

Supplemental information for “ Interactions between single cellulose chain and water molecules and their temperature dependences: I. Pristine cellulose chain”

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S1. Structure of a single bare cellulose chain

We take the structure shown in Fig.S1(a) as the structure of the bare cellulose chain, in which the C6-OH group directs to C2-O atom. The total energy of this structure (Fig.S1(a)) is less by 0.35 eV than that in Fig.S1(b), where the C6-OH group does not direct to the C2-O atom, but the C2-OH group to the C6-O atom. It is noted that the strongest binding energy of a water molecule is almost the same for the structures in Figs.S1 (a) and (b). The results in Ref.([Fukuhara et al. 2026](#)) have been obtained by using Fig.S1(b).

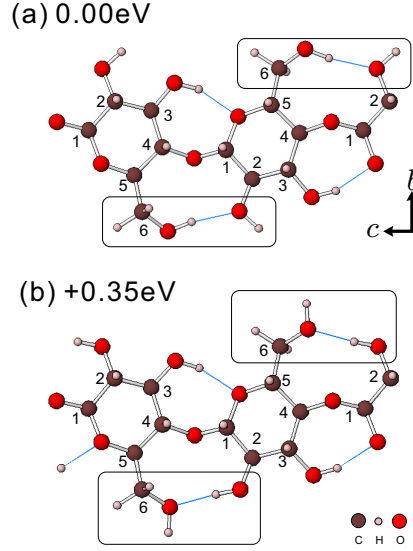


Fig.S1 Two optimized structures of the single bare cellulose chain. The structure shown in (a) is less by 0.35 eV than that in (b).

S2. Partial coordinates of bare cellulose chain and those of thirty-two bound single water molecules

The lattice vectors employed in the present study are listed in Table S1 as those components in the Cartesian coordinates. The lattice vectors correspond to $8 \times 8 \times 1$ of those in the cellulose I_β unit cell experimentally obtained (Nishiyama et al. 2002).

Table S1 Cartesian components ($\text{\AA}$) of Lattice vectors employed in the present study.

	x	y	z
$\vec{a}$	62.27200	0.00000	0.00000
$\vec{b}$	-7.42704	65.18626	0.00000
$\vec{c}$	0.00000	0.00000	10.38000

The partial coordinates of the optimized structure of the bare cellulose chain(in Fig.S1(a)) based on the lattice vectors in Table S1 are listed in Table S2, and those

of thirty-two single water molecules shown in Fig.1 are in Table S3. The partial coordinates of the water-bound cellulose chain are of course slightly changed by binding a water molecule.

Table S2 Partial coordinates of the optimized structures of the bare cellulose chain.

	<i>a</i>	<i>b</i>	<i>c</i>		<i>a</i>	<i>b</i>	<i>c</i>
C	0.00180	-0.00544	0.03915	H	0.01959	-0.00209	0.05063
	-0.00181	0.00545	0.53915		-0.01960	0.00209	0.55062
	-0.00377	-0.02272	0.94309		-0.02159	-0.02570	0.93730
	0.00377	0.02272	0.44308		0.02158	0.02570	0.43730
	0.00535	-0.01642	0.81156		-0.02020	0.00154	0.75576
	-0.00535	0.01643	0.31155		0.02020	-0.00154	0.25576
	-0.00249	0.00385	0.77098		0.02324	-0.01391	0.81883
	0.00249	-0.00385	0.27099		-0.02324	0.01391	0.31881
	0.00268	0.02047	0.87378		0.02043	0.02385	0.88397
	-0.00268	-0.02047	0.37380		-0.02044	-0.02385	0.38399
	-0.00698	0.04055	0.84467		-0.02427	0.03675	0.81942
	0.00698	-0.04055	0.34472		0.02427	-0.03674	0.31949
O	-0.00123	-0.03298	0.72661		-0.00621	0.04959	0.93445
	-0.00812	-0.01133	0.15500		0.00621	-0.04958	0.43453
	0.00448	0.05292	0.75044		0.00407	-0.05038	0.91955
	-0.00448	-0.05292	0.25051		-0.00407	0.05038	0.41951
	-0.00675	0.01284	0.99417		0.00366	-0.02886	0.63883
	0.00675	-0.01284	0.49418		-0.00366	0.02886	0.13882
	0.00528	-0.04040	0.98978		0.00112	0.04724	0.66403
	-0.00528	0.04040	0.48974		-0.00112	-0.04724	0.16410
	0.00528	-0.04040	0.98978				
	-0.00528	0.04040	0.48974				

Table S3 Partial coordinates of the bound water molecules at site (*i*).

<i>i</i>	O			H1			H2		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
1	0.0083	0.0712	0.3249	0.0069	0.0595	0.2638	0.0231	0.0776	0.3179
2	-0.0068	-0.0706	0.8253	-0.0065	-0.0591	0.7638	-0.0216	-0.0770	0.8292
3	-0.0452	-0.0319	0.7113	-0.0299	-0.0348	0.7127	-0.0526	-0.0424	0.6556
4	0.0454	0.0316	0.2107	0.0303	0.0350	0.2127	0.0533	0.0424	0.1600
5	-0.0027	0.0790	0.5052	0.0122	0.0844	0.4867	-0.0028	0.0758	0.5976
6	-0.0001	-0.0807	0.0132	-0.0143	-0.0883	0.0009	0.0004	-0.0769	0.1047
7	0.0494	0.0498	0.7835	0.0342	0.0519	0.7653	0.0572	0.0635	0.7825
8	-0.0498	-0.0497	0.2834	-0.0347	-0.0520	0.2660	-0.0578	-0.0634	0.2831
9	-0.0025	0.0916	0.6365	0.0000	0.0806	0.6971	0.0080	0.1032	0.6593
10	0.0024	-0.0914	0.1380	-0.0004	-0.0802	0.1966	-0.0082	-0.1028	0.1609
11	0.0537	0.0107	0.6719	0.0382	0.0110	0.6572	0.0581	0.0232	0.7201
12	0.0515	-0.0394	0.0018	0.0356	-0.0414	0.0004	0.0556	-0.0493	0.0646
13	-0.0537	-0.0106	0.1747	-0.0383	-0.0113	0.1578	-0.0585	-0.0234	0.2187
14	-0.0518	0.0386	0.5061	-0.0360	0.0403	0.5065	-0.0561	0.0486	0.5672
15	0.0529	-0.0114	0.4732	0.0375	-0.0114	0.4919	0.0599	0.0009	0.5142
16	-0.0528	0.0113	0.9716	-0.0375	0.0112	0.9921	-0.0600	-0.0008	0.0143
17	-0.0056	0.0722	0.1174	-0.0032	0.0607	0.1742	0.0088	0.0776	0.0884
18	0.0055	-0.0723	0.6215	0.0028	-0.0605	0.6754	-0.0087	-0.0780	0.5913
19	-0.0562	0.0018	0.7520	-0.0645	0.0123	0.7177	-0.0551	0.0046	0.8440
20	0.0563	-0.0019	0.2522	0.0647	-0.0123	0.2181	0.0553	-0.0046	0.3443
21	-0.0575	-0.0229	0.3895	-0.0676	-0.0182	0.3276	-0.0582	-0.0376	0.3746
22	0.0578	0.0231	0.8898	0.0677	0.0183	0.8265	0.0582	0.0377	0.8732
23	0.0558	0.0002	0.0545	0.0643	0.0067	0.1251	0.0537	-0.0143	0.0762
24	-0.0557	0.0000	0.5553	-0.0645	-0.0065	0.6244	-0.0541	0.0146	0.5757
25	-0.0593	-0.0273	0.9388	-0.0663	-0.0155	0.9654	-0.0571	-0.0346	0.0187
26	0.0593	0.0273	0.4402	0.0663	0.0155	0.4669	0.0572	0.0346	0.5201
27	0.0603	-0.0152	0.8163	0.0752	-0.0102	0.8377	0.0592	-0.0131	0.7239
28	-0.0604	0.0151	0.3150	-0.0753	0.0101	0.3365	-0.0594	0.0129	0.2226
29	0.0613	-0.0374	0.3151	0.0671	-0.0412	0.3975	0.0576	-0.0503	0.2702
30	-0.0619	0.0372	0.8137	-0.0674	0.0411	0.8970	-0.0579	0.0502	0.7698
31	-0.0240	0.0816	0.9543	-0.0396	0.0817	0.9526	-0.0194	0.0837	0.8651
32	0.0238	-0.0820	0.4550	0.0395	-0.0819	0.4503	0.0189	-0.0830	0.3659

S3. Example of energy surface of a water molecule rotating around the binding axis to the cellulose chain

Because the binding energy is not always sensitive to the direction of the unbound H atom in a bound water molecule, we re-calculate the binding energy by re-optimizing the structure of the cellulose chain and the water molecule with the angles of the unbound H atom rotating around the binding axis, 0, 45, 90, 135, 180, 225, 270, 315 degree as the initial structures.

Figure S2 shows an example of the energy surface of the water molecule rotating around the binding axis to the O atom of C6-O site (6) in Fig.1.

The difference of the binding energy is at most 0.03 eV except for the position g (just above C6 atom).

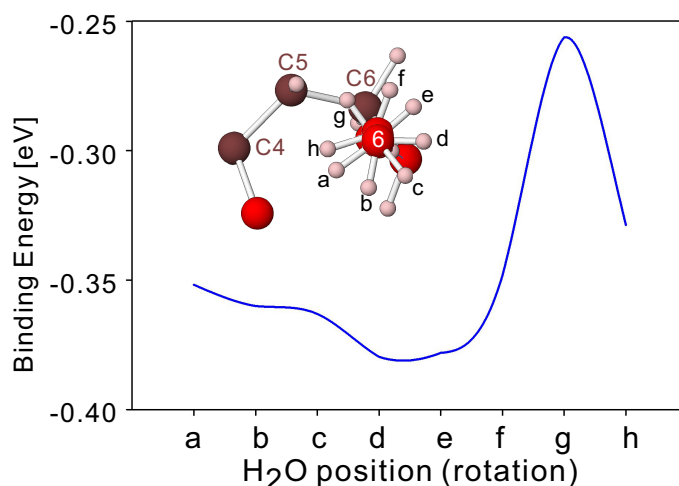


Fig.S2 Energy surface of a water molecule at C6-O site (6) by rotating the direction of the unbound H-atom around the binding axis.

S4. Density of electronic states in cellulose chain by hybrid method

For comparison with the results by GGA calculations shown in the subsection 2.3, we demonstrate the density of electronic states (DOS) in the single bare cellulose chain calculated by the hybrid method HSE06(Heyd et al. 2003). All electron atomic-bases with the TZ2P(triple *zeta* with two polarization functions) Slater-type orbitals are employed for the DOS calculations(te Velde and Baerends 1991). The calculations are performed under the 1-dimensional periodic boundary condition along the *c*-axis (10.31Å).

Figure S3 shows the same as Fig.7(a), the DOSs calculated by the GGA method.

As shown in Fig.S3, the basic DOS profile is similar to that in Fig.7(a). Only the difference is that the bandgap (6.8 eV) by HSE06 in Fig.S4 is much larger than that (5.3 eV) by GGA. It is said in general that the GGA method underestimates bandgaps in semiconductors and insulators and the hybrid method well reproduces the bandgaps experimentally obtained. However, the GGA gives a bandgap better than the HSE06 for the cellulose case; the UV-absorption estimates the band gap at 4.5 eV (Simão et al. 2015).

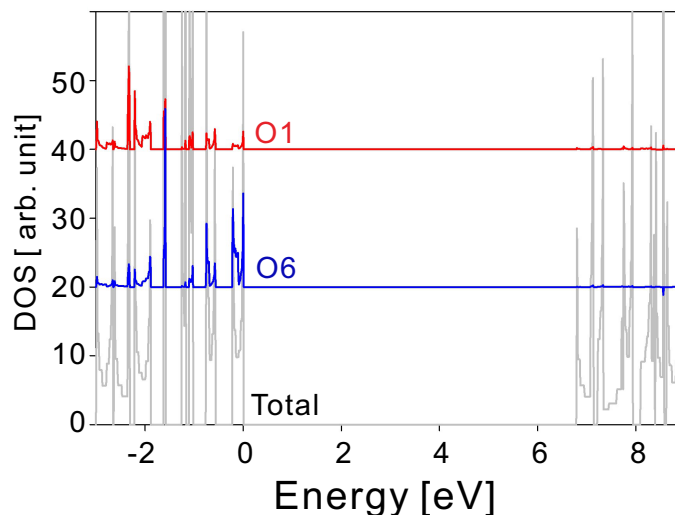


Fig.S3 Density of electronic states of the bare cellulose chain by the hybrid method(HSE06).

References

- Fukuhara M, Yokotsuka T, Samoto T, et al (2026) Electronic conduction in water-adsorbed kenaf cellulose. *Sci Rep* 16:1971. <https://doi.org/10.1038/s41598-025-33249-3>
- Heyd J, Scuseria GE, Ernzerhof M (2003) Hybrid functionals based on a screened Coulomb potential. *J Chem Phys* 118:8207–8215. <https://doi.org/10.1063/1.1564060>
- Nishiyama Y, Langan P, Chanzy H (2002) Crystal Structure and Hydrogen-Bonding System in Cellulose I β from Synchrotron X-ray and Neutron Fiber Diffraction. *J Am Chem Soc* 124:9074–9082. <https://doi.org/10.1021/ja0257319>

Simão CD, Reparaz JS, Wagner MR, et al (2015) Optical and mechanical properties of nanofibrillated cellulose:toward a robust platform for next-generation green technologies. Carbohydrate Polymers 126:40–46. <https://doi.org/10.1016/j.carbpol.2015.03.032>

te Velde G, Baerends EJ (1991) Precise density-functional method for periodic structures. Phys Rev B 44:7888–7903. <https://doi.org/10.1103/PhysRevB.44.7888>