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Supporting Information

Ambipolar Transistor Properties of 2,2′-Binaphthosemiquinones

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Synthesis

All chemicals and solvents were used as purchased. All reactions were carried out under ambient conditions. Column chromatography was carried out using silica gel (Wako Wakogel C-200). For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F254, 0.25 mm) were used. The ^{1}H-NMR (300 MHz) spectra were recorded using a JEOL JNM-AL300 spectrometer. Chemical shifts were given in δ values (ppm) using TMS as the internal standard. Mass spectra were taken on a Shimadzu GC–MS-QP-5000 mass spectrometer.

General procedures for the synthesis of 4-alkoxy-1-naphthol.[9]

To a solution of 1,4-naphthoquinone (1.58 g, 10.0 mmol) in methanol (20 mL) was added dropwise a solution of $SnCl_2$ (6.64 g, 35.0 mmol) in 12 M HCl (7 mL) at room temperature. The solution was refluxed for 3 hours and cooled to room temperature. Then, methanol was removed to one fifth of the starting volume and the residue was poured in cold water to give a precipitate, which was filtered and dissolved in CH_2Cl_2. The organic solution was dried over $MgSO_4$, and the solvent was removed *in vacuo* to give **1a**, which was purified by silica-gel chromatography ($CHCl_3$, $R_f = 0.3$) to obtain the pure product (1.1 g, 60%) as a white solid.

4-methoxy-1-naphthol (1a)

White solid (60% yield). ^{1}H NMR (300MHz, $CDCl_3$) δ 8.22 (1H, d, *J* = 9.3 Hz, H-8), 8.11 (1H, d, *J* = 9.3 Hz, H-5), 7.48-7.55 (2H, m, H-6 and H-7), 6.74 (1H, d, *J* = 8.1 Hz, H-2), 6.64 (1H, d, *J* = 8.1 Hz, H-3), 4.87 (1H, br, OH), 3.96 (3H, s, CH_3). EI-MS *m/z* = 174 (M^+).

4-ethoxy-1-naphthol (1b)

By using ethanol and following the same procedure as **1a**, the ethoxy derivative was obtained as a white solid (64% yield). EI-MS *m/z* = 188 (M^+).

4-*i*-propoxy-1-naphthol (1c)

By using isopropyl alcohol and following the same procedure as **1a**, the *i*-propoxy derivative was obtained as a white solid (50% yield). EI-MS *m/z* = 400 (M^+).

4-cyclohexyloxy-1-naphthol (1d)

By using cyclohexanol and following the same procedure as **1a**, the cyclohexyloxy derivative was obtained as a white solid (42% yield). EI-MS *m/z* = 242 (M^+).

4-*n*-hexyloxy-1-naphthol (1e)

By using *n*-hexanol and following the same procedure as **1a**, the *n*-hexyloxy derivative was obtained as a white solid (45% yield). EI-MS *m/z* = 244 (M^+).

General procedures for the synthesis of 4,4′-dialkoxy-2,2′-binaphthosemiquinone.

To a solution of **1a** (0.47 g, 2.7 mmol) in $CHCl_3$ (30 mL) was added Ag_2O (0.75 g, 3.2 mmol) at room temperature. After the mixture was stirred for 3 hours, inorganic precipitates were filtered off. The solvent was removed *in vacuo* to give **2a**, which was purified by silica-gel chromatography ($CHCl_3$, R_f = 0.8) and recrystallization from toluene to obtain the pure product (0.38 g, 83%) as needle-like black crystals.

4,4′-dimethoxy-2,2′-binaphthosemiquinone (2a)

Needle-like black crystals (83% yield). ^{1}H NMR (300MHz, $CDCl_3$) δ 8.41 (2H, s, H-3), 8.17 (2H, d, *J* = 7.8 Hz, H-8), 7.79 (2H, d, *J* = 7.8 Hz, H-5), 7.62 (2H, t, *J* = 7.8 Hz, H-7), 7.48 (2H, t, *J* = 7.8 Hz, H-6), 4.08 (6H, s, CH_3). EI-MS *m/z* = 344 (M^+).

4,4′-diethoxy-2,2′-binaphthosemiquinone (2b)

By using the starting material **1b** and following the same procedure as **1a**, the ethoxy species was obtained as needle-like black crystals (51% yield). ^{1}H NMR (300MHz, $CDCl_3$) δ 8.40 (2H, s, H-3), 8.17 (2H, d, *J* = 7.5 Hz, H-8), 7.84 (2H, d, *J* = 7.5 Hz, H-5), 7.63 (2H, t, *J* = 7.5 Hz, H-7), 7.49 (2H, t, *J* = 7.5 Hz, H-6), 4.33 (4H, q, *J* = 6.9 Hz, CH_2), 1.58 (6H, t, *J* = 6.9 Hz, CH_3). EI-MS *m/z* = 372 (M^+).

4,4′-di-*i*-propoxy-2,2′-binaphthosemiquinone (2c)

By using the starting material **1c** and following the same procedure as **1a**, the *i*-propyloxy species was obtained as needle-like black crystals (43% yield). ^{1}H NMR (300MHz, $CDCl_3$) δ 8.40 (2H, s, H-3), 8.16 (2H, d, *J* = 7.8 Hz, H-8), 7.82 (2H, d, *J* = 7.8 Hz, H-5), 7.60 (2H, t, *J* = 7.8 Hz, H-7), 7.46 (2H, t, *J* = 7.8 Hz, H-6), 4.95-4.87 (2H, m, *J* = 6.0 Hz, CH), 1.52 (12H, d, *J* = 6.0 Hz, CH_3). EI-MS *m/z* = 400 (M^+).

4,4′-dicyclohexyloxy-2,2′-binaphthosemiquinone (2d)

By using the starting material **1d** and following the same procedure as **1a**, the cyclohexyloxy species was obtained as needle-like black crystals (40% yield). ^{1}H NMR (300MHz, $CDCl_3$) δ 8.39 (2H, s, H-3), 8.17 (2H, d, *J* = 7.5 Hz, H-8), 7.84 (2H, d, *J* = 7.5 Hz, H-5), 7.61 (2H, t, *J* = 7.5 Hz, H-7), 7.46 (2H, t, *J* = 7.5 Hz, H-6), 4.73-4.63 (2H, m, CH), 2.15-2.05 (2H, m, CH_2), 1.92-1.72 (4H, m, CH_2), 1.65-1.50 (4H, m, CH_2). EI-MS *m/z* = 480 (M^+).

4,4′-di-*n*-hexyloxy-2,2′-binaphthosemiquinone (2e)

By using the starting material **1e** and following the same procedure as **1a**, the *n*-hexyloxy species was obtained as needle-like black crystals (60% yield). ^{1}H NMR (300MHz, $CDCl_3$) δ 8.38 (2H, s, H-3), 8.16 (2H, d, *J* = 7.8 Hz, H-8), 7.81 (2H, d, *J* = 7.8 Hz, H-5), 7.62 (2H, t, *J* = 7.8 Hz, H-7), 7.47 (2H, t, *J* = 7.8 Hz, H-6), 4.25 (4H, t, *J* = 6.3 Hz, CH_2), 2.00-1.85 (4H, m, CH_2), 1.50-1.30 (8H, m, CH_2CH_2), 0.94 (6H, t, *J* = 6.6 Hz, CH_3). EI-MS *m/z* = 484 (M^+).

Redox and optical properties

Cyclic voltammograms were measured on an ALS model 701E electrochemical analyzer in 0.1 M tetra-*n*-butylammonium hexafluorophosphate (n-$Bu_4N \cdot PF_6$) solutions of dichloromethane at a scan rate of 20, 50, and 100 mV/s. The reference electrode was $Ag/AgNO_3$ with a glassy carbon working electrode and a Pt supporting electrode. All the measured potentials were normalized assuming the ferrocene/ferrocenium redox potential to be –4.80 eV from the vacuum level.[10] UV/vis spectra were collected on a JASCO V-630 spectrometer in 10^{-5} M solutions of chloroform.

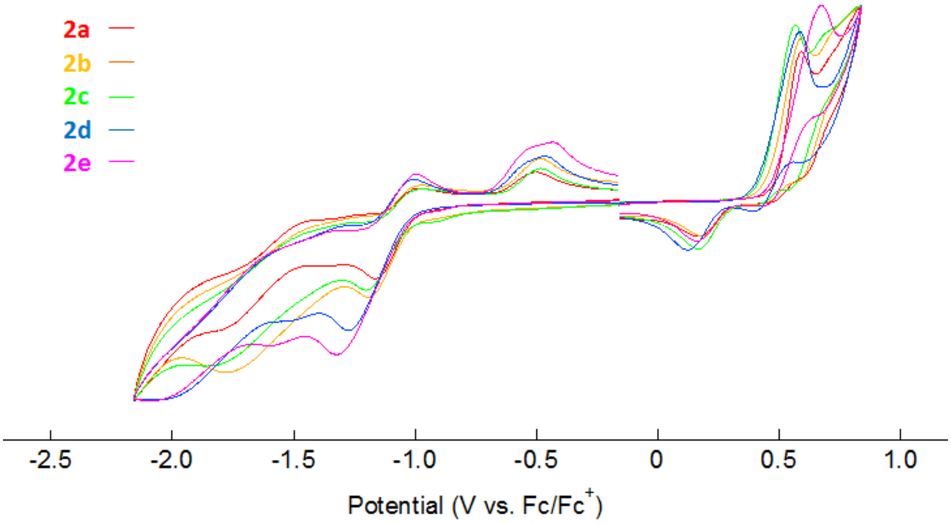

Fig. S1 Cyclic voltammograms of **2a-e** measured at a scan rate of 100 mV/s.

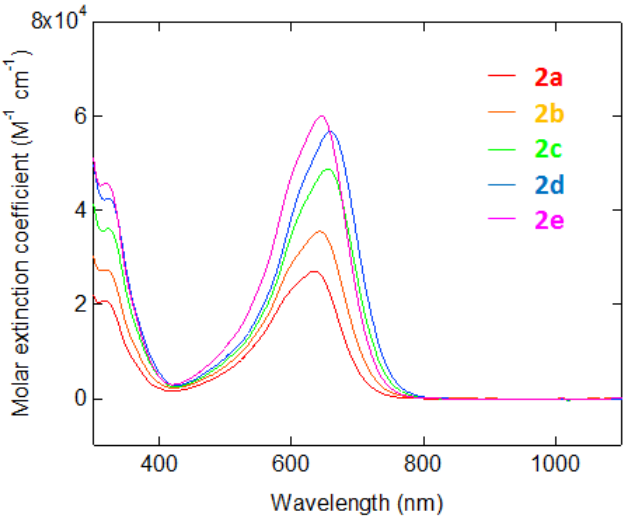

Fig. S2 UV/vis spectra of **2a-e** measured in chloroform.

Crystal structures and band calculations

The reflection data were collected on a Rigaku R-AXIS RAPID-II diffractometer using CuKα X-ray from a rotating anode source with a confocal multilayer X-ray mirror (λ = 1.54187 Å) around 273 K. The temperature was controlled by a Rigaku cryostat system. Empirical absorption correction was applied with the ABSCOR program. The structures were solved by the direct method (SIR 2008) and refined by full-matrix least-squares by applying anisotropic temperature factors for all non-hydrogen atoms using the SHELX-97 programs.[S1, S2] The hydrogen atoms were placed at geometrically calculated positions. The respective intermolecular transfer integrals t_i between the HOMO-HOMO and LUMO-LUMO were calculated on the basis of the extended Hückel molecular orbital calculation and the intermolecular overlaps of HOMO and LUMO obtained from the MOPAC, AM1 molecular orbital calculation.[S3, S4]

Device fabrication

Thin-film transistors were fabricated on a highly doped n-type silicon wafer with a thermally grown silicon oxide layer of 300 nm thickness (C = 11.5 nF/cm^2) by the following procedure. Tetratetracontane ($C_{44}H_{90}$, TTC, ε = 2.5) was deposited on the substrate with a thickness of 20 nm,[S5] where the resulting overall capacitance of the gate dielectrics was 10.4 nF/cm^2.[S6] The BNQ derivatives were vacuum deposited on the TTC thin-film with a thickness of 40 nm as the active layer. The top-contact electrodes were patterned by thermal deposition of Au using a shadow mask; the channel length (L) and width (W) were 100 μm and 1000 μm, respectively. The transistor characteristics were measured under the vacuum of 10^{-4} Pa by using a Keithley 4200 semiconductor parameter analyzer, and the mobility was evaluated from the transconductance in the saturated region.

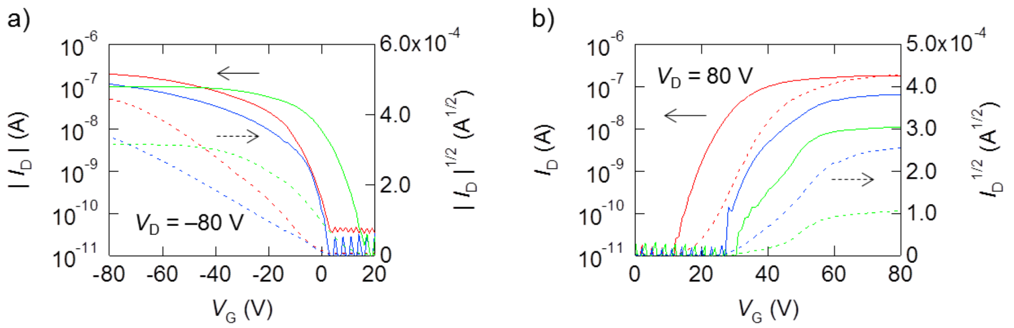

Fig. S3 Characteristics of the ambipolar transistors based on **2a** deposited on TTC. Transfer characteristics in the (a) p-channel, and the (b) n-channel regions, measured under vacuum (red curves), after five months (blue curves), and under ambient conditions (green curves).

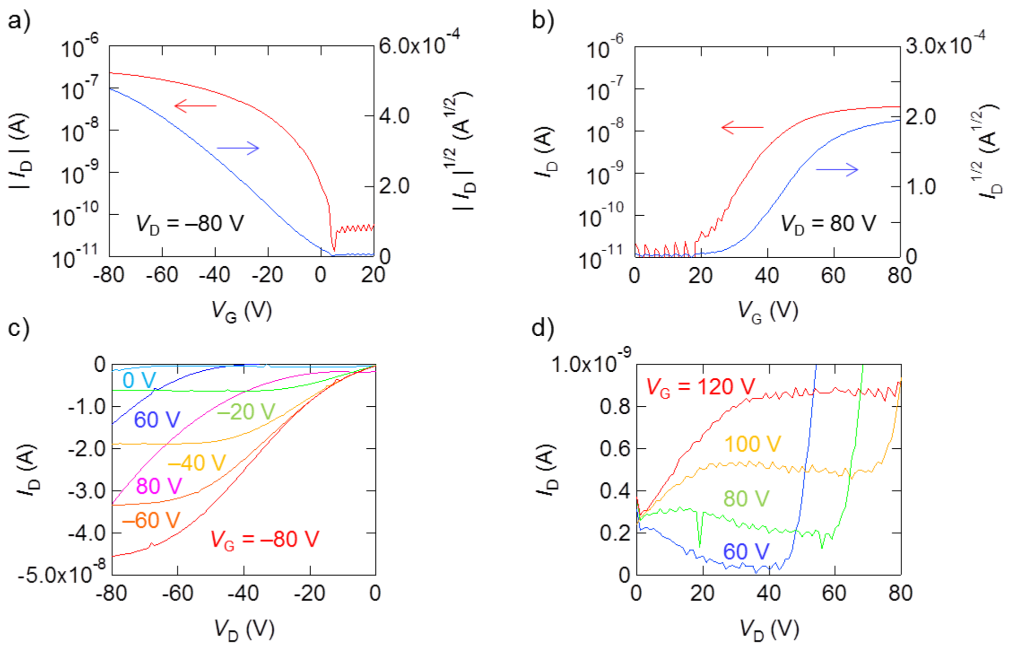

Fig. S4 Characteristics of the ambipolar transistors based on **2a** deposited on TTC. (a) Transfer characteristics in the p-channel region, and (b) the n-channel region. (c) Output characteristics in the p-channel region, and (d) the n-channel region.

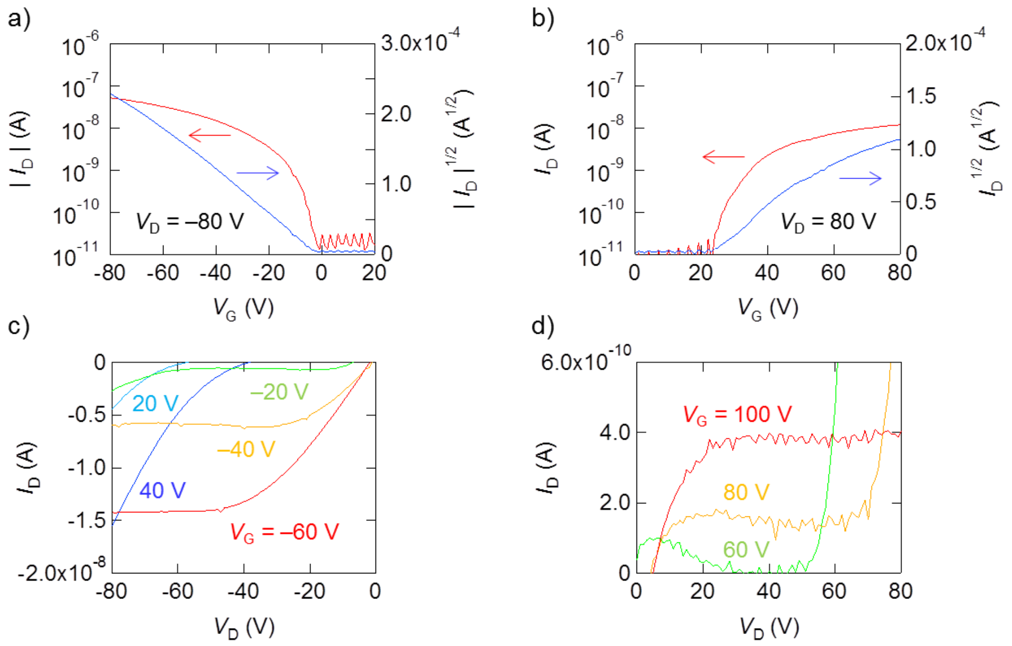

Fig. S5 Characteristics of the ambipolar transistors based on **2c** deposited on TTC. (a) Transfer characteristics in the p-channel region, and (b) the n-channel region. (c) Output characteristics in the p-channel region, and (d) the n-channel region.

Thin film properties

X-ray diffraction patterns of BNQs thin films (40 nm) deposited on TTC (20 nm)|SiO_2 substrates were obtained by a Phillips X'Pert-Pro-MRD with a monochromated CuKα radiation (λ = 1.541838 Å) in air. AFM images of BNQs thin films on TTC (20 nm)|SiO_2 were taken by an SII scanning probe microscope system SPI3800N and SPA-300 by using an Si_3N_4 cantilever in air.

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