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PAPER

Generic nature of long-range repulsion mechanism on a bulk insulator?†

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Dynamic atomic force microscopy measurements are reported that provide evidence for the presence of long-range repulsion in molecular self-assembly on a bulk insulator surface. We present the structures formed from four different benzoic acid derivatives on the (10.4) cleavage plane of calcite kept in ultra-high vacuum. These molecules have in common that they self-assemble into molecular stripes when deposited onto the surface held at room temperature. For all molecules tested, a detailed analysis of the stripe-to-stripe distance distribution reveals a clear deviation from what would be expected for randomly placed, non-interacting stripes (*i.e.*, geometric distribution). When excluding kinetic effects during growth, this result gives evidence for a long-range repulsion mechanism acting during the assembly of these stripes. The fact that this finding is robust against changes in the molecular structure indicates a generic nature of the observed mechanism, implying a ubiquitous origin such as electrostatic repulsion. Finally, we discuss parameters that might affect the unambiguous observation of this generic repulsion under specific experimental conditions.

1 Introduction

Molecular self-assembly is recognized as a most versatile tool to create molecular structures at surfaces.[1–3] Tuning the subtle balance between intermolecular as well as molecule–surface interactions is known to allow for tailoring the resulting supramolecular network in a rational fashion.[4] So far, the majority of the systems investigated make use of short-range attraction between the molecular building blocks. Besides van der Waals and attractive electrostatic forces, hydrogen bonds constitute a popular binding motif for molecular self-assembly due to their selectivity and directionality.[5,6] Exploiting intermolecular attraction has resulted

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in an impressive control over the order of the resulting structures, which range from clusters,[7,8] one-dimensional chains,[6,7] two-dimensional overlayers to most complex assemblies such as host–guest networks.[9] In contrast, intermolecular repulsion has been comparatively little explored for inducing order during molecular structure formation on surfaces in a rational fashion.[10–16] In most of the reported examples, electrostatic interaction has been identified as the origin of the repulsion.[17] While polar molecules carry an intrinsic dipole moment that can directly affect the ordering,[18,19] adsorption-induced dipoles of apolar molecules have also been shown to result in long-range repulsion.[13,14] An example for the latter is tetrathiafulvalene deposited onto Au(111), which has been shown to arrange in an ordered fashion with a range of up to 4 nm.[13] In a recent study, we have shown that 3-hydroxybenzoic acid (3-HBA) on calcite (10.4) self-assembles into molecular stripes.[16] These stripes exhibit an ordered arrangement induced by long-range repulsion that can be observed even at distances as large as 16 nm.

It should be noted, however, that the observation of an ordered arrangement of molecular structures is not necessarily a proof of the existence of repulsive interaction, but it can be due to kinetic effects during growth.[20–22] Such correlated growth kinetics have been demonstrated experimentally, *e.g.*, during the growth of pentacene islands on silicon oxide surfaces.[22,23] A possible way to exclude such deposition-dependent effects is comparing the structures obtained from different deposition protocols. For the structures formed from 3-HBA we have shown that the specific deposition protocol appears to be irrelevant,[16] indicating that the observed order is not determined by the specific diffusion and desorption kinetics,[22] but is, indeed, caused by long-range repulsion.

Here, we address the question of whether this example of long-range repulsion is special for 3-HBA or represents a general mechanism that might be used for rationally controlling molecular self-assembly on a bulk insulator surface. To this end, we have investigated twenty-eight different benzoic acid derivatives (for a full list, see the ESI†). We select those four molecules (including 3-HBA) that self-assemble into stable, uni-directional stripes when deposited on calcite (10.4) held at room temperature. A detailed analysis of the next-neighbour stripe distance distribution reveals that none of the molecules tested exhibits a geometric distance distribution,‡ which would be the distribution expected for randomly placed, non-interacting stripes. When excluding correlated growth kinetics, our results provide experimental evidence for the presence of a long-range repulsive interaction, regardless of the specific molecular structure. This robustness against variations in the molecular structure and the inner structure of the resulting stripes points towards a ubiquitous origin of the long-range repulsion, supporting the interpretation of an electrostatic repulsion mechanism. We discuss possible scenarios that might affect the unambiguous observation of this long-range repulsion under specific experimental conditions, such as elevated temperatures or kinetic trapping that might prevent to arrive at the thermodynamically favoured spacing. Keeping these parameters in mind might allow for a controlled use of long-range repulsion in future studies, enriching the available parameter space for tuning molecular self-assembly.

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‡ For a full derivation of the geometric distribution and the validity to apply this to randomly placed, non-interacting stripes see the supporting information in ref. 16.

2 Experimental details

2.1 Dynamic atomic force microscopy measurements

Dynamic atomic force microscopy (AFM) measurements were performed with a variable-temperature AFM from ScientaOmicron (Taunusstein, Germany) operated under ultra-high vacuum (UHV) conditions. We used doped silicon cantilevers from Nanosensors (Neuchâtel, Switzerland) with a typical spring constant of 40 N m^{-1} and eigenfrequency of 300 kHz in UHV. A phase-locked loop and amplitude controller from NanoSurf (Liestal, Switzerland) was used for signal demodulation and amplitude stabilization. A typical oscillation amplitude of 10 nm was used. All measurements shown here were taken with the sample kept at room temperature.

2.2 Sample preparation

The calcite samples used were purchased from Korth GmbH (Altenholz, Germany). Prior to each experiment, the sample was cleaved *in situ* and annealed at 640 K for one hour to obtain a clean (10.4) cleavage plane (Fig. 1a). The molecules were obtained from Sigma-Aldrich (Munich, Germany), Alfa Aesar (Karlsruhe, Germany) or, in the case of 4-ethynylbenzoic acid (4-EBA), were synthesized from commercial 3-iodobenzoic acid by analogy with literature procedures.[24,25] A home-built Knudsen cell was used for depositing the molecules onto the freshly prepared calcite surface held at room temperature. Twenty-eight different benzoic acid derivatives were tested in this study in total (for a full list and molecular

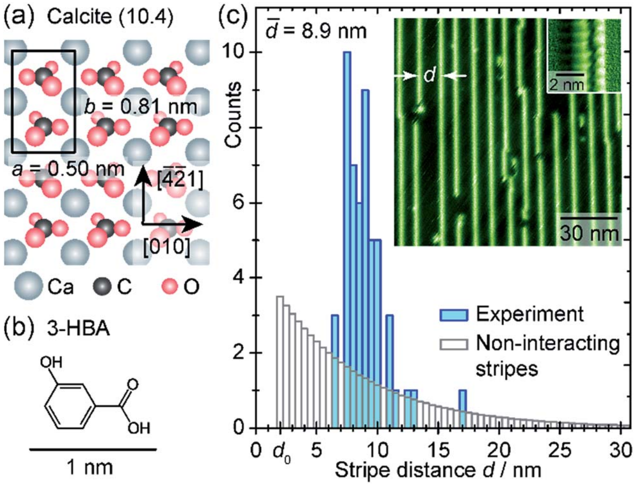

Fig. 1 (a) Model of the calcite (10.4) cleavage plane. The surface unit cell consists of two calcium cations and two carbonate groups. (b) Structural formula of 3-hydroxybenzoic acid (3-HBA). (c) Molecular double rows formed from 3-HBA on calcite (10.4). As can be seen, these stripes align along the [$\bar{4}\bar{2}1$] substrate direction. From the AFM image, an equidistant appearance of the stripes is evident. Inset: zoom onto a stripe showing the internal zig-zag structure of the stripe. The experimentally obtained next-neighbour stripe distance distribution (blue bars) clearly deviates from the distance distribution that would be obtained for randomly placed, non-interacting stripes (grey bars, geometric distribution). The minimum or nearest possible stripe distance is denoted by d_0.

structures, see the ESI†). Here, we focus on four molecules, namely 3-hydroxybenzoic acid (3-HBA, Fig. 1b), 3-aminobenzoic acid (3-ABA), 3,5-dihydroxybenzoic acid (3,5-DHBA), and 4-EBA. The sublimation parameters to arrive at submonolayer coverages were obtained from a different setup equipped with a quartz crystal microbalance.

3 Results and discussion

3.1 Proof-of-principle: molecular stripes from 3-HBA

As reported previously, when deposited onto calcite (10.4) kept at room temperature, 3-HBA self-assembles into molecular zig-zag rows (see inset in Fig. 1c) aligned along the $[\bar{4}\bar{2}1]$ substrate direction, indicating that short-range attraction dominates along the row direction.[16] The specific nature of this attraction remains speculative at the moment but appears irrelevant for the generic repulsion discussed in this work.§ The molecular stripes exhibit a strikingly ordered arrangement on the surface with an equidistant appearance, as seen in the AFM image shown in Fig. 1c. To obtain further insights into this ordering, we analyse the stripe distance distribution (blue bars in Fig. 1c) and use its standard deviation to quantify the degree of order. For randomly placed, non-interacting stripes, a geometric distribution is obtained (indicated by the grey bars in Fig. 1c). As can be seen in Fig. 1c, the distance distribution for 3-HBA at the given coverage (quantified using the mean stripe distance $\bar{d}$ of 8.9 nm) is clearly different from a geometric distribution. Moreover, the standard deviation of the distance distribution for 3-HBA (1.8 nm) is significantly smaller than the standard deviation of the corresponding geometric distribution (7.2 nm). Clearly, the stripes exhibit an ordering that corresponds to a non-random distribution.

For molecules deposited on a surface, such a non-random distribution can have two different origins. It is known that correlated growth kinetics can result in an ordered arrangement even in the absence of intermolecular interactions.[20,21] Thus, only when such growth kinetic effects can be excluded can the deviation from the geometric distribution be unambiguously assigned to the presence of a long-range repulsion mechanism. To exclude correlated growth effects for 3-HBA, we have previously performed experiments with varying deposition protocols and confirmed that the same stripe distance distribution is obtained regardless of the specific deposition sequence.[16] In a deposition sequence, we have demonstrated that the stripe distribution is adjusted to changes in the molecular coverage. This is clear evidence for the existence of a repulsive driving force causing this re-arrangement. Here, we further discuss a sequence of AFM images collected at the same sample position to assess the molecule's mobility at a fixed coverage (see the ESI for a complete 13 hours video†). In Fig. 2a, an AFM image with the characteristic 3-HBA stripe structure is shown. Fig. 2b shows the changes to another AFM image obtained at the same position about three hours later. We mark vanishing structures by blue colour in the initial image (Fig. 2c), while red colour is associated with newly-formed structures in the final image (Fig. 2d). As can be seen, the stripes do not only shrink and grow in size at the stripe ends, but entire stripes appear and vanish. This indicates sufficient

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§ Analysing the stripe length distribution should shed light on the strength of this short-range attraction. However, for simplicity we ignore the finite stripe length in this work.

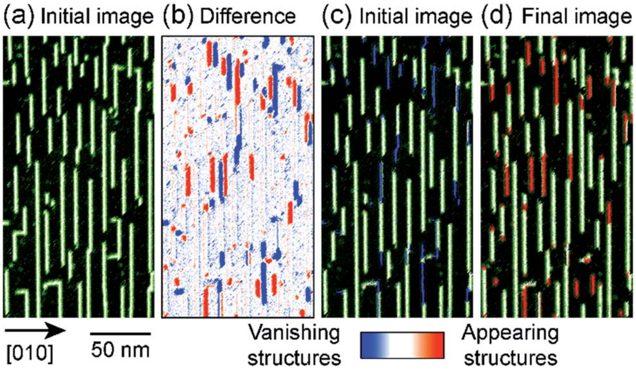

Fig. 2 Two AFM images from a series of images (see the ESI for the complete series†) illustrating the mobility of 3-HBA. (a) Initial image showing the characteristic 3-HBA stripe structure. (b) Changes to an image taken at the same sample position about three hours later, calculated according to: difference equals final image minus initial image. Blue colour marks vanishing structures in the initial image (c) and red colour marks appearing structures in the final image (d).

mobility for adopting the thermodynamic equilibrium structure within the time span given by the experiment, *i.e.*, any initial processes such as nucleation and ripening are completed and do, therefore, not affect the discussion made here. Even if an initial arrangement might be affected by correlated growth kinetics, the experimentally proven mobility would eventually result in a geometric distribution if long-range repulsion would be absent. The fact that the observed distance distribution deviates from the geometric distribution is, thus, clear experimental evidence for a long-range repulsion between the stripes. In our previous work,[16] we speculated that this repulsion arises from electrostatic repulsion of adsorption-induced dipoles. While we cannot prove that the observed repulsion is of electrostatic origin, we can calculate from a simple model – ignoring details such as diffusing single molecules and finite stripe lengths – that electrostatic repulsion of adsorption-induced dipoles with a reasonable dipole moment is of sufficient strength to explain the observed ordering.[16] In this previous work, we made an estimate as to how large an adsorption-induced dipole moment is needed for observing the standard deviation as we did in our experiments. For this, we performed MC simulations that gave a necessary dipole moment of 30 D/$\sqrt{(n)}$, where n is the number of molecules in a critical stripe interacting with infinitely long neighbouring stripes. When we assume that a single (neutral) molecule creates an adsorption-induced dipole normal to the surface of about 5 D, then only critical stripes of at least 7 nm length would reveal the observed order (to arrive at the total dipole moment of 30 D). If we assume the molecules to deprotonate, then a single molecule would have a dipole moment of about 15 D, which then reduces the necessary number of molecules in a critical stripe to four.

3.2 Generic nature: further evidence

Here, we address the question of whether the observed long-range repulsion is specific for 3-HBA or might be of a general nature. When considering electrostatic repulsion of adsorption-induced dipoles, we should expect the effect to be present for other molecules forming molecular stripes as well. To this end, we have investigated the self-assembly of twenty-eight different benzoic acid derivatives and focused on those that form uni-directional rows. We found three further molecules, 3-ABA, 3,5-DHBA and 4-EBA, that form stable molecular stripes orienting along the $[\bar{4}\bar{2}1]$ direction. Representative images of the stripes along with the corresponding stripe distance distributions are given in Fig. 3. In each distance histogram, the experimentally obtained distance distribution (blue bars) is compared with the geometric distribution for the respective coverage (grey bars).

As can be seen from the clear deviation of the experimental results from the geometric distribution, none of these experimentally obtained distributions can be explained by randomly placed, non-interacting stripes. Thus, when excluding correlated growth kinetics, a long-range repulsion mechanism must be present for all the molecules shown here.

It is interesting to note that this finding is not limited to the specific zig-zag structure of the stripes, which we identify not only for 3-HBA (see inset in Fig. 1c), but also for 3-ABA and 3,5-DHBA. To demonstrate this, we refer to the stripes that are formed by 4-EBA. These stripes are qualitatively different from the zig-zag structure of the three other molecules discussed before as they exhibit a (1 × 1) internal structure (see inset in Fig. 3c). Still, the distribution of these stripes shows a clear deviation from the geometric distribution. Excluding correlated growth kinetics during the assembly, these results again give evidence for the presence of a long-range repulsion. From this finding we can clearly deduce that the long-range repulsion is not linked to a specific stripe structure, indicating the generic nature of this mechanism.

3.3 Which parameters affect the degree of manifestation?

In the following, we want to discuss parameters that might affect a pronounced manifestation of long-range repulsion during molecular self-assembly in an equidistant arrangement. Obviously, at elevated temperatures the manifestation will become less pronounced. Also, short-range attractions can disturb an equidistant arrangement. Furthermore, we address the impact of kinetic trapping. These parameters need to be considered when aiming for taking advantage of

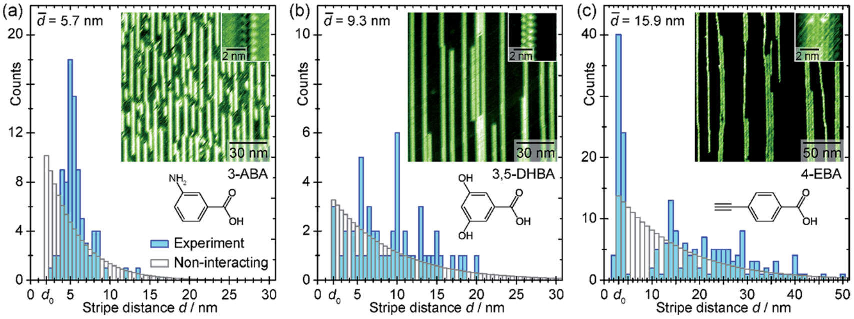

Fig. 3 Representative images and corresponding next-neighbour stripe distance distributions (blue bars) for (a) 3-ABA, (b) 3,5-DHBA and (c) 4-EBA. The geometric distribution calculated for the same coverage is shown with grey bars.

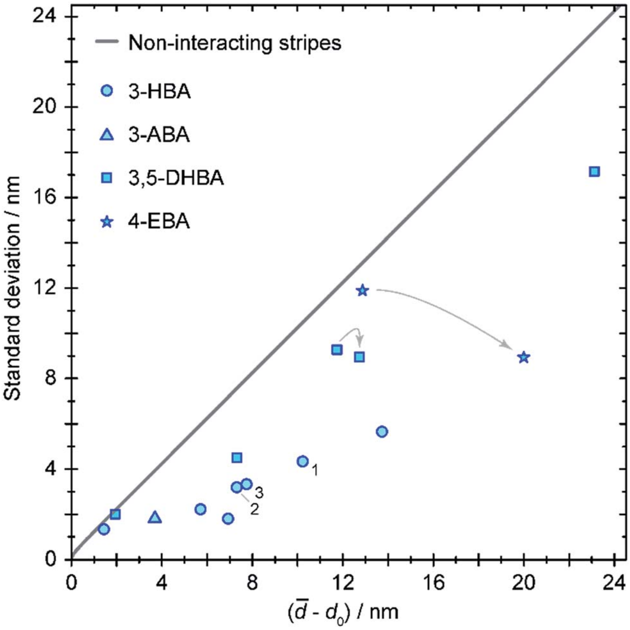

Fig. 4 Experimentally obtained standard deviation as a function of coverage for the four molecules discussed here. The grey line shows the standard deviation that is expected for randomly placed, non-interacting stripes (*i.e.*, a geometric distribution). Two distance distributions, namely one for 3,5-DHBA and one for 4-EBA, were analysed in two ways: first taking all stripe distances into account (origin of arrows) and, second, using all stripe distances except for the peak at d_0 (end of arrows). To exclude correlated growth effects, sequential deposition experiments can be carried out. We tested this for 3-HBA by comparing an experiment obtained after sequential deposition (corresponding standard deviations are marked by (1) for the first and (2) for the additional second deposition) with the situation obtained after a single deposition arriving at a similar coverage (marked by (3)). The similarity between the obtained values for (2) and (3) indicates sufficient stripe mobility.

a rational design of attractive short-range and repulsive long-range interactions in molecular self-assembly.

Elevated temperatures. When increasing the temperature, excited states become increasingly populated, which will inevitably result in a deviation from the ground state, *i.e.*, a perfect equidistant arrangement. Eventually, at a given temperature, the order might become difficult to detect in the experimental data.

Short-range attraction. The fact that stripes can be found directly next to each other for 4-EBA even for the low coverage shown in Fig. 3c sheds light onto a further interesting aspect: for 4-EBA, the short-range intermolecular attraction along the [010] direction (perpendicular to the long island axis) appears to favour broader islands composed of up to four stripes to be formed as compared to single stripes. Obviously, the above discussed long-range repulsion must also be present within the islands, but if the short-range attraction is large enough, islands can form. In fact, the observed island width is governed by the interplay between short-range attraction and long-range repulsion. This short-range attraction is evident in the displayed histogram for 4-EBA from a clear additional peak at d_0, the nearest possible neighbour distance. Such a peak is also present, but less dominant, in the displayed histogram for 3,5-DHBA in Fig. 3b. For high molecular coverages, the peak at the nearest neighbour distance gets more and more pronounced for all molecules. To quantify the degree of order, we plot the experimentally obtained standard deviation as a function of coverage and compare this standard deviation with what would be expected for randomly placed, non-interacting stripes (Fig. 4). As can be seen, all experimentally obtained standard deviations are clearly smaller than the value for a geometric distribution with the same coverage. We attribute the peak at d_0 to nearest neighbour attraction. In such a case, the standard deviation is clearly no longer a good measure for the induced order. Thus, in this case, we need to discard this first peak from the analysis of the distance distribution. We have done that for two cases of 3,5-DHBA and 4-EBA. The resulting two values for the standard deviation (square for 3,5-DHBA and star for 4-EBA) move towards even lower values as indicated by the two arrows in Fig. 4.

Kinetic trapping. Kinetics can have two different effects on the self-assembly. While correlated growth kinetics – as discussed above – can induce an ordered arrangement even in the absence of long-range repulsion, kinetic effects can also hamper the manifestation of long-range repulsion in the obtained structures. This situation occurs when the stripe mobility is not sufficient to arrive at the thermodynamic equilibrium. In such a case, a possibly existing repulsion might not manifest itself in the corresponding distance distribution.

4 Conclusions

In conclusion, we have presented four molecules that self-assemble into molecular stripes due to short-range attractive interactions. A detailed analysis of the next-neighbour stripe distance distributions reveals that all these arrangements clearly deviate from randomly placed, non-interacting stripes. When excluding correlated growth kinetics, this deviation provides unambiguous evidence for a long-range repulsion being present during the assembly of the stripes. The fact that the repulsion is observed regardless of the molecular structure and also regardless of the inner structure of the molecular stripes indicates a generic mechanism. We propose electrostatic interaction as a possible origin for the repulsion because of its ubiquitous nature. We discuss parameters that might hamper an experimental manifestation of the long-range repulsion during self-assembly in an equidistant arrangement. Obviously, elevated temperatures result in a deviation from the ground state, which counteracts an equidistant ordering. Short-range attraction can result in island formation which gives rise to an additional peak in the distance histogram at the nearest neighbour distance. Additionally, high diffusion barriers might result in a kinetically trapped structure that cannot develop into an ordered arrangement. With these insights, adjusting the balance between (anisotropic) short-range attraction and long-range repulsion appears to be a promising strategy for a rational design of the resulting structures in terms of the distance distribution.

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