an n+-doped Si wafer with a 220 nm thick thermally grown SiO2 layer, as a substrate for the lamination process, and this was treated with a thin film (ca. 310 nm thick) of a polystyrene (PS) insulator. The polymer insulator was spin-coated at 2000 rpm from a toluene solution and then annealed at 90 °C for 1 h on a hot plate under a N2 atmosphere. A thin and defect-free single crystal of a 21DNFU derivative was carefully selected and attached to the substrate. Source and drain electrodes were incorporated using a colloidal graphite paste.

The transfer and output characteristics of the devices were measured using an Agilent 4155C semiconductor parameter analyzer under vacuum at room temperature. The field-effect mobility (μFET) was estimated via a saturated drain current (I_d) regime, using the equation I_d = (WC/2L) μFET (V_g−V_th)^2, where C is the capacitance of the insulator, and V_g and V_th are the gate and threshold voltages, respectively. The on/off current ratio (I_on/I_off) was determined from the maximum (I_on) and minimum (I_off) I_d values.

Molecular orbital (MO) calculations were performed using density functional theory (DFT) methods at the B3LYP/6-31G(d) level, using the Gaussian09 program [15].

3. Results and discussion

The alkylphenyl substituted 21DNFU derivatives were successfully synthesized from DNFU using the two-step procedure shown in Scheme 1. The resulting 21DNFU derivatives were thermally stable and soluble in common organic solvents such as CHCl3 and toluene. We successfully performed the X-ray single crystal structural analysis on the planar, transparent crystals of the 21DNFU derivatives that had been reprecipitated from toluene and ethanol. The DNFU core of the 3P-21DNFU molecule had a twisted structure with a molecular torsion angle of 21° (Figure 2(a)). The molecular torsion angles for 5P-21DNFU and 7P-21DNFU were 22° and 25°, respectively. As shown in Figure 2(b), the 3P-21DNFU crystal system was monoclinic with a = 13.05 Å, b = 12.95 Å and c = 17.02 Å. In this packing structure, the nearest π-π distance between neighboring naphthalene rings was estimated to be 3.56 Å, which should be short enough for charge transport to occur. The 5P-21DNFU crystal system was also monoclinic, and the nearest π-π distance between neighboring naphthalene rings was 3.46 Å. However, the 7P-21DNFU molecules stacked alternately, that is the 21DNFU cores and alkyl chains were stacked in an alternating sequence.

We fabricated single crystal OFETs to allow their carrier transporting properties to be evaluated. A top-contact type single crystal OFET device was fabricated using a crystal lamination technique.
Figure 3. (a) A schematic illustration of single crystal OFET device. (b) Output characteristics for 5P-21DNFU based single crystal OFET device.

(Figure 3(a)). Figure 3(b) shows the typical output characteristics for OFETs based on single crystals of 5P-21DNFU with PS-treated SiO2 insulators. The devices showed typical output profiles for metal-oxide-semiconductor field-effect transistors. The channel conductance increased as \( V_g \) became more negative, indicating that the 5P-21DNFU behaved as a \( p \)-type semiconductor. The saturation of the drain current in the output permitted us to evaluate its carrier mobility from the slope of the transfer curve. The charge carrier mobility of the hole was calculated using the saturation current equation. The field-effect characteristics of the single crystal OFETs based on 21DNFU derivatives with PS insulators are summarized in Table 1. The devices based on 3P-21DNFU and 5P-21DNFU had good FET characteristics with \( \mu_{\text{FET}} = 0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) and \( I_{\text{on}}/I_{\text{off}} \) ratio of \( 10^3 \) for 3P-21DNFU and 5P-21DNFU. The field-effect characteristics of the single crystal OFETs were strongly affected by the chain lengths of the alkyl groups and packing structures of the molecules.

Acknowledgements

The authors thank H. Aihara for help with the X-ray crystal structural analyses. This study was financially supported in part by a Grant-in-Aid for Science Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References