

Supporting Information for

Angular-shaped naphthodifurans, naphtho[1,2-*b*;5,6-*b'*]- and naphtho[2,1-*b*;6,5-*b'*]- difuran : Are they isoelectronic with chrysene?

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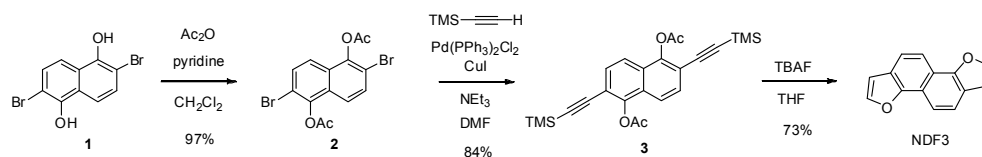
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1. Synthesis of NDFs

1-1. Synthesis of NDF3



Scheme S1. Synthesis of NDF3.

General: All chemicals and solvents are of reagent grade unless otherwise indicated. *N,N*-dimethylacetamide (DMA) was purified with a standard distillation procedure prior to use. 2,6-dibromo-1,5-naphthalenediol was synthesized as reported.^{S1} Melting points were uncorrected. All reactions were carried out under nitrogen atmosphere. Nuclear magnetic resonance spectra were obtained in deuterated chloroform (CDCl_3) with TMS as internal reference unless otherwise stated; chemical shifts (δ) are reported in parts per million. IR spectra were recorded using a KBr pellet for solid samples. EI-MS spectra were obtained using an electron impact ionization procedure (70 eV). UV-vis spectra were measured in dichloromethane or THF solution (concentration: 10^{-5} – 10^{-6} M) on a Shimadzu UV-3600 spectrometer. Cyclic voltammograms (CVs) were recorded on an ALS Electrochemical Analyzer Model 612D in dichloromethane containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple (Fc/Fc^+ : $E^{1/2} = +0.41$ V measured under identical conditions).

1,5-Diacetoxy-2,6-dibromonaphthalene (2)

To a suspension of 1,5-dibromo-2,6-dihydroxynaphthalene (3.18 g, 0.010 mol) and pyridine (2.0 mL, 0.21 mol) in CH_2Cl_2 (300 mL) was added acetic anhydride (5.0 mL, 0.060 mol) at rt. After the mixture was stirred for 15 h at the same temperature, diluted hydrochloric acid (1M, 10 mL) was added. The resulting mixture was separated, and the aqueous layer was extracted with dichloromethane (100 mL $\times$ 2). The combined organic layer was dried (MgSO_4) and concentrated in vacuo, and the resulting residue was purified by column chromatography on silica-gel eluted with chloroform ($R_f = 0.5$) to give **2** (3.92 g, 97%) as a white solid. Mp 218.7–219.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.51, (s, 6H), 7.60 (d, $J = 8.9$ Hz, 2H), 7.69 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.0, 144.9, 131.4, 128.5, 120.8, 114.9, 20.8; EIMS (70 eV) $m/z = 402$ (M^+); IR (KBr) $\nu = 1770$ (C=O) cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{Br}_2\text{O}_4$: C, 41.84; H, 2.51%. Found: C, 42.14; H, 2.41%.

1,5-Diacetoxy-2,6-bis(trimethylsilyl)ethynynaphthalene (3)

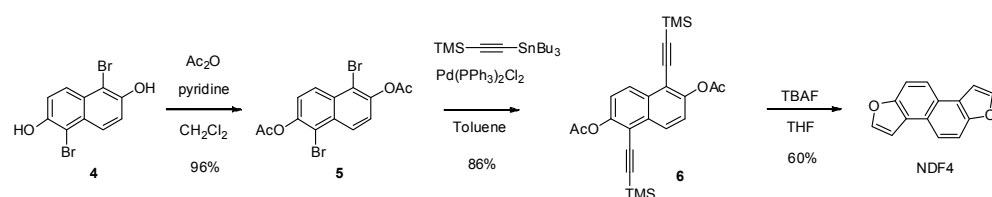
To a degassed solution of 1,5-diacetoxy-2,6-dibromonaphthalene (10 g, 24.8 mmol) and triethylamine (60 mL) in DMA (60 mL) was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (2.0 g, 0.16 mmol, 10 mol%), CuI (1.2 g, 0.35

mmol, 20 mol%) and trimethylsilylacetylene (TMSA, 25 mL, 177 mmol). After the mixture was stirred for 20 h at 60 °C, water (1 mL) and 1 N hydrochloric acid (1 mL) was added. The resulting mixture was extracted with dichloromethane, and combined organic layer was dried (MgSO₄) and concentrated in vacuo. The residue was purified by column chromatography on silica-gel eluted with chloroform to give a mixture of **3** (9.1 g, 84%) as a brown solid. Mp 221.4–222.3 °C; ¹H NMR (400MHz, CDCl₃) δ 0.27 (s, 18H) 2.47 (s, 6H) 7.54 (d, *J* = 8.6 Hz, 2H) 7.68 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 168.3, 149.3, 129.8, 127.8, 119.5, 115.2, 102.1, 99.9, 20.9, 0.0; EIMS (70 eV) *m/z* = 436 (M⁺); IR (KBr) ν = 1769 (C=O) cm⁻¹, 2155 (C≡C) cm⁻¹ Anal. Calcd for C₂₄H₂₈O₄Si₂: C, 66.02; H, 6.46%. Found: C, 65.91; H, 6.73%.

Naphtho[1,2-*b*:5,6-*b'*]difuran (NDF3)

A mixture of tetrabutylammonium fluoride (1 mol/L in THF, 14.6mL, 14.6mmol) in the presence of molecular sieves 4A (3.6 g) in THF (183 mL) was degassed with argon and the resulting solution was stirred at room temperature for 1 h. Then a solution of **3** (2.0 g, 4.58 mmol) in THF (60 mL) was added and whole was stirred at 60 °C for 21 h. The suspension was cooled to room temperature and filtered to remove any solid impurity. The filtrate was extracted with dichloromethane. Combined organic phase was washed with brine, dried over MgSO₄, and evaporated to dryness. The residue was purified by column chromatography on silica-gel eluted with hexane to give naphtho[1,2-*b*:5,6-*b'*]difuran (696 mg, 73%) as a white solid. Mp 149.8–150.4 °C (ref.^{S2} 145–146 °C); ¹H NMR (400 MHz, CDCl₃) δ 6.95 (d, *J* = 2.0 Hz, 2H) 7.79 (d, *J* = 2.0 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H) 8.17 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 151.1, 144.0, 122.6, 120.2, 119.0, 115.6, 107.7; EIMS (70 eV) *m/z* = 208 (M⁺); Anal. Calcd for C₁₄H₈O₂: C, 80.76; H, 3.87%. Found: C, 80.58; H, 3.79%.

1-2. Synthesis of NDF4



Scheme S2. Synthesis of NDF4.

2,6-Diacetoxy-1,5-dibromonaphthalene (**4**)

To a suspension of 2,6-dibromo-1,5-dihydroxynaphthalene (3.18 g, 0.010 mol) and pyridine (2.0 mL, 0.021 mol) in CH₂Cl₂ (30 mL) was added acetic anhydride (5 mL, 0.060 mol) at r.t.. After the mixture was stirred for 15 h at the same temperature, diluted hydrochloric acid (1M, 10 mL) was added. The resulting mixture was separated, and the aqueous layer was extracted with dichloromethane (100 mL ×

2). The combined organic layer was dried (MgSO_4) and concentrated in vacuo, and the resulting residue was purified by column chromatography on silica-gel eluted with chloroform ($R_f = 0.5$) to give 2,6-diacetoxy-1,5-dibromonaphthalene (3.90 g, 96%) as a white solid. Mp 221.5–222.3°C; ^1H NMR (400 MHz, CDCl_3) δ 2.44, (s, 6H), 7.38 (d, $J = 9.0$ Hz, 2H), 8.32 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 147.1, 131.8, 128.4, 123.9, 115.5, 20.7; EIMS (70 eV) $m/z = 402$ (M^+); IR (KBr) $\nu = 1750$ (C=O) cm^{-1} .

2,6-diacetoxy-1,5-bis(trimethylsilylethynyl)naphthalene (5)

To a 2-5 mL microwave pressurized vial equipped with a stirring bar, 1,5-diacetoxy-2,6-dibromonaphthalene (0.3 g, 0.75 mmol), tributyl(trimethylsilylethynyl)tin (0.664 g, 1.71 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (53.0 mg, 0.075 mmol, 10 mol%) and Toluene (5.0 mL) was added. Then the tube was sealed and refilled with argon. After the mixture was put into microwave reactor and heated to 120°C for 3 h., water (1 mL) and 1 N hydrochloric acid (1 mL) were added. Resulting mixture was extracted with dichloromethane, and combined organic layer was dried (MgSO_4) and concentrated in vacuo. The residue was purified by column chromatography on silica-gel eluted with chloroform to give a 2,6-diacetoxy-1,5-bis(trimethylsilylethynyl)naphthalene (0.281 g, 86%) as white solid. Mp 198.5–199.5°C; ^1H NMR (400 MHz, CDCl_3) δ 0.34 (s, 18H), 2.42, (s, 6H), 7.35 (d, $J = 8.8$ Hz, 2H), 8.31 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 151.5, 132.0, 128.3, 122.8, 106.2, 97.4, 21.2, 0.2; EIMS (70 eV) $m/z = 436$ (M^+); IR (KBr) $\nu = 1771$ (C=O) cm^{-1} , 2155 ($\text{C}\equiv\text{C}$) cm^{-1} .

Naphtho[2,1-*b*:6,5-*b'*]difuran (NDF4)

A mixture of tetra *n*-butylammonium fluoride (1 mol/L in THF, 14.6 mL, 14.6 mmol) in the presence of molecular sieves 4A (3.6 g) in THF (183 mL) was degassed with argon and the resulting solution was stirred at room temperature for 1 h. Then a solution of 2,6-diacetoxy-1,5-dibromonaphthalene (0.25 g, 5.73 mmol) in THF (35 mL) was added and whole was stirred at 60°C for 20 h. The suspension was cooled to room temperature and filtered to remove any solid impurity. The filtrate was extracted with dichloromethane (20 mL $\times$ 2). Combined organic phase was washed with brine, dried over MgSO_4 , and evaporated to dryness. The residue was purified by column chromatography on silica-gel eluted with hexane to give naphtho[2,1-*b*:6,5-*b'*]difuran (72 mg, 60%) as white solid. Mp 174.5–175.5°C (ref.^{S3} 175 °C); ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J = 7.5$ Hz, 2H), 7.76 (d, $J = 9.0$ Hz, 2H), 7.78 (d, $J = 7.5$ Hz, 2H), 8.03 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.9, 144.5, 124.3, 123.8, 120.4, 112.4, 105.7; EIMS (70 eV) $m/z = 208$ (M^+).

2. Cyclic voltammogram of NDF1/NDT1, 1,5-dimethoxynaphthalene and 2,6-dimethoxynaphthalene

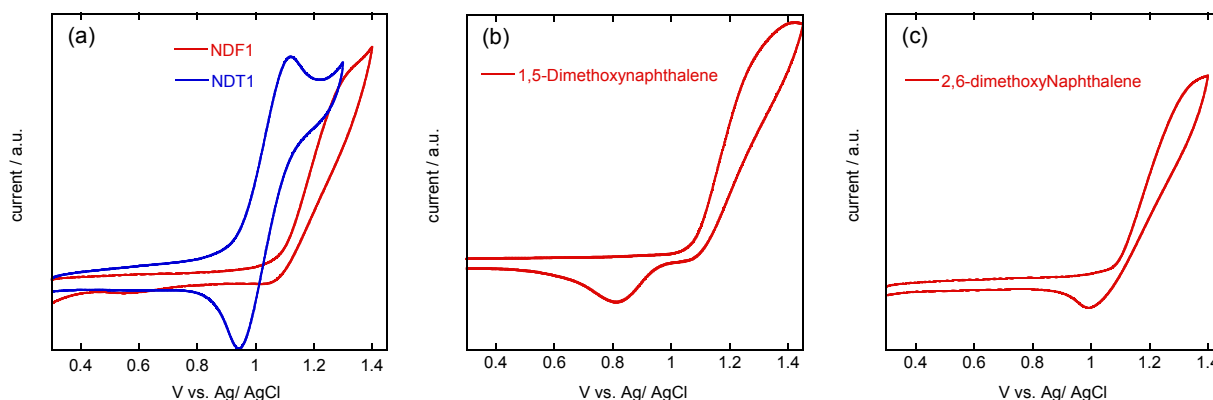


Figure S1. Cyclic voltammogram of NDF1/NDT1 (a), 1,5-dimethoxynaphthalene (b) and 2,6-dimethoxynaphthalene (c).

3. DFT calculations of NDF3

Geometry optimization and normal mode calculations of NDF3 and NDF4 were performed at the B3LYP/6-31G(d) level using the Gaussian03 program package.^{S4}

4. Energy diagrams of NDT1/NDF1, NDT3/NDF4 and NDT4/NDF4 based on the MO calculations^{S5,S6}

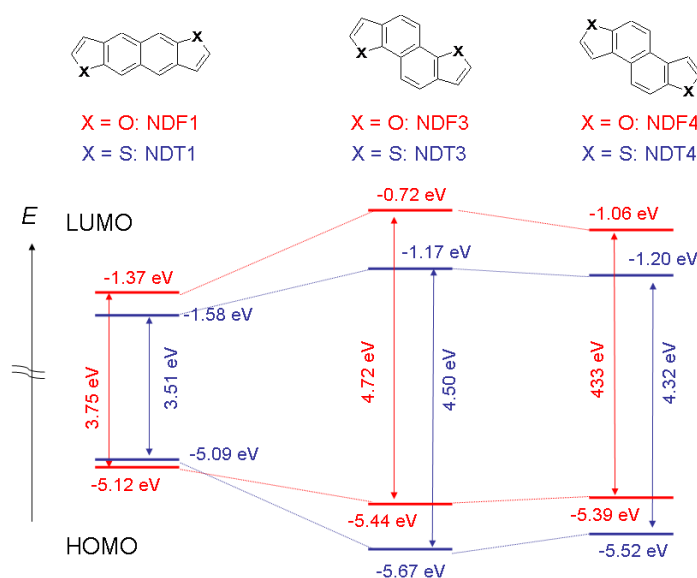


Figure S2. Schematic representation of calculated energy levels of NDF1/NDT1, NDF3/NDT3 and NDF4/NDT4.

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