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Structure and stability of 2D molecular networks comprising asymmetric cross-shaped molecular building blocks

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Abstract

We use the Monte Carlo simulation method to study the self-assembly of model cross-shaped molecules adsorbed on a square lattice. The molecules were assumed to consist of discrete segments arranged in a rigid planar structure having a central part called core and four arms attached to it. The calculations were performed for the selected cross-shaped molecules equipped with arms of adjustable length. The main purpose of our study was to examine how the changes in molecular shape can affect the structure formation in the adsorbed overlayer. For these building blocks we studied the effect of temperature and surface density on the morphology and stability of the self-assembled networks. The obtained results indicated clearly that a suitable modification of the molecular geometry can be used to create 2D self-assembled nanoporous grids with programmable architecture.

Introduction

Functional organic molecules with ramified structure are promising candidates for nanopatterning of solid surfaces via controlled adsorption either from gas of liquid phase. The bottom-up approach based on the self-assembly of these building blocks on such substrates as graphite[1,2] and metallic crystals [3,4] allows for fine tuning of the resulting two-dimensional architectures by suitable manipulation of size, shape and functionality of the molecular bricks at play. To date numerous organic molecules, including dehydrobenzo[12]annulenes (DBAs) derivatives [5,6], stilbenoid compounds [7,8], alkyl-substituted phthalocyanines[9], trimesic acid [10,11] and larger tricarboxylic acids [12] have been used to construct ordered patterns with adjustable geometric features. An unique property of the branched star-shaped molecules is that they can easily self-assembly into porous networks with regular nanometer-sized cavities having for example square[9] and hexagonal [5-8,10-12] shape. Occurrence of this process is largely facilitated by the long molecular arms and/or specific directional interactions which prevent close packing of the adsorbed molecules, so that an open porous structure can be formed. The resulting networks are typically stabilized by hydrogen bonds [10-12], metal-ligand coordination [13] or van der Waals interactions [5-9] and in many cases they are readily observable at room temperatures by means of scanning tunneling microscopy (STM). A distinct advantage of the porous networks, which make them of special interest to nanoscience, is that the nanocavities can be filled with foreign matter having desired physico-chemical and biological properties, including specific magnetic, optical or catalytic activity etc.. Achieving control over architecture and composition of such functional matrices opens up a way to fabricate novel materials for separation and catalytic purposes, molecular sensing and light harvesting [14-15].

The most prevalent star-shaped building blocks used for the creation of 2D porous networks from liquid phase and in ultra high vacuum (UHV) conditions are those having C_3 (tripod-shaped) and C_4 (cross-shaped) symmetry axis. In the case of the networks sustained by van der Waals interactions, the building molecules usually consist of flat core substituted with alkyl chains of different length [5-9]. Interdigitation of the long alkyl chains (molecular arms) leads to a highly ordered chiral superstructure. To model the self assembly of such symmetric building blocks we have recently proposed a coarse grained Monte Carlo model which revealed to be able to predict correctly pattern formation in adsorbed overlayers comprising molecules of DBA [16-19] and phthalocyanines [19,20]. Moreover, the proposed approach allowed us to identify basic structural parameters of the assemblies comprising asymmetric tripod- and cross-shaped molecular bricks. In this work we extend our studies and use the Monte Carlo method to explore the effect of adsorbate density and temperature on the morphology of the corresponding molecular networks.

1. Theoretical modeling

In the proposed model the cross-shaped molecules were assumed to be flat, rigid and composed of identical discrete segments, each of which occupies one site on a square lattice. Figure 1 shows schematically three selected molecular structures used in the simulations.

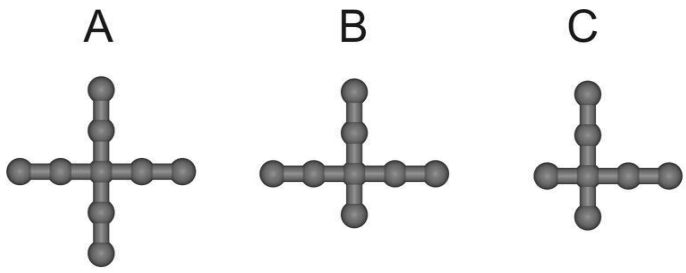

Figure 1. Schematic view of the cross-shaped molecules used in the simulations.

As seen in Fig. 1, molecule **A** is a C_4-symmetric structure with two-membered arms. The two additional molecules **B** and **C** can be treated as reduced versions of **A**, in which one arm (**B**) and two neighboring arms (**C**) were trimmed by one segment. The main purpose of choosing these additional structures was to examine how the change of symmetry of **A** affects structure formation in the corresponding molecular assemblies. The adsorbed molecules were assumed to interact via a short-ranged segment-segment interaction potential limited to nearest-neighbors on a square lattice (i.e. up, down, left, right). In all cases, the energy of interaction between a pair of segments was characterized by the parameter ε expressed in kT units. For the sake of convenience we assumed that both k and T are dimensionless.

The simulations were performed on a square 200 by 200 lattice of equivalent adsorption sites using the conventional canonical ensemble Monte Carlo method with

Metropolis sampling[19,20]. To eliminate edge effects periodic boundary conditions in both planar directions were imposed. At the initial step of the simulation a starting configuration was created by randomly distributing N molecules over the surface. Next, a molecule was selected at random and an attempt was made to move the molecule to a new position. To that end the potential energy of the molecule in the actual configuration, U_{old} was calculated by summing up segment-segment interactions between the selected molecule and neighboring molecules. To move the molecule over the surface a cluster of adsorption sites matching the shape of the molecule was chosen randomly. If none of the selected cluster sites was occupied the interaction energy in the new configuration U_{new} was calculated using the same procedure as for U_{old}. To decide if the move was successful the transition probability $p=\min\{1,\exp[-(U_{new}-U_{old})/kT]\}$ was calculated and compared with a randomly generated number $r \in (0,1)$. If $r<p$ the molecule was moved to the next position, otherwise it was left in the original one. The above sequence was repeated for each adsorbed molecule constituting one MC step. In all of the simulations described here we used up to 10^8 MC steps and assumed that $\varepsilon=-2$.

To examine and compare the effect of temperature on the stability of the self-assembled molecular structures formed by **A**, **B** and **C** we calculated also the associated heat capacities, C using the method based on the average fluctuation of the potential energy, E of the adsorbed phase [21]. To that end the following classical thermodynamic equality was used

$$C=\frac{1}{kT^2}(\langle E^2\rangle-\langle E\rangle^2) \qquad (2.1)$$

where: C-heat capacity,

E-potential energy of the adsorbed phase,

k-Boltzmann constant,

T-temperature.

and implemented in the simulation algorithm.

2. Results and Discussion

To study the influence of adsorbate density on the structure formation in the overlayers comprising **A**, **B** and **C** we performed the simulations in which 1500 and 2000 molecules of each type were adsorbed on the lattice. Figure 2 shows the equilibrium configurations obtained from the calculations.

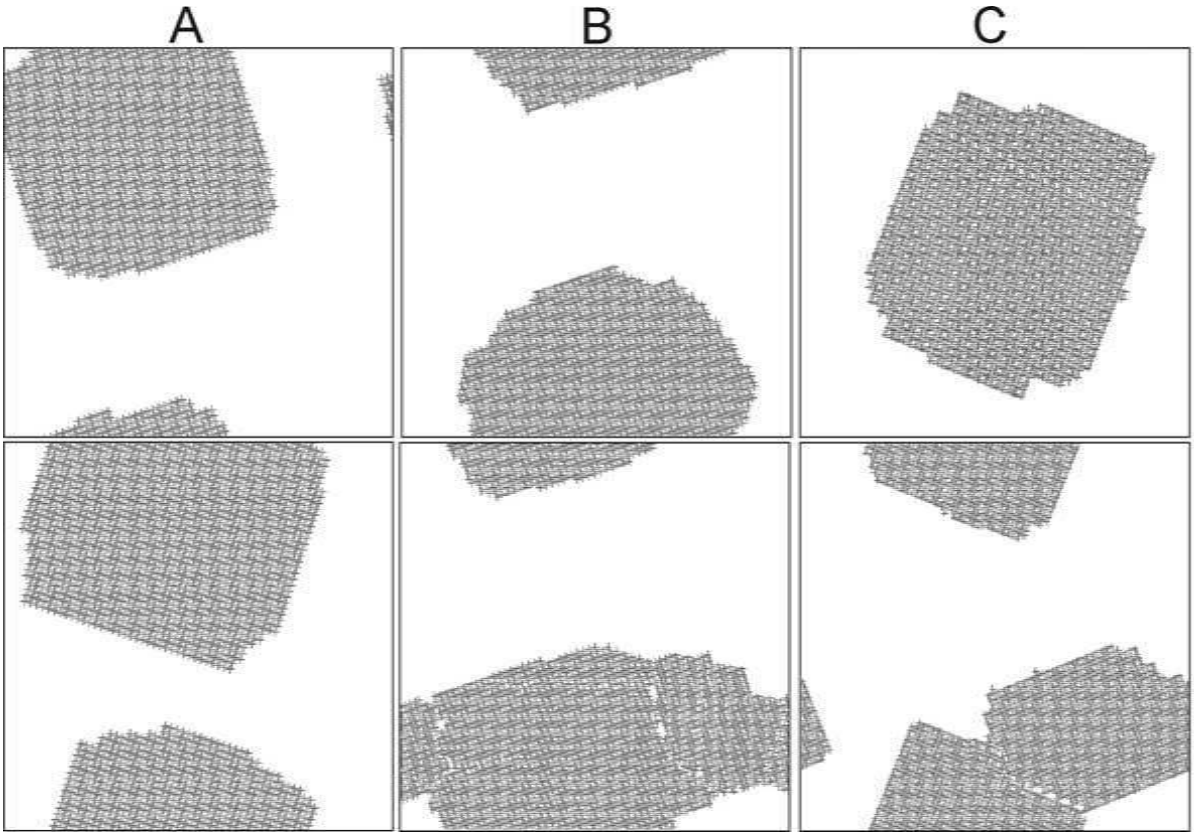

Figure 2. Snapshots of the adsorbed overlayer comprising 1500 (upper row) and 2000 (bottom row) molecules **A**-**C** adsorbed on the square 200 by 200 lattice. These results were obtained for ε=-2 and T=1.

As it follows from Fig.2, the considered molecules self-assembly into well-defined extended domains having mostly straight edges[20]. Although, the domains formed by molecules **A-C** look similar their internal structure is markedly different. To demonstrate this, in Fig. 3 we plotted magnified fragments of the corresponding ordered patterns from Fig.2.

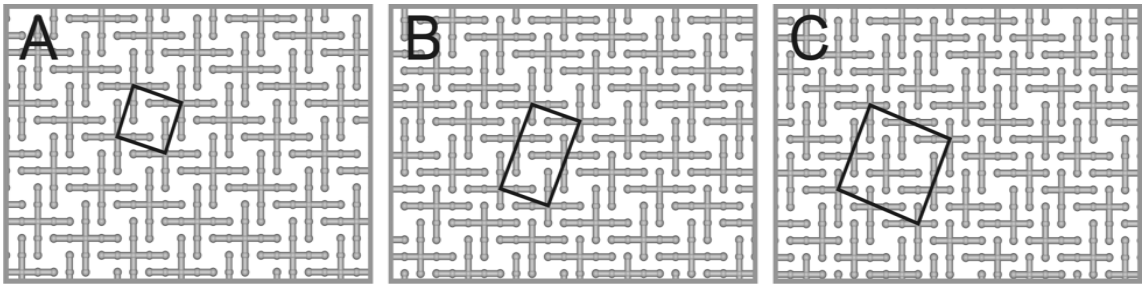

Figure 3. Magnified fragments of the ordered porous patterns formed by the molecules **A**-**C** adsorbed on the square lattice. The black solid lines delimit the corresponding unit cells.

This figure highlights structural details by which the adsorbed patterns comprising molecules of **A**, **B** and **C** differ form each other. A common feature of these porous grids is that they all contain cavities having size of one lattice site. However, depending on the assumed molecular geometry, the spatial distribution of the cavities within the overlayer is different. This effect can be easily seen in the local structure of the adsorbed phase that is shown in each unit cell (square for **A** and **C** and parallelogram for **B**). The resulting density of the simulated patterns, which we define as the fraction of occupied lattice sites within the unit cell is equal to 0.9, 0.96 and 0.97 for **A**, **B** and **C**, respectively. As the main structural parameters of the ordered assemblies form Fig. 3 were described elsewhere [20], in the following we focus on the energetic properties of the simulated structures. To calculate the potential energy of a single molecule of **A**, **B** and **C** in the corresponding pattern, U^* it is enough to sum up foreign segments adjacent to each segment of the selected molecule. The resulting number multiplied by 0.5ε gives the average potential energy of a single molecule within an infinite defect-free overlayer. The values of U^* obtained for **A**, **B** and **C** expressed in ε units are 8.8 and 7.5, respectively.

To compare relative thermodynamic stability of the patterns formed by molecules **A-C** we calculated the associated heat capacities as a function of temperature. For comparative purposes these simulations were performed at constant adsorbate density, that is at constant number of molecular segments adsorbed on the lattice. To achieve this, the number of molecules **A**(9 segments), **B**(8 segments) and **C**(7 segments) was adjusted to have 12096 and 16128 segments in total in each case which gives the density equal to 0.3 and 0.4 segment/lattice site, respectively. The appearance of a peak on the $C(T)$ plot indicates a structural transition in the adsorbed phase that is induced by changing temperature. The position of the peak maximum on the temperature axis allows for the estimation of the transition temperature at which the ordered pattern (**A**, **B** and **C**) melts and turns into 2D lattice gas. The higher the transition temperature, the more stable the pattern. Figure 4 presents the heat capacities calculated for the molecules **A-C**, at the density equal to 0.3 and 0.4.

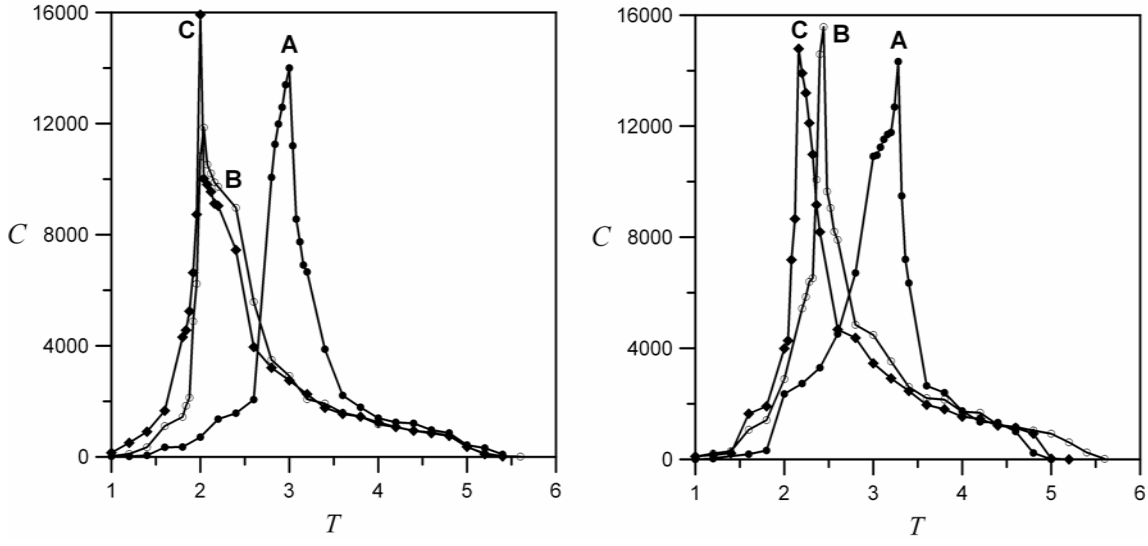

Figure 4. Heat capacities calculated for the molecules **A-C**, at the constant density equal to 0.3 (left) and 0.4 right segments/lattice site, for ε=-2.

The results plotted in Figure 4. were obtained in a single simulation run within the temperature interval 1.0-5.6 and they are rough estimates of the *C*(*T*) dependence for the explored systems. Nevertheless, basic qualitative information on the relative stability of the molecular networks **A**, **B** and **C** can be extracted from the simulated data. In particular, it can be observed that changing symmetry of molecule **A** by cutting its one or two arms by one segment shifts the heat capacity peak towards lower temperatures (**B**, **C**). This effect is visible for the adsorbate density equal to 0.3 as well as to 0.4 segments/lattice site. The approximate positions of the peak maxima corresponding to the lower and the higher density are: 3.0 (**A**) and 2.0 (**B**,**C**) for 0.3 and 3.30 (**A**), 2.47 (**B**) and 2.19 (**C**) for 0.4. The obtained results suggest that the 2D superstructure formed by molecules of **A** is more stable compared to those created by **B** and **C**. Moreover, the close position of the *C* peaks corresponding to **B** and **C** at both adsorbate densities indicates that the phase behavior of **B** and **C** is quite similar, but it is different form **A**. The preliminary results on the stability of the molecular networks reported in this contribution are the starting point for more detailed studies, in which the proposed methodology can be used to explore stability of adsorbed overlayers comprising cross-shaped molecules with altered aspect ratio and chemical composition.

3. Conclusions

The results of this work demonstrate that the formation of complex molecular patterns in adsorbed overlayers composed of such cross-shaped molecules as phthalocyanines and prorphyrins can be predicted and analyzed using the coarse-grained Monte Carlo modeling. The adopted approach allowed us to explore the effect of slight changes in the shape of the considered building blocks (arm elongation/shortening) on the morphology and stability of the corresponding self-assembled 2D structures. In particular, the obtained findings showed that the porosity and distribution of void spaces within the simulated porous networks can be controlled by fine tuning of the length of one or more arms of the building brick. Moreover, it was observed that the structural changes in the molecule affect stability of the patterns, as revealed by the shifts in the heat capacity curves calculated for A and for B and C. Our theoretical results can be helpful in custom designing porous molecular networks with selective (also chiral) adsorption and catalytic purposes.

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