Supramolecular Self-Assembly Driven by Electrostatic Repulsion: The 1D Aggregation of Rubrene Pentagons on Au(111)

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ABSTRACT At present, organic molecules are among the best candidate "building blocks" for the construction of self-assembling nanoscale devices based on metal substrates. Control of the formation of specific patterns in the submonolayer regime is usually achieved by appropriate choice and/or functionalization of the adsorbates. The effect of this intervention, though, is limited by the typically short-range character of the bonding. We present here a theoretical study on the system rubrene/gold to show that substrate-induced molecular charging can instead determine the assembly on larger scales. DFT calculations and electrostatic considerations are used to discuss the charge transfer at the metal/organic interface. This allows rationalization of previous puzzling experimental results and, in particular, of the unusual molecular gap broadening upon adsorption observed in STS spectra. The self-assembly process is further studied by means of classical molecular dynamics simulations. The charged adsorbates are modeled as mutually repulsive standing dipoles, with van der Waals interactions intervening at short distances. The striking resemblance between the experimental STM images and the results of our MD simulations shows that this simple model is able to capture the key effects driving the assembly in this system. The competition between long-range repulsive interactions and short-range attractive forces leads to characteristic and easily recognizable 1D patterns. We suggest that experimental evidence of the presence of similar patterns in other metal/organic systems can provide crucial information on the electronic level alignment at the interface, that is, on the occurrence of charge-transfer processes between metal and organic adsorbates.

KEYWORDS: supramolecular self-assembly · metal/organic interfaces · molecular dynamics · charge transfer · polycene · long-range repulsion

The self-organization of organic molecules on metal surfaces is attracting growing interest for its potential applications to nanodevices and biomaterials.[1] The observed supramolecular arrangements can have remarkable complexity and variety, and their investigation often reveals a subtle balance between competing interactions.[2,3] The assembly is typically the result of short-range attraction (*e.g.*, van der Waals forces or hydrogen bonding) between adsorbed monomers, and two-dimensional (2D) close-packed arrangements are by far the most commonly observed overlayer structures.[4] If the adsorbed molecules are charged with equal sign, usually following deprotonation, their mutual electrostatic repulsion is expected to hinder their assembly. However, the leading interaction term is not a Coulomb $1/r$ term but a weaker $1/r^3$ repulsion between parallel standing dipoles, due to the image-charge screening produced by the metallic substrate. As a result, self-assembly can still occur if strong short-range attraction prevails over the longer-range $1/r^3$ electrostatic repulsion. This still typically yields close-packed 2D structures, unless the presence of strongly polar molecules,[3] the formation of strongly directional H-bonds,[2] or asymmetric charge localization following deprotonation of specific linkage groups[5] induce some directionality in the assembly structure, for example, yielding molecular chains.

In light of this discussion, the case of rubrene self-assembly on atomically flat gold surfaces is particularly intriguing. Rubrene

(5,6,11,12-tetraphenylnaphtacene, $C_{42}H_{28}$) is a fluorescent polycene (see Figure 1) with unique electronic properties, which make it one of the most promising organic electronic materials to date.[6,7] As nonpolar molecules (*i.e.*, missing any functional groups available to form strong directional bonds), rubrene adsorbates are expected to interact through van der Waals forces, and electrostatic effects seem ruled out since deprotonation is absent in this system. We would thus reasonably expect rubrene to cluster into compact phases, as at first sight it appears to have no reason to assemble in 1D
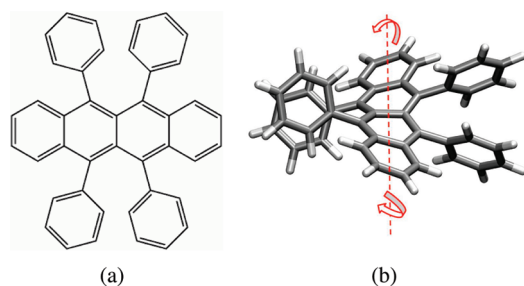
Figure 1. (a) Schematic for the rubrene molecule, $C_{42}H_{28}$, and **(b)** three-dimensional model for the molecule in gas phase, where the steric hindrance between the lateral phenyl rings leads to a twisted tetracene backbone.

superstructures. When the self-assembly of rubrene molecules on a Au(111) substrate is observed by STM, though, the results come at odds with such a picture.[8,9] The adsorption yields a progression of supramolecular structures with increasing coverage, ranging from randomly distributed small structures (mostly pentagons and hexagons) at 0.04 ML to extended honeycomb-like domains and hexagonal close-packed islands well above 0.3 ML. Remarkably, at about 0.25 ML, we observe zones enclosed by the growing hcp islands where rubrene molecules build pentagons, which in turn assemble into 1D meandering, open-ended chains and, occasionally, into regular decagons (Figure 2a). The occurrence of five-fold symmetries is an unusual phenomenon on its own, given how rarely they occur inside inorganic systems. The development of 1D structures comes as an even more remarkable surprise. Although no periodic tiling of the 2D plane can have pentagonal symmetry, the observed 1D assembly cannot be due to geometric hindrance of denser packing alone. Indeed, while dense aperiodic tilings based on pentagonal symmetry are possible and have been intensively studied,[10] any "amorphous" 2D assembly formed by mutually attractive pentagons could easily achieve a higher local density than observed here. Inside the 1D structures themselves, moreover, it is interesting to note that 72° "kinked" sections occur much less frequently than "straighter" 144° sequences (*cf.* Figure 2a), and that non-regular closed decamers are never observed; although

simple configurational statistics would predict these to be overwhelmingly more likely than regular decagons.[11]

Further available experimental results reveal even more puzzling incongruities. STS spectra recorded for different adsorbed molecules (*i.e.*, for molecules belonging to different supramolecular structures) can be remarkably different in terms of both gap and position of the HOMO level.[12] The HOMO level can shift by as much as ~1 eV, while the STS gap of molecules inside rubrene pentagons, in particular, appears to be as large as 5.1 eV, that is 0.6 eV wider than the 4.5 eV gas-phase gap, in striking contrast with the well-established picture of gap narrowing due to image-charge effects.[13] When the experiment is repeated on a similar noble metal surface, Ag(111), neither the open structures nor the gap variation are observed, suggesting that the substrate plays an important role in controlling both the electronic properties of the adsorbates and the dynamics of their self-assembly.[9]

In this work, we use electronic structure and molecular dynamics (MD) simulations to rationalize the observed 1D rubrene assembly. By analyzing the impact of surface screening response on the molecular electronic levels, we find that the renormalized rubrene HOMO level can rise above the Au(111) Fermi level, onsetting a charge-transfer (hole formation) mechanism, which transforms rubrene pentagons into positive supramolecular ions. We use this charge-transfer model to explain the apparent HOMO−LUMO gap variations measured by STS. Hole formation is instead not predicted on Ag(111) because of its lower electron affinity, explaining why no STS gap variation is ever observed on this otherwise similar substrate. The proposed model implies the presence of electrostatic repulsion between charged rubrene pentagons on Au(111), which we classify as "long-range", since it will prevail over "short-range" van der Waals attraction at distances exceeding the nearest neighbor linkage length. The interplay of such long-range repulsion and standard short-range attraction produces a tendency to
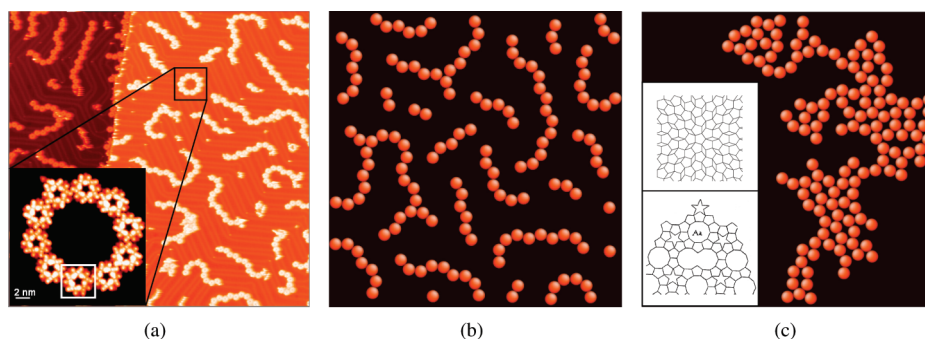

Figure 2. (a) Experimental image with 1D meandering sequences of rubrene pentagons, formed by five individual rubrene molecules, each imaged as a three-lobed unit (inset: the regular decagon of pentagons); **(b,c)** snapshots from the MD simulations of the self-assembly of rubrene pentagons at 0.14 molecules/nm² coverage: **(b)** assembly simulated with repulsive long-range term; **(c)** dense amorphous assembly obtained without repulsive electrostatic interaction (insets: dense tiling model by Dürer and "Aa" tiling by Kepler[11] with 144 and 72° pentagon sequences).
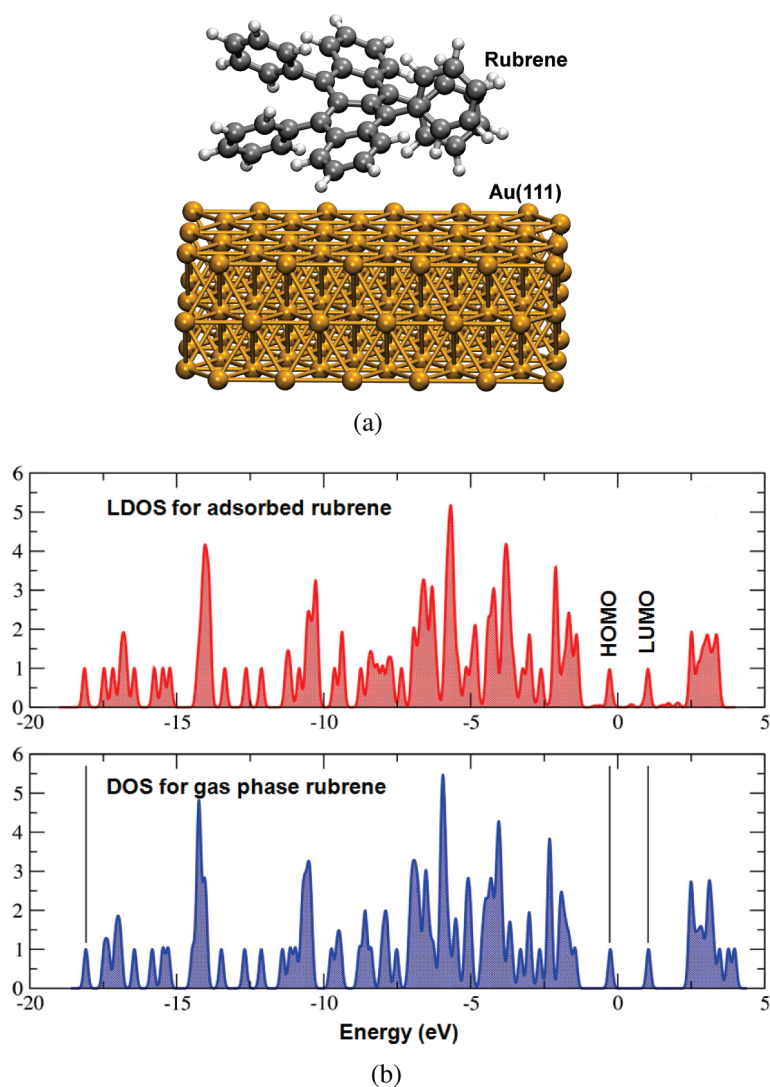
(a)

(b)

Figure 3. (a) Adsorption equilibrium structure as obtained from DFT-based calculations using the GGA for the exchange-correlation term. (b) Comparison between the LDOS of rubrene upon adsorption (in red, top) and the DOS of rubrene in the gas phase (in blue, bottom) aligned in order to match the HOMO−LUMO levels of the adsorbed one (a Gaussian broadening of 0.005 au, *i.e.*, ~0.136 eV, was applied). No appreciable hybridization or broadening of the molecular levels is observed.

maximize second neighbor distances within linked structures made of pentagonal units, leading to 1D assembly. We show this by a series of MD simulations where the inclusion of repulsive interactions between assembly units is found both necessary and sufficient to produce stable 1D supramolecular structures remarkably similar to those observed in the STM images (Figure 2).

RESULTS AND DISCUSSION

To understand the mechanism of adsorption of rubrene on Au(111), we first performed a set of first-principles density functional theory (DFT) GGA[14] calculations on the system. The Au(111) surface was represented by a periodically repeated three-layer slab with 36 atoms per layer (108 atoms in total). We deposited the rubrene molecule on one side of the slab only and corrected for the unphysical macroscopic field

across the vacuum layer (~10 Å thick) by introducing a compensating dipole.[15] Before performing calculations on the interacting system, we tested our models of the Au(111) surface and the rubrene molecule separately by computing their electronic properties. The calculated work function of Au(111) is $W_{Au} = 5.3$ eV, and the calculated (by means of the ∆SCF method)[16] gas-phase ionization potential of rubrene is $I_R^{(\Delta SCF)} = 6.35$ eV, both in excellent agreement with the experimental values, respectively, of 5.3[17] and 6.4 eV.[18]

In Figure 3, we show our results for the relaxed geometry and the local density of states of an isolated rubrene molecule adsorbed on the Au(111) surface. Two features are immediately apparent. First, both the local density of states and the equilibrium structure of the adsorbed molecule are remarkably similar to those of the gas-phase molecule, which indicates that there is no chemical interaction (covalent bonding) taking place between rubrene and Au(111).[19] Such a weak-bonding picture is in good agreement with the experimental observation of a high surface mobility.[20] Second, the Fermi level is pinned by the HOMO level of the molecule, which is only partially filled (there is a net transfer of 0.45 electrons from the molecule to the surface).[21] This is an important result, as it indicates a clear tendency of rubrene to accept holes when adsorbed on Au(111). However, at first sight, this charging effect appears inconsistent with our calculations of the non-interacting objects: the initial situation is a Au work function of 5.3 eV and a rubrene ionization potential of 6.35 eV, which raises a question of what might be at the origin of an extra driving force in excess of 1.05 eV capable of causing electron transfer from rubrene upon molecular adsorption onto the surface.

To answer this question, it is instructive to have a closer look at the electronic structure of the gas-phase molecule. In our GGA calculation, the HOMO level of the gas-phase rubrene lies at $\varepsilon_{HOMO} = 4.41$ eV below vacuum. This differs considerably with the ∆SCF value of the ionization potential, $I_R^{(\Delta SCF)} = 6.35$ eV. This discrepancy is a well-known failure of approximate DFT func-

tionals such as LDA or GGA (in exact DFT, the two values should be identical)[22] and can be traced back to the self-interaction error (SIE)[23−25] that affects the strongly localized 2p orbitals of C. Since ε_{HOMO} lies *above* the Fermi level of Au, when the molecule and the surface are equilibrated to the same electron chemical potential, some charge will be transferred from the molecular orbital, even if the "physical" ionization potential IP lies much lower in energy. As a consequence of the SIE, depletion of the localized HOMO orbital induces, in turn, a downward shift of the corresponding Kohn−Sham eigenvalue that tends to move ε_{HOMO} below the Fermi level. At equilibrium, ε_{HOMO} will therefore almost exactly pin the Fermi level and will be associated with a fractional occupation number, which is exactly what we get from our Au/rubrene calculation.

While the above considerations show that our GGA results are mutually consistent, they also bring up some concerns about the reliability of the physical picture that emerges. In particular, the question arises whether the tendency to transfer charge is a robust conclusion, or whether it might be an artifact of the self-interaction error—indeed, within a SIE-free (exact) theory, we would have for gas-phase rubrene $\varepsilon_{HOMO} = -IP \sim -6.4$ eV, which is, again, well below the work function of Au. In other words, is there any physical mechanism that might induce an upward shift of the "exact" HOMO level, and possibly bring it *above* (or in close vicinity of) the Fermi level upon physisorption? As seen above, the tendency of rubrene to form holes on Au is a potentially valuable indication of GGA, suggesting a positive answer to this question. Some further analysis shows that such a mechanism does indeed exist and is the dynamical screening of the molecular levels due to the image-charge effect.

Within many-body perturbation theory (MBPT), the energetics of charge-transfer processes (in particular, electron removal and addition) can be directly related to the spectrum of the quasiparticle energies (this is unlike Kohn−Sham DFT, where the eigenvalue spectrum is essentially a mathematical construction). A crucial ingredient of MBPT is the relaxation of the many-electron system upon electron removal or addition; we shall refer to this relaxation process as "screening" henceforth. Screening, which depends on the polarizability of the local environment where the perturbation is created, will inevitably lower the energy cost of, for example, creating a hole. As the quasiparticle energy exactly corresponds to the removal energy, this means that better screening will tend to shift the occupied levels *upward*. On the basis of this reasoning, it is natural to expect that the energy spectrum of a rubrene molecule approaching a highly polarizable metallic surface will be renormalized with respect to its gas-phase values by a quantity related to the distance d from the surface itself. This was indeed demonstrated recently by means of large-scale GW calculations.[13]
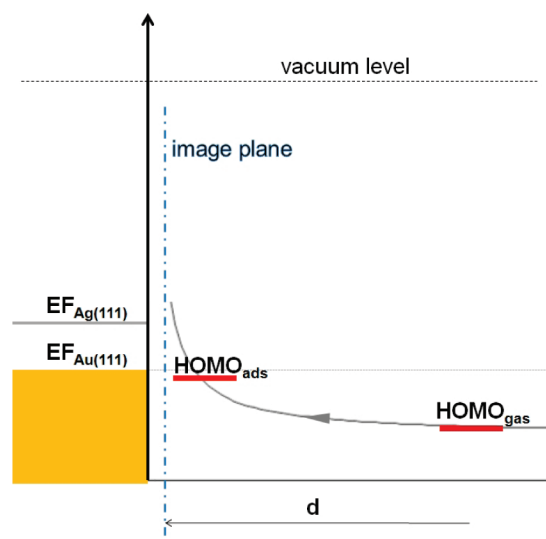

Figure 4. Simplified energy level diagram for the adsorption of rubrene on a metal substrate. The HOMO level of the molecule is predicted to rise while approaching the substrate due to the image-charge effect, which contributes with an energy term $E_{im} = e^2/4d$ (d is the distance between the molecular centroid and the image plane of the surface).

The leading correction term is given by the image-charge energy that binds a point-like hole to the underlying metal substrate and can thus be expressed in the form $E_{im} = e^2/4d$ (see Figure 4). In our case, d is the distance between the Au(111) image plane (located at $z_{im} = 1.1−1.2$ Å above the first surface layer[26]) and the molecular centroid, which can be directly extracted from our DFT calculations. With the value $d_{GGA} = 4.85$ Å that we extracted from the relaxed GGA geometry, we obtain an estimate of $E_{im}^{GGA} = 0.75$ eV.[27] We also computed a more accurate estimate of E_{im} by using the charge density distribution of the HOMO orbital, as suggested by Neaton *et al.*,[13] obtaining a very similar HOMO level upshift, $E_{im}^{HOMO} = 0.85$ eV (note that this is a conservative estimate—in a hypothetical full GW calculation further raising of the HOMO level on the order of 0.1−0.2 eV[28] is expected to occur because of the internal screening response of the molecule to surface polarization). On top of the distance-related image-charge effects, a non-negligible further HOMO level upshift is expected to occur in molecules within pentagonal units, due to the polarization of the surrounding molecules which contribute to stabilizing the hole.[29] This means that not only the distance from the surface but also the local environment, in terms of proximity to other polarizable adsorbates, can affect the relative stability of the neutral and charged states. In conclusion, even in a very conservative estimation, adsorption-related effects are very likely to lift the HOMO level above the Au(111) substrate Fermi energy, supporting the GGA indication of molecular charging upon adsorption. This makes rubrene, an exceptionally good hole conductor in its solid phase,[6] behave as a hole acceptor when adsorbed on Au(111). Conversely, our arguments practically rule out

any charging when rubrene is adsorbed on a substrate like Ag(111) because of the 0.8 eV lower work function.[30]

Remarkably, our charge-transfer model predicts a crossover, as a function of distance and/or nearest neighbor environment, from a neutral to a charged state. The molecule might charge up directly upon adsorption or might first physisorb in a neutral state at a certain distance d higher than the crossover one. Then, an external perturbation (*e.g.*, a thermal fluctuation or the electric field of the STM tip) brings it closer to the surface, and the image-charge effect triggers charge transfer, fully stabilizing the charge-adsorbate system. Furthermore, from the above arguments, it is natural to expect that the integer charge transfer (ICT)[31] might be a self-limiting mechanism. When an increasing number of adsorbates carrying a net standing dipole is created, the energy cost of further dipole formation would in fact increase, up to preventing any further charge transfer in densely populated areas. These predictions are in excellent agreement with the available STS data and UPS spectra, as we shall discuss in the following.

As mentioned before, STS measurements reveal a puzzling variety of spectra for different adsorbates, with ~1 eV lowered STS HOMO level peaks for molecules in open structures. It has been proposed[12] that these level shifts could be due to conformational effects. Our DFT gas-phase calculations, anyway, show that conformational changes in the neutral molecule yield negligible HOMO level variations of at most ~0.1 eV and cannot therefore be considered responsible for these much larger variations. If we assume that the rubrene pentagons are positively charged, instead, low-lying HOMO level peaks in the spectra become quite reasonable. The presence of a hole on the adsorbate implies indeed significant electrostatic lowering of all occupied levels, and the electron tunneling in negative bias conditions must proceed from levels lying lower than the predicted neutral molecule HOMO position. Furthermore, it has been experimentally proved that local changes in the spectra can be indeed induced by the STM tip,[12] as speculated above.

Spectra acquired on dense phases also confirm the picture of a charge-transfer dependence on the local environment. While molecules in open structures are always characterized by low-lying HOMO levels, at increasing coverage, a spread of HOMO level positions is observed (consistent with the picture of different degrees of hole localization). In dense rubrene islands, low-lying HOMO levels are measured only for few, sparse adsorbates, while the STS spectra obtained for the vast majority of molecules are identical to those acquired on a Ag(111) substrate (where no charge transfer is expected to take place), rigidly shifted with respect to the Fermi level by the 0.8 eV work function difference between Au(111) and Ag(111).[12,32]

The picture of a charge-transfer process at the interface is also fully consistent with our room temperature UPS measurements. In the 0.1 to 0.3 ML coverage range, we observe a work function decrease of 0.1 eV,[12] in agreement with the 0.2 eV value measured in ref 33. At higher coverage of about 1 ML, our UPS measurements show a further work function reduction of 0.6 eV, again consistent with the reported values.[33] These work function changes indicate the formation of an interface dipole that can be related with the presence of charged adsorbates.

We conclude that the simple vacuum-level alignment model assumed in ref 12, where the molecular levels of the adsorbed molecule would remain unperturbed upon adsorption, represents a drastic oversimplification for this system. Here, STS variations derive rather from nontrivial charge-transfer processes induced by correlation and screening, further modulated by the presence of the interface dipole. Consistent with these arguments, such variations are completely absent on the Ag(111) substrate, where charging is not expected.

We show in the following that these molecular charging effects are directly responsible for the observed 1D assembly behavior. We use a simple force field to model the interaction of rubrene pentagons, including a Lennard-Jones term yielding the edge sharing linkage, and a (standing) dipole−dipole repulsive term between charged pentagons:

$$U_{2b}(r) = \xi\left[\left(\frac{\sigma}{r'}\right)^{12} - 2\left(\frac{\sigma}{r'}\right)^6\right] + \frac{p^2}{2r^3}$$

where $r' = r - r_{eq} + \sigma$ with (in au, throughout) $p = e(z - z_{im}) = 18.0$ and $r_{eq} = 60.47$ from the STM images. The values of $\xi = 0.0022$ and $\sigma = 20.0$ were tuned so as to ensure that the short-range attractive term prevails over the repulsion at the experimental bonding distance. To incorporate the five-fold symmetry in the model, we further introduce a standard three-body U_{3b} term[34] with minima at 144 and 72°. Starting from random initial positions, we performed several simulated annealing runs in the experimental 0.1−0.18 molecules/nm² coverage range to determine the general features of stable supramolecular assemblies. Our results are illustrated in Figure 2, where the rubrene pentagons are represented by circles moving on a periodically repeated square cell. Direct comparison reveals a close resemblance between a typical STM image and the typical structure produced by our simulations (Figure 2b), sharing the same general pattern of approximately equidistant meandering chain segments of variable length, which only rarely split into two branches. This means that the presence of an electrostatic repulsive force between the interacting units is at least *sufficient* to obtain the observed self-assembly behavior. To prove that it is furthermore a *necessary* condition, we re-

peated the simulations after setting $p = 0$. The calculation produces very dissimilar patterns (Figure 2c) with rubrene pentagons clustering into relatively dense domains, as should be expected in the presence of purely attractive interactions. Keeping $p = 0$ to exclude repulsive forces and allowing the 144° binding angle only in the three-body term yields very similar results, with formation of dense disordered 2D domains. This suggests that the 1D patterns observed in the experiments are not due to a steric hindrance of the 72° angle in the edge-sharing linkage of neutral rubrene pentagon sequences. We thus conclude that the coexistence of long-range repulsion with short-range attraction is a key property of the interaction in this system.

CONCLUSIONS

As shown in this work, the existence of long-range repulsive interactions among molecular adsorbates can play a fundamental role in controlling the self-assembly patterns and achieve even unusually regular structures. For instance, the observed selective assembly of rubrene into perfectly regular decagons (Figure 2a) is easily rationalized in terms of their relative stability once electrostatic repulsion is accounted for, as the regular decagon shape maximizes the relative distance between non-neighboring pentagons. Indeed, just including the effect of repulsion in the simple force model described above singles out the regular decagon as the lowest energy decamer structure (0.02 eV lower than the next most stable one). This provides one of the very first examples of how controlling the electronic

properties (rather than the composition or the conformation) of the adsorbed monomer population by an appropriate choice of substrate and coverage can selectively determine the synthesis of a specific regular assembled superstructure within a numerous family of possible isomers. Charge-transfer processes leading to repulsive intermolecular interactions have been reported only recently in the literature, and in most cases they were shown to cause a gas-like behavior, with dispersed adsorbates.[35] Long-range ordering appears to have been discussed only in a single recent work[36] pointing out how similar effects might have been overlooked so far in previously studied systems.

We suggest that the present study may provide a novel route to identify the systems where electrostatic interactions are present and to acquire precious information on the electronic properties of metal−organic interfaces. Relatively inexpensive calculations at the DFT level can be used to screen efficiently a set of molecule/metal systems and identify the best candidates in terms of energy level alignment.[37] STM images can unambiguously reveal the emergence of peculiar 1D patterns at the submolecular level, which, as shown here, could be regarded as a strong indication of charge transfer at the adsorbate/substrate interface. This combined approach could be especially useful for the molecular electronics field,[31] where no general consensus has been reached yet on how to model such metal−organic interfaces properly, and device design is often still a trial-and-error process.

METHODS

First-principles density functional theory (DFT) calculations were performed within both the generalized-gradient approximation (GGA) and the local density approximation (LDA) using the projector-augmented wave method[38] as implemented in the "in-house" code Lautrec.[39]

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Formschneyder, Nürenberg, 1525), Kepler investigated mixed patterns such as the "Aa" tiling in Figure 2c (bottom inset), which includes one of the first reported "decagon of edge-sharing pentagons" motifs (*cf.* Kepler, *J. Harmonices Mundi Libri V* Francof., 1619). Interestingly, this structure (Figure 2a) is the largest regular polygon that can be built from edge-sharing equal regular polygons.

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27. Note that the GGA generally overestimates adsorption distances (see Silva *et al. Phys. Rev. Lett.* **2003**, *90*, 066104), which means that we are very likely underestimating the actual correction term. It is well known, anyway, that LDA tends to behave in the opposite way, *i.e.*, to underestimate adsorption distances; this provides a cost-effective way to bracket the image-charge correction (*cf.* Gao and Zheng *J. Phys.: Condens. Matter* **2007**, *19*, 386220 and Rusu *et al. J. Phys. Chem. C* **2009**, *113*, 9974). We thus performed an additional LDA calculation to complement our GGA structural data. We obtain $d_{LDA} = 3.65$ Å, which gives $E_{im}^{LDA} = 0.97$ eV.

28. The contribution of the molecular internal screening

29. In rubrene molecular crystals the IP is ∼1.1 eV lower than in gas phase, due to hole polarization screening. In smaller assemblies, though, each molecule has fewer neighbors (only two in a pentagon); therefore, the effect is expected to be less pronounced and minor with respect to the other contributions.

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32. Conversely, these observations are incompatible with an induced density of states (IDIS) in the molecular gap due to molecule−substrate hybridization effects, as this would imply fractional charging for all molecules, and a smaller energy shift than the "Shockley Mott" 0.8 eV value.[31] Thus, of the two main models currently used to investigate level alignment in organic/metal interfaces, the rubrene/Au(111) system is better described by the ICT model[31] than by the IDIS model (Vazquez, H. *et al. Appl. Surf. Sci.* **2004**, *234*, 107−112). This is consistent with the low degree of mixing of the rubrene π-electronic wavefunctions with the substrate states, due to the non-flat adsorption geometry. For a discussion of dynamical screening for weak molecule−metal couplings, see Thygesen arXiv:0810.5214v1 [cond-mat.mtrl-sci].

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