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Long-Range Alignments of Single Fullerenes by Site-Selective Inclusion into a Double-Cavity 2D Open Network

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Multicomponent supramolecular 2D networks are attracting considerable interest as highly ordered functional materials for applications in nanotechnology and organic electronic devices.[1] The challenge consists in controlling the ordering of two or more molecular species into specific architectures over an extended length scale with molecular precision. Highly organized supramolecular arrays can be obtained by self-assembly of complementary molecules which can interlock via intermolecular interactions such as hydrogen bonds.[2] An alternative approach aimed at tailoring multicomponent 2D networks consists of trapping guest molecules into a host open network to form guest−host architectures.[3] These networks can be produced on various metallic surfaces in either ambient or UHV conditions and are usually stable at room temperature. Various guest−host architectures have been recently prepared such as coronene-containing nanoporous networks of annulene derivatives,[3b,c] C_{60} molecules trapped into Kagome networks,[4] network-SAM hybrid structures obtained by filling the cells of a PTCDI-melamine network with thiols,[5] or isolated short alignments of single C_{60} molecules using Fe-containing terephthalic acid as the host.[1b]

However one key objective in molecular electronics remains the formation of extended 2D arrays of single molecules made of long and continuous alignments. We show here by means of scanning tunneling microscopy (STM) at the liquid−solid interface[6] that a self-organized nanocavity array of a star-shaped oligothiophene **1** (Figure 1a) can be used as a nanotemplate to produce long-range alignments of single C_{60} guest molecules. **1** self-assembles on highly oriented pyrolitic graphite (HOPG) into a long-range network made of two types of elongated cavities having different sizes and shapes. Postdeposition of C_{60} leads to the formation of defect-free alignments of single C_{60} molecules by site-selective inclusion into one of the two cavities.

Compound **1** was synthesized according to a procedure described elsewhere.[7] It consists of a planar rigid trithienobenzene core connected to three bithiophene arms, each of them being terminated by a hexyl chain. The procedures for deposition of **1** and C_{60} as well as STM imaging at the *n*-tetradecane/HOPG interface are reported in the Supporting Information (SI). Figure 1b shows that **1** self-organizes into long-range domains up to 200 nm in lateral size. High resolution STM (Figure 1c) reveals that the 2D lattice is an open network consisting in vertical and horizontal cavities of different sizes and shapes, each of them being delimited by six molecules. The length of the vertical cavity is 4.0 nm while that of the horizontal one is 4.5 nm. Both cavities have an elongated shape with an average width of ~1.0 nm. However, the key difference is that the right end of the horizontal cavity is much larger with a width of 1.5 nm. The width of molecule **1** as measured by STM is ~20 Å, in good agreement with the calculated width without the carbon chains (19.9 Å, Figure 1a). The lattice constants of the unit cell are $a = 6.5$ nm, $b = 3.8$ nm, $\alpha \approx 96°$. Figure 1c also reveals that the conjugated cores are T-shaped instead of having the expected star shape. This can be explained by a 180° rotation of one branch around the single bond connecting the bithiophene moiety to the conjugated rigid core. The resulting *syn*-conformation would then align two of the three branches along the same axis and reduce the angle with the third one (see SI for detailed conformational models of **1**). Such a T-shape has already been observed by STM on another oligothiophene having a ternary symmetry.[8] Note that the hexyl chains are not visible in the STM image. A model for the open network is shown Figure 1d. Finally, comparison of STM images of Figure 1 show that their respective unit cells are mirror images and that the double cavity open network is chiral (see SI).

After the double-cavity open network of **1** is formed, a droplet of a solution of C_{60} in *n*-tetradecane is added onto the sample. Figure

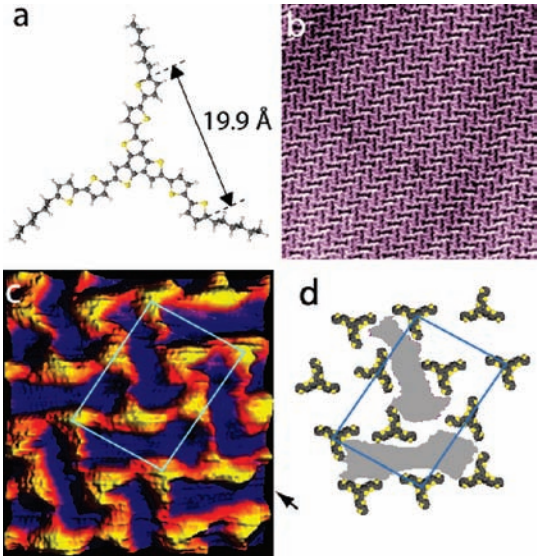

Figure 1. (a) Chemical structure of oligothiophene **1** used to generate the host network (yellow balls correspond to sulfur atoms). (b) STM image of the double-cavity self-assembly of compound **1** on graphite (70 × 70 nm^2; $V_s = 0.35$ V, $I_t = 70$ pA). Vertical and horizontal cavities are clearly visible in dark contrast. (c) High resolution 3D STM image[9] (10 × 10 nm^2; $V_s = 0.4$ V; $I_t = 20$ pA). Molecules of **1** appear in yellow-red while both types of cavities appear in blue. The unit cell is materialized as a parallelogram. (d) Model of the open network with the two cavities represented as gray areas.

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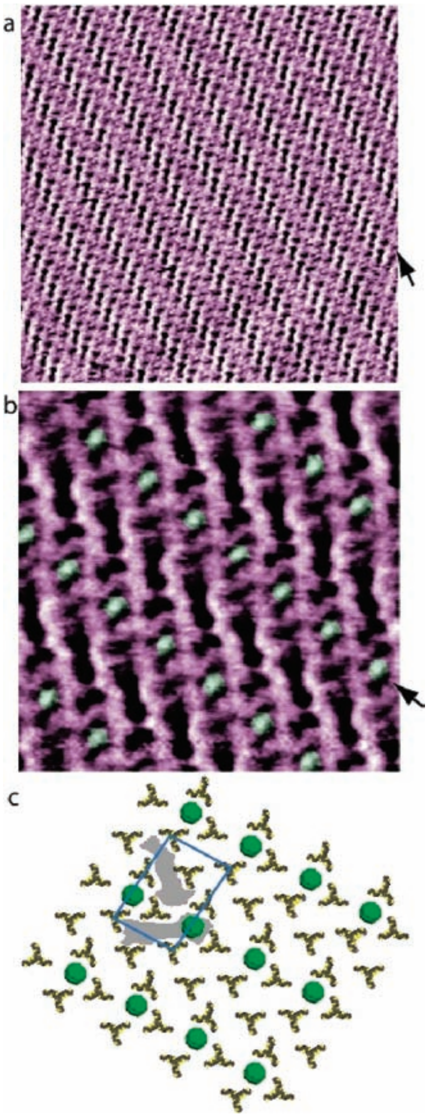

Figure 2. STM images of the 1-C_{60} guest−host network on graphite. (a) 70 × 70 nm^2; $V_s = 0.30$ V; $I_t = 40$ pA. All vertical cavities remain empty and appear in dark contrast. All horizontal cavities are filled with a C_{60} and are no longer visible. (b) 21 × 21 nm^2; $V_s = 0.3$ V; $I_t = 40$ pA. Individual C_{60} molecules appear in green and are indicated by an arrow. (c) Model of the long-range alignments of single C_{60} in the open network of **1** (see Figure 1d).

2a is a typical STM image recorded after postdeposition of C_{60}. Periodic parallel stripes appear in the network (indicated by black arrows) while the horizontal cavities disappear and the vertical cavities remain clearly visible in dark contrast. The unit cell of the network is the same as that of the original C_{60}-free open network. A high resolution STM image (Figure 2b) highlights that these linear stripes consist of alignments of single C_{60} molecules inside the original network of **1**. Comparison between STM images of Figures 1c and 2b indicates that the C_{60} molecules are nested inside the largest extremity of the horizontal cavities. The C_{60} molecules occupy all of these specific sites, and no intra- or intercavity hopping or displacement is observed. Then, under ambient conditions the C_{60} molecules can only be trapped in the largest cavity, the vertical cavity being too small to host C_{60}.

A number of networks have been obtained by exploiting noncovalent directional bonding interactions such as H-bonds. However, C_{60} molecules lack such directional bonding attributes. Comparison between Figures 1 and 2 shows that the initial 2D network of **1** is not modified by inclusion of C_{60}. Furthermore, the model in Figure 2c clearly shows that one molecule out of four in the unit cell is not in direct contact with C_{60}. We also note that the C_{60}/**1** ratio is 1:4, which is largely deficient in C_{60}, and that increasing the C_{60} concentration in the solution used for postdeposition does not modify this ratio. These characteristics suggest that the C_{60}/**1** network is not stabilized by donor−acceptor charge transfer interactions. Besides, although the hexyl chains of **1** are not visible on STM images, they can only occupy a small area of the cavities thus minimizing lateral C_{60}/**1** interaction. Finally, the overall C_{60}/**1** interaction is weak, and the site-selective inclusion of C_{60} into the largest cavity seems to be essentially governed by diffusion and interaction with the graphite surface.

In conclusion, we demonstrate that C_{60} can be trapped into specific sites of a 2D double-cavity open network, thus forming long-range alignments of single molecules. Since only one of the two cavities has the right size to host C_{60}, the smallest cavity remains empty and is thus available to trap additional species of smaller size. We are currently investigating the selectivity of the two cavities as potential host sites for chemical guest species of various sizes. Growing the C_{60}−**1** guest−host open network into the third dimension is another exciting challenge and could lead to segregated columnar stacks of both components. With compound **1** and C_{60} being respectively electron-donating[10] and -accepting molecules, the C_{60}−**1** guest−host system could thus constitute a model system to explore photoinduced charge transfer at the molecular level and be useful for future photovoltaic devices.

Supporting Information Available: Additional experimental details and molecular models. This material is available free of charge via the Internet at http://pubs.acs.org.

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