Electronic Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

Hexagonal columnar phase formed in lateral fluorinate bent-shaped molecules based on 1,7-naphthalene central core

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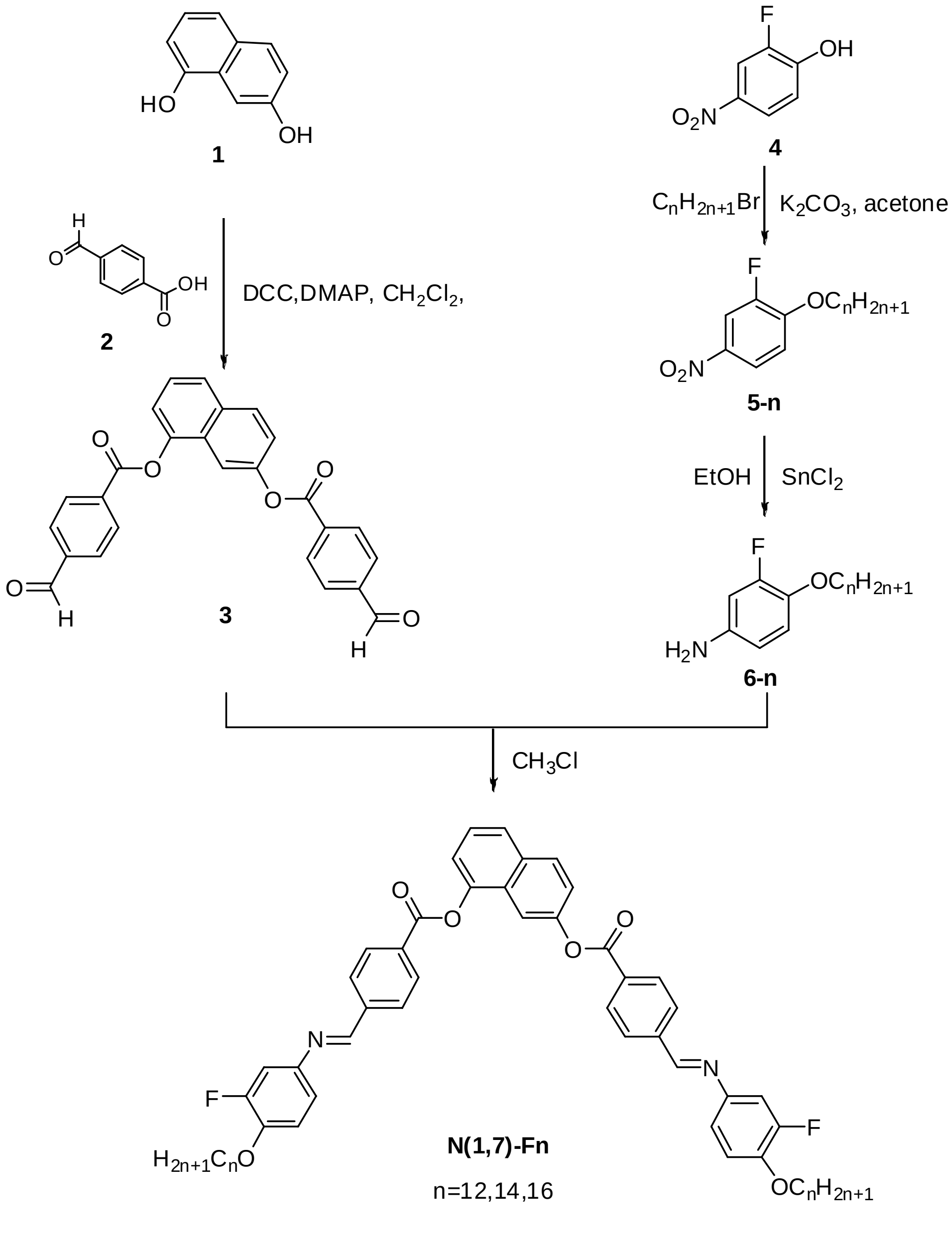
Synthesis and analytical data

The synthetic routes were illustrated in Schemes S1.



Scheme S1. Synthesize route to N(1,7)-Fn compounds

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Synthesis of dialdehydes 3

To a solution of 1,7-dihydroxynaphthalene **1** (1.00 g, 6.24 mmol) in CH_2Cl_2 (100 ml) was added 1,3-dicyclohexylcarbodiimide (DCC) (3.22 g, 15.60 mmol), 4-dimethylaminopyridine (DMAP) (catalyst amount), and 4-formylbenzoic acid **2** (2.06 g, 13.72 mmol). The mixture was stirred at room temperature for 3 days. After filtration to remove precipitated materials, the filtrate was chromatographed on silica gel (CH_2Cl_2) and then recrystallized from dichloromethane/ethanol to isolate **3** (1.35 g, 51%) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-8.07 (m, 6H), 8.37 (d, *J*=8.4 Hz, 4H), 8.48 (d, *J*=8.4 Hz, 4H), 10.14 (s, 1H), 10.16 (s, 1H).

Synthesis of 1-(dodecyloxy)-2-fluoro-4-nitrobenzene 5-12

A mixture of 2-fluoro-4-nitrophenol **4** (2.00 g, 12.7 mmol), 1-bromododecane (3.50 g, 14.0 mmol), potassium carbonate (5.80 g, 42.1 mmol) and potassium iodide (catalyst amount) in acetone (100 ml) was heated under reflux for 24 h. To this solution was added water (50 ml) and the produce was extracted with diethyl ether (30 ml × 3). The combined organic layers were dried ($MgSO_4$), concentrated and recrystallized from ethanol to give **5-12** (3.56 g, 86.0%) as yellow solid.

For **5-12**, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.25-1.60 (m, 18H), 1.87 (quin, *J*=6.6 Hz, 2H), 4.13 (t, *J*=6.6 Hz, 2H), 7.02 (dd, *J*=8.4 Hz, 1H), 7.95-8.07 (m, 2H).

For **5-14**, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.25-1.60 (m, 22H), 1.87 (quin, *J*=6.6 Hz, 2H), 4.13 (t, *J*=6.6 Hz, 2H), 7.02 (dd, *J*=8.4 Hz, 1H), 7.95-8.07 (m, 2H).

For **5-16**, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.25-1.60 (m, 26H), 1.87 (quin, *J*=6.6 Hz, 2H), 4.13 (t, *J*=6.6 Hz, 2H), 7.02 (dd, *J*=8.4 Hz, 1H), 7.95-8.07 (m, 2H).

Synthesis of 4-(dodecyloxy)-3-fluoroaniline 6-12

An ethanol (50 ml) solution of **6-12** (3.2 g, 9.80 mmol) and Stannous chloride dehydrate (11.1 g, 49.03 mmol) was refluxed for 12h, cooled to room temperature, and poured onto ice. The pH was adjusted to 8 using NaOH (2 mol L^{-1}) and the colorless mixture was extracted with ethyl acetate (200ml). The ethyl acetate layer was dried over anhydrous $MgSO_4$ and evaporated under reduced procure. The brownish solid was recrystallized from an ethanol/water, filtered, and vacuum dried. The whitish solid 4-(dodecyloxy)-3-fluoroaniline 6-12 obtained after recrystallization is 1.40 g, yield 48.4 %.

For **6-12**, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.25-1.60 (m, 18H), 1.75 (quin, *J*=6.8 Hz, 2H), 3.48 (br s, NH_2), 3.94 (t, *J*=6.6 Hz, 2H), 6.33-6.47 (m, 2H), 6.79 (t, *J*=8.8 Hz, 1H).

For **6-14**, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.25-1.60 (m, 22H), 1.75 (quin, *J*=6.8 Hz, 2H), 3.48 (br s, NH_2), 3.94 (t, *J*=6.6 Hz, 2H), 6.33-6.47 (m, 2H), 6.79 (t, *J*=8.8 Hz, 1H).

For **6-16**, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.25-1.60 (m, 26H), 1.75 (quin, *J*=6.8 Hz, 2H), 3.48 (br s, NH_2), 3.93 (t, *J*=6.6 Hz, 2H), 6.33-6.47 (m, 2H), 6.79 (t, *J*=8.8 Hz, 1H).

Synthesis of 1,7-naphathalene bis[4-(4-dodecyloxy-3-fluorophenyliminomethyl)benzoate] N(1,7)-F12

A solution of **6-12** (0.10 g, 0.24 mmol) and dialdehyde **3** (0.15 g, 0.52 mmol) in chloroform (50 ml) was heated under reflux for 3 hr. The reaction mixture was concentrated and recrystallized from chloroform/ethanol twice to give a yellow crystal of **N(1,7)-F12** (0.18 g, 78%). Target compounds **N(1,7)-F16**, **N(1,7)-F20** were similarly prepared in 72%, 68% yield, respectively.

For **N(1,7)-F12**, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 6H), 1.16-1.75 (m, 36H), 1.82 (quin, *J*=6.8 Hz, 4H), 4.05 (t, *J*=6.6 Hz, 4H), 6.96-7.13 (m, 6H), 7.42-7.50 (m, 2H), 7.56 (t, *J*=8.4 Hz, 1H), 7.77 (d, *J*=4.2 Hz,1H), 7.85 (d, *J*=8.4 Hz, 1H), 8.00 (dd, *J*=8.4 Hz, 3H), 8.06 (d, *J*=8.4 Hz, 2H), 8.29 (d, *J*=8.4 Hz, 2H), 8.40 (d, *J*=8.4 Hz, 2H), 8.54 (d, *J*=8.8 Hz, 2H).

^{13}C-NMR (400 MHz, $CDCl_3$) δ 14.16, 22.73, 25.95, 29.24, 29.39, 29.41, 29.59, 29.63, 29.68, 29.70, 31.96, 69.76, 109.05, 109.07, 109.25, 109.26, 112.74, 114.97, 114.99, 117.79, 117.80, 117.81, 117.82, 119.25, 122.27, 125.67, 126.22, 127.67, 128.82, 128.97, 130.05, 130.79, 130.92, 131.31, 131.47, 133.00, 140.80, 140.97, 144.24, 144.31, 146.50, 146.61, 146.68, 149.44, 151.77, 154.23, 157.52, 157.57, 164.76, 164.94.

Elemental analysis: calculated for $C_{67}H_{72}F_2N_2O_6$: C 76.04, H 7.41, N 2.86, F 3.88, O 9.80; found, C 76.27, H 7.45, N 2.94, O(+ F) 12.34.

For **N(1,7)-F14**, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 6H), 1.16-1.75 (m, 44H), 1.83 (quin, *J*=6.8 Hz, 4H), 4.06 (t, *J*=6.6 Hz, 4H), 6.96-7.13 (m, 6H), 7.42-7.50 (m, 2H), 7.57 (t, *J*=8.4 Hz, 1H), 7.77 (d, *J*=4.2 Hz,1H), 7.85 (d, *J*=8.4 Hz, 1H), 8.00 (dd, *J*=8.4 Hz, 3H), 8.06 (d, *J*=8.4 Hz, 2H), 8.30 (d, *J*=8.4 Hz, 2H), 8.41 (d, *J*=8.4 Hz, 2H), 8.54 (d, *J*=8.8 Hz, 2H).

^{13}C-NMR (400 MHz, $CDCl_3$) δ 14.16, 22.73, 25.95, 29.25, 29.41, 29.60, 29.64, 29.70, 29.74, 31.97, 69.77, 109.06, 109.07, 109.25, 109.26, 112.74, 114.99, 117.78, 117.80, 117.81, 117.83, 119.25, 122.27, 125.67, 126.22, 127.67, 128.82, 128.97, 130.05, 130.80, 130.92, 131.32, 131.48, 133.00, 140.81, 140.97, 144.25, 144.32, 146.51, 146.62, 146.63, 146.69, 149.44, 151.78, 153.24, 154.25, 157.53, 157.58, 164.77, 164.95.

Elemental analysis: calculated for $C_{67}H_{72}F_2N_2O_6$: C 76.56, H 7.79, N 2.71, F 3.67, O 9.27; found, C 76.38, H 7.84, N 2.80, O(+ F) 12.98.

For **N(1,7)-F16**, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 6H), 1.16-1.75 (m, 52H), 1.83 (quin, *J*=6.8 Hz, 4H), 4.06 (t, *J*=6.6 Hz, 4H), 6.96-7.13 (m, 6H), 7.42-7.50 (m, 2H), 7.57 (t, *J*=8.4 Hz, 1H), 7.77 (d, *J*=4.2 Hz,1H), 7.85 (d, *J*=8.4 Hz, 1H), 8.00 (dd, *J*=8.4 Hz, 3H), 8.06 (d, *J*=8.4 Hz, 2H), 8.30 (d, *J*=8.4 Hz, 2H), 8.41 (d, *J*=8.4 Hz, 2H), 8.54 (d, *J*=8.8 Hz, 2H).

^{13}C-NMR (400 MHz, $CDCl_3$) δ 14.16, 22.73, 25.95, 29.25, 29.41, 29.60, 29.64, 29.70, 29.72, 29.74, 29.75, 31.97, 69.79, 109.05, 109.07, 109.25, 109.27, 112.74, 114.99, 115.02, 117.77, 117.79, 117.81, 117.83, 119.26, 122.29, 125.67, 126.23, 127.67, 128.83, 128.98, 130.06, 130.81, 130.94, 131.32, 131.49, 133.02, 140.82, 140.97, 144.26, 144.33, 146.51, 146.52, 146.62, 146.63, 146.69, 149.44, 151.78, 153.25, 154.25, 157.56, 157.61, 164.79, 164.97.

Elemental analysis: calculated for $C_{67}H_{72}F_2N_2O_6$: C 76.04, H 7.41, N 2.86, F 3.88, O 9.80; found, C 76.81, H 8.28, N 2.60, O(+ F) 12.31.

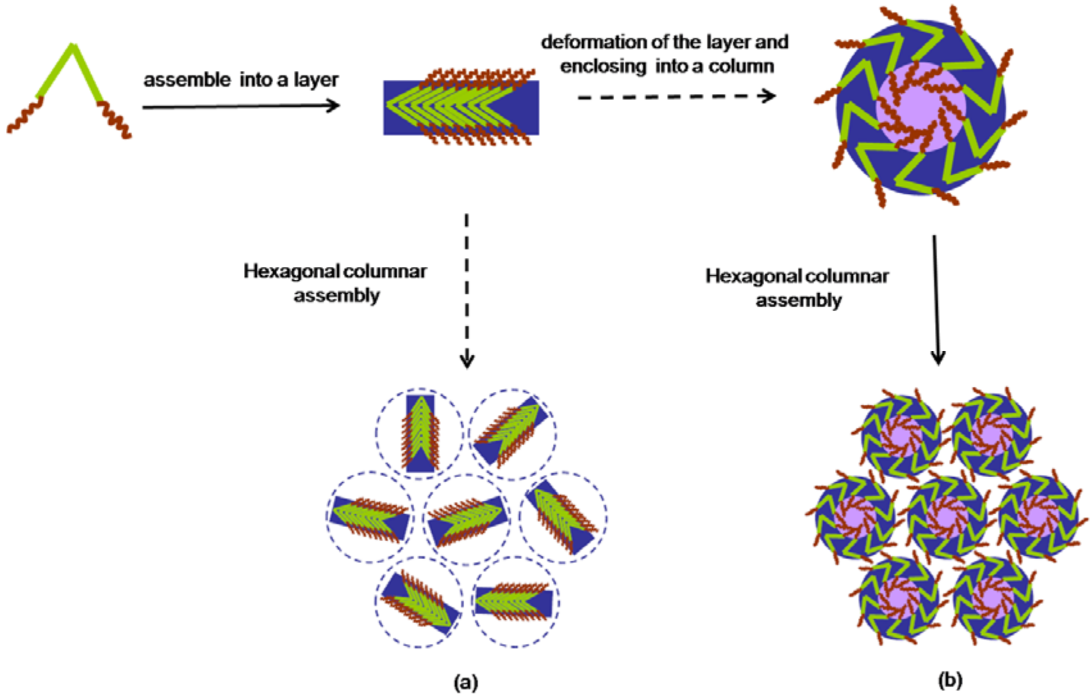

Figure S2 Two possible model of molecular assembly in columnar phase of N(1,7)-Fn compound (a) groups (or ribbons) of parallel molecules packed without any orientational corelation along the column axis, which is similar to the self-assembly proposed for phasmidic molecules. (b) the column is constructed from a tube-like assembly of molecules and cylindrically symmetric deformation of layers was assumed. The alkoxy tails of molecules are protruding outside of the column wall and inside of the enclosed mesogenic layer respectively.