Structure and Epitaxial Registry on Graphite of a Series of Nanoporous Self-Assembled Molecular Monolayers

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ABSTRACT We have analyzed by STM the detailed structures of a series of nanoporous honeycomb networks stabilized by alkyl chain interdigitation on graphite at the liquid—solid interface, that is, clip-like noncovalent bonding. The variations observed as a function of the length of the peripheral aliphatic chains show that the assembly is directed not only by lateral intermolecular interactions but also by the adsorption site on the substrate. We derive an atomically accurate model for the registry with graphite of our nanoporous model series of systems. In full agreement with the quantitative model, the pore areas vary step-by-step by more than one order of magnitude along the whole series while preserving the detailed features of the graphite-induced alkyl chain interdigitation. The largest pores observed correspond to a ratio of uncovered substrate area as large as 35%.

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Molecular self-assembly is a promising route for the bottom-up manufacturing of nanostructures on atomically flat surfaces. The mechanisms of molecular self-organization have been the subject of numerous investigations aimed at the realization of building blocks designed so as to spontaneously form 2D monolayers with specific topologies. Intermolecular interaction may be driven by various molecular recognition processes, from steric hindrance to hydrogen bonding or interdigitation of alkyl chains. The latter may be strongly favored by adsorption on the surface of highly oriented pyrolytic graphite (HOPG). As a matter of fact, the value of the alkyl-chain period allows an adsorption in registry with HOPG along its ⟨1,0,0⟩ axis according to the Groszek model. It has been noticed that the distance which minimizes the energy of side interaction between alkyl chains, 4.26 Å, exactly matches a period of ⟨1,0,0⟩ rows. Thus, molecular moieties able to “clip” together by interdigitation on HOPG have been designed by finely adjusting the lateral distance between chains.

Among the various geometries based on alkyl chain clips demonstrated so far at the solution—solid interface, one forms a nanoporous matrix, a generic structure which currently attracts strong interest. This specific nanoporous system presents intriguing molecular sieve and dynamic properties. The structure of its building block molecule is represented in Figure 1 together with the honeycomb structure that it forms. The possibility to finely tune the pore dimensions constitutes a prerequisite toward the control and exploitation of these properties. From the structure of the above-mentioned network, one may anticipate that varying the length of peripheral alkyl chains will result in changes of pore dimensions. Yet, although the influence of the substrate is seldom considered in interpreting self-assembled molecular structures, in the present case, the core role of HOPG on clip formation requires a more careful account of the substrate. In the above series of molecules, the step-by-step variation of alkyl chain lengths offers a unique opportunity to analyze the influence of adsorbate—adsorbent interactions.

In this paper, we analyze the evolution of the epitaxial relationships of nanoporous networks formed on HOPG by interdigitation of alkyl side-chains with various lengths. We show that the molecular lattices stay in registry with HOPG following a common atomically accurate model while pore areas vary by more than one order-of-magnitude.

Molecules of 1,3,5-tristerylbenzene substituted by alkoxy peripheral chains presenting n = 6, 8, 10, 12, or 14 carbon atoms (TSB3,5-Cn; see Figure 1) were deposited on the HOPG surface. They have been synthesized and purified by adapting the procedure described in the literature, using the corresponding 3,5-dialkoxybenzaldehydes. The solvent was 1-phenylclocatane (98%, Aldrich), which is well suited for in situ scanning tunneling microscopy (STM) because it is hydrophobic, highly...

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insulating, and poorly volatile. The substrate was a freshly cleaved HOPG (Goodfellow). The self-assembled monolayers formed from TSB3,5-C6, TSB3,5-C8, and TSB3,5-C10 were deposited from $10^{-5}$ to $10^{-4}$ mol L$^{-1}$ solutions immediately after cleaving the substrate and were then imaged by STM. Special care must be taken for the deposition of TSB3,5-C12 and TSB3,5-C14, which result in large pores and thus low-density monolayers. Solutions with lower concentration were then used ($10^{-5}$ to $10^{-6}$ mol L$^{-1}$) to avoid formation of alternate denser networks. Moreover, those solutions were deposited onto gently heated substrates (60 °C) before the system was progressively cooled down to room temperature for STM observation. In turn, this method happens to favor the formation of large domains. As an example, a typical large-area image of a self-assembled monolayer is presented in Figure 1. By applying the above procedure, domains larger than typically 100 nm were routinely observed. The tips used for STM imaging were mechanically formed in a 250 μm Pt–Ir wire (Pt80/Ir20, Goodfellow). The STM was a conventional fully digital system. The images reported here were obtained in the current mode, with slow height regulation, at a sample bias of $\sim$1000 mV and tunnel current set points in the range of 3–17 pA. The scan angle was adjusted in such a way as to keep the fast-scan axis nearly perpendicular to the sample slope. Images acquired simultaneously in forward and backward fast-scan directions were systematically recorded and compared. All images were corrected by homemade software for the drift of the instrument, which was evaluated by correlating successively acquired images with the opposite slow-scan direction. For angle measurements between domains, a hexagonal lattice with 60° angles between the lattice directions was assumed. Then, the combination of the measurements with the three axes, together with averaging over all domains present in the image, permitted accuracies of typically 0.5°.

For molecules comprising both aliphatic and conjugated parts, the conjugated moieties appear much brighter in STM images. On the basis of the observation of the star-shaped conjugated cores, it appears that each of the five molecules self-assembles on HOPG, forming large domains of honeycomb network (see Figure 2). The unit cells appear to have hexagonal symmetry. Their parameters evolve monotonously from 3.1 (TSB3,5-C6) to 4.5 nm (TSB3,5-C14) with increasing alkyl chain lengths. In each case, only two kinds of domains are formed, displaying mirror-symmetric STM images. Specifically, it can be observed that, depending on the orientation of the domain, two neighboring molecules are tilted either both clockwise or both counterclockwise with respect to the axis defined by the pair of molecule centers. The angles formed by the unit cell axes of two domains of opposite left- and right-handed orientations grown on the same terrace are shown in Figure 2 for TSB3,5-C6, TSB3,5-C8, and TSB3,5-C14 and reported below their respective images. TSB3,5-C12 is a specific case where both types of domains have the same direction, within experimental uncertainties (0.8°). A thorough observation of STM images of the unit cell still permits one to discern two distinct mirror-symmetric variants of domains, their unit cell axes being parallel one to the other. Thus, the angle $\theta$ between the two sets of domains varies uniformly from 23.6 (TSB3,5-C6) to 0° (TSB3,5-C12). In the case of TSB3,5-C14, the only operational deposition procedure, employing the lowest concentration and high substrate temperature during the self-assembly, yields very large single domains occupying entire terraces. Then, the angle can not be reproducibly measured, but the two sets of mirror-symmetric domains are still observed. The measured lattice parameters, that is, the unit cell dimensions $a$ and the angles $\theta$, are reported in Figure 2.

The qualitative features of self-assembled monomolecular layers can often be explained solely in terms of intermolecular interactions, the substrate contribution to lateral order being limited to the interplay between coverage maximization and steric hindrance. Yet, the existence of fixed lattice orientations, observed even for disjoined domains, can only be explained by interactions with the underlying HOPG substrate. To understand quantitatively the structure of the molecular assembly, an important point is whether the above-described lattice variations with alkyl chain length are governed only by intermolecular distances or are quantified by conditions of registry of the molecular lattice with HOPG.

To address this question, let us assume an optimal registry with the substrate. This means that all molecules are adsorbed in the same, most stable, geometry relative to the surface of the HOPG substrate. This hypothesis is consistent with the high similarity between STM images of different molecules,
including between those having different orientations. As a matter of fact, it has been predicted\textsuperscript{28,29} and observed\textsuperscript{30,31} that the appearance in STM images of such graphene-like conjugated structures changes considerably with the adsorption site. This imposes a six-fold rotation invariance around the center of a pore, for both the molecular layer and the topmost atomic layer of HOPG substrate. The molecular pores are thus necessarily centered over alveoli of HOPG as sketched in Figure 3 (points labeled C6\textsuperscript{3}). Notice however that, if one accounts for the second underlying atomic layer, the six-fold symmetry is broken and reduced to a three-fold rotation invariance. Then, two molecules rotated by 60° cannot be strictly equivalent. The stability of the adsorption is however governed mainly by interactions with the substrate surface, which justifies considering only one atomic layer of HOPG.

Similarly, the centers of the molecules correspond to a three-fold symmetry axis of the molecular layer (points labeled C3 in Figure 3) and are thus necessarily aligned on at least a three-fold symmetry axis of HOPG. There are three possible such situations, represented below Figure 3a (referred to as C3−1, C5−1\textsuperscript{4}, and C3−2). Each type corresponds to a different adsorption geometry and stability of the molecule. If we still assume that the molecules systematically arrange themselves so as to adopt the most stable one, then this point must remain of the same type when varying the length of the alkyl chains. This quantifies and reduces the possible periods of the lattice structures adopted for the various lengths, as shown in Figure 3b in the case of a C3−1 type. A detailed examination of the few possibilities thus left shows that the experimentally observed series of lattice parameters and angles between mirror-symmetric domains exactly matches the series of possible periods displayed in Figure 3b. This series of lattice vectors is fully consistent with the molecular model depicted in Figure 3a extrapolated to the other chain lengths. Specifically, it allows preservation of both the Groszek-type adsorption of the alkyl chains and their “clip”-like interdigitation over the whole series. The lattice epitaxial relation with HOPG follows the general form [(91 + 15n + 3n\textsuperscript{2})\textsuperscript{1/2} × (91 + 15n + 3n\textsuperscript{2})\textsuperscript{1/2}]R\theta and tan θ = 3\textsuperscript{1/2}(n−6)/(5n + 16), where n is the number methylene pairs in the alkyl chain (from n = 3 for TSB3,5-C6 to n = 7 for TSB3,5-C14). The corresponding data are reported in Figure 2 below each STM image. Notice that the angle between the lattice vectors of mirror-symmetric domains is 2θ. The agreement between experimental and theoretical data fully confirms the principles developed here.

The agreement with the model of epitaxial adsorption enables a derivation of the pore dimensions as a function of the chain length. As reported in Figure 2 (last row), the diameter (respectively area) of the circumscribed of the pores increases monotonously from 0.62 (0.30 nm\textsuperscript{2}) to 2.31 nm (4.2 nm\textsuperscript{2}) from TSB3,5-C6 to TSB3,5-C14. The ratio of the HOPG area not covered by molecules also increases, from ∼5% for TSB3,5-C6 up to ∼35% for TSB3,5-C14. In the latter case, the energy cost corresponding to the lack of molecule adsorption on a considerable proportion of the available substrate surface explains the difficulty in forming the layer and the necessity of a thorough control of the thermodynamics and kinetics of the self-assembly process.

Finally, the observation that the molecule adsorption strictly preserves the Groszek model structure for alkyl chain interaction with HOPG further supports the role of the so-called
Figure 5. Epitaxial relationship with HOPG. (a) Close-up showing the molecular positioning relative to HOPG (superimposed light gray chicken wire). For clarity, the case of shorter chains, TSB3,5-C6, has been represented. One lattice vector connecting two C6 points is represented (solid arrow). Two vectors connecting C6 and C3 points are also represented (dotted arrow). By symmetry, they must form a 120° angle and have the same lengths. (b) Variations of the lattice vector with chain length, from TSB3,5-C6 to TSB3,5-C14, constrained by the preservation of the nature of the C3 point relative to HOPG. (Here a C3–1 type). The mirror-symmetric lattice is also represented in the upper part, showing the variations of the angle between simultaneously observed domains. In all schemes, the centers of molecular pores, forming six-fold symmetry axes, are labeled C6. The centers of the molecules are analogously labeled C3.

In conclusion, we have analyzed the detailed structures of a series of nanoporous honeycomb networks formed by tristilbene derivatives on HOPG by STM at the liquid—solid interface. The variations observed as a function of the length of the peripheral aliphatic chains shows that the assembly is directed not only by lateral intermolecular interactions, that is, steric hindrance and chain interdigitation, but also by the search for the most stable adsorption site on the substrate. We have thus been able to derive an atomically accurate model for the registry with HOPG of our nanoporous model series of systems. The pore areas vary step-by-step by more than one order of magnitude along the whole series, while preserving the detailed features of the HOPG-induced alkyl chain interdigitation. The largest pores observed correspond to a ratio of uncovered substrate area as large as 55%.

**SUPPORTING INFORMATION AVAILABLE** Direct comparison of the molecular lattice orientation and the HOPG(110) axis and derivation of the lattice epitaxial registry formula. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).

**REFERENCES**


