Mechanisms of the Adsorption and Self-Assembly of Molecules with Polarized Functional Groups on Insulating Surfaces

B. Hoff,[†] M. Gingras,[†] R. Peresutti,^{†,§} C. R. Henry,[†] A. S. Foster,[‡] and C. Barth^{*,†}

[†]Aix-Marseille University, CNRS, CINaM UMR 7325, Campus de Luminy, Case 913, 13288 Marseille, France

[‡]COMP, Department of Applied Physics, Aalto University School of Science and Technology, PO Box 11100, FI-00076 Helsinki, Finland

Supporting Information

ABSTRACT: The adsorption and self-assembly of several pentahelicene molecules with polarized and rigid functional groups have been studied on the Suzuki (001) surface in ultrahigh vacuum by noncontact AFM and KPFM, with the assistance of DFT calculations. It is shown that the adsorption strongly depends not only on the functional groups but also on the ionic substrate lattice. In particular, the local dipole of the functional groups, the adsorption geometry with respect to the cation lattice, and the ionic structure of the surface play a dominant role with a considerably large impact on the self-assembly of the helicene molecules. The work provides a detailed insight into the interaction of functionalized molecules with ionic insulator surfaces and into self-assembly.



INTRODUCTION

Ordered organic thin films are believed to be important surface systems for a variety of applications, in particular, for conducting devices.¹⁻³ For optimal properties, the films must be 2-D and well-ordered (crystalline),¹ which is realized by supramolecular self-assembly in most cases.⁴ Insulating substrates are of particular importance because the intrinsic electronic properties of the molecules can be decoupled from the substrate,⁵ which is essential in microelectronics.^{1,2,6} To tailor organic thin films and optimize their properties on insulating surfaces, the adsorption and self-assembly of molecules needs to be understood on the molecular scale. This can be best achieved on model surfaces with selected molecules by noncontact atomic force microscopy (nc-AFM) and Kelvin probe force microscopy (KPFM).^{7,8} In the past few years, the (001) surfaces of alkali halides have been shown to be adequate substrates because they are almost atomically flat, providing easy access for nc-AFM and KPFM, even if molecules are supported on them.⁹⁻²⁰

An important aspect is the adsorption and diffusion of the molecules and, in particular, the influence of the ionic sublattices of the alkali halide substrate. A common finding is that the adsorption of molecules is relatively weak on such surfaces, resulting in a high mobility of the molecules. The molecules either form molecular nanowires at surface steps^{11,12} or self-assemble into large 2-D ordered films.^{9,10,13,14,17,18,20,21} The current tentative picture for the adsorption considers not only the van der Waals but also electrostatic contribution in the molecule–surface interaction: van der Waals forces are not strongly site-specific, and the molecules can occupy almost any position on the surface.^{15,19} However, as soon as a molecule

includes polar groups or atoms carrying a partial charge, the molecule can directly bind via a stronger electrostatic interaction with the ionic surface lattice 16,19,20,22,23 (charge matching).

In view of the increasing amount of work, the detailed adsorption mechanisms of the molecule-surface interaction are still under debate, and work including a comparison between experiment and theory is very limited. Furthermore, not much is known with respect to the impact of adsorption on selfassembly (and vice versa), and the precise mechanisms of selfassembly have not been considered much in the past. By a combination of nc-AFM/KPFM experiments and density functional theory (DFT), we give detailed insights into the adsorption and self-assembly mechanisms of molecules with rigid polar functional groups on a nanostructured insulating surface. We select racemic [5]helicene derivatives (pentahelicene) as model molecules because they are chiral, helical polyaromatic compounds that can have enhanced chiral and optoelectronic properties for future applications.^{24–27} Most importantly, such molecules can be functionalized and have the tendency to self-assemble into larger structures due to $\pi - \pi$ orbital interactions of their benzenoid rings.²⁷ Furthermore, helicene molecules, in general, can be vacuum-deposited onto surfaces, as shown on metal $^{28-32}$ and even insulating surfaces.^{19,33} We study a large spectrum of functionalizations by considering either one or two rigidly bound bromine atoms or cyano groups (Figure 1), which are all electroattractive with

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Figure 1. All four functionalized [5]helicene molecules used in this work: MonoBromo (a), DiBromo (b), MonoCyano (c), and DiCyano (d). The distances d (nm) and dipoles p (Debye) in the table were calculated by DFT for free molecules.

different localized partial negative charges. The adsorption and the self-assembly of the [5]helicene derivatives are studied by varying the functional groups and as a function of surface chemistry, which is accomplished on the nanostructured (001) Suzuki surface of NaCl:Cd²⁺. We show that the adsorption depends on the dipole strength of the molecules, the adsorption geometry, and the surface chemistry, with a strong impact on the self-assembly of the molecules.

METHODS

Experiments. All details of the synthesis of the helicene molecules can be found in the Supporting Information. The CdCl₂-doped (4 mol %) NaCl crystals were outgased by annealing at ~200 °C in an oven. After the cooling of the crystals and sample holders, the (001) surfaces were prepared by cleavage of the crystals along the (001) plane at room temperature. The crystals were then annealed a second time in the oven at ~200 °C for a few hours to reconstruct the surface as described in ref 34.

For depositing functionalized [5]helicene derivatives onto a crystal surface, a self-made Knudsen cell is used. The molecules are evaporated at a temperature of ~140 °C onto the surface held at room temperature (base pressure: upper 10^{-10} mbar range). A large quantity of molecules (\gg one molecular layer (ML)) was deposited at once onto the Suzuki surface during the deposition. The outgazing and preparation of the Suzuki surfaces, the deposition of molecules, and the scanning force microscopy experiments were done in one single UHV chamber.³⁵ More details can be found in the Supporting Information.

Frequency-modulated noncontact AFM (nc-AFM) and Kelvin probe force microscopy (KPFM) experiments were performed in the low 10^{-10} mbar pressure range and at room temperature with an Omicron RT-AFM/STM. Conducting silicon cantilevers from Nanosensors (NanoWorld AG, Neuchatel, Switzerland) and a demodulator (EasyPLL) from NanoSurf were used. KPFM measurements were performed in the frequency modulation mode,³⁶ where a dc and ac voltage (U_{ac}) with frequency f_{ac} are applied between tip and surface (tip at ground). On the Suzuki surfaces, the distribution of charges and dipoles on the surface is measured.^{37,38} All topography nc-AFM images shown in this work were acquired in the active KPFM mode, which is important for extracting reliable height values from such images.³⁹ More details of the techniques and most important parameters of the AFM and KPFM measurements can be found in the Supporting Information.

Calculations. First-principles calculations were performed using the periodic plane-wave basis VASP code,^{40,41} implementing the spin-polarized DFT and the generalized gradient approximation. Noncovalent interactions are described by means of the most recent version of the Langreth–Lundqvist density functional vdW-DF2.⁴² The nonlocal term in it was evaluated using the adaptive real-space approach.⁴³

The properties of the bulk and surface of NaCl and NaCl:Cd²⁺ and isolated molecules were carefully checked within this methodology, and excellent agreement was achieved with experiments. The lattice constants of NaCl (5.70 Å) and NaCl: Cd^{2+} (11.30 Å) were found to be within 1% of reported experimental values.^{44,45} Because no experimental structural results exist for isolated helicene molecules, key bond lengths and angles for all isolated molecules, starting from equilibrium structures, were compared using different van der Waals and hybrid functionals, and variations were less than 0.1 Å and 0.2° across the methods. All adsorption energies are calculated with respect to the dipole-corrected total energies provided by the DFT simulations. Note that calculations of charge transfer between the molecules and surface showed that it had a minimal role, with the interactions dominated by van der Waals and electrostatic interactions. The adsorption energy per molecule (ΔE_{ad}) is calculated as the total energy difference between the complete molecule-surface system and the isolated surface and isolated molecule. More details of the calculations and the energies of all molecule-surface systems can be found in the Supporting Information.

RESULTS

Experiment: Brominated and Cyanated [5]Helicene. A *charge matching* between a polar substituent of a helicene molecule with a partial negative charge and the surface cations was recently exemplified by 7-bromo[5]helicene (MonoBromo, Figure 1a) on the nanostructured Suzuki surface.¹⁹ The molecules adsorb only in the Suzuki regions, forming one ML thin islands,¹⁹ and no vertical stacking of the molecules can be observed. The molecules are lying flat on the surface (height: $h_{\text{MonoBromo}} = 0.8 \pm 0.1 \text{ nm}$) with the partially negatively charged bromine atom charge-matched above the surface.

In contrast with MonoBromo, DiBromo (Figure 1b) shows completely different characteristics (see Figure 2): DiBromo adsorbs on the Suzuki surface forming wide and flat islands, preferentially in the Suzuki regions of the surface but also partially in the NaCl regions. However, the molecules completely desorb from the surface within a few hours after the deposition (Figure 2a-c), as verified by several repeated deposition experiments on the surfaces of different Suzuki crystals. After about half a day the surface is clean and no molecular islands can be found, whereas the Suzuki surface remains completely intact. It is important to mention that all AFM images reveal that the height of the islands is ~ 2 Å higher $(h_{\text{DiBromo}} = 1.0 \pm 0.1 \text{ nm})$ than the height of MonoBromo. As will be discussed later, the larger height is a signature that the molecules are rather standing upward on the surface, in contrast with MonoBromo.



Figure 2. Temporal evolution of the desorption of DiBromo from the Suzuki surface. Panel a was obtained 1.5 h after the deposition of the molecules. The time interval between the successively recorded images is 35 min.

The height and adsorption characteristics of MonoBromo and DiBromo show that the substituents – here the number of attached bromine groups – have a significant impact on the adsorption of [5]helicene derivatives. To obtain further insight into the adsorption/desorption of functionalized [5]helicene molecules, the adsorption of [5]helicene derivatives incorporating either one (MonoCyano, Figure 1c) or two cyano groups (DiCyano, Figure 1d) has been considered. Such molecules have a three times larger dipole with respect to their bromine counterparts, MonoBromo and DiBromo, whereas the dipole of MonoCyano is already two times larger than the one of DiBromo. (See the table in Figure 1.)

In contrast with MonoBromo and DiBromo, the whole Suzuki surface is covered by the cyanated molecules right after the deposition, which is illustrated by the AFM images in Figure 3a,b. In the case of MonoCyano (Figure 3a), the surface is covered by islands of different heights, which are a multiple of $h_{\rm MC}$ = 1.10 ± 0.05 nm, as verified by topography profiles (Supporting Information). Heights below 1.1 nm could never be observed, suggesting that the height ($h_{\rm MC}$) is equivalent to one ML. A different situation is found for DiCyano (Figure 3b): one single ML covers the whole Suzuki surface (see discussion later), perfectly reshaping the steps of the Suzuki surface. On top of this layer, some large islands of up to 100 nm diameter can be found (bright), which have a height of up to 10 nm.

The evolution in time of the MonoCyano and DiCyano films at room temperature is quite fascinating: after the deposition of the molecules, a large part of them desorb from the Suzuki surface over time. In the case of MonoCyano, nanometer large aggregates of molecules desorb from the islands, one unit after another, such that many islands just disappear from the surface after 2 days. (See the Supporting Information.) In the case of DiCyano, the large round islands (Figure 3b) desorb within a day (see Supporting Information) such that the Suzuki surface is perfectly covered by one ML of DiCyano. However, the desorption does not stop (Figure 3c,d), in particular, in the NaCl regions, where the film breaks, creating holes with a depth of $h_{\rm DC} = 1.1 \pm 0.05$ nm about one or 2 days after the deposition (Figure 2c1-4). As in the case of MonoCyano, the height $h_{\rm DC}$ corresponds to one molecular layer because smaller heights could never be observed. As the film breaks and desorbs more and more, only some regions of NaCl are covered (Figure 2d), whereas no molecule desorbs from the Suzuki regions.

After a certain time, a surface state is reached for both cyanated [5]helicene molecules, where 1 ML of MonoCyano or DiCyano decorates only the Suzuki regions, as in the case of MonoBromo (Figure 4). In the case of MonoBromo, a decoration of only the Suzuki regions is reached right after the deposition without any adsorption of MonoBromo in the NaCl regions and without any vertical stacking of the molecules (Figure 4a). In the case of MonoCyano, a similar state is obtained after 2 days, during which a large part of the molecules desorbed from the surface (Figure 4b), whereas at some places some multilayered, ~ 6 nm high islands are still present on the



Figure 3. Adsorption and desorption phenomena of MonoCyano (a) and DiCyano (b–d) on the Suzuki surface (topography images). Panels a and b were acquired 2 and 8 h, respectively, after the deposition of the molecules. Image series c shows the time-dependent desorption of DiCyano, which creates holes in the 1 ML thick molecular film (68 min each image). The molecules only desorb from the NaCl regions but not from the Suzuki regions (arrow in image c4). (d) Snapshot of the single DiCyano ML desorbing from the NaCl regions, 8.3 days after the deposition.



Figure 4. Perfect decoration of the Suzuki regions by MonoBromo (instantaneously) (a), MonoCyano (after ~2 days) (b), and DiCyano (after ~1 week) (c). Color: topography images; b/w: Kelvin images.

Table 1. Adsorption Energy Per Molecule (ΔE_{ad}) in Electronvolts for All Functionalized [5]Helicene Derivatives Used in This Work^{*a*}

surface	position	site	MonoBromo	DiBromo	MonoCyano	DiCyano
S _{NaCl}	\perp	Na _{Cl}	0.31	0.23	0.48	0.73
	=	Na _{Cl}	0.84	0.99	1.10	1.23
Ss	\perp	Cd_{Cl}	0.32	0.23	0.52	0.75
	=	Cd _{Cl}	0.91	1.04	1.19	1.03
NaCl	\perp	Na _{Cl}	0.31	0.26	0.42	0.65
	=	Na _{Cl}	0.82	0.92	1.09	1.22
NaCl(nn)	\perp	Na _{Cl}		0.34		0.62
	=	Na _{Cl}		0.82		1.07

^{*a*}Identifiers S_{NaCl} and S_s denote the NaCl- and Suzuki-terminated Suzuki surfaces, respectively. The vertical and flat positions (Pos) of the molecule are labeled by the identifiers \perp and =, respectively. The surface sites Na_{Cl} and Cd_{Cl} correspond to a Na^+ and Cd^{2+} surface ion, which are above a $Cl^$ ion of the second layer. Above these sites the polarized substituents of the helicene molecules are located. (See Figure 5 and Supporting Information.) All energies for DiBromo and DiCyano were calculated for substitutents located above next-neighbor cations, except the last row (NaCl (nn)), which includes the energies of substitutents located above next-neighbor cations.

surface. In contrast, DiCyano needs more time to only decorate the Suzuki regions: after about 1 week, all molecules desorb from the NaCl region, leaving the Suzuki regions covered by 1 ML islands (Figure 4c). With respect to the film height, MonoBromo has a height of 0.8 nm because it is lying flat on the surface, whereas DiBromo, MonoCyano, and DiCyano are positioned vertically on the surface because they have a larger height of ~1.1 nm, respectively. (See the discussion later.)

Another striking difference between the cyanated [5]helicene molecules and MonoBromo is the stability of the films inside the Suzuki regions. MonoBromo remains on the surface all time;¹⁹ however, MonoCyano and DiCyano completely desorb from the Suzuki regions about 3 weeks after the deposition (Supporting Information). Note that the molecules desorb into the UHV chamber and probably adsorb on diverse metal parts where they remain; we never observed readsorption onto the Suzuki surfaces by time.

Theory: Adsorption Mechanisms. All results clearly show that the adsorption and desorption of [5]helicene derivatives strongly depend on the functional groups (substituents) of the molecule. To understand the differences in the adsorption of all four helicene molecules, we performed first-principles calculations using DFT,^{40,41} including self-consistent van der Waals interactions.⁴³ (See the Supporting Information.) The molecules were placed either in a horizontal or vertical position on the Suzuki surface, with the polarized substituents placed above specific cation sites: the two substituents of DiBromo and DiCyano were placed above next-neighbor cations and for some calculations above next-next-neighbor cations. Any configuration where the substituents are located above anion sites yielded smaller energies (Supporting Information). The adsorption energies of the most important molecule–surface systems are summarized in Table 1, whereas the complete set of results is documented in the Supporting Information.

Apart from the intermolecular interaction (self-assembly), which will be discussed later, the adsorption of a single molecule depends on the dipole strength of the functional group(s), on the surface site, and also on the mismatch/match between the ionic lattice and the two substituents in the case of DiBromo and DiCyano (Figure 5). Considering MonoBromo, the adsorption energy is around $\Delta E_{ad} \approx 0.3$ eV when the molecule is in its vertical position with the bromine chargematched at the cations. Because only the bromine atom is the closest atom to the surface, the interaction is dominated by



Figure 5. Model of charge-matching for the adsorption of MonoBromo (bottom left), DiBromo (bottom right), MonoCyano (middle), and DiCyano (top left and right). The substitutents of the molecules couple to the positive cations of the Suzuki (left) and pure NaCl (right) regions. The radius of the circle (top left, DiCyano) is the distance of the two nitrogens ($d_{\rm CN-CN} = 0.41$ nm), which almost equals the next-neighbor distance Na⁺–Na⁺ or Na⁺–Cd²⁺ ($d_{\rm Na-Na} = d_{\rm Na-Cd} = 0.40$ nm). The substitutents of the DiCyano molecule on the top right are placed above two next–next neighbor cations.

electrostatics, and van der Waals is minimal. When the molecule is flat, with the bromine still charge-matched at the cations (Figure 5, bottom left), the adsorption energy increases to $\Delta E_{\rm ad} \approx 0.8$ to 0.9 eV due to the additional, rather non-sitespecific van der Waals interaction between the benzene rings of the molecule and the surface. When a second bromine atom is bound to the molecule (DiBromo), the energies do not change so much; they are a bit smaller or higher when the substitutents are located above either next-neighbor or next-next neighbor (on NaCl) cations, respectively. This result is quite surprising because one might expect that the adsorption should increase with the number of functional groups, that is, with the increasing dipole strength of DiBromo. (See Figure 1.) However, as it becomes clear later this result is partially due to the mismatch between the Br-Br distance of the functional groups ($d_{Br-Br} = 0.34$ nm) and the cation distances (next neighbor: $d_{\text{Na-Na}} = d_{\text{Na-Cd}} = 0.40 \text{ nm}$), in combination with the relatively small dipole strength of DiBromo in comparison with, for example, DiCyano.

MonoCyano and DiCyano have a three times larger dipole strength than MonoBromo and DiBromo, respectively, whereas the dipole of MonoCyano is already two times larger than the one of DiBromo (Figure 1). These quite strong dipoles lead to larger adsorption energies: when MonoCyano is placed in a vertical position with the cyano group charge-matched above a surface cation (Figure 5, center), the adsorption energy considerably increases ($\Delta E_{\rm ad} \approx 0.4$ to 0.5 eV), in comparison with both brominated molecules. When the molecule is lying flat on the surface, the energies also increase ($\Delta E_{ad} \approx 1.1 \text{ eV}$). With respect to DiCyano in its vertical position (Figure 5, top), the adsorption energy significantly increases compared with MonoCyano ($\Delta E_{ad} \approx 0.7$ eV), which is not observed in the case of MonoBromo versus DiBromo. The adsorption above next-neighbor cations is preferred in comparison with the one above next-next neighbor cations. The reason is that the distance between the two nitrogen atoms ($d_{\text{CN-CN}} = 0.41 \text{ nm}$) almost equals the one of two next-neighbor surface cations $(d_{\text{Na-Na}} = d_{\text{Na-Cd}} = 0.40 \text{ nm})$; the two nitrogen atoms can be perfectly charge-matched at two surface cations, and the large dipole even favors a stronger adsorption.

From the latter considerations an agreement between experiment and theory can be found: in contrast with the flat lying MonoBromo, both cyano molecules are in a vertical position, the origin of which is explained in the next two sections. Two-third of the adsorption energy of MonoBromo is due to the van der Waals interaction, which is missing in the case of MonoCyano and DiCyano in their vertical position. As a result, the adsorption energies are smaller but thanks to the strong dipole strength of both cyanated molecules still somewhat comparable to that of MonoBromo. It qualitatively explains why MonoCyano and DiCyano desorb during a long time of days and weeks from the surface, whereas MonoBromo remains on the surface all time.

Furthermore, the calculations show that the adsorption energy for both cyanated molecules in their vertical position is 0.1 to 0.2 eV larger in the Suzuki region than in the pure NaCl regions, which is obviously due to the two positive valences of the cadmium ion (Cd^{2+}) . To some extent, this explains why the cyano molecules desorb first from the NaCl regions, as observed in our experiments. In comparison with MonoCyano, the adsorption energy is considerably larger for DiCyano with its two substituents. This explains why the desorption in the NaCl and Suzuki regions is faster for MonoCyano than for DiCyano, which is again in agreement with the experimental observations.

Self-Assembly. Despite the fairly good agreement of the experimental and theoretical results, a key question remains open regarding the position of the molecules. Why are DiBromo, MonoCyano, and DiCyano in a vertical position whereas MonoBromo lies flat on the surface? So far, the previously described results describe the adsorption for only single molecules but not for an ensemble of molecules. In the following sections, it will be shown that self-assembly and other mechanisms need to be taken into account for a full description.

Molecular Resolution. In contrast with MonoBromo, molecular resolution could be obtained for MonoCyano and DiCyano by nc-AFM high-resolution imaging (Figure 6). In the Suzuki regions, the AFM images show self-assembled molecules of MonoCyano (Figure 6a,b), which form molecular rows along equivalent (001) surface directions. On a large scale, up to 50 nm wide domains can be observed, in which any of the two $\langle 001 \rangle$ directions can be found from domain to domain. The rows have a distance of $d_{MC,row} = 1.44 \pm 0.03$ nm (Figure 6c) and are composed of bright dots with a distance of $d_{MC,spot}$ = 0.56 ± 0.01 nm (Figure 6d). In many images, we observed that the dots have sometimes an asymmetric shape, as can be seen in image Figure 6b. They are either elongated, forming \sim 6.5 Å thick bands (right row), or exhibit two maxima, one that is very bright and one which is very faint (left row), both separated by a distance of 4.5 Å. As discussed in the next section, the dots correspond to single MonoCyano molecules, which keep a distance of one unit cell of NaCl (a_{NaCl}) to each other along the rows.

Surprisingly, the situation of DiCyano contrasts the one of MonoCyano: molecular resolution shows self-assembled molecular rows in only the NaCl regions but never in the Suzuki regions (Figure 6e,f). In the latter Suzuki regions, the molecular structure is irregular, pointing to an amorphous structure. In contrast, molecular rows can be found along equivalent $\langle 001 \rangle$ surface directions in the NaCl regions, in domains with a length of up to 100 nm. As in the case of MonoCyano, each row is composed of bright dots with a mean



Figure 6. Molecular resolution of self-assembled MonoCyano (a-d) and DiCyano (e-h). (a-d) In the Suzuki region, MonoCyano self-assembles into rows (a,b), which have a distance of 1.44 ± 0.03 nm, as shown in panel c taken at the green dotted line in panel a. Each row exhibits equidistant bright dots with a distance of 0.56 ± 0.01 nm (panel d, blue dotted line in panel a). (e-h) Self-assembly of DiCyano can be observed only in the NaCl regions (e,f) but not in the Suzuki regions. The panels g and h were taken at the green and blue dotted lines in panel f, showing important features that are discussed in the main text.

distance of $d_{\text{DC,spot}} = 0.54 \pm 0.01$ nm along a row (Figure 6h). Depending on the imaging conditions and the tip, we observed a rather complex structure of the rows; Figure 6f,g shows typical contrast features: the periodicity is determined by two minima (M), which have a distance of $d_{\text{DC,row1}} = 2.8 \pm 0.2$ nm. Several maxima (A–E) determine the contrast and divide the latter long periodicity (M–M = A–E) into smaller sections: first, a second maxima can be seen (C), which halves the long periodicity A–E onto a value of $d_{\text{DC,row2}} = 1.4 \pm 0.1$ nm (A–C = C–E). Furthermore, two small maxima (B and D) divide the sections A–C and C–E. They are not exactly in the middle of the sections but are closer to maxima A and C, with distances of A–B = C–D \approx 5 Å and B–C = D–E \approx 8 Å. As discussed in the next subsection, we tentatively address the small distance of ~5 Å to the lateral size of a molecule.

Model for Self-Assembly. The high-resolution images acquired on MonoCyano and DiCyano films clearly show that the self-assembly phenomena need to be taken into account for a complete description. In particular, a synergy between supramolecular lateral interactions (self-assembly) and the substrate-molecule interactions previously described needs to be considered. A first key mechanism for the self-assembly is $\pi-\pi$ orbital interactions between the benzenoid rings of the helicene molecules.^{46,47} The importance of these interactions is already known for helicene in the crystalline state and in solution.²⁷ They consist of partial overlapping of π -orbitals from adjacent molecules, thus stabilizing the self-assembled molecules.^{48,49} The $\pi-\pi$ stacking of helicenes generates peculiar morphologies such as molecular columns or wires.²⁷

If similar lateral supramolecular interactions are anticipated for the helicene molecules on the Suzuki surface, both enantiomers of the molecules need to be arranged on the surface fulfilling the following criteria:

- Adsorption via the charge-matching model from above
- Formation of $\langle 001 \rangle$ rows with the molecules in a perpendicular orientation
- A $\pi \pi$ stacking along the rows with a bonding distance in the order of ~3.5 Å⁴⁷⁻⁴⁹

Surprisingly, considering many $\langle 001 \rangle$ row configurations of cyanated helicene molecules on the Suzuki surface leads to only two possible configurations. These are shown in the form of DFT simulation results for DiCyano on NaCl(001) in Figure 7.

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In the first configuration, rows of vertical DiCyano molecules can only be formed by one type of enantiomer (Figure 7a,b); the rows are therefore homochiral. The substituents are placed above two next—next neighbor cations (Figure 6d) so that the short axis of a molecule is perpendicular to the $\langle 001 \rangle$ direction of the row. Because only one type of enantiomer is used for building a row, some benzenoid rings of adjacent molecules are all parallel-displaced, face-to-face oriented. In fact, only two benzenoid rings of the helicene are, in principle, close enough to involve $\pi - \pi$ stacking because the helical nature of the molecule is preventing a full overlap with all rings. Such benzenoid rings of adjacent molecules have a distance of ~5.4 Å, which is larger than the distance of 3.5 Å for $\pi - \pi$ stacking (green cube).

In the second configuration (Figure 7c,d), both enantiomers are alternately placed along the $\langle 001 \rangle$ surface direction, with their two substituents always above two next-neighbor cations. Because of the $\langle 011 \rangle$ alignment of the two cations the short axis of each molecule is rotated by ~45° with respect to the $\langle 001 \rangle$ direction of the row. Some benzenoid rings of adjacent molecules are very close to each other, with a distance comparable to 3.5 Å (green cube). The calculations reveal that the skeleton of a helicene molecule is slightly deformed with respect to that of a free molecule because of the $\pi - \pi$ interactions. Although being almost face-to-face the adjacent benzenoid rings are not parallel to each other, and a hydrogen (yellow dotted circle) is quite close to such a benzene—benzene configuration.

With respect to the adsorption energy of the two row configurations (Table 2), a striking observation can be made: considering the first configuration with the substituents placed above next-next-neighbor cations (Figure 7a,b), the energy per molecule ($\Delta E_{\rm ad} = 0.57$ eV) is similar to that from a single molecule ($\Delta E_{\rm ad} = 0.62$ eV). Obviously, the stacking does not increase the adsorption energy of the system. However, considering the second-row configuration with the substitutents

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Figure 7. Self-assembled rows of DiCyano along the $\langle 001 \rangle$ surface direction on NaCl(001). (a,b) Cyano substitutents are placed above next-next-neighbor cations, with the molecules in their perpendicular orientation. (c,d) Cyano substitutents are placed above next-neighbor cations, with the molecules in their tilted orientation. Both enantiomers are represented in different colors (bright and dark), whereas in panels a and b only one type of enatiomer is shown. (e) Tilt of 20° (right) with respect to the vertically positioned DiCyano molecules (left). The height of the molecule is assumed to be the distance from the center of the last NaCl surface layer to the center of topmost hydrogen atoms. The green cubes have a side length of 3.5 Å, which is the typical distance for π - π stacking.

Table 2. Adsorption Energies Per Molecule (ΔE_{ad}) in Electronvolts for All Row Configurations of DiCyano on NaCl(001)

cations	position	row distance	ΔE_{ad}
single molecule	\perp		0.62
next-next neighbor	\perp	$4 \times a_{\text{NaCl}}$	0.57
next neighbor	\perp	$4 \times a_{\text{NaCl}}$	0.72
next neighbor	20°	$4 \times a_{\text{NaCl}}$	0.83
next neighbor, exp. distance	\perp	$2.5 \times a_{\rm NaCl}$	0.68
next neighbor, half distance	\perp	$2 \times a_{\text{NaCl}}$	0.60
next neighbor, exp. distance	20°	$2.5 \times a_{ m NaCl}$	0.75
next neighbor, half distance	20°	$2 \times a_{\text{NaCl}}$	0.70

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placed above next-neighbor cations (Figure 7c,d), the adsorption energy per molecule ($\Delta E_{ad} = 0.72 \text{ eV}$) is larger in comparison with the latter two energies and with that from a single molecule ($\Delta E_{ad} = 0.65 \text{ eV}$). The energy increases furthermore ($\Delta E_{ad} = 0.83 \text{ eV}$) if the molecules are tilted by 20° (Figure 7e), where the benzenoid rings get closer to each other.

Therefore, a stacking of DiCyano into rows increases the overall energy of the system only if the distance is comparable to the typical distance for π - π stacking (~3.5 Å), which is the case for the second row configuration with tilted molecules. An energy gain of 0.83 – 0.62 = 0.21 eV is obtained, which is in perfect agreement with the expected gain of energy for aromatic–aromatic π - π interactions, which is on the order of 0.1 to 0.2 eV.⁴⁹ However, if the distance between the benzenoid rings is too large, as is the case for the first row configuration (~5.4 Å), no energy gain is obtained.

The second-row configuration perfectly explains the selfassembly of DiCyano but also of MonoCyano because the cyano substituents do not play a major role in the π – π stacking. Most importantly, the structure is in perfect agreement with our experimental observations: the molecules have a distance of one unit cell of NaCl (a_{NaCl}), which equals the distances of the white dots along a row found in our AFM images for Mono and DiCyano (Figure 6). Furthermore, the calculations indicate a height of the molecules of $h_{\text{theo}} \approx 1.15$ nm (Figure 7e), which is also in perfect agreement with the experimental value of $h_{\text{exp}} =$ 1.10 ± 0.05 nm. A fair agreement between theory and experiment can be found with respect to the width of the molecular rows, which is ~5.5 Å large considering only the topmost hydrogen atoms.

Apart from the latter good agreement between experiment and theory a very important conclusion can be drawn considering the self-assembly of Mono- and DiCyano in the Suzuki regions: if DiCyano molecules are placed in the Suzuki region (Figure 8a, bottom row), the system is not anymore stable: for half of the molecules (yellow dotted circles) one of the partially negative cyano groups is positioned above the negative vacancies, where the adsorption energy is considerably much smaller ($\Delta E_{ad} = 0.18 \text{ eV}$). Obviously, these molecules do not adsorb at the latter sites so that half of the molecules are missing (top row), destroying the overall self-assembly in the



Figure 8. Self-assembled cyanated [5]helicene molecules in the Suzuki region. (a) Bottom row: The substitutents of half of the DiCyano molecules are located above the vacancies of the Suzuki structure (yellow circle), which is not a preferred adsorption site. They must be removed (top row), which destroys the overall self-assembly of DiCyano. (b) Bottom: by a 180° rotation of MonoCyano around its long axis, a cyano substituent above a vacancy can be positioned above a cation. Top: possible configuration for a self-assembled row of MonoCyano.

Suzuki regions. This probably leads to the more open and probably amorphous structure we observed in the AFM images (Figure 6e,f).

The latter match with experimental observations becomes even better when MonoCyano is considered: this molecule has only one substituent, which can be positioned at any of the two surface sites, vacancy or cation (Figure 8b, bottom): the position of the substituent (left) can be "switched" without changing the positions of the carbon and hydrogen atoms by a 180° rotation around the long axis of the molecule; the cyano group can therefore always be placed above a cation (right). This perfectly explains why MonoCyano can self-assemble in the Suzuki regions, as exemplified by the top row of molecules in Figure 8b.

So far, the architecture of self-assembled helicene molecules inside of a single row has been considered. With respect to the arrangement of the rows, we can conclude from the experiments that the rows have a rather large distance to each other ($d_{\rm row} = 1.4$ nm, Figure 6) and that there are two types of rows in the DiCyano case since a double periodicity ($d_{\rm DC,row1} = 2.8$ nm) could be observed. Although the latter can be principally explained by two rows, which are rotated to each other by 180° (they are not equivalent), a complete and precise description of the rows remains challenging due to the various possible configurations for rows on the surface; a row can be principally shifted by $a_{\rm NaCl}$ along the row and by $a_{\rm NaCl}/2$ perpendicular to it.

To qualitatively understand the large distance of 1.4 nm, we conducted a set of numerical simulations, in which the distance between the rows was varied by changing the size of the NaCl slab used for the calculations. (See the Supporting Information.) We simulated large and small row distances of $4 \times a_{\text{NaCl}}$ and $2 \times a_{\text{NaCl}}$, respectively (Figure 9a,c), and rows, which have



Figure 9. DFT results of rows build by self-assembled DiCyano on NaCl(001). The second row configuration with 20° tilted DiCyano molecules (Figure 7c,d) was used for the calculations. The rows in panels a and c are examples for a large $(4 \times a_{\text{NaCl}})$ and close $(2 \times a_{\text{NaCl}})$ row distance, respectively. (b) Distance of the rows (2.5 × $a_{\text{NaCl}})$ equals the row distance measured in the experimental AFM images (Figure 6).

the same distance of $2.5 \times a_{\text{NaCl}} \approx 1.4$ nm as the experimental one (Figure 9b). The adsorption energy per molecule (Table 2) decreases from $\Delta E_{\text{ad}} = 0.83$ (Figure 9a) to 0.75 eV (Figure 9b) and finally to 0.70 eV (Figure 9c) when the large row distance (Figure 9a) is reduced. This suggests that a repulsive interaction between molecular rows exists if they get close to each other, although differences of <0.1 eV are close to the limit of accuracy. In any case, the calculations do not find a clear energetic minimum at the row distance 2.5 × a_{NaCb} suggesting that a more extensive study, including finite temperature effects and more accurate methods, may be necessary to resolve this phenomenon.

Formation of Self-Assembled Molecules. After having characterized the adsorption and self-assembly of the helicene molecules, the important question remains why DiBromo, MonoCyano, and DiCyano are in a vertical position, whereas MonoBromo is lying flat on the surface. Considering the cyanated helicene molecules, the energy per molecule in the self-assembly configuration is around $\Delta E_{\rm ad} \approx 0.8$ eV and is smaller in comparison with that of a flat-lying molecule (in mean: $\Delta E_{\rm ad} \approx 1.1$ eV). From this perspective, the flat configuration should be the preferred one for the cyanated helicene molecules, which is, however, not the case.

A key mechanism for the perpendicular configuration could be the dipole of the surface and molecules. For instance, because the Suzuki surface already has a net dipole (negative end sticking from the surface),³⁴ the polar molecules try to compensate this surface dipole by orienting their dipole into the opposite direction (positive end sticking from the surface). However, if the dipole of the molecule is too small, as is the case of MonoBromo, the system seems to place the molecule rather flat onto the surface.

Qualitative support for this kind of dipole compensation comes from the Kelvin measurements, which were conducted on the MonoBromo, MonoCyano, and DiCyano films (Figure 4): with respect to MonoBromo, the Kelvin image exhibits a bright contrast (Figure 4a), which corresponds to a more negative electrostatic surface potential with respect to the neutral and stoichiometric NaCl regions.³⁸ In comparison, the Kelvin contrast is more or less dark for MonoCyano (Figure 4b) and clearly dark for DiCyano (Figure 4c). In the latter case, the DiCyano film is more positive with respect to the NaCl regions. All of this shows that the negative potential of the Suzuki regions^{34,50} is conserved in the MonoBromo case, which might be due to the negative bromine atoms that can be "seen" by the tip, and the small dipole of the molecule that is parallel to the surface. In the case of the cyanated molecules, the negative substituents are covered by the skeleton of the helicene molecules. The tip therefore "feels" the dipole with its positive part at the end of the helicene skeleton, which leads to a less negative (MonoCyano) or even positive electrostatic potential (DiCyano), depending on the dipole strength of the helicene molecule.

CONCLUSIONS AND OUTLOOK

On the nanostructured Suzuki surface, the adsorption, desorption, and self-assembly of [5]helicene (pentahelicene) molecules functionalized with one or two polar bromine or cyano substituents were studied by UHV nc-AFM and KPFM and by DFT calculations. The good agreement between experiment and theory shows that all three phenomena strongly depend on the substituents (dipole strength and number), the adsorption geometry for two substituents above the surface cations, and also on the surface chemistry of the Suzuki surface (lattice site).

With respect to the molecular adsorption, we conclude that the stronger the dipole of the molecule, the larger the adsorption energy. If more than one substituent is attached to the molecule skeleton, the largest adsorption energies are obtained in the case of a perfect match between the distance of the substituents and the next-neighbor cation distance (multiple charge-matching). Because of their large dipole, the

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cyano molecules exhibit the largest adsorption energies. They are in a perpendicular position, with the substituents chargematched at the cations of the surface, which allows a compensation of the net surface dipole of the Suzuki regions.

A perpendicular position permits a self-assembly of the molecules into molecular rows along the $\langle 001 \rangle$ surface direction. The self-assembly reduces the adsorption energy of the system and is mainly characterized by a stacking of adjacent molecules with $\pi - \pi$ orbital interactions of two benzenoid rings per molecule. Because of the previously described adsorption mechanism and the specific sizes of the cation sublattices, self-assembly is possible only for one specific row configuration where the benzenoid rings have to keep a distance of ~3.5 Å. The self-assembly is possible in NaCl for both cyano molecules, whereas in the Suzuki regions self-assembly is possible only for MonoCyano.

Our work is one of the first demonstrating that it is possible to characterize molecular surface phenomena in detail by a variation of polar substituents of a molecule and, at the same time, by varying the surface chemistry using a nanostructured insulating surface. Furthermore, it is a first-time comparison between experiment and DFT theory, which both explain the detailed mechanisms of self-assembly. In the future, our model could be benchmarked by using other surfaces like KBr(001) and LiF(001), which ionic lattices are much larger or smaller, respectively. We expect that varying the ionic lattice will have a large impact on the adsorption and, in turn, on the selfassembly of the molecules.

Our work supports the perspective that a general model for predicting, for example, helicene adsorption, and self-assembly can be created and used to tailor molecular films with specific properties on ionic surfaces. For instance, helicene molecules could be functionalized with three substitutents, which meet the charge matching criteria so that they bind more selectively the whole molecule in a flat and stable position. Such flat molecular templates can then be used for chiral recognition and templating of other molecules or even metal clusters. In a second step, chiral surfaces could be constructed and studied with enantiopure helicenes, which do not racemize at room temperature. A selective molecular adsorption with an impact onto self-assembly and chirality will help in the design of future molecular sensors and devices based on surface discrimination.

ASSOCIATED CONTENT

Supporting Information

Details of the synthesis of molecules, preparation of sample surfaces, deposition of the helicene molecules, numerical simulations, AFM/KPFM scanning parameters, and supporting experiments.

This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: barth@cinam.univ-mrs.fr. Phone: +33(0) 6.60.36.28.19.

Present Address

[§]R.P.: Institut Charles Gerhardt de Montpellier, UMR CNRS 5253, ENSCM-AM2N, 8, rue de l'école normale, 34296 Montpellier Cedex 05, France.

Notes

The authors declare no competing financial interest.

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