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Two-dimensional molecular sieves: structure design by computer simulations

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Abstract Nanoporous molecular networks formed spontaneously by organic molecules adsorbed on solid substrates are promising materials for future nanotechnological applications related to separation and catalysis. With their unique ordered structure comprising nanocavities of a regular shape planar networks can be treated as 2D analogs of bulk nanoporous materials. In this report we demonstrate how the Monte Carlo simulation method can be effectively used to predict morphology of self-assembled porous molecular architectures based on structural properties of a building block. The simulated results refer to the assemblies created by cross-shaped organic molecules which are stabilized by different intermolecular interactions, including hydrogen bonding and van der Waals interactions. It is demonstrated that tuning of size and aspect ratio of the building block enables the creation of largely diversified extended structures comprising pores of a square and rectangular shape. Our theoretical predictions can be helpful in custom design of functional adsorbed overlayers for controlled deposition, sensing and separation of guest molecules.

Keywords Self-assembly · Adsorption · Porous overlayers · Computer simulations

1 Introduction

Fabrication of ordered porous materials is a rapidly developing area in which the bottom-up synthesis has recently drawn considerable attention. In this approach the final structure of a porous material, including pore size and shape, can be usually designed based on individual properties of a building functional unit(s). A telling example are self-assembled metal–organic frameworks (MOFs) which comprise metal ions or clusters and organic bridging ligands forming framework structures sustained by coordination bonds (James 2003). The structural and physico-chemical properties of MOFs can be finely tuned by modification of their components, making those adsorbents highly applicable in separation, gas storage and heterogeneous catalysis.

So far, most efforts have focused on the bottom-up synthesis of bulk porous materials with predefined structure and functionality. Interestingly, the bottom-up method has been demonstrated to be highly effective also in the case of two-dimensional porous networks self-assembled on solid substrates such as metals and graphite, in ultra-high vacuum conditions and from liquid phase. There have been reported numerous experimental results on the spontaneous formation of nanoporous molecular overlayers comprising different organic molecules able to form directional hydrogen bonds and metal–organic coordination bonds (Kudernac et al. 2009; Stepanow et al. 2008). Moreover, it has been shown that those superstructures can be sustained via van der Waals interactions, for example by interdigitation of long alkyl chains of star shaped building blocks such as alkyl-substituted phthalocyanines (Miyake et al. 2008), dehydrobenzoannulenes (DBAs) (Tahara et al. 2009) and stilbenoid compounds (Schull et al. 2006). For those systems, a suitable choice of the building block results in the formation of networks with regular pores of different size and shape (Kudernac et al. 2009), e.g. square (Kühne et al. 2009), rhombic (Ahn et al. 2009), hexagonal (Tahara et al. 2009) and so on (Gutzler et al. 2009), as ob-

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served in scanning tunneling microscopy (STM) imaging. The distinct advantage of the porous networks is the regular spatial arrangement of nanometer-sized cavities with uniform well-defined shape. Guest molecules such as thiols (Madueno et al. 2008), coronenes (Schull et al. 2006; Lei et al. 2008), fullerenes (Piot et al. 2009), can often be selectively adsorbed in a reversible way, rendering these networks of interest for adsorption and separation processes in future nanotechnological applications. Moreover, they can be also used as templates for crystal growth in three dimensions or to spatially confine molecular motion (Schlickum et al. 2007). A variety of structural and functional modifications of these networks are possible.

An intriguing feature of the self-assembled porous networks is that in many cases their structure is determined mainly by the shape of the building block not by its chemistry. For example, it has been observed that chemically different tripod organic molecules are able to form isomorphic chiral porous networks with hexagonal cavities (Mu et al. 2008; Liu et al. 2010; Tahara et al. 2009). A similar situation refers to cross-shaped molecules such as derivatized phthalocyanines, for which square pores were observed (Miyake et al. 2008). The above property makes those systems highly attractive form the point of view of theoretical modeling, as the number of necessary parameters related to chemical composition of a building brick can be substantially reduced. In consequence, the self-assembly of a large set of molecules can be accurately reproduced with relatively simple coarse-grained models, of which the Monte Carlo lattice approach seems most appropriate here. This was recently demonstrated by us for both C_3-symmetric (Szabelski et al. 2010) and asymmetric (Adisoejoso et al. 2012) tripod DBA molecules adsorbed on a graphite surface as well as for molecules with other shapes (Szabelski and Kasperski 2011; Tahara et al. 2011). The simulated results were in a good agreement with the corresponding STM images and the proposed model revealed to be able to predict the polymorphism observed in DBA overlayers (Adisoejoso et al. 2012).

In this contribution we use the MC model to explore the effect of aspect ratio and relative position of molecular arms in a cross-shaped molecule on the morphology of the corresponding self-assembled overlayer. Our study was inspired by the experimental results which have been recently reported for phthalocyanines and their alkyl-substituted analogs self-assembled on graphite (Miyake et al. 2008) and metallic surfaces (Calmettes et al. 2008).

2 The model and simulation

The cross-shaped molecules used in the simulations 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 an example of a cross-shaped molecule (*ijkl*) consisting of a central segment called core connected with four arms of adjustable length i, j, k and l.

The adsorbed molecules were assumed to interact via a short-ranged segment-segment interaction potential limited to nearest-neighbors on a square lattice. The energy of interaction between a pair of segments was characterized by ε expressed in kT units. 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 (Szabelski et al. 2010; Szabelski and Kasperski 2011). 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 1000 molecules (*ijkl*) 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 $p = \min\{1, \exp[-(U_{\mathrm{new}} - U_{\mathrm{old}})/kT]\}$ 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 10^7 MC steps and assumed that $\varepsilon = -2$. For each considered structure (*ijkl*) the number of molecules fixed in the simulations (1000) corresponds to submonolayer coverage, at which ordered domains are readily formed.

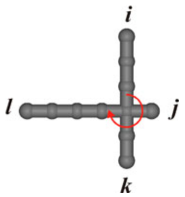

Fig. 1 Schematic structure of the cross-shaped (*ijkl*) molecules used in the simulations. The letter codes i, j, k and l denote the number of segments in each arm. The *red arrow* indicates clockwise numbering of arm segments around the core. A molecular building block (3124) is shown as an example (Color figure online)

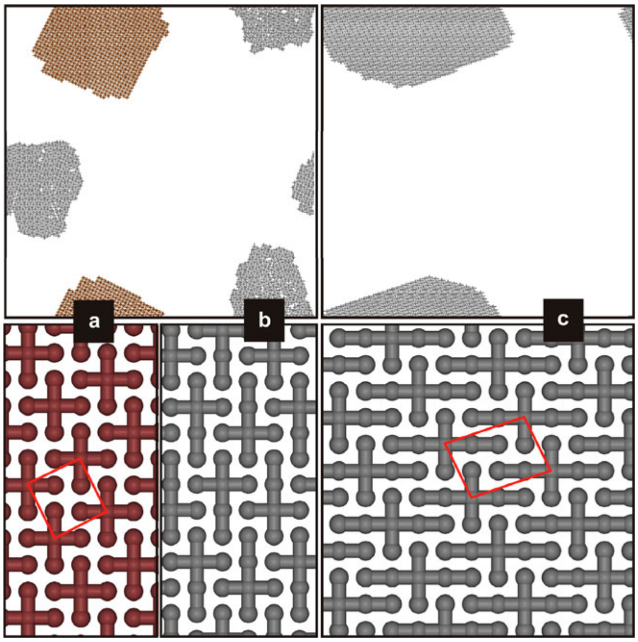

Fig. 2 Snapshots of the simulated nonporous overlayers comprising 1000 molecules of (**a**) (1111), (**b**) (2111) and (**c**) (2121). The snapshots obtained for (1111) (*brown*) and (2111) (*gray*) were superimposed. The *red lines* in the magnified fragments in the bottom part delimit the corresponding unit cells (Color figure online)

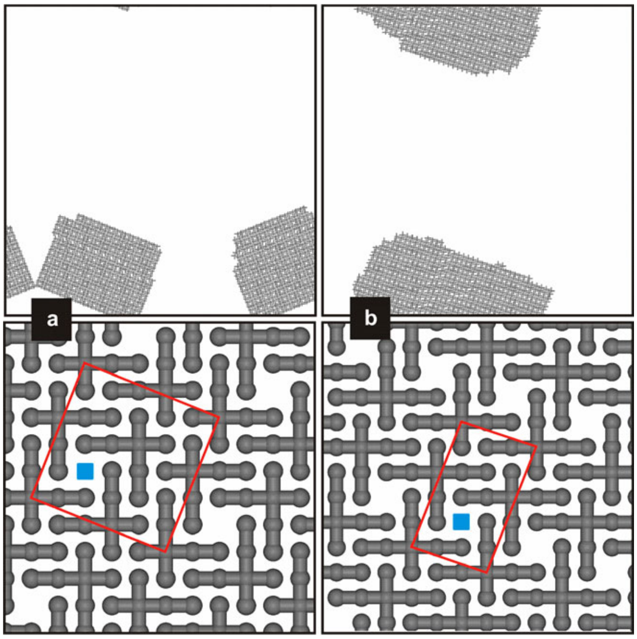

Fig. 3 Snapshots of the simulated porous overlayers comprising 1000 molecules of (**a**) (2211) and (**b**) (2221). The *red lines* in the magnified fragments in the bottom part delimit the corresponding unit cells. The pores inside the unit cells are marked in *blue* (Color figure online)

3 Results and discussion

To explore the influence of geometric properties of the cross-shaped building block on the morphology of the resulting assemblies we consider a few selected cases. In particular we focus on those molecules which are not prochiral, that is they do not deconvolute into mirror-image structures upon adsorption. The simplest example of a molecule of this kind is the C_4-symmetric molecule (1111) whose structure resembles that of small phthalocyanines or porphyrins (Calmettes et al. 2008). Figure 2a shows a snapshot of the simulated overlayer comprising 1000 molecules of (1111) (brown).

As seen in the figure, the smallest cross-shaped molecules self-assembly into nonporous domains in which they form closely packed ordered pattern with a square unit cell. An interesting feature of this superstructure is that it is globally chiral even though the building block is achiral being C_4-symmetric (Szabelski and Kasperski 2011). The molecular arrangement shown in Fig. 2a has been observed experimentally in numerous systems comprising phthalocyanines and porphyrins adsorbed on graphite and metallic surfaces in ultra high vacuum and from liquid phase (Drain et al. 2009; Miyake et al. 2008). The lack of void spaces in the self-assembled (1111) domains can be observed also for the two molecules (2111) and (2121) which were constructed by increasing the number of segments in one and two parallel arms of the parent (1111) molecule, respectively. For these molecules the simulated assemblies are also tightly packed but they differ in the range of order. In the case of (2111) we can observe the formation of a locally periodic pattern comprising a random mixture of small perfectly interlocked subdomains in which the molecules are aligned either horizontally or vertically. Figure 2b shows a magnified fragment of this structure (gray) comprising vertically aligned (2111) molecules with long arms pointing opposite directions. Because of the particular shape, the molecules of (2111) having three short arms are able to form globally aperiodic compact overlayer and stay fully coordinated with minimum potential energy. A different situation is encountered for the bigger molecule (2121), for which the self-assembly process results in an extended periodic structure with parallelogram unit cell, as illustrated in Fig. 2c. Note that in this case the pattern formed by the molecules of (2121) is not superimposable with its mirror image (see the magnified fragment) and thus it is chiral.

The self-assembled structures discussed so far comprise no nanocavities which can be filled with foreign matter and thus they are of limited application potential for adsorptive separation processes, etc. Interestingly, changing of the shape of the building block comprising two longer arms leads to the creation of a porous overlayer. This is clearly seen if Fig. 3a showing a domain formed by molecules of (2211).

The molecule (2211) has the same number of segments as the molecule (2121), but it differs in the arrangement of the long arms which are orthogonal. This property excludes the possibility of tight packing and its is responsible for the creation of void spaces having size of one adsorption site (blue squares in Fig. 2). Like for the smallest molecule (1111), the obtained overlayer is chiral. The same refers to the next system comprising molecules of (2221) equipped with three longer arms. As seen in Fig. 3b, these molecules self-assembly into a porous network characterized by a parallelogram unit cell. The type and number of nanocavities within the unit cell of the (2221) domain are the same as for the (2211) unit cell. A noticeable difference between these two structures is the number of unoccupied adsorption sites per dimensionless unit area which is equal to 0.03 and 0.06 for (2211) and (2221), respectively. The higher porosity of the latter system originates mainly from the presence of the third long arm which enables the formation of pores separated by a thin wall formed by two long arms of neighboring molecules. A general conclusion coming form the results discussed above is that, for the small cross-shaped molecules which normally self-organize into a compact overlayer the creation of porous structure can be induced by elongation of a pair of orthogonal arms or elongation of three arms. In practice this can be achieved, for example by a suitable attachment of longer alkyl chains to a square phtalocyanine core (Miyake et al. 2008; Qiu et al. 2000).

The size of the nanocavities created in the assemblies comprising molecules of (2211) and (2221) is relatively small compared to the dimensions of the network-forming building blocks. A simple route to enlarge void spaces in supramolecular networks comprising cross-shaped molecules is to elongate further their molecular arms. In the following we focus on one typical example, in which selected arms of the parent molecule (2222) were elongated by two segments. Figure 4a shows a snapshot of the simulated overlayer composed of 1000 molecules of (2222).

As seen in the figure, the molecules form an extended, perfectly ordered domain characterized by a square unit cell. The obtained superstructure is chiral and it comprises void spaces with the smallest available size of one adsorption site. Uniform elongation of the arms of the molecule (2222), by two segments each, produces the molecule (4444) which can be treated as an isotropically rescaled analog of the parent structure. For this molecule we can observe the formation of an isomorphic chiral porous network shown in Fig. 4b. The pores within that structure are 3 × 3 lattice site squares separated by two parallel molecular arms. To compare the simulated results with the corresponding experimental patterns in the bottom part of Fig. 4 we showed the STM images of the self-assembled overlayers comprising derivatized phthalocyanines (PC). The images shown in Fig. 4 have been recorded for the PC molecules equipped with eight alkyl chains build of 4 (c) and 6 (d) carbon atoms (Miyake et al. 2008). As seen in Fig. 4, the predicted effect of the uniform elongation of molecular arms on the morphology of the overlayer agrees well with the experiment. In both cases we can observe that increasing of the length of the molecular arms leads to the creation of square pores with a longer side. For the simulated system it is straightforward to establish a link between the pore size and the number of segments n in a single arm of the ($nnnn$) molecule. Namely, the pore area and porosity of the simulated structures comprising molecules ($nnnn$) scale with n as $(n-1)^2$ and $(n-1)^2/(n^2+2n+2)$, respectively. The simple scaling relation obtained for the model C$_4$-symmetric molecules allows for designing molecular overlayers with square pores of a predefined size. In this case, the outcome is an ordered structure with unimodal pore-size distribution.

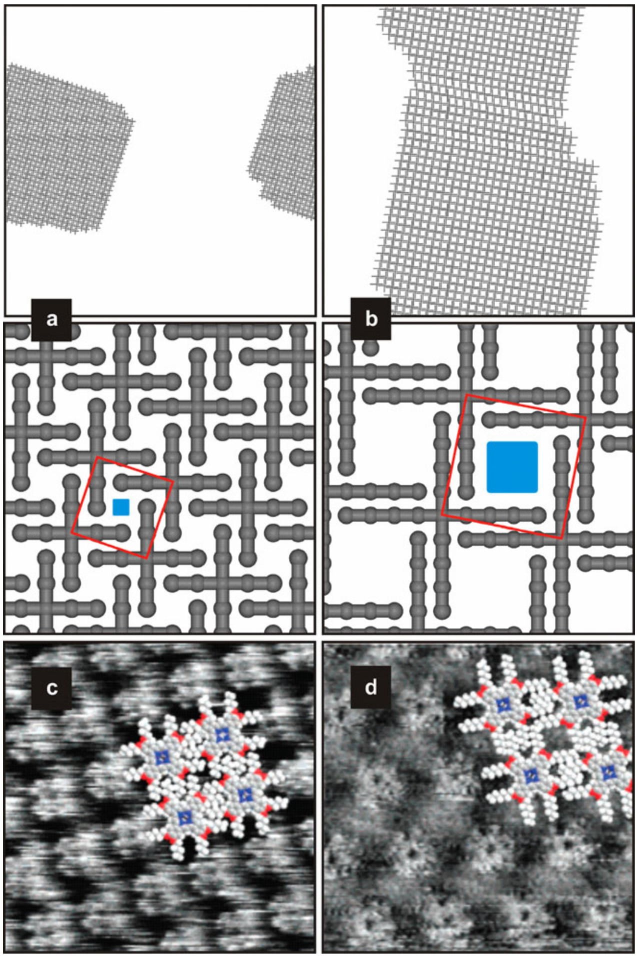

Fig. 4 Snapshots of the simulated porous overlayers comprising 1000 molecules of (**a**) (2222) and (**b**) (4444). The *red lines* in the magnified fragments in the middle part delimit the corresponding unit cells. The pores inside the unit cells are marked in *blue*. The *bottom part* shows STM images of the monolayers comprising alkyl-substituted phthalocyanine derivative (**c**) C$_4$OPc and (**d**) C$_6$OPc self-assembled at the phenyloctane/graphite interface. The CPK models of each structure were superimposed on each STM image. Reprinted and adapted with permission from Miyake et al. (2008). Copyright (2008) American Chemical Society (Color figure online)

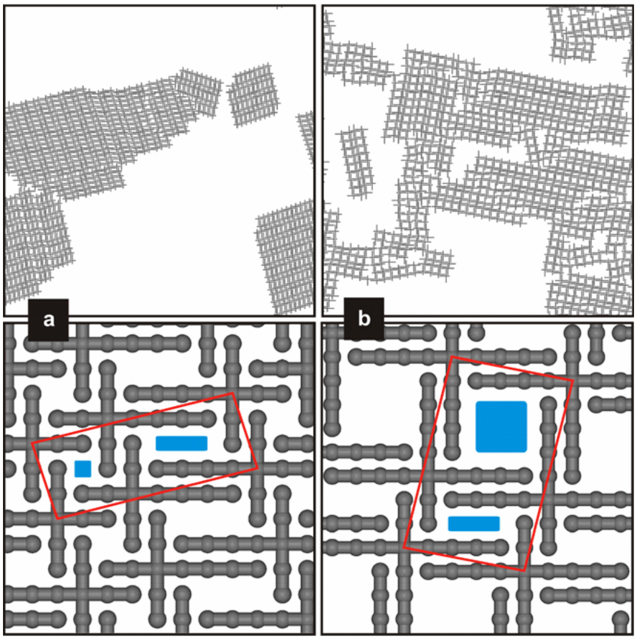

Fig. 5 Snapshots of the simulated porous overlayers comprising 1000 molecules of (**a**) (2224) and (**b**) (4442). The *red lines* in the magnified fragments in the bottom part delimit the corresponding unit cells. The pores inside the unit cells are marked in *blue* (Color figure online)

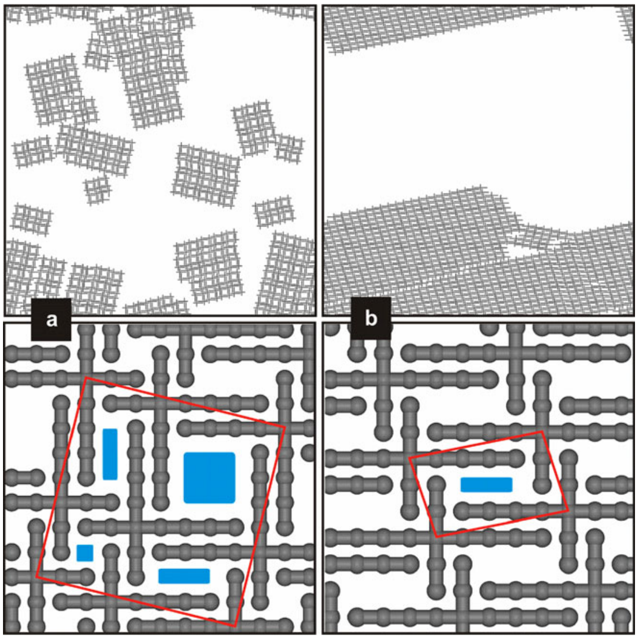

Fig. 6 Snapshots of the simulated porous overlayers comprising 1000 molecules of (**a**) (2244) and (**b**) (2424). The *red lines* in the magnified fragments in the middle part delimit the corresponding unit cells. The pores inside the unit cells are marked in *blue* (Color figure online)

All of the self-assembled porous networks discussed previously comprised void spaces of one shape and size (one lattice site or 3 × 3 squares). This structural property vanishes when anisotropic scaling is applied to the parent (2222) molecule. For example, for the (4222) molecule with one arm elongated by 2 segments we can observe the creation of a network with two types of pores which can be clearly seen in Fig. 5a.

The simulated structure is also chiral and it is characterized by a parallelogram unit cell with one rectangular (1 × 3) pore and one square (1) pore. A similar bimodal pore distribution was obtained for the (4442) molecule, for which the chiral self-assembled network shown in Fig. 5b comprises one rectangular (1 × 3) and one square (3 × 3) pore inside the parallelogram unit cell. A common element of these networks is the presence of the rectangular pore. What differs them is the size of the square pore within the unit cell, that (1) for (4222) and (3 × 3) for (4442). This feature can be used for example to create hybrid materials in which the rectangular pores are of primary interest and the size of square pores can be tuned to enable co-adsorption of smaller (for (4222)) or larger (for (4442)) molecules.

In the last example we demonstrate how the relative position of two longer arms within the rescaled cross-shaped molecule influences the network morphology. In this case, the presence of two longer neighboring orthogonal arms in a molecule of (4422) is responsible for the creation of a chiral porous structure of a new type. Figure 6a presents the simulated ordered domains comprising three types of nanocavities.

As seen in the figure, the pores within the square unit cell are of the same type as already observed for the structures discussed above, that is (1), (1 × 3) and (3 × 3). However, a new structural feature is the presence of these void spaces together in one network. The pair of orthogonal 4-membered arms of (4422) enables the formation of the square (3 × 3) pore, while the pair of orthogonal 2-membered arms creates rims of the small (1) square pore. An additional result of this particular attachment of the short and long arms of (4422) are the two perpendicularly oriented (1 × 3) rectangular pores. As demonstrated previously for the smaller molecules (2211) and (2121), changing of the aspect ratio of a cross-shaped molecule while keeping its composition fixed can result in a substantial change in the network structure. This is true also in the present case and it can be seen in Fig. 6b which corresponds to the molecule (4242) with a pair of collinear elongated arms. Here the altered arm arrangement makes the surface less heterogeneous—that is comprising adsorption centers of just one type. The above result can be helpful in selecting and synthesizing structural isomers of porphyrin and phthalocyanine based building blocks to produce porous networks with unimodal or multimodal 2D pore distribution.

To compare the obtained assemblies in a qualitative way in Table 1 we listed their structural parameters.

As it follows from the table, the porosity generally increases with the number of long arms in a molecule. More-

Table 1 Structural parameters of the simulated overlayers

Structure type	Unit cell shape and parameters[a]	Porosity[b]	Number and type of pores per unit cell
Nonporous			
(1111)	Square, $\sqrt{5}$	0	0
(2111)	n/a	0	0
(2121)	Parallelogram, $\sqrt{5} \times \sqrt{10}, 81.87$	0	0
Porous			
(2211)	Square, $\sqrt{29}$	0.03	1(1)
(2221)	Parallelogram, $\sqrt{10} \times \sqrt{29}, 85.24$	0.06	1(1)
(2222)	Square, $\sqrt{10}$	0.10	1(1)
(4222)	Parallelogram, $\sqrt{10} \times \sqrt{68}, 85.60$	0.15	1(1), 1(1 × 3)
(4422)	Square, $\sqrt{68}$	0.24	1(1), 2(1 × 3), 1(3 × 3)
(4242)	Parallelogram, $\sqrt{10} \times \sqrt{26}, 82.88$	0.19	1(1 × 3)
(4442)	Parallelogram, $\sqrt{26} \times \sqrt{68}, 87.27$	0.29	1(1 × 3), 1(3 × 3)
(4444)	Square, $\sqrt{26}$	0.35	1(3 × 3)

[a] Unit cell dimensions and angle are expressed in lattice constant units and degrees, respectively

[b] Number of unoccupied lattice sites within the unit cell divided by the area of the unit cell expressed in lattice constant units squared

over, for those molecules for which isomeric structures are possible ((2211) and (2121) and (4422) and (4242)) the orthogonality of longer arms is responsible for the formation of overlayers with higher porosity compared to those created by molecules with longer collinear arms. An obvious requirement for constructing a porous network comprising cross-shaped molecules considered here is the use of a building block with sufficiently long arms. The smallest molecule of this kind is the (2211) molecule. Further elongation of one or more arms of this minimal molecule, as performed in this study, will result in a porous overlayer with either one two or three types of adsorption centers. This rule holds for any achiral cross-shaped molecule with arms build of more than two segments (results not shown). In consequence, with the simple theoretical method outlined here it is possible to design a cross-shaped building block to obtain a surface with square and rectangular void spaces (adsorption centers) of a presumed size and abundance.

4 Conclusions

The theoretical results of this work demonstrate that the morphology of self-assembled two-dimensional overlayers comprising cross-shaped molecules can be largely influenced by the details of architecture of the building blocks at play. With the simple lattice MC model proposed here we were able to establish a link between the aspect ratio and size of the molecular brick and the structure of the resulting porous network. It was shown that by a suitable tuning of the molecular arm length and position of the arms around the core it is possible to create chiral compact and porous overlayers with different type and number of cavities. The minimum requirement for the cross-shaped molecules to self-assembly into a porous network was found to be the presence of at least two two-membered orthogonal arms in the molecule. In general, the orthogonality of arms promotes the formation of more open networks with more types of cavities, making the surface more structurally (energetically) heterogeneous. An important feature of the obtained results is that they are easily scalable, that is they can be used to predict morphology of adlayers comprising larger molecules having the same shape and aspect ratio.

The findings reported in this contribution can be helpful in preliminary screening of molecular libraries or in designing new structures such as alkyl substituted phtalocyanines etc. to create molecular overlayers with square and rectangular nanocavities of a predefined size. Those functional matrices can serve as selective adsorbents for separation or catalytic purposes, providing nanoconfinement for chemical reactions.

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