The following is a comment on the published paper shown on the preceding page.

Programmable Hierarchical Three-Component 2D Assembly at a Liquid-Solid Interface: Recognition, Selection, and Transformation

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Introduction

Construction of two-dimensional (2D) molecular networks on solid surfaces based on self-assembly is a subject of intense interest owing to the perspective of various applications in the field of nanoscience and nanotechnology.[1] Supramolecular self-assembly can become an alternative for current lithographic techniques to create surface patterns in the low nanometer regime. Among various types of molecular networks, porous 2D molecular networks have received a lot of attention because such surface-confined molecular networks can accommodate guest molecules or atomic clusters via so-called 2D host-guest chemistry,[2] resulting in the formation of multicomponent nanostructures. These molecular networks are typically observed by means of scanning tunneling microscopy (STM) under ultrahigh vacuum conditions or at the liquid-solid interface.

The formation of crystalline multicomponent 2D lattices, containing more than two different organic molecular building blocks has been reported rarely, since optimized recognition and selection processes are required to achieve the targeted multicomponent surface-confined patterns. The hydrogen bonded porous network formed by melamine and perylene tetracarboxydiimide of which pores are filled by clusters consisting of seven C_{60} molecules is one of representatives.[3] However, such well-defined multicomponent structures do not form upon simultaneously bringing all components to the surface. We succeeded in the formation of hierarchical self-assembly consisting of three-components, isopthalic acid (**ISA**), coronene (**COR**), and a dehydrobenzo[12]annulene derivatives (**DBA1**, Figure 1), at the liquid-solid interface based on a host-guest strategy, in which we highlighted the recognition and selection processes involved.

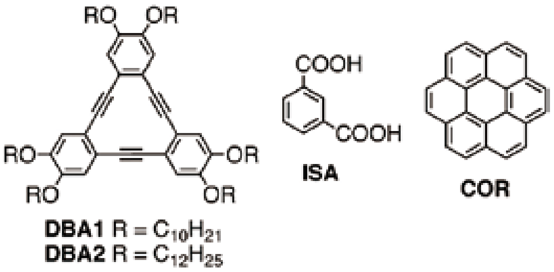

Fig.1 Chemical structures of **DBA1**, **DBA2**, isophthalic acid (**ISA**), and coronene (**COR**).

Bicomponent (ISA-COR) Supramolecular Assembly

In view of the typical hydrogen bonding pattern between carboxylic acid groups, **ISA** is expected to assemble into a zig-zag chain or into a cyclic hexamer, in which **ISA** adopts an extended or bent form, as shown in Figure 2a. While the former structure is closely packed, the latter possesses a pore with a diameter of ca. 1.4 nm. Indeed, at the 1-octanoic acid/graphite interface, **ISA** forms zig-zag chains which further assemble into 2D crystalline domains via van der Waals interactions between the chains. **ISA** molecules are resolved as small bright circles with a diameter of about 0.7 nm in the STM image (Figure 2b).

When **COR** was added to the solution of **ISA**, however, a dramatic difference was observed (Figure 2c). The repetitive unit contains one big bright disk (ca. 1 nm in diameter) surrounded by six small, less bright circles. These images are attributed to a **COR** molecule which is surrounded by a cyclic hexamer of **ISA** molecules. The interactions between the **ISA** hexamer and **COR** are mainly van der Waals (Figure 2a). These heteroclusters further assemble into 2D close-packed domains through van der Waals interactions.

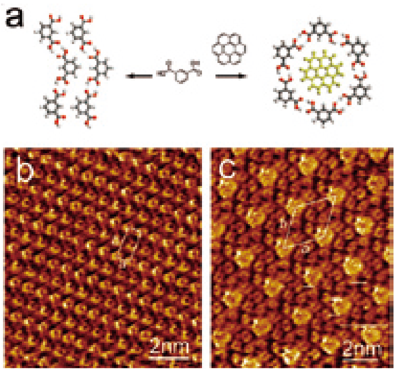

Fig.2 (a) Molecular Mechanics optimized structures of (left) the 'zig-zag' pattern of **ISA** and (right) the **COR$_1$-ISA$_6$** cluster. (b,c) STM images recorded at the 1-octanoic acid/graphite interface of self-assembled patterns of **ISA** (b) in absence of **COR** and (c) in the presence of **COR**.

Molecular mechanics (MM) calculations (with the PCFF force field) support the formation of **ISA$_1$-COR$_6$** heteromolecular clusters. MM calculations indicate that there is a significant stabilizing interaction between **COR** and the surrounding **ISA** molecules (–13 kcal/mol), reflecting the perfect structural fit of **COR** into the cavity of the cyclic **ISA** hexamer. Therefore, **COR** is a proper molecular 'template' to induce the transformation of the monocomponent **ISA** zig-zag network into a 2D bicomponent network of heteromolecular **COR$_1$-ISA$_6$** clusters. The shape of **COR** is well-resolved in the STM images, showing even submolecular details, indicating that **COR** molecules are immobilized and not rotating within the pore. This means that **COR** is stabilized into the **ISA** matrix by the geometrical match within the **ISA** cyclic hexamer.

Three-component (ISA–COR–DBA1) Supramolecular Assembly

We had found that **DBA1** formed at the 1,2,4-trichlorobenzene/graphite interface a honeycomb molecular network having pores with a diameter of 3.0 nm due to van der Waals interactions between the interdigitated alkyl chains which served as direction-

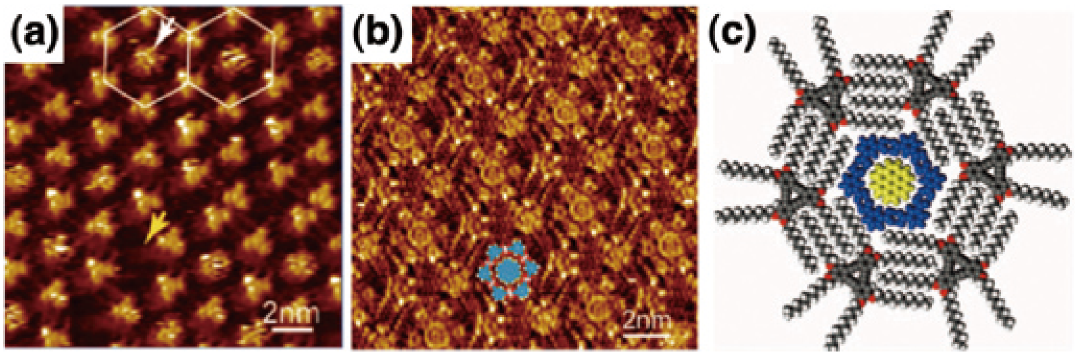

Fig.3 (a,b) STM images of **DBA** at the 1-octanoic acid/graphite interface (a) in the absence and (b) in the presence of **ISA** and **COR**. (a) The yellow arrow points to a distorted honeycomb cavity, while the white arrow highlights a **DBA1** molecule self-trapped in a honeycomb cavity. (b) A high-resolution image of the tricomponent architecture shows its submolecular detail. A model of the cluster **COR_1-ISA_6** is overlaid on the image. (c) An optimized model of the three-component hierarchical assembly of **COR_1-ISA_6-$DBA1_6$** on graphite with MM calculations.

al intermolecular linkages.[4] On the other hand, at the 1-octanoic acid/graphite interface, **DBA1** forms a close-packed pattern with some distorted honeycomb defects (marked with the yellow arrow in Figure 3a). Most of the DBA cores appear with a clear triangular shape, but some of them appear fuzzy (the white arrow in Figure 3a). We attribute these fuzzy ones to mobile DBA molecules self-trapped in the honeycomb cavities. When a drop of octanoic acid solution containing **ISA** and **COR** was added to the pre-assembled network of **DBA1**, a remarkable structural transformation was observed: the network of **DBA1** transformed from a close-packed network to a 2D honeycomb pattern, and **COR_1-ISA_6** clusters occupied the honeycomb cavities (Figures 3b and 3c). All the clusters have identical composition and symmetry. The **ISA** molecules, in their hexagonal H-bonded arrangement, are located at the corner of the hexagonal pore formed by **DBA1** molecules. Thus **COR_1-ISA_6** clusters fit perfectly in the hexagonal cavity, leading to an appreciable interaction between the **DBA1** host and the **COR_1-ISA_6** supramolecular guest, around –18 kcal/mol estimated by MM calculations. The submolecular resolution of **COR** and the **ISA** molecules in the host-guest matrices confirms that they are immobilized and no rotation occurs. Note that the **ISA** hexamer involves hydrogen bonding while the surrounding network of **DBA1** is stabilized by van der Waals interactions: different non-covalent interactions are at play at the two hierarchical assembly levels.

Guest-induced Structural Transformations

Patterns that are intrinsically non-porous can be transformed into the porous network upon adding an appropriate guest to the pore. Such transformations are explained by the gain in energy resulting from guest-substrate interactions, increased host–substrate interactions, and host-guest interactions which overcome the loss of stability inherent to the formation of "pore" and low-density host matrices.[5] In addition, the host-guest networks must be more stable than formation of phase-separated non-porous host and pure guest phases. The structural transformation of the molecular network of **DBA1** specifically induced by **COR_1-ISA_6** heterocluster indicates again the perfect structural match between the guest heterocluster and the hexagonal cavity of the host.

Dynamics and Recognition at the Interface

It is important to note that the sequence of addition of the three components to the surface does not affect the outcome of the network structure. This is a strong indication that the multicomponent architecture involving **DBA1**, **ISA**, and **COR** is formed in an equilibrium process. Furthermore, it suggests that recognition is involved between the heteromolecular cluster and the host matrix, possibly due to a selection process based on size and shape/symmetry commensurability of the cluster and cavity. To confirm this hypothesis, the host properties of **DBA1** have been compared with those of **DBA2**, an analogue with longer alkyl chains, which intrinsically should give rise to larger cavities upon self-assembly. The **DBA2** host matrix was also transformed into a porous network upon addition of an excess of **ISA**/**COR**. However, no well-ordered three-component assembly was observed. Only very few heteromolecular clusters are accommodated in some highly distorted cavities. The majority of the cavities appear fuzzy and featureless and are most possibly filled with **COR** molecules or mobile **COR-ISA_6** clusters. Only **DBA1** supports the uptake and stabilization of well-defined **COR_1-ISA_6** clusters in its cavities, emphasizing specific supramolecular recognition at the solid/liquid interface.

Conclusion

We have demonstrated a successful multicomponent and hierarchical templating approach to construct a three-component crystalline lattice, involving both hydrogen bonding and van der Waals interactions. The efficient recognition and selection processes allow for a programmable fabrication of highly complex hierarchical architectures. This approach paves the way for using the nanoporous DBA networks for instance as nanoreactors to create oligomers with well-defined size, symmetry, and composition. Moreover, thanks to the dynamic nature of the liquid-solid interface, the design and formation of more complex highly ordered substrate-based patterns would become possible.

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