

Electrostatic-Field-Driven Alignment of Organic Oligomers on ZnO Surfaces

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(Received 28 December 2010; published 30 September 2011)

We study the physisorption of organic oligomers on the strongly ionic ZnO(10 $\bar{1}$ 0) surface by using first-principles density-functional theory and nonempirical embedding methods. It turns out that the in-plane variation of the molecule-substrate interaction energy and the bonding dipole in the vertical direction are linked up by a linear relationship originating from the electrostatic coupling of the molecule with the periodic dipolar electric field generated by the Zn-O surface dimers. Long oligomers with a highly axial π -electron system such as sexiphenyl become well oriented with alignment energies of several 100 meV along rows of a positive electric field, in full agreement with recent experiments. These findings define a new route towards the realization of highly ordered self-assembled arrays of oligomers or polymers on ZnO(10 $\bar{1}$ 0) and similar surfaces.

DOI: 10.1103/PhysRevLett.107.146401

PACS numbers: 71.15.-m, 31.15.E-, 34.35.+a

Hybrid structures made of conjugated organic molecules and inorganic semiconductors exhibit an enormous application potential, as they combine the favorable features of both components in a single new material [1]. However, interfacing of organic molecules with the typically highly reactive semiconductor is a complex issue. Rupture and fragmentation are frequently observed leading to ill-defined interfaces [2]. On the other hand, the electronic structure of the semiconductor surface might be exploited for developing novel strategies of molecular aggregation. In this Letter, we demonstrate that the electrostatic interaction between the semiconductor and the π -electron system indeed gives rise to a well-ordered attachment for a wide class of organic molecules.

The chemistry of ZnO surfaces has been largely investigated in the context of catalysis [3,4], and, more recently, much attention has been paid to the linkage with organic dyes and polymers, driven, e.g., by photovoltaic applications [5–7]. In particular, it has been found experimentally that *p*-sexiphenyl (6P) absorbs flat-lying on the ZnO(10 $\bar{1}$ 0) surface with the long axis of the molecule perpendicular to the polar [0001] direction [8]. In that study, the hybrid interface has been formed entirely under ultrahigh vacuum conditions, suggesting that intrinsic features of the hybrid interface are behind this observation. The theoretical analysis presented below not only confirms this conjecture but reveals systematic tendencies common to many oligomers that can be used to engineer the growth of semiconductor hybrid structures.

ZnO is a strongly ionic crystal. Specifically, the (10 $\bar{1}$ 0) surface consists of Zn-O dimer rows of opposite charge, which generate a dipolar electrostatic surface field with peak strengths on the order of 10 V/nm [9]. It is likely that the spatial structure of a such strong surface field plays an

essential role in the molecular attachment. To validate this assumption, we consider initially biphenyl (2P) as a model oligomer and then extend the analysis to larger molecules. Figures 1(a) and 1(b) depict the configuration examined. We start from a clean, nonreconstructed ZnO(10 $\bar{1}$ 0) surface optimized by using density-functional theory (DFT) [10]. The origin of the reference coordinate system is

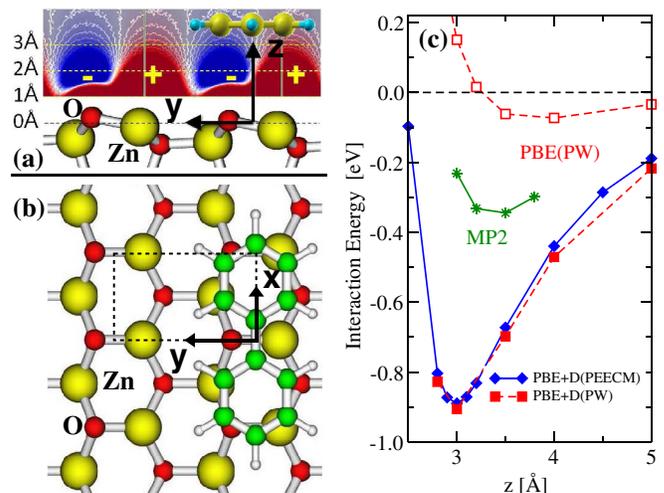


FIG. 1 (color online). (a) Side view of 2P on the ZnO(10 $\bar{1}$ 0) surface and the electric field (z component) close to the surface as obtained from PBE calculations. The color map covers the range from -5 V/nm (blue) to $+5$ V/nm (red). Note that the uppermost Zn-O dimers are tilted with respect to the surface plane. (b) Top view of 2P on the ZnO(10 $\bar{1}$ 0) surface (dotted rectangle: surface unit cell). (c) Molecule-substrate interaction energy for 2P versus vertical distance z ($x = y = 0$), as computed by different theoretical methods (see the text).

located at the center of a Zn-O surface bond, the z - and y -axis point along the surface normal and the [0001] direction, respectively. The position of the molecule is denoted by the coordinates of its center of mass.

In a first step, to obtain information on the molecule-substrate distance (z_0), we set the molecule at $x = y = 0$ with the long axis aligned in the x direction ($\theta = 0$) and the molecular plane parallel to the surface. The molecule-substrate interaction energy (E_{int}) of this configuration keeping both the molecular and ZnO(10 $\bar{1}$ 0) surface configuration frozen is plotted versus z in Fig. 1(c). The curves are computed at the Perdew-Burke-Ernzerhof (PBE) level [11], also with a dispersion correction (PBE + D) [12], by using two different computational methods: a periodic pseudopotential plane-wave (PW) approach at low coverage [9] and the periodic electrostatic embedded cluster method (PEECM) [13], the latter also allowing us to perform reference second-order Møller-Plesset (MP2) calculations [9].

Figure 1(c) shows that the PBE functional leads to weak binding [12,14,15], while the inclusion of dispersion corrections overestimates the binding with respect to MP2 [15–17]. These DFT shortcomings are unproblematic in the present context, as our goal is not the calculation of the total adsorption energy, but we are interested in the *variation* of E_{int} when changing molecular position and alignment in the surface plane. In the calculations presented below, the molecule-substrate distance is fixed to the MP2 value ($z_0 = 3.5$ Å).

As a next step, knowing z_0 with sufficient accuracy, we consider the variation of E_{int} when translating the molecule in the y direction. As displayed in Fig. 2(a), the computations performed at both PBE(PW) and PBE + D(PW) levels produce a sinusoidal curve with a minimum when the center of the molecule is close to a position atop a Zn atom ($y = 3.7$ Å). The fact that both plots cannot be distinguished demonstrates that dispersion interactions are not essential for the energy change [18]. We next move the molecule in this minimum and consider two other degrees of freedom: a shift of the x position [Fig. 2(b)] and a rotation (θ) around the z axis [Fig. 2(c)]. It turns out that E_{int} depends only smoothly on x , although distinctly different interaction configurations with the ZnO ions are probed. The θ scan does not resemble the threefold rotational symmetry of an (ideal) ZnO surface cell, indicating a prevailing mechanism with lower symmetry.

While not providing evidence that interactions on the atomic scale are involved, the variation of E_{int} in Figs. 2(a)–2(c) is consistent with the topology of the dipolar surface field (\vec{F}). For symmetry reasons, $F_x \approx 0$ and F_y and F_z can be approximated [see Fig. 1(a) and Ref. [9]] in the relevant z range by

$$\begin{aligned} F_y(y, z) &\approx Ae^{-kz} \cos(ky), \\ F_z(y, z) &\approx -Ae^{-kz} \sin(ky), \end{aligned} \quad (1)$$

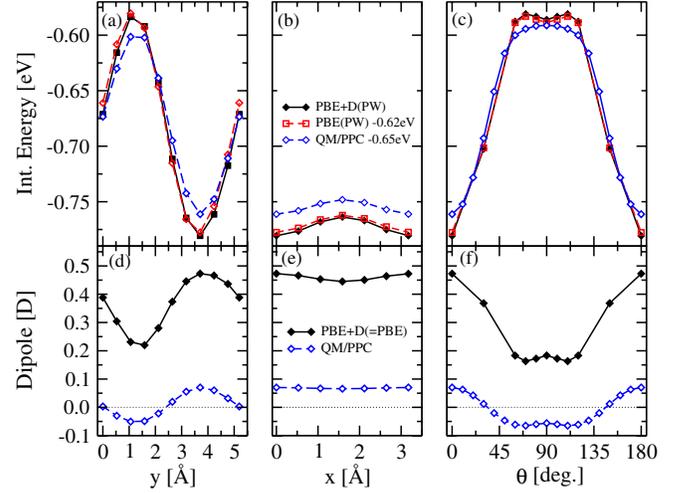


FIG. 2 (color online). Molecule-substrate interaction energy E_{int} (top panels) and bonding dipole μ_z (bottom panels) for different methods ($z = z_0$). Left: Variation with the y position ($x = 0, \theta = 0$). Center: Variation with the x position ($y = 3.7$ Å, $\theta = 0$). Right: Variation with θ ($x = 0, y = 3.7$ Å). The x and y plots cover the extension of the (10 $\bar{1}$ 0) surface unit cell.

where $k = 2\pi/a$, a is the length of the surface unit cell in the y direction, and A scales the field strength. The sinusoidal shape of E_{int} in Fig. 2(a) is in line with $F_z(y, z_0)$ and the smooth change in Fig. 2(b) with $\partial\vec{F}/\partial x = 0$. To elaborate the field-induced correlations more cogently, we describe the ZnO surface region classically by a periodic arrangement of point charges (PPC) with values $+q$ and $-q$ at the lattice positions of Zn and O atoms, respectively. By fitting the electrostatic field generated by the PPC with an Ewald summation technique [19] to the electrostatic field calculated in PBE(PW), we obtain $q = 0.95$ with a mean error in F of only 0.2 V/nm over the whole surface unit cell and 2.5 Å $< z < 4.5$ Å. The molecule is then treated quantum mechanically (QM) in this external potential at the PBE level. This QM/PPC approach (as a simplified version of PEECM) is capable of describing correctly the molecular polarization induced by the surface field but ignores charge transfer between the molecule and ZnO. As seen in Figs. 2(a)–2(c), the shape of the E_{int} curves computed in QM/PPC agrees very well with those of the DFT calculations, clearly verifying the leading role of the molecular electrostatic contribution in the in-plane energy variation. As the size of 2P (and, *a fortiori*, of the larger oligomers we are interested in) is larger than the surface unit cell, the molecular orbitals interact simultaneously with several Zn and O atoms so that exchange-correlation effects are averaged out.

To test the role of all other degrees of freedom, geometry optimizations at the PBE + D(PW) level relaxing all atomic positions in the molecule and in the two uppermost ZnO layers were carried out. Starting from different configurations ($\theta = 0$ or $\theta = 90^\circ$ and different y), we did not

find any interring torsions or molecular bending, though PBE + D overestimates the interaction energies and reduces z_0 [Fig. 1(c)]. The absence of these features is in accord with a recent DFT treatment of sextiophene on ZnO(10 $\bar{1}$ 0) [7]. In some configurations with $\theta = 0$, a small tilting angle of the molecule plane with respect to the x axis ($\approx 15^\circ$) occurred which follows the tilt of the Zn-O surface dimers [Fig. 1(a)]. Consideration of rigid, planar geometries is thus well justified, as such a small tilt is not substantially modifying the electrostatic coupling, in particular, for larger oligomers.

The prevalence of physisorption is corroborated by the bonding dipole along the z direction defined (in the present case of nonpolar molecules) by $\mu_z = \mu_z^{\text{tot}} - \mu_z^{\text{ZnO}}$ [20], where μ_z^{tot} and μ_z^{ZnO} represent the dipole of the total system and the bare ZnO surface, respectively. The PBE (PW) calculations reported in Figs. 2(d)–2(f) show that μ_z is in the range of 0.1–0.5 D, i.e., always positive but small. Calculations in the QM/PPC frame, where only the molecular polarization is accounted for, provide curves with similar profile but down-shifted by 0.3–0.4 D.

We may hence conclude that also the in-plane variation of the bonding dipole is governed by the electrostatic coupling. Plane-averaged density profiles further corroborate this conclusion [9]. From the offset to the PBE(PW) data, an upper limit of only $0.02e$ for the charge transfer contribution to μ_z is estimated, excluding that chemical bond formation is an essential factor. Note that PBE even overestimates charge transfer as it produces a too small ZnO band gap [7,10].

As \vec{F} determines the in-plane variation of both E_{int} and μ_z , there should be a correlation between the latter quantities. The comparison of the upper and lower panels in Fig. 2 reveals a strikingly concise relationship: The molecule-substrate interaction energy is virtually a linearly decreasing function of the field-induced dipole moment in the vertical direction. That is, the molecule attaches such that it maximizes this dipole moment. This important finding becomes more transparent in an analytical model treating the molecule-substrate electrostatics classically. The energy of a molecule with a zero static dipole but finite quadrupole moment M_{ij} in a weak but nonuniform electric field ($F_x \approx 0$) is [21]

$$\Delta E \approx -\frac{1}{2} \sum_{i=y,z} [M_{ii}(\nabla F_i)_i + \alpha_{ii}F_i^2], \quad (2)$$

where α_{ij} is the molecule's polarizability tensor. This expression is derived from perturbation theory: The first term represents the electrostatic interaction between the external nonuniform perturbing field and the unperturbed molecule, the second one the induction energy accounting for the molecular polarization created by the field. Equation (2) is valid for a large class of planar, symmetric oligomers characterized by vanishing off-diagonal elements of M_{ij} and α_{ij} . From (1), it follows that

$$(\nabla F_y)_y \approx kF_z, \quad (\nabla F_z)_z \approx -kF_z. \quad (3)$$

Using that $\mu_i = \alpha_{ii}F_i$ and inserting (3) in (2), we obtain

$$\Delta E \approx -B\mu_z - C\mu_z^2 - \frac{1}{2}\alpha_{yy}A^2e^{-2kz_0} \quad (4)$$

with $B = k(M_{yy} - M_{zz})/2\alpha_{zz}$ and $C = (\alpha_{yy} - \alpha_{zz})/2\alpha_{zz}^2$.

Table I compiles the values of the relevant parameters for 2P and three other representative molecules (6P, 5A = pentacene, 5PV = penta-phenylene-vinylene), all widely used in organic optoelectronics. As C is typically more than an order of magnitude smaller than B , the induction term quadratic in μ_z is negligible in (4) at the field strengths considered here. Therefore, the classical model not only shows that the linear energy-dipole relation originates from the electrostatic coupling but also signifies that this relation is of quite general validity. However, the alignment of a specific molecule and its stability cannot be derived by considering the quadrupole moment only. These features depend critically on the symmetry properties of the molecular π -electron system, and higher multipole terms cannot be ignored. The QM/PPC approach is an ideal tool in this context, because it includes exactly all electrostatic contributions. Moreover, QM/PPC is nonempirical, as it accurately reproduces the PBE(PW) results for 2P and it allows for scanning of the whole potential energy surface (PES) at reasonable numerical costs.

Figure 3 summarizes QM/PPC computations for 2P, 6P, 5A, and 5PV, where 1470 configurations in the space of x , y , and θ were considered. Again, all these molecules follow a linear $E_{\text{int}} - \mu_z$ relation [Fig. 3(a)], and it can indeed be shown that this linearity is maintained in all orders of the electrostatic coupling [9]. However, the specific alignment in the surface plane exhibits marked differences [Fig. 3(b)]. For 2P, studied merely for reference, we find two minima for $\theta = 0$ and 90° , energetically separated only by 22 meV, so that no definite alignment can be concluded at the electrostatic level. In contrast, the

TABLE I. PBE quadrupole moments (M_{yy} , M_{zz}) and polarizabilities (α_{yy} , α_{zz}) as well as B and C coefficients (see the text) for different molecules.

Molecule	M_{yy} (a.u.)	M_{zz} (a.u.)	α_{yy} (a.u.)	α_{zz} (a.u.)	B (eV/D)	C (eV/D ²)
2P	-46	-57	138	68	0.558	0.032
6P	-136	-168	377	190	0.589	0.011
5A	-83	-101	251	115	0.557	0.022
5PV	-145	-180	402	208	0.574	0.009

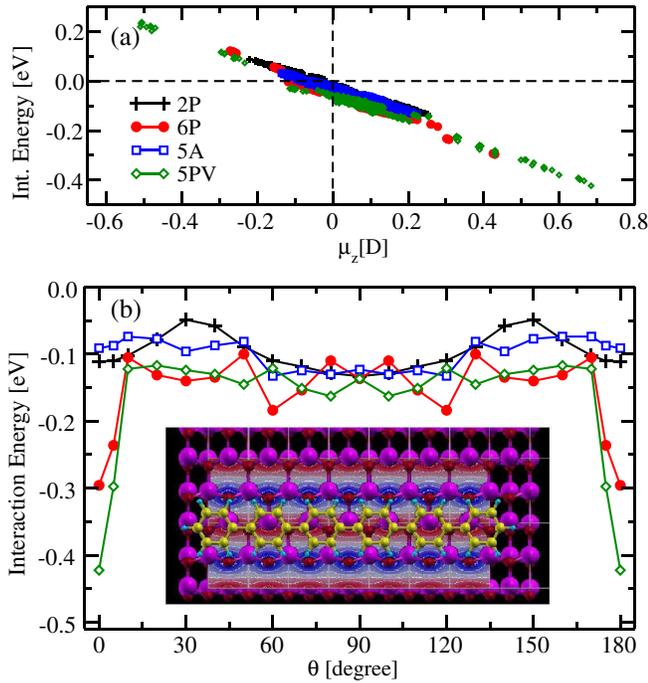


FIG. 3 (color online). Interaction energy for 2P, 6P, 5A, and 5PV on ZnO(10 $\bar{1}0$) in QM/PPC ($z_0 = 3.5$ Å). (a) E_{int} versus μ_z . (b) E_{int} versus rotation angle θ at the x and y positions of minimum energy. The 90° minimum of 2P is not present in Fig. 2(c) as it occurs for different x and y . Inset: Orientation of 6P at the global minimum shown on a color map of F_z .

PES of both 6P and 5PV features deep global minima at $\theta = 0$, in agreement with the experimental observation for 6P [8]. The alignment energies measured relative to the next stable arrangement are $E_{\text{al}} = 112$ ($\theta \approx 60^\circ$) and 260 meV ($\theta \approx 80^\circ$), respectively. The lateral position of the adsorption site is also uniquely defined, with $y \approx 3.7$ Å and $x = 0$ for both 6P and 5PV. Thus, as illustrated in the inset for 6P, the energy is minimized when the long axis of the molecule matches with the lines of largest positive F_z , where the electrostatic coupling and thus μ_z are maximized. The longer the molecule, the more stable the alignment.

PBE + D(PW) calculations for the full 6P/ZnO(10 $\bar{1}0$) interface [9] confirm the leading role of the surface field. Considering specifically the energy E_{al}^* required for a rotation from the minimum-energy QM/PPC configuration to $\theta = 90^\circ$, we obtain $E_{\text{al}}^* = 220$ meV at $z_0 = 3.5$ Å, which coincides with the QM-PPC value (221 meV). Account of a 15° tilt increases E_{al}^* to 325 (PBE + D) and 317 meV (QM/PPC). Even at $z_0 = 3.0$ Å, 2/3 of the energy is still given by the electrostatic contribution ($E_{\text{al}}^* = 622$ meV and 384 meV in PBE + D and QM-PPC, respectively). QM/PPC PES scans for $z_0 = 3.0$ Å provide the same alignment as in Fig. 3 for all four oligomers [9]. However, we emphasize that, for molecules which adsorb markedly closer to the surface and/or which are smaller in

size, exchange-correlation effects beyond QM/PPC can have a significant influence on the alignment energy.

The PES of 5A is instead less deep and structured. Contrary to 6P and 5PV, no preferred orientation can be thus anticipated here. This finding can be rationalized by the fact that 5A has no carbon atoms exactly on the long molecular axis which can be most easily polarized by the electric field, as is the case for 6P and 5PV.

In conclusion, we found that the dipolar electric field of the ZnO(10 $\bar{1}0$) surface plays a key role in the adsorption of typical oligomers. Provided the molecules are physisorbed at distances $z_0 \gtrsim 3.0$ Å and their π -electron system is axially oriented, the electrostatic molecule-substrate coupling induces a well-defined molecular alignment, stabilized against reorientation by energies $E_{\text{al}} > 100$ meV. The electrostatic coupling is characterized by a linear relation between the molecule-substrate interaction energy and the induced vertical molecular dipole moment, which can be employed to predict or design the molecular orientation on the surface, also by modifying the oligomer appropriately. The presence of a dipole layer shifts the vacuum level at the inorganic-organic interface [20]. The strategy of maximizing the induced dipole moment in the vertical direction when the oligomer attaches to the surface is thus also important for the energy level alignment in hybrid structures. Finally, we note that the single-molecule alignment will be perpetuated and results in molecular assemblies reflecting the topology of the surface field. The induced dipole moment can be modified by depolarization effects [22], but the resultant energy change is negligible on the scale of the electrostatic molecule-substrate coupling controlling the surface alignment. Therefore, our findings define a route towards the realization of highly ordered self-assembled arrays of oligomer or polymers on ZnO(10 $\bar{1}0$) and similar surfaces.

We thank TURBOMOLE GmbH for the TURBOMOLE program package and M. Sierka, G. Heimel, and I. Ciofini for discussions. This work is partially funded by the ERC-Starting-Grant Project DEDOM (No. 207441).

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