

Controlling intramolecular hydrogen transfer in a porphycene molecule with single atoms or molecules located nearby

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1. Introduction

- Atomic-scale surroundings are important for adsorbed molecules on a well-ordered surface because adsorbate-adsorbate interactions can change the potential energy.
- Previously some studies tried to control the state of adsorbed molecules by adding other adsorbates or changing the surface, but adding atoms with the exactly determined adsorbing site was rarely reported.
- More recently, tautomerization of phthalocyanine weakly bound to a semiconductor surface was controlled by two single indium adatoms (atoms added on the surface).¹
 - Phthalocyanine physisorbed on the InAs(111)A-(2x2) surface has three equivalent rotational orientations (Figure 1a).
 - The rotation was excited by inelastic electron tunneling, which causes fluctuation of the STM images at high voltage.
 - A phthalocyanine molecule was dragged to between two indium adatoms positioned on the surface with a certain distance in order to “pin” phthalocyanine (Figure 2).
 —> Rotation was disturbed, and intramolecular hydrogen transfer started to be observed.
 - Phthalocyanine originally shows tautomerization, which is disturbed by excitation of rotation, and that adatom-induced single-molecule pinning leaves the tautomerization undisturbed by preventing the molecule from being excited to rotation.
- Much effort was focused on controlling single molecules on a surface, however, tuning interaction energy with adatoms of well-designed adsorbing sites and following control of the adsorbed molecules have not been reported.

In this work, the authors observed intramolecular hydrogen transfer in a porphycene molecule by low-temperature scanning tunneling microscopy (STM), and tuned the tautomerization by adding single atoms, which changed the electronic (and slightly elastic) interaction energy. Cooperative effects on the tautomerization were also studied in the case that porphycene molecules made oligomers on the surface.

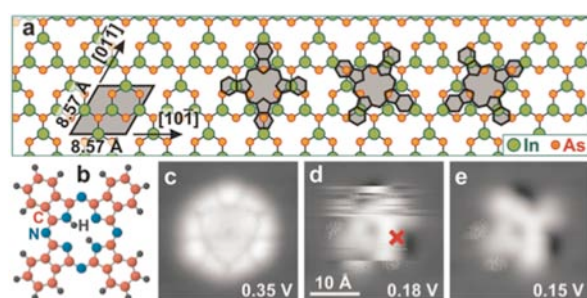


Figure 1. Rotation of phthalocyanine on the InAs(111)A-(2x2) surface.

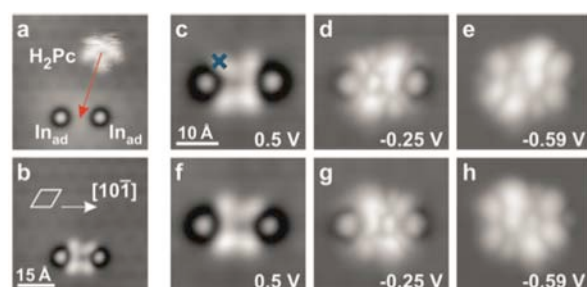


Figure 2. A phthalocyanine molecule pinned with indium adatoms.

2. Results and Discussion

2.1. STM-induced tautomerization of porphycene attached on a Cu(110) surface

- At first porphycene molecules were deposited onto a Cu(110) surface to study it by scanning tunneling microscopy (STM) at 5 K ($I_t = 10$ nA, $V = 100$ mV) (Figure 3a,b) → Crescent-shape
- Density functional theory calculations of porphycene on Cu(110) were also conducted (Figure 3c-h) → Image for *cis-1* is in good agreement with the experimentally observed ones.
- Next STM observation was conducted at high voltage ($V = 300$ mV), which caused fluctuation of images (Figure 4a,b). → Corresponding to *cis-cis* tautomerization (Figure 4e)

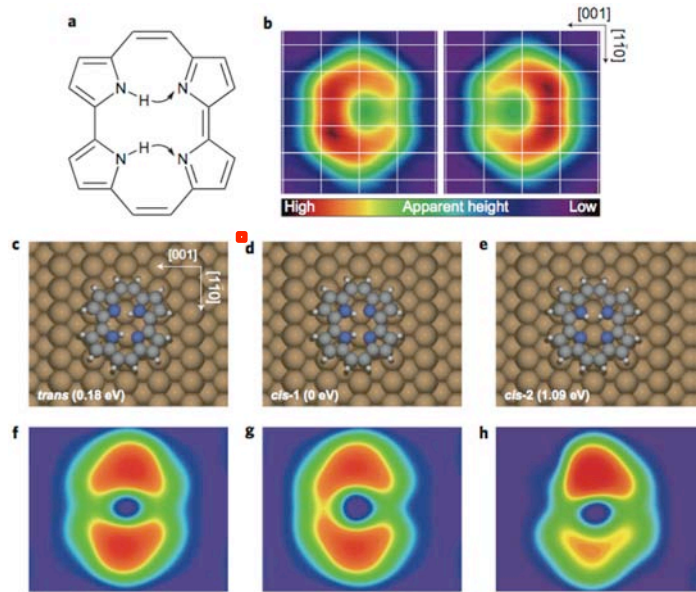


Figure 3. Porphycene molecules on a Cu(110) surface.

- Threshold voltage was about 150 meV for hydrogen-transfer process.
- The hydrogen transfer was monitored in real time by recording the tunneling current at a certain point (marked with a star in Figure 4a). → Telegraph noise between the two *cis-1* states (Figure 4c) without other states.
- Peak areas of histogram were obtained from the counts for each tunneling current → Fractional occupations of the two *cis-1* states (P_H and P_L)

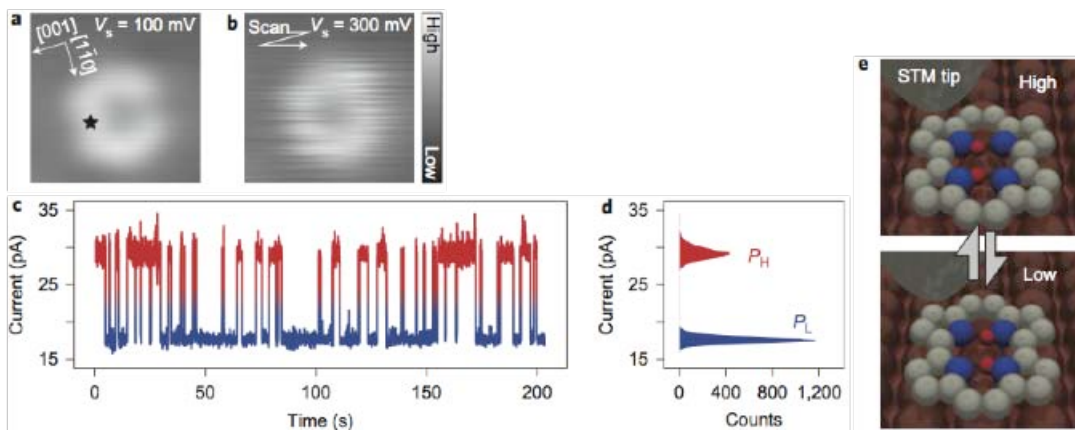


Figure 4. STM-induced tautomerization of single porphycene molecules

2.2. Control of the tautomerization by individual adatoms nearby

- To study the proximity effect in detail, single copper atoms were put at well-defined adsorption sites near the molecules by STM manipulation.
- Tautomerization of the compound with Cu atoms in the vicinity was observed (Figure 5a-k).
 - Molecules without adatom (Fig 5a) $P_H/P_L = 0.67 \pm 0.15$, which did not change in the case with adatom at a relatively large distance (Fig 5b,c).

- However, if adatom was closer to the molecule, P_H/P_L increased to 1.5 (Fig 5d,e).
 - > Presence of a single adatom was able to modify tautomerization at the distance of about 0.9 nm, which was larger than van der Waals radius of a porphycene molecule (0.65 nm).
- When the adatom was placed at the closest position (Fig 5f), the tautomerization was almost quenched.
- Two-adatom cases were also demonstrated (Fig 5h-k)
 - The first adatom was put at the left of the molecule shown in Fig 5h.
 - Then the second adatom was added symmetrically on both sides of molecule (Fig 5i).
 - > Compensated for each other and the same current distribution was observed as Fig 5a.
 - Finally the left adatom was removed to make the state same as Fig 5e (Fig. 5j).

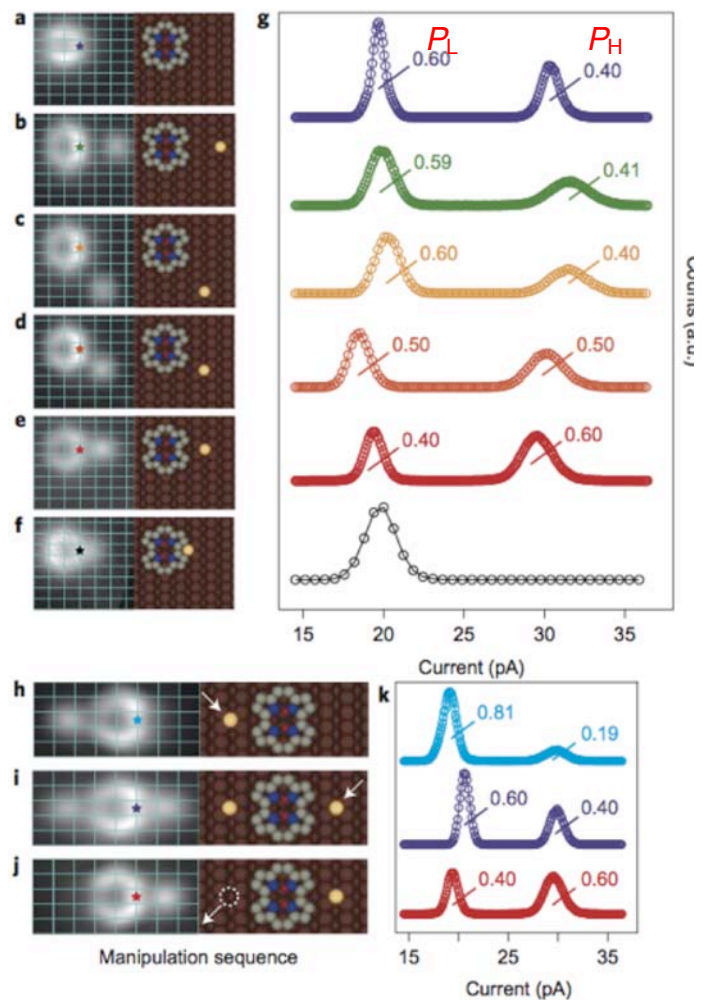


Figure 5. Controlling tautomerization by single adatoms.

- Total energy calculations of the complete surface-molecule-adatom system were also conducted to study potential well deformation by a single copper adatom (Figure 6e).
 - In absence of adatom, the two states are local minima of a double well potential and are degenerate in energy (Figure 6a).
 - For configuration I, smaller total energy for left potential minima —> the “High” tautomer state was favored.
 - $\Delta E = 5$ meV ($\ll 160$ meV, activation energy of thermally induced tautomerization) —> Modified tautomerization rate
 - For configuration II (very short molecule-adatom distance), opposite deformation of the double-well potential takes place. —> the “Low” state was favored.
 - $\Delta E = 117$ meV is a large fraction of the activation energy —> Quenching of the high state.
- Absorbate-absorbate interactions can have contributions from electronic interactions (caused by both absorbates and surface) and elastic interactions (caused by surface).
 - At a large adatom-molecule distance (configuration I), ΔE is governed mainly by the electronic interactions between absorbates.
 - At short distances (configuration II), substrate-related electronic interactions become dominant.
 - Elastic interactions (caused by surface lattice distortions) are small both at configuration I and configuration II.

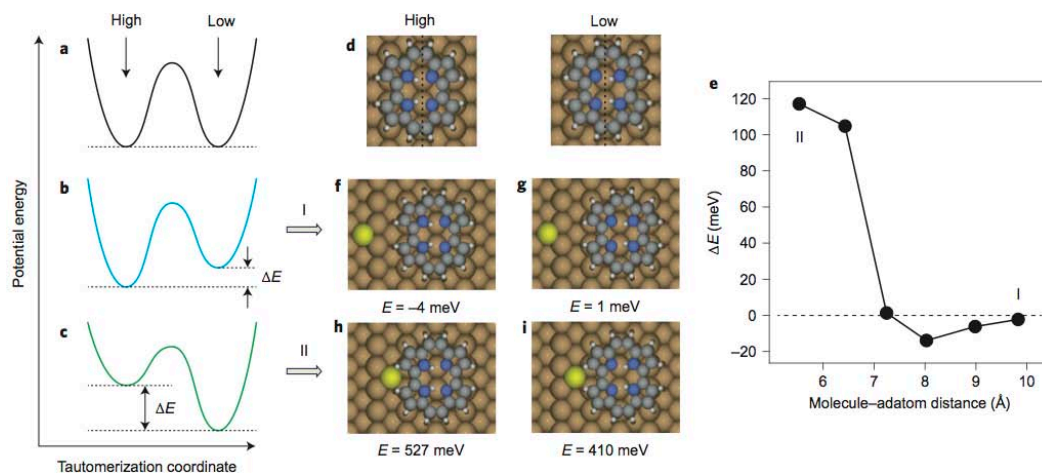


Figure 6. Potential well deformation by a single copper atom.

2.3. Cooperative effects of tautomerization properties modified by the tautomer state of neighboring molecules of the same compound

- Some molecules in a row were found around oxygen rows (the surface containing oxygen atoms in a row) and cooperative effects of tautomerization were studied.
 - In the dimer case, the tautomerization was almost quenched (Figure 7a).
 - In the trimer or longer molecular chain case, the outer molecules scarcely showed the tautomerization whereas the inner molecules showed tautomerization (Figure 7c–e).
- To study the cooperative effect in detail, distribution of the tunneling current was measured at a certain point (marked with a star) on an inner molecule from all possible tautomer states (Figure 7f–j). —> Variation of distribution was obtained
- In the longer molecular chain case, tautomerization of each individual molecule was determined predominantly by its two adjacent molecules, and second neighbor molecules were negligible.

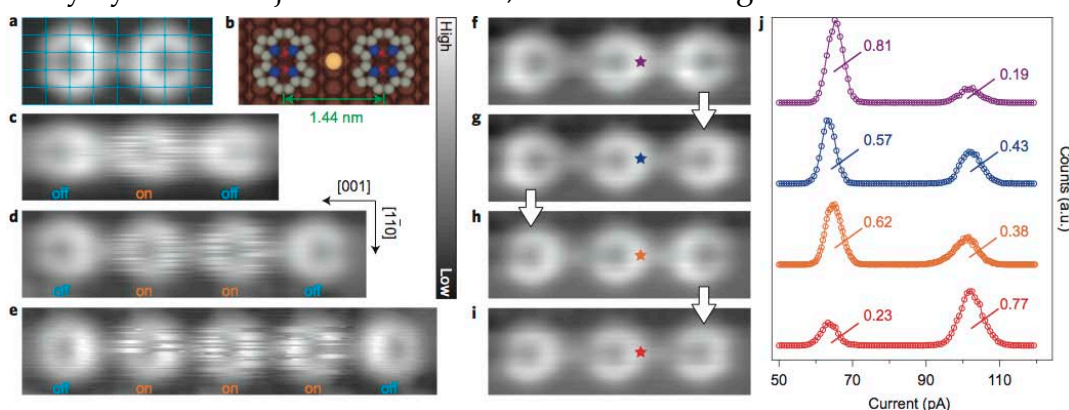


Figure 7. Cooperativity in switching single molecules within assemblies.

3. Conclusion

- Single-molecule tautomerization and its control by the exact position of individual atoms and molecules in the vicinity were observed by STM.
- Further study could be applied to design molecular devices for information processing at a single-molecule level.

References

- ¹ Nacci, C.; Erwin, S. C.; Kanisawa, K.; Folsch, S. *ACS Nano* **2012**, *6*, 4190–4195.