

A combined experimental and theoretical study of 1,4-bis(phenylethynyl)-2,5-bis(ethoxy)benzene adsorption on Au(111)

Mani Lokamani^{*,a,b,c}, Jeffrey Kelling^a, Robin Ohmann^{b,d}, Jörg Meyer^b, Tim Kühne^e, Gianarelio Cuniberti^b, Jannic Wolf^f, Thomas Huhn^f, Peter Zahn^c, Francesca Moresco^e, Sibylle Gemming^g

^a Department of Information Services and Computing, Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Bautzner Landstraße 400, Dresden 01328, Germany

^b Institute for Materials Science, Technische Universität Dresden, Dresden, 01062, Germany

^c Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Bautzner Landstraße 400, Dresden 01328, Germany

^d Department Physik, Universität Siegen, Walter-Flex-Straße 3, Siegen 57072, Germany

^e Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany

^f Department of Chemistry, Universität Konstanz, Konstanz 78457, Germany

^g Institute of Physics, Technische Universität Chemnitz, Chemnitz 09107, Germany

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ABSTRACT

The electronic and geometrical structure of 1,4-bis(phenylethynyl)-2,5-bis(ethoxy)benzene (PEEB) molecules adsorbed on a Au(111) surface is investigated by low temperature scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) in conjunction with density-functional-based tight-binding (DFTB) simulations of the density of states and the interaction with the substrate. Our density functional theory calculations indicate that the PEEB molecule is physisorbed on the Au(111) substrate, with negligible distortion of the molecular geometry and charge transfer between molecule and substrate.

1. Introduction

In recent times, conjugated oligomers and polymers have gained considerable interest due to their photo physical properties. Many molecules with pi-conjugated backbones have been reported in the literature [1], e.g. phenylenes, phenyleneethynylenes and thiophenes, exhibiting photo electrical properties which render them suitable candidates for solar cells, display applications and flexible electronics. What makes these conjugated molecules interesting is the fact that the photo electrical properties of these molecules can be engineered using functional groups to modify the conjugated pi-backbone. Many studies involving experimental and theoretical techniques have confirmed and demonstrated the tunability of conductance properties of conjugated molecules via functional groups [2,3]. For example, functionalizing conjugated molecules with nitro groups may induce a negative differential resistance behavior in the conductance properties [4]. Apart from the tunability of the electronic properties of conjugated molecules, the effect of the interaction of the molecules with the surroundings has also been the focus of many experimental and theoretical studies [5–8]. The

interaction between organic molecules and inorganic substrate at the atomic level plays a crucial role in the device characteristics. It is essential to understand the underlying mechanism of such interactions in order to design and synthesize new molecules with enhanced functionality and stability for organic electronic devices [9]. Commonly, the Tersoff-Hamann approach is employed to analyse STM and STS data by first-principles calculations [10]. Its applicability has been discussed controversially for molecules with strong coupling to the surface [11], but recent studies indicate that even subtle geometry details can be analyzed in weakly interacting molecules [12,13]. In this article, we present the results of a combined theoretical and experimental study of PEEB molecules deposited on Au(111). The electronic and geometric structure of the molecule on the surface is investigated using low-temperature STM in conjunction with DFTB [14] simulations of the density of states (DOS) and the interaction with the substrate. Our analysis reveals not only a negligible change of geometrical structure upon adsorption but also negligible charge-reordering and charge-transfer indicating that the PEEB molecules are physisorbed on Au(111).

* Corresponding author.

E-mail address: m.lokamani@hzdr.de (M. Lokamani).

2. Methods

2.1. Experimental setup

PEEB molecules were studied on the Au(111) surface with a LT-STM at a temperature of 5K under ultrahigh vacuum conditions ($< 10^{-10}$ mbar). The gold single crystal surface was cleaned by repeated cycles of Ne ion sputtering and subsequent annealing at 720K. The molecules were deposited from a Knudsen cell at 420K onto the Au(111) substrate which was kept at room temperature. After the deposition, the sample was transferred to the STM where it was cooled down. A bias voltage was applied between the sample and the tip. Differential conductance spectra and conductance maps were measured using lock-in detection with a modulation frequency of 833Hz and a modulation amplitude of 40mV.

2.2. Theoretical methods

We performed self-consistent DFTB simulations for geometrical and electronic structural properties as implemented in the program package DFTB+ [14]. The parameter set "auorg-1-1" has been utilized in all our calculations [15], which is an extension of the "mio-1-1" [16] parameter set. The "mio-1-1" set has been developed for organic molecules including O, N, C, H, and Au atoms and works well for conformational energies and geometries of H-bonded systems [17,18]. The "auorg-1-1" set is designed to describe optical excitations of thiolates on gold nanoclusters. The maximum angular momenta included in our calculations are: H:s, C:p, N:p, O:p, S:d and Au:d.

In order to model an isolated molecule and its adsorption geometries on the gold substrate, the unit cell was spanned using following lattice vectors: $a_1 = [28.85\text{\AA}, 0, 0]$, $a_2 = [14.43\text{\AA}, 24.985\text{\AA}, 0]$ and $a_3 = [0, 0, 25\text{\AA}]$. The Au(111) substrate was modelled using three layers ($10 \times 10 \times 3$) [7,19], which were kept fixed (see Figure S1 in supplements).

The relaxations were performed until the maximum force components reduced to $0.0001\text{eV}/\text{\AA}$. All structural relaxation calculations were performed using the conjugate gradient algorithm including the universal force field for dispersion corrections as implemented in DFTB+ [20]. The local density of states (LDOS) to simulate STM linescans was obtained by averaging over the energy range -0.11eV to Fermi level (E_F). The constant current images were evaluated using iso-surfaces with constant LDOS. The height of the iso-surfaces spanned over the xy-plane defines the simulated STM linescan.

3. Results

Experimental and Theoretical: Isolated Molecule + Adsorbed Molecule

The STM experiments reveal, that the adsorption of PEEB molecules occurs preferentially on the fcc-region of the reconstructed Au(111) surface. In Fig. 1 isolated PEEB molecules are observed as a collection of bright spots, which are associated with the phenyl rings and sidearms, as represented by the schematic overlay (refer to SI for preferred azimuthal orientation).

The relaxed geometry for the isolated PEEB molecule was calculated using DFTB+ (see Fig. 2). The PEEB molecule consists of a molecular backbone (MB) comprised of three phenyl rings each connected via a triply bonded alkyne ($C \equiv C$) unit and two functional oxy-ethyl groups (FG) attached to the central phenyl ring. The MB is indicated using the grey shaded area in the top view. The side chains are aligned symmetrically with respect to the MB. The relaxed geometries obtained using density-functional-based tight-binding plus (DFTB+) suggest that the molecule in the gas phase is planar (var $Z = 0.073\text{\AA}$ considering the carbon atoms of the molecular backbone only).

Both, the Kohn-Sham highest occupied molecular orbital (HOMO) at -5.04eV and Kohn-Sham lowest unoccupied molecular orbital (LUMO) at -2.61eV consist primarily of carbon bonding and anti-bonding

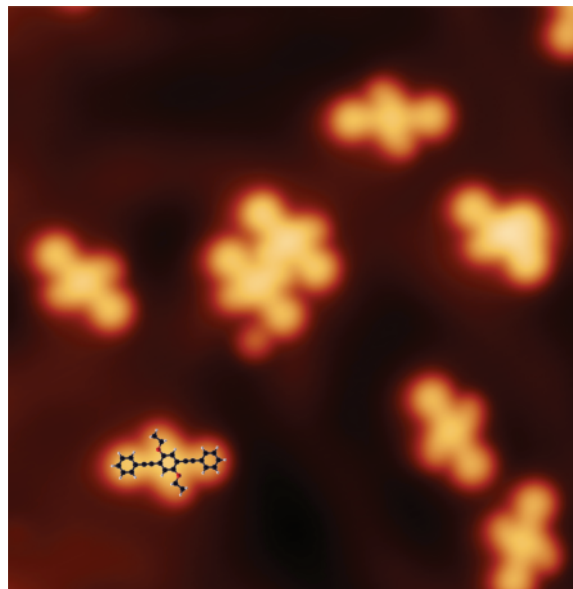


Fig. 1. STM images of PEEB adsorbed on Au(111) at low coverage (Image size: $10 \times 10\text{nm}^2$, $V_{\text{appl}} = -110\text{mV}$, $I = 120\text{pA}$). The schematic of PEEB resolves the bright lobes associated with individual phenyl rings and sidearms.

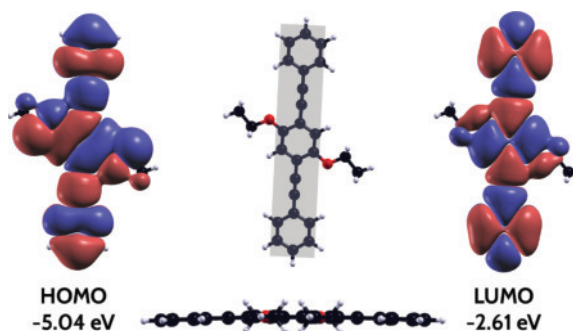


Fig. 2. Top and side view of a single PEEB molecule in the gas state. HOMO and LUMO are extended over the entire molecule. The grey shaded area indicates the MB.

orbitals, respectively, and contributions from the oxygen orbitals (lone pairs) of the functional groups (see Fig. 2). The extended HOMO is characterized by a nodal plane coinciding with the MB plane. The extended LUMO is, on the other hand, characterized by a sectioned four clover leaf form and two nodal planes over the phenyl rings along the MB. The calculated HOMO-LUMO gap amounts to 2.43eV using DFTB+. The experimentally measured HOMO-LUMO gap amount to 3.4eV for the family of molecules [21] very similar to PEEB suggesting that DFTB+ calculations tend to underestimate the size of the HOMO-LUMO gap for this molecule.

The preferential adsorption site for phenyl rings on metal(111) surfaces has been reported in the literature, mainly in studies on the adsorption behavior of organic molecules on metal surfaces using both wavefunction-based methods as well as density functional theory (DFT) [22,23]. Considering the molecular structure of PEEB comprised of three phenyl rings and the local 3-fold surface symmetry of Au(111) w.r.t. top, fcc-hollow and hcp-hollow sites and 2-fold surface symmetry of Au(111) w.r.t. the bridge-sites (see Figure 3), a preferred adsorption site for PEEB cannot be readily determined. In order to determine the global binding site for PEEB on Au(111), an adequate sampling of the configurational space incorporating the C_2 -symmetry of the PEEB molecule and the surface symmetry of Au(111) is imperative. The gold surface is modeled

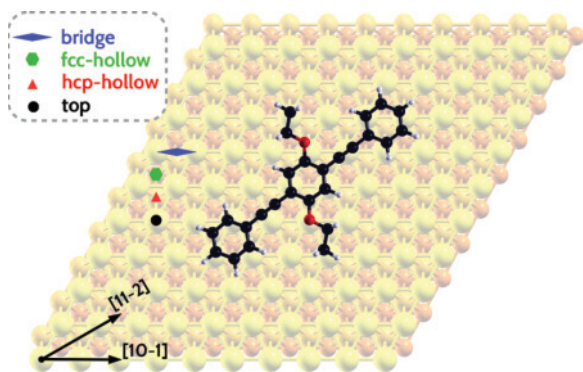


Fig. 3. The global binding site: The central phenyl ring lies staggered over an fcc-hollow and a bridge site. Peripheral phenyl rings lie over an hcp- and fcc-hollow site, respectively. The molecular backbone is rotated by 4.8° to $[11-2]$ direction. The bridge-, fcc-hollow, hcp-hollow and top-sites are shown schematically by a blue skewed diamond, green hexagon, red triangle and black circle, respectively.

using a $10 \times 10 \times 3$ cell of gold atoms with a Au-Au spacing of 2.855 \AA and is kept fixed during the relaxation. The configurational space is generated by placing the PEEB molecule in its isolated planar configuration, separated by a distance of 4.0 \AA from the top layer of gold. The central phenyl ring is aligned over the triangle formed by three adjacent metal atoms centered either on an fcc-hollow site or a hcp-hollow site. In addition, adsorption with the central phenyl ring over the Au-Au bridge and on top of an Au atom are investigated.

In order to determine the global binding site for a single PEEB molecule on Au(111), we sampled the configurational space in the following manner. Initially, the MB is aligned along the $[11-2]$ direction and is rotated counter clockwise in steps of 5° until 60° incorporating the 3-fold local symmetry of Au(111) w.r.t. the top, fcc-hollow and hcp-hollow sites. Configurations with the central phenyl ring placed over a bridge site are also included. In this case too, the MB is initially aligned along the $[11-2]$ direction but is now rotated in steps of 5° until 180° , in order to incorporate the 2-fold symmetry of Au(111) w.r.t. the bridge sites. The molecule is allowed to relax without any constraints.

The energetically most favorable binding site for a single PEEB molecule on Au(111) is shown in Fig. 3. The central phenyl ring lies staggered over an fcc-hollow and a bridge site. The remaining peripheral phenyl rings are adsorbed over an hcp- and an fcc-hollow site, respectively. The MB is inclined at an angle of 4.8° to the $[11-2]$ direction. The molecule exhibits a nearly planar geometry comparable to that of the isolated molecule. The average distance of the carbon atoms to the top gold layer amounts to 3.6 \AA . The variance of the separation of carbon and oxygen atoms to the top gold layer amounts to 0.024 \AA (Here, only carbon atoms of the molecular backbone were considered). The binding energy of a single PEEB molecule amounts to -0.78 eV (Also refer to adhesion energetics in the SI). The net electronic charge distribution of the PEEB molecule in the adsorbed state on Au(111) and is shown in Fig. 4 in units of $|e|$. The main redistribution occurs on the central phenyl ring (CPR) and the side arms. However, the charge differences per site are negligibly small with up to $0.006 |e|$. The total charge transfer from the molecule to the gold substrate amounts to 0.14 electrons. This suggests, that the molecule is physisorbed on Au(111).

4. Discussion: comparison of theory and experiments

4.1. Topography

Linescans performed over a single adsorbed molecule in the STM experiments are compared with the linescans calculated using DFTB at the E_F for the optimized geometry (see Fig. 5). Both the theoretical and the experimental linescans are performed across the MB over the side

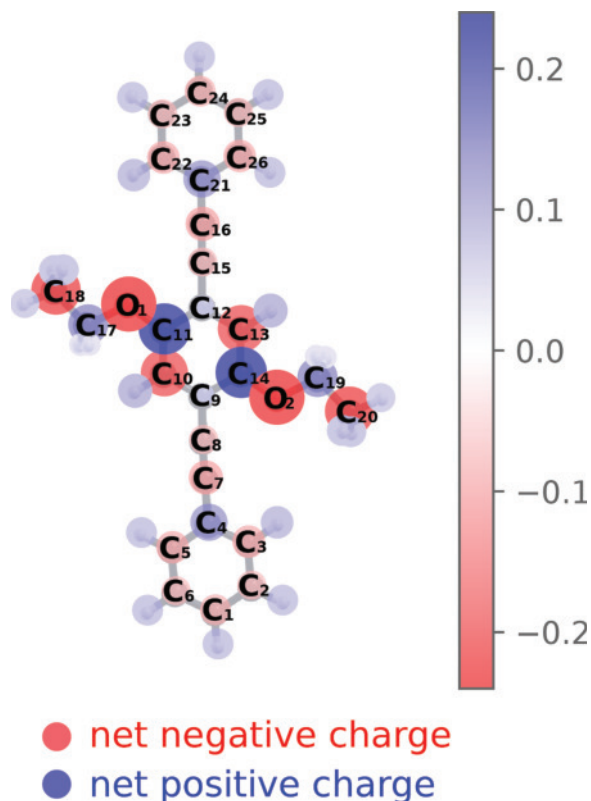


Fig. 4. The net electronic charge distribution on PEEB adsorbed on Au(111) at the global binding site. The red and blue circles represent net negative and net positive charge, respectively. Furthermore, the size of the circles corresponds to the amount of additional charge present on the atoms. Total charge transfer to the substrate amounts to $0.14|e|$.

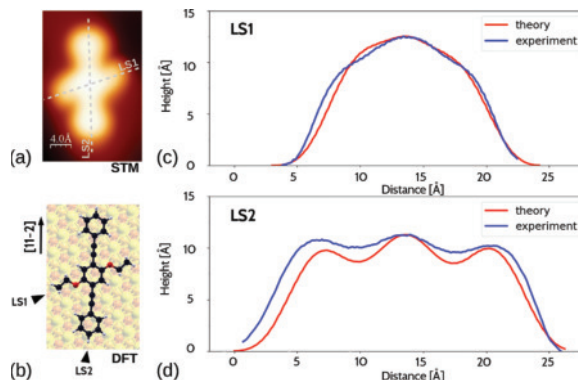


Fig. 5. Comparison of experimental and theoretical linescans (a) Experimental topographical image with linescans LS1 over the side chains and LS2 along the MB (grey dotted line). (b) Schematic of global binding site of PEEB on Au(111) and positions of linescans in DFTB simulations. (c,d) The experimental and theoretical linescans are differentiated using blue and red lines, respectively.

chains (LS1) and along the MB (LS2), respectively.

LS1 is characterized by a bell shaped curve with shoulders on the left and right corresponding to the positions of oxygen atoms of the side chains. The height of the central protrusion amounts to about 12.5 \AA . The exterior protrusions are not bilaterally symmetric: the right one is marginally higher than the left one. Although the side chains lie at about 0.25 \AA higher than the MB, in experimental linescans as well as in theoretical linescans the respective protrusions at a comparable height of 9 \AA , lie lower than the central protrusion belonging to the MB. This is due to the fact that the contribution of the states of the side chains to the

density of states (DOS) at E_F is considerably smaller than the contribution of the states of the MB (see Section IV B) linescan. LS2 is characterized by three distinct protrusions along the MB, with the central protrusion by the central phenyl ring being marginally higher than the exterior protrusions which belong to the outer phenyl rings. The theoretical linescan across the MB reflects quite well the behavior of the experimental result.

4.2. Electronic properties

The STS measurements were performed both on single molecules as well as on molecular clusters adsorbed on the bare Au(111)-surface. On applying bias voltages $|V_{\text{bias}}| > 1.3\text{V}$ the single molecules and the pairs tend to change their orientation and diffuse across the gold surface, due to the electron-induced mobility of the molecules [19,24]. Thus, spectroscopy measurements are not possible for single and cluster of molecules on Au(111). However, agglomerations of few molecules remained stable and could thus be successfully probed even upon applying bias voltages $|V_{\text{bias}}|$ as high as 2.5V.

The STS measurements on molecular clusters reveal two strong peaks: one at -1.3V and the other at +2.4V (see Fig. 6a). The spatial extent of these molecular resonances is visualized by 3 conductance spectra taken at the energy of the states (see Fig. 6(a) onset HOMO and LUMO). The state at positive voltages is most intense in the central region of the molecule. The state at negative voltages, that is in the region of occupied states, is strongly localized at the position of the side-groups. The latter is thus very important for the design of organic photo electrodes because it shows the specific influence of the side-groups on the electronic properties of the overall molecule.

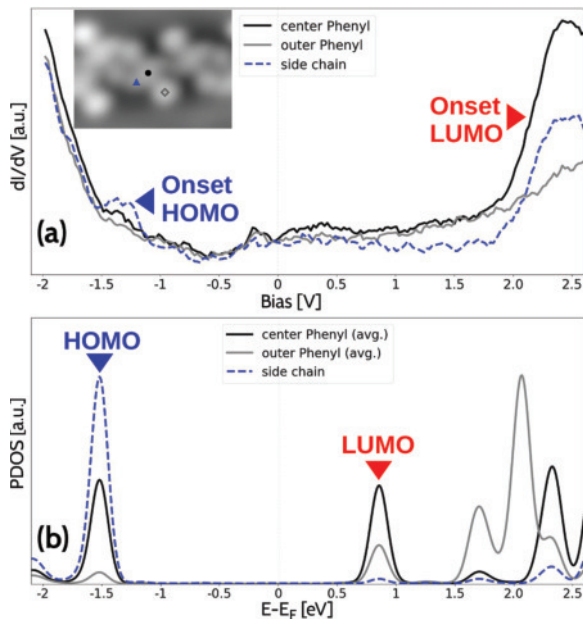


Fig. 6. (a) STS on central phenyl ring, outer phenyl ring and side chain are shown using black (thick), grey (thin) and blue (dashed) curves, respectively. The positions of the gold tip during STS measurements on the central phenyl ring, outer phenyl ring and side chain are shown using black dot, grey diamond and blue triangle, respectively, in the inset showing a mixed clustering. The onset of HOMO and LUMO emerges at -1.2V and +2.1V reaching a maximum at -1.3V and +2.4V, respectively. The experimental band-gap measures 3.7eV. [Inset: Topographical image measured at -0.1V and 50pA] (b) Calculated projected density of states (PDOS) for central phenyl ring, outer phenyl ring and side chain are shown using black (thick), grey (thin) and blue (dashed) curves respectively. HOMO and LUMO are located at approximately -1.51eV and +0.86eV, respectively. The theoretical band gap amounts to 2.37eV.

The PDOS shown in Fig. 6b reveals two strong peaks at -1.52eV and at +0.86eV which correspond to the HOMO and LUMO in STS measurements, respectively. Like the experimental HOMO peak, the theoretical HOMO peak is dominated by contributions from the side chains and the central phenyl ring. The contributions from outer phenyl rings are small. Likewise, the theoretical LUMO peak is dominated by the contributions from central phenyl ring as observed in the experimental LUMO peak. The calculated contributions of the outer phenyl rings however outweigh the contributions of the side chains, which does not coincide with the experimental observation. Furthermore, the shift in the energy of the theoretical LUMO peak towards the Fermi level reflects the problem that ground state Kohn–Sham DFT has describing the unoccupied states [25].

The calculated HOMO–LUMO gap amounts to 2.37eV which is significantly lower than the measured band-gap of 3.7eV.

5. Conclusion

In this paper, we have studied the electronic and geometrical structure of PEEB molecules adsorbed on the Au(111) surface using low temperature STM and STS measurements in conjunction with density functional theory based simulations. Our DFT based calculations indicate a net charge transfer of 0.14e to the substrate and an absolute charge transfer of less than 0.006 |e| per atom, implying that individual PEEB molecules are physisorbed on the gold substrate. The observed peak at -1.3V in STS measurements coincides quite well with the calculated PDOS peak at -1.56eV with good agreement of the dominant contribution from the side chains. The dominance of the central phenyl ring contribution in the HOMO derived peak can be confirmed by the calculations.

CRediT authorship contribution statement

Mani Lokamani: Conceptualization, Methodology, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. **Jeffrey Kelling:** Conceptualization, Methodology, Writing - review & editing. **Robin Ohmann:** Investigation, Writing - review & editing. **Jörg Meyer:** Investigation, Writing - review & editing. **Tim Kühne:** Data curation, Writing - review & editing. **Gianaurelio Cuniberti:** Writing - review & editing. **Jannic Wolf:** Resources. **Thomas Huhn:** Resources, Writing - review & editing. **Peter Zahn:** Conceptualization, Methodology, Visualization, Writing - review & editing. **Francesca Moresco:** Investigation, Writing - review & editing. **Sibylle Gemming:** Resources, Funding acquisition, Conceptualization, Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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