Supporting Information

Insights from molecular dynamics simulations for interaction between cellulose microfibrils and hemicellulose

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Table S1. Number of water molecules in different systems

Cellulose microfiber		Water molecular numbers
Planes	Polymerization degrees	
Hydrophilic plane (110)	10	1200
	20	2800
Hydrophobic plane (200)	10	1240
	20	2600

Table S2. The number of hydrogen bonds between xylans(Uxyl, Gxyl, Axyl, and Faxyl) and the (110) and (200) planes of cellulose microfibrils.

Cellulose hydrophilic plane									
		Uxyl		Gxyl		Axyl		Faxyl	
		1-5	6-10	1-5	6-10	1-5	6-10	1-5	6-10
H-bond numbers	1st	23	25	16	17	21	25	26	23
	2nd	22	23	16	19	20	22	15	19
	3rd	21	26	19	18	19	23	20	23
Cellulose hydrophobic plane									
		Uxyl		Gxyl		Axyl		Faxyl	
		1-5	6-10	1-5	6-10	1-5	6-10	1-5	6-10
H-bond numbers	1st	7	8	9	8	10	7	7	8
	2nd	9	8	8	6	9	10	6	8
	3rd	7	8	7	5	8	9	5	9

Note: H-bond numbers represented the sum between five xylans and cellulose microfibril planes. 1st, 2nd, and 3rd represented the number of simulations.

Criteria for H-bond: Bond angle less than 30°, the distance between heavy atoms less than 3.5Å.

Table S3. The number of hydrogen bonds between xylans(Gxyl and Gxyl2) and cellulose microfibrils (100) plane with different water molecule numbers.

Xylans			H-bond numbers			
			Gxyl (parallel)	Gxyl (anti-parallel)	Gxyl2 (parallel)	Gxyl2 (anti-parallel)
Water molecule numbers	0	1st	13	12	16	17
		2nd	13	11	13	14
		3rd	14	11	15	15
	700	1st	10	5	12	10
		2nd	9	5	11	9
		3rd	9	5	10	10
	1400	1st	9	5	6	9
		2nd	12	8	7	6
		3rd	9	5	8	11
	2800	1st	6	5	7	6
		2nd	6	5	5	3
		3rd	6	4	4	5

Note: H-bond numbers represented the sum between two xylans and the cellulose microfibril (110) plane. 1st, 2nd, and 3rd represented the number of simulations.

Criteria for H-bond: Bond angle less than 30°, the distance between heavy atoms less than 3.5Å.

Table S4. The sum of φ and ψ of Uxyl in the initial state and the cellulose microfiber plane, corresponding to Figure 6.

Glycosidic oxygen		1	2	3	4	5	6	7	8	9
Uxyl	Σ	-151.01	-174.37	-175.10	-175.78	-177.03	-174.62	-175.95	-171.48	-169.02
Hydrophilic planes (non-water)										
Uxyl-1	Σ	-56.63	-176.14	-141.46	-211.82	-180.58	-139.70	-65.99	-207.66	-163.10
Uxyl-2	Σ	-286.60	-250.93	-228.94	-243.97	-69.95	-51.90	-149.14	-164.27	-156.77
Uxyl-3	Σ	-227.97	-169.97	-52.12	-62.94	-103.85	-118.93	-140.92	-53.48	-50.84
Uxyl-4	Σ	-251.83	-149.87	-63.03	-12.00	-136.25	-96.15	-146.72	17.11	-154.51
Hydrophilic planes (Aqueous)										
Uxyl-1	Σ	-172.82	-289.29	-169.23	-177.54	-162.24	-166.54	-172.83	-234.76	-177.28
Uxyl-2	Σ	-179.22	-245.69	-138.08	-167.86	-163.86	-166.92	-168.38	-140.40	-151.51
Uxyl-3	Σ	-161.15	-173.52	-119.06	-95.81	-245.63	-173.49	-163.46	-141.42	-100.09
Uxyl-4	Σ	-171.94	-145.18	-171.55	-150.28	-159.72	-142.76	-157.22	-154.61	-170.70
Hydrophobic planes (non-water)										
Uxyl-5	Σ	-106.98	-48.08	-165.98	-152.15	-242.81	-57.90	-61.88	-58.52	-110.27
Uxyl-6	Σ	-219.63	-129.62	-225.01	-264.36	-200.26	-268.34	-236.10	-248.61	-230.00
Uxyl-7	Σ	-120.95	-161.34	-46.65	-54.84	-51.83	-128.52	-47.43	-113.17	-147.63
Uxyl-8	Σ	-137.25	-59.26	-52.70	-136.38	-42.61	-55.41	-56.62	-227.91	-141.80
Hydrophobic planes (Aqueous)										
Uxyl-5	Σ	-222.56	-168.61	-160.73	-155.32	-104.26	-143.62	-155.61	-147.30	-258.35
Uxyl-6	Σ	-147.07	-206.95	-258.20	-234.36	-244.16	-238.28	-176.06	-176.52	-144.66
Uxyl-7	Σ	-165.74	-162.29	-113.67	-136.78	-148.04	-161.60	-172.10	-244.39	-243.35
Uxyl-8	Σ	-168.88	-173.93	-165.47	-250.58	-175.42	-145.09	-158.86	-156.50	-166.06

Note: all values were the average of 0.1 ns before the end of the simulation, except for Uxyl in the initial state.

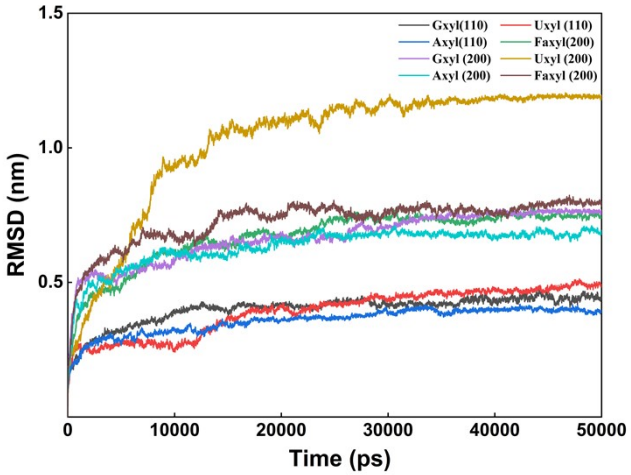

Figure S1. RMSD plots of xylan on the hydrophilic (110) and hydrophobic (200) planes of cellulose.

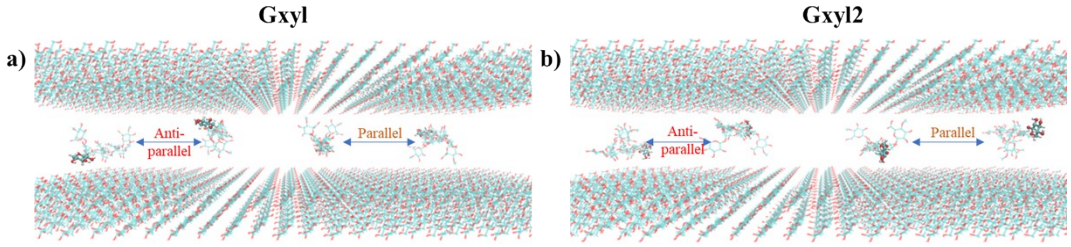

Figure S2. The initial state of the a) Gxyl and b) Gxyl2 systems.

Note: The water molecule layer was between the cellulose microfibrils and xylan with a thickness of 3Å.

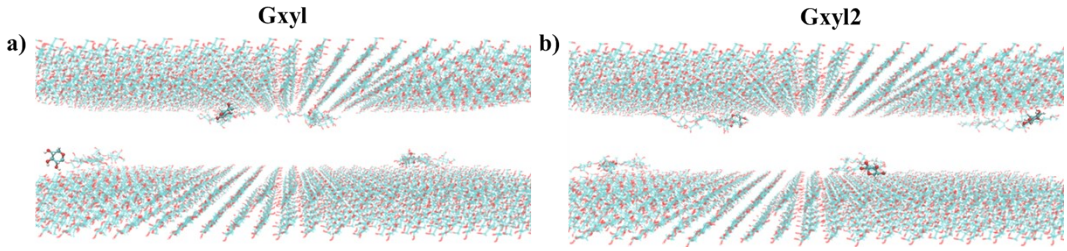

Figure S3. The final state of the a) Gxyl and b) Gxyl2 systems (without water molecules).

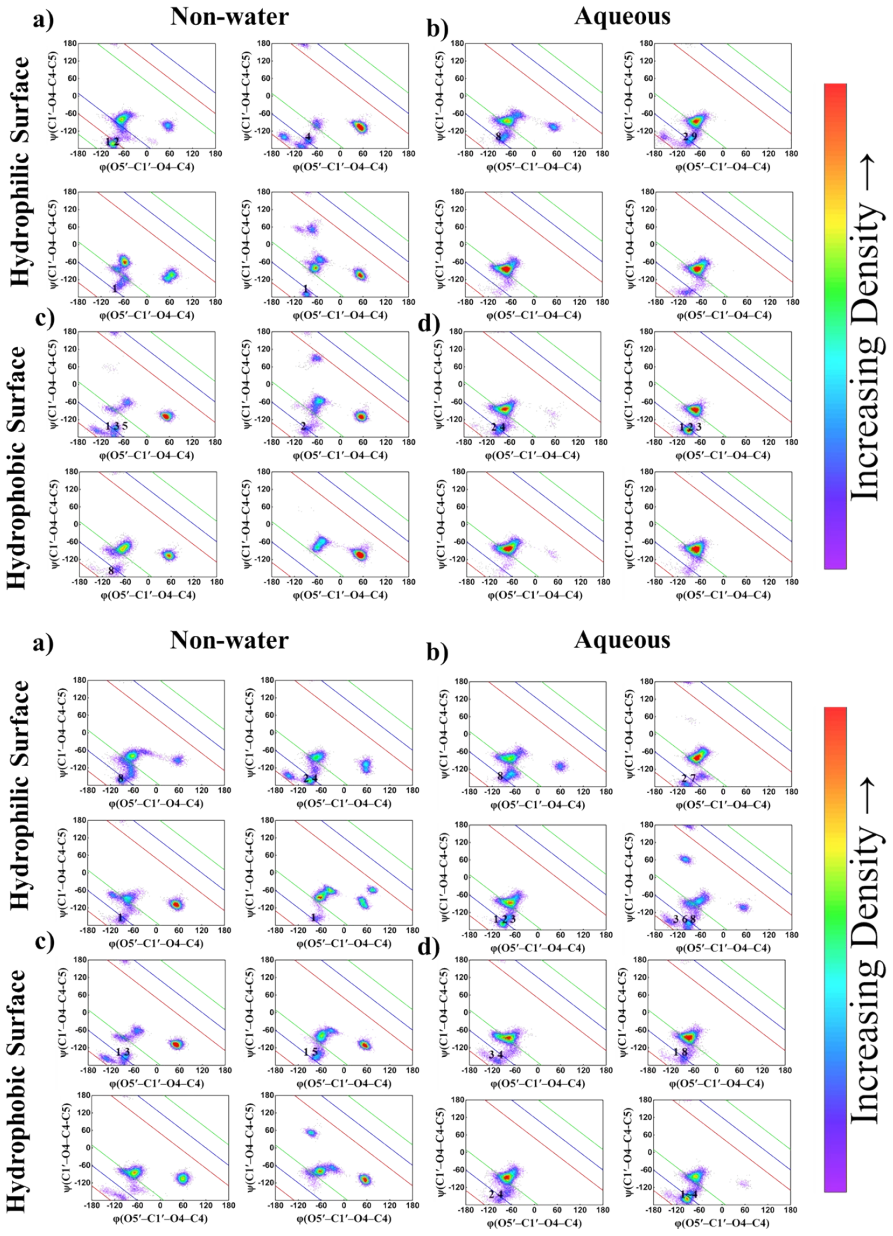

Figure S4. The results of two replicate simulations under the same conditions about the distribution of the dihedral angles, φ(O5'-C1'-O4-C4) and ψ(C5-C4-O4-C1') at the glycosidic linkage of Uxyl.

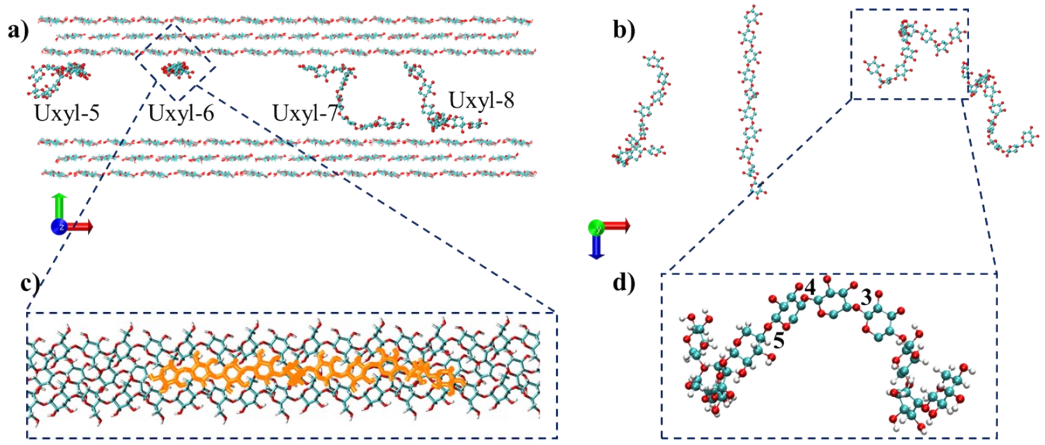

Figure S5. Main view (a), top view (b), and partial enlargement (c, d) of the final state of Uxyl on the 200 planes in the absence of water molecules.

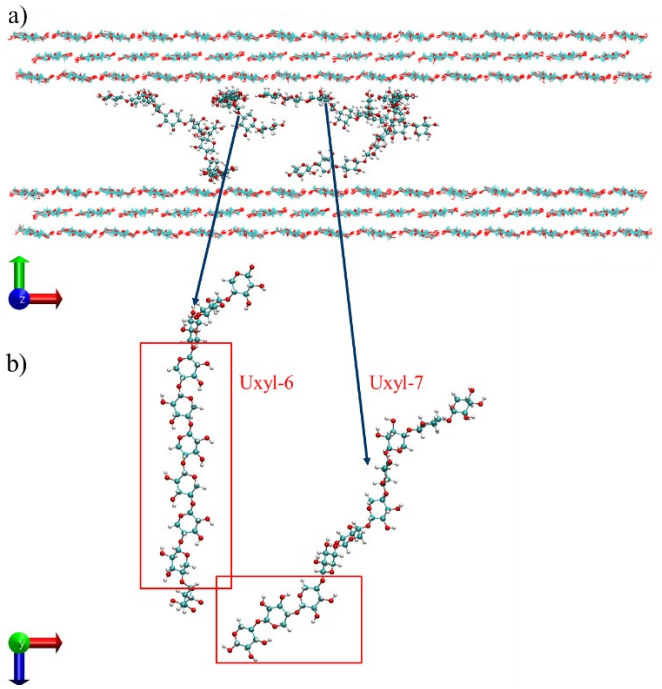

Figure S6. Main view (a) and top view of Uxyl-6,7 (b), of the final state of Uxyl on the 200 planes in the presence of water molecules.

Note: The xylan in the red box was in a 2-fold helical conformation, and the xylose ring in this part was close to the 200 planes of the cellulose microfibril.