



Self-assembly of a chiral porphyrin at surfaces

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Abstract

Evaporation of solutions of a new synthetic tetra meso-amidophenyl-substituted porphyrin derivative on graphite leads to different morphologies at the air–solid interface, whose nature depends on the solvent in which the molecule was dissolved. Fibres – which were shown to be a stable aggregate form of the compound by molecular modelling – are observed by AFM, although they do not seem to have the structure which was predicted. The reason for this situation appears to be the dominance of surface–molecule interactions over those between the molecules themselves. On mica surfaces, dewetting takes place, leading to relatively well-defined monolayer and bilayer domains.

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1. Introduction

Molecules organised on surfaces have found a variety of applications of late, and one of the most important challenges in this area is controlling the ordering of molecules in the 2D monolayer structures. Directional non-covalent modes of interaction, such as hydrogen bonding, are of great help and importance in the self-assembly of molecules on solids [1–6]. In addition to their directional properties, hydrogen bonds may control intermolecular distances and as a result dictate the molecular conformation and properties. Amide groups have been chosen to stabilize the interactions between contiguous molecules by hydrogen bonds [7] and form helices as the one shown in Fig. 1, which is a model aggregate (vide infra) of the target compound of this study: A chiral porphyrin.

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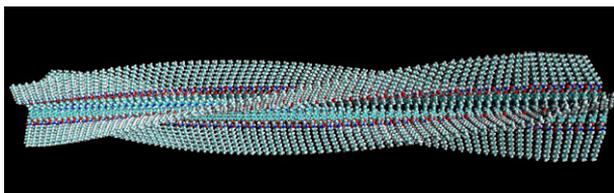


Fig. 1. A molecular model of a helical arrangement of hydrogen-bonded, chiral supramolecular fibre of porphyrin molecules.

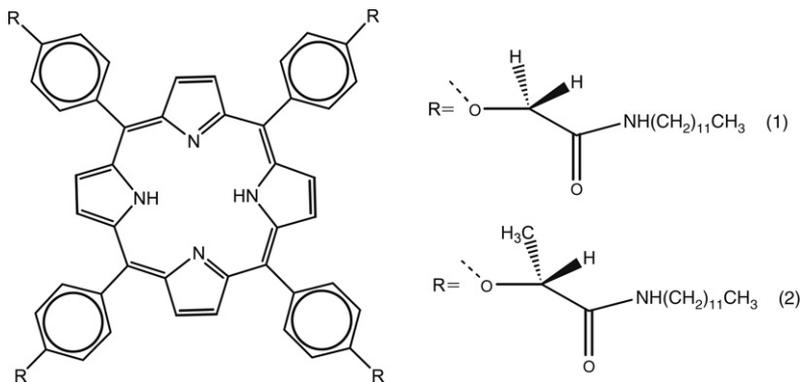
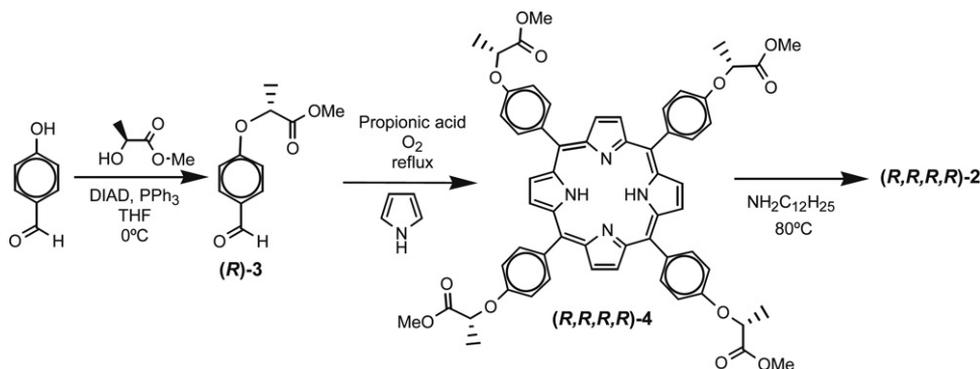


Fig. 2. An achiral porphyrin (**1**) and the chiral porphyrin (**2**) which is the subject of this study.

Porphyrins are an important and versatile group of organic compounds which show a number of interesting properties – ranging from electron transfer phenomena, to catalysis, photodynamic therapy and magnetism – which depend on the substituents attached to the tetrapyrrolic macrocyclic core, the metal ion incorporated in the core [8–10] and their supramolecular arrangement [11].

We are interested in creating chiral supramolecular assemblies of porphyrins to be able to study stereochemical effects on superstructure, charge transport and magnetism. The ultimate challenge here is to try and form helical structures at a surface such that they could be probed electronically. Amide bonds are a very good way to assemble molecules, and this has been done for the achiral porphyrin **1** (Fig. 2) [12]. We considered that the incorporation of stereogenic centres into the alkyl chains of this compound could generate helical assemblies, and for this reason we decided to focus on compound **2** which has chiral substituents. Importantly, the methyl group which breaks the symmetry of the molecule is located adjacent to the amide group which should give hydrogen bonds between the molecules.

To investigate whether the stereogenic centres in **2** could create a helical arrangement in an assembly of the molecules, we conducted a molecular modelling study. A helical arrangement could be driven by a combination of three main forces: (i) The propeller conformation of the phenyl rings with respect to the porphyrin core, (ii) the formation of hydrogen bonds between the amide groups, and (iii) π – π interactions between the cores of porphyrins. For this reason, computations were carried out with the TINKER molecular modelling package [13] and using the MM3 force field [14]. This force field is very accurate to take into account the π – π stacking (between the porphyrin cores) and hydrogen bonds (between the amide groups). To build an infinite helix, a periodic boundary condition was used.



Scheme 1. Synthetic route to the chiral porphyrin (R, R, R, R) -2.

Modelling of the chiral porphyrin **2** in this way gives an *M* helical structure (shown in Fig. 1) which is much more stable than the corresponding *P* arrangement. The stabilization energy in the stack, with respect to the isolated molecule is approximately -59.5 kcal/mol per porphyrin for *M*, and -49.3 kcal/mol per porphyrin molecule in the *P* arrangement. Therefore, the stereogenic centres are clearly able to favour the formation of a single handed helical superstructure in the supramolecular fibres of this compound.

Compound **2** was prepared in its enantiopure (R, R, R, R) form by the stereoselective synthesis shown in Scheme 1. In the first step, 4-hydroxybenzaldehyde was condensed with (*S*)-methyl lactate in the presence of triphenylphosphine and diisopropyl azodicarboxylate to afford (R) -**3** in 65% yield. This aldehyde was then condensed with pyrrole in refluxing propionic acid giving the porphyrin derivative (R, R, R, R) -**4** (15% yield), and amidation with *N*-dodecylamine gave the desired (R, R, R, R) -**2** in 84% yield. The compound was fully characterised by elemental analysis, NMR spectroscopy, mass spectrometry as well as by circular dichroism spectroscopy to check its optical activity.

The self-assembly of sub-monolayer amounts of (R, R, R, R) -**2**, at the air–substrate interface was studied by the acoustic mode Atomic Force Microscopy (AFM) after depositing a drop of a solution of the compound on the freshly cleaved substrate (either graphite or mica) and allowing the solvent to evaporate. The solvent has been shown to play an important role on the aggregation of small molecules upon casting, [15–20] and for this reason we chose to deposit the porphyrin from liquids with very different properties; methanol, toluene and chloroform. These solvents have very different hydrogen bonding capabilities and capacity to enter into interactions with aromatic groups. Toluene is expected to favour hydrogen bonding between molecules more than chloroform, and much more than methanol which is a very good hydrogen bond acceptor and donor [21]. The stacking of aromatic systems is generally believed to be favoured for either very polar [22] or very apolar solvents [23], such as methanol and toluene, respectively. In all cases, when (R, R, R, R) -**2** was deposited on the surfaces areas of higher and lower density were observed because of the non-uniform evaporation of the solvent in the drop, but the general features were similar in the different zones.

Deposition of the porphyrin **2** onto mica from toluene produced morphologies which can be ascribed to dewetting of the system from the hydrophilic surface [24,25]. However, simple dewetting is not the only effect at play in the formation of the layers: In the AFM images (Fig. 3) a clear step corresponding to relatively smooth monolayer and bilayer can be observed: Each increment is 3.5 nm. The bilayer is apparently grown randomly over the monolayer domains.

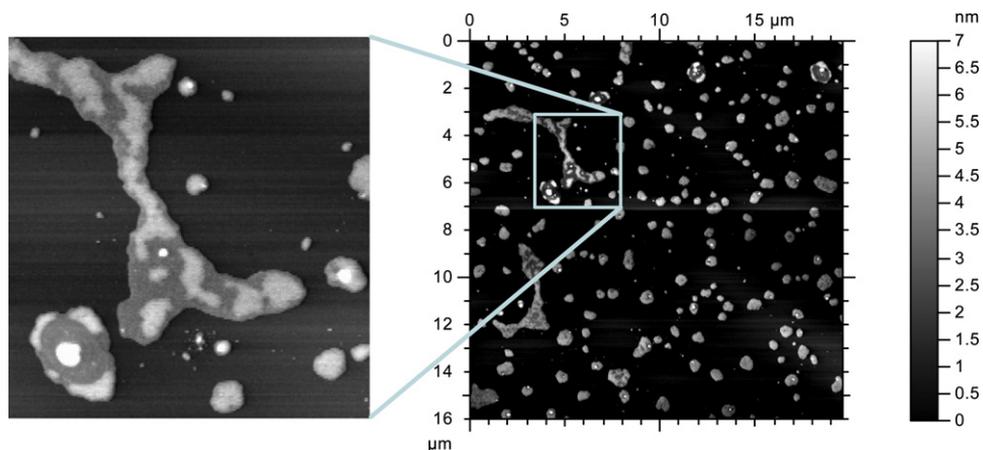


Fig. 3. Topographic AFM image of **2** deposited on freshly cleaved mica from a toluene solution (10^{-4} M).

Furthermore, higher areas corresponding to the deposition of several molecules are observed in some of the islands, as in the circular ones in the image on the left of Fig. 3. No fibres were observed. The molecule measures approximately 0.4 nm thick and a little over 4 nm long in its fully extended form, and therefore we assume that the layers contain molecules oriented practically perpendicular to the surface.

Deposition of the same toluene solution of **2** onto highly oriented pyrolytic graphite (HOPG) reveals a very different morphology to that of the aggregates seen on mica. A monolayer structure is formed with straight fibres growing over the top of it (Fig. 4), along with a few unstructured aggregates (possibly arising from material precipitated in solution). The height of the monolayer structure is around 1.5 nm, and the height of the fibres is of the same order. This data implies that in these aggregates the porphyrins are much more tilted than in the monolayer structure formed on the mica surface, meaning a different supramolecular arrangement, which is evident in the fibrillar morphology of the second layer. No indication of any helical structure was evident in the AFM images. The width of the fibres when imaged by the AFM is approximately 20 nm, which, after tip correction (using the formula $D = 4\sqrt{R_1 R_2}$, where D is the measured width, R_1 is the tip radius – in this case 5 nm – and R_2 is the real fibre radius) corresponds to a width of 5 nm, which would be consistent with a single molecule wide chain if the fully extended form was taken.

From methanol, the porphyrin shows an apparent monolayer on the HOPG with protruding objects which have a measured diameter of approximately 12 nm (Fig. 5). No fibrils were observed. The layer is composed of areas that are 0.6 nm thick and others that are 1 nm thick. These would correspond to porphyrins lying coplanar with the surface, and to either a double layer of this type or a slightly more tilted layer, respectively. The protrusions have a thickness of between 1 and 2 nm above the monolayer. Therefore, their dimensions imply that they could be composed of very few or even single molecules which could be oriented perpendicular to the ones which wet the surface of the hydrophobic substrate.

When deposited from chloroform onto HOPG, **2** forms yet another different morphology; a complex web of short fibres (Fig. 6). The height of the aggregates is only 0.4–0.5 nm, corresponding to the height of the molecule, approximately. It appears, therefore, that the molecule enters into a side-to-side interaction. It should be noted that there is no preferential

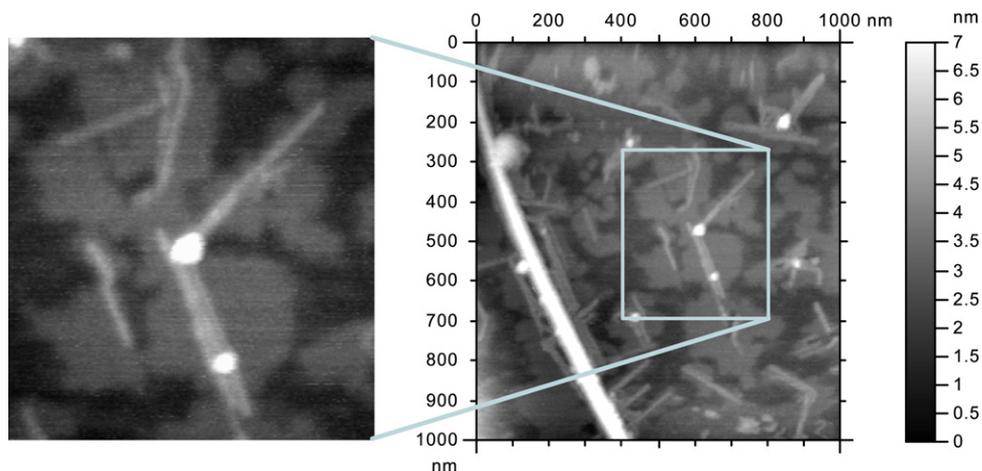


Fig. 4. A topographic AFM image of **2** deposited on freshly cleaved HOPG from a toluene solution (10^{-4} M).

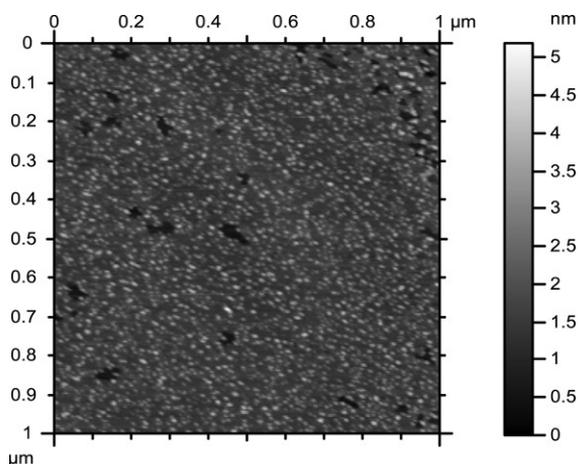


Fig. 5. Topographic AFM image of **2** deposited on freshly cleaved HOPG from a methanol solution (10^{-4} M).

orientation of the fibres (as proven by FFT analysis), a surprising observation given that there are four alkyl chains on the molecule which are presumably in contact with the surface in this coplanar arrangement of the molecules with respect to the surface. This might indicate assembly in solution prior to deposition [20], an idea backed up by variable concentration nuclear magnetic resonance studies of the compound in CDCl_3 , which do indicate aggregation.

2. Conclusions

The deposition of porphyrin derivative **2** onto graphite from different solvents leads to diverse superstructures at the surface after evaporation of the liquid. From toluene, the orientation of the molecule in the monolayer is tilted with respect to the surface with fibres growing over the top, while in chloroform very fine flat fibres are imaged, and from methanol a complex mixture of orientations of the molecules with respect to the surface is measured. All of these situations seem qualitatively different from morphologies seen for other porphyrins cast onto flat

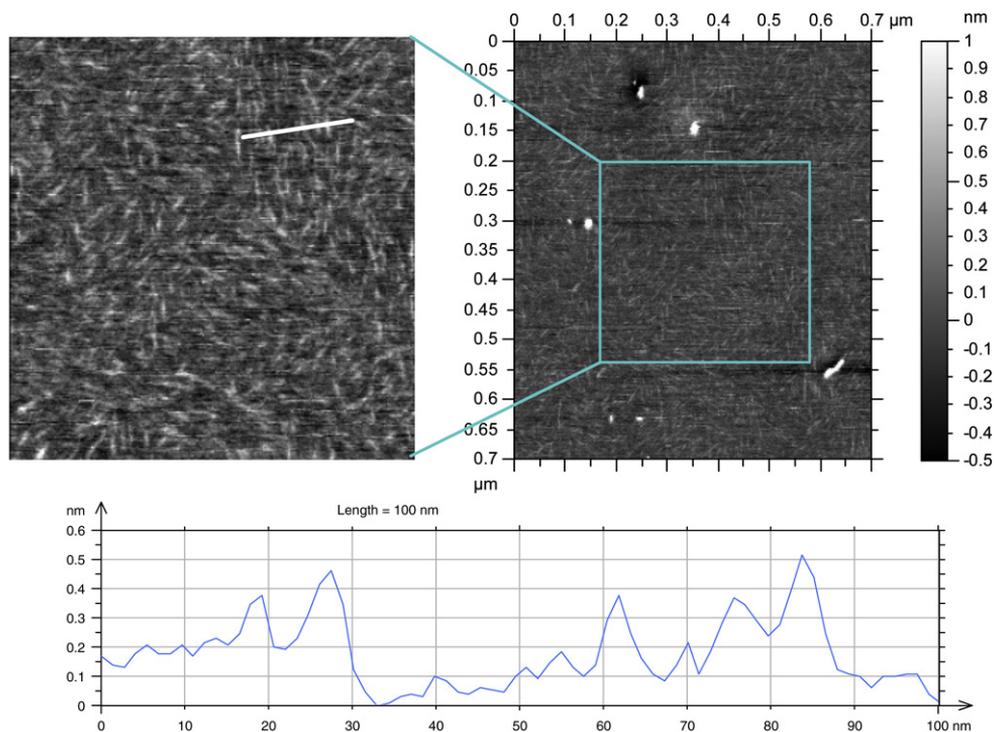


Fig. 6. Topographic AFM image of **2** deposited on freshly cleaved HOPG from a chloroform solution (10^{-4} M).

surfaces [26,27], although it should be pointed out that the structure of the substituents attached to the porphyrin described here is quite different from these literature precedents.

This situation is clearly a result of the modification of the interactions of the molecule with itself and with the surface when using different solvents. While molecular modelling implies that helical arrangements in fibres should be available upon aggregation, it appears that in the systems tried up to now the molecule–molecule interaction is not sufficient to overcome the effects of the surface on evaporation. However, it is clear that non-covalent interactions are playing a very important role in the morphology of the films, which are new and intriguing. We are presently varying the molecular composition and constitution in order to explore the origins of these effects.

Acknowledgements

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