



## Patterned monolayers of nitronyl nitroxide radicals

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### ABSTRACT

We report here the results of the preliminary characterization of the monolayer obtained both by self-assembling and microcontact printing of a di-alkyl sulfide nitronyl nitroxide derivative, 11-decyl sulfanyl-decanyl nitronyl nitroxide of which we describe the synthesis. The sulfide unit has been introduced in order to allow the grafting of the molecule to the gold surface as well as to improve the stability of the organic radical with respect to different grafting agents like thiols, whereas the two long alkyl chains have been introduced to enhance the packing order of the molecules in a self assembled monolayer structure.

X-band ESR was used to demonstrate the persistence of the paramagnetic character of the radical in the self-assembled monolayers, and to study its relatively large mobility. The microcontact printed monolayer was characterized by AFM, suggesting a non-negligible mobility of the molecules on the surfaces and a strong tilting of the molecules on the surface.

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## 1. Introduction

Organic radicals represent an important class of compounds in molecular magnetism. They are widely investigated with the aim of obtaining purely organic ferromagnets [1,2], as well as for assembling complex magnetic structures in which they act as building blocks, providing chemical and magnetic links between transition metal ions [3]. On this respect, nitronyl nitroxide radicals (NitR) are particularly versatile units which are able to yield magnetic polymers giving rise either to long range ordered structure, or to single chain magnets (SCMs) [4]. More recently NitR have been proposed also as candidate for obtaining quantum logic devices [5] and for the development of spintronics applications; in particular, NitR function were suggested to be used to increase the spin polarization of the current in molecular junction [6].

This purpose obviously requires the ability of handling these materials down to the molecular scale and to organize them in ordered monolayers. For this reason in the recent past we devoted strong efforts in their organization on surface via self-assembly [7]. Encouraging results have been obtained by depositing aromatic NitR derivatives on gold surfaces [8] and different functionalizations of the NitR moiety have been investigated in order to

enhance the local ordering as well as to explore the advantage offered by different deposition technique like the microcontact printing one [9].

In this paper we report our preliminary results on the preparation and the deposition on surface of a NitR based di-alkyl sulfide group. The structure of this molecule has been designed in order to couple different properties related to their grafting on surfaces: (i) sulfide unit has been introduced in order to allow the grafting of the molecule as well as to improve the stability of the organic radical with respect to different grafting agents like thiols; (ii) long chains (10 C atoms) units have been introduced to enhance the packing order of the molecules in a self-assembled monolayer structure; (iii) the second chain has been designed to be composed by the same number of C atoms in order to improve this packing [10].

## 2. Results and discussion

The synthesis of 11-decyl sulfanyl-decanyl nitronyl nitroxide (**6**) required the *ex-novo* preparation of the aldehyde based on the direct reduction of the decylthioundecanoic acid (**3**) to the corresponding 11-(decylthio)undecanal (**4**) through the use of the theryl(bromo)borane-dimethyl sulfide that allows the quantitative reduction of aliphatic carboxylic acids without damaging the dialkyl sulfide moiety [11]. The first step of the preparation involves

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the coupling of two aliphatic chains by the substitution of the bromine group of the 11-Br-undecanoic acid (**1**) reagent by the deprotonated thiol group of 1-decanthiol (**2**). The obtained decylthioundecanoic acid (**3**) is treated with thexylbromoborane-dimethylsulfide (ThxBHBr·SMe<sub>2</sub>) to form a thexyl(acyloxy)borane; the acyloxy group is then easily reduced to aldehyde by another equivalent of the reagent probably via a cyclic intermediate. The aldehyde is then recovered from the reaction mixture exploiting the Bertagnini reaction, yielding a bisulfide adduct by which the aldehyde (**4**) is then regenerated by basic catalysis [12]. The obtained aldehyde (**4**) was then condensed, (**5**), and oxidized to the corresponding nitronyl nitroxide radical (**6**) as described in the general procedure with standard oxidation with NaIO<sub>4</sub>. Further details concerning this synthesis, resumed in Fig. 1, are described in the experimental part.

In order to exclude the presence of over-oxidized species and to have a bulk fingerprint as a reference for the structure of the monolayer, the final product was characterized by electron spin resonance. ESR spectrum of the fluid solution (Fig. 2a) confirmed the effective purity of the compound. The spectral pattern corresponds to the expected one for an aliphatic nitronyl nitroxide derivative [13]. A quintet of triplet spectrum centred at  $g = 2.009$ , due to the coupling of the electron spin with two equivalent <sup>14</sup>N nuclei ( $I = 1$ ,  $A_{iso} = 7.6$  G) and two equivalent <sup>1</sup>H nuclei ( $I = 1/2$ ,  $A_{iso} = 2.6$  G) in  $\alpha$  position with respect to the nitronyl nitroxide function is observed as well.

As already demonstrated for different derivatives [8,14] ESR techniques allow the characterization of monolayer of radicals. We exploited this sensitivity to characterize self-assembled monolayers (SAMs) of (**6**). The preparation of the SAMs of (**6**) is described in the experimental part. The obtained room temperature ESR spectrum shows the presence of a submonolayer deposit of radicals with a quite large mobility. In particular, the five line of the hyperfine structure of the signal, centred at  $g = 2.009$ , indicates that the deposited species are NitR molecules. The angular independence of the signal (not shown) suggests that the averaging of the anisotropic interaction is effective. However, the shape of the spectrum also indicates a partially reduced mobility of the radical, constrained by the gold surface. These features are in agreement with those already reported by our group for a class of aromatic derivatives of NitR [8]. As a conclusion, at variance with the observed behaviour for simpler dialkyl-sulfide derivatives [10], the radical monolayer is not forming a rigid film. This also explains the difficulties we found in imaging these monolayers by scanning tunnelling microscopy in contrast to what we observed for aromatic derivatives of NitR [8].

The structure of the molecule (long aliphatic chain) and its chemical properties (solubility in ethanol, presence of the S-terminated linker group) allowed us to use also the microcontact printing technique ( $\mu$ CP) [9], to create patterned SAMs of the molecule on gold surfaces following the same procedure we followed for

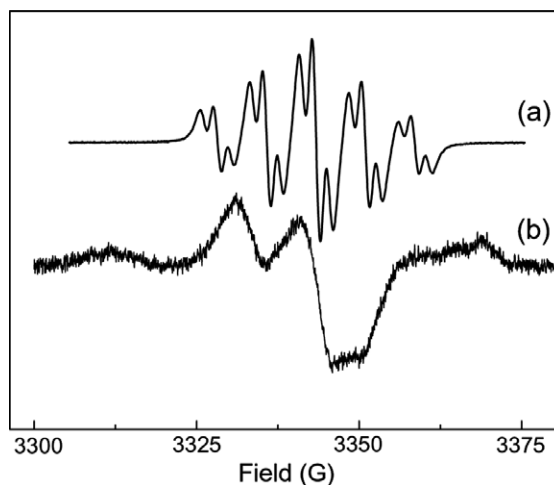


Fig. 2. Room temperature X-band ESR spectra of (**6**): (a) in CH<sub>2</sub>Cl<sub>2</sub> solution; (b) as monolayer deposited on gold surface.

complex magnetic molecules [15]. This soft-lithographic technique has never been used for NitR radicals but similar approaches recently permitted the deposition of polychlorotriphenylmethyl radicals [16]. Its main advantage relies on the enhancement of the possibility to access single molecule properties. In particular the achievement of reproducible and stable patterned surfaces of these radicals would trigger an easier first test of the detection of their magnetic properties via scanning probe microscopy based techniques [17–21]. Fig. 3 shows our preliminary microcontact printing results. PDMS elastomer with protrusions of 5  $\mu$ m wide stripes separated by 3  $\mu$ m spacing was used as stamp and the solution of (**6**) used in the SAM preparation was used as ink.

Atomic force microscopy characterization of the patterned monolayer was possible due to the soft approach of the semi-contact mode method [22] and allowed us to make some hypothesis on the organization of this molecules on surface. From the profiles, we can extrapolate that a strong tilting of the molecules on the surface occurs; moreover, due to the small interaction within the sulfide linking group and the gold surface, a non-negligible spreading of these molecules on the surfaces was observed, what is in agreement with the ESR analysis results. However these data are not conclusive and further characterization is required.

### 3. Conclusions

We presented the synthesis of a new nitronyl nitroxide derivative and the results from AFM and ESR characterization of the corresponding monolayers obtained by two different techniques, the self-assembling from solution and the microcontact printing tech-

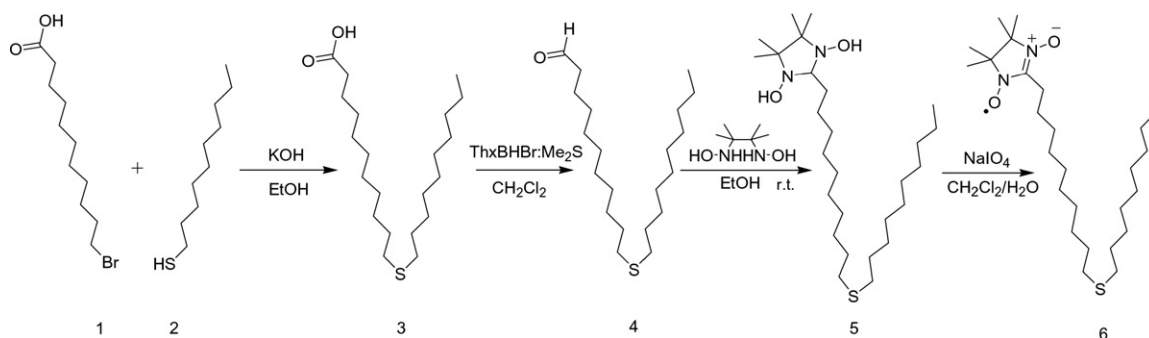
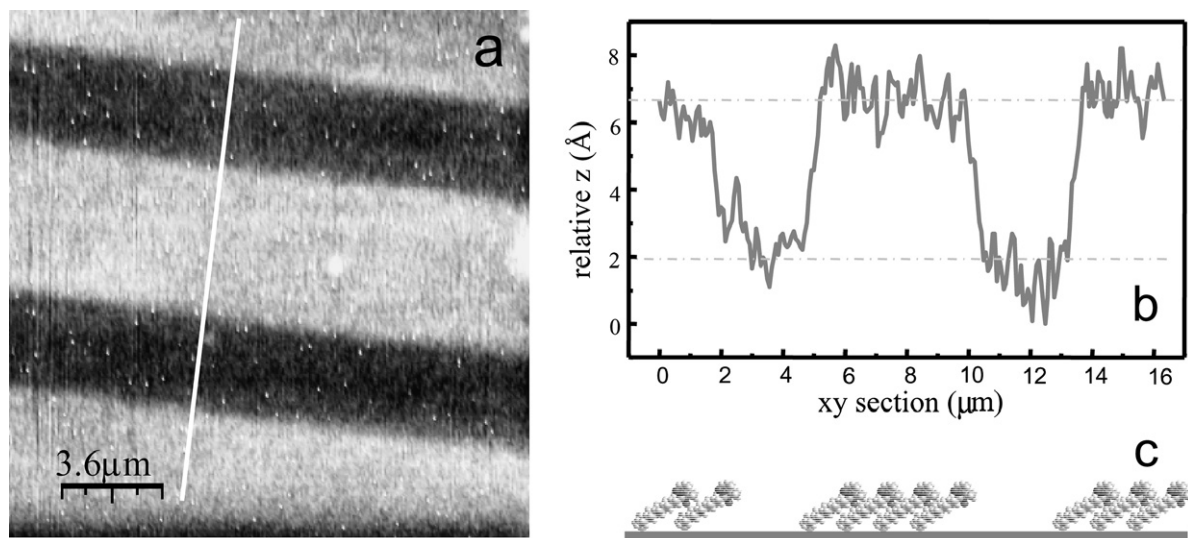


Fig. 1. Scheme of the preparation of **6**.



**Fig. 3.** AFM image ( $18 \times 18 \mu\text{m}^2$ ) of **(6)** microcontact printed in stripes on gold with a PDMS stamp ( $5 \mu\text{m}$  stripes spaced  $3 \mu\text{m}$  apart). Dotted line indicates the xy section presented in (b). In (c) a schematic view of the expected packing of molecules on the basis of the measured profiles is presented.

nique. The ESR analysis demonstrated the persistence of the paramagnetic character of the SAM and its relatively large surface mobility. AFM analysis of the microcontact printed monolayer confirmed the non-negligible surface mobility of the molecules on the surfaces. AFM measurements demonstrated that the microcontact printed molecules are strongly tilted on the surface.

Possible future developments of this investigation requires the exploration of different linking groups and a complete chemical characterization of these patterned structures.

The optimization of this kind of magnetic nanostructures will play a key role in the further development of magnetic local probe techniques like electron spin noise-scanning tunneling microscopy (ESN-STM) that has been recently proved to be well suited for the characterization of molecular based magnetic materials [23–25].

## 4. Experimental

### 4.1. Synthesis

The decylthioundecanoic acid (**3**) has been prepared by coupling 1-decanthiol (**2**) and 11-Br-undecanoic acid (**1**) as described elsewhere [26]: 1-decanthiol (10.7 g; 61.5 mmol), 11-bromoundecanoic acid (12.8 g; 48.3 mmol), powdered KOH (6.7 g; 119.6 mmol) and 125 mL EtOH were stirred and heated at reflux overnight. The mixture was allowed to cool down to room temperature, water was added and the aqueous solution was extracted twice with hexane to remove apolar contaminants. Thereafter, the water layers was acidified with HCl solution and extracted twice with ether. The combined ether layers were washed with NaCl solution and dried with  $\text{MgSO}_4$ . Evaporation and recrystallization from hexane gave 13.7 g pure decylthioundecanoic acid (**3**).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.85 (3H, t), 1.45–1.15 (26H, m), 1.7–1.5 (6H, m), 2.35 (2H, t), 2.50 (4H, t), 11.8–11.0 (1H, br s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 180.03, 34.0, 32.1, 31.8, 29.67, 29.52, 29.50, 29.39, 29.30, 29.27, 29.22, 29.16, 28.99, 28.91, 24.6, 22.6, 14.0.

An oven-dried 250 mL flask, fitted with a side arm and bent adaptor connected to a Hg bubbler, was charged with 9.5 g of decylthioundecanoic acid (**3**) and 17.5 mL of distilled  $\text{CS}_2$ . The flask was immersed in a cold bath and maintained at  $-20^\circ\text{C}$ . A pre-cooled 3 M solution of  $\text{ThxBHBr} \cdot \text{SMe}_2$  [11] in  $\text{CH}_2\text{Cl}_2$  (8.3 mL, 26.5 mmol) was added dropwise with stirring. After complete evolution of  $\text{H}_2$ , the cold bath was removed, and the reaction mixture

was warmed to room temperature. An additional 1.1 equiv of  $\text{ThxBHBr} \cdot \text{SMe}_2$  (9.2 mL, 29.2 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was then transferred via a double-ended needle to a flask containing 25 mL of water in an ice-water bath and was hydrolyzed with vigorous stirring for 1 h at room temperature. The mixture was saturated with NaCl and the separated organic layer was treated with  $\text{NaHCO}_3$  in order to neutralize the acidity. This solution was poured in a 40 mL saturated solution of  $\text{NaHSO}_3$  and 85 mL of THF was added maintaining under vigorous stirring for 1 h. Then the reaction mixture was cooled observing the precipitation of the adduct as expected [27].

Under vigorous stirring 26 g of this adduct was gradually added to a mixture heated to  $90^\circ$  of an aqueous solution of  $\text{Na}_2\text{CO}_3$  (40 g in 400 mL) and heptane (400 mL). When  $\text{CO}_2$  production ceased this mixture was added to 500 mL of water and the organic layer was separated. Removing the solvent a pure 11-(decylthio)undecanal (**4**) was obtained. Elemental Anal. (%) on a vacuum-dried sample Calc. for  $\text{C}_{21}\text{H}_{42}\text{OS}$ : C, 73.62; H, 12.36. Found: C, 73.92; H, 12.86%.  $^1\text{H}$  NMR 300 MHz,  $\text{CDCl}_3$  (ppm) = 9.79 (s, 1H, CHO), 2.52 (t, 4H,  $J = 2\text{Hz}$ ,  $\text{CH}_2\text{S}$ ), 2.45 (t, 2H,  $J = 2\text{Hz}$ ,  $\text{CH}_2\text{CHO}$ ), 1.60 (m, 6H), 1.28 (m, 26H), 0.9 (q, 3H,  $\text{CH}_3$ ).

### 4.2. SAM formation in solution

Monolayers of **(6)** were obtained by the standard method for preparations of SAMs in a solution [7]. A gold slide (gold evaporated on mica and flame annealed with hydrogen flame) was immersed in a 1 mM solution of **(6)** in ethanol at room temperature. After 20 h of incubation the slides were rinsed with pure ethanol and dichloromethane and dried under a nitrogen steam.

### 4.3. Deposition via $\mu\text{CP}$

Microcontact printed stripes were prepared similarly to an earlier described procedure, using a PDMS stamp replicated from a silicon master with gratings of 5–3  $\mu\text{m}$ . The stamp was inked with  $10^{-3}$  M solution of **(6)** in ethanol and dried, then the molecules were printed on the gold substrate by placing the stamp on the substrate and forming the conformal contact between the stamp and the gold surface. 20 nm thick gold layers were prepared by

evaporation on the titanium adlayer (2 nm) on the silicon wafer and cleaned by the same cleaning procedure described in Ref. [15].

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