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[9] In addition, the terminal oxide is enriched by approximately 50 % with ^{18}O, presumably by an acid-catalyzed exchange with ^{18}O-enriched water produced in the oxidation of tetrahydrofuran.

[10] Of the three major oxidation products, two have been identified as 2-methyl-1,3-dioxane and γ-butyrolactone. The identity of the third product and the reaction mechanism of the oxidation reaction are under current investigation.

[11] Although not proposed, the reaction could proceed by a similar route via a superoxovanadium(V) intermediate. Here, however, in contrast to the reaction depicted in Scheme 2, the hydroxovanadyl(IV) species itself acts as reducing reagent, therefore rendering bis(oxo)vanadium(V) and oxoperoxovanadium(V) complexes in equimolar amounts.

[12] Preliminary ESR studies with partially ^{17}O-enriched superoxo complex have shown that at $-30\,^{\circ}$C the superoxide unit is either symmetrically side-on-bound or that an end-on-bound superoxide undergoes a rapid rearrangement reaction, interchanging the bound and the unbound oxygen atoms faster than the ESR time scale.

Self-Assembly and Manipulation of Crown Ether Phthalocyanines at the Gel–Graphite Interface**

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The design, synthesis, and manipulation of supramolecular structures having well-defined geometries are great challenges. Such structures have possible applications in diverse fields such as materials science, molecular electronics, and sensor development.[1–3] The major source of inspiration for the generation of supramolecular architectures is the biological world.[4] On the other hand, new synthetic routes need to be developed that allow the constriction of molecular systems in such a way that the desired arrangements of components is obtained on the nanometer scale.[5, 6] Phthalocyanines (Pcs) constitute a widely investigated class of compounds which are interesting building blocks for the construction of supramolecular architectures.[7–11] Phthalocyanines have been self-assembled in solution and they can be deposited by using the Langmuir–Blodgett (LB) technique[9, 11] as well as by sublimation in ultra-high vacuum (UHV).[8, 12–14] The deposited assemblies have been visualized using scanning force microscopy (SFM)[11, 12] and scanning tunneling microscopy (STM).[13, 14]

Herein we report on the self-assembly and manipulation of monomeric Pcs from gels into layers at surfaces, studied by STM imaging. The Pcs (such as **1**) are functionalized with four benzocrown ether rings, which are each disubstituted with enantiomerically pure (*S*)-3,7-dimethyloctyl chains. The peculiar physicochemical properties of these chiral molecules arise from the fact that 1) they have an extended π-conjugated core which plays a key role in the charge-transfer properties of stacked Pcs; 2) they contain crown ethers which can host alkaline ions, and 3) they possess alkyl side chains which can induce a liquid crystalline behavior. In organic solvents **1** forms a gel in which helical fibers are present. The helicity of these fibers, which are composed of Pc stacks, can be tuned by the addition of alkaline ions, namely K^{+}.[15] The overall diameter of the fibers is equal to the diameter of the Pc discs with extended tails (6 nm), and the distance (*d*) between two Pc discs is 0.335 nm.

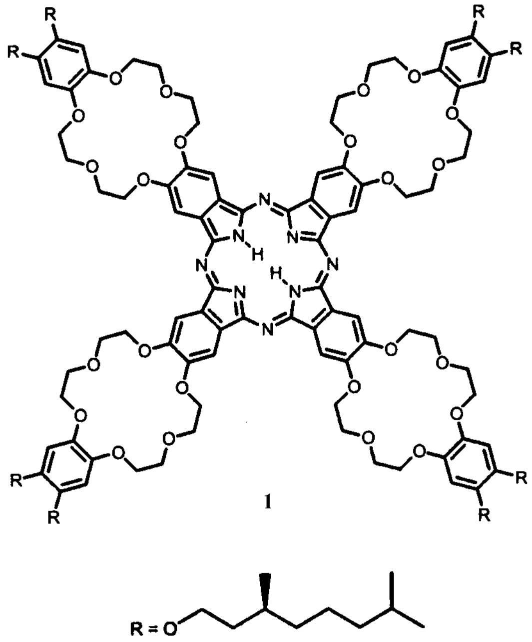

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Figure 1 shows sub-molecularly resolved STM images of the monomeric **1** moieties self-assembled at the interface between a gel and highly oriented pyrolitic graphite (HOPG). The molecular arrangement comprises two "face-on" phases (1 and 2 in Figure 1 a), and one "edge-on" lamellar phase (3 and 4 in Figure 1 a).

The "edge-on" lamellae, which are made up of π–π stacked Pcs (Figures 1 b and 2) exhibit widths (*w*) of (4.7 ± 0.2) nm (Figure 1) and lengths up to hundreds of nanometers (image

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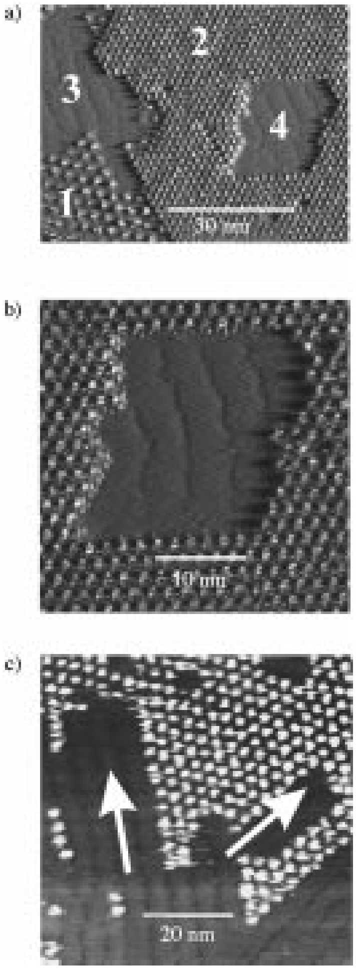

Figure 1. STM images of **1** at the gel–HOPG interface: a) and b) current image ($U_t = 0.58$ V, average $I_t = 53$ pA), c) height image ($U_t = 0.58$ V, average $I_t = 53$ pA). Image a exhibits four main features: a thermodynamically stable, relatively loosely packed hexagonal lattice (1), a metastable, more densely packed hexagonal phase (2), lamellae (3)—which are also visible in the area 4 where this molecular order has been induced by the STM tip. A zoom-in of area 4 revealing the π–π stacked Pcs forming the lamellae is shown in b. In image c the large hexagonal lattice is aligned along the main axes of the lamellae which are marked by the white arrows.

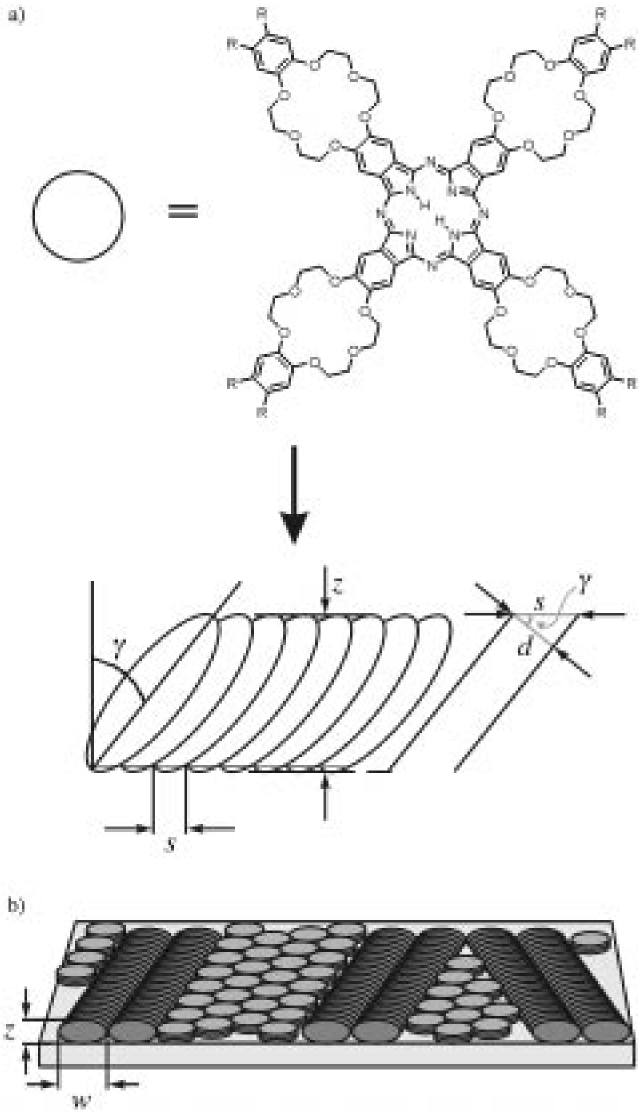

Figure 2. Schematic representation showing the packing of molecules of **1** at the solid–gel interface. a) Single Pcs are stacked forming a lamellar architecture with an intralamellar spacing (s) and a tilt angle with respect to the surface (γ). The thickness (z) of the lamellar layer can be calculated by assuming a typical π–π stacking with distance d between two discs. b) The surface of the HOPG is coated with molecules packed in both "edge-on" (lamellae) and "face-on" structures. The latter packing can also exist in an isolated object at the lamellar boundaries. The lamella width (w) is indicated.

not shown). The distance (d) between two Pc discs is expected to be 0.335 nm in the case of a typical π–π stacking interaction. The intralamellar spacing (s) between neighboring monomeric discs, however, is (0.44 ± 0.03) nm, as determined from the STM profiles on images such as Figure 1 b. This value suggests that the molecules are tilted from the normal by an angle γ, which can be calculated from $d/s = \cos\gamma$ to be 40°. For a molecular structure of the loosely packed hexagonal phase (see below) having an average unit cell vector of $a = (3.5 \pm 0.2)$ nm, the total area occupied by a molecule amounts to $a^2 \sin 60° = (10.6 \pm 1.2)$ nm^2. Given the lamellar widths (w) of (4.7 ± 0.2) nm, in the approximation of a rectangular shaped molecule packed "edge-on", the thickness (z) of the lamellae self-assembled on HOPG can be calculated to be $(10.6/4.7)$ nm $= (2.3 \pm 0.4)$ nm. Since the conjugated core has a diameter of about 1 nm, the remaining part of the lamella, which has a thickness of roughly 1.3 nm, consists of aliphatic moieties. It is worth noting that the possibility of tunneling electrons through such a 2.3 nm-thick layer of the lamellar phase indicates a remarkable conductivity of the hybrid saturated–unsaturated molecule in the direction parallel to the disc. These lamellar architectures, which have also been observed at the solution–HOPG interface (image not shown), are similar to the tubular nanostructures monitored by SFM in LB films of other Pc derivatives.[11]

Interestingly, the lamellar phase coexists with two different hexagonal phases (1 and 2 in Figure 1 a): A metastable phase with a cell of $a = (1.83 \pm 0.02)$ nm and $\alpha = 60°$, which disappears after a couple of hours, and a more loosely packed, almost hexagonal structure with $a = (3.4 \pm 0.2)$ nm, $b = (3.7 \pm 0.2)$ nm, and $\beta = (56 \pm 4)°$, which is more stable and lasts for at least several days. In both these arrangements the conjugated discs are oriented "face-on" on the basal plane of the graphite substrate. These phases are similar to the ones observed recently for a simpler Pc derivative at the HOPG–solution interface.[16] In our case the dimensions of the crystal lattices indicate that in both "face-on" packings the lateral substituents (crown ethers and aliphatic chains) are not fully extended, and thus adopt a coiled conformation. The main lattice axes of the thermodynamically stable phase are aligned along the main lamella directions (white arrows in Figure 1c and shown schematically in Figure 2), whereas the spacings of the two structures in the *xy* plane are not in registry. By raising the average tunneling current and decreasing the applied voltage one can increase substantially the forces exerted by the STM tip on the organic film. This process allowed us to manipulate the film of **1** at the molecular level. A structural rearrangement from the small hexagonal lattice ("face-on") to the lamellae ("edge-on") could be induced. After returning to the standard imaging condition of the adsorbate, the manipulation was visible in area 4 in Figure 1a, which indicated the occurrence of mechanochemical switching. The "face-on" oriented molecules in Figure 2a are present both as packed crystals with sizes of hundreds of square nanometers and as isolated objects embedded where defects in the lamellar structure are located, that is, at lamella boundaries. This unusual type of molecular inclusion in a tightly packed lamellar array, together with the high viscosity of the gel phase, may be the reason for the markedly low mobility of the single Pc molecules, which differs from results obtained in previous studies on Pc films grown and characterized in UHV.[14]

In STM height imaging (Figure 1c) a feedback loop controls the vertical position of the tip in such a way that a preset tunneling current flowing between the substrate and the tip is maintained constant while the tip scans in a horizontal plane above the sample. Since the conductivity of columnar stacks of Pcs is higher through the stacks than perpendicular to the stacks,[9c] the thickness of the self-assembled "face-on" phase in the tip–substrate gap is probably larger than the 2.3 nm distance discussed above for the lamellae. This means that the first type of architectures consists of stacks of Pc discs. Unfortunately, however, this type of measurement does not allow a determination of the exact number Pcs in the stacks.

The low mobility of the Pcs at the surface is of particular interest for future scanning tunneling spectroscopy investigations on single Pc molecules or stacks of them. Moreover, STM investigations at the solid–gel interface as presented here have a great advantage over the well-established method of performing studies at the solid–liquid interface,[17] because of the greater stability of the former gel phase (up to several days). We believe that this approach can be extended to a large variety of low molecular mass molecules which can form gels.

In summary, we have shown that the interplay of intramolecular, intermolecular, and interfacial forces can be used to construct highly organized two- and three-dimensional architectures from phthalocyanine building blocks at the gel–HOPG interface. The switching between different nanostructures co-existing at the surface can be stimulated with the tip of the STM with a resolution on the molecular scale. These results should be of interest for future applications in areas such as molecular electronics, optoelectronics, and sensor development.

Experimental Section

Scanning tunneling microscopy: The STM investigations were carried out with a home-built beetle-type, low-current STM.[18] A drop of an almost saturated solution of **1** in a 50:1 mixture of $CHCl_3$ and 1,2,4-trichlorobenzene (Aldrich) was applied to a freshly cleaved HOPG substrate. Evaporation of the solvent occurred slowly and gave rise to the slow (on a time scale of several hours) formation of a stable gel phase adsorbed on HOPG, which was visible to the naked eye. By varying the tunneling parameters, namely, decreasing the voltage and increasing the average tunneling current, it was possible to visualize the HOPG lattice underneath the gel and therefore to calibrate the piezo in situ. This procedure was also used to induce a structural rearrangement in domain 4 of Figure 1. The tunneling tips were mechanically cut from a 0.25 mm Pt:Ir (80:20) wire. Unit cells and backbone spacings were averaged using several images after their correction for the piezo drift (using a scanning probe image processor (SPIP), Version 1.720, Image Metrology ApS, Lyngby, Denmark).

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