Aromatic Polycycles

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Subliming the Unsublimable: How to Deposit Nanographenes**

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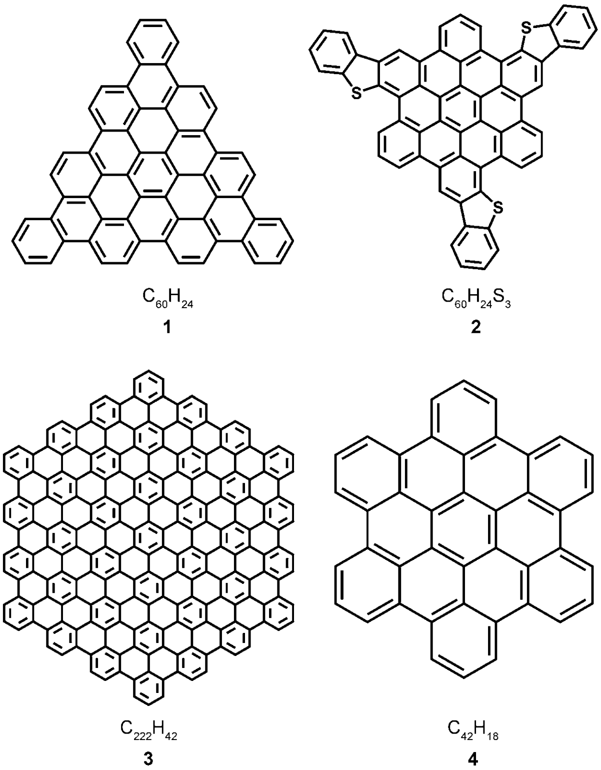
Graphene, as an integral part of graphite, is a two-dimensional aromatic lattice of carbon atoms.[1] In contrast to the popular belief that graphene cannot exist freely in nature, it was unexpectedly discovered by Novoselov et al. in 2004.[2] Subsequent experiments demonstrated the quantum Hall effect in graphene[3] and unique charge-transport properties, in which the carriers mimic massless relativistic particles.[4] These discoveries resulted in a surge of interest in the field of graphene synthesis. Although mechanical exfoliation of highly oriented pyrolytic graphite[2] (as a top-down method) or heating of silicon carbide wafers[5] (as a bottom-up method) is an effective laboratory-scale preparation of graphene for fundamental investigations, large-scale production of processable graphene is still a major challenge. Our approach to synthesize well-defined segments of graphene by cyclodehydrogenation of polyphenylene precursors is capable of producing large and giant polycyclic aromatic hydrocarbons (PAHs), which are often termed molecular- or nanographenes because of their structural similarity to the infinite graphene lattice. Furthermore, we hypothesize that well-organized molecular domains of large PAHs might undergo fusion upon thermolysis to produce graphene layers in a bottom-up approach. Moreover, molecular layers of large PAHs are also potential new candidates for electronic devices, such as organic photovoltaic cells[6] and organic field-effect transistors.[7,8]



Scheme 1. Chemical formulae of nanographenes **1**–**4**.

A crucial point of large PAHs, however, is processability, which traditionally requires either solubility or volatility. PAHs exceeding the size of hexabenzocoronene ($C_{42}H_{18}$; Scheme 1) are neither soluble in common organic solvents, nor sublimable without decomposition,[9] and thus not applicable for devices. Solubility could be achieved by attachment of long flexible aliphatic chains to the aromatic cores,[8] thus allowing easy processing by spin-coating, drop-casting, and inkjet printing,[10–12] but the long insulating aliphatic side chains induce severe steric hindrance, inhibiting efficient intermolecular packing, and thus result in poor charge-carrier mobility in test devices. New techniques are therefore called for to make the unprocessable molecules processable without changing the molecular structure. Herein, we describe for the first time the application of pulsed laser deposition (PLD) for the fabrication of thin layers of nanographenes that were previously considered unprocessable.

To date, PLD has mainly been used to deposit thin films of inorganic materials, such as high-temperature superconductors, ferroelectrics, and magnetoresistance oxides.[13] The deposition of large PAHs by PLD, however, is almost completely unexplored.[14,15] In our case, PLD allows very large PAHs to be "evaporated" much beyond their thermal evaporation limit with the help of a pulsed nitrogen laser (Figure 1).

The molecules, placed on a rotating sample holder inside a vacuum system, are irradiated by short laser pulses, causing their phase transition from the solid state into the gas phase. A narrow plume of molecules is thus formed, expanding with approximately supersonic speed[16] towards a substrate surface in close vicinity (ca. 1 cm), where the molecules are deposited as a thin layer. By careful adjustment of the laser power (irradiation density), an intact "sublimation" of the large PAHs can be achieved that is not feasible by equilibrium

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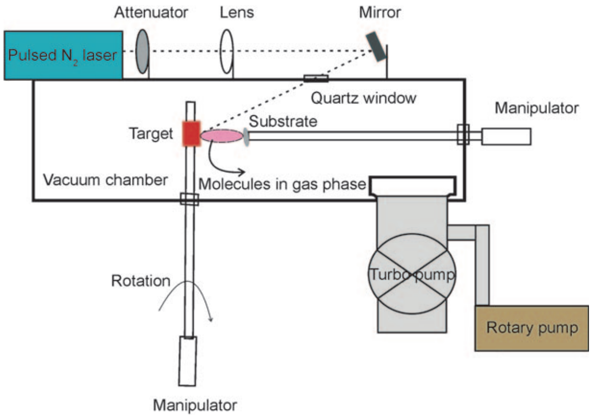

Figure 1. The pulsed laser setup used for the deposition of large PAHs.

processes such as thermal evaporation. The large PAHs under investigation exhibit significant absorption around the fundamental wavelength of a nitrogen laser ($\lambda = 337$ nm), thus exhibiting resonant absorption conditions which lower the threshold laser irradiance. Therefore, desorption of PAH molecules takes place under soft non-equilibrium conditions at relatively low temperatures. In comparison to our recently published method of PAH "soft landing,"[17] in which mass-selected ions are deposited, PLD produces mainly neutral species in a significantly higher yield; it is thus predestined for practical thin-film applications, such as organic electronics.

In the following, we describe the deposition of large discotics, such as $C_{60}H_{24}$ (**1**), $C_{60}H_{24}S_3$ (**2**), and $C_{222}H_{42}$ (**3**) (Scheme 1), by PLD on highly oriented pyrolytic graphite (HOPG) and stainless steel (SS) substrates. To date, these molecules could not be deposited by vacuum sublimation. The deposition on HOPG surfaces allows the characterization of such nanographenes by scanning tunneling microscopy (STM)[18] for the first time, and the deposition on matrix-modified stainless steel substrates enables an independent check of purity by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry.

Figure 2a shows the STM current image of a thin layer of PAH **1** ($C_{60}H_{24}$) on the basal plane of HOPG with high resolution as obtained by PLD. The triangular shape of the individual PAH molecules can easily be recognized in the inset of Figure 2, and even submolecular features are visible. On a larger scale, the "triangles" form a long-range order of packed two-dimensional polycrystalline molecular domains extending over several hundred square nanomometers, and lay approximately on a hexagonal motif, with a nearest-neighbor distance of about 2.9 nm.

Figure 2b shows the STM image of PAH **2** ($C_{60}H_{24}S_3$) deposited on HOPG. Again, the triangular shape of the individual molecules is clearly visible, and a regular pattern can be observed on a larger scale. As opposed to the PAH **1**, PAH **2** exhibits a different packing, with triangular voids between the triangular molecules. The voids have a side length of circa 1.5 nm. These observations are in agreement with those that we previously reported for the two-dimensional self-assembly of the same molecule on HOPG but deposited classically from solution, as PAH **2** is partly soluble in 1,2,4-trichlorobenzene.[19]

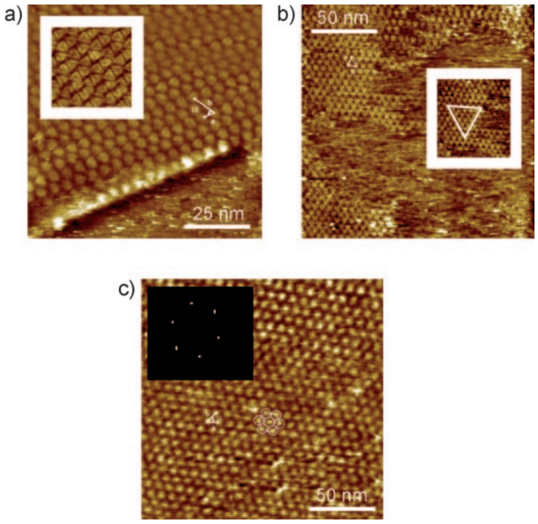

Figure 2. STM current images at the HOPG–dodecane interface of a) $C_{60}H_{24}$ (**1**; bias voltage $V_b = 425$ mV, tunneling current $I_t = 1.5$ pA), b) $C_{60}H_{24}S_3$ (**2**; $V_b = 550$ mV, $I_t = 1.6$ pA), and c) $C_{222}H_{42}$ (**3**; $V_b = 400$ mV, $I_t = 1.3$pA). Insets in (a) and (b) show the corresponding enlarged and filtered high-resolution images of the self-assembled layers; inset (c) shows the hexagonal arrangement from a two-dimensional Fourier transformation.

Unsubstituted $C_{222}H_{42}$ is the largest molecule to date with a fully condensed aromatic π system[20] that has been deposited as thin film by any kind of technique. The molecule is completely insoluble in common organic solvents and decomposes during sublimation attempts. Figure 2c shows the STM image of the giant PAH **3** on HOPG. The molecules, having a calculated diameter of 3.1 nm, show a nearest-neighbor distance of about 4.5 nm, and it is exciting to note that almost defect-free molecular domains could be obtained that are more than a few hundred square nanometers in size and have a hexagonal packing of the hexagon-shaped $C_{222}H_{42}$ molecules.

To ensure the chemical integrity of the molecules, we also applied MALDI-TOF mass spectrometry as an independent method to analyze the PAHs before and after PLD. The PAHs were deposited on top of stainless steel substrates covered with a thin layer of TCNQ (7,7,8,8-tetracyanoquinodimethane), which acts as a matrix molecule. This procedure enables a matrix-assisted laser desorption analysis of the deposited molecules directly at the surface under soft ionization conditions. The mass spectra of the three PAHs (Figure 3) reveal that the most intense signals appear at $m/z = 744$, 840, and 2708 for $C_{60}H_{24}$ (**1**), $C_{60}H_{24}S_3$ (**2**), and $C_{222}H_{42}$ (**3**), respectively, which correspond to the expected masses of the molecular ions. The spectra do not provide any evidence for fragmentation, and indicate that the PAHs retain their structural integrity during the deposition process by PLD.

In case of the giant PAH **3**, the molecules even have an improved purity after deposition (see the Supporting Information), which is very valuable as traditional methods of purification also fail for such giant molecules because of their insolubility and nonvolatility.

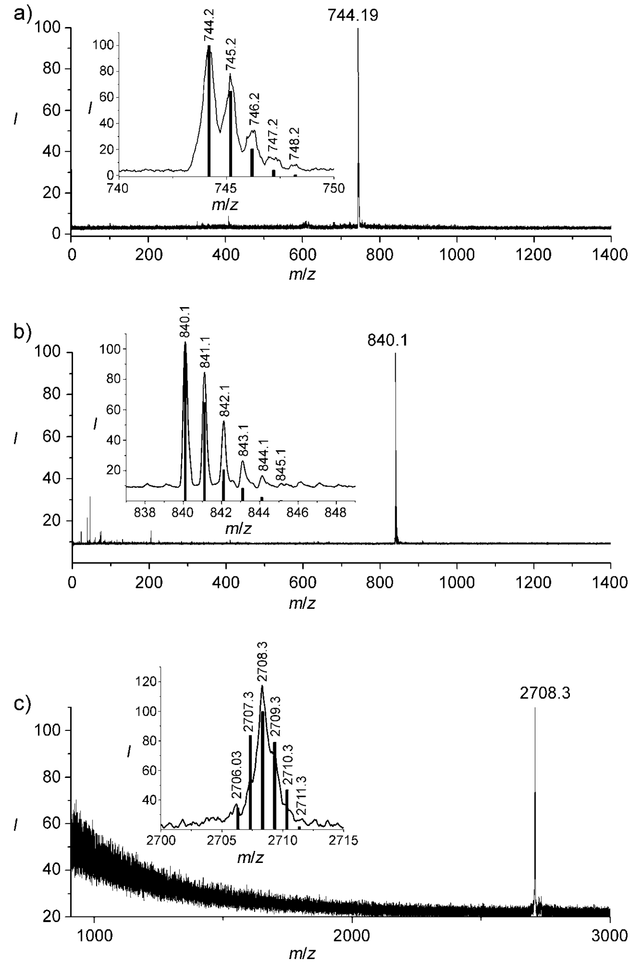

Figure 3. MALDI-TOF mass spectra of thin layers of a) $C_{60}H_{24}$ (**1**), b) $C_{60}H_{24}S_3$ (**2**), and c) $C_{222}H_{42}$ (**3**) deposited by PLD. Insets: enlarged spectra of the respective molecular peaks, with simulated signals (bars) corresponding to the natural isotopic mass distribution of the individual molecules.

In the work described above, thin films of large PAHs were fabricated by PLD, which was previously not possible by other conventional techniques, such as vacuum sublimation and solution processing. The process to obtain thin films of intact large PAHs by PLD is a valuable alternative sample preparation technique for STM investigations. Moreover, PLD will provide a new class of highly interesting but previously unprocessable large semiconducting PAHs for applications in electronic devices. Furthermore, we are attempting to thermally fuse the PLD layers of our well-organized “molecular graphenes” to a real graphene monolayer as a new bottom-up approach towards this challenging goal.

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