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Electronic Supplementary Information for

Why Do the Structural Properties of Complexes Formed by Glucans and Carbon Nanotubes Differ So Much?

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Table S1. Detail of the molecular assays and the simulations.

Composition[a]	Type	No. of atoms	No. of water molecules	Box size (Å^3)	Simulation Time (ns)[b]	No. of runs
β-1,4 glucan+ (6,6) SWCNT	Spontaneous wrapping	36177	11336	157×50×50	40+100	3[c]
α-1,4 glucan + (6,6) SWCNT	Spontaneous wrapping	37302	11711	157×51×51	110	3[c]
β-1,3 glucan + (6,6) SWCNT	Spontaneous wrapping	41367	13066	157×51×55	110+100	3[c]
β-1,4 glucan + (6,6) SWCNT	Tightly pre-wrapped	36912	11581	157×50×51	100	1
α-1,4 glucan + (6,6) SWCNT	Tightly pre-wrapped	37302	11711	157×51×51	100+100	1
β-1,3 glucan + (6,6) SWCNT	Tightly pre-wrapped	41367	13066	157×51×55	100	1
α-1,4 glucan + (6,6) SWCNT	Loosely pre-wrapped	34461	10764	157×49×49	80	1
β-1,4 glucan + (8,8) SWCNT	Pre-wrapped	35090	10803	157×49×50	100	1
β-1,4 glucan + (10,10) SWCNT	Pre-wrapped	40249	12352	157×52×54	100	1

β-1,4 glucan + (10,0) SWCNT	Pre-wrapped	35413	11100	157×49×50	100	1
β-1,4 glucan	Free sugar	14061	4476	172×32×30	20	1
α-1,4 glucan	Free sugar	12849	4072	140×32×32	20	1
β-1,3 glucan	Free sugar	14967	4778	149×33×34	20	1
β-1,4 glucan	Disaccharides/1D free-energy calculation	5148	1701	40×38×37	80	1
α-1,4 glucan	Disaccharides/1D free-energy calculation	4929	1628	40×38×35	80	1
β-1,3 glucan	Disaccharides/1D free-energy calculation	4989	1648	40×34×40	80	1
β-1,4 glucan	Disaccharides/2D free-energy calculation	5148	1701	40×38×37	320	1
α-1,4 glucan	Disaccharides/2D free-energy calculation	4929	1628	40×38×35	320	1
β-1,3 glucan	Disaccharides/2D free-energy calculation	4989	1648	40×34×40	320	1

[a]Unless otherwise specified, all the polysaccharide chains consist of 30 monomers.
[b]The number after plus sign is the time of additional equilibration of the wrapping configuration.
[c]Independent runs with distinct initial conditions.

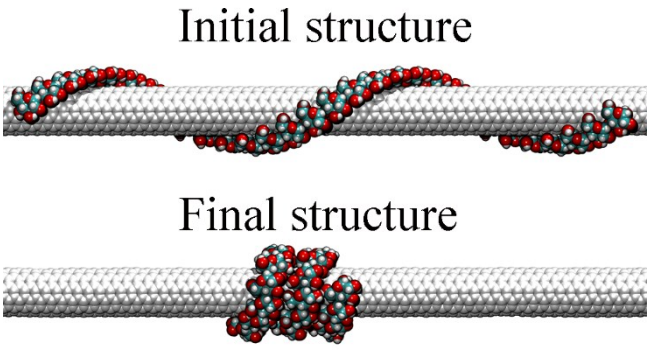

Figure S1. MD simulation of a α-1,4 glucan chain in water starting with a pre-wrapped SWCNT. After 80 ns simulation, the helical chain, initially extended, compressed like a spring, to become ultimately very compact. The final spatial arrangement of the polysaccharide-SWCNT complex is similar to that shown in Figure 2C.

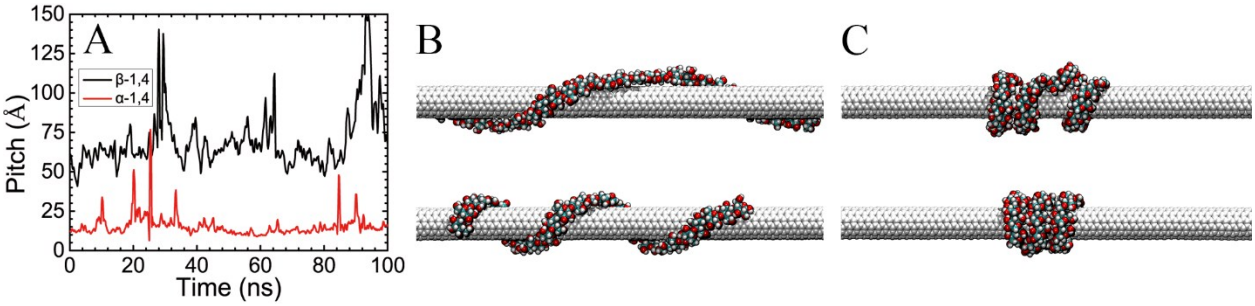

Figure S2. (A) Time evolution of the pitch in β-1,4, and α-1,4 glucan during the 100-ns equilibration. (B) and (C), stretched and compressed states of β-1,4 and α-1,4 glucan helix, respectively.

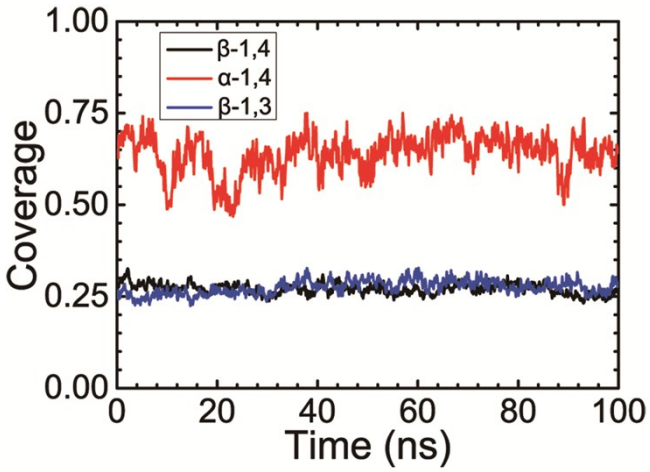

Figure S3. Time evolution of the coverage of SWCNT in the wrapped structures during the 100-ns equilibrium simulation.

Table S2. Binding free energy and its decomposition for the complex formed by α-1,4 glucan and SWCNT depicted in Fig. 1B. All quantities in kcal/mol.

	ΔG	ΔE_{bond}	ΔE_{angle}	$\Delta E_{dihedral}$	ΔE_{elec}	ΔE_{VDW}	ΔG_{PB}	ΔG_{SA}
α-1,4 glucan:SWCNT	-191.4	-0.1	6.9	2.5	-99.0	-126.9	64.7	-39.6

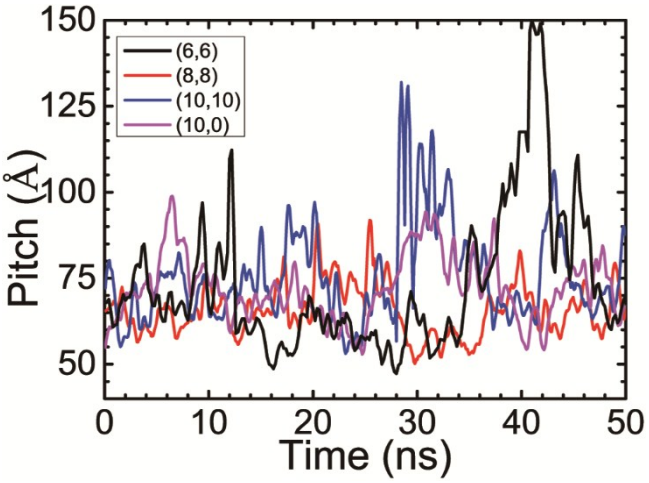

Figure S4. Pitch of different β-1,4 glucan-SWCNT complexes.

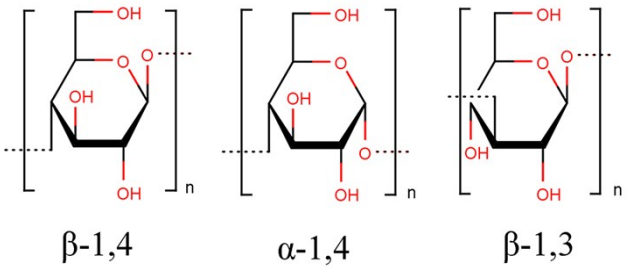

Figure S5. Structural formula of β-1,4, α-1,4 and β-1,3 glucans.

Table S3. Binding free energies per repeat unit of the polysaccharide chains and the glucoses. All quantities in kcal/mol.

	Repeat unit			Monomer	
	β-1,4 glucan	α-1,4 glucan	β-1,3 glucan	β-glucose	α-glucose
ΔG	-8.5	-9.5	-7.7	-8.4	-9.4

Table S4. Mean pitches and their standard deviations of different β-1,4 glucan-SWCNT complexes.

SWCNT	Diameter (Å)	Type	Mean pitch (Å)	Standard Deviation (Å)
(6,6)	8.136	Armchair	72.88472	20.79033
(8,8)	10.848	Armchair	71.39422	18.25159
(10,10)	13.560	Armchair	75.75254	13.44483
(10,0)	7.829	Zigzag	70.49537	10.09653

Table S5. Binding free energies for the complexes formed by β-1,4 glucan and different SWCNTs. All quantities in kcal/mol.

	β-1,4 glucan: (6,6) SWCNT	β-1,4 glucan: (8,8) SWCNT	β-1,4 glucan: (10,10) SWCNT	β-1,4 glucan: (10,0) SWCNT
ΔG	-256.0	-298.5	-319.9	-263.6

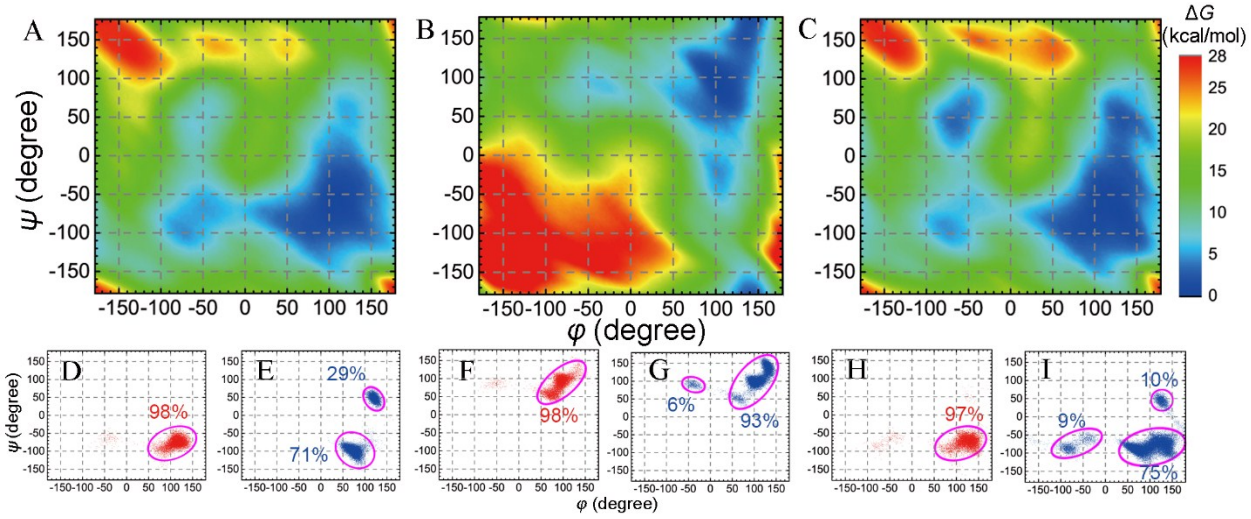

Figure S6. Distributions of dihedral angles (φ,ψ) in the polysaccharide chains with and without SWCNT, as well as the free-energy profiles as a function of (φ,ψ). The red and blue points show the distributions of (φ,ψ) for the polysaccharides free in water and wrapping around SWCNT, respectively.

RESULTS AND DISCUSSION

Differences between the Three Polysaccharide-SWCNT Hybrids.

Helicity. The helicity of the three types of polysaccharide chains on the hollow tubular surface can be directly observed from the stable conformations (Figure 1A, 1C and 2C), i.e. left-handed, left-handed and right-handed for β-1,4, α-1,4 and β-1,3 glucan, respectively. Considering that the α-1,4 and β-1,3 glucan chains are both left-handed and right-handed in crystal structures,[1-2] these polysaccharide chains seem to preserve their inherent chirality when wrapping around SWCNTs. Helicity of β-1,4 glucan in its crystal structure, however, is still under debate.[3] Our findings of a left-handed helix indirectly support the majority of experimental results,[3] that the crystal structure of β-1,4 glucan is possibly left-handed.

Pitch. Pitch is a crucial property for the determination of the overall fold of polymer chains. We, therefore, measured the pitch of the helices formed by β-1,4 and α-1,4 glucan chains on the SWCNT surface, using a fitting procedure.[4] As shown in Figure S2A, the pitch of β-1,4 glucan, larger than that of α-1,4 glucan, is the most significant difference between the two corresponding hybrids. Interestingly enough, although the pitches of the two helix polysaccharide chain are essentially constant during the 100 ns equilibrium simulation, there are spring-like stretching vibrations in the helical chains, mirrored in the abnormal high value in Figure S2A. The stretched and compressed states of the β-1,4 and α-1,4 glucan helix are depicted in Figure S2B and S2C. Although the intermediate structures between the stretched and compressed states emerged much more often in our simulation, the potential of spring-like vibration of the polysaccharide helix implies the possibility of existing a large range of polysaccharide/SWCNT ratio in supramolecular wrapping complexes. When polysaccharide is in excess, the helix may be in the compressed motif.

While it is hard to determine with a suitable precision the pitch in the irregular helix formed by β-1,3 glucan, experiment reveals that the mean pitch of the helical chain in β-1,3 glucan-SWCNT hybrids is about 10 nm.[5]

Coverage. The coverage of the SWCNT plays a key role in the determination of how much the surface property of the nanotube is screened. The extent of the coverage of the SWCNTs in the three assays is intuitively different from what might be inferred from a simple glance at Figure 1A, 2B and 1C. To quantify the concept of coverage, we adopted the following definition,

$$\text{coverage} = 1 - \frac{SASA_{\text{complex}}}{SASA_{\text{nanotube}}} \tag{1}$$

where $SASA_{\text{complex}}$ is the solvent accessible surface area (SASA) per unit length of SWCNT in the glucan-SWCNT hybrid, and $SASA_{\text{nanotube}}$ is the SASA per unit length of SWCNT.

As shown in Figure S3, the coverage of SWCNT in three assays remains fairly constant during the 100-ns equilibrium simulation. The average coverage of the SWCNT in the β-1,4, α-1,4 and β-1,3 glucan-SWCNT hybrids amounts to 27%, 64% and 28%, respectively. The α-1,4 glucan chain has the tightest helix and covers the SWCNT the most. It, therefore, screens most of the hydrophobic surface of the SWCNT. The much extended β-1,4 and β-1,3 glucans, however, cover less than one third of the surface of the SWCNTs. This extended helix can preserve most of the surface properties of SWCNTs. In practical applications, to obtain the desired features, we can take advantage of the varying degree of coverage of the SWCNT when wrapped by different polysaccharides.

Chain Length of the Polysaccharides Participating in the Wrapping

We calculated the binding free energies per repeat unit of the glucan chains and those of the α- and β-glucose. The former were derived by averaging the binding affinity of a chain over the number of monomers, i.e., 30. The latter were obtained from two additional simulations characterizing the spontaneous adsorption of one α- and β-glucose molecule on the surface of the SWCNT. As shown in Table S3, the binding free energies per repeat unit of the 1,4-linked polysaccharide chains are very similar to those of the corresponding glucoses, whereas the interaction of the structural unit in the β-1,3 glucan chain with the SWCNT is weaker than that of the free β-glucose molecule. This difference suggests a significant effect of the glycosidic bond linkage on the wrapping of the chain. It can also be conjectured that for the 1,4-linked glucan, the chain length slightly impacts the binding ability of the repeat unit of glucan to the SWCNT, but for the 1,3-linked glucan, such influence becomes significant. Further study would still be needed to make this point clear.

Effects of the Concentration of the Glucan and the Entanglement of the Chain

When the concentration in polysaccharides increases, interchain effects may be observed, to the extent that the CNT can be wrapped by more than one polysaccharide chain. In experiment, however, the polysaccharide is usually dispersed in solution by means of ultrasound and its concentration is usually very low,[5] pleading in favor of using a single chain to mimic mono-dispersed CNTs in solution. This work mainly focuses on the interaction of glucans with CNTs, under the assumption that the polymer concentration is not too high and interchain effects are overall marginal.

In our simulations, entanglement of the glucan chain was not observed, because the chain was located near the tubular surface and is too short relative to the infinitely long tube. From a kinetic standpoint, wrapping of an entangled chain around a CNT may become more difficult, because of the additional energy barriers from the disentanglement of the chain, the investigation of which is out of the scope of the present work.

METHODS

Preparation of the Initial Structures for the Spontaneous Wrapping and Simulations Starting with Initially Wrapped Configurations

The initial conformations of β-1,4, α-1,4 and β-1,3 glucan used in this study were generated by the GLYCAM carbohydrate builder, which assembles polysaccharides chains close to their crystal structures. The geometry of each polysaccharide and SWCNT was optimized separately using a conjugate gradient energy-minimization algorithm. The polymer chains were then placed in the vicinity of the SWCNT surface within the cutoff distance for short-range, van der Waals interactions, and the complexes were immersed into the aqueous solution. Each molecular assay underwent 2 ns of equilibration with harmonic restraints applied to the position of all heavy

atoms, thereby allowing water to relax around the supramolecular complex. The production simulations were then carried out, where the SWCNT was restrained with the aid of a weak harmonic potential.

The initially wrapped structures were generated by means of a VMD script in which the user defines the radius and the pitch helix. The radius of the helix is equal to that of a perfect helix formed spontaneously by β-1,4 glucan (see Figure 1A). For the compact artificial helix in Figure 2A, the helical pitch was set to ~9 Å. For the extended conformation depicted in Figure S1, the pitch was set to ~70 Å.

Detailed Discussions on Temperature Control

In Langevin dynamics, the friction term is chosen in such a way that coupling to the thermal bath is tight enough to maintain the temperature constant with reasonable fluctuations, but self-diffusion is not hampered. This friction term was set to 1.0 ps-1 in our simulations and there was no special setting for angular momentum. The evolution of the temperature in one of the equilibrium simulations is provided in Figure R3. As can be seen, the temperature was well-controlled over the entire simulation. The wrapping simulations were performed in the canonical ensemble. The pressure was not controlled. In the wrapping simulations, the initial velocity of each atom was randomly taken from a Boltzmann distribution at the desired temperature.

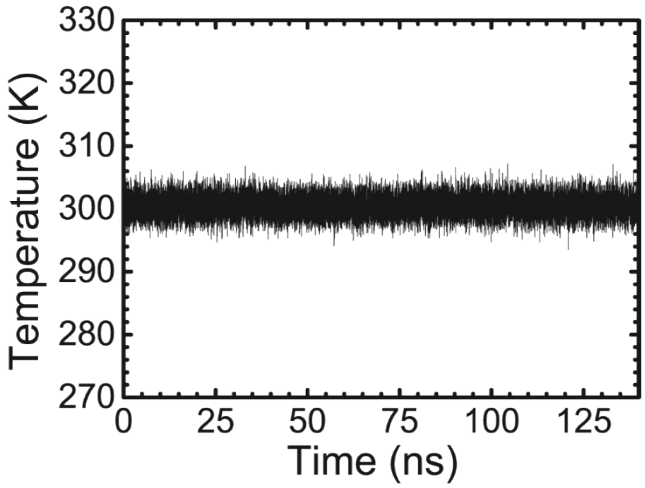

Figure S7. Time evolution of the temperature in the 140 ns simulation characterizing the spontaneous wrapping of β-1,4 glucan.

To address whether or not the temperature-control algorithm affects the results of this work, an additional 80-ns simulation characterizing the spontaneous wrapping of β-1,4 glucan around the SWCNT was performed, using the Lowe-Anderson thermostat, while keeping other parameters

unchanged. As shown in Figure S8, the perfect wrapping mode of the β-1,4 glucan is also obtained employing this alternate thermostat, suggestive that the algorithm for temperature control, as long as it yields the expected canonical distribution, has little effect on the spontaneous wrapping process.

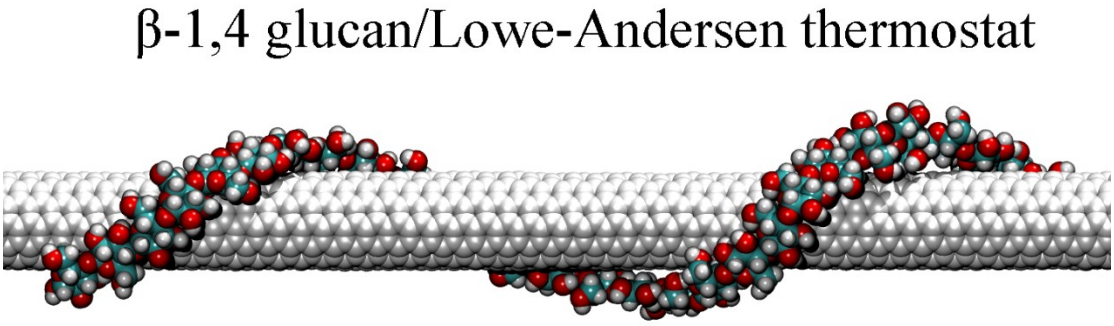

Figure S8. Final configuration of β-1,4 glucan-SWCNT complex.

REFERENCES

1. Popov, D.; Buléon, A.; Burghammer, M.; Chanzy, H.; Montesanti, N.; Putaux, J.-L.; Potocki-Veronese, G.; Riekel, C., Crystal Structure of A-amylose: A Revisit from Synchrotron Microdiffraction Analysis of Single Crystals. *Macromolecules* **2009,** *42* (4), 1167-1174.
2. Okuyama, K.; Otsubo, A.; Fukuzawa, Y.; Ozawa, M.; Harada, T.; Kasai, N., Single-Helical Structure of Native Curdlan and Its Aggregation state. *J. Carbohyd. Chem.* **1991,** *10* (4), 645-656.
3. French, A. D.; Johnson, G. P., What Crystals of Small Analogs are Trying to Tell us about Cellulose Structure. *Cellulose* **2004,** *11* (1), 5-22.
4. Kang, Y. K.; Lee, O.-S.; Deria, P.; Kim, S. H.; Park, T.-H.; Bonnell, D. A.; Saven, J. G.; Therien, M. J., Helical Wrapping of Single-Walled Carbon Nanotubes by Water Soluble Poly (p-phenyleneethynylene). *Nano. Lett.* **2009,** *9* (4), 1414-1418.
5. Numata, M.; Asai, M.; Kaneko, K.; Bae, A.-H.; Hasegawa, T.; Sakurai, K.; Shinkai, S., Inclusion of Cut and As-Grown Single-Walled Carbon Nanotubes in the Helical Superstructure of Schizophyllan and Curdlan (β-1, 3-glucans). *J. Am. Chem. Soc.* **2005,** *127* (16), 5875-5884.