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Crystalline C_{60} monolayers at the solid–organic solution interface†

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Crystalline monolayers of fullerene have been self-assembled at the interface between a 1,2,4-trichlorobenzene solution and an Au(111) surface. *In situ* scanning tunneling microscopy shows the adsorbate arrangement to be structurally equivalent to that found in films grown by sublimation in ultra-high vacuum. This new kind of ordered monolayer might be useful for performing reactions on fullerenes at the interface between their organic solutions and a solid substrate.

Since their discovery, fullerenes (C_{60}) have attracted a great deal of attention because they are structurally defined π-conjugated nano-objects with interesting physico-chemical properties.[1,2] In particular, several of their derivatives have proven to be outstanding electron acceptors,[3,4] which render them candidates for active components in solar cells.[3,5,6] Since fullerenes have a strong tendency to form clusters of different sizes, especially in polar solvents,[7,8] remarkable variations in their photophysical and photochemical properties have been observed.[4] Recently, it has been shown that functionalized C_{60} with polar tails and other moieties can self-assemble from aqueous solutions into a variety of well-defined 3D nano-structures with pre-programmed shapes.[9] Highly ordered thin films of fullerenes have been grown on surfaces by sublimation in ultra high vacuum (UHV) and studied by scanning tunneling microscopy (STM).[10,11] At the air–water interface, Bard *et al.* prepared fullerene Langmuir films and explored their electrochemical properties.[12] These films were then transferred onto iodine-modified Pt(111) (I/Pt) surfaces. Electrochemical STM in aqueous solutions revealed that C_{60} on I/Pt did not assemble into highly ordered structures because of strong interactions between I/Pt and C_{60}. This caused trapping of the C_{60} on the surface that hindered the search for the energetically most favorable states. Recently, some of us succeeded in preparing epitaxial C_{60} films on Au (111) by simple transfer of a C_{60} Langmuir film.[13] This was possible most probably because of weak admolecule–substrate interactions, which enabled the fullerenes to diffuse on the Au surfaces. Furthermore, taking advantage of the low solubility of unsubstituted fullerenes in aqueous solutions and exploiting the slow electrochemical replacement from iodine to fullerene adlayers, C_{60} epitaxial films that are structurally equivalent to those sublimed in UHV have been grown.[14] On the other hand, the fullerenes are reasonably soluble in organic solvents,[15] which opens new avenues for the formation of crystalline layers of unsubstituted C_{60} from organic solutions. Here, we report the molecular scale STM observation of the self-assembly of C_{60} at the interface between Au(111) and a solution in 1,2,4-trichlorobenzene (TCB) into highly ordered structures.

The STM investigations at the solid–liquid interface were carried out with a home-built low current STM.[16] First, the bare Au(111) surface, sublimed in high vacuum on muscovite mica was visualized (see ESI). A drop of an almost saturated C_{60} (99.5%, MTR Ltd.) solution in 1,2,4-trichlorobenzene (Aldrich) was applied to the Au(111) surface. The tunneling tip, mechanically cut from a 0.25 mm Pt–Ir (80 : 20) wire, was immersed in the solution during the investigation. Both STM height and current signals were recorded simultaneously. TCB was chosen because of its aromaticity, coupled with its fairly high dipole moment, which makes this solvent very suitable for the solubilization of unsubstituted conjugated molecules.[17]

Fig. 1 shows a typical survey STM current image of a monolayer of C_{60} at the interface between its TCB solution and a freshly sublimed Au(111) surface. It reveals small domains of ordered 2D nanostructures exhibiting a hexagonal arrangement. The bright spots in the current STM image are ascribed to resonance-enhanced tunneling through the π-conjugated fullerenes.[18] A closer view of the hexagonal structure is shown in the STM height image in Fig. 2. The hexagonal pattern is characterized by a unit cell with a = 1.08 ± 0.07 nm and

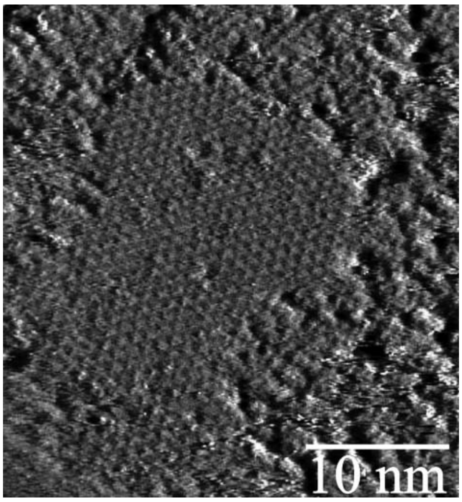

Fig. 1 STM current survey image of a C_{60} monolayer at the Au(111)–TCB solution interface. Among a disordered phase, some crystalline domains exhibiting a hexagonal arrangement are visible. Substrate bias voltage, U_t = −500 mV; average tunneling current, I_t = 800 pA.

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† Electronic supplementary information (ESI) available: constant current STM image of the Au(111) surface onto which the C_{60} was adsorbed. See http://www.rsc.org/suppdata/jm/b2/b207656j/

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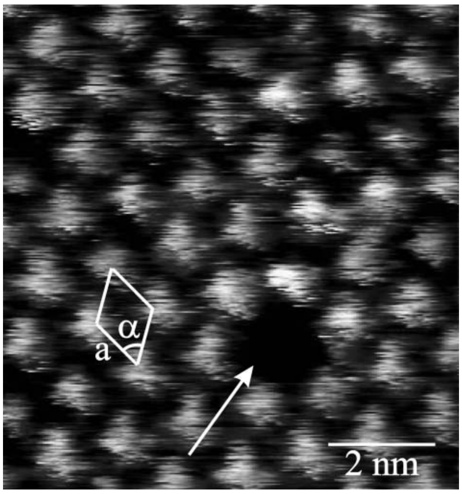

Fig. 2 STM height image of the Au(111)–TCB solution interface showing the hexagonally packed crystal. The white arrow indicates a missing molecule within the crystal. $U_t = -100$ mV, $I_t = 200$ pA.

$\alpha = 59 \pm 2°$. This packing is in very good agreement with that found in epitaxial C_{60} films prepared by deposition of Langmuir films from aqueous solutions onto Au(111)[14] and films sublimed in UHV on the same substrate.[19] The crystal also exhibits a point defect, which provides evidence that the visualized arrangement is neither an artifact nor a superstructure of the hexagonal substrate lattice.

The self-assembly of C_{60} is possible due to an interaction between molecule and substrate that is neither too weak (which would favor the dissolution of the molecules rather than their adsorption) nor too strong (trapping of the molecules at the surface). Moreover, a critical factor is the good solubility of fullerenes in TCB (up to 10.4 g L^{-1}). Several attempts at growing C_{60} films at the solid–liquid interface on highly oriented pyrolytic graphite (HOPG) substrates failed, although ordered C_{60} films on HOPG have previously been prepared by UHV sublimation.[20] We believe that, due to the very weak interaction between C_{60} and HOPG, the molecules prefer to remain solvated rather than adsorbing at the interface.

After completing our work, we learnt about similar experiments performed by Marchenko and Cousty[21] using a poorer solvent, namely tetradecane. They have been able to form highly ordered nanostructures of C_{60} on Au(111) by depositing dilute solutions on the substrate surface. However, upon applying concentrated solutions, a very rough overlayer was observed, which can be explained by the high tendency of C_{60} in a poor solvent to create clusters that collapse on the surface. Here, we have used 1,2,4 trichlorobenzene, which is a much better solvent for C_{60} due to its aromaticity and relatively high dipole moment. Exploiting this solvent, we could form crystalline monolayers with almost saturated solutions thanks to a more balanced competition between physisorption and dissolution. Nevertheless, a decrease in solubility was found in the course of re-solubilizing the C_{60} adsorbed on Au(111), after evaporation of the solvent, by simple addition of pure TCB solvent. The same hexagonal pattern was observed, but characterized by reduced size and stability of the C_{60} crystals. This is likely due to competition between adsorption and solubilization that does not exist when the molecules are dissolved by immersion of a crystalline powder in a pure solvent.

In summary, crystalline nanostructures of C_{60} can be formed at the interface between its solution in TCB and an Au(111) substrate. These structures are similar to those prepared by UHV sublimation and also by deposition of Langmuir films from aqueous solutions. With a view to exploiting the chemical reactivity of fullerenes,[22] the ability to assemble ordered C_{60} monolayers from organic solutions provides opportunities for performing reactions on C_{60} at the interface between its organic solutions and a solid substrate.

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