Supporting information:

Fivefold Helical Cellulose Trapped in Sulfuric Acid Framework

Wei Li, [1] Yu Ogawa, [1] Javier Perez, [2] Karim Mazeau, [1] Isabelle Morfin, [3] Yoshiharu Nishiyama[1]

1 Univ. Grenoble Alpes, CNRS, CERMAV, 38000 Grenoble, France.

2 Soleil Synchrotron, L'Orme des Merisiers, 91192 Gif-sur-Yvette, France

3 Universite Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France

Samples

96 wt% sulfuric acid (H_2SO_4) was purchased from Acros Organics, France. Flax fibers were purchased from a textile dealer.

Synchrotron X-ray scattering

The wide-angle X-ray scattering experiments were conducted with X-rays of 16 keV (λ = 0.77489 Å) at SWING beamline of SOLEIL Synchrotron (Paris, France). Three pipette glass tubes were sealed by flame (inner diameter of about 1.3 mm, wall thickness of 0.15 mm). Each tube contained about 3.75 mg of flax fibers, and then about 15 mg of H_2SO_4 solution were added into the tube by centrifugation, and it took approximately 15 mins before taking the first diffraction pattern. The tube with the sample was placed in a temperature-controlled specimen holder (Linkam THMS 600) and was cooled down from room temperature around 23 ˚C to -20 ˚C, then staying at -20 ˚C for 1 hour, then the temperature was increased to 20 ˚C. During this process, the diffraction patterns were taken every 5 mins, and the exposure time was 2 s for each frame.

Lab-source X-ray diffraction

X-ray was generated by a pin-hole flat-plate camera mounted on a Philips PW3830 generator operating at 30 kV and 20 mA (Ni filtered CuKα radiation, λ = 1.5418 Å). X-ray diffraction (XRD) patterns were recorded on Fujifilm imaging plates in a Warhus vacuum chamber, read by a Fujifilm BAS 1800-II bioimaging analyzer.

Solid-state ^{13}C CP/MAS NMR

The solid-state ^{13}C CP/MAS (cross-polarization magic-angle spinning) NMR spectra were measured with a Bruker Avance III 400 spectrometer operating at 100 MHz for ^{13}C. The spinning speed was set at 12 kHz, the sweep width at 29761 Hz, the recycle delay at 2 s and the cross-polarization contact at 2 ms. The ^{13}C chemical shifts were calibrated with the glycine carboxyl group at 176.03 ppm.

Exhaustive search of unit cell parameters

We carried out an exhaustive search of the unit cell parameters by assuming an orthorhombic unit cell. The unit cell parameter, *a*, is allowed to vary from 4 Å to 20 Å, nad *b* is constrained to be larger than *a* and smaller than 20 Å, both with steps of 0.01 Å. The *d*-spacing, d_{hkl}, was calculated as follow,

$$d_{hkl} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

where h ($0 \le h \le 10$), k ($0 \le k \le 10$) and l ($0 \le k \le 6$) were Miller indices.

The sum of the difference between d_{obs} and d_{hkl} of the 12 reflections (marked in Figure 1), φ_s, was calculated as:

$$\varphi_s = \sum_{i=1}^{12} \min_{\substack{0 \le h \le 10 \\ 0 \le k \le 10}} \frac{(d_{hkl}(i) - d_{obs}(i))^2}{\varepsilon(i)}$$

where $\varepsilon(i)$ was the error of the $d_{obs}(i)$.

Figure S1a shows a φ_s map as a function of unit cell parameters, a and b. Red spots indicated good agreement between d_{obs} and d_{hkl} for the 12 reflections. There were more red spots when the unit cell parameters *a* and *b*, hence the unit cell volume were large (Fig. S1). This is reasonable as a larger unit cell is more likely to get smaller φ_s due to its denser reciprocal lattice. To eliminate the influence of the unit cell volume, the φ_{Vu} was calculated as follows:

$$\varphi_{Vu} = \varphi_s \times V_u \times V_u$$

It was found the tendency of φ_{Vu} with increasing volume was nearly flat, so the volume effect was considered roughly cancelled. The smallest φ_{Vu} corresponded to the unit cell parameters a = 9.12 Å, b = 12.99 Å, c = 25.08 Å.

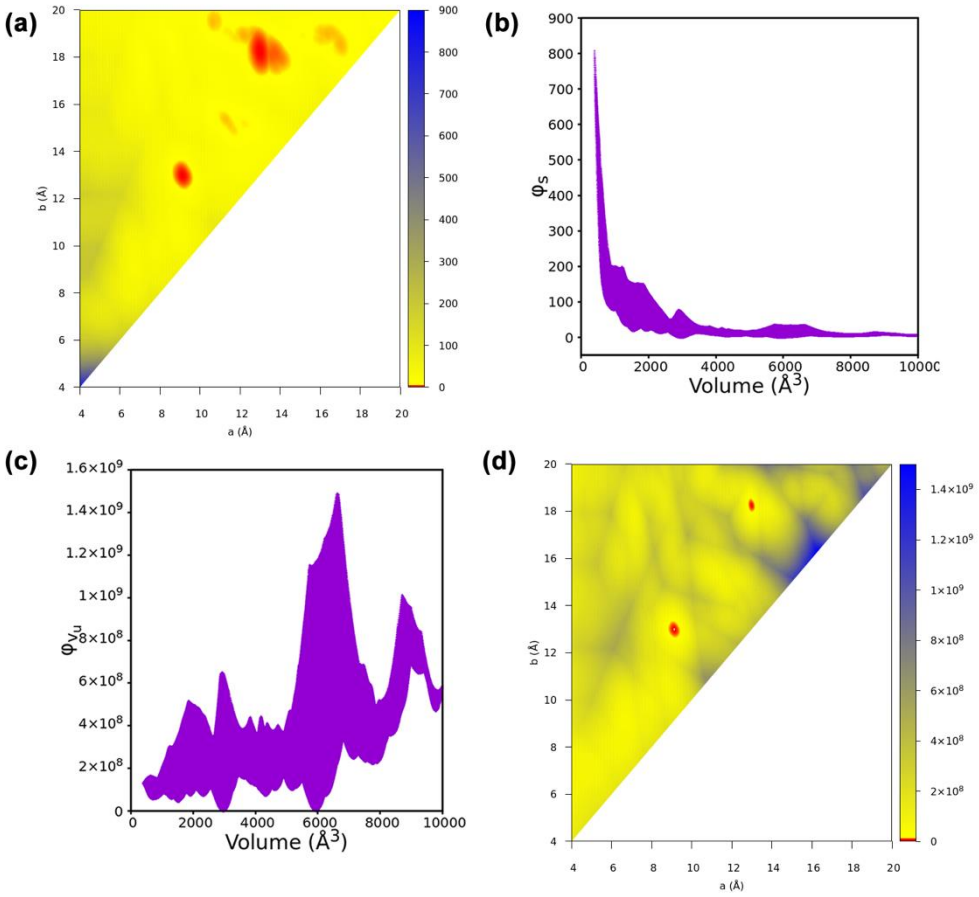

Figure S1. (a) φ_s map as a function of unit cell parameters, a and b. Red regions represent φ_s below 10. (b) φ_s as a function of unit cell volume. (c) φ_{Vu} as a function of unit cell volume. (d) φ_{Vu} map as a function of unit cell parameters, a and b.

Table S1. *The d-spacings (d_{obs}), errors of d-spacings (ε), the possible l values of Miller indices of the 12 reflections marked in Figure III.3b.*

Reflections	d_{obs} (Å)	*Error of* d_{obs} ε (Å)	d_{cal} (Å)	$\lvert d_{obs}-d_{cal}\rvert/d_{obs}$ (%)	Miller indices
No. 1	3.92	0.03	3.91	-0.216	130
No. 2	4.30	0.04	4.30	0.060	210
No. 3	5.29	0.05	5.29	0.009	120
No. 4	6.50	0.06	6.50	-0.077	020
No. 5	7.46	0.07	7.46	0.055	110
No. 6	9.13	0.08	9.12	-0.110	100
No. 7	5.77	0.05	5.77	-0.046	022
No. 8	5.12	0.05	5.13	0.176	023
No. 9	4.51	0.04	4.51	0.022	024
No. 10	5.63	0.05	5.64	0.295	014
No. 11	4.66	0.05	4.68	0.413	015
No. 12	3.98	0.03	3.98	0.077	016

Regeneration of flax cellulose swollen in 64 wt% sulfuric acid

Flax fibers swollen in 64% H_2SO_4 at -20 °C for 1 hour were washed by cold water until the pH reached neutral. The flax fibers were then subjected to X-ray diffraction in the wet state and after freeze-drying (Fig. S2a). Upon regeneration, the peak intensities weakened as can be seen in the diffraction pattern taken in the wet state. After drying, the diffraction pattern of the regenerated flax fibers shows some features of cellulose I, but the reflections are much blurrier arcs. No cellulose-II feature is observed, indicating that cellulose chains have not been in an antiparallel arrangement during the complexation with the acid, unlike in the case of alkali-swollen cellulose. The solid-state ^{13}C NMR spectra of flax fibers and the regenerated dry flax fibers are shown in Figure S2b. Judging from the C4 signals, the regenerated dry flax fibers contains more amorphous or disordered portions than the initial flax fibers, which was in agreement with the results of X-ray diffraction.

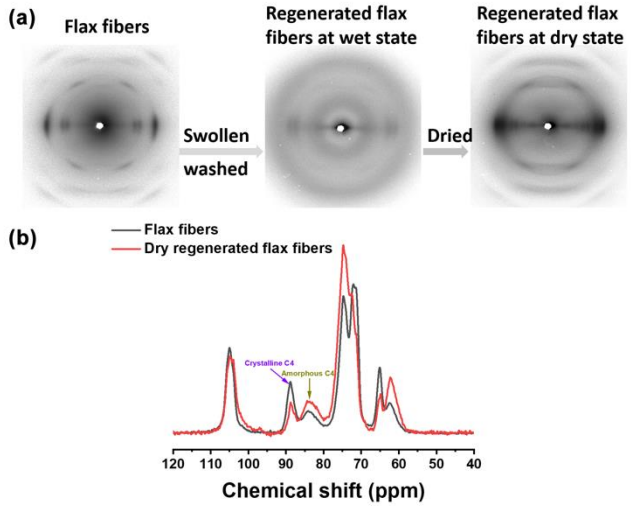

Figure S3. *(a) Two-dimensional X-ray diffraction patterns of flax fibers, the regenerated flax fiber at wet and dry state. (b) Solid state CP/MAS ^{13}C NMR spectra of flax fibers and the regenerated flax fibers at dry state.*

Figure S4. Simulated diffraction pattern of the cellulose-sulfuric acid complex based on the packing model shown in Fig. 3 in the main text.