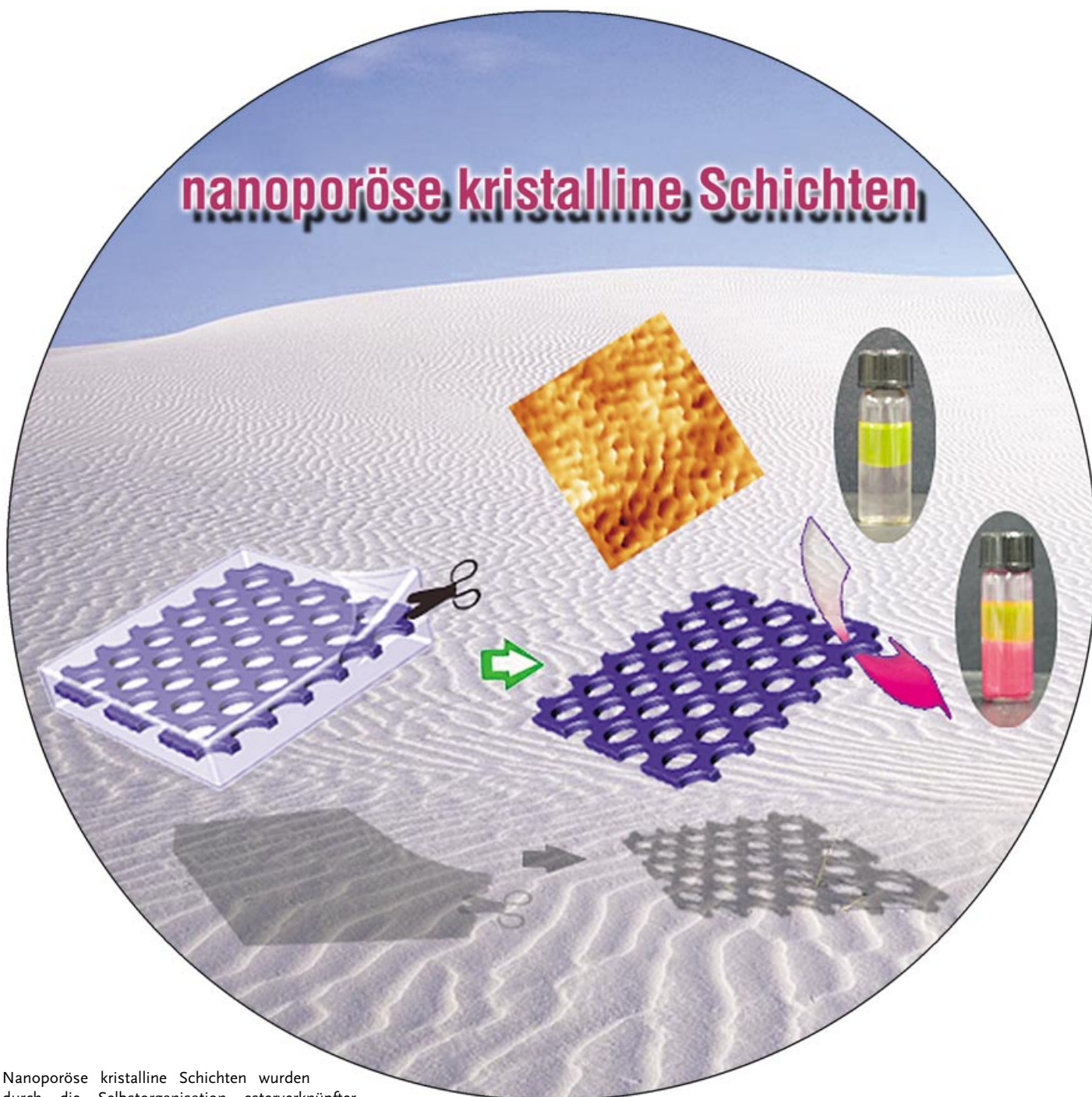


Zuschriften

nanoporöse kristalline Schichten



Nanoporöse kristalline Schichten wurden durch die Selbstorganisation esterverknüpfter Stab-Knäuel-Moleküle zu einer durchbrochenen Struktur erhalten. Nach Hydrolyse der Esterbindungen und Entfernen der Knäuelsegmente verblieb eine kristalline Schicht mit Nanoporen, die unpolare Farbstoffe wie Nilrot einlagern und aus einer Hexanlösung in die wässrige Phase überführen können. Details dazu enthält die Zuschrift von M. Lee et al. auf den folgenden Seiten.

Supramolecular Crystalline Sheets with Ordered Nanopore Arrays from Self-Assembly of Rigid-Rod Building Blocks**

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The design and construction of well-defined nanoporous materials is an area of great interest, because they have broad applications in catalysis, lithography, membrane filtration, and ion-selective membranes.^[1–6] Development of such well-defined porous materials requires the rational design of molecular components that are programmed to assemble through noncovalent intermolecular forces. We previously demonstrated that self-assembled structures based on rod building blocks could be manipulated through attachment of flexible parts with different lengths to their ends.^[7] Depending on the relative length of the rigid segments, these blocks self-assemble into perforated supramolecular layers with in-plane, ordered coil perforations that are able to self-organize into a three-dimensional (3D) hexagonal superlattice.^[8] One can envision that selective removal of coil segments from this ordered structure would provide a novel strategy to generate nanoporous layered materials with in-plane nanopore arrays.

Here we report the preparation of supramolecular crystalline sheets with in-plane nanopore arrays by hydrolysis with aqueous KOH and subsequent removal of coil segments from the perforated layered structure (Figure 1). The synthesis of a self-assembling rod-coil molecule consisting of penta-*p*-phenylene and poly(propylene oxide) was performed in a stepwise fashion starting with esterification of poly(propylene oxide) and 4-bromobenzoic acid, and continuing with Suzuki cross-coupling to generate the rod building block. The rod-coil molecule was characterized by ¹H and ¹³C NMR spectroscopy, elemental analysis, and gel-permeation chromatography (GPC) and shown to be in full agreement with

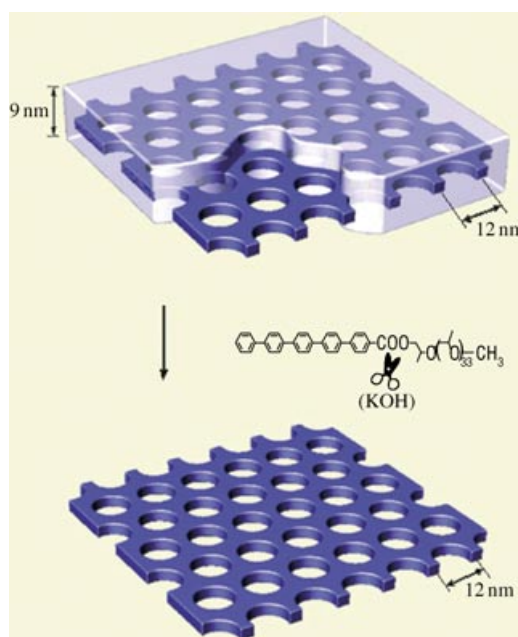


Figure 1. Preparation of supramolecular porous crystalline sheets by selective removal of coil segments from a perforated layer structure.

the structure presented. The ester linkage grafting the rod and coil segments can be easily cleaved by hydrolysis with alkali metal hydroxide solution.

The rod-coil compound melts into an isotropic liquid at 203 °C, as evidenced by differential scanning calorimetry (DSC) and thermal optical polarized microscopy. The TEM image of a microtomed film of the material (stained with RuO₄) showed a honeycomblike supramolecular structure with a hexagonal array of light coil perforations in a dark rod matrix (Figure 2a). Small-angle X-ray scattering (SAXS) measurements showed a number of well-resolved reflections, which can be indexed as a 3D hexagonal order (*P*6₃/*mmc* space-group symmetry) with lattice constants *a* = 12.7 and *c* = 18.0 nm (Figure 2b).^[8] The diameter of a perforation, determined from the lattice constants and density measurements, appeared to be 9 nm, consistent with the TEM analysis.

Wide-angle X-ray diffraction patterns showed three sharp reflections (Figure 3a), that is, the rod segments are packed

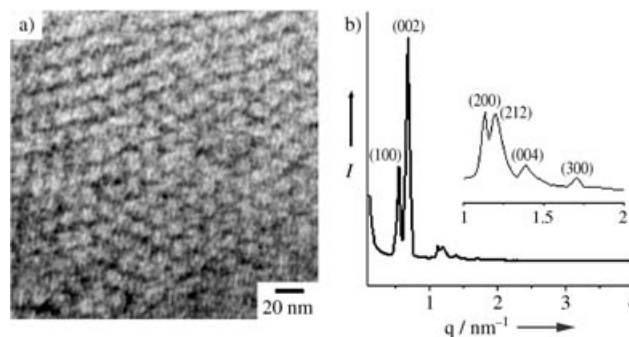


Figure 2. a) TEM image of a microtomed film of the rod-coil compound stained with RuO₄. b) Small-angle XRD pattern of the rod-coil compound. Inset: SAXS reflections for *q* = 1.0–2.0 nm^{−1} with an intensity scale expansion of ×10.

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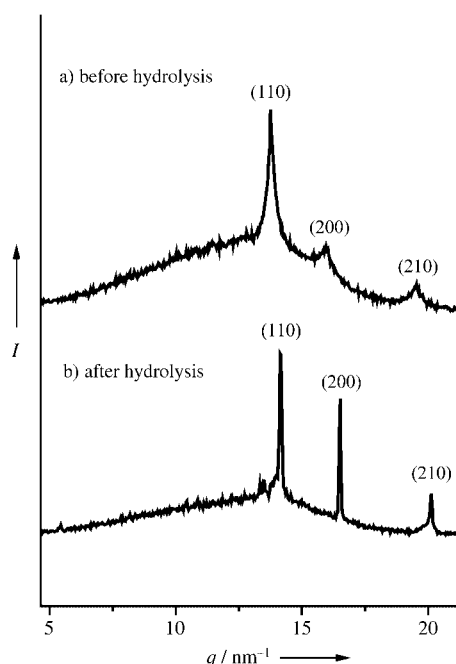


Figure 3. Wide-angle XRD patterns measured a) before and b) after hydrolysis of the rod-coil compound at 25 °C.

into a rectangular lattice ($P2gg$ space group) with unit cell dimensions $a = 0.79$ and $b = 0.56$ nm. These results demonstrate that the rod segments crystallize into a perforated layered structure, in which perforations are filled by coil segments, and subsequently the perforations organize into a 3D hexagonal superlattice.

Cleavage of the ester groups followed by selective removal of coil segments in the ordered state is a possible strategy for constructing nanoporous supramolecular crystalline sheets with well-defined pore size. To obtain initial proof of this concept, the thin film with coil perforations was placed in water/methanol containing potassium hydroxide at room temperature to cleave the ester groups grafting the rod and coil segments. Under these conditions, the crystalline layers consisting of rod segments are insoluble and inert. After one week, the rigid and insoluble film was removed from the hydrolysis solution, thoroughly washed with aqueous HCl and methanol, and dried at room temperature under vacuum.

Solid-state ^{13}C NMR spectra of the films showed that the signals associated with the poly(propylene oxide) chain had completely disappeared after hydrolysis (Figure 4). The FT-IR spectrum showed a broad O–H absorption in the region from 3400 to 2400 cm^{-1} and a C=O stretching band centered at 1720 cm^{-1} , which shifts to 1690 cm^{-1} after hydrolysis, indicative of conversion of an ester to a carboxylic acid. These data are consistent with the formation of rigid organic frameworks consisting only of aromatic rod segments by selective removal of the poly(propylene oxide) coils. The resulting film is completely insoluble in water and common organic solvents such as CHCl_3 , methanol, CH_2Cl_2 , toluene, hexane, and ethyl acetate and does not exhibit any noticeable swelling.

The TEM image of a microtomed film of the hydrolyzed sample stained with RuO_4 showed nanopore arrays (Figure 5a), indicative of the formation of nanopores on hydroly-

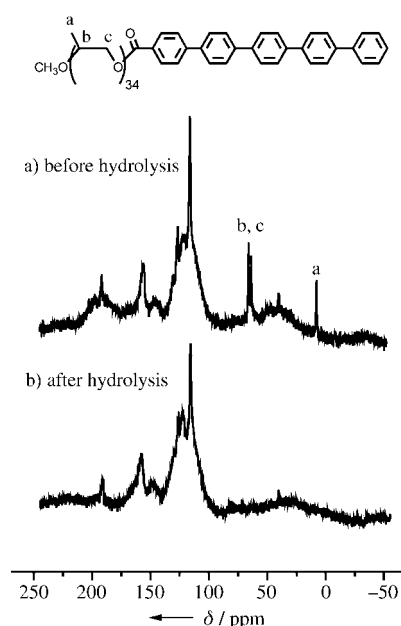


Figure 4. Solid-state ^{13}C NMR spectra of the rod-coil compound a) before and b) after hydrolysis.

ysis. This was also confirmed by atomic force microscopy (AFM) images. The amplitude images of a hydrolyzed film showed an ordered array of circular pores at the positions of the coil perforations (Figure 5b and 5c). The line scan in Figure 5b (inset) shows a pore to pore distance of approximately 12 nm, that is, the fundamental spacing is not changed on hydrolysis. The SAXS pattern exhibited four sharp scattering peaks corresponding to a lamellar structure with

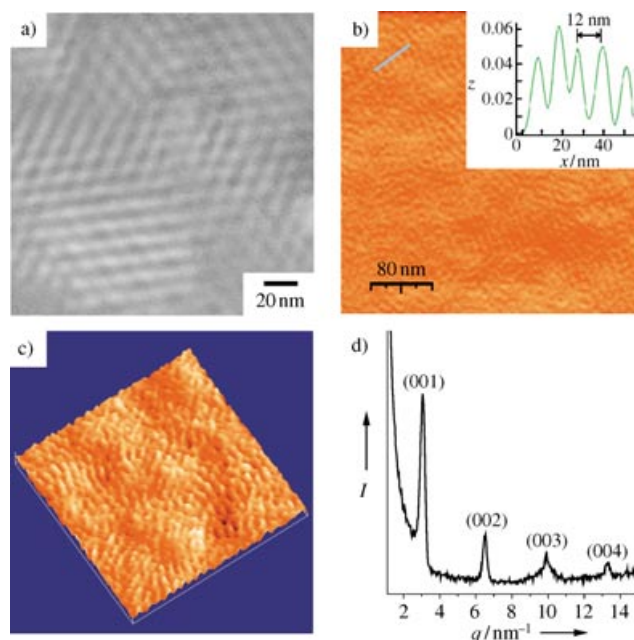


Figure 5. a) TEM image of a hydrolyzed film stained with RuO_4 . Tapping-mode AFM amplitude images presented as b) two- and c) three-dimensional graphics ($250\text{ nm} \times 250\text{ nm}$ area). d) Small-angle XRD pattern of the hydrolyzed sample.

a layer thickness of 2.1 nm (Figure 5d), which implies that perforation order is not maintained on removal of the coil segments. Since the length of carboxylic-acid-terminated penta-*p*-phenylene is 2.1 nm, the measured lattice constant indicates that the coil segments are extracted from the perforated layered structure after hydrolysis. These results demonstrate that the crystalline rod layers with in-plane nanopore arrays are stacked into a lamellar structure with a thickness corresponding to the length of a rod, while pore order along the *c* direction is lost on extraction of PPO coil segments. The wide-angle XRD pattern of the hydrolyzed sample revealed the same diffraction pattern but with peak narrowing compared to that of the rod-coil molecule (Figure 3b).^[9] These data are consistent with the preservation of the crystal structure within the rod layers, with enhanced crystallinity due to selective etching of the amorphous coil segments from the perforated layers. These results demonstrate that hydrolysis and subsequent removal of the flexible-coil segments in ordered nanostructures formed by rod-coil systems can provide a strategy for constructing nanoporous crystalline materials with uniform pore size.

Remarkably, the nanoporous solid proved capable of entrapping highly nonpolar dyes such as Nile Red in aqueous solution; this is indicative of the presence of nanoholes with hydrophobic interiors. In one experiment, Nile Red was dissolved in hexane and added to an aqueous dispersion of the nanoporous solid. The mixture was treated by ultrasonication

for 12 h. After this time, the water subphase turned violet, and the significant decrease in the intensity of the absorption peak corresponding to Nile Red in the hexane phase indicated that dye molecules had been transferred to the aqueous phase (Figure 6). This unique amphiphilic behavior is most probably attributable to hydrophobic and π - π interactions between the hydrophobic interiors of the nanopores and aromatic dye molecules.

In summary, a rod-coil compound in which an ester linkage grafts rod and coil segments exhibited a honeycomb-like supramolecular structure with 3D hexagonal symmetry. Hydrolysis with aqueous KOH and subsequent removal of the coil segments from the ordered structure with in-plane, hexagonally ordered perforations produced a crystalline layer with in-plane nanohole arrays. These results indicate that this approach allows novel, highly ordered nanoporous crystalline sheets to be produced, which potentially have applications as diverse as biomimetic transport membranes,^[1d] periodic porous materials,^[10] and nanopatterning.^[11]

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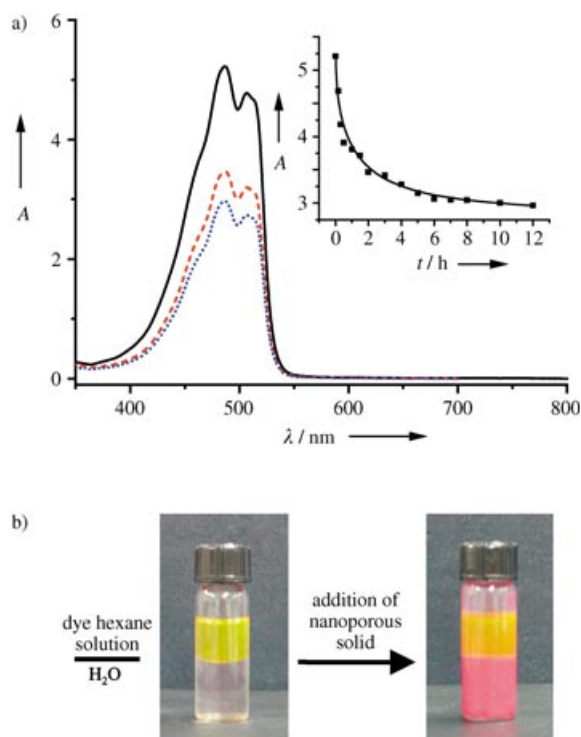


Figure 6. a) UV/Vis spectra of Nile Red in the hexane phase with a pure water phase before sonication (solid line) and with the water phase containing 7 wt% of the nanoporous crystals after 2 h (dashed red line) and 12 h sonication (dotted blue line). Inset: UV/Vis absorbance at $\lambda_{\text{max}} = 486$ nm as a function of time. b) Encapsulation of non-polar guest molecules in the nanoporous solid in an aqueous environment.

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