Oxadiazole–Metal Interface: from Isolated Molecules to \( \pi \)-Stacking

Ki-Young Kwon,* Xing Lin, Greg Pawin, Kin Wong, and Ludwig Bartels

Pierce Hall, University of California—Riverside, Riverside, California 92521

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Derivatives of 2,5-diaryl-1,3,4-oxadiazole are used widely for electron transport in organic light emitting diodes (OLED). This study addresses the structure of 2,5-diphenyl-1,3,4-oxadiazole (PPD) molecules on Cu(111) using scanning tunneling microscopy (STM) and density function theory (DFT): at incomplete coverage, PPD molecules are found horizontally on the surface; once the surface area is insufficient to accommodate all adsorbates in this fashion, a \( \pi \)-stacked film of vertically arranged molecules is formed. In contrast to bulk PPD, in this film, the molecules are arranged face-to-face at a separation of \( \sqrt{3}a_0 = 4.4 \) Å as imposed by the substrate interatomic spacing along the [\(-2\ 1\ 1\)] direction.

Since the discovery of electroluminescence in poly(p-phenylenevinylene) (PPV), organic conjugated polymers have been intensively investigated for their potential in applications such as LEDs, photovoltaic cells, and field effect transistors. Their properties are governed by the band gap between valence and conduction bands, which are composed of delocalized \( \pi \)-bonding (\( \pi \)) and \( \pi \)-antibonding (\( \pi^* \)) orbitals along the polymer main chain. A crucial factor for the performance of a LED device is the efficiency of charge injection into conduction and valence band from the metal electrodes (typically, indium–tin oxide (ITO) at the anode, low work function metals or their alloys at the cathode). Electron injection into the conduction band is often more difficult than hole injection into the valence band for organic conjugated oligo- or polymers of p-type semiconducting behavior. This imbalance limits the efficiency of organic polymer-based LED devices.\(^3\) To improve the quantum efficiency of organic LEDs, efforts have been made to facilitate electron injection. One common strategy is the insertion of high electron-affinity materials either directly into the polymer chains or between the cathode and the emitting layer as an electron transporting (ET) layer.\(^2\) 2-(4-Biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) (Figure 1a) has been studied widely as an ET material (Figure 1b) has the simplest diaryl-oxadiazole, as a model compound. In the bulk, this species is planar (due to intramolecular hydrogen bonding) and exhibits a herringbone structure at an intermolecular spacing of 3.4 Å. \( \pi \)-Stacking at metal surfaces has been previously observed for species such as pentacene\(^{16,17}\) and perylene.\(^{18}\) Recently Wolkow’s

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* To whom correspondence should be addressed. E-mail: ki-young.kwon@email.ucr.edu.

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Figure 1. Molecular structures of PBD (a) and PPD (b).

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Figure 2. (a) STM image of PPD molecules at submonolayer coverage (90 × 90 Å, *I* = 75 pA, *V*₀ = −1.1 V, 16 K). (b) High-resolution STM image of a single PPD molecule (22 × 22 Å, *I* = 59 pA, *V*₀ = −0.6 V, 16 K). (c) Model of the lowest-energy planar adsorption configuration of PPD.

group showed that similar π-stacking can also be achieved by covalent bonding to a semiconductor surface utilizing a “self-directing” mechanism.19

Our experiments use two home-built beetle-type STMs that are each surrounded by two gold-plated thermal shields to prevent contamination and drift. Scanning was performed under ultrahigh vacuum condition (less than 1 × 10⁻¹⁰ Torr) at 16 and 80 K for submonolayer and monolayer coverage, respectively. Electrochemical etched tungsten wire was used for STM tips. The clean Cu(111) samples (Monocrystals and MaTecK GmbH) were prepared by several cycles of argon ion sputtering (up to 3 kV) and annealing (500 K). Sample cleanliness was ascertained by STM both at room temperature and at 80 K prior to thermal deposition of PPD. Dosing proceeded at 80 K sample temperature and involved exposure to 1 × 10⁻⁸ Torr for 20 s and 1.2 × 10⁻⁸ Torr for 30 s for preparation of isolated molecules and monolayer coverages, respectively.

Density functional theory calculations of the electronic and geometric structures and adsorption energy of PPD on Cu(111) were carried out using the generalized gradient approximation (GGA) for the exchange-correlation functional²⁰ and the plane-wave pseudopotential method.²¹ Ultrasoft pseudopotentials were used for all atoms in the system. The cutoff energy for the plane-wave expansion is taken to be 300 eV, and a 3 × 3 × 1 Monkhorst-Pack K-point mesh in Brillouin zone sampling is used to obtain converged results for the total energy of the system. During lattice relaxation, atoms were allowed to move along all directions. The structures and energies that are shown in this study result from relaxation of the forces acting on each atom to better than 0.02 eV/Å. All supercells contain three layers of substrate atoms. We estimate the relative uncertainty between calculated minimum energies to be ≈ ±15 meV, but we wish to caution that GGA occasionally underestimates the absolute binding energy in physisorbed systems.²⁴

Figure 2 shows STM images of a monolayer coverage (1 PPD molecule per 150 Cu atoms, i.e., ≈6.7 × 10⁻⁹ monolayers) obtained at 16 K. Oxadiazoole molecules appear as dumbbell shapes oriented parallel to the substrate high-symmetry axes. At closer inspection, the shapes appear as fanning out further to one side of their long axis than to the other, yet they retain mirror symmetry with regards to a plane normal to their long axis. In Figure 2a, the molecules are annotated according to the substrate high symmetry axis they are aligned with. Species indicated with a prime fan out to the right of the respective axis, whereas the remainder fan out to the left. The presence of both species in one image rules out that this feature represents a tip artifact. It rather indicates that the molecule is adsorbed coplanar to the surface as indicated in the high-resolution image of Figure 2b: the phenyl rings appear as bright protrusions, whereas the center five membered ring appears less prominent especially at the oxygen position. This resembles a recent report by the Chiang group, where they found that the oxygen atom of furan appear as an indentation of the ring.²²

We performed density functional theory (DFT) calculations of PPD on a 6 × 4 substrate atoms supercell. Minimization proceeded from a large variety of different initial configurations, and we found the adsorption configuration of Figure 2c to be the lowest in energy. Here the center heterocycle is placed almost symmetrically above a substrate atom and the molecule’s long axis is aligned with one of the substrate high-symmetry axes. This agrees well with the experimental observation. Inversion of the molecule with respect to the substrate high-symmetry axis results in an inequivalent adsorption configuration due to the lack of inversion symmetry of the substrate; our calculations show, however, that the energetic difference between the two configurations is only minute (i.e., the calculated value is 1 meV, far below the uncertainty of our calculations.). This is in good agreement with the experimental observation of equal distribution of the molecules between these two configurations (i.e., 88 vs 85 molecules in 25 STM images of different surface areas).

We wish to note that individual PPD molecules cannot be imaged by STM at 80 K presumably due to rapid diffusion. At temperatures below 40 K, their diffusive motion can be captured by STM, and below 25 K, their motion is frozen out. A detailed analysis of the diffusive behavior of PPD is, however, beyond the scope of this study. Thermally programmed desorption experiments find desorption of intact PPD from the multilayer at 250–280 K followed by two desorption peaks from the monolayer at 320 and 350 K, respectively. The previous section addressed the coverage associated with the latter; higher coverages will be discussed below. The absence of dissociative desorption is a further manifestation of the weak interaction of PPD with Cu(111).

If the coverage is increased beyond that of Figure 2, initially we observe formation of dimers, trimers, and larger islands of flat lying oxadiazole molecules. Once the surface area is insufficient to accommodate all molecules horizontally, a distinct surface pattern emerges, which can be imaged even at 80 K (Figure 3) presumably due to mutual blocking of diffusion. To generate a surface film as ordered as shown here, annealing to room temperature between deposition and scanning at 80 K is required.

The film of Figure 3 is governed by short (two–seven-members) sequences of molecules at $\sqrt{3}a_0$ (4.4 Å) separation. (Figure 3b). The sequences run in the [1 1 2] direction and repeat along the [7 4 3] direction. The sequences are terminated by what appears as dislocation lines running along the same [7 4 3] direction. Albeit the short sequence length and inconsistent number of molecules between dislocation lines, we find quite extended order on the surface: even across step-edges, the direction of the sequences and dislocations remains conserved. Figure 4 shows a model of this setup. Inside the sequences, the molecules are aligned with the substrate high-symmetry direction. Their spacing of $\sqrt{3}a_0$ is far too short to accommodate a horizontally adsorbed molecule. DFT calculations of the adsorption of molecules at the experimental spacing results in a vertical adsorption configuration with the nitrogen atoms placed symmetrically across the top of a substrate atom which aligns the molecule with the substrate high-symmetry direction (in good agreement with the experimental data). These calculations utilize a supercell encompassing two face-to-face adsorbed molecules.

If we choose a height close to the top carbon atom of the benzene rings (in order to minimize any substrate influence), a slice through the calculated charge density shows significant interaction between the $\pi$-systems of neighboring molecules (Figure 4, bottom). The resultant conduit of delocalized electron density has a high likelihood of providing good electron mobility along the $\pi$-stacking direction.

Figure 3. (a) STM image of a complete film of PPD molecules. The change in color represents a step-edge of the underlying substrate (320 by 237 Å, $I = 74$ pA, $V = -3.0$ V, 80 K). (b) High-resolution STM image of the same pattern showing the molecules lying side-by-side (100 by 46 Å, $I = 110$ pA, $V = -1.8$ V, 80 K).

To elucidate whether the molecules experience compressive stress in this configuration, we calculated the total energy of our supercell also for the cases (a) that every other of the $\pi$-stacked molecules is missing and (b) for the bare copper surface. The calculated difference in adsorption energy per molecule for the second compared to the first molecule per unit cell is $\approx 8$ meV, i.e., less than the error of our calculation, which suggests the absence of significant compressive strain in the $\pi$-stack. It is also consistent with the intermolecular separation of PPD in the bulk herringbone structure of 3.4 Å.

To conclude, we wish to point out that there have been a lot of efforts to create face-to-face $\pi$-stacking of extended aromatic molecules in the fields of organic thin film transistors (OTFT) and molecular wires in the hope of thus improving in-plane charge mobility. These efforts generally focused on introducing substituents into the molecules that may facilitate $\pi$-stacking (e.g., a number of pentacene derivatives have been synthesized to transform the herringbone packing of unsubstituted pentacene to an optimal $\pi$-stacked configuration) rather than an exploration of the effects of an underlying substrate. Our results show that the latter can cause $\pi$-stacking even in the case of relatively weak interaction without the need for any substituents. This suggests that engineering of the substrate–adsorbate interface may pose a fruitful and direct avenue to thin $\pi$-stacked organic films.

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