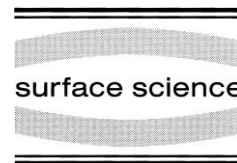




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Functionalized fullerenes on silicon surfaces

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Abstract

We have investigated the influence of phenyl addends on the packing and adsorption of C₆₀ on a solid substrate. On the Ag/Si(111)-(√3 × √3)R30° surface, the interactions of the unmodified part of the fullerene cages are not strongly affected by the addition of the phenyl groups although pronounced differences in molecular packing are observed. Phenylated C₆₀ may rotate to its optimum configuration and diffuse freely on this surface. In contrast it can neither rotate nor diffuse on Si(111)7 × 7, while on C₆₀/Si(111)-7 × 7 it can diffuse but the presence of the phenyl groups inhibits the formation of ordered layers. © 1998 Elsevier Science B.V. All rights reserved.

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Many of the properties of buckminsterfullerene, C₆₀, [1] are closely related to the equivalence of all 60 C atoms which make up this highly symmetric molecule. The symmetry may be reduced by attaching various groups to the molecule and research in this area constitutes an important part of fullerene chemistry [2–4]. It is particularly interesting to consider how the modification of one part of the cage will influence the properties of the remaining, unmodified, part of the fullerene molecule. This is of particular relevance when multiple additions to the fullerene cage have taken place. It is possible that modifications which affect one or a small number of neighbouring C atoms will have a limited effect on the chemistry of the rest of the cage so that C₆₀ may be considered as a

closed surface on which a number of chemical additions may be made independently [5].

In this Letter we address a related issue by considering the effect that addition of groups to a C₆₀ molecule has on its adsorption on a solid surface. We find that, as expected, the addends modify the ordering and packing of molecules. However, the modified parts of the cage experience interactions with the surface and with other molecules which do not appear to be strongly influenced by the chemical modifications. Our results imply that, at least for simple fullerene derivatives, the interactions of the fullerene cage and attached groups with the surface may be considered to be independent. Thus the fullerene cage may be used as an intermediate “glue” to attach a functional group to a surface.

The molecule we have used for this study, penta-

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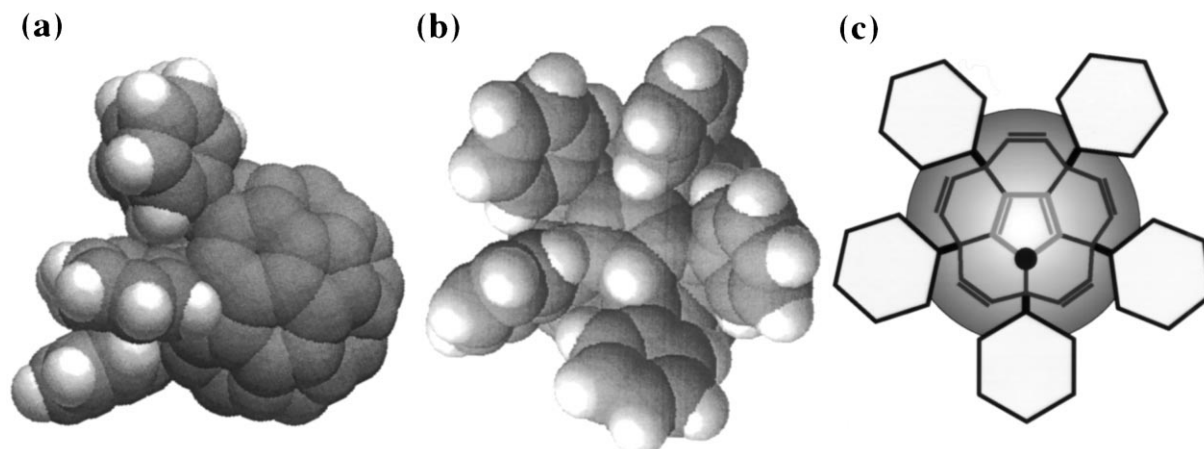


Fig. 1. A schematic diagram of $C_{60}Ph_5H$: (a) and (b) are space filling models. The filled black circle in (c) represents an H atom which is attached to the pentagonal face.

phenyl[60]fullerene, $C_{60}Ph_5H$, is synthesized using the method described by Birkett et al. [6]. As shown in Fig. 1 a phenyl group is attached to each of the five C atoms which are bonded to the vertices of one pentagon. One of the C atoms of the associated pentagonal face is bonded to a H atom and there are two double bonds between the two remaining pairs of C atoms on this face. The bonds from the vertices of the pentagon to the C atoms in the neighbouring hexagonal faces are single bonds as a consequence of the addition of the phenyl groups.

We have investigated the deposition of $C_{60}Ph_5H$ on the Si(111)- 7×7 surface, the Ag/Si(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface and a C_{60} monolayer adsorbed on Si(111)- 7×7 . Approximately 25 mg of $C_{60}Ph_5H$ was loaded into an ultra-high vacuum (UHV) chamber and heated to $300^\circ C$. This results in the sublimation of $C_{60}Ph_5H$ at ~ 0.5 monolayer (ML) per hour (one monolayer is defined as the coverage required for one ordered layer on Ag/Si(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$). To prepare the surfaces a 7×3 mm² piece of Si was cut from a (111) wafer (B doped, resistivity $> 1 \Omega cm$), loaded into the UHV system and outgassed overnight at $\sim 700^\circ C$. The Si was then heated to $1200^\circ C$ for 1–2 min after which it was allowed to cool to room temperature. This procedure resulted in a clean, defect free, 7×7 reconstruction. To form the Ag/Si(111)-

$(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction, Ag was evaporated onto the Si(111)- 7×7 surface while the sample was heated to $\sim 550^\circ C$ as described previously [7–9]. The C_{60} monolayer was formed by first evaporating 3–4 monolayers of C_{60} onto Si(111)- 7×7 and then annealing at $\sim 200^\circ C$ [10]. Constant current images of sample surfaces were recorded using a scanning tunnelling microscope (STM)¹ operating at room temperature within the UHV system. Electrochemically etched W tips which are cleaned by heating within the UHV system were used for STM image acquisition.

Fig. 2 shows STM images of $C_{60}Ph_5H$ adsorbed on the Ag/Si(111)- $\sqrt{3} \times \sqrt{3} R30^\circ$ surface. At low coverage (Fig. 2a) we observe molecules adsorbed at step edges and defect sites together with small ordered islands. High resolution scans show that much of the surface (the darker contrast regions in Fig. 2a) remains unaffected by the deposition of $C_{60}Ph_5H$ and are identical to images of the clean Ag/Si(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface (see inset to Fig. 2a and compare with images in Refs. [7–9]). These observations imply that $C_{60}Ph_5H$ is free to diffuse on Ag/Si(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ and may rotate to optimize its configuration on the surface. The arrangement of molecules in the ordered islands may be determined from higher resolution

¹ The STM, electronics and software were provided commercially by Oxford Instruments SPM Group.

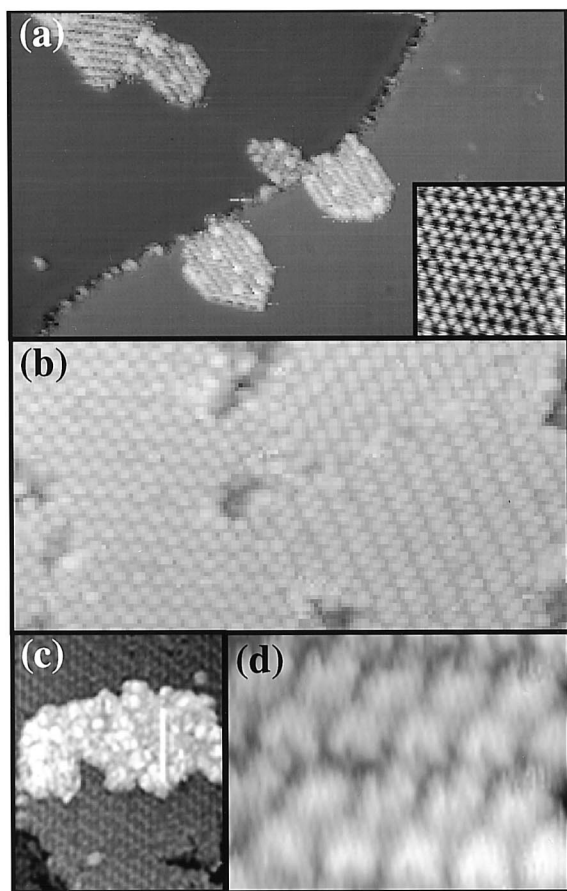


Fig. 2. STM images showing the adsorption of $C_{60}Ph_5H$ on the $Ag/Si(111)-\sqrt{3} \times \sqrt{3} R30^\circ$ surface. (a) 100×59 nm, sample bias -3 V, tunnel current 50 pA. The coverage is 0.1 monolayers. $C_{60}Ph_5H$ is adsorbed at step edges and defects and forms ordered islands. Inset shows a higher resolution image (6×6 nm) of the $Ag/Si(111)-(\sqrt{3} \times \sqrt{3}) R30^\circ$ surface. (b) 33×17 nm, 3 V, 100 pA. This image shows the regular arrangement of $C_{60}Ph_5H$ molecules. Three domains are observed. The coverage is ~ 1 monolayer and is produced by annealing a $C_{60}Ph_5H$ multilayer [see (c)] at $\sim 200^\circ C$ causing the second layer $C_{60}Ph_5H$ to desorb. (c) 43×52 nm, 3 V, 100 pA. This image show a disordered second layer island. Coverage 1.1 monolayers. (d) 6.5×4.9 nm, 2 V, 200 pA. In this image lobes on the molecules which correspond to phenyl groups are observed. The molecular orientation may be determined from such images.

images in which features, which we associate with the fullerene cage, may be identified and, form rows of parallel zig-zags which run across the surface. Three orientations of the ordered islands

are found with the zig-zag rows aligned with each of the principal axes of the $Ag/Si(111)-(\sqrt{3} \times \sqrt{3})R30^\circ$ surface. The presence of three domains is shown more clearly in an STM image (Fig. 2b) for which the coverage of $C_{60}Ph_5H$ is close to one monolayer. The height of the islands is 0.75 ± 0.05 nm.

From images such as Fig. 2a in which the molecular islands and the $Ag/Si(111)-(\sqrt{3} \times \sqrt{3})R30^\circ$ may be simultaneously resolved, it is possible to determine the ordering of the $C_{60}Ph_5H$. A schematic diagram of this arrangement is shown in Fig. 3. Also shown (Fig. 3a) is the accepted model for $Ag/Si(111)-(\sqrt{3} \times \sqrt{3})R30^\circ$ in which the surface is terminated by Si trimers and groups of three Ag atoms (referred to as Ag trimers) each of which is bound to a neighbouring Si trimer [11]. The surface may be represented by a hexagonal network in which the centre of each hexagon is a Si trimer and each vertex corresponds to a Ag trimer. Fig. 3b shows the arrangement of $C_{60}Ph_5H$ overlaid on this hexagonal network. The cage and phenyl groups are represented by bold circles and a single hexagon, respectively. The cage sits above either a vertex or a centre of a hexagon (Ag or Si trimer, respectively) with a centre-centre cage separation within the row of $a_0\sqrt{7} = 1.016$ nm [$a_0 = 0.384$ nm is the lattice constant of the unreconstructed Si(111) surface]. The three rows shown in Fig. 3b are not equivalent. In one of the rows all molecules sit above Ag trimers while in the other two half of the molecules sit above Si trimers and half above Ag trimers. The overall periodicity in the direction normal to the zig-zag is therefore three times the row separation, $15a_0/\sqrt{2} = 5.76$ nm.

To characterize fully the molecular configuration it is necessary to establish the orientation of the phenyl groups with respect to the surface. Fig. 2d shows an STM image in which intramolecular features may be resolved. There are two bright lobes on the side of each molecule facing away from the zig-zag backbone of the ordered structure. These observations provide evidence that the molecules are in the configuration shown in Fig. 1c in which the pentagon points "down" towards the surface so that one phenyl group and a hexagonal

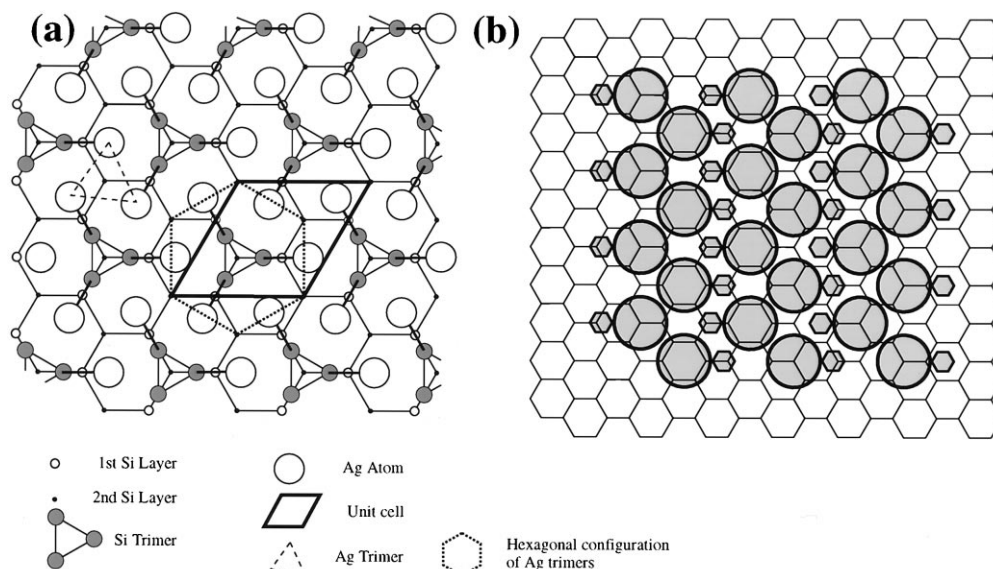


Fig. 3. A schematic diagram showing (a) the atomic configuration of the Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° surface (b) the ordered arrangement of C₆₀Ph₅H on the Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° surface.

face of the cage are in contact with the surface. In this configuration two phenyl groups are directed up from the molecule corresponding to the lobes in Fig. 2d. It is possible to pack model C₆₀Ph₅H molecules in this orientation in the zig-zag pattern shown in Fig. 3b. Molecules in an alternative configuration (rotated by 180° from that shown in Fig. 1b) with the pentagon pointing “up” have two phenyl groups and a C–C single bond within the cage in contact with the surface. It is *not* possible to pack molecules in this configuration into the zig-zag due to clashes between the phenyl groups of neighbouring rows. Note that there are five alternative configurations for the pentagon “down” orientation — as shown in Fig. 1c or rotated by $\pm 72^\circ$ or $\pm 144^\circ$. However it is not possible to distinguish between these orientations from our STM data.

A comparison with a recent study of the adsorption of C₆₀ on the Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° surface reveals some remarkable results. C₆₀ forms hexagonally close packed ordered islands (intermolecular spacing $a_0\sqrt{7}$) in which 1/3 of molecules are adsorbed above Si trimers and 2/3 above Ag trimers. It is, therefore, clear that while the packing of C₆₀Ph₅H is different due to the presence of the

phenyl addends, its adsorption site and the centre–centre cage separation are exactly the same as found for the unmodified C₆₀ molecule. This implies that for C₆₀Ph₅H the addition of the phenyls has not strongly influenced the remaining unmodified part of the C₆₀ cage.

While the presence of phenyl groups modifies the packing of two-dimensional ordered layers they completely inhibit the formation of ordered three dimensional structures. Fig. 2c shows an STM image recorded following the deposition of 1.1 monolayers of C₆₀Ph₅H. Second layer islands may be observed (brighter areas in Fig. 2c) which do not exhibit any local order. The presence of the phenyl groups directed away from the surface (see Fig. 3b and discussion above) inhibits the sequential stacking of layers with the molecular ordering shown in Fig. 3b.

For a sub-monolayer coverage both C₆₀ and C₆₀Ph₅H may diffuse on Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° until they are adsorbed at step edges, at defects or at the edges of growing islands. In contrast, STM images (Fig. 4a) show that C₆₀Ph₅H, like C₆₀ [12–14] is unable to diffuse on Si(111)-7 × 7. Note that the shape of the features in Fig. 4a varies from molecule to molecule. In

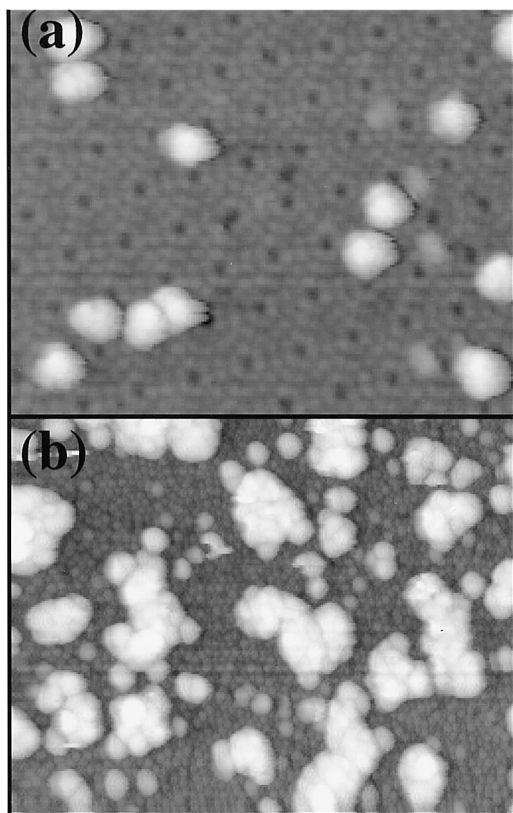


Fig. 4. $C_{60}Ph_5H$ adsorbed on (a) Si(111)- 7×7 $30 \text{ nm} \times 20 \text{ nm}$, 2 V, 100 pA, coverage 0.02 monolayers (b) C_{60} terminated Si(111)- 7×7 , $60 \times 47 \text{ nm}$, -3.5 V, 100 pA, coverage 0.1 monolayer.

addition the height of the features varies from 0.65 to 0.9 nm and it is possible to resolve intramolecular contrast for some molecules. The shape and contrast variations of individual molecules are unchanged from image to image. These observations imply that at room temperature the $C_{60}Ph_5H$ is unable either to rotate or diffuse on Si(111)- 7×7 . In the light of the discussion above the lack of rotation of $C_{60}Ph_5H$ implies that C_{60} itself is unable to rotate on Si(111)- 7×7 . This may not be deduced directly as C_{60} has a symmetric appearance in STM images.

Finally we consider the deposition of $C_{60}Ph_5H$ on Si(111)- 7×7 terminated by a single monolayer of C_{60} [10]. The C_{60} provides an inert van der Waals termination and is hexagonally ordered with a centre–centre cage separation of $a_0\sqrt{7}$.

Fig. 4b shows an STM image taken after the deposition of 0.1 monolayers of $C_{60}Ph_5H$ on $C_{60}/Si(111)-7 \times 7$. There are many bright topographic features with widths ranging from 3 to 7 nm and heights from 0.7 to 1.1 nm. These correspond to clusters of $C_{60}Ph_5H$ molecules. Higher magnification images show that molecules within these clusters do not form ordered arrangements. Note that C_{60} diffuses on $C_{60}/Si(111)-7 \times 7$ and forms higher ordered layers. Our results provide further evidence that while the diffusion, and therefore, the interaction of $C_{60}Ph_5H$ on this surface is rather similar to that of C_{60} the presence of phenyl groups strongly modifies the molecular packing.

In conclusion we have shown that the addition of addends to a small region of the C_{60} cage results in pronounced differences in the packing and ordering which the modified molecule may adopt. However the unmodified part of the fullerene cage within the $C_{60}Ph_5H$ molecule undergoes a chemical interaction with the Ag/Si(111)- $\sqrt{3} \times \sqrt{3} R30^\circ$ surface which is essentially identical to that of C_{60} . Our results imply that a fullerene cage may be used as an intermediate medium to attach arbitrary functional groups to a solid surface.

Acknowledgements

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