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Irreversible or reversible self-assembly procedures yield robust zirconium (IV)-porpyrinphosphonate cones or μm-long fibers of monomolecular thickness

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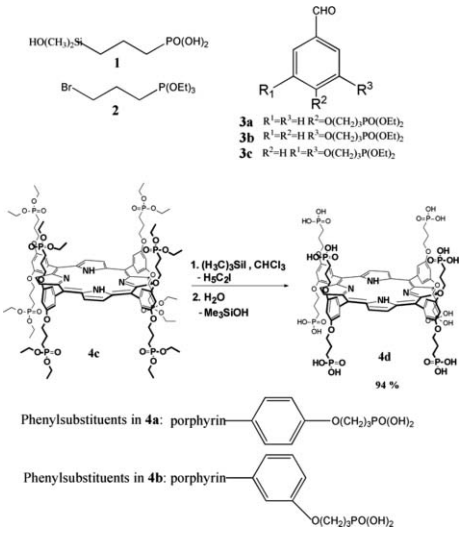
Stepwise, irreversible self-assembly of porphyrinphosphonates by zirconium(IV) produces cones of 20 nm height and similar widths. Side-on growth cannot be prevented. Reversible fiber growth without metal ions gave micrometer long fibers on mica of 2 nm width, because charge repulsion allowed only for end-on growth.

Molecular assemblies of metalloporphyrins are useful for the collection, conduction and conversion of light and redox energy. All three processes may be studied and optimized in organized molecular stacks on smooth electrodes with the tips of scanning electron microscopes (SFM), which may mechanically manipulate, electrochemically oxidize and instrumentally measure currents and photocurrents. Porphyrins have been deposited on smooth substrates as molecular monolayers,[1–3] multilayers[4,5] or as heterodimers in nanometer gaps of rigid monolayers.[6] Attempts to produce isolated porphyrin elevations suitable for AFM and STM manipulations failed, however. The intermolecular forces applied, namely dipolar and electrostatic interactions between axial ligands and central metal ions, were too weak to avoid the dissipation of porphyrin stacks on the solid substrate.[7–9]

We report here on hard porphyrinphosphonate particles on silicon wafers, which were covered by silylphosphonate **1** and on the hydrogen bond assisted assembly of ultrathin fibers on mica.

For the preparation of stable nanometer-sized objects we chose four zirconium(IV)-phosphonate bonds each on both sides of the porphyrin plane as a cement.[11,12] Phosphonate and zirconium(IV) ions are known to fit perfectly together in crystals of bolaamphiphiles.[13,14] **4a–d** were prepared from pyrrole and 3,5-dihydroxybenzaldehyde (Scheme 1). The bis-phenol was dialkylated with (3-bromopropyl)-phosphonic acid diethylester **2**,[15] and **3 a–c**, which was then refluxed with equimolar amounts of pyrrole in propionic acid to give the ethylester **4c** in 7–10% overall yields. Its hydrolysis to the octaacid **4d** was achieved using first iodotrimethylsilane at −40° C, followed by treatment with water[16] at room temperature. The phosphonate-covered wafer was then treated with an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ for 15 minutes, followed by an aqueous solution of porphyrin **4d**. Washing and repeated alternating treatment of the wafer with $ZrOCl_2$ and aqueous solutions of porphyrin **4d** yielded ill-defined porphyrin multilayers only. No island-like structures were detected in AFM pictures.

Transmission electron micrographs (TEM) of dried aqueous suspensions of **4d** on carbon grids before and after addition of $ZrOCl_2 \cdot 8H_2O$ also showed no extended fibers, only crystallites. Four self-assembly cycles using acetonitrile solution of **4d** alternately with $ZrOCl_2 \cdot 8H_2O$ yielded a rocky landscape corresponding to a high density of porphyrin assemblies. The average height was 10 nm, the maximum height about 30 nm. The density of porphyrin objects was, however, so high that no individual manipulation with the AFM tip was possible. We therefore developed an efficient capping procedure using upright-standing crystallites of Alizarin S,[17] which is also a good ligand for zirconium(IV) The desired number of about ten islands per 10^4 nm^2 was thus achieved. The shape of individual objects remained unchanged for several months on the silicon wafer's surface. Transmission electron microscopy (TEM) of the surface of AFM tips which had been in contact with the porphyrin **4d** coatings showed some pyramids with a height of about 10–20 nm and a width of about 10 nm at the base. Attempts to produce thin and high towers by stepwise self-assembly failed. We then investigated the possibility of attacking and moving individual objects with the AFM tip in the tapping mode.[10] It was found,



Scheme 1

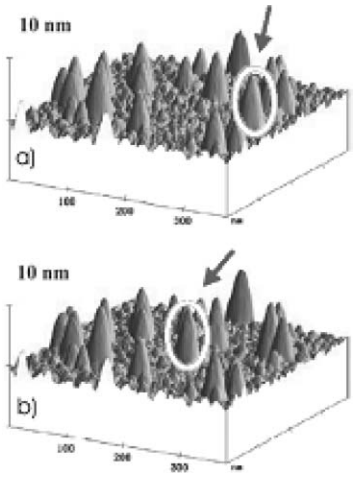


Fig. 1 Porphyrinphosphonate **4d**–zirconium(IV) multilayered rocks on silicon substrates covered with bolaamphiphile **1**, Zr(IV) and Alizarin S. The rock indicated by the arrow was moved by 200 nm with the AFM tip in the tapping mode. The width of the rocks is about 40 nm at the base.

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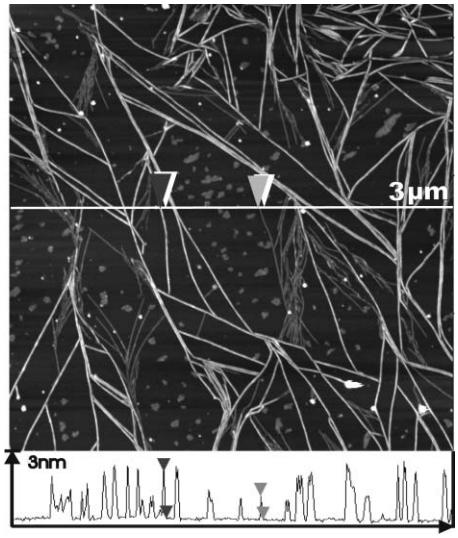

Fig. 2 SFM (tapping mode) of fibers obtained from a basic solution of porphyrin **4d** (pH 13) on mica.

that the 20 nm high objects slid on the Alizarin S ground or, in some cases, broke. Fig. 1 shows a typical 200 nm displacement. There was no change of shape or shift of neighboring objects or a dragging trace in the Alizarin S layer. The porphyrin rocks obtained are rigid enough to survive all kinds of surface modification.

For the construction of porphyrin wires we avoided heavy metal cements and connected the phosphonate groups simply by hydrogen bonds. This was most successful on a mica surface. We prepared a hot solution of the porphyrin-phosphonates **4b** and **4d** at pH 12 (NaOH), removed aggregates by ultrafiltration and applied the 10^{-4} M solution directly to freshly cleaved mica. A short-lived monolayer of flat-lying porphyrins was thus formed on the hydrophilic surface of mica. It was 0.5 nm thick and hydrophobic as shown by phase contrast AFM. Upon longer standing this monolayer broke up completely to form micrometer-long fibers with the desired uniform height of 2.8 nm corresponding to the diameter of a single porphyrin molecule (Fig. 2). These rigid, linear fibers constitute the thinnest and longest non-covalent porphyrin wires reported so far. They are obtained in quantitative yield and proved to be stable on mica for several months. Observed helicity is probably an AFM artefact.[18]

The model of Fig. 3 illustrates the differences between the irreversible growing process initiated by stepwise additions and phosphonate and zirconium(IV) salts and the reversible formation of polyanionic fibers, which are stabilized by weak hydrogen bonds and van der Waals forces only in co-facial arrangements at the ends of the growing fibers.

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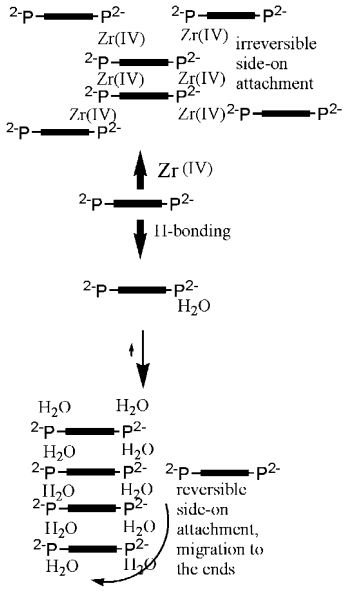

Fig. 3 Model of irreversible growth of porphyrinphosphonate rocks and fibers of monomolecular thickness.

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