Hierarchical Self-Assembly

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Surface Noncovalent Bonding for Rational Design of Hierarchical Molecular Self-Assemblies

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Self-assembly is a promising bottom-up route towards atomically precise fabrication of functional systems.[1] Nanoporous networks[2] that can host guest molecules[3,4] were obtained on metal surfaces under ultrahigh vacuum. Various supramolecular chemistry approaches have been applied[5–9] to obtain thermally[10,11] or chemically controlled[12,13] polymorphs. The spontaneous formation of patterns with hexagonal,[14] porous honeycomb,[15,16] or Kagomé[17] geometries has been also observed at the solution/solid interface.[18,19] The topologies, as well as the drastic structural changes often induced by minute changes in molecular structure[20] or solvent,[21] are usually explained a posteriori on the basis of molecular symmetry, molecule–substrate interactions, and molecule–molecule interactions. Interdigitation of alkyl chains is an example of the last-named[15,16,22,23] which is of practical interest since it is specific to the surface and does not occur in the bulk of the solution. Surprisingly, close-packed epitaxy of *n*-alkanes on highly ordered pyrolytic graphite (HOPG)[24–26] has not yet inspired the design of molecular linker exploiting this behavior.

Hence, we designed a new molecular unit acting as a functional linking group able to form strong surface-assisted intermolecular "clips" which, by interdigitation, strictly mimic the atomically precise organization of *n*-alkanes on HOPG. It forms the basis of a design strategy which parallels polymer chemistry in that mono-, bi-, and trifunctional clip-bearing building blocks form noncovalent surface dimers, polymers, and two-dimensional (2D) networks, respectively. We can then chemically steer the organization of these entities themselves at a higher supramolecular level.

The adsorption of *n*-alkanes on HOPG results in the formation of close-packed 2D lamellae of parallel-aligned rectilinear chains, oriented along the ⟨100⟩ direction of graphite[19,25,26] according to the Groszek model[24] (Figure 1 A). Organization of the adsorbed monolayers is driven by two main factors: The first is the correspondence between the zigzag alternation of methylene groups and the ⟨100⟩ direction of HOPG, with a stabilization energy of about 64 meV per methylene group.[27] The second is the parallel packing of alkane molecules, which, besides steric hindrance, results from a stabilization energy between nearest chains 4.1 Å apart. From theoretical estimations,[28] we can infer 2D crystallization energies on the order of 20–25 meV per pair of facing methylene groups. Molecular moieties that can "clip" together in the presence of HOPG may thus be designed by connecting, through a rigid link, every other alkane in a lamella in such a way that the Groszek geometry is strictly preserved.

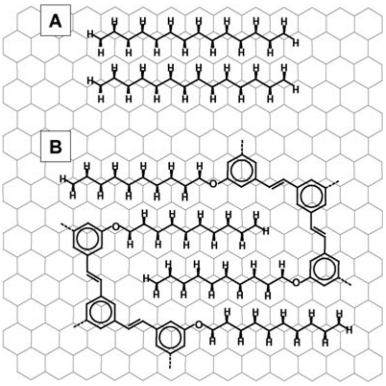

Figure 1. Clip design and principle. A) Linear *n*-alkane adsorption in correspondence with HOPG after the Groszek model,[24] and B) clip adsorption showing the rigorous preservation of the Groszek structure for the *n*-alkyl chains.

One of the simplest clip structures conforming to this model is based on two pairs of alkoxyl chains bonded through a π-conjugated bistilbene-like bridge, as sketched in Figure 1 B. The adsorption energy of the four decyloxy chains is about 2.6 eV and their clipping energy is around 0.7 eV. This functional group is highly versatile and amenable to diverse synthetic procedures. For instance, the bridge based on a 1,3,5-tristilbene or a 2,4,6-tristyrylpyridine core is the smallest single unit that can bear one clip (**I**), or two or three such clips (**II** and **III**, respectively) at the angles of 60° required for their simultaneous adsorption on HOPG (Figure 2 A–C). Thus, molecules with various number of clips can be considered to be monomers that are expected to form, after epitaxial reaction, dimers or chains (cyclic oligomers or linear polymers), as well as 2D networks (Figure 2 D–F).

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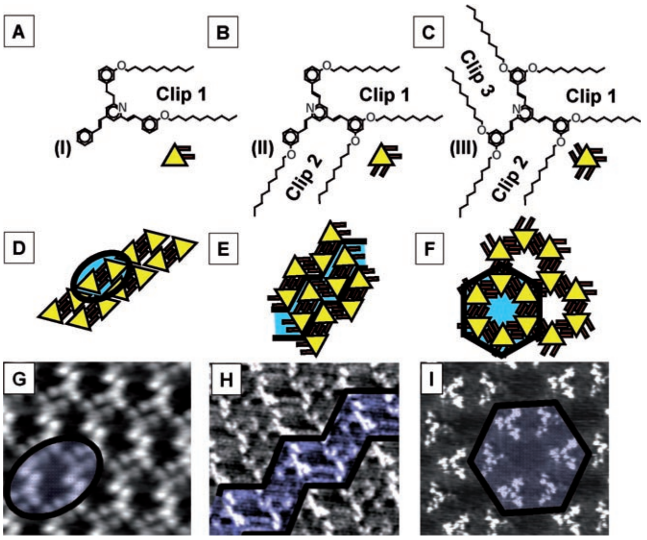

Figure 2. Realization of dimer-, polymer-, and networklike topologies from a given rigid core and differently placed clips. Molecular structures of **I**–**III** (A–C), anticipated self-assembly (D–F), and obtained STM images (G–I) corresponding to the monofunctional (A, D, G), bifunctional (B, E, H), and trifunctional (C, F, I) molecules, all based on the same 2,4,6-tristyrylpyridine core. For the three STM images the average tunnel current was $I_T \approx 15$ pA and the sample bias was $V_T \approx -1.0$ V. The scanned areas were 7.8×7.3 (G), 8.1×7.5 (H), and 8.9×8.3 nm^2 (I).

We first synthesized the mono-, di-, and trifunctional derivatives of Figure 2A–C, that is, compounds **I**–**III**, all based on the same 2,4,6-tristyrylpyridine central core, in order to analyze the influence of the number and location of the alkoxyl substituents. To extend the clip concept to various cores and to prove the resulting atomically precise placement, a bifunctional elongated molecule was designed (**IV**, see Figure 3), in which two functional groups end-cap a benzene central core.

Figure 2 shows the predicted assemblies (D–F) and the obtained STM images (G–I) for organizations of **I**–**III**. Bright three-arm patterns, observed in all images, are unambiguously assigned to the conjugated cores. This allows accurate analysis of their relative positions, from which the less contrasted organization of the alkyl groups can be inferred. When organization of the alkyl groups is clearly visible (e.g., in Figure 2H) it matches the deduced structures. In particular the two facing geometries corresponding to clipping of the two pairs of alkyl chains can be easily recognized and confirmed quantitatively. As anticipated, mono- (Figure 2D and G), bi- (Figure 2E and H), and trifunctional (Figure 2F and I) molecules form supramolecular dimers, polymers, and networks, respectively. The dimers (Figure 2D and G) are themselves packed so as to maximize their density, with unsubstituted sides closely facing each other. The supramolecular polymers (Figure 2E and H) adopt a linear configuration through alternation of molecular orientation, which permits the most compact packing. The engagement of all three clips with neighboring molecules (Figure 2F and I) results in the observed honeycomb network structure. The areas of the alveoli correspond to about 20 uncovered graphene hexagons. The maximum deficit in adsorption energy induced by the uncovered voids corresponds to the removal of one methylene group per hexagon, and is thus about 1.2 eV. It is compensated by the formation of two additional clips, as compared with the polymerlike structure, and this confirms quantitatively the strength of the clipping.

These results show that the organization obtained with a given tristilbene rigid core is controlled by the number and location of the alkoxyl side chains. The clip concept validated above is generalized by the results obtained with the bifunctional molecule with an elongated core **IV** (Figure 3). As expected, the molecules arrange in a polymerlike configuration. Compared to **II**, the clips are now parallel, and all molecules in a polymer row are equivalent.

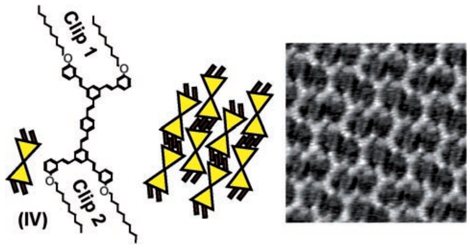

Figure 3. Polymerlike topology imposed by a different elongated rigid core. Molecular structure of **IV** (left), anticipated self-assembly scheme (middle), and obtained STM image (right) corresponding to bifunctional molecules based on an elongated core. The average tunnel current was $I_T \approx 12$ pA and the sample bias was $V_T \approx -1.0$ V. The scanned area was 8.0×8.0 nm^2.

The final step exploits the dynamic character of supramolecular chemistry. More particularly, the predicted fluxionality of the close-packed alkyl chains[25,29] suggests a degree of lability of the noncovalent clips and the possibility of dynamic constitutional diversity. For example, the geometrical structure of the bifunctional monomer (Figure 2B) should also allow its assembly into cyclic hexamers, thanks to the 60° angle between its two clips. However, because of the energetic cost associated with uncovered voids, the more compact linear polymer conformation is preferred (Figure 2E).

In an attempt to induce rearrangement into a cyclic hexamer, we added hexabenzocoronene (HBC), a flat discotic polyaromatic molecule known to be adsorbed on HOPG and to fit exactly in the 1.3-nm hexagonal alveolus of the honeycomb lattice in Figure 2F.[15] A droplet (ca. 5 μL) of a dilute solution of HBC was applied, the system was then heated to 60 °C, kept at this temperature for about 10 min, and cooled to room temperature. The polymer domains were found to be progressively replaced by domains exhibiting the new structure shown in Figure 4: HBC molecules induced cyclization of the non-covalent polymer as six-membered rings. In other words, HBC behaves as a block which cancels the energetic cost for the formation of the alveoli. After rearrangement, all the clips had formed again, in confirmation of the determinant structural role of these groups. The structure of the resulting hexamers is the same as the honeycomb units in the network of Figure 2F, but since the

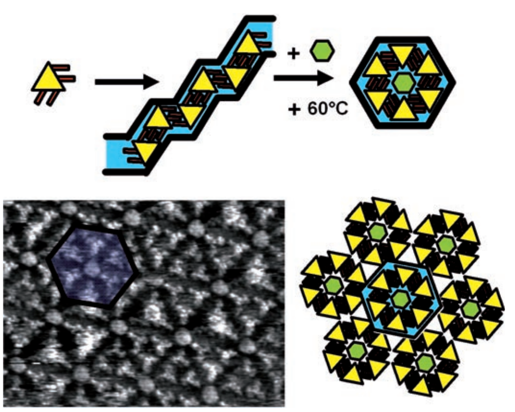

Figure 4. Dynamic reorganization of polymerlike topology into six-membered rings around discotic blocks. Scheme of the rearrangement reaction illustrating dynamic constitutional diversity of the self-assembled entities formed by bifunctional molecules with a 2,4,6-tristyrylpyridine core (top). STM image after rearrangement induced by addition of hexabenzocoronene (bottom left) and scheme of the obtained hierarchical structure (bottom right). The average tunnel current was $I_T \approx 14$ pA and the sample bias was $V_T \approx -1.0$ V. The scanned area was 25.7×18.7 nm^2.

outward-pointing clips are absent, the cyclic hexamers do not bond to each other. Consequently, they are themselves able to form a higher scale compact hexagonal superlattice. The resulting hierarchical assembly, in which HBC is encircled by a supramolecular hexamer which itself is hexagonally surrounded, is still in perfect atomic correspondence with the HOPG substrate. This multiscale assembly has an unprecedented overall periodicity of $\sqrt{607} \times \sqrt{607}$ R 6.02° relative to HOPG, as determined from the consistency of possible relationships with experimental lattice parameters and angles between domains.

In summary, by combining molecule–substrate epitaxial adsorption and intermolecular packing interactions we have designed a new type of surface-specific supramolecular bonding. We have demonstrated its validity by designing building blocks specifically aimed at the realization of various target topologies, such as dimers, linear (polymerlike), and cyclic (hexamers) chains, as well as 2D networks. Moreover, we have exploited the dynamic constitutional diversity of such systems to form hierarchical self-assemblies. These findings should encourage the design of other functional units and the realization of complex static and dynamic functional architectures, as are required for bottom-up nanotechnologies.

Experimental Section

Compounds **I**–**III** were synthesized by standard techniques starting from 2,4,6-trimethylpyridine and adding the appropriate arms by Siegrist reaction[30,31] with the corresponding imine. **IV** was synthesized by coupling of the functional group based on a benzene core with 1,3-dibenzaldehyde under standard Wittig conditions[32] (see the Supporting Information).

STM images were acquired with a homemade digital system. The images were obtained in current mode, with slow height regulation. The fast-scan axis was kept perpendicular to the sample slope. All images were corrected for drift of the instrument by combining two successive images with downward and upward slow-scan directions. The solvent was 1-phenyloctane (98%, Aldrich), which avoids the coadsorbtion observed with linear alkanes. The substrate was HOPG (Goodfellow) and the tips were mechanically formed from a 250-μm Pt–Ir wire (Pt80/Ir20, Goodfellow). The monolayers were formed by immersing the STM junction in a droplet (ca. 10 μL) of a ca. 10^{-4} M solution immediately after cleaving the substrate and approaching the STM tip. Imaging was then carried out in situ at the liquid–solid interface.

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