Towards the detection of single polychlorotriphenylmethyl radical derivatives by means of Electron Spin Noise STM

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Abstract

The Electron Spin Noise Scanning Tunnelling Microscopy (ESN-STM) technique is one of the most promising techniques detecting one single spin, combining the spatial resolution of the STM with the ability of spectral resolution and spin manipulation of Electron Spin Resonance. After its first observation, the effectiveness of this technique has been tested by different groups to study the properties of small aggregates or single organic radical molecules.

We report on the ongoing ESN-STM study on nano-aggregates of tris(2,4,6-thrichlorophenyl)methyl radical (TTM) derivatives, whose possibility to be used as wires, switches and memory devices has already been investigated in bulk. After deposition on Au(111), TTM radicals preserved their magnetism. To treat the collected noise data we followed a statistical approach; some peculiar characteristics of this analysis will be addressed.

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1. Introduction

Up to now, one of the most promising techniques to detect one single spin carrier molecule deposited on surface is the Electron Spin Noise Scanning Tunnelling Microscopy (ESN-STM) technique that combines the spatial resolution of the STM with the spectral resolution of the Electron Spin Resonance [1]. After its first application to detect defects in oxidized silicon surfaces [1], the effectiveness of this technique has been tested by various groups who focused their attention

on different instrumental set ups using well known ESR standards, such as BDPA [2,3], DPPH [3], TEMPO [4] or TEMPOL [5] free radicals. Very recently the ESN-STM has been used to complete the characterization of self-assembled monolayers of nitronyl nitroxide radicals [6], especially engineered for self-assembling and gold surface grafting through covalent bonding.

We report here on the use of the ESN-STM technique to address the behaviour of polychlorotriphenylmethyl (PTM) radical derivatives at a single molecule level. These molecules are persistent radicals that find application in nanotechnology as molecular wires, switches and memory devices [7]. PTM molecules can be variously functionalized and moreover present electroactive properties that allow the on−off switching of their magnetic nature [8]. In addition, PTM can be used as building block for organo-metallic complexes [9] and used for the synthesis of biradical species presenting interesting

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intramolecular electron transfer phenomena [10]. Making use of the ESN-STM set up already tested on DPPH and BDPA [3], we investigated the tris(2,4,6-thrichlorophenyl)methyl radical (TTM) derivative depicted in Fig. 1.

This radical appeared to be an excellent candidate for the ESN-STM measurements since we proved, with preliminary STM and CW ESR characterizations here reported, that it fulfils the requirements of this technique, *i.e.* (a) ability to self-organize on surfaces forming either small aggregates (nano-dots) or well-spaced regular monolayer organizations with significant molecular separations and (b) preservation of its magnetism when dispersed on such surfaces.

2. STM characterization

The TTM physisorbed Au(111) samples for STM were prepared using the dip and rinse procedure [3]. Dichloromethane solution (1 ml, 10^{-3} M) of the radical under study was freshly prepared before every set of measurements. In it, a small piece (9 mm^2) of 150 nm gold evaporated over mica (Molecular Imaging – Agilent Inc.), previously hydrogen flame annealed and washed in ultra pure ethanol and dichloromethane, was immersed for 30 s. Then the same gold was rinsed in ultra pure dichloromethane to wash out the molecules that were not physisorbed and gently dried under nitrogen flux. On such prepared gold samples, well-resolved STM images were obtained working in nitrogen environment and using tunnelling currents of 15 pA. STM measurements were performed with a P47-Pro system (NT-MDT, Zelenograd, Moscow, Russia) equipped with a customized low-current STM head and Pt/Ir 90/10 mechanically-cut tips prepared immediately before use. As shown in Fig. 2a TTM molecules are adsorbed on the entire gold surface forming aggregates of a diameter of less than 8 nm. Four hours after sample preparation, ordered domains were observed (Fig. 2b). A high resolution image (Fig. 2c) reveals the detailed structures that are characterized by periodic rows, distant 1.5 ± 0.1 nm one from the other. The periodicity of the rows, as well as their dimension, is consistent with the molecular size of TTM (Fig. 1) [11].

3. CW ESR measurements

By ESR, we demonstrated that the TTM derivative radicals preserve their magnetism when deposited on the surface, which is a fundamental requirement for performing ESN-STM experiments.

The grafting of the radical molecules on Au(111) was performed with the dip and rinse procedure, in the same way as for the STM characterization, and inserted inside a quartz EPR tube. Spectra were taken at room temperature on the sample freshly prepared as well as after a few days. These measurements unambiguously show that not only these radicals preserve their magnetism on surface, but they are also stable in time even when physisorbed on Au(111) surface. The spectrum (Fig. 3) shows only one line as a result of the immobilization of the molecule on the solid surface.

4. ESN-STM characterization

The main concept of ESN-STM is that a spin, in the presence of an external magnetic field, starts precessing and hence generates a modulation in the tunnelling current at its Larmor frequency [1]. Unlike ESR, in this technique no external rf stimulus is used, and instead, the noise created by the spin at the Larmor frequency is detected. As known, the Larmor frequency (ν_L) is directly related to the *g*-value of a paramagnetic centre by the relation: $\nu_L = g\mu_B B/h$. On this basis, for a fixed external applied magnetic field, it is possible to identify a paramagnetic species just by looking at the AC component of the tunnelling current at the frequency value at which resonance occurs. The radio frequency (rf) modulation generated by the spin precession sums up to the direct tunnelling current (DC) and by its revelation it is possible to determine the location of the spin site on the surface [12]. By following this rf component of the tunnelling current flowing through the STM tip, we can get local information about the paramagnetic centres located on the surface: the high frequency component of the tunnelling current is decoupled by the continuous one – which is fed into a low-pass band *I*–*V* converter and used as
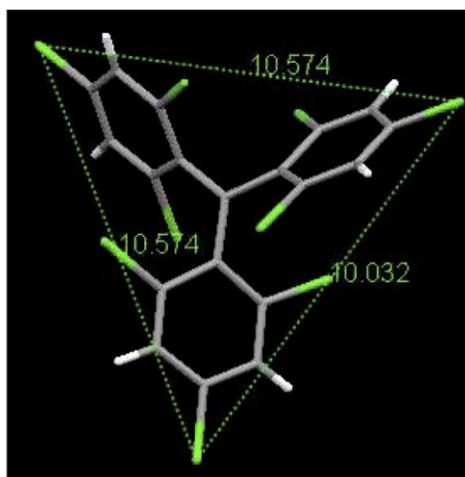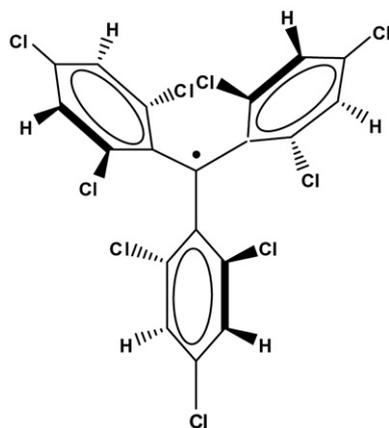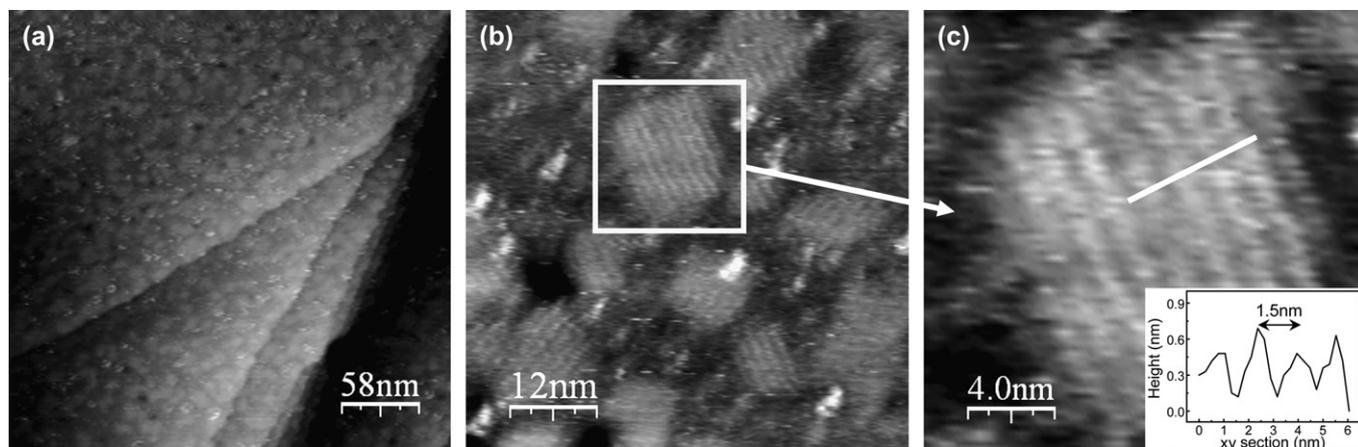

Fig. 1. Molecular structure of the TTM radical and its crystal structure representation with indication of the distances between the *para*-chlorine atoms [12].

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Fig. 2. (a) STM image (322 × 322 nm) of TTM dispersed on Au(111). Tip sample bias 0.3 V and tunnelling current 15 pA. (b) STM image (60 × 60 nm) of TTM dispersed on Au(111). Tip sample bias 0.3 V and tunnelling current 15 pA. (c) Zoom of one of the ordered domains: the periodicity of the rows corresponds to 1.5 ± 0.1 nm as shown in the inset figure.

a feedback to perform standard STM operations − so to be amplified and then monitored by a spectrum analyzer.

An important aspect to deal with when performing these experiments is the transient nature of the signal, *i.e.* the intrinsic instability in frequency that may cause failure in detecting the paramagnetic centres. Therefore, it appears mandatory to repeat the experiment on many single molecules or aggregates to get statistically significant results. Moreover, the level of the signal we want to detect is quite low [3], and only a large number of spectra and a statistical analysis of the collected data can make these measurements reliable. The phase sensitive detection (PSD) method, implemented by one of the authors [13], has been used in order to distinguish between spurious signals which might accidentally exist at the frequency

Fig. 3. Top: the signal of the dip and rinse TTM sample. MW frequency 9.40388 GHz, power 20 mW, Mod. Amp. 1 G, field modulation frequency 100 kHz. *g*-Value 2.00343; ESR cavity: standard TE102. The over-modulated spectrum shows one line arising from TTM of $L_w = 3.14$ G. The small signal at lower *g*-value is arising from the Au/mica substrate, as shown in the bottom spectrum. Bottom: the ESR spectrum of the substrate under the same experimental conditions.

examined and the real signals; this is accomplished by applying an AC magnetic field so as to modulate the Larmor frequency with a modulation frequency to be fed as a reference in a lock-in amplifier. The proper ratio between the modulation intensity to be chosen and the modulation frequency is 2 and a sketch of the complete apparatus used for all the measurements reported here can be found in Ref. [3]. While recording the STM image, we localized the tip on the TTM aggregates and recorded an rf spectrum in the frequency range around the Larmor frequency; during this spectroscopy operation, the tunnelling current was temporarily raised to 1 nA.

The parameter chosen as statistical indicator of the intensity of the candidate signals is the difference of the maximum positive peak and the minimum negative peak divided by the standard deviation $(P_k - P_k/\sigma)$. For each of the spectra, the $P_k - P_k/\sigma$ parameter was determined using an automatic routine especially written to analyze this type of data [14]. Nevertheless, each of the spectra has been individually checked to control the possible presence of a proper derivative shape as well as that the distance between the maximum and the minimum peak was of some kHz, *i.e.* comparable with the concerned parameters of the measurement (the corresponding modulation intensity of the frequency and the resolution band width of the spectrum analyzer). Only after this check we could finally consider the candidate signal as an ESN signal, as it is the case for the spectrum reported in Fig. 4.

Even though the set up has been designed and realized to be free of any kind of environmental noise in the radio frequency range [3], it is important to distinguish between ESN-STM signal and the environmental noise at the same working frequency. Therefore, we first took over 1000 spectra on the gold substrate with the tip slightly retracted and out of tunnelling. We could in this way establish the threshold value corresponding to the radio frequency noise level. Once the threshold was established, we worked in tunnelling conditions on the radical molecules. The $P_k - P_k/\sigma$ histogram for each set of measurements refers to a set of experiments performed at one working frequency and with a span of 3 MHz. Due to
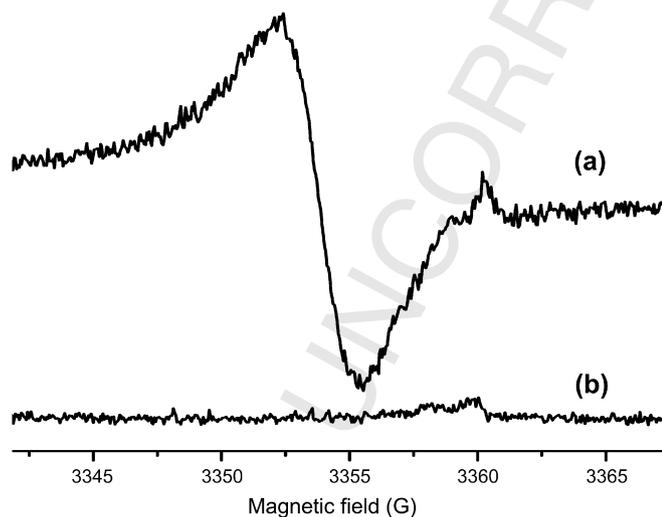
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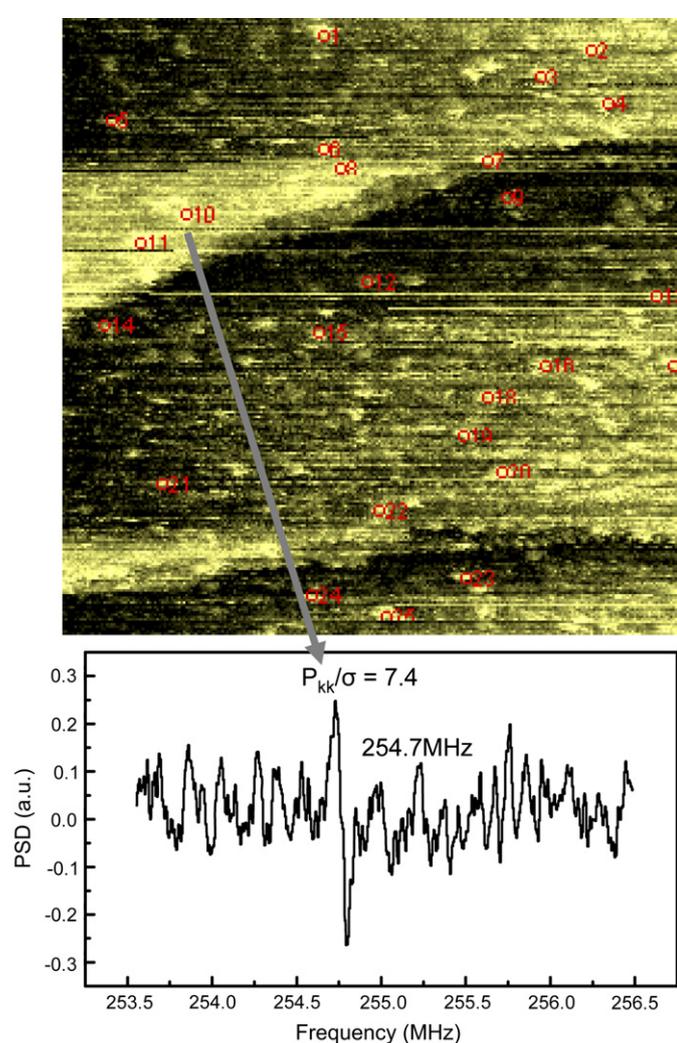4 *V. Mugnaini et al. / Solid State Sciences xx (2007) 1–5*

Fig. 4. Top: ESN-STM image of TTM dispersed on gold, without any filtering. The sample was prepared by the dip and rinse procedure. While scanning ESN spectra are acquired in correspondence of detected objects, in particular the ESN spectrum presented in the bottom part corresponds to the aggregate number 10.

the uncertainty in the value of the applied magnetic field, experiments were performed in different frequency ranges. The statistical analysis of all the recorded data shows some peculiar characteristics of the TTM radical with respect to the noise, opening the way towards the use of ESN-STM to detect single spins on the surface. While the noise distribution is symmetric around the central value and fitted properly by Gaussian symmetric function (Fig. 5), the histogram for TTM aggregates is right skewed and well fitted by the asymmetric Gaussian function [15]:

$$y = y_0 + B\exp\left(-(x - x_c)/2\sigma_1^2\right) \text{ and } B$$
$$= A/(\sigma_1 + \sigma_2/2) \times (2\pi)^{0.5}, \quad \text{if } x \le x_c \qquad (1)$$

$$y = y_0 + B\exp\left(-(x - x_c)/2\sigma_2^2\right) \text{ and } B$$
$$= A/(\sigma_1 + \sigma_2/2) \times (2\pi)^{0.5}, \quad \text{if } x > x_c \qquad (2)$$

where the centre of the distribution (x_c) and the widths σ_1 and **Q5** σ_2 are free parameters optimized during the fitting. When using this function to fit the noise data, σ_1 and σ_2 turned out to be coincident, as expected for a symmetric distribution. Instead, the best fitting of the TTM histogram gave a slightly higher value for the centre and, which is more interesting, a difference between σ_1 and σ_2 of 0.21, a clear indication of the asymmetry in the distribution. This asymmetry means that the total number of events whose $P_k - P_k/\sigma$ is larger than the x_c value of the noise histogram is higher for the TTM than for the noise. Therefore, we can conclude that not only the percentage of spectra above the threshold, but also considerations on the asymmetry of the statistical distributions must be taken into account when performing ESN-STM experiments on molecules deposited onto a solid surface. We are currently working on the elaboration of a physical model able to explain the asymmetry in our results.
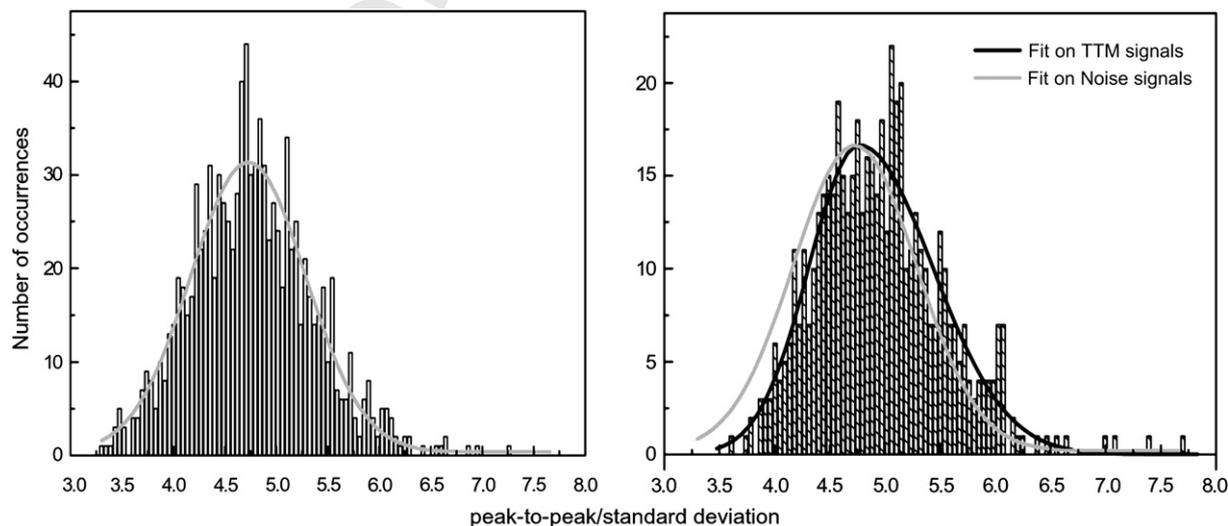

Fig. 5. Left: the histogram of the out of tunnelling noise (1024 spectra) at 255 MHz and its Gaussian fit. Right: the histogram of the TTM radicals (532 spectra) at the same frequency and in black its asymmetric fit. As a comparison the fit of the noise (in grey) is superimposed to the TTM one.

5. Conclusions

We have demonstrated the effectiveness of the ESN-STM in locating and studying TTM radical derivatives physisorbed as small aggregates lower than 10 nm in diameter on gold surface. The obtained promising results prompt us in improving the control of the dimension of the radicals deposited on gold and then exploit the possibilities of this technique following how the spin noise signal depends on the nanometer size of the aggregate. In conclusion, these molecules retain their paramagnetic character, as shown by ESR, which allowed us to detect a few good ESN spectra. The performed statistical analysis makes us confident about our results. The preliminary results so far obtained look promising, although a proper implementation of the equipment is still required to exploit the possibilities of this new technique. Further improvements of the experimental system are in progress. These include improving the matching between the detector and the STM, adding a reactive component in parallel to the STM tunnelling junction (tuning) and cooling to 4 K. We expect that these steps will significantly improve our ability to study the paramagnetic molecules at the single spin level.

Acknowledgements

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