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Nanopatterning of a Covalent Organic Framework Host-Guest System

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We have used a boroxine-based COF as a template for C_{60}-fullerene self-assembly on graphite. Local removal of the COF by STM based nanomanipulation creates nanocorrals that may host other species.

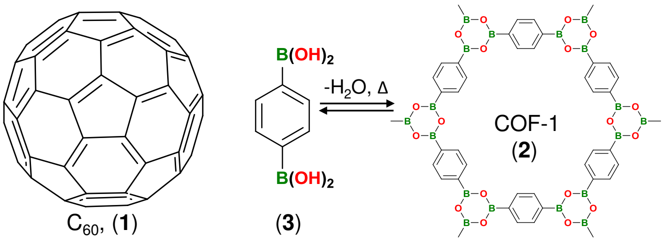
The fabrication of regularly ordered host-guest architectures on surfaces may lead to applications in various domains of nanotechnology that rely on the controlled patterning of functional surfaces. As host networks, many supramolecular systems have been designed and tested. Bound through Van der Waals-interactions,[1-3] hydrogen bonding[4-6], metal-organic coordination,[7] and other supramolecular interactions, they can be easily tuned to fit the nature and dimensions of the guest molecules.

Unfortunately together with this power of flexibility come limitations. Supramolecular interactions forming the host framework are comparable in strength and sometimes in nature to those binding the host and guest together thus making it difficult to manipulate/replace the guest without affecting the host. Furthermore, the dynamic nature of self-assembly being the blessing for the design of large highly ordered domains is also the curse when it comes to the stability of the created nanopatterns since any change in concentration, temperature or the composition of the media in contact with the surface may result in reassembly, formation of a different polymorph or even complete desorption from the surface.[8] An interesting alternative to supramolecular hosts is the use of two-dimensional covalent organic frameworks (2D COFs).[9]

In recent years, the synthesis of 2D COFs has gained a lot of interest and has been successfully performed both in ultra-high vacuum (UHV)[10-15] and ambient conditions[16-20]. Linking the building blocks together by covalent bonds creates strong sheets of material with well-defined composition and porosity. Polycondensation reactions involving Schiff bases[17, 19, 21] or boronic acid derivates [16, 18, 22] are the most studied so far and under optimal conditions can yield extended porous networks that compete with supramolecular systems, both in terms of domain size and structuralquality.[19, 20, 22]

In this communication, we provide the characterization of a COF based host-guest system and highlight some new possibilities that were impossible or rather difficult for previously reported host-guest assemblies. Our system consists of fullerene C_{60} (**1**) as the guest and polyboroxine framework (COF-1) (**2**) as the host.

Monolayers of COF-1 were synthesized via polycondensation of benzene-1,4-diboronic acid (**3**) using a slightly altered protocol reported by Dienstmaier et al.[16] Prepared COF-1 samples were heterogeneous, with areas differing in the coverage (regions with bare graphite, COF mono- and bilayers) and morphology (with varying domain size, and the nature and number of defects). Such sample heterogeneity was beneficial for our all-around investigation of fullerene-COF interactions and co-assemblies.



Scheme 1 Chemical structures of the guest (**1**), the host (**2**) and synthesis of **2** from the precursor **3**.

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Electronic Supplementary Information (ESI) available: [Synthesis of COF-1, details of DFT calculations and STM measurements, simultaneous visualization of COF-1/C_{60}, visualization of defects in COF-1, model of C_{60} multilayers on COF-1 and sandwich-like structures, clustering of C_{60} molecules, STM as an invasive tool for multilayers, multilayer formation of COF-1, increasing the C_{60} coverage through tip-scanning, details of scratching experiments]. See DOI: 10.1039/x0xx00000x

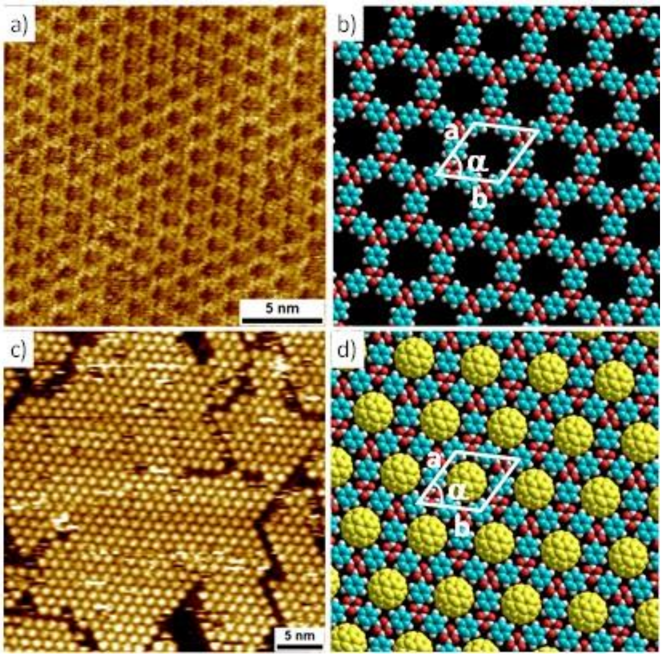


Fig. 1 STM images of the parent COF-1 (a) and its host-guest co-assembly with C_{60} (c), respectively. Tentative molecular models for COF-1 (b) and C_{60}@COF-1 host-guest co-assembly (d). Fullerenes adsorb inside the pore and for the convenience of assignment are highlighted in yellow. (a) V_{bias} = -0.600 V, I_{set} = 0.06 nA60 pA. (c) V_{bias} = -0.900 V, I_{set} = 0.02 nA.

Applying a saturated (c ≈ 2.9 mM) solution of C_{60} in 1-phenyloctane (PO) on top of a COF-1/HOPG substrate results in a hexagonal pattern of bright blobs, assigned to the individual C_{60} molecules (Fig 1). Differing from the close-packed arrangement of C_{60} on graphite ($a = b = 1.00 \pm 0.10$ nm, $\alpha = 60°$),[23] the unit cell parameters of this self-assembled structure $a = b = 1.50 \pm 0.10$ nm, $\alpha = 60°$ are the same as those of the parent COF-1. Each unit cell contains one C_{60} molecule that occupies the pores of the host network (Fig 1) as evidenced from the perfect superposition between the positions of fullerenes and the centers of the pores (Fig S5).

The surface is not fully covered with C_{60} molecules. There are point defects where a C_{60} molecule is missing. In general, the C_{60} molecules cluster together forming islands that are separated from each other by dark troughs or cracks. Interestingly by mapping out these fullerene islands it is possible to determine if they were formed on the same COF domain or on different ones, thus helping to visualize the defects in the COF monolayer as well (Fig S6).

C_{60} on its own does not form a stable self-assembly at the 1-phenyloctane-graphite interface at room temperature. Thus, fine supramolecular interactions between C_{60} and COF-1/graphite must play a role in the stabilization of this host-guest self-assembly. DFT modelling shows that the interaction energy is sensitive to the pore size and the periodicity of the host network, suggesting the importance of both host-guest and guest-guest interactions (Fig S3, S4). Through-space interactions between C_{60} guests result in a high degree of guest clustering in monolayers with low C_{60} coverage (Fig S8).

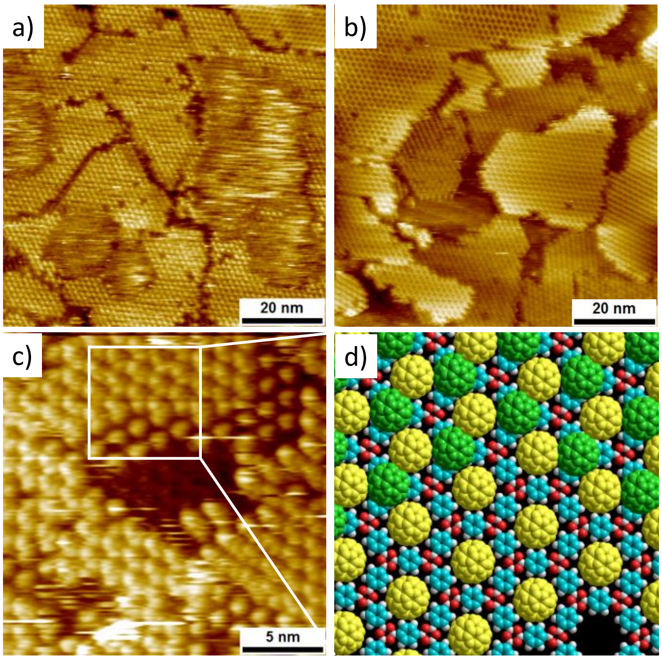


Fig. 2 Epitaxial growth of the 2nd fullerene layer. (a), (b) STM appearances of the multilayer growth imaged with unstable and stable tips, respectively. A representative high resolution STM image (c) and a tentative molecular model (d) of an area with empty COF-1, host-guest assembly C_{60}@COF-1 and assembly with two layers of fullerene. Fullerenes of the first and the second layers are colored yellow and green respectively. (a, b, c) V_{bias} = -0.900 V, I_{set} = 0.02 nA.

While imaging the self-assembly from concentrated fullerene solutions we noticed formation of persistent regions partly covering the domains of the C_{60}-filled COFs (Fig 2a). With more stable tips it became clear that these regions consist of fullerene molecules organized into the 2nd layer on top of C_{60}@COF-1. They form a distinct honeycomb-like pattern (Fig 2c). A tentative model is shown in Fig 2d. Here, the 2nd layer of fullerenes has the same structure and symmetry as the 1st one. It is shifted with respect to the first one. Such shift allows for efficient close contact interactions with three neighboring fullerenes from the other layer. Interestingly, the formation of the 2nd fullerene adlayer implies the possibility of further 3D growth (Fig S7) in which the symmetry, spacing and orientation are predefined by COF-1 (epitaxial growth of C_{60} multilayers on top of COF-1/graphite). Unfortunately, STM appears to be too invasive (Fig S9), and thus the possibility of the COF-directed growth of ultrathin films of fullerene warrants a separate investigation using a suitable technique (e.g. AFM).

Formation of multilayers is also possible for COFs.[18] Due to their size, the fullerene guests can only access the pores of the top-most layers of COF-1, yielding anticipated variations in the STM contrast of the molecular adsorbates on mono- or bilayers of the COF (Fig S10). Inspired by the work of Blunt et al.[24] we attempted the creation of COF-C_{60}-COF sandwich-like heterostructures (Fig S7), albeit unsuccessfully - formed highly inhomogeneous films made it difficult to scan the samples and to identify molecular constituents and morphology.

BesidesThe structural diversity programmed into the two-dimensional host-guest systems at the structural level of the building blocks, available supramolecular interactions and self-assembly processes (i.e. bottom-up approach) provides the means to control and engineer supramolecular structures. Another complementary and equally exciting possibility to engineer a given structure, property or function in new materials at the nanoscale is offered by direct local manipulations of the host, guest and/or both, for example using SPM lithography (i.e. top-down approach to nanofabrication). Below we present preliminary results of our work in this direction.

The STM tip is a macroscopic physical object, the position and precise movement of which can be controlled with sub-nm spatial resolution, necessary for the STM imaging.

As a consequence, molecules and nanoscale objects interact with the tip and can be moved in response to its movement, speeding up all adsorption/desorption and diffusion-related processes. Indeed, similarly to the previous work, some fullerene molecules leaving or coming into COF pores can be easily spotted in STM as semi-circular (instead of the usual circular) shapes (Fig 3a). Furthermore, local reshuffling of filled and empty positions has been routinely observed in sequential STM images of C$_{60}$@COF-1 (Fig 3b), illustrating the high speed of molecular events when compared to that of the STM measurement. Finally, upon prolonged continuous scanning of low-coverage fullerene samples significant local concentration of adsorbed fullerenes has been observed in the scanned area (Fig S11). This might be due to the high polarizability of C$_{60}$[25] and the strong local electric field between the tip and the sample, trapping fullerene molecules in the scan area.

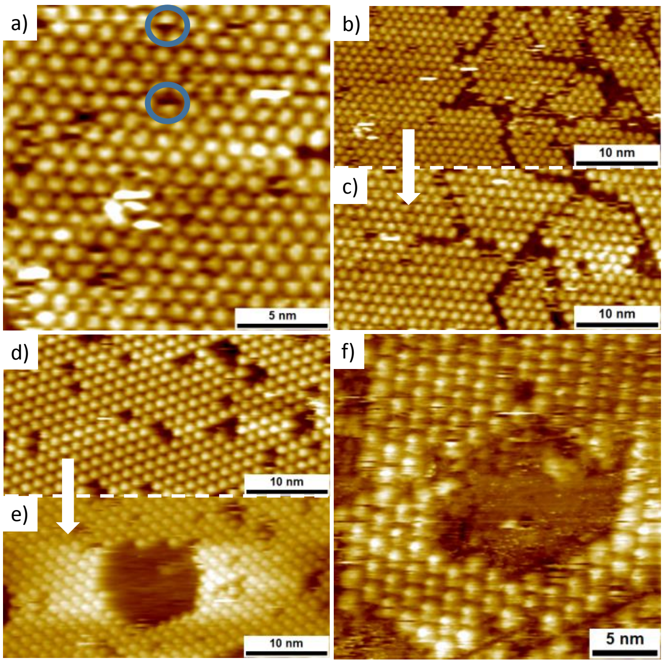


Fig. 3 Visualization and STM-assisted manipulations at nanoscale: a) adsorption and desorption events recorded in a single image, b)→c) sequential images showing changes in the positional order ("reshuffling") of C$_{60}$-guests. d)→e) the result of STM lithographic patterning of C$_{60}$@COF-1 host-guest assembly. f) Importance of the crystallographic directions and pattern symmetry on the preferential cleavage of the covalent framework. (a-f) V_{bias} = -0.900 V, I_{set} = 0.02 nA.

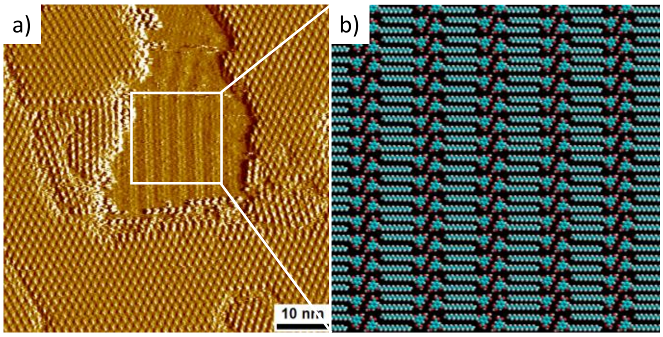
Maintaining a set-point tunneling current enforces a certain tip-sample separation, and thus weakly bound, poorly-conductive matter can be removed upon continuous scanning (Fig. S8). Earlier mentioned difficulties in imaging the 2nd layer fullerenes (Fig 2a) have the same origin- STM tip is too invasive due to its macroscopic inertia, technical limitations of the STM feedback system and the high local electric field.

Notably, the boroxine COF layer can also be "scratched" by STM tip (Fig. 3). This happens at relatively high tunneling current (0.3nA-0.7nA). The magnitude and the sign of the bias voltage have a much lower importance with a preference towards the smaller bias (typically, we use V_{bias}= -0.001V -1 mV). In our tests for this work, we focused on the lithography of small (~10-20 nm) rectangles. At this scale, the ~1.5 nm periodicity of COF-1 is too grainy to form straight lines, ideally resulting in hexagonal shapes (Fig. 3f). Also, defects present in the original COF layer adversely affect the scratched pattern often removing much larger areas than originally intended (Fig S12).

Among possible mechanisms for the spatially localized rupturing of the boroxine COF, some kind of an electron-assisted oxidative cleavage of C-B bonds appears to be the most plausible. Energy gain from breaking C-B bond in favor of C-O and especially B-O is a huge drive behind such reactions.[26] Indeed, boroxines are relatively labile to oxidants including molecular oxygen.[27]

STM lithography was successfully applied to nanopattern various substrates and materials, usually under rather harsh scanning parameters.[28] For example, the STM lithography of graphite can be done with nanometer precision at single graphene layers by scanning at 2.2-2.6V bias voltage.[29, 30] This is necessary to achieve the oxidation of C$_{sp2}$-C$_{sp2}$ bonds to C-O bonds and volatile products (CO, CO$_2$, etc.). Laterally controlled removal of the boroxine COF on the other hand, uncovers pristinegraphite surface for further functionalization. An example of such functionalization is shown in Figure 4 where a scratched area inside C$_{60}$@COF-1 monolayer was filled with self-assembled 5-tetradecyloxyisophthalic acid lamella by adsorption from the supernatant solution (Fig S13).

Fig. 4 Self-assembly of ISA-OC14 on the freshly exposed (after lithographic removal of COF-1) HOPG surface. (a) V_{bias} = -0.900 V, I_{set} = 0.02 nA.



In conclusion, we have shown that fullerene C_{60} forms a host-guest networkwith boroxine COF-1. Advantageously, the C_{60} decoration can additionally be used as a marker to visualize even tiny flakes of COF-1 with STM. High fullerene occupancy of the COF pores and relatively small (a=b= 1.5 nm) periodicity of the framework result in additional stabilizing interactions between the guest molecules and facilitates epitaxial growth of fullerene adlayer(s). Thus, ultrathin films of COF-1 might be of interest as insulating coatings for directed layered growth of fullerene and its derivatives. Finally, we have demonstrated that these host-guest monolayers can be easily patterned with STM lithography under very mild conditions, which opens up possibilities for the design of advanced functional nanoarchitectures.

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