Supporting Information for

The Unexpected Flexibility of Natural Cellulose at the Single-chain Level and Its Implications to the Design of Nano Materials

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The Experimental Details

Sample preparation. The IL, 1-allyl-3-methylimidazolium chloride (AMIMCl), was synthesized following the literature.[1] Natural cellulose (NC, Sigma Inc., Mw ~60,000, Product No. C6288) was dissolved in AMIMCl by stirring the mixture at 60 ^{o}C for ~2 h to a concentration of 0.01 mg/mL. A drop of the cellulose solution (~10 μL) was deposited on a clean glass slide for 10 min, followed by thorough rinse with DI water.

Force measurements. The sample was mounted in the AFM (Nanowizard II, JPK Instruments AG, Germany). Prior to the measurements, a drop of liquid was introduced between the Si_3N_4 AFM cantilever (Bruker Corp., CA) and the sample. Then during the AFM manipulation, the data was collected at the same time and then converted into force-extension curves (in brief, force curves) later. The spring constant of the AFM cantilever was measured by the thermo excitation method, ranging from 30 to 40 pN/nm.

The resulting single-molecule force curves were analyzed with Igor Pro V6.0 with custom-build procedures. The details of the instrumentation can be found elsewhere.[2-6]

Various stretching velocities have been applied in the force measurements (0.05-5 μm/s). However, there is no remarkable deviation between the force curves see Fig. S1. This result is consistent with the fact that the time scale of the chain segment movements of NC is much shorter than the time scale in our experiments, which implies that the single-molecule experiments are carried out in a quasi-thermodynamic equilibrium condition.[7]

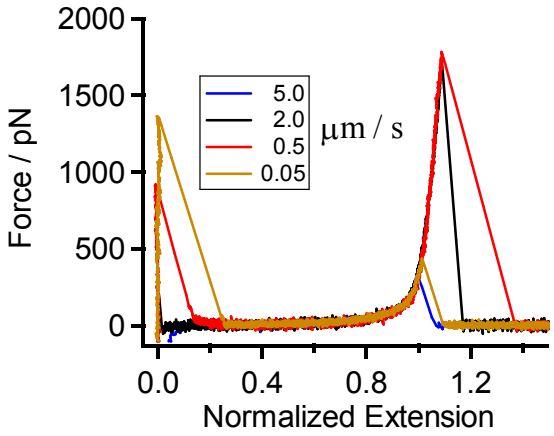
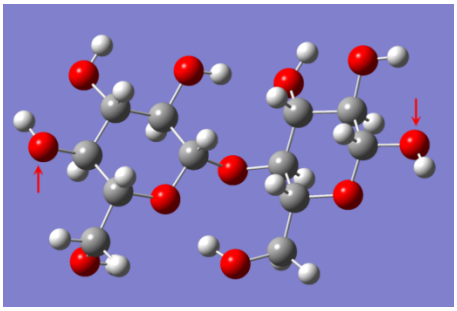


Fig. S1. Normalized force curves of NC obtained in octane at various stretching velocity.

The details of QM calculations



Scheme S1. NC dimer used in the calculation. Red arrows indicate the two ending oxygen atoms.

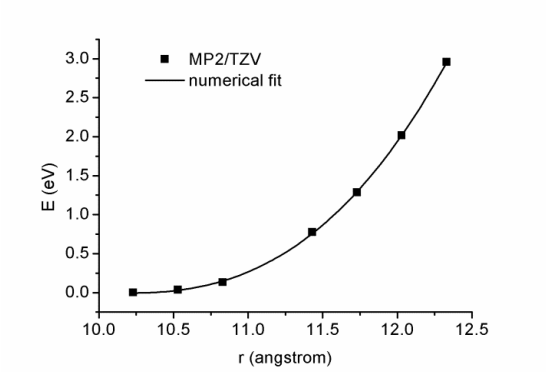


Fig. S2. The energies of stretched configurations at fixed distances between two ending oxygen atoms calculated at the MP2/TZV//B3LYP/TZV dual-level of theory. Solid line denotes the polynomial fit with Eq S1.

All quantum mechanical (QM) calculations are carried out using the GAUSSIAN 09 program. We consider NC dimers (as shown in Scheme S1) consisting of two pyranose rings in the calculations. The distance between the two ending oxygen atoms (labeled by red arrows in Scheme S1) is fixed at different values in our calculations, while the positions of all other atoms are optimized to minimize the total energy. The calculations are performed at the MP2/TZV//B3LYP/TZV dual-level of theory. Fig. S2 presents the energy difference by stretching NC dimer at fixed distances between two ending oxygen atoms, taking the unstreched NC dimer ground state as the energy reference. The solid line in Fig. S2 denotes polynomial fit according to

$$E = E_0 - a_0 \sum_{n=2}^{4} \gamma_{n-1} (a[E]/a_0 - 1)^n / n \qquad \text{Eq S1}$$

where a_0 is the length of the repeating unit at zero force, $a[E]$ is the length at a given extension with energy E. Fitting QM data to Eq S1 gives γ_1 = 10.57 nN, γ_2 = 90.23 nN, and γ_3 = -44.12 nN (see also Table S1). The derivative of this equation leads to the force expression, which is actually measurable experimentally,

$$F = \frac{\partial E}{\partial a} = \sum_{n=1}^{3} \gamma_n \left(a[F]/a_0 - 1 \right)^n \qquad \text{Eq S2}$$

where $a[F]$ is the length at the given force, F.

Table S1. The elastic constants of NC and polyacrylamide (PAAm) obtained from QM calculations. According to these elastic constants, the relationship between the contour length at a given F ($L[F]$) and that at zero force (L_0) can be obtained by Eq S3.

	γ_1 [nN]	γ_2 [nN]	γ_3 [nN]
PAAm	28.7	-42.0	16.9
NC	10.57	90.23	-44.12

The details of the QM-FJC fitting curves

Since the minor changes of bond angle and bond length are already considered in the calculations on one repeating unit, the equation can be easily rewritten to describe the whole polymer chain, see Eq S3:[6, 8, 9]

$$F = \sum_{i=1}^{3} \gamma_n \left(L[F]/L_0 - 1 \right)^n \qquad \text{Eq S3}$$

where L_0 is the contour length of the chain at zero force, $L[F]$ is the contour length at a given force F.

During the elastic stretching of a single polymer chain, the value of $L[F]/L_0$, starting from 1.0, increases with the increasing of F. Therefore, $L[F]/L_0$ is a monotonic increasing function of F and vice versa. During the elongation of the polymer chain, $L[F]/L_0$ is an ergodic value ranging from 1.0 to a number corresponding to the rupture of the polymer bridge. Here, we utilize the strength of a typical covalent bond as the upper limit for the stretching force, *e.g.* 2000 pN.[10] Thus, the upper limit for $L[F]/L_0$ is about 1.103,

according to Eq S3. In the range from 1.0 to 1.103, any value of $L[F]/L_0$ is reasonable and corresponds to a mapping value of F in the fitting curve, which can be calculated with Eq S3.

Since $L[F]/L_0$ can be an ergodic value in the proper range (1.0-1.103 in this study), the model now has only one free parameter left (the Kuhn segment length l_k). For a given value of l_k, the fitting curve can be generated as described below. In the range of 1.0 - 1.103, any value of $L[F]/L_0$ will correspond to a mapping point in the force curve. For this point, F can be calculated with Eq S3, and then R/L_0 can be calculated with Eq S4. In this way, the whole fitting curve can be generated when the value of $L[F]/L_0$ varies from 1.0 to 1.103 (see the dotted line in Fig. 2 in the main text). The modified FJC model (Eq S4), which is integrated with the QM results (Eq S3), is called QM-FJC model.

$$R/L_0 = (L[F]/L_0)\cdot\{\coth[(F\cdot l_k)/(k_BT)] - (k_BT)/(F\cdot l_k)\} \qquad \text{Eq S4}$$

The details of the QM-WLC fitting curves

The QM-WLC model (Eq. S5) can be described by the equation below:[8]

$$F\frac{l_p}{k_BT} = \frac{R/L_0}{L[F]/L_0} + \frac{1}{4\left(1-(R/L_0)/(L[F]/L_0)\right)^2} - \frac{1}{4} \qquad \text{Eq. S5}$$

For a certain value of l_p, a QM-WLC fitting curve can be generated by Eq. S5. To find out the proper l_p, the value was changed from 0.2 nm to 3 nm. As shown in Fig. S3, the high force regime can be fitted well only if l_p is larger than 1 nm. In the case that l_p is larger than 1 nm, however, a large deviation can be observed in the low force regime. That is to say, there is no such a value of l_p leads to good performance in the whole force range. This result indicates that the WLC model is not suitable for NC, even if the QM results are integrated.

Fig. S3. The QM-WLC fitting curve (dotted line) with various values of l_p vs the normalized experimental curve (red solid line). The data are zoomed in to show the deviation. The values of l_p are 0.2, 1, 2 and 3 nm, from left to right, respectively.

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