Supporting Information

The transition between triangular and square tiling patterns in liquid crystalline honeycombs formed by tetrathiophene-based bolaamphiphiles

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1. Synthesis

1.1 General

For the structures of the compounds see Scheme 1 in the main text. Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 °C). Tetrahydrofuran (THF) was distilled from sodium prior to use. Commercially available chemicals were used as received. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker-DRX-500 spectrometer. HRMS were performed on an Agilent LC/Msd TOF instrument. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. Thin-layer chromatography was performed on aluminum plates precoated with 5735 silica gel 60 PF254 (Merck). Column chromatography was performed on Merck silica gel 60 (230-400 mesh).

1.2 3-Alkylthiophenes 4/*n*

Compounds **4/6**[S1,S2], **4/8,** and **4/12**[S3] were previously reported. All 3-alkylthiophenes except 3-octadecylthiophene[S3] are commercially available from Aldrich company or could be prepared by a modified literature procedure of Kumada outlined by Zimmer *et al*.[S3,S4]

3-Pentylthiophene (4/5) yield: 75%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.19-7.18 (m, 1 H, Ar**H**), 6.90-6.87 (m, 2 H, 2 Ar**H**), 2.61-2.58 (t, J = 7.7, 2 **H**, ArC**H**$_2$), 1.62-1.59 (m, 2 H, ArCH$_2$C**H**$_2$), 1.31-1.24 (m, 4 H, 2 C**H**$_2$), 0.89-0.87 (t, J = 6.5, 3 H, C**H**$_3$).

3-Hexylthiophene (4/6) yield: 75%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.26-7.25 (m, 1 H, Ar**H**), 6.97-6.94 (m, 2 H, 2 Ar**H**), 2.67-2.64 (t, J = 7.7, 2 **H**, ArC**H**$_2$), 1.67-1.63 (m, 2 H, ArCH$_2$C**H**$_2$), 1.34-1.25 (m, 6 H, 3 C**H**$_2$), 0.90-0.83 (m, 3 H, C**H**$_3$).

3-Heptylthiophene (4/7) yield: 75%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.24-7.20 (m, 1 H, Ar**H**), 6.92-6.89 (m, 2 H, 2 Ar**H**), 2.62-2.59 (t, J = 7.7, 2 H, ArC**H**$_2$), 1.62-1.58 (m, 2 H, ArCH$_2$C**H**$_2$), 1.31-1.26 (m, 8 H, 4 C**H**$_2$), 0.89-0.87 (t, J = 6.6, 3 H, C**H**$_3$).

3-Octylthiophene (4/8) yield: 76%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.26-7.25 (m, 1 H, Ar**H**), 6.97-6.94 (m, 2 H, 2 Ar**H**), 2.67-2.64 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.68-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.34-1.30 (m, 10 H, 5 C**H**$_2$), 0.93-0.90 (t, J = 6.7, 3 H, C**H**$_3$).

3-Nonylthiophene (4/9) yield: 75%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ =

7.22 (m, 1 H, Ar**H**), 6.93-6.90 (m, 2 H, 2 Ar**H**), 2.63-2.60 (t, *J* = 7.6, 2 H, ArC**H**$_2$), 1.62-1.60 (m, 2 H, ArCH$_2$C**H**$_2$), 1.31-1.26 (m, 12 H, 6 C**H**$_2$), 0.89-0.87 (t, *J* = 6.4, 3 H, C**H**$_3$).

3-Decylthiophene (4/10) yield: 75%; colorless liquid. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.21-7.19 (m, 1 H, Ar**H**), 6.92-6.89 (m, 2 H, 2 Ar**H**), 2.62-2.59 (t, *J* = 7.6, 2 H, ArC**H**$_2$), 1.62-1.59 (m, 2 H, ArCH$_2$C**H**$_2$), 1.30-1.26 (m, 14 H, 7 C**H**$_2$), 0.89-0.87 (t, *J* = 6.6, 3 H, C**H**$_3$).

3-Undecylthiophene (4/11) yield: 77%; colorless liquid.^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.22-7.19 (m, 1 H, Ar**H**), 6.91-6.88 (m, 2 H, 2 Ar**H**), 2.61-2.59 (t, *J* = 7.6, 2 H, ArC**H**$_2$), 1.61-1.58 (m, 2 H, ArCH$_2$C**H**$_2$), 1.30 (m, 16 H, 8 C**H**$_2$), 0.89-0.87 (t, *J* = 6.6, 3 H, C**H**$_3$).

3-Dodecylthiophene (4/12) yield: 82%; colorless liquid. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.24-7.21 (m, 1 H, Ar**H**), 6.93-6.90 (m, 2 H, 2 Ar**H**), 2.63-2.60 (t, *J* = 7.6, 2 H, ArC**H**$_2$), 1.64-1.54 (m, 2 H, ArCH$_2$C**H**$_2$), 1.31-1.26 (m, 18 H, 9 C**H**$_2$), 0.89-0.87 (t, *J* = 6.6, 3 H, C**H**$_3$).

3-Tridecylthiophene (4/13) yield: 78%; colorless liquid. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.24-7.23 (m, 1 H, Ar**H**), 6.92-6.89 (m, 2 H, 2 Ar**H**), 2.62-2.59 (t, *J* = 7.5, 2 H, ArC**H**$_2$), 1.63-1.56 (m, 2 H, ArCH$_2$C**H**$_2$), 1.31-1.25 (m, 20 H, 10 C**H**$_2$), 0.89-0.87 (t, *J* = 6.6, 3 H, C**H**$_3$).

3-Tetradecylthiophene (4/14) yield: 80%; colorless liquid. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.22-7.20 (m, 1 H, Ar**H**), 6.91-6.88 (m, 2 H, 2 Ar**H**), 2.60-2.58 (t, *J* = 7.6, 2 H, ArC**H**$_2$), 1.64 (m, 2 H, ArCH$_2$C**H**$_2$), 1.32-1.25 (m, 22 H, 11 C**H**$_2$), 0.89-0.87 (t, *J* = 6.6, 3 H, C**H**$_3$).

3-Hexadecylthiophene (4/16) yield: 70%; colorless liquid. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.27-7.22 (m, 1 H, **ArH**), 6.93-6.90 (m, 2 H, 2 Ar**H**), 2.62-2.59 (t, *J* = 7.7, 2 H, ArC**H**$_2$), 1.61-1.50 (m, 2 H, ArCH$_2$C**H**$_2$), 1.30-1.26 (m, 26 H, 13 C**H**$_2$), 0.89-0.80 (m, 3 H, C**H**$_3$).

3-Octadecylthiophene (4/18) yield: 75%; yellow wax. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.27-7.21 (m, 1 H, Ar**H**), 6.93-6.90 (m, 2 H, 2 Ar**H)**, 2.63-2.60 (t, 2 H, ArC**H**$_2$), 1.62-1.50 (m, 2 H, ArCH$_2$C**H**$_2$), 1.31-1.26 (m, 30 H, 15 C**H**$_2$), 0.89-0.79 (t, *J* = 6.6, 3 H, C**H**$_3$).

1.3 3-Alkyl-2-bromothiophenes 5/*n*

The synthesis of compounds **5/*n*** was carried out as described in ref.[S5]; compounds **5/6, 5/10, 5/12** and **5/18**[S6] have been reported by us; compound **5/6** is also commercially

available from Aldrich company.

2-Bromo-3-pentylthiophene (5/5) yield: 95%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.18-7.17 (d, J = 5.5, 1 H, Ar**H**), 6.80-6.78 (d, J = 5.7, 1 H, Ar**H**), 2.57-2.54 (t, J =7.6, 2 H, ArC**H**$_2$), 1.60-1.52 (m, 2 H, ArCH$_2$C**H**$_2$), 1.36-1.32 (m, 6 H, 3 C**H**$_2$), 0.91-0.88 (t, J = 6.7, 3 H, C**H**$_3$).

2-Bromo-3-hexylthiophene (5/6) yield: 95%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.18-7.17 (d, J = 5.6, 1 H, Ar**H**), 6.79-6.77 (d, J = 5.6, 1 H, Ar**H**), 2.56- 2.54 (t, J =7.7, 2 H, ArC**H**$_2$), 1.60-1.53 (m, 2 H, ArCH$_2$C**H**$_2$), 1.36-1.31 (m, 6 H, 3 C**H**$_2$), 0.90-0.87 (t, J = 6.5, 3 H, C**H**$_3$).

2-Bromo-3-heptylthiophene (5/7) yield: 90%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.19-7.18 (d, J = 5.6, 1 H, Ar**H**), 6.80-6.78 (d, J = 5.6, 1 H, Ar**H**), 2.58-2.56 (t, J =7.5, 2 H, ArC**H**$_2$), 1.59-1.55 (m, 2 H, ArCH$_2$C**H**$_2$), 1.32-1.27 (m, 8 H, 4 C**H**$_2$), 0.90-0.87 (t, J = 6.6, 3 H, C**H**$_3$).

2-Bromo-3-octylthiophene (5/8) yield: 90%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.19-7.18 (d, J = 5.5, 1 H, Ar**H**), 6.80-6.78 (d, J = 5.5, 1 H, Ar**H**), 2.58- 2.56 (t, J =7.6, 2 H, ArC**H**$_2$), 1.58-1.55 (m, 2 H, ArCH$_2$C**H**$_2$), 1.31-1.27 (m, 10 H, 5 C**H**$_2$), 0.89-0.87 (m, 3 H, C**H**$_3$).

2-Bromo-3-nonylthiophene (5/9) yield: 89%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.18-7.17 (d, J = 5.5, 1 H, Ar**H**), 6.80-6.79 (d, J = 5.6, 1 H, Ar**H**), 2.59-2.57 (t, J =7.6, 2 H, ArC**H**$_2$), 1.59-1.55 (m, 2 H, ArCH$_2$C**H**$_2$), 1.32-1.25 (m, 12 H, 6 C**H**$_2$), 0.90-0.87 (m, 3 H, C**H**$_3$)

2-Bromo-3-decylthiophene (5/10) yield: 91%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.26-7.25 (d, J = 5.6, 1 H, Ar**H**), 6.98-6.97 (d, J = 5.6, 1 H, Ar**H**), 2.61-2.59 (t, J = 7.7, 2 H, ArC**H**$_2$), 1.62-1.58 (m, 2 H, ArCH$_2$C**H**$_2$), 1.34-1.30 (m, 14 H, 7 C**H**$_2$), 0.88-0.86 (t, J = 6.7, 3 H, C**H**$_3$).

2-Bromo-3-undecylthiophene (5/11) yield: 92%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.25-7.24 (d, J = 5.6, 1 H, Ar**H**), 6.97-6.96 (d, J = 5.5, 1 H, Ar**H**), 2.60-2.58 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.60-1.56 (m, 2 H, ArCH$_2$C**H**$_2$), 1.36-1.27 (m, 16 H, 8 C**H**$_2$), 0.87-0.85(t, J = 6.7, 3 H, C**H**$_3$).

2-Bromo-3-dodecylthiophene (5/12) yield: 91%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.19-7.18 (d, J = 5.6, 1 H, Ar**H**), 6.80-6.79 (d, J = 5.6, 1 H, Ar**H**), 2.57 -2.55 (t. J =7.8, 2 H, ArC**H**$_2$), 1.58-1.53 (m, 2 H, ArCH$_2$C**H**$_2$), 1.31-1.25 (m,18 H, 9 C**H**$_2$), 0.89-0.87 (t, J = 7.1, 3 H, C**H**$_3$).

2-Bromo-3-tridecylthiophene (5/13) yield: 89%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.18-7.17 (d, J = 5.6, 1 H, Ar**H**), 6.80-6.79 (d, J = 5.6, 1 H, Ar**H**), 2.58 -2.55 (t. J =7.5, 2 H, ArC**H**$_2$), 1.60-1.53 (m, 2 H, ArCH$_2$C**H**$_2$), 1.32-1.28 (m, 20 H, 10 C**H**$_2$), 0.91-0.88 (t, J = 6.7, 3 H, C**H**$_3$).

2-Bromo-3-tetradecylthiophene (5/14) yield: 90%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.19-7.18 (d, J = 5.6, 1 H, Ar**H**), 6.80-6.79 (d, J = 5.6, 1 H, Ar**H**), 2.66-2.64 (t, J = 8.0, 2 H, ArC**H**$_2$), 1.64-1.62 (m, 2H, ArCH$_2$C**H**$_2$), 1.33-1.28 (m, 22H, 11C**H**$_2$), 0.91-0.89 (t, J = 5.8, 3 H, C**H**$_3$).

2-Bromo-3-hexadecylthiophene (5/16) yield: 91%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.18-7.17 (d, J = 5.5, 1 H, Ar**H**), 6.79-6.78 (d, J = 5.4, 1 H, Ar**H**), 2.56-2.54 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.57-1.54 (m, 2 H, ArCH$_2$C**H**$_2$), 1.32-1.25 (m, 26 H, 13 C**H**$_2$), 0.89-0.87 (t, J = 6.6, 3 H, C**H**$_3$).

2-Bromo-3-octadecylthiophene (5/18) yield: 91%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.19-7.18 (d, J = 5.4, 1 H, Ar**H**), 6.79-6.78 (d, J = 5.4, 1 H, Ar**H**), 2.56-2.54 (t. J = 7.6, 2 H, ArC**H**$_2$), 1.56-1.54 (m, 2 H, ArCH$_2$C**H**$_2$), 1.30-1.25 (m, 30 H, 15 C**H**$_2$), 0.89-0.87 (t, J = 6.5, 3 H, C**H**$_3$).

1.4 2-Bromo-5-(4-methoxyphenyl)thiophene (8)

A mixture of the 2,5-dibromo-thiophene (**7**) (13.3 g, 55.0 mmol), (4-methoxyphenyl)boronic acid (8.2 g, 54.0 mmol), Pd(PPh$_3$)$_4$ (15 mg), ethyleneglycol dimethyl ether (8 mL), and K_2CO_3 solution (2 M, 8 mL) was refluxed for 6 h under an argon atmosphere. After staying overnight at RT, the reaction mixture was extracted with $CHCl_3$ (3×50 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by column chromatography (petroleum ether);.yield: 64%; white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.43 (d, J = 8.8, 2 H, 2 Ar**H**), 6.99-6.98 (d, J = 3.9, 1 H, Ar**H**), 6.94-6.93 (d, J = 3.8, 1 H, Ar**H**), 6.90-6.89 (d, J = 8.8, 2 H, 2 Ar**H**), 3.83 (s, 3 H, OC**H**$_3$).

1.5 3-Alkyl-5'-(4-methoxyphenyl)-2,2'-bithiophenes 9/*n*

Compounds **9/*n*** were prepared by a modified procedure of Kumada outlined by Zimmer *et al*.[S2] Accordingly, the appropriate 3-alkyl-2-bromothiophene (**5/*n***) (32.0 mmol) was dissolved in dry THF (20 mL). Magnesium turnings (960 mg, 40.0 mmol) were covered by such THF solution of **5/*n***. After the reaction had started, the remaining **5/*n*** solution was added dropwise, maintaining the Grignard solution under reflux. Stirring was continued under reflux for 1 h, and then the mixture was cooled to RT, and added

dropwise to a mixture of 2-bromo-5-(4-methoxyphenyl)thiophene (**8**) (8.6 g, 32.0 mmol) and Ni(dppp)Cl_2 (120 mg) in THF (35 mL) at 0°C, maintaining the temperature of the solution below 5°C. Stirring of the mixture was continued for additional 15 h under reflux, and the reaction mixture was cooled to RT, quenched with crushed ice (50 g), and HCl (2 M) was added until the precipitate was dissolved. Diethyl ether (100 mL) was added, the diethyl ether layer was separated and the aqueous layer was extracted with diethyl ether (3×100 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by column chromatography (eluent: petroleum ether).

5'-(4-Methoxyphenyl)-3-pentyl-2,2'-bithiophene (9/5) yield: 74%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.53 (d, J = 8.0, 2 H, 2 Ar**H**), 7.16-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 2.1, 1 H, Ar**H**), 6.93-6.91 (m, 3 H, 3 Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.79-2.76 (t, J = 7.7, 2 H, ArC**H**$_2$), 1.66-1.63 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.35 (m, 4 H, 2 C**H**$_2$), 0.88-0.86 (t, J = 6.5, 3 H, C**H**$_3$).

3-Hexyl-5'-(4-methoxyphenyl)-2,2'-bithiophene (9/6) yield: 77%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.52-7.50 (d, J = 7.7, 2 H, 2 Ar**H**), 7.14-7.12 (m, 2 H, 2 Ar**H**), 7.02-7.01 (d, J = 2.6, 1 H, Ar**H**), 6.91-6.89 (m, 3 H, 3 Ar**H**), 3.81 (s, 3 H, OC**H**$_3$), 2.77-2.74 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.65-1.59 (m, 2 H, ArCH$_2$C**H**$_2$), 1.35-1.22 (m, 6 H, 3 C**H**$_2$), 0.86-0.84 (t, J = 6.5, 3 H, C**H**$_3$).

3-Heptyl-5'-(4-methoxyphenyl)-2,2'-bithiophene (9/7) yield: 72%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.7, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.06-7.05 (d, J = 3.8, 1 H, Ar**H**), 6.95-6.90 (m, 3 H, 3 Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.80-2.77 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.68-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.38-1.26 (m, 8 H, 4 C**H**$_2$), 0.89-0.86 (t, J = 6.8, 3 H, C**H**$_3$).

5'-(4-Methoxyphenyl)-3-octyl-2,2'-bithiophene (9/8) yield: 74%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.7, 2 H, 2 Ar**H**), 7.16-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.4, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.80-2.77 (t, J = 7.7, 2 H, ArC**H**$_2$), 1.68-1.64 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.26 (m, 10 H, 5 C**H**$_2$), 0.89-0.86 (t, J = 6.8, 3 H, C**H**$_3$).

5'-(4-Methoxyphenyl)-3-nonyl-2,2'-bithiophene (9/9) yield: 79%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.53 (d, J = 8.6, 2 H, 2 Ar**H**), 7.16-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.91 (m, 3 H, 3 Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.79-2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.68-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.25 (m, 12 H, 6 C**H**$_2$), 0.88-0.86 (t, 3 H, C**H**$_3$).

3-Decyl-5'-(4-methoxyphenyl)-2,2'-bithiophene (9/10) yield: 71%; yellow liquid. ^{1}H

NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.8, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.8, 1 H, Ar**H**), 6.94-6.91 (m, 3 H, 3 Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.79-2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.68-1.62 (m, 2 H, $ArCH_2C$**H**$_2$), 1.37-1.25 (m, 14 H, 7 C**H**$_2$), 0.89-0.86 (t, J = 6.9, 3 H, C**H**$_3$).

5'-(4-Methoxyphenyl)-3-undecyl-2,2'-bithiophene (9/11) yield: 72%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.53-7.52 (d, J = 7.3, 2 H, 2 Ar**H**), 7.13-7.12 (m, 2 H, 2 Ar**H**), 7.04-7.03 (m, 1 H, Ar**H**), 6.92-6.90 (m, 3 H, 3 Ar**H**), 3.83 (s, 3 H, OC**H**$_3$), 2.78-2.75 (m, 2 H, ArC**H**$_2$), 1.71-1.64 (m, 2 H, $ArCH_2C$**H**$_2$), 1.37-1.25 (m, 16 H, 8 C**H**$_2$), 0.88-0.86 (m, 3 H, C**H**$_3$).

3-Dodecyl-5'-(4-methoxyphenyl)-2,2'-bithiophene (9/12) yield: 79%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.58-7.56 (d, J = 8.5, 2 H, 2 Ar**H**), 7.20-7.17 (m, 2 H, 2 Ar**H**), 7.08-7.07 (m, 1 H, Ar**H**), 6.97-6.95 (m, 3 H, 3 Ar**H**), 3.87 (s, 3 H, OC**H**$_3$), 2.83-2.80 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.70-1.65 (m, 2 H, $ArCH_2C$**H**$_2$), 1.40-1.28 (m, 18 H, 9 C**H**$_2$), 0.92-0.90 (t, J = 6.8, 3 H, C**H**$_3$).

5'-(4-Methoxyphenyl)-3-tridecyl-2,2'-bithiophene (9/13) yield:78%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.8, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.06-7.05 (d, J = 3.5, 1 H, Ar**H**), 6.95-6.92 (m, 3 H, 3 Ar**H**), 3.85 (s, 3 H, OC**H**$_3$), 2.79-2.76 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.68-1.57 (m, 2 H, $ArCH_2C$**H**$_2$), 1.40-1.28 (m, 20 H, 10 C**H**$_2$), 0.89-0.86 (t, J = 6.9, 3 H, C**H**$_3$).

5'-(4-Methoxyphenyl)-3-tetradecyl-2,2'-bithiophene (9/14) yield:95%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.33-7.32 (d, J = 8.6, 2 H, 2 Ar**H**), 6.95-6.93 (m, 2 H, 2 Ar**H**), 6.84-6.83 (d, J = 3.7, 1 H, Ar**H**), 6.73-6.70 (m, 3 H, 3 Ar**H**), 3.63 (s, 3 H, OC**H**$_3$), 2.58-2.55 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.45-1.41 (m, 2 H, $ArCH_2C$**H**$_2$), 1.16-1.03 (m, 22 H, 11 C**H**$_2$), 0.68-0.65 (t, J = 6.5, 3 H, C**H**$_3$).

3-Hexadecyl-5'-(4-methoxyphenyl)-2,2'-bithiophene (9/16) yield:79%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57-7.56 (d, J = 8.5, 2 H, 2 Ar**H**), 7.19-7.17 (m, 2 H, 2 Ar**H**), 7.07-7.06 (d, J = 3.5, 1 H, Ar**H**), 6.97-6.94 (m, 3 H, 3 Ar**H**), 3.87 (s, 3 H, OC**H**$_3$), 2.81-2.79 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.69-1.65 (m, 2 H, $ArCH_2C$**H**$_2$), 1.39-1.28 (m, 26 H, 13 C**H**$_2$), 0.91-0.89 (t, J = 6.5, 3 H, **CH**$_3$).

5'-(4-Methoxyphenyl)-3-octadecyl-2,2'-bithiophene (9/18) yield: 78%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56-7.55 (d, J = 8.6, 2 H, 2 Ar**H**), 7.18-7.17 (m, 2 H, 2 Ar**H**), 7.06-7.04 (d, J = 3.5, 1 H, Ar**H**), 6.96-6.94 (m , 3 H, 3 Ar**H**), 3.86 (s, 3 H, OC**H**$_3$), 2.80-2.79 (t, J = 7.7, 2 H, ArC**H**$_2$), 1.69-1.65 (m, 2 H, $ArCH_2C$**H**$_2$), 1.40 -1.28 (m, 30 H, 15 C**H**$_2$), 0.91-0.89 (t, J = 6.7, 3 H, C**H**$_3$).

1.6 3-Alkyl-5'-(4-allyloxyphenyl)-2,2'-bithiophenes 11/*n*

4-[3'-Alkyl-(2,2'-bithiophen)-5-yl]phenols 10/*n*: The appropriate bithiophene **9/*n*** (1.0 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled to -78°C, BBr_3 (0.11 mL, 1.1 mmol) was added and the solution was stirred at RT overnight. Water (10 mL) was carefully added, the mixture was extracted by $CHCl_3$ (3×15 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by column chromatography (eluent: petroleum ether / ethyl acetate V / V = 7 / 1). The obtained product was used directly for the next step.

3-Alkyl-5'-(4-allyloxyphenyl)-2,2'-bithiophenes 11/*n*: Allyl bromide (0.18 g, 1.5 mmol) was added to a mixture of **10/*n*** (1.0 mmol) and K_2CO_3 (0.41 g, 3.0 mmol) in dry CH_3CN (10 mL) under an argon atmosphere. The mixture was refluxed for 2 h and then CH_3CN was evaporated in vacuo. Water and ethyl acetate were added to the residue. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×10 mL), the combined extracts were washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo. The crude product was purified by chromatography (eluent: petroleum ether).

5'-(4-Allyloxyphenyl)-3-pentyl-2,2'-bithiophene (11/5) yield: 75%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.6, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.6, 1 H, Ar**H**), 6.95-6.93 (m, 3 H, 3 Ar**H**), 6.08-6.06 (m, 1 H, C**H**=), 5.46-5.42 (d, J = 17.2, 1 H, C$\mathbf{H}_2$=), 5.33-5.31 (d, J = 10.5, 1 H, C$\mathbf{H}_2$=), 4.58-4.57 (d, J = 5.1, 2 H, ArOC$\mathbf{H}_2$), 2.79-2.76 (t, J = 7.8, 2 H, ArC$\mathbf{H}_2$), 1.66-1.61 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.37-1.25 (m, 4 H, 2 C$\mathbf{H}_2$), 0.89-0.86 (t, J = 6.8, 3 H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-hexyl-2,2'-bithiophene (11/6) yield: 71%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.6, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.95-6.93 (m, 3 H, 3 Ar**H**), 6.10-6.05 (m, 1 H, C**H**=), 5.45-5.42 (d, J = 17.3, 1 H, C$\mathbf{H}_2$=), 5.32-5.30 (d, J = 10.5, 1 H, C$\mathbf{H}_2$=), 4.58-4.57 (m, 2 H, ArOC$\mathbf{H}_2$), 2.80-2.77 (t, J = 7.8, 2 H, ArC$\mathbf{H}_2$), 1.66-1.62 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.37-1.26 (m, 6 H, 3 C$\mathbf{H}_2$), 0.88 (m, 3 H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-heptyl-2,2'-bithiophene (11/7) yield: 81%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.53-7.52 (d, J = 8.9, 2 H, 2 Ar**H**), 7.16-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 6.10-6.03 (m, 1 H, C**H**=), 5.45-5.41(d, J = 17.3, 1 H, C$\mathbf{H}_2$=), 5.32-5.29 (d, J = 10.6, 1 H, C$\mathbf{H}_2$=), 4.57-4.56 (d, J = 5.1, 2 H, ArOC$\mathbf{H}_2$), 2.79-2.76 (t, J = 7.8, 2 H, ArC$\mathbf{H}_2$), 1.68-1.62 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.36-1.23 (m, 8 H, 4 C$\mathbf{H}_2$), 0.89-0.86 (t, J = 6.8, 3 H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-octyl-2,2'-bithiophene (11/8) yield: 74%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.7, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 6.09-6.04 (m, 1 H, C**H**=), 5.45-5.42 (d, J = 17.3, 1 H, C$\mathbf{H}_2$=), 5.32-5.30 (d, J = 10.5, 1 H, C$\mathbf{H}_2$=), 4.58-4.57 (d, J = 5.1, 2 H, ArOC$\mathbf{H}_2$), 2.79-2.76 (t, J = 7.8, 2 H, ArC$\mathbf{H}_2$), 1.66-1.62 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.37-1.25 (m, 10 H, 5 C$\mathbf{H}_2$), 0.88-0.86 (t, J = 6.7, 3H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-nonyl-2,2'-bithiophene (11/9) yield: 71%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.7, 2 H, 2 Ar**H**), 7.16-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 6.09-6.04 (m, 1 H, C**H**=), 5.45-5.42 (d, J = 17.3, 1 H, C$\mathbf{H}_2$=), 5.32-5.30 (d, J = 10.6, 1 H, C$\mathbf{H}_2$=), 4.58-4.57 (d, J = 5.1, 2 H, ArOC$\mathbf{H}_2$), 2.79-2.76 (t, J = 7.8, 2 H, ArC$\mathbf{H}_2$), 1.66-1.62 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.37-1.25 (m, 12 H, 6 C$\mathbf{H}_2$), 0.88-0.86 (t, J = 6.7, 3 H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-decyl-2,2'-bithiophene (11/10) yield: 76%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.51 (d, J = 7.1, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 6.10-6.04 (m, 1 H, C**H**=), 5.45-5.42 (m, 1 H, C$\mathbf{H}_2$=), 5.32-5.30 (m, 1 H, C$\mathbf{H}_2$=), 4.58-4.56 (m, 2 H, ArOC$\mathbf{H}_2$), 2.79-2.76 (t, J = 7.8, 2 H, ArC$\mathbf{H}_2$), 1.67-1.61 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.38-1.24 (m, 14 H, 7 C$\mathbf{H}_2$), 0.89-0.86 (t, J = 6.9, 3 H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-undecyl-2,2'-bithiophene (11/11) yield: 70%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.7, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 6.10 -6.05 (m, 1 H, C**H**=), 5.46-5.42 (m, 1 H, C$\mathbf{H}_2$=), 5.32-5.30 (m, 1 H, C$\mathbf{H}_2$=), 4.58- 4.57(d, J = 5.2, 2 H, ArOC$\mathbf{H}_2$), 2.79-2.76 (t, J = 7.8, 2 H, ArC$\mathbf{H}_2$), 1.67-1.61 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.37-1.24 (m, 16 H, 8 C$\mathbf{H}_2$), 0.89-0.86 (t, J = 6.8, 3 H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-dodecyl-2,2'-bithiophene (11/12) yield: 71%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.53 (d, J = 8.5, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.4, 1 H, Ar**H**), 6.95-6.93 (m, 3 H, 3 Ar**H**), 6.10- 6.05 (m, 1 H, C**H**=), 5.46-5.42 (d, J = 17.2, 1 H, C$\mathbf{H}_2$=), 5.32-5.30 (d, J = 10.6, 1 H, C$\mathbf{H}_2$=), 4.58-4.57 (d, J = 5.2, 2 H, ArOC$\mathbf{H}_2$), 2.80-2.77 (t, J = 7.8, 2 H, ArC$\mathbf{H}_2$), 1.67 -1.62 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.37-1.26 (m, 18 H, 9 C$\mathbf{H}_2$), 0.90-0.87 (t, J = 6.8, 3 H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-tridecyl-2,2'-bithiophene (11/13) yield: 76%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.5, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.4, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 6.10-6.05 (m, 1 H, C**H**=), 5.45-5.42 (d, J = 17.3, 1 H, C$\mathbf{H}_2$=), 5.32-5.30 (d, J = 10.6, 1 H, C$\mathbf{H}_2$=), 4.58-4.57 (d, J = 4.8, 2 H, ArOC$\mathbf{H}_2$), 2.79-2.76 (t, J = 7.8, 2 H, ArC$\mathbf{H}_2$), 1.68-1.61 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.37-1.25 (m, 20 H, 10 C$\mathbf{H}_2$), 0.89-0.86 (t, J = 6.6, 3 H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-tetradecyl-2,2'-bithiophene (11/14) yield: 78%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.3, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.0, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 6.09- 6.05 (m, 1 H, C**H**=), 5.46-5.42 (d, J = 17.6, 1 H, C$\mathbf{H}_2$=), 5.33-5.31 (d, J = 10.4, 1 H, C$\mathbf{H}_2$=), 4.58-4.57 (d, J = 4.8, 2 H, ArOC$\mathbf{H}_2$), 2.79-2.76 (t, J = 7.9, 2 H, ArC$\mathbf{H}_2$), 1.65- 1.61 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.37-1.24 (m, 22 H, 11 C$\mathbf{H}_2$), 0.89-0.86 (t, J = 6.2, 3 H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-hexadecyl-2,2'-bithiophene (11/16) yield: 71%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.53-7.52 (d, J = 8.3, 2 H, 2 ArH), 7.16-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.3, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 6.10- 6.04 (m, 1 H, C**H**=), 5.45-5.42 (d, J = 17.1, 1 H, C$\mathbf{H}_2$=), 5.32-5.30 (d, J = 10.6, 1 H, C$\mathbf{H}_2$=), 4.57-4.56 (d, J = 4.5, 2 H, ArOC$\mathbf{H}_2$), 2.79-2.76 (t, J = 7.6, 2 H, ArC$\mathbf{H}_2$), 1.66- 1.62 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.37-1.25 (m, 26 H, 13 C$\mathbf{H}_2$), 0.89-0.86 (t, J = 6.2, 3 H, C$\mathbf{H}_3$).

5'-(4-Allyloxyphenyl)-3-octadecyl-2,2'-bithiophene (11/18) yield: 79%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.7, 2 H, 2 Ar**H**), 7.16-7.14 (m, 2 H, 2 Ar**H**), 7.06-7.05 (d, J = 3.5, 1 H, Ar**H**), 6.98-6.95 (m, 3 H, 3 Ar**H**), 6.11- 6.05 (m, 1 H, C**H**=), 5.46-5.45 (d, J = 17.5, 1 H, C$\mathbf{H}_2$=), 5.33-5.31 (d, J = 10.5, 1 H, C$\mathbf{H}_2$=), 4.58-4.57 (d, J = 4.5, 2 H, ArOC$\mathbf{H}_2$), 2.79-2.77 (t, J = 7.6, 2 H, ArC$\mathbf{H}_2$), 1.67-1.62 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.37-1.25 (m, 30 H, 15 C$\mathbf{H}_2$), 0.89-0.87 (t, J = 6.5, 3 H, C$\mathbf{H}_3$).

1.7 3-{4-[3'-Alkyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diols 12/*n*

11/*n* (0.7 mmol) and NMMNO (0.6 mL, 60% solution in water) were dissolved in acetone. Osmium tetroxide (0.7 mL, 0.004 M solution in *tert*-butanol) was added, and the solution was stirred for 24 h at RT. Afterwards, sat. aq. Na_2SO_3 (5 mL) was added, and the mixture was stirred for 30 min at RT. The mixture was filtered. Ethyl acetate (30 mL) and 10% H_2SO_4 (5 mL) were added into the liquid and the organic layer was separated, washed with sat. aq. $NaHCO_3$ (50 mL) and H_2O (50 mL), dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. Purification of the product was done by chromatography (eluent: petroleum ether / ethyl acetate V / V = 1 / 2).

3-{4-[3'-Pentyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/5) yield: 85%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.53-7.52 (d, J = 8.7, 2 H, 2 Ar**H**), 7.16-7.14 (m, 2 H, 2 Ar**H**), 7.04-7.03 (d, J = 3.6, 1 H, Ar**H**), 6.93-6.91 (m, 3 H, 3 Ar**H**), 4.13-3.75 (m, 5 H, ArOC$\mathbf{H}_2$, C**H**OH, C$\mathbf{H}_2$OH), 2.77-2.74 (t, J = 7.8, 2 H, ArC$\mathbf{H}_2$), 1.67-1.62 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.32-1.25 (m, 4 H, 2 C$\mathbf{H}_2$), 0.88-0.86 (t, J = 6.5, 3 H, C$\mathbf{H}_3$).

3-{4-[3'-Hexyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/6) yield: 71%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.54 (d, J = 8.3, 2 H, 2 Ar**H**), 7.18-7.16 (m, 2 H, 2 Ar**H**), 7.06-7.05 (d, J = 3.1, 1 H, Ar**H**), 6.95-6.94 (m, 3 H, 3 Ar**H**), 4.15-3.75 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.80-2.77 (t, J = 7.7, 2 H, ArC**H**$_2$), 1.65-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.40-1.26 (m, 6 H, 3 C**H**$_2$), 0.95-0.93 (t, J = 6.6, 3 H, C**H**$_3$).

3-{4-[3'-Heptyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/7) yield: 71%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56-7.54 (d, J = 8.6, 2 H, 2 Ar**H**), 7.18-7.16 (m, 2 H, 2 Ar**H**), 7.06-7.05 (d, J = 3.6, 1 H, Ar**H**), 6.95-6.93 (m, 3 H, 3 Ar**H**), 4.15-3.80 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.80-2.77 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.65-1.59 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.26 (m, 8 H, 4 C**H**$_2$), 0.89-0.87 (t, J = 6.9, 3 H, C**H**$_3$)

3-{4-[3'-Octyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/8) yield: 77%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 6.7, 2 H, 2 Ar**H**), 7.16-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.5, 1 H, Ar**H**), 6.95-6.93 (m, 3 H, 3 Ar**H**), 4.14-3.78 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.78-2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.66-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.25 (m, 10 H, 5 C**H**$_2$), 0.89-0.87 (t, J = 6.6, 3 H, C**H**$_3$).

3-{4-[3'-Nonyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/9) yield: 81%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.54 (d, J = 8.7, 2 H, 2 Ar**H**), 7.18-7.16 (m, 2 H, 2 Ar**H**), 7.06-7.05 (d, J = 3.7, 1 H, Ar**H**), 6.95-6.93 (m, 3 H, 3 Ar**H**), 4.15-3.79 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.80-2.76 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.66-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.25 (m, 12 H, 6 C**H**$_2$), 0.89-0.86 (t, J = 6.9, 3 H, C**H**$_3$).

3-{4-[3'-Decyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/10) yield: 69%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.7, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 4.14-3.77 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.79-2.76 (t, J = 7.9, 2 H, ArC**H**$_2$), 1.67-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.24 (m, 14 H, 7 C**H**$_2$), 0.89-0.86 (t, J = 6.9, 3 H, C**H**$_3$).

3-{4-[3'-Undecyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/11) yield: 71%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.8, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.8, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 4.14-3.77 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.79-2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.68-1.63 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.24 (m, 16 H, 8 C**H**$_2$), 0.89-0.86 (t, J = 6.8, 3 H, C**H**$_3$).

3-{4-[3'-Dodecyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/12) yield: 75%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.58-7.57 (d, J = 8.5, 2 H, 2 Ar**H**), 7.19-7.17 (m, 2 H, 2 Ar**H**), 7.07 (d, J = 3.5, 1 H, Ar**H**), 6.97-6.94 (m, 3 H, 3 Ar**H**), 4.16-3.79 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.79-2.77 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.67-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.32-1.25 (m, 18 H, 9 C**H**$_2$), 0.89-0.87 (t, J = 6.5, 3 H, C**H**$_3$).

3-{4-[3'-Tridecyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/13) yield: 71%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.54 (d, J = 8.7, 2 H, 2 Ar**H**), 7.19-7.17 (m, 2 H, 2 Ar**H**), 7.06-7.05 (d, J = 3.7, 1 H, Ar**H**), 6.97-6.94 (m, 3 H, 3 Ar**H**), 4.16-3.79 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.80-2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.66-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.32-1.25 (m, 20 H, 10 C**H**$_2$), 0.89-0.86 (t, J = 6.8, 3 H, C**H**$_3$).

3-{4-[3'-Tetradecyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/14) yield: 94%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.2, 2 H, 2 Ar**H**), 7.18-7.16 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.1, 1 H, Ar**H**), 6.95-6.93 (m, 3 H, 3 Ar**H**), 4.14-3.79 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.79-2.76 (t, J = 7.5, 2 H, ArC**H**$_2$), 1.65-1.61 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.24 (m, 22 H, 11 C**H**$_2$), 0.89-0.86 (t, J = 6.5, 3 H, C**H**$_3$).

3-{4-[3'-Hexadecyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/16) yield: 71%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.7, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.6, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 4.14-3.76 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.79-2.76 (t, J = 7.7, 2 H, ArC**H**$_2$), 1.66-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.25 (m, 26 H, 13 C**H**$_2$), 0.89-0.86 (t, J = 6.8, 3 H, C**H**$_3$),

3-{4-[3'-Octadecyl-(2,2'-bithiophen)-5-yl]phenoxy}propane-1,2-diol (12/18) yield: 78%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.3, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.4, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 4.14-3.75 (m, 5 H, ArOC**H**$_2$, C**H**OH, C**H**$_2$OH), 2.79-2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.67-1.61 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.25 (m, 30 H, 15 C**H**$_2$), 0.89-0.86 (t, J = 6.4, 3 H, C**H**$_3$).

1.8 4-{4-[3'-Alkyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-2,2-dimethyl-1,3-dioxolanes 13/*n*

12/*n* (0.4 mmol) was dissolved in 2,2-dimethoxypropane (5 mL). After addition of pyridium p-toluenesolfonate (50 mg), the mixture was stirred at RT until the reaction was

complete. The solvent was evaporated and the residue was taken up in ethyl acetate (100 mL). The solution was washed with sat. aq. $NaHCO_3$ (50 mL), H_2O (50 mL) and brine (50 mL) and the organic layer was dried with anhydrous Na_2SO_4. Purification of the product was done by chromatography (eluent: petroleum ether / ethyl acetate V / V = 20 / 1).

2,2-Dimethyl-4-{ 4-[3'-pentyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-1,3-dioxolane (13/5) yield: 92%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54- 7.52 (d, J = 8.6, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 4.50-3.92 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.79- 2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.66-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.42 (s, 3 H, OCC**H**$_3$), 1.37-1.25 (m, 4 H, 2 C**H**$_2$), 0.89-0.86 (t, J = 6.9, 3 H, C**H**$_3$).

4-{ 4-[3'-Hexyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-2,2-dimethyl-1,3-dioxolane (13/6) yield: 95%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.6, 2 H, 2 Ar**H**), 7.18-7.16 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.6, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 4.51-3.92 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.80-2.77 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.65-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.42 (s, 3 H, OCC**H**$_3$), 1.30-1.25 (m, 6 H, 3 C**H**$_2$), 0.88-0.85 (t, J = 6.7, 3 H, C**H**$_3$).

4-{ 4-[3'-Heptyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-2,2-dimethyl-1,3-dioxolane (13/7) yield: 89%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54- 7.52 (d, J = 8.7, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.8, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 4.50-3.92 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.79- 2.76 (t, J = 7.9, 2 H, ArC**H**$_2$), 1.68-1.61 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.42 (s, 3 H, OCC**H**$_3$), 1.38-1.25 (m, 8 H, 4 C**H**$_2$), 0.89-0.86 (t, J = 6.9, 3 H, C**H**$_3$).

2,2-Dimethyl-4-{ 4-[3'-octyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-1,3-dioxolane (13/8) yield: 90%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54- 7.52 (d, J = 8.8, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 4.51-3.90 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.79- 2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.67-1.61 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.41 (s, 3 H, OCC**H**$_3$), 1.38-1.24 (m, 10 H, 5 C**H**$_2$), 0.89-0.86 (t, J = 6.8, 3 H, C**H**$_3$).

2,2-Dimethyl-4-{ 4-[3'-nonyl-(2,2'-bithiophen)-5-yl)phenoxymethyl}-1,3-dioxolane (13/9) yield: 91%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54- 7.52 (d, J = 7.6, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.6, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 4.51-3.91 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.79- 2.76 (t, J = 7.7, 2 H, ArC**H**$_2$), 1.74-1.63 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.42 (s, 3 H, OCC**H**$_3$), 1.37-1.26 (m, 12 H, 6 C**H**$_2$), 0.89-0.86 (t, J = 6.4, 3 H, C**H**$_3$).

4-{ 4-[3'-Decyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-2,2-dimethyl-1,3-dioxolane (13/10) yield: 95%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.53- 7.52 (d, J = 8.4, 2 H, 2 Ar**H**), 7.16-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.3, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 4.50-3.90 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.79- 2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.68-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.41 (s, 3 H, OCC**H**$_3$), 1.37-1.30 (m, 14 H, 7 C**H**$_2$), 0.89-0.86 (m, 3 H, C**H**$_3$).

2,2-Dimethyl-4-{ 4-[3'-undecyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-1,3-dioxolane (13/11) yield: 93%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54- 7.52 (d, J = 8.7, 2 H, 2 Ar**H**), 7.17-7.15 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 4.51-3.91 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.79- 2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.68-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.42 (s, 3 H, OCC**H**$_3$), 1.37-1.34 (m, 16 H, 8 C**H**$_2$), 0.89-0.86 (t, J = 6.7, 3 H, C**H**$_3$).

4-{ 4-[3'-Dodecyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-2,2-dimethyl-1,3-dioxolane (13/12) yield: 95%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54- 7.52 (d, J = 8.7, 2 H, 2 Ar**H**), 7.16-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.7, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 4.51-3.90 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.79- 2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.67-1.61 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.41 (s, 3 H, OCC**H**$_3$), 1.36-1.25 (m, 18 H, 9 C**H**$_2$), 0.89-0.86 (t, J = 6.7, 3 H, C**H**$_3$).

2,2-Dimethyl-4-{ 4-[3'-tridecyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-1,3-dioxolane (13/13) yield: 95%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54- 7.52 (d, J = 8.6, 2 H, 2 Ar**H**), 7.16-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.5, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 4.51-3.90 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.79- 2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.64-1.61 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.42 (s, 3 H, OCC**H**$_3$), 1.36-1.25 (m, 20 H, 10 C**H**$_2$), 0.89-0.86 (t, J = 6.5, 3 H, C**H**$_3$).

2,2-Dimethyl-4-{ 4-[3'-tetradecyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-1,3-dioxolane (13/14) yield: 90%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.71- 7.69 (d, J = 8.6, 2 H, 2 Ar**H**), 7.34-7.32 (m, 2 H, 2 Ar**H**), 7.27-7.26 (d, J = 3.2, 1 H, Ar**H**), 7.10-7.09 (m, 3 H, 3 Ar**H**), 4.69-4.08 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.97- 2.93 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.83-1.79 (m, 2 H, ArCH$_2$C**H**$_2$), 1.65 (s, 3 H, OCC**H**$_3$), 1.60 (s, 3 H, OCC**H**$_3$), 1.52-1.41 (m, 22 H, 11 C**H**$_2$), 1.06-1.04 (t, J = 6.5, 3 H, C**H**$_3$).

4-{ 4-[3'-Hexadecyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-2,2-dimethyl-1,3-dioxolane (13/16) yield: 91%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54- 7.52 (d, J = 8.7, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.6, 1 H, Ar**H**), 6.94-6.93 (m, 3 H, 3 Ar**H**), 4.52-3.91 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.80- 2.77 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.66-1.60 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.42 (s, 3 H, OCC**H**$_3$), 1.37-1.26 (m, 26 H, 13 C**H**$_2$), 0.89-0.86 (t, J = 6.8, 3 H, C**H**$_3$).

2,2-Dimethyl-4-{ 4-[3'-octadecyl-(2,2'-bithiophen)-5-yl]phenoxymethyl}-1,3-dioxolane (13/18) yield: 97%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54- 7.52 (d, J = 8.4, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.0, 1 H, Ar**H**), 6.94-6.92 (m, 3 H, 3 Ar**H**), 4.51-3.90 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.79- 2.76 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.64-1.60 (m, 2 H, ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.42 (s, 3 H, OCC**H**$_3$), 1.33-1.24 (m, 30 H, 15 C**H**$_2$), 0.89-0.86 (t, J = 6.2, 3 H, C**H**$_3$).

1.9 Compounds 14/*n*

Under an argon atmosphere, **13/*n*** (0.3 mmol) was dissolved in anhydrous THF (10 mL) and cooled to -60°C, then *n*-BuLi (1.6 M in *n*-hexane, 0.3 mL, 0.4 mmol) was added dropwise and the solution was stirred for 30 min. The solution was warmed slowly to -40°C, then anhydrous powdered $CuCl_2$ (54 mg, 0.4 mmol) was added in one portion. The mixture was stirred for 15 h at RT, The mixture was poured into water (20 mL) containing 10 mL of 1 M hydrochloric acid and extracted with diethyl ether (3×15 mL). The combined organic phase was washed with water and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by column chromatography (eluent: petroleum ether/ethyl acetate V / V = 10 / 1).

14/5: yield: 85%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.2, 4 H, 4 Ar**H**), 7.16-7.15 (d, J = 3.1, 2 H, 2 Ar**H**), 7.07-7.06 (d, J = 3.2, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.95-6.93 (d, J = 8.2, 4 H, 4 Ar**H**), 4.51-3.91 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.78-2.75 (t, J = 7.7, 4 H, 2 ArC**H**$_2$), 1.69-1.67 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.48 (s, 6 H, 2 OCC**H**$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.33-1.24 (m, 8 H, 4 C**H**$_2$), 0.90-0.87 (m, 6 H, 2 C**H**$_3$**),**

14/6: yield: 86%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.53-7.51 (d, J = 8.4, 4 H, 4 Ar**H**), 7.15-7.14 (d, J = 3.1, 2 H, 2 Ar**H**), 7.06-7.05 (d, J = 3.2, 2 H, 2 Ar**H**), 6.98 (s, 2 H, 2 Ar**H**), 6.94-6.92 (d, J = 8.3, 4 H, 4 ArH), 4.50-3.91 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.76-2.75 (t, J = 6.9, 4 H, 2 ArC**H**$_2$), 1.69-1.67 (m, 4 H, 2ArCH$_2$C**H**$_2$), 1.48 (s, 6 H, 2 OCC**H**$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.33-1.25 (m, 12 H, 6 C**H**$_2$), 0.89-0.86 (m, 6 H, 2 C**H**$_3$).

14/7: yield: 85%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.53 (d, J = 8.4, 4 H, 4 Ar**H**), 7.16-7.15 (d, J = 3.6, 2 H, 2 Ar**H**), 7.08-7.07 (d, J = 3.2, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.95-6.93 (d, J = 8.6, 4 H, 4 Ar**H**), 4.51-3.91 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.79-2.75 (t, J = 7.7, 4 H, 2 ArC**H**$_2$), 1.70-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.48 (s, 6 H, 2 OCC**H**$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.32-1.24 (m, 16 H, 8 C**H**$_2$), 0.90-0.86 (m, 6 H, 2 C**H**$_3$).

14/8: yield: 89%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.6, 4 H, 4 Ar**H**), 7.17-7.16 (d, J = 3.7, 2 H, 2 Ar**H**), 7.08-7.07 (d, J = 3.4, 2 H, 2 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.96-6.94 (d, J = 8.7, 4 H, 4 Ar**H**), 4.51-3.93 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.79-2.76 (t, J = 7.5, 4 H, 2 ArC**H**$_2$), 1.68-1.67 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.49 (s, 6 H, 2 OCC**H**$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.33-1.25 (m, 20 H, 10 C**H**$_2$), 0.90-0.87 (t, J = 6.7, 6 H, 2 C**H**$_3$).

14/9: yield: 91%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.1, 4 H, 4 Ar**H**), 7.16-7.15 (m, 2 H, 2 Ar**H**), 7.08-7.07 (m, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.95-6.94 (d, J = 8.1, 4 H, 4 Ar**H**), 4.52-3.91 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.77-2.74 (m, 4 H, 2 ArC**H**$_2$), 1.68-1.47 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.49 (s, 6 H, 2 OCC**H**$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.33-1.25 (m, 24 H, 12 C**H**$_2$), 0.90-0.87 (m, 6 H, 2 C**H**$_3$).

14/10: yield: 85%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.53 (d, J = 8.7, 4 H, 4 Ar**H**), 7.16-7.15 (d, J = 3.7, 2 H, 2 Ar**H**), 7.08-7.07 (d, J = 3.7, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.95-6.93 (d, J = 8.7, 4 H, 4 Ar**H**), 4.52-3.91 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.79-2.76 (t, J = 7.8, 4 H, 2 ArC**H**$_2$), 1.70-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.48 (s, 6 H, 2 OCC**H**$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.39-1.27 (m, 28 H, 14 C**H**$_2$), 0.89-0.86 (t, J = 6.8, 6 H, 2 C**H**$_3$).

14/11: yield: 80%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 7.5, 4 H, 4 Ar**H**), 7.17-7.16 (d, J = 3.0, 2 H, 2 Ar**H**), 7.08-7.07 (m, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.95-6.94 (d, J = 7.7, 4 H, 4 Ar**H**), 4.51-3.92 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.79-2.76 (t, J = 7.4, 4 H, 2 ArC**H**$_2$), 1.68-1.53 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.49 (s, 6 H, 2 OCC**H**$_3$), 1.43 (s, 6 H, 2 OCC**H**$_3$), 1.39-1.25 (m, 32 H, 16 C**H**$_2$), 0.89-0.86 (t, J = 6.4, 6 H, 2 C**H**$_3$).

14/12: yield: 85%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.4, 4 H, 4 Ar**H**), 7.16-7.15 (d, J = 3.5, 2 H, 2 Ar**H**), 7.07-7.06 (d, J = 3.5, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.95-6.93 (d, J = 8.5, 4 H, 4 Ar**H**), 4.51-3.91 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.78-2.75 (t, J = 7.7, 4 H, 2 ArC**H**$_2$), 1.69-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.48 (s, 6 H, 2 OCCH$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.39-1.25 (m, 36 H, 18 C**H**$_2$), 0.89-0.86 (t, J = 6.4, 6 H, 2 C**H**$_3$).

14/13: yield: 85%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.6, 4 H, 4 Ar**H**), 7.17-7.16 (d, J = 3.7, 2 H, 2 Ar**H**), 7.08-7.07 (d, J = 3.7, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.95-6.93 (d, J = 8.7, 4 H, 4 Ar**H**), 4.51-3.91 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.78-2.75 (t, J = 7.8, 4 H, 2 ArC**H**$_2$), 1.68-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.49 (s, 6 H, 2 OCCH$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.28-1.24 (m, 40H, 20 C**H**$_2$), 0.88-0.86 (t, J = 5.9, 6 H, 2 C**H**$_3$).

14/14: yield: 81%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.2, 4 H, 4 Ar**H**), 7.15-7.14 (d, J = 3.4, 2 H, 2 Ar**H**), 7.07-7.06 (d, J = 3.6, 2 H, 2 Ar**H**), 6.99 (s, 2 H, 2 Ar**H**), 6.94-6.93 (d, J = 8.4, 4 H, 4 Ar**H**), 4.50-3.90 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.78-2.75 (t, J = 7.7, 4 H, 2 ArC**H**$_2$), 1.68-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.47 (s, 6 H, 2 OCC**H**$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.38-1.25 (m, 44 H, 22 C**H**$_2$), 0.89-0.86 (t, J = 6.3, 6 H, 2 C**H**$_3$).

14/16: yield: 87%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.53 (d, J = 8.5, 4 H, 4 Ar**H**), 7.16-7.15 (d, J = 3.6, 2 H, 2 Ar**H**), 7.07-7.06 (d, J = 3.7, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.95-6.93 (d, J = 8.6, 4 H, 4 Ar**H**), 4.51-3.91 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.78-2.75 (t, J = 7.7, 4 H, 2 ArC**H**$_2$), 1.69-1.66 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.48 (s, 6 H, 2 OCC**H**$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.38-1.25 (m, 52 H, 26 C**H**$_2$), 0.89-0.86 (t, J = 6.6, 6 H, 2 C**H**$_3$).

14/18: yield**:** 85%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.6, 4 H, 4 Ar**H**), 7.16-7.15 (d, J = 3.8, 2 H, 2 Ar**H**), 7.07-7.06 (d, J = 3.7, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.95-6.93 (d, J = 8.7, 4 H, 4 Ar**H**), 4.51-3.90 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.78-2.75 (t, J = 7.5, 4 H, 2 ArC**H**$_2$), 1.69-1.66 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.48 (s, 6 H, 2 OCC**H**$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.38-1.24 (m, 60 H, 30 C**H**$_2$), 0.89-0.86 (t, J = 6.6, 6 H, 2 C**H**$_3$).

1.10 Bolaamphiphiles 2/*n*

A mixture of **14/*n*** (0.2 mmol) and 10% HCl (5 mL) in MeOH (30 mL) was heated under reflux for 6 h. After cooling to RT, the solvent was evaporated and $NaHCO_3$ solution (20 mL) was added. The residue was filtered and washed with water (3×20 mL). The product was purified by preparative centrifugal thin layer chromatography (eluent: ethyl acetate) and repeated crystallized from ethyl acetate/CH_3OH**.**

2/5: yield: 85%; orange solid. ^{1}H NMR (DMSO, 500 MHz): δ = 7.62-7.60 (d, J = 8.4, 4 H, 4 Ar**H**), 7.41-7.40 (m, 2 H, 2 Ar**H**), 7.27 (s, 2 H, 2 Ar**H**), 7.19-7.18 (d, 2 H, 2 Ar**H**), 7.02-7.01(d, J = 8.4, 4 H, 4 Ar**H**), 5.02-5.01 (d, J = 5.1, 2 H, ArOC**H**$_2$), 4.74-4.72 (d, J = 5.4, 2 H, ArOC**H**$_2$), 4.06-3.81 (m, 6 H, 2 C**H**$_2$OH, 2 C**H**OH), 2.77-2.76 (t, J = 7.6, 4 H, 2 ArC**H**$_2$), 1.66-1.63 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.35-1.26 (m, 8 H, 4 C**H**$_2$), 0.90-0.87 (t, J = 6.5, 6 H, 2 C**H**$_3$); ^{13}C NMR (DMSO, 125MHz): 159.1 (2 C), 143.8 (2 C), 140.6 (2 C), 133.9 (2 C), 133.4 (2 C), 129.5 (2 C), 127.5 (4 C), 127.0 (4 C), 126.2 (2 C), 123.6 (2 C), 115.6 (4 C), 70.3 (2 C), 70.2 (2 C), 63.1 (2 C), 31.5-22.2, 14.3 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{44}H_{51}O_6S_4$ $[M+H]^+$ 803.2563, found 803.2596; Elemental analysis calcd (%) for $C_{44}H_{50}O_6S_4$ (803.12): C 65.80, H 6.28; Found: C 65.53, H 6.37.

2/6: yield: 85%; orange solid. ^{1}H NMR (DMSO, 500 MHz): δ = 7.57-7.55 (d, J = 8.6, 4

H, 4 Ar**H**), 7.37-7.36 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.20 (s, 2 H, 2 Ar**H**), 7.14-7.13 (d, *J* = 3.7, 2 H, 2 Ar**H**), 6.98-6.97 (d, *J* = 8.7, 4 H, 4 Ar**H**), 5.00-4.99 (d, *J* = 5.2, 2 H, ArOC**H**$_2$), 4.72-4.70 (d, *J* = 5.6, 2 H, ArOC**H**$_2$), 4.13-3.61 (m, 6 H, 2 C**H**$_2$OH , 2 C**H**OH), 2.72-2.70 (t, *J* = 7.6, 4 H, 2 ArC**H**$_2$), 1.61-1.57 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.32-1.24 (m, 12 H, 6 C**H**$_2$), 0.84-0.81 (t, *J* = 6.7, 6 H, 2 C**H**$_3$); ^{13}C NMR (DMSO, 125 MHz): 158.2 (2 C), 143.8 (2 C), 140.2 (2 C), 134.8 (2 C), 133.7 (2 C), 129.8 (2 C), 127.7 (4 C), 126.6 (4 C), 126.3 (2 C), 122.5 (2 C), 115.1 (4 C), 70.3 (2 C), 69.5 (2 C), 63.6 (2 C). 31.6-22.4, 14.3 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{46}H_{55}O_6S_4$ $[M+H]^+$ 831.2876, found 831.2858; Elemental analysis calcd (%) for $C_{46}H_{54}O_6S_4$ (831.18): C 66.47, H 6.55; Found: C 66.24, H 6.67.

2/7: yield: 85%; orange solid. ^{1}H NMR (DMSO, 500 MHz): δ = 7.61-7.59 (d, *J* = 8.6, 4 H, 4 Ar**H**), 7.41-7.40 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.25(s, 2 H, 2 Ar**H**), 7.18-7.17 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.02-7.00 (d, *J* = 8.7, 4 H, 4 Ar**H**), 5.00-4.99 (d, *J* = 5.2, 2 H, ArOC**H**$_2$), 4.72-4.70 (d, *J* = 5.7, 2 H, ArOC**H**$_2$), 4.06-3.80 (m, 6 H, 2 C**H**$_2$OH , 2 C**H**OH), 2.76-2.73 (t, *J* = 7.4, 4 H, 2 ArC**H**$_2$), 1.66-1.61 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.36- 1.26 (m, 16 H, 8 C**H**$_2$), 0.86-0.83 (t, *J* = 6.6, 6 H, 2 C**H**$_3$); ^{13}C NMR (DMSO, 125 MHz): 159.1 (2 C), 143.7 (2 C), 140.4 (2 C), 133.9 (2 C), 133.4 (2 C), 129.5 (2 C), 127.3 (4 C), 126.9 (4 C), 126.2 (2 C), 123.4 (2 C), 115.5 (4 C), 70.3 (2 C), 70.2 (2 C), 63.1 (2 C), 31.7-22.5, 14.3 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{48}H_{59}O_6S_4$ $[M+H]^+$ 859.3189, found 859.3174; Elemental analysis calcd (%) for $C_{48}H_{58}O_6S_4$ (859.23): C 67.10, H 6.80; Found: C 66.89, H 6.93.

2/8: yield: 85%; orange solid. ^{1}H NMR (DMSO, 500 MHz): δ = 7.61-7.59 (d, *J* = 8.6, 4 H, 4 Ar**H**), 7.41-7.40 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.25 (s, 2 H, 2 Ar**H**), 7.18-7.17 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.01-6.99 (d, *J* = 8.7, 4 H, 4 Ar**H**), 4.99-4.98 (d, *J* = 5.2, 2 H, ArOC**H**$_2$), 4.71-4.68 (d, *J* = 5.7, 2 H, ArOC**H**$_2$), 4.05-3.79 (m, 6 H, 2 C**H**$_2$OH , 2 C**H**OH), 2.76-2.73 (t, *J* = 7.5, 4 H, 2 ArC**H**$_2$), 1.65-1.63 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.35- 1.23 (m, 20 H, 10 C**H**$_2$), 0.83-0.81(t, *J* = 6.5, 6 H, 2 C**H**$_3$); ^{13}C NMR (DMSO, 125 MHz): 159.1 (2 C), 143.8 (2 C), 140.6 (2 C), 133.9 (2 C), 133.3 (2 C), 129.5 (2 C), 127.5 (4 C), 126.9 (4 C), 126.2 (2 C), 123.6 (2 C), 115.6 (4 C), 70.3 (2 C), 70.1 (2 C), 63.0 (2 C), 31.6-22.4, 14.3 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{50}H_{63}O_6S_4$ $[M+H]^+$ 887.3502, found 887.3514; Elemental analysis calcd (%) for $C_{50}H_{62}O_6S_4$ (887.28): C 67.68, H 7.04; Found: C 67.49, H 7.17.

2/9: yield: 85%; orange solid. ^{1}H NMR (DMSO, 500 MHz): δ = 7.60-7.59 (d, *J* = 8.7, 4 H, 4 Ar**H**), 7.40-7.39 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.23 (s, 2 H, 2 Ar**H**), 7.17-7.16 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.01-6.99 (d, *J* = 8.7, 4 H, 4 Ar**H**), 5.00-4.99 (d, *J* = 5.2, 2 H, ArOC**H**$_2$), 4.72-4.70 (d, *J* = 5.7, 2 H, ArOC**H**$_2$), 4.06-3.80 (m, 6 H, 2 C**H**$_2$OH , 2 C**H**OH), 2.76-2.73 (t, *J* = 7.6, 4 H, 2ArC**H**$_2$), 1.65-1.62 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.35- 1.23 (m, 24 H, 12 C**H**$_2$), 0.84-0.81 (t, *J* = 6.7, 6 H, 2 C**H**$_3$); ^{13}C NMR (DMSO, 125 MHz): 159.1 (2 C),

143.7 (2 C), 140.4 (2 C), 133.9 (2 C), 133.4 (2 C), 129.5 (2 C), 127.4 (4 C), 126.9 (4 C), 126.2 (2 C), 123.4 (2 C), 115.5 (4 C), 70.3 (2 C), 70.2 (2 C), 63.1 (2 C), 31.7-22.5, 14.3 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{52}H_{67}O_6S_4$ $[M+H]^+$ 915.3815, found 915.3827; Elemental analysis calcd (%) for $C_{52}H_{66}O_6S_4$ (915.34): C 68.23, H 7.27; Found: C 68.01, H 7.41.

2/10: yield: 85%; orange solid. ^{1}H NMR ($CDCl_3$ + DMSO, 500 MHz): δ = 7.54-7.53 (d, *J* = 8.7, 4 H, 4 Ar**H**), 7.18-7.17 (d, *J* = 3.8, 2 H, 2 Ar**H**), 7.08-7.07 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.97-6.95 (d, *J* = 8.8, 4 H, 4 Ar**H**), 4.07-3.81 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.79-3.72 (m, 4 H, 2 C**H**$_2$OH), 2.68-2.60 (m, 4 H, 2 ArC**H**$_2$), 1.68-1.67 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.43-1.27 (m, 28 H, 14 C**H**$_2$), 0.87-0.83 (m, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$ + DMSO, 125 MHz): 158.9 (2 C), 143.6 (2 C), 140.1 (2 C), 133.9 (2 C), 133.5 (2 C), 129.5 (2 C), 127.0 (4 C), 126.8 (4 C), 126.2 (2 C), 123.2 (2 C), 115.4 (4 C), 70.3 (2 C), 70.1 (2 C), 63.1 (2 C), 31.7-22.5, 14.2 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{54}H_{71}O_6S_4$ $[M+H]^+$ 943.4128, found 943.4160; Elemental analysis calcd (%) for $C_{54}H_{70}O_6S_4$ (943.39): C 68.75, H 7.48; Found: C 68.57, H 7.59.

2/11: yield: 85%; orange solid. ^{1}H NMR (DMSO, 500 MHz): δ = 7.57-7.56 (d, *J* = 8.6, 4 H, 4 Ar**H**), 7.35-7.34 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.17 (s, 2 H, 2 ArH), 7.14-7.13 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.00-6.98 (d, *J* = 8.6, 4 H, 4 Ar**H**), 4.05-3.29 (m, 10 H, 2 C**H**$_2$OH , 2 ArOC**H**$_2$, 2 C**H**OH), 2.74-2.71 (t, *J* = 7.5, 4 H, 2 ArC**H**$_2$), 1.63-1.59 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.32-1.20 (m, 32 H, 16 C**H**$_2$), 0.83-0.80 (t, *J* = 6.8, 6 H, 2 C**H**$_3$); ^{13}C-NMR (DMSO; 125 MHz): 158.7 (2 C), 143.7 (2 C), 140.2 (2 C), 134.7 (2 C), 134.7 (2 C), 129.8 (2 C), 127.7 (4 C), 126.9 (4 C), 126.2 (2 C), 122.5 (2 C), 115.1 (4 C), 70.3 (2 C), 69.5 (2 C), 63.6 (2 C), 31.7-22.5, 14.2 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{56}H_{75}O_6S_4$ $[M+H]^+$ 971.4441, found 971.4430,; Elemental analysis calcd (%) for $C_{56}H_{74}O_6S_4$ (971.44): C 69.24, H 7.68; Found: C 69.01, H 7.79.

2/12: yield: 85%; orange solid. ^{1}H NMR ($CDCl_3$+DMSO, 500 MHz): δ = 7.53-7.52 (d, *J* = 7.8, 4 H, 4 Ar**H)**, 7.16-7.15 (m, 2 H, 2 Ar**H**), 7.07-7.06 (m, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.96-6.95 (d, *J* = 7.9, 4 H, 4 Ar**H**), 4.06-3.82 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH,), 3.80-3.72 (m, 4 H, 2 C**H**$_2$OH), 2.78-2.75(m, 4 H, 2 ArC**H**$_2$), 1.70-1.67 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.41-1.26 (m, 36 H, 18 C**H**$_2$), 0.88-0.86 (t, *J* = 6.2, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$+DMSO, 500 MHz): 159.1 (2 C), 143.8 (2 C), 140.5 (2 C), 133.9 (2 C), 133.4 (2 C), 129.5 (2 C), 127.5 (4 C), 126.9 (4 C), 126.2 (2 C), 123.5 (2 C), 115.5 (4 C), 70.3 (2 C), 70.2 (2 C), 63.1 (2 C), 31.6-22.4, 14.3 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{58}H_{79}O_6S_4$ $[M+H]^+$ 999.4754, found 999.4778; Elemental analysis calcd (%) for $C_{58}H_{78}O_6S_4$ (999.50): C 69.70, H 7.87; Found: C 69.54, H 7.95.

2/13: yield: 87%; orange solid. ^{1}H NMR ($CDCl_3$+DMSO, 500 MHz): δ = 7.54-7.53 (d, *J*

= 7.9, 4 H, 4 Ar**H)**, 7.16-7.15 (d, *J* = 3.5, 2 H, 2 Ar**H**), 7.07-7.06 (d, *J* = 3.5, 2 H, 2 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.96-6.95 (d, *J* = 7.9, 4 H, 4 Ar**H**), 4.07-3.82 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH,), 3.81-3.72 (m, 4 H, 2 C**H**$_2$OH), 2.78-2.75(m, 4 H, 2 ArC**H**$_2$), 1.70-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.41-1.26 (m, 40 H, 20 C**H**$_2$), 0.89-0.87 (t, *J* = 6.5, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$+DMSO, 125 MHz): 158.9 (2 C), 143.7 (2 C), 140.3 (2 C), 133.7 (2 C), 133.2 (2 C), 129.5 (2 C), 127.5 (4 C), 126.8 (4 C), 126.1 (2 C), 123.4 (2 C), 115.3 (4 C), 70.3 (2 C), 70.2 (2 C), 63.1 (2 C), 31.8-22.6, 14.2 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{60}H_{83}O_6S_4$ $[M+H]^+$ 1027.5067, found 1027.5072; Elemental analysis calcd (%) for $C_{60}H_{82}O_6S_4$ (1027.55): C 70.13, H 8.04; Found: C 69.99, H 8.13.

2/14: yield: 95%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, *J* = 8.5, 4 H, 4 Ar**H**), 7.15-7.14 (d, *J* = 3.6, 2 H, 2 Ar**H**), 7.07-7.06 (d, *J* = 3.6, 2 H, 2 Ar**H**), 6.99 (s, 2 H, 2 Ar**H**), 6.94-6.92 (d, *J* = 8.5, 4 H, 4 Ar**H**), 4.13-4.08 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.86-3.74 (m, 4 H, 2 C**H**$_2$OH), 2.78-2.75 (t, *J* = 7.6, 4 H, 2 ArC**H**$_2$), 1.71-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.39-1.25 (m, 44 H, 22 C**H**$_2$), 0.88-0.80 (m, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): 158.1 (2 C), 143.7 (2 C), 140.2 (2 C), 134.7 (2 C), 134.6 (2 C), 129.7 (2 C), 127.6 (2 C), 126.9 (4 C), 126.5 (2 C), 126.4 (2 C), 122.5 (2 C), 115.0 (4 C), 70.3 (2 C), 69.4 (2 C), 63.6 (2 C), 31.8-22.7, 14.0 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{62}H_{87}O_6S_4$ $[M+H]^+$ 1055.5380, found 1055.5359; Elemental analysis calcd (%) for $C_{62}H_{86}O_6S_4$ (1055.60): C 70.54, H 8.21; Found: C 70.32, H 8.30.

2/16: yield: 85%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.58-7.56 (d, *J* = 8.6, 4 H, 4 Ar**H**), 7.20-7.19 (d, *J* = 3.7, 2 H, 2 Ar**H**), 7.10-7.09 (d, *J* = 3.6, 2 H, 2 Ar**H**), 7.03 (s, 2 H, 2 Ar**H**), 6.98-6.96 (d, *J* = 8.6, 4 H, 4 Ar**H**), 4.17-4.06 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.91-3.79 (m, 4 H, 2 C**H**$_2$OH), 2.81-2.78 (t, *J* = 7.8, 4 H, 2 ArC**H**$_2$), 1.71-1.69 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.43-1.25 (m, 52 H, 26 C**H**$_2$), 0.91-0.88 (t, *J* = 6.5, 6 H, 2 C**H**$_3$); ^{13}C NMR (DMSO, 125 MHz): 159.1 (2 C), 143.8 (2 C), 140.4 (2 C), 134.0(2 C), 133.4 (2 C), 129.6 (2 C), 127.4 (4 C), 126.9 (4 C), 126.3 (2 C), 123.4 (2 C), 115.6 (4 C), 70.4 (2 C), 70.3 (2 C), 63.2 (2 C), 31.6-22.4, 14.2 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{66}H_{95}O_6S_4$ $[M+H]^+$ 1111.6006, found 1111.6006; Elemental analysis calcd (%) for $C_{66}H_{94}O_6S_4$ (1111.71): C 71.31, H 8.52; Found: C 71.19, H 8.61.

2/18: yield: 85%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, *J* = 8.3, 4 H, 4 Ar**H**), 7.16-7.15 (d, *J* = 3.4, 2 H, 2 Ar**H**), 7.07-7.06 (d, *J* = 3.4, 2 H, 2 ArH), 6.99 (s, 2 H, 2 Ar**H**), 6.95-6.93 (d, *J* = 8.3, 4 H, 4 Ar**H**), 4.14-4.09 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**$_2$OH), 3.88-3.79 (m, 4 H, 2 C**H**$_2$OH), 2.78-2.75 (t, *J* = 7.4, 4 H, 2 ArC**H**$_2$), 1.71-1.62 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.40-1.24 (m, 60 H, 30 C**H**$_2$), 0.88-0.86 (t, *J* = 6.2, 6 H, 2 C**H**$_3$); ^{13}C NMR (DMSO, 125 MHz): 158.9 (2 C), 143.6 (2 C), 139.7 (2 C), 134.0 (2 C), 133.6 (2 C), 129.8 (2 C), 128.2 (4 C), 126.7 (4 C), 126.2 (2 C), 122.9 (2 C), 115.3 (4 C), 70.4 (2 C), 70.1 (2 C), 63.2 (2 C), 31.7-22.4, 13.9 (multicarbons in alkyl chains); HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{70}H_{103}O_6S_4$ $[M+H]^+$ 1167.6712, found 1167.6728; Elemental analysis calcd (%) for $C_{70}H_{102}O_6S_4$ (1167.82): C 71.99, H 8.80; Found: C 71.78, H 8.91.

2. Additional XRD data

Table S1 Crystallographic data of compounds **2/*n***.[a]

Comp.	T/°C	phase	$2\theta_{obs}$/°	d_{obs}/nm	*hk*	d_{calc}/nm	d_{obs}-d_{calc}	a/nm
2/5	140	SmA	2.913	3.03	01	3.03	0.00	d = 3.03
			5.831	1.52	02	1.52	0.00	
			19.356	0.46	diff			
2/6	150	$Col_{hex}/p6mm$	2.827	3.13	10	3.13	0.00	a_{hex} = 3.61
			4.812	1.84	11	1.86	-0.02	
			19.385	0.46	diff			
	120	$Col_{hex}/p6mm$	2.760	3.20	10	3.20	0.00	a_{hex} = 3.70
			4.841	1.83	11	1.85	-0.02	
			5.510	1.60	20	1.60	0.00	
			19.527	0.45	diff			
2/7	160	$Col_{hex}/p6mm$	2.880	3.07	10	3.07	0.00	a_{hex} = 3.54
			5.021	1.76	11	1.77	-0.01	
			5.703	1.55	20	1.53	0.02	
			19.270	0.46	diff			
	80	$Col_{hex}/p6mm$	2.688	3.29	10	3.29	0.00	a_{hex} = 3.80
			4.674	1.89	11	1.90	-0.01	
			5.381	1.64	20	1.61	0.03	
			19.920	0.45	diff			
2/8	160	$Col_{hex}/p6mm$	2.854	3.10	10	3.09	0.01	a_{hex} = 3.57
			4.918	1.80	11	1.79	0.01	
			19.346	0.46	diff			
	80	$Col_{hex}/p6mm$	2.731	3.23	10	3.24	-0.01	a_{hex} = 3.74
			4.757	1.86	11	1.87	-0.01	
			5.427	1.63	20	1.62	0.01	
			19.766	0.45	diff			
2/9	160	$Col_{hex}/p6mm$	2.877	3.07	10	3.07	0.00	a_{hex} = 3.55
			4.915	1.80	11	1.77	0.03	
			5.748	1.54	20	1.54	0.00	
			19.107	0.46	diff			
	80	$Col_{hex}/p6mm$	2.706	3.26	10	3.26	0.00	a_{hex} = 3.77
			4.698	1.88	11	1.88	0.00	
			5.368	1.64	20	1.63	0.01	
			19.591	0.45	diff			

[a] (θ_{obs}: experimental scattering angle; d_{obs}: experimental and d_{calc}: calculated d spacing; *hk*: assigned indices for 2D phases (Col_{squ}, Col_{hex}), Parameter used: Lattice parameters used to calculate d_{calc} with an error of the calculated parameters in the order of 0.1 nm).

Table S1 continued

Comp.	T/°C	phase	$2\theta_{obs}$/°	d_{obs}/nm	*hk*	d_{calc}/nm	d_{obs}-d_{calc}	a/nm
2/10	140	Col_{hex}/*p6mm*	2.799	3.16	10	3.15	0.01	a_{hex} = 3.64
			4.831	1.83	11	1.82	0.01	
			5.570	1.59	20	1.58	0.01	
			19.262	0.46	diff			
	60	Col_{squ}/*p4mg*	1.697	5.21	11	5.20	0.01	a_{squ} = 7.36
			2.419	3.65	20	3.68	-0.03	
			2.696	3.28	21	3.29	-0.01	
			3.827	2.31	31	2.33	-0.02	
			4.346	2.03	32	2.04	-0.01	
			19.870	0.45	diff			
2/11	120	Col_{hex}/*p6mm*	2.852	3.10	10	3.10	0.00	a_{hex} = 3.58
			4.892	1.81	11	1.79	0.02	
			5.697	1.55	20	1.55	0.00	
			19.346	0.46	diff			
	100	Col_{squ}/*p4mg*	1.800	4.91	11	4.91	0.00	a_{squ} = 6.94
			2.568	3.44	20	3.47	-0.03	
			2.800	3.16	21	3.10	0.06	
			3.977	2.22	31	2.20	0.02	
			4.484	1.97	32	1.93	0.04	
			19.483	0.46	diff			
2/12	130	N	2.719	3.25				*d* = 3.25
			3.876	2.28				*d* = 2.28
			19.159	0.46				
	110	Col_{squ}/*p4mm*	2.511	3.52	10	3.52	0.00	a_{squ} = 3.52
			3.554	2.49	11	2.49	0.00	
			5.017	1.76	20	1.76	0.00	
			19.243	0.46	diff			
2/13	135	Col_{squ}/*p4mm*	2.535	3.49	10	3.49	0.00	a_{squ} = 3.49
			3.575	2.47	11	2.47	0.00	
			5.071	1.74	20	1.75	-0.01	
			19.150	0.46	diff			
2/14	140	Col_{squ}/*p4mm*	2.541	3.48	10	3.48	0.00	a_{squ} = 3.48
			3.593	2.46	11	2.46	0.00	
			5.058	1.75	20	1.74	0.01	
			19.418	0.46	diff			

Table S1 continued

Comp.	T/°C	phase	$2\theta_{obs}$/°	d_{obs}/nm	*hk*	d_{calc}/nm	d_{obs}-d_{calc}	a/nm
2/16	130	Col_{squ}/*p*4*mm*	2.519	3.51	10	3.51	0.00	a_{squ} = 3.51
			3.568	2.48	11	2.48	0.00	
			5.037	1.75	20	1.75	0.00	
			19.368	0.46	diff			
	60	Col_{squ}/*p*4*mm*	2.434	3.63	10	3.63	0.00	a_{squ} = 3.63
			3.449	2.56	11	2.57	-0.01	
			4.873	1.81	20	1.81	0.00	
			19.848	0.45	diff			
2/18	120	Col_{squ}/*p*4*mm*	2.482	3.56	10	3.56	0.00	a_{squ} = 3.56
			3.504	2.52	11	2.52	0.00	
			4.974	1.78	20	1.78	0.00	
			19.442	0.46	diff			
	80	Col_{squ}/*p*4*mm*	2.435	3.63	10	3.63	0.00	a_{squ} = 3.63
			3.448	2.56	11	2.57	-0.01	
			4.881	1.81	20	1.81	0.00	
			19.702	0.45	diff			

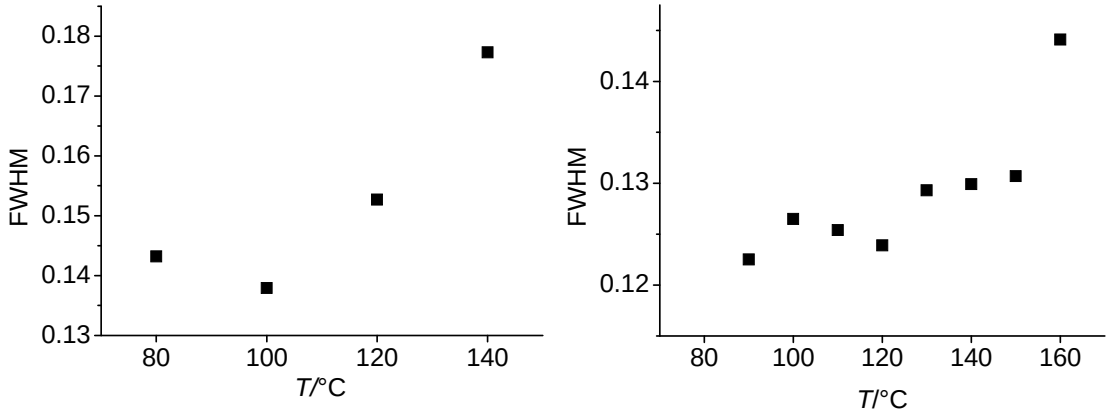

Fig. S1 Temperature dependence of the FWHM for compounds a) **2/7** and b) **2/9**; for compound **2/7** the enhanced FWHM at 80 °C is most probably due to the presence of the mesophase M close to this temperature, which is assumed to represent a kind of distorted layer structure.

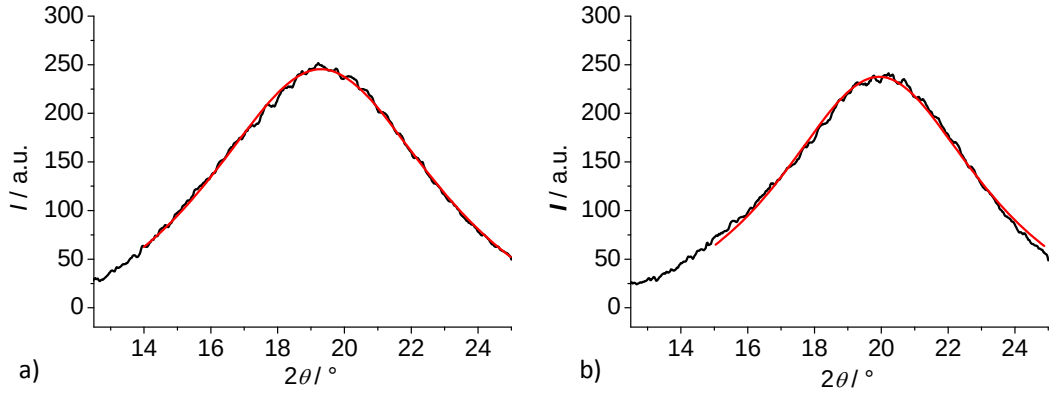

Fig. S2 Diffuse scattering in the wide angle region of the Col_{hex} phase of compound **2/7** at a) 160 °C and b) 80 °C showing a fit by one Lorentz function (red line).

3. Discussion of the honeycomb walls

More details about the structure of the honeycomb LC phases were gained from the analysis of the molecular packing in the honeycombs based on the XRD data in Table S1 and the calculated parameters collated in Table S2. The number of molecules in a hypothetical 3D unit cell was calculated from the volume of this unit cell (V_{cell}) and the volume of a molecule (V_{mol}, calculated using crystal volume increments[S7]) according to $n_{cell} = V_{cell}/V_{mol}$. V_{cell} was estimated based on the experimental 2D lattice parameters and an assumed one-molecule thickness of h = 0.45 - 0.46 nm corresponding to the experimentally determined maxima of the diffuse wide angle scatterings as collated in Table S1. The fitted wide angle scatterings (see Figure S2) do not show any shoulder or additional peak which would allow the distinction of different distances between the distinct molecular segments. Therefore, it assumed that the aromatic cores are rotationally disordered around their long axes and a mean distance corresponding to the position of the wide angle scattering maximum is used for the calculations.
The n_{cell} values were corrected for an assumed packing density of 0.63 in the LC phase, which is intermediate between a crystal (0.7) and a liquid (0.55), see Table S2. The values n_{cell}(average) obtained in this way are in good agreement with those determined from the molecular mass (M), the Avagadro constant (N) and the density (ρ) according to $n_{cell}(\rho) = a^2\, h\, N\rho/M$ (Table S3); the density was determined for compounds **2/6** as ρ = 1.178 g cm^{-3} and for compound **2/18** as ρ = 1.073 g cm^{-3} in the supercooled LC phase at 25 °C. This indicates that the obtained values are reliable, especially considering that the density at higher temperature should be a bit lower and in this way $n_{cell(\rho)}$ becomes smaller and approaches even closer to n_{cell}(average).
For the triangular honeycomb structure of compound **2/7**, as an example, the obtained values is n_{cell}(average) = 3.9 at T = 160 °C. Since in a triangular honeycomb there are 3 walls per unit cell the calculated average thickness of each honeycomb wall ($n_{wall} = n_{cell}/3$)

is slightly larger than just one rod-like core (n_{wall} = 1.3). Similar values of n_{wall}, typically ranging between 1.2 and 1.5 were observed for the Col_{hex} phases of all compounds **2/6-2/11** (see Table S2).

Table S2 Calculations of molecular volumina (V_{mol}), volumina of the hypothetical unit cells (V_{cell}), number of molecules in these unit cells (n_{cell}) and calculated average number of molecules in the cross section of the cylinder walls (n_{wall}) of compounds **2/*n*.**[a]

Comp.	*a*/nm	*T*/°C	V_{cell}/nm^3	V_{mol}/nm^3	f_R	n_{cryst}	n_{liq}	n_{cell} (average)	n_{wall} (average)	n'_{wall}
2/6	3.61	150	5.19	1.080	0.29	4.81	3.78	4.29	1.4	1.2
	3.70	120	5.34	1.080	0.29	4.94	3.88	4.41	1.5	1.3
2/7	3.54	160	4.99	1.130	0.32	4.42	3.47	3.94	1.3	1.1
	3.80	80	5.63	1.130	0.32	4.98	3.91	4.45	1.5	1.3
2/8	3.57	160	5.08	1.179	0.35	4.31	3.38	3.84	1.3	1.1
	3.74	80	5.45	1.179	0.35	4.62	3.63	4.13	1.4	1.2
2/9	3.55	160	5.02	1.229	0.37	4.09	3.21	3.65	1.2	1.1
	3.77	80	5.54	1.229	0.37	4.51	3.54	4.03	1.3	1.2
2/10	3.64	140	5.28	1.279	0.40	4.13	3.24	3.68	1.2	1.1
	7.36	60	24.38	1.279	0.40	19.06	14.98	17.02	1.7	1.5
2/11	3.58	120	5.11	1.328	0.42	3.84	3.02	3.43	1.1	1.0
	6.94	100	22.16	1.328	0.42	16.68	13.11	14.90	1.5	1.3
2/12	3.25	130	4.86	1.378	0.44	3.53	2.77	3.15	1.6	1.4
	3.52	110	5.70	1.378	0.44	4.14	3.25	3.69	1.8	1.6
2/13	3.49	135	5.60	1.427	0.46	3.93	3.08	3.51	1.8	1.5
2/14	3.48	140	5.57	1.477	0.48	3.77	2.96	3.37	1.7	1.5
2/16	3.51	130	5.67	1.576	0.51	3.60	2.83	3.21	1.6	1.4
	3.63	60	5.93	1.576	0.51	3.76	2.95	3.36	1.7	1.5
2/18	3.56	120	5.83	1.675	0.54	3.48	2.73	3.11	1.6	1.3
	3.63	80	5.93	1.675	0.54	3.54	2.78	3.16	1.6	1.4

[a] V_{cell} = volume of the unit cell defined by a^2 x 0.45 nm for square columnar phases and a^2 x sin(60°) x *h* nm for hexagonal phases (a height *h* = 0.45, 0.46 nm was used as indicated in Table 1 for the considered temperature); V_{mol} = molecular volume as calculated using crystal volume increments; [S7] n_{cryst} = number of molecules in the unit cell, calculated according to $n_{cell} = V_{cell}/V_{mol}$ (average packing coefficient in the crystal is *k* = 0.7; n_{liqu} = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient *k* = 0.55, calculated according to n_{liqu} = 0.55/0.7 x n_{cryst}; n_{cell} (average) = number of molecules in the unit cell in the LC phase estimated as the average of that in the n_{cryst} and n_{liqu}; n_{wall} (average) = number of molecules in the cross section of the cylinder walls as calculated from n_{cell} (average); n'_{wall} = 0.87 n_{wall} (average).

The deviation from being exactly one has different origins; at first it must be considered that the diffuse wide angle scattering represents an average value and the local packing is most likely close to hexagonal. Accordingly, the packing distance along the cylinder walls could be smaller by the factor $3^{1/2}/2$ (0.87), leading to values n'_{wall} between 1.0 and

1.3. Values above 1.0 are thought to be either due to a denser packing of the aromatic cores or a staggering of the aromatics along the cylinder walls, which both can improve the core-core interactions. On the other hand, the value n'_{wall} for the Col_{hex} phase of compound **2/11** becomes 1.0 due to the presence of a significant concentration of rhombic cylinders. Also thermal expansion of the chains effectively decreases the number of rod-like cores in the cross section of these triangular honeycomb walls. For compound **2/7**, as an example, n'_{wall} goes down from 1.3 at T = 80 °C to 1.1 at T = 160 °C due to the rising concentration of rhombic cylinders, the number of molecules per unit cell, and hence n_{wall}, decreases with growing alkyl chain length, because the concentration of rhombic cylinders increases by elongation of the lateral chains. For **2/7** n'_{wall} is 1.2 (T = 150 °C) and it goes down to a value of only n'_{wall} = 1.0 for compound **2/11** (T = 130 °C). For all square honeycomb phases (*p*4*gm* and *p*4*mm*) the thickness of the cylinder walls is in the range n'_{wall} = 1.3-1.6, which is in line with a nondistorted structure as mentioned in the main text. Also the temperature dependence of n'_{wall} is much smaller in the *p*4*mm* phases than for the Col_{hex} phases, confirming that no holes are formed in the cylinder walls of the square honeycombs.

Table S3. Comparison of n_{cell}(average) and n'_{cell} values for compounds **2/6** and **2/18**.

Comp.	T/°C	n_{cell}(average)	$n_{cell(\rho)}$
2/6	150	4.20	4.33
2/6	120	4.41	4.55
2/18	120	3.04	3.15
2/18	80	3.16	3.28

n_{cell}(average) = V_{cell}/V_{mol}; $n_{cell(\rho)}$ was determined based on the measured density.

4. Additional Textures

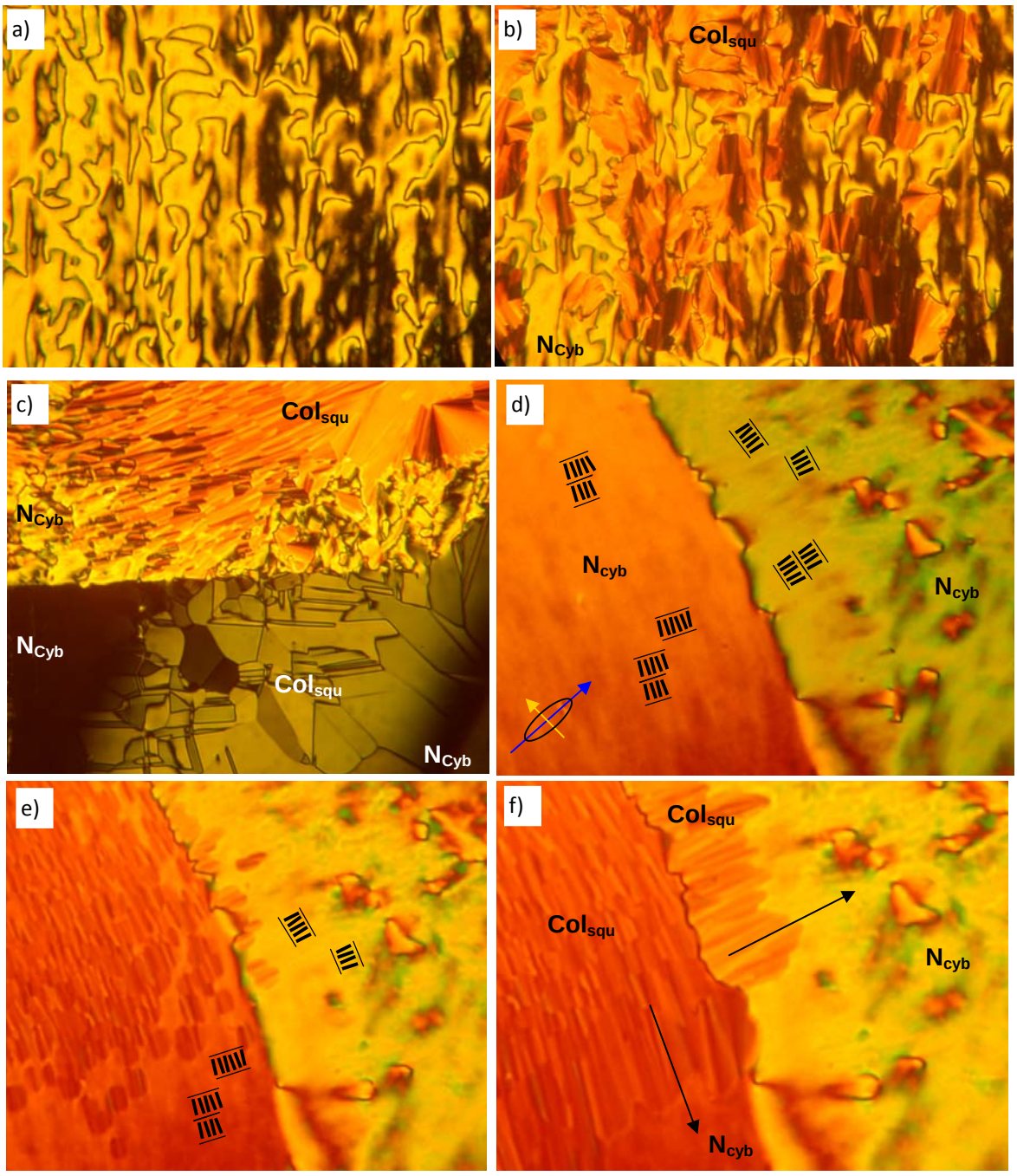

Fig. S3. Textures of compound **2/12** at the N_{cyb}- Col_{squ}/*p*4*mm* transition at ~ 125°C as observed between crossed polarizers (horizontal and vertical in all figures) under different alignment condition in 2μm cell: a) nematic Schlieren texture (homogeneous alignment) and b) growth of the Col_{squ} phase on slow cooling (rubbing direction of the surfaces is horizontal), the fans grow perpendicular to the rubbing direction, which means that the cylinder/cylinder fragments are aligned parallel to the rubbing direction and the

molecules are perpendicular to the rubbing direction; c) Col_{squ}-N_{Cyb} transition on slow heating, as seen in two adjacent domains with different alignment; in the upper part the square columns/column segments are parallel to the surfaces (homeogeneous alignment), leading to high birefringence; in the lower part they are perpendicular to the surfaces (homeotropic alignment), providing only small birefringence; this figure indicates the difference in birefringence between these two domains and in the lower part the fading of the texture of the Col_{squ} at the transition to the N_{Cyb} phase is visible (no sharp boundary between Col_{squ} and N_{Cyb} areas), this indicates that this transition is not associated with a fundamental reorientation of the cylinder axis and hence the direction of the honeycomb cylinders in the Col_{squ} phase should indeed be the same as the orientation of the cylinder fragments in the nematic phase; d-e) sample with alignment of columns/column segments parallel to the surface (homogeneos alignment) and with additional λ--retarder plate, (the indicatrix direction is shown in d); d) in the N_{Cyb} phase, e,f) at the transition to the Col_{squ} phase, indicating the two growth directions of the Col_{squ}-domains (arrows in f), the cylinders are aligned perpendicular to the direction of the arrows.

5. References

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