

Supporting Information for:

**Paper title:** Shear deterioration of the hierarchical structure of cellulose microfibrils under water condition: all-atom molecular dynamics analysis

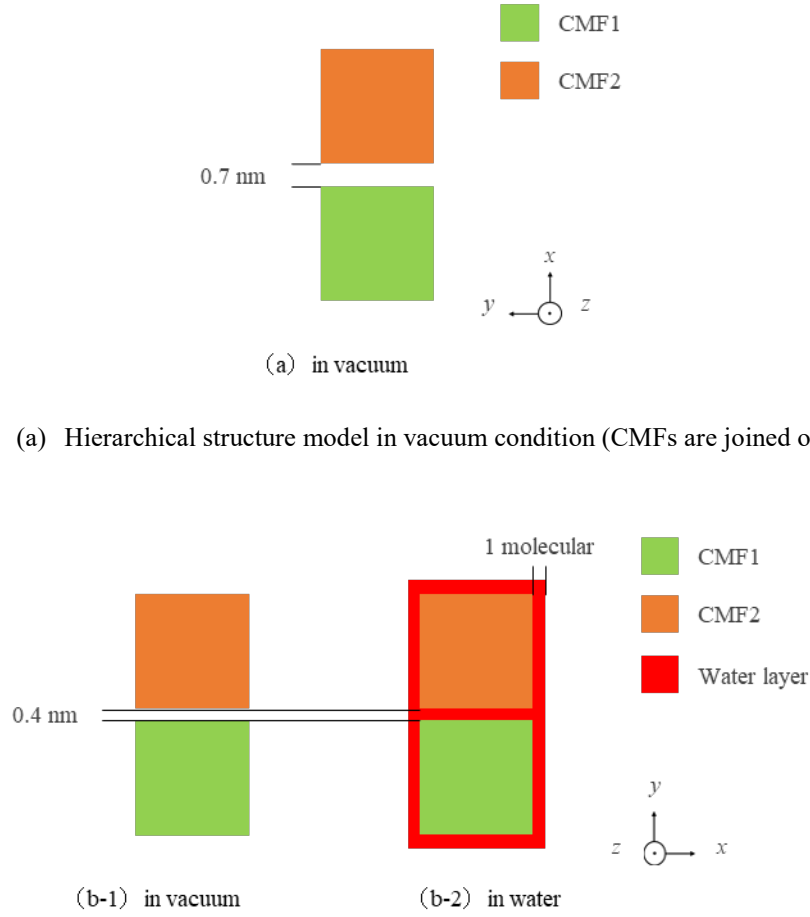
**Authors:** Yukihiro Izumi, Ken-ichi Saitoh, Tomohiro Sato, Masanori Takuma and Yoshimasa Takahashi

## 1. Calculation Condition for Hierarchical Structure Simulation Using Two CMFs

This section describes the supplementary simulation results which were omitted in the main text. In the main text, basically, two cellulose microfibrils (CMFs) were joined on the  $x$ -plane in **Figures 1 and 2** (where CMFs were attached perpendicular to the molecular sheets) to obtain the model of a hierarchical CMF structure in water. Not only that condition, in addition, but another type of hierarchical structural models were obtained by joining CMFs on the  $y$ -plane (where CMFs were attached parallel to the molecular sheets), too. Thus, molecular dynamics (MD) simulations were conducted with the models joined on  $x$ - and  $y$ - planes, either in vacuum or water condition. After an adequate structural relaxation was applied to the initial state, the shearing calculation was performed for all the models. Note that, throughout our studies, the  $x$ -direction was always perpendicular to the stacking plane of molecular sheets of CMF.

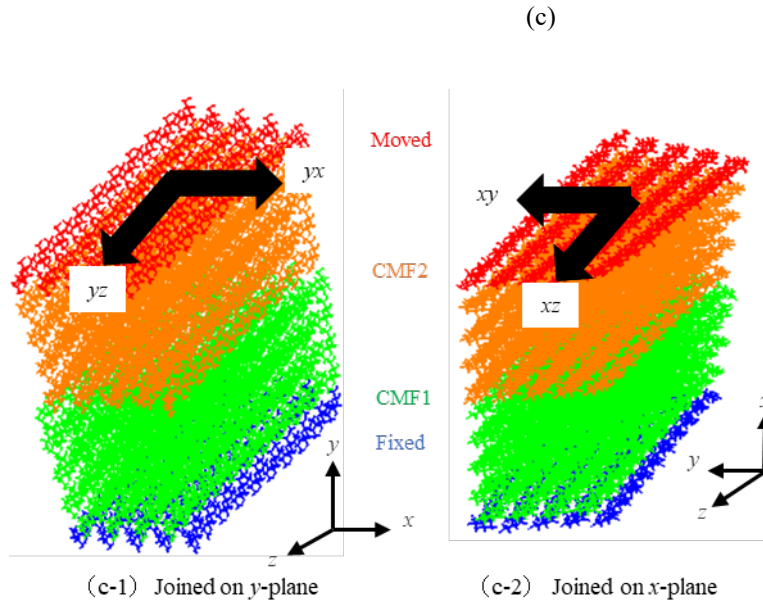
A single CMF structure was relaxed in a predetermined temperature as explained in **Section 3.1** of the main text. The relaxed CMF structure was duplicated by two and they were placed so that the spacing was 0.7 nm in the  $x$  direction (when the model was joined on the  $x$ -plane) or 0.4 nm in  $y$  direction (when the model was joined on  $y$ -plane), respectively. The resulted structures are shown in **Figure S1 (a)** for vacuum condition and **Figure S1(b)** for the model joined in  $y$ -direction (the model in water condition was described **Figure 3(a)** in the main text). As for the arrangement of water molecules, the “solvate” function integrated in VMD software was used in the same way as explained in the main text. The hierarchical models joining CMFs on the  $y$ -plane in vacuum and in water are shown in **Figure S1 (b-1) and (b-2)**, respectively.

Shear simulations were performed by using steered molecular dynamics (SMD), in the same way as explained in the main text. **Figure S2 (c-1) and (c-2)** show the way of applying shear deformation to the specimen. Some atoms which belong to molecular chains at one end in the  $y$ - or the  $x$ -direction (located in CMF2 in the figure) were assigned as SMD atoms and were forcibly moved with constant velocity. They are marked by "Moved" and are colored in red in the figure. Atoms which are contained in molecular chains at other end in the  $y$ - or the  $x$ -direction (located in CMF1) were completely fixed at initial positions and are marked by "Fixed" and are colored in blue in the figure. Other atoms colored in green or orange in the figures had no constraint and could freely move. Shear simulations either in vacuum or in water comprised four cases each, which were combinations of directions for the joining plane ( $x$  or  $y$ ) and the shearing ( $z$  or  $x$ ). Consequently, the conditions and results for four conditions are denoted by “ $xz$ -shear” and “ $xy$ -shear” for the model joined on the  $x$ -plane, and by “ $yz$ -shear” and “ $yx$ -shear” for the model joined on the  $y$ -plane. For example, for the case of “ $xz$ -shear”, the model was joined on the  $x$ -plane and then it was being sheared parallel to the  $z$ -direction. Also, four conditions of temperature, i.e., 10, 100, 200, and 300 K, were compared. As explained in the main text, the shear stress  $\tau$  and shear strain  $\gamma$  which were defined by the assumption of continuum mechanics of materials were used to analyze the shearing simulations.



(b) Hierarchical structure model in vacuum condition and in water (CMFs are joined on  $y$ -plane)

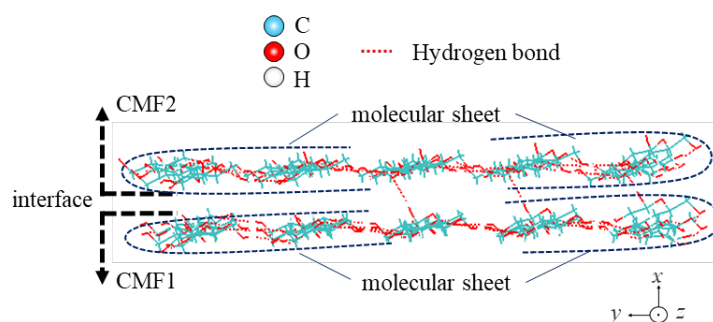
**Figure S1.** MD simulation models of the hierarchical structure (others not in the main text).



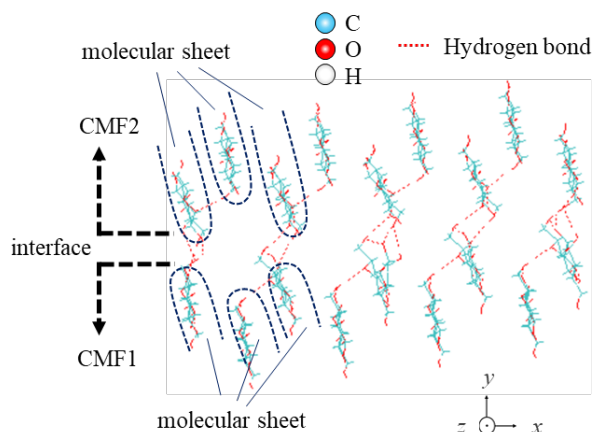
**Figure S2.** MD simulation models for the shear simulation of hierarchical structure.

## 2. Result for the Shearing Simulations of Hierarchical Structures (in vacuum or in water)

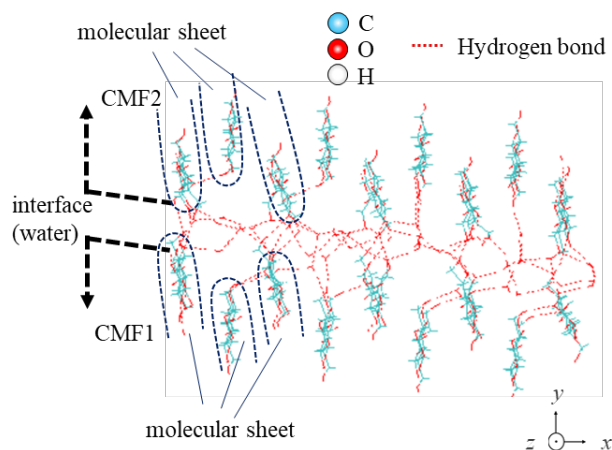
**Figure S3(a)** and **(b)** show the cross-sectional view in the vicinity of the interface between CMF surfaces before the shearing in vacuum or in water at 10 K (i.e., **Figure S3(a)** is no-water version of **Figure 6** in the main text, where CMFs were joined on the  $x$ -plane at 10 K and being sheared in water). When two CMFs are bonded in vacuum as shown in **Figure S3 (a)** or **(b-1)**, hydrogen bonds directly connect two CMF surfaces. On the other hand, when CMFs are surrounded by water as shown in **Figure S3 (b-2)**, hydrogen bonds are generated via water molecules between two surfaces. **Figure S4** shows views of molecular conformation before and after shear deformation. As shown in **Figures S4 (a)** and **(b)**, where the hierarchical structure was built by joining on the  $x$ -plane in vacuum, the structures broke inside of one CMF. On the other hand, as shown in **Figure S4 (c), (d), (e)** and **(f)**, in which shearing was applied to in the  $yx$ - or  $yz$ - direction in vacuum or in water, the structures made a sliding plane at the interface and exhibited a relative motion.



(a) in vacuum: joined on  $x$ -plane

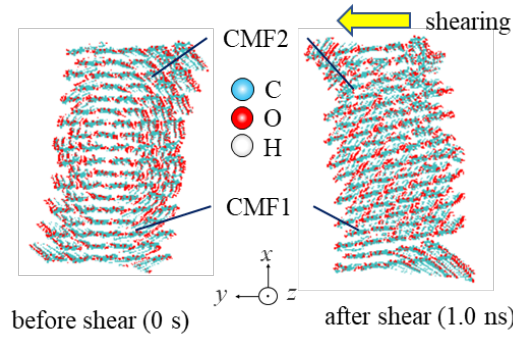


(b-1) in vacuum: CMFs were joined on  $y$ -plane.

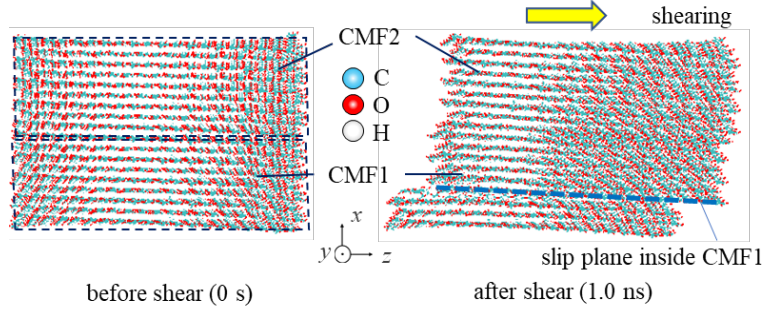


(b-2) in water: CMFs were joined on  $y$ -plane.

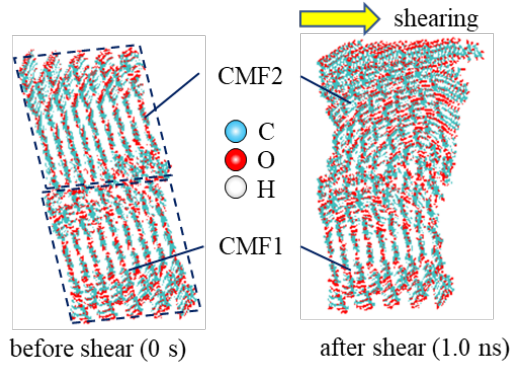
**Figure S3.** Cross sectional views of the interface in the hierarchical structure (at temperature 10 K)



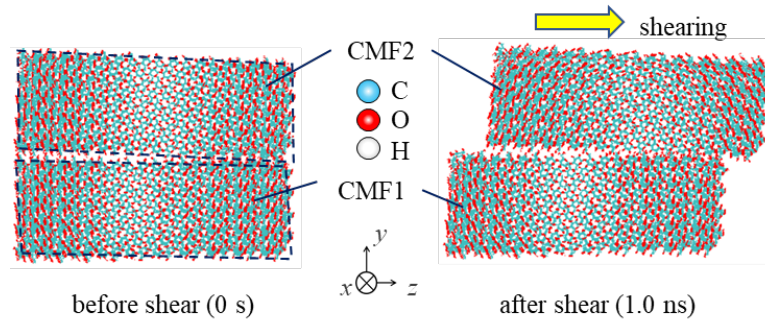
(a)  $xy$ -shear (in vacuum): CMFs were joined on  $x$ -plane, and then being sheared in  $y$  direction.



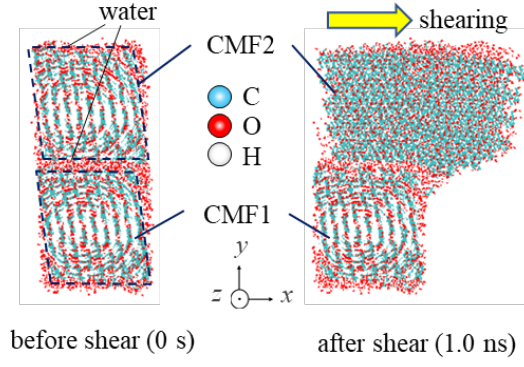
(b)  $xz$ -shear (in vacuum): CMFs were joined on  $x$ -plane, and then being sheared in  $x$  direction.



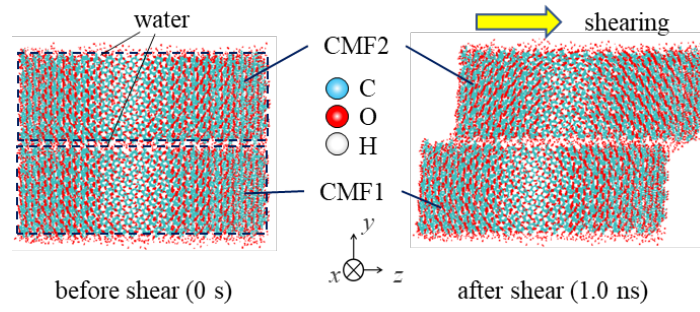
(c)  $yx$ -shear (in vacuum): CMFs were joined on  $y$ -plane, and then being sheared in  $x$  direction.



(d)  $yz$ -shear (in vacuum): CMFs were joined on  $y$ -plane, and then being sheared in  $z$  direction.



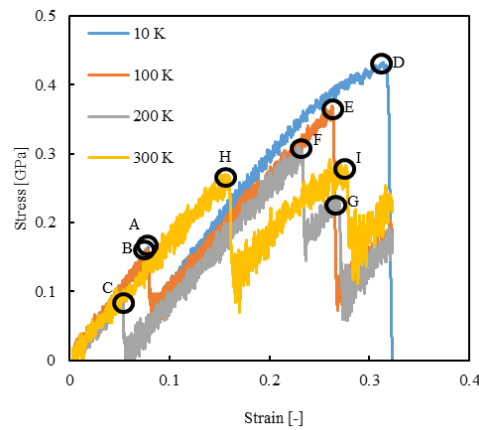
(e)  $yx$ -shear (in water): CMFs were joined on  $y$ -plane, and then being sheared in  $x$  direction.



(f)  $yz$ -shear (in water): CMFs were joined on  $y$ -plane, and then being sheared in  $z$  direction.

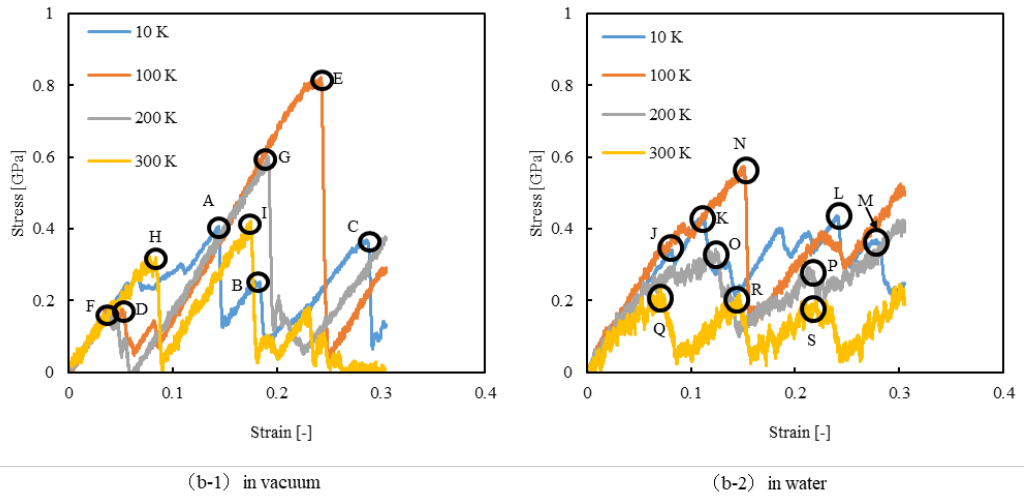
**Figure S4.** Change of molecular conformations in shear simulation of hierarchical structures (at temperature 10 K)

The shear stress-strain relations obtained in shearing simulations are shown in **Figure S5**. The shear moduli were calculated for the strain range of 0 to 0.04 in the same way as for the model in the main text. The relationship between moduli and system temperature is shown in **Figure S6 (a)** in vacuum and **Figure S6 (b)** for in water. The values,  $G_{xy}$ ,  $G_{xz}$ ,  $G_{yx}$ , and  $G_{yz}$ , mean shear moduli obtained in simulations of the “ $xy$ -”, “ $xz$ -”, “ $yx$ -”, and “ $yz$ -shear”, respectively.

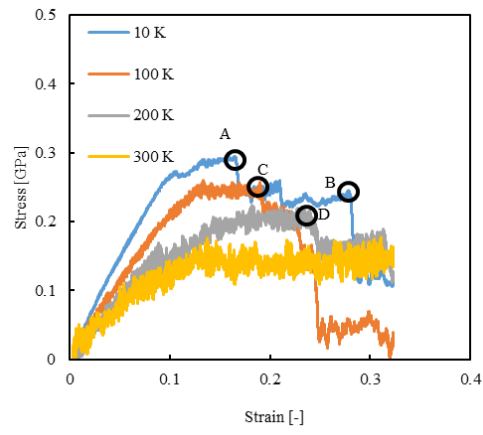


(a)  $xz$ -shear simulation (in vacuum)

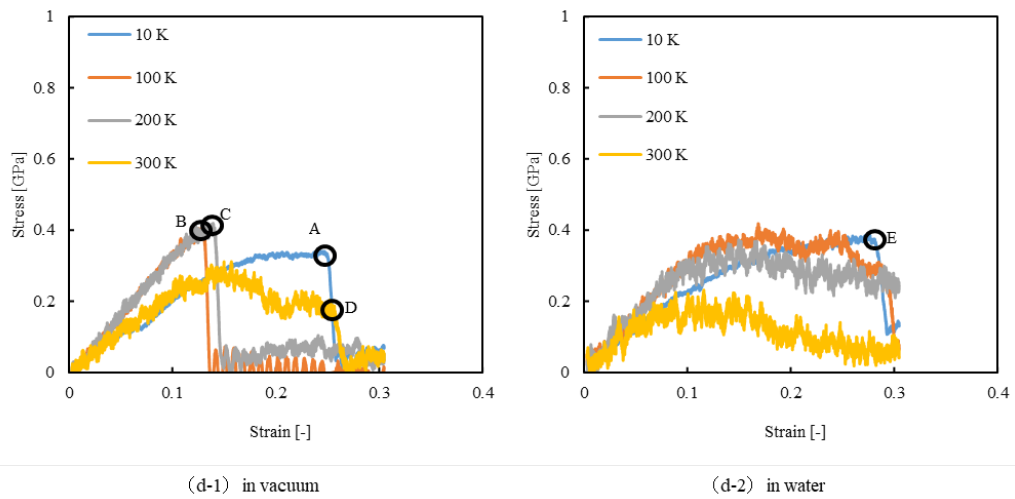
\*) results in water condition are described in the main text



(b) yz-shear simulation

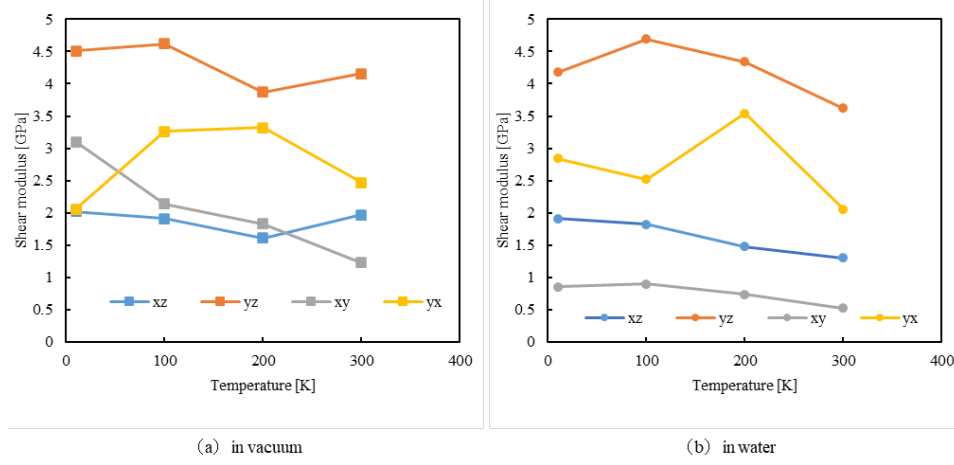


\*) results in water condition are described in the main text



(d) yx-shear simulation

**Figure S5.** Stress-strain diagrams obtained by shear simulations for the hierarchical structure



**Figure S6.** Relationship between shear moduli and system temperature (summarized for the model in vacuum or in water)

As a whole, elastic moduli obtained for  $yz$ - and  $yx$ -shear (where CMFs were joined on the  $y$ -plane) are larger than those obtained for  $xz$ - and  $xy$ -shear (where CMFs were joined on the  $x$ -plane). The shearing behavior of hierarchical structures joined on the  $x$ -plane are affected strongly by water molecules, such that the moduli in water are very smaller than in vacuum. On the other hand, when CMFs were joined on the  $y$ -plane, the hierarchical structures do show little effect of water, but rather show large thermal fluctuation as temperature rises. It is guessed that the model joined on the  $x$ -plane (the cases:  $xz$ - or  $xy$ -shear) makes easy sliding on the interface between CMFs, because water molecules are uniformly dispersed onto the molecular sheets as shown in **Figure S3 (a)**. In these cases, being helped by water molecules, the sliding on the interface occurs even in very small strain (it will happen in elastic range), and therefore the shear moduli in water becomes smaller than in vacuum. Whereas, in the model joined on the  $y$ -plane (the cases:  $yz$ - or  $yx$ -shear), water molecules are not so much uniformly dispersed in the interface, as observed in **Figure S3 (b-1)** or **(b-2)**, and therefore the sliding hardly occur there.

As captured in **Figure S6**, the shear modulus of the model joined on the  $x$ -plane (the case of  $xz$ - or  $xy$ -shear) obviously decreases with increase of temperature, while, for the model joined on the  $y$ -plane (the case of  $yz$ - or  $yx$ -shear), the dependency on the temperature is not clear. It is supposed that, as explained in the main text, the mobility of water molecules in the interface between CMFs tremendously changes depending on temperature range. But, for the case of  $yz$ - or  $yx$ -shear, as observed in **Figure S3 (b-1)** or **(b-2)**, molecular sheets are formed perpendicular to the interface. In such arrangement, any movement of water (oscillation, migration, or rotation, etc.) is always restrained independent on temperature.

**Table S1** summarizes the averaged shear moduli for all conditions. The moduli in vacuum largely depends on the direction of shear. This elastic anisotropy in vacuum is explained as follows. When the CMFs are joined in the  $x$  direction, i.e. perpendicular to the molecular sheets, the shear moduli  $G_{xy}$  (2.08 GPa) and  $G_{xz}$  (1.88 GPa) are almost the same. It is because, in vacuum, the hydrogen bonds between CMFs are directly formed between molecular sheets as shown in **Figure S3 (a)** and the bonding strength is supposed to be independent of the direction of stretching. On the other hand, in water, as explained in the main text,  $G_{xz}$  (1.63 GPa) was almost twice of  $G_{xy}$  (0.753 GPa). The hydrogen bonds must be intervened by water molecules, and they continually switch the places of bonds via water molecules.

**Table S1.** Average value of shear modulus obtained in all shear directions (models in vacuum and in water)

	Shear modulus [GPa]	
	in vacuum	in water
$G_{xy}$ (averaged value)	2.08	0.753
$G_{xz}$ (averaged value)	1.88	1.63
$G_{yx}$ (averaged value)	2.78	2.74



$G_{yz}$ (averaged value)	4.29	4.21
Experimental value for Larch [45].	1~3	

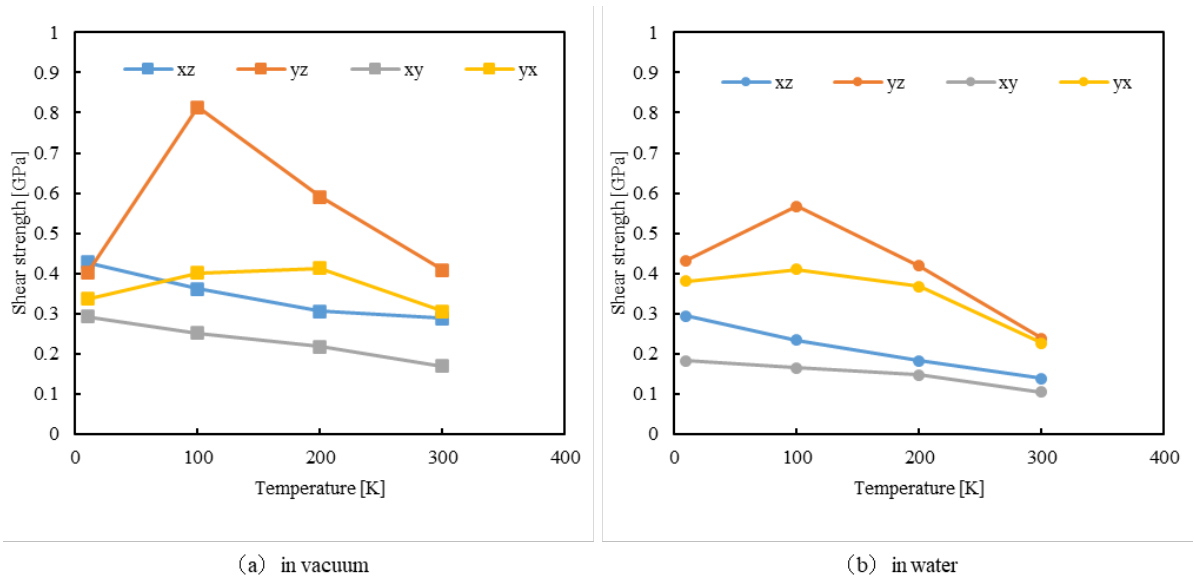
As mentioned in the main text and shown in **Figure 2 (a)**., when the CMFs are bonded in the  $y$  direction, there are many hydrogen bonds on the molecular sheet at the surface. Because of the geometrical arrangement of hydrogen bonds, they are apt to be stretched when the CMF is sheared in the  $z$  direction more than in the  $x$  direction, and consequently  $G_{yz}$  becomes higher than  $G_{yx}$ .

Shear moduli already reported for a single CMF, which corresponds to our three conditions,  $xy$ -,  $xz$ - and  $yz$ -shear, were 1.2~2.7 GPa, 1.66~2.6 GPa, or 4.4~6.8 GPa, respectively [45]. Thus, our values,  $G_{xy}$  and  $G_{xz}$  ( $xy$ - and  $xz$ -shear) as shown in **Table S1**, agree well with the previous research for single CMF. But, only  $G_{yz}$  for  $yz$ -shear exhibits lower value than the previous one.

The plastic region beyond the elastic region is recognized by the stress-strain curves in **Figure S5**. For the  $xz$ -shear in vacuum, as shown in **Figure S5 (a)**, interface slip occurred at the mark A and some fracture events inside one CMF occur repeatedly at the marks B~I. For the  $yz$ -shear in vacuum, as shown in **Figure S5 (b-1)**, interface slips were recognized many times at the marks A~D and F~H in the figure. But the shear stress was almost recovered after each slip events (i.e., stick-and-slip behavior). At the marks E~I in **Figure S5 (b-1)**, some molecular chains with velocity constraint were peeled off. For the  $yz$ -shear in water as shown in **Figure S4 (b-2)**, interface slips occurred at the marks J~S, recovering the shear stress each time.

In lower temperatures, hydrogen bonds were relatively fixed at the same place between CMFs and waters. Therefore, in need of shearing motion, the interface had to slip suddenly. In higher temperature, water molecules always move freely at the interface. In high temperature such as 300 K, periodic increase and decrease of the shear stress were clearly observed. This is because water molecules at the interface between CMFs always altered their locations.

The shear strength can be defined as the maximum value in shearing direction. The dependency of the shear strength on temperature in vacuum or in water is summarized in **Figure S7 (a)** or **(b)**, respectively. The hierarchical structure which was joined in  $x$ -direction (i.e. joined in perpendicular to molecular sheets) lowers the shear strength with increase of temperature, but the structure joined in  $y$ -direction (i.e. joined in parallel to molecular sheets) does not show clear dependency.



**Figure S7.** Relationship between shear strength and temperature (summarized for the model in vacuum or in water)

\* Some of calculation results were already appeared in the main text, so was omitted in this supplementary material.

\* Reference numbers in this supplementary material correspond to the main text.