

Asymmetric saddling of single porphyrin molecules on Au(111)S. Müllegger,^{1,*} M. Rashidi,¹ T. Lengauer,¹ E. Rauls,² W. G. Schmidt,² G. Knör,³ W. Schöfberger,³ and R. Koch¹¹*Institute of Semiconductor and Solid State Physics, Johannes Kepler University, Linz, Austria*²*Lehrstuhl für Theoretische Physik, Universität Paderborn, Germany*³*Institute of Inorganic Chemistry, Johannes Kepler University, Linz, Austria*

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The interaction of organometallic molecules with metal surfaces affects their conformation and accordingly their functionality. Surprising conformational complexity is revealed in single Au-porphyrin molecules on Au(111) exhibiting a variety of different asymmetric conformers. A combination of low-temperature scanning tunneling microscopy and spectroscopy experiments with density functional theory calculations discloses different registries of the pyrroles with the substrate lattice (determined and quantified with atomic precision) that cause asymmetric sub-Å buckling of the macrocycle and, furthermore, a redshift of the frontier-orbital energy gap.

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I. INTRODUCTION

The intimate relation between the conformation of a molecule and its functionality is of key importance for developing molecule-based nanoapplications in solution and on surfaces. This relation is strikingly evident in metal-porphyrin molecules providing functionality, e.g., for spectroscopic markers,¹ gas sensors,² tailored molecular catalysts,³ molecular switches,^{4,5} engineered molecular nanostructures,⁶ or molecular spintronics.^{7,8} Conformational changes are triggered by low-energy interactions of the porphyrin molecule with its local environment, e.g., by axial ligation^{9,10} or adsorption on solid surfaces,^{11–15} thus providing a handle for controlling functionality.

One of the most prominent conformational changes in porphyrins is the transition from a planar-core configuration in the gas phase to a C_{2v} -symmetric saddle configuration upon adsorption on metal surfaces¹⁶ investigated recently by scanning tunneling microscopy (STM) for various metal-base tetraphenylporphyrin (TPP) molecules.^{11–15} Despite the atomic-scale lateral resolution of the STM, it remains difficult to unambiguously separate topographical and electronic information from tip effects on a submolecular level. This, however, is essential for unambiguously determining the exact conformations of individual molecules in order to rule out small intramolecular distortions that will affect electronic properties, as well.

Here, we demonstrate that the tetrapyrrole-macrocycles of metal-TPP molecules exhibit a much richer conformational complexity that goes beyond the C_{2v} -symmetric saddle conformation upon adsorption on a metal surface. By employing low-temperature (LT) STM we succeeded in reliably identifying several conformers of Au 5,10,15,20-tetraphenylporphyrin (Au-TPP) with different asymmetric buckling deformations of their macrocycles. For the respective conformers, our STM-based adsorption-site mapping experiments reveal different adsorption sites and registries with the substrate lattice in agreement with our density functional theory (DFT) calculations. The observed different bonding of the pyrrole units to the substrate induces a redshift of the frontier orbital energies determined by scanning tunneling spectroscopy (STS), which we quantitatively relate to the magnitude of asymmetric buckling.

II. EXPERIMENTAL

The experiments were carried out in ultrahigh vacuum with a LT-STM operated at 7 K using electrochemically etched and *in situ* annealed polycrystalline tungsten tips with the bias voltage applied to the sample. The Au(111) single crystal substrate was cleaned by repeated cycles of Ar sputtering and annealing until a $22 \times \sqrt{3}$ diffraction pattern was obtained. [Au(III)-TPP]⁺Cl[−] was evaporated at 463 K out of a glass tube at substrate temperatures of 300 K.¹³ DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP)¹⁷ and the PW91 functional¹⁸ of the generalized gradient approximation complemented with an empirical dispersion correction¹⁹ to model the electron exchange and correlation. The latter yielded a meaningful approximation to the missing energy contributions for similar systems.²⁰ The Au(111) surface was modeled by periodically repeated slabs of four Au layers separated by 25 Å vacuum. The topmost two layers and all atoms of the molecule were allowed to relax during optimization. Electron-ion interaction was described by the projector-augmented wave (PAW) method.²¹ For the Brillouin zone sampling, only the gamma point was used together with an energy cutoff of 450 eV.

III. RESULTS AND DISCUSSION

At room temperature and ultralow coverages,²² the preferred nucleation sites of Au-TPP molecules on Au(111) are the bulged and pinched elbow sites²³ of the x -type corrugation line²⁴ of the $(22 \times \sqrt{3})$ herringbone reconstruction pattern (see Fig. 1 and high-resolution image in Fig. 2). Figure 1 displays four Au-TPP molecules (I–IV) imaged at identical tip conditions, clearly revealing that individual Au-TPP molecules have different azimuthal orientations relative to the substrate. A closer look on the topographic appearance discloses discernible features related to the main intramolecular structural units [pyrrole and phenyl moieties; see also Fig. 4(a)]. In a single molecule, some pyrroles appear higher than others, which has been attributed to their tilting away from the surface.²⁵ Employing a nonlinear color code accentuates even small apparent-height variations as illustrated by the insets of Fig. 1. Since tip and contamination effects are reliably ruled

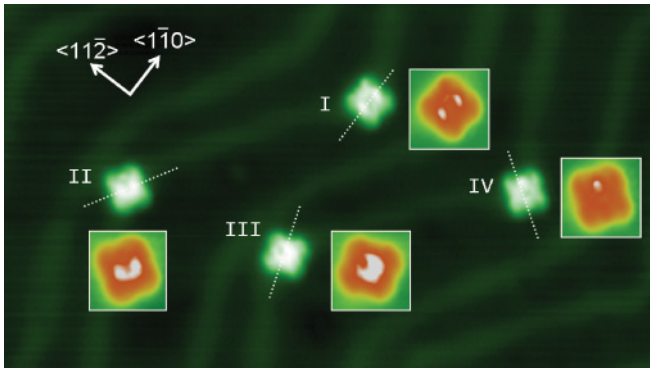


FIG. 1. (Color online) Constant-current STM image (58 pA, -1 V) of four Au-TPP molecules on Au(111) with different saddle-like conformations; dotted lines mark the main molecular axes; insets show the molecules with nonlinear color-code.

out, a comparison of the four Au-TPP molecules indicates that, in particular, the respective macrocycles exhibit different out-of-plane deformations. Obviously, four different Au-TPP conformers distinguished by their characteristic topographs have been imaged in Fig. 1. Apart from the C_{2v} -saddle conformer (I), the symmetry is reduced to C_{1v} or C_1 in the conformers (II–IV) by different buckling of the macrocycle (saddling-asymmetries).

Intuitively, the different conformations observed in Fig. 1 are related to variations in the positions and registries of the individual molecules relative to the local lattice configuration of their adsorption sites (elbows). The apex of each elbow exhibits a dislocation defect²⁴ inducing anisotropy to the local lattice. As shown in Fig. 2, the dislocation is characterized by an additional atomic row (marked by an arrow) that terminates at the elbow apex, while the neighboring atomic rows run distorted but steadily between hcp and fcc regions (dashed lines). At the apex, a section of an atomic row in the $\langle 1\bar{1}0 \rangle$ direction is pushed out of the surface plane as indicated by the apparent-height profiles in Fig. 2.

In order to determine the adsorption site and registry of different observed conformers relative to the anisotropic lattice

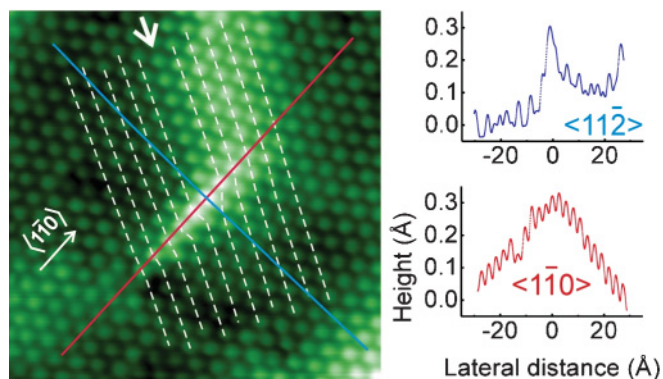


FIG. 2. (Color online) Left: Atomic resolution STM image (1 nA, $+0.25$ V) of the reconstructed Au(111) surface over the apex of a bulged elbow; dashed lines are a guide to the eye indicating atomic rows neighboring the half-row marked by the arrow; right: apparent-height profiles along the $\langle 11\bar{2} \rangle$ (blue) and $\langle 1\bar{1}0 \rangle$ (red) direction across the apex of the elbow defect.

at the elbow (Fig. 2), we performed STM-based adsorption-site mapping experiments: In a first step, a high-resolution close-up image of the selected conformer was recorded [Figs. 3(a) and 3(b)]. By keeping position and size of the image frame constant, the molecule was laterally moved away from its initial adsorption position out of the image frame by means of inelastic tunneling at a constant tunneling resistance (32 $M\Omega$). Finally, the substrate lattice at the position of the initially adsorbed molecule was imaged with atomic resolution and overlaid with the DFT structure of Au-TPP [Fig. 3(c)] in order to identify the initial position and orientation of the selected conformer [Figs. 3(a) and 3(b)]. This procedure was repeated for four different C_{2v} - and four different asymmetric-saddle conformers. The lateral drift of the image frame during our adsorption-site mapping experiments was negligibly small ($\ll 1$ Å); however, apparent lateral shifts of < 1 Å due to minor tip changes between subsequent images cannot be excluded.

To rationalize why different saddling asymmetries occur, we compare different conformers with respect to the location of their Au ions and the C atoms of their pyrroles. Figures 3(c)

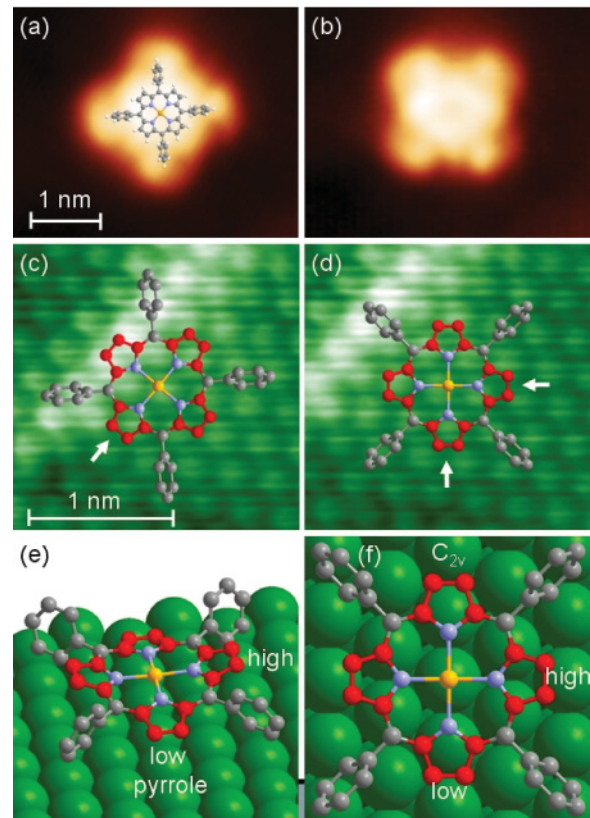


FIG. 3. (Color online) Adsorption site mapping experiments: (a), (b) STM topograph ($+1$ V, 50 pA) of an initially (a) C_{2v} -symmetric and (b) C_{1v} -symmetric Au-TPP molecule adsorbed near a bulged elbow site on Au(111); the molecular structure of Au-TPP is overlaid in (a); (c), (d) atomic-resolution STM images ($+0.26$ V, 1 nA) recorded after laterally removing the molecules (a) and (b) from their initial adsorption site; molecular structure models are overlaid at the original adsorption position; arrows indicate the pyrroles appearing darker in STM; pyrrole C atoms are highlighted in red. (e), (f) DFT calculations of the geometric structure of a single Au-TPP molecule adsorbed on idealized flat Au(111).

and 3(d) juxtapose two representative adsorption-site maps obtained for a C_{2v} conformer (c) and a low-symmetry conformer (d); pyrroles appearing darker in the STM topographs are marked by arrows. Statistical evaluation yields that all studied Au-TPP conformers preferentially adsorb within a radius of four surface lattice-constants around the elbow dislocation defect (intersection point of the red and blue lines in Fig. 2). The Au centers occupy on-top positions or are shifted by less than 1 Å in direction of a bridge position. In all observed C_{2v} conformers the atoms of the darker appearing (lowered) pair of opposite pyrroles adopt similar (i. e., nearly equivalent) adsorption sites. The lowered pyrroles of this pair are typically located near top positions in such a way that their outermost C atoms lie near threefold hollow positions [arrows in Fig. 3(c)]. The asymmetric saddles C_{1v} and C_1 have no such pair of opposite pyrroles with equivalent adsorption sites (low and high pair) [Fig. 3(d)]. Higher appearing pyrroles are less sensitive to lattice corrugations due to their larger separation from the surface (see below).

Figures 3(e) and 3(f) depict the molecular structure of Au-TPP on unreconstructed Au(111) calculated by DFT. Upon adsorption on Au(111), the molecule distorts into a C_{2v} -symmetric saddle [Fig. 3(e)]. In the most stable adsorption configuration the Au ion is in an on-top position, in good agreement with the experiments. Similar results were found for other d -metal centers.²⁶ It lies 4.15 Å above the underlying Au surface atom, which itself is displaced by 0.06 Å out of the surface plane. One pair of opposite pyrroles is tilted closer toward the surface and the other pair away from it by an angle of 15° [low and high pyrroles in Fig. 3(e)]. The outermost C atoms of the low pyrroles are stabilized in threefold hollow positions as depicted in Fig. 3(f), again in good agreement with experiment [Fig. 3(c)]. This allows them to move closer to the substrate plane by 0.6 Å compared to the C atoms of the high pyrroles occupying bridge like positions elevated by 0.65 Å relative to the Au ion. The N atoms lie ± 0.07 Å higher/lower relative to the Au ion. The phenyls are tilted by an angle of 67° relative to the surface plane, i.e., considerably larger than predicted by gas-phase calculations neglecting the metal surface.¹³

The DFT adsorption energy amounts to 5.55 eV and a negative charge of 0.1 e is transferred from the substrate to the [Au-TPP]⁺ molecule. Compared with an adsorption at a bridge or hollow site there is an energy difference of only 0.02 eV in agreement with earlier studies on a similar system.²⁶ An energy of 1.47 eV is stored in the distortion of the molecule²⁷ comparable to 1.16 eV reported for H₂-TBPP on Au(111).²⁸ The contribution of the long-range dispersive interactions to the adsorption energy amounts to 2.94 eV. We remark that for our simulations the molecule plus Au(111) slab were put in a singly positive charge state,²⁷ since our STM experiments indicate that the Cl⁻ counter ions have dissociated from the Au-TPP molecule after adsorption on the Au(111) surface³⁰ similar to the case of [Cu-corrole]⁺Cl⁻ complexes.²⁹

Our LT-STM experiments reveal that compared to the DFT calculations on unreconstructed Au(111) both symmetric and asymmetric conformers coexist on the reconstructed surface. Figure 4(a) compares representative STM topographs of a C_{2v} -conformer (1) and two different asymmetric conformers

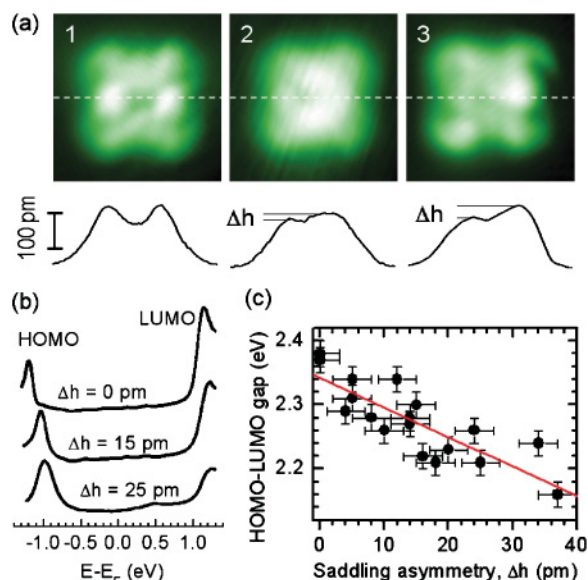


FIG. 4. (Color online) (a) STM topographs (-1 V, 50 pA) showing a C_{2v} symmetric-saddle conformer (1) and two different C_{1v} asymmetric-saddle conformers (2) and (3) together with the respective apparent-height profiles recorded along the dashed lines. (b) Representative dI/dV spectra of conformers with different Δh values exhibiting stronger shifts of HOMO compared to LUMO. (c) Redshift of the HOMO-LUMO energy gap for different Au-TPP conformers in dependence of the saddling-asymmetry, Δh ; red dashed line indicates a linear fit of the data.

(2, 3). Analyzing the apparent-height profiles across the most asymmetric pyrrole pair of the investigated conformers yields a quantitative measure, Δh , for characterizing their different degrees of saddling asymmetry [see line scans recorded along dashed lines in Fig. 4(a)]. The latter is accompanied by a shift of the respective highest occupied and lowest unoccupied molecular orbitals (HOMO, LUMO) as determined by STS with the tip centered over the molecule [Fig. 4(b)]. Plotting $|\Delta h|$ of various conformers against their HOMO-LUMO energy gap reveals an approximately linear red-shift in the accessible Δh range with increasing saddling asymmetry [Fig. 4(c)]. The maximum Δh value of 37 pm corresponds to a redshift of 210 meV ($\approx 8\%$ change) compared to the C_{2v} conformer. The change in the gap energy is dominated by a shift of the HOMO toward higher energies, thus having direct consequences on the molecular properties. A comparison of symmetric and asymmetric conformers with respect to the apparent-height profiles across the phenyl substituents indicates the effect of steric repulsion between neighboring pyrrole and phenyl moieties: Asymmetrical lowering of a pyrrole forces its two neighboring phenyls to adapt a steeper orientation as compared to the C_{2v} conformer, which appears as an increased apparent height of the respective phenyls of about 25 pm.

IV. CONCLUSION

In conclusion, we have studied variations of the adsorption sites and registries of single Au-TPP molecules relative to the Au(111) lattice with atomic-scale precision. LT-STM reveals

a variety of reduced-symmetry conformations in addition to the well-known C_{2v} saddle. Different registries of the pyrroles with the substrate lattice give rise to different sub-Å buckling of the saddled macrocycles. Local LT-STs of various conformers discloses a redshift the HOMO-LUMO gap that is quantitatively related to the magnitude of the saddling asymmetry and contains structural information about the local environment. The presented results improve the understanding of the molecule/environment interaction with impact on

tailoring and control of molecular properties for future porphyrin applications.

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*Corresponding author: stefan.muellegger@jku.at

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