Supplementary Material (ESI) for Soft Matter

Electronic Supplementary Information for

Evidence for general tilt columnar liquid crystalline phase

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Experimental

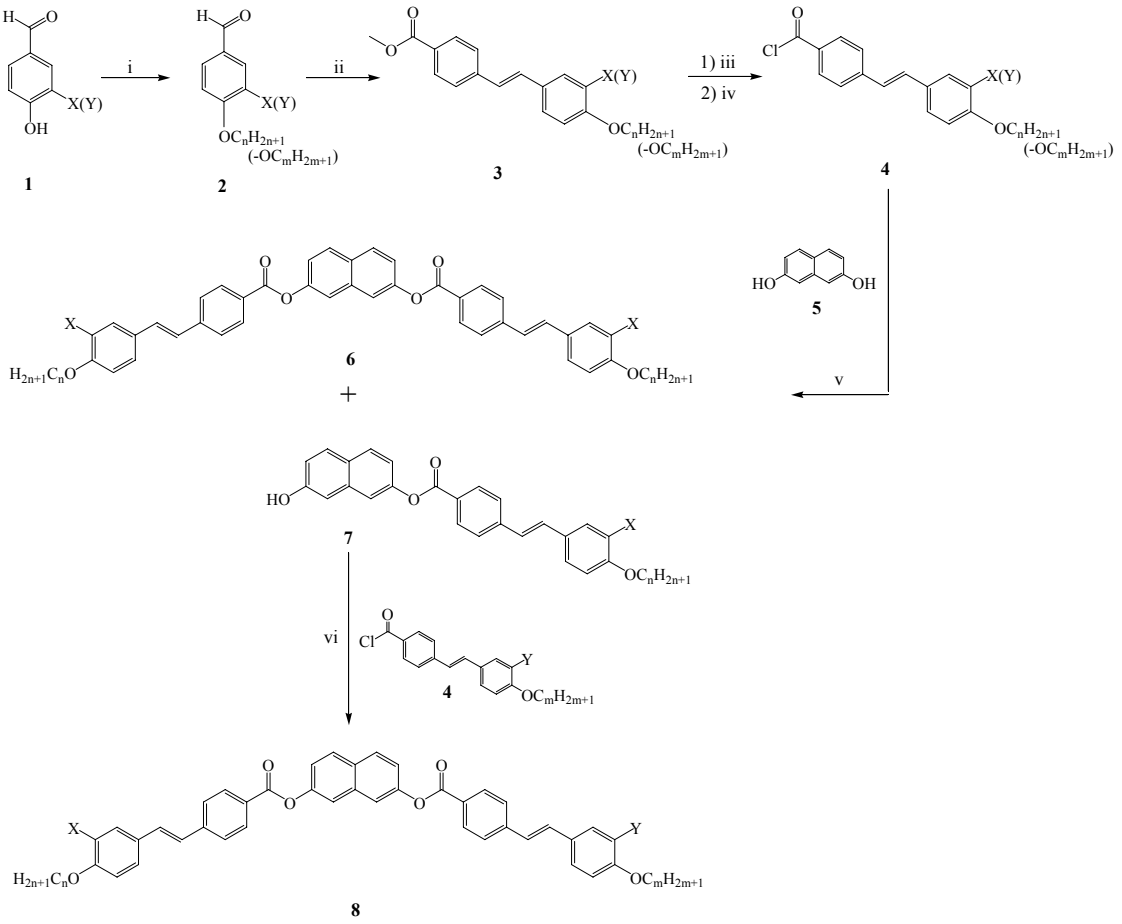
The molecular structures of synthesized compounds were confirmed by the following analytical methods. The carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Varian Unity Plus spectrometer operating at 50, 75 and 125 MHz, whereas ^{1}H NMR spectra were recorded at 200, 300 and 500 MHz. Tetramethylsilane was used as an internal standard. Chemical shifts were reported in ppm. Thin layer chromatography (TLC) analyses were performed on Merck 60 F_{254} silica gel aluminum plate. Column chromatography was carried out at atmospheric pressure using silica gel (100-200 mesh, Merck).

Synthesis

The synthesis of novel bent-core compounds was achieved by following the route depicted on Scheme 1.

Alkoxy aldehyde **2** was prepared from hydroxyaldehyde **1** and appropriate alkyl bromide using Williamson etherification. Compound **2** was treated with metyl 4-(triphenylphosphoniummethyl)-benzoate bromide in the presence of anhydrous potassium carbonate. Obtained stilbene derivative **3,** after transformation into benzoic acid chloride **4,** and esterification reaction with 2,7-dihydroxynaphthalene **5,** gave a mixture of disubstituted **6** and monosubstituted **7** products**,** which were separated by

column chromatography. Monoderivative **7** was treated with appropriated benzoic acid chloride, which resulted in formation of asymmetrical bent-core compound.



X = NO_2; n = 12, 16, 18

Y = Cl; m = 8, 10, 12, 15, 16, 18

Scheme 1. Synthetic route for the preparation asymmetric bent-core molecules i) $C_nH_{2n+1}Br$, $C_mH_{2m+1}Br$, K_2CO_3, KI, DMF, 80 °C, 8-10 h ii) metyl 4-(triphenylphosphoniummethyl)-benzoate bromide, 18-crown-6, CH_2Cl_2, THF, rfx., 20 h iii) KOH, EtOH, 60 °C, 10-12 h iv) $(COCl)_2$, toluene, rfx., 8 h v) TEA, THF, DMAP, rt., 4-5 h vi) TEA, THF, DMAP, reflux 8 h.

*Synthesis of 4-hydroxy-3-nitrobenzaldehyde **2***

The mixture of 3-hydroxy-4-nitrobenzaldehyde **1** (10 g, 60 mmol), K_2CO_3 (10.7 g, 77 mmol), KI (12.9 g, 77 mmol) and 1-dodecyl bromide (17.4 ml, 72 mmol) in DMF (200 ml) was heated at 80 °C for 8-10 h. After addition of water, product was extracted with toluene (3×20 ml) and the organic phase was dried over $MgSO_4$. The solvent was evaporated and the crude product was crystallized several times from ethanol. Yield 70%.
2: NMR: δ^1H (200 MHz, $CDCl_3$) 9.87 (s, 1H, CHO), 8.63 (d, J = 2.2 Hz, 1H, Ar), 7.98 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 1H, Ar), 6.98 (d, J = 8.8 Hz, 1H, Ar), 4.00 (t, J = 6.8 Hz, 2H, O<u>H</u>$_2$CH$_2$), 1.87 – 1.63 (m, 2H, CH_2), 1.55 – 1.13 (m, 18H, CH_2), 0.88 (t, 3H, J = 6.9 Hz, CH_3) δ^{13}C (50 MHz, $CDCl_3$) 189.76, 159.78, 140.10, 134.60, 131.24, 125.43, 115.60, 69.53, 32.52, 29.59, 29.52, 29.42, 29.29, 29.26, 23.02, 14.13
All alkoxy-derivatives were synthesized using similar procedure.

*Synthesis of 4-{(E)-2-[(4-dodecyloxy- 3-nitro-phenyl]ethenyl}benzoic acid methyl ester **3***

To the solution of methyl 4-(triphenylphosphoniummethyl)-benzoate bromide (6.83 g, 14 mmol), dissolved in dry methylene dichloride (70 ml) and tetrahydrofuran (100 ml), anhydrous potassium carbonate (6.9 g, 69 mmol) followed by 18-crown-6 (20 mg, 0.07 mmol) were added. Reaction mixture was stirred in room temperatures for 1 h. 4-dodecyloxy-3-nitrobenzaldehyde **2** (7.0 g, 21 mmol) was added to the yellow reaction mixture which was heated under reflux for 20 h. After the filtration of inorganic salts, reaction mixture was evaporated to dryness and ethanol was added to the oily residue, which led to the crystallization of product **3**. According to the spectral data, only (*E*)-stilbene was crystallized from the reaction mixture. Yield 45 %.
3: NMR: **δ^1H (200 MHz, $CDCl_3$)**: 8.03 (d, J = 8.2 Hz, 2H, Ar), 7.98 (d, J = 2.2 Hz, 1H, Ar), 7.64 (dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz, 1H, Ar), 7.53 (d, J = 8.4 Hz, 2H, Ar), 7.16 - 6.98 (m, 3H, Ar, C<u>H</u>=C<u>H</u>), 4.11 (t, J = 6.4 Hz, 2H, O<u>H</u>$_2$CH$_2$), 3.92 (s, 3H, OCH_3), 1.93 – 1.74 (m, 2H, CH_2), 1.55 – 1.18 (m, 18H, CH_2), 0.88 (t, J = 6.5 Hz, 3H, CH_3).
δ^{13}C (75 MHz, $CDCl_3$): 166.76, 152.16, 141.13, 140.05, 131.96, 130.10, 129.25, 128.32, 128.10, 126.33, 123.35, 114.69, 69.89, 52.12, 31.93, 29.65, 29.60, 29.52, 29.36, 29.28, 28.93, 25.83, 22.70, 14.14.
All stilbene derivatives were synthesized using similar procedure.

*Synthesis of 4-{(E)-2-[4-dodecyloxy-3-nitro-phenyl]ethenyl}benzoic acid chloride **4***

To the solution of 4-{(*E*)-2-[4-dodecyloxy-3-nitro]phenyl]ethenyl}benzoic acid methyl ester **3** (3 g, 6.41 mmol) in ethanol (200 ml), a solution of potassium hydroxide (1.10 g, 19.2 mmol) in ethanol (15 ml) was added and the mixture was heated under reflux for 10-12 h. After cooling the solution, crude product precipitated as a potassium salt. After drying under vacuum over sodium hydroxide, obtained salt was suspended in toluene (200 ml) and treated with excess of oxalyl chloride (5 ml). The reaction mixture was heated under reflux for 8 h. After filtration of precipitated potassium chloride, the remaining solution was evaporated to dryness. The product slowly solidified at room temperature with a yield of 98 %.

All benzoic acid chlorides were synthesized using similar procedure.

*Synthesis of asymmetric bent-core compounds **8** (**12/12**)*

To the solution of 2,7-dihydroxynaphthalene (1.4 g, 9.12 mmol), triethylamine (1 ml, 7.13 mmol) and DMAP (20 mg, 0.16 mmol) in tetrahydrofuran (100 ml), 4-{(*E*)-2-[4-dodecyloxy-3-nitro-phenyl]ethenyl}benzoic acid chloride **4** (0.86 g, 1.85 mmol) in dichloromethane (30 ml) was added dropwise. The reaction mixture was stirred at room temperature for 4-5 h, then solvent was evaporated to dryness under reduced pressure. Obtained mixture of disubstituted **6** and monosubstituted **7** products were separated by column chromatography. Yield of monosubstituted derivative – 40 %, disubstituted – 30 %. To the mixture monosubstituted derivative **6** (0.40 g, 0.67 mmol), triethylamine (1 ml, 7.13 mmol), tetrahydrofuran (100 ml), and DMAP (20 mg, 0.16 mmol), (*E*)-2-[3-chloro-4-(dodecyloxy)phenyl]ethenyl}benzoic acid **4** (0.37 g, 0.80 mmol) were added and the mixture was kept under reflux for 8 h. The asymmetric final product **12/12** was purified by column chromatography and double recrystallization from ethyl acetate. Yield for **12/12** – 20 %. The range of yields of this step varied from 20 – 40 %

All asymmetrical products were synthesized using the same procedure.

Spectral characterization of all final compounds

12/8

NMR: δ^{1}H (200 MHz, $CDCl_3$) 8.32 – 8.16 (m, 4H, Ar), 8.03 (d, 1H, J = 2.2 Hz, Ar), 7.94 (d, 2H, J = 9.0 Hz, Ar), 7. 76 - 7. 54 (m, 8H, Ar), 7. 44 – 7. 32 (m, 3H, Ar), 7.43 – 7.02 (m, 5H, Ar, C<u>H</u>=C<u>H</u>), 6.92 (d, 1H, J = 8.6 Hz, Ar), 4.22– 3.96 (m, 4H, OC<u>H_2</u>CH_2), 1. 93 – 1. 76 (m, 4H, CH_2), 1.57 – 1.18 (m, 28H, CH_2), 0.96 – 0.82 (m, 6H, CH_3);
δ^{13}C (50 MHz, $CDCl_3$) 164.92, 154.72, 152.27, 149.38, 149.32, 142.59, 141.95, 134.44, 132.06, 130.80, 130.75, 130.10, 129.57, 129.42, 129.27, 128.85, 128.48, 128.21, 128.00, 126.56, 126.37, 123.47, 121.21, 118.59, 114.71, 113.23, 69.91, 69.29, 31.93, 31.81, 29.64, 29.59, 29.52, 29.36, 29.31, 29.22, 29.07, 28.93, 25.95, 25.84, 22.67, 14.12.

12/10

NMR: δ^{1}H (200 MHz, $CDCl_3$) 8.33 – 8.14 (m, 4H, Ar), 8.03 (d, 1H, J = 2.2 Hz, Ar), 7.94 (d, 2H, J = 8.8 Hz, Ar), 7.76 - 7.53 (m, 8H, Ar), 7.44 – 7.30 (m, 3H, Ar), 7.13 – 7.02 (m, 5H, Ar, C<u>H</u>=C<u>H</u>), 6.92 (d, 1H, J = 8.8 Hz, Ar), 4.20– 3.98 (m, 4H, OC<u>H_2</u>CH_2), 2.00 – 1.73 (m, 4H, CH_2), 1.65 – 1.10 (m, 30H, CH_2), 0.88 (t, 6H, J = 6.6 Hz, CH_3),
δ^{13}C (50 MHz, $CDCl_3$) 165.00, 154.72, 152.26, 149.32, 142.59, 141.95, 134.43, 132.06, 130.80, 130.10, 129.42, 128.84, 128.47, 128.21, 127.98, 126.56, 126.37, 123.46, 121.20, 118.59, 114.71, 113.23, 69.91, 69.29, 31.91, 29.64, 29.56, 29.34, 29.07, 28.93, 25.95, 25.83, 22.70, 14.13.

12/12

NMR: δ^{1}H (200 MHz, $CDCl_3$) 8.32 – 8.14 (m, 4H, Ar), 8.02 (d, 1H J = 2.2 Hz, Ar), 7.93 (d, 2H, J = 9.0 Hz, Ar), 7.73 – 7.53 (m, 8H, Ar), 7.42 – 7.30 (m, 3H, Ar), 7.20 – 7.01 (m, 5H, Ar, C<u>H</u>=C<u>H</u>), 6.91 (d, 1H, J = 8.6 Hz), 4.24 – 3.94 (m, 4H, OC<u>H_2</u>CH_2), 1.95 - 1.75 (m, 4H, CH_2), 1.65 – 1.10 (m, 32H, CH_2), 0.88 (t, 6H, J = 6.6Hz, CH_3);
δ^{13}C (50 MHz, $CDCl_3$) 164.90, 154.72, 152.25, 149.31, 142.58, 141.94, 140.07, 134.42, 132.05, 130.79, 130.08, 129.56, 129.40, 129.24, 128.84, 128.46, 128.20, 127.96, 126.55, 126.36, 123.45, 121.20, 118.58, 114.70, 113.22, 69.91, 69.28, 31.93, 29.65, 29.60, 29.36, 29.06, 28.93, 25.94, 25.83, 22.70, 14.13.

12/15

NMR: δ^1H (200 MHz, $CDCl_3$) 8.33 – 8.16 (m, 4H, Ar), 8.02 (d, 1H, J = 2.2 Hz, Ar), 7.93 (d, 2H, J = 8.9 Hz, Ar), 7.76 – 7.52 (m, 8H, Ar), 7.42 – 7.30 (m, 3H, Ar), 7.22 – 7.00 (m, 5H, Ar, C<u>H</u>=C<u>H</u>), 6.92 (d, 1H, J = 8.6 Hz), 4.22 – 3.96 (m, 4H, OC<u>H</u>$_2$CH_2), 1.94 - 1.76 (m, 4H, CH_2), 1.54 – 1.16 (m, 42H, CH_2), 0.88 (t, 6H, J = 6.2 Hz, CH_3);

δ^{13}C (50 MHz, $CDCl_3$) 164.91, 154.72, 152.26, 149.32, 142.58, 141.94, 140.09, 134.42, 132.05, 130.79, 130.09, 129.56, 129.40, 129.26, 128.84 , 128.46, 128.20, 127.98, 126.56, 126.36, 123.46, 121.29, 118.58, 114.70, 113.22, 69.91, 69.29, 31.93, 29.67, 29.59, 29.36, 29.06, 28.93, 25.94, 25.83, 22.70, 14.13.

16/16

NMR: δ^1H (300 MHz, $CDCl_3$) 8.24 – 8.19 (m, 4H, Ar), 7.99 (d, 1H, J = 2.1 Hz, Ar), 7.91 (d, 2H, J = 9.0 Hz, Ar), 7.69 – 7.58 (m, 8H, Ar), 7.39 – 7.33 (m, 3H, Ar), 7.20 – 6.99 (m, 5H, Ar, C<u>H</u>=C<u>H</u>), 6.91 (d, 1H, J = 8.7 Hz), 4.12 (t, 2H, J = 6.3 Hz), 4.05 (2H, J = 6.6 Hz, OC<u>H</u>$_2$CH_2), 1.88 - 1.80 (m, 4H, CH_2), 1.50 – 1.44 (m, 4H, CH_2), 1.41 – 1.29 (m, 48H, CH_2), 0.88 (t, 6H, J = 6.3 Hz, CH_3);

δ^{13}C (75 MHz, $CDCl_3$) 164.92, 164.83, 154.83, 152.26, 149.48, 149.42, 142.64, 141.95, 140.34, 134.48, 131.92, 130.78, 130.73, 130.24, 130.16, 129.58, 129.41, 129.35, 128.90 , 128.62, 128.28, 128.10, 126.56, 126.51, 126.37, 123.16, 123.42, 121.17, 118.56, 114.85, 113.43, 70.03, 69.42, 31.93, 29.69, 29.65, 29.58, 29.54, 29.50, 29.35, 29.64, 29.11, 28.97, 25.95, 25.84, 22.67, 14.07.

18/18

NMR: δ^1H (500 MHz, $CDCl_3$) 8.26 – 8.18 (m, 4H, Ar), 8.02 (d, 1H, J = 2.0 Hz, Ar), 7.93 (d, 2H, J = 8.0 Hz, Ar), 7.69 (d, 1H, J = 2Hz, Ar), 7.68 – 7.58 (m, 7H, Ar), 7.42 – 7.34 (m, 3H, Ar), 7.19 – 7.00 (m, 5H, Ar, C<u>H</u>=C<u>H</u>), 6.92 (d, 1H, J = 9.0 Hz), 4.13 (t, 2H, J = 7 Hz, OC<u>H</u>$_2$CH_2), 4.06 (t, 2H, J = 7 Hz, OC<u>H</u>$_2$CH_2), 1.89 - 1.81 (m, 4H, CH_2), 1.54 – 1.44 (m, 4H, CH_2), 1.42 – 1.20 (m, 56H, CH_2), 0.88 (t, 6H, J = 7.0Hz, CH_3);

δ^{13}C (125 MHz, $CDCl_3$) 164.97, 164.88, 154.78, 152.27, 149.44, 149.38, 142.62, 141.98, 140.22, 134.47, 132.00, 130.81, 130.75, 130.17, 130.14, 129.58, 129.40, 129.34, 128.88, 128.55, 128.25, 128.05, 126.57, 126.44, 126.38, 123.53, 123.45, 121.28, 121.19,

118.59, 114.78, 113.33, 69.98, 69.36, 31.94, 29.71, 29.67, 29.59, 29.56, 29.53, 29.37, 29.35, 29.29, 29.10, 28.97, 25.96, 25.85, 22.70, 14.11.