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Liquid Crystalline Octaalkoxycarbonyl Phthalocyanines: Design, Synthesis, Electronic Structure, Self-aggregation and Mesomorphism

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Synthesis and characterization of 1a,b,d,e, 2, 3

2,3,9,10,16,17,23,24-Octakis(octyl-1-oxycarbonyl)-(29H, 31H)-phthalocyanine (1a).
Prepared similarly to **1c** from **3** (200 mg, 0.23 mmol) and 1-octanol (**4a**) (4 mmol, 0.63 cm^3) with the following amendment: flash chromatography (SiO_2, CH_2Cl_2/AcOEt 20 : 1) provided analytically pure product and further purification was not necessary. Green solid. Yield 260 mg (64%). λ_{max} ($CHCl_3$)/nm 350 (ε/dm^3 mol^{-1} cm^{-1} 85 600), 648 (55 700), 668 (172 000), 705 (179 000); δ_H (300 MHz, 0.01 mol dm^{-3} in $CDCl_3$, Me_4Si, 25 °C) 9.67 (8 H, s, arom. H), 4.67 (16 H, t, *J* 7.0, CH_2O), 2.03 (16H, quint, *J* 7.0, CH_2CH_2O), 1.30–1.70 (80 H, m, CH_2), 0.91 (24 H, t, *J* 6.9, Me), –1.20 (2 H, br s, NH); δ_C (75 MHz, 0.01 mol dm^{-3} in $CDCl_3$, Me_4Si, 25 °C) 167.6, 137.4, 134.5, 124.7, 66.7, 31.9, 29.4, 29.3, 28.8, 26.1, 22.7, 14.1; *m*/*z* (MALDI) 1763.1 (M^+).

2,3,9,10,16,17,23,24-Octakis(dodecyl-1-oxycarbonyl)-(29H, 31H)-phthalocyanine (1b).
Prepared similarly to **1c** from **3** (433 mg, 0.5 mmol) and 1-dodecanol (**4b**) (10 mmol, 1.86 g) with the following amendment: the crude product was isolated by flash chromatography (SiO_2, CH_2Cl_2/AcOEt 50 : 1). Then it was dissolved in hexane (50 cm^3), and MeOH was added until precipitation of **1b** was complete and the supernatant was nearly colorless. The supernatant was decanted, the residue re-dissolved in hexane and the precipitation with MeOH was repeated three times to give analitically pure **1b** after drying *in vacuo* as a green solid. Yield 664 mg (60 %). λ_{max} ($CHCl_3$)/nm 350 (ε/dm^3 mol^{-1} cm^{-1} 93 400), 649 (55 600), 668 (170 000), 705 (188 000); δ_H (300 MHz, 0.01 mol dm^{-3} in $CDCl_3$, Me_4Si, 25 °C) 9.58 (8 H, s, arom. H), 4.66 (16 H, t, *J* 7.3, CH_2O), 2.04 (16 H, quint, *J* 7.3, OCH_2CH_2), 1.20–1.67 (144 H, m, CH_2), 0.84 (24 H, t, *J* 7.0, Me), –1.65 (2 H, br s, NH); δ_C (75 MHz, 0.01 mol dm^{-3} in $CDCl_3$, Me_4Si, 25 °C) 167.5, 137.1, 134.5, 124.3, 66.7, 31.9, 29.8, 29.7, 29.7, 29.5, 29.4, 26.2, 22.7, 14.1 (2 signals of CH_2 missing due to overlap); *m*/*z* (MALDI) 2211.6 (M^+).

2,3,9,10,16,17,23,24-Octakis(2-hexyldecyl-1-oxycarbonyl)-(29H, 31H)-phthalocyanine (1d).

Prepared similarly to **1c** from **3** (433 mg, 0.5 mmol) and 2-hexyl-1-decanol (**4d**) (10 mmol, 2.90 cm^3) with the following amendment: the crude product was isolated by flash chromatography with CH_2Cl_2. The crude product was applied on the SiO_2 column, excess of **4d** was eluted with MeOH, and then **1d** was eluted with CH_2Cl_2. Viscous green oil. Yield 838 mg (63 %).

λ_{max} ($CHCl_3$)/nm 350 (ε/dm^3 mol^{-1} cm^{-1} 97 700), 649 (55 900), 668 (175 000), 705 (194 000); δ_H (300 MHz, 0.01 mol dm^{-3} in $CDCl_3$, Me_4Si, 25 °C) 9.88 (8 H, s, arom. H), 4.52 (16 H, d, *J* 6.2, CH_2O), 2.02 (8 H, m, C*H*CH_2O), 1.17–1.65 (192 H, m, CH_2), 1.00 (24 H, t, *J* 7.0, Me), 0.87 (24 H, t, *J* 6.9, Me), –0.17 (2 H, br s, NH). δ_C (75 MHz, 0.01 mol dm^{-3} in $CDCl_3$, Me_4Si, 25 °C) 167.8, 137.9, 134.7, 124.6, 69.6, 37.5, 31.9, 31.4, 30.1, 29.8, 29.7, 29.4, 26.8, 26.8, 22.7, 22.6, 14.1, 14.0 (2 signals of CH_2 missing due to overlap); *m*/*z* (MALDI) 2660.0 (M^+).

2,3,9,10,16,17,23,24-Octakis(2-octyldodecyl-1-oxycarbonyl)-(29H, 31H)-phthalocyanine (1e).

Prepared similarly to **1d** from **3** (200 mg, 0.23 mmol) and 2-octyl-1-dodecanol (**4e**) (1.44 cm^3, 4 mmol). Viscous green oil. Yield 407 mg (57%).

λ_{max} ($CHCl_3$)/nm 350 (ε/dm^3 mol^{-1} cm^{-1} 95 900), 649 (55 000), 668 (172 000), 705 (189 000); δ_H (300 MHz, 0.01 mol dm^{-3} in $CDCl_3$, Me_4Si, 25 °C) 9.88 (8 H, s, arom. H), 4.51 (16 H, d, *J* 6.0, CH_2O), 2.02 (8 H, m, C*H*CH_2O), 1.10–1.65 (256 H, m, CH_2), 0.79 (24 H, t, *J* 6.2), 0.75 (24 H, t, *J* 6.8), –0.17 (br s, 2H); δ_C (75 MHz, 0.01 mol dm^{-3} in $CDCl_3$, Me_4Si, 25 °C) 167.8, 137.9, 134.7, 124.6, 69.6, 37.5, 31.9, 31.8, 31.4, 30.1, 29.8, 29.7, 29.7, 29.4, 29.3, 26.8, 22.7, 22.6, 14.1, 14.0 (4 signals of CH_2 missing due to overlap); *m*/*z* (MALDI) 3108.7 (M^+).

2,3,9,10,16,17,23,24-Octacyano-(29H, 31H)-phthalocyanine (2).

Solid state NMR: δ_C (75 MHz, 25 °C) 140.6 (C=N), 137.5, 126.4 (CH), 117.3, 111.3 (CN); *m*/*z* (FD in the presence of $CuCl_2$): found: *m*/*z* 775.04 (M^+); $C_{40}H_8CuN_{16}$ requires 775.05.

2,3,9,10,16,17,23,24-Octacarboxy-(29H, 31H)-phthalocyanine (3).

δ_C (75 MHz, NaOD/D_2O, 25 °C, $Me_3SiCH_2CH_2COONa$ as internal standard) 177.9 (COOH), 157.2, 139.1, 138.8, 120.8. *m/z* (MALDI) 866 (M^+, 100), 848 ($[M - H_2O]^+$, 48), 823 ($[M - CO_2 + H]^+$, 43).

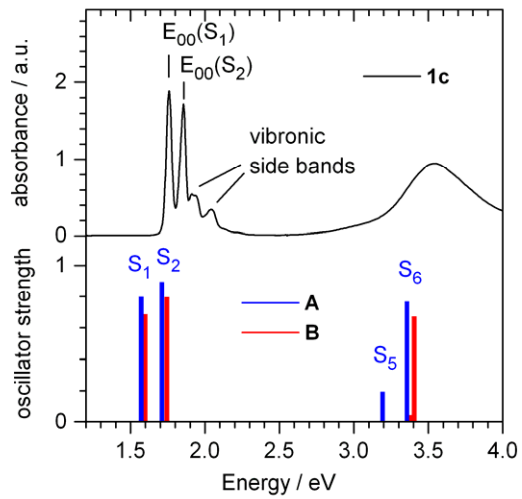

Fig. S1. Absorption spectra of phthalocyanines. Top: experimental spectrum of **1c** in $CHCl_3$; $E_{00}(S_1)$ and $E_{00}(S_2)$ are the adiabatic transition energies of the lowest electronic states; the vibronic side bands of S_1 (*ca.* 1.94 eV) and of S_2 (*ca.* 2.04 eV) are indicated. Bottom: Calculated stick spectra of the vertical electronic transition energies of **A** (blue) and **B** (red); geometry optimization: DFT B3LYP/6-31G*; electronic structure: ZINDO/S.

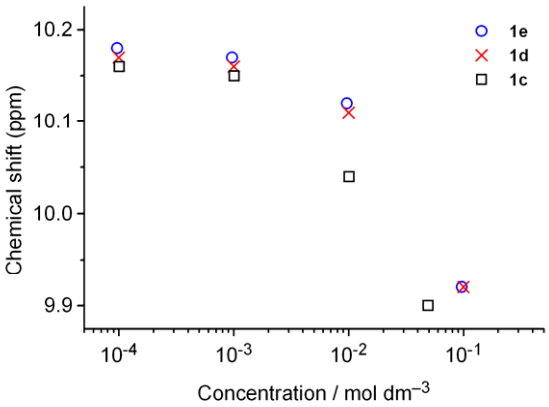

Fig. S2. Concentration-dependent ^1H chemical shifts of aromatic protons in **1c**, **1d** and **1e** recorded at 25 °C in C_6D_6.

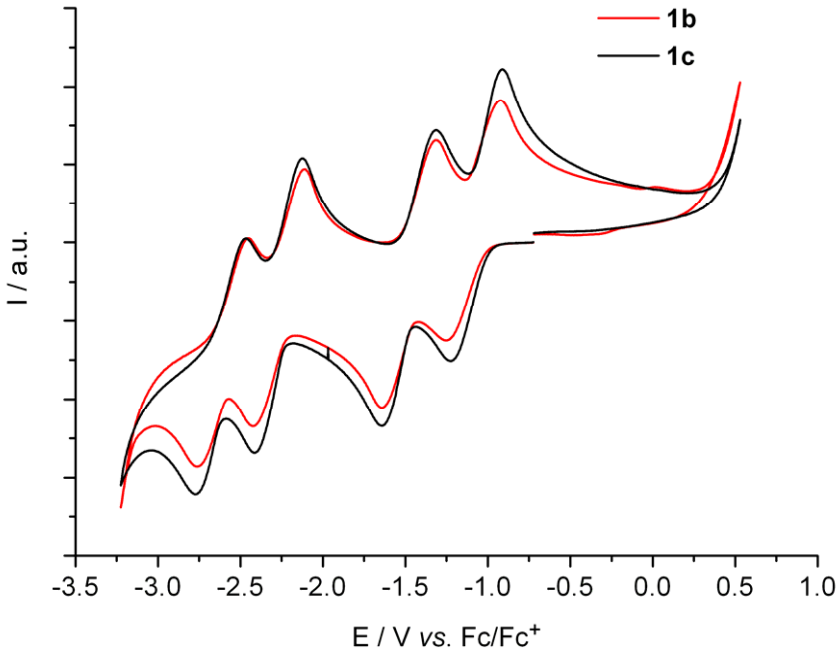

Fig. S3. CV curves of **1b** (red) and **1c** (black) in THF (10^{-3} mol dm^{-3}) containing $TBAPF_6$ (0.1 mol dm^{-3}); 25 °C, scan rate 100 mV s^{-1}; potentials *vs*. Fc/Fc^+.

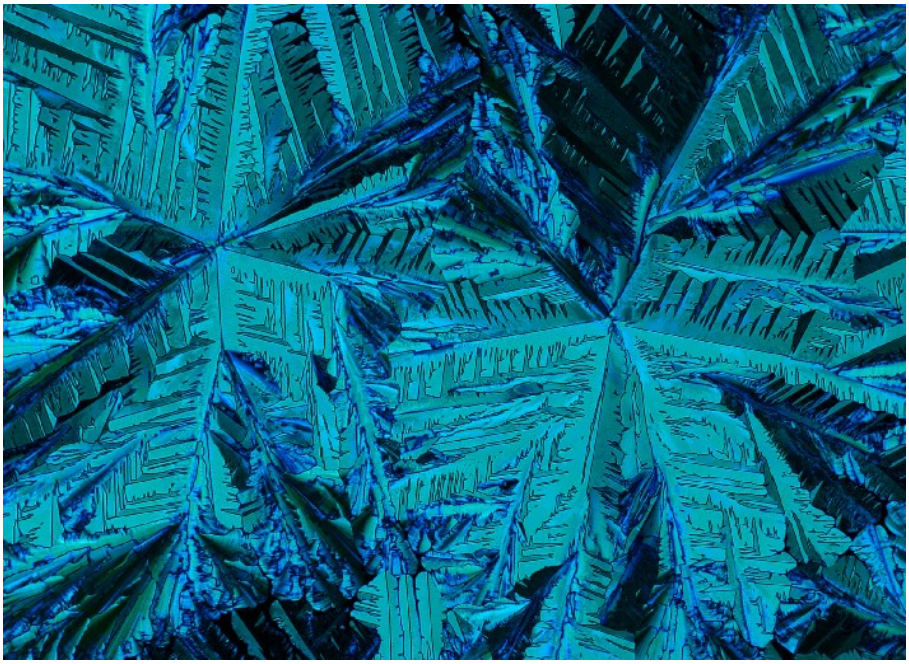

Fig. S4. Cross-polarized optical microscopy image of **1c** after cooling from isotropic liquid (160 °C) to columnar mesophase (140°C).

Table S1. Detailed indexation of liquid crystalline phase of **1c** at different temperatures.[a]

1c	*h*	*k*	*l*	d_{calc} (Å)	d_{exp} (Å)	Lattice parameters[a]
	1	1		23.7	23.7	a = 40.3 Å
Col$_r$ at 25°C	2	0		20.1	20.2	b = 29.4 Å
	1	3		9.5	9.5	
					4.5 (broad halo)	γ= 90.0°
	0	0	1		No apparent reflection	S = 1184.8 Å²
	1	1		23.7	23.7	a = 40.2 Å
Col$_r$ at 50°C	2	0		20.1	20.1	b = 29.3 Å
	1	3		9.5	9.5	
					4.5 (broad halo)	γ= 90.0°
	0	0	1		No apparent reflection	S = 1177.9 Å²
	1	1		23.6	23.6	a = 39.8 Å
Col$_r$ at 100°C	2	0		19.9	19.9	b = 29.3 Å
	1	3		9.5	9.5	
					4.6 (broad halo)	γ= 90.0°
	0	0	1		No apparent reflection	S = 1166.1 Å²
	1	1		23.5	23.5	a = 39.6 Å
Col$_r$ at 140°C	2	0		19.8	19.8	b = 29.2 Å
	1	3		9.4	9.4	
					4.6 (broad halo)	γ= 90.0°
	0	0	1		No apparent reflection	S = 1156.3 Å²

[a] d_{calc} and d_{exp} are the calculated and experimental diffraction spacings, respectively; *hk* is the indexation of the two-dimensional lattice (Miller indices); a, b and γ are the lattice parameters; S is the lattice area; Col$_r$: 2D rectangular columnar phase.

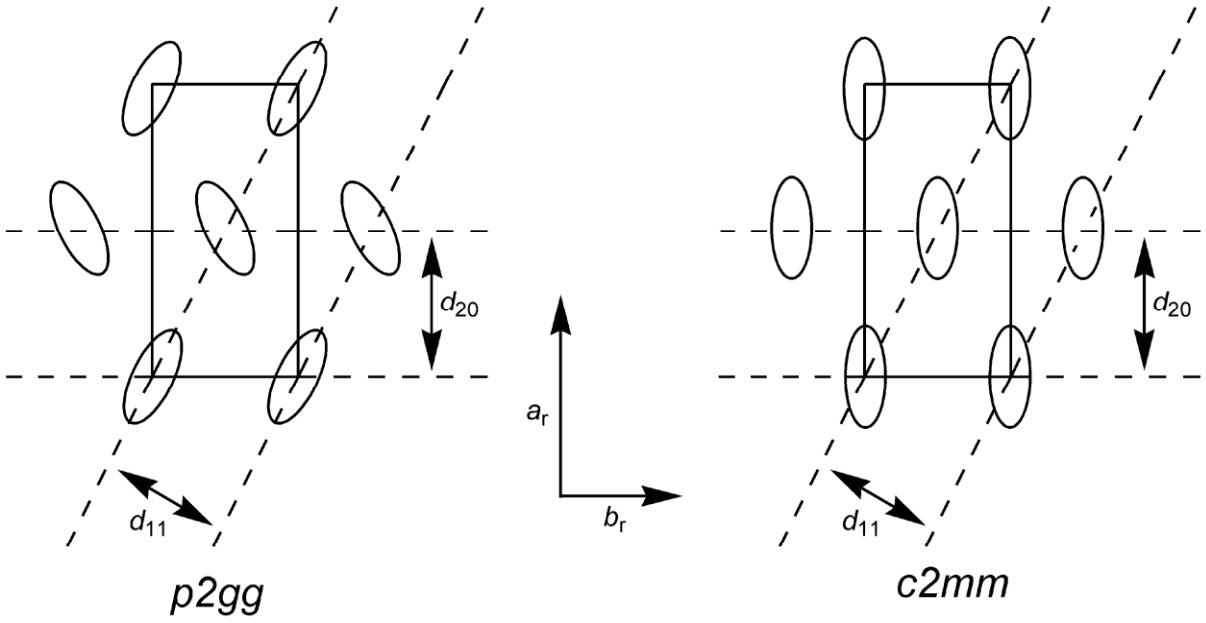

Fig. S5. Lateral structures of rectangular columnar phases and their respective plane groups (Hermann-Mauguin nomenclature)[S1]. Schematic representation of the 2D lattices of the two rectangular columnar mesophases: with a *p2gg* plane group (left) and with a *c2mm* plane group (right).[S2] These two arrangements include two columns per lattice and the elementary 3D cell is orthorhombic.

Solid state NMR

Instrumentation

All solid state NMR experiments were performed on a Bruker spectrometer with a ^{1}H frequency of 700.13 MHz and a ^{13}C frequency of 176.05 MHz. A Bruker double resonance probe supporting rotors of 2.5 mm outer diameter was used at a spinning frequency of 25 kHz for ^{13}C cross-polarization (CP) magic angle spinning (MAS) experiments. The RF precession frequencies were set to 100 kHz for both channels. The ^{13}C CP MAS measurement have been recorded with 2 s recycle delay, 1 ms CP contact time using a variable amplitude contact pulse (80–100%)[S3] and two-pulse phase-modulation (TPPM) ^{1}H decoupling during the acquisition.[S4]

At high spinning frequencies, additional heating effects caused by bearing gas friction become significant. The given sample temperature has been corrected for the frictional heating effect following the described procedure.[S5]

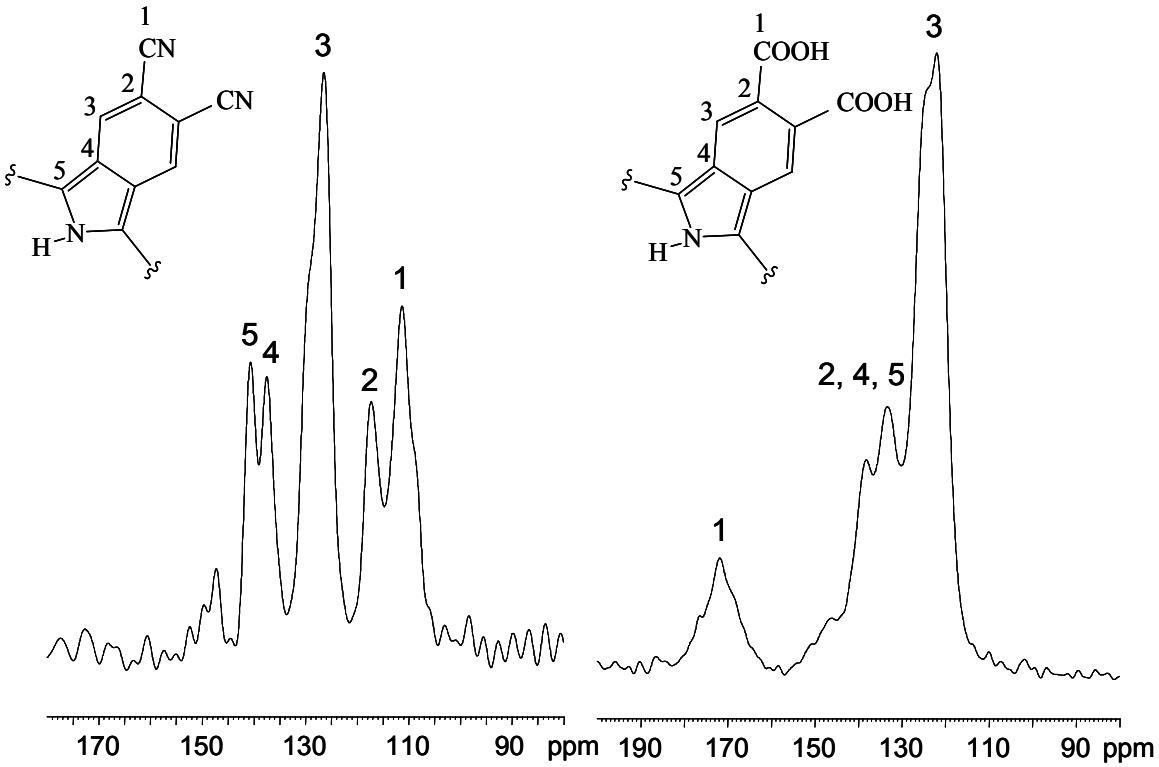

Fig. S6. ^{13}C CP MAS NMR spectra of **2** (left, 3 k transients) and **3** (right, 20 k transients) at 313 K. Due to the unfavorable distribution of the ^{13}C chemical shifts of the quaternary carbons in the case of compound **3**, the aromatic signals could not unambiguously be assigned from the CP MAS spectrum.

References

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