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Depolarization Effects in Self-Assembled Monolayers: A Quantum-Chemical Insight**

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Many recent experimental studies have demonstrated that the deposition of a self-assembled monolayer (SAM) made of polar molecules on a metal surface can significantly modulate its work function and hence the barrier for hole and electron injection in optoelectronic devices. The permanent dipole moment associated with the backbone of the molecules plays a key role in defining the amplitude and direction of the work-function shift. We illustrate here via quantum-chemical calculations performed on model systems that the dipole moment of molecules is significantly reduced going from the isolated state to the SAM. Such depolarization effects that are most often neglected thus reduce the work-function shift and have to be taken in account to control and understand charge-injection barriers in devices at a quantitative level.

1. Introduction

Charge injection from metallic electrodes to organic layers is a key mechanism governing the overall performance of organic-based devices such as light-emitting diodes and field-effect transistors.^[1,2] The injection barrier for holes/electrons is often defined in first approximation as the energy difference between the work function of the electrode and the highest occupied/lowest unoccupied molecular orbital (HOMO/LUMO) of the organic material. These barriers have to be minimized to reduce the operating voltage of the devices; moreover, in light-emitting displays, the injection barriers at the two electrodes should have a similar height in order to best balance the hole versus electron injection and hence avoid the accumulation of one kind of carrier in the device. Over the years, several strategies have been developed to modulate energy barriers. The simplest is to change the work function of the electrode by varying the nature of the metal or conducting polymer used.^[3] This is, however, of limited applicability owing to the reduced number of suitable materials, especially for electron injection. Another approach is to modify the energy of the HOMO and LUMO levels of an attractive compound by decorating its main backbone with electroactive substituents.^[4,5] A subtle in-

terplay of mesomeric versus inductive effects dictates the amplitude of the shift, with a donor character leading to a destabilization and an acceptor character to a stabilization of the frontier electronic levels. Since a single compound cannot generally provide an optimized barrier both for hole and electron injection at the same time, several layers are typically introduced in light-emitting devices. This has led to the concept of electron- and hole-transporting layers that are used to independently optimize carrier injection in the devices.^[6]

Recently, a large number of experimental studies have demonstrated that the work function of metallic systems such as gold, silver, copper, or indium tin oxide (ITO) can also be tuned by depositing a self-assembled monolayer (SAM), that is, a dense 2D array of molecules, onto them.^[7–16] Note that SAMs further contribute to the reduction of image charge effects that can trap the charges at the proximity of the electrodes.^[9] The backbone of the molecules forming SAMs is typically substituted by an anchoring group that promotes a strong binding to the surface and, in some instances, by a terminal group bearing some chemical functionalities. A prototypical case is the deposition of alkanethiol molecules on a gold surface;^[17–19] in this case, the thiol group of the molecule acting as the anchor is broken during the adsorption to promote the formation of a covalent bond between the sulfur atom and the gold surface. The modulation of the work function relies on the presence of an array of dipoles at the metal/SAM interface, which generates an abrupt shift in the electrostatic potential at the interface (also referred to as a vacuum level shift, VLS). Thus, the interface dipole also induces a change in the amplitude of the injection barriers compared to a situation where there is a full alignment of the vacuum level at the interface (i.e., the Schottky–Mott limit). When the dipole (whose direction is defined as going from the negative to the positive pole) points towards the organic layer, the work function of the metallic electrode is reduced and the hole [electron] injection barrier is increased [lowered], see Figure 1. The opposite holds true when the dipole points towards the metallic surface.

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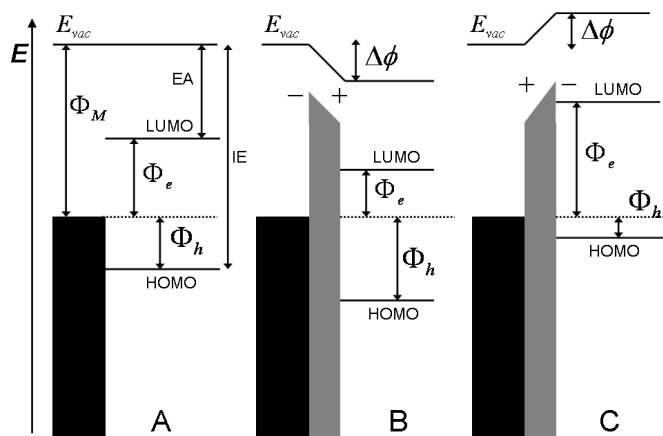


Figure 1. Electronic structure of A) a metal/organic interface in the Mott-Schottky limit and when a SAM of dipolar molecules is inserted with the dipole pointing towards B) the organic layer and C) towards the metallic surface. Φ_M is the work function of the metallic electrode, Φ_h the barrier for hole injection, Φ_e the barrier for electron injection, and $\Delta\phi$ the vacuum level shift.

The total interface dipole is made of different contributions: i) the dipole originating from a possible local charge transfer between the anchoring group and the metallic surface; in the case of thiolated compounds, the amplitude of this dipole is generally not influenced by the nature of the molecular backbone;^[20,21] and ii) the permanent dipole moment of the molecular backbone of the SAM-forming molecules. Also, it is important to consider that the electron tail protruding out of a bare metallic surface is repelled into the bulk as soon as molecules of any kind are deposited on its surface. This “pillow” effect thus systematically leads to a reduction of the work function of the electrode by a few tenths of an electronvolt.^[1,22,23] Moreover, the deposition of the molecules can be accompanied by a significant charge redistribution at the metal/organic interface that creates a dipole in the metal and/or around the anchoring group of the molecule in the absence of a charge transfer, as suggested by recent density functional theory (DFT) calculations.^[20,24]

It is now highly desirable to perform a large number of experimental and theoretical studies on metal/SAM interfaces to determine the relative weight of the various effects responsible for the interface dipole build-up and to establish structure-property relationships. At the theoretical level, a deep insight into such interfacial effects can be gained by performing first-principle calculations on metallic slabs covered by a SAM. Though being very powerful, this kind of theoretical modeling typically performed at the DFT level is still in its infancy and considerable efforts are still required to assess the reliability of such approaches and the choice of the best functionals and basis set. Simple expressions have also been used to estimate the work-function shift as a function of a limiter number of parameters. When considering separately the molecular and interfacial contributions, the work-function shift $\Delta\phi$ is given by classical electrostatics as:

$$\Delta\phi = N \left(\frac{\mu_{\text{Mol}}}{\epsilon_0 \epsilon_{\text{Mol}}} + \frac{\mu_{\text{M-S}}}{\epsilon_0 \epsilon_{\text{M-S}}} \right) \quad (1)$$

where N is the number of molecules per unit area, μ_{Mol} is the component perpendicular to the metallic surface of the dipole moment of the molecular backbone, $\mu_{\text{M-S}}$ is the dipole moment created locally between the anchoring unit of the molecules and the metallic surface due to the charge transfer and/or reorganization; ϵ_0 is the permittivity of free space, and ϵ the static dielectric constant. Note that the shift of the work function, induced by the pillow effect, is not accounted for in Equation 1; in the case of a gold surface, this shift has been estimated to be on the order of 0.5 eV.^[8,25,26] Recent experimental ultraviolet photoelectron spectroscopy (UPS) studies of alkanethiol molecules and derivatives on gold further indicate from a careful analysis of the chain-size dependence of the vacuum-level shift that the interfacial contribution is very small (between +0.02 eV and -0.05 eV).^[8] According to Equation 1, this suggests that the shift can be assessed in that case only from the amplitude of the permanent dipole moment of the molecule and the dielectric constant of the layer (which varies with the size of the molecules^[27] and with the layer density^[28]). In general, since the number of attractive anchoring groups is limited, the simplest strategy to vary the direction of the VLS shift is to modulate the permanent dipole moment of the molecular backbone, thus pointing to the key role played by the first term in Equation 1.

In many recent papers, the permanent dipole moment of the isolated molecules forming the SAMs has been calculated at the quantum-chemical level to shed light into the expected amplitude and direction of the VLS on the basis of Equation 1.^[7-9] This is clearly an approximation in situations where the anchoring group is involved in both the interfacial and molecular dipole moment. More importantly, this approach neglects possible depolarization effects in the SAMs, namely, the electric field generated by the permanent dipole of a molecule is likely to perturb the charge distribution and hence the dipole moment of the neighboring molecules and vice versa. Thus, this interaction is likely to reduce the permanent dipole moment of the individual molecules. Depolarization effects have been reported for the interface dipole generated by depositing atoms on a metallic surface.^[29,30] Such effects have been treated explicitly so far at the classical level, which yields the dipole of a molecule in a SAM as:^[31,32]

$$\mu = \mu_0 (1 + 9\alpha N^{3/2})^{-1} \quad (2)$$

with μ and μ_0 the dipole of the molecule in the SAM and in the isolated state, α the polarizability of the molecule, and N the number of molecules per unit area. This approach describes the dipole in a point representation, which works well only when the size of the molecule is smaller than the intermolecular separation;^[33] as this is practically never the case in actual systems, it is necessary to expand the dipoles into atomic contributions to provide a more reliable description of their interaction.^[34] This can only be achieved at a quantum-chemical level and has thus motivated the present theoretical study, the main goal of which is to estimate quantitatively the extent of depolarization effects in SAMs. We thus focus here exclusively on the molecular contribution to the work-function shift. We

will show below that such effects are significant in SAMs and should be accounted for in simple expressions developed to estimate these shifts. Our theoretical methodology is described in Section 2 and the results of our calculations are collected in Section 3.

2. Theoretical Methodology

We have first built model molecular clusters of increasing size with three different molecules; they all contain a thiol and a nitro group as terminal substituents and six carbon atoms in the molecular backbone (i.e., a benzene ring for **1**, a hexatriene spacer for **2**, and a saturated chain for **3**). In order to determine the amplitude of depolarization effects in longer segments, we have also considered the three series of push-pull molecules displayed in Figure 2, with n varying from 0 to 3 ($n=0$ corresponds to the small molecules initially used); the same terminal substituents and the same number of carbon atoms in the molecular backbone are found among the members of these three series. The geometry of the isolated molecules have been optimized at the semiempirical Hartree–Fock Austin Model 1 (AM1)^[35] level with the MOPAC software by imposing a constraint of planarity for the conjugated molecules and an all-trans configuration for the saturated chains. The substituents are forced to lie in the same plane as that defined by the carbon atoms of the molecular backbone. In order to compare the extent of depolarization effects for the different molecules in the same conditions, we have built one- and two-dimensional model clusters with the molecules packed in a similar way; the geometry of the molecules is not reoptimized when building the clusters. The extent of depolarization has been quantified from

the reduction of the dipole moment going from a value characteristic of a single molecule to the average value in the clusters. The choice of the semi-empirical AM1 technique has been validated for small clusters by performing similar calculations at the Hartree–Fock ab initio level with a 6-31G** basis set (vide infra). Note that DFT has not been applied in view of the known limitations of most current functionals in describing the dipole moment and linear polarizability of push-pull molecules.^[36] The charge distribution and the amplitude of the individual dipole moments have been estimated in the clusters by a population analysis performed within the zero differential overlap (ZDO) approximation; this is applicable owing to the fact that there is no charge transfer between the molecules in the clusters.

3. Results and Discussion

Figure 2 shows the size evolution of the permanent dipole moment for the three series of molecules. As expected, the dipole is the smallest for the saturated chains where only inductive effects can promote a charge transfer between the substituents and the molecular backbone; the permanent dipole is amplified via mesomeric effects in the presence of a conjugated backbone. The fast saturation of the dipole with molecular size (around 9 debyes (D ; $1 D = 3.335 \times 10^{-30}$ Cm) for series **1**, 7D for series **2**, and 4D for series **3**) demonstrates that the dipole should not be seen as having one negative pole on the nitro and one positive pole on the thiol; indeed, this would lead to a continuous increase of the dipole with the size of the spacer. Instead, the results, supported by a detailed population analysis, indicate that the molecules are made of two local dipoles located around the chain ends, thus rationalizing why the dipole does not further increase when the central part of the backbone is elongated; this description is clearly more approximate for the smallest molecules of the three series.

Figure 3 illustrates the evolution of the extent of depolarization in one-dimensional stacks formed by the smallest molecules of the three series ($n=0$) as a function of the number of molecules in the stack; the molecules are separated here by an intermolecular distance of 5 Å, which is typical for a SAM.^[19] The depolarization is quantified as $(\mu_0 - \mu_{av})/\mu_0$, with μ_0 being the dipole moment of the isolated molecule and μ_{av} the average dipole moment in the stack (estimated as the total dipole divided by the number of molecules). The results show that the amplitude of the depolarization effects saturates very quickly (around 20 molecules). The dipole moment of **1** saturates at a value of 5.62D compared to 6.19D for the isolated molecule, thus representing a loss

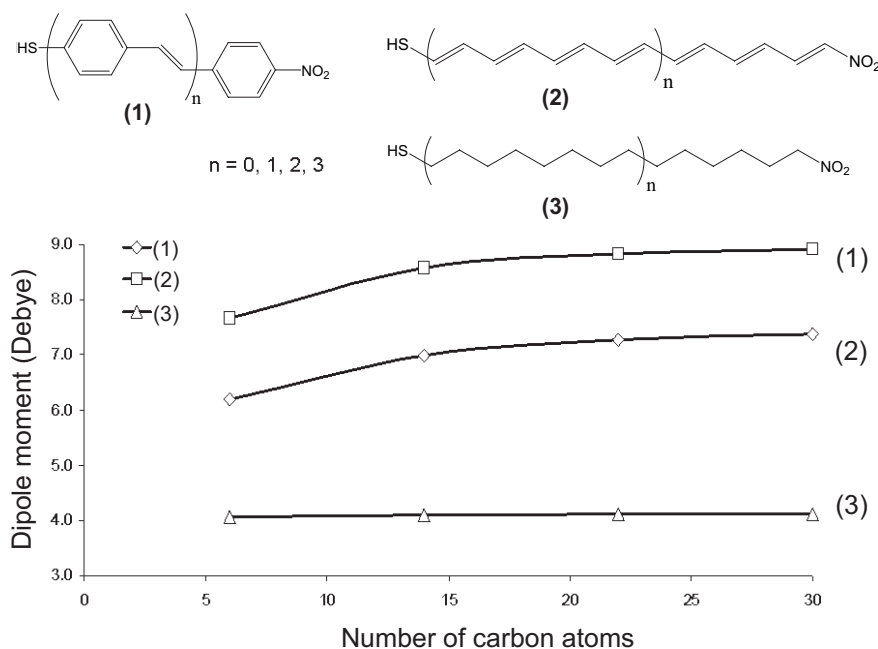


Figure 2. Chemical structure of the three series of push-pull molecules under study (top); AM1-calculated evolution of the permanent dipole moment in the three series of molecules as a function of the molecular size (bottom).

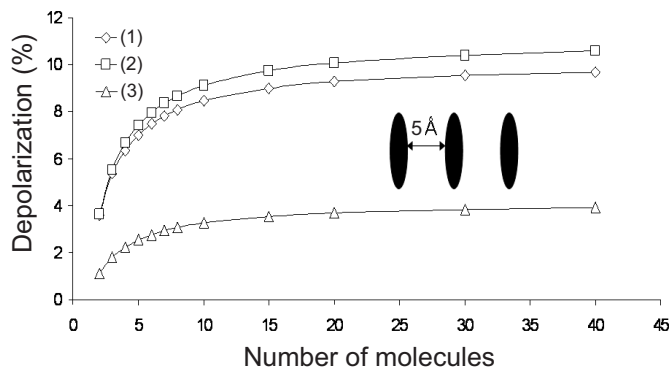


Figure 3. AM1-calculated evolution of the degree of depolarization in a one-dimensional stack built with the smallest molecules of the three series ($n=0$), in a cofacial configuration and an intermolecular distance fixed at 5 Å, as a function of the number of molecules in the stack.

of 9.3%. A similar depolarization is calculated for **2** (from 7.66D to 6.89D, a loss of 10.1%), whereas a less-pronounced effect prevails for **3** (from 4.07D to 3.92D, a loss of 3.7%; note that this percentage is further amplified by the initial small amplitude of the dipole moment of the isolated molecule). The dipole moment of the three molecules is reduced by a similar amount when repeating the same calculations on clusters containing up to 15 molecules at the Hartree–Fock level with a 6-31G** basis set, thus validating the choice of the AM1 method. The saturated values are fully consistent with those obtained by performing AM1 calculations with periodic conditions. The use of a large unit cell (at least five molecules in our case) is required to minimize the errors with the band-structure approach implemented in MOPAC,^[37] this has actually prevented the use of periodic conditions for two-dimensional stacks.

At first sight, the results shown in Figure 2 are readily explained by the higher polarizability of molecular backbones possessing π electrons. However, the average static polarizability values calculated with the AM1 Hamiltonian coupled to a finite field (FF) approach^[38] are similar for **1** and **3** (25.5 vs. $22.3 \times 10^{-24} \text{ cm}^3$, respectively) and are both smaller than the value obtained for **2** ($36.6 \times 10^{-24} \text{ cm}^3$). The somewhat surprising result that a benzene ring has a polarizability comparable to that of a corresponding saturated chain is supported by experimental data^[39] ($10.74 \times 10^{-24} \text{ cm}^3$ for benzene and $11.9 \times 10^{-24} \text{ cm}^3$ for *n*-hexane); this can be rationalized by the fact that the large energy resonance (i.e., aromaticity) of the benzene ring tends to strongly limit polarization effects. The polarizability of the molecules is therefore not the only factor driving the calculated evolutions. Another key parameter is the initial permanent dipole moment of the molecules, which is larger for **1** and **2** (6.91D and 7.66D, respectively) than for **3** (4.07D). Since a larger dipole moment generates a larger electric field, the extent of depolarization is thus expected to be more pronounced for **1** and **2**. The lower static polarizability and lower permanent dipole moment of **3** rationalize the reason for which the extent of depolarization is the least pronounced for the saturated chain. However, these two sole parameters cannot yet explain why **1** and **2** exhibit similar depolarization effects despite the fact that **2** is much more

polarizable. This points to the fact that the spatial distribution of the charges forming the two local dipoles is yet an additional parameter to consider. All together, the results demonstrate that a subtle interplay between the amplitude of the static polarizability, the amplitude of the permanent dipole moment, and the spatial location of the atomic charges dictates the calculated evolutions.

When calculating the individual dipole moments of the molecules in the stacks via a population analysis performed at the ZDO level, we observe that the dipole moment of the inner molecules is significantly reduced and that border effects contribute to an increase of the average dipole moment; this is why a critical cluster size has to be reached before obtaining converged results. The evolution of the average dipole moment in a cofacial dimer as a function of the intermolecular distance further indicates that the depolarization effects become clearly significant for intermolecular distances shorter than 20 Å, that is, in a range of distances where a point-dipole representation is not applicable for quantitative analysis.

The extent of depolarization is found to be reduced when increasing the size of the molecular backbone for the three series of compounds; this is shown in Figure 4 reporting the extent of depolarization in a one-dimensional stack formed by **1**, for n

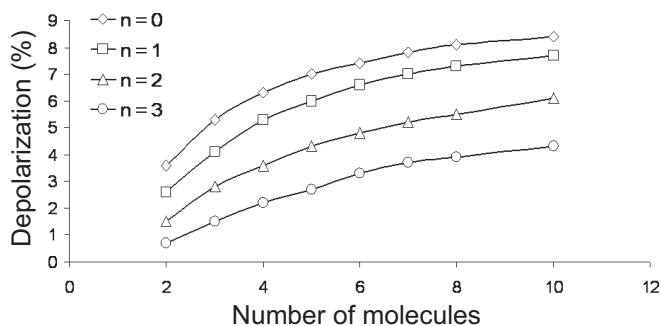


Figure 4. AM1-calculated evolution of the degree of depolarization in a one-dimensional stack built with the molecules of series **1** ($n=0-3$), in a cofacial configuration and an intermolecular distance fixed at 5 Å, as a function of the number of molecules in the stack.

varying from 0 to 3, as a function of the number of molecules. These results suggest that the local polarizability is not uniform over the conjugated backbone and that the external units become less polarizable when the chain size grows. This appears to be consistent with the results of recent work introducing a submolecular partitioning scheme of the hyperpolarizability in push-pull compounds.^[40]

We evaluated the amplitude of depolarization in two-dimensional stacks, which are more representative of the actual SAMs. Calculations have been performed on model stacks built from the smallest molecules of the three series ($n=0$) in order to investigate the influence of packing density and geometry. The two-dimensional square clusters are limited in size to 49 (7×7) molecules owing to computational limits in MOPAC: note also that the maximum size of the unit cells that we can consider (less than 200 atoms) are too small to perform reliable band-structure calculations. We have considered four different

packing structures for the three molecules in order to compare the extent of depolarization in similar conditions. We distinguish in Figure 5: i) the “model” packing obtained by translating laterally by 8 Å the one-dimensional stacks previously dis-

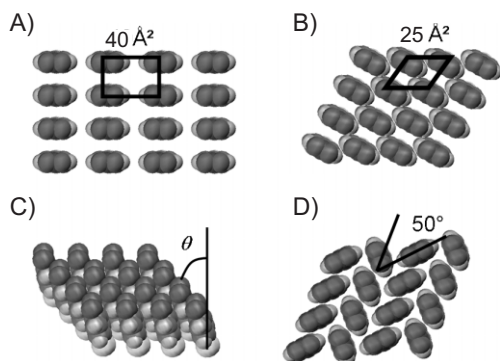


Figure 5. Illustration of the various packings considered for the two-dimensional square ($n \times n$) clusters: A) model packing; B) compact packing; C) tilted packing; and D) herringbone packing. See text for more details.

cussed (with an intermolecular separation fixed at 5 Å); the surface per molecule is thus 40 Å², which is much larger than corresponding experimental values (about 21.6 Å² both for alkanethiols and oligophenylthiols,^[19] respectively); ii) the “compact” packing where the surface per area has been scaled down to 25 Å²; iii) the “tilted” packing where the chains in the compact geometry have been tilted by 15° for **1** and 30° for **2** and **3** with respect to the normal to the molecular layer while keeping a surface per molecule of 25 Å²; such tilting angles are characteristic of those reported in the literature for alkanethiol and arenethiol molecules;^[41,42] and iv) the “herringbone” packing where two inequivalent molecules are introduced by rotating one column of molecules by 50° while keeping the same surface area as in (ii) and (iii); such a packing is characteristic of phenylene-based molecules in SAMs^[43] and of many small unsubstituted conjugated molecules in the crystalline state.^[44]

Figure 6 shows the degree of depolarization as a function of the number of molecules in the four different packing structures for the three molecules. For **1**, the increase in the packing density going from 40 to 25 Å² per molecule promotes an increase in the extent of depolarization (from ca. 15% to 25% or, similarly, from a loss of 0.93D to a loss of 1.55D). Strikingly, variations in the packing geometry for a given areal density hardly impacts the depolarization effects. The insensitivity to the rotational angle is readily explained by the cylindrical symmetry of the molecule with respect to the long molecular axis. For such symmetrical molecules, the degree of depolarization thus appears to be exclusively governed by the packing density. This symmetry is lost in molecules **2** and **3** where the nitro group is tilted with respect to the long molecular axis. For molecule **2**, the increase in the packing density has a much larger impact than the variations in the packing geometry, while the opposite holds true for molecule **3**. The tilt angle is found to slightly reduce the degree of depolarization in both cases and the rotation to increase it by promoting shorter separations be-

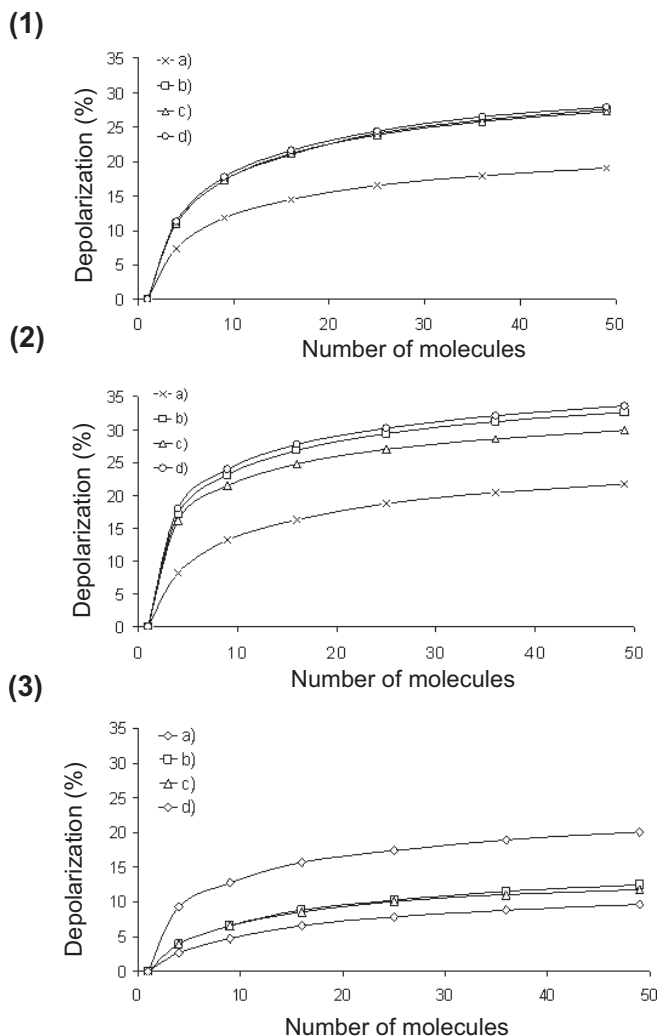


Figure 6. AM1-calculated evolution of the degree of depolarization in the four packing structures considered for the two-dimensional clusters built with the smallest molecules of the three series (**1** at the top, **2** in the center, and **3** at the bottom) as a function of the number of molecules in the cluster.

tween the nitro groups of adjacent chains. The weaker impact of the packing density for molecule **3** is reflected in Figure 5, which shows that the evolution of the depolarization with the interchain distance has a larger slope for a molecule displaying a larger dipole moment. This is rationalized by the fact that the dipole moment around the nitro group is more localized in **3** than in **2**; only the charges of the two neighboring carbon atoms are affected by the introduction of the nitro group in **3**, whereas those of all carbon atoms are affected in **2**. As a result, stronger interactions are promoted in the former case by the rotation when the nitro groups get closer.

4. Conclusions

Quantum-chemical calculations performed on model one- and two-dimensional clusters formed by push-pull molecules il-

lustrate that the dipole moment of the individual molecules is strongly reduced going from the isolated state to the aggregate. Such depolarization effects also act to accommodate dipolar molecules in dense two-dimensional arrays by reducing their dipole–dipole interactions. The reduction in the dipole moment obtained for the model compounds under study can be as high as 30%; this behavior is governed by the interplay between several parameters: the amplitude of the dipole and the spatial distribution of the atomic charges at the molecular level, and the packing density and geometry at the supramolecular level. The subtle effects revealed by the quantum-chemical calculations cannot be accessed from traditionally used classical descriptions based on the severely limited point-dipole approximation. The present results are applicable to all dipolar molecules currently used to modulate the work function of metallic electrodes via the deposition of a SAM. In view of their significant impact, these depolarization effects have to be fully taken into account to understand, and control at a quantitative level, the work-function shift of metallic electrodes and hence the charge-injection barriers in organic-based devices. Such corrections are on the order of a few tenths of an electronvolt. Our study further demonstrates that estimates of VLS shifts based on the dipole moment of an isolated molecule can prove very misleading.

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