

# 1 Introduction

Molecular magnetism is an interdisciplinary research field where chemists and physicists work together to design and characterise the magnetic properties of molecular based materials. Among these a central role is played by the so called Single Molecule Magnets (SMMs) [1]. The evocative name derives from the magnetic property of these molecular systems, which behave as tiny magnets. They are characterised, albeit at cryogenic temperatures, by slow relaxation of the magnetisation, which is molecular in origin [1]. This behaviour arises from a ground state characterised by the coexistence of two different states separated by an energy barrier; a property known as magnetic bistability. Moreover the molecular nature leads to the observation of quantum effects in static and dynamic magnetic properties [1]. SMMs combine the advantages of the molecular scale with the properties of bulk magnetic materials. This has made them attractive, though still at a fundamental level given the low operational temperatures, for high-density information storage, for quantum computing [2–4] and for spintronic applications [5]. In the latter research field the electronic and spin degrees of freedom are exploited for technological purposes [5–8].

In order to explore the possibilities offered by SMMs it is mandatory to achieve the control of the magnetic state at the single molecule level. Typically this is achieved by creating hybrid nano-architectures, i.e. SMM on a conducting surface or inserted in a nanogap between electrodes. For this reason in the last decade many efforts have been devoted to the preparation and the characterisation of SMMs hybrid surfaces [9]. As demonstrated by the first attempts based on the archetypal SMM, a dodecanuclear manganese complex ( $\text{Mn}_{12}$ ) [10,11], the preparation of such a hybrid surface has proved to be a critical issue. In fact, due to structural modifications induced by the substrate, the  $\text{Mn}_{12}$  molecules lose their SMM character. To

overcome such problems more stable SMMs are needed, requiring synthetic efforts, as well as a fine control of the deposition method, a task that necessitates competences in surface-science. This work is indeed devoted to the surface-science aspect.

The first relevant result in the preparation of a SMM hybrid surface was achieved by employing a chemical grafting method for the molecular deposition [12]. However this surface preparation method requires a specific molecular moiety able to bind the surface. This represents a limitation because it does not allow the molecular functionalization of different surfaces using the same molecule. Moreover, the preparation from solution did not allow a fine control of the surface quality. This hampers the possibility to address the single molecule properties by employing Scanning Tunnelling Microscopy (STM) and its derived techniques. In order to be able to exploit the great potentiality of these techniques, recently demonstrated in the investigation of atomic structures on surfaces [13–18], other deposition methods must be employed, such as the electrospray beam deposition, employed by Kern's group [19,20], and the more traditional molecular sublimation method. In fact, both methods allow the preparation of the surfaces employing the ultimate controlled conditions provided by the Ultra High Vacuum (UHV) environment. These methods overcome the substrate limitation of the chemical grafting procedure allowing the preparation of different hybrid surfaces by using the same SMM. Moreover, highly reactive surfaces, like ferromagnetic 3d metals, can be employed. However, the sublimation procedure requires a high thermal stability of the single molecule magnet that strongly reduces the number of SMMs suitable for this type of deposition.

In this work we present a study concerning two sublimable molecular systems. We start by presenting the results of our investigation on one of the most studied class of SMMs: the rare earth ions bis(phthalocyaninato) complexes [21]. In particular the terbium(III) bis(phthalocyaninato) ( $\text{TbPc}_2$ ) has been considered as the archetypal of sublimable SMMs. It exhibit slow relaxation of the magnetisation at temperatures as high as 15 K, which is remarkable

for a SMM. As a result of its flat structure the  $\text{TbPc}_2$  molecule has proven to be a good candidate for STM and scanning tunnelling spectroscopy (STS) investigations [22–25]. These studies have provided crucial information about the electron transport properties of the  $\text{TbPc}_2$  SMM [8]. A keen interest has been also focused on the study of hybrid architectures made by magnetic molecules deposited on magnetic substrates [26–28]. The presence of molecule–substrate magnetic interaction could indeed open new perspectives for spintronics and data storage applications. Albeit the consistent number of publications on this SMM some issues concerning its magnetic behaviour when organized in nanostructures, like the strong reduction of its magnetic hysteresis when deposited on conducting substrates, are still open and have been the object of this thesis.

The other SMM investigated here belongs to the  $\text{Fe}_4$  SMM class. It has been recently shown that a particular derivative of this family can be sublimated [29]. However, also due to the intrinsic difficulties related to the very low blocking temperature (below 1 K) of this SMM, an accurate picture of the magnetic and structural properties of sublimated  $\text{Fe}_4$  hybrid surfaces is still lacking. This despite the fact that in the last years the  $\text{Fe}_4$  family of SMM has proven to be a good model system for the rationalization of the relationship between the magnetic properties and the chemical structure [30].

The  $\text{Fe}_4$  molecules are robust and chemically stable. They can be chemically functionalised with different moieties to promote the interaction with surfaces or to introduce functionalities able to promote a photomodulation of the magnetic properties [31]. Moreover the magnetic properties of the  $\text{Fe}_4$  molecules are less influenced by intermolecular interactions [32] than the  $\text{TbPc}_2$  class. This has allowed to observe also in monolayer films the molecular magnetic bistability and the quantum phenomena, such as the tunnelling of the magnetisation, characterising this SMM.

In this work we present the results of our study of the two molecular systems mentioned above. Chapter 3 is devoted to the investigation of the magnetic behaviour of  $\text{TbPc}_2$  and the correlation of its hysteretic behaviour with the surrounding environment. In

particular we focus our attention on the hysteretic loops of TbPc<sub>2</sub> molecule during the sublimation process, highlighting some anomalies. In order to shed some light on this phenomenon, in section 3.3 we present the results obtained by exploiting the low energy muons implantation technique to perform depth-resolved investigations of the magnetic properties of TbPc<sub>2</sub> thick films. In the last part of chapter 3 (section 3.4) we report a characterisation of thin films of TbPc<sub>2</sub> sublimated on two magnetic substrates, namely lanthanum-strontium manganite and metallic cobalt. Our choice has fallen on these two because they are the most employed ferromagnetic substrates for the realisation of electrodes in organic spin valve [6], thus preparing the ground for future applications.

Chapter 4 is dedicated to the investigation of hybrid surfaces prepared by sublimation of Fe<sub>4</sub> SMMs. We exploit the controlled preparation of the UHV techniques to perform a photoelectron characterisation (PES) of Fe<sub>4</sub> deposited on Au(111) surface (section 4.2). The PES investigation has allowed to tune the preparation of the hybrid surfaces getting sub-monolayer Fe<sub>4</sub> coverage. This has allowed to investigate low coverage Fe<sub>4</sub> samples on different surfaces by means of STM techniques. Thanks to all the efforts in the optimization of the preparation procedure and the in depth characterisation of our films it has been possible to perform experiments in one of the most performing STM platform to record inelastic electron tunnelling spectra. This technique is one of the few that allow the investigation of the electronic and magnetic properties of molecules on surface at the single molecule level.

## References

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