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## STM imaging of molecules on well defined substrates

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**Abstract.** Scanning tunnelling microscopy (STM) has been used to obtain images, in ultra-high vacuum (UHV), of molecules of  $\eta$  5-cyclopentadienyl-bis triphenylphosphine ruthenium 4-pentaoxybenzotrile hexafluorophosphate ( $Ru^*$  complex) and a monolayer of polymerized polydiacetylene (PDA) deposited on Au substrates in the form of Langmuir–Blodgett (LB) films. Tunnelling spectroscopy has been used to detect the electronic structure on the surface due to  $Ru^*$  complex molecules. Ultra-violet photoelectron spectroscopy (UPS) was used to confirm this electronic structure.

### 1. Introduction

Although of great interest, imaging of molecular structure by scanning tunnelling microscopy (STM) has hitherto entailed some difficulties and uncertainties. In particular, there are specific requirements for the substrate and its interaction with the molecule, which are necessary to give reliable images. We discuss these in detail elsewhere [1], but in brief, they include the following.

(i) The need for the substrate to be conducting and atomically flat to allow easy distinction between substrate and the adsorbed molecule.

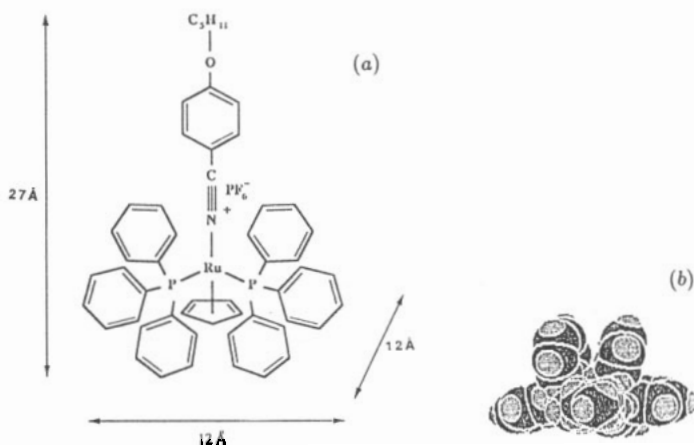
(ii) Imaging artefacts must be avoided. Highly oriented pyrolytic graphite (HOPG) is now known to be generally unsuitable as a substrate because of the considerable likelihood of substrate-generated artefacts in the STM [2]. We have found gold deposited epitaxially on silver on mica to be a suitable surface for molecules solving (i) and (ii).

(iii) Tip–sample interaction can distort molecules and in cases of weakly adsorbed molecules displace them laterally. Reasonably strong fixation to the substrate is therefore needed.

(iv) There may be difficulties encountered during the subsequent interpretation of the images, primarily because the process of charge transfer through these molecules under the STM is not fully understood.

In this article we present some of our results taken on a class of materials deposited, on Au substrates, by the well known Langmuir–Blodgett (LB) technique [3] and describe how tunnelling spectroscopy can help establish the presence of molecules on surface. Numerous attempts to image simply fatty acid mono- and multi-layers were unsuccessful. The best results were obtained on molecules with large substituted groups and materials that were crosslinked laterally (because of (iii)). Images of

an organo-ruthenium compound ( $\eta$  5-cyclopentadienyl-bis triphenylphosphine ruthenium 4-pentaoxybenzotrile hexafluorophosphate). (Ru\* complex) [4] figure 1 and 16-8 polydiacetylene (PDA) ( $\text{CH}_3(\text{CH}_2)_{16}-\text{C}=\text{C}-\text{C}=\text{C}-(\text{CH}_2)_8-\text{COOH}$ ) [5] polymerized in the solid state ([5] and references therein) are presented later. Both systems studied were specifically chosen for their high electrical conductivity.



**Figure 1.** (a) Molecule of the Ru\* complex with dimensions predicted from the space-filled model. (b) View from above of space-filled model.

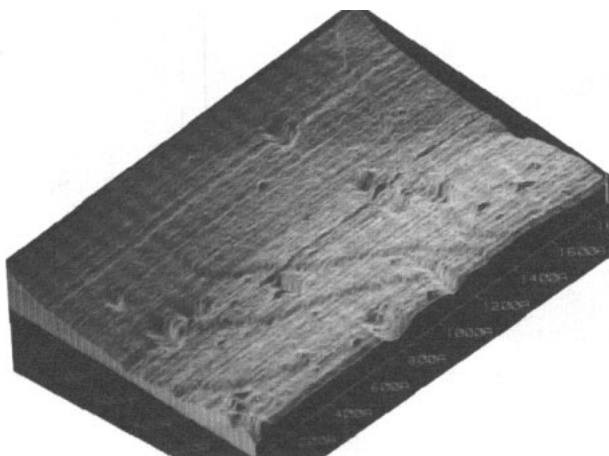
## 2. Deposition and imaging

One-half of the 10 mm<sup>2</sup> Au substrate was covered with the molecular material; this allows direct comparison between images with and without molecules. Monolayers of a Ru\* complex (surface pressure (SP) 22 mN m<sup>-1</sup>, subphase pH 5.8, transfer rate (TR) 1.55 mm min<sup>-1</sup>) and a monomer of 16-8 PDA (SP 25 mN m<sup>-1</sup>, subphase pH 5.9, TR 1.55 mm min<sup>-1</sup>) were transferred from a water subphase. The monomer was polymerized by exposure to UV radiation for several minutes. The presence of molecules on the surface was confirmed by using UV-vis spectroscopy.

The images were taken in ultra-high vacuum (UHV),  $p = 2-5 \times 10^{-10}$   $\tau$ , using a commercial Omicron STM. A fast entry load lock system meant bakeout of the system was not needed, no heating of samples therefore occurred. The typical procedure for STM imaging was as follows.

- (i) The tungsten tip, electrochemically etched, was electron beam heated *in situ*.
- (ii) It was then used to scan a freshly prepared Si(111) sample.
- (iii) Once the  $7 \times 7$  reconstruction on the Si surface was observed, the tip was then immediately used to image different areas of the naked Au substrate to thoroughly characterize the substrate.

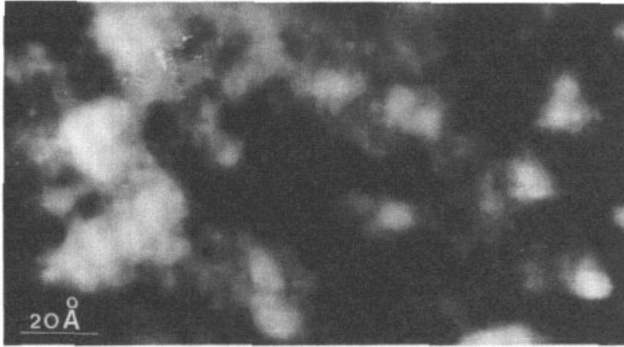
(iv) The tip was then moved to the area covered with molecules to proceed on to molecular imaging. All the imaging was performed in constant current mode. Current image tunnelling spectroscopy (CITS) is performed by interrupting the feedback loop at each pixel and ramping the voltage through a specified range taking simultaneous  $I-V$  curves with the constant current image. The voltage is applied with respect to the sample.



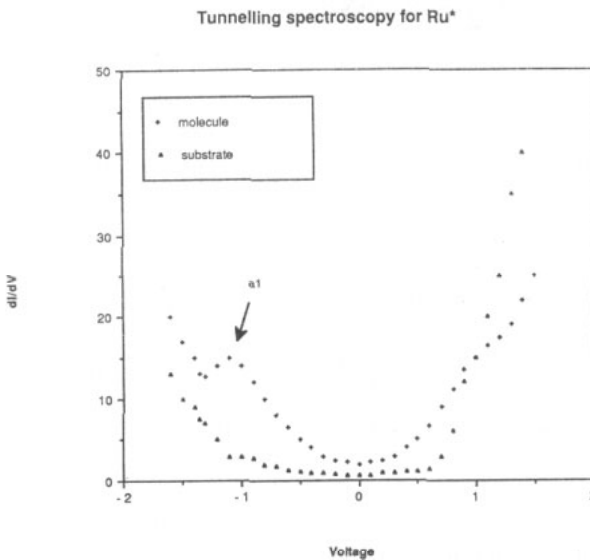
**Figure 2.** Au surface ( $2000 \text{ \AA} \times 2000 \text{ \AA}$ ) used for molecular imaging. The image shows both the steps and the presence of holes as discussed in the text.

### 3. Results and discussion

Figure 2 shows an image of a typical Au surface used for our molecules. Besides showing the characteristic steps,  $2.5\text{--}3 \text{ \AA}$  high, the regular presence of holes was also observed which seems to be a feature of our substrates. Figure 3 shows a CITS image taken on an area covered with the  $\text{Ru}^*$  complex. The best contrast was obtained at certain voltages only. The resolution obtained during repeated topographic scanning on the same area prior to CITS was much poorer. This shows the importance of CITS in cases where good contrast is only available at certain voltages. Scattered features are seen with a length scale of  $12\text{--}14 \text{ \AA}$ . This is in agreement with the expected dimensions for single molecules, figure 1. The larger adsorbates observed towards the left of the image are likely to be groups of more than one molecule. Such features were never seen on similar scans on the substrate alone. Figure 4 shows a  $dI/dV$  against  $V$  plot for sites over molecules and substrate sites. Such plots are an indication of the variation of local density of states with energy of substrate with and without adsorbate. The small peak (labelled a1) at around  $-1.1 \text{ V}$  corresponds to a local increase of states brought about due to the adsorbed molecules on Au. We have confirmed the presence of this electronic structure for the molecule–substrate system by carrying out ultraviolet photoelectron spectroscopy (UPS) (see for example [6] and references therein) on the same samples. UPS is surface-sensitive to within  $2 \text{ nm}$  and the spectrum can yield a direct picture of the filled density of states. It is thus well suited for comparative study of the tunnelling spectroscopy obtained with the STM. Figure 5 shows such a spectrum taken with a helium discharge lamp as the UV source (strongest line at  $21.2 \text{ eV}$ ). It shows a broad peak (labelled a2) with energy range  $0.6$  to  $1.8 \text{ eV}$  below the Fermi level of Au. Another peak, at around  $2.7 \text{ eV}$ , is seen further to the right sitting on the edge of a larger peak. In a complicated molecule like the  $\text{Ru}^*$  complex such peaks are difficult to assign to specific bonds. One conclusion can confidently be drawn, however. The energy range agrees with the one observed in the STM. This gives further confidence in the assignment of the observed images to the  $\text{Ru}^*$  molecules. We note finally that the scattered arrangement in figure 3 may be partially a result of



**Figure 3.** CITS image for Ru\* complex on Au. Scattered arrangements of molecules is seen.



**Figure 4.**  $dI/dV$  against  $V$  plot for sites with and without molecules. Note the different variations of the two plots.

tip-induced lateral motion of molecules during repeated scanning of the same area.

Numerous scanning on the unpolymerized monomer of PDA on Au revealed no reproducible structures. One of the unique features of the PDA polymer is the fully conjugated, rigid backbone consisting of alternating double and triple bonds, figure 6. Figure 7 shows an image of the PDA monolayer polymerized in the solid state. The width of the linear features varied between 8 and 10 Å with the spacing between them between 5 and 13 Å. Such features were repeatedly seen on numerous different areas with their angle with respect to the dipping direction changing over different regions of the film. The image shown was irreproducibly destroyed by performing CITS. Such features were never seen on the substrate alone. This combined with the absence of any reproducible structure during numerous scans on the monomer alone suggests these features are related to the backbone. Leung *et al* [7] has also noted that some cross linking of the monomer is required to give visibility in the STM. Such linear features have also been reported by R J Young ([5] and references therein)

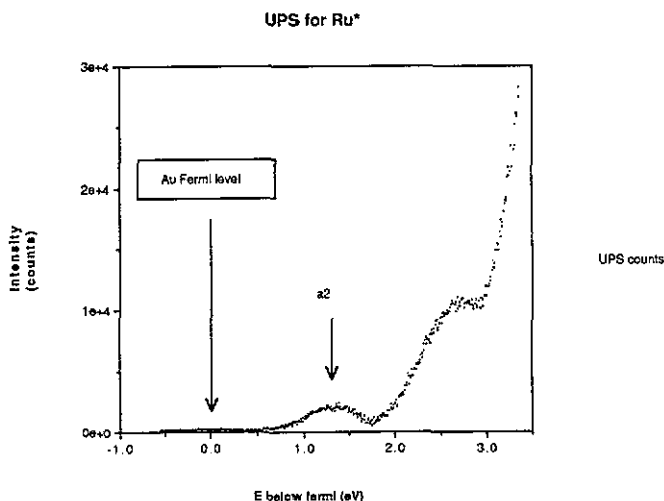


Figure 5. UPS spectrum for Ru\* complex on Au showing filled density of states.

during TEM studies of single crystal PDA. The varying distance between the imaged lines suggests the existence of unpolymerized molecules. This has implications on the rotational and distance packing of molecules. Various orientations of the backbone with respect to the dipping direction suggests the existence of domains in the film [3]. Lastly we note that during CITS the charge injection per pixel increased, compared to topographic imaging, by over three orders of magnitude (to  $1 \times 10^{-10} \text{ C nm}^{-2}$ ). Such a large increase may contribute to the irreproducibility of the image. This need not necessarily imply polymer destruction or mass loss. Mere rearrangement of monomers will yield the same result.

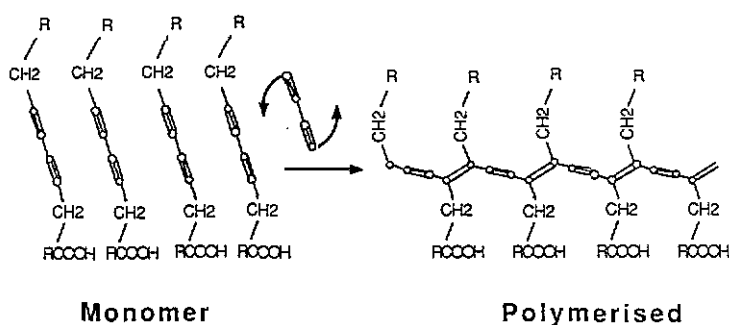
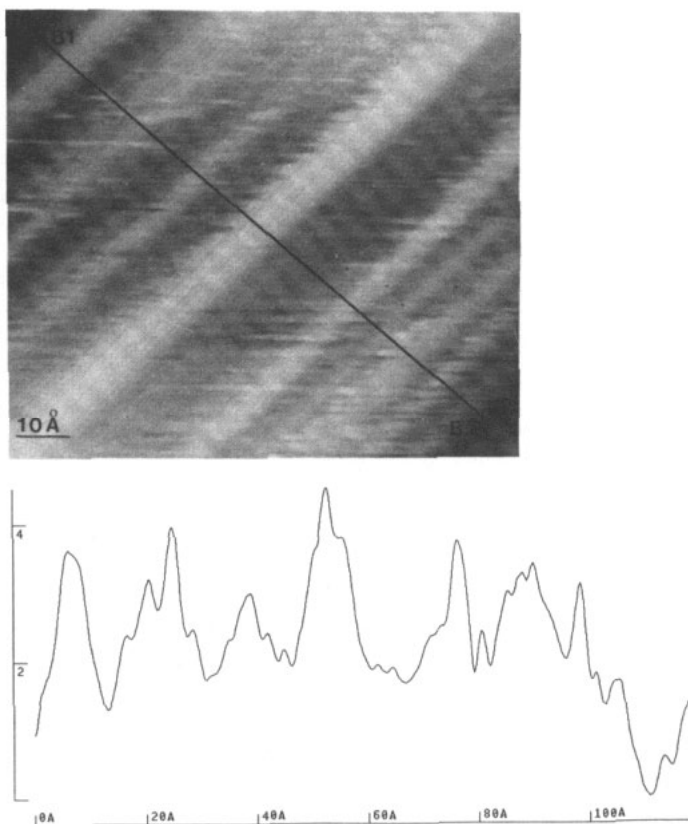


Figure 6. Polymerization of PDA monomers leading to the conjugated backbone.

#### 4. Conclusions

LB films, in general, are very difficult to image, especially long alkane chains. By use of CITS satisfactory voltages are found to allow sufficient contrast to image Ru\* complex molecules. For the PDA, cross linking of the monomers seems essential for visibility in STM. This provides mechanical stability and increased conductivity, both allowing STM imaging.



**Figure 7.** Topographic image of polymerized PDA. The lower panel shows a line scan across (B)1, (B)2. The linear features are at about  $90^\circ$  to the dipping direction.

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