Supplementary Information

Self-Organized Spiral Columns in Laterally Grafted Rods

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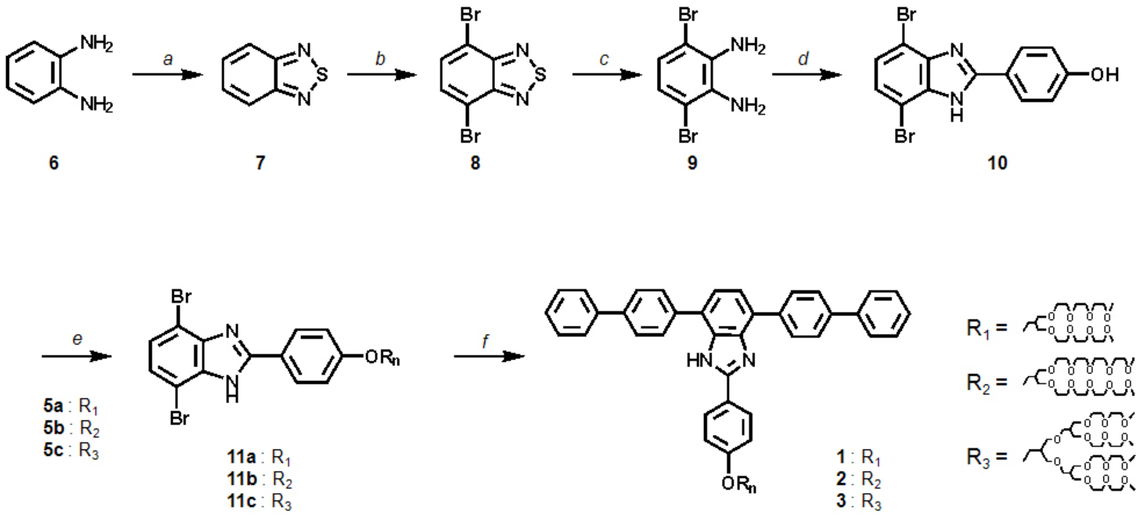
1. Generals. 1, 2-diamino benzene, triethylene glycol monomethyl ether, tetraethylene glycol, and 4-hydroxy benzaldehyde from Aldrich were used as received. NaH (60 %) and *p*-toluenesulfonyl chloride (98 %) from TCI and Tokyo Kasei were used as received. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, TCI, Acros, etc.) and were used without purification. Hexane, dichloromethane, and ethyl acetate were distilled before use. Visualization was accomplished with UV light, iodine vapor. Flash chromatography was carried out with Silica Gel 60 (230-400 mesh) from EM Science. Dry THF was obtained by vacuum transfer from sodium and benzophenone. 4-biphenylboronic acid and tosylated tri, tetra ethylene 1st generation dendrimer and diethylene oxide 2nd generation dendrimer were prepared according to the similar procedures described previously.[S1, S2]

2. Techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded from $CDCl_3$ or DMSO solutions on a Bruker AM 250 spectrometer. The purity of the products was checked by thin-layer chromatography (TLC; Merck, silica gel 60). Recycling preparative high-pressure chromatography (HPLC) was performed for further purification by using HITACHI model pump L-7110, JAI model UV detector 310 and JAI model RI detector RI-7S. A Perkin Elmer Diamond-DSC differential scanning calorimeter equipped with 1020 thermal analysis controller was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks. The transmission electron microscopy (TEM) was performed at 120 kV using JEOL 2010.

3. X-ray experiment. To identify microstructure, X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 10C1 and 4C1 X-ray beam line at the Pohang Accelerator Laboratory, South Korea. The wavelength of X-ray source was 1.54 Å. In order to confirm molecular packing in nanostructure, X-ray scattering measurements were conducted with an apparatus consisting of an 18kW-rotating anode X-ray generator(Rigaku Co.) operated at 46kV × 20mA, mirror optics with point focusing. The CuKα radiation(=1.54 Å) from a 0.1 × 1mm microfocus cathode was used. Two-dimensional (2-D) diffraction patterns were recorded on imaging plates. The distance between sample and imaging plate was 68 cm for small-angle scattering. The sample was held in an aluminum sample holder, which was sealed with the window of 7 μm thick Kapton films in both sides. The sample was heated with two cartridge heaters and the temperature of the samples was monitored by thermocouple placed close to the sample.

4. TEM experiment. Before TEM experiment, the samples were annealed under vacuum at melting temperature and cooled down to room temperature. The samples for TEM analysis of untreated materials were quenched in liquid nitrogen and microtomed by cryo-ultramicrotomy (MTXL system, Boeckeler Ins. Inc. USA equipped with CR-X cryogenic system). Thin sections of samples were transferred to carbon-coated Cu-grid substrates. In order to improve mass thickness contrast and radiation sensitivity, the thin films were slightly exposed to staining agent vapor (0.5 wt % aqueous RuO_4). Direct imaging was carried out at 120 kV accelerating voltage, using the images acquired with a Dual vision 300W and SC 1000 CCD camera (Gatan, Inc.; Warrendale, PA).

5. Synthesis of compounds 1 - 3



Reagents and conditions : (a) Et_3N, CH_2Cl_2, $SOCl_2$, reflux; (b) Br_2, HBr, reflux; (c) $NaBH_4$, EtOH, 25℃; (d) 4-hydroxybenzaldehyde, TsOH, EtOH, reflux; (e) **5a**-**c**, K_2CO_3, EtOH/CH_3CN, reflux; (f) 4-biphenylboronic acid, 2M Na_2CO_3, tetrakis-triphenylphosphine palladium(0), THF, reflux.

Scheme 1. Synthesis of compounds **1-3**.

Compound 7. To a 1000 mL flask were added compound **6** (10.0 g, 92.5 mmol), 300 mL of CH_2Cl_2 and triethylamine (37.4 g, 370.0 mmol). The solution was stirred until compound **6** was dissolved clearly. Thionyl chloride was added dropwise very slowly and the mixture refluxed for 4h. The solvent was removed in a rotatory evaporator and 700 mL of water added. Concentrated HCl was added to a final pH of 2. The desired compound was purified by direct steam distillation following addition of water to the mixture. The steam distilled mixture was extracted three times with 200 mL of CH_3Cl_2, dried over $MgSO_4$ and filtered. The solvent was removed, affording pure compound **7** in 85 % yield white solid (10.7 g, 78.6 mmol). ^1H NMR (250 MHz, $CDCl_3$, δ, ppm): 7.99 (dd, $J = 3.3, 4.6$ Hz, 2H), 7.57 (dd, $J = 3.1, 6.8$ Hz, 2H).

Compound 8. To a 500 mL two-necked round bottom flask were added compound **7** (10.00 g, 73.4 mmol) and 150 mL of HBr (47 %). A solution containing Br_2 (35.2 g, 220.3 mmol) in 100 mL of HBr was added dropwise very slowly (slow addition is essential). If necessary, an additional 100 mL of HBr can be added to the solution. After total addition of the Br_2, the solution was refluxed for 6h. Precipitation of an orange solid was noted. The mixture was allowed to cool to room temperature and sufficient saturated solution of $Na_2S_2O_5$ added to consume completely any excess Br_2. The mixture was filtered under vacuum and washed exhaustively with water. The solid was then washed once with cold diethyl ether and dried under vacuum for ca. 20h, affording the desired dibrominated compound **8** in 72 % yield yellow solid (15.5g, 52.9 mmol). ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 7.73 (s, 2H).

Compound 9. To a suspension of compound **8** (5.0 g, 17 mmol) in EtOH (170 mL), $NaBH_4$ (6.4 g, 170 mmol) was added portionwise at 0 °C. The mixture was stirred for 20h at room temperature (25 °C). After evaporation in rotatory evaporator, H_2O (100 mL) added, and the mixture was extracted with diethyl ether. The organic phase was washed with sat. NaCl solution and dried over $MgSO_4$. Evaporation in *vacuo* gave compound **9** in 54% yield white solid (2.4 g, 9.0 mmol). ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 6.84 (s, 2H), 3.89 (s, 4H).

Compound 10. A compound **9** (2.4 g, 9.0 mmol), 4-hydroxybenzaldehyde (1.3 g, 9.9 mmol), *p*-toluenesulfonic acid (152 mg, 0.9 mmol), and 50 mL of EtOH were refluxed for 24h under an argon atmosphere. The solvent was removed, H_2O (100 mL) added, and the mixture was extracted with ethyl acetate. The organic phase was dried over

$MgSO_4$, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel, methylene chloride /MeOH : 10/1 eluent) to yield 65%, white solid (2.1 g, 5.9 mmol). ^{1}H NMR (250 MHz, DMSO-d_6, δ, ppm): 13.02 (s, 1H), 10.07 (s, 1H), 8.21 (d, J = 7.5 Hz, 2H), 7.22 (s, 2H), 6.92 (d, J = 7.5 Hz, 2H).

Compounds 11a-c. Compounds **11a-c** were all synthesized using the same procedure. A representative example is described for **11a**. Compound **10** (0.37 g, 0.7 mmol), compound **5a**[S2] (0.4 g, 0.8 mmol) and K_2CO_3 (1.1g, 7.0 mmol) were dissolved in 50 mL of DMF. The mixture was heated at reflux for 48 hours and then cooled to room temperature. The solvent was removed in a rotary evaporator, and the resulting mixture was poured into water and extracted with ethyl acetate. The ethyl acetate solution was dried over anhydrous magnesium sulfate and filtered. After the solvent was removed in a rotary evaporator, the crude products were purified by column chromatography (silica gel) using methanol : ethyl acetate (1:10 v/v) as eluent to yield 73% (0.37 g, 0.5 mmol) of colorless liquid.

Compound 11a ^{1}H-NMR (250MHz, $CDCl_3$, δ, ppm): 10.37-10.20 (s, 1H), 8.08 (s, 2H), 7.27 (m, H), 6.94 (d, J = 7.5 Hz, 2H), 4.09 (d, J = 7.5 Hz, 2H), 3.68-3.41 (m, 28H), 3.37 (s, 6H), 2.10-2.05 (m, 1H).

Compound 11b ^{1}H-NMR (250MHz, $CDCl_3$, δ, ppm): 10.23-10.16 (s, 1H), 8.11 (s, 2H), 7.30 (m, 2H), 7.05 (d, J = 8.3 Hz, 2H), 4.07 (d, J = 7.5 Hz, 2H), 3.71-3.39 (m, 36H), 3.35 (s, 6H), 2.12-2.08 (m, 1H).

Compound 11c ^{1}H-NMR (250MHz, $CDCl_3$, δ, ppm): 10.21 (s, 1H), 8.14 (s, 2H), 7.28 (m, 2H), 6.95 (d, J = 7.5 Hz, 2H), 4.05 (d, J = 7.5 Hz, 2H), 3.62-3.35 (m, 60H), 2.15-

2.04 (m, 3H).

Compounds 1 – 3. Compounds **1 - 3** were all synthesized using the same procedure. A representative example is described for **1**. Compound **11a** (0.4 g, 0.5 mmol) and 4-biphenylboronic acid (0.25 g, 1.25 mmol, 4 eq.) were dissolved in degassed THF (30 mL). Degassed 2M aqueous Na_2CO_3 (30 mL) was added to the solution and then tetrakis(triphenyl-phosphine) palladium (0) (0.06 g, 0.05 mmol, 0.1 eq.) was added. The mixture was heated at reflux for 48 hours with vigorous stirring under argon. Cooled to room temperature, the layers were separated, and the aqueous layer was then washed twice with methylene chloride. The combined organic layer were dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using ethyl acetate : methanol (10:1 v/v) as eluent and then further purified by prep-HPLC to yield 0.38 g (80 %) of white solid.

Compound 1 ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 9.84 (s, 1H), 8.31 (d, J = 8.3 Hz, 2H), 7.75-7.44 (m, 20H), 7.05 (d, J = 8.5 Hz, 2H), 4.09 (d, J = 7.5 Hz, 2H), 3.68-3.41 (m, 28H), 3.37 (s, 6H), 2.10-2.05 (m, 1H).; ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ = 157.5, 152.9, 141.8, 136.5, 135.4, 129.3, 128.4, 127.9, 123.4, 122.4, 114.9, 72.7, 71.1, 70.8, 67.9, 59.3, 37.2; MALDI-TOF-MS $[MH]^+$ calcd. for $C_{55}H_{62}N_2O_9$: m/z = 895.45; Found: 895.06.

Compound 2 ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 9.54 (s, 1H), 8.24 (d, J = 7.5 Hz, 2H), 7.75-7.44 (m, 20H), 7.06 (d, J = 7.5 Hz, 2H), 4.07 (d, J = 7.5 Hz, 2H), 3.71-3.39 (m, 36H), 3.35 (s, 6H), 2.12-2.08 (m, 1H).; ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ = 157.5, 152.9, 141.8, 136.5, 135.4, 129.3, 128.1, 127.7, 123.4, 122.3, 114.9, 72.7, 71.1,

70.5, 70.2, 67.9, 59.3, 37.2; MALDI-TOF-MS $[MH]^+$ calcd. for $C_{59}H_{70}N_2O_{11}$: m/z = 938.5; Found: 938.63.

Compound 3 ^{1}H-NMR (250 MHz, $CDCl_3$, *δ*, ppm): 9.50 (s, 1H), 8.30 (d, *J* = 7.8 Hz, 2H), 7.79-7.38 (m, 20H), 7.06 (d, *J* = 8.6 Hz, 2H), 4.05 (d, *J* = 7.5 Hz, 2H), 3.62-3.35 (m, 60H), 2.15-2.04 (m, 3H).; ^{13}C-NMR (100 MHz, $CDCl_3$, *δ*, ppm): 157.5, 152.9, 141.8, 136.5, 135.4, 129.3, 128.4, 127.9, 127.7, 123.4, 122.3, 114.9, 72.7, 71.1, 70.8, 70.2, 67.9, 59.3, 37.2; MALDI-TOF-MS $[MH]^+$ calcd. for $C_{69}H_{90}N_2O_{15}$: m/z 1187.63; Found: 1187.78.

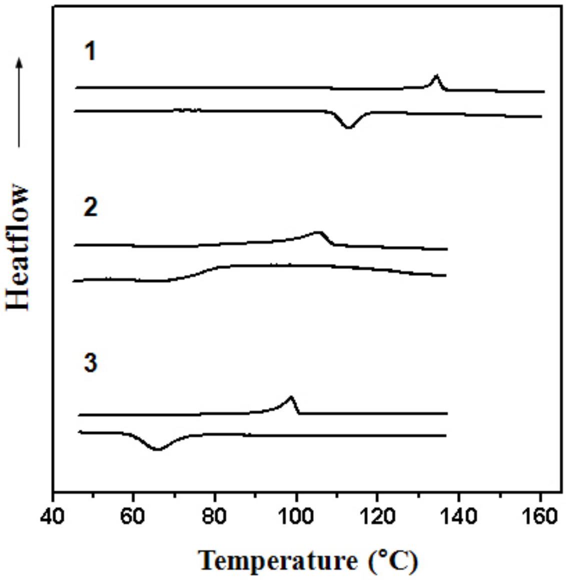


Figure S1. DSC traces of compounds **1-3** during the second heating scans and the first cooling scans (scan rate : 10°C/min).

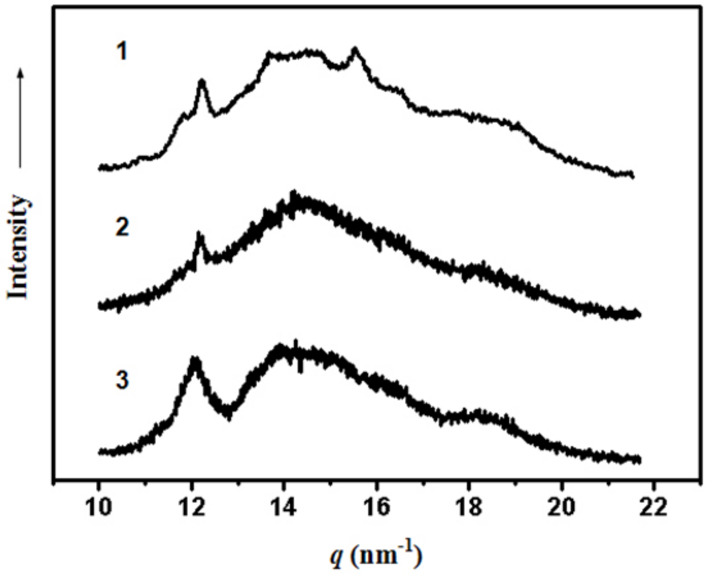


Figure S2. Wide angle diffraction pattern of molecule **1-3**.

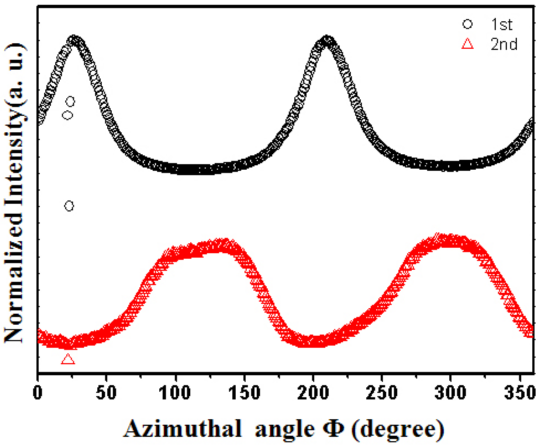


Figure S3. Azimuthal profiles in 2D small-angle X-ray diffraction pattern, showed two intensity maxima at approximately 90° above and below the equator, obtained from **1** at 25 °C. Azimuthal profile averaged around {100}, {010} reflections (q range ◯:2.0~2.5, Δ:4.0~4.5 nm^{-1})

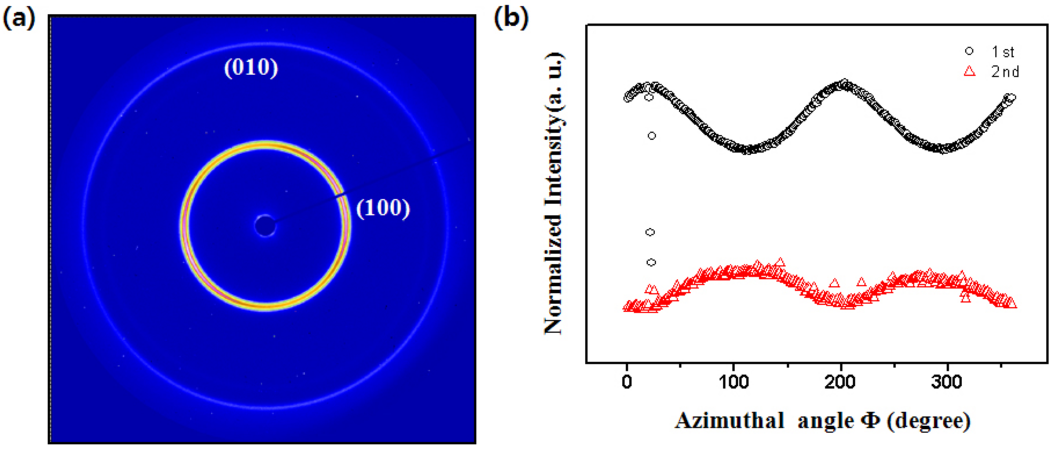


Figure S4. (a) 2D-SAXS pattern obtained from **2** at 25°C. The diffraction pattern shows {100}, {010} reflections. (b) Azimuthal profiles in 2D SAXS pattern obtained from **2** at 25 °C. Two intensity maxima at approximately 90º above and below the equator, suggesting that the rectangular structure. Azimuthal profile averaged around {100}, {010} reflections (q range ○:1.6~2.0, Δ:3.8~4.3 nm^{-1}).

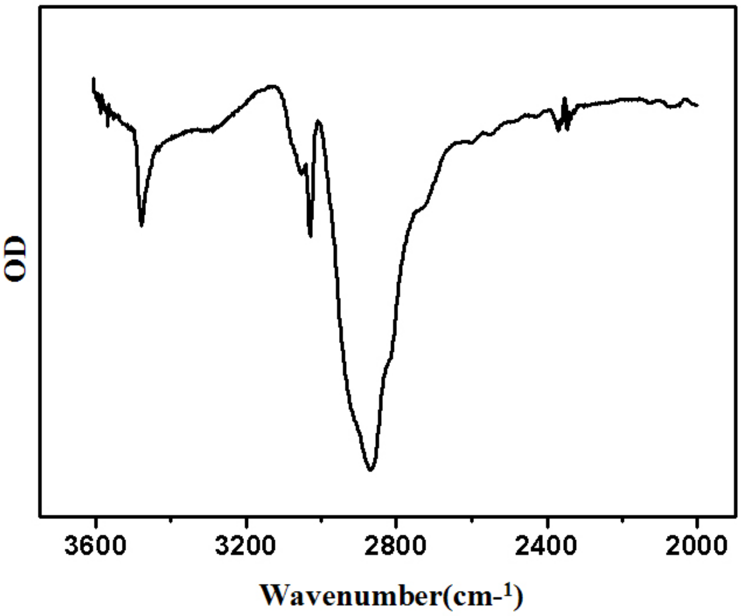


Figure S5. FT-IR spectroscopy of compound **1**.

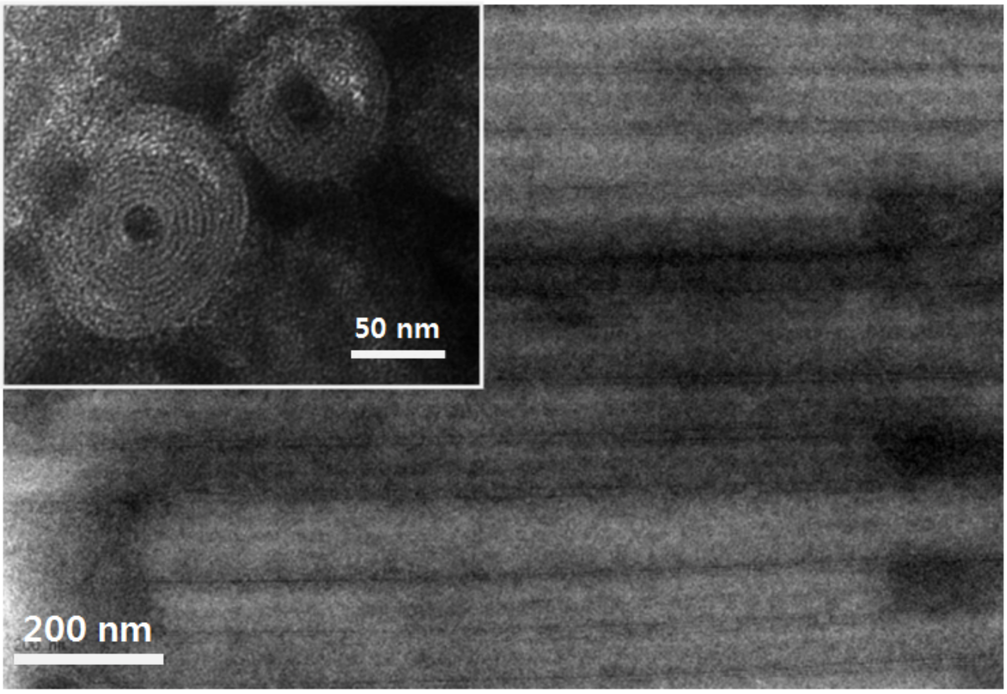


Figure S6. TEM image of a microtomed film of **3**.

Table S1. Thermal Transition of compounds **1-3**.

	Phase transition (°C) and corresponding enthalpy changes (*kJ*/mol)	
	Heating	Cooling
1	col_{rect} 134 (7.2) i	i 112 (8.32) col_{rect}
2	col_{rect} 105 (5.3) i	i 68 (1.89) col_{rect}
3	col_{rect} 98 (8.2) i	i 66 (9.43) col_{rect}

Table S2. Compound Parameters[a]

	Mw (g/mol)	ρ (g/cm^3)	*L* (nm)	a (nm)	b (nm)	γ (°)	V_{cell} (nm^3)	n
1	895	1.23	2.16	2.94	1.54	90	9.78	8.09
2	983	1.21	2.16	3.45	1.54	90	11.48	8.50
3	1187	1.18	2.16	3.78	1.56	90	12.74	7.62

[a] Molecular weight (M), density (ρ), molecular lengths (L, distances between the head groups in the most extended conformation, CPK models), lattice parameters (a, b, γ), calculated volumes of the unit cells (V_{cell}), n was calculated according to the formula $n_2 = V_{\text{cell}}(N_A/M)\ \rho$, where N_A is the Avogadro constant

Table S3. Small angle X-ray diffraction data for oblique columnar lattice of compound **1** measured at 25 °C.[a]

h	***k***	***l***	q_{obsd} **nm^{-1}**	q_{calcd} **nm^{-1}**
1	0	0	2.134	2.134
0	1	0	4.082	4.082
1	1	0	4.568	4.602

[a] q_{obsd} and q_{calcd} are the scattering vectors of the observed reflections, and calculated for the rectangular columnar structure with lattice parameters a = 2.94 nm, b = 1.54 nm.

Table S4. Small angle X-ray diffraction data for oblique columnar lattice of compound **2** measured at 25 °C.

h	*k*	*l*	q_{obsd} nm^{-1}	q_{calcd} nm^{-1}
1	0	0	1.823	1.823
0	1	0	4.074	4.074
1	1	0	4.464	4.464

[a] q_{obsd} and q_{calcd} are the scattering vectors of the observed reflections, and calculated for the rectangular columnar structure with lattice parameters a = 3.45 nm, b = 1.54 nm.

Table S5. Small angle X-ray diffraction data for rectangular columnar lattice of compound **3** measured at 25 °C.

h	*k*	*l*	q_{obsd} nm^{-1}	q_{calcd} nm^{-1}
1	0	0	1.663	1.663
0	1	0	4.027	4.027
1	1	0	4.337	4.361
3	0	0	4.973	4.989

[a] q_{obsd} and q_{calcd} are the scattering vectors of the observed reflections, and calculated for the rectangular columnar structure with lattice parameters a = 3.78 nm, b = 1.56 nm.

Reference

S1. Kim, B.-S., Hong, D.-J., Bae, J., Lee, M., *J. Am. Chem. Soc.* **2005**, *127*, 16333.

S2. Kim, H.-J. Lee, E. Kim, M. G. Kim, M.-C. Sim, E. and Lee, M. *Chem. Eur. J.* **2008**, *14*, 3883.