

Self-assembly and electronic effects of $\text{Er}_3\text{N}@C_{80}$ and $\text{Sc}_3\text{N}@C_{80}$ on Au(111) and Ag/Si(111) surfaces

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Abstract. We have investigated self-assembled island formation, molecular detail and interesting contrast reversal effects for $\text{Er}_3\text{N}@C_{80}$ and $\text{Sc}_3\text{N}@C_{80}$ on Au(111) and Ag/Si(111) surfaces using variable temperature scanning tunnelling microscopy (STM) and spectroscopy (STS). The trinitride containing fullerenes have been evaporated onto Ag-passivated Si(111) at room temperature and self-assembled into close-packed 2-D islands. Gentle annealing at 200 – 300 °C is required for the formation of close-packed islands with 20 – 50 nm diameter on the Au(111) surface. Variable-voltage STM reveals bias-dependent contrast anomalies within the islands, and at low temperatures (< 90K), intra-molecular resolution of the fullerenes has been achieved. STS measurements indicate that the bright/dark anomalies may be caused by different electron densities of states for the “normal” and “anomalous” fullerenes.

1. Introduction

Trimetallic nitride endohedral fullerenes were first discovered in 1999 [1] and can be produced in higher yields than other metal containing endohedral fullerenes. Another advantage is that the $\text{M}_3\text{N}@C_{80}$ molecules, where M is a metal such as Er or Sc in a planar M_3N unit, are thermally stable and are therefore suitable for deposition onto substrates in ultrahigh vacuum (UHV) by evaporation from Knudsen cells. The otherwise unstable icosahedral (I_h) C_{80} cage is stabilized by charge transfer due to the donation of six electrons from the nitride cluster to the carbon cage. Therefore, this family of fullerenes is often described as trinitride template fullerenes (TNTs) due to the trinitride cluster acting as a template for the carbon cage. TNT fullerenes may have potential for use in future optoelectronic devices, especially $\text{Er}_3\text{N}@C_{80}$ which is magneto-optically active in the near-infrared and shows characteristics that could be employed as a readout pathway for fullerene-based quantum information processing [2-4]. Such applications would require the fabrication of well-ordered arrays of these fullerenes, as has already been shown for $\text{Er}_3\text{N}@C_{80}$ on different surfaces [5-7]. In this paper we have investigated self-assembled close-packed islands of $\text{Er}_3\text{N}@C_{80}$ and $\text{Sc}_3\text{N}@C_{80}$ on Au(111) and Ag/Si(111) surfaces using variable temperature scanning tunnelling microscopy (STM) and

spectroscopy (STS), paying particular attention to the appearance of bias-dependent contrast anomalies that seem to be caused by different electron densities of states on the fullerenes.

2. Experimental

$\text{Sc}_3\text{N@C}_{80}$ and $\text{Er}_3\text{N@C}_{80}$ were supplied by Luna Innovations. $\text{Sc}_3\text{N@C}_{80}$ was characterized by mass spectrometry showing the molecular peak at 1109 m/z. The sample was dissolved in toluene and purified by high performance liquid chromatography (HPLC) in recycling mode using a 5PYE column. After a few cycles of operation, it was observed that a second chromatographic peak started to appear from the main peak. At the 8th cycle of operation the two peaks were collected separately. Based on peak areas, it is calculated that the first peak constitutes approximately 80% of the total, while the remaining 20% correspond to the second peak. The chromatographic separation is shown in figure 1. The two HPLC peaks were further characterized by UV-Vis spectroscopy as shown in fig. 2.

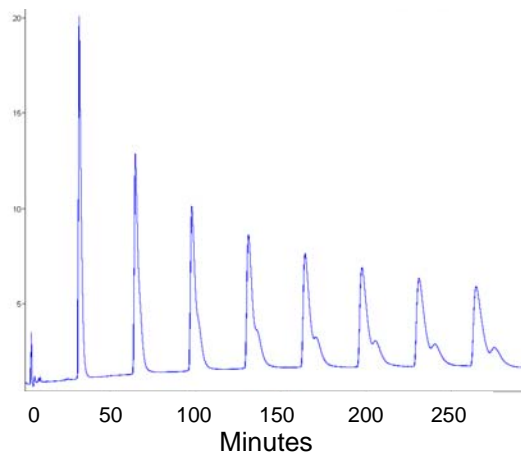


Figure 1. Recycling HPLC trace of $\text{Sc}_3\text{N@C}_{80}$ in toluene (5PYE column, 10 x 250 mm, flow rate 6 ml/min). Two peaks were separated after 8 cycles of operation.

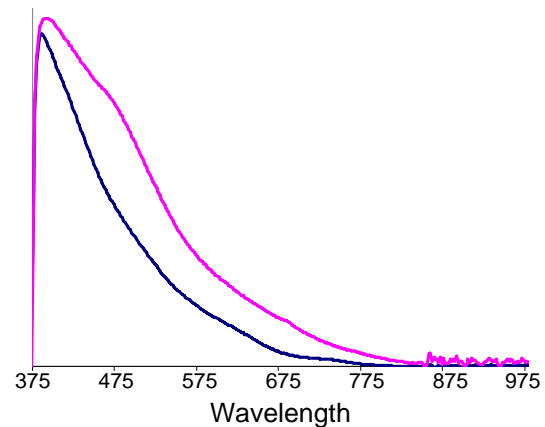


Figure 2. UV-Vis spectra of $\text{Sc}_3\text{N@C}_{80}$ -I (—) and $\text{Sc}_3\text{N@C}_{80}$ -II (—) in CS_2 solution. The y-axis shows absorbance in arbitrary units. Both spectra have absorbance onset at 848 nm. $\text{Sc}_3\text{N@C}_{80}$ -I shows peaks at 737 and 385 nm. $\text{Sc}_3\text{N@C}_{80}$ -II shows peaks at 467 and 387 nm.

Both spectra have absorbance onset at 848 nm. The major HPLC fraction ($\text{Sc}_3\text{N@C}_{80}$ -I) shows salient peaks at 737 and 385 nm. The minor HPLC fraction ($\text{Sc}_3\text{N@C}_{80}$ -II) shows peaks at 467 and 387 nm. These results correspond very well with the two isomers of $\text{Sc}_3\text{N@C}_{80}$ that were described previously to have (I_h) and (D_{5h}) symmetries, respectively [8]. Therefore we assign the two HPLC fractions to be the major and minor isomers of $\text{Sc}_3\text{N@C}_{80}$. The same purification procedure was followed for $\text{Er}_3\text{N@C}_{80}$. Some higher fullerene impurities were removed from the sample but after extensive recycling no isomers of $\text{Er}_3\text{N@C}_{80}$ were detected.

The isomerically pure $\text{Er}_3\text{N@C}_{80}$ and $\text{Sc}_3\text{N@C}_{80}$ molecules were evaporated *in-situ* from separate Knudsen cells at 480-500°C onto Au(111)/mica and Ag/Si(111) substrates in a variable-temperature (VT) UHV STM system (JEOL 4500S) in Oxford, as well as in Omicron VT STM/AFM systems in Milano and Swansea, and were subsequently imaged both at ambient and liquid nitrogen temperatures using electrochemically etched tungsten tips.

3. Results and Discussion

$\text{Er}_3\text{N@C}_{80}$ and both isomers of $\text{Sc}_3\text{N@C}_{80}$ have been evaporated in UHV in separate experiments onto Ag-passivated Si(111) at room temperature and self-assembled into close-packed 2-D islands (10-30 nm diameter) at step edges. The fullerenes form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ coincidence lattice on the underlying silver surface [5]. When the TNT fullerenes are deposited onto Au(111) substrates, gentle

annealing at 200-300°C encourages the formation of close-packed monolayer-high islands with 20-50 nm diameter (Fig. 3). The intermolecular spacing between the fullerenes is $1.15 \text{ nm} \pm 0.01 \text{ nm}$ and the close-packed directions are parallel to $\text{Au}\langle 110 \rangle$, suggesting a (4×4) coincidence lattice. All fullerenes in the islands are therefore expected to occupy identical lattice positions with respect to the underlying substrate lattice.

Bias-dependent STM reveals bright and dark anomalies within the islands, both for isomerically pure $\text{Sc}_3\text{N@C}_{80}$ and $\text{Er}_3\text{N@C}_{80}$ on $\text{Ag/Si}(111)$ [5] as well as on $\text{Au}(111)/\text{mica}$ (Fig. 4). In filled states images (Fig. 4a), some fullerenes appear brighter than the others, while in empty states images (Fig. 4b) the contrast is reversed and the same molecules (marked by circles) now appear darker. This effect is reproducible again and again for many hours with always the same molecules showing the effect. At large bias voltages ($> \pm 2.5 \text{ V}$) the “bright/dark” molecules are indistinguishable from the neighbouring “normal” fullerenes ruling out topographic effects. Fullerene vacancies in the islands appear as black holes at any bias voltage, as can be seen in Figure 4, and adsorbates always appear bright. The density of the “bright/dark” fullerenes varies between 2% and about 20% and seems to be independent of the type and isomer of the TNT fullerenes and the type of substrate.

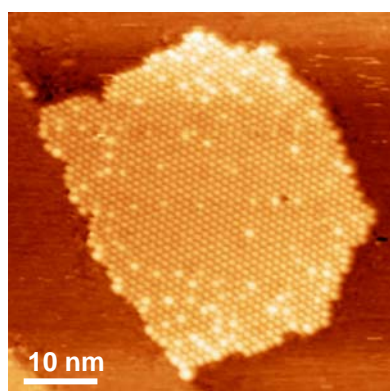


Figure 3: STM image of $\text{Er}_3\text{N@C}_{80}$ island on $\text{Au}(111)/\text{mica}$ ($V_{\text{SB}} = -1 \text{ V}$, $I_t = 0.02 \text{ nA}$)

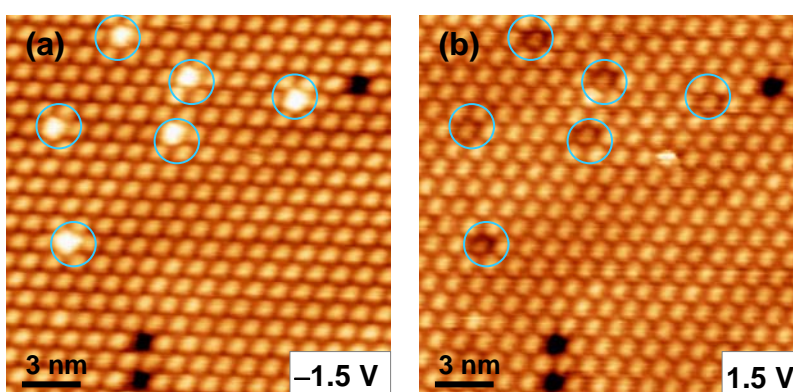


Figure 4: (a) filled states ($V_{\text{SB}} = -1.5 \text{ V}$) and (b) empty states STM image ($V_{\text{SB}} = 1.5 \text{ V}$) of close-packed $\text{Sc}_3\text{N@C}_{80}$ on $\text{Au}(111)/\text{mica}$ ($I_t = 0.08 \text{ nA}$). The circled molecules appear bright in filled states and dark in empty states. Vacancies always show as black holes.

When the samples are imaged at low temperatures (77–90 K) where the rotation of the fullerenes on the substrates is frozen, intra-molecular detail becomes visible on the fullerenes (Fig. 5). When the bias voltage is reduced from -1 V (Fig. 5a) to -0.6 V (Fig. 5b), the “bright/dark” fullerenes become indistinguishable from the surrounding molecules showing the same molecular orbital structure, which suggests that they have the same orientation on the substrate. We can also rule out impurities as the purity of the samples has been confirmed by mass spectrometry, and the crucibles are thoroughly cleaned before each set of evaporations. We therefore deduce that the observed “bright/dark” effect is an electronic effect.

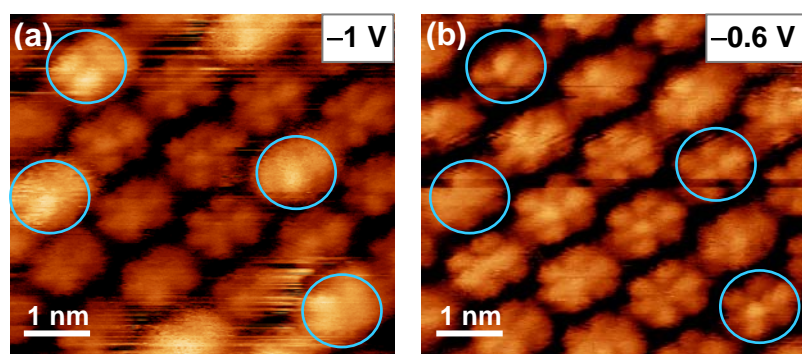


Figure 5: Filled states images showing molecular detail of $\text{Er}_3\text{N@C}_{80}$ on $\text{Ag/Si}(111)$. Circles show identical molecules in each image. The bright molecules at -1 V sample bias (a) become indistinguishable from their neighbours at $V_{\text{SB}} = -0.6 \text{ V}$ (b) suggesting they are identical molecules with the same orientation on the surface.

Normalized STS spectra (Fig. 6) of “normal” and “bright/dark” fullerenes suggest a different electronic density of states for the anomalous fullerenes. For the “normal” fullerenes, the position of the peak attributed to the HOMO energy level at -1.81 V is in good agreement with UPS spectra of $\text{Sc}_3\text{N@C}_{80}$ [9], and the observed HOMO–LUMO gap is similar to the values obtained by UV-Vis measurements and DFT calculations [10]. The “bright/dark” fullerenes seem to have a higher density of occupied states and a lower density of unoccupied states which explains why they appear brighter than the “normal” fullerenes in filled states STM images and darker in empty states images.

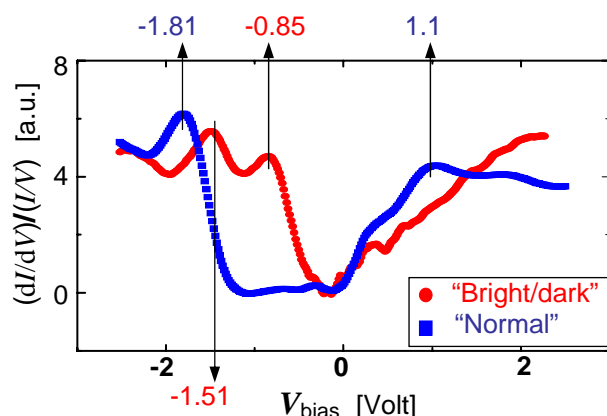


Figure 6: Normalized STS spectra of “normal” and “bright/dark” $\text{Sc}_3\text{N@C}_{80}$ molecules on Au(111)/mica as seen in figure 4. The curves are obtained as an average of the I/V -normalized curves taken at different tip-sample distance (i.e. bias-current setpoint) and are the result of an average of more than 20 curves in order to increase the signal to noise ratio. $I_{(\text{setpoint})} = 0.04$ nA. The spectra suggest different electronic states for the anomalous fullerenes.

4. Conclusion

We have observed the self-assembly of TNT fullerenes into close-packed islands on Au(111)/mica and Ag/Si(111) surfaces. Intra-molecular resolution can be achieved at liquid nitrogen temperature when the rotation of the molecules on the surface is frozen. The appearance of bias-dependent contrast anomalies has been investigated using variable-voltage STM and STS, and seems to be caused by different electron densities of states for the “normal” and “bright/dark” fullerenes. After ruling out the presence of impurities or different isomers in the sample, it is thought that the contrast anomalies are an electronic effect, possibly caused by different charge transfer from the substrate. Comparison with atomistic modeling and detailed spectroscopy will be necessary to elucidate the exact nature of these contrast anomalies.

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