



High resolution scanning-tunneling-microscopy imaging of individual molecular orbitals by eliminating the effect of surface charge

Z.H. Cheng^a, S.X. Du^a, N. Jiang^a, Y.Y. Zhang^a, W. Guo^a, W.A. Hofer^b, H.-J. Gao^{a,*}

^a Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100190, PR China

^b Liverpool University, Liverpool L69 3BX, UK

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ABSTRACT

Ultrathin Iron(II) Phthalocyanine (FePc) monolayers have been employed to decouple individual FePc molecules electronically from the metallic substrate, which allows the intrinsic electronic structure of the free molecule to be preserved and imaged by means of low-temperature scanning tunneling microscopy (STM). High-resolution images reveal the standard “cross” structure for molecules adsorbed at the metal surface, but a detailed electronic structure, corresponding to the highest occupied molecular state (HOMO), for molecules adsorbed at the buffer layer. Different STM images of the molecules in the first and second layer are referred to different interactions between molecules and substrate. This interpretation is verified by control experiments on a second molecule, tetra-*tert*-butyl zinc Phthalocyanine ((*t*-Bu)₄ZnPc). We therefore conclude that this effect is generic and can be used to investigate a molecule's electronic structure in detail.

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1. Introduction

Scanning tunneling microscopy (STM) is remarkably well suited to probe not only the configuration of self-assembled structures of molecules and even individual molecular structures at the atomic scale, but also their intrinsic electronic properties [1,2]. As STM relies on nonzero conductance within the tunneling junction to produce an image, the majority of the STM studies of individual molecules have so far been limited to molecules on metal or semiconductor substrates. In these cases, the electronic structure of the molecules is usually strongly influenced by the substrate either due to strong coupling between molecules and the substrate [3], or the fact that the molecular states are merged with the surface electrons to produce a convoluted STM image [4]. Except for specific weakly-adsorbed systems, for example pentacene on Au(111) [5], it is desirable to decouple molecules electronically from a substrate to investigate the intrinsic electronic properties of an individual molecule [6]. Ultra-thin insulating films on a metallic substrate or passivated surface of a semiconductor have been used in the past to this end [7–10]. Alternatively, organic thin films can form buffer layers to provide the decoupling [11–13]. However, so far no intra-molecular features for individual orbitals of Iron(II) Phthalocyanine (FePc) have been observed. Even adsorbed on a thin decoupling layer of NaCl on Cu (111) the molecule is imaged as a cross without intrinsic features [14]. Here, we report on the direct observation of detailed electronic

structures of the molecule using the decoupling effect of a molecular buffer layer. The FePc monolayer on Au(111) substrate provides electronic decoupling to allow spatial variation of single electron states of individual FePc molecules to be studied. To verify that this is a generic effect, and not a feature of only one particular system, experimental observations were also conducted on another molecular system, tetra-*tert*-butyl Zinc Phthalocyanine ((*t*-Bu)₄-ZnPc) on Au (111).

2. Experimental and calculation details

The experiments were performed with an Omicron low-temperature STM system with a base pressure of 1×10^{-10} mbar. The bare Au(111) surface was prepared by several cycles of Ar⁺ ion sputtering and annealing to 700 K. FePc and (*t*-Bu)₄-ZnPc (Aldrich, 98+%) were thermally evaporated at 540 K onto Au(111) surface held at 370 K, respectively. Subsequently, the sample was cooled down to 5 K. All the STM images were obtained at 5 K.

In order to gain a detailed understanding, the experimental STM results were compared to simulations based on density functional theory (DFT) calculations for single molecules. The Perdew–Wang exchange–correlation functional with generalized-gradient corrections [15], projector augmented waves (PAW) [16], and plane waves, as implemented in the VASP code [17] were used. The energy cutoff in the simulations was 400 eV, the structures were relaxed until the net force on every atom was smaller than 0.02 eV/Å. The highest occupied molecular orbitals were simulated by charge density contours, the constant current contours obtained by a tungsten tip were simulated with the bSKAN code [18].

* Corresponding author.

E-mail address: hjgao@iphy.ac.cn (H.-J. Gao).

3. Results and discussion

FePc is a typical planar metal-Pc molecule, which is composed of a flat Pc skeleton with an iron ion completely immersed in the central cavity, as schematically shown in Fig. 1(a) top. To determine the interaction between the molecules and the substrate, we constructed an Au(111) supercell model with four layers containing one FePc molecule. The optimized configuration shows that the distance between the molecule and the gold substrate is ~ 3.28 Å, indicating physisorption of the molecule, but no decisive changes of the molecular electronic structure due to hybridization of single electron states. The adsorption site of FePc on Au(111) is shown in Fig. 1(a) bottom. For comparison we also show a (tBu)₄-ZnPc molecule (Fig. 1(b) top) and its adsorption configuration on Au(111) (Fig. 1(b) bottom). Both molecules are composed of a similar frame of nitrogen and carbon atoms, their key differences are the chemical identity of the metal center and the (t-Bu) groups attached to the benzene rings. As seen in Fig. 1(a) and (b), these differences substantially change the appearance of the density contour of the highest occupied molecular state (HOMO). For FePc, the density contour remains fairly flat with the ligands at approximately the same height as the molecular center (Fig. 2(a)). For (tBu)₄-ZnPc the highest protrusion of the contour is at the position of the (t-Bu) attachments, while the molecular center appears as a depression. These differences will have implications for the appearance of the molecule in actual STM experiments. An isolated FePc (or (tBu)₄-ZnPc) molecule on top of an FePc (or (tBu)₄-ZnPc) monolayer interacts only weakly via van der Waals forces, and will be situated in a distance above the surface, where the charge background from the surface has decayed enough to become effectively zero. In this case the electronic structure of the molecule is expected to be close to its state in the vacuum.

Experimentally, a highly-ordered FePc monolayer has been fabricated by evaporating FePc molecules onto the Au(111) surface kept at 390 K [19], showing a commensurate superstructure with a square unit cell. The FePc molecules of the monolayer are imaged as a four-lobed “cross” structure with a central round protrusion, which is consistent with its chemical structure. It indicates that the FePc molecules are in a flat-lying geometry on the terraces. Fig. 3(a) shows

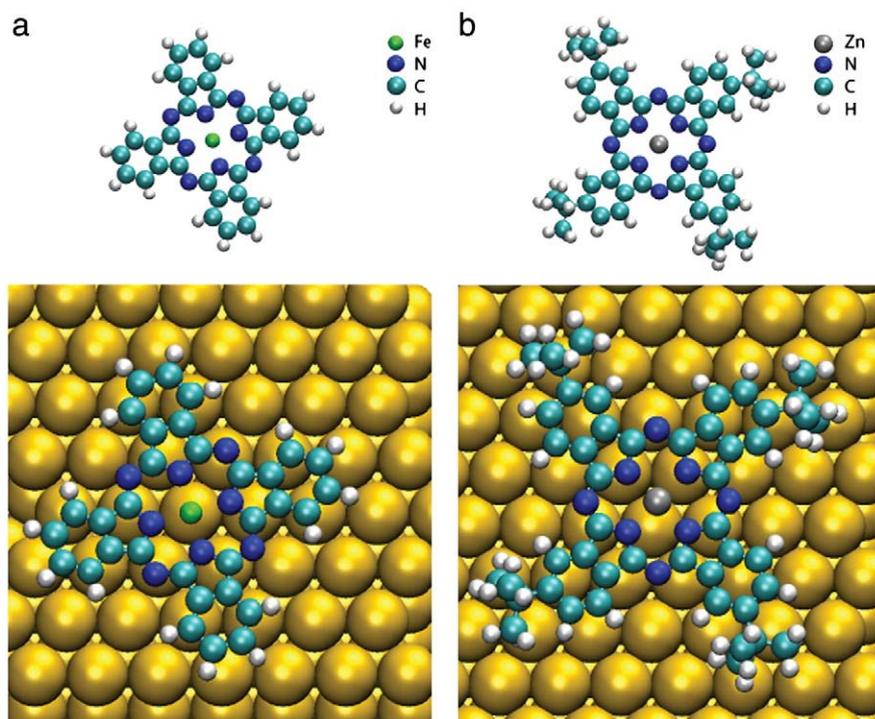


Fig. 1. Phthalocyanine molecules on Au(111). (a) FePc molecular structure (top) and adsorption configuration at the surface (bottom). The metal center of the molecule is adsorbed on top of an Au atom. (b) (tBu)₄-ZnPc molecular structure (top) and its adsorption configuration on Au(111). In this case the metal center of the molecule adsorbs at a bridge site.

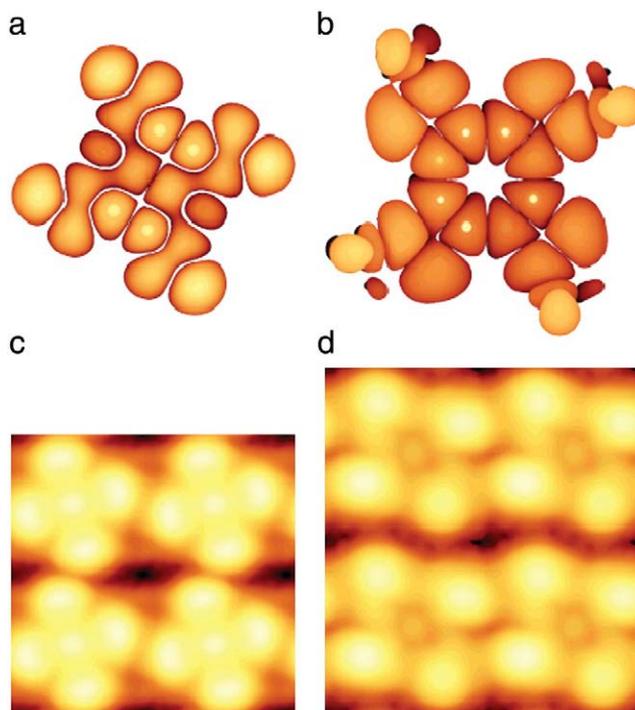


Fig. 2. Charge density contours and current contours. (a) and (c) show the charge density contour of the highest occupied electronic state of FePc (a), and the constant current contour (-2 V, 0.05 nA, four unit cells) of a simulated STM measurement using a tungsten tip (c). (b) and (d) show the corresponding state for (tBu)₄-ZnPc (a) and an equivalent constant current contour (-2 V, 0.05 nA, four unit cells), again using a tungsten tip in the simulations (d). While the simulated current contour for FePc is a cross (c), it corresponds to four distinct protrusions for (tBu)₄-ZnPc on Au(111).

a constant-current STM image of an isolated FePc molecule adsorbed on the well-ordered FePc monolayer on Au(111). In Fig. 3(b) it is seen that features within this molecule appear distinctly only on the FePc buffer layer.

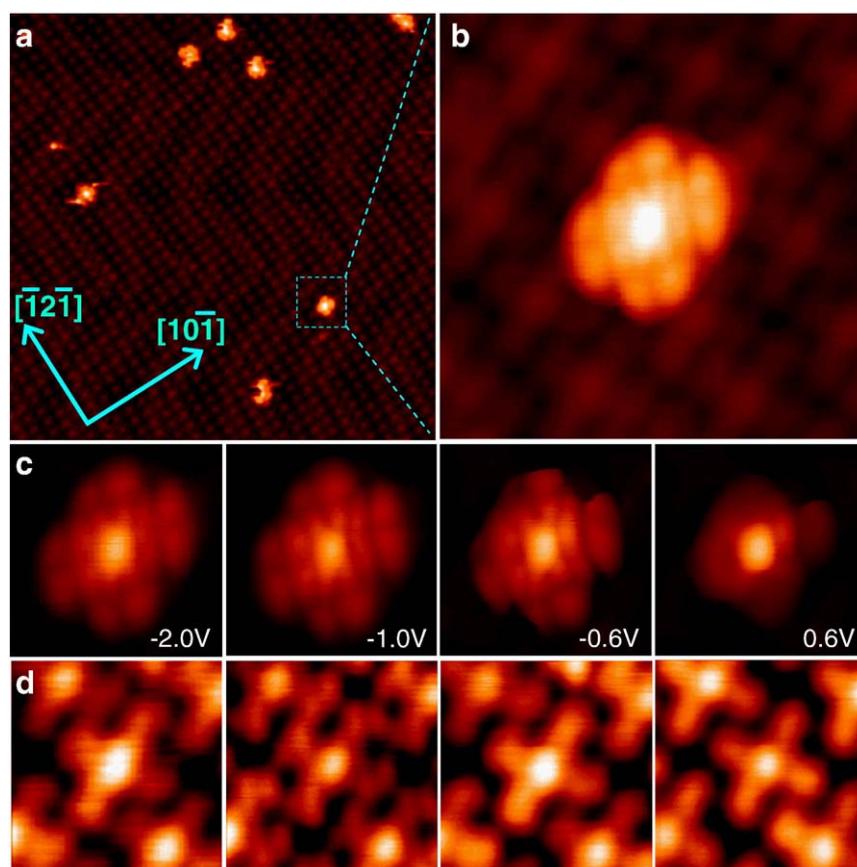


Fig. 3. (a) Large-scale STM image ($50 \text{ nm} \times 50 \text{ nm}$, $U = -2.0 \text{ V}$, $I = 0.05 \text{ nA}$, 77 K) of FePc molecules on highly ordered FePc monolayer on Au(111). (b) High-resolution STM image ($6 \text{ nm} \times 6 \text{ nm}$, $U = -2.0 \text{ V}$, $I = 0.05 \text{ nA}$, 77 K) showing the adsorption site and configuration of an isolated FePc molecule on the ordered FePc monolayer. (c) High-resolution STM images ($3 \text{ nm} \times 3 \text{ nm}$, $I = 0.05 \text{ nA}$) of the isolated FePc molecule adsorbed on the monolayer, taken at indicated sample biases. (d) The corresponding STM images ($3 \text{ nm} \times 3 \text{ nm}$, $I = 0.05 \text{ nA}$) of FePc molecule directly adsorbed on Au(111).

High-resolution bias-dependent STM images are shown in Fig. 3(c) and (d). Fig. 3(c) depicts an isolated FePc molecule adsorbed on the FePc monolayer, while Fig. 3(d) shows one FePc molecule within the buffer layer. The isolated FePc molecule on the monolayer exhibits spatially resolved internal structures at the indicated bias voltages; these internal structures are moreover bias-dependent. It should be noted that the internal structures at -2.0 , -1.0 V and -0.6 V are very similar, while the images at -1.0 V are somewhat different. The internal structure at $+0.6 \text{ V}$ differs from those at negative bias voltages and is much less distinct. In case of molecules adsorbed directly on Au(111), no spatially resolved inner structures are observed at these bias voltages. The experiments reveal also that the FePc molecules within the first monolayer are imaged in a rather similar fashion by STM and nearly independent of the bias voltage applied. We attribute this fact to the influence of the metallic substrate. The only slight deviation from this rule is found at -1.0 V , as shown in Fig. 3(d). A comparison of STM images of the molecules within the buffer layer (Fig. 3(d)) and simulated scans with a tungsten tip (Fig. 2(c)) allows the conclusion that the experimental image is due to the convolution of molecular states and electron states of the metal substrate, which cannot be clearly distinguished in measurements or simulations with a tungsten tip. This result is in line with early STM simulations, which actually came to the conclusion that the spatial resolution of tungsten tips is rather poor [20].

This effect of an organic buffer layer on the resolution of the electronic structure can also be observed at other systems, such as $(t\text{-Bu})_4\text{-ZnPc}$ molecules on Au(111). Isolated $(t\text{-Bu})_4\text{-ZnPc}$ molecules are dispersed and separate on an ordered $(t\text{-Bu})_4\text{-ZnPc}$ monolayer on Au(111), as shown in the large-scale STM image of Fig. 4(a). The $(t\text{-Bu})_4\text{-ZnPc}$ molecules of the monolayer are imaged as a four-lobed structure with a central hole. The

four protrusions of one molecule show a rectangle, square or trapezoid due to the different substitution position of the *tert*-butyl groups on the benzene rings. Three $(t\text{-Bu})_4\text{-ZnPc}$ molecules with different shapes directly on Au(111) are outlined in Fig. 4(b). This image structure indicates a flat-lying geometry. No spatially resolved inner structures can be observed within the molecules of the first monolayer on Au(111). The adsorption configurations of $(t\text{-Bu})_4\text{-ZnPc}$ molecules on the first monolayer are clearly shown in the STM image of Fig. 4(c). It represents a roughly flat-lying geometry with molecular features not observed within the molecules adsorbed directly on Au(111). This proves that the elimination of the background charge from the surface, which prevents imaging of detailed molecular states, is not a special feature of any particular molecule/substrate system. Rather, it is a generic result whenever the states of a molecule are sufficiently far from the enveloping density of electrons at a metal surface. A comparison with simulated STM scans, shown in Fig. 2(d), is in good agreement with experimental data: the molecule in low resolution scans is imaged as four distinct protrusions. Only in high resolution scans on the buffer layer does the molecular appearance change to one close to the structure of the highest occupied orbital.

4. Conclusions

In summary, we have presented a proof that an organic molecular layer on a metallic substrate provides sufficient decoupling from the metal charge background to allow the inherent electronic properties of individual molecules to become visible in STM. In one example, FePc monolayers have been employed to decouple individual FePc molecules electronically from the Au(111) substrate. In this case the intrinsic electronic states of the free molecule are preserved and can

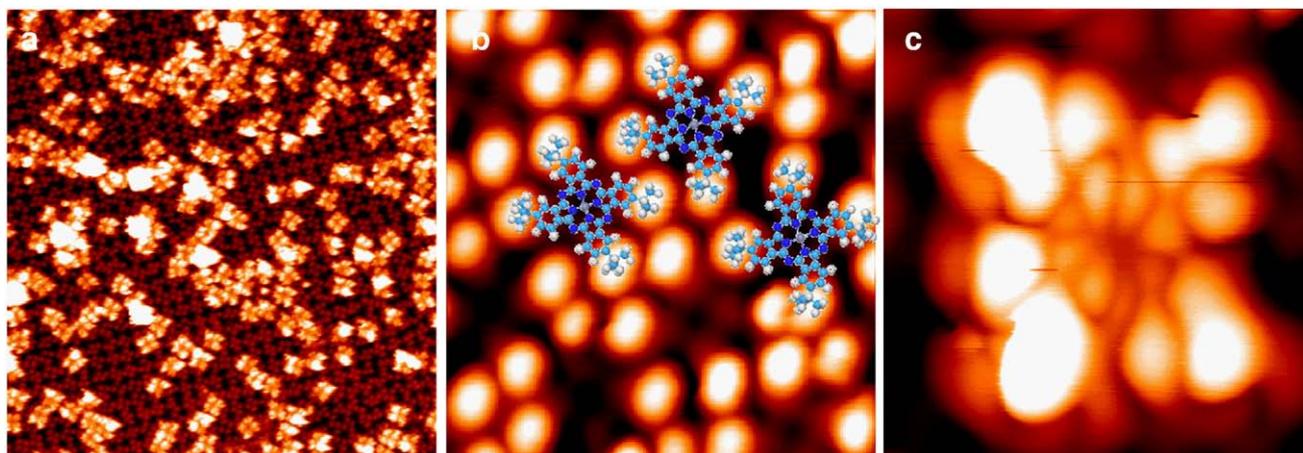


Fig. 4. Isolated (t-Bu)₄-ZnPc molecules adsorbed on the ordered (t-Bu)₄-ZnPc monolayer on Au(111). (a) Large-scale STM image (50 nm × 50 nm, $V = -2.0$ V, $I = 0.05$ nA) of the distribution of (t-Bu)₄-ZnPc molecules on the monolayer. (b) Close-up STM image (5 nm × 5 nm, $V = -1.9$ V, $I = 0.03$ nA) of the ordered (t-Bu)₄-ZnPc monolayer on Au(111) surface. (c) Close-up STM image (4.5 nm × 4.5 nm, $V = -1.9$ V, $I = 0.03$ nA) showing the intramolecular features of the (t-Bu)₄-ZnPc molecule on the monolayer.

be imaged. Because the surface charge spilled out into the vacuum vanishes for larger distances of the FePc molecule, its molecular states become visible. The corresponding STM image is interpreted as the HOMO of a single molecule, an interpretation verified by density functional theory calculations. This phenomenon is not system specific, as subsequent measurements for (t-Bu)₄-ZnPc showed. The effect is thus generic and can be generally employed to obtain a detailed analysis of a molecule's electronic structure.

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