Molecules for organic electronics studied one by one

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The electronic and geometrical structure of single difluoro-bora-1,3,5,7-tetraphenyl-aza-dipyrromethene (aza-BODIPY) molecules adsorbed on the Au(111) surface is investigated by low temperature scanning tunneling microscopy and spectroscopy in conjunction with ab initio density functional theory simulations of the density of states and of the interaction with the substrate. Our DFT calculations indicate that the aza-BODIPY molecule forms a chemical bond with the Au(111) substrate, with distortion of the molecular geometry and significant charge transfer between the molecule and the substrate. Nevertheless, most likely due to the low corrugation of the Au(111) surface, diffusion of the molecule is observed for applied bias in excess of 1 V.

1 Introduction

Opto-electronically active organic materials offer several advantages over traditional solid-state semiconductors in the fabrication of devices such as solar cells and light emitting diodes including their low cost, low weight, and flexibility. Aza-BODIPY molecules have been known for more than 15 years and BODIPY derivatives have been recently investigated in more detail for applications as electron donor material for organic solar cells and their optical properties are presently optimized through the synthesis of new compounds. Here, we use difluoro-bora-1,3,5,7-tetraphenyl-aza-dipyrromethene; the same structure without the BF2 complex was originally synthesized in 1943 as a synthetic dye.

There are two key reasons for the interest in aza-BODIPY for applications in organic electronics, especially in solar cells. First of all, these molecules possess a tunable infrared absorption, and can convert a part of the incident light spectrum into electricity that only a few other currently existing organic compounds can. The second reason is their chemical stability, which eases processing requirements during solar cell production. There have already been other BODIPY derivatives incorporated in solar cell devices, but these lack the strong infrared absorption behavior of aza-BODIPY.

To better control the properties of the molecule in the final photovoltaic device, it is important to investigate the influence of different environmental factors on the absorption behavior and on the electronic properties of single molecular species or even single molecules. Several scanning tunneling microscopy (STM) and spectroscopy (STS) investigations of molecules which are of interest for organic photovoltaics have been reported in recent years, especially concerning metal phthalocyanines and fullerenes which currently serve as standard materials for photovoltaic heterojunctions, where phthalocyanines act as the electron donor and C60 as the electron acceptor.

Recently, research on the nature of the interaction between single organic dye molecules such as aza-BODIPY and inorganic substrates was reported, showing the relevance of such interactions to the development of dye-sensitized solar cells, which use an organic donor in combination with an inorganic acceptor. The understanding of the basic mechanisms governing the interactions between organic molecules and inorganic surfaces at the atomic level is essential for further progress in organic electronics, because it allows for the exploitation of the details of the molecular photo-physical properties as well as for the design of new molecules, which can enhance the functionality and stability of these devices.

In this article, we present the results of a combined theoretical and experimental study of single aza-BODIPY molecules deposited on Au(111). This is the first systematic, single molecule study of the adsorption behaviour of this class of molecules on any substrate. The electronic and geometric structure of the molecule on the surface is investigated using low temperature scanning tunneling microscopy (STM) in conjunction with ab initio density functional theory (DFT) simulations of the density of states (DOS) and of the interaction with the substrate.

2 Methodology

Experiments were performed by scanning tunneling microscopy (STM) and spectroscopy (STS) in ultra high vacuum.
(UHV) conditions (base pressure below $1 \times 10^{-10}$ mbar) at a temperature of $5\,\text{K}$. The STM is kept at $5\,\text{K}$ by thermal contact with a liquid He cryostat and it is completely shielded from radiation by a double screen. The cryogenic pumping preserves the sample surface uncontaminated for several days after preparation.

The Au(111) surface was cleaned by several cycles of sputtering and annealing at $450\,\text{C}$ followed by flashing to $550\,\text{C}$, forming a clean herringbone reconstruction. Aza-BODIPY molecules were evaporated from a Knudsen cell for a few seconds at a temperature of about $220\,\text{C}$ onto the clean Au(111) surface kept at room temperature. The sample was then transferred to the STM without breaking the vacuum. Images were taken in constant current mode typically at a bias voltage $V_{\text{bias}} = -0.5\,\text{V}$ and at a tunneling current $I = 0.1\,\text{nA}$. Voltages are applied to the sample with respect to the tip.

STS spectra were recorded by measuring the first derivative of the tunneling current ($dI/dV_{\text{bias}}$). After positioning the tip above a molecule and switching off the feedback loop, the bias voltage was varied over the energy range of interest with a sinusoidal modulation of about $20\,\text{meV}$. Using standard lock-in detection techniques, the first derivative of the tunneling current was extracted. Before measuring the STS spectrum on the molecule, STS spectra were recorded on the bare Au(111) terraces. Only those tips showing the Au(111) surface state preference for the fcc domains is known for many organic molecules. Nevertheless, by lateral manipulation we can easily move a single aza-BODIPY molecule from a fcc to a hcp domain and back without changing its conformation.

An enlarged STM image of a molecule is shown in Fig. 1(b). The aza-BODIPY molecule consists of a central BODIPY core and four phenyl rings attached and the carbon atom in the meso-position replaced by nitrogen, as shown in the schematic figure.

Fig. 1 Aza-BODIPY molecules adsorbed on the Au(111) surface. (a) Overview STM image showing several adsorbed molecules with different orientation (image size $284\,\text{Å} \times 152\,\text{Å}$). (b) STM image of a single aza-BODIPY molecule (image size $25\,\text{Å} \times 25\,\text{Å}$). (c) Simulated STM image generated from the local DOS (LDOS) at $-0.5\,\text{eV}$ calculated with DFT-LDA for aza-BODIPY on Au(111) (image size $19.2\,\text{Å} \times 19.2\,\text{Å}$). The fluorine atom on the other hand is...
not visible in the experimental images. This can be clearly seen by comparing the experimental line scans with the theoretical ones in Fig. 2(c,d). No significant differences in the STM images and line scans are observed by varying the tunneling conditions up to a voltage of about 1 V. However, when a bias voltage of $|V_{\text{bias}}| \geq 1$ V is applied, the molecule starts to diffuse and changes its orientation, as reported in the example of Fig. 3, thus limiting the possible range of STS measurements.

Typical STS spectra measured on the centre of aza-BODIPY molecules and on the bare Au(111) surface are shown in Fig. 4(a). The spectra recorded on the molecule show a single broad and intense peak centred approximately at $V_{\text{bias}} = 0.7$ V corresponding to unoccupied electronic states. Further spectra measured on different positions on the molecule, show similar results and indicate that the energy state observed at $V_{\text{bias}} = 0.7$ V is delocalized over the molecule.

4 Theory results

The relaxed geometry and orbital-resolved DOS were first calculated with DFT-LDA for the gas-phase aza-BODIPY molecule (see Fig. 5). Both the geometry and the electronic structure were found to be in good agreement with those obtained from calculations using B3LYP exchange–correlation functionals which gives adequate results for various organic molecules.34,35 According to both the LDA and GGA calculations described here, the two phenyl rings on either side of the F atoms are rotated at an angle approximately $21^\circ$ to the plane of the BODIPY core, while the rotation angle for the other two phenyl rings is approximately $15^\circ$. The Kohn–Sham highest occupied molecular orbital (HOMO) for the isolated gas phase molecule was found in the LDA calculations to have a value of $\epsilon_{\text{HOMO}} = 5.65$ eV. For exact Kohn–Sham DFT, $\epsilon_{\text{HOMO}} = -IP$, where $\epsilon_{\text{HOMO}}$ is the energy of the Kohn–Sham HOMO and $IP$ is the exact ionization potential.27,36 However, in practice, the value of the Kohn–Sham $-\epsilon_{\text{HOMO}}$ calculated using approximate exchange–correlation functionals such as LDA is typically several eV less than the true value for the ionization potential.37,38 The lowest unoccupied molecular orbital (LUMO) was calculated to have
an energy of $-4.40 \text{ eV}$, although as DFT is a ground state theory the unoccupied Kohn-Sham states do not have a physical meaning in the way that the occupied ones do. The ionization potential was measured experimentally using UPS to have a value of $5.62 \text{ eV}$ for a thin film,\(^3\) although the similarity of this result to the $-\varepsilon_{\text{HOMO}}$ value calculated with LDA is probably coincidental as the gas phase ionization potential would be expected to be somewhat larger than this. The LUMO energy was measured using cyclic voltammetry to have a value of $-4.01 \text{ eV}$.\(^3\) Therefore, DFT-LDA calculations tend to underestimate the size of the HOMO–LUMO gap for this molecule, which is a common problem with LDA calculations, and which needs to be taken into consideration when interpreting the results. Calculations with GGA gave values for the HOMO and LUMO energies of $-5.43 \text{ eV}$ and $-4.19 \text{ eV}$, respectively, and so give a similar sized HOMO–LUMO gap to LDA. For calculations with both types of exchange–correlation functionals, the orbital resolved DOS showed that both the HOMO and LUMO orbitals consisted primarily of carbon $\pi$ orbitals which are delocalized over the entire molecule, with a significant contribution also coming from the $\pi$ orbitals on the N atoms in the BODIPY core.

In order to simulate the situation in the STM measurements, the relaxed geometry for the molecule on a Au(111) surface was first calculated. The interaction with the surface results in the phenyl rings rotating, so that they are now in the same plane as the BODIPY core. The BODIPY core is slightly raised on the N atoms in the BODIPY core.

Concerning the STS experiment (see Fig. 4(a)) the strong peak observed at around $0.7 \text{ V}$ can be seen in the calculated DOS, although it is shifted towards the Fermi energy and is now centered around $0.2 \text{ eV}$ above the Fermi level. This error in the energy value for the LUMO is similar to that for the gas phase molecule which was also seen in other calculations, and again is most likely due to the inability of ground state Kohn-Sham DFT to reliably describe unoccupied states\(^4\) and the tendency of LDA to underestimate the HOMO–LUMO gap.\(^3\) Both the experimental and the calculated LDA LUMO resonances have similar widths, in the range of $0.4 \text{ eV}$ to $0.5 \text{ eV}$ at half maximum. Calculations with GGA produce a spectrum with narrower resonances due to the
weakened bonding to the substrate, in which the HOMO and LUMO are both shifted upward in energy by approximately 0.2 eV compared to the LDA results shown in Fig. 4(b), so that they are at approximately $-0.7$ eV and 0.5 eV, respectively.

During STM measurements, the molecule was observed to diffuse across the substrate when biases of greater than $\pm 1$ V were applied, limiting the measurement of STS spectra to values between $-1$ V and 1 V. In order to understand why the molecule was diffusing on the surface, the total energy differences of different adsorption positions were calculated, with the results shown in Fig. 6. These calculations show that the maximum energy difference between two sites is approximately 0.5 eV. The experimental results indicate that the energy transfer between the tunneling electrons and the molecule via inelastic scattering at an applied bias of the order of 1 V is sufficient to overcome this diffusion potential barrier.

The results of the DFT-LDA calculations suggest that the aza-BODIPY molecule is at least weakly chemisorbed on the Au(111) surface. The geometry of the molecule is significantly altered during the adsorption process, and the orbitals of the molecule are broadened in energy indicating hybridization with the Au states. This is somewhat surprising as Au(111) has a relatively low reactivity compared to other metallic surfaces. Other planar organic dye molecules such PTCDA only physisorb on Au(111),41 although they chemisorb on other metallic surfaces.41,42 In order to further investigate the nature of the interaction between aza-BODIPY and the Au(111) substrate, the net charge distributions (i.e. the difference between the molecular charge distribution and the superposition of the atomic charge distributions) were plotted for the molecule on the substrate as shown in Fig. 7. This function was also integrated over the Voronoi cell of each atom. Phenyl rings 3 and 5 are the lower phenyl rings, i.e. those on either side of the F atoms, and rings 1 and 7 are the upper phenyl rings, while the “BODIPY core” excludes the B and F atoms, which are shown separately. Charge differences are in units of the electronic charge $e$.

### Table 1

<table>
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<th>Molecule section</th>
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<td>Total</td>
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In this paper, we have studied the adsorption and the electronic properties of single aza-BODIPY molecules on Au(111). Our DFT-LDA results indicate that due to the charge transfer from the Au substrate to the aza-BODIPY molecule, the latter is chemically bound to the surface. The geometry of the adsorbed molecule is weakly distorted compared to the gas phase, assuming a slightly conical shape with the phenyl rings being rotated so that they are aligned almost parallel to the plane of the surface. The STS peak experimentally observed at $V_{bias} \approx 0.7$ eV primarily consists of carbon $\pi$ states broadened by the interaction with the substrate. However, it should be noted that it is possible that the LDA calculations are overestimating the extent to which the molecule is charged. While the peak in the calculated DOS straddles the Fermi level indicating that this orbital is partially occupied, the resonance in the experiments corresponding to this orbital is further from the Fermi level as shown in Fig. 4(a), and so probably contains less charge than would be suggested by the calculations.

### 6 Conclusion

In this paper, we have studied the adsorption and the electronic properties of single aza-BODIPY molecules on Au(111). Our DFT-LDA results indicate that due to the charge transfer from the Au substrate to the aza-BODIPY molecule, the latter is chemically bound to the surface. The geometry of the adsorbed molecule is weakly distorted compared to the gas phase, assuming a slightly conical shape with the phenyl rings being rotated so that they are aligned almost parallel to the plane of the surface. The STS peak experimentally observed at $V_{bias} \approx 0.7$ eV primarily consists of carbon $\pi$ states broadened by the interaction with the substrate. However, it should be noted that it is possible that the LDA calculations are overestimating the extent to which the molecule is charged. While the peak in the calculated DOS straddles the Fermi level indicating that this orbital is partially occupied, the resonance in the experiments corresponding to this orbital is further from the Fermi level as shown in Fig. 4(a), and so probably contains less charge than would be suggested by the calculations.
surface, with the F atom not being visible in the STM images due to the contribution to the DOS from the states on this atom being situated at \( \approx 3.5 \) eV below the Fermi level.

To overcome the actual limits of organic electronics in terms of functionality and stability, it is of fundamental importance to understand in detail the properties of the single molecules used in the devices and their interaction with substrates and other molecules. The present work is a first contribution in this direction. Further studies of model systems for organic electronics are planned, where in addition to the molecule-substrate interaction, the donor–acceptor interaction at the atomic level can open new pathways in the development of devices based on a few or even single molecules.

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**References**