Self-assembled Two-dimensional Supramolecular Architectures of Zinc Porphyrin Molecules on Mica

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Abstract. The assembly of two-dimensional molecular structures of zinc porphyrin molecules arising from the dewetting of a porphyrin solution on a mica substrate is investigated using the atomic force microscope (AFM). Both a near equilibrium nucleation and growth process, and a far from equilibrium spinodal dewetting process are observed. By choosing a zinc porphyrin molecule with a prefabricated structure, we are able to control the morphology of the single layer molecular films formed on the substrate.

1. Introduction
The electronic and optical properties of a molecular architecture depend on the character of the individual molecules as the building blocks, and on how these molecules are connected to each other. It is possible to synthesize a particular type of molecule with a predetermined property and structure such that when the molecules are brought into close contact, they self-assemble into a two-dimensional or a three-dimensional molecular architecture that exhibits a desired physical or chemical property. Among the many molecules studied for the purpose of developing model molecular electronic devices, phthalocyanines and porphyrins have attracted particular attentions due to their interesting electronic properties and the possibility of tailoring their properties by molecular engineering. [1-8] Here we report the formation of single molecular layers of zinc porphyrin molecules on a solid substrate. We show that whilst maintaining the intrinsic property of the molecule itself, we can alter the way the molecules are bonded to one another by adding different side chains to the main frame of the molecule, and hence control the structure of the supramolecular assembly.

2. Experimental
Zinc porphyrin molecules 1 and 2 employed in our investigation are synthesized in Cambridge University. [9] Fig. 1 shows the structures of the two zinc porphyrin derivatives. Both derivatives have the same macrocycle as the main frame of the molecule. This common feature gives the two derivatives the same electronic and optical properties arising from the molecular orbitals associated with the macrocycle. For 1, there are two trimethylsilane (TMS) groups bonded to the macrocycle via phenyl groups and acetylene linkers. For 2, there are two (CH₂)₁₁ units, connected together via a S-S bond, forming a structure resembling the handle of a basket. This handle has a strong influence on the bonding between porphyrin molecules in a solid aggregate by hindering the interaction between neighbouring porphyrin molecules.
The molecules were first dissolved into tetrahydrofuran (THF) to a concentration of $2 \times 10^{-5}$ M. A droplet of the solution ($\sim 2 \text{ ml}$) was then applied onto the surface of mica and left to dry in air. The initial thickness of the liquid film is estimated to be $20 \text{ nm}$ over a $1 \text{ cm}^2$ area. The concentration and the volume of the solution were carefully chosen so that the number of zinc porphyrin molecules deposited on the mica surface was not sufficient to cover the whole surface with more than a single molecular layer. Tapping mode atomic force microscopic (AFM) imaging of the molecular thin films was performed in air at room temperature with a Dimension 3100 SPM (Digital Instruments, Santa Barbara).

![Figure 1. The structures of the two types of zinc porphyrin molecules used in our experiment.](image)

**Results and discussion**

Figs. 2 (a) and (b) show two AFM images of the structure formed from zinc porphyrin 1 on mica. Needle-like structures, as those shown in the figure, are observed over most part of the surface. These needles are $1.6 \text{ nm}$ high above the mica substrate, and are assigned to a single molecular layer of zinc porphyrin 1. [8] The average size of the needles, however, depends on the concentration of the solution, with larger needles formed at higher concentrations. Due to the nature of liquid phase deposition, the concentration of the solution on the mica substrate varies with time during evaporation. Moreover, concentration gradients across the surface are also expected to exist as a result of surface tension induced liquid flow, which is responsible for the observation of different sized needles seen at different parts of the surface. [8] The needles shown in Fig. 2 (a) have an average width of $200 \text{ nm}$ whilst those in Fig. 2 (b) $350 \text{ nm}$.

![Fig. 2. AFM images of molecular monolayers of zinc porphyrin 1 on mica. (a) $6 \times 6 \text{ nm}$ (b) $5 \times 5 \text{ nm}$. (c) Schematic diagram showing the proposed orientation of the zinc porphyrin molecules within the monolayer needles. Each disk in (c) represent a single zinc porphyrin 1 molecule.](image)

According to the AFM images, the growth of the zinporphyrin needles follows a layer-by-layer mode. The minimum height of the molecular structures observed on mica is $1.6 \text{ nm}$, corresponding to a single molecular layer, with taller structures appear multiples of $\sim 1.6 \text{ nm}$ in height. The needle shape of the porphyrin assemblies shown in Fig. 2 arises from a direction-dependent growth rate. The preferred bonding configuration between molecules like zinc porphyrin 1 is the co-facial stacking of the macrocycle planes as a result of the strong $\pi-\pi$ interaction. [10] In the porphyrin solution, once a nucleus of molecular aggregate is formed, the fast growth direction is expected to be roughly perpendicular to the plane of the macrocycle. The rather regular shape of the needles also suggests
that the molecular assemblies are two-dimensional molecular crystals. The growth of molecular needles inside the liquid film is in competition with the evaporation of the solvent. There is a point when the liquid film becomes unstable and breaks apart due to dewetting. Before that happens, a needle grows by capturing diffusion molecules to its edges and the growth process is more or less close to equilibrium.

In great contrast to what is observed for zinc porphyrin 1, the structure formed from zinc porphyrin 2 on mica under the same experimental condition is completely different. Fig. 3 shows two AFM images of the dried zinc porphyrin 2 assemblies on mica at room temperature. In Fig. 3 (a), one sees a large number of small molecular islands of various sizes. The height of all the islands is 2 nm which is independent of the lateral size of the features. For this reason, all the islands shown in Fig. 3 (a) are identified as monolayer islands. The appearance of the structure has some similarity with the patterns formed from the dewetting process on solid surfaces by a liquid film, \[11-14\] and is rather consistent with a spinodal dewetting process. \[15-20\] During the evaporation of the solvent, the concentration of porphyrin molecules within the liquid film increases and the temperature of the liquid decreases. This induces phase separation and the formation of molecular aggregates according to a universal phase diagram of this type of system. \[21\] When a nucleus of molecular aggregate forms, it creates a capture zone around it such that porphyrin molecules within the capture zone get incorporated into the existing nucleus. As a consequence, no new nucleus can form within the capture zone of an existing one because of a reduced molecular concentration in the neighbourhood of an existing nucleus. This process effectively controls the distance between two molecular aggregates next to each other. The average distance between most neighbouring islands in Fig. 3(a) is 175 nm. Thus the average diffusion length of a zinc porphyrin 2 molecule inside the liquid film is in the order of 85 nm.

![AFM images of monolayer islands of zinc porphyrin 2 on mica. (a) 15 x 15 μm. (b) 5 x 5 μm.](image)

Larger islands of zincporphyrin 2 molecules are found only at surface defect sites such as shown in Fig. 3(b). The bright circular structure, 12 nm in height, in Fig. 3(b) is associated with a defect on mica. Around this defect, a densely packed disk of zinc porphyrin 2 (~12 μm in diameter) is found. This disk has the same height as the smaller islands in the surrounding area, as well as those shown in Fig. 3(a). The defects on mica act as strong pinning sites for the solution and thus promote the nucleation of porphyrin aggregates around them. Because the liquid film is pinned at the defect sites, as the solvent evaporates, a directional flow of the solvent molecules towards a pinning site should take place. This flow thus carries porphyrin molecules toward the protrusion where molecular monolayer is formed. This process is similar to the formation of colloidal monolayers \[22,23\] reported before. Because the disks are formed at an early stage in the whole drying process, there is plenty of time for them to grow ahead of spinodal dewetting.

Neither the large circular disks around surface defects, nor the smaller islands formed due to spinodal dewetting show any trace of a preferential growth direction or a crystalline structure of the zinc porphyrin 2 aggregates. In the case of zinc porphyrin 1, the strong interaction between the molecules in the co-facial packing scheme favours crystallisation at an early stage when the concentration of molecules is still low. Subsequent growth of the needles consumes all the molecules inside the liquid film ahead of spinodal dewetting. The result is the formation of relatively large (μm
sized) crystalline structures. For zinc porphyrin 2, the addition of the curved hydrocarbon chain over the macrocycle plane, prevents the effective co-facial stacking of the molecule, although co-facial packing between two molecules is still possible. In the absence of surface defects, the zinc porphyrin 2 molecules stay as isolated molecules, or pairs of molecules until the spinodal dewetting process occurs. At that point, phase separation drives the molecules into small islands as the liquid film dries up.

Because of the common macrocycle main frame of the two zinc porphyrin derivatives, the electronic and optical properties of the two molecules are similar. However, by introducing a basket handle to the macrocycle, the intermolecular interaction within a supramolecular assembly is completely altered. For the porphyrin needles, a large anisotropy in electrical conductivity and response to optical excitation is expected, whilst the properties of the non-crystalline film from zinc porphyrin 2 are expected to be rather isotropic. The co-facial stacking of porphyrin 1 should give the molecular needles a relatively high electrical conductivity along the length of the needles. In this regard, the structure formed from zinc porphyrin 2 would behave as an isotropic molecular resistance. The resistivity of such a molecular resistance can further be modified by adding various side chains to the macrocycle. The method described here is quite general and should be applicable to a large number of systems, such as suspended nanocrystals and magnetic structures assembled from magnetic molecules.

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