Supporting Information

Furan Fused V-Shaped Organic Semiconducting Materials with High Emission and High Mobility

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Synthesis Materials

Reagents and Starting Materials

1.0 M Boron tribromide in dichloromethane, 2-methoxy-6-bromonaphthalene and NiCl₂(dppp) was purchased from TCI. All Grignard reagents, Fe(acac)₃ and trimethoxy(2-phenylethyl)silane were purchased from Sigma–Aldrich Inc. *N*-methylpyrrolidone, 1,2-dichlorobenzene were purchased from WAKO chemicals. 1.6 M n-BuLi in hexane and all anhydrous solvents were purchased from KANTO chemicals. Zeolite HSZ-360 was purchased from TOSOH Corp. 7-Methoxy-2-naphthyltrifluoromethanesulfonate¹ and 6-decyl-2-methoxynaphthalene² were prepared according to literature procedure.

1.2 Methods

General for Synthesis and Characterization

All the reactions were carried out under an atmosphere of nitrogen. Air- or moisture-sensitive liquids and solutions were transferred via a syringe or a Teflon cannula. Analytical thin-layer chromatography (TLC) was performed on glass plates with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator (Merck Silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet lamp (254 nm and 365 nm) and by dipping with 10% phosphomolybdic acid in ethanol and heating on a hot plate. Flash column chromatography was performed on Kanto silica gel 60. Open column chromatography was performed on Wakogel C-200 (75-150 µm). All NMR spectra were recorded on a JEOL ECA600 and JEOL ECS400 spectrometers. Chemical shifts are reported in parts per million (ppm, δ scale) from residual protons in the deuterated solvent for ¹H NMR (δ 7.26 ppm for chloroform and δ 5.93 ppm for 1,1,2,2-tetrachloroethane) and from the solvent carbon for ¹³C NMR (δ 77.16 ppm for chloroform and δ 74.00 ppm for 1,1,2,2-tetrachloroethane). The data were presented in the following format: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant in Hertz (Hz), signal area integration in natural numbers, assignment (*italic*). Mass spectra were measured on a JEOL JMS-T100LC APCI/ESI mass spectrometer. Melting points and elemental analyses were collected on a Mettler Toledo MP70 Melting Point System and J-Science Lab JM10 MICRO CORDER, respectively.

1.3 Experimental Section

7-Decyl-2-methoxynaphthalene (Iron-catalyzed alkylation reaction³)



To a solution of 7-methoxy-2-naphthyltrifluoromethanesulfonate (22.8 g, 74.4 mmol) and Fe(acac)₃ (525 mg, 1.49 mmol, 2 mol%) in THF (330 mL) and *N*-methylpyrrolidone (33 mL) was added decylmagnesium bromide (1.0 M in Et₂O, 96.7 mL, 96.7 mmol, 1.3 mol amt.) dropwise at room temperature. The color immediately changed into dark brown and the reaction was exothermic. After stirring for 2 h at ambient temperature, the reaction was quenched with water. The organic layer was extracted with ethyl acetate and washed with water and brine. After the solvent of combined organic layer was removed *in vacuo*, the crude material was purified by silica gel column chromatography (hexane:chloroform = 97:3) to afford the titled compound (17.0 g, 57.0 mmol, 77%) as white solid. The spectral data of this compound was identical to the literature previously.²

General procedure of homo-coupling reaction:

6,6'-Didecyl-3,3'-dimethoxy-2,2'-binaphthalene (for synthesis of C₁₀–DNF–VW)



To a solution of 7-decyl-2-methoxynaphthalene (7.46 g, 25.0 mmol) in THF (100 mL) was added 1.62 M *n*-BuLi in hexane (17.0 mL, 27.5 mmol, 1.1 mol amt.) at 0 °C. After stirring at 0 °C for 2 h, Fe(acac)₃ (9.71 g, 27.5 mmol, 1.1 mol amt.) was added at 0 °C

and the resultant mixture was stirred at room temperature for 10 h. After the reaction finished, the crude material was passed through a short pad of Celite[®] to remove the inorganic salt. After removing the solvent *in vacuo*, the crude material was purified by silica gel column chromatography (hexane:chloroform = 90:10) to afford the titled compound (5.43 g, 9.13 mmol, 73%) as white solid. M.p.: 68.4–71.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.89 (t, J = 6.8 Hz, 6H, CH_3), 1.26–1.40 (m, 28H, $(CH_2)_7$), 1.70 (quin, J = 7.2 Hz, 4H, ArCH₂CH₂), 2.76 (t, J = 7.2 Hz, 4H, ArCH₂), 3.86 (s, 6H, OCH₃), 7.16 (s, 2H, ArH), 7.19 (d, J = 8.4 Hz, 2H, ArH), 7.56 (s, 2H, ArH), 7.68–7.71 (m, 4H, ArH). ¹³C NMR (150 MHz, CDCl₃): δ 14.3, 22.9, 29.2 (two carbons), 29.75, 29.82 (two carbons), 31.6, 32.1, 36.4, 55.8, 105.1, 125.2, 125.4, 127.2, 127.6, 129.2, 130.1, 134.6, 141.0, 156.5. TOF HRMS (APCI): Calcd for C₄₂H₅₉O₂ [M+H] 595.4515, found 595.4537. Anal. Calcd for C₄₂H₅₈O₂: C, 84.79; H, 9.83. Found: C, 84.85; H, 9.72.

7,7'-Didecyl-3,3'-dimethoxy-2,2'-binaphthalene (for synthesis of C₁₀-DNF-VV)



White solid. Yield: 66%. M.p.: 65.4–66.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.88 (t, J = 6.8 Hz, 6H, CH₃), 1.26–1.35 (m, 28H, (CH₂)₇), 1.69 (quin, J = 7.6 Hz, 4H, ArCH₂CH₂), 2.74 (t, J = 7.6 Hz, 4H, ArCH₂), 3.86 (s, 6H, OCH₃), 7.19 (s, 2H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.55 (s, 2H, ArH), 7.68 (s, 2H, ArH), 7.70 (d, J = 8.4 Hz, 2H, ArH), 7.55 (s, 2H, ArH), 7.68 (s, 2H, ArH), 7.70 (d, J = 8.4 Hz, 2H, ArH), 1³C NMR (150 MHz, CDCl₃): δ 14.3, 22.9, 29.48, 29.51, 29.7, 29.80 (two carbons), 31.7, 32.1, 36.1, 55.8, 105.3, 126.3, 126.4, 127.9, 129.0, 129.9, 130.1, 132.8, 138.3, 155.9. TOF HRMS (APCI): Calcd for C₄₂H₅₉O₂ [M+H] 595.4515, found 595.4509. Anal. Calcd for C₄₂H₅₈O₂: C, 84.79; H, 9.83. Found: C, 84.73; H, 9.56.

General procedure of demethylation reaction:

6,6'-Didecyl-2,2'-binaphthalene-3,3'-diol (for synthesis of C₁₀-DNF-VW)



To a solution of 6,6'-didecyl-3,3'-dimethoxy-2,2'-binaphthalene (4.46 g, 7.50 mmol) in dichloromethane (30 mL) was added 1.0 M BBr₃ in dichloromethane (16.5 mL, 16.5 mmol, 2.2 mol amt.) at 0 °C and the resulting mixture was stirred at room temperature for 1 h. After the crude material was poured into ice water, organic layer was extracted with EtOAc, washed with water and brine, and dried over MgSO₄. After removing the solvent *in vacuo*, the crude material was purified by silica gel column chromatography (hexane:EtOAc = 80:20) to afford the titled compound (4.12 g, 7.27 mmol, 97%) as white solid. M.p.: 117.5–118.8 °C. ¹H NMR (600 MHz, CDCl₃): δ 0.89 (t, *J* = 7.2 Hz, 6H, *CH*₃), 1.26–1.41 (m, 28H, (*CH*₂)₇), 1.72 (quin, *J* = 7.2 Hz, 4H, ArCH₂CH₂), 2.77 (t, *J* = 7.2 Hz, 4H, Ar*CH*₂), 5.51 (s, 2H, O*H*), 7.24 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.36 (s, 2H, Ar*H*), 7.54 (s, 2H, Ar*H*), 7.73 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.80 (s, 2H, Ar*H*). ¹³C NMR (150 MHz, CDCl₃): δ 14.3, 22.9, 29.51, 29.53, 29.7, 29.78, 29.80, 31.5, 32.1, 36.4, 111.0, 124.8, 125.0, 126.1, 127.7, 127.8, 130.8, 135.2, 142.0, 151.3. TOF HRMS (APCI): Calcd for C₄₀H₅₅O₂ [M+H] 567.4202, found 567.4199. Anal. Calcd for C₄₂H₅₄O₂: C, 84.75; H, 9.60. Found: C, 84.81; H, 9.34.

7,7'-Didecyl-2,2'-binaphthalene-3,3'-diol (for synthesis of C₁₀-DNF-VV)



White solid. Yield: 97%. M.p.: 105.4–106.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.88 (t, J = 6.4 Hz, 6H, CH₃), 1.26–1.35 (m, 28H, (CH₂)₇), 1.72 (quin, J = 7.6 Hz, 4H, ArCH₂CH₂), 2.76 (t, J = 7.6 Hz, 4H, ArCH₂), 5.63 (s, 2H, OH), 7.34 (d, J = 8.4 Hz, 2H, ArH), 7.39 (s, 2H, ArH), 7.58 (s, 2H, ArH), 7.69 (d, J = 8.4 Hz, 2H, ArH), 7.79 (s, 2H,

Ar*H*). ¹³C NMR (100 MHz, CDCl₃): δ 14.3, 22.8, 29.5, 29.70, 29.76, 29.78 (two carbons), 31.6, 32.1, 36.1, 111.4, 125.9, 126.3, 126.4, 128.9, 129.5, 130.6, 133.4, 139.1, 150.7. TOF HRMS (APCI): Calcd for C₄₀H₅₅O₂ [M+H] 567.4202, found 567.4213.

General procedure of synthesis of C₁₀–DNF–V derivatives: 3,9-Didecyldinaphtho[2,3-*b*:2',3'-*d*]furan (C₁₀–DNF–VW)



To a solution of 6,6'-didecyl-2,2'-binaphthalene-3,3'-diol (998 mg, 1.76 mmol) in 1,2-dichlorobenzene (35 mL) was added zeolite HSZ-360 (200 mg) and the reaction mixture was heated at 160 °C for 16 h. After the reaction finished, organic material was dissolved by hot 1,1,2,2-tetrachloroethane, which was passed through a short pad of silica gel column employing 1,1,2,2-tetrachloroethane to remove the zeolite. After reducing the solvent to c.a. 10 mL *in vacuo*, addition of MeOH gave the white precipitate (909 mg, 1.66 mmol, 94%), which was collected by vacuum filtration. The obtained white solid was purified by vacuum sublimation with diffusion pump (High temp. = 280 °C, Low temp. = 180 °C, pressure < 0.003 Torr).

M.p.: 209.4–210.4 °C. ¹H NMR (600 MHz, CDCl₂CDCl₂): δ 0.82 (t, J = 6.6 Hz, 6H, CH₃), 1.22–1.36 (m, 28H, (CH₂)₇), 1.68 (quin, J = 7.2 Hz, 4H, ArCH₂CH₂), 2.75 (t, J = 7.2 Hz, 4H, ArCH₂), 7.31 (d, J = 8.4 Hz, 2H, ArH), 7.67 (s, 2H, ArH), 7.75 (s, 2H, ArH), 7.90 (d, J = 8.4 Hz, 2H, ArH), 8.40 (s, 2H, ArH). ¹³C NMR (150 MHz, CDCl₂CDCl₂, 100 °C): δ 14.0, 22.6, 29.3, 29.4, 29.51, 29.59 (two carbons), 31.1, 31.9, 36.2, 106.1, 119.6, 124.6, 126.1, 126.3, 128.3, 128.9, 134.1, 141.2, 156.2. TOF HRMS (APCI): Calcd for C₄₀H₅₃O [M+H] 549.4096, found 549.4095. Anal. Calcd for C₄₀H₅₂O: C, 87.54; H, 9.55. Found: C, 87.59; H, 9.62.

2,10-Didecyldinaphtho[2,3-*b*:2',3'-*d*]furan (C₁₀–DNF–VV)



White solid. Yield: 98%. The obtained white solid was finally purified by vacuum sublimation with diffusion pump (High temp. = 250 °C, Low temp. = 150 °C, pressure < 0.003 Torr).

M.p.: 173.9–174.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.89 (t, J = 6.4 Hz, 6H, CH₃), 1.26–1.40 (m, 28H, (CH₂)₇), 1.75 (quin, J = 7.2 Hz, 4H, ArCH₂CH₂), 2.82 (t, J = 7.2 Hz, 4H, ArCH₂), 7.40 (d, J = 8.4 Hz, 2H, ArH), 7.81 (s, 2H, ArH), 7.83 (s, 2H, ArH), 7.88 (d, J = 8.4 Hz, 2H, ArH), 8.43 (s, 2H, ArH). ¹³C NMR (150 MHz, CDCl₂CDCl₂): δ 14.4, 22.9, 29.5, 29.6, 29.70, 29.77, 29.79, 31.5, 32.0, 36.1, 106.5, 119.6, 125.1, 126.8, 127.6, 128.3, 130.3, 132.0, 139.3, 155.4. TOF HRMS (APCI): Calcd for C₄₀H₅₃O [M+H] 549.4096, found 549.4128. Anal. Calcd for C₄₀H₅₂O: C, 87.54; H, 9.55. Found: C, 87.61; H, 9.50.

2. Ionization Potentials

Photoelectron yield spectroscopy (PYS) was performed on a Sumitomo Heavy Industries Advanced Machinery PYS-202. For PYS measurements, thin films (100 nm) of **DNF–V** derivatives were thermally evaporated on ITO coated quartz substrates and measurements were performed in vacuum. The photoelectron yield spectra are depicted in Figure S1.



Figure S1. Photoelectron yield spectra of **DNF–V** derivatives in thin films after light illumination from a D_2 lamp *in vacuo*.

3. Absorption Spectra in Evaporated Thin Film and Solution

UV-vis absorption spectra were measured with a JASCO V-570 spectrometer. Thin films were prepared by vacuum deposition with the thickness of 100 nm on quartz substrates. **DNF–V** derivatives in solutions were prepared in degassed and analytical grade 1,2-dichloroethane.



Figure S2. Absorption spectra of **DNF–V** derivatives (**DNF–V**: blue, **C₁₀–DNF–VV**: green, **C₁₀–DNF–VW**: red) in vacuum deposited thin films on quartz substrate.



Figure S3. Absorption spectra of **DNF–V** (blue) **C**₁₀–**DNF–VV** (green) and **C**₁₀–**DNF–VW** (red) in 1,2-dichloroethane solution (**DNF–V**: $C = 2.5 \times 10^{-5}$ M, **C**₁₀–**DNF–VV**: $C = 1.9 \times 10^{-5}$ M, **C**₁₀–**DNF–VW**: $C = 5.73 \times 10^{-6}$ M).

4. Fluorescent Spectra

Photoluminescence spectra and absolute quantum yields were recorded with a Hamamatsu Photonics C9920–02 Absolute PL Quantum Yield Measurement System. The samples in solution were prepared in degassed and analytical grade 1,2-dichloroethane.



Figure S4. Fluorescent spectra of **DNF–V** (**DNF–V**: blue, **C**₁₀–**DNF–VV**: green, **C**₁₀–**DNF–VW**: red) derivatives in solids.



Figure S5. Fluorescent spectra of **DNF–V** derivatives (**DNF–V**: blue, **C**₁₀–**DNF–VV**: green, **C**₁₀–**DNF–VW**: red) in a 1,2-dichloroethane solution.

Table S1. Summarized optical properties of DNF–V, C₁₀–DNF–VV and C₁₀–DNF–VW

	UV/Vis absorption	Fluorescence in solution		Fluorescence in solid state	
Compound	$\lambda_{\max} \left(\mathrm{nm} ight)^a$	$\lambda_{\max} \left(nm ight)^b$	$\Phi(sol.)$	$\lambda_{\max} \left(nm ight)^c$	$\Phi(\text{solid})$
DNF-V	322, 337, 362, 382	389, 410, 431 (sh)	0.83	408 (sh), 427, 455, 488, 524	0.72
C ₁₀ -DNF-VV	323, 340, 369, 389	398 419, 444 (sh)	0.82	411, 435, 456 (sh)	0.18
C ₁₀ -DNF-VW	331, 348, 359 (sh), 381	388, 409, 431(sh)	0.88	407 (sh), 424, 448	0.40

^{*a*} Wavelength of absorption intensity maximum in 1,2-dichloroethane. ^{*b*} Wavelength of emission intensity maximum in 1,2-dichloroethane. ^{*c*} Wavelength of emission intensity in solid state.

5. Thermal Analyses

5.1 Thermogravimetric–Differential Thermal Analyses (TG–DTA)

TG–DTA measurement was carried out with a Rigaku Thermo Plus EVO II TG 8120. Sample was placed in aluminum pan and heated at the rate of 5 K/min, under N_2 purge at a flow rate of 100 mL/min. Al₂O₃ was used as reference material.



Figure S6. TG-DTA charts of C_{10} -DNF-VV (green) and C_{10} -DNF-VW (red). Dotted and solid lines represent TGA and DTA, respectively.

5.2 Differential Scanning Calorimetric (DSC) Analyses

DSC measurement was carried out with a Rigaku Thermo Plus EVO II DSC8270. Sample was placed in aluminum pan and heated at the rate of 5 K/min, under N_2 purge at a flow rate of 100 mL/min. Al₂O₃ was used as reference material.



Figure S7. DSC charts of C₁₀–DNF–VV (green line) and C₁₀–DNF–VW (red line).

6. Single-Crystal Analyses

We have obtained the single crystals of C_{10} –DNF–VV and C_{10} –DNF–VW by means of recrystallization from a mixture of toluene and 2-propanol. Single crystal diffraction data were collected on a Rigaku R-AXIS RAPID II imaging plate diffractometer with CuK α radiation or synchrotron radiation at SPring-8.

Crystal data for C₁₀–DNF–VV: C₄₀H₅₂O, M = 548.84, a colorless plate, 0.100 × 0.100 × 0.100 mm, orthorhombic, *Pnma*, a = 6.0634 (7), b = 72.208 (8), c = 7.6952 (9) Å, V = 3369.2 (7) Å³, Z = 4, $\rho_{calcd} = 1.058$ g cm⁻³, T = 296 K, 2 $\theta_{max} = 82.1^{\circ}$, synchrotron radiation, $\lambda = 1.01060$ Å, $\mu = 0.141$ mm⁻¹, 9113 reflections measured, 2378 unique reflections, $R_{int} = 12.96\%$, 187 parameters, $R_1 = 0.0984$ ($I > 2 \sigma$ (I)), $wR_2 = 0.3247$ (all data), CCDC–964194.

Crystal data for **C**₁₀–**DNF**–**VW**: C₄₀H₅₂O, M = 548.84, a colorless plate, $0.487 \times 0.144 \times 0.010$ mm, orthorhombic, *Pnma*, a = 5.9067 (3), b = 72.191 (4), c = 7.3415 (4) Å, V = 3130.5 (3) Å³, Z = 4, $\rho_{calcd} = 1.081$ g cm⁻³, T = 296 K, $2 \theta_{max} = 136.7 \circ$, CuK α radiation, $\lambda = 1.54187$ Å, $\mu = 0.500$ mm⁻¹, 30615 reflections measured, 2886 unique reflections, $R_{int} = 23.16\%$, 187 parameters, $R_1 = 0.1552$ ($I > 2 \sigma$ (I)), $wR_2 = 0.3751$ (all data), CCDC–964195.

7. Theoretical Calculations

Frontier molecular orbitals and energy levels of **DNF–V** derivatives were calculated for a single molecule at the B3LYP/6-31G* level.



Figure S8. HOMO and LUMO of DNF-V derivatives.

8. Experimental Details for OFET Device Fabrication and Evaluation Procedure

The surface of the substrates with 500 nm or 200 nm thick thermally oxidized SiO₂ on doped Si is first cleaned in an ultra-sound bath with acetone and 2-propanol for 5 min, consecutively. The surface of the cleaned substrates is treated with vapor-deposited decyltriethoxysilane (DTS) or trimethoxy(2-phenylethyl)silane (β -PTS). To form the crystalline thin films, a 0.2 wt% solution of C₁₀-DNF-VV or C₁₀-DNF-VW is prepared and the prepared droplet (approximately 50–100 µL) is sustained at an edge of a structure on an inclined substrate, so that the crystalline domain grows in the direction of the inclination through evaporation of the solvent. The structure to support the droplet can be a small piece of a silicon wafer and can be removed after the growth of the crystalline film. Then, the source and drain gold electrodes are then evaporated on the film through a shadow mask. The doped-Si layer acts as a gate electrode with

dielectric constant of 3.9. A picture of a representative single crystal for FET device is given in Figure S9. Electrical characterization was performed using a semiconductor parameter analyzer (Keithley 4200). Field-effect mobilities (μ_{FET}) values were estimated from the saturation regime using the following the equation:

$$I_d = (WC_i/2L)\mu_{\text{FET}}(V_{\text{g}}-V_{\text{th}})^2$$

Where μ_{FET} is the carrier mobility in saturated region, W is the channel width, L is the channel length, I_d is the drain current, V_g is the gate voltage, C_i is the capacitance of gate insulator and V_{th} is the threshold voltage. Especially, device which consists of **C**₁₀-**DNF**-**VW** crystalline film on β -PTS treated 200 nm SiO₂ substrate was washed with acetonitrile to reduce the effect of oxygen or water as a trap site.



Figure S9. (a) Schematic image of the crystalline thin film formation by edge-cast method. (b) Representative photo of single crystal transistors using C_{10} -DNF-VV. (c) Schematic device structure based on C_{10} -DNF-V derivatives.



Figure S10. OFET characters of C_{10} -DNF-VV. Transfer (left)- and output (right) characteristics (L/W = 295/880, SiO₂: 500 nm). Solution crystallized film was prepared from 0.2 wt% chloroform solution on the DTS-treated substrate at room temperature.



Figure S11. OFET characters of C_{10} -DNF-VW. Transfer (left)- and output (right) characteristics (L/W = 195/490, SiO₂: 500 nm). Solution crystallized film was prepared from 0.2 wt% *o*-DCB solution on the DTS-treated substrate at 80 °C.



Figure S12. OFET characters of C₁₀–DNF–VW (washed with acetonitrile). Transfer (left)- and output (right) characteristics (L/W = 7/30, SiO₂: 200 nm). Solution crystallized film was prepared from 0.2 wt% *o*-DCB solution on the β -PTS-treated substrate at 60 °C.

9. X-ray-diffraction Measurements for Solution-crystallized Thin Film

The X-ray-diffraction measurements were performed using the high-energy X-ray source of the photon-factory at SPring-8.



Figure S13. The Laue spots of the solution-crystalized C_{10} –DNF–VW thin film on the imaging plate in the (a) in-plane and (b) out-of-plane measurements.



Figure S14. The Laue spots of the solution-crystalized C_{10} -DNF-VV thin film on the imaging plate in the (a) in-plane and (b) out-of-plane measurements.

10. AFM Images of Solution-crystallized Thin Film of C₁₀–DNF–VW



Figure S15. AFM images of the solution grown films of C_{10} -DNF-VW: (a) top view, (b) bird's view, and (c) schematic illustration of the crystal structure of C_{10} -DNF-VW.

11. References

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