Phase selectivity triggered by nanoconfinement: the impact of corral dimensions

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By using a novel protocol to spatially confine molecules in well-defined small 2D areas, the so-called nanocorrals, we show using scanning tunneling microscopy (STM) how this kind of confinement affects self-assembled molecular network (SAMN) formation at a liquid-solid interface. The 2D lateral confinement, imposed by the size of the nanocorrals, has a clear impact on the phase selectivity of a molecule that can form both low-density and high-density SAMNs, the high-density phase being promoted by the confinement.

Many functional and sometimes structural properties of materials change upon spatial confinement. Among the many cases, the particle size dependent emissive properties of inorganic nanoparticles such as CdSe is a textbook example.¹ But also in organic materials such size dependent properties arise.^{2,3} For instance, the deviation from bulk values of the glass transition temperature of polymer thin films has been attributed to the existence of confinement effects.^{4–6} Also, properties of small molecules, such as their viscosity, can change dramatically when confined in thin films.^{7,8} Nanoconfinement of materials in nanopores has led to a range of interesting observations. For example, freezing and melting points are often depressed in nanopores.^{9,10} Or the polymorphism of some organic compounds can be significantly affected as well.^{11,12}

“Polymorphism” is a phenomenon that also occurs in monolayer thin films of molecules self-assembled into supramolecular networks on solid substrates. The liquid-solid

interface is an attractive environment to support the formation of such self-assembled supramolecular networks (SAMNs). If an atomically flat and conductive substrate is used, scanning tunneling microscopy (STM) is an ideal local probe microscopy technique to characterize the structure and dynamics in these SAMNs, at the liquid-solid interface, at the nanoscale. Numerous aspects, structural as well as functional, have been investigated, for such SAMNs. A rather intriguing phenomenon is their concentration dependent phase behavior. The SAMN structure might differ depending on the concentration of the solute in the liquid-phase. In such cases, quite often low-density SAMNs are favored at low concentrations while upon increasing the solute concentration a transition towards one or more high-density phases is observed.^{13–15} A similar effect can be obtained upon changing the temperature.^{16,17} The gradual concentration or temperature dependent transition of one SAMN structure

Fig. 1(a) Schematic illustration of the self-assembly of DBA derivatives on bare HOPG and in confined spaces. (b) Chemical structures of DBA derivatives. (c) Schematic models for porous and non-porous patterns. (d) Chemical structure and schematic model of a covalently bound 3,4,5-trimethoxy phenyl group on a graphene flake.

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into another one can be explained based on thermodynamic grounds, albeit also kinetic effects may contribute. Motivated by the impact of nanopores on the polymorphism of certain organic systems,^{11,12,18,19} we reasoned that lateral confinement conditions could also reveal similar phenomena for SAMN formation at the liquid-solid interface.

Herein we report the first observation of phase-selectivity in molecular self-assembly under lateral nanoconfinement (Figure 1a). This was done for a well-investigated model system – SAMNs based on alkoxyated dehydrobenzo[12]annulene (DBA) derivatives.^{13,20} Controlled nanoconfinement was realized on arylated highly oriented pyrolytic graphite (HOPG), the substrate-of-choice for the custom design, *in-situ* modification and convenient STM characterization of graphite corrals.^{21–23} Some rationales behind our system design choices are given below, while more technical aspects are detailed out in ESI.

The selected DBA-OC13 (Figure 1b) is a medium-size DBA building block that, just like other alkoxyated DBA derivatives,^{13,24,25} when assembled from 1-phenyloctane (1-PO), can form two polymorphs: porous and linear (Figures 1c and 2). Control experiments (Figure S4, Table S1) on unmodified HOPG have shown that ~ 50% : 50% porous : non-porous composition is achieved in 5.6×10^{-6} M solution. That is why all nanoconfinement experiments were done at this concentration. Furthermore, 1-PO leads to stable *in-situ* nanoshaving conditions. It also turned out that the DBA pores are easier to identify than non-porous assemblies (especially, when analyzing the content of the smallest nanocorrals (24–60 nm) in which STM images often lacked sub-molecular resolution). Hence the surface coverage analysis was primarily

done by measuring porous phase, and the 50% surface coverage of porous phase was taken as the sign of ‘no discernable selectivity towards either of the phases’.

For the nanoconfinement experiments, HOPG surface was fully grafted with a dense layer of 3,4,5-trimethoxyphenyl groups (ESI, section S5).^{26,27,28} The most relevant factor to choose this aryl species was that even in low-resolution STM images 3,4,5-trimethoxyphenyls can be readily distinguished from DBA-OC13. Via an *in-situ* STM based nanolithography protocol removing locally grafted molecules at the interfaces of the grafted graphite and a 1-phenyloctane solution containing DBA-OC13, areas defined in size and shape are formed, the so-called nanocorrals.^{22,23} The direct exposure of the newly-generated surface to DBA-OC13 solution prevented contamination, otherwise, frequently observed when DBA-OC13 solution was introduced after *ex-situ* corral formation.

To probe the potential impact of the geometrical nanoconfinement, square nanocorrals of different sizes were created, ranging from $24 \times 24 \text{ nm}^2$ to $201 \times 201 \text{ nm}^2$. From here on, we denote the size of the nanocorral by referring to the length of its side. The nanoshaving experiments were carried out at a DBA-OC13 concentration of 5.6×10^{-6} M, which on pristine graphite surface ensures an equal surface coverage of the porous and non-porous phases. The surface coverage of the porous and non-porous phases for each of the nanocorrals is summarized in Table S4 and presented in Fig. 3c. The trend is clear. In contrast to experiments carried out on pristine graphite, hardly any porous phase is observed in the smaller corrals. Only locally, some hexagonal pores, indicated by green dots in Fig. 3a, b, are observed. The larger the nanocorrals, the larger the fraction of the porous phase, but it remains always lower than the one observed on pristine graphite. Only, at a corral size of about 200 nm, the surface coverage of the non-porous phase equals the surface coverage of the porous phase, reflecting the situation on pristine graphite. Note that we also looked at the effect of DBA concentration, showing that regardless of the nanocorral size, the porous : non-porous ratio increases with decreasing DBA-concentration (Figure S7). The larger the nanocorral, the more pronounced this trend is, as expected based on the data for unmodified HOPG.

To rule out that odd-even effects are at play at the level of the alkyl chains, similar experiments were carried out with DBA-OC12 (ESI, Section S7–S8). Qualitatively and even quantitatively, the results are very similar as those obtained with DBA-OC13.

We not only used square nanocorrals (in the main text), but also circular and triangular corrals (Figure S12 and S13). Irrespective of the shape of the nanocorrals, the results showed similar tendency. So, the confinement effect is independent on the corral shape.

Time-dependent effects were not investigated in detail, as continued scanning leads to an increased risk of unintended nanoshaving and deterioration of the image quality. *In-situ* cleaning of the tip via a voltage pulse is not an option as it resets the self-assembly process. Nevertheless, some dynamics was observed which however did not affect the non-porous to porous ratio (Figure S14). In addition, for the smallest corral dimensions, nanoshaving was performed at elevated

Fig. 2 High-resolution STM images and the corresponding structural models of (a, b) porous and (c, d) non-porous self-assembled monolayers of DBA-OC13 at the 1-phenyloctane/HOPG interface. Concentration: (a) 2.0×10^{-6} M; (c) 6.7×10^{-5} M. Scanning parameters: $V_s = -0.20 \text{ V}$, $I_t = 200 \text{ pA}$. Unit cells are overlaid on the STM images. (a) Porous phase: unit cell parameters $a = 4.7 \pm 0.1 \text{ nm}$, $b = 4.7 \pm 0.1 \text{ nm}$, $\gamma = 60 \pm 1^\circ$; area density per molecule is 9.57 nm^2 . (c) Non-porous phase: unit cell parameters $a = 2.5 \pm 0.1 \text{ nm}$, $b = 4.7 \pm 0.1 \text{ nm}$, $\gamma = 90 \pm 3^\circ$; area density per molecule is 5.88 nm^2 .

Fig. 3 (a, b) STM images of the self-assembly of DBA-OC13 at the 1-phenyloctane/graphite interface, in corrals of different size (approximately $24 \times 24 \text{ nm}^2$, $39 \times 39 \text{ nm}^2$ and $60 \times 60 \text{ nm}^2$). These are the average dimensions of 15 nanocorrals of each type. Scanning parameters: $V_s = -0.80 \text{ V}$, $I_t = 80 \text{ pA}$. The nanocorrals are formed via a nanoshaving process (Scanning parameters: $V_s = -0.001 \text{ V}$, $I_t = 200 \text{ pA}$) at the interface between the 1-phenyloctane solution of DBA-OC13 and graphite. DBA-OC13 concentration is $5.6 \times 10^{-6} \text{ M}$. Green dots represent hexagonal pores. (c) Dependence of the surface coverage of porous and non-porous structures as a function of the size of the square corrals. Each data point results from the average values of 15 corrals (24 , 39 and 60 nm) or 40 zoom-in ($50 \times 50 \text{ nm}^2$) images (90 , 114 , 145 , 177 and 201 nm). The standard deviation is indicated. For nanocorrals reaching a diameter of about 201 nm , there is no nanoconfinement effect anymore.

temperature to assess the kinetic stability of the assemblies. Compared to room temperature experiments, the porous : non-porous ratio at 50°C remained unaltered (Table S7). Thus, the assembly composition in nanocorrals is kinetically stable up to at least 50°C .

In all these experiments, the relative orientation of the square nanocorrals with respect to the symmetry axes of the graphite surface is not known, and not controlled. To rule out that there is an effect of substrate symmetry on the geometrical nanoconfinement effects, we ran some tests on DBA-OC13 where we varied the orientation of the square nanocorrals with respect to the HOPG lattice. In addition to the fact that these experiments confirm that the alkyl chains run parallel to one of the symmetry axes of graphite (Figure S15), the more important outcome of this set of experiments is that regardless the relative orientation of the square nanocorrals with respect to the graphite lattice, the results are not different from those discussed before (Figure S16, Table S8). Also the absence of preferential molecular alignment with respect to the slow nanoshaving direction, a phenomenon that was observed for a chainlike molecule,²² suggests that the nanoshaving process is

not at play in defining the outcome of the self-assembly process. All of this suggests that the phenomena as observed are independent of the nanoshaving process itself. The reason can be found in the different geometries of the molecules.

Obviously, the question rises what is the mechanism behind the nanoconfinement effect. Both kinetics and thermodynamics are at play in the formation of self-assembled molecular networks. A priori, it is not possible to state which will dominate the network formation.²⁹ Previously we have shown that self-assembly of these alkoxyated DBA derivatives represents a thermodynamic composition of linear and porous structure at the interface between 1,2,4-trichlorobenzene (TCB) and graphite. A similar, gradual decrease in the surface coverage of the porous phase (and increase in the linear phase) as a function of DBA-OC13 concentration, but now in 1-phenyloctane, suggests that this is also the case in this system. Note though that kinetic blockades cannot be ruled out. So, the equal surface coverage of the linear and porous phases at $5.6 \times 10^{-6} \text{ M}$, does not necessarily represent an equilibrated surface composition at the thermodynamic minimum. We have identified two effects to explain the favored formation of the high-density phase in smaller nanocorrals.

From a thermodynamic point of view, phase selectivity can be explained as the result of additional interactions between DBA-OC13 or DBA-OC12 and the walls of the corral. Such interactions are simple in nature and their strength is additive.²⁷ As such, the larger the interaction between the molecular network and the wall, the larger the expected energy gain. Higher flexibility in packing of linear phase allows easier accommodation to the irregularities of grafts at the wall of the corral. This effect becomes the more pronounced the larger the perimeter to area ratio of the nanocorrals, i.e. for the smaller nanocorrals. Hence, observed phase selectivity could be interpreted as preferential stabilization of the linear phase by the walls of the corral. However, we don't find a bias for linear phase formation at the corral walls.

From a kinetics point of view, the nanocorral size could affect the relative rates of nucleation of the porous and the linear phase.³⁰ This could be due to size differences of the critical nuclei of linear and porous phases: being more dense, the critical nucleus of the linear phase can fit in a smaller confinement than the honeycomb phase, and hence can have higher nucleation probability. At present it is not possible to distinguish between the two interpretations.

In conclusion, we have systematically investigated geometrical confinement effects on the self-assembly of alkoxyated DBAs that form two concentration dependent phases at the interface between 1-phenyloctane and HOPG. The effect of nanoconfinement is expressed by a strongly increased tendency to form the non-porous phase. This nanoconfinement is indeed size dependent as the effect disappears when the corrals reach a size of about $200 \times 200 \text{ nm}^2$. This behavior can be explained based both on thermodynamics as well as kinetics considerations, or a combination of both. Temperature dependent studies on polymorph selection might shine some light on the relative importance of both mechanisms. Also chain length dependent studies are of potential interest. Overall, this

new approach to study confinement effects is an interesting platform to reveal aspects of 2D supramolecular chemistry.

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Conflicts of interest

There are no conflicts to declare.

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