Supporting Information

Dithiophene Based X-Shaped Bolaamphiphiles: Liquid Crystals with Single Wall Honeycombs and Geometric Frustration

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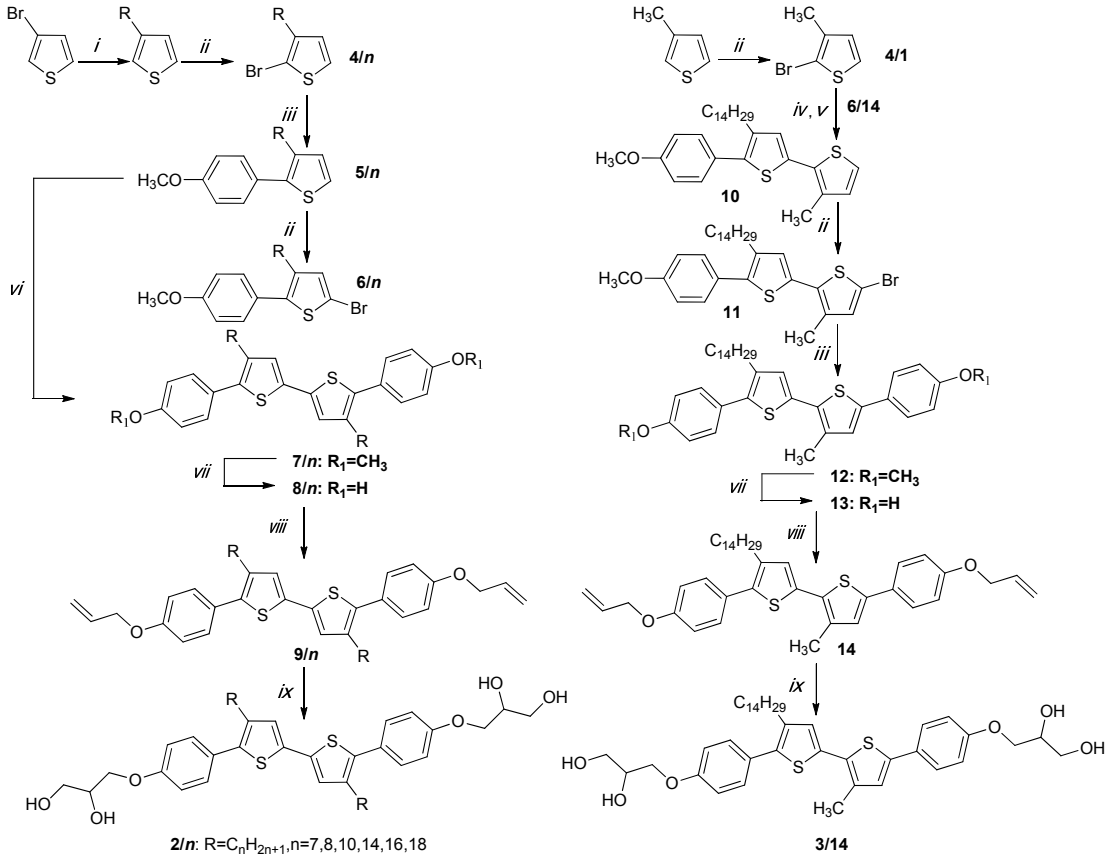
1. Synthesis

1.1 General



Scheme 1 Synthesis of compounds **2/*n*** and **3/14**; *Reagents and conditions*: *i*) $C_nH_{2n+1}MgBr$, $Ni(dppp)Cl_2$, THF, reflux, 15 h; *ii*) NBS, THF, 0-5°C, 15 h; *iii*) 4-methoxybenzene boronic acid, $Pd(PPh_3)_4$, $NaHCO_3$, glyme, H_2O, reflux, 15 h; *iv*) Mg, THF, reflux, 0.5 h; *v*) $Ni(dppp)Cl_2$, THF, reflux, 15 h; *vi*) *n*-BuLi, THF, $CuCl_2$, -60°C, 15 h; or CH_2Cl_2, $FeCl_3$, CH_3NO_2, RT, 7min; *vii*) BBr_3, -78°C, CH_2Cl_2, RT, 24 h; *viii*) K_2CO_3, CH_3CN, allylbromide, reflux, 6 h; *ix*) OsO_4, NMMNO, H_2O, acetone, RT.

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. 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

The 3-alkylthiophenes were prepared by a modified Kumada coupling reaction as described in the literature[S1] and reported previously.[S2]

1.3 3-Alkyl-2-bromothiophenes 4/*n*

The synthesis of compounds **4/n** was carried out as described in ref.[S3]; compounds **4/10** and **4/18** have been reported previously.[S4]

2-Bromo-3-methylthiophene 4/1 yield: 89%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.18-7.16 (d, J = 5.5, 1 H, Ar**H**), 6.79-6.78 (d, J = 5.5, 1 H, Ar**H**), 2.21 (s, 3 H, C**H**$_3$).

2-Bromo-3-heptylthiophene 4/7 yield: 90%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.26-7.24 (d, J = 5.6, 1 H, Ar**H**), 6.98-6.96 (d, J = 5.6, 1 H, Ar**H**), 2.57-2.54 (t, J = 7.7, 2 H, ArC**H**$_2$), 1.61-1.54 (m, 2 H, ArCH$_2$C**H**$_2$), 1.33-1.31 (m, 8 H, 4 C**H**$_2$), 0.90-0.87 (t, J = 6.1, 3 H, C**H**$_3$).

2-Bromo-3-octylthiophene 4/8 yield: 88%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ=7.19-7.17 (d, J = 5.6, 1 H, Ar**H**), 6.80-6.79 (d, J = 5.6, 1 H, Ar**H**), 2.62-2.55 (m, 2 H, ArC**H**$_2$), 1.58-1.55 (m, 2 H, ArCH$_2$C**H**$_2$), 1.30-1.27 (m, 10 H, 5 C**H**$_2$), 0.90-0.87 (t, J = 6.4, 3 H, C**H**$_3$).

2-Bromo-3-decylthiophene 4/10S4[S5] 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**) , 2.58-2.55(t. J =7.5, 2 H, ArC**H**$_2$), 1.60-1.57(t, J = 6.7, 2 H, ArCH$_2$C**H**$_2$), 1.32-1.28 (m, 14 H, 7 C**H**$_2$), 0.91-0.88 (t, J = 6.7, 3 H, C**H**$_3$).

2-Bromo-3-tetradecylthiophene 4/14 yield: 87%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.19-7.17 (d, J = 5.6, 1 H, Ar**H**), 6.80-6.79 (d, J = 5.6, 1 H, Ar**H**), 2.57 -2.54 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.55 (m, 2 H, ArCH$_2$C**H**$_2$), 1.30-1.26 (m, 22 H, 11 C**H**$_2$), 0.89-0.87 (t, J = 6.8, 3 H, C**H**$_3$).

2-Bromo-3-hexadecylthiophene 4/16 yield: 88%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.18-7.17 (d, J = 5.4, 1 H, Ar**H**), 6.79-6.78 (d, J = 5.4, 1 H, Ar**H**), 2.57 -2.54 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.56-1.55 (m, 2 H, ArCH$_2$C**H**$_2$), 1.30-1.25 (m, 26 H, 13 C**H**$_2$), 0.89-0.87 (t, J = 6.2, 3 H, C**H**$_3$).

2-Bromo-3-octadecylthiophene 4/18S4 yield: 92%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.18-7.17 (d, J = 5.4, 1 H, Ar**H**), 6.79-6.78 (d, J = 5.4, 1 H, Ar**H**), 2.57 -2.54 (t, J = 7.6, 2 H, ArC**H**$_2$), 1.56-1.55 (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 = 6.2, 3 H, C**H**$_3$).

1.4 3-Alkyl-2-(4-methoxyphenyl)thiophenes 5/*n*

The synthesis of compounds **5/*n*** was carried out as described in ref.[S3]; compounds **5/10** and **5/18** have been reported previously. [S4]

3-Heptyl-2-(4-methoxyphenyl)thiophene 5/7 yield 82%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ= 7.36-7.34 (d, *J* = 8.5, 2 H, 2 Ar**H**), 7.18-7.17 (d, *J* = 5.0, 1 H, Ar**H**), 6.96 (d, 1 H, Ar**H**), 6.95-6.93 (d, *J* = 8.5, 2 H, 2 Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.63-2.60 (t, *J* = 7.9, 2 H, ArC**H**$_2$), 1.59-1.55 (m, 2 H, ArCH$_2$C**H**$_2$), 1.26-1.16 (m, 8 H, 4 C**H**$_2$), 0.86-0.80 (m, 3 H, C**H**$_3$).

2-(4-Methoxyphenyl)-3-octylthiophene 5/8 yield 78%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ= 7.36-7.34 (d, *J* = 8.7, 2 H, 2 Ar**H**), 7.18-7.17 (d, *J* = 5.1, 1 H, Ar**H**), 6.96-6.93 (m, 3 H, 3 Ar**H**), 3.84 (s, 3 H, OCH_3), 2.62-2.59 (t. *J* = 7.9, 2 H, ArC**H**$_2$), 1.60-1.57 (m, 2 H, ArCH$_2$C**H**$_2$), 1.27-1.23 (m, 10 H, 5 C**H**$_2$), 0.88-0.82 (m, 3 H, C**H**$_3$).

3-Decyl-2-(4-methoxyphenyl)thiophene 5/10[S4] yield 67%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): *δ* = 7.36-7.34 (d, *J* = 8.6, 2 H, Ar**H**), 7.17-7.16 (d, *J* = 5.2, 1 H, Ar**H**), 6.95-6.92 (m, 3 H, 3 Ar**H**), 3.83 (s, 3 H, OC**H**$_3$), 2.63-2.60 (t, *J* = 7.8, 2 H, ArC**H**$_2$), 1.61-1.55 (m, 2 H, ArCH$_2$C**H**$_2$), 1.28-1.24 (m, 14 H, 7 C**H**$_2$), 0.89-0.87 (t, *J* = 6.7, 3 H, C**H**$_3$).

2-(4-Methoxyphenyl)-3-tetradecylthiophene 5/14 yield 51%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): *δ* = 7.35-7.34 (d, *J* = 8.0, 2 H, 2 Ar**H**), 7.18-7.17 (d, *J* = 5.0, 1 H, 1 Ar**H**), 6.96-6.93 (m, 3 H, 3 Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.62-2.59 (t, *J* = 7.7, 2 H, ArC**H**$_2$), 1.58-1.55 (m, 2 H, ArCH$_2$C**H**$_2$), 1.25 (m, 22 H, 11 C**H**$_2$), 0.89-0.86 (t, *J* = 6.3, 3 H, C**H**$_3$).

3-Hexadecyl-2-(4-methoxyphenyl)thiophene 5/16 yield 50%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): *δ* = 7.33-7.31 (d, *J* = 7.0, 2 H, 2 Ar**H**), 7.15-7.14 (d, *J* = 5.2, 1 H, 1 Ar**H**), 6.93-6.90 (m, 3 H, 3 Ar**H**), 3.82 (s, 3 H, OC**H**$_3$), 2.60-2.57 (t, *J* = 7.7, 2 H, ArC**H**$_2$), 1.59-1.53 (m, 2 H, ArCH$_2$C**H**$_2$), 1.23-1.21 (m, 26 H, 13 C**H**$_2$), 0.87-0.84 (t, *J* = 6.7, 3 H, C**H**$_3$).

2-(4-Methoxyphenyl)-3-octadecylthiophene 5/18[S4] yield 40%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): *δ* = 7.35-7.34 (d, *J* = 8.5, 2 H, 2 Ar**H**), 7.18-7.17 (d, *J* = 4.8, 1 H, Ar**H**), 6.96-6.93 (m, 3 H, 3 Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.62-2.61 (m, 2 H, ArC**H**$_2$), 1.56 (m, 2 H, ArCH$_2$C**H**$_2$), 1.25 (m, 30 H, 15 C**H**$_2$), 0.88-0.84 (t, *J* = 7.3, 3 H, C**H**$_3$).

1.5 5-Bromo-2-(4-methoxyphenyl)-3-alkylthiophenes 6/*n*

The synthesis of compounds **6/*n*** was carried out as described in ref.[S3]

5-Bromo-2-(4-methoxyphenyl)-3-octylthiophene 6/14 yield 92%; colorless liquid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.29-7.27 (d, J = 8.6, 2 H, 2 Ar**H**), 6.93-6.91 (d, J = 8.6, 2 H, 2 Ar**H**), 6.89 (s, 1 H, Ar**H**), 3.83 (s, 3 H, OC**H**$_3$), 2.54-2.51 (t, J = 7.5, 2 H, ArC**H**$_2$), 1.56-1.51 (m, 2 H, ArCH$_2$C**H**$_2$), 1.25-1.22 (m, 22 H, 11 C**H**$_2$), 0.89-0.86 (t, J = 6.7, 3 H, C**H**$_3$).

1.6 5'-(4-Methoxyphenyl)-3-methyl-4'-tetradecyl-2,2'-bithiophene 10

Compound **10** was prepared by a modified literature procedure of Kumada outlined by Zimmer *et al* [S1,S6] Accordingly, magnesium turnings (960 mg, 40 mmol) were covered by dry THF (10 mL) and 2-bromo-3-methylthiophene **4/1** (0.28g , 0.16 mmol in 0.5ml THF) was added. After the reaction had started, the remaining **4/1** (5.33 g, 31.5 mmol) dissolved in dry THF (9.5 mL) was added dropwise, maintaining the Grignard solution under reflux. Stirring was continued under reflux for 0.5 h, and then the mixture was cooled to RT, and added dropwise to a mixture of 5-bromo-2-(4-methoxyphenyl)-3-tetradecylthiophene **6/14** (14.91 g, 32 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 3 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 Na_2SO_4, and the solvent was removed in *vacuo*. The residue was purified by column chromatography (petroleum ether).

5'-(4-Methoxyphenyl)-3-methyl-4'-tetradecyl-2,2'-bithiophene 10 yield: 75%; yellowish solid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.39-7.37 (d, J = 8.5, 2 H, 2 Ar**H**), 7.12-7.11 (d, J = 5.0, 1 H, Ar**H**), 6.99 (s, 1 H, Ar**H**), 6.96-6.94 (d, J = 8.5, 2 H, 2 Ar**H**), 6.88-6.87 (d, J = 5.1, 1 H, Ar**H**), 3.85 (s, 3 H, OC**H**$_3$), 2.63-2.60 (t, J = 7.8, 2 H, ArC**H**$_2$), 2.42 (s, 3 H, ArC**H**$_3$), 1.63-1.60 (t, J = 6.1, 2 H, ArCH$_2$C**H**$_2$), 1.29-1.25 (m, 22 H, 11 C**H**$_2$), 0.89-0.86 (t, J = 6.5, 3 H, C**H**$_3$).

1.7 5-Bromo-5'-(4-methoxyphenyl)-3-methyl-4'-tetradecyl-2,2'-bithiophene 11

The synthesis of compound **11** was carried out as described in ref.[S3]

5-Bromo-5'-(4-methoxyphenyl)-3-methyl-4'-tetradecyl-2,2'-bithiophene 11 yield: 91%; ^{1}H NMR ($CDCl_3$; 500 MHz): yellow solid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.39-7.37 (d, J = 8.5, 2 H, 2 Ar**H**), 6.99 (s, 1 H, Ar**H**), 6.96-6.94 (d, J = 8.5, 2 H, 2 Ar**H**), 6.88-6.87 (d, J = 5.1, 1 H, Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.62-2.59 (t, J = 7.7, 2 H, ArC**H**$_2$), 2.41 (s, 3 H, ArC**H**$_3$), 1.63-1.60 (t, J = 6.1, 2 H, ArCH$_2$C**H**$_2$), 1.27-1.25 (m, 22 H, 11 C**H**$_2$), 0.88-0.85 (t, J = 6.4, 3 H, C**H**$_3$).

1.8 5,5'-Bis(4-methoxyphenyl)-3-methyl-4'-tetradecyl-2,2'-bithiophene 12

The synthesis of compound **12** was carried out as described in ref.[S3]

5,5'-Bis(4-methoxyphenyl)-3-methyl-4'-tetradecyl-2,2'-bithiophene 12 yield: 56%; yellow solid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.52-7.50 (d, J = 8.6, 2 H, 2 Ar**H**), 7.39-7.38 (d, J = 8.6, 2 H, 2 Ar**H**), 7.01 (s, 1 H, Ar**H**), 7.00 (s, 1 H, Ar**H**), 6.96-6.95 (d, J = 8.6, 2 H, 2 Ar**H**), 6.92-6.90 (d, J = 8.6, 2 H, 2 Ar**H**), 3.85 (s, 3 H, OC**H**$_3$), 3.84 (s, 3 H, OC**H**$_3$), 2.62 (t, 2 H, ArC**H**$_2$), 2.42 (s, 3 H, ArC**H**$_3$), 1.63-1.61 (m, 2 H, ArCH$_2$C**H**$_2$), 1.25 (m, 22 H, 11 C**H**$_2$), 0.89-0.86 (t, J = 6.4, 6 H, 2 C**H**$_3$).

1.9 4,4'-Dialkyl-5,5'-bis(4-methoxyphenyl)-2,2'-bithiophenes 7/n

Method 1:[S7] Under an argon atmosphere, 3-alkyl-2-(4-methoxyphenyl)thiophene **5/n** (3 mmol) was dissolved in anhydrous THF (10 mL) and cooled to -60 °C, then *n*-BuLi (1.6 M in *n*-hexane, 1.88 mL, 3 mmol) was added dropwise and the solution was stirred for 30 min. Then anhydrous powdered $CuCl_2$ (405 mg, 3 mmol) was added in one portion. The mixture was stirred until it returned to room temperature, then warmed to 40 °C for 12 h. The mixture was poured into 20 mL of water 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 Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1).

Method 2:[S8] At 25 °C, 3-alkyl-2-(4-methoxyphenyl)thiophene **5/n** (3 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL), then anhydrous $FeCl_3$ (0.6 M in CH_3NO_2 10 mL, 11.1 mmol) was added and the solution was stirred for 7 min. Then CH_3OH (20 mL) was added and stirred for 3 min at which point Zn powder (361 mg, 5.55 mmol) was added and further stirred for 5 min., the mixture was filtrated and the residue was washed with ethyl acetate. The combined organic phase was dried over Na_2SO_4, and the solvent was removed in *vacuo*. The residue was purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1).

4,4'-Diheptyl-5,5'-bis(4-methoxyphenyl)-2,2'-bithiophene 7/7 (Method 1) yield: 40%; yellow solid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.36-7.35 (d, J = 8.5, 4 H, 4 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.94-6.92 (d, J = 8.6, 4 H, 4 Ar**H**), 3.84 (s, 6 H, 2 OC**H**$_3$), 2.60-2.57 (t, J = 7.6, 4 H, 2 ArC**H**$_2$), 1.60 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.26-1.23 (m, 16 H, 8 C**H**$_2$), 0.89-0.86 (m, 6 H, 2 C**H**$_3$).

5,5'-Bis(4-methoxyphenyl)-4,4'-dioctyl-2,2'-bithiophene 7/8 (Method 2) yield: 72%; yellow solid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.38-7.36 (d, J = 8.25, 4 H, 4 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.95-6.94 (d, J = 8.25, 4 H, 4 Ar**H**), 3.85 (s, 6 H, 2 OC**H**$_3$),

2.61-2.58 (t, J = 7.7, 4 H, 2 ArC**H**$_2$), 1.61-1.57 (t, J = 6.95, 4 H, 2 ArCH$_2$C**H**$_2$), 1.24 (m, 20 H, 10 C**H**$_2$), 0.88-0.86 (t, J = 6.2, 6 H, 2 C**H**$_3$).

4,4'-Didecyl-5,5'-bis(4-methoxyphenyl)-2,2'-bithiophene 7/10 (Method 1) yield: 26%; yellow solid. ^{1}H NMR (CDCl$_3$; 500 MHz): δ = 7.38-7.36 (d, J = 8.5, 4 H, 4 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.95-6.94 (d, J = 8.6, 4 H, 4 Ar**H**), 3.85 (s, 6 H, 2 OC**H**$_3$), 2.61-2.58 (t, J = 7.8, 4 H, 2 ArC**H**$_2$), 1.61-1.56 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.24 (m, 28 H, 14 C**H**$_2$), 0.89-0.86 (t, J = 6.7, 6 H, 2 C**H**$_3$).

5,5'-Bis(4-methoxyphenyl)-4,4'-ditetradecyl-2,2'-bithiophene 7/14 (Method 1) yield: 40%; yellow solid. ^{1}H NMR (CDCl$_3$; 500 MHz): δ = 7.37-7.35 (d, J = 8.7, 4 H, 4 Ar**H**), 7.00 (s, 2 H, 2 Ar**H**), 6.95-6.93 (d, J = 8.7, 4 H, 4 Ar**H**), 3.84 (s, 6 H, 2 OC**H**$_3$), 2.60-2.57 (t, J = 7.4, 4 H, ArC**H**$_2$), 1.60-1.56 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.27-1.24 (m, 44 H, 22 C**H**$_2$), 0.88-0.84 (t, 6 H, 2 C**H**$_3$).

4,4'-Dihexadecyl-5,5'-bis(4-methoxyphenyl)-2,2'-bithiophene 7/16 (Method 1) yield: 39%; yellow solid. ^{1}H NMR (CDCl$_3$; 500 MHz): δ = 7.37-7.36 (d, J = 8.6, 4 H, 4 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.95-6.93 (d, J = 8.6, 4 H, 4 Ar**H**), 3.85 (s, 6 H, 2 OC**H**$_3$), 2.60-2.57 (t, J = 7.8, 4 H, ArC**H**$_2$), 1.61 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.25 (m, 52 H, 26 C**H**$_2$), 0.88-0.85 (m, 6 H, 2 C**H**$_3$).

5,5'-Bis(4-methoxyphenyl)-4,4'-dioctadecyl-2,2'-bithiophene 7/18 (Method 1) yield: 34%; yellow solid. ^{1}H NMR (CDCl$_3$; 500 MHz): δ = 7.37-7.36 (d, J = 8.9, 4 H, 4 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.94-6.92 (d, J = 8.7, 4 H, 4 Ar**H**), 3.85 (s, 6 H, 2 OC**H**$_3$), 2.60-2.58 (t, J = 7.6, 4 H, ArC**H**$_2$), 1.60-1.51 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.30-1.25 (m, 60 H, 30 C**H**$_2$), 0.87-0.85 (t, J = 6.4, 6 H, 2 C**H**$_3$).

1.10 4,4'-(3-Methyl- 4'-tetradecyl-[2,2'-bithiophene]-5,5'-diyl)diphenol 13 and 4,4'-(4,4'-dialkyl -2,2'-dithiophene-5, 5'-diyl)diphenols 8/n

12 or **7/n** (1 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to –78 °C, BBr_3 (0.22 mL, 2.2 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 Na_2SO_4, and the solvent was removed in vacuo at 40 °C for 4 h. The obtained product was used directly for the next step without further purification.

1.11 5,5'-Bis(4- (allyloxy)phenyl)-3-methyl-4'-tetradecyl-2,2'-bithiophene 14 and 5,5'-bis (4-allyloxyphenyl)-4,4'-dialkyl-2,2'-bithiophenes 9/*n*

Allyl bromide (363 mg, 3 mmol) was added under an argon atmosphere to a mixture of **13** or **8/n** (1 mmol) and K_2CO_3 (552 mg, 4 mmol) in dry CH_3CN (15 mL). 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 Na_2SO_4 and the solvent were evaporated in vacuo. The crude product was purified by chromatography (eluent: petroleum ether/ethyl acetate V / V = 20 / 1) and crystallized from $CHCl_3/CH_3OH$.

5,5'-Bis(4-(allyloxy)phenyl)-3-methyl-4'-tetradecyl-2,2'-bithiophene 14 yield: 50%; yellow wax. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.51-7.49 (d, J = 8.8, 2 H, 2 Ar**H**), 7.38-7.37 (d, J = 8.6, 2 H, 2 Ar**H**), 7.01 (s, 1 H, Ar**H**),7.00(s, 1 H, Ar**H**), 6.97-6.96 (d, J = 8.4, 2 H, 2 Ar**H**), 6.93-6.92 (d, J = 8.5, 2 H, 2 Ar**H**), 6.08-6.05 (m, 2 H, 2 C**H**=), 5.47-5.42 (m, 2 H, C$\mathbf{H}_2$=), 5.33-5.31 (m, 2 H, C$\mathbf{H}_2$=), 4.59-4.57 (m, 4 H , 2 ArOC$\mathbf{H}_2$), 2.64-2.61 (t, J = 6.9, 2 H, ArC$\mathbf{H}_2$), 2.42 (s, 3 H, ArC$\mathbf{H}_3$), 1.57 (m, 2 H, ArCH$_2$C$\mathbf{H}_2$), 1.25 (m, 22 H, 11 C$\mathbf{H}_2$), 0.89-0.86 (t, J = 6.8, 3 H, C$\mathbf{H}_3$).

5,5'-Bis(4-(allyloxy)phenyl)-4,4'-diheptyl-2,2'-bithiophene 9/7 yield: 74%; yellow wax. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.36-7.34 (d, J = 8.6, 2 H, 2 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.96-6.94 (d, J = 8.6, 4 H, 4 Ar**H**), 6.12-6.04 (m, 2 H, 2 C**H**=), 5.47-5.45 (d, J = 17.2, 4 H, 2 C$\mathbf{H}_2$=), 5.33-5.31 (d, J = 10.5, 2 H, C$\mathbf{H}_2$=), 4.57 (m, 4 H, 2 ArOC$\mathbf{H}_2$), 2.60-2.58 (t, J = 7.9, 4 H, 2 ArC$\mathbf{H}_2$), 1.61-1.50 (m, 4 H, 2 ArCH$_2$C$\mathbf{H}_2$), 1.30-1.29 (m, 8 H, 4 C$\mathbf{H}_2$), 0.80-0.78 (t, J = 6.8, 6 H, 2 C$\mathbf{H}_3$).

5,5'-Bis(4-(allyloxy)phenyl)-4,4'-dioctyl-2,2'-bithiophene 9/8 yield: 87%; yellow wax. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.36-7.35 (d, J = 8.3, 4 H, 4 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.96-6.95 (d, J = 8.4, 4 H, 4 Ar**H**), 6.11-6.05 (m, 2 H, 2 C**H**=), 5.46-5.43 (d, J = 17.2, 2 H, C$\mathbf{H}_2$=), 5.33-5.31 (d, J = 10.4, 2 H, C$\mathbf{H}_2$=), 4.58-4.57 (d, J = 4.9, 4 H , 2 ArOC$\mathbf{H}_2$), 2.61-2.57 (t, J = 7.7, 4 H, 2 ArC$\mathbf{H}_2$), 1.61-1.57 (t, J = 6.85, 4 H, 2 ArCH$_2$C$\mathbf{H}_2$), 1.24 (m, 20 H, 10 C$\mathbf{H}_2$), 0.88-0.86 (t, J = 6.4, 6 H, 2 C$\mathbf{H}_3$).

5,5'-Bis(4-(allyloxy)phenyl)-4,4'-didecyl-2,2'-bithiophene 9/10 yield: 89%; yellow wax. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.36-7.35 (d, J = 8.0, 4 H, 4 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.96-6.95 (d, J = 8.1, 4 H, 4 Ar**H**), 6.11-6.06 (m, 2 H, 2 C**H**=), 5.46-5.43 (d, J = 17.4, 2 H, C$\mathbf{H}_2$=), 5.32-5.30 (d, J = 10.5, 2 H, C$\mathbf{H}_2$=), 4.58-4.57 (d, J = 4.5, 4 H, 2 ArOC$\mathbf{H}_2$), 2.60-2.57(t, J = 7.5, 4 H, 2 ArC$\mathbf{H}_2$), 1.62-1.59(t, J = 6.7, 4 H, 2 ArCH$_2$C$\mathbf{H}_2$), 1.24 (m, 28 H, 14 C$\mathbf{H}_2$), 0.89-0.86 (t, J = 6.2, 6 H, 2 C$\mathbf{H}_3$).

5,5'-Bis(4-(allyloxy)phenyl)-4,4'-ditetradecyl-2,2'-bithiophene 9/14 yield: 81%; yellow wax. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.36-7.35 (d, J = 8.5, 4 H, 4 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.96-6.95 (d, J = 8.5, 4 H, 4 Ar**H**), 6.12-6.05 (m, 2 H, 2 C**H**=), 5.46-5.31 (m, 4 H, 2 C$\mathbf{H}_2$=), 2.61-2.57 (t, J = 7.4, 4 H, 2 ArC$\mathbf{H}_2$), 1.61-1.57 (m, 4 H, 2 ArCH$_2$C$\mathbf{H}_2$), 1.25 (m, 44 H, 22 C$\mathbf{H}_2$), 0.89-0.86 (t, J = 6.6, 6 H, 2 C$\mathbf{H}_3$).

5,5'-Bis(4-(allyloxy)phenyl)-4,4'-dihexadecyl-2,2'-bithiophene 9/16 yield: 85%; yellow wax. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.36-7.34 (d, J = 8.6, 4 H, 4 Ar**H**), 7.01

(s, 2 H, 2 Ar**H**), 6.96-6.94 (d, *J* = 8.5, 4 H, 4 Ar**H**), 6.12-6.04 (m, 2 H, 2 C**H**=), 5.45-5.43 (d, *J* = 17.2, 2 H, C$\mathbf{H}_2$=), 5.33-5.31 (d, *J* = 10.5, 2 H, C$\mathbf{H}_2$=), 4.59-4.58 (m, 4 H, 2 ArOC$\mathbf{H}_2$), 2.59 (t, *J* = 7.5, 4 H, 2 ArC$\mathbf{H}_2$), 1.61-1.57 (m, 4 H, 2 ArCH_2C$\mathbf{H}_2$), 1.32-1.26 (m, 52 H, 26 C$\mathbf{H}_2$), 0.89-0.87 (t, *J* = 6.2, 6 H, 3 C$\mathbf{H}_3$).

5,5'-Bis(4-(allyloxy)phenyl)-4,4'-dioctadecyl-2,2'-bithiophene 9/18 yield: 72%; yellow wax. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.39-7.34 (m, 4 H, 4 Ar**H**), 7.29 (s, 1 H, Ar**H**), 7.01 (s, 1 H, Ar**H**), 6.98-6.95 (m, 4 H, 4 Ar**H**), 6.11-6.06 (m, 2 H, 2 C**H**=), 5.46-5.31 (m, 4 H, 2 C$\mathbf{H}_2$=), 4.59-4.58 (d, *J* = 4.6, 4 H, 2 ArOC$\mathbf{H}_2$), 2.64-2.59 (m, 4 H, 2 ArC$\mathbf{H}_2$), 1.60-1.51 (m, 4 H, 2 ArCH_2C$\mathbf{H}_2$), 1.25 (m, 60 H, 30 C$\mathbf{H}_2$), 0.89-0.86 (t, *J* = 6.7, 6 H, 2 C$\mathbf{H}_3$).

1.12 2,5'-Diphenyl-2,5-dithiophene based bolaamphiphiles 2/n and 3/14

9/n or **14** (1 mmol) and NMMNO (1.2 mL, 60% solution in water) were dissolved in acetone. Osmium tetroxide (1.3 mL, 0.004 M solution in *tert*-butanol) was added, and the solution was stirred for 24 h at RT. Afterwards, saturated aqueous Na_2SO_3 solution was added, and the mixture was stirred for 30 min at RT. The mixture was filtered. Ethyl acetate and 10% H_2SO_4 were added into the liquid and the organic layer was separated, washed with saturated $NaHCO_3$ solution and H_2O, dried over Na_2SO_4, and the solvent was evaporated in vacuo. Purification of the product was done by chromatography (eluent: ethyl acetate) and crystallized from $CHCl_3$/CH_3OH (10/1).

2/7: yield: 76%. ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 7.33-7.32 (d, *J* = 8.5, 4 H, 4 Ar**H**), 7.02 (s, 2 H, 2 Ar**H**), 6.99-6.97 (d, *J* = 8.6, 4 H, 4 Ar**H**), 4.84-3.94 (m, 10 H, 2 ArOC$\mathbf{H}_2$, 2 C**H**OH, 2 C$\mathbf{H}_2$OH), 2.60-2.57 (m, 4 H, 2 ArC$\mathbf{H}_2$), 1.60-1.58 (m, 4 H, 2 ArCH_2C$\mathbf{H}_2$), 1.27-1.21 (m, 16 H, 8 C$\mathbf{H}_2$), 0.87-0.85 (t, *J* = 6.1, 6 H, 2 C$\mathbf{H}_3$). ^{13}C-NMR ($CDCl_3$; 500 MHz): δ=158.0 (2 C), 139.2 (2 C)**,** 137.4 (2 C), 135.5 (2 C), 133.9 (2 C), 129.5 (4 C), 125.8 (2 C), 125.0 (2 C), 114.2 (4 C), 69.7 (2 C), 69.0 (2 C), 62.6 (2 C), 30.8-21.9, 13.5 (carbons in alkyl chain). Elemental analysis calcd (%) for $C_{40}H_{54}O_6S_2$ (694.98): C 69.13, H 7.83; Found: C 68.89, H 8.01.

2/8: yield: 78%. ^{1}H NMR (DMSO; 500 MHz): δ = 7.31-7.30 (d, *J* = 8.3, 4 H, 4 Ar**H**), 7.12 (s, 2 H, 2 Ar**H**), 6.99-6.98 (d, *J* = 8.4, 4 H, 4 Ar**H**), 4.02-4.00 (m, 2 H, ArOC$\mathbf{H}_2$), 3.89-3.86 (m, 2 H, ArOC$\mathbf{H}_2$), 3.80-3.79 (m, 2 H, 2 C**H**OH), 3.46-3.44 (m, 4 H, 2 C$\mathbf{H}_2$OH), 2.52-2.49 (m, 4 H, 2 ArC$\mathbf{H}_2$), 1.52 (m, 4 H, 2 ArCH_2C$\mathbf{H}_2$), 1.16 (m, 20 H, 10 C$\mathbf{H}_2$), 0.81-0.79 (t, *J* = 6.4, 6 H, 2 C$\mathbf{H}_3$). ^{13}C-NMR (DMSO; 500 MHz): δ = 159.3 (2 C), 139.4 (2 C)**,** 136.6 (2 C), 134.7 (2 C), 130.8 (4 C), 126.7 (2 C), 126.6 (2 C), 115.6 (4 C), 70.8 (2 C), 70.5 (2 C), 63.6 (2 C), 32.2-22.9, 14.8 (multicarbons in alkyl chains). Elemental analysis calcd (%) for $C_{42}H_{58}O_6S_2$ (723.04): C 69.77, H 8.09; Found: C 69.56, H 8.34.

2/10: yield: 85%. ^{1}H NMR (DMSO; 500 MHz): δ = 7.35-7.33 (d, *J* = 8.5, 4 H, 4 Ar**H**),

7.17 (s, 2 H, 2 Ar**H**), 7.02-7.01 (d, *J* = 8.6, 4 H, 4 Ar**H**), 4.05-4.02 (m, 2 H, ArOC**H**$_2$), 3.92-3.88 (m, 2 H, ArOC**H**$_2$), 3.83-3.80 (m, 2 H, 2 C**H**OH), 3.47-3,45 (m, 4 H, 2 C**H**$_2$OH) 2.58-2.55 (t, *J* =7.3, 4 H, 2 ArC**H**$_2$), 1.56-1.55 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.20-1.16 (m, 28 H, 14 C**H**$_2$), 0.85-0.82 (t, *J* = 6.6, 6 H, 2 C**H**$_3$). ^{13}C-NMR (DMSO; 500 MHz): *δ* = 159.3 (2 C), 139.5 (2 C)**,** 136.7 (2 C), 134.7 (2 C), 130.8 (4 C), 126.8 (2 C), 126.6 (2 C), 115.7 (4 C), 70.8 (2 C), 70.6 (2 C), 63.6 (2 C), 32.2-22.9, 14.8 (carbons in alkyl chains). Elemental analysis calcd (%) for $C_{46}H_{66}O_6S_2$ (779.14): C 70.91, H 8.54; Found: C 70.79, H 8.83.

2/14: yield: 90%. ^{1}H NMR (DMSO; 500 MHz): *δ* = 7.34-7.32 (d, *J* = 8.7, 4 H, 4 Ar**H**), 7.14 (s, 2 H, 2 Ar**H**), 7.01-6.99 (d, *J* = 8.8, 4 H, 4 Ar**H**), 4.98-4.97 (d, *J* = 5.2, 2 H, ArOC**H**$_2$), 4.69-4.67 (m, 2 H, ArOC**H**$_2$), 4.04-3.79 (m, 6 H, 2 C**H**$_2$OH, 2 C**H**OH), 2.57-2.54 (t, *J* = 7.4, 4 H, 2 ArC**H**$_2$), 1.55 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.20-1.14 (m, 44 H, 22 C**H**$_2$), 0.84-0.81 (t, *J* = 6.7, 6 H, 2 C**H**$_3$). ^{13}C-NMR (DMSO; 500 MHz): δ = 158.7 (2 C), 138.6 (2 C)**,** 136.2 (2 C)，134.3 (2 C), 130.1 (4 C), 126.1 (2 C), 125.7 (2 C), 115.0 (4 C), 70.3 (2 C), 70.0 (2 C), 63.1 (2 C), 30.5-22.5, 14.2 (carbons in alkyl chain). Elemental analysis calcd (%) for $C_{54}H_{82}O_6S_2$ (891.36): C 72.76, H 9.27; Found: C 72.52, H 9.51.

2/16: yield: 81%. ^{1}H NMR (DMSO; 500 MHz): *δ* = 7.29-7.27 (d, *J* = 7.6, 4 H, 4 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.96-6.95 (d, *J* = 8.1, 4 H, 4 Ar**H**), 4.99-3.80 (m, 10 H, 2 ArOCH$_2$, 2 C**H**OH, 2 C**H**$_2$OH), 2.65-2.51 (m, 4 H, 2 ArC**H**$_2$), 1.51 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.17 (m, 52 H, 26 C**H**$_2$), 0.81-0.77 (m, 6 H, 2 C**H**$_3$). ^{13}C-NMR (DMSO; 500 MHz): *δ* = 158.5 (2 C), 138.2 (2 C)**,** 136.2 (2 C), 134.3 (2 C), 130.0 (4 C), 126.0 (2 C), 124.9 (2 C), 114.8 (4 C), 70.3 (2 C), 69.8 (2 C), 63.1 (2 C), 31.8-22.5, 13.9 (carbons in alkyl chain). Elemental analysis calcd (%) for $C_{58}H_{90}O_6S_2$ (947.46): C 73.52, H 9.57; Found: C 73.39, H 9.84.

2/18: yield: 75%. ^{1}H NMR ($CDCl_3$; 500 MHz): *δ* = 7.39-7.36 (m, 4 H, 4 Ar**H**), 7.01 (s, 2 H, 2 Ar**H**), 6.99-6.95 (m, 4 H, 4 Ar**H**), 4.15-3.78 (m, 10 H, 2 ArOCH$_2$, 2 C**H**OH, 2 C**H**$_2$OH), 2.61-2.57 (m, 4 H, 2 ArC**H**$_2$), 1.59-1.56 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.25 (m, 60 H, 30 C**H**$_2$), 0.89-0.86 (t, *J* = 6.7, 6 H, 2 C**H**$_3$). ^{13}C-NMR ($CDCl_3$; 500 MHz): *δ* = 158.3 (2 C), 138.4 (2 C)**,** 136.5 (2 C)，135.5 (2 C), 130.9 (4 C), 129.2 (2 C), 128.1 (2 C), 115.0 (4 C), 70.8 (2 C), 69.7 (2 C), 64.1 (2 C), 30.1-23.1, 14.5 (carbons in alkyl chain). Elemental analysis calcd (%) for $C_{62}H_{98}O_6S_2$ (1003.57): C 74.20, H 9.84; Found: C 73.99, H 10.03.

3/14: yield: 80%. ^{1}H NMR (DMSO; 500 MHz): *δ* = 7.55-7.53 (d, *J* = 8.5, 2 H, 2 Ar**H**), 7.36-7.35 (d, *J* = 8.5, 2 H, 2 Ar**H**), 7.25 (s, 1 H, Ar**H**), 7.09 (s, 1 H, Ar**H**), 7.02-7.00 (d, *J* = 8.5, 2 H, 2 Ar**H**), 6.98-6.96 (d, *J* = 8.5, 2 H, 2 Ar**H**), 4.95 (m, 2 H, ArOC**H**$_2$), 4.66 (m, 2 H, ArOC**H**$_2$), 4.04-3.79 (m, 6 H, 2 C**H**OH, 2 C**H**$_2$OH), 2.59-2.57 (m, 2H, ArC**H**$_2$), 2.36 (s, 3 H, ArC**H**$_3$), 1.56-1.55 (m, 2H, ArCH$_2$C**H**$_2$), 1.20, (m, 22 H, 11 C**H**$_2$), 0.83-0.81 (m, 3 H, C**H**$_3$). ^{13}C-NMR (DMSO; 500 MHz): *δ* = 159.0, 158.8,

140.6, 138.7**,** 136.9, 134.9, 133.5, 130.4 (2 C), 129.0 (2 C), 128.0, 127.3, 126.8, 126.2, 126.1, 115.5 (2 C), 115.2 (2 C), 70.3 (2 C), 70.2 (2 C), 63.1 (2 C), 31.6-22.4, 15.8, 14.3 (multicarbons in alkyl chain). Elemental analysis calcd (%) for $C_{41}H_{56}O_6S_2$ (709.01): C 69.45, H 7.96; Found: C 69.12, H 8.18.

2. XRD data

Table S1. Crystallographic data of compounds **2/*n*** and **3/14**.[a]

Comp	T/°C	phase	$2\theta_{obs}$/°	d_{obs}/nm	*hk*	d_{calc}/nm	d_{obs}-d_{calc}	a/nm
2/7	50	Col_{hex}/*p6mm*	3.644	2.42	10	2.43	-0.01	a_{hex} = 2.80
			6.223	1.42	11	1.40	0.02	
			7.129	1.23	20	1.21	0.02	
			20.124	0.46	diff			
2/10	60	Col_{squ}/*p4mm*	3.241	2.73	10	2.73	0.00	a_{squ} = 2.73
			4.577	1.93	11	1.93	0.00	
			6.466	1.37	20	1.36	0.01	
			19.786	0.45	diff			
2/14	40	Col_{squ}/*p4mm*	3.083	2.87	10	2.87	0.00	a_{squ} = 2.87
			4.337	2.04	11	2.03	0.01	
			6.121	1.44	20	1.44	0.00	
			19.530	0.45				
2/16	30	Col_{squ}/*p4gm*	1.766	5.00	11	5.00	0.00	a_{squ} = 7.07
			2.497	3.54	20	3.54	0.00	
			2.773	3.19	21	3.16	0.03	
			3.897	2.27	31	2.24	0.03	
			4.451	1.99	32	1.96	0.03	
			5.117	1.73	40	1.77	0.04	
			19.949	0.45	diff			
2/18	40	Col_{hex}/*p6mm*	2.219	3.98	10	3.98	0.00	a_{hex} = 4.60
			3.838	2.30	11	2.30	0.00	
			4.435	1.99	20	1.99	0.00	
			19.570	0.45	diff			
3/14	50	Col_{squ}/*p4mm*	2.861	3.09	10	3.09	0.00	a_{squ} = 3.09
			4.011	2.20	11	2.19	0.01	
			19.63	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).

The X-ray diffraction patterns were recorded with a 2D detector (HI-STAR, Siemens). Ni filtered and pin hole collimated CuK_α radiation was used. The exposure time was normally 60 min. The sample to detector distance was 8.8 cm and 26.9 cm for the

wide angle and small angle measurements, respectively. Alignment was achieved upon slow cooling (rate: 1 K·min^{-1} – 0.1 K·min^{-1}) of a small droplet of the sample on a glass plate and takes place at the sample–glass or at the sample–air interface, with domains fiber-like disordered around an axis perpendicular to the interface. The samples were held on a temperature-controlled heating stage. The investigations of the solvent induced mesophase of compound **2/8** was done by mixing the compound with an excess of water and heating the mixture to 50 °C

Table S2 Calculations of molecular volumina (V_{mol}), volumina of the hypothetical unit cells (V_{cell}) and number of molecules in these unit cells (n_{cell}) of compounds **2/*n*** and **3/14.** [a]

Comp.	a/nm	V_{cell}/nm^3	V_{mol}/nm^3	f_R	n_{cryst}	n_{liq}	n_{cell}	n_{wall}
1/12	3.04	4.16	0.895	0.34	4.65	3.65	4.15	2.08
2/6	2.81	3.08	0.895	0.35	3.44	2.70	3.07	1.02
2/7	2.80	3.06	0.945	0.38	3.24	2.55	2.90	0.97
2/8			0.995	0.41				
2/10	2.73	3.35	1.094	0.46	3.06	2.40	2.73	1.37
2/12	2.78	3.48	1.193	0.51	2.92	2.29	2.60	1.30
2/14	2.87	3.71	1.292	0.55	2.87	2.26	2.57	1.29
2/16	7.07	22.49	1.391	0.58	16.17	12.71	14.44	1.44
2/18	4.60	8.25	1.491	0.61	5.53	4.35	4.94	1.65
3/14	3.09	4.30	0.970	0.40	4.43	3.48	3.96	1.98

[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 0.45 nm for hexagonal phases; V_{mol} = molecular volume as calculated using crystal volume increments;[S9] 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} = 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} = number of molecules in the cross section of the cylinder walls as calculated from n_{cell}.

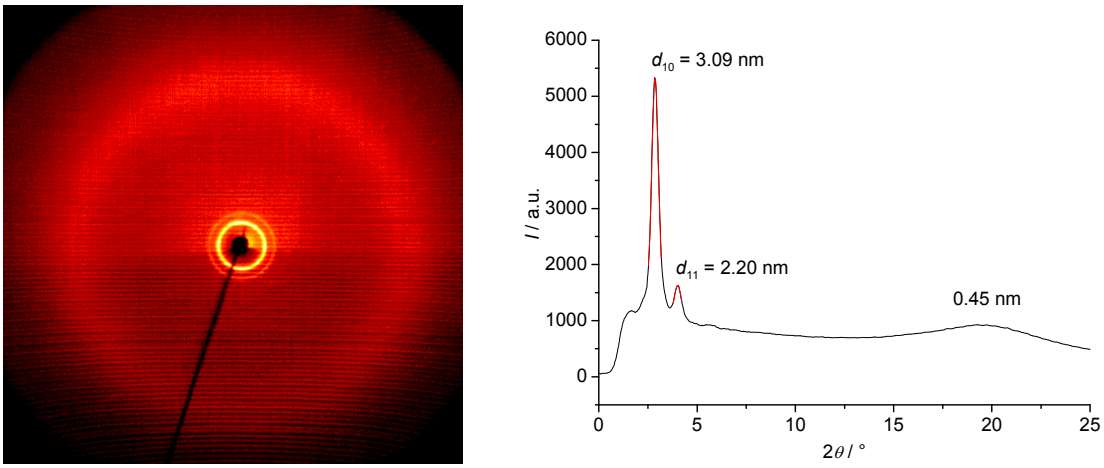


Fig. S1 WAXS diffraction pattern of the $Col_{squ}/p4mm$ phase of compound **3/14** at T = 50 °C and θ-scan of the diffraction pattern.

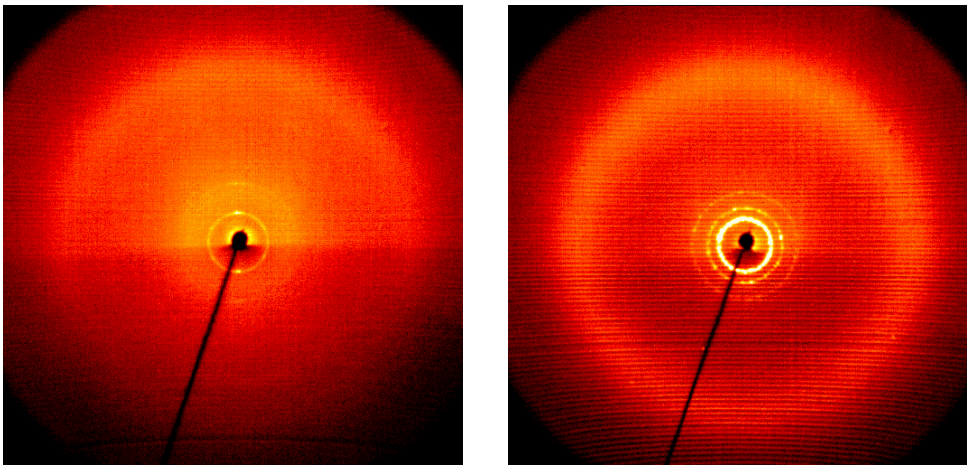


Fig. S2 WAXS diffraction pattern a) of the $Col_{hex}/p6mm$ phase of compound **2/7** at T = 50 °C and b) of the $Col_{squ}/p4mm$ phase of compound **2/10** at T = 60 °C.

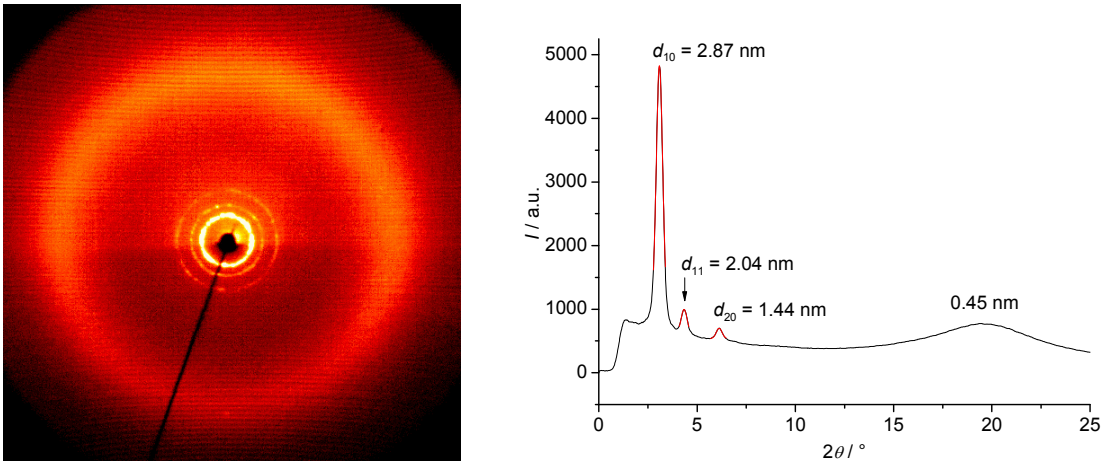


Fig. S3 WAXS diffraction pattern of the $Col_{squ}/p4mm$ phase of compound **2/14** at T = 40 °C and θ-scan of the diffraction pattern.

3. References

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