Supporting Information for

# [2,2']Bi[naphtho[2,3-*b*]furanyl]: a versatile organic semiconductor with a furan-furan junction

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## 1. Synthesis of BNF (4)



Scheme S1. Synthesis of BNF (4).

**Experimental:** All chemicals and solvents are of reagent grade unless otherwise indicated. All reactions were carried out under nitrogen atmosphere. Melting points were uncorrected. Nuclear magnetic resonance spectra were obtained in deuterated chloroform with a JEOL EX-270 or a JEOL Lambda 400 spectrometer operating at 270 or 400 MHz, respectively, for <sup>1</sup>H, and a JEOL Lambda 400 or a Varian 500 MR spectrometer operating at 100 or 125 MHz, respectively, for <sup>13</sup>C with TMS as internal reference; chemical shifts ( $\delta$ ) are reported in parts per million. EI-MS spectra were obtained on a Shimadzu QP-5050A spectrometer using an electron impact ionization procedure (70 eV).

## 2-Bromo-3-methoxynaphthalene

To a solution of 2-methoxynaphthalene (47 g, 300 mmol) in THF (350 mL) was added 1.67 M hexane solution of n-BuLi (186 mL, 310 mmol) at -78 °C. After the mixture was stirred for 1 h at room temperature, 1,2-dibromoethane (27 mL, 320 mmol) was added to the solution at -78 °C, and the resulting mixture was stirred for 20 h at room temperature. The mixture was poured into a saturated aqueous ammonium chloride solution (100 mL) and was extracted with ether (30 mL × 3). The combined ethereal extracts were washed with brine (50 mL × 3), dried (MgSO<sub>4</sub>), and concentrated in vacuo. The residue was purified by recrystallization from hexane to give 3-bromo-2-methoxynaphthalene **1** (64 g, 90%) as a colorless solid. Analytical sample was obtained with recrystallization from hexane. Mp 65–66 °C (ref<sup>S1</sup> 76 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.98 (s, 3H), 7.13 (s, 1H), 7.38 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 7.48 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 5.2 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  56.4, 106.8, 113.5, 124.9, 126.8, 126.9 (×2), 129.6, 132.4, 133.7, 153.6; EI-MS (70 eV) m/z = 236 (M<sup>+</sup>)

#### 3-Bromo-naphthalen-2-ol

To a solution of 2-bromo-3-methoxynaphthalene **1** (60 g, 253 mmol) in dichloromethane (500 mL) was added dropwise a dichloromethane solution of BBr<sub>3</sub> (ca. 4 M 100 mL, 400 mmol) at -78 °C. After the stirring was maintained for 20 h at room temperature, the mixture was added ice (approximately 100 g) at 0 °C. The resulting mixture was extracted with dichloromethane (200 mL × 3). The combined organic layer was washed with brine (100 mL × 3), dried (MgSO<sub>4</sub>) and concentrated in vacuo. The residue was purified by recrystallization from hexane to give 3-bromo-naphthalen-2-ol **2** (56 g, quantitative yield) as a colorless solid. Mp 79–80 °C (ref<sup>S1,2</sup> 80–81 °C); <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  5.61 (s, 1H), 7.34 (dd, *J* = 8.0 Hz, 7.9 Hz, 1H), 7.38 (s, 1H), 7.44 (dd, *J* = 8.0 Hz, 7.9 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 8.01 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  111.0, 112.9, 124.8, 126.9, 127.0, 127.2, 129.8, 131.5, 134.8, 149.7; IR (KBr) v = 3421 cm<sup>-1</sup> (-OH); EI-MS (70 eV) *m/z* = 222 (M<sup>+</sup>)

# 2-Acetoxy-3-bromonaphthalene

To a solution of 3-bromo-2-hydroxynaphthalene **2** (20 g, 90 mmol) and triethylamine (37.8 mL, 278 mmol) in dichloromethane (500 mL) was added acetic anhydride (9.6 mL, 102 mmol) at 0 °C. After stirring for 16 h at room temperature, the mixture was diluted with water (100 mL) and hydrochloric acid (4 M, 100 mL). The resulting mixture was extracted with dichloromethane (100 mL × 3). The combined organic layers were washed with brine (200 mL × 3), dried (MgSO<sub>4</sub>), and concentrated in vacuo to give practically pure 2-acethyloxy-3-bromonaphthalene **6** (23.8 g, quantitative yield) as a yellow solid. Mp 82–83 °C; <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  2.40 (s, 1H), 7.45–7.52 (m, 2H), 7.59 (s, 1H), 7.74–7.78 (m, 2H), 8.11 (s, 1H), 8.10 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  21.2, 115.4, 121.2, 127.0, 127.1, 127.2, 127.8, 132.6, 132.7, 133.0, 145.7, 169.3; IR (KBr) v = 1785 cm<sup>-1</sup> (C=O); EI-MS, *m*/*z* = 264 (M<sup>+</sup>); Anal. Calcd for C<sub>12</sub>H<sub>9</sub>BrO<sub>2</sub>: C, 54.37; H, 3.42%. Found: C, 54.41; H, 3.30%

#### 2-Acethyloxy-3-(trimethylsilylethynyl)naphthalene

To a deaerated solution of 2-acethyloxy-3-bromonaphthalene (2.6 g, 10 mmol) in triethylamine (30 mL) and DMF (30 mL) was added trimethylsilylacetylene (1.7 mL, 12mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (211 mg, 0.3 mmol, 3mol%) and CuI (114 mg, 0.6 mmol, 6 mol%). After stirring for 15 h at room temperature, the mixture was diluted with water (100 mL) and hydrochloric acid (4 M, 60 mL). The resulting mixture was extracted with dichloromethane (50 mL × 3). The combined organic layers were washed with brine (50 mL × 3), dried (MgSO<sub>4</sub>), and got through silicagel pad. The solution was concentrated in vacuo to give 2-acethyloxy-3-(trimethylsilylethynyl)naphthalene (2.8 g, quantitative yield) as a pale yellow solid. Mp 85–87 °C; <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  0.27 (s, 9H), 2.38 (s, 3H), 7.44–7.52 (m, 2H), 7.75–7.79 (m, 2H), 8.04 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  0.29, 21.2, 99.7, 100.3, 116.6, 119.7, 126.7, 127.7, 127.8, 128.0, 131.4, 133.7, 134.1, 148.6, 169.4; IR (KBr) v = 1767 cm<sup>-1</sup> (C=O); EI-MS, *m*/*z* = 282 (M<sup>+</sup>); Anal. Calcd for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>Si: C, 72.30; H, 6.42%. Found: C, 72.24; H, 6.71%.

#### Naphtho[2,3-b]furan (6)

To a suspension of cesium carbonate (1.3 g, 4.0 mmol) in N,N-dimethylacetamide (40 mL) and water (2 mL) was added 2-acethyloxy-3-(trimethylsilylethynyl)naphthalene (282 mg, 1.0 mmol), then stirred at 80 °C for 5 h. After poured into 200 mL of saturated aqueous ammonium chloride solution, the precipitation was collected by filtration and washed with water. The solid was solved with chloroform and purified by flash column chromatography on silica gel to give naphtho[2,3-*b*]furan (131 mg, 78%) as pale yellow crystals. Mp 110–112 °C (ref.<sup>S3</sup> 119 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.88 (dd, *J* = 2,3 Hz, 0.88 Hz, 1H), 7.39–7.47 (m, 2H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.91–7.96 (m, 3H), 8.07 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  106.6, 107.3, 119.4, 124.3, 125.2, 128.2, 128.4, 128.8, 130.7, 131.9, 147.6, 154.1; EI-MS, *m*/*z* = 168 (M<sup>+</sup>).

# [2,2']Bi[naphtho[2,3-b]furanyl] (BNF, 4)

To a solution of naphtho[2,3-*b*]furan (336 mg, 2 mmol) in THF (30 mL) was added 1.67 M hexane solution of n-BuLi (1.5 mL, 2.5 mmol) at -78 °C. After the mixture was stirred for 1 h at room temperature, CuCl<sub>2</sub> (403 mg, 3.0 mmol) was added to the solution at -78 °C, and the resulting mixture was stirred for 20 h at room temperature. The mixture was poured into a saturated aqueous ammonium chloride solution (50 mL) and the precipitation was collected by filtration and washed with water. The solid was purified by repetitive gradient sublimation in vacuo (ca. 230 °C at <  $10^{-2}$  Pa under nitrogen atmosphere) to give analytical and device grade sample of BNF as yellow-green crystals (94 mg, 28% yield). Mp > 300 °C; EI-MS (70 eV) *m/z* = 334 (M<sup>+</sup>). Anal. Calcd for C<sub>24</sub>H<sub>14</sub>O<sub>2</sub>: C, 86.21; H, 4.22%. Found: C, 85.98; H, 3.93%.

#### 2. X-ray structural analysis of BNF (4)

Recrystallization from chlorobenzene gave single crystals of **4** suitable for X-ray analysis. The X-ray crystal structure analysis was made on a Rigaku RAPID-IP (Mo $K\alpha$  radiation,  $\lambda = 0.71069$  Å, graphite monochromator, T = 296 K,  $\omega$  scan,  $2\theta_{max} = 55.0^{\circ}$ ) or on a Rigaku Mercury-CCD (Mo $K\alpha$  radiation,  $\lambda = 0.71069$  Å, graphite monochromator, T = 296 K,  $2\theta_{max} = 55.0^{\circ}$ ). The structure was solved by the direct methods.<sup>S4</sup> Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the calculations but not refined. All calculations were performed using the crystallographic software package TeXsan 1.2.<sup>S5</sup>





Figure S1. Molecular structure of BNF (a) and packing structure (b).

# 3. MO calculation for BNF (4) and BNT (5)

MO calculations were carried out with the DFT/TD-DFT method at the B3LYP/6-31g(d) level using Gaussian 03 program package.<sup>S6</sup>



Figure S2. Calculated HOMO and LUMO of BNF (4) and BNT (5).

	$E_{\rm ox} \stackrel{\rm onset}{\sim} /$	$\lambda_{\max}$ ( $\lambda_{e}$	edge) /	$\lambda^{ m PL}$ max /	$\phi_{\rm em}$ b	$E_{ m HOMO}$ /	$E_{\rm g}$ / eV	IP / eV $^{\rm c}$	$E_{\rm HOMO,}~E_{\rm LUMO}$
	V <sup>a</sup>	nm		nm		eV			(Calcd) <sup>d</sup>
BNF (4)	+1.20	368,	390	400, 430	0.88	-5.6	3.00	5.68	-5.27, -1.93
		(410)							
BNT $(5)^{\mathrm{e}}$	+1.36	369,	392	430, 435	0.014	-5.73	2.99	5.61	-5.28, -2.01
		(415)							

Table S1. Electronic properties of 4 and 5.

<sup>a</sup> V vs. Ag/AgCl. All the potentials were calibrated with the Fc/Fc<sup>+</sup> ( $E^{1/2} = +0.43$  V measured under identical conditions). <sup>b</sup> determined by the relative method using 9,10-diphenylanthoracene ( $\phi_{em}$  0.90) as the standard. <sup>c</sup> determined by photoemission yield spectroscopy in air. <sup>d</sup> see Figure S2. <sup>e</sup> Mamada, M.; Nishida, J.-i.; Kumaki, D.; Tokito, S.; Yamashita, Y. *J. Mater. Chem.* **2008**, *18*, 3442–3447.

## 4. Thin film deposition and fabrication of OFET and OPV devices based on BNF (4)

**OFETs**: OFETs were fabricated in a "top-contact" configuration on a heavily doped n<sup>+</sup>-Si (100) wafer with a 200 nm thermally grown SiO<sub>2</sub> ( $C_i = 17.3 \text{ nF cm}^{-2}$ ). The substrate surfaces were treated with octyltrichlorosilane (OTS), octadecyltrichlorosilane (ODTS), or hexamethyldisilazane (HMDS) as reported previously.<sup>S7</sup> A thin film BNF (**4**) as the active layer was vacuum-deposited on the Si/SiO<sub>2</sub> substrates maintained at various temperatures ( $T_{sub}$ ) at a rate of 1 Å s<sup>-1</sup> under a pressure of ~10<sup>-3</sup> Pa. On top of the organic thin film, gold films (80 nm) as drain and source electrodes were deposited through a shadow mask. For a typical device, the drain-source channel length (*L*) and width (*W*) are 50 µm and 1.5 mm, respectively. Characteristics of the OFET devices were measured at room temperature under ambient conditions with a Keithley 4200 semiconducting parameter analyzer. Field-effect mobility ( $\mu_{FET}$ ) was calculated in the saturation regime ( $V_d = -60$  V) of the I<sub>d</sub> using the following equation,

 $I_{\rm d} = C_{\rm i} \ \mu_{\rm FET} \ (W/2L) \ (V_{\rm g} - V_{\rm th})^2$ 

where  $C_i$  is the capacitance of the SiO<sub>2</sub> insulator, and  $V_g$  and  $V_{th}$  are the gate and threshold voltages, respectively. Current on/off ratio ( $I_{on}/I_{off}$ ) was determined from the I<sub>d</sub> at  $V_g = 0$  V ( $I_{off}$ ) and  $V_g = -60$  V ( $I_{on}$ ). The  $\mu_{FET}$  data reported are typical values from more than ten different devices.



Figure S3. FET characteristics of vapor processed 4-based OFETs: (a) transfer and (b) out-put curves.



Figure S4.AFM image (a) and XRD (b) of vapor deposited thin film of 4.

**OPVs:** Standard bilayer solar cells were fabricated by using sequential vacuum depositions on ITO-coated glass substrates. Twice vacuum sublimed NDF (**4**), C<sub>60</sub>, C<sub>70</sub>, and BCP in our laboratory were used. The ITO substrates (110 nm thickness on glass, sheet resistance  $< 20 \ \Omega$  square<sup>-1</sup>) were successively washed by ultrasonication in a neutral detergent, deionized water, distilled water, acetone, and isopropanol for 10 min. Then, they were treated with UV ozone for 20 min immediately prior to loading into a vacuum chamber ( $\sim 3 \times 10^{-3}$  Pa). Thin films of NDF (deposition rate: 1 Å s<sup>-1</sup>, 40 nm), C<sub>60</sub> (deposition rate: 2 Å s<sup>-1</sup>, 30 nm), and BCP (2 Å s<sup>-1</sup>, 10 nm) were subsequently deposited, and then Al (1 Å s<sup>-1</sup>, 100 nm) used as the cathode was evaporated through a shadow mask with 2.0 mm diameter openings. Current-voltage (*J-V*) characteristics of cells were measured under simulated AM1.5G solar illumination (Asahi-Bunko Co., Ltd.) in air without encapsulation using a Keithley 2400 source meter. ND filters were used to adjust the light intensity measured with a calibrated broadband optical power meter (Newport Instruments).

Power conversion efficiency ( $\eta$ ) was calculated using

$$\eta = (J_{\rm sc} V_{\rm oc} FF)/P_{\rm o}$$

where  $V_{oc}$  is the open circuit voltage,  $J_{sc}$  is the short-circuit current density,  $P_o$  is the power of the incident light and *FF* is the fill factor.



Figure S5. Absorption spectra of  $BNF/C_{60}$  (or  $C_{70}$ )/BCP films.

# 5. OLET devices on vapor-grown single crystals of BNF (4)

Single crystals of BNF (4) were prepared by using physical vapor transport method with a flow of pure argon gas (50  $cm^3 min^{-1}$ ). As the organic active layer, large thin plate-like crystals, typical crystal size of 0.3 to 1 mm, were selected. The thicknesses of the single crystals of BNF (4) were typically 0.3 to 0.6 µm, as characterized by a Dektak profilometer. The light emitting OFETs (LE-OFET, or OLET) devices were fabricated with bottom-gate and top-contact configuration. A 300 nm-thick  $SiO_2$  layer on a highly doped n<sup>++</sup>-Si wafer was used as an insulator. To cover unwarranted electron traps on the SiO<sub>2</sub> surface, a 20 nm-thick poly(methyl methacrylate) (PMMA) layer was dip-coated from a toluene solution (10 mg ml<sup>-1</sup>) onto the surface of SiO<sub>2</sub> gate insulators. After the PMMA deposition, the substrates were first pre baked at 80 to 90 °C for 8 h in the nitrogen atmosphere condition, then baked at 100 to 110 °C for 15 min. Then, a BNF (4) single crystal was carefully placed on the substrate by utilizing the electrostatic force between the organic single crystal and the substrate. The substrates were transferred from the glove box to the metal chamber without exposing to air. The alignment of a shadow mask on the single crystal was hand-operated and checked by a charge-coupled device (CCD) camera in the glove box. A source and drain electrode was formed by using conventional thermal evaporation of gold and calcium metals through a shadow mask under a vacuum of  $< 3 \times$  $10^{-4}$  Pa. Their deposition rate and thickness were 0.3 nm s<sup>-1</sup> and 50 nm, respectively. To improve the hole injection, MoOx was inserted between organic single crystal and gold electrode. The channel lengths and width were carefully checked by optical microscope. The devices were then transferred to a measurement chamber without exposing to air. The dependence of the source-drain current ( $I_d$ )-external EL quantum efficiency ( $\eta_{ext}$ ) characteristics on gate voltage  $(V_g)$  were measured by using a semiconductor parameter analyzer (Agilent B 1500) under vacuum of  $1 \times 10^{-3}$  Pa at room temperature. Light-emission intensity from the top of device was captured by using calibrated Si-photodiode and external quantum efficiency directly obtained by and optical power meter (Model 1835-C, New port).



Figure S6. Emission of BNF (4) single crystal under the backlight irradiation.

#### 6. Emission spectra of BNF single crystal and thin film

The PL characteristics of the vapor-grown crystals and the evaporated thin films were measured on a spectrophotometer (FP-6500-A-51, Jasco Co., Tokyo, Japan).



Figure S7. Emission spectra of BNF (4): single crystal (a) and evaporated thin film (b).

# 7. References

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S10



S11





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Low solubility of BNF (4) prevented to obtain its <sup>13</sup>C NMR specvtrau,.