

Two-Dimensional Ordered Porous Patterns by Molecular Design

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We demonstrate by computer experiments that the spontaneous formation of two-dimensional regularly patterned molecular networks containing voids may be an entirely entropy-driven process. On the basis of a simple model of core–(soft) shell half-disk-shaped particles, we show that, even without the mediation of any attractive interparticle forces, such particles self-organize to stable and macroscopically ordered patterns with regularly distributed voids. The morphology of these supramolecular porous motifs depends critically on the size of the core relative to the coronal halo. The reverse engineering analysis of these precise two-dimensional supramolecular porous templates suggests molecular-shape complementarity and polyphilicity as key design parameters for the bottom-up engineering of such functional substrates.

Introduction

Molecular self-organization is a key concept in creating highly ordered assemblies of molecules, standing as one of the most promising fields in nanotechnology research.^{1–3} Understanding the principles and the underlying molecular mechanisms behind self-assembly and self-organization, in addition to a scientific and technological challenge, is a central concern for chemistry and biology and a required step toward molecular engineering of new materials. Given specific molecular properties and thermodynamic conditions, self-organization may involve molecular self-assembly. In this case, the system is driven toward self-organization in parallel with the development of supramolecular entities with well-defined structure and spatial dimensions through molecular recognition events. These entities may involve a few or several hundreds of molecules. In all known cases of supramolecular self-organization, the formation of the supramolecular entities and their structural integrity are based upon relatively weak in strength but selective intermolecular interactions.^{1,2} The driving force for this hierarchical type of self-organization is the interplay between the energetic and entropic contributions toward minimization of the system's free energy.

Supramolecular chemistry offers a plethora of methods and ideas toward complex self-organization through molecular self-assembly.⁴ In addition, a number of relevant computer simulation experiments clearly demonstrate how the inclusion of selectively interacting sites at prescribed locations on the surface of hard particles may enable the self-organization into fascinating structures,⁵ induce liquid crystallinity by particles which are not mesogenic without the selective interactions,⁶ or phase separate without these interactions.⁷ However, effectively predicting and describing the self-organization behavior of highly complex nanoscopic building blocks using the *interparticle* interactions

as a starting point remains a great scientific challenge.^{5–13} Computer simulations based on a nearly exact representation of the short-range intermolecular correlations may indicate certain directions toward molecular engineering of new materials with novel and possibly desirable properties.

Below three dimensions, surface nanopatterning and two-dimensional (2D) crystal engineering have been strongly developing fields of research in recent years. By utilizing both interparticle and particle–substrate interactions, a great variety of intriguing and possibly technologically interesting 2D nanopatterns have been achieved.^{14–22} As a special class of nanopatterned surfaces, 2D molecular networks containing voids provide interesting opportunities in host–guest chemistry, heterogeneous catalysis, separation, molecular electronics, and sensor devices. However, only a few examples of such networks have been reported.^{20–22} In this work, we utilize computer simulations in an attempt to provide molecular design rules for the generation of 2D motifs with regularly distributed open pores. We demonstrate how molecular polyphilicity, an inherent property of the so-called core–shell or core–corona particles, together with their molecular shape complementarity may provide such patterned surfaces.

Core–shell (CS) particles represent a broad class of systems that have been intensively investigated during the past few years. The generic term of CS accommodates a diversity of molecular structures such as tethered metal or glass nanoparticles,²³ block

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copolymer micelles,²⁴ and globular dendrimers.^{25–27} All of the above share the same structural topology of an internal, usually inaccessible, core and a soft shell with different chemical affinity (phylicity). Apart from globular or highly symmetric dendrons, properly functionalized fullerenes,²⁸ organic–inorganic hybrids,^{29,30} or even small molar mass, properly designed and functionalized aromatic derivatives^{21,22} are all examples of polyphilic CS molecules with nonconventional shapes, i.e., conical, rod-like, wedge-like, half-sphere-like or, in 2D, triangular, polygonal or half-disk-shaped.^{31–33} Usually, the macroscopic order of systems composed from such anisotropic particles is supramolecular in nature, and the form of the self-assembled aggregates is determined by the coupling of shape anisotropy and molecular polyphilicity.

In this work, we focus on the molecular organization and the self-assembling properties of half-disk-shaped CS particles. On the basis of a minimal intermolecular potential for such particles in 2D, we utilize Monte Carlo (MC) computer simulations to show that such systems exhibit rich phase polymorphism that involves ordered phases with open pores. Studying the self-organization behavior and rich accompanying pattern formation of such systems is anticipated to elucidate the role of the molecular polyphilicity and molecular shape complementarity in the self-organization and to provide design rules for nanoparticles or molecules to be utilized for the creation of templated surface structures.

Molecular Model and Computational Details

We begin by considering the highly idealized model of two-dimensional CS disks in which each particle consists of an internal hard core with radius r_{core} , decorated with a shell of radius r_{shell} . To quantify the relative thickness of the molecular parts, the dimensionless molecular parameter $\chi \equiv r_{\text{core}}/r_{\text{shell}}$ is introduced which assumes values in the interval $0 \leq \chi \leq 1$. We assume that the pair potential is infinite if the core or coronal part of a disk overlaps with the core of a second disk and zero otherwise. In this minimalistic approach the coronal parts of the particles can interpenetrate without any energetic cost or gain (perfectly soft shells), but the extent of the interpenetration is limited by the presence of the internal hard cores. Thus, the distance of shortest approach between any pair of disks is $\sigma_0 = r_{\text{shell}}(1 + \chi)$, and the system is isomorphic to the two-dimensional system of hard disks, which has been extensively studied, during the past decades. This athermal system crystallizes upon compression into a hexagonal crystal (possibly through a Kosterlitz–Thoules phase transition³⁴) when the surface coverage (or packing fraction, $\eta = N(\pi\sigma_0^2/4)/A$, where N and A are the number of particles and the area of the system, respectively) is about 0.7, with

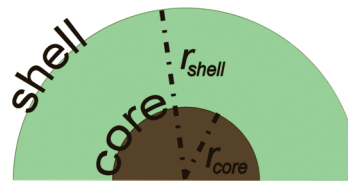


Figure 1. Model of a half-disk-shaped core–shell particle. The internal hard core and the soft shell are defined by the radii r_{core} and r_{shell} , respectively.

the close packing limit corresponding to packing fraction $\eta_{\text{cp}} = 3^{1/2}\pi/6 \approx 0.9$.

With this isomorphism in mind, we focus our study on the phase behavior and on the molecular organization of systems of half-disk-shaped particles (shown in Figure 1) that result on splitting the CS disk in two identical parts. By breaking the cylindrical symmetry, the intermolecular potential of the half-disks becomes highly anisotropic, depending on both interparticle separation and relative orientations.

Intuitively, one might expect that at high densities a system comprising half-disk-like CS particles forms physical dimers with pairs of particles assembling into supramolecular disks as the system drives itself toward efficient packing. These disks in turn are expected to occupy the sites of the usual highly packed triangular lattice. In the remainder of the article, we show that this is correct only in the case of particles with thin or absent coronal shells. Contrary to the aforementioned scenario, when the shell thickness exceeds a certain threshold, the supramolecular aggregates comprise more than two particles and their shape delimits an empty interior. These aggregates, in turn, self-organize into thermodynamically stable periodic motifs exhibiting open pores and extended intercoronal overlapping.

To simulate the phase behavior of the half-disk particles, we have performed standard constant pressure (tension) Metropolis MC simulations with periodic boundary conditions, following a simulated annealing approach.^{35,36} Starting from a well-equilibrated low-pressure isotropic state of N particles, the system was gradually compressed with small pressure jumps. The simulation at each pressure involved $\sim 10^5$ MC cycles for equilibration, and statistical data were obtained during the next 10^6 MC cycles. Each MC cycle involved on average one random translation and/or reorientation per particle and one random change of the surface of the system. To avoid the development of internal stresses, especially in the high-pressure ordered phases, and to diminish the possibility of biasing the equilibrium state, the sides of the simulation box were allowed to vary independently. Generally, the interactions between molecular species and the substrate have an important effect on the final self-assembled structure as also does the presence of external fields. In our model, however, no such interactions or forces were assumed, implying particles physisorbed onto a structureless, perfectly flat substrate.

Results and Discussion

Several systems comprising particles with a relative thickness parameter in the range $0 < \chi \leq 1$ were simulated. In Figure 2 we present the calculated compressibility vs packing fraction ($z^* - \eta$) equations of state (EoS) of systems of half-disks with no ($\chi = 1$), thin ($\chi = 0.50$), moderate ($\chi = 0.24$), and thick ($\chi = 0.17$) soft shell. The average packing fraction at a given pressure P was

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calculated as $\eta = Na/\langle A \rangle$, where $\langle A \rangle$ is the average surface area of the system and $a = \pi\sigma_{\min}^2/8$ serves as a measure of the particle surface. The compressibility was calculated as $z^* = p^*/\eta$, by defining the dimensionless pressure $p^* = pa/k_B T$ and with $k_B T$ the thermal energy. For comparison reasons, the EoS of a system of whole disks with molecular surface area $2a$ is also plotted in Figure 2.

A clear density jump, indicating a first-order transition, was observed upon compression for all the systems but the one with half-disks of moderate shell ($\chi = 0.24$). A first insight into the molecular organization in the high-pressure phases is obtained by simple visual inspection of the representative snapshots shown in Figure 3. These snapshots hint that the particles' ordering depends critically on the shell thickness and also reveal a trend behind the open pore formation mechanism. Clearly, the repeating units in the ordered phases are not single half-disks but rather a collection of them as they spontaneously form supramolecular aggregates with well-defined shape, strongly dependent on the shell thickness. In systems of particles with no ($\chi = 1$) or thin ($\chi = 0.50$) coronal shells the supramolecular aggregates comprise two half-disks in an arrangement resembling a whole disk. These clusters in turn self-organize in a hexagonal lattice (shown in Figure 3a,b). The ordered phase of the $\chi = 1$ system has an almost identical EoS with the ordered phase of the hard disks system. Similar supramolecular organization is observed for the moderate shell ($\chi = 0.50$) half-disks system. The situation dramatically changes for systems with thick shell ($\chi = 0.17$). In this case the high-pressure phase consists of supramolecular aggregates that

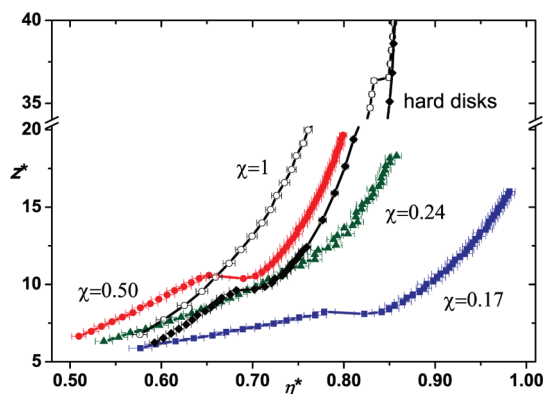


Figure 2. Calculated equations of state (EoS) of systems of half-disk shaped core-shell particles with no ($\chi = 1$), thin ($\chi = 0.50$), moderate ($\chi = 0.24$), and thick ($\chi = 0.17$) shell, together with a plot corresponding to the hard disks system.

self-organize into a well-defined pattern of rhombic pores as shown in Figure 3d. Systematic search for the shell thickness at which there is a crossover between the two- and four-particles aggregates revealed that there is a narrow range of shell thicknesses, around $\chi = 0.24$, for which the high-pressure phase is dominated by triangular aggregates as Figure 3c clearly shows. The existence of this narrow range of stable patterns with triangular pores is also confirmed by simple analytic calculations of the densities of the highest packed arrangements assuming triangular symmetry with repeating units of two-, three-, and four-particle aggregates. These simple geometric calculations indicate, in accordance with the simulation findings, that around $\chi = 0.24$ the pattern with the triangular pores is indeed the pattern that allows for the highest packing fraction.

Several pair correlation functions were used to quantify the positional and orientational order of the studied systems (for details see Supporting Information and ref 12). All the results confirmed the thermodynamic stability of the ordered phases and verified, on quantitative grounds, the structural organization of both the supramolecular entities on the molecular length scale and of the ordered phases on large scales. To quantify the degree of aggregation and monitor the evolution of the clustering process with pressure, we calculated the population distribution of the various aggregates during the simulation runs. The ensemble average of the fraction of the particles participating in clusters of different types and sizes was calculated using the distribution function $h_m(p^*) \equiv \langle N_m(p^*) \rangle / N$, where $N_m(p^*)$ is the number of particles participating in aggregates composed by m particles. Details on the clustering procedure are given in the Supporting Information.

Cluster distribution plots are presented in Figure 4. These plots clearly show that even in the low-pressure isotropic phases the particles form short-living clusters of various types that coexist in well-defined proportions. At the phase transition pressure the systems of no or thin ($\chi = 0.50$) and thick ($\chi = 0.17$) shell particles show an abrupt change in the populations of the supramolecular clusters with those comprising two or four particles, respectively, dominating in the ordered phase (shown in Figure 3a,c). On the other hand, in the case of the system with moderate ($\chi = 0.24$) shell half-disks, although an abrupt jump is not present in the respective clustering plot, the evolution of the relative populations of the various aggregates clearly reveal the gradual formation of an ordered phase built from three-particle clusters at high pressures as the cluster distribution plot of Figure 4b shows. This is in agreement with the absence of a clear density jump on the EoS of this system, indicating the trapping of the system in transient and possibly metastable states.

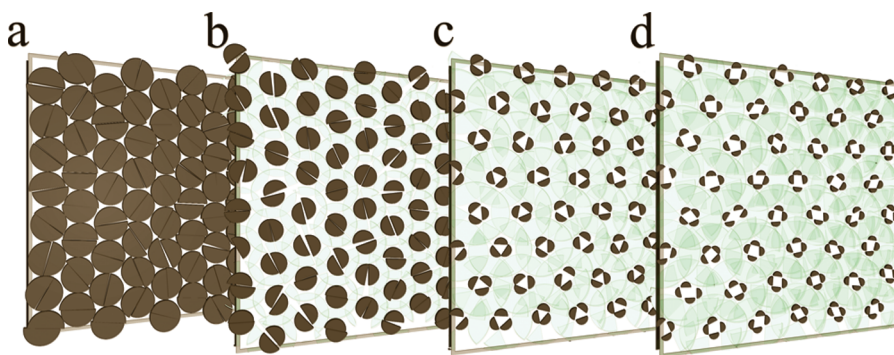


Figure 3. Representative snapshots of high-pressure ordered states of systems of half-disk-shaped core (gray)–shell (light color) particles with (a) no, (b) thin, (c) moderate, and (d) thick shell at high densities. Supramolecular clusters with triangular and rhombic open pores characterize the self-assembled structures in the case of the moderate and thick shell systems.

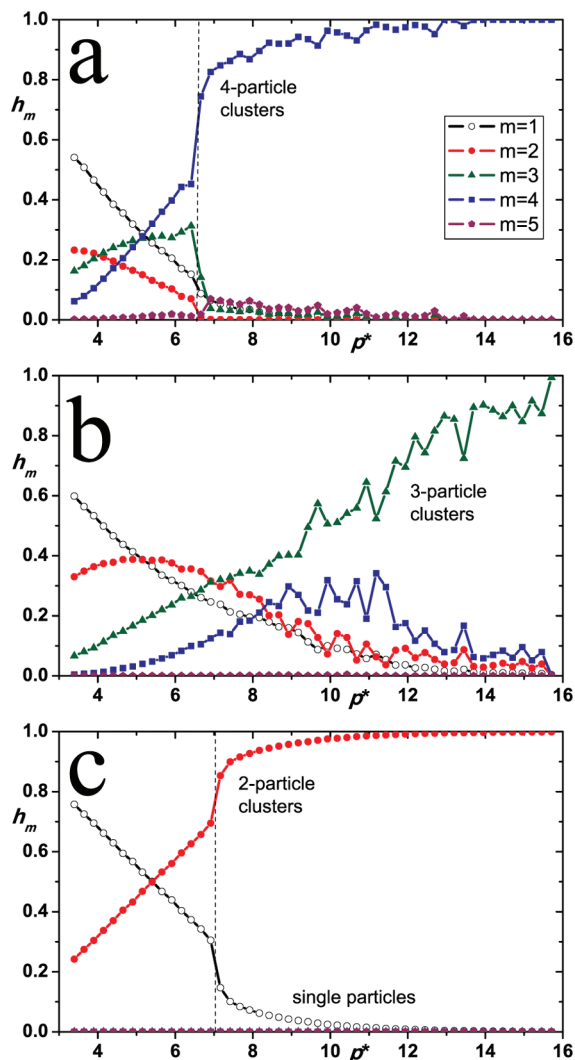


Figure 4. Cluster distribution plots of systems of half-disk-shaped core-shell particles with (a) thick, (b) moderate, and (c) thin shell. For both the thick and thin shell systems, an abrupt change in the percentages suggests a phase transition (dashed line). Clusters of four or two particles dominate the anisotropic states. Clusters of three or two particles dominate at high pressures for the moderate shell system, although a clear phase transition is not observed.

It should be noted here that, for the systems of particles with thick shells, the morphology of the most favorable clusters in the low concentration regime does not reflect the type of the dominant supramolecular entity in the ordered phases. Thus, for the system with the thick shell ($\chi = 0.17$) particles, aggregates with rectangular ($m = 4$) and triangular ($m = 3$) pores appear with similar probability with the nonclustered particles at pressures just below the phase transition pressure (shown in Figure 4a), after which aggregates with rectangular pores dominate entirely (shown in Figures 4a and 3d). Similar behavior is observed with the systems of half-disks with moderate shell thickness, in which all the $m = 1-4$ aggregates have similar populations close to the transition point (shown in Figure 4b). This fact reveals clearly that the dominant aggregates and the final structure of the ordered phases for the systems of half-disks with moderate to thick shells cannot be safely predicted from the study of the precursor supramolecular aggregates formed in the low pressure (or density) phases.

Our findings suggest that systems of half-disks with thin soft shells self-assemble into disk-like physical dimers, which in turn

self-organize into triangular periodic motifs. There is a narrow range of shell thicknesses, around $\chi = 0.24$, for which the half-disk-shaped CS particles tend to self-assemble into triangular aggregates with an empty interior. Particles with thicker shells ($\chi \leq 0.24$) form quadruplets which delimit rectangular pores and dominate over all the other types of clusters in the ordered phase. We note here that in the theoretical limit of $\chi \rightarrow 0$ clusters of infinite numbers of particles are expected due to the ultrasoft shell assumed for this model. Such extreme situations are prevented by modeling the soft shell-shell interactions on more realistic grounds, assuming for instance soft interparticle repulsion upon shell-shell overlap with strength proportional to the overlap area of the particle shells. We have confirmed this with extensive simulations on a parameter space which included the pressure, temperature, shell thickness, and strength of the intershell interactions. With properly chosen shell-shell interaction parameters, all the aforementioned motifs for the ordered phases were observed again with the variation of the outer shell thickness. Thus, adjusting soft interactions serves as a fine-tuning mechanism allowing precise control of the shape and size of the open pores. There are several ways to physicochemically control both the strength of the intershell repulsion and the shell thickness. For example, for particles with polymeric shells of flexible chains on the particle's periphery, the grafting density, the quality of the solvent, and/or the temperature could be the appropriate shell-shell interaction control factors. Such control of the shell thickness could lead to responsive smart surfaces which, with the control of the solvent quality or temperature, could give rise to patterned surfaces with switchable pores.

We stress the fact that although we have used a simple model for our simulation agents, their behavior proved to be not intuitively predictable. Contrary to intuition, the existence of empty spaces in the form of regular open pores (whenever these are observed) proves to be a requisite for the studied systems to achieve thermodynamic stability at high densities. This contradictory situation stems from the fine interplay between two opposing forces as the presence of the soft shells drives the system in a direction opposite to which the close packing of the hard cores alone would dictate.

Conclusion

We have demonstrated by means of Monte Carlo simulations that the two-dimensional spontaneous formation of ordered porous patterns may be an entirely entropy driven process. The coarse-grain, highly idealized, molecular model introduced captures the essential molecular properties of 2D half-disk-shaped core-shell amphiphiles with use of a minimum number of modeling parameters of clear significance. The minimal approach adopted for our molecular model and the interactions involved should not, by any means, be considered as a strict recipe for the experimentalist. It aims to illustrate that a "smart" design of the molecular "shape" could drive molecular self-assembly even when specific attractive interactions are not present. We believe that this notion is of great importance, especially when aiming at targeted applications through molecular engineering. Despite the simplicity of the model, the studied systems exhibit a surprisingly rich phase behavior. By varying the density and/or the amphiphilic shell thickness, novel, thermodynamically stable, patterns covering a variety of porous topologies may be produced. We have obtained insights into the underlying physics governing the thermodynamic behavior of such systems and the principal mechanisms driving the self-organizing processes. A two-way direct link has been established between the molecular architecture and interactions of our model particles and the morphology

of the resulting patterns. Thus, our study could also serve as a guide for experiments in the area of self-assembling systems for synthesizing particles to be used as building blocks for the fabrication of porous nanostructured materials with desired morphological features. Finally, given the very limited simulation studies¹⁰ on the cluster formation mechanisms of three-dimensional soft matter particles that interact via purely repulsive interactions, extension of the present model to 3D is in progress.

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Supporting Information Available: Notes on cluster analysis and brief characterization of phases with pair correlation functions. This material is available free of charge via the Internet at: <http://pubs.acs.org>.