PHYSICAL REVIEW B **77**, 085410 (2008)

Conformational change of tetrahydroxyquinone molecules deposited on Ag(111)

Mathieu Abel,* Vincent Oison, Mathieu Koudia, and Louis Porte
Aix-Marseille Université CNRS UMR 6242, IM2NP, campus Saint Jérôme case 142, 13397 Marseille cedex 20, France

(Received 8 October 2007; published 7 February 2008)

We report a joint experimental and theoretical study of the deposition of tetrahydroxyquinone (THQ) molecules on a Ag(111) surface. Scanning tunneling microscopy and low-energy electron diffraction experiments at room temperature reveal the formation of large two-dimensional domains composed of flat-lying molecules which match exactly with the surface network. Density functional theory calculations give evidence of an original self-assembly process in which the molecules have to change their conformation to self-assemble on the Ag(111) surface. The intermolecular and molecule-substrate interactions are studied by electron density topology. This reveals the formation of strong O-H$\cdots$O hydrogen bonds between adjacent molecules and Ag$\cdots$O bonds between molecule and substrate, inducing a large charge transfer from the surface to the lowest unoccupied molecular orbital of THQ.

DOI: 10.1103/PhysRevB.77.085410 PACS number(s): 68.43.Hn, 68.37.Ef, 68.43.Bc

I. INTRODUCTION

The growing interest in molecule-based miniature devices arises from the premise that collective optical and electronic properties can be systematically manipulated through molecular design.[1,2] Supramolecular aggregation can create spontaneously controlled structures thanks to selective and directional noncovalent interactions, such as van der Waals, hydrogen bonding, or metal center coordination. This approach, which has been widely exploited both in the solid state and in solution,[3] has been extended to create controlled self-assemblies of functional molecular species on well-defined surfaces in order to design novel nanoscale architectures.[4–7] Chemical synthesis allows us to obtain a large variety of functional organic molecules which interact by hydrogen bonds. These strong intermolecular interactions are used to control the two-dimensional architecture of the molecular thin films.[8–12] In a first approximation one would like to take advantage of supramolecular chemistry to predict the geometry of the molecular network simply from the molecule symmetry. In this study, we show that this simple supramolecular concept is not always sufficient to predict the molecular networks at surfaces. Herein the molecules are first adsorbed in their most stable conformation and then they transform themselves into a metastable conformer so that they can self-assemble. The prediction of such supramolecular aggregations on surfaces needs a detailed understanding of both molecule-molecule and molecule-substrate interactions.

This work focuses on the self-assembly of tetrahydroxyquinone (THQ) on Ag(111) surface. THQ consists in a phenyl ring with two carbonyl groups in para position and four hydroxyl groups around the phenyl. In its most stable conformation (conformation 0 in Fig. 1), the symmetry of the molecule is D_{2h}. Scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) experiments reveal that the deposition of THQ onto a Ag(111) surface gives a hexagonal molecular network hardly compatible with the D_{2h} symmetry. A theoretical study based on density functional theory (DFT) calculations shows how a conformational change of this molecule makes possible this hexagonal packing. DFT represents a unique tool for the analysis of molecular self-assemblies, in particular when hydrogen bonds are involved[11–13] and also for a realistic study of molecule-surface interactions.[14,15] Figure 1 shows the three different metastable conformers of THQ studied in this paper: conformations 1 and 2 are obtained by the rotation in the molecular plane of one or two hydroxyl groups (-OH), respectively. One can notice that conformations 0 and 2 are naturally present in three-dimensional molecular crystals and conformers obtained by the rotation of three or four -OH are definitely less stable due to strong hydrogen-hydrogen repulsion.[16]

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A. Experiments

Sample preparation and characterization were carried out in an ultrahigh-vacuum (base pressure 3×10^{-10} mbar) apparatus providing well-defined conditions for STM (VT-Omicron) and LEED (Omicron) experiments. The Ag(111) surface was cleaned by repeated cycles of Ar$^+$ sputtering and annealing at 750 K, which accounts for an atomically flat and clean surface. THQ molecules were deposited onto the substrate held at room temperature by organic molecular beam epitaxy (OMBE) from effusion cell evaporators. STM measurements were performed in the constant-current mode at room temperature, with bias voltage around 1.5 V and tunneling current around 0.4 nA. Post-processing was done using WSXM software.[17]

FIG. 1. (Color online) Representation of three THQ conformers: the energy loss with respect to the most stable structure (conformer 0) is 0.13 and 0.26 eV for conformers 1 and 2, respectively.

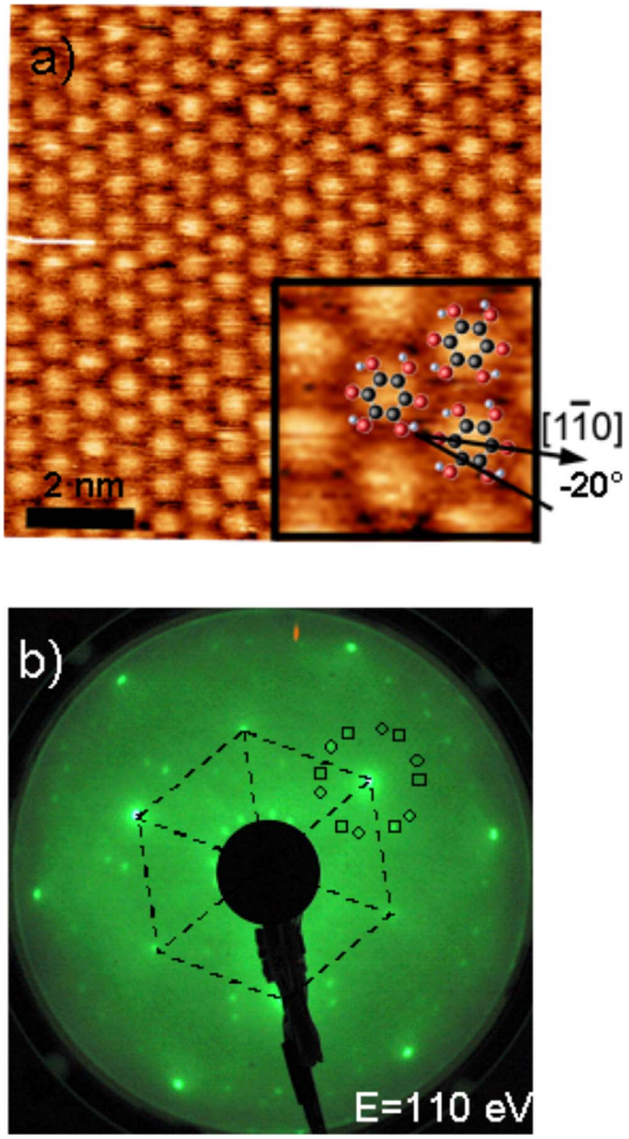

FIG. 2. (Color online) Structure of one monolayer film of THQ on Ag(111) (a) STM image (10 nm × 10 nm) of the regular hexagonal structure of THQ rotated by -20° with respect to the [1-10] direction, the inset is 2 nm large. (b) LEED pattern recorded at an electron energy of 110 eV. The dashed line represents the Ag(111) pattern; circles and squares represent $(\sqrt{7}\times\sqrt{7})R20^\circ$ and $(\sqrt{7}\times\sqrt{7})R\text{-}20^\circ$, respectively, with some extinction.

B. Calculations

Electronic structure calculations were performed within the framework of density functional theory using both SIESTA (spanish initiative for electronic simulations with thousands of atoms) (Refs. 18 and 19) and PAW (projector augmented wave) codes.[20] The exchange-correlation energy is treated within the generalized gradient approximation (GGA) using a parametrization proposed by Perdew, Burke, and Ernzerhof.[21] When using PAW, the wave function of the valence electrons is expanded in a plane-wave basis set with a cutoff energy of 40 Ry. For the calculations using SIESTA, the wave function of the valence electrons is expanded in a localized basis set consisting of finite-range pseudoatomic orbitals:[22] a double-ζ basis set was used for each atom. The core electrons are treated within the frozen core approximation with norm-conserving Troullier-Martins pseudopotentials.[23] The utilization of a basis set of atomic orbital requires one to take into account the basis set superposition error (BSSE) for cohesive energy calulations.[24] Moreover, the parametrization of the atomic orbitals used in the SIESTA code was checked carefully by comparison of of numerous calculations using SIESTA and PAW codes. In all the calculations, the Ag(111) surface was simulated using a slab of six Ag layers. The first three layers were fixed in the bulk geometry and the last three (i.e., the surface) could fully relax. We used a $4\times4\times1$ k-mesh grid: four k points along each direction of the reciprocal space of the molecular packing and one k point along the [111] direction of the substrate.

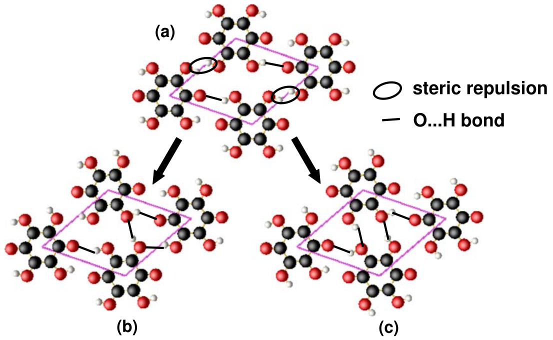

FIG. 3. (Color online) Representation of the two-dimensional self-assemblies of THQ molecules (a) in conformation 0, (b) in conformation 1, and (c) in conformation 2. O-H···O bonds are represented by black lines and steric repulsion between hydrogen are materialized by circles.

III. RESULTS AND DISCUSSION

A. STM and LEED analysis of the first monolayer

The deposition of one monolayer of THQ molecules on the Ag(111) surface results in two equivalent structures consisting of regular hexagons of side 7.6 Å rotated by ±20° with respect to the Ag(111) close-packed direction as determined by STM. The structure rotated by -20° is represented in the STM image in Fig. 2. These two structures are related by a mirror symmetry with respect to a plane perpendicular to the surface and passing through one of the close-packed directions of the substrate. LEED experiments evidence two unit cells: $(\sqrt{7}\times\sqrt{7})R20^\circ$ and $(\sqrt{7}\times\sqrt{7})R\text{-}20^\circ$ fully commensurable with the underlying silver hexagonal lattice. These two molecular patterns are represented in Fig. 2(b) by circles and squares, respectively, with some extinctions due to interferences. As shown in Fig. 2(a) the molecules are adsorbed in flat-lying configuration with their phenyl ring parallel to the substrate in round-shaped islands of one monolayer thick. This isotropic shape is unexpected since the symmetry of the most stable THQ conformer is D_{2h} and should not give a network of D_{3h} symmetry by hydrogen bonding between hydroxyl and carbonyl functional groups. We will demonstrate

TABLE I. Comparison between the three adsorption sites calculated for THQ molecules in conformation 0: the adsorption energies (E_{ads}) are compared to the most stable top site. The charge transfers are deduced from the Mulliken population analysis. *d* is the average distance between molecule and surface.

	E_{ads} (eV)	Charge CT (electrons)	d (Å)
Top	0.00	0.67	2.86
Hollow	0.14	0.49	3.18
Bridge	0.13	0.47	3.16

further that the formation of this two-dimensional (2D) network implies both a strong molecule-substrate interaction, leading to the commensurate epitaxial relation between the THQ monolayer and the Ag(111) surface, and the necessary conformational change of THQ molecule from the most stable conformer 0 to conformer 1 or 2, in order to increase the molecule-molecule interactions.

B. Intermolecular interaction

The intermolecular interactions were first simulated neglecting the influence of the substrate. The hexagonal symmetry was imposed in agreement with experiments. Figure 3 represents the experimental unit cell with molecules positioned with conformations 0, 1, and 2, respectively. In conformation 0, the steric repulsion between hydrogen atoms of neighboring molecules (circles in Fig. 3) does not allow short-range interactions between molecules and consequently makes a compact two-dimensional arrangement strictly impossible. Then molecules can self-assemble as observed only if they change their conformation to conformation 1 or 2. The energy loss due to the rotation of one or two hydroxyl group (0.13 and 0.26 eV, respectively) is counterbalanced by the formation of four O-H···O bonds per molecule. Their lengths are comprised between 2.0 and 2.2 Å. They are responsible for a cohesive energy with respect to the most stable conformation 0 of 0.42 eV and 0.20 eV within conformations 1 and 2, respectively.[25] Such a large difference suggests that conformation 1 is preferred for self-assembly.

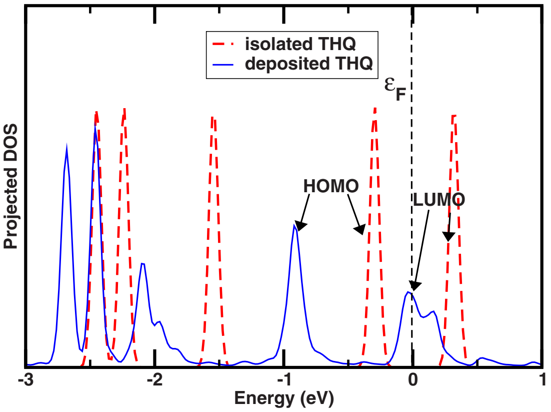

FIG. 4. (Color online) Densities of electronic states projected on valence atomic orbitals (i.e., on the 1*s* orbitals of hydrogen atoms and on the 2*s* and 2*p* orbitals of carbon and oxygen atoms) of the isolated THQ molecule (dotted line) and of the adsorbed molecules (solid line).

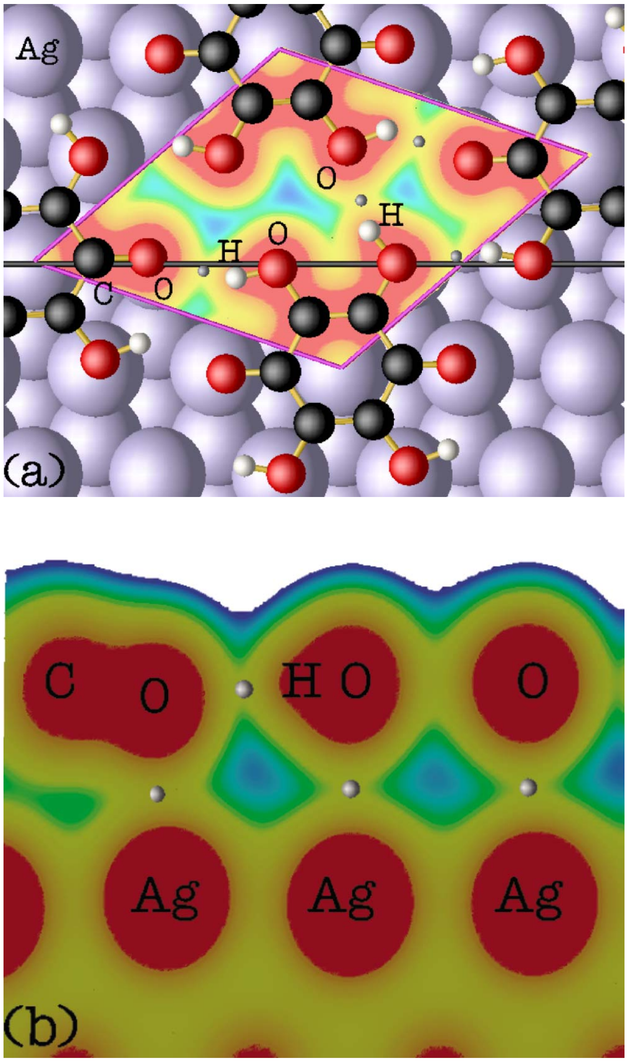

FIG. 5. (Color online) Electron density obtained from PAW calculations for the self-assembly of THQ adsorbed at top site: (a) in the molecular plane and (b) in the perpendicular plane cutting through it along the black line in figure (a). Intermolecular O-H···O and Ag···O bond CPs are represented by tiny gray spheres. The isodensity values increase from 0.013e^- Å^{-3} (blue isoline) to 0.67e^- Å^{-3} and more (red isoline): the yellow isoline corresponds to the isovalue 0.07e^- Å^{-3}.

C. Molecule substrate interaction

The influence of the substrate on the self-assembly process is determined by the comparison of three adsorption sites (top, bridge, and hollow), the center of the phenyl group being located at either top, bridge, or hollow site (Table I). In all cases, the geometry of the molecule corresponds to the conformation 0 but there is no influence of the conformation on the adsorption since the hydrogen atoms are not involved in the adsorption process. The two carbonyl bonds of the molecule are aligned with one of the close-packed directions of the substrate. This alignment was checked to be the most favorable orientation. The reference energy (0 eV) is attributed to the top site, which is energetically more favorable by over 0.1 eV than the two other adsorption sites (hollow and bridge). Thus, we can conclude that the molecules are adsorbed on the top site of the Ag(111) surface as represented in Fig. 5(a), below. In this configuration, all six oxygen atoms are located on top of an Ag atom and form Ag⋯O bonds. The formation of these bonds induces a distortion of the molecule: the distance between the oxygen atoms of the carbonyl (hydroxyl) groups and the substrate is shorter by 0.22 Å (0.11 Å) than the distance between the carbon atoms of the phenyl group and the surface. When THQ is adsorbed at the bridge site or hollow site, the oxygen atoms are not located on top of Ag atoms, and thus the Ag⋯O contacts are very weak. Consequently, the geometry of the molecule is almost planar and the average distance between the molecule and the surface is longer: 3.2 Å instead of 2.9 Å when THQ is adsorbed on top site. The adsorption process is associated with a charge transfer (CT) from the surface to the molecule, which plays the role of electron acceptor, which amounts to $0.7e^-$ at the top site instead of $0.5e^-$ at both the other sites. The projected density of states of Fig. 4 reveals that charge transfer results from a partial filling of the lowest unoccupied molecular orbital (LUMO) of the molecule, which is mainly localized on the $2p$ states of the oxygen and carbon atoms. This charge transfer mechanism is very close to the one reported in the case of the adsorption of NTCDI on Ag(110) (Ref. 15) or PTCDA on Ag(111) (Ref. 14). On the whole, adsorption on the top Ag site, combined with the necessary conformation change of THQ molecules, perfectly explains the hexagonal commensurate epitaxy of the THQ monolayer revealed by STM and LEED experiments.

D. Analysis of the first monolayer of THQ adsorbed on Ag(111)

To fully describe the adsorption process we still have to make precise the mutual influence of molecule-substrate interactions on molecule-molecule interactions. Intermolecular bonds have been determined for the complete monolayer with molecules adsorbed in conformation 1 on top sites of Ag(111) using both SIESTA and PAW codes (Fig. 5). The topological analysis was performed following Bader's approach to electron densities, $n(\mathbf{r})$, given on 3D grids.[26,27] It allowed us, in particular, to characterize critical points (CPs) which correspond to the extrema of $n(\mathbf{r})$. At a bond CP, the value of the electron density $n(\mathbf{r}_{CP})$ is minimum along the bond direction and maximum in the perpendicular plane. Herein the value of $n(\mathbf{r}_{CP})$ was used in order to quantify the strength of the intermolecular contacts. As revealed by Fig. 5, the strengths of the intermolecular O-H⋯O and Ag⋯O contacts are similar because of very close electron densities (around $0.07e^-$ Å^{-3}) at the corresponding CPs. In comparison with the two-dimensional arrangement without substrate, the strength of the O-H⋯O bonds is weakened by less than 20%, due to the elongation of the corresponding bond lengths (less than 0.06 Å). The molecule-surface interactions are also affected by the intermolecular interactions. The molecules are less distorted and the average distance between molecule and surface increases from 2.86 to 2.95 Å, thus reducing the adsorption energy and the charge transfer. It finally emphasizes that the self-assembly of THQ molecules onto the Ag(111) surface results from balanced contributions of both molecule-molecule and molecule-substrate interactions.

IV. CONCLUSION

In summary, this STM and LEED study of the deposition of THQ molecules on Ag(111) surface revealed the coexistence of two domains of molecular self-assemblies related by a mirror symmetry and perfectly commensurable with the unit cell of the Ag(111) surface. The detailed DFT analysis of intermolecular and molecule-substrate interactions showed that molecules can self-assemble only if they change their conformation to a less stable conformer by the rotation of one O-H group. This allowed the formation of four O-H⋯O hydrogen bonds per molecule which were analyzed together with the molecule-surface interactions by electron density topology. The adsorption at the top site involved a large charge transfer from the surface to the LUMO of the molecule and the formation of Ag⋯O electronic contacts inducing a distortion of the molecule. Finally, the large molecule-substrate interaction leads to the formation of a perfectly commensurate molecular layer. Thus a detailed description of intermolecular and molecule substrate interactions is mandatory for supramolecular designs at surfaces.

ACKNOWLEDGMENTS

We thank M. Mossoyan, J. C. Mossoyan A. Bliek, and D. Catalin for helpful discussions and experimental support. Calculations were partially supported by Centre Informatique National de l'Enseignement Supérieur' (CINES-France). This work was supported by the "Agence Nationale de la Recherche" under Contract No. PNANO 06-0251.

---

*Mathieu.Abel@univ-cezanne.fr; mathieu.abel@im2np.fr

[1] T. Verbiest, S. V. Elshocht, M. Kauranen, L. Hellemans, J. Snauwaert, C. Nuckolls, T. J. Katz, and A. Persoons, Science **282**, 913 (1998).

[2] K. Ray, S. P. Ananthavel, D. H. Waldeck, and R. Naaman, Science **283**, 814 (1999).

[3] J. M. Lehn, Science **260**, 1762 (1998).

[4] J. V. Barth, G. Constantini, and K. Kern, Nature (London) **437**, 671 (2005).

[5] S. de Feyter and F. C. de Schryver, Chem. Soc. Rev. **32**, 139

(2003).

[6] G. Whitesides, J. Mathias, and C. Seto, Science **254**, 1312 (1991).

[7] J. V. Barth, Annu. Rev. Phys. Chem. **58**, 58 (2007).

[8] J. V. Barth, J. Weckesser, C. Cai, P. Günther, L. Bürgi, O. Jeandupeux, and K. Kern, Angew. Chem., Int. Ed. **39**, 1230 (2000).

[9] S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, E. Delvigne, N. Lin, X. Deng, C. Cai, J. Barth, and K. Kern, Nat. Mater. **3**, 229 (2004).

[10] J. A. Theobald, N. Oxtoby, M. Phillips, N. R. Champness, and P. Beton, Nature (London) **424**, 1029 (2003).

[11] M. Abel, V. Oison, M. Koudia, C. Maurel, C. Katan, and L. Porte, ChemPhysChem **7**, 82 (2006).

[12] V. Oison, M. Koudia, M. Abel, and L. Porte, Phys. Rev. B **75**, 035428 (2007).

[13] V. Oison, Surf. Sci. **601**, 1040 (2007).

[14] A. Hauschild, K. Karki, B. C. C. Cowie, M. Rohlfing, F. S. Tautz, and M. Sokolowski, Phys. Rev. Lett. **94**, 036106 (2005).

[15] A. Alkauskas, A. Baratoff, and C. Bruder, Phys. Rev. B **73**, 165408 (2006).

[16] Cambridge crystallographic database.

[17] Computer code WSXM, Nanotech Electronic (http://www.nanotech.es).

[18] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J. M. Soler, Int. J. Quantum Chem. **65**, 543 (1997).

[19] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).

[20] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[21] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[22] J. Junquera, O. Paz, D. Sánchez-Portal, and E. Artacho, Phys. Rev. B **64**, 235111 (2001).

[23] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[24] H. B. Jansen and P. Ros, Chem. Phys. Lett. **3**, 140 (1969).

[25] The cohesive energy is the difference between the energy of the isolated molecule in conformation 0 and the energy of the 2D molecular structure in conformation 1 or 2.

[26] R. F. W. Bader, *Atoms in Molecules: A quantum theory, The International Series of Monographs on Chemistry* (Clarendon Press, Oxford, 1990).

[27] C. Katan, P. Rabiller, C. Lecomte, M. Guezo, V. Oison, and M. Souhassou, J. Appl. Crystallogr. **36**, 65 (2003).