Electronic Supplementary Information

Ferroelectric mobile water

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1. Supplementary Text

We calculate the water density inside the effective inner space of the (*m,m*) CNTs. Inside the CNTs of sufficiently large diameter, the water density is close to that of bulk. The smaller the diameter, the lower the density. For example, 0.99, 0.98, 0.97, 0.85, and 0.73 g/cc for m = 20, 16, 12, 7, and 6, respectively (280 K, CNT length 2.1 nm). Interestingly, anomalies occur at m = 9 and 8. The density increases to about 1.07 g/cc for m = 9, and reaches no less than about 1.23 g/cc for m = 8. That is, the 'ferroelectric mobile water (FMW)' is an anomalous high-density phase. Figure S1a shows the water density inside the (8,8) CNT at 280K. The net axial polarization per molecule (Figure 1b) is nearly constant at about -0.79 (units are the magnitude of a single dipole of TIP5P-E water). The ferroelectric direction is seen unchanged over 40 ns.

At a higher temperature (290 K), the high density phase (FMW) and a low density phase of about 1.02 g/cc alternatively appear (Figure S1c). This tendency is observed to continue also during the subsequent additional 50 ns, and is expected to continue further. The direction of the net axial polarization undergoes a series of abrupt changes (Figure S1d). Comparing Figure S1c and S1d, we notice that the changes occur in the low density phase. That is, the ferroelectric direction is reversed via the low density phase. The potential energy per molecule in the high density phase is 0.89 kcal/mol lower than

that in the low density phase. Here, the potential energy is calculated as follows. For each snapshot, we calculate the following quantity,

$$E_{pot} = E_{ele}(WAT_{in} - WAT_{in}) + E_{LJ}(WAT_{in} - WAT_{in}) + E_{LJ}(WAT_{in} - CNT) + \{ E_{ele}(WAT_{in} - WAT_{out}) + E_{LJ}(WAT_{in} - WAT_{out}) \} / 2, \quad (1)$$

where,

E_{ele}(X-Y) : sum of electrostatic interaction energy between X and Y,

E_{LJ}(X-Y) : sum of Lennard-Jones interaction energy between X and Y,

WAT_{in} : water molecules inside CNT,

WAT_{out} : water molecules outside CNT.

The snapshots in the high and the low density phases are collected separately based on the results of the water density in Figure S1c. The resultant sum is equivalent to 8.9 nsec (18.1 nsec) for the high (low) density phase. They are equally divided into ten, for which each average of E_{pot} is calculated. These averages are used to derive the final value of the potential energy (the standard deviation is at most 0.13 % of the final value).

The dominant contribution to the potential energy difference arises from the electrostatic energy. In the high density phase, the hydrogen atom distribution near the oxygen atom is very close to that of bulk water (Figure S2). Though the low density phase resembles bulk water in density, the first maximum of the hydrogen atom distribution is clearly low compared to both bulk water and the high density water. The recurrent change of the ferroelectric direction and the density of the FMW ensures the effect of the reservoir water fluctuation through the open ends of the CNT. Here, we demonstrate the effect of the CNT length. In the simulation employing a CNT about twice as long (4.0 nm), both the water density and the net axial polarization become

nearly constant even at 290 K (Figure S1e and f, respectively), resembling those in the simulation employing the 2.1 nm-long CNT at 280 K (Figure S1a and b). Roughly speaking, employing the longer CNTs has an effect similar to reducing the temperature.

2. Supplementary Figures

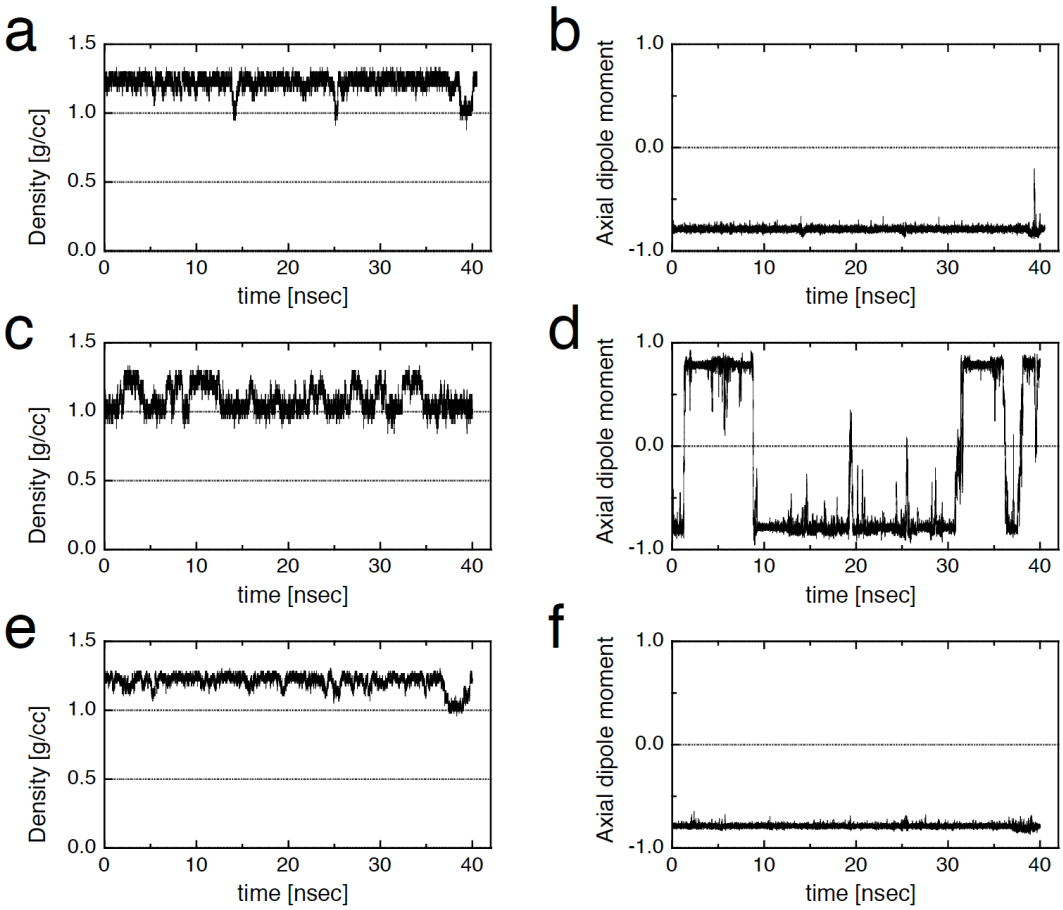

Figure S1. Effect of temperature and CNT length.
Density (a)(c)(e) and net axial polarization (b)(d)(f) of water inside (8,8) CNT.
(a)(b) CNT length 2.1 nm. 280K. (c)(d) CNT length 2.1 nm. 290K.
(e)(f) CNT length 4.0 nm. 290K.

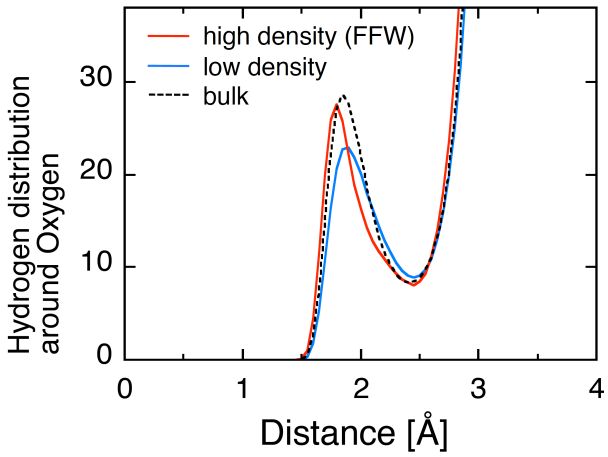

Figure S2. Hydrogen distribution around Oxygen inside (8,8) CNT.
CNT length 2.1 nm. 290 K. Quantities proportional to number (not density) of hydrogen atoms at between r and $r + \Delta r$ from oxygen atom are plotted (center oxygen atoms near CNT edges are excluded from distribution calculation).

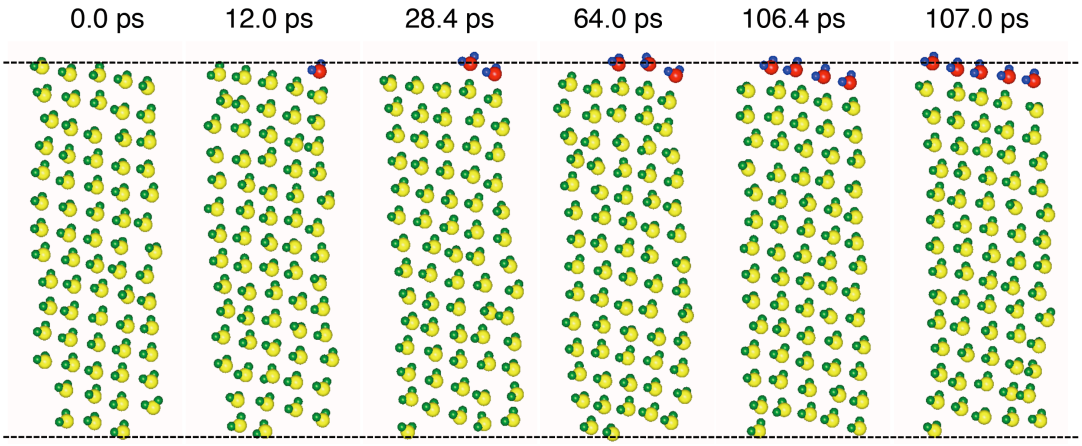

Figure S3. Mechanism of proton-ordered diffusion inside (8,8) CNT.
CNT length 4.0 nm. 280K. Only water molecules inside CNT are shown. Two dotted lines represent positions of CNT edges. 'Vacant pocket' near top edge of CNT is filled molecule by molecule with reservoir water molecules (whose oxygen atoms are coloured red).

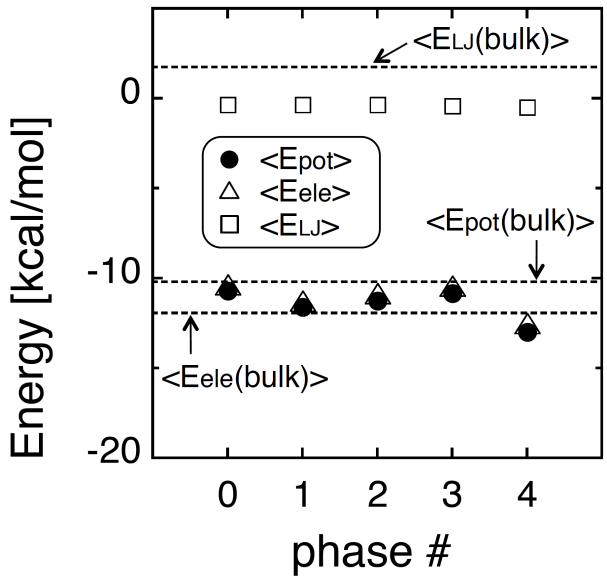

Figure S4. Energy of five water phases inside (9,9) CNT.
CNT length 2.1 nm. 280K. $<E_{pot}>$ is final average of potential energy (see Eq. 1 and its subsequent explanation). $<E_{ele}>$ and $<E_{LJ}>$ are final averages of

$E_{ele} = E_{ele}(WAT_{in} - WAT_{in}) + E_{ele}(WAT_{in} - WAT_{out}) / 2,$

$E_{LJ} = E_{LJ}(WAT_{in} - WAT_{in}) + E_{LJ}(WAT_{in} - CNT) + E_{LJ}(WAT_{in} - WAT_{out}) / 2,$

respectively. Bulk values are also shown.

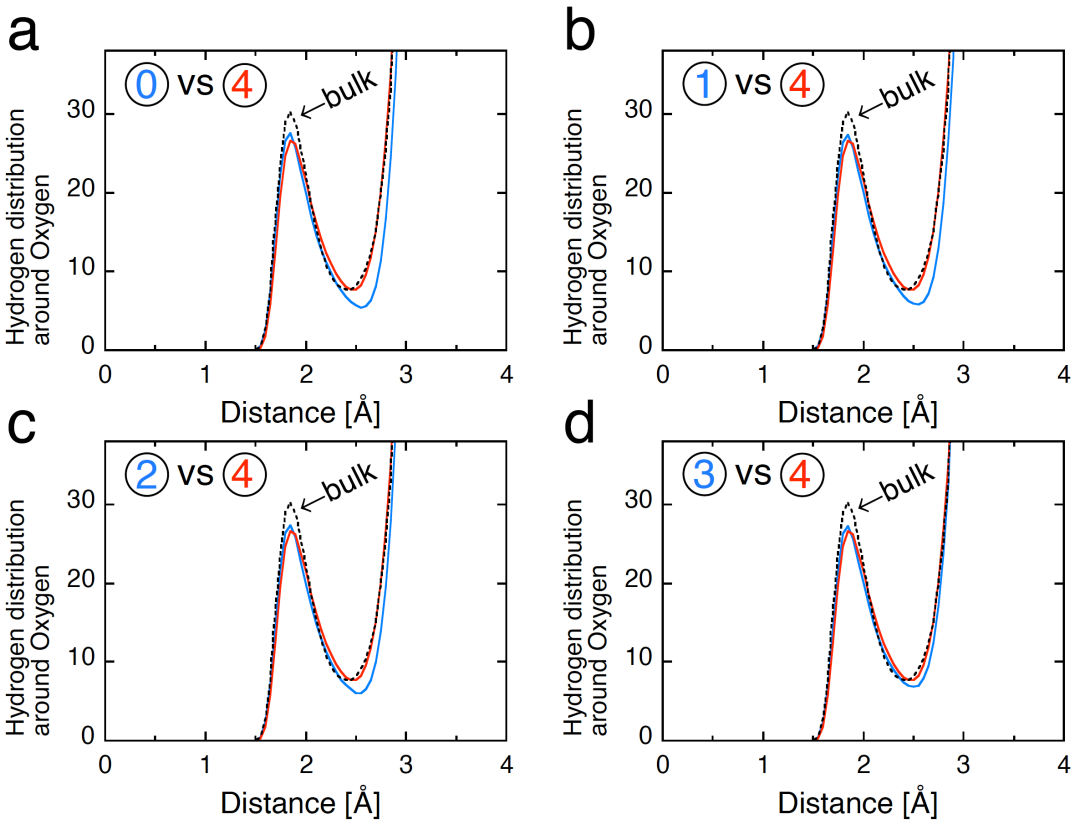

Figure S5. Hydrogen distribution around Oxygen inside (9,9) CNT.
CNT length 2.1 nm. 280 K. Five water phases inside CNT are compared in corresponding colours, together with bulk water (black dotted line). Quantities proportional to number (not density) of hydrogen atoms at between r and $r + \Delta r$ from oxygen atom are plotted (center oxygen atoms near CNT edges are excluded from distribution calculation).

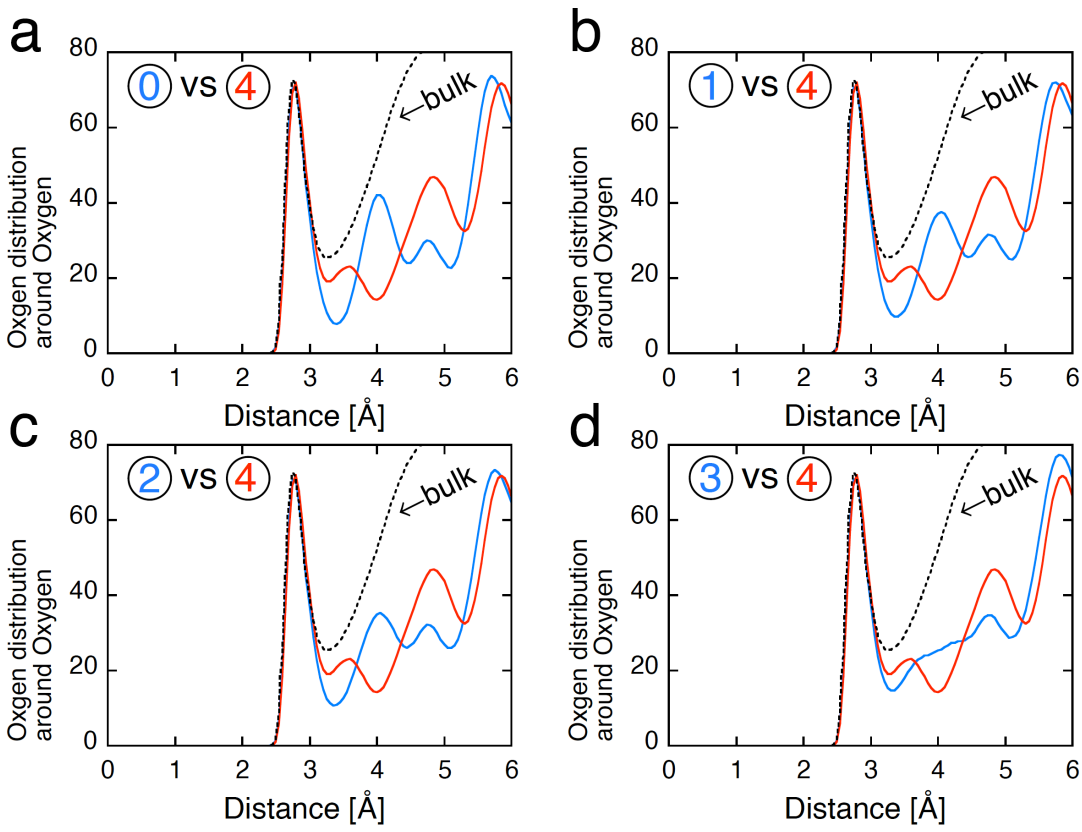

Figure S6. Oxygen distribution around Oxygen inside (9,9) CNT.
CNT length 2.1 nm. 280 K. Five water phases inside CNT are compared in corresponding colours, together with bulk water (black dotted line). Quantities proportional to number (not density) of oxygen atoms at between r and $r + \Delta r$ from oxygen atom are plotted (center oxygen atoms near CNT edges are excluded from distribution calculation).

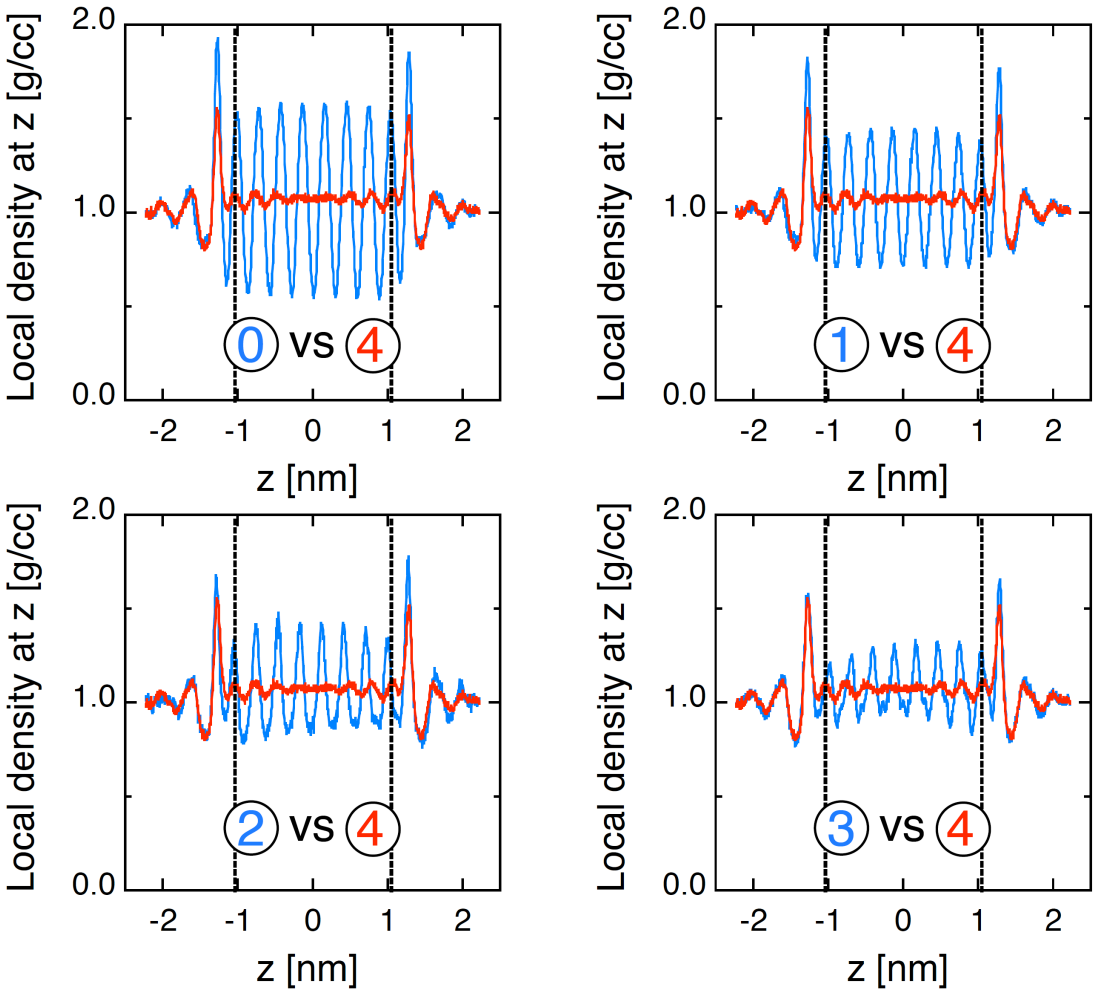

Figure S7. Local water density along CNT axis.

CNT length 2.1 nm. 280K. Five water phases inside CNT are compared in corresponding colours. Two vertical dotted lines represent CNT edges.

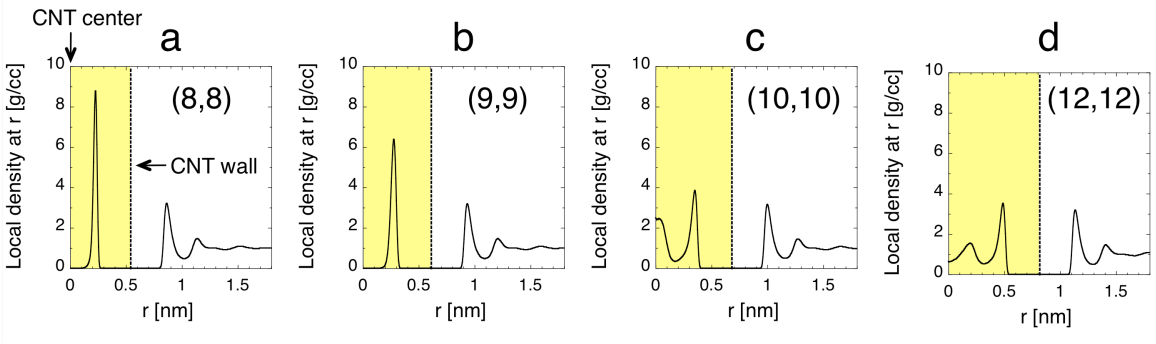

Figure S8. Local water density along radial direction of CNT.
(a) (8, 8), (b) (9, 9), (c) (10, 10) and (d) (12, 12) CNT (2.1nm length). 280K. 1 atm. Data obtained from equilibrated MD trajectories lasting 10 nsec. Yellow region represents inner space of CNT.

3. Supplementary Movies

Movie S1

This movie shows the proton-ordered diffusion of water molecules inside (8,8) carbon nanotube open to water reservoir. CNT length 4.0 nm. Side (left) and unfolded views at 280K. Five neighbouring molecules are coloured for guide for eyes. Simulation time 5 nsec. (QuickTime; 6.5 MB)

Movie S2

This movie shows 'go-stop-go' motion of water molecules inside (9,9) carbon nanotube open to water reservoir. CNT length 4.0 nm. Side (left) and unfolded view at 290K. Six neighbouring molecules are coloured for guide for eyes. Simulation time 2.4 nsec. (QuickTime; 7.3 MB)