Molecular Wire of Urea in Carbon Nanotube: A Molecular Dynamics Study

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Supplementary Information

1. System Preparation.

Table S1. Setup of systems for the simulations of (6, 6) armchair single-walled carbon nanotubes (SWNTs) in aqueous urea at various urea concentrations. (A): 336-carbon SWNT case. (B): 144-carbon SWNT case. C_{urea} (mol/L) denotes the urea concentrations; N_{urea} and N_{water} denote the number of urea and water molecules in the system.

A:

$N_{solvent}$ \ C_{urea}	0.5 M	1 M	8 M
N_{urea}	24	47	376
N_{water}	2612	2490	1659

B:

C_{urea} / $N_{solvent}$	1 M	2 M	3 M	4 M	5 M	6 M	7 M	8 M	9 M	10 M
N_{urea}	31	62	93	124	155	186	216	248	277	310
N_{water}	1615	1536	1455	1409	1302	1217	1161	1080	1005	957

2. Recalculating the Number of Inner Urea/Water by Excluding the Molecules Adjacent to the Edge of the SWNT

We have recalculated the number of inner urea/water molecules by excluding the molecules adjacent to the edge of the 336-carbon (6, 6) SWNT (see Table S2). Compared to the results of Table 1 in the main text, the results in Table S2 confirm that the residual water inside the SWNT commonly locates adjacent to the edge of the SWNT.

Table S2. Average number of urea ($\overline{N}_{urea}$) and water molecules ($\overline{N}_{water}$) inside the 336-carbon (6, 6) SWNT in equilibrium [here, only the axially central region of SWNT (2.72 nm in length) is considered when counting water/urea molecules for comparison], as well as the occurrence probabilities for "perfect wire" ($P_{perfect}$[a]), with KBFF and OPLS urea models.

C_{urea}	KBFF			OPLS		
	$\overline{N}_{urea}$	$\overline{N}_{water}$	$P_{perfect}$	$\overline{N}_{urea}$	$\overline{N}_{water}$	$P_{perfect}$
0.5 M	5.78	0.06	94.1%	5.71	0.67	39.6%
1 M	5.84	0.001	99.9%	5.96	0.20	81.4%
8 M	5.88	0.001	99.9%	6.09	0.03	96.9%

[a] $P_{perfect}$ is defined as the occurrence probability for "perfect" urea wire (at this time, there is no water molecules inside the axially central region of SWNT) in equilibrium.

3. Average Dipole Orientation of Urea Molecules inside the 144-carbon (6, 6) SWNT and Flipping Behavior of Urea Wire.

In addition to the study of the urea wire inside the 336-carbon SWNT, we also

performed separated simulations of 144-carbon (6, 6) SWNT in 8 M urea. The nanotube is essentially filled with ~ 3 urea molecules (on average, there are 2.94 urea molecules and 0.03 water molecules inside SWNT for the KBFF urea case; for OPLS urea case, the corresponding numbers are 2.70 for urea and 0.33 for water[1]). We have computed the average dipole orientation of inner urea molecules, $\bar{\phi}$ (ϕ is defined as the angle between a urea dipole and the nanotube axis), as a function of simulation time, shown in Fig. S1. Although the urea wire is short, we have not observed any flipping event for the KBFF urea, and only observed 1~2 flipping events for the OPLS urea, during several independent simulations, each with 100 ns.

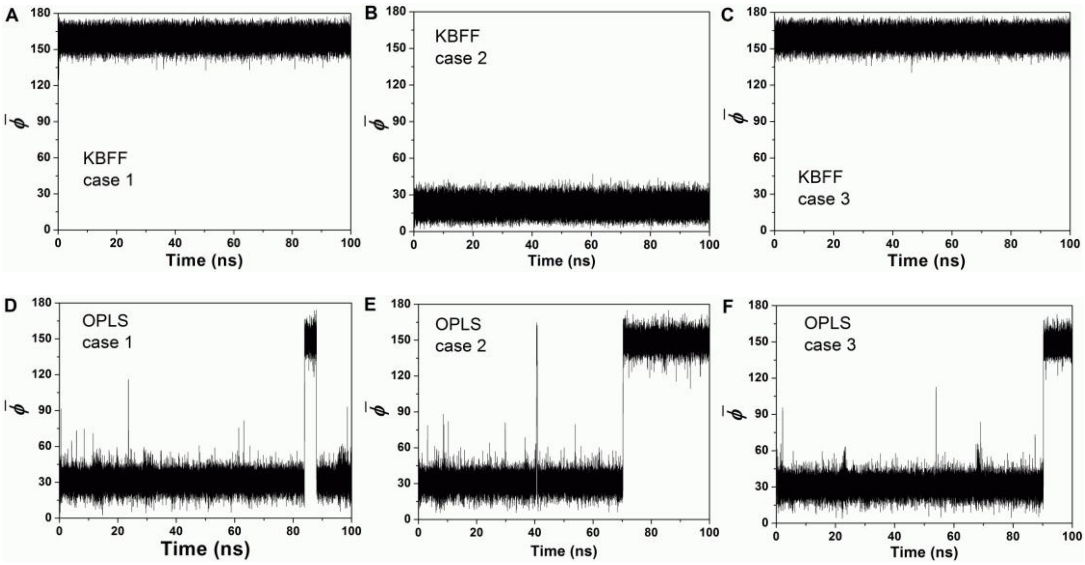

Figure S1. Average inner urea's dipole orientation versus time and flipping behavior of urea wire inside the 144-carbon (6, 6) SWNT. (A-C): Cases for the KBFF urea. (D-F): Cases for the OPLS urea. Each plot stands for an independent simulation.

4. Axial Density Profile for Water inside SWNT and Comparison with that for Urea.

Fig. S2 displays the average water position distribution along the SWNT axis (blue curve in this figure and in Fig. 2 of the main text). As mentioned in the main text, the water molecules are much less sharply distributed compared to the urea molecules. In the following, we show that this difference comes mainly from the different molecular sizes of urea and water. Since a water molecule is much smaller than a urea molecule

(urea's volume is approximately 2.5 times larger than that of water[2]), it can better accommodate its position inside the nanotube, thus resulting in a "two-state" water wire, corresponding to 12 or 13 inner water molecules (N_{water}), with the occurrence probabilities of 31.2% and 63.3%, respectively. As shown in Fig. S2, the axial positions are sharply distributed for both N_{water} = 12 case and N_{water} = 13 case. However, the peak positions in the axial density profile of the N_{water} =12 case overlap with those valley positions of the N_{water} =13 case. Consequently, the sharp position distributions for the N_{water} =12 case and the N_{water} =13 case average out, leading to an indistinct overall water distribution. In contrast, when the "perfect" urea wire is formed inside the 336-carbon (6, 6) SWNT (in 8 M urea), the average number of inner urea molecules is 7.1, with the most dominant number of 7 and an occurrence probability of 89.0%. That is, due to the relatively larger physical dimension of urea, the urea wire has only one dominant state (N_{urea} = 7), leading to a distinct urea distribution along the nanotube axis.

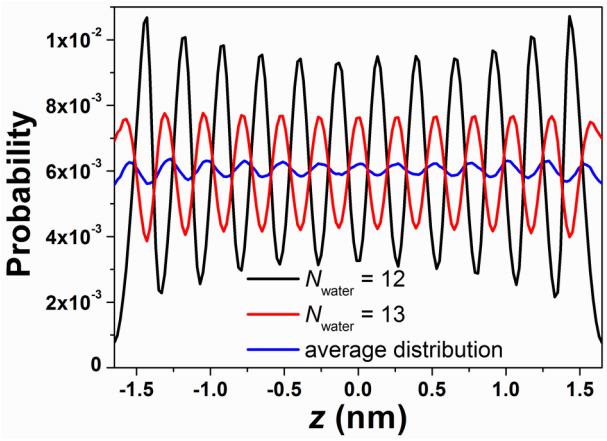

Figure S2. The axial density profiles for water molecules inside the 336-carbon (6, 6) SWNT, when the SWNT is immersed in pure water. The blue curve represents the average water position distribution, while the black and red curves represent the water position distributions when the inner water molecules (N_{water}) are 12 and 13, respectively.

In addition, we have compared the simulation results (using KBFF urea model and 8 M urea concentration for illustration) with different vdW cutoff distances, d_{cutoff} (1.0

nm, 1.2 nm, and 1.5 nm), and found that they are not sensitive to the cutoff distances used and 1.2nm cutoff distance should be sufficient (see Table S3).

Table S3: Average number of urea ($\overline{N}_{urea}$) and water molecules ($\overline{N}_{water}$) inside 336-carbon (6, 6) SWNT and 144-carbon (6, 6) SWNT in equilibrium (using KBFF urea model and 8 M urea concentration for illustration), as well as the occurrence probabilities for "perfect wire", P_{perfect}, with various vdW cutoff distances, d_{cutoff}.

d_{cutoff}	336-carbon (6, 6) SWNT			144-carbon (6, 6) SWNT		
	$\overline{N}_{urea}$	$\overline{N}_{water}$	P_{perfect}	$\overline{N}_{urea}$	$\overline{N}_{water}$	P_{perfect}
1.0 nm	7.10	0.02	97.6%	2.94	0.03	97.7%
1.2 nm	7.10	0.03	96.7%	2.94	0.03	97.9%
1.5 nm	7.08	0.04	95.8%	2.94	0.03	97.8%

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