Supplementary Material (ESI) for Soft Matter

Supporting Information

Chiral Supermolecular Liquid Crystalline Tetrapedes

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Experimental procedures

4- Experimental section

11-(4-cyanobiphenyl-4'-yloxy)undecanol 2a

4-Cyano-4'-hydroxybiphenyl (20 g, 102 mmol) 1, 11-bromo-1-undecanol (25.17 g, 98 mmol), potassium carbonate (58.40 g, 422.6 mmol) and a catalytic amount of KI were heated under reflux in butanone (300 ml) for 18 h. The solids were removed by filtration and washed with acetone. The combined solvents were removed on a rotary evaporator to give a residue, which was recrystallised from acetonitrile to afford a white solid (34.34 g, 96%).
1H NMR (CDCl3, 400 MHz, Me4Si): δ (ppm) 1.22-1.41 (6CH2, m)), 1.47 (CH2, quint), 1.57 (CH2, quint), 1.81 (CH2, quint), 3.64 (OCH2, t), 4.00 (OCH2, t), 6.96-7.02 (2CH, d), 7.49-7.55 (2CH, d), 7.61-7.71 (4CH, q).
13C NMR (CDCl3, 100 MHz, Me4Si): δ(ppm) 25.64 (CH2), 25.91 (CH2), 29.10 (CH2), 29.26 (CH2), 29.31 (CH2), 29.40 (CH2), 29.43 (CH2), 29.47 (CH2), 32.66 (CH2), 62.83 (CH2OH), 68.04 (CH2OAr), 109.83 (Cq), 114.96 (CH), 119.00 (CN), 126.91 (CH), 128.18 (CH), 131.06 (C_q), 132.42 (CH), 145.13 (C_q), 159.68 (C_q).

6-(4-cyanobiphenyl-4'-yloxy)hexanol 2b

4-Cyano-4'-hydroxybiphenyl (5.76 g, 29.51 mmol), 1, 6-bromo-1-hexanol (97%) (6.17 g, 33.05 mmol, 1.12 eq), potassium carbonate (11.4 g, 82.49 mmol, 2.80 eq) and a catalytic amount of KI were heated under reflux in butanone (100 ml) for 18 h. The solids were removed by filtration and washed with acetone. The combined solvents were removed on a rotary evaporator to give a residue, which was recrystallised from EtOH to afford a white solid (6.53 g, 92 %).
^{1}H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ (ppm) 1.35-1.72 ($3CH_2$, m), 1.83 (CH_2, quint), 3.67 (OCH_2, t), 4.01 (OCH_2, t), 6.96-7.02 (2CH, d), 7.49-7.55 (2CH, d), 7.61-7.71 (4CH, dd).
^{13}C NMR ($CDCl_3$, 100 MHz, Me_4Si): δ(ppm) 25.49 (CH_2), 25.83 (CH_2), 29.13 (CH_2), 32.60 (CH_2), 62.80 (CH_2OH), 67.94 (CH_2OAr), 109.95 (C_q), 115.00 (CH), 119.09 (CN), 127.02 (CH), 128.28 (CH), 131.23 (C_q), 132.52 (CH), 145.21 (C_q), 159.68 (C_q).

Typical procedure for the synthesis of the mesogenic arms carboxylic acids 3a and 3b
To a vigorously stirred solution of 11-(4-cyanobiphenyl-4'-yloxy)undecanol 2a 1 [or 6-(4-cyanobiphenyl-4'-yloxy) hexanol 2b] 2 (67.72 mmol) in acetone (1 L) was added the chromic acid oxidizing reagent (2.67 M, 42 mL) dropwise at 0 °C. The mixture was stirred at the same temperature for 15 min and at room temperature for 30 min. The reaction was then quenched with i-PrOH (20 mL) and the mixture was filtered to remove the solids. The filtrate was diluted with water (1 L) to precipitate a white solid which was filtered and dried to yield pure acid 3a in 95 % yield [or 3b in 96 % yield].

11-(4-cyanobiphenyl-4'-yloxy)undecanoic acid 3a
^{1}H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ (ppm) 1.22-1.41 (5CH2, m), 1.47 (CH2, quint), 1.64 (CH2, quint), 1.81 (CH2, quint), 2.35 (CH2, t), 4.00 (CH2O, t), 6.96-7.02 (2CH, d), 7.49-7.55 (2CH, d), 7.61-7.71 (4CH, m).
^{13}C NMR ($CDCl_3$, 100 MHz, Me_4Si): δ (ppm) 24.65 (CH2), 26.00 (CH2), 29.02 (CH2), 29.19 (CH2), 29.32 (CH2), 29.46 (CH2), 33.86 (CH2), 68.13 (CH2O), 109.99 (Cq-CN), 115.06 (CHar), 119.13 (CN), 127.06 (CHar), 128.31 (CHar), 131.23 (Cq), 132.56 (CHar), 145.28 (Cq), 159.77 (CqO), 179.14 (CO2).

6-(4-cyanobiphenyl-4'-yloxy)hexanoic acid 3b
^{1}H NMR ($DMSO-d_6$, 400 MHz): δ (ppm) 1.47 (CH_2, quint), 1.62 (CH_2, quint), 1.76 (CH_2, quint), 2.26 (CH_2CO, t), 3.99 (CH_2O, t), 6.95-7.05 (2CH, d), 7.55-7.70 (2CH, d), 7.70-7.85 (4CH, m).
^{13}C NMR ($DMSO-d_6$, 100 MHz): δ (ppm) 24.16 (CH_2), 25.05 (CH_2), 28.32 (CH_2), 33.52 (CH_2), 67.29 (CH_2O), 109.07 (C_q-CN), 114.77 (CH_{ar}), 118.66 (CN), 126.56 (CH_{ar}), 127.97 (CH_{ar}), 130.17 (C_q), 132.37 (CH_{ar}), 144.18 (C_q), 159.18 (C_q), 174.28 (CO_2).

Typical procedure for the synthesis of the tetrapedes Gn and Mn (n=1, 2)

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[1] S. J. Cowling, A.W. Hall, J. W. Goodby, Y. Wang, H. F. Gleeson, J. Mat. Chem., 16, 22, 2006, 2181–2191.
[2] T. Mihara, M. Tsutsumi, N. Koide, Mol. Cryst. Liq. Cryst. Sci. Tech. Mol. Cryst. Liq. Cryst., 382, 2002, 53 – 64.

Under nitrogen atmosphere and to a oven-dried round-bottomed flask containing a solution of 11-(4-cyanobiphenyl-4'-yloxy)undecanoic acid **3a** [or 6-(4-cyanobiphenyl-4'-yloxy)hexanoic acid **3b**] (9.70 mmol) and methyl α-D-mannopyranoside [or methyl α-D-glucopyranoside] (340 mg, 1.62 mmol) in dry CH_2Cl_2 (50 mL) were added DCC (2.2 g, 10.66 mmol) and *N*,*N*-dimethylaminopyridine (119 mg, 0.97 mmol). The resulting mixture was stirred for 14 days at room temperature and the reaction progress was monitored by gel permeation chromatography (GPC). The resulting solution was filtered and the DCU washed with CH_2Cl_2. The solvent was then evaporated in vacuo to afford an oily crude residue, which was submitted to column chromatography (CH_2Cl_2 / EtOAc) to give the tetramers **Gn / Mn** (n=1, 2) in 100 % yields.

Methyl-tetra-O-[11-(4-cyanobiphenyl-4'-yloxy)undecanoyl]-α-D-glucopyranoside G1
^{1}H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ (ppm) 1.15-1.40 (20CH_2, m), 1.40-1.50 (4CH_2, m), 1.50-1.70 (4CH_2, m), 1.70-1.85 (4CH_2, m), 2.14-2.44 (4CH_2, m), 3.41 (MeO, s), 3.92-4.04 (4CH_2 +1CH, m), 4.09-4.18 (1H, m), 4.19-4.27 (1H, dd), 4.87-4.94 (1H, dd), 4.94-4.98 (1H, d), 5.10 (1H, t), 5.53 (1H, t), 6.92-7.01 (8CH, m), 7.46-7.54 (8CH, m), 7.56-7.69 (16CH, m).
^{13}C NMR ($CDCl_3$, 100 MHz, Me_4Si): δ (ppm) 24.73 (CH_2), 24.85 (CH_2), 24.89 (CH_2) , 26.01 (CH_2), 28.99 (CH_2), 29.07 (CH_2), 29.11 (CH_2), 29.20 (CH_2), 29.25 (CH_2), 29.35 (CH_2), 29.36 (CH_2), 29.48 (CH_2), 29.52 (CH_2), 33.98 (CH_2), 34.01 (CH_2), 34.14 (CH_2), 55.41 (MeO), 61.76 (CH_2O), 67.29 (CH), 68.07 (CH_2O), 68.21 (CH), 69.69 (CH), 70.69 (CH), 96.80 (CHO_2), 109.95 (C_q-CN), 115.01 (CH_{ar}), 119.07 (CN), 126.98 (CH_{ar}), 128.26 (CH_{ar}), 131.12 (C_q), 132.51 (CH_{ar}), 145.13 (C_q), 145.15 (C_q), 145.18 (C_q), 159.74 (C_qO), 172.23(CO_2), 172.59 (CO_2), 172.90 (CO_2), 173.37 (CO_2).
MALDI-TOF MS m/z: observed data 1639.9 (M^+, 55 %), 1662.9 (MNa^+, 100.0%); calculated 1639.9 (M^+), 1662.9 (MNa^+).
Elemental analysis: Found C, 74.11; H, 7.80; N, 3.36. Calc. for $C_{103}H_{122}N_4O_{14}$: C, 75.43; H, 7.50; N, 3.42.

Methyl-tetra-O-[11-(4-cyanobiphenyl-4'-yloxy)undecanoyl]-α-D-mannopyranoside M1
^{1}H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ (ppm) 1.20-1.40 (20CH_2, m), 1.40-150 (4CH_2, m), 1.51-1.72 (4CH_2, m), 1.73-1.85 (4CH_2, m), 2.15-2.50 (4CH_2, m), 3.40 (MeO, s), 3.92-4.03 (4CH_2+1H, m), 4.12-4.20 (1H, dd,), 4.22-4.31 (1H, dd), 4.70-4.73 (1H, d), 5.25-5.40 (3H, m), 6.93-7.00 (8CH, m), 7.47-7.53 (8CH, m), 7.56-7.68 (16CH, m).
^{13}C NMR ($CDCl_3$, 100 MHz, Me_4Si): δ (ppm) 24.66 (CH_2), 24.75 (CH_2), 24.82 (CH_2), 24.89 (CH_2), 26.00 (CH_2), 29.03 (CH_2), 29.05 (CH_2), 29.08 (CH_2), 29.11 (CH_2), 29.18 (CH_2), 29.22 (CH_2), 29.23 (CH_2), 29.35 (CH_2), 29.50 (CH_2), 34.03 (CH_2), 34.08 (CH_2), 55.21 (MeO), 62.36 (CH_2O), 65.85 (CH), 68.07 (CH_2O), 68.52 (CH), 68.90 (CH), 69.25 (CH), 98.58 (CHO_2), 109.98 (C_q-CN), 115.00 (CH_{ar}), 119.04 (CN), 126.98 (CH_{ar}), 128.25 (CH_{ar}), 131.18 (C_q), 132.50 (CH_{ar}), 145.16 (C_q), 159.72 (C_qO), 172.37 (CO_2), 172.42 (CO_2), 172.70 (CO_2), 173.32 (CO_2).
MALDI-TOF MS m/z: observed data 1639.9 (M^+, 13%), 1662.9 (MNa^+, 100.0%); calculated 1639.9 (M^+), 1662.9 (MNa^+).
Elemental analysis: Found C, 75.36**;** H, 8.05**;** N, 3.76. Calc. for $C_{103}H_{122}N_4O_{14}$: C, 75.43; H, 7.50; N, 3.42.

Methyl-tetra-O-[6-(4-cyanobiphenyl-4'-yloxy)hexanoyl]-α-D-glucopyranoside G2
^{1}H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ (ppm) 1.35-1.90 (12CH_2, m), 2.20-2.50 (4CH_2, m), 3.41 (MeO, s), 3.88-4.05 (4CH_2+1H, m), 4.10-4.18 (1H, dd), 4.22-4.31 (1H, dd), 4.89-4.99 (2H, m), 5.13 (1H, t), 5.53 (1H, t), 6.90-7.00 (8CH, m), 7.46-7.54 (8CH, m), 7.55-7.70 (16CH, m).
^{13}C NMR ($CDCl_3$, 100 MHz, Me_4Si): δ (ppm) 24.38 (CH_2), 24.45 (CH_2), 24.50 (CH_2), 25.40 (CH_2), 25.45 (CH_2), 25.47 (CH_2), 28.72 (CH_2), 33.76 (CH_2), 33.89 (CH_2), 55.37 (MeO), 61.59 (CH_2O), 67.13 (CH), 67.49 (CH_2O), 67.51 (CH_2O), 67.63 (CH_2O), 68.11 (CH), 69.79 (CH), 70.61 (CH), 96.67 (CHO_2), 109.85 (C_q-CN), 109.88 (C_q-CN), 109.90 (C_q-CN), 114.83 (CH_{ar}), 114.85 (CH_{ar}), 114.86 (CH_{ar}), 114.90 (CH_{ar}), 118.95 (CN), 118.98 (CN), 126.85 (CH_{ar}), 126.86 (CH_{ar}), 126.88 (CH_{ar}), 126.89 (CH_{ar}), 128.16 (CH_{ar}), 128.18 (CH_{ar}), 131.13(C_q), 131.15 (C_q), 131.18 (C_q), 132.42 (CH_{ar}), 144.88 (C_q), 144.95 (C_q), 145.02 (C_q), 159.43 (C_qO), 159.44 (C_qO), 159.48 (C_qO), 159.52 (C_qO), 171.93 (CO_2), 172.30 (CO_2), 172.54 (CO_2), 173.02 (CO_2).
MALDI-TOF MS m/z: observed data data 1358.5 (M^+, 50%), 1381.5 (MNa^+, 100.0%); calculated 1358.5 (M^+), 1381.5 (MNa^+).
Elemental analysis: Found C, 73.08; H, 5.76; N, 4.02. Calc. for $C_{83}H_{82}N_4O_{14}$: C, 73.32; H, 6.08; N, 4.12.

Methyl-tetra-O-[6-(4-cyanobiphenyl-4'-yloxy)hexanoyl]-α-D-mannopyranoside M2
^{1}H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ (ppm) 1.35-1.90 (12CH_2, m), 2.20-2.31 (CH_2, m), 2.31-2.38 (CH_2, m), 2.38-2.55 (2CH_2, m), 3.42 (MeO), 3.88-4.05 (4CH_2+1H, m), 4.15-4.21 (1H, dd), 4.27-4.35 (1H, dd), 4.71-4.75 (1H, d), 5.27-5.44 (3H, m), 6.90-7.00 (8H, m), 7.46-7.54 (8H, m), 7.55-7.70 (16H, m).
^{13}C NMR ($CDCl_3$, 100 MHz, Me_4Si): δ (ppm) 23.99 (CH_2), 24.09 (CH_2), 24.17 (CH_2), 24.33 (CH_2), 25.04 (CH_2), 25.07 (CH_2), 25.13 (CH_2), 28.41 (CH_2), 28.46 (CH_2), 33.44 (CH_2), 33.47 (CH_2), 33.61 (CH_2), 54.83 (MeO), 61.82 (CH_2O), 65.34 (CH), 67.21 (CH_2O), 67.31 (CH_2O), 68.12 (CH), 68.79 (CH), 68.86 (CH), 98.21 (CHO_2), 109.44 (C_q-CN), 114.55 (CH_{ar}), 114.58 (CH_{ar}), 118.58 (CN), 126.40 (CH_{ar}), 127.77 (CH_{ar}), 130.54 (C_q), 130.56 (C_q), 132.03 (CH_{ar}), 144.41 (C_q), 144.43 (C_q), 159.17 (C_qO), 159.21 (C_qO), 159.23 (C_qO), 171.73 (CO_2),171.76 (CO_2), 171.95 (CO_2), 172.57 (CO_2).
MALDI-TOF MS m/z: observed data 1358.5 (M^+, 22%), 1381.5 (MNa^+, 100.0%)%); calculated 1358.5 (M^+), 1381.5 (MNa^+).
Elemental analysis: Found C, 71.28; H, 6.16; N, 3.68. Calc. for $C_{83}H_{82}N_4O_{14}$: C, 73.32; H, 6.08; N, 4.12