Supplementary Information:

Water-methanol separation with carbon nanotubes and electric fields

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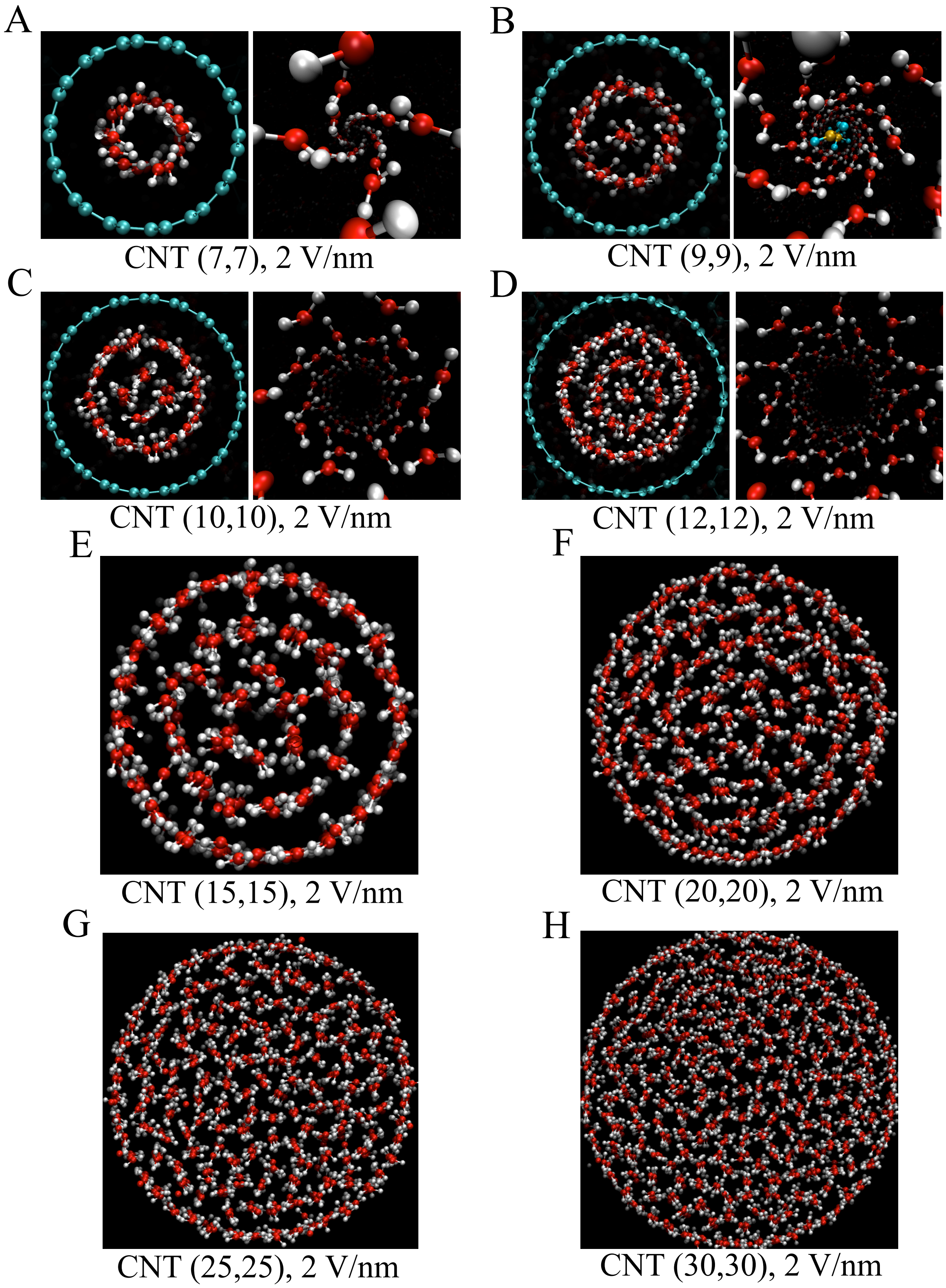
1. Molecules structures in carbon nanotubes

Figure S1 shows snapshots of water molecules structures in CNT (7,7) to (30,30) with 2 V/nm. The structures are helical for CNT (7,7) to (9,9). For the larger CNTs, water molecules have multi-walls structures and they tend having non-helical structures, such as in CNT (10,10) and (12,12).



CNT (7,7), 2 V/nm

CNT (9,9), 2 V/nm

CNT (10,10), 2 V/nm

CNT (12,12), 2 V/nm

CNT (15,15), 2 V/nm

CNT (20,20), 2 V/nm

CNT (25,25), 2 V/nm

CNT (30,30), 2 V/nm

Figure S1: Snapshots of water molecules in CNTs under 2 V/nm of electric filed. The simulation condition is $\chi_{\mathrm{water}} = 0.81$ in reservoirs. (A) in CNT (7,7) with orthographic and perspective projections for the left and the right figures, respectively. Water molecules form helical structure. (B) in CNT (9,9), water molecules have outer and inner structures. The outer structure is helical and the inner one is single-file structure as shown with orange and blue colors in the right figure. (C) in CNT (10,10), water molecules form double-walls structure. The outer structure is not helical (the right figure). (D) in CNT (12,12), the outer structure is not helical (the right figure). (E) to (H) in CNT (15,15), (20,20), (25,25) and (30,30), respectively. Water molecules form multi-walls structures.

Figure S2 shows radial density distribution of water and methanol molecules in CNT (8,8) with 0 V/nm, where mole fraction of water molecules χ_{water} in the CNT is 0.2. Water and methanol molecules are concentrated at a narrow region in the radial direction as confirmed by the snapshot in the Figure S2-B.

With 0.5 V/nm or stronger fields, χ_{water} in the CNT (8,8) is 1.0, that means only water molecules occupy in the CNT. With an increase of the electric field, the peak width of the radial density becomes narrower and shifted from the CNT axis as shown in Figure S3-A, B for 0.5- and 2 V/nm, respectively. Thus, water molecules form tube-like structures as shown by the snapshots.

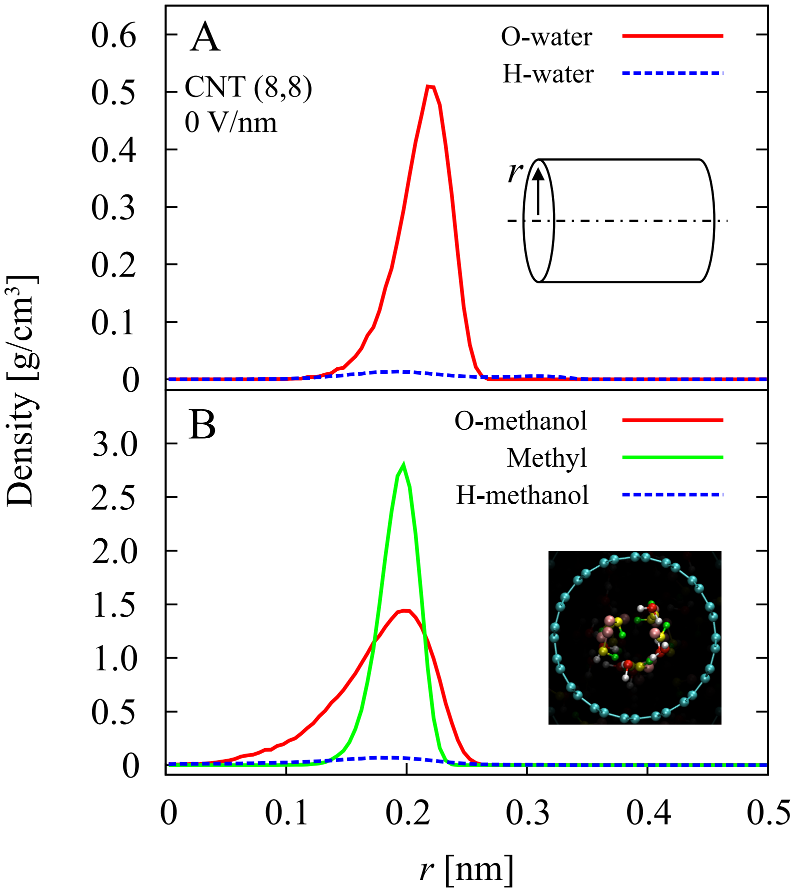


Figure S2: Radial density distribution of atoms in CNT (8,8) with 0 V/nm, (A) for water molecules, and (B) for methanol molecules. Simulation was performed with $\chi_{\mathrm{water}} = 0.81$ in reservoirs. Snapshot in figure B shows structure of water and methanol molecules in the CNT.

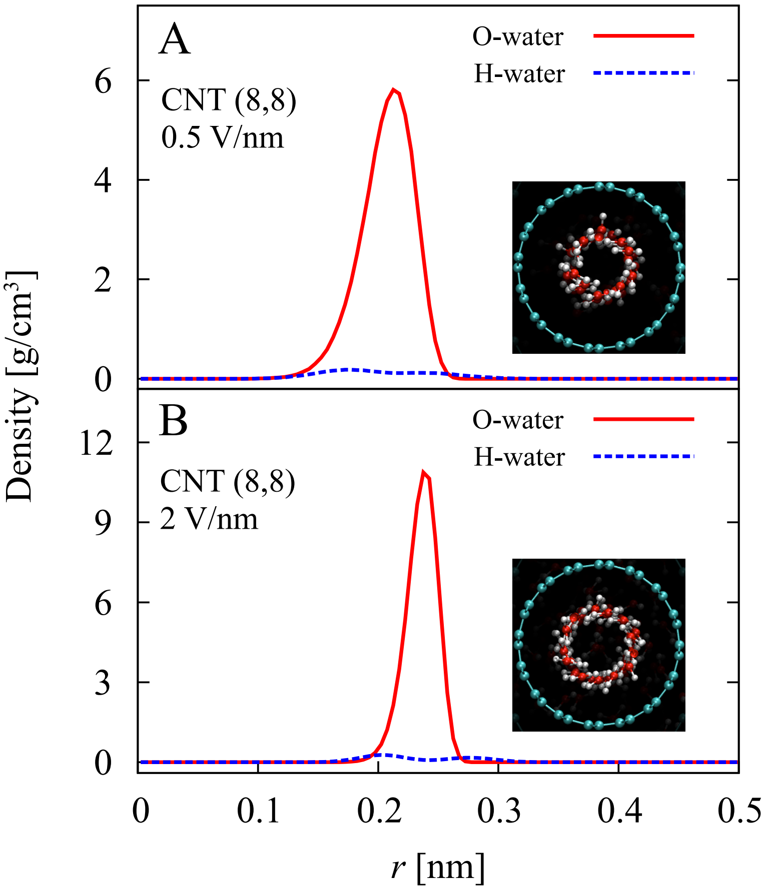
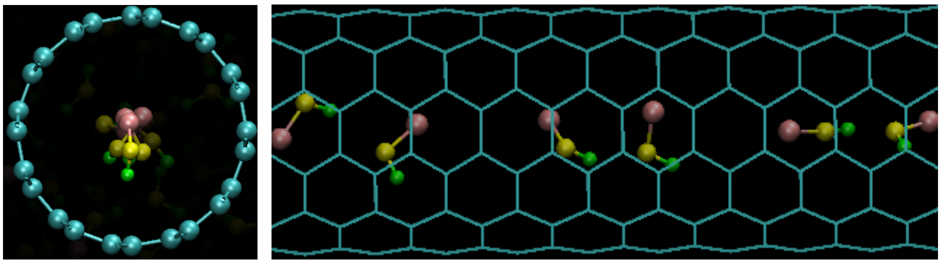


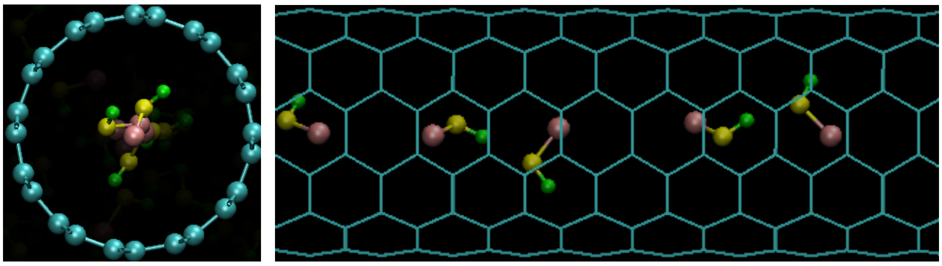
Figure S3: Radial density distribution of water molecules in CNT (8,8), (A) with 0.5 V/nm, and (B) with 2 V/nm. χ_{water} in reservoirs was set to 0.81.

Figure S4 represents the molecules structures in CNT (6,6). With 0 to 0.5 V/nm, methanol molecules prefer to occupy in the CNT where their structure is single-file. With an increase of the electric field, 1 V/nm or stronger fields, water molecules prefer to fill in the CNT instead of the methanol molecules. Under this field, the water molecules form zig-zag structures where every molecule is bonded to each other by hydrogen bond. It makes the water molecules structure more stable.

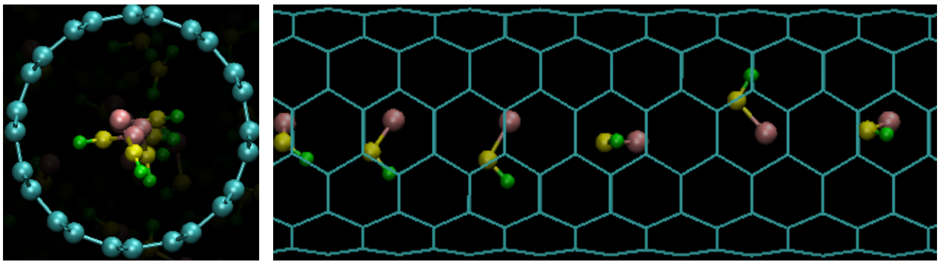
CNT (6,6), 0 V/nm



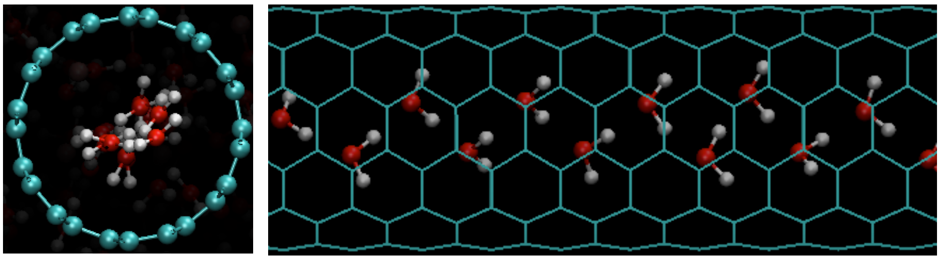
CNT (6,6), 0.25 V/nm



CNT (6,6), 0.5 V/nm



CNT (6,6), 1 V/nm



CNT (6,6), 2 V/nm

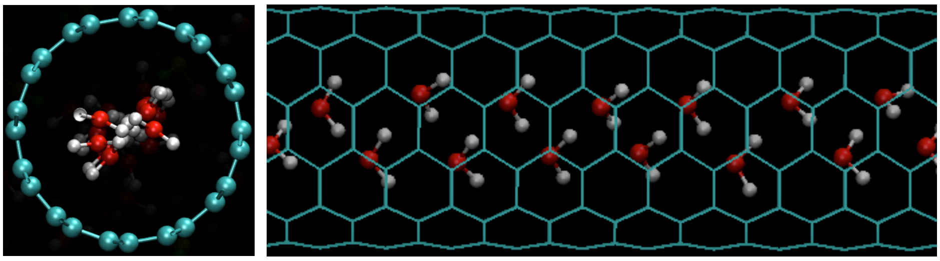


Figure S4: Structures of molecules in CNT (6,6), with 0, 0.25, 0.5, 1, and 2 V/nm. Methanol molecules are represented with yellow, green, and pink for oxygen, hydrogen, and methyl, respectively. Water molecules are red and white for oxygen and hydrogen. With 1 and 2 V/nm, water molecules prefer to fill the CNT and they form zig-zag single-file structure. Simulation condition was set to $\chi_{water} = 0.81$ in the reservoirs.

2. Water molecules *vs.* methanol molecules in carbon nanotubes under electric field

To compare effect of axial electric field on the water molecules and methanol molecules in carbon nanotubes (CNTs), we performed simulations by filling the reservoir with water molecules only (water-CNT-graphene system) and methanol molecules only (methanol-CNT-graphene system). Then, we compared the dipole moment orientation, occupancy of molecules in CNTs, potential energies, structures, and hydrogen bond network. Dipole moment orientation, occupancy, and structures for the water molecules have been reported in our previous study [1].

2.1 Orientation of dipole moment

Figure S5 shows direction of dipole moment for methanol molecules in CNT (6,6) and (8,8) with 0, 1, and 2 V/nm. The direction of dipole moment is represented with angle α, which is the angle between the dipole moment μ and electric field E. The vertical axis denotes probability distribution function (pdf). With 0 V/nm, the peaks are at $\cos \alpha = -1$ and 1 for CNT (6,6) and −0.8 and 0.8 for CNT (8,8). Those mean the dipole moment of methanol molecules in CNTs has two orientations that are opposite to each other. With the electric field, the peak of $\cos \alpha$ is shifted to 1 implying the direction of the dipole moment tends to be parallel to that of the field. It is same as for water molecules where the electric field aligns the dipole moment direction parallel to the field.

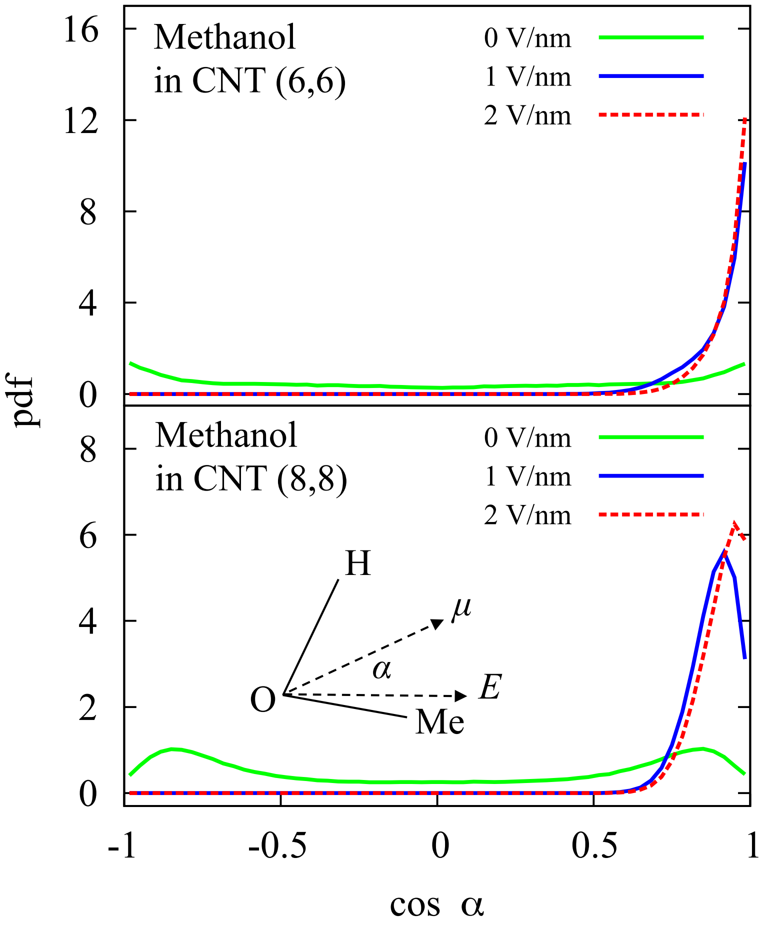


Figure S5: Effect of electric field on the dipole moment orientation of methanol molecules in CNT (6,6) and (8,8). Direction of dipole moment is indicated with angle α, which is the angle between the dipole moment μ and electric field E. O, H, and Me represent oxygen, hydrogen, and methyl, respectively. The vertical axis shows probability distribution function (pdf). Under the field, direction of dipole moment tends to be parallel to that of the field.

2.2 Occupancy of molecules in CNTs

The numbers of methanol molecules inside CNTs are shown in Table S1. Same as for the water molecules, the occupancy of methanol molecules in the CNTs increases with the electric field. Although the number of methanol molecules in the CNTs decreases slightly from 1 to 2 V/nm, but it is still larger than that with 0 V/nm. Hence, same as to the water molecules, electric field makes methanol molecules prefer to fill into CNTs.

Table SI: Average numbers of methanol molecules in CNTs. (with standard deviation)

E [V/nm]	CNT (6,6)	CNT (8,8)
0	6.4 ± 0.5	16.7 ± 1.1
1	7.0 ± 0.4	19.7 ± 0.7
2	6.7 ± 0.5	19.3 ± 0.7

2.3 Potential energies

2.3.1 Lennard-Jones potential energy

To compare effect of CNT wall on the water and methanol molecules, we calculated Lennard-Jones (LJ) potential energy per molecules in the reservoir and in the CNT (8,8). Distributions of the LJ potential energy for water and methanol molecules with 0 and 2 V/nm are shown in Figure S6-A and B, respectively. Difference of LJ potential energy in the CNT and in the reservoir ($\Delta U_{\mathrm{LJ}} = U_{\mathrm{CNT}} - U_{\mathrm{res}}$) indicates van der Waals interaction of water-CNT and methanol-CNT (see Table S2, S3). With 0 V/nm, ΔU_{LJ} for water molecules is higher than that for methanol molecules, which are −10.37 kJ/mol and −18.23 kJ/mol, respectively. This means that van der Waals attraction for methanol-CNT is stronger than that for water-CNT. With 2 V/nm, ΔU_{LJ} for methanol and water molecules are −12.87 kJ/mol and 6.29 kJ/mol, respectively. This means that attraction of methanol-CNT decreases slightly with the field. In contrast, with 2 V/nm, ΔU_{LJ} for water becomes positive denoting repulsive interaction between water and CNT. Thus, we can conclude that the preferential occupancy of water molecules over methanol molecules in the CNT with electric field is not due to the van der Waals interaction between water and CNT. The result suggests that electrostatic interaction (hydrogen bond network) in the water structure is a key factor for the separation effect with electric field.

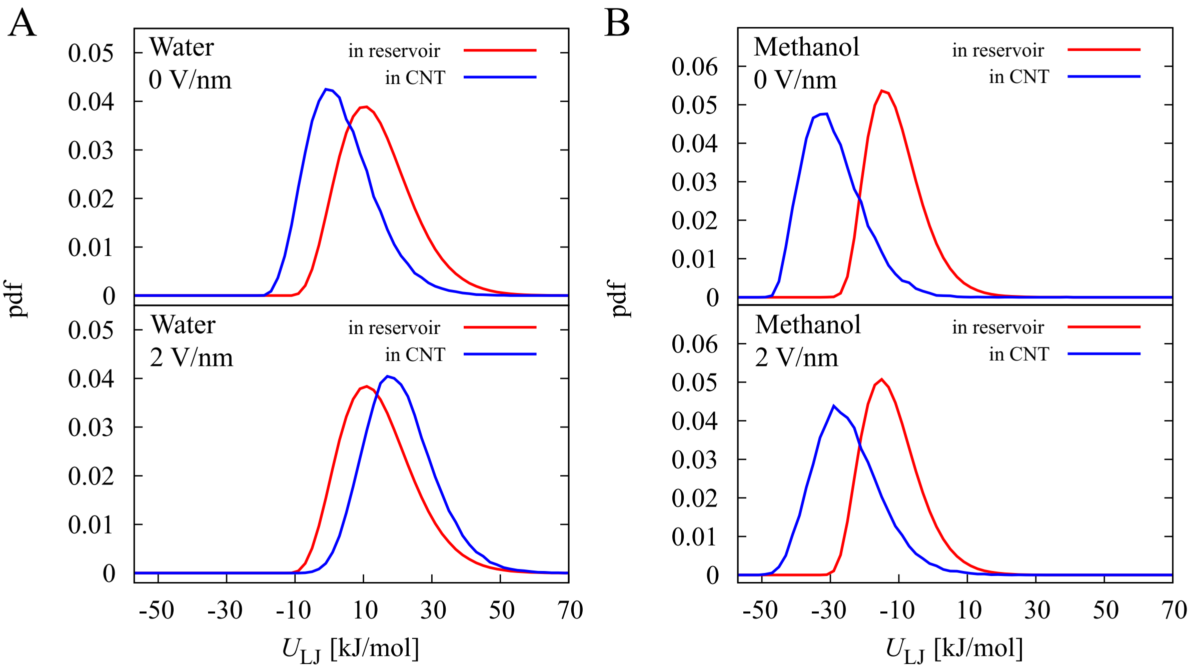


Figure S6: Distribution of Lennard-Jones (LJ) potential energy for molecules in the reservoir and in the CNT (8,8) with 0 and 2 V/nm; (A) for water molecules, and (B) for methanol molecules. Difference of LJ potential energy in the reservoir and in the CNT indicates van der Waals interaction of water-CNT and methanol-CNT. The difference of LJ potential in CNT and in reservoir (ΔU_{LJ}

$=U_{\mathrm{CNT}} - U_{\mathrm{res}}$) for methanol is lower than that for water. This implies that van der Waals attraction of methanol-CNT is stronger than that of water-CNT.

2.3.2 Coulomb potential energy

Figure S7-A, B show distribution of coulomb potential energy in reservoir and in CNT (8,8) for water and methanol molecules, respectively. Coulomb potential energy for water and methanol in CNT decreases significantly with the electric field. Difference of coulomb potential energy in the CNT and in the reservoir ($\Delta U_{\mathrm{coul}} = U_{\mathrm{CNT}} - U_{\mathrm{res}}$) for water decreases from 12.13 kJ/mol to −31.55 kJ/mol with 0 and 2 V/nm, respectively (Table S2). ΔU_{coul} for methanol decreases as well from 7.51 kJ/mol to −17.97 kJ/mol with 0 and 2 V/nm, respectively (Table S3). Those results reveal that under electric field, electrostatic interaction within structures of molecules in CNT facilitates water and methanol molecules filling CNT.

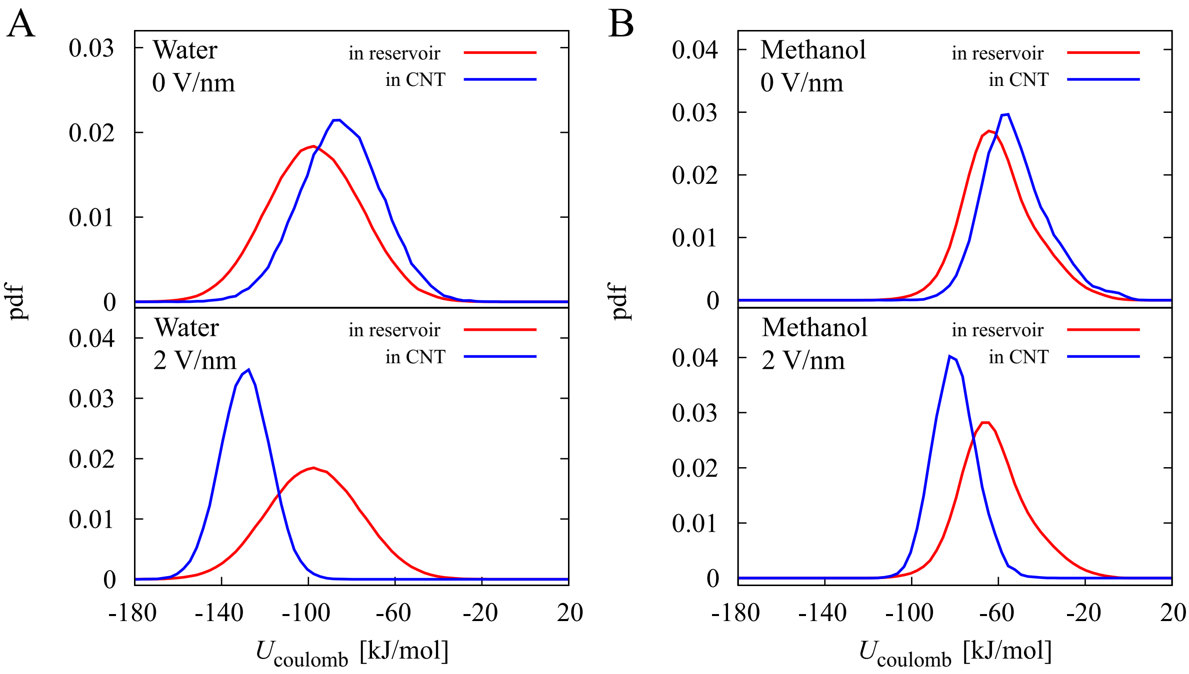


Figure S7: Distribution of coulomb potential energy for molecules in the reservoir and in the CNT (8,8) with 0 and 2 V/nm; (A) for water molecules, and (B) for methanol molecules. With electric field, coulomb potential energy in CNT decreases significantly both for water and methanol. This means that under electric field, the coulomb potential energy drives water and methanol to fill in the CNT.

2.3.3 Dipole potential energy

When a dipole is subjected to external electric field, it has the following potential energy

$$U_{dipole} = -\vec{\mu} \cdot \vec{E} \qquad (1)$$

where $\vec{\mu}$ is vector of dipole moment and $\vec{E}$ is the electric field. Thus, U_{dipole} will be minimum when the direction of dipole moment is parallel to that of the electric field. Figure S8-A, B show distribution of U_{dipole} in the reservoir and in the CNT (8,8) under 2 V/nm for water and methanol molecules, respectively. Distribution of U_{dipole} in the reservoir is broader than in the CNT. It is because direction of a dipole moment under electric field is not statically parallel to the field but it oscillates around the direction of the field. Amplitude of the oscillation for molecules in the reservoir is larger than that of in the CNT. This is due to the effective electric field working in the reservoir is lower than that in the CNT. As we have discussed in our previous study that graphene sheet induces polarization [1]. This means that the polarization induces internal electric field in the direction opposite to the external electric field. Thus, the effective electric field in the reservoir is the external field subtracted by the internal field. Distribution of dipole potential energy in the reservoir for methanol decays faster than that for water (Figure S8-B). It indicates that internal electric field due to the polarization for methanol is lower than that for water. Dipole moment of methanol is lower than that of water, which are 2.22 D and 2.27 D, respectively. That makes charge density for methanol is lower than that for water. As a result, effect of polarization for methanol is weaker.

Because peaks of U_{dipole} distribution in CNT are narrower than those in reservoir, the averages of dipole potential energy in the CNT are lower than those in the reservoir. As a result, differences of dipole potential energy in CNT and in the reservoir ($\Delta U_{\mathrm{dipole}}$) for water and methanol molecules are negative, which are −5.06 kJ/mol and −1.30 kJ/mol, respectively (Table S2, S3). This means the dipole potential energy helps water and methanol molecules to fill CNT.

Total of ΔU per molecule in Table S2 and S3 decreases with electric field. For water, total of ΔU per molecule decreases from 1.76 kJ/mol to −30.32 kJ/mol with 0 and 2 V/nm, respectively. For methanol, those values are −10.72 kJ/mol to −32.14 kJ/mol with 0 and 2 V/nm, respectively. Decreasing of total ΔU per molecule support the notion that under the electric field, water and methanol molecules prefer to fill CNT. Those results confirm the occupancy data where the number of molecules in CNTs increases with electric field.

From the occupancy data, we determined the ratios of the number of water molecules to the number of methanol molecules in CNT (8,8). Those values are 2.15 and 2.57 with 0 and 2 V/nm, respectively. Thus, with 0 V/nm, ΔUs for all molecules in CNT (8,8) are 3.78 kJ/mol and −10.72 kJ/mol for water and methanol, respectively. The ΔU for methanol is lower than that for water. It suggests that methanol molecules prefer to fill in the CNT over water molecules. With 2 V/nm, those values are −77.92 kJ/mol and −32.14 kJ/mol for water and methanol, respectively. The ΔU for water is much lower than that for methanol. It suggests that water molecules strongly prefer to occupy in the CNT over methanol molecules.

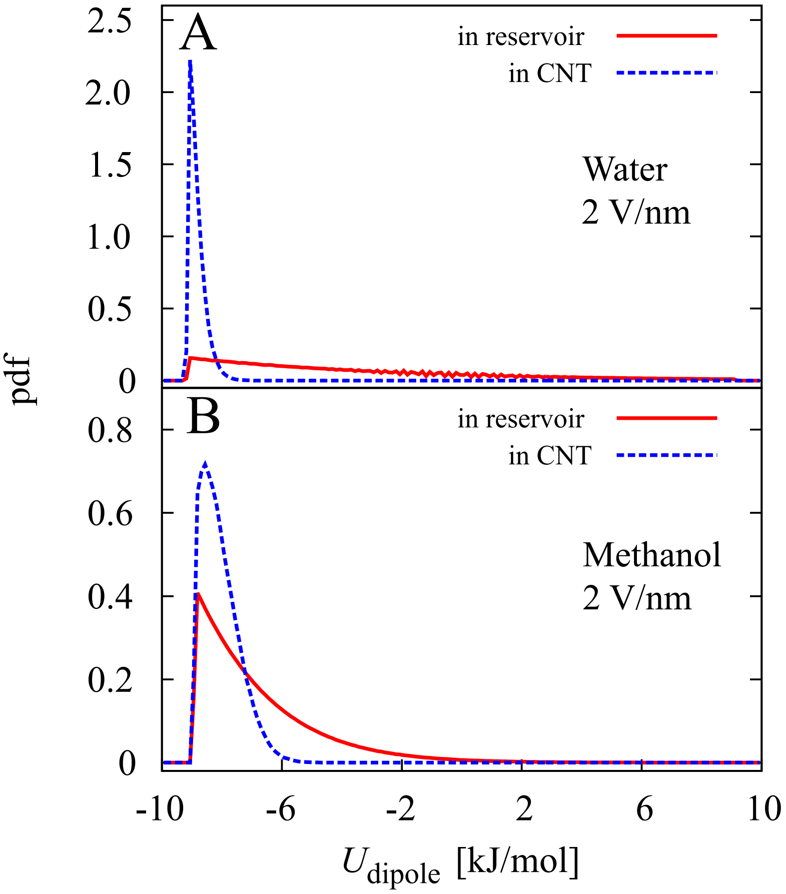


Figure S8: Distribution of dipole potential energy for molecules in the reservoir and in the CNT (8,8) with 2 V/nm; (A) for water molecules, and (B) for methanol molecules.

Table S2: Average potential energies per molecule in reservoir and in CNT (8,8) for water. ΔU is the difference between potential energy in CNT (U_{CNT}) and in reservoir (U_{res}).

E [V/nm]	Energy (U)	in reservoir [kJ/mol]	in CNT [kJ/mol]	$\Delta U = U_{\text{CNT}} - U_{\text{res}}$
0	LJ	14.08	3.71	−10.37
	Coulomb	−97.20	−85.07	12.13
			Total :	1.76 [kJ/mol]
2	LJ	14.52	20.81	6.29
	Coulomb	−97.46	−129.01	−31.55
	Dipole	−3.76	−8.82	−5.06
			Total :	−30.32 [kJ/mol]

Table S3: Average potential energies per molecule in reservoir and in CNT (8,8) for methanol. ΔU is the difference between potential energy in CNT (U_{CNT}) and in reservoir (U_{res}).

E [V/nm]	Energy (U)	in reservoir [kJ/mol]	in CNT [kJ/mol]	$\Delta U = U_{\mathrm{CNT}} - U_{\mathrm{res}}$
0	LJ	−10.87	−29.10	−18.23
	Coulomb	−59.68	−52.17	7.51
			Total :	−10.72 [kJ/mol]
2	LJ	−11.93	−24.80	−12.87
	Coulomb	−62.08	−80.05	−17.97
	Dipole	−6.76	−8.06	−1.30
			Total :	−32.14 [kJ/mol]

2.4 Structures and hydrogen bond network

Figure S9 shows structure of methanol molecules in CNT (8,8) with 2 V/nm. The molecules form two line-structures. The methyl groups from each line-structure are close to each other implying that each line-structure is not hydrogen bonded to one another. Similar structure is shown for methanol molecules in CNT (8,8) with 1 V/nm. The structures of methanol molecules differ from those of water molecules, which are helical structures in CNT (8,8) with 1 and 2 V/nm.

For analyzing hydrogen bond (HB), we employed the following geometrical criteria. For water molecules: $R_{\mathrm{OO}} < 0.36$ nm, $R_{\mathrm{OH}} < 0.24$ nm, and angle of HO---O < 30° [2] and for methanol molecules: $R_{\mathrm{OO}} < 0.35$ nm, $R_{\mathrm{OH}} < 0.26$ nm, and angle of HO---O < 30° [3]. Average numbers of HB per molecule for water in CNT (8,8) are 2.84, 2.93 and 2.77 with 0, 1 and 2 V/nm, respectively. Those for methanol in CNT (8,8) are 1.70, 1.89 and 1.83 with 0, 1 and 2 V/nm, respectively. Because the methyls cannot form HB, the number of HB of methanol is lower than that of water. Electric field does not affect the number of HB per molecules significantly both for water and methanol molecules. However, the field makes lifetime of HBs in the water structure becomes very long. The electric field strengthens the HBs in the water structure [1]. We determined dynamics of HBs with the HB autocorrelation function [4]:

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

where $h(t)$=1 if a pair of molecules is bonded at time t and $h(t)$=0 otherwise. The denominator $\langle h \rangle$ is for normalization, which is the number of HBs tagged at t=0. Same as to the water molecules, HB autocorrelation function for methanol with electric field slightly decreases and then constant (Figure S10). It indicates that the lifetime of HBs is very long. The field strengthens HBs of methanol structure in CNT as well.

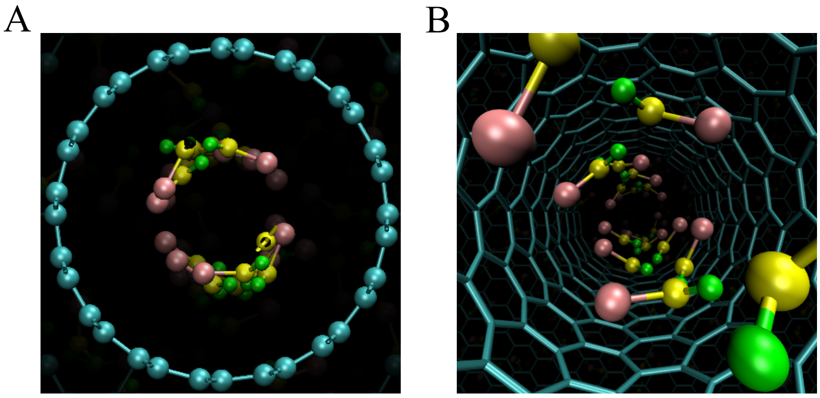


Figure S9: Structure of methanol molecules in CNT (8,8) with 2 V/nm. The molecules form two line-structures where the methyl groups from each line-structure are close to each other. This indicates that each line-structure is not hydrogen bonded to one another.

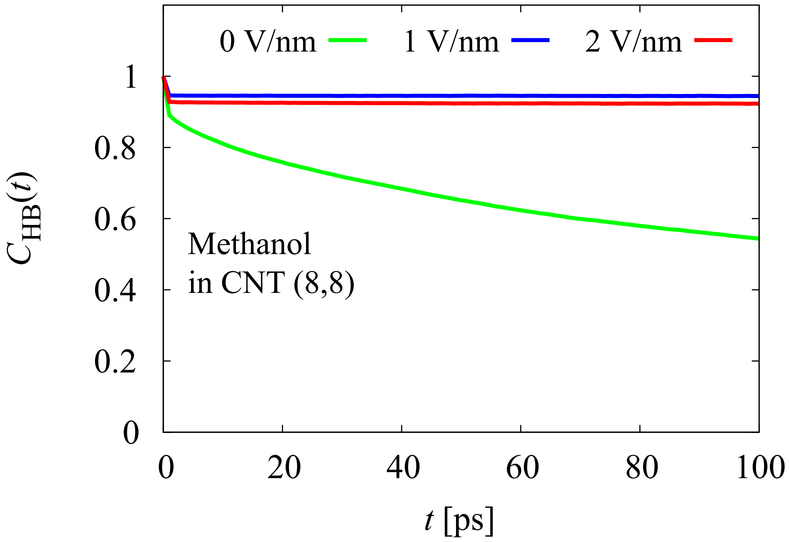


Figure S10: HB autocorrelation function for methanol molecules in CNT (8,8) under 0, 1, and 2 V/nm. With the electric field, the lifetime of HBs of methanol molecules is very long.

To clarify the HB network in the water and methanol structures, we calculated distribution of HB direction. The pairs of molecules bonded with HB were determined from the three-dimensional (3D) structures. Then, the structures were unrolled to obtained 2D structures as shown in Figure S11-A and B for water and methanol molecules in CNT (8,8) with 2 V/nm, respectively. Direction of HB in 2D structure is indicated with angle α, which is measured from the z-axis to the clockwise direction. As an example, for the molecule i-th in Figures S11-A, we identified all HBs from the i-th to all other molecules at $z \geq 0$. Position of the chosen molecules i-th was set to $z = 0$ at the time, and i-th was applied all molecules in the CNT. We calculated from 22 ns of simulation time. The result is shown in Figure S11-C for water (red line) and methanol (dotted blue-line). There are two main-peaks at $\alpha_{w1} = 23^\circ$, $\alpha_{w2} = 303^\circ$, and a low peak at $\alpha_{w3} = 75^\circ$ for HBs in water molecules structure. The angle α_{w1} and α_{w2} are related to the column direction (magenta dashed-line) and the row direction (green dashed-line). That means the HB network is composed of a group of parallel lines in the column direction and a group of parallel lines in the row direction. In other word, water molecules structure consists of some line-structures that are hydrogen bonded to each other such as a net structure. In addition, few molecules make HB in the direction of α_{w3} (orange arrow-line). The 2D structure in Figure S11-B confirms the explanation before that methanol molecules have two line-structures. There are two peaks of HB direction, which are at $\alpha_{m1} = 25^\circ$ and $\alpha_{m2} = 334^\circ$ (Figure S11-C). The angle α_{m1} and α_{m2} are related to the directions of magenta line and green line (Figure S11-B), respectively. There are two directions of HB within a line-structure because methanol molecules form zig-zag configuration. There is no hydrogen bond from a line-structure to the other line-structure. Hence, the two line-structures are independent. They are not hydrogen bonded to each other. Consequently, the methanol structure in the CNT is weaker than the water structure. With 2 V/nm, ΔU of coulomb potential energy per molecule for water molecules is lower than that for methanol molecules, which are −31.55 kJ/mol and −17.97 kJ/mol, respectively (Table S2, S3). Those data indicate that electrostatic interaction in the water structure is stronger than that in the methanol structure.

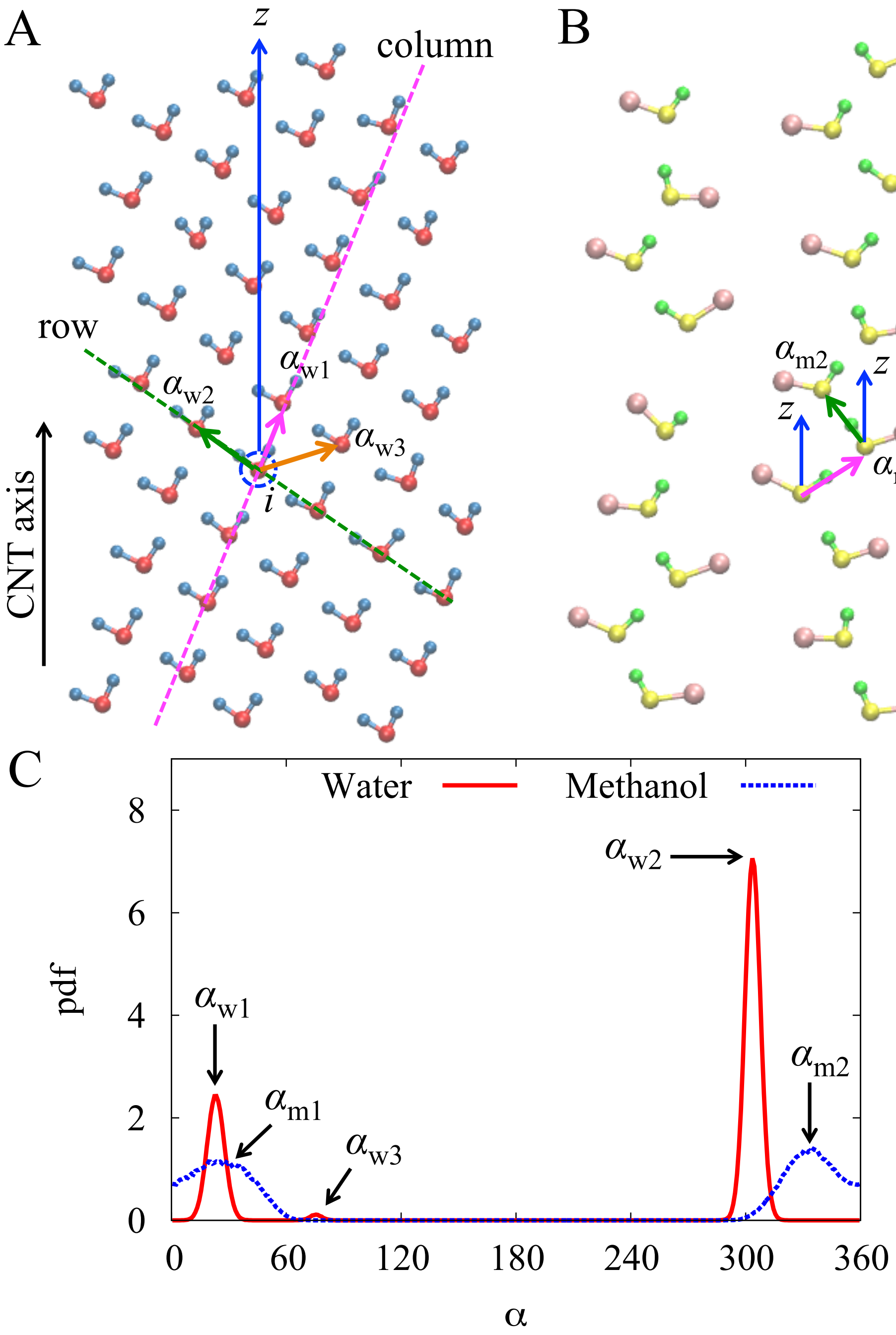


Figure S11: (A) Two-dimensional (2D) structure of water molecules in CNT (8,8) with 2 V/nm. (B) 2D structure of methanol molecules in CNT (8,8) with 2 V/nm. (C) Distribution of hydrogen bond direction in the water and the methanol structures. The direction is indicated with angle α, which is measured from the z-axis to the clockwise direction.

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