Electrostatic Field Driven Alignment of Organic Oligomers on ZnO Surfaces

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We study the physisorption of organic oligomers on the ZnO(1010) surface using first-principles density-functional theory and non-empirical embedding methods. We find that both in-plane location and orientation of the molecules are completely determined by the coupling of their quadrupole moments to the periodic dipolar electric field present at the semiconductor surface. The adsorption is associated with the formation of a molecular dipole moment perpendicular to the surface, which bears an unexpected linear relation to the molecule-substrate interaction energy. Long oligomers such as sexiphenyl become well-aligned with stabilization energies of several 100 meV along rows of 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/polymers on ZnO(1010) and similar surfaces.

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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. 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. 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 gives indeed rise to the self-assembly of stable and highly ordered monolayers for a wide class of conjugated organic molecules.

The specific surface under consideration is the non-polar (1010) crystal plane of ZnO. The chemistry of ZnO surfaces, see e.g. Ref. [8], has been largely investigated in the context of catalysis [4] and, more recently, much attention is paid to the linkage with organic dyes and polymers, driven, e.g., by photovoltaic applications [5, 6]. In particular, it has been found experimentally that p-sexiphenyl (6P) absorbs flat on the ZnO(1010) surface with the long axis of the molecule perpendicular to the polar [0001] direction [2]. In this study, the hybrid interface has been formed entirely under ultra-high vacuum conditions suggesting that intrinsic features of the semiconductor-molecule system are behind that type of aggregation. The theoretical analysis presented below not only confirms this conjecture but reveals systematic tendencies common to all oligomers that can be used to engineer the growth of inorganic/organic structures.

In order to establish a proper and efficient methodical framework, we start with biphenyl (2P) as a short model oligomer. Fig. 1a and b depict the configuration examined. The origin of the reference coordinate system is located at the center of a surface Zn-O bond, the z- and y-axis point along the surface normal and the polar [0001] direction, respectively. The position of the molecule is denoted by the coordinates of its center of mass. We consider a clean, non reconstructed surface optimized using density functional theory (DFT) as described in Ref. [8].

Our goal is the construction of the ground-state potential energy surface (PES) of the molecule-semiconductor system. In a first step, we set the center of the molecule on top of the Zn-O bond (x=y=0) with its long axis aligned in x-direction and the molecular plane parallel to the surface. The interaction energy of this arrangement keeping both the molecular and ZnO(1010) surface configuration frozen is plotted versus distance from surface (z) in Fig. 1c. The curves are computed at the PBE level [9] and with dispersion correction (PBE+D) [10], using two different computational methods: a periodic pseudopotential plane-wave (PW) approach [11] and the periodic electrostatic embedded cluster method (PEECM) [11, 12], as implemented in the TURBOMOLE [13] program.

Figure 1: shows that the PEECM results agree very well with the PW ones. The practical advantage of PEECM lies in the fact that it considers only a single molecule in interaction with the surface. Unlike the PW method, where a whole periodic organic monolayer (of hypothetical structure) has to be treated, PEECM defines thus a cost effective way to tackle the initial adsorption step of the molecule. As expected from previous studies, see e.g. Ref. [14], the PBE functional leads to weak binding, while the dispersion correction increases the binding energy and reduces the molecule-substrate distance. In order to verify the accuracy of PBE+D for
ZnO surfaces, we performed reference MP2 calculations within the PEECM scheme. Figure 1 exposes that PBE+D is quite far from MP2 and thus cannot be safely used for ZnO surfaces. The MP2 predicts an interaction energy of 370 meV with an equilibrium distance \( z_0 \approx 3.5 \text{ Å} \). This molecule-substrate distance will be used in all the following calculations.

As a next step, we now consider the change of the molecule-substrate interaction energy (\( \Delta E \)) when the molecule is translated along \( y \)-direction. As displayed in Fig. 2a, the computations performed again in different approximations commonly reveal a distinct minimum for \( y \approx 3.7 \text{ Å} \), i.e., when the center of the molecule is close to a position atop a Zn atom. Interestingly, the relative energies of the PBE(PW) approach are practically not modified by inclusion of the dispersion. In order to save computation time for the examination of the complete PES below, we performed the same procedure but modeling the ZnO(10\bar{1}0) surface only by point-charges with values \( +q \) and \( -q \) at the lattice positions of the Zn and O atoms, respectively. We call this method QM/PPC (quantum mechanics/periodic point-charges), because the molecule is treated quantum mechanically at PBE level, while the ZnO surface is classically described. Hence, only the electrostatic interaction between the molecule and the substrate is considered in this approach. For \( q=1.2 \), excellent agreement with the PBE(PW) result is indeed achieved. This value \( q \) is very close to what is found in the Mulliken population analysis of the ZnO(10\bar{1}0) surface. Therefore, we conclude that exchange-correlation forces determine the absolute energy (see Fig. 1c), but the energy variation when moving the molecule within the surface plane is completely dominated by the electrostatic coupling. Exchange-correlation effects vary on the atomic length scale, but are averaged out as the molecule is larger than the ZnO(10\bar{1}0) unit cell.

The alternating point charges which characterize the ZnO(10\bar{1}0) surface create a periodic dipolar electric field \( \vec{F} \). An important consequence of this field is that it generates in turn an induced dipole moment \( \vec{\mu} \) in the 2P molecule. For symmetry reasons, \( F_z \) is negligible, while \( F_y \) and \( F_z \) reach values of several V/nm. The resultant \( \mu_y \) and \( \mu_z \) are plotted versus \( y \)-position in Fig. 2c. Over the length \( a \) of the unit cell, they change sign with a relative shift of \( a/4 \). This behavior reflects the dipolar character of \( \vec{F} \), as illustrated in Fig. 2d. The electric field is largely inhomogeneous, but sufficiently far from the surface where the molecule is located, it has oscillating character. When \( y \approx 2.5 \text{ Å} \), \( \mu_y \) reaches its negative maximum. At this position, as schematized in Fig. 2d, the molecule experiences a negative electric field over almost its whole size, whereas the average of \( F_z \) is almost zero and thus \( \mu_z \approx 0 \).

The knowledge gained above enables us now to search for the global minimum of the PES by changing the residual degrees of freedom - translation of the molecule along the \( x \)-direction and rotation around the \( z \)-axis. The QM/PPC approach makes it possible to scan a set of 1500 different molecular configurations. The results are condensed in Fig. 3. The QM/PPC interaction energy (relative to the isolated molecule) is represented in Fig. 3a, as a function of the rotation angle \( \theta \) for the whole set...
of x- and y-positions sampled over the ZnO(10\bar{1}0) surface unit cell.

![Fig. 3: Adsorption scenario of 2P on the ZnO(10\bar{1}0) surface as computed by the QM/PPC method. a) Molecule-substrate interaction energy versus rotation angle \(\theta\) for all x- and y-positions counted. \(\theta = 0\): long molecular axis along x-direction (see Fig 1a). In b) and c), the interaction energy is plotted versus the z- and y-component, respectively, of the induced dipole moment.](image)

The absolute minimum is found at \(\theta = 90^\circ\) (long 2P axis \(\parallel\) y). However, there is also a second minimum at \(\theta = 0\), which corresponds to the one in Fig. 2b. The energy difference between the two minima is only 20 meV and hence within the numerical error range. We conclude that the 2P molecule can be arranged on the ZnO(1010) surface in two different cross-aligned orientations which makes the formation of a well ordered monolayer rather questionable.

The central question to be answered is about the mechanism controlling the alignment of the molecule. The interplay between the surface electrostatic field, the induced dipole moment, and the interaction energy becomes evident from Fig. 3b and c. There is a distinct linear relation between the \(\Delta E\) and \(\mu_z\). The energy is minimized if and only if the dipole moment along z is maximized. On the other hand, as seen in Fig. 3c, it holds \(\mu_y \approx 0\) at the energy minimum, but there is no direct relation like in the case of \(\mu_z\).

The above findings become more transparent in an analytical model gathering the leading features of the molecule. The energy of a molecule with zero static dipole but finite quadrupole moment \(M_{ij}\) in a weak but non-uniform electric field \((F_z \approx 0)\) is

\[
\Delta E \approx \frac{-1}{2} \sum_{i=x,y,z} \left( M_{ii} \frac{dF_i}{dr_i} + \alpha_{ij} F_j^2 \right),
\]

where \(\alpha_{ij}\) is the molecule’s polarizability tensor. This expression is derived from perturbation theory: the first term represents the electrostatic interaction between the external non-uniform perturbing field and the unperturbed molecule, the second one the induction energy [10] accounting for the molecular polarization created by the field. Eq. 1 is valid for a large class of planar, symmetric oligomers characterized by vanishing off-diagonal elements of \(M_{ij}\) and \(\alpha_{ij}\). The ZnO(1010) surface periodic dipolar electric field seen by the molecule can be approximated by (see Fig 2c,d and Ref. [11])

\[
F_y(y, z) \approx A e^{-k z} \cos(k y), \quad F_z(y, z) \approx -A e^{-k z} \sin(k y)
\]

with \(k = 2\pi/a\) so that its norm \((F \approx A e^{-k z})\) is independent on \(y\) and

\[
\frac{dF_y}{dy} \approx k F_z, \quad \frac{dF_z}{dz} \approx -k F_z.
\]

Using that \(\mu_i = \alpha_{ii} F_i\) and inserting (2) in (1), we obtain

\[
\Delta E \approx -B \mu_z - C \mu_z^2 - \frac{\alpha_{yy} F^2}{2}
\]

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

| molecule | \(M_{yy}\) | \(M_{zz}\) | \(\alpha_{xx}\) | \(\alpha_{zz}\) | B | C |
|----------|----------|----------|-------------|-------------|----|----|
| a.u. | a.u. | a.u. | eV/D | eV/D^2 |
| 2P | -46.2 | -57.3 | 217.4 | 68.2 | 0.558 | 0.068 |
| 6P | -135.7 | -168.4 | 1257.6 | 190.5 | 0.589 | 0.062 |
| 5A | -82.6 | -101.4 | 645.2 | 115.2 | 0.557 | 0.084 |
| 5PV | -145.3 | -180.1 | 2052.9 | 207.8 | 0.574 | 0.090 |

**TABLE I: PBE quadrupole moments \((M_{yy}, M_{zz})\), polarizabilities \((\alpha_{xx}, \alpha_{zz})\) as well as B and C coefficients (see text) for different molecules.**

Table II 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 opto-electronics. Though the anisotropy of \(\alpha\) can be quite significant, the term quadratic in \(\mu_z\) in (3), originating from the induction energy, is negligible against the linear term (i.e., the quadrupolar contribution) for weak fields. Hence, the analytical model fully recovers the numerical results of Fig. 3b. A linear fit to the data in Fig. 3d for 2P provides a slope of -0.48 eV/D in very good agreement with the value expected from Table I.

The analytical treatment suggests that the electrostatic scenario found for 2P is of general validity. Indeed, the full numerical analysis confirms this for 6P, 6A, and 5PV. A global optimization for molecules of this size cannot be carried out using first-principles methods only and, usually, semi-empirical approximations have to be employed [17]. The QM/PPC approach is instead non-empirical because the only parameter (q) is fixed from a first-principles (PBE/PW) calculations. We thus were able to perform the same global scan of the PES as for 2P. Fig. 4 demonstrates that the linear relation between...
interaction energy and vertical dipole moment is a common feature for this class of non-polar molecules. Even, the slope of the curves is almost the same (-0.46 ± 0.58 eV/D), consistent with the similar values of $B$ in Tab. [I]

FIG. 4: Interaction energy for 6P, 5A and 5PV on ZnO(10¯10) in QM/PPC. a) Linear relation between molecule-substrate interaction energy and induced vertical dipole moment. b) Interaction energy versus rotation angle, only the minimum values from all $x$- and $y$-positions scanned are shown. Inset (color-online): Orientation of 6P at the global minimum shown on a colormap of the $z$-component of the surface electric field.

Although the linear energy-dipole relation holds for all these molecules, the specific alignment on the substrate can be substantially different. This is documented in Fig. [4b], where the energy is plotted as a function of $\theta$ at $x$- and $y$-positions with minimized energy. In contrast to 2P, the PES of both 6P and 5PV exhibits deep global minima at $\theta = 0$, clearly separated by 140 meV and 330 meV, respectively, from other arrangements. Not only the orientation but also the lateral position of the adsorption site is uniquely defined, with $y \approx 3.7$ Å and $x = 0$ for both 5PV and 6P. 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 $\mu_z$ are maximized. The longer the molecule, the more stable the alignment. The PES of 5A is instead less deep and structured. In contrast to 6P/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 it is for 6P/5PV.

In conclusion, we found that the periodic dipolar electric field of the ZnO(1010) surface plays a key role in the adsorption of typical oligomers. When the molecules exhibit an axially oriented $\pi$-electron system, a well-defined molecular alignment, stabilized by energies larger than 100 meV against reorientation, is established, as observed experimentally for 6P [7]. 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 and/or to design the molecular orientation on the surface. Moreover, this dipole moment is directly associated with workfunction changes [18], and thus provides a tool for engineering the energy level adjustment of inorganic/organic hybrid structures [7]. Finally, we note that the single-molecule adsorption described above will be perpetuated and will result in molecular assemblies reflecting the topology of the surface field. Although the induced dipole moment is modified by depolarization effects [18, 19], this energy scale is certainly significantly smaller than the electrostatic molecule-substrate coupling controlling the alignment on the surface. Therefore, we believe that our findings define a route towards the realization of highly-ordered self-assembled arrays of oligomer/polymers on ZnO(1010) and similar surfaces.

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