

Tuning the packing density of host molecular self-assemblies at the solid–liquid interface using guest molecule†

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The use of THB molecules as a guest template tunes the formation of a two-dimensional honeycomb network in preference to alternative close packed structures of TECDB self-assembled on HOPG surface at the solid–liquid interface.

In view of developing novel nanostructured functional materials, the controlled arrangement of organic molecules on surfaces has attracted a lot of research interest.¹ In particular, molecular patterns with two-dimensional honeycomb networks are used to immobilize functional units as guest molecules in a repetitive and spatially ordered arrangement. Compared with solution-phase self-assembly² and solid-state crystal engineering,³ surface-based supramolecular chemistry is less well understood.^{4,5} Except for the substrate and the chemical structure of molecules, the environmental conditions such as light irradiation,⁶ electric and magnetic fields,^{7,8} time,⁹ concentration,¹⁰ ratio¹¹ and temperature¹² also play important roles in governing supramolecular self-assemblies. One strategy to favor the formation of nanoporous networks is to tune the solution concentration. Another strategy is the use of guest molecules to influence and to transform the configurations of a two-dimensional surface assembly. This method has been used in honeycomb networks that utilize alkyl-chain interdigitation for network formation.^{13–15}

Due to the stronger hydrogen bonding, carboxylic groups are frequently used to drive the self-assembly process, for instance, the self-assembly of trimesic acid and 1,3,5-benzenetricarboxylic acid.¹⁶ However, it is difficult for 1,3,5-trihydroxybenzene (THB, Scheme 1) with weak intermolecular hydrogen bonding to adsorb on a HOPG surface at the solid–liquid interface. In this work, we first utilize THB as the guest molecule to tune the packing motifs of 1,3,5-tris(10-ethoxycarbonyldecyloxy) benzene (TECDB, Scheme 1) self-assembly and form the honeycomb structure. Our study illustrates that by sensible choice of guest molecule, intermolecular interactions, weak hydrogen bonding and spatial effects can control two-dimensional networks directly and form host–guest nanostructures.

TECDB was synthesized according to the reported procedure.¹⁷ Fig. 1 shows typical STM images of monolayers formed at

different concentrations of TECDB. The bright spots correspond to the π -conjugated benzene rings due to their high electronic density and the strip features are the side chains. Close observation of magnifications of the monolayers (Fig. S1, ESI†) reveals that TECDB molecules form dimers with different stacking fashions. The corresponding molecular models are superimposed in Fig. 1a–c. Pairing phenomena have already been observed on symmetrical molecules with peri-hexabenzocoronene¹⁸ and T₁₁¹⁹ adlayers on solid surfaces. Under higher concentrations, the TECDB molecules form dimers side by side and pack into a porous structure along the direction of the HOPG lattice after the interdigitation of their chain groups in adjacent lamellae (Fig. 1a). When the concentration decreases, because one side chain of a molecule interdigitates with that of another molecule, a different type of dimer forms and arranges with a relative higher-density structure (Fig. 1b). The molecular models in Fig. 1d depict the intermolecular interactions. After the solvent evaporates completely, the coexisting self-assembly pattern of both single molecules and dimers appears as shown in Fig. 1c. This stacking pattern remedies the hole defect of dimer assembly.

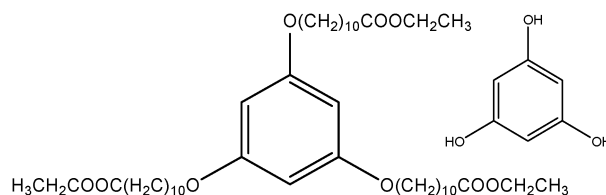
Since the side chains interdigitate and lie on the surface, it can be inferred that the featured adlayer structure is influenced by intermolecular and molecule–substrate interactions. To identify the orientation relation between the TECDB adlayer and underlying HOPG lattice, composite STM images are obtained in Fig. S2, ESI†. In the porous structure, all side chains are found to stretch along one of the main symmetry axis of HOPG (Fig. S2a, ESI†). In the linear structure, side chains in the dark contrast troughs are horizontal and parallel to the HOPG lattice, while in the bright contrast troughs, alkyl chains are tilted. Because of steric restrictions, the tilted chains cannot be directed along the HOPG lattice (Fig. S2b†). The incommensurability of the tilted chain is the origin of their flexibility on the substrate and thus of the bright contrast generated in STM image.¹⁹

Self-assembly at the solid–liquid interface is mainly controlled by the interplay of adsorbate–adsorbate, adsorbate–substrate interactions. The assembly process is dynamic and depends on the adsorption–desorption equilibrium toward a minimum of the

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Scheme 1 Chemical structures of 1,3,5-tris(10-ethoxycarbonyldecyloxy) benzene (TECDB) and 1,3,5-trihydroxybenzene (THB).

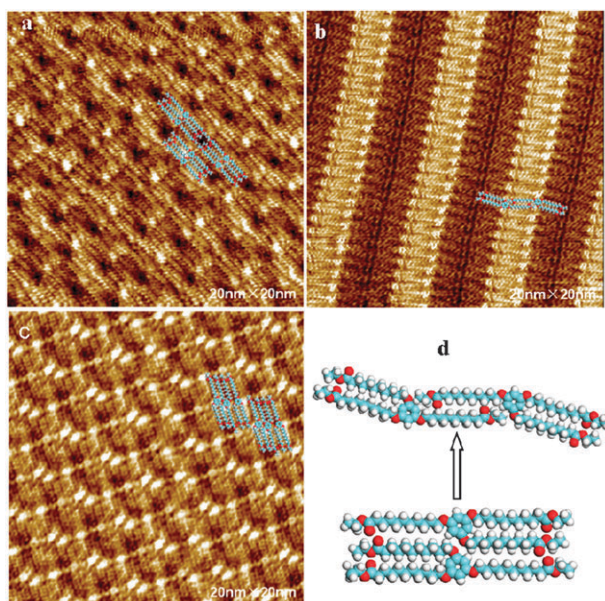


Fig. 1 A series of STM images of the self-assembled TECDB molecules on HOPG at different concentrations: (a) porous pattern, $5.0 \times 10^{-4} \text{ mol L}^{-1}$ ($V_{\text{bias}} = 620 \text{ mV}$; $I_t = 436 \text{ pA}$) and (b) linear pattern, $2.1 \times 10^{-6} \text{ mol L}^{-1}$ ($V_{\text{bias}} = 817 \text{ mV}$; $I_t = 436 \text{ pA}$). These images show the typical transition from a porous pattern to a close-packed linear structure when the TECDB concentration decreases. (c) Self-assembled structure after the solvent evaporated completely. (d) Scheme illustrating the structures and the transition from a porous pattern to a linear arrangement.

overall free energy. At relatively low concentrations (less than $1.0 \times 10^{-5} \text{ mol L}^{-1}$), it is interesting that a transition process from a porous motif to a linear polymorph is obtained by consecutive STM images (Fig. S3, ESI†), which indicates that the porous structures are not optimal from a free-energy point of view. The transition of self-assembled structures can be ascribed to the polarity of the solvent molecules and related solvent–solution interactions, which play an important role in the van der Waals interactions of the assembly structure. Additionally, the TECDB dimer constitutes a building block for the TECDB adlayer which further self-assembles in a lamellar packing.

So we conclude that the concentration dependence is directly related to the difference of stability in the porous and linear polymorphs and their respective molecular densities. These results provide not only insight into the thermodynamics of the formation of surface-confined nanopatterns at the solid–liquid interface, but also some general guidelines for the successful control of polymorphism at such surfaces.

Although the concentration can tune the self-assembled structure, the anticipated honeycomb network is not obtained. The self-assembly of TECDB on HOPG also demonstrates that low-density structures are not optimal from a free-energy viewpoint because no honeycomb structure is observed. However, guest molecules can overcome the energy cost of forming a low-density pattern by initiating the formation of the targeted porous pattern and stabilizing it by coadsorption.^{15,20} We are interested in investigating whether the formation of the honeycomb network structure can be enhanced *via* the use of a guest species to act as a template for this structure. Thus, THB

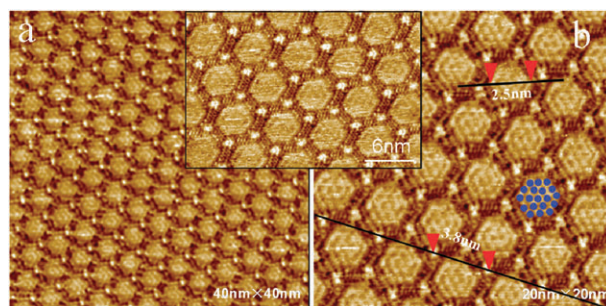


Fig. 2 (a, b) STM images of the honeycomb structures formed from a mixture of TECDB and THB at the phenyloctane–HOPG interface. (a) In the presence of THB, a structural transformation occurs and a supramolecular two-component architecture forms. ($V_{\text{bias}} = 818 \text{ mV}$; $I_t = 400 \text{ pA}$). (b) High-resolution image reveals the hexagonal pores are filled in by clusters of THB. ($V_{\text{bias}} = 800 \text{ mV}$; $I_t = 300 \text{ pA}$). The insert highlights the structural motif for the packing details of TECDB molecules under relative higher voltage. ($V_{\text{bias}} = 1000 \text{ mV}$; $I_t = 300 \text{ pA}$).

is chosen as a guest molecule that is anticipated to act as a suitable template to favor the formation of the honeycomb network. The choice of THB is based on previous studies, which have demonstrated that trimesic acid²¹ and isophthalic acid¹³ form a honeycomb network on HOPG and because it is of a suitable size and shape to fit within hexagonal pores. Due to the weak hydrogen bonding between THB molecules, THB cannot form a self-assembled monolayer on a HOPG surface. However, when THB was added to a phenyloctane solution of TECDB prior to surface deposition, we surprisingly found that TECDB and THB molecules coadsorbed on HOPG and formed the expected host–guest honeycomb network.

In contrast to the results obtained for a TECDB only system, which was transformed upon the addition of THB from porous or linear structures to a honeycomb lattice with THB-filled hexagonal pores identical in size to those anticipated (Fig. 2). Following the addition of THB to the deposition solutions there is no evidence for the formation of the porous or linear structures. Indeed only the honeycomb network with co-adsorbed THB is observed and covers the entire surface (Fig. S4, ESI†). These images (Fig. 2 and S4, ESI†) clearly demonstrate the successful use of a guest template in promoting the formation of a network arrangement that is less stable in the absence of the guest molecule.²² The formation of a honeycomb network in the presence of the guest molecules is thermodynamically favoured, which overcomes the instabilities related to the formation of “voids” and the lower density of the host matrix.

The high stability of the TECDB adlayer due to the van der Waals interactions between side chains and HOPG surface allows one to obtain intermolecular resolution, which reveals details of the molecular packing by applying a higher bias voltage (the insert in Fig. 2). In the honeycomb pattern, the three side chains on the benzene ring spread out radically and are interdigitated with those of neighboring molecules. At a low bias voltage, the bright feature inside the cavities is strong evidence for the coadsorption of THB molecules (Fig. 2a). The repeating period for the honeycomb network is 3.8 nm and the pore diameter is 2.5 nm as shown in Fig. 2b. The orientation of THB is clearly defined by the pore shape of TECDB molecule: the benzene rings of THB run parallel to the long axis of the

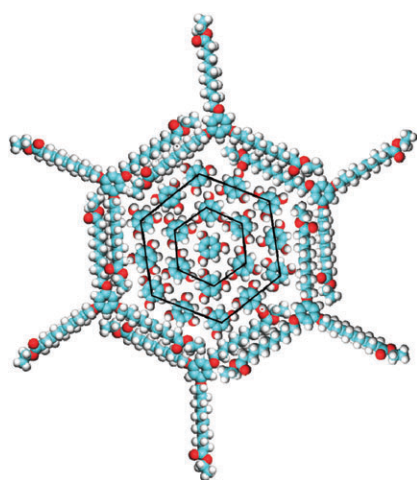


Fig. 3 Proposed schematic representation of the honeycomb network supramolecular arrangement of TECDB with nineteen THB molecules positioned in the circular hexagonal pore.

chains forming the pore. The bright hexagonal shape is not very obvious due to the mobility of THB inside the pore.⁵ Although we cannot clearly resolve the structure from the STM images, the number of guest molecules inside the cavity can be determined. A model for the experimentally observed stabilization of THB within the honeycomb network by intermolecular hydrogen bonding is shown in Fig. 3. It can be seen from the schematic representation, twelve hydrogen-bonded THB molecules fit well into the hexagonal “void” of the honeycomb network of TECDB molecules and form the second hexagonal structure. It is interesting that the third hexagonal structure with six hydrogen-bonded THB molecules resides in the smaller hexagonal pore because of the space complementarity and hydrogen-bonding interactions. The middle space is filled in by a single THB molecule. Thus the network acts as a well-defined structure to template the formation of regular 2-D cluster of THB with hydrogen bonds and well-defined spacings.

In conclusion, we have demonstrated that the concentration of TECDB influences its self-assembled structure. Furthermore, the successful application of a templating approach to tune the self-assembled structures of TECDB by the use of a suitably designed guest molecule, THB, enhances the stability of the honeycomb network. Such a guest selectivity creates an opportunity to immobilize specific functional molecules on the surface. We are currently developing these studies with other guest molecules with suitable geometric size to further elaborate the TECDB-based supramolecular architecture to surface-based self-assembly.

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