

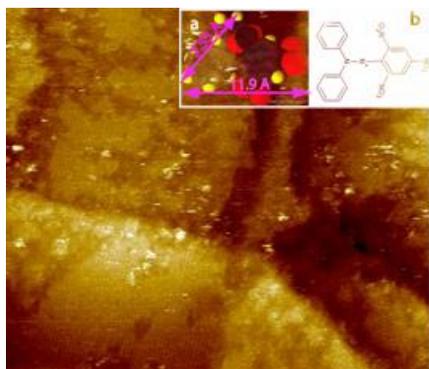
NANOSTRUCTURING PARAMAGNETIC MOLECULES AT METAL SURFACES AS A TEMPLATE FOR ESN-STM

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INTRODUCTION

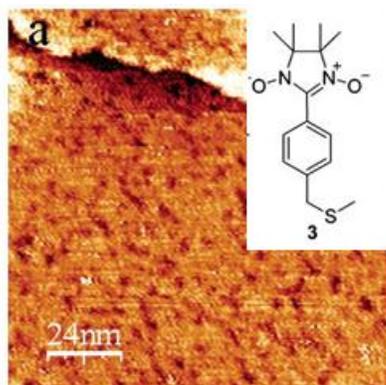
Both the measurement of spin dynamics at the single molecular level¹⁻³ and the exploration of paradigms to implement quantum computing at the nanoscale require a precise spatial control on the position of the spin. Unpaired electron spins in organic molecules are interesting candidates for this purpose: the low spin orbit coupling of the unpaired electron in an organic molecule and the synthetic flexibility in adding molecular moieties, make these molecules appealing for surface constrained nanostructuring. In this work we present three different approaches to the nanostructuring of paramagnetic organic molecules at the surface. We use the Au(111) surface for the three methods.



STM image of ordered arrays of 1-10 phenantroline. The white protrusions are DPPH single molecules or dimers

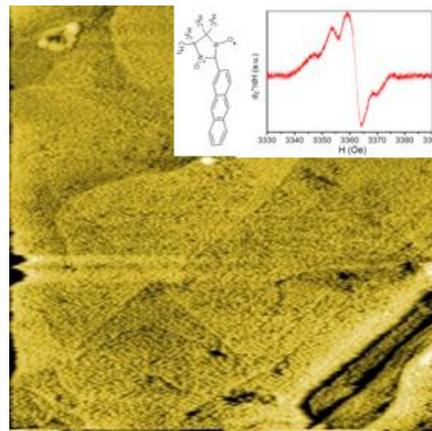
RESULTS

In the first approach a nitronyl nitroxide radical (NIT) moiety is functionalized with three different linking groups (Ph-R; with R = CH₂SCH₃, SCH₃, PhSCH₃) including in all cases a sulfur atom⁴ promoting the interaction with gold. Depending on the tail structure self assembling of ordered monolayers of spins are observed. In this way a commensurate lattice of spin centers is created. Electron Spin Resonance (ESR) measurements are obtained from these monolayers. These measurements show that the monolayers preserve the molecular paramagnetism, in addition they also provide evidence that the molecules are subject to slow movements around their axis.



STM image of ordered arrays of the nitronyl nitroxide (NIT-PhR) derivative shown in the inset.

In the second approach paramagnetic molecules of DPPH are embedded into a 2D-ordered diamagnetic molecular matrix⁵. This approach is particularly useful to provide a test sample for Scanning Tunneling Microscope (STM) single molecular spectroscopy at room temperature at the solid air-interface. Ordered arrays of the molecule 1-10 phenantroline are created on Au(111) by dipping method followed by sample annealing to 80 C⁰. Specifically a mixture containing the paramagnetic molecule DPPH and the 1-10-phenantroline is used to produce the nanostructure. ESR measurements provides insights on the thermal resilience of the DPPH molecules. The STM data are interpreted making use of ENDOR and FT-ESR measurements obtained from solid and liquid dilute solutions of DPPH.



STM image of ordered arrays of NIT-anthracene phenantroline. The inset shows the NIT-anthracene molecular structure and the ESR image.

In the third approach we make use of a Nitroxyl Nitroxides (NIT) moiety bringing an anthracene tail. This tail allows the formation of ordered monolayers of NIT-anthracene molecules on the Au(111) surface. ESR spectra are obtained from the monolayer surface showing that the paramagnetism of the NIT moiety is preserved at the contact with the surface. Electron Nuclear Double Resonance (ENDOR) and Electron Spin Envelope Echo Measurement (ESEEM) measurements from dilute solid and liquid solution are also presented. The ENDOR measurements provide the relaxation time for the N nuclei, which assists the interpretation of single molecule spectroscopy measurements. STM measurements from diamagnetic anthracene films intercalated with NIT-anthracene molecules will be also presented.

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