



# Chemisorption of azafullerene on silicon: isolating $C_{59}N$ monomers

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## Abstract

We find that  $C_{59}N$  exists as a monomer on Si(111) and Si(100) surfaces, in contrast to the dimerised state ( $(C_{59}N)_2$ ) it adopts in the bulk azafullerene solid. A combination of scanning tunnelling microscopy, photoelectron spectroscopy and X-ray absorption measurements indicates that, as for  $C_{60}$ , the chemical bond between  $C_{59}N$  and the Si(111)-(7 × 7) surface involves the formation of covalent Si–C bonds. We argue that the strong  $C_{59}N$ -surface interaction on both Si(111) and Si(100) precludes molecular diffusion and thus prohibits the formation of dimers. The dominant role of molecule–surface, as opposed to intermolecular interactions is confirmed by scanning tunnelling microscope-based molecular manipulation experiments. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Azafullerene; Monomer; Silicon

## 1. Introduction

The azafullerene molecule  $C_{59}N$  represents an exciting addition to the fullerene family [1]. Early theoretical work [2] on the properties of both  $C_{59}N$  and  $C_{59}B$  indicated that a close parallel existed between the role of the B and N atoms in these molecules and that of deep impurity states in semiconductors. That work demonstrated that  $C_{59}N$  can loosely be thought of as an ‘n doped’ molecule with the N-related state being strongly localised and, energetically, lying relatively deep within the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap of fullerene (0.27 eV from the LUMO).

The addition of an extra electron to the  $\pi$ -bonded fullerene cage produces a very reactive molecular radical and it was found that  $C_{59}N$  readily bonds to a like radical (via a weak intercage C–C bond) to form a ( $C_{59}N$ ) dimer [3]. Detailed density functional calculations, supported by photoemission and core-level exci-

tation spectra of bulk ( $C_{59}N$ )<sub>2</sub> provided strong support for the localisation of the extra electron on the N atom and, thus, a weak perturbation of both the occupied and unoccupied molecular states compared to the parent  $C_{60}$  molecule [4].

Very recently, we have demonstrated that it is possible to isolate the  $C_{59}N$  monomer through sublimation from the ( $C_{59}N$ )<sub>2</sub> solid and subsequent adsorption on a reactive Si(111)-(7 × 7) or Si(100)-(2 × 1) surface [5]. The isolation of the  $C_{59}N$  monomer raises a number of fascinating questions related to its chemical and electronic properties and how these might differ from those of an adsorbed  $C_{60}$  molecule. In this paper, in addition to presenting STM imaging and manipulation results, we discuss our photoemission and C 1s near edge X-ray absorption fine structure (NEXAFS) measurements on adsorbed  $C_{59}N$  which indicate that the azafullerene–Si surface interaction involves like  $C_{60}$ , covalent bonding. This similarity in the adsorption character leads to little difference in the response of  $C_{59}N$  and  $C_{60}$  molecules to STM manipulation. In particular, we find that the  $C_{59}N$ –Si interaction prohibits the STM-induced re-dimerisation of azafullerene molecules.

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## 2. Experimental

The STM measurements and photoemission/NEXAFS experiments were carried out in separate ultra high vacuum (UHV) chambers at Nottingham and the VUV beamline, ELETTRA, respectively. In each case, clean Si surfaces were prepared by direct current resistive heating to temperatures of  $\sim 1200^\circ\text{C}$  while maintaining the pressure in the  $10^{-10}$ -mbar range.  $\text{C}_{59}\text{N}$  was sublimed onto the Si surface from a standard Knudsen cell operating at a temperature of  $550^\circ\text{C}$ . As discussed by Haffner et al. [6], we also observed a reduction in the evaporation rate as a function of prolonged sublimation times but for the experiments described in this paper the sublimation rate was constant over the deposition period (as judged from STM images and the ratio of the C 1s and Si 2p core-level integrated intensities).

The STM imaging and manipulation experiments were carried out at room temperature using electrochemically etched W tips which were cleaned by electron bombardment in UHV.

The photoemission data were acquired at normal emission using an angle resolving analyser, acceptance

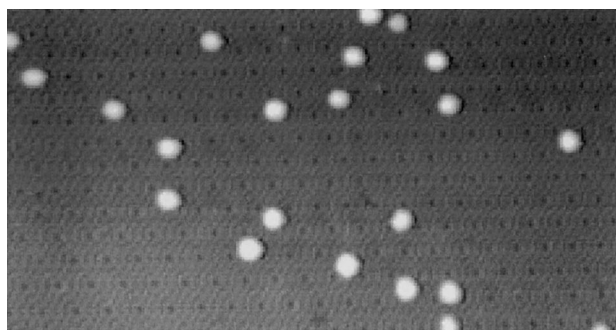


Fig. 1. A  $60 \times 30 \text{ nm}^2$  STM image of a submonolayer coverage of  $\text{C}_{59}\text{N}$  on  $\text{Si}(111)-(7 \times 7)$ . Bias voltage,  $+3.0 \text{ V}$ ; tunnel current,  $0.2 \text{ nA}$ .

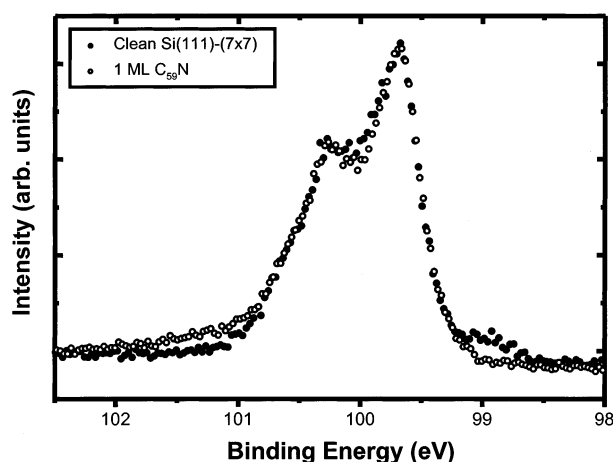


Fig. 2. Si 2p core-level spectra taken at normal emission with  $h\nu = 138.125 \text{ eV}$ .

angle,  $\pm 1^\circ$ . C 1s NEXAFS data were recorded by measuring the drain current from the Si sample (equivalent to the total electron yield) as a function of photon energy. The spectra were acquired at approximately  $20^\circ$  off normal incidence and were normalised to spectra taken from the clean  $\text{Si}(111)$  surface. This normalisation procedure accounts for the throughput of the beamline in the photon energy range of interest. The photon energy was calibrated using the C 1s  $\rightarrow$  LUMO edge for a thick  $\text{C}_{60}$  film, which is well established as falling at an energy of  $284.5 \text{ eV}$  (see [7]).

## 3. Results and discussion

Fig. 1 is a filled state STM image of the  $\text{Si}(111)-(7 \times 7)$  surface with a submonolayer  $\text{C}_{59}\text{N}$  coverage. It is clear from this image that the azafullerene molecules, just as observed for  $\text{C}_{60}$  submonolayers on the  $(7 \times 7)$  surface [8], are isolated, showing no preference for clustering or preferential adsorption at step edges. (That the molecular positions are truly uncorrelated have been checked by analysing the nearest neighbour separations. These are described by Poisson statistics indicating a lack of molecular clustering). The apparent diameters (broadened from the real molecular diameter due to the finite radius of curvature of the STM tip) and heights of the molecules are very similar to those found for  $\text{C}_{60}$ .

$(\text{C}_{59}\text{N})_2$  dimers were not observed in our STM images, indicating that not only is the azafullerene molecule sublimed as a monomer from the azafullerene crystal (possible due to the low value of the  $\text{C}_{59}\text{N}-\text{C}_{59}\text{N}$  bond energy ( $0.78 \text{ eV}$ ) [3] but also that it is not free to diffuse and redimerise on the  $\text{Si}(111)-(7 \times 7)$  surface. As described in [5], a lack of diffusion is observed also for  $\text{C}_{59}\text{N}$  on the  $\text{Si}(100)-(2 \times 1)$  surface but significant diffusion lengths for  $\text{C}_{59}\text{N}$  were found on the much less reactive hydrogen-passivated  $\text{Si}(100)-(2 \times 1)$  surface.

The lack of diffusion of  $\text{C}_{60}$  on  $\text{Si}(111)$  and, thus the presence of a strong  $\text{C}_{60}-\text{Si}(111)$  interaction has recently been shown to result from the formation of covalent Si-C bonds [9,10] and not, as previously suggested [11], from the transfer of a large amount of electronic charge from the Si surface to the fullerene LUMO. (Note, however, that Sakamoto et al. [10] have suggested that over 70% of the fullerene molecules in a close packed monolayer on  $\text{Si}(111)$  are physisorbed — a result that is somewhat at odds with our recent photoemission measurements of this system [12].

We used Si 2p photoemission to examine whether the  $\text{C}_{59}\text{N}-\text{Si}(111)$  interaction is also of covalent character. Fig. 2 shows an Si 2p core-level spectra (taken at normal emission with a photon energy of  $138.125 \text{ eV}$ ) of a clean  $(7 \times 7)$  surface and a 1 ML coverage of  $\text{C}_{59}\text{N}$  on the  $\text{Si}(111)$  surface. As for  $\text{C}_{60}$  [10,12], the most

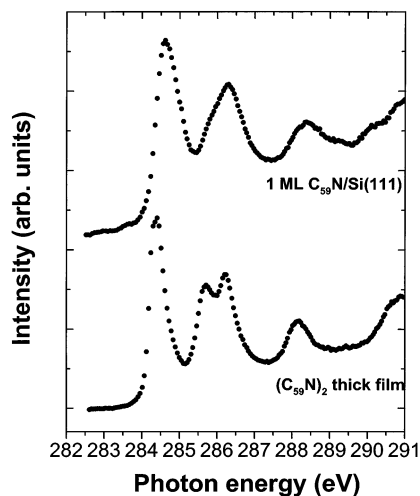


Fig. 3. NEXAFS spectra for a thick (bull-like)  $(C_{59}N)_2$  film and for a  $C_{59}N$  monolayer on the Si(111)-(7 × 7) surface.

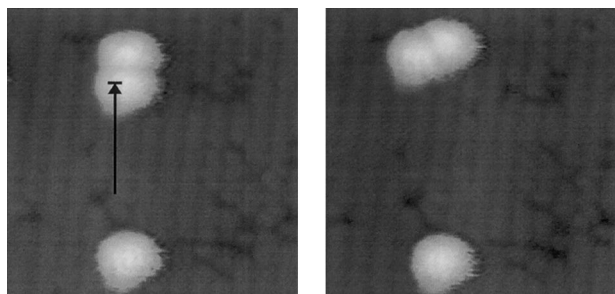


Fig. 4. Result of an attempt to redimerise two  $C_{59}N$  molecules on the Si(100)-(2 × 1) surface using STM molecular manipulation. Both STM images are 10 × 10 nm<sup>2</sup>. The arrow in the image on the left represents the length of excursion of the STM tip used in manipulating the lower molecule.

prominent differences between the two spectra are the removal of the shoulder on the low binding energy side of the spectrum (which is due to the rest atoms of the (7 × 7) reconstruction) and the appearance of a broad shoulder on the high binding energy side. This shoulder has been attributed to Si–C bond formation for  $C_{60}$  [10] and the similarity of the spectral-line shape with the Si 2p spectrum for a 1 ML  $C_{60}$  coverage on Si(111) suggests that covalent Si–C bonding also underlines the strong  $C_{59}N$ –Si(111) interaction. Note that the complexity of high resolution Si 2p spectra from Si(111)-(7 × 7) (which, for the clean surface have been shown to consist of six separate surface core-level shifted components in addition to the bulk peak [13]) makes the reliable application of a fitting procedure to ascertain the relative intensities of the  $C_{60}$ - and Si surface-related features problematic.

Further strong evidence for a covalent  $C_{59}N$ –Si(111) interaction is provided by the NEXAFS data shown in Fig. 3. The  $(C_{59}N)_2$  NEXAFS spectrum is in very good agreement with the electron loss spectroscopy (EELS)

core-level excitation spectrum of  $(C_{59}N)_2$  published by Pichler et al. (see, Fig. 1 of [4]). (Both NEXAFS and EELS core-level excitation probe the unoccupied density of states of the azafullerene molecule (albeit in the presence of a core-hole)). The primary difference between a bulk  $C_{60}$  NEXAFS spectrum (see, [7]) and the  $(C_{59}N)_2$  spectrum is an additional broadening of the spectral features of the latter.

As is clear from Fig. 3, for a 1 ML coverage of  $C_{59}N$  on Si(111), the NEXAFS spectral features are significantly broader than those for the corresponding  $(C_{59}N)_2$  spectrum. Importantly, there is also a 0.2 eV shift of the LUMO to higher photon energy (compared to the thick film spectrum) for the azafullerene monolayer. As discussed by Maxwell et al. ([7] and references therein), both the broadening of the  $\pi^*$  levels and the shift of the LUMO to higher energy may be associated with covalent fullerene–substrate bonding. The shift to higher energy of the LUMO has been found to follow increases in fullerene–substrate bond strength [7]. We observe an identical LUMO shift of 0.2 eV for a  $C_{60}$  monolayer on Si(111) [12], strongly suggesting that the  $C_{60}$ - and  $C_{59}N$ –Si(111) bonding interactions are very similar.

We have previously used the anisotropic reconstruction of the Si(100)-(2 × 1) surface to precisely position  $C_{60}$  molecules using the STM tip [14]. This surface consists of rows of dimers with the preferential site for both  $C_{60}$  [15] and  $C_{59}N$  [16] being in the trough between dimer rows. The procedure we used to manipulate individual  $C_{60}$  and  $C_{59}N$  molecules has been described in detail in [14] but, briefly, involves exploiting the repulsive interaction that exists between the fullerene molecule and STM tip at small tip–molecule separations to push a molecule, with sub nanometre precision, across the Si surface. Manipulation of  $C_{59}N$  molecules both parallel and perpendicular to the Si(100) dimer rows is possible with success rates of 90 and 30%, respectively, — very similar to the values found for  $C_{60}$  manipulation.

An attempt to redimerise two  $C_{59}N$  molecules using STM manipulation is shown in Fig. 4. The extent of excursion of the STM tip was chosen so that it interacted only with the lower molecule — this molecule is therefore pushed towards the upper molecule reducing the intermolecular separation. After, just as was found for  $C_{60}$ , repeating this experiment many times, we find that it was impossible to reduce the separation of two  $C_{59}N$  molecules in the same trough to below 1.15 nm (i.e. 3 × the Si(100) surface lattice constant). Invariably, either the upper or lower molecule moves into an adjacent trough as has also been observed for  $C_{60}$  [14].

Both our inability to reduce the  $C_{59}N$ – $C_{59}N$  separation to below 1.15 nm and the fact that this spacing is commensurate with the underlying Si surface lattice strongly suggest that the  $C_{59}N$ –Si interaction dominates

over the  $C_{59}N-C_{59}N$  interaction. It is however possible that alternative or additional mechanisms may prohibit  $C_{59}N-C_{59}N$  redimerisation in our manipulation experiments. For example, it may be that there is large activation energy for dimer formation that is not surmounted simply by moving the molecules together. This is somewhat analogous to the factor that prevented Eigler et al. [17] from ‘building’ a  $CO_2$  molecule by moving an oxygen atom and a CO molecule together using the STM tip. In their case, it was the low temperature (4 K) at which their experiment was carried out, that prevented the  $CO + O \rightarrow CO_2$  reaction from taking place.

It is clear from photoemission measurements that at a substrate temperature of  $\sim 293$  K (the temperature at which the manipulation experiments were carried out)  $C_{59}N$  molecules that impinge from the vapour phase onto the surface of an azafullerene thick film redimerise [5]. In addition, the morphology of  $C_{59}N$  films on H:Si(100) surfaces is consistent with a redimerisation of the azafullerene molecules [5]. Both these results suggest that when neither translational nor rotational motion of the molecules is hindered (i.e. for adsorption on a chemically unreactive surface) they form dimers at room temperature and this in turn indicates a rather low activation energy for dimerisation for weakly adsorbed  $C_{59}N$ . Thus, we believe it is the strong molecule–surface interaction that underlies our inability to redimerise two  $C_{59}N$  molecules on Si(100)-(2 × 1).

In conclusion,  $C_{59}N$  sublimes and adsorbs as a monomer on Si(111)-(7 × 7) and Si(100)-(2 × 1) surfaces. Core-level photoemission and NEXAFS support a covalent bonding mechanism for  $C_{59}N$  on Si(111)-(7 × 7), very similar to that found for  $C_{60}$ . The covalent interaction prohibits molecular diffusion and thus  $C_{59}N$  redimerisation at room temperature. The strength of

the molecule–surface interaction is such that STM-induced redimerisation is also not possible.

### Acknowledgements

We thank the UK Engineering and Physical Sciences Research Council (EPSRC) for financial support. The experiments at ELETTRA were funded under the EU Large Scale Facilities Programme. We gratefully acknowledge M. Pedio for both supplying a copy of [9] before publication and useful discussion.

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