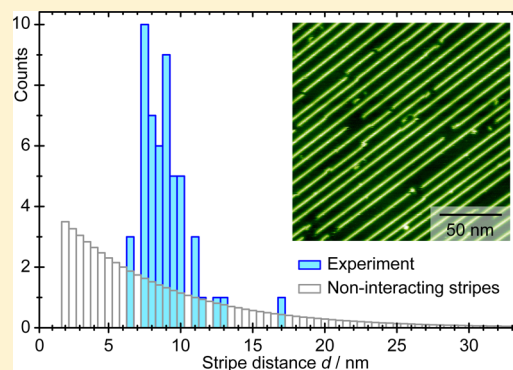


Long-Range Order Induced by Intrinsic Repulsion on an Insulating Substrate

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Supporting Information

ABSTRACT: An ordered arrangement of molecular stripes with equidistant appearance is formed upon the adsorption of 3-hydroxybenzoic acid onto calcite (10.4) held at room temperature. In a detailed analysis of the next-neighbor stripe distances measured in noncontact atomic force microscopy images at various molecular coverages, we compare the observed stripe arrangement with a random arrangement of noninteracting stripes. The experimentally obtained distance distribution deviates substantially from what is expected for a random distribution of noninteracting stripes, providing direct evidence for the existence of a repulsive interaction between the stripes. At low molecular coverage, where the average stripe distance is as large as 16 nm, the stripes are significantly ordered, demonstrating the long-range nature of the involved repulsive interaction. The experimental results can be modeled with a potential having a $1/d^2$ distance dependence, indicating that the observed long-range repulsion mechanism originates from electrostatic repulsion of adsorption-induced dipoles solely. This effect is particularly pronounced when local charges remain unscreened on the surface, which is characteristic of nonmetallic substrates. Consequently, the observed generic repulsion mechanism is expected to play a dominant role in molecular self-assembly on electrically insulating substrates.



INTRODUCTION

The success of future molecular electronics will critically rely on our capability to fine-tune the structure of functional molecules on surfaces.¹ Adjusting the subtle balance between intermolecular and molecule–surface interactions is known to provide a versatile strategy for tailoring the on-surface structure formation.² In the past, short-range attractive forces between the molecules have been in the focus to control the resulting structure, especially benefiting from directional attractions, as provided by, e.g., hydrogen bonding.³ In contrast, long-range repulsive interactions have been explored only rarely, despite their potential in offering a powerful additional option for controlling the formation of ordered molecular arrangements on the surface of interest.⁴

Long-range order has been reported for metal adatoms on metal surfaces, induced by Friedel oscillations of the surface electronic states.^{5,6} This substrate-mediated interaction can be identified by its characteristic periodicity, which is defined by the Fermi wavelength and, thus, independent of the coverage.

The formation of unidirectional rows of pentacene molecules on Cu(110) has been ascribed to another type of substrate-mediated interaction originating from adsorption-induced charge density waves in the electronic states of the surface.⁷ In this system, row spacings of 2.8 ± 0.2 nm have been observed.

Repulsion between rows formed by pentagonally arranged water molecules has been presented to result in spacings on the order of 1 nm.⁸ In this work, a $1/d$ interaction has been revealed, indicative of a monopole–monopole rather than a dipole–dipole repulsion.

For molecules exhibiting a permanent electrical dipole moment normal to the surface, repulsive dipole–dipole interactions can be present.^{9,10} On a metal surface, this repulsion can be enhanced due to the presence of mirror dipoles. This repulsion has been shown to result in a coverage-dependent separation of pyridine derivatives on a Cu(111) surface with a characteristic spacing of 4 nm at a coverage of 0.02 molecules per nm^2 .⁹ Charge transfer between the molecule and the surface can further enhance the electrostatic repulsion of polar molecules. This has been shown for phthalocyanine on Ag(111), causing the formation of an ordered thin film with a periodicity of 2.5 nm at a coverage of 0.33 monolayer (ML).¹¹

Charge transfer has also been reported as the origin for dipole–dipole repulsion between apolar molecules, namely, tetrathiafulvalene on Au(111).^{12,13} In the latter work, a coverage-dependent spacing has been revealed with a

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molecule–molecule distance of 3.5 nm at a coverage of 0.03 ML. Another system along this line has been rubrene molecules on the same surface, revealing long-range repulsion that has been ascribed to substrate-induced molecular charging.¹⁴ These studies have demonstrated that even for molecules carrying no permanent dipole moment, the surface-normal dipole moment induced by charge transfer upon interaction with the surface can be large enough to induce long-range order. This is interesting as surface electrons of the metal substrate are known to screen the local charges. Along this line of argumentation, it can be speculated that long-range repulsion based on charge transfer due to molecule–surface interaction should be significantly more pronounced on electrically insulating substrates, as charge screening is largely suppressed. To the best of our knowledge, no example exists so far demonstrating long-range repulsive interactions of organic molecules on a bulk insulator surface.

Here we present a generic mechanism for the formation of an ordered array of molecular stripes on an insulating substrate based on long-range repulsive interactions. Upon adsorption of 3-hydroxybenzoic acid (HBA) (see Figure 1a) onto calcite

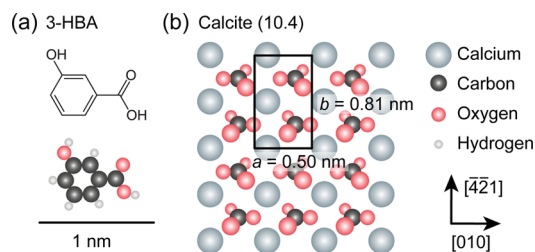


Figure 1. Model of (a) the 3-hydroxybenzoic acid (HBA) molecule and (b) the calcite (10.4) surface. The scale bar applies to both.

(10.4) (see Figure 1b) held at room temperature, molecular stripes are formed.¹⁵ A detailed analysis of the next-neighbor stripe distances obtained from noncontact atomic force microscopy (NC-AFM) images reveals an equidistant appearance with a periodicity, which is inversely proportional to the molecular coverage.

Periodicities as large as 16 nm are obtained at a coverage of 0.127 ML, demonstrating the long-range nature of the present repulsion. The degree of order is revealed by analyzing the

standard deviation of the coverage-dependent stripe spacing, which is substantially smaller than what is expected for a random distribution of noninteracting stripes.

We propose the origin of this repulsion to be the charge redistribution associated with the interaction between adsorbed molecules and the surface. In summary, our work demonstrates that adsorption-induced dipole moments appear to be sufficiently large for causing a strikingly long-range repulsion on an insulating substrate, i.e., in the absence of charge screening effects.

METHODS

NC-AFM measurements were performed with a variable-temperature AFM (Omicron) operated under ultrahigh vacuum conditions and at room temperature. Calcite substrates were purchased from Korth Kristalle and cleaved in situ to obtain atomically flat calcite (10.4) surfaces. The HBA molecules with a purity of 99% were purchased from Sigma-Aldrich. Before deposition, the molecules were thoroughly degassed. The molecules were deposited in situ using a home-built Knudsen cell. A crucible temperature of 320 K was used, yielding a deposition rate of approximately 0.005 ML/min. Note that the coverages stated in the following were calculated from the obtained average stripe distance as outlined below. Typically, for each experiment a freshly cleaved calcite crystal was used.¹⁶

RESULTS AND DISCUSSION

After 45 min of HBA deposition onto calcite (10.4) held at room temperature ($T = 305$ K), the surface is covered by molecular stripes that are oriented along the $[421]$ direction, as shown in Figure 2a. In this image, the entire surface area is uniformly covered by stripes, which are separated by similar distances. Only small areas without stripes can be found at regions where one stripe ends and the next one has not started yet. Furthermore, no shortest-distance neighbor stripes exist: Whenever two stripes meet, both of the stripes end, instead of the two stripes continuing directly next to each other. In images with and without step edges, the length of the stripes typically ranges from 50 to 300 nm. These findings result in an overall well-ordered, equidistant appearance of the stripe arrangement. High-resolution images (Figure 2b and c) reveal that the stripes consist of molecular double rows. This arrangement can be readily rationalized by molecules forming intermolecular

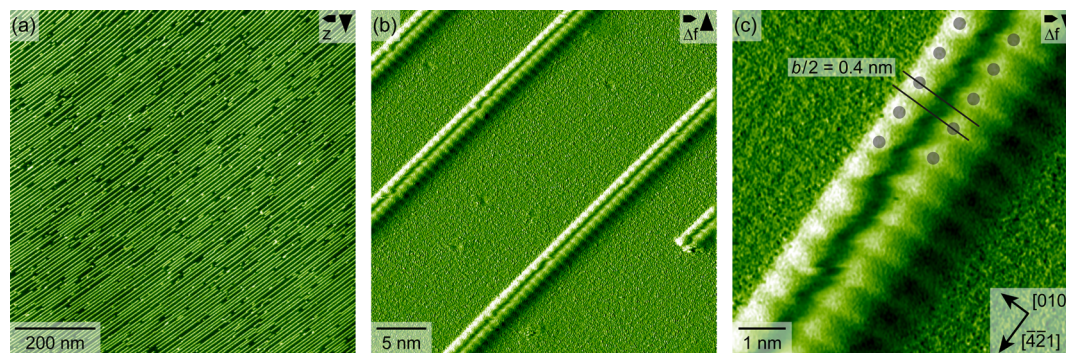


Figure 2. Stripes formed by HBA on calcite (10.4) held at room temperature. (a) NC-AFM topography image exhibiting molecular stripes after 45 min deposition of HBA (corresponding to 0.224 ML). The molecular stripes reveal an equidistant appearance. (b) Frequency shift image showing a zoom onto the stripe structures after 25 min deposition of HBA (corresponding to 0.127 ML). The stripes are oriented along the $[421]$ direction. (c) Drift-corrected frequency shift image of a single stripe revealing the double-row structure with a periodicity of $b/2 = 0.4$ nm in the $[421]$ direction commensurate with the calcite surface. Note that the asymmetric appearance of the row is ascribed to an asymmetric tip, as can be deduced from experiments with different tips.

hydrogen bonds in a zigzag fashion. Detailed, drift-corrected images elucidate a molecular arrangement with a periodicity of $b/2 = 0.4$ nm in the $[421]$ direction, as shown in Figure 2c, where b is the calcite surface unit cell length in that direction (cf. Figure 1b). Thus, the molecular arrangement is, indeed, commensurate with the underlying substrate, and the molecules are therefore expected to adopt equivalent adsorption positions.

To analyze the long-range nature of the involved ordering mechanism, we performed coverage-dependent NC-AFM measurements. The qualitative observation obtained from NC-AFM images is complemented by a statistical analysis of the stripe-to-stripe distances. The center-to-center distances d of next neighbors were obtained by analyzing $174 \text{ nm} \times 174 \text{ nm}$ large images. In total, over 600 stripe distances were analyzed. For each coverage, the distances were summarized in a histogram with a bin size of 0.5 nm. The coverage was calculated from the average stripe distance \bar{d} and the finite stripe width d_0 according to $c = d_0/\bar{d}$.

In the following, we compare the experimental data with histograms that would be obtained for randomly placed, noninteracting stripes. The probability distribution describing the occurrence of stripe distances d is given by

$$P(d) = s(1 - s)^{(d-d_0)/a} \quad (1)$$

for noninteracting stripes. Here, $(d - d_0)/a$ is the number of free adsorption spots between two stripes and $s = 1/(1 + (\bar{d} - d_0)/a)$ is the probability of finding a spot occupied.¹⁷

Some of the experimentally obtained histograms are presented in Figure 3. Next to each histogram, a representative NC-AFM image for the respective coverage is shown. Together with the experimental data (blue bars), the distribution for noninteracting stripes according to eq 1 is drawn (gray bars). All histograms deviate substantially from the distribution of noninteracting stripes and reveal a comparatively narrow stripe distance distribution. The histogram at a relatively high coverage of 0.579 ML (Figure 3a) shows two distinct peaks, around 2 nm and around 5 nm. The first peak indicates the minimum stripe distance resulting from the finite stripe width of $d_0 = 2$ nm found in full monolayer-coverage images. This first peak presumably results from short-range attraction between the stripes. The second peak is indicative of a repulsive interaction, which outweighs the short-range attraction at larger distances. Upon reducing the coverage, several effects can be noted in the histograms. The peak around 2 nm disappears. The average stripe distance shifts to larger values, because it is inversely proportional to the coverage. In Figure 3b an average stripe distance of $\bar{d} \approx 9$ nm is observed (corresponding to a coverage of 0.224 ML), while in Figure 3c, the average stripe distance is $\bar{d} \approx 16$ nm (0.127 ML). Additionally, the stripe distance distribution becomes broader with decreasing coverage, as can be seen from the standard deviation of the stripe distances indicated by the double arrows in Figure 3. However, even at the smallest coverage shown here, the standard deviation is only 5.7 nm, which is small compared to the standard deviation of randomly placed noninteraction stripes of 14 nm at this coverage. This finding provides direct evidence for the existence of a long-range repulsion between the stripes. From this statistical analysis, we can readily conclude that the periodicity of the stripe pattern can be tuned by the molecular coverage. Most importantly, periodicities as large as 16 nm are observed, demonstrating the long-range nature of the involved repulsion.

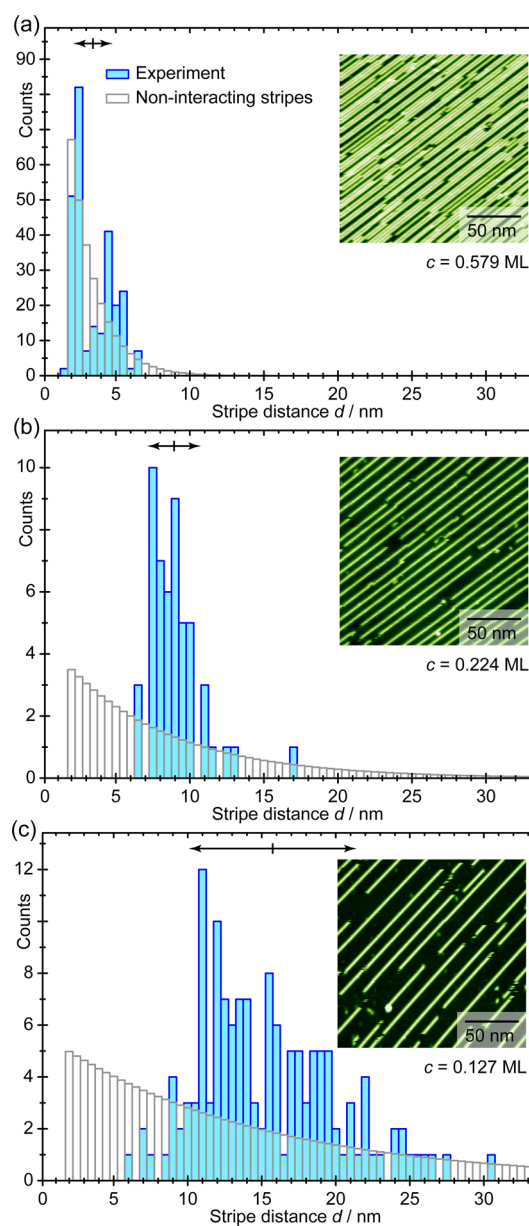


Figure 3. Histograms of measured next-neighbor stripe distances (blue bars) and representative NC-AFM images at different HBA coverage as indicated in the figure. The double arrows mark the average stripe distance and standard deviation in each experimental data set. The calculated histograms for noninteracting stripes (eq 1) are shown for comparison (gray bars).

The degree of order of the stripe arrangement can be deduced from the standard deviation of the stripe distances as a function of the average stripe distance. For perfectly equidistant spacing, the standard deviation of the stripe distance is zero. When considering noninteracting stripes, the standard deviation σ scales with the average stripe distance \bar{d} according to $(\bar{d} - d_0)(1 + a/(\bar{d} - d_0))^{1/2}$ (gray line in Figure 4a). In other words, the standard deviation of the stripe distance at a given average stripe distance (which is inversely proportional to the coverage) can be considered as a measure for the degree of order. The experimentally obtained values for the data from HBA are shown by blue circles in Figure 4a. As can be seen, these data deviate significantly from those expected for noninteracting stripes.

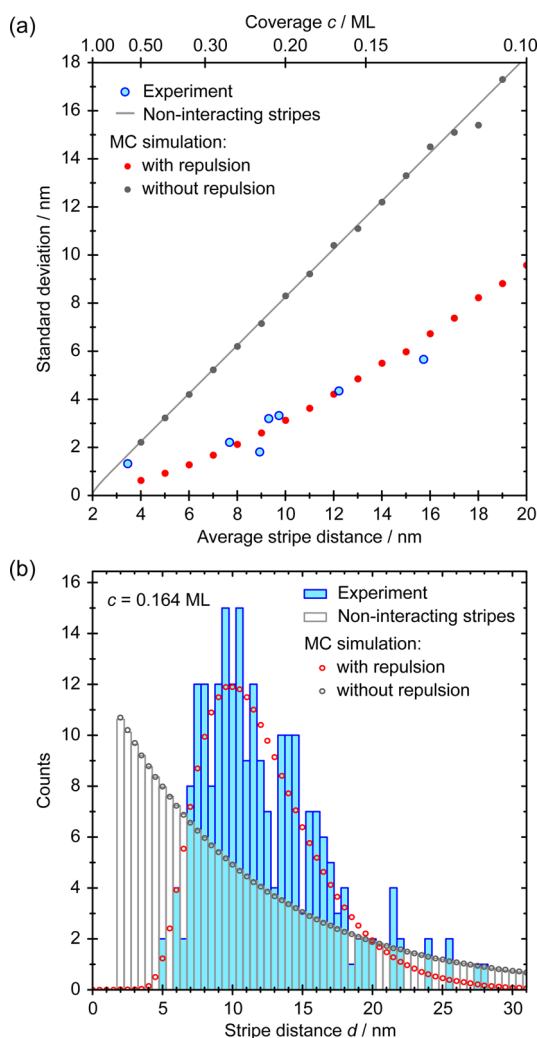


Figure 4. (a) Experimentally obtained standard deviation of the next-neighbor stripe distances as a function of the average stripe distance (blue circles). Note that the data point for a coverage of 0.579 ML is added although short-range attraction is visible at this high coverage. The standard deviation of noninteracting stripe distances scales with the average stripe distance as shown by the gray line. The points show MC simulation results with our dipole model using a dipole moment of 0 D (gray points), corresponding to noninteracting stripes and a dipole moment of $30 \text{ D}/\sqrt{n}$ (red points). (b) Next-neighbor stripe distance histogram from an experiment with HBA molecules (blue bars) compared with a distance histogram for noninteracting stripes (gray bars) as well as simulated histograms with and without (gray circles) dipole–dipole repulsion. The dipole moments were the same as in (a).

Next, we discuss a possible physical origin of the observed long-range repulsive interaction. Direct dipole–dipole interaction between the molecular building blocks has rarely been considered as an origin for repulsive interaction on the order of several nanometers when investigating metal surfaces.¹⁸ Instead, to explain the formation of periodic gratings on metal surfaces, indirect, substrate-mediated interactions have been speculated as a possible source for long-range repulsion.^{4,18} When other effects influencing the molecular arrangement are present, such as charge screening by the surface-state electrons, the electrostatic dipole–dipole interaction might, indeed, be too small to be decisive for a structural arrangement with a long-range order.

On insulator surfaces, however, charge screening is largely absent, and the substrate templating effect is known to be rather weak.¹⁹ Therefore, we propose a generic electrostatic repulsion mechanism for any ensemble of molecules adsorbed on a flat surface occupying equivalent adsorption positions.

No matter how complex or unique the molecule–surface bond might be, a characteristic charge distribution pattern establishes between molecule and surface. Note that this picture applies irrespective of the detailed adsorption geometry and does not require the molecule itself to carry a permanent dipole moment. Consequently, there will be electrostatic repulsion between these molecules due to their identically oriented charge distribution patterns. In the most simple case, the molecule–surface bond might be modeled as an electric dipole of strength $p = ql$ perpendicular to the surface. Here, q would be the charge transfer associated with the bond while l reflects the binding length.

To validate this picture, we performed Monte Carlo (MC) simulations²⁰ to model the repulsion originating from adsorption-induced electric dipoles. This simulation is intended to demonstrate that adsorption-induced dipoles appear sufficient for causing a strikingly long-range repulsion on an insulating substrate.²¹ We assume that each stripe is a one-dimensional array of identical molecular dipoles p perpendicular to the surface. From our AFM data, we were not able to directly follow the nucleation of stripes on the surface, but it is plausible to assume a critical stripe length $nb/2$ (corresponding to a critical number of molecular dipoles n with a dipole moment of in total np) has to form before extended stripes can grow. Therefore, we model the electrostatic repulsion between a short stripe segment and an infinitely long stripe at distance d , which is given by the electrostatic potential energy $U(d) = \hat{p}np / (2\pi\epsilon_0 d^2)$ of this arrangement. Here, $\hat{p} = 2p/b$ is the dipole density within the stripe, $b/2$ is the distance between two molecular dipoles (see Figure 2), and ϵ_0 is the vacuum permittivity. The dipoles are confined to a two-dimensional surface lattice and interact via the above-mentioned $1/d^2$ potential solely (cf. Supporting Information).

In this model, the standard deviation of the stripe distance can be determined as a function of the average stripe distance. For a vanishing dipole moment, the simulation data (Figure 4a, gray symbols) follow the standard deviation of noninteracting stripes (eq 1). For a nonvanishing dipole moment, the simulated standard deviation at a given average stripe distance (Figure 4a, red symbols) is always smaller than the standard deviation obtained for noninteracting stripes. This simple estimate readily shows that electrostatic dipole–dipole interactions must not be disregarded as long as other influencing effects are absent. We obtain an excellent agreement with the experimentally obtained values when considering a dipole moment of $p = 30 \text{ D}/\sqrt{n}$, which is a very reasonable value.²² To further validate our model, we consider a distance histogram for a molecular coverage of 0.164 ML as shown in Figure 4b. The experimental data are given by a blue bar chart, again showing a narrow stripe distance distribution in sharp contrast to the broad distribution of noninteracting stripes given by the gray bar chart. The experimentally obtained distribution is perfectly reproduced by our MC simulations (red symbols) with the same dipole moment as in Figure 4a, giving further justification for the model used here.

CONCLUSION

In summary, we present the formation of an ordered molecular stripe arrangement with equidistant appearance on an insulating substrate. The spacing periodicity can be tuned by the molecular coverage. The underlying repulsive interaction exhibits a long-range nature, which is significant even at average stripe-to-stripe distances as large as 16 nm. We propose a generic repulsion mechanism based on adsorption-induced charge transfer to explain the observed ordering. Using a simple dipole–dipole repulsion model, we demonstrate that the experimentally observed order can be readily explained by electrostatic repulsion solely. The dipole moment required to model the observed data is well conceivable when considering adsorption-induced charge transfer. We speculate that the observed mechanism is of generic nature for self-assembly on insulator surfaces, which are characterized by the absence of charge screening and other surface templating effects.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b08829.

Detailed deviation of the probability distribution and details on the Monte Carlo simulation (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

ML, monolayer; HBA, 3-hydroxybenzoic acid; NC-AFM, noncontact atomic force microscopy; MC, Monte Carlo

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- (17) A derivation of these equations is given in the [Supporting Information](#).

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- (20) Distance distributions can be calculated from a general analytic expression given in Bakhti, B. Statistically Interacting Vacancy Particles. *Phys. Rev. E* **2014**, *89*, 012137, if the stripe interaction is limited to next neighbors. When considering a $1/d^2$ potential, the calculated data agree very well with the presented experimental as well as the simulated results (cf. [Supporting information](#)).

- (21) The observation of equidistant stripes of HBA on calcite has provided the impetus for this work. As we aim for presenting a generic mechanism, the specific binding situation of 3-HBA, however, is not our focus.

- (22) Considering a typical adsorption-induced dipole moment of about 5 D, the value of $p = 30 \text{ D}/\sqrt{(n)}$ allows for estimating a critical stripe length of about 7 nm. When assuming deprotonation of the carboxylic acid group, the dipole moment would be on the order of 15 D. In this case, the critical stripe segment would include four molecules.