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**Figure 1 ǀ Porphycene molecule on Cu(110) and schematic of the measurement configuration.** **a** and **b,** STM images of a single porphycene molecule at 5 K (gap conditions: *V*bias = –100 mV, *I*t = 10 nA, size: 1.49 × 1.42 nm2). The white grid represents the surface lattice of Cu(110). The white star indicates the lateral tip position during force spectroscopy in **Fig. 2a–c**. **c,** Molecular structure of *cis* porphycene that can be reversibly switched between the two mirror reflected configurations. The curved arrows depict the hydrogen transfer during tautomerization. **d,** Schematic of the tip-induced tautomerization experiment. The tip mounted on a tuning fork sensor oscillates at the resonance frequency (*f*0) of ~23 kHz with the amplitude (*A*OCS) of a few Å. The frequency shift (Δ*f*) caused by the interaction (yellow column) between the tip apex and molecule (or surface) is recorded while moving the tip down and up (Δ*z*).

** Figure 2 ǀ Force spectroscopy of a single porphycene molecule. a,** Background-subtracted Δ*f*(Δ*z*) curves (green: approach, light green: retraction). The inset shows the Δ*f*(Δ*z*) over a molecule (green) and the bare Cu(110) surface (black) before subtraction. The lateral tip position is indicated in **Fig. 1a** and *V*bias was set to 0 V during the measurement. The initial tip height was fixed at a gap resistance of 10 GΩ (*V*bias = 100 mV, *I*t = 10 pA) over the bare Cu(110) surface and then laterally moved over a molecule with the feedback loop disabled. **b,** Background-subtracted *F*(Δ*z*) curves measured with three different tip conditions (labeled Tip 1–3). The black dashed lines represent the fitted result to the Morse potential model $F\_{M}=-E\_{d}2κ[e^{-κ\left(z-z\_{e}\right)}-e^{-2κ\left(z-z\_{e}\right)}]$, where *E*d is the bond energy, *κ* the decay constant, and *z*e the equilibrium distance (fitting parameters are listed in Supplementary Table 1). The ∆*z* is the relative tip height with respect to *z*e of each approach curve. The inset shows the STM images before and after measurement (white arrow indicates the measured molecule). **c,** Background-subtracted *U*(Δ*z*) curves for the three different tips. The inset shows the histogram of the threshold potential (*U*th) collected from 21 different tip conditions. **d‒f**, Background-subtracted *F*(Δ*z*) maps for approach measured along the [001] direction and obtained with Tip 1. The upper edge of the black area in **e** and **f** indicates the vertical tip position at which tautomerization takes place. **g**, Adsorption geometry of porphycene determined by the DFT calculations. The black dashed lines represent the recorded lines of the force maps in **d–f**. **h,** Schematic of the initial and final state of tautomerization. **i,** Background-subtracted *U*(Δ*z*) curves measured at three different positions over a molecule indicated in **g** (obtained with Tip 1). For clarity, the curves (i) and (iii) are vertically offset. **j,** Δ*U* (= *U*initial – *U*final) curves at the three different positions. The ∆*z* for **d**–**f** and **i**, **j** represents the relative tip height with respect to *z*e of the approach curve at the position (ii). Measurement parameters: Tip 1; *A*ocs = 1 Å, *f*0 = 22653 Hz, Q = 18274, Tip 2; *A*ocs = 1 Å, *f*0 = 22645 Hz, Q = 33855, Tip 3; *A*ocs = 1 Å, *f*0 = 22646 Hz, Q = 39143.



**Figure 3 ǀ Force spectroscopy of a single porphycene molecule with a xenon-terminated tip.** **a**, Schematic of the experimental configuration. **b**, and **c,** STM images with a xenon-tip before and after the measurement (*V*bias = 100 mV, *I*t = 30 pA, 1.4 × 1.4 nm2). The white star indicates the lateral tip position during the measurement. **d,** Δ*f*(Δ*z*) curve measured over Cu(110) (black) and over porphycene (blue: approach, light blue: retraction). The inset shows the background-subtracted Δ*f*(Δ*z*). The subtraction is implemented in the regime before the second decrease of Δ*f*(Δ*z*) takes place (indicated by the dashed line). **e,** Background-subtracted *U*(Δ*z*) curve. The inset shows the *F*(Δ*z*) curve and the solid lines represent the best fitted result of the approach curve to the Morse potential model with the parameters; [*E*d (eV), *κ* (Å-1)] = [0.114(±0.004), 0.98(±0.08)]. The ∆*z* is the relative tip height with respect to *z*e. Measurement parameters: *A*ocs = 1 Å, *f*0 = 22646 Hz, Q = 39143.

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**Figure 4** | **Calculated force curves and MEPs for the tip‒porphycene‒surface system.** **a** and **b,** Optimized structure and modeled copper tip. **c** and **d,** Simulated background-subtracted *U*(Δ*z*) and Δ*U*(Δ*z*) curves. The lateral tip position is indicated by the colored dots in **b**. “Initial” and “Final” represent the curves over the donor and the acceptor pyrroles, respectively (*i.e.*, corresponding to the curves before and after tautomerization). The ∆*z* is defined with respect to the potential minimum of the “Initial” curve at the position (ii). The curves for the position (i) and (iii) are vertically offset for clarity. **e,** Simulated 2D force map over a molecule (only the *F* < 0 regime is shown). **f,** MEP for the *cis* → *cis* tautomerization of the adsorbed porphycene on Cu(110) determined by the nudged elastic band method. **g,** 2D plot of the N‒H bond length as a function of the tip position. The black line indicates the *F* = 0 contour. **h,** MEPs in the presence of the tip. The corresponding geometry is displayed on the right. The cross markers in **f** and **h** represent the ZPE corrected energies. The path length was obtained from the Euclidean distance between the images in configurations space.