Supporting Information

Phasmidic indigoid liquid crystals

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Instruments

IR: Infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FTIR spectrometer
and are given in cm⁻¹ units. All samples were measured as attenuated total reflection (ATR)
spectra on a ZnSe crystal. Signals are characterized by b, broad; w, weak; m, medium; s,
strong.

1H-NMR: The 1H-NMR spectra were recorded on Bruker AC 300 or Bruker DPX 300
spectrometers operating at 300 MHz or on a Bruker DRX 500 instrument operating at 500
MHz. Chemical shifts are reported as δ in ppm with the coupling constants J in Hz. In all
spectra solvent peaks were used as internal standard. As solvent DMSO-d6 (δ = 2.49 ppm)
was used. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q,
quartet; m, multiplet; br, broad.
13C-NMR: The 13C-NMR spectra were recorded as APT spectra either on a Bruker AC 300 spectrometer instrument operating at 75 MHz or on a Bruker DRX 500 instrument operating at 125 MHz.

LR-MS: Finnigan MAT Incos 50 Galaxy System.

Elemental analysis: CHN-combustion analyses were measured using an Elementar Vario EL instrument.

Experimental section

Synthetic procedures and analytical data

1-Bromo-2,3,4-tridodecyloxybenzene (4)

30 mmol (18.92 g) 1,2,3-tridodecyloxybenzene (3) were dissolved in 100 ml tetrachloromethane and reacted for 20 hours with 36 mmol (6.41 g) NBS at 70 °C. The reaction solution was filtered and washed three times with water. After evaporation of the solvent the crude product was purified by column chromatography (Silica gel, cHex) with cyclohexane yielding 8.06 g (11.4 mmol, 38%) 4 as viscous, colorless oil.

nD²³: 1.4923; TLC (Silica gel, cHex / EtOAc = 30:1): Rf = 0.63; FT-IR (ATR): ν = 2920 (s), 2850 (s), 1570 (w), 1463 (m), 1439 (m), 1376 (m), 1294 (m), 1254 (w), 1209 (m), 1085 (s), 1001 (m), 916 (w), 787 (w), 720 (m); ¹H-NMR (300 MHz, CDCl₃): δ = 7.13 (d, J = 8.9 Hz, 1H; 6-H), 6.52 (d, J = 9.0 Hz, 1H; 5-H), 3.95 (m, 6H; 3 × α-CH₂), 1.75 (m, 6H; β-CH₂), 1.45 (m, 6H; γ-CH₂), 1.53-1.38 (m, 48H; CH₂), 0.86 (t, J = 6.6 Hz, 9H; CH₃); ¹³C-NMR (75.5 MHz, CDCl₃): δ = 153.08 (s; C-4), 150.62 (s; C-2), 143.10 (s; C-3), 126.49 (d; C-6), 109.35 (d; C-5), 108.58 (s; C-1), 73.99, 73.87 (2 × t; C-2-OCH₂ and C-3-OCH₂), 68.89 (t; C-4-OCH₂), 31.93, 30.24, 29.69, 29.66, 29.55, 29.49, 29.38, 29.29, 26.08, 22.69 (10 × t; CH₂), 14.11 (q; CH₃); LR-MS (EI, 70 eV) m/z (%): 711 (23) [M⁺ für ⁸¹Br], 709 (24) [M⁺ für ⁷⁹Br], 631 (3) [M⁺ -Br], 542 (6) [M⁺-C₁₂H₂₅ für ⁸¹Br], 540 (7) [M⁺-C₁₂H₂₅ für ⁷⁹Br], 463 (5) [M⁺-C₁₂H₂₅ -Br], 374 (69) [M⁺-2(C₁₂H₂₅) für ⁸¹Br], 372 (68) [M⁺-2(C₁₂H₂₅) für ⁷⁹Br], 294 (18) [M⁺-2(C₁₂H₂₅) -Br].

2,3,4-Tridodecyloxyphenylboronic acid (5)

10.3 mmol (7.39 g) of 1-bromo-2,3,4-tridodecyloxybenzene (4) were dissolved in 350 ml dry THF and cooled to -78 °C. Thereafter, 11 mmol (4.4 ml) of a 2.5M n-BuLi solution were added slowly over a time span of 90 minutes. 30 minutes after completion 30.0 mmol (3.1 ml) trimethyl borate were added rapidly and the solution was allowed to warm up to room
temperature. Subsequently, 100 ml 2M HCl were added and THF was removed under reduced pressure. After addition of ethyl acetate the organic phase was washed twice with water and once with brine and dried over MgSO₄. The solvent was evaporated and the crude product recrystallized from petrol ether (40-60 °C) yielding pure 2,3,4-tridodecyloxyphenylboronic acid (5, 6.01 g, 8.9 mmol, 86%) as a colourless solid.

**Mp.** (Petrol ether 40-60°C): 49 °C; **TLC** (Silica gel, cHex / EtOAc = 3:1): Rᵣ = 0.51; **FT-IR** (ATR): ν = 3380 (bw), 2917 (s), 2848 (s), 1593 (m), 1464 (m), 1372 (m), 1339 (m), 1291 (m), 1222 (m), 1083 (s), 1018 (w), 997 (w), 957 (w), 889 (w), 808 (w), 771 (w), 719 (m); **¹H-NMR** (300 MHz, CDCl₃): δ = 7.47 (d, J = 8.3 Hz, 1H; 6-H), 6.68 (d, J = 8.4 Hz, 1H; 5-H), 6.36 (s, 2H; B(OH)₂), 4.16 (t, J = 6.5 Hz, 2H; 4-OCH₂), 3.92 (t, J = 6.5 Hz, 2H; 3-OCH₂), 1.77 (m, 6H; β-CH₂), 1.45 (m, 6H; γ-CH₂), 1.38 -1.18 (m, 48H; CH₂), 0.86 (t, J = 6.5 Hz, 9H; CH₃);

13C-NMR (75.5 MHz, CDCl₃): δ = 158.36 (s; C-2), 156.33 (s; C-4), 140.26 (s; C-3), 130.87 (d; C-6), 114.89 (s; C-1), 108.43 (d; C-5), 74.70 (t; C-2-OCH₂), 73.59 (t; C-3-OCH₂), 68.55 (t; C-4-OCH₂), 56.92, 30.32, 29.69, 29.66, 29.39, 29.26, 26.17, 26.10, 25.86, 22.69 (11 × t; CH₂), 14.11 (q; CH₃).

5-(2,3,4-Tridodecyloxyphenyl)indolin-2,3-dione (7)

5-Bromoisatin (6, 2.0 mmol, 452 mg) was dissolved in 15 ml dry DME under argon atmosphere together with 2,3,4-tridodecyloxyphenylboronic acid (5, 2.4 mmol, 735 mg) and tetrakis(triphenyl)phosphin palladium(0) (0.04 mmol, 42 mg) and heated to 80 °C. After complete resolution 4 ml of a degassed aqueous 1M potassium phosphate solution was added and the mixture was stirred for 7 hours before 35 ml of 1M hydrochloric acid were added. After 12 hours the product was obtained as dark red precipitate, filtered, dried and purified chromatographically (silica gel, DCM/MTBE 15:1), yielding 5 (0.777 g, 1.0 mmol, 50%) as a dark red, wax like solid.

**Mp.** (DCM / MTBE = 15:1): Cr 78.9 °C (52.9 kJ/mol) I; **TLC** (Silica gel, DCM / MTBE = 15:1): Rᵣ = 0.47; **FT-IR** (ATR): ν = 3287 (bw), 2921 (s), 2850 (s), 1762 (m), 1746 (m), 1623 (m), 1592 (w), 1464 (m), 1425 (w), 1377 (w), 1310 (w), 1292 (w), 1269 (w), 1200 (w), 1104 (m), 1075 (m), 1007 (w), 837 (w), 797 (w), 718 (w); **UV-Vis** (EtOH, 10 mg/L) λ_max: 222 nm (s), 265 nm (m), 454 nm (w); **¹H-NMR** (300 MHz, CDCl₃): δ = 9.22 (s, 1H; NH), 7.75 (s, 1H; 4-H), 7.73 (dd, J = 8.2 Hz, J = 1.7 Hz, 1H; 6-H), 6.99 (d, J = 8.0 Hz, 1H; 7-H), 6.92 (d, J = 8.6 Hz, 1H; 6’-H), 6.67 (d, J = 8.7 Hz, 1H; 5’-H), 4.01 (t; J = 6.5 Hz, 2H; 3-OCH₂), 3.97 (t; J = 6.5 Hz, 2H; 4-OCH₂), 3.78 (t; J = 6.5 Hz, 2H; 2-OCH₂), 1.80 (m, 6H; β-CH₂), 1.47 (m, 6H; γ-CH₂), 1.40-1.10 (m, 48H; CH₂), 0.86 (m, 9H; CH₃); 13C-NMR (75.5 MHz, CDCl₃): δ = 183.42 (s; C-3), 160.16 (s; C-2), 153.42 (s; C-4’), 150.69 (s; C-2’), 147.79 (s; C-7a),...
142.18 (s; C-3’), 139.74 (d; C-6), 134.82 (s; C-5), 126.46 (zwei Signale: (s; C-1’) und (d; C-4’)), 123.75 (d; C-6´), 117.80 (s; C-3a), 112.06 (d; C-7), 108.43 (d; C-5´), 73.78 (2 × t; C-2’-OCH2 and C-3’-OCH2), 68.74 (t; C-4’-OCH2), 31.90 (t; CH2), 30.38 (t; C-3’-OCH2CH2), 30.13 (t; C-2’-OCH2CH2), 29.63 (t; C-4’-OCH2CH2), 29.35, 26.15, 26.11, 26.00, 22.66 (5 × t; CH2), 14.08 (q; CH3);

LR-MS (EI, 70 eV, Teilspektrum) m/z (%): 776 (74) [M+], 607 (14) [M+-C12H25], 452 (6), 439 (100) [M+-2C12H25], 411 (29) [M+-2C12H25-CO], 382 (9) [M+-2C12H25-2CO];

EA (%) calc. for C50H81NO5: C 77.37, H 10.52, N 1.80, found: C 77.54, H 10.44, N 1.77.

6-(2,3,4-Tridodeyloxyphenyl)indolin-2,3-dione (9)

The same procedure as for 5 was applied, but with 6-bromoisatin (8, 2 mmol, 452 mg) yielding 1.18 g (1.52 mmol, 76%) of 6 as an orange wax like solid.

Mp. (DCM / MTBE = 15:1): Cr 89 °C I; TLC (Silica gel, DCM / MTBE = 15:1): Rf = 0.71;

FT-IR (ATR): \( \tilde{\nu} = 3304 \) (bw), \( 2915 \) (s), \( 2847 \) (s), \( 1760 \) (m), \( 1737 \) (s), \( 1613 \) (s), \( 1590 \) (s), \( 1465 \) (m), \( 1380 \) (m), \( 1336 \) (m), \( 1294 \) (s), \( 1226 \) (w), \( 1200 \) (w), \( 1170 \) (w), \( 1108 \) (s), \( 1078 \) (m), \( 1013 \) (w), \( 953 \) (w), \( 903 \) (w), \( 840 \) (w), \( 795 \) (w), \( 720 \) (m); UV-Vis (EtOH, 10 mg/L) \( \lambda_{max} \): 215 nm (s), 252 nm (m), 356 nm (m); \( \text{^1}H\text{-NMR} \) (300 MHz, CDCl3): \( \delta = 9.04 \) (s, 1H; NH), 7.57 (d, \( 3J = 7.9 \) Hz, 1H; 4-H), 7.25 (d, \( 3J = 8.2 \) Hz, 1H; 5-H), 7.15 (s, 1H; 7-H), 7.00 (d, \( 3J = 8.6 \) Hz, 1H; 6’-H), 6.70 (d, \( 3J = 8.7 \) Hz, 1H; 5’-H), 4.02 (t; \( 3J = 6.7 \) Hz, 2H; 3’-OCH2), 3.99 (t; \( 3J = 6.6 \) Hz, 2H; 4’-OCH2), 3.80 (t; \( 3J = 6.4 \) Hz, 2H; 2’-OCH2), 1.80 (m, 6H; \( \beta\text{-CH2} \), 1.49 (m, 6H; \( \gamma\text{-CH2} \), 1.40-1.13 (m, 48H; CH2), 0.86 (m, 9H; CH3);

\( \text{^13}C\text{-NMR} \) (75.5 MHz, CDCl3): \( \delta = 182.52 \) (s; C-3), 160.51 (s; C-2), 154.42 (s; C-4’), 151.15 (s; C-2’), 149.93 (s; C-6), 149.11 (s; C-7a), 142.27 (s; C-3’), 126.76 (s; C-1’), 125.26 (d; C-4), 124.91 (d; C-5), 124.31 (d; C-6’), 116.10 (s; C-3a), 113.38 (d; C-7), 108.42 (d; C-5’), 78.73 (t; t; C-3’-OCH2), 73.87 (t; C-3’-OCH2), 68.77 (t; C-4’-OCH2), 31.90 (t; CH2), 30.38 (t; C-3’-OCH2CH2), 30.13 (t; C-2’-OCH2CH2), 29.64 (t; C-4’-OCH2CH2), 29.35, 26.15, 26.11, 26.00, 22.66 (5 × t; CH2), 14.08 (q; CH3);

LR-MS (EI, 70 eV) m/z (%): 776 (74) [M+], 607 (2) [M+-C12H25], 452 (6), 439 (100) [M+-2C12H25], 411 (29) [M+-2C12H25-CO], 382 (9) [M+-2C12H25-2CO];

EA (%) calc. for C50H81NO5: C 77.37, H 10.52, N 1.80, found: C 77.54, H 10.44, N 1.77.

5,5’-Bis-(2,3,4-tridodeyloxyphenyl)indigo (1)

To a solution of 7 0.60 mmol (0.465 g) in 6 ml dry toluene 0.63 mmol (0.131 g) phosphorouspentachloride was given and the reaction was heated to 100 °C for 4 hours. Subsequently the dark red reaction mixture was cooled to 50 °C, 1.32 mmol (0.145 g)
thiophenol were added and kept on this temperature for 16 hours. To the green solution 20 ml of methanol were given to precipitate the crude product, which was filtered off and purified by column chromatography with a 2:1 mixture of cyclohexane and chloroform and adjacent recrystallization from ethanol yielding 0.11 g (23%) 1 as blue solid.

**M.p.** (CHCl3/cHex 2:1): Cr 61.7 °C (50.8 kJ/mol) Col 1 77.6 °C (14.1 kJ/mol) Col 2 219.6 °C (32.8 kJ/mol) I; **TLC** (Silica gel, CHCl3): Rf = 0.33; **FT-IR** (ATR): ν = 3372 (w), 2916 (s), 2847 (s), 1629 (s), 1585 (w), 1464 (s), 1425 (w), 1401 (w), 1374 (w), 1313 (w), 1296 (w), 1273 (m), 1259 (w), 1198 (m), 1183 (m), 1141 (m), 1122 (s), 1085 (s), 807 (w), 718 (w), 657 (w); **UV-Vis** (CHCl3, 10 mg/L) λmax: 240 nm (s), 308 nm (s), 367 nm (m), 624 nm (m); **1H-NMR** (300 MHz, CDCl3): δ = 8.93 (s, 2H; NH), 7.85 (d, J = 1.2 Hz, 2H, 4-H), 7.69 (dd, J = 8.4 Hz, 2H, 6-H), 7.03 (d, J = 8.4 Hz, 2H, 7-H), 6.79 (d, J = 8.6 Hz, 2H, 6´-H), 6.67 (d, J = 8.7 Hz, 2H, 5´-H), 4.02 (t; J = 6.6 Hz, 4H, 3´-OCH2), 3.98 (t; J = 6.4 Hz, 4H, 4´-OCH2), 3.77 (t; J = 6.4 Hz, 4H, 2´-OCH2), 1.80 (m, 12H, β-CH2), 1.47 (m, 12H, γ-CH2), 1.40-1.10 (m, 96H, CH2), 0.84 (m, 18H, CH3); **13C-NMR** (75.5 MHz, CDCl3): δ = 188.77 (s; C-3), 153.00 (s; C-4´), 150.82 (s; C-2´), 150.56 (s; C-7a), 142.26 (s; C-3´), 137.78 (d; C-6), 131.65 (s; C-5), 127.66 (s; C-1´), 124.82 (d; C-4), 124.00 (d; C-6´), 121.83 (s; C-2), 120.02 (s; C-3a), 111.43 (d; C-7), 108.45 (d; C-5´), 73.75, 73.69 (2 × t; C-2´-OCH2 and C-3´-OCH2), 68.78 (t; C-4´-OCH2), 31.93, 30.44, 30.16, 29.70, 29.39 (5 × t; CH2), 26.19, 26.15, 26.07 (3 × t; γ-CH2), 22.69 (t; CH2), 14.11 (q; CH3); **EA (%)** calc. for C100H162N2O8: C 79.00, H 10.74, N 1.84, found: C 78.75, H 10.71, N 1.79.

6,6´-Bis-(2,3,4-tridodeyloxyphenyl)indigo (2)

Same procedure as 1, but starting with 6 (1.00 mmol, 0.776 g) yielding 0.569 g (70%) 2 as green solid.

**M.p.** (CHCl3 / cHex 2:1): Cr 126.2 °C (66.1 kJ/mol) Col 1 143.1 °C (18.4 kJ/mol) I; **TLC** (Silica gel, CHCl3): Rf = 0.35; **FT-IR** (ATR): ν = 3351 (w), 2917 (s), 2849 (s), 1610 (s), 1588 (m), 1504 (m), 1463 (m), 1438 (s), 1376 (m), 1316 (s), 1279 (m), 1221 (w), 1191 (w), 1133 (s), 1100 (s), 1072 (s), 871 (w), 797 (w), 776 (w), 709 (w); **UV-Vis** (NMP, 10 mg/L) λmax: 239 nm (s), 297 nm (s), 412 nm (m), 611 nm (m); **1H-NMR** (300 MHz, CDCl3): δ = 8.95 (s, 2H; NH), 7.70 (d, J = 8.0 Hz, 2H, 4-H), 7.21 (s, 2H, 7-H), 7.12 (dd, J = 8.2 Hz, J = 1.0 Hz, 2H, 5-H), 7.02 (d, J = 8.6 Hz, 2H, 6´-H), 6.71 (d, J = 8.8 Hz, 2H, 5´-H), 4.03 (t; J = 6.6 Hz, 4H, 3´-OCH2), 3.99 (t; J = 6.4 Hz, 4H, 4´-OCH2), 3.79 (t; J = 6.4 Hz, 4H, 2´-OCH2), 1.81 (m, 12H, β-CH2), 1.49 (m, 12H, γ-CH2), 1.40-1.10 (m, 96H, CH2), 0.84 (m, 18H, CH3); **13C-NMR** (75.5 MHz, CDCl3): δ = 188.16 (s; C-3), 153.86 (s; C-4´), 151.85 (s; C-7a), 151.14 (s; C-2´), 147.05 (s; C-6), 142.31 (s; C-3´), 127.80 (s; C-1´), 124.38 (d; C-6´), 123.77
(d; C-4), 122.48 (d; C-5), 122.06 (s; C-2), 118.35 (s; C-3a), 112.86 (d; C-7), 108.36 (d; C-5’), 74.09 (t; C-2’-OCH2), 73.83 (t; C-3’-OCH2), 68.77 (t; C-4’-OCH2), 31.93, 30.44, 30.18, 29.71, 29.42 (4 × t; CH2), 26.19, 26.14 (2 × t; γ-CH2), 22.69 (t; CH2), 14.11 (q; CH3); EA (%) calc. for C100H162N2O8: C 79.00, H 10.74, N 1.84, found: C 79.00, H 10.72, N 1.81.

NMR Spectra

1H-NMR spectrum of 5,5’-bis-(2,3,4-tridodeyloxyphenyl)indigo (1)
$^{13}$C-NMR (APT) spectrum of 5,5'-Bis-(2,3,4-tridodeyloxyphenyl)indigo (1)

$^1$H-NMR spectrum of 6,6'-bis-(2,3,4-tridodeyloxyphenyl)indigo (2)
$^{13}$C-NMR (APT) spectrum of 6,6'-bis-(2,3,4-tridodeyloxyphenyl)indigo (2)
$^1$H-NMR spectrum of 1-bromo-2,3,4-tridodecyloxybenzene (4)

$^{13}$C-NMR (APT) spectrum of 1-bromo-2,3,4-tridodecyloxybenzene (4)
$^1$H-NMR spectrum of 2,3,4-tridodecyloxyphenylboronic acid (5)

$^{13}$C-NMR (APT) spectrum of 2,3,4-tridodecyloxyphenylboronic acid (5)
\(^1\)H-NMR spectrum of 5-(2,3,4-tridodeyloxyphenyl)indolin-2,3-dione (7)

\(^{13}\)C-NMR (APT) spectrum of 5-(2,3,4-tridodeyloxyphenyl)indolin-2,3-dione (7)
$^1$H-NMR spectrum of 6-(2,3,4-tridodeyloxyphenyl)indolin-2,3-dione (9)

$^{13}$C-NMR (APT) spectrum of 6-(2,3,4-tridodeyloxyphenyl)indolin-2,3-dione (9)
Polarizing microscopy textures of the mesophases of 1 and 2

**Figure S1:** Texture of the Col₂ phase of 1 at 211 °C between crossed polarizers, showing focal conical domains, helical filaments and elongated domains of uniform birefringence.

**Figure S2:** Texture of the Col₂ phase of 1 at 210 °C between crossed polarizers.
Figure S3: Texture of the Col$_2$ phase of 1 at 118 °C between crossed polarizers.

Figure S4: Texture of the Col$_3$ phase of 2 at 140 °C between crossed polarizers.
Figure S5: Texture of the Col₁ phase of 2 at 144 °C between crossed polarizers.

Figure S5: Texture of the Col₁ phase of 2 at 144 °C with one horizontal polarizer.
Figure S7: Texture of the Col3 phase of 2 at 144 °C between crossed polarizers.

Figure S8: Texture of the Col3 phase of 2 at 144 °C with one horizontal polarizer.