Supporting Information

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S. Ⅰ Diffusion coefficient of bulk water

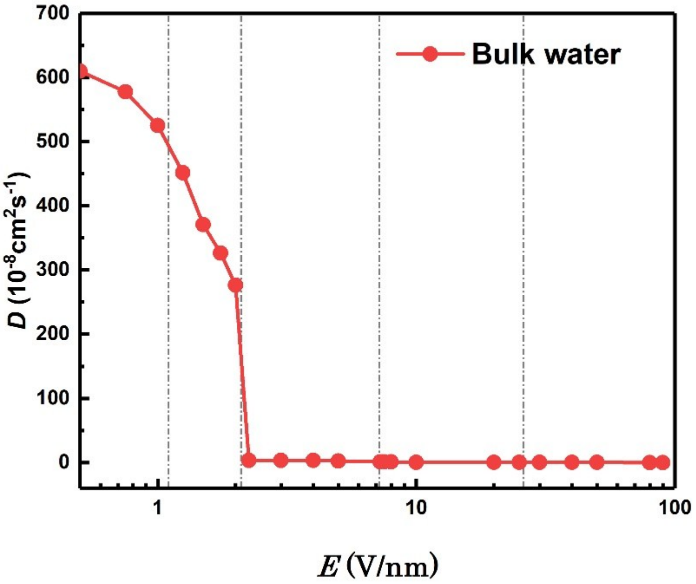
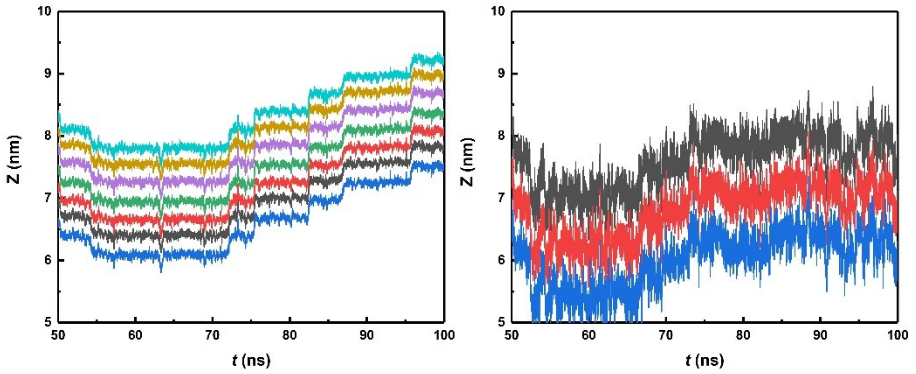


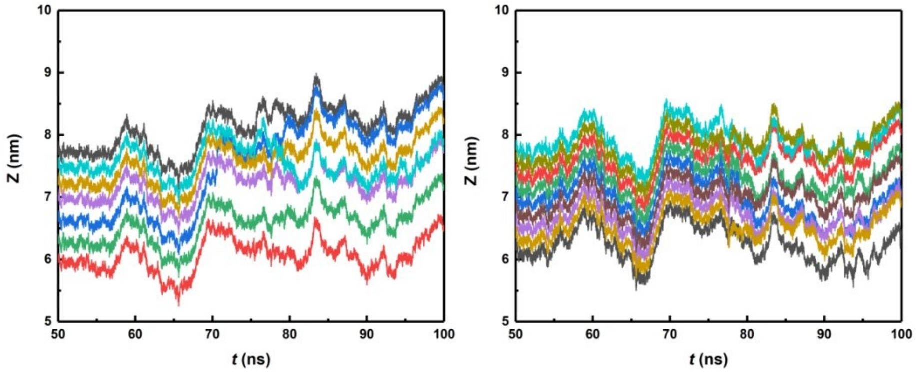
Fig. S1. Diffusion coefficient of water as a function of electric field. The black dots represent diffusion coefficient of water in SWNT, and the red dots represent that of bulk water out of SWNT.

Our simulation results indicate that water diffusion coefficient of bulk water is larger than that of water molecules confined in the carbon nanotube. For type A, Q1D nitrogen hydrate is solid-like, while the bulk water is still liquid. But when the electric field is larger than 1 V/nm, diffusion coefficient of bulk water decreases sharply too. For $E > 2.25$ V/nm, bulk water is transformed into polar ice, which is consistent with the recent research.[1]

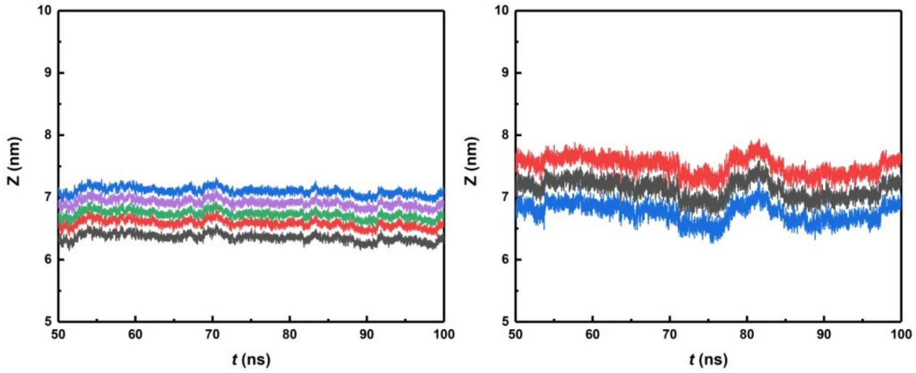
S. Ⅱ Motions z(t) of individual molecules inside the carbon nanotube



(a) z(t) of H_2O of ice nanotube for type A. (b) z(t) of N_2 inside the ice nanotube for type A.



(c) z(t) of H_2O of ice nanotube for type B. (d) z(t) of H_2O of the center water chain for type B



(e) z(t) of H_2O of ice nanotube for type C_1. (f) z(t) of N_2 inside the ice nanotube for type C_1.

Fig. S2. Motions z(t) of indivial water molecules and nitrogen molecules shown as colored lines. (a) z coordinates of typical seven water molecules inside the nanotube for type A. (b) z coordinates of typical three nitrogen molecules inside the ice nanotube as a function of time for type A. (c) z coordinates of typical seven water molecules of ice nanotube for type B. (d) z coordinates of typical water molecules of a water chain in the core-sheath ice nanotube for type B. (e) z coordinates of typical water molecules of ice nanotube for type C_1. (f) z coordinates of typical nitrogen molecules inside the ice nanotube for type C_1.

Fig. S2 shows motions z(t) of indivial water molecules and nitrogen molecules. For type A, the water molecules form an octagonal ice nanotube with a nitrogen wire sitting in its core region. From Fig. S2 (a), we can see that water molecules of an ice nanotube, which are bonded each other with hydrogen bonds, are not motionless. They vibrate around their equlibrium positions, which is induced from thermal energy. The ampitudes are typically of the order of 0.1 nm. But, the octagonal ice nanotube can drift slowly along the nanotube axis as a whole due to the fluctations of water molecules outside the carbon nanotube. Similarly, nitrogen molecules vibrate with larger amplitudes. Meanwhile, the nitrogen wire in the core region can move as a whole relative to the ice nanotube. It is very different from the 3D gas hydrate.

For type B, the diffusion coefficent increases abruptly. From Fig. S2(c)-(d), we can see that colored lines disperse slowly. This inidcates that motions of water molecules are not so highly collective. Water molecules exchange takes place occationally between the water chain in core region and the octagonal ice nanotube.

For type C_1, water molecules and nitrogen molecules all vibrate around their equlibrium positions. The drift-like motion of the Q1D hydrate was not observed in our whole simulations for type C_1.

S.Ⅲ Structural difference between type B and type C_1

The structure of type B is similar to that of type C_1, but they are still different. The 2D surface by unwrapping the ice nanotubes of type B is shown in Fig. S3.

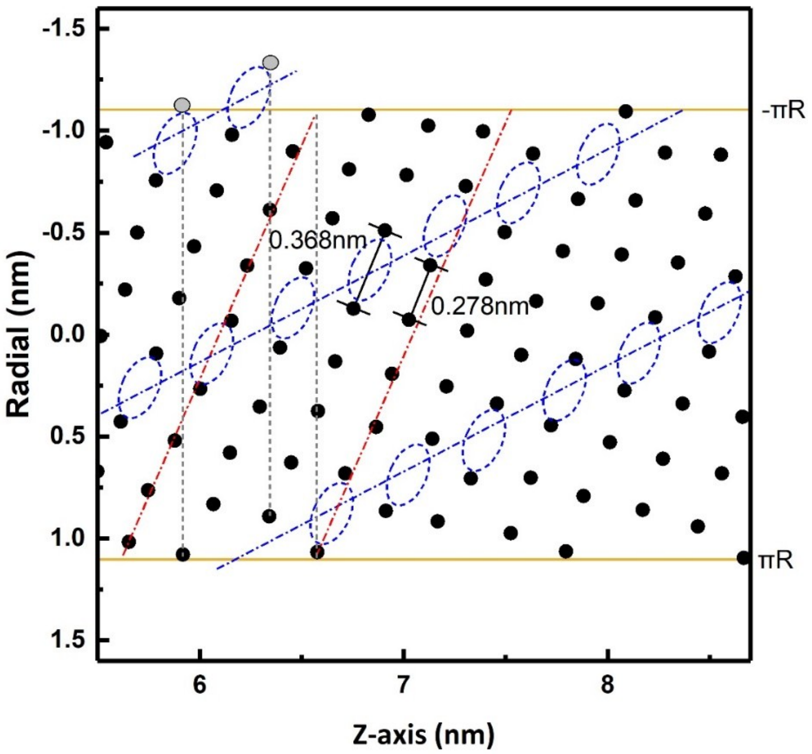


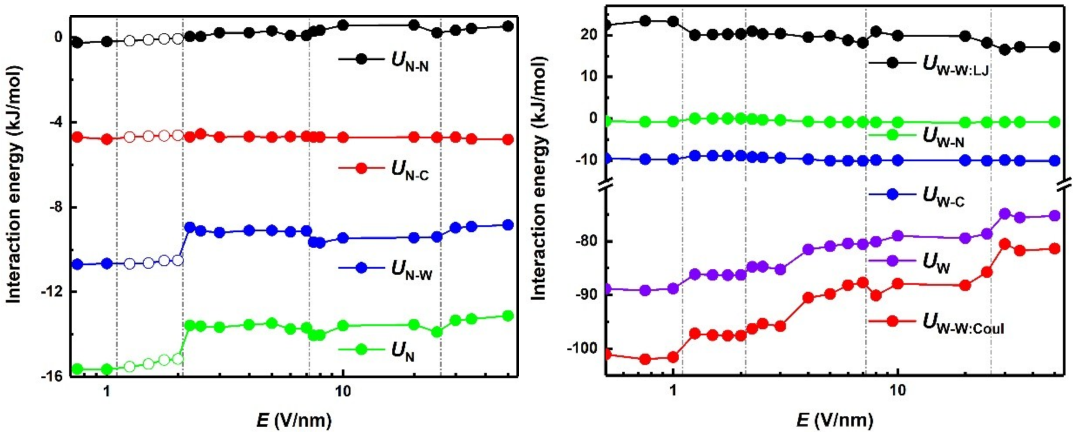
Fig. S3. 2D surface by unwrapping the ice nanotubes of type B.

For type B, there are defects in the helical ice nanotube due to a water chain in the center. Defect is defined as the distance between neighboring water molecules is larger than 0.35 nm (blue dashed ellipse). Generally, distance between two adjacent water molecules is about 0.278 nm in the ice nanotube (INT). The water chain in the center is zigzag. Each water molecule of the zigzag water chain inside the ice nanotube is usually joined to other two water molecules at two sides of the defect by hydrogen bonds resulting in the water chain diverging from the center.

S.Ⅳ Interactions

We have calculated water-water, water-N_2, water-SWNT, N_2-SWNT and water-external field interactions. In Fig. S4 (a), we show the interaction energies per nitrogen molecule inside the SWNT. Note the interaction energies for type B which were calculated before N_2 released from the SWNT (see hollow dots in Fig. S4(a)). With the increase of electric field, N_2-N_2 interaction energy per nitrogen molecule, $U_{N\text{-}N}$, increases slowly and N_2-SWNT interaction energy, $U_{N\text{-}C}$, barely changes. The change of the total interaction energy per nitrogen molecule, U_N, is mainly attributed to the change in N_2-Water ($U_{N\text{-}W}$).

Similarly, from Fig. S4 (b), we can see that Water-N_2 ($U_{W\text{-}N}$) and Water-SWNT ($U_{W\text{-}C}$) interaction energies per water molecule barely change as well. However the Water-Water Coulomb interaction energy, $U_{W\text{-}W:Coul}$, significantly increases and Water-Water LJ interaction energy, $U_{W\text{-}W:LJ}$, decreases slightly. Thus, the interaction energy change of water molecules inside the SWNT and water-electric field interactions play a key role in structure transition from type A to type B.



(a) (b)

Fig. S4. (a) Average N_2-N_2, N_2-SWNT, N_2-Water interactions and the total interaction energy for nitrogen molecules inside SWNT (b) Average Water-Water (LJ and Coulomb included), Water-SWNT, Water-N_2 interactions and the total interaction energy for water molecules inside SWNT.

1. Zhu, W.; Huang, Y.; Zhu, C.; Wu, H.-H.; Wang, L.; Bai, J.; Yang, J.; Francisco, J. S.; Zhao, J.; Yuan, L.-F. *Nat. Commun.* **2019,** 10, (1), 1-7.