Perfectly Straight Nanostructures of Metallosupramolecular Coordination-Polyelectrolyte Amphiphile Complexes on Graphite**

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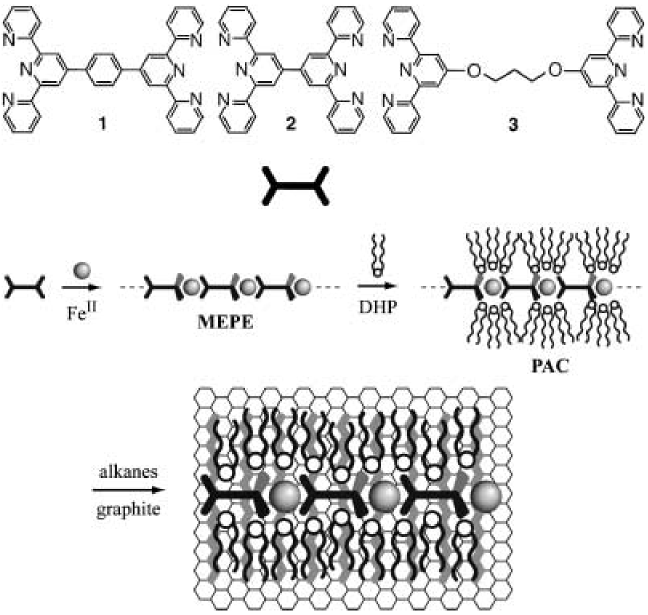
The progression of structural hierarchy from the atom to the molecule, the supermolecule, and the supramolecular assembly corresponds to an increase in diversity and complexity.[1] At each level of the hierarchy, characteristic structural or functional features emerge that do not exist at lower levels. Multistep auto-assembly of architectures with structures of different length scales has, therefore, become a central objective in supramolecular chemistry and materials science.[2] Important advances toward this goal were reported, particularly in the domain of metal-ion-induced superstructures.[3] The intriguing prospects of supramolecular devices and materials have, in addition, stimulated research in this area recently.[4] To address, manipulate, and operate functional devices individually at the nanoscopic level it is particularly interesting to assemble them on a surface.[5]

We have developed a modular approach based on metallosupramolecular coordination polyelectrolytes (MEPEs)[6] and the corresponding polyelectrolyte–amphiphile complexes (PACs)[7] that provides a facile entry towards hierarchical architectures. These materials are readily self-assembled from metal ions, ditopic ligands, and amphiphiles as shown in Scheme 1. The composition of PAC-**1** formed under the particular assembly conditions is such that six dihexadecyl phosphate molecules (DHPs) bind per repeat unit.[8] Presumably, DHPs form a charged hydrogen-bonded network, which binds to the MEPE through electrostatic interactions as schematically depicted in Scheme 1. In contrast, the composition of PAC-**2** and PAC-**3** are such that two DHPs bind per repeat unit. The association of MEPE and DHP has a profound impact on the properties of the final material. PACs dissolve in common organic solvents spread at the air–water interface[8] and form thermotropic liquid-crystalline mesophases.[9] Herein we describe the self-assembly of perfectly straight and epitaxially oriented nanostructures of PACs based on the multicomponent sequential self-assembly process depicted in Scheme 1.



Scheme 1. Metal-ion-induced self-assembly of iron acetate and ditopic bisterpyridines, **1**, **2**, and **3**, results in metallosupramolecular coordination polyelectrolytes (MEPEs). A linear, positively charged macromolecule is formed as a consequence of the octahedral coordination geometry (indicated by the wedges). Sequential self-assembly of MEPE and dihexadecyl phosphate (DHP) gives the polyelectrolyte–amphiphile complex (PAC). Finally, PAC and alkanes auto-assemble on graphite. The bottom part schematically depicts the proposed model for the resulting nanostructures (simplified representation, not to scale). The alkanes (thick rods) adsorb epitaxially on the lattice of the basal plane of the underlying graphite surface. This alkane monolayer serves as a template for orienting the rigid rods of type PAC-**1** and PAC-**2**.

In a first series of experiments, submonolayers of PACs were spin-coated on bare graphite. Tapping-mode scanning force microscopy (SFM) images (not shown) revealed 2D objects with an average diameter of about 100 nm which one could ascribe either to single long coiled polymers or, alternatively, to aggregates of a few shorter polymer molecules. The objects made from PAC-**1** and PAC-**2** exhibit relatively short (< 50 nm) straight chain segments, while PAC-**3** is completely coiled, which indicates that the flexible spacer in **3** hinders the formation of straight rods. Spin-coating a dilute solution of a mixture of PAC and a long chain alkane at a mass ratio around 1:10 then leads to perfectly straight nanostructures of PAC-**1** and PAC-**2**, with lengths up to 200 nm being obtained. Figure 1 shows SFM images of a submonolayer of PAC on top of an alkane monolayer. Imaging the bottom layer reveals regular highly ordered lamellae, which are characteristic for self-assembled monolayers of alkanes on graphite (Figure 1b, inset).[10] The long chain alkanes seem to preferentially wet the graphite surface, while the PACs assemble on top of the interface and became oriented parallel to the alkane lamellae axis and, therefore, 30° relatively to a graphite lattice axis.[11] We note that the distance between the PAC rods is always (5.5 ± 0.3) nm, irrespective of the length of the alkanes utilized, which indicates that the alkane layer orients and straightens the PAC, but does not determine the distances between adjacent PACs. The width of the PAC can be as large as 6 nm if the alkyl chains are fully extended. We, therefore, conclude that the imaged objects correspond to individual PAC rods.

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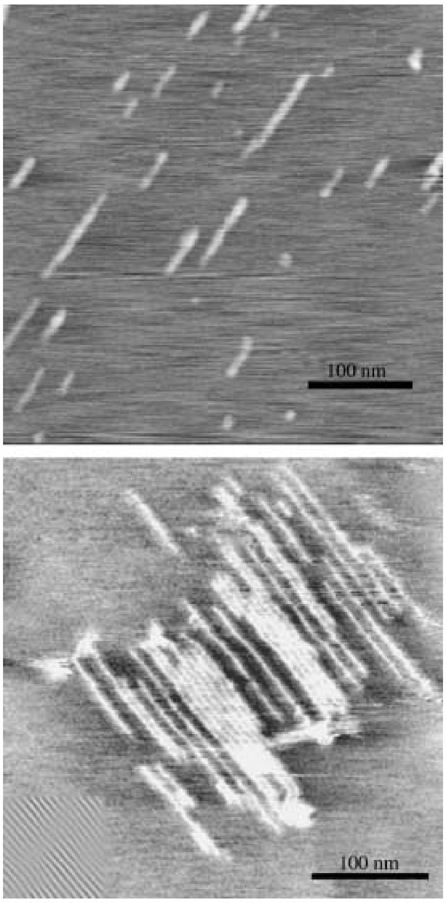

Figure 1. Top: Representative SFM image of PAC-**1** adsorbed in the presence of $C_{32}H_{66}$ on the basal plane of graphite. Bottom: SFM image of a sample prepared from about twice the concentration and recorded with harder tapping than usual. The bottom layer consists of regular ordered lamellae of the self-assembled alkane monolayer (inset shows a filtered image of a part of the surface with the pure alkane monolayer). Perfectly straight PAC rods are observed on top of the alkane template layer.

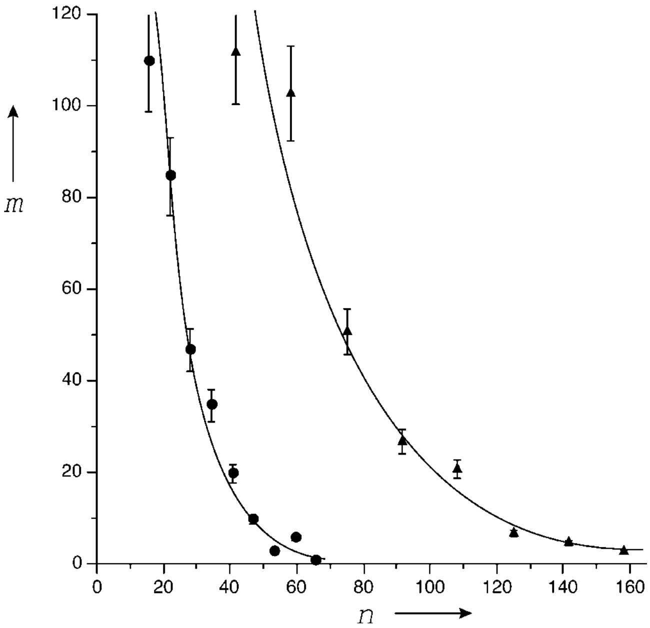

Figure 2. Experimental length distribution of PAC-**1** (▲) and PAC-**2** (●) determined by SFM and calculated length distribution (——) based on binding energies of $21.5\,k_BT$ (53.4 kJ mol^{-1}, PAC-**1**) and $19\,k_BT$ (47.2 kJ mol^{-1}, PAC-**2**). n = number of repeat units, m = occurrence.

The distributions of rod lengths P of PAC-**1** and PAC-**2** are displayed in Figure 2 for rods which were longer than 30 nm. The error bars indicate the statistical error of each data point. If an association equilibrium is assumed, the length distribution P of assemblies is given by $P \cong C_n = e^{-\alpha} n (C_1 e^{\alpha})^n$, where n is the number of repeat units in an assembly, α is the binding energy per repeat unit in units k_BT, and C_n is the concentration of assemblies consisting of n monomers.[12] The resulting total concentration is then given by $C = \sum_{n=1}^{\infty} C_n = \frac{C_1}{(1-C_1 e^{\alpha})^2}$. By combining the two equations, one can solve for the binding energy α since the concentration C is known and C_n is determined experimentally. The resulting binding energies are $(21.5 \pm 1)\,k_BT$ (53.4 kJ mol^{-1}) for PAC-**1** and $(19 \pm 1)\,k_BT$ (47.2 kJ mol^{-1}) for PAC-**2**.[13] We propose that coordination of the metal ion is the major contributor to the overall binding energy for two reasons: first, the cohesive energy of alkanes is much smaller compared to metal ion coordination and, second, it is further reduced because two or six DHPs per repeat unit cannot form a continuous close-packed structure. Additional evidence is provided by the observation that ordering by the amphiphiles is not strong enough to induce orientation of the flexible PAC-**3**. A possible contribution of DHP to the overall binding energy might be reflected in the fact that PAC-**1** (6 DHPs) has a slightly higher binding energy than PAC-**2** (2 DHPs). Within the experimental error, the binding energies of both PACs are in agreement with that of mononuclear bisterpyridine Fe^{II} complexes in solution, which suggests that the assumption of an association equilibrium proposed above is reasonable.[14]

The observations can be explained by the following model. In the absence of alkanes, PACs are not oriented because the potential ripple of the graphite surface is very small.[11b] Immediately after spin-coating, the PACs are still mobile—since traces of remaining solvent facilitate molecular diffusion—which results in interfacial reorganization including polymerization and/or aggregation up to a point when all the solvent has evaporated. The PACs are now immobilized and can be visualized with SFM. In contrast, co-adsorption of PAC and alkanes results in perfectly straight PAC rods because the alkane molecules can form a stable, highly ordered monolayer at the solid/liquid interface[10] and the surface potential ripple of an alkane monolayer is larger than that of a graphite surface (see also ref. [11d]). We, therefore, propose that the PAC and alkane molecules co-assemble at the interface such that the alkane molecules act as a template to orient the PACs.

It is interesting to note that the lengths of the PACs directly adsorbed on graphite are much longer than if they are co-adsorbed with alkanes, which reflects a higher concentration of PAC at the surface than in solution. In fact, the average length of self-aggregating macromolecules with a binding energy of $21.5\,k_BT$ or $19\,k_BT$ at the same concentration as observed at the surface should be around 560 and 270 nm, respectively, which is indeed of the order of the total contour lengths of PAC-**1** and PAC-**2** on bare graphite. On the other hand, at the solution concentration the equilibrium chain lengths are expected to be 56 and 27 nm for PAC-**1** and PAC-**2**, respectively, which correspond approximately to the actual average PAC lengths adsorbed in the presence of alkanes. Therefore, we suggest that the length distribution of PACs in solution is preserved upon co-adsorption of PAC and alkanes. Apparently, PACs and alkanes co-assemble at the interface without interfacial reorganization.

In summary, almost perfectly straight and epitaxially oriented chains of metallosupramolecular coordination-polyelectrolyte–amphiphile complexes formed from rigid ditopic metal ion receptors are self-assembled on the basal plane of graphite by using long chain alkanes as an orienting template layer. Through a sequence of molecular recognition steps comprising metal ion coordination, electrostatic interactions, and amphiphilic self-assembly the adsorption of nanoscopic assemblies can be performed at an interface in a predictable manner. Controlling the correlation of position and orientation is of paramount importance for encoding new properties and functions.[15] On-going research in our laboratories indicates that this approach is of general utility. The modularity of this approach provides an entry to encode the value-adding physicochemical properties of metallosupramolecular devices into nanoscopic architectures that can be addressed and manipulated individually by scanning probe techniques.

Experimental Section

Ligands **1**, **2**, and **3** were prepared according to literature procedures.[16] The assembly of MEPE and PAC was carried out according to previously published procedures.[8] Alkanes ($C_{32}H_{66}$, $C_{44}H_{90}$, $C_{50}H_{102}$, Aldrich) were used as received. Solutions of neat PACs ($1.3\times10^{-3}\,\mathrm{g\,L^{-1}}$) or mixtures of PAC ($1.3\times10^{-3}\,\mathrm{g\,L^{-1}}$) with $C_{32}H_{66}$, $C_{44}H_{90}$, $C_{50}H_{102}$ ($1.3\times10^{-2}\,\mathrm{g\,L^{-1}}$) were spin-coated onto the basal plane of highly oriented pyrolytic graphite (HOPG, Advanced Ceramics Co., USA, quality ZYH at 40 rps). The coated graphite samples were dried for 10 min at 40 °C before SFM investigations were carried out with a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) in the tapping mode. An E-scanner over a range of scan lengths from 5 to 0.3 μm, and commercial Si cantilevers (length 125 μm and width 30 μm) with spring constants between 17 and 64 N m^{-1} were used.

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$(C_2H_{10}N_2)[Cr(HPO_3)F_3]$: The First Organically Templated Fluorochromium(III) Phosphite**

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In recent years the search for new open-framework materials with transition metal elements has become the focus of much interest due to the potential application of these materials as absorbents, ion exchangers, solid-state electrolytes, and catalysts in heterogeneous catalysis.[1] Such applications are not possible with main group systems of tetrahedral framework zeolites. The syntheses of these materials usually involve organic templates, for example organic diamines, for generating large cavities and are performed under mild hydrothermal conditions to avoid the formation of dense phases.

Microporous behavior has been successfully extended to the phosphate and arsenate systems of at least 14 elements of the periodic table, but examples dealing with chromium have not been reported.[1b,2] The pattern of behavior of these kinds of compounds is underpinned by the strength of the P–O

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