

Supporting Information

High Performance Oxygen-bridged N-shaped Semiconductors with Stabilized Crystal Phase and Blue Luminescence

Chikahiko Mitsui,^a Yuji Tanaka,^b Shota Tanaka,^b Masakazu Yamagishi,^a Katsumasa Nakahara,^c Masafumi Yano,^b Hiroyasu Sato,^d Akihito Yamano,^d Hiroyuki Matsui,^a Jun Takeya,^{a,c} and Toshihiro Okamoto*^{a,c,e}

^aDepartment of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.

^bGraduate School of Science and Engineering, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan.

^cThe Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan.

^dRigaku Corp., 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666, Japan.

^ePRESTO, Japan Society and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

Contents

1. Synthesis
2. Absorption Spectra in Evaporated Thin Film
3. Fluorescent Spectra
4. Ionization Potentials
5. Thermal Analyses
6. Single-Crystal Analyses
7. Theoretical Calculations
8. OFET Device Fabrication and Evaluation Procedure
9. X-ray-diffraction Measurements for Solution-crystallized Thin Film
10. Photograph of solution-crystallized thin film of C₁₀-DNBDF-NV
11. References

1. Synthesis

1.1 Materials

Reagents and Starting Materials

1.0 M boron tribromide in dichloromethane and PdCl₂(dppp) was purchased from TCI. 1,4-Dibromo-2,5-dimethoxybenzene and zinc chloride (99.999% trace metals basis) were purchased from Sigma–Aldrich Inc. *n*-BuLi and 1,2-dichlorobenzene were purchased from Kanto chemicals. Zeolite HSZ-360 was purchased from TOSOH Corp. All anhydrous solvents were purchased from Kanto chemicals. 2-Decyl-6-methoxynaphthalene was prepared by the reported procedure.^[1] 2,5-Bis(3-hydroxynaphthalen-2-yl)benzene-1,4-diol and 2,5-bis(6-decyl-3-hydroxynaphthalen-2-yl)benzene-1,4-diol were synthesized according to the previously reported procedure.^[2]

1.2 Methods

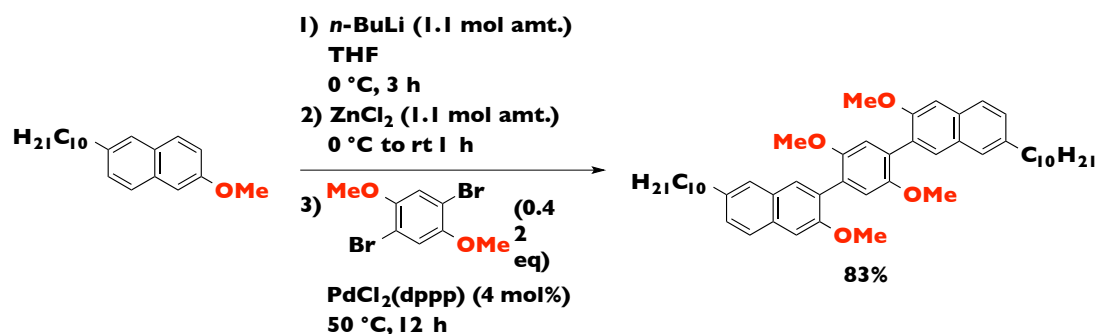
General for Synthesis and Characterization

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 either exposure to ultraviolet lamp (254 nm and 365 nm) or by dipping with 10% phosphomolybdic acid in ethanol and then 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, δ 5.93 ppm for 1,1,2,2-tetrachloroethane, and δ 1.73 ppm for tetrahydrofuran) and from the solvent carbon for ¹³C NMR (δ 77.16 ppm for chloroform and δ 25.5 ppm for tetrahydrofuran). 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

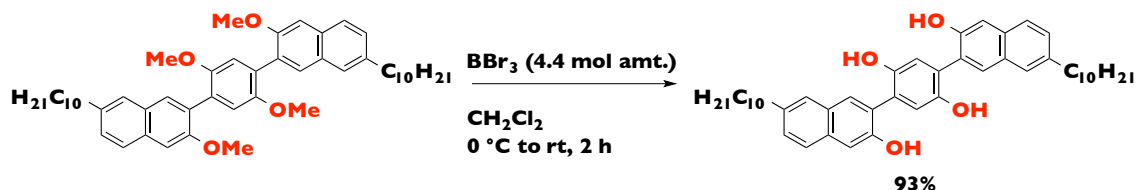
3,3'-(2,5-dimethoxy-1,4-phenylene)bis(6-decyl-2-methoxynaphthalene)



To a solution of 2-decyl-6-methoxynaphthalene (10.3 g, 34.5 mmol, 2.4 mol amt. for 1,4-dibromo-2,5-dimethoxybenzene) in THF (138 mL) was added 1.65 M *n*-BuLi in hexane (23.0 mL, 38.0 mmol, 1.1 mol amt. for 2-decyl-6-methoxynaphthalene) at 0 °C. After stirring at 0 °C for 3 h, 1.0 M zinc chloride in THF (38.0 mL, 38.0 mmol, 1.1 mol amt. for 2-decyl-6-methoxynaphthalene) was added at 0 °C and the resultant mixture was stirred at room temperature for 1 h. To the resulting pale yellow solution were added 1,4-dibromo-2,5-dimethoxybenzene (4.26 g, 14.4 mmol) and PdCl₂(dppp) (340 mg, 0.576 mmol) and the reaction mixture were stirred at 50 °C for 12 h. After addition of water, organic layer was extracted with EtOAc, washed with brine, and dried over MgSO₄. After removing the solvent to c.a. 60 mL *in vacuo*, addition of MeOH and CHCl₃ afforded the titled compound (6.38 g, 9.45 mmol, 66%) as white solid, which was collected by filtration as a major part. In a mother liquor, there still remained small amount of the products. After removing the solvent in the mother liquor, the crude material was purified by silica gel column chromatography (hexane:chloroform = 80:20 to 50:50) to afford the titled compound (1.67 g, 2.47 mmol, 17%) as white solid. Total yield: 83%. M.p.: 167.3–167.9 °C. ¹H NMR (600 MHz, CDCl₃): δ 0.89 (t, *J* = 6.6 Hz, 6H, CH₃), 1.27–1.35 (m, 28H, (CH₂)₇), 1.69 (quin, *J* = 7.2 Hz, 4H, ArCH₂CH₂), 2.75 (t, *J* = 7.2 Hz, 4H, ArCH₂), 3.75 (s, 6H, OCH₃), 3.94 (s, 6H, OCH₃), 6.99 (s, 2H, ArH), 7.22 (s, 2H, ArH), 7.30 (d, *J* = 8.4 Hz, 2H, ArH), 7.56 (s, 2H, ArH), 7.70 (d, *J* = 8.4 Hz, 2H, ArH), 7.74 (s, 2H, ArH). ¹³C NMR (150 MHz, CDCl₃): δ 14.27, 22.84, 29.47, 29.49.

29.73, 29.77 (two carbons), 31.71, 32.05, 36.11, 55.85, 56.72, 105.51, 115.37, 126.32, 126.45, 127.82, 127.95, 128.95, 129.73, 130.20, 132.66, 138.39, 151.35, 155.51. HRMS (APCI+): Calcd for $C_{50}H_{67}O_4$ [M+H] 731.5039, found, 731.5031. Anal. Calcd for $C_{50}H_{66}O_4$: C, 82.15; H, 9.10. Found C, 82.27; H, 9.11.

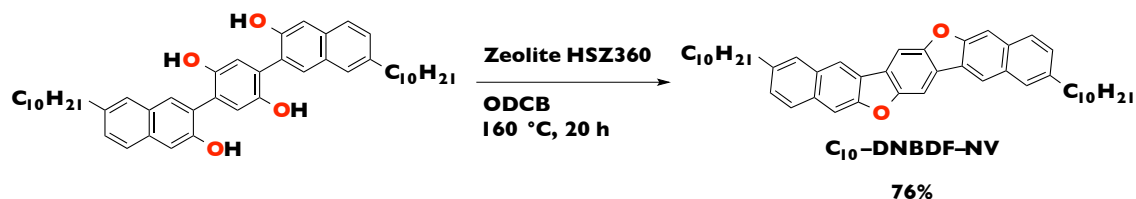
2,5-bis(7-decyl-3-hydroxynaphthalen-2-yl)benzene-1,4-diol



To a suspension of 3,3'-(2,5-dimethoxy-1,4-phenylene)bis(6-decyl-2-methoxynaphthalene) (4.00 g, 5.47 mmol) in dichloromethane (22 mL) was added 1.0 M BBr_3 in dichloromethane (24.1 mL, 24.1 mmol, 4.4 mol amt.) at 0 °C and then was stirred at room temperature for 2 h. After the crude mixture was poured into ice water, organic layer was extracted with THF and EtOAc, washed with water and brine, and dried over $MgSO_4$. After removing the solvent to 30 mL *in vacuo*, addition of acetone and dichloromethane afforded the titled compound (2.83 g, 4.19 mmol, 77%) as white precipitate, which was collected by filtration as a major part. In a mother liquor, there still remained small amount of the products. After removing the solvent in the mother liquor, the crude material was purified by silica gel column chromatography (hexane:AcOEt = 90:10 to 75:25) to afford the titled compound (588 mg, 0.87 mmol, 16%) as white solid. Total yield: 93%. M.p.: 229.9–231.1 °C. 1H NMR (400 MHz, $THF-d_8$): δ 0.89 (t, $J = 6.8$ Hz, 6H, CH_3), 1.26–1.42 (m, 28H, $(CH_2)_7$), 2.74 (t, $J = 7.6$ Hz, 4H, $ArCH_2$), 6.97 (s, 2H, ArH), 7.22 (s, 2H, ArH), 7.25 (d, $J = 8.4$ Hz, 2H, ArH), 7.56 (s, 2H, ArH), 7.60 (d, $J = 8.4$ Hz, 2H, ArH), 7.76 (s, 2H, ArH), 7.92 (s, 2H, OH), 8.41 (s, 2H, OH) 4 protons for $ArCH_2CH_2$ were overlapped with those of THF. ^{13}C NMR (150 MHz, $THF-d_8$): δ 15.04, 24.16, 30.88, 30.90, 31.15, 31.21 (two carbons), 33.09, 33.47, 37.39, 111.98, 120.90, 127.11, 127.56, 128.29, 128.82, 130.35, 130.67, 131.61, 134.51, 138.83, 149.30, 153.91. HRMS (APCI+): Calcd for $C_{46}H_{59}O_4$ [M+H] 675.4413, found, 675.4412. Anal. Calcd for $C_{46}H_{58}O_4$: C, 81.86; H, 8.66. Found C, 81.72; H, 8.58.

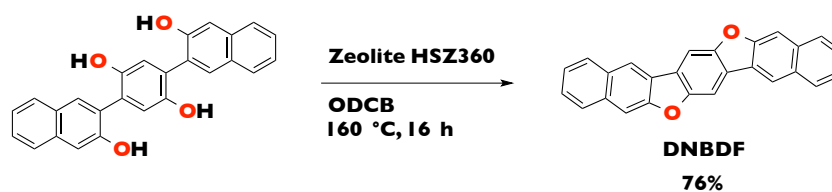
General procedure for dehydration reaction

2,10-Didecyldinaphtho[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]difuran (C_{10} -DNBDF-NV)



To a white suspension of 2,5-bis(7-decyl-3-hydroxynaphthalen-2-yl)benzene-1,4-diol (810 mg, 1.20 mmol) in 1,2-dichlorobenzene (24 mL) was added Zeolite HSZ-360 (324 mg) and the reaction mixture was stirred at 160 °C for 20 h. The resultant mixture was passed through a short pad of Celite® to remove the Zeolite by hot filtration. After addition of MeOH to the filtrate, the formed precipitate was collected by filtration to afford the titled compound (579 mg, 0.91 mmol, 76%) as pale yellow solid. The obtained compound was purified by vacuum sublimation with diffusion pump (High temperature region: 330 °C, Low temperature region: 230 °C, pressure: ca. 10^{-3} Torr). M.p.: 313 °C (determined by DSC). ^1H NMR (600 MHz, $\text{CDCl}_2\text{CDCl}_2$, 100 °C): δ 0.88 (t, $J = 7.2$ Hz, 6H, CH_3), 1.26–1.43 (m, 28H, $(\text{CH}_2)_7$), 1.77 (quin, $J = 7.8$ Hz, 4H, ArCH_2CH_2), 2.82 (t, $J = 7.8$ Hz, 4H, ArCH_2), 7.39 (d, $J = 8.4$ Hz, 2H, ArH), 7.81 (s, 2H, ArH), 7.87 (d, $J = 8.4$ Hz, 2H, ArH), 7.89 (s, 2H, ArH), 8.13 (s, 2H, ArH), 8.38 (s, 2H, ArH). ^{13}C NMR spectra could not be recorded due to the low solubility. HRMS (APCI+): Calcd for $\text{C}_{46}\text{H}_{55}\text{O}_2$ [$\text{M}+\text{H}$] 639.4202, found, 639.4199. Anal. Calcd for $\text{C}_{46}\text{H}_{54}\text{O}_2$: C, 86.47; H, 8.52. Found C, 86.56; H, 8.53.

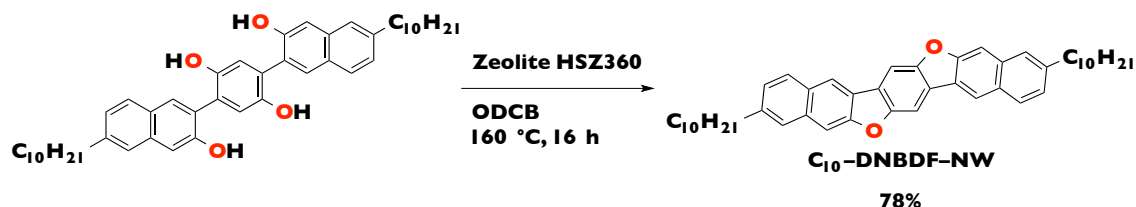
Dinaphtho[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]difuran (DNBDF)



Yield: 76%. The obtained compound was purified by vacuum sublimation with diffusion pump (High temperature region: 300 °C, Low temperature region: 170 °C, pressure: ca. 10^{-3} Torr). Pale yellow solid. M.p.: N.A. ^1H NMR (600 MHz, $\text{CDCl}_2\text{CDCl}_2$, 120 °C): δ 7.49 (dd, $J = 8.4$ Hz, 8.4 Hz, 2H, ArH), 7.53 (dd, $J = 8.4$ Hz, 8.4 Hz, 2H, ArH), 7.94 (s, 2H, ArH), 7.97 (d, $J = 8.4$ Hz, 2H, ArH), 8.05 (d, $J = 8.4$ Hz, 2H, ArH), 8.17 (s, 2H, ArH), 8.46 (s, 2H, ArH). ^{13}C NMR spectra could not be recorded due to

the low solubility. HRMS (APCI+): Calcd for $C_{26}H_{15}O_2$ [M+H] 359.1072, found, 359.1067. Anal. Calcd for $C_{26}H_{14}O_2$: C, 87.13; H, 3.94. Found C, 87.15; H, 4.08.

3,11-Didecyldinaphtho[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]difuran (C_{10} -DNBDF-NW)



Yield: 78%. The obtained compound was purified by vacuum sublimation with diffusion pump (High temperature region: 330 °C, Low temperature region: 230 °C, pressure: ca. 10^{-3} Torr). Pale yellow solid. M.p.: 371 °C (determined by DSC). 1H NMR (600 MHz, $CDCl_2/CDCl_2$ at 100 °C): δ 0.89 (t, $J = 6.6$ Hz, 6H, CH_3), 1.25–1.44 (m, 28H, $(CH_2)_7$), 1.78 (quin, $J = 7.2$ Hz, 4H, $ArCH_2CH_2$), 2.83 (t, $J = 7.2$ Hz, 4H, $ArCH_2$), 7.34 (d, $J = 8.4$ Hz, 2H, ArH), 7.72 (s, 2H, ArH), 7.86 (s, 2H, ArH), 7.95 (d, $J = 8.4$ Hz, 2H, ArH), 8.12 (s, 2H, ArH), 8.40 (s, 2H, ArH). ^{13}C NMR spectra could not be recorded due to the low solubility. HRMS (APCI+): Calcd for $C_{46}H_{55}O_2$ [M+H] 639.4202, found, 639.4197. Anal. Calcd for $C_{46}H_{54}O_2$: C, 86.47; H, 8.52. Found C, 86.63; H, 8.14.

2. Absorption Spectra in Evaporated Thin Film

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. **DNBDF** derivatives in solution were prepared in degassed 1,2-dichlorobenzene.

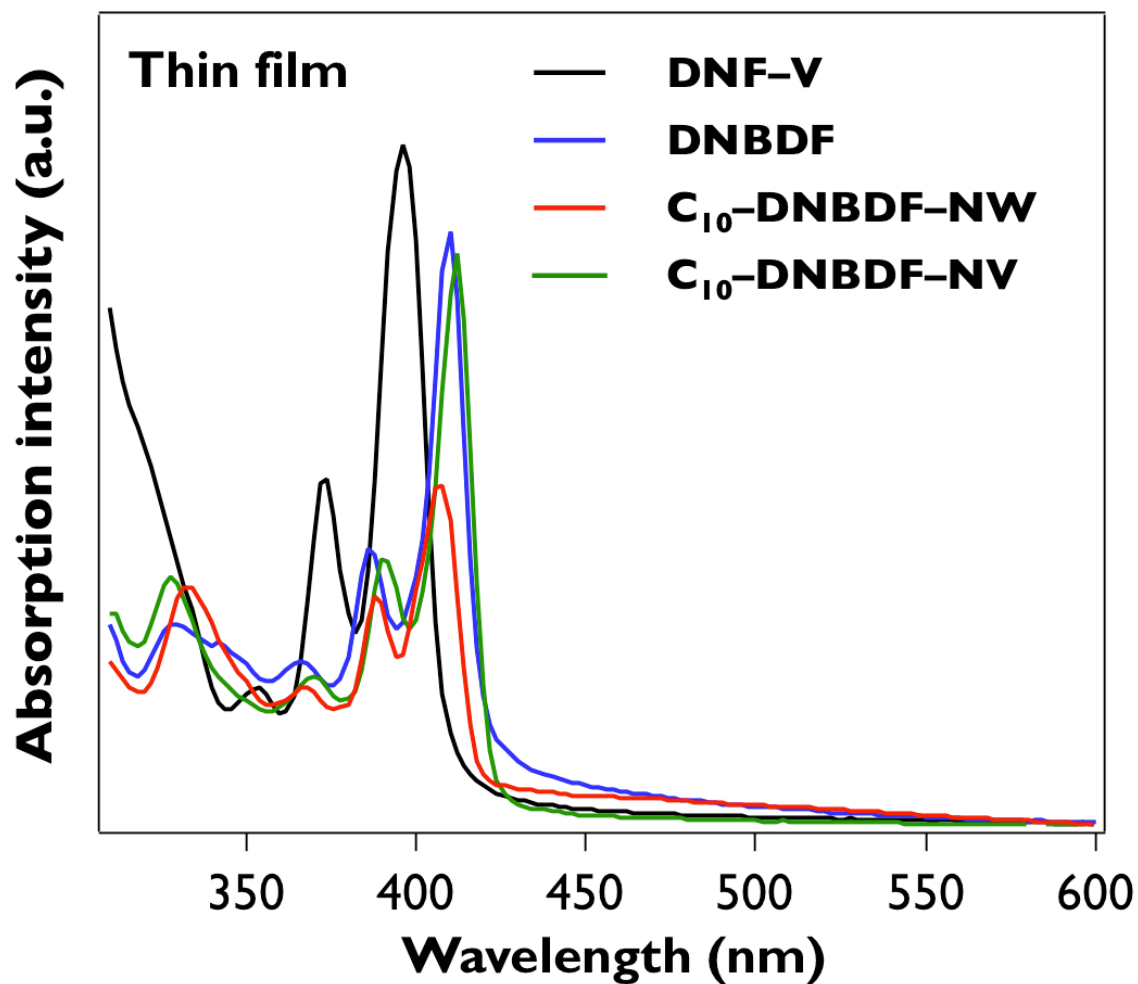


Figure S1. Absorption spectra of **DNBDF** derivatives and **DNF-V** (**DNBDF**: blue, **C₁₀-DNBDF-NW**: red, **C₁₀-DNBDF-NV**: green, **DNF-V**: black) in vacuum deposited thin films on quartz substrate.

3. 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 1,2-dichlorobenzene.

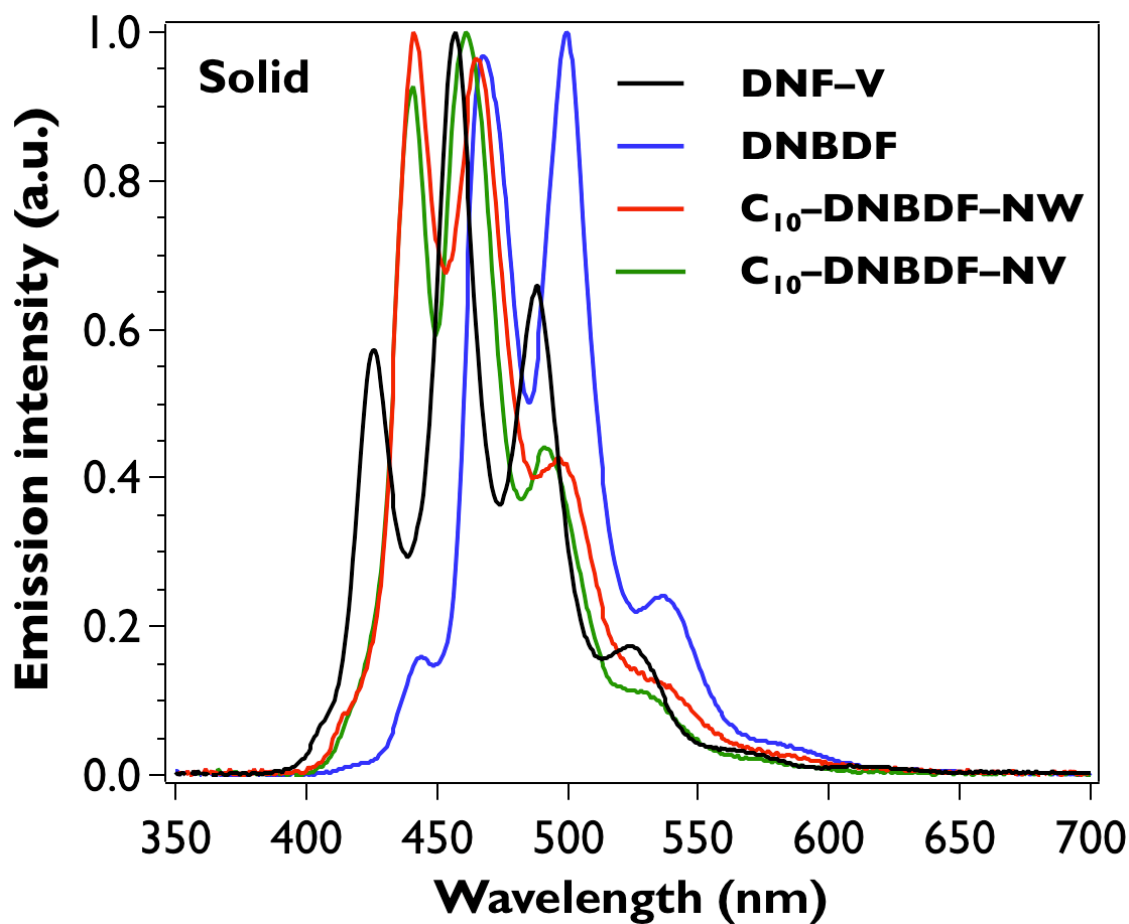


Figure S2. Fluorescent spectra of DNBDF derivatives and DNF-V (DNBDF: blue, C₁₀-DNBDF-NW: red, C₁₀-DNBDF-NV: green, DNF-V: black) in solid state.

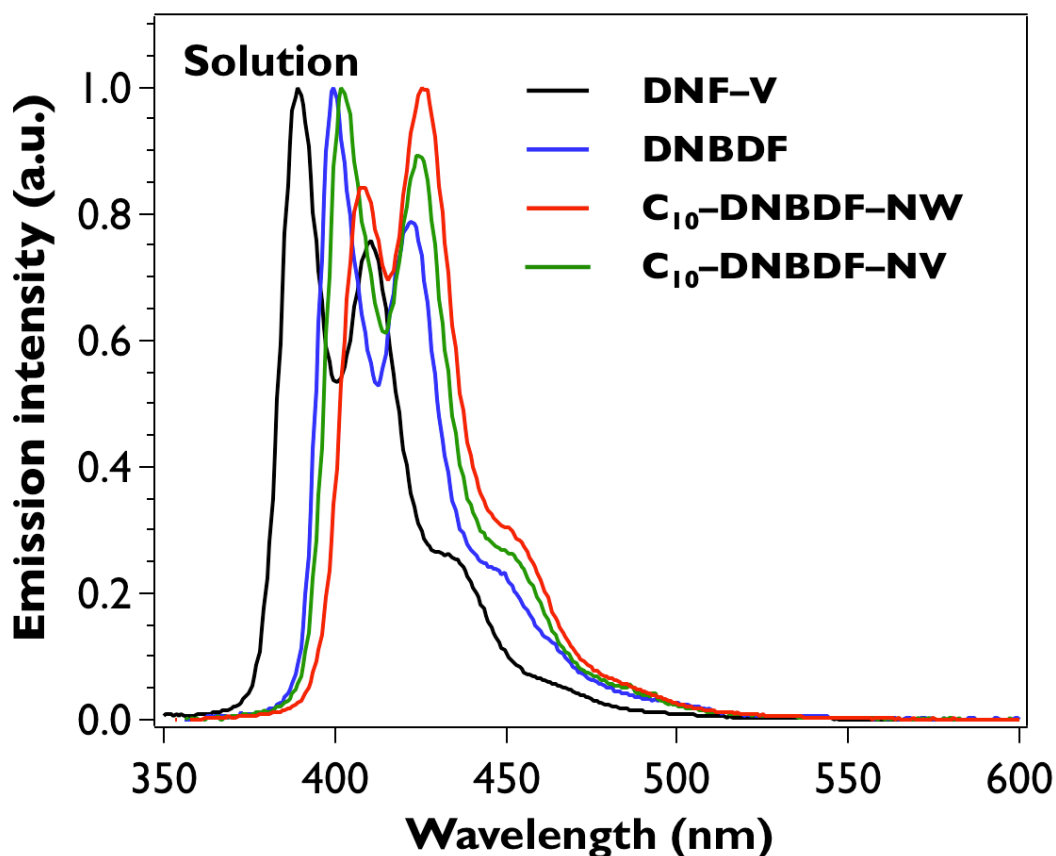


Figure S3. Fluorescent spectra of **DNBDF** derivatives in 1,2-dichlorobenzene solution and **DNF-V** in 1,2-dichloroethane. (**DNBDF**: blue, **C₁₀-DNBDF-NW**: red, **C₁₀-DNBDF-NV**: green, **DNF-V**: black)

Table S1. Summarized optical properties of **DNF-V**, **DNBDF**, **C₁₀-DNBDF-NW**, and **C₁₀-DNBDF-NV**

| Compound | UV/Vis absorption | Fluorescence in solution | | Fluorescence in solid state | |
|--------------------------------|------------------------------------|------------------------------------|----------------|------------------------------------|----------------|
| | λ_{\max} (nm) ^a | λ_{\max} (nm) ^b | Φ (solu.) | λ_{\max} (nm) ^c | Φ (solid) |
| DNF-V ^d | 322, 337, 362, 382 | 389, 410, 431 (sh) | 0.83 | 408 (sh), 427, 455, 488, 524 | 0.72 |
| DNBDF | 295, 346, 362, 394 | 400, 422, 446 (sh) | 0.65 | 444, 468, 500, 536 | 0.71 |
| C₁₀-DBDNF-NW | 294, 349, 367, 396 | 408, 425, 452 (sh) | 0.78 | 441, 465, 497, 535 (sh) | 0.36 |
| C₁₀-DNBDF-NV | 294, 349, 367, 397 | 402, 424, 450 (sh) | 0.69 | 441, 461, 491, 527 (sh) | 0.42 |

^a Wavelength of absorption intensity maximum in 1,2-dichlorobenzene. ^b Wavelength of emission intensity maximum in 1,2-dichlorobenzene. ^c Wavelength of emission intensity in solid state. ^d Measured in 1,2-dichlorobenzene.

4. Ionization Potentials

Photoelectron yield spectroscopy (PYS) was performed on a Sumitomo Heavy Industries Advanced Machinery PYS-202. For PYS measurements, thin films (*ca.* 100 nm) of **DNBDF** derivatives were thermally evaporated on ITO coated quartz substrates and measurements were performed in vacuum. The photoelectron yield spectra are depicted in Figure S4.

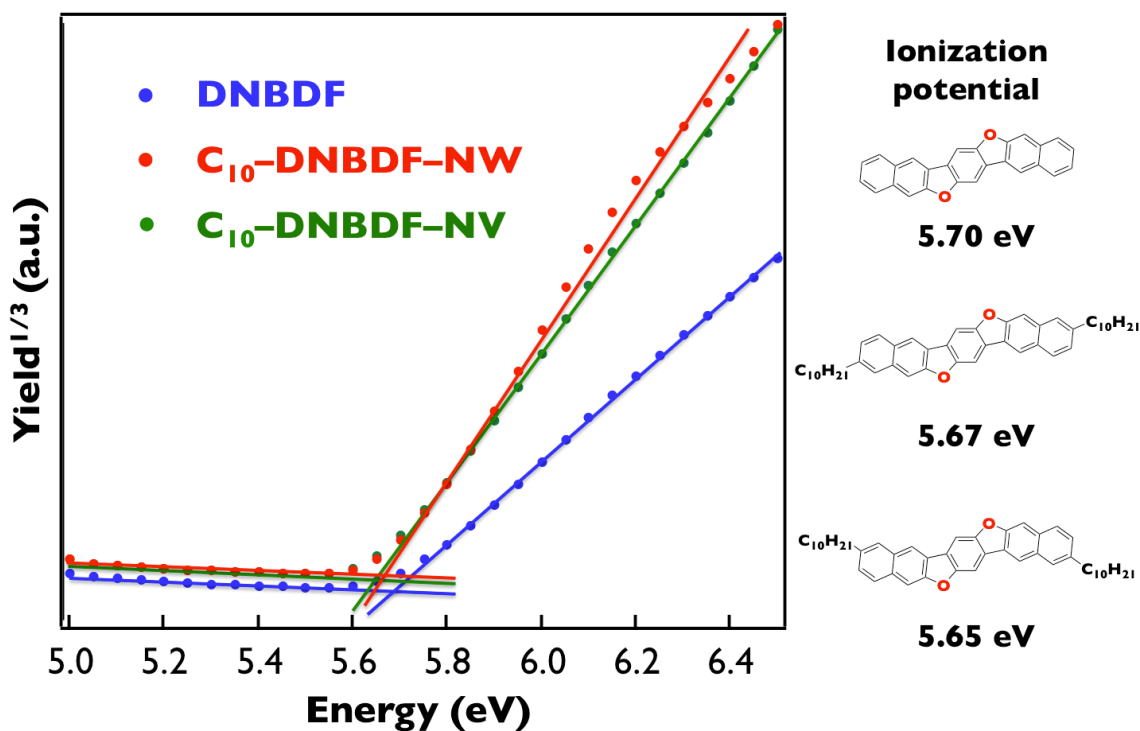


Figure S4. Photoelectron yield spectra of **DNBDF** derivatives in thin films after light illumination from a D₂ lamp *in vacuo*.

5. Thermal Analyses

5.1 Thermogravimetric Analyses (TGA)

TGA measurements were 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 N₂ purge at a flow rate of 100 mL/min. Al₂O₃ was used as reference material.

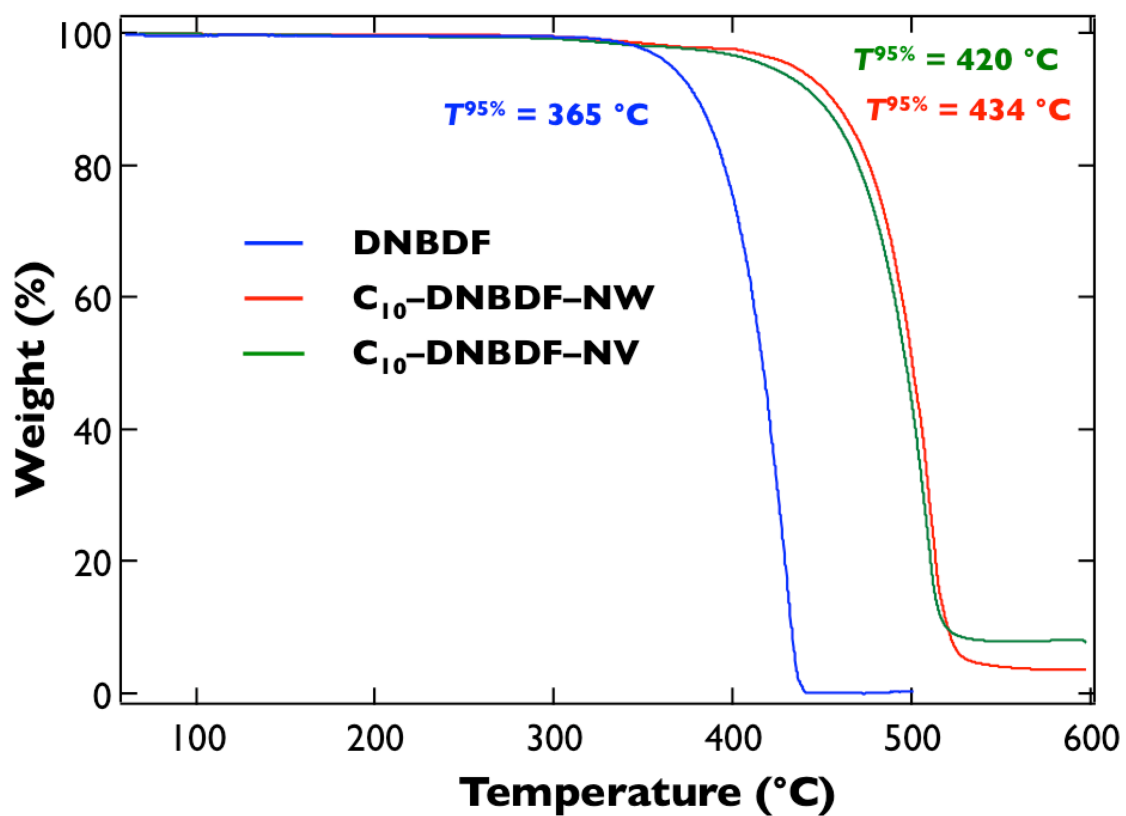


Figure S5. TGA charts of DNBDF derivatives.

5.2 Differential Scanning Calorimetric (DSC) Analyses

DSC measurements were 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 N₂ purge at a flow rate of 100 mL/min. Al₂O₃ was used as reference material.

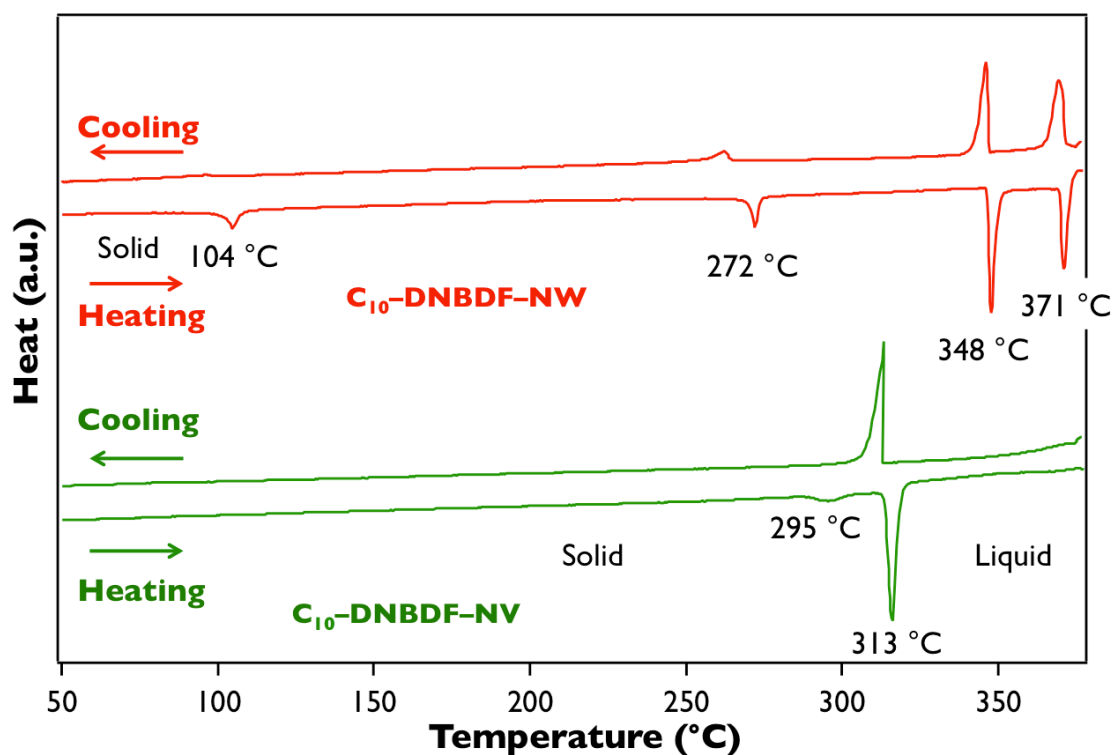


Figure S6. DSC charts of C₁₀-DNBDF-NW (red line) and C₁₀-DNBDF-NV (green line).

6. Single-Crystal Analyses

We have obtained the single crystals of **DNBDF** by physical vapor transport technique. Single crystals of **C₁₀-DNBDF-NV** and **C₁₀-DNBDF-NW** were prepared by means of recrystallization from a mixture of 1,2-dimethoxybenzene. Single crystal diffraction data were collected on a Rigaku R-Axis RAPID II imaging plate diffractometer with CuK α radiation.

Crystal data for **DNBDF**: C₂₆H₂₂O₂, $M = 366.46$, a colorless plate, $0.623 \times 0.454 \times 0.01$ mm, triclinic, $P-1$, $a = 5.946(3)$, $b = 7.516(4)$, $c = 18.704(10)$, Å, $\alpha = 96.63(2)^\circ$, $\beta = 91.21(2)^\circ$, $\gamma = 90.083(18)^\circ$, $V = 830.1(7)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.466$ g cm⁻³, $T = 296$ K, $2\theta_{\text{max}} = 128.1^\circ$, CuK α radiation, $\lambda = 1.54187$ Å, $\mu = 0.714$ mm⁻¹, 9927 reflections measured, 2926 unique reflections, $R_{\text{int}} = 16.28\%$, 253 parameters, $R_1 = 0.2121$ ($I > 2\sigma(I)$), $wR_2 = 0.5037$ (all data), CCDC-1400150.

Crystal data for **C₁₀-DNBDF-NW**: C₄₆H₅₄O₂, $M = 638.93$, a colorless plate, $0.523 \times 0.302 \times 0.005$ mm, orthorhombic, $Pbca$, $a = 7.3950(5)$, $b = 5.8775(4)$, $c = 80.760(6)$ Å, $V = 3510.2(4)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.209$ g cm⁻³, $T = 296$ K, $2\theta_{\text{max}} = 136.5^\circ$, CuK α radiation, $\lambda = 1.54187$ Å, $\mu = 0.545$ mm⁻¹, 36598 reflections measured, 3204 unique reflections, $R_{\text{int}} = 19.86\%$, 217 parameters, $R_1 = 0.1178$ ($I > 2\sigma(I)$), $wR_2 = 0.3051$ (all data), CCDC-1400149.

Crystal data for **C₁₀-DNBDF-NV**: C₄₆H₅₄O₂, $M = 638.93$, a colorless plate, $0.332 \times 0.165 \times 0.005$ mm, monoclinic, $P2_1/c$, $a = 41.774(10)$, $b = 7.4659(17)$, $c = 5.9023(13)$ Å, $\beta = 93.859(7)^\circ$, $V = 1836.6(7)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.155$ g cm⁻³, $T = 296$ K, $2\theta_{\text{max}} = 134.3^\circ$, CuK α radiation, $\lambda = 1.54187$ Å, $\mu = 0.521$ mm⁻¹, 7636 reflections measured, 1335 unique reflections, $R_{\text{int}} = 16.57\%$, 218 parameters, $R_1 = 0.1540$ ($I > 2\sigma(I)$), $wR_2 = 0.4401$ (all data), CCDC-1400151.

7. Theoretical Calculations

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

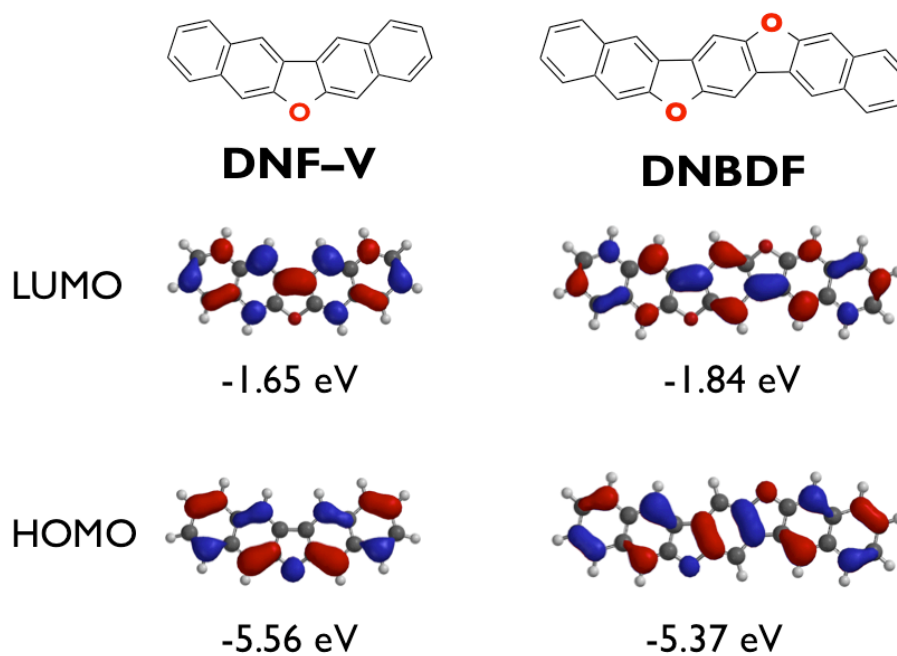


Figure S7. HOMO and LUMO of **DNF-V** and **DNBDF**.

Electronic band structure calculations were conducted based on the packing structure by way of 2-dimensional periodic boundary condition at the PBE/PBE/6-31G(d) level. The energies are plotted and labeled as $\Gamma = (0, 0, 0)$, $S = (0.5, 0.5, 0)$, $T = (0, 0.5, 0.5)$, $U = (0.5, 0, 0.5)$, $X = (0.5, 0, 0)$, $Y = (0, 0.5, 0)$, $Z = (0, 0, 0.5)$ in the crystallographic coordinates. Effective hole masses were calculated as $m^* = \hbar^2 \left(\frac{\partial^2 E(k)}{\partial k^2} \right)^{-1}$ along respective directions.

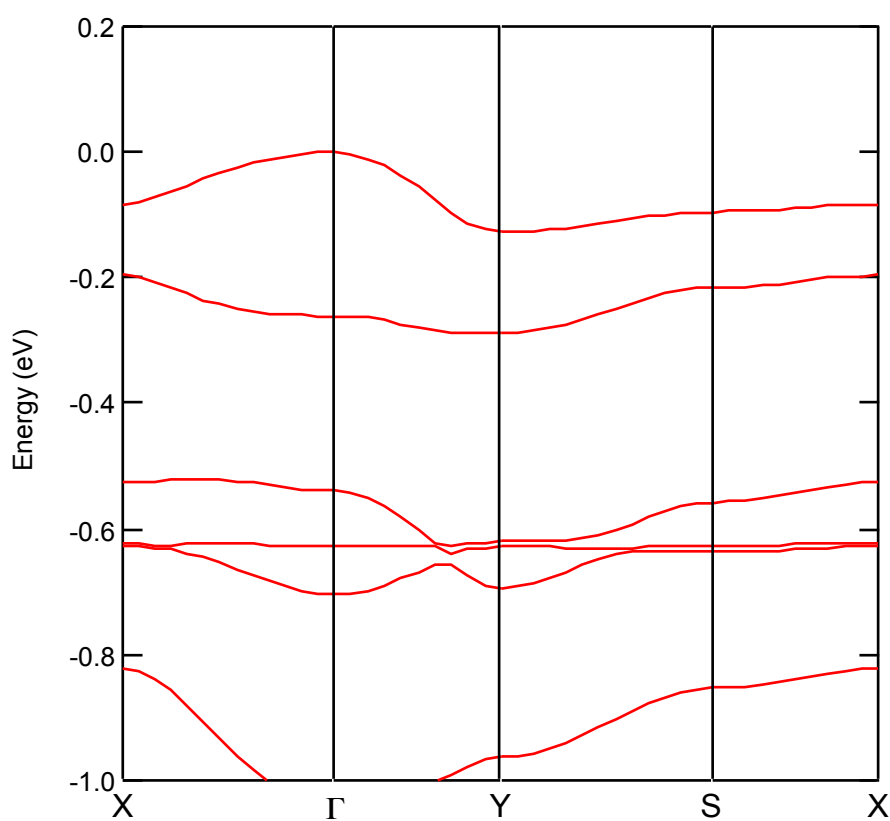


Figure S8. Electronic band structure of **DNBD** crystal (a - b plane). Left axis is the energy relative to the top of the valence band.

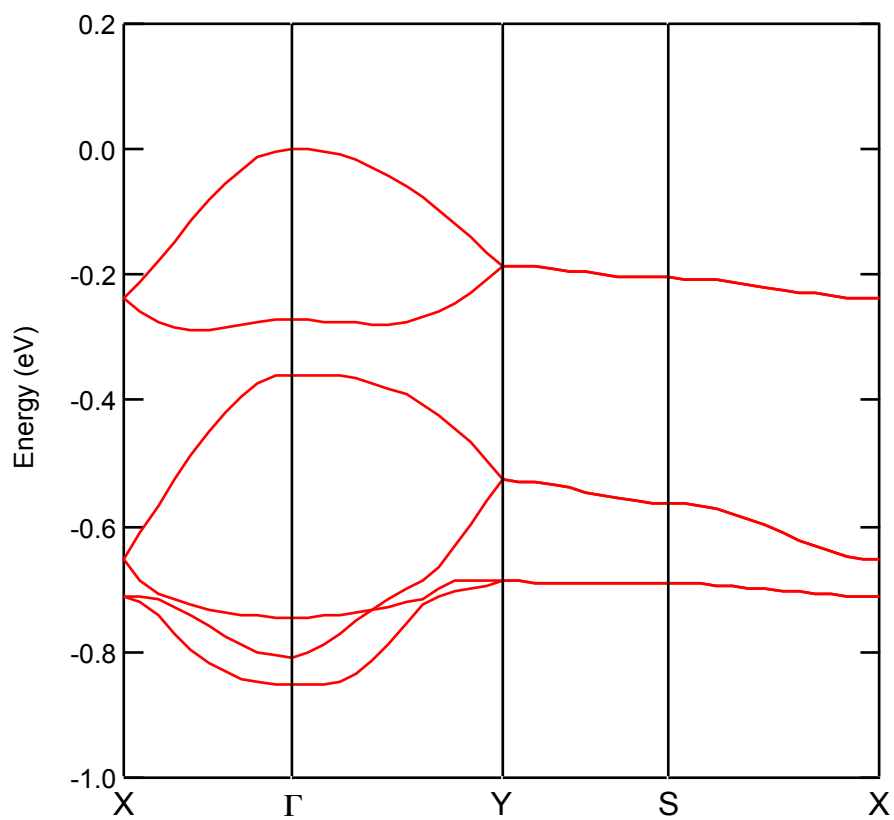


Figure S9. Electronic band structure of C_{10} -DNBDF-NW crystal (a - b plane). Left axis is the energy relative to the top of the valence band.

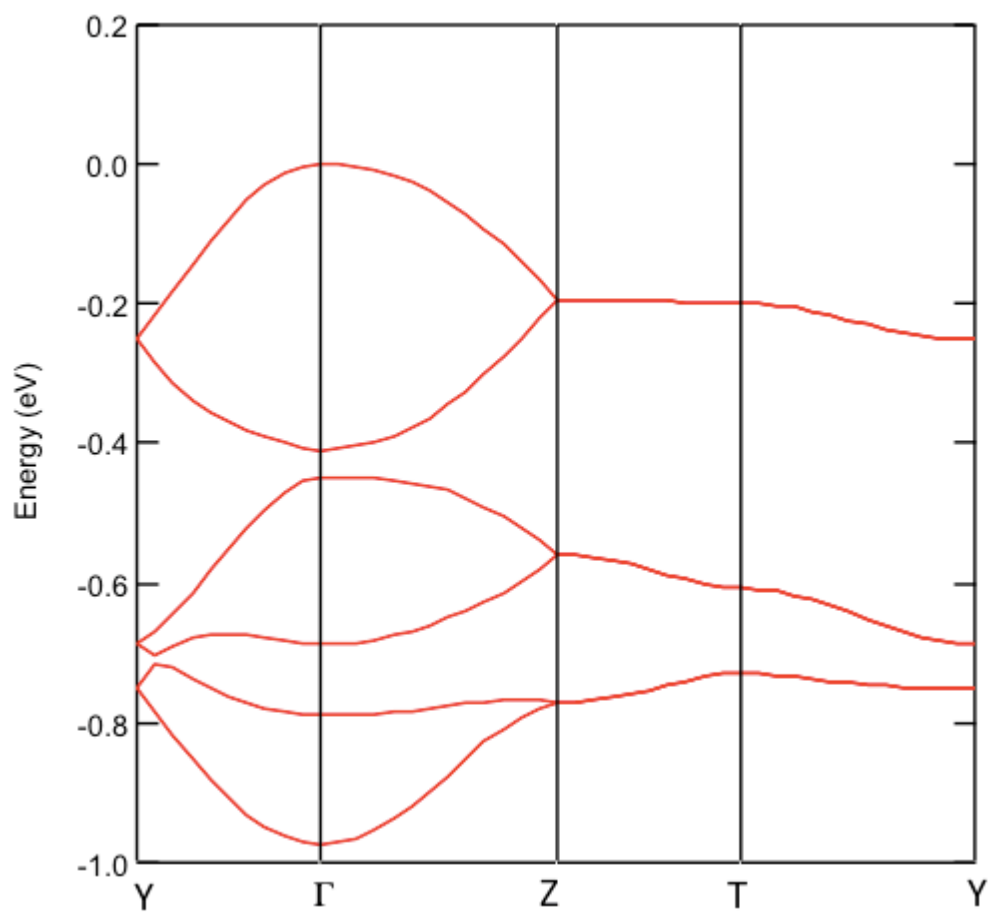


Figure S10. Electronic band structure of C_{10} -DNBDF-NV crystal (b - c plane). Left axis is the energy relative to the top of the valence band.

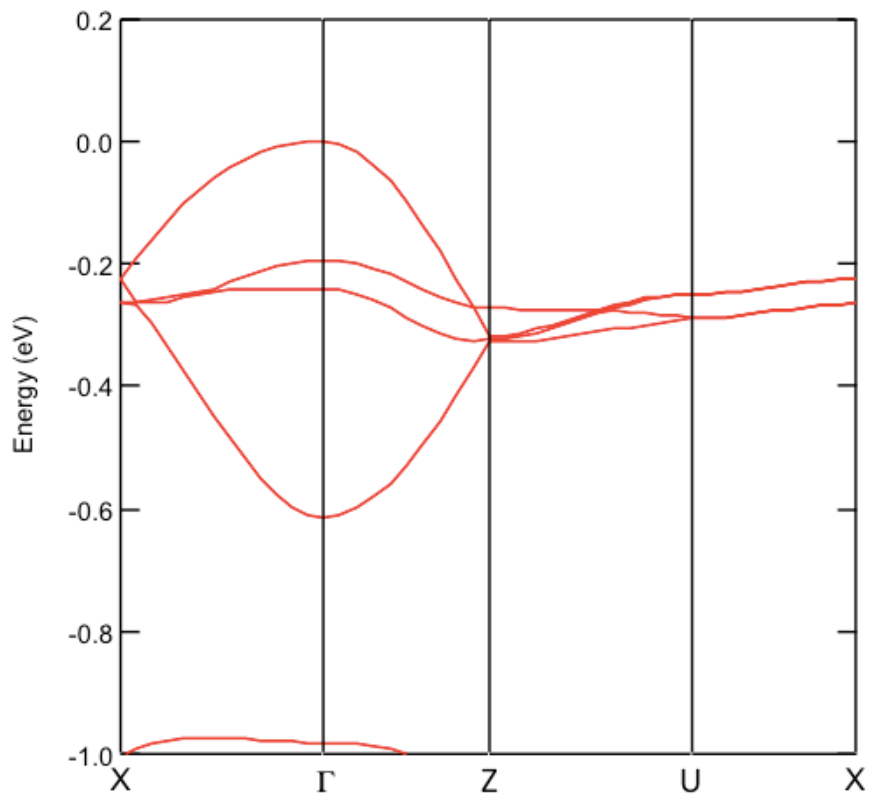


Figure S11. Electronic band structure of **C₁₀-DNF-VW** crystal (*a-c* plane). Left axis is the energy relative to the top of the valence band.

8. OFET Device Fabrication and Evaluation Procedure

The surface of the substrates with 500-nm-thick thermally oxidized SiO₂ on doped Si is first sonificated in acetone and 2-propanol for each 5 min, followed by UV-ozone exposure for 30 min. The surface of the cleaned substrates is treated with β -phenylethyltrichlorosilane (β -PTS) in toluene solution. To form the crystalline thin films, a 0.05 wt% solution of **C₁₀-DNBDF-NV** in 1,2,4-trichlorobenzene dissolved at 120 °C is dropped at an edge of a sustaining structure on a heated substrate at 90 °C and the crystalline domains grow in the direction of evaporation of the solvent. The structure to support the droplet can be removed after the growth of the crystalline film. Then, F₄-TCNQ (thickness: 1–2 nm) and the Au electrodes (thickness: 40 nm) are evaporated on the **C₁₀-DNBDF-NV** film through a shadow mask. The doped-Si layer acts as a gate electrode and SiO₂ layer as a dielectrics with relative permittivity of 3.9. A schematic illustration of FET is given in Figure S12. Electrical characterization was performed in ambient condition using a semiconductor parameter analyzer (Keithley 4200). Field-effect mobility (μ_{FET}) values were estimated from the saturation regime using the following equation:

$$I_{\text{D}} = (WC_{\text{i}}/2L)\mu_{\text{FET}}(V_{\text{G}} - V_{\text{th}})^2,$$

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.

Representative 5 device performances are depicted in Figure S14–18.

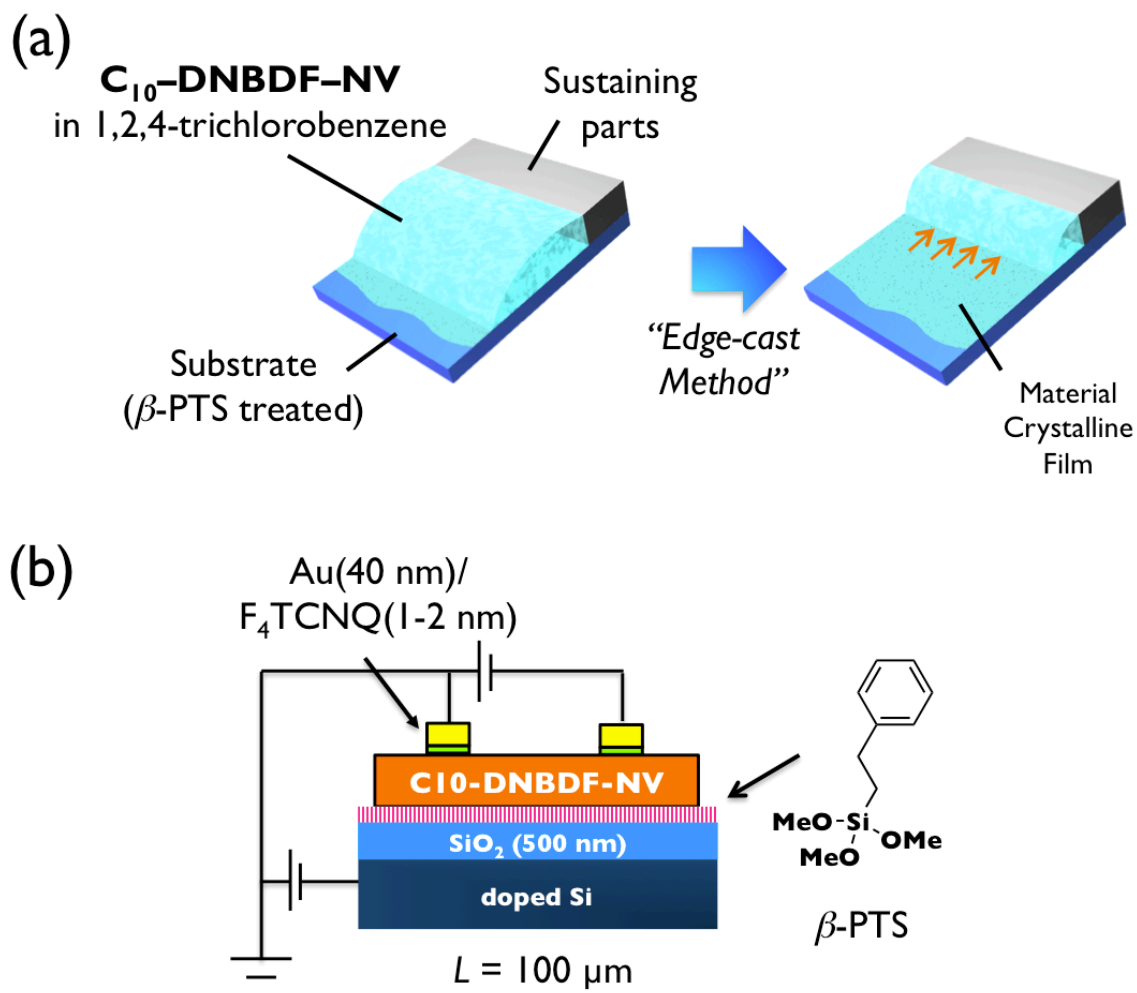


Figure S12. (a) Schematic image of the crystalline thin film formation by edge-cast method. (b) Schematic device structure based on **C₁₀-DNBDF-NV**.

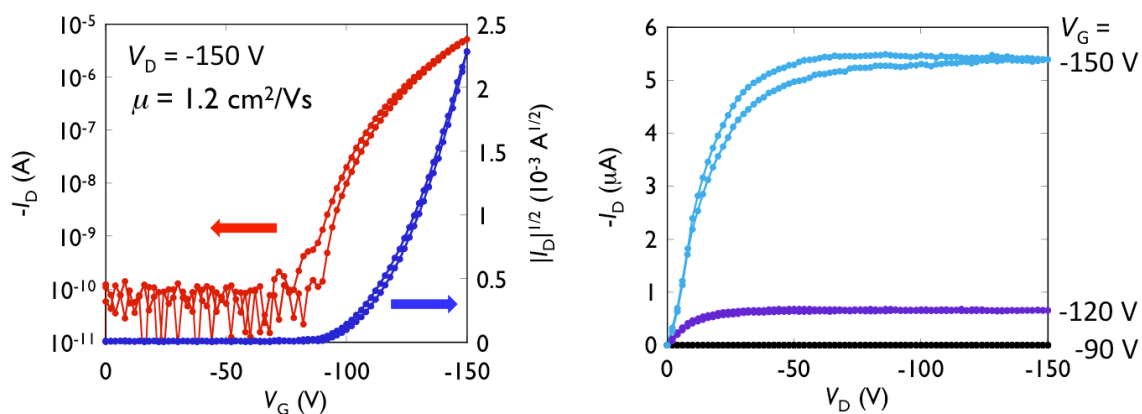


Figure S13. OFET characters of **C₁₀-DNBDF-NV** (Device 1). Transfer (left)- and output (right) characteristics ($L/W = 100/60$, SiO₂: 500 nm).

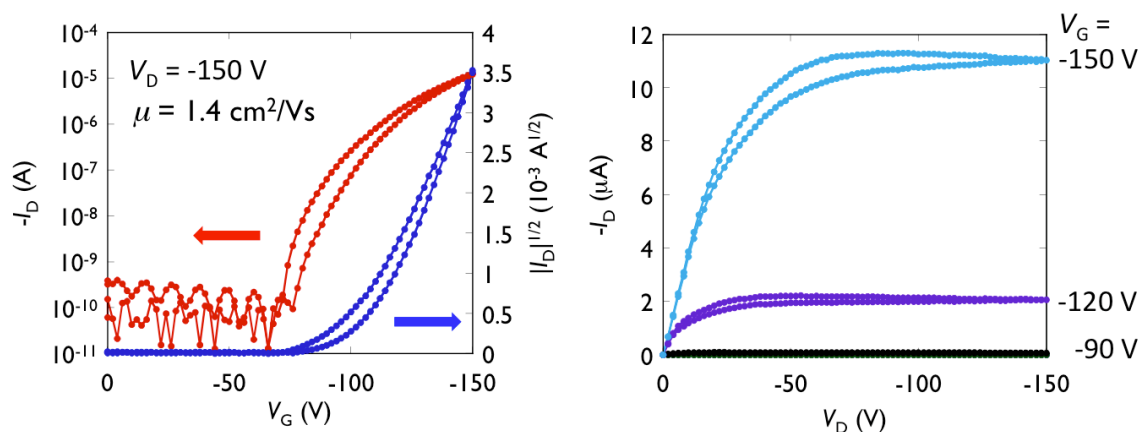


Figure S14. OFET characters of C_{10} -DNBDF-NV (Device 2). Transfer (left)- and output (right) characteristics ($L/W = 100/113$, SiO_2 : 500 nm).

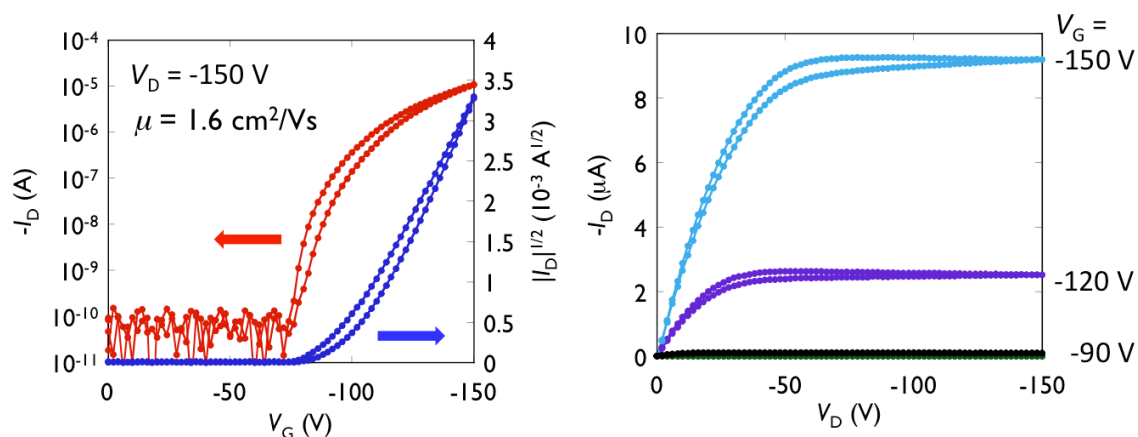


Figure S15. OFET characters of C_{10} -DNBDF-NV (Device 3). Transfer (left)- and output (right) characteristics ($L/W = 100/69$, SiO_2 : 500 nm).

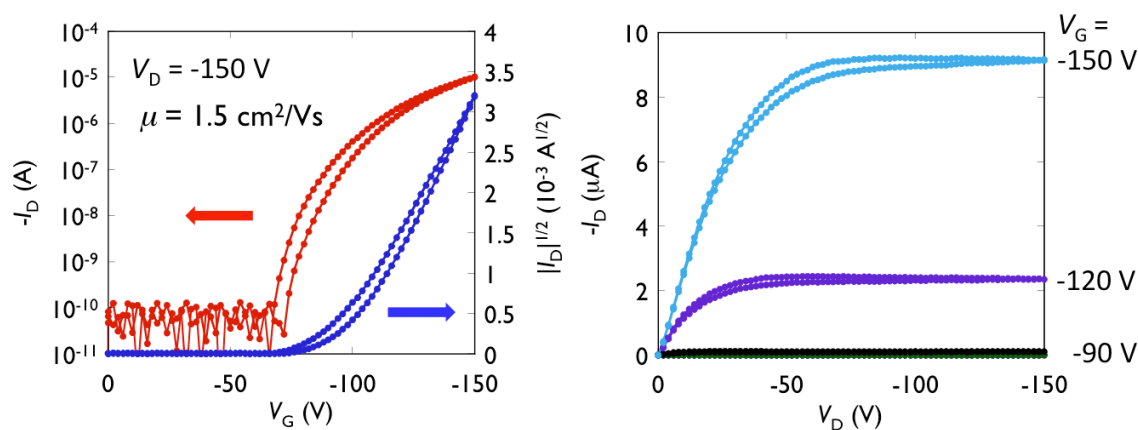


Figure S16. OFET characters of C_{10} -DNBDF-NV (Device 4). Transfer (left)- and output (right) characteristics ($L/W = 100/56$, SiO_2 : 500 nm).

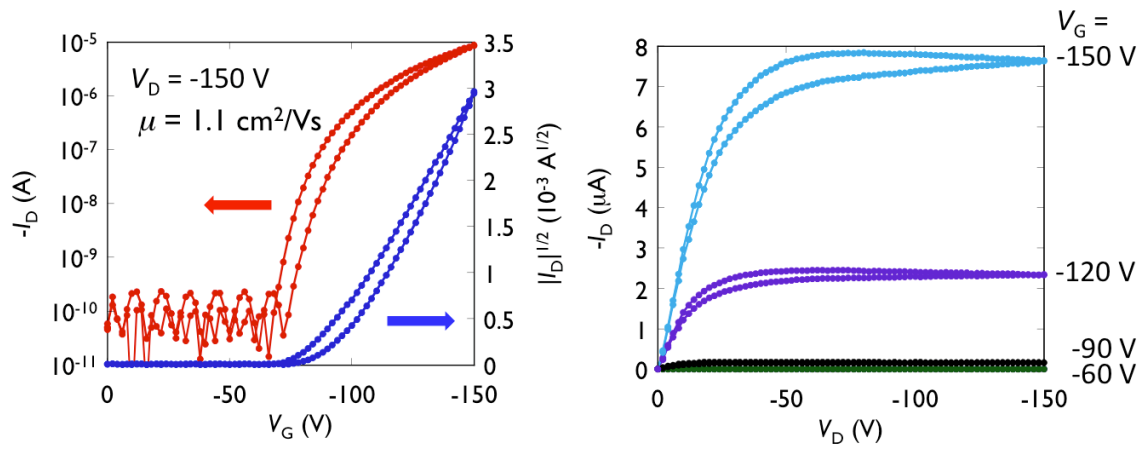


Figure S17. OFET characters of **C₁₀-DNBDF-NV** (Device 5). Transfer (left)- and output (right) characteristics ($L/W = 100/62$, SiO_2 : 500 nm).

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

The X-ray-diffraction measurements were performed using Rigaku Mercury 70 with $\text{CuK}\alpha$ radiation.

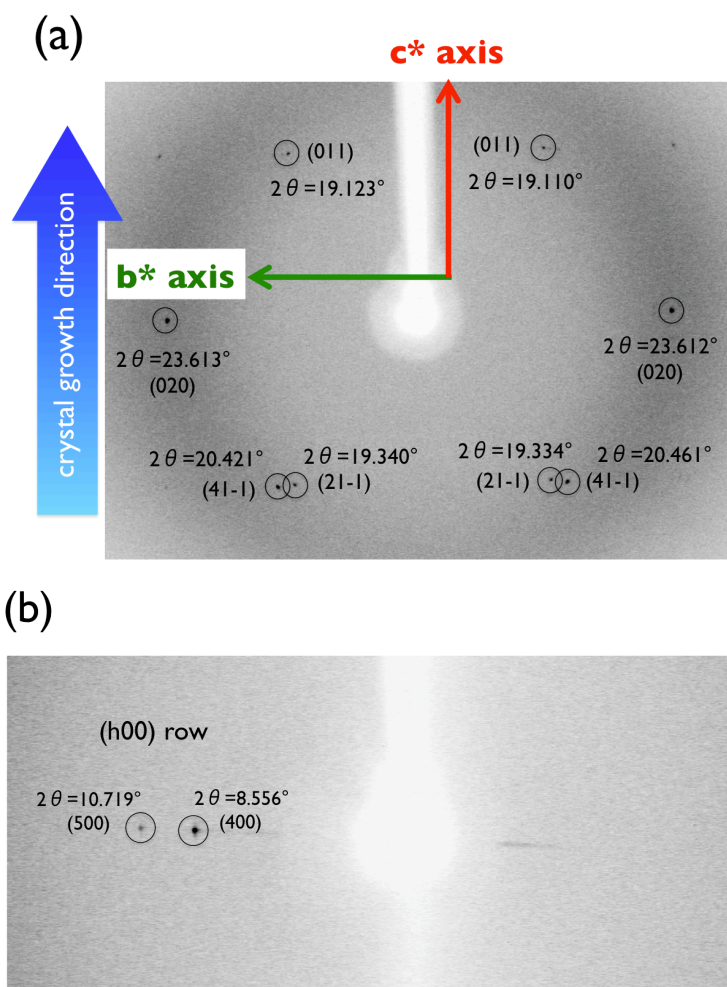


Figure S18. The Laue spots of the solution-crystallized C_{10} -DNBDF-NV thin film on the imaging plate in the (a) in-plane and (b) out-of-plane measurements.

10. Photograph of solution-crystallized thin film of C₁₀-DNBDF-NV

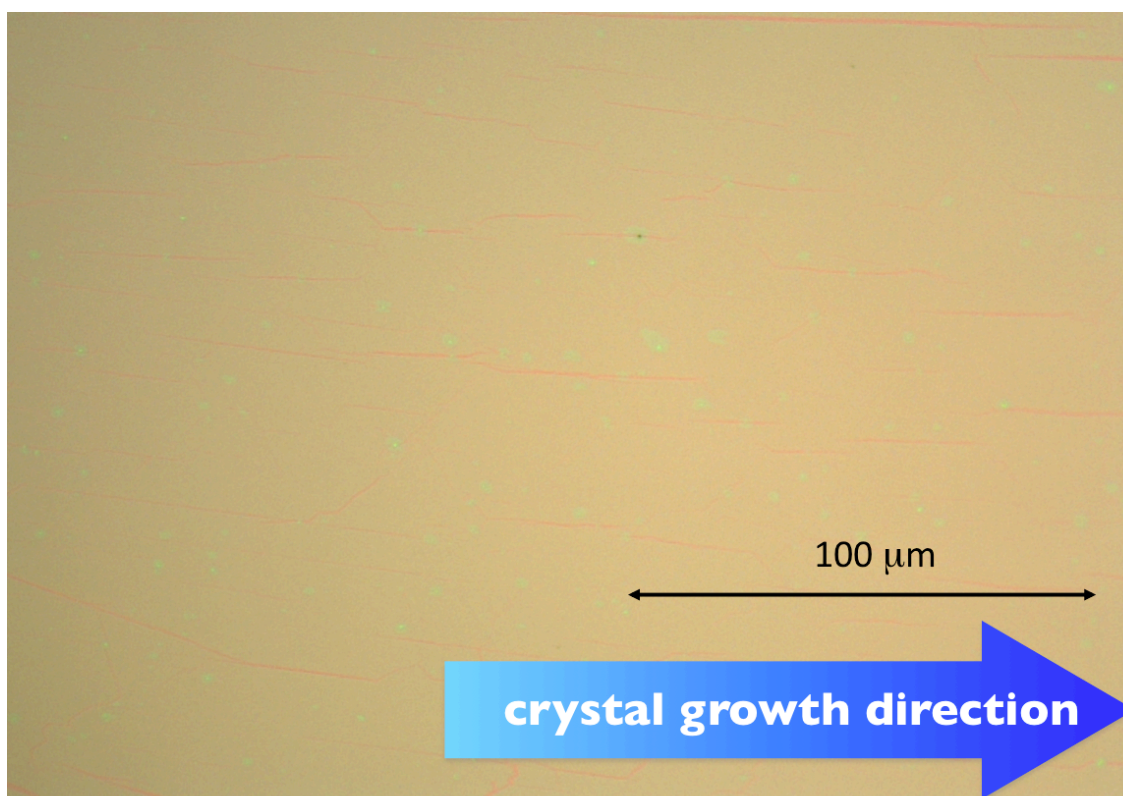


Figure S19. Representative photo of solution-crystallized thin film of C₁₀-DNBDF-NV.

11. References

- (1) K. Niimi, M. J. Kang, E. Miyazaki, I. Osaka, K. Takimiya, *Org. Lett.*, 2011, **13**, 3430–3433.
- (2) C. Mitsui, T. Okamoto, M. Yamagishi, J. Tsurumi, K. Yoshimoto, K. Nakahara, J. Soeda, Y. Hirose, H. Sato, A. Yamano, T. Uemura, J. Takeya, *Adv. Mater.*, 2014, **26**, 4546–4551.