Direct Visualization of 3-Dimensional Force and Energy Map of a Single Molecular Switch

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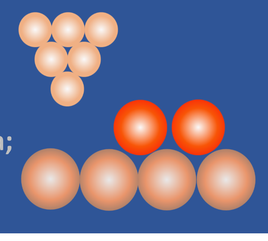

ABSTRACT

Fundamental researches on mechanical and flexure properties of molecules adsorbed on materials surface can greatly advance applications of molecular thin films on devices. Here, we mechanically induce conformational change on a single molecule and quantify the driving force required for such molecular shape switch via a low temperature (~ 5K) Scanning Tunneling Microscope (STM) and Qplus Atomic Force Microscope (Q+AFM). Our measurement maps a three-dimensional landscape for mechanical potential and force at single molecule level with high spatial resolution of a few angstrom (10^{-10} m) in all three dimensions. Our preliminary results indicate that an energy barrier of ~400meV needs to be overcome for rings flipping of TBrPP-Co.

METHODOLOGY

Sample Preparation

- A single crystal metal substrate Au(111) is cleaned to atomic level by repeated cycles of Ar^+ ion bombardment and annealing at ~600°C.
- Molecule TBrPP-Co is subsequently deposited on substrate via thermal evaporation in an ultra-high vacuum preparation chamber (~ 10^{-9} torr).

Data Collection

- The fabricated sample is transferred to analysis chamber in-situ for manipulation experiment.
- A sharp Pt/Ir tip (apex radius of a few nanometers) is mounted on a fine tuning fork (~1mm in length) and is driven to vibrate at f_0 = 30414Hz.
- Tip scans the molecule at different heights with 0.1Å as increment till approaches threshold distance, and meanwhile tip-molecule interaction strength is recorded in the form of tip frequency change Δf, a method first demonstrated by Ternes et al.[1].
- At threshold distance, mechanical force between tip and molecule become large sufficient and cause pentagon rings flip their direction.
- Frequency change Δf is translated into vertical stiffness of the tunning fork, vertical force between tip and molecule, and potential energy of the molecule using Sader-Jarvis method[2].
- By mapping a mechanical potential landscape for a single molecule TBrPP-Co with spatial resolution of a few angstrom in all three dimensions, the energy barrier to be overcome and force required for such molecular conformation switch can be quantified with accuracy of a few tens meV and a few pico-Newton pN.

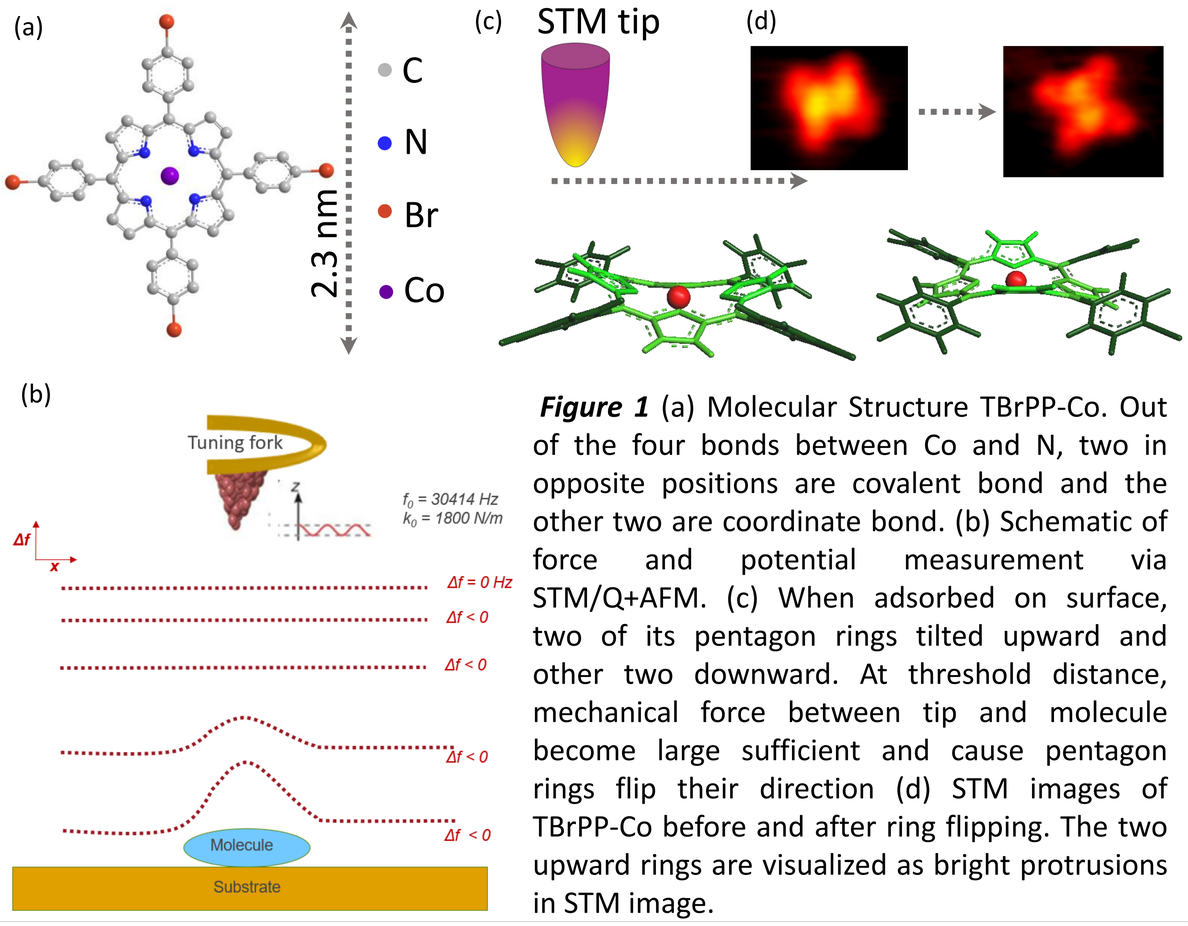

Figure 1 (a) Molecular Structure TBrPP-Co. Out of the four bonds between Co and N, two in opposite positions are covalent bond and the other two are coordinate bond. (b) Schematic of force and potential measurement via STM/Q+AFM. (c) When adsorbed on surface, two of its pentagon rings tilted upward and other two downward. At threshold distance, mechanical force between tip and molecule become large sufficient and cause pentagon rings flip their direction (d) STM images of TBrPP-Co before and after ring flipping. The two upward rings are visualized as bright protrusions in STM image.

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INSTRUMENT

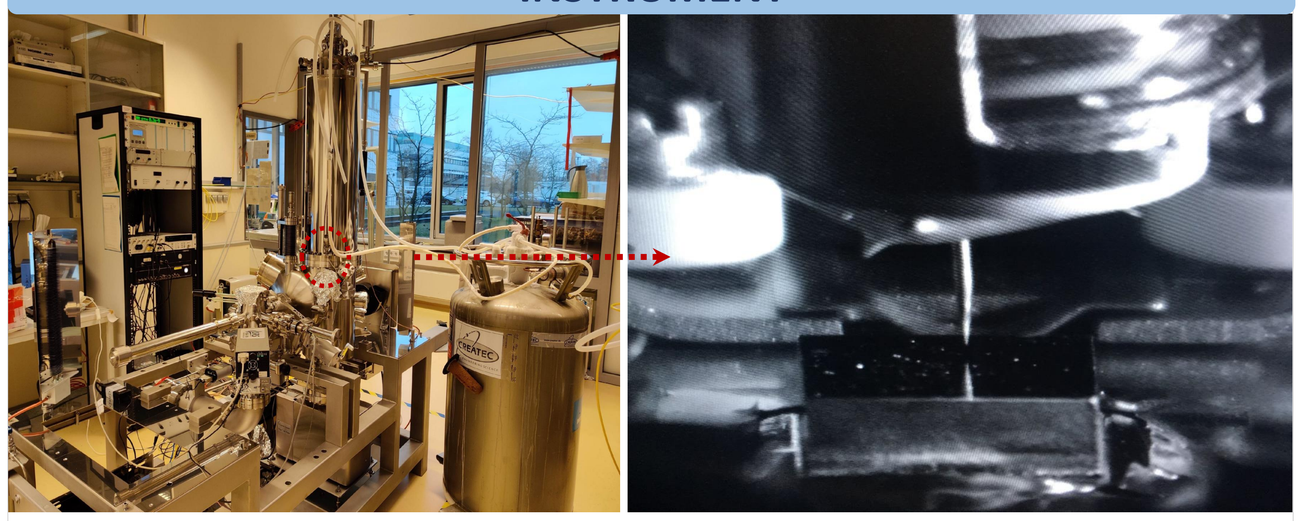

Figure 2 Left: Low Temperature Scanning Tunneling Microscope (STM) and Qlus Atomic Force Microscope (Q+AFM). Ultra-high vacuum: 10-10 torr; Temperature: 4K. Red oval represents the area where scanning head is housed. Right: Scanning head of STM. Lateral spatial resolution of a few angstrom.

EXPERIMENT RESULTS

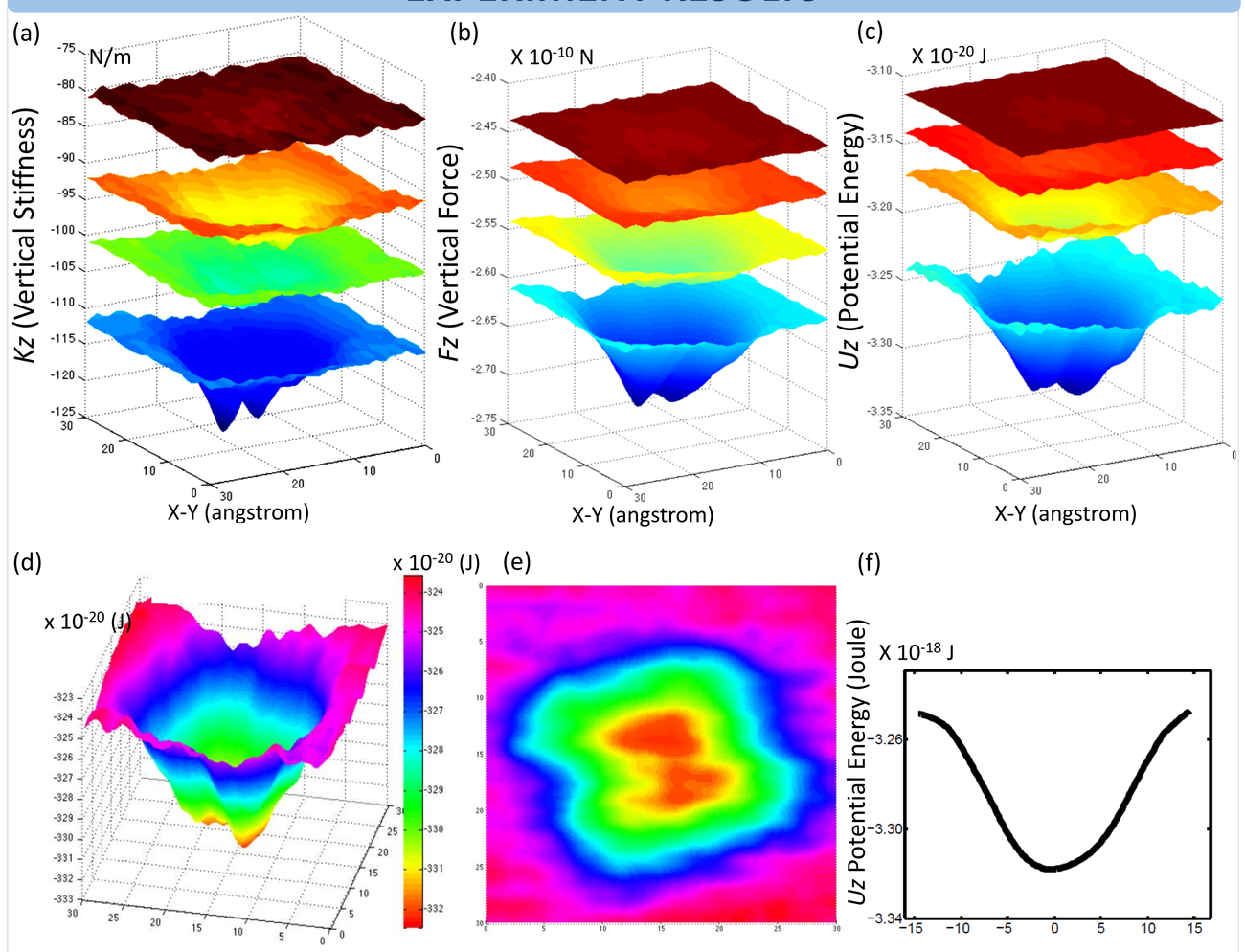

Figure 3 3D landscape of vertical stiffness of the tunning fork (a), vertical force between tip and molecule (b), and mechanical potential energy of the single TBrPP-Co molecule. Side view (d) and top view (e) of the potential energy at threshold distance. (f) Energy barrier of ~400meV is required to be overcome for rings flipping of TBrPP-Co.

CONCLUSION & OUTLOOK

Conclusion

- TBrPP-Co molecular conformation switch can be successfully induced in a mechanical manner via STM/Q+AFM.
- Out preliminary results indicate that an energy barrier of ~400meV needs to be overcome for rings flipping of TBrPP-Co.
- Results presented here are based on analysis of preliminary data. With more data collected and further analysis, results are subject to adjustment before research finalizing stage.

Critical Questions Remain for Further Study

- Force direction for conformational switch needs to be identified. The study by Ternes et al.[1] reveals that lateral component *Fx* of the total force play the critical role in molecular movement across the surface. However, it is unclear if it is lateral *Fx* or vertical *Fz* component of the total force that cause molecular conformation change. Further analysis is needed.
- Theoretical calculations are ongoing to find whether conformational change is accompanied by bond change from covalent bond to coordinate bond.

REFERENCE

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