

Mirror Symmetry Breaking and Chiral Amplification in Foldamer-Based Supramolecular Helical Aggregates

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SUPPORTING INFORMATION

Materials and methods

The synthesis and characterization of **1** are described elsewhere.^{1,2}

General sample preparation – In an attempt to ‘erase’ any solid-state chiral memory, **1** was dissolved in CHCl₃ prior to solvent evaporation and subsequent addition of the solvent that promotes fiber formation. However, it must be noted that the K_a for dimerization in chloroform at 35 °C is very strong (*ca.* 6000 M⁻¹) and may preclude attempts to remove all traces of chirality.^{1,2} A measured amount of **1** (Mettler Toledo MX5 microbalance) in a tin capsule was dissolved in CHCl₃ and the solvent was removed with a stream of nitrogen. The appropriate amount of solvent was then added to make the desired concentration. This solution was sealed and sonicated in a bath sonicator (Elma Ultrasonic LC20H bath sonicator with a frequency of 35 kHz) for 10 minutes. Immediately after sonication, the solution is considered a ‘day 0’ sample and the figure captions indicate the age of the solution being used for the various experiments. Stirring (370 RPM) caused a decrease in the rate of chiral amplification, likely due to the disruption of fiber growth. In one series of experiments an equal mixture or an unequal mixture of mature fibers (‘day 112’ in CH₂Cl₂) of opposite chirality were mixed together and the CD spectra were monitored with time (over a period of 10 days). In both cases no significant changes at 330 nm were observed.

CD - Circular dichroism (CD) spectra were recorded using a Jasco J-710 or J-815 spectropolarimeter equipped with a Peltier temperature controller. Typical operating parameters were: 400 to 250 nm; 1 nm bandwidth, 0.1 step resolution, 0.25 s response, 100 nm/min scan speed and 5 accumulations. Spectra were collected at room temperature unless otherwise stated. The CD curves were smoothed with a convolution width of 13 using the Means-Movement method (Jasco Spectra Analysis software version 1.53.04). CD spectra were recorded in a 1 or 2 mm cuvette or as a KBr pellet (13 mm) as indicated in the figure caption.

CD Sample preparation: The chiral additive experiments were carried out using a 0.75 mg/mL solution of **1** with sonication for 10 minutes. From this vial, 160 µL were transferred to 640 µL of solvent that contained 6.25% (v/v) diethyl L-tartrate or diethyl D-tartrate. This corresponds to a final tartrate concentration of 5% (v/v) and to 0.15 mg/mL of **1**. This procedure was repeated for a control experiment with no chiral additive from the same solution. CD spectra were recorded after 15 minutes. Inducing an asymmetric perturbation of transition moments, may perturb the equilibrium between the left- and right-handed helical conformations of **1** causing a preference for one chirality of the hierarchical fibers formed and thus giving a negative or positive CD band. Intermolecular stabilization of the lock-washer building block or fibrillar substructures are likely at play. We believe that these diastereomeric interactions are

strong enough to cause an energy difference between the M- and P-helix to such an extent that the chirality of the initial fibers is specifically influenced. Tartaric acid is a chiral species, widely used as a chiral reagent, chiral-resolving agent, and chiral auxiliary in organic synthesis, and it may induce CD in achiral molecules. Diethyl tartrate was used previously in our labs to induce chirality in helical oligopyridinedicarboxamide molecular strands. The diethyl tartrate additive is well-suited for this study since diethyl L- and D-tartrate show CD bands below 240 nm whereas the absorption band of **1** displays a maximum at 330 nm.³ The temperature studies of **1** in 1,2-dichloroethane with chiral additive (Figure 4b and Figure SI-4) were carried out as follows: the appropriate solution was heated to 80 °C and held at this temperature for 15 minutes. The temperature was subsequently reduced to -10 °C over a period of *ca.* 5 minutes. After remaining at -10 °C for 15 minutes a CD spectrum was recorded and the temperature was increased. For all temperature studies, each spectrum at the indicated temperature was recorded after equilibrating for 5 minutes. In one series of experiments an equal mixture, or an unequal mixture of mature fibers (day 112) of opposite chirality were mixed together and the CD spectra were monitored with time (over a period of 10 days). In both cases no changes at 330 nm were observed.

TEM - Transmission electron microscopy (TEM) was carried out using an FEI Tecnai 12 TEM equipped with an AMT XR80C CCD camera system. The images were obtained in bright field mode at an accelerating voltage of 120 kV.

TEM Sample preparation: Approximately 2 µL of sample (*ca.* 0.15 mg/mL in CH₂Cl₂) was applied directly to a carbon support film of 15-24 nm thickness (carbon type A) on a 300 mesh Cu grid (Ted Pella #01820)

AFM - Atomic force microscopy (AFM) was carried out under ambient conditions using a Bruker Nanoscope MultiMode scanning probe microscope. The AFM was operated in the tapping mode using 125 µm etched silicon probes (Digital Instruments Nanoprobe RTESP) with a 10 nm apex or high aspect ratio silicon nitride probes (NanoWorld, SuperSharpSiliconTM) with a 2 nm apex. The amplitude set point was about 70% of the pop off voltage, the scan rate was typically from 0.6 to 1 Hz, the integral gain was between 1 and 3 and the proportional gain between 2 and 5. Images were flattened using the Nanoscope 6.14r2 software.

AFM Sample preparation: Approximately 1 µL of sample (*ca.* 0.15 mg/mL) was spin-coated onto a freshly cleaved mica plate rotating at 4000 rpm.

SEM – Scanning electron microscopy (SEM) was carried out using a Hitachi S-4700 FE-S/TEM equipped with the Oxford Inca EDS. The images were obtained with an accelerating voltage of 2.0 kV and 10 µA.

SEM Sample preparation: Approximately 15 µL of sample (*ca.* 0.15 mg/mL in CH₂Cl₂) was applied directly a freshly cleaved mica substrate and left to dry. Approximately 3 nm of platinum was subsequently evaporated onto the sample to improve its conductivity.

References

1. Cuccia, L. A.; Lehn, J. M.; Homo, J. C.; Schmutz, M. *Angew. Chem. Int. Ed.* **2000**, *39*, 233-237.
2. Cuccia, L. A.; Ruiz, E.; Lehn, J. M.; Homo, J. C.; Schmutz, M. *Chem. Eur. J.* **2002**, *8*, 3448-3457.
3. Kolomiets, E.; Berl, V.; Lehn, J.-M. *Chem. Eur. J.* **2007**, *13*, 5466-5479.

Supplemental Figures

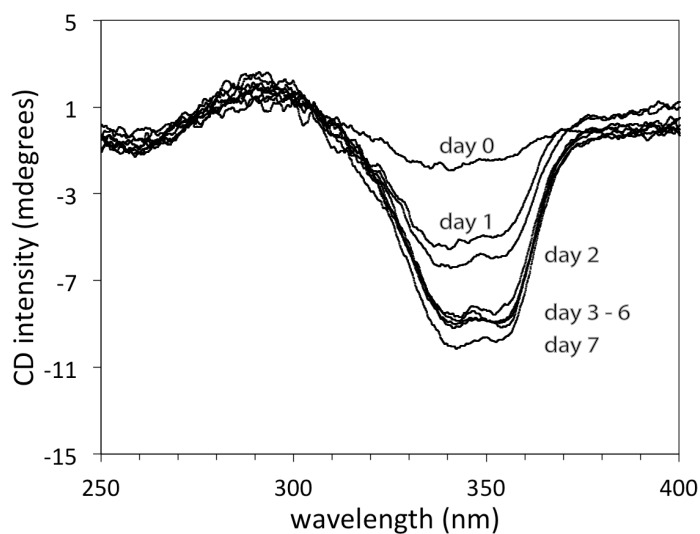


Figure SI-1. CD spectra of **1** with increasing time (ca. 0.15 mg/mL in CH_2Cl_2 ; 2 mm path length).

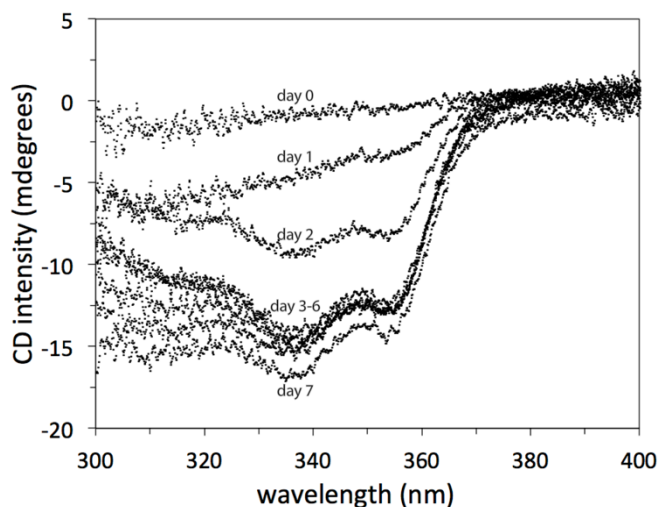


Figure SI-2. CD spectra of **1** with increasing time (ca. 0.2 mg/mL in pyridine; 1 mm path length).

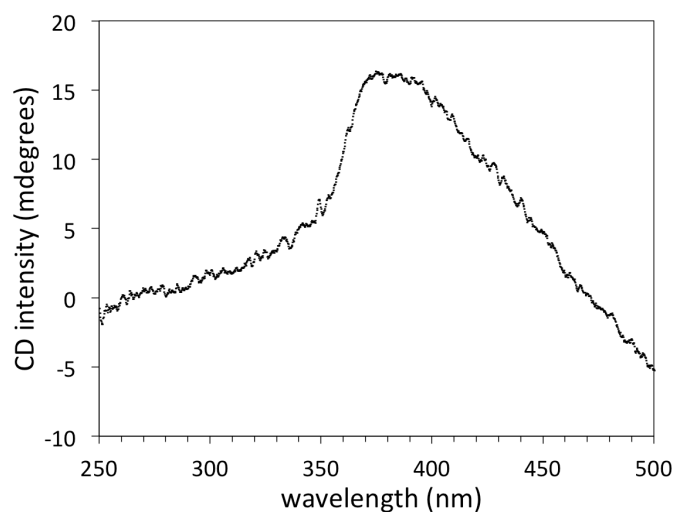


Figure SI-3. CD spectrum of **1** in KBr (125 mg KBr and *ca.* 5 mg of **1**; 13 mm diameter)

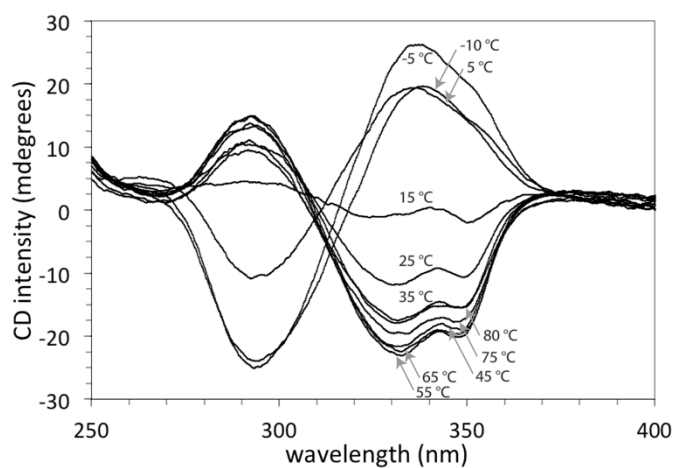


Figure SI-4. CD spectra of **1** with 5% diethyl D-tartrate and increasing temperature as indicated (*ca.* 0.15 mg/mL in 1,2-dichloroethane; 15 minutes; 2 mm path length).

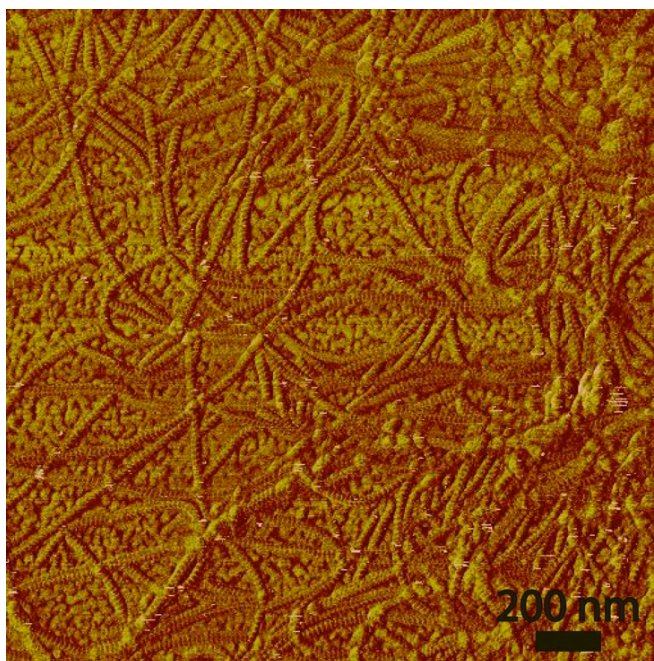


Figure SI-5. Tapping mode AFM phase image of **1** (*ca.* 0.15 mg/mL in CH₂Cl₂; day 4).

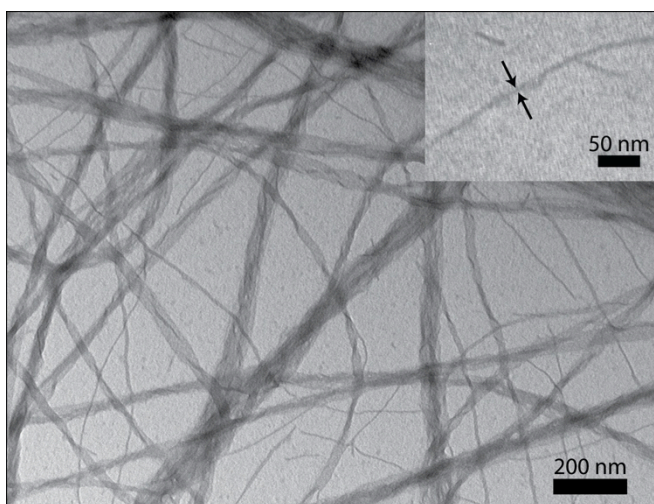


Figure SI-6. TEM micrograph of **1** with 5.2 nm fiber highlighted in inset (*ca.* 0.15 mg/mL in CH₂Cl₂; day 7).

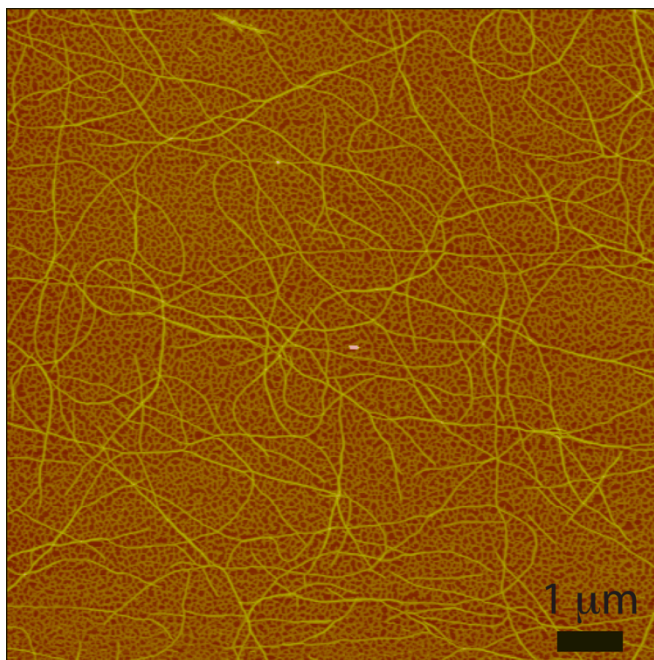


Figure SI-7. Tapping mode AFM height image of **1** with 21 nm height scale (*ca.* 0.15 mg/mL in CH₂Cl₂; day 7).

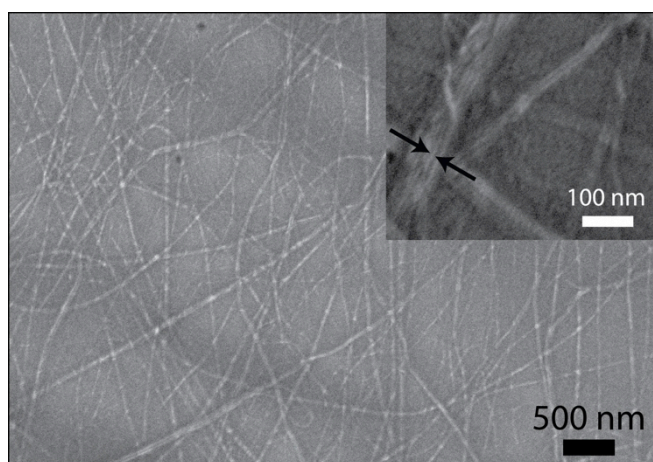


Figure SI-8. SEM micrograph of **1** with 13 nm fiber highlighted in inset (*ca.* 0.15 mg/mL in CH₂Cl₂; day 11)

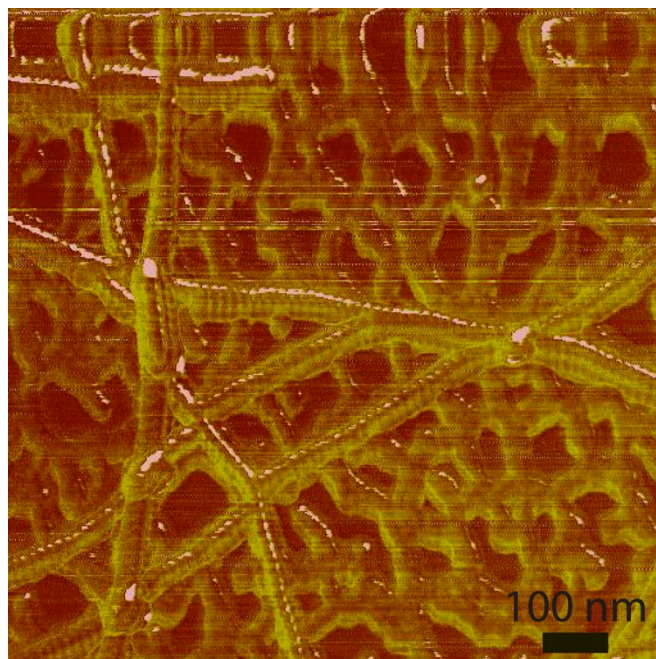


Figure SI-9. Tapping mode AFM phase image of **1** (*ca.* 0.15 mg/mL in 1,2-dichloroethane; day 13).

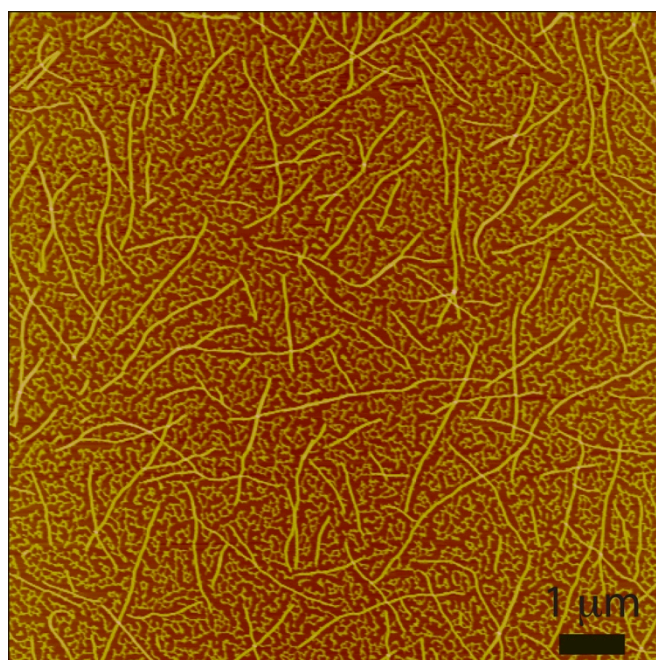


Figure SI-10. Tapping mode AFM height image of **1** with 10 nm height scale (*ca.* 0.15 mg/mL in CH₂Cl₂; day 14).

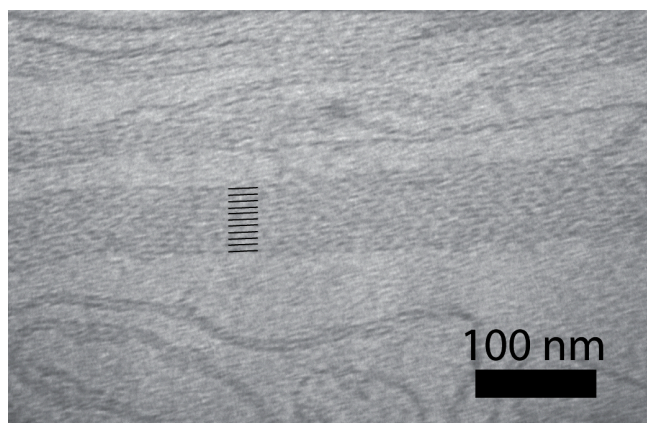


Figure SI-11. TEM micrograph of **1** with a 2D array of 2.6 nm fibrils highlighted (*ca.* 0.15 mg/mL in CH₂Cl₂; day 14).

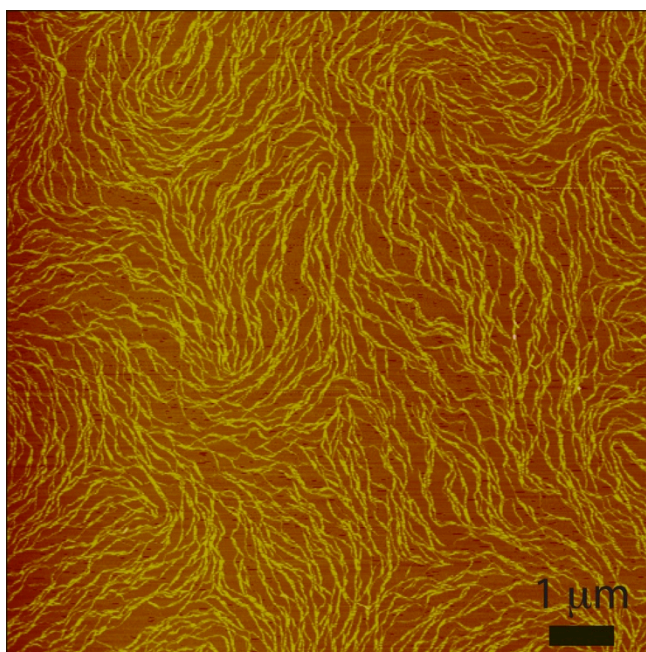


Figure SI-12. Tapping mode AFM height image of **1** with 10 nm height scale (*ca.* 0.15 mg/mL in pyridine; day 25).

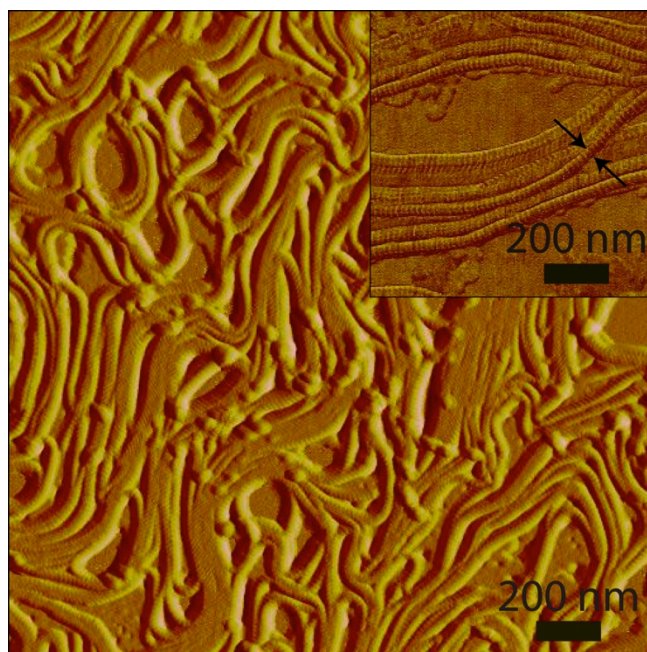


Figure SI-13. Tapping mode AFM amplitude image of **1** (*ca.* 0.15 mg/mL in CH₂Cl₂; day 38); inset: tapping mode AFM phase image of **1** with 24 nm fiber highlighted (*ca.* 0.10 mg/mL in CH₂Cl₂; day 20).

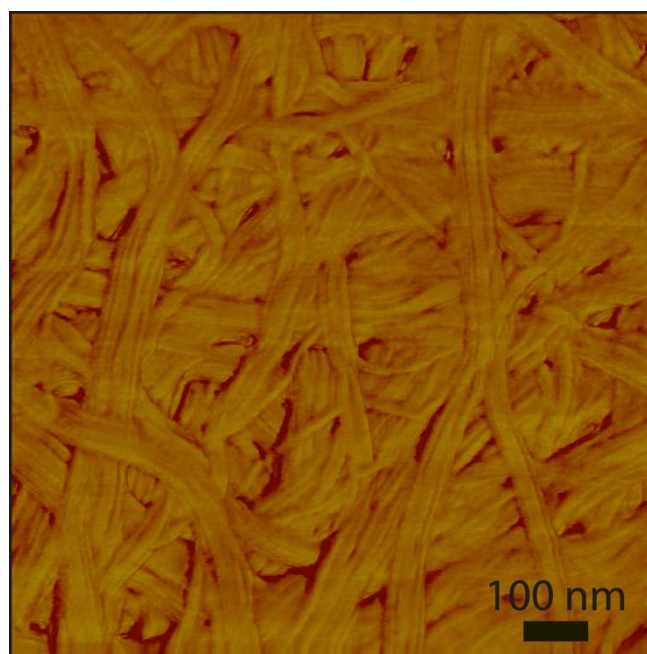


Figure SI-14. Tapping mode AFM amplitude image of **1** (*ca.* 0.15 mg/mL in CH₂Cl₂; day 38).