Rationalization of the Mechanism of Bistability in Dithiazolyl-based Molecular Magnets

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Chapter 1

Introduction

This introductory Chapter is organized in order to guide the reader through the different steps that have brought to the research and development of molecular magnets. The history of magnetism and its technological applications evolve in parallel with our own history. The first examples of compasses date back to the ancient China, although the real source of magnetism has remained unknown until the end of the 19th century. Since then, the new-born quantum mechanical theory gave an extraordinary contribution to the interpretation of this property. Magnetism has been extensively exploited in a countless set of devices. A brief summary of the most important results achieved in the past, as well as the current state-of-the-art in the field, are here reported. Finally, the motivations and goals for the research developed in this doctoral thesis are provided.

1.1 From Stones to Molecules

Since the early stages of human history, natural phenomena have triggered a continuum of experiences and discoveries, contouring the different human communities and their expansion, or extinction. As a rule of thumb, the more the society was technologically advanced, the higher were the chances to survive. At their time, the Chinese, the Egyptian and the Roman empires witnessed long periods of prosperity thanks to their technological supremacy with respect to the neighbouring populations. Nowadays, although still valid, the technological supremacy is only one of the different ways to compete in a globalized society.
In the plethora of discoveries that enhanced our knowledge of nature, magnetism is to be considered one of the most relevant. Evidences of knowledge of magnetism date back to both ancient China and Greece. The first source of magnetism discovered were the magnetite-based ($\text{Fe}_3\text{O}_4$) rocks, called lodestones. These natural bulk magnets, if properly suspended, align with the Earth magnetic field\cite{1,2}. Soon, the ancient populations realized that also a small piece of iron can become magnetic, once it gets in touch with a lodestone. Believed to have magical origin, this fascinating property found a practical application in the magnetic iron needles of the first compasses already around 1088 a.c., as described by Sheng Kua\cite{3}. Before the advent of compasses, people used to “sail by sight”. The introduction of these tools marked a new era into navigation systems, enabling the discovery of new places and navigation routes in the following centuries. Despite the remarkable use of it in primitive compasses, it is only in the last two centuries that magnetism saw its “golden age”. The real contribution towards the rationalization and understanding of magnetism in its basic concepts started only in the late 19\textsuperscript{th} century, to be extensively investigated along all the 20\textsuperscript{th} century. The 19\textsuperscript{th} century, defined as the “electromagnetic age”, saw the unification of apparently separate phenomena like light, electricity and magnetism thanks to Maxwell, as reported in his famous paper entitled “A Dynamical Theory of the Electromagnetic Field”\cite{4} published in 1865; the 20\textsuperscript{th} century, instead, witnessed the birth of the modern quantum theory, and in turn, the “understanding age” of magnetism according to Coey’s classification of the history of magnetism in seven ages\cite{5}. Since then, magnetism has been employed in an extended class of devices. Currently, we are living in the “Age of spin electronics”, the time in which\cite{5}

“we are just now beginning to learn how to manipulate spin currents and to make good use of them”.

Deciphering such a complex phenomenon like magnetism led us to reach technological breakthroughs. Nowadays, it can be found in daily common tools used, like clocks, smartphones and storage devices for example; but it plays also a fundamental role in the most advanced experiments that are currently being performed, like in the Large Hadron Collider (LHC) at CERN\cite{6} or in the new generation of plasma reactors\cite{7}.

\subsection{From Bulk to Molecular Magnets: A Glimpse of the Future}

The natural reservoirs of transition elements, the natural sources\cite{8} of strong magnetism known since the very beginning, are running out. This drawback is pushing the research for new and more environmental friendly solutions. This does
not mean to look for exotic elements or to make use of futuristic technologies. We have, instead, to consider the use of more abundant elements at our disposal[9–12] (e.g. carbon, nitrogen, sulphur, oxygen, selenium) and to better engineer what is already known, and, eventually, to drive the synthesis of new compounds.

Thanks to organic and supramolecular chemistry, nowadays we have at our disposal an incredible number of molecular compounds, with a wide spectrum of properties (e.g. optical, electronic, magnetic). One of the most challenging goals that supramolecular chemistry is trying to achieve is to reproduce the bulk properties of magnets by manipulation at a molecular level. But moving from bulk systems composed of transition metals, which are intrinsically favorable to generate magnetic compounds, to organic-based ones, offers some non-trivial challenges to overcome, like the material stability, lifetime, etc. Nevertheless, potentially, there are many advantages related to the use of molecular systems, like the possibility of thin films deposition, transparency, low density, limited production costs, and so on. An ideal molecular crystal should be customizable in order to present a specific spatial molecular arrangement, favoring ferromagnetism or paramagnetism, depending on the final application of the material. Moreover, it should be stable also at room temperature, and it should have an extended lifetime use.

Molecular magnets are among the most suitable potential candidates for advanced devices like data storage, sensors and quantum computers. The structural arrangement is mainly governed by covalent bondings or weaker forces, like hydrogen bonds. Moreover, the synthesis of molecule-based materials can be done under mild conditions of temperature and pressure. The magnetic materials based on carbon, sulphur, oxygen and nitrogen requires a fraction of the energy of the inorganic counterpart. On top of that, they can be recycled, avoiding the disposal of environmentally dangerous wastes.

1.2 Short History of Molecular Magnets

The first example of ferromagnetic ordering in molecular magnets was reported by Miller and co-workers[13–15], for [Fe(C₅Me₅)₂]⁺[TCNE]⁻ (TCNE=tetracyanoethylene) (see Fig. 1.1). Although remarkable, the magnetic property of this compound arises only below a certain critical temperature (Tc < 5 K). Clearly, this material was not suitable for practical applications for devices operating at room temperature (RT). Since then, a lot of effort has been devoted to the synthesis of RT molecular magnets. This breakthrough was achieved in 1991, with the synthesis of the charge-transfer salt V(TCNE)ₓ(CH₂Cl₂)ᵧ[16]. Then, around 1995/1996, some Prussian-blue
Figure 1.1: Crystal structure of the \([\text{Fe(C}_5\text{Me}_5)_2]^{\cdot+}[\text{TCNE}]^{\cdot-}\) compound, showing the (a) chain and (b) the crystal packing.

derivatives were added to the list of RT molecular magnets[17–20]. Three decades later, the list of these organic compounds has been greatly extended. Nowadays, the principal families of free radicals and corresponding derivatives investigated are verdazyl[21, 22], triphenylmethyl[23–31], phenalenyl[32, 33], nitroxide[34–42] and dithiazolyl[43–47] based radicals (see Fig. 1.2). These organic molecular magnets have all of the properties commonly attributed to metal-based (or atom-based) magnets, like, for example, coercivity[48]. While many examples of organic molecular magnets have been studied[49–58], we are still far from a complete control over their properties, and, in turn, a practical application. For a detailed description of the evolution of molecule-based magnets, the reader is encouraged to read the review “Organic magnets, a history” by Miller[59].

The basic building blocks composing molecular crystals with magnetic ordering are either pristine organic radicals, coordination compounds or a combination of both. Each single unit must host, at least, an unpaired electron. In the case of neutral radicals, many strategies have been applied to prevent their high reactivity. Among the most relevant, it is worth to mention the steric protection and the use of
heteroatoms. The first can suppress the dimerization reaction and can dramatically change the crystal structure, while the latter, for example, exploits the lone pair electrons to control the intermolecular electronic interactions. The use of heteroatoms
also affects the spin density over the molecular skeleton[60]. While in the case of the ferrocenium ion of the coordination compound (e.g. [Fe(C₅Me₅)₂]⁺[TCNE]⁻), the unpaired electrons are highly localised in the d or f shells of the transition metal, in the case of purely organic compounds based on light elements (H, C, N, O), the unpaired electrons reside in the s and p orbitals. More recently, Oakley and co-workers have reported that making use “heavy atoms” like S or Se, is a good strategy to increase the critical temperature of magnetically-ordered systems[61]. The formation of molecule-based magnets is a consequence of the alignment of spins due to unpaired electrons with suitable interactions through π electrons[60].

As highlighted by Ratera and Veciana[60], the skeleton of stable neutral radicals plays an important role in the 1) good stabilization of the spin and 2) modulating and controlling the electronic structure which will control the intermolecular interactions responsible for the physical-chemical properties of the material.

### 1.2.1 The Molar Magnetic Susceptibility

Experimentally, the magnetic response of a material is evaluated by means of the magnetic susceptibility (χ), which measures to which extent a material is magnetized by an applied external magnetic field. The molar magnetic susceptibility[62] is equivalent to the ratio between the molar magnetization $M$, and $H$, the magnetic field applied to the material

$$\chi = \frac{M}{H}$$

(1.1)

This formulation of $\chi$ is only valid at 1) not too low temperatures and 2) very small magnetic fields. The molar susceptibility units of $\chi$ are, in CGS[63] units, [emu·mol⁻¹]. A more advantageous and easier interpretation of the susceptibility is provided when $\chi$ is multiplied by the corresponding temperature value

$$\chi T = \frac{M}{H} \cdot T$$

(1.2)

The units of $\chi T$ are [emu K mol⁻¹]. In the manuscripts reported in the thesis we made use of the second definition of the susceptibility, because it provides a more sensitive means to detect small magnetic variations associated with the structural arrangement as a function of the temperature range. If $\chi T$ is constant as the temperature decreases, it means that the Curie’s law is obeyed. On one hand, if $\chi T$ increases as the temperature decreases, it means that there are dominant ferromagnetic interactions. On the other hand, if $\chi T$ decreases as the temperature decreases, it means that there are dominant antiferromagnetic interactions.
Magnetic materials, in the most general classification, may be diamagnetic, paramagnetic or ferromagnetic. Diamagnetic materials (e.g. pyrolytic carbon), are repelled by an external magnetic field. On the contrary, paramagnetic materials (e.g. platinum), are weakly attracted by an external magnetic field., while ferromagnetic materials (e.g. cobalt, iron, neodymium,..) are strongly attracted by an external magnetic field.
1.2.2 The Dithiazolyl-Based Molecular Magnets

In recent years we have witnessed incredible developments in the study of organic molecular magnets based on the dithiazolyl (DTA) moiety (see Fig. 1.4). The attention paid to the DTA-based crystals comes from the possibility to have a wide range of structural arrangements that can be obtained while maintaining radical open-shell character, qualifying the corresponding compounds as persistent and stable. Banister[64] pioneered the research of these compounds, with an accurate analysis of the C/N/S rings[65]. Oakley[43, 44] and Chivers[46], among others, gave a remarkable contribution to the synthesis of these compounds, based on the original idea from Haddon[47]. The DTA radical family is composed of circa 40 compounds[66], presenting a spectrum of magnetic behaviors. In particular, two sets of compounds received a lot of attention in the last years. The first set contains

Figure 1.4: Examples of DTA-based compounds, where the DTA moiety (d) is added to different possible substituents (a), (b) and (c), creating the corresponding compounds (a)-TTTA, (b)-PDTA and (c)-TDPDTA.
spin-crossover (also known as spin-switch)\cite{67–70} materials (SCO). In this case, the spin state of the material changes without affecting the crystalline structure of the system. The second case, instead, contains compounds presenting bistability, where

Bistability is the ability of a material to present two stable phases that can both exist within a given range of temperatures, but above and below that range, only one or the other phase exists”

The technological advantage associated with a compound with such magneto-structural behavior would be enormous. The prototype crystal presenting this bistable property and that has been extensively investigated is the 1,3,5-trithia-2,4,6- triazapentalenyl (TTTA) (see Figure 1.5). This system presents a susceptibility curve with a wide hysteresis loop that encompasses room temperature. The LT phase has a triclinic habit, whereas the HT phase is monoclinic. The structure at equilibrium of the first polymorph presents dimers. Hence, this phase is magnetically silent. The HT polymorph, instead, has been identified as an averaged structure, since a continuous coupling/decoupling mechanism occurs between dimers within the columns along the stacking direction. In turn, it has been shown that this phase is paramagnetic. A more detailed analysis of this compound will be provided in Chapter 3. Here, it is sufficient to mention that the static and dynamical analysis of this crystal, as reported in recent papers\cite{71–74}, gave for the first time a unique chance to decipher how the transition from the low temperature polymorph to the high temperature one occurs in thermodynamical terms, and how magnetic interactions within the crystal are affected. Unfortunately, the structural variables involved in the LT$\leftrightarrow$HT phase transition still remain unknown. It is also due to the fact that simulating phase transitions is by no means an easy task.
Figure 1.5: The susceptibility curve of the TTTA materials (a) and the HT (b) and LT (c) polymorphs studied. It is possible to see the particular geometrical arrangement of the two polymorphs, where the LT phase presents eclipsed dimers while the HT phase presents a uniform stack. Both these structures have been experimentally resolved at 298K.

1.3 Thesis Goals and Outlook

The general motivation that justify the effort to study DTA-based compounds mainly concerns with the possibility of employing the DTA-based compounds to promote a new generation of more efficient devices, especially targeting the ones for memory storage. In this sense, theory plays a key role in elucidating the common and different properties between different systems, especially if they belong to the same family, in the light of the same model approach. The main goal I aim to accomplish in this work is to justify the possibility of different magnetic behaviors as a function of the kind of substituent attached to the DTA moiety and, in turn, their corresponding crystal packing. On the line of the work performed by Vela and co-workers[72–74] on the prototype TTTA material, both from a static and dynamical point of view,
the investigation of PDTA, TDPDTA and 4-NCBDTA compounds, respectively (see Fig. 1.6), will be presented. The interest on these particular structures lies on their bistable character. The PDTA and TDPDTA compounds will be analysed in details because of their rather large bistable range, as will be discussed in Chapter 3. The 4-NCBDTA instead, which is not bistable but spin-switchable, will be account for sake of comparison with respect to TTTA, PDTA and TDPDTA materials.

Different techniques and methodologies have been used to investigate this set of compounds from different points of view. The ultimate intent is to depict a more clear reason why some specific arrangements of some compounds favor a diamagnetic rather than a paramagnetic behavior, or vice versa. Moreover, a possible explanation of the driving force triggering the phase transition of these organic molecular magnets will be provided, in the light of the results achieved.

In the past, a solid computational protocol called First-Principles Bottom-Up[75, 76] (FPBU) approach has been successfully used in an extended analysis of the magnetic topology (i.e. the propagation of the magnetic interactions within the molecular crystal along the 3D axes) for a multitude of different molecular magnets. This technique is also used here with the same intent, and it will be discussed in details in Chapter 2. The derivation of the magnetic exchange interactions values have been performed at different levels of theory and methods, as will be discussed later, employing both Density Functional Theory and the (high level) wavefunction methods like Complete Active Space Self-Consistent-Field and Difference Dedicated Confi-
configuration Interaction. On top of the magnetic analysis, also geometry/variable-cell optimizations in the solid state and interaction energy calculations are performed. On one hand the optimized structures are fundamental to study the equilibrium configuration of the system and, eventually, to later extrapolate intermediate structures, sampling the evolution of the system as a function of time and temperature in Ab-Initio Molecular Dynamics calculations. On the other hand, the study of how the columns pack and how energetically they contribute to stabilize the system is a fundamental aspect for understanding the mechanisms that drive the phase transition.

The thesis is organized following the natural development of the research during the last three years, as follows:

Chapter 2: in this Chapter, an overview of the different theoretical methodologies used to investigate the systems is presented. In the first part of this chapter, the Hartree-Fock (HF) method will be briefly reported, with its limits. Then, the post-HF methods used to recover the correlation term will be shortly presented. In particular, attention will be put on the relation with the magnetic coupling[77]. In the second part, the Density Functional Theory (DFT) method will be presented, with particular emphasis on the DFT method applied to periodic systems, used to simulate the crystalline phases of the systems mentioned above. In the third part, a brief overview of the theory behind the AIMD method will be reported. Finally, will be presented a detailed description of the First-Principles Bottom-Up (FPBU) methodology. The Hartree-Fock and Post-Hartree-Fock theory provided here can be explored in deep in the reference manual "Modern Quantum Chemistry"[78], while for DFT theory is referenced to "Electronic Structure: Basic Theory and Practical Methods"[79];

Chapter 3: in this Chapter, a detailed description of the DTA-based compounds investigated is reported. The crystalline structures as well as the chemical properties of each single compound will be presented, underlining the similarities and differences with respect to the prototype TTTA material;

Chapter 4: in this Chapter, a systematic computational study of the intermolecular interactions characterising the LT and HT polymorphs of the prototype TTTA material is provided, elucidating the origin of the energy difference between them and rationalising the crystal packing of the two phases, respectively.
Chapter 5: in this Chapter, the different magnetic responses of the different phases of the PDTA and TDPTDA materials have been rationalised employing the FPBU approach. The detailed analysis shows that, while the PDTA material resembles the TTTA prototype compound, the TDPDTA instead deviates, showing both in the LT and HT phases a weaker magnetic coupling. The source of this difference is found in the inter-column interactions (see Appendix A.3). Thanks to the FPBU method, it was possible to unveil this hidden effect. This unusual behaviour of the TD-PDTA compound is also investigated by studying the magnetic interactions as a function of the structural arrangements for each DTA-based material. To validate the FM trend predicted by DFT, supplementary in silico experiments are performed by means of the wave function Difference Dedicated Configuration Interaction method. To conclude, the interaction energy maps (IEMs) are provided, giving a quantitative estimation of the energetic cost necessary for each compound to be in a FM arrangement.

Chapter 6: in this Chapter, a new spin transition mechanism, found to operate in the TDPDTA material, is proposed for the first time, by directly comparing the results from the AIMD simulations for a set of structures sampled at different temperatures, both for the PDTA and TDPDTA systems. The comparison of the two systems is mainly focused on the respective HT phases, the most interesting ones for technological purposes. The data from the respective variable-cell (VC) optimisations as well as the analysis of the trajectories from the AIMD simulations and their post-processing elaboration are reported, complemented with several in silico experiments to prove the phases stability with respect to some metastable structures and the key role that some geometrical variables play in the new stabilization process featuring the TDPDTA material. The TTTA and 4-NCBDTA dynamical results have already been reported[73, 80].

Chapter 7: in this Chapter, some final remarks and suggestions for further research are reported as well as a discussion of the implications that the discovery reported in Chapter 6 might have in the quest for controlling the properties of the DTA-based materials for technological purposes.
Bibliography


[63] Quantum Mechanics, by Littlejohn, R. 
http://bohr.physics.berkeley.edu/classes/221/1718/221.html.


[66] The Cambridge Crystallographic Data Centre (CCDC), https://www.ccdc.cam.ac.uk/structures/?.


