Host–Guest Chemistry

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Structural Transformation of a Two-Dimensional Molecular Network in Response to Selective Guest Inclusion**

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Dedicated to Professor Klaus Müllen on the occasion of his 60th birthday

The self-assembly of molecular building blocks on surfaces has been widely employed to produce well-defined, two-dimensional (2D) molecular networks.[1] Especially, molecular networks with void spaces, so-called "2D porous networks", are of great interest because such networks offer the possibility to immobilize functional units as guest molecules in a repetitive and spatially ordered arrangement.[2] Thus, these networks serve as templates for the controlled self-assembly of single-molecule-based devices, which will be of use in future nanotechnological applications.

Recently, the host properties of 2D porous networks for organic guest molecules and the dynamic behavior of guests inside the pores have been studied under ultrahigh vacuum (UHV) conditions[2a–e] as well as at the solid/liquid interface[2f,g] by means of scanning tunneling microscopy (STM). A key feature of those reported host–guest systems is the rigidity of the molecular network involving permanent porosities. In contrast, a flexible host network that undergoes conformational changes to accommodate guest molecules would provide a high guest selectivity similar to bioenzymes, such as metalloproteins, which recognize their target substrates by an induced fit mechanism.[3] The solid/liquid interface is an excellent environment for the creation of such flexible host networks thanks to a high degree of dynamics related to molecular adsorption–desorption processes (out-of-plane mobility) and in-plane molecular diffusion.

Our strategy to construct such a flexible guest-responsive network on a surface is to use directional but weak molecule–molecule interactions based upon alkyl-chain interdigitation (van der Waals interactions), rather than hydrogen bonds or coordination bonds, which are stronger and lead to more rigid networks. Herein we demonstrate the first example of the structural transformation from a nonporous network into a porous network as a response to the addition of guest. The guest selectivity depends not only on molecular size, but also on the electronic properties; the host matrix only recognizes and captures flat molecules containing large π-conjugated moieties.

Among numerous molecular building blocks, dehydrobenzo[12]annulene (DBA) derivatives are promising candidates for the construction of flexible networks at the solid/liquid interface: the appropriately sized cores can be linked through directional alkyl-chain interdigitation.[4] Moreover, the careful choice of the core shape and the solvent allows selective construction of a desired pattern out of the many different network topologies.[5] During the course of our studies, we found that elongation of alkyl chains at the periphery of triangular DBA cores (**1**, Scheme 1a) strongly affects the network structures at the interface between highly oriented pyrolytic graphite (HOPG) and 1,2,4-trichlorobenzene (TCB);[5] whereas compounds containing shorter alkyl chains (C_{10} for **1a** and C_{12} for **1b**) lead to the formation of porous honeycomb-type networks, compounds **1c**–**1e** with chain lengths of C_{14}, C_{16}, and C_{18}, respectively, show nonporous linear-type structures (Scheme 1b). In the honeycomb network, all six alkyl chains of the DBA core are adsorbed on HOPG. In the linear structure, two of the six alkyl chains are desorbed. The adsorbed alkyl chains are fully extended and interdigitated. The DBA molecules with longer alkyl chains prefer to form the linear-type pattern rather than the honeycomb structure because of the instability imposed by the increased diameter of the voids as a result of the too-low density of the surface coverage. From this point of view, **1c** with C_{14} chains is an interesting case: the linear pattern with honeycomb-shaped defects at domain boundaries is dominant.

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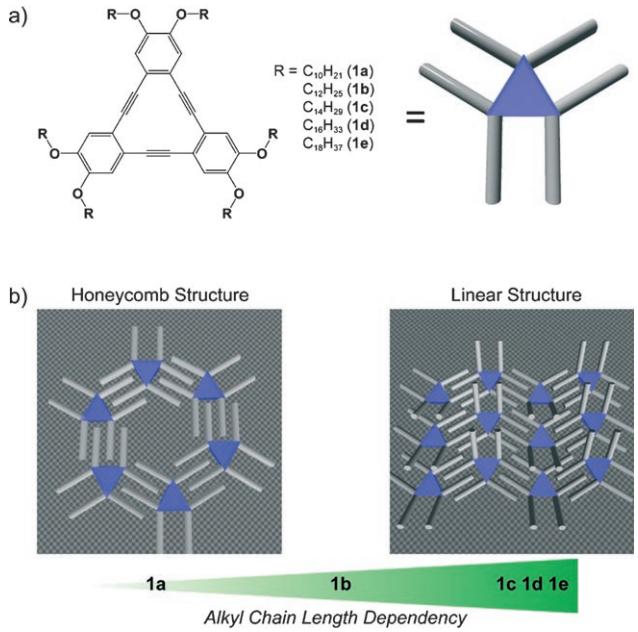


Scheme 1. a) Molecular structure of annulenes. b) Alkyl chain length dependency of the 2D networks formed.

To investigate the anticipated host capability and evaluate the usefulness of STM in probing host–guest interactions with (sub)molecular resolution, a tenfold excess of coronene was added to the liquid phase after the formation of the porous honeycomb network of **1a**. Coronene is the best candidate as a guest molecule because of its planar π-conjugated core with C_6 symmetry, which should fit into the hexagonal cavities of the honeycomb network. In Figure 1a, the bright triangular

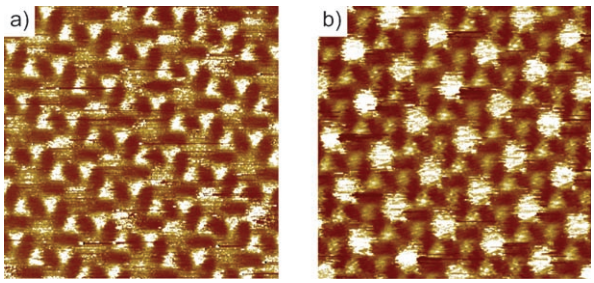


Figure 1. STM images of the honeycomb network of **1a** with an excess of coronene (17.5×17.5 nm^2): a) at low bias voltage ($V_{bias}=-1.00$ V, $I_{set}=0.7$ nA); b) at high bias voltage ($V_{bias}=-0.27$ V, $I_{set}=0.7$ nA).

DBA cores are clearly visible and some low-contrast featureless structures are observed in the hexagonal cavities at a low bias voltage (−1.00 V). In contrast, bright but fuzzy spots appear in the cavities by applying a higher bias voltage (−0.27 V), which was not observed in the absence of coronene molecules (Figure 1b). The bright feature inside the cavities is strong evidence for the coadsorption of coronene molecules. From the STM images and molecular modeling studies, the diameter was estimated to be about 2 nm. The exact number of coronene guests could not be determined, but probably ranges from one to a maximum of three. The featureless bright disk shape is attributed to the mobility of coronene inside the pore, which results in an averaged image sampling all possible locations of coronene inside the pore.

Nonporous linear structures are the dominant pattern types of **1c**–**1e**. However, honeycomb structures can be observed as defects in the domain boundaries of the linear networks. Surprisingly, upon addition of a tenfold excess of guest coronene molecules dissolved in TCB to the already formed linear-type pattern at the solid/liquid interface, a drastic change of network structure was observed for **1c**: a nearly complete conversion of the linear structure into the honeycomb structure. The guest coronene molecules were observed as bright features inside hexagonal cavities in the same manner as observed for **1a**. In case of **1d**, the linear structure did not transform completely into the honeycomb structure. Although several honeycomb domains were observed, the linear network was still dominant. From the tentative model of the honeycomb structure of **1c** (Figure 2a), a maximum of seven coronene molecules can fit in a pore. This network conversion is solely due to the addition of guest molecules and can be described as shown in Equation (1).

$$\mathbf{1c}\ (\text{linear, nonporous}) + \text{G} \rightarrow \mathbf{1c} \supset \text{G}\ (\text{honeycomb, porous}) \qquad (1)$$

It is notable that a honeycomb network with coadsorbed coronene molecules was also formed upon application of a mixed solution of both compounds in TCB to the substrate: the formation of the honeycomb network in presence of the guest molecules is thermodynamically favored. This result can be explained by the gain in energy resulting from molecule–substrate interactions of physisorbed hosts (**1c**) and guests (coronene) with the graphite, which overcomes the instabilities related to the formation of "voids" and the lower density of the host matrix. In contrast, **1d** with longer alkyl chains and a stronger adsorption energy on HOPG does not favor coadsorption of coronene, and the linear structure remains the dominant one.

To investigate the detailed mechanism of the structural transformation, a titration experiment was carried out; coronene molecules were gradually added to the linear structure of **1c**, and the area fraction of the honeycomb structure was determined (average of ten large-area STM images (96 nm × 96 nm) in different areas for each guest/host ratio). Figure 2b shows a plot of the area fraction of the honeycomb structure versus the guest/host (G/H) molecular ratio. In these large-scale STM images, each DBA molecule is imaged as a small spot: parallel double rows of small spots represent the linear structure whereas hexagons with a central void are characteristic for the honeycomb structure as shown in Figure 2c–f. Identification of the network types upon coadsorption of the coronene molecules is simplified because of their specific contrast. A small fraction of honeycomb structures (13%) was observed in absence of guest molecules (G/H = 0) at the boundaries between linear-type domains. In the intermediate range between G/H = 1 and G/H = 4, the growth of the honeycomb network is observed. All the STM images in this range have small spots of **1c** and bright features

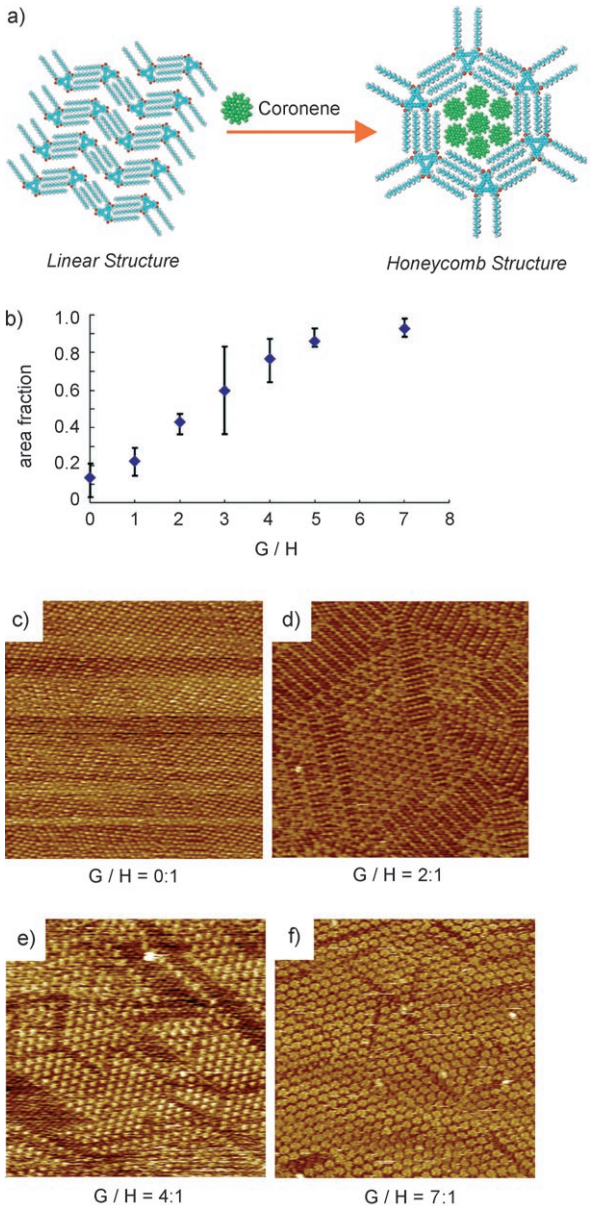
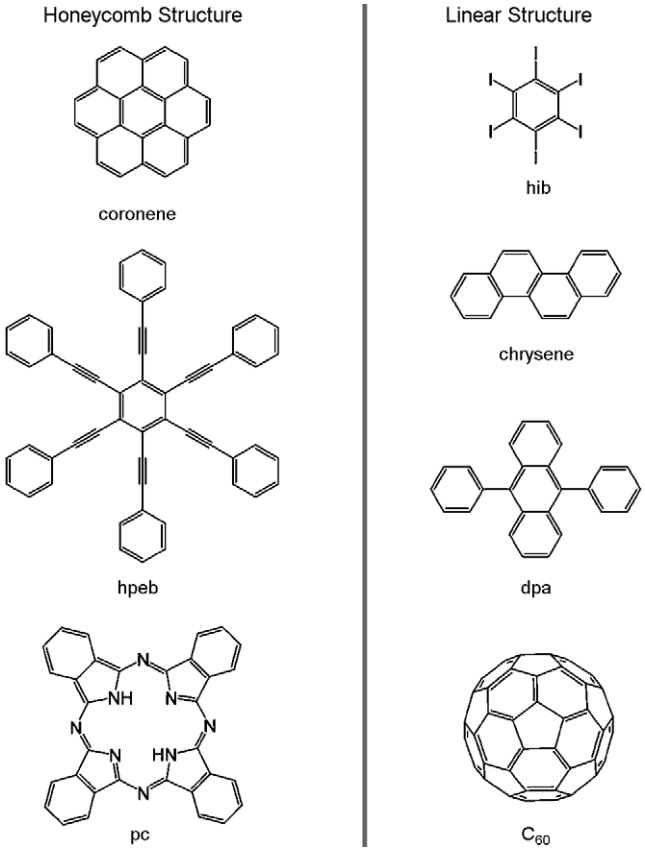


Figure 2. a) Tentative models of the surface patterns of **1c**. Left: linear structure of **1c** without coronene; right: honeycomb structure capturing at most seven coronene molecules. b) Plot of the area fraction of the honeycomb structure versus the guest/host molecular ratio (G/H). c–f) Large-area STM images (96×96 nm^2) of the network structures of **1c** with or without coronene ($V_{bias}=0.7$ V, $I_{set}=0.04$ nA): c) guest/host = 0:1; d) guest/host = 2:1; e) guest/host = 4:1; f) guest/host = 7:1.

of coronene aggregates inside hexagonal pores. Upon increasing the amount of coronene molecules in solution, the honeycomb domains grow and cover almost the entire surface (93%) at G/H = 7. In the intermediate range, the honeycomb structures form heterogeneously shaped domains rather than "isolated" cyclic hexamers. Cavities with different contrast (bright and dark) were observed for the lower ratios (e.g. G/H = 2), which implies the coexistence of filled and empty cavities. Unfortunately, the in-plane diffusion of the guests inside the cavity makes it difficult to determine the number of guest molecules. On the basis of these observations, we suggest the following tentative mechanism for the structural transformation from the linear to the honeycomb network: coronene molecules captured in the cavities in the domain boundary between linear structures stabilize the honeycomb structure and might initiate its growth, which leads to empty cavities at low coronene concentrations. This process might involve conformational changes (e.g. reorientation of alkyl chains) and in-plane motion of adjacent DBA molecules, which now have all alkyl chains adsorbed. In addition, out-of-plane desorption–adsorption processes are likely to be involved: the decreased density of annulene molecules requires at least the partial desorption of the annulene population.

Guest selectivity is also a significant issue in host–guest chemistry on surfaces. A rigid network system leads to size selectivity; guests smaller than the cavity can be accommodated inside, whereas the bigger ones are excluded. To investigate which properties of guest molecules, such as symmetry, size, and planarity, induce the structural changes of the flexible network of **1c**, a number of other guest molecules were probed: hexakis(phenylethynyl)benzene (hpeb), [60]fullerene (C_{60}), 9,10-diphenylanthracene (dpa), chrysene, hexaiodobenzene (hib), and phthalocyanine (pc) (Scheme 2). A tenfold excess of guest molecules was added to the solution of **1c** in TCB and a drop of the mixed solution was applied to the substrate. Planar guest molecules with large π-conjugated cores such as hpeb and pc led to the formation of the



Scheme 2. Guest molecules.

honeycomb network, whereas small π-conjugated molecules such as hib and chrysene, as well as the nonplanar molecules such as dpa and C_{60}, did not affect the linear network structure of **1c**.

The adsorption energy of guest molecules on HOPG is key in showing guest selectivity. Coronene, hpeb, and pc have relatively strong adsorption energies as a result of their large planar π-conjugated cores: they reside in the cavities at domain boundaries and stabilize the honeycomb structure of **1c**. The molecule–substrate interactions of the other guests are not strong enough to change the original host network structure. Furthermore, the symmetry of guest molecules does not seem to affect the coadsorption phenomenon. This selectivity is quite unique and contrasts with rigid networks in terms of the exclusion of smaller molecules.

In conclusion, we demonstrated the structural transformation of molecular networks on a surface—from a linear nonporous structure to a honeycomb porous network—as a response to the addition of guest molecules. The network of **1c** acts as a filter to capture only planar guests with large π-conjugated moieties. Such guest selectivity creates an opportunity to align and immobilize specific functional molecules on the surface.

Experimental Section

All experiments were performed at 20–22 °C with a Discoverer scanning tunneling microscope (Topometrix, Santa Barbara, USA) along with an external pulse/function generator (model HP 8111A) with negative sample bias or a PicoSPM (Molecular Imaging, Arizona, USA). Pt/Ir STM tips were prepared by mechanical cutting or electrochemical etching from Pt/Ir wire (80%/20%, diameter 0.2 mm) in a 2 N KOH/6 N NaCN solution in water.

Prior to imaging, the compounds under investigation were dissolved in 1,2,4-trichlorobenzene (Aldrich) at a concentration of approximately 10^{-4} M, and a drop of this solution was applied on a freshly cleaved surface of HOPG (grade ZTB, Advanced Ceramics Inc., Cleveland, USA). Then, the STM tip was immersed into the solution. The bright (dark) contrast refers to a high (low) current (constant-height mode: Discoverer STM) or to a high (low) topography (constant-current mode: PicoSPM). The bias voltage was applied to the sample in such a way that at negative bias voltage, electrons tunnel from the sample to the tip. All images presented are raw data.

To investigate host–guest systems, the samples were prepared in two different ways: 1) The solution of the host molecules in TCB was first measured to confirm the network structure, and then a drop of the solution of the guest molecules was added to the sample. 2) A mixed solution of the host and guest molecules was prepared and then a drop was applied to the substrate.

The titration experiment was carried out as follows: A solution of **1c** (15 μL, 6.7×10^{-4} M, 1.0×10^{-7} mol) in TCB was dropped on an HOPG surface and measured by STM (G/H = 0). A solution of coronene (3 μL, 3.3×10^{-3} M, 1.0×10^{-7} mol) in TCB was added to the already existing solution of **1c** on the HOPG surface (G/H = 1) and then imaged by STM. Coronene (3 μL) was added stepwise to achieve the following guest/host ratios: G/H = 2, 3, 4, 5, and 7. For each ratio, more than ten large-scale STM images (96×96 nm^2) were measured to obtain an area fraction of the honeycomb structure. Note that the volume is not constant during the measurement owing to solvent evaporation.

The molecular modeling studies were carried out by using HyperChem.

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