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Liquid Crystals with Novel Complex Superstructures

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1. Synthesis and analytical data:

1.1. Lithium 14-(4,4"-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (10-Li): 14-(4,4"-Didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoic acid[S1] (0.50 g, 0.63 mmol) was dissolved in diethyl ether (50 mL), then LiOH (15 mg, 0.63 mmol), dissolved in water (2 mL) was added, the salt was precipitated as soon as the base was added (stirring was avoided, because after stirring the solid become too finely distributed to be filtered), the reaction mixture was, then, kept at r.t. over night to complete the reaction. After that, the solid was filtered and washed with water and dried in air, the crude product was purified by repeated crystallized from ethyl acetate. Yield 0.23 g (45.7 %); transition temperatures, s. Tab. S7. ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz) δ = 7.50 (d, ^3J(H,H) = 8.8, 2 H, Ar-H), 7.49 (d, ^3J(H,H) = 8.8, 2 H, Ar-H), 7.30 (d, ^3J(H,H) = 7.8, 1 H, Ar-H), 7.16 (dd, ^3J(H,H) = 7.8, ^4J(H,H) = 1.6, 1 H, Ar-H), 7.10 (d, ^4J(H,H) = 1.6, 1 H, Ar-H), 7.94-6.85 (m, 4 H, Ar-H), 4.11 (t, ^3J(H,H) = 4.5, 2 H, OCH_2), 3.97-3.93 (m, 4 H, OCH_2), 3.87 (s, 2 H, OCH_2COO), 3.74-3.72 (m, 2 H, OCH_2), 3.56-3.50 (m, 12 H, OCH_2), 1.81-1.73 (m, 4 H, CH_2), 1.46-1.26 (m, 28 H, CH_2), 0.89-0.85 (m, 6 H, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 175.4, 158.7, 158.0, 155.8, 140.8, 133.1, 130.7, 130.5 (2C), 130.3, 128.9, 127.9 (2C), 119.5, 114.7 (2C), 113.9 (2C), 111.5, 70.8, 70.6, 70.4, 70.2, 70.0, 69.7, 69.6, 69.4, 68.3, 68.1, 68.0, 31.9 (2C), 29.6 (2C), 29.6 (2C), 29.5, 29.5, 29.4, 29.4 (3C), 26.2, 26.1, 22.7 (2C), 14.2 (2C). $C_{48}H_{71}O_9Li{\cdot}0.5H_2O$ (Cal) C:71.35 %, H:8.98 %, (Found) C:71.21 %, H:8.81 %.

1.2. Sodium 14-(4,4"-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (10-Na): Methyl 14-(4,4"-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate[S1] (0.81 g, 1 mmol) and aqueous NaOH (1 M, 50 mL) were heated for 16 h under reflux. After cooling to r.t., the precipitated solid was filtered off and dried in air, the crude product was purified by column chromatography on silica gel with $CHCl_3/CH_3OH$ as Eluent, and repeated crystallized from ethyl acetate or $CHCl_3$/n-hexane. Yield 0.74 g (64.9 %); transition temperatures, s. Tab. S7. ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz) δ = 7.49 (d, ^3J(H,H) = 8.8, 2 H, Ar-H), 7.48 (d, ^3J(H,H) = 8.8, 2 H, Ar-H), 7.29 (d, ^3J(H,H) = 7.8, 1 H, Ar-H), 7.14 (dd, ^3J(H,H) = 7.8, ^4J(H,H) = 1.6, 1 H, Ar-H), 7.09 (d, ^4J(H,H) = 1.6, 1 H, Ar-H), 6.91 (d, ^3J(H,H) = 8.6, 2 H, Ar-H), 6.87 (d, ^3J(H,H) = 8.6, 2 H, Ar-H), 4.10 (t, ^3J(H,H) = 4.5, 2 H, OCH_2), 3.96-3.91 (m, 4 H, OCH_2), 3.83 (s, 2 H, OCH_2COO), 3.72-3.69 (m, 2 H, OCH_2), 3.58-3.51 (m, 12 H, OCH_2), 1.78-1.72 (m, 4 H, CH_2), 1.43-1.26 (m, 28 H, CH_2), 0.89-0.85 (m, 6 H, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 176.2, 159.3, 158.6, 156.4, 141.3, 133.6, 131.3, 131.0 (2C), 130.9, 129.4, 128.4 (2C), 120.0, 115.3 (2C), 114.4 (2C), 112.0, 71.5, 71.3, 71.0, 70.7, 70.5, 70.2, 70.1, 69.6, 68.7, 68.6, 68.5, 32.4 (2C), 30.1 (2C), 30.0 (2C), 30.0 (2C), 29.9, 29.9 (3C), 26.7, 26.6, 23.2 (2C), 14.7 (2C). EA: $C_{48}H_{71}O_9Na{\cdot}H_2O$ (Cal.) C:69.20 %, H:8.83 %, (Found) C:69.12 %, H:8.83 %.

1.3. Potassium 14-(4,4"-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (10-K): Synthesized in an analogous way as **10-Li** from 14-(4,4"-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoic acid[S1] (0.50 g, 0.63 mmol) and KOH (35 mg, 0.63 mmol). Yield 0.24 g (45.8 %); transition temperatures, s. Tab. S7. ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz)

δ = 7.49 (d, ^3J(H,H) = 8.6, 2 H, Ar-H), 7.45 (d, ^3J(H,H) = 8.6, 2 H, Ar-H), 7.27 (d, ^3J(H,H) = 7.8, 1 H, Ar-H), 7.16-7.13 (m, 1 H, Ar-H), 7.11 (s, 1 H, Ar-H), 6.91 (d, ^3J(H,H) = 8.8, 2 H, Ar-H), 6.86 (d, ^3J(H,H) = 8.8, 2 H, Ar-H), 4.13 (t, ^3J(H,H) = 4.5, 2 H, OCH_2), 3.96-3.91 (m, 4 H, OCH_2), 3.78 (s, 2 H, OCH_2COO), 3.77-3.74 (m, 2 H, OCH_2), 3.55-3.35 (m, 12 H, OCH_2), 1.80-1.73 (m, 4 H, CH_2), 1.45-1.22 (m, 28 H, CH_2), 0.87 (t, ^3J(H,H) = 6.7, 6 H, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 174.8, 158.7, 158.0, 155.7, 140.8, 133.0, 130.7, 130.5 (2C), 130.4, 128.9, 127.9 (2C), 119.5, 114.7 (2C), 113.9 (2C), 111.6, 71.3, 70.4, 70.0, 70.0, 69.6 (2C), 69.4, 68.9, 68.7, 68.1, 68.0, 31.9 (2C), 29.6 (2C), 29.6 (2C), 29.5, 29.5, 29.4, 29.4 (3C), 26.2, 26.1, 22.7 (2C), 14.2 (2C). $C_{48}H_{71}O_9K{\cdot}H_2O$ (Cal) C:67.89 %, H:8.66 %, (Found) C:67.78 %, H:8.74 %.

1.4. Cesium 14-(4,4”-didecyloxy-p-terphenyl-2’-yloxy)-3,6,9,12-tetraoxatetradecanoate (10-Cs): Synthesized in an analogous way as **10-Li** from 14-(4,4”-didecyloxy-p-terphenyl-2’-yloxy)-3,6,9,12-tetraoxatetradecanoic acid[S1] (0.50 g, 0.63 mmol) and Cs_2CO_3 (102 mg, 0.31 mmol). Yield 0.30 g (51.4 %); transition temperatures, s. Tab. S7. ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz) δ = 7.51 (d, ^3J(H,H) = 8.8, 2 H, Ar-H), 7.46 (d, ^3J(H,H) = 8.8, 2 H, Ar-H), 7.29 (d, ^3J(H,H) = 7.8, 1 H, Ar-H), 7.16 (dd, ^3J(H,H) = 7.8, ^4J(H,H) = 1.6, 1 H, Ar-H), 7.12 (d, ^4J(H,H) = 1.6, 1 H, Ar-H), 6.93 (d, ^3J(H,H) = 8.8, 2 H, Ar-H), 6.90 (d, ^3J(H,H) = 8.8, 2 H, Ar-H), 4.17 (t, ^3J(H,H) = 4.5, 2 H, OCH_2), 3.97-3.93 (m, 4 H, OCH_2), 3.79 (s, 2 H, OCH_2COO), 3.77-3.75 (m, 2 H, OCH_2), 3.56-3.40 (m, 12 H, OCH_2), 1.78-1.73 (m, 4 H, CH_2), 1.48-1.22 (m, 28 H, CH_2), 0.86 (t, ^3J(H,H) = 6.8, 6 H, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 174.2, 158.8, 158.2, 155.6, 141.0, 133.0, 130.9, 130.6 (2**C**), 130.4, 128.8, 128.0 (2**C**), 119.7, 114.8 (2**C**), 114.0 (2**C**), 111.6, 71.9, 70.5 (2C), 70.1, 70.0, 69.9, 69.4, 69.1, 68.5, 68.1, 68.0, 31.9 (2**C**), 29.6 (2C), 29.6 (2C), 29.5, 29.4, 29.4, 29.3 (3**C**), 26.1, 26.1, 22.7 (2**C**), 14.1 (2**C**). $C_{48}H_{71}O_9Cs{\cdot}0.5H_2O$ (Cal.) C:61.13 %, H:7.80 %, (Found) C:61.01 %, H:7.99 %.

1.5. Sodium 14-(4,4”-dihexadecyloxy-p-terphenyl-2’-yloxy)-3,6,9,12-tetraoxatetradecanoate (16-Na): Synthesized as reported for **10-Na** from methyl 14-(4,4”-dihexadecyloxy-p-terphenyl-2’-yloxy)-3,6,9,12-tetraoxatetradecanoate[S1] (1.3 g, 1.3 mmol). Yield 1.0 g (76.2 %); transition temperatures, s. Tab. S7. ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz) δ = 7.48 (d, ^3J(H,H) = 8.6, 2 H, Ar-H), 7.47 (d, ^3J(H,H) = 8.7, 2 H, Ar-H), 7.28 (d, ^3J(H,H) = 7.9, 1 H, Ar-H), 7.14 (dd, ^3J(H,H) = 7.9, ^4J(H,H) = 1.7, 1 H, Ar-H), 7.09 (d, ^4J(H,H) = 1.7, 1 H, Ar-H), 6.91 (d, ^3J(H,H) = 8.7, 2 H, Ar-H), 6.86 (d, ^3J(H,H) = 8.7, 2 H, Ar-H), 4.09 (t, 2H, ^3J(H,H) = 4.8, OCH_2), 3.96-3.87 (m, 6 H, OCH_2, OCH_2COO), 3.70 (t, ^3J(H,H) = 4.8, 2 H, OCH_2), 3.63-3.43 (m, 12 H, OCH_2), 1.78-1.73 (m, 4 H, CH_2), 1.43-1.38 (m, 4 H, CH_2), 1.37-1.23 (m, 48 H, CH_2), 0.88-0.84 (m, 6 H, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 176.1, 158.7, 158.0, 155.8, 140.7, 133.0, 130.7, 130.4 (2C), 130.3, 128.9, 127.9 (2C), 119.5, 114.7 (2C), 113.9 (2C), 111.5, 70.9, 70.8, 70.5, 70.4, 70.2, 69.9, 69.6, 69.4, 68.2, 68.2, 68.0, 32.0 (2C), 29.8 (6C), 29.7 (2C), 29.7 (4C), 29.7 (2C), 29.7, 29.6, 29.6, 29.5, 29.4 (4C), 26.2, 26.2, 22.8 (2C), 14.2 (2C). $C_{60}H_{95}O_9Na{\cdot}0.2H_2O$ (Cal.) C:73.01 %, H:9.74 %, (Found) C:72.95 %, H:9.64 %.

1.6. Cesium 14-(4,4”-dihexadecyloxy-p-terphenyl-2’-yloxy)-3,6,9,12-tetraoxatetradecanoate (16-Cs): Synthesized in an analogous way as **10-Li** from 14-(4,4”-dihexadecyloxy-p-terphenyl-2’-yloxy)-3,6,9,12-tetraoxatetradecanoic acid[S1] (0.234 g, 0.24 mmol) and Cs_2CO_3 (39.8 mg, 0.12 mmol). Yield 0.164 g (62.5%); transition temperatures, s. Tab. S7. ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz) δ = 7.50 (d, ^3J(H,H) = 8.7, 2 H, Ar-H), 7.48 (d, ^3J(H,H) = 8.7, 2 H, Ar-H), 7.29 (d, ^3J(H,H) = 7.9, 1 H, Ar-H), 7.17 (dd, ^3J(H,H) = 7.9, ^4J(H,H) = 1.7, 1 H, Ar-H), 7.11 (d, ^4J(H,H) = 1.5, 1 H, Ar-H), 6.93 (d, ^3J(H,H) = 8.7, 2 H, Ar-H), 6.90 (d, ^3J(H,H) = 8.7, 2 H, Ar-H), 4.19-4.17 (m, 2H, OCH_2), 3.98-3.94 (m, 4 H, OCH_2), 3.84 (s, 2 H, OCH_2COO), 3.77-3.75 (m, 2 H, OCH_2), 3.57-3.46 (m, 12 H, OCH_2), 1.79-1.74 (m, 4 H, CH_2), 1.46-1.41 (m, 4 H, CH_2), 1.40-1.20 (m, 48 H, CH_2), 0.86 (t, ^3J(H,H) = 7.3, 6 H, CH_3).^{13}C-NMR ($CDCl_3$, 100

MHz) δ = 174.1, 158.7, 158.1, 155.4, 141.0, 132.9, 130.9, 130.6 (2C), 130.3, 128.7, 127.9 (2C), 119.7, 114.7 (2C), 114.0 (2C), 111.5, 71.1, 70.5, 70.4, 70.2, 70.1, 70.0, 69.6, 69.4, 68.3, 68.2, 68.1, 32.0 (2C), 29.8 (6C), 29.8 (2C), 29.7 (2C), 29.7 (4C), 29.6 (2C), 29.5 (2C), 29.5 (2C), 29.5 (2C), 26.2, 26.2, 22.8 (2C), 14.2 (2C). $C_{60}H_{95}O_9Cs$ (Cal.) C:65.91 %, H:8.76 %, (Found) C:65.63 %, H:8.55 %.

2. Experimental conditions for X-ray scattering

Powder X-ray investigations were carried out with a Guinier film camera (Huber). Samples in glass capillaries (∅ 1 mm) in a temperature-controlled heating stage, quartz-monochromatized CuK_α radiation, 30 min exposure time, calibration with the powder pattern of $Pb(NO_3)_2$, indices as found for aligned samples on a glas plate on a temperature-controlled heating stage (alignement at the sample–glas or at the sample–air interface, sample disordered around an ∞-fold axis perpendicular to this interface) with a 2D detector (HI-STAR, Siemens). Synchrotron small-angle diffraction experiments were performed on Station 16.1 at the SRS at Daresbury, U.K. Powder samples in capillaries were held in a modified Linkam temperature-controlled stage. A double focused highly collimated monochromatic beam was used, with a Daresbury quadrant multiwire detector. Sample to detector distance was 1.3 metres.

θ_{exp} = Bragg angle measured from Guinier patterns
θ_{calc} = Bragg angle calculated from the lattice parameters according to:

$$\sin^2\theta_{calc} = \frac{\lambda^2}{4a^2}\left[\frac{4}{3}\left(h^2 + k^2 + hk\right) + \left(\frac{a}{c}\right)^2 l^2\right]$$

a, c = lattice parameters

2.1. Rhombohedral phase of 16-Na

Assumed space group from model considerations: $R\bar{3}m$

Table S1. X-ray data of compound **16-Na**, T = 50 °C.

hkil	θ_{exp} (°)	θ_{calc} (°)	θ_{exp}-θ_{calc} (°)
0003	1,04	1,04	0.00
10-11	1.54	1.54	0.00
-1012	1.65	1.65	0.00
0006	2.08	2.08	0.00
1100	2.62	2.60	0.02

Lattice parameters (hexagonal setting of axes) a = 3.4 nm, c = 12.8 nm
Observed reflections: *hkil* with $-h + k + l = 3n$

2.2. Channeled layer phases

Assumed space group from model considerations: *P*6/*mmm*

Table S2. X-ray data of compound **16-Cs**, T = 103 °C, a = 3.9 nm, c = 4.1 nm

hkil	θ_{exp} (°)	θ_{calc} (°)	θ_{exp}-θ_{calc} (°)
0001	1.09	1.08	-0.01
10-10	1.30	1.31	-0.01
10-11	1.68	1.69	-0.01
0002	2.14	2.16	-0.03

Table S3. X-ray data of compound **10-Li**, T = 75 °C,. a = 3.8 nm, c = 3.6 nm

hkil	θ_{exp} (°)	θ_{calc} (°)	θ_{exp}-θ_{calc} (°)
0001	1.23	1,23	0.00
10-10	1.35	1,34	0.01
10-11	1.79	1.82	-0.03
1100	2.34	2.33	0.01
0002	2.45	2.46	-0.01

Tabble S4. X-ray data of compound **10-Na**, T = 70 °C, a = 3.9 nm, c = 3.7 nm

hkil	θ_{exp} (°)	θ_{calc} (°)	θ_{exp}-θ_{calc} (°)
0001	1.22	1.19	0.03
10-10	1.30	1.31	-0.01
1100	2.24	2.27	-0.03
0002	2.41	2.39	0.02
10-12	2.74	2.72	0.02

Table S5. X-ray data of compound **10-K**, T = 115 °C, a = 3.8 nm, c = 3.6 nm

hkil	θ_{exp} (°)	θ_{calc} (°)	θ_{exp}-θ_{calc} (°)
0001	1.23	1.23	0.00
10-10	1.34	1.34	0.00
1100	2.32[a]	2.32	0.00
0002	2.43[a]	2.45	-0.02
1101	2.61[a]	2.63	-0.02
10-12	2.77[a]	2.80	-0.03

[a] Values from the 2D-detector patterns (too weak in the Guinier pattern)

2.3. Electron density reconstruction for the hexagonal channeled layer (ChL_{hex}) phase of compound 10-Cs

Table S6. d-spacings (d_{obs}: experimental; d_{calc}: calculated), intensities and phases of reflections used in the reconstruction of electron densities for the Chl_{hex} phase of compound 10-Cs at 80°C.

hkl	d_{obs} (nm)	d_{calc} (nm)	$I(hkl)$	$\phi(hkl)$
001	3.72	3.72	53.8	0
100	3.53	3.53	100	0
101	2.56	2.56	1.09	π
110	2.03	2.04	0.83	0
002	1.86	1.86	0.70	π

The space group is $P6/mmm$, with unit cell parameters a = 4.08 nm and c = 3.72 nm. Diffraction intensities $I(hkl)$ were measured from the powder diffraction pattern recorded at 80ºC, after cooling the sample from the isotropic liquid. Fourier reconstruction of the electron density is carried out using the general formula:

$$\rho(xyz) = \Sigma_{hkl} F(hkl) \exp[2\pi i(hx+ky+lz)] = \Sigma_{hkl} \sqrt{I(hkl)} \exp[2\pi i(hx+ky+lz) + i\phi(hkl)].$$

Here $\phi(hkl)$ is the phase of the (hkl) reflection.

Reference:

[S1] Synthesis will be reported in a separate paper