Predicting the influence of a *p2*-symmetric substrate on molecular self-organization with an interaction-site model†

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An interaction-site model can *a priori* predict molecular self-organisation on a new substrate in Monte Carlo simulations. This is experimentally confirmed with scanning tunnelling microscopy on Fréchet dendrons of a pentacontane template. Local and global ordering motifs, inclusion molecules and a rotated unit cell are correctly predicted.

Self-organization of supramolecular monolayers constitutes a major challenge for surface functionalization, sensors, catalysis, and molecular electronic devices.[1] The difficulty has been neatly summarized recently by Tomba *et al.*[2] who state "[…] the increasing complexity of the assembly units used makes it generally more difficult to control the supramolecular organization and *predict* the assembling mechanisms." Various approaches,[3] *via* synthetic routes, atomistic modelling or coarse-grained Monte-Carlo methods, have been adopted to predict patterns in a particular experiment. The ultimate goal is a generalized model, which can be fitted to individual experimental circumstances *e.g.* molecules, conformations, substrates, solvents while retaining its predictive power. Based on an interaction-site model, developed in a multi-modelling approach, we recently found with Monte-Carlo simulations that geometry as well as a few salient weak interaction-sites encode a large variety of structural motifs of a particular molecular conformation on a graphite substrate.[4]

In this communication, we demonstrate the versatility of interaction site models by predicting patterns on a new substrate with Monte Carlo simulations prior to measurements. Fréchet dendrons[5] exhibit a wide range of self-organized ordering motifs on highly oriented pyrolytic graphite (HOPG).[4] By employing pentacontane modified HOPG, we change the substrate's symmetry, lattice constant and adsorption energy. This serves

as an intricate test for the applicability of the recently introduced interaction-site model[4] to a wider variety of experimental systems. New simulations have been performed on a rectangular lattice and successfully compared with scanning tunnelling microscopy (STM) images of Fréchet dendrons, growing on top of a pentacontane monolayer. Hence, we corroborate the predictive power of interaction site models for molecular self-organization. In particular, we highlight the importance of substrate symmetry on pattern formation.

The Fréchet dendron[6] methyl (3-[3,5-bis(dodecyloxyphenyl)-methoxy]-5-[3,5-bis(octyloxyphenyl)methoxy]benzoate) displays seven different ordering motifs on HOPG.[4] This second generation Fréchet dendron consists of three benzene rings, two of which carry flexible alkoxychains[6] which interact with the surface and drive the molecular self-organization *via* chain inter-digitation,[7] see Fig. 1c. A variety of ordering motifs is expected,
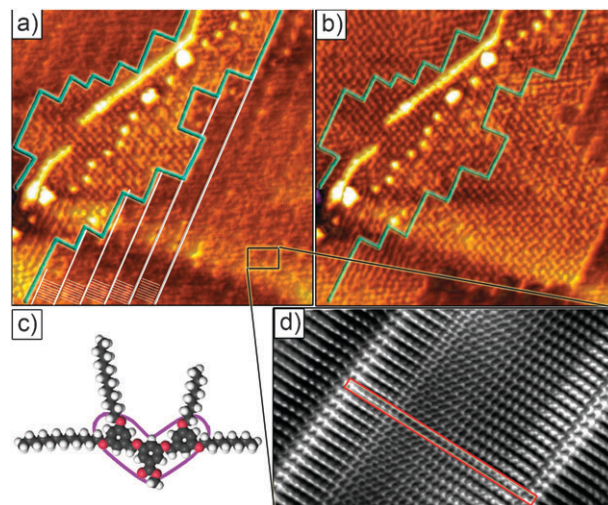

Fig. 1 Self-organized Fréchet dendron domains on top of a pentacontane monolayer: the upper STM images display the domain growth over time. (a) Rows of pentacontane are indicated in white, Fréchet dendron domain borders in green. The green outline of the Fréchet dendron domain follows the pentacontane rows. (b) Subsequent STM¶ image of the same spot. The distinct HOPG surface defects serve as recognition markers. The domain size from the left image is outlined in green. This indicates that the Fréchet dendron domains grow on top of pentacontane. (c) Space filling structure of the Fréchet dendrons with outlined molecular core. (d) High resolution image of a pentacontane monolayer on HOPG. The row like structure changes the HOPG surface from a sixfold to a twofold symmetry. Parameters: (a), (b) $U_{Bias} = -400$ mV, $|I_T| = 0.5$ pA, 80 nm × 80 nm; (d) $U_{Bias} = -150$ mV, $|I_T| = 30$ pA, 10 nm × 6 nm.

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when these Fréchet dendrons organize on the new pentacontane modified HOPG substrate. The feasibility of modifying substrates with pentacontane was successfully introduced by Bai and Fichou et al.,[8] allowing us to change the surface symmetry to p2 and the lattice constants to (x = 0.4 nm, y = 0.3 nm).

Pentacontane was dissolved in tetradecane before applying a droplet onto the HOPG surface and raising the substrate temperature to 50 °C to evaporate the tetradecane. The Fréchet dendrons were applied from 0.2 mM solution in phenyloctane or ethanol. We have performed high-resolution STM imaging under ambient conditions employing a Nanoscope Multimode III equipped with a low-current converter.

In the STM images (see Fig. 1a and b) the uncovered row structure of pentacontane is visible, emphasized by white lines. A high-resolution close-up reveals the ladder-like pentacontane pattern with a unit cell of 6.5 nm × 0.4 nm in atomic resolution, see Fig. 1d. On pentacontane monolayers Fréchet dendrons self-organize in domains, encased in green in Fig. 1a. These domains precisely follow the row structure of the pentacontane substrate. We use the distinct bright HOPG defect features as position markers. A follow-up image of the same location has been taken, see Fig. 1b: the domain size indicated by the green borders shows that Fréchet dendrons domains grow on the pentacontane monolayer.

Two ordering motifs of self-organized Fréchet dendrons, "jigsaw" and "tiretrack", are identified on pentacontane. These domains grow and show Ostwald ripening over minutes to hours. An extended domain of a p2 symmetric "jigsaw" pattern is shown in Fig. 2a adjacent to rows of unoccupied pentacontane (indicated by white lines). In the "jigsaw" ordering two molecules arrange in a tip-on-tip geometry in a nearly rectangular unit cell, see inset Fig. 2a. This ordering motif is also found on HOPG.[4] The unit cell a = 3.2 nm, b = 2.6 nm, α = 86° is tilted with respect to the pentacontane rows and features an additional bright protrusion in the middle of four adjacent molecules. This might be an included molecule, which partially fits into the provided host cavity. On HOPG yet another pattern, referred to as "tiretrack",
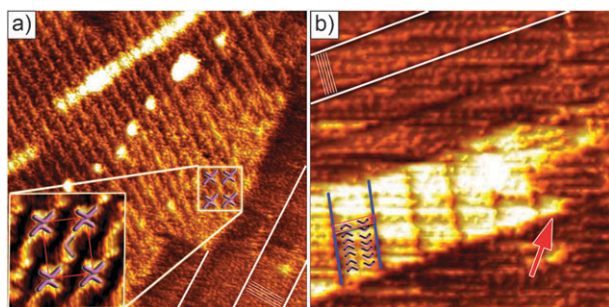
emerges.[4] There Fréchet dendrons interdigitate in a p2 symmetric double-row ordering. Such Fréchet "tiretrack" rows (blue lines) are found to run roughly perpendicularly to the pentacontane rows (white lines), as indicated in Fig. 2b. The unit cell parameters are a = 6.0 nm, b = 1.0 nm, α = 87°. The unit cells of all patterns show no measurable difference to HOPG within the error. The width of the Fréchet dendrons double-rows amounts to 6.0 nm which is close to the width of pentacontane rows (6.5 nm). Nevertheless, an easy identification is possible, since single Fréchet dendrons, measuring half the width of a double-row, accompany the regular double-row structure (marked with a red arrow in Fig. 2b). A third ordering motif, the "wave" patterns, resembles a similar pattern found on HOPG, the wave pattern.[4] This rarely occurring pattern is displayed in the ESI.† In summary, Fréchet dendrons grow on a pentacontane monolayer exhibiting twofold symmetry in two (three) ordering motifs, all with a p2 symmetric unit cell.

Prior to the STM measurements, we have predicted ordering motifs on a p2-symmetric lattice by independent Monte Carlo (MC) simulations. Based on a coarse-grained interaction-site model[4] the essential geometric features of the molecule and the substrate are condensed without including every chemical detail. The patterns discussed in this communication are obtained for two different pairs of internal angles (see Fig. 3e): conformer ε, 60° and 120°, conformer ζ, 60° and 180°, for long and short pairs of alkoxy chains. More chain angles on a hexagonal substrate are described elsewhere.[9] Here a new lattice is implemented in this interaction site model. The twofold symmetric substrate is realized via (a) model molecules arranged on a rectangular lattice and via allowing (b) four possible orientations of each model molecule.

Fig. 2 Ordering motifs of Fréchet dendrons on pentacontane imaged by STM. (a) "Jigsaw" domain: the pentacontane rows are indicated in white. The black rectangle marks a 6 nm × 6 nm sized area. The inset in the lower left corner shows a high resolution image. Molecular backbones are overlaid and a unit cell is marked in red. (b) "Tiretrack" domain: again, pentacontane rows are marked in white. Fréchet dendron "tiretrack" rows are indicated in blue with a unit cell in red. The schematic representation of the molecular backbones illustrates the ordering.[4] The red arrow marks half a double-row of Fréchet dendrons (discussion see text). Parameters: (a) U_{Bias} = −400 mV, $|I_T|$ = 0.5/1 pA, 50 nm × 50 nm/6 nm × 6 nm; (b) U_{Bias} = −1000 mV, $|I_T|$ = 8 pA, 50 nm × 50 nm.
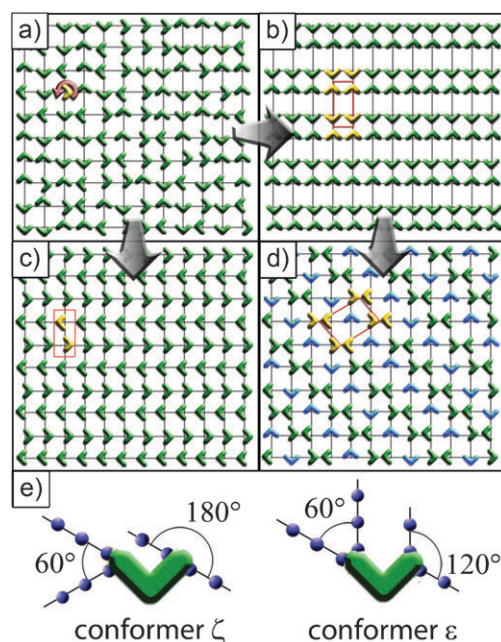

Fig. 3 Pattern prediction based on MC simulations of an interaction-site model. (a) Random starting configuration. The individual model molecules can rotate in fixed π/2 angles in a Monte-Carlo step. Slow cooling predicts the following patterns: (b) "jigsaw" and (d) "jigsaw with inclusion" for the chain configuration ε and: (c) "tiretrack" for the chain configuration ζ (two other patterns are displayed in the ESI†). (e) Detailed view of the chain configurations ζ and ε.

The MC simulations have been performed by preparing random starting configurations (see Fig. 3a) and slowly "cooling" them. The aspect ratio of the two lattice constants is held at a value of 7/8, which approximately reflects reaching equivalent positions perpendicular and along pentacontane rows. In a Monte Carlo step, $\pi/2$-rotations are possible on each lattice site. Allowing only π rotations would limit the freedom of orientations and would hence possibly restrict the so found patterns. The lattice constant a (and $b = 8/7a$) has been varied between $2.8a/\sigma$ and $4.2a/\sigma$, corresponding to a change in coverage density by a factor of 1.5, while the dimensionless inverse temperature $\varepsilon/k_B T$ ranges from 0.025 to 6. All simulated patterns proved stable in the simulations up to 300 °C and are therefore considered to be stable at room temperature.

Fig. 3 displays three of the five found patterns for the conformers ε and ζ. Conformer ε: the first ordering exhibits dimeric units in a $p2$ symmetric tip-on-tip arrangement (for $3.8a/\sigma$), see Fig. 3b. Such a tip-on-tip arrangement matches the experimentally found "jigsaw" pattern (see Fig. 2a). When the lattice constant is increased ($4.0a/\sigma$) an "interlaced jigsaw" structure can be observed with inclusions of one model molecule per unit cell in non-fixed orientation, see Fig. 3d. The unit cell is then rotated with respect to the lattice axis, for another "interlaced jigsaw" pattern see ESI.† Conformer ζ: a $p2$ symmetric double-row pattern is found, comparable to the experimental "tiretrack" pattern ($3.8a/\sigma$), see Fig. 3c. (For this conformer an interlaced double-row structure can be obtained for a few other a/σ, see ESI.†) In the double-row pattern the third experimentally discovered pattern, "wave", is also encoded (again, see ESI†). Hence, the predicted patterns reflect the local and global symmetry of the experimentally identified ordering motifs as well as the interlacing with non-fixed molecules.

Fréchet dendrons on pentacontane molecules have a reduced adsorption energy (80.3 kJ mol^{-1} nm^{-2}) compared to Fréchet dendrons on HOPG (167.1 kJ mol^{-1} nm^{-2}), which we calculated using molecular mechanics (MM)‖ in Material Studio.[10] This reduced adsorption energy leads to a high orientational freedom ($\pi/2$ rotations instead of π-rotations) on the lattice sites. The experimentally observed inclusions in the "jigsaw" pattern can only be obtained in simulations when $\pi/2$ rotations are allowed.

The prediction of local molecular arrangements by the interaction-site model in its detail goes beyond considerations feasible by group theory. Nevertheless let us comment on the influence of a lower symmetric substrate for molecular self-organization. The symmetry groups of a twofold symmetric substrate are included in four-fold, $e.g.$ Cu(100), or six-fold symmetric substrates, $e.g.$ HOPG. Therefore, ordering motifs found on twofold surfaces can be expected to occur also on $e.g.$ six-fold symmetric surfaces. The "tiretrack", "wave", and "jigsaw" ordering motifs observed on pentacontane are also found on the six-fold HOPG surface. Yet on HOPG two more hierarchical flat lying patterns are recognized exhibiting molecules with $\pi/3$ orientations relative to each other.[4] Strong molecule–surface interactions can constrain the molecular orientation along the symmetry axis of the substrate; hence, $\pi/3$ symmetric patterns are omitted on pentacontane. This underlines that the substrate, despite reduced adsorption energy, has a big influence and that substrates symmetry dictates molecular ordering.

In conclusion, we gain $a priori$ predictability of ordering motifs of Fréchet dendrons on a new substrate. We have generalized the interaction-site approach to the most general surface symmetry ($p2$). The general applicability has been successfully demonstrated in a template experiment. Additionally, we find that a $p2$ symmetric substrate selects a subset of $p2$ symmetric patterns from a larger pattern variety observed on higher-symmetry substrates. Hence, substrate symmetry constrains the allowed ordering motifs. Prediction of ordering motifs on new substrates, prior to experimental observation, will not only greatly ease future surface functionalization, in particular of layered assemblies (3D), but also allow application directed chemical synthesis.

Notes and references

¶ All images are flattened, drift-corrected. Fig. 1d and the inset of Fig. 2a are correlation averaged. The color scale ranges from dark brown, over light brown, yellow to white.

‖ Molecular mechanics is performed with the Forcite module of Materials Studio 4.4 employing a universal force field. Energy calculations were performed on the "jigsaw" pattern.

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