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H-shape mesogenic dimers – spacer parity effect

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Details of synthesis

Materials and methods

The compounds: 4-(dodecyloxy)benzoyl chloride (**3**), 3,4-didodecyloxy benzoyl chloride (**4**), 3,4,5-tridodecyloxy benzoyl chloride (**5**), 4’ -hydroxybiphenyl-4-yl 3,4-didodecyloxybenzoate (**7**), 4’-hydroxybiphenyl-4-yl 3,4,5-tridodecyloxybenzoate (**8**), ethyl 4-dodecyloxy-2-hydroxybenzoate (**13**) were previously obtained and described.[1,2] 4,4’-cyjanobiphenol (**9**) was used as received without further purification. Solvents: ethanol (EtOH), methanol (MeOH), trichloromethane ($CHCl_3$), dichloromethane (CH_2Cl_2), toluene, tetrahydrofuran (THF) and N,N-Dimethyloformamide (DMF) were of p.a. quality. Unless otherwise specified, substrates were obtained from Sigma-Aldrich. Solvents DMF and THF were dried and purified over 3 Å molecular sieves. All other solvents were used as received without further purification. Purification of products was carried out by column chromatography using Rushan Taiyang silica gel 60 (230-400 mesh). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 Å F_{254} (Merck) pre-coated glass plates (0.25 mm thickness) and visualized using iodine vapor and/or UV lamp (254 nm). ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Unity Plus 200 MHz and/or 500 MHz instrument in $CDCl_3$. 1H NMR peaks were referenced to the signals for the residual protiochloroform at 7.26 ppm. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration.

Synthetic procedures

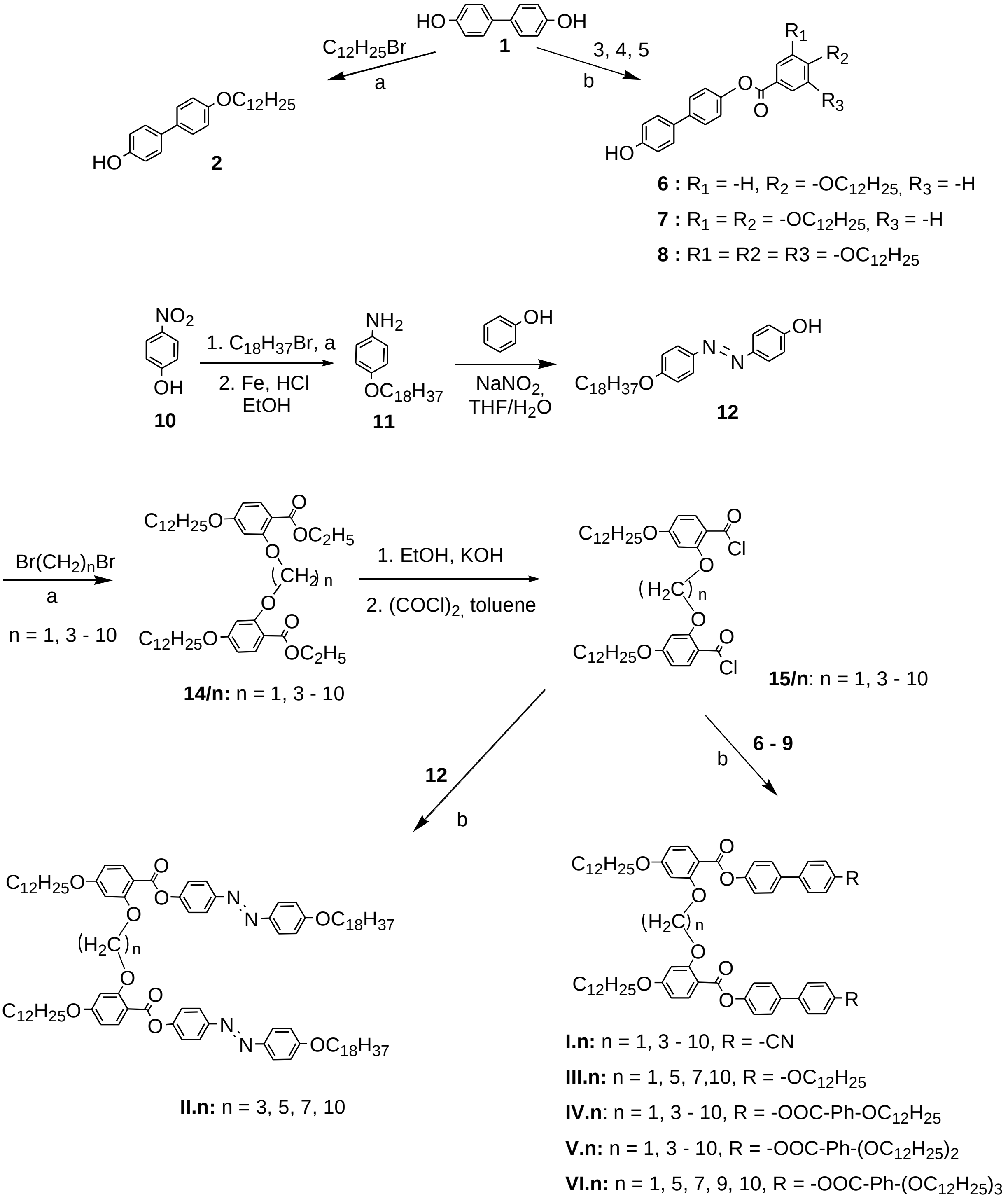
The synthetic path is shown at the Scheme 1 and the details of synthesis are described below.

SYNTHESIS OF 4’-DODECYLOXYBIPHENYL-4-OL (2):
To a solution of 4,4’-biphenol **(1)** (20 g, 107 mmol) in anhydrous DMF (300 mL), potassium carbonate (29.5 g, 214 mmol) and potassium iodide (35.3 g, 214 mmol) were added. The reaction was heated up to 45˚ C and the 1-Bromododecane (26.7 g, 107 mmol) was added. The reaction mixture was refluxed at 110-120° C for 18 h. The reaction mixture was removed from the heat and allowed to cool to room temperature (RT), then poured into water with ice. The precipitate was separated and purified by recrystallization (toluene) to yield a white solid (24.65 g, 65%). ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.47 – 7.41 (m, 4H); 6.96 – 6.86 (m, 4H); 3.98 (t, 2H, J= 6.8); 1.96-1.76 (m, 2H); 1.27 (s, 18H); 0.88 (t, 3H, J= 6.6).

SYNTHESIS OF 4’-DODECYLOXY - 4-HYDROXYBIPHENYL-4-YL BENZOATE (6):
To a solution of 4,4’-biphenol **(1)** (17.2 g, 92.4 mmol) in anhydrous THF (320 mL), TEA (20 mL) and DMAP (catalytic amount) were added. After 40 minutes of stirring, the solution of **(3)** in THF (40 mL) was added. The reaction was refluxed and monitored by TLC (15 h). The reaction mixture was removed from the heat and allowed to cool to room temperature (RT). The organic solvent (THF) was removed by rotary evaporation and the crude product was purified by column chromatography (1% MeOH/$CHCl_3$) to yield a white powder (21.35 g, 73 %). ^{1}H NMR (200 MHz, d-THF) δ [ppm]: 8.13 – 8.08 (m, 2H); 7.59 – 7.55 (m, 2H); 7.46 – 7.42 (m, 2H); 7.24 – 7.20 (m, 2H); 7.04 – 6.99 (m, 2H); 6.83 – 6.79 (m, 2H); 4.06 (t, 2H, J= 6.4); 1.87-1.74 (m, 2H); 1.53- 1.20 (m, 18H); 0.88 (t, 3H, J= 6.6)

SYNTHESIS OF 4-OCTADECYLOXY-PHENYLAMINE (11):
To a solution of 4-nitro-phenol **(10)** (25 g, 180 mmol) in anhydrous DMF (350 mL) , potassium carbonate (27.5 g, 200 mmol) and potassium iodide (35.6 g, 216 mmol) were added. The mixture was heated up to 45˚ C and the 1-bromooctadecane (66g, 198 mmol) was added. The reaction mixture was refluxed at 110-120° C and after 10 h removed from the heat, allowed to cool to room temperature (RT), and poured into water. The precipitate was separated and recrystallized (toluene) to yield a white solid (65.55 g, 93%) (*1-Nitro-4-octadecyloxybenzene).* **^{1}H NMR (200 MHz w $CDCl_3$) δ [ppm]:** 8.18 (d, 2H, J = 8.2), 6.93 (d, 2H, J = 8.2), 4.13 (t, 2H, J = 6.8), 1.82 (m, 2H), 1.44 – 1.20 (m, 30 H), 0.88 (t, 3H, J = 6.8).

The intermediate 1-Nitro-4-octadecyloxybenzene (30 g, 77 mmol) was dissolved in EtOH (600 mL) and iron filings (30 g), and 10M HCl (1 mL) were added. The reaction was refluxed and monitored by TLC, until consumption of the nitro derivative was complete. The reaction mixture was removed from the heat and allowed to cool to room temperature (RT). The crude reaction was filtered through celite, and the filtrate was concentrated via rotary evaporation to yield an oil (solid after a few hours) (23.67 g, 85 %). **^{1}H** NMR (200 MHz, $CDCl_3$) δ [ppm]: 6.69 (d, 2H, J = 8.6), 6.63 (d, 2H, J = 8.8), 3.92 (t, 2H, J = 6.4), 1.82 (m, 2H), 1.38 – 1.20 (m, 30H), 0.88 (t, 3H, J = 7.0).



Scheme 1. Synthesis of the H-dimers; a: K_2CO_3, KI, DMF, b: DMAP, TEA, THF

SYNTHESIS OF 4-HYDROXY-4'(4-OCTADECYLOXY)DIAZOBENZENE (12):

The 4-octadecyloxy-phenylamine **(11*)*** (15 g, 42 mmol) was dissolved in THF/H_2O (9:1, 200 mL) and cooled down to 0° C. To obtain the acidic environment, 10M HCl was added (acidity of solution was controlled with pH indicator). A fresh prepared solution of sodium nitrite (4.83 g, 70 mmol) in H_2O (10 mL), and solution of phenol (11.86 g, 126 mmol) in 3M NaOH (40 mL) were added to the reaction. After 2 h the crude reaction mixture was poured into water. Obtained brown solid was separated and recrystallized (hexane) to yield an yellow powder (17.27 g, 88 %). ^{1}H NMR (200 MHz, d-THF) δ [ppm]: 7.79 (d, 4H, J = 8.2), 6.95 (d, 4H, J = 8.4), 4.06 (t, 2H, J = 6.4), 1.79 (m, 2H), 1.39 – 1.20 (m, 30H), 1.05 (t, 3H, J = 7.0)

H-shaped unit ***(14/7):*** Ethyl 4-dodecyloxy-2-hydroxybenzoate **(13)** (20 g, 57.1 mmol) was dissolved in anhydrous DMF (350 mL), then potassium carbonate (8.0 g, 58.0 mmol) and potassium iodide (9.63 g, 58.0 mmol) were added. Solution was heated up to 60° C and 1,7-dibromheptane (7.40 g, 28.7 mmol) was added. The reaction mixture was refluxed at 140° C, and monitored by TLC until consumption of the aromatic ester was complete (12h). The reaction mixture was removed from the heat and allowed to cool to room temperature (RT), then poured into water with ice. The precipitate was separated and purified by column chromatography (toluene) to yield a white powder (65%). ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.83 (d, 2H, J= 9.6); 6.49 – 6.44 (m, 4H); 4.31 (q, 4H, J= 7.0); 4.02 – 3.94 (m, 8H); 1.85-1.78 (m, 8H); 1.60 – 1.20 (m, 48H); 0.86 (t, 6H, J= 6.6).

SYNTHESIS OF THE OTHER HOMOLOGUES

The other homologues **(14/8 – 14/10)** were prepared as described for **(14/7).** The homologues **(14/1, 14/3 – 14/6*)*** were prepared as previously described. [1] Appropriate dibromoalkanes $Br(CH_2)_nBr$ (n = 1, 3 ÷ 10) were used.

H-shaped unit (14/8): ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.83 (d, 2H, J= 9.6); 6.50 – 6.44 (m, 4H); 4.30 (q, 4H, J= 7.2); 4.02 – 3.94 (m, 8H); 1.92-1.60 (m, 8H); 1.54 – 1.20 (m, 50H); 0.86 (t, 6H, J= 6.6).

H-shaped unit (14/9): ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.82 (d, 2H, J= 9.0); 6.49 – 6.44 (m, 4H); 4.31 (q, 4H, J= 7.0); 4.02 – 3.94 (m, 8H); 1.95-1.62 (m, 8H); 1.60 – 1.20 (m, 52H); 0.88 (t, 6H, J= 6.0).

H-shaped unit (14/10): ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.76 (d, 2H, J= 9.2); 6.41 – 6.37 (m, 4H); 4.25 (q, 4H, J= 7.0); 3.90 (t, 8H, J= 6.3); 1.95-1.62 (m, 8H); 1.50 – 1.10 (m, 54H); 0.88 (t, 6H, J= 6.6).

SYNTHESIS OF *H*-SHAPED ACID CHLORIDE (15/7):

A solution of potassium hydroxide (10 g, 178.2 mmol) in ethanol (20 mL) was added to suspension of H-shaped unit **(14/7)** (10g, 12.6 mmol) in ethanol (100 mL). The reaction mixture was refluxed for 8 h. The precipitate was separated and dried. In the second step obtained salt was suspended in anhydrous toluene (200 mL) and excess of oxalyl chloride (10 mL, 116.6 mmol) was added. The reaction mixture was refluxed, and monitored by TLC. The inorganic salt was filtered off and the hot solution of crude product was allowed to cool to room temperature (RT). The organic solvent (toluene) was removed by rotary evaporation to yield yellowish solid (95%). The crude solid was used without further purification in the final reaction.

The other homologues **(15/8 – 15/10)** were prepared as described for **(15/7).** The homologues **(15/1, 15/3 – 15/6)** were prepared as previously described.[1]

SYNTHESIS OF THE DIMERS

Dimer – series I ***(I/1):*** Into the solution of 4,4'-cyanobiphenyl **(9)** (0.81 g, 7.14 mmol) in anhydrous THF (70 mL) with presence of triethylamine (2 mL) a solution 2.4 g (3.50 mmol) of dichloride **(15/1)** in anhydrous THF (7 mL) was added. The reaction mixture was gently stirred at room temperature and after 15 minutes DMAP was added. The reaction mixture was refluxed for 12 h. The organic solvent (THF) was removed by rotary evaporation and the crude solid was purified by recrystallization (methanol) to yield a white powder (65%). ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.06 (d, 2H, J= 9.0); 7.77 - 7.61 (m, 12H); 7.31 (d, 4H, J= 8.6); 7.10 – 7.00 (m, 2H); 6.66 (dd, 2H, J_1= 2.6, J_2= 9.2); 5.93 (s, 2H); 3.96 (t, 4H, J= 6.6); 1.80-1.55 (m, 4H); 1.23 (s, 36H); 0.88 (t, 6H, J= 6.8); Elemental analysis for $C_{65}H_{74}N_2O_8$ (M= 1011.9): calc. C 77.20, H 7.38, N 2.77%; found C 77.26, H 7.41, N 2.81%;

The other homologues **(I/3 – I/10)** were prepared as described for **(I/1)**.

Dimer – series I ***(I/3):*** ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.03 (d, 2H, J= 8.5); 7.72 (dd, 4H, J_1= 2.0, J_2= 6.5); 7.66 (dd, 4H, J_1= 1.8, J_2= 6.8); 7.59 (dd, 4H, J_1= 2.0, J_2= 6.5); 7.26-7.25 (m, 4H); 6.53 – 6.49 (m, 4H); 4.31 (t, 4H, J=5.5); 3.94 (t, 4H, t, J= 6.5); 2.37-2.33 (m, 2H); 1.76-1.70 (m, 4H); 1.43-1.37 (m, 4H); 1.36 – 1.20 (m, 32H); 0.88 (t, 6H, J = 7.0). ^{13}C-NMR (125 MHz, $CDCl_3$) δ [ppm]: 164.71, 163.60, 161.68, 151.65, 144.91, 136.38, 132.59, 128.25, 127.60, 122.70, 118.82, 110.92, 110.48, 105.87, 100.09, 77.28, 77.03, 76.77, 68.33, 64.90, 31.88, 29.63, 29.60, 29.57, 29.52, 29.34, 29.32, 29.08, 25.93, 22.66, 14.10; Elemental analysis for: $C_{67}H_{78}N_2O_8$ (M=1039.34): calc. C 77.43; H 7.56; N 2.70%; found C 77.47; H 7.59; N 2.73%;

Dimer – series I ***(I/4):*** ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.05 (d, 2H, J= 8.0); 7.70-7.57 (m, 12H); 7.29 (d, 4H, J= 7.0); 6.54 – 6.49 (m, 4H); 4.11 (br., 4H); 3.98 (br., 4H); 2.12 (br. 4H); 1.77 (br., 4H); 1.44-1.27 (m, 36H); 0.88 (br., 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ [ppm]: 164.64, 163.63, 161.67, 151.63, 144.88, 136.33, 134.46, 132.58, 128.24, 127.60, 122.69, 118.88, 110.81, 110.49, 105.47, 99.95, 77.28, 77.03, 76.77, 68.34, 68.16, 31.89, 29.61, 29.57, 29.53, 29.32, 29.06, 25.93, 25.76, 22.67, 14.12; Elemental analysis for: $C_{68}H_{80}N_2O_8$ (M=1053,37): calc. C 77.53; H 7.65; N 2.66%; found C 77.51; H 7.63; N 2.62%;

Dimer – series I ***(I/5)****:* ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.03 (d, 2H, J= 8.5); 7.71 – 7.55 (m, 12H); 7.29-7.27 (m, 4H); 6.53 (dd, 2H, J_1= 2.5, J_2= 9.0); 6.46 (d, 2H, J= 2.0); 4.02 – 3.97 (m, 8H); 1.93-1.87 (m, 4H); 1.81 – 1.73 (m, 4H); 1.48 – 1.42 (m, 4H); 1.38 – 1.20 (m, 34H); 0.88 (t, 6H, J=7.0); Elemental analysis for: $C_{69}H_{82}N_2O_8$ (M=1067.40): calc. C 77.64; H 7.74; N 2.62%; found C 77.62; H 7.71; N 2.59%;

Dimer – series I ***(I/6)****:* ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.05 (d, 2H, J= 8.6); 7.72 – 7.54 (m, 12H); 7.31 – 7.24 (m, 4H); 6.57 – 6.46 (m, 4H); 4.06 – 3.98 (m, 8H); 1.80-1.76 (m, 8H); 1.46 – 1.20 (m, 40H); 0.89 (t, 6H, J=6.6); Elemental analysis for: $C_{70}H_{84}N_2O_8$ (M=1081.42): calc. C 77.74; H 7.83; N 2.59%; found C 77.78; H 7.86; N 2.62%;

Dimer – series I ***(I/7)****:* ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.99 (d, 2H, J= 8.6); 7.68– 7.54 (m, 12H); 7.30 – 7.26 (m, 4H); 6.54 – 6.38 (m, 4H); 4.03 – 3.98 (m, 8H); 1.88-1.74 (m, 8H); 1.42 – 1.20 (m, 42H); 0.88 (t, 6H, J=6.8); Elemental analysis for: $C_{71}H_{86}N_2O_8$ (M=1095.45): calc. C 77.85; H 7.91; N 2.56%; found C 77.89; H 7.94; N 2.60%;

Dimer – series I ***(I/8)****:* ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.97 (d, 2H, J= 8.8); 7.61 – 7.50 (m, 12H); 7.21 (d, 4H, J= 9.6); 6.50 – 6.40 (m, 4H); 3.95 – 3.92 (m, 8H); 1.90-1.70 (m, 8H); 1.38 – 1.20 (m, 44H); 0.88 (t, 6H, J=6.6); Elemental analysis for: $C_{72}H_{88}N_2O_8$ (M=1109.48): calc. C 77.94; H 7.99; N 2.52%; found C 77.97; H 8.03; N 2.57%;

Dimer – series I ***(I/9)****:* ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.02 (d, 2H, J= 8.6); 7.70 – 7.56 (m, 12H); 7.29 – 7.24 (m, 4H); 6.54 – 6.44 (m, 4H); 3.99 – 3.97 (m, 8H); 1.82-1.78 (m, 8H); 1.48 – 1.20 (m, 46H); 0.88 (t, 6H, J=6.6); Elemental analysis for: $C_{73}H_{90}N_2O_8$ (M=1123.50): calc. C 78.04; H 8.07; N 2.49%; found C 78.09; H 8.11; N 2.53%

Dimer – series I ***(I/10)****:* ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.04 (d, 2H, J= 8.8); 7.72 – 7.58 (m, 12H); 7.31 – 7.26 (m, 4H); 6.57 – 6.48 (m, 4H); 4.06 – 3.97 (m, 8H); 1.84-1.78 (m, 8H); 1.46 – 1.20 (m, 48H); 0.88 (t, 6H, J=6.6); Elemental analysis for: $C_{74}H_{92}N_2O_8$ (M=1137.53): calc. C 78.13; H 8.15; N 2.46%; found C 78.17; H 8.16; N 2.48%

The same procedure was applied to obtain series II **(II/n),** using dichloride (**15/n**) and ligand (**2**) instead of (**9**):

Dimer – series II ***(II/1)****:* ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.89 (d, 2H, J= 8.8); 7.47-7.40 (m, 8H); 6.96 – 6.87 (m, 4H); 6.71 (dd, 4H, J_1= 2.4, J_2= 8.8); 6.49 (d, 4H, J= 2.2); 5.63 (s, 2H); 3.97-4.03 (m, 8H); 1.83 – 1.76 (m, 8H); 1.50-1.20 (m, 72H); 0.88 (t, 12H, J= 7.0); Elemental analysis for: $C_{87}H_{124}O_{10}$ (M=1329.91): calc. C 78.57; H 9.40%; found C 78.61; H 9.46%;

Dimer – series II ***(II/3)****:* ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.02 (d, 2H, J= 9.0); 7.54 (d, 4H, J= 8.5); 7.49 (d, 4H, J= 9.0); 7.17 (d, 4H, J=8.5); 6.96 (d, 4H, J= 9.0); 6.52- 6.48 (m, 4H); 4.31 (t, 4H, J= 5.5); 3.99 (t, 4H, J= 6.5); 3.92 (t, 4H, J= 6.5); 2.38 – 2.32 (m, 2H); 1.83 – 1.78 (m, 4H); 1.75 – 1.70 (m, 4H); 1.50-1.20 (m, 72H); 0.90 – 0.87 (m, 12H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ [ppm]: 164.58, 164.02, 161.63, 158.70, 150.04, 138.27, 134.34, 132.88, 128.04, 127.62, 122.17, 114.75, 110.75, 105.93, 99.92, 77.28, 77.03, 76.77, 68.30, 68.08, 64.82, 31.94, 29.69, 29.67, 29.63, 29.61, 29.57, 29.44, 29.41, 29.37, 29.32, 29.12, 26.09, 25.97, 22.71,14.14; Elemental analysis for: $C_{89}H_{128}O_{10}$ (M=1357.96): calc. C 78.72; H 9.50%; found C 78.73; H 9.52%;

Dimer – series II ***(II/4)****:* ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.01 (d, 2H, J= 9.0); 7.52 (d, 4H, J= 9.0); 7.46 (d, 4H, J= 9.0); 7.20 (d, 4H, J=8.5); 6.94 (d, 4H, J= 8.5); 6.52- 6.48 (m, 4H); 4.11 (sz., 4H); 4.00 – 3.95 (m, 8H); 2.10 (br., 4H); 1.83 – 1.73 (m, 8H); 1.50-1.22 (m, 72H); 0.89 – 0.87 (m, 12H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ [ppm]: 164.52, 163.99, 161.64, 158.76, 150.20, 138.28, 134.38, 133.01, 128.08, 127.62, 122.14, 114.85, 111.23, 105.70, 100.15, 77.28, 77.03, 76.77, 68.38, 68.33, 68.17, 31.94, 29.69, 29.68, 29.65, 29.63, 29.61, 29.57, 29.44, 29.40, 29.36, 29.15, 26.11, 26.00, 25.86, 22.70,14.10; Elemental analysis for: $C_{90}H_{130}O_{10}$ (M=1371.99): calc. C 78.79; H 9.55%; found C 78.86; H 9.59%;

Dimer – series II ***(II/5)****:* ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.02 (d, 2H, J= 9.0); 7.51 (d, 4H, J= 8.5); 7.46 (d, 4H, J= 9.0); 7.20 (d, 4H, J=8.5); 6.94 (d, 4H, J= 8.5); 6.51 (dd, 2H, J_1= 2.3, J_2= 8.8); 6.45 (d, 2H, J= 2.0); 4.02 – 3.94 (m, 12H); 1.92 – 1.87 (m, 4H); 1.83 – 1.74 (m, 8H); 1.50 – 1.41 (m, 8H); 1.36 – 1.23 (66H); 0.88 (t, 12H, J= 7.0); Elemental analysis for: $C_{91}H_{132}O_{10}$ (M=1386.02): C 78.86; H 9.60%; found C 78.88; H 9.61%;

Dimer – series II ***(II/6)****:* ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.95 (d, 2H, J= 8.6); 7.48 – 7.38 (m, 8H); 7.13 (d, 4H, J=8.6); 6.87 (d, 4H, J= 8.8); 6.46 - 6.40 (m, 4H); 4.00 – 3.80 (m, 12H); 1.82 – 1.70 (m, 12H); 1.48 – 1.18 (m, 76H); 0.81 (t, 12H, J= 6.6); Elemental analysis for: $C_{92}H_{134}O_{10}$ (M=1400.04): calc. C 78.93; H 9.65%; found C 78.91; H 9.63%;

Dimer – series II ***(II/7)****:* ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.03 (d, 2H, J= 8.6); 7.55 – 7.45 (m, 8H); 7.21 (d, 4H, J=8.8); 6.94 (d, 4H, J= 8.8); 6.54 - 6.47 (m, 4H); 4.01 – 3.95 (m, 12H); 1.80 – 1.76 (m, 12H); 1.48 – 1.18 (m, 78H); 0.88 (t, 12H, J= 6.8); Elemental analysis for: $C_{93}H_{136}O_{10}$ (M=1414.07): calc. C 78.99; H 9.69%; found C 79.03; H 9.74%;

Dimer – series II ***(II/8)****:* ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.96 (d, 2H, J= 8.6); 7.49 – 7.38 (m, 8H); 7.14 (d, 4H, J=8.6); 6.87 (d, 4H, J= 9.0); 6.47 - 6.41 (m, 4H); 3.93 – 3.87 (m, 12H); 1.76 – 1.69 (m, 12H); 1.50 – 1.20 (m, 80H); 0.81(t, 12H, J= 6.8); Elemental analysis for: $C_{94}H_{138}O_{10}$ (M=1428.10): calc. C 79.06; H 9.74%; found C 79.10; H 9.77%;

Dimer – series II ***(II/9)****:* ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.03 (d, 2H, J= 8.8); 7.58 – 7.46 (m, 8H); 7.21 (d, 4H, J=8.6); 6.94 (d, 4H, J= 8.8); 6.54 - 6.48 (m, 4H); 4.04 – 3.94 (m, 12H); 1.83 – 1.76 (m, 12H); 1.46 – 1.20 (m, 82H); 0.88 (t, 12H, J= 6.8); Elemental analysis for: $C_{95}H_{140}O_{10}$ (M=1442.12): calc. C 79.12; H 9.78%; found C 79.17; H 9.84%;

*Dimer – series II **(II/10):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.03 (d, 2H, J= 8.6); 7.57 – 7.46 (m, 8H); 7.22 (d, 4H, J=8.6); 6.94 (d, 4H, J= 8.6); 6.54 - 6.50 (m, 4H); 4.04 – 3.94 (m, 12H); 1.82 – 1.77 (m, 12H); 1.57 – 1.20 (m, 84H); 0.88 (t, 12H, J= 6.8); Elemental analysis for: $C_{96}H_{142}O_{10}$ (M=1456.15): calc. C 79.18; H 9.83%; found C 79.21; H 9.83%;

The same procedure was applied to obtain series III **(III/n),** using appropriate dichloride **(15/n)** and ligand **(12)** instead of **(9):**
*Dimer – series III **(III/3):*** ^{1}H NMR (500 MHz, CDCl$_3$) δ [ppm]: 8.00 (d, 2H, J= 9.0); 7.90 (dd, 8H, J$_1$= 3.5, J$_2$= 9.0); 7.26 (d, 4H, J= 9.0); 6.99 (d, 4H, J= 9.0); 6.52 – 6.47 (m, 4H); 4.32 (t, 4H, J= 5.5); 4.04 (t, 4H, J= 6.5); 3.92 (t, 4H, J= 6.5); 2.38 – 2.32 (m, 2H); 1.84 – 1.81 (m, 4H); 1.75 – 1.72 (m, 4H); 1.50-1.20 (m, 96H); 0.88 (t, 12H, J= 6.5). ^{13}C-NMR (125 MHz, CDCl$_3$) δ [ppm]: 164.78, 163.61, 161.77, 161.75, 152.85, 146.94, 134.39, 124.74, 123.48, 122.48, 114.77, 106.20, 100.14, 77.28, 77.03, 76.78, 68.47, 68.42, 64.96, 31.95, 29.72, 29.69, 29.63, 29.60, 29.58, 29.43, 29.41, 29.37, 29.27, 29.15, 26.07, 26.00, 22.70, 14.10; Elemental analysis for: $C_{101}H_{140}N_4O_{10}$ (M=1570.21): calc. C 77.26; H 8.99; N 3.57%; found C 77.30; H 9.01; N 3.59%;
*Dimer – series III **(III/5):*** ^{1}H NMR (500 MHz, CDCl$_3$) δ [ppm]: 8.00 (d, 2H, J= 8.5); 7.88 (dd, 8H, J$_1$= 2.5, J$_2$= 8.5); 7.30 (d, 4H, J= 8.5); 6.98 (d, 4H, J= 9.0); 6.52 – 6.45 (m, 4H); 4.07 – 4.00 (m, 8H); 3.97 (t, 4H, J= 6.5); 1.94 – 1.86 (m, 4H); 1.84 – 1.72 (m, 8H); 1.52-1.20 (m, 98H); 0.88 (t, 12H, J= 7.0). ^{13}C-NMR (125 MHz, CDCl$_3$) δ [ppm]: 164.85, 163.91, 161.93, 153.11, 150.44, 147.14, 134.66, 124.94, 123.87, 122.66, 114.95, 111.31, 105.95, 100.46, 77.49, 77.24, 76.99, 69.00, 68.65, 68.61, 32.15, 29.93, 29.89, 29.86, 29.83, 29.81, 29.78, 29.63, 29.60, 29.58, 29.60, 26.47, 29.37, 29.01, 26.27, 26.21, 22.91, 14.31; Elemental analysis for: $C_{103}H_{144}N_4O_{10}$ (M=1598.27): calc. C 77.40; H 9.08; N 3.51%; found C 77.42; H 9.11; N 3.53%;
*Dimer – series III **(III/7):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.02 (d, 2H, J= 8.8); 7.92 - 7.79 (m, 8H); 7.32 – 7.25 (m, 4H); 6.98 (d, 4H, J= 9.0); 6.54 – 6.46 (m, 4H); 4.05 – 3.99 (m, 12H); 1.92 – 1.82 (m, 12H); 1.58-1.20 (m, 102H); 0.88 (t, 12H, J= 6.8); Elemental analysis for: $C_{105}H_{148}N_4O_{10}$ (M=1626.32): C 77.54; H 9.17; N 3.45%; found C 77.56; H 9.18; N 3.44%;
*Dimer – series III **(III/10):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.03 (d, 2H, J= 8.6); 7.95 - 7.87 (m, 8H); 7.34 – 7.25 (m, 4H); 6.98 (d, 4H, J= 9.0); 6.58 – 6.45 (m, 4H); 4.05 – 3.97 (m, 12H); 1.90 – 1.76 (m, 12H); 1.60-1.20 (m, 108H); 0.88 (t, 12H, J= 6.8); Elemental analysis for: $C_{108}H_{154}N_4O_{10}$ (M=1668.40): calc. C 77.75; H 9.30; N 3.36%; found C 77.77; H 9.32; N 3.35%;

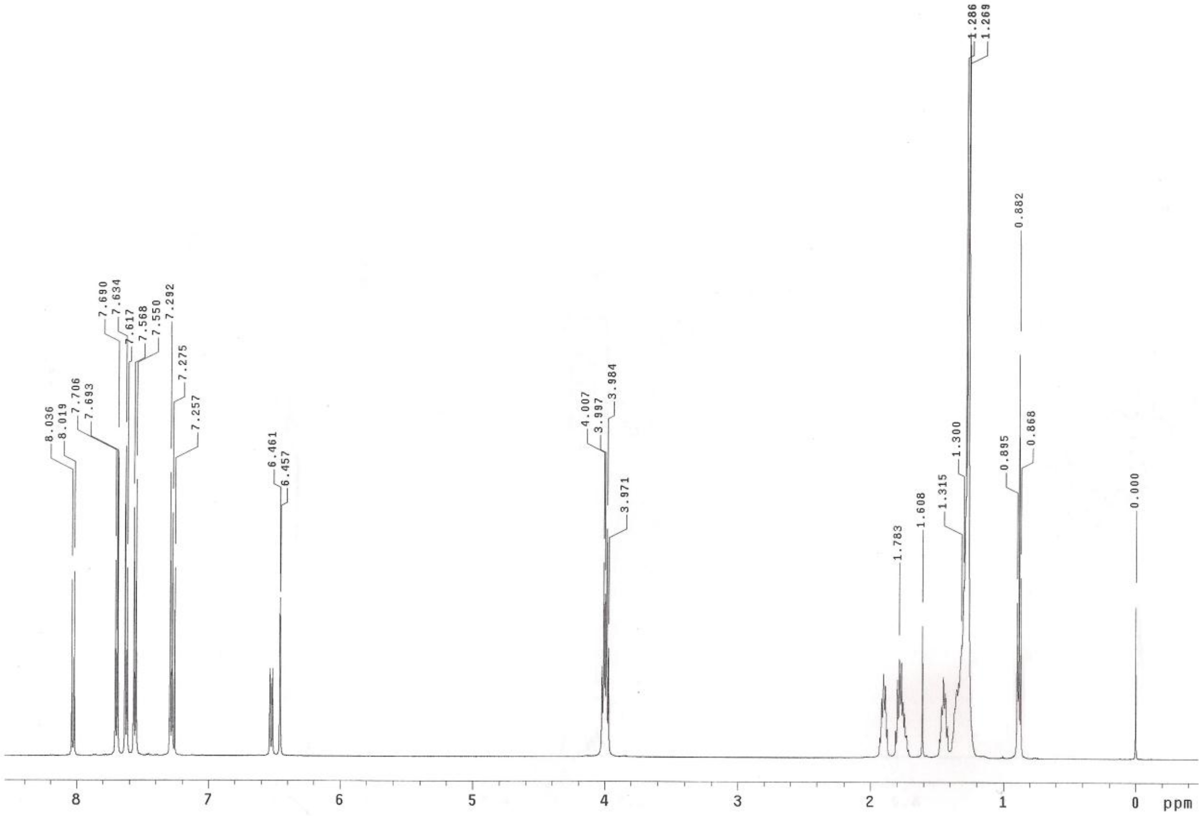
The same procedure was applied to obtain series IV (18/n), using dichloride **15/n** and ligand ***6*** instead of ***9***:
*Dimer – series IV **(IV/1):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.17 (d, 4H, J= 9.0); 8.06 (d, 2H, J= 8.8); 7.62 (d, 8H, J= 8.0); 7.31 – 7.24 (m, 8H); 7.02 – 6.96 (m, 4H); 6.70 – 6.63 (m, 4H); 5.94 (s, 2H); 4.08 – 3.92 (m, 8H); 1.84 – 1.70 (m, 8H); 1.60 – 1.20 (m, 72H); 0.88 – 0.83 (m, 12H); Elemental analysis for: $C_{101}H_{132}O_{14}$ (M=1570.12): calc. C 77.26; H 8.47%; found C 77.31; H 8.50%;
*Dimer – series IV **(IV/3)**:* ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.15 (d, 4H, J=8.8); 8.04 (d, 2H, J= 8.8); 7.60 (m, 8H); 7.33 – 7.22 (m, 8H); 7.01 – 6.95 (d, 4H, J=8.8); 6.55 – 6.48 (m, 4H); 4.22 (br., 4H); 4.05 (t, 4H, J=6.6); 3.96 (t, 4H, J=6.5); 2.3 (br., 2H); 1.95 – 1.70 (m, 8H); 1.60 – 1.20 (m, 72H); 0.88 – 0.83 (m, 12H); Elemental analysis for: $C_{103}H_{136}O_{14}$ (M=1598.17): calc. C 77.41; H 8.58%; found C 77.42; H 8.61%;
*Dimer – series IV **(IV /4):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.09 (d, 4H, J= 8.8); 7.98 (d, 2H, J= 8.8); 7.58 – 7.49 (m, 8H); 7.23 – 7.16 (m, 8H); 6.91 (d, 4H, J= 9.0); 6.47 – 6.42 (m, 4H); 4.04 – 3.88 (m, 12H); 2.06 (sz.4H); 1.80 – 1.70 (m, 8H); 1.50 – 1.18 (m, 72H); 0.81 – 0.78 (m, 12H); Elemental analysis for: $C_{104}H_{138}O_{14}$ (M=1612.20): calc. C 77.48; H 8.63%; found C 77.50; H 8.67%;
*Dimer – series IV **(IV /5):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.09 (d, 4H, J= 8.8); 7.97 (d, 2H, J= 8.6); 7.53 – 7.47 (m, 8H); 7.21 – 7.15 (m, 8H); 6.91 (d, 4H, J= 9.0); 6.47 – 6.40 (m, 4H); 4.01 – 3.88 (m, 12H); 1.82 – 1.60 (m, 12H); 1.50 – 1.16 (m, 74H); 0.81(t, 12H, J= 6.0); Elemental analysis for: $C_{105}H_{140}O_{14}$ (M=1626.23): calc. C 77.55; H 8.68%; found C 77.52; H 8.64%;
*Dimer – series IV **(IV /6):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.16 (d, 4H, J= 8.8); 8.03 (d, 2H, J= 8.6); 7.59 (dd, 8H, J$_1$= 2.2, J$_2$= 8.8); 7.28 – 7.23 (m, 8H); 6.98 (d, 4H, J= 8.8); 6.55 – 6.40 (m, 4H); 4.08 – 3.97 (m, 12H); 1.88 – 1.76 (m, 12H); 1.56 – 1.20 (m, 76H); 0.88(t, 12H, J= 6.6); Elemental analysis for: $C_{106}H_{142}O_{14}$ (M=1640.25): calc. C 77.62; H 8.73%; found C 77.68; H 8.77%;
*Dimer – series IV **(IV /7):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.16 (d, 4H, J= 8.6); 8.03 (d, 2H, J= 8.6); 7.52 (dd, 8H, J$_1$= 2.4, J$_2$= 8.6); 7.21 – 7.14 (m, 8H); 6.94 (d, 4H, J= 8.8); 6.54 - 6.47 (m, 4H); 4.00 – 3.95 (m, 12H); 1.80 – 1.74 (m, 12H); 1.51 – 1.21 (m, 78H); 0.88 (t, 12H, J= 6.8); Elemental analysis for: $C_{107}H_{144}O_{14}$ (M=1654.28): calc. C 77.69; H 8.77%; found C 77.74; H 8.81%;
*Dimer – series IV **(IV /8):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.04 (d, 4H, J= 8.6); 7.94 (d, 2H, J= 8.6); 7.48 (dd, 8H, J$_1$= 2.2, J$_2$= 8.6); 7.16 – 7.09 (m, 8H); 6.86 (d, 4H, J= 8.8); 6.49 - 6.42 (m, 4H); 4.02 – 3.90 (m, 12H); 1.81 – 1.72 (m, 12H); 1.50 – 1.20 (m, 80H); 0.81(t, 12H, J= 6.8); Elemental analysis for: $C_{108}H_{146}O_{14}$ (M=1668.31): calc. C 77.75; H 8.82%; found C 77.77; H 8.85%;
*Dimer – series IV **(IV /9):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.14 (d, 4H, J= 8.8); 8.05 (d, 2H, J= 8.6); 7.50 (dd, 8H, J$_1$= 2.2, J$_2$= 8.6); 7.21 – 7.16 (m, 8H); 6.94 (d, 4H, J= 8.8); 6.52 - 6.46 (m, 4H); 4.03 – 3.94 (m, 12H); 1.81 – 1.75 (m, 12H); 1.46 – 1.20 (m, 82H); 0.88 (t, 12H, J= 6.6); Elemental analysis for: $C_{109}H_{148}O_{14}$ (M=1682.33): calc. C 77.82; H 8.87%; found C 77.84; H 8.90%;
*Dimer – series IV **(IV /10):*** ^{1}H NMR (200 MHz, CDCl$_3$) δ [ppm]: 8.08 (d, 4H, J= 8.8); 7.96 (d, 2H, J= 8.4); 7.52 (dd, 8H, J$_1$= 1.2, J$_2$= 8.6); 7.20 – 7.19 (m, 8H); 6.90 (d, 4H, J= 9.0); 6.47 – 6.43 (m, 4H); 4.01 – 3.91 (m, 12H); 1.80 – 1.72 (m, 12H); 1.48 – 1.18 (m, 84H); 0.81(t, 12H, J= 6.6); Elemental analysis for: $C_{110}H_{150}O_{14}$ (M=1696.36): calc. C 77.88; H 8.91%; found C 77.91; H 8.94%;

The same procedure was applied to obtain series V **(V/n),** using dichloride **(15/n)** and ligand **(7)** instead of **(9):**
Dimer – series V ***(V/1):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.06 (d, 2H, J= 8.8); 7.84 (dd, 2H, J_1= 2.0, J_2= 8.6); 7.65 – 7.60 (m, 10H); 7.31 – 7.26 (m, 8H); 7.02 – 6.93 (m, 4H); 6.66 (dd, 2H, J_1= 2.4, J_2= 9.0); 5.94 (s, 2H); 4.18 – 4.02 (m, 8H); 3.96 (t, 4H, J= 6.4); 1.98 – 1.80 (m, 8H); 1.74 – 1.62 (m, 4H); 1.58 – 1.20 (m, 108H); 0.91 – 0.83 (m, 18H); Elemental analysis for: $C_{125}H_{180}O_{16}$ (M=1938.76): calc. C 77.44; H 9.36%; found C 77.45; H 9.39%;
Dimer – series V ***(V /3):*** ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.03 (d, 2H, J= 9.0); 7.83 (dd, 2H, J_1= 2.0, J_2= 8.0); 7.69 (d, 2H, J= 2.0); 7.59 – 7.56 (m, 8H); 7.27 – 7.24 (m, 8H); 6.93(d, 2H, J= 8.5); 6.52 (dd, 2H, J_1= 2.0, J_2= 9.0); 6.46 (d, 2H, J = 2.0); 4.12 – 4.05 (m, 8H); 4.04 – 3.97 (m, 8H); 1.94 – 1.74 (m, 14H); 1.53 – 1.42 (m, 12H); 1.40 - 1.22 (m, 96H); 0.90 – 0.87 (m, 18H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ [ppm]: 165.04, 164.50, 164.06, 161.60, 153.85, 150.69, 150.50, 148.69, 137.75, 128.09, 128.05, 124.39, 122.27, 122.05, 121.56, 114.67, 111.96, 111.10, 105.49, 100.15, 77.28, 77.03, 76.77, 69.36, 69.07, 68.67, 68.33, 31.92, 31.91, 29.70, 29.66, 29.63, 29.61, 29.60, 29.56, 29.42, 29.39, 29.38, 29.36, 29.34, 29.19, 29.12, 29.06, 28.79, 26.02, 25.98, 22.68, 22.64, 14.11; Elemental analysis for: $C_{127}H_{184}O_{16}$ (M=1966.81): calc. C 77.55; H 9.43%; found C 77.59; H 9.46%;
Dimer – series V ***(V /4):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.98 (d, 2H, J= 8.6); 7.77 (dd, 2H, J_1= 2.0, J_2= 8.6); 7.61 (d, 2H, J= 2.0); 7.55 – 7.49 (m, 8H); 7.23 – 7.18 (m, 8H); 6.86 (d, 2H, J= 8.6); 6.47 – 6.42 (m, 4H); 4.04 – 3.88 (m, 16H); 2.05 (sz. 4H); 1.85 – 1.70 (m, 12H); 1.51 – 1.20 (m, 108H); 0.81 (t, 18H, J= 7.6); Elemental analysis for: $C_{128}H_{186}O_{16}$ (M=1980.84): calc. C 77.61; H 9.46%; found C 77.59; H 9.42%;
Dimer – series V ***(V /5):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.03 (d, 2H, J= 8.8); 7.83 (dd, 2H, J_1= 2.0, J_2= 8.8); 7.68 (d, 2H, J= 2.0); 7.59 – 7.55 (m, 8H); 7.27 – 7.23 (m, 8H); 6.94 (d, 2H, J= 8.6); 6.55 – 6.47 (m, 4H); 4.11 – 3.96 (m, 16H); 2.0 – 1.72 (m, 16H); 1.60 – 1.20 (m, 110H); 0.88 (t, 18H, J= 7.4); Elemental analysis for: $C_{129}H_{188}O_{16}$ (M=1994.86): calc. C 77.67; H 9.50%; found C 77.71; H 9.52%;
Dimer – series V ***(V /6):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.03 (d, 2H, J= 8.4); 7.84 (dd, 2H, J_1= 1.8, J_2= 8.4); 7.69 – 7.57 (m, 10H); 7.31 – 7.23 (m, 8H); 6.94 (d, 2H, J= 8.4); 6.55 – 6.46 (m, 4H); 4.11 – 3.97 (m, 16H); 1.90 – 1.70 (m, 16H); 1.60 – 1.16 (m, 112H); 0.88 (t, 18H, J= 6.8); Elemental analysis for: $C_{130}H_{190}O_{16}$ (M=2008.89): calc. C 77.72; H 9.53%; found C 77.70; H 9.52%;
Dimer – series V ***(V /7):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.00 (d, 2H, J= 8.6); 7.82 (dd, 2H, J_1= 2.0, J_2= 8.6); 7.66 – 7.54 (m, 10H); 7.29 – 7.22 (m, 8H); 6.92 (d, 2H, J= 8.6); 6.57 – 6.46 (m, 4H); 4.08 – 3.97 (m, 16H); 1.88 – 1.72 (m, 16H); 1.58 – 1.18 (m, 114H); 0.88 (t, 18H, J= 7.0); Elemental analysis for: $C_{131}H_{192}O_{16}$ (M=2022.92): calc. C 77.78; H 9.57; found C 77.77; H 9.61%;
Dimer – series V ***(V /8):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.84 – 7.78 (m, 4H); 7.66 – 7.50 (m, 10H); 7.24 – 7.19 (m, 10H); 6.92 (d, 4H, J= 8.6); 4.10 – 3.94 (m, 16H); 1.94 – 1.72 (m, 16H); 1.48 – 1.20 (m, 116H); 0.88 (t, 18H, J= 6.6); Elemental analysis for: $C_{132}H_{194}O_{16}$ (M=2036.94): calc. C 77.83; H 9.60%; found C 77.86; H 9.62%;
Dimer – series V ***(V /9):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.01 – 7.92 (m, 4H); 7.80 – 7.68 (m, 10H); 7.54 – 7.36 (m, 10H); 6.90 (d, 4H, J= 8.6); 4.11 – 3.97 (m, 16H); 1.88 – 1.70 (m, 16H); 1.58 – 1.20 (m, 118H); 0.88 (t, 18H, J= 6.8); Elemental analysis for: $C_{133}H_{196}O_{16}$ (M=2050.97): calc. C 77.89; H 9.63%; found C 77.93; H 9.65%;
Dimer – series V ***(V /10):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.78 – 7.75 (m, 4H); 7.62 – 7.51 (m, 10H); 7.23 – 7.19 (m, 10H); 6.87 (d, 4H, J= 8.8); 4.10 – 3.98 (m, 16H); 1.90 – 1.72 (m, 16H); 1.50 – 1.18 (m, 120H); 0.81 (t, 18H, J= 6.0); Elemental analysis for: $C1_{34}H_{198}O_{16}$ (M=2065.00): calc. C 77.94; H, 9.66%; found C 77.96; H, 9.69%;

The same procedure was applied to obtain series VI **(VI/n)**, using appropriate dichloride **(15/n)** and ligand **(8)** instead of **(9)**.
Dimer – series VI ***(VI/1):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.90 (d, 2H, J= 8.8); 7.46 (dd, 8H, J_1= 1.8, J_2= 8.6); 7.27 (s, 4H); 7.11 (d, 8H, J= 7.4); 6.86 – 6.82 (m, 2H); 6.52 – 6.48 (m, 2H); 5.78 (s, 2H); 3.93 – 3.80 (m, 16H); 1.80 – 1.52 (m, 16H); 1.40 – 1.10 (m, 144H); 0.72 (t, 24H, J = 6.4); Elemental analysis for: $C_{149}H_{228}O_{18}$ (M=2307.39): calc. C 77.56; H 9.96%; found C 77.57; H 9.98%;
Dimer – series VI ***(VI/5):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.97 (d, 2H, J= 8.6); 7.51 (dd, 8H, J_1= 2.8, J_2= 8.6); 7.36 (s, 4H); 7.20 – 7.16 (m, 8H); 6.47 – 6.40 (m, 4H); 4.02 – 3.89 (m, 20H); 1.85 – 1.60 (m, 20H); 1.45 – 1.15 (m, 146H); 0.81 (t, 24H, J = 7.2); Elemental analysis for: $C_{153}H_{236}O_{18}$ (M=2363.50): calc. C 77.75; H 10.06%; found C 77.78; H 10.09%;
Dimer – series VI ***(VI/7):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.92 (d, 2H, J= 8.8); 7.48 (dd, 8H, J_1= 2.8, J_2= 8.6); 7.34 (s, 4H); 7.18 – 7.09 (m, 8H); 6.51 – 6.46 (m, 4H); 3.92 – 3.80 (m, 20H); 1.83 – 1.62 (m, 20H); 1.42 – 1.10 (m, 150H); 0.81 (t, 24H, J = 6.6); Elemental analysis for: $C_{155}H_{240}O_{18}$ (M=2391.55): calc. C 77.84; H, 10.11%; found C 77.89; H, 10.15%;
Dimer – series VI ***(VI/10):*** ^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.89 (d, 2H, J= 8.2); 7.45 (dd, 8H, J_1= 2.0, J_2= 8.6); 7.27 (s, 4H); 7.13 – 7.07 (m, 8H); 6.42 – 6.34 (m, 4H); 3.93 – 3.83 (m, 20H); 1.70 – 1.58 (m, 20H); 1.42 – 1.10 (m, 156H); 0.72 (t, 24H, J = 6.6); Elemental analysis for: $C_{158}H_{246}O_{18}$ (M=2433.63): calc. C 77.98; H 10.19%; found C 78.02; H 10.23%;

^{1}H NMR spectra for representative compounds: homologues n=5 from each series **I – VI**

I.5



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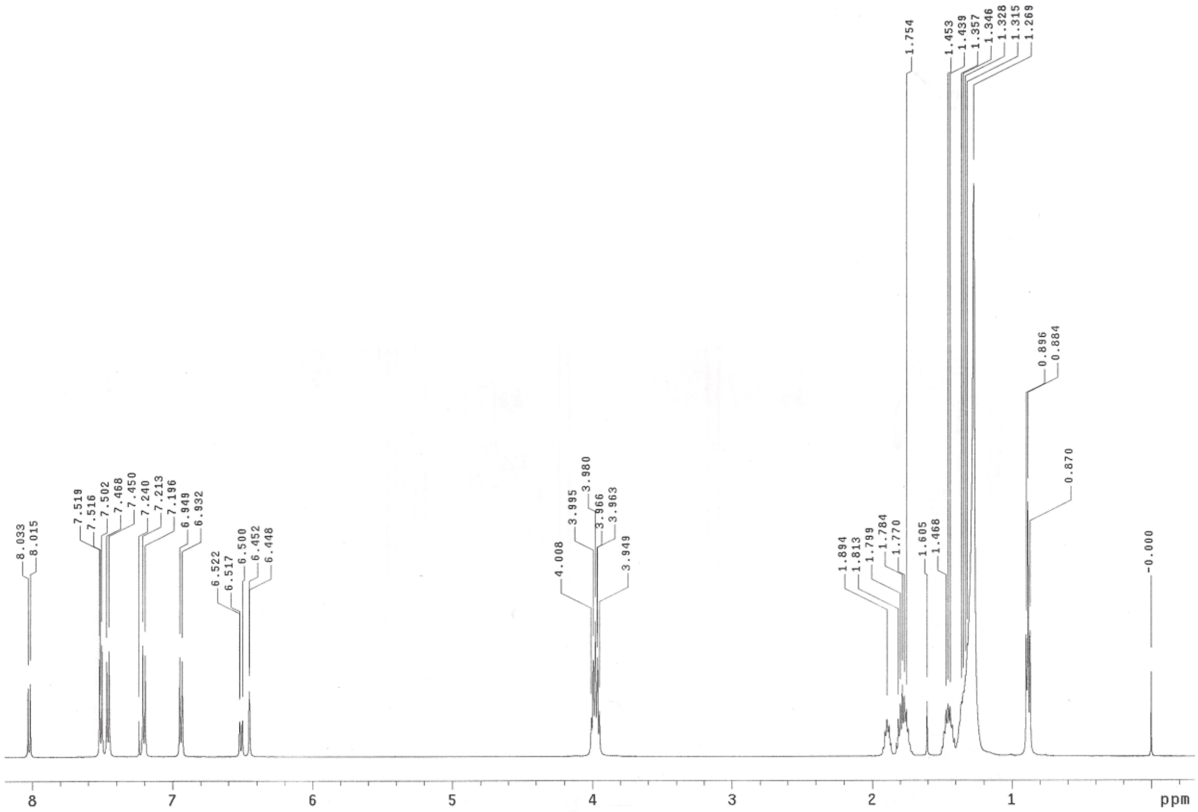

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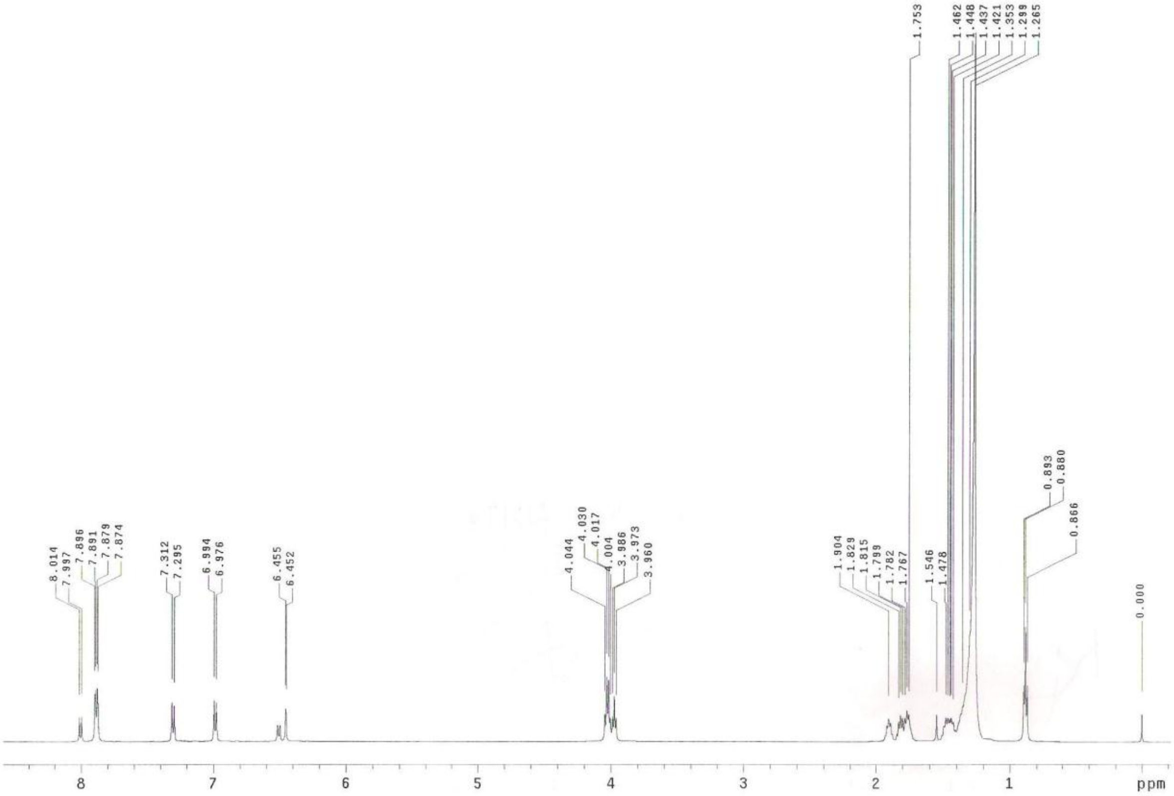
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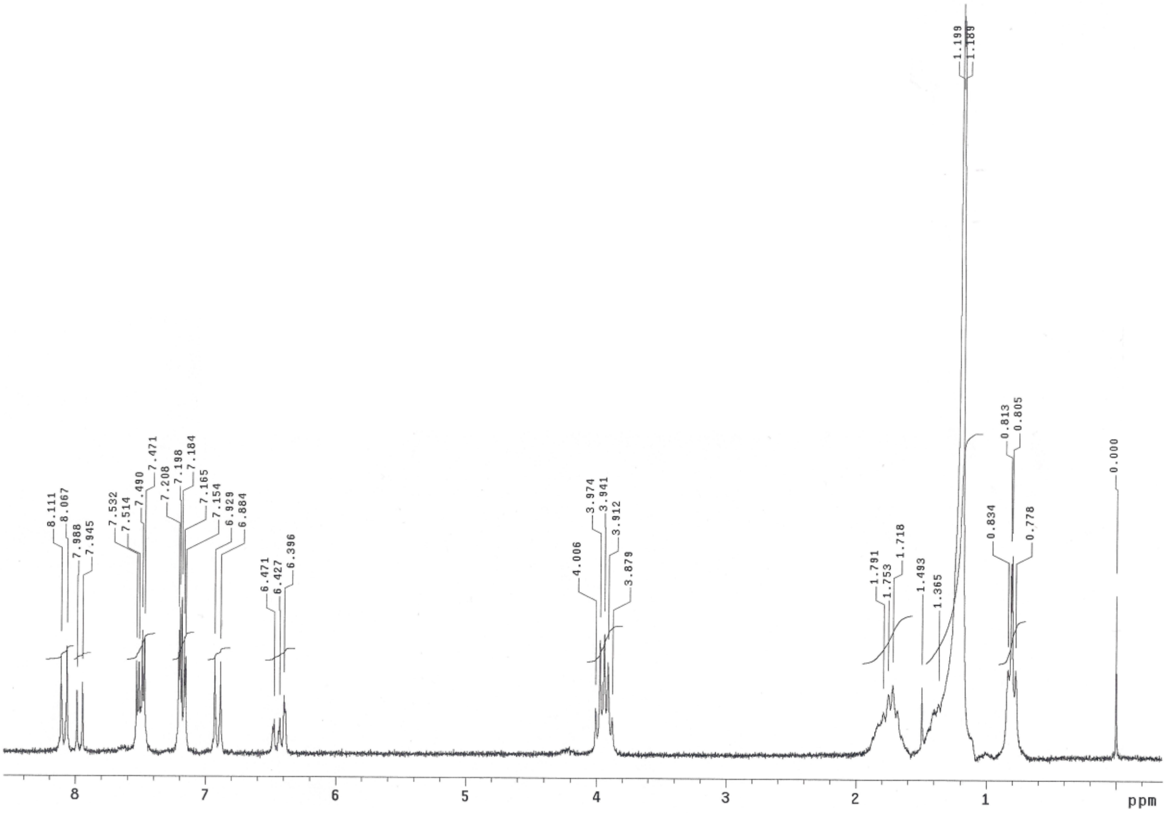
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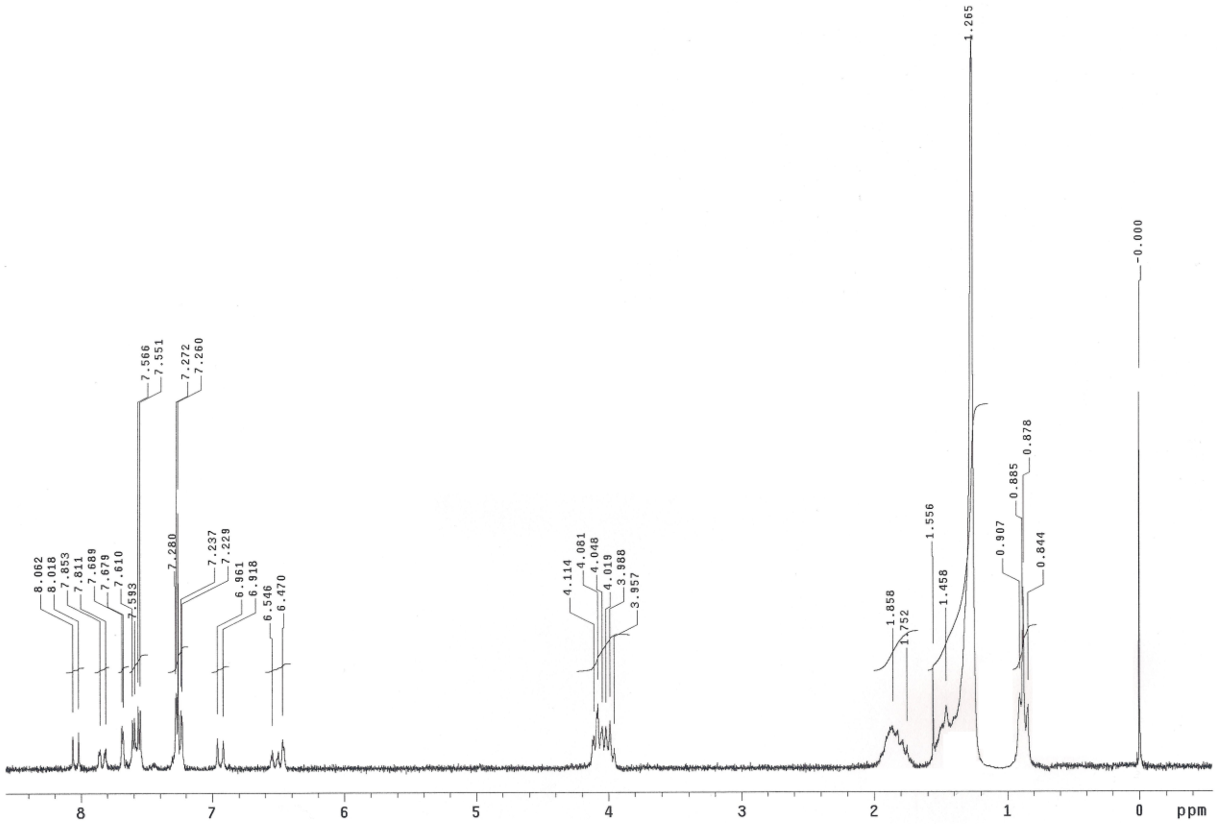
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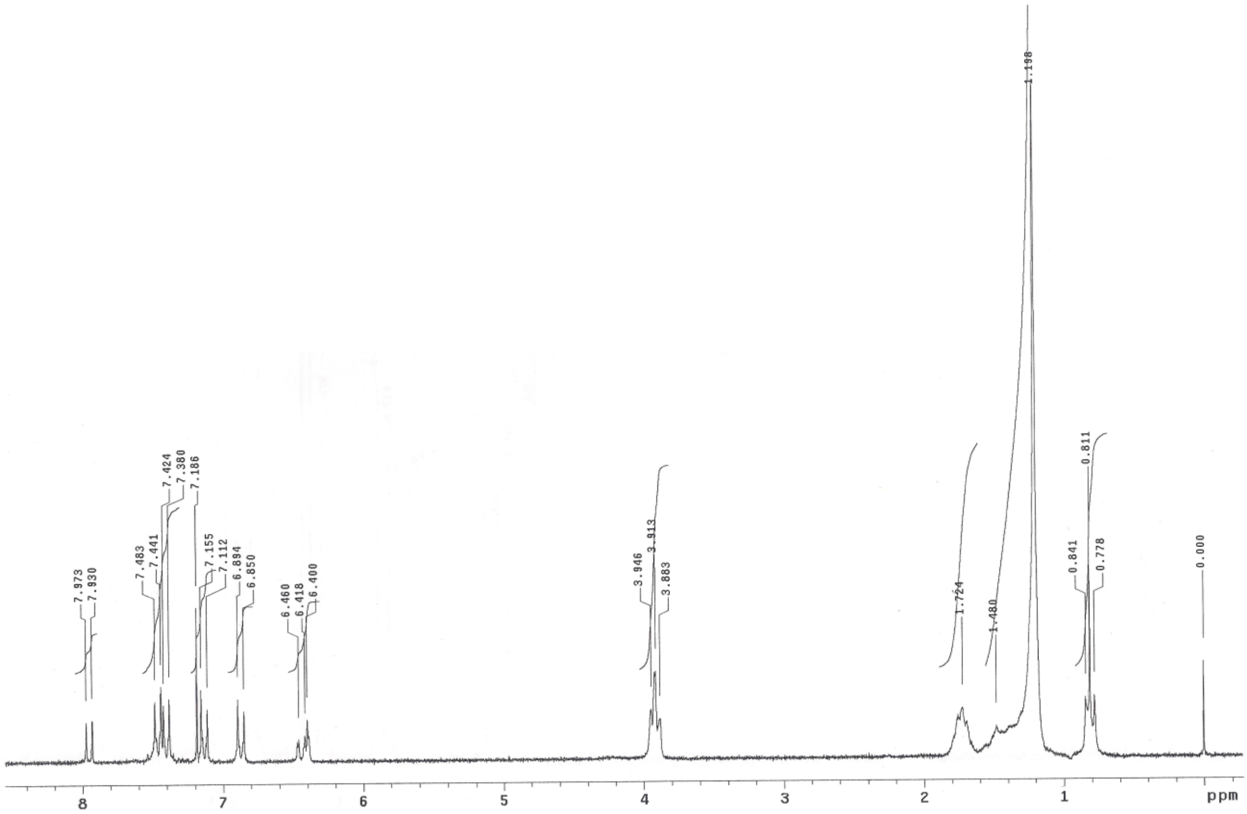
ppm

VI.5


7.973
7.930
7.483
7.441
7.424
7.380
7.186
7.155
7.112
6.894
6.850
6.460
6.418
6.400
3.946
3.913
3.883
1.724
1.480
1.198
0.841
0.811
0.778
0.000
8
7
6
5
4
3
2
1
ppm

DSC measurements

DSC thermograms (1st heating, red line and 1st cooling, blue line) are presented for representative compounds: homologues n=5 from each series **I** – **VI**, and those, which showed different LC phase sequence.

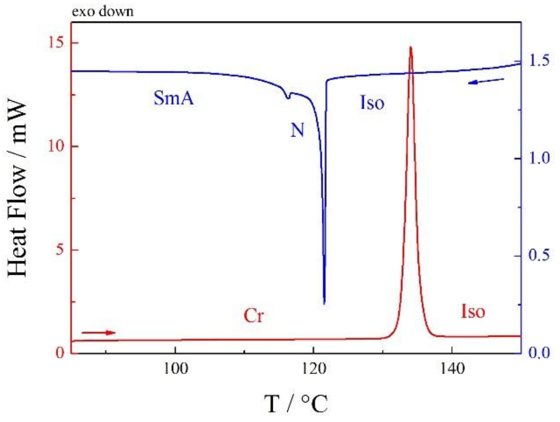


Figure S1. DSC thermograms for compound **I.5**

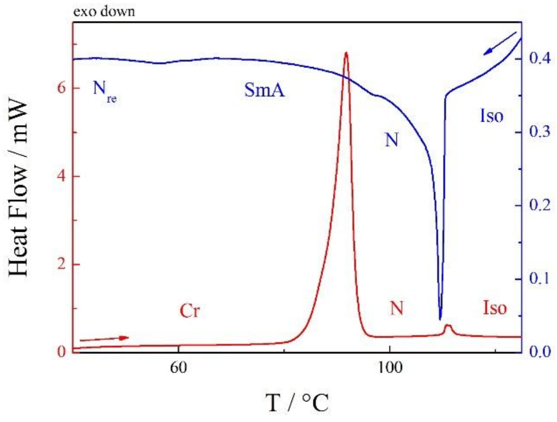


Figure S2. DSC thermograms for compound **I.7**

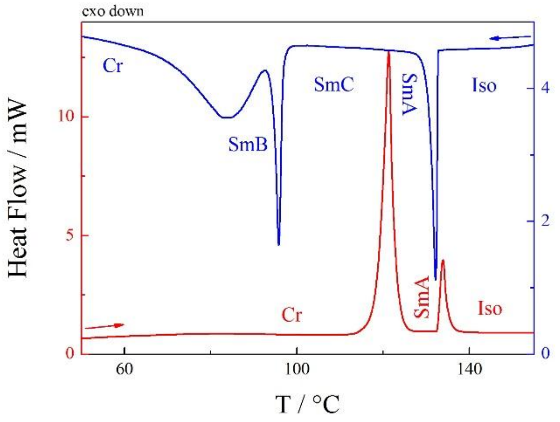


Figure S3. DSC thermograms for compound **II.4**

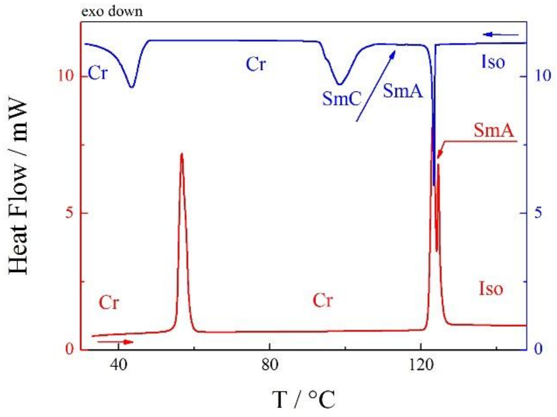


Figure S4. DSC thermograms for compound **II.5**

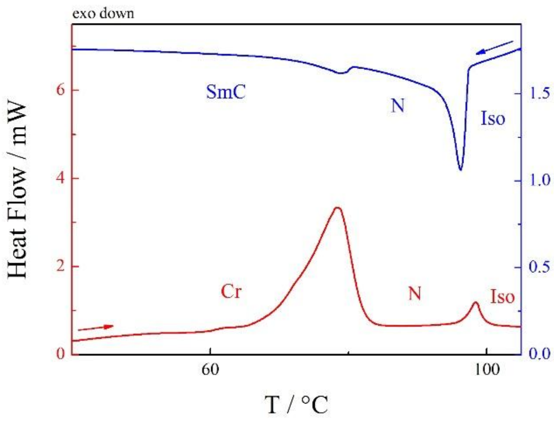


Figure S5. DSC thermograms for compound **II.10**

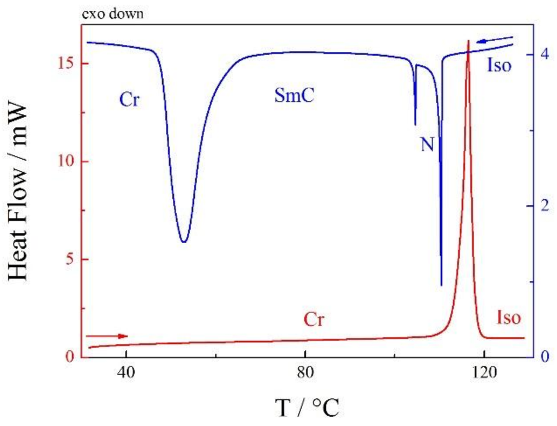


Figure S6. DSC thermograms for compound **III.5**

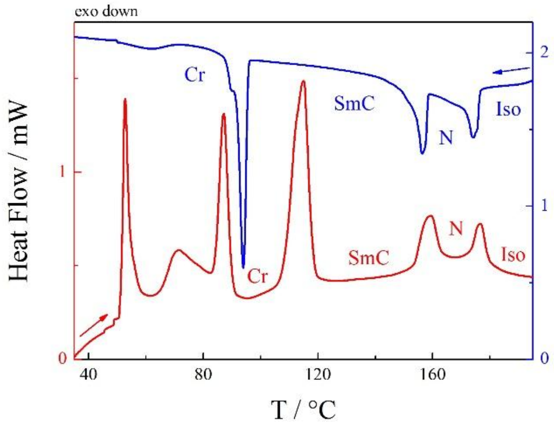


Figure S7. DSC thermograms for compound **IV.5**

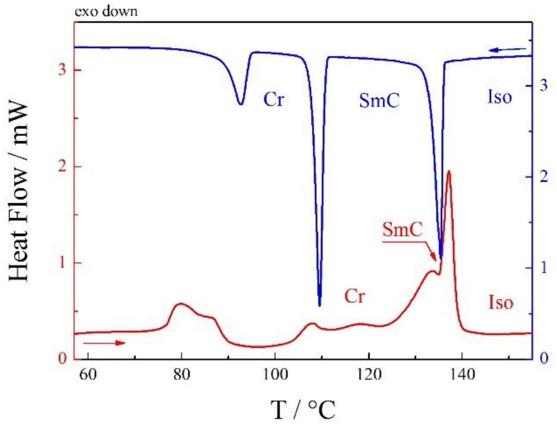


Figure S8. DSC thermograms for compound **V.5**

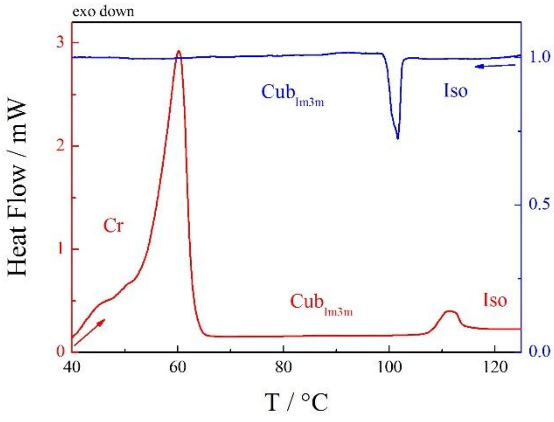


Figure S9. DSC thermograms for compound **VI.1**

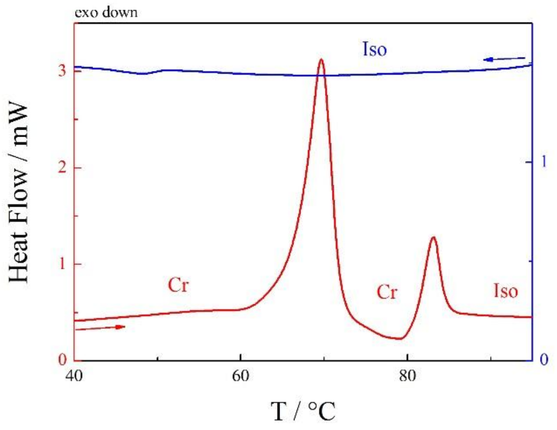


Figure S10. DSC thermograms for compound **VI.5**

XRD measurements

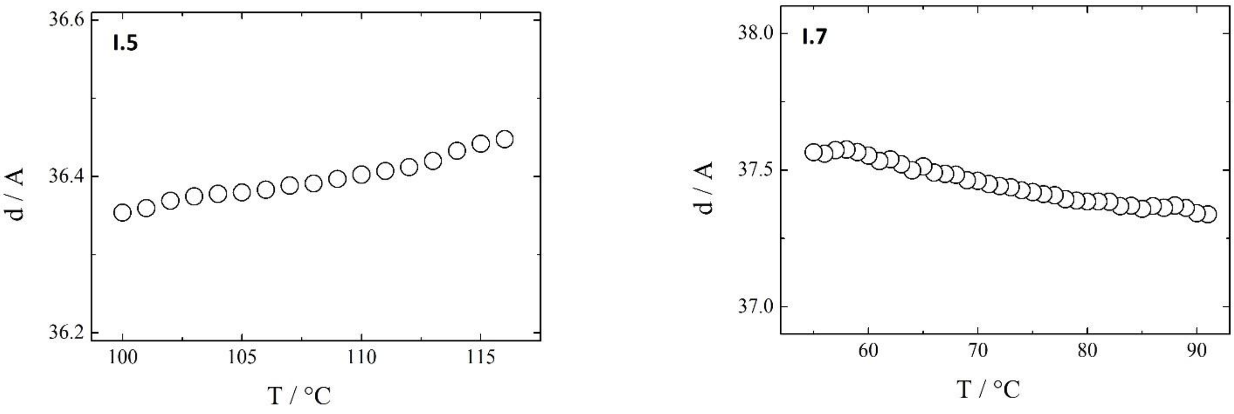


Figure S11. Smectic layer thickness measured as a function of temperature for homologues of **Series I** forming SmA phase.

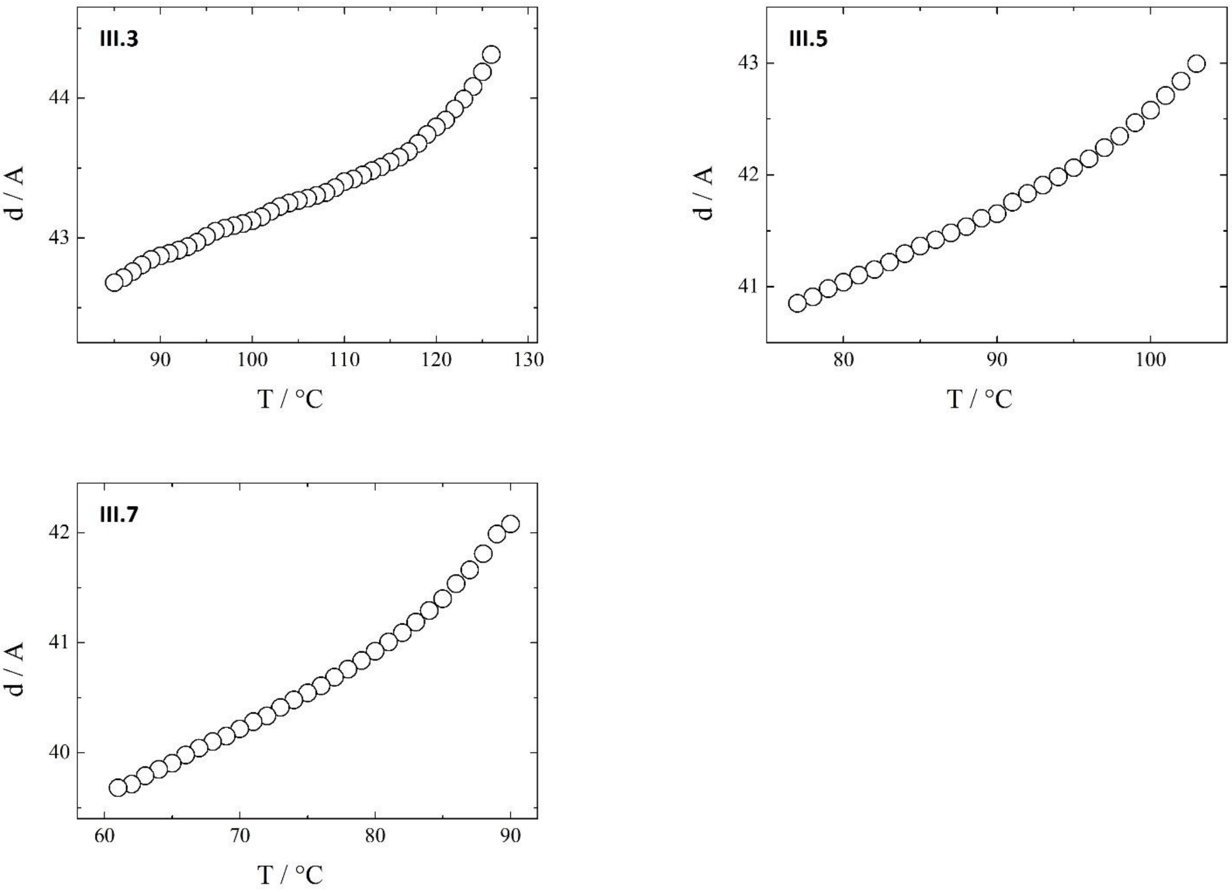


Figure S12. Smectic layer thickness measured as a function of temperature for homologues of **Series III**

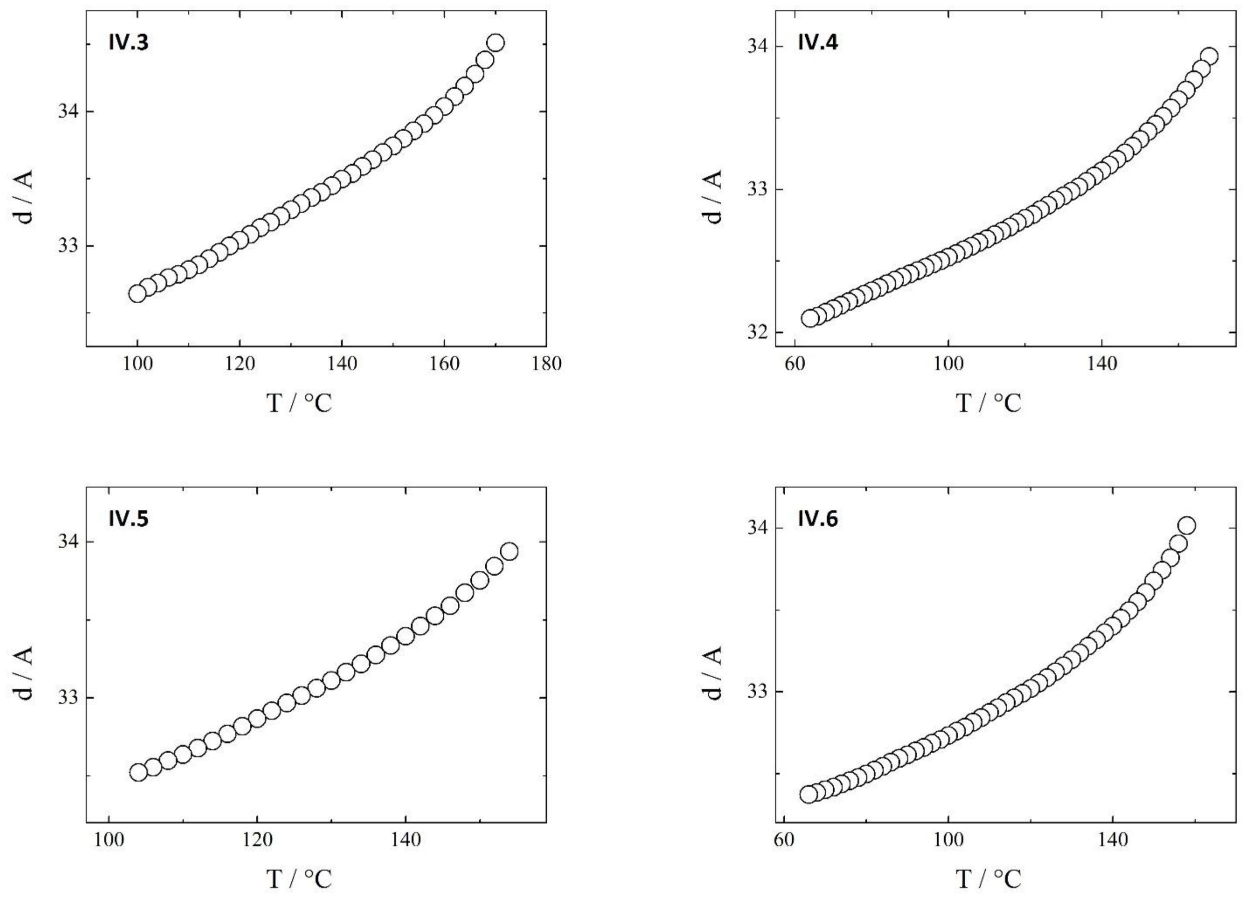


Figure S13. Smectic layer thickness measured as a function of temperature for consecutive homologues of **Series IV** with odd an even number of carbon atoms in the linkage chain.

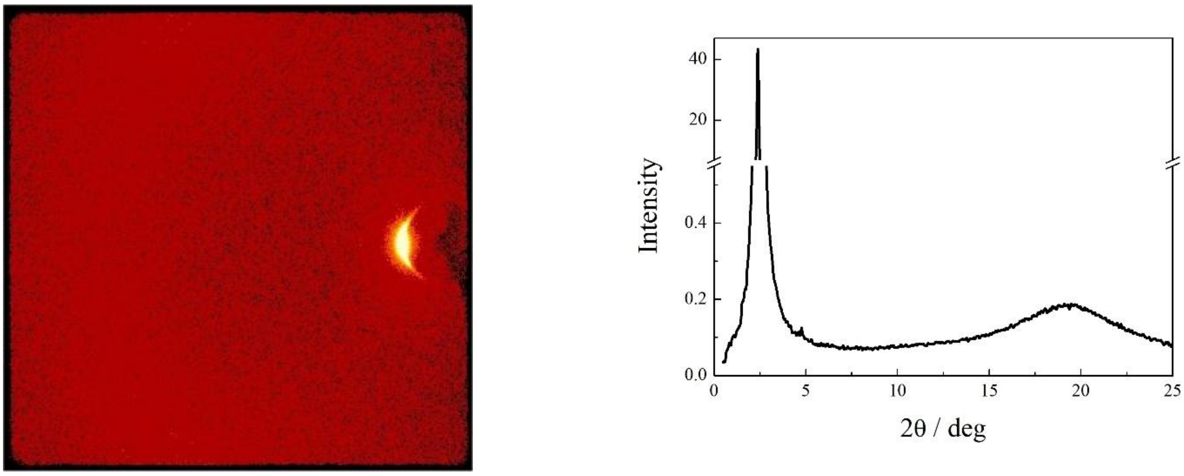


Figure S14. 2D wide angle xrd pattern (left) and corresponding plot of diffracted intensity vs. diffraction angle obtained by integration of the 2D pattern over azimuthal angle (right), for compound **V.5** in SmC phase.

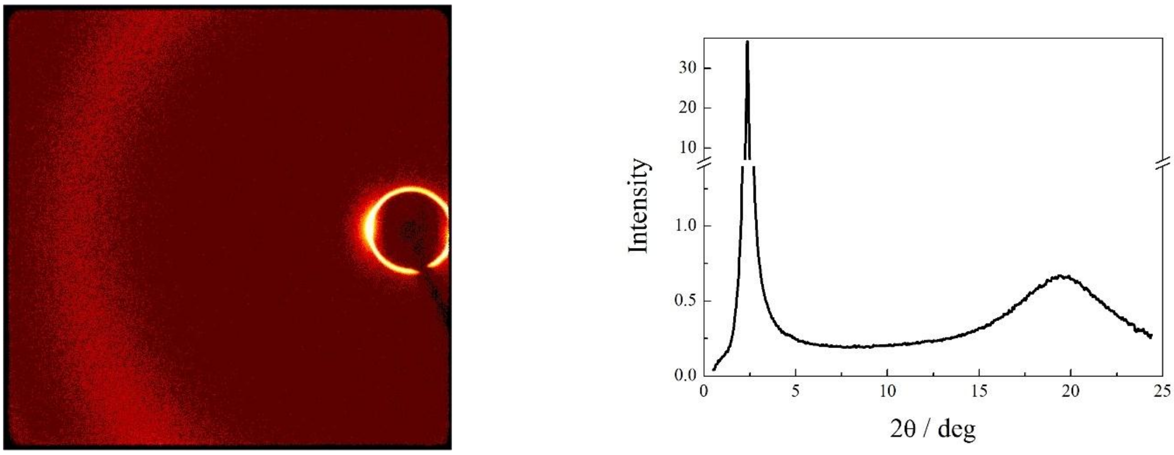
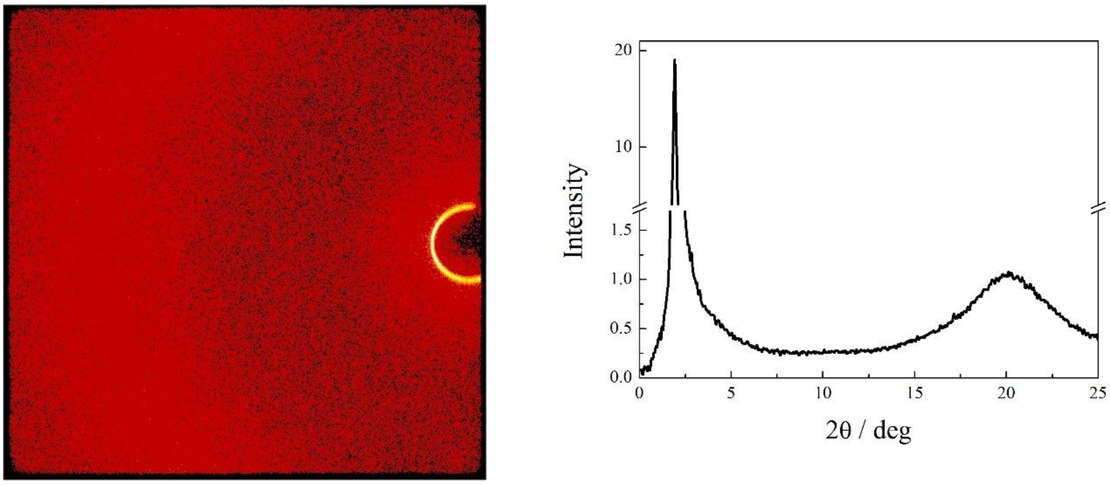
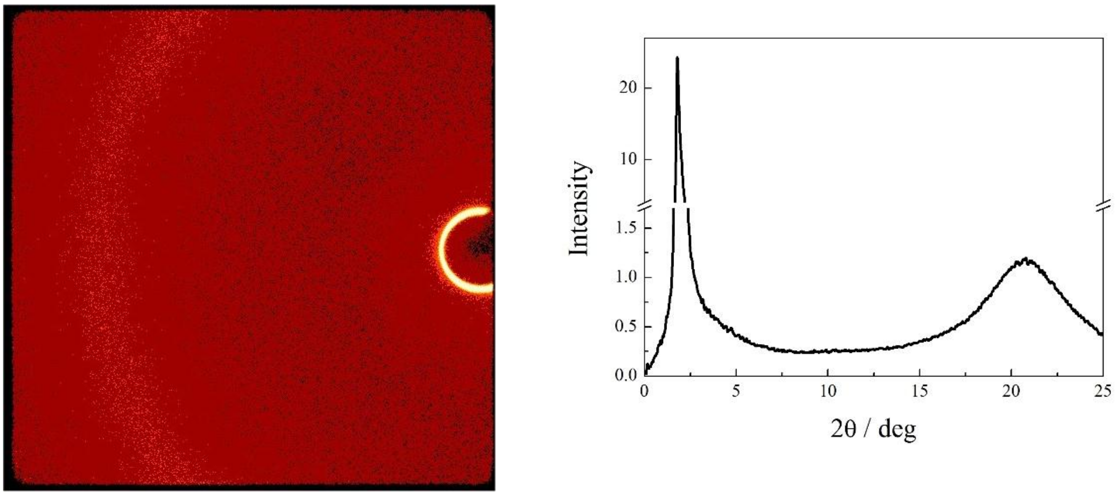


Figure S15. 2D wide angle xrd pattern (left) and corresponding plot of diffracted intensity vs. diffraction angle, obtained by integration of the 2D pattern over azimuthal angle (right), for compound **V.6** in SmC phase.



T = 60 °C, SmA



T = 35 °C, SmC

Figure S16. 2D wide angle xrd patterns (left) and corresponding plot of diffracted intensity vs. diffraction angle, obtained by integration of the 2D pattern over azimuthal angle (right), for compound **VI.9** in SmA phase (T = 60 °C) and SmC phase (T = 35 °C).

UV – Vis measurements

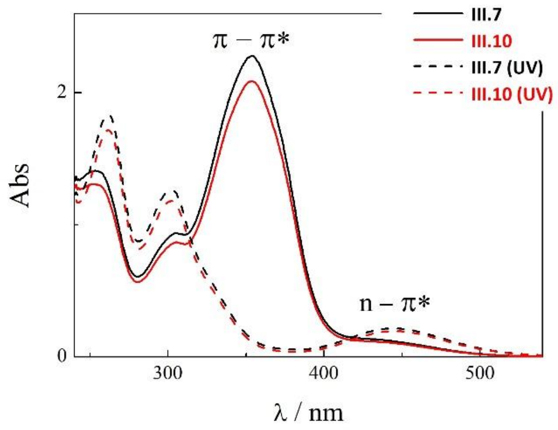


Figure S17. UV – Vis absorption spectra for solutions of Azo compounds **III.7** (black) and **III.10** (red) in CHCl3, (4 x 10^{-5} mol/dm^3). Solid lines show the absorption of trans form and dashed lines - cis form obtained by irradiation of the samples with UV light (365 nm).

Notes and references

1 M. Kolpaczynska, K. Madrak, D. Pociecha, J. Mieczkowski, and E. Gorecka, *Liquid Crystals*, 2011, **38**, 149
2 M. Wojcik, M. Kolpaczynska, D. Pociecha, J. Mieczkowski, and E. Gorecka, *Soft Matter*, 2010, **6**, 5397