

Supporting Information

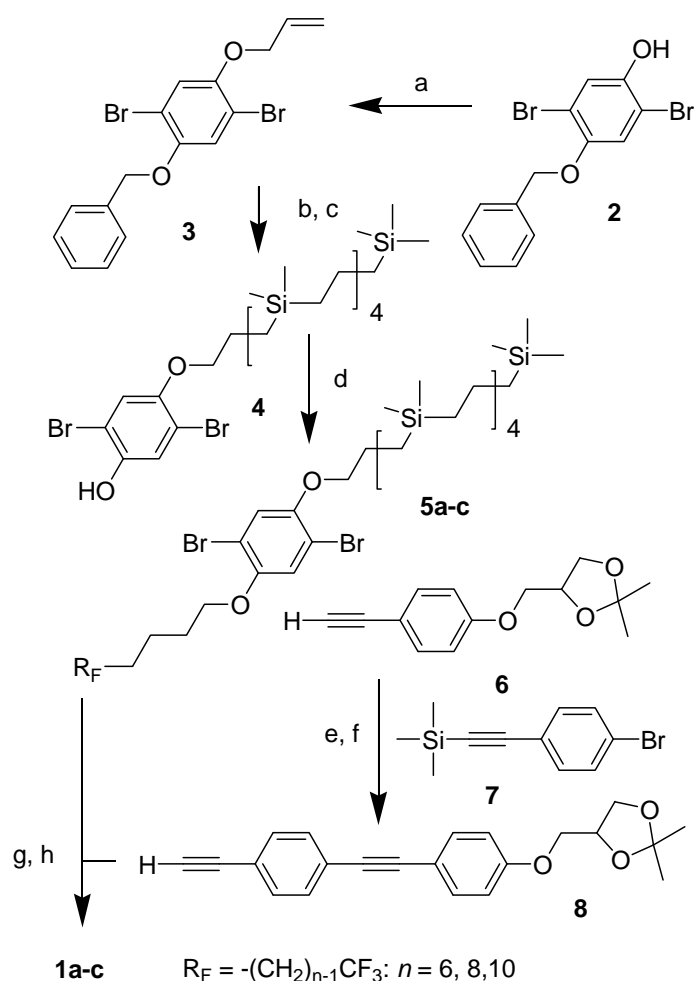
Soft Self-assembled Sub-5 nm Scale Chessboard and Snub-Square Tilings with Oligo(*para*-phenyleneethynylene) Rods

Constance Nürnberger, Huanjun Lu, Xiangbing Zeng, Feng Liu, Goran Ungar, Harald Hahn,
Heinrich Lang, Marko Prehm, and Carsten Tschierske

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1. Syntheses and analytical data of the materials



Scheme S1. Synthesis of compounds **1a-c**. *Reagents and conditions:* a) allyl bromide, K_2CO_3 , CH_3CN , reflux, 6 h; b) $H-[SiMe_2(CH_2)_3]_4SiMe_3$,^{S7} H_2PtCl_6 , Et_2O , r.t., 2d; c) H_2 , Pd/C, THF, 8 h; d) $R_F(CH_2)_4Br$,^{S1} K_2CO_3 , CH_3CN , reflux, 16 h; e) $Pd[PPh_3]_4$, CuI, Et_3N , reflux, 5 h; f) NaOH, MeOH/THF, r.t., 3h; g) $Pd[PPh_3]_4$, CuI, Et_3N , reflux, 6 h; h) PPTS, MeOH/THF, reflux, 6 h.

1.1 Intermediates

1.1.1 Semiperfluoroalkyl bromides

The synthesis has been carried out as described previously^{S1}

1.1.2 1-Allyloxy-4-benzyloxy-2,5-dibromobenzene 3

The synthesis has been reported in^{S2,S3}

1.1.3 4-{4-[(2,2-Dimethyl-1,3-dioxolane-4-yl)methoxy]phenylethynyl}phenylacetylene 8

The synthesis has been reported in ^{S4, S5, S2}

1.1.4 1-Benzyloxy-2,5-dibromo-4-(4,4,8,8,12,12,16,16,18,18-decamethyl-4,8,12,16,18-pentasilaheneicosyloxy)benzene (3) ^{S6}

Under an atmosphere of argon a solution of 1-allyloxy-4-benzyloxy-2,5-dibromobenzene (1.8 g, 5.5 mmol) and 1,1,5,5,9,9,13,13,17,17-decamethyl-1,5,9,13,17-pentasilaoctadecan ^{S7} (2.5 g, 5.7 mmol) in anhydrous Et₂O (50 ml) is treated with H₂PtCl₆ (13 mg) and the mixture is stirred at room temperature for two days. The reaction mixture is evaporated under reduced pressure and the residue is taken up in Et₂O and H₂O. The organic layer is separated and the H₂O phase is extracted twice with Et₂O. The combined organic phases are washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: *n*-hexane with 20% CHCl₃). Yield: 2.92 g (3.3 mmol; 61 %); colorless oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.46-7.31 (m, 5H, OCH₂C₆H₅), 7.14 (s, 1H, Ar-H); 7.08 (s, 1H, Ar-H), 5.05 (s, 2H, OCH₂C₆H₅), 3.91-3.88 (m, 2H, OCH₂), 1.80-1.76 (m, 2H, OCH₂CH₂), 1.36-1.25 (m, 8H, CH₂CH₂CH₂), 0.62-0.51 (m, 18H, SiCH₂), -0.02 (s, 6H, Si(CH₃)₂), -0.05 (s, 9H, Si(CH₃)₃), -0.07 (m, 18H, Si(CH₃)₂).

1.1.5 2,5-Dibromo-4-(4,4,8,8,12,12,16,16,18,18-decamethyl-4,8,12,16,18-pentasilaheneicosyloxy)phenol (4) ^{S8}

Under an atmosphere of argon compound **3** is dissolved in THF (30 ml) and Pd/C (0.1 g, 10 % Pd) is added. After rinsing with hydrogen (3x) the hydrogen pressure is set to 3.2 bar and the temperature to 40 °C. After 8 h the solution is filtered and the filtrate is washed with THF (200 ml). Finally, the solvent is evaporated. The residue is purified by column chromatography on silica gel (eluent: CHCl₃). Yield: 1.53 g (1.95 mmol; 59 %), colorless oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.21 (s, 1H, Ar-H), 6.95 (s, 1H, Ar-H), 5.32 (s, 1H, OH), 3.87 (t, ³J(H,H) = 6.8 Hz, 2H, OCH₂), 1.75 (m, 2H, OCH₂CH₂), 1.37-1.29 (m, 8H, CH₂CH₂CH₂), 0.62-0.51 (m, 18H, SiCH₂), -0.02 (s, 6H, Si(CH₃)₂), -0.05 (s, 9H, Si(CH₃)₃), -0.08 (m, 18H, Si(CH₃)₂).

1.1.6 4-(4,4,8,8,12,12,16,16,18,18-Decamethyl-4,8,12,16,18-pentasilaheneicosyloxy)-1-semiperfluoroalkyl-2,5-dibromobenzenes 5a-c

1,4-Dibromo-2-(4,4,8,8,12,12,16,16,18,18-decamethyl-4,8,12,16,18-pentasilaheneicosyloxy)-5-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecylfluorodecyloxy)benzene (5a)

A mixture of **4** (0.35 g, 0.48 mmol), 1-bromo-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecylfluorodecan ^{S1,S2} (0.24 g, 0.53 mmol) and K₂CO₃ (1.0 g, 7.2 mmol) in CH₃CN (40 ml) is stirred under reflux for 16 h. H₂O is added and the reaction mixture is extracted thrice with Et₂O. The combined organic phases are washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: *n*-hexane with 20% (V/V) CHCl₃). Yield: 0.45 g (0.38 mmol; 81 %), colorless solid, colorless oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.07 (s, 1H, Ar-H), 7.06 (s, 1H, Ar-H), 3.99-3.96 (m, 2H, OCH₂), 3.91-3.87 (m, 2H, OCH₂), 2.24-2.03 (m, 2H, CH₂CF₂), 1.98-1.83 (m, 4H, (CH₂)₂CH₂CF₂), 1.82-1.74 (m, 2H, OCH₂CH₂), 1.37-1.26 (m, 8H, CH₂CH₂CH₂), 0.62-0.51 (m, 18H, SiCH₂), -0.02 (s, 6H, Si(CH₃)₂), -0.05 (s, 9H, Si(CH₃)₃), -0.07 ppm (m, 18H, Si(CH₃)₂).

1,4-Dibromo-2-(4,4,8,8,12,12,16,16,18,18-decamethyl-4,8,12,16,18-pentasilaheneicosyloxy)-5-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-pentadecafluorododecyloxy)benzene (5b)

A mixture of **4** (0.35 g, 0.48 mmol), 1-bromo-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecylfluorododecan^{S1,S2} (0.29 g, 0.53 mmol) and K₂CO₃ (1.0 g, 7.2 mmol) in CH₃CN (40 ml) is stirred under reflux for 16 h. H₂O is added and the reaction mixture is extracted thrice with Et₂O. The combined organic phases are washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: *n*-hexane with 20% (V/V) CHCl₃). Yield: 0.50 g (0.40 mmol; 83 %), colorless solid, mp. 34-35 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.07 (s, 1H, Ar-H), 7.06 (s, 1H, Ar-H), 3.99-3.96 (m, 2H, OCH₂), 3.91-3.87 (m, 2H, OCH₂), 2.21-2.17 (m, 2H, CH₂CF₂), 1.93-1.82 (m, 4H, (CH₂)₂CH₂CF₂), 1.80-1.74 (m, 2H, OCH₂CH₂), 1.35-1.24 (m, 8H, CH₂CH₂CH₂), 0.62-0.51 (m, 18H, SiCH₂), -0.02 (s, 6H, Si(CH₃)₂), -0.05 (s, 9H, Si(CH₃)₃), -0.07 ppm (m, 18H, Si(CH₃)₂).

1,4-Dibromo-2-(4,4,8,8,12,12,16,16,18,18-decamethyl-4,8,12,16,18-pentasilaheneicosyloxy)-5-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorotetradecyloxy)benzene (5c)

A mixture of **4** (0.35 g, 0.48 mmol), 1-bromo-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heneicosafuorotetradecan^{S1,S2} (0.35 g, 0.53 mmol) and K₂CO₃ (1.0 g, 7.2 mmol) in CH₃CN (40 ml) is stirred under reflux for 16 h. H₂O is added and the reaction mixture is extracted thrice with Et₂O. The combined organic phases are washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: *n*-hexane with 20% (V/V) CHCl₃). Yield: 0.47 g (0.35 mmol; 73 %), colorless solid, mp. 48-50 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.07 (s, 1H, Ar-H), 7.06 (s, 1H, Ar-H), 3.99-3.96 (m, 2H, OCH₂), 3.90-3.87 (m, 2H, OCH₂), 2.22-2.17 (m, 2H, CH₂CF₂), 1.90-1.85 (m, 4H, (CH₂)₂CH₂CF₂), 1.80-1.75 (m, 2H, OCH₂CH₂), 1.35-1.25 (m, 8H, CH₂CH₂CH₂), 0.62-0.50 (m, 18H, SiCH₂), -0.02 (s, 6H, Si(CH₃)₂), -0.05 (s, 9H, Si(CH₃)₃), -0.07 - -0.08 ppm (m, 18H, Si(CH₃)₂).

1.1.7 Acetonides

1-(4,4,8,8,12,12,16,16,18,18-Decamethyl-4,8,12,16,18-pentasilaheneicosyloxy)-2,5-bis(4-{4-[(2,2-dimethyl-1,3-dioxolane-4-yl)methoxy]phenylethynyl}phenylethynyl)-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecylfluorododecyloxy)benzene (1a-acetonide)^{S9}

Under an atmosphere of argon a mixture of **5a** (0.45 g, 0.39 mmol), **8** (0.31 g 0.93 mmol), Pd[PPh₃]₄ (0.004 g, 3 mol-%) and CuI (0.002g, 2 mol-%) in anhydrous Et₃N (25 ml) is stirred under reflux for 6 h. H₂O is added and the reaction mixture is extracted thrice with Et₂O. The combined organic phases are washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: CHCl₃ with 1% (V/V) Et₂O). Yield: 0.40 g (0.24 mmol, 62 %); yellow solid, mp. 127-128 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.43 (m, 12H, Ar-H), 6.99 (s, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.89-6.87 (m, 4H, Ar-H), 4.48-4.45 (m, 2H, OCH), 4.18-4.14 (m, 2H, OCH₂), 4.08-3.88 (m, 10H, OCH₂), 2.18 (m, 2H, CH₂CF₂), 1.94 (m, 4H, (CH₂)₂CH₂CF₂), 1.87-1.80 (m, 2H, OCH₂CH₂), 1.45 (s, 6H, CH₃), 1.39 (s, 6H, CH₃), 1.34-1.25 (m, 8H, CH₂CH₂CH₂), 0.71-0.49 (m, 18H, SiCH₂), -0.01 (s, 6H, Si(CH₃)₂), -0.06 (s, 9H, Si(CH₃)₃), -0.08 ppm (s, 6H, Si(CH₃)₂), -0.08 ppm (s, 6H, Si(CH₃)₂), -0.09 ppm (s, 6H, Si(CH₃)₂).

1-(4,4,8,8,12,12,16,16,18,18-Decamethyl-4,8,12,16,18-pentasilaheneicosyloxy)-2,5-bis(4-{4-[(2,2-dimethyl-1,3-dioxolane-4-yl)methoxy]phenylethynyl}phenylethynyl)-4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-pentadecafluorododecyloxy)benzene (1b-acetonide)

Under an atmosphere of argon a mixture of **5b** (0.50 g, 0.40 mmol), **8** (0.32 g 0.96 mmol), Pd[PPh₃]₄ (0.004 g, 3 mol-%) and CuI (0.002g, 2 mol-%) in anhydrous Et₃N (30 ml) is stirred under reflux for 6 h. H₂O is added and the reaction mixture is extracted thrice with Et₂O. The combined organic phases are washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: CHCl₃ with 1% (V/V) Et₂O). Yield: 0.12 g (0.06 mmol, 15 %); yellow solid, mp. 137-139 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.43 (m, 12H, Ar-H), 7.00 (s, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.89-6.87 (m, 4H, Ar-H), 4.49-4.44 (m, 2H, OCH), 4.18-4.14 (m, 2H, OCH₂), 4.08-4.04 (m, 4H, OCH₂), 4.00-3.95 (m, 4H, OCH₂), 3.94-3.88 (m, 2H, OCH₂), 2.18 (m, 2H, CH₂CF₂), 1.94-1.93 (m, 4H, (CH₂)₂CH₂CF₂), 1.86-1.81 (m, 2H, OCH₂CH₂), 1.45 (s, 6H, CH₃), 1.40 (s, 6H, CH₃), 1.35-1.24 (m, 8H, CH₂CH₂CH₂), 0.71-0.50 (m, 18H, SiCH₂), -0.01 (s, 6H, Si(CH₃)₂), -0.06 (s, 9H, Si(CH₃)₃), -0.08 ppm (s, 6H, Si(CH₃)₂), -0.08 ppm (s, 6H, Si(CH₃)₂).

1-(4,4,8,8,12,12,16,16,18,18-Decamethyl-4,8,12,16,18-pentasilaheneicosyloxy)-2,5-bis(4-{4-[(2,2-dimethyl-1,3-dioxolane-4-yl)methoxy]phenylethynyl}phenylethynyl)-4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorotetradecyloxy)benzene (1c-acetonide)

Under an atmosphere of argon a mixture of **5c** (0.45 g, 0.33 mmol), **8** (0.26 g 0.80 mmol), Pd[PPh₃]₄ (0.004 g, 3 mol-%) and CuI (0.001g, 2 mol-%) in anhydrous Et₃N (30 ml) is stirred under reflux for 6 h. H₂O is added and the reaction mixture is extracted thrice with Et₂O. The combined organic phases are washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: CHCl₃ with 1% (V/V) Et₂O). Yield: 0.42 g (0.02 mmol, 70 %); yellow solid, mp. 140-143 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.47-7.43 (m, 12H, Ar-H), 7.00 (s, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.89-6.86 (m, 4H, Ar-H), 4.50-4.44 (m, 2H, OCH), 4.18-4.14 (m, 2H, OCH₂), 4.08-4.04 (m, 4H, OCH₂), 4.00-3.93 (m, 4H, OCH₂), 3.91-3.88 (m, 2H, OCH₂), 2.24-2.11 (m, 2H, CH₂CF₂), 1.94-1.90 (m, 4H, (CH₂)₂CH₂CF₂), 1.87-1.80 (m, 2H, OCH₂CH₂), 1.45 (s, 6H, CH₃), 1.39 (s, 6H, CH₃), 1.37-1.24 (m, 8H, CH₂CH₂CH₂), 0.71-0.50 (m, 18H, SiCH₂), -0.01 (s, 6H, Si(CH₃)₂), -0.05 (s, 9H, Si(CH₃)₃), -0.08 ppm (s, 6H, Si(CH₃)₂), -0.08 ppm (s, 6H, Si(CH₃)₂), -0.08 ppm (s, 6H, Si(CH₃)₂).

1.2 Compounds 1a-c

1a - A mixture of **1a-acetonide** (0.40 g, 0.24 mmol), pyridinium 4-toluenesulphonate (0.05 g, 0.2 mmol), MeOH (20 ml) and THF (20 ml) is stirred under reflux for 12 h. The reaction mixture is evaporated under reduced pressure and the residue is taken up in Et₂O and H₂O. The organic layer is separated and the H₂O phase is extracted twice with Et₂O. The combined organic phases are washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product is purified by preparative centrifugal thin layer chromatography with EtOAc as eluent and crystallized from THF/MeOH. Yield: 0.08 g (0.05 mmol, 21 %), yellow solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.44 (m, 12H, Ar-H), 7.00 (s, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.88 (d, ³J(H,H) = 8.5 Hz, 4H, Ar-H), 4.11-4.02 (m, 8H, OCH₂, OCH), 4.00-3.97 (m, 2H, OCH₂), 3.87-3.72 (m, 4H, OCH₂), 2.18 (m, 2H, CH₂CF₂), 1.93-1.90 (m, 4H, (CH₂)₂CH₂CF₂), 1.86-1.81 (m, 2H, OCH₂CH₂), 1.37-1.24 (m, 8H, CH₂CH₂CH₂), 0.71-

0.50 (m, 18H, SiCH₂), -0.01 (s, 6H, Si(CH₃)₂), -0.05 (s, 9H, Si(CH₃)₃), -0.08 ppm (s, 18H, Si(CH₃)₂); ¹³C-NMR (100 MHz, CDCl₃): δ = 158.53, 153.90, 153.15, 133.14, 131.44, 131.37, 131.33, 123.50, 122.93, 122.79, 117.20, 116.98, 115.94, 114.66, 114.10, 94.93, 91.24, 91.18, 88.24, 87.74, 87.47 (C≡C), 72.45, 70.37, 70.37, 69.36, 68.90, 63.67 (OCH₂, OCH), 29.04, 24.17, 21.53, 20.34, 20.30, 20.18, 20.09, 18.60, 17.53, 11.67 (CH₂), -1.33, -2.98, -3.19 ppm (SiCH₃); ¹⁹F-NMR (188 MHz, CDCl₃): δ = -81.19 (m, 3F, CF₃), -114.70 (m, 2F, CH₂CF₂), -122.28 (s, 2F, CF₂), -123.25 (s, 2F, CF₂), -123.84 (s, 2F, CF₂), -126.50 (s, 2F, CF₂CF₃); HR-ESI-MS: m/z [M+Cl]⁻ 1615.5987 (calc. 1615.6031).

1b - A mixture of **1b-acetonide** (0.12 g, 0.06 mmol), pyridinium 4-toluenesulphonate (0.05 g, 0.2 mmol), MeOH (10 ml) and THF (10 ml) is stirred under reflux for 12 h. The reaction mixture is evaporated under reduced pressure and the residue is taken up in Et₂O and H₂O. The organic layer is separated and the H₂O phase is extracted twice with Et₂O. The combined organic phases are washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product is purified by preparative centrifugal thin layer chromatography with EtOAc as eluent and crystallized from THF/MeOH. Yield: 0.08 g (0.05 mmol, 83 %), yellow solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.44 (m, 12H, Ar-H), 7.00 (s, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.88 (d, ³J(H,H) = 8.7 Hz, 4H, Ar-H), 4.12-4.05 (m, 8H, OCH₂, OCH), 4.00-3.97 (m, 2H, OCH₂), 3.87-3.72 (m, 4H, OCH₂), 2.18 (m, 2H, CH₂CF₂), 1.93-1.90 (m, 4H, (CH₂)₂CH₂CF₂), 1.86-1.81 (m, 2H, OCH₂CH₂), 1.37-1.24 (m, 8H, CH₂CH₂CH₂), 0.71-0.50 (m, 18H, SiCH₂), -0.01 (s, 6H, Si(CH₃)₂), -0.05 (s, 9H, Si(CH₃)₃), -0.08 ppm (s, 18H, Si(CH₃)₂); ¹³C-NMR (100 MHz, CDCl₃): δ = 158.53, 153.91, 153.15, 133.15, 133.13, 131.44, 131.37, 131.33, 123.44, 122.92, 122.79, 116.98, 115.94, 114.64, 114.11, 94.93, 91.23, 88.24, 87.74, 87.47 (C≡C), 72.44, 70.37, 69.36, 68.90, 63.66 (OCH₂, OCH), 29.04, 24.16, 21.53, 20.34, 20.30, 20.18, 20.09, 18.60, 17.53, 11.67 (CH₂), -1.33, -2.98, -3.19 ppm (SiCH₃); ¹⁹F-NMR (188 MHz, CDCl₃): δ = -81.16 (m, 3F, CF₃), -114.66 (m, 2F, CH₂CF₂), -122.21 (s, 4F, CF₂), -123.06 (s, 2F, CF₂), -123.77 (s, 2F, CF₂), -126.44 (s, 2F, CF₂CF₃); HR-ESI-MS: m/z [M+Cl]⁻ 1715.5939 (calc. 1715.68).

1c - A mixture of **1c-acetonide** (0.42 g, 0.23 mmol), pyridinium 4-toluenesulphonate (0.05 g, 0.2 mmol), MeOH (20 ml) and THF (20 ml) is stirred under reflux for 12 h. The reaction mixture is evaporated under reduced pressure and the residue is taken up in Et₂O and H₂O. The organic layer is separated and the H₂O phase is extracted twice with Et₂O. The combined organic phases are washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product is purified by preparative centrifugal thin layer chromatography with EtOAc as eluent and crystallized from THF/MeOH. Yield: 0.11 g (0.06 mmol, 24 %), yellow solid; ¹H NMR (400 MHz, CDCl₃): δ = 7.49-7.40 (m, 12H, Ar-H), 7.00 (s, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.88 (m, 4H, Ar-H), 4.12-4.02 (m, 8H, OCH₂, OCH), 4.00-3.97 (m, 2H, OCH₂), 3.87-3.73 (m, 4H, OCH₂), 2.18 (m, 2H, CH₂CF₂), 1.93 (m, 4H, (CH₂)₂CH₂CF₂), 1.87-1.79 (m, 2H, OCH₂CH₂), 1.36-1.24 (m, 8H, CH₂CH₂CH₂), 0.71-0.50 (m, 18H, SiCH₂), -0.01 (s, 6H, Si(CH₃)₂), -0.06 (s, 9H, Si(CH₃)₃), -0.08 ppm (s, 18H, Si(CH₃)₂); ¹³C-NMR (100 MHz, CDCl₃): δ = 158.56, 153.94, 153.18, 133.16, 133.14, 131.45, 131.38, 131.34, 123.50, 123.44, 122.92, 122.78, 116.97, 115.93, 114.65, 114.62, 114.08, 94.90, 91.20, 88.20, 87.69, 72.38, 70.31, 69.29, 68.84, 63.60 (OCH₂, OCH), 28.93, 24.05, 21.42, 20.23, 20.18, 20.07, 19.97, 18.49, 17.41, 11.55 (CH₂), -1.47, -3.12, -3.19 ppm (SiCH₃); ¹⁹F-NMR (188 MHz, CDCl₃): δ = -81.15 (m, 3F, CF₃), -114.66 (m, 2F, CH₂CF₂), -122.09 (m, 10F, CF₂), -123.03 (s, 2F, CF₂), -123.76 (s, 2F, CF₂), -126.44 ppm (s, 2F, CF₂); HR-ESI-MS: m/z [M+Cl]⁻ 1815.5857 (calc. 1815.5904).

2. Additional Data

2.1. Experimental Methods

Phase transitions were determined by polarizing optical microscopy (Optiphot 2, Nikon) in conjunction with a heating stage (FP 82 HT, Mettler) and by differential scanning calorimetry (DSC-7, Perkin Elmer) at heating/cooling rates of 10 K min⁻¹.

SAXS experiments were recorded on Beamline I22 at Diamond Light Source and Beamline BL16B1 at Shanghai Synchrotron Radiation Facility, SSRF. Samples were held in evacuated 1 mm capillaries. A modified Linkam hot stage with a thermal stability within 0.2 °C was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side. A MarCCD detector was used. q calibration and linearization were verified using several orders of layer reflections from silver behemate and a series of n -alkanes. The measurement of the positions and intensities of the diffraction peaks is carried out using Galactic PeakSolveTM program, where experimental diffractograms are fitted using Gaussian shaped peaks. The diffraction peaks are indexed on the basis of their peak positions, and the lattice parameters and the space groups are subsequently determined. Once the diffraction intensities are measured and the corresponding plane group determined, electron density maps can be reconstructed, on the basis of the general formula

$$E(xy) = \sum_{hk} F(hk) \exp[i2\pi(hx+ky)] \quad (\text{Eqn. 1})$$

Here $F(hk)$ is the structure factor of a diffraction peak with index (hk) . It is normally a complex number and the experimentally observed diffraction intensity.

$$I(hk) = K \cdot F(hk) \cdot F^*(hk) = K \cdot |F(hk)|^2 \quad (\text{Eqn. 2})$$

Here K is a constant related to the sample volume, incident beam intensity etc. In this paper we are only interested in the relative electron densities, hence this constant is simply taken to be 1. Thus the electron density

$$E(xy) = \sum_{hk} \sqrt{I(hk)} \exp[i2\pi(hx+ky) + \phi_{hk}] \quad (\text{Eqn. 3})$$

As the observed diffraction intensity $I(hk)$ is only related to the amplitude of the structure factor $|F(hk)|$, the information about the phase of $F(hk)$, ϕ_{hk} , can not be determined directly from experiment. However, the problem is much simplified when the structure of the ordered phase is centrosymmetric, and hence the structure factor $F(hk)$ is always real and ϕ_{hk} is either 0 or π .

This makes it possible for a trial-and-error approach, where candidate electron density maps are reconstructed for all possible phase combinations, and the “correct” phase combination is then selected on the merit of the maps, helped by prior physical and chemical knowledge of the system. This is especially useful for the study of nanostructures, where normally only a limited number of diffraction peaks are observed.

WAXS patterns (quartz-monochromatized CuK _{α} radiation, 30 to 60 min exposure time) were recorded with a HI-STAR detector, Siemens.

2.2. Calorimetric data

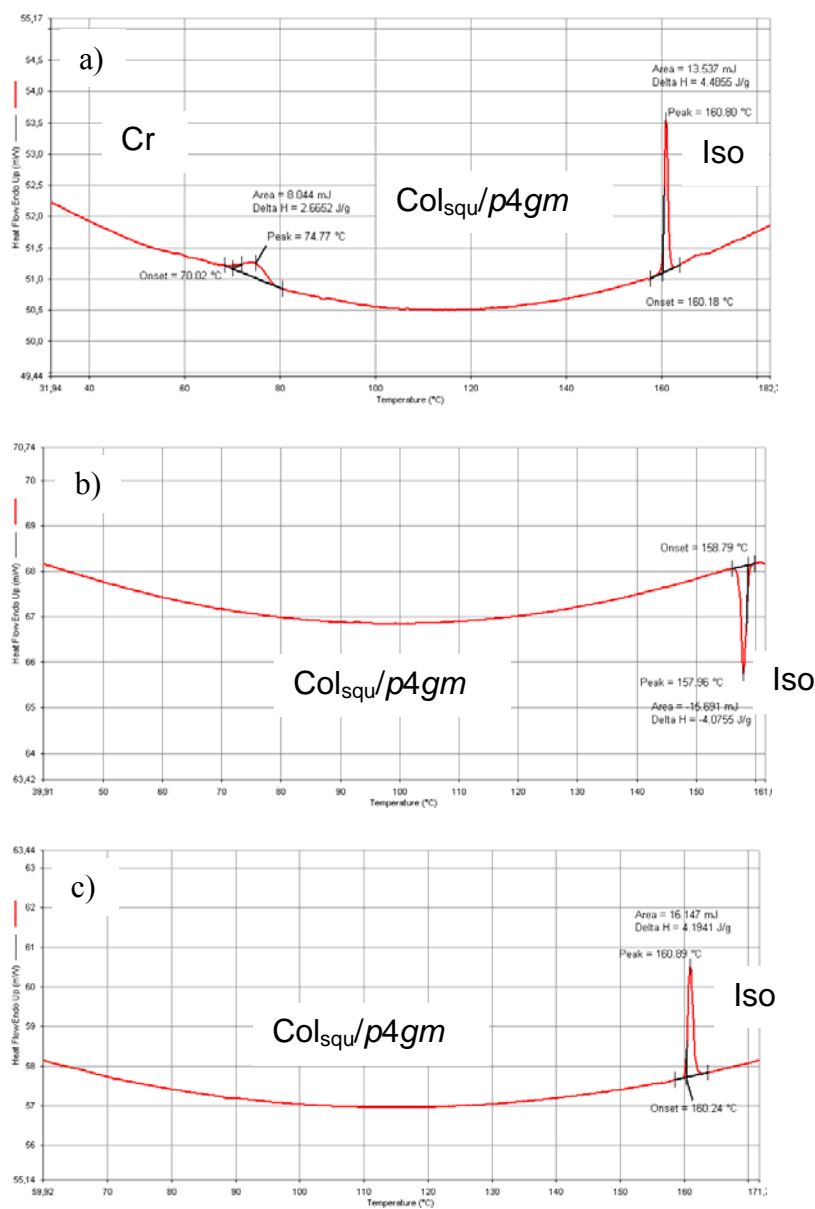


Figure S1: DSC scans of compound **1a** recorded at 10 K min⁻¹; a) first heating, b) first cooling and c) second heating after 1 year storage at 20 °C.

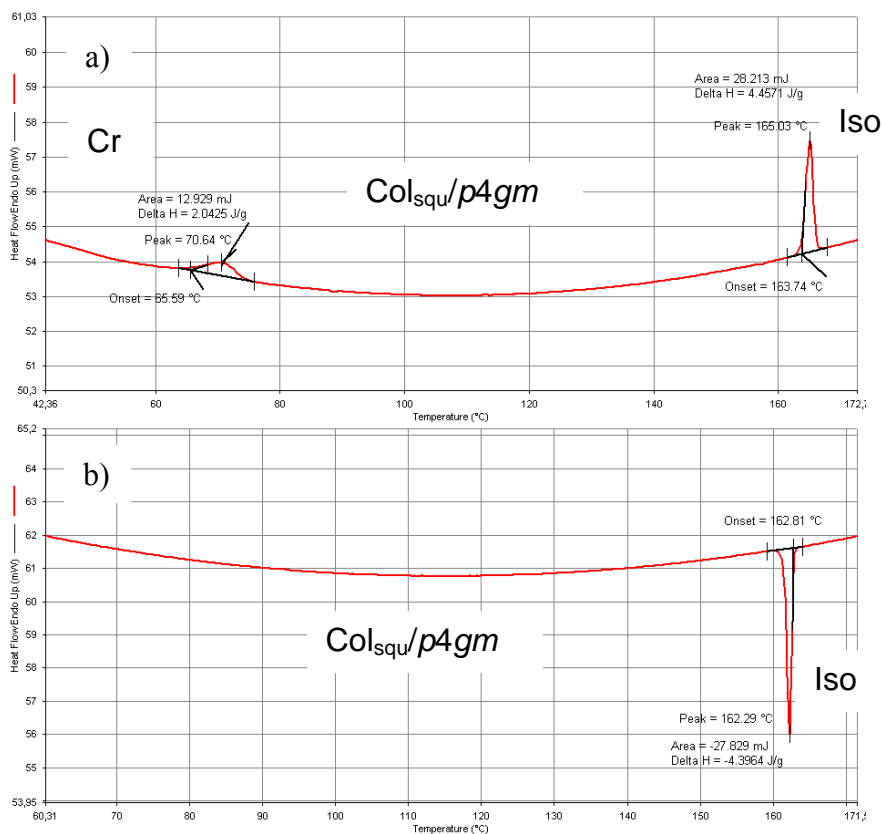


Figure S2: DSC scans of compound **1b** recorded at 10 K min⁻¹; a) first heating, b) cooling.

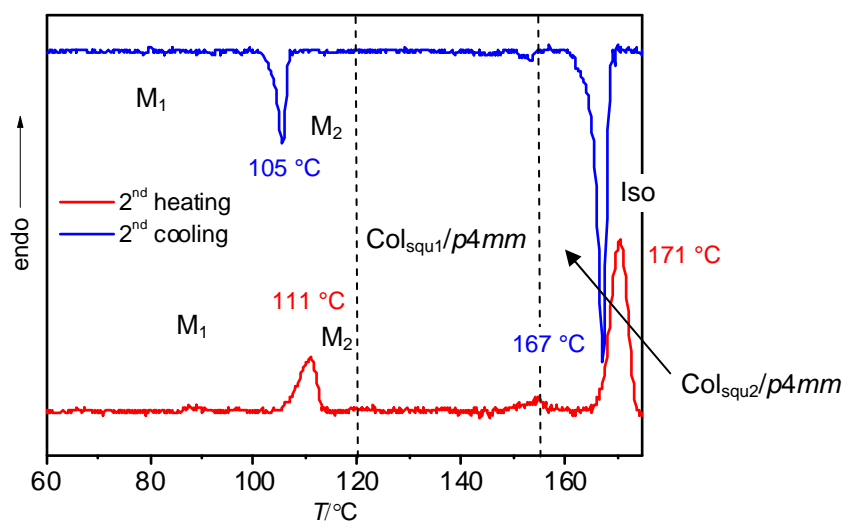


Figure S3: DSC scans of compound **1c** recorded at 10 K min⁻¹; dashed lines indicate the phase transitions M₂- Col_{squ1}/p4mm and Col_{squ1}/p4mm - Col_{squ2}/p4mm.

2.3 Contact area between 1b and 1c

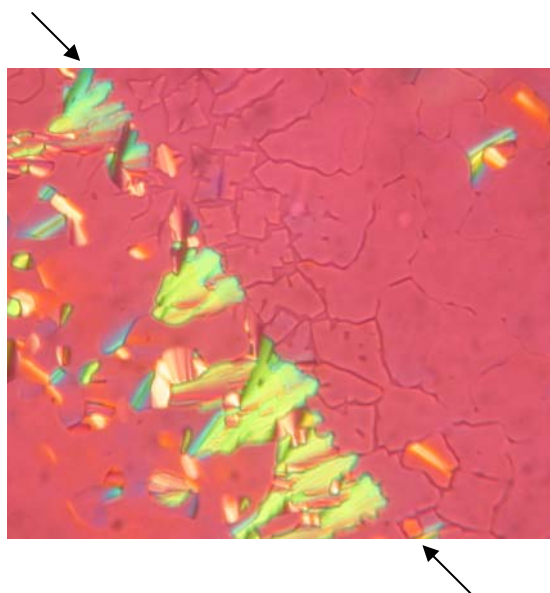


Figure S4: Contact region between **1b** and **1c** at $T = 160\text{ }^{\circ}\text{C}$ (with λ -retarder plate and slightly uncrossed polarizers, left $p4mm$ phase of **1c**, right $p4gm$ phase of **1b** (predominately homeotropic alignment)); position of phase boundary is indicated by arrows. In the contact region between **1b** and **1c** no additional intermediate mesophase could be observed, though the mixing of the two molecules with different R_F chain length in the contact region would allow a continuous change of the effective R_F chain volume. In the contact area the stability of both mesophases is slightly reduced to $T_{cl} \sim 161\text{ }^{\circ}\text{C}$ and only one sharp boundary between $p4mm$ and $p4gm$ can be observed. Therefore it is concluded that the formation of the rhomb-square tiling is disfavoured.

2.4 Additional XRD data

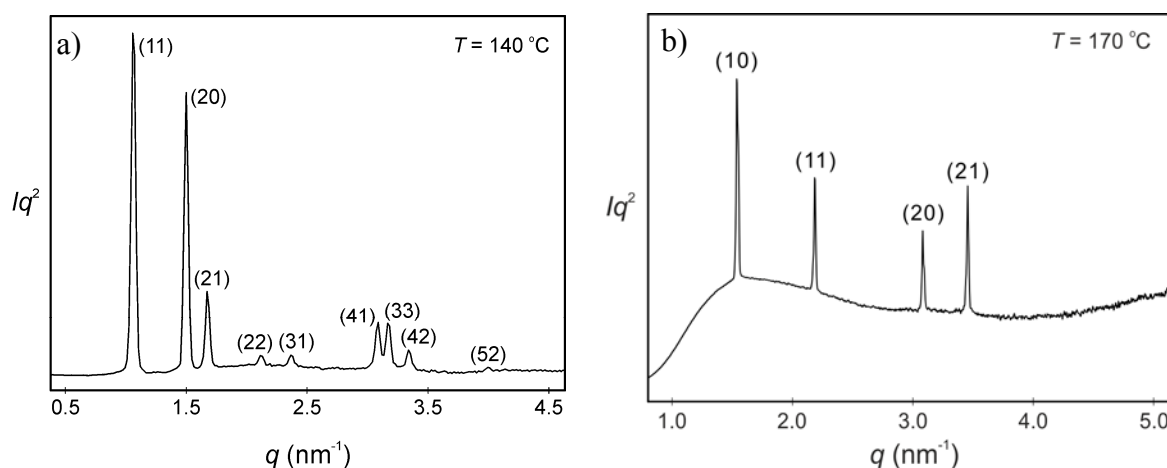


Figure S5. Powder diffraction pattern of (a) the $p4gm$ phase of compound **1b** at $T = 140\text{ }^{\circ}\text{C}$ and (b) the $p4mm$ phase of compound **1c** at $T = 170\text{ }^{\circ}\text{C}$.

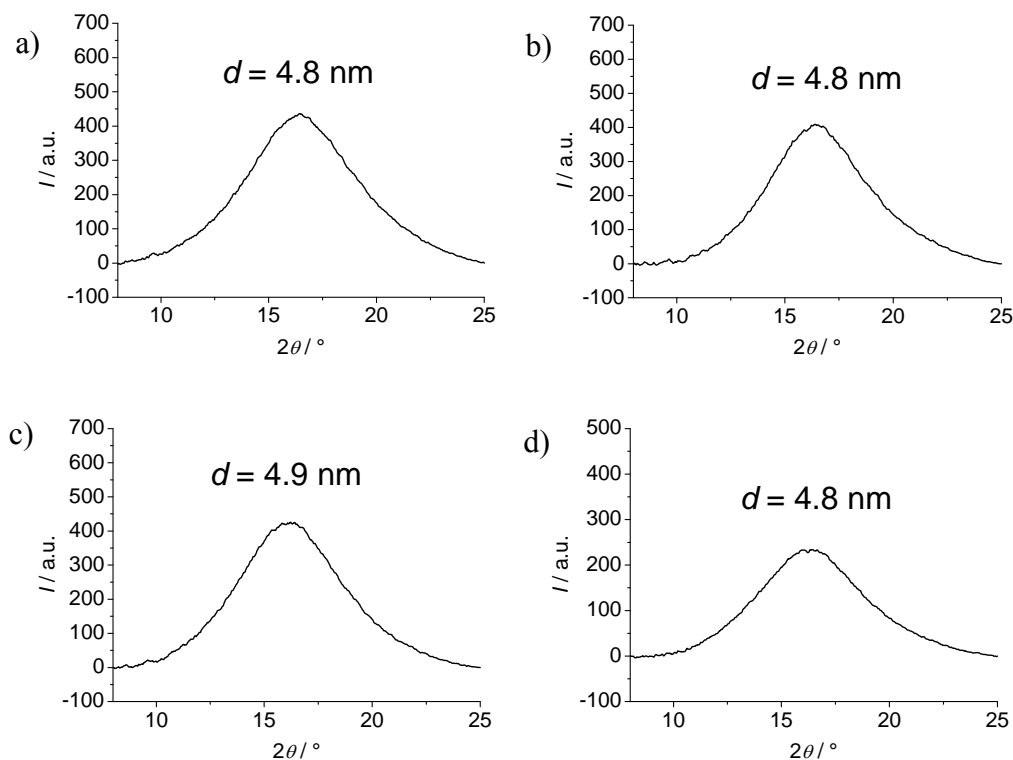


Figure S6. θ -scans over the wide angle scattering for a) **1a** ($T = 145$ °C, $d_{\max} = 0.54$ nm); b) **1b** ($T = 100$ °C, $d_{\max} = 0.54$ nm); c) **1b** ($T = 160$ °C, $d_{\max} = 0.55$ nm) and d) **1c** ($T = 130$ °C, $d_{\max} = 0.54$ nm).

2.5. Additional electron density maps

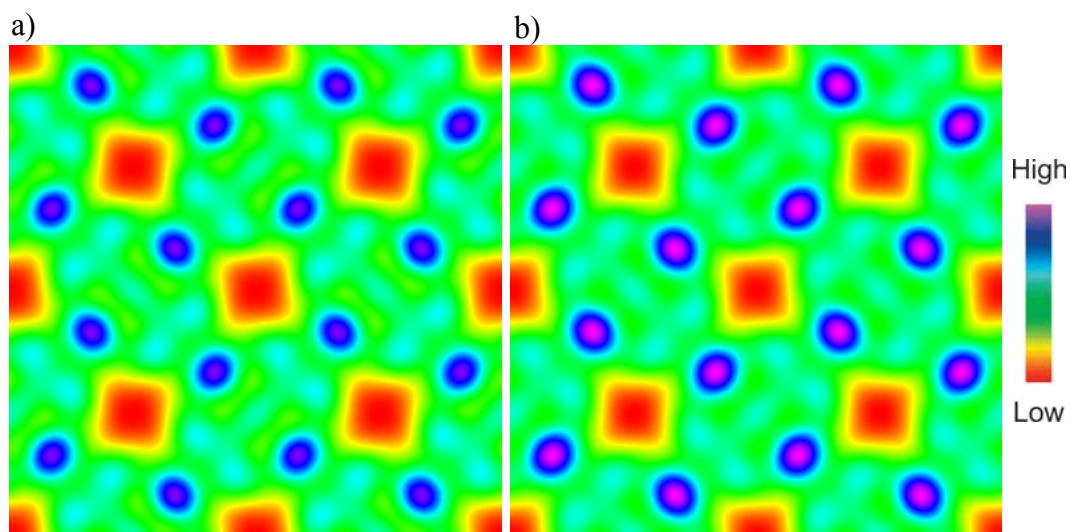


Figure S7. Reconstructed electron density map of the $p4gm$ phase of compounds **1a** and **1b** from the data in Tables S1 and S2. To check that the phases (+/-) were chosen correctly in ED map construction we use a simple version of the “isomorphous replacement” method;^{S10} by comparing the maps of compounds **1a** and **1b** scaled so as to keep the lowest (R_{Si}) and the medium level ED areas (OPE) the same colour, we see that the ED level associated with the

R_F regions is higher and larger for compound **1b** in (b) than for compound **1a**, shown in a), as expected from their fluorine content.”

2.6. Determination of the molecular length

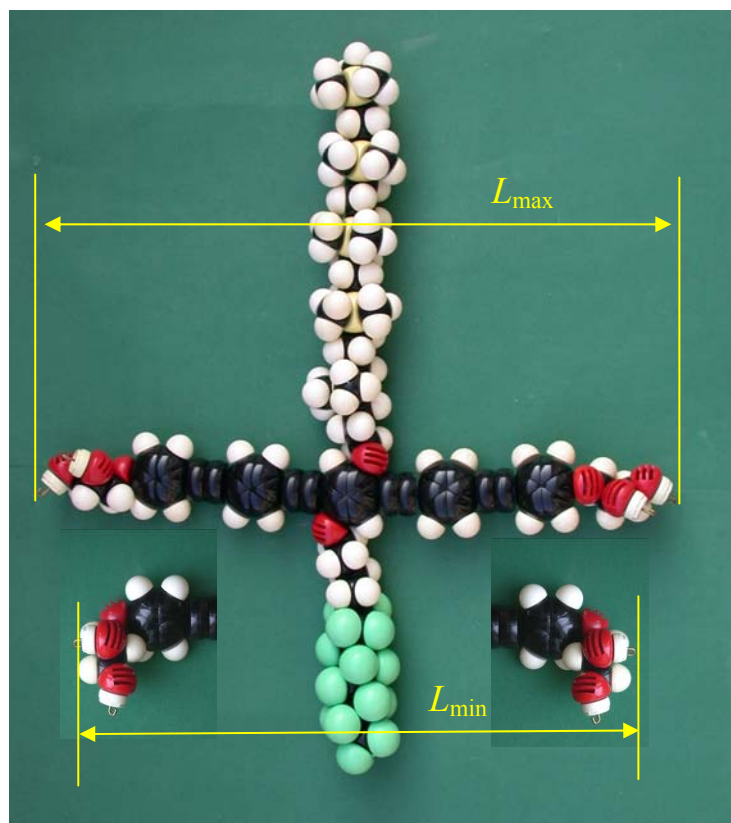


Figure S8. CPK molecular models showing compound **1b** in the most stretched conformations; L_{max} is the distance between the primary hydroxyl groups of the glycerol groups; L_{min} corresponds to the distance between the secondary hydroxyl groups of the glycerol units assuming a compact conformation of the glycerol units (see insets): $L_{max} = 4.5$ nm; $L_{min} = 4.1$ nm; average: $L = 4.3$ nm.

2.7 Tabular XRD data

Table S1. Experimental and calculated d -spacings, relative integrated intensities, and phases used in the reconstruction of electron densities for the $CoI_{\text{sq}}/p4gm$ phase of compound **1a** at 60 °C. All intensity values are Lorentz and multiplicity corrected in this and the following tables.

| (hk) | $d_{\text{obs.}} - \text{spacing (nm)}$ | $d_{\text{cal.}} - \text{spacing (nm)}$ | $intensity$ | $phase$ |
|-----------------------------------|---|---|-------------|---------|
| (11) | 5.90 | 5.90 | 100.0 | π |
| (20) | 4.18 | 4.18 | 88.3 | π |
| (21) | 3.74 | 3.73 | 2.8 | π |
| (22) | 2.96 | 2.95 | 3.2 | π |
| (31) | 2.65 | 2.64 | 1.1 | 0 |
| (41) | 2.03 | 2.03 | 9.5 | 0 |
| (33) | 1.98 | 1.97 | 15.4 | π |
| (42) | 1.88 | 1.87 | 5.4 | 0 |
| (52) | 1.55 | 1.55 | 0.8 | π |
| (62) | 1.34 | 1.32 | 1.7 | 0 |
| (63) | 1.25 | 1.24 | 1.0 | 0 |
| $a_{\text{sq}} = 8.35 \text{ nm}$ | | | | |

Table S2. Experimental and calculated d -spacings, relative integrated intensities, and phases used in the reconstruction of electron densities for the $CoI_{\text{sq}}/p4gm$ phase of compound **1b** at 140 °C.

| (hk) | $d_{\text{obs.}} - \text{spacing (nm)}$ | $d_{\text{cal.}} - \text{spacing (nm)}$ | $intensity$ | $phase$ |
|-----------------------------------|---|---|-------------|---------|
| (11) | 5.91 | 5.91 | 100.0 | π |
| (20) | 4.19 | 4.18 | 76.3 | π |
| (21) | 3.75 | 3.74 | 10.7 | π |
| (22) | 2.96 | 2.96 | 3.3 | π |
| (31) | 2.65 | 2.65 | 1.7 | 0 |
| (41) | 2.04 | 2.03 | 7.4 | 0 |
| (33) | 1.98 | 1.97 | 15.4 | π |
| (42) | 1.88 | 1.87 | 3.5 | 0 |
| (52) | 1.57 | 1.55 | 0.6 | π |
| $a_{\text{sq}} = 8.37 \text{ nm}$ | | | | |

Table S3. Experimental and calculated d -spacings, relative integrated intensities, and phases used in the reconstruction of electron densities for the $\text{Col}_{\text{squ}1}/p4mm$ phase of compound **1c** at 130 °C.

| (hk) | $d_{\text{obs.}} - \text{spacing (nm)}$ | $d_{\text{cal.}} - \text{spacing (nm)}$ | <i>intensity</i> | <i>phase</i> |
|------------------------------------|---|---|------------------|--------------|
| (10) | 5.76 | 5.76 | 100.0 | π |
| (11) | 4.07 | 4.07 | 0.49 | 0 |
| (20) | 2.88 | 2.88 | 0.05 | π |
| (21) | 2.58 | 2.58 | 0.33 | π |
| (22) | 2.04 | 2.04 | 2.4 | 0 |
| (30) | 1.92 | 1.92 | 0.1 | π |
| (31) | 1.82 | 1.82 | 1.6 | 0 |
| (32) | 1.60 | 1.60 | 0.2 | 0 |
| (41) | 1.40 | 1.40 | 0.02 | 0 |
| (33) | 1.36 | 1.36 | 0.04 | π |
| (42) | 1.29 | 1.29 | 0.2 | π |
| $a_{\text{squ}} = 5.76 \text{ nm}$ | | | | |

Table S4. Experimental and calculated d -spacings, relative integrated intensities, for the $\text{Col}_{\text{squ}2}/p4mm$ phase of compound **1c** at 170 °C.

| (hk) | $d_{\text{obs.}} - \text{spacing (nm)}$ | $d_{\text{cal.}} - \text{spacing (nm)}$ |
|------------------------------------|---|---|
| (10) | 4.07 | 4.07 |
| (11) | 2.87 | 2.88 |
| (20) | 2.04 | 2.04 |
| (21) | 1.82 | 1.82 |
| $a_{\text{squ}} = 4.07 \text{ nm}$ | | |

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