

Single-Crystal Organic Field-Effect Transistors of Naphthodifurans

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Received: January 26, 2015; Accepted: February 25, 2015; Web Released: June 15, 2015

Three types of naphthodifurans (NDFs) have been designed as active organic materials in organic field-effect transistors (OFETs), and one of them, naphtho[2,1-*b*:6,5-*b'*]difuran, has been found to show an excellent OFET mobility of up to $3.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Based on the crystal-packing structure and theoretical analyses, we attribute the high carrier mobility of the NDF derivatives to large intermolecular interactions and small reorganization energies. The NDF compounds show very high thermal and electrochemical stability. Together with some previous studies, the present study indicates that fused furan compounds show a performance that is equal to or better than that of the corresponding thiophene compounds.

Thiophene derivatives are popular organic semiconductor materials for the fabrication of printed plastic electronics, and research on organic field-effect transistors (OFETs) is no exception.¹ In contrast, furan derivatives had rarely been examined for device applications^{2,3} until we explored the p-type and ambipolar properties of benzodifuran (BDF) derivatives (Figure 1)⁴⁻⁷ to find their utility in hetero- and homojunction organic light-emitting diode (OLED) devices. Encouraged by the results, we envisioned that fused furan are also useful for single-crystal OFETs, because of the small van der Waals radius of the oxygen atom that permits denser packing of the molecules in a single crystal than seen for thiophenes. Considering strong intermolecular electronic coupling caused by dense packing, along with a small reorganization energy because of the effective π -electron conjugation over the fused aromatic framework. the carrier mobility of the single crystals of these molecules may



Figure 1. Structures of benzodifurans (BDFs) and naphthodifurans (NDFs).

be significantly enhanced.⁸ Herein we report the synthesis of three classes of naphthodifuran derivatives (Figure 1), naphtho[2,1-*b*:6,5-*b'*]difuran (**NDF1**),⁹ naphtho[1,2-*b*:5,6-*b'*]difuran (**NDF2**), and naphtho[2,3-*b*:6,7-*b'*]difuran (**NDF3**), and also the excellent charge-transporting properties of one of the **NDF1** compounds in a single-crystal OFET¹⁰ device. We prepared single crystals for the devices by a physical vapor transport (PVT)¹¹ method and by a solution process. The highest hole mobility that we recorded was $3.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$: a value among the highest for solution-processed OFETs. These values are much higher than those recently reported for nonfused furan derivatives, such as oligofurans, which showed a mobility value of less than $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and suggests that the fusion of the furan rings to the rigid naphthalene structure is an important structural feature of the new NDF materials.¹⁴

Experimental

All of the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen or argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a Teflon cannula. Flash column chromatography was performed employing Kanto Silica gel 60 (spherical, neutral, 140–325 mesh).

Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on JEOL ECA-500 (500 MHz) and JEOL ECA-600 (600 MHz) NMR spectrometers. High-vacuum train sublimation (pressure



Scheme 1.

below 30 mTorr) was performed on a P-100HT instrument (ALS Technology Co., Ltd.). Melting points of solid materials were determined on a Mel-Temp II capillary melting-point apparatus and are uncorrected. Mass spectra were obtained on a JEOL Accu TOF JMS-T100LC instrument. Cyclic voltammetry (CV) measurements were performed on a HOKUTO DENKO HZ-5000 voltammetric analyzer at room temperature in a one-compartment cell under N₂ gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag⁺ reference electrode. Thermogravimetry–differential thermal analysis (TG–DTA) was performed on a Rigaku Thermo plus 2 thermal analyzer (TG 8120).

Synthesis. General Procedure for the Zinc-Mediated Double Cyclization Reaction: 2,7-Bis(4-octylphenyl)naphtho[2,1-b:6,5-b']difuran (C₈-DPNDF1); The general synthetic strategy is shown in Scheme 1 and discussed in the following section.

A solution of butyllithium in hexane $(0.37 \text{ mL}, 1.62 \text{ mol L}^{-1}, 0.60 \text{ mmol})$ was added to a solution of 1,5-bis[(4-octylphenyl)ethynyl]naphthalene-2,6-diol (**1b**, 175 mg, 0.300 mmol) in THF (1.2 mL) at 0 °C. The resulting yellow suspension was allowed to warm to ambient temperature and stirred for 30 min. After a solution of zinc chloride in THF (0.60 mL, 1.0 mol L⁻¹, 0.60 mmol) was added, the volatiles were removed in vacuo, and then toluene (1.2 mL) was added. The resulting mixture was heated to 120 °C and stirred for 3 h at this temperature. After cooling to ambient temperature, H₂O was added to quench the reaction. The organic layer was extracted with CHCl₃ and dried over MgSO₄. After removal of solvent in vacuo, the crude material was purified by silica gel column chromatography (hexane:CHCl₃ = 90:10) to afford the title compound (168 mg, 96%) as a white powder. Mp: 302–303 °C. ¹H NMR (600 MHz, CDCl₃): δ 0.89 (t, J = 7.2 Hz, 6H), 1.26–1.39 (m, 20H), 1.67 (q, J = 7.2 Hz, 4H), 2.65 (t, J = 7.2 Hz, 4H), 7.30 (d, J = 8.4 Hz, 4H, C₆H₄), 7.50 (s, 2H), 7.79 (d, J = 9.0 Hz, 2H), 7.86 (d, J = 8.4 Hz, 4H), 8.04 (d, J = 9.0 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 14.1, 22.7, 29.3, 29.4, 29.5, 31.4, 31.9, 35.9, 99.9, 112.0, 120.1, 124.2, 124.8, 125.9, 128.2, 128.9, 143.5, 151.8, 156.0. MS (APCI+): 585 (M + H⁺). Anal. Calcd for C₄₂H₄₈O₂: C, 86.26; H, 8.27%. Found: C, 86.34; H, 8.23%.

2,7-Diphenylnaphtho[**2,1-***b***:6,5-***b'***]difuran (DPNDF1); White powder. Mp: 318–319 °C. ¹H NMR (600 MHz, CDCl₃): \delta 7.37 (t, J = 7.2 Hz, 2H), 7.49 (dd, J = 7.2, 7.2 Hz, 4H), 7.57 (s, 2H), 7.81 (d, J = 7.8 Hz, 2H), 7.96 (d, J = 7.2 Hz, 4H), 8.07 (d, J = 7.8 Hz, 2H). ¹³C NMR (125 MHz, CDCl₂CDCl₂): \delta 99.7, 111.4, 119.6, 123.1, 123.9, 124.8, 127.7, 128.1, 129.5, 150.9, 154.7. MS (APCI+): 361 (M + H⁺). Anal. Calcd for C₂₆H₁₆O₂: C, 86.65; H, 4.47%. Found C, 86.35; H, 4.81%.**

2,7-Diphenylnaphtho[**1,2-***b***:5,6-***b'***]difuran** (DPNDF2); White solid. Mp: 283–284 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.21 (s, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.50 (dd, J = 7.7, 7.7 Hz, 4H), 7.80 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 7.7 Hz, 4H), 8.25 (d, J = 8.3 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 102.7, 116.0, 119.0, 120.1, 124.7, 124.8, 128.3, 128.9, 130.9, 151.2, 155.5. MS (TOF, APCI+): 361.13 (M + H⁺). Anal. Calcd for C₂₆H₁₆O₂: C, 86.65; H, 4.47%. Found: C, 86.53; H, 4.59%.

2,7-Diphenylnaphtho[2,3-*b*:6,7-*b'*]difuran (DPNDF3); Yellow solid. Mp: Not available because of sublimation. ¹H NMR (500 MHz, CDCl₂CDCl₂, 120 °C): δ 7.16 (s, 2H),



Figure 2. Performances of OFET devices using NDFs. (a) DPNDF1, (b) DPNDF2, and (c) DPNDF3. Transfer characteristics are shown in the left column (inset: photograph of device), and the output characteristics are shown in the right column.

7.44 (t, J = 7.6 Hz, 2H), 7.52 (dd, J = 7.6, 7.6 Hz, 4H), 7.98 (d, J = 7.6 Hz, 4H), 8.03 (s, 2H), 8.13 (s, 2H). ¹³C NMR could not be measured because of the poor solubility. MS (TOF, APCI+): 360.09 (M + H⁺). Anal. Calcd for C₂₆H₁₆O₂: C, 86.65; H, 4.47%. Found: C, 86.42; H, 4.67%.

OFET Fabrication and Evaluation. Fabrication Procedure of Laminated Single-Crystal OFET Device with **Bottom-Gate–Bottom-Contact Architecture (Device A):** This type of device was fabricated for **DPNDF1** and **DPNDF3** because these compounds afforded platelet single crystals by the physical-vapor transport (PVT) method.

A substrate that consists of a 500-nm thick thermally oxidized SiO_2 surface on n-doped Si was consecutively ultrasonicated with acetone and 2-propanol each for 5 min. The cleaned substrate was covered with perfluorotriethoxysilane (F-SAM).¹⁵ On the surface-treated substrate, chromium and gold were successively deposited under vacuum using a shadow mask to thicknesses of 3 and 27 nm, respectively. A thin single crystal of the PVT-grown DPNDF was attached electrostatically to the prepared substrate to construct a bottom-contact single-crystal transistor. A picture of a representative device is given in Figure 2a. The doped-Si layer acts as a gate electrode that has a dielectric constant of 3.9. Electrical characterization was performed using a semiconductor parameter analyzer (Keithley 4200). Field-effect mobility (μ) values were estimated in the saturation regime using eq 1:

$$I_{\rm d} = (WC_{\rm i}/2L)\mu(V_{\rm g} - V_{\rm th})^2$$
(1)

Table 1. OFET Characteristics and Properties of DPNDFs

Compound	Device type	$\mu / { m cm}^2 { m V}^{-1} { m s}^{-1} { m a})$	$V_{ m th}$ /V ^{b)}	$I_{\rm on}/I_{\rm off}$ ratio	$E_{\rm ox}$ /V ^{c)}	$T_{\rm m}$ /°C ^{d)}	<i>T</i> _{95%} ∕°C ^{e)}
DPNDF1	А	0.8-1.3	-10	$10^4 - 10^5$	0.68	302-303	322
	С	0.6-1.0	-50	$10^{4}-10^{5}$			
C ₈ -DPNDF1	С	1.5-3.6	-100	$10^{4}-10^{5}$	0.62	318-319	404
DPNDF2	В	0.1-0.2	0	$10^{3}-10^{4}$	0.70	283-284	307
DPNDF3	А	0.4-0.6	10	$10^4 - 10^5$	0.63	ND (sub) ^{f)}	369

a) OFET mobility in the saturated regime. b) Threshold voltage of the OFET device. c) Oxidation potential (vs. Fc/Fc^+). d) Melting point. e) 5% weight loss temperature determined using TG–DTA. f) Not determined because of sublimation.

where I_d is the source–drain current, W and L are the channel width and length, respectively, C_i is the capacitance of the SiO₂ insulator and V_{th} is the threshold voltage.

Fabrication Procedure of a Single-Crystal OFET Device with Top-Gate–Top-Contact Architecture Using a Parylene Gate Insulator (Device B): This type of device was fabricated for DPNDF2, which afforded needle crystals by PVT. On the top of the PVT-grown single crystals, source and drain electrodes were drawn using carbon paste, and gold wire was attached to each electrode. Parylene SR was deposited as a dielectric with relative dielectric constant of 3.0 (800 nm thickness) on the processed crystal. Afterward, carbon paste was drawn as a gate electrode on the surface of the parylene-coated single crystals. A picture of a representative device is given in Figure 2b. The OFET performances were evaluated in a similar manner to that used for device A.

Fabrication Procedure of a Solution-Crystallized OFET Device with Bottom-Gate–Top-Contact Architecture (Device C) by the Oriented Crystal-Growth Method:¹⁶ This type of device was fabricated for DPNDF1 and C₈-DPNDF1 because they have acceptable solubility. The fabrication process using C₈-DPNDF1 is described as a representative example.

On the surface of the cleaned Si/SiO₂ (same as the one used for device A), decyltriethoxysilane (DTS) was vapor-deposited. A droplet of 0.2-wt % solution of **C₈-DPNDF1** in chlorobenzene was placed at room temperature at an edge of a solution-sustaining piece on a slightly inclined substrate to grow a crystalline domain in the direction of the inclination through evaporation of the solvent. The source and drain gold electrodes were then vacuum-deposited on the organic film by the use of a shadow mask. The OFET performance was evaluated in a manner similar to that used for device A.

Results and Discussion

Synthesis of NDFs. We synthesized the NDFs by a zincmediated intramolecular cyclization reaction (Scheme 1).^{4,17} Thus, dialkynes 1a and 1b synthesized from β , β' -naphthalenediol (syntheses of these compounds are shown in Supporting Information) were deprotonated with butyllithium, converted to the corresponding zinc salt by treatment with zinc chloride, heated at 120 °C, and the reaction mixture was quenched with water to obtain 2,7-diphenylnaphtho[2,1-*b*:6,5-*b'*]difuran (DPNDF1) and 2,7-bis(*p*-octylphenyl)naphtho[2,1-*b*:6,5-*b'*]difuran (C₈-DPNDF1), respectively, in excellent yield (Scheme 1a). Other diphenyl-substituted NDFs, DPNDF2 and DPNDF3, were prepared in the same manner from dialkynes 2 and **3**, which were synthesized from α, α' - and β, β' -naphthalenediol, respectively (Schemes 1b and 1c). Details are shown in Supporting Information.

OFETs Using PVT-Grown DPNDF Single Crystals (Devices A and B). Performance of Single-Crystal OFETs: We employed two types of device structure depending on the shape of PVT-grown single crystals. As to the platelet and flexible DPNDF1 and DPNDF3, the single crystals could be manually laminated on the substrates with patterned gold electrodes to form a bottom-gate-bottom-contact structure (device A). On the other hand, DPNDF2, forming the sturdy needle shaped crystal, is not suitable for FET evaluation in the form of the device A, due to the imperfect contact on the substrate. Thus, the single crystal transistors based on DPNDF2 were fabricated in top-gate-top-contact structure using carbonpaste electrodes and a parylene gate dielectric (device B). The OFET performances of the DPNDF-based devices are shown in Figure 2 and summarized in Table 1. These devices showed hole-transporting characteristics. The transfer characteristics of DPNDF1 and DPNDF3 showed slight hysteresis (Figures 2a and 2c), and that using DPNDF2 showed no hysteresis (Figure 2b). This fact suggests that carrier injection from the electrode to the organic material occurs without a significant barrier. Among OFET devices using the three types of PVTgrown DPNDFs, the bottom-gate-bottom-contact devices using platelet crystals of DPNDF1 showed the highest hole mobility. The calculated hole mobility of the DPNDF1-based device was up to $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the saturation regime with an $I_{\rm on}/I_{\rm off}$ ratio of 10⁵ and a threshold voltage of -10 V. The DPNDF3-based devices having the same configuration showed hole mobilities of 0.4–0.6 cm² V⁻¹ s⁻¹ with I_{on}/I_{off} ratios of 10⁴-10⁵ and a threshold voltage of 10 V. The top-gate-topcontact devices using a needle crystal of **DPNDF2** (type B) showed a low threshold voltage (0V) and somewhat lower mobility (0.1–0.2 cm² V⁻¹ s⁻¹) and I_{on}/I_{off} ratios (10³–10⁴) than the other NDFs.

Packing Structures in Single Crystal and Theoretical Calculations on Carrier-Transporting Abilities: To obtain some insights into the difference in the mobility among three compounds, we revealed the packing structures of **DPNDFs** by means of X-ray single crystal structural analyses (Figure 3b).¹⁸ **DPNDF1** and **DPNDF3** were found to represent layer-bylayer structures with the herringbone-packing motifs, which are preferable for two-dimensional carrier transport. In contrast, **DPNDF2** stacks in slipped herringbone packing manner with a large tilt angle of 129° and thus forms a one-dimensional stacking arrangement. We then calculated and compared the



Figure 3. Crystal structures of DPNDFs. (a) Molecular structures and reorganization energies (λ), (b) Packing structures, (c) Herringbone structures and calculated electronic coupling elements (V, in meV).

electronic coupling elements $(V)^{19}$ among HOMOs in the crystal, because their reorganization energies for hole formation (λ) based on Marcus theory²⁰ are small and comparable (Figure 3a). In crystal, DPNDF1 and DPNDF3 exhibited a herringbone-type packing with the different two-dimensional interactions among the molecules as judged by the V values (Figure 3c). DPNDF1 possesses well-balanced and moderate V values of 27.7 and 39.9 meV for stacking and transverse directions, respectively. On the other hand, **DPNDF3** shows anisotropic and smaller V values; only 6.5 meV for the stacking direction and 40.3 and 20.8 meV for two transverse directions. Thus, the OFET based on **DPNDF1** recorded higher mobility than that of DPNDF3. Here the reorganization energies for hole formation (λ) in **DPNDF1** and **DPNDF3** are also small, as small as 178 and 199 meV, respectively, as calculated for a single molecule using the B3LYP/6-31G* level of theory.²¹ The origin of these smaller values than those for α -oligofurans (237-370 meV)²² can be ascribed to the effective π -electron conjugation over the rigid fused aromatic framework, which supports their high carrier transporting abilities. In contrast to these compounds, DPNDF2 exhibits a one-dimensional columnar packing in a single crystal, and shows highly anisotropic V values of which one is very large (105 and 2.2 meV for the stacking and the transverse directions, respectively). An OFET using such a highly anisotropic crystal is known to be sensitive to the quality of the specimen crystal,¹⁰ and the inhomogeneity in a single crystal (e.g., impurity or defect in a crystal) creates carrier traps, which often limit the measured mobility.⁷¹ This may be one of the origins of the lower mobility of the OFETs using needle crystals of DPNDF2.

Solution-Processed OFETs Using DPNDF1 and C₈-DPNDF1 (Device C). The solution-processed OFETs (device C) using a solution of DPNDF1 or C₈-DPNDF1 were found to show high hole mobilities (Figure 4 for an OFET using C₈-DPNDF1. Data are summarized in Table 1). The hole mobilities are 0.6–1.0 and 1.5–3.6 cm² V⁻¹ s⁻¹, for DPNDF1 and C₈-DPNDF1, respectively, in the saturation regime with a high I_{on}/I_{off} ratio of 10⁴–10⁵. These FET mobilities are among the highest for solution-processed OFETs.

An effective intermolecular interaction in the crystal state as well as the homogeneity of the solution-grown crystals of C₈-**DPNDF1** was verified by X-ray diffraction (XRD) and atomic force microscopy (AFM) analyses (Figure 5). The crystal packing of C₈-DPNDF1 was characterized as a herringbone packing with highly anisotropic electronic coupling elements of 59.3 and 0.3 meV along the stacking and the transverse directions, respectively (Figure 5a). Transmission XRD measurements revealed the molecular arrangement (See SI). By the out-of-plane XRD measurement, diffraction peaks corresponding to (001) and (002) were observed, suggesting that the C_8 -DPNDF1 stands on the substrate and forms lamella-like layer-by-layer structure and the carrier conduction *a*–*b* plane is parallel to the substrate. On the basis of the in-plane XRD for a C₈-DPNDF1 film, the crystal-growth direction, along which the source and drain channels were constructed, was not entirely parallel to the molecular stacking direction (b axis) but tilts ca. $20-30^{\circ}$ against the b axis, that is, not the most deal orientation for efficient carrier transportation. We consider that the mobility data obtained here $(3.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ can be improved further in the future by controlled installation of the source and drain channels.



Figure 4. Performances of solution-processed OFET devices using C₈-DPNDF1. (a) Transfer characteristics (inset: photograph of device) and (b) Output characteristics.



Figure 5. Molecular orientation and homogeneity of a solution-grown single crystal of C₈-DPNDF1. (a) Packing structure.
(b) Schematic illustration of the crystal structure. (c) Top view of the AFM image (inset: bird's-eye view). (d) Cross-sectional profile along the white dotted line in (c).

Such high apparent mobility of the C₈-DPNDF1-based OFET device can be attributed to the homogeneity of the C₈-DPNDF1 crystal as confirmed by AFM analyses (Figures 5b–5d). The AFM image of the C₈-DPNDF1 crystal showed a molecularly flat area extending to a micrometer area with only a few steps each with a height of ca. 2.4 nm, which corresponds to a single molecular layer supported by the out-of-plane XRD measurement. From the diffraction peak at $2\theta = 4.825^{\circ}$ (002), the *d* spacing is calculated to be 2.37 nm. Considering that the molecular length is 3.7 nm based on the X-ray single crystal analysis, we concluded that the molecular long axis stands on the substrate with a tilt angle of ca. 40°.

Thermal and Electrochemical Stabilities. Thermal and electrochemical stability are also important factors for materials. Indeed, **DPNDF**s are found to be stable (Table 1): both the melting (T_m) and 5%-weight loss temperatures ($T_{95\%}$) are higher than 300 °C (see Figure S1 in Supporting Information). Unlike those of the nonfused furans,^{7q,12,13} cyclic voltammographic data for **DPNDF**s indicated reversible oxidation waves (Figure S2). The oxidation potential of **DPNDF**s ranges from 0.62 to 0.70 V (vs. Fc/Fc⁺), from which we estimate the HOMO energy level to be between -5.42 and -5.50 eV.²³ These HOMO energy levels allow smooth hole injection from the gold electrode to **DPNDF**, and work as p-type organic semiconductors. We consider that the observed stability stems from the rigid and extended π -conjugated framework of the naphthalene-fused furan core.

Conclusion

In conclusion, we have designed and synthesized a new class of p-type semiconducting materials: naphtho-fused furan compounds (NDFs), and found that they show high OFET mobility and high thermal and electrochemical stability. The hole mobility data of up to $3.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been recorded for a solution-grown single-crystal device using **C**₈-**DPNDF1**. These data rival those of the other known organic semiconductors. The present OFET data suggest that solution-processable devices can surpass the performance of amorphous silicon devices. We consider that the present data provide further support for our initial conjecture that furan compounds rival the corresponding thiophene compounds for organic electronics devices.

We thank MEXT for financial support (KAKENHI for H.T., No. 20685005; and the Global COE Program for Chemistry Innovation). This work was partly supported by the Strategic Promotion of Innovative R&D, JST (E.N.) and PRESTO, JST (H.T.).

Supporting Information

Synthetic details and properties of the compounds. This material is available electronically on J-STAGE.

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