The Second Quantum Revolution: Role and Challenges of Molecular Chemistry

The Second Quantum Revolution: Role and Challenges of Molecular Chemistry

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ABSTRACT: Implementation of modern Quantum Technologies might benefit from the remarkable quantum properties shown by molecular spin systems. In this perspective we highlight the role that molecular chemistry can have in the current second quantum revolution, *i.e.* the use of quantum physics principles to create new quantum technologies, in this specific case by means of molecular components. Herein, we briefly review the current status of the field by identifying the key advances recently made by the molecular chemistry community, such as for example the design of molecular spin qubits with long spin coherence and the realization of multiqubit architectures for quantum gates implementation. With a critical eye to the current state-of-the-art, we also highlight the main challenges needed for the further advancement of the field toward quantum technologies development.

Introduction

Quantum Technologies (QT) exploit the quantum properties of matter such as superposition, tunneling, and entanglement to develop new functional tools and devices.[1–3] These are based on components that obey quantum physics laws discovered during *the first quantum revolution*. The latter refers to the development of concepts - such as the wave-particle duality - which have allowed us to better understand the principles behind fundamental technologically relevant phenomena not explained by classical mechanics.[1] These range from the understanding of the chemical reactions that govern chemistry to the photoelectric effect at the basis of semiconductor physics.

The first quantum revolution has now evolved to a higher level of complexity. Currently, we are in the middle of *the second quantum revolution*, where the quantum physics laws are not only simply understood. Thanks to our ability to control matter at the nanoscale, where quantum properties, such as quantum coherence, are efficiently preserved, we can develop novel technologies, such as quantum information, quantum sensing, quantum optics, quantum cryptography, *etc.*[1] This evolution is driven by the continuous need of device miniaturization and the great promise that quantum mechanical principles offer with respect to the classical ones.[2,3] For example, quantum computation,[4] the novel computational paradigm based on the quantum bit, or qubit, is expected to speed up current computational performances, but more importantly, it is expected to solve problems that are unsolvable with the current classical paradigm.[2]

The core of this approach is the qubit. A qubit has the property to be placed in a coherent superposition state, $\psi = \alpha|0\rangle + \beta\,|1\rangle$, other than the two 0 and 1 states of the computational basis as in a classical bit (Figure 1), thus accessing multiple states.[2]

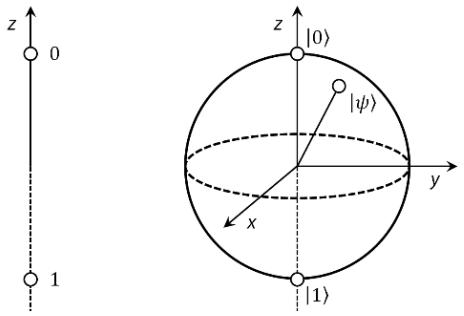

Figure 1. Schematic representation of two states available for a classical bit 0 and 1 (left) and those available for a quantum bit $|\psi\rangle$ (right). All points on the surface of the Bloch sphere represents superposition states for the qubit.

Qubits can be used to build quantum computers,[5] and their construction is recognized as one of the fundamental steps for QT.[6] Realization of quantum computers requires the ability to perform single qubits manipulations, but this is not the sole requirement. As in any logic process both control and target elements must be present. A qubit must therefore "feel" and "react" to other qubits, and in particular to their coherent superposition state. This is possible if

two qubits are "entangled", *i.e.* the total state is not simply the product of the individual qubit states.[2,6,7]

In 2000, D. P. DiVincenzo has formalized for the first time five requirements for a qubit to be viable for the realization of quantum computers.[8] A qubit should be or have: *i)* a long coherence time, which is the lifetime of the superposition state, *ii)* initialized in a specific initial state, *iii)* well-defined and scalable, *iv)* individually measurable, *v)* able to devise universal quantum gates. These stringent and somehow antithetic criteria should be simultaneously satisfied, making the quest for viable qubits a real challenge for chemistry, physics and materials science.[9]

Several physical realizations of qubits are currently investigated, for example polarized photons,[10] ionic traps,[11] superconducting circuits,[12] quantum dots,[13] and spins, both nuclear[14,15] and electronic.[16] Among them, the superconducting circuits technology is so far the most advanced one,[5] leading to some archetype quantum computers, although with a limited number of operating qubits. However, extension to a larger number of qubits, which is needed not only to perform complex algorithms but also to mitigate the errors induced by the finite lifetime of the coherence, is still an open issue.[17]

The use of electronic and nuclear spin has attracted considerable interest. The spin is intrinsically a two-level quantum system which can easily be manipulated by electromagnetic radiations,[18] as magnetic resonance techniques have been showing us for almost 80 years. Spin impurities in inorganic semiconductors have been proposed 20 years ago by Kane as a potential platform for quantum computing.[19] Exceptionally long coherence times are encountered when paramagnetic defects are created in solid-state materials such as phosphorous defects in silicon[20] or silicon carbide (Figure 2a).[21] Another appealing spin based platform is constituted by nitrogen-vacancy (NV) centers in diamond, which are also characterized by long coherence times (Figure 2b).[22–24] However, in these systems the realization of operating quantum gates appears difficult by the scarce control over qubit-qubit distance - and thus qubit-qubit coupling - during defect implantations. Still, the rational control of the properties of these paramagnetic sites remains challenging due to the lack of chemical tunability.

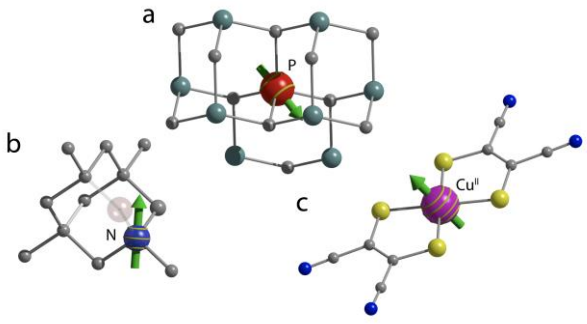

Figure 2. Spin qubit physical realizations: phosphorous defect in silicon carbide (a), nitrogen and vacancy center in diamond (b), a paramagnetic metal complex with long spin coherence (c).

An alternative approach consists in exploiting electronic or nuclear spins of magnetic molecules prepared through molecular chemistry approaches (Figure 2c).[25] In this case the spin degree of freedom can be intrinsically associated to the nuclear spin of certain atoms or associated to the electronic spin of a metal ion in a precise oxidation state, a transition metal or a lanthanide in a molecular complex.[26–28] Equally relevant are organic radicals stabilized either by electron delocalization or by steric hindrance.[29]

In this context, nuclear spins have the advantage to be easily manipulated with Nuclear Magnetic Resonance (NMR) techniques[30] and to show long coherence times. Compared to electrons, they are more protected against environmental perturbations that induce a collapse of the superposition state, a phenomenon called decoherence (*vide infra*). However, nuclear spins are scarcely tunable and a switchable interaction between them is not easily accomplished within a molecular structure. Electronic spins are instead well-suited to behave as qubits because they can be more rapidly manipulated with Electron Paramagnetic Resonance (EPR) techniques, thanks to the larger Zeeman splitting.

The quantum properties of magnetic molecules are expected to be relevant for the development of spin-based QT. Molecular chemistry has already demonstrated to be a rich playground for the preparation of tailor-made molecules that can serve for the realization of potential components of a quantum computer. While molecules with low spin values are currently investigated in quantum computation as "fast and switchable" dynamic computational units, molecules with a large spin and magnetic anisotropy showing magnetic bistability at the single molecule level (single-molecule magnets, SMMs) have been proposed since 1990s as ideal media for "long-term" information storage.[31] Notably, in these systems quantum effects are accessible and controllable with available experimental techniques.[32]

The research methodology to increase the performance of SMM, developed and applied during almost three decades of research, has been based on the optimization of the spin Hamiltonian parameters by chemical design. By following this approach, recent significant improvements have been reached, such as the observation of magnetic bistability up to 80 K in a SMM formulated as $[(\eta\text{-}Cp^{iPr5})Dy(\eta\text{-}Cp^*)][B(C_6F_5)_4]$ (Cp^{iPr5} = penta-*iso*-propylcyclopentadienyl, Cp* = pentamethylcyclopentadienyl).[33] The blocking temperature is above the temperature at which nitrogen liquifies (77 K) and ca. 40 times higher than the archetypal SMM, Mn_{12} acetate.[31]

A similar chemical approach is expected to be of crucial importance for molecular spin qubits (MSQs) as well. Indeed, increasing the operable temperature range of these molecular spin components is fundamental for wide spread applications because it will avoid the use of specific refrigerators, with significant improvements in terms of device-dimensions and operational costs.[3] Still, extending operative temperatures up to room temperature will open a much broader range of applications.

The interest in molecules for QT is rapidly expanding and several perspective or review articles have been published recently focusing on molecules (S. Sproules),[29] transition metal complexes (D. Freedman *et al.*),[34] or lanthanides (A. Gaita-Ariño *et al.*)[35] as spin qubits.

This perspective focuses mainly on coordination compounds, although stable organic radicals can show superior coherence properties and biradical molecules have been extensively employed. Indeed, proposals for adiabatic quantum computation[36] have been formulated[37] and quantum gating demonstrated for biradicals.[38] The motivation of our choice is the higher tunability of single center spin Hamiltonian parameters, in particular the spin manifold, the anisotropy of the g tensor and of the hyperfine coupling, as well as quadrupolar interaction for lanthanide ions. The organization of molecular spin centers in bi- and three-dimensional architectures, e.g. in metal-organic frameworks, and the possibility to evaporate magnetic molecules on clean surfaces are also very appealing. The relevance of these features will become clear in the following when we will address the challenges that, from the authors point-of-view, have to be pursued by the molecular science community in order to promote molecular spins as an alternative platform for QT. The combination of different expertise, from synthetic chemistry to theoretical modeling, passing from experimental molecular physics to nanoscience, is mandatory. In order to address all crucial points raised by DiVincenzo, we dedicate a section to each of them. With a critical eye to what has been already done and what is important to disclose in the near future, we aim at pushing forward the role of molecular chemistry in QT development.

Long coherence times

A long coherence time, that is, a long life-time of the quantum superposition state, is a fundamental requisite for a system to behave as a qubit. This requirement represents only a first step toward qubits practical implementation. However, it can be considered the *sine qua non* condition for a system to behave as a qubit candidate. Pulsed EPR spectroscopy techniques allow for an easy access to qubits' relaxation times and control of the superposition state through nutation experiments and detection of Rabi oscillations.[18] Indeed, two parameters are used to evaluate qubits performances, the spin-lattice relaxation time T_1, which represents the time required for an excited spin to relax back to its ground state, and the phase memory time or coherence time T_m, which is a measure of the lifetime of the superposition state before the loss of quantum information. T_m is obtained by incrementally increasing τ, the time difference between $\pi/2$- and π-pulses, in Hahn echo sequences and measuring the decay of the integrated echo.[39] It differs from the characteristic time of pure spin-spin relaxation, T_2, as T_m comprises all mechanisms of decoherence eventually involved, such as nuclear spin diffusion.[40]

Decoherence is principally induced by electron-electron and electron-nuclear spin-spin interactions. The former depends linearly on the paramagnetic species concentration, in agreement dependence of the dipolar field with the distance (d) as d^{-3}. A random paramagnetic dilution in diamagnetic matrices lead to a distribution of relaxation times, which is often modeled with a stretched exponential decay. Simulations of the spin echo time dependence by quantum unitary dynamics on an ensemble of hundreds of spins have shown to be able to satisfactorily reproduce the stretched exponential parameter.[41]

For low concentrations of paramagnetic species, interactions with the nuclear spin bath dominate. The strength of the interaction depends on the nuclear magnetic moment and the hyperfine interaction, the latter having a through-bond and through-space contribution. The use of atomic species without or with reduced nuclear magnetic moment is a straightforward strategy to increase the lifetime of the coherent state, while the distance between the electronic spin and the magnetic nuclei provides more subtle effects. The dynamics of the nuclear spin bath is, in fact, generally dominated by nuclear spin diffusion involving flip-flop transitions.[40] It should be however noted that the nuclei close to the electronic paramagnetic center experience a different resonance frequency and do not participate to the spin flip-flop transitions leading to spin diffusion. This creates a "black sphere" or a "diffusion barrier" with a characteristic radius of the order of ca. 6 Å.[40,42–44] Nuclear spin inside the sphere are therefore less efficient in promoting decoherence.

A simple relation allows to easily quantify if experimentally observed coherence times are viable to perform quantum logic operations: $\Omega_R T_m > 10^4$–10^5 where $\Omega_R \propto g\mu_B B_1/\hbar$ is the Rabi frequency, *i.e.* the reciprocal of the time required to perform an individual quantum operation, and B_1 the magnetic field of the microwave radiation. As Ω_R is of the order of tens of MHz, then $T_m > 100$ μs is required to satisfy the previous relation.

For the reasons mentioned above, is not common to observe-coherence time of the order of hundreds of microseconds for transition metal ion or lanthanide complexes. Current research in this direction is taking advantage of decades of investigations by pulsed EPR experiments on diluted paramagnetic systems performed for other purposes.[45,46] For instance, in order to use paramagnetic labels for the elucidation of structure in biological systems, optimization of coherence times is necessary. A wide literature is available on this topic, showing that organic radicals and simple complexes of light transition metal ions exhibit coherence times of interest for quantum computation.[29,40]

The observation of moderately long coherence times in polynuclear metal complexes, in particular heterometallic antiferromagnetic rings with $S = ½$ ground spin state, has prompted in depth studies to improve quantum coherence times. Moreover, the organization of these units in supramolecular assemblies that can be operated as quantum gates has been investigated. T_m as high as ca. 15 μs, were observed for deuterated carboxylate ligands and dilution in deuterated solvents.[47]

Having in mind the previously mentioned goal of 100 μs for T_m, it is evident that a more efficient optimization can be achieved on simpler paramagnetic units. In 2015, J. M.

Zadrozny, D. E. Freedman and coworkers have reported on a vanadium(IV)-based complex with a nuclear spin-free dithiolene ligand formulated as $C_8S_8^{2-}$.[27] This tris-chelated complex of formula $[V(C_8S_8)_3]^{2-}$ (Figure 3), when diluted in the nuclear spin-free solvent CS_2, has shown at cryogenic temperatures an increase of the T_m by ca. 2 orders of magnitude with respect to the same complex measured in the nuclear spin-active solvent d_8-DMF/d_8-toluene.[27] A record T_m, of the order of the millisecond (ca. 0.7 ms), has thus been obtained.

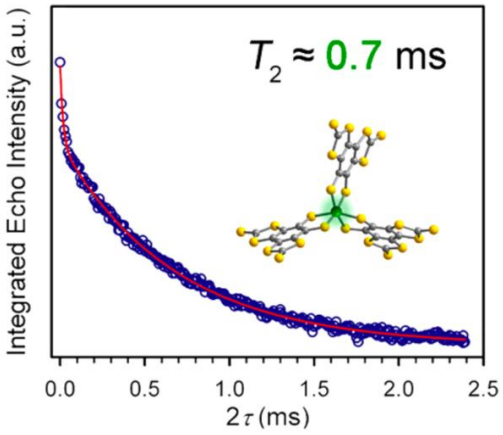

Figure 3. Molecular structure (inset) and pulsed EPR echo decay trace for $[P(Ph)_4]_2[V(C_8S_8)_3]$ in CS_2 at T = 10 K. Adapted with permission form ref. [27]. Copyright 2015 American Chemical Society.

This result clearly shows that molecular spin systems are intrinsically competitive with respect to solid-state defects in inorganic materials if most of the decoherence sources are removed from the environment.[9] Thus, a strategy that relies on the complete removal of nuclear spins from ligands and counterions, as in paramagnetic defects in diamond, silicon or silicon carbide, where the use of nuclear spin free ^{28}Si and ^{12}C isotopes reduces decoherence significantly, seems a winning strategy. However, it cannot be easily translated in the organic chemistry world where nuclear spin-active atoms such as ^{14}N, ^{31}P and especially ^{1}H are ubiquitous.

It should be also noted that a value of T_m of ca. 1 ms has been achieved by working in frozen solutions, which is far from the solid-state framework that would enable operating devices. In this context a step toward the observation of such a long coherence time in a crystalline solid-state material will be highly beneficial to prove that MSQs can show comparable properties with respect to the classical inorganic counterparts. In such a case, both the solid-state and the long coherence times requirements will be satisfied, with the additional advantage of a potential tunability of the magnetic/electronic properties at the synthetic level.

In order to address this issue, K. Bader, J. Van Slageren and coworkers investigated the coherence times of a Cu^{II} complex with a dithiolene ligand $[P(Ph)_4]_2[Cu(mnt)_2]$ (mnt = maleonitriledithiolate) diluted in the Ni^{II} diamagnetic analogue, that has shown preservation of coherence up to room temperature.[26] Then, our group has applied the same principle to study the coherence times and the spin dynamics of an S = ½ spin system based on V(IV), VOPc, diluted in the diamagnetic analogue TiOPc, that has shown a coherence times of ca. 1 μs at room temperature.[28] Importantly, this coherence time has been reveled sufficiently long to control the superposition state through nutation experiments with first observation of Rabi oscillations at ambient conditions for a MSQ also in a relatively high concentration of paramagnetic species (10 %).[28]

Considering that the spin will be ultimately exposed to the external environment, an encapsulation strategy can be highly beneficial as a protection tool from decoherence sources. This approach has been extensively employed in group-V elements endohedral fullerenes, mainly ^{14}N@C_{60} and ^{31}P@C_{60}, with T_m of the electronic spin S = 3/2 of the orders of few ms at liquid helium temperatures,[48] and of 250 μs at 170 K. Also these record values have been observed by dilution in the almost nuclear-spin free solvent CS_2.[49] Similarly, S = 1/2 metallofullerenes of formula M@C_{82}, with M = Sc, Y, and La, have shown T_m around 200 μs in the same temperature range.[50] The combination of the long coherence time of the nuclear spins with the fast manipulation of the electronic spins has been also exploited for these systems.[51]

The rich and versatile - although low yield - chemistry of endohedral fullerenes has allowed to insert a variety of spins inside fullerene cages. For instance, $Dy_2ScN@C_{80}$ behaves as a SMM with a very high anisotropy energy barrier,[52] while $Er_3N@C_{80}$ shows an interesting spin dependent luminescence at low temperature.[53] The cage can be engineered to stabilize an electron originated by the addition of a benzyl group or by a N defect on a C_{80} molecule. This electron couples ferromagnetically to the lanthanide spins (Figure 4).

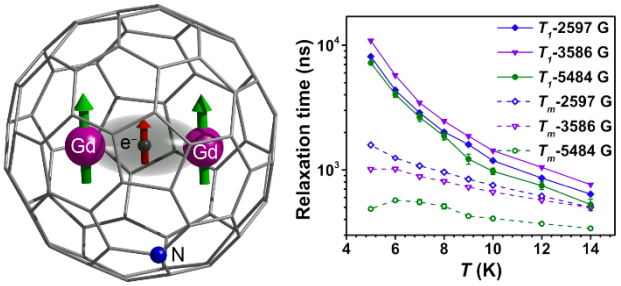

Figure 4. Molecular structure of a $C_{79}N$ fullerene entrapping two Gd^{III} ions bridged by an unpaired electron able to transmit a strong ferromagnetic interaction as reported in ref. [54] (left), and temperature dependence of T_1 (open symbols) and T_m (solid symbols) extracted from pulsed-EPR spectra recorded in toluene frozen solution (right). Assignment of the investigated transitions inside the S = 15/2 total spin manifold can be found in the original work. Right panel adapted with permission from ref. [54]. Copyright 2017 American Chemical Society.

While $[Dy_2]$-@C_{80}-benzyl is a SMM with a blocking temperature of 18 K, the $[Gd_2]$-@$C_{79}N$ shows a record ferromagnetic interaction (J ~ 350 cm^{-1} in the JS_aS_b formalism) stabilizing the S = 15/2 total spin state.[55] Remarkable coherence times (ca. 1.6 μs at 5 K) have been observed for such a large

spin multiplicity based on lanthanide ions, thanks to the protection from decoherence sources in an almost nuclear spin free environment.[54] However, this coherence time is not sufficiently long to reach the 100 μs limit previously indicated. Considering that the investigated lanthanide-based qubit has, although low, a magnetic anisotropy that favors a rapid decoherence due to the fast spin-lattice relaxation as the temperature increase from 5 to 14 K, we can envisage very interesting outcomes if this strategy will be extended to endohedral fullerenes containing transition metal ions with low spin-orbit coupling, such as titanium or vanadium.[56] Ti(III) containing species have been reported but not magnetically investigated,[57] while some EPR data are available for $V_xSc_{3-x}@C_{80}$ but the dynamic properties are still unexplored.[58]

Although in the field of quantum computation all physical realizations of qubits are operated at low temperature, for other applications such as quantum sensing, a long spin coherence at high temperature, possibly room-temperature, is required to make them practical. In such high temperature regime, the spin coherence time is limited by the spin-lattice relaxation time. Thus, a control of T_1 is of paramount importance to preserve long coherence times as the temperature increases.

In the last few years, several studies aimed at understanding the relation between molecular structural features and spin-lattice relaxation behavior have been reported.[59–61] Among them, one remarkable result is the significant difference in the temperature dependence of the spin-lattice relaxation observed for two vanadium(IV) complexes of the same ligand and counterion, featuring a different coordination geometry.[59] This study has highlighted the key role of the square pyramidal coordination environment of the vanadyl moiety, in comparison to the more flexible distorted octahedral geometry of the non-oxido vanadium(IV), in preserving a long spin-lattice relaxation, and consequently a long spin coherence up to room-temperature (Figure 5).[59]

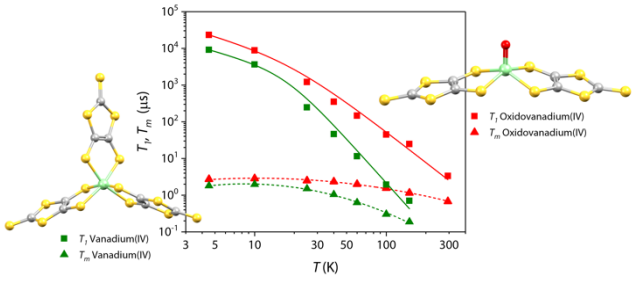

Figure 5. Temperature dependence of spin-lattice (T_1) and coherence (T_m) times of the two oxidovanadium(IV) and vanadium(IV) complexes (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) investigated to understand the role of the molecular coordination geometry on spin-lattice relaxation (ref. [59]). Adapted with permission from ref. [59]. Copyright 2016 American Chemical Society.

Recent theoretical studies have corroborated the hypothesis that this is related to the differences in the internal vibrational modes for the two molecules, especially those involving the first coordination sphere of the metal ion carrying the spin. Indeed, the more abrupt temperature dependence of T_1 for the octahedral coordination is clearly associated to a more efficient spin-phonon coupling mechanism of the low energy (< 400 cm^{-1}) vibrations in the octahedral surrounding.[62]

A recent report has also highlighted that promising results towards an increase of the operable temperature range of MSQs can be achieved by exploiting the highly isotropic hyperfine coupling and minimal *g*-anisotropy of certain lanthanide metal ion in peculiar oxidation states. Indeed, it has been shown that the family of divalent rare-earth molecules formulated as [K(2.2.2-cryptand)][Ln(Cp')$_3$] (Ln = Y, Lu, La; Cp' = $C_5H_4SiMe_3$) has a negligible magnetic anisotropy and an electronic s-like ground spin state that allows to observe coherence times of 0.4 μs at room temperature for the Y derivative doped (ca. 2%) in the isostructural diamagnetic analogue of Yb.[63]

A practical implementation of highly coherent molecular spin qubits also requires a precise organization of electronic qubit molecular components into extended framework. Realization of spatial control over qubit–qubit distances can be in principle achieved by coordination chemistry approaches as it will be highlighted in the scalability section. However, translating single qubit molecular building units into extended arrays might not guarantee retention of long spin–lattice relaxation times and long spin coherence up to room temperature because of the modifications over qubit–qubit reciprocal distances and molecular crystal lattice phonon structure. Recently, studies have been reported on the preparation on an extended bi-dimensional (2D) array of Cu^{II}-based spin qubits[64] and on the preparation of three-dimensional (3D) metal–organic frameworks based on vanadyl units,[65] or Cu^{II},[66] all employing tetracarboxylphenylporphyrinate as ligand. They have demonstrated that the long spin coherence of the representative molecular building blocks is preserved at high temperatures also in these extended molecular structures.[64,65]

Magnetic dilution in diamagnetic analogues introduces a random distribution of paramagnetic sites in the material. From this point-of-view, the results of this approach are not far from that used to introduce NV centers into diamond or phosphorous in silicon. However, MOF engineering allows to exploit sufficiently long linkers to induce a separation between spin qubits in concentrated highly ordered molecular structures. First results in this direction have been reported by Freedman and coworkers, with coherence times detected in a concentrated MOF based on Cu^{II}-phtahlocyanine moieties.[66]

Initialization

To perform a reliable quantum logic operation, it is necessary that all operable qubits involved in the sequence of quantum gates assume a well-defined and known initial state. This process is called initialization and can be achieved in different ways.[2] For example, for spin qubits one can rely on thermal initialization. This method consists in cooling the material down to the lowest achievable temperature in the presence of a sufficiently strong

magnetic field to induce a spin polarization toward a well-defined spin sublevel of the electronic ground spin state. This method can be considered adequate for electronic spins because the Zeeman energy is usually sufficiently high to separate the spin sublevels.[67] However, when nuclear spin states are used to encode qubits this method is not efficient because the small Zeeman splitting of nuclear energy levels does not induce a selective population at the lowest experimentally achievable temperatures in most cases.[67–69] This poses substantial limitations to practical experiments of quantum computing with NMR based schemes.[67]

When dealing with hybrid nuclear/electronic approaches the initialization of the hyperfine sublevels can be accomplished by using the dynamic nuclear polarization (DNP) technique, which is largely employed to enhance NMR signals.[70–72] In the case of spin qubits, the flip-flop transition, *e.g.* a simultaneous change of both m_S and m_I, involves the electronic and nuclear spin of the same atom, while in DNP the electronic spin is that of an external paramagnetic agent.

A particularly efficient initialization process relying on DNP but taking advantage also of optical transitions is that employed in NV centers in diamonds.[69] It consists in using laser pulses to selectively populate one state of the $|m_S = 0, m_I>$ manifold of the ground $S = 1$ state thanks to the inter-system crossing (ISC) from the excited triplet to the excited singlet state (Figure 6). Because the fluorescent emission is faster than electronic spin flipping (T_1), a condition not common for paramagnetic metal ions, the $m_S = 0$ state of the ground triplet state can be selectively populated even at room temperature thanks to the high efficiency of the ISC transitions (thick blue lines in Figure 6 by), in contrast to the poorly efficient transitions (thin lines).

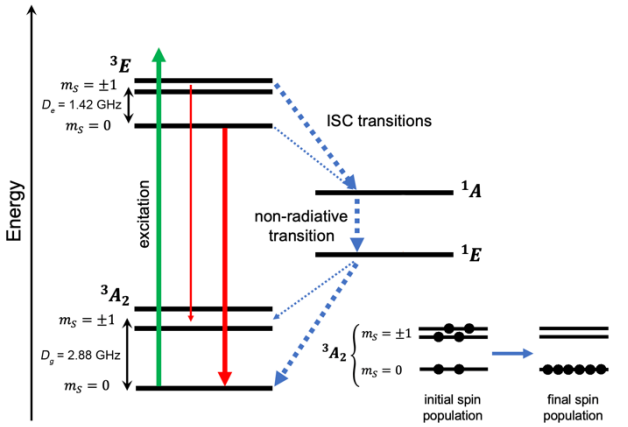

Figure 6. Simplified energy level scheme of a NV defect in diamond in the absence of strain and in zero static field. The energy separations are not in scale, and the ZFS of the ground and excited triplets are given in GHz. The system is optically excited with green light (green arrow) and emits red fluorescence (red arrows) whose intensity is affected by the very different efficiency of ISC transitions involving different m_S components (thick and thin blue arrows).

The same phenomenon gives to NV centers in diamonds also the advantage of an optical readout of the spin state. The intensity of the red fluorescence corresponding to the excited triplet → ground triplet transition is maximum for the $m_S = 0$ ground state because it is not quenched by the ISC transitions. This allows for local, and single spin detection. [73]

More subtle is the procedure to selectively populate one hyperfine level, *i.e.* to achieve nuclear spin initialization. Here a series of microwave (mw) and radiofrequency (rf) pulses is used. It must be noted that a very high efficiency is obtained when working in static fields that are close to the avoided level crossings of the m_S components of the $S = 1$ manifold of the electronic excited state, *ca.* 500 G. In this condition m_S is no more a good quantum number and flip-flop transitions are highly probable.[74] In this process, the ground electronic state $|m_s = 0, m_I>$ of Figure 6 is optically excited to the $|m_s = 0, m_I>^*$ excited state at a field where an avoided level crossing between $|m_s = 0, m_I>^*$ and $|m_s = -1, m_{I+1}>^*$ occurs due to non-diagonal hyperfine terms. The nuclear spin projection is therefore not conserved, unless it has reached its maximum value. If the lifetime of the excited electronic state is longer than the time required for this transition, the efficiency of electronic spin initialization can be transferred to the nuclear spin. All these features make NV centers a unique platform for spin-based QT because both optical initialization and long coherence times criteria are simultaneously satisfied.

For MSQs candidates, to observe such combination of features is rather difficult, although not impossible. Indeed, first efforts in the direction of achieving an optical initialization and addressing for molecular candidates has been recently paved by Fataftah and Freedman.[75] Their proposal consists in miming the electronic principles observed in NV centers in diamond, *i.e.* taking advantage of the electronic spin sublevels of $S = 1$ ground spin state systems for an optical initialization process consisting in a selective ISC, a phenomenon rather unexplored for molecular compounds.[75] Furthermore, radiative emission properties (either fluorescence of phosphoresce) are also requested to provide a way for optical read-out.[34]

It should not be forgotten that such properties need to be also accompanied by a long coherence time of the electronic $S = 1$ spin sublevels. Such combination of features has not been achieved yet for MSQs candidates, thus indicating that considerable efforts in this direction are still needed to verify if optical initialization and addressing of electronic molecule-based spins can be implemented.

Quantum Gates

Quantum computation requires the implementation of a universal set of quantum gates.[7] Quantum algorithms typically consist in a sequence of one and two-qubits gates that are able to solve a broad class of computational problems through a common computational scheme.[2,4,7] For spin qubits, a one-qubit operation is for example the inversion of the phase of the qubit, *i.e.* the bit-flip gate, corresponding to the NOT operation in the classical representation. A two-qubit gate is for example the controlled-NOT gate, where the state of a target qubit is modified as a function of the state of a control qubit. Another two-qubit gate

is the SWAP gate, where the state of two qubits is exchanged, for example, from |01⟩ to |10⟩.

Clearly, to perform complex quantum computation, the challenge is to be able to devise diverse sequence of gates within the same platform by accessing a sufficient number of operable qubits as target inputs and controls.

Molecular chemistry can be a powerful tool to implement quantum logic gates by means of well-developed synthetic strategies aimed at the preparation of polynuclear homo and heterometallic molecular architectures, also exploiting the principles of molecular self-assembling.[25,76–78] In such structures, qubits can be encoded on metal ions of different nature, and for each of them a fine-tuned environment can be created by playing with the nature of the surrounding ligands and resulting coordination geometries.[79]

Molecule-based proposals for the implementation of two- or three-qubit gates have been presented in recent years. Different approaches have been reported. They range from supramolecular assemblies of antiferromagnetically coupled heterometallic rings with S = ½ ground spin states,[76,77] to ligand design to obtain dinuclear lanthanides[80] or oxidovanadium(IV)[81] moieties weakly interacting within a discrete molecular architecture. Yet, purely organic molecules containing stable radicals[38] as well as photogenerated radical pairs,[82] have been proposed as quantum gates.

A feature common to all previously cited examples is the way to entangle two spins. The simplest and most investigated approach consists in positioning two spin centers at a fixed distance and exploit magnetic interactions (superexchange or dipolar) to allow them to communicate. The optimal strength of the interaction depends on the gate implementation scheme. In general, the interaction must be not too strong to allow single spin control, but comparable or larger than the difference in the interaction (hyperfine or Zeeman) of the individual qubits. Both design and operation of weakly interacting qubits benefit of the research performed on the development of double electron-electron resonance for the determination of the distance between spin labels of relevance in structural biology.[45,46]

In the simplest schemes interactions are permanent,[80] but a fixed interaction is not a satisfactory condition for the systems to implement sequences of gates or to be used as quantum simulators. It is extremely important to introduce a switchable interaction between qubits to allow for practical gate operations and avoid unwanted many-body spontaneous evolutions - typical of permanent couplings - that require additional correction schemes.[81]

The first remarkable efforts to control the magnetic interaction between MSQs candidates have been performed by R. E. P. Winpenny and collaborators.[76,78] They have pursued the challenge of controlling the interaction between heterometallic paramagnetic rings as potential qubits by adjusting the length and the nature of the spacers. In general, it is necessary to have two distinguishable connected qubits in order to be separately manipulated by electromagnetic radiation thanks to different resonance conditions. This can be achieved by selecting different paramagnetic centers or by taking advantage of the different spatial orientation if magnetic anisotropy is present. This is for instance the case of the molecular system reported in Figure 7, where the two connected rings are differently oriented.[77] In other similar derivatives the two qubits are connected by a redox-active spacer that acts as a switchable auxiliary qubit that can turn on and off the effective interaction between target-qubits through an external manipulation. This consists in a redox-active high spin Co^{II} ion octahedrally coordinated by two ditopic ligands that link together two Cr_7Ni rings. The central Co^{II} ion can undergo chemical oxidation towards a Co^{III} diamagnetic ion, switching off the magnetic interaction. Remarkably, the redox-active control is reversible.[77]

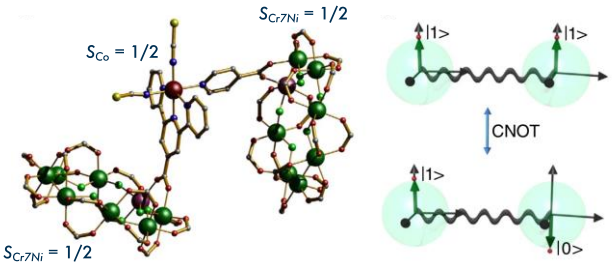

Figure 7. Molecular structure of the supramolecular architecture exploited as quantum gates and schematic representation of the C-NOT operation involving target qubits. Adapted with permission from ref. [77].

Although this example represents an elegant realization of a switchable magnetic interaction between MSQs, the realization of viable gates appears difficult. Cr_7Ni rings have a S = ½ ground state that is selectively populated only at low temperatures (< 10 K) due to the intrinsic polynuclear nature of these molecular architectures. Thus, coherent spin manipulations can be performed only at cryogenic temperatures. On the other hand, if redox control of the $Co^{II/III}$ switch has to be achieved by chemical means, high temperatures and a fluid medium seem necessary.

A switchable interaction between two target-qubits might be alternatively achieved by exploiting the properties of a complex that undergoes spin-crossover transition or redox isomerism[83,84] upon application of an external stimulus (temperature, light, magnetic or electric fields) or by the insertion of a photoactive spacer.[85] Although to date these methods have not been deeply examined, an efficient and fast enough switching of the interaction between qubits is needed to be exploited in real applications.

Under this respect, photo-generation of spin triplets states from radical ligands[86] or radical pairs from diamagnetic ligands[87] can be regarded as one of the few viable ways to achieve fast exchange switching between qubits. Such a phenomenon shows a dynamics with a timescale of the order of the μs, thus comparable to coherence times of state-of-the-art MSQs.

An alternative strategy to introduce a fast and switchable interaction between qubits consists in the implementation

of a hybrid nuclear/electronic approach. Examples of this approach can be found in pnictide endohedral fullerenes.[88] Our group and collaborators have recently reported on two weakly interacting vanadyl qubits that are linked together through ditopic bis-catecholate ligands in a discrete molecular architecture.[81] In this system, two qubits are encoded on two of the vanadium nuclear spin states and the entanglement between them is mediated by the weak dipolar coupling between the two electronic spins of vanadium IV (Figure 8). Here, rf pulses can be used to induce single-qubit operation on the target qubits, such as the change of their state from $|0\rangle$ to $|1\rangle$, while fast electronic spin excitation through mw pulses can be used to switch the effective interaction between them and to perform a controlled-Z gate operation where a selective phase switch of both target qubits in the $|0\rangle$ state is changed from $-|00\rangle$ to $|00\rangle$ (Figure 8).[81]

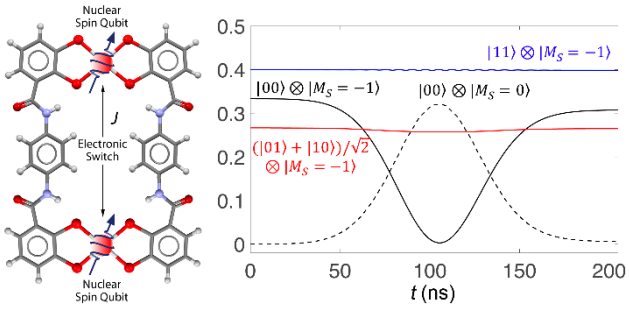

Figure 8. Molecular structure of the dinuclear vanadyl architecture based on ditopic bis-catecholate ligands and temporal evolution of the electronic states' composition upon mw pulses excitation. Adapted with permission from ref. [81]. Copyright 2018, Royal Society of Chemistry.

The experimentally determined spin Hamiltonian parameters of the system, which shows remarkably long electronic coherence times, have been used to simulate the system dynamics under a specific sequence of pulses, demonstrating its potential use as a quantum simulator.[81]

This approach, as the others reported above, has some drawbacks that need to be highlighted to push forward molecular platforms for QT applications. In the latter system, metal ion sites are undistinguishable due to the molecular symmetry. This is not an issue for its use as a quantum simulator when symmetric quantum mechanical problems are considered, such as the simulation of the quantum tunneling dynamics for an S = 1 spin system. However, having two distinguishable and selectively addressable qubits will be beneficial to extend the simulation potentials of the platform. Moreover, qubits encoded on nuclear spin states, although associated to long coherence times, are more difficult to initialize than electronic qubits. Finally, the experimental set-up necessary to implement such a computational scheme requires both rf and mw excitations but differs from an ENDOR spectrometer in the detection mode, here based on the nuclear spins.

To overcome these difficulties, we can try to get inspired from strategies under development for other physical platforms, such as donor spin qubits in silicon. A very appealing one is the use of electric fields to polarize the electron density around the donor atoms. This induces an electric dipole on the qubit and modifies the hyperfine interaction with the nuclear spin of the phosphorous atom, thus inducing flip-flop transitions.[89]

Electric fields are becoming an important tool in molecular magnetism, mainly because they are much more local than magnetic fields and can allow single molecule addressing (vide infra). When applied to macroscopic samples, electric fields can be used to slightly tune the spin Hamiltonian parameters.[90] Most investigations refer to a modification of the *g* factor and of the magnetic anisotropy parameters through the spin-orbit coupling, but equally appealing is the possibility to tune the energy of interaction between coupled spin centers.[91–94] Recent experiments based on EPR spectroscopy of macroscopic samples under electric fields, either static,[95] pulsed,[96] or modulated,[97] have revealed effects that are too weak to switch completely off the magnetic interaction, but are however able to tune the system in and out of the resonance conditions.[98] Of particular relevance are antiferromagnetic triangles.[91,93] These systems, that have been widely theoretically investigated, lack inversion symmetry thus allowing first order electric field effects. Moreover, they exhibit spin frustration, *i.e.* the impossibility to satisfy all antiferromagnetic interactions, resulting in energy degeneracy of spin levels. These systems are therefore very sensitive to external perturbations, such as the application of an electric field.

The scenario changes significantly if single molecules in contact with a substrate are considered. In such a case, much stronger local electric field can be achieved and used to manipulate the spin states, as described in the following section.

Addressability

Manipulation and read out of spin states at the single-spin level is one of the biggest challenges to address in order to turn molecular spin systems from simpler qubits candidates to viable computational units. A rather straightforward way to address single molecule is to organize them on a surface and employ a probe with sufficient lateral resolution, or to insert a single molecule in a nanocircuit. From a conceptual point-of-view, it should be kept in mind that a drastic modification of the environment for a molecule can ultimately induce drastic changes in the spin response. Thus, experiments aimed at investigating the robustness of selected molecules once deposited on a surface are fundamental to understand if the spin dynamics is significantly changed or not.

Indeed, the most advanced spin-based quantum computational platforms, such as phosphorous defects on silicon or silicon carbide, exploit technological tools and techniques that allow the addressing of single qubits.[20] Single spin addressing has also the advantage that initialization can be achieved by a measurement that collapse the state in a pure state.[2]

It should be however noted that, when dealing with molecular platforms, every single unit is intrinsically equal to

all surrounding molecules from both structural and electronic points of view. Thus, one can think that a measurement performed on an ensemble of molecules can provide, in principle, the same response as a single unit, avoiding the hard task of performing manipulations on the single molecule. Unfortunately, our vision of an ensemble of identical molecules is an idealization that is broken by the presence of non-uniform interactions between the molecules and the decoherence sources. This makes our molecular ensembles an inhomogeneous system, with a response to an external stimulus that is different with respect to that expected for a single-molecule. Moreover, the intrinsic miniaturization down to the single molecule will be lost with ensembles measurements.

Recently, fundamental experiments in the direction of MSQs single molecule addressing have been performed on the double-decker SMM formulated as [$TbPc_2$] (Pc = phthalocyaninate). These systems have been the first complexes containing a single paramagnetic ion exhibiting magnetic bistability because the crystal field separates very efficiently (ca. 600 cm^{-1}) the $m_J = \pm 6$ ground doublet from other doublets of the ground $J = L + S = 6$ manifold of Tb^{III}.[99] An unpaired electron is delocalized on the two ligands and is moderately coupled to the lanthanide magnetic moment. A considerable amount of results has been obtained mainly by Wernsdorfer and coworkers working on this class of molecules. An exhaustive review of these results is beyond the scope of this perspective. However, it is important to stress here what has made [$TbPc_2$] such a unique platform for single spin (either electronic or nuclear) detection and manipulation. First of all, the chemical and structural stability of the compound allows processing in ultra-high vacuum and from solution.[100,101] The remarkable magnetic anisotropy makes the tunneling of the anisotropy energy barrier the principal mechanism of relaxation of the electronic magnetic moment at low temperatures. Quantum tunneling is enhanced at the avoided level crossings of the hyperfine levels of the nuclear spin $I = 3/2$ that characterizes the ^{159}Tb isotope with 100 % of natural abundancy.[99] The sizeable splitting induced by nuclear quadrupolar is also very important because allows differentiation between transitions involving different m_I levels. The nuclear and electronic spin dynamics are strongly connected with the advantage that the former can be investigated by measuring the latter, which, on its turn, can be detected at the single molecule level through transport measurements. A single molecule has been embedded inside a nanometric electric junction forming a three-terminal single-molecule magnet transistor,[102] similarly to what previously done on endohedral fullerenes.[103] Of relevance here is the fact that the hopping electrons responsible of the transport process do not involve the Tb atom but rather the Pc ligand. The unpaired electron on the latter is however interacting with the Tb magnetic moment. This unique chain of indirect detection has been fundamental to have access to the nuclear spin dynamics without significantly altering the properties of the [$TbPc_2$] SMM. Even more important is how manipulation of the nuclear spin state can be performed.[104] It relies on the Stark effect on the hyperfine interaction; Wernsdorfer and coworkers have estimated a relative change in the hyperfine interaction of the order of 0.1–1% for an applied electric field of 10^6 V/m, an effect at least an order of magnitude larger than what observed by Mims in pulsed EPR experiments on three-positive lanthanide ions in inorganic lattices.[105]

Thanks to the unique combination of properties of the [$TbPc_2$] molecule and the outperforming experimental setup, the Grover algorithm proposed to find an element in an unsorted list,[106] has been implemented using the nuclear spin of a single [$TbPc_2$] molecule.[107] This represents one of the most important achievements in quantum information processing with molecular spins.

A more versatile platform for single molecule addressing could be realized with advanced techniques based on scanning probe microscopy. It is well established that STM can be used to manipulate atoms and molecules on surfaces to realize artificial structures.[108] Moreover, when combined with a magnetic tip, it can probe the spin state of the investigated object, thus its spin dynamics.[109] The spin state can be manipulated by sending a rf or mw pulse at the frequency in resonance with the spin system. This corresponds to performing a spatially resolved single spin EPR experiment.[110]

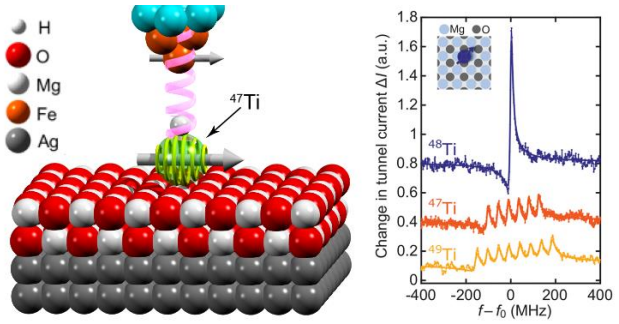

Figure 9. Schematic view of an STM-EPR experiment investigating the hyperfine splitting of the $S = 1/2$ of a hydrogenated Titanium atom deposited on a MgO bilayer grown on Ag. The tip is magnetic due to its termination with Fe atoms. AC frequency pulses are sent through the tip and a change in the tunneling current is observed when the frequency matches energy level splitting (left). Results of the EPR experiment performed ($T = 1.2$ K, $B = 0.9$ T) on three different isotopes of Ti sitting on a bridge site. The six and eight hyperfine lines of ^{47}Ti and ^{49}Ti are well evident. The data are rescaled with f_0 slightly different in the three cases but close to 23 GHz (right). Right panel adapted with permission from ref. [112].

The technique is able to capture also fine details such as the dipolar interaction between $S = 1/2$ of hydrogenated Ti adatoms[111] or the dependence of the hyperfine splitting of ^{47}Ti and ^{49}Ti adatoms on the binding site - oxygen or bridging - on the MgO surface (Figure 9).[112]

The mechanism inducing the ESR transition in the STM experiment is still debated but it has been suggested that the motion of the adatom caused by the oscillating electric field exposes the magnetic atom to an effective time-varying magnetic field generated by the magnetic tip.[111] If such

a mechanism can also be active for molecules deposited on a surface remains an open question, though the detection of the hyperfine levels of a molecular spin in a STM-ENDOR experiment has been recently reported.[113]

The rapidly expanding capability of scanning probe techniques has recently allowed to control and quantify the magnetic interaction between two $[Ni(Cp)_2]$, $S = 1$, molecules, one attached to the scanning probe tip and the other deposited on a Ag surface.[114]

Molecules have also the advantage, compared to single adatoms, that the electrons can tunnel through the ligand orbitals. This could in principle mitigate the decoherence induced by tunnel events, recently observed for Fe adatoms on MgO.[109]

Scalability

Scalability can be defined as the property of a computational system to be adaptive to a potential increase in the algorithm's complexity. This can be achieved by increasing the intrinsic performance of the single computational units, here the qubits, or the connections and nodes between them, here the number of interconnected qubits within a quantum gate. The former and the latter can be defined as vertical and horizontal scalability, respectively.[115,116] Both should be improved to allow for better computational outcomes.

In the field of MSQs, one can consider vertical scalability as the potential of a qubit to act as a qudit by accommodating a manifold of electronic transitions[117,118] associated to either a ground spin state > ½, or to the hyperfine coupling. Such manifolds of transitions, each one considerable as a qubit, can be used to implement schemes of error correction without the need of an interaction with another independent qubit unit. Since vertical scalability is an intrinsic property of a given qubit, it can be quite easily tuned by playing with the nature of the ligands, the metal and the metal ions' coordination geometry.

A recent report has highlighted such vertical scalability potential for a Ln-based electronic spin qubit of formula [Yb(trensal)], H3trensal = 2,2',2'' -Tris(salicylideneimino)triethylamine,[17] which is characterized by relatively long coherence times at low temperature.[119] S. Carretta and coworkers have shown that the effective $S = ½$ electronic spin of Yb(III) can act as an electronic qubit coupled with its $I = 5/2$ nuclear spin (a six-level qudit) that can be coherently manipulated by rf pulses. The multilevel structure of the nuclear qudit and its coupling with the electronic spin allows implementing a scheme of quantum error correction that can be used against amplitude shift errors that might affect nuclear spin levels.[120,121] This method requires a smaller number of qudits to solve errors of the same computational basis with respect to the more classical qubit block encoding scheme, which is based on redundancy principles.[17] It should be however pointed out that one cannot rely uniquely on vertical scalability because the finite number of states available as qubits is somehow limited. A purely vertical approach to scalability has indeed killed the NMR approach to quantum computing.[122]

Augmenting the horizontal scalability might consists instead in increasing the number of interconnected qubits by finding an efficient pathway to allow them to communicate selectively and through switchable interactions with external control. Molecular chemistry can have a major impact in addressing the challenge of horizontal scalability by extending the principles of molecular quantum gates preparation illustrated above to an increased number of interconnected control- and target-qubits by means of supramolecular, coordination chemistry and self-assembling principles. For example, preparation of 2D or 3D solid-state arrays of qubits with good performance in terms of coherence times have been already achieved.[64–66,123,124] 1D architectures, on the contrary, have the advantage of better controlled dipolar interactions and the possibility to use the gradient of the magnetic field for selective addressing.[125]

For an effective scale up a fundamental principle might be that of entangling finite ensembles of interacting qubits within precisely designed molecular architectures in a controlled manner. For example, one can think about realization of hierarchical covalent superstructure[126] or bio-inspired self-organizational structures like peptides and DNA.[127]

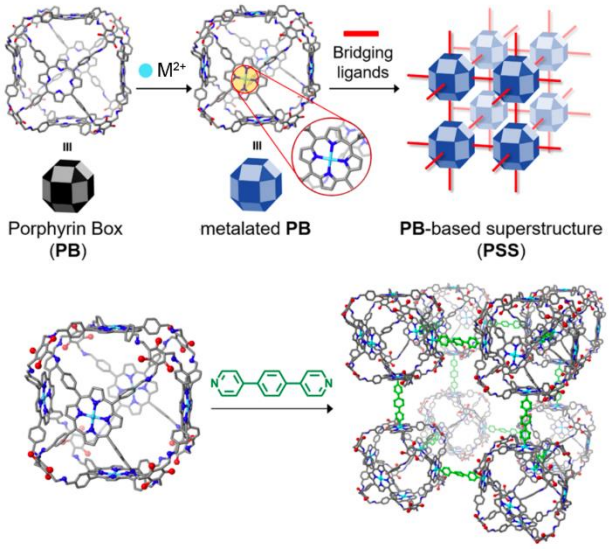

Figure 10. Concept behind the realization of hierarchical superstructures based on metallated-porphyrin boxes (top) and practical realization using Zn-porphyrins and dipyridyl terminated bridging ligands (bottom). Adapted with permission from ref. [126]. Copyright 2018 American Chemical Society.

The hierarchical superstructure approach might be a way to connect in a chemically controllable manner discrete structural units constituted by a finite number of interacting metal ions. This is for example the case of zinc-metallated porphyrin boxes connected by dipyridyl terminated bridging ligands that lead to the hierarchical superstructure reported in Figure 10.[126]

If these units are *"ad hoc"* electronically and structurally designed, meaning that each porphyrin units contains metal ions with long spin coherence that can communicate efficiently only with the metal ions inside the box, we can

foresee each unit as a molecular quantum gate. These units can be connected through a bridging ligand of tunable length in a superstructure of higher hierarchy.[126] If the linker is designed to allow communication between different boxes outputs in a switchable and scalable manner, this can lead to the realization of molecular quantum circuits. In order to achieve a control with timescale comparable to that of available T_ms, we can foresee the use of radical or diamagnetic bridging ligand able to generate triplet state upon photoexcitation,[86,87] while for a local control, we can rely in the current advances in the use of local electric fields to tune spin exchange interactions.[97]

The bio-inspired approach might instead consist in the use of chiral moieties, *i.e.* aminoacidic binding sites, to link metal ions or lanthanides in asymmetric coordination environments, thus making the metal ions in principle distinguishable through EPR. Moreover, by taking advantage of the self-organizational properties of such moieties, one can envisage the preparation of infinite different sequences of fragments to encode qubits and related quantum gates.[127]

Although also for these approaches one can identify some criticisms related to the addressing of all DiVincenzo criteria, for example the control of the interaction between units, they can be certainly considered a step-forward with respect to the preparation of paramagnetically diluted 2D and 3D molecular networks.

Another strategy might rely on a hybrid approach consisting in the preparation of complex molecular architecture containing a discrete number of operable qubits by controlled self-assembly on surface. On a surface, local electric field can reach amplitudes as high as 10^9 V/m, e.g. under the tip of a scanning tunnel microscope. These fields are in principle strong enough to switch on-off interaction between the qubits. Simultaneous spin-manipulation through mw radiation and local readout are however difficult to realize, unless performed with other means, *e.g.* optically.

Conclusion and Outlook

Every single approach that relies on a specific qubit physical realization for QT development presents both pros and cons. As clearly stated in this perspective, the molecular approach is not immune to that, presenting its own advantages and disadvantages. On the basis of the criteria highlighted here, the use and manipulation of molecular spin systems for QT applications appears a step behind to alternative physical realizations. However, for a field that is still in its infancy, with a limited investment in terms of funding and researchers involved, remarkable advancements in a restricted time-frame have been already achieved, while plenty of room for significant improvements is still available.

The understanding of the fundamental principles behind quantum coherence properties optimization in molecular spin systems by chemical design can be considered already advanced. Indeed, a rational strategy, which is fundamental for significant improvements and progresses in the near future, has been already paved in the last few years.

Even more promising, though mainly unexplored, appears a transversal approach to the second quantum revolution that touches different qubit physical realizations. Indeed, it would be possible to collect and combine all the advantages of the different approaches together. As an example of this cross-fertilization between different platforms we can mention here the emergent field of topological quantum computation based on Majorana fermions, an approach that is predicted to be much more fault-tolerant than gated superconductors used in the existing quantum computers.[128]

A possible realization of Majorana states is based on a spin chain deposited on a bidimensional superconductor.[129,130] This has boosted the interest on the investigation of the interaction between magnetic impurities and a superconducting substrate that can lead to a coupled state between the spin of the impurity and the Cooper pairs, also known as Yu-Shiba-Rusinov coupled states.[131–133] While magnetic atoms have a permanent coupling with the substrate, it has been recently shown that a MSQ such as VOPc shows ON-OFF state of this coupling with the Pb substrate depending on the orientation of this asymmetric molecule.[134] Even more interesting is the possibility to tune the interaction of the oxygen-up-conformer by exerting pressure with the STM tip. This example highlights that the remarkable progress made by nanoscience and nanotechnology has already broken the boundaries between these different approaches. Thus, the realization and exploitation of hybrid architectures can be seen as one of the most promising strategies in the direction of QT development and its practical applications.

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Notes

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