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Supporting Information

Synthesis and self-assembly of 5,5'-Bis(phenylethynyl)-2,2'-bithiophene-based bolapolyphiles in triangular and square liquid crystalline honeycombs

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1. Synthesis

1.1 General

For the structures of the compounds see Scheme 2 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. 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). The X-ray diffraction patterns of aligned or partially aligned samples were recorded with a 2D detector (HI-STAR, Siemens). Ni filtered and pin hole collimated Cu-K_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 aligned samples were held on a temperature-controlled heating stage.

1.2 3-Alkylthiophenes 2/*n*

Compounds **3/6**[S1,S2] and **3/10**[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 (2/5) yield: 85%; 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 Hz, 2 H, ArC**H**$_2$), 1.63-1.59 (m, 2 H, ArCH$_2$C**H**$_2$), 1.42-1.21 (m, 4 H, 2 C**H**$_2$), 0.89-0.87 (t, J = 6.5 Hz, 3 H, C**H**$_3$).

3-Octylthiophene (2/8) yield: 86%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.22-7.21 (m, 1 H, Ar**H**), 6.93-6.90 (m, 2 H, 2 Ar**H**), 2.63-2.60 (t, J = 7.6 Hz, 2 H, ArC**H**$_2$), 1.64-1.59 (m, 2 H, ArCH$_2$C**H**$_2$), 1.40-1.26 (m, 10 H, 5 C**H**$_2$), 0.89-0.86 (t, J = 6.7 Hz, 3 H, C**H**$_3$).

3-Decylthiophene (2/10) yield: 78%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.21-7.19 (m, 1 H, Ar**H**), 6.91-6.86 (m, 2 H, 2 Ar**H**), 2.61-2.58 (t, J = 7.6 Hz, 2 H, ArC**H**$_2$), 1.61-1.58 (t, J = 6.5 Hz, 2 H, ArCH$_2$C**H**$_2$), 1.42-1.26 (m, 14 H, 7 C**H**$_2$), 0.89-0.86 (t, J = 6.6 Hz, 3 H, C**H**$_3$).

3-Dodecylthiophene (2/12) yield: 82%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.24-7.22 (m, 1 H, Ar**H**), 6.94-6.91 (m, 2 H, 2 Ar**H**), 2.63-2.60 (t, J = 7.7 Hz, 2 H, ArC**H**$_2$), 1.63-1.58 (m, 2 H, ArCH$_2$C**H**$_2$), 1.41-1.26 (m, 18 H, 9 C**H**$_2$), 0.89-0.87 (t, J = 6.6 Hz, 3 H, C**H**$_3$).

3-Tetradecylthiophene (2/14) 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 Hz, 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 Hz, 3 H, C**H**$_3$).

3-Octadecylthiophene (2/18) yield: 75%; yellow wax. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.24-7.22 (m, 1 H, Ar**H**), 6.94-6.91 (m, 2 H, 2 Ar**H**), 2.63-2.60 (t, J = 7.7 Hz, 2 H, ArC**H**$_2$), 1.62-1.58 (m, 2 H, ArCH$_2$C**H**$_2$), 1.40-1.25 (m, 30 H, 15 C**H**$_2$), 0.89-0.87 (t, J = 6.6 Hz, 3 H, C**H**$_3$).

1.3 3-Alkyl-2-iodothiophene 3/*n*

The synthesis of compounds **3/*n*** was carried out as described in ref.[S5]

2-Iodo-3-pentylthiophene (3/5) yield: 95%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.36-7.34 (d, J = 5.3 Hz, 1 H, Ar**H**), 6.74-6.73 (d, J = 5.5 Hz, 1 H, Ar**H**), 2.55-2.52 (t, J = 7.7 Hz, 2 H, ArC**H**$_2$), 1.59-1.51 (m, 2 H, ArCH$_2$C**H**$_2$), 1.41-1.24 (m, 4 H, 2 C**H**$_2$), 0.91-0.88 (t, J = 6.8 Hz, 3 H, C**H**$_3$).

2-Iodo-3-octylthiophene (3/8) yield: 92%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.36-7.35 (d, J = 5.2 Hz, 1 H, Ar**H**), 6.74-6.73 (d, J = 5.2 Hz, 1 H, Ar**H**), 2.55-2.52 (t, J =7.4 Hz, 2 H, ArC**H**$_2$), 1.56-1.53 (m, 2 H, ArCH$_2$C**H**$_2$), 1.31-1.27 (m, 10 H, 5 C**H**$_2$), 0.89-0.87 (t, J = 5.6 Hz, 3 H, C**H**$_3$).

3-Decyl-2-iodothiophene (3/10) yield: 94%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.37-7.36 (d, J = 5.3 Hz, 1 H, Ar**H**), 6.75-6.74 (d, J = 5.2 Hz, 1 H, Ar**H**), 2.55-2.52 (t, J =7.5 Hz, 2 H, ArC**H**$_2$), 1.61-1.54 (m, 2 H, ArCH$_2$C**H**$_2$), 1.41-1.24 (m, 14 H, 7 C**H**$_2$), 0.89-0.87 (t, J = 6.1 Hz, 3 H, C**H**$_3$).

3-Dodecyl-2-iodothiophene (3/12) yield: 95%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.37-7.36 (d, J = 5.4 Hz, 1 H, Ar**H**), 6.75-6.74 (d, J = 5.4 Hz, 1 H, Ar**H**), 2.56-2.53 (t, J =7.7 Hz, 2 H, ArC**H**$_2$), 1.56-1.54 (t, J =7.2 Hz, 2 H, ArCH$_2$C**H**$_2$), 1.41-1.23 (m, 18 H, 9 C**H**$_2$), 0.90-0.87 (t, J = 6.5 Hz, 3 H, C**H**$_3$).

2-Iodo-3-tetradecylthiophene (3/14) yield: 92%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.37-7.36 (d, J = 5.4 Hz, 1 H, Ar**H**), 6.75-6.74 (d, J = 5.4 Hz, 1 H, Ar**H**), 2.56-2.53 (t, J = 7.6 Hz, 2 H, ArC**H**$_2$), 1.57-1.55 (t, J = 7.1 Hz, 2 H, ArCH$_2$C**H**$_2$), 1.40-1.23 (m, 22 H, 11 C**H**$_2$), 0.89-0.86 (t, J = 6.4 Hz, 3 H, C**H**$_3$).

2-Iodo-3-octadecylthiophene (3/18) yield: 90%; white solid, m.p. 41-43 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.38-7.37 (d, J = 5.4 Hz, 1 H, Ar**H**), 6.75-6.74 (d, J = 5.4 Hz, 1 H, Ar**H**), 2.56-2.53 (t, J = 7.6 Hz, 2 H, ArC**H**$_2$), 1.58-1.56 (m, 2 H, ArCH$_2$C**H**$_2$), 1.41-1.23 (m, 30 H, 15 C**H**$_2$), 0.89-0.87 (t, J = 6.5 Hz, 3 H, C**H**$_3$).

1.4 1-Allyloxy-4-iodobenzene (5)

The synthesis of compound **5** was carried out as described in ref.[S6] Yield: 92%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54-7.52 (d, J = 8.6 Hz, 2 H, 2 Ar**H**), 6.73-6.71 (d, J = 8.7 Hz, 2 H, 2 Ar**H**), 6.05-5.98 (m, 1 H, C**H**=CH_2), 5.40-5.37 (d, J = 17.1 Hz, 1 H, CH=C**H**$_2$), 5.26-5.24 (d, J = 10.5 Hz, 1 H, CH=C**H**$_2$), 4.52-4.51 (d, J = 4.9 Hz, 2 H, ArOC**H**$_2$).

1.5 3-(4-Iodophenoxy)propane-1,2-diol (6)

The synthesis of compound **6** was carried out as described in ref.[S6] Yield: 80%; colorless crystal; m.p. 94-95°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57-7.56 (d, J = 8.3 Hz, 2 H, 2 Ar**H**), 6.70-6.69 (d, J = 8.1 Hz, 2 H, 2 Ar**H**), 4.10-4.09 (m, 1 H, ArOC**H**$_2$), 4.01-4.00 (m, 2 H, ArOC**H**$_2$, C**H**$_2$OH), 3.85-3.83 (m, 1 H, C**H**$_2$OH), 3.75-3.73 (m, 1 H, C**H**OH).

1.6 4-(4-Iodophenoxymethyl)-2,2-dimethyl-1,3-dioxolane (7)

The synthesis of compound **7** was carried out as described in ref.[S6] Yield: 96%; white solid; m.p. 41-42°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56-7.54 (d, J = 8.2 Hz, 2 H, 2 Ar**H**), 6.70-6.69 (d, J = 8.2 Hz, 2 H, 2 Ar**H**), 4.48-4.45 (m, 1 H, C**H**O), 4.17-4.15 (m, 1 H, ArOC**H**$_2$), 4.02-4.00 (m, 1 H, C**H**$_2$O), 3.92-3.87 (m, 2 H, ArOC**H**$_2$, C**H**$_2$O), 1.46 (s, 3 H, OCC**H**$_3$), 1.40 (s, 3 H, OCC**H**$_3$).

1.7 4-{4-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]phenyl}-2-methylbut-3-yn-2-ol (8)

The synthesis of compound **8** was carried out as described in ref.[S6] Yield: 89 %; yellow solid; m.p. 57-58°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.35-7.34 (d, J = 7.6 Hz, 2 H, 2 Ar**H**), 6.84-6.83 (d, J = 7.7 Hz, 2 H, 2 Ar**H**), 4.49-4.47 (m, 1 H, C**H**O), 4.17-4.15 (m, 1 H, ArOC**H**$_2$), 4.06-4.03 (m, 1 H, C**H**$_2$O), 3.95-3.89 (m, 2 H, ArOC**H**$_2$, C**H**$_2$O), 1.68 (s, 6 H, 2 HOCC**H**$_3$), 1.47 (s, 3 H, OCC**H**$_3$), 1.41 (s, 3 H, OCC**H**$_3$).

1.8 4-(4-Ethynylphenoxymethyl)-2,2-dimethyl-1,3-dioxolane (9)

The synthesis of compound **9** was carried out as described in ref.[S6] Yield: 88 %; yellow liquid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43-7.41 (d, J = 8.7 Hz, 2 H, 2 Ar**H**), 6.86-6.84 (d, J = 8.7 Hz, 2 H, 2 Ar**H**), 4.49-4.45 (m, 1 H, C**H**O), 4.17-4.14 (m, 1 H, ArOC**H**$_2$), 4.06-4.03 (m, 1 H, C**H**$_2$O), 3.95-3.92 (m, 1 H, ArOC**H**$_2$), 3.90-3.87 (m, 1 H, C**H**$_2$O), 3.01 (s, 1 H, C≡C**H**), 1.46 (s, 3 H, OCC**H**$_3$), 1.40 (s, 3 H, OCC**H**$_3$).

1.9 Compounds 10/*n*

Compounds **10/*n*** were prepared by the related literature procedure of Sonogashira reaction.[S7] Under an argon atmosphere, A mixture of 3-alkyl-2-iodothiophene (**3/*n***) (3.0 mmol) and 4-[(4-Ethynylphenoxy)methyl]-2,2-dimethyl-1,3-dioxolane (**9**) (696 mg, 3.0 mmol) was dissolved in dry THF (10 mL) and dry triethylamine (5 mL) under a nitrogen atmosphere. Then $Pd(PPh_3)_4$ (50 mg, 0.04 mmol), CuI (30 mg, 0.16 mmol) was added, and the mixture was stirred over night at room temperature. Ethyl acetate (50 mL) was added, and the mixture was washed with brine

(3×20 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography (petroleum ether : ethyl acetate = 7: 1).

10/5: yield: 85%; yellow-brown liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.42 (d, J = 8.7 Hz, 2 H, 2 Ar**H**), 7.15-7.14 (d, J = 5.2 Hz, 1 H, Ar**H**), 6.89-6.86 (m, 3 H, 3 Ar**H**), 4.49-3.88 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.75-2.72 (t, J = 7.7 Hz, 2 H, ArC**H**$_2$), 1.68-1.63 (m, 2 H, ArCH$_2$C**H**$_2$), 1.47 (s, 3 H, OCC**H**$_3$), 1.40 (s, 3 H, OCC**H**$_3$), 1.35-1.32 (m, 4 H, 2 C**H**$_2$), 0.91-0.88 (t, J = 6.6 Hz, 3 H, C**H**$_3$).

10/8: yield: 81%; yellow-brown liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43-7.41 (d, J = 8.6 Hz, 2 H, 2 Ar**H**), 7.14-7.13 (d, J = 5.1 Hz, 1 H, Ar**H**), 6.88-6.85 (m, 3 H, 3 Ar**H**), 4.49-3.87 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.75-2.72 (t, J = 7.5 Hz, 2 H, ArC**H**$_2$), 1.66-1.59 (m, 2 H, ArCH$_2$C**H**$_2$), 1.46 (s, 3 H, OCC**H**$_3$), 1.40 (s, 3 H, OCC**H**$_3$), 1.33-1.25 (m, 10 H, 5 C**H**$_2$), 0.87-0.85 (t, J = 6.1 Hz, 3 H, C**H**$_3$).

10/10: yield: 82%; yellow-brown liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43-7.42 (d, J = 8.5 Hz, 2 H, 2 Ar**H**), 7.14-7.13 (d, J = 5.1 Hz, 1 H, Ar**H**), 6.88-6.86 (m, 3 H, 3 Ar**H**), 4.50-3.88 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.75-2.72 (t, J = 7.6 Hz, 2 H, ArC**H**$_2$), 1.65-1.63 (t, J = 6.5 Hz, 2 H, ArCH$_2$C**H**$_2$), 1.47 (s, 3 H, OCC**H**$_3$), 1.40 (s, 3 H, OCC**H**$_3$), 1.32-1.24 (m, 14 H, 7 C**H**$_2$), 0.88-0.85 (t, J = 6.6 Hz, 3 H, C**H**$_3$).

10/12: yield: 80%; yellow-brown liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43-7.41 (d, J = 8.6 Hz, 2 H, 2 Ar**H**), 7.13-7.12 (d, J = 5.1 Hz, 1 H, Ar**H**), 6.88-6.85 (m, 3 H, 3 Ar**H**), 4.48-3.87 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.75-2.72 (t, J = 7.5 Hz, 2 H, ArC**H**$_2$), 1.65-1.63 (t, J = 6.6 Hz, 2 H, ArCH$_2$C**H**$_2$), 1.46 (s, 3 H, OCC**H**$_3$), 1.40 (s, 3 H, OCC**H**$_3$), 1.32-1.24 (m, 18 H, 9 C**H**$_2$), 0.89-0.86 (t, J = 6.5 Hz, 3 H, C**H**$_3$).

10/14: yield: 77%; yellow-brown liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43-7.41 (d, J = 8.7 Hz, 2 H, 2 Ar**H**), 7.14-7.13 (d, J = 5.1 Hz, 1 H, Ar**H**), 6.88-6.85 (m, 3 H, 3 Ar**H**), 4.48-3.87 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.74-2.71 (t, J = 7.6 Hz, 2 H, ArC**H**$_2$), 1.65-1.61 (m, 2 H, ArCH$_2$C**H**$_2$), 1.46 (s, 3 H, OCC**H**$_3$), 1.40 (s, 3 H, OCC**H**$_3$), 1.32-1.23 (m, 22 H, 11 C**H**$_2$), 0.88-0.85 (t, J = 6.5 Hz, 3 H, C**H**$_3$).

10/18: yield: 84%; white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.42 (d, J = 8.6 Hz, 2 H, 2 Ar**H**), 7.16-7.15 (d, J = 5.1 Hz, 1 H, Ar**H**), 6.89-6.86 (m, 3 H, 3 Ar**H**), 4.50-3.89 (m, 5 H, ArOC**H**$_2$, OC**H**, OC**H**$_2$), 2.75-2.72 (t, J = 7.4 Hz, 2 H, ArC**H**$_2$), 1.66-1.63 (t, J = 6.6 Hz, 2 H, ArCH$_2$C**H**$_2$), 1.47 (s, 3 H, OCC**H**$_3$), 1.41 (s, 3 H, OCC**H**$_3$), 1.33-1.25 (m, 30 H, 15 C**H**$_2$), 0.89-0.86 (t, J = 6.6 Hz, 3 H, C**H**$_3$).

1.10 Compounds 11/*n*

Under an argon atmosphere, compound (**10/*n***) (2.4 mmol) was dissolved in anhydrous THF (10 mL) and cooled to -60 °C, then n-BuLi (1.6 M in n-hexane, 1.6 mL, 2.6 mmol) was added dropwise and the solution was stirred for 30 min. The solution was warmed slowly to -40 °C, then

anhydrous powdered $CuCl_2$ (324 mg, 2.4 mmol) was added in one portion. The mixture was stirred for 12 h at room temperature. The mixture was poured into 20 mL of water and extracted with diethyl ether (3×20 mL). The combined organic phase was washed with water and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo. The residuewas purified by column chromatography (petroleum ether : ethyl acetate = 7 : 1).

11/5: yield: 80%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.42 (d, J = 8.7 Hz, 4 H, 4 Ar**H**), 6.94 (s, 2 H, 2 Ar**H**), 6.90-6.89 (d, J = 8.7 Hz, 4 H, 4 Ar**H**), 4.50-3.90 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.71-2.68 (t, J = 7.7 Hz, 4 H, 2 ArC**H**$_2$), 1.68-1.66 (t, J = 7.0 Hz, 4 H, 2 ArCH$_2$C**H**$_2$), 1.47 (s, 6 H, 2 OCC**H**$_3$), 1.41 (s, 6 H, 2 OCC**H**$_3$), 1.38-1.30 (m, 8 H, 4 C**H**$_2$), 0.92-0.89 (t, J = 6.7 Hz, 6 H, 2 C**H**$_3$).

11/8: yield: 78%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.42 (d, J = 8.0 Hz, 4 H, 4 Ar**H**), 6.93 (s, 2 H, 2 Ar**H**), 6.90-6.88 (d, J = 8.0 Hz, 4 H, 4 Ar**H**), 4.50-3.89 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.71-2.68 (t, J = 7.4 Hz, 4 H, 2 ArC**H**$_2$), 1.67-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.47 (s, 6 H, 2 OCC**H**$_3$), 1.41 (s, 6 H, 2 OCC**H**$_3$), 1.35-1.26 (m, 20 H, 10 C**H**$_2$), 0.88-0.85 (m, 6 H, 2 C**H**$_3$).

11/10: yield: 75%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.42 (d, J = 8.0 Hz, 4 H, 4 Ar**H**), 6.93 (s, 2 H, 2 Ar**H**), 6.90-6.88 (d, J = 8.1 Hz, 4 H, 4 Ar**H**), 4.50-3.89 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.71-2.68 (t, J = 7.0 Hz, 4 H, 2 ArC**H**$_2$), 1.68-1.60 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.47 (s, 6 H, 2 OCC**H**$_3$), 1.41 (s, 6 H, 2 OCC**H**$_3$), 1.35-1.24 (m, 28 H, 14 C**H**$_2$), 0.88-0.86 (t, J = 5.1 Hz, 6 H, 2 C**H**$_3$).

11/12: yield: 71%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.42 (d, J = 8.5 Hz, 4 H, 4 Ar**H**), 6.93 (s, 2 H, 2 Ar**H**), 6.90-6.88 (d, J = 8.5 Hz, 4 H, 4 Ar**H**), 4.50-3.90 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.71-2.68 (t, J = 7.5 Hz, 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**$_3$), 1.41 (s, 6 H, 2 OCC**H**$_3$), 1.35-1.25 (m, 36 H, 18 C**H**$_2$), 0.89-0.86 (t, J = 6.4 Hz, 6 H, 2 C**H**$_3$).

11/14: yield: 65%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.42 (d, J = 8.6 Hz, 4 H, 4 Ar**H**), 6.93 (s, 2 H, 2 Ar**H**), 6.90-6.88 (d, J = 8.7 Hz, 4 H, 4 Ar**H**), 4.50-3.90 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.71-2.68 (t, J = 7.4 Hz, 4 H, 2 ArC**H**$_2$), 1.66-1.64 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.47 (s, 6 H, 2 OCC**H**$_3$), 1.41 (s, 6 H, 2 OCC**H**$_3$), 1.35-1.25 (m, 22 H, 11 C**H**$_2$), 0.89-0.86 (t, J = 6.7 Hz, 6 H, 2 C**H**$_3$).

11/18: yield: 67%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.42 (d, J = 8.6 Hz, 4 H, 4 Ar**H**), 6.93 (s, 2 H, 2 Ar**H**), 6.90-6.88 (d, J = 8.7 Hz, 4 H, 4 Ar**H**), 4.50-3.89 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.71-2.68 (t, J = 7.5 Hz, 4 H, 2 ArC**H**$_2$), 1.67-1.64 (t, J = 6.6 Hz, 4 H, 2 ArCH$_2$C**H**$_2$), 1.47 (s, 6 H, 2 OCC**H**$_3$), 1.41 (s, 6 H, 2 OCC**H**$_3$), 1.35-1.25 (m, 60 H, 30 C**H**$_2$), 0.89-0.86 (t, J = 6.4 Hz, 6 H, 2 C**H**$_3$).

1.11 Bolapolyphiles 2ET/*n*

A mixture of **11/*n*** (0.5 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), then dried over anhydrous Na_2SO_4. The solvent was removed in *vacuo*. The product was purified by preparative centrifugal thin layer chromatography (petroleum ether : acetone = 4 : 3) and repeated crystallized from petroleum ether : ethyl acetate = 1 : 1.

2ET/5: yield: 67%; yellow solid. ^{1}H NMR ($CDCl_3$+DMSO, 500 MHz): δ = 7.42-7.40 (d, J = 8.3 Hz, 4 H, 4 Ar**H**), 6.96 (s, 2 H, 2 Ar**H**), 6.93-6.92 (d, J = 8.2 Hz, 4 H, 4 Ar**H**), 4.58-4.57 (d, J = 3.4 Hz, 2 H, ArOC**H**$_2$), 4.28-4.27 (d, J = 4.9 Hz, 2 H, ArOC**H**$_2$), 4.09-4.00 (m, 6 H, 2 C**H**$_2$OH, 2 C**H**OH), 3.69-3.64 (m, 4 H, 2 CH$_2$O**H**, 2 CHO**H**), 2.71-2.68 (t, J = 7.6 Hz, 4 H, 2 ArC**H**$_2$), 1.68-1.66 (t, J = 6.5 Hz, 4 H, 2 ArCH$_2$C**H**$_2$), 1.37-1.33 (m, 8 H, 4 C**H**$_2$), 0.91-0.89 (m, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$+DMSO, 125 MHz): 159.3, 148.4, 136.4, 132.8, 125.0, 117.8, 115.1, 115.0, 96.9, 81.1, 70.4, 69.6, 63.5, 31.5-22.5, 14.2 (multicarbons in alkyl chains); Elemental analysis calcd (%) for $C_{40}H_{46}O_6S_2$ (686.92): C 69.94, H 6.75; Found: C 69.85, H 6.78.

2ET/8: yield: 61%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.42 (d, J = 8.4 Hz, 4 H, 4 Ar**H**), 6.92 (s, 2 H, 2 Ar**H**), 6.89-6.88 (d, J = 8.6 Hz, 4 H, 4 Ar**H**), 4.11-4.03 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.85-3.75 (m, 4 H, 2 C**H**$_2$OH), 2.74 (s, 2 H, 2 CH$_2$O**H**), 2.71-2.68 (t, J = 7.6 Hz, 4 H, 2 ArC**H**$_2$), 2.20 (s, 2 H, 2 CHO**H**), 1.67-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.35-1.26 (m, 20 H, 10 C**H**$_2$), 0.88-0.85 (m, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): 158.9, 148.8, 137.0, 133.2, 125.2, 118.1, 116.5, 115.1, 96.7, 81.8, 70.8, 69.6, 64.0, 32.3-23.1, 14.5 (multicarbons in alkyl chains); Elemental analysis calcd (%) for $C_{46}H_{58}O_6S_2$ (771.08): C 71.65, H 7.58; Found: C 71.58, H 7.61.

2ET/10: yield: 65%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.45-7.44 (d, J = 8.7 Hz, 4 H, 4 Ar**H**), 6.94 (s, 2 H, 2 Ar**H**), 6.91-6.89 (d, J = 8.7 Hz, 4 H, 4 Ar**H**), 4.15-4.07 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.89-3.75 (m, 4 H, 2 C**H**$_2$OH), 2.71-2.68 (t, J = 7.6 Hz, 4 H, 2 ArC**H**$_2$), 2.58-2.57 (m, 2 H, 2 CH$_2$O**H**), 1.99-1.97 (m, 2 H, 2 CHO**H**), 1.68-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.35-1.25 (m, 28 H, 14 C**H**$_2$), 0.89-0.86 (t, J = 6.5 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): 158.9, 148.8, 137.0, 133.3, 125.2, 118.1, 116.5, 115.1, 96.7, 81.8, 70.7, 69.7, 64.0, 32.3-23.1, 14.5 (multicarbons in alkyl chains); Elemental analysis calcd (%) for $C_{50}H_{66}O_6S_2$ (827.19): C 72.60, H 8.04; Found: C 72.53, H 8.06.

2ET/12: yield: 67%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.42-7.40 (d, J = 8.6 Hz, 4 H, 4 Ar**H**), 6.90 (s, 2 H, 2 Ar**H**), 6.87-6.86 (d, J = 8.7 Hz, 4 H, 4 Ar**H**), 4.10-4.02 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.83-3.72 (m, 4 H, 2 C**H**$_2$OH), 2.97-2.96 (m, 2 H, 2 CH$_2$O**H**), 2.70-2.67 (t, J = 7.6 Hz, 4 H, 2 ArC**H**$_2$), 2.48 (s, 2 H, 2 CHO**H**), 1.67-1.63 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.35-1.25 (m, 36 H, 18 C**H**$_2$), 0.89-0.86 (t, J = 6.5 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): 159.0, 148.7, 137.0, 133.2, 125.2, 118.2, 116.7, 115.2, 96.7, 81.8, 70.9, 69.8, 64.1, 32.3-23.0, 14.4 (multicarbons in alkyl chains); Elemental analysis calcd (%) for $C_{54}H_{74}O_6S_2$ (883.29): C 73.43, H 8.44; Found: C 73.37, H 8.46.

2ET/14: yield: 67%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43-7.41 (d, J = 8.4 Hz, 4 H, 4 Ar**H**), 6.91 (s, 2 H, 2 Ar**H**), 6.88-6.87 (d, J = 8.4 Hz, 4 H, 4 Ar**H**), 4.12-4.04 (m, 6 H, 2 ArOC**H**$_2$,

2 C**H**OH), 3.84-3.75 (m, 4 H, 2 C**H**$_2$OH), 2.91 (s, 2 H, 2 CH$_2$O**H**), 2.70-2.67 (t, J = 7.5 Hz, 4 H, 2 ArC**H**$_2$), 2.41 (s, 2 H, 2 CHO**H**), 1.67-1.64 (t, J = 6.5 Hz, 4 H, 2 ArCH$_2$C**H**$_2$), 1.34-1.24 (m, 22 H, 11 C**H**$_2$), 0.89-0.86 (t, J = 6.4 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): 159.0, 148.8, 137.0, 133.3, 125.2, 118.1, 116.5, 115.1, 96.7, 81.8, 70.8, 69.6, 64.0, 32.3-23.1, 14.5 (multicarbons in alkyl chains); Elemental analysis calcd (%) for $C_{58}H_{82}O_6S_2$ (939.40): C 74.16, H 8.80; Found: C 74.09, H 8.83.

2ET/18: yield: 60%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.42-7.40 (d, J = 8.4 Hz, 4 H, 4 Ar**H**), 6.89 (s, 2 H, 2 Ar**H**), 6.86-6.85 (d, J = 8.5 Hz, 4 H, 4 Ar**H**), 4.13-4.01 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.85-3.73 (m, 4 H, 2 C**H**$_2$OH), 3.47 (s, 2 H, 2 CH$_2$O**H**), 3.04 (s, 2 H, 2 CHO**H**), 2.69-2.66 (t, J = 7.2 Hz, 4 H, 2 ArC**H**$_2$), 1.65-1.63 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.34-1.25 (m, 60 H, 30 C**H**$_2$), 0.89-0.87 (t, J = 6.5 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): 158.8, 148.8, 137.0, 133.3, 125.1, 118.0, 116.5, 115.0, 96.7, 81.8, 70.9, 69.6, 64.0, 32.4-23.1, 14.5 (multicarbons in alkyl chains); Elemental analysis calcd (%) for $C_{66}H_{98}O_6S_2$ (1051.61): C 75.38, H 9.39; Found: C 75.31, H 9.41.

2. Additional figures

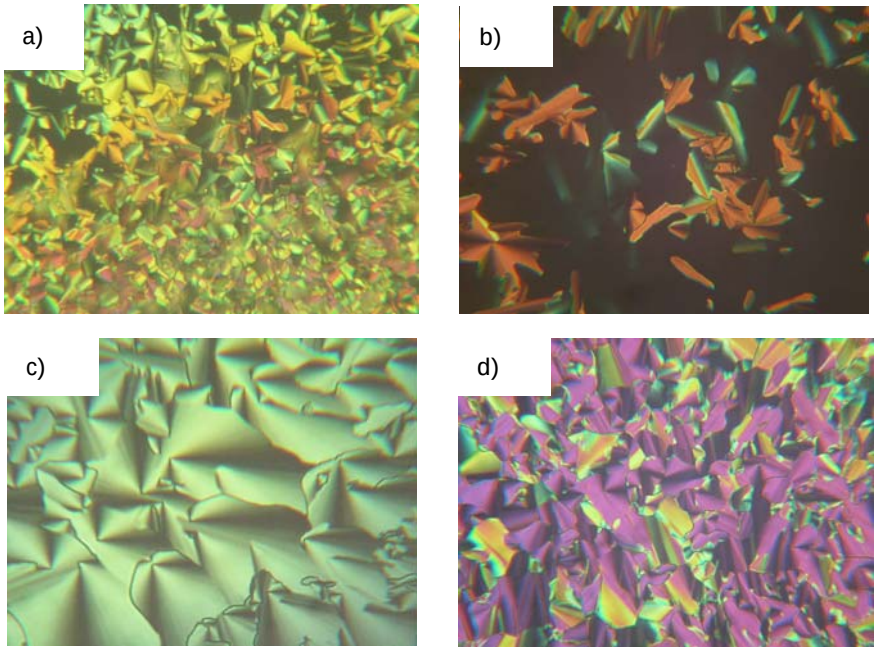


Fig. S1 Representative textures as seen between crossed polarizers: (a) Col$_{hex}$Δ/*p6mm* phase of compound **2ET/8** at T = 95 ºC; (b) Col$_{hex}$Δ/*p6mm* phase of compound **2ET/10** at T = 100 ºC; (c) Col$_{hex}$Δ/*p6mm* phase of compound **2ET/12** at T = 85 ºC; (d) Col$_{squ}$/*p4mm* phase of compound **2ET/14** at T = 60 ºC (dark areas represent homeotropically aligned region).

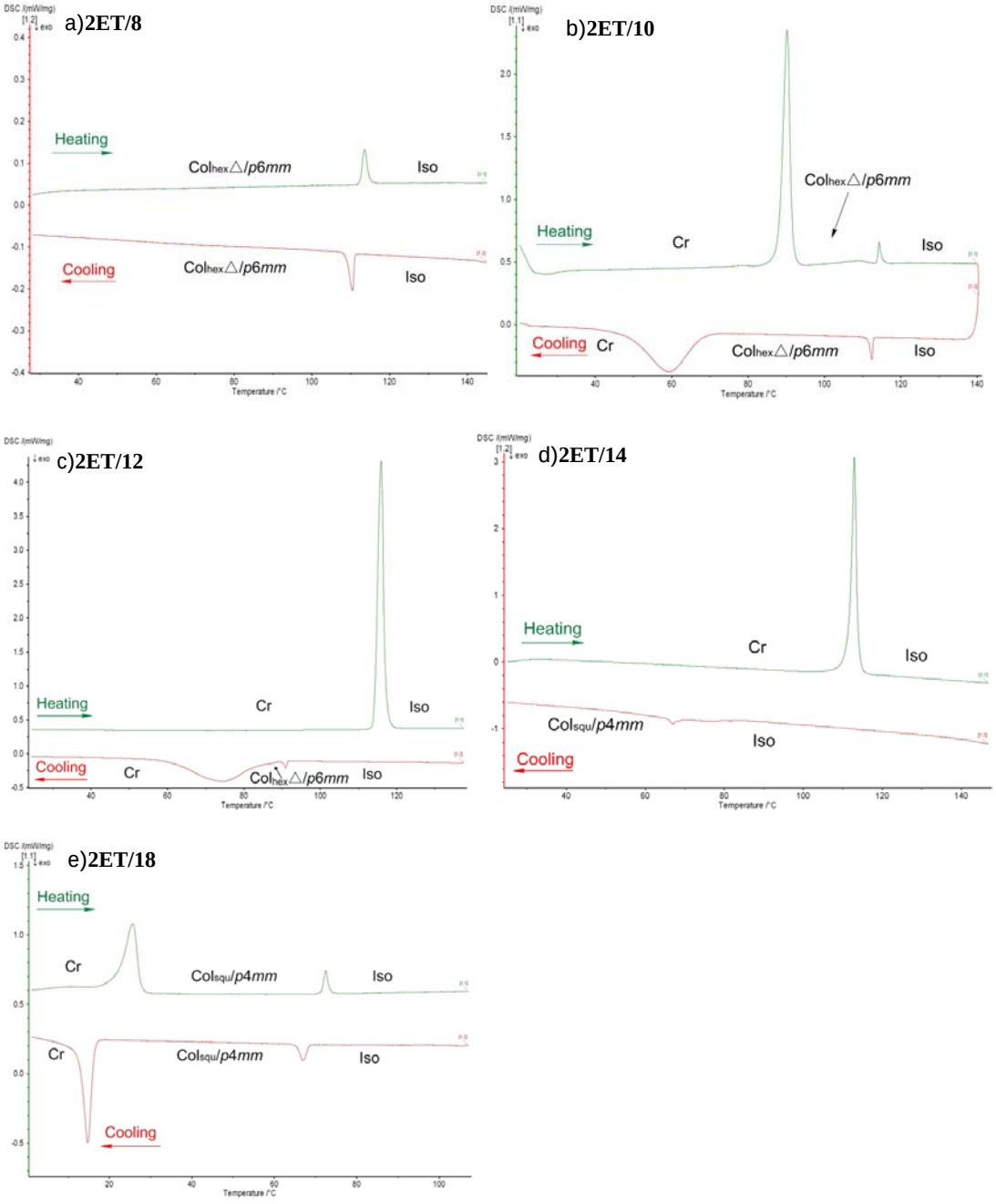
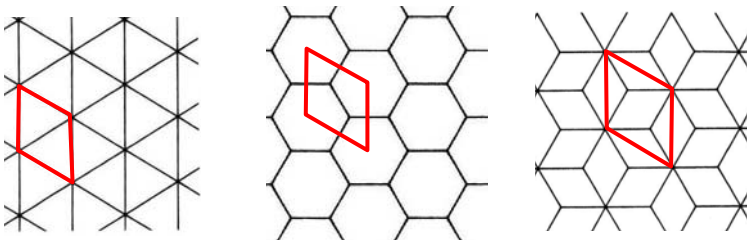


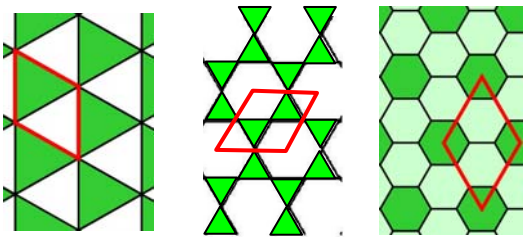
Fig. S2 DSC heating and cooling scans of compounds **2ET/*n*** (5 K min^{-1}, second scans).

Simple tilings (identical cells)



$a_{hex} = L_{mol}$ $a_{hex} = 3^{1/2} L_{mol}$ $a_{hex} = 3^{1/2} L_{mol}$

Two color tilings (two different kinds of cells)



$a_{hex} = L_{mol}$ $a_{hex} = 2 L_{mol}$ $a_{hex} = 3 L_{mol}$

Fig. S3 Tiling patterns of LC honeycombs with hexagonal symmetry (*p6mm* with exception of the two-color triangle tiling which has trigonal *p*3*m*1 symmetry) and the relations between lattice parameter a_{hex} and length of the rod-like molecular backbone L_{mol}. With exception of the hexagonal rhomb tiling all these tiling patterns have been found experimentally (see references given in the main text).

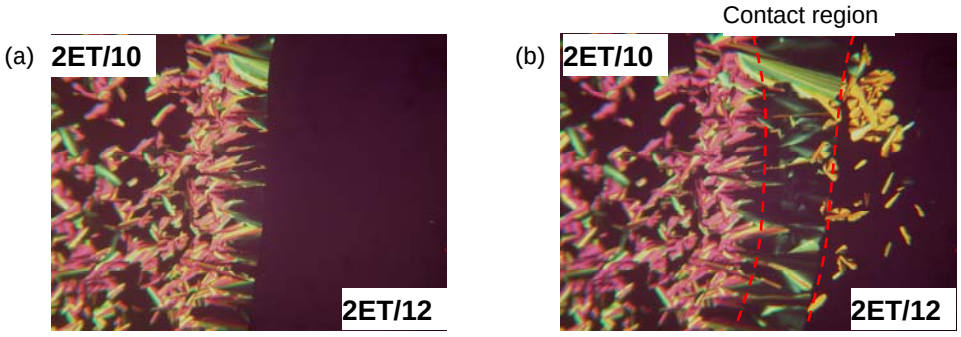


Fig. S4 Contact region between the triangular honeycomb of **2ET/10** and **2ET/12** (a) at T = 100 °C and (b) at T = 92 °C, which shows the growth of **2ET/12** from left to right.

3. Additional XRD data

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

Comp.	T/°C	phase	$2\theta_{obs}$/°	d_{obs}/nm	*hk*	d_{calc}/nm	d_{obs}-d_{calc}	a/nm
2ET/8	100	$Col_{hex}\Delta$/*p6mm*	3.192	2.77	10	2.77	0.00	3.20
			6.267	1.41	20	1.39	0.02	
			19.43	0.46	diff			
2ET/10	100	$Col_{hex}\Delta$/*p6mm*	3.190	2.77	10	2.77	0.00	3.20
			6.242	1.42	20	1.39	0.03	
			19.17	0.46	diff			
2ET/10	25	$Col_{hex}\Delta$/*p6mm*	3.140	2.81	10	2.81	0.00	3.25
			6.252	1.41	20	1.41	0.00	
			20.65	0.43	diff			
2ET/14	25	Col_{squ}/*p4mm*	2.802	3.15	10	3.15	0.00	3.15
			3.958	2.23	11	2.23	0.00	
			5.600	1.58	20	1.58	0.00	
			20.37	0.44	diff			
2ET/18	60	Col_{squ}/*p4mm*	2.717	3.25	10	3.25	0.00	3.25
			3.812	2.32	11	2.30	0.02	
			5.447	1.62	20	1.63	-0.01	
			19.49	0.46	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 S2 Estimations 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 **2ET/*n***[a]

Comp.	a/nm	V_{cell}/nm^3	V_{mol}/nm^3	f_R	n_{cryst}	n_{liq}	n_{cell}	n_{wall}
2ET/8	3.20	3.99	1.056	0.39	3.78	2.97	3.38	1.13
2ET/10	3.20	3.99	1.155	0.44	3.45	2.71	3.08	1.03
	3.25	4.12	1.155	0.44	3.57	2.81	3.19	1.06
2ET/14	3.15	4.47	1.353	0.52	3.30	2.59	2.95	1.48
2ET/18	3.25	4.75	1.552	0.58	3.06	2.40	2.73	1.37

[a] V_{cell} = volume of the unit cell defined by $a_{squ}^2 \times 0.45$ nm for square columnar phases and $a_{hex}^2 \times \sin(60°) \times 0.45$ nm for hexagonal phases; V_{mol} = molecular volume as calculated using crystal volume increments;[S8] n_{cryst} = number of molecules in the unit cell, estimated 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 $n_{liqu} = 0.55/0.7 \times n_{cryst}$; n_{cell} = number of molecules in the unit cell in the LC phase estimated as the average of n_{cryst} and n_{liqu}; n_{wall} = average number of molecules in the lateral cross section of the cylinder walls as calculated from n_{cell} by deviding *n*cell by the number of honeycomb walls per unit cell (3 for the triangular tilings and 2 for the square tilings).

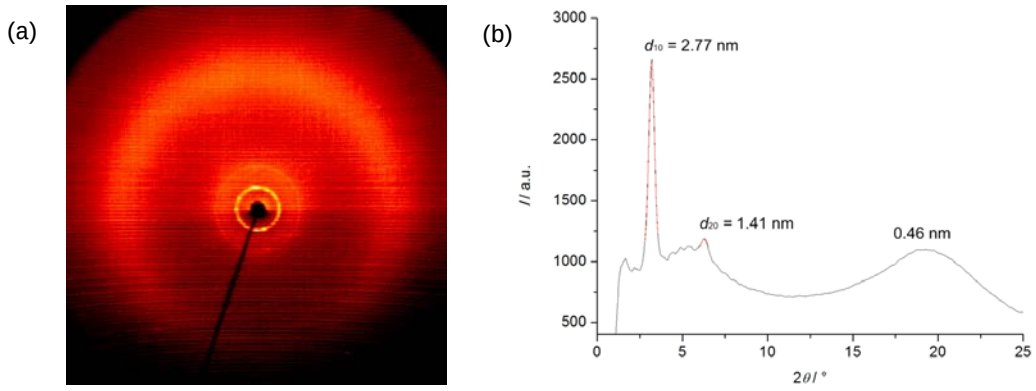


Fig. S5 (a) WAXS diffraction pattern of the $Col_{hex}\Delta/p6mm$ phase of compound **2ET/8** at T = 100 °C and (b) θ-scan of the diffraction pattern.

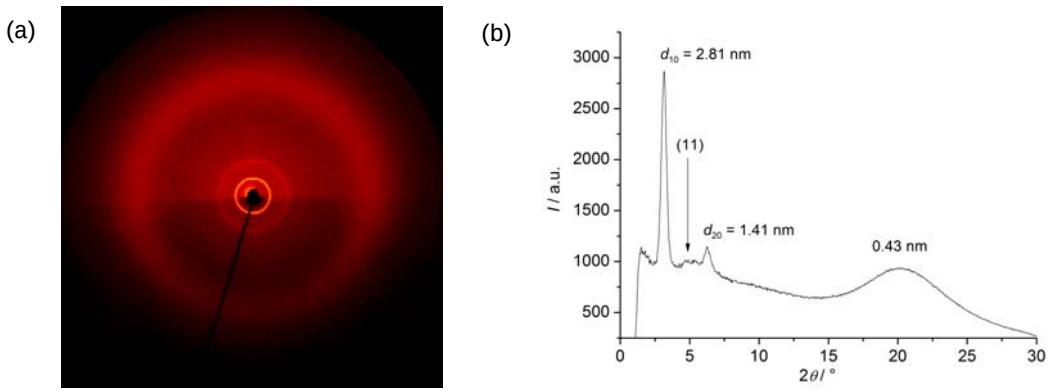


Fig. S6 (a) WAXS diffraction pattern of the $Col_{hex}\Delta/p6mm$ phase of compound **2ET/10** at T = 25 °C and (b) θ-scan of the diffraction pattern, arrow indicates the position expected for the 11 reflection of the hexagonal lattice.

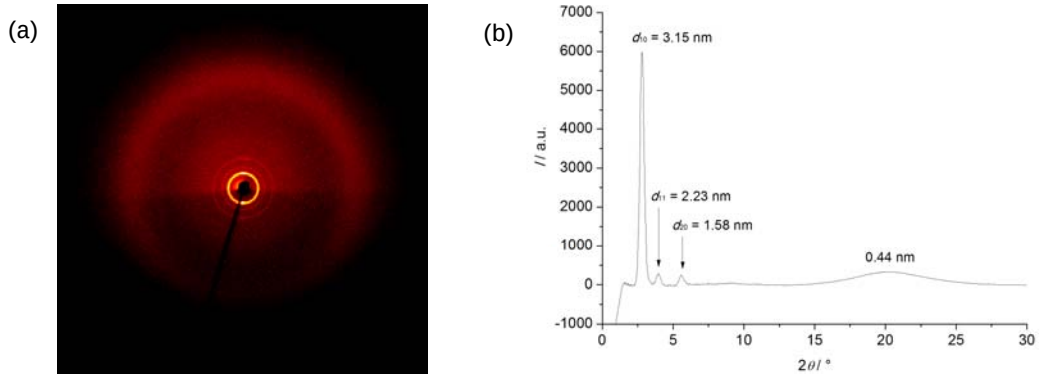


Fig. S7 (a) WAXS diffraction pattern of the $Col_{squ}/p4mm$ phase of compound **2ET/14** at 25 °C and (b) θ-scan of the diffraction pattern.

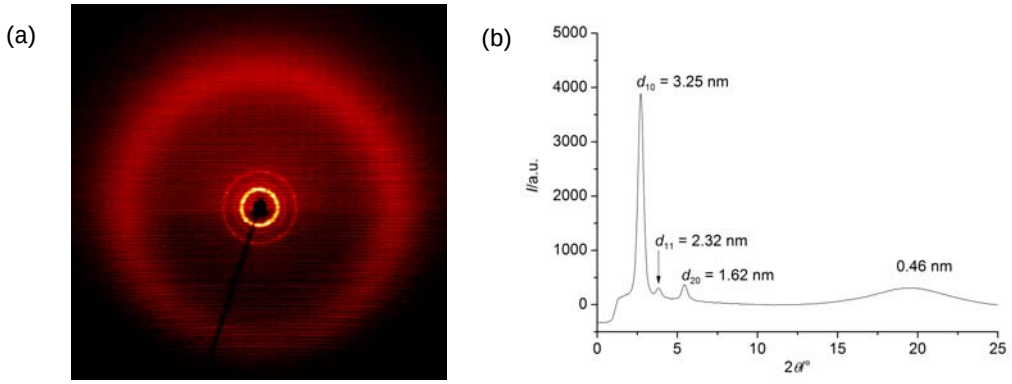


Fig. S8 (a) WAXS diffraction pattern of the $Col_{squ}/p4mm$ phase of compound **2ET/18** at T = 60 °C and (b) θ-scan of the diffraction pattern.

4. References

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