Supporting Information

Asymmetric ether-linked liquid crystalline dimers with a highly polar end group

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1. Synthesis of the intermediates

1.1. Ethyl-3,4,5-trishexyloxybenzoate (1).

This was prepared using similar method to that reported in ref.[S1] as following: to ethyl 3,4,5-trihydroxybenzoate (8.00 g; 40.4 mmol) in 200 mL butanone, 1-bromohexane (18.12 mL; 129 mmol), anhydrous potassium carbonate K₂CO₃ (33.45 g; 242.4 mmol) and a catalytic amount of KI were added. The reaction mixture was stirred under reflux for 18 hours. The suspension obtained was filtered, washed several times with hot butanone. The solvent was removed under vacuum and the remaining oil was poured into 500 mL of hot methanol and cooled slowly under strong stirring. The ester compound 1 was formed as a white precipitate which was filtrated, affording 16.33 g (89.77 %). ¹H-NMR (400 MHz, CDCl₃) δ ppm: 7.24 (s, 2H, Ar-H), 4.34 (qua, *J* = 6.7 Hz, 2H, -OCH₂CH₃), 4.01 (t, *J* = 6.9 Hz,

6H, Ar-OCH₂CH₂), 1.70 – 1.85 (m, 6H, Ar-OCH₂CH₂), 1.49-1.28 (m, 6H, -CH₂-), 1.38 (t, = 6.7 Hz, 3H, -OCH₂CH₃), 1.21 – 1.35 (m, 18H, -CH₂-), 0.88 (t, *J* = 6.7 Hz, 9H, CH₃).

1.2. 3,4,5-Trihexyloxybenzoic acid (2).

Compound **1** (15.00 g, 33.3 mmol) was dissolved in 100 mL of ethanol at 55 °C. After complete dissolution (1.6 g, 40 mmol) of NaOH dissolved in water were added slowly and the mixture refluxed until complete hydrolysis as indicated from TLC. The solution was poured into ice, acidified to pH = 1 with concentrated HCl, filtered and the obtained white solid was washed with excess amount of water. The crude material was recrystallized from methanol, affording 13.52 g (96.11 %) of the pure acid **2**. ¹H-NMR (400 MHz, CDCl₃) δ ppm: 7.33 (s, 2H, Ar-H), 4.03 (m, 6H, Ar-OCH₂CH₂), 1.73 – 1.84 (m, 6H, Ar-OCH₂CH₂), 1.19-1.38 (m, 18H, -CH₂-), 0.88 (t, *J* = 6.9 Hz, 9H, CH₃).

1.3. 4'-Hydroxybiphenyl-3,4,5-trihexyloxyphenylbenzoate (3).

This was synthesized using similar method to that described in ref.[S2] as following: The acid **2** (3 g, 7.1 mmol) was heated under reflux with excess thionyl chloride (15 mL) and a catalytic amount of DMF for one hour. The excess thionyl chloride was removed under reduced pressure followed by the addition of 4,4'-biphenyldiol (6.6 g, 35.5 mmol), 4-dimethylaminopyridine (DMAP, 1.3 g, 10.7 mmol) dissolved in 50 ml of dichloromethane and 10 ml of pyridine under nitrogen atmosphere to the obtained acid chloride. The reaction mixture was stirred at room temperature under nitrogen for 24 hours. The resulting solution was poured into ice and acidified to pH=1 with concentrated HCl followed by filtration and the obtained white solid was washed with excess amount of water and dried over anhydrous CaCl₂ overnight. The crude material was purified by column chromatography using methylene chloride as the eluent affording 2.3 g (54.8%) of **3** as a white solid. ¹H-NMR (400 MHz, CDCl₃) δ ppm: ¹H-NMR (400 MHz, CDCl₃) δ: 7.55 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.50 – 7.38 (m, 4H, Ar-H), 7.33 – 7.15 (m, 2H, Ar-H), 6.89 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.98 (s, 1H, Ar-OH), 4.18 – 3.95 (m, 6H, Ar-OCH₂CH₂), 1.95 – 1.67 (m, 6H, Ar-OCH₂CH₂), 1.65 – 1.21 (m, 18H, CH₂), 1.06 – 0.73 (m, 9H, CH₃).

1.4. 1-Bromo-5-(4-cyanobiphenyl-4'-oxy)pentane (4).

This was synthesized using similar method to that reported in ref.[S3] Thus to 4-cyano-4'-hydroxybiphenyl (2.5 g, 12.8 mmol), 1,5-dibromopentane (17.4 g, 128 mmol) and K₂CO₃ (13.3 g, 96mmol) were added to dry acetone (250 mL), and the reaction mixture was

refluxed with stirring for 24 h. The solution was filtered and the inorganic residues were washed several times with acetone. The acetone was removed under vacuum and the obtained oil was poured into cooled petroleum ether (350 mL) and kept in the refrigerator for several hours. The precipitated white solid was filtered off and washed thoroughly with petroleum ether followed by recrystallization twice from aqueous ethanol to afford 3.2 g (72.7%) of white crystals. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 7.74 – 7.58 (m, 4H, Ar-H), 7.53 (d, J = 8.6 Hz, 2H, Ar-H), 6.99 (d, J = 8.6 Hz, 2H, Ar-H), 4.04 (t, J = 6.1 Hz, 2H, Ar-OCH₂), 3.45 (t, J = 6.7 Hz, 2H, -CH₂Br), 2.03 – 1.91 (m, 2H, -OCH₂CH₂-), 1.91 – 1.80 (m, 2H, BrCH₂CH₂-), 1.71 – 1.60 (m, 2H, -CH₂-).

1.5. 1-(4-Cyanobiphenyl-4'-oxy)-5-(4-formylphenyl-4'-oxy)pentane (5).

This was synthesized using similar method to that described in ref.[S3] To compound **4** (2.75 g, 8 mmol), 4-hydroxybenzaldehyde (1.2 g, 9.8 mmol), and K_2CO_3 (5.5 g, 40 mmol) in *N,N*-dimethylformamide (20 mL) were refluxed with stirring for 6 hours. After cooling the reaction mixture it was poured into water (250 mL). The resulting precipitate was filtered off and purified using column chromatography using methylene chloride as the eluent to yield 2.2 g (71.45%) of **5** as a pale yellow material. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 9.88 (s, 1H, Ar-CHO), 7.83 (d, 2H, J = 8.7 Hz, Ar-H), 7.73 – 7.59 (m, 4H Ar-H), 7.53 (d, 2H, J = 8.6 Hz, Ar-H), 6.99 (d, 4H, J = 8.7 Hz, Ar-H), 4.16 – 3.99 (m, 4H, Ar-OCH₂), 2.00 – 1.83 (m, 4H, Ar-OCH₂CH₂), 1.78 – 1.63 (m, 2H, -CH₂-).

1.6. 4-[5-(4'-Cyanobiphenyl-4-yloxy)pentyl]oxy]benzoic acid (6).

The aldehyde **5** was oxidized to the corresponding acid **6** according to the oxidation procedure reported in Ref.[S4] as following: the aldehyde, **5** (1.7 g, 4.44 mmol) and resorcinol (0.52 g, 4.75 mmol) were dissolved in *tert*-butyl alcohol (120 mL). To the previous solution sodium chlorite (1.91 g, 17.38 mmol) and sodium dihydrogenphosphate (1.28 g, 10.70 mmol) dissolved in water (30 mL) were added in a drop wise manner over a 10-min period. The reaction mixture was stirred at room temperature overnight. Volatile components were removed under vacuum and the residue was dissolved in water (100 mL). 1 N Aqueous HCl was added till pH 3 and the obtained white precipitate was isolated, washed successively with water and hexane, and dried in air to give 1.72 g (97.2 %) of **6**. The obtained acid **6** needed no further purification. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6) δ ppm: 12.54 (s, 1H, Ar-COOH), 7.93 – 7.76 (m, 6H, Ar-H), 7.67 (d, 2H, J = 8.8 Hz, Ar-H), 7.07 – 6.93 (m, 4H, Ar-H), 4.08 – 3.99 (m, 4H, Ar-OCH₂CH₂), 1.91 – 1.68 (m, 4H Ar-OCH₂CH₂), 1.65 – 1.46 (m, 2H, -CH₂-).

2. Analytical data of compounds An/m

Compound A4/5

Yield = 67 %, white crystals. ¹H-NMR (400 MHz, CDCl₃) δ: 8.17 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.76 – 7.59 (m, 8H, Ar-H), 7.53 (d, *J* = 9.1, 2H, Ar-H), 7.44 (s, 2H, Ar-H), 7.35 – 7.21 (m, 4H, Ar-H overlapped with CDCl₃), 7.06 – 6.92 (m, 4H, Ar-H), 4.16 – 4.00 (m, 10H, Ar-OCH₂CH₂), 2.02 – 1.64 (m, 12H, Ar-OCH₂CH₂), 1.63 – 1.42 (m, 6H, CH₂), 1.07 – 0.92 (m, 9H, CH₃). ¹³C-NMR (400 MHz, CDCl₃) δ ppm: 13.81, 13.85, 19.13, 19.24, 22.71, 28.85, 28.94, 31.32, 32.32, 67.84, 68.03, 68.97, 73.19, 108.62, 110.10, 114.29, 115.07, 119.04, 121.64, 122.08, 122.10, 123.84, 127.06, 128.14, 128.15, 128.33, 131.43, 132.31, 132.54, 138.02, 138.16, 143.09, 145.20, 150.51, 150.55, 152.97, 159.64, 163.41, 164.90, 165.03. Elemental Analysis: Calc. for **C₅₆H₅₉NO₉** C, 75.57; H, 6.68; N, 1.57. Found C, 75.53; H, 6.65; N, 1.52 %.

Compound A10/5

Yield = 65 %, white powder. ¹H-NMR (400 MHz, CDCl₃) δ ppm: 8.17 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.75 – 7.57 (m, 8H, Ar-H), 7.53 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.43 (s, 2H, Ar-H), 7.33 – 7.21 (m, 4H, Ar-H overlapped with CDCl₃), 7.05 – 6.92 (m, 4H, Ar-H), 4.18 – 3.98 (m, 10H, Ar-OCH₂CH₂), 2.04 – 1.62 (m, 12H, Ar-OCH₂CH₂), 1.61 – 1.14 (m, 42H, CH₂), 1.01 – 0.75 (m, 9H, CH₃). ¹³C-NMR (400 MHz, CDCl₃) δ ppm: 14.08, 22.66, 22.68, 22.72, 26.04, 26.07, 28.85, 28.94, 29.30, 29.32, 29.37, 29.56, 29.61, 29.65, 29.71, 30.34, 31.89, 31.92, 67.84, 68.03, 69.29, 73.57, 108.63, 110.10, 114.29, 115.07, 119.04, 121.64, 122.08, 122.10, 123.82, 127.06, 128.13, 128.15, 128.33, 131.43, 132.31, 132.54, 138.03, 138.16, 143.09, 145.2, 150.52, 150.55, 152.96, 159.64, 163.41, 164.90, 165.03. Elemental Analysis: Calc. for **C₇₄H₉₅NO₉** C, 77.79; H, 8.38; N, 1.23. Found C, 77.75; H, 8.38; N, 1.20 %.

Compound A4/7

Yield = 66 %, white powder. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : δ 8.22 – 8.09 (m, 2H, Ar-H), 7.73 – 7.59 (m, 8H, Ar-H), 7.57 – 7.48 (m, 2H, Ar-H), 7.44 (s, 2H, Ar-H), 7.33 – 7.23 (m, 4H, Ar-H, Ar-H overlapped with CDCl_3), 7.06 – 6.92 (m, 4H, Ar-H), 4.15 – 3.95 (m, 10H, Ar- OCH_2CH_2), 1.95 – 1.68 (m, 10H, Ar- OCH_2CH_2), 1.65 – 1.40 (m, 12H, CH_2), 1.07 – 0.92 (m, $J = 7.3$ Hz, 9H, CH_3). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ ppm: 13.81, 13.85, 19.13, 19.25, 25.93, 25.96, 29.01, 29.06, 29.13, 31.32, 32.32, 68.03, 68.20, 68.96, 73.19, 108.62, 110.06, 114.30, 115.06, 119.06, 121.54, 122.08, 122.11, 123.85, 127.04, 128.13, 128.15, 128.31, 131.31, 132.30, 132.53, 138.01, 138.16, 143.08, 145.22, 150.51, 150.56, 152.97, 159.73, 163.50, 164.92, 165.03. Elemental Analysis: Calc. for $\text{C}_{58}\text{H}_{63}\text{NO}_9$ C, 75.87; H, 6.92; N, 1.53. Found C, 75.82; H, 6.92; N, 1.49 %.

Compound A6/7

Yield = 62 %, white powder. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 8.16 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.73 – 7.59 (m, 8H, Ar-H), 7.53 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.43 (s, 2H, Ar-H), 7.33 – 7.21 (m, 4H, Ar-H overlapped with CDCl_3), 7.04 – 6.92 (m, 4H, Ar-H), 4.14 – 3.93 (m, 10H, Ar- OCH_2CH_2), 1.93 – 1.71 (m, 10H, Ar- OCH_2CH_2), 1.64 – 1.22 (m, 24H, CH_2), 1.00 – 0.82 (m, 9H, CH_3). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ ppm: 13.99, 14.06, 22.59, 22.66, 25.68, 25.73, 25.93, 25.96, 29.01, 29.06, 29.13, 29.25, 30.28, 31.53, 31.71, 68.03, 68.20, 69.28, 73.57, 108.62, 110.07, 114.30, 115.06, 119.06, 121.54, 122.08, 122.11, 123.83, 127.04, 128.13, 128.15, 128.31, 131.31, 132.30, 132.53, 138.01, 138.16, 143.08, 145.22, 150.51, 150.56, 152.96, 159.73, 163.50, 164.91, 165.03. Elemental Analysis: Calc. for $\text{C}_{64}\text{H}_{75}\text{NO}_9$ C, 76.69; H, 7.54; N, 1.40. Found C, 76.60; H, 7.51; N, 1.37 %.

Compound A10/7

Yield = 64 %, $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 8.16 (d, $J = 8.9$ Hz, 2H, Ar-H), 7.74 – 7.58 (m, 8H, Ar-H), 7.53 (d, 2H, Ar-H), 7.43 (s, 2H, Ar-H), 7.34 – 7.21 (m, 4H, Ar-H overlapped with CDCl_3), 7.06 – 6.90 (m, 4H, Ar-H), 4.13 – 3.96 (m, 10H, Ar- OCH_2CH_2), 1.92 – 1.69 (m, 10H, Ar- OCH_2CH_2), 1.64 – 1.16 (m, 48H, CH_2), 0.96 – 0.80 (m, 9H, CH_3). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ ppm: 14.08, 22.66, 22.68, 25.93, 25.96, 26.04, 26.07, 29.01,

29.06, 29.13, 29.30, 29.32, 29.37, 29.56, 29.61, 29.65, 29.71, 30.34, 31.89, 31.92, 68.03, 68.20, 69.28, 73.57, 108.63, 110.07, 114.29, 115.06, 119.05, 121.54, 122.08, 122.10, 123.82, 127.04, 128.13, 128.15, 128.30, 131.32, 132.30, 132.53, 138.02, 138.16, 143.09, 145.22, 150.51, 150.56, 152.96, 159.73, 163.50, 164.91, 165.03. Elemental Analysis: Calc. for $C_{76}H_{99}NO_9$ C, 77.98; H, 8.52; N, 1.20. Found C, 77.97; H, 8.50; N, 1.19 %.

3. 1H -NMR Spectra of compounds *An/m*

Figure S1. 1H -NMR Spectrum of **A4/5** in $CDCl_3$.

Figure S2. 1H -NMR Spectrum of **A6/5** in $CDCl_3$.

Figure S3. ^1H -NMR Spectrum of **A10/5** in CDCl_3 .

Figure S4. ^1H -NMR Spectrum of **A4/7** in CDCl_3 .

Figure S5. ^1H -NMR Spectrum of **A6/7** in CDCl_3 .

Figure S6. ^1H -NMR Spectrum of **A10/7** in CDCl_3 .

4. ^{13}C -NMR Spectra of compounds An/m

Figure S7. ^{13}C -NMR Spectrum of A4/5 in CDCl_3 .

Figure S8. ^{13}C -NMR Spectrum of A6/5 in CDCl_3 .

Figure S9. ^{13}C -NMR Spectrum of A10/5 in CDCl_3 .

Figure S10. ^{13}C -NMR Spectrum of A4/7 in CDCl_3 .

Figure S11. ^{13}C -NMR Spectrum of A6/7 in CDCl_3 .

Figure S12. ^{13}C -NMR Spectrum of A10/7 in CDCl_3 .

5. References

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