

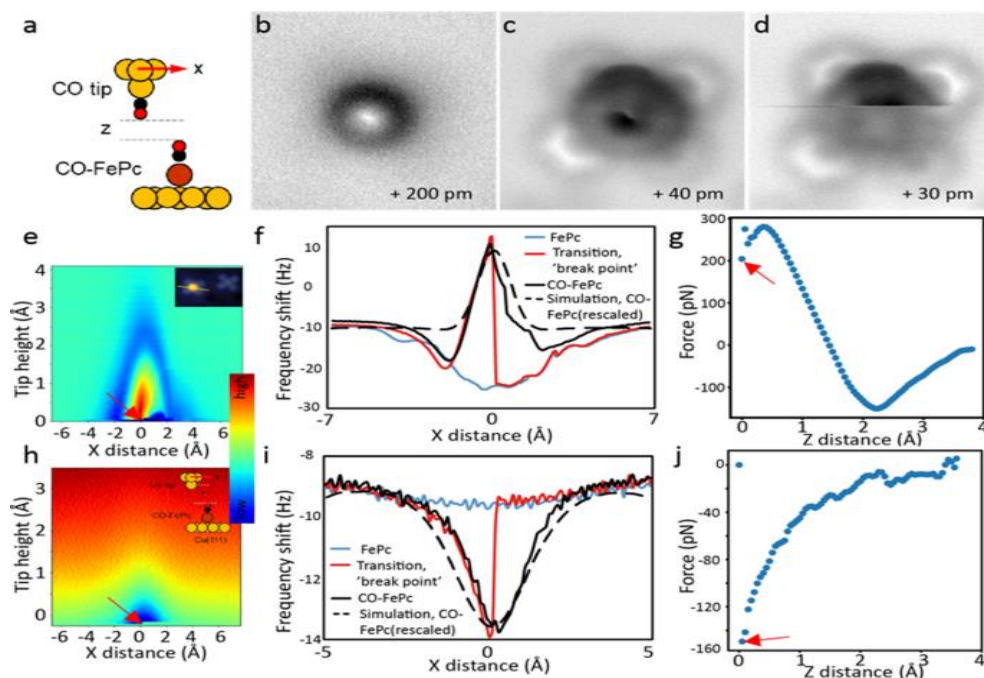
## Probing and Manipulating a Single Chemical Bond Using Scanning Probe Microscopy

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The ability to obtain images of organic molecules with atomic resolution using qPlus type AFM opened doors for a wide range of applications, including directly characterizing molecular structures [1], probing molecular properties [2], creating new structures [3], and even providing a tool for studying various types of chemical bonds [4]. Using AFM tips to manipulate chemical bonds provided insights into the bond-forming process which is involved in many surface interactions. This is essential for obtaining insights into the physical nature of a chemical bond and its role in many chemical and catalytic mechanisms. However, the controlled breaking of a chemical bond using mechanical forces, along with accurate measurements of these forces, is extremely challenging and its detailed process has not yet been fully understood [5]. Dative bonds are commonly found in transition metal complexes and play vital roles in catalysis, organometallic chemistry, and biochemistry. We studied the break of a single dative bond between a CO molecule and a ferrous phthalocyanine (FePc) complex using AFM together with real-space pseudopotential density functional theory (DFT) calculations. Our results reveal detailed mechanisms of bond breaking by both repulsive and attractive forces. This work advances understanding of the origins of measured forces in dative bond breaking.

After dosing CO and FePc on Cu(111) surface at 5 K, some CO molecules can land on FePc and form a OC-Fe bond, high resolution AFM image can identify the chemical structure of the bonded molecule complex [6]. After applying a controlled force to break the bond, the chemical structure of the molecules can be imaged again. The forces acted on the AFM tip during the bond rupture process are recorded. Figure 1 showed the process of dative bond breaking. Our results show that the bond can be ruptured either by applying an attractive force of ~150 pN with a Cu tip or by a repulsive force of ~220 pN with a CO tip. During the bond breaking, a significant contribution of shear forces was identified, accompanied by changes of the spin state of the system. In addition, our results show that, with a CO tip, the dative bond ruptured after passing a maximal force at ~300 pN, which may related with the symmetry of the bond. Our combined experimental and computational studies provide a deeper understanding of the chemical bond breaking process [7].



**Figure 1.** **a** Schematic of a CO-AFM tip interacting with CO-FePc (Cu: yellow; C: black; O: red; Fe: brown). **b–d** Non-contact AFM images obtained at different tip heights ( $z$ ); the final dislodging of CO occurs at  $z = +30$  pm. **e** 3D force map of the frequency shift ( $\Delta f$ ) vs. AFM tip heights ( $z$ ) and horizontal position ( $x$ ), with a CO tip. Step size is 5 pm in  $z$ , and the scan path in  $x$  is across the center of the Fe, as shown in the inset. The tip position at bond rupture is indicated by the breakpoint (arrow). **f** Frequency shift ( $\Delta f$ ) obtained in the horizontal ( $x$ ) direction before, during (indicated by the disjointed curve), and after the bond rupture. **g** The force curve deconvoluted from  $\Delta f$  at the breakpoint in the vertical ( $z$ ) direction. **h** 3D force map of the frequency shift ( $\Delta f$ ) showing quantitative rupture of the dative bond, obtained using a Cu tip; the insert shows schematic of interaction between a Cu tip and CO-FePc. **i** Frequency shift ( $\Delta f$ ) obtained using a Cu tip scanned in the horizontal ( $x$ ) direction. **j** The deconvoluted force curve at the breakpoint in the vertical ( $z$ ) direction using a Cu tip. (Red arrows indicate the bond rupture point. Long-range background forces are subtracted in Figures **g** and **j**).

#### References:

- [1] L Gross et al., *Science* **325** (2009), p. 1110.
- [2] L Gross et al., *Nat. Chem.* **2** (2010), p. 821.
- [3] K Kaiser et al., *Science* **365** (2019), p. 1299.
- [4] J Zhang et al., *Science* **342** (2013), p. 611.
- [5] C Wagner et al., *Phys. Rev. Lett.* **109** (2012), p. 076102.
- [6] P Chen et al., *Nat. Commun.* **12** (2021), p. 5635.
- [7] The authors acknowledge the support of ExxonMobil and the Imaging and Analysis Center operated by the Princeton Institute for the Science and Technology of Materials at Princeton University, which is supported in part by the Princeton Center for Complex Materials, a National Science Foundation Materials Research Science and Engineering Center (Grant No. DMR-2011750).