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From high quality packing to disordered nucleation or phase separation in donor/acceptor interfaces: ClAlPc-C$_{60}$ on Au(111)

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The dramatic consequences that the orientation adopted by the molecular dipoles, in diverse arrays of chloroaluminum phthalocyanine (ClAlPc) on Au(111), have on the ulterior adsorption and growth of C$_{60}$ are explored by means of an all scanning probe microscopy approach. The unidirectional downwards organization of the molecular dipoles at the first layer reduces charge transfer from the metal to C$_{60}$. Imbalance between attractive and repulsive interactions of the fullerenes are crucial for their ordered supramolecular aggregation. The effect at the basis of such self-assembling seems to be released by the all upwards dipole orientation adopted on the ClAlPc second layer. The low electronic corrugation of the bilayer repercussions in a higher mobility of the fullerenes which for similar coverages diffuse large distances to reach uncovered first layer regions. Density functional theory calculations corroborate the experimental observations indicating the relevance of charge transfer, potential energy surface corrugation, C$_{60}$ on-surface diffusion barriers and screening. The structure of the co-adsorbed C$_{60}$ and ClAlPc layers strongly depends on the deposition sequence. Phase-separation, where each molecule adopts the single-component assembly, occurs if C$_{60}$ is deposited first. The present results contribute to understanding the influence of the dipolar nature of molecular layers on the electronic and structure of donor/acceptor heterojunctions, which is crucial for device design via engineering the energy levels alignment at the organic-organic and organic-metal interfaces.

Introduction

Understanding the fundamental processes taking place between organic molecules at the donor/acceptor interface, as well as the role of the metal surface, is of enormous importance to optimize organic electronic devices, such as organic displays, organic field effect transistors, and organic photovoltaic cells. In particular, how competing intermolecular interactions at different scale lengths influence molecular assembling, affecting the interfacial structure, is relevant for practical applications because it controls the band alignment of the molecular systems. Investigating these issues implies, however, the complex task of considering several weak interactions, such as van der Waals, hydrogen bonding and electrostatic interactions. Moreover, supramolecular organization and self-assembly$^{1,2}$ (the “bottom-up” fabrication method with the lowest energy consumption) on metals and charge transfer between metal surfaces and molecules$^{3,4}$ (essential for charge injection/extraction in molecular electronics) depend on a delicate balance between inter and intramolecular interactions and molecule-surface interactions, which are highly system-dependent. Therefore, the relevance of describing the electronic processes at the molecule/molecule and molecule/metal interfaces, in connection with the structure of the interfaces themselves, is evident for application in devices that involve molecular species in contact with metallic electrodes.

In the workbench of electronic interface design, sandwich structures, where one thin organic layer, acting as spacer, is intercalated between the metallic substrate and the electron acceptor material, have been routinely employed to tune surface work function and control charge transfer from the metal. Self-assembled monolayers covalently bonded to the metal are the most common dielectric spacers used to this end.$^{5,6,7,8}$ Richer though much complex scenarios are open at the donor/acceptor interface using small organic semiconductor molecules.

For years, C$_{60}$ fullerenes have been considered as the archetypal electron acceptor materials due to their large electron affinity and good stability. Because their practical relevance, a good deal of experimental and theoretical investigations have been devoted to both, electronic properties and structural details, for fullerenes on close-packed metals.$^9$ Fewer exist concerning the growth of C$_{60}$ on top of ordered organic monolayers on metals.$^{10,11,12,13}$ In all cases, the subtle balance between molecule-molecule and molecule-substrate...
interactions is invoked. In particular, the observation of serpentine one dimensional chains or disordered phases have been interpreted in terms of repulsion between fullerene molecules that result charged to some extent after charge transfer from the metal to the fullerene through the intercalated layer. The possibility of modulating the weight of the contributing interactions by incorporating, under the acceptor molecules, layers made out of molecules with permanent dipolar moment of diverse orientation emerges as an appealing benchmark. Wei et al. investigated how polymorphism of well-organized monolayers of the polar titanyl phtalocyanine (TiOPc) affects the interface built upon polymorphism of well-organized monolayers of the polar titanyl TiOPc molecules initially packed in a tilted (non-planar) configuration were displaced by the C60 deposited on top.

In this context, the system formed by C60 and chloroaluminum phtalocyanine (CIAIpc) results attractive, because both are known to separately yield well-ordered monolayers on Au(111) which have been as well electronically studied. Herein, the effect of the molecular dipoles within a layer intercalated between C60 and the metal is studied by depositing C60 molecules at room temperature (RT) on diverse ordered CIAIpc layers. To understand the influence of dipoles orientation, three different scenarios are studied: all Cl-up monolayer, alternated Cl-up and Cl-down monolayer and a bilayer consisting of Cl-up and Cl-down molecules adopting a staggered stacking. Additionally, in an attempt to pursue the role of relative orientation between molecules, the reverse deposition order is also analyzed.

CIAIpc is a nonplanar molecule with permanent electric dipole perpendicular to its molecular π-plane that can adopt two distinct planar configurations (Cl-up and Cl-down) when adsorbed on metallic surfaces. Competing molecule-molecule and molecule-metal interactions make the adsorption of this dipolar molecules particularly complex. The CIAIpc/Au(111) system has been extensively studied and it is known that, after a moderate post-deposition annealing, the monolayer consists of a highly ordered array of all Cl-up molecules, where the interaction of the conjugated plane and the metal (π-σ coupling) overcomes the dipolar interaction between molecules. Molecules in the second layer adopt the Cl-down configuration and a fourfold adsorption that leads to a staggered stacking, optimizing the electrostatic interaction between first and second layers. It has been also reported that depending on the strain degree of the reconstructed topmost surface of the Au(111) substrate (that can vary with substrate preparation and post-growth annealing temperature) the first layer can be built up by the coexistence of Cl-down and Cl-up configurations, as reported for Au(111)/mica.

The combination of scanning tunneling microscopy (STM) and frequency modulation atomic force microscopy (FM-AFM) with ab initio calculations provide a vast description of the created C60/CIAIpc interfaces. The consistency of the energetic and structural landscapes in this particular donor/acceptor system provides some general clues to envisage future fine-tuning of surface work function and design controlled interfaces.

METHODS

Experimental details. The Au(111) single crystal (Mateck GmbH, Germany) was prepared by repeated cycles of Ar⁺ sputtering (0.8 keV) plus annealing at 600°C in a preparation chamber equipped with a Low Energy Electron Diffraction (LEED) optics and diverse evaporators connected to the STM/AFM characterization chamber. After several cleaning cycles, the observation of a sharp pattern by LEED and the herringbone (HB) reconstruction by STM confirmed a well-ordered clean Au(111). The HB double rows of discommensuration lines (DL) along the <112> directions were used to establish the crystal azimuth orientation for the structural analysis throughout the present work. This in-situ reference is of relevance since the HB pattern, driven by tensile surface stress, can have a very different local appearance on diverse areas of the same surface. Two different cases are the so called rosetta structure where HB domains converge in a complex star-like structure and the simplest pairwise parallel stripes with consequences on the characteristics of deposited molecular overlayers. It is worth mentioning that differences in Au(111) strain release have been shown to affect the orientation of the CIAIpc molecules within the monolayer leading to short-order and disordered mixed (Cl-up and Cl-down) monolayers. Conversely, the HB patterns have been reported to change upon adsorption of perylene and FePc due to an anisotropic stress induced by charge transfer at the Au interface.

The CIAIpc molecules (Sigma-Aldrich) were purified twice by gradient thermal annealing before being introduced in the ultra-high vacuum (UHV) chamber where they were degassed and sublimated employing a Knudsen cell at 345°C. Well-ordered layers were obtained in samples annealed for 10 min at 150°C immediately after deposition (post-growth annealing). The C60 molecules were as well in-situ deposited from the vapour phase using deposition rates of about 2-3 Å/min using a Knudsen cell (380°C). The diverse molecular coverages (θ) at the surface have been estimated from topographic STM images.

The experiments were carried out at RT under a base pressure of 1×10⁻¹⁰ mbar, using a commercial combined STM/AFM-UHV system Aarhus SPM 150 with KolibriSensor probes (f₀ ~ 1 MHz, Q ~ 25000) and a Nanonis Control System (SPECS Surface Nano Analysis GmbH). The sharp metallic tip was cleaned in-situ via Ar⁺ sputtering and, during STM measurements, was maintained oscillating at a constant amplitude (A = 200 pm) so that the tip-sample interaction was reflected in a frequency shift (Δf) from f₀. Topographic STM was conducted in the constant current mode and the simultaneous Δf was recorded. Typical tunnelling parameters were: sample bias voltages of 1.2 V and currents of 100-200 pA. The in-plane lattice constant, in high resolution images, and step heights, in large-scale images of the in-situ cleaned Au(111) were employed for calibration of the STM piezo scanner. In the employed setup, the bias voltage is applied to the sample. The local contact potential difference (CPD) of the surfaces was
Experimental results. Well-ordered monolayers of all Cl-up CIAIPc on Au(111) were prepared using a moderate post-growth annealing as described in the experimental section. The molecules self-arrange in the square lattice \((a_{\text{Cl-AlPc}} = b_{\text{Cl-AlPc}} = 1.38 \pm 0.02 \text{ nm})\) shown in Figure 1 and fully detailed in a previous work.\(^{19}\) In this monolayer, all molecules adopt the Cl-up configuration, that is, the layer consists of dipoles with unidirectional downwards orientation \((\mu_i)\) and their aromatic plane at about \(\sim 3 \text{ Å}\) parallel to the surface and rotated \(10^\circ\) respect the square unit cell axes.

As it can be seen in wide scan STM images (Figure 1b, 1c), large domains of the HB pattern of the reconstructed gold surface are visible underneath and are used to determine the substrate main crystallographic directions. In general, the persistence of the HB is interpreted as an indication of molecular physisorption on a non-strained Au(111) surface. It is worth mentioning here that the HB reconstruction is a manifestation of strain relief due to an increased density \((\sim 4\%)\) of the topmost surface relative to a bulk-truncated (111) surface. Subtle differences in surface relaxation have been observed, for example, in gold films grown on mica, Au(111)/mica.\(^{16}\) Creation of highly mobile adatoms during the preparation procedure may also lead to small density variability and subsequent layer strain fluctuations manifested through HB domain distribution. Since the quality of the organic overlay depends on it, we will come back to this fact later in this work.

On bare metal (111) surfaces, the C\(_60\) molecules are known to form close-packed hexagonal phases. In particular, on Au(111) it forms diverse well-ordered monolayers with commensurate structures among which the more frequently observed are: \((2\sqrt{3} \times 2\sqrt{3})R30^\circ\) and \((7 \times 7)R0^\circ,\)\(^{32}\) where \(R\) is the relative angle between the lattice orientation of the C\(_60\) overlayer and one nearest neighbour (NN) direction of the (111) substrate. Figure 2 illustrates the result of depositing a monolayer coverage \((0 - 0.3 \text{ ML})\) of C\(_60\) on a complete Cl-up monolayer. The particular surface region shown in Figure 2a contains two terraces separated by a monoatomic step of Au(111). As expected from the symmetry relationship between the square adlayer and the hexagonal planes of the fcc crystal, the relative orientation of the square lattices of CIAIPc at each
The side of the step is 60°. The excellent quality of the C₆₀ close-packed assemblies indicates a good mobility of these molecules at RT on highly ordered regions of the CIAIPc monolayer. The C₆₀ islands have an apparent height of 0.5 ± 0.5 nm with respect to the underlying CIAIPc monolayer and display a remarkable flatness, with a corrugation of 65 ± 0.5 pm. The molecules exhibit a smooth hemispherical shape. The unit cell of a₃C₆₀ = 0.98 ± 0.05 nm, oriented along the NN directions of the Au(111). The magnification images of Figures 2b and 2c and their corresponding two-dimensional fast Fourier transform (2D-FFT) in Figure 2d, permit deriving that the unidirectional epitaxial relationship of the two lattices is 5aClAlPc = 7aC₆₀ along the common [011]. In contrast to the large well-ordered 2D islands, wrinkled chains, isolated molecules and small disordered nuclei of C₆₀ are observed at the lower step edge and at less extended defects of the underlying monolayer on both terraces of Figure 2a. Such defects are associated either to the presence of disordered regions of CIAIPc molecules close to the steps or to domain boundaries of the square lattice. This is the case shown in Figure 2e. The existence of equivalent domains laterally displaced half unit cell, with the subsequent frontier along [1 1 2], is highlighted by the white dotted lines drawn in the Δf image of Figure 2f.

The similarity between the close-packed hexagonal phase, formed on the ordered CIAIPc monolayer (Figure 2a, 2c), and those found for C₆₀ layers on bare metal substrates is remarkable and manifestly contrasts with the quasi-one dimensional organization and low density disordered phases of C₆₀ over zinc phthalocyanine (ZnPc), pentacene or α-sexithiophene (α-6T) layers on (111) oriented Au and/or Ag surfaces. The lack of 2D order in those systems has been attributed to the competitive weight of attractive forces and long-range repulsive interactions, regardless of the supramolecular structure of the underlying layers. It is clear that the presence of an intercalated layer between the metal and C₆₀ may alter the C₆₀ intermolecular interactions. For example, in the absence of interlayer, the repulsive electrostatic interaction between charged molecules, due to charge transfer from the metal to the fullerenes, is effectively screened. Therefore, allowing molecular self-assembly. Even if charge transfer persist in the presence of an interlayer, the larger distance between the charged C₆₀ and the metal results in diminished screening. For non-charged or weakly charged fullerenes, the hexagonal packing is favoured by strong van der Waals attractions between molecules but is also an indication of their facile diffusion favoured by weak intermolecular interactions with the underlying organic molecules. Indeed, as we will describe below, electronic corrugation influencing diffusion barriers also plays a role and, in the case of an interlayer made out of non-planar molecules with permanent dipole, the scenario can get much more complicated.
As it is known, the work function ($\phi$) of the metals surface is modified by the adsorption of molecules through different processes among which, for example, molecule-substrate charge redistribution and “push-back” effect compete with permanent dipoles in the case of CIAIPc. Because the cases of the single layer (Cl-up) and the bilayer (Cl-down on Cl-up) have been already reported\(^{19}\) (see also Figure S1 in the ESI) we only briefly discuss here the consequences of the CIAIPc interlayer on the fullerene layer. Compared to the spatially averaged values obtained by UPS, CPD values obtained by local probes allow spatially resolved measurements on coexisting differentiated regions. Therefore, to get a picture of the energy level alignment, we performed systematic local CPDs on the similarly ordered layers of $\text{C}_60$ on the bare and on the CIAIPc monolayer. The result is presented in Figure 3, where the clean Au(111) work function ($\phi = 5.35$ eV) as measured separately by UPS is shown as a reference. On top of the well-ordered $\text{C}_60$ islands directly grown on gold (see for example Figure 5a), the work function is reduced by $\Delta \phi = -100$ meV. This reduction is lower than the reported by UPS for one monolayer.\(^{33}\) Otherwise, the effect of depositing an ordered CIAIPc monolayer on Au(111) is increasing the work function by $\Delta \phi = +70$ meV, a value that falls by $\Delta \phi = -50$ meV when $\text{C}_60$ islands are grown on top. In summary, the intercalation of an ordered Cl-up CIAIPc monolayer between $\text{C}_60$ and the metal surface slightly raises the work function above the Fermi level of Au(111). As we will discuss later, a direct consequence of this vacuum level offset is that electron transfer from the metal surface to $\text{C}_60$ becomes unfavourable. Though in this particular system, the absolute value of the changes are small, the results open new avenues for interface modification via surface engineering using dipolar molecular layers.

Despite the neat results described above for the all Cl-up monolayer formed over the highly ordered HB reconstruction of the relaxed Au(111) substrate, the situation becomes more complex if Cl-up and Cl-down configurations coexist on the very same molecular layer. In fact, in the absence of substrate influence, the dipolar interaction between CIAIPc neighbour molecules would favour assemblies with antiparallel orientation of the dipoles (Cl-up and Cl-down). Indeed, disordered or short-range order mixed 2D layers of CIAIPc have been reported for Au(111)/mica and ascribed to differences in the gold surface relaxation.\(^{16}\) Such a CIAIPc layer can be seen in Figure 4a and 4b, for a coverage slightly over the monolayer, with the concurrence of the first layer and some individual and small aggregates of a second layer. Close inspection to the lower level reveals that, in addition to the rounded protuberances (bright in both topography and $\Delta f$) typical of molecules in the Cl-up configuration, molecules with Cl-down are also seen (flat four lobes appearance in topography and featureless aspect in Figure 5).

![Figure 4](image_url)

**Figure 4.** (a) STM topography and (b) simultaneously measured $\Delta f$ for a mixed (Cl-up and Cl-down) monolayer of CIAIPc. Few second layer molecules are also seen. (c) and (d) STM topographic images of the same surface after deposition of 0.1ML of $\text{C}_60$. STM parameters: $I = 200$ pA and $V = +2.0$ V. The bicolor scale of (c) highlights the disordered nucleation of $\text{C}_60$ (red).
The distribution of each dipole orientation is estimated to be ~50% in the first layer. In the topographic image shown in Figure 4c a bicolour scale has been used to clearly differentiate the deposited C60 (red) from the ClAlPc molecules (green). The contrast between the disordered C60 aggregates on the mixed layer monolayer and the well-packed hexagonal assemblies on the all Cl-up monolayer (Figure 2a) is obvious. The lack of ordered packing of the fullerenes on the mixed surface is evidenced in the large-scale image of Figure 4d. Molecules accumulate in long vacancies at small single layer patches, but no order takes place. Then, we can conclude that though the mobility of the molecules is considerably high so they meet and nucleate together, the repulsive interactions seem enough to impede optimal close packing.

After knowing that the misaligned disposition of the permanent dipoles in the first layer (top Figure 5a) hinders organization of the fullerenes, we explore C60 deposition on an incomplete and defective bilayer. The staggered configuration of dipoles with opposite orientation within first and second layers is shown in bottom Figure 5a. Figures 5c-5f show different areas of the resulting surface after deposition of C60 (0–0.2ML). The most striking observation is that no matter how large the region is, there is neither adsorption nor nucleation on the second ClAlPc layer (Figure 5c). In fact, and contrary to what happens in the case of the Cl-up monolayer, no nucleation is observed at punctual defects (vacancies) or extended defects (domain boundaries). The molecules diffuse long distances (several tens of unit cells) over this layer to reach empty first layer regions, where due to the Cl-up and Cl-coexistence, they nucleate in a disordered manner (Figure 5c and 5d) as schematically depicted in the cartoon of Figure 5e. Remarkably, this process takes place even for relatively large amounts of deposited C60 (Figure 5f). In the corresponding Δf map of Figure 5g, the presence of two different domains and the downwards orientation of the ClAlPc molecules forming the second layer are clearly seen. A large amount of fullerenes, individually recognized in the images, huddle together at the domain boundary. Outstandingly, at the tallest region of the C60 pile (circled at the Δf image centre) some short-range order is detected, likely indicating the vanishing influence of the layer underneath. The lack of C60 adsorption on the second ClAlPc layer, even for a sufficiently large coverage, is certainly a consequence of a high mobility and large diffusion path of the molecules on the upper level. However, the origin of such low energy barrier for surface diffusion is elusive. As commented above, the key will be found at the electronic corrugation of the ClAlPc layer.

In an attempt to rationalize from a theoretical perspective the different scenarios experimentally observed after the deposition of C60 molecules on: i) well-ordered monolayers of all Cl-up ClAlPc on Au(111), and ii) ClAlPc bilayer on Au(111), we have carried out a large and time-consuming battery of DFT-based calculations. A detailed structural description of the two types of ClAlPc adlayers on Au(111) can be found elsewhere.19 The factors employed for the choice of the possible configurations, for C60 on both adlayers as well as for the gas-phase interaction geometries, are described in the ESI.

Interestingly, in the gas phase, the calculation indicates charge transfer and interaction energy strongly depend on the interaction geometry and relative orientation between the C60 and ClAlPc molecules (ESI, Figure S5). We have computed equilibrium geometries (keeping fixed the two bottommost Au(111) layers during the optimization process), adsorption energies and Bader charge transfers from the substrate for a C60 molecule (per unit cell) on a monolayer of Cl-up ClAlPc on Au(111) on three representative adsorption sites (for each}

![Figure 6](image_url)

**Figure 6.** Top and side (insets) pictorial views of the DFT-optimized structural models for the adsorption of C60 molecules on an ordered monolayer of all Cl-up ClAlPc on Au(111) for six representative adsorption sites (a–f). Unit cell used in the calculations is shown as a light-green dashed-lined box. Blue and red shadowed regions represent the Cl-up ClAlPc and C60 molecules, respectively. Computed Cl-NEB diffusion barriers (AE_{diff} in eV) are indicated along specified directions (black arrows) for each case. More details in Figure S2 of the ESI.

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governed by vdW interactions, nonetheless sufficient to anchor the molecules to the surface.

We have also computed the charge transfer processes (see Methods section) occurring after the formation of the interface of C₆₀ on the Cl-up CIAIPc/Au(111). We obtain charge transfers from the substrate to the C₆₀ molecules of 0.22 and 0.16 e⁻ for the configurations in Figures 6a and 6b, respectively. Within the theoretical formalism employed in this work, the charge transfer from the Au(111) to the C₆₀ in its most stable and fully relaxed (2√3x2√3)R30° periodic geometry is 0.28 e⁻. A value significantly lower than the 0.8 e⁻ estimated by resonant photoemission for the C₆₀/Au(111) interface. Although the computed values are of the same order with or without the CIAIPc monolayer, they are higher by a 30% and a 75% for C₆₀/Au(111) than for the configurations in Figures 6a and 6b. This can be considered as a non-negligible reduction of the charge transfer to C₆₀ in the presence of the unidirectional dipole interlayer. Therefore diminishing the charge-induced repulsion between molecules. Besides, upon higher adsorption the CIAIPc adlayer accumulates, in average per molecule, an excess of electronic charge of 0.19 e⁻, appreciably lower than without C₆₀ molecules (0.32 e⁻). The consequences in molecular assembling are reinforced by the calculation of diffusion barriers from the most stable configurations in Figure 6. The calculations yield on-surface diffusion barriers ranging between 0.36 eV and 1.71 eV, justifying only relative RT diffusion of the C₆₀ molecules on the Cl-up CIAIPc monolayer. The low repulsion between C₆₀ molecules, their moderate diffusion, summed to the intensity of the interaction with the underlying CIAIPc, favours the stabilization of the C₆₀ molecules and leads to the formation of the robust close-pack of the fullerenes observed in Figures 2a and 2c.

In a following step, we have computed equilibrium geometries, adsorption energies and Bader charge transfers from the substrate for a C₆₀ molecule (per unit cell) on the CIAIPc bilayer on Au(111). Figure 7 shows the 4 different adsorption sites studied (two with the interacting lowest part of the C₆₀ being a C₂-bridge and two being a C₆-ring), and the corresponding optimized geometries. In this case the most stable configurations are those with the C₆₀ molecule lying on the Al atom of the Cl-down CIAIPc molecules with a bottommost C₂-bridge (Figure 7a) and a C₆-ring (Figure 7b). The adsorption energies per C₆₀ in each configuration are 0.48 and 0.56 eV, respectively, with charge transfers below 0.02 e⁻, in a clear physisorption regime. For the other two cases (Figure 7c and 7d), adsorption energy and charge transfer are around 0.4 eV and <0.01 e⁻, respectively. The net charge accumulated in the bilayer of around 0.1 e⁻ in all cases. The scenario has completely changed with respect to the adsorption on the Cl-up CIAIPc monolayer. Now, the nature of the interaction is merely vdW and adsorption energies are rather low. In order to evaluate the diffusion rate of the C₆₀ molecules, we have computed the diffusion barriers, similarly to the previous case. Result of these calculations shows in all cases diffusion barriers < 0.11 eV independently on the diffusion direction tested, which justifies a high diffusion capability of the molecules deposited on the bilayer. This effect is clearly driven by the low electronic corrugation of the bilayer, leaving the C₆₀ molecules free to diffuse long distances on the surface until reaching highly-reactive on-surface defects or empty first layer regions, as experimentally evidenced.

With a last experimental case study, we will show that the structure of co-adsorbed C₆₀ and CIAIPc layers strongly depends on the deposition sequence. As already known, if C₆₀ is deposited first, islands of compact hexagonal packing are formed on the bare Au(111). For a coverage of θ–0.5ML, the surface is made out of crystalline C₆₀ patches surrounded by bare substrate (Figure 8a-8c). Some defects in the form of individual fullerenes with lower apparent height (darker in the image) is characteristic of C₆₀ on Au(111). The result of the subsequent deposition of 1ML of CIAIPc on such a surface is shown in Figure 8b. Remarkably, instead of covering the entire exposed surface (bare gold and C₆₀), the impinging phthalocyanines, do not adsorb on the fullerene layer but
balance between attractive and repulsive interactions and, therefore, in the aggregation of the fullerenes. On top of the unidirectional monolayer of CIAIpc, with all molecules in the Cl-up configuration (downwards dipoles), CIAIpc self-assembles in a robust close-packed hexagonal order. Conversely, CIAIpc molecules are arranged disorderedly when deposited on a monolayer with mixed orientation of the molecular dipoles (disordered coexistence of Cl-up and Cl-down). The overall compensation of dipoles in such mixed configuration would allow competition, between van der Waals intermolecular attraction and repulsion between charged C60 molecules, to manifest by a lack of order in their packing. Remarkably, despite the expected low electrostatic repulsion due to small charge transfer, C60 does not adsorb on the CIAIpc bilayer (topmost layer made out of all Cl-down, upwards dipoles) but nucleates at uncovered patches of the first layer. We ascribe this experimental evidence at the early stages of formation to a lower adsorption energy and the lower diffusion barriers calculated over the bilayer stack with respect to the monolayer. The structure of co-adsorbed C60 and CIAIpc layers strongly depends on the deposition sequence. If fullerenes are deposited first, phase-separation occurs, where each molecule adopts the structure of the single component cases on clean Au(111).

CONCLUSIONS

We provide experimental evidence of the influence of an intercalated layer of permanent dipole CIAIpc molecules on the charge transfer between Au(111) and the electron acceptor C60. Both electronic and structural details of the CIAIpc layers become relevant for the organic-organic interface properties. The significance of the charge transfer and energy alignment through the intercalated CIAIpc film has consequences in the

**Conflicts of interest**

There are no conflicts to declare.

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