Supporting Information

Supramolecular microtubes based on 1,3,5-benzenetricarboxamides prepared by self-assembly upon heating

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S1: Synthesis and characterization of 1,3,5-benzenetricarboxamides 1 – 3

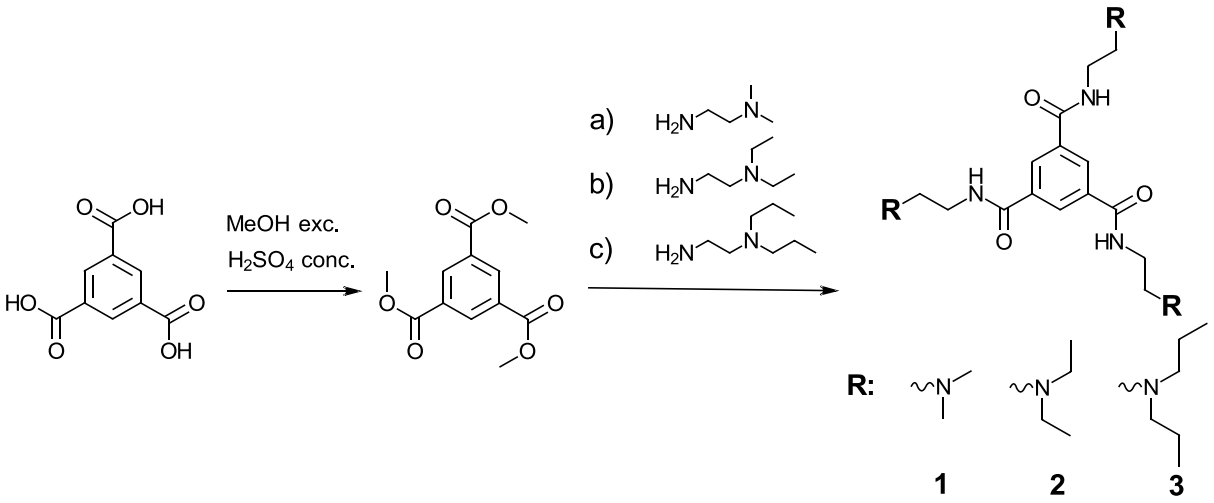

Figure S1. Two step synthesis of 1,3,5-benzenetricarboxamides **1** – **3**: Esterification of trimesic acid to 1,3,5-benzenetricarboxylic acid trimethyl ester and subsequent synthesis of the respective 1,3,5-benzenetricarboxamides, (N^1,N^3,N^5-tris[2-(dimethylamino)-ethyl]-1,3,5-benzenetricarboxamide) **1**, (N^1,N^3,N^5-tris[2-(diethylamino)-ethyl]-1,3,5-benzenetricarboxamide) **2**, and (N^1,N^3,N^5-tris[2-(dipropylamino)-ethyl]-1,3,5-benzenetricarboxamide) **3**.

Synthesis of trimesic acid trimethyl ester (1,3,5-benzenetricarboxylic acid trimethyl ester)

All chemicals were used as received without further purification. 100 g of trimesic acid (1,3,5-benzenetricarboxylic acid) (0.476 mol) were dissolved in 1.5 L of methanol. 7 mL of concentrated H_2SO_4 were added, and the mixture was heated under reflux for two days. Complete conversion was determined by thin layer chromatography. After cooling to room temperature, the precipitated product was filtrated, washed with small amounts of methanol and dried under reduced pressure, yielding 108.0 g (0.465 mol, 90 %) of trimesic acid trimethyl ester as a white powder.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.99 (s, 9H), 8.85 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 52.6, 131.2, 134.6, 165.4.

MS-EI (m/z): 252 (M·+), 222, 221, 193.

*Synthesis of N^1,N^3,N^5-tris[2-(dimethylamino)-ethyl]-1,3,5-benzenetricarboxamide **1***

10.0 g (0.04 mol) of trimesic acid trimethyl ester were dispersed in 22.0 mL (17.6 g, 0.2 mol) of *N*,*N*-dimethyl-ethylenediamine under argon atmosphere. The mixture was heated to 125 °C, stirred overnight and subsequently allowed to cool down to room temperature. The resulting mixture was dispersed in acetone and heated until an almost clear solution was obtained. The

hot solution was filtrated using a sintered funnel. The solvent was removed and the product was dried in a vacuum oven at 50 °C over night resulting in 5.3 g (32 %) of **1** as a white powder.
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.30 (s, 18H), 2.56 (m, 6H), 3.57 (quartet, 6H), 7.21 (t(br), 3H), 8.48 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 37.3, 45.0, 57.7, 135.0, 165.6.
MS-EI (m/z): 420 (M·+), 350, 72, 71, 58.
Anal. calcd. for $C_{21}H_{36}N_6O_3$: C 60.0, H 8.6, N 20.0; found: C 58.8, H 8.0, N 18.7.

*Synthesis of N^1,N^3,N^5-tris[2-(diethylamino)-ethyl]-1,3,5-benzenetricarboxamide **2***
10.0 g (0.04 mol) of trimesic acid trimethyl ester were dispersed in 28.1 mL (23.2 g, 0.2 mol) of *N*,*N*-diethyl-ethylenediamine under argon atmosphere. The mixture was heated to 125 °C, stirred overnight and subsequently allowed to cool down to room temperature. The crude product was recrystallized from ca. 450 mL of acetic acid ethyl ester and washed with hexane, yielding after drying 8.98 g (45 %) of **2** as a white powder.
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.06 (t, 18H), 2.60 (quartet, 12H), 2.68 (m, 6H), 3.53 (quartet, 6H), 7.20 (t(br), 3H), 8.44 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 11.6, 37.4, 46.6, 51.3, 128.2, 135.2, 165.6.
MS-EI (m/z): 504 (M·+), 99, 87, 86, 58.
Anal. calcd. for $C_{27}H_{48}N_6O_3$: C 64.3, H 9.6, N 16.7; found: C 64.4, H 9.1, N 16.6.

*Synthesis of N^1,N^3,N^5-tris[2-(diproylamino)-ethyl]-1,3,5-benzenetricarboxamide **3***
1.75 g (0.0069 mol) of trimesic acid trimethyl ester were dispersed in 6.25 mL (5.0 g, 0.03 mol) of *N*,*N*-dipropyl-ethylenediamine under nitrogen atmosphere. The mixture was heated to 125 °C, stirred overnight and subsequently allowed to cool down to room temperature. The crude product was recrystallized from DMF with some drops of water. The product was filtrated and dried under reduced pressure, yielding 2.1 g (52 %) of **3** as a light yellowish powder.
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.89 (t, 18H), 1.48 (sextet, 12H), 2.44 (m, 12H), 2.67 (t, 6H), 3.52 (quartet, 6H); 7.12 (t(br), 3H); 8.38 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 11.9, 20.1, 37.5, 52.4, 55.8, 128.0, 135.3, 165.6.
MS-EI (m/z): 588 (M·+), 559, 286, 128, 115, 114, 86, 72.
Anal. calcd. for $C_{33}H_{60}N_6O_3$: C 67.3, H 10.3, N 14.3; found: C 67.3, H 9.8, N 14.0.

Methods

Nuclear magnetic resonance spectroscopy:

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) experiments were carried out on a Bruker Avance AC 300 spectrometer at room temperature. The compounds were dissolved in $CDCl_3$.

Mass spectroscopy:

Mass spectra were recorded on a Finnigan MAT 8500 spectrometer (Thermo Fisher Scientific) (EI, 70 eV) using direct injection mode. Only molecule peak ($M^{\cdot+}$) and peaks with relative intensities ≥ 30 % are reported in the corresponding characterization data.

Elemental analysis:

Elemental analysis (C, H, N) was carried out with a Unicube from Elementar Analysen-Systeme with sulfanilamide as a standard. The samples were placed in tin boats and measured twice. The theoretical amount of all elements was calculated using Chemicalize. Values are given in weight %.

S2: FT-IR investigation of 1,3,5-benzenetricarboxamides 1 – 3

FT-IR spectra of bulk materials as obtained from synthesis were recorded with a Perkin-Elmer Spectrum 100 FT-IR spectrometer in ATR mode.

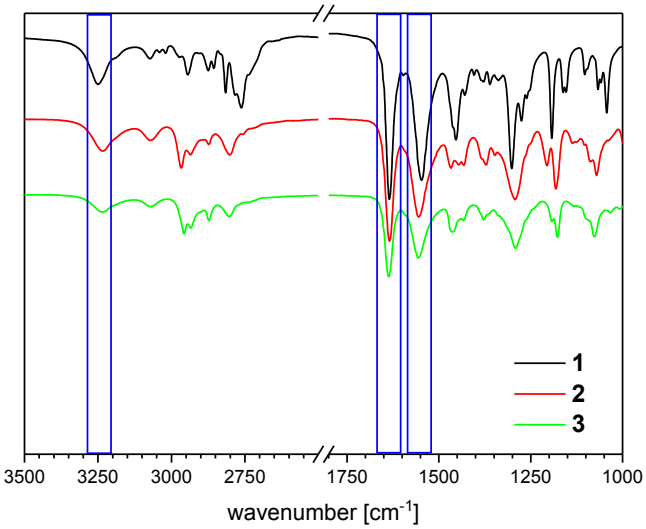

Figure S2. FT-IR spectra of **1** – **3** as obtained from synthesis. The BTAs show IR signals (see blue boxes) at around 3240 cm^{-1} (Amide A, N-H stretch vibrations), at around 1640 cm^{-1} (Amide I, C=O stretch vibrations) and at around 1560 cm^{-1} (Amide II; superposition of N-H bend and C-N stretch vibrations). The position of the signals indicates a columnar stacking due to threefold hydrogen bonds between the BTA building blocks.[1]

[1] P. J. M. Stals, M. M. J. Smulders, R. Martín-Rapún, A. R. A. Palmans and E. W. Meijer, *Chem. Eur. J.*, 2009, **15**(9), 2071.

S3: Differential scanning calorimetry of 1,3,5-benzenetricarboxamides 1 – 3

DSC were performed on a Mettler Toledo DSC^{3+} STAR^{e} System. Typically, 10 mg of the compound were weighed in a crucible. Three heating and cooling curves were recorded from -50 °C to 250 °C with a rate of 10 K min^{-1} under nitrogen atmosphere.

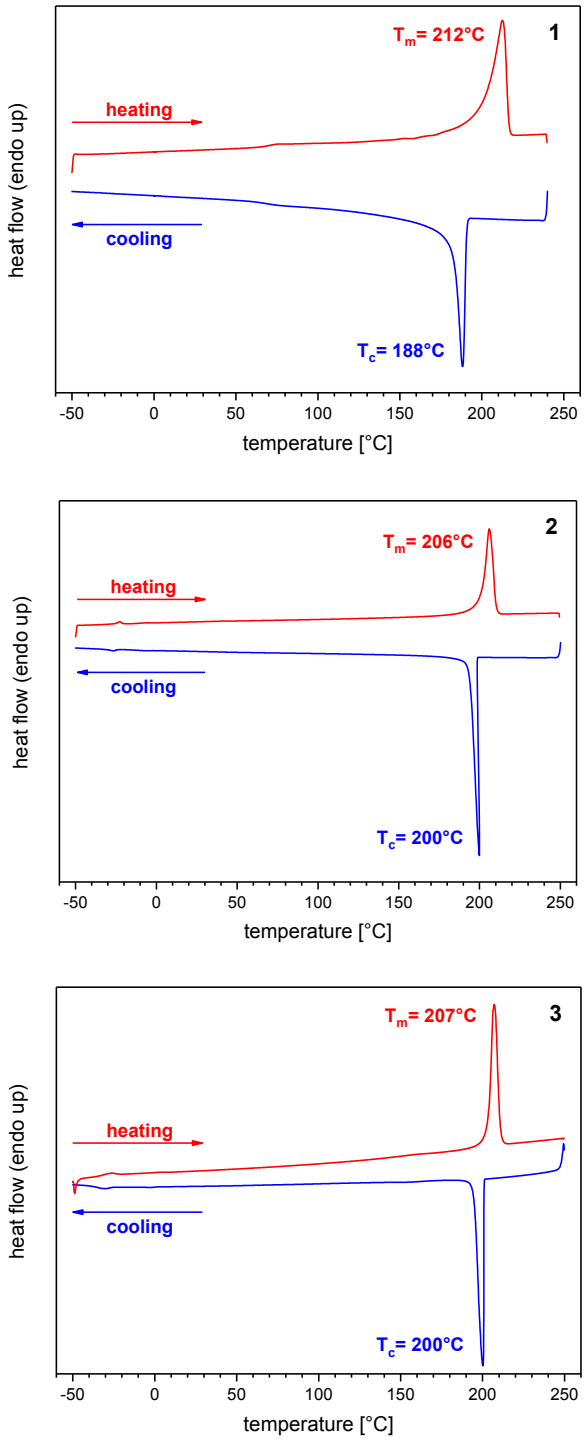

Figure S3. DSC 2nd heating and 2nd cooling curves of **1** – **3** at a rate of 10 K min^{-1} under nitrogen atmosphere. The melting peak and the crystallization peak are labeled as T_m and T_c, respectively.

S4: Polarizing optical microscopy of 1,3,5-benzenetricarboxamides 1 – 3

Temperature-dependent polarizing optical microscopy of 1,3,5-benzenetricarboxamides 1 – 3 in bulk:

A small portion of the powder was placed on a glass slide (Menzel-Gläser), covered with a cover slide and heated to 250 °C. Images were recorded between crossed polarizers using a Nikon Diaphot 300 microscope equipped with a camera and a Mettler Toledo hotstage.

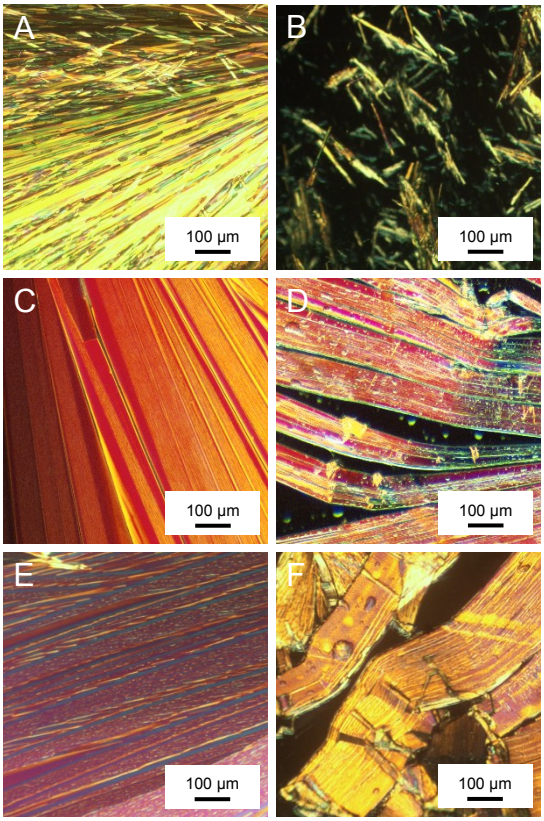

Figure S4.1. A – F: Temperature-dependent polarized optical micrographs in bulk of **1**, **2** and **3** at 180 °C, before (A, C and E) and after (B, D and F) shearing the sample. All three compounds show birefringent textures. **1** shows a brittle behavior and breaks upon shearing, confirming a crystalline structure (B). **2** and **3** show deformable textures and bending, which is indicative for a plastic crystalline behavior (D and F).

Temperature-dependent polarizing optical microscopy of aqueous solution of 1,3,5-benzenetricarboxamides 2:

An aqueous solution with a concentration of 20 g L^{-1} of **2** was placed on a glass slide (Menzel-Gläser) and covered with a smaller cover slide. The liquid sample was then sealed with silicon high-vacuum grease to prevent evaporation. Images were taken between crossed polarizers in the presence of a λ/4 plate using a Nikon Diaphot 300 microscope equipped with a camera and a Mettler Toledo hotstage.

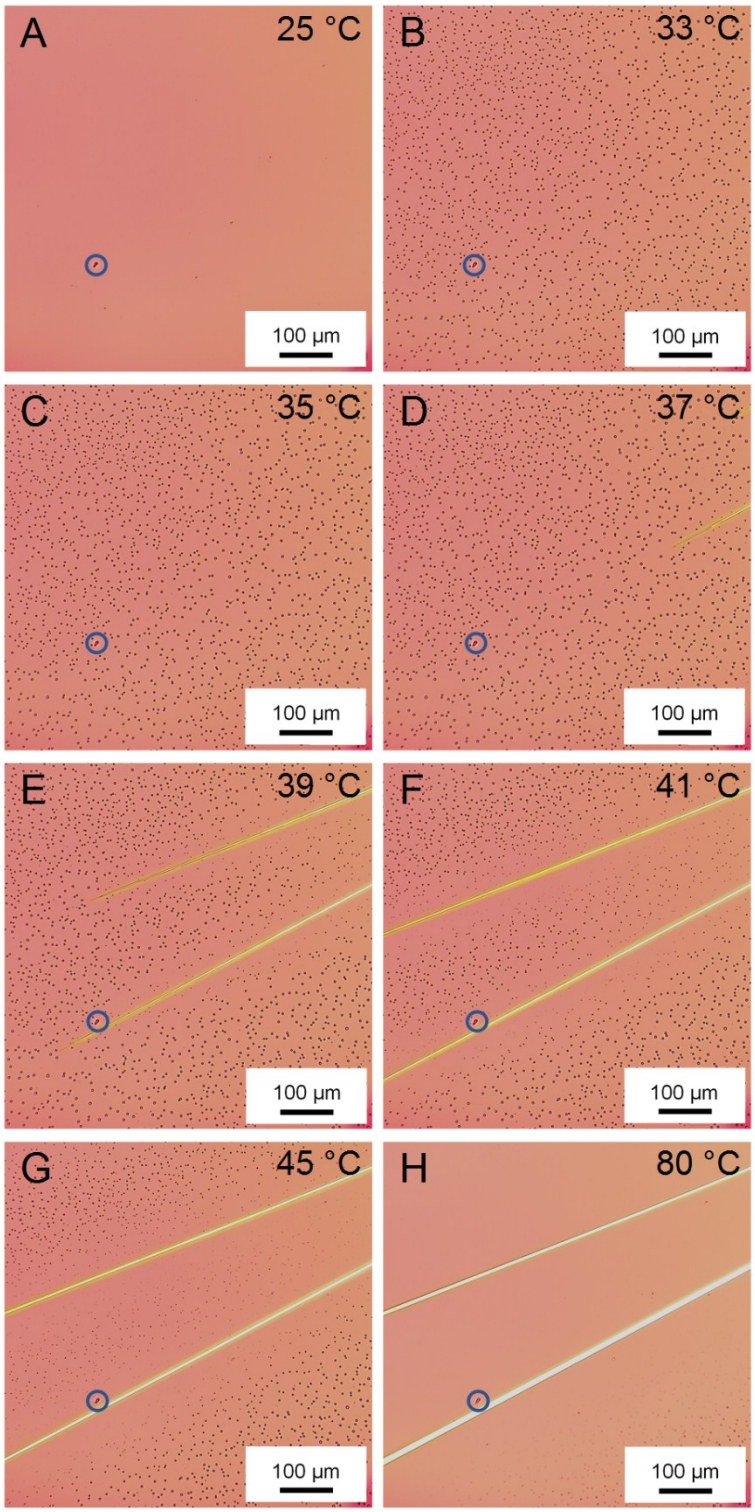

Figure S4.2. A – H: Series of polarized optical micrographs with λ/4 plate of 20 g L^{-1} of **2** in water. Heating the sample (blue circle indicates same position) from 25 °C to 80 °C with a heating rate of 1 K min^{-1} reveals phase separation of the solution followed by self-assembly of **2** into supramolecular fiber-like structures.

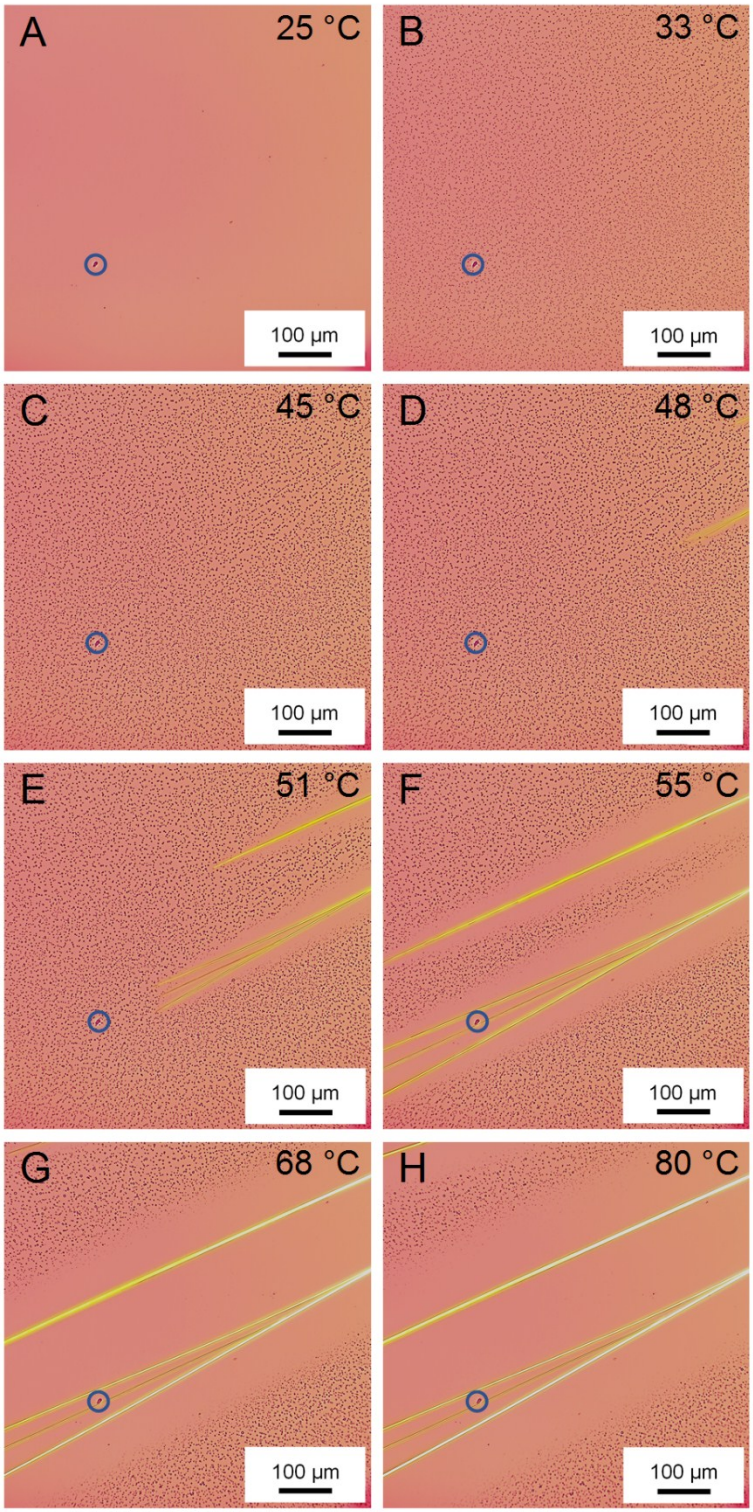

Figure S4.3. A – H: Series of polarized optical micrographs with λ/4 plate of 20 g L^{-1} of **2** in water. Heating the sample (blue circle indicates same position) from 25 °C to 80 °C with a heating rate of 5 K min^{-1} reveals phase separation of the solution followed by self-assembly of **2** into supramolecular fiber-like structures.

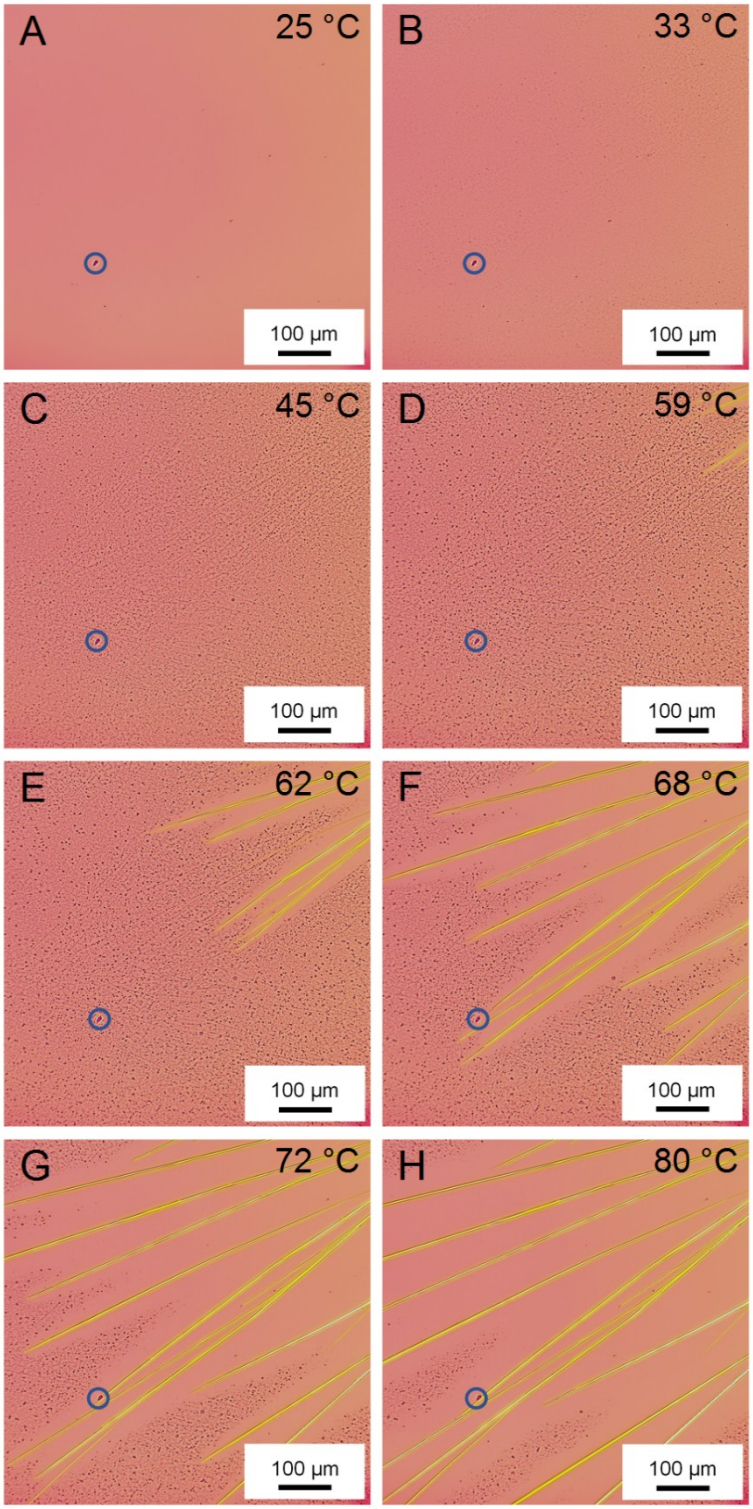

Figure S4.4. A – H: Series of polarized optical micrographs with λ/4 plate of 20 g L^{-1} of **2** in water. Heating the sample (blue circle indicates same position) from 25 °C to 80 °C with a heating rate of 10 K min^{-1} reveals phase separation of the solution followed by self-assembly of **2** into supramolecular fiber-like structures.

S5: X-ray powder diffraction patterns of 1,3,5-benzenetricarboxamide 2

X-ray powder diffraction (XRD) measurements of the bulk material and of aqueous samples were performed on a Huber Guinier diffractometer 600, equipped with a Huber germanium monochromator 611 to receive a $Cu_{K\alpha 1}$ radiation of $\lambda = 154.051$ pm. A custom-made oven was installed into the diffractometer to investigate the samples at different temperatures. For the measurements, Mark tubes with an outer diameter of 1 mm were used for the bulk material and Mark tubes with an outer diameter of 2 mm for the aqueous samples, respectively. In all cases, the wall thickness of the Mark tubes was 0.01 mm.

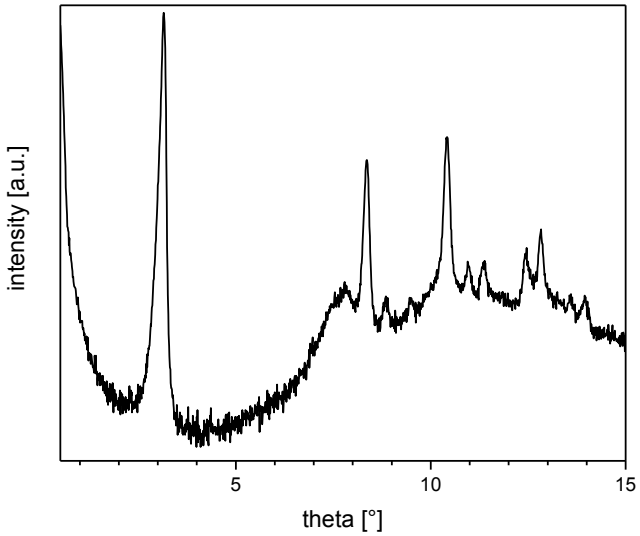

Figure S5.1. X-ray powder diffraction pattern of **2** at room temperature as obtained from synthesis.

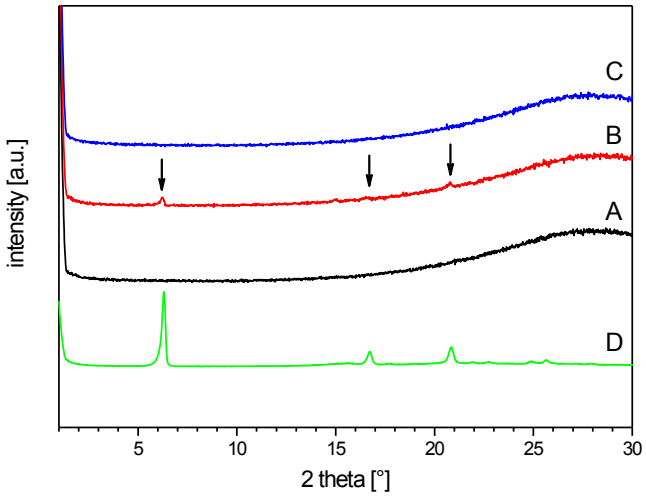

Figure S5.2. X-ray powder diffraction patterns of **2** in water with a concentration of 20 g L^{-1} measured at room temperature before heating (A), measured at 40 °C featuring weak diffraction peaks indicated by arrows (B), and at room temperature after cooling (C). X-ray powder diffraction pattern of **2** as obtained from synthesis as reference (D).

S6: Cloud and clearing point determination of 1,3,5-benzenetricarboxamide 2 in water

The cloud and clearing points of **2** were determined optically for 16 concentrations in parallel using the crystallization system Crystal16 (Technobis Crystallization Systems). Concentrations of 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90 and 100 g L^{-1} of **2** in water were prepared at room temperature. The samples were stirred at 600 rpm and the transmission of each sample was recorded for two cycles in the range of 5 °C to 80 °C. Each cycle consists of a heating step with a rate of 0.5 K min^{-1}, an isothermal hold at 80 °C for 5 min, a subsequent cooling step with a rate of 0.5 K min^{-1}, and an isothermal hold at 5 °C for 30 min.

Here, we define transmission at 0 % as cloud point and at 100 % as clearing point. Exemplarily, the 1st heating and 1st cooling cycle and the recorded transmission for the sample **2** with a concentration 20 g L^{-1} are shown in Figure S6. During heating, clouding of the sample occurs at around 33 °C and leads to a rapid change in the transmission from 100 % to 0 %. Upon subsequent cooling, a clear solution is obtained at around 27 °C, indicated by the rapid change of the transmission from 0 % to 100 %.

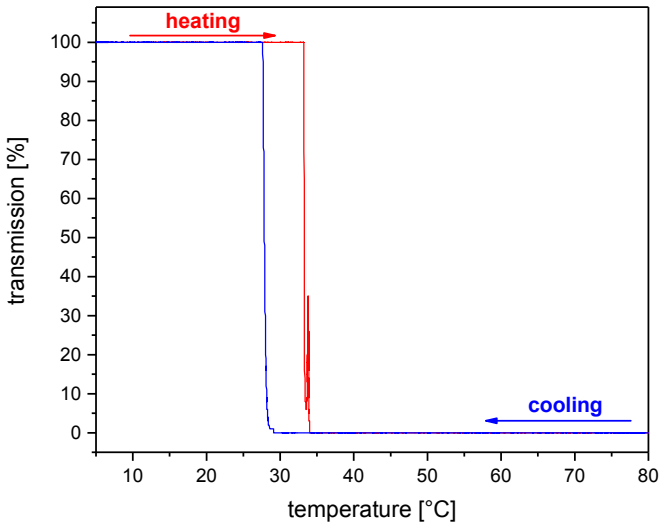

Figure S6. Cloud and clearing point determination. The 1st heating and 1st cooling cycle and the recorded transmission for **2** with a concentration 20 g L^{-1} is shown. Upon heating, the cloud point of the sample was determined at around 33 °C (change of transmission from 100 % to 0 %). Upon cooling, the clearing point was indicated at around 27 °C (change of transmission from 0 % to 100 %).

S7: Micro-differential scanning calorimetry of 1,3,5-benzenetricarboxamide 2 in water

Micro-differential scanning calorimetry (μDSC) measurement was performed on a Setaram MicroDSC III. A solution of the compound under investigation (about 0.7 mL) was filled into a Hastelloy C276 sample cell which was immediately sealed to avoid evaporation. The reference cell was filled with an equal amount of water and sealed. Prior to measurement, the cells were kept at the desired starting temperature for at least 1 h to ensure thermal equilibration. The measurement was carried out applying a heating and cooling rate of 0.1 K min^{-1}.

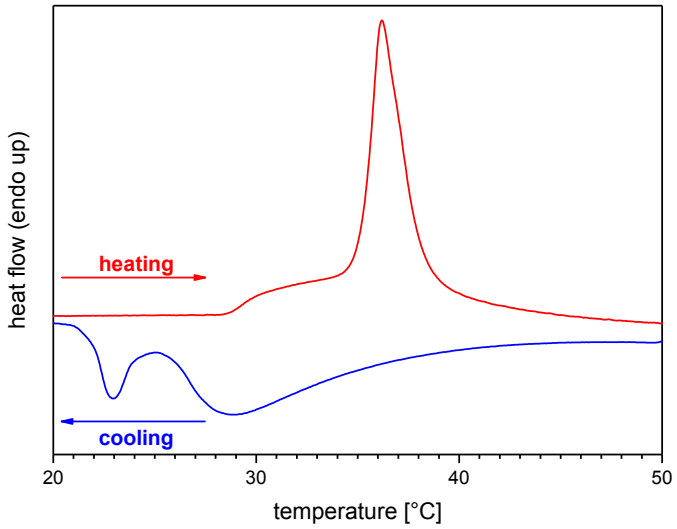

Figure S7. Micro-differential scanning calorimetry curves of **2** in water with a concentration of 20 g L^{-1} at a heating and cooling rate of 0.1 K min^{-1}. Upon heating, a smaller peak with an onset at about 29 °C followed by a stronger peak with a maximum at 36 °C is observed. Upon cooling, two peaks are visible demonstrating the reversibility of the process.

S8: Scanning electron microscopy of 1,3,5-benzenetricarboxamide 2

Measurements were conducted on different scanning electron microscopes, namely, Ultra plus (Zeiss), Dual-Beam FIB-SEM, 1540XB-CrossBeam (Zeiss) and FEI Quanta FEG 250 (Thermo Fisher Scientific). For the measurement on the Ultra plus microscope, the samples were mounted on a sample holder using an adhesion graphite pad and sputtered with platinum (1.3 – 2 nm) to ensure sufficient conductivity. Furthermore, the supramolecular microtubes were investigated with the focused ion beam FIB-SEM with a Ga-focused ion source. Here, the samples were attached on a sample holder using an adhesive conductive graphite pad. Cross-sections were produced with cutting lengths between 5 µm and 20 µm. The cutting line width was up to 30 µm. The used FIB current was between 200 pA and 500 pA, and a step size of 20 nm min^{-1} was applied. The FEI Quanta FEG 250 was conducted in the environmental scanning electron microscopy (ESEM) mode. 2 µL of a clear solution of **2** in water with a concentration of 20 g L^{-1} was placed at 60 °C in the sample holder (Figure S8A). At 60 °C, the solution turned turbid and supramolecular fiber-like structures were formed (B and C). Figure S8B and S8C show the supramolecular structures at different positions of the sample.

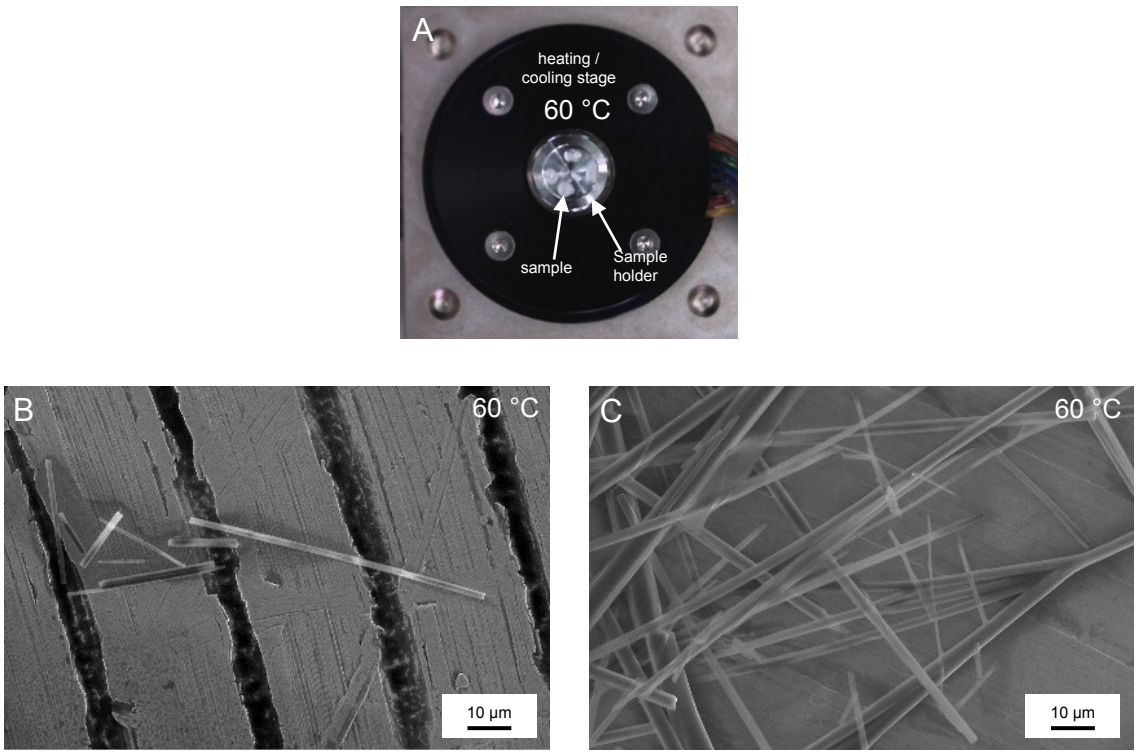

Figure S8. A: Optical micrograph of the cooling / heating stage in the environmental scanning electron microscope. B – C: Scanning electron micrographs of supramolecular microtubes at different positions of the sample.

S9: Optical micrograph and fiber diameter histogram of supramolecular microtubes of 1,3,5-benzenetricarboxamide 2

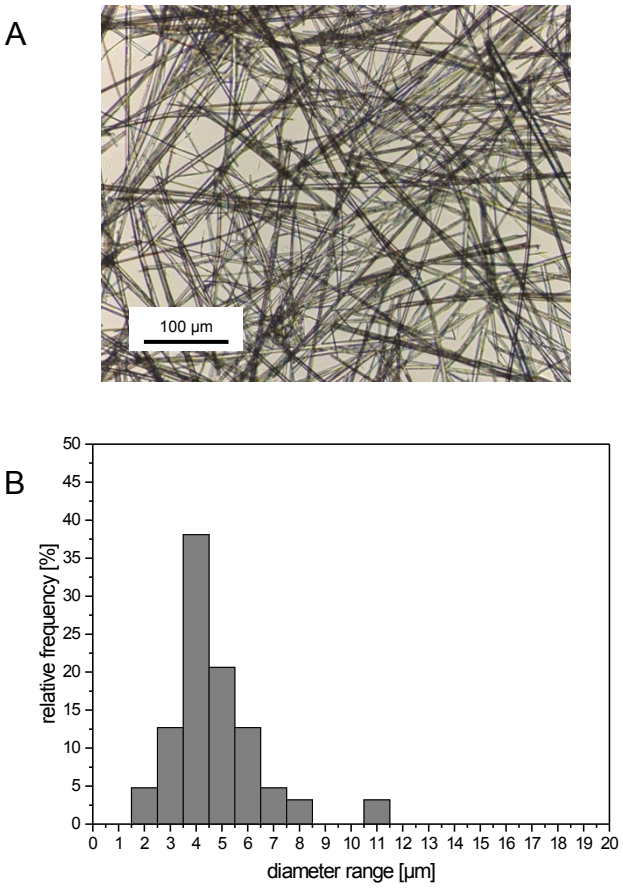

Figure S9. A: Optical micrograph of isolated supramolecular structures of **2** prepared by dropping a small amount of an aqueous solution of **2** with a concentration of 10 g L^{-1} onto a glass surface preheated to 80 °C and subsequently evaporation of water at this temperature. Hollow supramolecular microtubes with lengths of several hundreds of µm are visible. B: Histogram of the diameters of supramolecular microtubes based on at least 60 individual microtubes from micrograph A. The mean diameter was determined to be 4.7 ± 1.6 µm.