

Direct observation of molecular dynamics using scanning tunneling microscopy

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Controlling over and understanding molecular processes are of fundamental importance in nature and also play a key role for future molecular devices. Amongst the processes, H-bonding dynamics, i.e., exchange and transfer of H-atom/proton, is one of the most common elementary processes in chemistry and biology, yet the microscopic mechanism is imperfectly understood in condensed phase, especially at interfaces. We have employed low-temperature scanning tunneling microscopy to directly control and observe H-bonding dynamics and revealed the mechanism at the single-molecule level [1].

I will show the direct observation of H-bond exchange and H-atom transfer reactions within water-based model systems assembled on a Cu(110) surface using STM manipulation [2,3], and the precise control of intramolecular hydrogen transfer reactions (that is tautomerization) in single porphycene molecules on a Cu(110) surface [4]. The H-bond exchange that occurs via quantum tunneling is visualized in water dimer (Fig.1). The sequential H-atom relay reaction (Grotthuss mechanism) that is induced by vibrational excitation is controlled in water-hydroxyl complexes (Fig.2). The potential landscape of tautomerization is precisely tuned by changing the surroundings of individual porphycene molecules (Fig.3).

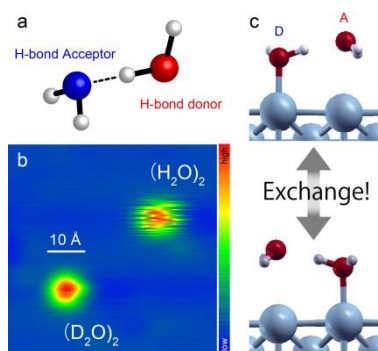


Fig.1 H-bond exchange in water dimer. **a**, Schematic of dimer. **b**, STM image of H₂O and D₂O dimer. **c** Structure on Cu(110).

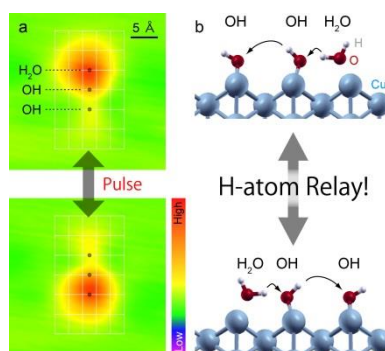


Fig.2 H-atom transfer reaction in water-hydroxyl complex. **a**, STM images. **b**, Structure of the complex on Cu(110).

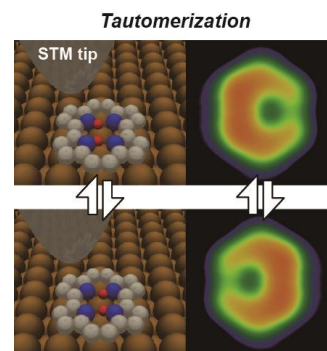


Fig.3 Tautomerization of a single porphycene molecule on Cu(110). (Left) Schematic model. (Right) STM images.

- [1] T. Kumagai, Visualization of hydrogen-bond dynamics, Springer Verlag (2012).
- [2] T. Kumagai *et al.* Phys. Rev. Lett. 100, 166101 (2008).
- [3] T. Kumagai *et al.* Nature Materials 11, 167 (2012).
- [4] T. Kumagai *et al.* Nature Chemistry, accepted (2013).