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Barrier Formation at Organic Interfaces in a Cu(100)-benzenethiolate-pentacene Heterostructure

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The energy level alignment at the metal-organic and organic-organic interfaces of the Cu(100)/benzenethiolate/pentacene heterostructure is studied by photoemission spectroscopy and discussed theoretically using a model that includes, in a consistent way, charge transfer, Pauli repulsion, intrinsic molecular dipoles, and interface screening as a function of coverage. Despite the different nature of the two interfaces, our model provides a unified explanation for the work-function changes at both junctions and enables us to determine the benzenethiolate orientation as a function of coverage.

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The energy level alignment at organic-organic (OO) and metal-organic (MO) interfaces is a crucial physical property determining the behavior of advanced molecular devices [1–3]. Considerable effort has been devoted to pentacene (C₂₂H₁₄), due to its efficiency as an active layer in organic thin film transistors (OTFTs) [4,5] for having high charge carrier mobility at room temperature (RT) [5,6]. Recently, self-assembled monolayers (SAMs) [7–9] have been used as buffer layers to obtain pentacene with standing-up orientation, by suppressing the direct interaction between the pentacene molecules and the metal substrate, reducing the gate-voltage and enhancing the on/off ratio in OTFTs [8,10]. It is also a case study where the level alignment and the barrier formation of different organic interfaces can be analyzed, a line of research that has been recently the focus of considerable theoretical and experimental work.

Since the Schottky-Mott model was disproved [11,12] by the observation of interface dipoles, several mechanisms have been proposed to explain the energy level alignment at organic interfaces: chemical reaction and the formation of gap states in the organic material [13]; orientation of molecular dipoles [14]; or compression of the metal electron tails at the MO interface due to Pauli repulsion [15,16]. Recently, some of us suggested [17] that an additional important mechanism is the tendency of the charge neutrality level (CNL) of the organic material to align with the metal Fermi level (at MO interfaces) or the CNL of the other organic material (at heterojunctions). Pentacene on a well-ordered benzenethiolate (C₆H₅S – , Bt) SAM adsorbed on the Cu(100) surface is a case study for analyzing these mechanisms. A compact Bt-SAM can be prepared on Cu(100) surface, forming an ideal well-ordered MO interface [9,18]. Then, a standing-up single-layer of pentacene can be grown on top of the Bt-SAM forming an ideal well-ordered [18] OO heterostructure. In this work we analyze the MO and OO energy level align-

ment, interface dipole and barrier formation as a function of Bt and pentacene coverage (Θ). Using high-resolution ultraviolet photoelectron spectroscopy (HR-UPS) we study the work-function (ϕ) evolution and determine the charge injection barrier, ionization energy (IE), and energy level diagram at these interfaces. This information is discussed theoretically by means of an unified induced density of interface states (IDIS) model that takes into account the effects of charge transfer, orientation of molecular dipoles, and Pauli repulsion on the formation of these interfaces. The Cu(100)/Bt-SAM and Bt-SAM/pentacene interfaces exhibit a very different behavior. The former is reactive (Sulfur is chemically bonded to Cu, although not forming a very strong bond [19], see also below), involves a large molecular dipole [20] and presents strong screening and depolarizing effects from the Cu substrate and surrounding organic material. The OO heterojunction, on the other hand, is weakly interacting, nonpolar, and lacks permanent molecular dipoles [20]. Thus, it would be desirable to have a theoretical model which could explain the behavior of both interfaces as a function of Θ and, at the same time, analyze separately those effects. A full density-functional theory (DFT) calculation for these interfaces would not allow an accurate calculation of the charge transfer at the interface [21], since DFT yields organic-molecular energy gaps that can be underestimated [19] by several eVs. This serious limitation points to the need of going beyond DFT for an accurate description of molecule-metal interfaces [19]. In our approach, instead of attempting a full DFT calculation for the Cu(100)/Bt-SAM/pentacene system, we calculate the electronic structure of the MO and OO interfaces in two steps. First, we determine the molecular electronic structure, by means of a local-orbital DFT [22] calculation; many-body levels (e.g., ionization and affinity levels) are then determined by means of total energy calculations for molecular configurations with ± 1 electron, neglecting orbital relaxation (see Ref. [23] for de-

tails). In a second step we introduce the interaction between the two media forming the interface, including the effects of charge transfer, Pauli repulsion, molecular permanent dipoles, screening, and image potential; the description of these effects in a unified IDIS model is given below.

The experiments have been carried out at the LOTUS laboratory by HR-UPS, preparing the heterostructure in ultra-high-vacuum environment ensuring contaminant-free organic layers [9,18]. Normal-emission HR-UPS data were acquired using a He discharge lamp ($h\nu = 21.218$ eV), and the photoemitted electrons were analyzed in the plane of incidence with a hemispherical SCIENTA SES-200 analyzer (energy resolution 15 meV, integration angle $\pm 8^\circ$). ϕ was estimated from the high binding-energy (BE) cutoff of the photoemission spectrum [9], after negatively biasing the sample (-9 V). The Cu(100) surface, cleaned by repeated sputtering-annealing cycles, was exposed to benzenethiol (C_6H_5SH) vapors, to form a saturated Bt-SAM [9], with a nearly up-right orientation (about 20° off-normal), and $c(2 \times 6)$ symmetry [18,24]. Pentacene was evaporated *in situ* from an organic-molecular beam epitaxy cell on the Cu(100)/Bt-SAM system at RT, and the thickness was monitored by a quartz microbalance.

The work-function evolution at the Cu(100)/Bt interface upon Bt-SAM formation is shown in Fig. 1. It decreases as a function of Θ , leading to a variation $\Delta_{MO} = -1.00 \pm 0.05$ eV at saturation coverage ($\Theta = 1$), and presents a slope change at $\Theta \sim 0.33$, interpreted [24] as due to a structural phase change, from flat-lying to

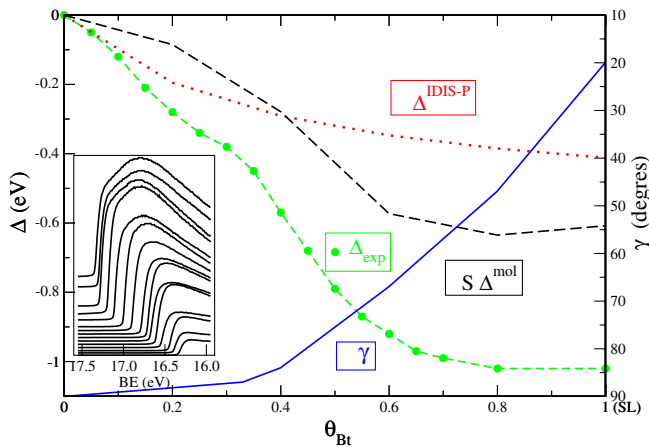


FIG. 1 (color online). Work-function change (Δ) as a function of benzenethiol exposition on Cu(100). $\Theta_{Bt} = 1$ corresponds to completion of the $c(2 \times 6)$ single-layer phase [9,18]. Experimental Δ data (large dots, dashed guideline); IDIS-pillow contribution to Δ (dotted line); molecular dipole contribution to Δ (dashed line). Calculated molecular orientation angle (γ) with respect to the surface normal (continuous line). Inset: High BE (in eV) cutoff of the photoemission data for the Cu(100)/Bt interface, at increasing Θ , from clean Cu (bottom spectrum) to one single-layer Bt (top spectrum).

standing-up molecules (with Sulfur atoms interacting with the Cu surface). Pentacene deposition on the Bt-SAM produces an increase in work function, saturating at $\Delta_{OO} = 0.09 \pm 0.05$ eV with respect to the Bt-SAM when a single-layer is completed (Fig. 2). A defect-free layer is achieved using benzenethiol to produce the SAM, avoiding S contamination produced by use of diphenyl-disulfide [25]. The energy band diagram for the present heterostructure is illustrated in Fig. 3. The measured interface dipole variation Δ at the MO and OO interfaces is of opposite polarity. From the HR-UPS data [9], the IE defined by the highest-occupied molecular-orbital (HOMO) onset relative to the vacuum level is 4.75 ± 0.05 eV and 4.61 ± 0.05 eV for Cu(100)/Bt-SAM and Bt-SAM/pentacene, respectively. The hole injection barrier (ϕ_h) is 1.18 ± 0.05 eV (MO) and 0.95 ± 0.05 eV (OO). The ϕ_h value for this standing-up pentacene layer (0.95 eV) is smaller than that for flat-lying pentacene (1.05 eV) [3].

In our theoretical approach, we analyze the barrier formation for these two organic interfaces combining several effects: (a) charge transfer at both interfaces as described by the IDIS model, (b) Pauli repulsion, and (c) molecular permanent dipoles which, for the polar thiol molecules at the Cu/Bt-SAM interface, represent an important contribution. Within the IDIS model [17], the charge transfer between the metal and the organic (or between two organics) is controlled by the energy difference between the metal Fermi level, E_F , and the organic CNL (or between the CNLs of both organics for an OO interface), and by the screening parameter S , which depends on the interface polarizability [17]. In this approach, the Pauli repulsion or “Pillow” dipole, Δ_0^P , can be incorporated in the model [26] by calculating the corresponding reduction in ϕ [27], in such a way that now the joint work-function change, Δ^{IDIS-P} , is

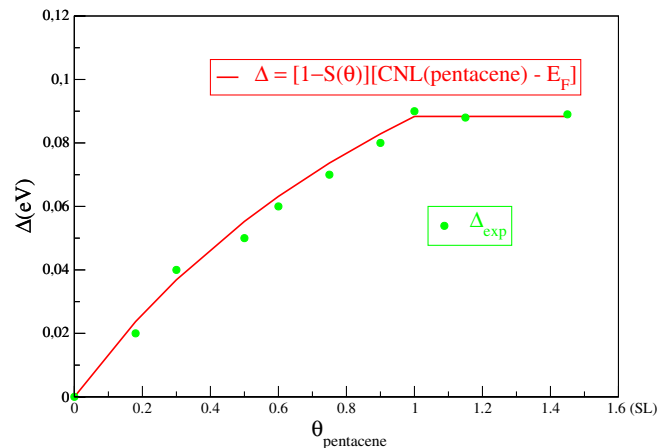


FIG. 2 (color online). Work-function change (Δ) as a function of pentacene deposition on top of the Cu(100)/Bt-SAM system, with respect to the Cu(100)/Bt-SAM surface. $\Theta_{pentacene} = 1$ corresponds to completion of a single-layer [9,18]. Experimental Δ data (large dots); IDIS-calculated Δ (line).

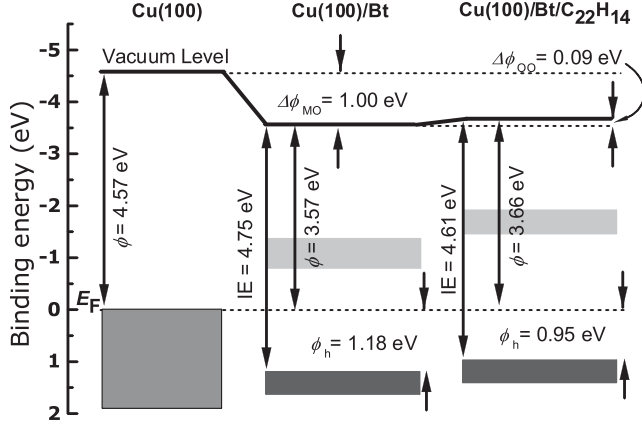


FIG. 3. Energy level diagram of the Cu(100)/Bt-SAM/pentacene heterostructure based on the present results. Highest-occupied molecular-orbitals and lowest-unoccupied molecular orbitals are denoted by thick dark and light-gray lines, respectively. Experimental uncertainty ± 0.05 eV.

$$\Delta^{\text{IDIS-P}} = (1 - S)(E_{\text{CNL}} - E_F) + S\Delta_0^P, \quad (1)$$

where $S = 1/[1 + 4\pi e^2 D_s(E_F)\delta/A]$ depends on the IDIS in the organic molecule at E_F , $D_s(E_F)$, the effective distance δ between the metal and organic induced charges, and the area A per organic molecule. The effect of having molecules with a permanent dipole P^0 is to modify, on a first approximation, the metal work function by a quantity given by $\Delta^0 \cos\gamma$ ($\Delta^0 = 4\pi P^0/A$), where γ is the angle between the molecule and the surface normal. However, this dipole is screened by the molecular susceptibility, χ , as described by the Topping model [28]:

$$\Delta^{\text{mol}} = \Delta^0 \cos\gamma / (1 + \alpha), \quad (2)$$

where α can be approximated by $2\chi/a^3$ ($A = \pi a^2$). In our model, Eqs. (1) and (2) can be generalized to

$$\Delta^T = S\Delta^{\text{mol}} + S\Delta_0^P + (1 - S)(E_{\text{CNL}} - E_F), \quad (3)$$

which combines the IDIS dipole, the pillow dipole (screened by S) and the molecular permanent dipole (screened by the molecular polarizability and S). Notice that in Eq. (3) for an OO interface Δ_0^P can be neglected and $(E_{\text{CNL}} - E_F)$ should be replaced by $(E_{\text{CNL}}^1 - E_{\text{CNL}}^2)$.

We first discuss the Cu/Bt interface using this approach. The IDIS model has been applied to cases having a weak metal-organic interaction; for Cu/Bt-SAM, while the metal-S bond is covalent, the interaction is presumably not very strong as shown by calculations on Au [19], where the Bt-molecular orbitals are not significantly disturbed with respect to the isolated molecule. Thus, we start by analyzing the free phenylethyl molecule by means of local-orbital DFT calculations [22] that yield a good description of the molecular covalent bonds. Many-body corrections to the DFT levels are determined by calculating

the total energy change when an electron or hole is added to a specific molecular level; see Ref. [23] for details. The molecular CNL is calculated from these ‘‘corrected’’ energy levels, as discussed in Ref. [17]. Our calculations yield an energy gap of 5.0 eV (in good agreement with Ref. [19]) and a CNL located 3.5 eV above the center of the HOMO level, E_{HOMO} . We find that, upon adsorption, image potential effects [29] strongly reduce the energy gap to around 1.9 eV, and $E_{\text{CNL}} - E_{\text{HOMO}}$ to 1.0 eV. These effects are calculated using a classical image potential with a metal image plane located 1.25 Å [30] from the outermost Cu layer. Our DFT calculations yield a molecular permanent dipole, P^0 , of 3.0 debyes: for a full Bt-monolayer, assuming the molecule oriented perpendicularly to the surface, the associated potential drop is $\Delta^0 = 8.5$ eV. Finally, the reduction of the metal work function due to the Pauli repulsion between the Cu and S orbitals has been calculated to be $\Delta_0^P = 0.4$ eV for a full monolayer. This effect is associated with the overlap between the Cu and the Sulfur doubly occupied orbitals which push the Cu orbitals toward the metal [31]. We analyze the Cu/Bt interface (see Fig. 1) starting from Eq. (3) and extending it to the case of a fraction of monolayer, $0 < \Theta < 1$. Notice first that $\Theta \propto 1/a^2 \propto 1/A$; this allows us to define $S(\Theta) = 1/(1 + \sigma\Theta)$, and $\alpha(\Theta) = \beta\Theta^{3/2}$, σ and β being constants to be fitted from experiment at $\Theta = 0$ and $\Theta = 1$. Furthermore, we introduce the Θ -dependent molecular dipole, $\Delta^0(\Theta) = \Theta\Delta^0$, and the pillow dipole, $\Delta_0^P(\Theta) = \Theta\Delta_0^P$, these dipoles increasing linearly with the number of molecules on the surface. With these definitions, Eq. (3) can be extended to

$$\Delta^T(\Theta) = S(\Theta)\Delta^0(\Theta)\cos\gamma/[1 + \alpha(\Theta)] + S(\Theta)\Delta_0^P(\Theta) + [1 - S(\Theta)](E_{\text{CNL}} - E_F) \quad (4)$$

For $\Theta \rightarrow 0$, $\cos\gamma \rightarrow 0$ (flat-lying molecule [24]) and

$$\Delta^T(\Theta) \rightarrow \Delta^{\text{IDIS-P}} = (E_{\text{CNL}} - E_F)\sigma\Theta/(1 + \sigma\Theta) + \Delta_0^P\Theta/(1 + \sigma\Theta); \quad (5)$$

from this equation and the slope of Δ_{exp} in Fig. 1 for $\Theta \rightarrow 0$, we find σ to be 2.6; this yields $S(1) = 0.28$, in good agreement with systems where the pinning of the Fermi level is strong [17]. The calculated $\Delta^{\text{IDIS-P}}$ is shown in Fig. 1: this joint contribution is only 0.37 eV for a full monolayer; the difference 0.63 eV to the total dipole should be associated with the permanent molecular dipole P^0 that yields the dominant contribution to the total work function change [31]. On the other hand, with $S(1) = 0.28$ and [32] $\gamma = 20^\circ$, we find $S(1)\Delta^0(1)\cos\gamma = 2.24$ eV, so that $1 + \alpha(1) = 3.6$, and $\beta = 2.6$. We can then use Eq. (4) to obtain the molecular orientation angle γ as a function of Θ (also shown in Fig. 1): this angle changes almost linearly between $0.33 < \Theta < 1$, the molecule starting to tilt at the transition ($\Theta \sim 0.33$) between the flat-lying and the standing-up ‘‘phases’’ (Fig. 1).

The Bt/pentacene case can be more easily discussed because the Bt-permanent dipole is only operative at the Cu/Bt interface [20]. We therefore analyze this case taking $\Delta^0 = 0$ and $\Delta_0^p = 0$ in Eq. (3), and write

$$\Delta_{\text{Bt/Pentacene}} = (1 - S)[E_{\text{CNL}}^{\text{Pentacene}} - E_F(\text{Bt})], \quad (6)$$

where the Bt-Fermi level is used because of the IDIS in the energy gap. Our DFT calculations for pentacene [17,33] yield a CNL located 3.8 eV below the vacuum level, so that $E_{\text{CNL}}^{\text{pentacene}} - E_F(\text{Bt}) = 0.23$ eV. Then, taking $S = 0.6$, a value similar to the screening parameter typical of other OO interfaces [34], we obtain $\Delta_{\text{Bt/Pentacene}} = 0.09$ eV. We can also extrapolate Eq. (6) as follows:

$$\Delta(\Theta) = [1 - S(\Theta)][E_{\text{CNL}}^{\text{Pentacene}} - E_F(\text{Bt})], \quad (7)$$

where $S(\Theta) = 1/(1 + 0.65\Theta)$ (such that $S = 0.6$ for $\Theta = 1$). Figure 2 shows $\Delta(\Theta)$ for $0 < \Theta < 1$, in excellent agreement with experimental evidence. Notice that for $\Theta > 1$, Δ should not change with Θ , as found experimentally, since the interface is already formed for 1 single layer. In summary, the energy level diagram for the Cu(100)/Bt-SAM/Pentacene heterostructure, where weakly interacting OO and reactive MO interfaces coexist, is derived from a photoemission study. The MO interface involves a large molecular dipole, strong screening, and depolarizing effects from the Cu substrate and surrounding organic material; also the OO heterojunction, despite its weak interaction, exhibits an induced dipole. These data have been analyzed as a function of coverage by a unified IDIS model, which takes into account the main physical ingredients governing the interface formation: the reduction of the metal work function at the metal-organic interface due to the compression of the metal electron tails, the Bt-molecular permanent dipole and the charge transfer between Bt and Cu (or between Bt and pentacene) using the concept of CNL. We believe these to be the dominant electrostatic components, as they allow for a very good description of the experimental data, and the determination of the Bt orientation as a function of coverage. We therefore conclude that the unified IDIS model yields an excellent description of the energy level alignment at MOO heterostructures.

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