

Tailoring the Mobility of a 3D Molecule Adsorbed on a Metal Surface

Tomaso Zambelli,* Jérôme Lagoute, Carlos J. Villagomez Ojeda, Christophe Coudret, and Sébastien Gauthier

Groupe Nanosciences, CEMES-CNRS, 29 rue Jeanne Marvig, F-31055 Toulouse Cedex, France

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Because of its tetrahedral structure, spirobifluorene is an innovative molecule for molecular mechanics studies by means of scanning tunneling microscopy. On Cu(100), it was observed only anchored at defects because of its mobility at room temperature. To frustrate its diffusion, it was functionalized with phenyl and thiophene groups. Tetraphenylspirobifluorene is also mobile on Cu(100), whereas tetrathienylspirobifluorene is fixed in the middle of the terraces. This very different behavior is an original and unexpected result because both benzene and thiophene are reported to be weakly bound to Cu(100) with almost the same adsorption energy.

Giving the possibility to observe, address, and manipulate molecules adsorbed on conductive substrates, scanning tunneling microscopy (STM) is pioneering the way toward monomolecular electronics.¹ STM investigations have been mostly focused on either planar molecules^{2–7} or molecules with a central planar core but equipped with vertical legs.⁸ Nevertheless, this flat geometry is responsible for a strong interaction between the molecule and the surface, modifying the electronic and optical properties of the adsorbed molecule. As palliative, it was recently proposed to coat metallic surfaces with ultrathin insulating films,⁹ exerting a decoupling function.^{10,11} An alternative strategy consists of using “three-dimensional” (3D) molecules so that a part of it is not directly interacting with the substrate whatever its adsorption geometry. In this perspective, we studied the adsorption of spirobifluorene (SbF, Figure 1a).

SbF is a promising object for molecular mechanics studies because of its rigidity and its aptness to be functionalized. It is constituted of two couples of benzene rings connected to a central carbon atom in sp^3 configuration. This structure together with the C–C bond between the two phenyl groups of every couple bestows rigidity on SbF, as was recently investigated by STM on Cu(111) at 5 K.¹² At the same time, its tetrahedral symmetry allows the molecule to be unavoidably adsorbed with three phenyl groups interacting with the surface and one remaining “free”, pointing toward the vacuum region (Figure 1b). This is an interesting aspect because SbF phenyls can be further functionalized by attaching another group to them. The group bound to the free phenyl would be consequently decoupled from the substrate, and for example, its mechanical behavior as a rotation around the bonding axis could thus be detected with the STM tip kept directly over it. Promising tetrahedral molecules were synthesized having an adamantane core with terminating carboxylic acids¹³ adapted for TiO_2 nanoparticles or a silicon atom core with terminating thiols adapted for gold surfaces¹⁴ but were not the object of STM studies.

We observed that SbF is very mobile at room temperature (RT). Molecular mobility is crucial for auto-organization

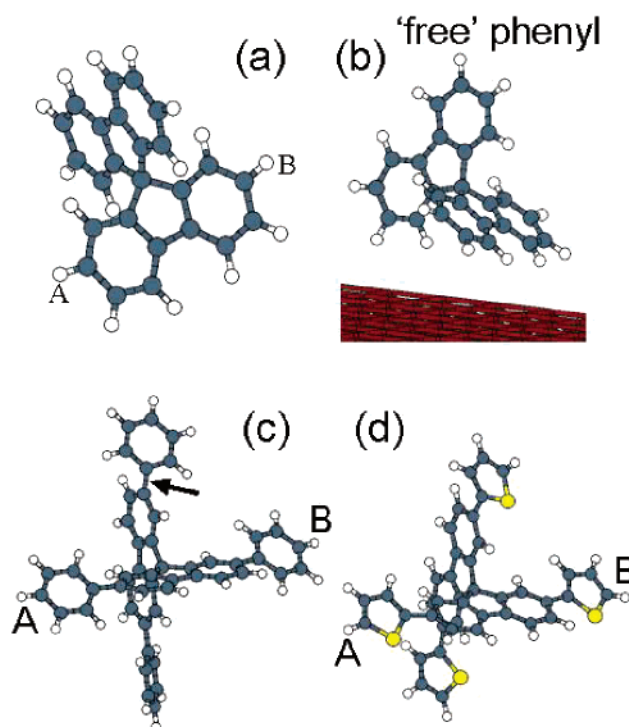


Figure 1. Ball-and-stick models of (a) spirobifluorene (SbF), (b) SbF adsorbed on Cu(100), (c) tetraphenylspirobifluorene (TPh), and (d) tetrathienylspirobifluorene (TTh). Configurations a, c, and d were optimized with the program Cerius 4.2 using a force-field procedure. The distance between hydrogen atoms A and B corresponds to 9 Å for SbF, to 17.5 Å for TPh, and to 16.3 to Å for TTh.

processes but becomes a hindrance when experiments are focused on the behavior of a single molecule. Because of their mobility, molecules cannot be observed on a flat terrace but only trapped by a defect. The presence of the defect is not straightforwardly taken into account in the calculations of the corresponding STM images, hampering the determination of the adsorption geometry from the comparison between experimental

* Corresponding author. E-mail: zambelli@cemes.fr.

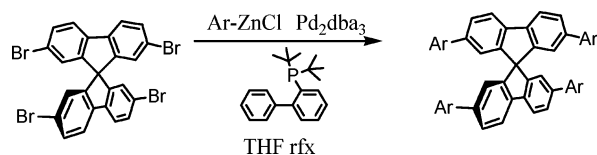


Figure 2. Synthesis mechanism of TPh and TTh (Ar = phenyl or thienyl aromatic group).

and calculated images. Moreover, molecular mobility forbids direct intervention on a chosen molecule for spectroscopic or manipulation experiments because the STM tip cannot be reliably positioned over the molecule. To frustrate the SbF mobility at RT, we explored the way represented by attaching phenyl or thiophene groups to SbF. The underlying idea is twofold: The appended groups (i) increase the contact area between the molecule and surface and (ii) strengthen the bond between the molecule and the metal substrate.

Concerning molecular adsorption on monocrystalline surfaces, functionalization is very current for investigations of self-assembled monolayers, carbon nanotubes, and fullerene. On the contrary, functionalization is only finding its beginning in ultrahigh vacuum (UHV) environments, not the least because of the problems related to the deposition of large organic molecules. Examples are the tetra-arylated porphyrins¹⁵ and the lander family,¹⁶ whereby functionalization consists of equipping a central core with lateral groups, or the wheelbarrow,¹⁷ whereby the whole molecule is conceived to exert a function once adsorbed on a surface. A very illustrative experiment was carried out by Yokohama et al.,¹⁸ whereby the lateral groups of porphyrins were substituted with cyanophenyl groups in order to tune their intramolecular interactions and thus their aggregation pattern. In this letter, we originally interpret functionalization as a way to adapt the physical properties of a molecule to the requirements of a scanning probe experiment at room temperature by modifying its mobility on a metal surface. We demonstrate that providing it with phenyl groups (TPh, Figure 1c) does not change its mobility significantly. On the contrary, thiophene groups (TTh, Figure 1d) completely block its mobility at RT. In this way, we add a contribution not only to the understanding of the interactions between metal surfaces and adsorbed large organic molecules but also to the future applications of this understanding for nanoscience.

SbF was obtained in three steps according to ref 15. TPh and TTh molecules were prepared following previously described strategies, starting from the readily available 2,2',7,7'-tetrabromospirofluorene using a Negishi coupling.¹⁹ Thus, the tetrabromo starting material was treated with the suitable commercially available arylzinc chloride, in refluxing tetrahydrofuran in the presence of a palladium catalyst, using a hindered phosphine²⁰ (Figure 2). Compounds were isolated by chromatography (phenyl groups) or by recrystallization (thienyl groups) and gave analyses consistent with the proposed structure (Ar/phenyl) or with published data²¹ (Ar/thienyl).

The UHV-STM system used for this study has already been described elsewhere.²² The Cu(100) sample (Surface Preparation Laboratory, Zaandam, NL) was cleaned by the usual cycling procedure of Ar⁺ ion sputtering (600 eV, 4 $\mu\text{A}/\text{cm}^2$) and annealing at 800 K. The three molecules were sublimated by heating a crucible with the sample positioned in front of it. As reported in ref 21, no molecular fragmentation was noticed with mass spectroscopy; hence, monodisperse adsorbates in the STM images could be interpreted as intact molecules. STM tips were obtained by electrochemically etching a tungsten wire (0.25 mm),²³ heated in situ to eliminate the oxide, and sharpened with Ne⁺ autosputtering.^{24,25} Since molecules were found agglomer-

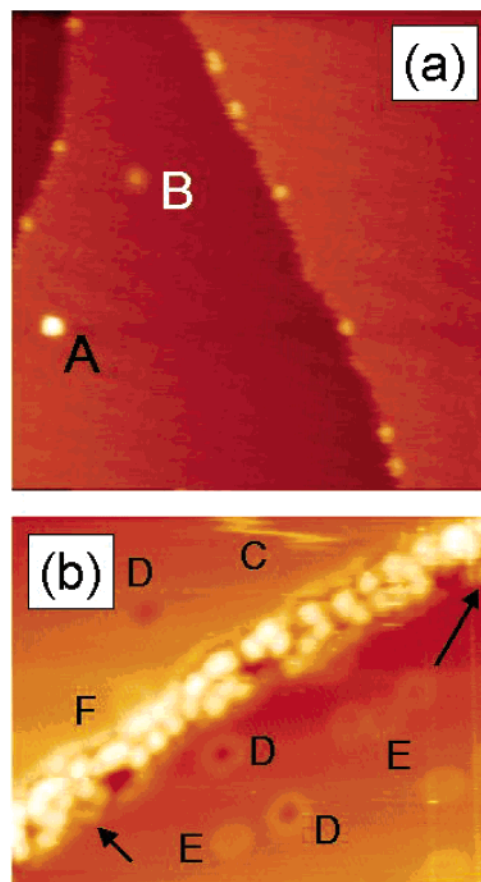


Figure 3. STM images of Cu(100) after the sublimation of 10^{-3} L and of 0.08 L of SbF, respectively: (a) 47 nm \times 47 nm, $I_t = 11$ pA, $V_{\text{bias}} = -2$ V; (b) 15 nm \times 11 nm, $I_t = 8$ pA, $V_{\text{bias}} = 3$ V.

ated in the scanned area at tunnel current values higher than 35 pA, low tunneling currents below 10 pA and high bias voltages from 2 to 4 V were necessary to keep the tip far away from the surface, avoiding uncontrolled manipulations. Both molecular sublimation and STM experiments were performed with the sample at RT. The presented STM images were processed only with subtraction of a least-squares-fit plane. No filtering procedure was applied.

Figure 3a shows a region with three terraces separated by two monatomic steps after the adsorption of a small amount of SbF. Molecules are imaged as white spots and are clearly located at the upper edge of the steps. The bigger spot A is not a SbF but an impurity. On the contrary, B also lying in the middle of a terrace is a SbF. Nevertheless, closer images show that it is anchored on a defect. SbF's are 2.8 ± 0.3 Å high and 10 ± 2 Å fwhm large. SbF's are imaged in a slightly fuzzy way. This is usually a sign of mobility. By comparing a sequence of images of the same area, we could actually observe that SbF's diffuse along the step edge. Figure 3b shows two terraces separated by a monatomic step after a higher exposure to SbF. SbF's form an irregular pattern along the upper edge of the step. Arrows indicate the first SbF trapped at the lower edges. Since SbF's completely decorate the edges of the steps, they cannot diffuse anymore along their edge; hence, they are no longer blurred but are imaged with a definite contrast. It must be noted that no SbF can be observed in the middle of the terraces yet. C is probably a SbF manipulated by the STM tip. A halo can be discerned around the impurities (D and E) and along the row of SbF at the step (F). Impurities D imaged as depressions are ascribed to sulfur atoms that are a known contaminant of copper crystals. Since they are not imaged surrounded by an halo before

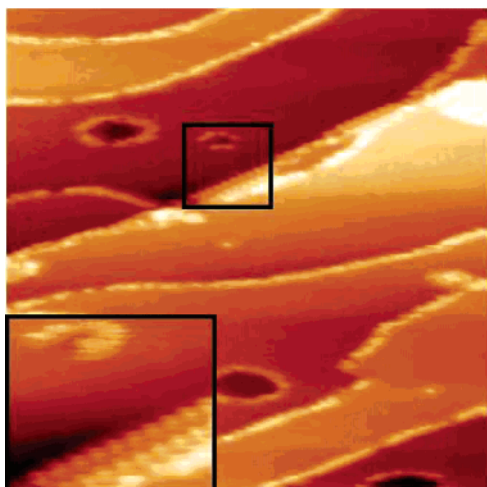


Figure 4. STM image of Cu(100) after the sublimation of 0.05 L of TPh. The vacancies in the middle of terraces were fabricated by gentle Ar^+ ion sputtering ($0.7 \mu\text{A}/\text{cm}^2$ for 30 s) to increase the step density. $100 \text{ nm} \times 100 \text{ nm}$, $I_t = 9 \text{ pA}$, $V_{\text{bias}} = 1.5 \text{ V}$.

SbF adsorption, we propose that halos originate by SbF trapped by the defect but with a mean dwelling time much shorter than that necessary to acquire a pixel (1 ms).

SbF's, which are only found trapped at monatomic steps or at defects in the middle of terraces, are mobile on Cu(100) at room temperature. To limit their mobility, they were functionalized with phenyl groups. Every phenyl group of TPh is connected with a phenyl of SbF through a C–C bond indicated with an arrow in Figure 1c. While the structure of SbF is supposed to be “rigid”, the added phenyls can rotate around the C–C axis and the same C–C bond can eventually be bent as it was already measured for the C–C bond connecting a conjugated board with a 3,5-(bis-*tert*-butyl)-phenyl leg.²⁶ The added phenyls may thus find a more stable configuration on the metal surface and TPh be less mobile than SbF.

In Figure 4, a large region of Cu terraces is imaged after sublimation of 0.05 L of TPh. All steps are decorated with a thin fuzzy white line. On the contrary, the detail shows a portion of steps where molecules are individually resolved. In light of images taken also at higher coverage, we interpret the fuzzy line as being due to TPh diffusing along the step edge. When their density becomes high enough to block their mobility, TPh's can be imaged one by one. However, we could not univocally establish whether they lie on the upper or on the lower edge of a step. We cannot also exclude that they straddle the step. No molecules could be found in the middle of the terraces. As for the SbF, it can be concluded that TPh's are mobile on Cu(100) at RT too. From experiments at higher coverage, we measured that TPh's are $5.0 \pm 0.4 \text{ \AA}$ high and $14 \pm 3 \text{ \AA}$ fwhm large, but these values are affected by the uncertainty that they were obtained from the profile of molecules arranged in an island.

Finally, SbF's were functionalized with thiophene groups. As the phenyls of TPh, every thiophene of TTh is attached with a phenyl of SbF via a C–C bond (Figure 1d). Rotation around the C–C axis and bending of the C–C bond can also occur to stabilize the adsorption energy of TTh on the Cu terraces.

Figure 5 shows a portion of four terraces separated by monatomic steps after the sublimation of 0.07 L of TTh. TTh's are imaged as protrusions $4.5 \pm 0.3 \text{ \AA}$ high and $15 \pm 2 \text{ \AA}$ fwhm large. The height of the imaged TTh's is not common; for example, C_{60} molecules having a diameter of 10.18 \AA are imaged between 3 and 4 \AA high when adsorbed on Au(110).²⁷ This is an important point: TTh's are still conductive enough

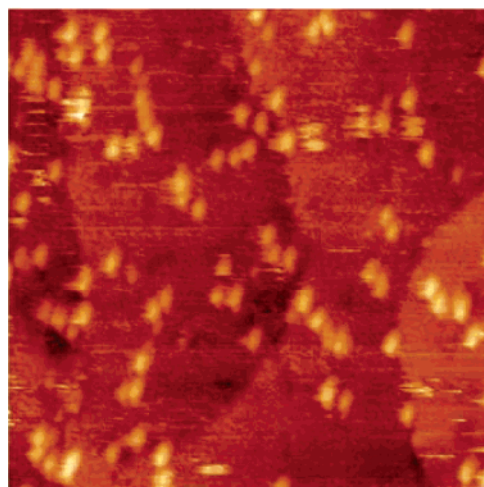


Figure 5. STM image of Cu(100) after the sublimation of 0.07 L of TTh. $45 \text{ nm} \times 45 \text{ nm}$, $I_t = 6 \text{ pA}$, $V_{\text{bias}} = 2.7 \text{ V}$.

so that the STM tip can follow their profile without sweeping them away from the scanned area.

The striking effect is that they are adsorbed not only at steps but also in the middle of the terraces and that they do not change their position in the time scale of an hour. Functionalization of SbF with thiophene groups thus provided the wished result of inhibiting the mobility at RT.

SbF has been the object of a parallel study with STM at 5 K on Cu(111) by Berndt's group in Kiel, Germany, focused onto its adsorption conformation and its self-assembly properties.¹² They found that SbF is very mobile on Cu(111) at RT too. Applying molecular mechanics, they proposed that SbF is physisorbed on Cu(111) with an adsorption energy of -1.36 eV and a diffusion barrier of 0.074 eV . Such a small value of the diffusion barrier may explain the high mobility of SbF at RT also on Cu(100).

On the contrary, the so different mobilities of TPh and TTh are surprising in light of the theoretical descriptions for the adsorption of benzene and thiophene on Cu(100).

Isolated benzene molecules have been imaged with STM on Cu(100) at very low temperature²⁸ but without measuring their diffusion. The first cluster calculations for benzene/Cu(100) were obtained by Triguero et al.: Benzene is found in a chemisorbed state, with the molecular plane parallel to the surface without important deformation.²⁹ Recently, Lorente et al. confirmed these results with *ab initio* density functional theory (DFT) evaluating an adsorption energy of -0.68 eV .³⁰ The energy was not calculated for tilted geometries.

No UHV-STM experiments about the adsorption of isolated thiophene molecules have been reported yet, but one has been reported on self-assembled films and Au(111).³¹ Recently, DFT calculations were published for the system thiophene/Cu(100).³² In accordance with experimental results by means of EELS and TPD³³ and of S K-edge XAFS,^{34,35} thiophene was reported to lie with its molecular plane parallel to the surface. The adsorption energy for this configuration is of -0.47 eV , whereas configurations tilted around the sulfur atom are still bounded weaker to the surface.

Since they interact with the surface only through phenyl and thiophene groups, respectively, TPh and TTh should hence be weakly bound on Cu(100) too. As the attached groups may be not perfectly parallel to the surface, TTh's possibly interact slightly stronger with the copper because tilted thiophene groups still interact with the surface via their sulfur atoms. For atoms and simple molecules adsorbed on metallic surfaces, it was

experimentally observed that the diffusion barrier is a fraction between $1/5$ and $1/10$ of the adsorption energy.³⁶ On the basis of this rule of thumb, TPh and TTh should hence exhibit a comparable mobility at room temperature. Nevertheless, TPh and TTh are not simple molecules because they interact with the surface at three separated sites. Since no trace of diffusing TPh's is observed in the pixels (corresponding to 1 ms) in the middle of the terraces, we estimate their dwelling time to be of the order of 10 μ s, whereas it is of 1 h for the TTh's. From the Arrhenius equation, a difference for the diffusion barrier of approximately 500 mV is derived. Such a different value of the diffusion barrier cannot originate from a different adsorption energy but from a different diffusion mechanism.³⁷ Thiophene groups are bounded to the copper surface mostly through the electrons of the sulfur atoms, whereas phenyl groups, through the delocalized electrons of the carbon atoms. For a molecule, it may cost more energy to break the three localized sulfur bonds than to slide on the phenyl groups.

In conclusion, spirobifluorene was functionalized first with phenyl and then with thiophene groups in order to inhibit its diffusion. TPh was also found to be mobile on Cu(100) terraces, whereas TTh was found fixed in the middle of the terraces. Functionalization with thiophene groups to immobilize molecules on copper surfaces is very promising because it is not restricted only to spirobifluorene but can be extended to other molecules.

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References and Notes

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- (37) We exclude that the different diffusion rates of TPh and TTh are due to a different interaction with the STM tip. If immobile TPh were swept away from the scanned area, a corresponding signal of pushed molecules would be noticed in the current signal and features such as C in Figure 3b would be recorded in the middle of the terraces.