Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information:

Separation of Water–Ethanol Solution with Carbon Nanotubes and Electric Fields

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1. Separation effect for TIP4P water–ethanol solution

To clarify the effect of water molecule model on the separation, we performed simulation with (8,8) CNT and filled the reservoirs with TIP4P water–ethanol solution. Mole fraction of water (χ_{TIP4P}) in the reservoirs was 0.19 (the numbers of molecules in each reservoir were N_{TIP4P} = 964 and $N_{ethanol}$ = 4000). Table S1 shows χ_{TIP4P} in the (8,8) CNT. At 0 V/nm, χ_{TIP4P} in CNT is lower than that in the reservoir, which means ethanol prefer to fill the CNT. At 0.25 V/nm, χ_{TIP4P} in CNT increases to 0.66 ± 0.08. With $E \geq 0.5$ V/nm, only water molecules occupy in the CNT (χ_{TIP4P} = 1 in the CNT). Under an electric field, TIP4P water prefers to fill CNT over ethanol, resulting in a separation effect. This result is same as when the reservoirs are filled with SPC water–ethanol solution. Moreover, TIP4P water in the CNT also forms a helical structure as shown in Figure S1. Therefore, this suggests that the separation effect with CNTs and an electric field is little dependent on the choice of water molecule model.

Table S1 Mole fractions of TIP4P water (χ_{TIP4P}) in (8,8) CNT (with standard deviation) for χ_{TIP4P} = 0.19 in the reservoirs.

E [V/nm]	χ_{TIP4P} in CNT
0	0.04 ± 0.06
0.25	0.66 ± 0.08
0.50	1.00
1.00	1.00
2.00	1.00

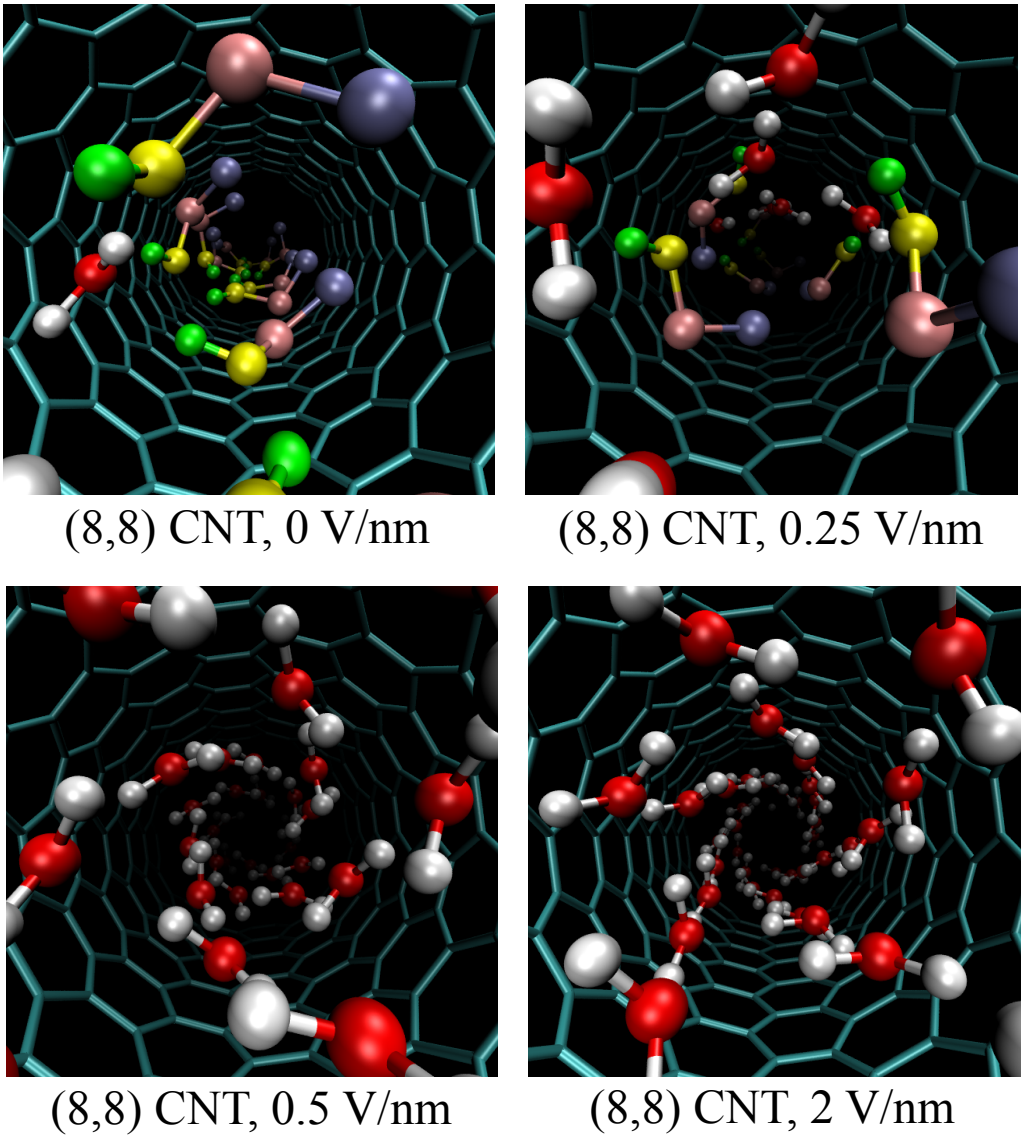

Figure S1 Snapshots of molecules in (8,8) CNT under 0, 0.25, 0.5, and 2 V/nm of electric field. The reservoirs were filled with TIP4P water–ethanol solution for the concentration χ_{TIP4P} = 0.19. Green, yellow, pink, and blue atoms represent hydrogen, oxygen, methylene, and methyl of ethanol molecules, respectively. Red and white atoms represent oxygen and hydrogen of TIP4P water molecules, respectively. At $E \geq 0.5$ V/nm, only TIP4P water molecules occupy the CNT and they form an ordered (helical) structure.

2. Structures of water molecules in (20,20), (25,25), and (30,30) CNTs

Figure S2 shows structures of water molecules in (20,20), (25,25), and (30,30) CNTs at 1 V/nm and 2 V/nm for χ_{water}= 0.81 in the reservoirs. Under these conditions, only water molecules occupy in the CNTs (χ_{water} = 1 in the CNT). We calculated hydrogen bond (HB) autocorrelation function to investigate the dynamics of HBs in the water structures, [1, 2]

$$C_{HB}(t) = \frac{\langle h(0)h(t)\rangle}{\langle h^2\rangle}$$

where $h(t)$ = 1 if a pair of molecules is bonded at time t and $h(t)$ = 0 otherwise. The denominator $\langle h^2\rangle$ is for normalization and is the number of HBs tagged at t = 0. HBs between water molecules in the CNTs are obtained with the following geometrical conditions: R_{OO} < 0.36 nm, R_{OH} < 0.24 nm, and angle of HO---O < 30°.[3, 4] Figure S3 shows the HB autocorrelation function ($C_{HB}(t)$) of water structures in (20,20), (25,25), and (30,30) CNTs at 1 V/nm and 2 V/nm. The $C_{HB}(t)$ of water molecules in (25,25) CNT is higher than that in (20,20) and (30,30) CNTs. This implies that under an electric field, the lifetime of HBs within the water structure in (25,25) CNT is longer than that in (20,20) and (30,30) CNTs. This means the water structure in (25,25) CNT is stronger than that in (20,20) and (30,30) CNTs. This result confirms that the separation effect with (25,25) CNT is stronger than that with (20,20) and (30,30) CNTs.

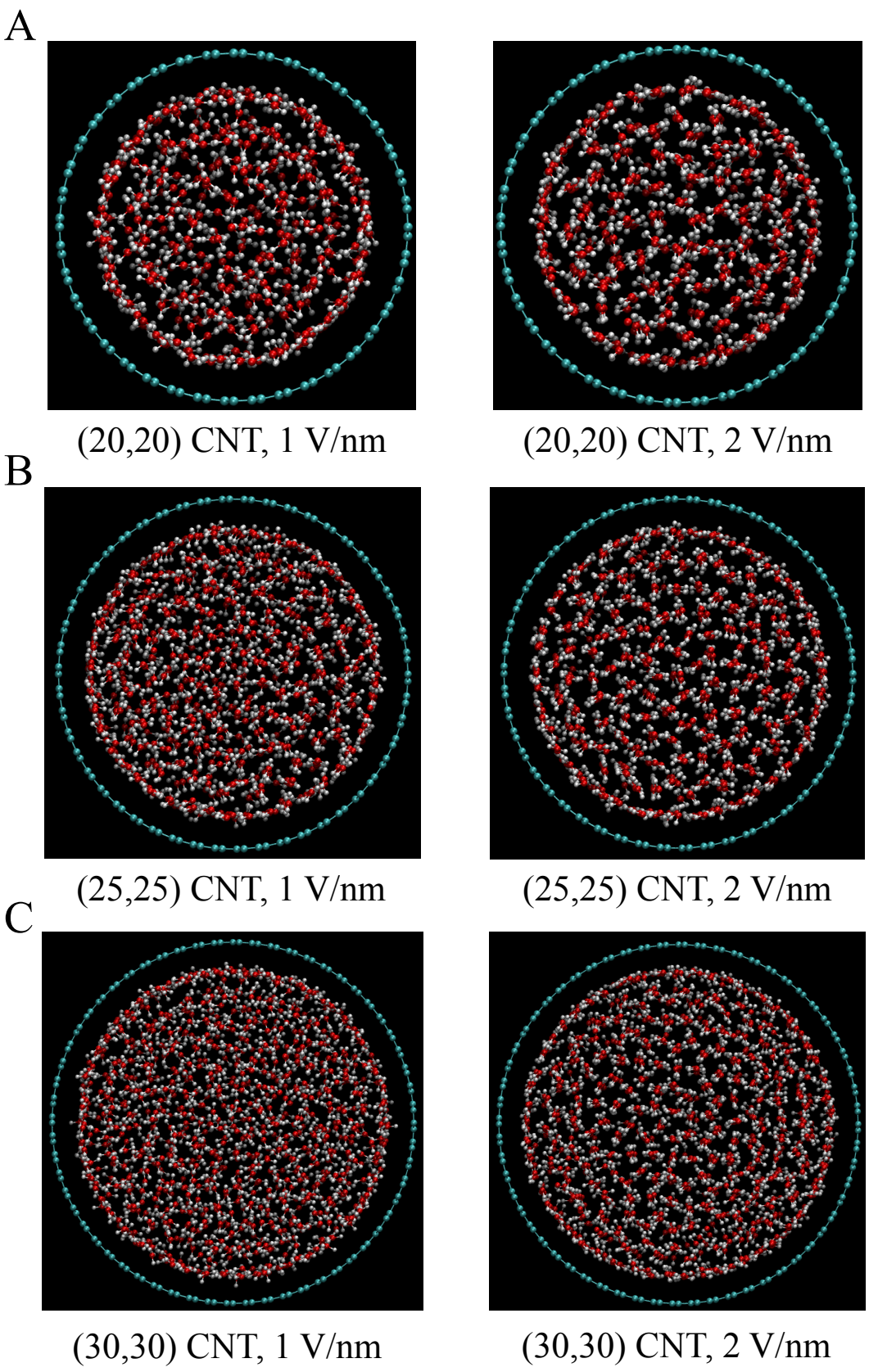

Figure S2 Snapshots of water molecules structures in CNTs at 1 V/nm and 2 V/nm of electric fields and χ_{water} = 0.81 in reservoirs. (A) in (20,20) CNT, (B) in (25,25) CNT, and (C) in (30,30) CNT.

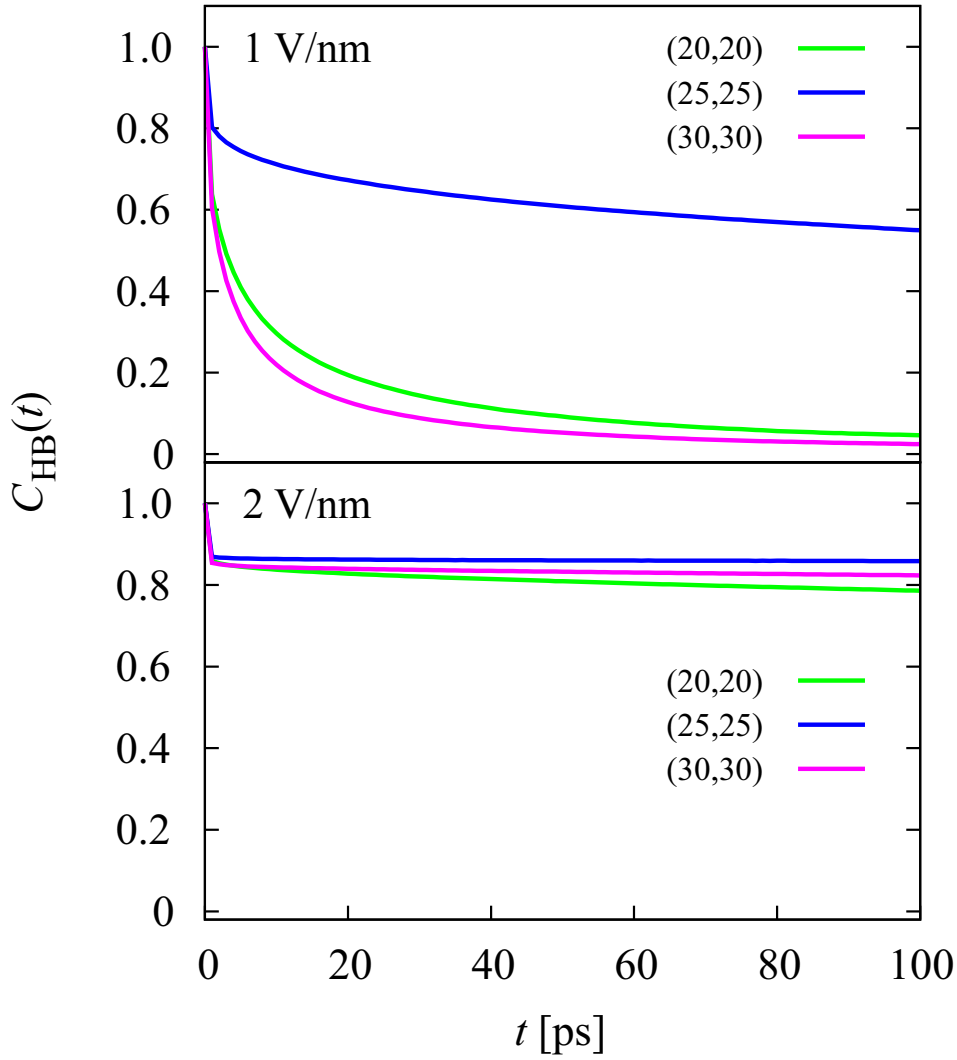

Figure S3 Hydrogen bond (HB) autocorrelation function of water molecules in (20,20), (25,25), and (30,30) CNTs at 1 V/nm (top) and 2 V/nm (bottom). The lifetime of HBs of water molecules in (25,25) CNT is longer than that in (20,20) and (30,30) CNTs. This indicate the water structure in (25,25) CNT under an electric field is stronger than that in (20,20) and (30,30) CNTs.

References

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