Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Thermal stability of surface-confined assemblies comprising functional cross-shaped molecules: Insights from Monte Carlo modeling

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ARTICLE INFO

Article history:
Received 27 November 2015
Received in revised form 15 January 2016
Accepted 15 January 2016
Available online xxx

Keywords:
Self-assembly
Adsorption
Chiral porous networks
Monte Carlo simulations ;, Functional molecules

ABSTRACT

Self-assembly of star-shaped organic molecules on solid surfaces provides an effective approach to construct 2D functional nanostructures such as supramolecular networks with programmable architecture and functions. As it has been often observed experimentally, small changes in geometry and functionality of a building-block can directly influence the morphology and stability of the resulting two-dimensional molecular assemblies. In this contribution, we used the Monte Carlo simulation method in the Canonical Ensemble to explore the effect of shape and intramolecular distribution of interaction centers within a model cross-shaped building-block on the thermal stability of the resulting low-dimensional chiral structures. Specifically, for the cruciform molecular units we calculated heat capacities as a function of temperature and linked the position of the corresponding peak maxima with the structural parameters of the molecules. The obtained results indicate, that the heat capacities and the phase behaviour of the studied systems strongly depend on the properties of the building molecule, such as the number and position of interaction centers and molecular symmetry. The insights from this study can be helpful in designing molecular architectonics on solid surfaces, especially when building blocks such as porphyrins and phthalocyanines are at play.

1. Introduction

Recent progress in both manipulation of matter at the nanoscale and imaging of supramolecular assemblies opens up new ways to create ordered low-dimensional structures with tunable physico-chemical properties. One of such structures are the surface-confined molecular arrays formed spontaneously by building blocks with suitably encoded functions [1,2]. Among these molecular bricks star-shaped units have been long recognized as versatile material, especially in the creation of nanoprous 2D adsorbed overlayers, either in ultra high vacuum and at the liquid/solid interface. The beneficial ramified geometry of tripod- and cross-shaped molecular bricks often enables the formation of ordered superstructures with regular nanosized void spaces which can be filled with foreign matter to produce functional, also chiral, matrices [2]. Moreover, structure of such porous grids can be additionally modified by changes in external conditions such as temperature [3], type of solvent [4] and guest species [5]. These unique features make the self-assembling 2D porous networks highly attractive medium from the point of view of future application in nanotechnology, adsorption, catalysis and material science.

In most of experimental studies on the 2D self-assembly of porous networks C_3- and C_4-symmetric organic molecules have been used, including for example tricarboxylic acids [6], dehydrobenzoannulenes (DBAs) derivatives [7,8], alkyl-substituted phthalocyanines [9] and naphthalocyanine [10]. In these cases the formation of porous networks (often chiral) with hexagonal and square voids has been observed, respectively. However, much less attention has been given to asymmetric tripod- and cross-shaped building blocks. One example in this area has been the self-assembly of the asymmetric tripod-shaped DBA molecules equipped three arm alkyl chains of unequal length [11]. For this molecule, the deviation from the C_3-symmetry was found to be the source of polymorphism which led to the formation of two coexisting porous patterns with different symmetries. Very recently tricarboxylic acids with reduced symmetry have been also used to create diversified patterns at the organic solvent/graphite interface [12]. In the case of cross-shaped molecules, however, analogous studies have been, to the best of our knowledge, limited to derivatized porphyrins [13–15] and creation of extended arrays has been

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http://dx.doi.org/10.1016/j.apsusc.2016.01.140
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Please cite this article in press as: A. Kasperski, P. Szabelski, Thermal stability of surface-confined assemblies comprising functional cross-shaped molecules: Insights from Monte Carlo modeling, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.01.140

reported only for the asymmetric tectons with one longer arm [14,15].

One of central questions in designing 2D molecular architectures is how structural and constitutional modifications of the building block affect the resulting assembly. This information is particularly useful, as it enables reduction of time and resources needed to select the optimal molecule able to form the target superstructure. For example, some molecular geometries and intermolecular distributions of functional groups in a building block can stabilize certain ordered superstructures while others can prevent their formation. This refers, for instance, to thermal stability of porous networks whose application would require operating in ambient conditions. A useful route to determine the influence of molecular features on the properties of self-assembled structures is to perform computer simulations with the help of such methods as Monte Carlo and Molecular Dynamics. These techniques have been successfully applied to 2D assemblies comprising chemically different tripod-shaped molecules, both C_3-symmetric [16–19] and asymmetric [11]. In these cases, it was possible to predict accurately possible molecular patterns and determine conditions for their coexistence. Generalized statistical–mechanical models for the self-assembly of tripods have been also developed to describe phase behaviour of a wide class of molecules [20]. However, for cross-shaped molecules only a few computational studies on the 2D self-assembly have been carried out using MC and MD methods. These investigations have been devoted mainly to specific systems in which C_4-symmetric molecules such as phtalocyanines [21] and porphyrins served as building material [22–24]. Recently also a more general theoretical model has been proposed by Akimenko et al. who investigated small simplified C_4-symmetric tectons adsorbed on a square lattice [25]. However, systematic studies on the effect of molecular features on the morphology of the corresponding supramolecular patterns were first reported in our recent papers [26–30]. The obtained results demonstrated that the self-assembly of cruciform building blocks can be guided by a suitable manipulation of molecular geometry and composition to create largely diversified 2D architectures.

In this contribution we extend our investigations and study thermal stability of surface-confined assemblies built of cross-shaped units differing in size, aspect ratio and functionality. In particular we focus on the effect of temperature on the specific heat curves simulated for the investigated molecules. Our main objective is to identify the relation between intrinsic properties of the building block and transition temperature (specific heat maximum) at which the molecular units self-assemble to form ordered structures. This approach will help us understand how the building block can be modified to achieve persistent periodic assemblies characterized by the highest temperature resistance.

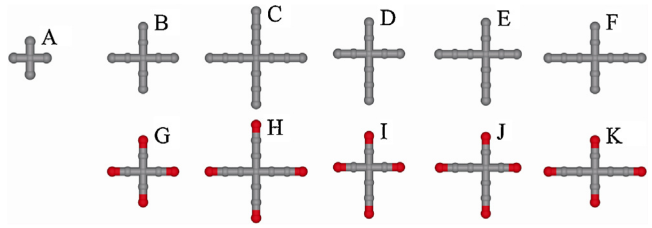

Fig. 1. Schematic structure of the cross-shaped building blocks used in the simulations. For those molecules in which only certain segments are active (G–K) we used red coloring to highlight them. The active segments are normally plotted in grey for all of the molecules with uniform composition (A–F). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2. Methods

To construct surface confined supramolecular assemblies we used different cross-shaped building blocks which are shown schematically in Fig. 1. These basic structural units were assumed to consist of discrete segments, each of which occupies one site on a square lattice. The molecules were allowed to interact via short-range segment-segment interaction potential whose range was limited to nearest neighbors on the lattice. The energy of interaction between adjacent foreign segments was characterized by the parameter ε. If not specified otherwise, all of the molecular segments were active and able to interact. The simulations of the self-assembly were carried out using the lattice gas MC technique in the Canonical Ensemble combined with the orientationally-biased sampling. A detailed description of the simulation algorithm can be found in our previous work [27]. The simulations started with N molecules of a selected type which were randomly distributed over the square lattice with side L equal to 100. The adsorbed overlayer was next equilibrated in a series of attempts to move and rotate in-plane each molecule and a single attempt is further called one MC step. In the simulations the adsorbed overlayer was slowly cooled down from temperature $T = 4.0$ down to $T = 0.1$ within 400 decrements. In each of these temperature intervals we performed $N \times 10^6$ MC steps of which last ten percent was used for averaging. The associated specific heat per molecular segment at a given T was calculated based on the fluctuation theorem

$$C_v = \frac{\left\langle U^2 \right\rangle - \left\langle U \right\rangle^2}{NskT^2} \qquad (1)$$

where U is the potential energy of the adsorbed phase, s is the number of segments in the molecule and k is the Boltzmann constant. For comparative purposes all of the simulations were run at constant adsorbate density equal to 0.32 segment/site. Accordingly, different number of molecules, N was used depending on molecular size and shape. This density was chosen as being optimal for random, unrestricted (no overlaps) placement of the molecules of each type on the surface. The results presented in the following are averages over ten independent runs. All of the model parameters are assumed to be dimensionless that is the energies and temperature are expressed in units of ε and $|\varepsilon|/k$, respectively. Snapshots of the ordered structures formed by all of the investigated molecules can be found in the Supporting Information (SI).

3. Results and discussion

3.1. Molecules with uniform composition

To examine the effect of temperature on the self-assembly in our systems we first performed the calculations for the simplest C_4-symmetric molecules with homogeneous composition. Fig. 2 shows the specific heat curves obtained for these building blocks. The simulated curves are rather sharp peaks centered at the transition temperature, T_{tr} which is equal to about 1.345 (**A**), 1.600 (**B**) and 1.925 (**C**), respectively. The transition temperature increases as the molecule becomes bigger which is a clear manifestation of the larger number of intermolecular interactions provided by the longer arms. To visualize this dependency in the right panel of Fig. 2 we plotted T_{tr} as a function of the mean potential energy of a molecule **A**–**C** in an infinite defect-free overlayer. Let us remind that, the molecules **A**–**C** under the investigated conditions form chiral nanoporous networks with scalable square void spaces [29,30]. Magnified fragments of these networks are shown in the Supporting Information. The obtained dependency between T_{tr} and E is linear (with slope equal to 0.14 and intercept equal to 0.46), similar to the effect of the arm length on T_{tr} (results not shown). The

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