# Preface

The general idea of quantum computing was born in the late 20th century thanks to the works of outstanding scientists like R. Feynman, C. H. Bennett, D. Deutsch, and many others. The idea of overcoming the limitations of classic computation in understanding nature's laws by adopting a universal machine capable of "speaking" the same language of the microscopic quantum world appeared absolutely sensible. Seminal results were initially obtained by physicists, mathematicians, and even philosophers, who laid the groundwork of this interdisciplinary subject, i.e., the quantum information science. Nowadays, the scientific community rides the wave of the second quantum revolution, thus presenting formidable examples of quantum architectures for implementing a new kind of computation. For instance, leading groups such as IBM and Google have already presented superconductive circuits for quantum processors operating with 65 (Falcon processor) and 53 (Sycamore processor) quantum bits, respectively. Companies provide online and cloud platforms, thus giving them the possibility to access such powerful quantum computers to solve different problems.

Although their calculation power was proven to be incredibly high, these architectures present practical limitations that must be overcome to reach a fast, fault-tolerant, and universal computation.

Among the proposed strategies, electron spin-based molecular qubits aroused a specific interest in the community because of the tunability properties of molecules. In this respect, chemistry can give the chance of getting various and tailored molecular systems that might be adopted for different purposes, e.g., for implementing qubits and quantum logic gates, encoding quantum error correction algorithms, for quantum sensing applications, and so on. Nevertheless, combining the need for a specific molecular design and target quantum properties is not trivial. Efforts are still needed to reach essential objectives and overcome common

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problems in different physical and chemical systems. For example, a crucial parameter for qubits is the so-called coherence time, roughly the time in which a certain state of the system can store the encoded information, and it is strictly correlated to the spin dynamics of the system. This specific parameter is not easily controllable since a blend of contributions (magnetic coupling interactions, spin-phonon interactions, etc.) may cause its reduction. Up to now, the effect of various contributions on this parameter is still unclear, and more investigations are mandatory to untangle further the different phenomena originating in its loss.

The author of this thesis mainly worked as a synthetic and inorganic chemist. He synthesized and probed different molecular systems based on transition metal complexes, principally of $Cu^{II}$ and $V^{IV}$ ions, for reaching more performant spin qubits and quantum logic gates. Consequently, this thesis work aims mainly to give a complete overview of the different molecular strategies proposed during these three years as a PhD student at the University of Florence and to show important results and limitations of the employed systems.

The thesis will start with an extensive introduction to the subject of quantum computing, mainly presenting the logic and working principles of quantum computers' fundamental units (Chap.1). Then, different chemical and physical strategies for the obtaining of qubits will be presented in Chap.2, focusing on those based on nuclear and electron spins. In the same chapter, the electron spin relaxation subject will also be treated. An overview of the most promising molecular systems proposed so far is then reported in Chap.3. The general introduction given within these three chapters provides the theoretical bases of quantum information science necessary for understanding the following chapters.

The first principal subject of the thesis will be presented in Chap.4, where different examples of molecular qubits synthesized and characterized by the author will be discussed. Here, we will focus on phenomena originating from the spin-spin and spin-lattice relaxation processes in molecular qubits and the proposed molecular strategy for overcoming the present limitations. In particular, this chapter is mainly devoted to presenting those systems fulfilling three main requirements for the optimization of molecular qubits: i.e., i) a multilevel structure of electronic or nuclear states; ii) a nuclear spin-depleted environment; iii) neutral charge and appreciable thermal stability so that they can be employed for surface deposition experiments. Two examples of hydrogen-free neutral copper(II) molecular qubits will be presented. In particular, the syntheses and magnetic investigations of two complexes of porphyrazine- and dithiolene-like ligands are reported in Sec.4.1 and Sec.4.2, respectively. This section will also focus on the rationalization of the systems' spin dynamics, followed by the experimental and theoretical approaches employed. Furthermore, the treatment of the spin-lattice relaxation phenomenon and its investigation will be extended to the case of lanthanide-based single-molecule magnets. In Sec.4.3, it is reported a comparative experimental and *ab initio* study conducted on an archetypical SMM, i.e., the dysprosium(III) complex of acetylacetonate ligand, aimed at unveiling the role of phonons in the relaxation of this class of compounds.

A relevant part of this thesis work is also related to the application of molecular qubits for advanced EPR experiments. In this respect, there will be presented two studies conducted on the archetypical oxovanadium(IV) qubit with the tetraphenyl porphyrin ligand, i.e., [VO(TPP)]. In Sec.5.1, we will show some intriguing results obtained from the collaboration with the University of Modena and Reggio Emilia (Prof M. Affronte's Group). In that work, single crystals and polycrystalline samples of [VO(TPP)] are coupled with superconductive coplanar resonators and employed for the storage and retrieval of the information in a molecular spin ensemble, i.e., for implementing "quantum memories". In Sec.5.2, we will further show some preliminary results on the investigation of coherence properties of a [VO(TPP)] single crystal by working at the so-called atomic clock transitions, thus exploiting the multilevel nature of the vanadium element. This work was conducted in collaboration with Prof J. R Friedman's group (Amherst University). Additionally, we report a short treatment on the purification procedure employed for obtaining iron(III)-free porphyrins (Sec.5.3). The main objective of the author here was that of removing iron(III) contaminants found in [VO(TPP)].

In the end, the last part of the work will focus on the molecular approaches employed for the realization of two molecular spin-based quantum logic gates. In Chap.6, two examples of porphyrin-based oxovanadium(IV) complexes suitable for the encoding of two- or multi-qubit gates will be presented. On the one hand, the chapter aims to discuss how porphyrins could be sensibly employed to get target multi-qubit architectures, thus allowing the possibility of scaling up the system dimension effectively. On the other hand, the chapter stresses how difficult rationalizing such a complex system's magnetic and coherence properties could be. An example of a multi-qubit system characterized by a switchable interaction is presented in Sec.6.1. This work was realized in collaboration with the University of Manchester, where the author spent three months as a visiting student under the supervision of Prof R. E. P. Winpenny and Dr G. Timco. The work will focus on preparing and synthesizing a vanadyl qubit with the tetrapyridyl porphyrin complex [VO(TPyP)]. The central qubit is linked through coordination bonds to four more purple-$Cr_7Ni$ rings qubits. Furthermore, we will show our results obtained on a two-qubit logic gate based on a vanadyl dimer obtained by condensing two A3B triphenyl porphyrin complexes (Sec.6.2). The dimer is characterized by two distinguishable and exchange-coupled vanadyl units suitable for the implementation of logical operations.