Supporting Information for

Atomic Insight into the Interfacial Effect on the Molecular Solvation

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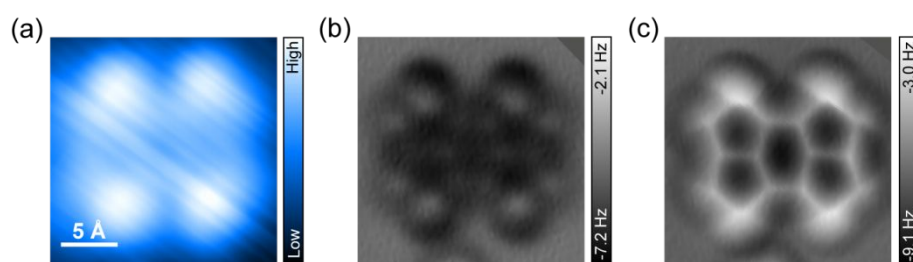
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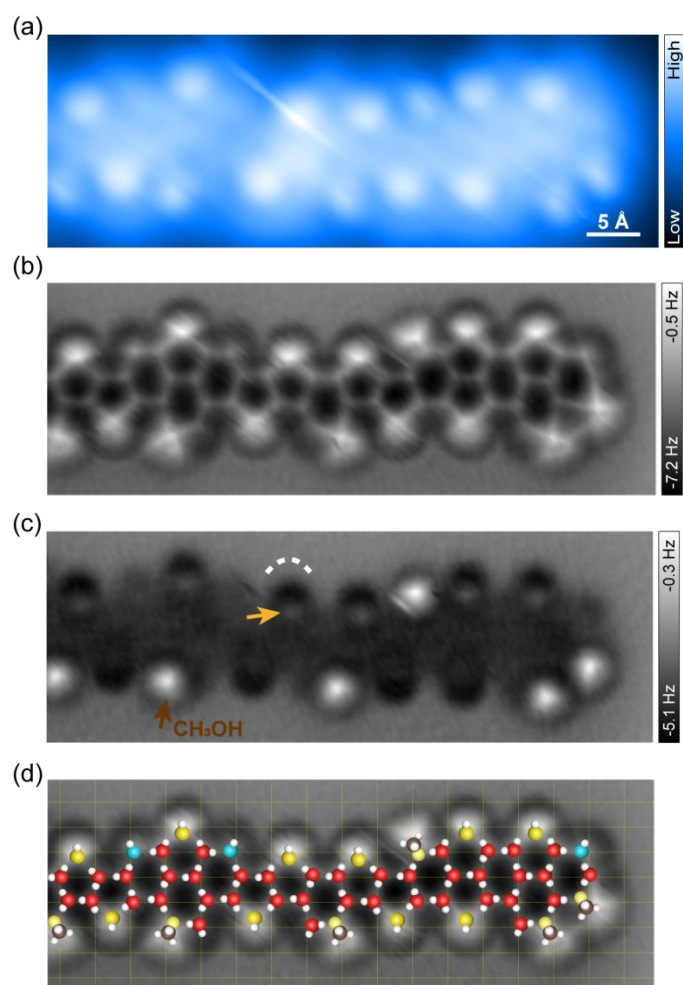[e]*Interdisciplinary Institute of Light-Element Quantum Materials and Research Center for Light-Element Advanced Materials, Peking University, Beijing, 100871, China*

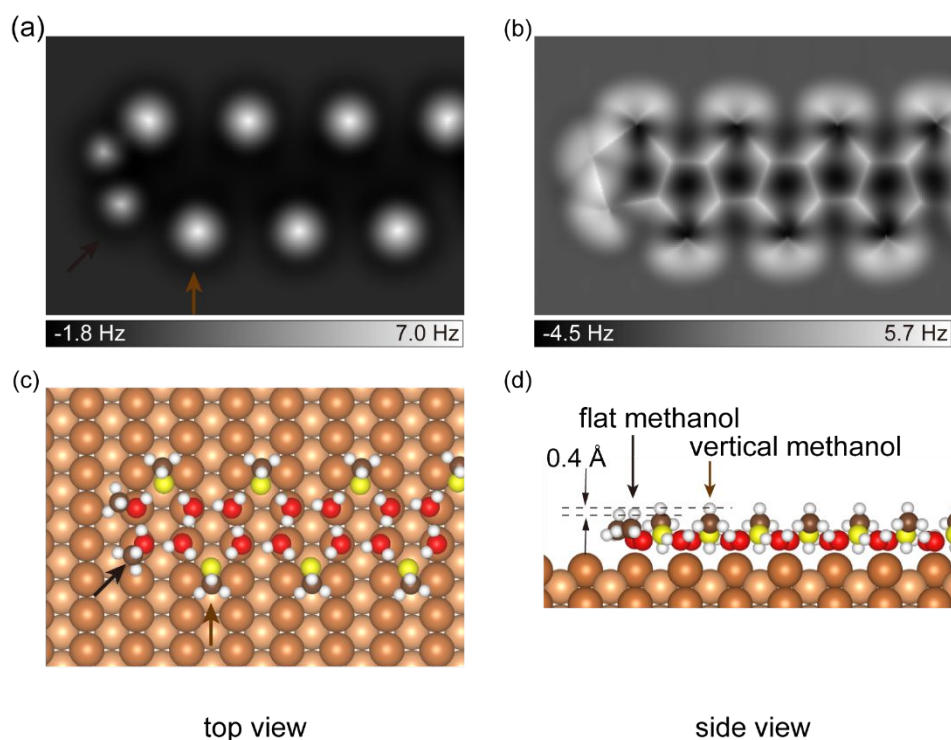[*] Corresponding authors. Email: dycao@bit.edu.cn (D. C.); jguo1294@bnu.edu.cn (J. G.)

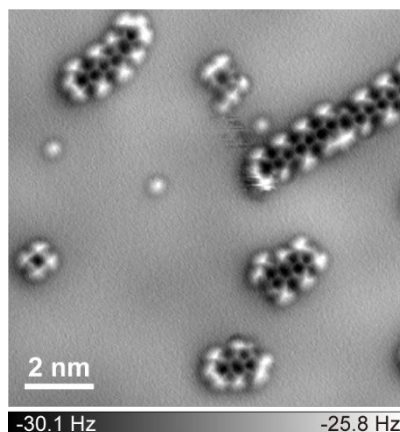[†] These authors contributed equally to this work.

Figure S1. Atomic-scale characterization of a tetraphyllous shaped water cluster on Cu(110) surface. (a) High-resolution STM image (set point: 100 mV, 50 pA). (b, c) Constant-height AFM imaging at the tip height of 0 pm (b) and -90 pm (c), respectively. The oscillation amplitudes of the AFM images are 100 pm. The tip heights of experimental AFM images are referenced to the STM set point on the Cu surface (100 mV, 50 pA).
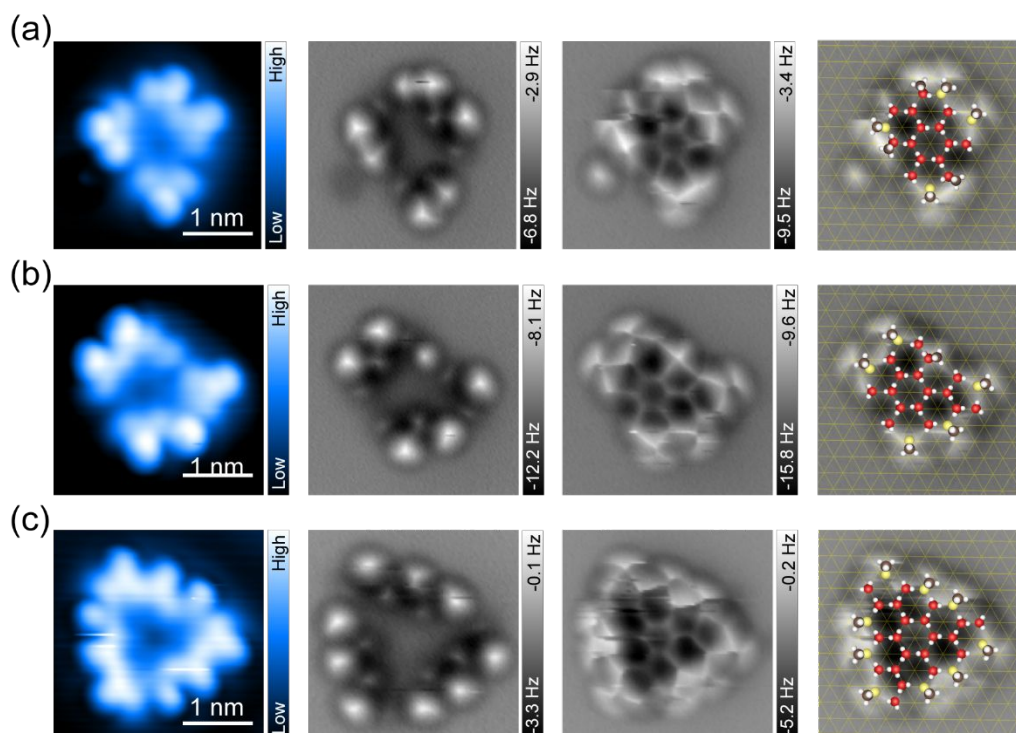
Figure S2. Water-methanol mixed 1D chain with the methanol to water ratio of 1:9. (a) High resolution STM image (set point: 20 mV, 120 pA). (b, c) Constant-height AFM imaging at the tip height of 0 pm (b) and -90 pm (c), respectively. (d) Proposed H-bonding configuration of the water-methanol complex overlaid on the AFM image. White dashed lines and yellow arrows shown in (c) denote the depression and faint protrusion features of vertical water molecules, respectively. Brown arrow shown in (c) highlights methanol molecule with vertical OH directionality with respect to the surface. H and C atoms are denoted as white and brown spheres, respectively. Red, yellow and blue spheres represent O atoms in the flat, vertical water (methanol) molecules and hydroxyls, respectively. The yellow grid denotes the underlying Cu(110) lattice. The tip heights are referenced to the STM set point on the Cu surface (100 mV, 50 pA). The oscillation amplitudes of the AFM images are 100 pm.

(a)

-1.8 Hz   7.0 Hz

(b)

-4.5 Hz   5.7 Hz

(c)

(d)

flat methanol
        vertical methanol
0.4 Å

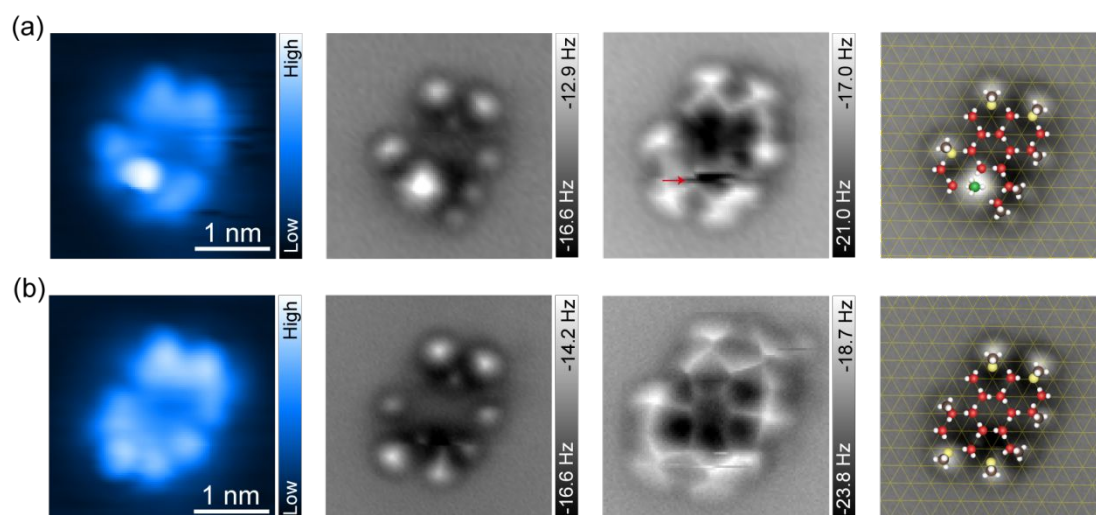top view   side view

Figure S3. Water-methanol mixed 1D pentagonal chain. (a, b) Simulated AFM images at the tip height of 11.3 Å (a), 9.9 Å (b). (c, d) Top and side views of the calculated adsorption configuration of the 1D chain. Brown and black arrows show methanol molecules with vertical and horizontal OH directionality, respectively, with respect to the surface. Cu atoms are denoted as dark and light ochre yellow spheres to highlight the anisotropic character of the Cu(110) surface. H and C are denoted as white and brown spheres, respectively. Red and yellow spheres represent O atoms in the flat and vertical water (methanol) molecules, respectively. The highest H atom of the vertical methanol shown in (d) is 0.4 Å more protruded than that of the flat methanol.
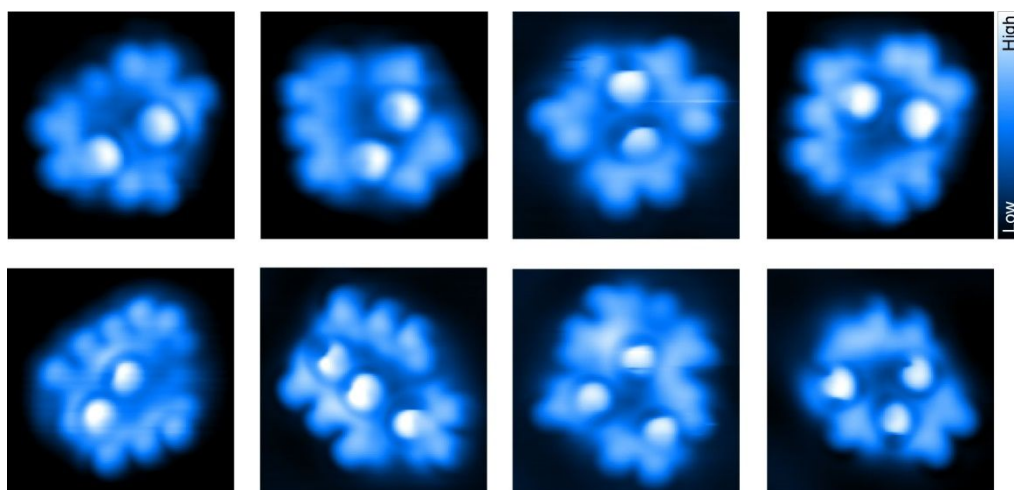
Figure S4. Overview AFM image of water-methanol complexes on Cu(110) surface with the methanol-water ratio of 2:3. The set point of AFM tip height is -100 pm. The tip height is referenced to the STM set point on the Cu surface (100 mV, 50 pA). The oscillation amplitude of the AFM image is 100 pm.

Figure S5. Water-methanol mixed clusters on Cu(111) surface. (a-c) High-resolution STM (the leftmost column), height dependent AFM images (the middle two columns) and the proposed atomic models overlaid on the AFM images (the rightmost column) of three typical types of larger water-methanol mixtures on Cu(111) surface, which were composed of interconnected hexamers and pentamers. The yellow grids indicate the underlying Cu(111) lattice. Set point of STM images: 100 mV, 50 pA. Experimental AFM images (the middle two panels) from left to right are obtained at the tip height of 50 pm, -70 pm (a, b), and 50 pm, -90 pm (c), respectively. The tip heights are referenced to the STM set point on the Cu surface (100 mV, 50 pA). The oscillation amplitudes of the AFM images are 100 pm.
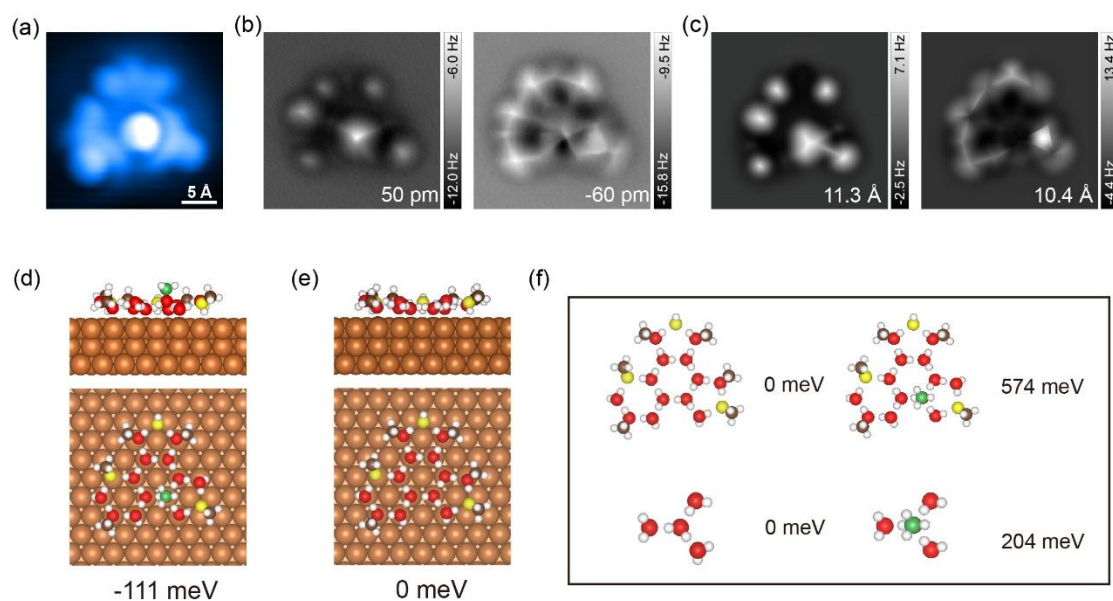
Figure S6. Configuration transformation of the water-methanol complex on Cu(111) with the interior methanol moving to the outside through tip manipulation. (a, b) High-resolution STM (the leftmost column), height dependent AFM images (the middle two columns) and the proposed atomic models overlaid on the AFM images (the rightmost column) of the cluster before (a) and after (b) structural transformation induced by the tip when scanning at small tip height (highlighted by the red arrow). C atom of the methanol molecule with the C-O bond perpendicular to the Cu(111) substrate is highlighted by green sphere. Red and yellow spheres represent O atoms in the flat and vertical water (methanol) molecules, respectively. The yellow grids indicate the underlying Cu(111) lattice. Set point of STM images: 100 mV, 50 pA. Experimental AFM images (the middle two panels) from left to right are obtained at the tip height of 50 pm, -50 pm (a), and 50 pm, -100 pm (b), respectively. The tip heights are referenced to the STM set point on the Cu surface (100 mV, 50 pA). The oscillation amplitudes of the AFM images are 100 pm.

Figure S7. STM images of water-methanol clusters on Cu(111) surface with two or three interior methanol molecules. Set point of STM images: upper panels from left to right: 50 mV, 10 pA; 100 mV, 50 pA; 100 mV, 50 pA; 100 mV, 50 pA; lower panels from left to right: 100 mV, 50 pA; 50 mV, 20 pA; 100 mV, 50 pA; 100 mV, 10 pA.

Figure S8. Atomic-scale characterization and energy analysis of a smaller water-methanol cluster (10-D_2O+6-CH_3OH) on Cu(111) surface. (a-d) Water-methanol mixed cluster with a methanol residing in the central hexamer. (a) STM image (100 mV, 50 pA). (b) Constant-height experimental AFM images. (c) Simulated AFM images. (d) Top and side views of the calculated adsorption configurations. (e) Top and side views of the calculated adsorption configurations of the cluster without interior methanol. The relative adsorption energies are added at the bottom of each structural model. (f) Comparison of the intermolecular interactions of the water-methanol complex and the corresponding internal clusters around the interior water that is replaced by methanol. The relative intermolecular binding energies are added at the right side of each atomic model. The structure shown in (e) is constructed by moving the interior methanol shown in (d) to the outside position, and is further optimized by DFT calculation. However, such a cluster (e) is not observed in the experiment. The intermolecular interaction energy increase (574 meV) of the cluster not only arises from the interior methanol site (204 meV) but is extended to the whole water-methanol network, through the collective H-bonding network relaxation.

Table S1. The influence of vibrational entropy on the mixing of water and methanol. The structures denote those shown in Figure 5b. ΔE_{ad}+TΔS_{vib} denotes the relative energy referenced to Cu(111)-1 with the contribution of the vibrational entropy, ΔS_{vib} denotes the relative vibrational entropy referenced to Cu(111)-1.

Structure	ΔE_{ad} +TΔS_{vib} (meV)				
	T=0 K	T= 25 K	T= 100 K	T= 150 K	T= 300 K
Cu(111)-1	0	0	0	0	0
Cu(111)-2	-97	-95	-69	-45	42

The entropy can be partitioned into configurational entropy and vibrational entropy and the magnitude of configurational entropy is directly related to the possible geometric configurations degenerated in energy[1]. With the consideration that the number of the molecules in the mixtures is small, the quantity difference of the degenerated geometric configurations in the energy of the mixture with or without the methanol inside the water network should be small. Thus, the contribution of configurational entropy to the relative stability of the different water-methanol mixtures can be neglected, leaving the vibrational entropy to be considered. The vibrational entropy of the mixture can be estimated in the harmonic approximation[1],
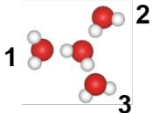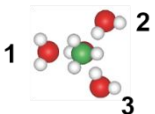
$$S_{vib} = k_b \Sigma [\frac{\hbar\omega_i}{k_bT}(\exp\left(\frac{\hbar\omega_i}{k_bT}\right) -1)^{-1} - \ln\left(1 - \exp\left(\frac{\hbar\omega_i}{k_bT}\right)\right)]$$

where $\hbar$ is the reduced Planck constant, k_b is the Boltzmann constant, and T is the temperature. The summation runs over all the Γ-point vibrational modes of the water-methanol mixture (ω_i), which was calculated using the finite displacement method with a fixed substrate after the structural relaxation.

The calculated relative adsorption energies of the mixtures on Cu(111) surface with the contribution of the vibrational entropy (ΔE_{ad}+TΔS_{vib}) were summarized in Table S1. It can be seen that the relative energy difference of the mixture on Cu(111) surface tends to decrease even invert as the temperature increase, indicating that the contribution of the vibrational entropy promotes the water-methanol mixing. It is worth mentioning that this result also supports the experimental observation of the

water-methanol complete mixing on Cu(111) surface.

Table S2. Binding energy between molecules in the internal cluster of the mixture on Cu(111). E_{bi} denotes the H-bonding energy between each water molecule (denoted by 1,2,3) and the central water/methanol molecule.

Internal cluster on Cu(111)	E_{bi} (meV)			Total E_{bi} (meV)
	1	2	3	
	-91	-52	-4	-147
	-28	123	147	242

The large ΔE_{bi-mix} is related to the compressed H-bonding network on Cu(111) and Cu(110), due to the small lattice spacing of Cu (~2.55 Å), which is significantly shorter than the favorable O-O distance between the nearest neighboring water molecules (~2.8 Å). A detailed energy analysis of the binding energy of the water-water molecules and the water-methanol molecules in the internal clusters around the replaced interior molecule can clarify this point. As shown in Table. S2, the binding energies between the water molecules are all negative, indicating the water-water repulsive interaction in the internal cluster. However, after replacing the central water molecule in the internal cluster with methanol, the binding energies between the water and methanol molecules are significantly larger than the previous water-water binding energies. Therefore, the large ΔE_{bi-mix} is induced due to the release of the strain of H-bonding network with interior methanol, although the number of H-bond seems to be unchanged.

Reference

(1) Costa, D. G.; Rocha, A. B.; Diniz, R.; Souza, W. F.; Chiaro, S. S. X.; Leitão, A. A. Structural Model Proposition and Thermodynamic and Vibrational Analysis of Hydrotalcite-Like Compounds by Dft Calculations. *J. Phys. Chem. C* **2010**, *114*, 14133-14140.