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Perfectly Straight Nanowires of Fullerenes Bearing Long Alkyl Chains on Graphite

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To handle, operate, and manipulate nanoscopic devices, self-organization of molecular modules on solid surfaces and interfaces has led to diverse research activities in nanotechnology and nanoscience.[1] Fine-tuning of interfacial and intermolecular interactions permits building well-defined, ordered structures over large areas, which have been visualized, characterized, and manipulated by scanning probe techniques.[2] Many molecules, such as derivatives of long alkyl chains, self-assemble at suitable interfaces, such as highly oriented pyrolytic graphite (HOPG),[3] giving rise to close to perfectly ordered structures. These ordered molecular structures can serve as a template layer for biological molecules[4] and for visualization of aromatic molecules.[5] Other examples include the topological reaction of diacetylenes at the nanoscale[6] or the expression of molecular chirality.[7]

One-dimensional (1-D) nanostructures of organic semiconductors are attractive candidates as active components in electronic nanodevices. A class of materials for which this is particularly relevant is that of nanocarbon materials, including fullerenes. While the 2-D arrangement of fullerenes on surfaces is well established,[8] alignment of fullerenes in 1-D architectures is far less common.[9] We, therefore, asked if it is possible to self-assemble nanowires in a predictable way by using tailored fullerenes. As a structure directing component, we attached to the fullerene long alkyl chains, which should induce epitaxial assembly on HOPG in a facile way. In addition, the alkyl chains act as insulating barriers, which spatially separate the fullerene nanowires. In this communication, we report the formation of 1-D lamellae, epitaxially oriented along the HOPG lattice, formed by fullerene derivatives bearing long alkyl chains (Figure 1a). The distance between adjacent nanowires can be regulated at nanometer level by the molecular design.

The fullerene derivative with three hexadecyl chains (**1**) was recently synthesized. In the volume phase, this molecule exhibits a variety of solvent-dependent hierarchical architectures, including fibers, spheres, disks, and cones.[10] On the basis of these findings, we decided to synthesize fullerene derivatives (**2**−**5**) and study their assembly on HOPG. The newly synthesized fullerenes were prepared following the same strategy as for **1** and were unambiguously characterized by ^{1}H and ^{13}C NMR, FT-IR, and UV−visible spectroscopy as well as MALDI-TOF mass spectrometry (Supporting Information).

Fullerenes **1**−**5** were spin-coated from chloroform solutions ($c = 2 \times 10^{-5}$ M) onto freshly cleaved HOPG under conditions to achieve submonolayer coverage in order to reveal structural details of the interfacial layers. AFM measurements were carried out in tapping-mode under ambient atmosphere, and STM measurements were performed at 100 K under ultrahigh vacuum.

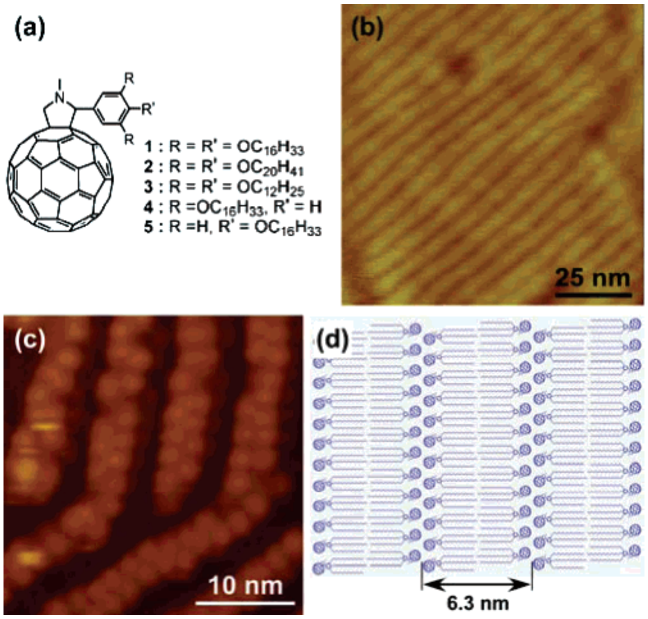

Figure 1. (a) Structure of fullerene derivatives (**1**−**5**). AFM image (b) of **1** on HOPG spin-coated from $CHCl_3$ solution (scan range 100 × 100 nm^2, Z range 2 nm). (c) High-resolution STM image of **1** on HOPG (scan range 30 × 30 nm^2; I_{set} = 40 pA; V_{bias} = +3.0 V). STM (c) reveals the organization of the C_{60} moieties within the lamellae. (d) Schematic illustration showing the molecular organization of **1** in the lamellae.

Tapping-mode AFM images reveal that fullerene **1** forms a 1-D lamellar structure on HOPG (Figure 1b). The length of the lamellae exceeds 100 nm. The lamellae are characteristic for alkyl chain nanostructures on graphite.[3] Presumably, the alkyl chains assemble along the underlying lattice axis of the basal plane of graphite, thus arranging the fullerene moieties on the surface. This hypothesis is supported by the observation that stripes in different domains are rotated by multiples of 60° with respect to each other, reflecting the symmetry of the underlying lattice. The periodicity of the nanostripes is determined to be 6.3 nm. On the basis of molecular modeling, the length of **1** in an *all-trans* conformation is estimated to be 3.1 nm,[10] that is half the lamellar width. Therefore, we propose that the lamellae are composed of fully extended alkyl chains, and that the molecules are arranged in a head-to-head bilayer architecture. The AFM image reveals a height difference in the dark and bright regions (Figure 1b) of 0.4−0.5 nm. Alkanes are expected to have a height of 2.5 Å and C_{60} of 7 Å.[11] We associate the bright regions with the C_{60} moieties and the darker ones with the alkyl tails. The data suggest that all three alkyl chains adsorb to the surface. In Figure 1c, the high-resolution STM image, measured under the optimized conditions, shows lamellae composed of C_{60} arranged in a zigzag-type fashion. The periodicity of the lamellae

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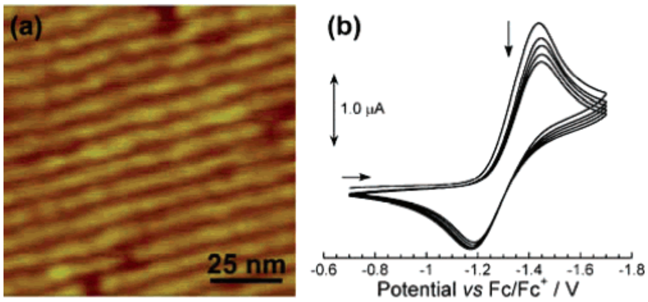

Figure 2. AFM image (a) of **2** on HOPG spin-coated from $CHCl_3$ solution (scan range 100 × 100 nm^2, *Z* range 2 nm). Cyclic voltammogram of **2** (b) on HOPG (0.1 M *n*-Bu_4NClO_4, CH_3CN, Ar atmosphere, scan rate 0.1 V s^{-1}, 20 °C).

is again 6.3 nm. The C_{60} moieties appear larger (approximately 1.8 nm) than their actual size (approximately 1 nm)[9,12] perhaps because of the tip-object convolution. Apparently, the C_{60} moieties are not close packed as one would expect from the spatial mismatch of three alkyl chains and C_{60}. The organization of **1** within the lamellae is schematically illustrated in Figure 1d. Epitaxial ordering of the alkyl chains on the basal planes of graphite forces the molecules into a lamellar architecture, while intermolecular $\pi-\pi$ interaction gives rise to the zigzag ordering of the C_{60} moieties.

To further verify the hypothesis of the ordering process, we synthesized fullerene derivatives with different alkyl chain length. We expected that longer alkyl chains should result in a larger periodicity of the lamellae. Derivative **2** has three eicosanyl chains in the 3,4,5-positions of the phenyl group and an estimated length of 3.6 nm in a fully extended conformation. Similar to **1**, AFM imaging of **2** shows close to perfect lamellae (Figure 2a). In contrast to **1**, the length of the lamellae is several hundred nanometers, and the domain sizes of lamellae are larger than that of **1** (Supporting Information). The periodicity of the nanostripes is determined to be 7.2 nm, which corresponds nicely to twice the molecular length of **2**, indicating the same structural motive as derivative **1**. This result supports the structural model as shown in Figure 1d.

In contrast, molecules having three dodecyl chains (**3**) in the 3,4,5-positions or two hexadecyl chains in the 3,5-positions of the phenyl group (**4**) do not form ordered lamellae but random aggregates. The findings correlate with the thermal and structural properties determined by DSC[13] and FT-IR.[14]

In the case of derivative **5**, which has just one hexadecyl chain, the length and the domain size of the lamellae are smaller than those found in **1** and **2** (see Figure S3). Interestingly, the periodicity of the nanostripes is only 4.3 nm, which is much shorter than twice the molecular length as in the previous examples. Apparently, derivative **5**, with an estimated molecular length of approximately 3.1 nm, forms a different arrangement. We propose that **5** forms interdigitated lamellae with a head-to-tail configuration. Such an arrangement maximizes the van der Waals interactions of adjacent alkyl chains as well as C_{60} moieties. The alternative structure of a tilted bilayer is discarded because of the significant spatial mismatch of the C_{60} moiety and the alkyl chain.

These results demonstrate that the distance between adjacent fullerene nanowires can be tailored at the nanoscopic level through the molecular design (**1**, 6.3 nm; **2**, 7.2 nm; and **5**, 4.3 nm).

Cyclic voltammetry (CV) of **1** and **2** (Figure 2b) on HOPG shows a single redox event corresponding to the generation of the fullerene monoanion[15] at a potential of $E_{1/2} = -1.29$ V for **1** and -1.30 V for **2**. The current passed during the reduction process, and the electroactive quantity is calculated to be 25% for **1** and 63% for **2** of full monolayer coverage. These results are comparable with the surface coverage determined by AFM (Supporting Information). The electrochemical activity of the C_{60} groups is fully maintained in the surface-confined assemblies.

In summary, we presented an approach to direct the assembly of C_{60} groups on graphite in a predictable way. We used alkanes as structure directing components, covalently bonded to C_{60}. The epitaxial assembly of the alkyl chains on graphite results in formation of lamellar structures and a 1-D alignment of the fullerenes. Derivatives with three alkyl chains adsorb in a head-to-head bilayer structure. The C_{60} moieties are organized in a zigzag-type fashion within the lamellae. If only one alkyl chain is present, an interdigitated lamella is formed. The spacing between lamellae is determined by the alkyl chain length. Our work indicates that the substitution pattern and the chain length of the alkyl chains determine the order and packing motive. We show that the C_{60} moieties are electroactive, opening the way to address individual C_{60} and to investigate the conductivity of individual (polymerized) nanowires.

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Supporting Information Available: Synthetic procedures for compounds **2**−**5**, AFM, and CV in solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Differential scanning calorimetry (DSC) patterns showed a phase transition behavior with the endothermic peak at 30.6 °C for **1**, at 58.9 °C for **2**, and at −37.1 °C for **3**; in contrast, there were no phase transition peaks for **4**.
(14) FT-IR at room temperature displays CH_2 stretching vibrations for **1** and **2** at 2849 (ν_{sym}) and 2918 cm^{-1} (ν_{asym}), indicating an *all-trans* conformation of alkyl chains, while **3** and **4** show peaks at 2852 and 2922 cm^{-1}, characteristic of *disordered* alkyl chains.
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