Physisorption of three amine terminated molecules (TMBDA, BDA, TFBDA) on the Au(111) Surface: The Role of van der Waals Interactions

Maral Aminpour¹, Duy Le¹, Adam Kiejna² and Talat S. Rahman¹

¹ Department of Physics, University of Central Florida, Orlando, Florida 32816
² Institute of Experimental Physics, University of Wroclaw, Pl M Borna 9, 50-204 Wroclaw, Poland

Abstract

Recently, the electronic properties and alignment of tetramethyl-1,4-benzenediamine (TMBDA), 1,4-benzenediamine (BDA) and tetrafluoro-1,4-benzenediamine (TFBDA) molecules were studied experimentally. Discrepancies were found for both the binding energy and the molecule tilt angle with respect to the surface, when results were compared using density functional theory calculations [1]. We have included the effect of vDW interactions both between the molecules and that of the molecule with the Au(111) surface and find binding energies which are in very good agreement with experiments. We also find that at low coverages each of these molecules would adsorb almost parallel to the surface. N-Au bond lengths and charge redistribution on adsorption of the molecules are also analyzed. Our calculations are based on DFT using vDW-DF exchange correlation functionals. For BDA (since we are aware of experimental data), we show that for higher coverage, inclusion of intermolecular van der Waals interactions leads to tilting of the molecules with respect to the surface and formation of line structures. Our results demonstrate the central role played by intermolecular interaction in pattern formation on this surface.

Introduction

1. Amin-terminated molecules are applied as single molecule electrical junctions. In particular 1,4-diaminobenzene (BDA) seems to be particularly useful as it provides less variation and hence better control in conductance than that observed for other linkers [2].

2. Experiment and DFT calculations [1]:

Experiment

<table>
<thead>
<tr>
<th>Molecule</th>
<th>TiL Angle [°]</th>
<th>Binding Energy [eV]</th>
<th>N-Au distance [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFBDA</td>
<td>34</td>
<td>-0.26</td>
<td>2.18</td>
</tr>
<tr>
<td>BDA</td>
<td>27</td>
<td>-0.26</td>
<td>2.18</td>
</tr>
<tr>
<td>TMBDA</td>
<td>27</td>
<td>-0.26</td>
<td>2.18</td>
</tr>
</tbody>
</table>

DFT

<table>
<thead>
<tr>
<th>Molecule</th>
<th>TiL Angle [°]</th>
<th>Binding Energy [eV]</th>
<th>N-Au distance [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFBDA</td>
<td>34</td>
<td>-0.26</td>
<td>2.18</td>
</tr>
<tr>
<td>BDA</td>
<td>27</td>
<td>-0.26</td>
<td>2.18</td>
</tr>
<tr>
<td>TMBDA</td>
<td>27</td>
<td>-0.26</td>
<td>2.18</td>
</tr>
</tbody>
</table>

The authors find good “agreement” for the tilt angle for BDA. The disagreement for the others was ascribed to the lack of vDW interactions in the DFT calculations.

Why would a symmetric molecule with a benzene ring adsorbs on Au(111) with a large tilt angle, while benzene itself prefers to align almost parallel to the surface?

Can PBE functional predict quantitatively reliable results for systems in which vDW interactions are expected to play a role?

Computational details

Simulations are carried out using Density Functional Theory

Code: QUANTUM ESPRESSO

Ultrasoft Pseudopotential


The Roman-Perez and Soler algorithm [5] is used to speed up the calculation.

Simulation model:

- Au(111) slab: 5 atomic layers of (4x4) and 3x1x1 surface unitcells parallel to surface.
- 17Å of vacuum
- Brillouin Zone: (3x3x1) uniform mesh of K-points for (4x4) substrate and (5x5x1) mesh for 3x1x1 substrate.

BDA Case: Interaction Energy Between Molecules

The PBE functional does not lead to a noticeable attractive interaction energy between the molecules, while vDW-DF show the formation of such an interaction with an energy of 70 meV.

Very interestingly, the interaction energy of two interacting BDA molecules separated by d0 is found to be maximum at 26° (vDW-DF). The difference in the interaction energy between 0° and 26° is as high as 620 meV (; 70 versus + 550 meV with vDW-DF).

References

[7] Prof. Tony F. Heinz Lab, Columbia University

For detailed information: