

Two-dimensional structures composed of cross-shaped molecules adsorbed on solid surfaces – a computational model

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The ability of simple molecular building blocks to form extended ordered patterns by adsorption and self-assembly on solid substrates is an advantageous property that has been widely used to create nanostructured surfaces. In this contribution we demonstrate how the lattice Monte Carlo simulation method can be used to predict morphology of adsorbed overlayers comprising simple functional cross-shaped molecules resembling phthalocyanines and porphyrins. In particular, we focus on the influence of the distribution of active interaction centers within a model cross-shaped molecule on the structure of the resulting molecular networks. Additionally, we investigate how using racemic mixtures of input prochiral molecules affects the chirality and porosity of the corresponding ordered patterns. The obtained results show that suitable manipulation of the chemistry of cross-shaped building block allows for the controlled creation of largely diversified molecular porous networks.

Keywords: adsorption, self-assembly, computer simulations, porous overlayers.

1. INTRODUCTION

Designing two-dimensional porous networks by controlled self-assembly of organic molecules on solid substrates is a quickly developing area which links individual characteristics of molecular building blocks and physico-chemical properties of the resulting 2D porous material. Most experimental results related to bottom-up synthesis of such materials are based on the self-assembly on graphite or metal surfaces in ultra-high vacuum conditions and from liquid phase. It has been shown that self-assembled porous networks can be sustained not only by directional hydrogen bonds [1-4] and metal-organic coordination bonds [5-7] but also via van der Waals interactions, for example by interdigitation of long alkyl chains of the adsorbed, star-shaped molecules, such as alkyl-substituted phthalocyanines [8], dehydrobenzoannulenes (DBAs) [9,10] and stilbenoid compounds [11]. The advantageous feature of nanoporous networks is the presence of nanometer-sized cavities with uniform well-defined shape [12,13], which can be filled by foreign molecules, e.g. thiols, coronenes and fullerenes [14-16], having required chemical, biological, magnetic or optical properties. Moreover, tuning of chemistry and geometry of such building bricks allows for custom fabrication of 2D nanomaterials for adsorption, separation and catalytic processes.

Controlling and directing the on-surface patterning requires the optimal choice of shape and functionality of the building block. However, it appears that the structure of the porous networks depends mostly on the geometry and distribution of interaction centers in the input-molecule and not on its specific chemistry, limiting the number of necessary parameters needed to describe such systems. In consequence, the self-assembly can be effectively predicted by theoretical modeling. Among computational methods, Monte Carlo lattice approach seems to be the most effective, allowing for investigation of system with large number of molecules under variable conditions, where the geometry of building blocks as well as interactions can be described with relatively low number of adjustable parameters [17-26]. This simple coarse-grained MC model was recently used by us to explore the effect of aspect ratio and relative position of molecular arms in cross-shaped molecules [25] and the role of the number and position of the interaction centers on the morphology of the corresponding 2D assemblies. In this contribution we use the adopted approach to investigate the effect of intramolecular distribution of active centers in an asymmetric building block on the superstructures formation

in adsorbed overlayers. In particular, we explore the self-assembly of racemic mixtures of prochiral molecules with no symmetry elements in which three interaction centers were activated.

2. THE MODEL AND SIMULATIONS

The self-assembling molecules were modeled as flat, rigid structures composed of identical discrete segments, each of which occupies one site on a square lattice. Selected segments were activated to represent different intramolecular distribution of the active centers. The interactions between the activated segments were described by a short range segment-segment interaction potential limited to nearest neighbors on a square lattice and characterized by $\varepsilon = -1$ expressed in kT units [25, 26]. Fig. 1. shows an exemplary molecule on the lattice with the corresponding interactions. In all simulations we used a square $L \times L$ lattice with $L = 200$ representing the underlying surface. Periodic boundary conditions in both planar directions were imposed to eliminate edge effects. To simulate the on-surface self-assembly we use the Monte Carlo method in canonical ensemble with orientationally biased sampling [26]. The simulation algorithm can be described in the following way. At the beginning of the simulation N molecules of the same type (or $2 \times N/2$ in case of racemic mixtures) were randomly distributed over the surface. Next, up to 10^6 MC steps were performed, with the MC step being defined as an attempt to move and rotate each of the molecules in the system. Each trial to change the configuration began with a random choice of a molecule and the associated displacement. Then, by rotating the molecule around its central segment, four trial orientations $\{b_{n1}, b_{n2}, b_{n3}, b_{n4}\}$ in the new position were generated. By summing up the interactions between the active segments of the selected molecule and neighboring molecules, the potential energy in each trial orientation $U(b_{ni})$, for $I = 1, 2, 3, 4$ was calculated. Then, the Rosenbluth factor in the new position $W(n)$, was determined as:

$$W(n) = \sum_{j=1}^4 \exp[-\beta U(b_{nj})] \quad (1)$$

where $\beta = kT$, k is the Boltzmann factor and T is temperature. Out of these four orientations one, denoted b_{nk} , was selected with a probability:

$$p(b_{nk}) = \exp[-\beta U(b_{nk})] / \sum_{j=1}^4 \exp[-\beta U(b_{nj})] \quad (2)$$

The same procedure was repeated for the old position, by generating three trial orientations $\{b_{o2}, b_{o3}, b_{o4}\}$ and calculating the corresponding potential energies $U(b_{oi})$, for $i = 2, 3, 4$. The Rosenbluth factor in the old position was given as:

$$W(o) = \exp[-\beta U(b_{o1})] + \sum_{j=2}^4 \exp[-\beta U(b_{oj})] \quad (3)$$

where b_{o1} refers to the initial orientation of the molecule.

To decide if the move was successful, the transition probability P was calculated:

$$P = \min(1, W(n)/W(o)) \quad (4)$$

and compared with a random number $r \in (0,1)$. If $r < p$ the move was accepted and otherwise the molecule was left in the original position. Additionally, we used the annealing procedure [27], slowly cooling the overlayer from $T = 1$ to target temperature $T = 0.1$, minimizing the risk of trapping the system in metastable states. In all of the simulations, the number of molecules correspond to submonolayer coverage, allowing for unrestricted development of ordered domains.

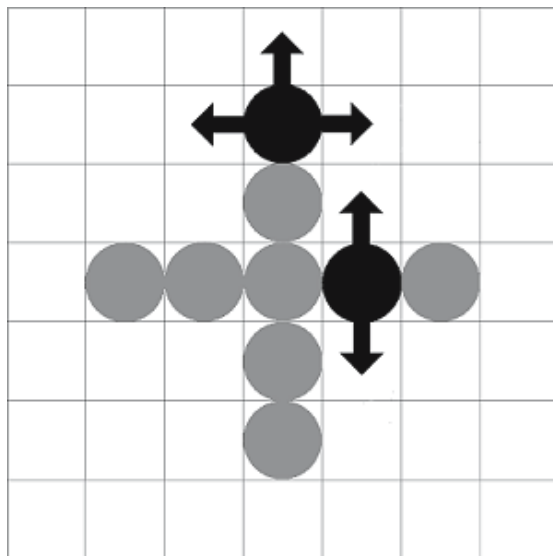


Fig. 1. Schematic drawing of the model molecule adsorbed on a square lattice. The active segments are shown in black. The arrows indicate directions and range of intermolecular interactions allowed in the model.

3. RESULTS AND DISCUSSION

To explore how the distribution of active segments in the input molecule affects the pattern formation, we consider a few selected simple cases. In particular, we focus on racemic mixtures of prochiral molecules. Two shapes of building blocks were taken into account, which were obtained by elongating one arm or two orthogonal arms of the parent C_4 molecule. In addition, selected molecular segments were activated. To explore pattern formation in the racemic mixtures we used four types of molecules, (presented in Fig. 2.) and their opposite enantiomers (not shown).

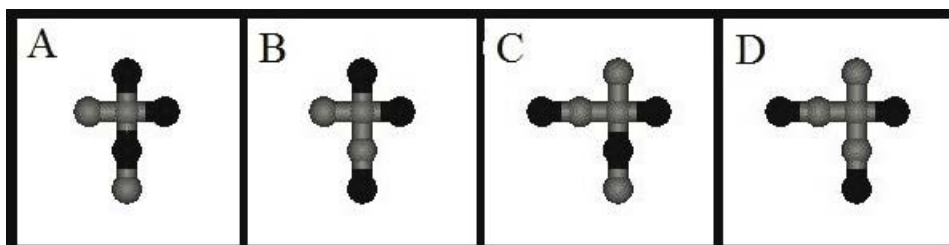


Fig. 2. Types of molecules used in the simulations. Only one enantiomer of each structure is shown. Black segments correspond to the interaction centers.

Let us first discuss the structures simulated for the molecules with one longer arm. Fig. 3. shows the results obtained for the molecule of type A. The interaction centers in this building block are located on two orthogonal short arms and on the middle segment of the longer arm of the molecule. The performed calculations show that such an arrangement leads to the formation of small dispersed clusters, randomly distributed over the surface and comprising four molecules each, as can be seen in Fig. 3a. Because the described molecule is chiral in 2D, it is possible to simulate phase behavior of the racemic mixture. In this case, mirror images of the clusters observed previously are present on the surface (Fig. 3b) and the introduction of the other enantiomer does not induce substantial changes in the morphology.

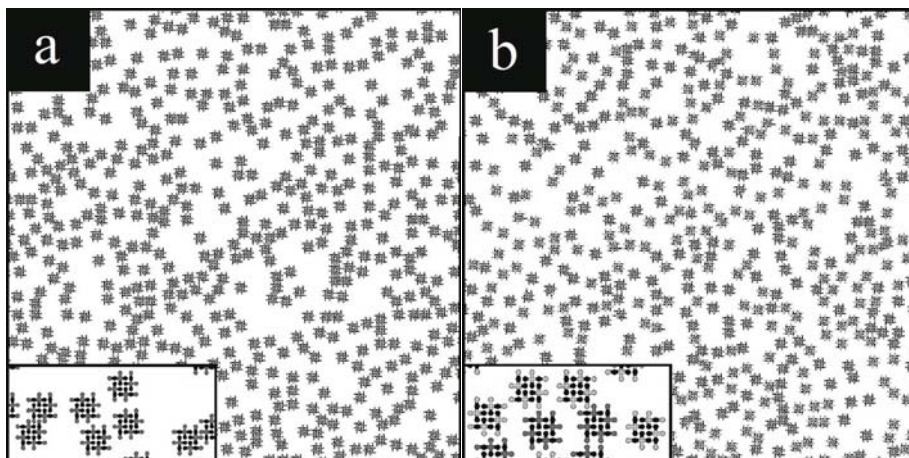


Fig. 3. Adsorbed structures formed by a) 2134 molecules of type A b) 2134 molecules of molecules A and their mirror images (racemic mixture). The insets show magnified fragments of the simulated snapshots. Black segments represent the active centers.

The molecular building-block denoted by **B** differs from molecule **A** only in the position of the activated segment in the longer arm. Namely, now this segment is moved to the terminal position of the longer arm. Fig. 4. presents the pattern formed by the molecules of **B**.

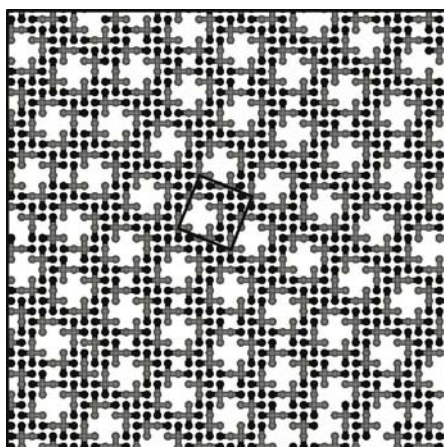


Fig. 4. Magnified fragment of the porous phase observed in the simulations performed for 2134 molecules of type B. The solid black line delimits the corresponding unit cell.

The molecules of **B** form an extended, periodic pattern, composed of a large number of interlocked subdomains characterized by square $\sqrt{29} \times \sqrt{29}$ unit cell. Moreover, we can observe cross-shaped nanocavities in the structure, as well as, smaller unitary pores surrounded by four active segments.

We also investigated the patterns formed by the molecules with two orthogonal longer arms and mixed racemic structures comprising these molecules. A molecule of type **C** has three active centers located on the ends of two collinear arms (one- and two-membered) and one center on the segment close to the core of the other two-membered arm. Fig. 5. presents the results of the simulations carried out for molecule **C** and for the corresponding racemic mixture.

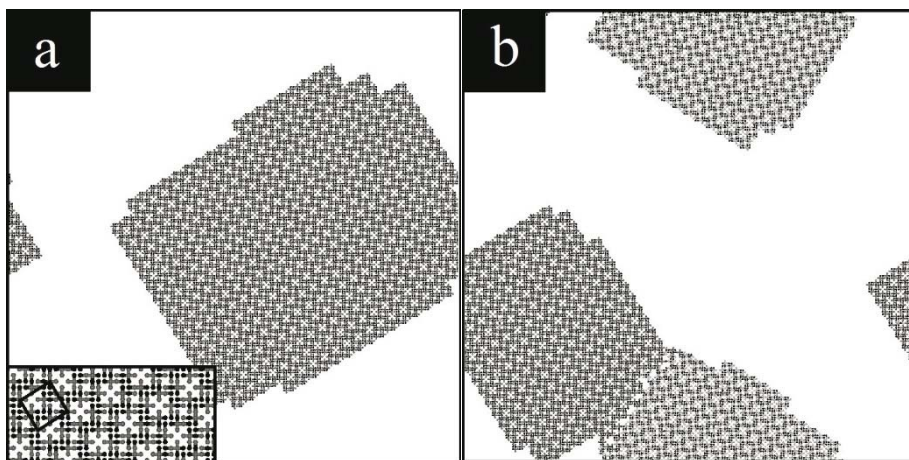


Fig. 5. Ordered chiral patterns formed by a) 1828 molecules of type **C**; b) corresponding racemic mixture of enantiomers. The inset shows magnified part of the structure. The unit cell is delimited by the black lines.

The arrangement of interaction centers in molecule **C** promotes the formation of ideally periodic, chiral domains with complex structure comprising five pores of unitary area (i.e. one lattice site) per $\sqrt{34} \times \sqrt{34}$ square unit cell. In the case of the corresponding racemic mixture, we can observe the chiral resolution of enantiomers into two equally large domains, one being mirror image of the other. This situation changes significantly when all of the three active segments occupy terminal positions in the molecular building brick, forming the molecule of type **D**.

In this last example, shown in Fig. 6., the presence of a single enantiomer in the system leads to the creation of one large homochiral domain, characterized by parallelogram $\sqrt{26} \times \sqrt{10}$ unit cell. Although this behavior is similar to that observed already for **C**, the self-assembly of the corresponding racemic mixture results in the formation of a mixed crystal with $\sqrt{101} \times \sqrt{34}$ unit cell. Moreover, the mixed molecular network of **D** comprises three kinds of cavities: 1×1 , 1×2 , and S-shaped ones, versus only one type (2×2) observed for the enantiopure structure from Fig. 6a. Apparently, these results demonstrate how the small change in the functionality of the building block can result in a substantial difference in the morphology of the self-assembled networks.

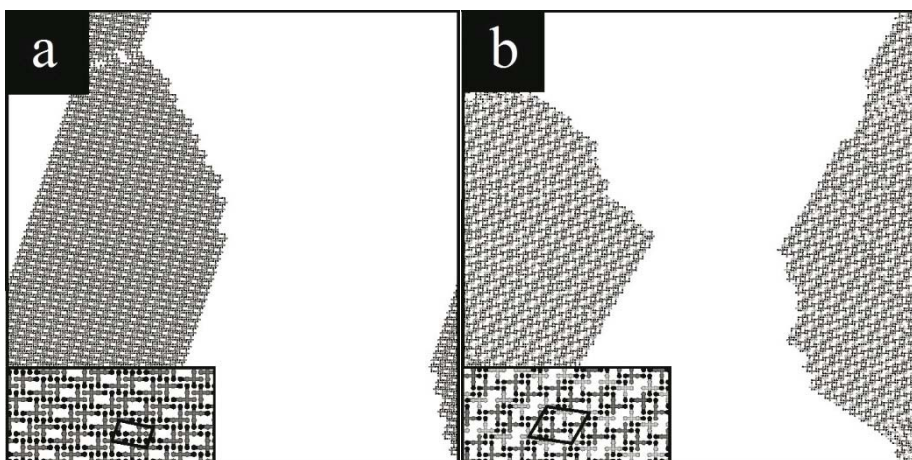


Fig. 6. Porous molecular networks formed by 1828 molecules of type D a) and by the molecules of the corresponding racemate b). The insets show magnified parts of the structures, while the solid black lines delimit the unit cells.

4. CONCLUSIONS

The results presented in this contribution show that the simple lattice MC model can be helpful in finding the relation between the intramolecular distribution of active centers in the cross-shaped input molecule and the architecture of the resulting adsorbed structures. In particular it is demonstrated how by using racemic mixtures of functional building blocks it is possible to direct the self-assembly towards separated chiral porous networks or mixed surface crystals with diversified pore

structure. The findings reported in this work can be used for designing surface overlayers sustained by intermolecular interactions between cross-shaped building blocks resembling derivatized porphyrins or phthalocyanines. The proposed methodology can reduce the number of necessary test syntheses needed to obtain the optimal building molecule.

5. ACKNOWLEDGMENT

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