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 $\delta$ 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$_2$Cl$_2$. 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$_2$O (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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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\(_3\)) \( \delta \) 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\(_2\)CH\(_2\)), 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\(_4\)N·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.\(^1\)\(^0\) UV/vis spectra were collected on a JASCO V-630 spectrometer in \( 10^{-5} \) M solutions of chloroform.

![Cyclic voltammograms of 2a-e](image)

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

**Fig. S2** UV/vis spectra of 2a-e measured in chloroform.
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 \((C = 11.5 \text{ nF/cm}^2)\) by the following procedure. Tetratetracontane \((\text{C}_{44}\text{H}_{90}, \text{TTC}, \varepsilon = 2.5)\) was deposited on the substrate with a thickness of 20 nm,\(^{55}\) where the resulting overall capacitance of the gate dielectrics was 10.4 \text{nF/cm}^2.\(^{56}\) 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 \(10^{-4} \text{ Pa}\) by using a Keithley 4200 semiconductor parameter analyzer, and the mobility was evaluated from the transconductance in the saturated region.

![Characteristics](image.png)

**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)\(\text{SiO}_2\) substrates were obtained by a Phillips X’Pert-Pro-MRD with a monochromated CuK\(\alpha\) radiation (\(\lambda = 1.541838 \text{ Å}\)) in air. AFM images of BNQs thin films on TTC (20 nm)\(\text{SiO}_2\) were taken by an SII scanning probe microscope system SPI3800N and SPA-300 by using an Si\(_3\)N\(_4\) cantilever in air.

References


