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Two-Dimensional Crystal Engineering: A Four-Component Architecture at a Liquid–Solid Interface**

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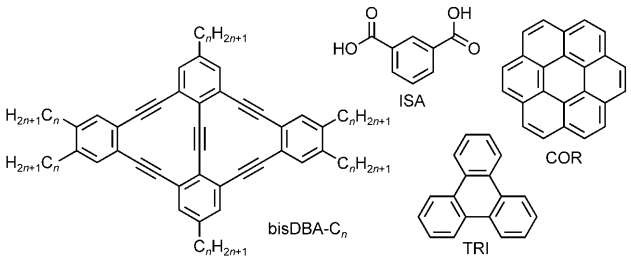
Molecular assemblies of increasing complexity can be spontaneously formed, based on a multitude of noncovalent interactions. Three-dimensional (3D) crystalline assemblies are most often homomeric, meaning that they are formed from (enantiomeric) copies of the same molecule.[1] Designing multicomponent heteromeric architectures is challenging, and ternary or quaternary cocrystals are extremely rare.[2] Similarly, the spontaneous formation of multicomponent heteromeric two-dimensional (2D) crystals requires efficient recognition and selection.[3] 2D molecular crystals are typically formed by self-assembly at the liquid–solid interface[4] or under ultrahigh-vacuum conditions (UHV)[5] on atomically flat (conductive) substrates, and their structures are frequently probed by scanning tunneling microscopy (STM). The confinement to two dimensions makes the self-assembly of multicomponent systems less problematic in terms of design and controlling intermolecular interactions (homomeric versus heteromeric). However, balancing molecule–substrate interactions is absolutely crucial. At the liquid–solid interface, solvent–molecule and solvent–substrate interactions must also be considered. Therefore, three-component assemblies are still rare both at the liquid–solid interface[3b,6] and under vacuum conditions,[7] and to our knowledge, no four-component crystalline architectures have been realized to date.

Herein we report the successful self-assembly of a four-component 2D crystal at a liquid–solid interface upon simple mixing of the four molecular components in the appropriate solvent at room temperature and application of a drop of this mixture to the basal plane of highly oriented pyrolytic graphite (HOPG). Equally important to the successful realization of this four-component network are the 2D crystal engineering and self-assembly concepts involved.

The strategy to form such a multicomponent network is based on the structural properties of low-density, so-called nanoporous, networks[8–10] and their ability to host guest species.[3b,7,11–13] A Kagomé type network has been fabricated with a rhombic-shaped fused dehydrobenzo[12]annulene (DBA) derivative with decyl chains (bisDBA-C_{10}, Scheme 1) at the liquid–solid (TCB–HOPG) interface



Scheme 1. Chemical structures of bisDBA-C_n, isophthalic acid (ISA), coronene (COR), and triphenylene (TRI).

(TCB = 1,2,4-trichlorobenzene).[13a] Kagomé[14] networks are characterized by two types of pores that differ in size and symmetry, that is, equally spaced hexagonal pores, each of which is surrounded by six smaller triangular pores.[13a,15]

From an engineering or structural point of view, our approach to formation of a four-component 2D crystalline network is straightforward: a heterocluster of coronene (COR, Scheme 1) surrounded by six hydrogen-bonded isophthalic acid (ISA, Scheme 1) molecules is predicted to fit into the hexagonal void of the Kagomé network of bisDBA-C_{12}. This surface-confined heterocluster (COR_1-ISA_6), with a diameter of 2.5 nm, is a stable entity and was previously hosted in a honeycomb network.[3b] Molecular modeling foresees triangular guests such as triphenylene (TRI, Scheme 1), trimethyltriphenylene, or trichlorotriphenylene (see the Supporting Information) to reside in the smaller triangular pores because of size and shape complementarity.

1-Octanoic acid was chosen as the liquid medium as it is able to dissolve ISA. After simple application of a drop of the 1-octanoic acid solution containing bisDBA-C_{12} (3.8×10^{-6} M), COR (4.5×10^{-4} M), ISA (2.5×10^{-3} M), and TRI (6.0×10^{-4} M) [0.0084 (bisDBA-C_{12}): 1 (COR): 5.5 (ISA): 1.3 (TRI)][16] on

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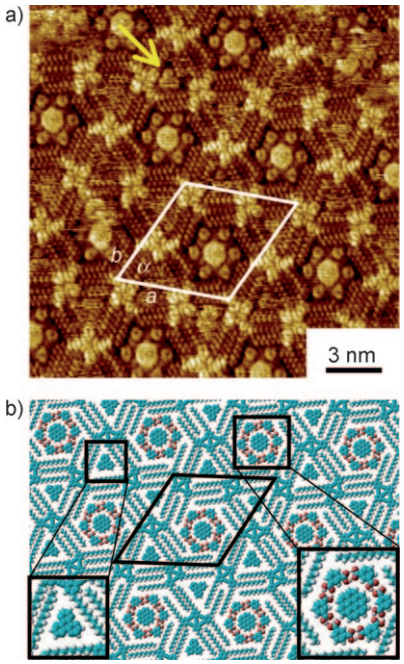

Figure 1. a) STM image of a mixture of bisDBA-C_{12} (3.8×10^{-6} M), COR (4.5×10^{-4} M), ISA (2.5×10^{-3} M), and TRI (6.0×10^{-4} M; $I_{set}=0.053$ nA, $V_{set}=-1.10$ V). b) Tentative network model showing the Kagomé structure of bisDBA-C_{12} hosting the COR_1-ISA_6 cluster and TRI in the hexagonal and triangular voids, respectively. The arrow points to a defect site with a distorted cavity shape: the cavity sides are formed by two, three, and four parallel alkyl chains, respectively, while in the regular crystal, each side is formed by three parallel alkyl chains. As a result, the guest molecule is trapped at the corner of a triangle.

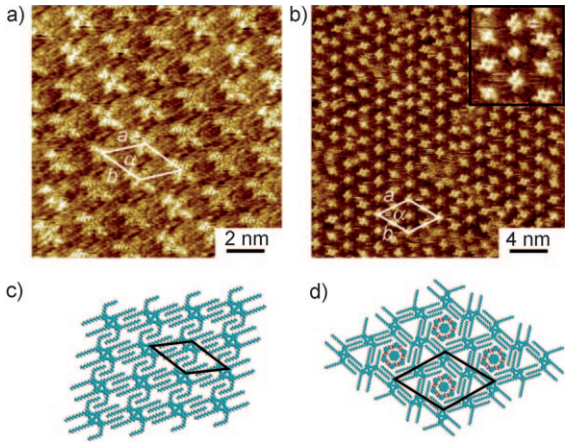

Figure 2. a,b) STM images of bisDBA-C_{12} (4.5×10^{-6} M) at the 1-octanoic acid–HOPG interface in the absence (a) and in the presence (b) of ISA (2.9×10^{-3} M) and COR (5.3×10^{-4} M). a) BisDBA-C_{12} forms a nonporous packing in the absence of any guest molecules ($I_{set}=0.10$ nA, $V_{set}=-0.86$ V). b) In the presence of COR and ISA, a structural transformation occurs, and a supramolecular three-component architecture forms. ($I_{set}=0.058$ nA, $V_{set}=-0.90$ V). The inset (side length = 7 nm) clearly shows the COR_1-ISA_6 cluster trapped inside the hexagonal void of the Kagomé structure. c) Tentative network model of the nonporous polymorph of bisDBA-C_{12}. d) Tentative network model of the Kagomé structure of bisDBA-C_{12} hosting the COR_1-ISA_6 cluster.

the basal plane of graphite, monolayer formation sets in (Figure 1): all six alkyl chains of bisDBA-C_{12} are adsorbed. A Kagomé structure is formed and covers the entire surface (see the Supporting Information). Each hexagonal void is filled with a COR_1-ISA_6 cluster. The triangular voids are filled by TRI molecules. The contrast reflects the signature of TRI, namely three fused aromatic rings. The orientation of TRI is clearly defined by the shape of the pore: the sides of TRI run parallel to the long axis of the alkyl chains forming the pore. The triangular pores are often characterized by streaky features, which is a signature for the mobility of the TRI species. The other triangular guests were adsorbed too, but the immobilization was most successful for TRI (see the Supporting Information). Note that the unit cell ($a=b=(5.5\pm0.1)$ nm, $\alpha=(61\pm5)°$) consists of 12 molecules: three bisDBA-C_{12}, one COR, six ISA, and two TRI.

Though the approach seems straightforward, the outcome of this self-assembly process is not obvious:

1) Polymorphism. In contrast to the targeted Kagomé structure, in 1-octanoic acid bisDBA-C_{12} forms a nonporous pattern at all concentrations probed (from 4.5×10^{-6} M to 4.5×10^{-4} M; Figure 2a,c). The unit-cell parameters are $a=(3.0\pm0.1)$ nm, $b=(2.8\pm0.2)$ nm, and $\alpha=(47\pm2)°$. In octanoic acid, the Kagomé pattern is therefore not the thermodynamically favored polymorph.

2) Templates. Low-density structures are not optimal from a free-energy point of view. However, template molecules can overcome the energy cost of forming these low-density patterns by initiating the formation of the targeted porous polymorph and stabilizing it by coadsorption.[3b,9e,13c,e,17] The highest efficiency is expected for (clusters of) template molecules with a high adsorption energy and a shape complementary to the pores.

In contrast to results obtained for a related alkylated DBA system, which was transformed upon addition of COR from a nonporous network to a honeycomb lattice with COR-filled hexagonal pores identical in size to those of the anticipated Kagomé pattern,[13c] mixing of bisDBA-C_{12} and COR only leads to the nonporous bisDBA-C_{12} pattern. Upon mixing bisDBA-C_{12}, COR, and ISA, however, the Kagomé network was indeed achieved, and the central hexagonal pore was filled by an immobilized COR_1-ISA_6 heterocluster (Figure 2b,d).[18] The unit-cell parameters of the Kagomé lattice containing COR_1-ISA_6 are $a=b=(5.6\pm0.1)$ nm and $\alpha=(62\pm3)°$. The ideal fit of the COR_1-ISA_6 heterocomplex is much more effective than COR or ISA alone to template the formation of the Kagomé lattice. It is a unique example of a templating supramolecular complex. Moreover, neither COR nor ISA fits (stabilizes) the triangular pores well, and combined with their poor performance in stabilizing the hexagonal pores, these monocomponent templates are not efficient in driving the formation of the porous polymorph.

In contrast, a mixture of bisDBA-C_{12} and TRI does lead to Kagomé formation (Figure 3a). TRI fills the hexagonal pores as well as the triangular pores. Modeling suggests that both the size and shape of a cluster of six TRI molecules are complementary to the hexagonal void (see the Supporting Information), while one TRI molecule fits a triangular pore,

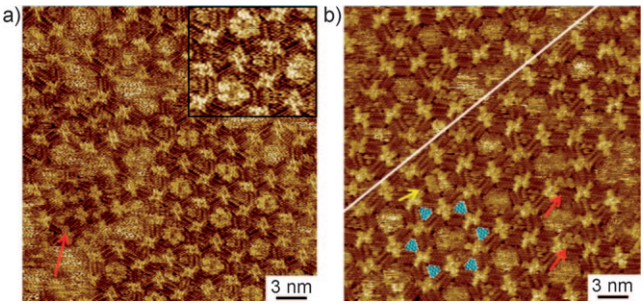

Figure 3. a) STM image of a Kagomé pattern formed from a mixture of bisDBA-C_{12} (3.8×10^{-6} M) and TRI (6.0×10^{-4} M) at the 1-octanoic acid–HOPG interface. ($I_{set}=0.095$ nA, $V_{set}=-0.90$ V). The fuzzy areas contain mobile molecules. The red arrow indicates a defect area. The inset (side length = 9 nm) reveals that hexagonal pores of the Kagomé lattice are filled by clusters of TRI. The triangular pores host one TRI molecule. b) STM image of a monolayer formed from a mixture of bisDBA-C_{12} (6.0×10^{-6} M), COR (5.3×10^{-4} M), and TRI (6.0×10^{-4} M) at the 1-octanoic acid–HOPG interface. ($I_{set}=0.095$ nA, $V_{set}=-1.0$ V). Six molecular models of TRI are superimposed on the STM image. The white line indicates a domain boundary, separating mirror-image domains. Some TRI-dimer defects are indicated by red arrows. A hexagonal pore filled with immobilized guests is indicated by a yellow arrow.

as verified experimentally. A mixture of bisDBA-C_{12}, TRI, and COR also leads to Kagomé formation (Figure 3b). In this case, TRI fills the triangular pores, while the hexagonal pores are filled with mobile guests (clusters of TRI and/or clusters of TRI and COR), which exhibit a fuzzy contrast.

3) Concentration. For the three-component network consisting of bisDBA-C_{12}, COR, and ISA, systematic studies show that only an approximate 100-fold excess of COR (5.3×10^{-4} M) and ISA (2.9×10^{-3} M) leads to the exclusive formation of heterocomplex-filled Kagomé domains of bisDBA-C_{12} (4.5×10^{-6} M) [0.0085 (bisDBA-C_{12}): 1 (COR): 5.5 (ISA)].[16] In other words, bisDBA-C_{12} is adsorbed much more effectively than the other components (excluding any potentially involved kinetic effects). An overall increase in concentration at a constant ratio of network components (achieved spontaneously upon solvent evaporation) did not affect the outcome of the self-assembly process. Decreasing the overall concentration while keeping the ratio constant also resulted exclusively in heterocomplex-filled Kagomé domains.[19] For the four-component system, the optimized conditions for the three-component system were kept constant and TRI was added at the same concentration as COR. These observations confirm the importance of concentration and stoichiometry control at a liquid–solid interface for multicomponent self-assembly, as reported recently.[3e]

4) Dynamics. The multicomponent patterns are thermodynamically stable, and complete surface coverage showing exclusively the Kagomé pattern is achieved after roughly one hour under optimized concentration conditions. This result was experimentally verified for the multicomponent system consisting of bisDBA-C_{12}, COR, and ISA. Under favorable imaging conditions, initially the coexistence of guest-filled Kagomé domains and nonporous bisDBA-C_{12} domains is observed. Over time, the nonporous domains disappear in favor of the guest-filled Kagomé domains (see the Supporting Information).

Systematic experiments in which the four different components were added in sequence were not performed, as it is hard to control the relative ratio and concentration in this way. However, adding a mixture of COR and ISA on top of an already existing nonporous bisDBA-C_{12} pattern results in the formation of Kagomé patterns filled with the COR_1-ISA_6 heterocomplex in addition to COR_1-ISA_6 domains. Preformation of COR_1-ISA_6 domains and subsequent addition of bisDBA-C_{12} gave qualitatively the same results: heterocomplex-filled Kagomé patterns are formed (see the Supporting Information). Thus, it is fair to conclude that the sequence in which the different compounds are added does not fundamentally affect the outcome of the supramolecular self-assembly process: the described patterns are the thermodynamically favored ones. However, premixing is required to promote the fast and defect-poor formation of the targeted multicomponent architectures.

We suggest that the four-component 2D crystallization is a cooperative process involving the action of all components at the same time and not a sequential process in which first the heterocomplex-stabilized Kagomé pattern is formed with subsequent host–guest complexation of the triangular compound, or inversely in which stabilization of the triangular pores by TRI is followed by occupation of the hexagonal pores by the COR_1-ISA_6 heterocomplex. Although it is not clear which factor is more important, it is deduced that the exact size matching of the guests (clusters) to both types of pores is crucial for attaining stable four-component self-assembly.

In summary, we have demonstrated the successful 2D crystal engineering of a complex four-component network at the liquid–solid interface, as revealed by scanning tunneling microscopy. After optimizing the concentration of the four components and their ratio, simply mixing the components and bringing the solution in contact with the graphite substrate leads to spontaneous formation of the 2D four-component crystal. Furthermore, we identified the conditions necessary to induce the structural transformation of an initially nonporous network into a porous one (at the level of the bisDBA-C_{12} molecules) by coadsorbing the appropriate template molecules, which fill and stabilize the pores. Size matching between guest molecule or cluster and network pore is very important for the formation of well-defined multicomponent networks. The dynamic nature of this complex supramolecular self-assembly process was established. Unraveling the concepts of 2D crystal engineering paves the way to the formation of more complex and functional surface nanopatterns, also at a liquid–solid interface. If stabilized, networks that are designed to host different species could, for example, turn out to be useful for chemistry in nanoconfined spaces or for covalent capture, leading to the formation of previously inaccessible compounds.[20] Or they could be used as templates for directed self-assembly.

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[16] The imperfect stoichiometric ratio COR/ISA (1:5.5 instead of 1:6) was not intentional. The ratio COR/TRI is 1:1.3 rather than 1:2 owing to the limited solubility of TRI. As these conditions gave rise to successful guest-stabilized Kagomé patterns, the solution composition was not adjusted. These results further demonstrate that a perfect stoichiometric composition of the solution is not a prerequisite for successful multicomponent self-assembly.

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[18] Given the fact that benzoic acid does not form dimers in a polar solution through hydrogen bonding (H. Yamada, K. Yajima, H.

Wada, G. Nakagawa, *Talanta* **1995**, *42*, 789), the formation of the heterocluster COR_1-ISA_6 in a dilute octanoic acid solution is very unlikely. It is likely formed upon surface confinement.

[19] Too low a concentration of bisDBA-C_{12} (3.0×10^{-6} M) [0.0056 (bisDBA-C_{12}): 1 (COR): 5.5 (ISA)] leads to the coexistence of COR_1-ISA_6 domains and heterocomplex-filled Kagomé domains. Too high a concentration of bisDBA-C_{12} (1.9×10^{-5} M) [0.036 (bisDBA-C_{12}): 1 (COR): 5.5 (ISA)] leads to the coexistence of Kagomé and nonporous features (see the Supporting Information).

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