Surface Patterning

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Molecular Self-Assembly across Multiple Length Scales**

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The generation of supramolecular architectures that exhibit a high degree of order across multiple length scales is of great importance for applications in various fields including (opto)electronics, magnetism, catalysis, and medicine.[1,2] While single, randomly distributed nanostructures are useful for basic studies on their physicochemical properties, the production of large-area arrays of nanoscale objects, such as nanowires, nanotubes, and nanocrystals spanning from the nanometer up to the millimeter scale, is of utmost importance for their technological application, for example, as active components for the fabrication of (opto)electronic devices like organic transistors or light-emitting diodes.[3] Indirect, slow, and multistep patterning approaches have been proposed,[4–9] but they are not easily applicable on scales spanning from 5 nm up to 10 mm and frequently they involve surface-invasive steps and chemically limiting procedures. Elemans et al.[10] instead described recently a simple method to prepare very large arrays of exceptionally long (i.e. up to 1 mm) lines of porphyrin trimers, each line being only one molecule thick. This result was obtained by mastering the complex balance of forces which are involved in self-assembly from solution on a solid surface.

Self-assembly of organic (supra)molecules from solution is nowadays one of the simplest methods to develop complex, nanostructured materials with innovative properties.[11,12] Among various molecular systems, alkylated polycyclic discotic molecules such as triphenylenes, hexabenzocoronenes, phthalocyanines, or porphyrins[13,14] are frequently chosen as starting building blocks to exploit their ability to stack and form columnar architectures and liquid-crystalline phases.[15] The formation of ordered thin films from these systems appears easy: just dissolve your molecules in the right solvent and at the right concentration, then deposit a drop of the solution on a substrate. The molecules will self-assemble, interacting with one another through weak forces such as van der Waals or electrostatic interactions. As noncovalent interactions can also be highly directional, upon solvent evaporation molecules can arrange on the substrate to form architectures such as crystals, layers, or fibrils.[16] The processability of these systems can be improved by covalently grafting substituents such as alkyl chains, which offer an enhanced solubility of the molecule in organic solvents, to the molecular periphery.[13] These side groups can incorporate moieties which act as poles for additional noncovalent interactions, such as amides to form hydrogen bonds.[17] The exact self-assembly behavior of a given molecular system is difficult to control a priori, but it is possible to adjust this behavior by employing a stepwise approach, that is, by systematically varying the chemical structure (e.g. the size of the molecule and the side groups) during synthesis.[13] The interactions involved are very weak; as a consequence, response to external stimuli, adaptability, and self-healing are hallmarks of supramolecular structures and materials,[18] leading to the formation of thermodynamically stable architectures with an extremely high degree of order at the ensemble level. In contrast, large molecules or polymers typically form materials that exhibit a kinetically governed morphology.[19]

Self-assembly of small molecules from solution frequently yields structures that exhibit a high degree of order on the nanometer scale, whereas on the micrometer scale they exhibit more disordered morphologies. Moreover, on the micrometer scale these structures usually adopt random positions and orientations on the substrate. This is primarily caused by the non-uniform evaporation of the solvent at surfaces. In fact, evaporation typically proceeds through dewetting of the solution, leading to the formation of holes in the liquid layer that eventually enlarge and coalesce until the solvent is completely evaporated. This process is typically called a pinhole mechanism.[20] The final morphology is the result of the interplay

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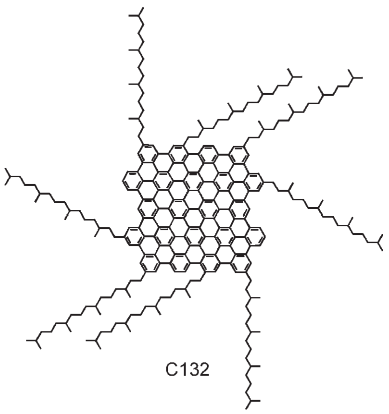
of intramolecular, intermolecular, and interfacial interactions, and also includes the shear forces applied to the solution during the dewetting process, which are due to surface tension forces.

Although the deposition from solution from the practical (experimental) viewpoint is apparently extremely simple, intrinsically it is a very complex phenomenon to predict and model theoretically, as it involves different materials and phases (the solid substrate, the liquid solvent, the molecules dissolved in the solvent, and the atmosphere in which the solvent evaporates) as well as their interfaces. To obtain a control over the morphology, a subtle balance of all the interactions involved must be achieved, as shown in Figure 1 a in which three major types of interactions are considered. Extreme cases, which are characterized by one of the three interactions dominating over the others, can lead to the following three scenarios:

1) If molecule–molecule interactions are too strong, the molecules will be poorly soluble in the chosen solvent, although small ordered aggregates (a few hundred molecules in size) can still be formed and deposited on a surface.[21]
2) If molecule–substrate interactions are dominant, the molecules will be kinetically trapped on the surface instead of interacting with each other and thus undergoing self-reparation or more generally reorganization. However, organized nanoassemblies can still be obtained with an order that is induced to a great extent by the structure of the substrate.[22]
3) If molecule–solvent interactions are too strong, the molecule–molecule interactions will be shielded and the molecules will tend to follow the solvent during the dewetting to ultimately give amorphous structures.

The effect of surface tension forces (here we primarily consider dewetting) is usually detrimental to self-assembly, although in some cases it has been successfully exploited for nanolithograpic patterning.[9] Dewetting effects can be minimized by slowing the solvent evaporation, for example, by performing the deposition in an atmosphere saturated with solvent vapors or by employing a low volatile solvent (i.e. a high-boiling-point solvent).[23] As an example, different morphologies can be obtained from an alkylated polycyclic aromatic hydrocarbon (C132) deposited from solution on a mica surface by changing the experimental conditions, that is, by altering the equilibrium between dewetting and intermolecular interactions as the major driving force of the self-assembly (Figure 2). In particular, by varying the nature of the solvent and the temperature employed during the deposition it was possible to form mesoscopic fibers or amorphous agglomerates as a result of a self-assembly process dominated by intermolecular interactions or dewetting, respectively.[24]



C132

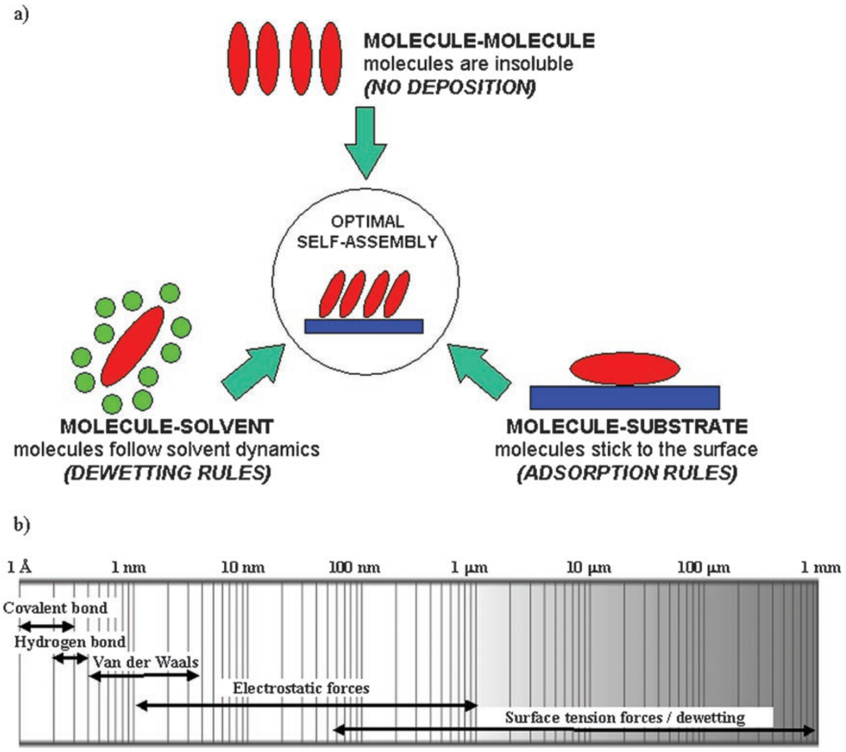


Figure 1. a) Schematic representation of the major types of interaction that play a role during solvent-assisted deposition. If one of the forces dominates over the others, ordered self-assembly is not achieved. b) Qualitative comparison of the relevant length scales over which each type of force dominates the self-assembly.

In the experiment performed by Elemans et al.,[10] instead, dewetting does not dominate over intermolecular interactions but acts in combination with them. These two forces act in a hierarchical manner, governing on distinct scales to achieve a high degree of order in both molecular and mesoscopic dimensions.[25] In this way, periodic patterns of exceptionally long, that is, up to 1 mm, lines of porphyrin trimers were produced (Figure 3 a).

When a drop of solution is applied to a mica surface, one-molecule-thick lines of porphyrin trimers with a length of up to almost one millimeter are generated on the surface while the solvent evaporates. These lines run parallel to the receding drop edges. The formation of lines is determined by the discontinuous shrinkage of the drop during evaporation of the solvent: the drop edge is pinned (probably by some irregularly

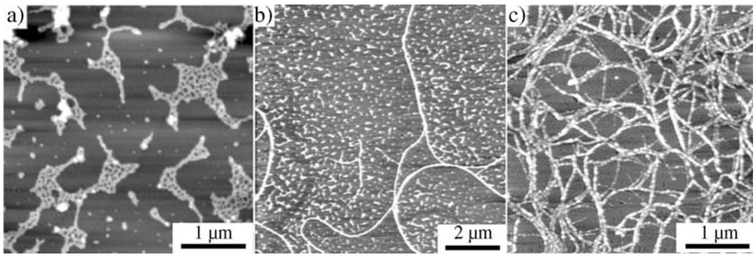
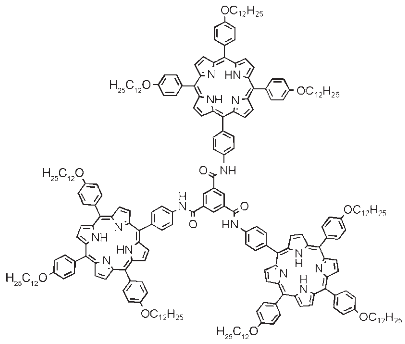


Figure 2. Example of competition between self-assembly and dewetting: topographical scanning force microscopy (SFM) images of C132 on mica. a) Deposition from a dichlorobenzene solution at room temperature: irregular aggregates are formed due to dewetting-dominated self-assembly. b) Deposition from a trichlorobenzene solution at room temperature: slower evaporation of the solvent allows some molecules to self-organize in fibers, while the others still give disordered aggregates. c) Deposition from a trichlorobenzene solution at 4 °C: evaporation is even slower and the process primarily leads to the formation of self-assembled fibers. Reproduced from Ref. [24].



porphyrin
trimer

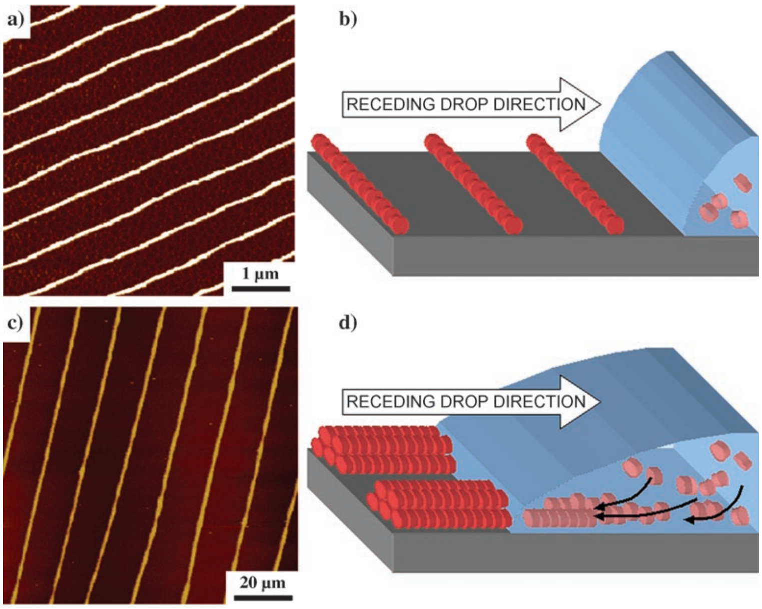


Figure 3. a) Topographical SFM image of porphyrin trimers self-assembled in lines with cross-sections of tens of nanometers. b) Schematic representation of the formation of nanoscopic lines. c) SFM image of lines with cross-sections of hundreds of nanometers obtained by using larger droplets. d) Schematic representation of the formation of large lines. Adapted from Ref. [10].

clustered porphyrin material or eventually by small structural defects of the surface) and thus it shrinks through discontinuous jumps. After each jump, the receding drop leaves a thin layer of solution on the surface which undergoes rapid dewetting. Ripples are formed within the thin unstable layer which forces the molecules to self-assemble into long lines parallel to the drop edge (Figure 3 b). Noteworthy, these lines do not only display a high aspect ratio but they also exhibit a surprisingly uniform lateral spacing on macroscopic scales: (640 ± 40) nm spacing on areas up to 3 mm^2. This takes place because the dewetting process, and consequently the line spacing, is not controlled by the kinetics of the receding drop but rather it is ruled by the energetics of the surface–solution system. Note that the line spacing, although varying in the different domains, always lies in the range 0.5–1 µm.

As described by Seeman et al.,[26] the dominant lateral wavelength of the dewetting process (in this case, the spacing between the ripples formed) depends on 1) the surface tension of the liquid and 2) the excess free energy $\Phi(h)$ of a layer of solution with thickness h deposited on a surface. The value of $\Phi(h)$ can be calculated from the Hamaker constant of the liquid on a given substrate and can also be obtained experimentally.[26]

In past years, most experimental studies on dewetting have been carried out by melting thin polymeric films because in this case there is no evaporation of the liquid and the process is slow enough to be monitored in real time.[27] In the case of dewetting involving highly volatile liquids, it is much more difficult to monitor the process. The scenario gets even more complicated when solutions of molecules that form liquid-crystalline phases are involved.[28–30]

In the report by Elemans et al.,[10] the authors were also able to dramatically change the self-assembly of the molecules simply by slowing down the evaporation process. By making use of larger droplets, which required a longer time to achieve complete evaporation of the solvent, the prime process governing the growth was no longer the pinning of the receding drop but rather the flow of molecules towards the drop edge as a result of solvent evaporation, which increased their concentration in the proximity of the edge. This is a well-known phenomenon which explains, for example, why coffee stains on a towel have edges that are darker than the center.[31] The radial flow of molecules toward the drop edges, together with their tendency to self-assemble, gives in this case lines of molecules which are *perpendicular* to the drop edge. These lines are not one molecule thick, but rather they consist of bundles of stacks with a spacing on the micrometer scale (Figure 3c,d).

The demonstration that a complete change of self-assembly behavior can be obtained just by changing drop size is a proof of the high versatility of the technique, but it also reveals the delicate dependence of the approach on the deposition parameters. Although very regular patterns can be obtained in a single experiment, the interplay of the different forces is truly complex and thus the formation of reproducible morphologies requires a high level of control over many deposition parameters such as the drop size, drop-edge pinning, temperature, humidity, nature of the surface (including hydrophobic versus hydrophilic character, flatness, cleanliness), and so on.

A limitation of this approach is the circular shape of the obtained pattern, which is dictated by the dynamics of the receding drop. A linear geometry of the patterning can be accomplished by making use of the zone-casting technique, which is based on the spreading of a drop by a dispenser that slowly slides over the substrate.[32] Parallel arrays of porphyrin fibers could be obtained with a well-defined macroscopic orientation by spreading the solution by zone-casting instead of drop-casting.

The periodic lines obtained by Elemans et al. were already successfully applied to align a thick layer of liquid crystals, thus showing the potential application of such self-assembled patterns in the fabrication of displays. Future explorations and exploitations of the electrical properties of these systems, such as charge transport enhanced by the high molecular order of the stacks, can also be of great interest for the development of organic, nanostructured transistors.

By and large, for a few centuries now, organic chemists have been able to control through molecular synthesis the behavior of single molecules in solution. Since a few decades, with the advent of supramolecular chemistry, the self-assembly of a few molecules into ordered nanoscopic structures has become possible by exploiting weak intermolecular interactions.[1] Nowadays, hierarchical self-assembly, through the concerted use of different physical and chemical forces that dominate over distinct multiple scales (see Figure 1b), makes it possible to extend this control up to macroscopic, visible scales.[33]

In conclusion, the careful control of the interplay of intermolecular and interfacial interactions can allow properly designed molecules to form very large and organized structures up to the millimeter-length scale. The factors and processes involved are indeed quite complex, spanning from simple van der Waals and other short-range noncovalent interactions to the physics of fluids, and surely a better understanding of the dewetting dynamics of solutions is needed. However, the results obtained by Elemans et al. show that although the theory of the process is complex and poorly known, the formation of large scale, regular nanometric patterns can be achieved by exploiting cheap, quick, and up-scalable methods. A greater control over this hierarchical self-assembly can be obtained through a systematic study performed by tuning the various boundary conditions and by unraveling the underlying principles governing the thermodynamics and the kinetics of the process through a temporal evolution study, that is, real-time mapping. A higher degree of complexity can be attempted by employing hierarchical self-assembly methodology to grow multicomponent architectures, even bio-hybrid ones, with a predetermined order or by exploiting it in conjunction with other (non)conventional patterning methodologies based on photo- or electron-beam lithography.[34] For example, complex highly conductive structures can be produced by combining dewetting and self-assembly of large biological units such as tobacco mosaic viruses and gold nanospheres.[35] Finally, future challenges include not only the manipulation of the nanostructures by exploiting poorly invasive methods, such as electrophoretic approaches[36,37] or magnetic fields[38] on properly designed architectures, or their further stabilization introducing cross-linkable moieties[39] but also their technological application, for example, in electronics and diagnostics.

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